The Structure, Redox Properties, and Reactions of Some Planar $[M^{II}N_4]$ Chelate Compounds of Cobalt, Nickel, and Copper, and their Oxidised Products, Including Paramagnetic Cobalt(III) Species

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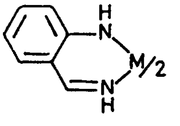
An investigation is reported of the structure and some reactions of the cobalt(II), nickel(II), and copper(II) compounds of several tricyclic quadridentate di-anionic Schiff's base ligands derived from *o*-aminobenzaldehyde and various diamines. The ligands are 1,2-bis-(*o*-iminobenzylideneamino)ethane (aben), 1,2-bis-(*o*-iminobenzylideneamino)propane (abpn), 1,3-bis-(*o*-iminobenzylideneamino)propane (abtn), and 1,2-bis-(*o*-iminobenzylideneamino)phenylene (abphen). The physicochemical data presented are supplementary to that of two recent papers in proving a four co-planar co-ordination polyhedron in the metal(II) compounds. In addition, a polarographic study of the redox behaviour of these compounds indicates that all should have chemically accessible higher oxidation states. Attempts to prepare the nickel and copper oxidation products of the type [M(L)X] (X = Br, I) gave only amorphous solids which have not been characterised. But the crystalline compounds [Co(L)X] (X = Cl, Br, I) which were readily isolated, are unique examples of paramagnetic cobalt(III) compounds with nitrogen-donor ligands. A square-pyramidal five-co-ordinate structure is postulated. These compounds react in donor solvents such as pyridine to form six-co-ordinate diamagnetic species of the type [Co(L)(solvent)X]. The crystalline diamagnetic compound [Co(aben)(py)Cl] has been isolated, and evidence is given for an equilibrium in the solutions in donor solvents between the diamagnetic and paramagnetic species.

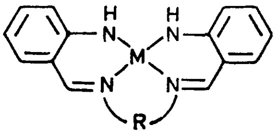
As part of a general investigation of the stereochemistry, the redox behaviour, and reactions of planar $[MN_4]$ chelate systems, we have studied the bisbidentate and the tricyclic quadridentate Schiff's base compounds (I) and (II) of cobalt, nickel, and copper; these are formed from *o*-aminobenzaldehyde and various amines.

The ligands will be abbreviated as follows: abNH for the bidentate ligand in (I); aben for the quadridentate ligand in (II; $R = \cdot CH_2 \cdot CH_2 \cdot$), abpn for that in [II; $R = \cdot CH(Me) \cdot CH_2 \cdot$], abtn for (II; $R = \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot$), and abphen for that in (II; $R = o\text{-}C_6H_4$).

Although many of the copper(II) and nickel(II) compounds were first reported by Pfeiffer and his co-workers[1] in 1937, no further data have been published on these species until the present work—a preliminary report[2] of which has already been given—and a parallel study by Green and Tasker of the nickel(II)[3] and cobalt(II)[4] systems.



(I)



(II)

Here we present data supplementary to those of Green and Tasker[3,4] on the inherently planar nature of the metal(II) compounds, and we give details of a study of some oxidation reactions and their products, especially in the cobalt series, where novel paramagnetic species have been observed.

EXPERIMENTAL

Preparation of Compounds.—The ligands aben and abphen were prepared in ethanol;[1] abtn was crystallised from ethanol. The ligand abpn was not isolated as a crystalline solid, and the preparations of compounds of this ligand started from solutions of the components of the Schiff's base in ethanol.

We usually give in the following only the preparations of the new compounds. References to the earlier preparations are given in Table 1 together with the analytical data for all species.

[Co(abNH)$_2$]. The method for preparing this compound parallels those for the nickel(II) and copper(II) compounds.[1] A solution of *o*-aminobenzaldehyde (0·55 g) in ethanol (25 ml) was added to cobalt(II) acetate tetrahydrate (1·3 g) in concentrated aqueous ammonia (50 ml). The brown solution was heated (10 min) when the brown-red compound precipitated. It was filtered off from the hot solution, washed with dilute aqueous ammonia, and dried in the air.

[Co(aben)]. The detail reported by Green and Tasker[4] for preparing this compound is unnecessary. Red crystals of the compound separate out when a hot aqueous solution (40 ml) of cobalt(II) acetate (0·6 g) is added to a boiling ethanol solution (40 ml) of the ligand (0·5 g). The compound was filtered off from the hot mixture, washed with ethanol, and dried in the air.

[Ni(abpn)] and [Cu(abpn)]. These compounds were obtained by the same method which Pfeiffer and his co-workers[1] used for the aben compounds.

[Co(abpn)]. This compound was obtained in good yield by the method used for the aben species.

[Co(abphen)]. We have not experienced the difficulties reported by Green and Tasker[4] for this compound. The method was the same as that used for [Co(aben)]. The dark green crystals, which separated from the red solution, were filtered off, washed with ethanol and water, and dried in the air. The compound could be recrystallised from pure dichloromethane (*cf.* the preparation of [Co(abphen)Cl]).

[Ni(abpn)],DMF. Crystals of the compound separated out when a solution of [Ni(abpn)] in dimethylformamide (DMF) was set aside overnight.

[Co(abpn)],DMF. Dark red-brown crystals of the solvate were obtained when, (*a*) a solution of [Co(abpn)] in DMF was set aside in the air (5 weeks); (*b*) water was added to a DMF solution which had been left overnight; and (*c*) a solution in DMF was treated with oxygen (2½ hours), and then diluted with water to precipitate the cobalt compound. The product in (*b*) was mixed with some [Co(abpn)], but this latter was not detected in the *X*-ray powder patterns of the other samples.

'Ni(abpn)I'. (a) *From acetone.* A solution of [Ni(abpn)] (0·43 g) in acetone (30 ml) was filtered, and iodine (0·16 g) in acetone (10 ml) was added dropwise to the stirred solution. A dark green solution formed, which soon deposited a dark green amorphous solid. This was filtered off, washed with acetone, and dried in the air.

(b) *From chloroform.* A solution of [Ni(abpn)] (0·55 g) in chloroform (50 ml) was treated under nitrogen with a solution of iodine (0·21 g) in chloroform (50 ml). The dark amorphous solid which precipitated was filtered off, and a further quantity of the same amorphous material was obtained by adding diethyl ether to the filtrate. The analytical data (Table 1) refer to this latter sample.

'Ni(abpn)Br'. This product was obtained by mixing chloroform solutions of [Ni(abpn)] (0·68 g) and bromine (0·10 g) as above. Light petroleum (b.p. 40—60°) was added to precipitate the dark amorphous solid from the resultant green-brown solution.

'Cu(abpn)Br'. A dark green solid was obtained by the method used for the nickel analogue.

[Co(aben)Cl]. (a) From CHCl$_3$. A suspension of [Co(aben)] in chloroform was left for 24 h. The greenish black residue was then repeatedly washed with chloroform, until the wash liquors no longer turned red. The product was dried in air.

(b) *From* CCl$_4$. The method was the same as for chloroform, except that the product was repeatedly washed with acetone to remove any remaining cobalt(II) species.

(c) The purest sample was obtained by suspending the pyridine species (*q.v.*) in CH$_2$Cl$_2$ overnight.

[Co(aben)Clpy],H$_2$O. The compound [Co(aben)Cl] from CHCl$_3$ (2 g) was dissolved in pyridine (brown solution). After several hours, black crystals of the compound separated out. These were filtered off, washed with pyridine, and dried in air.

Weight loss at 60° in *vacuo* over P$_4$O$_{10}$ was 17%—corresponding to loss of 1 mol. equiv. of pyridine. When either this dried product or the original pyridine compound were suspended in dichloromethane, both reverted to pure [Co(aben)Cl].

[Co(aben)Br]. A solution of [Co(aben)] (0·5 g) in dichloromethane (60 ml) was treated with bromine (0·12 g) in dichloromethane (200 ml). A dark greenish black precipitate of the crude material separated immediately. It was filtered off, washed with dichloromethane, and dried in the air. Poor analytical data were obtained (Table 1), but the *X*-ray data show that it is isomorphous with the chloro- and iodo-analogues.

[Co(aben)I]. The method for preparing this compound was the same as that used for the bromo-compound, but with

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[1] P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl, and H. Thielert, *J. prakt. Chem.*, 1937, **149**, 217.

[2] B. M. Higson and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 209.

[3] M. Green and P. A. Tasker, *J. Chem. Soc.* (*A*), 1970, 2531.

[4] M. Green and P. A. Tasker, *J. Chem. Soc.* (*A*), 1970, 3105.

iodine (0·20 g) instead of bromine; it was a dark brownish green solid.

[Co(abpn)Cl]. (a) *From cold* $CHCl_3$. The blue-black microcrystalline solid was obtained by dissolving [Co(abpn)] in chloroform at room temperature. The deep red solution quickly turned brown and very fine needles separated out. The same reaction occurred in chloroform containing a small amount of ethanol, pure chloroform, and in the dark. The initial product normally gave high chloride analyses (*cf.* product from hot soln. and CCl_4); it was obtained as dark green needles. The compound gives brown solutions in water and pyridine, but green in aqueous acetone, Me_2SO, and DMF.

TABLE 1

The compounds isolated, the analytical data, and room-temperature magnetic moments

	Analyses (%)								
	Found				Calculated				
Compound	C	H	N	Others	C	H	N	Others	μ (B.M.)
[Ni(abNH)$_2$] [a]	56·2	5·2	18·7		56·6	4·8	18·9		
[Ni(aben)] [a]	59·3	5·3	17·7		59·5	5·0	17·4		
[Ni(abpn)]	60·6	5·3	16·3		60·5	5·3	16·6		
[Ni(abtn)] [b]	60·4	5·6	16·8		60·5	5·3	16·6		
[Ni(abphen)] [a]	64·6	4·5	15·0		64·7	4·4	15·1		Dia.
[Co(abNH)$_2$]	56·4	4·8	19·2		56·6	4·7	18·9		
[Co(aben)]	59·4	5·0	17·7		59·4	5·0	17·3		2·1
[Co(abpn)]	60·6	5·3	16·5		60·5	5·3	16·6		2·2
[Co(abphen)]	64·9	4·5	15·4		64·7	4·3	15·1		2·0
[Cu(abNH)$_2$] [a]	55·1	4·6	18·2		55·7	4·6	18·6		
[Cu(aben)] [a]	58·1	5·2	17·3		58·5	4·9	17·1		
[Cu(abpn)]	59·5	5·5	16·9		59·7	5·3	16·4		
[Cu(abphen)] [a]	64·0	4·1	14·6		63·9	4·3	14·9		
[Ni(abpn)],DMF	58·7	6·1	16·9		58·6	6·2	17·1		
[Co(abpn)],DMF	58·9	6·1	17·1		58·5	6·1	17·1		
Ni(abpn)Br,H_2O	46·5	4·1	12·6	Br, 16·9	46·9	4·6	12·9	Br, 18·4	
Ni(abpn)I (*a*) [c]	44·8	3·9	11·9	I, 27·8	44·0	3·9	12·1	I, 27·4	Dia.
(*b*) [c]	43·8	3·9	12·0	I, 27·8					Dia.
Cu(abpn)Br,H_2O	43·4	3·9	11·5	Br, 19·7	46·4	4·6	12·7	Br, 18·2	1·6
[Co(aben)Cl] (*a*) [c]	52·8	4·0	15·1	Cl, 11·6	53·6	4·5	15·6	Cl, 9·9	2·7
(*b*) [c]	49·5	4·1	13·6	Cl, 13·7 Co, 14·3	48·8 [d]	4·1	14·2	Cl, 18·0 Co, 15·0	2·6 [g]
(*c*) [c]	53·7	4·5	15·8	Cl, 10·1	53·6	4·5	15·6	Cl, 9·9	2·7
[Co(abpn)Cl] (*a*) [c]	52·2	4·4	14·2	Cl, 11·0	54·8	4·9	15·0	Cl, 9·5	
(*b*) [c]	54·1	4·8	15·9	Cl, 9·8					2·7
(*c*) [c]	49·0	4·2	13·1	Cl, 12·2					
(*d*) [c]	44·0	4·3	12·1	Cl, 18·4 Co, 13·9	46·0 [e]	4·1	12·6	Cl, 24·0 Co, 13·3	2·4 [e]
	42·7	4·3	11·4	Cl, 20·5					
	40·8	4·2	11·2	Cl, 19·0					
[Co(abphen)Cl] (*a*) [c]	54·8	3·4	13·1	Cl, 9·2	59·1	4·0	13·8	Cl, 8·7	2·7
(*b*) [c]	53·3	3·9	12·7	Cl, 14·2 Co, 12·3	54·3 [d]	3·7	12·7	Cl, 16·0 Co, 13·3	2·5
Co(aben)Cl,py,H_2O	55·6	5·2	15·7	Cl, 7·4	55·3	5·1	15·4	Cl, 7·9	Dia. [h]
Co(abpn)Cl,py,H_2O	55·8	5·0	15·8	Cl, 8·2	56·3	5·4	14·9	Cl, 7·6	
[Co(aben)Br]	36·7 [f]	3·8	10·7	Br, 17·7	47·7	4·0	13·9	Br, 19·8	
[Co(abpn)Br]	48·5	4·7	13·0	Br, 18·8	49·0	4·4	13·4	Br, 19·2	2·7
[Co (abphen)Br]	49·1	4·5	11·6	Br, 26·1	53·2	3·6	12·4	Br, 17·7	
[Co(aben)I]	42·9	3·9	12·7	I, 28·7	42·7	3·6	12·4	I, 28·2	
[Co(abpn)I]	44·1	4·2	12·2	I, 28·4	44·0	3·9	12·1	I, 27·3	2·8
[Co (abphen) I]	48·8	3·4	11·1	I, 29·2	48·2	3·3	11·2	I, 25·5	

[a] The preparation is given in ref. 1. [b] The preparation is given in ref. 3. [c] These letters refer to the preparative method in the experimental. [d] These figures refer to Co(L)Cl_2. [e] These figures refer to Co(abpn)Cl_3. [f] This sample has an *X*-ray diffraction pattern which shows it to be isomorphous with [Co(aben)Cl]. Both the i.r. spectrum and the analyses indicate the presence of large quantities of water (*i.e.* $\sim 6H_2O$), which therefore must be occluded in the solid. [g] Molar susceptibilities here are calculated from the 'molecular weight' indicated by the cobalt analyses. Since the exact formulation of these compounds is unknown, the diamagnetic corrections are only rough estimates. [h] $10^6\chi_M = 180$ c.g.s.u.

(b) The purest sample was obtained by recrystallisation from DMF.

(c) *From* CCl_4. A stirred suspension of [Co(abpn)] in CCl_4 changed overnight to a greenish black precipitate. This was filtered off, washed with acetone until all unchanged [Co(abpn)] had been removed, and then dried in the air.

(d) *From hot* $CHCl_3$. When [Co(abpn)] was treated with boiling chloroform, the dark precipitate was amorphous and had a very high chlorine content (Table 1).

Co(abpn)Cl,H_2O,py. The compound [Co(abpn)Cl] (from $CHCl_3$) was dissolved in pyridine and dry diethyl ether was added. The green amorphous powder which precipitated, was filtered off, washed with ether containing pyridine and dried in the air.

[Co(abpn)Br]. A solution of [Co(abpn)] (0·5 g) in dichloromethane (40 ml) was treated with bromine (0·12 g) in dichloromethane (200 ml). The brown solution was filtered and evaporated under reduced pressure until dark green crystals of the compound separated out. These were filtered off, washed with dichloromethane, and dried in the air.

[Co(abpn)I]. The method used to prepare this compound was the same as that for the bromo-analogue, but with iodine (0·20 g) instead of bromine. The compound precipitated as soon as the solutions were mixed; it was a black solid.

[Co(abphen)Cl]. (a) *From* $CHCl_3$. A green-brown solution of [Co(abphen)] in chloroform was set aside for several days, when black crystals of the compound separated out.

(b) *From* CCl_4. A suspension of [Co(abphen)] in tetrachlorocarbon was stirred for four days. The greenish black solid was filtered off, washed, and dried in the air.

[Co(abphen)Br]. A solution of [Co(abphen)] (0·5 g) in dichloromethane (60 ml) was treated with bromine (0·11 g) in dichloromethane (300 ml). The green-brown solution was filtered and evaporated under reduced pressure, when dark green crystals of the compound separated out. The analytical data (Table 1) on this crude sample were not good, but the *X*-ray data (deposited with the National Lending Library as Supplementary Publication No. 20269; 8 pp) * characterise it as being isostructural with the chloro- and iodo-species.

[Co(abphen)I]. The method used to prepare this compound was the same as that used for the bromo-analogue, but with iodine (0·17 g) instead of bromine; it was a greenish black solid.

Physical Measurements.—The electronic spectra were recorded on a Unicam SP700 instrument, with diffuse-reflectance attachment (SP735) for the solid spectra.

The ^1H n.m.r. spectra were obtained on a Varian HA100 instrument.

The magnetic data were obtained on a Gouy-type balance, with permanent magnets of 5300 and 3040 G.

The i.r. spectra were recorded on a Perkin-Elmer PE457 grating instrument, using paraffin mulls.

The mass spectra were recorded on an AEI MS12 spectrometer, with source temperatures between 220 and 250 °C.

The *X*-ray powder diffraction patterns were obtained photographically on a Phillips 11·46 cm camera with Co-K_α radiation.

The voltammetric data were obtained on a Beckman Electroscan 90 instrument, using conventional H-type cells and a rotating Pt electrode at ambient temperatures (20 ± 2 °C), with a standard aqueous calomel electrode as reference. The three electrode system was used to correct for *iR* drop. Solutions in CH_2Cl_2 or DMF were 3×10^{-4}M in compound, and 0·05M in supporting electrolyte (NEt_4ClO_4). The limit to the working range for oxidation was $\sim +1{\cdot}7$ V.

Cyclic voltammetric studies used the stationary Pt electrode.

Microanalyses for C, H, N, and halogen were from the Microanalytical Laboratory of this Department.

RESULTS AND DISCUSSION

The Cobalt(II), *Nickel*(II), *and Copper*(II) *Species*.—The *X*-ray powder diffraction data show that, in all cases, the solid cobalt(II), nickel(II), and copper(II) compounds of the same ligand are isomorphous. The arguments for regarding the nickel(II) compounds as planar [MN_4] species have been given by Green and Tasker[3,4] and our data (Tables 1—3 and Supplementary Publication No. 20269) confirm and supplement, and in a few cases correct theirs.

This planar structure of the solid compounds is now fully confirmed by a three-dimensional *X*-ray structural study [5] of [Ni(abpn)] and supported by a two-dimensional study [6] of the copper compound [Cu(aben)]. The former gives an interesting example of an axial methyl group in a pn chelate ring.

The similarity of the electronic spectra of the various compounds in different solution and solid phases (refs. 3 and 4, and Table 2) shows that they also remain planar in solution even in donor solvents such as pyridine.

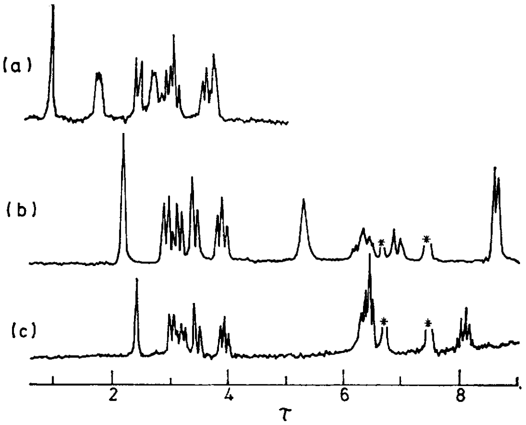

FIGURE 1 The ^1H n.m.r. spectra in $(CD_3)_2SO$ of (a) [Ni(abphen)], (b) [Ni(abpn)], and (c) [Ni(abtn)]. The asterisked, truncated peaks are the resonances from residual protons of the solvent and HOD

Both [Ni(abpn)] and [Co(abpn)] were obtained from DMF as 1 : 1 solvates [M(abpn)],DMF, which are isomorphous (*X*-ray data). That the DMF is not bonded to the metal in these solids, is shown by the identity of their diffuse-reflectance and solution spectra with those of the non-solvated species.

The contrasts of these planar [MN_4] species with the closely related salicylaldimine species are marked. The latter often expand their co-ordination number, either by dimerisation or polymerisation [7] [especially in the case of cobalt(II) [8] and copper(II) [9]] or by the addition of donor molecules,[7,10] whereas the former do not.

^1H *N.m.r.* The data for some of the diamagnetic nickel(II) compounds are listed in Table 3, and the spectra are shown in Figure 1.

These data are at variance with those of Green and Tasker.[3] For [Ni(abtn)] and [Ni(abpn)] we identify the NH signals at much higher field (τ 6·30 and 5·35, respectively), relying on the observation of rapid loss of these signals when D_2O is added to the solutions, as well

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* For details of Supplementary Publications see Notice to Authors No 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[5] N. A. Bailey and E. D. McKenzie, unpublished data.

[6] N. A. Bailey and B. D. Nicholson, unpublished data.

[7] R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

[8] S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, *B*25, 1671.

[9] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644; E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

[10] M. Calligaris, D. Minichielli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

TABLE 2

The electronic spectra of the metal(II) compounds in the region 30 ⟶ 5 kK. Bands appearing as ' shoulders ' are given in parentheses, and the extinction coefficients in square brackets

Compound	Phase	Observed bands (kK)
$[Co(abNH)_2]$	Solid	27·0(vbr) [a] (~23) [a] 19·0 16·25 11·3 6·7 [c]
	Py soln	27·0[10,300] 23·1[9300] (22·3)[7600] 19·15[2800] 16·3[470] [b]
[Co(aben)]	Solid	27·0(vbr) [a] 18·5(asym) 10·35 ~6 [c]
	CH_2Cl_2 soln	26·55[14,600] 22·95[20,200] (20·0)[3700] 18·8[4800] (16·2)[350] 11·0[120] ~7[50] [c]
	Py soln	26·2[24,000] 22·7[33,000] (20·0)[5800] 18·7[7300] (16·2)[390] 10·95[67] ~6·5[24] [c]
[Co(abpn)]	Solid	25·9(br) [a] 22·7 18·6 (16·4) (~12) 10·8 ~6 [c]
	CH_2Cl_2 soln	26·6[14,400] 22·95[19,300] 20·0[3800] 18·9[4600] (16·3)[300] 11·0[58] ~6[20] [c]
	Py soln	26·2[16,900] 22·7[23,200] (~20)[4400] 18·6[5600] (16·2)[360] 10·9[56] ~6[20] [c]
[Co(abphen)]	Solid	22(vbr) [a] (18·2) 17·5 15·8 10·5 ~6 [c]
	CH_2Cl_2 soln	(27·0)[15,600] 25·4[19,800] 23·3[17,900] (~22) (19·8)[4000] 18·5[3800] (17·8)[3700] (16·1) [2700] (14·3)[1200] (~10·6)[~100] [b]
	Py soln	27·0[13,600] (25·3)[11,600] 22·4[12,400] (19·7)[5300] (18·1)[5100] 17·5[5200] (~16) (14·1)[900] [b]
$[Ni(abNH)_2]$	Solid	28·0 20·8 (~19)
	Py soln	(28·6)[11,700] 20·8[3640] [b]
[Ni(aben)]	Solid	26·6 21·3 (20·6) (19·1)
	$CHCl_3$ soln	(27·5)[6700] (~21·2) 20·6[4800] (~19)[2000]
	Py soln	(27·3)[8300] (21·2) 20·3[5900] (~19)[3000]
[Ni(abpn)]	Solid	26·3 (21·2) 20·3 (19)
	$CHCl_3$ soln	(27·5)[7200] (~21) 20·5[5400] (~19)
	Py soln	(27·4)[8600] (~21·2) 20·35[6300] (~19)[3000]
[Ni(abtn)]	Solid	25·8(br) (22·0) 21·4 (20·3) 16·0
	$CHCl_3$ soln	(27·6[5400] 21·25[4300] 20·0[4200] (16·35)[270]
	Py soln	(27·6)[6100] 20·75[4600] 19·8[4700] (16·25)[320]
[Ni(abphen)]	Solid	24(vbr) [a] (18·1) 16·9 15·65 (~13·5)
	$CHCl_3$ soln	(~28) (~27) 25·8[23,600] 25·0[23,000] (~23·0) (19·0)[5000] 18·6[5100] (17·7)[4800] 16·1[5850]
	Py soln	(~28) (~27) 25·4[27,500] 24·9[27,400] (23·0) 19·3[5700] (18·6)[5300] 17·2[5800] 15·95[7200]
	$(CH_3)_2SO$ soln	(28·2)[10,200] (26·8)[17,800] 25·2(br)[24,000] (19·1[4400] 18·4[4600] 17·25[5000] 16·0[6000]
$[Cu(abNH)_2]$	Solid	25(vbr) [a] 22·6(br) [a] (19·2) 14·9(asym)
[Cu(aben)]	Solid	24·9 [a] (22·2) [a] 14·85
	$CHCl_3$ soln	(~25) (24·2) 23·8[11,100] (22·1) 14·6[170]
	Py soln	(~25) 23·65[13,200] (22·4) 14·7[190]
[Cu(abpn)]	Solid	24·4(br) [a] (22·5) [a] 14·75
	$CHCl_3$ soln	23·9[11,900] (22·2) 14·6[180]
	Py soln	23·6[12,900] 22·3) 14·8[210]
[Cu(abphen)]	$CHCl_3$ soln	28·8[14,200] 24·0[15,350] 20·7[16,600] (~16·2)[400] (~15·3)[340]
	Py soln	28·6[13,400] 23·75[15,900] 20·55[16,800] (~16·2)[600]

Abbreviations: br = broad, v = very, asym = asymmetric, py = pyridine, soln = solution.

[a] Because of the intensity of the spectra, these bands were poorly defined by our instrumentation, but the characteristic peaks in the visible region were usually well defined. [b] Because of the low solubility, only the most intense bands were observed. [c] The exact position and shape of these low-energy bands are obscured by vibrational overtone and combination bands.

TABLE 3

The ^1H n.m.r. data for the nickel(II) compounds [τ values, $(CD_3)_2SO$ solutions] [a]

Compound	CH=N	Aromatic CH	–NH– [b]	N–CH_2C and N–CH(CH_3)–C	C–CH_2–C	C–CH_3
[Ni(abpn)]	2·27(s2)	3·00(d2, $J \approx 7$) 3·19(t2, $J \approx 7$) 3·50(d2, $J \approx 8$) 3·95(t2, $J \approx 7$)	5·37(s2,br)	6·4(m2) 6·99(d1, $J \approx 12$)		8·71(d3, $J \approx 6$)
[Ni(abtn)]	2·43(s2)	3·04(d2, $J \approx 8$) 3·21(t2, $J \approx 7$) 3·48(d2, $J \approx 8$) 3·95(t2, $J \approx 7$)	6·30(s2)	6·45(t4, $J \approx 7$)	8·11(q2, $J \approx 7$)	
[Ni(abphen)]	0·98(s2)	1·8(m2) 2·48(d2, $J \approx 8$) 2·75(m2) 2·8 → 3·4(m4) 3·65(t2, $J \approx 7$)	3·81(s2)			

[a] The figure given in parentheses after the multiplicity is the relative integrated intensity of the resonance. [b] Deuteriation often causes diminution of these peaks, if the solution is left in the $(CD_3)_2SO$ for any appreciable time.

as the integrated intensities and cross-correlations of the different compounds.

The confusion in the earlier work [3] appears to have resulted from the presence of paramagnetic impurities. For some solutions of these compounds, we have found that the two higher field aromatic CH signals are markedly broadened and the NH signals lost. Perhaps the compound acts as a chelating ligand to the paramagnetic metal impurity in the solvent, in the same way as do [M(salen)]° species.[11]

I.r. spectra. The i.r. spectra of the various compounds, listing only the characteristic stretching frequencies above 1500 cm^{-1} are deposited with the National

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[11] E. Sinn and C. M. Harris, *Co-ordination Chem. Rev.*, 1969, **4**, 391; M. D. Hobday and T. D. Smith, *J. Chem. Soc.* (*A*), 1971, 1453.

Lending Library in Supplementary Publication no. 20269. Green and Tasker [3,4] have assigned separate stretching frequencies to the C=N (azomethine) group and the aromatic ring system of the ligand. The former are at distinctly lower energy than those in a variety of copper(II) compounds of Schiff base ligands derived from pyridine-2-carbaldehyde,[12,13] in which there are well-separated bands at *ca.* 1650 cm^{-1} (assigned to the azomethine group) and others at 1600—1610 cm^{-1} (assigned as pyridyl ring frequencies). Here the assignments are supported by the changes observed [13] when alcohol adds across one of the two azomethine groups, and the group frequency concept appears to hold. On the other hand, Dudek and Dudek [14] have shown that the group frequency concept is invalid in this region of the i.r. spectra of some salicylaldimines, and the same undoubtedly applies to the present compounds which have similar spectra.

Mass spectra. In Table 4 we list some of the peaks observed in the mass spectra, which serve to confirm the basic structure of the metal(II) compounds. No attempt has been made to characterise the cracking patterns. But, as for [15] the analogous quadridentate salicylaldimines, these spectra often have other peaks at *m/e* values corresponding to the loss of the 'bridging' aliphatic carbon fragments [CH_2–CH_2 of aben, and CH_3 and $CH(CH_3)\cdot CH_2$ of abpn].

TABLE 4

Some of the characteristic peaks in the mass spectra of the various compounds.[a] (Only the mass number of the ion with the most abundant isotopes is listed.)

	Observed *m/e* values					
Compound	Halogen	Hydrogen halide	Loss of hydrocarbon 'bridge'		Metal(II) parent	Higher peaks
[Ni(abpn)]				321 (7)	*336*	
[Ni(abtn)]					*336*	
[Co(aben)]			295 (1)		*323*	
[Co(abpn)]			295 (1)	322 (10)	*337*	
[Co(abphen)]					*371*	
[Cu(abpn)			299 (1·5)	326 (0·2)	*341*	
Ni(abpn)Br	79, 81 (220)	80, 82 (350)		321 (11)	334 (13) *336*	
Ni(abpn)I	127 (30)	128 (62)		321 (14)	334 (26) *336*	
Cu(abpn)Br					339 (110) *341*	
[Co(aben)Cl]	35 (5)	36 (17)	293 (1) 295 (14)		321 (85) *323*	
[Co(abpn)Cl]	35 (10)	36 (57)	293 (1) 295 (1·3)	320 (8) 322 (10)	335 (115) *337*	349 (0·6) 351 (0·5)[b]
[Co(abphen)Cl]	35 (8)	36 (40)	295 (1·5)		*371*	
[Co(aben)Br]	79, 81 (12)	80, 82 (31)	295 (0·7)	321 (120)	321 (120) *323*	351 (0·6) 400 (2·8) 402 (4·2) 404 (1·6) 479 (0·1) 481 (0·3) 483 (0·1) 558 (0·04) 561 (0·04)
[Co(abpn)Br]	79, 81 (15)	80, 82 (40)	295 (1)	320 (3) 322 (7)	335 (63) *337*	349 (1·7) 351 (0·7) 414 (0·4) 416 (1) 418 (0·7) 493 (0·2) 495 (0·3) 497 (0·1)
[Co(abphen)Br]	79, 81 (8)	80, 82 (23)	295 (0·6)		*371*	450 (2·1) 452 (2·2) 529 (0·3) 531 (0·5) 533 (0·3) 608 (0·2) 610 (0·2) 612 (0·1) 687 (0·1) 689 (0·1) 691 (0·1)
[Co(aben)I]	127 (8)	128 (15)	293 (0·2) 295 (0·4)		321 (43) *323*	
[Co(abpn)I]	127 (7·5)	128 (15)	293 (0·4) 295 (1)	320 (3) 322 (8)	335 (100) *337*	
[Co(abphen)I]	127 (2)	128 (2)			*371*	
[Co(aben)pyCl]H_2O[c]	35 (10)	36 (94)			321 (150) *323*	
[Co(abpn)pyCl]H_2O[c]	35 (4)	36 (44)	295 (2)	320 (13) 322 (14)	335 (110) *337*	349 (1·4) 351 (2·8)[b]

[a] The parent peaks are in italics, and relative intensities are given (in parentheses) on a scale in which this one is 100. For the metal(III) compounds, the most intense peak is usually the one corresponding to the metal(II) species, and here again we quote intensities with respect to the latter. [b] A set of peaks was observed typically as follows: 436 (1·1), 438 (0·6), 440 (0·6), and 442 (0·7), each with a weaker satellite one mass number higher. They do not correspond to a simple fragmentation pattern. [c] Also a strong pyridine peak at 79.

Protonation in acid solutions. Both the cobalt(II) and nickel(II) compounds dissolve in dilute aqueous acids to give yellow solutions, and in the case of [Ni(abphen)] a brown-yellow compound was isolated from dilute nitric acid. These species probably represent compounds of the parent (non-deprotonated) ligands, and the solid obtained in the latter case appears to be of the type $Ni(abphenH_2)(NO_3)_2,nH_2O$.

A number of attempts [16] to isolate the non-deprotonated copper(II) compounds, such as $Cu(abenH_2)(ClO_4)_2$, from ethanol solutions of the ligands and copper(II) perchlorate, gave black needles. But the analytical data persistently indicated partial deprotonation in the products.

The Electrochemical Data.—All metal(II) compounds of these ligands show oxidation waves. In a few cases, reduction behaviour also was studied. The results are listed in Table 5.

Often, for the processes studied, the measure of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ indicated reversible electrode behaviour, but seldom was reversible cyclic voltammetric behaviour observed

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[12] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1971, 1666.

[13] C. M. Harris and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1969, 746; M. Cressy, E. D. McKenzie, and S. Yates, *J. Chem. Soc.* (*A*), 1971, 2677.

[14] E. P. Dudek and G. Dudek, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 241.

[15] B. F. G. Johnson, personal communication.

[16] C. M. Harris and E. D. McKenzie, unpublished data, 1959.

(Table 5). This latter appears to be at least partially a result of electrode coating, which caused trouble with many of the measurements, especially at higher potentials. But, until the compounds have been studied in a further variety of non-donor and donor solvents, and with different electrode systems, we do not attempt to draw any firm conclusions about the nature of the electrode processes. The present data do at least indicate the main features of the redox behaviour.

We have not determined directly the number of electrons involved in the various electrode processes by coulometry. However, the measured wave-heights (all solutions were at the same concentration) generally were comparable with those of known one-electron processes. The several exceptions which appear to be two-electron processes are noted in Table 5.

TABLE 5

The electrochemical data

Compound	Solvent	$E_{\frac{1}{2}}$ (V)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ (mV) [a]	I_d/c (μA mmol^{-1})	PS[b]	Process
[Ni(abNH)$_2$]	DMF	+0·28	82			0→+1
		+1·10	110			+1→+2
		−1·14	~230			0→−1
[Ni(aben)]	CH_2Cl_2	+0·20	72	3·2		0→+1
		+0·79	90	3·3		+1→+2
	DMF	+0·21	58	1·5		0→+1
[Ni(abpn)]	CH_2Cl_2	+0·20	75	1·9	107	0→+1
		+0·77	134	1·7		+1→+2
[Ni(abtn)]	CH_2Cl_2	+0·24	70	4·2	i	0→+1
		~+1·0	Poorly defined			+1→+2
		−1·1	~200	5		0→−1
	DMF	+0·24	54	1·9	i	0→+1
[Ni(abphen)]	CH_2Cl_2	+0·40	57	2·6	i	0→+1
		+0·94	198	3		+1→+2
[Ni(salen)]	CH_2Cl_2	+1·03	110	15	i	0→+2(?) [c]
[Ni(saltn)]	CH_2Cl_2	+0·42	64	2		0→+1
		+0·80	~120	2		+1→+2
[Ni(salphen)]	CH_2Cl_2	+1·08	95	10		0→+2(?) [c]
[Co(aben)]	CH_2Cl_2	+0·07	58	3	i	0→+1
[Co(abpn)]	CH_2Cl_2	+0·10	54	4·2	108	0→+1
[Co(abphen)]	CH_2Cl_2	+0·23	127	7	180 [d]	0→+2(?) [d]
[Cu(aben)]	CH_2Cl_2	+0·32	71	4·2	i	0→+1
[Cu(abpn)]	CH_2Cl_2	+0·34	109	3	i	0→+1
[Cu(abphen)]	CH_2Cl_2	+0·38	71	4	i	0→+1
		~+1·15	Poorly defined			+1→+2

[a] Values of ~70 mV in CH_2Cl_2 and ~56 mV in DMF usually indicate reversible processes. [b] PS = Peak separation in the cyclic voltamagrams, *i.e.* $E_{\text{cathodic}} - E_{\text{anodic}}$. For reversible one-electron waves, PS ≈ 90 mV. The 'i' in this column means that no peak was observed for the reduction run. This probably results in some cases from electrode coating. [c] The I_d/c values indicate two-electron processes. [d] From the shape of the cyclic voltamagram and the other data this appears to be a *reversible* two-electron process. Trace amounts of water cause a drop in the voltage at which this wave occurs.

Nickel(II). All the nickel(II) compounds show two well-defined oxidation waves; but, whereas [Ni(abtn)] and [Ni(abNH)$_2$] show irreversible reduction waves at −1·1 V, neither [Ni(aben)] nor [Ni(abpn)] shows any reduction wave in our solutions down to the experimental limit of *ca.* −1·6 V. The differences in the oxidation waves of these two pairs of compounds also are significant (Table 5).

Such differences might result from different ligand conformations, and/or a distortion of the [NiN_4] plane in the case of [Ni(aben)] and [Ni(abpn)].

The electrochemical behaviour of these nickel(II) compounds parallels fairly closely that observed for two other planar [$Ni^{II}N_4$] species with delocalised ligand systems.[17,18] Some parallels also are observed with the analogous salicylaldimines, which have an N_2O_2 donor set (Table 5). In particular, the compound [Ni(saltn)] shows the same pattern of two oxidation waves. By contrast, both [Ni(salen)] and [Ni(salphen)] give only one wave at much higher potentials, and these appear to be two-electron processes.

Copper(II). The copper(II) compounds also give two oxidation waves, but at higher potentials than do the nickel(II) compounds. Again the more extensively delocalised system of [Cu(abphen)] gives waves at the highest potentials.

No attempt was made to compare the analogous salicyaldimine compounds, since they dimerise to give five-co-ordinate species.[9]

Cobalt(II). In contrast to the compounds of the other metals, those of cobalt(II) are characterised by single oxidation waves (Table 5). For [Co(aben)] and [Co(abpn)], these appear to be one-electron processes, and no further oxidation waves were observed in the region below +1·5 V. Yet the wave for [Co(abphen)] appears to be that of a two-electron process.

No attempt is made to compare these results with the extensive data obtained by Costa and his co-workers[19] on the Co(salen) systems, because of the marked influence of axial ligands on these latter N_2O_2 systems.

We do not consider that the ab compounds represent members of an electron-transfer series of the type defined

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[17] A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, 1966, **88**, 5201.

[18] O. A. Gansow, R. J. Olcott, and R. H. Holm, *J. Amer. Chem. Soc.*, 1967, **89**, 5470.

[19] G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc.* (*A*), 1970, 2870, and references therein.

by Holm *et al.*[17,18] The observed redox behaviour in the ab series is markedly dependent on the metal; and, in the case of the cobalt compounds, changes in the co-ordination number on oxidation to the +1 species are well-documented in the following. The electrode processes generally show some tendency towards irreversibility and this may be indicative of changes in the co-ordination number of the oxidised species—a not at all unexpected occurrence if the electrode processes involve a change more of metal than ligand ' oxidation state '.

Chemical Oxidations.—Nickel and copper. A spectrophotometric titration of [Ni(abpn)] with iodine in dichloromethane (Figure 2) showed an end-point, with well-defined isosbestic points, at a 1 : 1 ratio of reactants.

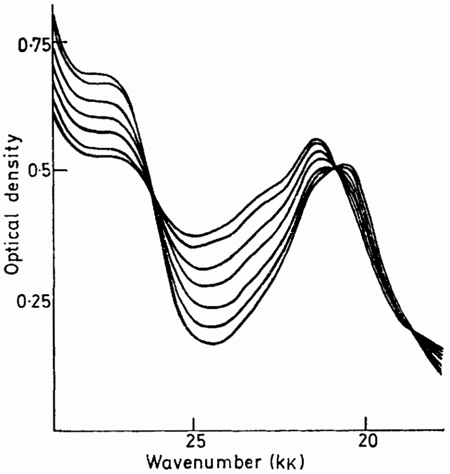
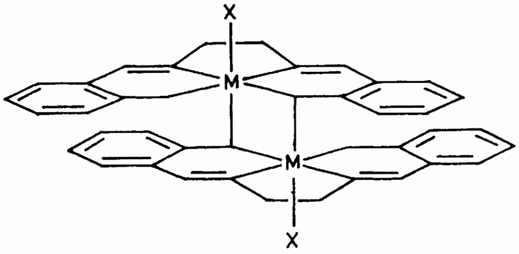


FIGURE 2 The spectrophotometric titration of [Ni(abpn)] with iodine in dichloromethane, showing the curves for I : Ni ratios of 0 : 1 to 1 : 1; the curve with the lowest energy peak in the visible region is that for pure [Ni(abpn)]. Solutions were 2 × 10^{-5}M in nickel compound

And a ' compound ' analysing as Ni(abpn)I was obtained from chloroform or acetone (Table 1).

However, these dark green products were *diamagnetic*, as was a bromine oxidation product obtained from chloroform (Table 1). Thus, if these materials do represent one-electron oxidation products of [Ni(abpn)], they must be magnetically non-dilute—perhaps with the dimeric structure (III). Similar results have been reported [20] for other iodine oxidation products of nickel(II) and palladium(II) species.

The data, however, are generally dissatisfying. All products were *amorphous*, as was a dark diamagnetic solid obtained from the reaction of [Ni(abphen)] with iodine in chloroform. And a dark green amorphous solid, obtained from [Cu(abpn)] and bromine in chloroform, had a large paramagnetism (Table 1)—typical of a copper(II) species.



(III)

At least the mass spectra (Table 4) indicate that halogenation has not occurred on the carbocyclic rings of the ligand. In such a case, we would expect to observe peaks in the spectra corresponding to the metal(II) compound of the halogen substituted ligand. [Nickel(II) compounds of chloro- and bromo-substituted salicylaldimines give strong parent-ion peaks [21].] No such peaks are observed for Ni(abpn)X (X = Br or I), but instead there are (Table 4) (*a*) strong peaks for HX and X, and (*b*) a prominent peak two mass numbers below [Ni(abpn)]. The latter may indicate that the imino-groups of the tetramine ligand are the source of the hydrogen atoms for HX. These peaks are not observed in the mass spectra of the metal(II) compounds. Similarly the mass spectrum for ' Cu(abpn)Br ' gave no peaks corresponding to a brominated ligand.

Cobalt. (a) *With oxygen.* No change was observed in the visible absorption spectra of [Co(abpn)] in dry pyridine or DMF when the solutions were saturated with molecular oxygen at atmospheric pressure. This contrasts with a great many other planar cobalt(II) compounds, such as the N_2O_2 systems of the salicylaldimines and related ligands,[22] and the N_4 systems of the porphyrin [23] and corrin [24] compounds.

Oxidation with oxygen does occur in hydroxylic solvents. Ethanol solutions turn brown irreversibly in the presence of oxygen, and so do DMF solutions when water also is added. For the latter, an intense band ($\varepsilon_{\max.} \approx 700$) appears at 12·6 kK in the electronic absorption spectrum, and this parallels the spectra of the paramagnetic cobalt(III) halogeno-compounds (*q.v.*).

A dark brown solid was obtained from the oxidised ethanol solution, but it was amorphous (even after dissolution in DMF and reprecipitation with ether).

On the other hand, well-defined crystalline products have been obtained from reactions with oxygen in the presence of β-diketones and malononitrile. These are six-co-ordinate diamagnetic species which have direct parallels in the salicylaldimine series. The former have

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[20] H. J. Keller and K. Seibold, *J. Amer. Chem. Soc.*, 1971, **93**, 1309; A. S. Foust and R. H. Soderberg, *ibid.*, 1967, **89**, 5507.

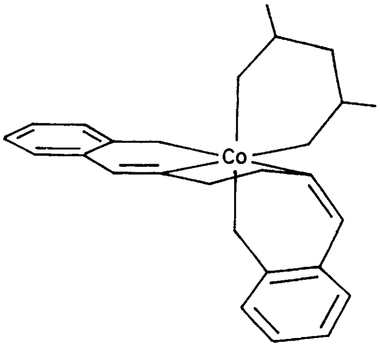
[21] E. D. McKenzie, unpublished data.

[22] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55; B. M. Hoffman, D. L. Diemente, and F. Basolo, *ibid.*, 1970, **92**, 61; C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946; T. Tsumaki, *Bull. Chem. Soc. Japan*, 1938, **13**, 252; R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886; M. Calvin, R. H. Bailes, and W. K. Wilmarth, *ibid.*, 1946, **68**, 2254; M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.* (*A*), 1970, 1069.

[23] F. A. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 4235; B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci.*, 1970, **67**, 637.

[24] J. H. Bayston, N. Kelso King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, 1969, **91**, 2775.

the structure (IV), with a non-planar arrangement of the donor atoms of the quadridentate ligand; [25,26] and the



(IV)

latter is a cobalt-alkyl species of the type now firmly characterised for the reaction of [Co(salen)] with malononitrile and oxygen.[27] These species will be discussed in detail elsewhere.

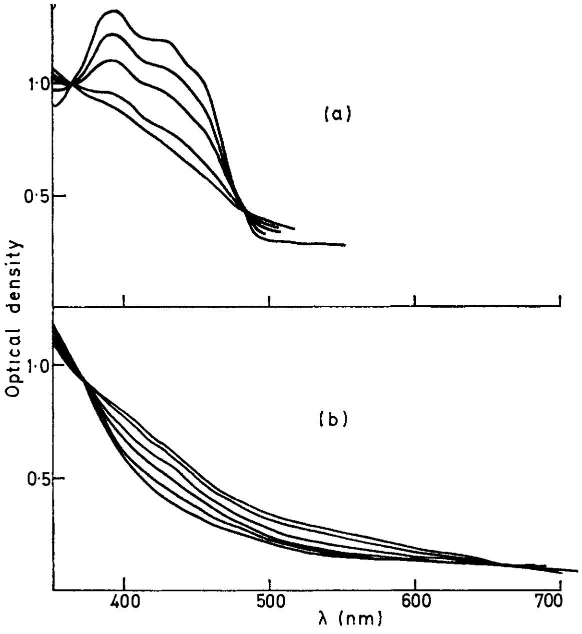


FIGURE 3 The spectrophotometric titration of [Co(abphen)] with bromine in dichloromethane. In (a), the curves are given for solutions with Br : Ni ratios up to 1 : 1, and in (b), those for the solutions between 1 : 1 and 2·5 : 1. Solutions were approximately 5 × 10^{-5}M in the cobalt compound. The isosbestic points for (a) are at 352 and 483 nm, whilst those for (b) are at 360 and ~675 nm

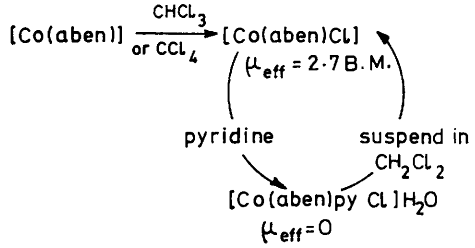
(b) *With halogens and halogenocarbons.* (i) Cobalt(III) compounds. The reactions of the cobalt(II) compounds with halogens or chloroform or tetrachlorocarbon give products of particular interest since they are the first fully characterised examples of paramagnetic cobalt(III) compounds with nitrogen-donor ligands, and they appear to have the unusual (for cobalt) $S = 1$ electronic ground state.

Spectrophotometric titrations of [Co(abpn)] and [Co(abphen)] with bromine and iodine give well-defined 1 : 1 end-points. Figure 3a shows a typical example. No titrations with chlorine were attempted, but it was possible to follow the reaction

$$[\mathrm{Co(abpn)}] + \mathrm{Cl} \longrightarrow [\mathrm{Co(abpn)Cl}]$$

in solution in laboratory reagent CH_2Cl_2. In various samples of this solvent the reaction had a half-life varying between several hours and a week, and well-defined isosbestic points were observed for the changing spectra.

Solid derivatives of the type [Co(L)X] (where X = Cl, Br, and I) were paramagnetic with moments between 2·7 and 2·8 B.M. (Table 1).* The reality of this paramagnetism was carefully checked and is fully confirmed by taking the same sample through the cycle of the Scheme.



SCHEME

That is, the paramagnetic [Co(aben)Cl] was converted quantitatively into the diamagnetic pyridine compound; and this latter reconverted (again quantitatively) into [Co(aben)Cl] simply by suspending it in dichloromethane. The latter product had the same magnetic moment and *X*-ray powder diffraction pattern as that of the original product.

For each ligand, the *X*-ray powder diffraction patterns of the compounds [Co(L)X] (where X = Cl, Br, I) indicate that they are isomorphous. One set of such patterns is given in Figure 4. The similarities are marked, especially the intensity distributions, and they are consistent with the same basic molecular species, in each case, packing in the same crystalline arrangement

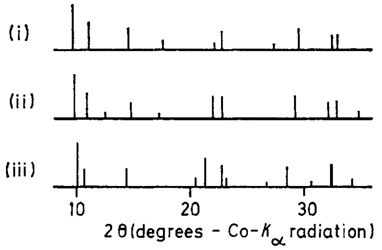


FIGURE 4 The *X*-ray powder diffraction patterns of (i) [Co(aben)Cl], (ii) [Co(aben)Br] and (iii) [Co(aben)I]

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* A detailed study of the paramagnetism of these compounds is being undertaken with Dr. M. Gerloch. Preliminary results indicate the presence of a thermal spin-state equilibrium.

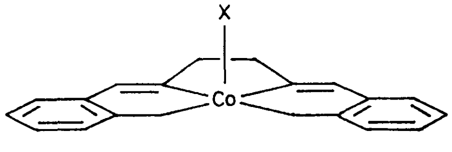
[25] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, in the press.

[26] M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1969, 1248.

[27] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 591.

(same space-group); and the differences between the chloride, bromide, and iodide can be rationalised as resulting from the different diffracting power of the different halogens together with minor changes in one or more of the cell dimensions (*cf.* the series [Co(phen)$_2$Cl$_2$]X,nH$_2$O in ref. 28).

We tentatively assign a five-co-ordinate square-pyramidal structure (V) to all the paramagnetic cobalt(III) compounds, partly because the quadridentate ligand is expected to prefer a planar configuration, and since this gives the most obvious rationalisation of the spin-state change when pyridine is added (see Scheme). Accordingly also the diamagnetic pyridine compound of the Scheme is assigned a ' normal ' octahedral structure [Co(abpn)(py)Cl]H$_2$O. These assignments will be checked by full three-dimensional *X*-ray structural studies when suitable crystals are available.



(V)

Because of solubility problems, no molecular-weight measurements are available, but the only compound with sufficient solubility—[Co(abpn)Cl]—is essentially a non-electrolyte in nitromethane (10 cm^2 mol^{-1} Ω^{-1} at 10^{-4}M and 20 °C).

Once again the mass spectra (Table 4) give good evidence in most cases that halogenation of the ligand has not occurred. (See the discussion on the nickel and copper halogenation products.) Only in the case of the bromo-compounds were peaks observed at *m/e* values corresponding to Co(L) + nX species, and here values of n up to 4 were observed. They appear to result from recombination reactions of the chelate compound with bromine atoms at the high temperature of the mass spectrometer. A similar reaction of methyl radicals with the cobalt-phthalocyanine nucleus occurs in the mass spectrum of methylcobaltphthalocyanine.[29]

TABLE 6

The electronic spectra of the cobalt(III) compounds in the region 30 ⟶ 5 kK. Bands appearing as shoulders are given in parentheses, and the extinction coefficients in square brackets

Compound	Phase	Observed bands (kK) [a]						
[Co(aben)Cl]	Solid				18·4	12·8br		6·0
	$(CH_3)_2SO$ soln	28·3br ([10,900]	(23·9) [6500]	(20·3) [1800]	19·4 [1900]	12·8 [6800]	(9·5) [430]	~5·5 [360]
	DMF soln	26·5 [12,100]	23·0 [15,200]	(19·5) [2100]	18·8 [2200]	13·2 [4800]	(9·6) [730]	~6 [500]
[Co(aben)Br]	Solid				18·4	12·3br		~6
	DMF soln	26·5 [11,400]	23·0 [13,400]		18·6 [1500]	12·9 [3200]	(9·4) [200]	~6 [200]
[Co(aben)I]	Solid				(18·4)	12·6br		~6
	DMF soln	26·5 [11,400]	23·0 [13,500]		18·7 [1600]	12·7 [3200]	(9·3) [300]	~5 [200]
[Co(abpn)Cl]	Solid				18·6	11·7br	(9·6)	~6
	$CHCl_3$ soln	28·2br [6000]			18·8 [1500]	13·0 [3500]	(9·5) [700]	7·1 [500] ~6 [350]
	$(CH_3)_2SO$ soln	27·8br [5600]	(23·7) [3500]		19·4 [1900]	12·8 [3700]	(9·4) [250]	~5·5 [200]
	DMF soln	26·6 [9100]	23·1 [8200]		18·9 [2000]	13·1 [4100]	(9·4) [300]	~5·5 [200]
[Co(abpn)Br]	Solid				18·6	11·7br	(9·6)	~6
	DMF soln	26·5 [11,400]	23·0 [13,200]		18·6 [1500]	12·8 [3000]	(9·3) [200]	~6 [150]
[Co(abpn)I]	Solid					13·1br		5·6
	CH_2Cl_2 soln	27·8 [6000]		19·6 [1600]	19·6 [1600]	12·4 [3200]	(9·5) [600]	~6 [300]
	DMF soln	26·4 [12,100]	23·0 [14,900]		18·7 [2100]	12·6 [5000]	(9·4) [350]	~5·5 [300]
[Co(aben)Cl]	Py soln		(22·0) [6000]	21·4 [6100]		12·4 [500]	(9·3) [70]	~6 [40]
[Co(aben)Br]	Py soln		(22·1) [6050]	21·4 [6100]		(12·6) [300]	(9·3) [80]	~6 [50]
[Co(aben)I]	Py soln	26·9 [4300]	(22·1) [7600]	21·5 [7700]	(17·5) [1100]	(12·6) [280]	(9·5) [40]	~5·5 [30]
[Co(abpn)Cl]	Py soln	26·4 [4300]	22·5 [5700]	21·4 [5500]	(18) [2000] (16·5) [1100]	12·3 [800]	(9·4) [100]	~6 [70]
[Co(abpn)Br]	Py soln	26·9 [7000]	22·9 [5900]	21·4 [6000]	17·4 [2600]	(12·6) [600]	(9·3) [170]	~6 [90]
[Co(abpn)I]	Py soln	26·5 [3500]	(22·2) [6400]	21·4 [6600]	(17·6) [1300]	12·6 [400]	(9·3) [50]	~5·5 [40]
[Co(abphen)Cl]	$(CH_3)_2SO$ soln		24·5 [11,000]		(18·9) [3800]	(17·7) [3100]		(12·3) [600]
	DMF soln		25·2 [14,100]	23·0 [13,900]	(18·6) [4600]	(17·6) [4400]	(15·5) [2400]	(12·5) [370]
[Co(abphen)Br]	CH_2Cl_2 soln		25·4 [15,000]	(23·3) [13,000]	(19·7) [4700] (18·5) [4000]	(16·2) [2200]	(15·6) [2000]	(14·2) [1000] 12 [400]
	DMF soln	(26·8) [13,300]	25·2 [15,000]	23·0 [14,000]	(19·7) [4900] (18·5) [4300]	(17·5) [4000]	(15·5) [2500]	(13·9) [1000] 12·4 [500]
[Co(abphen)I]	DMF soln	(26·7) [13,000]	25·2 [14,000]	23·0 [13,600]	(19·6) [4800]	(17·6) [4400]	(15·5) [2300]	(14·0 [1000] (12·4) [350]
[Co(abphen)Cl]	Py soln	27·0 [13,400]	21·7 [11,000]	(19·9) [8300]	17·3 [8000]			
[Co(abphen)Br]	Py soln	27·1 [14,000]	21·9 [10,500]	20·0 [8000]	17·4 [7800]			
[Co(abphen)I]	Py soln	27·1 [14,000]	22·1 [11,700]	19·5 [8500]	17·5 [8800]			

[a] For the reflectance spectra of the solids, we quote only the bands below 20 kK. The higher energy bands were not resolved by our instrumentation.

The electronic absorption spectra of the compounds

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[28] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1969, 2637.

[29] P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc.* (*A*), 1968, 90.

[Co(L)X] are quite unlike those of normal octahedral cobalt(III) compounds (Table 6 and Figures 5 and 6). The aben and abpn compounds have a band at ~13 kK in the solid state and in solutions in non-donor solvents (including here Me_2SO and DMF) with an extinction coefficient for the latter of 3000—7000, together with reasonably intense bands at *ca.* 9 and 6 kK. The solvent dependence of the intensity of these bands also is quite marked—compare [Co(aben)Cl] in Me_2SO and DMF. Rather different spectra are observed for the abphen compounds, as noted below.

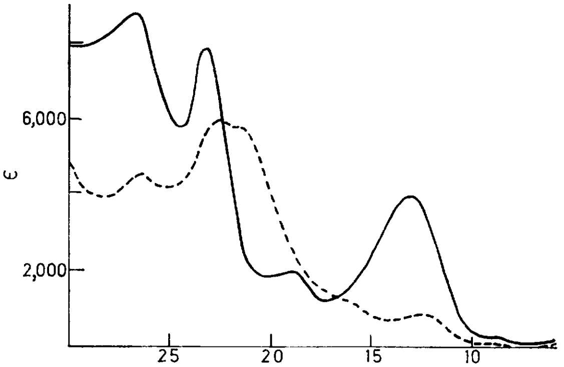

FIGURE 5 The electronic absorption spectra of [Co(abpn)Cl] in DMF (——) and pyridine (- - - -)

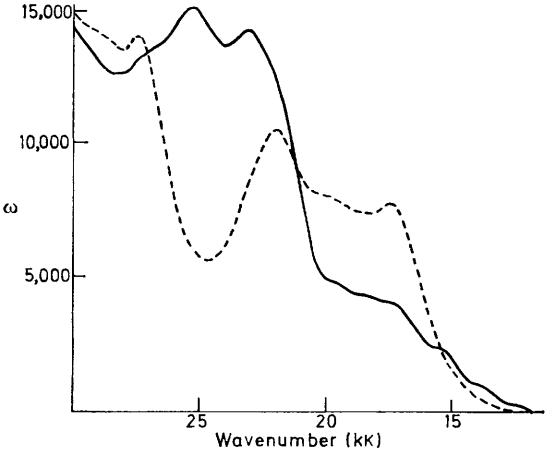

FIGURE 6 The electronic absorption spectra of [Co(abphen)Br] in DMF (——) and pyridine (- - - -)

Those of the aben and abpn compounds give a useful measure of the equilibria (VI) which exist in solutions in

$$[Co(L)X] + solvent \rightleftharpoons [Co(L)(solvent)X]$$

(VI)

donor solvents such as pyridine and water. For example, the compound [Co(abpn)Cl] in pyridine shows residual intensity in its spectrum the regions 13, 9, and 6 kK. This is consistent with the presence of 20—25% of the paramagnetic species [Co(abpn)Cl] in equilibrium in the solution with the diamagnetic six-co-ordinate species [Co(abpn)py)Cl].

In agreement with this, a figure of 20% paramagnetic species is calculated from the paramagnetic susceptibility (^1H n.m.r. method) of the pyridine solution [$\chi_M = 683$ (c.g.s. units × 10^6)]. Further evidence is given by the ^1H n.m.r. spectrum in perdeuteriopyridine. Here the resonances of the residual protons of the pyridine are sharp and not significantly shifted, whereas those of the protons of the quadridentate ligand are broad unresolved peaks, with large paramagnetic contact shifts.

From the various spectra, it appears that the amount of the paramagnetic species in the equilibria in pyridine decreases in the orders Cl > Br > I and abpn > aben (> abphen).

A solvation effect on the equilibria (VI) in water and aqueous acetone also is observed. In water, the brown solution of [Co(abpn)Cl] gives only a low intensity shoulder in its spectrum at ~13 kK. But, on the addition of an equal volume of acetone the solution turns green, and the intensity of the band which develops at 12·5 kK ($\varepsilon \geq 3200$) indicates that most, if not all, of the compound is now present in the paramagnetic form. There is an interesting parallel here with the Lifschitz nickel(II) compounds.[30]

Variations in colour of the aqueous solutions with pH also have been observed, but not yet investigated. These undoubtedly involve, at least partly, protonation and deprotonation of the terminal nitrogens of the quadridentate ligands.

The spectra of the abphen compounds (Figure 6) are rather different from those of aben and abpn. In particular, in DMF and chloroform there are a number of narrow bands—none fully resolved—in the visible region, and there is no prominent high intensity peak at *ca.* 13 kK. (A shoulder is generally evident here, but of much lower intensity than for the compounds of the other ligands.) We could not obtain reasonable diffuse-reflectance spectra of the solids—perhaps because of the lack of well-defined bands in the visible and near i.r. regions. So we are unable to correlate the solutions with the paramagnetic solids from their spectra. (They were insufficiently soluble for magnetic measurements in solution.) However, in pyridine the spectra are quite different (Figure 6) and thus consistent with a change in spin-state. If this is so, then, because of the complete change in spectra, it follows that the compounds [Co(abphen)X] are present almost if not completely as the six-co-ordinate diamagnetic species [Co(abphen)(py)X] in pyridine.

A further more detailed study of these systems is in progress, together with extensions to other related ligand systems and other metals.

The occurrence of the unusual paramagnetism in these compounds can be rationalised in various ways. In ligand-field terms, we see it as resulting from a tetragonal structure with a strong in-plane ligand-field of the Schiff's base ligand, and a weak axial ligand-field of the halogen.

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[30] I. Lifschitz, J. G. Bos, and K. M. Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97; I. Lifschitz and F. L. M. Schouteden, *Rec. Trav. chim.*, 1939, **58**, 411.

In simplest terms, this could result, for example, in the d_{xy} and d_{z^2} orbitals being of similar energy, and hence a $(d_{xz})^2(d_{yz})^2(d_{xy})^1(d_{z^2})^1$ configuration for the metal. An increase in the axial ligand-field with the addition of pyridine (in the diamagnetic species) could then separate the d_{xy} and d_{z^2} levels sufficiently to give a $(d_{xz})^2(d_{yz})^2$-$(d_{xy})^2$ configuration.

Of course, other rationalisations are possible and a molecular-orbital approach is probably more applicable; but the above approach allows one also to rationalise why such paramagnetic species have not been observed previously. None have been observed in the salicylaldimine and related N_2O_2 systems, and this is paralleled by the different stereochemistry of the metal(II) compounds of these N_2O_2 ligands and our N_4 ligands (see above discussion and refs. 3 and 4). Both can be rationalised in terms of the ligand-field strengths of the quadridentate ligands.[3,4]

The other related dianionic N_4 ligands which have been studied are largely macrocycles such as the porphyrins. Here the ' hole ' in the ligand may be too large to allow an in-plane ligand-field as strong as in the ab series of ligands. M–N Bond distances would be 2·01 Å for an undistorted porphyrin ligand framework, but can be very much shorter in our more flexible ligands.

The few other known examples of ' cobalt(III) ' compounds which appear to have a spin-triplet ground or close-lying excited state are several bisdithiolene compounds,[31] for which a four-co-planar structure is proven,[32] and the compound $[Co(PEt_3)_2Cl_3]$ which appears to have a trigonal bipyramidal structure.[33]

(ii) *' Second-stage ' reactions.* Second-stage reactions with halogens, as yet ill-defined, have been observed with most of these species. In the spectrophotometric titrations of [Co(abpn)] with bromine and iodine, changes in the spectra were observed beyond the 1 : 1 end-point and for the [Co(abphen)] titrations the second-stage reactions also gave isosbestic points (Figure 3b). Regular changes in the spectra were still occurring up to a 3 : 1 ratio of halogen to metal, so these changes probably indicate the formation of polyhalogen compounds such as $[Co^{III}(abphen)Br_3]$. One attempt to prepare the compound $[Co^{III}(abpn)Br_3]$ gave an amorphous black solid.

Less easily rationalisable is the observation of a second-stage reaction with $CHCl_3$ or CCl_4. The compounds [Co(L)Cl], as usually obtained from these solvents, gave high chlorine analyses (Table 1) and usually, but not invariably, the reaction in hot $CHCl_3$ gave solids with a Cl : Co ratio greater than 2 : 1. The *X*-ray powder photographs of these latter showed almost complete lack of crystallinity, and the samples gave very poorly defined i.r. spectra. Thus there is no way of determining purity and/or uniqueness of the species.

In Figure 7 we represent the *X*-ray diffraction patterns (powders) of several different preparations of Co(abpn)-Cl_x, in which x varies between 1 and *ca.* 2. As x increases, the crystallinity of the whole sample decreases—the lines become more diffuse—until when x is near 3 the samples are completely amorphous.

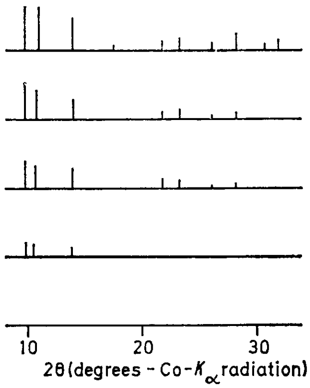

FIGURE 7 The *X*-ray powder diffraction patterns of the $Co(abpn)Cl_x$ species for which x varies between 1 and *ca.* 2·5. The value of x varies from the top to the bottom of the figure. For higher values of x, no significant diffraction of the *X*-rays was observed

These second-stage products were significantly less volatile in the mass spectrometer than the monochloro-compounds, but gave weak peaks corresponding to the species [Co(L)Cl] and very strong HCl peaks. Their magnetic moments (Table 1) are significantly smaller than those of the monochloro-compounds. Perhaps further work on related systems will help to clarify the problem of their structure.

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[1/1330 *Received, July 30th,* 1971]

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[33] K. A. Jensen, B. Nygaard, and C. Th. Pedersen, *Acta Chem. Scand.*, 1963, **17**, 1126.