

'Transition Metal Complexes of Quadridentate  
Nitrogen Ligands'

A thesis submitted for  
the Degree of D.Phil  
in the University of York

P.A. TASKER

DECEMBER 1968



## ABSTRACT

The properties of vitamin B<sub>12</sub> and various 'model' compounds are reviewed, and the criteria for ligands which might act as substitutes for the corrin system are discussed in chapters 1 and 2.

A series of possible 'model' ligands was prepared by the condensation of some diamines with o-aminoaryl carbonyl compounds in a 1:2 molar ratio. The properties of these free ligands were examined, and the effect of variation of structural features in the ligands on the geometry, conjugation and crystal field splitting when complexed, is discussed.

Nickel(II) complexes of dianionic forms of these ligands were prepared and studied. All the ligands gave planar nickel(II) complexes, even in cases where a tetrahedral arrangement of the donor atoms seemed to give a much less strained form of the ligand. In these complexes the nickel(II) ion showed no tendency to increase its coordination number, and this behaviour contrasted with that of analogous complexes of 'N<sub>2</sub>O<sub>2</sub>' ligands derived from salicylaldehyde. It is suggested that this difference results from electronic, rather than steric effects.

The cobalt(II) complexes were also judged

to be planar. They showed less tendency to be oxygenated or oxidized than similar complexes of 'N<sub>2</sub>O<sub>2</sub>' ligands. Some evidence is presented for reduction to a species analogous to vitamin B<sub>12s</sub> which contains cobalt with a formal oxidation state of one, but no alkyls analogous to vitamin B<sub>12</sub> coenzyme could be isolated.

The synthesis of macrocyclic ligands is discussed in chapter 6. A series of new macrocyclic complexes was prepared by the reaction of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione with some diamines in the presence of metal ions. Some aspects of the mechanisms of these reactions are discussed in chapter 7. Only for the reaction of 1,2-diaminoethane with the dialdehyde was a 'template' or organizational effect of the metal ion suggested.

The experimental section is divided into two parts. The first (chapter 10) gives general experimental details, and includes measurement of magnetic susceptibility in solution by Evans' NMR method, and a manometric study of gas absorption. The second part describes preparative methods and reaction details (chapter 11).

ACKNOWLEDGEMENTS.

I should like to thank Dr. M. Green for his friendly supervision and encouragement received during the course of this research.

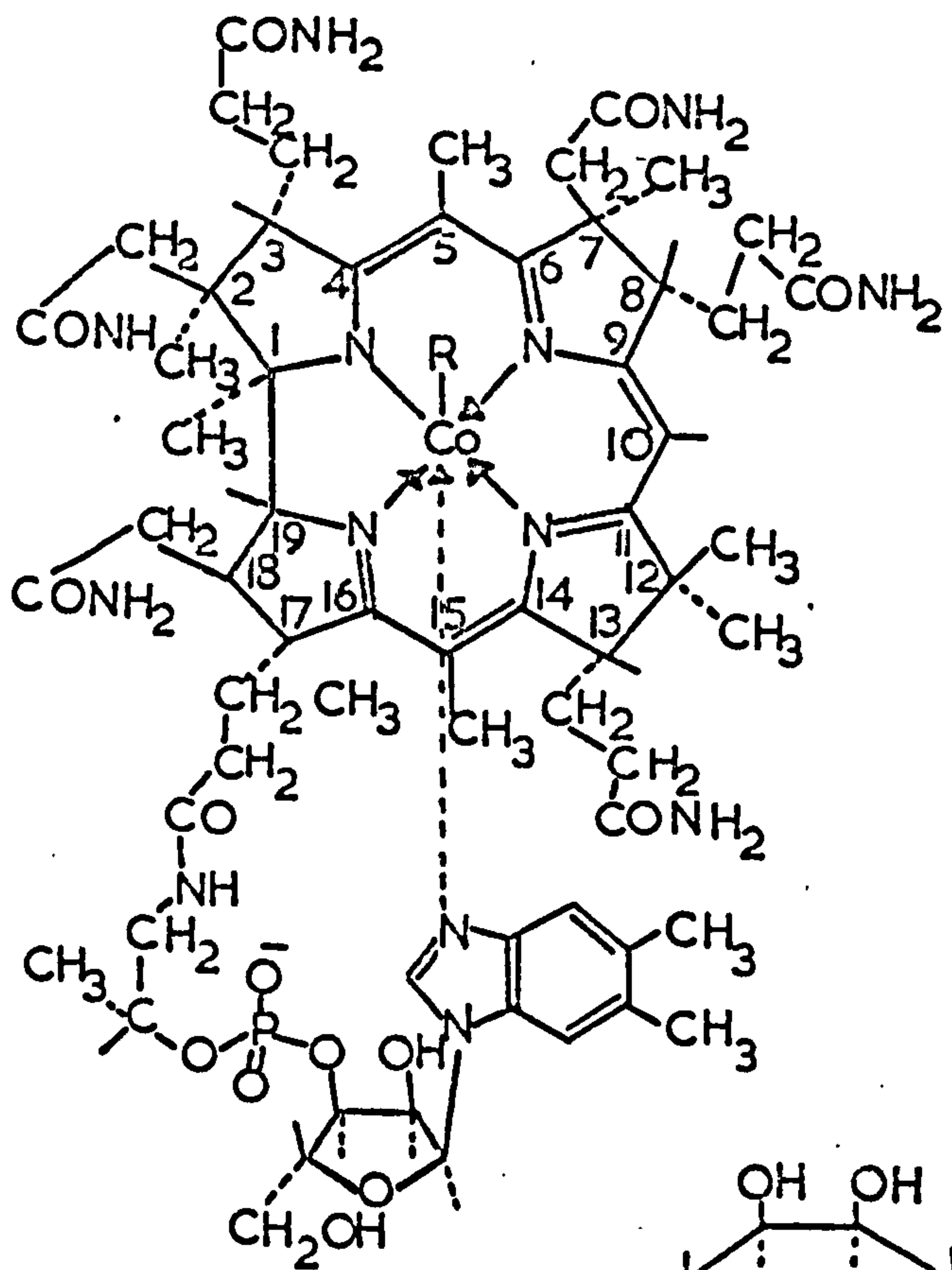
I should also like to express my gratitude to all the members of the department who have given assistance, in particular to Dr. J. Smith and R. Bratchley for helpful discussions, and to Mrs. M. Sutherland for running so many NMR spectra for me.

Finally I am indebted to my wife for her constant encouragement and help in the preparation of this thesis, and to my father who arranged for many of the diagrams and spectra to be reduced in size.

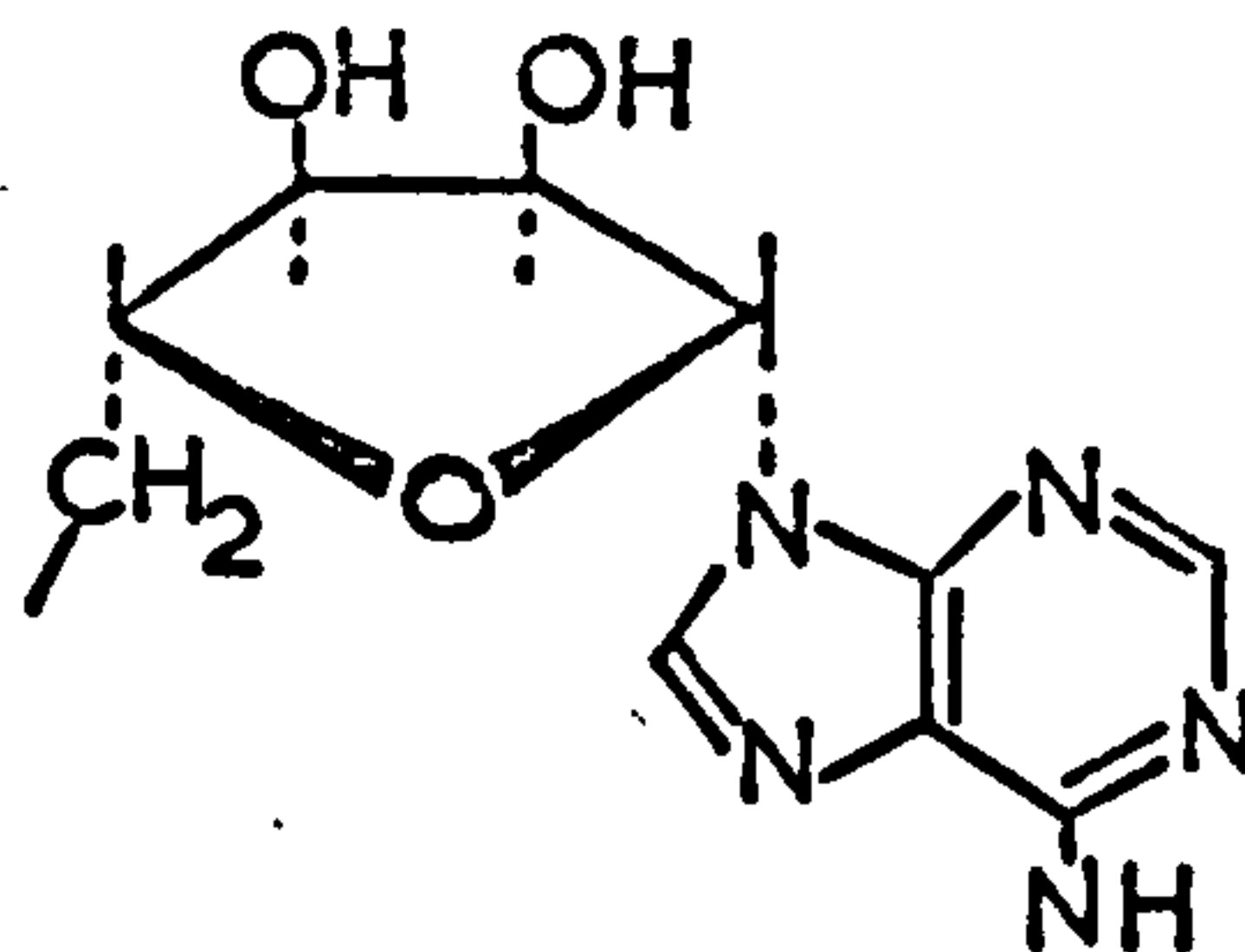
1961

CONTENTS

	page
Acknowledgements	ii
Contents	iii
Chapter 1. Vitamin B <sub>12</sub> and 'model' compounds	1
Chapter 2. Choice of 'model' ligand systems	21
Chapter 3. Acyclic 'model' ligand systems	30
Chapter 4. Nickel(II) complexes of acyclic quadridentate nitrogen ligands	59
Chapter 5. Cobalt complexes of the acyclic 'model' ligands	106
Chapter 6. The synthesis of macrocyclic ligands	141
Chapter 7. Some new quadridentate macrocyclic ligands	153
Chapter 8. Nickel(II) and copper(II) complexes of some new macrocyclic ligands	188
Chapter 9. Cobalt complexes of some new macro- cyclic ligands	209
Chapter 10. General experimental details	226
Chapter 11. Preparative details	265



(B)  
Vitamin B<sub>12</sub> coenzyme R=



(A)  
Vitamin B<sub>12</sub> R= CN<sup>-</sup>

[1.1]. The structure of vitamin B<sub>12</sub> and its coenzyme.

Derivatives differing by virtue of the nature of 'R' are called cobalamins, e.g. cyanocobalamin is vitamin B<sub>12</sub>. The tetrapyrrolic ring system will be referred to as the 'corrin' system.

## Chapter 1. Vitamin B<sub>12</sub> and 'Model' Compounds.

- 1.1 Vitamin B<sub>12</sub> and vitamin B<sub>12</sub> coenzyme.
  - 1.1.1 Ligand replacement in vitamin B<sub>12</sub> derivatives.
  - 1.1.2 Electronic spectra of vitamin B<sub>12</sub> derivatives.
  - 1.1.3 Reduction of vitamin B<sub>12</sub> derivatives.
- 1.2 'Model' systems for vitamin B<sub>12</sub>.
  - 1.2.1 Reduction of the 'model' compounds.
  - 1.2.2 'Model' compounds of vitamin B<sub>12</sub> coenzyme.
  - 1.2.3 Ligand replacement in 'model' compounds.
- 1.3 Other systems stabilizing low valency states and alkyls of cobalt.
- 1.4 References.

### 1.1 Vitamin B<sub>12</sub> and vitamin B<sub>12</sub> coenzyme.

The chemistry of vitamin B<sub>12</sub> has been studied extensively and reviews<sup>1,2,3,4</sup> deal with references up to 1967. The structure of vitamin B<sub>12</sub> [1.1,A] was derived mainly from X-ray crystallographic data by Hodgkin and co-workers<sup>5,6</sup>. Vitamin B<sub>12</sub> coenzyme [1.1,B] is a more functional form, but was isolated<sup>7,8</sup> twelve years after the vitamin, because it is highly sensitive to light and cyanide ions, and moderately sensitive to acid. Consequently any of these agents in all the

earlier isolation procedures would have destroyed it to give other forms of vitamin B<sub>12</sub>. It is the first known naturally-occurring organo-metallic compound.

For the inorganic chemist the main interest in vitamin B<sub>12</sub> lies in its unusual properties in comparison with other cobalt complexes. The many reactions of the peripheral groups in the molecule are of importance in studies of the biological properties of the vitamin, and were also important in establishing the complete structure of the molecule, but will not be dealt with here.

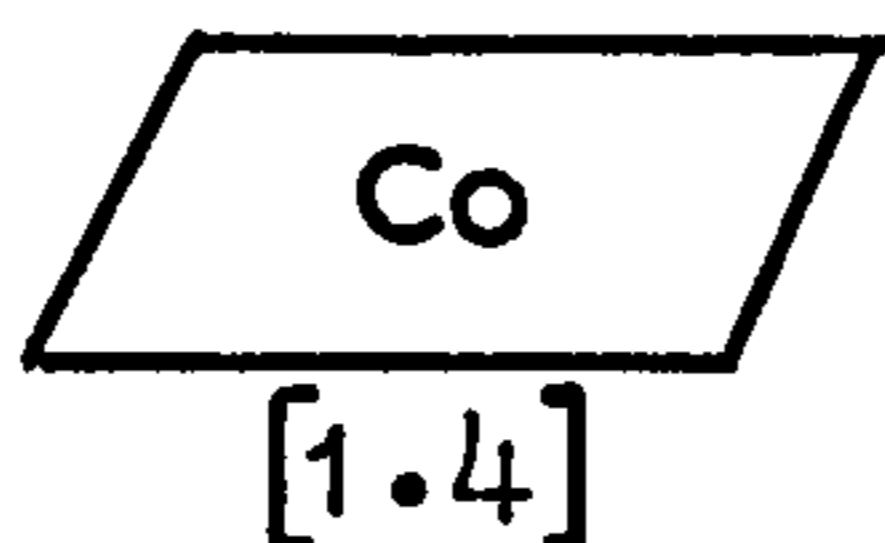
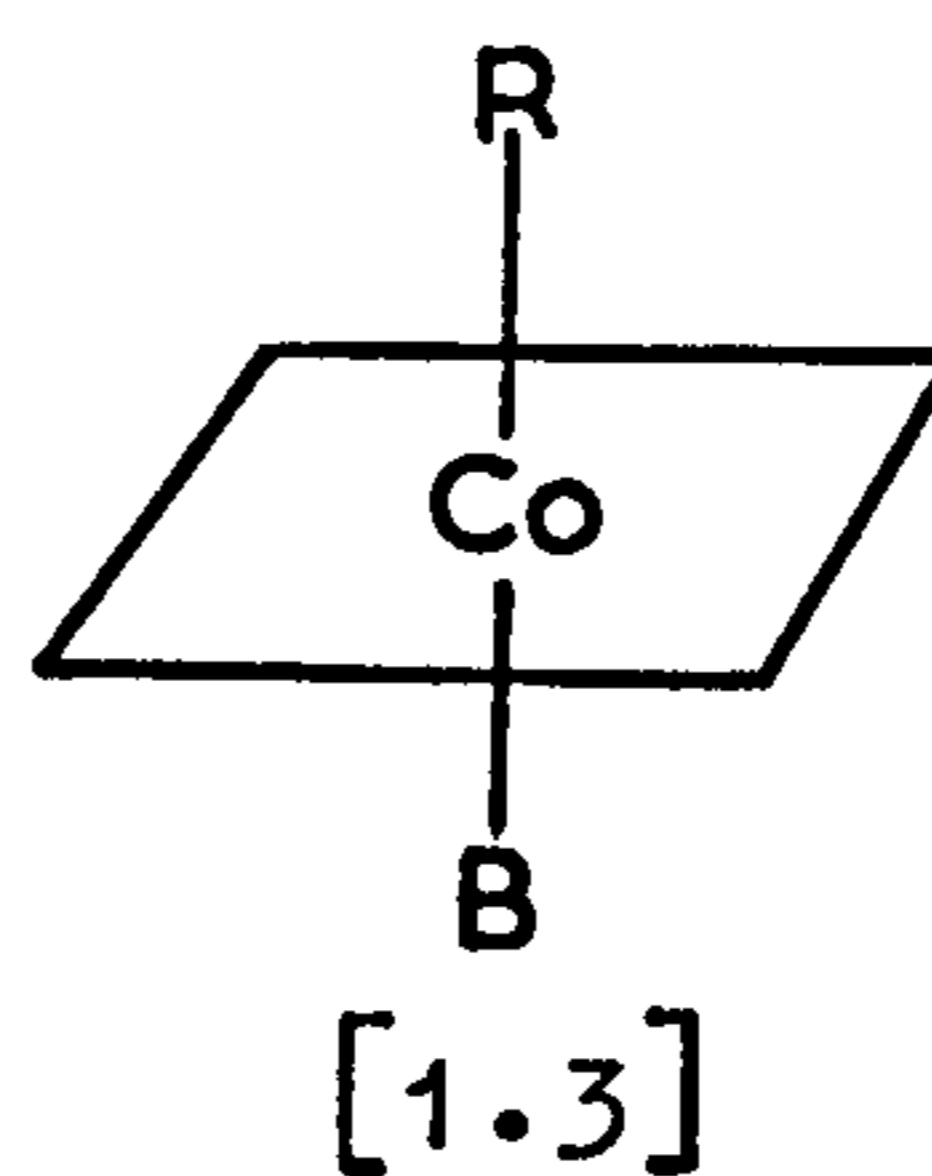
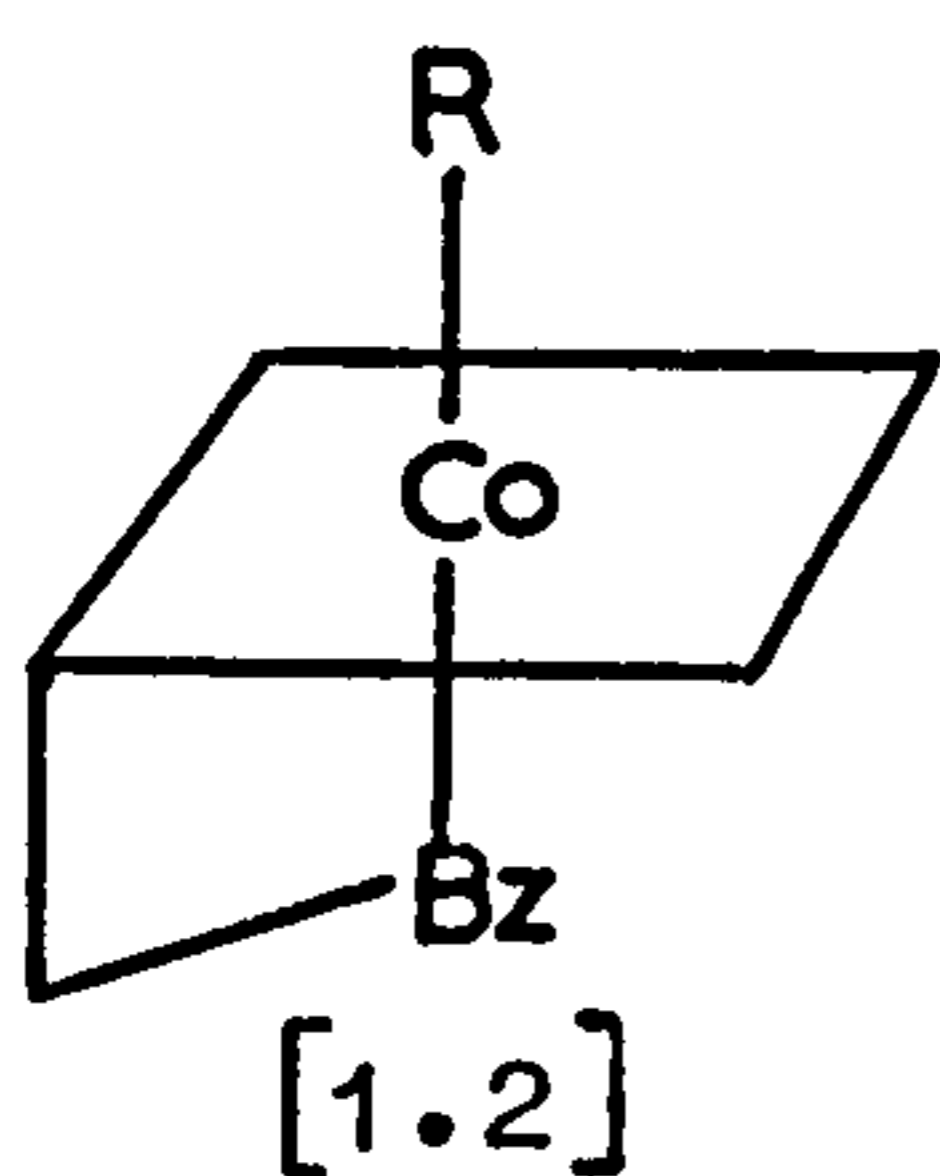
#### 1.1.1 Ligand Replacement in vitamin B<sub>12</sub> derivatives.

Both the cyanide or 5'-deoxyadenosyl group (R in [1.1]) and the benzimidazole moiety may be displaced from the coordination sphere of the cobalt atom by other ligands,<sup>9,10</sup> but the corrin ring system has not been removed without the use of reagents which cause its destruction.<sup>11</sup> Certain cobalt-free corrinoids have been isolated from photosynthetic bacteria, but have yet to be clearly characterized.<sup>12,13</sup>

The rigid equatorial ligand system of vitamin B<sub>12</sub> makes it an ideal system for studies of replacement reactions. In such studies<sup>14,15,16,17,18</sup> vitamin B<sub>12</sub> and



its derivatives are represented by the idealized structures [1.2] and [1.3]. In this way electronic transmission through the cobalt atom into cis and trans effects



[1.2] Vitamin B<sub>12</sub> and coenzyme

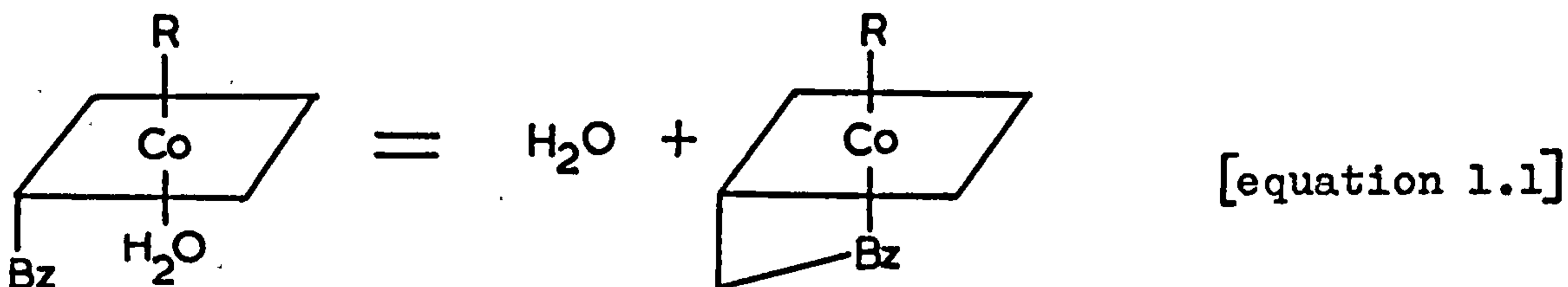
[1.3] Vitamin B<sub>12</sub> derivatives without the nucleotide

[1.4] Cobalt corrinoid

Cis-effects are illustrated by a dependence of the properties of the equatorial ring system on the nature of the axial ligands. For example it has been suggested that the main effect of an axial ligand on the electronic spectrum of the equatorial ring system (cis-effect) is related to the position of the ligand in the nephelauxetic series.<sup>14</sup> The N.M.R. spectrum of the equatorial ring system (in particular the C-10 hydrogen atom, see [1.1]) is also strongly dependent on the axial ligand (R)<sup>15,16</sup>,

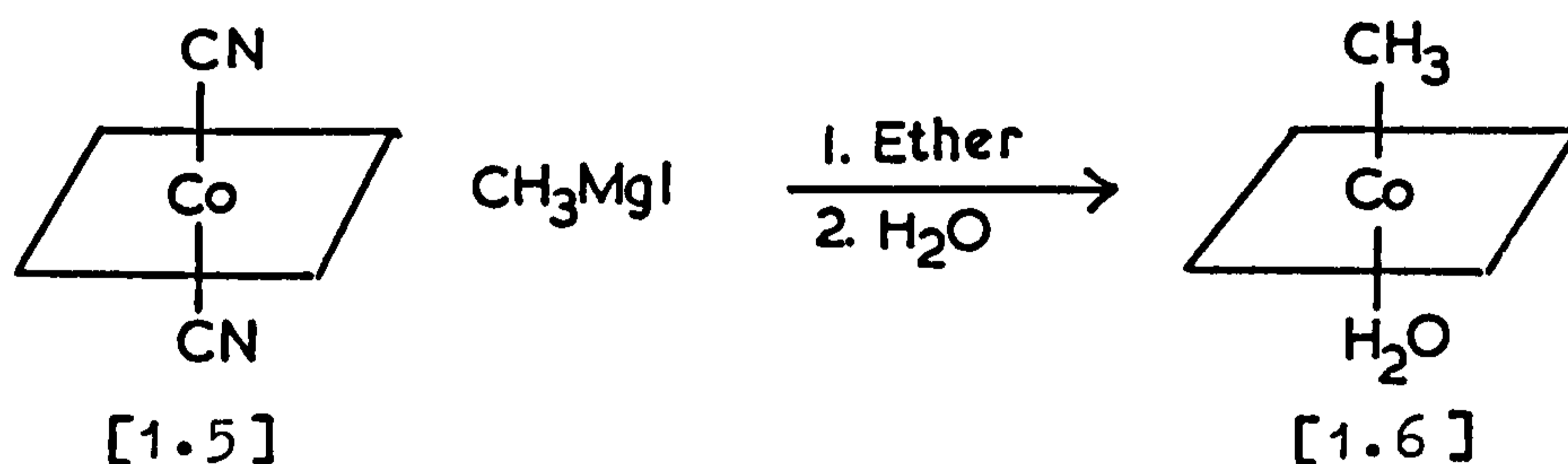
but no systematic variation with the nature of R has been recorded, and small changes in the ring shape might account for the effects.<sup>15</sup>

A trans-effect is manifest by a dependence of the properties of one axial ligand (e.g. R) on the nature of the other (i.e. B). For example, the equilibrium (equation [1.1] ) favours the coordination of the benziminazole moiety for the less polarizable axial ligand R.<sup>17</sup> In other words, increasing the polarizability of the group R decreases the stability of the cobalt-benziminazole bond relative to that of the cobalt-water bond. Similarly, by studying the cyanide stretching frequency in complexes ( [1.3] B = CN<sup>-</sup> ) it has been shown<sup>18</sup> that the strength of the cobalt cyanide bond decreases with polarizability of the group R.



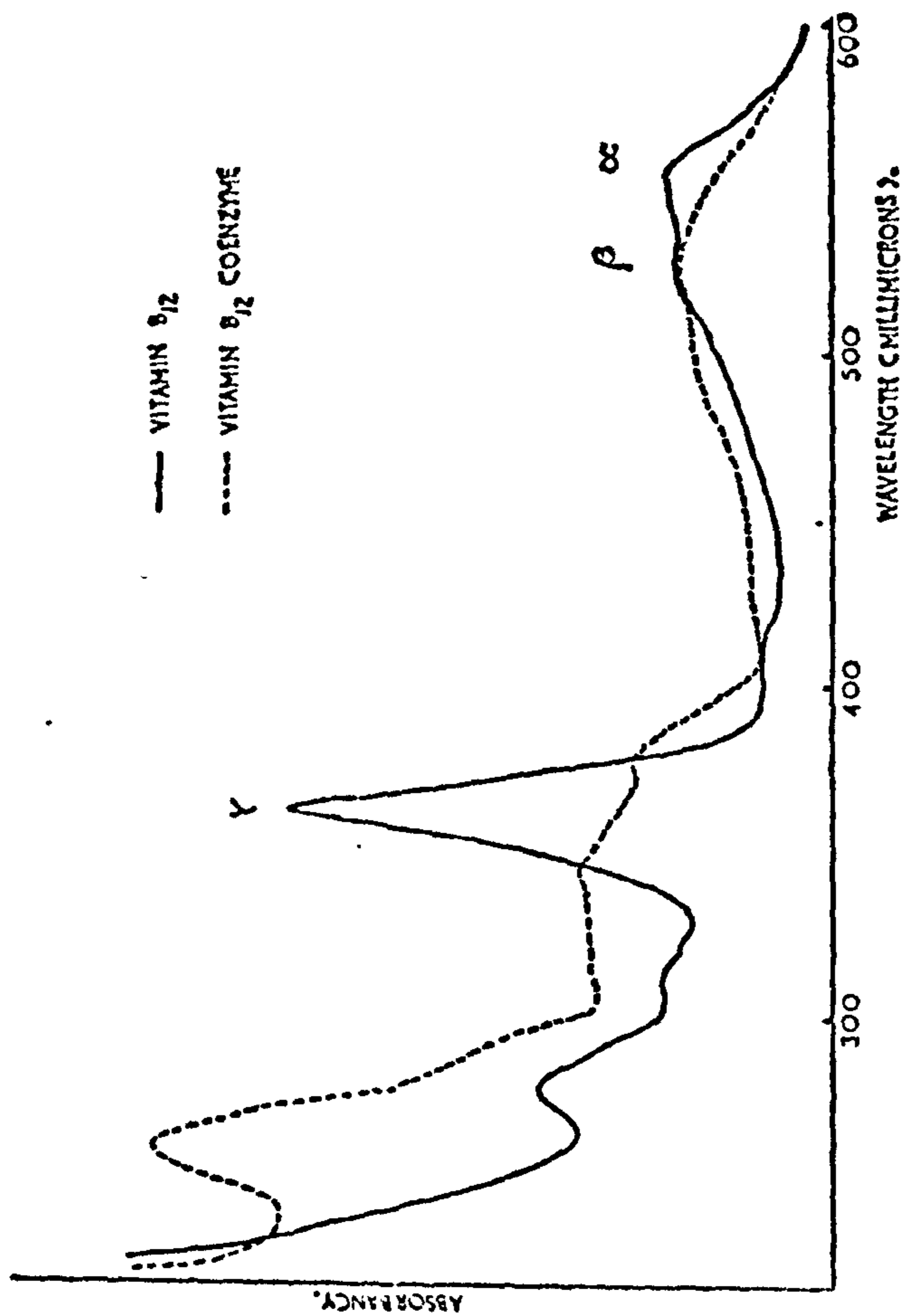
When the primary amide groups (see [1.1] ) of dicyanocobalamin were converted to the corresponding ethyl ester groups, an ether soluble cobalt (III) complex [1.5]

was obtained.<sup>19</sup> This was treated with an excess of methyl magnesium iodide and then hydrolysed, when a methyl cobalamin [1.6] was obtained in which the ethyl ester groups had been converted into the corresponding tertiary alcohol groups.<sup>19</sup> This is one of the two important routes to derivatives of vitamin B<sub>12</sub> containing alkyl-cobalt bonds.



### 1.1.2 Electronic spectra of vitamin B<sub>12</sub> derivatives.

The spectrum of vitamin B<sub>12</sub> is qualitatively similar to the spectra of the metalloporphyrins, apparently having a Soret ( $\gamma$ ) band (361 M $\mu$ ) and distinct  $\alpha$  and  $\beta$  bands (550 and 520 M $\mu$ ).<sup>20</sup> At first sight this is rather surprising since it was thought that tetra-pyrrole systems in which the conjugation around the macrocycle is interrupted, e.g. the porphyrinogens



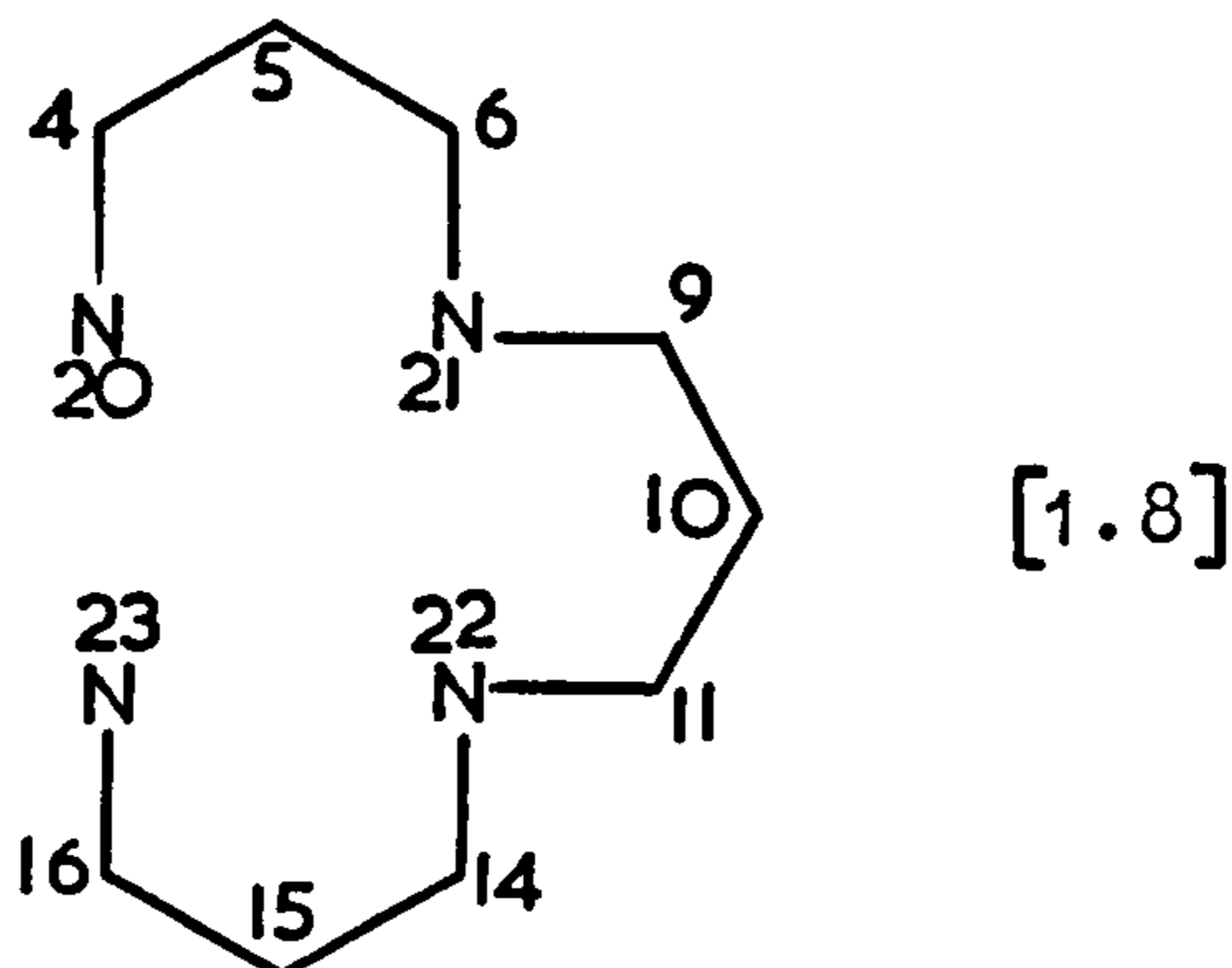
[1.7]. The spectra of vitamin B<sub>12</sub> and its coenzyme.

and corrins, would not show a Soret band.<sup>21</sup> A "conjugated pathway maintained by the cobalt atom" has been proposed to explain this apparent anomaly.<sup>21</sup> However, even the cobalt-free corrinoid compounds<sup>13</sup> contain bands which correspond closely to all those in the vitamin B<sub>12</sub> spectrum above 300 M $\mu$  and, hence, it does not seem necessary to postulate a completely cyclic conjugated system to explain the transitions responsible for the spectra of vitamin B<sub>12</sub> derivatives.

One of the most interesting features of the spectra of vitamin B<sub>12</sub> derivatives is their strong dependence on the nature of the axial substituents (see page 3 ). The spectra of vitamin B<sub>12</sub> and the coenzyme (see [1.7] ) are so different that at first there was some doubt as to whether they contained the same conjugated chromophore.<sup>22</sup>

A recent theoretical treatment<sup>22</sup> of the optical properties assumes that all the transitions in the visible and near ultraviolet spectra are of the  $\pi - \pi^*$  type, i.e. localized within the conjugated chain of thirteen atoms from N(20) to N (23) (see diagram [1.8] and cf. [1.1] ). The cis-effect of an axial ligand (e.g. R in [1.2] ) is approximated on the basis of the charge donation to the metal, which is then transmitted to the ligand nitrogen atoms. The treatment accounts

successfully for many features of the spectrum.

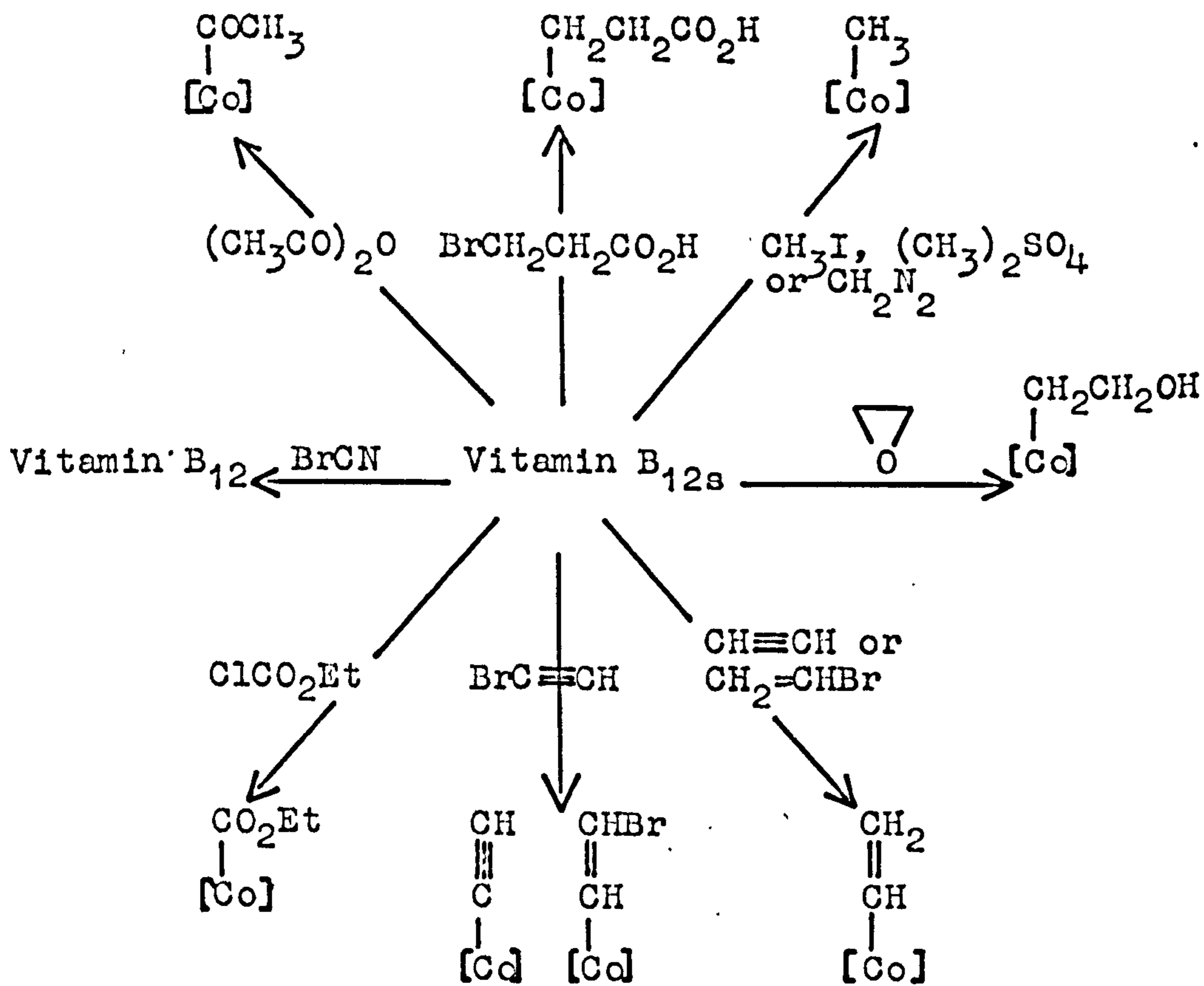


### 1.1.3 Reduction of Vitamin B<sub>12</sub> derivatives

Chemical or electrolytic reduction of vitamin B<sub>12</sub> initially gives a brown substance (vitamin B<sub>12r</sub>), which can be further reduced to green vitamin B<sub>12s</sub>.

Formation of vitamin B<sub>12r</sub> involves removal of the cyanide ligand as hydrogen cyanide for chemical reduction<sup>23</sup> or methylamine for catalytic reduction.<sup>24</sup> On aerial oxidation vitamin B<sub>12r</sub> gives aquocobalamin<sup>25</sup> ([1.1] with R = H<sub>2</sub>O). The cobalt atom in vitamin B<sub>12r</sub> has been assigned<sup>26,27</sup> a formal oxidation state of two after considerable doubt, and somewhat conflicting experimental evidence.

Further reduction of vitamin B<sub>12r</sub> with sodium borohydride<sup>28</sup> or chromous acetate<sup>29</sup> at pH 9.5 gives grey-green vitamin B<sub>12s</sub><sup>30</sup> which can still be oxidized to aquocobalamin, but when treated with alkylating agents



[1.9]. Reactions of vitamin B<sub>12s</sub>

[Co] represents the cobalamin system.

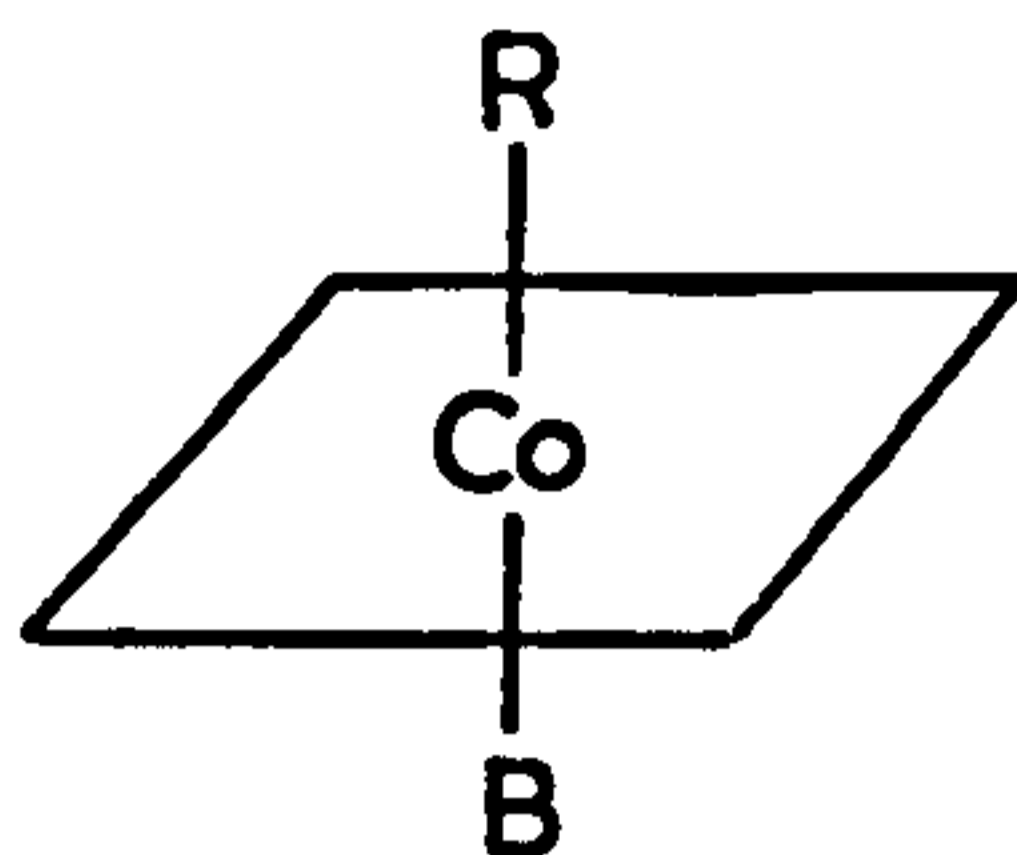
gives the corresponding alkylcobalamins.<sup>28</sup> Controlled potential reduction of<sup>26,27</sup> aquocobalamin to vitamin B<sub>12s</sub> suggested that it contained cobalt with a formal oxidation state of one.

Typical reactions of vitamin B<sub>12s</sub><sup>28,31</sup> are illustrated in diagram [1.9] .

## 1.2 'Model Systems' for vitamin B<sub>12</sub>

The reduction of a transition metal compound to a nucleophilic species which is reacted with an alkylating agent to give a derivative containing a metal-carbon  $\sigma$ -bond is a common procedure in the synthesis of organometallic compounds.<sup>32</sup> The range of stable cobalt alkyls derived from vitamin B<sub>12s</sub> (see [1.9] ) prompted a great deal of research into similar systems with stabilizing effect on cobalt-alkyl bonds. Such systems are commonly referred to in the literature as 'model' compounds of vitamin B<sub>12</sub>, and may generally be represented by a structure [1.10] similar to [1.3] page 3 , i.e. an equatorial quadridentate ligand system surrounding a cobalt (III) ion, with axial ligands R and B, one of which may be an alkyl group.

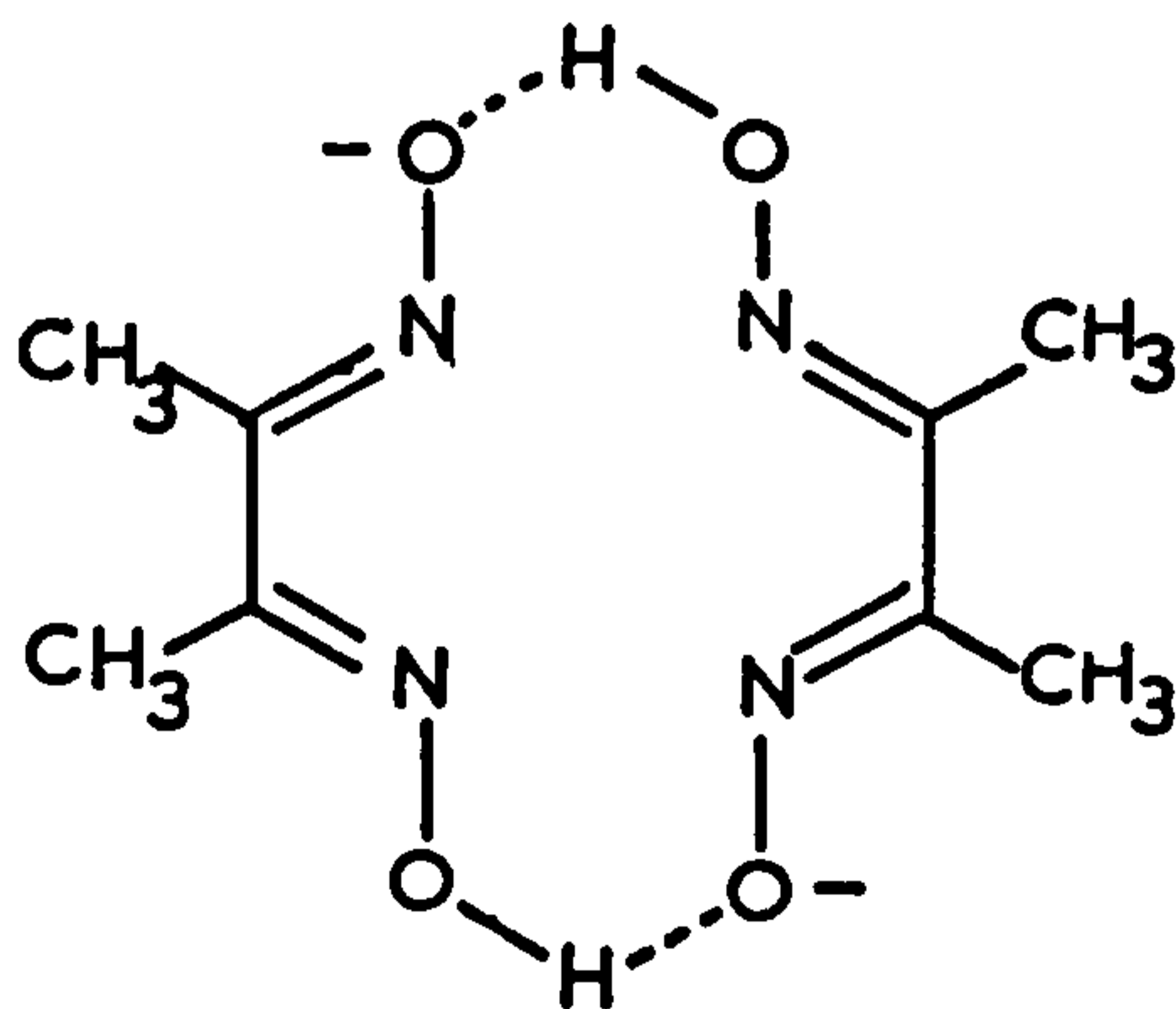




[1.10]

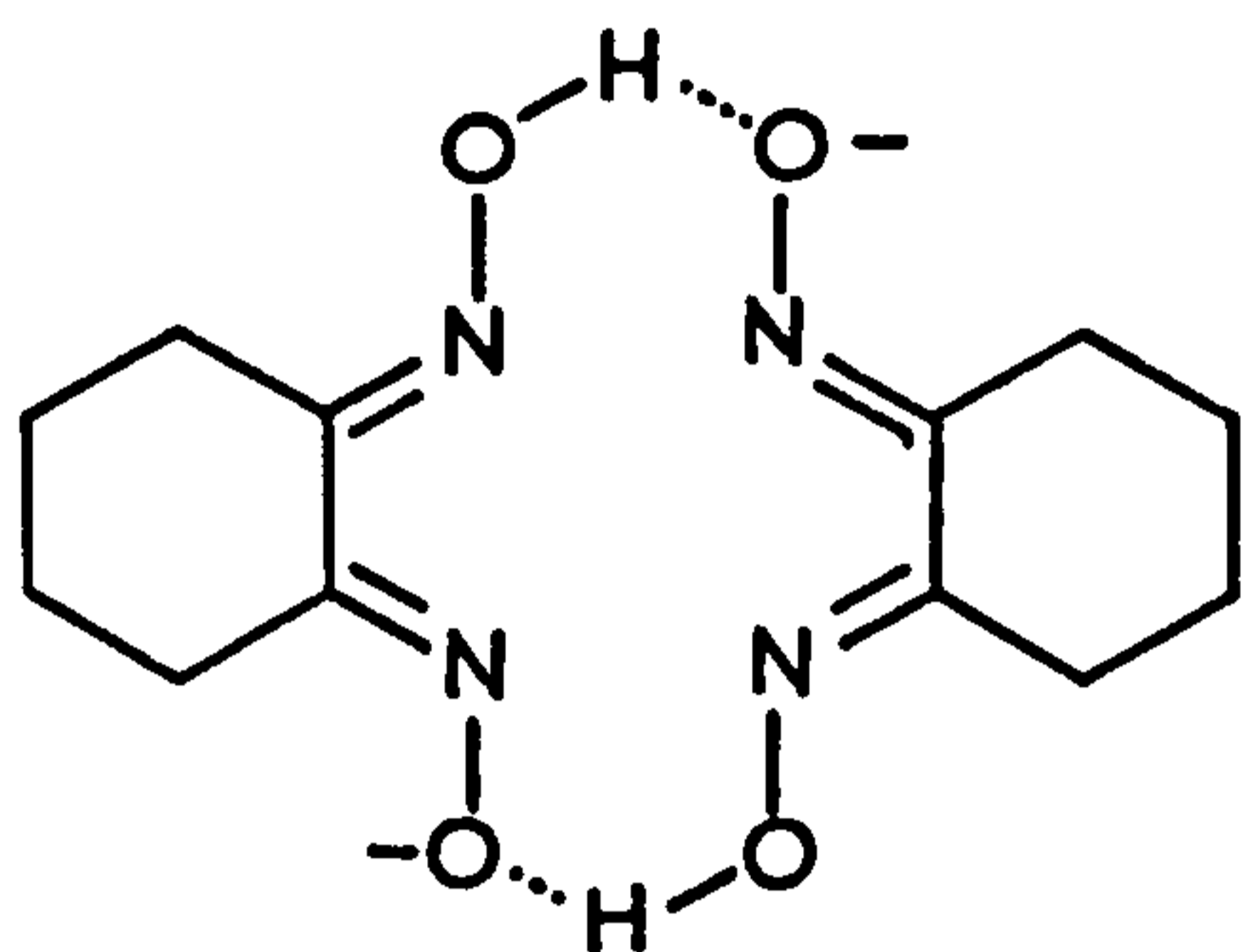
Throughout this thesis the term 'model ligand system' is used to represent such an equatorial ligand system.

When this work was commenced the only model ligand system which had been used successfully to stabilize cobalt-alkyl  $\sigma$ -bonds was the bis-dimethylglyoximate system (dmg) [1.11]<sup>34</sup> (N.B. see page 15 for systems not related to corrins)

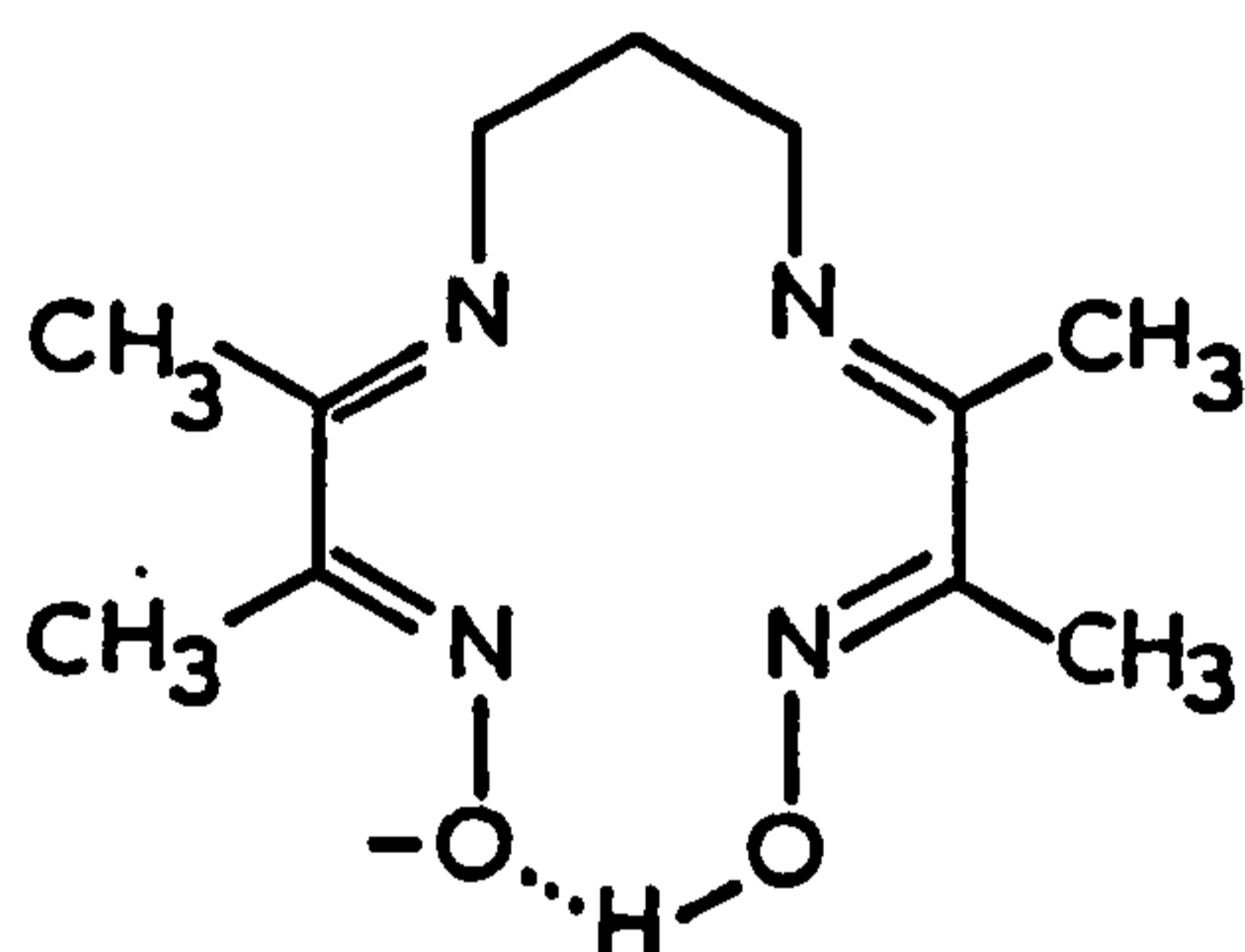


[1.11.]

However, in the last two years a number of other systems have appeared in the literature. Bis-(cyclohexane - 1,2-dionedioximato)<sup>34</sup>, [1.12] (c h d), and the mixed imine-oxime ligand bis-(diacetylmonoxime-imino) - 1,3 - propane,<sup>35</sup> [1.13] , are related to the bis-(dimethylglyoximato) system.

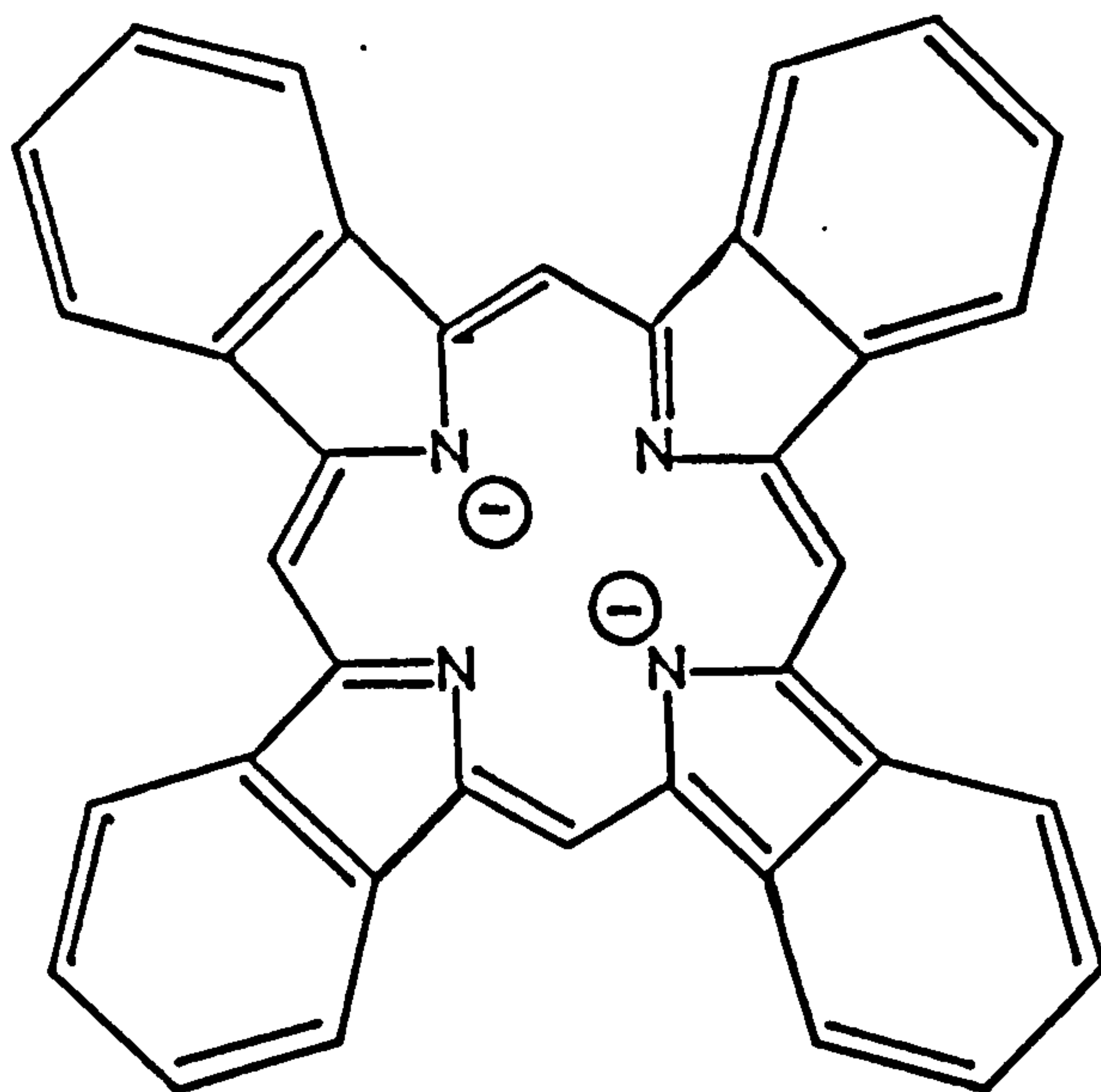


[1.12]

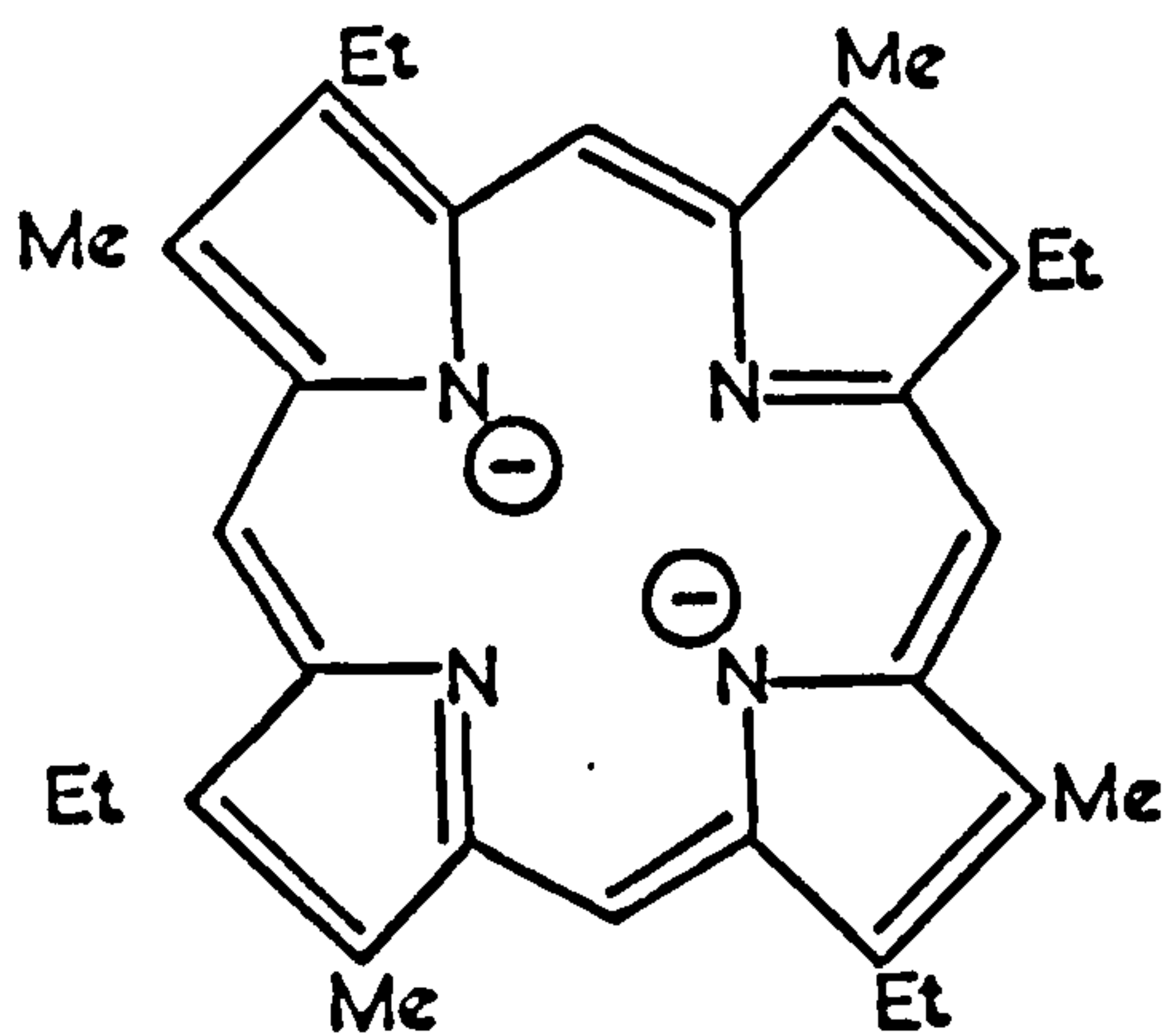


[1.13]

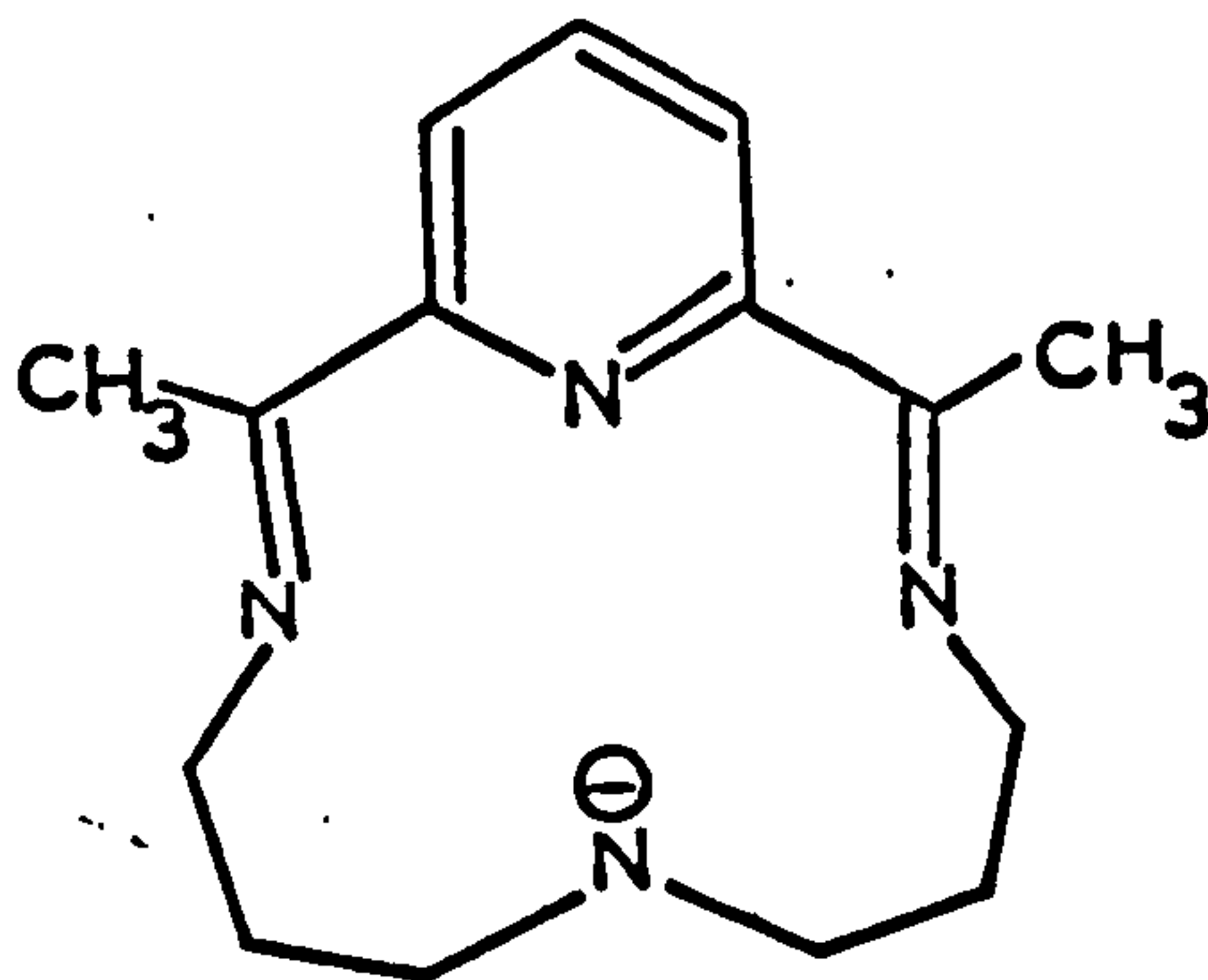
Application of the ligand N,N' - bis - (o-hydroxybenzylidene) - 1,2 - diaminoethane, [1.14] (salen), to the stabilization of cobalt-alkyl bonds was recorded almost simultaneously by Costa and his co-workers<sup>36</sup> and Calderazzo.<sup>37</sup> A similar 'N<sub>2</sub>O<sub>2</sub>' system, bis-(acetylacetonate)-ethylenediamine,<sup>38</sup> [1.15] (baen), had been earlier described by Costa's group.<sup>38</sup>



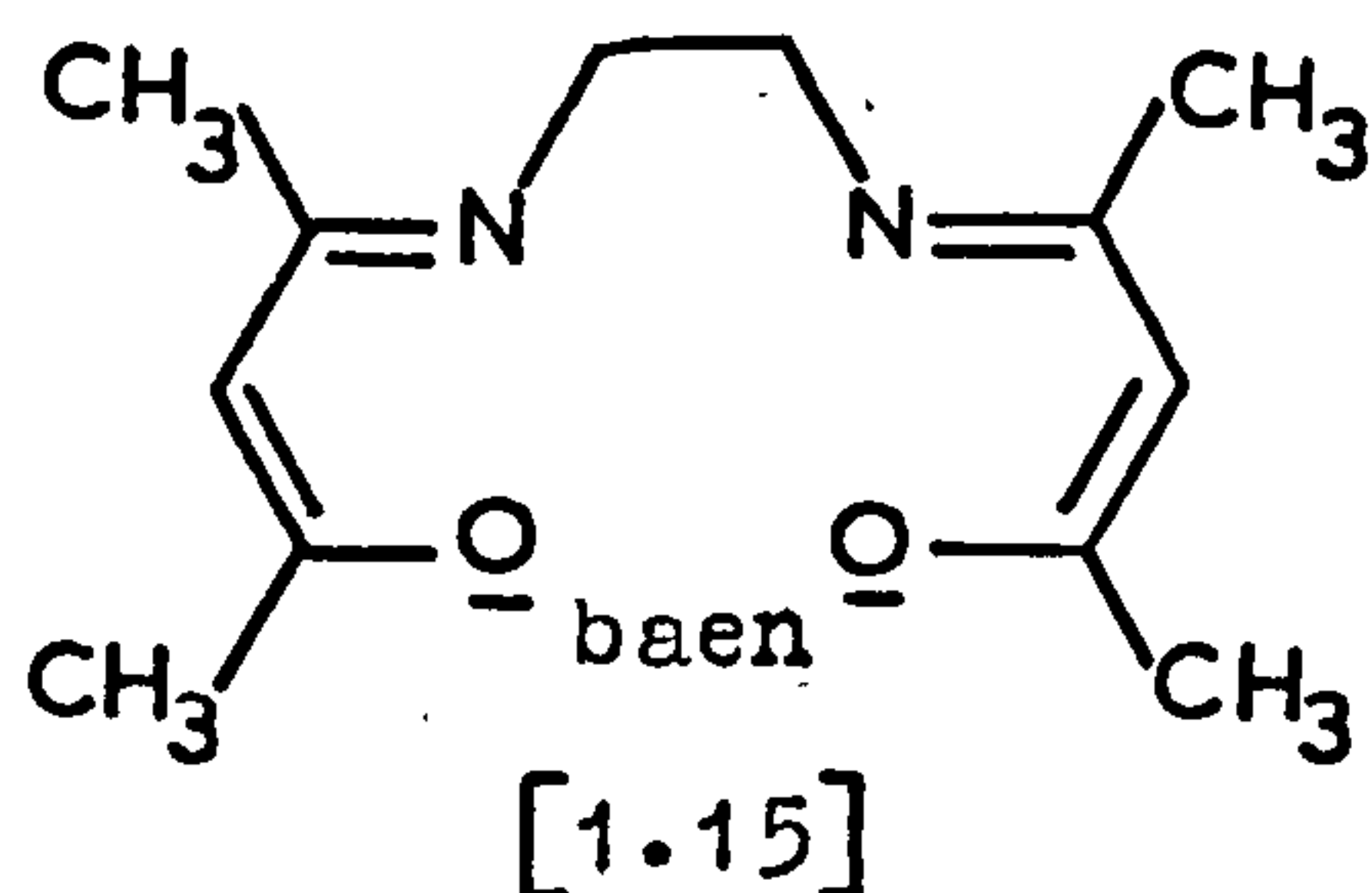
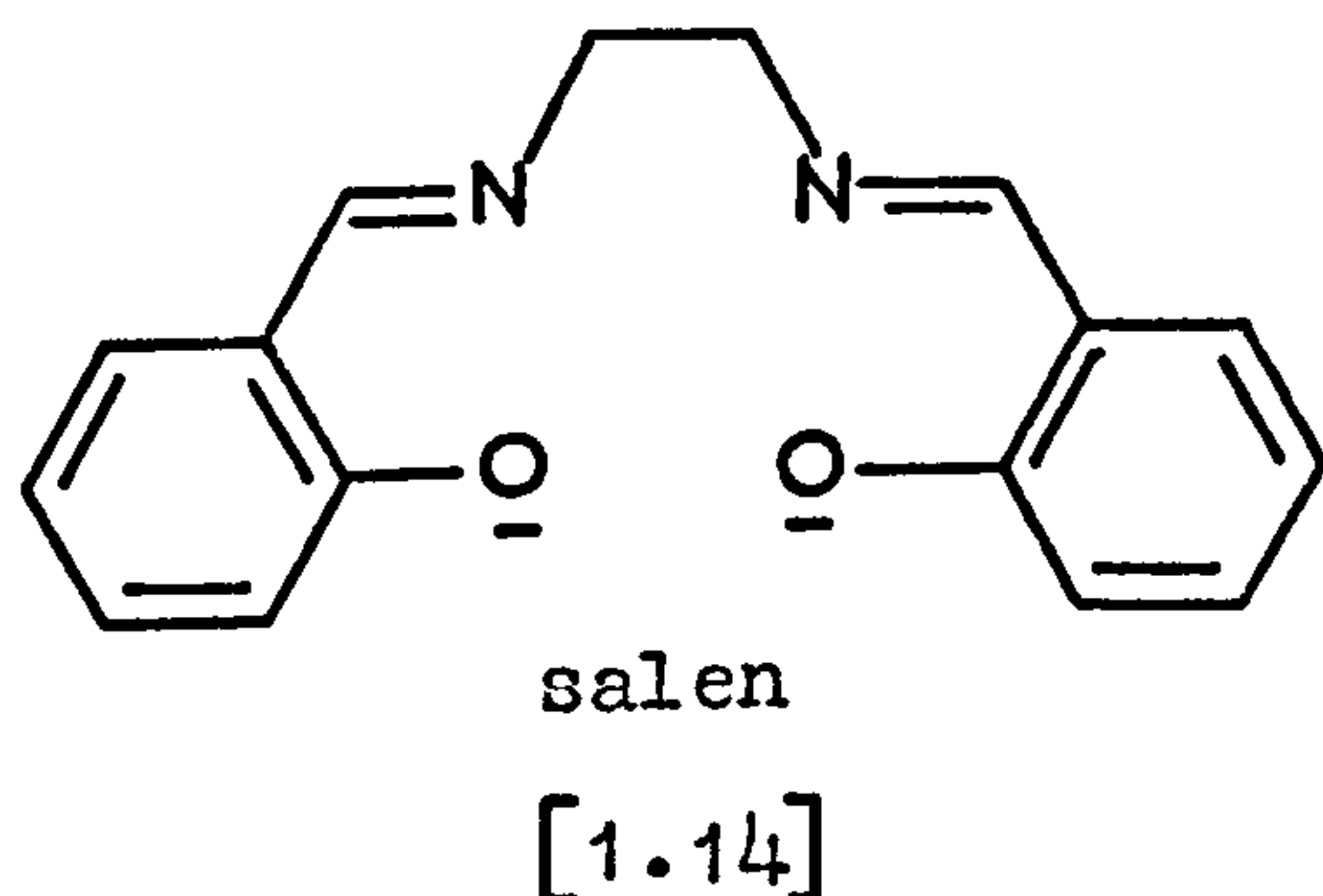
[1.17]



[1.16]



[1.18]



Some cyclic systems quite similar to the corrin system have been used, for example the porphyrin [1.16]<sup>39</sup>, and the phthalocyanine [1.17].<sup>40</sup> One other cyclic ligand system [1.18] has been recorded.<sup>41</sup>

### 1.2.1 Reduction of the model compounds.

For all the model compounds except [1.13] evidence has been presented for reduction to a compound which formally contains cobalt (I) and is analogous to vitamin B<sub>12s</sub>.<sup>33,37,39,40,41,42,43,44</sup> In most cases the reduced species is assumed to be anionic and there has been little convincing evidence to support the formulation of a hydrido-cobalt (III) complex. Studies with the salen system [1.14]<sup>45</sup> and cobalt (II) - 4,4',4'',4''' - tetrasulphonatophthalocyanine<sup>46</sup> have shown that the reduced (cobalt (I)) species are low-spin compounds

showing small residual paramagnetism. A solution containing the cobalt (I) - 4,4',4'',4''' - tetra-sulphonatophthalocyanine anion showed no evidence of a proton magnetic resonance absorption which could be attributed to the hydrido group.<sup>46</sup>

A preliminary report<sup>47</sup> of controlled potential reduction studies on some model compounds supports the assignment of a formal valency of one to the cobalt atom in the active nucleophilic reduced forms. It also suggests that the ease of reducing the cobalt (III) to cobalt (I) forms decreases in the order  $\text{dmg} > \text{salen} > \text{baen}$ .

The electrons introduced into the salen [1.14] compound on reduction are apparently<sup>45</sup> delocalized to the ligand system, and particularly to the azomethine bond. Infrared and magnetic evidence were used<sup>45</sup> to support this hypothesis. Since all the model compounds showing evidence for the existence of cobalt (I) species have some conjugation between the axial donor atoms, it is likely that some delocalization of the electrons to the ligand systems occurs in all the reduced forms.

### 1.2.2 Model Compounds of vitamin B<sub>12</sub> coenzyme.

These are the compounds type [1.10] (page 9 )

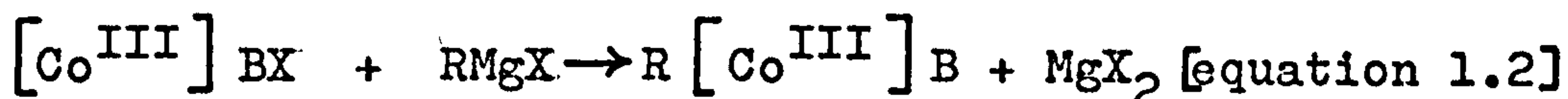
with R representing a  $\sigma$ -bonded alkyl group. There are two main synthetic routes to these alkyls, which correspond closely to those described for the syntheses of alkyl cobalamins (page 5 and 8).

The first, (equation [1.1]) involves the reaction of a reduced, nucleophilic species (c.f. vitamin B<sub>12s</sub>) presumed to contain cobalt (I) with an alkyl halide.



[ ] represents the equatorial ligand system.

The second is the reaction of a Grignard reagent with a cobalt (III) containing species as in equation 1.2 .

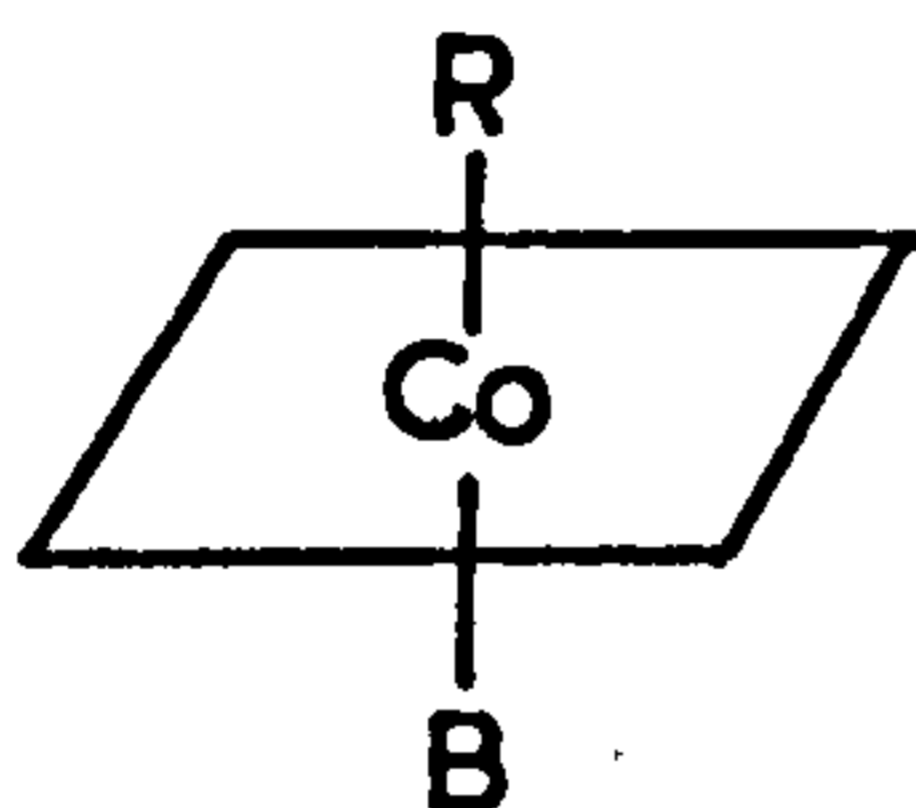


### 1.2.3 Ligand replacement in model compounds.

The cis- and trans- effects observed for the cobalamins (see page 3) have been studied in 'model' compounds, mainly using N.M.R. techniques, and evidence for transmission of electronic effects through the cobalt (III) atom has been presented.

A cis- effect has been observed for the chemical shift of the proton magnetic resonance of

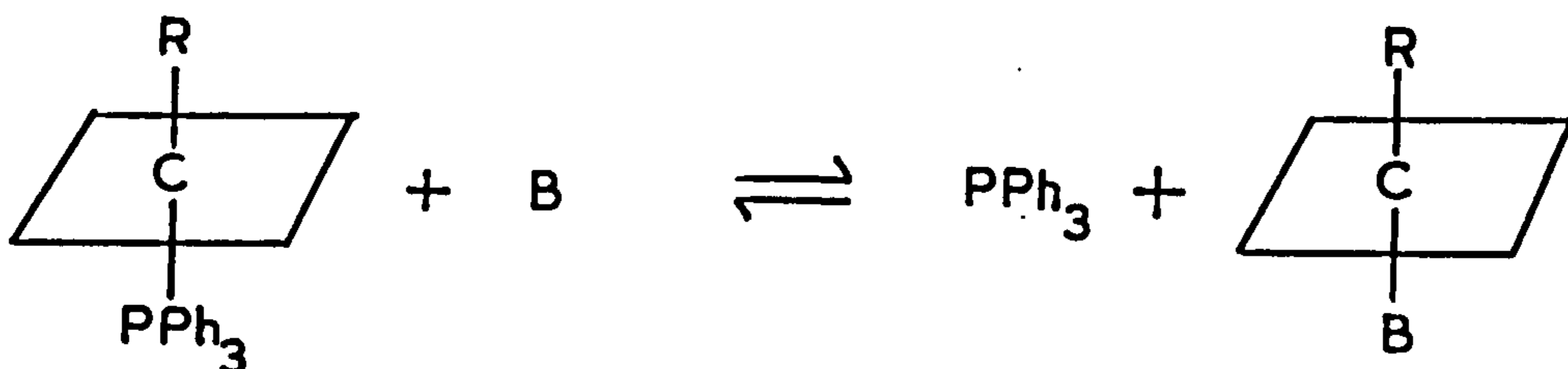
equatorial system groups in dmg,<sup>48,49</sup> salen<sup>50</sup> and baen<sup>50</sup>. The chemical shift of the methyl groups in the dmg system has been correlated with the Hammett  $\sigma_{\text{para}}$  functions of axial substituents R<sup>48</sup> (see [1.10] ), and the methine resonances in baen with the  $\sigma$ -donor properties of both substituents R and B<sup>50</sup> (see [1.10] ).



[1.10]

Both cis- and trans- transmission through the cobalt-(III) atom is indicated by the observed P<sup>31</sup>H spin-spin coupling, giving doublet proton magnetic resonances for both the dmg methyl groups and the alkyl group (R) for a series of model compounds with the dmg system having B = PPh<sub>3</sub> in [1.10].<sup>51</sup> Such compounds lend themselves to the study of trans-effects in the equilibria (equation [1.3] ) using N.M.R spectroscopy.<sup>49,51</sup> Exchange of triphenyl phosphine by a large variety of different bases has been studied.<sup>49</sup> Acceptor properties of the alkyl groups (R) favour the coordination of stronger  $\sigma$ -donor bases. Some steric effects were

found to operate, and the displacement of triphenyl phosphine was less favourable for bases (B) with bulky substituents.<sup>49</sup>



[equation 1.3]

Equilibria followed using electronic spectroscopy<sup>52</sup> for the baen and salen systems indicate strong trans - effects, but no details have yet been given to the nature of the effect.

It is hoped that dipole moment studies being carried out in this laboratory might also demonstrate trans-electronic transmission through the cobalt (III) ion.

### 1.3 Other ligand systems stabilizing low valency states and alkyls of cobalt.

There are other ligand systems which stabilize low valency states and alkyls of cobalt, which do not



resemble the equatorial vitamin B<sub>12</sub> system. These are the ligands which are often encountered in organometallic chemistry, and cannot be dealt with in length here, for example phosphines<sup>53, 54, 55</sup> cyclopentadienyl<sup>54, 55, 56</sup>, and carbonyl.<sup>56, 57</sup>

More unusual are the pentacyanatocobalt systems. Reaction of the pentacyanocobaltate(II) ion in water with alkyl halides gives solutions containing the alkylpentacyanocobaltate(III) ion (equation [1.4])<sup>58, 59, 60, 61</sup>



[equation 1.4]

The pentacyanohydridocobalt(III) ion,  $[\text{HCo}^{\text{III}}(\text{CN})_5]^{3-}$ , has been isolated<sup>62</sup> from aqueous solution by precipitation as the compound  $\text{Na}_2\text{CsCo}(\text{CN})_5\text{H}$

#### 1.4 References.

1. E Lester-Smith, "Vitamin B<sub>12</sub>", 3rd Ed., Methuen, 1965.
2. R. Bonnett, Chem. Rev., 63, 573, (1963).
3. K. Bernhauer, O. Müller and F. Wagner, Angew. Chem. (Internat. Ed.) 3, 200, (1964).

4. H.A. Barker, *Biochem. J.*, 105, 1, (1967)
5. Dorothy C. Hodgkin et al., *Proc. Roy. Soc. A.*, 242, 228, (1957).
6. Dorothy C. Hodgkin et. al., *Proc. Roy. Soc. A.*, 251, 306 (1959).
7. H.A. Barker et al., *J. Biol. Chem.*, 235, 480, (1960).
8. H.A. Barker, H. Weissbach and R.D. Smyth, *Proc. Natl. Acad. Sci. U.S.*, 44, 1093, (1958).
9. P. George, D.H. Irvine and S.C. Glauser, *Ann. N.Y. Acad. Sci.*, 88, 393, (1960).
10. J.A. Hill, J.M. Pratt and R.J.P. Williams, *J. Theoret. Biol.*, 3, 423, (1962).
11. As ref 2, page 575.
12. D. Perlman and J.I. Toohey, *Arch. Biochem. Biophys.*, 124, 462, (1968).
13. J.I. Toohey, *Proc. Natl. Acad. Sci. U.S.* 54, 934, (1965).
14. J.M. Pratt and R.G. Thorp, *J. Chem. Soc. (A)*, 187, (1966).
15. H.A.O. Hill, J.M. Pratt and R.J.P. Williams, *J. Chem. Soc.*, 2859, (1965).
16. H.A.O. Hill, B.E. Mann, J.M. Pratt and R.J.P. Williams, *J. Chem. Soc. (A)*, 564, (1968).
17. G.C. Hayward, H.A.O. Hill, J.M. Pratt, N.J. Vanston and R.J.P. Williams, *J. Chem. Soc.*, 6485, (1965).
18. R.A. Firth, H.A.O. Hill, J.M. Pratt, R.G. Thorp and R.J.P. Williams, *Chem. Comm.* 400, (1967).

19. F. Wagner and K. Bernhauer, *Ann. N.Y. Acad. Sci.*, 112, 580, (1962).
20. As reference 2, page 582.
21. J.E. Falk, "Porphyrins and Metalloporphyrins", Elsevier, 1964, page 73.
22. P. Day, *Theoret. Chim. Acta.*, 7, 328, (1967)
23. G.E. Boxer and J.C. Rickards, *Arch. Biochem. Biophys.*, 30, 382, (1951).
24. H. Schmid, A. Ebnöther and P. Karrer, *Helv. Chim. Acta*, 36, 65, (1953).
25. E.A. Kaczka, R.G. Denkwalter, A. Holland and K. Folkers, *J. Amer. Chem. Soc.*, 73, 335, (1949)
26. H.A.O. Hill, J.M. Pratt and R.J.P. Williams, *Chem. and Ind.*, 197, (1964).
27. J.A. Knowles, *Diss Abs.*, 27B, 1385, (1966).
28. A.W. Johnson, L. Mervyn, N. Shaw and E. Lester Smith *J. Chem. Soc.*, 4146 (1963).
29. G.H. Beavan and E.A. Johnson, *Nature*, 176, 1264 (1955).
30. O. Schindler, *Helv. Chim. Acta*, 34, 1356, (1951).
31. As reference 2, page 590.
32. M.L.H. Green, "Organometallic Compounds", Vol. 2, Methuen, 1968, page 205.
33. G.N. Schrauzer and J. Kohnle, *Chem. Ber.*, 97, 3056, (1964).
34. G.N. Schrauzer and R.J. Windgassen, *J. Amer. Chem. Soc.*, 88, 3738, (1966).

35. G. Costa and G. Mestroni, Tetrahedron Letters, 4005, (1967).
36. G. Costa, G. Mestroni and L. Stefani, J. Organometal Chem., 7, 493, (1967).
37. F. Calderazzo and C. Floriani, Chem. Comm., 139, (1967).
38. G. Costa, G. Mestroni, G. Tauzher and L. Stefani, J. Organometal. Chem., 6, 181, (1966).
39. D.A. Clarke, D. Dolphin, R. Grigg, A.W. Johnson and H.A. Pinnock, J. Chem. Soc. (C), 881, (1968).
40. P. Day, H.A.O. Hill and M.G. Price, J. Chem. Soc. (A), 90, (1968).
41. E.I. Ochiai and D.H. Busch, Chem. Comm. 905, (1968).
42. G. Costa and G. Mestroni, Tetrahedron Letters, 1783, (1967)
43. G. Costa and G. Mestroni, J. Organometal. Chem., 11, 325, (1968)
44. G. Costa, G. Mestroni and G. Pellizer, J. Organometal Chem., 11, 333, (1968).
45. C. Floriani, M. Puppis and F. Calderazzo, J. Organometal Chem., 12, 209, (1968).
46. D.H. Busch, J.H. Weber, D.H. Williams and N.J. Rose, J. Amer. Chem. Soc., 86, 5161, (1964).
47. G. Costa, A. Puxeddu and G. Tauzher, Inorg. Nuclear Chem. Letters, 4, 319 (1968).
48. H.A.O. Hill, K.G. Morallee and R.E. Collis, Chem. Comm., 888 (1967).

49. G. Swinden, D. phil. Thesis, York, 1967.
50. H.A.O. Hill, K.G. Morallee, G. Pellizer, G. Mestroni and G. Costa, *J. Organometal Chem.*, 11, 167, (1968).
51. Michael Green, R.J. Mawby and G. Swinden, *Chem. Comm.*, 127, (1967).
52. G. Costa et al., Abstracts, 3rd Internat. Symposium on Organometallic Chemistry, Munich, 1967, page 116.
53. J. Chatt and B.L. Shaw, *J. Chem. Soc.*, 289, (1961).
54. H. Yamakazi and N. Hagihara, *Bull. Chem. Soc. Japan*, 38, 2212, (1965).
55. R.B. King, *Inorg. Chem.*, 5, 82, (1966).
56. P.M. Treichel and G.P. Werber, *J. Organometal Chem.*, 2, 157, (1967).
57. R.F. Heck, *Adv. Organometal Chem.*, 4, 243, (1966).
58. J. Halpern and J.P. Maher, *J. Amer. Chem. Soc.*, 86, 2311, (1964).
59. J. Halpern and J.P. Maher, *J. Amer. Chem. Soc.*, 87, 5361, (1965).
60. M.O. Johnson, M.L. Tobe and Lai Yoong Wong, *J. Chem. Soc. (A)*, 491, (1967).
61. M.D. Johnson, M.L. Tobe and Lai Yoong Wong, *J. Chem. Soc. (A)*, 929, (1968).
62. R.G.S. Banks and J.M. Pratt, *Chem. Comm.* 776, (1967).

## Chapter 2. Choice of 'Model' Ligand Systems.

- 2.1 Criteria for good 'model' ligands.
- 2.2 General structure of systems chosen for study.
  - 2.2.1 Planarity of the ligand donor atoms.
  - 2.2.2 Loss of protons to give anionic ligands.
  - 2.2.3 Conjugation between the ligand donor atoms.
  - 2.2.4 Macrocyclic 'model' ligands.
  - 2.2.5 Ligand field splitting.
- 2.3 Related ligands with saturated nitrogen donors.
- 2.4 General layout of this thesis.
- 2.5 References.

### 2. Choice of 'model' ligand systems.

The properties of vitamin B<sub>12</sub> and various 'model' compounds have been discussed in chapter 1. When this work was commenced the only 'model' compounds which had appeared in the literature were those of the bis-(dimethylglyoximato) type (see page 9), which had been studied by Schrauzer and co-workers.

It was decided to synthesize some new ligand systems, and to test their properties as substitutes for the corrin system of vitamin B<sub>12</sub>. The choice of type of ligand molecule was based on the following criteria, which are all present in the corrin and

bis(dimethylglyoximato) systems.

### 2.1 Criteria for good 'model' ligands.

(1) The ligand must have four nitrogen donor atoms capable of adopting a square-planar arrangement about a metal atom.

(2) When complexed the ligand must be anionic.

(3) The ligand must show some conjugation between its donor atoms.

Of the 'model' systems which have recently appeared in the literature, most have four nitrogen donors, all are dianionic when complexed to cobalt except [1.13], page 10 and [1.18], page 11 which are monoanionic, and all show some conjugation between the donor atoms.

In order to study the relative importance of these properties it was hoped to study ligand systems which differed in the following ways.

(a) Deviations from square-planarity.

(b) Variation in conjugation through the ligand.

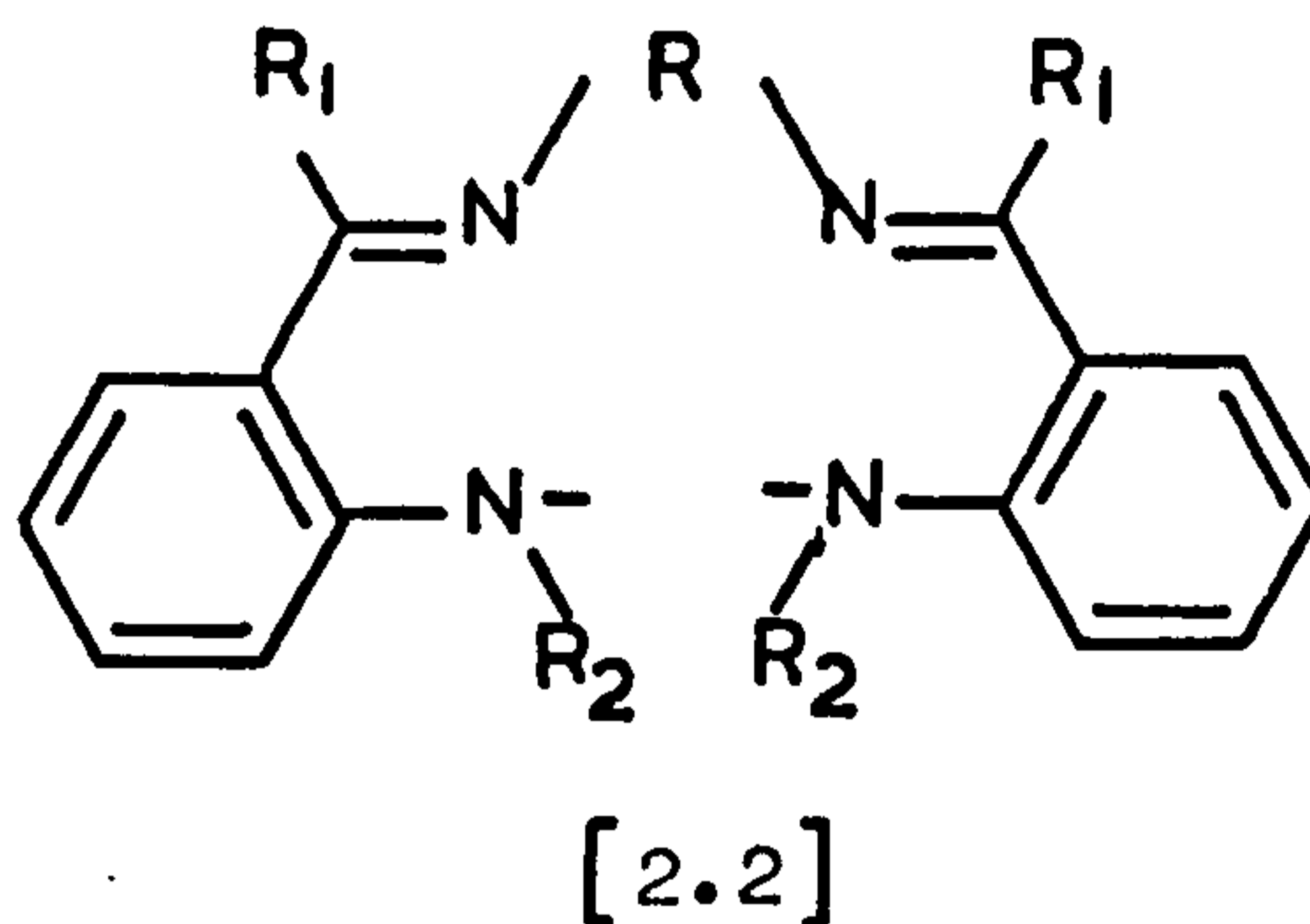
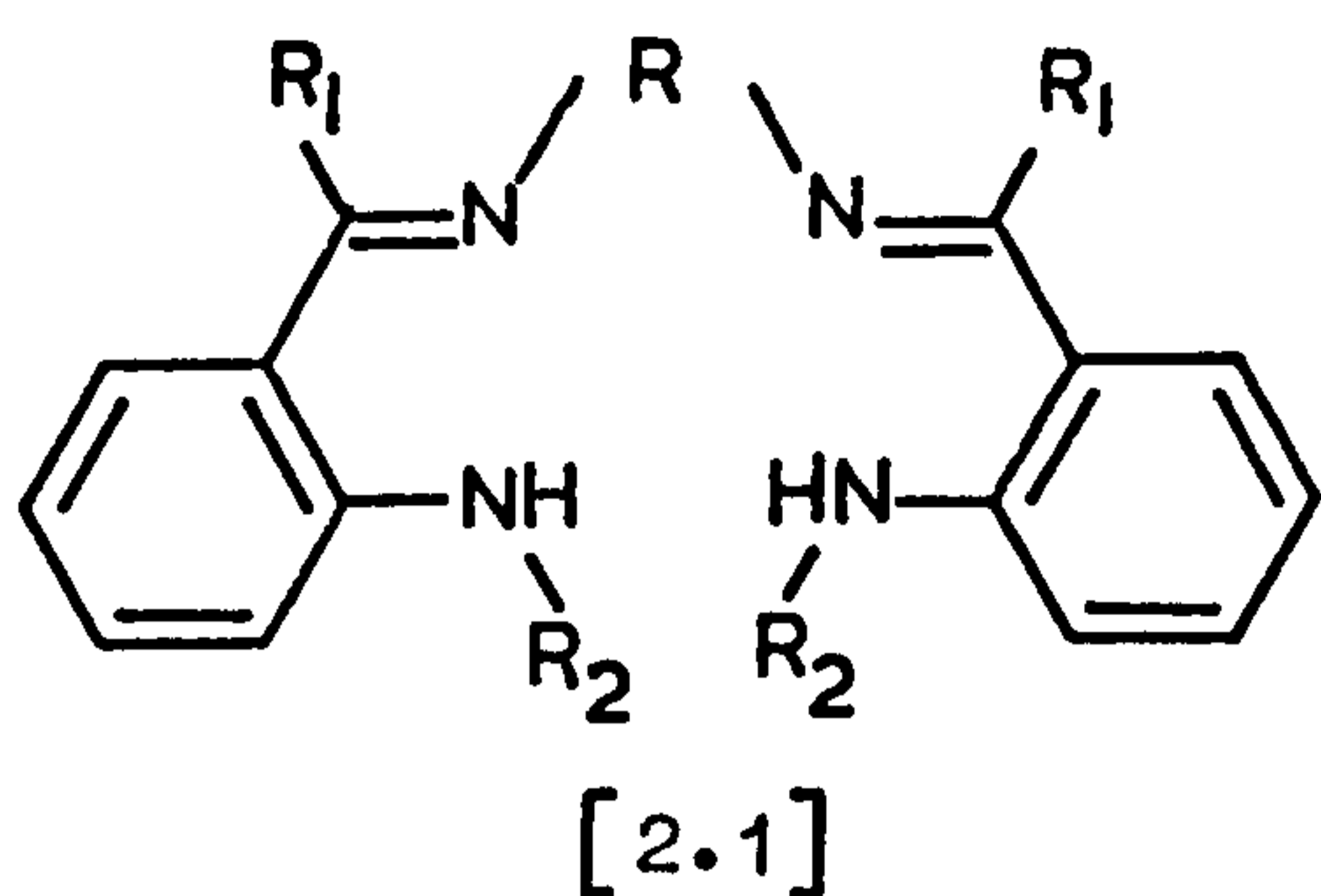
(c) Acyclic and cyclic ligands.

(d) Variation in ligand field splittings.

### 2.2. General structure of systems chosen for study.

For the reasons outlined above, it was decided to study ligands of the general structure [2.1] which could lose protons from the aromatic amine groups

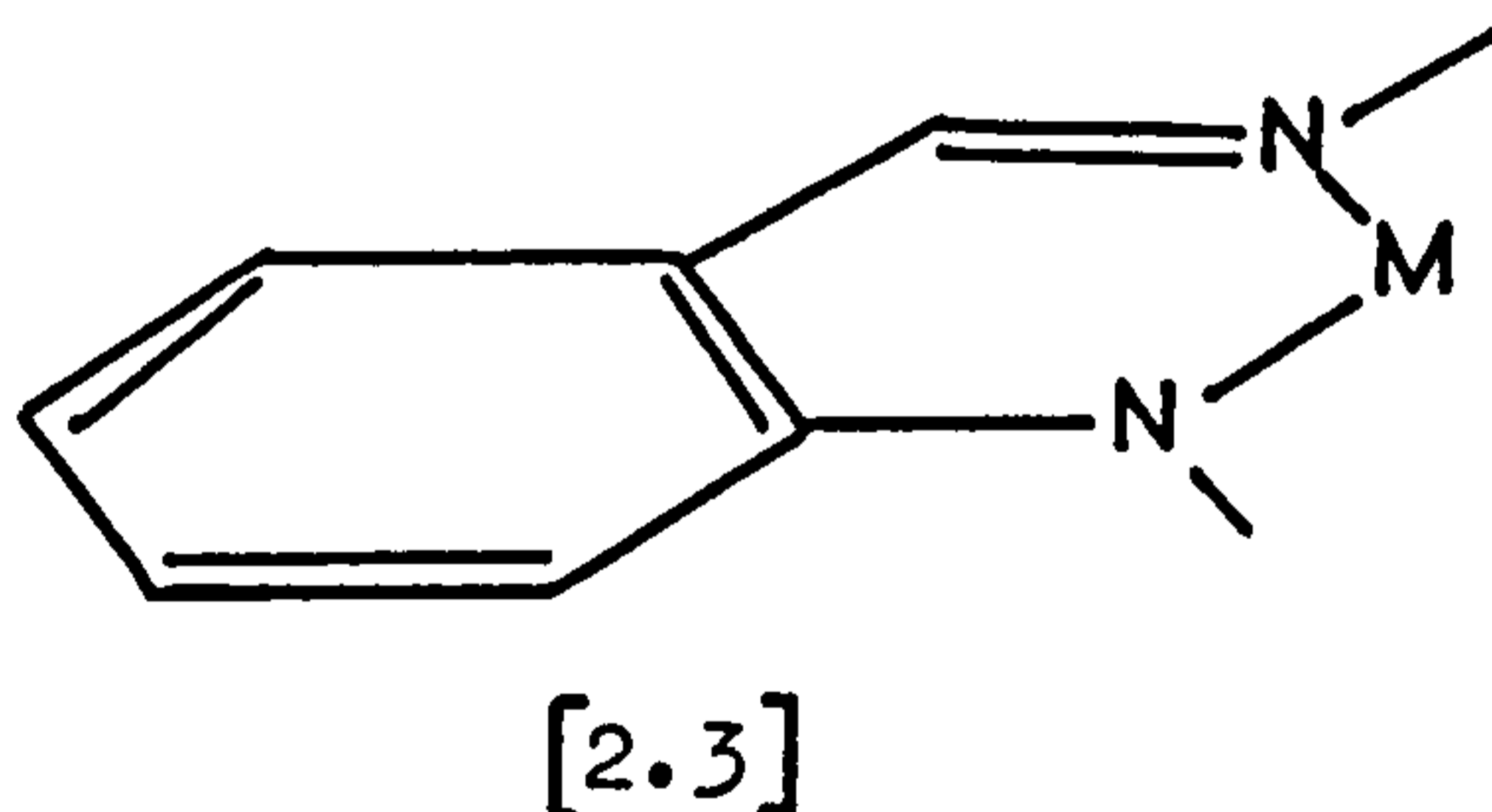
to give the dianionic ligands [2.2]



The possibilities of ligands [2.1] fulfilling the criteria of section 2.1 will be discussed in the following sections.

### 2.2.1 Planarity of the ligand donor atoms.

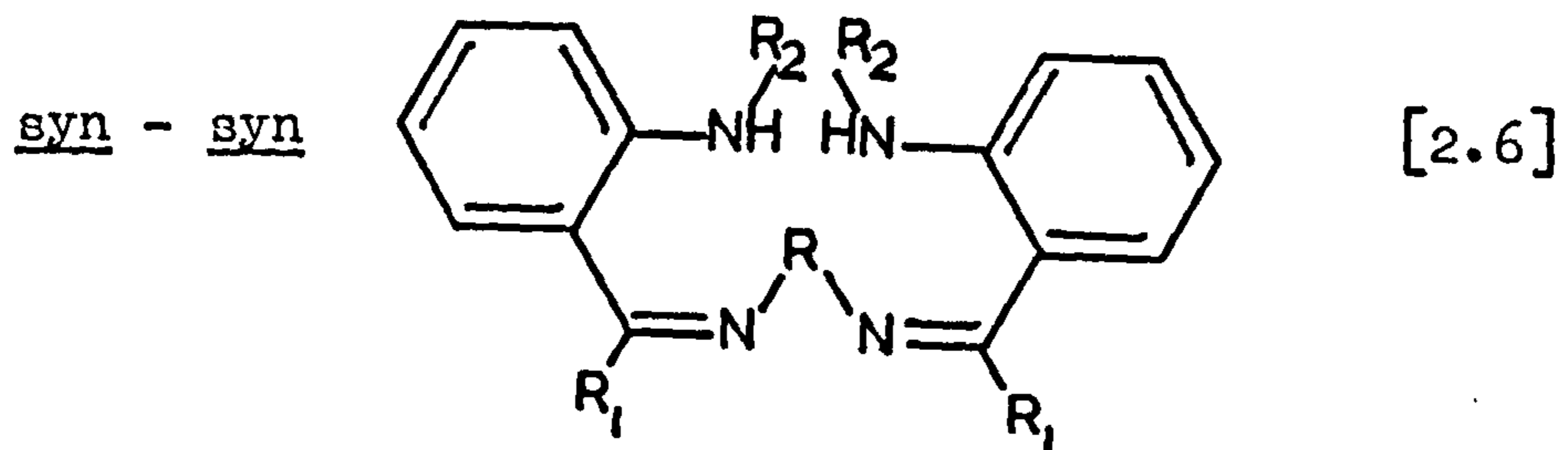
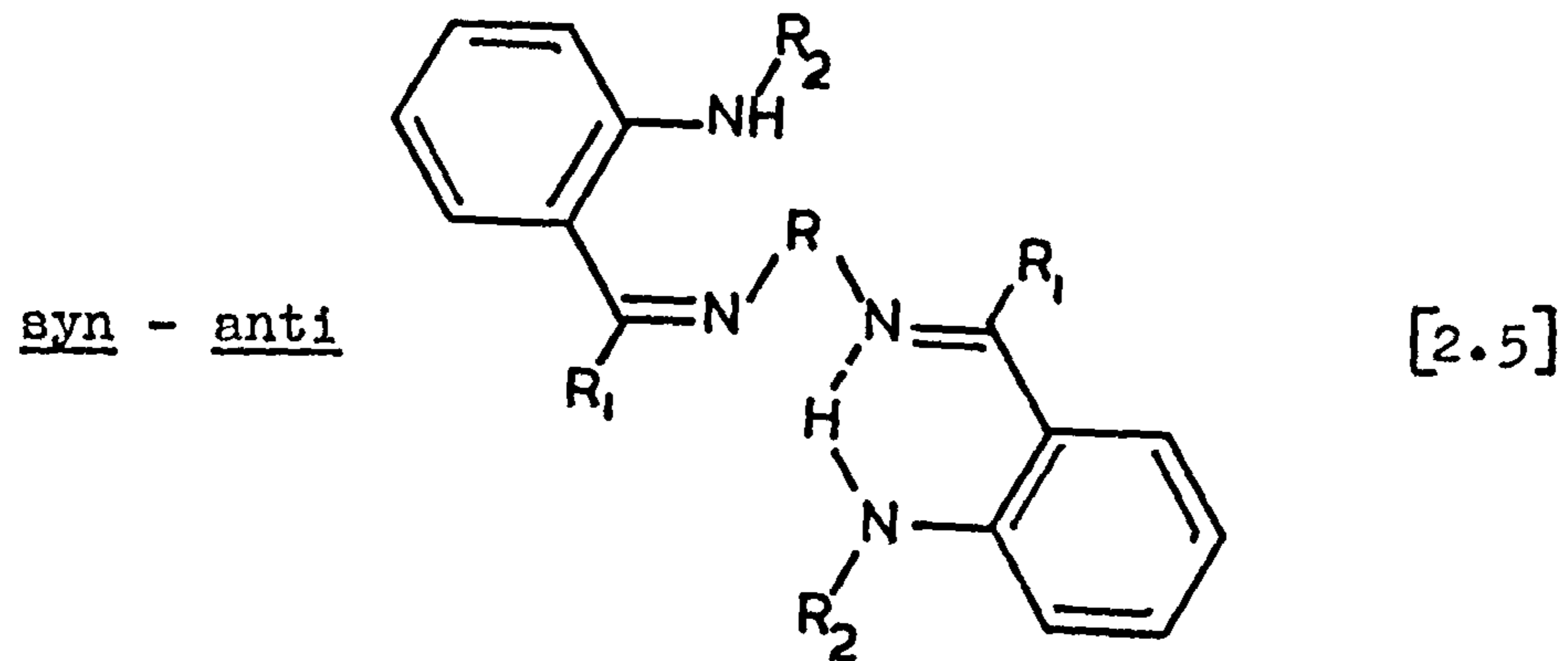
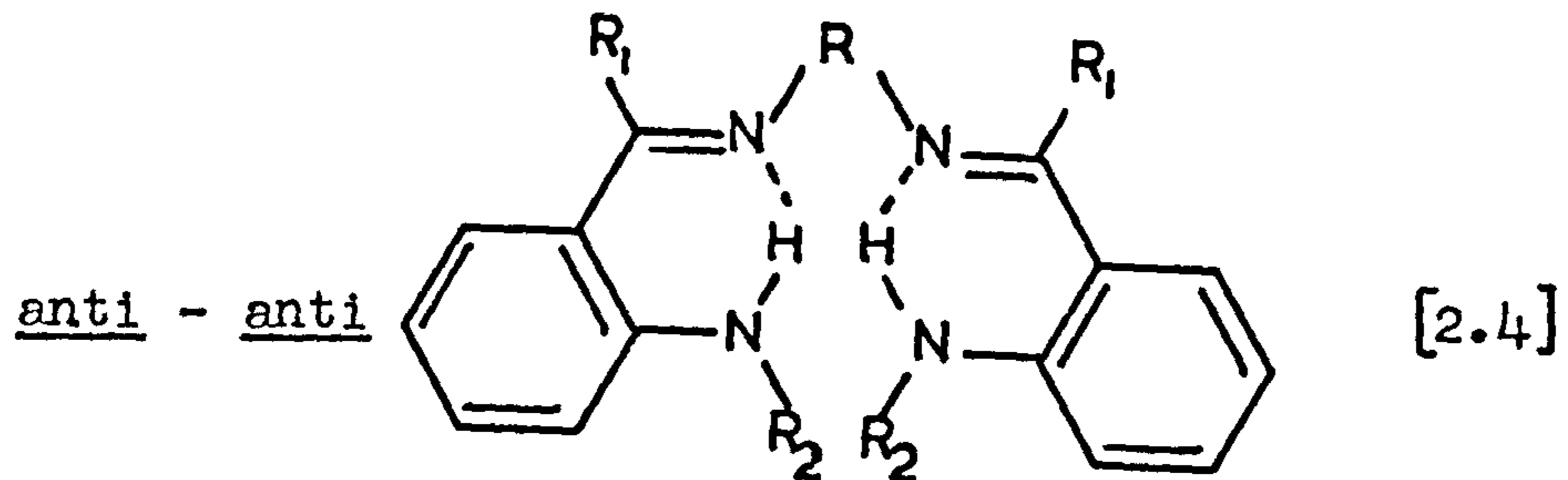
The bonds from the nitrogen atoms of fragment [2.3] to the metal ion should lie in the plane of the ring and the two nitrogen atoms, since the most probable hybridization for both nitrogen atoms is  $sp^2$  when bonded in this way.




In order that all four nitrogen atoms lie in the same plane it is necessary that the bridging group (R) between the fragments [2.3], should allow both



o-aminophenyl  
and R groups  
arranged:



azomethine groups to lie in the same plane as the two azomethine nitrogen donors and the metal atom. For a simple polymethylene bridging group ( $R = -(CH_2)_n^-$ ) it has been shown<sup>1</sup> that to increase the length of the bridge between two adjacent azomethine donors beyond 3 atoms ( $n > 3$ ) cases "serious steric difficulties" for the planar distribution of the metal atom and the two azomethine groups.

When  $R = -CH_2CH_2-$  or  we would expect the least strained arrangement of the ligand with its four nitrogen donors in a plane about the metal atom.

It was hoped that substitution of suitable groups for  $R_1$  and  $R_2$  might produce steric constraints which would favour deviation from square-planarity.

An azomethine group should show similar properties with regard to isomerism as a carbon-carbon double bond. Hence for a di-imine of the type [2.1] (p 23) there are formally three possible isomers [2.4], [2.5] and [2.6], and only one of these [2.4] theoretically has the chance of adopting a square-planar arrangement of its four nitrogens about a single metal atom.

In practice the anti-anti form [2.4] is expected to predominate since in this form both imine groups will be hydrogen-bonded to the o-amino groups of the aromatic

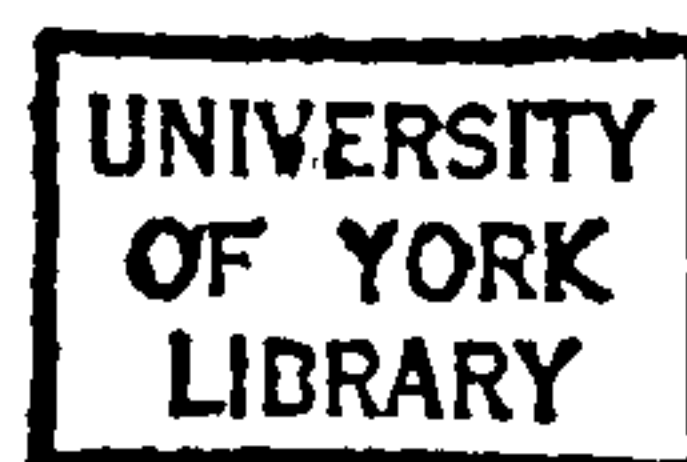
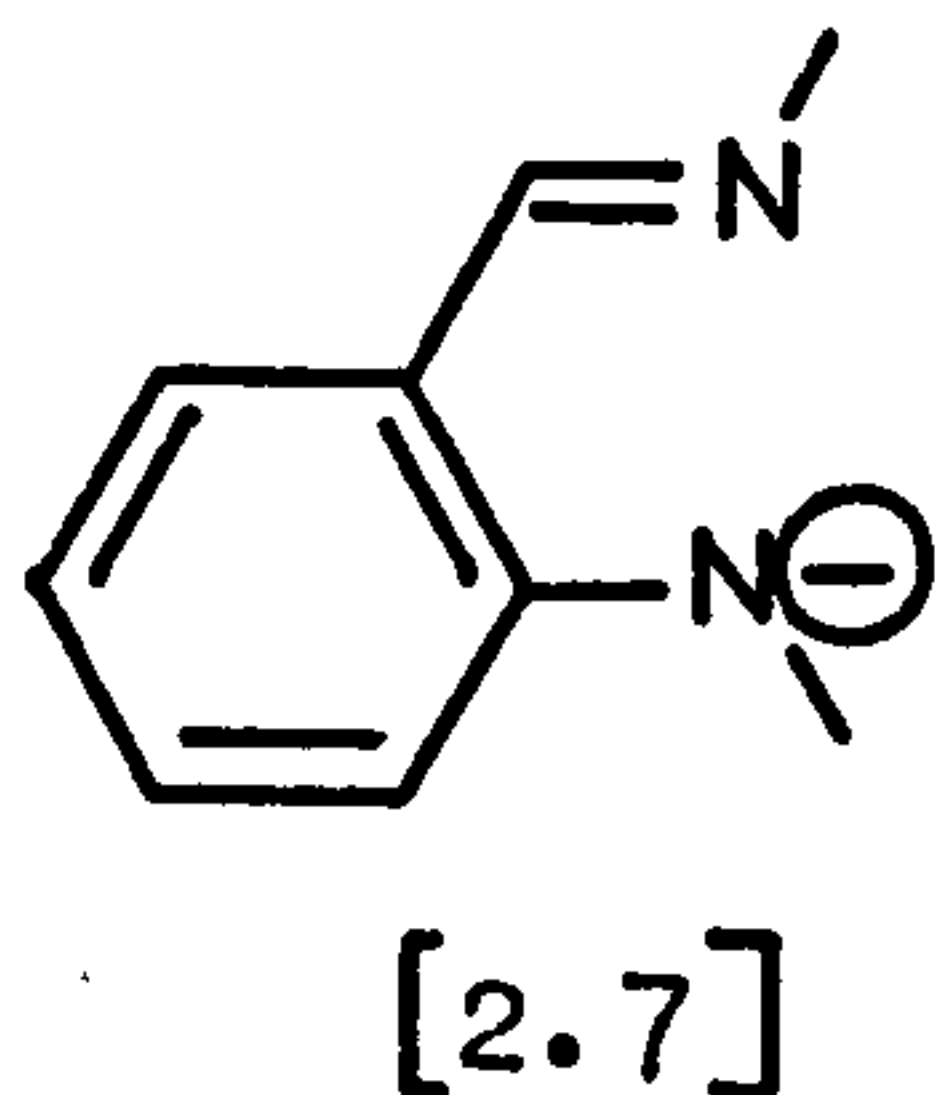
rings. Also interconversion of imines is quite fast in solution<sup>2</sup>, and so non-anti-anti forms will be able to adopt a square-planar arrangement about a metal ion in solution.

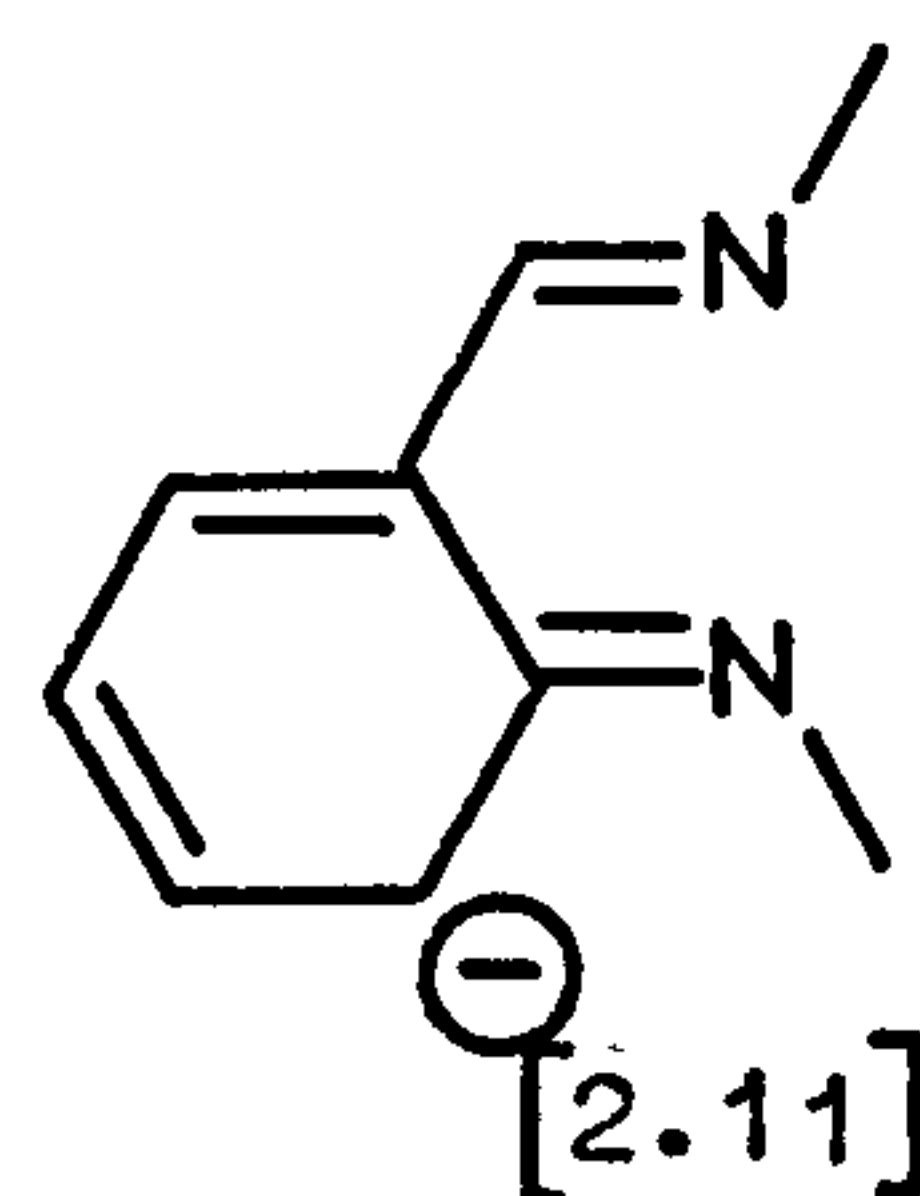
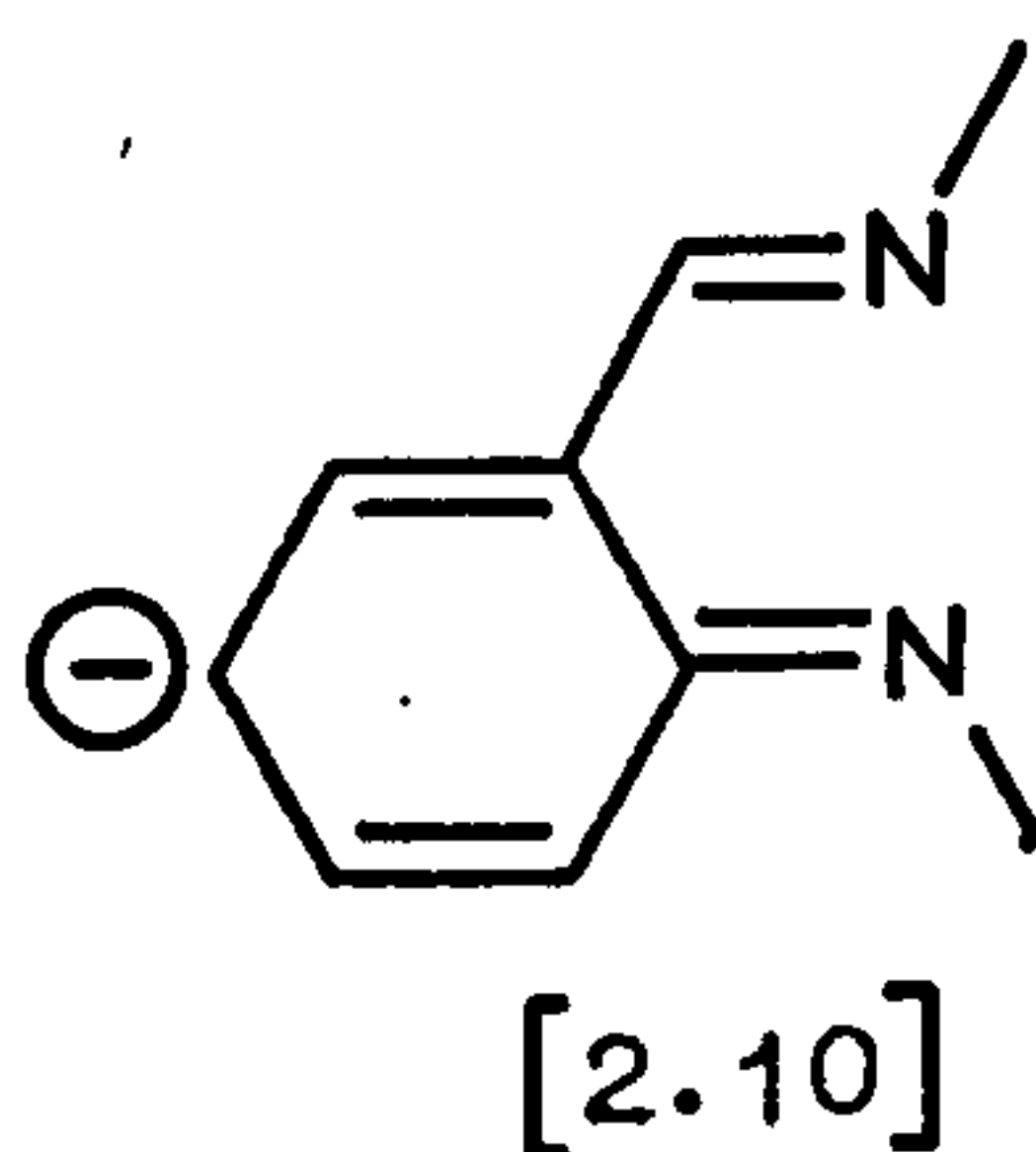
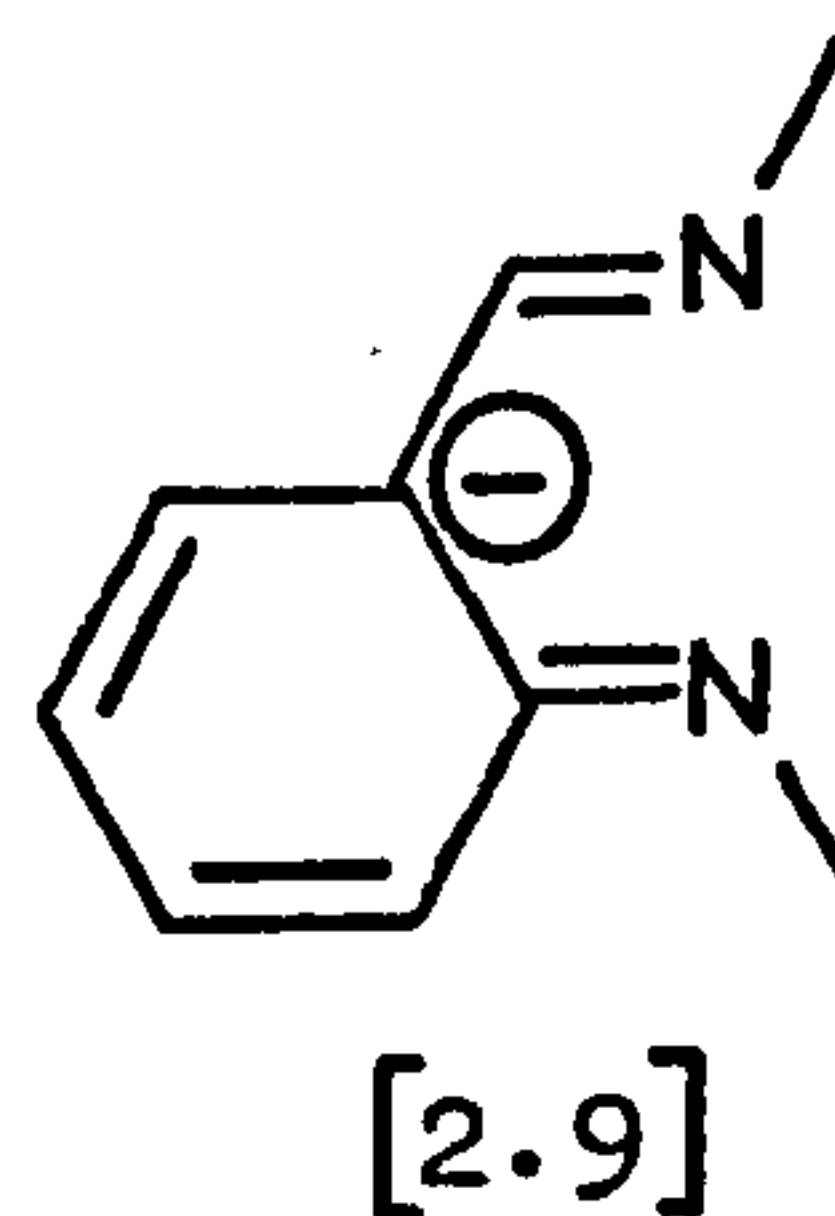
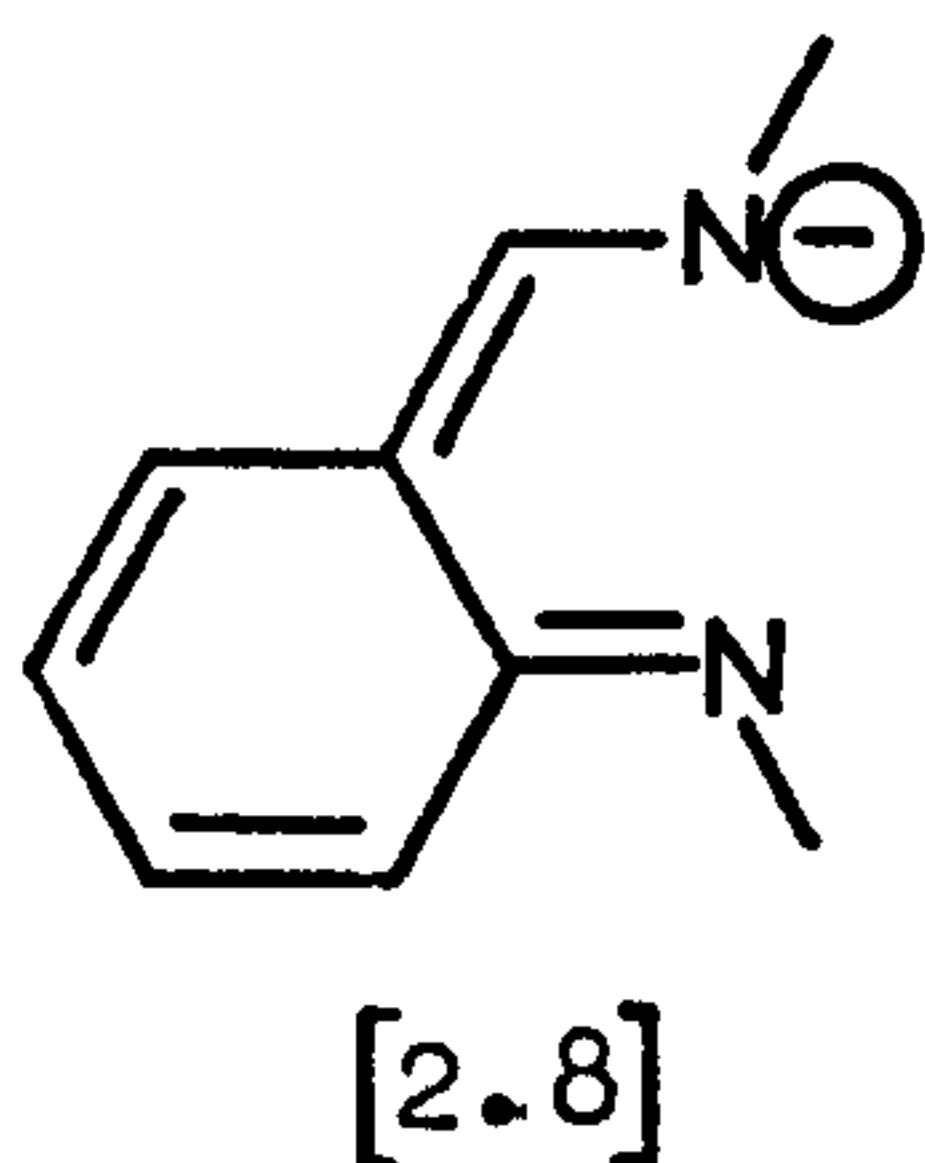
### 2.2.2 Loss of protons to give anionic ligands.

Pfeiffer and co-workers<sup>3</sup> showed that N,N'-bis(o-amino-benzylidene) - 1,2-diaminoethane ( [2.1] , R = -CH<sub>2</sub>CH<sub>2</sub> -, R<sub>1</sub> = R<sub>2</sub> = H) lost two protons on reaction with copper or nickel ions in basic media, and gave uncharged complexes (see also p. 68 ). It was hoped that by adjusting the reaction media the ligands could be made to lose protons on complexation with cobalt.

### 2.2.3 Conjugation between the ligand donor atoms.

The basic fragment [2.7] is conjugated between its two nitrogen atoms. The negative charge on the amine nitrogen atom can be delocalized to the azomethine nitrogen atom (resonance structure [2.8] ), or to the aromatic ring (resonance structures [2.9] , [2.10] and [2.11] )





In the full molecule ([2.1] p 23) conjugation between the nitrogen donors can be increased by using an unsaturated bridging group R, e.g.  $R = \text{C}_6\text{H}_5$  gives all four nitrogen atoms in a conjugated system.

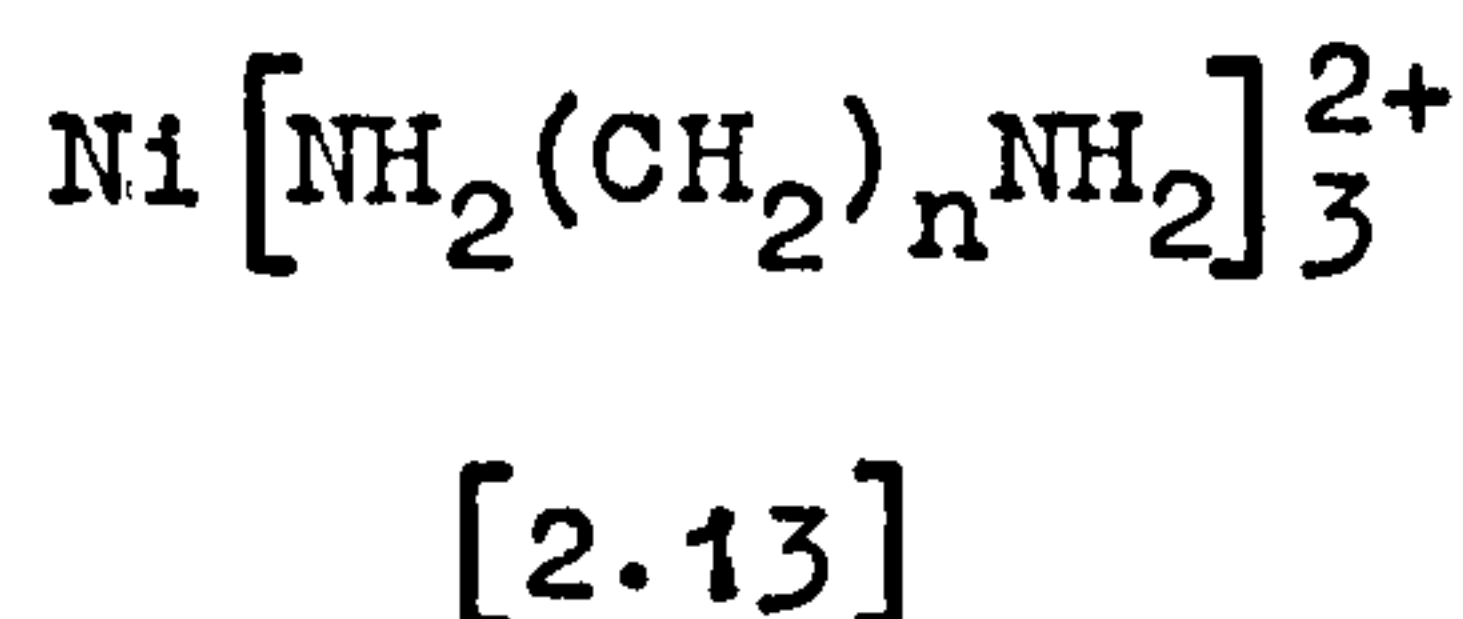
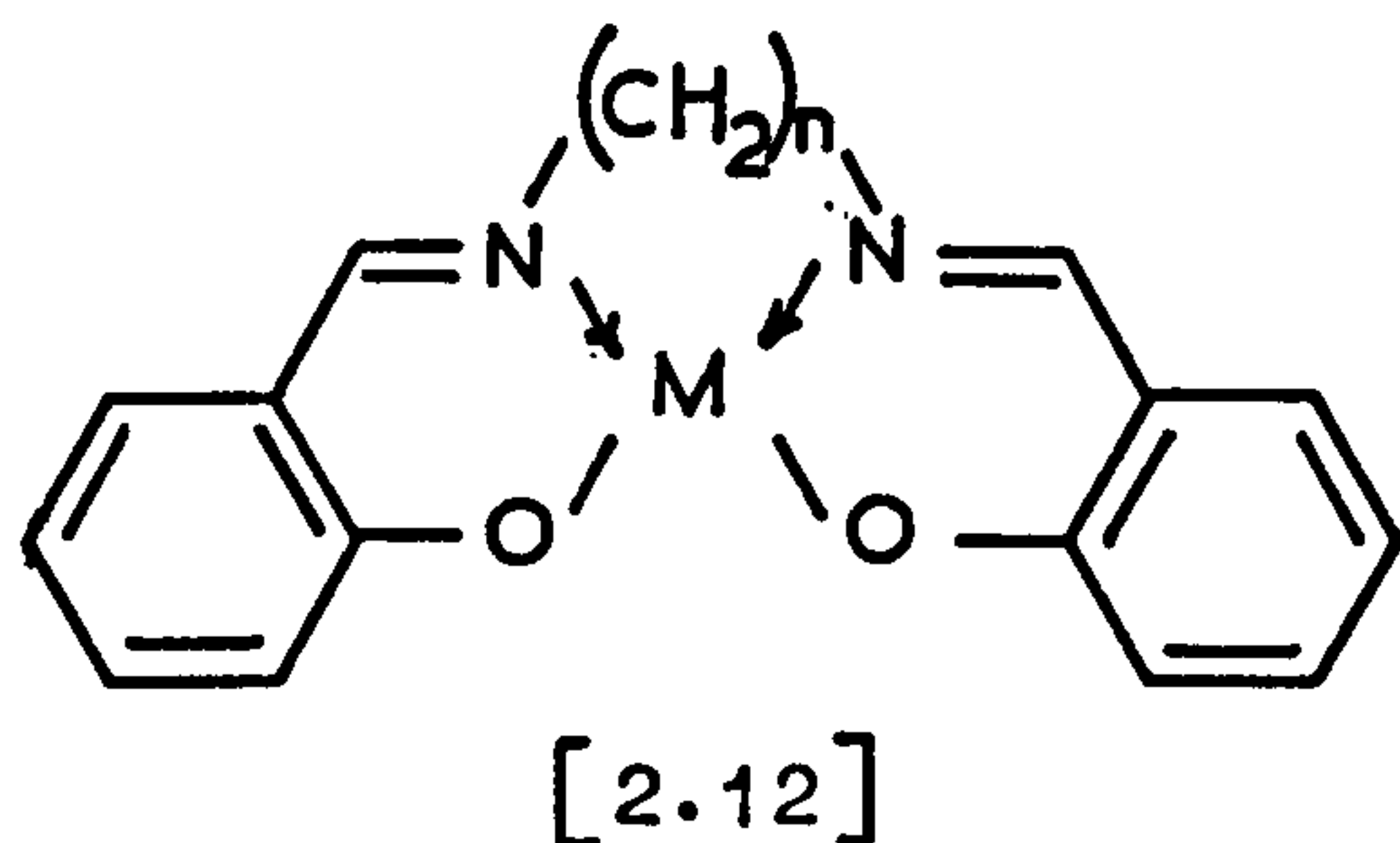
Delocalisation of charge to the ligand system could also be increased by substituting unsaturated groups for  $R_1$  and  $R_2$ .

#### 2.2.4 Macrocyclic 'model' ligands.

When both  $R_2$  groups of structure [2.1] are replaced by a bridging group, e.g.  $-\text{CH}_2\text{CH}_2-$ , we have a cyclic system. The problems of synthesis of macrocyclic ligand systems are dealt with in chapter 6.

### 2.2.5 Ligand field splitting.

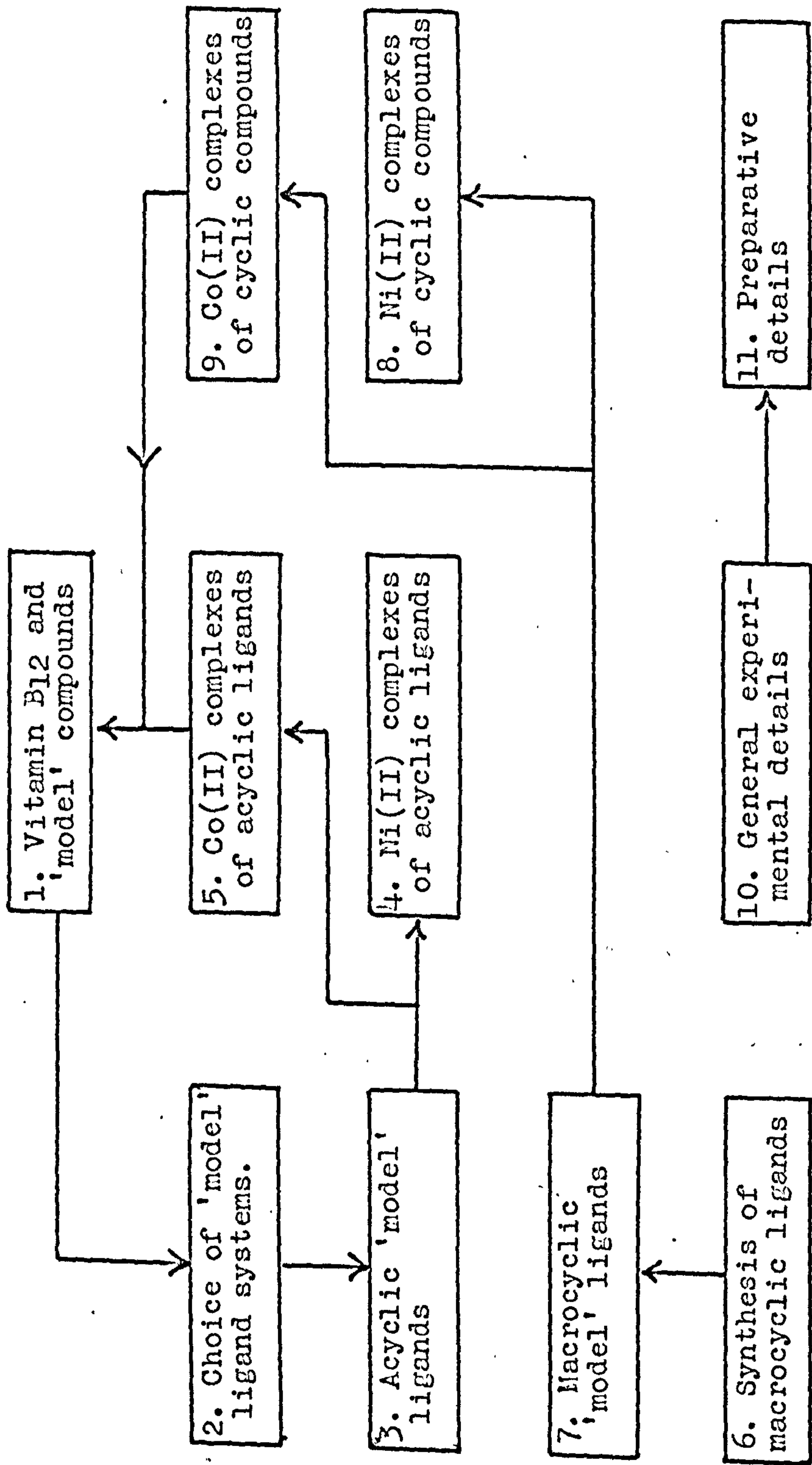
Increasing the length of a polymethylene bridging group R beyond two members causes increasing steric strain for a square-planar arrangement (see p. 24 ). To maintain a square-planar arrangement of the nitrogen atoms the distance of the azomethine donor atoms from the metal should be increased, with a corresponding decrease in the ligand field strength. Similar decreases in ligand field strength with increase in number of members of the chelate ring have been observed for the systems [2.12]<sup>5</sup> and [2.13]<sup>6</sup>



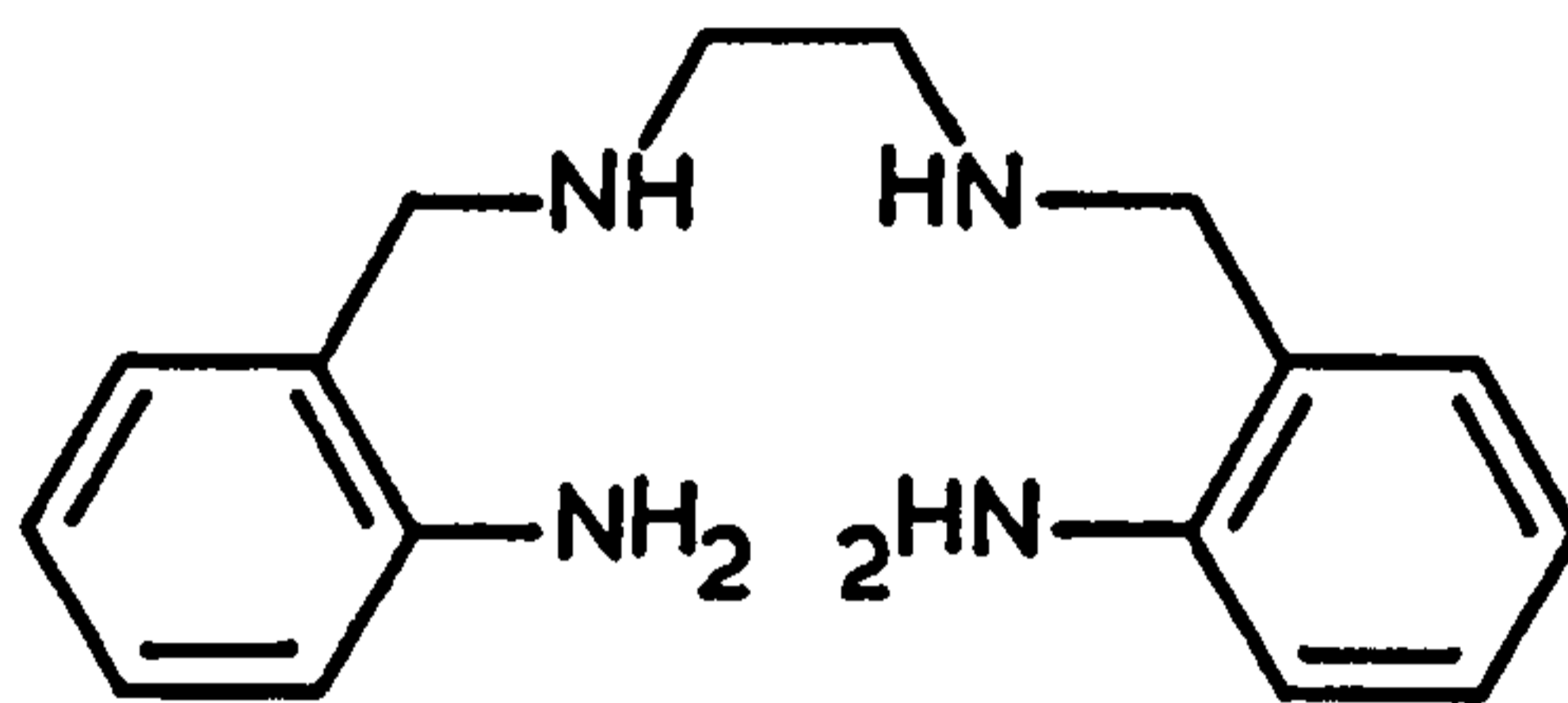
It was hoped that it might also be possible to vary the ligand field by replacement of groups R<sub>1</sub> and R<sub>2</sub> by electron donating and withdrawing groups.

### 2.3 Related ligands with saturated nitrogen donors.

Quite a number of quadridentate ligands with



saturated nitrogen donor atoms have been studied (see p. 60 for brief review ). We hoped to synthesize and study N,N'-bis-(o-aminobenzyl) - 1,2-diaminoethane [2.14] which is a reduced form of the simplest 'model' ligand (p. 23 ) ( [2.1] , R = -CH<sub>2</sub>CH<sub>2</sub>-, R<sub>1</sub>=R<sub>2</sub>=H) to illustrate the importance of conjugation in the ligands [2.1] in determining their manner of coordination and the properties of their complexes.



[ 2.14 ]

#### 2.4 General layout of this thesis.

The flow diagram on page F28 represents the order of presentation of material in this thesis, and the relationship between the contents of the chapters. The chapter numbers are included in the 'boxes'.


#### 2.4 References.

1. A.A. Goodwin and F. Lions, J. Amer. Chem. Soc., 82, 5013, (1960).
2. R.O. Clinton, J. Org. Chem., 27, 1148, (1962).
3. P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl and H. Thielert, J. prakt. Chem., 149, 217, (1937), Chem. Abs., 32, 512, (1938).
4. R.H. Holm, J. Amer. Chem. Soc., 82, 5832, (1962)
5. C.K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, 1962, page 297.



## Chapter 3. Acyclic 'Model' Ligand Systems.

- 3.1. Nomenclature and Abbreviations.
- 3.2. General Synthetic Route.
  - 3.2.1. Condensations of o-aminoacetophenone and o-aminobenzophenone.
  - 3.2.2. Condensation of o-aminobenzaldehyde with 1,2 - diaminobenzene.
  - 3.2.3. An alternative synthetic route for ligands derived from o-aminobenzaldehyde.
- 3.3 Characterization of the ligands.
  - 3.3.1 Analyses.
- 3.4. Mass spectra.
- 3.5. Infrared spectra.
- 3.6. Electronic spectra.
  - 3.6.1. Benzophenone imines.
  - 3.6.2. General Assignments.
- 3.7. N.M.R. spectra.
  - 3.7.1. Chemical shifts of NH protons.
  - 3.7.2. Systems containing N-methylanilino groups.
- 3.8. A related ligand with saturated nitrogen atoms.
- 3.9. References.

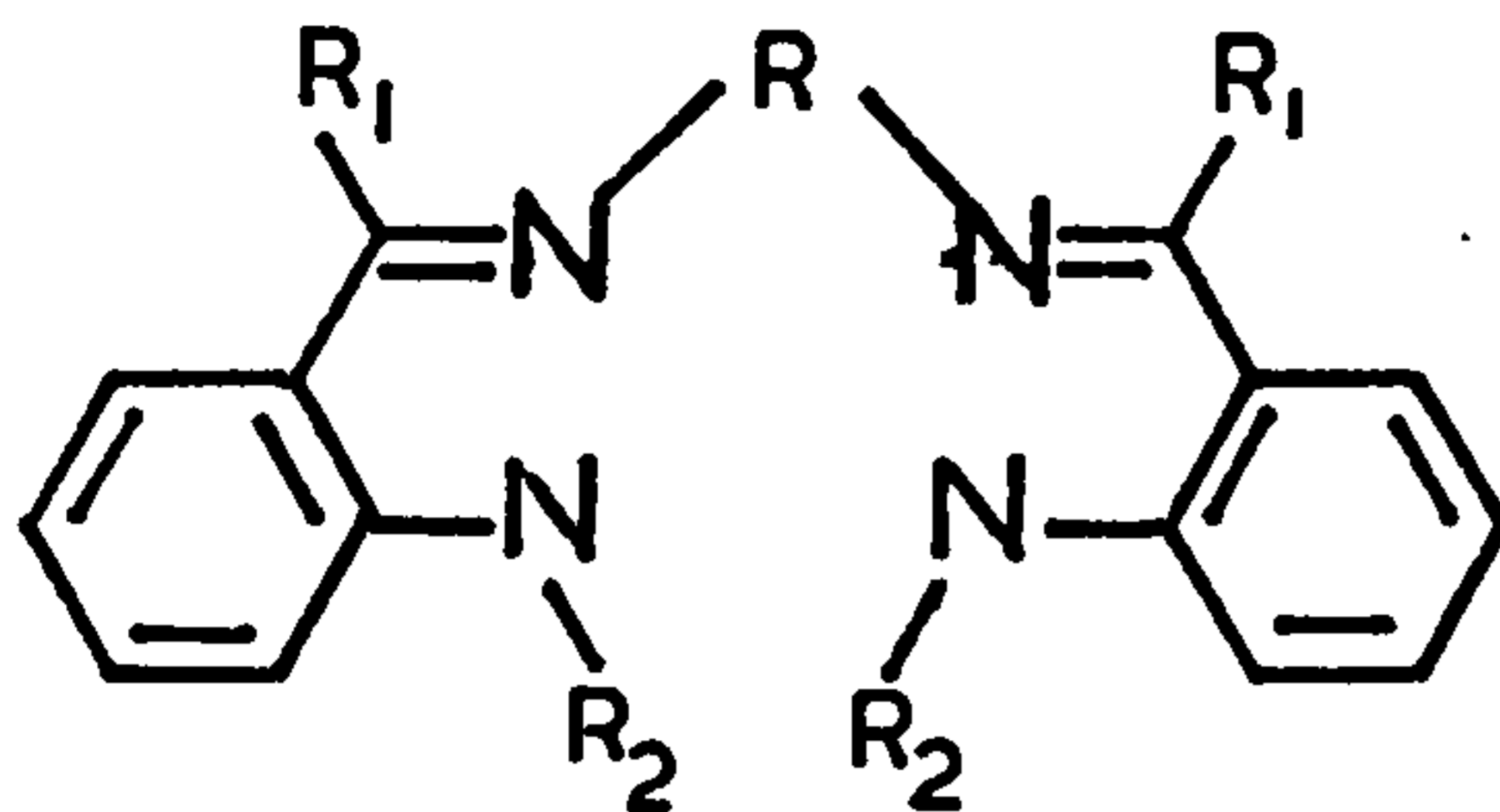
$R^a$	$R_1^a$	$R_2^a$	Name	Abbreviation.	m.p.
$-(CH_2)_2$	H	H	N,N'-bis-(o-amino-benzylidene) 1,2-diaminoethane	amben	182° (lit 178°)
$-(CH_2)_3$	H	H	N,N'-bis-(o-amino-benzylidene) 1,3-diaminopropane	ambtn	112°
$-(CH_2)_4$	H	H	N,N'-bis-(o-amino-benzylidene) 1,4-diaminobutane	ambbuten	133°
$-(CH_2)_{10}$	H	H	N,N'-bis-(o-amino-benzylidene) 1,10-diaminodecane	ambdecen	115°
	H	H	N,N'-bis-(o-amino-benzylidene) 1,2-diaminobenzene	ambphen	195°
$-(CH_2)_2$	$C_6H_5$	H	N,N'-bis-(o-amino-benzophenylidene) 1,2-diaminoethane	ampen	142°
$-(CH_2)_4$	$C_6H_5$	H	N,N'-bis-(o-amino-benzophenylidene) 1,4-diaminobutane	ampbuten	138°
$-(CH_2)_2$	$CH_3$	H	N,N'-bis-(o-amino-acetophenylidene) 1,2-diaminoethane	amaen	127°
$-(CH_2)_2$	H	$CH_3$	N,N'-bis-(N-methyl-o-aminobenzylidene) 1,2-diaminoethane	Me-amben	131°
$-(CH_2)_4$	H	$CH_3$	N,N'-bis(N-methyl-o-aminobenzylidene) 1,4-diaminobutane	Me-ambbuten	94°
$-(CH_2)_{10}$	H	$CH_3$	N,N'-bis(N-methyl-o-aminobenzylidene) 1,10-diaminodecane	Me-ambdecen	71°

Table[3.2]. Nomenclature and abbreviations of acyclic 'model' ligands.

(a) refers to the groups in general formula [3.1]  
 (b) dubious purity (see page 34 ).

### 3.1 Nomenclature and abbreviations.

Table [3.2] lists the acyclic ligands of general formula [3.1] prepared for this work.



[3.1]

Nomenclature is based on that commonly used for Schiff base ligands derived from salicylaldehyde and o-hydroxyacetophenone.<sup>1</sup>

The abbreviations are also similar to those widely used in the literature for ligands derived from salicylaldehyde. The first part of the abbreviation is derived from the parent aldehyde or ketone, while the second part is the common abbreviation for the parent diamine (see table [3.1] ).

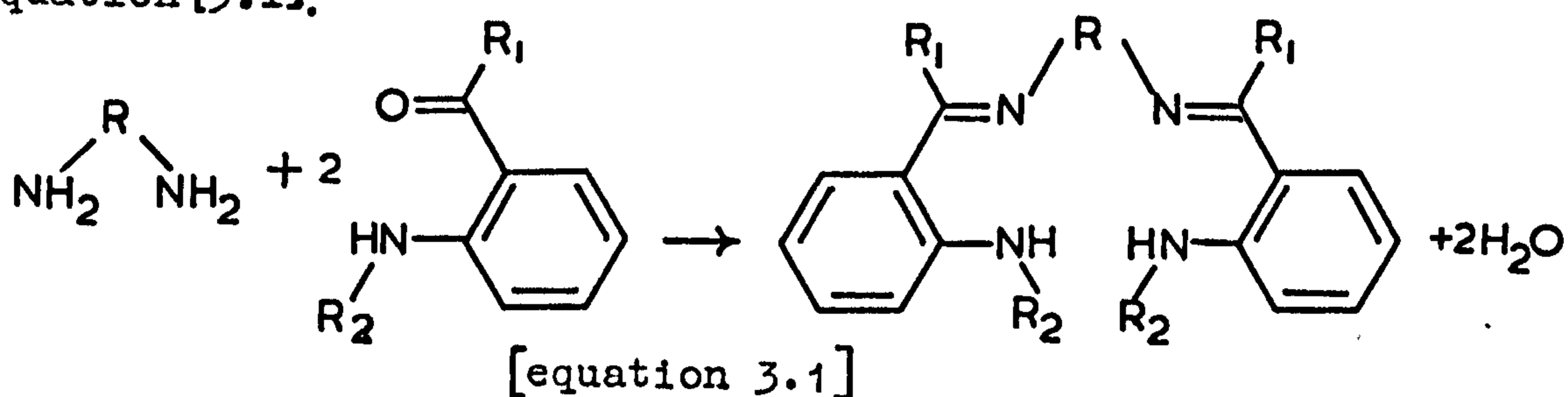
Parent aldehyde or ketone	Abbreviation
o-aminobenzaldehyde	amb.
o-aminoacetophenone	ama.
o-aminobenzophenone	amp.
N-methyl-o-aminobenzaldehyde	Me-amb.

Parent diamine	Abbreviation
1,2-diaminoethane	en.
1,3-diaminopropane	tn.
1,4-diaminobutane	buten
1,10-diaminodecane	decen
1,2-diaminobenzene	phen
1,8-diaminonaphthalene	naph

Table [3.1]. Derivation of abbreviations of the Ligands..

### 3.2. General Synthetic Route.

Synthesis was usually achieved by condensation of the appropriate diamine and o-aminoarylcarbonyl compound according to equation [3.1].



In most cases the reaction goes in good yields on refluxing in methanol for a short time. The main drawback with this route is the tedious

preparation of the o-aminoarylcarbonyl compound.

On no occasion was more than one isomer of [3.1] isolated. It is assumed that of the three possible geometric isomers of [3.1] (see p. 24.), only the most stable with both imine groups hydrogen-bonded to the amine groups can be isolated at normal temperatures, when interconversion between the forms will be rapid in solution.<sup>2,3.</sup>

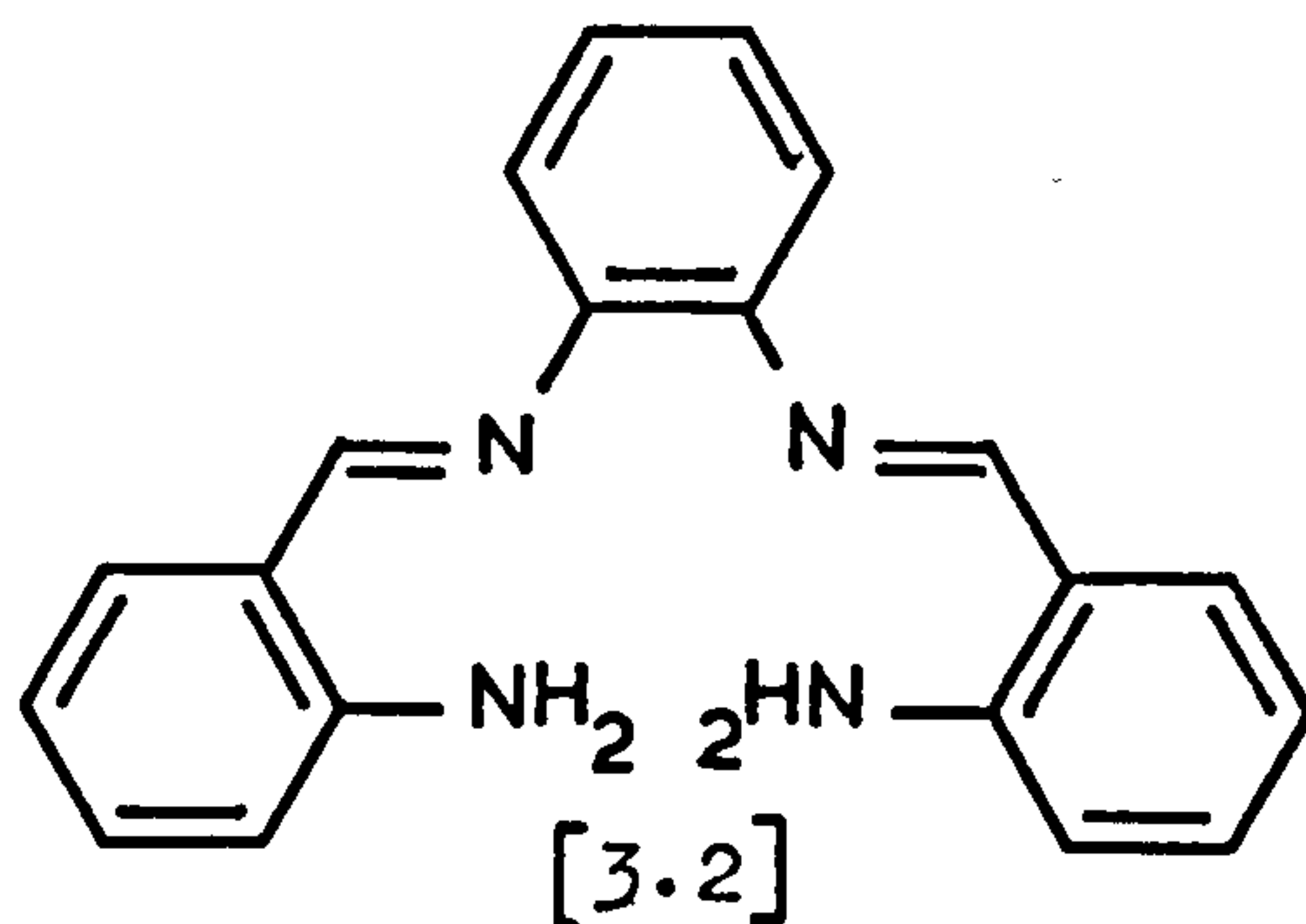
3.2.1 Condensation with o-aminoacetophenone ( $R_1=CH_3$   $R_2=H$ )  
and o-aminobenzophenone ( $R_1=C_6H_5$   $R_2=H$ ).

The condensation equation [3.1] is more difficult to achieve when the carbonyl group is sterically hindered ( $R_1=C_6H_5$ ), or electronically less active ( $R_1=CH_3$ ). o-Aminoacetophenone was refluxed with 1,2-diaminoethane containing a little anhydrous zinc chloride for two hours to give N,N'-bis-(o-aminoacetophenylidene) - 1,2-diaminoethane (amaen). The condensation of o-aminobenzophenone with aliphatic diamines was only achieved by prolonged heating in the presence of traces of Lewis acids.

The condensations involving o-aminobenzaldehyde required no Lewis acid catalyst and were complete on refluxing in methanol for a short time.

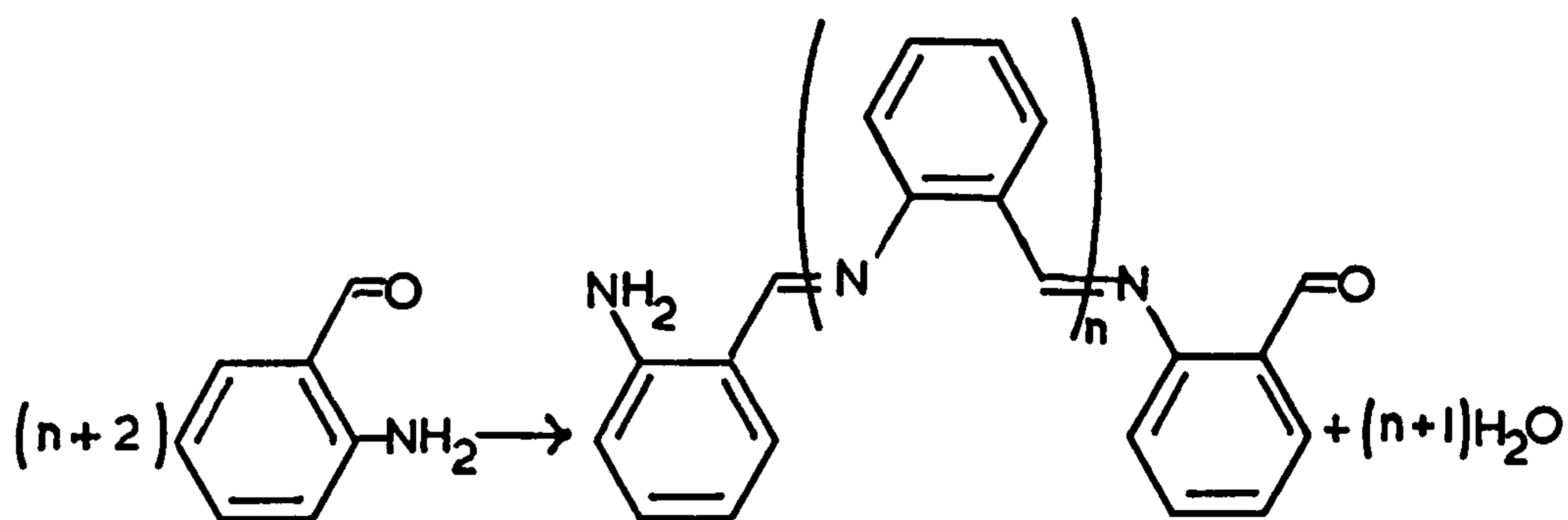
3.2.2 Condensation of o-aminobenzaldehyde with  
1,2-diaminobenzene.

It was found to be very difficult to isolate the free ligand ambphen [3.2].



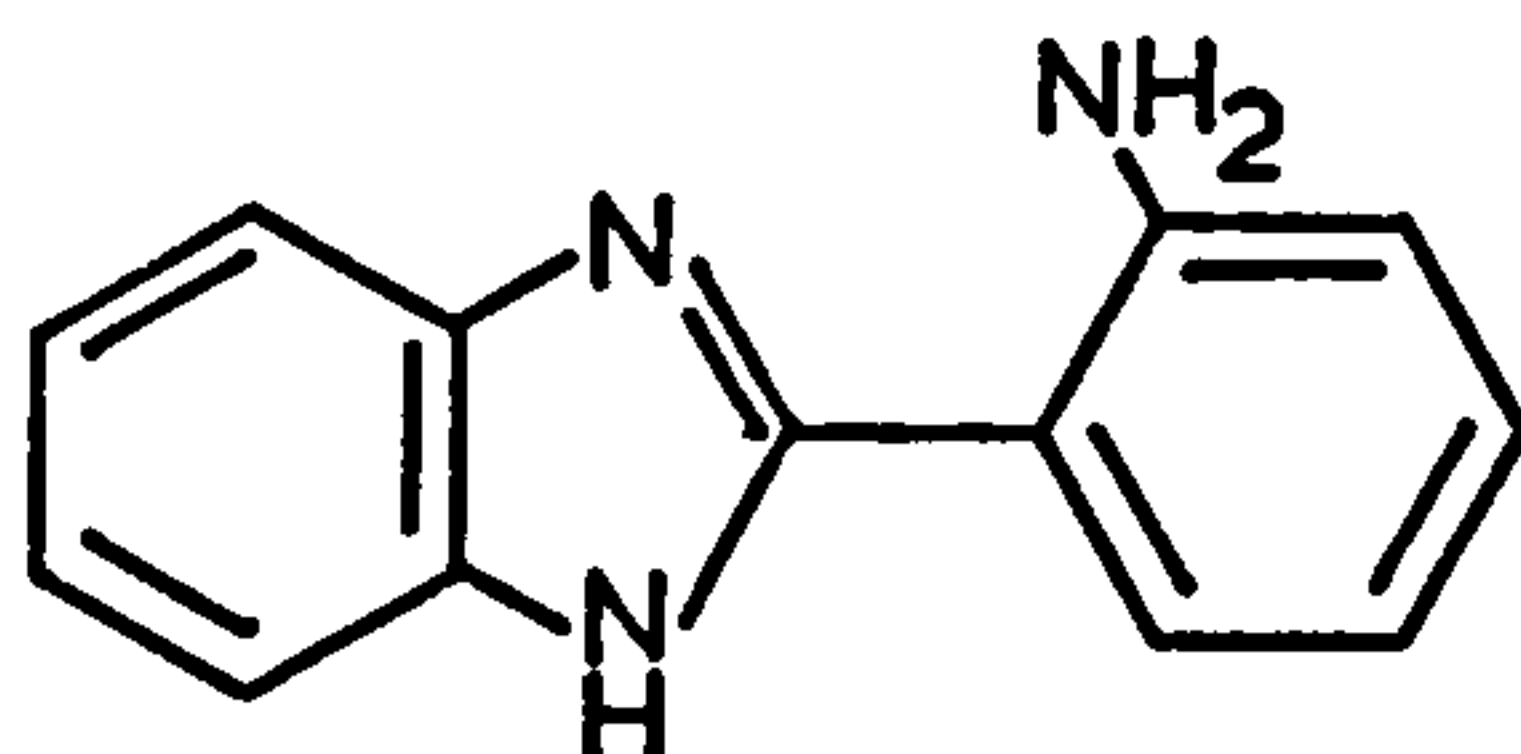
Condensation of 1,2-diaminobenzene with o-aminobenzaldehyde gave a yellow oil which usually could not be induced to crystallise. This oil may contain the desired product mixed with polymers from o-aminobenzaldehyde or even 2-(o-aminophenyl)-benzimidazole [3.3].

Polymerisation of o-aminobenzaldehyde (equation [3.2]) may occur at a rate comparable with the desired condensation because the basicity of the amine groups of 1,2-diaminobenzene is not very much greater than that of the amine group of o-aminobenzaldehyde.



[equation 3.2]

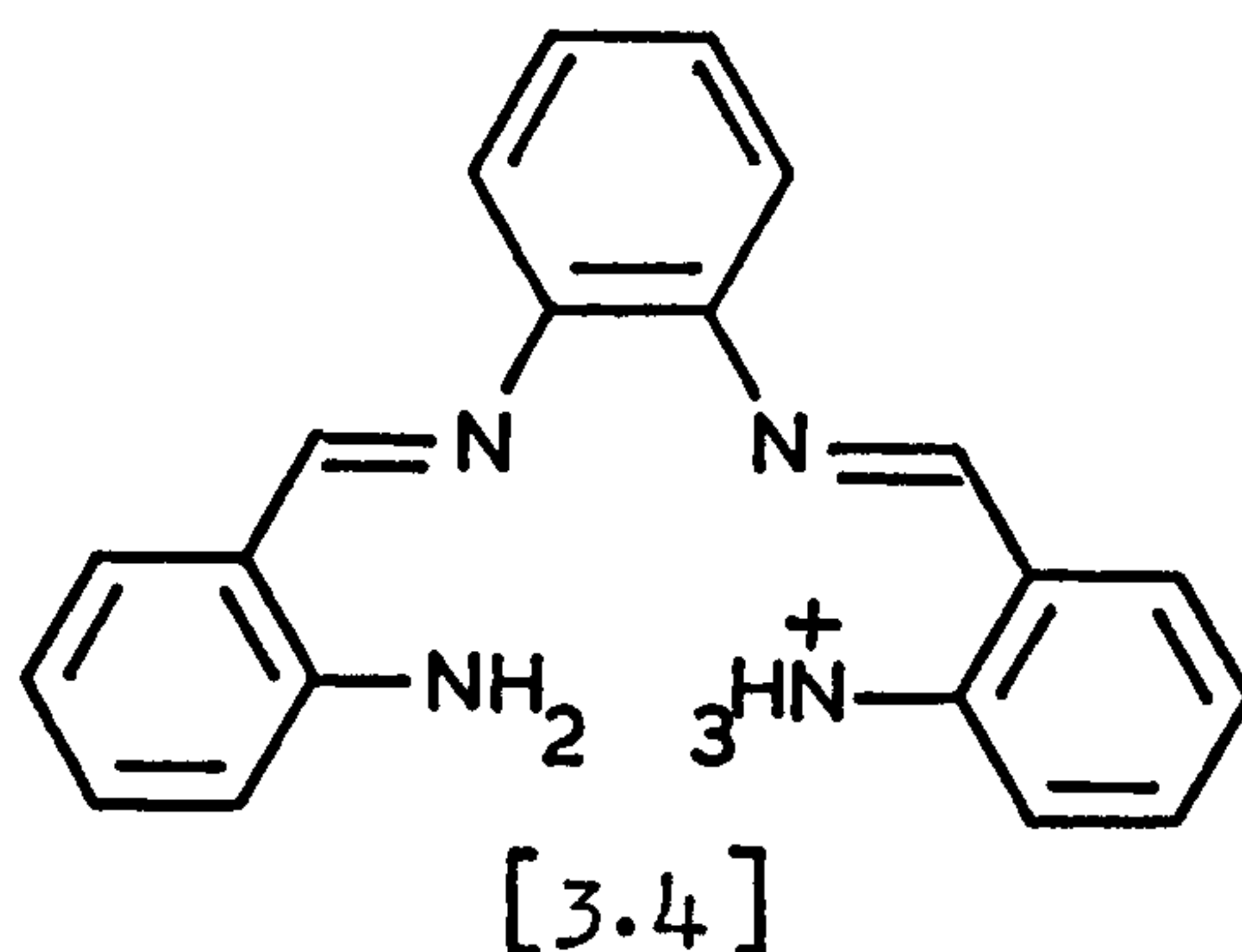
Formation of 2-(o-aminophenyl)-benzimidazole [3.3] will be favoured by oxidizing conditions.



[3.3]

A solid product was isolated from one condensation product after standing for two weeks and occasionally triturating with methanol. The material obtained after reprecipitation from acetone with petrol had a higher melting point than either starting material. It was judged to contain at least some of the desired ligand since the mass spectrum of the material has a peak at 315 m/e thought to be due to the species [3.4] and shows a breakdown pattern expected for the desired ligand (see also page 40). However, reaction

of this solid with nickel acetate in methanol gave only a very low yield of Ni ambphen, and it is therefore assumed to be composed mainly of low polymers from o-aminobenzaldehyde.



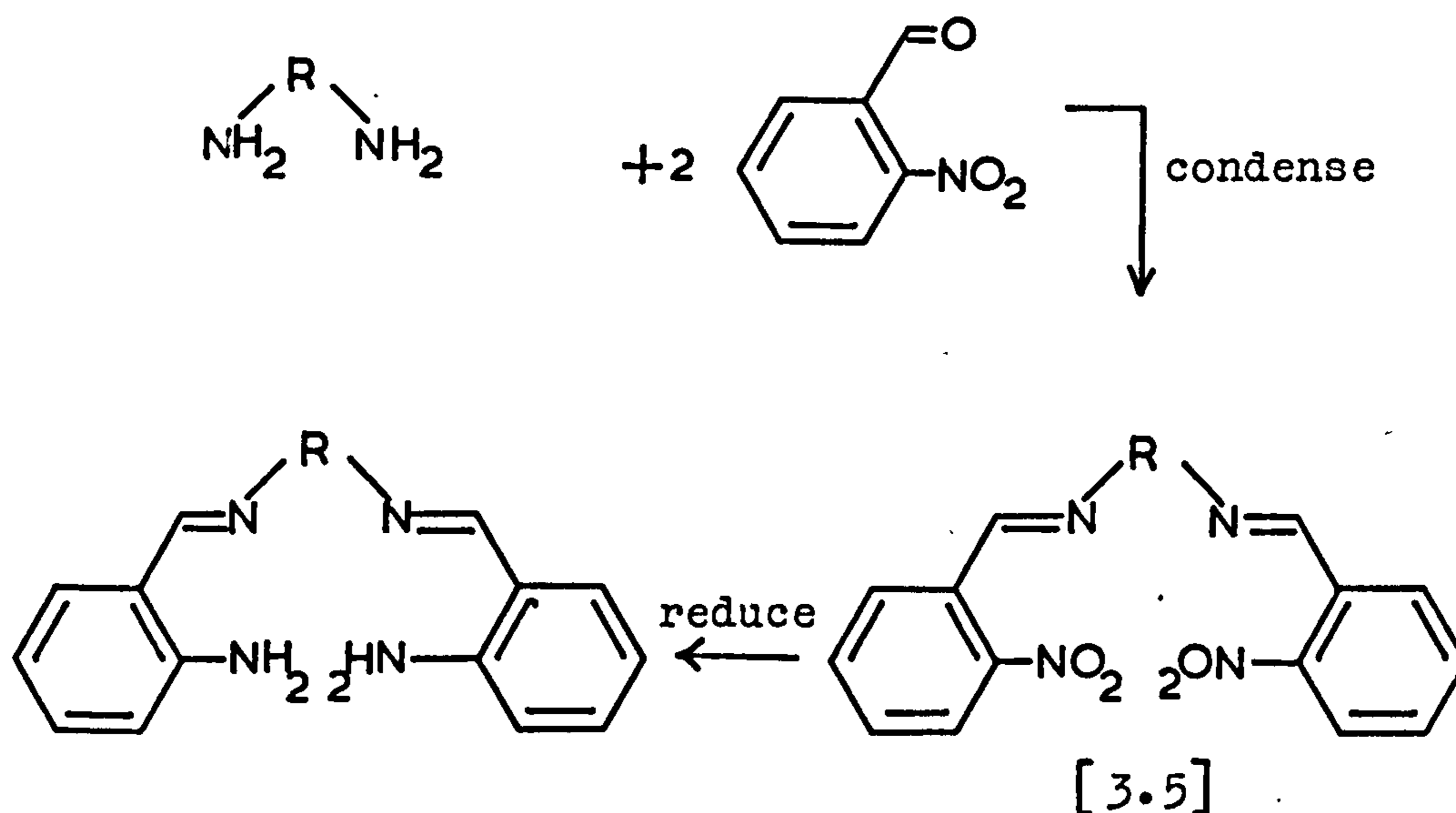
Pfeiffer et al.<sup>22</sup> obtained the complex Ni ambphen by reacting nickel acetate in situ with the condensation product of o-aminobenzaldehyde and 1,2-diaminobenzene.

We attempted to prepare the free ligand ambphen by displacement of nickel from Ni ambphen. It was found that reagents which frequently displace nickel from complexes e.g. hydrogen sulphide or strong cyanide solution would not react with the complex. Dimethylglyoxime appeared to give a small amount of bis(dimethylglyoximato)-nickel after standing with a dimethylformamide solution of Ni ambphen for several months, but most of the Ni ambphen was unchanged.



3.2.3. An alternative synthetic scheme for ligands derived from o-aminobenzaldehyde.

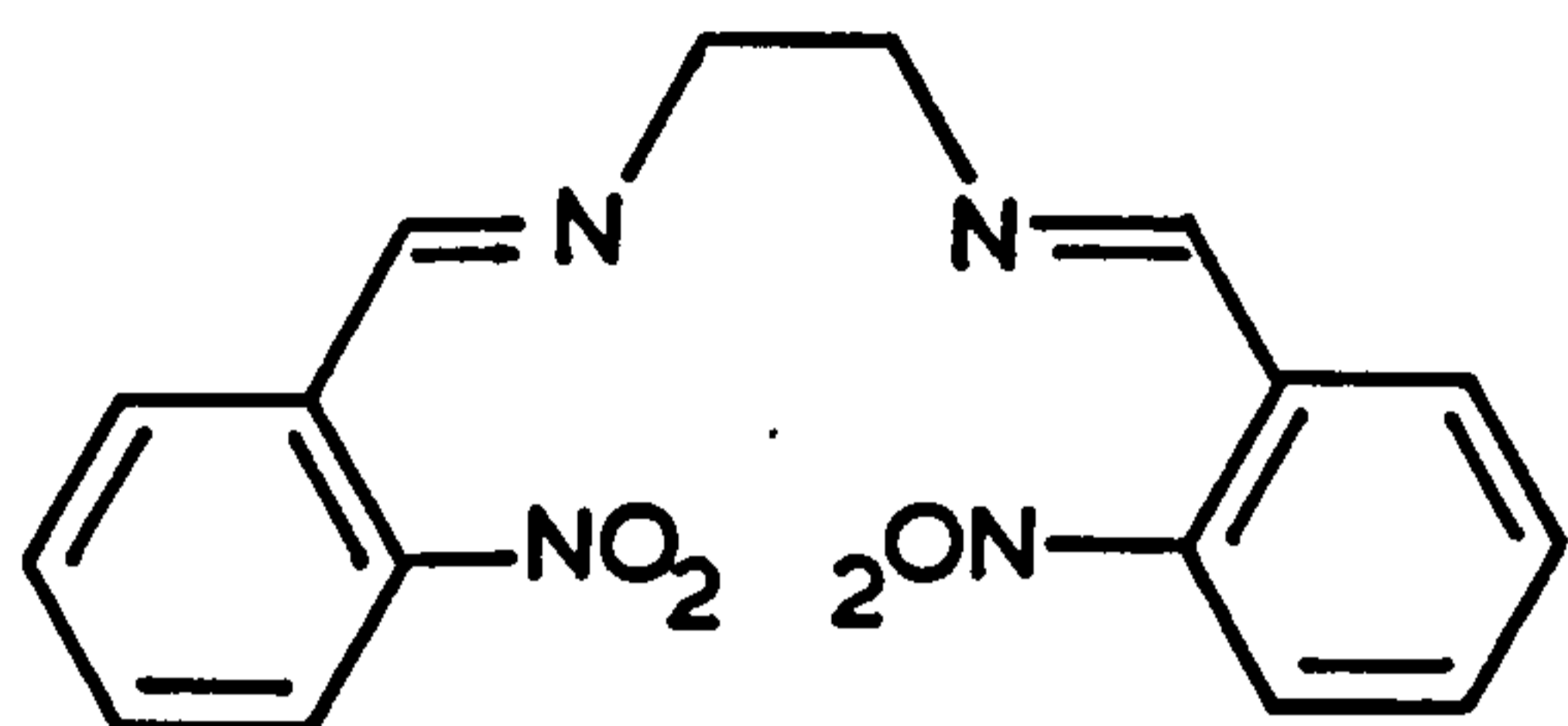
To avoid the synthesis of o-aminobenzaldehyde, which cannot be prepared in bulk and tends to polymerise on standing, the following scheme was tested for the ligands derived from o-aminobenzaldehyde.



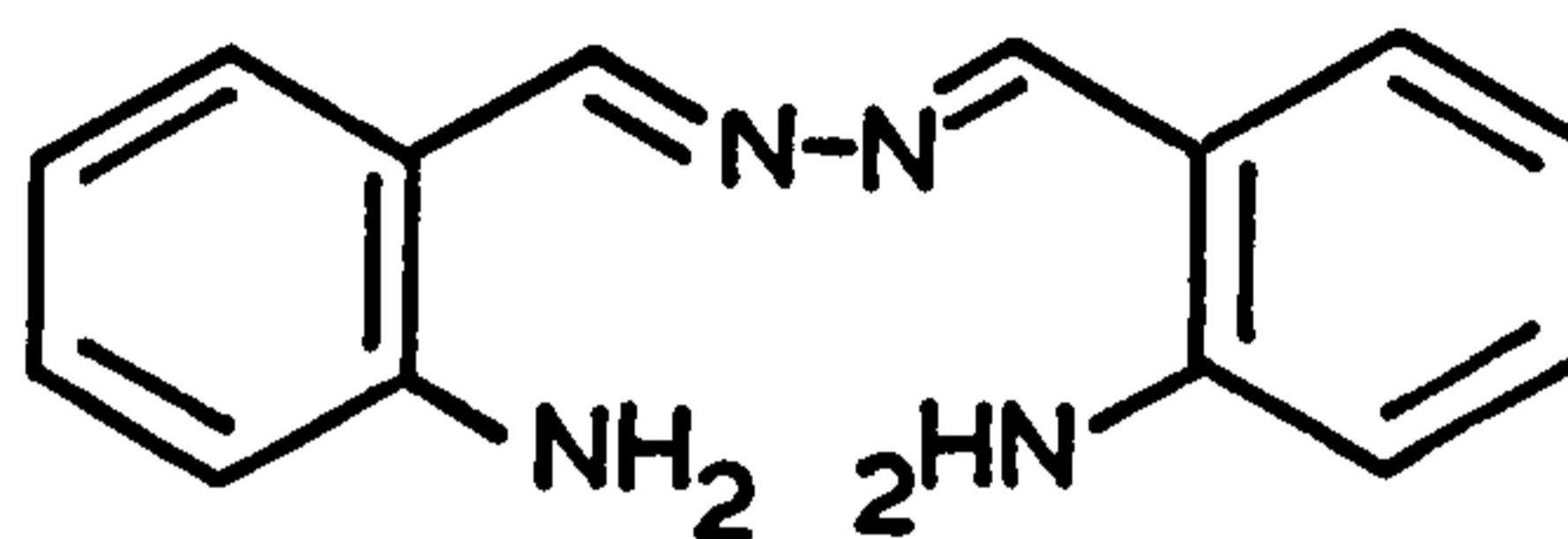
The reduction of the nitro compound [3.5] presented some difficulties. Strongly acidic or basic media had to be avoided owing to the tendency of the Schiff base to hydrolyse.

Hydrazine in the presence of palladium charcoal is a good reagent for reducing nitro groups.<sup>4</sup> Unfortunately, when N,N'-bis-(o-nitrobenzylidene) -

1,2-diaminoethane [3.6] was treated in this way a high yield of N,N'-bis-(o-aminobenzylidene)-hydrazone [3.7] was obtained.



[3.6]

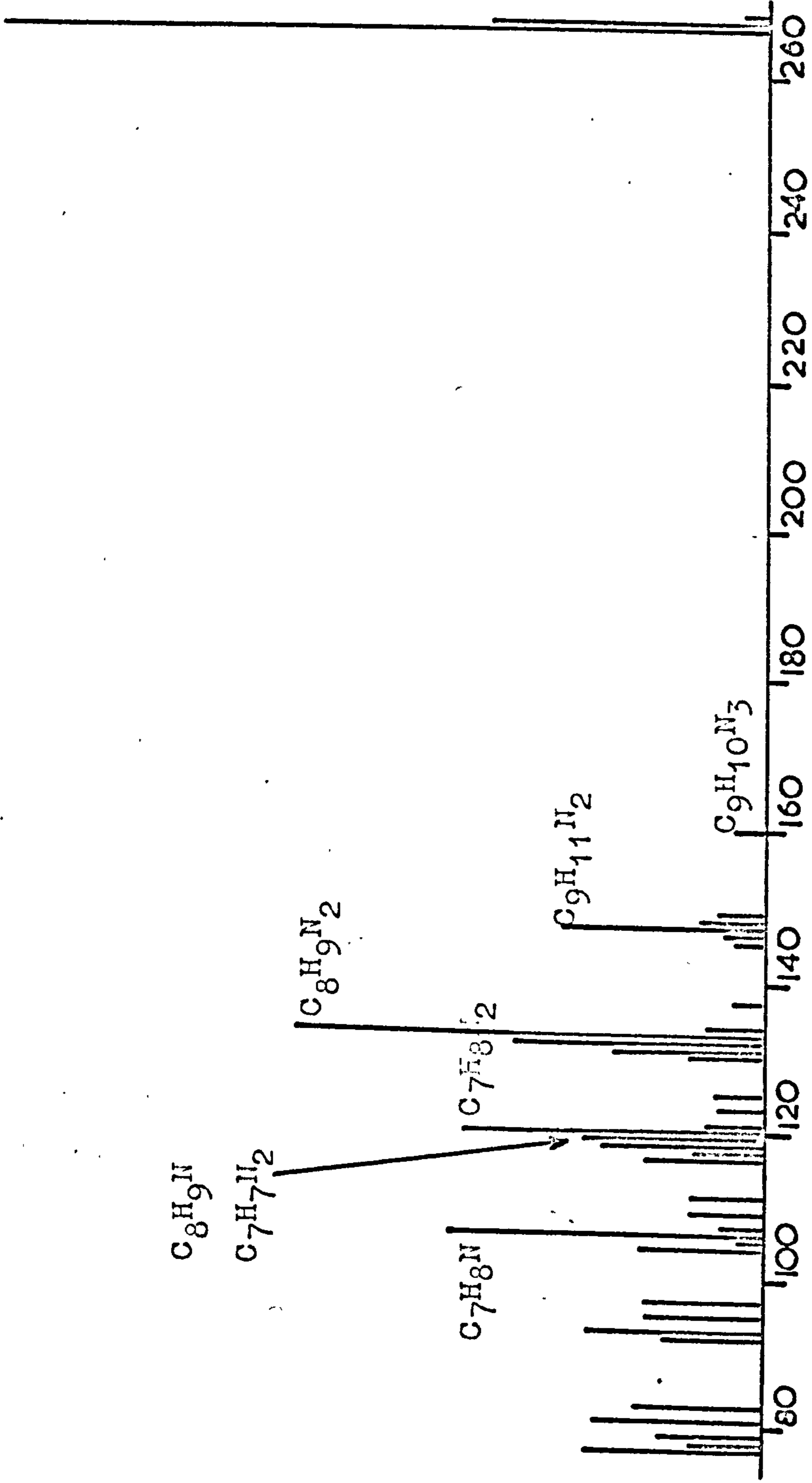


[3.7]

The nitro groups have been reduced, but hydrazine has displaced 1,2-diaminoethane. It has been shown<sup>5</sup> that in many cases hydroxylamine and hydrazine react faster with imines than with the corresponding aldehyde or ketone.

N,N'-bis-(o-aminobenzylidene)-hydrazone [3.7] was also obtained by reduction of o-nitrobenzaldehyde in the presence of hydrazine hydrate and palladium charcoal.

The reduction of [3.6] to amben was achieved by hydrogenation in methanol in the presence of platinum black. The method suffered from the limitations of the hydrogenation apparatus available, and had to be done quantitatively, since absorption of hydrogen beyond the stoichiometric amount required for the reduction of the nitro groups would have resulted in unwanted reduction of



The mass spectrum of arben.

the azomethine groups.

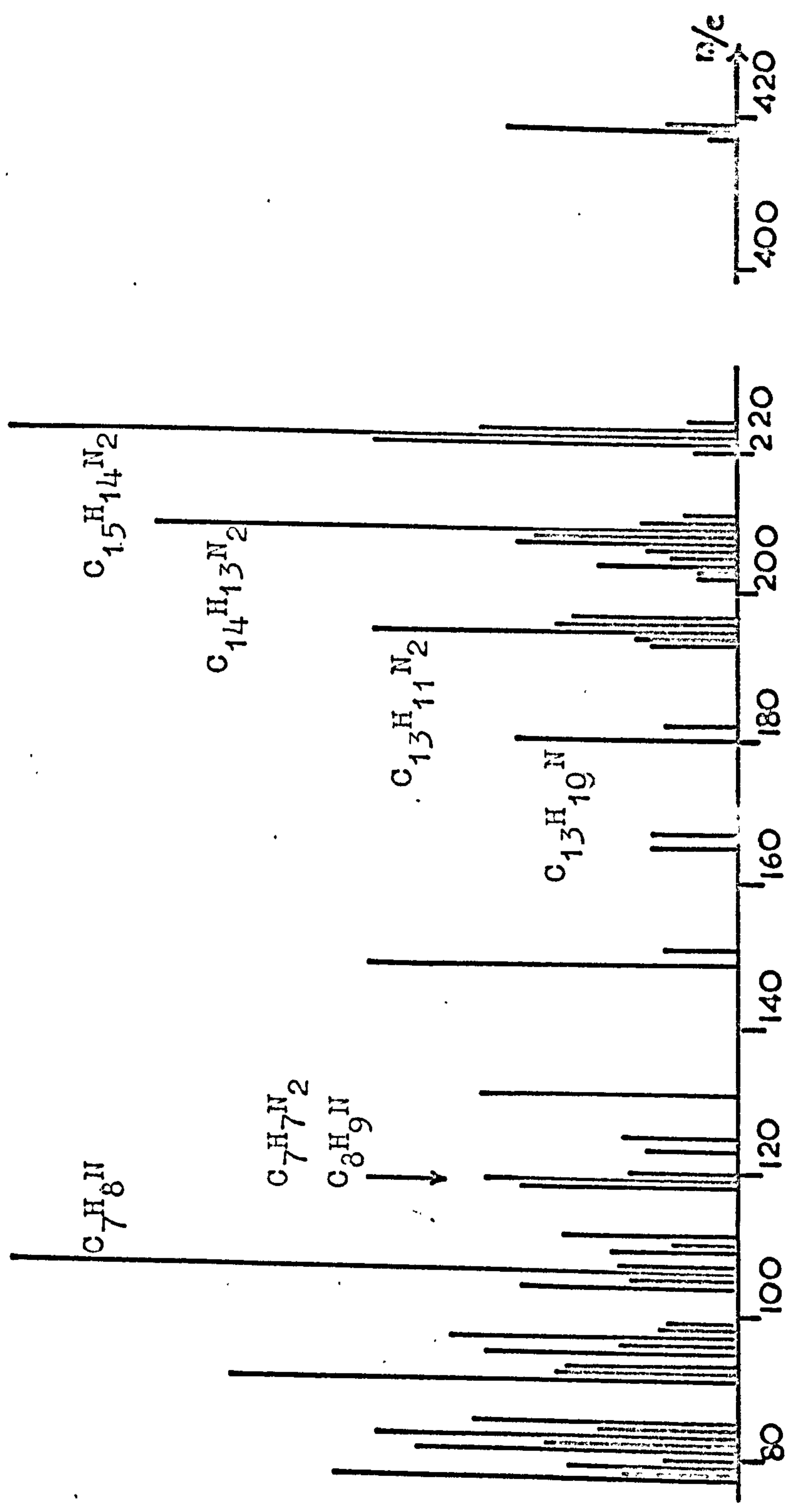
The best method for hydrogenation of this type of nitro precursor to the ligand was achieved with palladium charcoal catalyst in the presence of the metal ion required to be complexed by the ligand. The desired complex is obtained in one step, and it appears that complexation stabilizes the azomethine groups with respect to reduction by hydrogen in the presence of palladium charcoal (see page 72 ). Hence, the uptake of hydrogen did not have to be followed quantitatively. A slow stream of hydrogen was passed through a methanolic solution of the ligand and the required metal acetate, containing a suspension of the catalyst (see also page 291 and page 299).

### 3.3 Characterization of the ligands.

Of the ligands prepared, half were sent for analysis. At least one ligand derived from each o-aminoarylketone was analysed. The other ligands were characterized on the basis of their N.M.R. spectra and mass spectra, and, to a lesser extent their infrared and electronic spectra.

#### 3.3.1 Analyses.

The results of carbon, hydrogen and nitrogen



The mass spectrum of ampen.

Faint, illegible text at the bottom of the page, possibly bleed-through from the reverse side.

analyses are shown in table [3.3] .

Ligand	Formula	Molecular Weight	Composition %		
			C	H	N
amben	$C_{16}H_{18}N_4$	266.3	Calc. 72.17	6.81	21.04
			Found 72.09	6.80	20.90
ambtn	$C_{17}H_{20}N_4$	280.4	Calc. 72.82	7.19	19.98
			Found 72.56	7.34	20.73
ambdecen	$C_{24}H_{34}N_4$	378.6	Calc. 76.15	9.04	14.80
			Found 76.43	8.63	14.72
ampen	$C_{28}H_{26}N_4$	418.6	Calc. 80.38	6.22	13.39
			Found 80.35	6.26	13.38
amaen	$C_{18}H_{22}N_4$	294.4	Calc. 73.48	7.53	19.03
			Found 72.92	7.49	19.49
Me-amben	$C_{18}H_{22}N_4$	294.4	Calc. 73.48	7.53	19.03
			Found 72.77	7.53	19.58

Table [3.3] Analysis results for some 'acyclic' ligands.

### 3.4. Mass spectra.

Mass spectra were determined for all the ligands and have been tabulated in the experimental section (chapter 11) after the preparation of each ligand. They provide a useful method for characterizing the ligands, since a molecular ion peak is observed for each compound and the fragmentation pattern is similar in each case.

The mass spectra of amben and ampen are shown on pages F39 and F40, and some of the principal lines are assigned molecular formulae. These spectra were

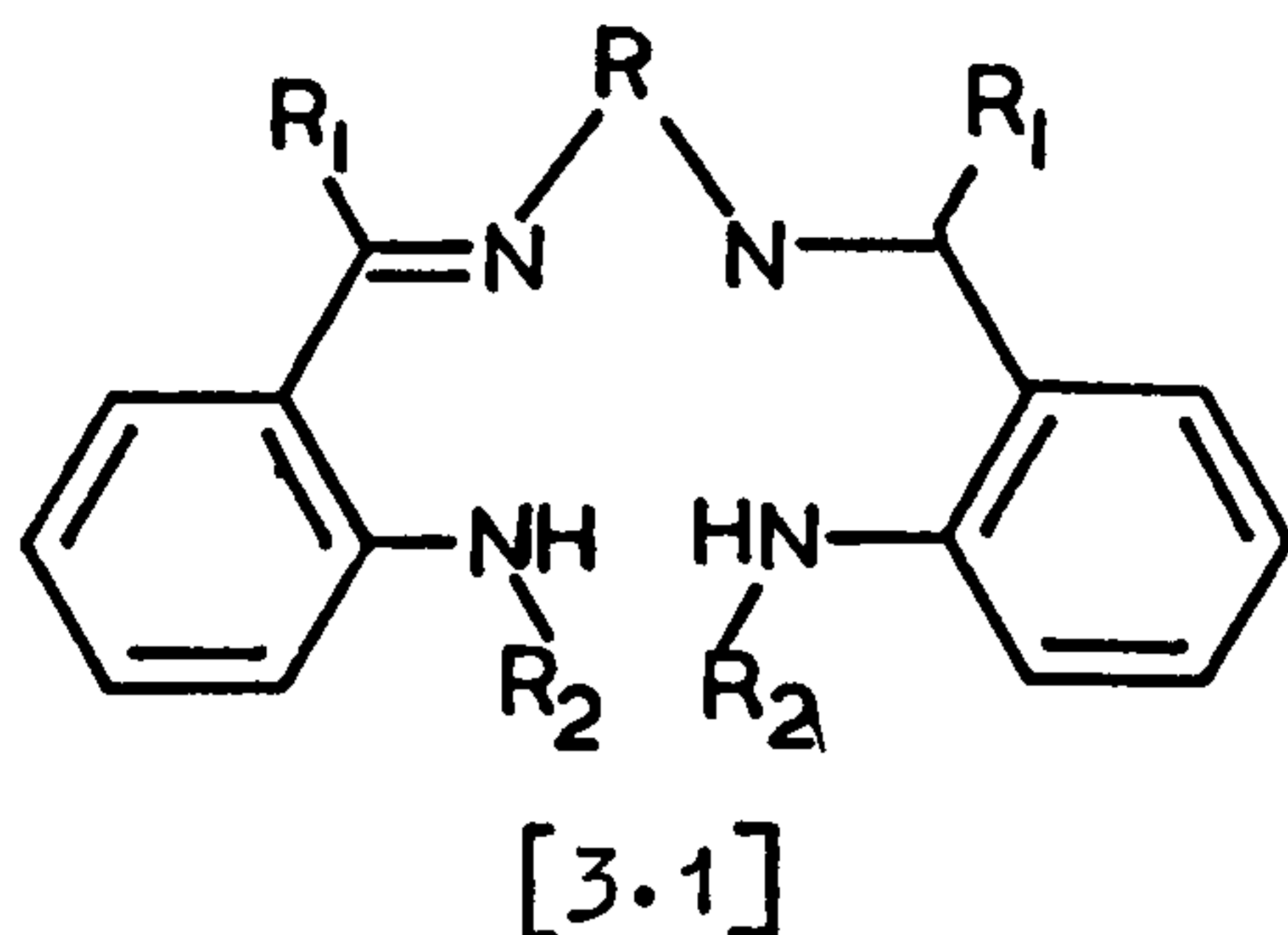
m/e	Accurate Mass		Ion formula (best fit)
	Determined	Calculated	
a	b	c	c
<u>amben</u>			
106	106.0658	106.0657	C <sub>7</sub> H <sub>8</sub> N
119	d 119.0729	119.0735	C <sub>8</sub> H <sub>9</sub> N
	119.0608	119.0609	C <sub>7</sub> H <sub>7</sub> N <sub>2</sub>
120	120.0683	120.0687	C <sub>7</sub> H <sub>8</sub> N <sub>2</sub>
133	133.0775	133.0766	C <sub>8</sub> H <sub>9</sub> N <sub>2</sub>
147	147.0927	147.0922	C <sub>9</sub> H <sub>11</sub> N <sub>2</sub>
160	160.0879	160.0875	C <sub>9</sub> H <sub>10</sub> N <sub>3</sub>
<u>ampen</u>			
106	106.0664	106.0657	C <sub>7</sub> H <sub>8</sub> N
119	d 119.0727	119.0734	C <sub>8</sub> H <sub>9</sub> N
	119.0608	119.0609	C <sub>7</sub> H <sub>7</sub> N <sub>2</sub>
180	180.0812	180.0813	C <sub>13</sub> H <sub>10</sub> N
195	195.0930	195.0922	C <sub>13</sub> H <sub>11</sub> N <sub>2</sub>
209	209.1100	209.1080	C <sub>14</sub> H <sub>13</sub> N <sub>2</sub>
222	222.1150	222.1157	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub>

Table [3.4] Accurate masses of some peaks in the mass spectra of amben and ampen.

(a) From A.E.I. M.S.12 instrument (b) A.E.I. M.S.9

(c) From tables.<sup>6</sup> (d) Doublet.

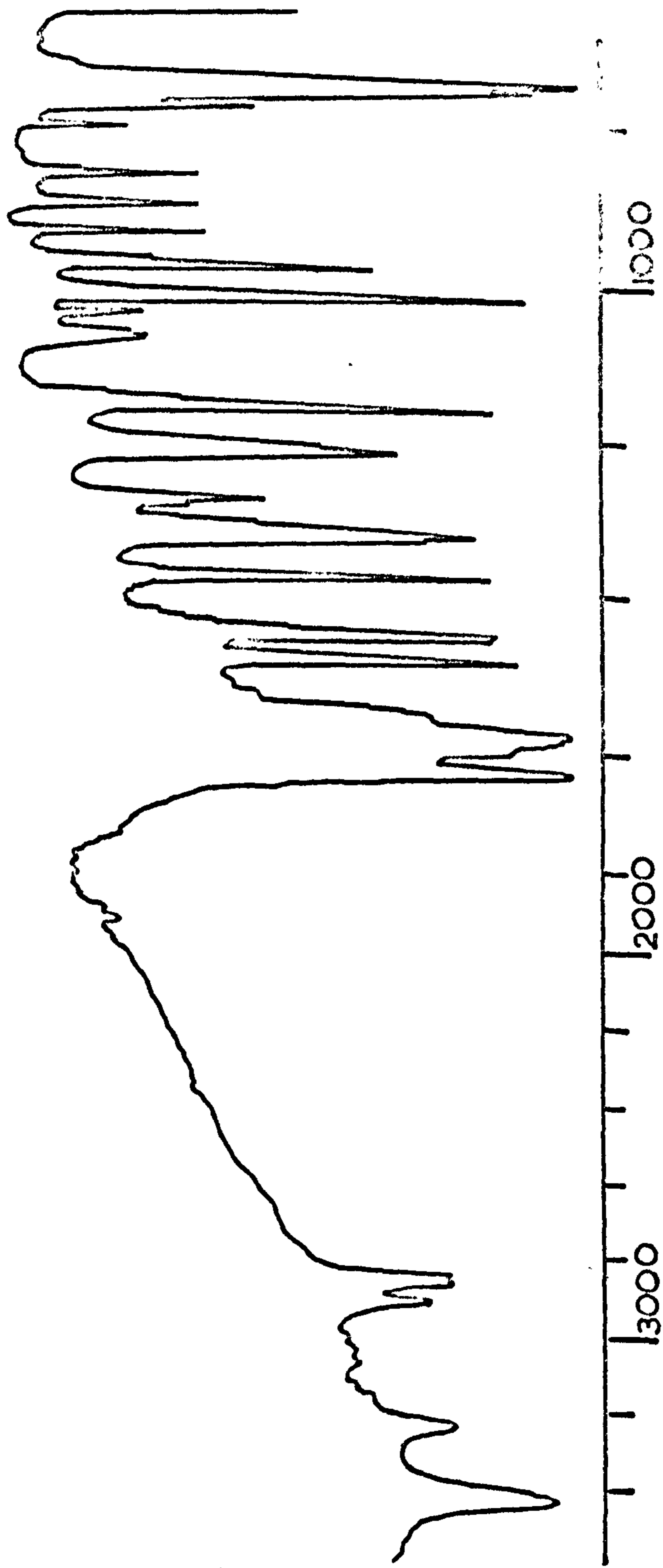
examined in more detail, and accurate masses of various peaks determined in order to make assignments more certain. The accurate mass values and "best fit" formulae for the lines assigned are given in table [ 3.4 ], page F41.



The principal peaks in the mass spectra of the ligands are due to fragmentation of the molecule [3.1] at the following points;

- (a) azomethine bond, e.g. in amben giving peaks  $m/e$ , 160 ( $C_9H_{10}N_3$ ) and 106 ( $C_7H_8N$ ),
- (b) bridging group (R) bonds, e.g. in amben giving the peak  $m/e$ , 133 ( $C_8H_9N_2$ ),
- (c) the bond between the bridging group (R) and the azomethine nitrogen atom, e.g. in ampen giving peaks  $m/e$ , 222 ( $C_{15}H_{14}N_2$ ) and 195 ( $C_{13}H_{11}N_2$ ) and metastable at  $m/e$  118,
- (d) the bond between the substituent ( $R_1$ ) and the azomethine carbon atom, e.g. in ampen peak,  $m/e$  131





Infrared spectrum of amben as a potassium bromide disc, (cm.<sup>-1</sup>)

( $C_8H_7N_2$ ) from peak m/e, 209 ( $C_{14}H_{13}N_2$ ).

(e) the bond between the substituent ( $R_2$ ) and the amine nitrogen atom, e.g. in Me-ambbuten (tabulated page 284) peak, m/e 308 ( $C_{19}H_{24}N_4$ ) from m/e 322 ( $C_{20}H_{26}N_4$ )

### 3.5 Infrared spectra.

The infrared spectra were obtained for all the ligands. The full spectrum of a ligand is useful for comparison when complexes are to be characterized, and these data ~~is~~ <sup>are</sup> included in the experimental section after the preparation of each ligand. The spectrum of amben is given on page F42.

The absorptions in the regions expected for stretching frequencies of NH groups and azomethine groups are arranged comparatively in table [3.5].

There is no absorption at  $3400 \pm 60 \text{ cm}^{-1}$  and  $1550 \pm 15 \text{ cm}^{-1}$  for the compounds Me-amben, Me-ambbuten and Me-ambdecen [3.8]. Since these compounds have no amine hydrogen atom apart from the hydrogen-bonded one we may assign absorptions at these frequencies to NH stretching and NH bending vibrations respectively for the 'free' hydrogen atom of the  $NH_2$  groups in the other compounds.

The other absorption in the NH region, occurs at slightly lower energy ( $3220 \pm 40 \text{ cm}^{-1}$ ) and is the NH

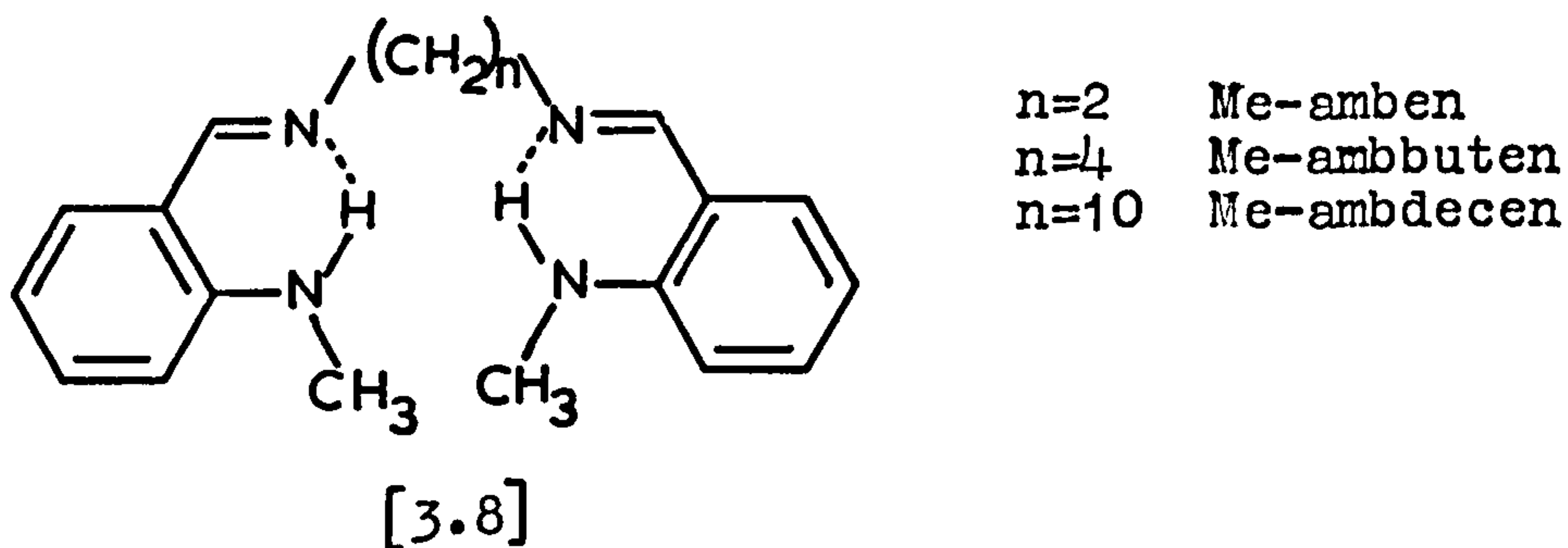
Ligand	NH(free) stretch	NH-N stretch	C=N stretch	ring stretch	NH bend
amben	3430(s)	3250(m)	1636(s)	1609(sh) 1585(s)	1559(sh)
ambtn	3427(s)	3254(m)	1633(s)	1606(sh) 1586(s)	1557(sh)
ambbuten	3405(s)	3250(m)	1633(s)	1608(sh) 1590(s)	1565(sh)
ambdecen	3405(s)	3252(m)	1633(s)	1608(sh) 1588(s)	1562(sh)
ambphen <sup>a</sup>	3340(s)	3200(m)	1614(s)	1592(s)	1548(m)
ampen	3463(s)	3190(b)	1613(s)	1585(s)	1555(m) 1545(m)
ampbuten	3470(s)	3200(b)	1606(s)	1592(m)	1562(m) 1537(s)
amaen	3349(s)	3110(b)	1620(s)	1585(m)	1550(sh)
Me-amben	-	3202(b)	1625(s)	1586(s)	- 1529(s)
Me-ambtn	-	3222(b)	1627(s)	1585(s)	- 1528(s)
Me-ambdecen	-	3223(b)	1625(s)	1585(s)	- 1530(s)

Table [3.5]. Infrared absorption spectra of the ligands in the NH and

C=N stretching regions. All measured as nujol mulls,  $\lambda_{\max}$  in  $\text{cm}^{-1}$

a. dubious purity, see text.

stretching vibration for the hydrogen-bonded amine hydrogen.



The azomethine stretching vibration appears at  $1620 \pm 15 \text{ cm}^{-1}$ , which falls within the range quoted by Smith ( $1610 - 1635 \text{ cm}^{-1}$ ) in his review.<sup>7</sup>

The absorption at  $1585 \pm 5 \text{ cm}^{-1}$  is assumed to be due to o-substituted benzene by analogy with other workers assignments.<sup>8,9.</sup>

Other absorptions in the infrared region can be assigned by comparison with other workers' results. Table [3.6] compares the spectra of amben and salen, in the regions where assignments have been made for the latter.<sup>8</sup> Some additional absorptions of amben are also assigned.

amben a	salen b	salen assignments	amben only
3440 (a)			NH (free) Stretch
3250 (m)			NH (H-bonded) Stretch
3070 (w)	3058	CH (aromatic) Stretch	
3030 (w)	3015	CH (aromatic) Stretch	
2930 (w)	2957	CH <sub>2</sub> (aliphatic) Stretch	
2875 (m)	2933	CH <sub>2</sub> (aliphatic) Stretch	
2855 (m)	2870	CH <sub>2</sub> (aliphatic) Stretch	
	2650	OH Stretch	
1636 (s)	1637	C = N Stretch	
1609 (sh.)	1612	C = C (aromatic) Stretch	
1585 (s)	1580	C = C (aromatic) Stretch	
1559 (s)			NH (free) Bend
1492 (s)	1499	C = C (aromatic) Stretch	
1461 (s)	1460	CH <sub>2</sub> (aliphatic) Bend	

Table [3.6] comparing the infrared absorption spectrum of amben with salen.

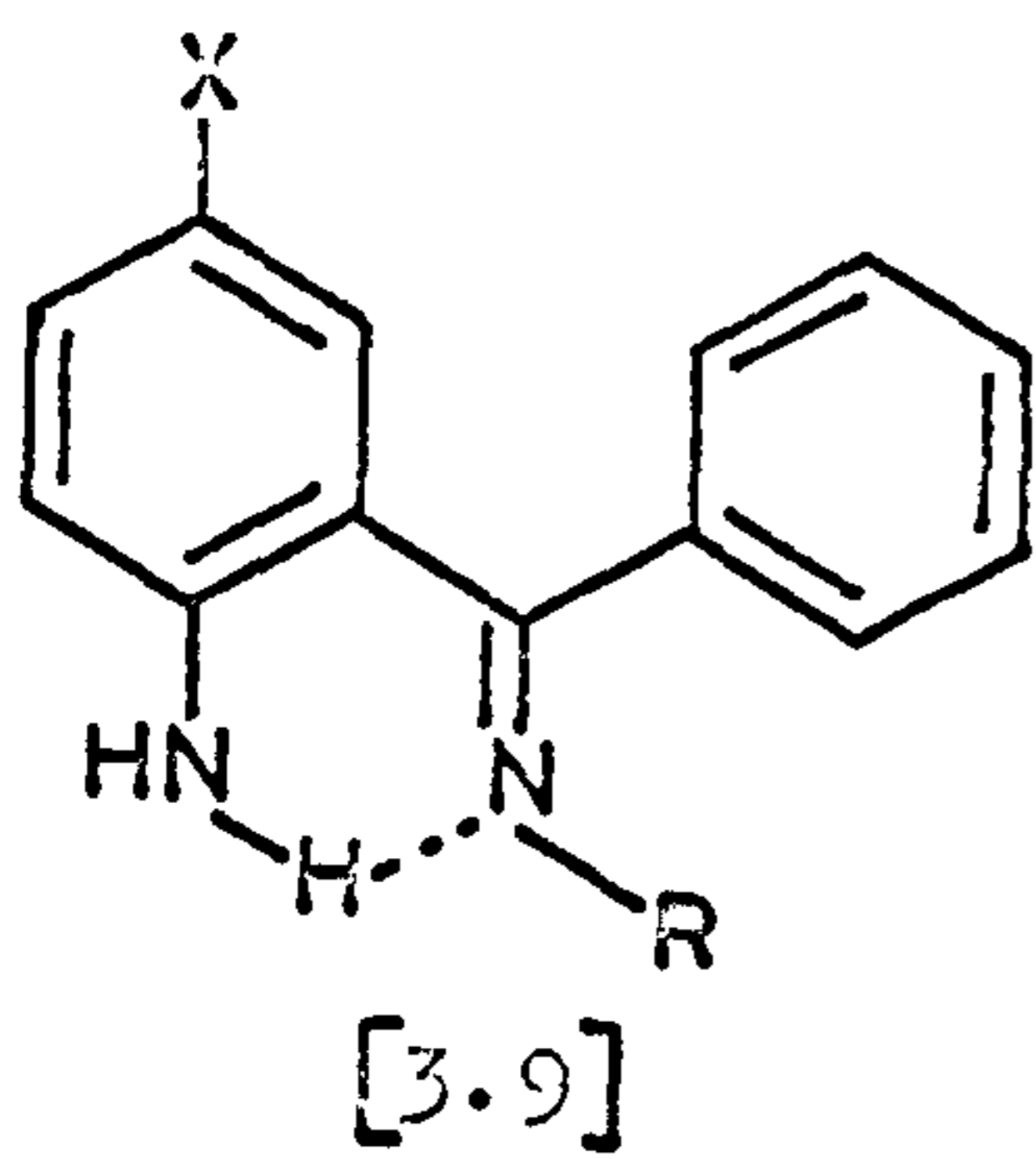
(a) KBr disc (  $\lambda_{\max}$  cm<sup>-1</sup> ) (b) Mulls<sup>8</sup>

### 3.6. Electronic spectra.

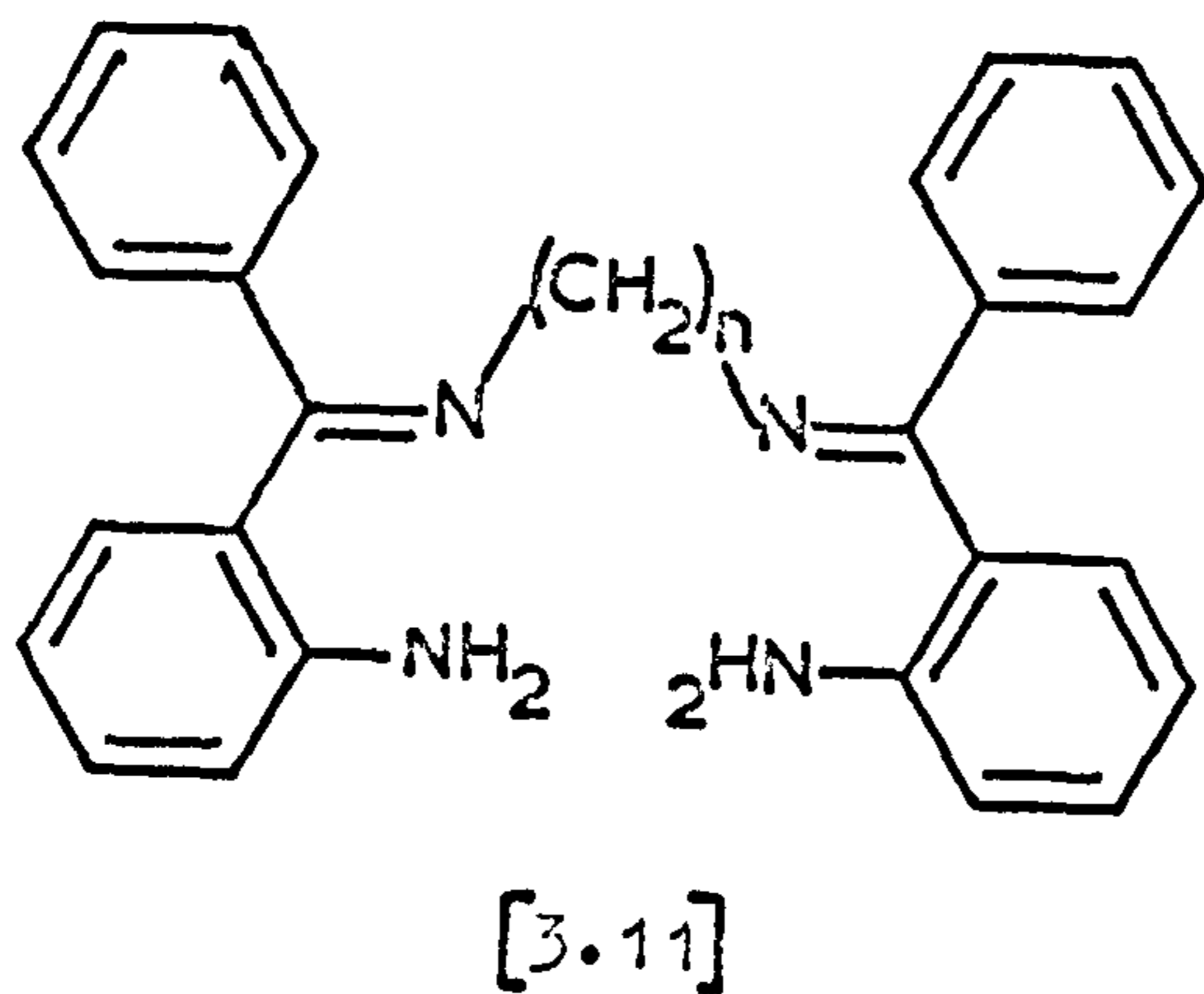
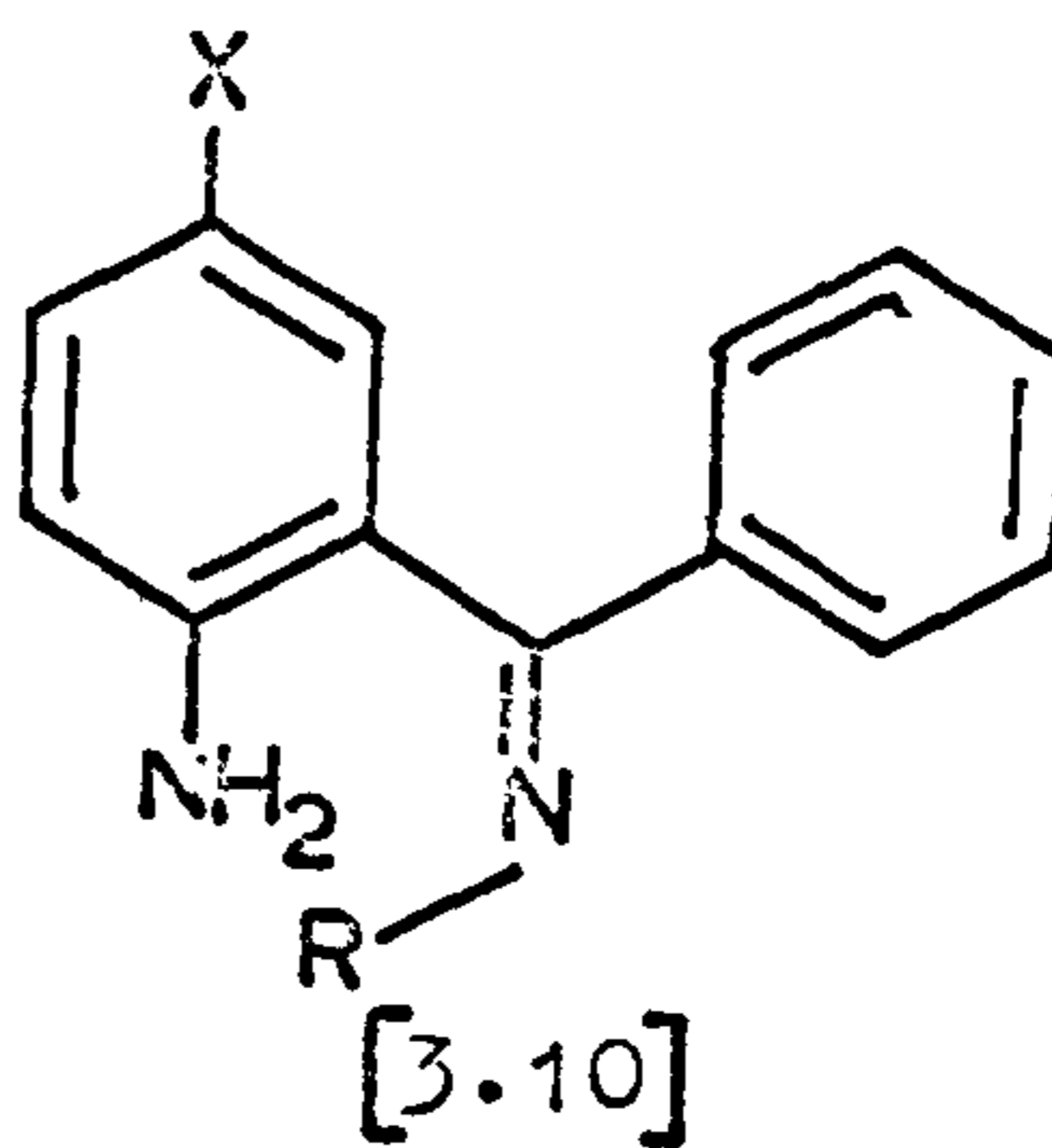
The electronic spectra of the ligands in methanol solutions are given in table [3.7]. All the compounds show two main bands, one at 340 - 360  $m\mu$  and a second, more intense, at 226 - 234  $m\mu$ . The spectra are more complex than those of simple Schiff bases.<sup>7</sup> The complexity of the electronic spectra of Schiff bases of aromatic aldehydes increases greatly with substituents in the aromatic ring, especially if these have non-bonding electrons.<sup>10,11</sup>

Ligand	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )
amben	343 (6940)	296 (6910)	260 (sh) (7860)	232 (24500)
ambtn	340 (6730)	293 (6260)	260 (sh) (9900)	230 (28100)
ambbuten	340 (6080)	290 (5420)	257 (sh) (10800)	228 (29200)
ambdecen	340 (6530)	292 (5600)	255 (sh) (9780)	227 (29100)
ampen	345	- (9680)	260 (sh) (17300)	234 (53000)
ampbuten	345 (7840)	-	260 (sh) (12600)	232 (48600)
amaen	360 (5700)	295 (4200)	260 (sh) (9670)	228 (25400)

anti- isomers



syn- isomers



Ligand	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )
Me-amben	362 (8630)	310 (3850)	260 (11860)	227 (44200)
Me-ambbuten	358 (11200)	270 (11100)	263 (11900)	226 (65400)
Me-ambdecen	355 (12000)	271 (9400)	263 (12200)	227 (78000)

Table [3.7]. Absorption maxima ( $m\mu$ ) of methanolic solutions of the ligands.

### 3.6.1. Benzophenone imines.

Benzophenone imine and methylimine show only single absorption bands at  $252 m\mu$  ( $\epsilon$ , 17500) and  $246 m\mu$  ( $\epsilon$ , 15400) respectively.<sup>7</sup>


The spectra of some substituted o-aminobenzophenone imines and the ligands ampen and ampbuten [3.11] synthesised in this work are compared in table [3.8]. The spectrum of o-aminobenzophenone is also included.

The syn-isomers [3.10] show two bands; one in the region  $238 - 248 m\mu$  ( $\epsilon$ , 17800 - 25300) and another, much weaker, in the region  $310 - 316 m\mu$  ( $\epsilon$ , 2300 - 2900), whereas the two bands for the anti-isomers [3.9] are found at  $221 - 231 m\mu$  ( $\epsilon$ , 26000 - 33900) and  $331 - 362 m\mu$  ( $\epsilon$ , 3300 - 5000). The absorption bands above  $320 m\mu$



are believed to be due to the chromophore arising from conjugation of the o-aminophenyl group with the imino bond, which is possible only when the nitrogen substituent is anti.<sup>2</sup> It is this band which we would expect to be fundamentally altered on chelation.

In the spectra of ampen and ampbuten the two bands occur in very similar positions to those of the anti-isomers [3.10]. Also the molar extinction coefficients for the bands are about twice the values for the anti-isomers, which is to be expected, since ampen and ampbuten have two benzophenone imine chromophores per molecule. All evidence from the electronic spectra points to the anti - anti configuration [3.11] being correct for ampen ampbuten.

Compound		$\lambda_{\max} (m\mu)$ ( $\epsilon$ )	$\lambda_{\max} (m\mu)$ ( $\epsilon$ )
<u>Syn</u> - isomers [3.10]			
X =	R =		
H	OH	238 (17800) <sup>b</sup>	310 (2900) <sup>b</sup>
Cl	OH	246 (21700) <sup>a</sup>	316 (2000) <sup>b</sup>
Cl	CH <sub>2</sub> CH <sub>2</sub> -N 	248 (25300) <sup>a</sup>	
Br	OH	244 (22000) <sup>b</sup>	314 (2300) <sup>b</sup>
o-aminobenzophenone		236 (21000) <sup>c</sup>	365 (5500) <sup>c</sup>

Compound		$\lambda_{\max}$ (m $\mu$ )	$\lambda_{\max}$ (m $\mu$ )
e		( $\epsilon$ )	( $\epsilon$ )
<u>anti-isomers</u> [3.9]			
X =	R =		
H	OH	221 (33900) <sup>b</sup>	331 (5000) <sup>b</sup>
Cl	OH	231 (26000) <sup>d</sup>	346 (3300) <sup>d</sup>
Cl	<chem>CH2CH2N1CCCC1O</chem>	233 (27100) <sup>d</sup>	362 (4840) <sup>d</sup>
Br	OH	227 (29000) <sup>b</sup>	344 (3900) <sup>b</sup>
<hr/>			
ampen, [3.11]	(n = 2)	234 (53000)	345 (9680)
ampbuten, [3.11]	(n = 4)	232 (48600)	345 (7840)

Table 3.8 Electronic spectra of some o-aminobenzophenone imines.

- (a) Ethanol solution, only this band quoted.<sup>2</sup>  
 (b) Isopropanol solution.<sup>12</sup>  
 (c) Ethanol solution.<sup>13</sup>  
 (d) Ethanol solution.<sup>2</sup>  
 (e) Substituents as in [3.9], [3.10] and [3.11].

### 3.6.2. Assignments for the principal bands.

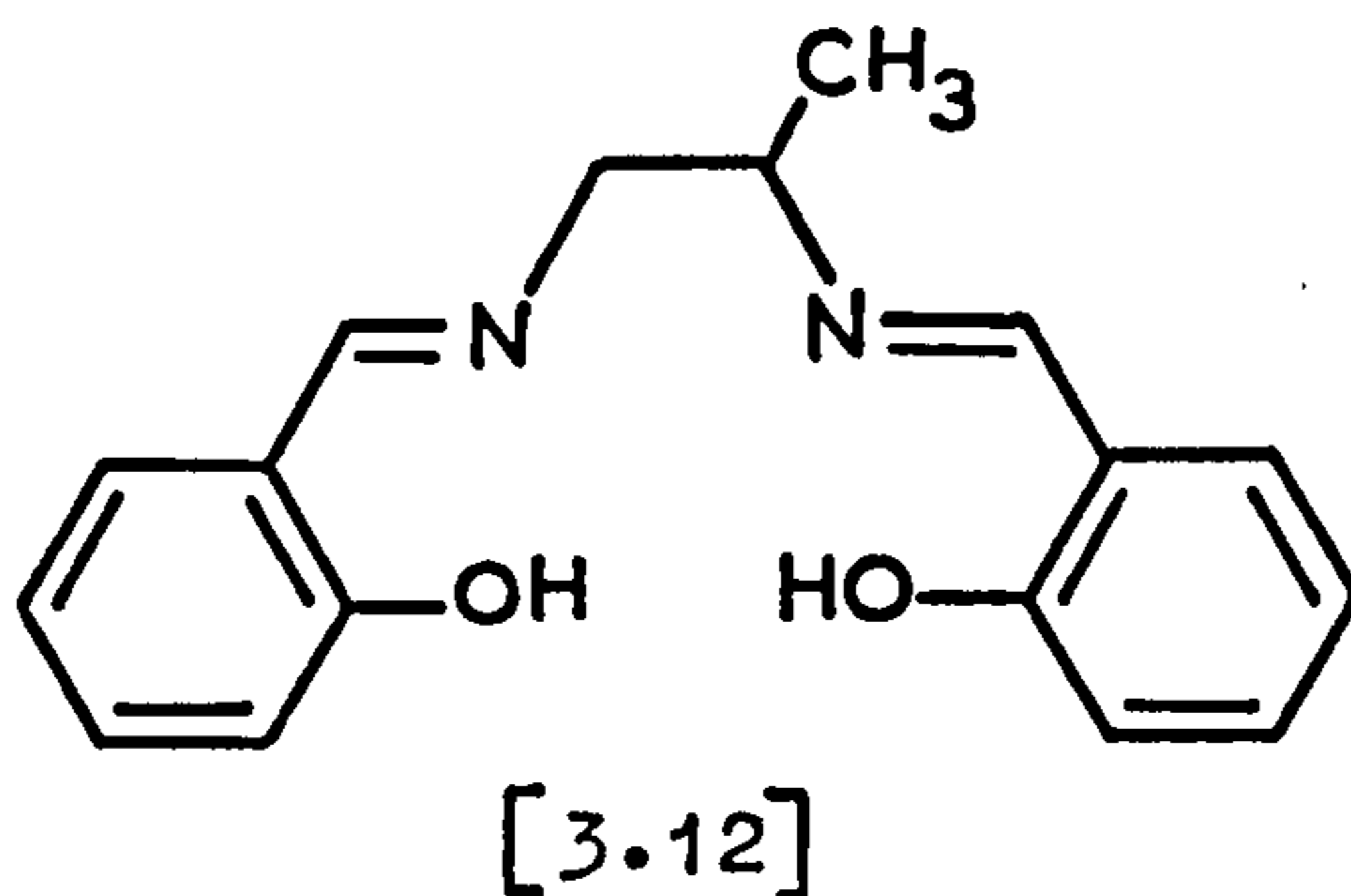
Following the normal practice<sup>14</sup> of assigning the lower energy transition to a  $n - \pi^*$  transition, it would seem reasonable to ascribe the bands at 340 - 362 m $\mu$  to a  $n - \pi^*$  transition, and the bands at 226 - 234 m $\mu$  to a  $\pi - \pi^*$  transition. We expect the  $n - \pi^*$  transition

to be more sensitive to effects altering conjugation to a substituent with a lone pair of electrons, and table [3.8] shows that the lower energy band changes position more on altering the configuration about the azomethine band from the anti to the syn form.

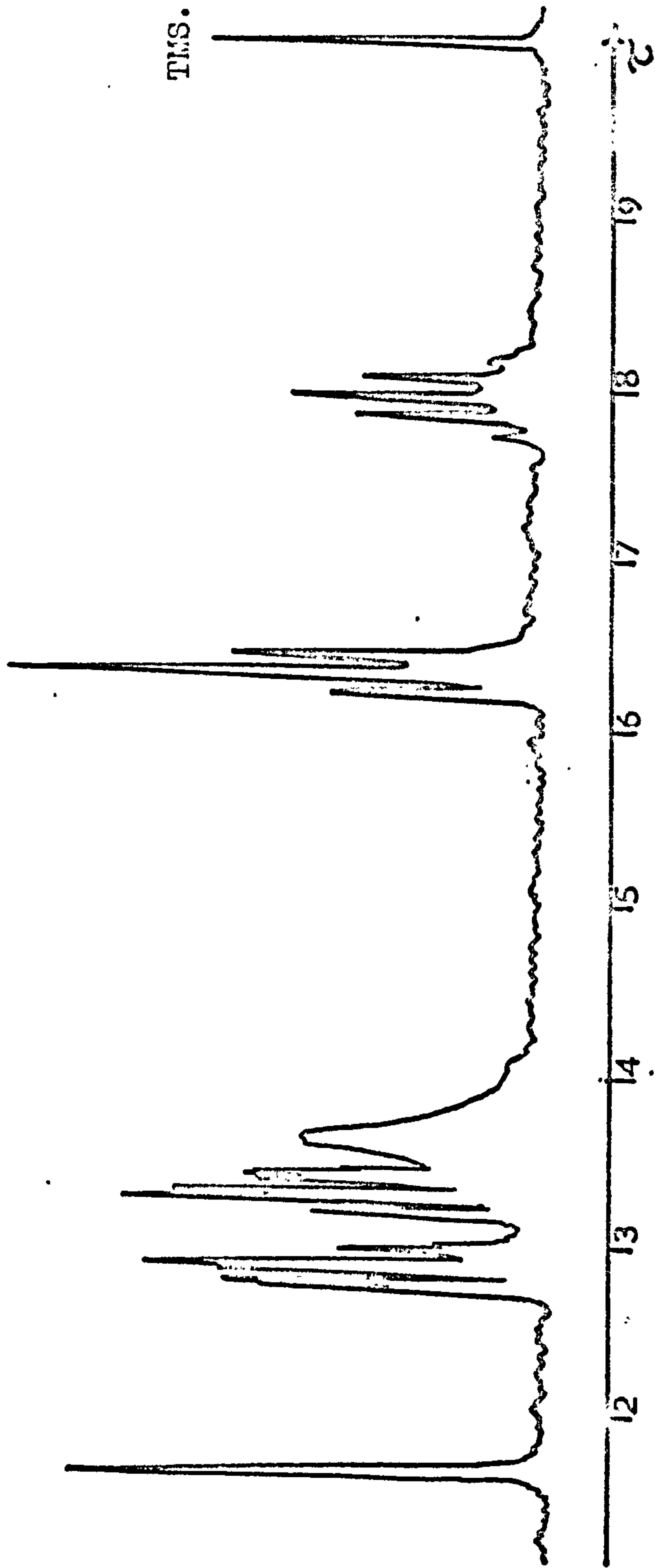
Extension of the above assignments from the o-aminobenzophenone imines to the other ligands is supported by the following :-

(a) methylating the amino group of o-aminobenzophenone imines causes a shift of the  $n - \pi^*$  transition to lower energies.<sup>12</sup> A shift from 343 to 362  $m\mu$  is observed on methylating amben (c.f. Me-amben, table [3.7] )

(b) Bosnich<sup>15</sup> assigned the  $n - \pi^*$  transition as the lower energy absorption for the ligand salpn [3.12]



(c) Examination of Me-ambdecen in different solvents shows (table [3.9]) that the position of the lower energy band is more sensitive to change of solvent, which is to



N.M.R. spectrum of amibtn as  $CDCl_3$  solution.

be expected of the transition is dependent on lone pair electrons associated with hydrogen-bonding. Unfortunately the shifts are small and somewhat inconclusive.

solvent	Methanol	Ether	$C_6H_{12}$ c	D.M.F a
$\lambda_{max}$ (m $\mu$ )	355	358	360	355
	271	271	272	272
	263	264	263	263
	227	228	227	- <sup>b</sup>

Table [3.9] Variation of positions of absorption bands for Me-ambdecen with solvent.

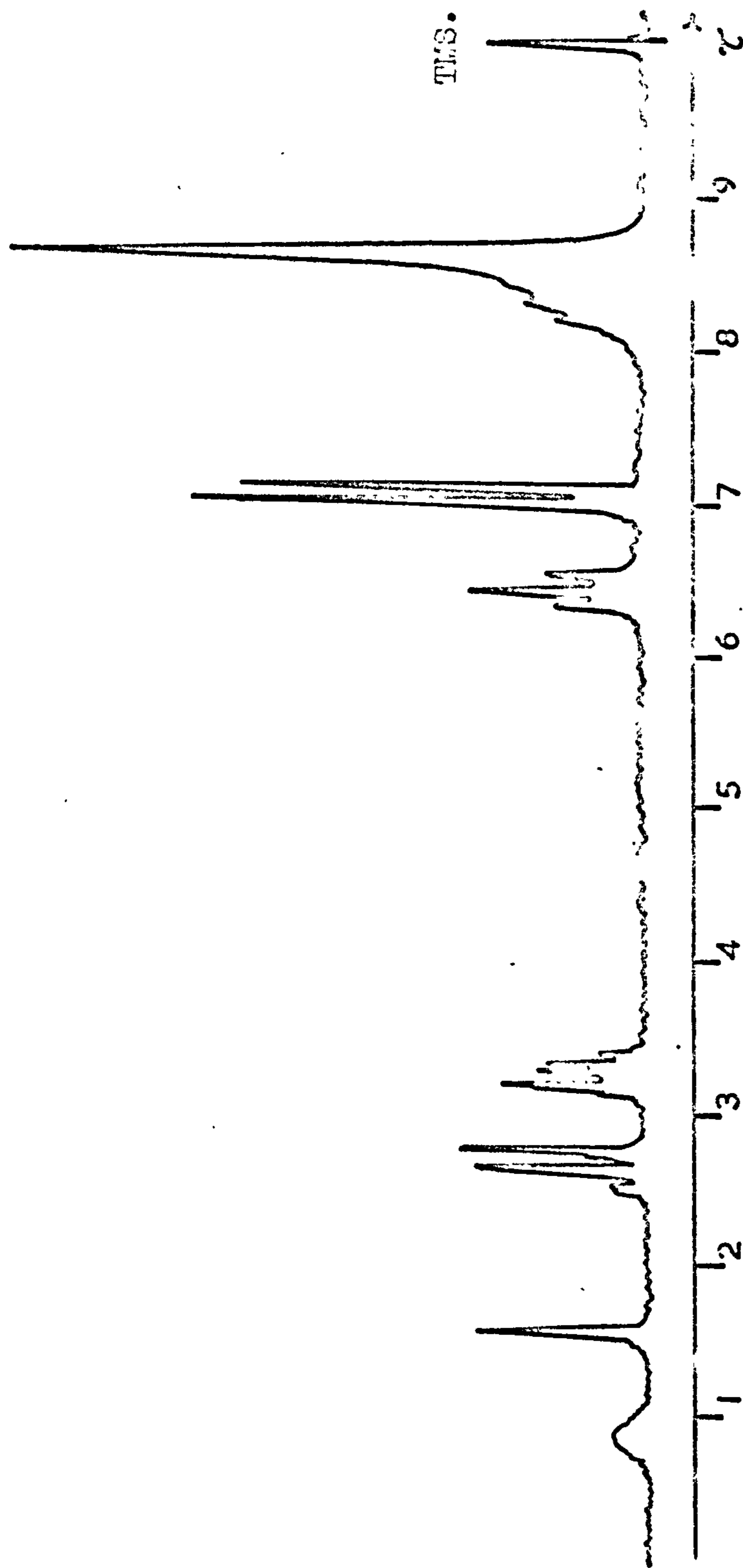
(a) Dimethylformamide (b) This region is obscured by solvent absorption (c) Cyclohexane.

### 3.7. N.M.R. spectra.

The N.M.R spectra are tabulated in the experimental section after the preparation of each ligand. The spectra of ambtn and Me-ambdecen are shown on pages F50 and F51 as typical examples.

#### 3.7.1. N-H proton resonances.

In all cases where solvent and solubility permitted the resonance signal for NH protons was assigned by addition of a few drops of deuterium oxide, which exchanges rapidly with the NH protons, and causes the



N.M.R. spectrum of Me-undecene as CDCl<sub>3</sub> solution.

signal to collapse (deuterium has  $I = 1$  and its N.M.R. frequency will be in a different range, e.g. for a 10 kilogauss field the  $^1\text{H}$  N.M.R. frequency is  $42.577 \text{ Mc sec}^{-1}$  while the  $^2\text{H}$  N.M.R. frequency is  $6.536 \text{ Mc sec}^{-1}$ ).<sup>16</sup>

Where the NH proton resonance occurs 'under' other large signals its presence has to be inferred by comparison of the integrated areas of the signals before and after the addition of  $\text{D}_2\text{O}$ .

The chemical shifts of the  $\text{NH}_2$  protons in substituted o-aminobenzophenone oximes have been claimed to be diagnostic of configurational isomerism.<sup>12</sup> The shifts are much lower ( $3.0 - 3.5 \tau$ ) for the anti-isomers ([3.9], page F46) than the corresponding syn-isomers ( $5.0 - 5.5 \tau$ ) ([3.10], page F46) when measured in dimethyl sulphoxide ( $\text{d}_6$ ) solution, due to the greater strength of hydrogen-bonding in the former.

The shifts of the  $\text{NH}_2$  protons observed in this work fall in the range  $2.9 - 3.6 \tau$ . This is further evidence for the configuration of the ligands being anti-anti about the two azomethine bonds as in [3.11] page F46. (see also page 33 and page 47).

### 3.7.2 N.M.R. spectra of systems containing an N-methyl-anilino group.

Of the ligands type [3.1] page 31, those

derived from N-methyl-o-aminobenzaldehyde showed the most interesting N.M.R spectra. The methyl resonance is a doublet when the spectra are recorded in deuteriochloroform. The splitting disappears after the addition of a small quantity of deuterium oxide, and is ascribed to spin-spin coupling between the methyl protons and the hydrogen-bonded amine proton.

Proton-proton spin-spin coupling in the system H-C-N-H is quite unusual.<sup>17</sup> The absence of coupling in strongly basic amines e.g. methylamine has been attributed to rapid proton exchange in solution promoted by traces of acid in the solvent.<sup>17,18</sup> Proton exchange is relatively slow for amide groups, and in N-alkylamides the  $\alpha$ -protons of the alkyl group are coupled ( $J = 5-6$  c.p.s) with the amide protons.

The N.M.R spectra of some compounds related to N-methyl-o-aminobenzaldehyde were investigated briefly. Table [3.10] shows the shifts of the NH and methyl protons and the coupling between them.

Compound	NH shift ( $\tau$ )	CH <sub>3</sub> shift ( $\tau$ )	$J_{\text{NH,CH}_3}$ (c.p.s.)
N-methylanthranilic acid a	1.63	7.11	0
N-methyl-o-aminobenzaldehyde b	1.63	7.14	5.1
N-methyl-o-aminobenzaldehyde- methyimine b	1.08	7.13	4.5



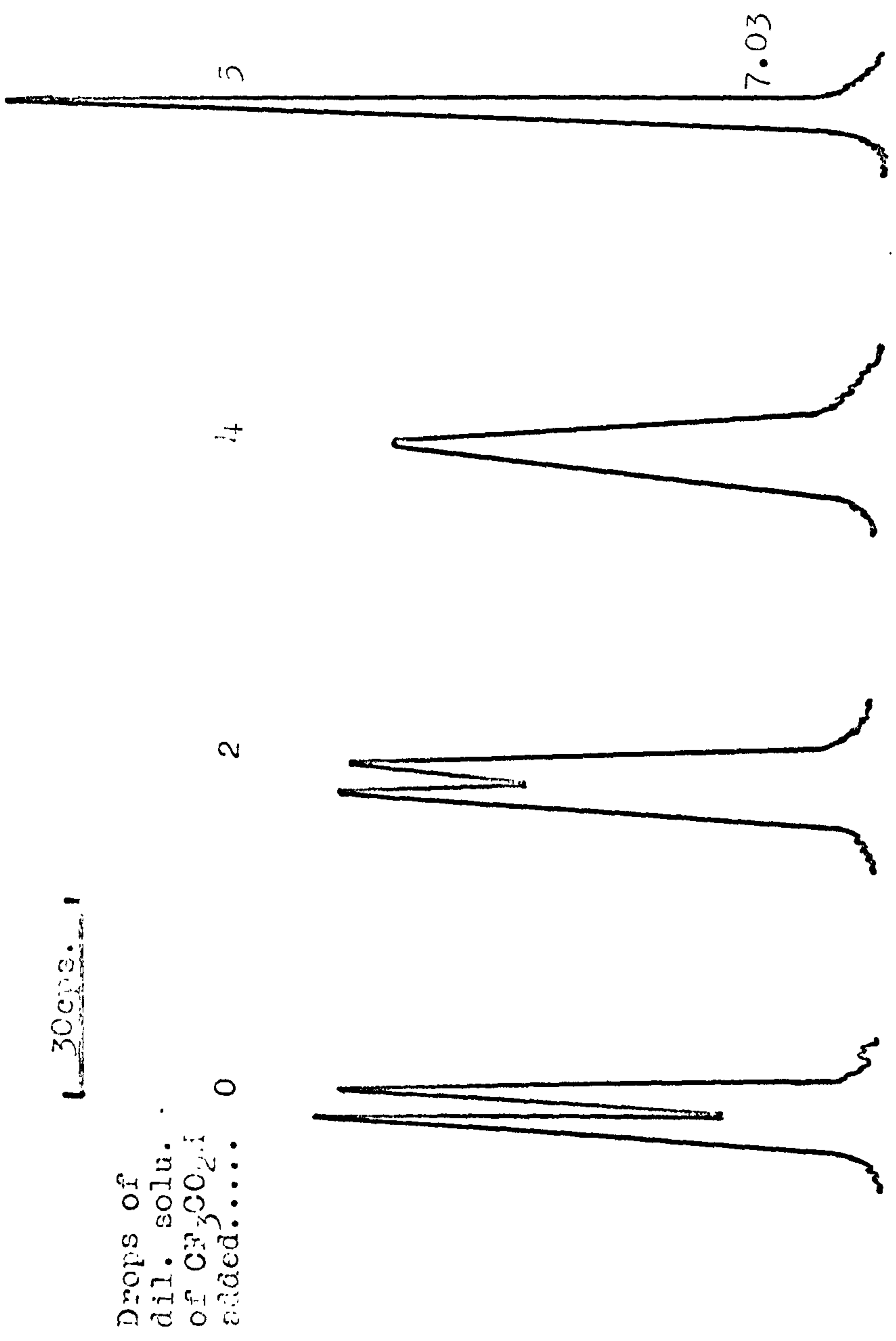
Compound		NH shift ( $\tau$ )	CH 3 shift ( $\tau$ )	J NH, CH <sub>3</sub> (c.p.s)
N-methyl-o-aminobenzaldehyde-oxime	b	-(c)	7.12	5.1
Me-amben	b	1.05	7.19	5.4
Me-ambbuten	b	1.20	7.15	5.4
Me-ambdecen	b	0.85	7.05	5.3

Table [3.10] N.M.R spectra of compounds related to N-methyl-o-aminobenzaldehyde.

(a) Solution in acetone - d<sub>6</sub> (b) Solution in deuteriochloroform.  
(c) Not observed, possibly very broad. Peak at 5.32 $\tau$  is more likely to be oxime proton.

Of the compounds studied, all except N-methyl-anthranilic acid showed a coupling of  $5 \pm 0.5$  c.p.s between the methyl and amino group protons. Possibly N-methyl-anthranilic acid gives a high enough concentration of protons in solution for amino protons exchange to be sufficiently fast to cause the doublet to collapse to a singlet (see page 55 ).

Me-ambbuten was chosen for study under varied conditions, due to its high solubility in most organic solvents.



[3.13]. The effect of addition of acid on the N.M.R. resonance of the methyl group in Fe-cr buten.

(1) Increase in temperature. The spectra of Me-ambbuten in various solvents were examined at temperature intervals up to just below the boiling points of the solvents.

The existence of a spin multiplet requires that the nuclei responsible should be coupled for a time greater than  $J^{-1}$ , where  $J$  = coupling constant for the two nuclei.<sup>16</sup> It was hoped that increasing temperature would increase the rate of proton exchange to the point where the average lifetime of a NH bond was less than 0.2 secs and the methyl doublet would collapse to a singlet.

The results are shown in table [3.11]. No indication of coalescence of the methyl doublet lines was observed, even in the polar solvent dimethyl sulphoxide -  $d_6$  at 150°

Solvent	Temp.	Methyl resonance		
		Shift ( $\tau$ )	Appearance.	J (c.p.s)
CDCl <sub>3</sub>	- 20	7.15	doublet	5.4
	+ 50	7.13	doublet	5.5
CCl <sub>4</sub>	- 20	7.13	doublet	5.4
	+ 75	7.12	doublet	5.5
Acetone- $d_6$	25	7.14	doublet	5.5
	50	7.13	doublet	5.3
DMSO $d_6$	a 15	7.18	doublet	5.3
	150	7.14	doublet	5.5

Table [3.11]. Temperature variation of N.M.R of methyl protons in Me-ambbuten. (a) Dimethyl sulphoxide.

(2) Hydrogen ion concentration. The concentration of exchangeable protons in a carbon tetrachloride solution of Me-ambbuten was steadily increased by addition of small quantities of a dilute solution of trifluoroacetic acid in carbon tetrachloride. As the proton concentration is increased the methyl doublet coalesces to give a broad singlet, and finally a sharp singlet at a slightly lower  $\tau$  value (see [3.13] on page F54 ).

Increasing the rate of exchange of amine protons causes confusion of their spin states experienced by the methyl protons and collapse of the doublet. When the exchange is fast enough the spin states of the amine protons are effectively completely 'averaged' and no coupling (a sharp singlet) is observed. The methyl resonance of a series of substituted N-methylanilines has been investigated.<sup>17</sup> Spin-spin coupling between methyl and amine protons was not observed for the more basic anilines due to a high rate of proton exchange, whereas the less basic anilines showed a doublet ( $J = 4.8 - 5.8$  c.p.s) for the methyl resonance.

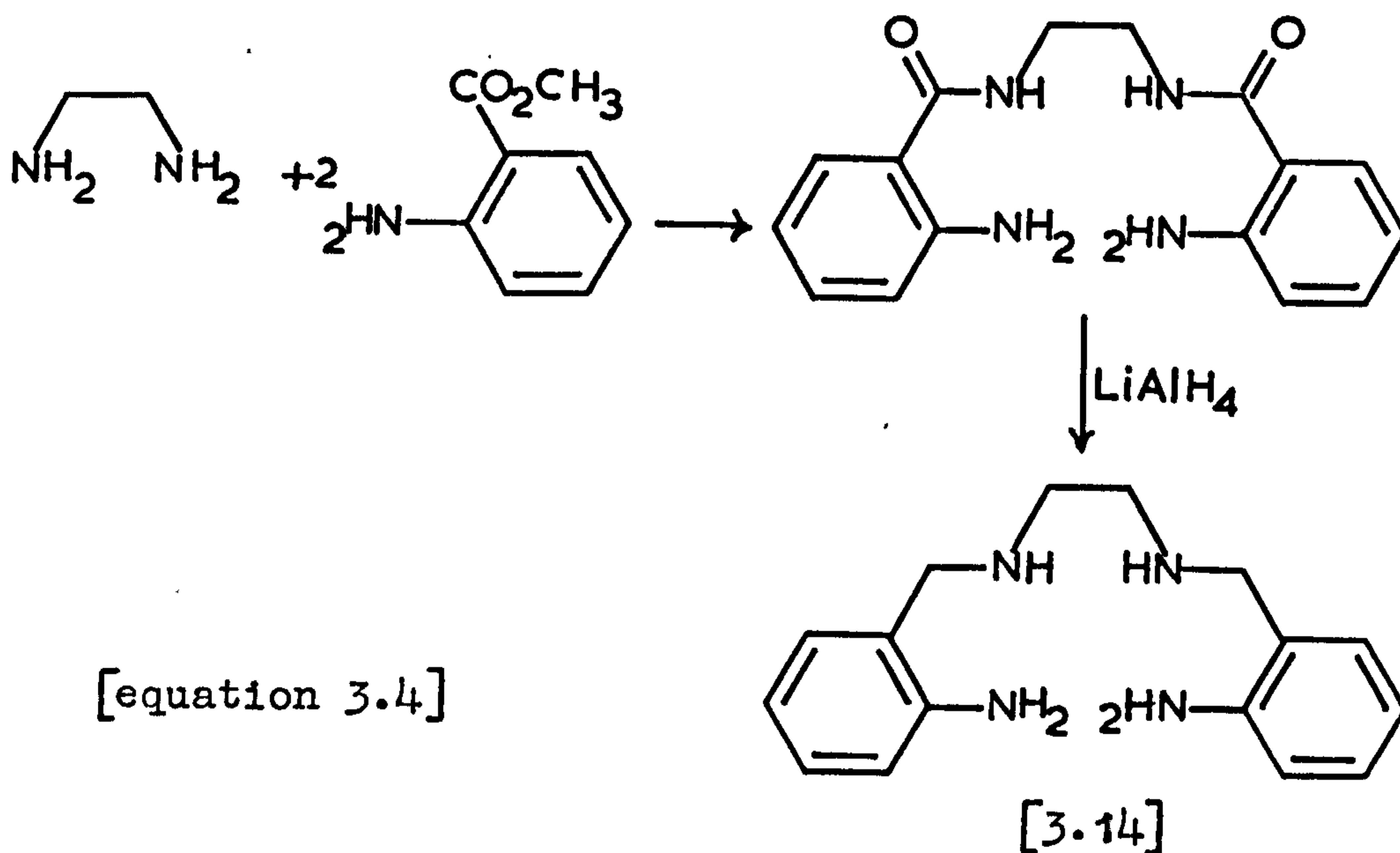
The change in position of the methyl resonance at high proton concentration is due to different shielding of methyl protons in the systems  $\text{CH}_3\text{-NH}$  and  $\text{CH}_3\text{-NH}_2^+$ . Such a change in chemical shift on protonation has been used<sup>21</sup> to establish the position of N-methyl proton

resonances in complex spectra.

3.8. A related ligand with saturated nitrogen atoms.

N,N'-Bis-(o-aminobenzyl)-1,2-diaminoethane, or 2,3:10,11-dibenzo-1,5,8,12-tetra-azadodecane [3.14] has a similar structure to amben, but differs in that there is no conjugation possible between its donor atoms.

A convenient synthetic route to 2,3:10,11-dibenzo-1,5,8,12-tetra-azadodecane is shown in equation [3.4]



The abbreviation amben 4H will be used for [3.14], emphasizing its relationship to amben.

### 3.9. References.

1. R.H. Holm, G.W. Everett and A. Chakravorty, Prog. Inor. Chem., 7, 83, (1966).
2. S.C. Bell, G.L. Conklin and S.J. Childress, J. Amer. Chem. Soc., 85, 2868, (1963).
3. D.Y. Curtin and J.W. Hausser, J. Amer. Chem. Soc., 83, 3474, (1961).
4. M.J.S. Dewar and T. Mole, J. Chem. Soc., 2556 (1956).
5. C.R. Hauser and D.S. Hoffenberg, J. Amer. Chem. Soc. 77, 4885, (1955).
6. J.H. Beynon and A.E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry", Elsevier, 1963.
7. P.A. Smith, "Open Chain Nitrogen Compounds", Benjamin 1965, page 294.
8. P. Teyssie and J.J. Charette, Spectrochim. Acta, 19, 1407, (1963).
9. E.J. Olszewski and D.F. Martin, J. Inorg. Nuclear Chem., 26, 1577, (1964).
10. "U.V. Atlas", Vol. VI, Butterworth's 1968, Table C6/T2.
11. "U.V. Atlas", Vol. III, Butterworth's, 1967, Spectra C6/1, C6/2, C6/3 and table C6/T1.
12. J.G. Pritchard, G.F. Field, K. Koch, G. Raymond, L.H. Sternbach, V. Toome and S. Traiman, Applied Spectroscopy, 20, 363, (1966).
13. G. Porter and P. Suppan, Trans. Faraday Soc., 61, 1664, (1965).

14. M. Kasha, *Discussions Faraday Soc.*, 9, 15 (1950).
15. B. Bosnich, *J. Amer. Chem. Soc.*, 90, 627, (1968).
16. J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon, 1965, page 589.
17. I.D. Rae, *Austral. J. Chem.*, 19, 409, (1966).
18. E. Grunwald, A. Loewenstein and S. Meiboom, *J. Phys. Chem.*, 27, 630, (1957).
19. O. Dudek and G.P. Volpp, *J. Org. Chem.*, 30, 50, (1965).
20. "High Resolution N.M.R. Catalog", Varian Associates, 1962 and 1963, Vol. I, Spectra 85 and 319 and Vol. II Spectrum 547.
21. J.B. Davis, *Chem. and Ind.*, 1094, (1968).

Chapter 4. Nickel (II) complexes of acyclic quadridentate nitrogen ligands.

- 4.1 Classification of acyclic quadridentate nitrogen ligands.
- 4.2 Compounds containing saturated nitrogen donors.
  - 4.2.1 Cis-trans isomerism in octahedral complexes.
  - 4.2.2 Unusual coordination numbers and geometries.
  - 4.2.3 A nickel (II) complex of N,N'-bis-(o-aminobenzyl)-1,2-diaminoethane.
- 4.3 Compounds containing unsaturated heterocyclic nitrogen donors.
- 4.4 Conjugated compounds which lose protons to give anionic ligands.
  - 4.4.1 Preparations and analyses.
  - 4.4.2 Infrared spectra.
  - 4.4.3 N.M.R. spectra.
  - 4.4.4 Magnetic behaviour.
  - 4.4.5 Electronic spectra.
- 4.5 Copper complex.
- 4.6. References.

This chapter describes a series of nickel complexes of ligands whose synthesis have been discussed in chapter 3. The nickel (II) complexes were chosen for



systematic study, prior to working with the corresponding cobalt (II) complexes, because of their presumed greater stability and resistance to oxidation. The copper complex was prepared only for comparison with cyclic analogues of chapter 9.

#### 4.1 Acyclic quadridentate nitrogen ligands.

Recently, as interest in polydentate ligands has grown, a considerable number of quadridentate nitrogen ligands have been studied. In this chapter we are concerned only with acyclic 'N<sub>4</sub>' ligands. Cyclic systems are reviewed in chapter 6.

For the purposes of this discussion it is convenient to group the known acyclic quadridentate nitrogen ligands in the following way.

- (A) Compounds containing saturated alicyclic nitrogen donors.
- (B) Compounds containing unsaturated heterocyclic nitrogen donors.
- (C) Conjugated compounds which lose protons to give anionic ligands.

#### 4.2 Compounds containing saturated alicyclic nitrogen donors.

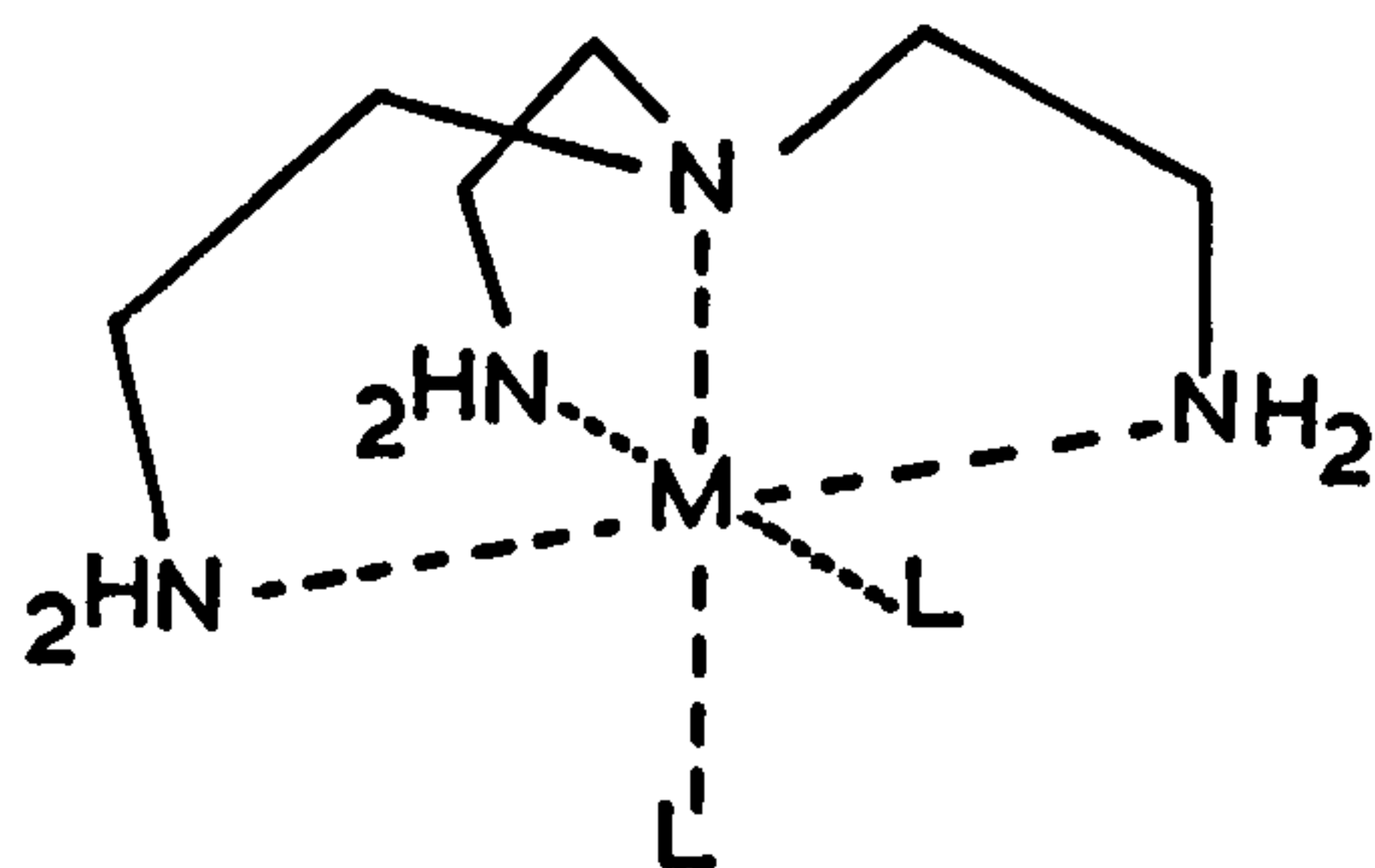
The main interest in this group is in stereo-

chemical effects, which are of two main types.

#### 4.2.1 Cis-trans isomerism in octahedral complexes.

The flexibility of the chains linking the donor atoms frequently allows the chelating ligand to adopt both types of arrangement about the metal ion. Lions<sup>1</sup> has proposed that a square-planar arrangement of four nitrogen atoms (a trans-complex) is more likely when alternate linking chains in the ligand have 2 and 3 carbon atoms.

Tris(2-aminoethyl)-amine was originally synthesized by Mann<sup>2</sup> because as a quadridentate ligand it could only give cis-octahedral complexes<sup>3,4</sup> [4.1].

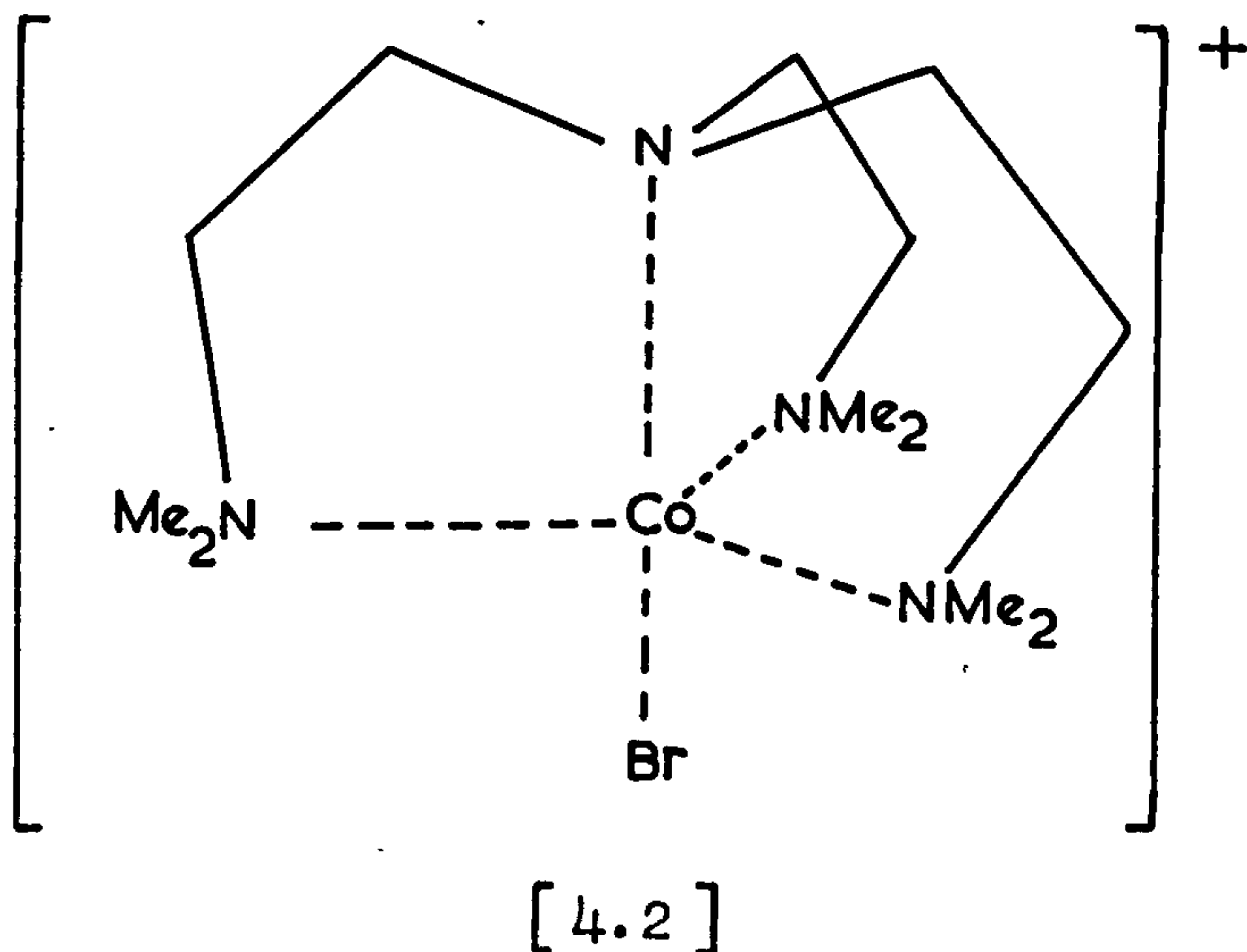


[4.1]

#### 4.2.2 Unusual coordination numbers and geometries.

Certain carefully chosen ligand molecules have steric properties such that when acting as quadridentate ligands they put constraints on the approach of further

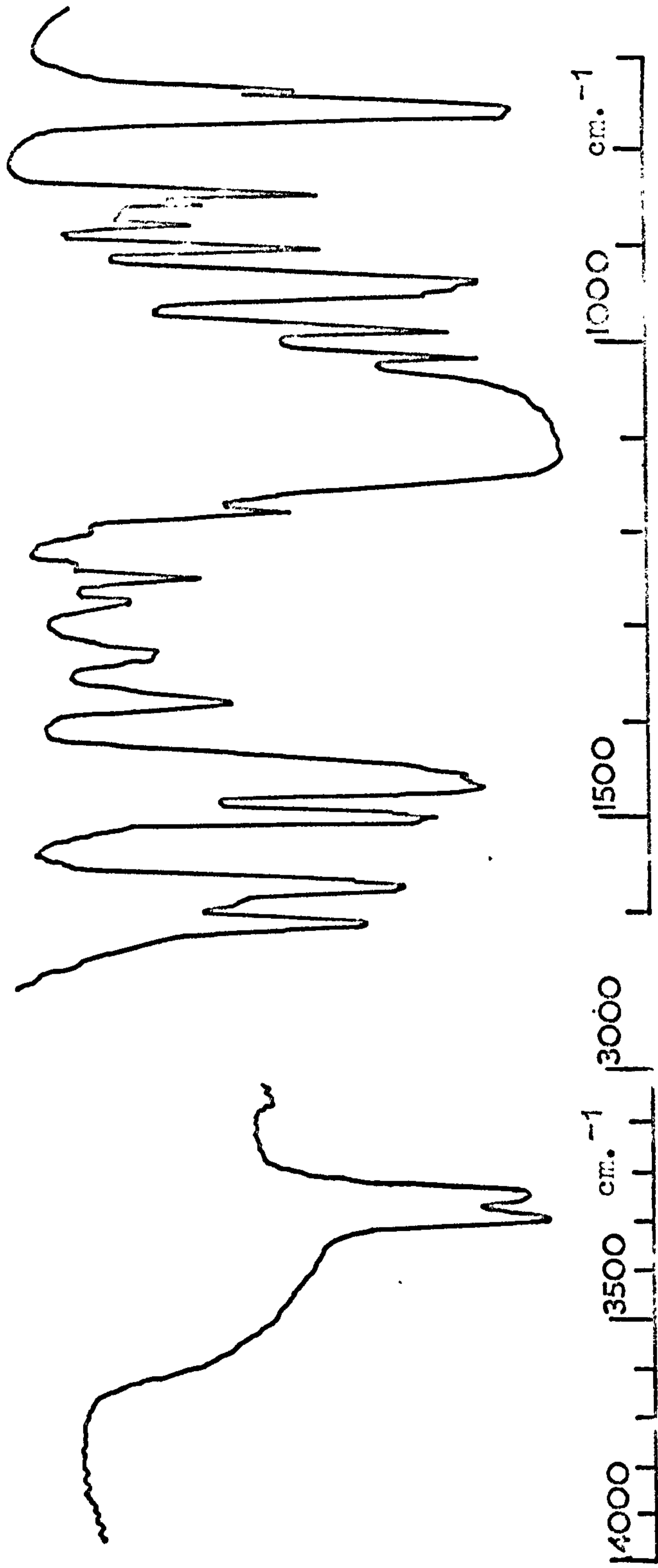
ligands. For example tris-(2-dimethylaminoethyl)-amine gives five coordinate complexes with cobalt (II), nickel (II) and copper (II) ions.<sup>5</sup> The steric crowding produced by the six N-methyl groups prevents the approach of a sixth ligand. The tris-(2-dimethylaminoethyl)-aminebromocobalt (II) ion [4.2] has a trigonal bipyramidal structure with  $C_3$  symmetry.<sup>6</sup>



#### 4.2.3 A nickel (II) complex of N,N'-bis-(o-aminobenzyl)-1,2-diaminoethane.

Pale purple-blue crystals separated when an aqueous nickel (II) chloride solution containing sodium perchlorate was allowed to stand for several days over N,N'-bis-(o-aminobenzyl)-1,2-diaminoethane, (amben 4H).

Analysis showed an atomic ratio of carbon :



[4.3]. The infrared spectrum of  $[\text{Ni}(\text{amben } 4\text{H})(\text{H}_2\text{O})_2]^{2+} (\text{ClO}_4^-)_2$ .

nitrogen of 4 : 1, indicating the presence of amben 4H in the material. The best formula fits the structure  $[\text{Ni}(\text{amben } 4\text{H})(\text{H}_2\text{O})_2]^{2+} (\text{ClO}_4^-)_2$ . Unfortunately the found carbon and nitrogen percentages were rather high (page 289). Perhaps the complex is contaminated with some free ligand, or some perchlorate ions had been replaced by chloride ions.

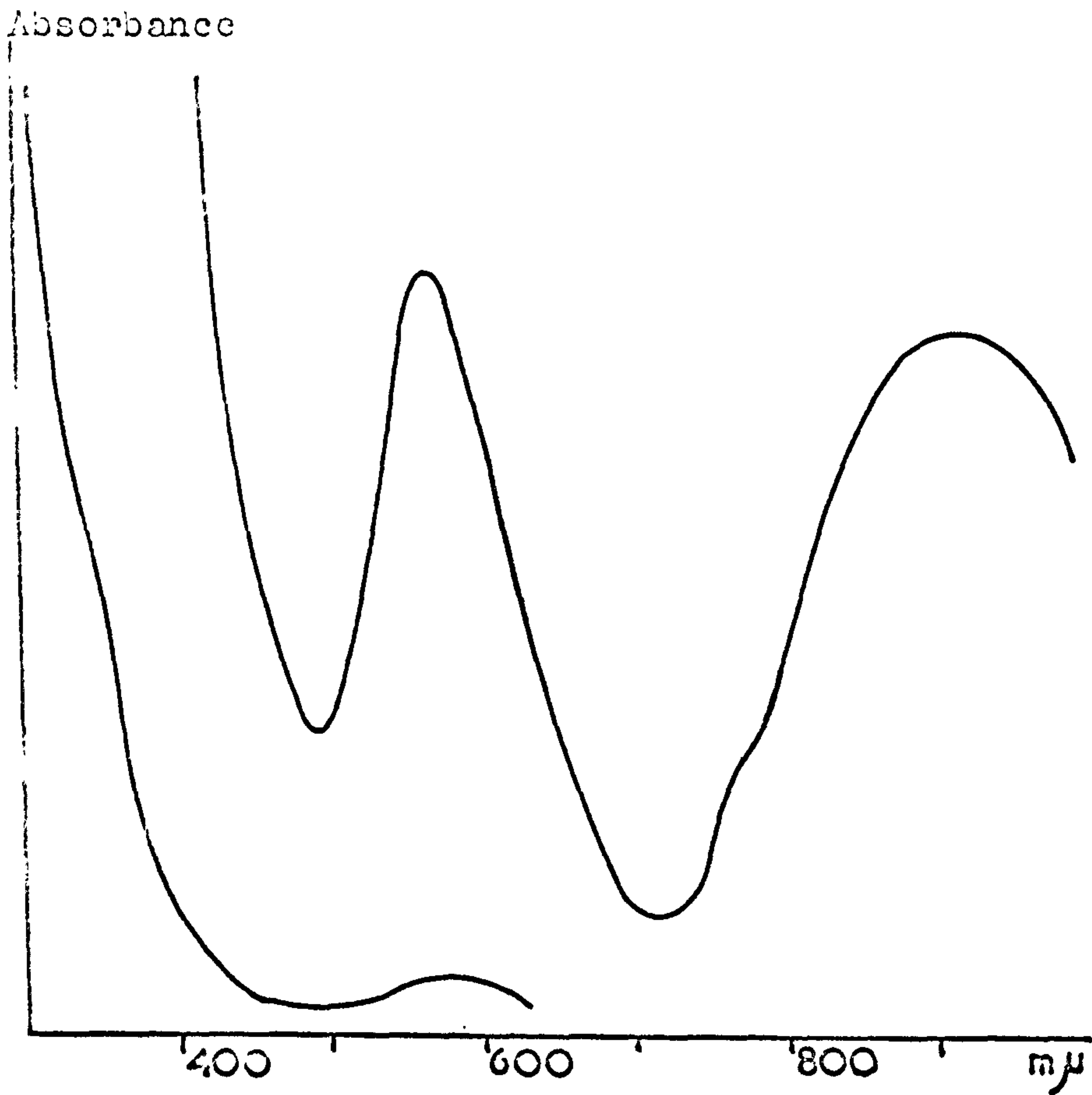
The infrared spectrum in the regions 4000 - 3000 and 1700 - 700  $\text{cm}^{-1}$  is shown in [4.3]. The broad band centred at 1090  $\text{cm}^{-1}$  is due to perchlorate ions, and the lack of splitting indicates that these ions are not coordinated.<sup>7</sup>

The magnetic moment of the nickel ion ( $2.82 \pm .08$  B.M) is consistent with a high spin octahedral configuration,<sup>8</sup> and the electronic spectrum of the complex (table [4.1]) closely resembles other paramagnetic quadridentate amine ligand complexes.

$\text{Ni}(\text{amben } 4\text{H})(\text{H}_2\text{O})_2^{2+}$		340(sh)	570	780(sh)	930
$\text{Ni}(\text{tren})(\text{H}_2\text{O})_2^{2+}$	a	360	561	782(sh)	950
$\text{Ni}(\text{trien})(\text{H}_2\text{O})_2^{2+}$	b	358	564	800(sh)	962

Table [4.1] Absorption maxima ( $m\mu$ ) of aqueous solutions of some quadridentate amine complexes of nickel (II)

- (a) Tren = tris(2-aminoethyl)amine, ref. 3  
 (b) Trien = triethylenetetramine, ref. 9



The visible spectrum of  $[\text{Ni}(\text{amben } 4\text{H})(\text{H}_2\text{O})_2]^{2+}$

in water at two concentrations.

In some cases<sup>9,10,11,12,13</sup>. nickel (II) octahedral complexes with four coordinated amine donors may be dehydrated to give yellow diamagnetic complexes with a presumed square-planar arrangement of the nitrogen donors about the nickel ion.  $[\text{Ni}-(\text{amben } 4\text{H})(\text{H}_2\text{O})_2]^{2+}(\text{ClO}_4^-)_2$  showed no tendency to lose water from its coordination sphere when heated at  $100^\circ\text{C}$  under high vacuum.

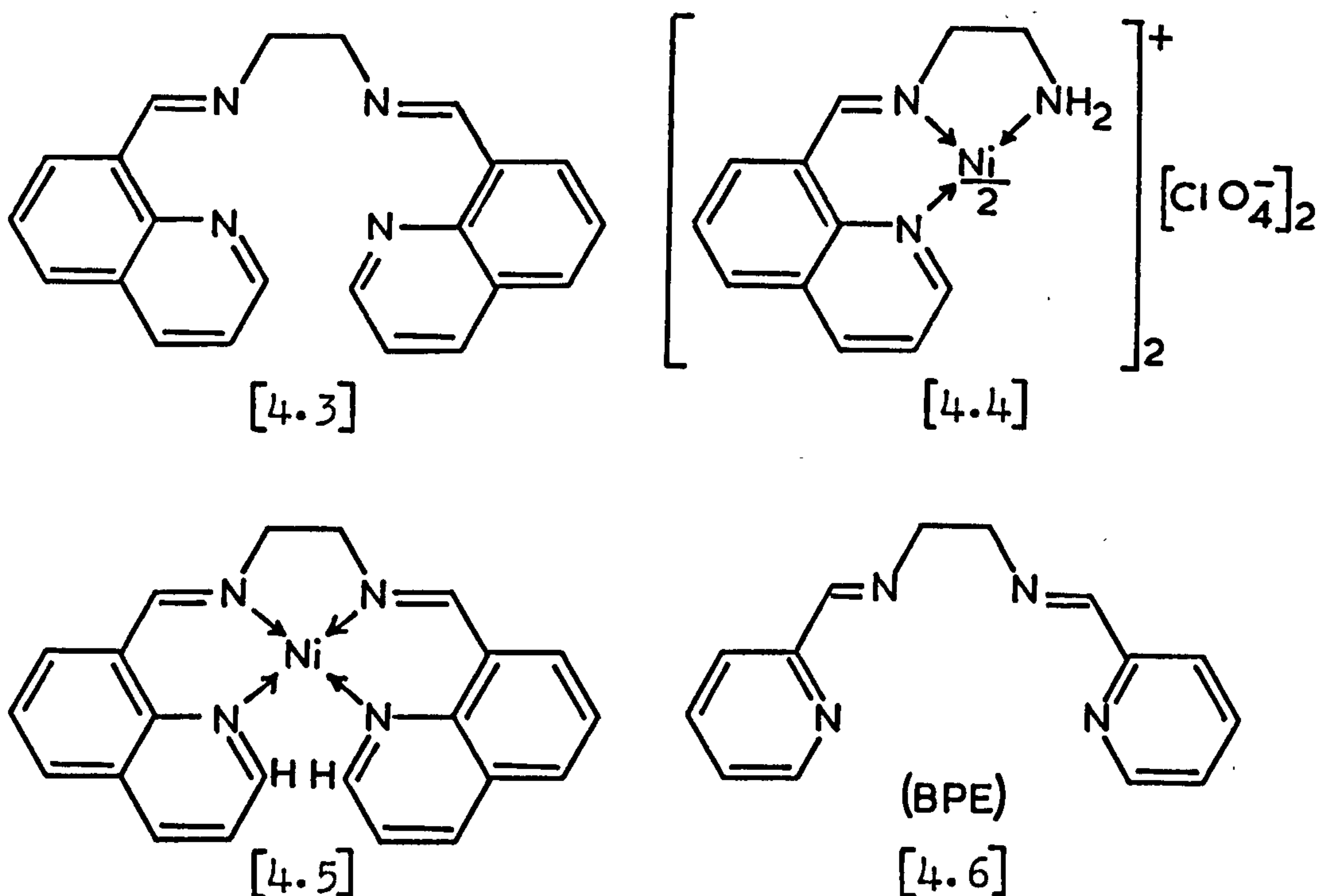
The more unsaturated ligand amben forms complexes of nickel (II) with quite different properties (see section 4.4). These differences must result in part from the conjugation in the ligand amben which facilitates loss of a proton on complexation, and the planarity of the two fragments ([2.3], chapter 2) of the coordinated ligand.

#### 4.3 Compounds containing unsaturated heterocyclic nitrogen donors.

Schiff bases of quinoline and pyridine aldehyde<sup>14,15</sup> and mixed molecules containing saturated nitrogen atoms in chains bridging heterocyclic rings<sup>16,17</sup> are the most important members of this group.

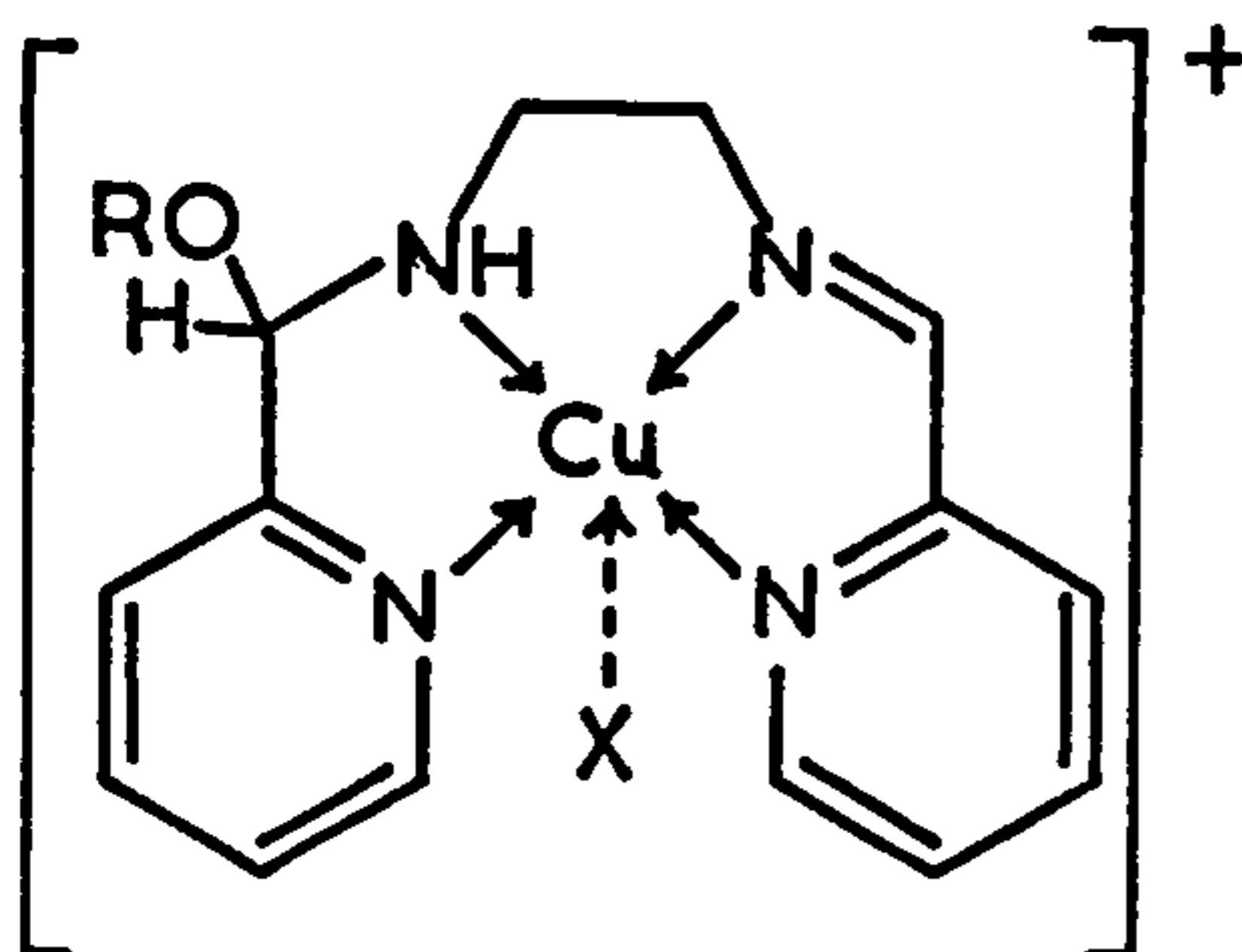
The Schiff base ligands often show interesting steric effects. 1,2-bis-(8-quinolylmethyleneimino)ethane [4.3] is hydrolysed by nickel(II) perchlorate solution and gives<sup>14</sup> bis-(1-amino-2-(8-quinolylmethyleneimino)

ethanato)nickel(II) perchlorate [4.4] . The square-planar arrangement of [4.3] about a nickel(II) ion (see [4.5] ) suffers from the strong interactions of the quinolyl 2-H atoms, but the octahedral complex [4.4] is much more thermodynamically stable.<sup>14</sup>

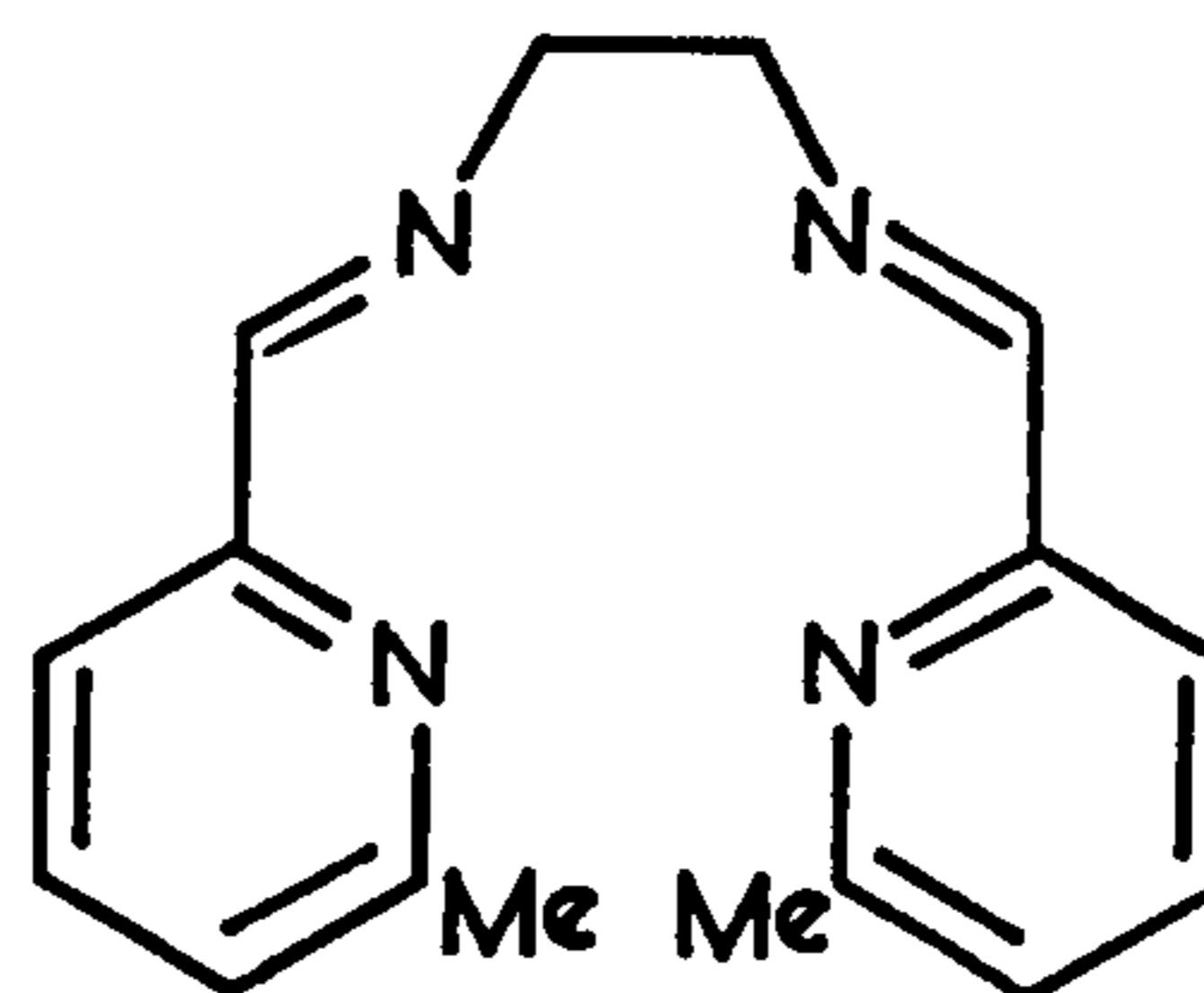


Similarly 1,2-bis-(2-pyridylmethyleneimino)-ethane [4.6] can give five-coordinate complexes<sup>18</sup>  $[\text{Cu}(\text{BPE})\text{X}]\text{X}$ , add a molecule of an alcohol to give<sup>18</sup> [4.7] in which some of the strain has been relieved, or partially hydrolyse to give<sup>14,19</sup> the bis(1-amino-2-(2-pyridylmethyleneimino)ethane)iron(II) complexes [4.8].



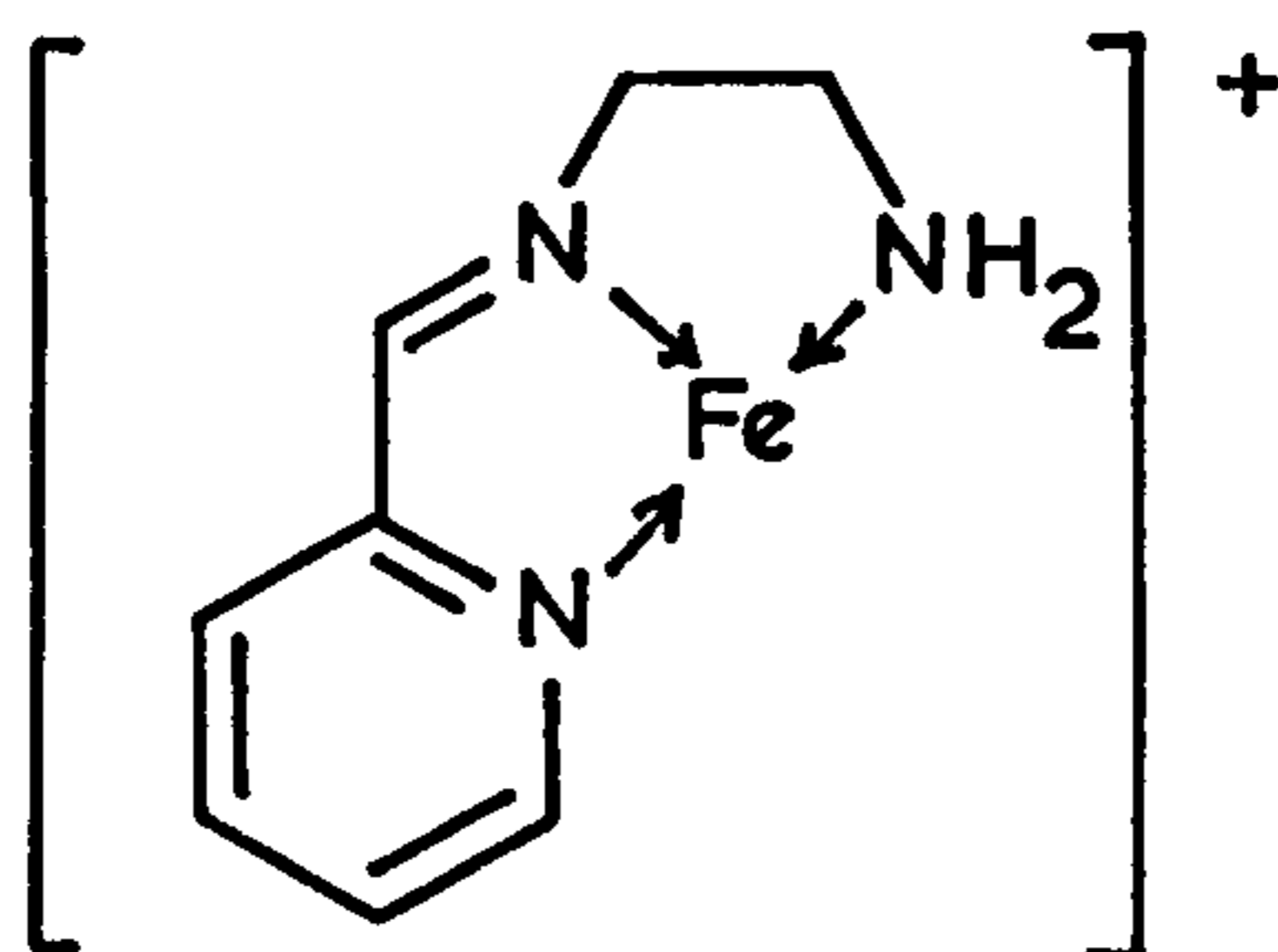


[4.7]

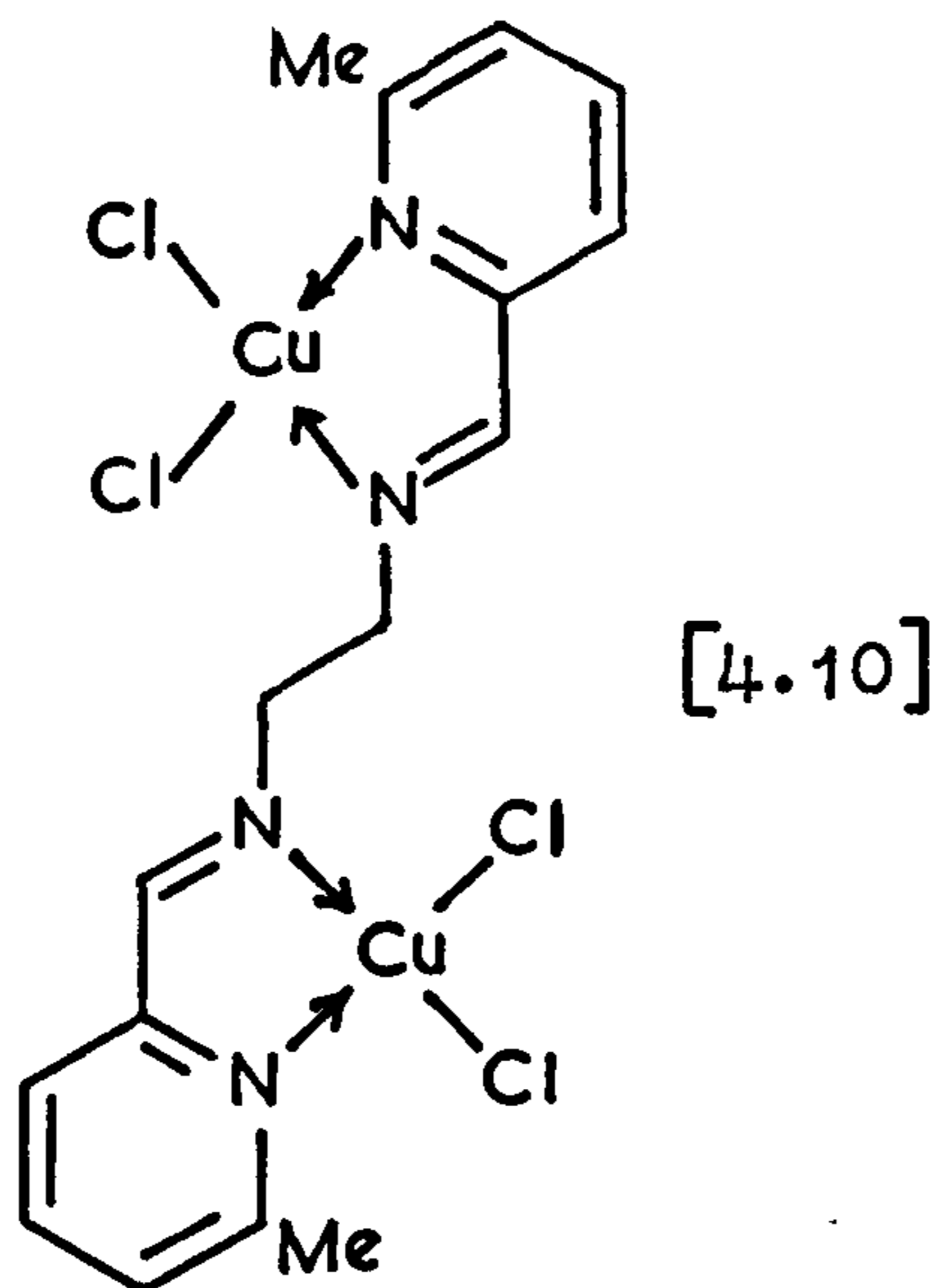


[4.9]

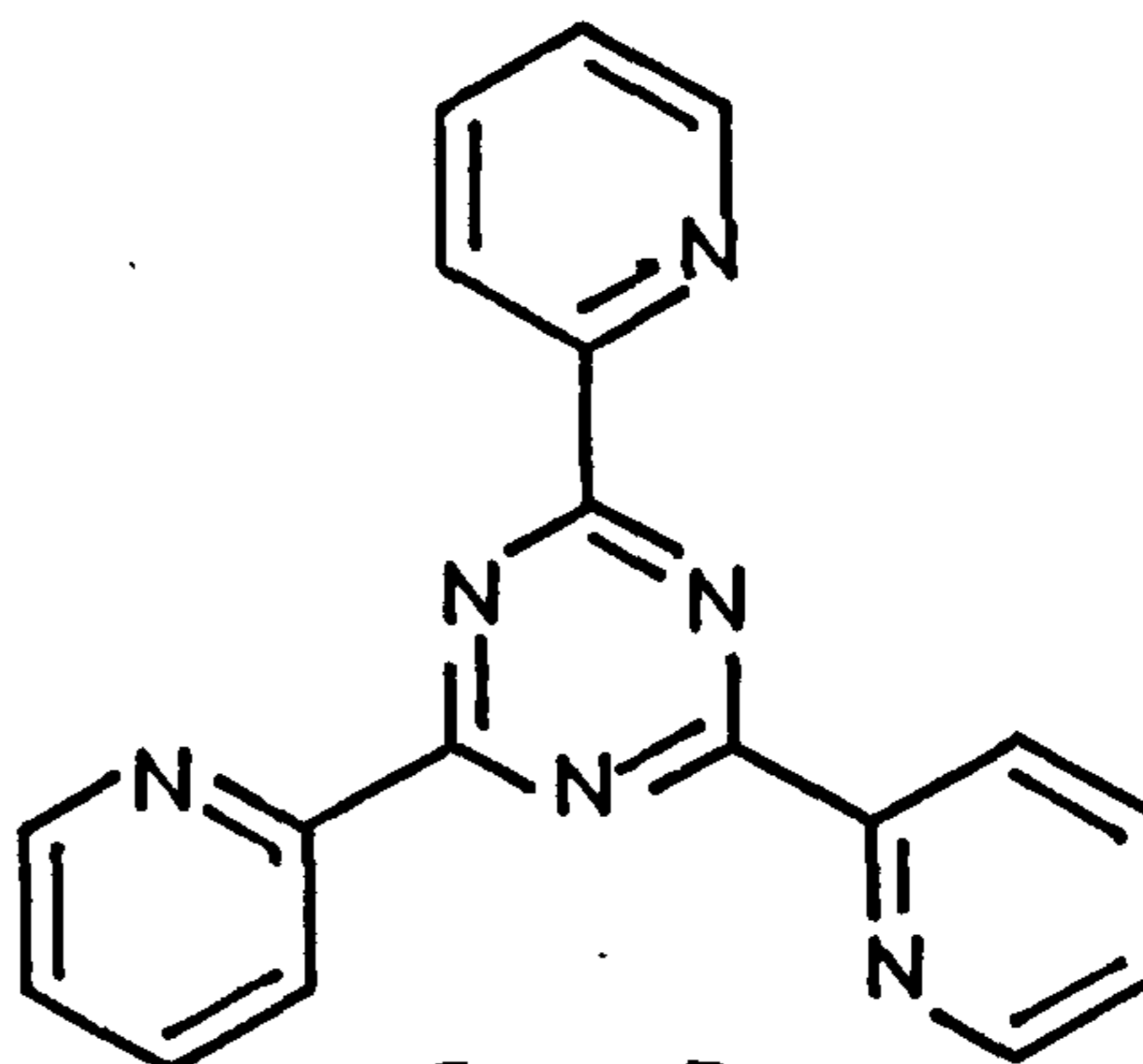
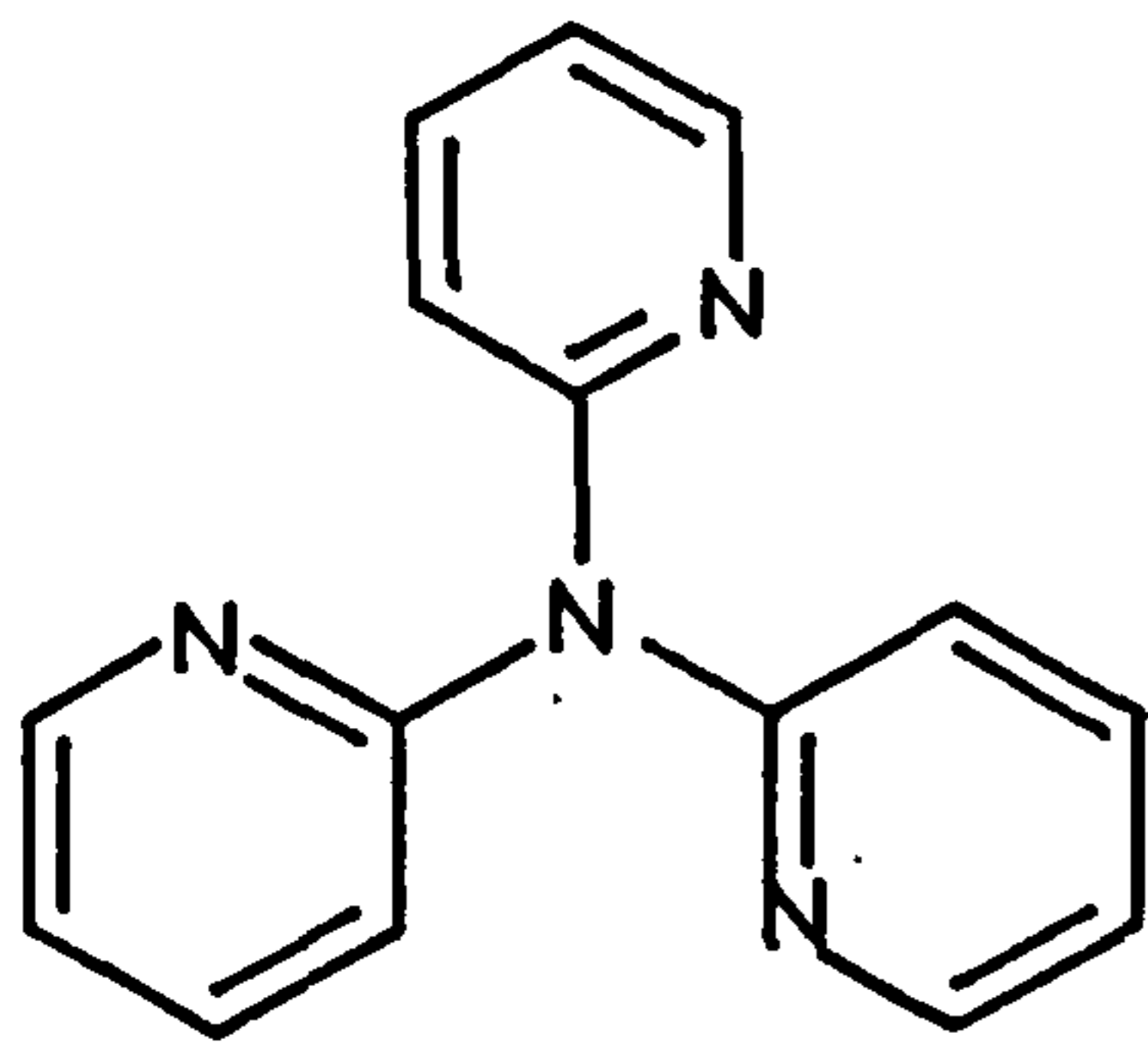
1,2-Bis-(6'-methyl-2'-pyridylmethyleneimino) ethane [4.9] shows even less tendency to form square-planar complexes.<sup>20</sup> Partial hydrolysis occurs readily to give octahedral complexes<sup>20</sup>, c.f. [4.8]<sup>14,19</sup> A bis-bidentate complex [4.10] has been isolated by reaction with copper(II) chloride.<sup>20</sup> When complexed in this manner the pyridine residue does not have its methyl group in a severely sterically hindered position.



[4.8]



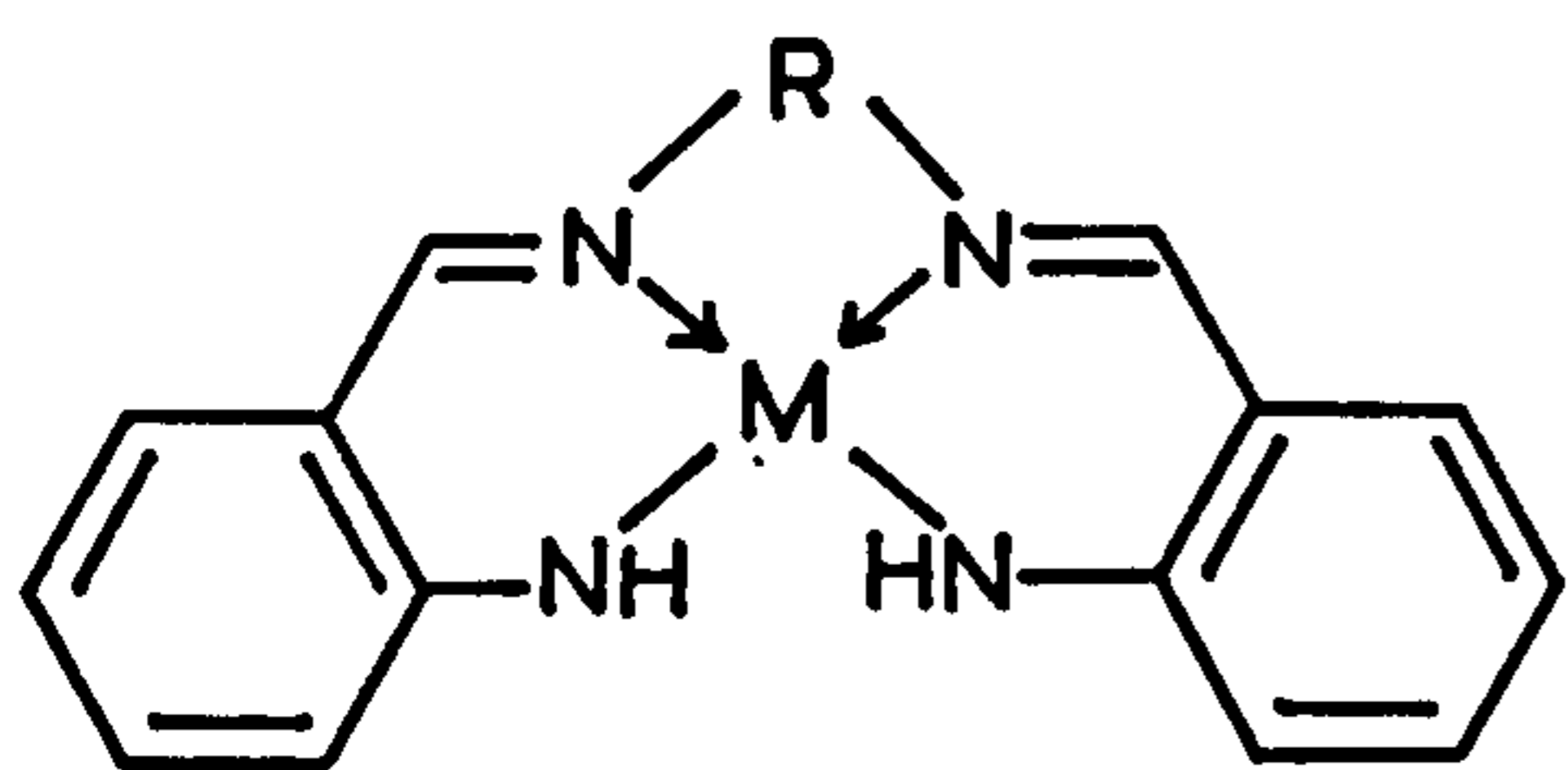
Many multipyridyl ligands do not exert their full donor capacity, due to unfavourable steric restrictions. Hence tri-(2-pyridyl)amine<sup>16,22</sup> [4.11] and 2,4,6-tri-(2-pyridyl)-1,3,5-triazine<sup>21</sup> [4.12] both act as tridentate ligands.



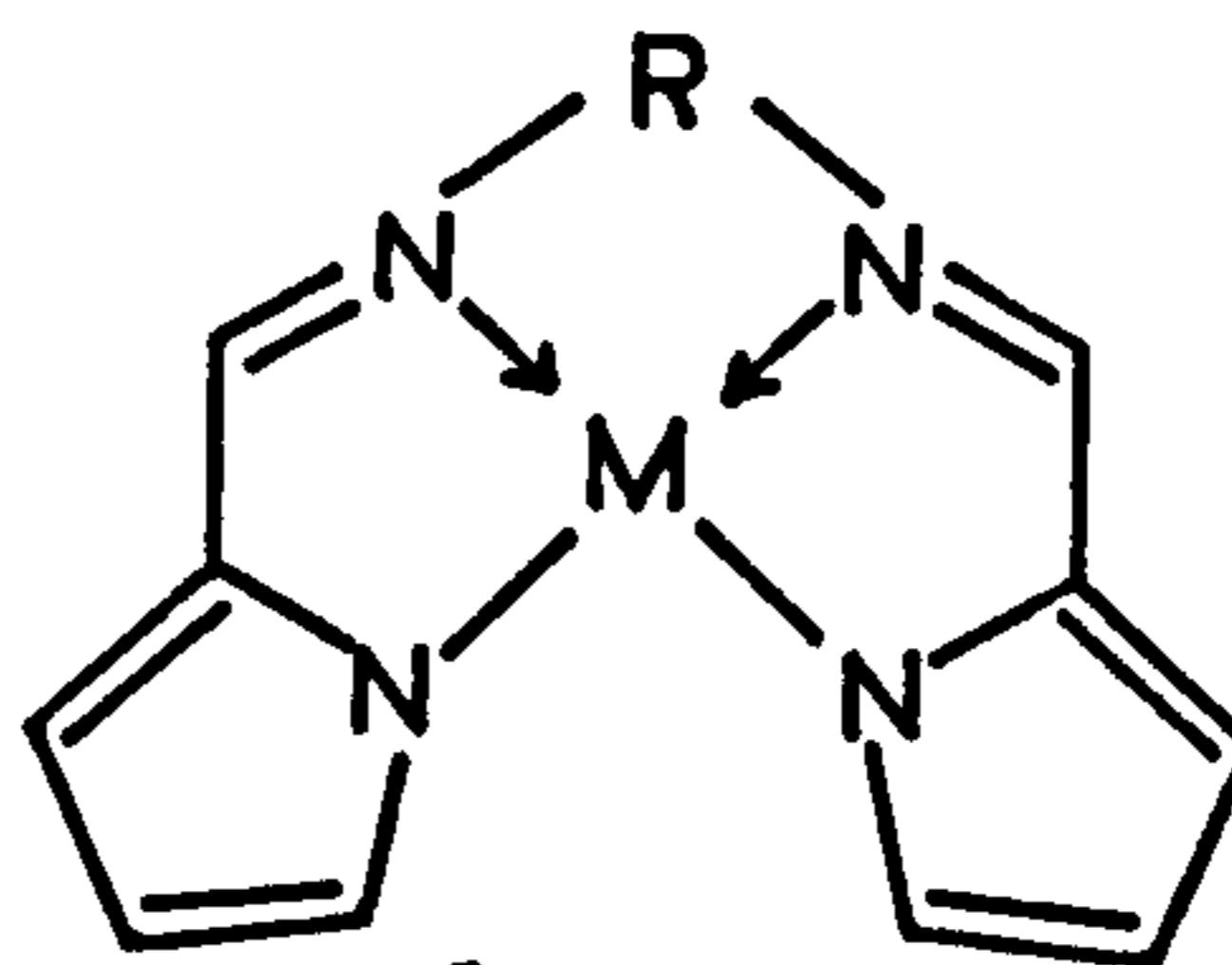
#### 4.4 Conjugated compounds which lose protons to give anionic ligands.

These chelating agents will be to some extent acyclic analogues of biologically important cyclic compounds such as porphyrins and corrins (see chapter 1). Also they should be similar to the much studied "N<sub>2</sub>O<sub>2</sub>" systems, the salicylaldimines and  $\beta$ -ketoimines (see reference 23 for review). However, there have been few systematic studies of such acyclic "N<sub>4</sub>" chelates.

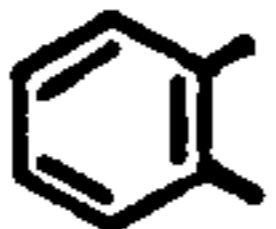
Pfeiffer and his co-workers<sup>24</sup> prepared the complexes [4.13] and [4.14] of quadridentate ligands derived from o-aminobenzaldehyde and pyrrole-2-aldehyde.

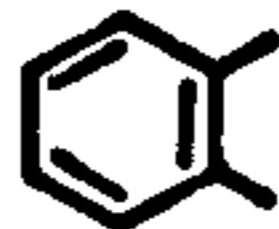


[4.13]



[4.14]

R = -CH<sub>2</sub>CH<sub>2</sub>- and   
M = Cu(II) and Ni(II)

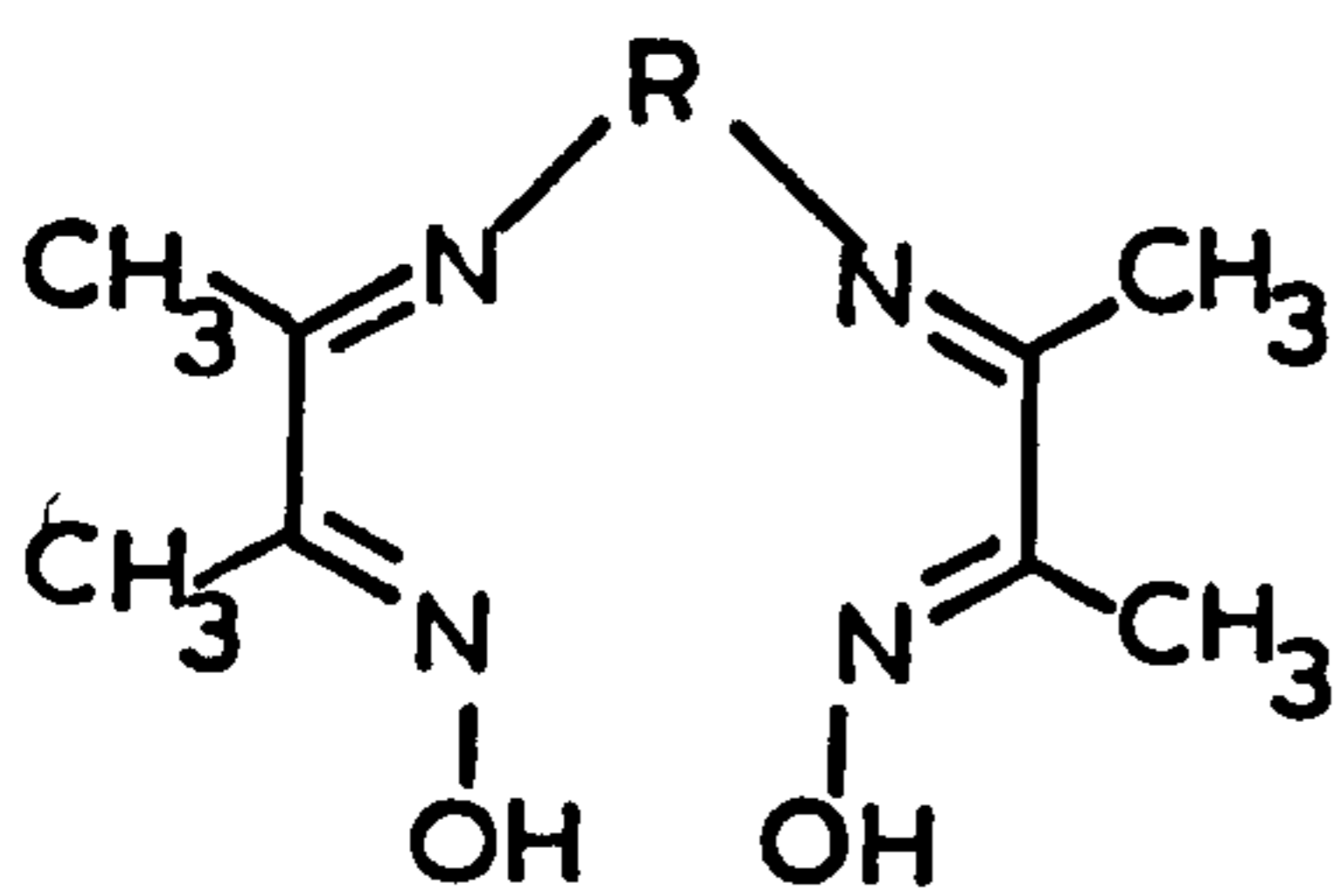
R = -CH<sub>2</sub>CH<sub>2</sub>- and   
M = Cu(II) and Ni(II)

Until recently these systems have not been further reported, except briefly as colorimetric agents<sup>25</sup> for the determination of nickel, and then only as

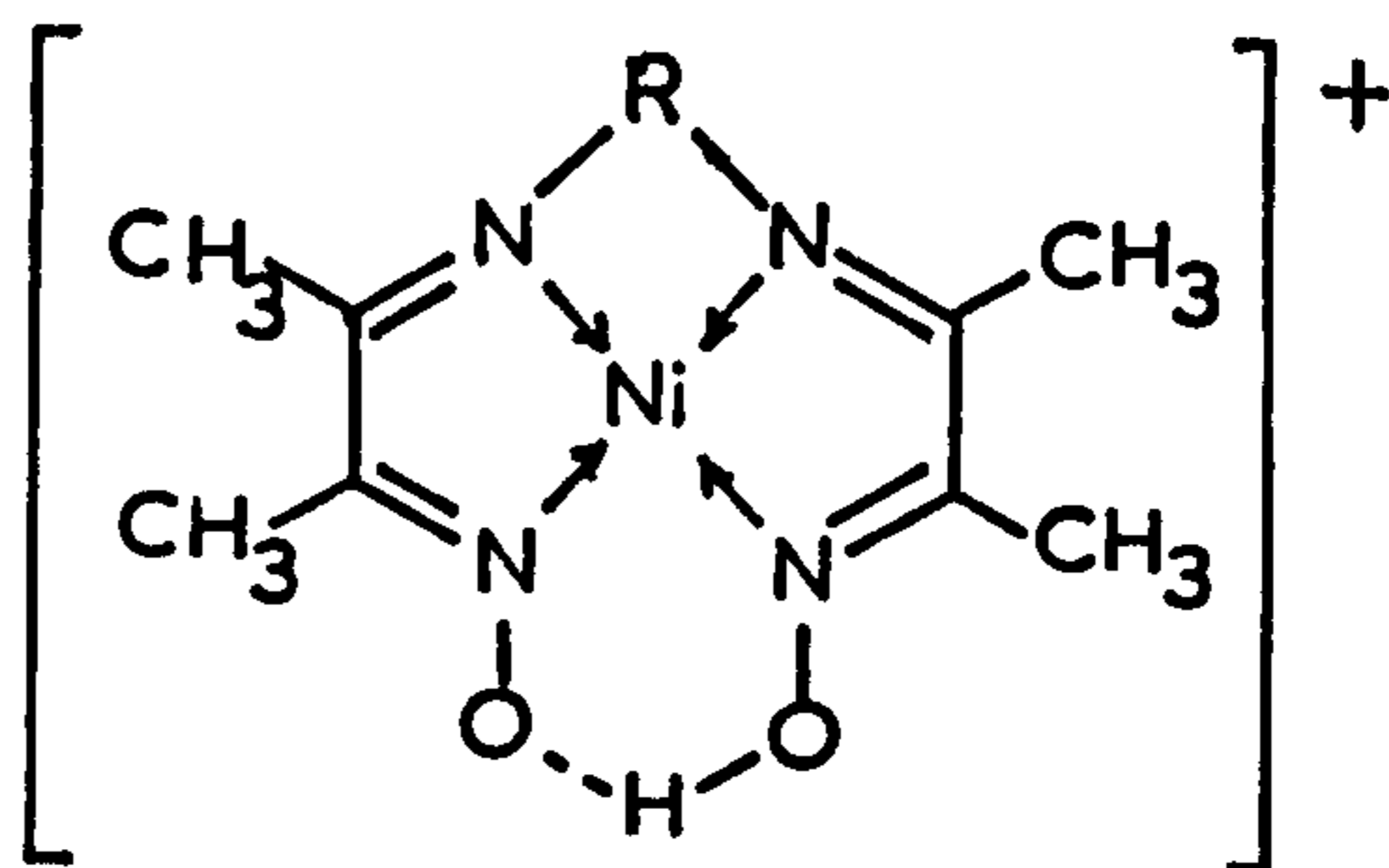
comparison with other similar "N<sub>2</sub>O<sub>2</sub>" ligands.

A series of nickel(II) complexes of quadridentate ligands derived from pyrrole-2-aldehyde similar to those of [4.14] has recently been prepared.<sup>26</sup> The effect of variation of the bridging group (R in [4.14] ) on the ligand field splitting and stereochemistry of the complex was studied. Diamagnetic, and hence presumed planar, complexes were obtained, even in cases where models revealed that the ligand would be much less strained in a tetrahedral configuration (e.g. R = pentamethylene or trans-1,2-cyclohexylene). The complexes remained square-planar and diamagnetic in chloroform. The ligand field splitting was found to decrease with length of the bridging group R.

Some mixed Schiff base-oxime ligands such as [4.15] can also give anionic quadridentate ligands.<sup>27</sup> The square-planar complexes of nickel (II) [4.16] are formally quite similar to bis-dimethylglyoximate complexes.



[4.15]



[4.16]

R. = -CH<sub>2</sub>CH<sub>2</sub>- , -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- . R = -CH<sub>2</sub>CH<sub>2</sub>- , -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- .


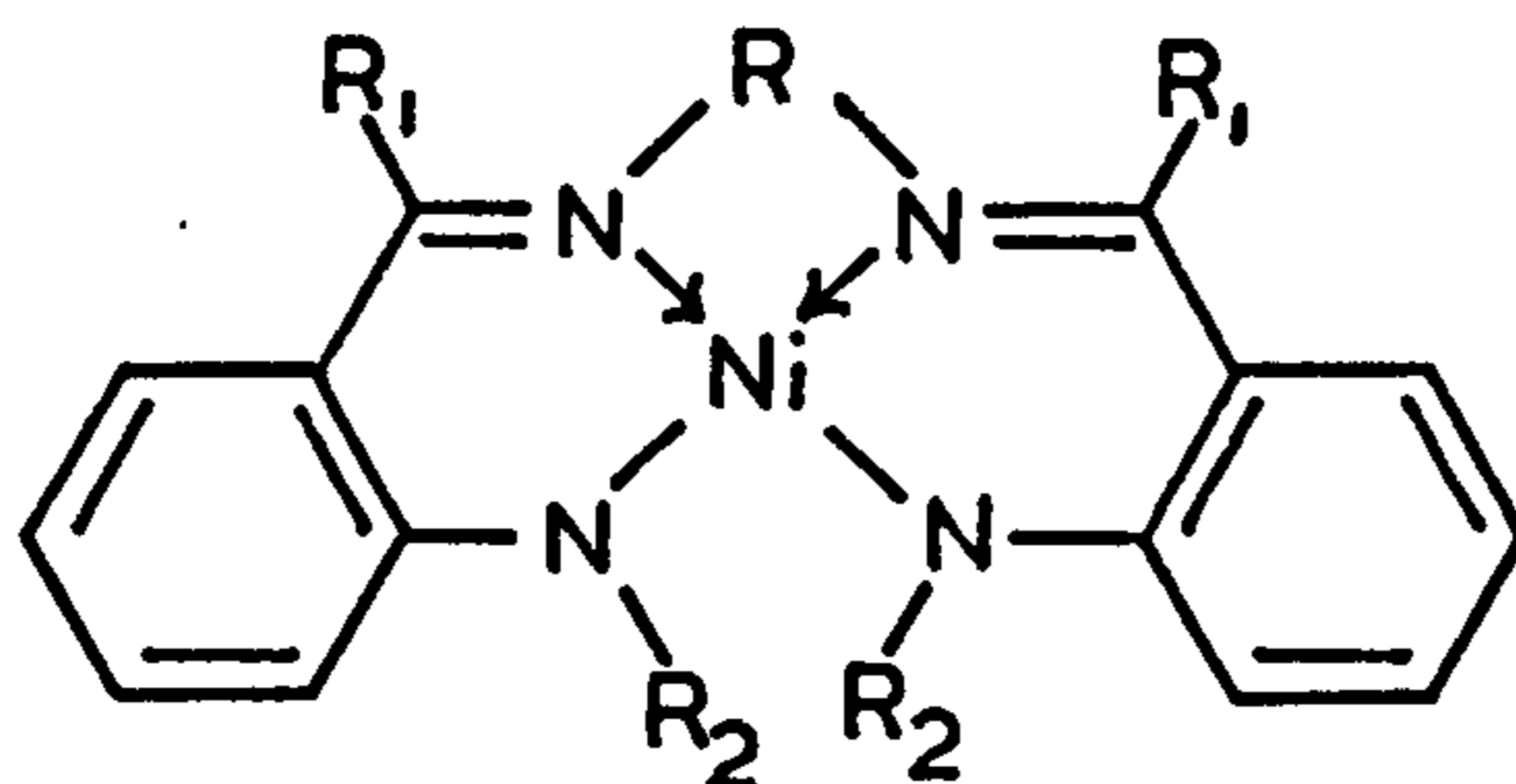
R <sub>a</sub>	R <sub>1</sub> a	R <sub>2</sub> a	Preparation b	Name c	Abbreviation c
-(CH <sub>2</sub> ) <sub>2</sub>	H	H	1,2,3,4 DMF d	N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanonickel(II)	Niamben
-(CH <sub>2</sub> ) <sub>3</sub>	H	H	2,3 THF e	N,N'-bis-(o-aminobenzylidene)-1,3-diaminopropanonickel(II)	Niambtn
-(CH <sub>2</sub> ) <sub>4</sub>	H	H	6 THF	N,N'-bis-(o-aminobenzylidene)-1,4-diaminobutanonickel(II)	Niambbuten
-C <sub>6</sub> H <sub>4</sub>	H	H	5 THF	N,N'-bis-(o-aminobenzylidene)-1,2-diaminobenzeneatonickel(II)	Niambphen
	H	H	5 DMF	N,N'-bis-(o-aminobenzylidene)-1,8-diaminonaphthaleneatonickel(II)	Niambnaph
-(CH <sub>2</sub> ) <sub>2</sub>	Ph	H	2,3 DMF	N,N'-bis-(o-aminobenzophenylidene)-1,2-diaminoethanonickel(II)	Niampen
-(CH <sub>2</sub> ) <sub>4</sub>	Ph	H	2 Ether	N,N'-bis-(o-aminobenzophenylidene)-1,4-diaminobutanonickel(II)	Niampbuten
-(CH <sub>2</sub> ) <sub>2</sub>	H	CH <sub>3</sub>	2 IPE f	N,N'-bis-(N-methyl-o-aminobenzylidene)-1,2-diaminoethanonickel(II)	NiMe-amben

Table [4.2]. Nickel(II) complexes of acyclic 'model' ligands.

(a) Substituents of formula [4.17]. (b) Numbers refer to methods, page 70 & solvents for recrystallization also given. (c) Based on the ligand abbreviations page 31. (d) Dimethylformamide (e) Tetrahydrofuran (f) Di-isopropyl ether.

In this work a series of nickel(II) complexes [4.17] of the anionic ligands type [2.2] (page 23) was studied. The ligands have been discussed in chapter 3.



[4.17]

#### 4.4.1 Preparation of the complexes.

It was found that the conditions required for preparation of the complexes varied considerably with the type of ligand used. As might be expected, generally, synthesis is most easily achieved for complexes of ligands which are expected to give the strongest ligand fields and the least strained square-planar arrangement of the four nitrogen donor atoms.

The following methods were used:

- (1) Addition of a methanolic solution of nickel(II) acetate to the ligand in refluxing methanol.
- (2) As (1) followed by the addition of a stoichiometric

amount of sodium methoxide.

(3) Addition of an aqueous mixture of nickel(II) sulphate and ammonia solution to the ligand in refluxing ethanol, based on the method of Pfeiffer et al.<sup>24</sup>

(4) Reduction of the aromatic nitro precursor of the ligand in a methanolic solution of nickel(II) acetate containing a little palladium/charcoal catalyst.

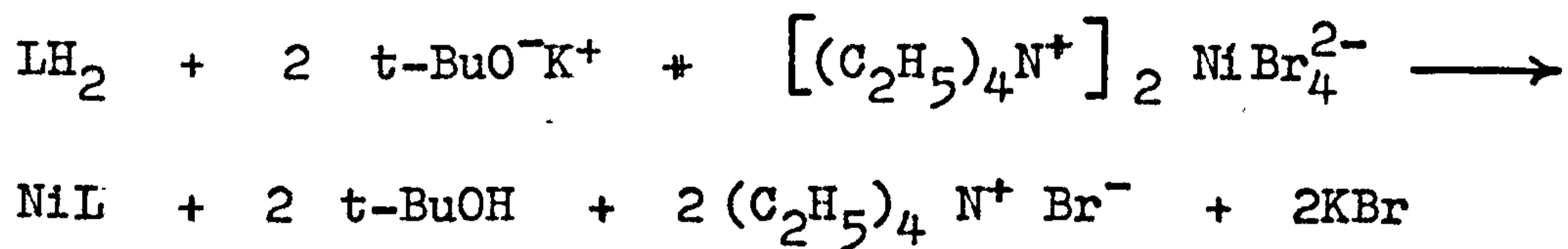
(5) Reaction of nickel(II) acetate with the condensation product of the appropriate aldehyde and diamine, corresponding to the ligand, without isolation, based on the method of Pfeiffer et al.<sup>24</sup>

(6) Addition of solid tetraethylammonium tetrabromonickelate(II) to a solution of the ligand and a stoichiometric amount of potassium t-butoxide in tetrahydrofuran, based on the method of Holm et al.<sup>28</sup>

More details are given in the experimental section, chapter 11.

Method(6) was attempted for the preparation of a complex from a given ligand when the simpler methods (1) and (2) had proved unsuccessful. The somewhat elaborate procedure of method (6) was developed<sup>28</sup> to ensure that the removal of the protons from the ligand (see equation [4.1] ) is facilitated by the presence of a strong base (potassium t-butoxide), which will not react preferentially with the source of metal ions,

effectively removing them by precipitation of a highly insoluble product.

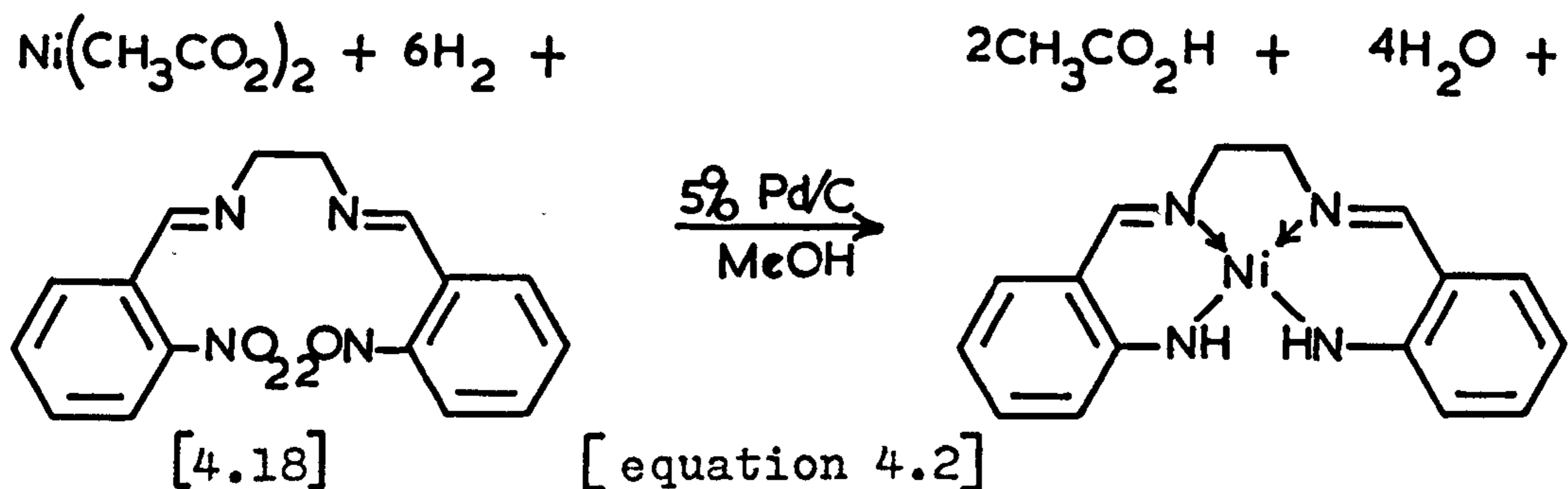


equation [4.1].  $\text{LH}_2$  = quadridentate nitrogen ligand type [3.1] page 31. t-Bu = tertiary butyl.

Method (5) is useful when isolation of the ligand is difficult (see page 34).

Method (4) avoids some difficult stages in the synthesis of the free ligand (see page 37), and is a convenient route to the complexes provided that a solvent is available to extract the product from palladium charcoal catalyst. Passing a stream of hydrogen through a methanolic solution of N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane [4.18] in the presence of 5% palladium charcoal and nickel (II) acetate produces a very intense red solution after about 30 min. which gradually fades to give a precipitate of Niamben. After 24 hr. the yield of Niamben after extraction with dimethylformamide was 64%. The product had the same infrared and electronic spectra as an authentic sample prepared from the ligand amben, and gave good analysis results for  $\text{C}_{16}\text{H}_{16}\text{N}_4\text{Ni}$ .



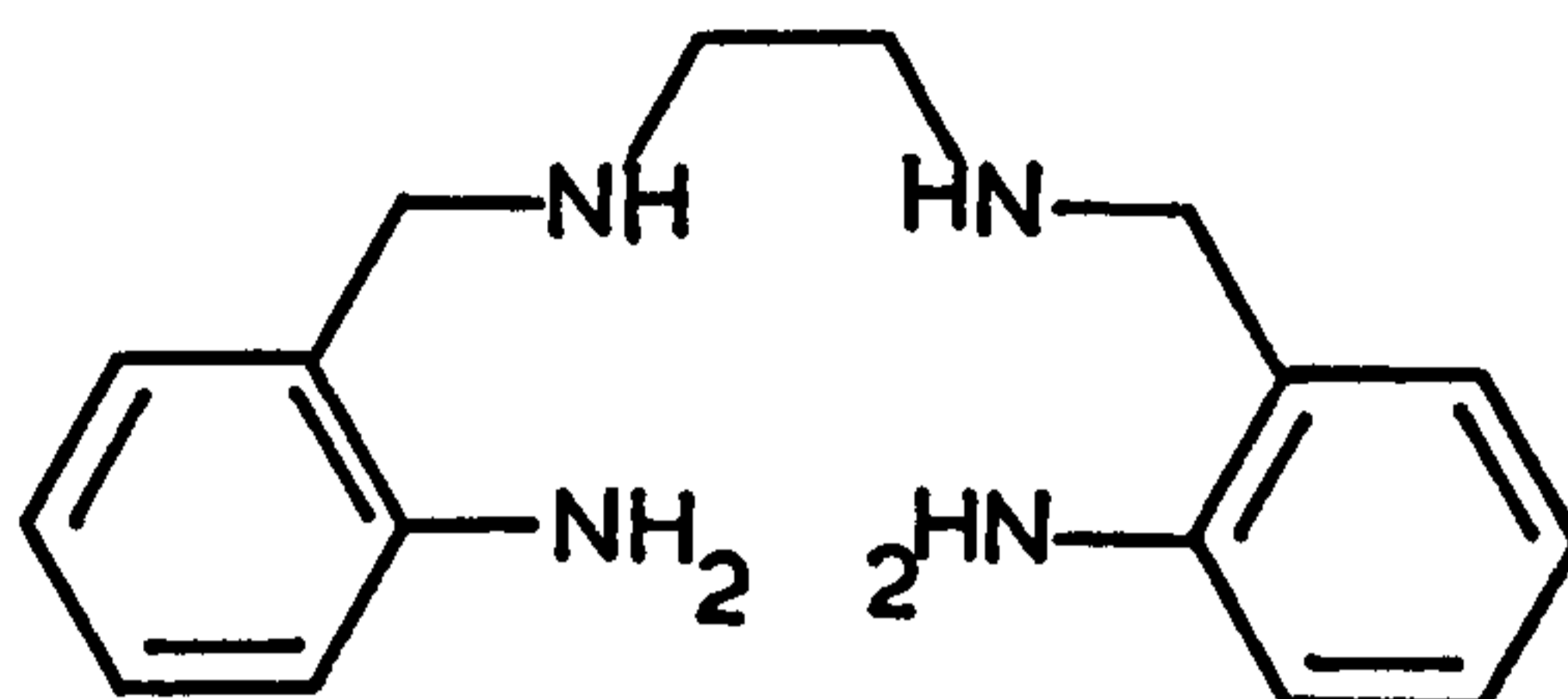


Attempts were made to isolate a complex of an intermediate reduction product from the deep red solution produced after passing hydrogen for 30 min. Only red oils could be obtained from repeated attempts at crystallization from various solvents.

Very recently it has been reported that complete hydrogenation of *N,N'*-bis-(*o*-nitrobenzylidene)-1,2-diaminoethane [4.18] in the presence of 10% palladium charcoal gives *N,N'*-bis-(*o*-aminobenzyl)-1,2-diaminoethane [4.19].<sup>17</sup>

In the presence of nickel(II) ions the intermediate product *amben* appears to be stabilized by complexation with respect to reduction of its imine groups to give [4.19]. There is some evidence for the increase in "aromatic character" of an imine group on complexation.<sup>26</sup>

It is to be expected that the polarity of the imine bond will be reduced by complexation (see also page 79)



[4.19]

The synthesis of Niamben by method (4) (equation 4.2) was attempted in the absence of catalyst, since it has recently been shown<sup>29</sup> that it is possible to reduce Nisalen to species which formally contain nickel(I) and nickel (0), and it was hoped that if any similar species were produced under these conditions, they would readily reduce the nitro-groups of the starting material. There was no evidence for reduction under these conditions.

Addition of a small quantity of Niamben was tried in case the reaction could be autocatalytic with this compound being reduced in small quantities to the nickel(I) or nickel(0) compound. There was no evidence for reduction after passing hydrogen for several days, and the N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane [4.18] was recovered unchanged.

Compound		Composition %			Molecular Weight
		C	H	N	
Niamben	Found	59.35	5.01	16.87	322.7
	Calc.	59.49	4.96	17.35	
Niambtn	Found	60.20	5.49	15.98	337.1
	Calc.	60.58	5.38	16.62	
Niambbuten	Found	61.47	5.55	15.12	351.5
	Calc.	61.58	5.74	15.96	
Niambphen	Found	64.77	4.62	15.25	371.1
	Calc.	64.74	4.35	15.09	
Niampen	Found	70.03	5.07	11.76	475.2
	Calc.	70.76	5.09	11.79	
Niampbuten	Found	71.52	5.59	11.84	503.3
	Calc.	71.59	5.61	11.13	
NiMe-amben	Found	61.48	5.63	16.15	351.1
	Calc.	61.58	5.74	15.96	

Table [4.3] Analysis results for nickel(II) complexes of  
table [4.2]

The nickel(II) complexes of acyclic quadridentate ligands, type[4.17](page 70), successfully prepared in this work are listed in table [4.2] , together with their methods of preparation and solvents of recrystallization. The full names and abbreviations used in this thesis are also included. It should be noted that in deriving abbreviations we shall adopt the common procedure<sup>23</sup> of not indicating loss of protons from a ligand on complexation. Hence the term 'amben' in Niamben refers to the ligand which is dianionic (see page 25) by loss of two protons.

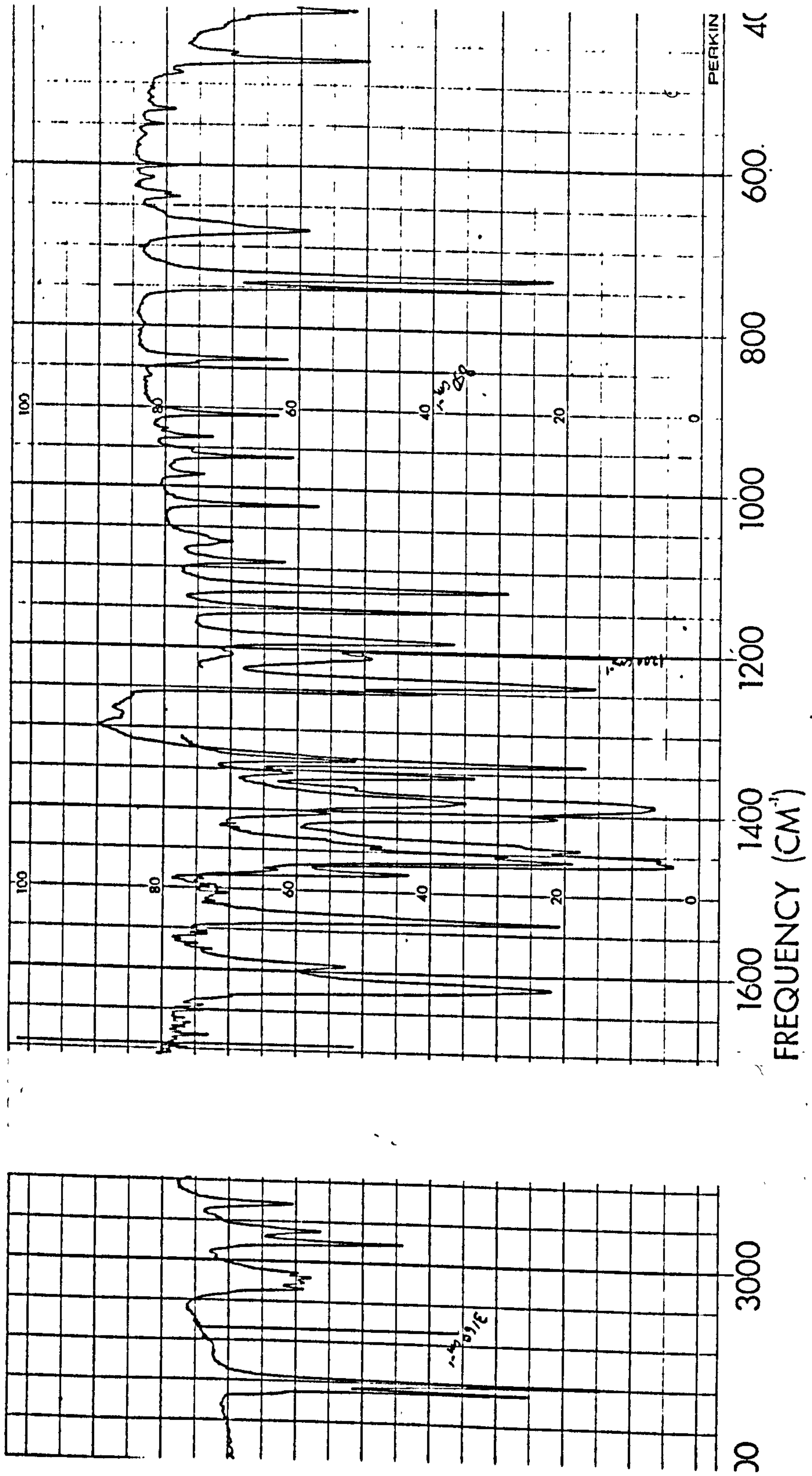
Analysis results of these compounds are tabulated separately (table [4.3] )

Nickel(II) complexes of the ligands ambdecen, Me-ambbuten and Me-ambdecen could not be prepared by methods (1), (2) and (6) page 70.

#### 4.4.2 Infrared spectra.

Initial identification of each ligand and complex was made on the basis of infrared spectra. The full spectra of the nickel(II) complexes are tabulated in the experimental section. The spectrum of Niamben is reproduced on page F 76 as a typical example. In table [4.4] the infrared absorptions in the ranges 3500 - 3200 and 2000 - 1500  $\text{cm}^{-1}$  are arranged comparatively for all

The infrared spectrum of Niamben as nujol and hexachlorobutadiene mulls.



the nickel complexes.

The hydrogen-bonded NH stretch in the ligand is usually a broad peak centred around  $3200\text{ cm}^{-1}$  (see page 42) which disappears upon complex formation. The 'free' NH stretch in the ligand is usually shifted downward by about  $130\text{ cm}^{-1}$  on complexation, see table [4.5]. The size of the shift varies very little with structural differences in the ligands. It is possibly due to a net decrease in the electronegativity of the nitrogen atom on losing a proton and bonding to the metal, resulting in a weaker NH bond in the complexes. For complexation of amines without loss of a proton a bigger shift is usually observed<sup>30</sup>, but the electronegativity change is expected to be larger.

In some of the complexes two absorptions were observed in the region of the NH stretching mode. At first it was thought that this might result from a coupling of the two NH stretching modes through the nickel atom. However, a 'splitting' is not observed in other complexes in table [4.4] and in many analogous copper and cobalt complexes (table [11.2]), which apparently offer the same facilities for coupling of vibrations through the metal atom. Perhaps stacking of molecular units in the crystal lattice leads to non-equivalence of the NH groups. Unfortunately the solubility of the complexes which showed

Niamben	3313	3293	1617	1593	-	1537
	(m)	(m)	(s)	(m)		(s)
Niambtn	3829	3281	1620	1590	1548	1538
	(m)	(m)	(s)	(m)	(s)	(m)
Niambbuten	3270	-	1612	1592	1549	1539
	(m)		(s)	(m)	(m)	(m)
Niambphen	3829	3308	1614	1574	1536	1529
	(w)	(w)	(s)	(s)	(s)	(m)
Niambnaph	3306	3285	1617	1592	-	1538
	(m)	(m)	(s)	(m)		(s)
Niampen	3350	-	1605	1560	-	1519
	(m)		(s)	(s)		(s)
Niampbuten	3335	3332	1604	1557	-	1510
	(m)	(m)	(s)	(s)		(s)
NiMe-amben	-	-	1615	1600	1527	1510
			(s)	(sh)	(s)	(m)

Table [4.4] , comparing the infrared spectra of the complexes in the regions 3500 - 3200 and 1700 - 1500 cm<sup>-1</sup>

All measured as mulls, cm<sup>-1</sup>.

the 'splitting' was too low in suitable solvents to test whether the NH groups became equivalent on breaking down the crystal lattice by solution.

The peak immediately above  $1600\text{ cm}^{-1}$  in the infrared spectra of the complexes is assumed to be due to the C=N stretch by comparison with other workers results.<sup>31</sup> Complexation causes the C=N stretch to be shifted downward by about  $10\text{ cm}^{-1}$  from the frequency observed in the corresponding ligand. Since the shifts are small the significance of their variation with ligand structure is doubtful. Increasing conjugation of the azomethine group with other unsaturated groups in the ligand, and metal-ligand  $\pi$ -bonding on complexation both tend to lower the energy of the C=N stretching vibration.<sup>32</sup>

Much larger shifts to lower frequencies are observed for the C=O group of salicylaldehyde on complex formation.<sup>33</sup>

Complex	$\Delta\text{C=N}$	a	$\Delta\text{N-H}$	b
Niamben	16	c	130	
Niambtn	8		116	
Niambbuten	18		135	
Niampen	8		128	
Niampbuten	0		132	
NiMe-amben	13		-	d

Table [4.5] Shifts of stretching frequencies associated with



Niamben	Nisalen	Assignments
a	b	c
3313(m)	-	NH
3293(m)		stretch
3060(w)		CH (aromatic)
3047(w)	3030(m)	stretch
3032(m)		
2948(m)		CH (aliphatic)
2915(w)	2930(m)	stretch
2855(w)	2860(sh)	
1617(s)	1621(s)	C = N
		Stretch
1593(s)	1600(s)	Conjugated ring interaction
1537(s)	1536(s)	C = C (aromatic) stretch
1478(w)	1465(s)	CH <sub>2</sub> (aliphatic)
1459(s)	1451(s)	bend
1452(sh)		

Table [4.6], comparing the infrared absorption spectra of Niamben and Nisalen.

- (a) Recorded as nujol and hexachlorobutadiene mulls on a Perkin Elmer 621 spectrometer.  
 (b) Recorded as KBr disc.<sup>34,35</sup>  
 (c) Assignments (apart from NH stretch) made in refs. 34 and 35.

the azomethine groups and anilino groups on complexation.

$$\begin{array}{l} \text{(a)} \quad \Delta_{\text{C=N}} = \nu_{\text{C=N}}(\text{ligand}) - \nu_{\text{C=N}}(\text{complex}) \\ \text{(b)} \quad \Delta_{\text{NH}} = \nu_{\text{NH}}(\text{ligand}) - \nu_{\text{NH}}(\text{complex}) \\ \text{(c)} \quad \text{cm}^{-1} \quad \text{(d) No NH group present in the complex.} \end{array}$$

Other absorptions in the infrared region can be assigned by comparison with other workers' results. Table [4.6] compares the spectra of Niamben and Nisalen, in the regions where assignments have been made for the latter.

#### 4.4.3. N.M.R. spectra.

Due to the generally low solubility of the complexes it was not possible to obtain N.M.R. spectra for all the compounds in table [4.2]. Those which were successfully determined are included in table [4.7]. The spectra of Niambtn and Niambphen are reproduced on pages F80 and F82.

The variety of substituents and structures of the ligands facilitated assignment of the resonance peaks in table [4.7]. Comparison of the spectra in table [4.7] with those of the free ligands shows some interesting changes on complexation.

#### 4.4.3(a) Methine resonances.

The resonance of the azomethine hydrogen nucleus is shifted to higher fields on complexation, see Table [4.8]. Further examples of this effect are given for the cyclic nickel(II) complexes in chapter 8.

Compound (Solvent)	Methine CH=N	Aro- matics	Amine -NH-	Methylene =N-CH <sub>2</sub> - -C-CH <sub>2</sub> -C-		Methyl -NMe
Niambtn (DMSO-d <sub>6</sub> )	2.36 <sup>c</sup> Singlet	2.8-3.6 Complex	3.94 Broad	6.47 Triplet <sup>a</sup>	8.15 Quintet <sup>a</sup>	- -
Niambbuten (DMSO-d <sub>6</sub> )	2.37 Singlet	2.8-3.9 Complex		6.52 Complex <sup>b</sup>	8.29 Complex <sup>b</sup>	- -
Niambphen (DMSO-d <sub>6</sub> )	0.91 Singlet	1.7-3.7 Complex	3.80 Broad	-	-	-
NiMe-amben (CDCl <sub>3</sub> )	2.48 Singlet	2.7-3.7 Complex	-	6.81 Singlet	-	7.25 Singlet
Niampbuten (CDCl <sub>3</sub> )	-	2.4-4.1 Complex		6.57 Complex <sup>b</sup>	8.20 Complex <sup>b</sup>	-

Table[4.7] N.M.R. spectra of nickel complexes type 4.17

- (a) J = 6 c.p.s.  
 (b) Broad singlet, showing signs of splitting on expansion.  
 (c) Chemical shift in  $\tau$ .

	ambtn	ambbuten	Me-amben
Ligand	1.66 <sup>a</sup>	1.67	1.65
Ni(II)complex	2.36	2.37	2.48

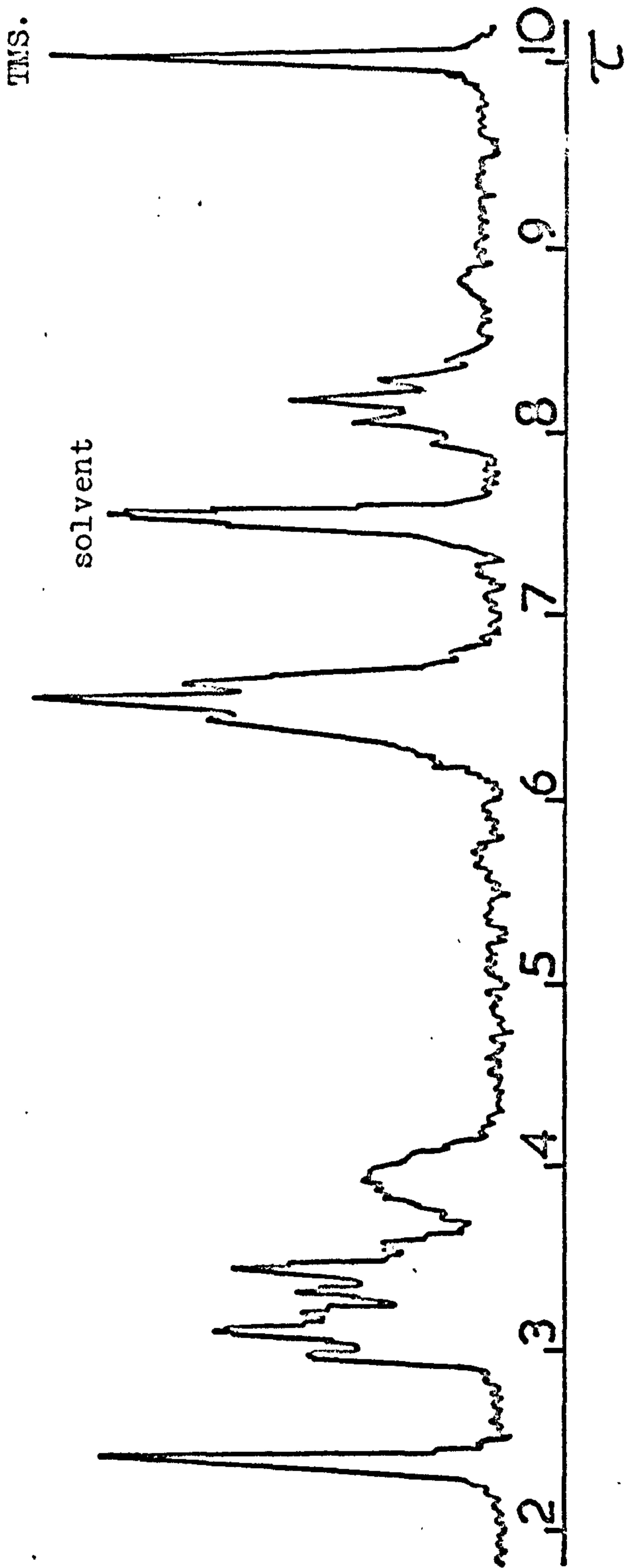
Table [4.8] Chemical shifts of methine resonances of ligands and corresponding nickel(II) complexes

(a)  $\tau$  values to  $\pm 0.02$  ppm.

Several factors might be expected to alter the chemical shift of the azomethine proton on complexation, among them -

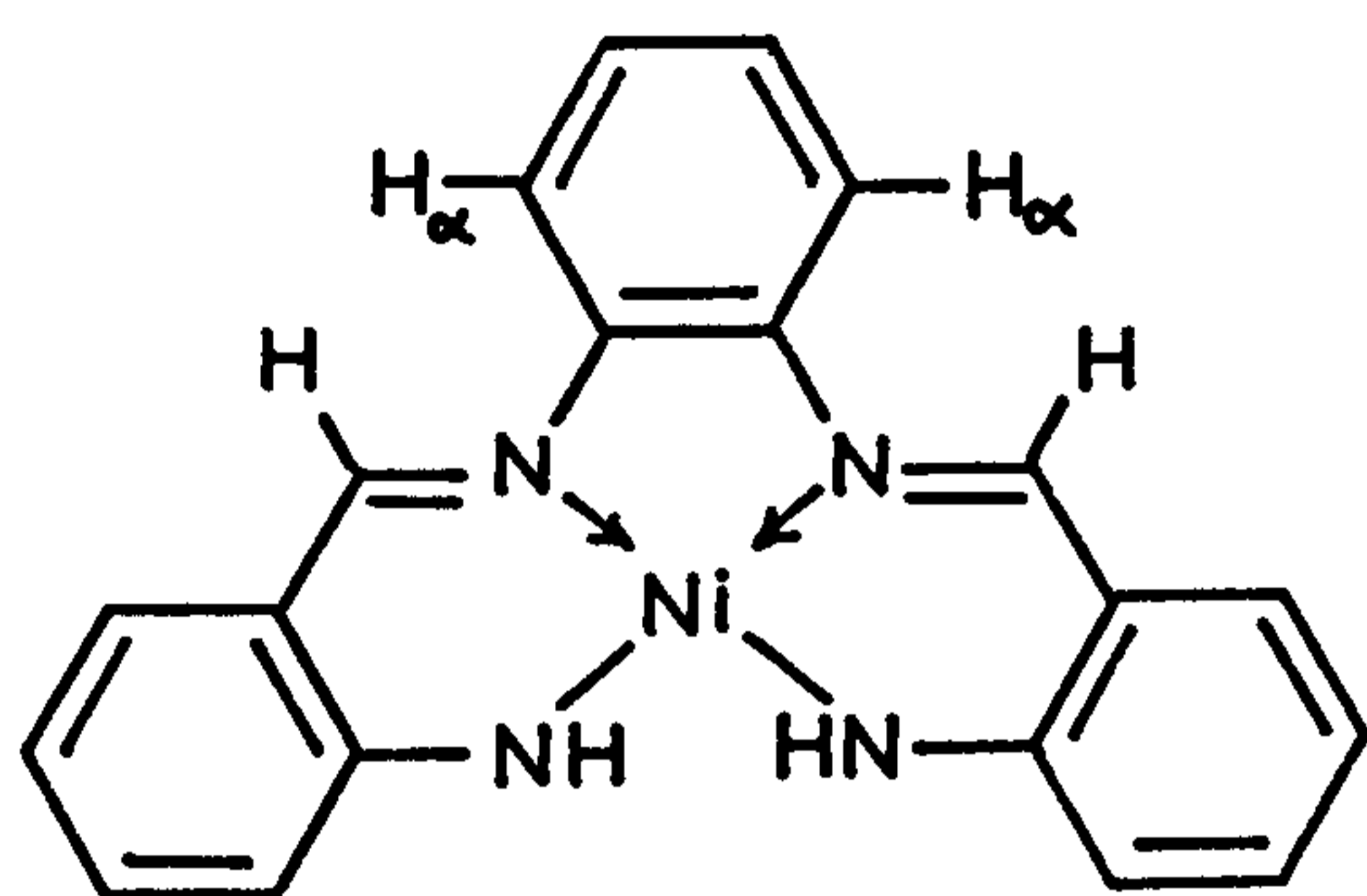
- (1) a change in effective electronegativity of the azomethine nitrogen atom.
- (2) The introduction of a new 'aromatic' ring system involving the nickel(II) ion.
- (3) a change in position of azomethine group relative to the bridging group.
- (4) Some unpaired spin density of a low-lying paramagnetic state being transmitted to the azomethine group.

The methine resonance of Niambphen occurs at much lower field ( $0.91\tau$ ) than in the other complexes. Unfortunately a N.M.R spectrum of the ligand is not available, since the ligand was not isolable in a pure form (page 34). The shielding of the azomethine hydrogen is probably ~~increased~~<sup>de</sup> increased by the conjugated system which links

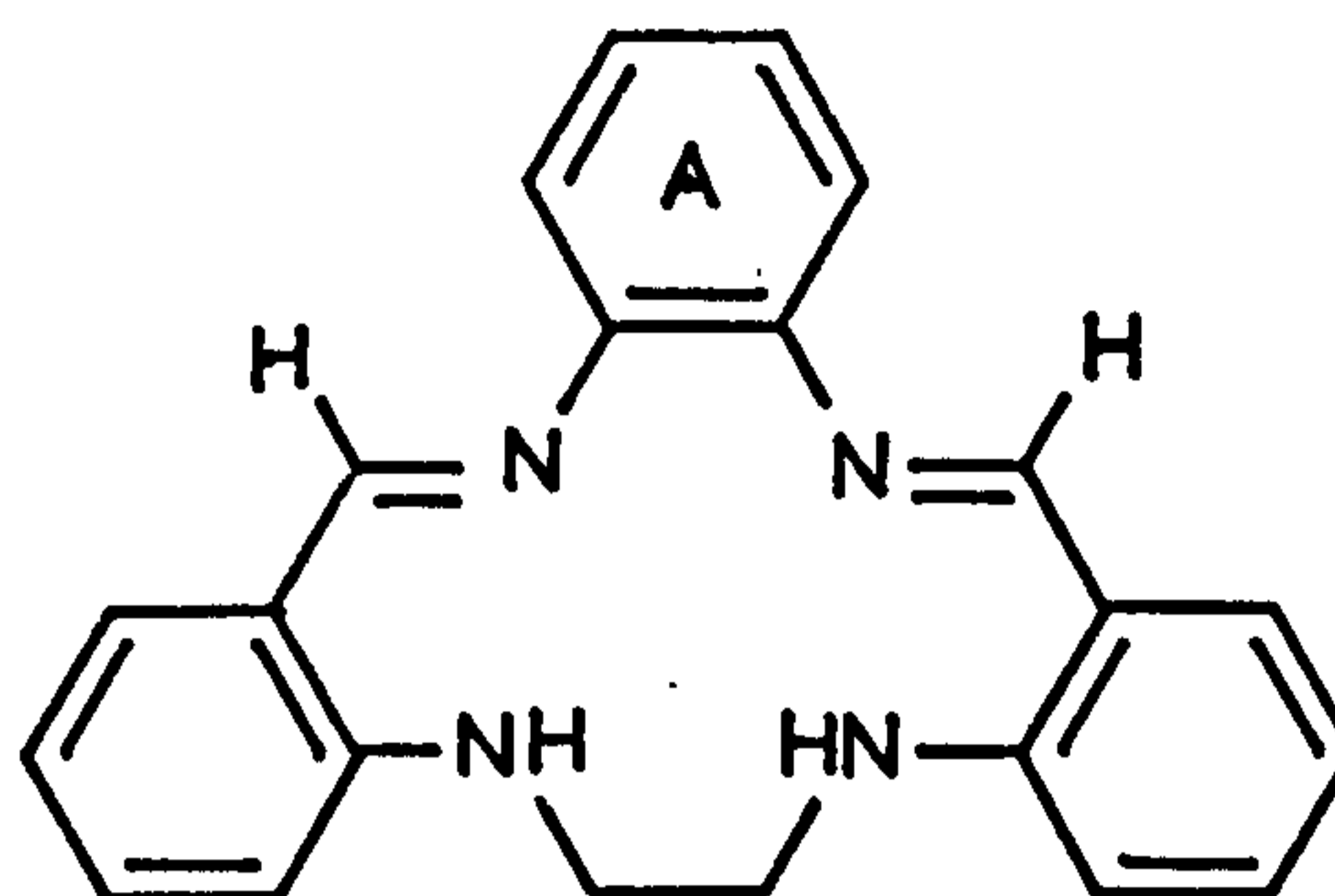


N.M.R. spectrum of Niambtn as a dimethyl sulphoxide ( $d_6$ ) solution.

the whole carbon-nitrogen skeleton of the molecule, and by the ring current of the bridging benzene ring which must lie in the same plane as the azomethine groups (see [4.20]).



[4.20]



[4.21]

Probably both effects contribute. The following observations support the above explanation.

Two aromatic hydrogen nuclei in Niambphen have resonance lines at lower fields than those observed for the aromatic hydrogens of the other complexes in table [4.7]. These are probably the two nuclei ( $H_{\alpha}$  [4.20]) which experience similar ring current effects to the azomethine hydrogens.

The azomethine resonance of the ligand [4.21] occurs at relatively low field ( $1.16\tau$ ).

The cyclic nature of [4.21] requires that the

	Chemical Shift of $\alpha$ -methylene group ( $\tau$ )			
	ambtn	ammbuten	Me-amben	Ampbuten
Ligand	6.33	6.32	6.18	6.78
Complex	6.47	6.52	6.81	6.57
Shift on complexation	+	+	+	-

Table [4.9]. Chemical shift of  $\alpha$ -methylene resonances of ligands and corresponding nickel(II) complexes.

	Chemical Shift of $\beta$ -methylene group ( $\tau$ )		
	ambtn	ammbuten	ampbuten
Ligand	7.95	8.21	8.30
Complex	8.15	8.29	8.20
Shift on complexation	+	+	-

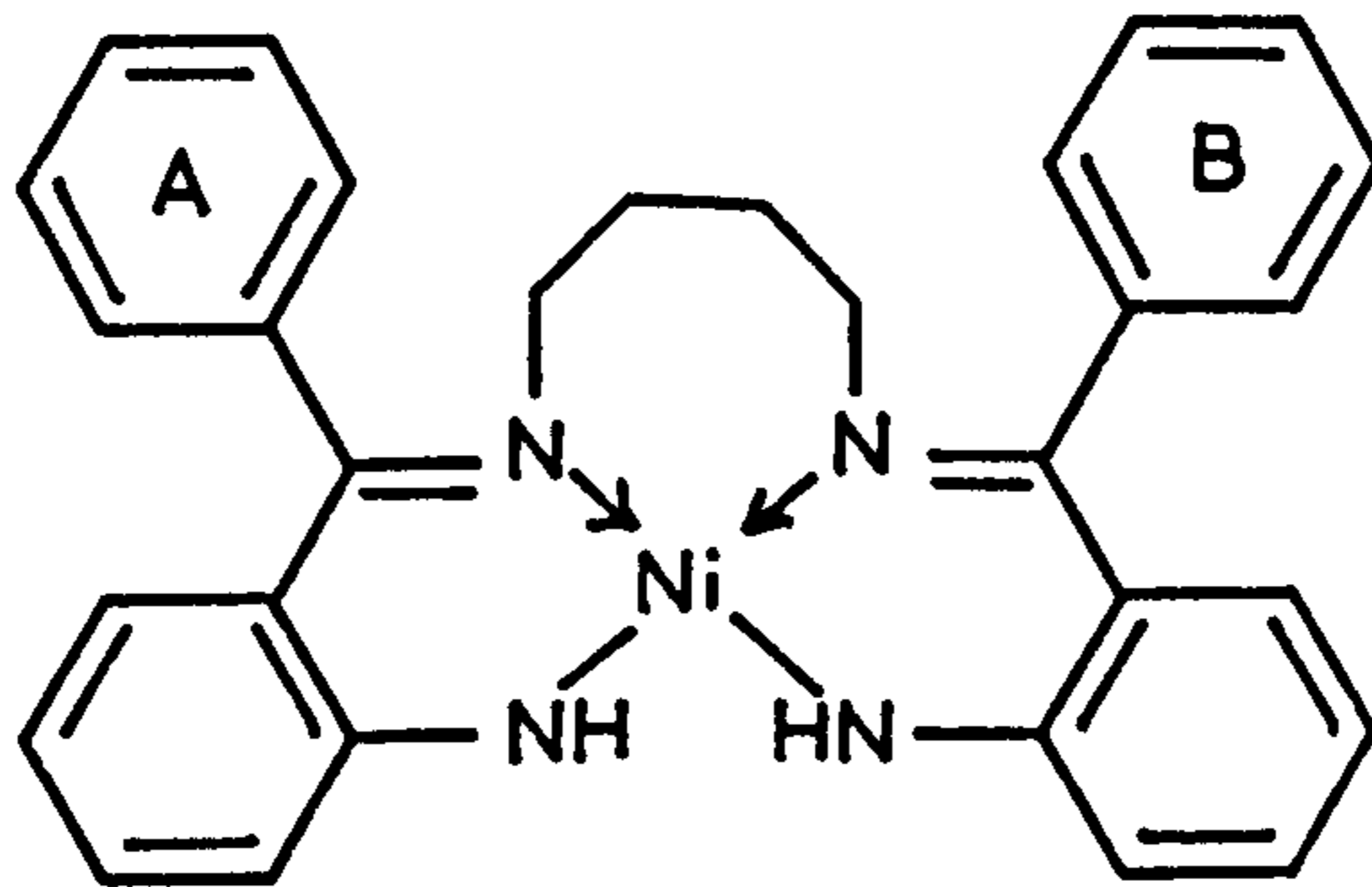
Table [4.10]. Chemical Shifts of  $\beta$ -methylene resonances of ligands and corresponding nickel(II) complexes.

azomethine hydrogen atoms lie approximately in the plane of the benzene ring (A) [4.21].

#### 4.4.3.(b) Methylene resonances.

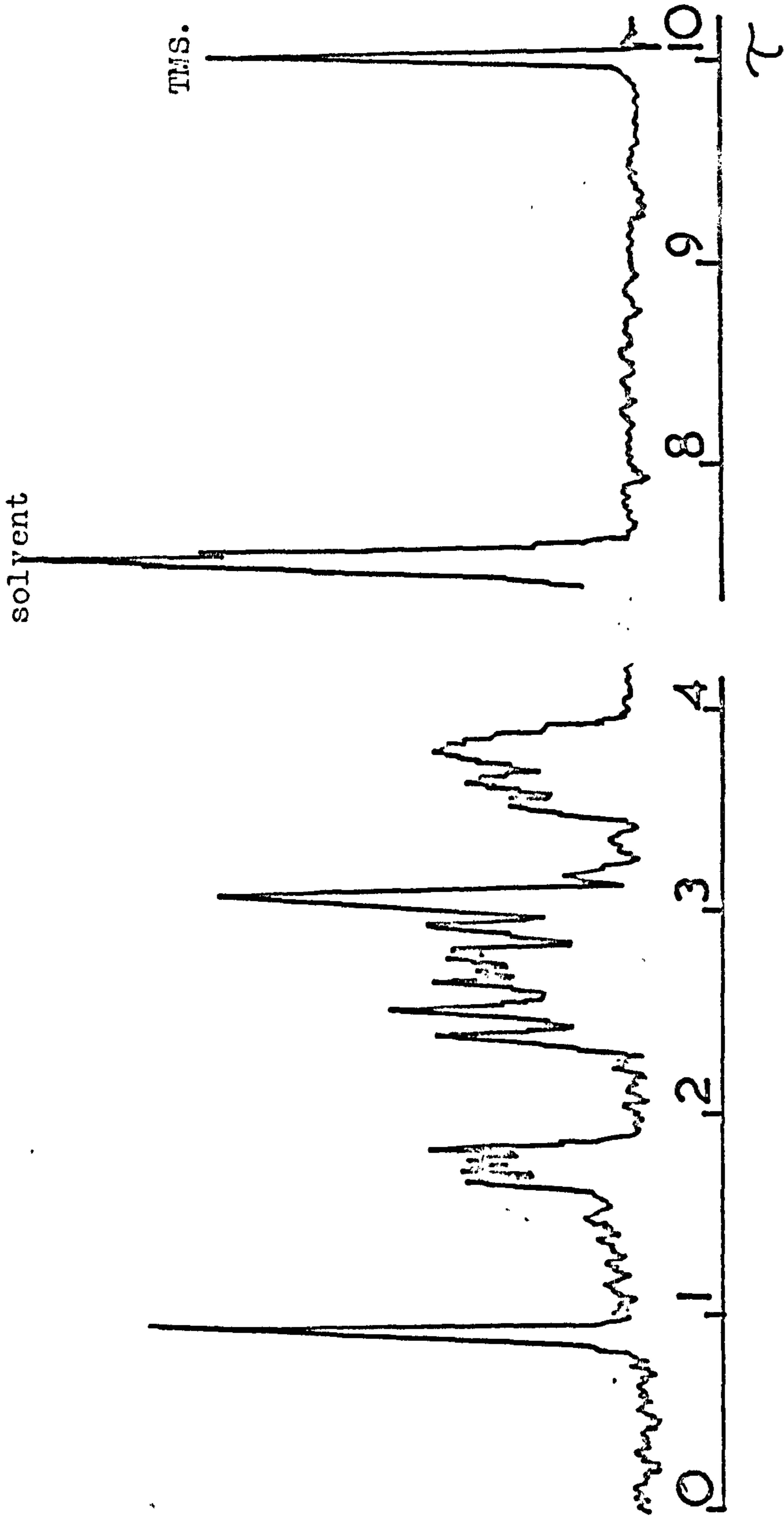
The methylene group resonances are shifted to higher fields on complexation for ambtn, ambuten and Me-amben, but to lower fields for ampbuten. The effect is greater for the  $\alpha$ -groups than the  $\beta$ -groups (relative to the azomethine bond) see tables [4.9] and [4.10].

The shielding effect of the azomethine groups is probably decreased by complexation and this accounts for the higher field resonances for the methylene groups of Niambtn, Niambbuten and NiMe-amben. Complexation of ampbuten may bring the methylene groups more into the plane of the phenyl substituents A and B, thus increasing their shielding, see [4.22].



[4.22]





N.M.R. spectrum of Niambphen as a dimethyl sulphoxide ( $d_6$ ) solution.

#### 4.4.3.(c) N-Methyl resonance.

The N-methyl protons of Me-amben give rise to a sharp doublet due to spin-spin coupling between the methyl protons and the anilino proton (page 51). On complexation the anilino proton is lost and the N-methyl resonance is observed as a sharp singlet at  $7.25\tau$ .

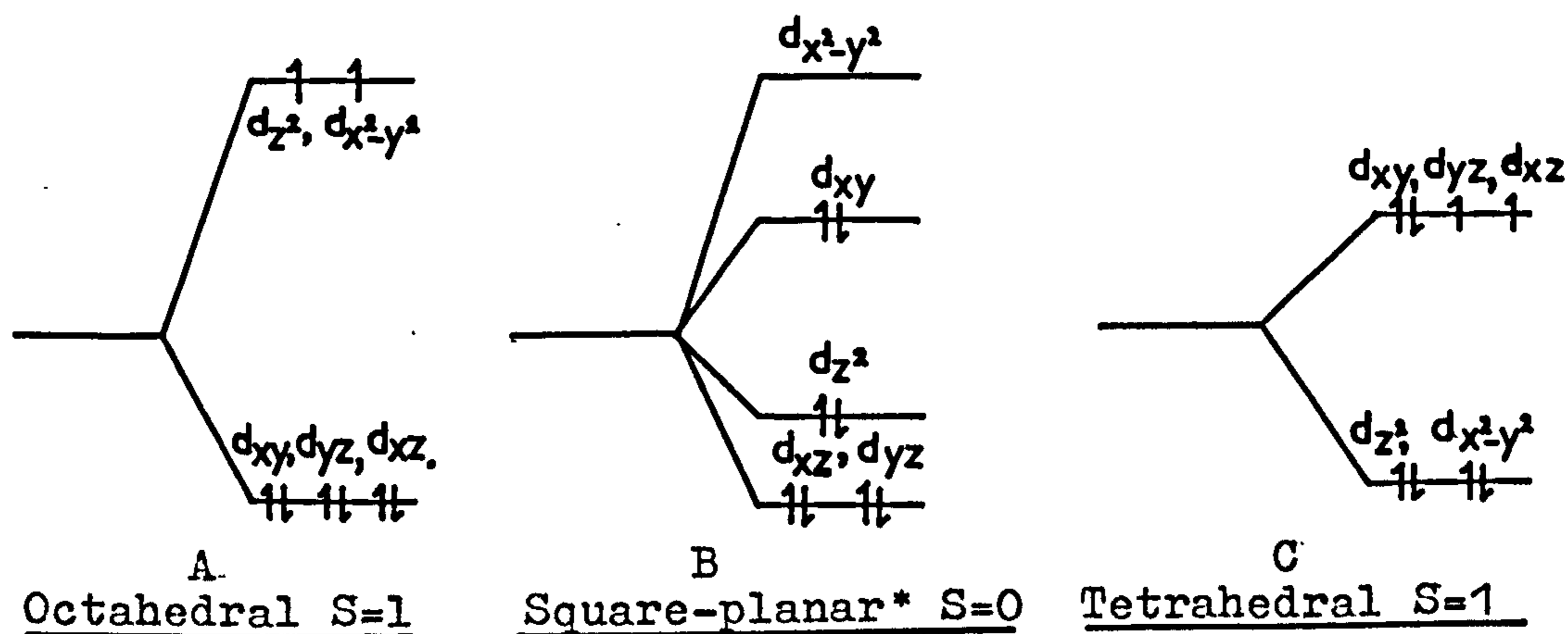
#### 4.4.4. Magnetic behaviour.

Most bivalent nickel complexes show magnetic properties of one of the following categories.<sup>8</sup>

(1) Six covalent, octahedral, paramagnetic complexes with a triplet ground state [4.23], A.

(2) Four covalent, square-planar, diamagnetic complexes with a singlet ground state [4.23], B.

(3) Four covalent, tetrahedral, paramagnetic complexes with a triplet ground state [4.23], C.

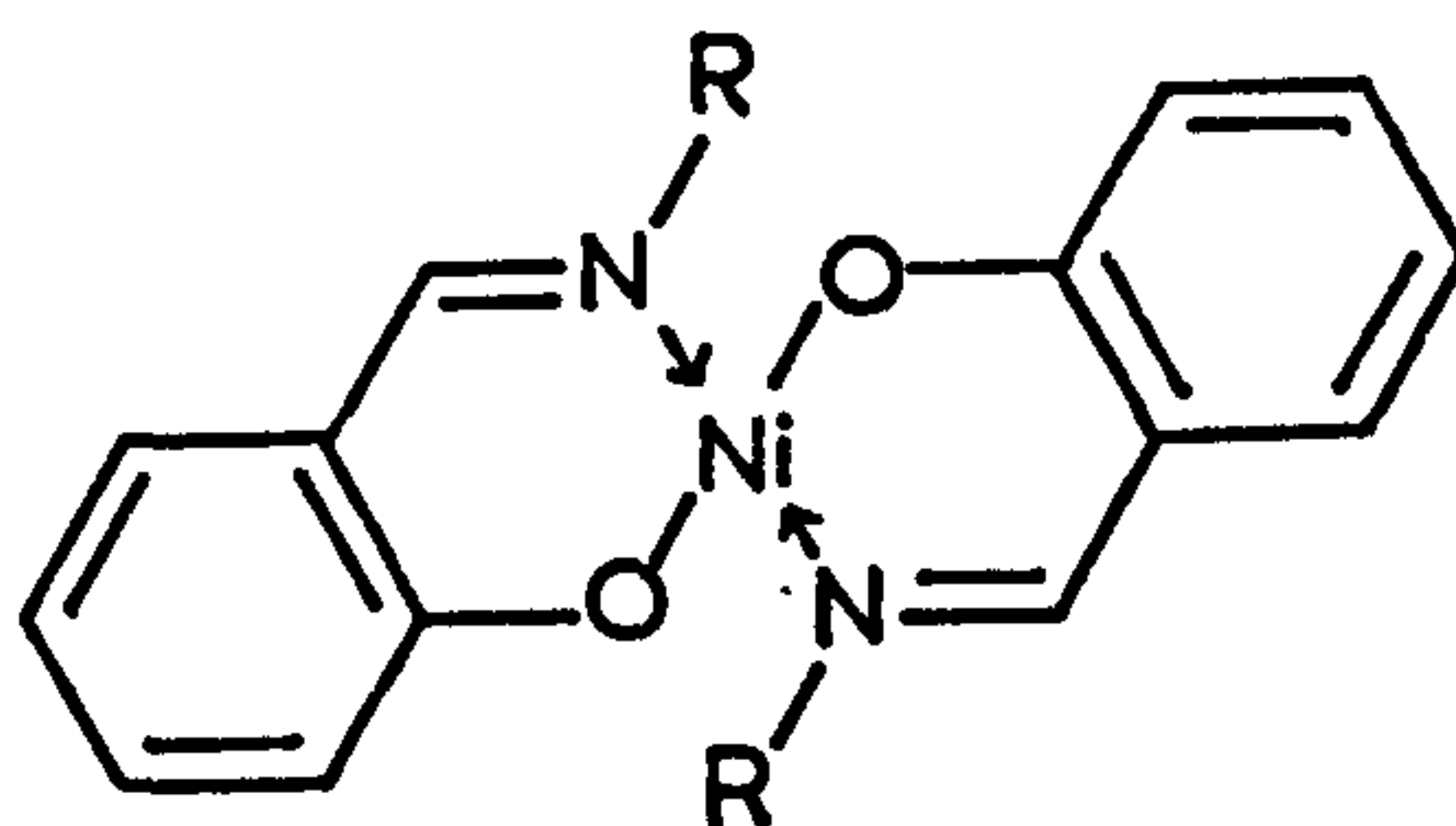


\*relative energies of  $d_{z^2}$  and  $d_{xz}$ ,  $d_{yz}$  orbitals are not known and probably depend on the nature of the ligand system.



Nisalen [4.24] gives diamagnetic solutions in pyridine. It was originally proposed<sup>40</sup> that this was due to a steric factor, the  $-\text{CH}_2\text{CH}_2-$  hydrogen atoms restricting the approach of further ligands, while no such restrictions are present, in the Nisalphen molecule. A more favourable explanation (page 92) will be presented in the light of studies made in this work.

The magnetic properties of the quadridentate complexes type [4.24] are considerably more straightforward than the analogous bis-bidentate complexes [4.25], which show varied types of magnetic properties according to the nature of the group R. Examples illustrating the possible types of magnetic behaviour will be given briefly.



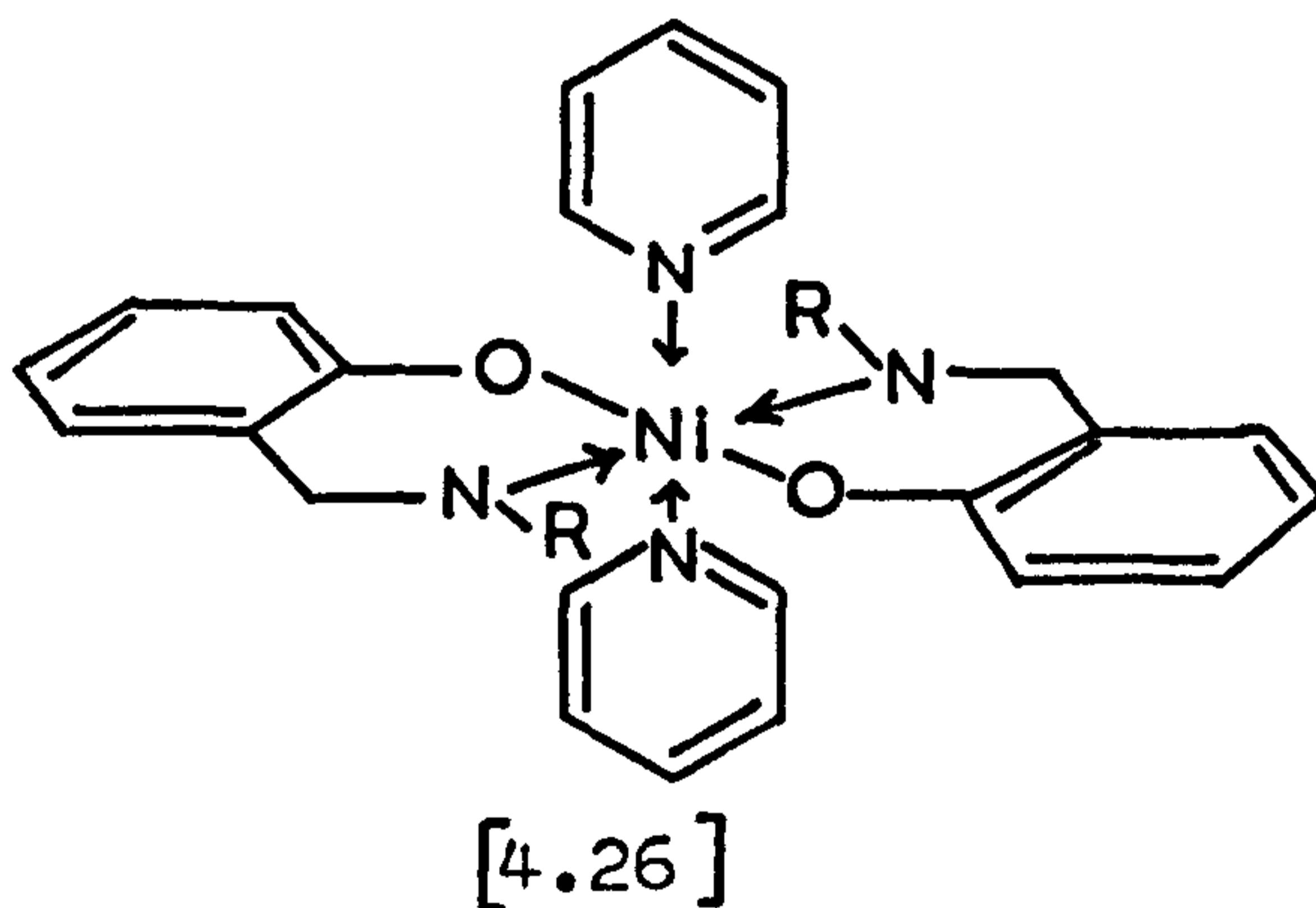
[4.25]

(1) Paramagnetic solid complexes.

Although most of the solid complexes are diamagnetic with a planar arrangement of the ligand donor atoms around the nickel atom, paramagnetic solids are known in which the planar arrangement is not present:

(a) a distorted octahedral configuration has been achieved by 'polymerization' of the planar units with oxygen atoms of one unit acting also as ligands for adjacent nickel ions, e.g. when  $R = CH_3$  the complex exists in two forms, one diamagnetic, and the other, isolated by heating to about  $180^\circ C$ , paramagnetic.<sup>41,42.</sup>

(b) a hexacoordinate configuration has been achieved by addition of further ligands to the coordination sphere, by crystallization in the presence of good donor molecules, e.g. diamagnetic complexes with  $R = OH$  and  $CH_3$  have been crystallized from pyridine to give<sup>36,43</sup> octahedral complexes [4.26]



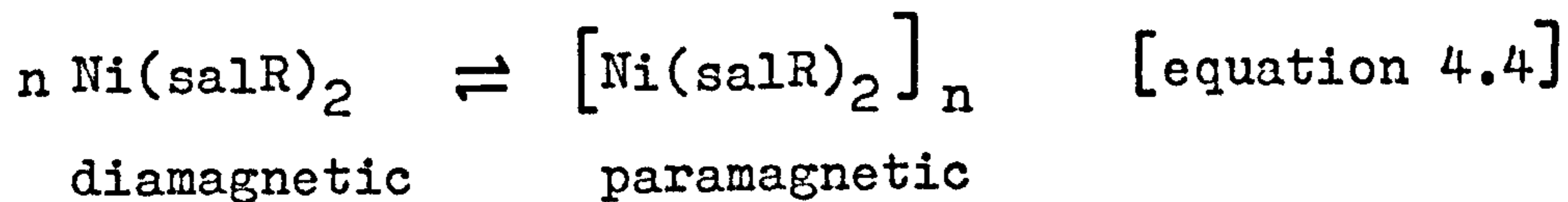
(c) a distorted tetrahedral configuration is achieved with certain bulky R groups. The magnetic moments of such complexes are above the maximum values expected for octahedral nickel(II) ( $3.2 \text{ B.M.}$ )<sup>8</sup> but well below the values predicted by theory for perfect

$T_d$  symmetry (3.9 - 4.2 B.M),<sup>44</sup> e.g. the complex with R=t-butyl has<sup>45</sup> a solid moment of 3.35B.M.

(2) Paramagnetic solutions in non-coordinating solvents.

There are three types of species responsible for the paramagnetism of solutions in non-coordinating solvents:

(a) Species in which the coordination number has been extended by association of planar units in a manner similar to (1)(a) above. The paramagnetic<sup>36,37</sup> solutions of the complex [4.25], R=CH<sub>3</sub> were shown to be due to associated species by R.H. Holm, who investigated<sup>46</sup> the dependence of the equilibrium, equation [4.4], on concentration of the complex.

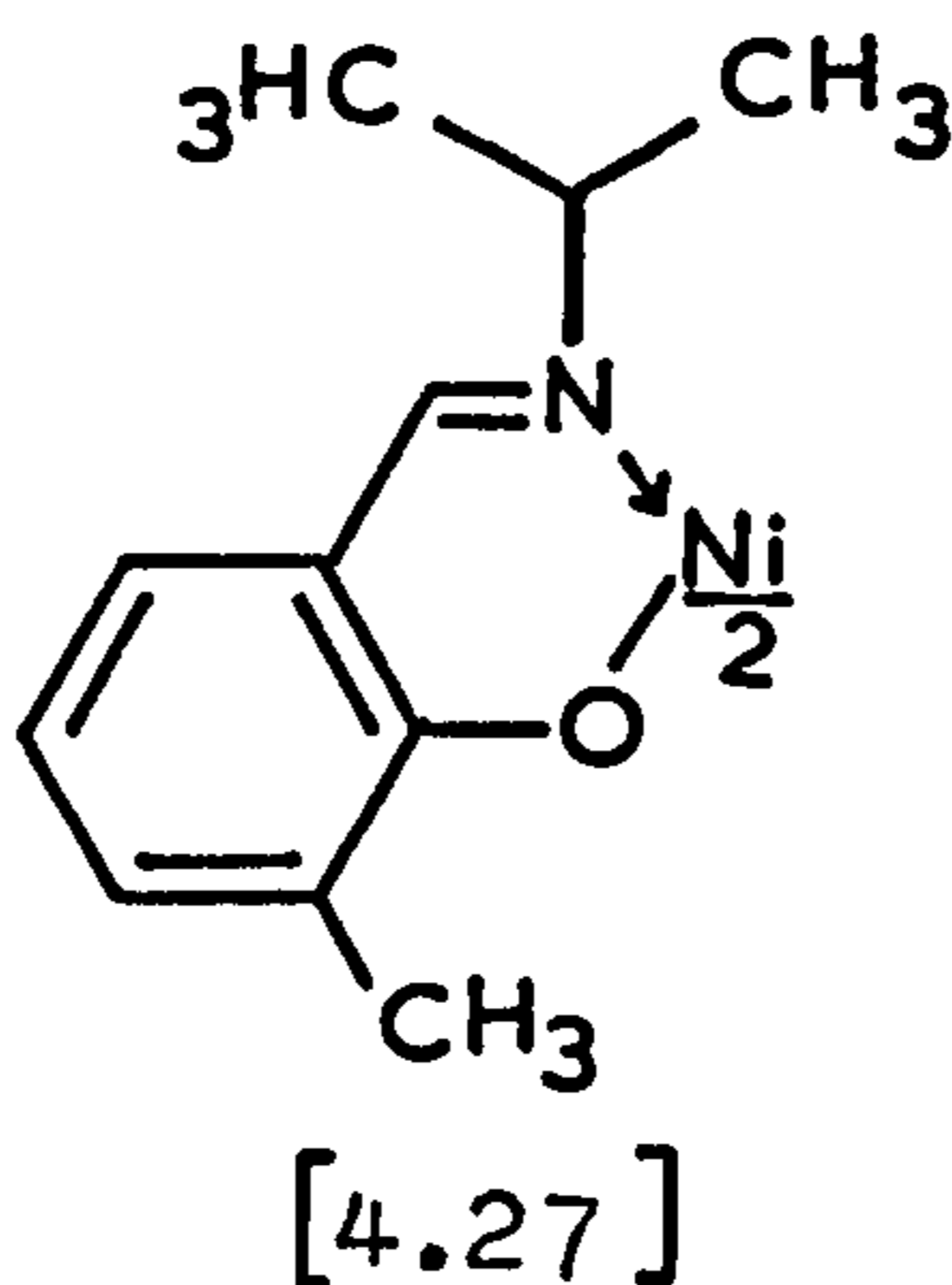


(b) distorted octahedral species in which the hexacoordination is made possible<sup>48</sup> by a donor atom located in the substituent R, e.g. when R = -CH(CH<sub>3</sub>)CH<sub>2</sub>OCH<sub>3</sub> an octahedral species is present<sup>47</sup> at low temperatures in chloroform solution.

(c) distorted tetrahedral species (c.f.(1)(c) above) for certain bulky R groups. Dissolving some complexes appears to aid the conversion of a strained planar form to a less strained distorted <sup>tet</sup>ahedral form, as does increase in temperature, e.g. [4.27] is a

diamagnetic solid but gives strongly paramagnetic solutions in chloroform.<sup>23</sup>

Tetrahedral species such as [4.27] have been studied carefully by Holm and co-workers using contact shift N.M.R. spectroscopy,<sup>23,49</sup> and the unpaired spin density on the ligand system estimated in several cases.



(3) Paramagnetism in molten complexes.

This effect is thought to be due to some conversion to a tetrahedral form.<sup>50</sup>

(4) Paramagnetism in coordinating solvents.

Formation of hexacoordinate species is assumed for this effect<sup>36,37</sup> in a similar manner to the quadridentate systems (see page 83)

The results of magnetic measurements on the solid complexes [4.17] are given in table [4.11]. These results were obtained by the Gouy method at room temperature, (see page 229).

Complex	Temp- erature °K	$\chi_g$ x10 <sup>6</sup>	$\chi_M$ x10 <sup>6</sup>	$\chi_L$ x10 <sup>6</sup>	$\chi_{M'}$ x10 <sup>6</sup>
Niamben	293	-0.24	-78	-146	68
Niambtn	293	-0.20	-67	-163	96
Niambbuten	290	0.04	14	-181	195
Niambphen	292	-0.32	-118	-168	50
Niampen	290	0.92	437	-240	677
Niampbuten	294	-0.17	-85	-261	175
NiMe-amben	293	0.04	13	-181	194

Table [4.11] Magnetic susceptibilities (cgs units) of the nickel complexes [4.17]

$\chi_g$  and  $\chi_M$  = mass and molar susceptibilities of the complexes.

$\chi_L$  = molar susceptibility of the ligand, from tables<sup>51</sup>

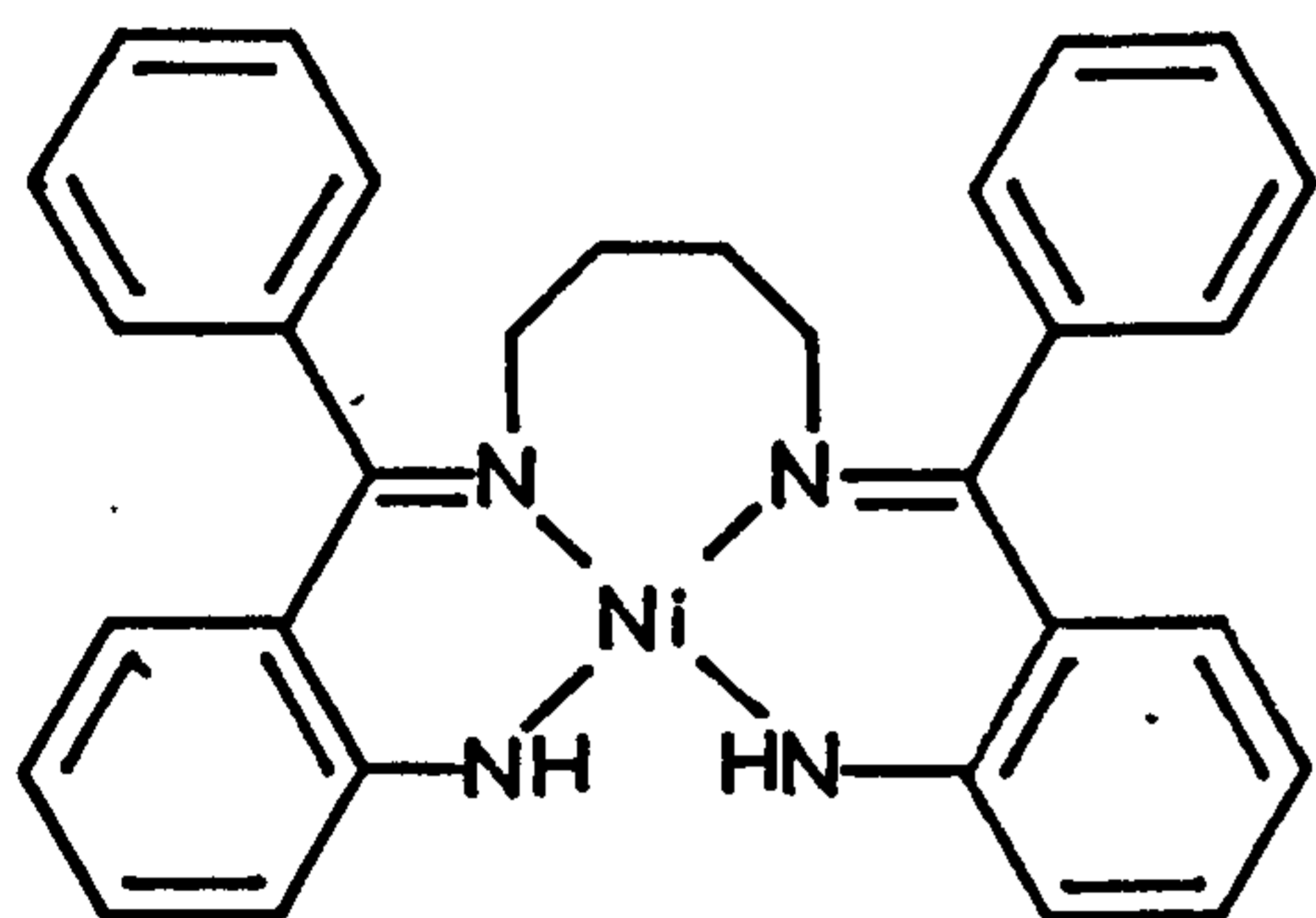
$\chi_{M'}$  = molar corrected susceptibility of the nickel ion.

A low-spin state is indicated for all the complexes in the solid state. The small positive corrected molar susceptibilities may be due to traces of paramagnetic impurities, or to small residual paramagnetism which has been described for low-spin  $d^6$  and  $d^8$  systems.<sup>52,53.</sup>

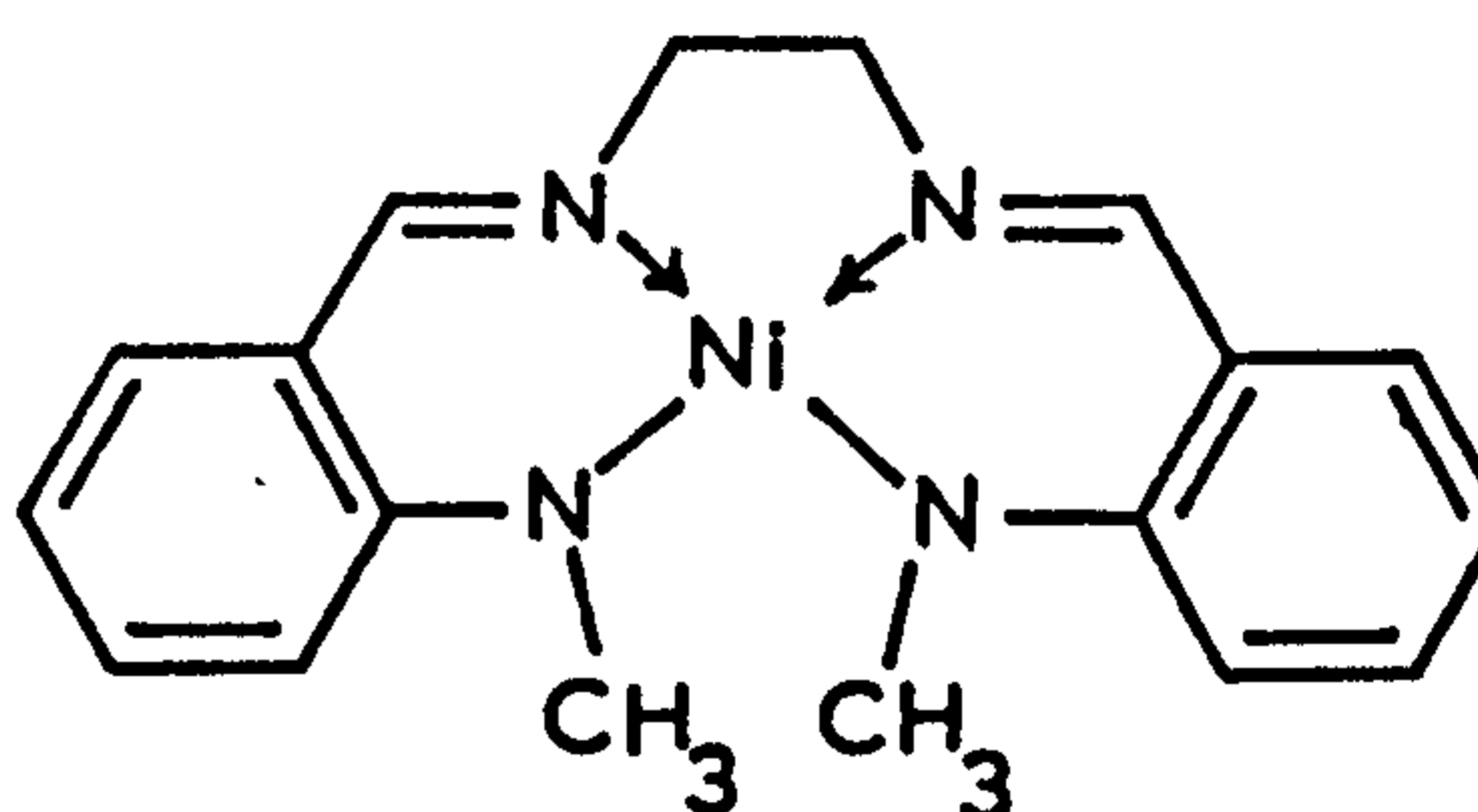
It is likely that all the complexes in Table [4.11] have a square-planar arrangement of the four donor nitrogen atoms about the nickel(II) ion, even when the ligands must be in somewhat strained configuration to



adopt this arrangement, e.g. in Niampbuten [4.22] where one of the chelate rings has seven members, with three fixed in the plane  $Ni(N_4)$ . Models show that the strain could be considerably reduced with a tetrahedral arrangement of the donors about the nickel(II) ion.



[4.22]



[4.28]

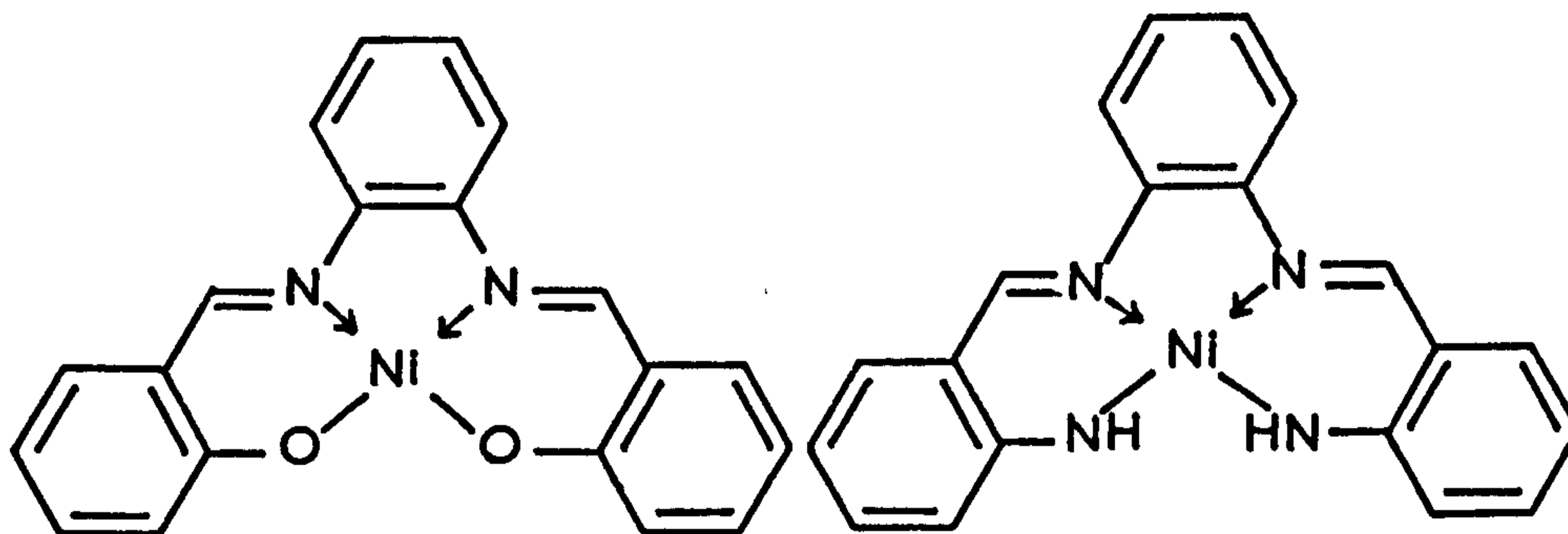
The molecule of NiMe-amben [4.28] would show considerable interaction between the two N-methyl groups if the whole carbon-nitrogen skeleton of the ligand were strictly planar and the four nitrogen atoms were situated at the corners of a square (c.f. the complexes of quadridentate Schiff base ligands of pyridine-2-aldehyde and quinoline-8-aldehyde, page 66). In solution N.M.R studies (page F79) show that the methyl protons of NiMe-amben [4.28] are equivalent. It is possible that either the whole molecule 'opens up' to allow the N-methylanilino groups to be further apart, or the methyl

carbons are situated symmetrically above and below the plane of the molecule.

Where solubility permitted the magnetic properties of the complexes were examined in pyridine solution by the N.M.R method (see page 231). Niambtn, Niambphen, Niampbuten and NiMe-amben were examined at 33°, in pyridine using tetramethylsilane as the N.M.R reference peak (see page 237). All gave diamagnetic solutions. The same results were obtained using cyclohexane as a reference in pyridine.

Niampbuten and NiMe-amben were examined at temperatures down to 238°K. The hexacoordinate solvated form of Nisalphen is favoured by decrease in temperature.<sup>36</sup> (see also page 248). Solutions of Niampbuten and NiMe-amben were still diamagnetic at 238°K. None of the complexes studied showed any tendency to solvate in pyridine to give paramagnetic species. These results are in agreement with the electronic spectra studies (page 97).

The reluctance of Niambphen to add molecules of pyridine contrasts with the behaviour of Nisalphen (see page 83). Sterically the two ligand systems are very similar (see [4.29] and [4.30] ), and so it seems unlikely that the resistance to addition of two pyridine molecules of Niambphen can be due to a steric restriction of approach of further ligands.

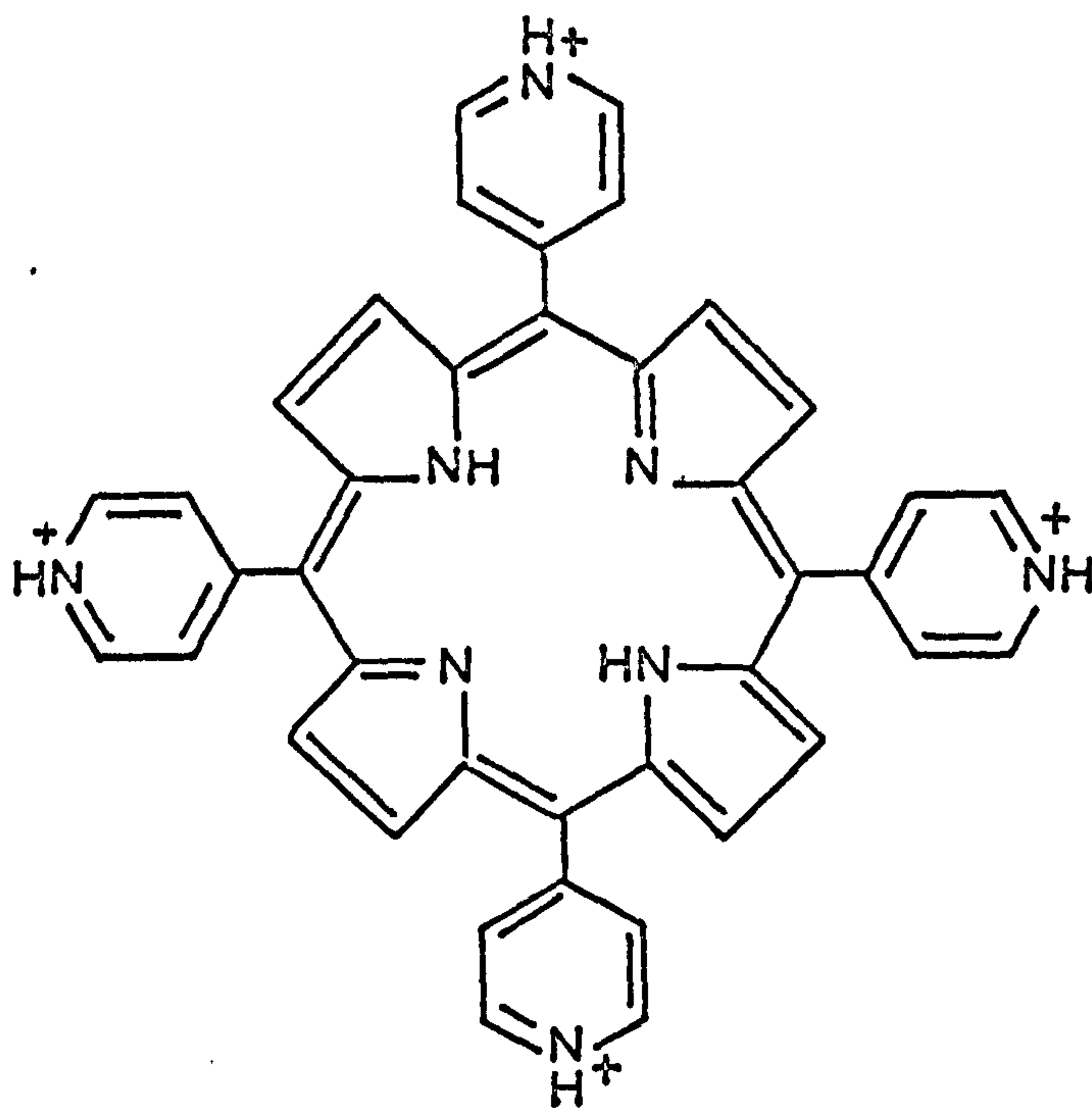
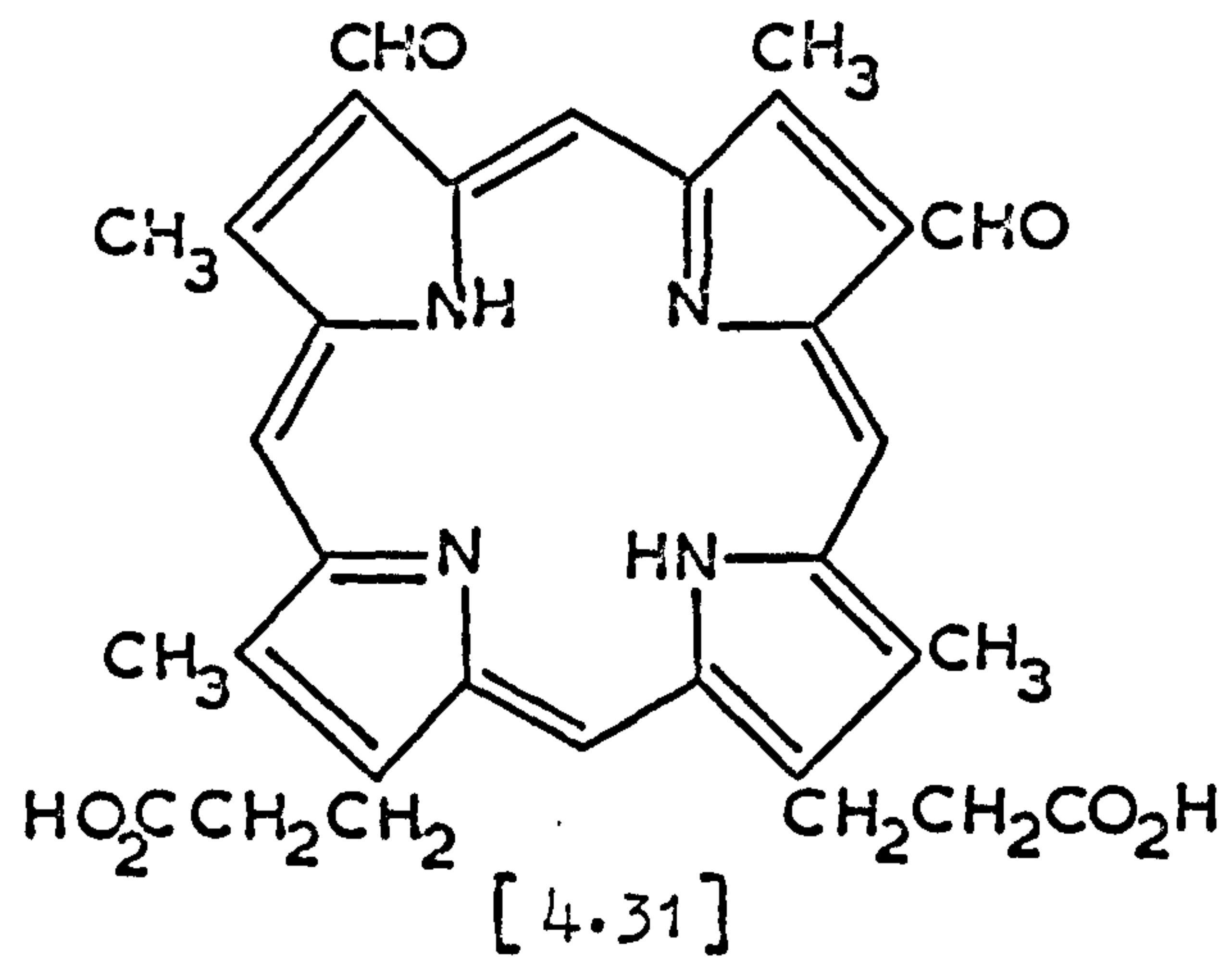


[4.29]

[4.30]

An explanation in terms of the different ligand field splittings produced by ' $N_4$ ' and ' $N_2O_2$ ' systems is more convincing. An ' $N_4$ ' system would be expected to produce a greater ligand field splitting than a comparable ' $N_2O_2$ ' system.

Calculations have shown<sup>54</sup> that the triplet state of a  $d^8$  ion in a tetragonal crystal field distorted towards a square-plane is lowered in energy by increasing the size of the electric dipoles on the octahedral axes, whereas the singlet state is increased in energy. For a given pair of dipoles on the octahedral axes the singlet ground state is favoured by increasing the size of the dipoles situated in the square-plane, until after a certain value is reached it has a lower energy than



the lowest energy triplet ground state. Hence, if the in-planar ligand field is greater than a certain critical value the complex will show no tendency to give paramagnetic species in the presence of a potential ligand.

This hypothesis is supported by several other workers' results. Nickel(II) porphyrins are normally diamagnetic in pyridine solution, but when the electron density on the coordinated nitrogen atoms is sufficiently decreased further coordination is possible.<sup>55</sup> The weakly basic porphyrins [4.31]<sup>56</sup> and [4.32]<sup>57</sup> give nickel(II) complexes which form hexacoordinate paramagnetic species by addition of two pyridine molecules in solution.

For a series of complexes  $\text{Ni}(\text{amine})_4(\text{ClO}_4)_2$  which have a square-planar arrangement of the amine donor atoms, with the two perchlorate ions more weakly coordinated in the axial positions it has been shown recently<sup>58</sup> that the axial crystal field parameter decreases as the planar field increases.

The different affinities of Nisalen and Nisalphen for the coordination of pyridine molecules (see page 84) may also be explained in terms of the greater ligand field splitting of salen due to the greater basicity of its two aliphatic imine nitrogen atoms.

Relative order for ligand field splitting (d)	R (e)			
	-(CH <sub>2</sub> ) <sub>2</sub> - ≈	-CH <sub>2</sub> CH(CH <sub>3</sub> )- >	-(CH <sub>2</sub> ) <sub>3</sub> >	-C <sub>6</sub> H <sub>4</sub>
NH <sup>-</sup>	No (a)	- (c)	No (a), (b)	No (a), (b)
X = (e)	>O <sup>-</sup>	No (a), (b) ref. 40, 37	No (a) 59	Yes (a) 59
		Yes (a), (b) 59, 37		

Table [4.12] Tendency of nickel(II) complexes of type [4.34] to coordinate pyridine.

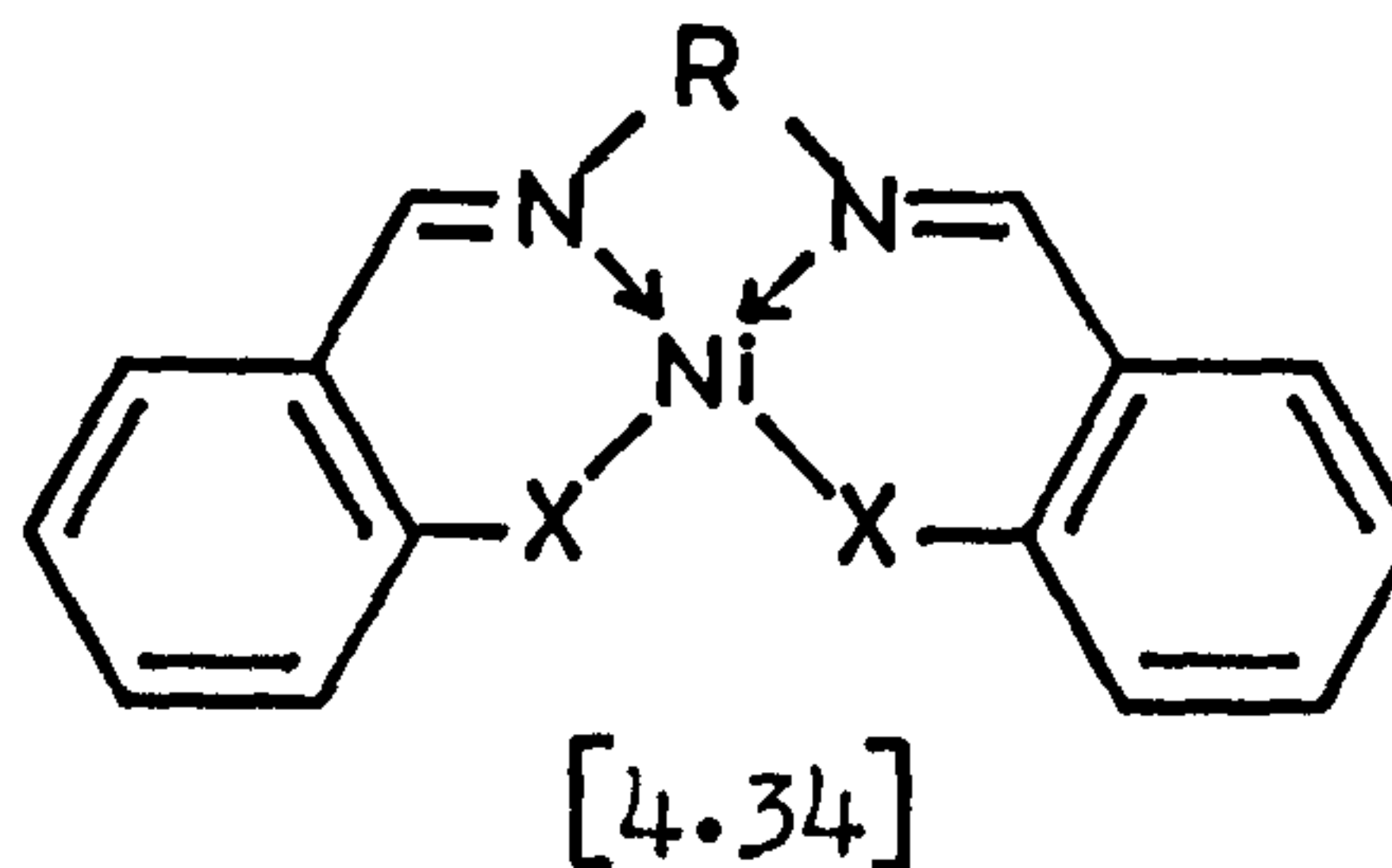
(a) Spectrophotometric evidence.

(b) Magnetic evidence.

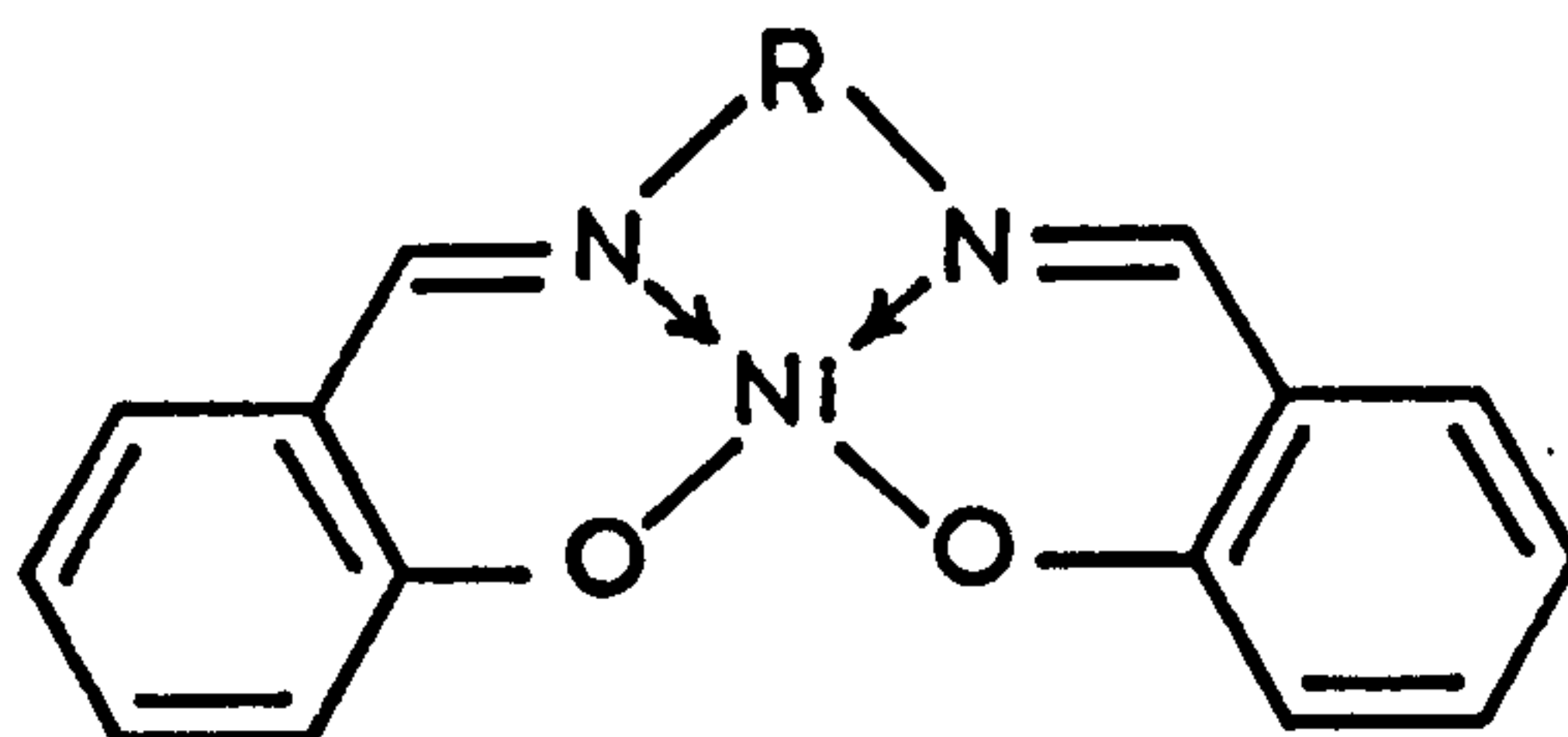
(c) Compound not prepared.

(d) c.f. references 59, 60.

(e) Substituents in formula [4.34].

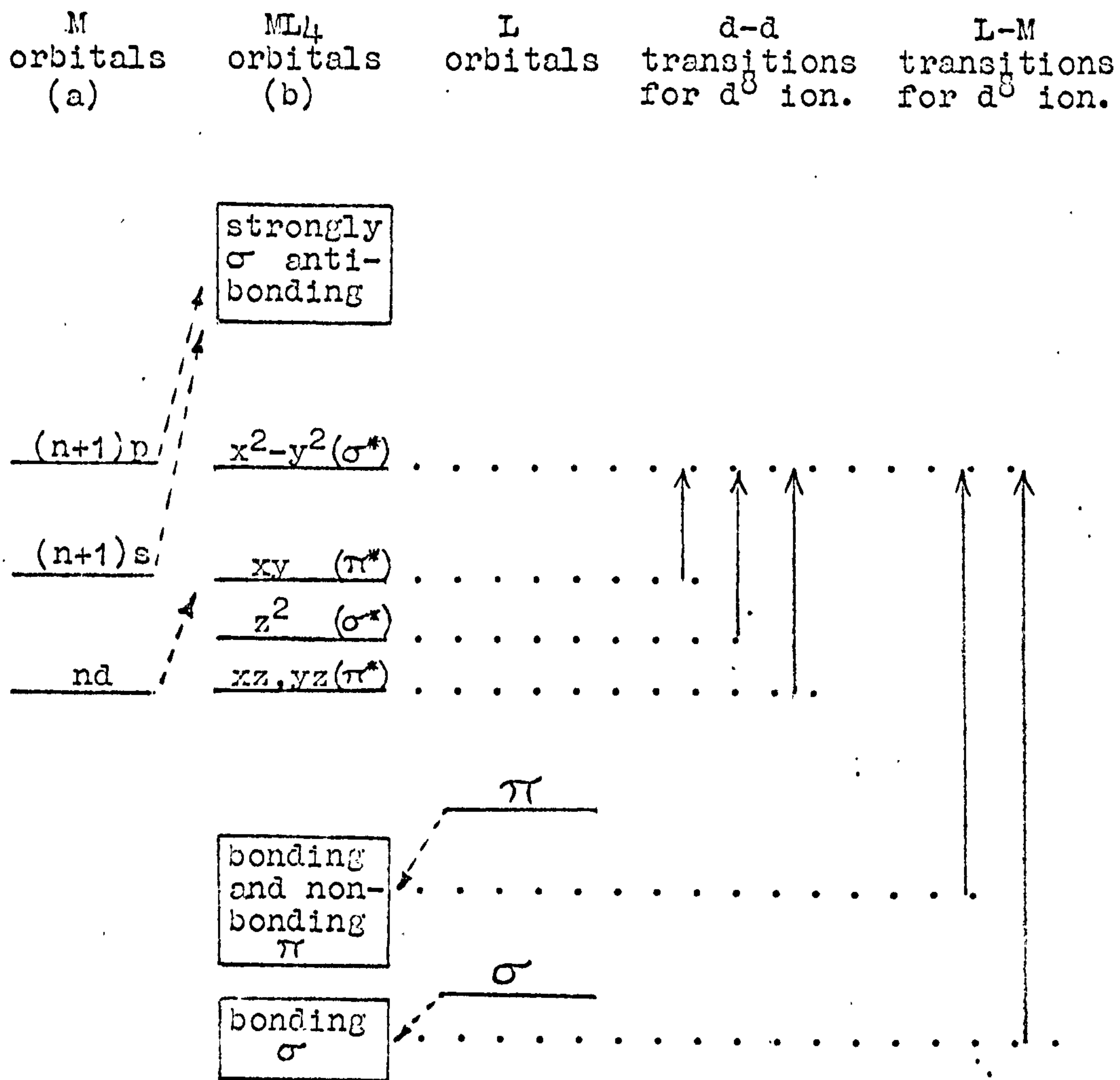


After this work had been completed a paper by Yamada and his co-workers was published<sup>59</sup> in which the tendency of Schiff base complexes of nickel(II) to assume coordination numbers greater than four was studied spectrophotometrically. Of the nickel(II) complexes of quadridentate salicyldimine ligands [4.33] those with the higher ligand field splittings (e.g. R =  $-\text{CH}_2\text{CH}_2-$  and  $-\text{CH}_2\text{CH}(\text{CH}_3)-$ ) did not add pyridine, while those with lower values (e.g. R =  $-(\text{CH}_2)_3-$  and  $-\text{C}_6\text{H}_4-$ ) did. These authors stressed that the best explanation of this behaviour is in terms of the ligand field strength of the ligands.



[4.33]

Results for the complexes of quadridentate nitrogen ligands of this work are compared with available data for quadridentate salicylaldehyde complexes in table [4.12].



[4.35]. Simplified energy level diagram for a square-planar complex with ligands having no  $\pi$  orbital systems, showing the spin-allowed transitions for a  $d^8$  diamagnetic complex.

(a) M = metal (b) L = ligand.

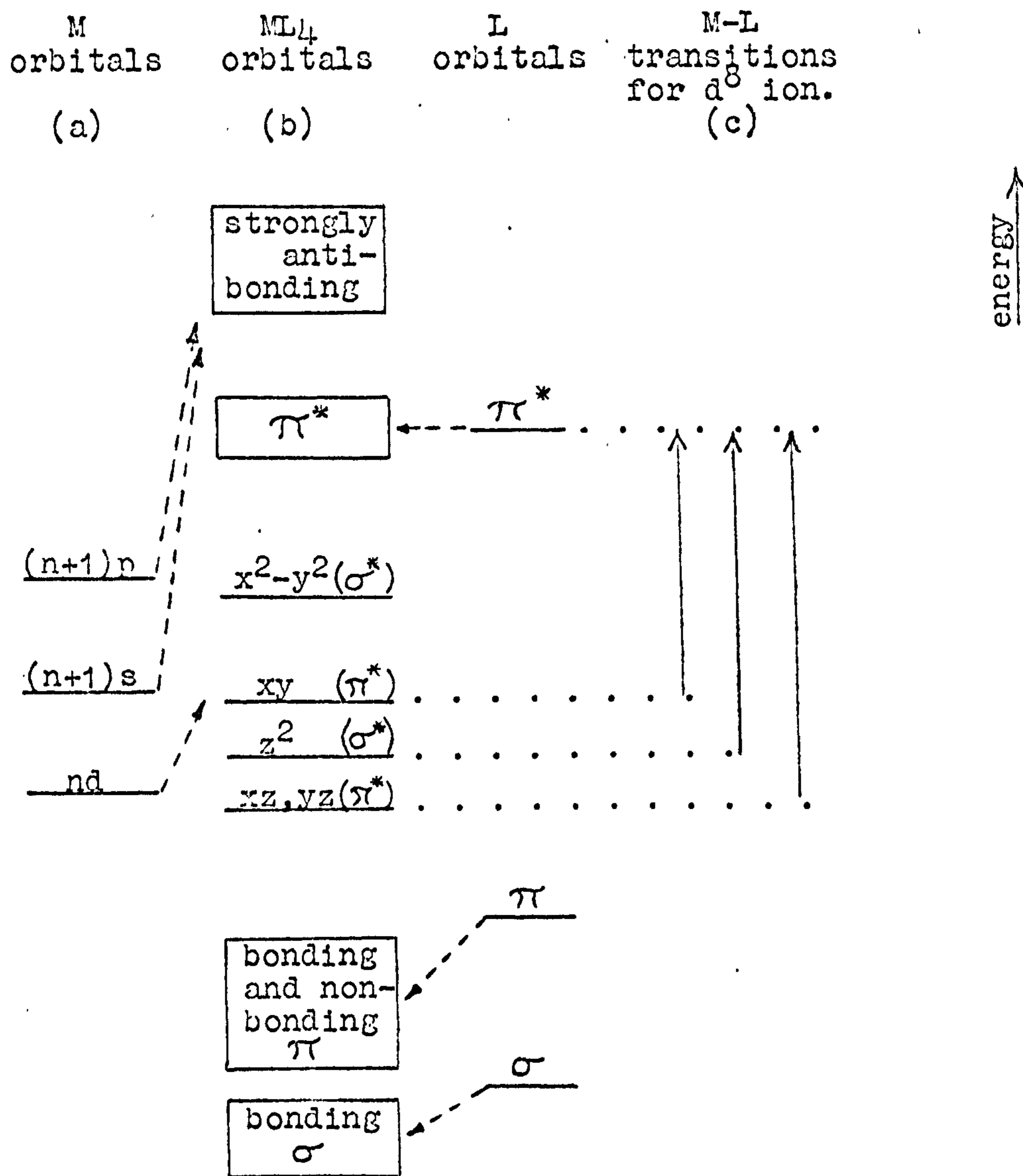


#### 4.4.6 Electronic spectra.

For square-planar complexes of transition metals with a  $d^8$  electronic configuration the assignment of electronic spectra absorption bands is relatively straightforward when the ligands possess no  $\pi$  orbital systems.<sup>61</sup> For this situation a simplified energy level scheme<sup>62</sup> for the complex is given in [4.35].

In favourable cases (e.g.  $\text{PdCl}_4^{2-}$ )<sup>61</sup> the three spin-allowed d-d transitions,  $d_{xy} \rightarrow d_{x^2-y^2}$ ,  $d_{z^2} \rightarrow d_{x^2-y^2}$ , and  $d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$  are observed. Charge transfer bands are thought to be of the "ligand to metal" type for complex ions similar to  $\text{PdCl}_4^{2-}$  since  $\text{Cl}^-$  is not expected to have any orbitals stable enough to accept metal electrons at the energies of the near ultraviolet region normally studied. Two intramolecular ligand to metal charge transfer bands are observed for the " $\text{PdCl}_4^{2-}$  type" ions, for the allowed transitions generally described as  $\sigma \rightarrow (x^2-y^2)$  and  $\pi \rightarrow (x^2-y^2)$ , (see [4.35]).

The situation is much more complex for systems in which the ligands have  $\pi$  orbital systems, because of a number of levels derived from  $\pi^*$  ligand orbitals may occur at energies slightly above the  $\sigma^* (x^2-y^2)$  level. Charge transfer transitions of the "metal to ligand" type are now also possible, see [4.36]. An example of a simple system of this type is the  $\text{Ni}(\text{CN})_4^{2-}$  ion,<sup>61</sup> which



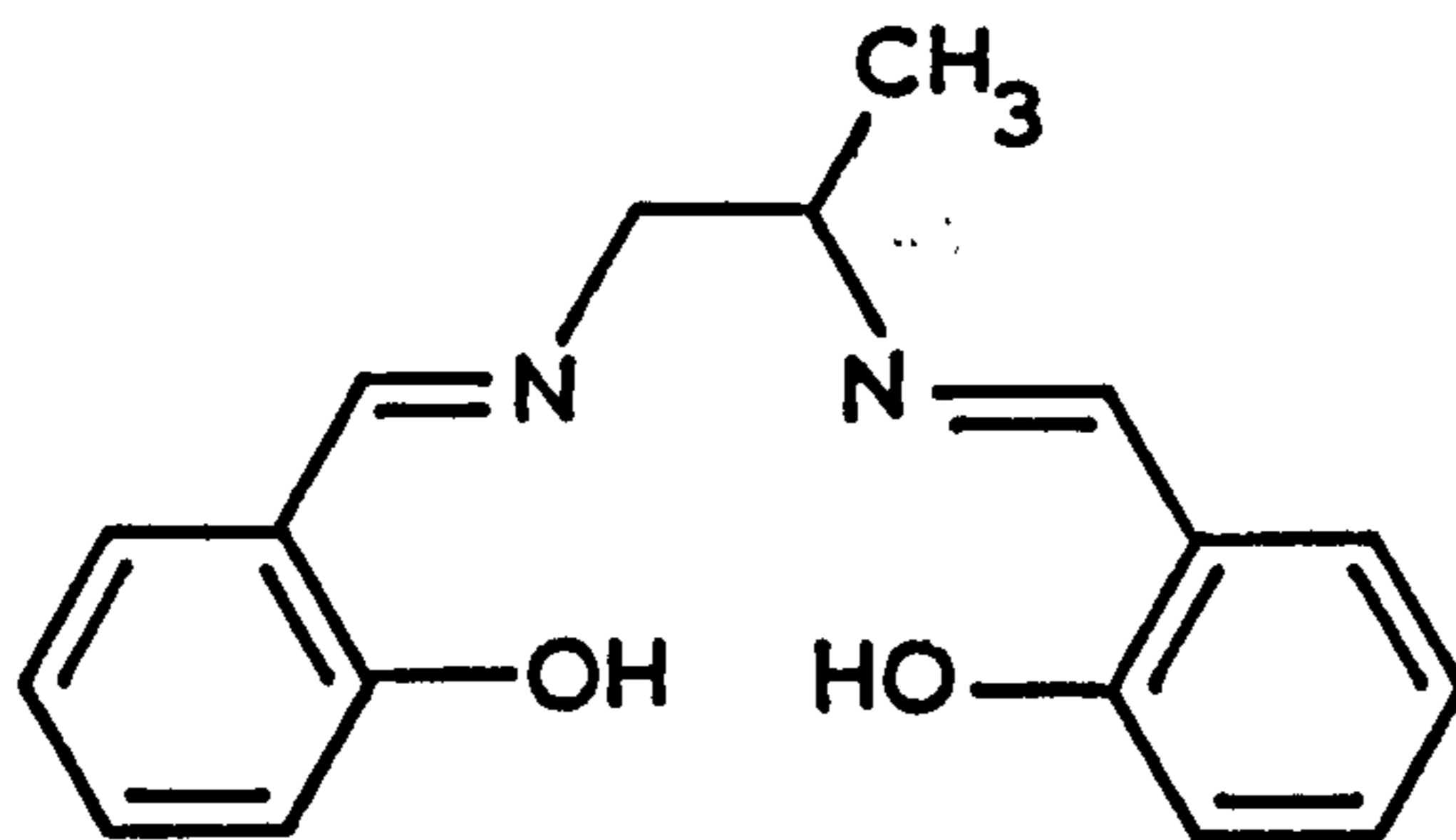
[4.36]. Simplified energy level diagram for a square-planar complex with ligands having  $\pi$  orbital systems, showing the additional spin-allowed transitions for a  $d^8$  diamagnetic complex.

(a) M = metal (b) L = ligand (c) see [4.35] for the d-d and L-M transitions.

gives rise to three charge transfer bands, thought to be due to transitions from the three filled "metal d" orbital levels to the first available ligand level (see [4.36] ). The presence of very intense low energy bands of this type makes the d-d spectrum hard to resolve.

For nickel(II) complexes of quadridentate Schiff base ligands derived from salicylaldehyde the d-d transitions have only been resolved in a few cases<sup>60</sup> without the use of circular dichroism.

The most complete assignment for spectra of the 'salen-type' nickel(II) complexes was made by Bosnich<sup>63</sup> recently, who studied the electronic spectrum of the nickel(II) complex of the optically active ligand salpn [4.37]. Comparison with the spectra of Zn(II)salpn, the free ligand, and bis-(N-methylsalicylaldiminato)-nickel(II) led to the assignments for the transitions shown in table [4.13], page F96.



[4.37]

Transition	$d \rightarrow d$	$M \rightarrow L$
Levels in [4.36] involved.	$d_{x^2-y^2} \uparrow$ $d_{xy}$ $d_{x^2-y^2} \uparrow$ $d_{z^2}$ $d_{x^2-y^2} \uparrow$ $d_{yz}, d_{zx}$	$\pi^* \uparrow$ $d_{xy}$ $\pi^* \uparrow$ $d_{z^2}$ $\pi^* \uparrow$ $d_{yz}, d_{zx}$
$\lambda_{max.}$ (m $\mu$ )	555 (sh) a (513) b	448 (sh) a 412 388 (sh) a

Table [4.13]. Assignments for the electronic transitions in the spectrum of a methanolic solution of Ni(II)(-)-salpn

(a) (sh) = shoulder. (b) ( ) = only seen in the circular dichroism spectrum.

The electronic spectra of the acyclic nickel(II) complexes prepared for this work are tabulated on page 99. Only in a few cases were low intensity bands resolved which might be d-d transitions. A complete assignment for the electronic transitions shown in [4.35] and [4.36] would only be possible after a separate research project of the type carried out by Bosnich.<sup>63</sup> However, certain useful information can be deduced from the spectra.

4.4.5 (a) Comparison of the ligand field splitting with analogous 'N<sub>2</sub>O<sub>2</sub>' systems.

The spectra of Nisalpn and Nisalpn show weak absorptions at 540<sup>60</sup> and 550<sup>63</sup> m $\mu$  respectively which are assumed to be due to the lowest energy d-d transition, ( $d_{xy} \rightarrow d_{x^2-y^2}$ , see [4.35]). A similar weak band is not observed in Niamben, and probably occurs at higher energies, being hidden under one of the intense metal to ligand charge transfer bands. This suggests that the nickel(II) d orbitals are split more by amben than by the comparable 'N<sub>2</sub>O<sub>2</sub>' systems salen and salpn.

4.4.5(b) Variation of ligand field splitting with length of the bridging chain R in [4.17].

Shoulders were observed in the spectra of Niambtn, Niambbuten and Niampbuten at around 600 m $\mu$ .

These weak bands may be due to the lowest energy d-d transition. Although energies cannot be assigned with any certainty, since the bands are too poorly resolved, they occur at lower energy than in Niamben, which suggests that the ligand field splitting is smaller for the ligands with longer bridging groups R in [4.17]. A similar trend was observed with comparable ligands derived from pyrrole-2-aldehyde.<sup>26</sup>

#### 4.4.5 (c) Increase in coordination number for the complexes.

The  $d_z^2 \rightarrow d_{x^2-y^2}$  transition is very sensitive to the approach of a ligand along the z-axis, and is expected to move to longer wavelengths the greater the field in the z-direction.<sup>64</sup> Certain nickel(II) complexes of Schiff bases extend their coordination number when dissolved in coordinating solvents, and this change is accompanied by the appearance of new band(s) in the lower energy region of the spectrum.<sup>40,59.</sup>

The possibility of the complexes extending their coordination number beyond four was examined spectroscopically. Unfortunately solutions concentrated enough to give appreciable absorptions were only obtainable in polar, and hence possibly coordinating solvents, and so comparison had to be made with spectra of solid samples, recorded as nujol mulls in the visible and near infrared regions.

All the bands occurring in the visible region of the solution spectra of the nickel complexes were detected in the nujol mulls. No striking change in the solution spectra was observed when the solvent systems were varied, for instance by the addition of pyridine. Apparently, the complexes show no tendency to increase their coordination number beyond that in the solid state on solution in the coordinating solvent systems used in table [4.14].

These results are compatible with those obtained by magnetic susceptibility determinations in solution and are discussed on page 90.

#### 4.4.5(d) Increased conjugation in the ligand system.

Niambphen has an intense band at lower energy than the other complexes. For this system in which all four donor atoms are linked by a conjugated chain a lower energy  $\pi^*$  orbital is available to accept 'metal d' electrons. A similar effect was observed for the salicylaldimines systems, where for the free ligands [4.38] the additional conjugation in the ligands with aromatic R results in red shifts for the  $n - \pi^*$  and  $\pi - \pi^*$  transitions.<sup>65</sup>

Increased conjugation by substituting phenyl groups for R<sub>1</sub> in [4.17] results in much smaller red shifts.

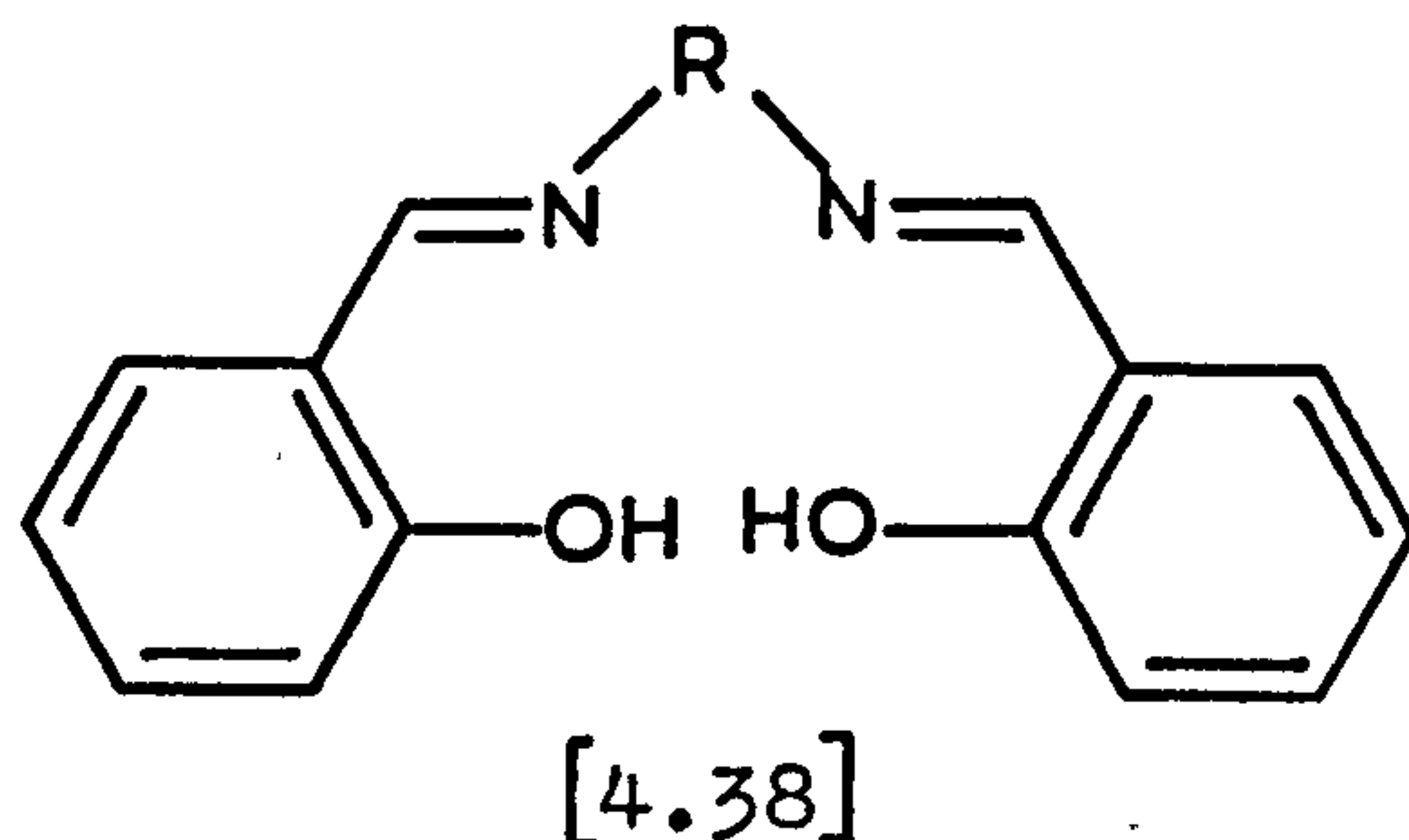


Table [4.14] Electronic Spectra of nickel(II) complexes  
[4.17] page 70.

(a)  $\lambda_{\max}$  in  $m\mu$  (b) ( ) Molar extinction coefficient.  
 (c) Scanned 300 - 1000  $m\mu$  (d) Scanned 260 - 1000  $m\mu$   
 (e) Scanned 400 - 1000  $m\mu$ .

Niamben (1) Dimethylformamide solution <sup>c</sup>; 481<sup>a</sup> (3900)<sup>b</sup>,  
 361 (5300), 320 (16000).

(2) Tetrahydrofuran solution and 20% pyridine -  
 tetrahydrofuran solution <sup>c</sup>; 480 (4200), 360 (sh) (6400),  
 320 (16000), 310 (sh) (15000)

(3) Nujol mull <sup>e</sup>; 485<sup>a</sup>, 470.

Niambtn (1) Dimethylformamide solution <sup>c</sup>; 495 (4700),  
 472 (4700), 357 (sh) (5800), 322 (19000).

(2) Nujol mull <sup>e</sup>; 600 (sh), 500, 475, 440 (sh)

Niambbuten (1) Dimethylformamide solution <sup>c</sup>; 620(sh) (800),  
 515 (3600), 475 (3700), 365 (5100), 323 (13000).

(2) Tetrahydrofuran solution <sup>c</sup>; 610 (sh), 518,  
 480, 365, 325.



(3) Nujol mull <sup>e</sup>; 620 (sh), 525(sh), 470.

Niambphen (1) Dimethylformamide solution <sup>d</sup>; 620 (7600), 575 (5900), 585(sh) (5300), 515(sh) (5100), 430(sh) (9300), 394(sh) (29000), 395 (29500), 370(sh) (21000), 350(sh) (8000), 292 (54000).

(2) Tetrahydrofuran solution and 20% pyridine - tetrahydrofuran solution <sup>c</sup>; 620 (6800), 572 (5300), 538 (5100), 516(sh)(5000), 425(sh)(8700), 388(sh)(26000), 377(28000), 355(sh)(19000), 340(sh)(12000), 3050 (49000).

(3) Nujol mull <sup>e</sup>; 630, 580, 540(sh), 420(sh).

Niambnaph (1) Dimethylformamide solution <sup>c</sup>; 475 (6100) 350 (10000), 313 (27000).

(2) Nujol mull <sup>e</sup>; 520(sh), 500, 480(sh).

Niampen (1) Dimethylformamide solution <sup>c</sup>; 555 (1800), 490 (4500), 365 (8300), 328 (17000).

(2) Nujol mull <sup>e</sup>; 530, 510, 480.

Niampbuten (1) Dimethylformamide solution <sup>c</sup>; 610(sh)(450), 510 (4200), 482(4300), 410(sh)(4500), 370(sh)(6000), 320(20000).

(2) Nujol mull <sup>e</sup>; 630(sh), 520, 490, 420(sh)

NiMe-amben (1) Dimethylformamide solution <sup>d</sup>; 620(sh) (390), 510 (5200), 480(sh)(4800), 380(7400), 347(7900), 295(17300).

(2) Tetrahydrofuran solution and 20% pyridine - tetrahydrofuran solution <sup>c</sup>; 500 (4900), 375(7100), 350(7300).

(3) Nujol mull <sup>e</sup>; 650(sh), 520, 485(sh)

#### 4.5. Copper complex.

The copper(II) complex of amben was prepared by the method used by Pfeiffer<sup>24</sup> and recrystallized from dimethylformamide. Its infrared spectrum was very similar to that of Niamben except that the NH stretch was observed as a sharp single peak.

The other properties of this complex are discussed in comparison with the cyclic systems on page 188.

#### 4.6 References.

1. F. Lions, Chem. in Brit. 3, 101, (1967).
2. F.G. Mann and W.J. Pope, J. Chem. Soc., 482, (1926).
3. C.K. Jørgensen, Acta. Chem. Scand., 10, 887, (1956).
4. S.E. Rasmussen, Acta. Chem. Scand., 13, 2009, (1959).
5. M. Campolini and N. Nardi, Inorg. Chem., 4, 41 (1966).
6. M. di Vaira and P.L. Orioli, Inorg. Chem., 6, 955, (1967).
7. B.J. Hathaway and A.E. Underhill, J. Chem. Soc., 3091, (1961).
8. B.N. Figgis and J. Lewis, Prog. Inorg. Chem., 6, 197, (1964).
9. C.K. Jørgensen, Acta. Chem. Scand., 11, 399, (1957).
10. D.A. House and N.F. Curtis, J. Chem. Soc., 3149, (1963).
11. I. Lifschitz, J.G. Bos and K.M. Dijkema, Z. Anorg. Chem., 242, 97, (1939).

12. J.H. Nelson and R.O. Ragsdale, *Inorg. Nuclear Chem. Letters*, 3, 585, (1967).
13. G. Narain, *Z anorg. Chem.*, 347, 215, (1966).
14. J. Dekkers and H.A. Goodwin, *Austral. J. Chem.* 19, 2241, (1966).
15. E. Hoyer and B. Lorenz, *Z anorg. Chem.*, 350, 160, (1967)
16. G.C. Kulasingam and W.R. McWhinnie, *J. Chem. Soc.(A)*, 1253 (1967).
17. D.W. Gruenwedel, *Inorg. Chem.*, 7, 495, (1968).
18. C.M. Harris and E.D. McKenzie, *Nature*, 196, 670, (1962).
19. P. Krumholz, *Inorg. Chem.*, 4, 612, (1965).
20. H.A. Goodwin and F. Lions, *J. Amer. Chem. Soc.*, 82, 5013, (1960).
21. R.S. Vagg, R.N. Warrenner and E.C. Watton, *Austral. J. Chem.* 20, 1841, (1967).
22. W.R. McWhinnie, G.C. Kulasingam and J.C. Draper, *J. Chem. Soc. (A)*, 1199, (1966).
23. G.W. Everett, R.H. Holm and A. Chakravorty, *Prog. Inorg. Chem.* 7, 83, (1966).
24. P. Pfeiffer, Th. Hesse, H.Pfitzner, W. Scholl and H. Thielert, *J. prakt. Chem.*, 149, 217, (1937).
25. H. Veda and M. Deguchi, *Hiroshima Daigaku Kogakuba Kenkyu Hokoku*, 13, 61 (1965), *Chem. Abs.* 63, 4938 (1965).
26. J.H. Weber, *Inorg. Chem.*, 6, 258, (1967).
27. E. Uhlig and M. Friedrich, *Z. anorg. Chem.*, 343, 299, (1966).

28. R.H. Holm, A. Chakravorty and L.J. Theriot, *Inorg. Chem.*, 5, 625, (1966).
29. F. Calderazzo and C. Floriani, *Chem. Comm.*, 417 (1968).
30. A.G. Hill and C. Curran, *J. Phys. Chem.*, 64, 1519, (1960).
31. As ref. 23, page 160.
32. H.M. Fischer and R.C. Stoufer, *Inorg. Chem.*, 5, 1172, (1966).
33. L.J. Bellamy and R.F. Branch, *J. Chem. Soc.*, 4487, (1954)
34. E.J. Olszewski and D.F. Martin, *J. Inorg. Nuclear Chem.* 26, 1577, (1964).
35. K. Ueno and A.E. Martell, *J. Phys. Chem.*, 60, 1270 (1956).
36. H.C. Clark and A.L. Odell, *J. Chem. Soc.*, 3431, (1955).
37. J.B. Willis and D.P. Mellor, *J. Amer. Chem. Soc.*, 69, 1237, (1947).
38. J.E. Falk and R.S. Nyholm, "Current Trends in Heterocyclic Chemistry", Ed. A. Albert, G.M. Badger and C.W. Shoppee, Butterworths, 1958, page 130.
39. H. Seuff and W. Klemm, *J. prakt. Chem.*, 154, 73, (1939).
40. G. Maki, *J. Chem. Phys.*, 29, 1129, (1958).
41. C.M. Harris, S.L. Lenzer and R.L. Martin, *Austral. J. Chem.*, 11, 331, (1958).
42. H.C. Clark and R.J. O'Brien, *Can. J. Chem.*, 39, 1030, (1961).
43. F. Basolo and W.R. Matoush, *J. Amer. Chem. Soc.*, 75, 5663, (1953).

44. B.N. Figgis, *Nature*, 182, 1568, (1958).
45. L. Sacconi, P. Paoletti and M. Ciampolini, *J. Amer. Chem. Soc.*, 85, 411, (1963).
46. R.H. Holm, *J. Amer. Chem. Soc.*, 83, 4683, (1961).
47. A. Chakravorty, J.P. Fennessy and R.H. Holm, *Inorg. Chem.*, 4, 26, (1965).
48. M. DiVaira and P.L. Orioli, *Inorg. Chem.*, 4, 490, (1967).
49. R.H. Holm, A. Chakravorty and G.O. Dudek, *J. Amer. Chem. Soc.*, 86, 879, (1964).
50. L. Sacconi, *J. Chem. Soc.*, 4608, (1963).
51. P.W. Selwood, "Magnetochemistry", 2nd Ed., Interscience, 1956, page 92.
52. J.S. Griffith and L.E. Orgel, *Trans. Faraday Soc.*, 53, 601, (1957).
53. C.J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, 1962, page 147.
54. G. Maki, *J. Chem. Phys.*, 28, 651. (1958).
55. J.E. Falk, "Porphyrins and Metalloporphyrins", Elsevier, 1964, page 41.
56. W.S. Caughey, R.M. Deal, B.D. McLees and J.O. Alben, *J. Amer. Chem. Soc.*, 84, 1735, (1962).
57. E.B. Fleischer, *Inorg. Chem.*, 1, 493, (1962).
58. A.V. Butcher, D.J. Phillips and J.P. Redfern, *J. Chem. Soc. (A)*, 1064, (1968).
59. S. Yamada et al., *Coordin. Chem. Rev.*, 3, 247, (1968).

60. R.H. Holm, J. Amer. Chem. Soc., 82, 5632, (1960).
61. H.B. Gray and C.J. Ballhausen, J. Amer. Chem. Soc., 85, 260, (1963).
62. H.B. Gray, "Transition Metal Chemistry", Vol. I. Ed. R.L. Carlin, Arnold, 1965, page 239.
63. B. Bosnich, J. Amer. Chem. Soc., 90, 627, (1968).
64. P.S. Braterman, R.C. Davies and R.J.P. Williams, Adv. Chem. Phys., 7, 359, (1964).
65. S.M. Crawford, Spectrochim. Acta, 19, 255 (1963).

## Chapter 5. Cobalt Complexes of the Acyclic 'Model' Ligands.

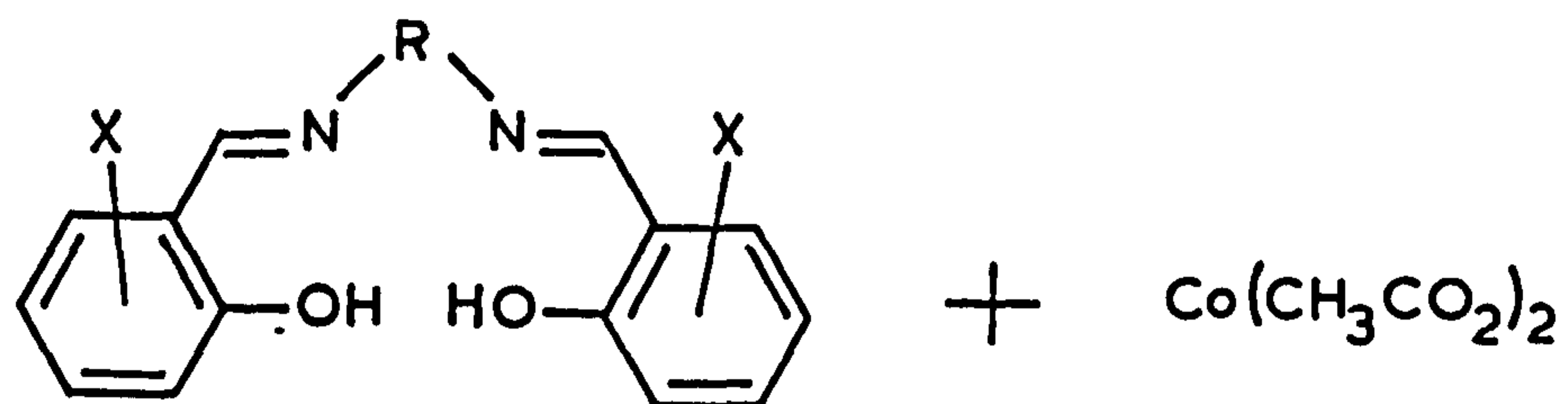
- 5.1 Cobalt(II) complexes.
- 5.1.1 Nomenclature and abbreviations:
- 5.2 Preparations and analyses.
- 5.3 Infrared spectra
- 5.4 Magnetic measurements.
- 5.4.1 Similar systems.
- 5.4.2 Solid magnetic moments.
- 5.5 Electronic spectra
- 5.6 Oxygenation and oxidation.
- 5.7 Reduction to cobalt(I).
- 5.8 References.

### 5.1 Cobalt(II) complexes.

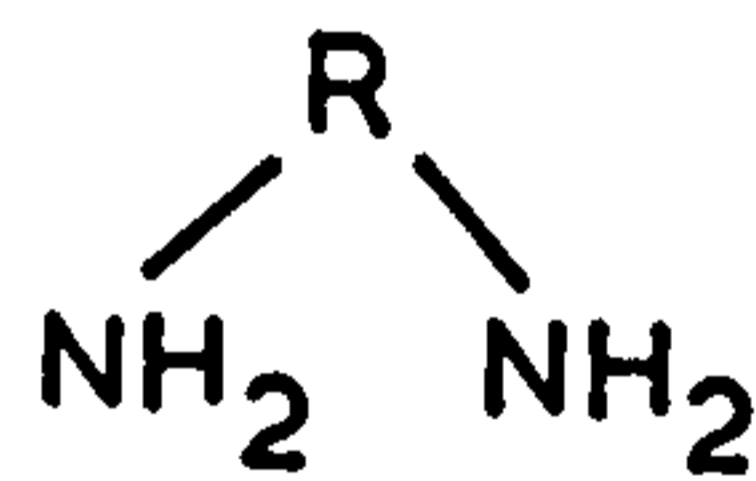
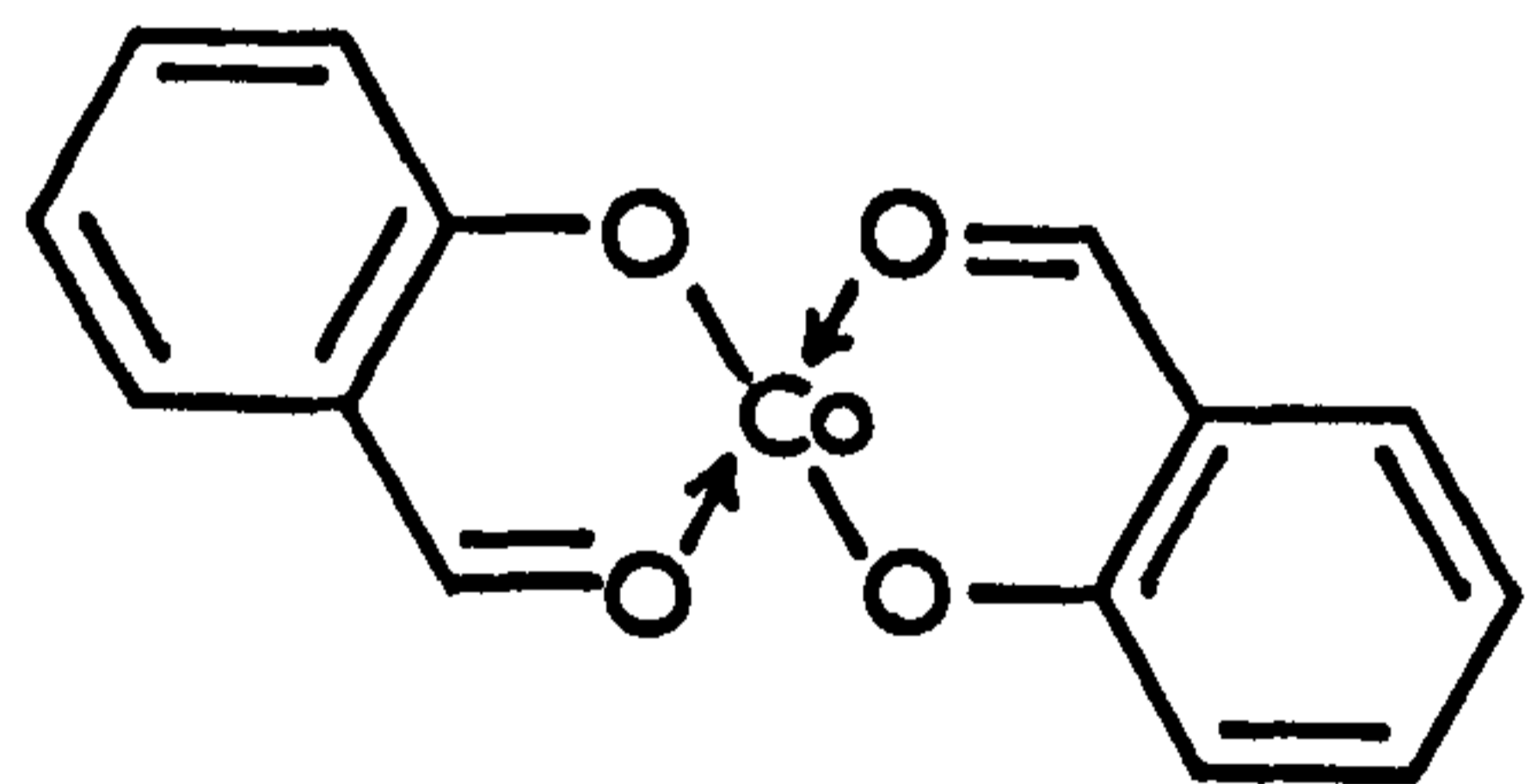
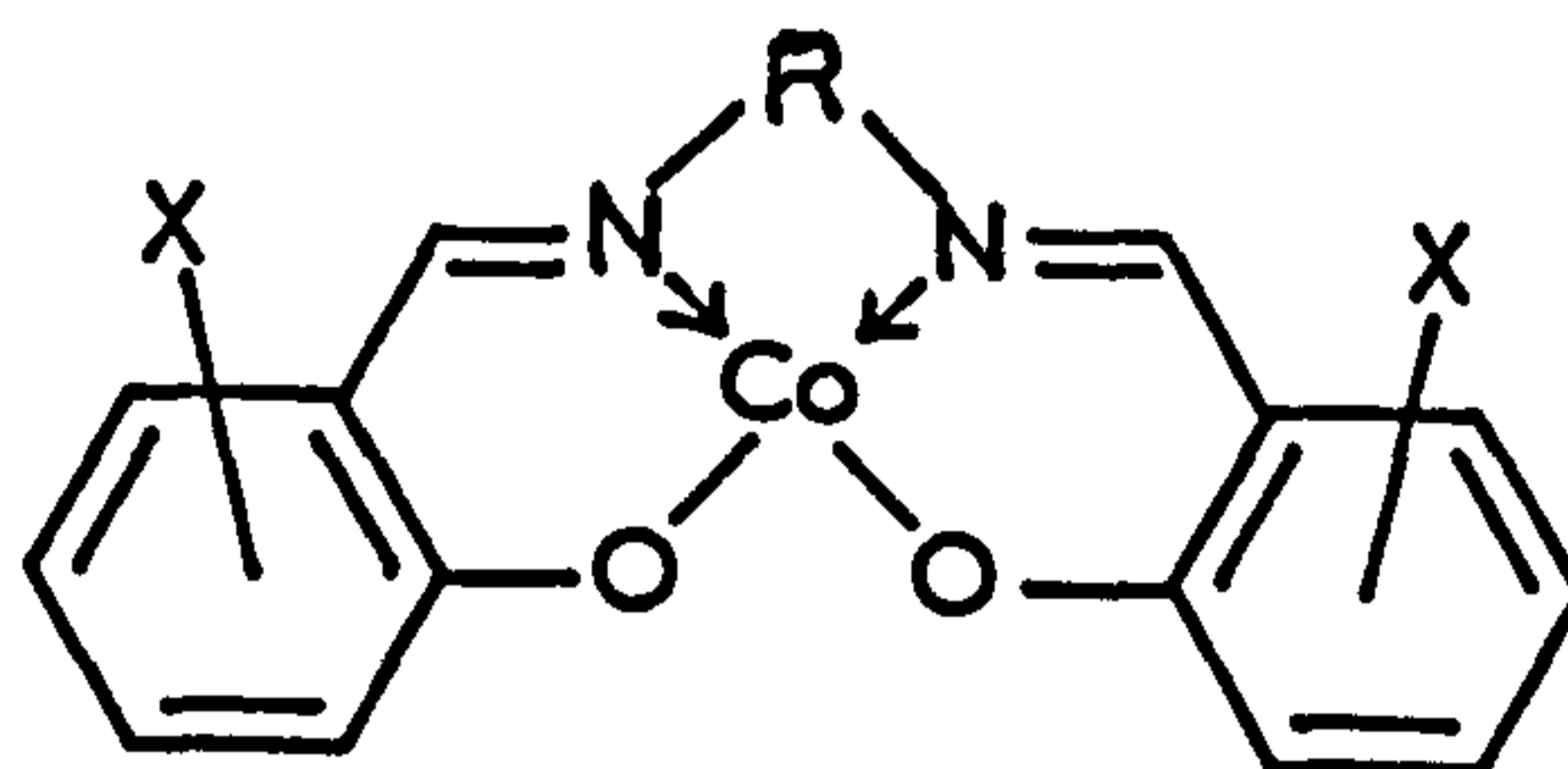
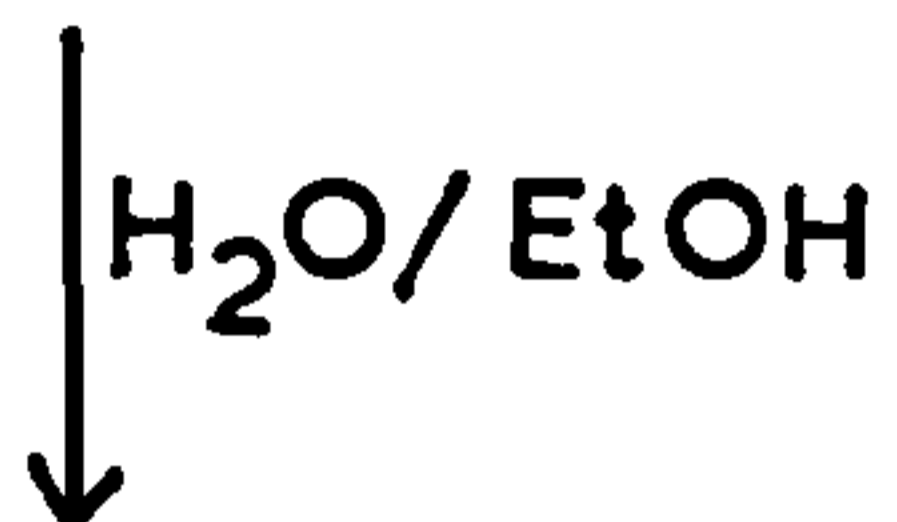
Some cobalt(II) analogues of the nickel(II) complexes described in chapter 4 were synthesized and their properties compared with the cobalt corrinoids.

#### 5.1.1. Nomenclature and abbreviations.

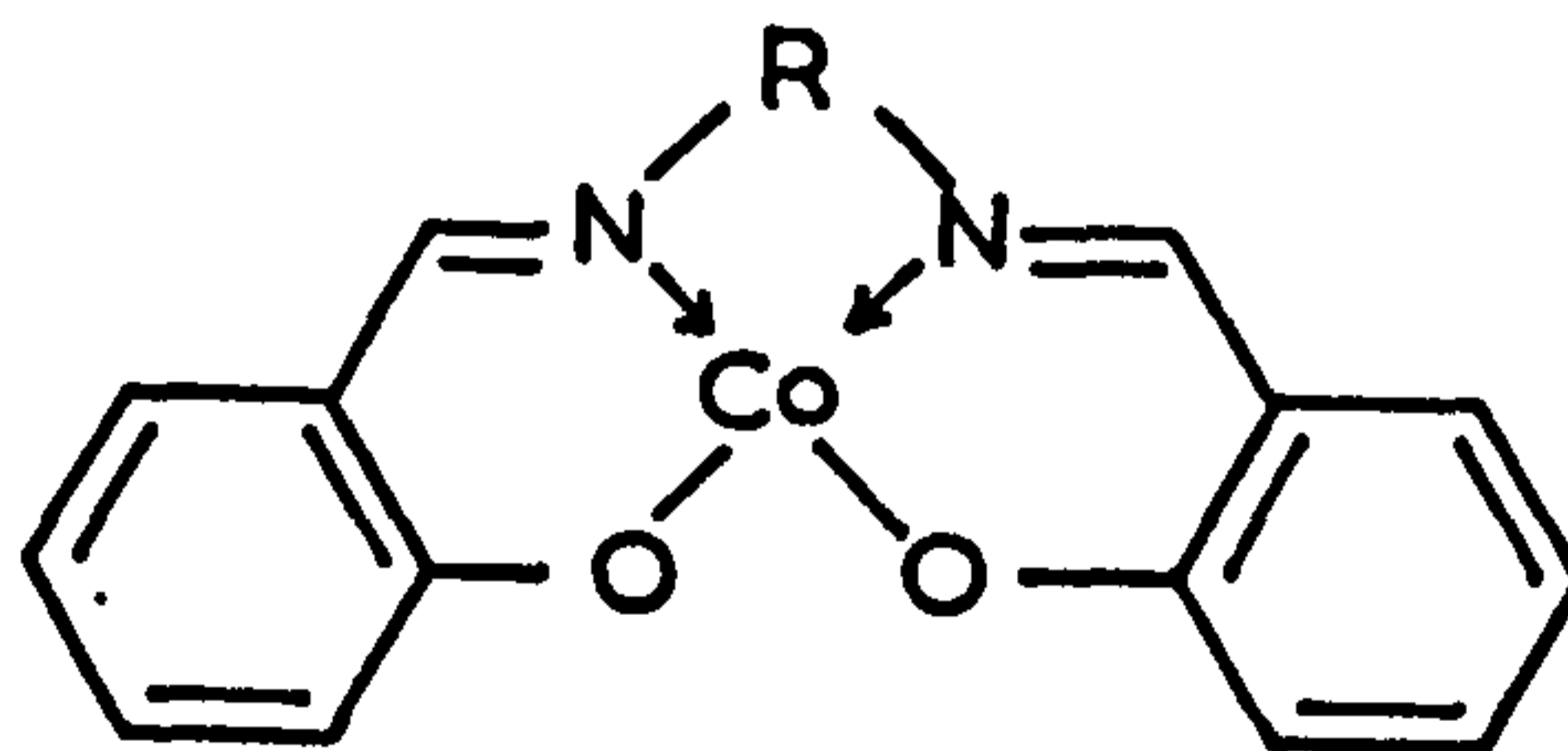
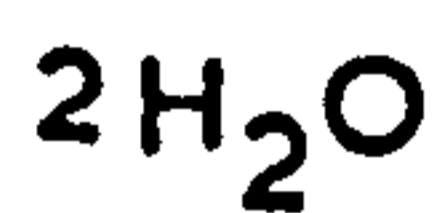
The same system of nomenclature and abbreviations will be used as was listed in full for the ligands (page 31) and nickel(II) complexes (page 70). Hence, for example, Coamben represents N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato-cobalt(II) [5.1]



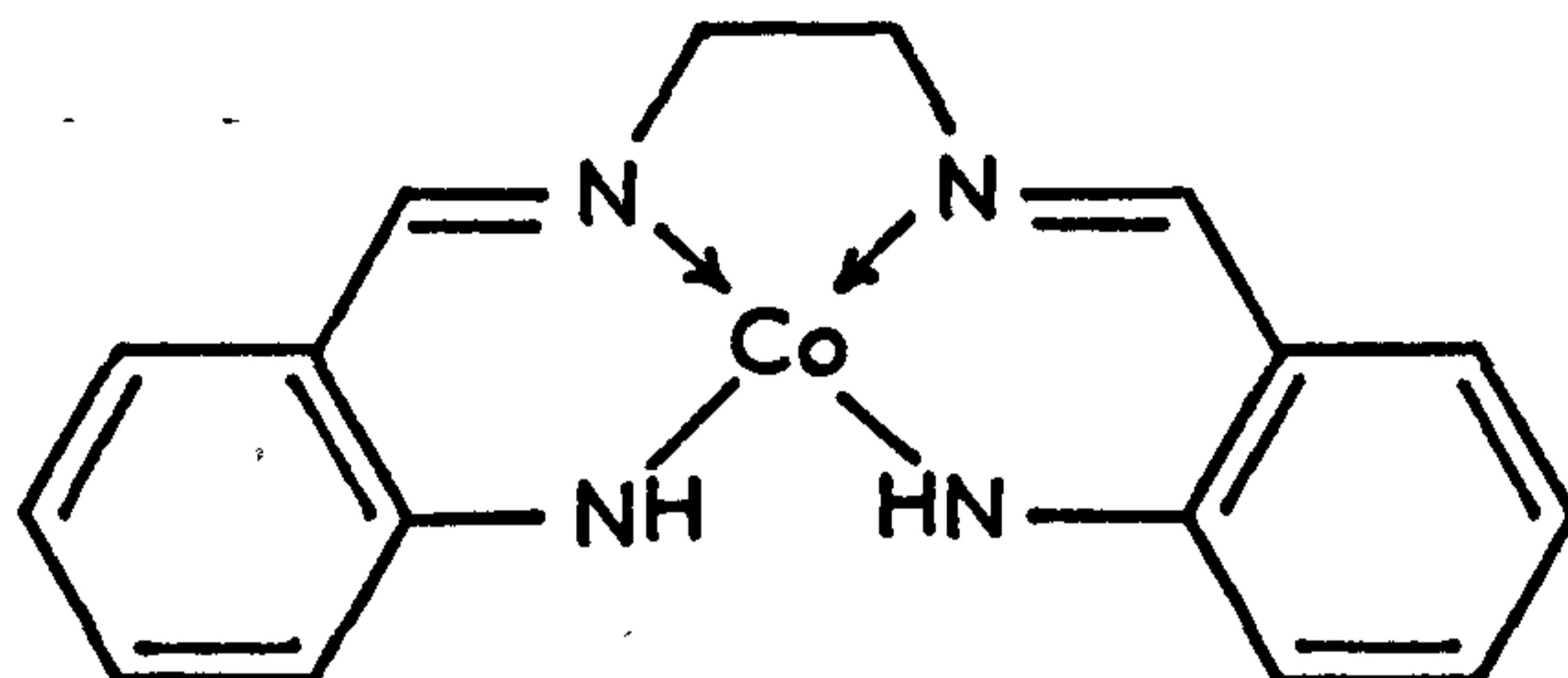
[ equation 5.1 ]



[ equation 5.2 ]







[5.1]

### 5.2 Preparations and analyses.

A large number of cobalt(II) chelates of quadridentate ligands derived from salicylaldehyde were made by Calvin and his co-workers<sup>1</sup> in their studies of oxygenation of Cosalen and its derivatives. Synthesis was usually achieved by addition of an aqueous solution of cobalt(II) acetate to a refluxing ethanolic suspension of the preformed ligand (equation [5.1]).

Some other chelates of quadridentate salicylaldehydines which could not be obtained by this method were prepared by B.O. West<sup>2</sup> from bis-(salicylaldehydato)-cobalt(II) and the appropriate diamine according to equation [5.2].

The methods used in this work for the preparation of cobalt(II) complexes of the dianionic forms of the ligands described in chapter 3 are listed below.

It was found that method(1), which is based on the Calvin<sup>1</sup> method (equation [5.1] ) was only useful for Coamben. Unfortunately, the method of B.O. West<sup>2</sup> (equation [5.2] ) could not be adapted to give complexes of ligands derived from o-aminobenzaldehyde, since the latter readily polymerizes, and hence bis-(o-aminobenzaldehyde)-cobalt(II) cannot be prepared.

(1) Addition of a methanolic solution of cobalt(II) acetate to the ligand in refluxing methanol.

(2) As (1) followed by the addition of a stoichiometric amount of sodium methoxide solution.

(3) Condensation of the appropriate diamine and o-aminoarylcarbonyl compound in a methanolic solution of cobalt(II) acetate.

(4) Reduction of the aromatic nitro precursor of the ligand in a methanolic solution of cobalt(II) acetate containing a little palladium charcoal catalyst.

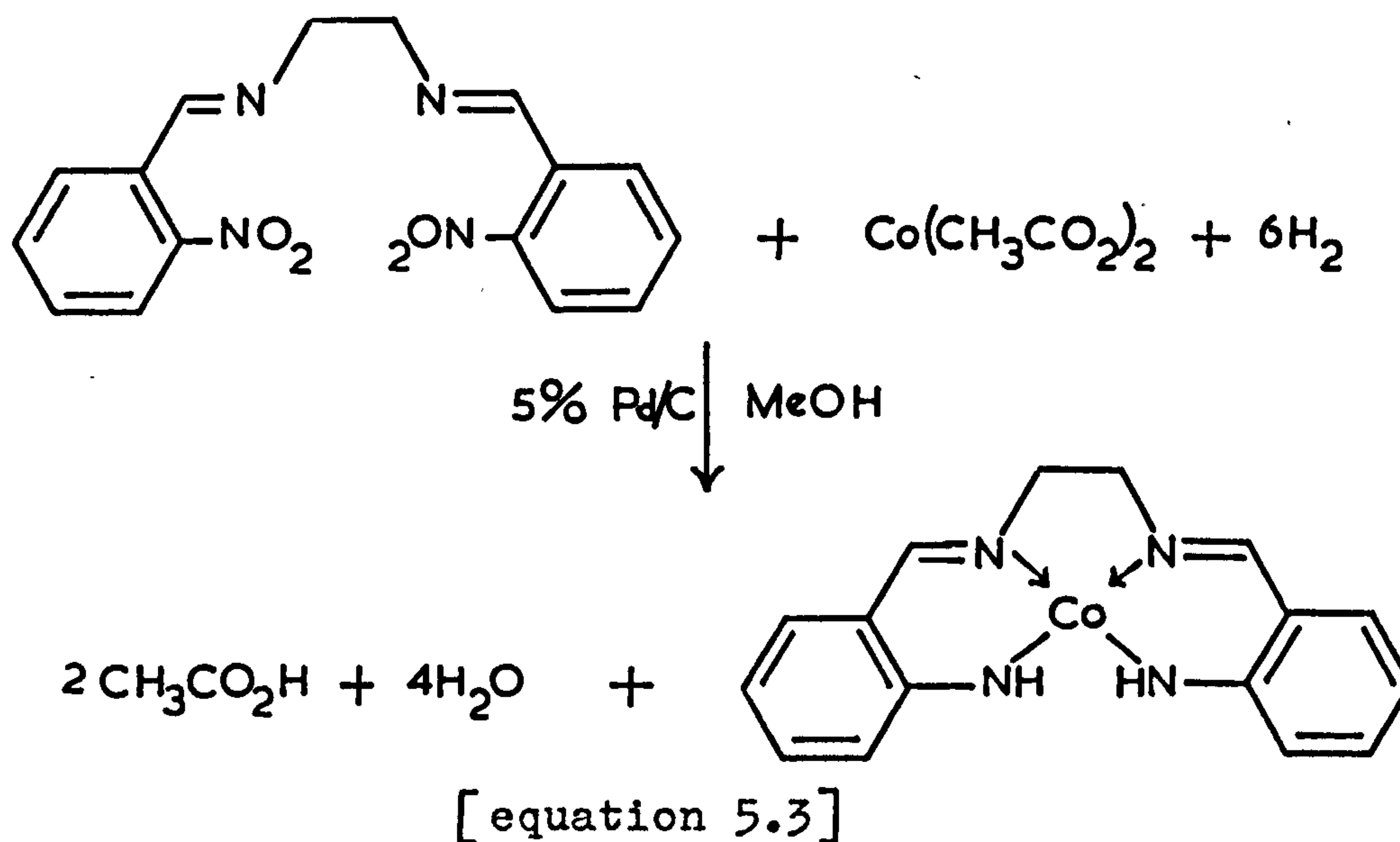
(5) Addition of solid tetraethylammonium tetrabromocobaltate(II) to a solution of the ligand and a stoichiometric amount of potassium t-butoxide in tetrahydrofuran.

The methods correspond closely to those used for the analogous nickel(II) complexes (page 70), and are described in detail in chapter 11.

It was found generally that the synthesis of

a cobalt(II) complex was more difficult to achieve than the analogous nickel(II) complex (chapter 4). All operations were performed under nitrogen as a precaution against oxidation to cobalt(III) complexes, or the formation of oxygen adducts. All the complexes required recrystallization from dimethylformamide before satisfactory analysis results were obtained.

Method (4) merits further mention. It provides a convenient route to the complexes, provided that a solvent is available to extract the product from palladium charcoal catalyst.



Complexation of the imine groups to cobalt appears to protect them from reduction (see also page 73).

The method would be more convenient if the palladium catalyst were unnecessary. Since certain cobalt

complexes have been used as catalysts for reduction and hydrogenations <sup>3,4,5,6</sup>. It was hoped that conditions could be found under which one of the cobalt species involved in method 4 might show catalytic properties for the reduction of nitro-groups. In view of the possible existence of a cobalt(I) species related to Coamben (see section 5.7) and the evidence for cobalt(I) compounds acting as reduction catalysts, <sup>5,6</sup>. the reaction (equation [5.3] ) was carried out in the presence of a little Coamben to see if it would be autocatalytic, with a reduced form of Coamben acting as the hydrogenation catalyst. No such evidence<sup>of</sup> hydrogenation was obtained.

The addition of catalytic quantities of cyanide ions was considered. Since the pentacyanocobaltate ion is known to be a hydrogenation catalyst<sup>7</sup> (the species  $\text{HCo}(\text{CN})_5^{3-}$  is thought<sup>7</sup> to be responsible) it may prove fruitful to attempt the reaction (equation [5.3] ) in the presence of cyanide ions. This was not tried in this work because of the possibility of cyanide catalysed hydrolysis of the imine groups, which has been shown<sup>8,9</sup> to occur readily in some imine complexes, which were otherwise extraordinarily resistant to hydrolysis, even in concentrated mineral acids.<sup>10</sup>

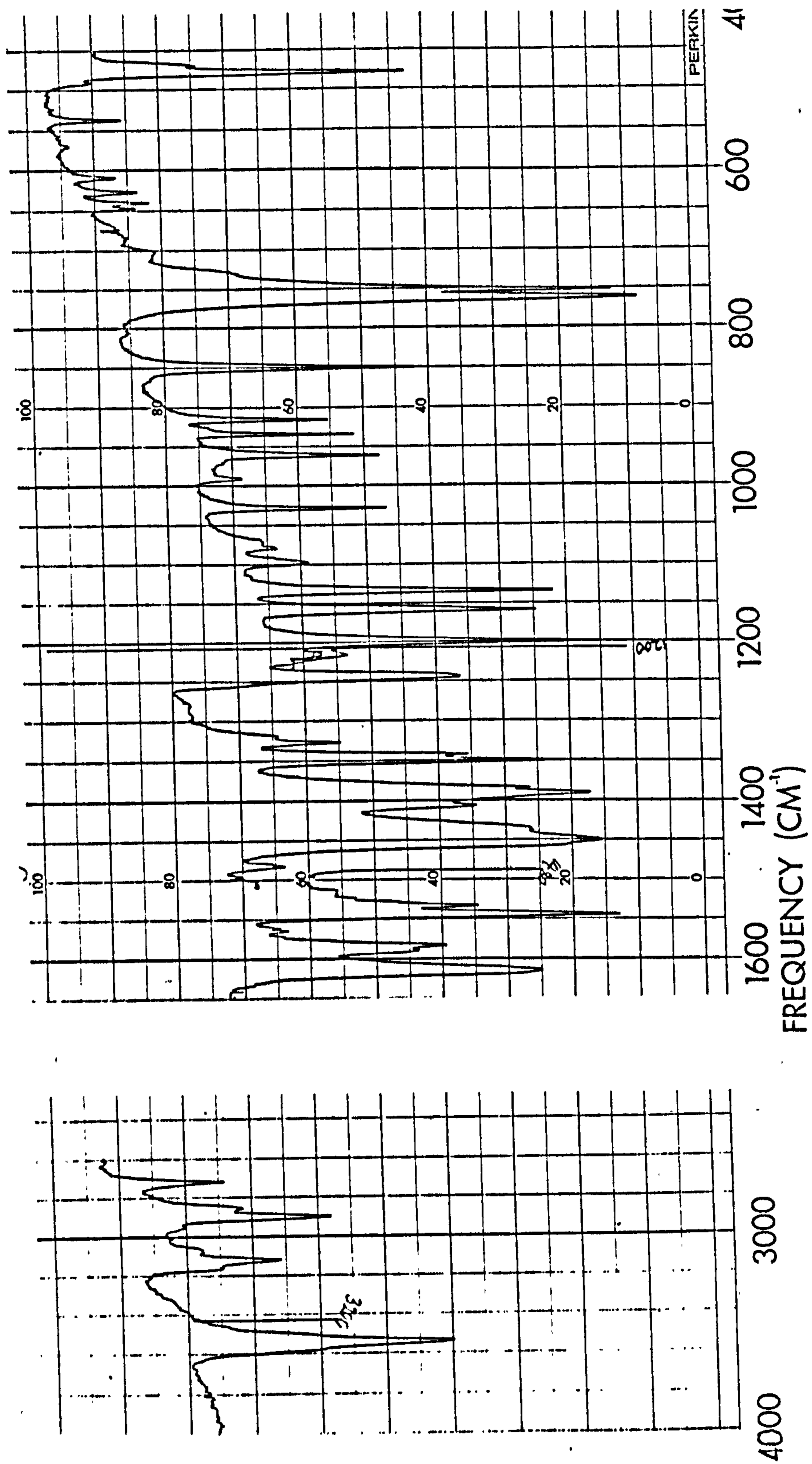
The preparation of Coambphen by method 3 was attempted several times. An impure product with an

infrared spectrum remarkably similar to Niambphen was isolated as an amorphous solid, which could not be induced to crystallize under conditions which were normally effective for recrystallization of the other cobalt(II) complexes (see chapter 11). Method 3 worked well for Coamben, but the product required careful purification.

Method 5 was attempted for complexes which could not be prepared by the other methods. It is based on the method used by Holm<sup>11</sup> for synthesis of cobalt(II) complexes of bidentate  $\beta$ -ketoimine ligands. Some success was achieved with CoMe-amben, but again purification proved difficult. Other workers<sup>1,2</sup> have reported poor analysis results in attempts to synthesize the analogous quadridentate salicylaldehyde imine complexes having long bridging groups (R) when the preformed ligands were used. The route analogous to that used successfully to synthesize these salicylaldehyde imine complexes with long bridging groups (see equation [5.2]) is not applicable for ligands derived from o-aminobenzaldehyde (page 108).

Only four complexes were prepared which were analytically pure. Analysis results for these compounds are shown in table [5.1].

The infrared spectrum of Coemben as nujol and hexachlorobutadiene mulls.



Complex	Molecular Formula	Composition %			
		C	H	N	
Coamben	$C_{16}H_{16}N_4Co$	Calc.	59.46	4.95	17.34
		Found	59.31	5.05	17.55
Coambtn	$C_{17}H_{18}N_4Co$	Calc.	60.05	5.33	16.60
		Found	59.76	5.32	16.31
Coamaen	$C_{18}H_{20}N_4Co$	Calc.	61.54	5.73	15.94
		Found	61.43	5.69	15.78
Coampen	$C_{28}H_{24}N_4Co$	Calc.	70.73	5.08	11.78
		Found	70.82	5.43	11.91

Table [5.1] Analysis result for cobalt(II) complexes of the 'acyclic' ligands.

### 5.3 Infrared spectra.

Initial identification of each complex was based on its infrared spectrum. The spectra are tabulated in full on page 301. The spectrum of Coamben is shown on page F112 as a typical example.

Most features of the spectra are very similar to the analogous nickel(II) complexes which have been discussed in section 4.4.2, e.g. the ligand's hydrogen-bonded NH stretching vibration disappears, and the imine stretching vibration moves to lower energy on complexation. The appearance and positions of the absorption bands are remarkably similar to those of the analogous nickel(II) complexes, and this greatly simplified

the characterization of some of the cobalt(II) complexes which were difficult to isolate in a pure state.

By comparison with the spectrum of Cosalen and Niamben for which some assignments have been made (references 12 and 13 and page F78) it is possible to identify many of the vibrations in Coamben (see table [5.2] )

Niamben	Cosalen	Coamben	Assignments
a	b	c	
3313 (m) 3293(m)	-	3253	NH (free stretch)
3060 (w) 3047 (w) 3032 (w) 3018 (w)	3062 (w) 3042(w) 3020 (sh)	3062 (sh) 3043 (m) 3023 (w)	CH(aromatic stretch)
2948 (m) 2915 (w) 2855 (w)	- d - d - d	2934 (m) 2912 (w) 2845 (w)	CH (aliphatic) stretch
1617 (s)	1625 (s)	1607 (s)	Imine stretch
1593 (m) 1537 (s)	1607 (s) 1533 (s)	1582 (s) 1537 (s)	C=C(aromatic) stretch
1478 (w) 1459 (s) 1452 (sh)	1471 (m) 1446 (s)	1473 (m) 1448 (sh) 1448 (s)	CH <sub>2</sub> (aliphatic) bend

Table [5.2] Infrared spectra of Niamben, Cosalen & Coamben

(  $\lambda_{\max}$ ,  $\text{cm}^{-1}$  )



- (a) As nujol and hexachlorobutadiene mulls (see page F78).
- (b) As nujol mull (3000 - 1700  $\text{cm}^{-1}$ ) The region  $< 1700 \text{ cm}^{-1}$  from reference 12 (as KBr disc)
- (c) As nujol and hexachlorobutadiene mulls.
- (d) Obscured by nujol absorptions.

Cosalen in some crystalline modifications absorbs oxygen in the solid state (see section 5.6) and Ueno and Martell<sup>12</sup> have suggested that a band occurring at  $565 \text{ cm}^{-1}$  in the infrared spectrum of oxygenated Cosalen is due to the stretching vibration of the cobalt oxygen bond. Samples of Coamben which had been allowed to stand in air for several weeks showed no new bands in this region of their infrared spectra.

Some of the cobalt(II) complexes show two closely spaced peaks in the NH stretch region (c.f. the nickel(II) complexes, section 4.4.2). The origin of this effect remains uncertain, as there seems to be no systematic variation with structural differences in the complexes, e.g. there are two peaks for Niamben and Coampen, but a single sharp peak for Coamben and Niampen. Possibly the effect is due to different "stacking arrangements" for the molecular units in the solid state (see also page 76).

#### 5.4 Magnetic measurements.

For cobalt(II) chelates of the ligands described

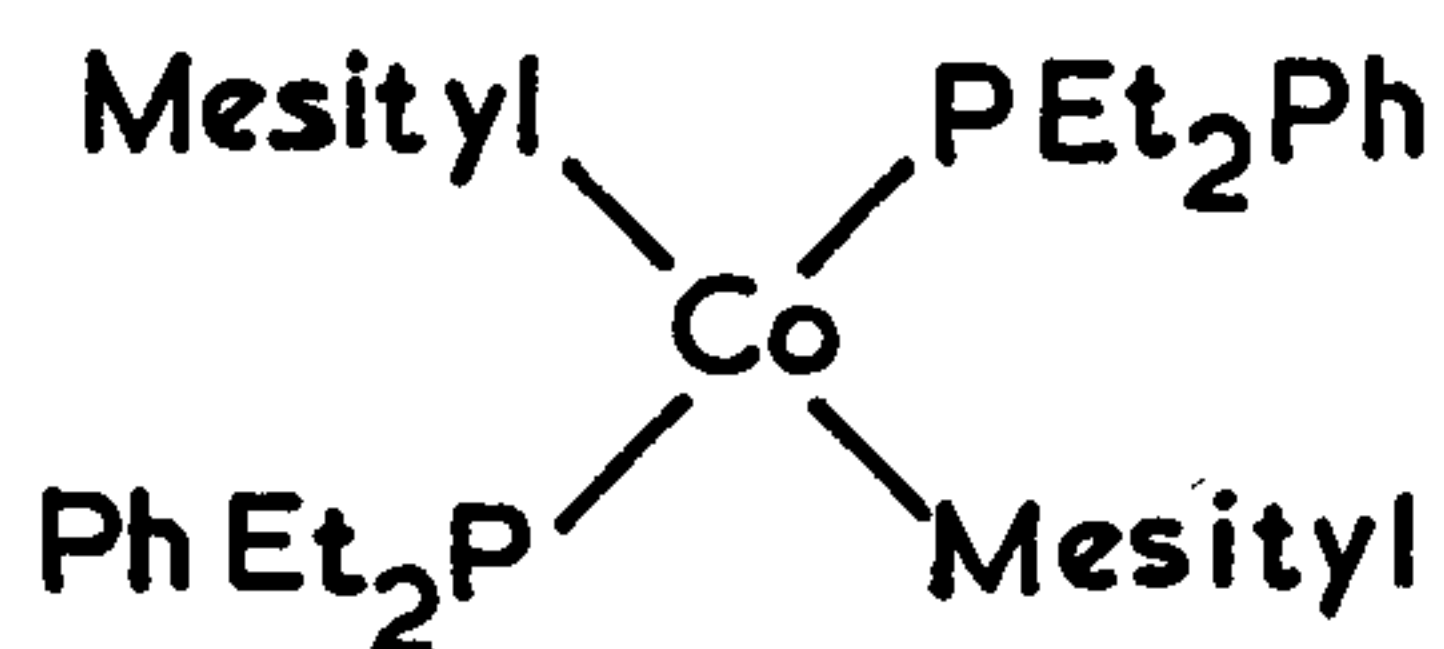
in chapter 3 several types of coordination geometry may be envisaged. Some of these possibilities will be considered briefly below, in order to indicate the types of magnetic behaviour which might be expected.

#### 5.4.1(a) Square-planar complexes.

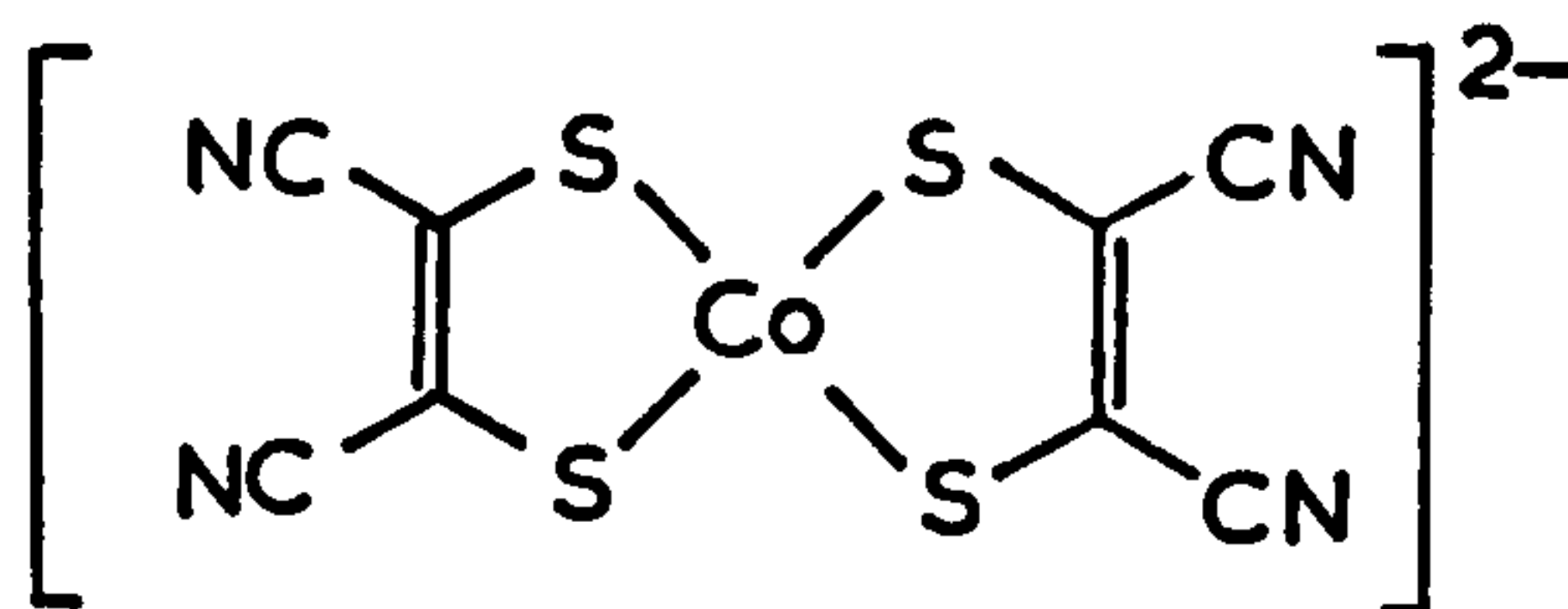
Many cobalt(II) complexes of Schiff bases derived from  $\beta$ -diketones and salicylaldehyde have been claimed to be square-planar (reviewed in references 14 and 15), but there have been no complete X-ray investigations to confirm these structural assignments. In particular, it is difficult to eliminate the possibility of extension of the coordination number of the cobalt atom beyond four by coordination to atoms, in neighbouring chelate molecules. A 'polymeric' structure of this type has been established for Cusalen<sup>16</sup> and it is not impossible for some forms of Cosalen.<sup>17</sup> Cobalt(II) phthalocyanine also suggests a stacking of planar units with cobalt atoms aligned with donor atoms in adjacent units.<sup>18</sup> However, the distance is probably too large for significant bonding interaction, and this compound has been quoted as a typical example of cobalt(II) square-planar complexes.<sup>19</sup>

Square planarity has been established<sup>20,21</sup> for cobaltous complexes of some other types of ligand, e.g.

[5.2]<sup>20,22</sup> and [5.3]<sup>21,23</sup>, which have magnetic moments of 2.5 B.M.<sup>22</sup> and 2.16 B.M.<sup>23</sup> respectively, falling within the range quoted<sup>24</sup> as 'normal' for cobalt(II) square-planar complexes.



[5.2]

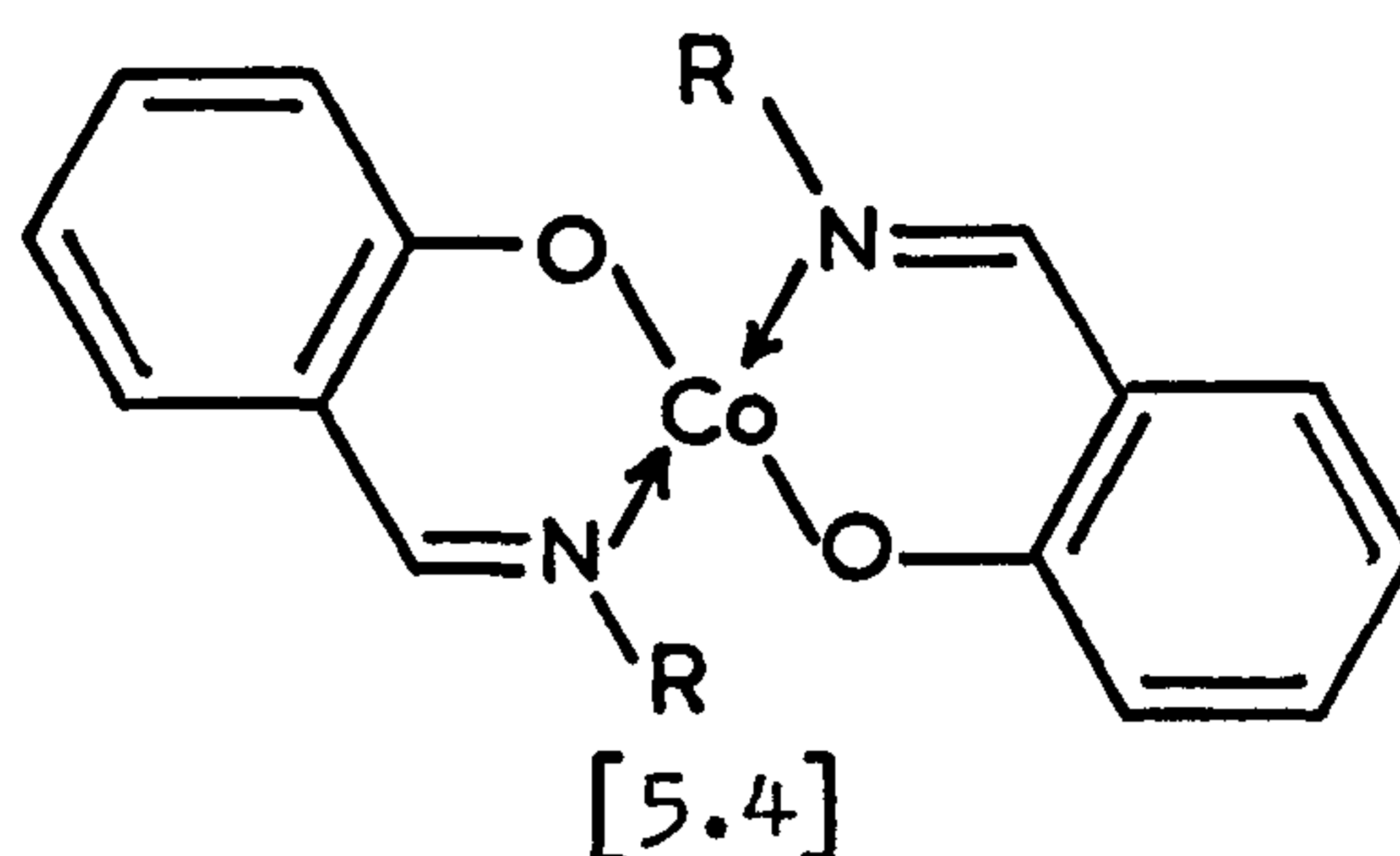


[5.3]

Planar quadricoordinate cobaltous complexes could be either spin-free or spin-paired,<sup>25</sup> but there is little evidence<sup>25,26</sup> for the spin-free state, and most show magnetic moments in the range 2.1 - 2.9 B.M. It is difficult<sup>25</sup> to account for the large increase in the magnetic moments over the spin only values of 1.73 B.M.

#### 5.4.1(b) Tetrahedral complexes.

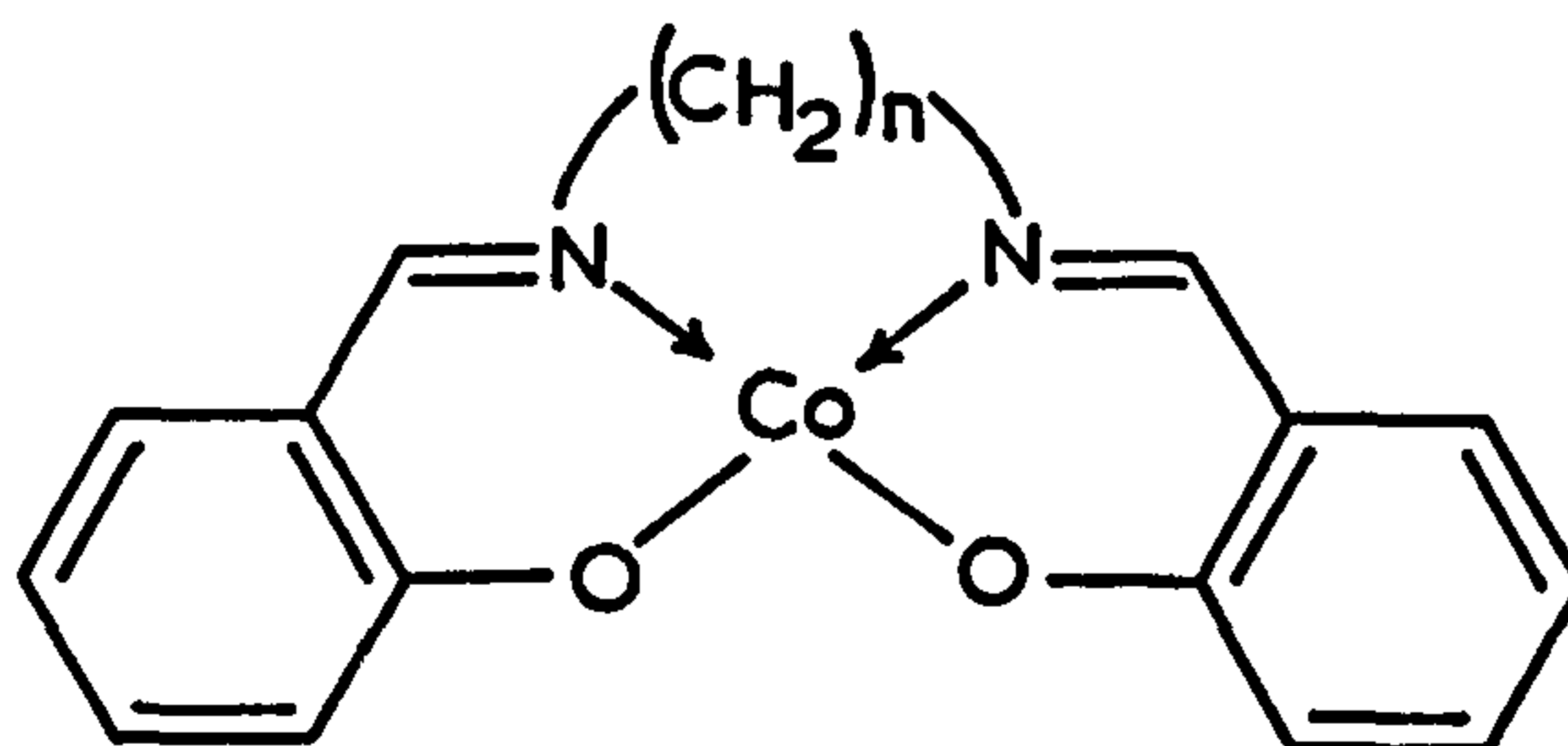
Most of the cobalt(II) complexes of the bidentate ligands derived from salicylaldehyde (see [5.4] for general formulation) fall into this class.<sup>27</sup> These have magnetic moments between 4.3 and 4.5 B.M.<sup>27</sup> which is within the range quoted<sup>15,19</sup> as 'normal' for cobaltous tetrahedral complexes.



There are a few examples of complexes [5.4] which are presumed<sup>27</sup> to have planar structures.

Certain effects are thought to favour square-planarity in these few examples<sup>27</sup>, namely:

- (i) Higher ligand fields produced by the ligands.
- (ii) Smaller substituents (R)
- (iii) Hydrogen-bonding between the two chelating ligands when R = H or OH.



[5.5]

Some complexes [5.5] related to Cosalen, but with longer polymethylene bridging groups are thought to be tetrahedral<sup>2</sup>. The moments<sup>2</sup> for the compounds ( [5.5] , n= 6 - 10) are 4.63 - 4.68 B.M. On this evidence it has been suggested<sup>2</sup> that the spin-pairing in Cosalen arises because a planar configuration is forced upon the complex due to the steric requirement of the ligand, and in the absence of such steric factors the preferred configuration will be as close to tetrahedral as the ligand will permit. Recently it has been suggested that Cosaltn ( [5.5], n = 3) also has a tetrahedral structure, but no value for the moment is quoted.<sup>28</sup>

#### 5.4.1(c) Octahedral complexes.

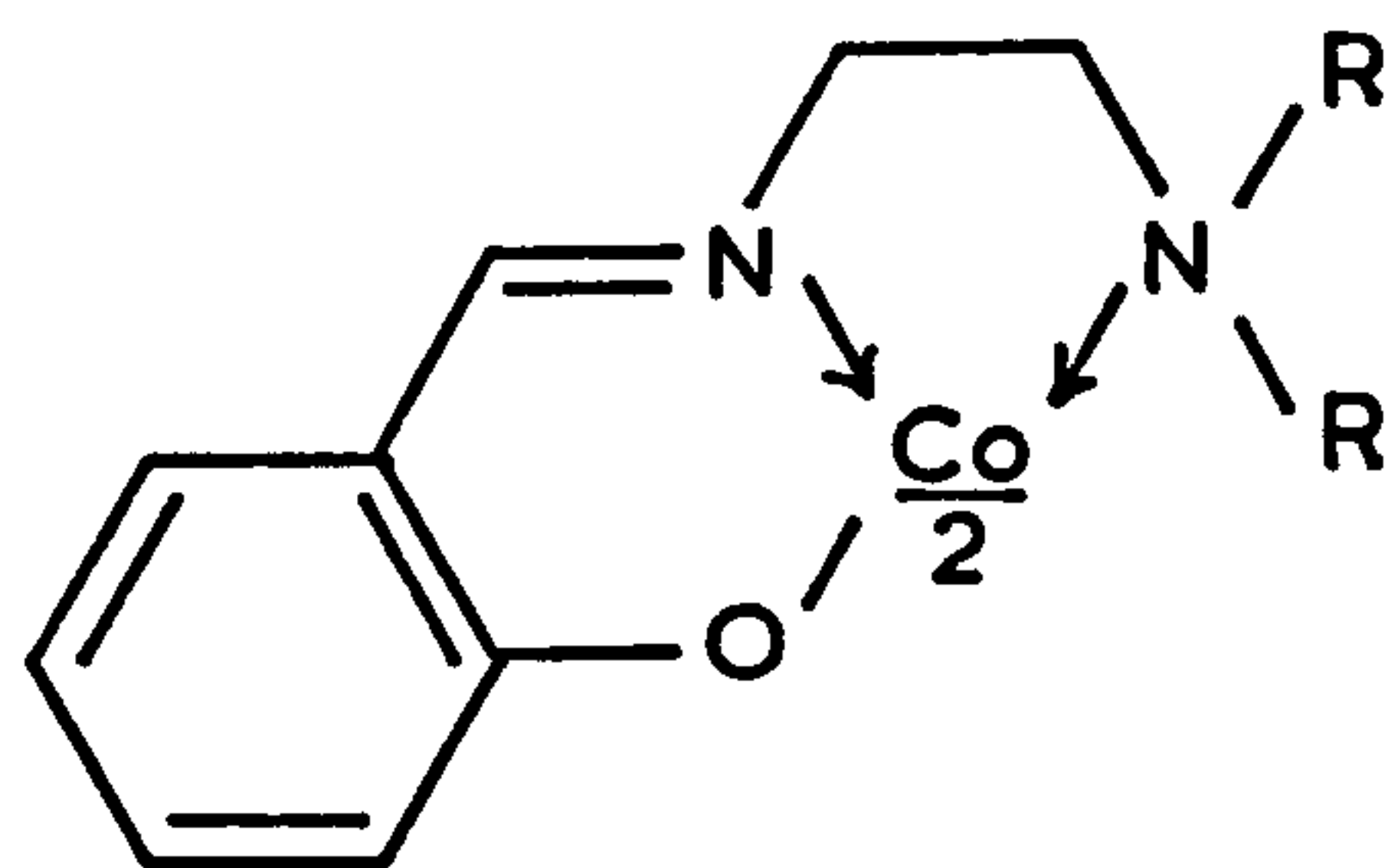
For Schiff base chelates of cobalt(II) octahedral coordination has been observed under the following circumstances.

##### (i) Solvation of quadricoordinate complexes.

When solutions of some of the complexes type [5.4] are treated with pyridine, sexacoordinate complexes are obtained<sup>27</sup> with magnetic moments in the range 4.8 - 5.2 B.M. For bulky substituents (R) solvation does not occur, but for slightly smaller substituents an equilibrium situation with the tetrahedral form being partially converted to pentacoordinate or sexacoordinate species has been suggested.<sup>27</sup>

(ii) Bis(tridentate Schiff base) complexes.

Cobalt(II) complexes of some ligands formed from salicylaldehyde and N-substituted ethylenediamines (see [5.6] ) have been shown<sup>29</sup> to have distorted octahedral structures and magnetic moments ranging between 4.1 and 4.7 B.M.



[5.6]

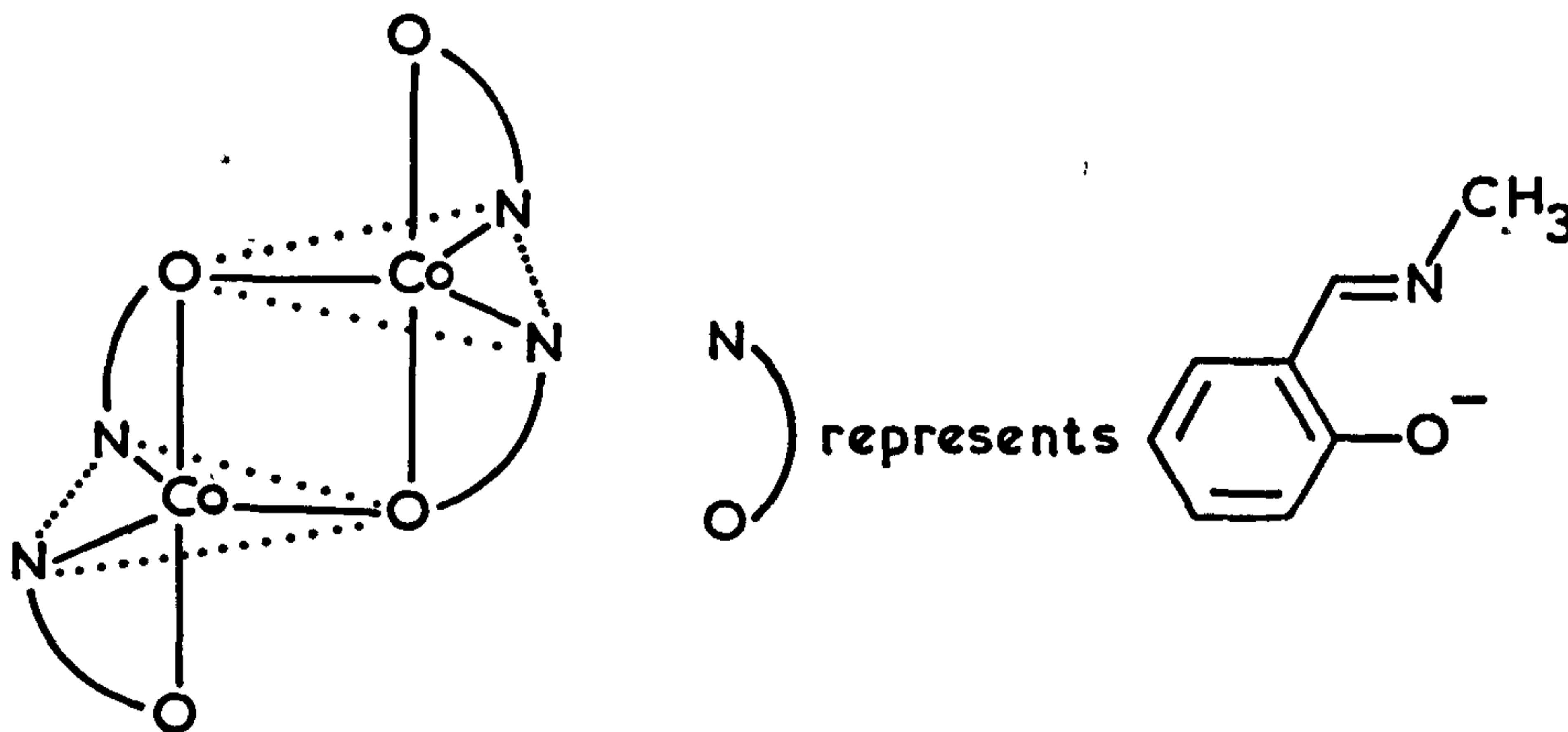
Both these types of sexacoordinate cobaltous complexes of Schiff base ligands show moments which fall within the range suggested<sup>15,19</sup> as typical for high spin distorted octahedral cobalt(II).

The possibility of low spin sexacoordinate cobalt(II) has rarely been considered for Schiff base complexes.<sup>30</sup> The magnetic behaviour of certain derivatives of Cosalen at low temperatures has been explained<sup>30</sup> on the basis of a low spin octahedral configuration for the cobalt atom. Such complexes should<sup>19</sup> show moments slightly above the spin-only value of 1.73 B.M.

#### 5.4.1(d) Pentacoordinate complexes.

Pentacoordinate cobalt(II) complexes of Schiff bases have been described which owe their existence to special effects similar to the types which have been described above.

Certain chelates whose stoichiometry would suggest a coordination number of four have structures in which this number is extended to five by coordination to atoms in neighbouring chelate units.<sup>29</sup> Bis(N-methylsalicylaldiminato)cobalt(II) exists as a dimer in the solid state with a structure<sup>31</sup> as in [5.7]. The magnetic moment<sup>29</sup> is 4.62 B.M.



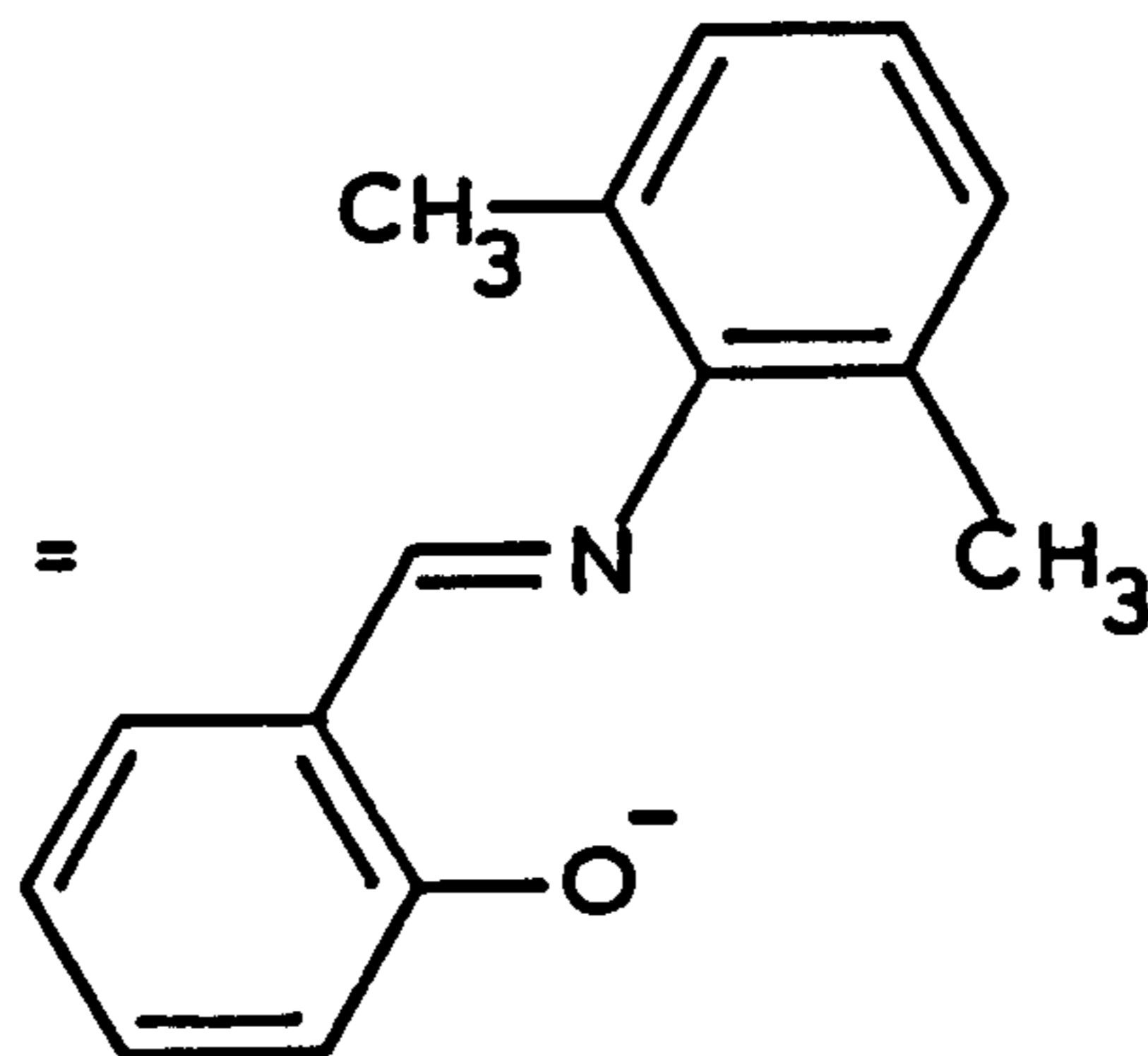
Pyridine solvates of some bis(N-substituted-salicylaldiminato)cobalt(II) complexes are thought to be pentacoordinate<sup>27</sup> but definitive structural data are

not available. A moment of "about 4.5 B.M." is quoted<sup>27</sup> for the presumed pentacoordinate complex [5.8].

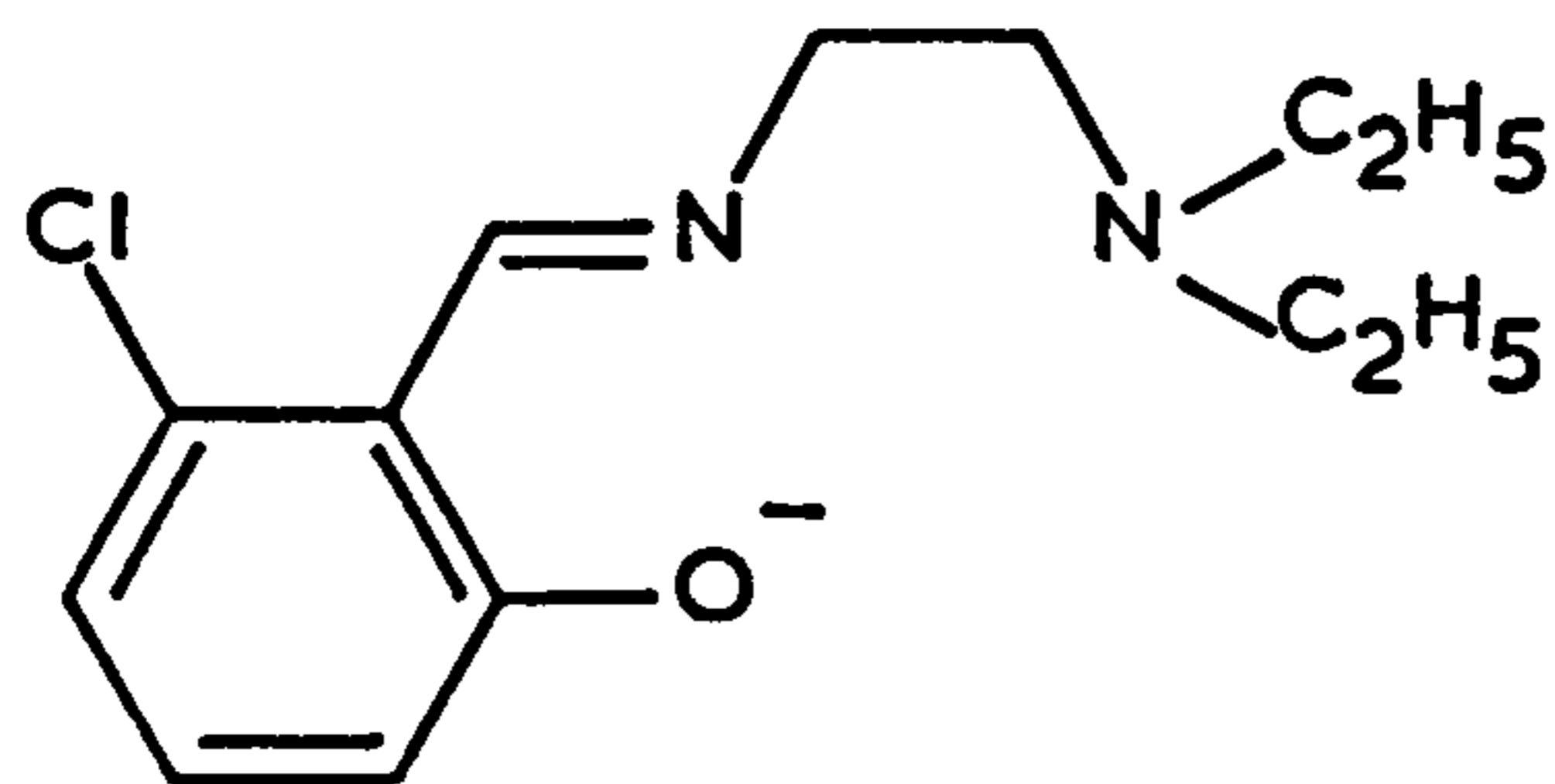
$\text{Co}(\text{sal-R})_2\text{py}$

[5.8]

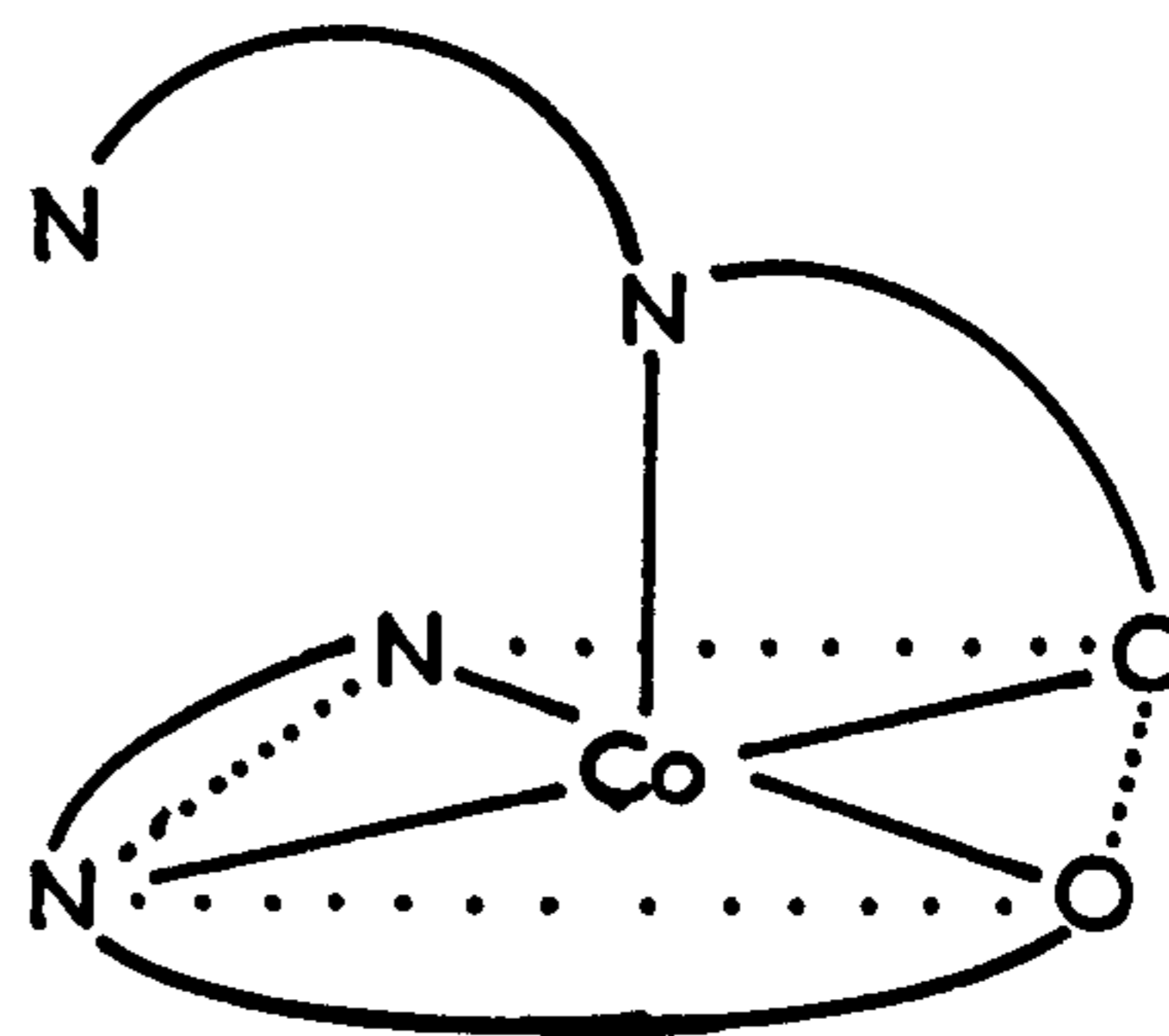
where sal-R =



For some bis(N-substituted salicylaldiminato) cobalt(II) complexes a pentacoordinate structure can be achieved by coordination of a donor atom located in the substituent,<sup>29</sup> e.g. the cobalt(II) complex of the ligand [5.9] has an distorted square-pyramidal structure [5.10] in which one molecule of [5.9] is bidentate and another tridentate.<sup>32</sup>



[5.9]



[5.10]



Complex	Temp. (°K)	$\chi_g$ $\times 10^6$	$\chi_m$ $\times 10^6$	$\chi_L$ $\times 10^6$	$\chi_m'$ $\times 10^6$	$\mu$ <sup>a</sup> (B.M)
Coamben	292-295	5.930	1957	-146	2103	2.22±0.04
Coambtn	290-294	5.305	1789	-157	1948	2.15±0.06
Coamaen	291-294	6.166	2160	-168	2328	2.35±0.07
Coampen	292-295	3.363	1599	-243	1842	2.10±0.06

Table [5.3] Magnetic susceptibilities (cgs units) of the solid complexes at room temperature.

(a) mean for values calculated for different temperatures (see page 230), other quantities ( $\chi_g$  etc. - symbols listed in chapter 10) are actual figures for a determination at an intermediate temperature.

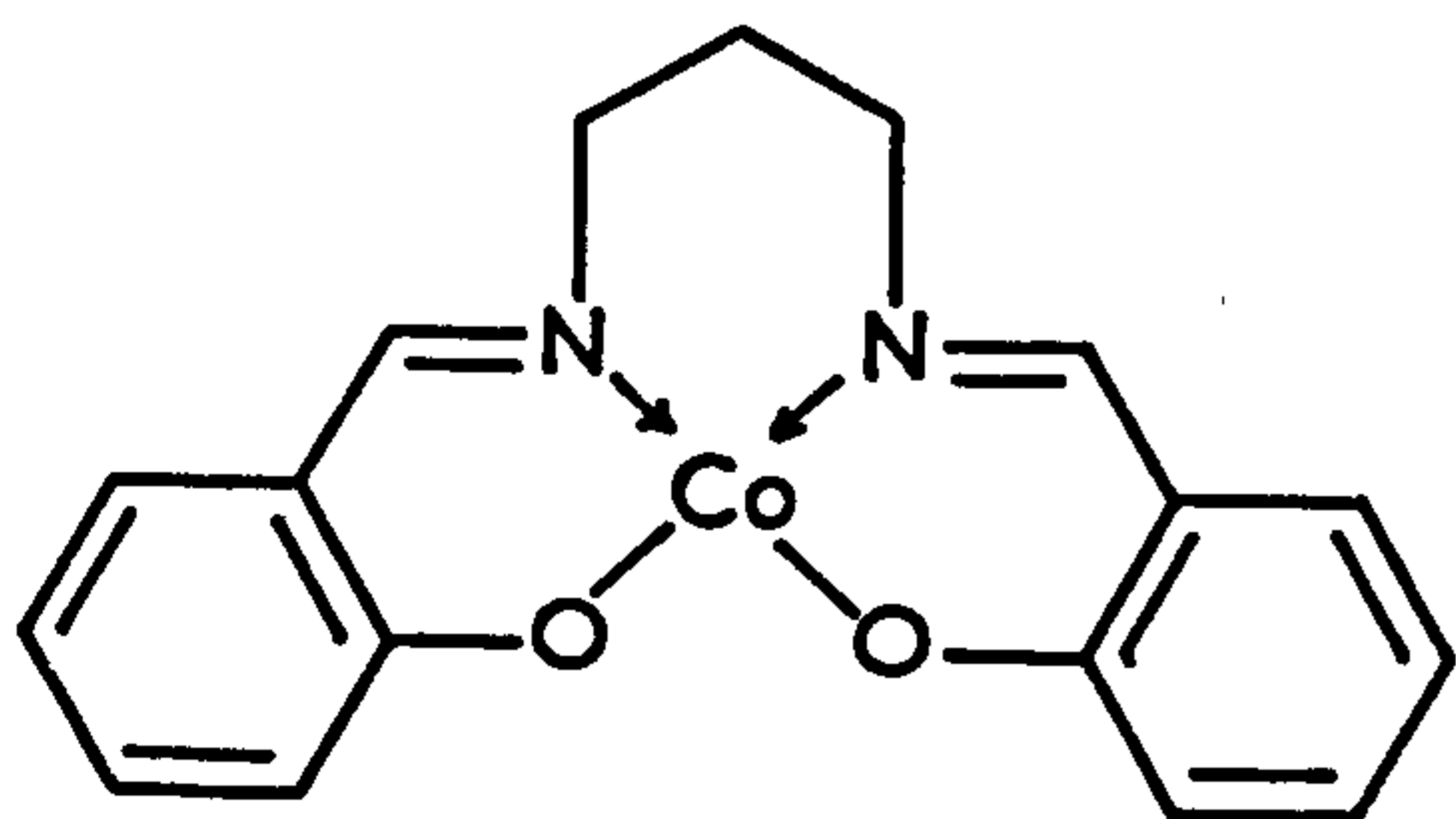
The magnetic moments<sup>33</sup> for compounds of the type [5.10] range between 4.10 and 4.70 B.M., and in general five coordinate cobalt(II) complexes of anionic Schiff base ligands have high-spin configurations with moments falling in this range.

#### 5.4.2 Magnetic moments of the solid complexes.

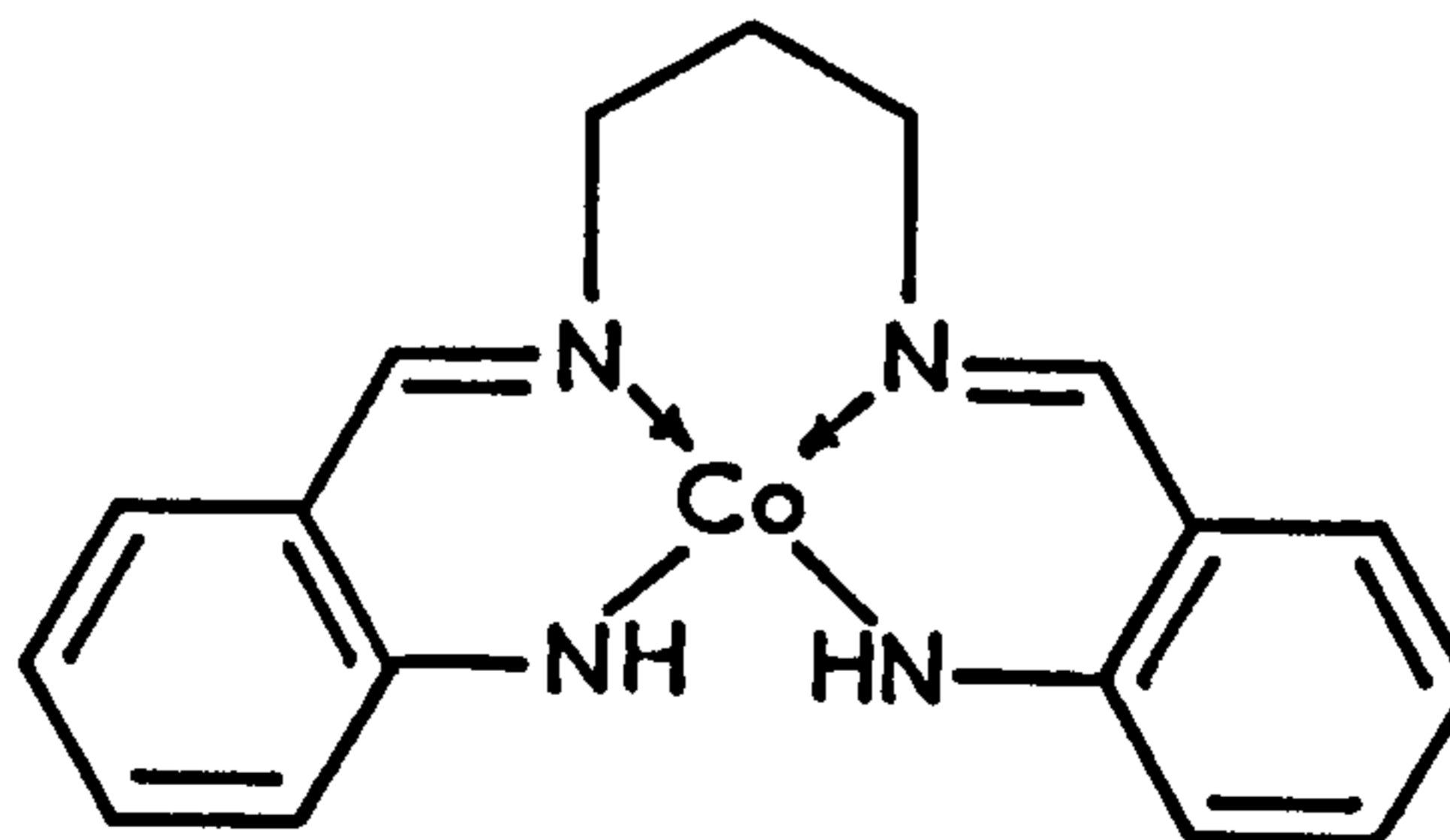
The results for the cobalt complexes of table [5.1] are shown in table [5.3] on page F 122.

All the compounds show a low-spin configuration for the cobalt(II) atom, with moments falling in the range regarded as 'typical' for quadricoordinate planar cobalt(II) complexes (see page 116).

Unfortunately the cobalt complexes of ligands with longer bridging groups which might adopt tetrahedral configurations (see page 118) were not available using the synthetic techniques described on page 108.



[5.11]

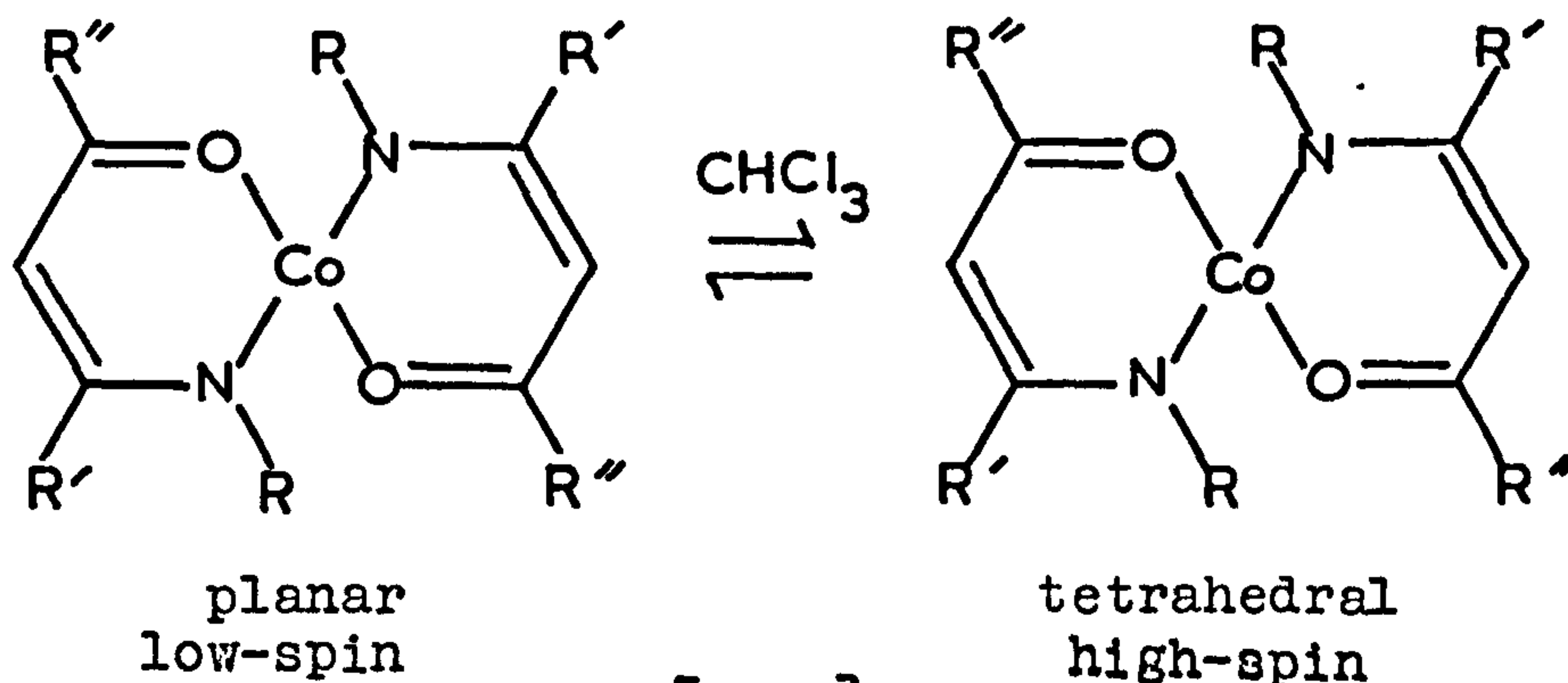


[5.12]

Cosaltn [5.11] has been claimed to have a tetrahedral structure<sup>28</sup>, but the comparable 'N<sub>4</sub>' complex Coambtn [5.12] synthesized in this work appears to be square-planar.

The simplest explanation of this observation is based upon the relative strengths of the ligand fields produced by 'N<sub>2</sub>O<sub>2</sub>' and analogous 'N<sub>4</sub>' ligands. The stronger field produced by the 'N<sub>4</sub>' ligand ambtn will favour the low-spin square-planar configuration, while saltn gives a high-spin system, which will be most stable with a tetrahedral geometry.

A planar-tetrahedral equilibrium has been observed<sup>11</sup> for chloroform solutions of certain quadricoordinate cobalt(II) complexes represented in [5.13]. The equilibrium favours the square-planar form for complexes [5.13] in which the substituent R is small. For these cases the tetrahedral form has been shown to be favoured by increase in temperature.



[5.13]

### 5.5 Electronic Spectra.

There seems to be considerable disagreement over the spectra characteristic of square-planar quadricoordinate Schiff base complexes of cobalt(II). Nishikawa and Yamada reported<sup>34</sup> the visible and near infrared spectrum of Cosalen and some closely related compounds, measured in chloroform solution, and claimed that an absorption band at  $1205\text{ m}\mu$  with an extinction coefficient of about 20 was indicative of a square-planar configuration. However Katagari and Endo have shown<sup>35</sup> that such complexes form monochloroform adducts which can be isolated as stable crystalline compounds, presumably containing five-coordinate cobalt(II), and hence the band at  $1205\text{ m}\mu$  may be more representative of

spin-paired cobalt(II) in a ligand field of possibly square-pyramidal symmetry. Solid Cosalen shows no band at  $1205\text{ m}\mu$ , but a pronounced absorption maximum at  $877\text{ m}\mu$ , but here again the possibility of a coordination number greater than four cannot be ignored<sup>17</sup> (see page 115).

Due to the unavailability of diffuse reflectance spectra equipment the transmission spectra of the solid complexes of table [5.1] were recorded as nujol mulls supported on filter paper, and as potassium bromide mulls pressed into thin transparent discs. The absorption maxima are shown in table [5.4].

Complex	Phase <sup>a</sup>	$\lambda_{\text{max}}$	$(\text{m}\mu)$		
Coamben	Nujol	(b)	430	530	935
	KBr <sup>c</sup>	380	430	535	958
Coambtn	Nujol	(b)	440	535	1030
	KBr	380	440	540	1025
Coamaen	Nujol	(b)	440	543	935
	KBr	376	440	542	955
Coampen	Nujol	(b)	440	555	925 (sh)
	KBr	373	435	545	920 (sh)

Table [5.4]. Absorption maxima of the solid complexes

- (a) as mulls, see text (b) Spectrum scanned 400 - 1200  $\text{m}\mu$   
(c) Spectrum scanned 350 - 1200  $\text{m}\mu$ .

Complex	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )	$\lambda_{\max}$ ( $\epsilon$ )
Coamben	375 (14450)	431 (20200)	530 (4450)	917 (57)
Coambtn	375 (9680)	435 (9900)	540 (3080)	960 (sh) (83)
Coamaen	376 (11800)	433 (14100)	542 (4100)	924 (90)
Coampen	375 (15100)	438 (18000)	543 (6100)	918 (114)

Table [5.5] Absorption maxima ( $m\mu$ ) of dimethylformamide solutions of the complexes.

(a) Scanned 350 - 1200  $m\mu$ .

Bands in very similar positions were recorded for dimethylformamide solutions of the complexes (see table [5.5]), suggesting that the configuration of the cobalt(II) atoms is the same in both the solid state and in solution. Pyridine was added to the dimethylformamide solutions of Coamben and Coampen, and was found to cause no noticeable change in their spectra. Under these conditions the spectra of ' $N_2O_2$ ' complexes<sup>27</sup> which solvate (see page 118) show considerable changes in the near-infrared region.

It seems likely that the complexes have approximately square-planar structures, both in the solid

state and in solution, since no change in axial perturbation was recorded for conditions in which the potential for addition of ligands in the axial positions was varied considerably.

It is possible that the band occurring at around  $1000 \text{ m}\mu$  is due to a d-d transition involving energy levels whose separation is dependent on the ligand field. To support this it may be pointed out that the band occurs at slightly lower energy in Coambtn (with a three-membered bridging group (R)) than in Coamben, Coamaen and Coampen (with two-membered bridging groups (R)). A decrease in ligand field splitting with length of chelating linkage has been observed in other systems (see page 27).

Since the splitting produced by an ' $\text{N}_2\text{O}_2$ ' system is expected to be less than the splitting of an ' $\text{N}_4$ ' system we might expect analogous ' $\text{N}_2\text{O}_2$ ' complexes to show the same band at lower energies. This is the case if the band at  $1205 \text{ m}\mu$  quoted by Nishikawa and Yamada as characteristic of ' $\text{N}_2\text{O}_2$ ' planar cobalt(II) complexes is due to the same transition.

### 5.6 Oxygenation and oxidation.

Many of the cobalt(II) complexes of Schiff base ligands derived from salicylaldehyde absorb oxygen

reversibly. These compounds are reviewed in reference 36.

The ability to absorb oxygen is very dependent on the crystalline forms of the complexes, and on the nature of substituents in the salicylaldehyde aromatic ring.

None of the solid complexes in table [5.1] showed any darkening colour or decrease in paramagnetic susceptibility on standing in air for several weeks. Changes in colour and magnetic susceptibility are characteristic of oxygenation of the solid 'Cosalen-type' of compounds.

In order to eliminate the complications of crystal-packing effects the oxygenation of 'Cosalen-type' compounds, some studies have been made in solution.<sup>1,37,38.</sup>

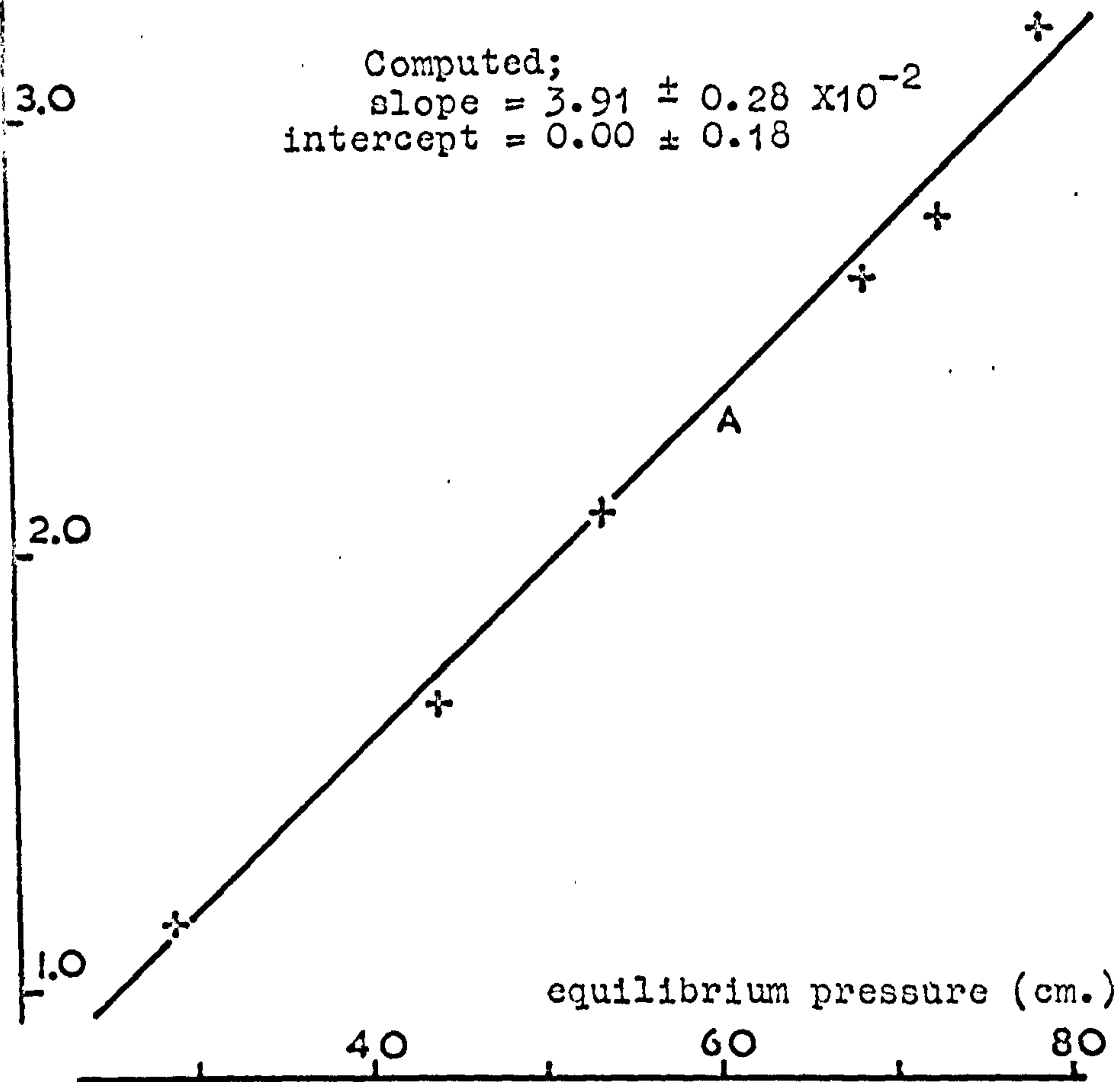
Solutions of Cosalen in certain non-aqueous solvents were found to absorb oxygen with a stoichiometry represented in equation [5.4].



The solid products so obtained analysed for a composition of two moles of solvent (S) and Cosalen for each mole of oxygen. Under different conditions the products decomposed to give the three components as in

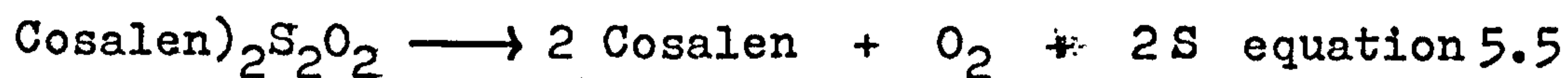


pressure  
drop (cm.)



[5.14]. Plot of pressure drop against equilibrium pressure for oxygen over pure dimethylformamide.

equation [5.5]



Pyridine<sup>1,37</sup>, dimethylformamide<sup>37</sup> and dimethyl sulphoxide<sup>37</sup> have been used as the solvents in these reactions.

In this work dimethylformamide solutions of Coamben were tested for an ability to absorb oxygen. The apparatus used in these experiments is described in chapter 10 page 252.

First the solubility of oxygen in dimethylformamide was determined by observing the pressure drop when oxygen was absorbed by 50 ml. of the pure degassed solvent at 26°C. The curve (A) in [5.14] shows the pressure drop in the apparatus for different equilibrium pressures of oxygen over dimethylformamide. Clearly, solutions of oxygen in dimethylformamide obey Henry's Law in the pressure range studied. From the previously calibrated volume of the apparatus (page 257) the solubility of oxygen in dimethylformamide at 26° and one atmosphere equilibrium pressure was calculated as  $4.83 \pm 0.36 \times 10^{-3}$  mole L<sup>-1</sup>.

The oxygen uptake by degassed solutions of Coamben in dimethylformamide was determined as described in chapter 10, and the results (recorded as decreases in

Coamben (mmole)	Equilibrium Pressure O <sub>2</sub> (cm)	Pressure Change (cm) (c)		
		Observed	Expected for pure D.M.F (d)	Further change expected for equation (a)
0.276	73.06	2.78	2.85	1.69
" (b)	71.66	2.75	2.80	1.69
0.521	78.92	3.10	3.08	3.20
" (b)	70.16	2.75	2.74	3.20

Table [5.6] Oxygen absorption by degassed solutions of Coamben in dimethylformamide (DMF).

- (a)  $2\text{Coamben} + \text{O}_2 + 2\text{DMF} = (\text{Coamben})_2\text{O}_2(\text{DMF})_2$   
 (b) Same solution deoxygenated and repeat.  
 (c) , Volume above solution = 151.6 ml. Temperature 299<sup>0</sup>K  
 (d) From curve A, [5.14].

pressure) for two solutions of Coamben are summarized in table [5.6]. The decreases in pressure corresponded closely to those expected for oxygen uptake by 50 ml. of pure degassed dimethylformamide alone, which were read from curve A [5.14] for the various final pressures of oxygen in the apparatus.

Also included in table [5.6] are the decreases in pressure which would be expected if oxygen was absorbed in the same molar ratio (1 O<sub>2</sub> : 2 Co) as was observed<sup>37</sup> for Cosalen. These are of a magnitude which easily would have been detected under the experimental conditions used.

Apparently Coamben behaves quite differently from Cosalen,<sup>37</sup> and shows no tendency to form stable oxygen adducts in dimethylformamide solution. It is difficult to see any simple explanation for this difference in behaviour. There are only small differences in the steric properties of the systems, and it seems unlikely that the NH groups of Coamben would restrict the approach of an oxygen molecule which is assumed<sup>36</sup> to be above the plane of the molecule in the 'Cosalen type' compounds.

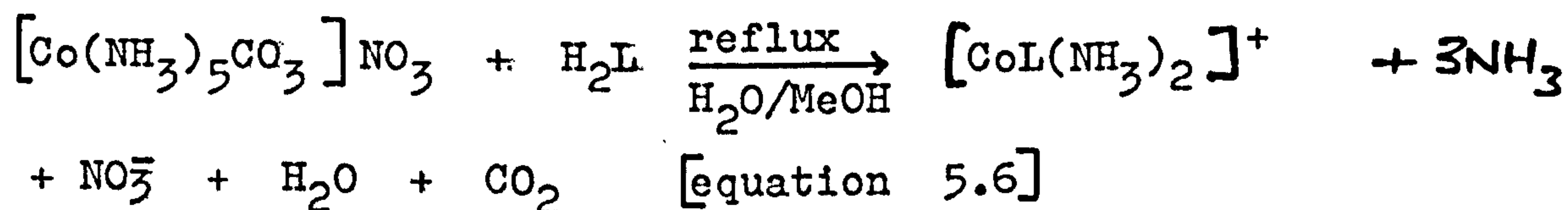
### Oxidation

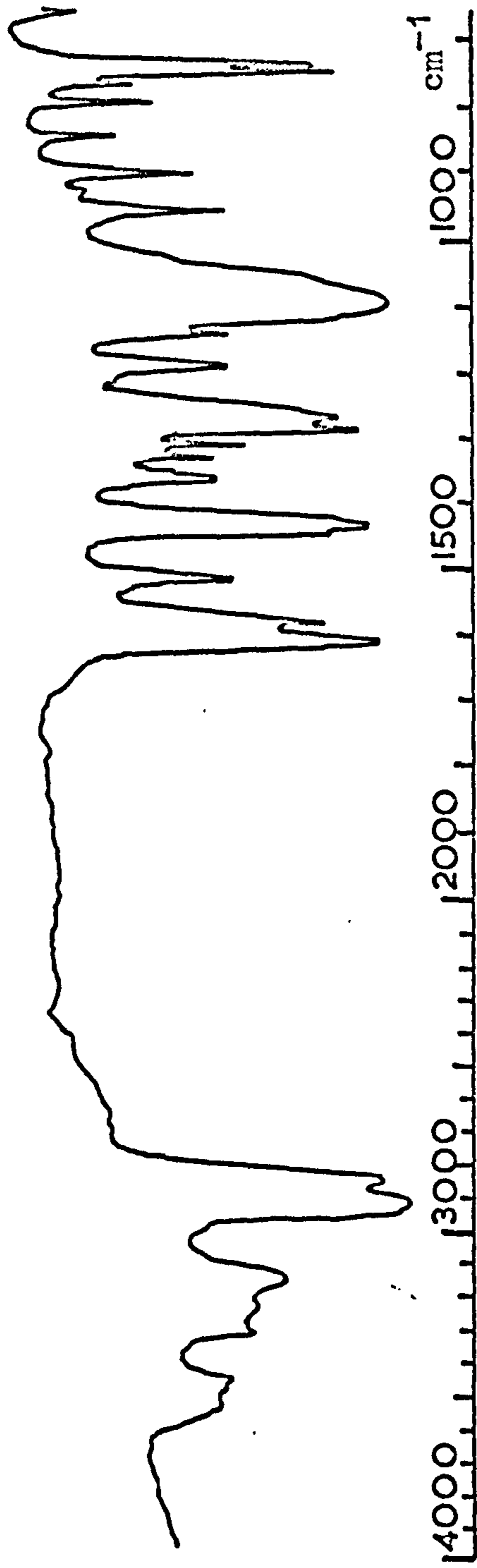
It was hoped to prepare cobalt(III) complexes of some of the ligands described in chapter 3.

Some comparable salen complexes formulated as  $[\text{Co}^{\text{III}}\text{salen X}_2] \text{Y}$  have been recorded by Yamada.<sup>39</sup> The complexes were isolated after treating a suspension of Cosalen in dilute acetic acid with hydrogen peroxide in the presence of a base X and a salt containing the anion Y. When we used comparable conditions to treat Coamben only uncharacterizable tars and solids were obtained.

Unfortunately no details of Yamada's method are available at present. Using Cosalen in attempts to improve on the experimental conditions which we had found unsuccessful for Coamben, often gave low yields of  $[\text{Co}^{\text{III}}\text{salen X}_2] \text{Y}$  in mixtures which were difficult to separate.

In the course of these investigations a very convenient method for the preparation of cobalt(III)salen complexes was discovered.<sup>40</sup> The method is shown in equation [5.6]. It involves the reaction of free salen ( $\text{H}_2\text{L}$ ) with a labile pentamminocobalt(III) complex, in refluxing aqueous methanol. The desired complex often crystallizes from the mixture on cooling, or can be precipitated as the perchlorate by the addition of sodium perchlorate.





[5.15]. The infrared spectrum of  $[\text{Cosalen}(\text{NH}_3)_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$  as a nujol mull.

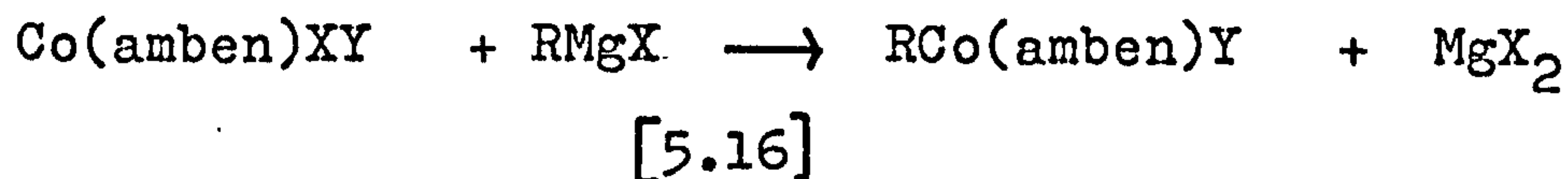
The infrared spectrum of the compound  $[\text{Cosalen}(\text{NH}_3)_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$  is shown in [5.15]. This formulation for the complex is supported by the analysis results (page 304) and the infrared spectrum which shows a single band at  $1080 \text{ cm}^{-1}$  which is characteristic of uncoordinated perchlorate ions.<sup>41</sup>

When the method shown in equation [5.6] was repeated under identical conditions, using amben instead of salen a most surprising result was obtained. A red solid was collected from the methanol mixture. After washing with water and drying this solid was found to be Coamben. Some of the cobalt(III) ions must be reduced during the course of the reaction, presumably at the expense of some of the free ligand amben, which must be oxidized. No other pure products could be obtained from the amorphous solids obtained on addition of sodium perchlorate to the filtrate or on evaporation of the filtrate from this mixture.

Some preliminary results from the controlled potential oxidation of Coamben and Cosalen solutions in dimethylformamide (see page 307 for a description of the apparatus) suggested that an oxidation wave is observed for Cosalen, but not for Coamben in the potential range accessible using platinum electrodes and potassium

perchlorate as the current carrier. The oxidation wave for Cosalen occurred at c.a. + 1.4 V relative to a calomel electrode but unfortunately appeared to be accompanied by some polarization of the electrodes, and was not reproducible or reversible.

Unfortunately our inability to prepare cobalt(III) complexes of amben rules out the synthesis of a cobalt alkyl using the route outlined in [5.16]. This synthetic scheme is very similar to that used for preparing alkyl derivatives of vitamin B<sub>12</sub> (see page 5 ) and that used recently for the synthesis of alkyls of Cosalen.<sup>42,43.</sup>

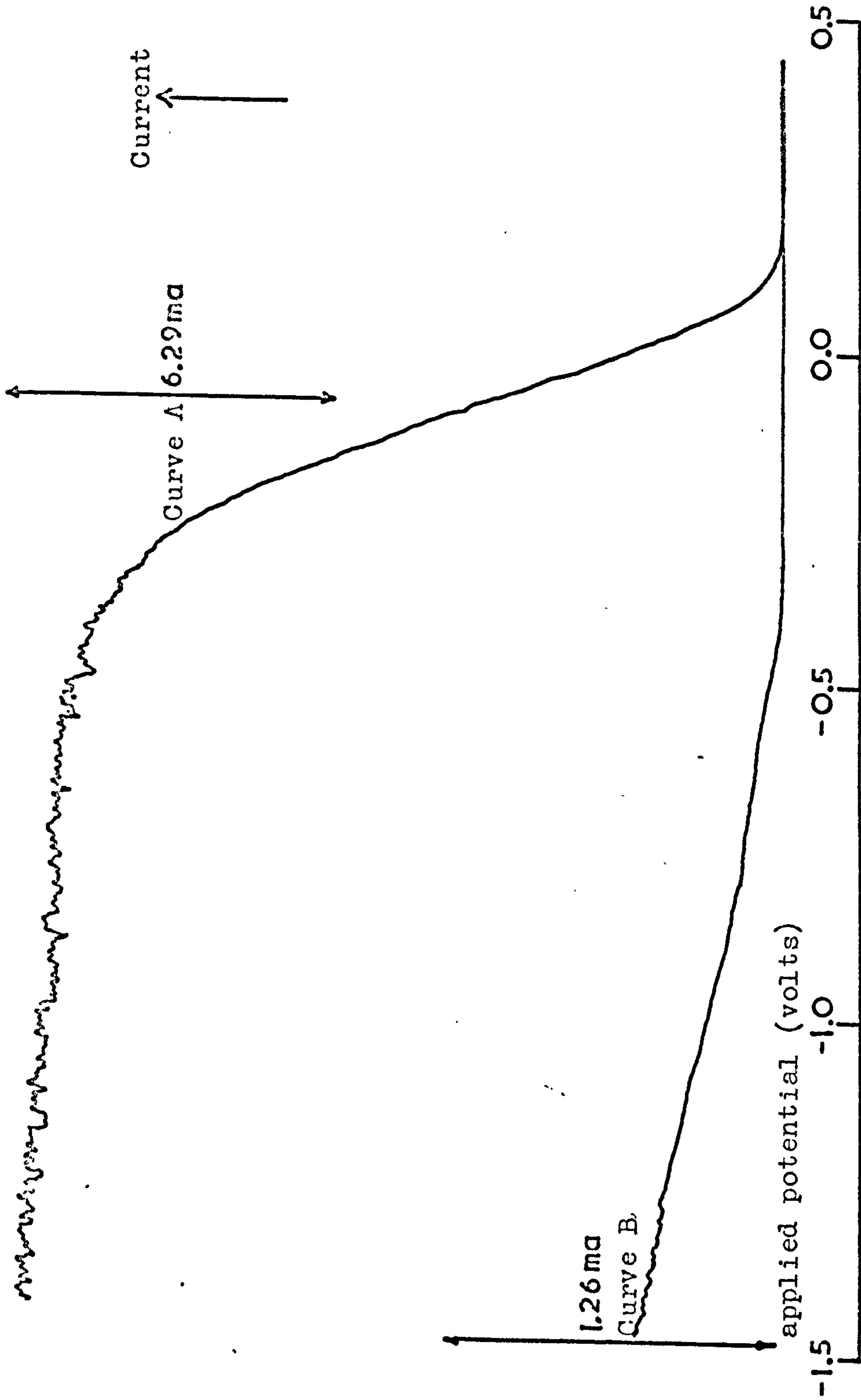


At present, investigations are in progress in this laboratory to elucidate the products obtained by oxidation of Coamben with iodine.

### 5.7 Reduction to species containing cobalt(I)

When a deoxygenated suspension of Coamben in tetrahydrofuran was stirred with sodium sand a very deep green solution was produced, which when removed from the sodium sand and treated with ethanol liberated a gas (assumed to be hydrogen) and deposited red crystals of

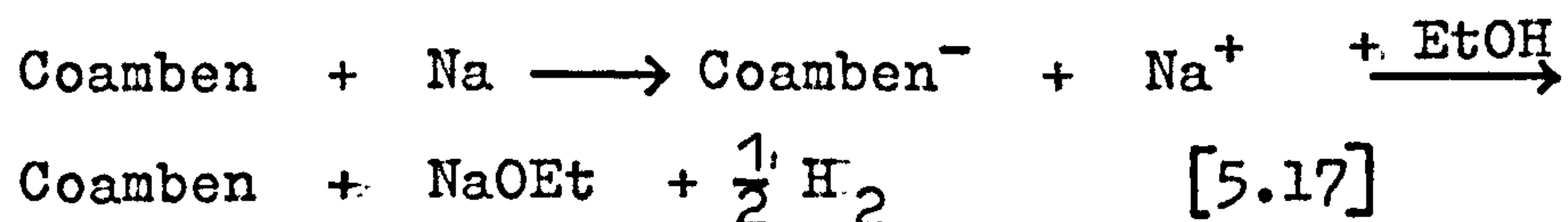




[5.18]. A plot of current against applied potential (relative to a S.C.E.) for a solution of Coamben in dimethylformamide (curve A), and solvent system (curve B).

Coamben.

It is proposed that an anion containing cobalt with a formal oxidation state of one is present in the green solution; and that the changes described above may be represented by the scheme [5.17]. The same changes were observed when 2% sodium amalgam was used instead of sodium sand.



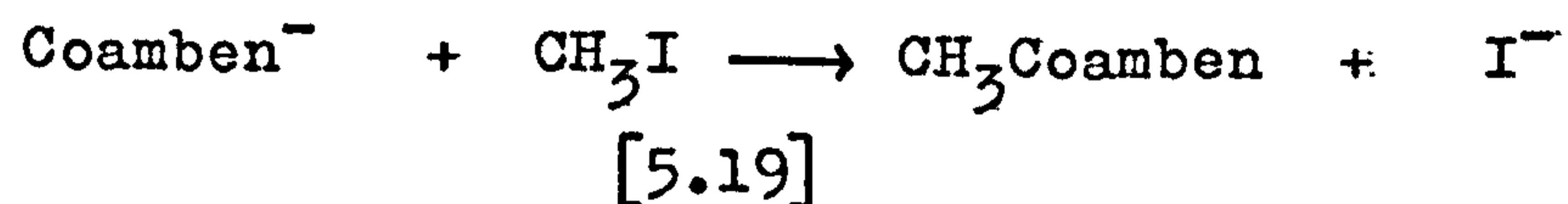
The reduction was also investigated qualitatively using controlled potential reduction. A deoxygenated solution of Coamben in dimethylformamide containing potassium perchlorate (0.1M) as a carrier was reduced using platinum electrodes (see section 11.3). A plot of current against applied potential (relative to a standard calomel electrode) is shown as curve A in [5.18]. Curve B is a plot at higher current sensitivity for the pure deoxygenated solvent system.

It is suggested that the reduction wave with  $E_{1/2} = -0.12 \text{ V}$  might be due to the change which can be formalized as  $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}} - e^-$ , but further experiments are needed to confirm this. It is hoped that by linking this reduction technique with electron spin resonance

spectroscopy, evidence may be obtained for the nature of species involved.

Using the same conditions as described above a similar reduction wave ( $E_{\frac{1}{2}} = -0.04$  V) was observed for Cosalen in dimethylformamide. The evidence for reduction of this substance to a species containing cobalt(I) has recently been well documented.<sup>43</sup>

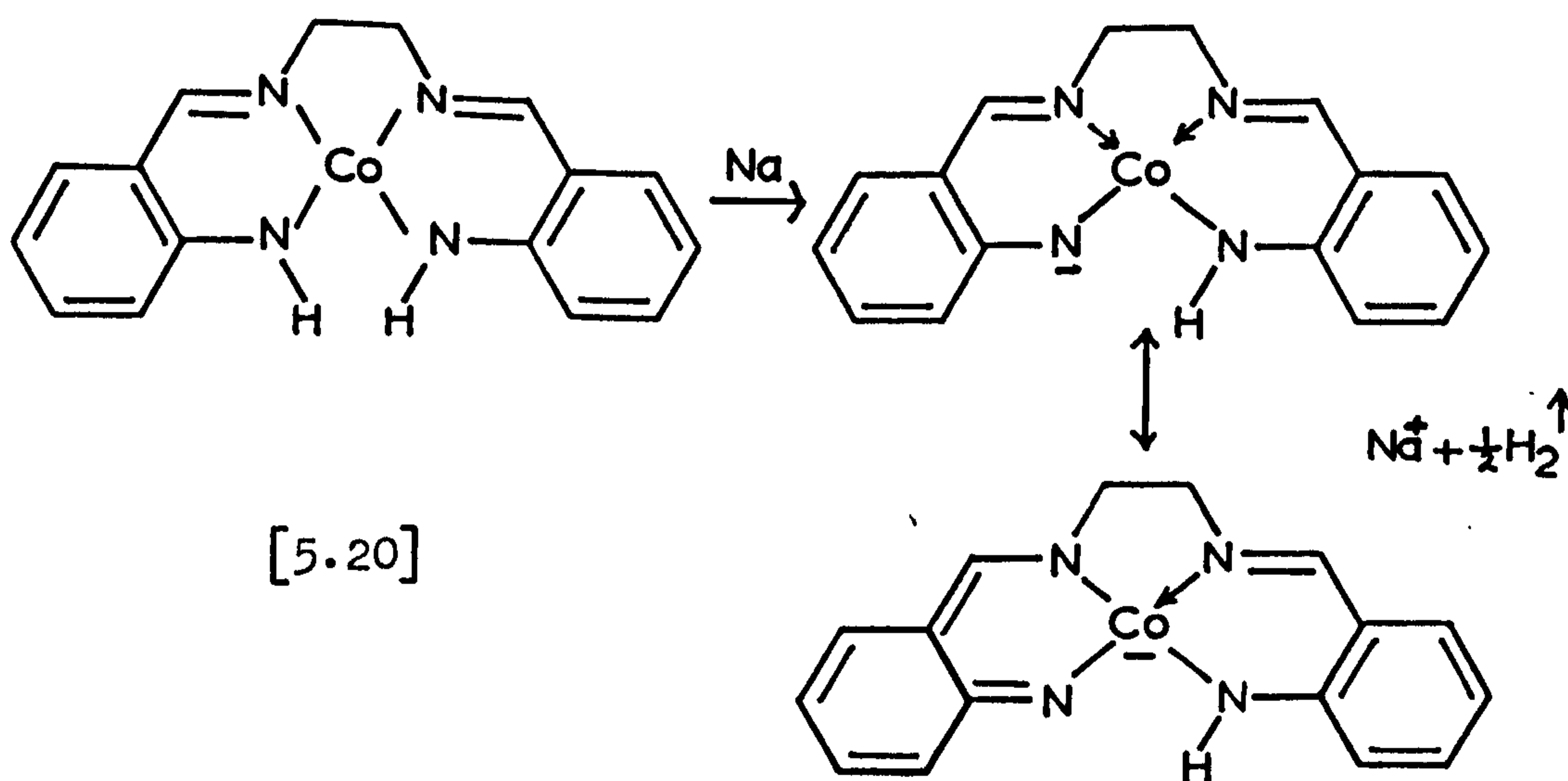
It was hoped that reaction of the cobalt(I) species  $\text{Coamben}^-$  with methyl iodide according to the scheme shown in [5.19] would give the corresponding methyl derivative having a cobalt-carbon  $\sigma$ -bond. The reaction was repeated several times without success, using reduction by both sodium sand and 2% sodium amalgam to produce the  $\text{Coamben}^-$ . When the reaction was repeated using Cosalen under a set of conditions which had failed for  $\text{Coamben}^-$  (see page 305), a reasonable yield of the methyl derivative was obtained. This reaction has also been described in the literature.<sup>43,44</sup>



Initially when attempts were made to synthesize  $\text{CH}_3\text{Coamben}$  by scheme [5.19] an equimolar quantity of methyl iodide was used. It was reasoned that perhaps

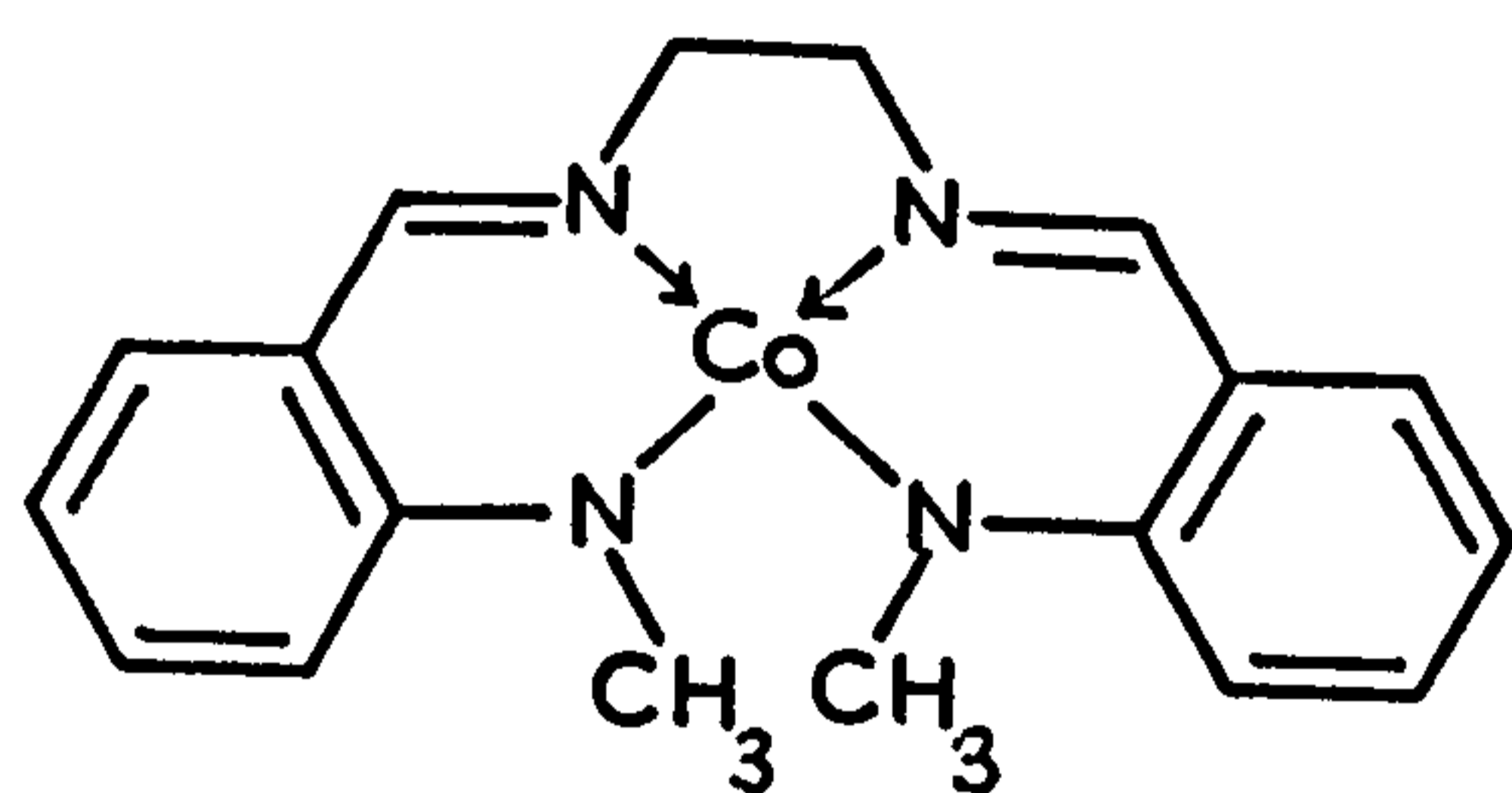
methylation of the anilino groups was a competing reaction, and that it would be worthwhile attempting the reaction with an excess of methyl iodide. This proved no more successful.

The presence of the anilino groups may well be significant in the failure to obtain a cobalt-alkyl under the comparatively accessible conditions which had proved successful for Cosalen. It even presents another possibility for the reduction of Coamben, which is illustrated in [5.20]. This reduced species could show two nucleophilic centres in the reaction with methyl iodide. Deprotonation of coordinated amino groups under strongly basic conditions has been observed for other systems.<sup>45,46,47</sup>

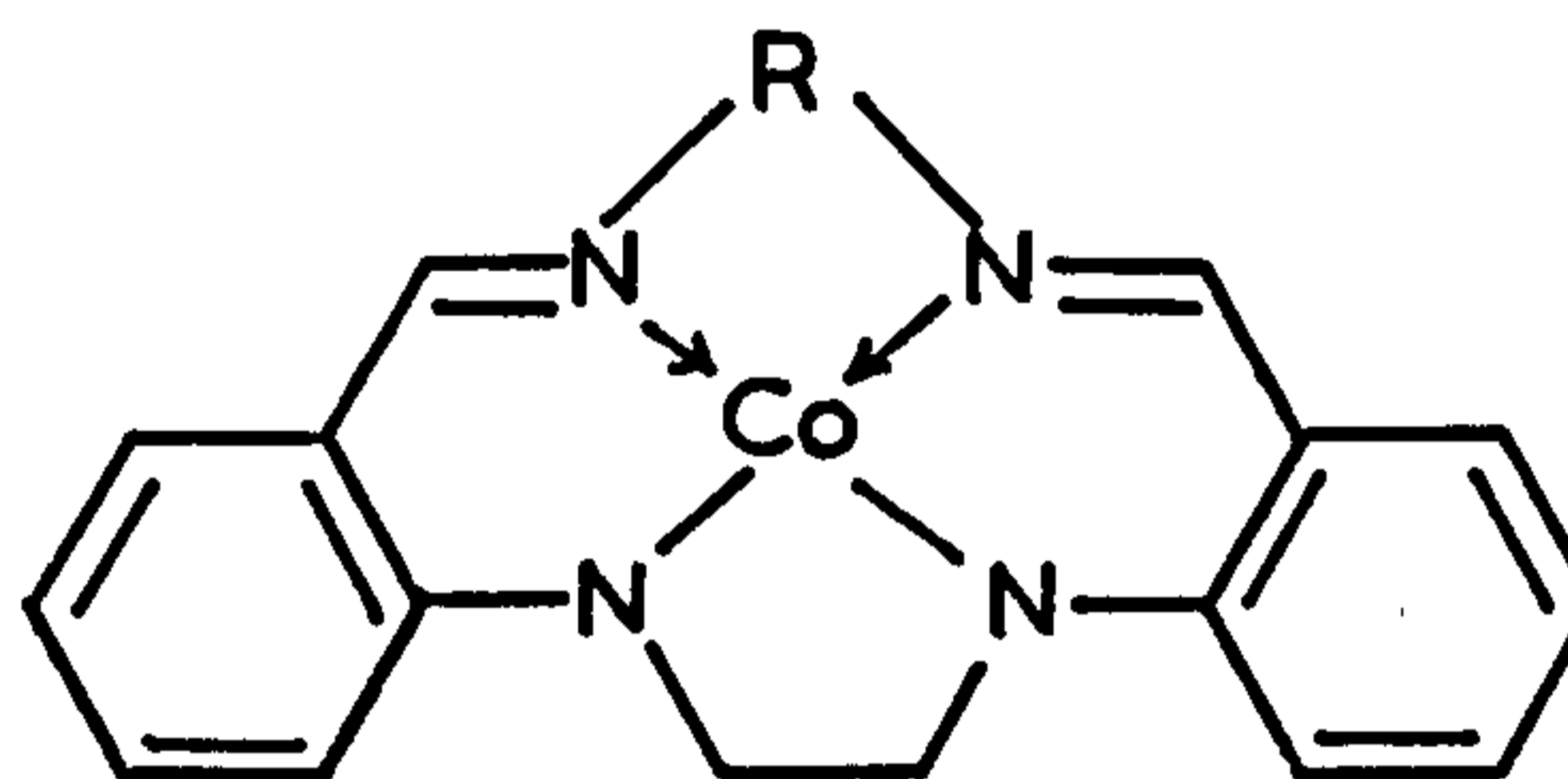


In view of these possible complications resulting from the presence of NH groups in the complexes it was decided to study analogous compounds in which the NH groups had been replaced by N-alkyl.

Since the complex CoMe-amben [5.21] could not be obtained pure (see page 111) it was decided to synthesize the completely cyclic complexes [5.22] which contain no NH groups. These systems will be discussed in the following chapters.



[5.21]



[5.22]

### 5.8 References.

1. R.H. Bailes and M. Calvin, J. Amer. Chem. Soc., 69, 1886, (1947).
2. H. Weigold and B.O. West, J. Chem. Soc. (A). 1310, (1967).

3. M.F.L. Johnson, "Cobalt, its Chemistry, Metallurgy and Uses," Ed. R.S. Young, Reinhold, 1960, page 293.
4. J. Bayston, N.K. King and M.E. Whinfield, Adv. in Catalysis, IX, 312 (1956).
5. Michael Green, R.J. Mawby and G. Swinden, Inorg. Nucl. Chem. Letters, 4, 73, (1968).
6. E.N. Salinkova and M.L. Khidekel, Izvest. Akad. Nauk. S.S.S.R., Ser. Khim., 223 (1967).
7. E.I. Ochiai, Coord. Chem. Rev. 3, 49, (1968).
8. Y.M. Curtis and N.F. Curtis, Austral. J. Chem., 18, 1933, (1965).
9. N.F. Curtis and D.A. House, Chem. and Ind., 1708, (1961)
10. N.F. Curtis, Coord. Chem. Rev., 3, 3, (1968).
11. G.W. Everett and R.H. Holm, J. Amer. Chem. Soc., 87, 5266, (1965).
12. K. Ueno and A.E. Martell, J. Phys. Chem., 60, 1270, (1956).
13. P. Teyssie and J.J. Charette, Spectrochim. Acta, 19, 407, (1963).
14. G.W. Everett, R.H. Holm and A. Chakravorty, Prog. Inorg. Chem., 2, 83, (1966).
15. D.H. Busch, as ref. 3, page 88.
16. D. Hall and T.N. Waters, J. Chem. Soc., 2644, (1960).
17. H. Weigold and B.O. West, J. Chem. Soc. (A), 1310, (1967).

18. A.B.P. Lever, *Adv. Inorg. Chem. and Radiochem.*, 7, 27, (1965).
19. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.* 6, 37, (1964).
20. P.G. Owston and J.M. Rowe, *J. Chem. Soc.*, 3410, (1963).
21. J.D. Forrester, A. Zalkin and D.H. Templeton, *Inorg. Chem.*, 3, 1500, (1964).
22. J. Chatt and B.L. Shaw, *J. Chem. Soc.*, 289, (1961).
23. A. Davison, N. Edelstein, R.H. Holm and A.H. Maki, *J. Amer. Chem. Soc.*, 85, 3049 (1963).
24. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 338, (1959)
25. R.L. Carlin, "Transition Metal Chemistry", Ed. R.L. Carlin, Vol. 1, Arnold, 1965, page 1.
26. H.B. Gray as reference 25, page 258.
27. S. Yamada, *Coord. Chem. Rev.* 1, 415, (1966).
28. M. Hariharan and F.L. Urbach, *Abs. 156th. Nat. Meeting A.C.S., Inorg. Div., Abs. 98.*
29. L. Sacconi, *Coord. Chem. Rev.* 1, 192, (1966).
30. A. Earnshaw, P.C. Hewlett, E.A. King, L.F. Larkworthy, *J. Chem. Soc. (A)*, 241, (1968).
31. P.L. Orioli, M. Di Vaira and L. Sacconi, *Chem. Comm.*, 103, (1965).
32. L. Sacconi, P.L. Orioli and M. Di Vaira, *J. Amer. Chem. Soc.*, 87, 2059, (1965).
33. L. Sacconi, M. Ciampolini and G.P. Speroni, *Inorg. Chem.*, 4, 1116, (1965).

34. H. Nishikawa and S. Yamada, Bull. Chem. Soc. Japan, 37, 8, (1964).
35. S. Katagari and J. Endo, J. Chem. Soc. Japan, 84, 197, (1963).
36. L.H. Vogl, H.M. Faigenbaum and S.E. Wiberley, Chem. Rev., 63, 269, (1963).
37. F. Calderazzo, C. Floriani and J.J. Salzmann, Inorg. Nuclear Chem. Letters, 2, 379, (1966).
38. H.P. Fritz and W. Gretner, Inorg. Nuclear Chem. Letters, 3, 141, (1967).
39. S. Yamada, H. Nishikawa and E. Yoshida, Proc. Japan Acad., 40, 211, (1964).
40. Michael Green, J. Smith and P. A. Tasker, unpublished observations.
41. B.J. Hathaway and A.E. Underhill, J. Chem. Soc., 3091, (1961).
42. G. Costa, G. Mestroni and L. Stefani, J. Organometal Chem., 7, 493, (1967).
43. C. Floriani, M. Puppis and F. Calderazzo, J. Organometal Chem., 12, 209, (1968).
44. F. Calderazzo and C. Floriani, Chem. Comm., 139, (1967).
45. D.G. Upchurch, Diss. Abs. 22B, 3027.
46. G.W. Watt and D.G. Upchurch, J. Amer. Chem. Soc., 89, 177, (1967).
47. G.W. Watt, P.W. Alexander and B.S. Manhas, J. Amer. Chem. Soc. 89, 6483, (1967).



## Chapter 6. The Synthesis of Macrocyclic Ligands.

6.1 General problems.

6.2 Template reactions

6.2.1 Kinetic template effect

6.2.2 Thermodynamic template effect

6.2.3 Template synthesis of cyclic quadridentate nitrogen ligands.

6.2.4 Other template syntheses of macrocyclic ligands.

6.3 Stability of the cyclic ligand

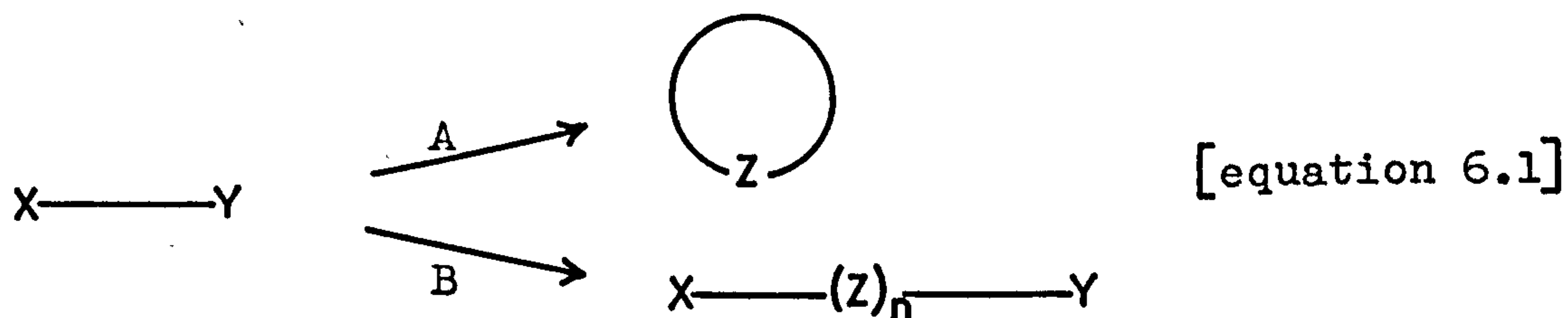
6.3.1 Conjugated cyclic ligands

6.3.2 Steric considerations

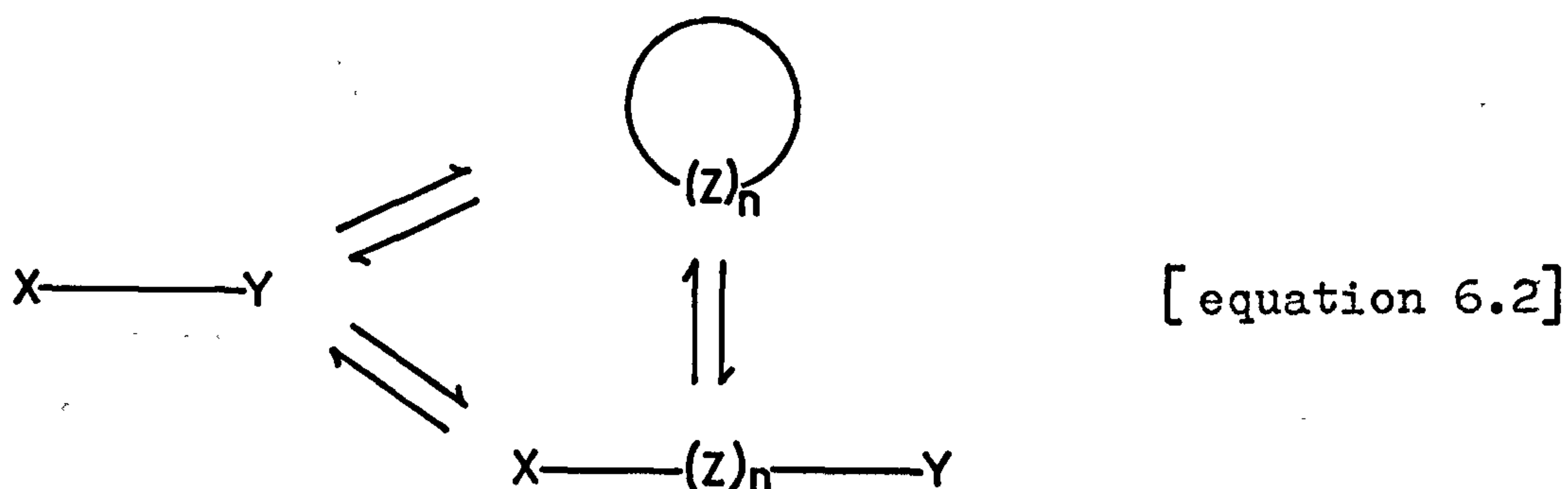
6.4 References:

### 6.1 General Problems.

The synthesis of macrocyclic ligands presents the same type of problem as the synthesis of large ring molecules. If two functional groups X and Y are required to be reacted intramolecularly to give the functional group Z in a large ring molecule (see equation [6.1](A) ) there is always the possibility of intermolecular reaction to give a polymeric system (see equation [6.1] (B) )



When the reaction of X and Y to give Z is reversible, an equilibrium situation can result, in which the coexistence of monomer units, polymer chains, and monomer or polymer rings is possible (equation [6.2])



We wish to find conditions which will favour the formation of a desired cyclic unit.

### 6.2 Template reactions.

The term 'template reaction' was first used by Busch<sup>1</sup> to describe, "reactions where a metal ion may serve as a 'template' to organize the course of a complex multistep reaction." Clearly, the use of a 'template' metal ion may simplify the problem of synthesis of a macrocyclic ligand complex.

Several recent reviews<sup>1,2,3,4</sup> of reactions of coordinated ligands use the term "template", but only one<sup>3</sup> attempts to distinguish between different types of template effect. A distinction is made between 'kinetic' and 'thermodynamic' template effects. The terms were

presumably originated by analogy to kinetic control and thermodynamic control of reaction pathways (see reference 5 for definitions).

### 6.2.1 Kinetic template effect.

In the kinetic template effect the important function of the metal ion is in lowering the free energy of activation of the desired process. Since  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ , decreasing  $\Delta H^\ddagger$  or increasing  $\Delta S^\ddagger$  lowers the free energy of activation  $\Delta G^\ddagger$ . In many cyclization reactions  $\Delta S^\ddagger$  may have a large negative value, but may be compensated for by a decrease in  $\Delta H^\ddagger$  due to bonding in the transition state with the template ion. Hence, the organizational action of the metal ion results from its ability to lower the free energy of the molecule in the transition state, in which the functional groups X and Y are arranged to react intramolecularly (i.e. favours (A) over (B) in equation [6.1]). Clearly it is important that this arrangement of the transition state suits the coordination geometry of the template ion.

Normally the configuration of atoms in the transition state prior to cyclization will be very similar to that of the cyclized molecule, and so, if there is appreciable bonding to the metal ion in the transition

state, it will remain after the cyclization has been completed. For this reason kinetic template reactions are seldom 'catalytic' and are often difficult to distinguish from thermodynamic template reactions (below)

### 6.2.2. Thermodynamic template effect.

In the thermodynamic template effect the main function of the metal template ion is to lower the free energy of a desired product, which has been formed by an equilibrium process. Hence, if a macrocyclic ligand is formed in small quantities in an equilibrium process (e.g. equation [6.2] ), strong complexation will lower its free energy relative to other species, and displace equilibria in favour of the macrocycle.

In practice it is normally difficult to decide which type of template effect is operating in a given case. No kinetic studies have been reported for any of the documented template cyclizations.

The presence of a metal ion complexed to the macrocycle is not clear evidence for a thermodynamic effect (see section 6.2.1). Also it would seem probable that thermodynamic template action would often be accompanied by kinetic action.

If the desired macrocycle is not obtained in the absence of a metal ion a kinetic template effect is

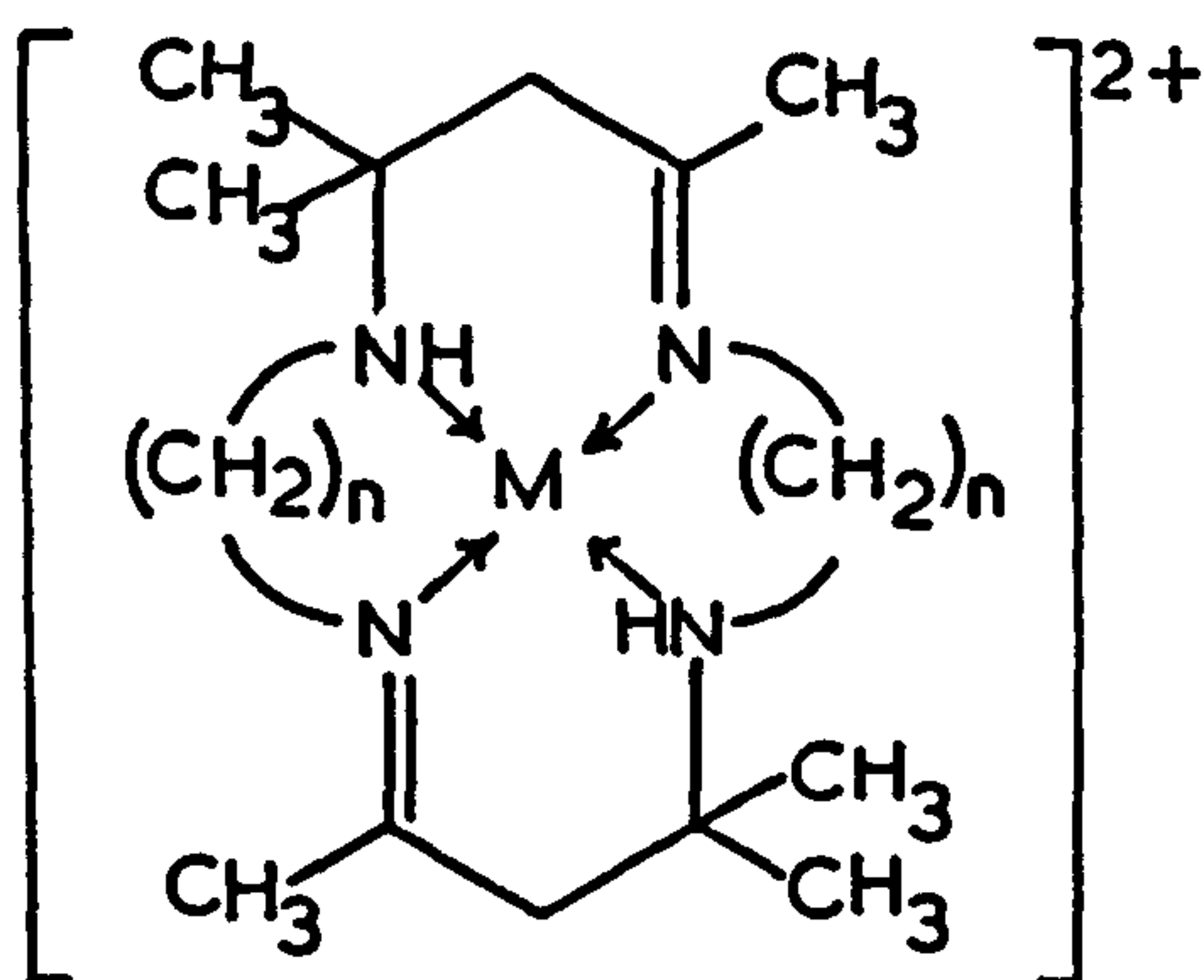
suggested. However, it is difficult to rule out the formation of a very low concentration of macrocycle in equilibrium with other species, and then thermodynamic control (thermodynamic template effect) giving the macrocyclic complex on the addition of the template ion.

### 6.2.3 Template reactions giving cyclic quadridentate nitrogen ligands.

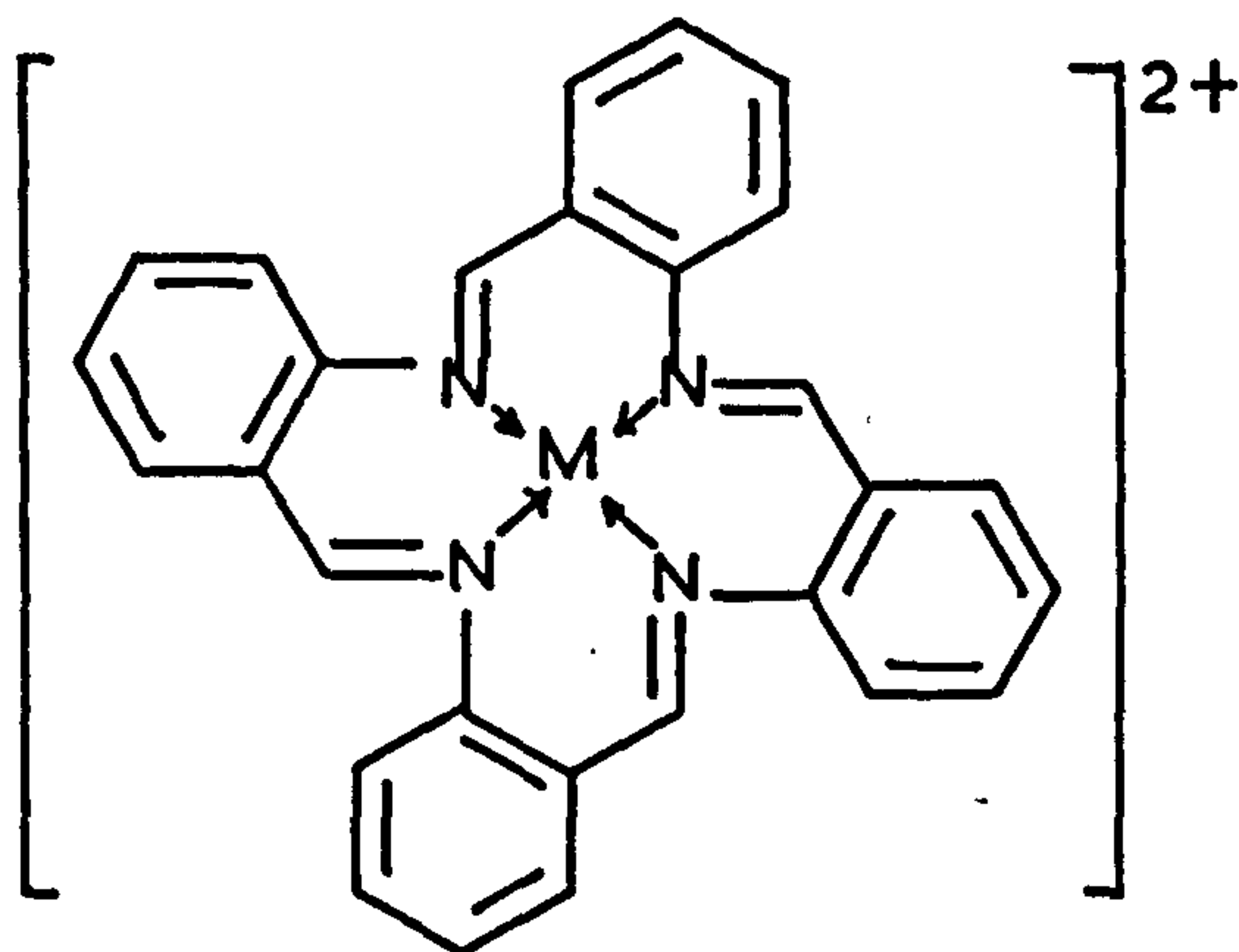
Most of the recorded template syntheses of macrocyclic ligands have resulted in the formation of square-planar quadridentate ligand complexes.

Curtis<sup>6</sup> found that acetone or mesityl oxide reacted with bis and tris-diamine complexes of copper(II) and nickel(II) to give macrocyclic complexes of the type [6.1]. Both cis and trans isomers differing in relative positions of the imine groups are possible, and also optical isomers due to restricted inversion about the secondary amine centres. These, and many other similar compounds prepared by reduction and oxidation have been recently reviewed.<sup>7</sup> A free ligand (n=2 in [6.1]) has been found<sup>8</sup> to form in the condensation of acetone or mesityl oxide with a protonic acid salt of 1,2-diaminoethane in the absence of a metal ion. Reactions to give [6.1] in the presence of a metal ion have therefore been considered,<sup>3</sup> to be examples of a thermodynamic template

effect. A free ligand was also obtained<sup>9</sup> when the condensation was attempted in the presence of ferrous ions.

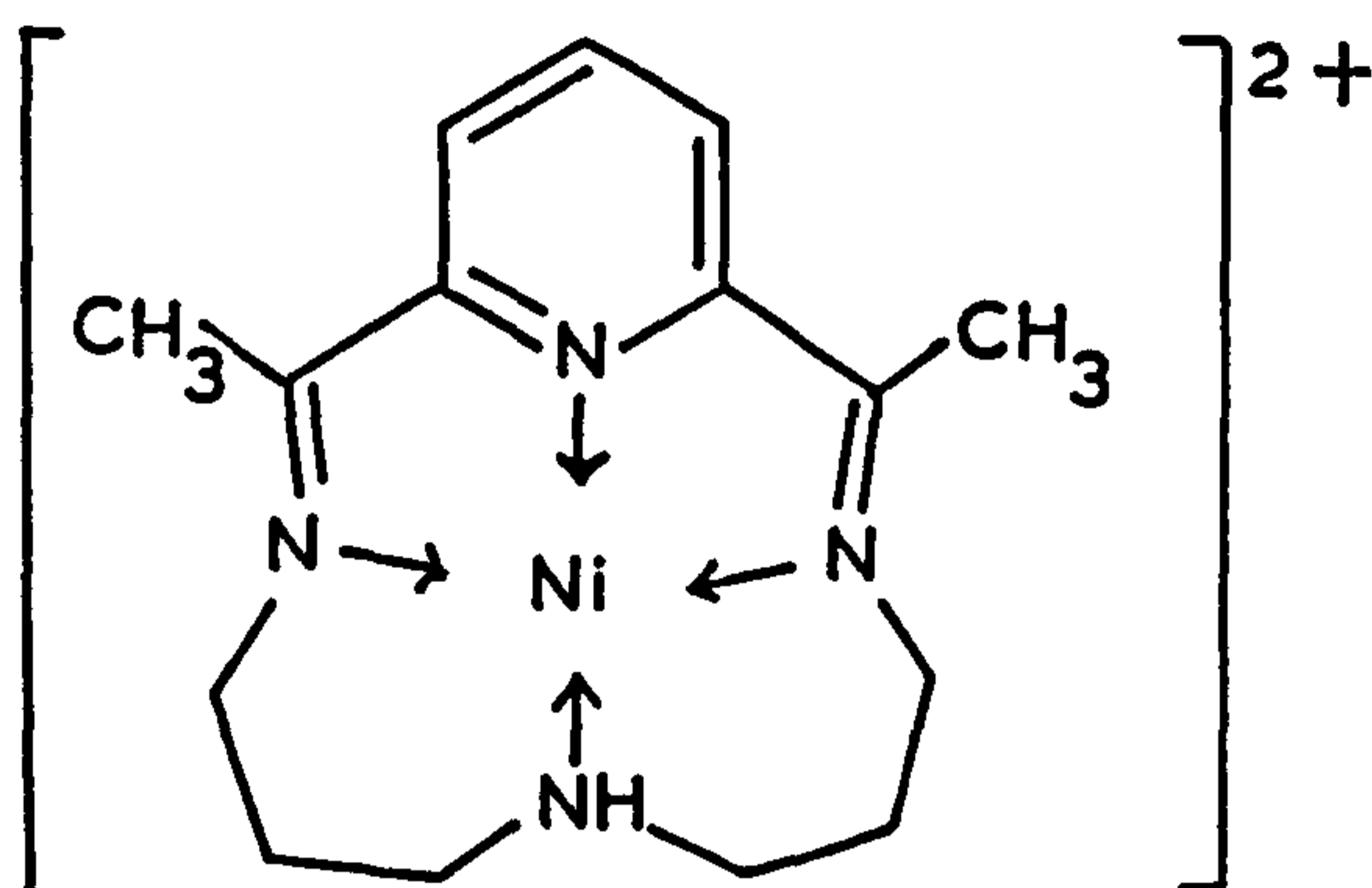


[6.1]



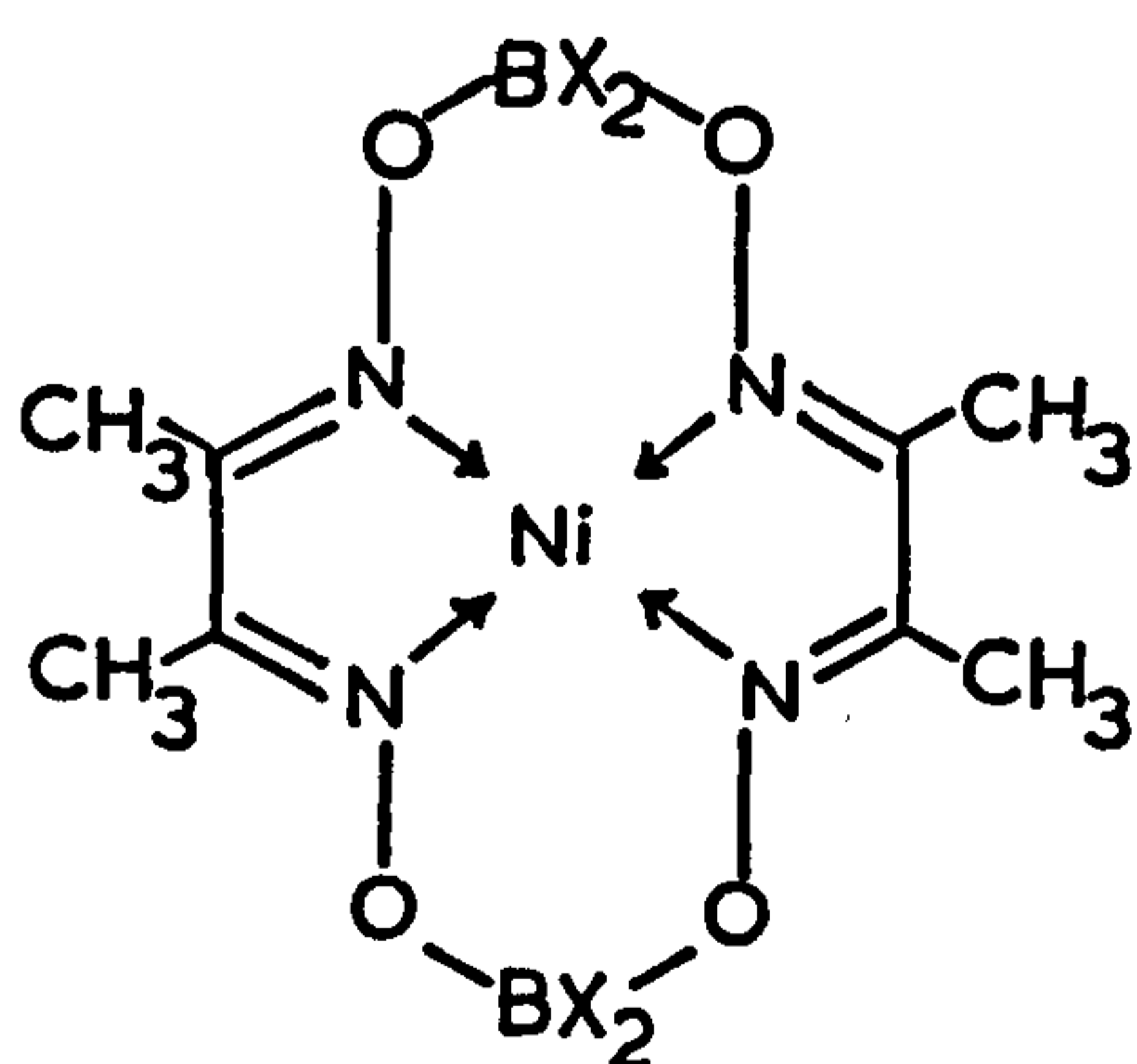
[6.2]

Condensation of *o*-aminobenzaldehyde in ethanolic solutions of nickel(II) and copper(II) ions gives<sup>10</sup> macrocyclic complexes of the type [6.2]. The reaction has been suggested<sup>3</sup> to be an example of a kinetic template effect, since the cyclic tetra-anhydro tetramer is not detected in the reaction of *o*-aminobenzaldehyde in the absence of metal ions.<sup>11,12</sup> Similar considerations apply to the condensation of 2,6-diacetylpyridine with 1,5,9-triazanonane which normally gives a resinous material, but in the presence of copper(II) and nickel(II) ions gives [6.3]<sup>13,14</sup>.



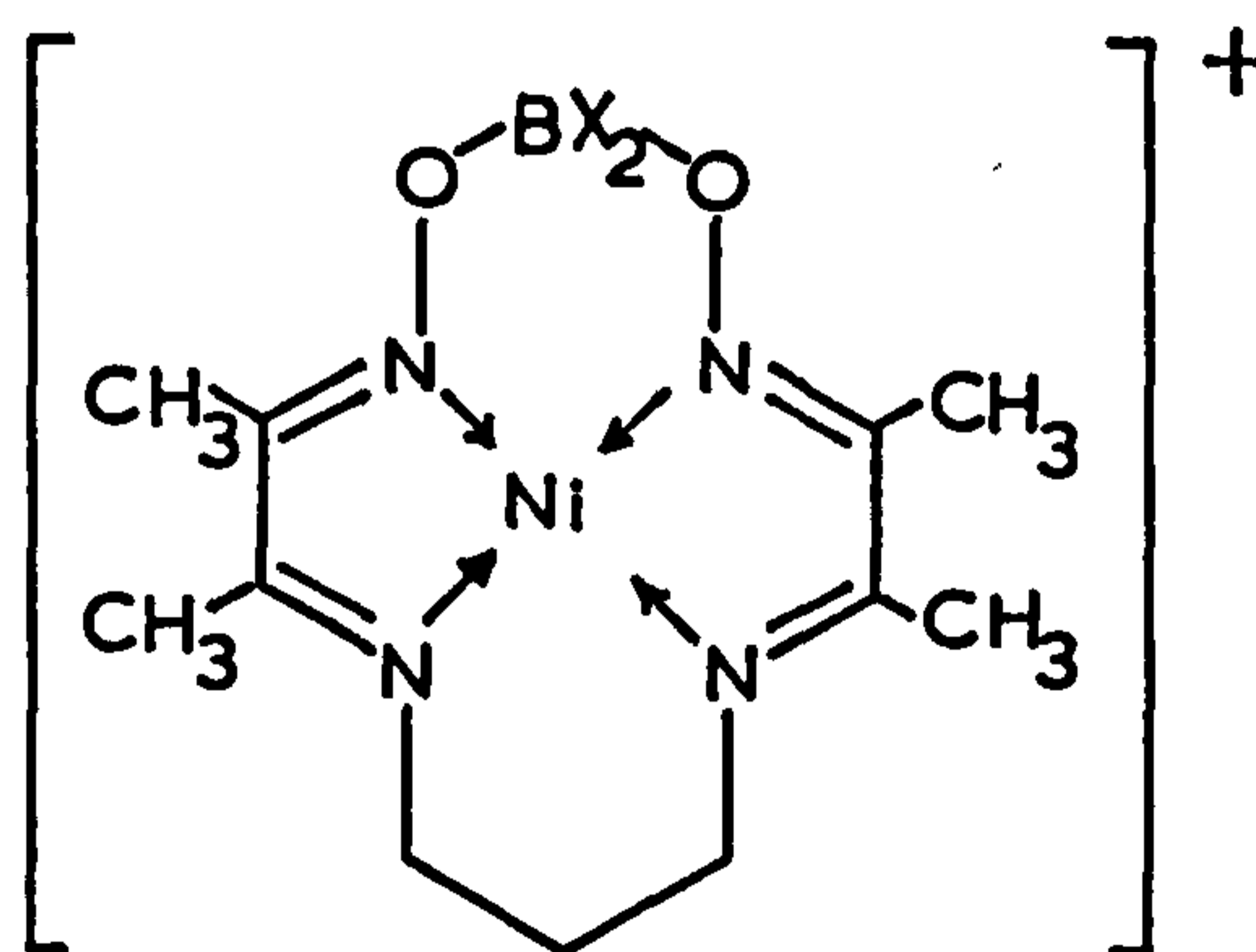
[6.3]

Complexes of certain oxime ligands may be bridged across adjacent oxygen atoms by reaction with borinic acid esters or boron trifluoride, to give cyclic quadridentate ligand complexes.<sup>15,16,17</sup> Examples are shown in [6.4] and [6.5].



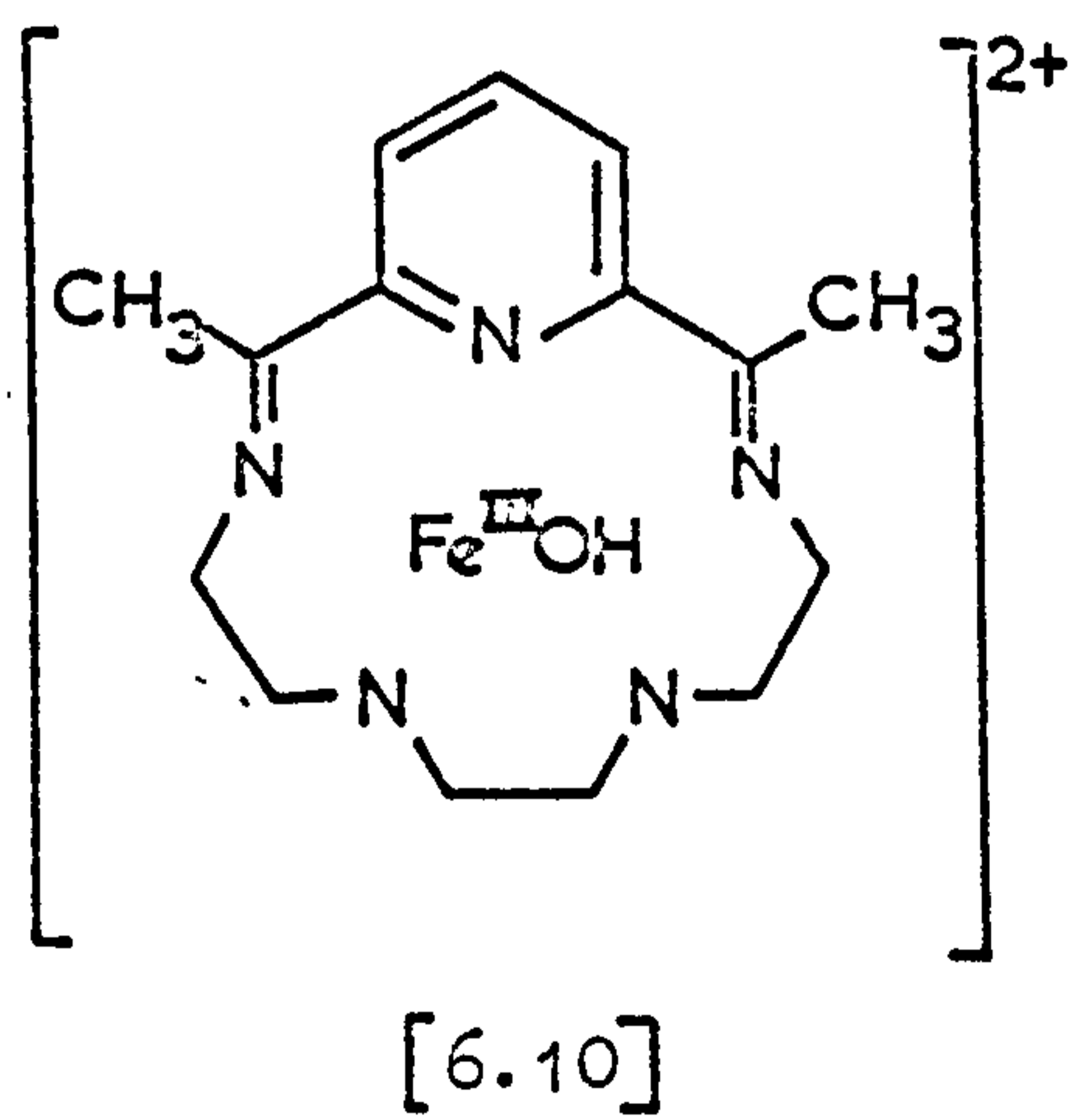
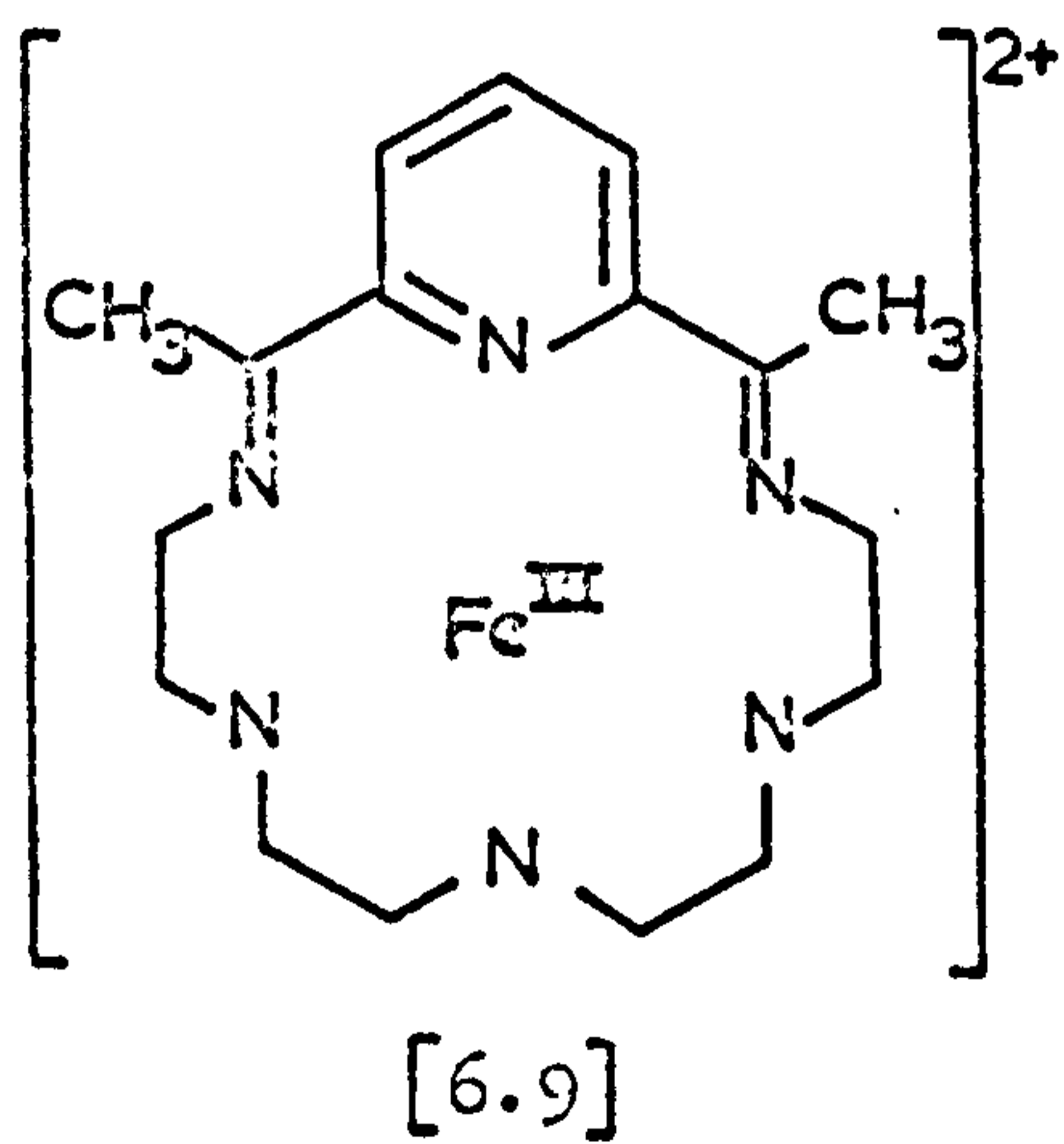
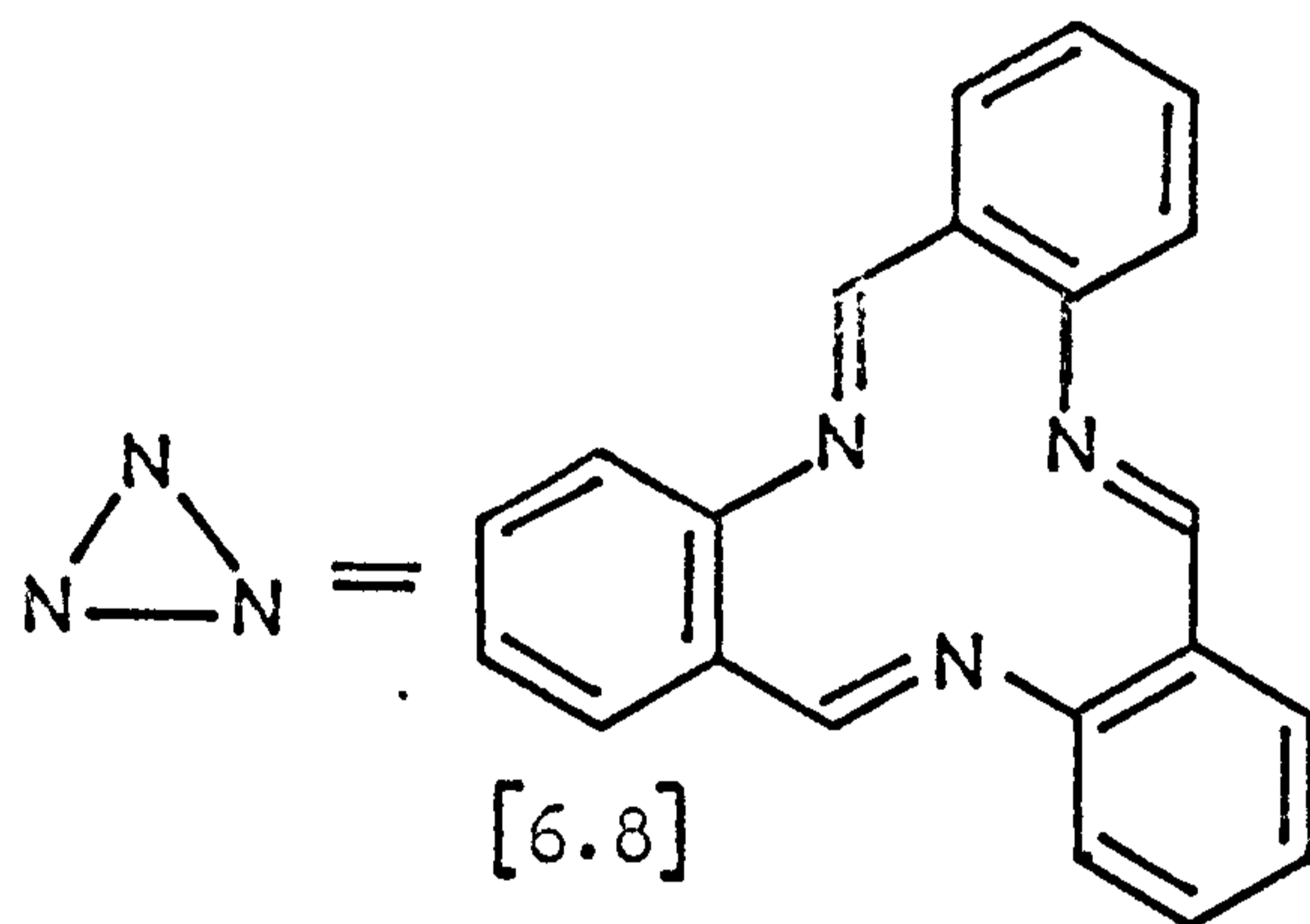
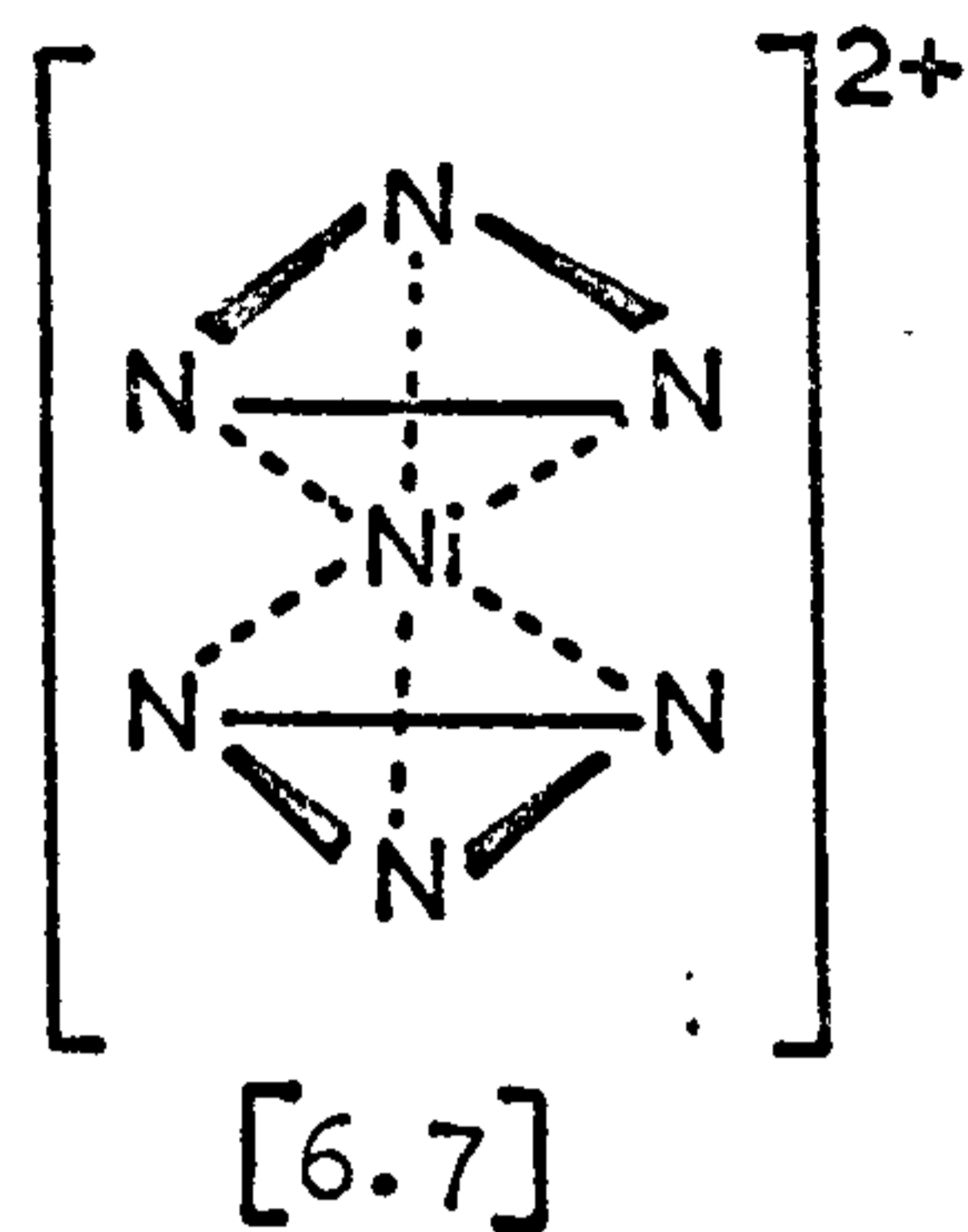
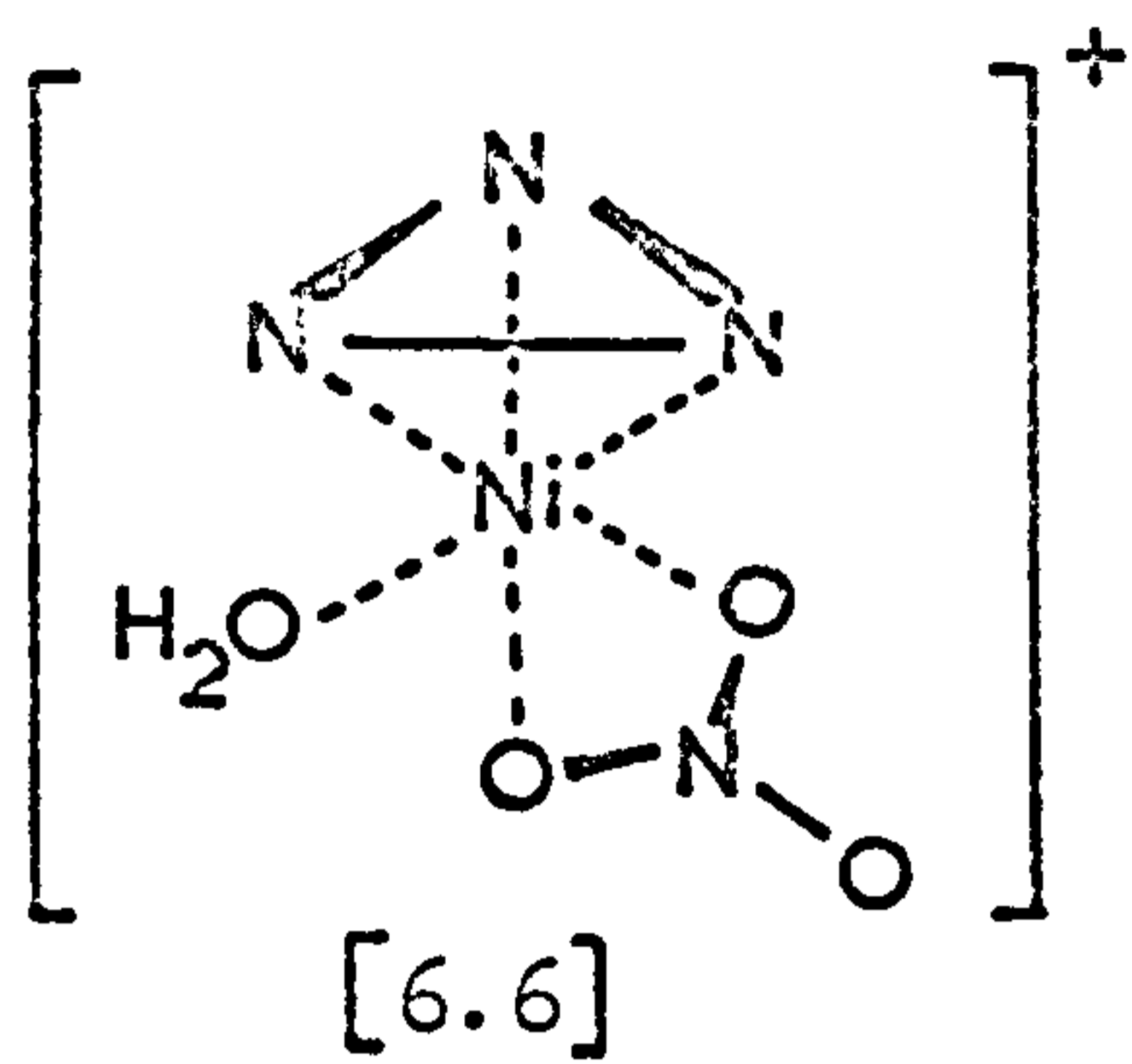
X = E, ref. 15  
X = C<sub>6</sub>H<sub>5</sub>, ref. 16

[6.4]



X = F, ref. 17

[6.5]



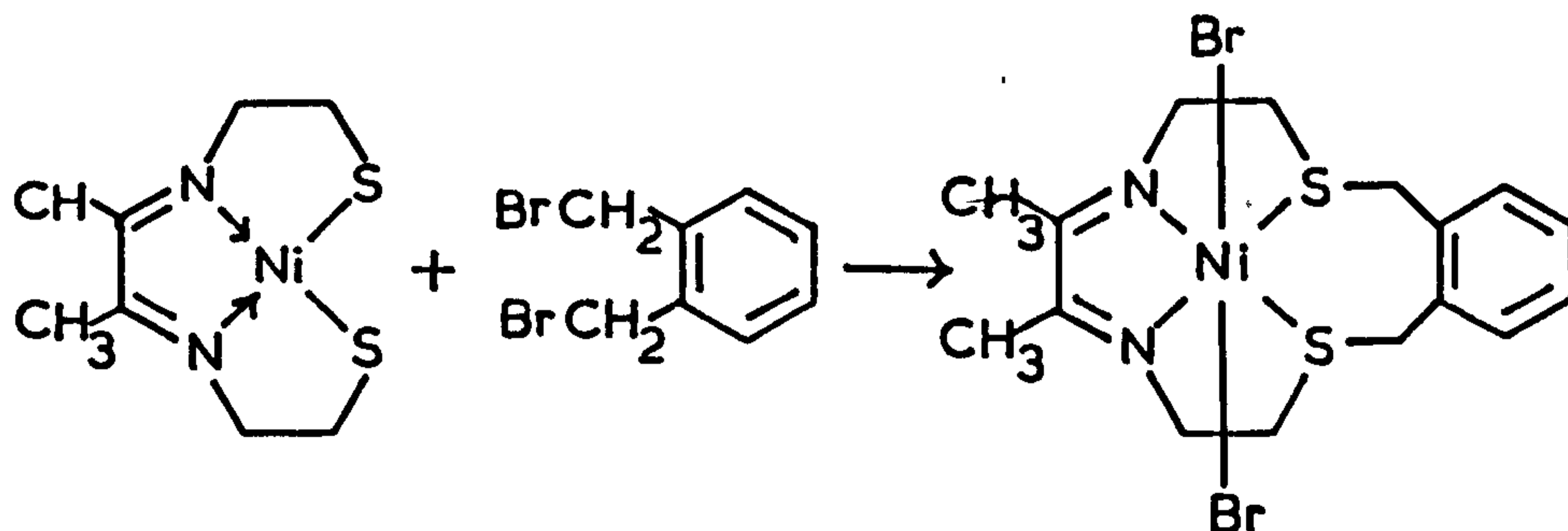


#### 6.2.4 Other template reactions giving macrocyclic ligands.

When products from the self condensation of o-aminobenzaldehyde were reacted with nickel(II) ions, complexes [6.6] and [6.7] of the cyclic trisanhydro trimer [6.8] were isolated<sup>18,19,20</sup>. Apparently a thermodynamic template effect operates in this case. The free trimer ligand will be much less strained than the tetramer, but is distorted<sup>18</sup> when complexed, to allow the three nitrogen atoms to bond to a nickel(II) ion.

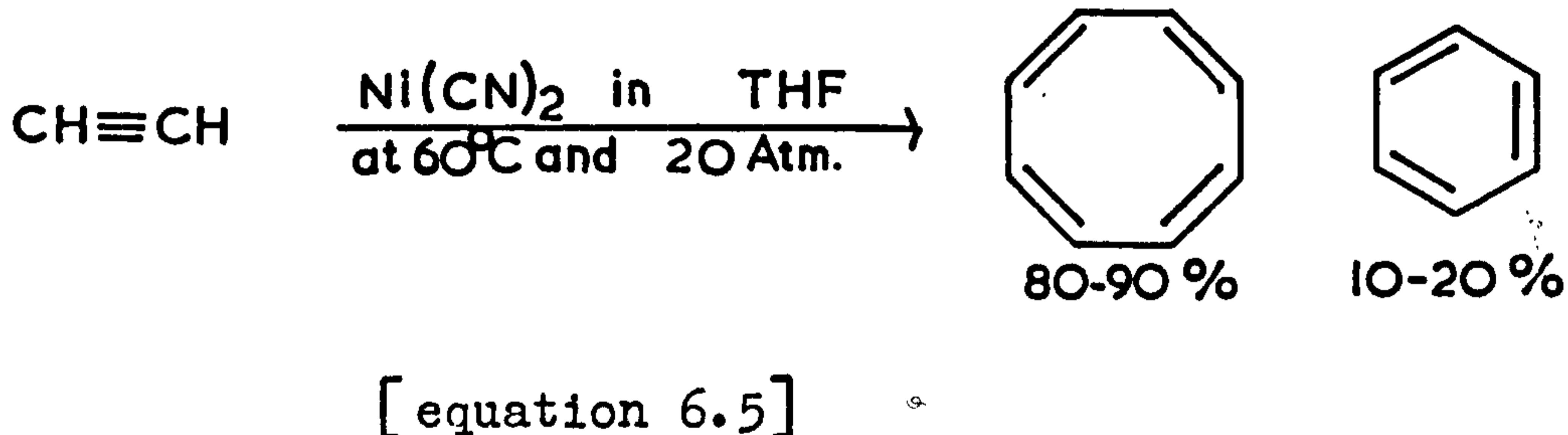
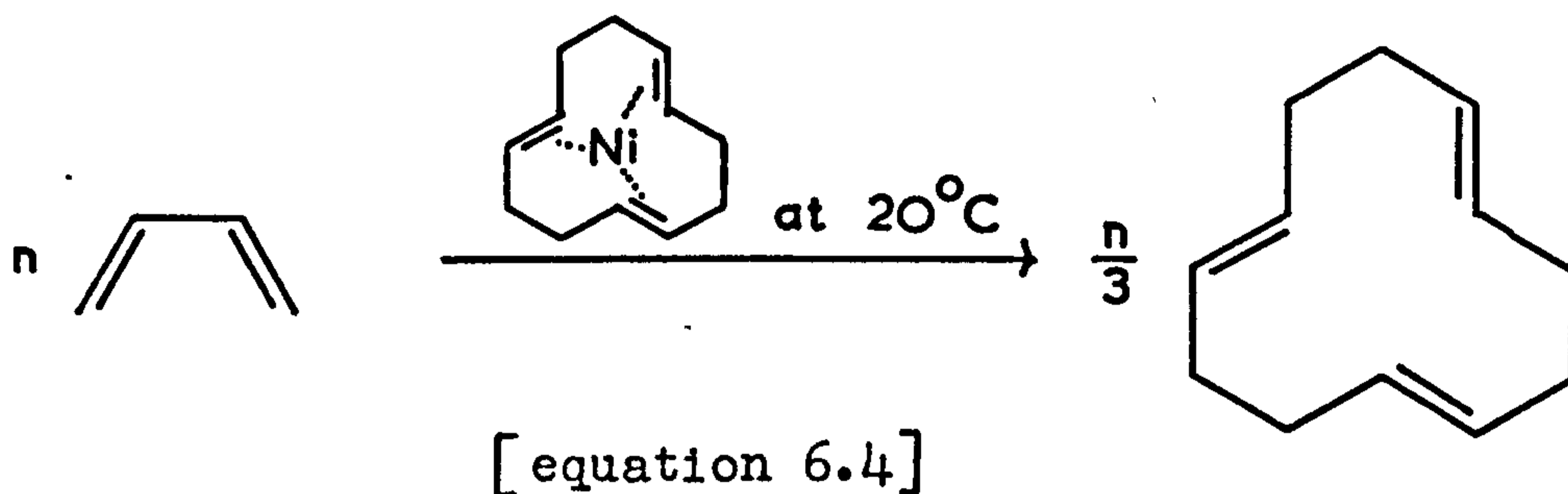
Complexes [6.9] and [6.10] containing hexadentate and pentadentate macrocyclic ligands have been isolated<sup>21</sup> by reaction of 2,6-diacetylpyridine with the appropriate polyamine in the presence of ferric ions. In [6.9] the macrocyclic ligand has lost a proton at an indetermined site.

A complex of a sulphur-containing macrocycle has been prepared<sup>22</sup> by the reaction shown in equation [6.3]



[equation 6.3]

Certain cyclization reactions of butadiene<sup>23</sup> and acetylene<sup>24,25</sup> are catalysed by metal ions or metal compounds, and are examples of truly catalytic, or kinetic, template reactions. Two examples are shown in equations [6.4] and [6.5].

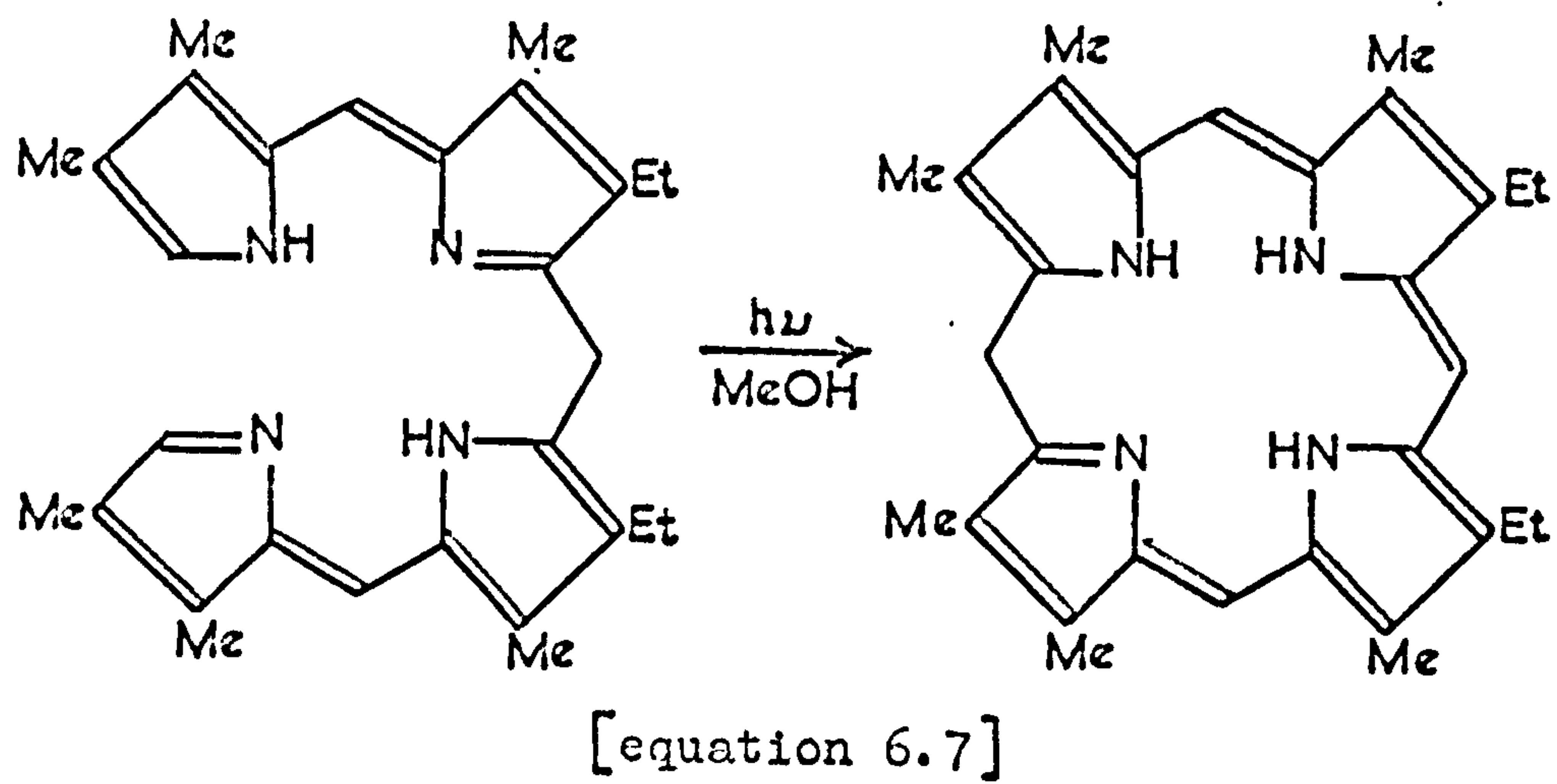
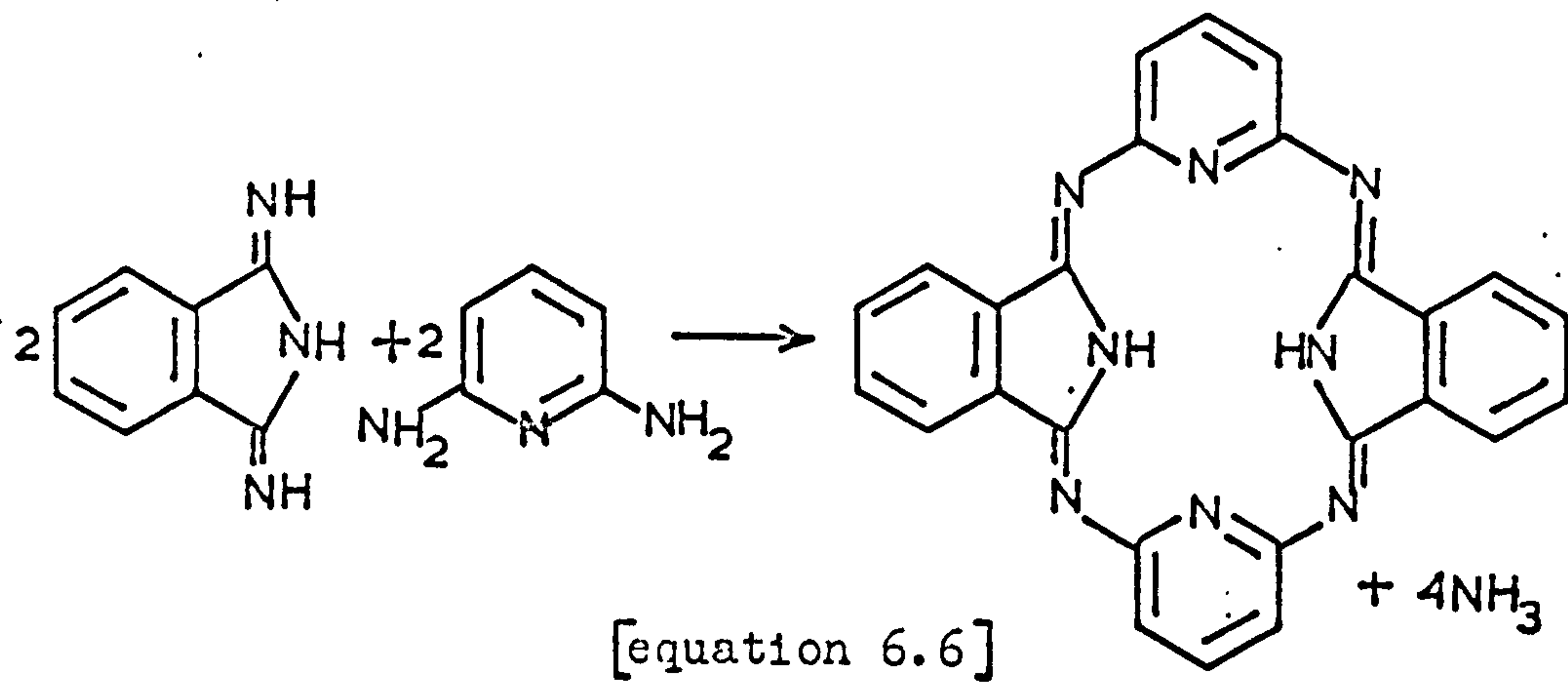


### 6.3 Stability of the cyclic ligand.

Certain properties of a particular ligand may lead to its formation in favourable quantities in an equilibrium situation such as that of equation [6.2].

#### 6.3.1. Conjugated cyclic ligands.

Phthalocyanines, porphyrins, corroles, and many



related compounds have a cyclic system of conjugation, and this aromaticity often makes them extremely stable, inert compounds. The cyclization of many of these compounds can be achieved in good yields in the absence of metal ions. Equation [6.6] shows a typical example.<sup>26</sup>

A corrole (a dehydrogenated corrin with the same carbon-nitrogen skeleton as the ring system in vitamin B<sub>12</sub> - see chapter 1) may be synthesized<sup>27</sup> by the light catalysed cyclization shown in equation [6.7].

In nearly all the examples of this type, cyclization is more readily achieved in the presence of a metal ion<sup>28,29,30,31</sup> where possibly both kinetic and thermodynamic template effects operate.

### 6.3.2 Steric considerations.

In both the kinetic and thermodynamic controlled syntheses of cyclic ligands (equations [6.1] and [6.2] respectively, page 141) the amount of cyclization as opposed to polymerization will depend critically on the length and conformation of the chain in the monomer. This effect will be referred to in chapter 7.

### 6.4. References.

1. D.H. Busch, Rec. Chem. Prog., 25, 107, (1964).
2. D.H. Busch, Adv. Chem. Series, 32, 1, (1963).

3. Ei Ochiai, *Coordin. Chem. Rev.*, 3, 49, (1968).
4. J.P. Collman, "Transition Metal Chemistry", Ed. Carlin, Vol 2., Arnold, 1966, page 1
5. R.O.C. Norman, "Principles of Organic Synthesis", Methuen, 1968, page 92.
6. N.F. Curtis, *J. Chem. Soc.*, 4409, (1960)
7. N.F. Curtis, *Coordin. Chem. Rev.* 3, 3, (1968).
8. N.F. Curtis and R.W. Hay, *Chem. Comm.*, 524, (1966).
9. N. Sadasivan and J.F. Endicott, *J. Amer. Chem. Soc.*, 88, 5468, (1966).
10. G.A. Melson and D.H. Busch, *J. Amer. Chem. Soc.*, 86, 4834, (1964).
11. L.T. Taylor, S.C. Vergez and D.H. Busch, *J. Amer. Chem. Soc.*, 88, 3170, (1966).
12. F. Seidel and W. Dick, *Ber.*, 60, 2018, (1927).
13. R.L. Rich and G.L. Stucky, *Inorg. Nucl. Chem. Letters*, 1, 61, (1965).
14. J.L. Karn, and D.H. Busch, *Nature*, 211, 160, (1966).
15. G.N. Schrauzer, *Chem. Ber.*, 95, 1438, (1962).
16. F. Umland and D. Thierig, *Angew. Chem. Internat.*, 1, 333, (1962).
17. N.J. Rose, D.A. Baldwin, V. Litvinov and D.H. Busch, *Abst. 156th Meeting A.C.S., Inorg. Div., Abs. 99.*
18. E.B. Fleischer and E. Klem, *Inorg. Chem.*, 4, 637, (1965)
19. G.A. Melson and D.H. Busch, *J. Amer. Chem. Soc.*, 87, 1706, (1965).

20. L.T. Taylor, S.C. Vergez and D.H. Busch, J. Amer. Chem. Soc., 88, 3170, (1966).
21. J.D. Curry and D.H. Busch, J. Amer. Chem. Soc., 86, 592, (1964).
22. M.C. Thompson and D.H. Busch, J. Amer. Chem. Soc., 86, 3651, (1964).
23. G. Wilke et al. Angew. Chem. Internat., 2, 105, (1963)
24. W. Reppe, O. Schlichtung, K. Klager, T. Toepel, Ann., 560, 1 (1948).
25. G.N. Schrauzer, P. Glockner and S. Eichler, Angew. Chem. Internat., 3, 185 (1964).
26. J.A. Elvidge and J.H. Golden, J. Chem. Soc., 700, (1957)
27. A.W. Johnson and I.T. Kay, J. Chem. Soc., 1620, (1965)
28. R. Grigg, A.W. Johnson and P. van den Broek, Chem. Comm. 502 (1967).
29. D. Dolphin, R.L.N. Harris, J.L. Huppertz, A.W. Johnson and I.T. Jay, J. Chem. Soc. (C), 30, (1966)
30. A.B.P. Lever, Adv. Inorg. Radiochem., 2, 28, (1965)
31. F.H. Moser and A.L. Thomas, "Phthalocyanine Compounds", Rheinhold, 1963.

## Chapter 7. Some New Quadridentate Macrocyclic Ligands.

### 7.1 Choice of systems.

7.1.1 Adaptation of the 'Curtis'<sup>4</sup> reactions.

7.1.2 More suitable systems for template synthesis.

### 7.2 Cyclic systems related to those of chapter 3.

7.2.1 Synthesis of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione.

7.2.2 Cyclic chelates from the dialdehyde.

7.2.3 Nomenclature and abbreviations.

### 7.3 Mechanism of the cyclization.

7.4 The reaction of 1,2-diaminoethane with the dialdehyde.

7.4.1 The effect of high dilution.

7.4.2 The effect of zinc (II) ions.

7.4.3 The effect of other metal ions.

7.5 The reaction of 1,3-diaminopropane and 1,4-diaminobutane with the dialdehyde.

7.6 The reaction of 1,2-diaminobenzene with the dialdehyde.

7.6.1 Acid catalysis.

### 7.7 The free macrocyclic ligands.

7.7.1 Analyses and molecular weight determinations.

7.7.2 Mass spectra.

7.7.3 Infrared spectra.

7.7.4 Electronic spectra.

7.7.5 N.M.R. spectra

7.8 References

It was decided to attempt the preparation of some cyclic 'model' ligands having the criteria which have been outlined in chapter 2.

### 7.1 Choice of systems.

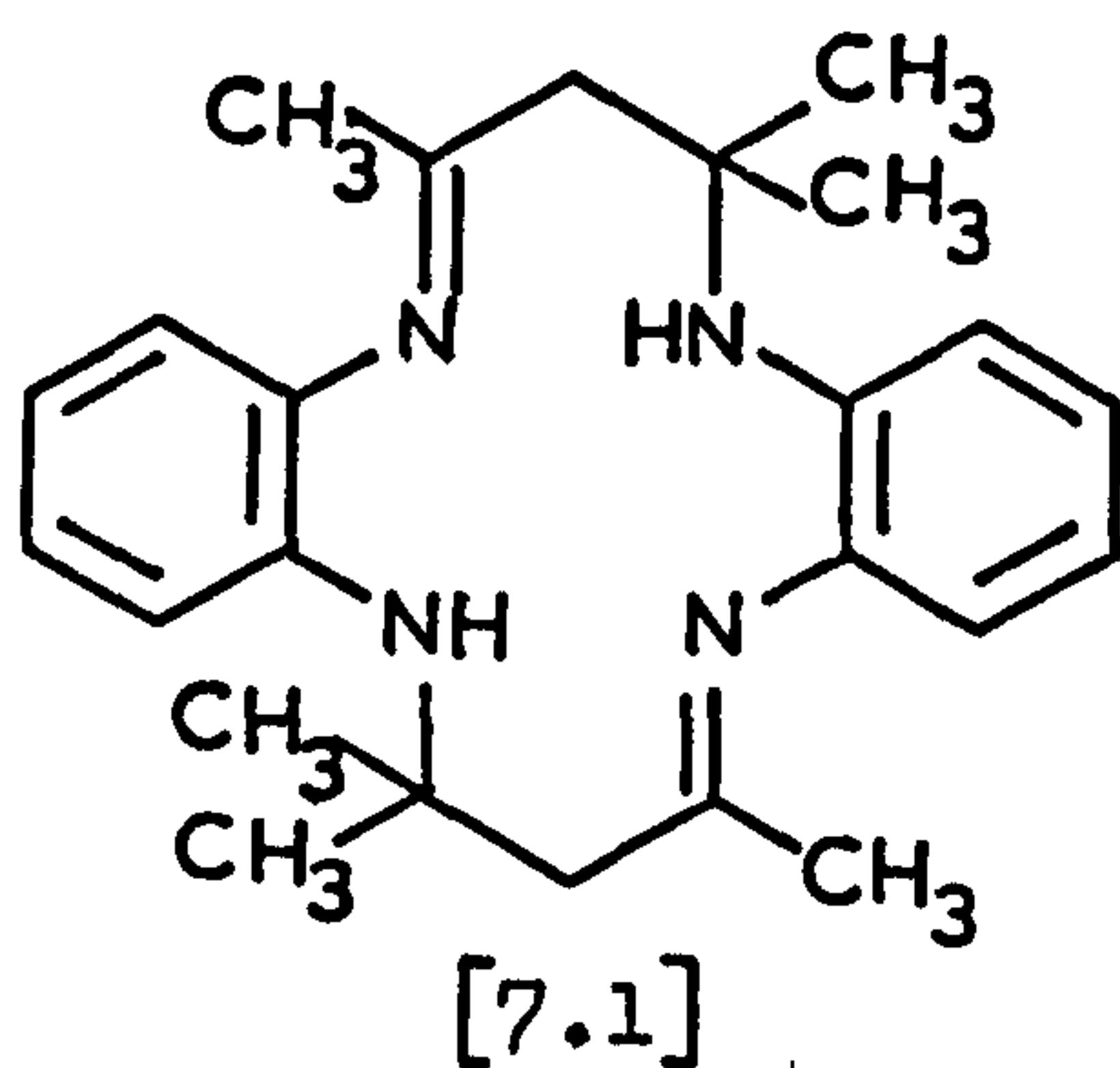
Of the macrocyclic ligands which have been prepared previously (see chapter 6), none were considered suitable as 'model' systems, and hence, it was proposed to synthesize some new systems. Some workers<sup>1,2,3</sup> have expressed their difficulties in preparing new macrocyclic planar chelates, and one<sup>3</sup> issued the impressive warning "we have been unable to prepare macrocyclic, approximately planar, chelates from 2,6-diacetylpyridine and diethylenetriamine and from various combinations of polyfunctional ketones, amines, esters, amides, acetals and other compounds".

Since template syntheses have apparently failed in so many cases it was decided to base our synthesis of macrocyclic planar chelates on reactions of functional groups for which some template activity of metal ions has already been substantiated.



### 7.1.1 Adaptation of the 'Curtis'<sup>4</sup> reactions.

The macrocyclic ligands resulting from the condensation of acetone or mesityl oxide with aliphatic diamines<sup>4</sup> (see page 146) do not lose protons to give anionic ligands, and hence, uncharged complexes of metal(II) ions. However, it was hoped that if the synthesis could be adapted to aromatic diamine compounds, the resulting macrocycle (e.g. [7.1]) might more readily lose two protons from the amino groups to give the required uncharged metal(II) complexes. 1,2-Diaminobenzene, for example, readily loses protons when acting as a chelate in square-planar complexes.<sup>5</sup>

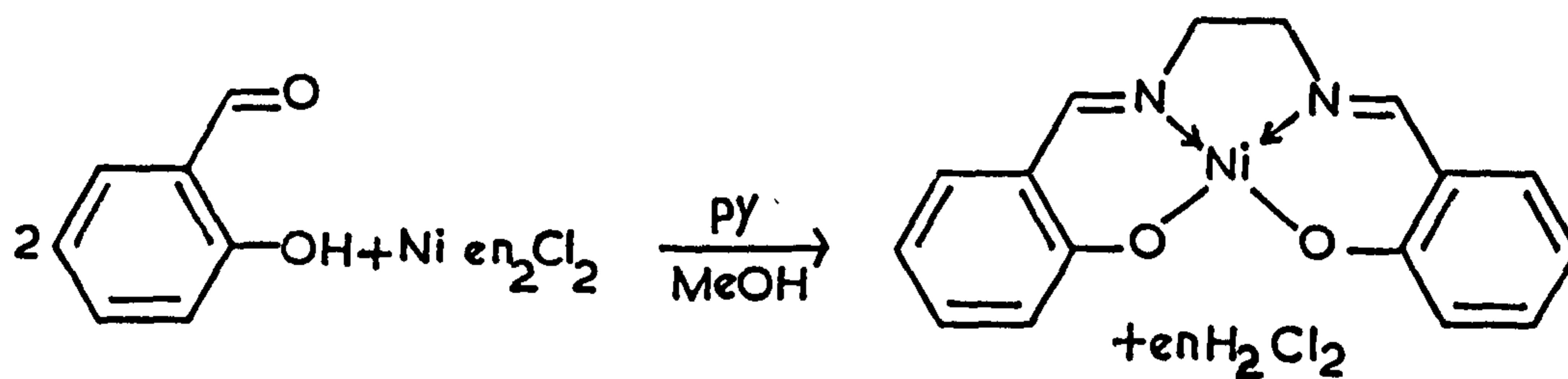


Many attempts using both 1,2-diaminobenzene and 1,8-diaminonaphthalene under comparable conditions to those used<sup>4</sup> for synthesis of metal chelates of the macrocycles [6.1] (page 146) failed to give anything

other than intractable tars.

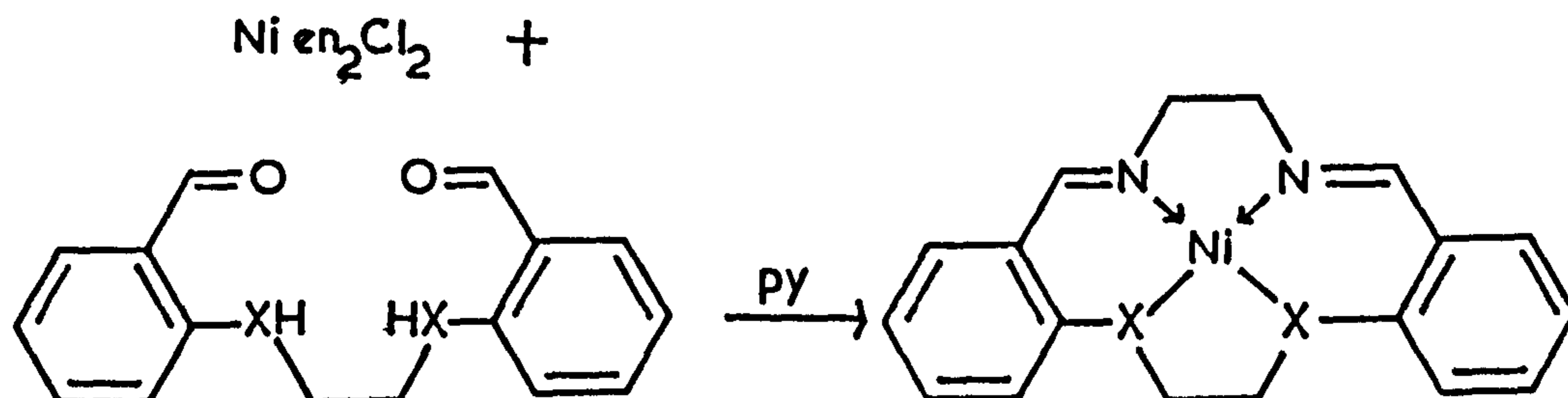
### 7.1.2. Suitable systems for template synthesis.

There have been indications<sup>6,7,8</sup> that metal ions show template action in reactions of  $\beta$ -diketones and of salicylaldehyde with amines to give chelate complexes. An example<sup>8</sup> is shown in equation [7.1]

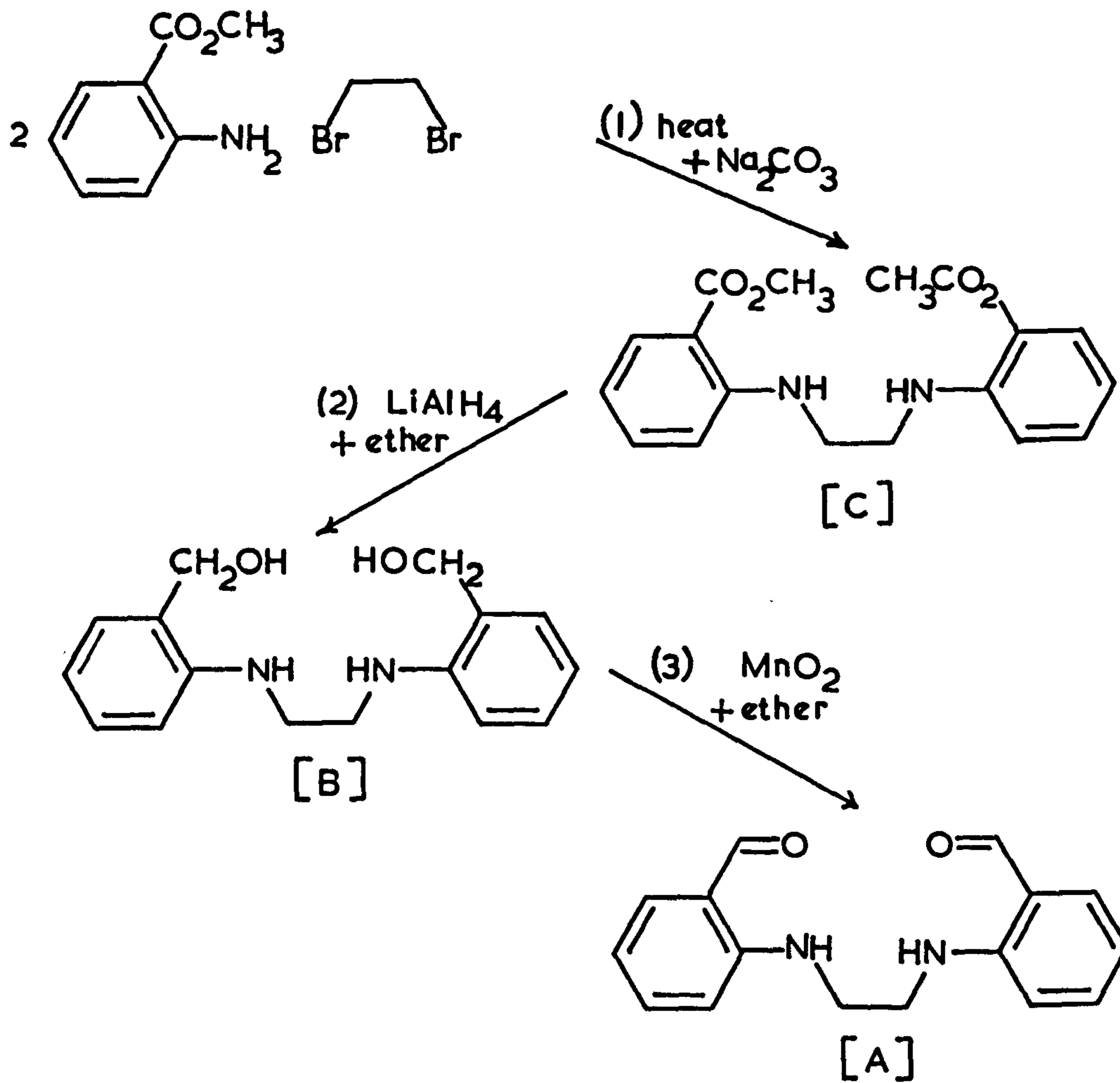


[equation 7.1]

This led to the idea that if a suitably bridged diketone were available a similar reaction might give a macrocyclic ligand complex, as in equation [7.2]. For our purposes (see chapter 2) it would be desirable for X to represent a nitrogen atom.



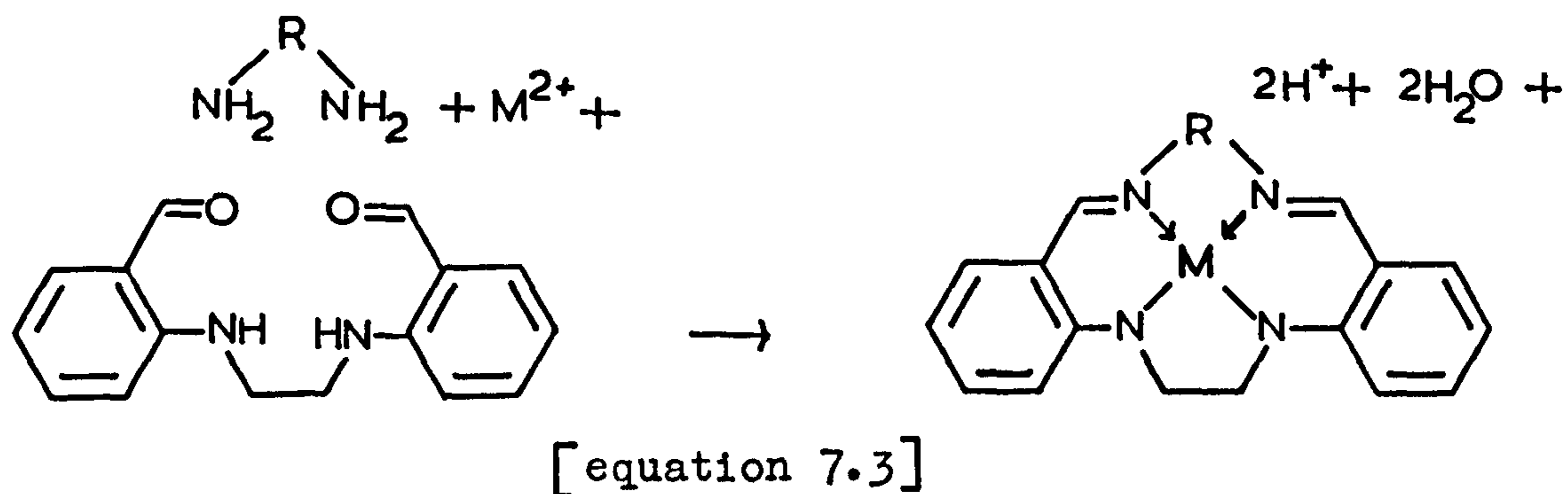
[equation 7.2]



[7.2]. The synthesis of 4,7-diaza-2,3:8,9-dibenzo-decane-1,10-dione.

## 7.2. Cyclic systems related to those of chapter 3.

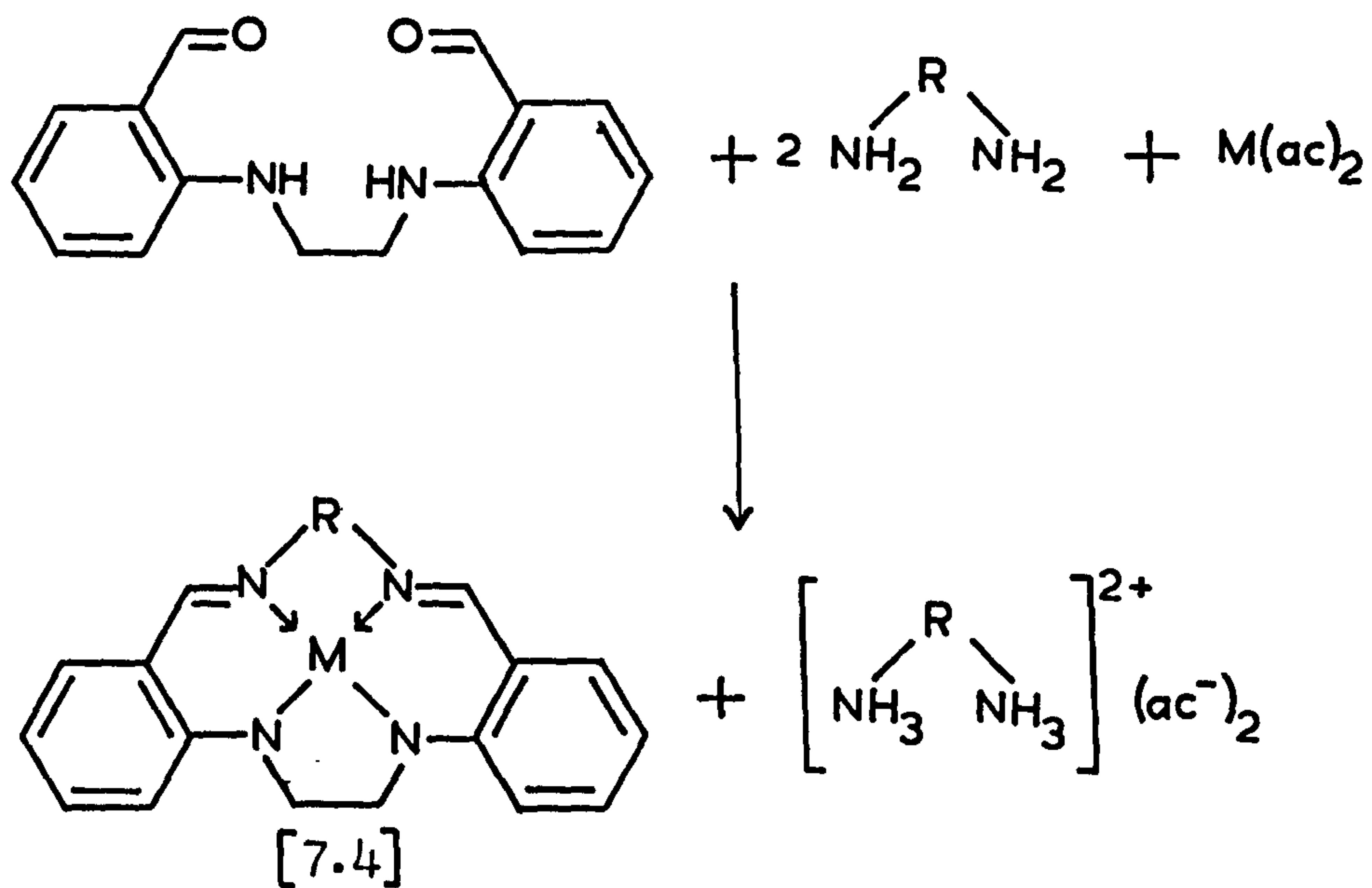
If the reaction shown in equation [7.2] could be extended to other metals and other diamines, as in equation [7.3], complexes of a range of cyclic ligands analogous to those of chapter 3 (general formula [3.1] page 31) would be available.



### 7.2.1 Synthesis of 4,7-diaza-2,3:8,9-dibenzodecane - 1,10 - dione.

The scheme outlined in [7.2] (opposite) was used to prepare 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione ([7.2] A), which will hereafter be referred to as the dialdehyde. The new compounds A, B and C are fully described in the experimental section.

The only problem experienced in scheme [7.2] occurred in what appears to be the simplest step, i.e.(1). Initially the reaction of methylanthranilate (excess) and 1,2-dibromoethane was attempted in the absence of



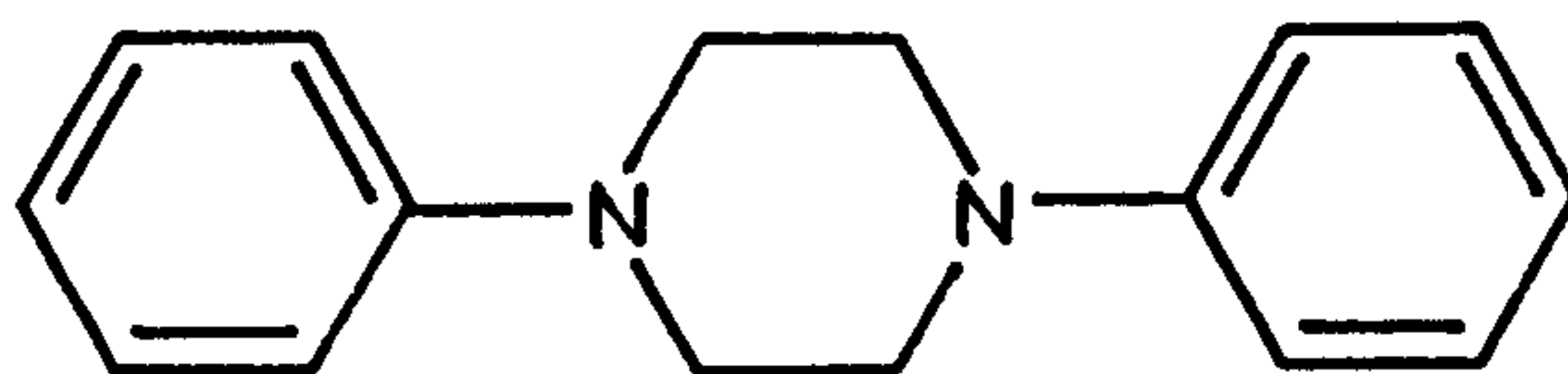
$\text{ac}^- = \text{acetate ion}$

$\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}.$

$\text{R} = -(\text{CH}_2)_2-, -(\text{CH}_2)_3-, -(\text{CH}_2)_4-, -\text{C}_6\text{H}_4-.$

[Equation 7.4]. The synthesis of the macrocyclic metal chelates.

solid sodium carbonate. After a short period of heating a reaction proceeded vigorously, with a rapid evolution of gas. The resulting mixture deposited N,N'-diphenylpiperazine [7.3] on cooling (see page 308 for details of characterization.) The N,N'-diphenylpiperazine must result by hydrolysis and decarboxylation of the methyl anthranilate ester group. Heating 1,2-dibromoethane and aniline together gives N,N'-diphenylpiperazine.<sup>9</sup>



[7.3]

The formation of N,N'-diphenylpiperazine was suppressed by heating methyl anthranilate and 1,2-dibromoethane together with an excess of solid sodium carbonate, and vigorously stirring. Sodium carbonate reacts with the liberated hydrogen bromide, thus reducing hydrolysis of the ester group.

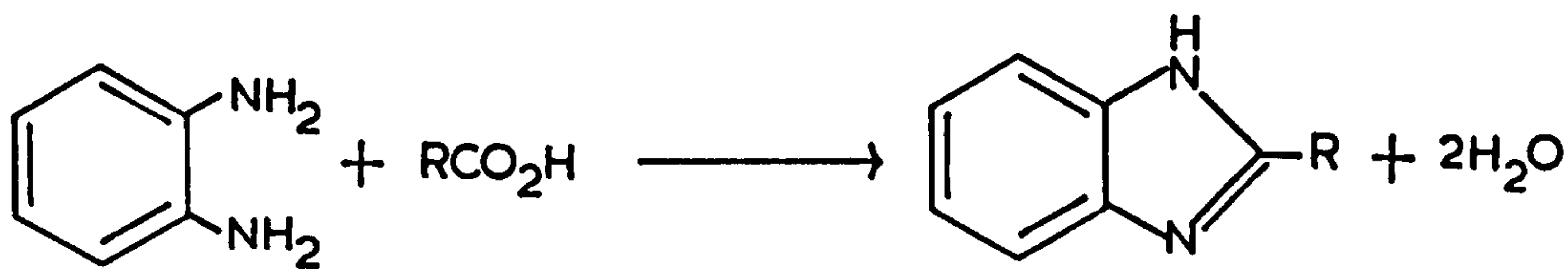
#### 7.2.2 Preparation of cyclic complexes from the dialdehyde.

It was found that the reaction outlined in equation [7.4] gave very good yields of cyclic complexes, general formula [7.4], for the three metal ions shown,

and for four different bridging groups R. Evidence for the formulation [7.4] will be presented in the chapters (8 and 9) describing the metal complexes.

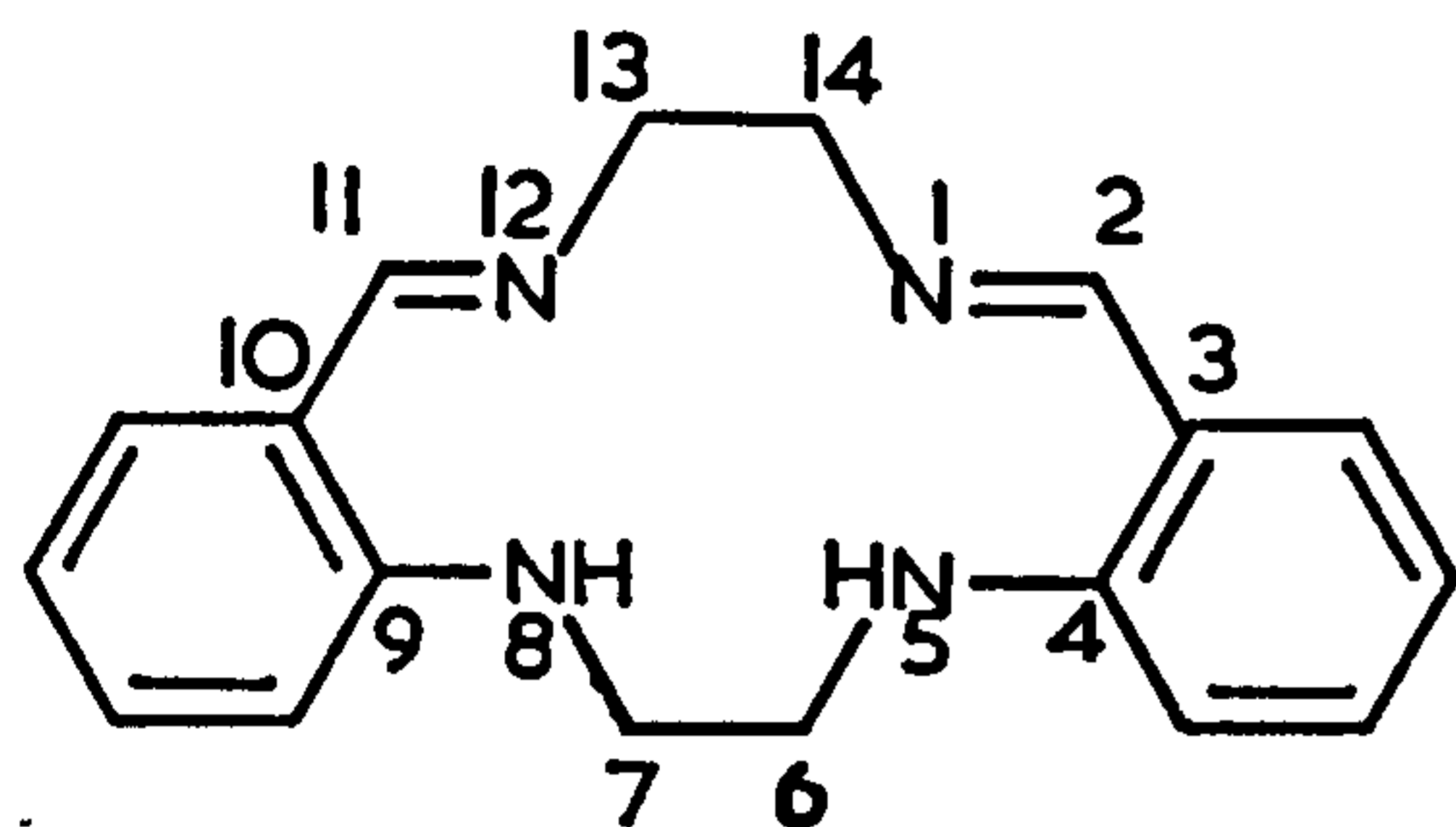
For the aliphatic bridging groups (R) the reaction was complete after refluxing in methanol for about six hours (vigorously stirring was required to reduce violent bumping), but longer reaction times (16-20hr.) were required for the complexes with a phenylene bridging group.

For the aliphatic bridging groups (R) two moles of the diamine were used, one of which was required to neutralize liberated acetic acid. Since 1,2-diaminobenzene can react with carboxylic acids<sup>10</sup> according to equation [7.5] it was judged expeditious to use three moles of this diamine.

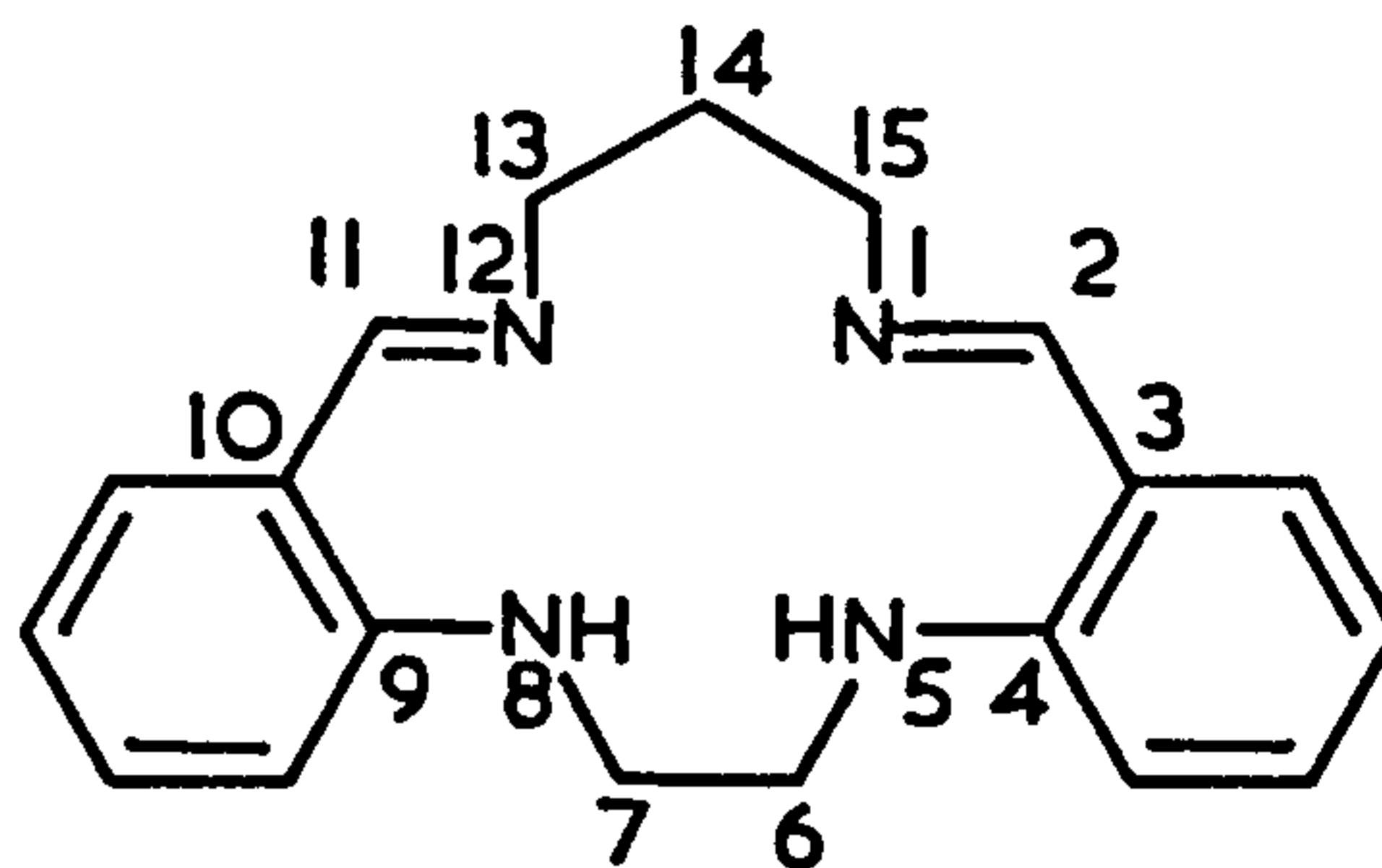


[equation 7.5]

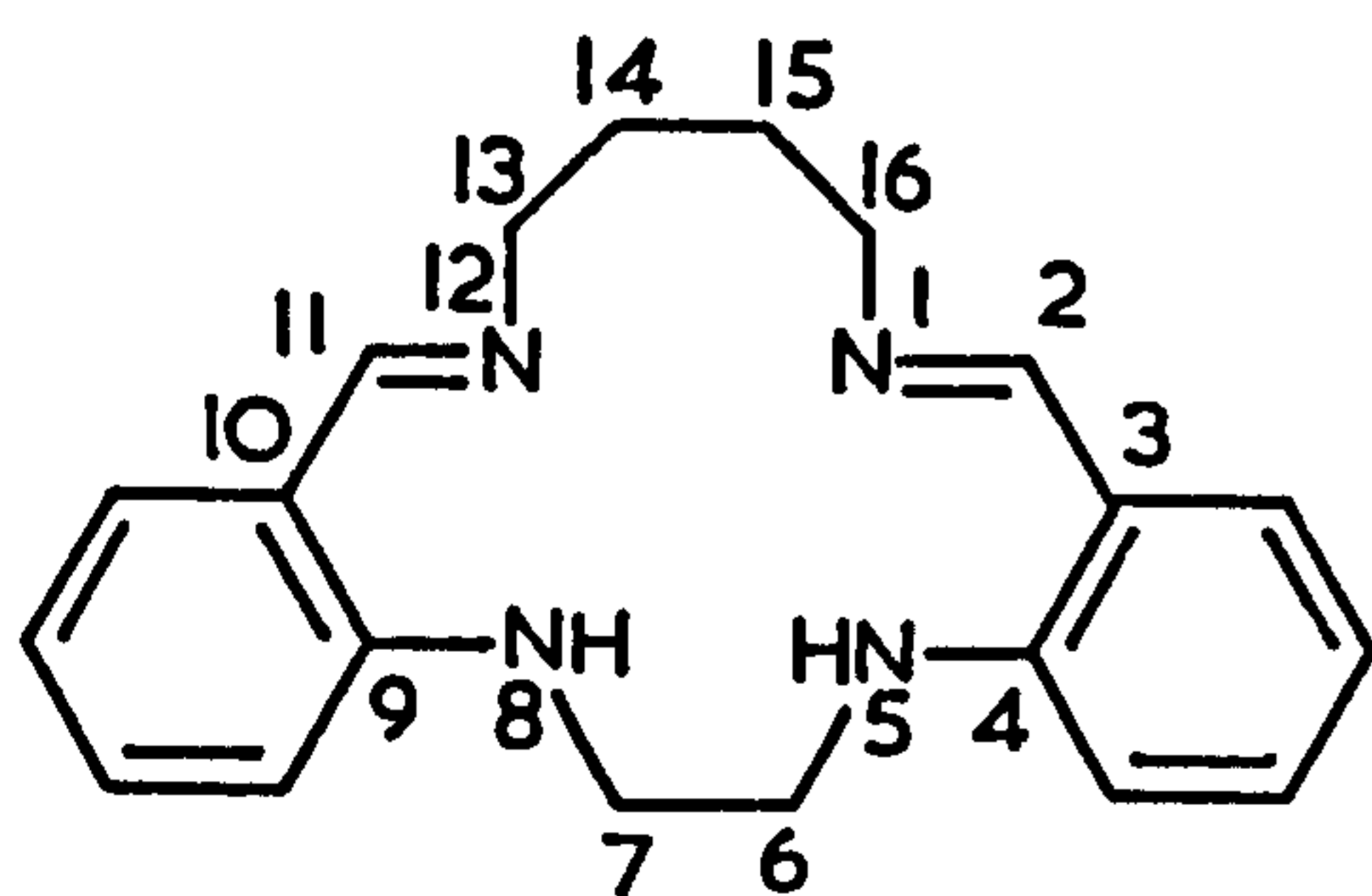
More complete details of the reaction are given in the experimental section (chapter 11).



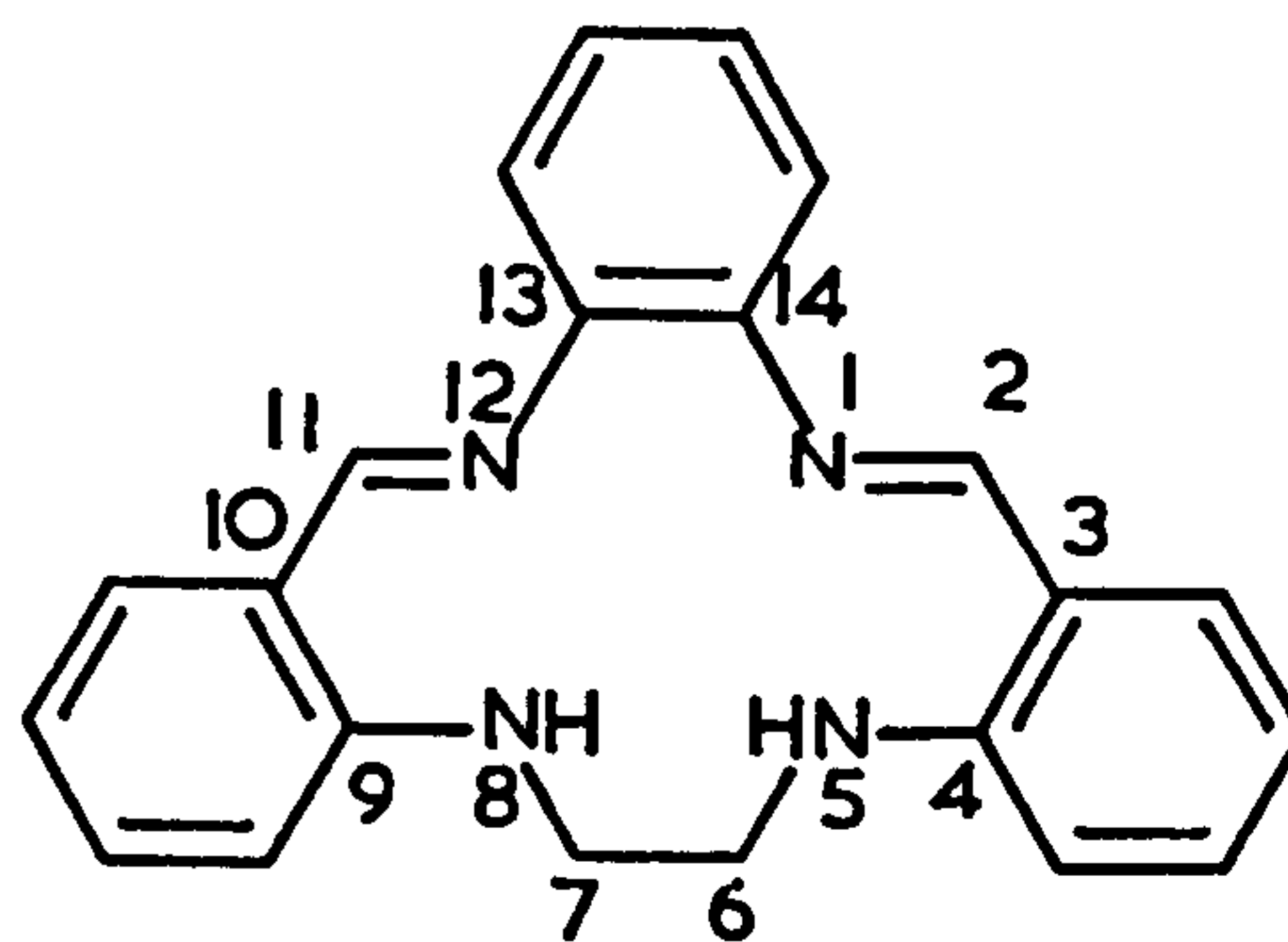
[7.5]



[7.6]



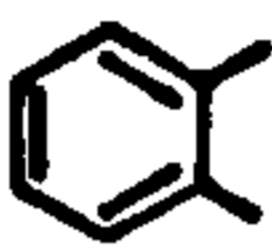
[7.7]



[7.8]



### 7.2.3 Nomenclature and abbreviations.

The nomenclature is based on the large ring of the free ligand, which has four nitrogen atoms. The full names of the ligands are given in table [7.1]. The numbering of the atoms is shown in structures [7.5], [7.6], [7.7] and [7.8]. A different system was used in our preliminary note<sup>11</sup>, which described only complexes of ligands with 2 carbon atoms in the bridge (i.e.  $R = -(CH_2)_2$  and ). The system adopted here allows the numbers 1 - 12 to represent atoms in the same portion of the molecule even when the length of the bridging group is varied.

Formula Number	Systematic Name	Abbreviation.
[7.5]	3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-diene.	cyen
[7.6]	3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclopentadecane-1,11-diene.	cytn
[7.7]	3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclohexadecane-1,11-diene.	cybuten
[7.8]	1,5,8,12-tetra-aza-3,4:9,10:13,14-tri-benzocyclotetradecane-1,11-diene.	cyphen

Table [7.1] Nomenclature and abbreviations of cyclic ligands.

Since the molecules differ only in the nature

of the group R (see [7.4] ) it is proposed to use the term 'cy' to refer to the rest of the molecule from azomethine nitrogen 1 to azomethine nitrogen 12, in conjunction with a suffix (en, tn, buten or phen) related to the bridging group R. The same abbreviations are used for the bridging group R in the acyclic ligands, see table [3.1] , page 32. The abbreviations for the macrocyclic ligands are also included in table [7.1] .

The complexes are named in the standard way<sup>12</sup>, by adding the suffix '-ato' to the ligand (denotes an anionic ligand), followed by the complexed metal and its formal oxidation state, e.g. the complex [7.4] ,  $R = -(CH_2)_2^-$ ,  $M = Ni(II)$  is called 3,4:9,10 - dibenzo - 1,5,8,12-tetra-azacyclotetradecane-1,11-dieneatonickel(II).

For the abbreviations of the complexes we shall follow the now standard practice of not indicating loss of protons from the ligand on complexation, e.g. Nicyen refers to the complex [7.4],  $R = -(CH_2)_2^-$ ,  $M = Ni(II)$  in which the ligand is dianionic by loss of two protons from the amine nitrogen atoms. Abbreviations for the complexes are listed in [8.1] (page 189) and [9.1] (page 210).

### 7.3 Mechanism of the cyclization.

The syntheses summarized in equation [7.4] appear to be examples of template reactions. It was

decided to examine in more detail the reaction of each diamine with the dialdehyde, in order to elucidate the mechanism of the cyclizations. The reactions are treated in sections 7.4, 7.5 and 7.6.

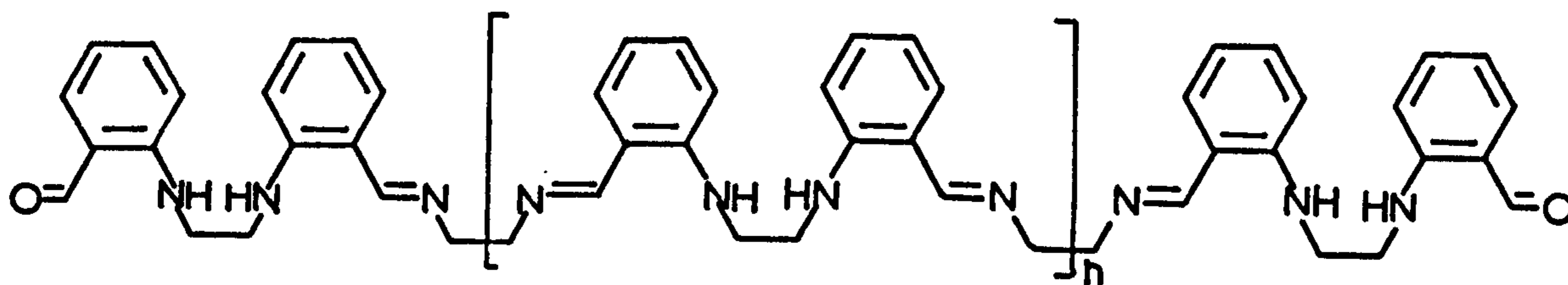
#### 7.4. The reaction of 1,2-diaminoethane with the dialdehyde.

When the dialdehyde was reacted alone with 1,2-diaminoethane under conditions similar to those used for the syntheses shown in equation [7.4] (i.e. refluxing in methanol for several hours), a white material, m.p. 283-288<sup>o</sup>, was obtained.

This substance is not the cyclic monomeric ligand [7.5], since this has a much lower melting point (see section 7.7). The mass spectrum showed no peaks which could be distinguished from background noise. In particular, no peak was detected at  $m/e = 292$  where the cyclic ligand [7.5] gives a strong line due to its molecular ion. This suggests that the white material does not contain any significant quantity of the cyclic ligand [7.5].

Formulation of the substance is hampered by its extremely low solubility in most solvents. The infrared spectrum as a nujol mull indicates the absence of carbonyl groups, and the presence of amino groups. Possibly the material is a low polymer, since analysis

results fit tolerably well with a structure [7.9] with  $n=5$  to 6.



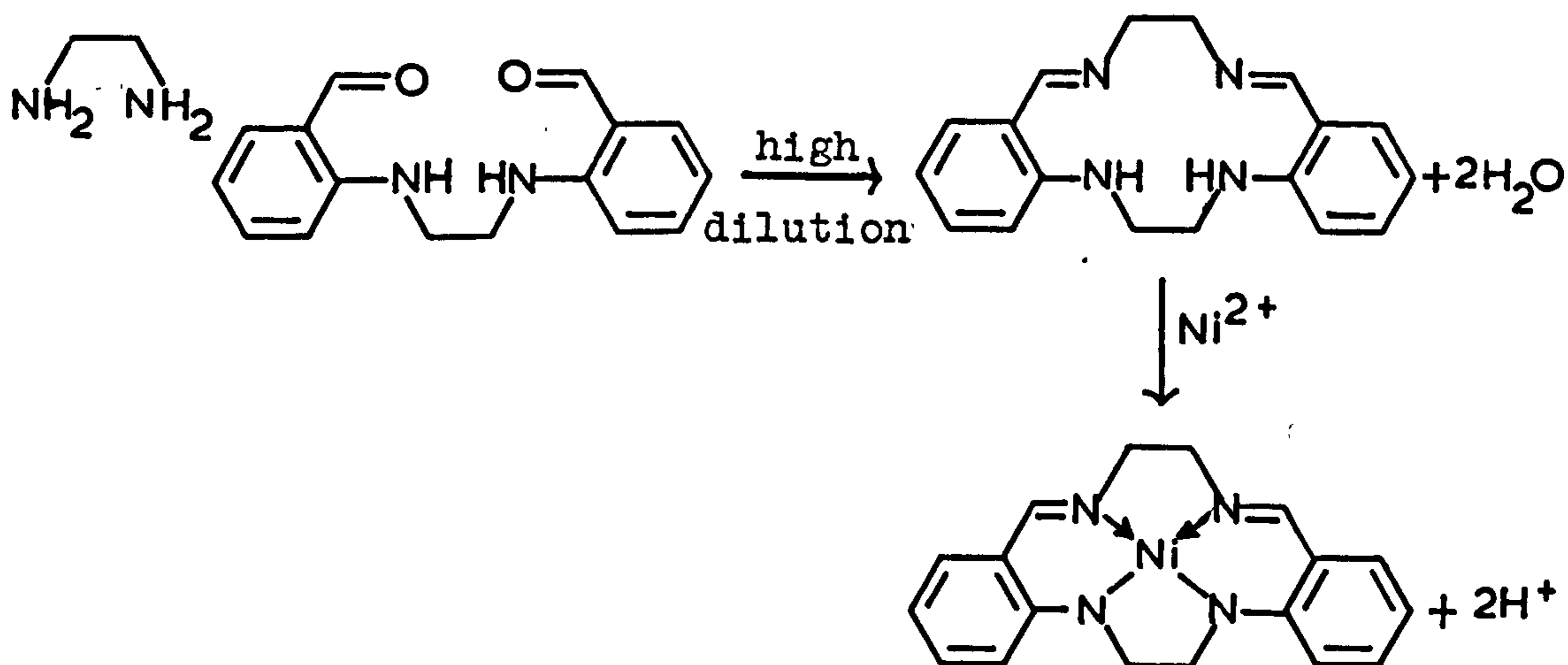
[7.9]

Only after treating the solid with a refluxing methanolic solution of nickel(II) acetate for 7 days was it possible to detect the formation of any Nicyen (identified by comparison of its electronic and infrared spectra with those of an authentic sample).

These facts suggest that in the synthesis of Nicyen by heating the dialdehyde in a methanolic solution of 1,2-diaminoethane and nickel(II) acetate the nickel(II) ion acts as a kinetic template (page 143). Thermodynamic template action (page 144) of the metal ion is less likely, because the product in the absence of metal ions seems to contain no free cyclic ligand, and requires a much longer period of reaction with nickel(II) ions to give the required complex Nicyen. However, there is another possible function of the metal ion, which fits the facts equally well. This is discussed in the following section.

#### 7.4.1 The effect of high dilution.

1,2-Diaminoethane forms very stable chelates with transition metal ions<sup>13</sup>, and so its concentration in solution in a non-complexed form will be very low under the conditions used in equation [7.4]. The dialdehyde is only sparingly soluble in methanol, and so its concentration in solution will also be low. For a kinetically controlled process which can lead to either rings or polymer chains (see equation [6.1] page 141) the formation of rings is favoured by high dilution.<sup>14</sup> It is possible that the conditions of equation [7.4] approximate to high dilution, and that the cyclic ligand is formed prior to complexation with nickel(II) ions (equation [7.6]).



Under "high dilution" conditions (see page 314) the reaction of 1,2-diaminoethane and the dialdehyde gave a solid product on evaporation, from which the free cyclic ligand (cyen) was extracted in approximately 50% yield.

Evidence for formulation of this material as [7.5] is presented in section 7.7.

Stirring the free ligand for a few minutes with a boiling methanolic solution of nickel(II) acetate gave Nicyen. Hence the 'pseudo high dilution' mechanism shown in equation [7.6] cannot be ruled out. It should be remarked that this 'pseudo high dilution' mechanism is also a possibility in other template reactions (chapter 6) which appear to be kinetically controlled. It is perhaps significant that many of these involve the condensation of amines with carbonyl compounds, in the presence of template ions which are known to form strong amine complexes.

#### 7.4.2. The effect of zinc(II) ions.

Reaction of the dialdehyde and 1,2-diaminoethane in a refluxing methanolic solution of zinc(II) acetate gave a good yield of the free cyclic ligand [7.5].

The function of the zinc(II) ion in aiding the cyclization may be due to either of two mechanisms closely related to those described in sections 7.4 and 7.4.1.

The zinc(II) ion is known<sup>13</sup> to form strong complexes with 1,2-diaminoethane, and so a 'pseudo high dilution' mechanism (see section 7.4.1) is possible.

Alternatively, zinc may act as a truly catalytic template ion, i.e. it may reduce the free activation energy in the transition state by complexing with the

ligand centres, but is displaced from the final cyclic ligand.

#### 7.4.3. The effect of other metal ions.

The reaction was carried out as described in section 7.4, but the products were studied to see the effect of addition of various metal ions on the reaction. The solid product was examined in the following ways to judge whether it contained appreciable quantities of cyen, or was entirely the unknown 'polymer' described in 7.4.

(1) Infrared spectrum as a nujol mull. The infrared spectra of cyen and the 'polymer' are remarkably similar, and so estimation of the relative quantities of both in the solid product could not be made in this way. The purpose of this test was to see if appreciable quantities of other materials were present, e.g. excess dialdehyde and metal acetate or metal 1,2-diaminoethane complexes or metal cyen complexes.

(2) Melting points. Surprisingly this provided a good method for detecting either material. If infrared spectroscopy had shown the absence of other materials then melting in the range  $165-175^{\circ}$  was taken to indicate the presence of cyen. The unknown 'polymer' shows a characteristic transformation to a more crystalline form

Metal ion	Mg <sup>2+</sup>	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Ag <sup>+</sup>	Cd <sup>2+</sup>
(M)	a	a	b	a	a	a	a	a	a

Formation of Mcyen

yes yes yes

Formation of cyen

yes f yes f yes f yes f

Log K <sub>1</sub> of en complex	0.37	2.73	4.28	5.89	7.66	10.72	5.71	6.00	5.63
	c	c	c	c	c	d	c	e	d

Table [7.2]. Summary of the effect of addition of metal ions on the reaction between the dialdehyde and 1,2-diaminoethane (en).

(a) Addition as the hydrated metal acetate. (b) Addition as ferrous ammonium sulphate (+ sodium acetate), and as ferrous oxalate (repeat experiment) (c) Ref. 13, in 1M. KOI (d) Ref. 13, in 1M. KNO<sub>3</sub> (e) Ref. 13, in 1M. KNO<sub>3</sub> (value approximate) (f) High melting 'polymeric' material also obtained.



above 200° and melts with decomposition above 280°.

(3) Thin layer chromatography. Chromatographs of chloroform extracts of the solids were compared with a dilute chloroform solution of cyen. An extract of the high melting unknown described in 7.4 was also run for comparison, (see chapter 11 for details). The extract from the unknown 'polymer' showed a very small trace of cyen. When an extract from a solid showed a similar trace quantity of cyen it was assumed that this solid had a similar composition to the 'polymer'. In some cases the extracts showed considerable quantities of cyen.

(4) Mass spectra. The mass spectra of all the solids were run under the same conditions. The spectrum of cyen is shown on page F178. The 'polymer' showed a small peak at  $m/e = 208$ , but otherwise few peaks which could be distinguished with any certainty from those of the background. For samples which the above tests had shown to contain appreciable quantities of cyen the characteristic lines (page F178) of cyen were observed.

The results of these experiments are summarized in table [7.2].

The cyclic metal complexes were only obtained for the cobalt(II), nickel(II) and copper(II) ions. The free cyclic ligand was obtained from the reaction in the presence of iron(II), zinc(II) and cadmium(II) ions.

Table [7.2] also lists the stability constants of 1,2-diaminoethane complexes of the metal ions. It can be seen that all the metals aiding the cyclization reaction form strong complexes with 1,2-diaminoethane. This is consistent with both the 'high dilution' and kinetic template mechanisms suggested in sections 7.4 and 7.4.1.

The silver ion does not assist the cyclization process, even though it forms strong complexes with amines. This may be very significant. For the 'high dilution' mechanism the function of the metal ion is merely to reduce the concentration of 1,2-diaminoethane in solution. Silver(I) ions should be as effective as many of the other 'cyclizing' ions in this respect.

Where the silver(I) ion differs noticeably from the other ions is in its normal coordination geometry. Silver(I) diamine complexes have a linear arrangement of amine donors about the metal, forming polymeric species in solution<sup>16,17</sup>, whereas the other metal ions commonly form octahedral or square-planar diamine complexes. If the inability of the silver(I) ion to assist the cyclization, is due to its unsuitable coordination geometry a 'template' mechanism for the function of the other ions is suggested.

Apart from this case such a template mechanism seems to be remarkably insensitive to small variations in the coordination geometries of the metal ions, e.g. zinc(II)

and cadmium(II) seem to show similar 'template' properties, despite their considerable difference in their ionic radii.

This study has shown that the formation of cyen from the dialdehyde and 1,2-diaminoethane is favoured by either 'high dilution' conditions, or the addition of metal ions forming strong 1,2-diaminoethane complexes, provided these do not have a linear arrangement of nitrogen donors about the metal ion.

#### 7.5 The reaction of 1,3-diaminopropane and 1,4-diaminobutane with the dialdehyde.

When 1,3-diaminopropane and 1,4-diaminobutane were reacted with the dialdehyde in boiling methanol long white needles separated from solution. These proved to be the free cyclic ligands cytn [7.6] and cybuten [7.7]. Evidence for formulation as [7.6] and [7.7] will be presented in section 7.7

It is quite surprising that cyclization occurred so readily and that no 'polymer' products were detected. A study of molecular models showed that after one imino group has been formed (see [7.10]) the possibility of the free amino group approaching the remaining aldehyde group is quite high. The features in the molecule restricting possible positions of the free amino group, and

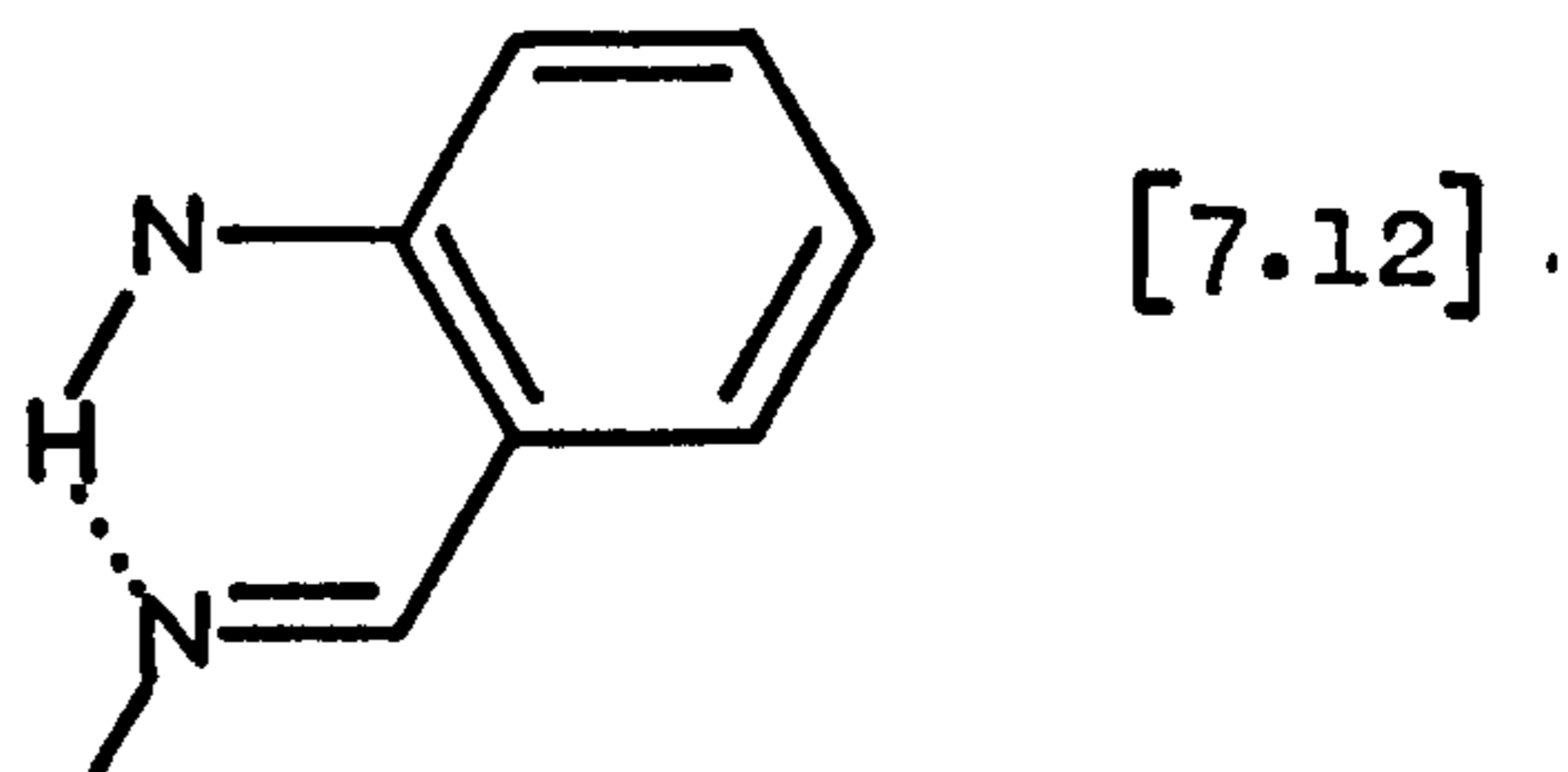
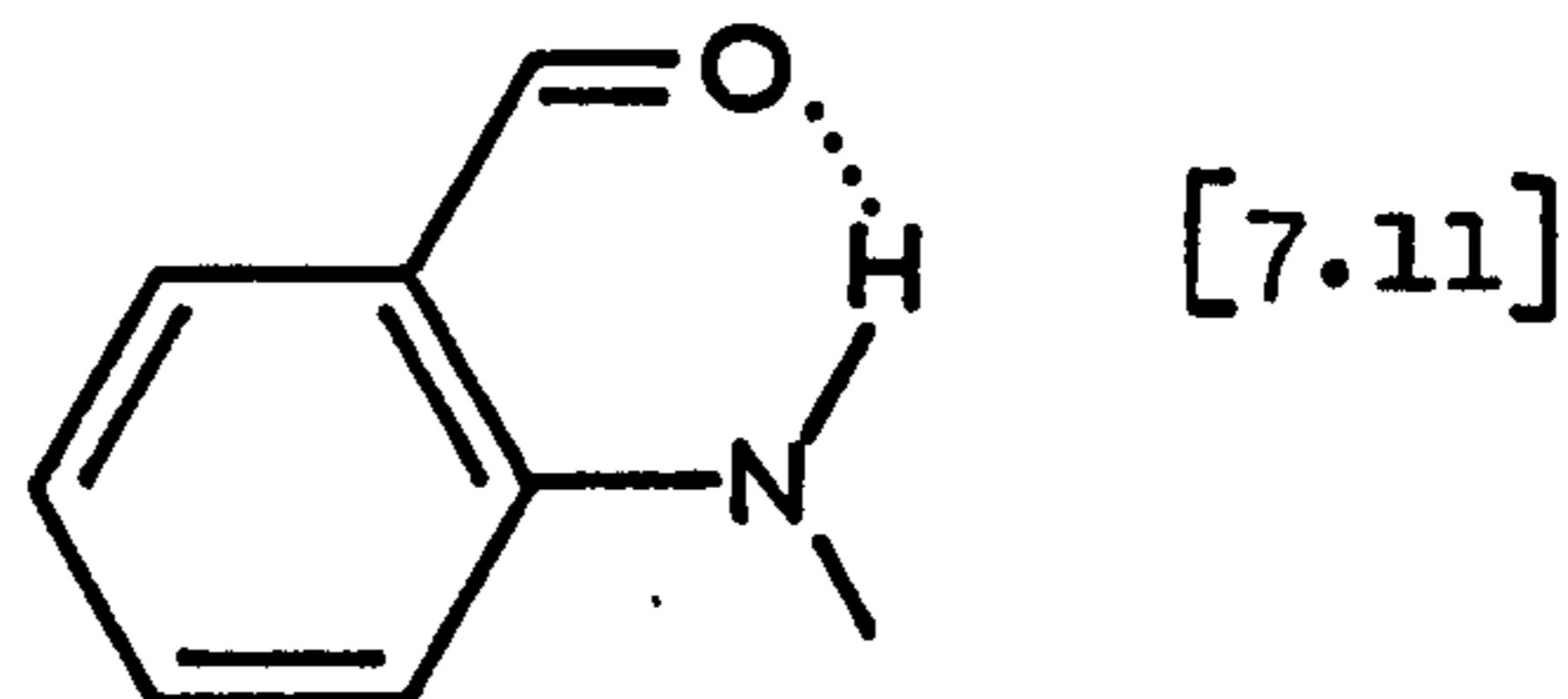
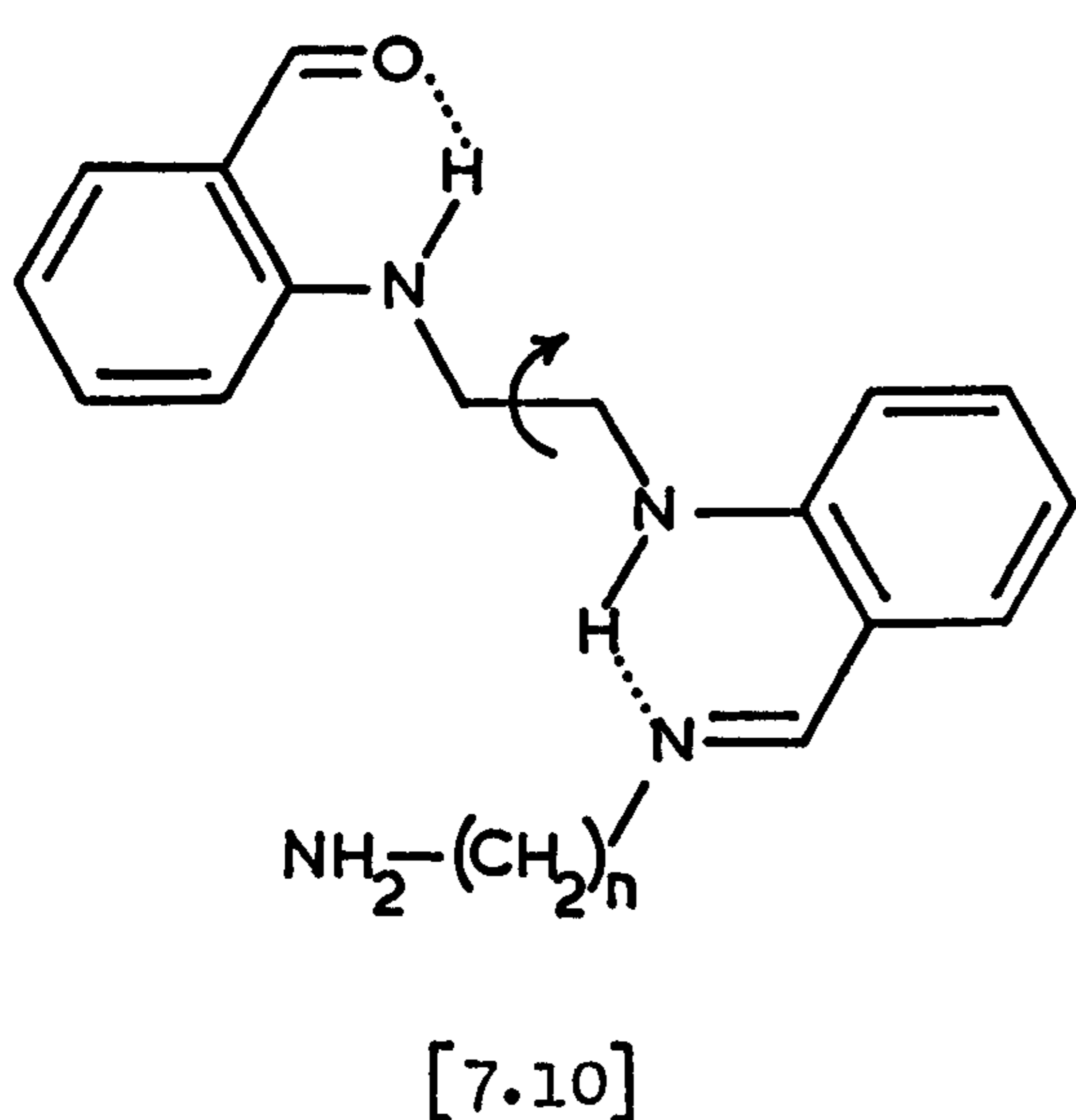
favouring its approach to the aldehyde group are;

(1) the assumed planarity and rigidity of the portions [7.11] and [7.12].

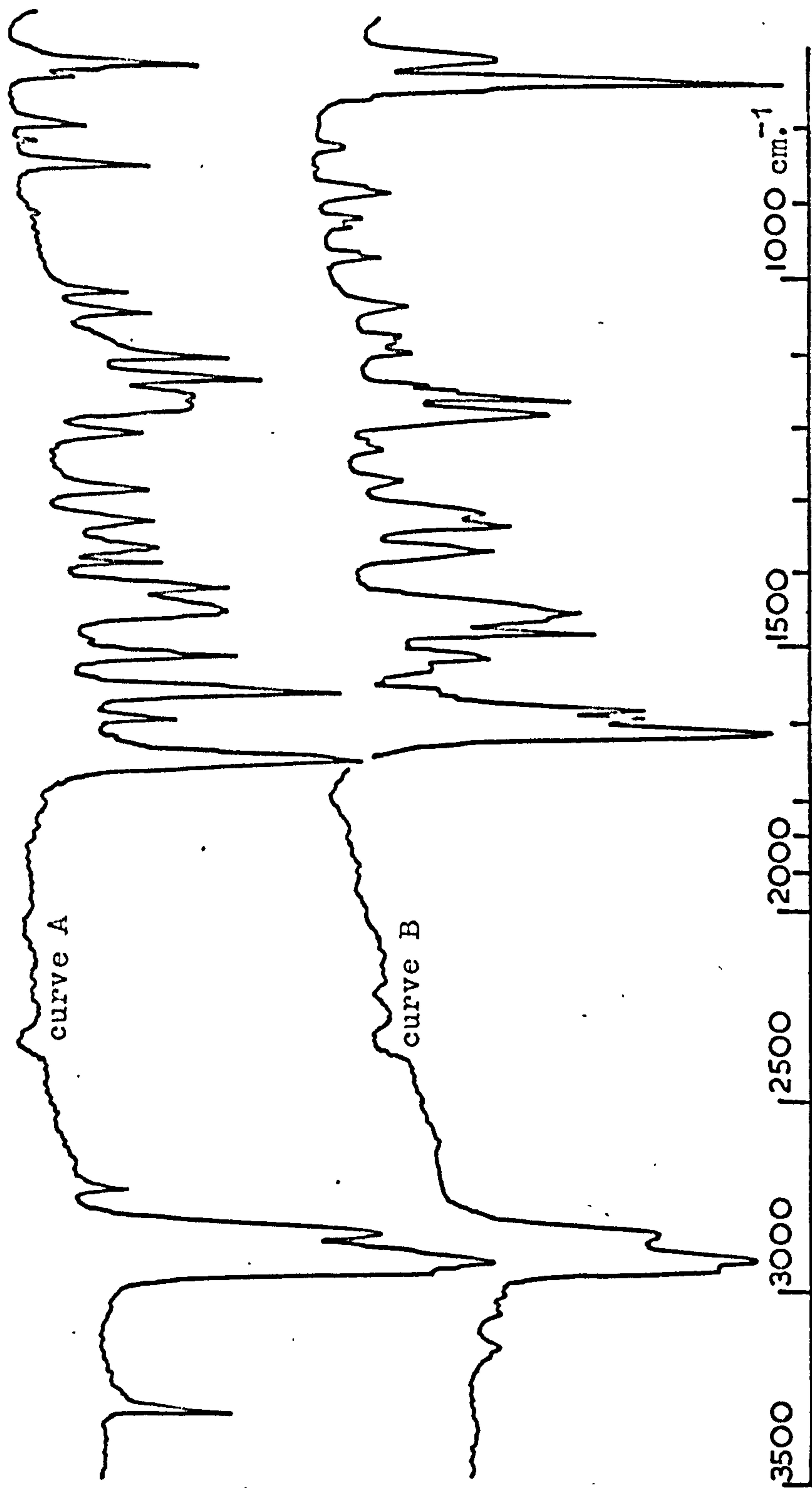
(2) the orientation of the  $\alpha$ -methylene group relative to the imino group bond.

(3) the assumed restricted rotation about the methylene to anilino nitrogen bonds.

(4) the rotation about the bridging methylene to methylene bond.



In order to explain the failure of 1,2-diaminoethane to cyclize under the same conditions it can only be supposed that the methylene chain ( $n=2$  in [7.10]) is too short for a reasonable frequency of the amino group



[7.13]. The infrared spectra of the dialdehyde (curve A) and the free cyclic ligand cypnen (curve B) as nujol mulls.

approaching the free aldehyde group. Hence, unless high dilution is used the aldehyde group will react preferentially with another amino group.

Since the free cyclic ligands cytn [7.6] and cybuten [7.7] reacted rapidly with nickel(II) acetate to give the corresponding nickel(II) complexes, there is no necessity to postulate any template activity of nickel(II) ions in the synthetic route to these complexes shown in equation [7.4] page 159.

#### 7.6 The reaction of 1,2-diaminobenzene with the dialdehyde.

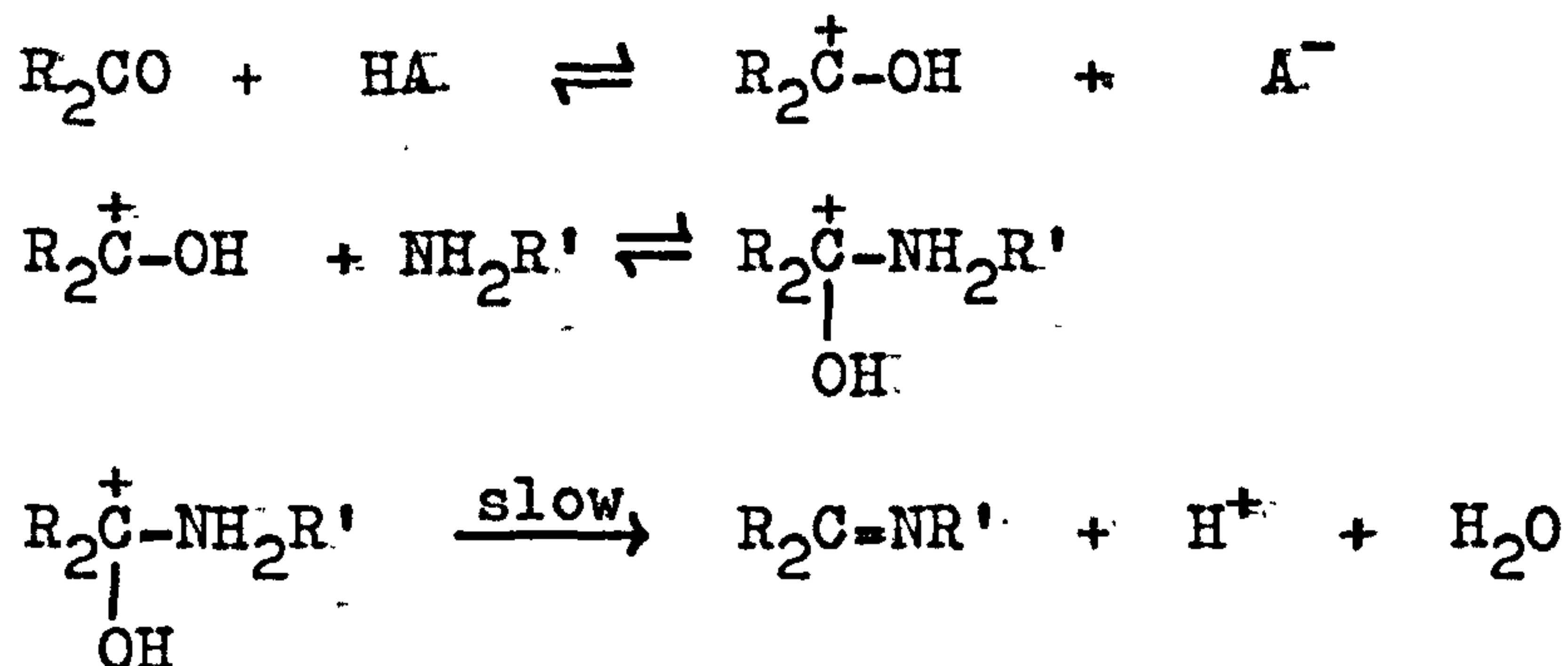
The dialdehyde was treated with a refluxing methanolic solution of 1,2-diaminobenzene, under an atmosphere of nitrogen. After six days the solid present (after washing with a little methanol) was judged to contain only the dialdehyde, by comparison of its infrared spectrum (nujol mull) with an authentic specimen. A small quantity of zinc(II) acetate was added and the reaction continued. After six hours the solid (treated as above) contained no dialdehyde, and was found to be (section 7.7) the free cyclic ligand cyphen [7.8]. The infrared spectra of the dialdehyde and cyphen may be compared in [7.13].

These results show that the formation of cyphen from 1,2-diaminobenzene and the dialdehyde is catalysed by zinc(II) and nickel(II) ions. Apparently the zinc(II)

ion is a better catalyst than the nickel(II) ion, since in the presence of the latter an appreciable amount of unreacted dialdehyde was detected after 6 hours (page 324).

### 7.6.1. Acid catalysts.

It has been shown<sup>18,19</sup> that the condensation of aldehydes and amines is catalysed by acids. Hammett<sup>20</sup> favoured a reaction scheme as in equation [7.7].



[equation 7.7]

It was decided to test the catalytic activity of acids in the reaction between the dialdehyde and 1,2-diaminobenzene. The conditions were the same as those described above, but in separate reaction vessels the effect of addition of small quantities of antimony trifluoride, anhydrous aluminium(III) chloride and pyridinium perchlorate (see page 322) was investigated.

Addition of antimony trifluoride and aluminium(III) chloride caused complete conversion to cyphen within one

hour. Pyridinium perchlorate was a less effective catalyst and complete conversion to cyphen was only achieved after approximately 5 hours. The results are summarized in table [7.3].

Substance added	Time for disappearance of solid dialdehyde	b
Nickel(II) acetate	<sup>a</sup> >10 hr	
Zinc(II) acetate	< 6 hr	
Pyridinium perchlorate	5 hr	
Antimony trifluoride	1 hr	
Aluminium trichloride	1 hr	

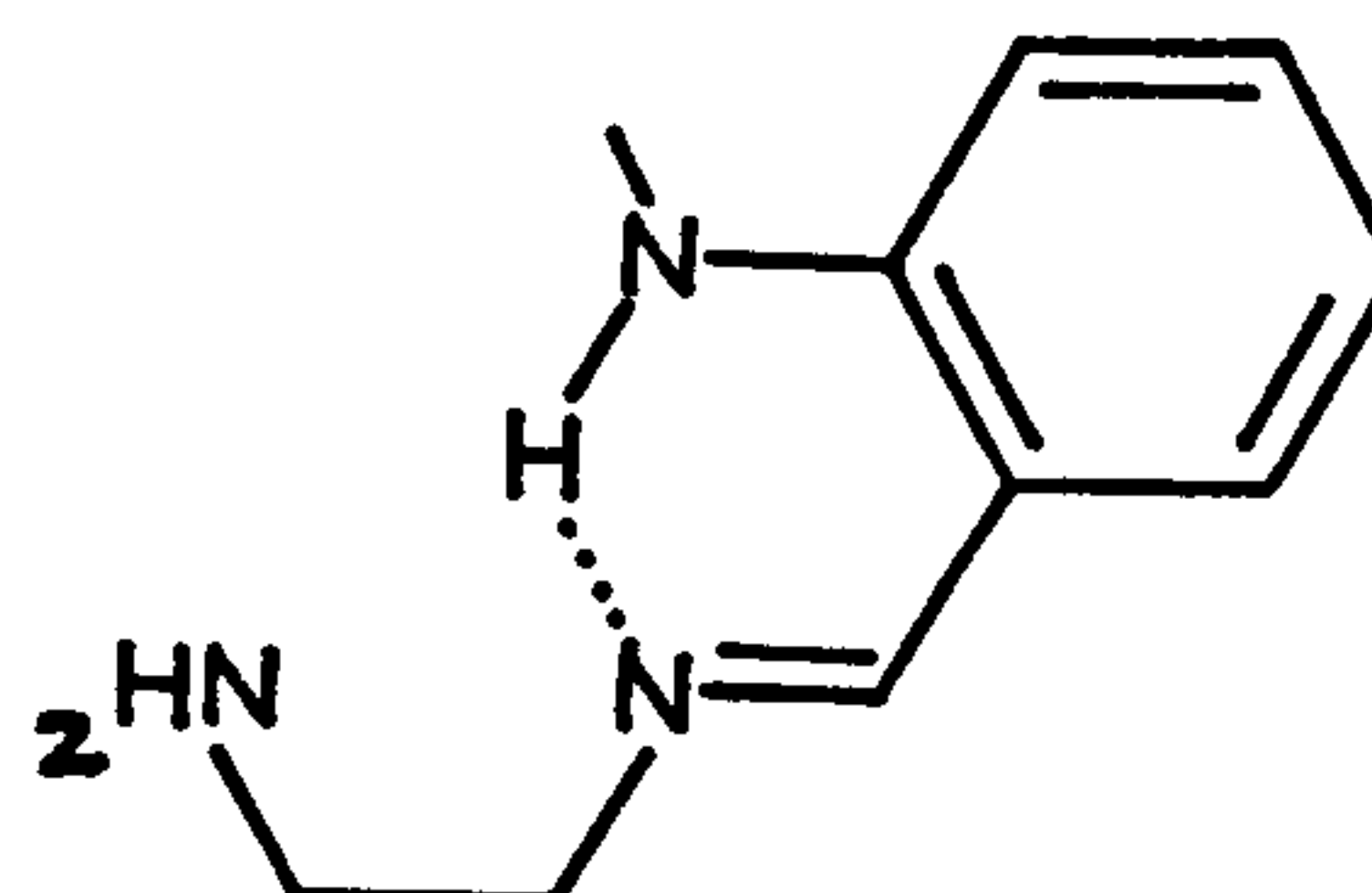
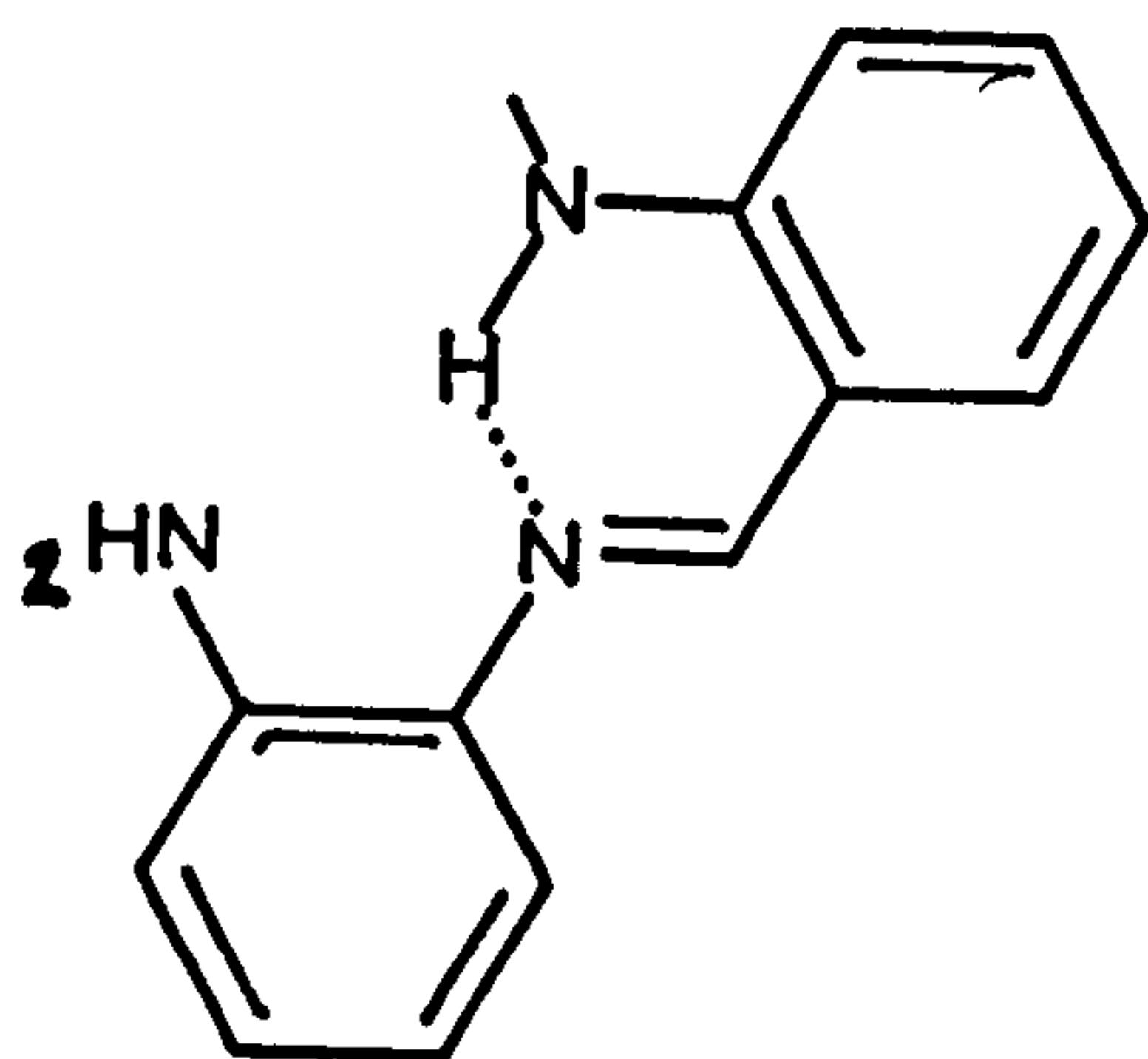
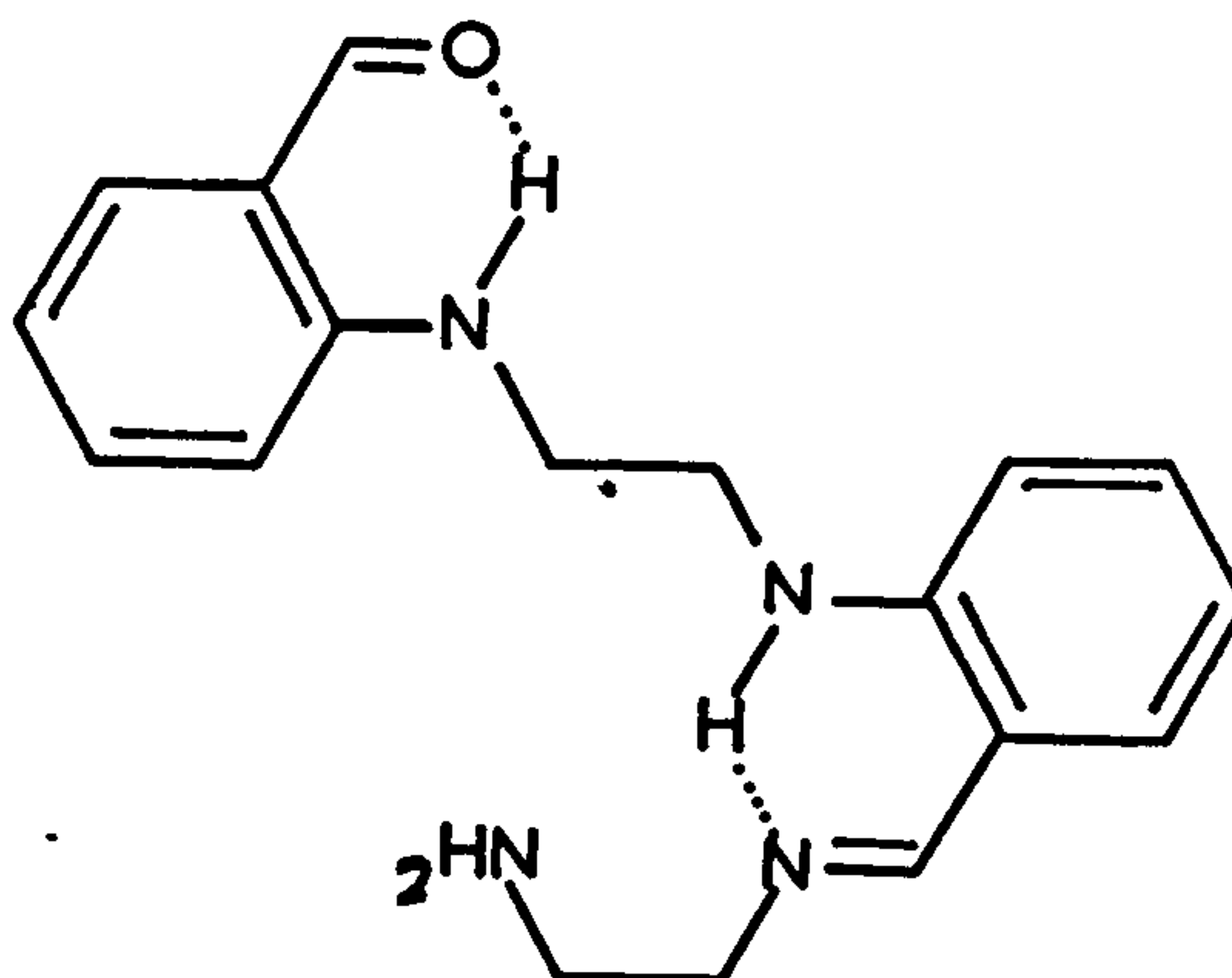
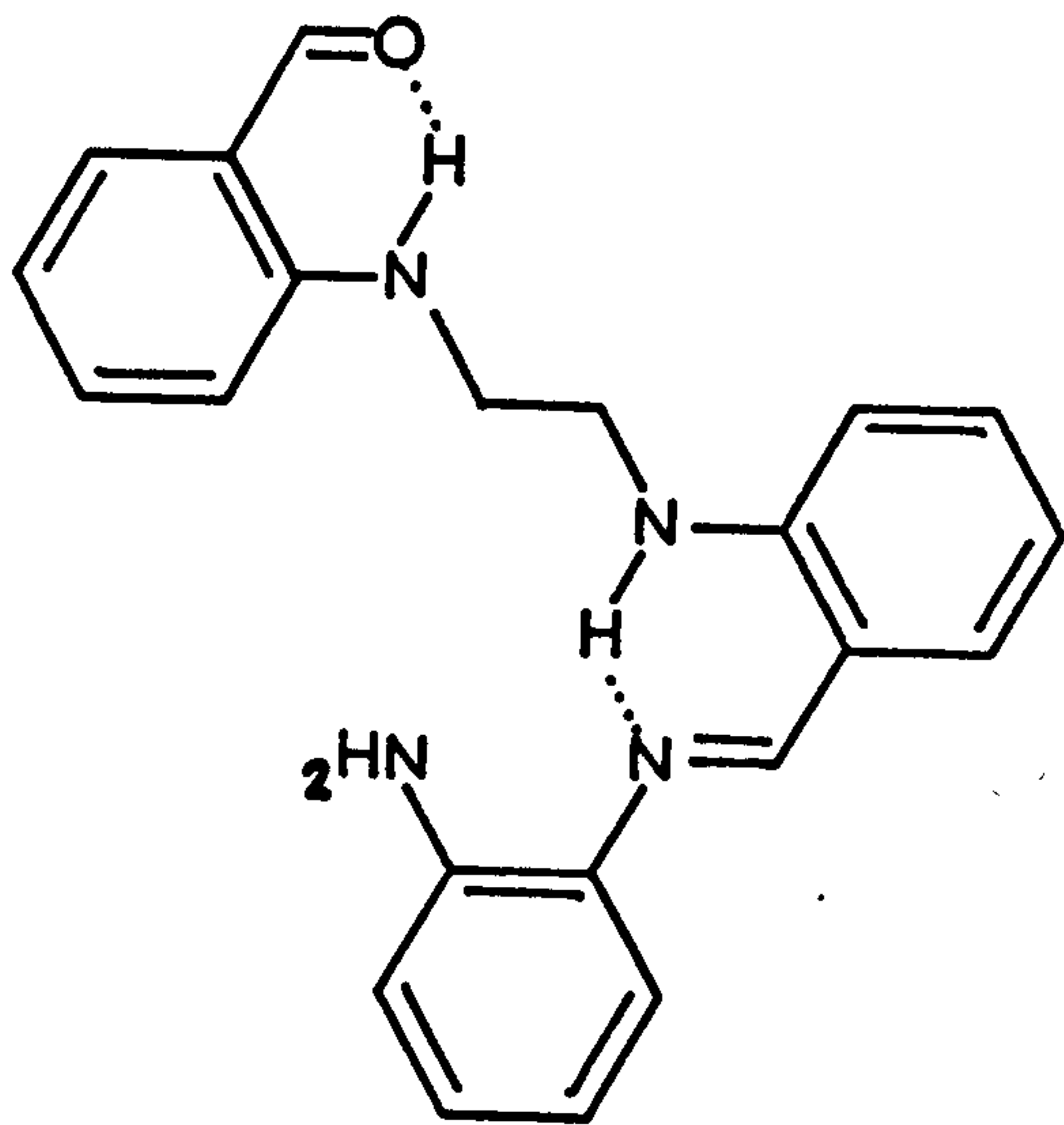
Table [7.3] Approximate reaction times for the formation of cyphen.

- (a) Not truly catalytic - nickel ions become complexed to cyphen.  
 (b) When solid matter shows no bands in the infrared region characteristic of the dialdehyde.

It is not unreasonable that the acid catalysis in this case could be represented by a similar mechanism to that proposed by Hammett (equation [7.7]).

It is possible that the important role of the metal ions  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  in the reaction equation [7.4] is not their organizational template activity (page 142) but activity as Lewis acid catalysts. It is possible that antimony trifluoride and aluminium(III) chloride





give rise to appreciable concentrations of protons in methanol, or may themselves function as catalysts. The catalytic activity of pyridinium perchlorate is probably due to its role as a source of protons.

An example where nickel(II) ions show similar catalytic activity is in the Beckmann rearrangement of aldoximes. The rearrangement is acid catalysed<sup>21</sup>, but nickel(II) acetate has also been used to effect the isomerization to amides, and has the advantage that it does not promote further reaction of the amide<sup>21</sup>.

It is possible that one of the factors contributing to the inferior 'catalytic' activity of the nickel(II) ion compared to the zinc(II) ion in the formation of cyphen is its continuous removal from solution by complexation with the product molecule.

No 'polymeric' products were detected in the reactions of 1,2-diaminobenzene with the dialdehyde, even in the cases where reaction was 'fast' and no ions were present which were capable of holding reaction centres in a configuration favouring cyclization (i.e. reactions after the addition of  $\text{SbF}_3$ ,  $\text{AlCl}_3$  and  $\text{C}_5\text{H}_5\text{NH}^+\text{ClO}_4^-$ ).

It is not clear why the product after one imine bond has been formed [7.14] should prefer to cyclize rather than react intermolecularly giving a 'polymer'. In particular few features of [7.14] seem more favourable.

for cyclization than in the 1,2-diaminoethane analogue [7.16] which in the absence of special conditions normally gives the 'polymer'. Perhaps the extra rigidity of the fragment [7.15] in comparison with [7.17] is all-important in increasing the frequency of approach of the amino group with the unreacted aldehyde group (see also page 170).

Several difficulties are likely in attempts to further elucidate the reaction of 1,2-diaminobenzene and the dialdehyde in the presence of metal ions (equation [7.4]). A careful kinetic study might reveal association between the dialdehyde and the metal ions in the activated complex, but it will be difficult to decide to which atoms the metal is bonded. Hence a distinction between the 'acid catalysis' mechanism (metal bonded to carbonyl oxygen) and a 'template' mechanism (involving also bonding to other atoms) may prove impossible.

This study has shown that it is not necessary to postulate 'template' activity of the metal ions in forming metal cyphen complexes according to equation [7.4].

### 7.7 The free macrocyclic ligands.

Provided that the right conditions are used (sections 7.4 to 7.6) it is not difficult to isolate the free cyclic ligands cyen, cytn, cybuten and cyphen. The properties of these compounds leading to the formulation

of their structures as in [7.5] to [7.8] (page F 160 ) will be discussed below.

### 7.7.1 Analyses and molecular weight determinations.

The results for carbon, hydrogen and nitrogen analyses are collected in table [7.4]. In each case the total carbon, hydrogen and nitrogen percentage was close to 100 and hence eliminated the possibility of oxygen from the dialdehyde remaining in the molecule. The atomic ratios of carbon, hydrogen and nitrogen agreed with the proposed molecular formulae and so it only remained to determine the molecular weights to confirm these molecular formulae.

Ligand	Molecular Formula		Composition %		
			C	H	N
cyen	$C_{18}H_{20}N_4$	Calc.	73.94	6.89	19.16
		Found	73.12	7.12	19.53
cytn	$C_{19}H_{22}N_4$	Calc.	74.47	7.24	18.29
		Found	73.91	7.21	18.98
cybuten	$C_{20}H_{24}N_4$	Calc.	74.96	7.55	17.48
		Found	74.88	7.60	17.35
cyphen	$C_{22}H_{20}N_4$	Calc.	77.62	5.92	16.46
		Found	76.99	5.78	15.99

Table [7.4] Analysis results for the macrocyclic ligands.

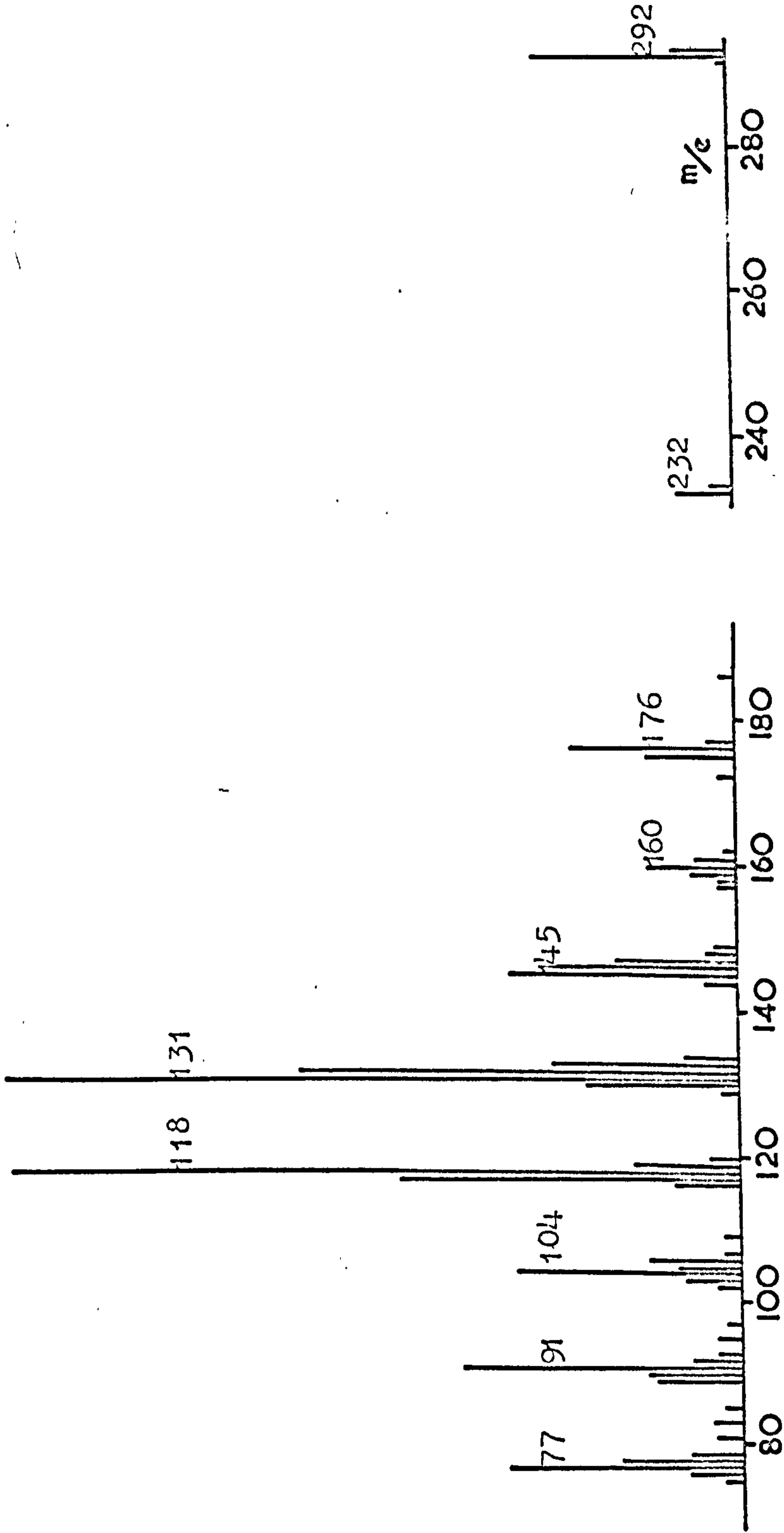
Molecular weights were determined using a Mechrolab 'Osmometer Model 301 A'. Results are summarized in table [7.5]. Unfortunately cyphen was not sufficiently soluble in a volatile solvent for which the apparatus could be calibrated, and its molecular weight could not be determined in this way.

Ligand	Solution (conc. g/l)	Molarity <sup>a</sup>	Molecular Weight	
			Found	Calc. <sup>b</sup>
cyen	chloroform	0.194	299	292
	(5.803)			
cytn	chloroform	0.190	306	306
	(5.805)			
cybuten	acetone	0.202	319	320
	(6.445)			
	(10.395)	0.320	325	320

Table [7.5] Molecular weight determinations for the free cyclic ligands.

- (a) From calibration curves for benzil in these solvents determined by Miss A. Wariss.  
 (b) For the molecular formulae in table [7.4].

The results show good agreement with the molecular weights of the formulae proposed in table [7.4], i.e. for products resulting from the condensation of one molecule of the dialdehyde with one molecule of the appropriate diamine.



The mass spectrum of cyan.

For cyphen the appearance of a molecular ion in its mass spectrum (see below) is evidence for its molecular formula as in table [7.4]. Molecular ions were also detected for the other ligands.

### 7.7.2 Mass spectra.

The mass spectra are tabulated in full in chapter 11 after the preparation of each ligand. In all cases the molecular ion was detected. Cyphen, unfortunately gave few other peaks which could be distinguished from background noise.

In general the breakdown patterns are very similar to those of the acyclic ligands (see section 3.4 page 41) and will not be considered here. The mass spectrum of cyen is shown on page F178 for comparison with amben, page F39.

### 7.7.3 Infrared spectra.

Infrared spectra are also tabulated in full in chapter 11. Comparison with the spectra of the acyclic ligands shows that many of the assignments made (section 3.5 page 42) may be extended to the macrocyclic ligands. In table [7.6] the spectra of amben and cyen are compared in the region  $4000 - 1450 \text{ cm}^{-1}$ , where assignments have been made for the former.

cyen $\lambda_{\max}$ (cm <sup>-1</sup> )	amben $\lambda_{\max}$ (cm <sup>-1</sup> )	Assignments for amben spectrum
a	a	b
-	3440 (s)	NH (free) stretch
3230 (w)	3250 (m)	NH (H-bonded) stretch
3075 (w) 3050 (w) 3015 (w)	3070 (w) 3030 (w)	CH (aromatic) stretch
2935 (w) 2925 (w) 2890 (w) 2855 (m)	2930 (w) 2875 (m) 2855 (m)	CH <sub>2</sub> (aliphatic) stretch
1638 (s)	1636 (s)	C = N stretch
1606 (s) 1583 (sh)	1609 (sh) 1585 (s)	C = C (aromatic) stretch
-	1559 (s)	NH (free) bend
1520 (s)	-	
1502 (a)	1499 (s)	C = C (aromatic) stretch
1463 (s) 1449 (s)	1461 (s)	CH <sub>2</sub> (aliphatic) bend

Table [7.6] comparing the infrared absorption spectra of cyen and amben.

- (a) measured as KBr discs.  
(b) see page 44



### 7.7.4 Electronic spectra.

The absorption bands of methanolic solutions of the macrocyclic ligands have been collected in table [7.7] .

Ligand	$\lambda_{\max}^a$	$\lambda_{\max}$	$\lambda_{\max}$	$\lambda_{\max}$
cyen	348 (8720) <sup>b</sup>	-	260 (13300)	232 (63900)
cytn	349 (10300)	278 (sh) (8570)	264 (12600)	228 (68800)
cybuten	352 (10400)	275 (sh) (9460)	265 (11900)	228 (62700)
cyphen	378 (13500)	337 (11600)	275 (sh) (25500)	246 (52300)

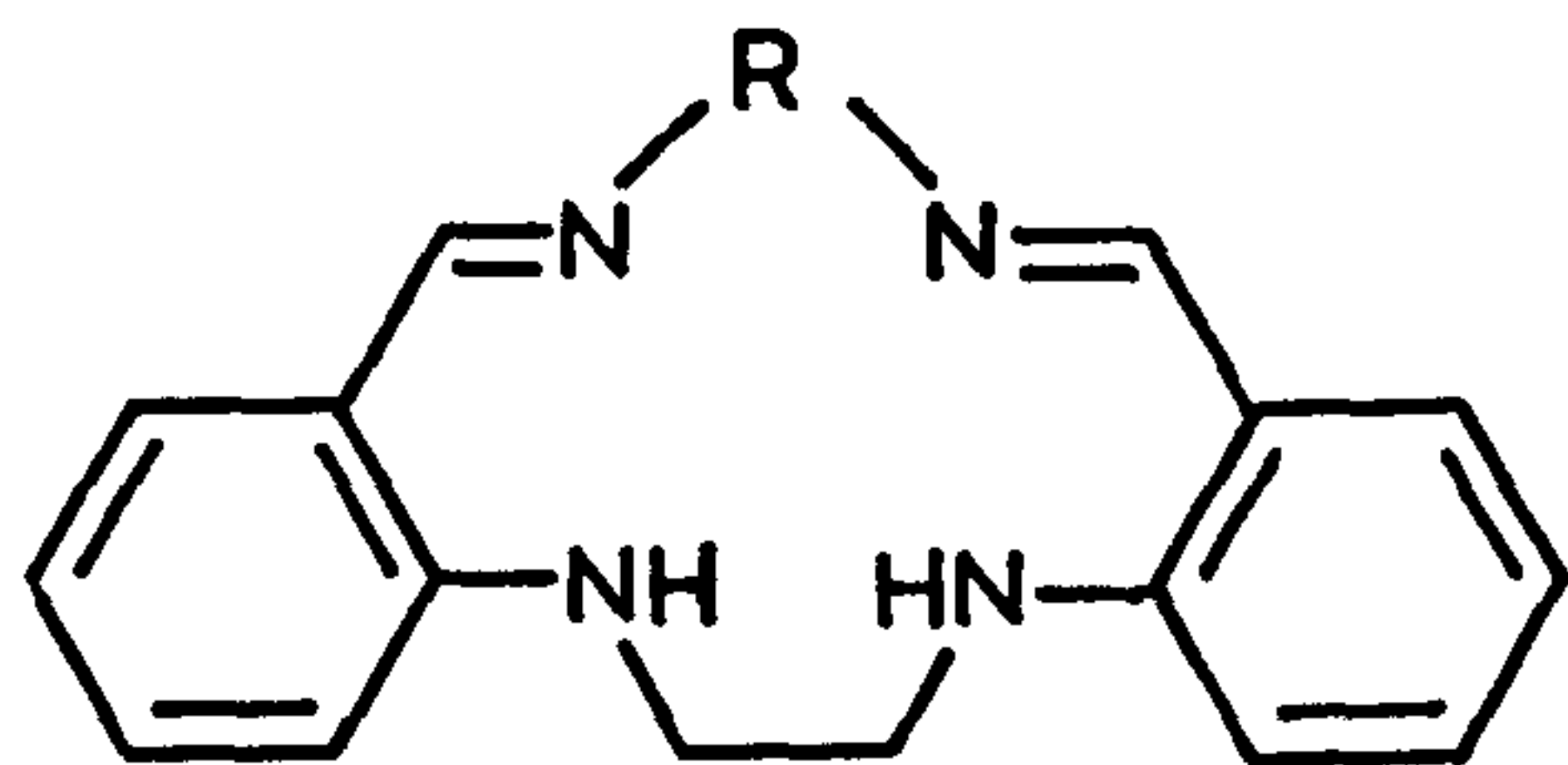
Table [7.7] . Electronic spectra of the macrocyclic ligands in methanol.

(a)  $\lambda_{\max}$  in  $m\mu$  (b) ( ), molar extinction coefficient.

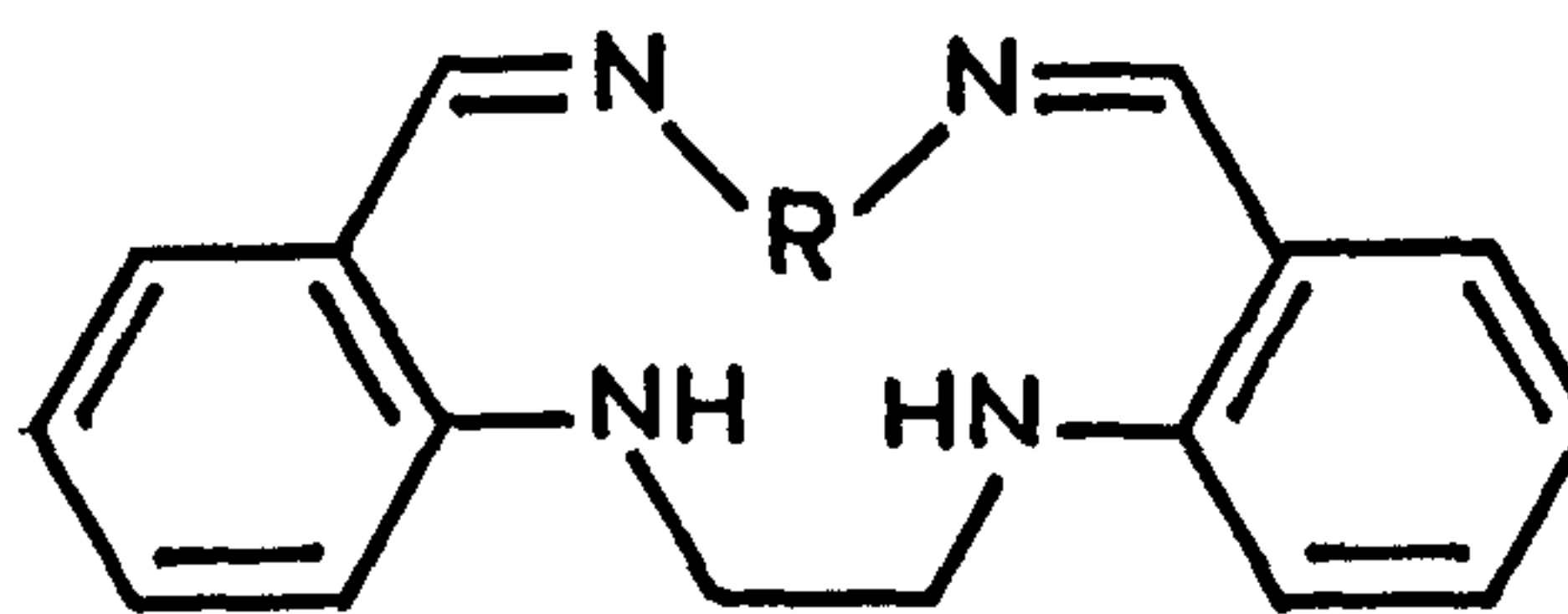
The cyclic nature of the ligands makes the syn-syn configurations of the bridging groups R relative to the N-alkyl-o-aminophenyl groups (about the imine bonds) [7.19] much less likely than the corresponding anti-anti arrangement [7.18] .

In chapter 3 (page 46) it was shown that anti-isomers of o-aminobenzaldehyde-alkylimines have absorption bands in the regions 221-233  $m\mu$  (  $\epsilon$  ,26000-34000) and

331-362  $m\mu$  ( $\epsilon$ , 3300-5000). The ligands cyen, cytn and cybuten also show bands in these regions, supporting their formulation in anti-anti configurations [7.18]. The extinction coefficients of the bands are approximately double those of the anti-o-aminobenzaldehyde-alkylimines, which is to be expected, since cyen, cytn and cybuten contain two such chromophores per molecule.

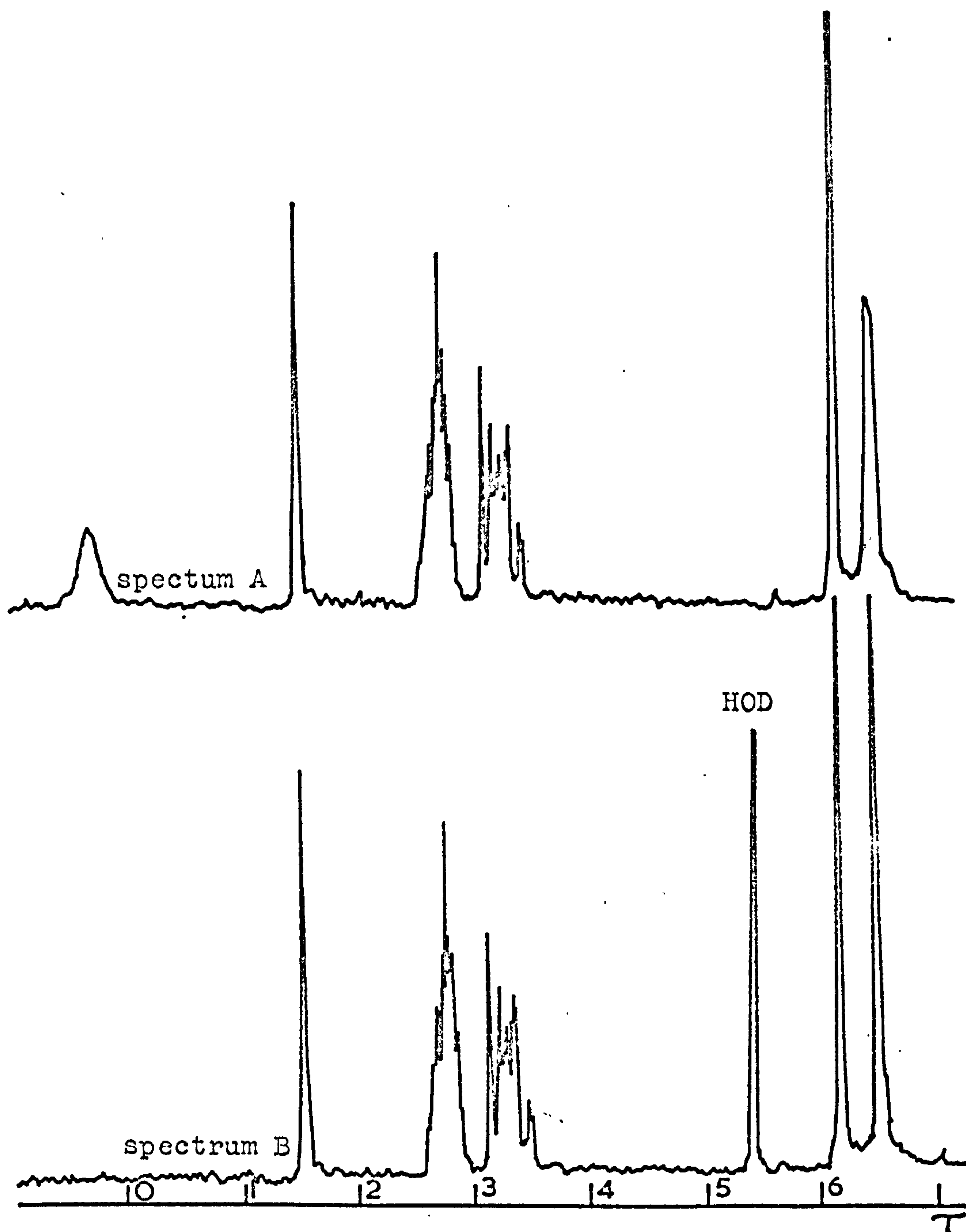


anti-anti configuration  
[7.18]



syn-syn configuration  
[7.19]

Cyphen is a special case since a conjugated bridging group links the  $\pi$ -systems of the two anti-o-aminobenzaldehyde-alkylimine chromophores. In this way the lowest  $\pi^*$  orbital is lowered in energy, and a band is observed at longer wavelengths than in the other ligands. It is probably the 'tailing' of this band into the visible region that is responsible for the yellow colour of cyphen.



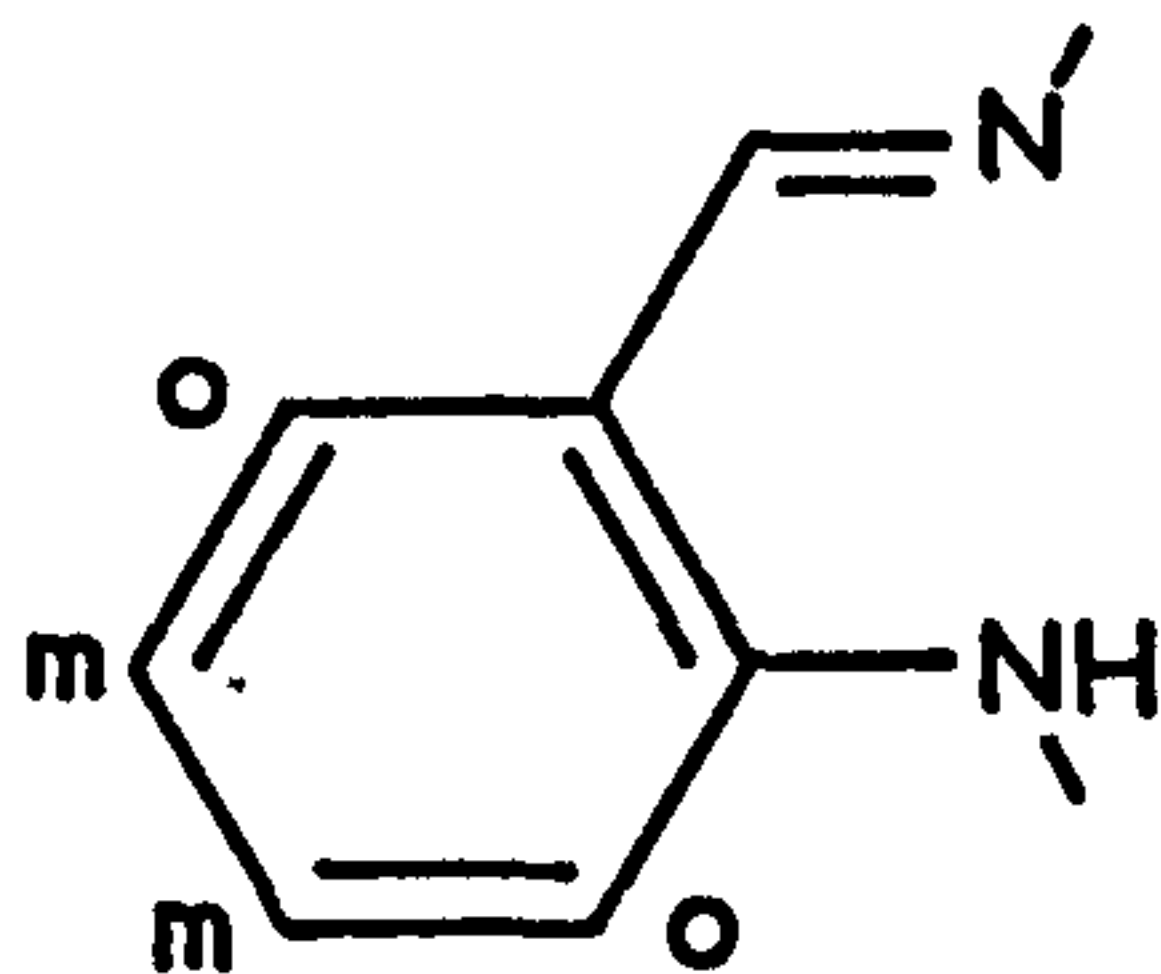
[7.21]. The N.M.R. spectrum of cyen as a  $\text{CDCl}_3$  solution (A), showing the effect of addition of a few drops of  $\text{D}_2\text{O}$  (B).

### 7.7.5 N.M.R spectra.

The N.M.R spectra are tabulated in full in chapter 11 after the preparation of each ligand. The spectrum of cyen is shown on page F182 as a typical example.

Many features of the spectra show a close resemblance to those of the acyclic ligands.

Resonances due to the protons of the bridging groups (R in [7.18] ) are very similar in appearance and chemical shift to those of the analogous acyclic ligands. For cybuten broad resonances for the methylene bridging groups are observed (c.f. ambuten), and this is thought to be due to the non-equivalence of protons caused by conformational isomerism. The resonance lines for the aromatic protons of the portions [7.20] are split into two groups, presumably for the protons ortho and meta to the substituted positions (c.f. spectrum of ambtn, page F50).

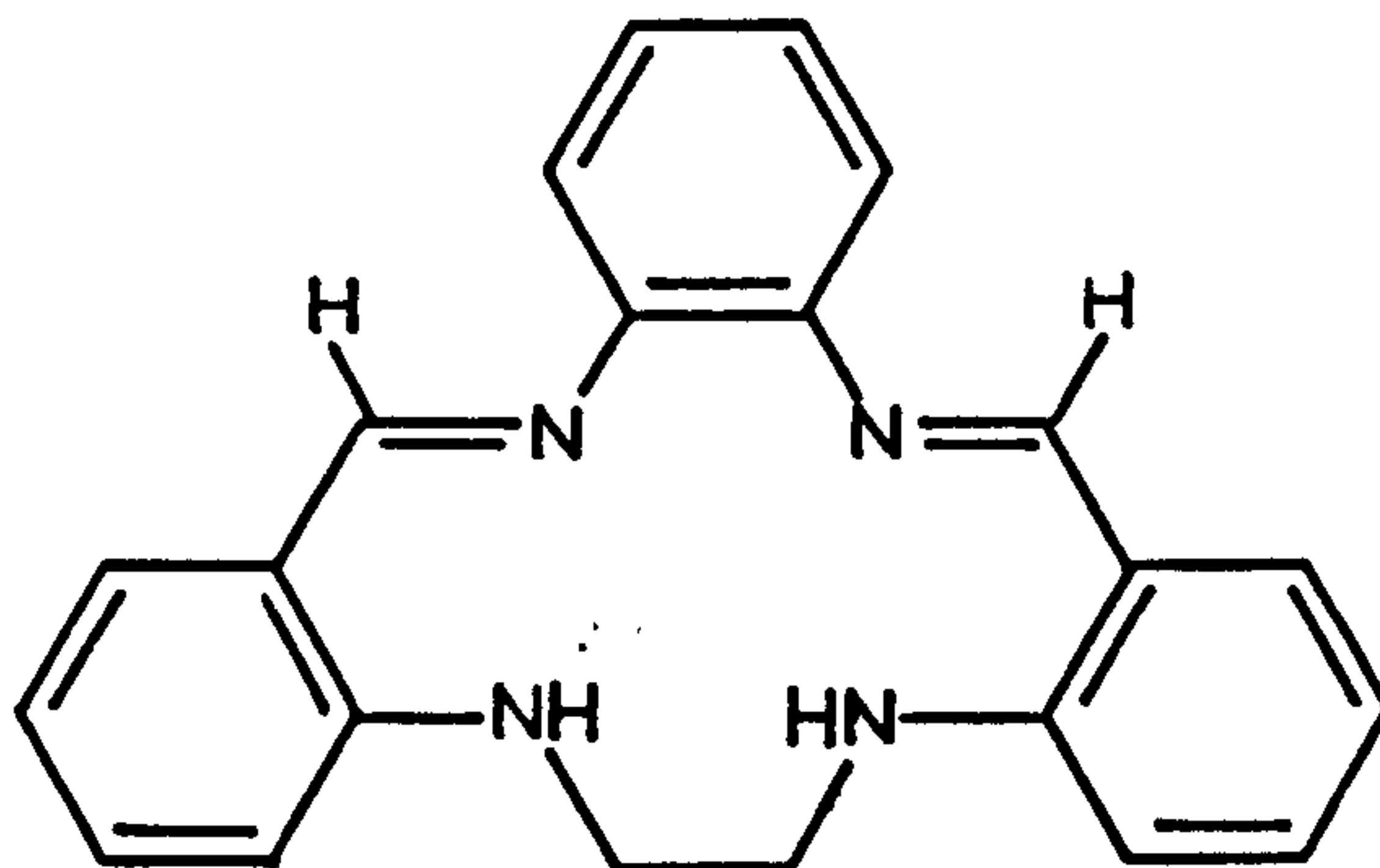


[7.20]

Spin-spin coupling between the anilino protons

and the 'anilino' methylene protons (see [7.21] ) is observed for all the macrocyclic ligands. This situation compares closely with the acyclic ligands containing a N-methyl-anilino group (see section 3.7.2). The effect of addition of a small quantity of D<sub>2</sub>O to a deuteriochloroform solution of cyen is also shown on page F182. The resonance of the 'anilino' methylene protons (6.48  $\tau$ ) becomes a sharp singlet since the anilino proton has been replaced by exchange with deuterium (causing collapse of the signal at -0.38  $\tau$ ). The same phenomenon was observed for the dialdehyde, and the related dialcohol [B] and diester [C] shown in [7.2], page F157, and the other macrocyclic ligands.

The methine resonance of cyphen occurs at considerably lower field than the methine resonances of all the other cyclic and acyclic ligands. It is thought that the shielding of this methine group in cyphen is ~~de~~ increased because it lies adjacent to and approximately in the plane of the bridging aromatic ring (see [7.22] ).



[7.22]

The chemical shifts of the hydrogen bonded anilino protons are shown in table [7.8]. It appears that as the length of the bridging group R increases the resonance position of the hydrogen bonded protons moves to higher field. In other words (c.f. section 3.7.1 and ref.22) the strength of hydrogen bonding decreases as the bridging group length is increased.

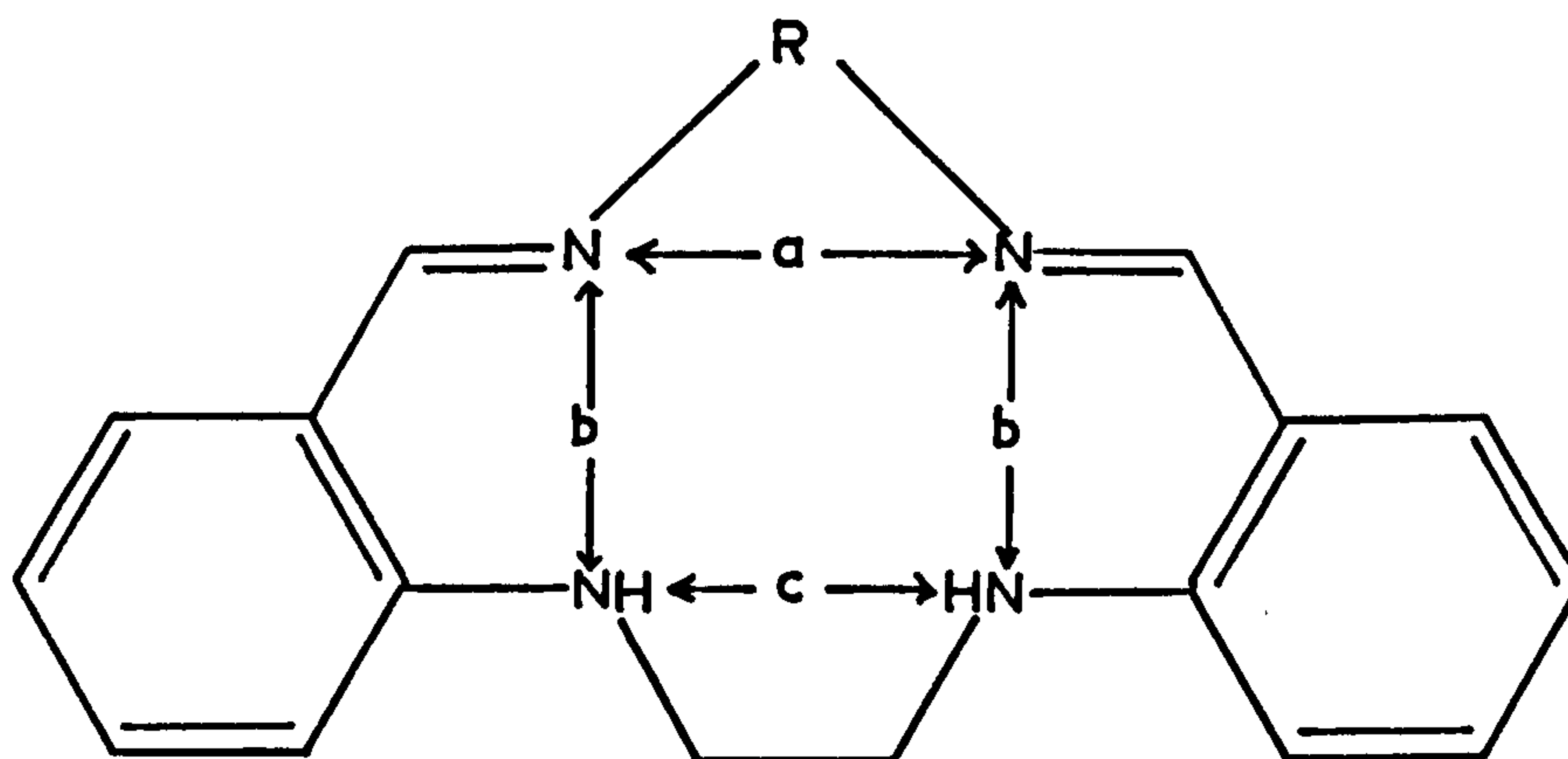
Ligand	No. atoms 'bridging' the azomethine nitrogens.	Chemical shift of NH protons.	
cyen	2	-0.38	a
cyphen	2	-0.32	b
cytn	3	0.45	a
cybuten	4	0.68	a

Table [7.8] Chemical shifts ( $\tau$ ) of NH protons in the macrocyclic ligands.

(a)  $\text{CDCl}_3$  solutions (b)  $\text{DMSO} (d_6)$  solution.

The effect may be explained by reference to diagram [7.23]. Increasing the bridging group length will 'open up' the molecule slightly, i.e. increase the distances a, b and c in [7.23]. Presumably the effect diminishes as one moves away from R, thus

$\Delta a > \Delta b > \Delta c$ . A weaker hydrogen-bond will result from increase in the distance  $b$ . The origin of this effect is very similar to that responsible for the decrease in ligand field splitting of the ligands with increasing length of the bridging chain  $R$  (see page 27).



[7.23]

### 7.8 References.

1. C.L. Honeybourne and G.A. Webb, Chem. Comm. 739, (1968).
2. G.A. Webb, personal communication (1966)
3. R.L. Rich and G.L. Stucky, Inorg. Nucl. Chem. Letters, 1, 61, (1965).
4. N.F. Curtis, Coord. Chem. Rev., 2, 3, (1968).
5. A.L. Balch and R.H. Holm, J. Amer. Chem. Soc., 88, 5201, (1966).
6. B. Kirson and H. Sechter, Bull. Soc. chim. France, 2236, (1966).

7. Kyu Sun Bai and D.L. Leussing, J. Amer. Chem. Soc., 89, 6126, (1967).
8. E.J. Olszewski and D.F. Martin, J. Inorg. Nucl. Chem., 26, 1577, (1964).
9. D.S. Pratt and C.O. Young, J. Amer. Chem. Soc., 40, 1429, (1918).
10. I.L. Finar, "Organic Chemistry", Vol. 2, 2nd Ed., Longmans, (1954) page 490.
11. Michael Green and P.A. Tasker, Chem. Comm., 518 (1968).
12. "Handbook for Chemical Society Authors", Chem. Soc. London, 1961, page 38.
13. "Stability Constants", Ed. L.G. Sillen and A.E. Martell, Chem. Soc. London, 1964, page 373.
14. P.J. Flory, "Principles of Polymer Chemistry", Cornell U.P., 1953, page 96.
15. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley, 1962, page 480.
16. G. Schwarzenbach, B. Maissen and G. Ackermann, Helv. Chim. Acta, 35, 2333, (1952).
17. G. Schwarzenbach, H. Ackermann, B. Maissen and G. Anderegg, Helv. Chim. Acta., 35, 2337, (1952).
18. R.W. Layer, Chem. Rev., 63, 489, (1963).
19. B.A. Porai-Koshits and A.L. Remizov, Problemy Mekhanizma Org. Reaktsii, Akad. Nauk. S.S.R., Otdel. Fiz. Mat. i Khim. Nauk, 238, (1953) (Chemical Abstracts, 50, 16686a).



20. L.P. Hammett, "Physical Organic Chemistry", McGraw Hill, 1940, page 333.
21. L. Field, P.B. Hughmark, S.H. Shumaker and W.S. Marshall, J. Amer. Chem. Soc., 83, 1983 (1961).
22. J.G. Pritchard, C.F. Field, K. Koch, G. Raymond, L.H. Sternbach, V. Toome and S. Traiman, Applied Spectroscopy, 20, 363, (1966).

Chapter 8. Nickel(II) and Copper(II) Complexes of  
some New Macrocyclic Ligands.

8.1 Syntheses.

8.2 Characterization of the complexes.

8.2.1 Infrared spectra.

8.2.2 N.M.R spectra.

8.2.3 Magnetic measurements.

8.2.4 Electronic spectra.

8.3 Protonation of the complexes.

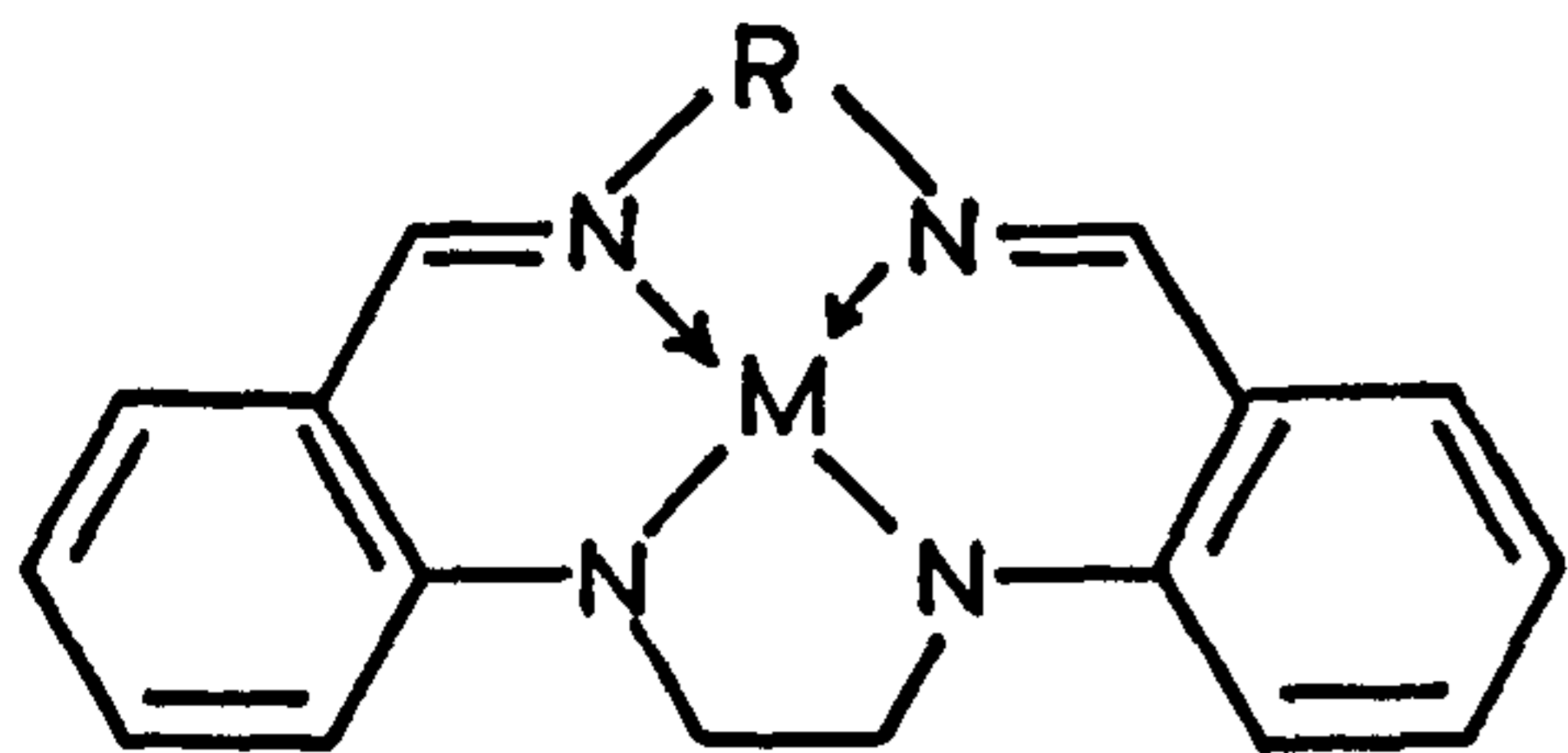
8.4 References.

8.1 Syntheses.

The complexes [8.1] were prepared by reaction of the appropriate diamine with the dialdehyde in the presence of the metal(II) acetate in refluxing methanol, (see page 158). Details of this method are given in chapter 11, and some aspects of its mechanism have been discussed in chapter 7.

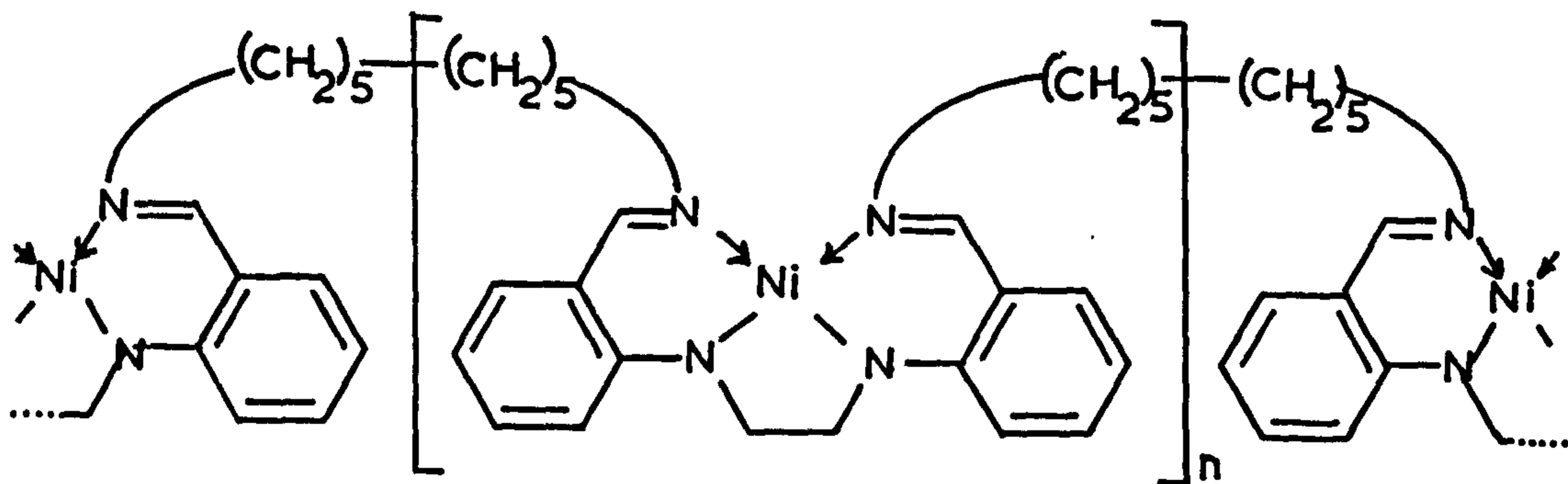
An alternative, but less practical route for the preparation of the complexes is from the pre-formed ligands, all of which can be isolated (see chapter 7).

A different type of product was isolated from the reaction of very long chain diamines with the dialdehyde under conditions which gave good yields of



[8.1]

	M(II)	R	Abbreviation
(A)	Ni	$-(\text{CH}_2)_2-$	Nicyen
(B)	Ni	$-(\text{CH}_2)_3-$	Nicytn
(C)	Ni	$-(\text{CH}_2)_4-$	Nicybuten
(D)	Ni	$-\text{C}_6\text{H}_4-$	Nicyphen
(E)	Cu	$-(\text{CH}_2)_2-$	Cucyen
(F)	Cu	$-(\text{CH}_2)_3-$	Cucytn



[8.2]

the complexes [8.1]. For example when 1,10-diaminodecane was reacted with the dialdehyde in a refluxing methanolic solution of nickel(II) acetate a dark red amorphous solid was obtained which analysed approximately for  $C_{26}H_{34}N_4Ni$ , but, unfortunately, its extremely low solubility in all the solvents available precluded purification. Its infrared spectrum (included in table [11.3], page 324) and near-infrared and visible spectra as nujol mulls were similar to the other nickel(II) complexes [8.1] and like these complexes it is diamagnetic. However, the extremely low solubility would suggest that this complex is better formulated as a polymeric material, possibly with a structure [8.2], or one in which the polymeric imine-amine chains are cross-linked by coordinated nickel(II) ions. Polymeric complexes formed by simple diamines with long bridging groups have been described in the literature.<sup>1,2.</sup>

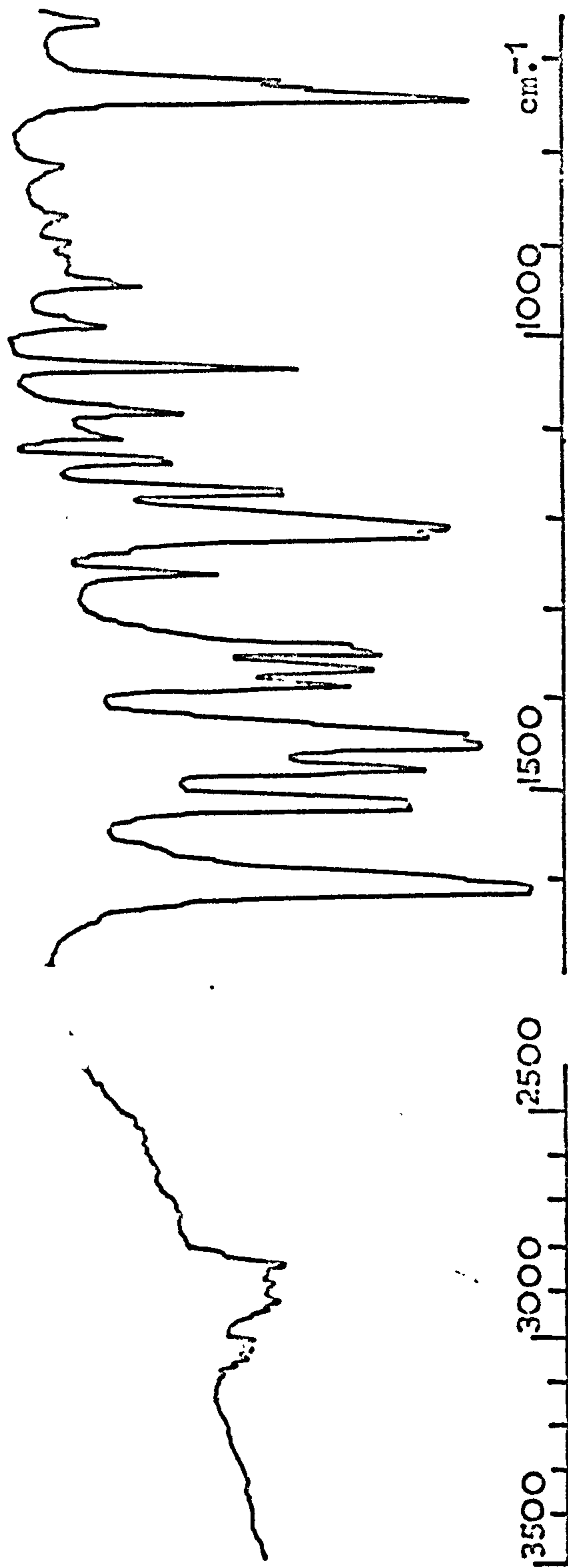
## 8.2 Characterization of the complexes.

The analysis results for the complexes (table [8.1]) fit the molecular formulae which would be expected for the structures shown on page F189.

Compound		Composition %			Molecular Weight
		C	H	N	
Nicyen	Found	61.78	5.37	15.46	349.1
	Calc.	61.93	5.19	16.05	
Nicytn	Found	62.62	5.71	15.58	363.1
	Calc.	62.84	5.55	15.43	
Nicybuten	Found	63.19	6.15	14.55	377.1
	Calc.	63.69	5.88	14.86	
Nicyphen	Found	66.43	4.59	14.14	397.1
	Calc.	66.54	4.57	14.10	
Cucyen	Found	60.00	5.45	15.44	353.9
	Calc.	61.08	5.13	15.83	
Cucytn	Found	62.56	5.76	15.45	367.9
	Calc.	62.02	5.48	15.22	

Table [8.1] Analysis results for complexes [8.1]

Two facts support the formulation of the complexes as the cyclic systems [8.1] rather than polymeric systems similar to [8.2]. Firstly the complexes could be obtained by reaction of the free cyclic ligands, (page 188) with the appropriate metal(II) acetate. Secondly the molecular weight of Nicyen was found to be 362 in a benzene solution, a value which compares reasonably well with 349 expected for the formula [8.1](A).



[8.3]. The infrared spectrum of Nicyen as a potassium bromide disc.

### 8.2.1 Infrared spectra.

The infrared spectra of the complexes are tabulated in full in chapter 11, and the spectrum of Nicyen as a potassium bromide disc is shown in [8.3] as a typical example.

The loss of protons from the 'anilino' groups on complexation is indicated by the absence of absorptions in the NH stretch region of the spectrum. Many features of the spectra are very similar to those of the analogous acyclic complexes which have been discussed in section 4.4.2, and most of the assignments may be extended to the cyclic complexes (see table [8.2]).

The spectra of the copper(II) complexes are almost identical to those of the analogous nickel(II) complexes. Table [8.2] also compares the spectrum of Cucyen with Nicyen and Niamben.

The imine groups shows a higher stretching frequency in the free ligands than when complexed. For cyen, cytn and cybuten the shifts to lower frequencies are of a similar magnitude (c.a.  $20 \text{ cm}^{-1}$ ) to those observed for the acyclic ligands (see page 77).

In the free ligand cyphen the C=N stretch occurs at lower energy. Probably this is due to the location of the imine group in a much more extensive conjugated system. Of the complexes of cyclic ligands

Niamben	Nicyen	Cucyen	Assignments
3313 (m)	-	-	NH
3293 (m)	-	-	stretch
3060 (w)	3075 (w)	3076 (w)	CH
3047 (w)	3055 (w)	3055 (w)	(aromatic)
3032 (w)	3020 (w)	3020 (w)	stretch
3018 (w)	3005 (sh)	3010 (w)	
2948 (m)	2945 (sh)	2943 (w)	CH
2915 (w)	2935 (w)	2920 (w)	(aliphatic)
2855 (w)	2917 (w)	2899 (m)	stretch
	2895 (m)	2864 (m)	
	2865 (sh)	2850 (m)	
	2855 (m)	2822 (m)	
	2832 (sh)	2790 (m)	
1617 (s)	1613 (s)	1614 (s)	C=N stretch
1593 (m)	1603 (sh)	1598 (sh)	C=C stretch
1537 (s)	1564 (m)	1565 (m)	
	1555 (sh)	1555 (sh)	
	1525 (s)	1525 (s)	
	1518 (s)	1518 (s)	

Table [8.2] The infrared spectra of Niamben, Nicyen and Cucyen in the region 1500 - 3500  $\text{cm}^{-1}$ .

(nujol and hexachlorobutadiene mulls.)



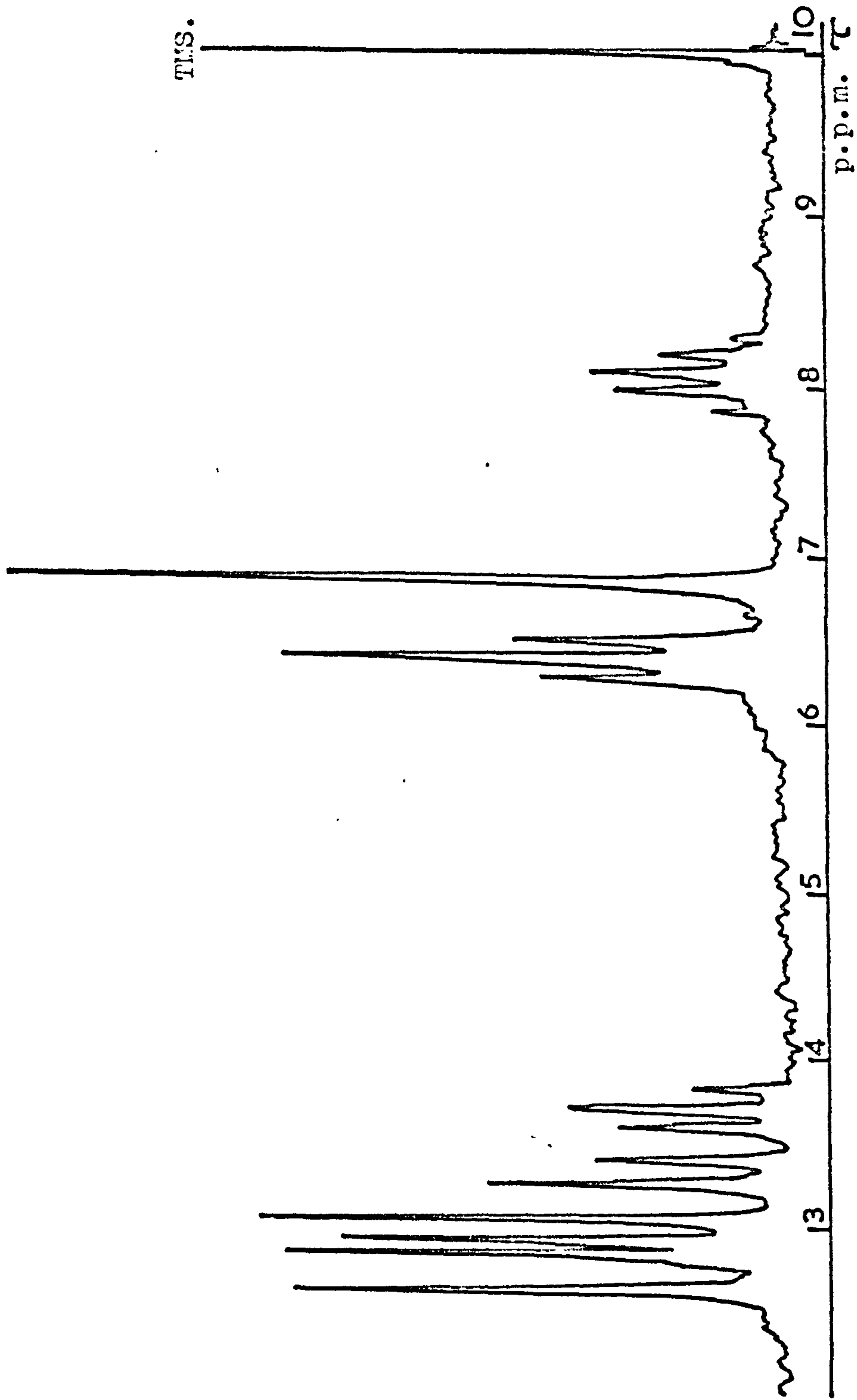
containing imine groups which have been prepared by other workers (see chapter 6), those in which the imine bond is conjugated to other groups, e.g. [6.2] and [6.3], show C=N stretching vibrations at lower energies,<sup>3,4</sup> than those in which the group is not conjugated<sup>5</sup>, e.g. [6.1].

For cyphen the shift of the C=N stretching frequency on complexation is much smaller ( $6\text{ cm}^{-1}$ ) than for cyen, cytn and cybuten, possibly because the increase in conjugation would be expected to be smaller.

### 8.2.2 N.M.R spectra.

Nicyen, Nicytn and Nicybuten were sufficiently soluble in deuterchloroform to allow their N.M.R spectra to be obtained. The appearance of proton resonances are very similar to those of the free ligands, except that no peak attributable to the NH group could be found in the complexes since these protons are presumably lost on complexation to give the uncharged products [8.1]. The spectrum of Nicytn is shown in [8.4] as a typical example.

The positions of some of the proton resonances change on complexation. Table [8.3] compares the chemical shifts of the azomethine protons of the complexes with those of the free ligands. Within experimental error the



[ 8.4 ]. The N.M.R. spectrum of Nicytin as a  $\text{CDCl}_3$  solution.

shift to higher field on complexation is the same for each ligand. Factors which could contribute to these shifts have been considered in the discussion of the N.M.R spectra of the acyclic nickel(II) complexes (page 79).

	Chemical shifts of -CH=N- ( $\tau$ )		
	cyen	cytn	cybuten
Ni(II) complex	2.40	2.65	2.66
Free ligand	1.54	1.80	1.81
Shift on complexation	+0.86	+0.85	+0.85

Table [8.3]. Chemical shifts of the azomethine protons in the Ni(II) complexes and the free ligands.

The resonances of all the methylene groups in the ligands are shifted to higher fields on complexation. The magnitudes of the shifts vary from ligand to ligand but the following order holds for each ligand; 'anilino' methylene > 'imino' ( $\alpha$ )methylene > 'imino' ( $\beta$ )methylene.

In the free ligands spin-spin coupling between the anilino proton and the 'anilino' methylene groups causes the resonance of the latter to be split. A sharp singlet is observed for this resonance in the nickel(II) complexes, again indicating the loss of the anilino protons

Complex	Temp. (°K)	$\chi_g$ $\times 10^6$	$\chi_M$ $\times 10^6$	$\chi_L$ $\times 10^6$	$\chi_{M'}$ $\times 10^6$	$\mu^a$ (B.M)
Nicyen	294	-.250	-87	-175	88	-
Nicytn	293	.062	21	-187	208	-
Nicybuten	294	-.181	-68	-199	131	-
Nicyphen	289	-.506	-201	-186	-15	-
Cucyen	289-295	3.701	1305	-175	1485	1.86
Cucytn	290-294	3.375	1242	-187	1429	1.85

Table [8.4]. Magnetic susceptibilities (cgs units) of the solid complexes at room temperature.

(a) Mean for six values, calculated for different temperatures assuming a Curie Law; other quantities ( $\chi_g$  etc.) are actual figures for a determination at one temperature.

on complexation.

### 8.2.3 Magnetic measurements.

Data from the determinations of magnetic susceptibility of the solid complexes are included in table [8.4].

The nickel(II) complexes are diamagnetic, and hence probably have an approximately planar arrangement of the four donor atoms about the nickel ion (see page 82). Models suggest that for the ligand cybuten this type of arrangement must involve considerable strain of the four methylene groups in the bridge R (see [8.1] (C)), and that this strain would be considerably reduced in an approximately tetrahedral arrangement of the four nitrogen atoms about the nickel ion. For the planar arrangement of the four nitrogen atoms about the nickel ion it would seem likely that the methylene groups of R will be puckered above and below the plane. Dr P. Main of the Physics Department, York has kindly agreed to attempt a single crystal X-ray structure determination of Nicybuten, in order to ascertain the arrangement of the carbon atoms in the tetramethylene bridging chain.

The magnetic moments of copper(II) complexes are insensitive to stereochemistry<sup>6</sup>, and moments of around 1.9 B.M. are shown by octahedral, square-planar, square-

pyramidal and approximately tetrahedral complexes.<sup>6</sup>

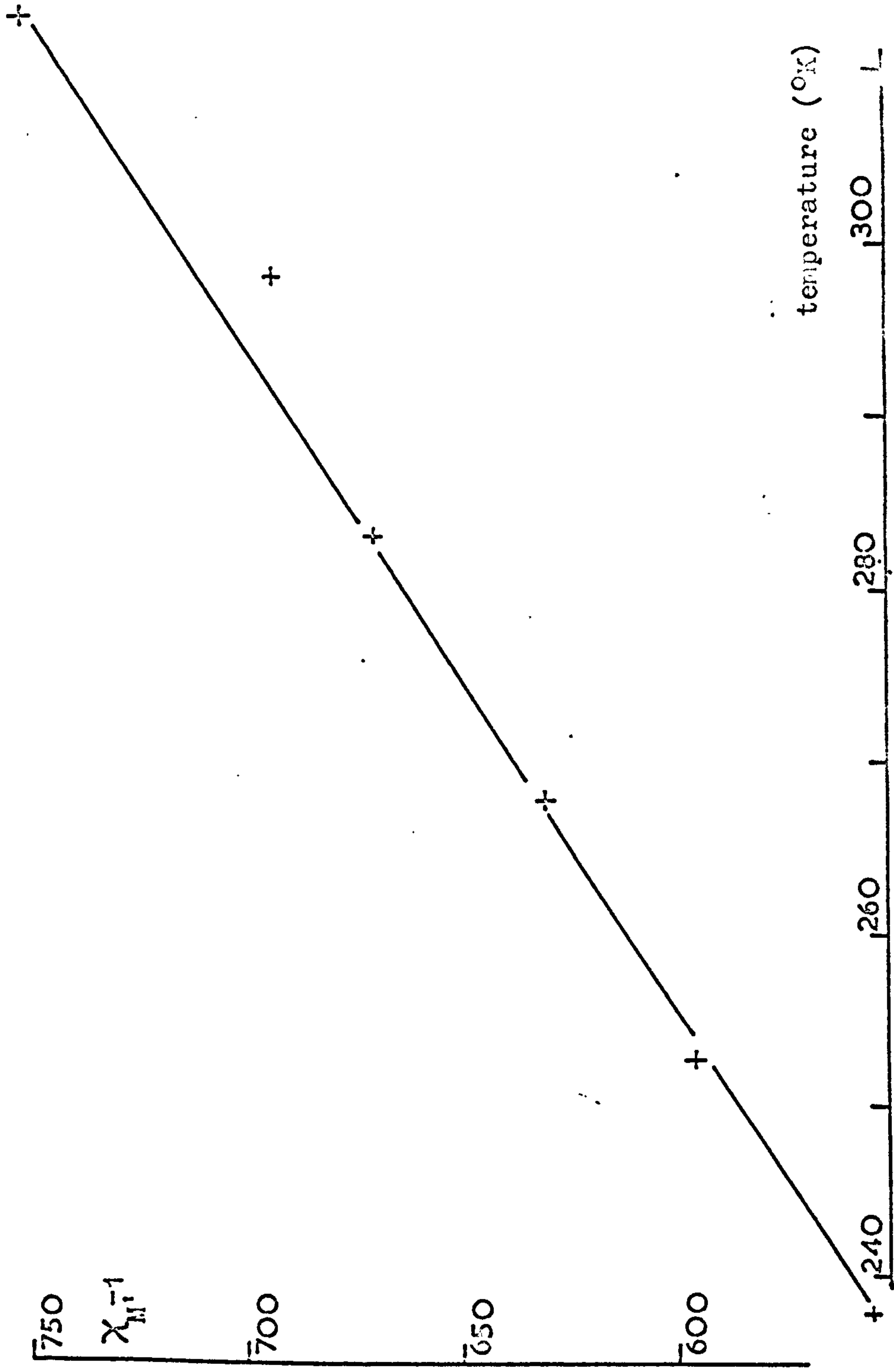
Only in cases where magnetic exchange occurs are appreciably different moments observed, e.g. the lower moments (c.a. 1.4 B.M) of the copper(II) salts of many carboxylic acids which are thought<sup>7,8</sup> to show direct exchange via the Cu-Cu bonds.

Moments of 1.86 and 1.85 for Cucyten and Cucytn do not give any indications to the geometries of the complexes, but suggest that dimerization by formation of a Cu-Cu bond is unlikely.

The magnetic susceptibility of a pyridine solution of Cucytn was examined using the N.M.R method described in chapter 10. Unfortunately Cucyten was not sufficiently soluble to allow the method to be applied.

Results for the Cucytn solution are shown in table [8.5]. The mass susceptibility of Cucytn in solution was calculated using the expression shown in equation [10.2] (page 235) with the calibration constant (c') = 7.96(2).

Temp. (°K)	$\Delta f$ (cps)	$\chi_g$ $\times 10^6$	$\chi_M$ $\times 10^6$	$\chi_{M'}$ $\times 10^6$	$\chi_M^{-1}$
312	5.0	3.15	1160	1330	751
298	5.5	3.47	1280	1450	692
283	5.7	3.60	1320	1490	670
268	6.1	3.85	1420	1590	631



[8.5]. A plot of  $\chi_M^{-1}$  against temperature for Cucytn in pyridine + 2% TMS.

253	6.5	4.10	1510	1680	596
238	7.0	4.42	1630	1790	557

Table [8.5]. Susceptibilities (cgs. units) of Cucytn in a pyridine solution containing 2% TMS.

(a) for symbols see chapter 10.

In [8.5] (page F196) values of  $\chi_M^{-1}$  are plotted against temperature. The straight line indicates that the paramagnetic susceptibility follows the Curie-Weiss law, with a Weiss constant of  $-12 \pm 14^\circ$ , calculated from the computed intercept. Unfortunately the error in the intercept is large because readings could only be taken in a limited temperature range a long way above  $T=0$ .

The computed slope gives the magnetic moment of the copper(II) ion as  $1.82 \pm .05$  B.M., a value quite close to that obtained in the solid state by the Gouy method (see table [8.4]).

Pyridine solutions of Nicytn and Nicybuten were examined by the N.M.R method in order to investigate the addition of pyridine to the complexes to produce hexacoordinate paramagnetic species similar to those discussed in section 4.4.4. page 83. No appreciable paramagnetism was detected even on lowering the temperature to  $238^\circ\text{K}$ , and thus it seems that these complexes



behave similarly to their acyclic analogues, and that coordination of pyridine is unfavourable because the planar ligand field is greater than a certain critical value (see page 91)

#### 8.2.4 Electronic spectra.

The electronic spectra of the complexes are included in table [8.6]. Dimethylformamide solutions of all the complexes shown in [8.1] were examined in order to compare the spectra with those of the acyclic nickel(II) complexes discussed in chapter 4.

In every case a cyclic complex type [8.1] showed a similar spectrum to its acyclic analogue, e.g. table [8.7] compares the principal absorption maxima of Nicybuten with Niambbuten and Cucyen with Cuamben. Comparison of the spectra of the two types of complex reveals that in all cases the absorptions in the region 350-700  $m\mu$  occur at slightly lower energies in the cyclic complexes. The shift of these intense bands to lower energies made the weak absorptions expected for the d-d transitions even more difficult to resolve in the cyclic complexes, and for dimethylformamide solutions of Nicyen, Nicytn, Nicybuten and Nicyphen no such bands could be observed.

		$\lambda_{\max}$ (m $\mu$ )			
Nicybuten	-	550	500	407 (sh)	385
Niambbuten	620 (sh)	515	475	-	365
Cucyen	650 (sh)	472 (sh)	430	-	358
Cuamben	670	460 (sh)	422 (sh)	415	350

Table [8.7] . Similarities between the spectra of dimethylformamide solutions of complexes [8.1] and their acyclic analogues.

When Nicyen, Nicytn and Nicybuten were measured as nujol mulls some poorly defined shoulders were detected which might be due to d-d transitions. A precise assignment of energies to these bands is difficult because of their poor resolution, but the relative energies clearly fall in the following order;

$$\text{Nicyen (560 m}\mu\text{)} > \text{Nicytn (620 m}\mu\text{)} > \text{Nicybuten (650 m}\mu\text{)}$$

This is the order which would be expected for the ligand field splittings produced by cyen, cytn and cybuten, and resembles that of the analogous acyclic complexes (page 97). The presumed greater distance between the nitrogen atoms as the length of the bridging group R is increased is probably responsible for this order, which is the same as that observed for the strength of hydrogen-bonding in the free cyclic ligands (see page 184)

The weak bands in the nickel(II) complexes [8.1] occur at slightly lower energy than in their acyclic analogues (see table [8.8]). If these bands are due to d-d transitions, the sizes of which are dependent on the ligand field, then the values in table [8.8] suggest that the cyclic ligands produce a slightly smaller field than their acyclic analogues. Such an effect might result from a shorter distance between the nickel ion and the anilino nitrogen atoms in the acyclic systems, since the dimethylene bridge in the cyclic systems might restrict the approach of the anilino nitrogen atoms after a certain point.

Nicyen	Nicytn	Nicybuten
(560)	(620)	(650)
Niamben	Niambtn	Niambbuten
(-a)	(600)	(620)

Table [8.8]. The positions ( $m\mu$ ) of the weak bands around 600  $m\mu$  in the complexes [8.1] and their acyclic analogues.

- (a) No band could be detected for this compound.  
 (b) All bands observed as shoulders in nujol mull spectra.

The spectra were examined qualitatively in solutions containing appreciable quantities of pyridine, and it was found that bands were observed in very similar positions to those of dimethylformamide and benzene

solutions and of the nujol mulls. In particular no new bands were detected in the near-infrared, and this provides further evidence for the reluctance of the nickel(II) complexes to increase their coordination number by addition of pyridine (see also page 196).

Table [8.6]. Electronic spectra of the complexes shown in [8.1].

(a) DMF = dimethylformamide (b) Scanned 280 - 1000  $m\mu$   
 (c)  $\lambda_{\max}$  ( $m\mu$ ) (d) Extinction coefficient  
 (e) Scanned 300 - 1000  $m\mu$  (f) Scanned 350 - 1000  $m\mu$   
 (g) Tetrahydrofuran = THF

Nicyen, as a DMF<sup>a</sup> solution<sup>b</sup>; 495<sup>c</sup>(5700)<sup>d</sup>, 372 (8800),  
 307 (24500),

as a benzene solution<sup>e</sup>; 565(sh) (2590), 510 (5300),  
 482 (sh) (4550), 376 (7700), 321 (sh) (19400),  
 305 (21500),

as a nujol mull<sup>f</sup>; 560 (sh), 525, 490 (sh), 380.

Nicytn, as a DMF solution<sup>b</sup>; 520 (4470), 480 (sh) (3900),  
 390 (sh) (5700), 376 (5800), 305 (19100), as a nujol  
 mull<sup>f</sup>; 620 (sh), 550, 490 (sh), 400, 380.

Nicybuten, as a DMF solution<sup>b</sup>; 550 (3740), 500 (3720),  
 407 (sh) (4680), 385 (5120), 305 (sh) (17540), as  
 a nujol mull<sup>f</sup>; 650 (sh), 580, 530, 420 (sh) 385,  
 360 (sh).

Nicyphen, as a DMF solution<sup>b</sup>; 632 (7100), 588 (5400), 550 (sh)

(4900), 441 (sh) (7000), 406 (2300), 388 (23000),  
370 (16300), 291 (49000),

As a THF<sup>g</sup> solution<sup>e</sup>; 640 (7030), 590 (5500),  
550 (sh) (4800), 440 (sh) (7500), 410 (24800),  
390 (24800) 370 (sh) (17000), 350 (sh) (9600),  
as a nujol mull<sup>f</sup>; 680, 630, 570, 440 (sh) 415,  
390 (sh).

Cucytn, as DMF solution<sup>b</sup>; 650 (sh) (180), 472 (sh) (3900),  
430 (12300), 358 (2670), 299 (15700),

as a benzene solution<sup>e</sup>; 675 (sh) (200), 482 (sh)  
(4130), 439 (13400), 369 (3160), 305 (15900),  
as a nujol mull<sup>f</sup>; 650 (sh), 480 (sh), 440, 370.

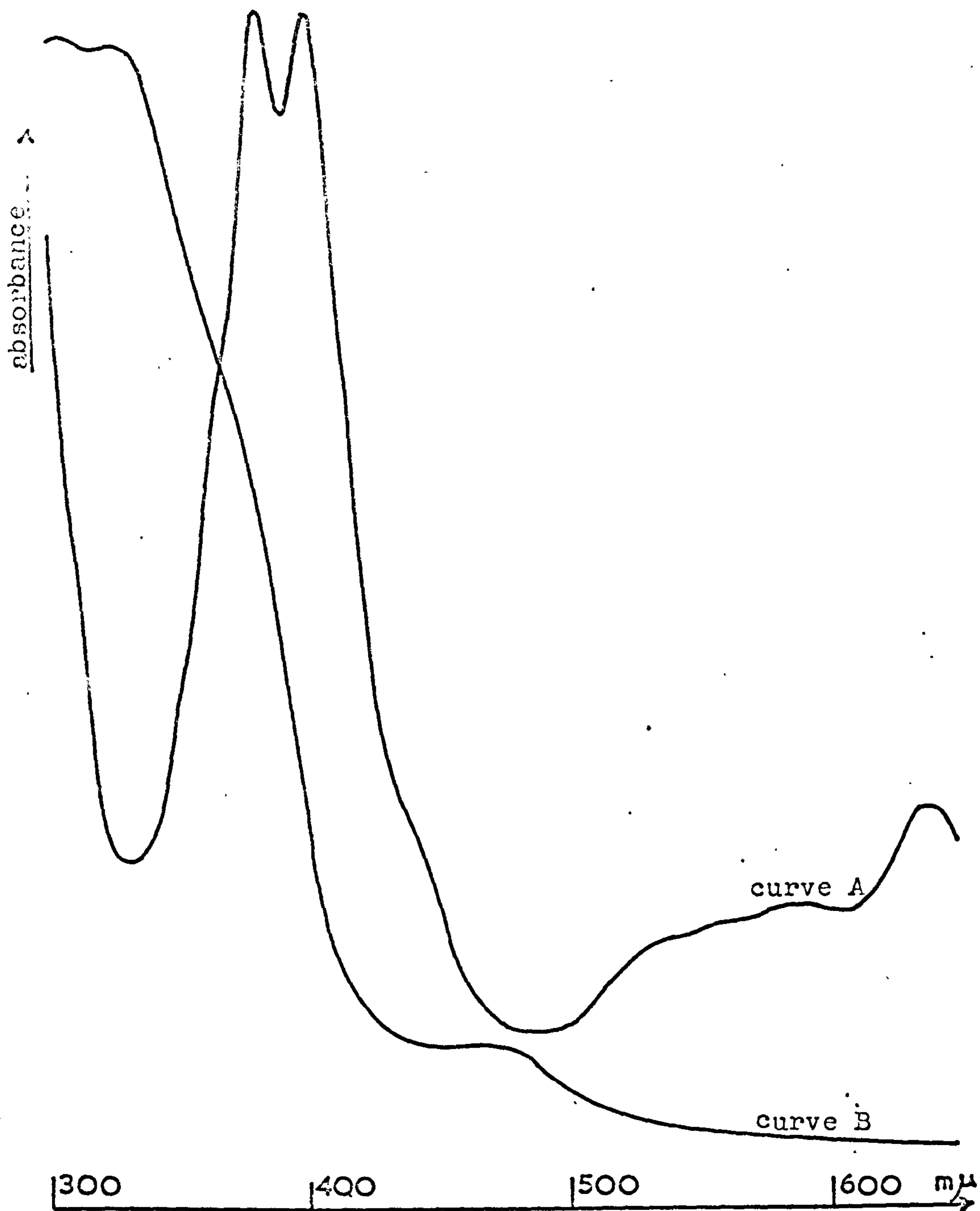
Cucytn, as DMF solution<sup>b</sup>; 740 (150), 439 (11000), 365 (sh)  
(2300), 300 (16000),

as a nujol mull<sup>f</sup>; 740, 490 (sh) 450, 370 (sh)

Cuamben, as DMF solution<sup>b</sup>; 675 (203), 460 (sh) (2100),  
422 (sh) (12000), 415 (13000), 395 (sh) (8500),  
350 (sh) (2500), 300 (12000).

### 8.3 Protonation of the cyclic complexes.

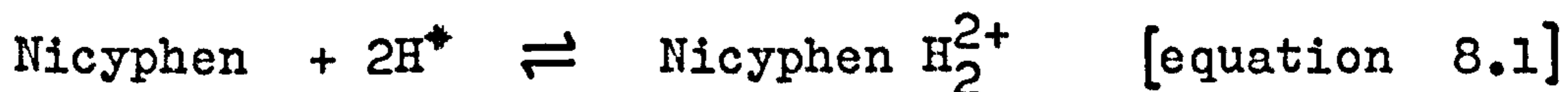
In the course of studying the spectra of the cyclic nickel complexes type [8.1] the effect of addition of protonic acids was investigated. Addition of perchloric acid to a tetrahydrofuran solution of Nicyphen causes a complete change in the electronic spectrum from curve (A)



[8.6]. The electronic absorption spectrum of a tetrahydrofuran solution of Nicyphen (A), showing the effect of addition of HClO<sub>4</sub>. (curve B).

to curve (B) in [8.6], corresponding to an observed colour change from deep-green to pale orange. The change is reversible, since addition of a few drops of sodium hydroxide solution or sodium methoxide solution causes reversion to (A) with a slight reduction in optical density due to dilution. The orange solution (B) appears to be quite stable on standing, and no change in the spectrum was detected after 8 hrs at room temperature.

This behaviour can be explained in terms of a reversible protonation of the complex Nicyphen in solution, according to the equilibrium shown in equation [8.1] .



A suspension of Nicyphen in tetrahydrofuran was treated with 70% perchloric acid, when a bright yellow-orange precipitate was produced. This material appeared to be indefinitely stable in air, and was not noticeably hygroscopic. It analysed for the diprotonated perchlorate 'adduct' of Nicyphen, i.e.  $[\text{Nicyphen H}_2]^{2+} (\text{ClO}_4^-)_2$  (see table [8.9] ). Similar results were obtained for the pale yellow product isolated by reaction of perchloric acid with Nicyen, except that this material appeared to be slightly hygroscopic, a factor which may be responsible for the rather low carbon and high hydrogen analysis figures.

$\lambda_{\text{max}}$ (m $\mu$ )	Solution (a, b, c)	Optical density	Conc. Nicyphen (g l <sup>-1</sup> x 10 <sup>2</sup> )	'Nicyphen' in orange material.
640	(b)	0.731	4.12	67.5%
	(c)	0.169	0.960	63.0%
590	(b)	0.572	4.08	67.0%
	(c)	0.141	1.001	65.6%
408	(c)	0.621	0.994	65.0%
388	(c)	0.634	1.015	66.5%

Table [8.10]. Spectrophotometric analysis of the conversion  
of  $[\text{Nicyphen H}_2]^{2+} (\text{ClO}_4^-)_2$  to Nicyphen.

- (a) Solution (a) contained 15.26 mg. of  $[\text{Nicyphen H}_2]^{2+} (\text{ClO}_4^-)_2$  made up to 50 ml. with tetrahydrofuran containing 5ml. N. sodium methoxide solution.
- (b) Solution (a) diluted by a factor of 5.
- (c) Solution (a) diluted by a factor of 20.



Compound			Composition %		
			C	H	N
[Nicyphen H <sub>2</sub> ] <sup>2+</sup>	(ClO <sub>4</sub> <sup>-</sup> ) <sub>2</sub>	Found	43.91	3.69	9.31
		Calc.(a)	44.18	3.37	9.31
[Nicyen H <sub>2</sub> ] <sup>2+</sup>	(ClO <sub>4</sub> <sup>-</sup> ) <sub>2</sub>	Found	38.33	4.03	9.99
		Calc.(b)	39.31	3.67	10.19

Table [8.9]. Analysis results for the perchloric acid 'adducts'.

(a) for molecular formula C<sub>22</sub>H<sub>20</sub>N<sub>4</sub>NiCl<sub>2</sub>O<sub>8</sub>.

(b) for molecular formula C<sub>18</sub>H<sub>20</sub>N<sub>4</sub>NiCl<sub>2</sub>O<sub>8</sub>.

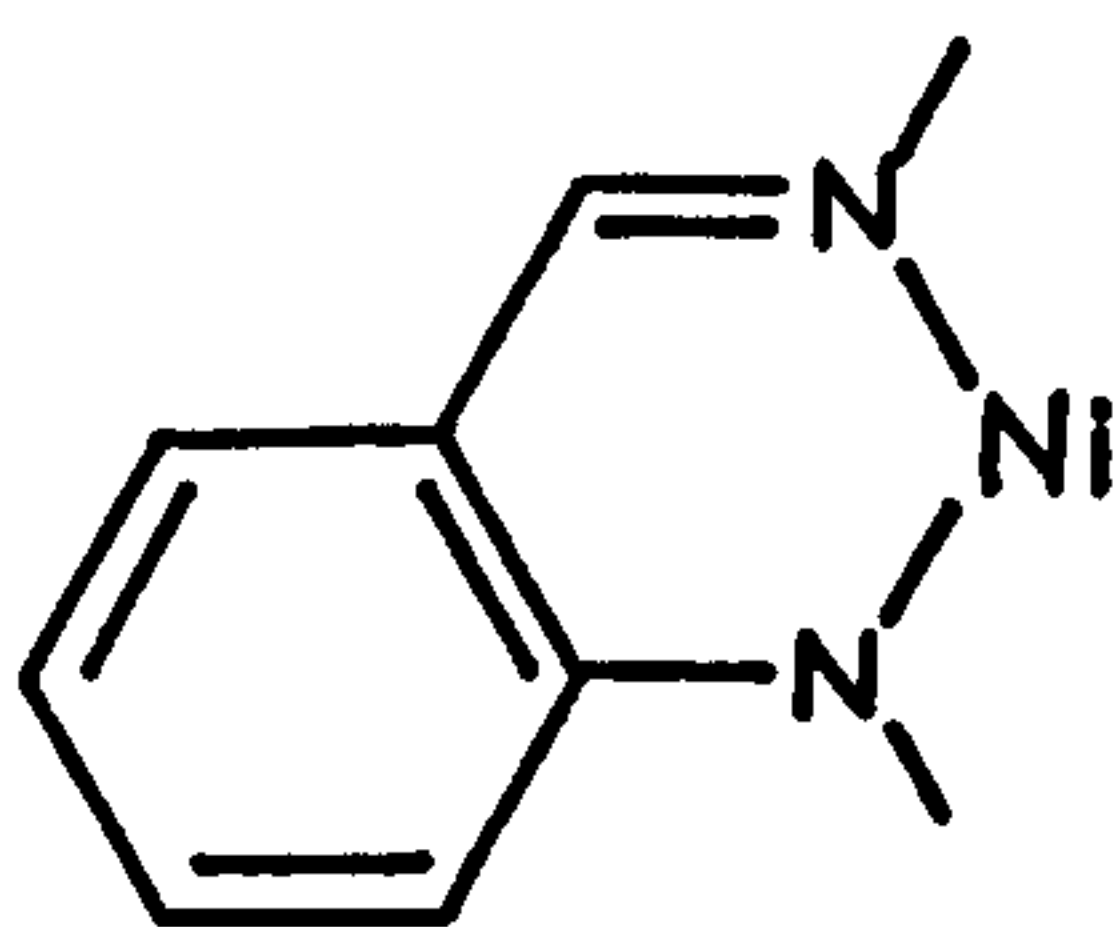
The conversion of [Nicyphen H<sub>2</sub>]<sup>2+</sup> (ClO<sub>4</sub><sup>-</sup>)<sub>2</sub> back to Nicyphen was studied spectrophotometrically. A small quantity of [Nicyphen H<sub>2</sub>]<sup>2+</sup> (ClO<sub>4</sub><sup>-</sup>)<sub>2</sub> was weighed into a volumetric flask, treated with a solution of methanolic sodium methoxide in tetrahydrofuran and made up to volume with tetrahydrofuran, and after the precipitate of sodium perchlorate had settled the spectrum was recorded for two diluted solutions (b) and (c). Since the extinction coefficients for Nicyphen in tetrahydrofuran are known (see page 201) the concentrations of Nicyphen in the solutions (b) and (c) could be estimated at several wavelengths (see table [8.10]). From these concentrations it was possible to calculate the percentage of C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>Ni ('Nicyphen') present in the orange material. The mean value was 65.8%

which compares favourably with a value of 66.4% predicted from the formula  $C_{22}H_{20}N_4NiCl_2O_8$  for  $[Nicyphen H_2]^{2+} (ClO_4^-)_2$ .

Besides illustrating the reversibility of the protonation, this method provides a convenient method for establishing the formulae of these type of 'adducts'.

The fact that a protonated form of the complexes can be isolated without displacement of the metal or hydrolysis of the ligand demonstrates a remarkable stability of these cyclic complexes. It would be interesting to investigate the possibility of similar 'adducts' for the acyclic systems discussed in chapter 4, to establish whether the exceptional stability of the compounds in table [8.9] is due primarily to the cyclic nature of the ligands.

It is not clear which centres in the molecule of Nicyphen are protonated on reaction with perchloric acid. The disappearance of some of the intense low-energy transitions from the electronic spectrum on protonation suggests that some of the  $\pi$ -orbital levels available for promotion of nickel(II) d-electrons are no longer present. The protonation of either the imino or anilino nitrogen atoms is consistent with this observation since either will reduce the conjugation or extensiveness of the  $\pi$  systems in the fragment [8.7].



[8.7]

It was hoped that an examination of the infrared spectra of the complexes in the C=N stretching region would furnish information as to whether the imine groups were protonated in the 'adducts'. New bands in the double bond stretching regions were observed for  $[\text{Nicyphen H}_2]^{2+} (\text{ClO}_4^-)_2$  and  $[\text{Nicyen H}_2]^{2+} (\text{ClO}_4^-)_2$ , and occur at slightly higher frequencies than for the starting material complexes. It is possible that these bands are the C=N stretching modes which are located at slightly higher frequencies due to the decrease in the conjugation in the systems (see page 191 and also reference 10) However, the possibility of this band being due to a deformation mode of the new NH group cannot be eliminated, since this is expected to occur somewhere in this region. This problem, and the general alteration of the C=C stretching modes which would also be expected for alteration of the conjugation in the rings makes this evidence inconclusive.

Unfortunately the protonated complexes are insufficiently soluble to allow their N.M.R spectra to

be obtained. An observation of spin-spin splitting of either the azomethine hydrogen or the 'anilino' methylene hydrogens would distinguish between protonation at either type of nitrogen atom.

The two 'adducts' shown in table [8.9] are diamagnetic, and the lack of splitting of the bands at  $1100\text{ cm}^{-1}$  in their infrared spectra indicates<sup>11</sup> that the perchlorate ions are not coordinated, and hence, a quadricoordinate planar arrangement of the nitrogen donor atoms is suggested (see section 4.4.4, page 82).

Many diamagnetic nickel(II) complexes of quadridentate amines show absorptions around  $500\text{ m}\mu$ .<sup>15</sup> Table [8.11] compares the absorption of  $[\text{Nicyphen H}_2]^{2+}(\text{ClO}_4^-)_2$  in this region with several comparable systems. The band in  $[\text{Nicyphen H}_2]^{2+}(\text{ClO}_4^-)_2$  lies in a position intermediate between those for the highly conjugated systems e.g. (TAAB) see [6.2], page 146 and the more saturated systems, e.g. (trans [14] diene) see [6.1], n=2, page 146.

Complex (a)	Position of 'yellow' <sup>15</sup> band. ( $\text{m}\mu$ )	Ref.
$[\text{NiTAAB}]^{2+}(\text{ClO}_4^-)_2$	526	12
$[\text{Nitrans}[14]\text{ diene}]^{2+}(\text{ClO}_4^-)_2$	435	13
$[\text{Nibeap}]^{2+}(\text{ClO}_4^-)_2$	450	14

$[\text{Nicyclam}]^{2+} (\text{ClO}_4^-)_2$	470	15
$[\text{Nicyphen H}_2]^{2+} (\text{ClO}_4^-)_2$	476	-

Table [8.11]. Positions of the 'yellow bands' in

$[\text{Nicyphen H}_2]^{2+} (\text{ClO}_4^-)_2$  and comparable systems.

- (a) TAAB (see [6.2] page 146), trans [14] diene<sup>16</sup>  
 (see [6.1], n=2, page 146), beap is 1,9-diamino-  
 3,7-diazazanonane and cyclam is 1,4,8,11-tetra-  
 azacyclotetradecane.

#### 8.4 References.

1. H.L. Schäfer and O. Kling, Z anorg. Chem., 309, 245, (1961).
2. V. Caglioti, C. Furlani, G. Dessy and C. Ibaria, Gazz. chim, 92, 1276, (1962).
3. G.A. Melson and D.H. Busch, J. Amer. Chem. Soc., 86, 4834, (1964).
4. J.L. Karn and D.H. Busch, Nature, 211, 160, (1966)
5. N. Sadasivan and J.F. Endicott, J. Amer. Chem. Soc., 88, 5468, (1966).
6. B.N. Figgis and J. Lewis, Prog. Inorg. Chem., 6, 37, (1964).
7. M. Kondo and M. Kubo, J. Phys. Chem., 62, 1558, (1958).
8. R.L. Martin and H. Waterman, J. Chem. Soc., 2545, (1957).
9. B. Bosnich, J. Amer. Chem. Soc., 90, 627, (1968)

10. H.M. Fischer and R.C. Stoufer, *Inorg. Chem.*, 5, 1172, (1966).
11. B.J. Hathaway and A.E. Underhill, *J. Chem. Soc.*, 3091, (1961).
12. G.A. Melson and D.H. Busch, *J. Amer. Chem. Soc.*, 86, 4834, (1964).
13. N.F. Curtis, Y.M. Curtis and H.K.J. Powell, *J. Chem. Soc. (A)*, 1015, (1966).
14. B. Bosnich, R.D. Gillard, E.D. McKenzie and G.A. Webb, *J. Chem. Soc. (A)*, 1331, (1966).
15. B. Bosnich, M.L. Tobe and G.A. Webb, *Inorg. Chem.* 4, 1109, (1965).

Chapter 9. Cobalt Complexes of some New Quadridentate  
Macrocyclic Ligands.

9.1 Syntheses and characterization.

9.1.1 Magnetic measurements

9.1.2 Electronic spectra.

9.1.3 Infrared spectra

9.2 'Model' compounds for vitamin B<sub>12</sub>

9.3. Oxidation

9.4 Reduction

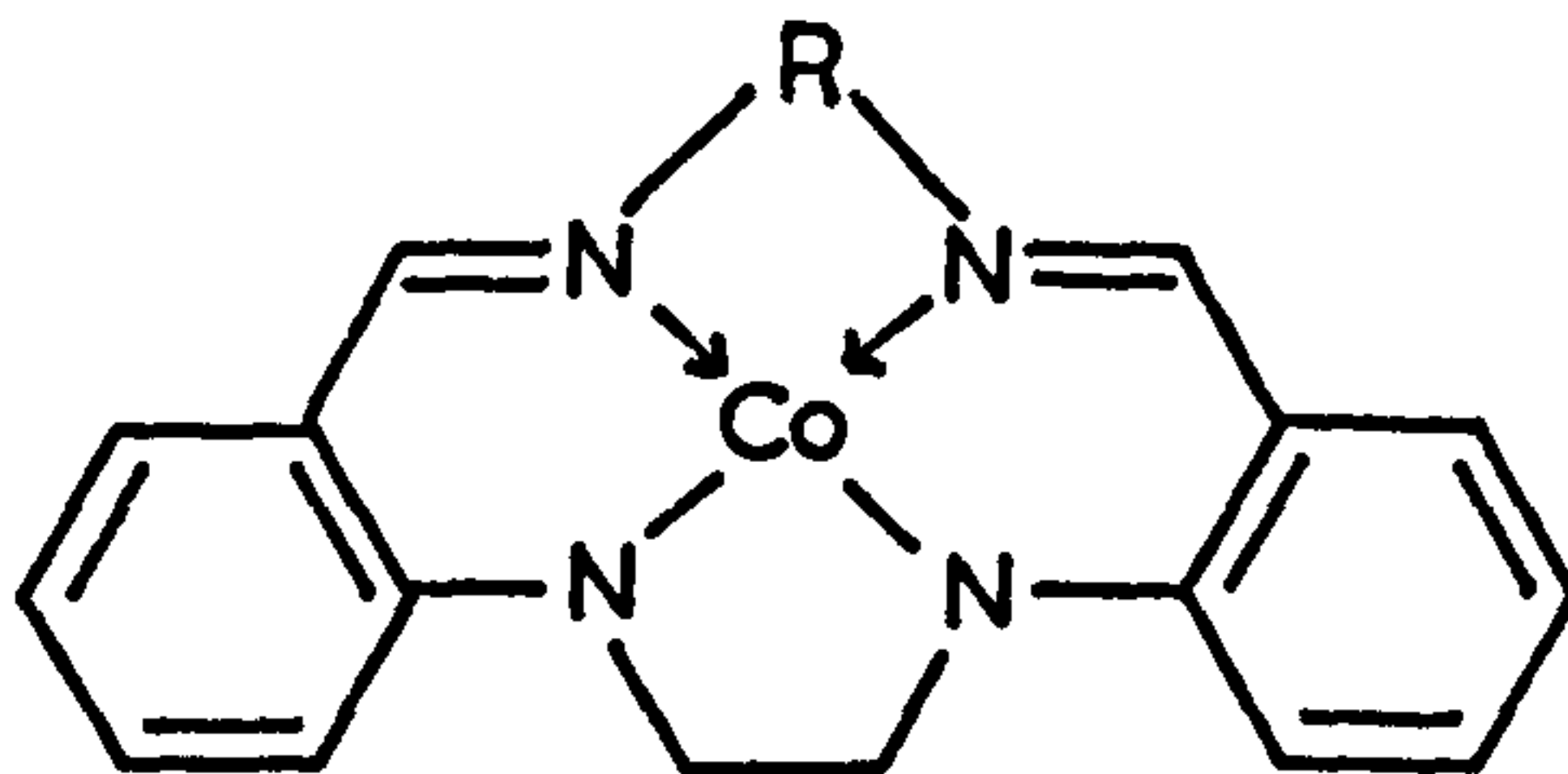
9.5 References

This chapter describes a series of cobalt(II) complexes of the cyclic ligands discussed in chapter 7.

[9.1] lists these complexes, and shows the abbreviations which will be used in this thesis.

9.1 Synthesis and characterization.

Synthesis of the complexes was achieved in a very similar manner to that used for the analogous nickel(II) and copper(II) complexes [8.1] page 189, i.e. by reaction of the appropriate diamine with 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione in a methanolic solution of cobalt(II) acetate. All operations were performed under an atmosphere of nitrogen as a precaution against oxidation and oxygenation, and the complexes were obtained as fine



R=	abbreviation
$-(\text{CH}_2)_2-$	Cocyen
$-(\text{CH}_2)_3-$	Cocytn
$-(\text{CH}_2)_4-$	Cocybuten
$-\text{C}_6\text{H}_4-$	Cocyphen

[ 9.1 ]



deep purple-red crystals. Attempts to recrystallize these products [9.1] from several solvents were unsuccessful, despite elaborate precautions to exclude oxygen, and so samples of the unrecrystallized products were sent for analysis.

A crystal of Cocyen suitable for an X-ray structure determination was grown from a reaction mixture of cobalt(II) acetate, 1,2-diaminoethane and 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione in dimethyl sulphoxide maintained for several weeks at c.a. 25° in the apparatus shown in [11.3] , page 329.

All the complexes shown in [9.1] appear to react slowly on standing in air to give materials which are much less soluble in organic solvents. Infrared spectra of mulls of these materials are similar to the freshly prepared complexes. The most striking change is observed for Cocyen, for which the purple-red needles crumble on exposure to air, giving a fine brown-orange powder. The other complexes remain crystalline, but darken slowly. It is not yet clear whether these changes are caused by reversible oxygenation (see page 127) or oxidation to cobalt(III).

Analysis results for the four cobalt(II) complexes are shown in table [9.1].

Compound	Molecular Formula	Composition %			
			C	H	N
Cocyen	$C_{18}H_{18}N_4Co$	Calc.	61.89	5.19	16.03
		Found	61.24	5.35	15.77
Cocytn	$C_{19}H_{20}N_4Co$	Calc.	62.81	5.55	15.42
		Found	62.55	5.58	15.47
Cocybuten	$C_{20}H_{22}N_4Co$	Calc.	63.66	5.87	14.85
		Found	62.95	5.94	14.12
Cocyphen	$C_{22}H_{18}N_4Co$	Calc.	66.50	4.57	14.10
		Found	65.68	4.49	14.45

Table [9.1] Analysis results for the cobalt(II) macrocyclic complexes.

In order to substantiate the cyclic formulation of the complexes and the consequent molecular formulae shown in table [9.1] the molecular weight of Cocytn was estimated using a Mecrolab 'Osmometer Model 301A'. Unfortunately this instrument is unsuitable for air-sensitive solutions, and readings of the volatility of a benzene solution had to be recorded before the apparatus had been allowed its 'normal' equilibration time of 2 min. Also Cocytn is only slightly soluble in benzene and so very dilute solutions had to be used (better solvents, e.g. chloroform and carbon tetrachloride appear to react with the complexes : see page 222). Under these circumstances the determined molecular weight of 402

Complex	Temp.	$\chi_g$	$\chi_M$	$\chi_L$	$\chi_{M'}$	$\mu$
	(°K)	$\times 10^6$	$\times 10^6$	$\times 10^6$	$\times 10^6$	b
Cocyen	290-291	5.132	1791	-175 <sup>a</sup>	1966	2.15±.05
Cocytn	291-296	4,850	1762	-187	1949	2.15±.02
Cocybuten	295-296	6.475	2443	-199	2642	2.51±.01
Cocyphen	291-292	5.201	2070	.186	2256	2.30±.06

Table [9.2] Magnetic susceptibilities (cgs units) of the solid cobalt(II) macrocyclic complexes at room temperature.

- (a) from tables<sup>1</sup>  
 (b) mean for values calculated for different temperatures (see page 230), other quantities ( $\chi_g$  etc - symbols listed in chapter 10) are actual figures for a determination at an intermediate temperature.

compares reasonably with the value of 363 predicted for the formula  $C_{19}H_{20}N_4Co$ .

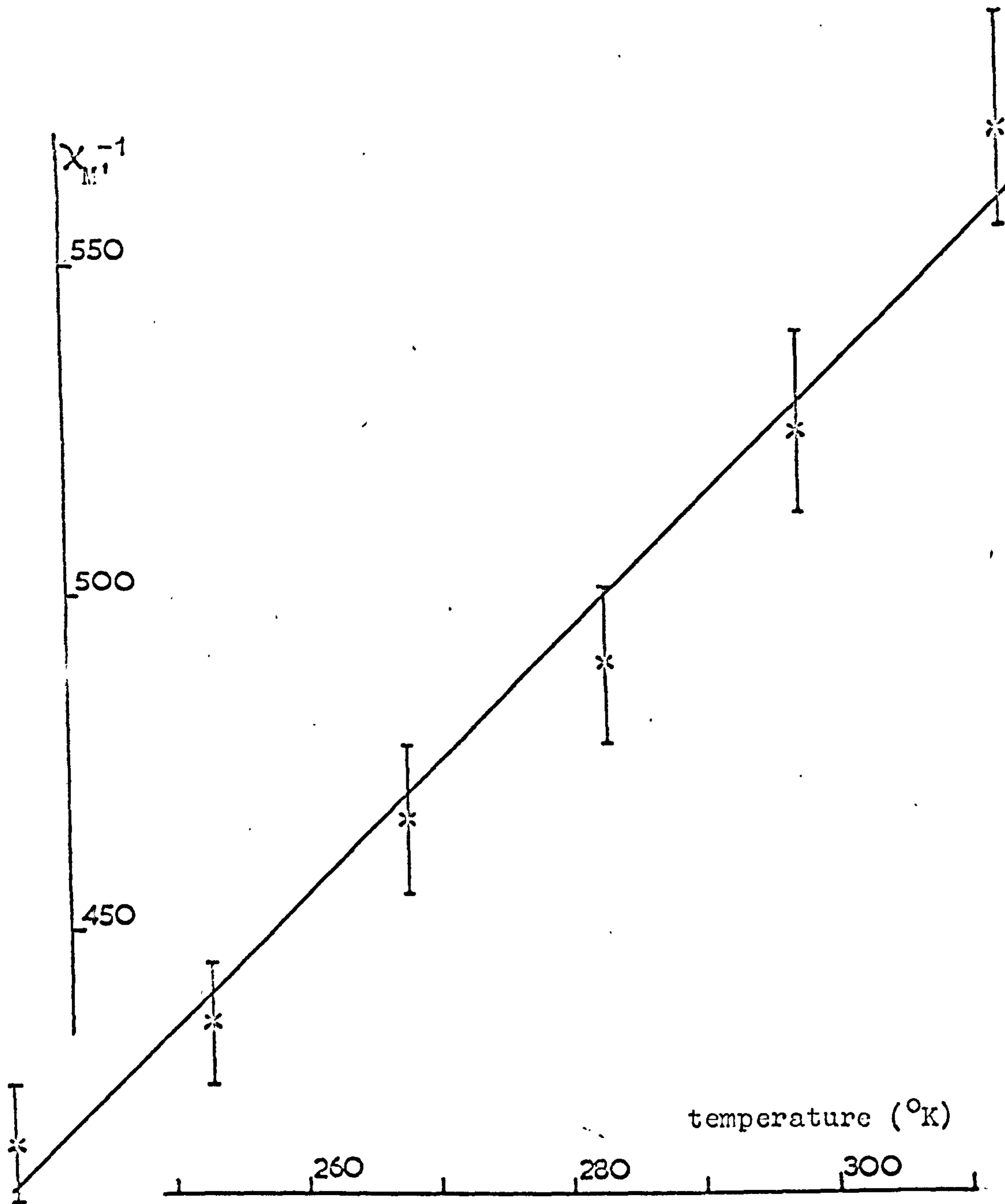
### 9.1.1 Magnetic Measurements.

The magnetic susceptibilities of the complexes are shown in table [9.2]. It was found that the more granular crystalline complexes Cocyt<sub>n</sub> and Cocybut<sub>n</sub> gave smaller errors for the determined quantities  $\chi_g$  and  $\mu$  than the fine needles of Cocy<sub>n</sub> and Cocyphen, which were more difficult to pack in a reproducible manner.

The values for the magnetic moments of the solid complexes all fall within the range which is typical of quadricoordinate cobalt(II) with a planar low-spin configuration (see page 116, chapter 5).

Molecular models indicate that in Cocybut<sub>n</sub>, the ligand would be capable of giving an approximately tetrahedral arrangement of its four nitrogen atoms about the cobalt ion, which would be less strained than a planar arrangement. Possibly the preference for the planar structure results from the high ligand field of cybut<sub>n</sub>, which favours a low-spin configuration, which is more stable for a tetragonal arrangement of the donor atoms.

Dr Main of the Physics Department has kindly agreed to attempt an X-ray determination of the structure of Cocybut<sub>n</sub> and several related compounds.



[9.2]. A plot of  $\chi_M^{-1}$  against temperature for a solution of Cocytin in pyridine + 2% tetramethylsilane.

For Cocytyn and Cocybuten, which are appreciably soluble in pyridine the magnetic susceptibilities were examined over a range of temperatures, using the N.M.R method described in chapter 10. The results are given in tables [9.3] and [9.4] and plots of  $\chi_{M'}^{-1}$  against temperature are shown in [9.2] and [9.3] on pages F213 and F214 .

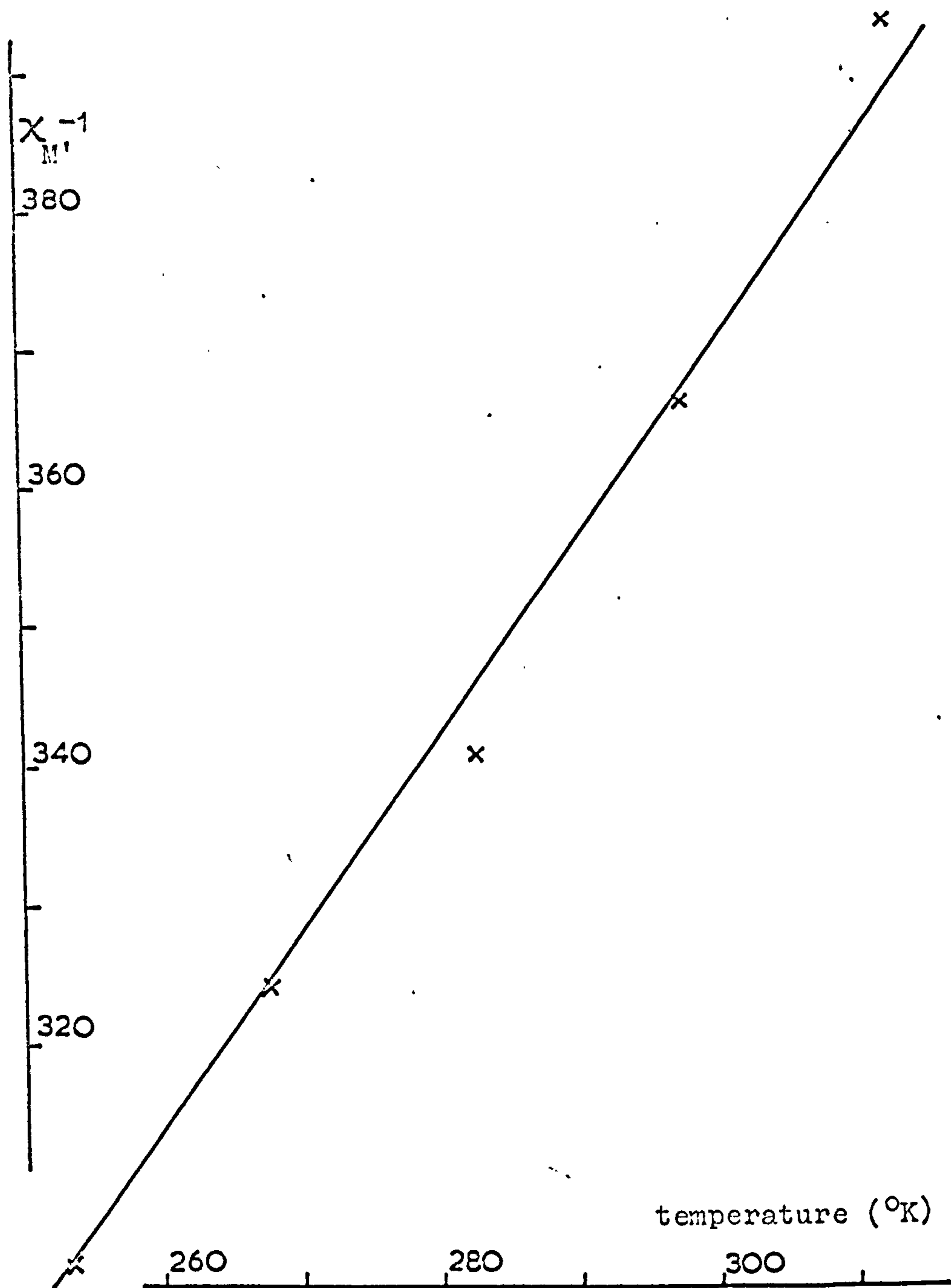
Temp. (°K)	$\Delta f$ (cps)	$\chi_g$ $\times 10^6$ a	$\chi_M$ $\times 10^6$	$\chi_{M'}$ $\times 10^6$ b	$\chi_{M'}^{-1}$
313	3.2	4.36	1582	1752	571
298	3.5	4.76	1730	1900	525
283	3.8	5.17	1879	2049	488
268	4.0	5.45	1977	2147	466
253	4.3	5.85	2126	2296	436
238	4.5	6.13	2225	2395	418

Table [9.3]. Magnetic susceptibilities (cgs units) of a pyridine solution of Cocytyn containing 2% TMS.

(a) Calculated using equation [10.2] page 235 and calibration constant  $(c')=7.96(2)$ .

(b) Corrected for the molar susceptibility of the ligand, see table [9.2] .

Temp. (°K)	$\Delta f$ (cps)	$\chi_g$ $\times 10^6$ a	$\chi_M$ $\times 10^6$	$\chi_{M'}$ $\times 10^6$ b	$\chi_{M'}^{-1}$
313	11.4	6.22	2345	2545	393
298	12.3	6.71	2531	2730	366
283	13.3	7.26	2737	2936	341



[9.3]. A plot of  $\chi_M^{-1}$  against temperature for a solution of Cocybuten in pyridine + 2% tetramethylsilane.

268	14.0	7.64	2881	3080	325
253	15.0	8.19	3087	3286	304

Table [9.4] Magnetic susceptibilities (cgs units) of a pyridine solution of Cocybuten containing 2% TMS

- (a) Calculated using equation [10.2] page 235 and a calibration constant ( $c'$ ) = 7.96(2).  
 (b) Corrected for the molar susceptibility of the ligand, see table [9.2].

The plots of reciprocal of corrected molar susceptibility against temperature suggest slight deviations from the Curie-Weiss law. However, it is doubtful whether these apparent deviations are significant since in [9.2] the errors in the values of  $\chi_M^{-1}$  resulting from an error of 0.1 cps in the estimation of

$\Delta f$  (see page 237) are shown to be such that all the points could fall on a line obtained by a least mean squares analysis for the six points. The large errors in estimating  $\chi_g$  etc. in this case are principally due to the low concentration of Cocytyn in solution and the consequent small values of  $\Delta f$ . An investigation over a larger temperature range might reveal if there is a genuine departure from Curie-Weiss behaviour.

It is unlikely that any solvation to give five or six-coordinate species occurs in pyridine solution,



since such species would probably have a high-spin configuration with magnetic moments greater than 4 B.M. (see page 118). The paramagnetic susceptibility of the pyridine solutions of Cocyt<sub>n</sub> and Cocyb<sub>u</sub>ten is satisfactorily accounted for by magnetic moments for the cobalt ions similar to those observed in the solid state (see below). Also, if solvation occurred to give high-spin species in equilibrium with the unsolvated low-spin form a large departure from Curie-Weiss law would be expected, since the solvated forms are likely to be strongly favoured by decrease in temperature (see page 248).

The best straight line through the points of [9.2] has a slope of  $2.01 \pm 0.15$  and gives a value of  $2.00 \pm .08$  B.M. for the magnetic moment of the cobalt(II) ion in a pyridine solution of Cocyt<sub>n</sub>. Similarly for Cocyb<sub>u</sub>ten the moment is 2.39 B.M. These values are quite close to those observed for the solid complexes (page 212).

The straight line shown in [9.2] gives an intercept at  $T=0$  of  $-70.6 \pm 42.5$  and hence a Weiss constant  $= -35 + 21^{\circ}$ . Similarly for Cocyb<sub>u</sub>ten the Weiss constant  $= -38^{\circ}$ . However it would be foolish to place any real significance on these constants in view of the large errors involved and the possibility of departure from Curie-Weiss behaviour.

### 9.1.2 Electronic spectra.

The electronic spectra of the complexes [9.1] (see table [9.6]) are very similar to those of the acyclic analogues which have been discussed in chapter 5. The intense bands of the acyclic complexes which occur in the region 400-600  $m\mu$  are found at slightly lower energy for the cyclic analogues, but the molar extinction coefficients for the absorption maxima, and the appearance of the bands are remarkably similar for both types of compound. Table [9.5] compares the absorption maxima of dimethylformamide solutions of Coambtn and Cocyttn to illustrate the similarities of the two spectra. Occurrence of the intense bands at slightly lower energies in the cyclic compounds was also recorded for the nickel(II) complexes (see page 197).

Compound	$\lambda_{\max}$ ( $\epsilon$ )			
Cocyttn	930 (70)	555 (3840)	448 (12200)	377 (9500)
Coambtn	960(sh) (83)	540 (3080)	435 (9900)	375 (9680)

Table [9.5] Absorption maxima ( $m\mu$ ) of dimethylformamide solutions of Cocyttn and Coambtn.

Both in nujol mulls and deoxygenated dimethylformamide solutions of the freshly prepared complexes it was possible to detect a fairly sharp absorption in the region  $900 - 1000 \text{ m}\mu$ , having a molar extinction coefficient of about 100. A similar band was observed for the acyclic complexes, and might correspond to the transition at  $1200 \text{ m}\mu$ , which has been quoted<sup>2</sup> as characteristic of planar quadricoordinate complexes of Schiff bases of the 'salen' - type (see also page 124). In some of the complexes type [9.1] another absorption was observed which might be due to a d-d transition occurring at  $600 - 650 \text{ m}\mu$  as a shoulder on the lowest energy intense band.

The near infrared region of the spectrum has been used quite often<sup>2,3,4,5,6</sup> to observe changes in the coordination geometry of cobalt(II) complexes, because, for a series of complexes, a particular arrangement of donor atoms about the cobalt ion produces a characteristic spectrum.

Since nujol mull spectra of the complexes [9.1] all contain a single sharp peak at  $900 - 1000 \text{ m}\mu$  it is probable that they all have a similar arrangement of the four nitrogen atoms about the cobalt ion (presumably planar - see section 9.1.1). The same arrangement also in both

dimethylformamide and pyridine solutions is suggested by the very similar spectra of these solutions. The failure of pyridine to coordinate to the cobalt atom in Cocyt<sub>n</sub> and Cocybut<sub>n</sub> has already been demonstrated by magnetic measurements (see page 215), and was also observed for the acyclic complexes.

Table [9.6] The electronic spectra of the cobalt(II) complexes type [9.1]

(a) Dimethylformamide (b)  $\lambda_{\max}$  in  $m\mu$  (c) Molar extinction coefficient (d) Shoulder (e) Scanned 300-1200  $m\mu$   
 (f) Scanned 350-1200  $m\mu$  (g) Scanned 300-650  $m\mu$   
 (h) Dimethyl sulphoxide (i) Tetrahydrofuran.

Cocy<sub>n</sub> as a DMF<sup>a</sup> solution<sup>e</sup>; 900<sup>b</sup> (110)<sup>c</sup>, 640(sh)<sup>d</sup> (430), 542(4200), 510(sh)(3300), 442(19100), 376(11200), as a nujol mull. f; 900, 615(sh), 560, 510(sh), 441, 380.

Cocy<sub>t<sub>n</sub></sub> as a DMF solution<sup>e</sup>; 930(70), 555(3840), 448(12200), 377(9500), 325(sh)(8500) as a nujol mull f; 930, 560, 450, 380.

Cocybut<sub>n</sub> as a DMF solution<sup>e</sup>; 940(80), 615(sh)(3100), 558(4200), 446 (13100), 384(9900), 332(sh)(9100), as a nujol mull. f; 950, 620(sh), 560, 450, 380.

Cocyphen as a DMSO<sup>h</sup> solution<sup>e</sup>; 950(90), 745 (1100), 660(2600), 582 (5300), 555(sh)(5000), 512(sh)(5100), 442(23100), 408(20600), 398(20600), 368(sh)(16900),

330(17700),

as a DMF solution  $\epsilon$ ; 580(4000), 550(sh)(8900),  
518(sh)(3900), 442(15100), 392(14800), 370(sh)  
(13300), 338(sh)(13900),

as a THF<sup>i</sup> solution  $\epsilon$ ; 580, 550, 515, 442, 395,  
368, 316,

as a nujol mull<sup>f</sup>; 930, 790, 690, 600, 480, 380.

### 9.1.3 Infrared spectra.

The infrared spectra of the complexes are tabulated on page 329 in the experimental section; and are very similar to the analogous nickel(II) complexes which have been discussed in chapter 8. Each of the complexes [9.1] was characterized initially on the basis of its infrared spectrum, which proved a useful criterion for judging whether the product was contaminated with 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione, since this has sharp characteristic absorptions at 3335 and 1660  $\text{cm}^{-1}$ .

### 9.2 'Model' compounds for vitamin B<sub>12</sub>

The full potential of the systems [9.1] as a source of 'model' compounds for vitamin B<sub>12</sub> has not yet been fully explored. Some preliminary results are presented below.

### 9.3 Oxidation of the complexes.

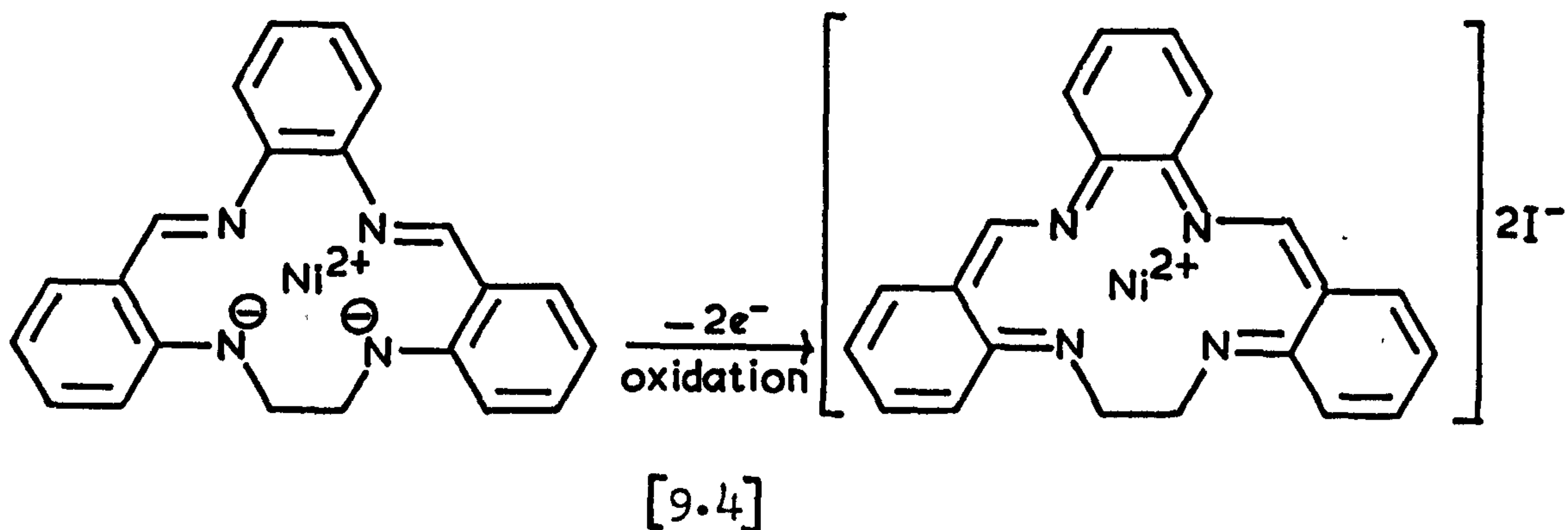
Tetrahydrofuran solutions of Cocyen and Cocyphen reacted almost instantaneously with solutions of iodine or bromine to give black amorphous solids which are almost insoluble in nearly all solvents, but sparingly soluble in pyridine to give intense red-brown solutions.

In order to elucidate these reactions it was decided to study the oxidation of the analogous nickel(II) complexes.

It was found that Nicyphen also gave a similar reaction with iodine, and the product isolated from the reaction of equimolar quantities analysed for NicyphenI<sub>2</sub>, and gave an infrared spectrum with many peaks similar to Nicyphen, but with clear differences in the region 700-1250 cm<sup>-1</sup>. It was thought initially that a substitution reaction of the aromatic rings had occurred. However, some acyclic complexes of chapter 4 did not appear to react in this way, and so another possibility was considered, i.e. that the Nicyphen had been oxidized to a species which contained nickel with a formal oxidation state of four.

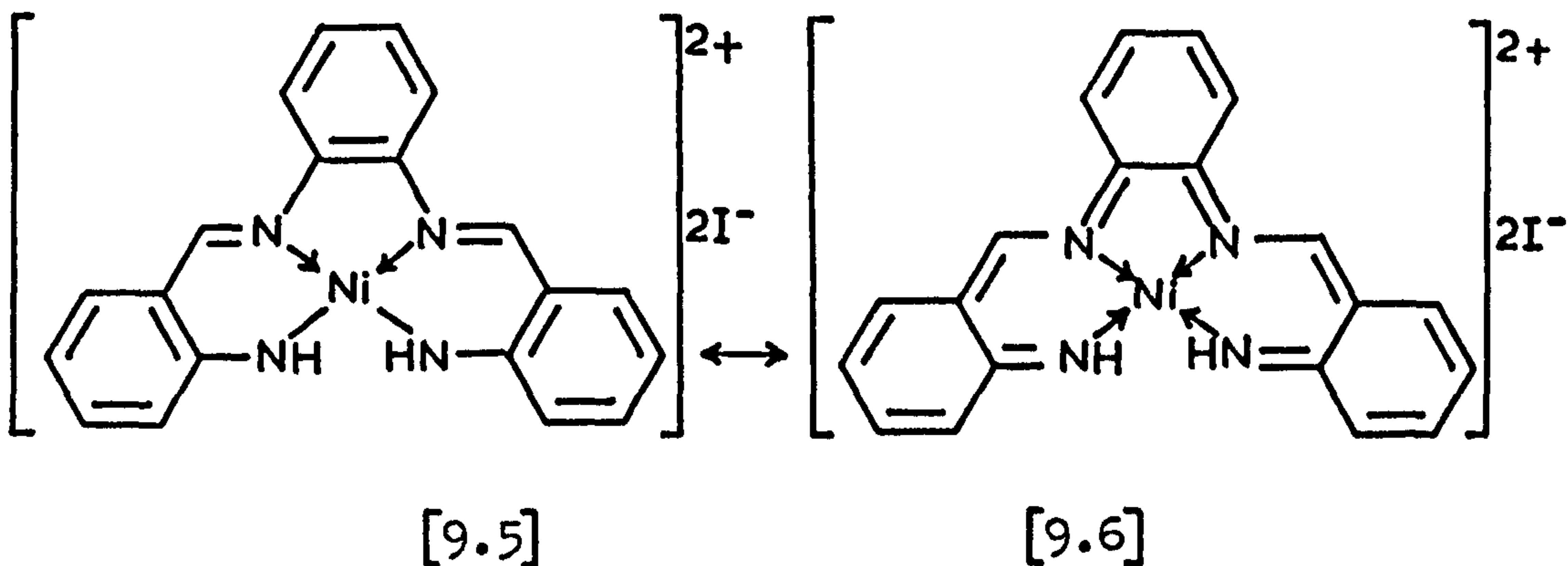
Some remarkable features of the ligand system would stabilize such an oxidation state. Diagram [9.4] shows that two electrons could be removed from the ligand system cyphen<sup>2-</sup> without formally involving the nickel ion

at all. The oxidized form has one more double bond, and a quinone structure for its benzene rings.



Certain other observations support this hypothesis:

(a) A complex analysing for  $\text{NiambphenI}_2$  was isolated after reaction of Niambphen with iodine. A similar resonance structure [9.6] involving quinone forms of the benzene rings is also possible for this oxidation product [9.5].



The ease of metal to ligand charge transfer suggested by [9.5] and [9.6] could account for the extremely strong absorptions in the visible spectrum.

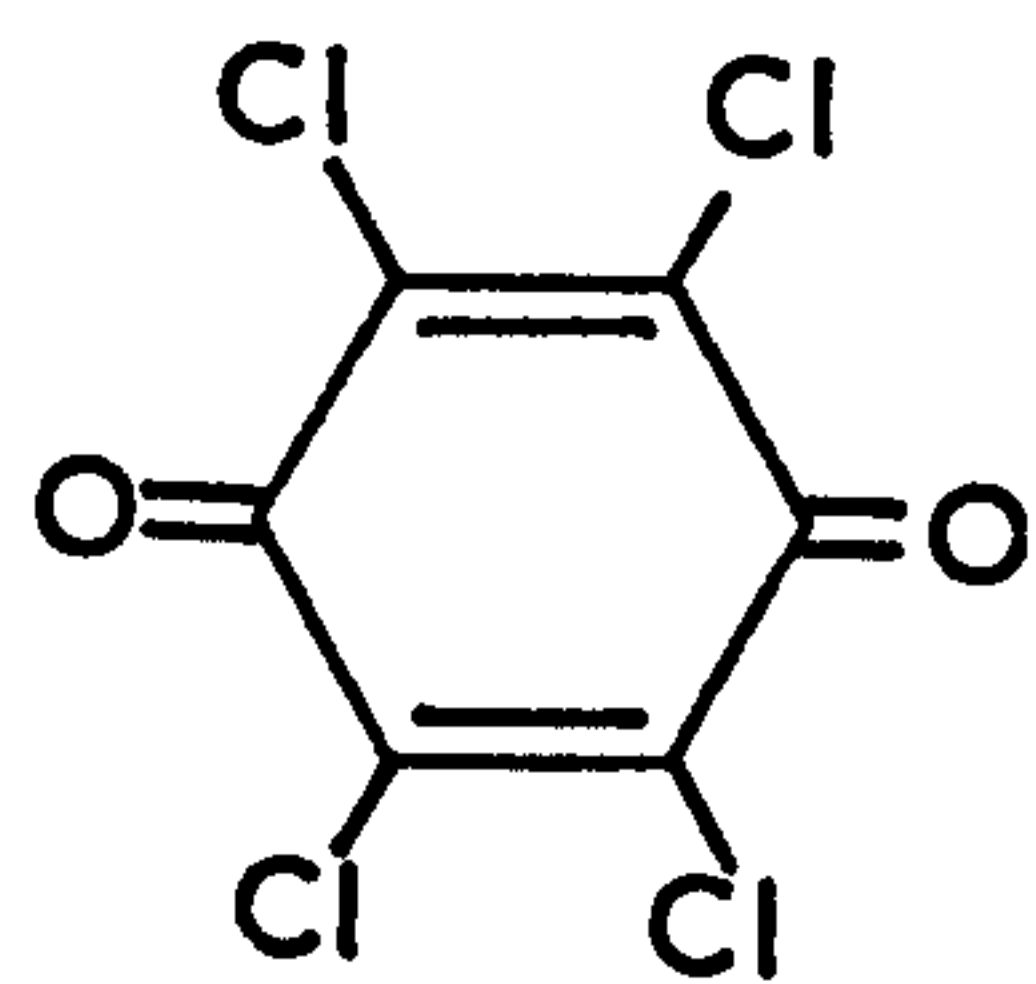
(b) R.H. Holm has presented<sup>7,8</sup> evidence for nickel complexes of anionic forms of 1,2-diaminobenzene being oxidized to species formally containing Ni(IV).

(c) Certain sulphur-containing ligands with extensive  $\pi$ -orbital systems stabilize unusual oxidation states of many metal ions in square-planar complexes.<sup>9</sup>

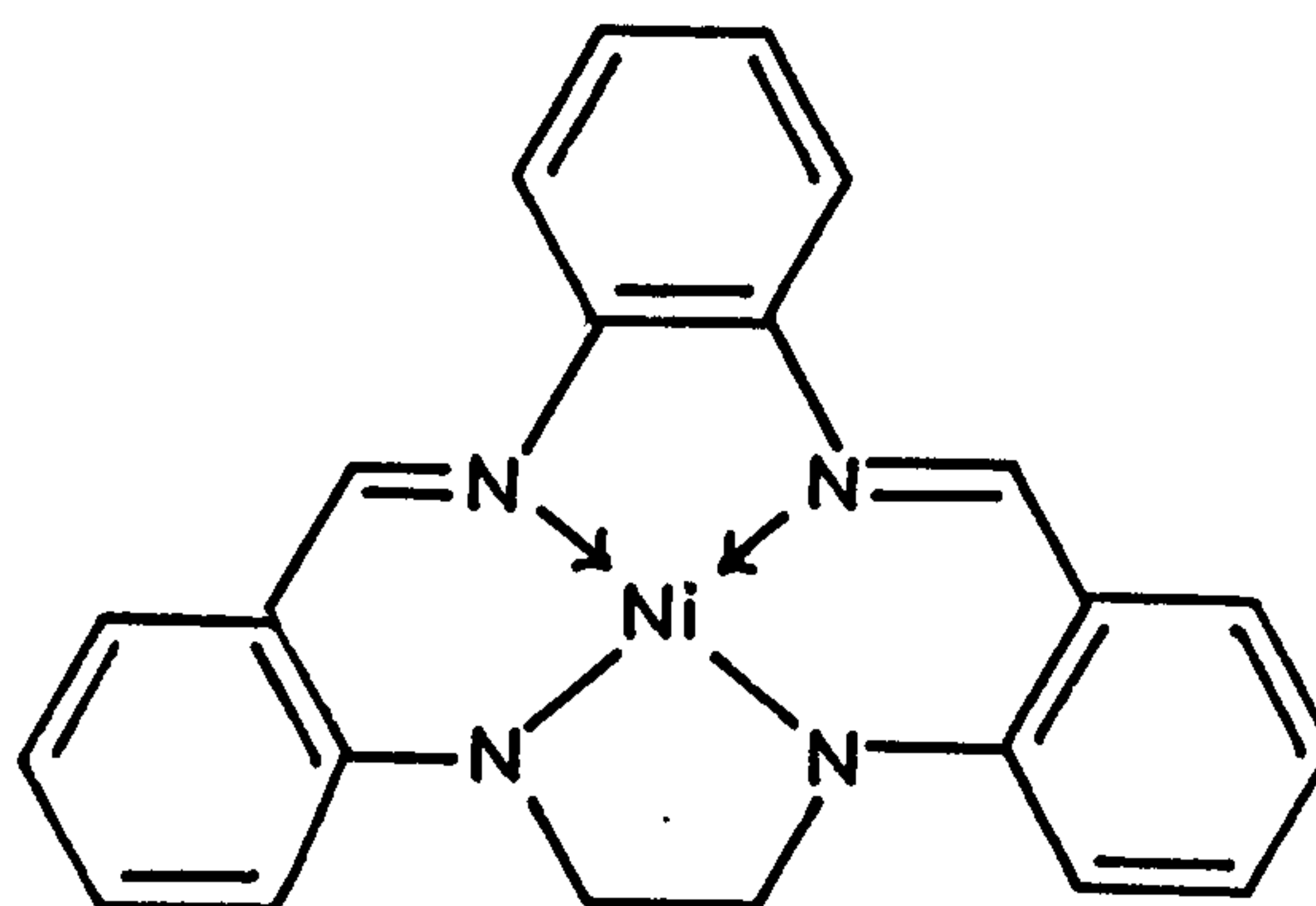
(d) The participation of a conjugated system (linking the four nitrogen donors) of the corrin ring of vitamin B<sub>12</sub> in stabilizing unusual oxidation states and alkyls of cobalt has already been suggested (see chapter 1 ).

During the course of spectroscopic investigations on both the cobalt(II) and nickel(II) complexes of the macrocyclic ligands it was observed that they appeared to react with chlorinated solvents. The reactions are strongly light catalysed, and occur faster in carbon tetrachloride than in chloroform. The products are highly insoluble amorphous materials which resemble those obtained from the reactions of the complexes with halogens. It is possible that the reactions may be analogous to the oxidation of Cosalen by chloroform, which has been reported by Katagari and Endo<sup>10</sup>.

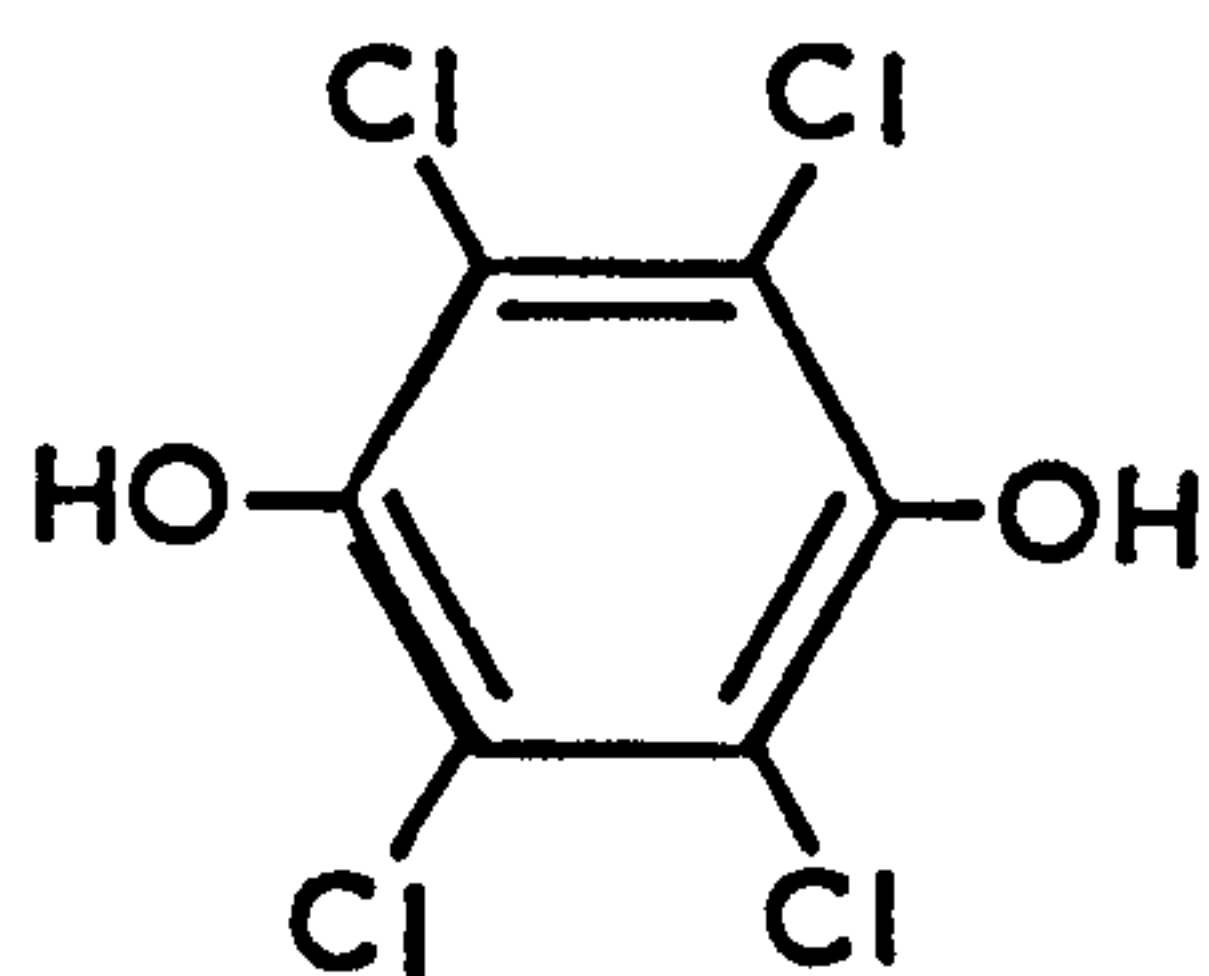




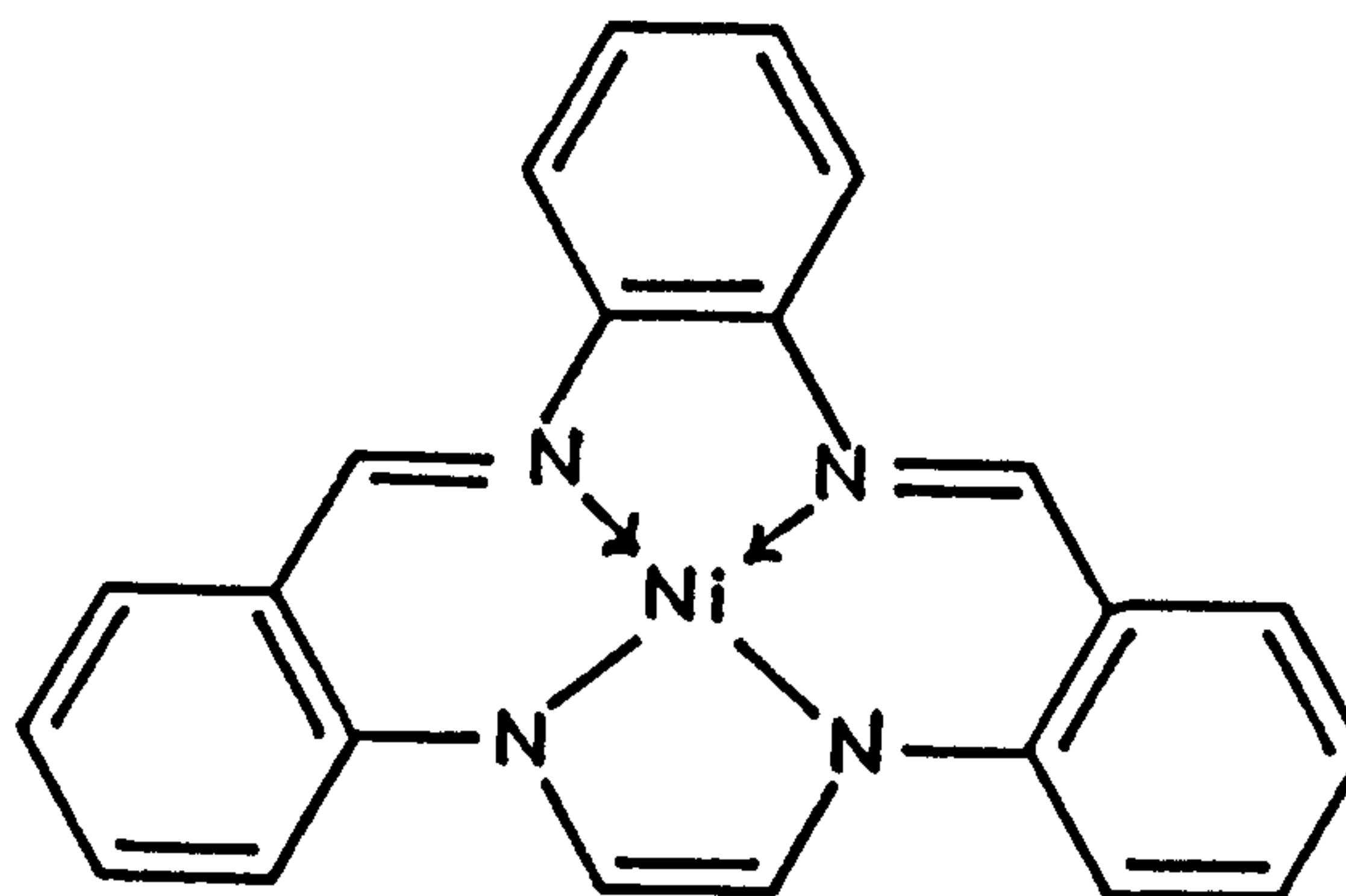
[9.7]



Benzene



[9.8]



From the reaction of Nicyphen with 2,3,5,6-tetra-chloro-p-benzoquinone [9.7] a product was obtained with an infrared spectrum remarkably similar to that of the compound analysing for NicyphenI<sub>2</sub> described above. This reaction was attempted because it was hoped that the dehydrogenating properties<sup>11,12</sup> of [9.7] could lead to the more conjugated cyclic complex [9.8]. Initial observations suggest that this dehydrogenation may also have been accompanied by further oxidation, since the product gave low carbon, hydrogen and nitrogen analysis figures and [9.8] should show very similar results to Nicyphen.

#### 9.4. Reduction.

Tetrahydrofuran solutions of Cocyen and Cocyphen were reduced with sodium sand or 2% sodium amalgam, and gave green, air-sensitive, solutions, which presumably contain cobalt with a formal oxidation state of one, by analogy with the results for the acyclic complexes discussed in chapter 5. The reaction of these green solutions with alkyl halides has given products which have not yet been characterized.

Since some cobalt phthalocyanines have been reduced with much milder reagents,<sup>13,14</sup> e.g. sodium

dithionite or hydrazine, these were employed in attempts to reduce Coccyphen, but without any apparent success.

### 9.5 References.

1. P.W. Selwood, "Magnetochemistry", 2nd Ed., Interscience, 1956, page 92.
2. H. Nishikawa and S. Yamada, Bull. Chem. Soc. Japan, 37, 8, (1964).
3. S. Yamada, Coordin. Chem. Rev., 1, 415, (1966).
4. S. Yamada and E. Yoshida, Bull. Chem. Soc. Japan, 40, 1298, (1967).
5. E. Yoshida and S. Yamada, Bull. Chem. Soc. Japan, 40, 1395, (1967).
6. L. Sacconi, Coordin. Chem. Rev. 1, 192, (1966).
7. A.L. Balch, F. Röhrscheid and R.H. Holm, J. Amer. Chem. Soc., 87, 2301, (1965).
8. A.L. Balch and R.H. Holm, J. Amer. Chem. Soc., 88, 5201, (1966).
9. H.B. Gray, "Transition Metal Chemistry", Vol. 1, Ed. R.L. Carlin, Arnold, 1965, page 239.
10. S. Katagari and J. Endo, J. Chem. Soc. Japan, 84, 197, (1963).
11. L.M. Jackman and D.T. Thompson, J. Chem. Soc. 4794 (1961).
12. E.A. Brande, L.M. Jackman and R.P. Linstead, J. Chem. Soc., 3548, (1954).

13. P. Day, H.A.O. Hill, M.G. Price, J. Chem. Soc. (A) 90, (1968).
14. D.H. Busch, J.H. Weber, D.H. Williams and N.J. Rose, J. Amer. Chem. Soc. 86, 5161, (1964).

## Chapter 10 General Experimental Details.

- 10.1 Mass spectra.
- 10.2 N.M.R. spectra.
- 10.3 Infrared spectra.
- 10.4 Ultraviolet, visible and near infrared spectra.
- 10.5 Magnetic susceptibility of solid samples.
- 10.6 A. N.M.R method for magnetic susceptibility in solution.
  - 10.6.1 Calibrant solutions.
  - 10.6.2 Measurement of bulk susceptibility shift.
  - 10.6.3 Results for calibrant solutions.
  - 10.6.4 Other measurements.
  - 10.6.5 Non-aqueous solvents.
  - 10.6.6 Variation of capillary mounting.
  - 10.6.7 Air-sensitive samples.
  - 10.6.8 Variable temperature measurements.
  - 10.6.9 Equilibrium studies.
  - 10.6.10 Summary.
- 10.7 Measurement of gas uptake by solutions.
  - 10.7.1 Measurement of pressure change.
  - 10.7.2 Thermostating.
  - 10.7.3 Determination of the volume of the apparatus.
  - 10.7.4 Reaction vessel and burette systems.
  - 10.7.5 Nitrogen line.
  - 10.7.6 Stirrer.

10.7.7 Solubility of the gas in the solvent system.

10.7.8 Gas uptake in solution.

10.8 Solvent purification.

10.8.1 Pyridine.

10.8.2 Dimethylformamide.

10.8.3 Dimethylsulphoxide.

10.8.4 Tetrahydrofuran.

10.8.5 Methanol.

10.8.6 Ethanol.

10.9 Miscellaneous details.

10.10 References.

### 10.1 Mass spectra.

Routine spectra were recorded on an A.E.I. M.S.12 instrument, using a direct insertion probe, normally maintained at approximately  $150^{\circ}$ .

Accurate masses of peaks were determined on an A.E.I. M.S.9 instrument at the University of Hull.

### 10.2 Nuclear magnetic resonance spectra.

Spectra were recorded by Mrs M. Sutherland on a Perkin Elmer R10  $60 \text{ Mc sec}^{-1}$  N.M.R. Spectrometer at  $33^{\circ}$ . In some cases the Perkin Elmer variable temperature probe accessory was used.

Under normal operating conditions chemical shifts were reproducible to  $0.02 \tau$ .

### 10.3 Infrared spectra.

Both mulls and potassium bromide discs were used to record spectra of solid samples. A Unicam 200 G instrument was used for routine work, but some spectra requiring finer resolution were run on a Perkin Elmer 621 instrument.

In the tabulation of absorption maxima the following abbreviations were used; m = medium, s = strong, w = weak (relative intensities) and b = broad, v = very, sh = shoulder (appearance)

### 10.4 Ultraviolet, visible and near-infrared spectra.

Solution spectra were recorded on a Cary 14 Spectrophotometer. Since a diffuse reflectance spectrum attachment was not available, solid spectra were recorded as nujol mulls supported either on strips of filter paper or between two potassium bromide plates.<sup>1</sup>

For solutions of air-sensitive materials in tetrahydrofuran, dimethylformamide and dimethylsulphoxide 'suba' seals could not be used to keep the cells air-free, since they dissolve in these solvents giving strong bands in the visible and ultraviolet regions. Special taps

with B10 'quickfit' joints were fitted to the cells for measurements of such air-sensitive solutions.

The abbreviations used in tabulation of spectra were the same as in section 10.3.

### 10.5 Measurement of magnetic susceptibility of solid samples.

For solid samples the Gouy method was used at room temperature with a procedure as outlined in reference 2.

An electromagnet manufactured by Newport Instruments (1½" - type C) was used (½" pole faces and a gap of approximately 1 cm.). The magnet was water cooled, and used in conjunction with a variable output d.c. supply unit (0-3 amp., 0-150 volt), also manufactured by Newport Instruments.

A balance manufactured by Stanton Instruments (type SM 12), capable of weighing to ±.02 mg was used to detect apparent changes in weight in subjecting the sample to a magnetic field. Modifications of the balance to allow the suspension of a Gouy tube from the balance pan were carried out as suggested by Newport Instruments.<sup>3</sup>

The Gouy tube was calibrated using mercury tetrathiocyanatocobalt(II)<sup>4</sup> and triethylenediaminenickel(II) thiosulphate<sup>5</sup> which have mass susceptibilities of  $16.44 \times 10^{-6}$  (±0.5%) and  $11.03 \times 10^{-6}$  (±1%) c.g.s. units respectively



at 20°C and follow the Curie-Weiss Law with  $\theta = 10$  and  $-43^\circ$  respectively<sup>4,5</sup>. These calibrants were prepared using identical conditions to those in the literature.<sup>4,5</sup> The values for the calibration constant  $\beta$  (see reference 2) for a single magnetic field agreed to within 1% and the mean value was used in determinations of unknown susceptibility.

Unknown susceptibilities were determined at two field strengths, approximately 7000 and 9000 gauss<sup>3</sup> (electromagnet currents of 0.8 and 1.1 amp. respectively) to test for ferromagnetic impurities.

When room temperature changed over a series of determinations for the same material, the magnetic moment was calculated assuming the Curie Law to be applicable over a small temperature range, and an error analysis was performed on the values for the magnetic moment. When the temperature remained constant an error analysis was carried out on the values of mass susceptibility.

Accuracy varied considerably with the nature of the sample. In the best cases (the granular complexes of cobalt(II) and copper(II) ) the mass susceptibility was reproducible to within 4% and the magnetic moment to 2%. The complexes existing in the form of matted needles or well-defined plates gave poorer results (mass susceptibility to within 5-9% and magnetic moment 3-5%), and were often ground to a powder before packing, or tamped down with a

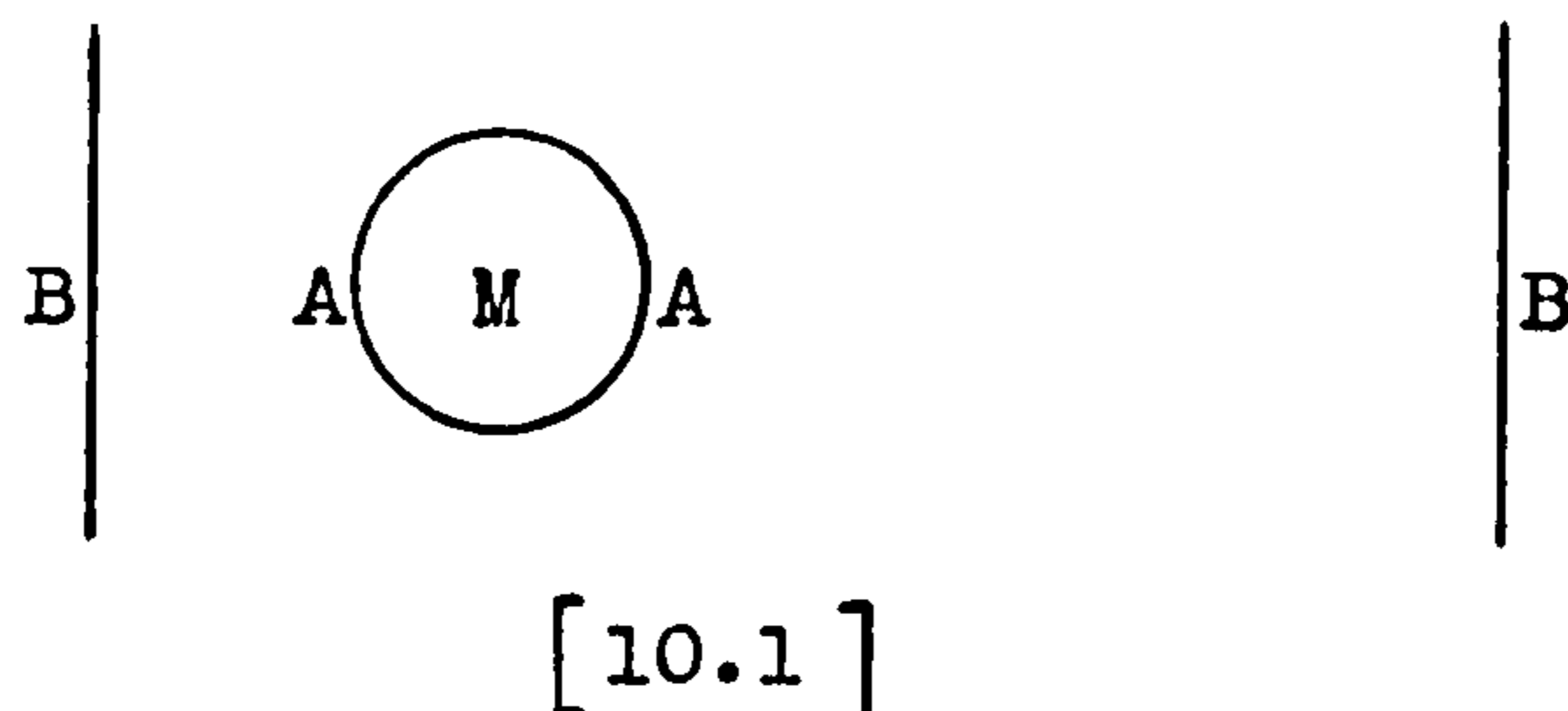
glass rod.

10.6 The N.M.R method for measurement of magnetic susceptibilities in solution.

The Gouy method involves certain difficulties when applied to the measurement of magnetic susceptibilities in solution. Especially when solutions are dilute, the weight changes are small when a magnetic field is applied, and to obtain values of the same precision as with solid samples a higher magnetic field (larger magnet) or more sensitive balance must be used. Due to the limitations of the Gouy equipment available it was decided to try the N.M.R method first described by Evans<sup>6</sup>.

The method is based on the theory of bulk susceptibility shifts, which was developed to make the necessary correction when working with an external reference in an N.M.R. tube, since the position of the resonance line for a nucleus in a molecule is affected by the bulk diamagnetic shielding of the medium in which the molecule is situated<sup>7</sup>.

The total volume of sample is divided into two regions by defining a sphere (surface A) around any given molecule (M) in the sample, large enough to be of macroscopic dimensions, but small in comparison with the size of the sample container (surface B).

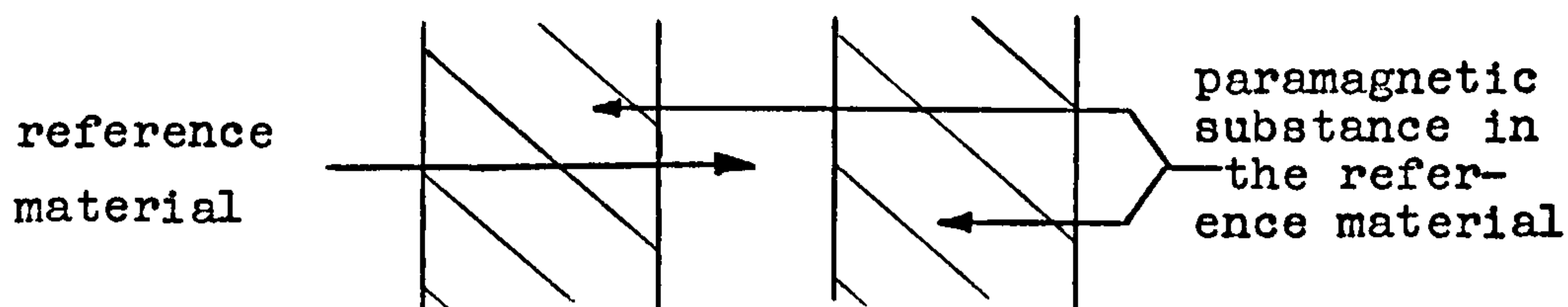


When a sample is placed in a uniform magnetic field,  $H_0$ , the field experienced at a nucleus in the molecule (M) is made up of

- (1) the external field  $H_0$ .
- (2) the field due to induced magnetism in the region between the surface of the sphere (A) and boundary of the sample (B).
- (3) the field due to induced magnetism in the inner sphere (the chemical shift).

The field acting upon the molecule in the inner sphere is<sup>8</sup>  $H = H_0 \left[ 1 + \frac{4\pi - \alpha}{3} \chi_v \right]$ , where  $\chi_v$  is the volume magnetic susceptibility of the sample and  $\alpha$  is a factor dependent upon the geometry of the container holding the sample ( $\alpha = \frac{4\pi}{3}$  for a perfect sphere and  $2\pi$  for a perfect cylinder). Hence for an imperfect cylindrical container  $H = H_0(1 - k\chi_v)$  where  $k$  depends upon the geometry, and the bulk susceptibility effect is equivalent to a contribution of  $k\chi_v$  to the screening constant.

Consider a section of two coaxial cylinders, the inner (1) containing a reference material (volume susceptibility  $\chi_{vr}$ ) and the outer (2) a dilute solution (volume susceptibility  $\chi_{vs}$ ) of a paramagnetic substance in the same reference material.



## 10.2

The fields experienced by molecules in the inner and outer cylinders are  $H_1 = H_0(1 - k_1 \chi_{vr})$  and  $H_2 = H_0(1 - k_2 \chi_{vs})$  respectively, where  $k_1$  and  $k_2$  depend upon the geometries of the cylinders.

The difference in positions of the resonance lines for the reference material in the two containers

$$= \Delta H = H_1 - H_2 = H_0(k_2 \chi_{vs} - k_1 \chi_{vr})$$

$$\therefore \frac{\Delta H}{H_0} = k_2 \chi_{vs} - k_1 \chi_{vr}$$

But  $\chi_{vs} = \chi'_{vr} + \chi'_{vp}$ , where  $\chi'_{vr}$  and  $\chi'_{vp}$  are the volume susceptibilities of the reference material and paramagnetic substance in solution.

$$\therefore \frac{\Delta H}{H_0} = k_2 \chi'_{vr} + k_2 \chi'_{vp} - k_1 \chi_{vr}$$

Converting to mass susceptibilities gives;

$$\frac{\Delta H}{H_0} = k_2 d'_r \chi_{gr} + k_2 d'_p \chi_{gp} - k_1 d_r \chi_{gr}, \text{ where}$$

$d'_r$  and  $d'_p$  are the densities of the reference material and paramagnetic substance in solution, and  $d_r$  the density of pure reference material. The density of the solution is  $d_s = d'_r + d'_p$

$$\therefore \frac{\Delta H}{H_0} = k_2 d_s \chi_{gr} - k_2 d'_p \chi_{gr} + k_2 d'_p \chi_{gp} - k_1 d_r \chi_{gr}$$

The density of the paramagnetic substance in solution ( $d'_p$ ) is its concentration in grams per ml. of solution ( $m'$ )

$$\therefore \frac{\Delta H}{H_0} = k_2 d_s \chi_{gr} - k_2 m' \chi_{gr} + k_2 m' \chi_{gp} - k_1 d_r \chi_{gr}$$

$$\chi_{gp} = \frac{\Delta H}{H_0 k_2 m'} - \frac{(k_2 d_s - k_1 d_r) \chi_{gr}}{m'} + \chi_{gr}$$

This expression reduced to that quoted by D.F. Evans<sup>6</sup> when the values  $k_1 = k_2 = \frac{2\pi}{3}$  are substituted.

For dilute solutions, assuming that  $k_1 \approx k_2$  gives  $k_2 d_s - k_1 d_r \approx 0$  and the expression reduced to that shown in equation [10.1].

$$\chi_{gp} = \frac{\Delta H}{H_0 k_2 m'} + \chi_{gr} \quad [\text{equation 10.1}]$$

Fritz and Schwarzhaus<sup>9</sup> employed a different expression to find susceptibilities in solution by N.M.R. They used a similar system of two coaxial cylinders, the

outer containing a paramagnetic solution and a N.M.R. reference material, miscible with the solvent, and the inner the solvent containing only the same N.M.R. reference material in the same concentration. They related the susceptibility ( $\chi_{gp}$ ) of the paramagnetic material to the separation ( $\Delta f$  c.p.s.) of the signals for the reference material in both cylinders by equation [10.2], where  $m$  is the concentration of paramagnetic substance in mg. per ml. of solution, and  $c'$  is a constant incorporating the operating frequency ( $f$ ) of the N.M.R. machine ( $\frac{\Delta f}{f} = \frac{\Delta H}{H_0}$ ).

$$\chi_{gp} = \frac{\Delta f}{m} \cdot c' \quad [\text{equation 10.2}]$$

These workers claim to obtain results which compare well with those obtained by the Gouy method, even for substances with quite low susceptibilities, when  $\chi_{gr} \approx \frac{1}{10} \cdot \chi_{gp}$  and it would not seem permissible to ignore the correction for the susceptibility of the solvent system in the Evans' expression (equation [10.1]).

It was decided to test the method to see which type of expression could be applied with our machine. An expression as in equation [10.3] was assumed, and the constants  $c$  and  $K$  determined by using calibrant solutions of known paramagnetic susceptibility.

$$\chi_{gp} = \frac{\Delta f}{m} \cdot c + K \quad [\text{equation 10.3}]$$

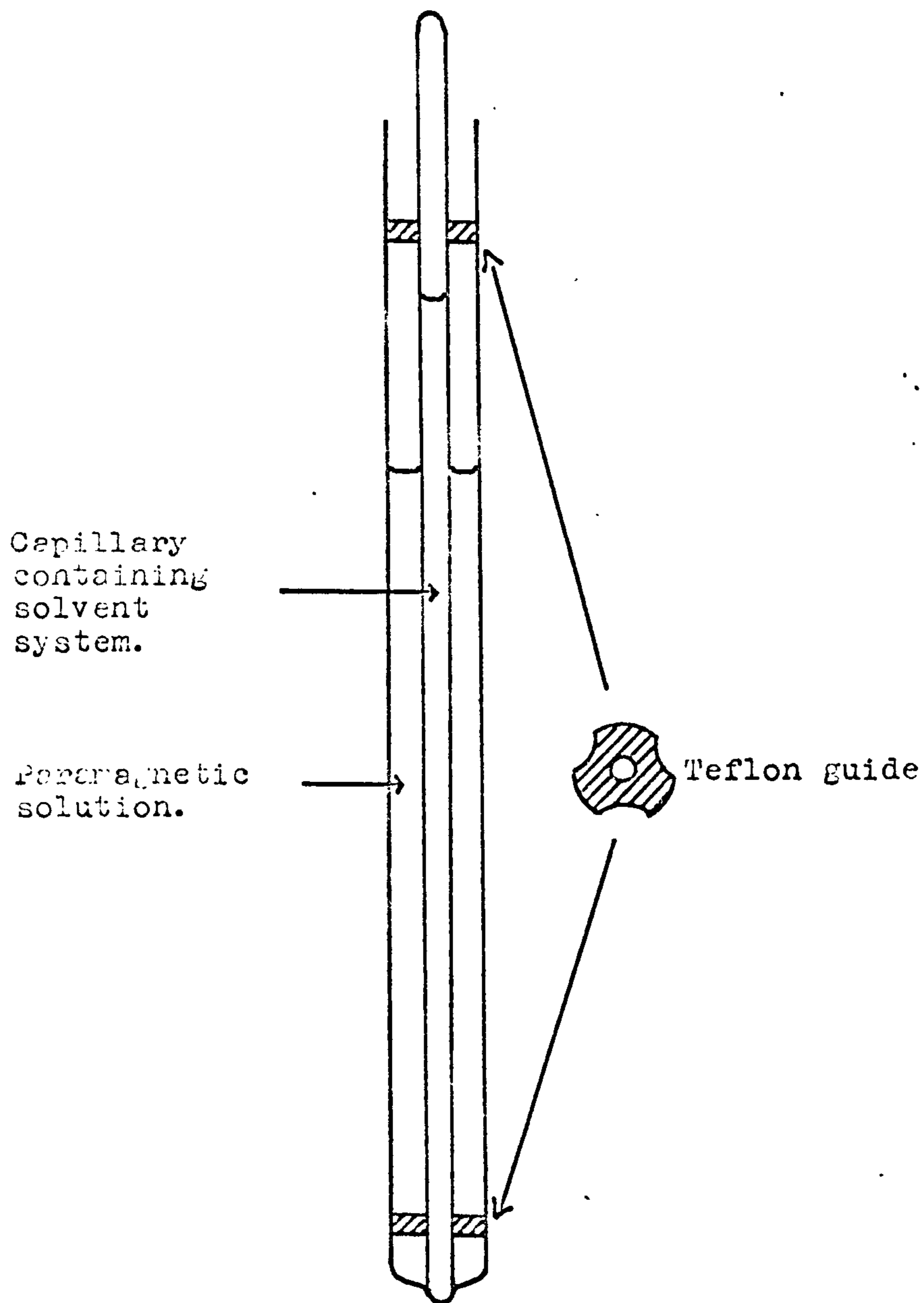
### 10.6.1 Calibrant Solutions.

Nickel(II) chloride solutions have been carefully studied as paramagnetic susceptibility standards,<sup>10</sup> and their temperature variation well documented<sup>10</sup>. Hence the mass susceptibility of nickel(II) chloride (calculated as the anhydrous material) at 33°C (the normal operation temperature of the N.M.R. machine)\* is  $32.77 \times 10^{-6}$  c.g.s. units.

A stock solution in deoxygenated water containing 2% t-butanol was prepared from Analar  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and analysed by taking two 5ml. and two 10 ml. portions, diluting, and precipitating with a slight excess of dimethylglyoxime<sup>11</sup>. The precipitate was filtered and washed at a sinter, and dried to constant weight at 120°. Found  $\text{NiCl}_2$  concentration (g./l.) 17.74, 17.70, 17.75, 17.74, Mean 17.73. Solutions of various concentrations were prepared by dilution of this master solution.

Choice of a second calibrant solution was more difficult. There have been few reliable measurements of solutions susceptibilities over a temperature range enabling the gram susceptibility to be extrapolated to 33°C. Potassium ferricyanide at 25°C has a mass susceptibility in solution of  $8.10 \times 10^{-6}$  c.g.s. units<sup>12</sup>. Assuming that

\* Perkin Elmer R10 60 Mc/s N.M.R. spectrometer.



[10.3]



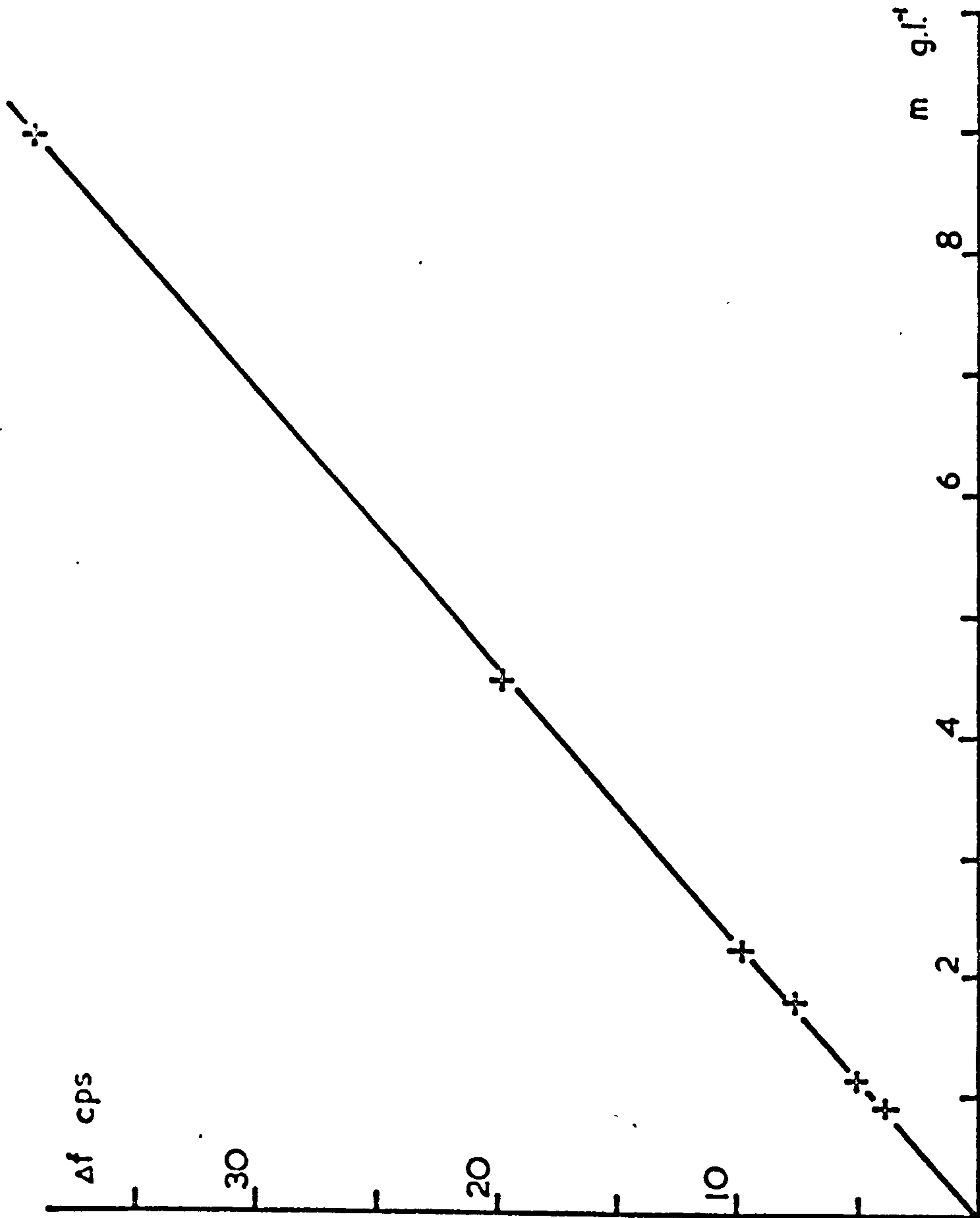
the Curie-Weiss Law is valid over the small temperature range ( $25^{\circ} - 33^{\circ}\text{C}$ ), with the same  $\theta$  value as the solid<sup>13</sup>, the mass susceptibility in solution at  $33^{\circ}\text{C} = 7.89 \times 10^{-6}$  c.g.s units. Solutions were prepared by weighing Analar  $\text{K}_3\text{Fe}(\text{CN})_6$ , and making up to volume with water containing 2% t-butanol.

#### 10.6.2 Measurement of Bulk Susceptibility Shift

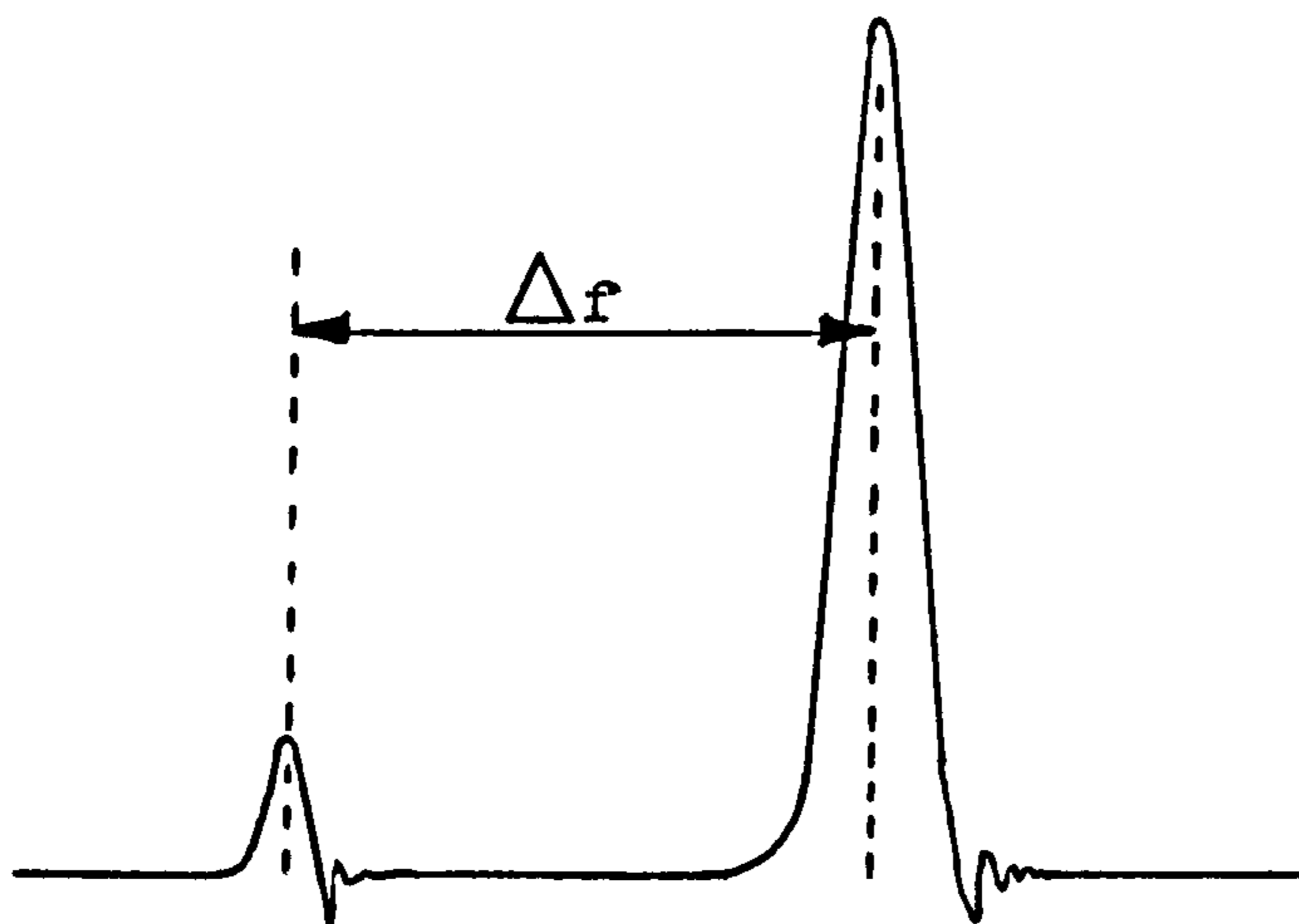
The paramagnetic solutions were introduced into a standard N.M.R. tube, and a capillary containing the solvent system (water containing 2% t-butanol) placed in the tube, and held coaxial with two teflon guides as in [10.3].

The shift of the t-butanol signals was found by standard techniques. A typical N.M.R. spectrum trace in this region is shown in [10.4]. The smaller signal is due to t-butanol in the capillary, and the larger (shifted upfield) t-butanol in the paramagnetic solution.

This region of the spectrum was recorded several times for a given paramagnetic solution, and it was found that  $\Delta f$  could be estimated to 0.1 c.p.s.



[10.5]. A plot of  $\Delta f$  against  $m$  for nickel(II) chloride solution.



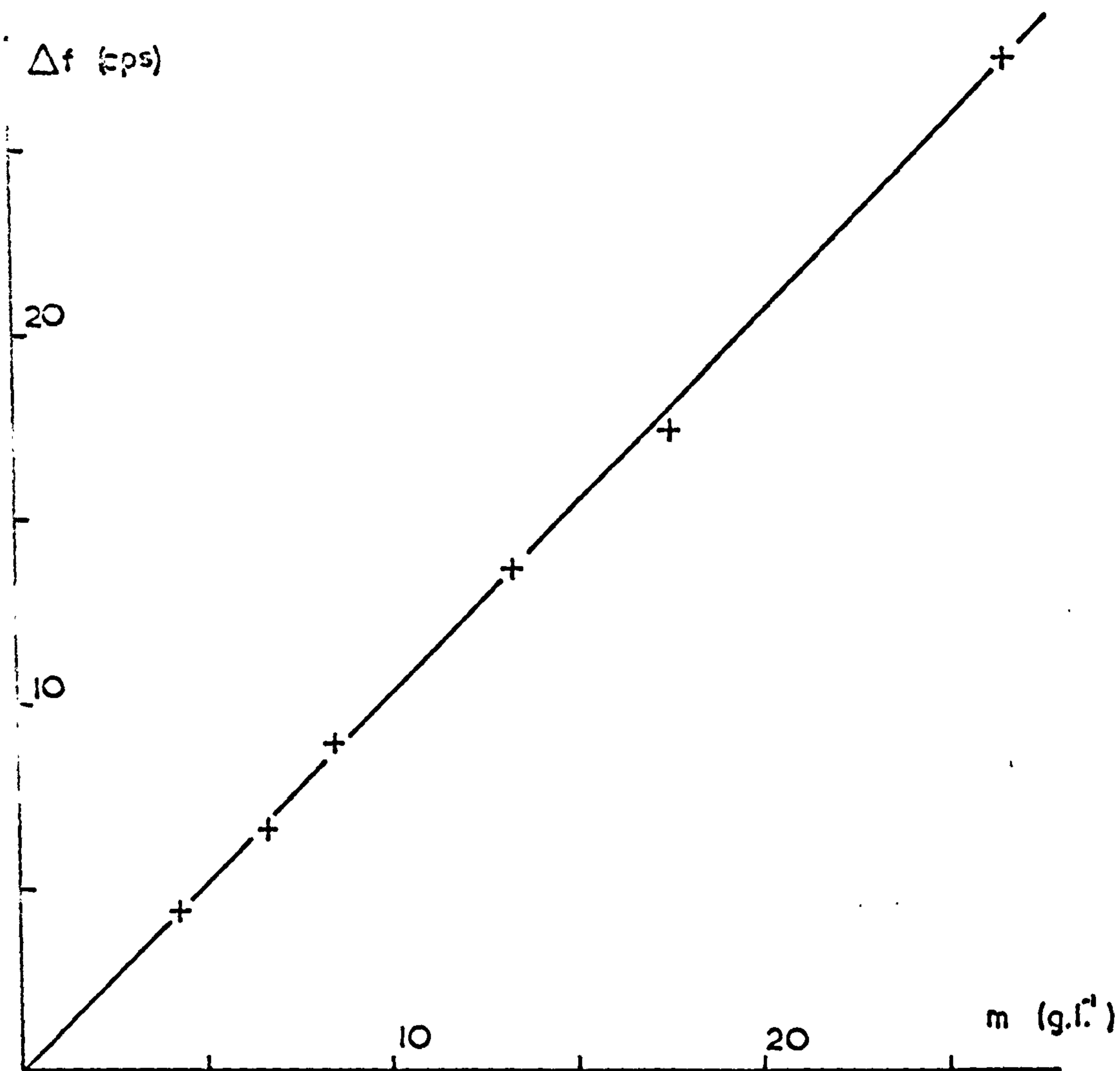
### 10.6.3 Results for calibrant solutions.

The theoretical expression giving the shift of the reference signal is  $\chi_{gp} = \frac{\Delta f}{m} \cdot c + K$  (equation [10.3]). For a perfect cylinder, and when the concentration of paramagnetic material is measured in g./l. or mg./ml. then  $c = 7.958 \times 10^{-6}$ .

Linear variation of  $\Delta f$  and  $m$ . From equation [10.3] it is apparent that  $\Delta f$  should be a linear function of  $m$ .  $\Delta f = \frac{(\chi_{gp} - K)m}{c}$ .

The experimental results for variation of  $\Delta f$  with  $m$  for nickel(II) chloride and  $K_3Fe(CN)_6$  solutions are shown in [10.5] and [10.6].

For the expression  $\Delta f = am + b$  the values of  $a$  and  $b$  were computed by least mean squares analysis. The



[10.6]. A plot of  $\Delta f$  against  $m$  for potassium ferricyanide solutions.

results are given in table[10.1]. In all cases  $b = 0$  within the calculated error.

13

Solute	Solvent	Slope (a)	Intercept (b)
$\text{NiCl}_2$	Water + 2% t-BuOH	$4.294 \pm 0.037$	$0.128 \pm 0.155$
$\text{K}_3\text{Fe}(\text{CN})_6$	Water + 2% t-BuOH	$1.008 \pm 0.018$	$0.020 \pm 0.275$
$\text{CuSO}_4$	i Water + 2% t-BuOH	$0.753 \pm 0.004$	$0.037 \pm 0.070$
$\text{Ni}(\text{Salox})_2$	ii Pyridine + 2% Cyclohexane	$1.535 \pm 0.028$	$-0.081 \pm 0.208$

Table [10.1]. Computed slopes and intercepts for plots of  $\Delta f$  against  $m$  for various solutions.

(i) Page 241 (ii) Nickel(II)-bis-(salicylaloximate), page 242

Values for constants  $c$  and  $K$  in equation [10.3].

The constant  $a = \frac{\chi_{gp}}{c} - K$ , and hence for nickel(II)

chloride  $a = 4.294 = \frac{32.77 \times 10^{-6}}{c} - K$  and for potassium

ferricyanide  $a = 1.008 = \frac{7.89 \times 10^{-6}}{c} - K$ .

Solving gives  $K = 0.248 \pm 0.280 \times 10^{-6}$  c.g.s units, making no allowance for errors in the values for mass susceptibilities of nickel(II) chloride<sup>10</sup> and potassium ferricyanide<sup>12</sup>. The value for  $K$  from the theoretical expression<sup>6</sup> (equation [10.2]) is the mass

Paramagnetic Substance (a)	$K_3Fe(CN)_6$	$CuSO_4 \cdot 5H_2O$	$Co(NO_3)_2$	$Ni(salox)_2$ (e)
Solvent System (b)	$H_2O/Bu^tOH$	$H_2O/Bu^tOH$	$H_2O/Bu^tOH$	Pyridine/ Cyclohexane
Computed $\frac{\Delta f}{m}$	$1.008 \pm 0.018$	$0.753 \pm 0.004$	$6.79$ (d)	$1.535 \pm 0.026$
Experimental $\chi_g \times 10^6$ (cgs units)	$7.69 \pm 0.20$	$5.75 \pm 0.08$	$51.9 \pm 0.4$	$11.72 \pm 0.30$
Literature $\chi_g \times 10^6$ (cgs units)	$7.89$ <sup>12</sup>	$5.78 \pm 0.05$ <sup>15</sup>	$51.65$ <sup>16</sup>	$11.24$ <sup>17,18</sup>
Experimental $\mu$ (B.M.)	2.57	1.95	4.86	3.15
Literature $\mu$ (B.M)	2.59	1.95	4.84	3.10

Table [10.3]. Susceptibility determination results compared with literature values.

- (a) Formula refers to species for which  $\chi_g$  is calculated.  
 (b) Solvent and N.M.R. reference material in 2% concentration.  
 (c) Extrapolated from data in the literature using the Curie-Weiss Law.  
 (d) Mean of two determinations only. (e) Bis-(salicylaloximato)-nickel(II)

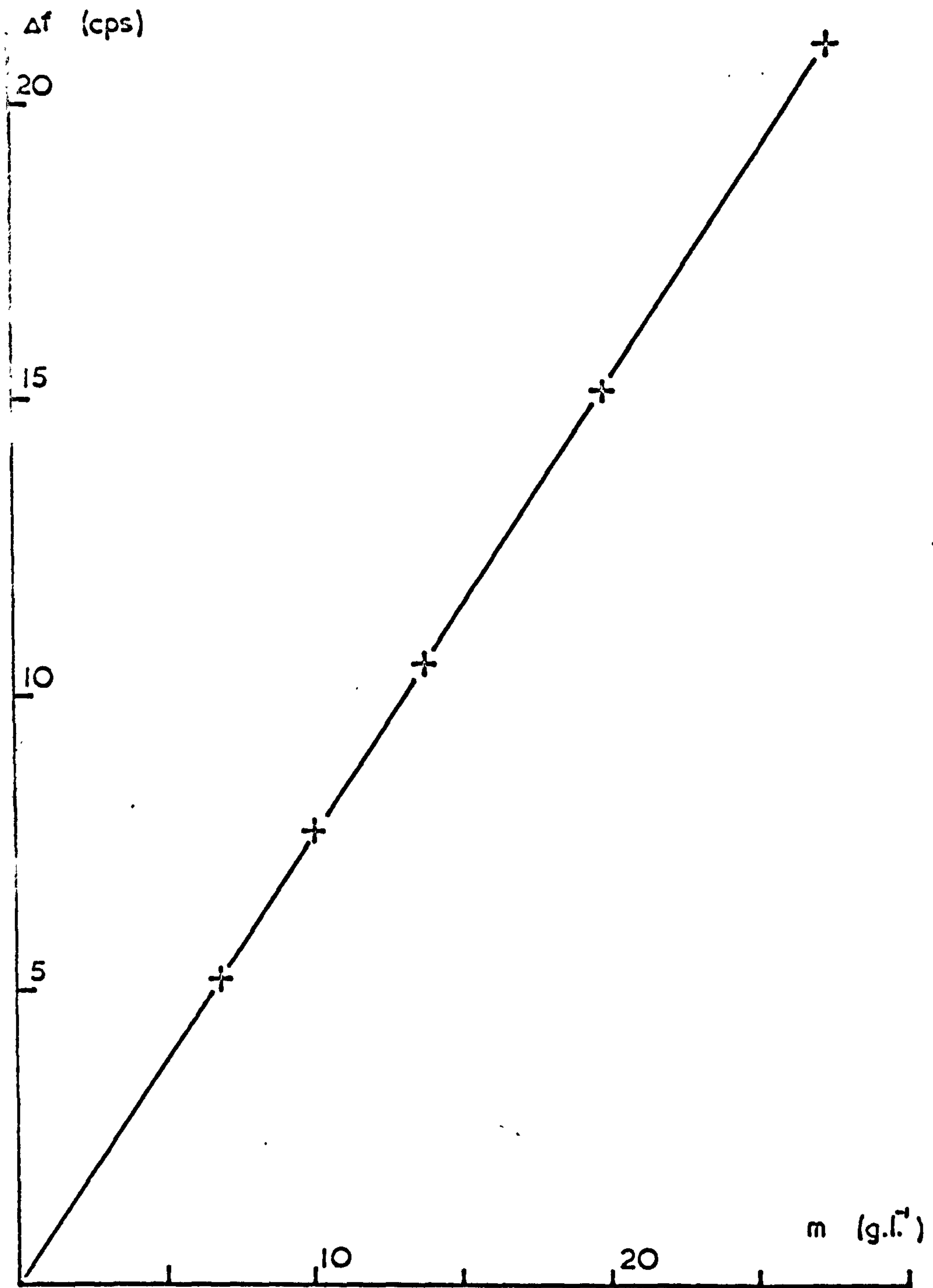
susceptibility for the solvent system. For water containing 2% t-butanol, this can be assumed to be  $-0.722 \times 10^{-6}$  c.g.s. units (the value for water at  $20^{\circ}\text{C}$ , which shows only small temperature variation<sup>14</sup>). It would appear that the expression used by Fritz and Schwarzhaus<sup>9</sup> (see page 235)  $\chi_{gp} = \frac{\Delta f c}{m}$  is valid in this case, since  $K=0$  in equation [10.3] within the calculated error.

It is difficult to see any theoretical grounds for ignoring the solvent susceptibility correction term. It is possible that dissolved oxygen in the solvent system reduces its diamagnetic susceptibility to a smaller value. In cases where the paramagnetic susceptibility is high the error in ignoring this correction is small, and this procedure was adopted in this work.

The value of  $c$  calculated for the calibrant solutions is  $7.572 + 0.125 \times 10^{-6}$  c.g.s. units:  $\text{cps}^{-1} \text{g}^{-1}$ , which compares well with the value from the theoretical expression for a perfect cylinder of  $7.598 \times 10^{-6}$  (see page 238).

#### 10.6.4 Other measurements to check the method.

The applicability of the Fritz expression  $\chi_{gp} = \frac{\Delta f}{m} c'$  (see page 235) was checked with other solutions. Substituting values for the nickel chloride solutions into equation [10.2] gives the calibration



[10.7]. A plot of  $\Delta f$  against  $m$  for copper(II) sulphate solution.



constant  $c' = 7.632 \pm .065$  c.g.s. units:  $\text{cps}^{-1} \text{g}^{-1} \text{l}^1$ .

A series of copper(II) sulphate solutions in water containing t-butanol were studied using the same NMR tube and capillary. The plot of  $\Delta f$  against  $m$  is shown in [10.7], page F 241. From the computed slope (table [10.1]) and calibration constant  $c'$  the mass susceptibility of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in solution was calculated to be  $5.75 \pm .08 \times 10^{-6}$  c.g.s. units.

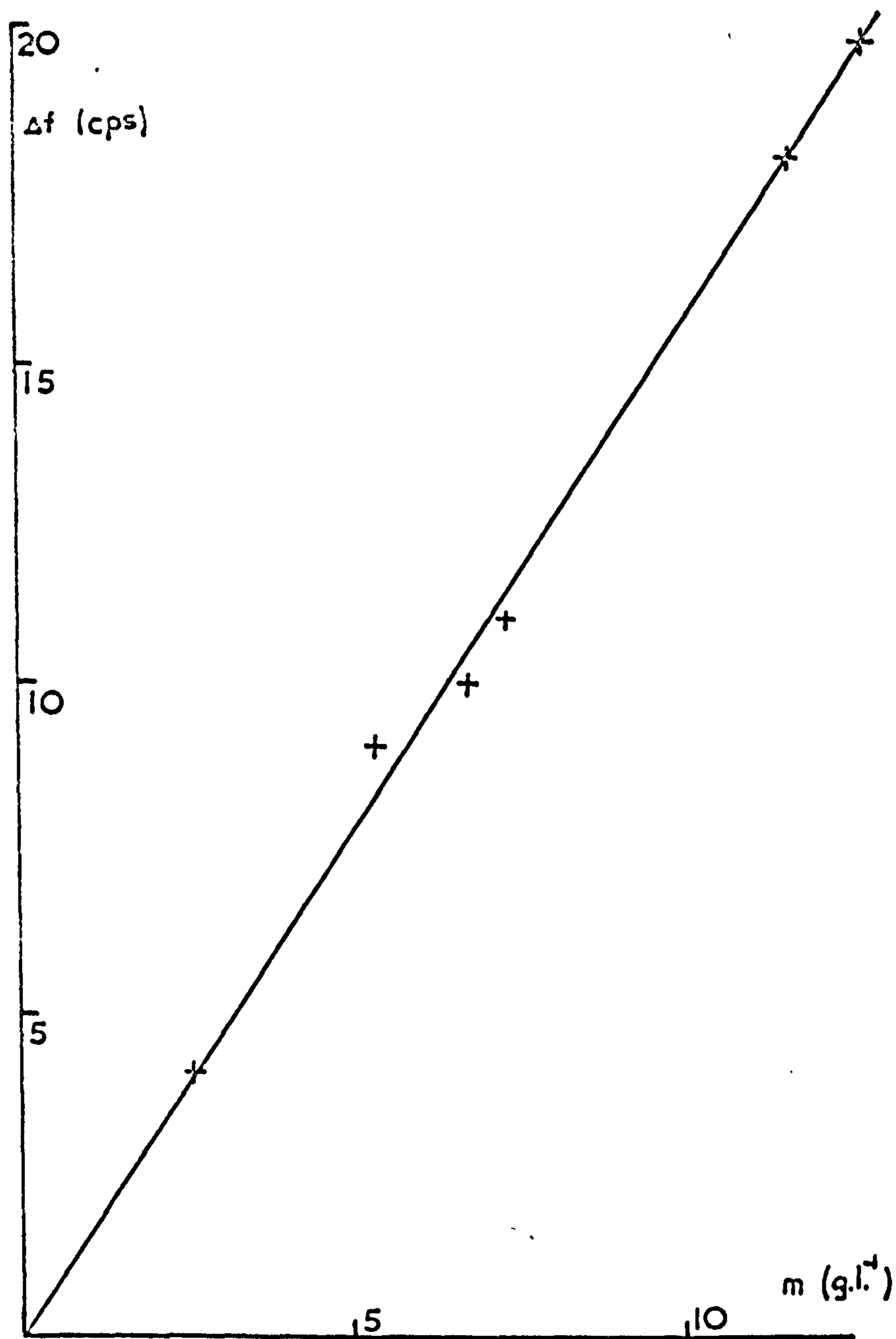
Two solutions of cobalt(II) nitrate in water containing 2% t-butanol were examined in the same way. The results are shown in table [10.2].

$m$ (mg/ml)	<sup>a</sup> $\Delta f$ (cps)	$\Delta f/m$	Mean $\Delta f/m$	$\chi_{\text{gp}}$ $\text{Co}(\text{NO}_3)_2$
5.69	38.2	6.71	6.79	51.9
2.85	19.6	6.87		

Table [10.2]. Results for solution susceptibility determination of cobalt(II) nitrate.

(a) Solutions were prepared from a stock solution standardized by R. Bratchley.

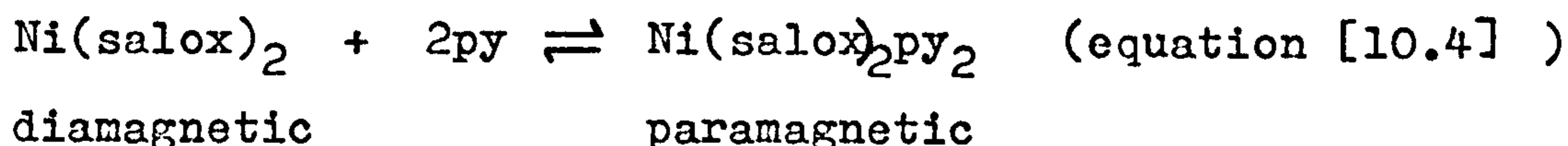
The susceptibilities determined using the tube and capillary calibrated with nickel(II) chloride solution are compared with literature values in table [10.3].



[10.8]. A plot of  $\Delta f$  against  $m$  for bis(salicylaldox-  
imato)nickel(II) in pyridine solution.

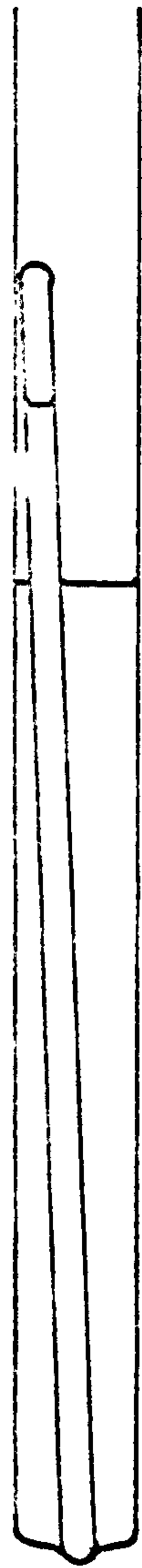
### 10.6.5. Non-aqueous solvent systems.

To test the validity of the method when applied to non-aqueous solvents and complexes similar to those we wished to study, measurements were made of the bulk susceptibility shifts of solutions of bis-(salicylaloximato)-nickel(II) in pyridine containing 2% cyclohexane. Willis and Mellor<sup>17</sup> showed that many diamagnetic nickel complexes of Schiff bases gave paramagnetic solutions in coordinating solvents, (see also page 93). For bis-(salicylaloximato)-nickel(II) the equilibrium in equation [10.4] between solvated and nonsolvated forms is shifted completely to the right.

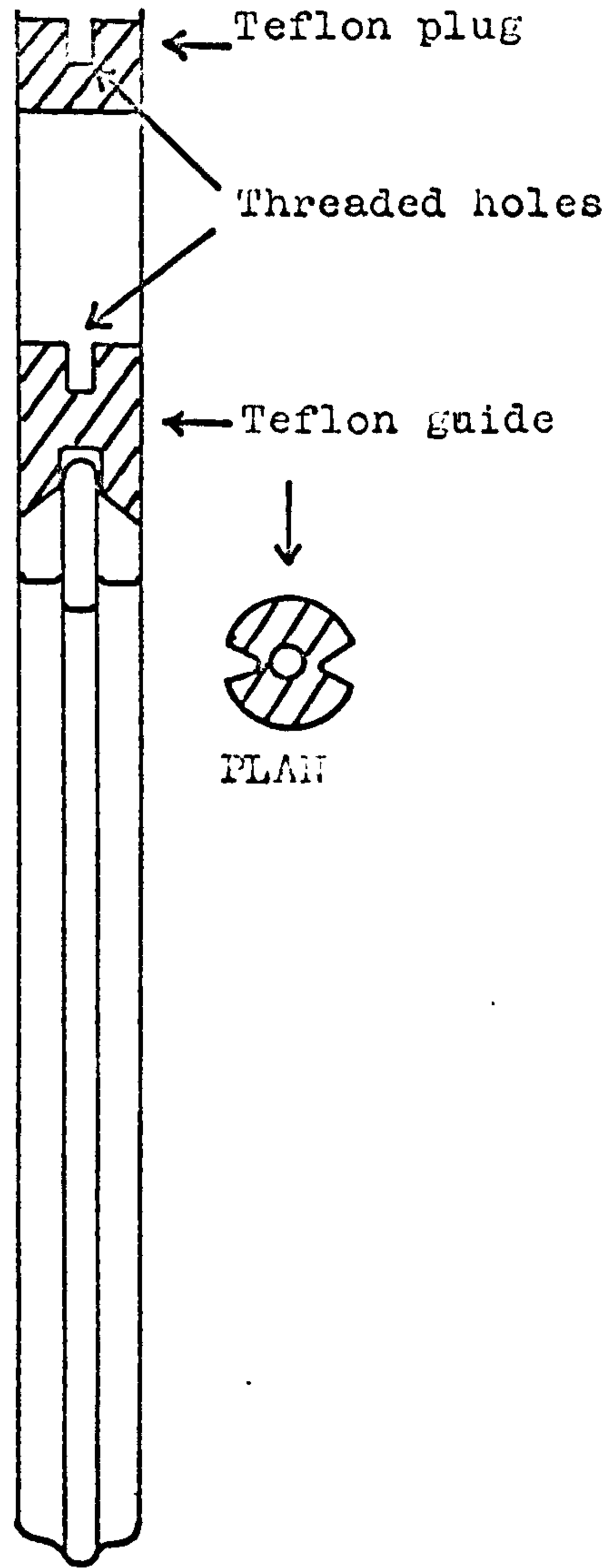


Subsequent examination<sup>18</sup> has shown that this compound obeys the Curie-Weiss Law in pyridine (198 - 316°K) with a moment of 3.1 B.M.

The same N.M.R. tube and capillary were used to examine the bulk susceptibility shifts for solutions of Ni(salox)<sub>2</sub> in pyridine containing 2% cyclohexane, and the plot of Δf against m is shown in [10.8]. From the computed slope (Table [10.1]) the gram susceptibility is calculated as 11.72 ± .30 c.g.s. units, which compared



[10.9]



[10.10]

favourably with the literature values (Table [10.3] ).

#### 10.6.6. Variation of capillary mounting

When the fixed capillary (see [10.3]) is replaced by a capillary which is not held strictly coaxial (see [10.9] ) the resolution of signals is poorer. It was found that the error in computing  $\Delta f/m$  for the loose capillary system was larger than that for the fixed capillary, e.g.  $\Delta f/m$  for tube (1) with a fixed capillary =  $4.294 \pm 0.037$  cps  $g^{-1}$  but  $\Delta f/m$  for tube (2) with a loose capillary =  $4.172 \pm 0.098$  cps  $g^{-1}$  (both for six nickel(II) chloride solutions).

#### 10.6.7. Measurement of air sensitive solution.

The tube system [10.3] is unsuitable for air sensitive solutions since the protruding capillary precludes effective stoppering of the tube. For these measurements a shorter capillary as in [10.10] was used.

The sequence of operations for introducing an air sensitive solution is;

- (1) The tube containing the capillary is flushed with nitrogen, introduced through a long thin syringe needle.
- (2) The solution is introduced, withdrawing the nitrogen needle above the level of the liquid.
- (3) The Teflon guide is inserted with the nitrogen needle

still in position (the cuts along the guide allow this).

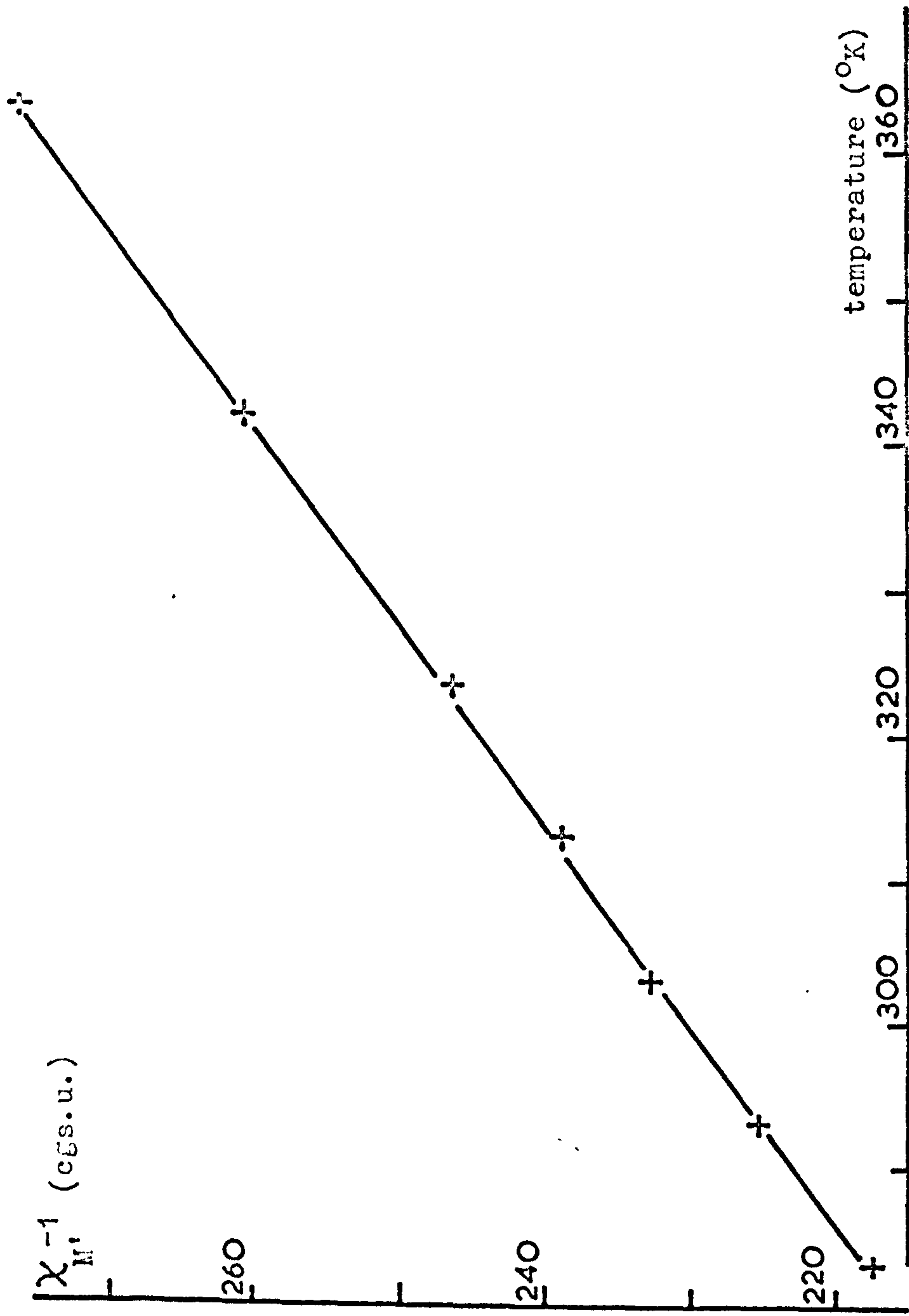
(4) The nitrogen needle is removed and a Teflon plug inserted.

#### 10.6.8. Variable temperature measurement.

Using the variable temperature probe the variation of bulk susceptibility shift with temperature was investigated to see if it was possible to study temperature dependence of susceptibilities in solution.

A tube assembly as in [10.10] was used with a nickel(II) chloride solution (concentration 7.09 g./l. in water containing 2% t-butanol). The variation of  $\Delta f$  with temperature is tabulated below. The calibration constant  $c'$  for the assembly was calculated from the  $\Delta f$  value at 293°K, when  $\chi_{gp} = 34.22^{10}$ . Using this value ( $c' = 7.962 \times 10^{-6}$ ) the mass susceptibility of nickel(II) chloride was calculated at the other temperatures. The results are included in table [10.4].

Temperature (°K)	Mean (cps)	$\Delta f$	$\chi_{gp} \times 10^6$ (c.g.s units)	$\chi_M \times 10^6$ (cgs units)	$\chi_M^{-1}$ (cgs units) <sup>-1</sup>
363	24.9		27.94	3621	276.2
343	26.4		29.62	3840	260.4
323	27.9		31.30	4058	246.4
313	28.8		32.31	4189	238.7



[10.11]. A plot of  $\chi_M^{-1}$  against temperature for nickel(II) chloride solution.

303	29.4	32.99	4276	233.9
293	30.5	34.22 <sup>10</sup>	4436 <sup>10</sup>	225.4
283	31.6	35.46	4596	217.6

Table [10.4]. Temperature variation for a nickel(II) chloride solution in water + 2% t-butanol (7.09 g/l).

(a) Calculated using a calibration constant  $c' = 7.96(2) \times 10^{-6}$  (see page 244).

(b) Molar susceptibility.

In [10.11] the calculated values of  $\chi_M^{-1}$  are plotted against temperature.

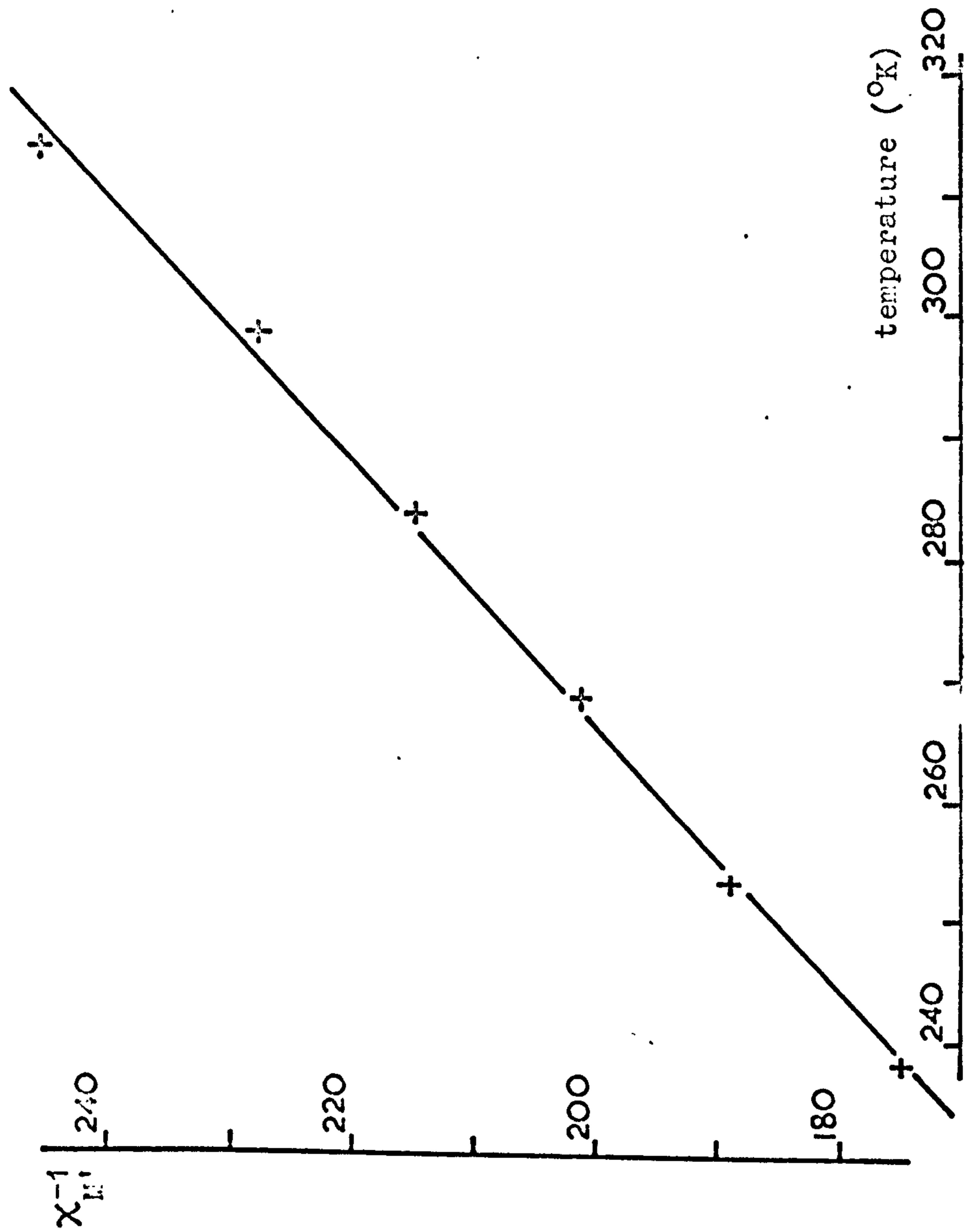
The Curie-Weiss dependence of  $\chi_M^{-1}$  on temperature is given in equation [10.5], where  $C$  and  $\theta$  are the Curie and Weiss constants respectively.

$$\frac{1}{\chi_M} = \frac{T}{C} + \frac{\theta}{C} \quad [\text{equation 10.5}]$$

The straight line of the graph [10.11] shows that in this case the variation of  $\Delta f$  with temperature is due to the Curie-Weiss temperature variation of the susceptibility of nickel chloride. The intercept of the line ( $14.5 \pm 4.3$  when  $T = 0$ ) was computed by a least mean squares analysis, and gives  $\theta = 25 \pm 5^\circ$ . This value compares favourably with that found for nickel(II) nitrate solution ( $\theta = 16^\circ$ ), using the Gouy method<sup>19</sup>.

In this analysis the variation of concentration





[10.12]. A plot of  $\chi_M^{-1}$  against temperature for a bis(salicylaloximato)nickel(II) solution in pyridine.

(m) due to density change with temperature has not been considered. For water the density changes over this temperature range by 2.5%. Considering that the change for water is only of the order of the experimental error in determination of  $\Delta f$ , the effect was ignored.

The result for the temperature variation of a bis-(salicylaloximato)-nickel(II) solution in pyridine containing 2% tetramethylsilane are given in table [10.5].

Temperature. (°K)	Mean $\Delta f$ (c.p.s)	$\chi_{gp} \times 10^6$ (cgs units)	$\chi_M \times 10^6$ (cgs units)	$\chi_M' \times 10^6$ (cgs units)	$\chi_M'^{-1}$ (cgs units)
313	14.8	11.88	3929	4074	245.5
298	16.0	12.83	4249	4394	227.6
283	17.0	13.64	4514	4659	214.6
268	18.2	14.60	4833	4978	200.9
253	19.4	15.57	5151	5296	188.8
238	20.9	16.77	5550	5696	175.6

Table [10.5]. Temperature variation of a bis-(salicylaloximato)nickel(II) solution in pyridine + 2% TMS (9.92 g./l.)

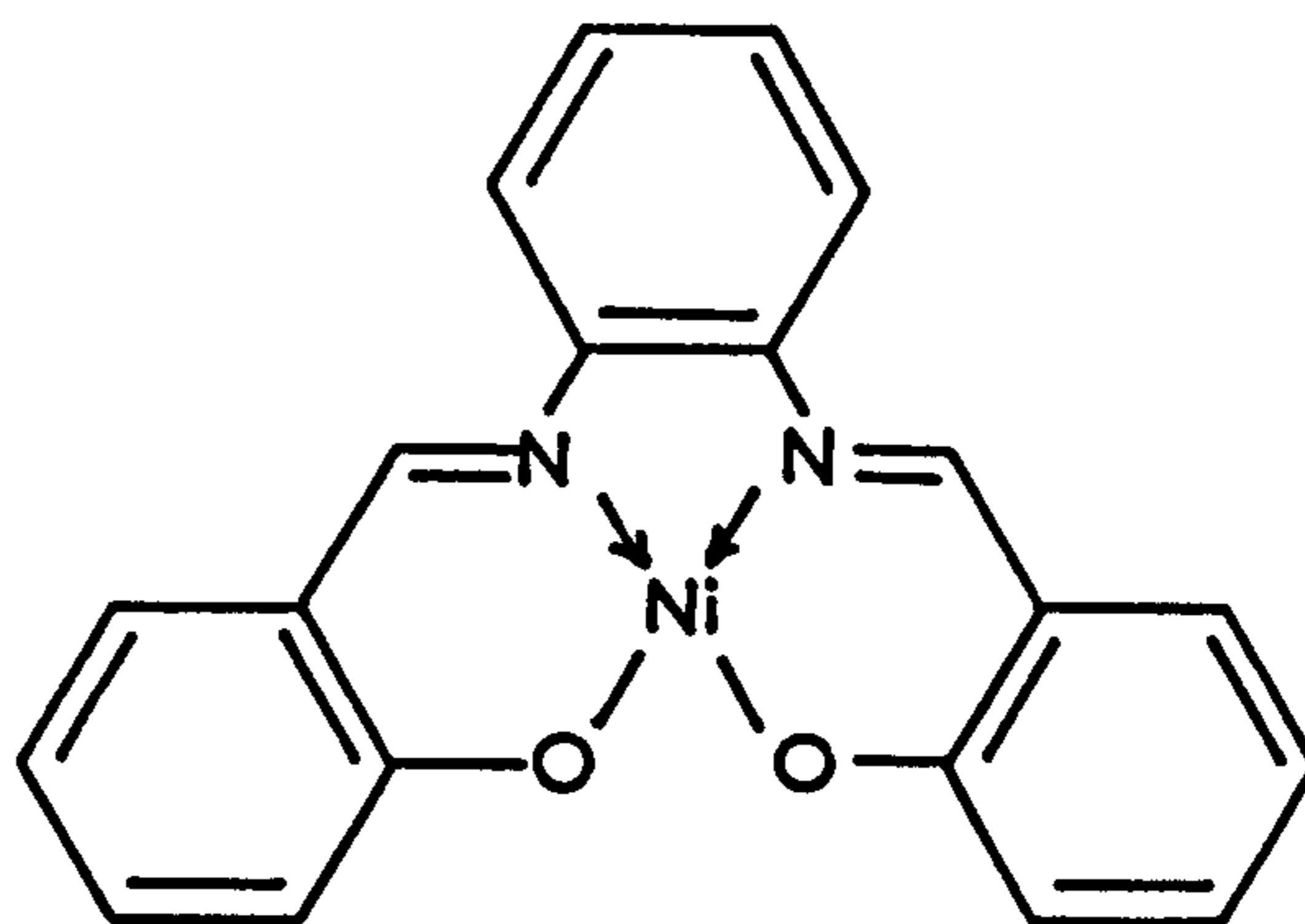
- (a) Calculated using calibration constant  $c' = 7.96(2) \times 10^{-6}$  (see page 244)  
 (b) Molar susceptibility  
 (c) Molar susceptibility corrected for the susceptibility of the ligand system, i.e.  $- 145 \times 10^{-6}$  c.g.s units.

In [10.12] the calculated values of  $\chi_M'^{-1}$  are plotted against temperature. Again the Curie-Weiss Law

holds for the temperature variation of susceptibility. The computed intercept ( $-42.8 \pm 7.8$  when  $T=0$ ) gives the Weiss constant =  $-47 \pm 10^\circ$ , which compares well with the value of  $-30^\circ$  obtained by Clark and Odell<sup>18</sup>, using the Gouy method.

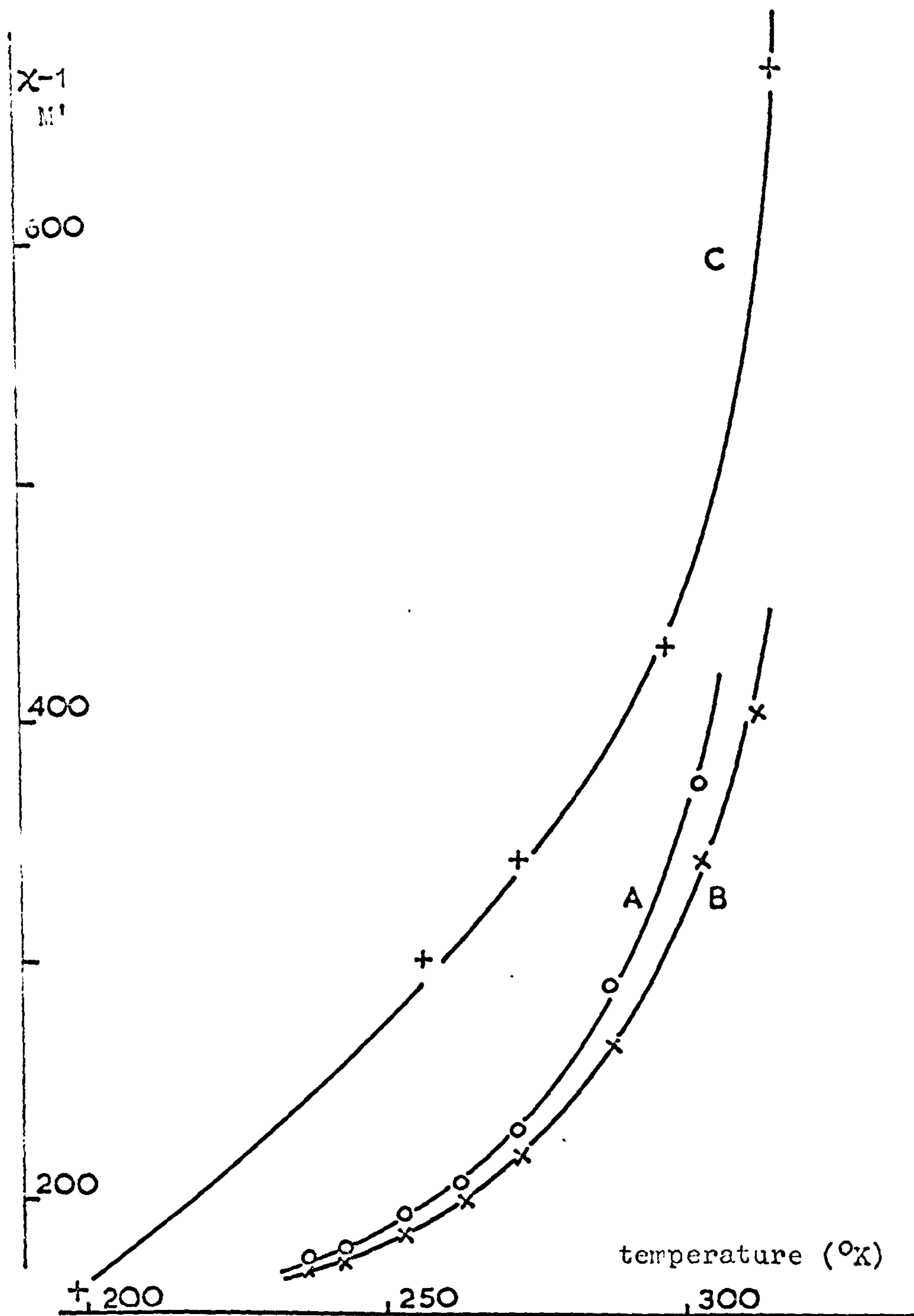
#### 10.6.9 Equilibrium studies.

The N.M.R method was applied to the study of an equilibrium between diamagnetic and paramagnetic species in solution. The equilibrium between Nisalphen [10.13] and its solvated form in pyridine solution was chosen for investigation, since this is a very similar reaction to those considered in chapter 4 page 90.



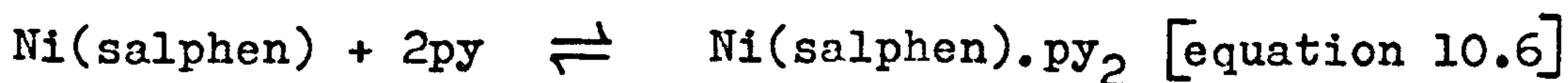
[10.13]

Clark and Odell<sup>18</sup> showed that Nisalphen gave diamagnetic solutions in non-coordinating solvents. In pyridine, however, an equilibrium between paramagnetic



[10.14]. A plot of  $\chi_{M'}^{-1}$  against temperature for a Nisalphen solution in pyridine.

solvated molecules and diamagnetic unsolvated molecules [equation 10.6] was postulated to explain the observed paramagnetism of solutions. The equilibrium favours the solvated molecules as the temperature is lowered, and at 198°K all the Nisalphen was assumed to be in the paramagnetic form, and then the magnetic moment of the nickel ion calculated to be 3.2 B.M.<sup>18</sup>



Our results for two solutions of Nisalphen in pyridine containing 2% tetramethylsilane are listed in table [10.6]. The reciprocals of corrected molar susceptibility are plotted against temperature in [10.14]

Solution (A), concentration 4.608 mg./ml.

Temperature.	Mean $\Delta f$ (c.p.s.)	$\chi_{gp} \times 10^6$ <sup>a</sup> (cgs units)	$\chi_M \times 10^6$ <sup>b</sup> (cgs units)	$\chi_{M'} \times 10^6$ <sup>c</sup> (cgs units)	$\chi_{M'}^{-1}$ (cgs units)
303	3.9	6.74	2514	2675	373
288	5.1	8.81	3287	3448	290
273	6.6	11.40	4253	4413	227
263	7.3	12.61	4704	4865	205
253	8.0	13.82	5156	5317	194
243	8.6	14.93	5570	5731	175
238	8.8	15.20	5671	5832	172

Solution (B), concentration 2.697 mg./ml.

Temperature.	Mean $\Delta f$ (c.p.s.)	$\chi_{gp} \times 10^6$ <sup>a</sup> (cgs units)	$\chi_M \times 10^6$ <sup>b</sup> (cgs units)	$\chi_{M'} \times 10^6$ (cgs units)	$\chi_{M'}^{-1}$ <sup>c</sup> (cgs units)
313	2.1	6.20	2313	2474	404
303	2.5	7.38	2753	2914	343
288	3.3	9.74	3634	3795	264
273	4.0	11.81	4406	4577	219
263	4.4	12.99	4947	5008	200
253	4.8	14.17	5287	5448	184
243	5.2	15.35	5727	5888	170
238	5.3	15.65	5838	5999	167

Table [10.6]. Temperature variation of N,N'-bis(o-hydroxybenzylidene)-1,2-diaminobenzeneatonicel(II) in pyridine + 2% TMS.

- (a) Calculated using calibration constant  $c' = 7.96(2) \times 10^{-6}$  (see page 244).  
 (b) Molar susceptibility (c) Molar susceptibility corrected for the susceptibility of the ligand system, i.e.  $-161 \times 10^{-6}$  cgs units.

The curves (A) and (B) illustrate that the paramagnetism does not follow a Curie-Weiss Law, and that the paramagnetism is favoured by decrease in temperature.

The results of Clark and Odell<sup>18</sup> (curve (C)) are also shown in [10.14]. Our values for the molar susceptibilities, obtained using the N.M.R. Method are

higher than those from the Gouy method<sup>18</sup>, but the values from the two methods appear to converge at low temperatures.

The determinations at 238°K using the N.M.R method require that the minimum value for the magnetic moment of a nickel atom in the solvated molecule be 3.35 (solution (A) ) or 3.38 (solution (B) ) B.M. This value is calculated assuming all the Nisalphen to be in the solvated form. The normal moments for magnetically dilute nickel(II) octahedral complexes lie in the range 2.9 - 3.3 B.M.<sup>20</sup>

It appears that the N.M.R method gives anomalously high values for the susceptibilities in this case, however it should be pointed out that there seems to be considerable disagreement between Gouy determinations of two sets of workers.<sup>17,18.</sup>

#### 10.6.10 Summary

The N.M.R procedure has proved useful in measuring susceptibilities of paramagnetic solutes, and for the study of temperature dependence of magnetic susceptibilities. The method shows certain advantages over the conventional Gouy procedure. For compounds of low solubility the accuracy ( $\chi_{gp}$  to within 2%) is higher than for the Gouy method. Smaller quantities of material are required, and no specialized equipment other than an N.M.R spectrometer

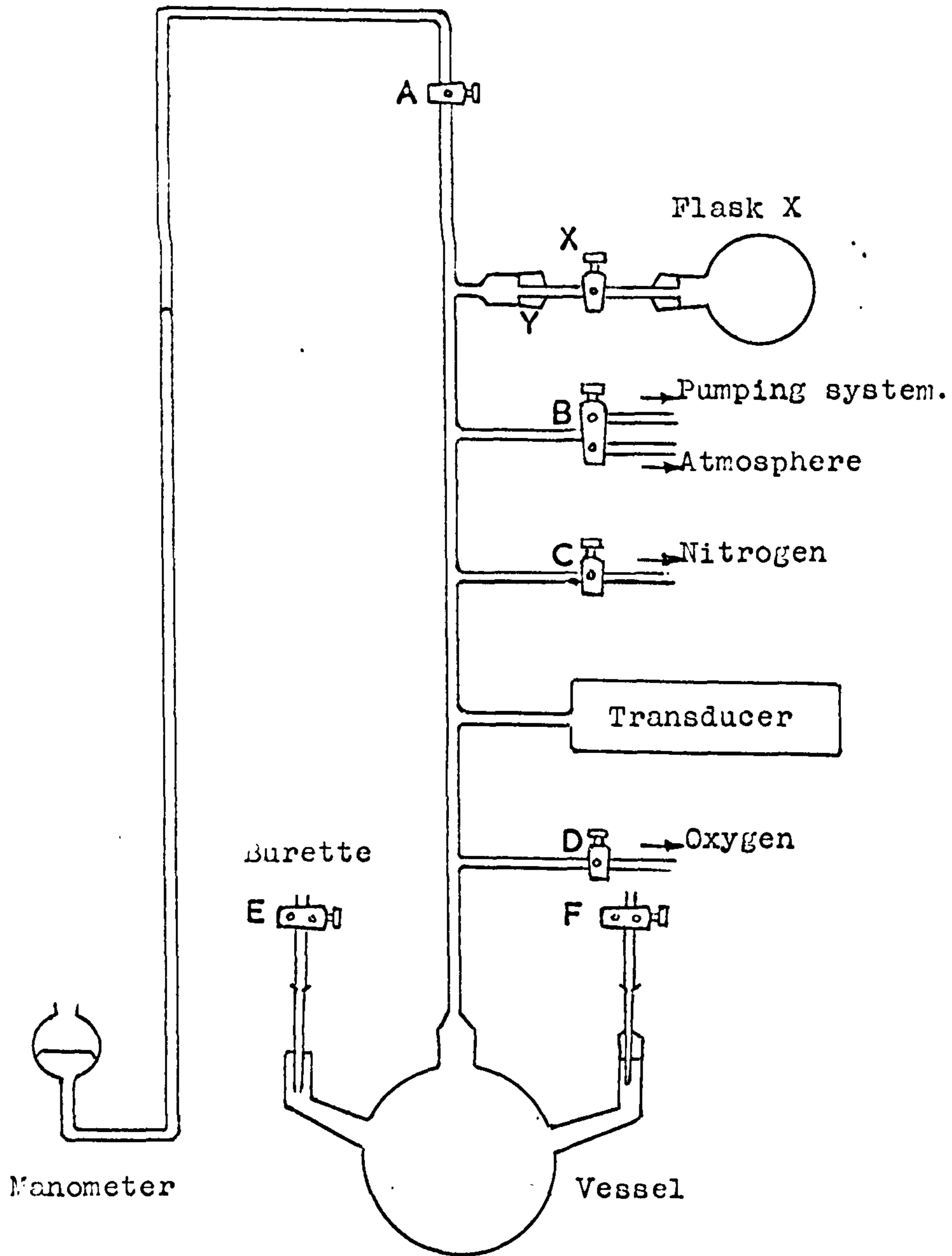
is required. Convenient investigation of temperature dependence of susceptibility is also possible provided that a variable temperature probe is available.

One of the main disadvantages is that the method is limited to solution susceptibilities. A N.M.R method has been described<sup>21</sup> in which two capillaries are embedded in a solid sample, so that they take up different orientations to the applied field. The resonance positions of nuclei contained within the two capillaries show different bulk susceptibility shifts due to different orientations to the applied field. It is suggested<sup>21</sup> that the geometric demagnetization factors may be calculated, or better, determined by use of a calibrant solid. The principal difficulties seem to be firstly, packing the tube with known (or reproducible) positions of the capillaries relative to the applied field, and secondly, the need for specialised N.M.R equipment with a Guloy coil large enough to accommodate a sample with appreciable differences in orientation of the two embedded capillaries.

Caution must be exercised in the use of the N.M.R method for solution susceptibilities, since situations can be envisaged in which equation [10.2] will no longer be applicable.

If the reference material molecules show any





[10.15]. Apparatus for measurement of gas uptake by solutions, (not to scale).

bonding interaction with the paramagnetic molecules anomalous chemical shifts may be produced due to finite spin density in the reference molecule. Contact shifts are reviewed in reference 22.

The derivation of equation [10.2] is based upon bulk properties of solutions. If there is any 'ordering' of the constituents of the solutions this simple relationship will no longer be valid. In view of recent evidence for large molecular aggregates in liquids this may prove to be the best explanation of anomalous results.

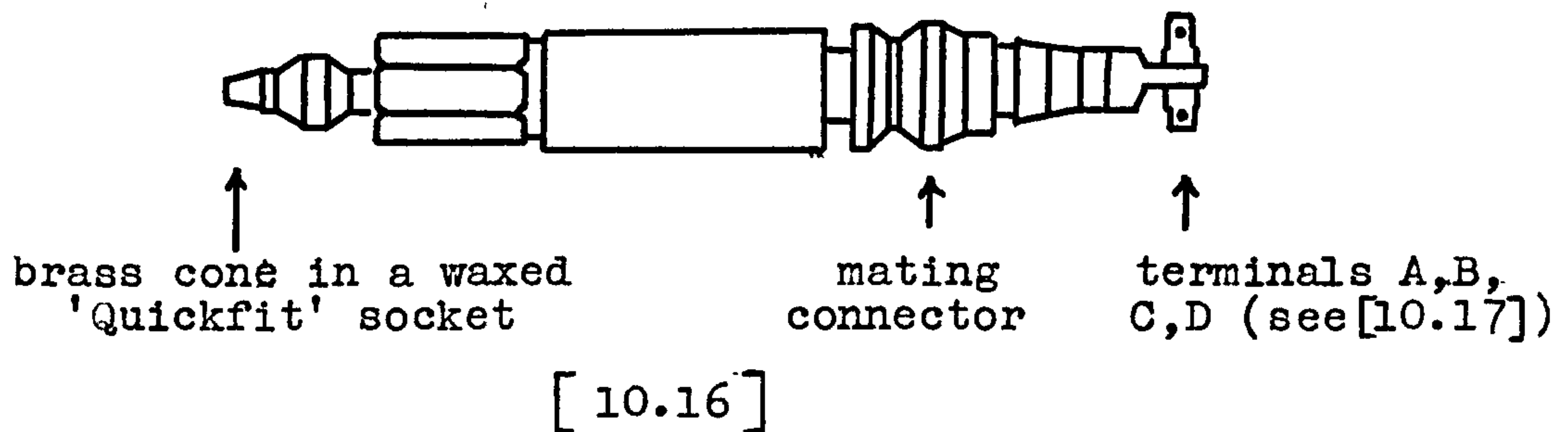
The Gouy method does not suffer from these latter situations, since it does not employ a molecular sized 'probe' to measure properties of macroscopic systems.

## 10.7 Apparatus for the measurement of gas uptake in solution.

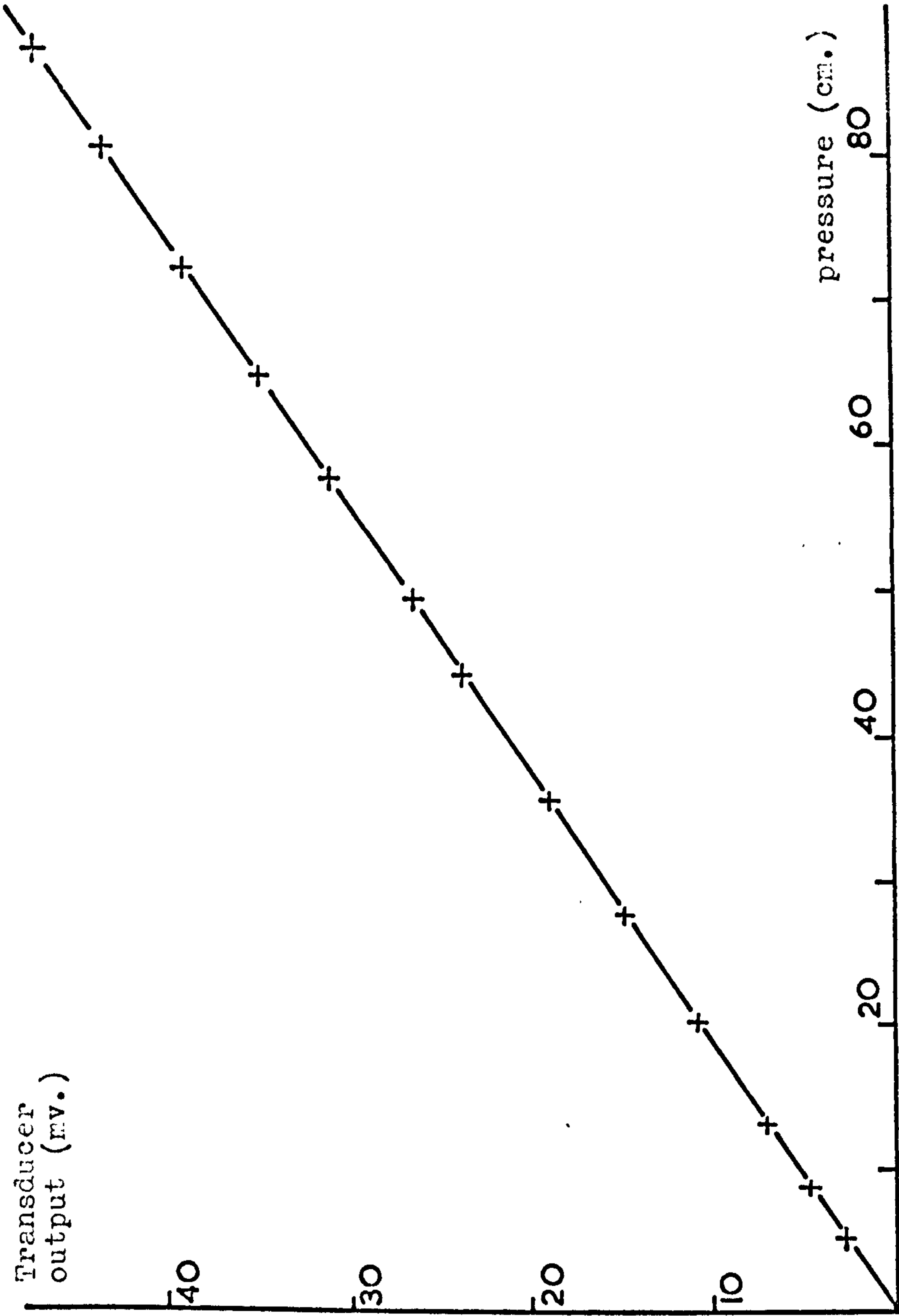
Oxygen uptake by solutions of cobalt(II) complexes was followed by pressure changes in an apparatus of fixed volume at constant temperature. The reaction vessel and gas leads are shown in [10.15].

### 10.7.1 Measurement of pressure change.

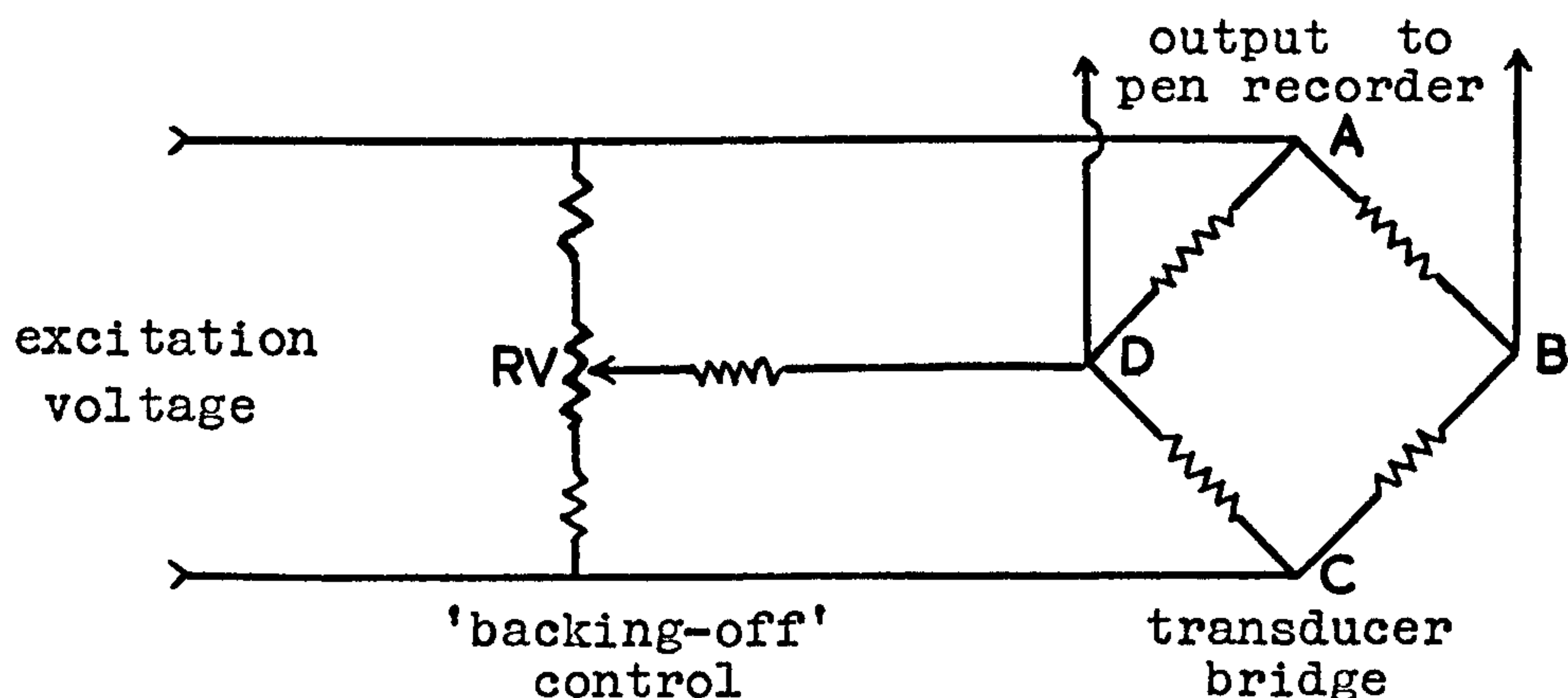
A pressure transducer manufactured by Bell and Howell Ltd., type 4-326 was used to measure pressure changes, and fitted to the apparatus as in [10.16].



A stable D.C. excitation voltage (10v) for the transducer was provided by an "Excitation Module" type L.230710, also manufactured by Bell and Howell Ltd., and the output from the transducer fed to a servoscribe recorder, (Georz, RE 511) as in [10.17]. The slide contact RV in [10.17] provided a 'backing-off' control, which enabled the bridge of the transducer to be balanced to give a zero reading on the recorder for any given pressure. In this way a sensitive scale on the recorder may be used for an appreciable pressure, and small pressure differences measured. Noise due to other circuits recorded by the servoscribe was reduced by passing its mains supply through a voltage stabilizer (Advance Voltstat, CV.50H).



[10.18]. Transducer output in mv. plotted against pressure in cm.



10.17

The linearity of output of the transducer with pressure was checked with the external manometer (M) in [10.15]. The results are shown in [10.18], page F 254, and were checked periodically.

### 10.7.2 Thermostating.

The whole apparatus was enclosed in an air thermostat built by R. Bratchley.<sup>23</sup> Expanded polystyrene sheets mounted on a Dexion frame provided an efficient insulating box in which the air was circulated by a fast electric fan. The air was heated by a 60 watt light-bulb close to the fan, connected to the mains supply via a relay operated by a toluene regulator (Gallenkamp TM - 462, fitted with proportioning head TM - 470).

To prevent the thermostat exceeding the desired temperature when the stirrer and fan motors had been operating for prolonged periods (or on a hot day) a small

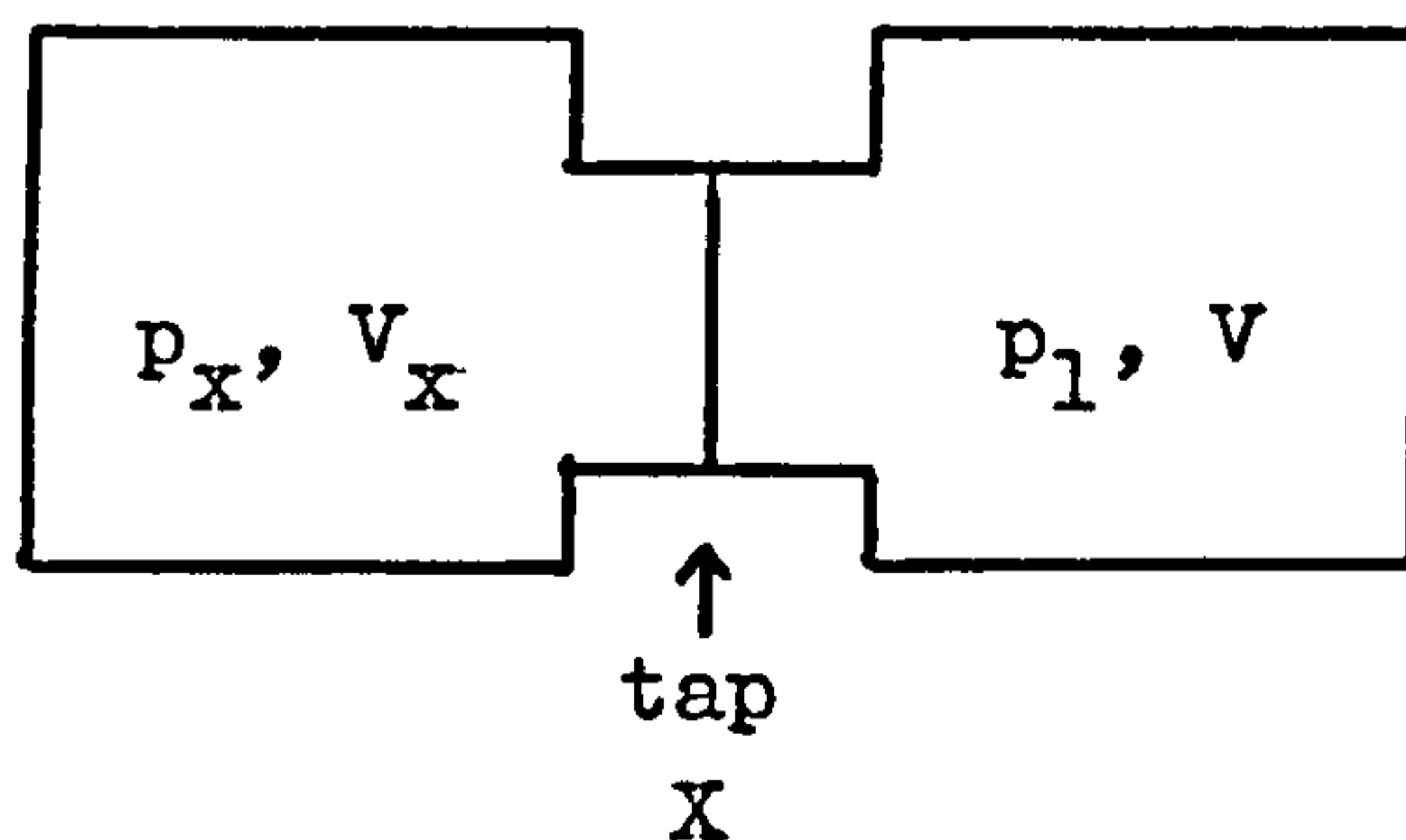
radiator was placed near the fan. A slow stream of tap water passed through the radiator.

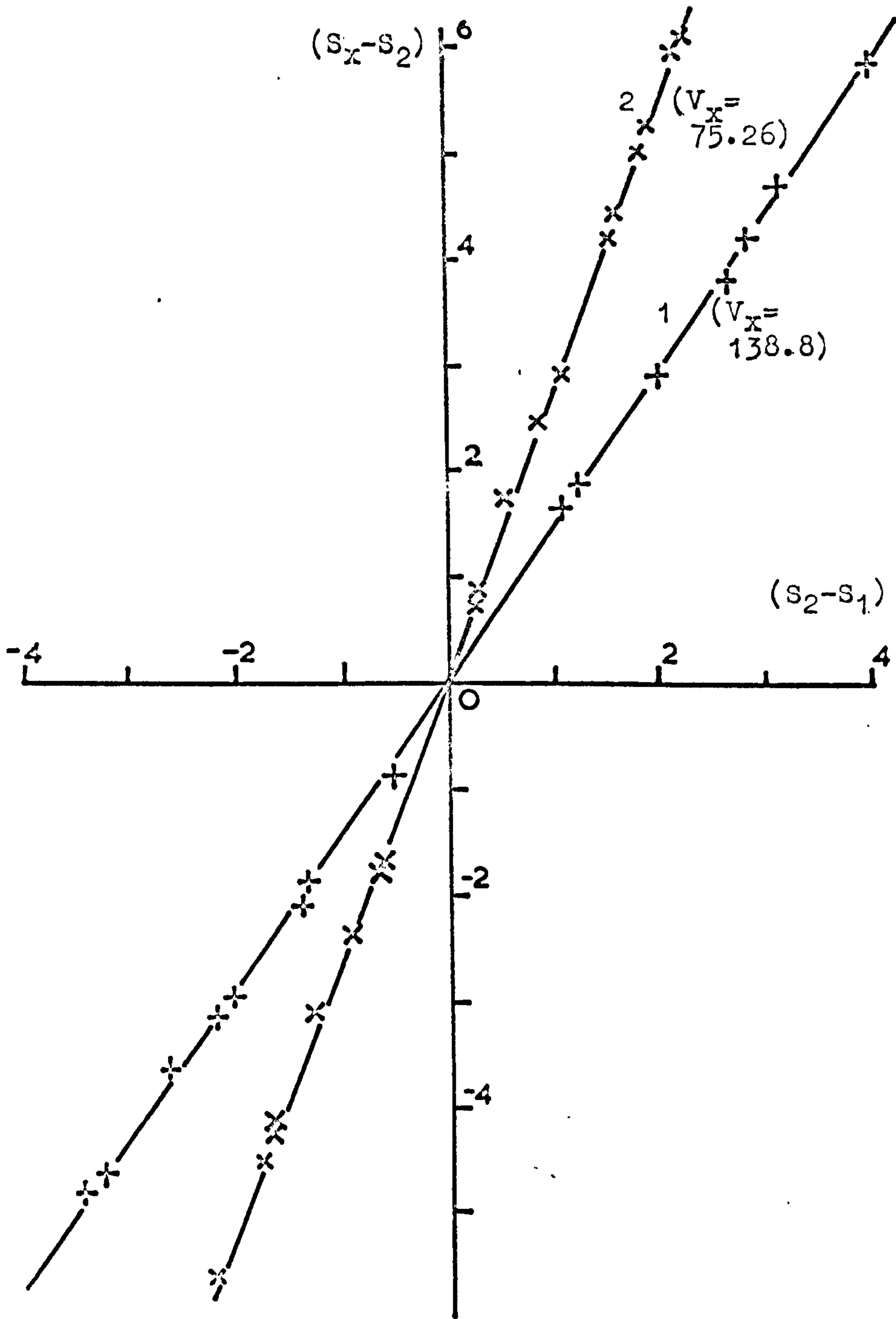
This system produced thermostating effective to  $\pm 0.2^{\circ}\text{C}$ , provided the trap-door into the box was not left open.

### 10.7.3 Determination of the volume of the apparatus.

The volume ( $V$ ) of the vessel and capillaries above upto taps A,B,C,D,E,F,X was determined by application of Boyle's law.

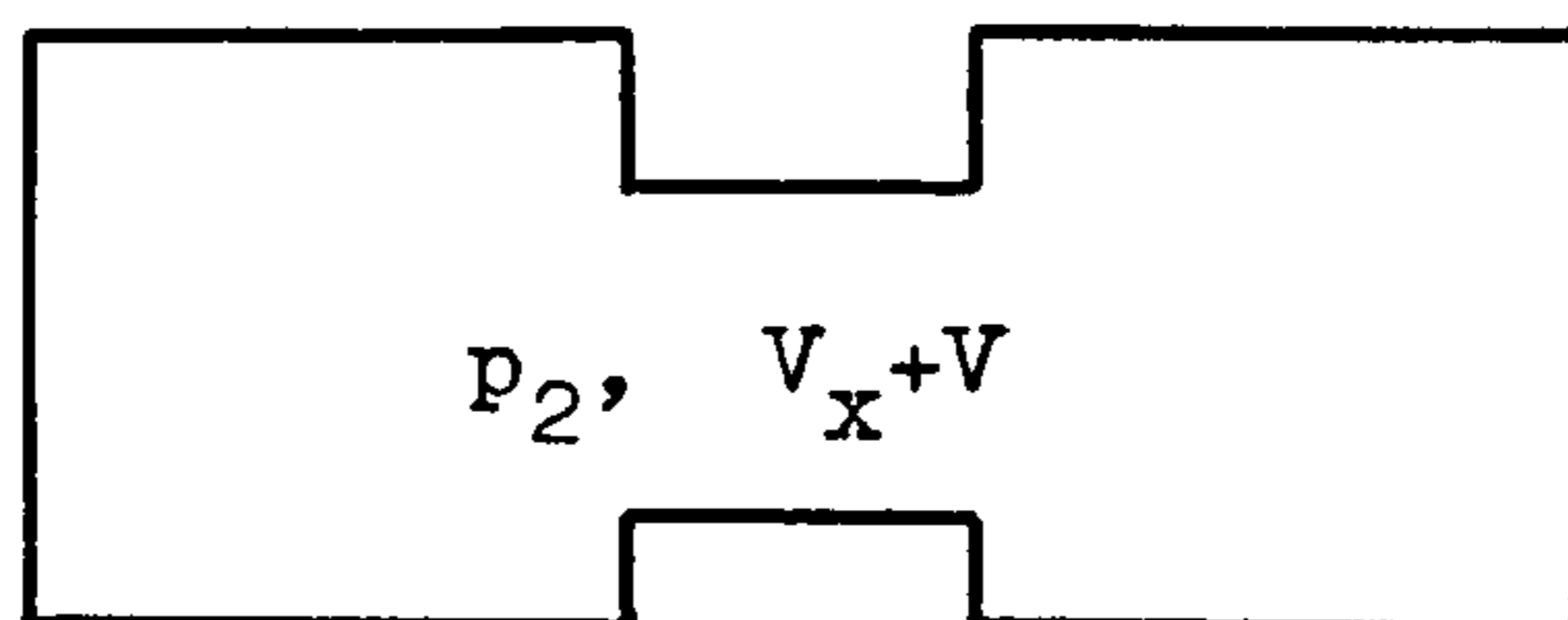
Let the volume of the flask X and capillary upto the point X in [10.15] be  $V_x$  (see also [10.19] ). With tap X open the pressure ( $p_x$ ) is recorded by the transducer output, measured on the servoscribe chart as  $S_x$ . Tap X is closed and the pressure in the vessel altered to a value  $p_1$  (servoscribe reading  $S_1$ ). With all other taps closed the tap X is opened and the resulting pressure ( $p_2$ ) again recorded as a servoscribe reading ( $S_2$ )





[10.20]. Plots of  $S_x - S_2$  against  $S_2 - S_1$ .

(S in 'Servoscribe' chart paper divisions (each 2cm.) ).



[10.19]

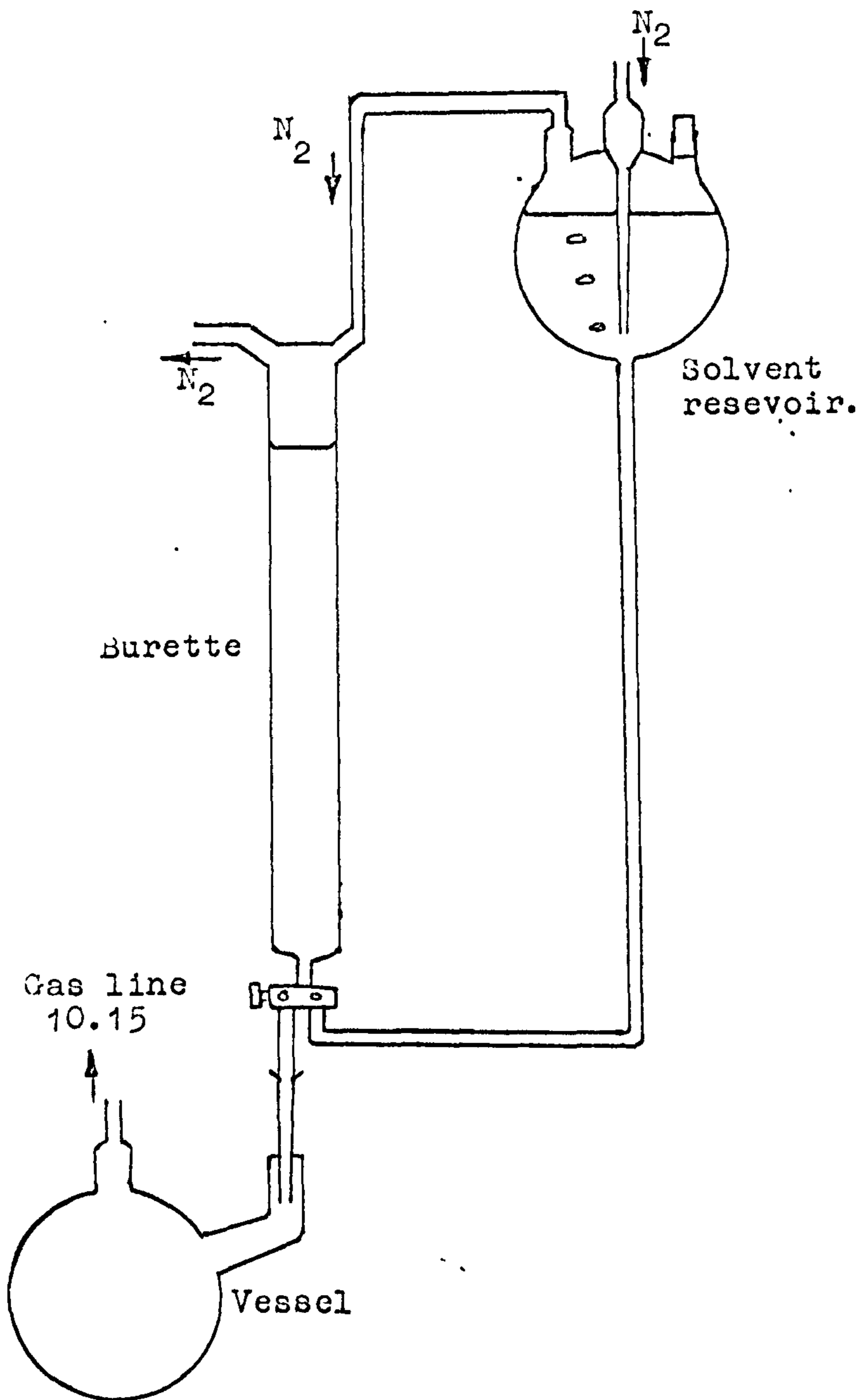
By Boyle's law  $p_x V_x + p_1 V = p_2 (V + V_x)$

$$\therefore \frac{p_x - p_2}{p_2 - p_1} = \frac{V}{V_x}$$

But the servoscribe reading ( $S$ ) is proportional to the pressure ( $p$ ), hence  $\frac{S_x - S_2}{S_2 - S_1} = \frac{V}{V_x}$  (equation [10.7] )

In [10.20], page F256, a series of values for  $S_x - S_2$  are plotted against  $S_2 - S_1$  for two different volumes  $V_x$ . The volumes  $V_x$  were determined by detaching the flask X and tap X at the 'quickfit' joint Y, and weighing the assembly empty and then filled with water to the point X. The temperature of the water was noted when the assembly was filled to the mark. Correction for the density of water at this temperature gave the volumes as





[10.21]. Burette system.

138.80 and 75.26 (mean for three determinations) for the two flasks used in [10.20].

For the measurement of different sets of  $S_x$ ,  $S_1$ , and  $S_2$  values different detection ranges of the servoscribe recorder were used, corresponding to 2,5,10,20 and 50 m.v. output change for a full deflection (10 divisions) of the pen on the chart paper. Points in [10.20] fell onto the straight lines (1) and (2) regardless of the sensitivity range used. In this way the linearity of the servoscribe detection was checked for different ranges.

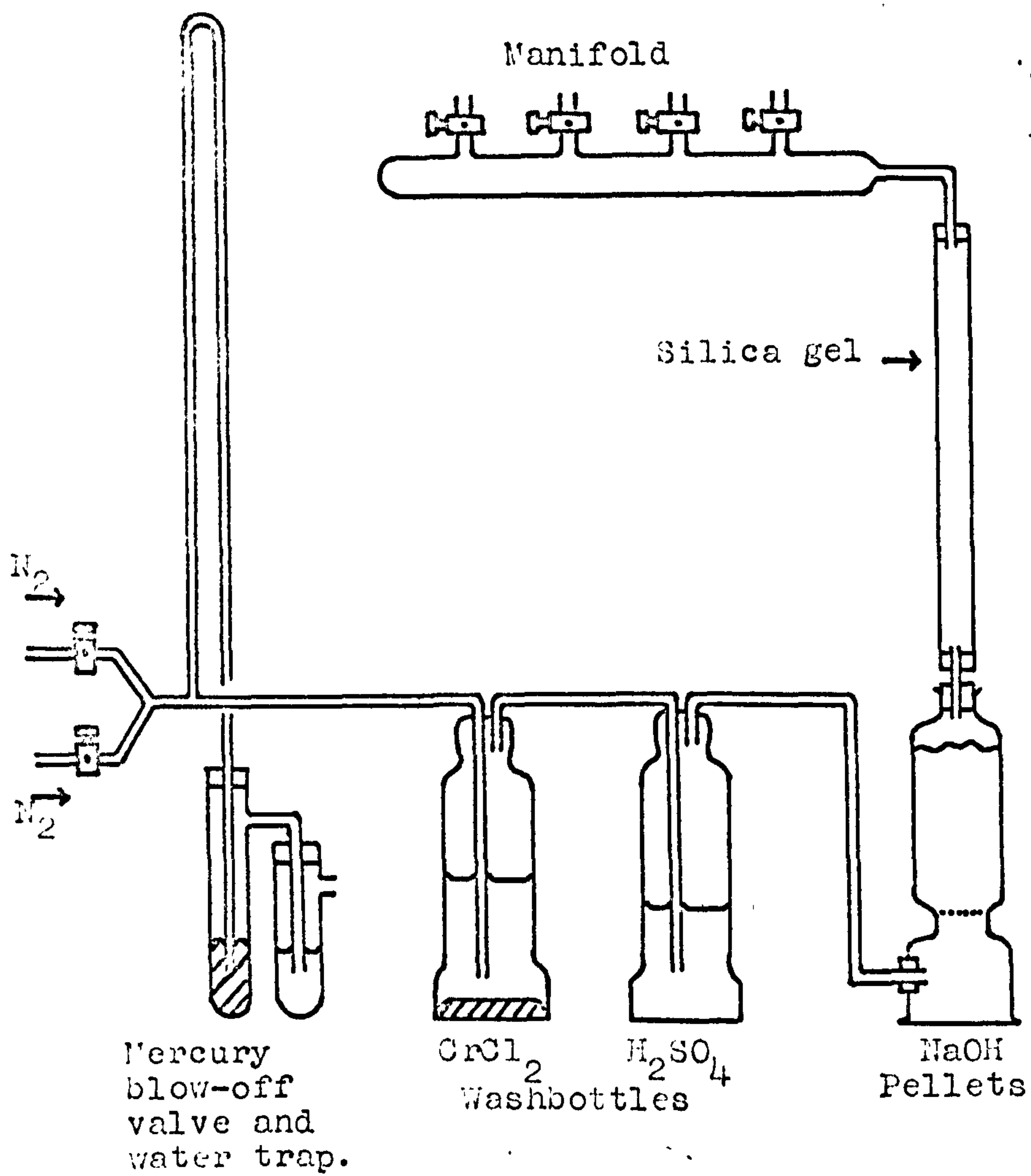
The computed slopes of the lines (1) and (2) in [10.20] gave values for the volume  $V$  as  $200.0 \pm 1.8$  ml. and  $202.9 \pm 1.6$  ml. respectively.

Taking the mean of these two values, weighting according to their individual standard errors<sup>24</sup> gave the most probable value of the volume of the apparatus as  $V = 201.6 \pm 2.1$  ml.

#### 10.7.4 Reaction vessel and burette systems.

The reaction vessel had two side-arms fitted with burettes which allowed the delivery of volumes of solvent in the absence of air. One of the burette and reservoir systems is illustrated in [10.21].

The same pressure of nitrogen above the solvent in the reservoir and burette permitted simple refilling



[10.22]. Nitrogen line.

of the burette. When a volume of solvent was to be delivered to the reaction vessel a stream of nitrogen was passed through the capillary system (taps C and B in [10.15] open). Both this stream and that over the burette were tapped from the same manifold in the nitrogen line (see [10.22], page F 258), and, hence, free flow of solvent into the vessel was not impeded by inequalities of nitrogen pressure in different parts of the apparatus.

#### 10.7.5 Nitrogen line.

'Oxygen-free' nitrogen (British Oxygen Company Ltd.) was passed through an acidic chromous chloride solution (continuously regenerated by contact with zinc amalgam) and dried by passing through columns of sodium hydroxide pellets and silica gel.

A 'blow-off' safety valve and a gas manifold fitted with sprung taps were also connected to the line, see [10.22].

#### 10.7.6 Stirrer.

The contents of the flask were stirred by a plastic covered magnetic follower driven by a rotating magnet. A constant speed motor (Parvalux Ltd., 1425 r.p.m) was used to rotate the magnet, and a series of speeds were made available by use of a gearing system involving pulleys

and belts manufactured by Goodyear and Glover and Wood Ltd. (pulleys - type XL037 and belts-type 120XL).

The stirrer motor was cooled by passing a stream of water through a coil of copper tubing which had been wound round the casing.

#### 10.7.7 Solubility of the gas in the solvent system.

With all the other taps in [10.15] closed the apparatus was evacuated by opening B, and checked for leaks by leaving under vacuum with transducer output recorded on the chart paper, for the most sensitive recorder range. The apparatus was filled with nitrogen by opening tap C and then flushed with a stream of nitrogen by opening tap B to the atmosphere.

The solvent was admitted from one of the burettes (taps E or F), and then degassed by pumping with vigorous stirring for 5 mins. (for dimethylformamide only a small solvent loss was detected by weighing after pumping for 15 min.) The stirrer was stopped and tap B closed and then oxygen was admitted to the apparatus to a desired pressure, recorded at a low sensitivity scale on the chart paper.

The 'backing-off' control was altered to give a reading of 9-10 divisions on the chart paper, for a sensitive recorder scale. The stirrer was started, and

the pressure drop recorded on the chart paper. The equilibrium pressure at the same sensitivity was measured relative to atmospheric pressure, which had been read from a mercury barometer.

The whole procedure was repeated for different initial pressures of oxygen in the apparatus.

#### 10.7.8 Gas uptake in solution.

The solute was weighed directly into the reaction flask, and then the whole procedure of section 10.7.7 repeated. The solute dissolved during the degassing and stirring operation.

After the gas uptake and equilibrium pressure had been recorded the solution was degassed and the procedure repeated to see if the process of gas absorption was reversible.

#### 10.8 Solvent purification.

In general the standard laboratory grade solvents were used. Exceptions and methods of purification are briefly listed below.

##### 10.8.1 Pyridine.

Analar pyridine was degassed, refluxed for 60 min. over calcium hydride in a slow stream of nitrogen,

and distilled, collecting a fraction b.p. 114 - 116°.

#### 10.8.2 Dimethylformamide.

After refluxing for 3 hours over anhydrous potassium carbonate dimethylformamide was distilled twice using a fractional distillation column packed with glass helices, heated by a jacket (Gallenkamp DT - 520), collecting the fraction, b.p. 151 - 153°

#### 10.8.3 Dimethylsulphoxide.

Dimethyl sulphoxide reacts explosively with some drying agents.<sup>25</sup> After standing overnight over calcium hydride in a water bath maintained at 20° dimethyl sulphoxide was distilled under reduced pressure, using a nitrogen 'bleed'.

#### 10.8.4 Tetrahydrofuran.

'Degassed' tetrahydrofuran containing a little benzophenone was refluxed under nitrogen over sodium wire, for a short time and then distilled under a slow stream of nitrogen, using a fractionating column and collecting the fraction, b.p. 63-65°.

#### 10.8.5 Methanol.

Commercial 'absolute' methanol was treated as

in reference 26.

#### 10.8.6 Ethanol

Commercial 'absolute' ethanol was purified to give 'superdry' ethanol by distillation from ethyl succinate and sodium.<sup>27</sup>

#### 10.9 Miscellaneous details.

Analyses were performed by Dr. A. Bernhardt in Mülheim.

Melting points were determined on a Kofler hot stage and are quoted uncorrected.

#### 10.10 References.

1. H. Weigold and B.O. West, J. Chem. Soc.(A), 1310, (1967)
2. B.N. Figgis and J. Lewis, "Technique of Inorganic Chemistry", IV, Interscience, 1965, page 137.
3. Newport Instruments Ltd., "User Handbook for 1½ in. Electromagnet Type C".
4. B.N. Figgis and R.S. Nyholm, J. Chem. Soc., 4190, (1958)
5. N.F. Curtis, J. Chem. Soc., 3147, (1961).
6. D.F. Evans, J. Chem. Soc., 2003, (1959).
7. D.F. Evans, Proc. Chem. Soc., 115, (1958).
8. J.A. Pople, W.G. Schneider and H.J. Bernstein, "High-resolution N.M.R. Spectroscopy", McGraw-Hill, 1959, p.81.



9. H.P. Fritz and K.E. Schwarzhaus, *J. Organometal. Chem.*, 1, 208, (1963).
10. H.R. Nettleton and S. Sugden, *Proc. Royal Soc.*, A173, 313, (1939).
11. A.I. Vogel, "Text-Book of Quantitative Inorganic Analysis", 3rd Ed., Longmans, 1961, page 526.
12. E.N. Sloth and G.S. Garner, *J. Chem. Phys.*, 22, 2064, (1954).
13. B.N. Figgis, *Trans. Faraday Soc.*, 57, 204, (1961).
14. P.W. Selwood, "Magnetochemistry", 2nd Ed., Interscience, 1956, page 86.
15. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.* 6, 213, (1964)
16. A. Lallemand, *Annales de Physique*, 3, 97, (1935).
17. J.B. Willis and D.P. Mellor, *J. Amer. Chem. Soc.*, 69, 1237, (1947).
18. H.C. Clark and A.L. Odell, *J. Chem. Soc.*, 3431 (1955)
19. F.H. Field and W.G. Vosburg, *J. Amer. Chem. Soc.*, 71, 2398, (1949).
20. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.* 6, 198, (1964)
21. G. Feher and W.D. Knight, *Rev. Scientific Instruments*, 26, 293, (1955).
22. D.R. Eaton and W.D. Phillips, *Adv. Magnetic Resonance*, 1, 103, (1965).
23. R. Bratchley, D. Phil Thesis, York, to be submitted.

24. J. Topping, "Errors of Observation and Their Treatment", Chapman and Hall, 1966, page 93.
25. W.W. Epstein and F.W. Sweat, Chem. Rev., 67, 247, (1967).
26. A.I. Vogel, "Text-Book of Practical Organic Chemistry", 3rd Ed., Longmans, 1962, page 169.
27. *ibid.*, page 168.

Chapter 11. Preparative Details.

11.1	Acyclic ligands, chapter 3	Page 265
11.2	Nickel complexes, chapter 4	Page 288
11.3	Cobalt complexes, chapter 5	Page 296
11.4	Cyclic ligands, chapter 7	Page 308
11.5	Nickel and copper complexes, chapter 8	Page 322
11.6	Cobalt complexes, chapter 9	Page 328
11.7	Miscellaneous compounds, chapter 10	Page 332
11.8	References	Page 334

11.1. Compounds of chapter 3.O-Aminobenzaldehyde.

The method of L.E. Smith and I.W. Opie<sup>1</sup> was used on double scale with some modifications. The flask was heated during reaction and steam distillation in an isomantle. A sealed stirrer was used, which was left in position during the steam distillation. The product from the ether extract (1.5 g.) m.p. 36-39<sup>o</sup> was not further distilled. The total yield of pale yellow plates, m.p. 37-39<sup>o</sup>, varied from 5.6 to 6.5 g (59-68%). The product was used immediately, as it undergoes self polymerisation on standing, especially in a dessiccator.

N.M.R. spectrum of a CDCl<sub>3</sub> solution ( $\tau$ ); 0.09 (methine, singlet), 2.35-3.40 (aromatics, complex), 3.85

(NH<sub>2</sub>, broad).

I.R. spectrum as KBr disc ( $\lambda_{\max}, \text{cm}^{-1}$ ); 3490(b)  
2980(w), 1661(s), 1605(s), 1595(s), 1485(s), 1460(m),  
1402(w).

N,N'-Bis-(o-aminobenzylidene)-1,2-diaminoethane.

(1) From o-aminobenzaldehyde. o-Aminobenzaldehyde (3.0g  
25 mmole) in methanol (50ml.) was refluxed with  
1,2-diaminoethane (0.8ml. 12 mmole), for 30 mins, whilst  
stirring vigorously to minimise bumping. After cooling,  
white crystals, m.p. 170-175°C, were collected at a sinter  
and recrystallized from boiling acetone (250 ml.) to give  
white plates of N,N'-bis-(o-aminobenzylidene)-1,2-  
diaminoethane (31g, 92%), m.p. 182-184°C (lit. 178°)<sup>2</sup>

Analysis found C, 72.09; H, 6.80; N, 20.09%

C<sub>16</sub>H<sub>18</sub>N<sub>4</sub> requires C, 72.17; H, 6.81; N, 21.04%

N.M.R. spectrum of dimethylsulphoxide (d<sub>6</sub>)  
solution ( $\tau$ ); 1.66 (methine, singlet), 2.6-3.6 (aromatics,  
complex), 2.90 (NH<sub>2</sub>, broad), 6.24 (methylene, singlet).  
Acetone solution: 1.58 (methine, singlet), 2.10 (NH<sub>2</sub>, broad),  
2.6-3.6 (aromatics, complex), 6.14 (methylene, singlet).

Mass spectrum (m/e); 267 (20%), 266 (100%)  
(molecular ion) 160 (2%), 148 (5%), 147 (14%), 133 (31%),  
132 (17%), 131 (10%), 120 (20%), 119 (12%), 118 (11%),  
116 (8%), 106 (21%), 93 (12%), 83 (10%), 81 (10%), 77 (12%).

IR. spectrum as nujol mull ( $\lambda_{\max}$ ,  $\text{cm}^{-1}$ ); 3430(s), 3250(s), 1636(s), 1609(sh) 1585(s), 1559(m), 1492(m), 1380(s), 1330(m), 1323(m), 1275(w), 1220(m), 1163(s), 1060(w), 1040(w), 1022(s), 982(m), 935(w), 900(w) 862(w), 805(w), 755(m), 747(s), 725(w) (KBr disc data p 44 ).

(2) From o-nitrobenzaldehyde.

(a) N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane. o-Nitrobenzaldehyde (1.03 g. 6.8 mmole) in ethanol (10 ml) was refluxed with 1,2-diaminoethane (.21 g, 3.4 mmole) for 30 mins. The solid separating was recrystallized from ethanol (30 ml) and gave N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane (.99g, 89%) as white needles, m.p. 109-110°C, which turn bright yellow in sunlight.

N.M.R spectrum of  $\text{CDCl}_3$  solution ( $\tau$ ), 1.09 (methine, singlet), 1.75-2.70 (aromatics, complex), 5.91 (methylene, singlet).

I.R. spectrum as KBr disc ( $\lambda_{\max}$ ,  $\text{cm}^{-1}$ ); 3020(w), 3010(w), 2880(w), 2750(w) 1635(s), 1603(m), 1569(s), 1520(s,b) 1505(sh), 1495(sh), 1440(m)

(b) Reduction of N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane. N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane (1.0g, 3.1 mmole) was hydrogenated in ethanol (200ml) using a platinum black catalyst (0.1g.),

which had been prepared from chloroplatinic acid as described by Adams<sup>3</sup>. 440 ml. of hydrogen at atmospheric pressure was absorbed (theoretical volume; 452 ml. at 752 mm. and 20°C). The catalyst was removed by filtration, and evaporation of the filtrate gave white plates m.p. 174-177°C, which were recrystallized from boiling acetone to give N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethane (0.46g., 56%), m.p. 182-183°C, mixed m.p. with authentic sample 182-184°C.

N,N'-bis(o-aminobenzylidene)-hydrazone.

(a) from N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane.

N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane (1 g. 3.1 mmole) was heated for 15 mins. in refluxing ethanol (100ml.) with hydrazine hydrate (10ml.) and 5% palladium charcoal (.5g). The mixture was filtered hot and evaporated under reduced pressure to remove excess hydrazine hydrate. The resulting bright yellow solid was recrystallized from ethanol to give bright yellow needles of N,N'-bis-(o-aminobenzylidene)-hydrazone (0.56g 76%), m.p. 248-250° (lit. 248°)<sup>4</sup>

Analysis found C, 70.20; H, 5.86; N, 23.11%

C<sub>14</sub>H<sub>14</sub>N<sub>4</sub> requires C, 70.55; H, 5.93; N, 23.51%

N.M.R. spectrum of acetone solution ( $\tau$ ); 1.31 (methine, singlet), 2.4-3.4 (aromatics, complex).

Mass spectrum (m/e); 239(16%), 238(100%)

molecular ion), 223(12%), 222(87%), 221(16%), 209(35%), 208(48%) 207(13%), 120(26%) 119(100%), 118(28%), 104(20%) 103(13%), 102(10%), 94(22%), 93(73%), 92(133%), 91(31%), 78%(12%), 77(25%).

IR. Spectrum as KBr disc ( $\lambda_{\max}, \text{cm}^{-1}$ ); 3410 (s) 3020(w), 1619(s), 1601(s), 1595(sh), 1580(sh), 1545(s) 1490(s), 1451(s).

(b) From o-nitrobenzaldehyde. o-Nitrobenzaldehyde (lg. 66mmole) was heated for 3 hours in refluxing ethanol (25ml.) with hydrazine hydrate (10ml.) and 5% palladium charcoal catalyst (.5g). The mixture was filtered hot and evaporated under reduced pressure until all the excess hydrazine hydrate had distilled. The resulting yellow solid was recrystallised from a 1:1 mixture of ethanol and acetone (10 ml), when N,N'-bis-(o-aminobenzylidene)-hydrazone (.54g., 69%) was obtained as yellow needles m.p. 248-249° (mixed m.p. 247-249° with sample prepared from N,N'-bis(o-nitrobenzylidene)-1,2-diaminoethane).

N,N'-bis-(o-aminobenzylidene)-1,3-diaminopropane

A solution of o-aminobenzaldehyde (3.79g 31 mmole) and 1,3-diaminopropane (1.3 ml. 16 mmole) in ethanol (30 ml.) was refluxed for 1 hr. The volume was reduced to approximately 15 ml. by evaporation under reduced pressure

when white crystals separated, m.p. 104-110C, which were recrystallized from hot ethanol to give white plates of N,N'-bis-(o-aminobenzylidene)-1,3-diaminopropane (3.07g. 69%) m.p. 112-114°C.

Analysis found C, 72.56; H, 7.34; N, 20.73%

$C_{17}H_{20}N_4$  requires C, 72.82; H, 7.19; N, 19.98%

N.M.R spectrum of  $CDCl_3$  solution ( $\tau$ ): 1.66 (methine, singlet) 2.7-3.5 (aromatics, complex), 3.62 ( $NH_2$ , broad), 6.33 ( $\alpha$ -methylene, triplet,  $J = 7$  c.p.s.), 7.95 ( $\beta$ -methylene, quintet,  $J = 7$  c.p.s.).

Mass spectrum (m/e); 280 (22%) (molecular ion), 177 (15%), 160 (18%), 147 (47%), 134 (81%), 133 (100%), 132 (33%), 131 (30%), 130 (66%), 120 (23%), 119 (76%), 118 (90%), 117 (18%), 116 (12%), 107 (10%), 106 (76%), 104 (35%), 103 (11%), 94 (10%), 93 (34%), 92 (37%), 91 (22%), 78 (19%), 77 (41%).

IR. spectrum as nujol mull ( $\lambda_{max}$ ,  $cm^{-1}$ ); 3427 (s) 3254(m), 3060(w), 3020(w), 1633(s), 1606(sh), 1586(s) 1557(m), 1491(s), 1370(s), 1339(m), 1219(m), 1163(s), 1108(w), 1088(w), 1067(w), 1034(w), 1020(m), 979(m) 942(w), 931(w), 893(w), 860(w), 774(w), 755(m) 747(s).

N,N'-bis-(o-aminobenzylidene)-1,4-diaminobutane.

A solution of o-aminobenzaldehyde (2.0g 16.5 mmole) and 1,4-diaminobutane (.72g 8.1 mmole) in methanol (50ml)



was refluxed for 2 hrs. The volume was reduced to approximately 10 ml. when white crystals separated which were recrystallized from a small volume of methanol to give N,N'-bis-(o-aminobenzylidene)-1,4-diaminobutane (1.5 g 63%) as white prisms m.p. 133-135°.

N.M.R. spectrum of  $\text{CDCl}_3$  solution ( $\tau$ ); 1.67 (methine, singlet), 3.4 ( $\text{NH}_2$  by integrating also after  $\text{D}_2\text{O}$  addition), 2.7-3.6 (aromatics, complex), 6.32 ( $\alpha$ -methylene, broad), 8.21 ( $\beta$ -methylene, broad).

Mass spectrum (m/e); 294 (13%) (molecular ion) 191 (13%), 175 (16%), 174 (100%), 173 (29%), 159 (10%), 151 (10%), 147 (23%), 146 (19%), 145 (20%), 139 (12%), 137 (17%), 133 (28%), 132 (25%), 131 (52%), 130 (17%), 127 (10%), 125 (23%), 123 (25%), 121 (23%) 120 (18%), 119 (30%), 118 (25%), 111 (40%) 107 (32%), 106 (61%), 97 (61%) 95 (51%), 93 (30%), 85 (46%), 81 (62%), 77 (24%).

IR. spectrum as nujol mull ( $\lambda_{\text{max}}$ ,  $\text{cm}^{-1}$ ); 3405(s), 3250(m), 3060(w), 3020(w), 1633(s), 1608(sh), 1590(s) 1565(m), 1494(s), 1372(s), 1350(m), 1219(m), 1179(w), 1159(s), 1113(w), 1056(m), 1028(w), 1007(m) 976(m) 937(w), 885(w), 855(w), 777(w), 753(m), 745(s)

N,N'-bis-(o-aminobenzylidene)-1,10-diaminodecane.

A solution of o-aminobenzaldehyde (3.71g 30.6 mmole) and 1,10-diaminodecane (2.64g 15.3 mmole) in methanol

(50 ml.) was refluxed for 1 hour. On cooling white crystals were deposited, m.p. 114-115<sup>o</sup>, which were recrystallised from ethanol containing a little chloroform and gave N,N'-bis-(o-aminobenzylidene)-1,10-diaminodecane (5.30 g 90%) as white prisms m.p. 115-116<sup>o</sup>.

Analysis found C, 76.43; H, 8.63; N, 14.72%

C<sub>24</sub>H<sub>34</sub>N<sub>4</sub> requires C, 76.15; H, 9.05; N, 14.80%

N.M.R. spectrum of CDCl<sub>3</sub> solution ( $\tau$ );

1.65 (methine, singlet), 2.6-3.5 (aromatics, complex),  
3.65 (NH<sub>2</sub>, broad), 6.46 ( $\alpha$ -methylene, triplet, J=7 c.p.s)  
8.70 ( $\beta$  -  $\epsilon$  -methylene, broad).

Mass spectrum (m/e); 378 (20% (molecular ion),  
275 (13%), 259 (10%), 258 (10%), 245 (10%), 231 (9%),  
217 (11%), 203 (12%), 189 (20%), 175 (23%), 169 (24%),  
161 (10%), 148 (11%), 147 (64%), 146 (14%), 144 (11%),  
134(50%), 133 (100%), 132 (68%), 131 (32%) 130 (29%),  
120 (40%), 119 (64%), 118 (64%), 117 (28%), 106 (95%),  
93 (31%), 77 (32%).

IR. spectrum as KBr disc ( $\lambda_{\max}$ ; cm<sup>-1</sup>); 3405 (s)  
3252(m), 3070(w), 3030(w), 2921(s,b), 2851 (s,b), 1633(s)  
1608(sh), 1588(s), 1562(sh), 1491(s), 1465(m), 1458(m)  
1390(m,b), 1310(w), 1281(m,b), 1224(m), 1163(m), 1079(w)  
1159(w), 1022(sh), 1012(m), 978(m) 944(w), 907(sh), 892(m)  
862(m), 779(m), 757(s), 749(s) 735(w).

o-Aminobenzophenone.

This was prepared by a Friedel Craft reaction of p-toluenesulphonylanthranyl chloride with benzene according to the method of Scheifele and DeTar<sup>5</sup>. Hydrolysis of the resulting sulphonamide gave o-amino-benzophenone, m.p. 105-106°, in 52% yield, after treatment with activated charcoal and recrystallization from 95% ethanol.

N.M.R. spectrum in CDCl<sub>3</sub> solution ( $\tau$ );  
2.3-3.0 (aromatics, complex), 3.3-3.7 (aromatics, complex)  
3.90 (NH<sub>2</sub>, broad).

IR. spectrum as KBr disc ( $\lambda_{\max}$ , cm<sup>-1</sup>); 3435(s), 3220(s), 3105(w), 3085(w), 3050(w), 1635(s), 1615(s), 1587(s), 1493(w), 1475(s) 1445(s).

N,N'-bis-(o-aminobenzophenylidene)-1,2-diaminoethane.

(1) o-Aminobenzophenone (3.5g. 18 mmole) was heated for 24 hours with 1,2-diaminoethane (.60ml. 9 mmole) under reflux in an oil bath maintained at 120°. The resulting oil was poured into water (20 ml.) to remove excess 1,2-diaminoethane, and extracted with chloroform (4 x 10 ml.) Evaporation under reduced pressure gave an oil which was induced to crystallise by dissolving in 50% ethanol : water and allowing to stand for several days. Recrystallising this solid twice from a small

volume of 95% ethanol gave N,N'-bis-(o-aminobenzophenylidene)-1,2-diaminoethane (1.2g 32%) as white prisms  
m.p. 142-146°.

Analysis found C, 80.35; H, 6.26; N, 13.38%

$C_{28}H_{26}N_4$  requires C, 80.38; H, 6.22; N, 13.39%

N.M.R. spectrum as  $CDCl_3$  solution ( $\tau$ );

2.5-3.8 (aromatics, complex), 3.2 ( $NH_2$ , by integration, also after  $D_2O$  addition), 6.49 (methylene, singlet).

Mass spectrum (m/e), 419 (10%), 418 (28%)

(molecular ion), 223 (35%), 222 (90%), 221 (50%), 210 (14%), 209 (60%), 208 (25%), 207 (30%), 204 (19%), 197 (23%)  
196 (22%), 195 (50%), 194 (15%), 182 (11%), 180 (30%), 167 (13%), 165 (14%), 151 (11%), 149 (50%), 131 (35%), 125 (16%), 120 (13%), 119 (35%), 118 (30%), 111 (24%), 106 (100%), 104 (30%), 97 (40%), 95 (35%), 93 (24%), 92 (22%)  
91 (60%), 85 (37%), 83 (50%), 81 (45%), 79 (24%), 77 (58%).

IR. spectrum as nujol and HCBD mull ( $\lambda_{max}, cm^{-1}$ ),  
3463(s), 3190(b), 3080(w), 3075(w), 3025(w), 2920(m),  
2860(m), 1613(s), 1585(s), 1555(m), 1545(m), 1483(s),  
1450(s), 1440(s), 1404(m), 1348(w), 1325(m), 1305(s)  
1256(s), 1160(s), 1088(w), 1072(w), 1022(m), 999(w), 962(s),  
912(m), 845(w), 772(m), 745(s), 706(s).

(2) Refluxing o-aminobenzophenone (3.0g. 15 mmole) in excess 1,2-diaminoethane (15 ml. 280 mmole) containing a few crystals of 1,2-diaminoethane dihydrochloride, and

working up the product as above, after evaporating the excess 1,2-diaminoethane under reduced pressure, gave a similar yield of N,N'-bis-(o-aminobenzophenylidene)-1,2-diaminoethane (0.9g. 29%).

(3) Heating o-aminobenzophenone (3.0g 15 mmole) and 1,2-diaminoethane (.53ml. 8 mmole) and a small quantity of anhydrous zinc chloride (approx. 1 mg.) in a sealed tube at 200°C for 24 hr. produced a brown tar, which after treatment with hot 50% ethanol : water and charcoal gave a pale yellow filtrate which deposited crystals of N,N'-bis-(o-aminobenzophenylidene)-1,2-diaminoethane (.25g 8%), m.p. 142-145°, after recrystallisation from ethanol.

(4) Refluxing o-aminobenzophenone (2.0g. 10 mmole) with 1,2-diaminoethane (.33ml. 5 mmole) in ethanol and methanol for 3 days gave no apparent reaction.

N,N'-bis-(o-aminobenzophenylidene)-1,4-diaminobutane.

o-Aminobenzophenone (3.0g. 15 mmole) was heated with 1,4-diaminobutane (.70g 8 mmole) containing anhydrous zinc chloride (approx. 1 mg.) under reflux for 36 hr. in an oil bath maintained at 125°. After cooling, methanol (10 ml.) was added and the crystals separating after several days were recrystallised from iso-propyl ether (200 ml.) to give pale yellow crystals of N,N'-bis-(o-amino

benzophenylidene)-1,4-diaminobutane (2.4g 67%), m.p.  
= 138-140°.

N.M.R. spectrum in  $\text{CDCl}_3$  solution ( $\tau$ ); 2.4-3.7 (aromatics, complex), 3.2 ( $\text{NH}_2$ , by integration also after addition of  $\text{D}_2\text{O}$ ), 6.78 ( $\alpha$ -methylene, broad), 8.30 ( $\beta$ -methylene, broad).

I.R. spectrum as nujol mull ( $\lambda_{\text{max}}, \text{cm}^{-1}$ ); 3470(s), 3190(b), 3070(w), 3010(w), 1606(s), 1592(m), 1562(s), 1537(s), 1487(w), 1455(s), 1445(w), 1379(m), 1335(w), 1308(s), 1256(s), 1183(w), 1164(s), 1072(w), 1067(w), 1045(w), 1025(w), 985(w), 977(w), 943(w), 921(w), 903(w), 852(w), 825(w), 775(m), 755(s), 704(s), 689(m), 642(m).

#### o-Aminoacetophenone.

This was purchased from Kodak Ltd., and used without further purification.

N.M.R. spectrum of  $\text{CDCl}_3$  solution ( $\tau$ ): 2.2-3.6 (aromatics, complex), 3.77( $\text{NH}_2$ , broad), 7.50 (methyl, singlet).

#### N,N'-bis-(o-aminoacetophenylidene)-1,2-diaminoethane.

o-Aminoacetophenone (10g. 74 mmole), 1,2-diaminoethane (2.5ml., 37mmole) and a small amount of anhydrous zinc chloride (approx. 1 mg.) were refluxed

together for 2 hours. After cooling, methanol (20 ml) was added, and on standing for 24 hours a solid separated, which was recrystallised from methanol containing a trace of water to give colourless needles of N,N'-bis-(o-aminoacetophenylidene)-1,2-diaminoethane (5.7g. 52%)  
m.p. 127-129°C.

Analysis found C, 72.92; H, 7.49; N, 19.49%

C<sub>18</sub>H<sub>22</sub>N<sub>4</sub> requires C, 73.48; H, 7.53; N, 19.03%

N.M.R. spectrum of CDCl<sub>3</sub> solution ( $\tau$ ); 2.4-3.5 (aromatics, complex), 3.60 (NH<sub>2</sub>, broad), 6.11 (methylene, singlet), 7.70 (methyl, singlet).

Mass spectrum (m/e); 295 (4%), 294 (21%) (molecular ion), 279 (2%), 234 (12%), 233 (11%), 219 (6%) 175 (5%), 160 (22%), 159 (10%), 148 (16%), 147 (60%), 146 (16%), 145 (45%), 135 (30%), 134 (16%), 133 (15%), 132 (43%), 120 (37%), 119 (21%), 118 (100%), 117 (25%) 106 (27%), 104 (6%), 92 (25%), 91 (39%), 90 (2%), 77 (15%).

I.R. spectrum as nujol mull ( $\lambda_{\max}$ , cm<sup>-1</sup>); 3349(s), 3110(m,b), 3080(sh), 3050(w), 3020(w), 1620(s), 1585(m), 1550(sh), 1492(m), 1460(sh), 1430(sh), 1363(m), 1318(w), 1295(sh), 1285(s), 1248(s), 1182(sh), 1152(s), 1105(m), 1075(w), 1055(m), 1025(s), 1002(sh), 932(w), 842(w) 775(w), 742(s), 737(s).

N-methylantranilic acid.

To a solution of anthranilic acid (100g. .73 mole) in 5% sodium hydroxide solution (650 ml) was added dimethyl sulphate (80 ml. .84 mole). The mixture was shaken vigorously for 5 min., cooled to 0°, and filtered. The residue was recrystallised twice from ethanol (1.5 l.) to give N-methylantranilic acid (93g. 84%), m.p. 178-179° (lit. 178-179°)<sup>6</sup>

N-methyl-o-aminobenzylalcohol.

Lithium aluminium hydride (20g. 0.53 mole) was added to dry diethyl ether (1 l.) (distilled from calcium hydride), contained in a 2 l. 3-necked flask fitted with a sealed mechanical stirrer and a Soxhlet extractor and condenser. N-methylantranilic acid (33.1g 0.219 mole) was placed in a thimble in the Soxhlet extractor. The ether was refluxed gently in a heating mantle, and after 2 hours all the N-methylantranilic acid had been introduced into the flask. (N.B. during the siphoning of ether solution from the Soxhlet extractor a vigorous evolution of hydrogen takes place, which sweeps ether vapour out of the top of the condenser. A length of tubing was fitted to a calcium chloride tube at the end of the condenser to lead ether vapour away from the sparking stirrer motor to a window.) After



refluxing for a further 30 mins. water (50 ml.) was added cautiously in small portions to destroy excess lithium aluminium hydride, followed by 10% sodium hydroxide solution (550 ml.) The ether layer was decanted and combined with ether from three extractions (3 x 200 ml.) of the aqueous layer, dried over magnesium sulphate (200 g.) and evaporated to give a pale yellow oil (26.2g 86%) of N-methyl-o-aminobenzylalcohol, which was used unpurified for the preparation of N-methyl-o-amino-benzaldehyde.

I.R. spectrum as liquid film ( $\lambda_{\max}, \text{cm}^{-1}$ ); 3500 (b,sh), 3420(s,b), 3060(w), 3042(w), 2982(w), 2920(m), 2865(m), 2810(m), 1608(s), 1585(s), 1512(s), 1468(s), 1426(m).

#### N-methyl-o-aminobenzaldehyde.

(1) A solution of N-methyl-o-aminobenzylalcohol (10 g. 73 mmole) in diethylether (100 ml) was added to active manganese dioxide, 'type  $\text{MnO}_2(\text{B})$ '<sup>7</sup> (50 g.), which had been prepared by heating manganous carbonate at 250° in a stream of air, washing with 15% nitric acid, followed by water, and drying at 250°.

The reaction mixture was shaken for two days and then filtered. The manganese dioxide was washed with ether (5 x 50 ml.) and hot chloroform (5 x 50 ml.). The combined

extracts were dried over magnesium sulphate (50 g) and evaporated when white needles and a yellow oil were obtained. The white needles (.27g) were removed by filtration and washed with diethyl ether. The yellow oil and washings were distilled and gave N-methyl-o-amino-benzaldehyde (5.2g. 51%) as a yellow liquid b.p. 75-78°/1mm. (lit 77-78°/1mm<sup>8</sup> and 112°/10mm.<sup>9</sup>).

N.M.R. spectrum of CDCl<sub>3</sub> solution ( $\tau$ ); 0.21 (methine, singlet), 1.63 (NH, broad), 2.4-3.4 (aromatics, complex), 7.14 (methyl, doublet, J = 5.1 c.p.s).

I.R. spectrum as liquid film ( $\lambda_{\max}$ , cm<sup>-1</sup>): 3350(s) 3070(w), 3048(w), 2980(w), 2905(s), 2870(m), 2850(m), 2815(w), 2741(m), 1660(s), 1613(w), 1606(m), 1580(s).

Recrystallisation of the white crystals from iso-propyl ether containing a little chloroform gave white needles of an unknown substance, m.p. 195-196°.

Analysis found C, 75.18; H, 5.19; N, 9.29%

C<sub>9</sub>H<sub>8</sub>NO requires C, 73.95; H, 5.51; N, 9.58%

N.M.R. spectrum as CDCl<sub>3</sub> solution, ( $\tau$  values and ratio of integrated areas); 2.13(singlet, 1), 2.5-3.9 (complex, 8), 3.86(singlet, 1), 4.83(four lines, 2).

Mass spectrum (m/e), 237(10%), 236(68%), 235(100%) 218(3%), 207(17%), 206(15%), 205(9%). 180(7%), 179(24%), 178(5%), 153(3%), 152(7%), 151(4%), 132(4%), 131(6%),

130(3%), 129(5%), 117(4%), 11.6(6%), 105(4%), 104(9%),  
103(7%), 102(7%), 91(8%), 90(9%), 89(13%), 78(9%), 77(52%)  
76(19%), 75(8%).

I.R. spectrum as nujol mull ( $\lambda_{\max}, \text{cm}^{-1}$ ); 3020(w)  
1618(s), 1601(s), 1588(m), 1572(s), 1498(w), 1480(m) 1375.

(2) When the procedure above was repeated using manganese dioxide, 'type  $\text{MnO}_2(\text{A})$ '<sup>7</sup>, which had not been washed with acid a similar yield of N-methyl-o-amino-benzaldehyde (47%) and the unknown substance was obtained.

(3) A vigorously stirred solution of N-methyl-o-aminobenzylalcohol (10g. 73 mmole) in diethyl ether (250 ml.) was refluxed with manganese dioxide (type 'MnO<sub>2</sub> A') (50g.) for 6 hours and worked up as above.  
Yield 5.5g (56%)

#### N-methyl-o-aminobenzaldoxime.

N-methyl-o-aminobenzaldehyde (3.7g 27 mmole) was shaken with hydroxylamine hydrochloride (10 g.) and N. sodium hydroxide solution (30 ml.) for 6 hr. The resulting oil was extracted with chloroform (3 x 10 ml). The extract was dried over magnesium sulphate (10 g.) and evaporated to a pale yellow oil. Crystals of N-methyl-o-aminobenzaldoxime were obtained by sublimation at 160°/1mm. onto a cold finger. Recrystallisation from petrol gave white prisms of N-methyl-o-aminobenzaldoxime

(1.1g. 27%), m.p. 49-51° (lit 50-51°).<sup>10</sup>

N.M.R spectrum of  $\text{CDCl}_3$  solution ( $\tau$ ); -0.52 (methine, singlet), 2.4-3.5 (aromatics, complex), 5.32 (OH, broad), 7.12 (methyl, doublet  $J = 5.1$  c.p.s).

N-methyl-o-aminobenzald-N'-methylimine.

N-methyl-o-aminobenzaldehyde (1g. 74 mmole) was shaken with 30% aqueous methylamine (20 ml.) for 24 hours. The mixture was cautiously evaporated to about half volume under reduced pressure, and extracted with carbon tetrachloride (3 x 10 ml). The extract was dried over magnesium sulphate (5g.) and distilled. N-methyl-o-aminobenzald-N'-methylimine (.8g 72%) was obtained as bright yellow oil b.p. 60 - 62°/1mm.

N.M.R spectrum of  $\text{CDCl}_3$  solution ( $\tau$ ); 1.08 (NH, broad), 1.65 (methine, singlet), 2.5-3.6 (aromatics, complex), 6.58 (imine-methyl, singlet), 7.13 (amine-methyl, doublet  $J = 4.5$  c.p.s).

N,N'-bis-(N-methyl-o-aminobenzylidene)-1,2-diaminoethane.

N-methyl-o-aminobenzaldehyde (2.1g 15.0 mmole) in methanol (10 ml) was heated with 1,2-diamino-ethane (0.45g. 7.5 mmole) under reflux for 30 mins. On cooling the mixture set solid and was crystallised slowly from methanol containing a little chloroform, when white

crystals separated which were recrystallised from methanol to give N,N'-bis(N-methyl-o-aminobenzylidene)-1,2-diaminoethane (1.7g 77%) as colourless plates, m.p. 131-133°.

Analysis found C, 72.77; H, 7.53; N, 19.58%

C<sub>18</sub>H<sub>22</sub>N<sub>4</sub> requires C, 73.48; H, 7.53; N, 19.03%

N.M.R. spectrum of CDCl<sub>3</sub> solution ( $\tau$ ); 1.05 (NH, broad), 1.65 (methine, singlet), 2.5-3.6 (aromatics, complex), 6.18 (methylene, singlet), 7.19 (methyl, doublet, J = 5.4 c.p.s).

Mass spectrum (m/e); 294 (13%) (molecular ion), 177(6%), 175(6%), 161 (12%), 148(8%), 147 (30%), 146 (11%), 145 (8%), 140 (7%), 133 (23%), 132 (40%), 131 (20%), 120 (18%), 119 (15%), 118 (100%), 117 (33%), 106 (17%), 104 (12%), 91 (42%), 78 (9%), 77 (22%).

I.R. spectrum as KBr disc ( $\lambda_{\max}$ , cm<sup>-1</sup>); 3200(b), 3099(w), 3070(w), 2922(m), 2860(m), 2820(w), 1629(s), 1586(s), 1529(s), 1471(sh), 1466(s), 1440(m), 1408(s), 1388(m), 1288(s,b), 1241(w), 1222(m), 1170(m), 1116(w), 1078(w), 1052(w), 1022(m), 984 (m), 942(w), 896(m), 848(w), 789(m), 756(s).

N,N'-bis-(N-methyl-o-aminobenzylidene)-1,4-diaminobutane.

N-methyl-o-aminobenzaldehyde (2.95 g. 21.8 mmole) in methanol (30ml.) was heated with 1,4-diaminobutane (0.96g 11 mmole) for 3 hours. On cooling white crystals

separated which were recrystallised from methanol (30 ml.) to give N,N'-bis-(N-methyl-o-aminobenzylidene) - 1,4-diaminobutane as pale yellow prisms (1.91 g 54%), m.p. 94-96°.

N.M.R. spectrum as  $\text{CDCl}_3$  solution ( $\tau$ ); 1.20 (NH, broad), 1.80 (methine, singlet), 2.8-3.7 (aromatics, complex), 6.45 ( $\alpha$ -methylene, broad), 7.15 (methyl, doublet,  $J = 5.4$  c.p.s), 8.25 ( $\beta$ -methylene, broad).

Mass spectrum (m/e); 323 (8%), 322 (35%) (molecular ion), 308 (5%), 203 (8%), 189 (6%), 188 (30%), 187 (22%), 173 (15%), 160 (9%), 147 (8%), 146 (6%), 145 (23%), 135 (12%), 133 (22%), 132 (17%), 120 (33%), 119 (19%), 118 (100%), 117 (21%), 106 (16%), 104 (8%), 91 (31%), 77 (14%).

I.R. spectrum as nujol mull ( $\lambda_{\text{max}}$ ,  $\text{cm}^{-1}$ ); 3222(m,b) 3090(w), 3065(w), 1627(s), 1585(s), 1528(s), 1460(s), 1425(m), 1380(m), 1315(m), 1210(m,b), 1165(s), 1158(sh), 1111(m), 1063(m), 1049(m), 1034(w), 1009(m), 976(m), 875(m), 848(w), 750(s), 739(m), 660(m).

N,N'-bis-(N-methyl-o-aminobenzylidene)-1,10-diaminodecane.

To a solution of 1,10-diaminodecane (4.1 g 24.1 mmole) in methanol (50ml.) was added N-methyl-o-amino-benzaldehyde (6.5g. 48.2 mmole) and the mixture refluxed for 30 mins, when a pale yellow oil separated. Benzene (200 ml)

was added to the hot mixture. On cooling white crystals separated which were recrystallised from a 3:1 methanol, benzene mixture to give white prisms of N,N'-bis-(N-methyl-o-aminobenzylidene)-1,10-diaminododecane (5.1g 52%) m.p. 71-72°.

N.M.R. spectrum as CDCl<sub>3</sub> solution ( $\tau$ ); 0.85 (NH, broad), 1.54 (methine, singlet), 2.4-3.5 (aromatics, complex), 6.42 ( $\alpha$ -methylene, triplet, J=7 c.p.s), 7.05 (methyl, doublet, J= 5.3 c.p.s), 8.65 ( $\beta$ - $\epsilon$  - methylene, broad).

Mass spectrum (m/e); 407 (7%), 406 (24%) (molecular ion), 289 (13%), 278 (37%), 287 (31%), 272 (5%), 259 (2%), 245 (2%), 231 (2%), 229 (2%), 217 (2%), 203 (3%), 189 (2%), 175 (3%), 173 (4%), 161 (5%), 148 (7%), 147 (20%), 146 (7%), 145 (7%), 133 (35%), 132 (13%), 131 (12%), 120 (27%), 119 (25%), 118 (100%), 117 (30%), 106 (14%), 91(21%), 77 (7%).

I.R. spectrum as a nujol mull ( $\lambda_{\max}$ , cm<sup>-1</sup>), 3223 (m,b), 3150(w), 3099(w), 3060(w), 1625(s), 1585(s) 1530(s), 1520(sh), 1460(s), 1430(w), 1360(m), 1290(s) 1260(w), 1210 (m,b) 1173(s), 1155(m), 1110(m), 1080(w), 1072(w), 1052(m), 1041(w), 1009(w), 987(w), 970(m), 882(m), 850(w), 754(s), 732(m), 655(m).

2,3:10,11-Dibenzo-1,5,8,12-tetra-azadodecane.

(a) 2,3:10,11-Dibenzo-1,5,8,12-tetra-azadodecane-

4,9-dione. 1,2-Diaminoethane (7ml. 105 mmole) and methyl anthranilate (50 ml. 387 mmole) were refluxed together for three days. The mixture solidified on cooling, was washed onto a sinter with ethanol and then further washed with portions of ethanol. The white residue was recrystallized from a 1:1 mixture of methanol and chloroform (500ml) and gave 2,3:10,11-dibenzo-1,5,8,12-tetra-azadodecane-4,9-dione (8 g. 25%) as white plates m.p. 246-248°.

Analysis found C, 64.41; H, 6.25; N, 18.61%

$C_{16}H_{18}N_4O_2$  requires C, 64.41; H, 6.08; N, 18.78%

N.M.R. spectrum of dimethyl sulphoxide ( $d_6$ ) solution: 1.70 $\tau$  (NH, broad), 2.3-3.5 $\tau$  (aromatics, complex), 3.63 $\tau$  (NH<sub>2</sub>, broad), 6.53 $\tau$  (methylene, singlet).

Mass spectrum : m/e 298 (11%) (molecular ion), 162 (11%), 150 (12%), 136 (13%), 120 (100%), 96 (35%).

I.R. Spectrum as KBr disc :  $\lambda_{max}(cm^{-1})$   
3480(s), 3375(s), 3300(s,b), 1630(s,b), 1582(s), 1550(s), 1490(m), 1452(m), 1403(m), 1348(m), 1322(m), 1292(w), 1268(m), 1222(m), 1170(sh), 1151(m), 1021(w), 942(w), 893(m), 779(w), 755(m), 750(s), 690(m).

(b) Reduction of 2,3:10,11-dibenzo-1,5,8,12-tetra-azadodecane-4,9-dione. Lithium aluminium hydride (2.9g 77 mmole) was added to dry ether (700 ml) (which had been distilled from calcium hydride), contained in a



in a 2l 3-necked flask fitted with a sealed mechanical stirrer and a Soxhlet extractor and condenser. 2,3:10,11-Dibenzo-1,5,8,12-tetra-azadodecane-4,9-dione (3.7 g 12.4 mmole) was placed in a thimble in the Soxhlet extractor. The ether was refluxed gently in a heating mantle, and after 16 hrs. all the solid had been introduced into the flask (see p278 for safety precautions). Water (3ml) was added cautiously, followed by 15% sodium hydroxide solution (3ml) and a further 8.5 ml. water. The mixture was filtered, and the residue washed with ether. The combined filtrates were dried over solid magnesium sulphate and evaporated to a pale yellow oil, of 2,3:10,11-dibenzo-1,5,8,12-tetra-azadodecane (2.5 g 74%) which darkens on standing.

N.M.R. of  $\text{CDCl}_3$  solution ( $\tau$ ); 2.7-3.6 (aromatics, complex), 6.33 ('benzyl'-methylene, singlet), 6.72 (NH singlet), 6.3-7.0 (NH broad and complex), 7.37 (methylene, singlet). Addition of deuterium oxide causes collapse of signals at 6.72 and 6.3-7.0  $\tau$ .

2,3:10,11-Dibenzo-1,5,8,11-tetra-azadodecane tetrahydrochloride.

A solution of 2,3:10,11-dibenzo-1,5,8,11-tetra-azododecane in ether from the lithium aluminium hydride reduction was dried over magnesium sulphate. Dry

hydrogen chloride was passed through the solution and the precipitate collected and dried in a vacuum desiccator. The solid darkens on exposure to light.

I.R. spectrum as KBr disc ( $\lambda_{\max}, \text{cm}^{-1}$ ); 3400 (m,wb), 3080(w), 2940(m), 2900(w), 2700(m,v,b), 2580(m,vb) 2420(sh), 3200(M,vb), 1635(m,vb), 1549(s,b), 1499(s), 1455(m), 1339(m), 1325(sh), 1310(sh), 1235(w), 1205(w), 1138(m,b), 1127(m,b), 992(w), 968(m), 898(w), 830(w), 858(m), 799(sh), 781(m), 766(s), 755(s), 674(m).

#### 11.2 Compounds of chapter 4.

##### Diaquo-(N,N'-bis-(o-aminobenzyl)-1,2-diaminoethane)-nickel(II) perchlorate.

A solution of nickel(II) chloride (1.0g.) in water was added to N,N'-bis-(o-aminobenzyl)-1,2-diaminoethane in a stoppered flask. A little dilute sodium hydroxide solution was added until the mixture became cloudy. Two drops of 2N hydrochloric acid were added, followed by hydrated sodium perchlorate (0.8 g), and the mixture allowed to stand, when purple crystals slowly separated. After a week diaquo(N,N'-bis-(o-aminobenzyl)-1,2-diaminoethane)nickel(II) perchlorate was removed by filtration, washed with a little acetone and recrystallised from 5% aqueous acetone.

Analysis found C, 36.15; H, 5.24; N, 11.89%

$C_{16}H_{26}N_4O_{10}Cl_2Ni$  requires C, 34.07; H, 4.64; N, 9.93%.

Mass susceptibility (Gouy method, 18°) was  $5.50 \pm 0.24$  c.g.s. units.

Preparation of nickel(II) complexes of the acyclic 'model' ligands type [3.1] (page 31).

One example of each preparative method outlined on page 70 is given below. Table [4.2] (page F70 ) lists the methods and solvents for recrystallisation used for preparation of all the nickel(II) complexes of the acyclic 'model' ligands.

Method (1) (page 70 ). N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanonickel(II), [ Niamben].

To a vigorously stirred suspension of N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethane (1 g., 3.8 mmole) in a refluxing methanol (25 ml.) was added a solution of nickel(II) acetate (1 g., 4.0 mmole) in methanol (50 ml.) Red prisms separated, and the mixture bumped violently when the stirring rate was reduced. After refluxing the mixture for 30 min. Niamben was collected at a sinter, washed with a little methanol, and recrystallized from dimethylformamide containing a small quantity of water, to give red-brown plates (1.0 g 81%).

When this procedure was repeated using nickel(II) sulphate and nickel(II) nitrate instead of nickel(II) acetate the yield of Niamben was lower (72% and 68%).

Method (2) (page 70). N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanonickel(II), [Niamben]

To a vigorously stirred suspension of N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethane (1 g., 3.8 mmole) in refluxing methanol (20 ml.) was added a solution of nickel(II) acetate (1 g., 4.0 mmole) in methanol (50 ml.) Freshly prepared 1M. sodium methoxide solution (7.5 ml., 7.5 mmole), was added in portions. After the addition of sodium methoxide the mixture was cooled and Niamben collected at a sinter and recrystallised from dimethylformamide to give red-brown plates (1.1 g., 90%).

Method (3) (page 70). N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanonickel(II), [Niamben].

To a suspension of N,N'-bis(o-aminobenzylidene)-1,2-diaminoethane (0.5g., 1.9 mmole) in refluxing ethanol (20 ml.) was added nickel(II) sulphate (0.5 g. 1.9 mmole) in 10% ammonia solution (10 ml.) After 30 mins. the mixture was cooled, the red-brown precipitate collected at a sinter, washed with 10% ammonia solution, water, and ethanol, and recrystallized from dimethylformamide containing

a little water to give red-brown plates of Niamben (0.44 g., 71%).

Method (4) (page 70). N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato nickel(II), [Niamben].

A slow stream of hydrogen was passed through a stirred solution of N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane (page 267) (1.54 g., 4.7 mmole) and nickel(II) acetate (1.70 g. 6.8 mmole) in methanol (50 ml.) containing a suspension of 5% palladium charcoal (100 m.g.) An intensely red solution was produced after about 30 mins. which gradually faded to give a suspension of brown-red solid in a pale brown solution. After 24 hr. the mixture was filtered, and the product was extracted from palladium charcoal with hot dimethylformamide (3 x 10 ml.) precipitated by the addition of methanol, and recrystallized from dimethylformamide containing a little water to give Niamben as red-brown plates (0.97 g., 64%).

In another experiment the initial intense red solution was filtered from palladium charcoal catalyst and evaporated in an attempt to isolate a nickel complex of partially reduced N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane. Only deep red oils could be obtained from a wide selection of solvents and recrystallization techniques.

Repeating the procedure of method (4) in the absence of palladium charcoal catalyst gave no evidence for reduction after passing hydrogen for 48 hr. The *N,N'*-bis-(*o*-nitrobenzylidene)-1,2-diaminoethane was recovered (90%) by evaporation of the reaction mixture under reduced pressure, washing the residue with water, and recrystallizing from 95% ethanol.

A similar experiment with no palladium charcoal catalyst performed in the presence of Niamben (20 mg.) gave only starting materials after 48 hours; Niamben (11 mg.) on filtration, and *N,N*-bis-(*o*-nitrobenzylidene)-1,2-diaminoethane (88%) on working-up as above.

Method (5) (page 70). *N,N'*-bis-(*o*-aminobenzylidene)-1,2-diaminobenzeneatonicel(II), [Niambphen].

*o*-Aminobenzaldehyde (2.0 g., 16.5 mmole) and 1,2-diaminobenzene (1 g., 9.1 mmole) were heated in water (10 ml.) containing 2N. sodium hydroxide solution (1.5 ml) on a water bath for 1 hr. The resulting oil was dissolved in ethanol (80 ml.) and a suspension of nickel(II) acetate (2.5g., 10.0 mmole) in water (5ml.) added. After refluxing for 30 min. a dark green precipitate was removed by filtration, washed with aqueous ammonia and ethanol, and recrystallized from tetrahydrofuran to give fine blue-green needles of Niambphen (2.7g., 89%).

Method (6) (page 70). N,N'-bis-(o-aminobenzylidene)-1,4-diaminobutanatonickel(II), [Niambbuten].

Technical t-butanol was dried over calcium sulphate and then refluxed over sodium and distilled. An approximately tenth molar solution of potassium t-butoxide was prepared by dissolving potassium in the redistilled t-butanol maintained at 30° under an atmosphere of dry nitrogen.

Tetraethylammonium tetrabromonickelate(II) was prepared by the method of Gill and Nyholm<sup>11</sup> and recrystallized from 'superdry'<sup>12</sup> ethanol.

To a solution of N,N'-bis-(o-aminobenzylidene)-1,4-diaminobutane (0.61 g., 2.07 mmole) in redistilled tetrahydrofuran (see page 261) (10 ml.) was added .13M potassium t-butoxide (31.5 ml., 4.10 mmole) in tetrahydrofuran (40 ml.). The solution was stirred and tetraethylammonium tetrabromonickelate(II) (1.33g., 2.08 mmole) added. After 10 hr. the mixture was filtered and the filtrate evaporated under reduced pressure when a dark red powder was obtained which was crystallized from tetrahydrofuran by slow evaporation under a stream of dry nitrogen. Niambbuten was obtained as deep red-purple prisms (0.2g., 27%)

Table [11.1]. Infrared spectra of nickel(II) acyclic complexes [4.17], p 70.

(a)  $\lambda_{\max}(\text{cm}^{-1})$  (b) Recorded on a Perkin Elmer 621 spectrometer (c) Recorded on a Unicam 200 G. spectrometer (d) Hexachlorobutadiene (e) For abbreviations see section 10.3.

Niamben as nujol and HCB<sup>d</sup> mull<sup>s</sup><sup>b</sup>; 3313<sup>a</sup>(m)<sup>e</sup>, 3293 (m), 3060(w), 3047(w), 3032(w), 3018(w), 2948(m), 2915(w), 2855(w), 1617(s), 1593(m), 1537(s), 1478(w), 1459(s), 1452(sh), 1442(sh), 1403(sh), 1388(s), 1355(m), 1339(s), 1251(m), 1240(s), 1180(s), 1151(s), 1124(s), 1092(w), 1068(w), 1021(m), 984(w), 961(m), 936(w) 908(m), 840(m), 760(s), 737(s), 679(m), 640(w), 635(w), 600(w), 550(w), 530(w), 470(m), 460(w), 408(m).

Niambtn as nujol and HCB mull<sup>s</sup><sup>b</sup>; 3320(m), 3281(m), 3060(sh) 3042(w), 3030(sh), 2948(m), 2930(sh), 2860(w), 1620(s), 1590(m), 1548(s), 1538(m), 1466(s), 1451(s), 1440(m), 1405(s), 1379(w), 1368(w), 1349(m), 1290(m), 1251(s), 1191(m), 1153(s), 1130(s), 1108(w), 1080(s), 1022(m), 983(w), 965(w), 935(w), 916(w), 907(m), 847(m), 700(m), 786(w), 750(s), 741(s), 689(m), 632(w), 625(w), 604(m), 566(w), 551(m), 506(w), 492(w), 463(s), 415(w).

Niambbuten as nujol mull<sup>c</sup>; 3270(m), 3060(sh), 3040(sh), 1612(s), 1592(m), 1549(m), 1539(m), 1475(sh), 1465(s), 1385(w), 1347(s), 1330(m), 1254(w), 1250(m), 1200(m), 1192(m), 1152(s), 1124(s), 1104(w), 1072(w), 1026(m),



1009(m), 964(w), 939(w), 912(w), 888(w), 864(w), 848(m),  
785(sh), 755(s).

Niambphen as nujol mull<sup>c</sup>; 3329(w), 3308(w), 3060(sh),  
3008(sh), 1614(s), 1574(s), 1536(s), 1529(m), 1489(m),  
1460(s), 1415(m), 1284(w), 1268(m), 1210(sh), 1190(s),  
1163(w), 1158(s), 1130(m), 1052(w), 1021(m), 968(w),  
940(m), 924(w), 842(w), 831(w), 781(m), 749(s), 740(sh),  
701(w), 672(m).

Niambnaph as KBr disc<sup>c</sup>, 3306(sh), 3285(s), 3065(w), 3042(w)  
2940(w), 2866(w), 1617(s), 1592(m), 1538(s), 1483(w),  
1450(s), 1392(s), 1372(m), 1340(m), 1287(m), 1237(s),  
1183(s), 1155(s), 1119(s), 1020(m), 975(w), 958(m), 843(w),  
799(s), 783(m), 749(s), 712(w), 705(m), 679(m).

Niampen as nujol and HCB mulls<sup>b</sup>; 3350(m), 3070(w),  
3050(w), 3030(w), 2981(m), 2930(w), 2855(w), 1605(s),  
1560(s), 1519(s), 1495(w), 1488(m), 1460(s), 1446(s),  
1399(m), 1372(s), 1342(s), 1265(s), 1220(m), 1180(w),  
1170(m), 1159(m), 1151(m), 1115(m) 1089(m), 1076(m),  
1029(m), 1000(m), 939(w), 912(w), 850(w), 835(m), 788(m),  
778(m), 760(m), 742(m), 741(s), 701(m), 688(w), 649(s),  
641(s), 610(w), 579(w), 565(w), 533(w), 509(w), 446(m).

Niampbuten as nujol and HCB mulls<sup>b</sup>; 3335(m), 3332(m),  
3060(w), 3039(w), 3018(w), 2995(w), 2940(m), 2919(m),  
2860(w), 1604(s), 1557(s), 1510(s), 1489(w), 1480(m),  
1450(m), 1442(m), 1398(m), 1370(w), 1359(s), 1334(w),

1323(w), 1264(s), 1230(m), 1180(m), 1158(s), 1119(m),  
1111(m), 1102(w), 1095(w), 1072(w), 1038(w), 1029(w),  
1012(m), 1002(m), 968(w), 930(w), 915(w), 885(w), 860(w),  
840(w), 809(w), 776(m), 769(m), 752(m), 742(s), 724(m),  
710(m), 702(m), 691(w), 665(m), 648(w), 630(w), 580(w),  
561(m), 530(m).

NiMe-amben as nujol mull<sup>c</sup>; 3070(w), 3030(w), 2790(m),  
1615(s), 1600(sh), 1527(s), 1510(m), 1460(s), 1375(m),  
1358(m), 1348(s), 1330(m), 1260(w), 1231(m), 1211(s),  
1177(s), 1169(m), 1150(m), 1128(m), 1086(s), 1076(w),  
1050(m), 1041(m), 1035(w), 948(w), 941(m), 922(w) 915(w),  
892(m), 830(m), 758(s), 750(s), 732(s), 670(w).

### 11.3 Compounds of chapter 5.

Preparation of cobalt(II) complexes of acyclic model  
ligands type [3.1] (page 31).

One example of each preparative method outlined on page 108 is given below. The complexes of table [5.1] were all recrystallized from dimethylformamide. A hot dimethylformamide solution was filtered under nitrogen and its volume reduced under vacuum.

Method (1) (page 108) N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato cobalt(II), [Coamben]

A slow stream of nitrogen was passed through a vigorously stirred solution of N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethane (lg., 3.8 mmole) in refluxing methanol (25 ml.) and a deoxygenated solution of cobalt(II) acetate (lg., 4.0 mmole) in methanol (60 ml.) added from a tap funnel. After refluxing the mixture for 30 mins. the red-brown solid was collected at a sinter and recrystallized from dimethylformamide as described above when Coamben (.86g 70%) was obtained as large crimson plates.

The yield was improved to 95% by using the conditions described in method (2).

Method(2) (page 108) N,N'-bis-(o-aminobenzophenylidene)-1,2-diaminoethanato cobalt(II), [Coampen].

A slow stream of nitrogen was passed through a stirred solution of N,N'-bis-(o-aminobenzophenylidene)-1,2-diaminoethane (0.61 g., 1.46 mmole) in refluxing methanol (10 ml) and a solution of cobalt(II) acetate (0.36 g., 1.63 mmole) in deoxygenated methanol added from a tap funnel. Freshly prepared 1M. sodium methoxide solution (3.5ml., 3.5 mmole) was added in portions, and the mixture refluxed for 30 mins. A bright red solid

was collected after cooling, and when crystallized from dimethylformamide (see above) gave Coampen (0.53 g. 77%) as deep red prisms.

Method (3) (page 108) N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato cobalt(II), [Coamben].

A slow stream of nitrogen was passed through a vigorously stirred solution of cobalt(II) acetate (1.2 g., 4.9 mmole) and 1,2-diaminoethane (.34 ml., 5.0 mmole) in ethanol (30 ml). A solution of o-aminobenzaldehyde (1.17g. 9.7 mmole) in ethanol (20 ml.) was added and the mixture refluxed under nitrogen for one hour. The resulting amorphous brown solid was collected and recrystallized twice from dimethylformamide when Coamben (0.3 g. 19%) was obtained as deep red prisms.

Attempted preparation of N,N'-bis-(o-aminobenzylidene)-1,2-diaminobenzeneato cobalt(II) [Coambphen].

o-Aminobenzaldehyde (1.0 g., 8.2 mmole) was heated with 1,2-diaminobenzene (0.5 g., 4.6 mmole) in water containing 2N sodium hydroxide solution (1ml) on a water bath under a stream of nitrogen for 1 hr. Ethanol (20 ml.) was added followed by a solution of cobalt(II) acetate (1 g., 4.0 mmole) in water (5ml.) The mixture was refluxed for 2 hr. under nitrogen and filtered when a flocculent black precipitate was obtained. This solid

gave an infrared spectrum remarkably similar to Niambphen, but would not crystallize from chloroform, pyridine, dimethylformamide or tetrahydrofuran.

Addition of a methanolic solution of o-amino benzaldehyde to cobalt(II) acetate and 1,2-diaminobenzene in methanol and treating as above gave very similar results.

Method (4) page (108). N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanocobalt(II), [Coamben].

A slow stream of hydrogen was passed through a stirred solution of N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane (page 267) (1.0g. 3.0 mmole) and cobalt(II) acetate in methanol (50 ml.) containing a suspension of 5% palladium charcoal (220 mg.). An intense red solution was produced after about 30 min., which gradually faded to give a suspension of a brown-red solid in a pale brown solution. After 48 hr. the mixture was filtered, and the product was extracted from the palladium charcoal with hot dimethylformamide, precipitated by the addition of methanol, and recrystallized from dimethylformamide (see above), when Coamben was obtained as red prisms (.64 g., 68%).

A similar experiment with no palladium charcoal catalyst, performed in the presence of Coamben (20 mg)

gave only starting materials after 48 hrs; Coamben (12 mg) on filtration, and N,N'-bis-(o-nitrobenzylidene)-1,2-diaminoethane (75%) after evaporation of this filtrate, washing with water and recrystallizing from 95% ethanol.

Method (5) (page 108). Attempted preparation of N,N'-bis-(N-methyl-o-aminobenzylidene)-1,2-diaminoethanato-cobalt(II), [CoMe-amben].

Tetraethylammonium tetrabromocobaltate(II) was prepared by the method of Gill and Nyholm<sup>11</sup> and recrystallized from 'superdry'<sup>12</sup> ethanol.

To a solution of N,N'-bis(N-methyl-o-amino-benzylidene)-1,2-diaminoethane (0.46 g., 1.56 mmole) in tetrahydrofuran (100 ml.) was added 0.1M potassium t-butoxide (31 ml. 3.1 mmole). The solution was stirred and a slow stream of nitrogen passed, and tetraethylammonium tetrabromocobaltate(II) (1.0 g., 1.56 mmole) added. After stirring for 16 hr. at room temperature the mixture was filtered under nitrogen and evaporated under reduced pressure. A dark red solid mixed with some white powder was obtained.

Repeated attempts to recrystallize the red solid (which gave deep red solutions in tetrahydrofuran, chloroform and dimethylformamide) produced only red oils.

Table [11.2]. Infrared spectra of cobalt(II) acyclic complexes p 112.

(a)  $\lambda_{\max}$  ( $\text{cm}^{-1}$ ) (b) Recorded on a Perkin Elmer 621 spectrometer (c) Recorded on a Unicam 200 G spectrometer. (d) Hexachlorobutadiene (e) Abbreviations section 10.3.

Coamben as nujol and HCB<sup>d</sup> mulls<sup>b</sup>; 3253<sup>a</sup> (s,b)<sup>e</sup>, 3062(sh), 3043(m), 3023(w), 2934(m), 2912(m), 2843(m), 1607(s), 1582(sh), 1575(m), 1547(s), 1525(m), 1473(w), 1448(sh), 1442(s), 1430(sh), 1398(m), 1383(s), 1375(m), 1342(s), 1320(m), 1237(s), 1192(s), 1151(s), 1127(s), 1090(w), 1072(w), 1021(m), 983(w), 953(m), 925(m), 918(m), 842(s), 753(s), 743(s), 640(w), 633(w), 620(w), 602(w), 530(w), 471(m).

Coambtn as nujol mull<sup>c</sup>; 3280(m), 3065(sh), 3050(m), 1613(s), 1580(m), 1575(sh), 1550(m), 1539'sh), 1470(sh), 1405(s), 1380(s), 1371(sh), 1339(s), 1280(m), 1245(s), 1215(s), 1200(s), 1151(s), 1128(s), 1102(w), 1077(m), 1019(m), 958(m), 928(w), 903(m), 849(m), 756(s), 745(sh).

Coamaen as nujol mull<sup>c</sup>; 3265(m), 3080(w), 3030(sh), 1605(s), 1560(w), 1552(w), 1510(sh), 1502(m), 1460(sh), 1452(m), 1330(w), 1359(sh), 1350(s), 1275(m), 1255(s), 1220(s), 1166(s), 1150(s), 1108(w), 1068(w), 1059(w), 1019(m), 999(m), 849(m), 878(m), 850(s), 767(s), 746(s), 715(w).

Coampen as nujol mull<sup>c</sup>; 3323(m), 3313(m), 3070(m)

3040(sh), 1602(s), 1560(sh), 1555(m), 1505(m), 1591(m)  
1583(m), 1442(s), 1400(m), 1339(s), 1325(m), 1260(s),  
1228(m), 1170(m), 1159(s), 1153(sh), 1115(m), 1087(m),  
1073(m), 1028(s), 1004(m), 970(w), 910(w), 850(m), 840(m),  
788(m), 778(m), 765(m), 749(s), 730(w), 702(s), 685(m).

Coambphen (impure) as nujol mull<sup>c</sup>; 3232(m), 3222(m),  
3075(w), 3030(w), 1612(s), 1575(m), 1562(s), 1532(s),  
1485(m), 1460(s), 1445(s), 1425(s), 1373(s), 1333(s),  
1285(w), 1262(m), 1249(m), 1217(m), 1192(s), 1160(m), 1149(s)  
1131(w), 1050(m), 1021(m), 961(w), 939(m), 930(m), 910(w),  
845(m), 837(m), 810(w), 755(s), 744(sh), 690(w).

CoMe-amben (impure) as nujol mull<sup>c</sup>; 3050(w), 3020(w),  
2780(m), 1606(s), 1585(s), 1525(s), 1515(sh), 1460(s),  
1380(m), 1355(m), 1342(s), 1330(m), 1261(s), 1209(s),  
1172(s), 1165(sh), 1090(s), 1040(s), 978(m), 942(w),  
910(sh), 891(m), 830(sh), 810(s,b), 756(s), 733(m), 670(w).

Attempted oxidation of N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato-cobalt(II), c.f. ref. 13.

N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato-cobalt(II) (421 mg.) was suspended in 50% aqueous methanol (50 ml.) containing a few drops of dilute acetic acid. 3-Methylpyridine (1 ml.) was added followed by 20 vol. hydrogen peroxide (5 ml.) in portions. The



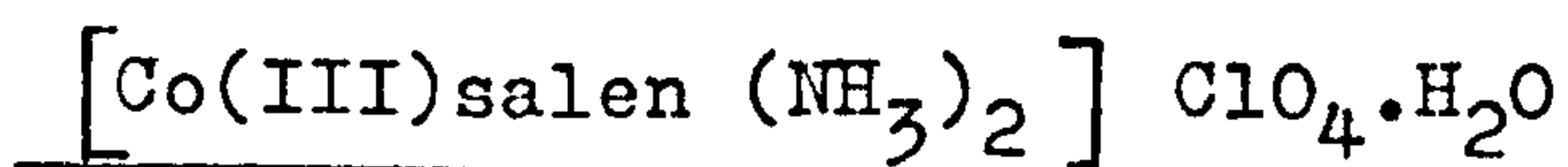
mixture was heated on a water bath for 1 hr. and the resulting amorphous black powder collected at a sinter. The filtrate precipitated an oil on evaporation of the methanol. The residue, after drying showed only a few broad peaks in the infrared region, and was sparingly soluble in pyridine, but insoluble in water and most organic solvents.

N,N'-bis(o-hydroxybenzylidene)-1,2-diaminoethanatocobalt(II)  
[Cosalen].

The following method gave consistently good yields of crystalline 'inactive' (see ref. 15) product.

To a vigorously stirred suspension of N,N'-bis(o-hydroxybenzylidene)-1,2-diaminoethane (10 g., 37 mmole) in methanol (200 ml.) refluxing under nitrogen was added a methanolic (400 ml.) solution of cobalt(II) acetate (9.29 g., 38 mmole), followed by N. sodium methoxide solution (75 ml.) After refluxing for 30 mins. the mixture was cooled, allowed to stand under nitrogen for 24 hr. and filtered, when N,N'-bis(o-hydroxybenzylidene)-1,2-diaminoethanatocobalt(II) was obtained as purple-red plates (8.1 g., 82%).

Diammino(N,N'-bis-(o-hydroxybenzylidene)-1,2-diamino-  
ethanato)cobalt(III) perchlorate monohydrate,



Equimolar quantities of pentamminocarbonatocobalt

(III) nitrate<sup>16</sup> and N,N'-bis-(o-hydroxybenzylidene)-1,2-diaminoethane were heated together in refluxing 50% aqueous methanol until no more ammonia was evolved, and all the material had passed into solution. On cooling orange needles of diammino(N,N'-bis-(o-hydroxybenzylidene)-1,2-diaminoethanato)cobalt(III) nitrate separated from solution.

Infrared spectrum as a nujol mull ( $\lambda_{\max}, \text{cm}^{-1}$ ); 3420(m,b), 3220(m,b), 3160(m,b) 3040(w), 3010(w), 1643(s), 1608(s), 1548(m), 1540(m), 1460(s), 1330(vb,NO<sub>3</sub><sup>-</sup>), 1380(sh), 1350(sh), 1330(sh), 1310(sh), 1290(s), 1235(w), 1205(s), 1154(s), 1131(s), 1087(m), 1057(m), 1038(m), 963(m), 905(s), 853(m), 830(m), 799(m), 765(sh), 746(s), 737(s), 665(w).

Addition of sodium perchlorate to the filtrate from above precipitated orange-yellow needles which were recrystallized from aqueous acetone and gave diammino-(N,N'-bis-(o-hydroxybenzylidene)-1,2-diaminoethanato)cobalt(III) perchlorate monohydrate as fine needles.

Analysis found C, 40.64; H, 4.74; N, 11.78%  
 $\text{C}_{16}\text{H}_{22}\text{N}_4\text{O}_7\text{CoCl}$  requires C, 40.33; H, 4.65; N, 11.76%

Reaction of pentamminocarbonatocobalt(III) nitrate with N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethane.

To a suspension of N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethane (0.25g. .93 mmole) in refluxing acetone

(15 ml.) was added a suspension of pentamminocarbonato-cobalt(III) nitrate (0.25g. .93 mmole) in water (10 ml). The mixture was refluxed for three hours, periodically changing the condenser and removing the sublimate of ammonium carbonate. The mixture was filtered hot and the red residue washed with water and a little methanol when N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato-cobalt(II), Coamben, was obtained (.113g 38%), identified by comparison of its infrared spectrum (nujol mull) and electronic spectrum (dimethylformamide solution) with an authentic sample.

To the filtrate which appeared to darken in air was added sodium perchlorate, when a dark brown solid was precipitated. Attempts to recrystallize this material were unsuccessful.

(N,N'-Bis-(o-hydroxybenzylidene)-1,2-diaminoethanato)methylcobalt(III), [CH<sub>3</sub>Cosalen].

Sodium sand was prepared by vigorously stirring a suspension of sodium in refluxing deoxygenated redistilled toluene, and stopping the stirrer 30 sec. after removing the source of the heat from the toluene. The toluene was removed by decantation and the sodium sand washed with redistilled tetrahydrofuran.

To approximately 1.5 g. of sodium sand was added

a suspension of N,N'-bis-(o-hydroxybenzylidene)-1,2-diaminoethanato-cobalt(III) (3.5g 10.8 mmole) in tetrahydrofuran (50 ml.) and the mixture stirred under nitrogen. After 1½ hours the mixture gave a deep green solution which was pushed through a glass-wool plug by an excess pressure of nitrogen into a flask containing iodomethane (0.7 ml., 11.4 mmole) in tetrahydrofuran (30 ml.) maintained at 0°C, when the solution immediately turned red-brown. Water (30 ml.) was added when a bright red solid was deposited which was recrystallized from a 4:6 chloroform-petrol (60 - 80°) mixture and gave aquo (N,N'-bis-(o-hydroxybenzylidene)-1,2-diaminoethanato)-methylcobalt(III),  $[\text{CH}_3\text{CoSalen}(\text{H}_2\text{O})]$  (1.66 g. 43%) as fine red needles.

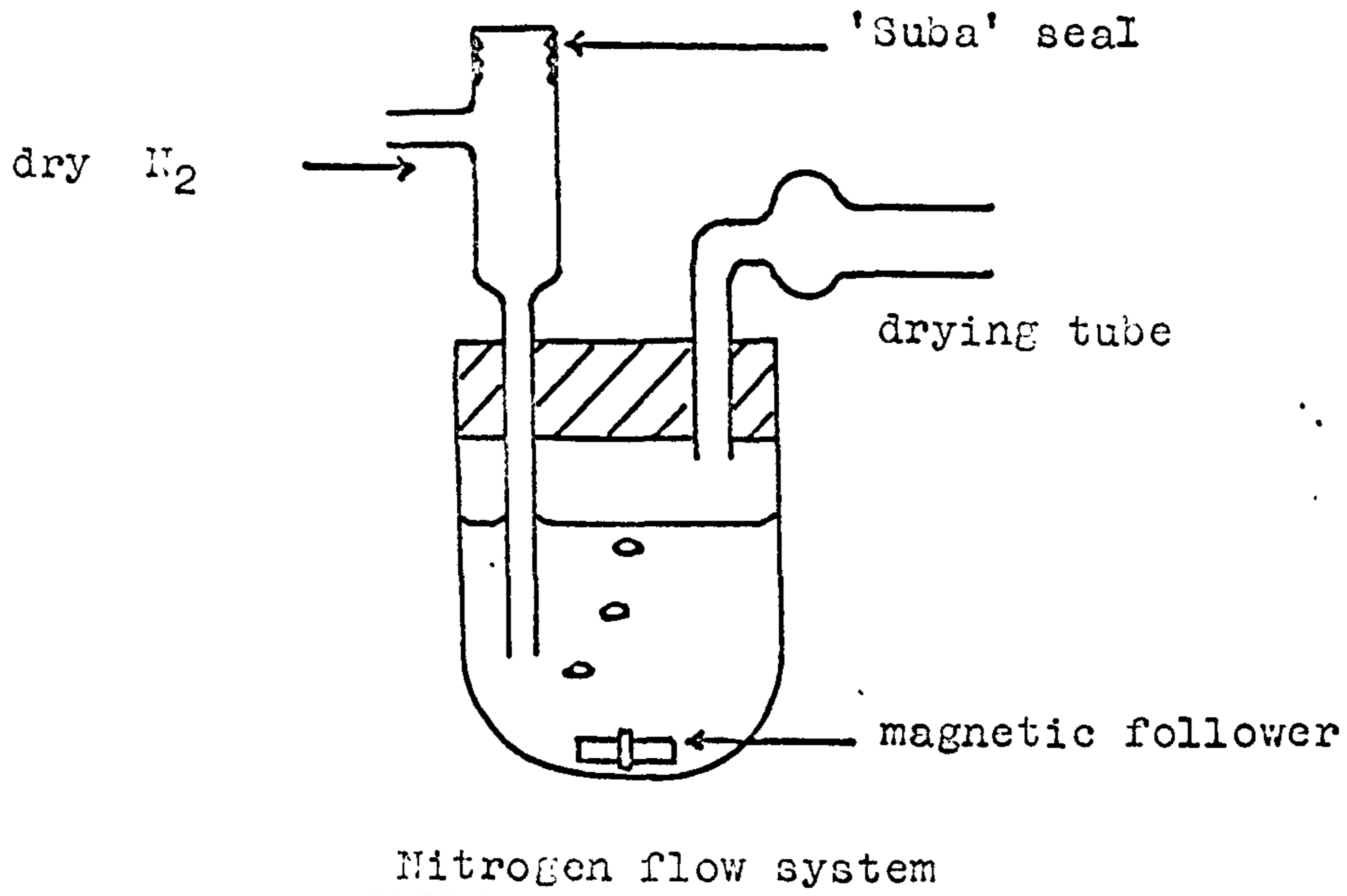
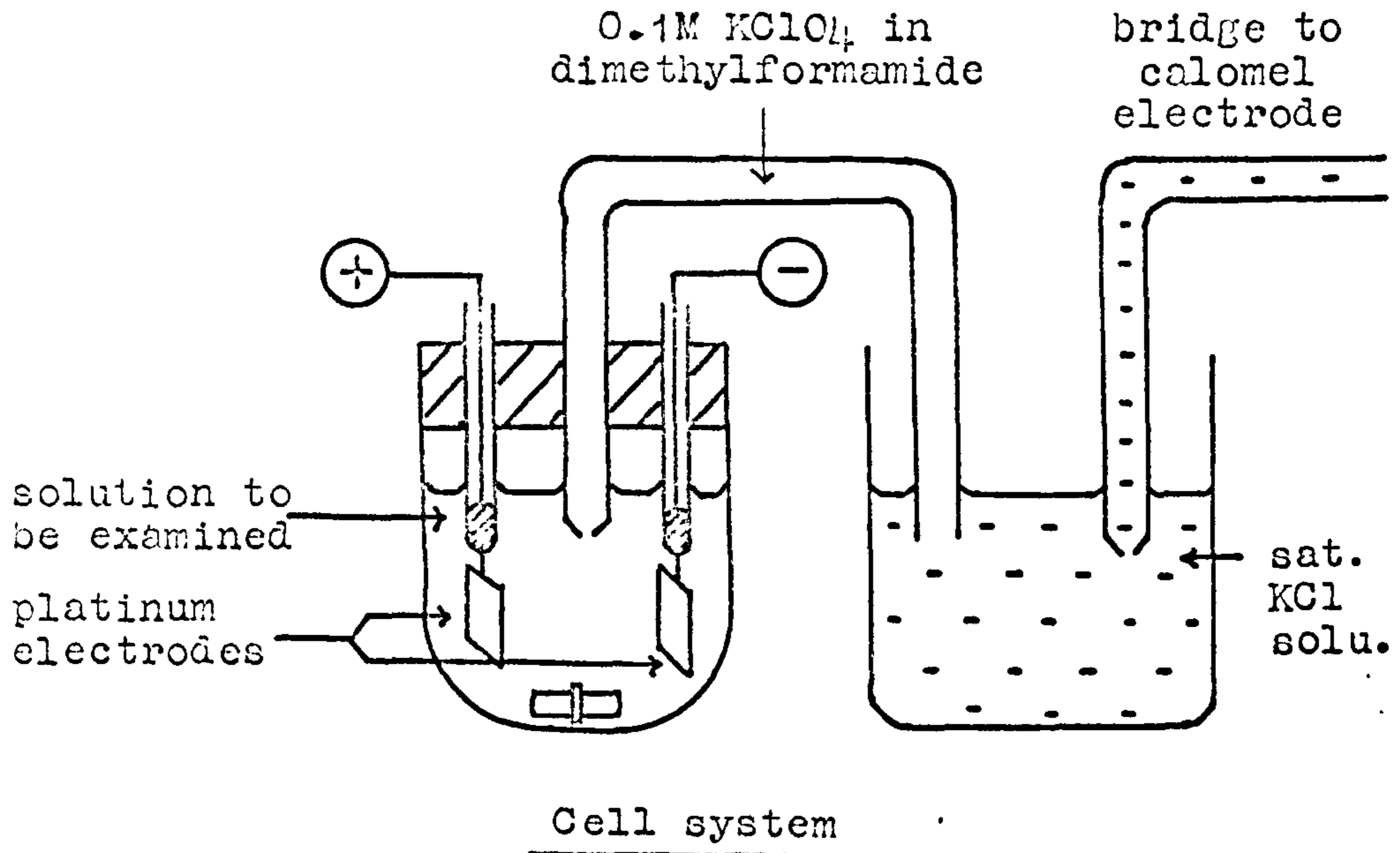
Dehydration of this compound in vacuo over  $\text{P}_2\text{O}_5$  gave green  $\text{CH}_3\text{CoSalen}$ .

The infrared and N.M.R. spectra supported the formulation for the compound, and corresponded closely to those published recently.<sup>14</sup>

Solutions of the aquo derivative in chloroform are deep green, but change to deep red on the addition of pyridine or aniline.

Reduction of N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato-cobalt(II) with sodium sand.

A deep green solution was produced when a



tetrahydrofuran solution of Coamben was treated with sodium sand in the same way as described above. A portion of this solution was added to ethanol. A gas was evolved and red plates of Coamben were deposited.

When the green solution was treated with iodomethane in the same way as described above a brown solution was produced, but no crystalline product could be isolated by treatment with water followed by attempts to recrystallize from various solvents. A pyridine solution of the brown solid obtained apparently had too much paramagnetic impurity to allow a N.M.R. spectrum to be obtained.

Similar results were obtained when a tetrahydrofuran solution of Coamben was stirred with 2% sodium amalgam under nitrogen.

Controlled potential reduction of N,N'-bis-(o-aminobenzylidene)-1,2-diaminoethanato-cobalt(II), [Coamben].

The cell is shown in [11.1]. Solutions were deoxygenated by passing a stream of nitrogen through the system (see lower diagram). The nitrogen lead was withdrawn until above the solution while measurements were taken. Samples were introduced by syringe through the 'suba' seal.

Redistilled dimethylformamide (see page 261) containing anhydrous potassium perchlorate (approx. 1M

solution was used as the solvent system and in the bridge to the saturated potassium chloride solution.

A potentiostat type TR40-3A, manufactured by the Chemical Electronics Co. Ltd., Newcastle, was used to provide a controlled potential (relative to the calomel electrode) to one of the platinum electrodes. The current flowing was recorded as the Y axis on a Bryans "XY Autoplotter" and plotted against the applied potential.

The solution was stirred to reduce polarization effects, but these presented a serious problem to reproducibility of scans in many cases. Substitution of rotating platinum electrodes or a dropping mercury electrode may alleviate this difficulty.

#### 11.4 Compounds of chapter 7.

##### N,N'-diphenylpiperazine.

Methyl anthranilate (117g. 0.77 mole) and 1,2-dibromoethane (28g. 0.15 mole) were heated gently on an isomantle, After a few minutes a violent reaction set in and large quantities of white fumes were produced. The flask was cooled, and heated very gently for a further 2 hr. when this vigorous reaction had subsided. On cooling the mixture solidified. Methanol (100 ml.) was

added and the solid washed onto a sinter. The white crystals were recrystallized from 10% aqueous ethanol and gave N,N'-diphenylpiperazine (12.03 g. 35%) as white plates m.p. 162-164° (lit. 163°).<sup>17</sup>

Analysis found C, 80.49; H, 7.43; N, 11.87%

C<sub>16</sub>H<sub>18</sub>N<sub>4</sub> requires C, 80.63; H, 7.61; N, 11.75%

N.M.R. spectrum of CDCl<sub>3</sub> solution ( $\tau$ );

2.50 - 3.42 (aromatics, complex), 6.71 (methylene, singlet).

Mass spectrum (m/e); 239(6%), 238 (35%)

(molecular ion), 196 (4%), 133 (9%), 132 (48%), 120 (4%), 119 (9%), 106 (12%), 105 (100%), 104 (38%), 78 (6%), 77 (44%).

N,N'-Bis-(o-carbo-methoxyphenyl)-1,2-diaminoethane.

Methyl anthranilate (292 g. 1.93 mole) was heated under gentle reflux with 1,2-dibromoethane (181g. 0.96 mole) in the presence of anhydrous sodium carbonate (250 g. 2.1 mole) for 2 days. The mixture was stirred constantly, and periodically the solid dislodged from the sides of the flask. On cooling the mixture set solid and was extracted with boiling chloroform (3 x 500 ml.). After filtering the extract was evaporated under reduced pressure to give a transparent oil which was recrystallized from a 5:1 petrol (80-100°): chloroform mixture. N,N'-bis-(o-carbo-



methoxyphenyl)-1,2-diaminoethane (105g. 34%) was obtained as large white needles, m.p. 118-120°.

Analysis found C, 65.72; H, 6.52; N, 8.68%  
 $C_{18}H_{20}N_2O_4$  requires C, 65.84; H, 6.14; N, 8.53%

N.M.R. spectrum of  $CDCl_3$  solution ( $\tau$ );  
 1.95-3.55 (aromatics, complex), 6.18 (methoxy, singlet),  
 6.50 (methylene, triplet).

Mass spectrum (m/e); 329 (4%), 328 (18%)  
 (molecular ion), 265 (5%), 166 (6%), 165 (56%), 164 (60%),  
 133 (11%), 132 (100%), 105 (7%), 77 (13%).

Infrared spectrum as KBr disc ( $\lambda_{max}$ ,  $cm^{-1}$ )  
 3345(m), 3030(w), 2990(w), 2945(m), 2935(m), 1670(s)  
 1497(m), 1572(s), 1510(s), 1498(sh), 1462(m), 1448(s),  
 1432(s).

#### 4,7-Diaza-2,3:8,9-dibenzodecane - 1,10 -diol

Lithium aluminium hydride (22.2 g 0.57 mole) was added to dry ether (1 l.) (which had been distilled from calcium hydride), contained in a 2 litre 3-necked flask fitted with sealed mechanical stirrer and Soxhlet extractor and condenser. N,N'-Bis-(o-carbomethoxy)-1,2-diaminoethane (73g. 0.22 mole) was introduced by packing into Soxhlet thimbles, which were extracted by the refluxing ether. (N.B. for safety precautions see page 278). After refluxing gently for 6 hr. all the

N,N'-bis-(o-carbomethoxy)<sup>phenyl</sup>-1,2-diaminoethane had been introduced into the flask. The excess lithium aluminium hydride was destroyed using the conditions which give a granular precipitate<sup>18</sup> (i.e. successive additions of water (22 ml.), 15% sodium hydroxide solution (22ml.) and water (67ml.) ). The mixture was filtered and the white solid extracted with boiling chloroform (4 x 500 ml.) The extracts and filtrate were combined, dried over magnesium sulphate and evaporated under reduced pressure to give a white solid which was recrystallized from a 50% chloroform-petrol (80-100°) mixture. Long white needles of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-diol (58 g. 95%) were obtained, m.p. 124-126°.

Analysis found C, 69.96; H, 6.96; N, 10.37%  
 $C_{16}H_{20}N_2O_2$  requires C, 70.56; H, 7.40; N, 10.28%

N.M.R. spectrum of  $CDCl_3$  solution ( $\tau$ ): 2.65-3.55 (aromatics, complex), 4.76 (NH or OH, broad), 5.46 ('benzyl' methylene, singlet), 6.57 ('anilino' methylene, broad).

Mass spectrum (m/e), 273 (3%), 272 (15%) (molecular ion), 138 (4%), 137 (45%), 136 (30%), 120 (3%), 119 (12%), 118 (100%), 117 (5%), 106 (6%), 91 (18%), 78 (3%), 77 (7%).

Infrared spectrum as nujol mull ( $\lambda_{max}$ ,  $cm^{-1}$ ); 3395(s), 3200(m,b), 1612(s), 1585(s), 1516(s), 1400(w).

4,7-Diaza-2,3:8,9-dibenzodecane-1,10-dione.

To a solution of 4,7-diaza-2,3:8,9-dibenzo-  
decane-1,10-diol (14 g. 52.5 mole) in diethyl ether (500 ml)  
was added active manganese dioxide 'type MnO<sub>2</sub> (B)'<sup>7</sup>  
(see page 279) (115 g.). The suspension was stirred  
vigorously and the ether gently refluxed for 6 hr. The  
manganese dioxide was removed by filtration and extracted  
with boiling chloroform (4 x 500 ml.). The filtrate and  
extracts deposited a yellow solid on evaporation under  
reduced pressure, which was dried in a dessicator and  
recrystallized from chloroform to give 4,7-diaza-2,3:8,9-  
dibenzodecane-1,10-dione (9.4 g. 67%) as large yellow  
plates m.p. 177-179°.

Analysis found           C, 71.74; H, 5.85; N, 10.19%

C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> requires   C, 71.62; H, 6.01; N, 10.44%

N.M.R. spectrum as a very dilute solution in  
CDCl<sub>3</sub> containing a little dimethyl sulphoxide (d<sub>6</sub>) (τ);  
0.02 (methine, singlet), 1.40 (NH, broad), 2.1-3.5  
(aromatics, complex), 6.34 ('anilino' methylene broad).

Mass spectrum (m/e), 269 (3%), 268 (17%)  
(molecular ion), 147 (3%), 136 (4%), 135 (37%), 134 (100%),  
118 (7%), 116 (7%), 107 (6%), 106 (23%), 91 (9%), 79 (8%),  
78 (6%), 77 (20%).

Infrared spectrum as nujol mull (λ<sub>max</sub>, cm<sup>-1</sup>);  
3335(m), 2755(m), 1660(s), 1610(m), 1572(s), 1528(m),  
1465(m), 1435(m).

The reaction of 1,2-diaminoethane and 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione.

To a stirred suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (200 mg. 0.75 mmole) in refluxing methanol (20 ml.) was added a solution of 1,2-diaminoethane (0.1 ml. 1.5 mmole) in methanol (10 ml.) The white solid was removed by filtration. The solid (0.24 g) was an amorphous powder (m.p. 280-288°) which showed a transition to a more crystalline form just below its melting point. An analysis sample was prepared by dissolving approximately 0.1 g in tetrahydrofuran, filtering and precipitating by reduction of volume under reduced pressure.

Analysis found C, 72.74; H, 6.74; N, 19.01%

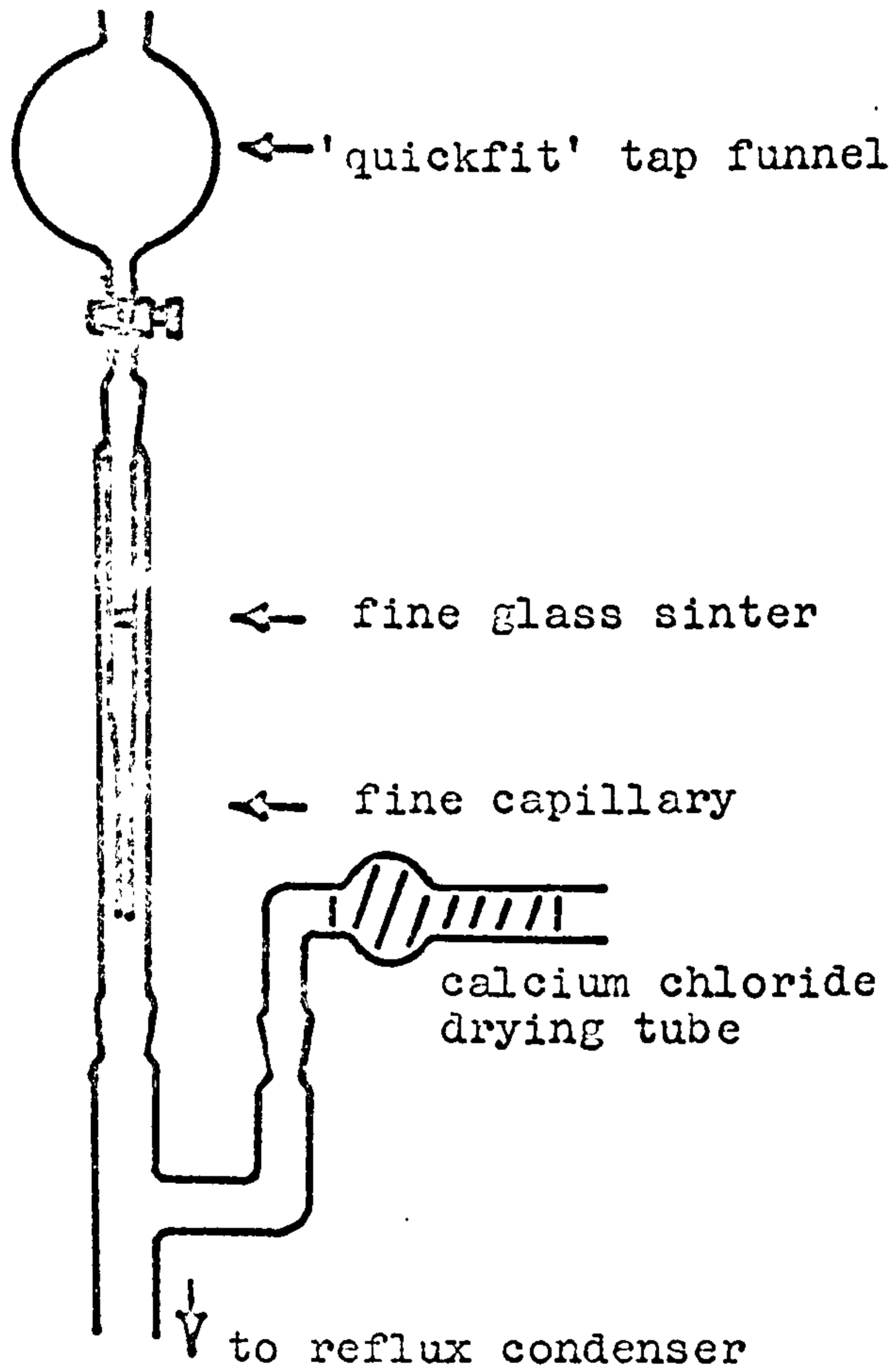
$C_{18}N_{20}N_4$  requires C, 73.94; H, 6.89; N, 19.16%

Infrared spectrum as nujol mull ( $\lambda_{max}$ ,  $cm^{-1}$ )  
3240 (m,b), 3090(w), 3060(w), 1634(s), 1604(w), 1580(s),  
1565(sh), 1512(s), 1465(s).

The same product was obtained from reaction of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (100 mg.) 0.37 mmole with a methanol (20 ml.) solution of 1,2-diaminoethane (0.05 ml. .75 mmole) after allowing to stand at room temperature for 4 weeks.

The reaction of unknown (above) with nickel(II) acetate.

To a stirred suspension of the unknown solid



(100 mg.) in refluxing methanol (20 ml.) was added a solution of nickel(II) acetate (150 mg.) in methanol (10 ml.). The mixture slowly turned red. After 7 days a red-brown amorphous solid and a white solid were detected in the reaction flask. After 10 days only the brown solid was obtained on filtration. After washing with a little water and methanol the dried solid showed the same infrared and electronic absorption spectra bands as an authentic sample of 3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-dieneatonicel(II) (page 322)

3,4:9,10-Dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-diene (cyen).

To a vigorously stirred solution of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (500 mg. 1.8 mmole) in refluxing methanol (1 l.) was added over a period of 8 hr. a solution of 1,2-diaminoethane (0.12 ml. 1.8 mmole) in methanol (250 ml.) using the apparatus shown in [11.2] to maintain a steady slow rate of addition.

After refluxing for 36 hr. the mixture was cooled and the volume reduced to 150 ml. by evaporation under reduced pressure at approximately  $10^{\circ}$ , when a white solid, m.p.  $155-174^{\circ}$ , was obtained. This solid was extracted with a small volume of tetrahydrofuran, and evaporation gave impure prisms of 3,4:9,10-dibenzo-1,5,

8,12-tetra-azacyclotetradecane-1,11-diene (270 mg. 51%)

m.p. 172-176°. Recrystallization from chloroform improved the melting point (175-177°) giving pale pink crystals.

Analysis found C, 73.12; H, 7.12; N, 19.53%

$C_{18}H_{20}N_4$  requires C, 73.94; H, 6.89; N, 19.16%

N.M.R. spectrum as  $CDCl_3$  solution ( $\tau$ );

-0.38 (NH, broad), 1.54(methine, singlet), 2.6-3.5(aromatics, complex), 6.17 ('imino' methylene, singlet), 6.45 ('anilino' methylene, broad).

Mass spectrum (m/e); 293 (7%), 292 (31%)

(molecular ion), 232 (8%), 176 (23%), 175 (12%), 174 (14%), 161 (4%), 160 (12%), 159 (6%), 146 (22%), 145 (31%), 133 (26%), 132 (61%), 131 (100%), 130 (21%), 119 (14%), 118 (130%), 117 (47%), 106 (12%), 104 (30%), 91 (37%), 90 (13%), 78 (16%), 77 (32%).

Infrared spectrum as nujol mull ( $\lambda_{max}$ ,  $cm^{-1}$ );

3230 (w,b), 1638(s), 1606(s), 1580(sh), 1520(m), 1502(w), 1460(s), 1332(m,b), 1272(w), 1263(m), 1225(sh), 1205(s), 1165(m), 1158(m), 1139(m), 1092(w), 1052(w), 1043(w), 1035(m), 979(w), 968(w), 919(m), 878(w), 850(w), 795(w), 756(sh), 748(s), 700(m,b).

The reaction of 1,2-diaminoethane and 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione in the presence of zinc(II) acetate

To a stirred suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (450mg. 1.7 mole) in refluxing

Metal ion added (mg.)	Mg <sup>2+</sup> (409)	Mn <sup>2+</sup> (502)	Fe <sup>2+</sup> (240)	Fe <sup>2+</sup> (900)	Cd <sup>2+</sup> (410)	Ag <sup>2+</sup> (490)
	a	a	b	c	a	a
Volume of methanol (ml.)	30	25	20	50	30	30
Dialdehyde taken (mg.)	428	512	310	552	400	410
1,2-diaminoethane taken (ml.)	.24	.25	.15	.25	.2	.2
Product m.p.	289- 293°	287- 292°	170- 175°	170- 180°	170- 175°	288- 292°

Table [11.4]. Quantities taken in reactions of 1,2-diaminoethane with the dialdehyde in the presence of metal ions.

(a) As the hydrated metal acetate. (b) As the hydrated oxalate (c) As ferrous ammonium sulphate - some sodium acetate also added



methanol 80 ml. containing zinc(II) acetate (500 mg. 2.3 mole), was added a solution of 1,2-diaminoethane (0.2 ml. 3.0 mole). After refluxing for a short time the mixture was allowed to stand for several days. The solid was removed and extracted with hot chloroform (most dissolves). The extract was dried over magnesium sulphate and evaporated under reduced pressure when 3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-diene (282 mg. 58%) was obtained as pale pink crystals, m.p. 175-177°. Recrystallization for chloroform produced no increase in m.p. Mixed melting point with sample from the 'high dilution' preparation, 174-177°.

The residue from the extraction (50 mg.), m.p. 270-280° had an identical infrared spectrum to the unknown compound (page 313).

The reaction of 1,2-diaminoethane and 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione in the presence of other metal ions.

The same general method was used in each case. The quantities of compounds taken are shown in table [11.4] To a stirred suspension of 4,7-diaza-2,3:8,9-dibenzo-decane 1,10-dione in methanol containing the metal salt was added a methanolic solution of 1,2-diaminoethane. The mixture was refluxed under nitrogen for six hours. The resulting solid was collected by filtration, washed with a little

methanol, followed by water and finally another small quantity of methanol. The solid was dried and its infrared spectrum and melting point recorded.

Approximately 50 mg. of the solid was extracted with hot chloroform (2 ml.) and one drop of the solution spotted onto a thin layer ( $300\mu$ ) of silica gel (containing calcium sulphate as a binder-Merck) on a glass plate.<sup>19</sup> The cyclic ligand cyen was eluted with a mixture of (60-80°)petrol (30%) in chloroform. The chromatograms were compared, on the same plate, with extracts obtained in a similar manner from the unknown material, m.p. 283-289°, from the reaction in the absence of metal ions (page 313) and the residue from the reaction in the presence of zinc(II) ions (page 316), and also with a dilute solution of the free cyclic ligand cyen (0.55 mg./ml). The  $R_f$  value for cyen under these conditions was 24%. The position of bands on the plates were ascertained by examination under ultraviolet light.

3,4:9,10-Dibenzo-1,5,8,12-tetra-azacyclopentadecane-1,11-diene (cytn)

To a suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (200 mg. 0.75 mmole) in methanol (20 ml.) was added a solution of 1,3-diaminopropane (0.13 ml. 1.6 mmole) in methanol (10 ml.) The mixture was maintained at approximately 60° for 6 hours in a stoppered flask. The long white needles were recrystallized from a mixture

methanol (50%) and dichloromethane to give 3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclopentadecane-1,11-diene (150 mg. 65%) as white needles, m.p. 187-188°.

Analysis found C, 73.91; H, 7.21; N, 18.98%

C<sub>19</sub>H<sub>22</sub>N<sub>4</sub> requires C, 74.47; H, 7.24; N, 18.29%

N.M.R. spectrum as a CDCl<sub>3</sub> solution ( $\tau$ ); 0.45 (NH, broad), 1.80 (methine, singlet), 2.7-3.6 (aromatics, complex), 6.30 ('imino' ( $\alpha$ ) methylene, triplet, J=5 c.p.s.), 6.51 ('anilino' methylene, complex), 7.99 ('imino' ( $\beta$ ) methylene, quintet, J=5 c.p.s.).

Mass spectrum (m/e); 307 (14%), 306 (60%) (molecular ion), 196 (24%), 190 (29%), 189 (32%), 188 (29%), 174 (10%), 173 (13%), 159 (18%), 155 (10%), 154 (79%), 149 (13%), 147 (18%), 146 (34%), 145 (34%), 139 (84%), 133 (18%), 132 (18%), 131 (37%), 119 (15%), 118 (100%), 117 (37%), 111 (24%), 91 (31%), 83 (18%), 77 (26%).

Infrared spectrum as nujol mull ( $\lambda_{\max}$  cm<sup>-1</sup>); 3220 (m,b), 3080(m), 3020(w), 1632(s), 1598(s), 1578(sh), 1532(m,b), 1460(s), 1380(s), 1352(m), 1342(s), 1330(m), 1282(w), 1270(w), 1252(w), 1210(s), 1169(m), 1139(m), 1112(m), 1085(w), 1168(s), 1144(m), 976(w), 968(w), 930(m), 920(m), 898(w), 875(m), 831(m), 750(s), 744(s), 734(w), 698(s).

3,4:9,10-Dibenzo-1,5,8,12-tetra-azacyclohexadecane-1,11-diene (cybuten)

To a suspension of 4,7-diaza-2,3:8,9-dibenzo-

decane-1,10-dione (200 mg. 0.75 mmole) in methanol (20 ml.) was added a solution of 1,4-diaminobutane (0.15 ml. 1.5 mmole) in methanol (5 ml.). The mixture was maintained at approximately 60° for 6 hours in a stoppered flask.

3,4:9,10 Dibenzo-1,5,8,12-tetra-azacyclohexadecane-1,11-diene (130 mg. 55%) was collected at a sinter and recrystallized from methanol containing a little dichloromethane to give long white needles m.p. 149-151°.

Analysis found C, 74.88; H, 7.60, N, 17.35%

C<sub>20</sub>H<sub>24</sub>N<sub>4</sub> requires C, 74.96; H, 7.55; N, 17.48%

N.M.R. spectrum as CCl<sub>4</sub> solution ( $\tau$ ); 0.68 (NH, broad), 1.81 (methine, singlet), 2.8-3.7 (aromatics, complex), 6.50 ('imino' and 'anilino' methylene, broad), 8.27 ('imino' ( $\beta$ ) methylene, broad).

Mass spectrum (m/e); 321 (12%), 320 (55%) (molecular ion), 204 (10%), 203 (22%), 204 (32%), 187 (15%), 185 (14%), 160 (14%), 159 (8%), 146 (9%), 145 (20%), 133 (35%), 132 (28%), 131 (62%), 130 (17%), 119 (17%), 118 (100%), 117 (45%), 106 (17%), 105 (17%), 104 (16%), 91 (32%), 77 (25%).

Infrared spectrum as a nujol mull ( $\lambda_{\max} \text{cm}^{-1}$ ); 3201(m), 3150(sh), 3080(sh), 3010(sh), 1630(s), 1604(sh), 1592(s), 1584(sh), 1570(sh), 1520(s), 1514(sh), 1460(s), 1381(s), 1332(s), 1283(m), 1252(w), 1210(m), 1198(m), 1160(s), 1130(w), 1111(w), 1086(m), 1078(m), 1048(m), 999(m), 983(m), 972(m), 927(w), 919(w), 837(w), 747(s), 735(m).

The reaction of 1,2-diaminobenzene and 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione.

A slow stream of nitrogen was passed through a refluxing methanolic (20 ml.) suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (300 mg. 1.1 mmole) contained in a three necked 100 ml. flask. A deoxygenated solution of 1,2-diaminobenzene (121 mg. 1.1 mmole) in methanol (10 ml.) was added, and the mixture allowed to reflux for 6 days, periodically adding methanol to replace that swept out of the condenser by the stream of nitrogen.

The solid in the flask was sampled daily by removing a small amount of the suspension with a dropping pipette, filtering, and washing the residue with a small amount of methanol. The infrared spectrum of this solid as a nujol mull showed only bands of the starting material after reaction for six days.

It was found in repeat experiments that if glassware was used which had not been carefully cleaned, some reaction of the dialdehyde was observed, giving the product described in the following section.

1,5,8,12-tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-diene, (cyphen).

To the reaction mixture above was added a solution of zinc(II) acetate (0.5 g. mmole) in methanol

(20 ml.). After refluxing for 6 hr. the mixture was sampled (as above) and found to contain no solid dialdehyde. The solid material showed a different infrared spectrum, and in particular an absence of absorptions at 3335 and 1660  $\text{cm}^{-1}$  characteristic of the dialdehyde. 1,5,8,12-Tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-diene (307 mg. 81%) was removed by filtration, and recrystallized from iso-propyl ether when fine yellow needles, m.p. 175-176° were obtained.

Analysis found C, 76.99; H, 5.78; N, 15.99%

$\text{C}_{22}\text{H}_{20}\text{N}_4$  requires C, 77.62; H, 5.92; N, 16.46%

N.M.R. spectrum of dimethyl sulphoxide ( $\text{d}_6$ ) solution ( $\tau$ ); -0.32 (NH, broad), 1.16 (methine, singlet), 2.3-3.6 (aromatics, complex), 6.42 ('anilino' methylene, complex).

Infrared spectrum as a nujol mull ( $\lambda_{\text{max}} \text{cm}^{-1}$ ); 3160(m,b), 3080(sh), 3060(sh), 3020(sh), 1615(s), 1597(m), 1585(m), 1573(m), 1563(m), 1520(s), 1502(w), 1483(s), 1462(s), 1378(s), 1338(s), 1325(m), 1275(w), 1235(w), 1225(w), 1186(s), 1168(s), 1159(sh), 1149(m), 1104(w), 1095(w), 1082(w), 1043(m), 978(m), 972(sh), 938(m), 925(m), 891(m), 883(m), 858(w), 850(w), 830(m), 755(sh), 742(s), 710(s).

The reaction of 1,2-diaminobenzene and 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione in the presence of acid catalysts.

The reaction was carried out as described above

except that small quantities of acid catalysts were added instead of a methanolic solution of zinc(II) acetate.

Pyridinium perchlorate was prepared by slow addition of 60% perchloric acid to a solution of pyridine in 95% ethanol. When no more white crystals were deposited they were removed at a sinter, washed with a little ethanol and dried in a dessiccator.

About 100 mg. portions of the catalyst was added in each case. The reactions were sampled as described above. Results are given in chapter 7.

#### 11.5 Compounds of chapter 8.

##### 3,4:9,10-Dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-dieneatonickel(II), [Nicyen].

To a stirred suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (0.73 g., 2.7 mmole) in refluxing methanol (20 ml.) was added nickel(II) acetate (0.68 g., 2.7 mmole), followed by 1,2-diaminoethane (0.36 ml., 5.5 mmole) in methanol (10 ml.) After six hours the mixture was filtered, and the infrared spectrum of the fine purple-red needles showed the absence of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione. Recrystallization of this product from a mixture (3:1) of benzene and petrol (80-100°) (c.a. 150 ml.) gave 3,4:9,10-dibenzo-1,5,8,12-tetra-aza-

cyclotetradecane-1,11-dieneatonickel(II) (.41 g. 45%)  
as fine purple needles.

N.M.R. spectrum as  $\text{CDCl}_3$  solution ( $\tau$ ); 2.40 (methine, singlet), 2.8-3.9 (aromatics, complex), 6.56 ('imino' methylene, singlet), 6.69 ('anilino' methylene, singlet).

Other compounds type [8.1] page 189.

The same procedure as above gave similar yields of Nicytn, Nicybuten, Cucyten and Cucytn (for abbreviations see page F189.)

N.M.R. spectrum of Nicytn as  $\text{CDCl}_3$  solution ( $\tau$ ); 2.65 (methine, singlet), 2.8-3.9 (aromatics, complex), 6.38 ('imino' ( $\alpha$ ) methylene, triplet,  $J = 7$  c.p.s), 6.84 ('anilino' methylene, singlet), 8.08 ('imino' ( $\beta$ ) methylene, quintet,  $J = 7$  c.p.s).

N.M.R. spectrum of Nicybuten as  $\text{CDCl}_3$  solution ( $\tau$ ); 2.66 (methine, singlet), 2.8-3.8 (aromatics, complex) 6.38 ('imino' ( $\alpha$ ) methylene, broad), 6.90 ('anilino' methylene, singlet), 8.30 ('imino' ( $\beta$ ) methylene, broad).

1,5,8,12-Tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-dieneatonickel(II), [Nicyphen].

To a stirred suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (0.53 g., 2.0 mmole) in a methanol (50 ml.) solution of nickel(II) acetate (0.52 g, 2.1 mmole) refluxing under nitrogen, was added a solution of 1,2-diaminobenzene (0.64 g., 5.9 mmole) in methanol (10 ml.).



After refluxing for 6 hr. the almost black mixture was sampled, and the solid found, from its infrared spectrum, to contain some of the starting dialdehyde. After 24 hr. no dialdehyde could be detected, and the mixture was filtered, and the mass of dark needles recrystallized from benzene by slow evaporation of the solution (c.a. 100 ml.) under a stream of nitrogen, when Nicyphen (0.46g., 58%), was obtained as deep blue-green fine needles.

Table [11.3]. Infrared spectra of the cyclic complexes of nickel(II) and copper(II), (chapter (8)).

(a)  $\lambda_{\max}$  (cm<sup>-1</sup>) recorded on a Unicam 200 G spectrometer.

(b) abbreviations section 10.3 (c) Hexachlorobutadiene.

Nicyen as nujol and HCB<sup>c</sup> mulls; 3075<sup>a</sup>(w)<sup>b</sup>, 3055(w), 3020(w), 3005(w), 2945(sh), 2935(w), 2917(w), 2895(m), 2865(sh), 2855(m), 2832(sh), 1613(s), 1603(sh), 1564(m), 1555(sh), 1525(s), 1518(s), 1482(s), 1455(s), 1442(s), 1391(m), 1364(m), 1358(m), 1350(m), 1344(m), 1270(w), 1235(w), 1218(s), 1203(s), 1174(m), 1169(m), 1140(w), 1135(w), 1112(w), 1084(w), 1037(m), 992(w), 982(w), 949(w), 860(w), 820(w), 746(s), 735(m), 726(m), 665(w).

Nicytn as a nujol mull; 3065(w), 3050(w), 3045(w), 3015(w), 2820(m), 2815(m), 1614(s), 1540(sh), 1529(s), 1520(sh), 1470(s), 1391(m), 1376(s), 1370(sh), 1358(s), 1348(m), 1268(w), 1226(m), 1218(m), 1210(s), 1172(m), 1143(m), 1136(m), 1111(m), 1102(w), 1072(m), 1035(m), 1002(w),

995(w), 946(m), 919(w), 863(m), 832(w), 745(s), 733(s).

Nicybuten as a nujol mull; 3060(w), 3045(w), 3040(w), 1608(s), 1584(m), 1528(s), 1520(sh), 1515(sh), 1470(s), 1461(sh), 1435(sh), 1395(w), 1385(sh), 1375(m), 1349(m), 1324(m), 1306(w), 1265(m), 1240(w), 1222(m), 1212(m), 1190(m), 1177(w), 1160(w), 1139(w), 1110(sh), 1098(m), 1085(m), 1060(sh), 1038(s), 1020(sh), 999(w), 989(w), 953(w), 876(w), 806(w,b), 758(s), 745(sh), 740(s), 732(s), 706(w), 670(w).

Nicyphen as nujol mull; 3082(w), 3062(w), 3050(w), 3042(w), 3012(w), 2962(sh), 2945(sh), 2922(m), 2885(m), 2845(m), 2815(sh), 1609(s), 1571(s), 1534(sh), 1514(s), 1510(s), 1470(s), 1452(s), 1442(m), 1430(s), 1390(s), 1371(s), 1355(s), 1348(sh), 1330(sh), 1267(m), 1242(w), 1194(s), 1177(m), 1143(m), 1124(w), 1110(w), 1045(sh), 1032(m), 940(m), 932(m), 922(w), 822(w), 815 (w), 742(s), 737(s), 729(m), 722(sh).

Ni(II) complex from  $\text{NH}_2(\text{CH}_2)_{10}\text{NH}_2$  and the dialdehyde, as nujol mull ( $< 2000 \text{ cm}^{-1}$ ); 1622(s), 1604(sh), 1582(s), 1580(s), 1570(s), 1535(s), 1532(m), 1517(m), 1505(sh), 1480(sh), 1460(s), 1452(s), 1433(sh), 1398(sh), 1388(sh), 1367(s), 1350(sh), 1260(w), 1235(s), 1205(sh), 1175( ), 1143(m), 1072(w), 1055(w), 1051(w), 1025(m), 1006(sh), 970(sh), 955(m,b), 905(m), 873(m), 822(w), 803(w). 744(s), 729(s), 679(m).

Cucyen as nujol and HCB mulls; 3076(w), 3055(w), 3020(w), 3010(w), 2943(w), 2920(w) 2899(m), 2864(m), 2850(m), 2822(m), 2790(m), 1614(s), 1598(sh), 1565(m), 1555(sh), 1525(s), 1518(s), 1479(s), 1456(s), 1545(s), 1440(s), 1430(sh), 1400(w), 1389(s), 1373(w), 1362(m), 1351(m), 1341(w), 1265(w), 1260(w), 1238(w), 1210(sh), 1199(s), 1169(s), 1140(s), 1087(m), 1067(m), 1040(m), 968(w), 960(m), 943(m), 934(w), 904(w), 895(w), 868(m), 834(w), 824(w), 793(w), 751(s), 743(s), 733(m), 728(s).

Cucytn as a nujol mull; 3062(w), 3040(w), 3020(w), 2815(m), 1612(s), 1590(sh), 1540(sh), 1531(m), 1476(s), 1465(s), 1445(sh), 1435(sh), 1399(w), 1390(sh), 1375(s), 1365(sh), 1350(sh), 1260(w), 1210(s,b), 1170(m), 1140(s), 1105(m), 1078(w) 1044(m), 1036(m), 965(sh), 960(m), 945(w), 913(w), 883(sh), 870(m), 835(w), 825(w), 793(w), 745(s), 729(s),

1,5,8,12-Tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-dienenickel(II) perchlorate, [Nicyphen H<sub>2</sub>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>.

To a stirred suspension of Nicyphen (0.1 g 0.25 mmole) in tetrahydrofuran (5 ml.) was added 70% perchloric acid (0.2 ml.) with caution. A bright orange precipitate was produced. The mixture was stirred for one hour. Addition of a further drop of perchloric acid caused no change. The orange precipitate of [Nicyphen H<sub>2</sub>]<sup>2+</sup>(ClO<sub>4</sub><sup>-</sup>)<sub>2</sub>

was collected at a sinter, washed with a little dry tetrahydrofuran and dried under vacuum (0.114 g. 76%).

Analysis found C, 43.91; H, 3.69; N, 9.31%  
 $C_{22}H_{20}N_4NiCl_2O_8$  requires C, 44.18; H, 3.37; N, 9.37%

Infrared spectrum as KBr disc ( $\lambda_{max}$   $cm^{-1}$ );  
 3140(m,b), 1624(s), 1595(s), 1570(sh), 1520(w), 1485(m),  
 1462(w), 1445(w), 1417(w), 1395(m), 1321(s), 1259(s),  
 1205(m), 1160(sh), 1100 (vs,b), 995 (sh), 985 (sh), 950 (sh),  
 930(m), 875(w), 815(w), 767(s), 752(sh), 732(sh).

Electronic spectrum as tetrahydrofuran solution,  
 $\lambda_{max}$  (m $\mu$ ) and ( ) extinction coefficients; 476 (6860),  
 380(sh)(14400), 340 (20000).

3,4:9,10-Dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-  
dienenickel(II) perchlorate,  $[Nicyen H_2]^{2+} (ClO_4)_2$

To a stirred suspension of Nicyen (40 mg. 0.11 mmole) in tetrahydrofuran (3 ml.) was added 70% perchloric acid (0.7ml) with caution. A pale yellow precipitate was formed almost immediately, but the mixture was stirred for a further 30 min. The pale yellow powder of  $[Nicyen H_2]^{2+} (ClO_4)_2$  was collected at a sinter, washed with a little dry tetrahydrofuran, and dried under vacuum (44 mg. 72%)

Analysis found C, 38.33; H, 4.03; N, 9.99%  
 $C_{18}H_{20}NiCl_2O_8$  requires C, 39.31; H, 3.67; N, 10.19%  
 Infrared spectrum as KBr disc ( $\lambda_{max}$   $cm^{-1}$ ); 3320(n,b),

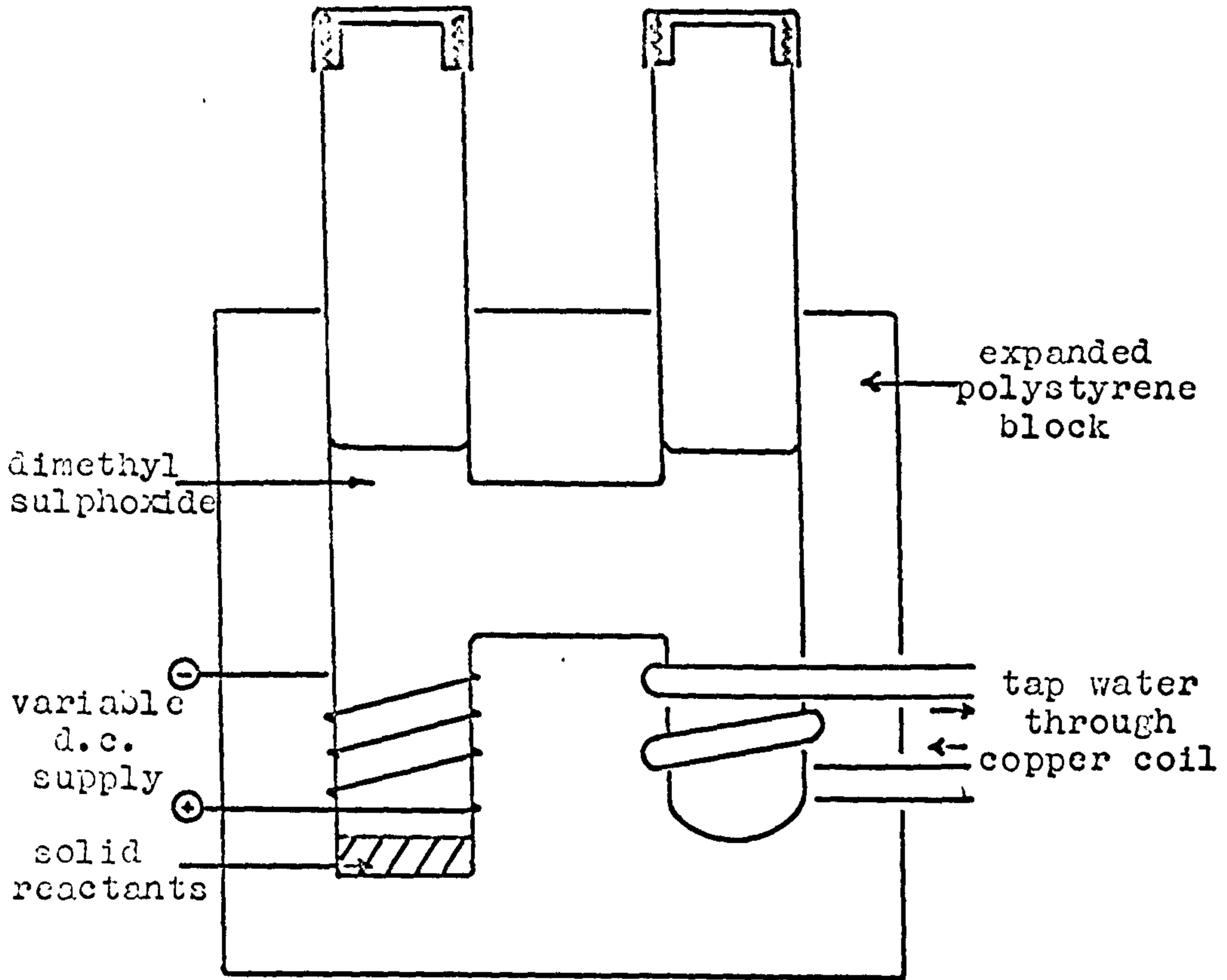
3040(w), 3030(w), 3020(w), 2960(w), 2950(w), 1641(s), 1600(s), 1585(sh), 1495(sh), 1488(m), 1475(sh), 1445(sh), 1435(sh), 1424(s), 1405(sh), 1359(w), 1303(s), 1280(sh), 1269(w), 1239(m), 1209(sh), 1192(m), 1170(m), 1145(sh), 1100(vs,b), 1080(sh), 1046(sh), 1001(m), 941(w), 929(w), 876(m), 807(m), 769(s), 734(m).

### 11.6 Compounds of chapter 9.

#### 3,4:9,10-Dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-dieneatocobalt(II) [Cocyen]

A suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (1.2g., 4.5 mmole) in methanol (60 ml.) was refluxed gently under a slow stream of nitrogen. The mixture was stirred vigorously and cobalt(II) acetate (1.2g., 4.8 mmole) was added, followed by a solution of 1,2-diaminoethane (0.64ml., 9.6 mmole) in methanol (10 ml). After two hours the matted crystals were broken into smaller lumps to reduce the violent bumping. After six hours the mixture was filtered under nitrogen, and the residue washed with a little methanol, when Cocyen was obtained as fine purple needles which were allowed to dry on the sinter by passing a slow stream of nitrogen over them (1.4 g. 86%).

These crystals could not be recrystallized from any of a wide range of solvents tested, and so a crystal sufficiently large for an X-ray structure determination was



[11.3]

grown from a reaction mixture using one tenth scale of reactants (above) in dimethyl sulphoxide (c.a. 20 ml.), using the apparatus shown in [11.3]. A small current was supplied to the heating coil sufficient to produce a temperature difference of approximately  $10^{\circ}$  between the two arms of the apparatus (tested before addition of any of the reagents). The reagents were added under an atmosphere of nitrogen, and the apparatus carefully sealed and allowed to stand for three weeks. Some reasonable sized crystals were deposited in the horizontal arm.

Other compounds type [9.1] page 210.

The reaction in methanol (page 328) gave similar yields when applied to the synthesis of Cocytin and Cocybuten (for abbreviations see page 210).

1,5,8,12-Tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-dieneatocobalt(II). [Cocyphen]

The method described for the analogous nickel(II) complex (see page 323) was used and gave a similar yield. The product was analysed and used in reactions without further purification, since all attempts at recrystallization failed.

Table [11.5]. Infrared spectra of the cyclic complexes of cobalt(II), (chapter 9).

(a)  $\lambda_{\max}(\text{cm}^{-1})$ , recorded on a Unicam 200G spectrometer.

(b) abbreviations section 10.3 (c) Hexachlorobutadiene.

Cocycen as nujol and HCB<sup>c</sup> mulls; 3060(w)<sup>b</sup>, 3050(w), 3025(w), 3005(w), 2980(sh), 2960(sh), 2945(w), 2940(m), 2905(w), 2880(w), 2865(m), 1602(s), 1585(m), 1572(sh), 1565(sh), 1523(s), 1517(sh), 1490(sh), 1479(w), 1438(s), 1427(s), 1398(w), 1373(m), 1338(s), 1326(m), 1266(m), 1244(w), 1230(sh), 1215(s), 1179(m), 1172(m), 1145(w), 1140(w), 1114(w), 1085(w), 1065(w), 1043(m), 995(w), 943(w), 938(w), 914(w), 907(w), 830(w), 821(w), 751(s), 739(s), 731(m).

Cocytu as KBr disc; 3080(w), 3060(w), 3050(w), 3010(w), 2980(w), 2945(w), 2935(w), 2920(m), 2860(m), 2820(m), 1603(s), 1580(s), 1572(sh), 1525(s), 1520(sh), 1515(sh), 1505(sh), 1475(s), 1450(sh), 1439(sh), 1429(s), 1395(sh), 1385(w), 1370(sh), 1350(s), 1335(sh), 1325(sh), 1292(w), 1263(m), 1222(sh), 1215(s), 1173(m), 1143(m), 1102(m), 1080(sh), 1070(w), 1035(m), 1003(w), 991(w), 952(sh), 941(w), 922(w), 872(m), 833(w), 751(s), 733(s), 728(sh).

Cocycbuten as nujol mull; 3060(w), 3040(w), 3015(w), 1602(s), 1578(s), 1527(s), 1523(s), 1520(sh), 1470(s), 1460(sh), 1440(sh), 1430(s), 1377(s), 1367(m), 1346(s), 1330(sh), 1310(w), 1279(w), 1259(w), 1222(s), 1215(sh), 1160(s), 1139(m), 1105(w), 1080(m), 1067(w), 1033(m), 1015(m), 975(w), 955(w), 944(w), 933(w), 914(w), 892(w), 860(w), 849(m), 801(m), 751(s), 742(s), 739(m), 733(m).



Cocyphen as nujol mull; 3080(w), 3050(w), 3035(w), 3020(w), 1608(s), 1597(sh), 1570(s), 1565(s), 1520(s), 1495(w), 1485(w), 1465(s), 1455(sh), 1439(sh), 1379(s), 1362(s), 1348(m), 1252(w), 1247(m), 1212(w), 1197(s), 1179(m), 1159(m), 1140(m), 1105(w), 1070(w), 1048(w), 1038(m), 965(w), 940(m), 922(w), 902(m), 840(w), 823(m), 813(w), 747(s), 740(s), 736(m).

Reactions of the complexes with iodine.

The reaction of Nicyphen with iodine will be described as a typical example. A similar procedure was used for the cobalt complexes except that tetrahydrofuran solutions were prepared under nitrogen, and air was excluded until after the reaction was complete.

To a solution of Nicyphen (330 mg., 0.84 mmole) in tetrahydrofuran (150 ml.) was added a solution of iodine (210 mg., 0.84 mmole) in tetrahydrofuran (10 ml.) The mixture was stirred for 20 mins. and centrifuged. The amorphous black solid was washed with tetrahydrofuran (4 x 25 ml.) and dried.

Analysis found C, 39.56; H, 3.08; N, 8.80; I, 39.76%  
 $C_{22}H_{18}N_4NiI_2$  requires C, 40.59; H, 2.79; N, 8.61; I, 38.99%

Infrared spectrum as a nujol mull ( $\lambda_{max}, cm^{-1}$ );  
 3060(w), 3035(w), 3000(w), 1612(s), 1594(m), 1581(m), 1555(s), 1520(m), 1490(sh), 1475(m), 1440(s), 1420(vs), 1380(s), 1361(w), 1399(m), 1315(sh), 1292(vs), 1265(w),

1250(w), 1215(vs), 1195(sh), 1186(vs), 1160(vs), 1116(vs), 1040(s), 1020(w), 960(w), 940(w), 935(w), 870(m), 827(m), 770(sh), 759(m), 749(vs).

A reaction under similar conditions using Niambphen gave a black amorphous powder.

Analysis found C, 37.65; H, 3.10; N, 7.82; I, 42.90%  
 $C_{20}H_{16}N_4NiI_2$  requires C, 36.97; H, 2.48; N, 8.62; I, 39.06%

### 11.7 Compounds of chapter 10.

#### Salicylaldoxime, [salox]

Salicylaldehyde (25 ml.) was added to a solution of hydroxylamine hydrochloride (50 g.) and sodium acetate (100 g.) in water (300 ml.). The mixture was stirred vigorously and heated under reflux for 4 hr. After cooling it was extracted with benzene (2 x 200 ml.) and the extract was dried over magnesium sulphate, and evaporated under reduced pressure. The resulting oil was crystallized by dissolving in a mixture of dichloromethane and (40-60°) petrol and allowing to stand when the solvent evaporated slowly, and salicylaldoxime was deposited as long white prisms (19.0 g 59%). Recrystallization as described above gave a product with m.p. 56-57° (lit. 57°)<sup>20</sup>

#### Bis(salicylaldoximato)nickel(II). [Ni(salox)<sub>2</sub>]

To a solution of salicylaldoxime (16.6 g., 121 mmole) in methanol (100 ml.) was added a hot solution

of nickel(II) acetate (20g., 80 mmole) in methanol (1 l.). The mixture was refluxed and stirred vigorously for 2 hrs. and filtered hot. The resulting pale green residue was recrystallized twice from large volumes of hot chloroform. Dark green prisms were obtained by the slow evaporation of a chloroform solution.

Found C, 50.72; H, 3.93; N, 9.02%

$C_{14}H_{12}N_2O_4Ni$  requires C, 50.81; H, 3.65; N, 8.46%

*N,N'*-bis(*o*-hydroxybenzylidene)-1,2-diaminobenzene, [salphen]

Salicylaldehyde (51.5 ml., .5 mole) in ethanol (350 ml.) was added slowly to a stirred solution of 1,2-diaminobenzene (27g., .25 mole) in refluxing ethanol (200 ml.) The mixture was refluxed for one hour and then allowed to cool slowly when orange-yellow needles of salphen were deposited (74 g., 94%), which were recrystallized from chloroform giving similar crystals m.p. 161-162°C (lit. 163°C)<sup>2</sup>

*N,N'*-bis(*o*-hydroxybenzylidene)-1,2-diaminobenzeneatonickel(II),

[Nisalphen]

Salphen (33 g., 105 mmole) was added in portions to a hot stirred solution of nickel(II) acetate (30g., 120 mmole) in methanol (600 ml.) The mixture was stirred at room temperature for 18 hr and then filtered, when Nisalphen (35 g., 89%) was obtained as red-orange needles. A portion of the product was recrystallized from pyridine

when fine crimson needles were produced which were washed with ether and recrystallized from chloroform.

Found C, 65.15; H, 3.99; N, 7.71%

$C_{20}H_{14}N_2O_2Ni$  requires C, 64.39; H, 3.78; N, 7.51%

### 11.8 References.

1. L.E. Smith and J.W. Opie, Organic Syntheses, Collected Volumes, III, 57.
2. Von. P. Pfeiffer, Th.Hesse, H. Pfitzner, W. Scholl and H. Thielert, J. prakt Chem. 149, 217, (1937).
3. V. Voorhees and R. Adams, J. Amer. Chem. Soc., 44, 1397, (1922).
4. P. Cohn and A. Blau, Monats. für Chem. 25, 374, (1904)
5. H.J. Scheifele Jr., and D.F. DeTar, Organic Syntheses, Collected Volumes, IV, 34.
6. Dictionary of Organic Compounds, Eyre and Spottiswoode, 4th Ed. page 2119.
7. M. Harfenist, A. Bavley and W.A. Lazier, J. Org. Chem., 19, 1608 (1954).
8. L. Sacconi, I. Bertini and R. Morassi, Inorg. Chem., 6, 1548, (1967).
9. E. Bamberger, Chem. Ber., 37, 979, (1904).
10. E. Bamberger, Chem. Ber., 37, 985, (1904).
11. N.S. Gill and R.S. Nyholm, J. Chem. Soc., 3997, (1959).

12. A.I. Vogel, "Text-Book of Practical Organic Chemistry", 3rd Ed. Longmans, 1962, page 167.
13. S. Yamada, H. Nishikawa and E. Yoshida, Proc. Japan. Acad., 40, 211, (1964).
14. C. Floriani, M. Fuppis and F. Calderazzo, J. Organometal Chem., 12, 209 (1968).
15. L.H. Vogt, H.M. Faigenbaum and S.E. Wiberley, Chem. Rev., 63, 269, (1963).
16. Gift from H.M. Jackson, prepared as described by F. Basolo and R.K. Murmann, Inorg. Syntheses, IV, 171, (1953).
17. J.F. Thorpe and A.S. Wood, J. Chem. Soc, 103, 1608, (1913).
18. V.M. Micovic and M.L. Mihailovic, J. Org. Chem., 18, 1190 (1953).
19. I. Smith and J.G. Feinberg, "Paper and Thin Layer Chromatography", Shandon Scientific Co. Ltd., 2nd Ed., 1965, page 159.
20. L.C. Raiford and E.P. Clark, J. Amer. Chem. Soc., 45, 1738, (1923).