

Paramagnetic Cobalt(III) Compounds of Chromophoric Type $[\text{Co}(\text{N})_4\text{X}]$. Part II¹. Further Preparations, Spectral Data, and Some Reactions.

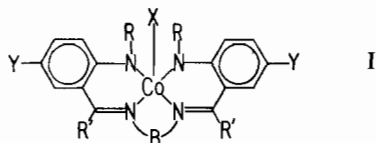
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A further extension is reported of the series of five-coordinate cobalt(III) compounds $[\text{Co}(\text{N})_4\text{X}]$ ($X = \text{Cl}, \text{Br}$), derived from quadridentate dianionic Schiff base ligands such as 1,2-bis-(*o*-iminobenzylideneimino)-ethane. In this new series, the effects of both electron-donating and -withdrawing ligand substituents have been investigated. Solid, crystalline compounds were isolated by oxidising the previously reported cobalt(II) species, and they were characterised by their *i.r.* spectra and X-ray powder diffraction patterns. All have room-temperature magnetic moments of ~ 3 B.M., attributable to thermal population of a triplet state of the molecule, and they have characteristic electronic spectra with a strong absorption at $12,000 \rightarrow 13,000 \text{ cm}^{-1}$ ($\epsilon \leq 9000 \text{ l M}^{-1} \text{ cm}^{-1}$).

No systematic trends were observed in the magnetic susceptibilities. In pyridine, the paramagnetic species are in equilibrium with two diamagnetic ones – $[\text{Co}(\text{N})_4\text{X}(\text{py})]$ and $[\text{Co}(\text{N})_4(\text{py})_2]^+$ – to an extent determined by the substituents on the quadridentate N_4 ligand. The compounds are not very robust, especially in solution. For example, in wet DMF, water causes quite rapid reduction to cobalt(II) and in dry DMF another, unidentified, slower reaction occurs. Such reactions led to errors in some of the details of the spectra reported in Part I. These are now corrected.

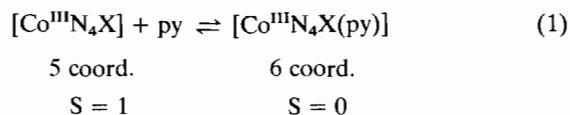
Introduction

We have previously reported^{1,2} that some cobalt(III) compounds of type I ($X = \text{Cl}, \text{Br}, \text{I}$)



have a thermally accessible $S = 1$ spin state (magnetic moments near 3 B.M. at room temperature) and that equilibria (1) exist in solutions in donor solvents such as pyridine.

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A further study of these was undertaken to obtain single crystals of one such compound suitable for an X-ray structural determination³, and to help define the origin and the limits of the $S = 1$ spin state here. To this end, we have studied the effect of both electron-withdrawing and electron-donating substituents on the ligands (R, R' and Y of I) and variations in the middle chelate ring (B of I).

Experimental

Preparation of Compounds

All compounds were prepared by oxidation of the cobalt(II) species⁴ as before¹. Bromine in dichloromethane was used for the bromo compounds, whereas the chlorides were usually prepared by dissolving the cobalt(II) compound in chloroform and setting the solution aside at room temperature. The crystalline solids isolated and characterised are listed in Table I.

The chloro compounds often separated as crystalline solvates, which showed the expected initial instability to loss of solvent, but some were surprisingly reluctant to lose all of this solvent. For example, $[\text{Co}(\text{cappn})\text{Cl}]\text{CHCl}_3$ lost solvent in the air at room temperature, reaching an apparent equilibrium at $\sim 0.8 \text{ CHCl}_3$; heating at 100°C for 15 h *in vacuo* reduced it to 0.4 CHCl_3 ; and further loss of solvent under these conditions was very slow (still 0.3 CHCl_3 after another 15 h). The X-ray powder diffraction patterns showed that the initial crystalline solvate was being replaced by a crystalline non-solvate.

The two different forms of $[\text{Co}(\text{appn})\text{Cl}]$ were obtained from two different preparations of the same CHCl_3 solvate. For the α -form, the sample had been set aside at room temperature for several days and then heated *in vacuo* for 6 h; for the β -form, a freshly prepared sample was heated *in vacuo* at 100°C for 17 h.

TABLE I. The Compounds Prepared, the Analyses, and the Key to the Ligand Abbreviations Used.

Compound	Abbreviation (refer I)				Analyses							
	R	R'	Y	B	Found				Calculated			
					C	H	N	Halogen	C	H	N	Halogen
[Co(abn)Br] ^a	H	H	H	CH ₂ C(Me) ₂	48.8	4.5	12.8	Br, 25.2	49.6	4.7	13.1	Br, 18.8
[Co(maben)Br] ^a	Me	H	H	(CH ₂) ₂	47.6	4.4	13.5	Br, 28.7	50.1	4.7	13.0	Br, 18.5
[Co(amen)Br]	H	Me	H	(CH ₂) ₂	49.1	4.4	12.5	Br, 18.5	50.1	4.7	13.0	Br, 18.5
[Co(appn)Cl]CHCl ₃	H	Ph	H	CH ₂ CH(Me)	61.3	4.1	7.6	Cl, 16.7	55.9	4.2	8.7	Cl, 22.0
α -[Co(appn)Cl]					65.4	5.0	10.7	Cl, 6.9	66.4	5.0	10.7	Cl, 6.8
β -[Co(appn)Cl]					65.3	5.1	10.9	Cl, 6.9	66.4	5.0	10.7	Cl, 6.8
[Co(capen)Cl]CHCl ₃	H	Ph	Cl	(CH ₂) ₂	50.4	3.6	7.5	Cl, 30.1	49.8	3.3	8.0	Cl, 30.4
[Co(capen)Cl]					57.9	4.1	9.5	Cl, 18.2	58.0	3.8	9.7	Cl, 18.3
[Co(capen)Br]					56.3	3.9	9.5	Cl, 11.6	53.9	3.6	9.0	Cl, 11.4
[Co(capen)Br]DMF					53.9	4.4	9.3	Br, 13.1 ^b	53.4	4.2	10.0	Br, 12.8
[Co(capen)Br](CH ₂ Br) ₂					43.5	3.5	6.8	Cl, 10.7	44.4	3.2	6.9	Cl, 10.2
[Co(cappn)Cl]nCHCl ₃ ^c	H	Ph	Cl	CH ₂ CH(Me)	52.0	3.9	8.0	Cl, 8.2	51.8	3.6	8.1	Cl, 8.7
					53.8	3.9	9.0	Br, 27.6 ^b	54.8	3.8	8.7	Br, 29.5
					55.6	3.9	9.0	Cl, 28.0	55.9	3.9	8.9	Cl, 28.0 (n=0.8)
					54.8	4.0	9.0	Cl, 24.0	54.6	3.8	8.8	Cl, 23.6 (n=0.4)
					54.8	4.0	9.0	Cl, 21.8	55.9	3.9	8.9	Cl, 22.0 (n=0.3)
					54.8	4.0	9.0	Cl, 10.9	54.6	3.8	8.8	Cl, 11.1
					57.1	4.2	9.4	Br, 12.3 ^b	58.7	4.1	9.4	Br, 12.5
[Co(cappn)Br]DMF ^d	H	Ph	Cl	(CH ₂) ₃	57.1	4.2	9.4	Cl, 20.2	58.7	4.1	9.4	Cl, 17.9
[Co(captn)Cl]					54.5	4.0	9.0	Cl, 11.1	54.6	3.8	8.8	Cl, 11.1
[Co(captn)Br]					54.5	4.0	9.0	Br, 12.5 ^b	54.6	3.8	8.8	Br, 12.5

^a These samples clearly were impure, but the electronic spectra prove that they were mainly the paramagnetic cobalt(III) species. ^b The analyses were for total halogen, and the figures are calculated on the assumption of the appropriate

Cl : Br ratio. ^c See Experimental. ^d It was obtained only in very small yield and was not analysed, but is characterised by the spectroscopic data.

$[Co(capen)Br]$ forms an unstable CH_2Cl_2 solvate, which readily loses all solvent in the air. It was successfully recrystallised from DMF, but not in good yield (see Results and Discussion on reactions in this solvent). The product was a DMF solvate; and a preparation from 1,2-dibromoethane, using bromoform as oxidant, gave a dibromoethane solvate.

$[Co(cappn)Br]$ also separated as an unstable CH_2Cl_2 solvate, and was obtained in very low yield as a DMF solvate when recrystallised from this solvent.

Preparations of $[Co(amen)Br]$ and $[Co(maben)Br]$ gave products with well-defined X-ray powder patterns, but the i. r. spectra usually had broad peaks and the microanalyses showed that they were impure.

Various attempts to prepare $[Co(abtn)Cl]$ and $[Co(abtn)Br]$ gave black powders. However, they were amorphous; the i. r. spectra had broad bands and the diffuse reflectance electronic spectra were featureless. An intermediate tan-brown compound separated when $[Co(abtn)]$ was added to CCl_4 . It was a well-defined crystalline species – probably a CCl_4 solvate – but we have not attempted to characterise it fully.

Physical Measurements

Details were given in Part I¹. The reactions in DMF were followed spectrophotometrically on a Unicam SP1800 instrument.

Results and Discussion

The cobalt(III) compounds (Table I) were all intensely coloured – usually dark green or black. They were characterised by their X-ray powder diffraction patterns and i. r. spectra (Table II).

The diffuse reflectance spectra (Table III), with the characteristic high intensity bands at $12 \rightarrow 13 \times 10^3 \text{ cm}^{-1}$ and weaker ones ($\epsilon_{\text{max}} \sim 500 \text{ l mol}^{-1} \text{ cm}^{-1}$) at ~ 9 and $4 \rightarrow 6 \times 10^3 \text{ cm}^{-1}$, characterise the present compounds as further examples of the five-coordinate³ paramagnetic cobalt(III) species previously described^{1,2}. Even when we have been unable to isolate pure samples of the cobalt(III) compounds of some of the ligands, these spectra are used as proof that the typical paramagnetic species are obtainable in these systems (Table III).

Magnetic moments (Table II) for the new species are all close to those previously described ($\sim 3 \text{ B.M.}$). No systematic variations are discernible in these room temperature moments.

Spectra and Reactions in Solution

The electronic spectra (Table III) have been measured in various solvents to define further the positions of the equilibria (1). As discussed in Part I¹, there is a marked diminution in the intensity of the band at 12

TABLE II. Some of the Physicochemical Data.

Compound	μ_{eff} (B.M.) ^a	I. r. (ν_{NH} in cm^{-1}) ^b	X-ray Powder Diffraction Lines (d spacings) ^c
$[Co(abbn)Br]$		3250s,sp	
$[Co(maben)Br]$		3240s,sp	11.4s, 9.34s, 6.95w, 5.92vw, 4.69vs, 4.51m
$[Co(amen)Br]$		3160s,br	12.7w, 12.2vw, 10.4vs, 9.09vw, 8.42m, 8.03w
$[Co(appn)Cl]CHCl_3$		3235s, (3215)m	13.0s, 11.8vw, 11.5w, 8.35m, 4.67m, 4.31m
α - $[Co(appn)Cl]$			10.9s, 9.17w, 8.03w, 7.24vw, 6.43m, 5.18w
β - $[Co(appn)Cl]$	2.8 (293)	3240s, 3215s	11.5m, 9.51w, 8.85w, 6.20vw, 5.88s, 5.51vw
$[Co(capen)Cl]CHCl_3$	3.0 (300)	3235s	13.9vs, 7.79m, 6.86w, 6.35m, 5.54w, 5.39s
$[Co(capen)Cl]$		3240s	15.3vw, 13.5vs, 12.5vs, 9.9vw, 7.50vw, 6.20s
$[Co(capen)Br]$	2.6 (300)	3245s,sp	13.2vs, 7.67m, 6.56w, 5.95s, 5.54w, 4.80vw
$[Co(capen)Br]CHCl_3$			13.9vs, 7.79m, 6.28m, 6.02w, 5.66w, 4.94w
$[Co(capen)Br]DMF$		3240s,sp	14.1vs, 8.03w, 7.85m, 6.86w, 6.64w, 6.20s
$[Co(capen)Br](CH_2Br)_2$		3245s,sp	14.1vs, 10.5vw, 8.10m, 7.04m, 6.35w, 6.09vw
$[Co(cappn)Cl]0.8CHCl_3$	2.8 (300)	3220s, (3200)m	d 12.2vs, 11.2w, 7.61w, 7.45w, 6.13m
$[Co(cappn)Cl]$			d 12.7vs, 11.7m, 8.16w, 7.61w, 7.04s, 6.32m
$[Co(cappn)Br]$	3.0 (301)	3230s,sp	14.1w, 13.0s, 11.7s, 7.14m, 7.04vw, 6.39m
$[Co(cappn)Br]DMF$		3235s,sp	13.2m, 12.1s, 11.4m, 8.49m, 7.79m, 7.45vw
$[Co(captn)Cl]$ ^e	3.1 (300)	3250s,sp, 3205s,sp	17.1vw, 12.1vs, 9.34m, 8.16s, 7.61w, 7.40m
$[Co(captn)Br]$ ^e	3.1 (298)	3245s,sp, 3210s,sp	16.8vw, 12.1vs, 9.42m, 8.57vs, 8.29m, 7.67vw

s = strong, m = medium, w = weak, v = very, sp = sharp

^a The temperature of the measurement is given in parentheses (Kelvin). ^b Bands occurring as shoulders are given in parentheses. The DMF solvates were characterised by a strong absorption at 1675 cm^{-1} . ^c Only the first six observed lines are listed. They should serve to identify species. ^d All the observed patterns were of mixtures. We include here only the lines which we can assign with confidence to the separate species. ^e These two are isomorphous.

TABLE III. The Electronic Spectra.

<i>Diffuse Reflectance and Solutions in CH₂Cl₂, CHCl₃, and DMSO</i>		
Compound		Observed Bands (10 ³ cm ⁻¹) ^a
[Co(abbn)Br]	[Solid] [CH ₂ Cl ₂]	30—22 ^b , 18.0, 12.0, (9), ~6 ^c 29.4[10000], (27.4)[9000], (24.9)[6800], 18.8[2000], 12.9[6600], (9.7)[1300], 5.8[500]
[Co(maben)Br]	[Solid]	30—22 ^b , (18), 12, ~6.5 ^c
[Co(amen)Br]	[Solid]	(poorly resolved) 13.5, ~7 ^c
[Co(caben)Cl]	[Solid]	(27), 25, (23), 17.8, 12.5, ~6 ^c
[Co(apen)Cl]	[CHCl ₃]	— d —, 13.0[3700], (9.9)[650], 6.5[400]
[Co(appn)Cl]	[Solid]	30—22 ^b , 18.2, 13.8, (9.4), ~5 ^c
	[DMSO]	27.5[10300], (23.4)[5800], 19.2[1900], 12.9[8500], (9.3)[400], ~5[550]
[Co(capen)Cl]	[Solid]	(27.0), 25.0 (23.5), 17.7, 12.7, ~5.5 ^c
	[DMSO]	— d —, 13.7[8000], (9.5)[600], ~5[600]
[Co(capen)Br]	[Solid]	30—21 ^b , 17.5, 12.5, ~5.5 ^c
	[CH ₂ Cl ₂]	28.9[11900], (24.0)[7900], (22.6)[6500], 18.0[2500], 12.5[9200], (9.6)[1000], 5.6[500]
	[DMSO]	27.4[12200], (26.6)[11900], (23.1)[6400], 18.5[2700], 12.5[9400], (9.4)[760], 5.3[700]
[Co(cappn)Cl]	[Solid]	(26.5), 25.3, (24.0), 17.7, 12.7, ~5 ^c
	[DMSO]	27.2[10400], (22.8)[4900], 18.4[1700], 12.6[9000], (9.3)[500], ~5[700]
[Co(cappn)Br]	[Solid]	26 ^b , (23.5), (21.5), 17.7, 12.7, ~5.5 ^c
	[CH ₂ Cl ₂]	28.0[11000], (23.0)[7300], (22.4)[5800], 18.0[2500], 12.7[8600], (9.5)[500], 5.5[500]
	DMSO	— d —, 18.6[2500], 12.7[9100], (9.5)[600], 5[750]
Co(captn)Cl	Solid	26 ^b , (23.2), 21.2, 18.0, 12.8, (8.7), ~4.0
	DMSO	— d —, 12.0[2100]
Co(captn)Br	Solid	26.5 ^b , (21.5), 18.0, 12.3, (8.7), ~5 ^c
	DMSO	— d —, 12.0[2000]

DMF Solutions

These were quite unstable (see text), but extrapolation of some kinetic data allowed the estimation of extinction coefficients for the band at 12 → 13 × 10³ cm⁻¹ as follows:

Co(appn)Cl	13.3[≥7200]
Co(cappn)Br	12.5[≥8900]

Pyridine Solutions

Compound	Observed Bands (10 ³ cm ⁻¹) ^a
[Co(abbn)Br]	(22.2)[5700], 21.4[5800], 12.2[2300], 9.1[590]
[Co(appn)Cl]	d 12.3[3600], (9.5)
[Co(capen)Cl]	(25.3)[3700], (21.0)[6800], 20.5[6900], (19)[4200], (12.5)[≤100]
[Co(capen)Br]	(25.3)[3700], (21.2)[6600], 20.5[6900], (19)[3500], (12.5)[≤60]
[Co(cappn)Cl]	(24.8)[4200], 21.3[6100], 20.5[6100], (19)[4000], 11.9[1000]
Co(cappn)Br	(24.8)[4300], (21.1)[6900], 20.4[7100], (19)[4300], 12.0[700]
Co(captn)Cl	(24.8)[3600], 21.8[6900], (17.6)[3900], (13)[~90]
Co(captn)Br	(24.9)[3700], 21.8[7400], (17.8)[2100], (13)[~60]

^a Band appearing as shoulders are given in parentheses, and extinction coefficients in square brackets. ^b A very broad envelope, in which the individual bands were not well-resolved. ^c Vibrational overtones obscure the exact position of the band here. ^d The u.v. region was not measured.

→ 13 × 10³ cm⁻¹ when the compounds are dissolved in pyridine, and this was explained by the formation of a diamagnetic six-coordinate species, as in (1).

Exact definition of such equilibria requires quantitative data on the spectra in various non-donor solvents, but there are problems here. Few of the compounds

were sufficiently soluble in such clearly non-donor solvents as CHCl₃ and CH₂Cl₂. Further, although DMF and DMSO were found to be good solvents, without apparent donor properties, a variety of decomposition reactions occur in them, and these limit attempts to determine extinction co-efficients (see below). Such

reactions also led to errors in the spectra reported in Part I for the region $18 \rightarrow 30 \times 10^3 \text{ cm}^{-1}$. So Figure 1 is given to show a fully characterised spectrum of one of the paramagnetic species in the range $5 \rightarrow 30 \times 10^3 \text{ cm}^{-1}$.

Nevertheless, it has been possible to construct a useful table (Table IV), in which estimates are given of the amount of the paramagnetic species present in solution in pyridine, and these reveal some interesting trends. Concentrations of the paramagnetic species in pyridine range between $\sim 40\%$ for $[Co(\text{appn})Cl]$ and $< 1\%$ (scarcely detectable) for $[Co(\text{capen})Cl]$.

The earlier data had shown that the concentration of the paramagnetic species decreases for different X in the order $Cl > Br > I$; we now also have for the quadridentate ligands $bn > pn > en \cong tn$, and $ap > ab > cap$ species. That is, methyl substituents on the middle chelate ring have a significant steric effect on the addition of pyridine to the sixth co-ordination site of the cobalt (the pyridine restricts the space available to the methyl at the extremity of its vibrations). Both the electron-donating phenyl substituents on the azomethine carbon (ap series), and the electron-withdrawing chlorine on the phenylene ring, through altering the electron-den-

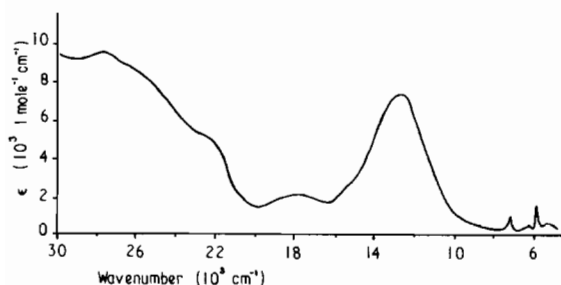


Figure 1. The electronic absorption spectrum of $[Co(\text{cappn})Br]$ in dichloromethane.

TABLE IV. Estimated Concentrations (%) of the Various Paramagnetic Species in Pyridine Solutions, Based on the Absorption Band at $12\text{--}13 \times 10^3 \text{ cm}^{-1}$ (the figure quoted in square brackets is the extinction coefficient used for the estimation. It was taken as the highest value observed for the various solutions in non-donor solvents).

Compound	% Paramagnetic		
	Cl	Br	I
$[Co(\text{aben})X]$	4 [6800]	2 [4000]	< 1 [3200]
$[Co(\text{abpn})X]$	15 [4000]	5 [4000]	2 [3200]
$[Co(\text{abbn})X]$		35 [6600]	
$[Co(\text{appn})X]$	40 [8500]		
$[Co(\text{capen})X]$	1 [9000]	0.5 [9400]	
$[Co(\text{cappn})X]$	11 [9000]	8 [9100]	
$[Co(\text{captn})X]$	4 [2100]	3 [2000]	

sity at the metal, have the expected effect on the addition of pyridine to the cobalt.

There is a further complication for the pyridine solutions, although it does not significantly alter the above discussion. This is the presence of a second (ionisation) equilibrium (2), which we were led to consider because of the long Co-Cl bond found in the X-ray



analysis³, and because of anomalies in the observed order for the amount of paramagnet present in solutions of the different halogeno species. The order $Cl > Br > I$ is contrary to that expected from the polarisabilities of the anions, and the magnitude of the differences between chloro- and bromo-species is variable (Table IV).

Certainly there is some ionisation in pyridine. Equivalent conductivities for freshly prepared $[Co(\text{appn})Cl]$, $[Co(\text{cappn})Cl]$ and $[PH_3MeAs]Cl$ in pyridine were found to be, respectively, 15, 10 and 42 mho (conc. = $2 \rightarrow 3 \times 10^{-4} M$). However, just these two results show that there is no direct relationship between the ionisation and the amount of paramagnet present, and that equilibrium (1) does predominate. Thus we have decided not to pursue the matter further.

There is an unexpected change in the electronic absorption spectrum of $[Co(\text{apen})Cl]$ when it is left in $CHCl_3$ (Figure 2). A strong, but different absorption is still present in the $12 \rightarrow 13 \times 10^3 \text{ cm}^{-1}$ region, which must indicate that a new paramagnetic cobalt(III) species is formed, and the most likely explanation is a reaction of $CHCl_3$ with the quadridentate ligand. In Part I, we described¹ amorphous compounds prepared from $CHCl_3$ solutions, and these had Cl:Co ratios of up to 3:1. They may be related to the reaction product of Figure 2, and all may represent products of chlorination of the donor NH groups.

Other reactions occur in DMSO and DMF. In the usual wet "lab reagent" solvents, reduction to Co^{II} occurs – characterised by the appearance of bands at

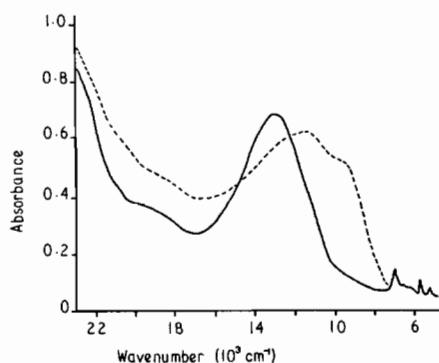


Figure 2. The electronic absorption spectrum of $[Co(\text{apen})Cl]$ in chloroform (full line – $1.93 \times 10^{-4} M$) and the change in spectrum observed after three days (dashed line).

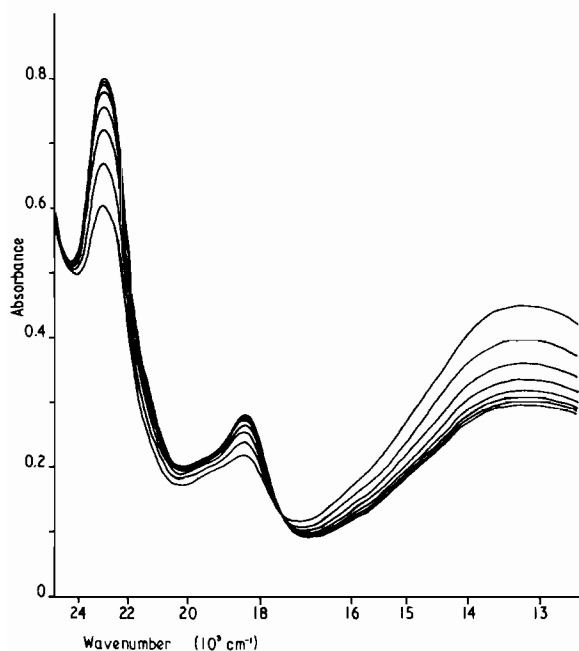


Figure 3. The electronic absorption spectra of [Co(appn)Cl] in wet DMF ($7.58 \times 10^{-5} M$), showing the decrease in intensity with time of the cobalt(III) band at $\sim 13,000 \text{ cm}^{-1}$ and the accompanying increase of the cobalt(II) bands at 18,500 and 23,000 cm^{-1} .

18.0 and $22.7 \times 10^3 \text{ cm}^{-1}$ (Figure 3). Suppression of this reaction by complete drying of the solvents indicates that water is the reductant. In DMF, in sealed spectrophotometer cells, the reactions are not first-order in metal compound, and markedly decelerate with time. No study has been made of the dependence on water concentration, nor of the presence of oxygen. However, the deceleration is probably associated with an approach to equilibrium (3), the forward reaction having been noted previously¹:



When the DMF solvent is pre-dried, another reaction occurs in which resolved bands are lost and no new ones appear (Figure 4). In several cases, when this reaction was being studied, the band at $\sim 23 \times 10^3 \text{ cm}^{-1}$, characteristic of cobalt(II), began to appear in the spectra, but this is attributable to the diffusion of water into the cell and the occurrence of the back reaction of equilibrium (3). For [Co(appn)Cl] and [Co(cappn)Br], the band characteristic of the paramagnetic cobalt(III) species at $\sim 13 \times 10^3 \text{ cm}^{-1}$ was monitored to give rate data and the extinction coefficient (by extrapolation to zero time). The reactions were initially first order in metal compound ($k = 0.41$ and 0.17 hr^{-1} , respectively, at 23°C) with a gradual deceleration after

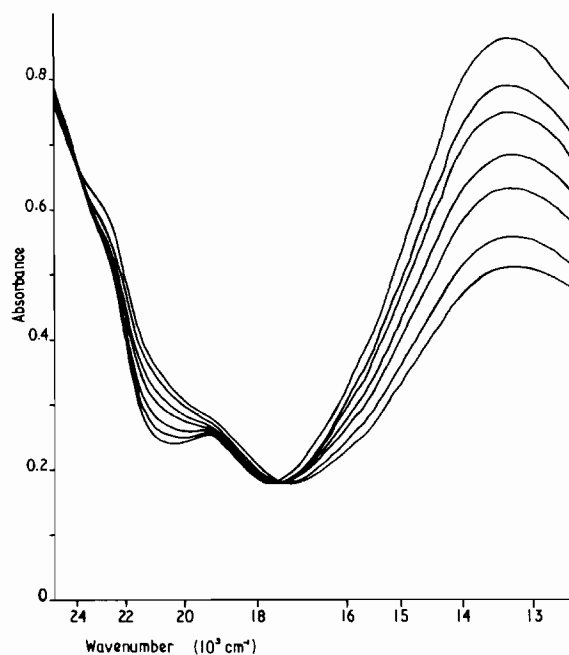


Figure 4. The electronic absorption spectra of [Co(appn)Cl] in dried DMF ($7.24 \times 10^{-5} M$), showing again the decrease in intensity of the cobalt(III) band at $\sim 13,000 \text{ cm}^{-1}$, but not this time accompanied by the formation of cobalt(II).

~ 3 and 0.5 hr , respectively. The reactant here has not been identified; it may be DMF, or some unidentified impurity.

Clearly, more work is required to characterise these reactions fully, but they do illustrate the instability of our cobalt(III) compounds.

Conclusions

It is clear from the X-ray structure³ that the magnetic results reported earlier² can now be accepted as resulting from a thermal equilibrium of $S = 0$ and $S = 1$ states. The solids are magnetically dilute and antiferromagnetism can be ruled out.

At least in the electronic spectra and room temperature magnetic moments of the solids, there is no significant effect observable of the present range of ligand skeletons and substituents, even though these markedly affect the redox properties of the metal(II) compounds. Differences may be observable in the populations of the triplet states at lower temperatures, but, from the present work, the only observable effect has been on the equilibria in pyridine.

The crystal structure³ of [Co(capen)Cl] shows that these compounds are definitely square-pyramidal five-coordinate; Co-N bond lengths are not abnormal, but

a remarkably long Co—Cl bond length is found {2.509 (7)Å}. These results are in keeping with the previous rationalisation of the paramagnetism^{1,2}; a low-lying triplet state could be explained, in crystal-field terms, to result from a strong in-plane ligand field and a weak axial field. Where the axial field is non-existent, as in the structurally related, but four-co-planar, anionic biuretato compounds⁵, the triplet state is fully populated even at low temperatures. This also is in keeping with the crystal field rationalisation, which, in such covalent compounds, must be partly fortuitous. However, we see no point at this stage in attempting a detailed molecular orbital description.

With the wide variety of macrocyclic and other anionic ligands now being studied, it will be interesting to see if other structural types of N_4 ligands can give similar paramagnetic cobalt(III) species.

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