Inorganica Chimica Acta, *74* (1983) 43–53

Metal Complexes with 2-Aminopyridine N-Oxide, Including N-Oxide-Bridged Complexes of Cobalt(II), Nickel(II) and Copper(II).
Further Studies on Related Pyridine N-Oxide Complexes

ARTHUR E. LANDERS and DAVID J. PHILLIPS*

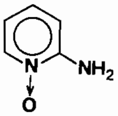
School of Chemistry, University of New South Wales, Kensington, N.S.W. 2033, Australia

Received March 11, 1983

Metal complexes of 2-aminopyridine N-oxide (Hapo) have been characterised by infrared spectra, X-ray powder diffraction spectra, and by magnetic measurements and electronic spectra to liquid nitrogen temperature. Neutral Hapo appears to be an O-donor ligand in almost every case, according to spectroscopic evidence. The $[M(Hapo)_6]X_2$ *complexes (M = Mn, Co and Ni; X drawn from* ClO_4, BF_4 *and* NO_3*) are octahedrally coordinated and* $[Cu(Hapo)_4](BF_4)_2$ *is square planar. The complexes* $Co(Hapo)_2Br_2 \cdot C_2H_5OH$, $Ni(Hapo)_2Br_2$, $Cu(Hapo)_2(NO_3)_2$*, and the copper(II) halide complexes, are all antiferromagnetic and N-oxide bridged. Such bridging pyridine N-oxide, whilst common with copper(II), is rare with cobalt(II) and nickel(II). The temperature dependence of the magnetism of* $Ni(Hapo)_2Br_2$ *has been compared to that for various models. Other Hapo complexes with cobalt(II) and nickel(II) halides appear to be halide-bridged. Some previously reported complexes with pyridine N-oxide (po), of the type* $M(po)Hal_2 \cdot H_2O$ *(M = Co, Ni), have been more fully characterised and are halide-bridged. The complexes* $[Fe(Hapo)_4Cl_2]Cl$ *and* $[(Cr(Hapo)_4Cl_2]Cl \cdot H_2O$ *have* trans-MO_4Cl_2 *coordination. The complex* $Cu(apo)_2$ *contains deprotonated O,N-bonded ligand. The complexes* $Cu(apo)_2$, $[Cu(Hapo)_4](BF_4)_2$, $Cu(Hapo)_2(NO_3)_2$ *and the metal perchlorate complexes have been previously reported, the remaining complexes are new.*

Introduction

There are many examples of pyridine N-oxide bridged copper(II) complexes and they often exhibit strong magnetic interaction [1]. Very few complexes of this type are known with other metal ions. We have been studying complexes of pyridine N-oxide ligands containing donor substituents in the 2-position, in an attempt to broaden the range of N-oxide-bridged complexes [2–6]. We report complexes of 2-aminopyridine N-oxide (I, Hapo). Some N-oxide-bridged cobalt(II), nickel(II) and copper(II) complexes have been obtained, and antiferromagnetic interaction is found to be present.



(I, Hapo)

Prior to our work, Sigel and Brintzinger [7, 8] isolated the deprotonated complex $Cu(apo)_2$ and the complexes $[M(Hapo)_6](ClO_4)_2$ (M = Mg, Mn, Fe, Co, Ni, Zn) and $M'(Hapo)_4(ClO_4)_2$ (M′ = Cu, Ba). Formation constant studies, infrared spectra and solution electronic spectra were reported [7, 8]. West and co-workers have made detailed studies of complexes with several N-alkyl and N,N-dialkyl derivatives of Hapo, which behave as O or O, N donors [9–18]. After the completion of our work, West reported a study of some copper(II) complexes with Hapo [19]. The only compounds common to his and our work are $Cu(Hapo)_4(BF_4)_2$ and $Cu(Hapo)_2(NO_3)_2$, and we report additional magnetic and infrared spectroscopic data. We reported part of our work in a preliminary communication [2].

Results and Discussion

The complexes are listed in Table I, with analyses. All complexes contain neutral ligand, except for $Cu(apo)_2$.

---

*Author to whom correspondence should be addressed.

0020-1693/83/£3.00

© Elsevier Sequoia/Printed in Switzerland

TABLE I. Analytical Data.

Compound	Analyses % (Calculated and Found)				
	C	H	N	M	
$Cu(apo)_2$	42.6	3.6	19.9	22.5	light green
	42.4	3.7	19.9	22.3	
$Cu(Hapo)Cl_2$*	24.6	2.5	11.5	26.0	dark brown
	25.1	2.8	11.9	26.2	
$Cu(Hapo)_2Cl_2 \cdot H_2O$*	32.1	3.8	14.9	17.0	brown-red
	32.5	3.8	14.6	16.8	
$Cu(Hapo)_2Br_2 0.5C_2H_5OH$*	28.3	3.2	12.0	13.6	brown-red
	28.8	3.3	11.8	13.8	
$Cu(Hapo)_2(NO_3)_2$	29.4	3.0	20.6	15.6	yellow-green
	29.1	3.0	19.8	15.3	
$Cu(Hapo)_4(BF_4)_2$	35.5	3.6	16.5	9.4	green
	35.0	3.6	16.2	9.7	
$Ni(Hapo)Cl_2 \cdot H_2O$*	23.3	3.1	10.9	22.8	light yellow
	23.8	3.4	10.7	23.0	
$Ni(Hapo)_2Br_2$	27.4	2.8	12.8	13.4	light yellow
	27.7	3.0	13.1	13.2	
$[Ni(Hapo)_6](NO_3)_2 \cdot H_2O$*	41.8	4.45	22.8	6.8	light yellow
	41.6	4.4	22.8	7.0	
$[Ni(Hapo)_6](BF_4)_2 \cdot 2H_2O$*	38.8	4.3	18.5	6.3	dark yellow
	39.1	4.2	17.9	6.0	
$[Ni(Hapo)_6](ClO_4)_2$	39.2	4.0	18.3	6.4	yellow-brown
	39.2	4.1	17.5	6.5	
$Co(Hapo)Cl_2 \cdot C_2H_5OH$*	29.4	4.2	9.8	20.6	mauve
	28.9	4.1	9.8	20.7	
$Co(Hapo)_2Br_2 \cdot C_2H_5OH$*	29.7	3.7	11.6	12.2	dark blue
	29.4	3.6	11.2	11.9	
$Co(Hapo)_2Br_2 \cdot H_2O$*	26.3	3.1	12.3	12.8	mauve
	26.4	3.1	12.1	12.9	
$[Co(Hapo)_6](NO_3)_2 \cdot H_2O$*	41.8	4.4	22.8	6.8	pink
	41.8	4.2	22.6	7.0	
$[Co(Hapo)_6](ClO_4)_2$	39.5	4.0	18.3	6.4	dark pink
	38.7	3.9	17.9	6.2	
$[Mn(Hapo)_6](ClO_4)_2$	39.4	4.0	18.4	6.0	yellow
	39.5	3.9	18.1	6.4	
$Fe(Hapo)_4Cl_3$*	39.9	4.0	18.6	9.3	bright red
	40.2	4.2	18.7	9.0	
$Cr(Hapo)_4Cl_3 \cdot H_2O$*	38.9	4.3	18.2	8.4	crimson
	39.0	4.3	16.7	8.7	
$Cu(po)Cl_2$	26.5	2.3	6.1	–	green
	26.3	2.5	5.9	–	
$Ni(po)Cl_2 \cdot H_2O$	24.7	2.9	5.8	–	yellow
	25.0	3.1	5.8	–	
$Co(po)Cl_2 \cdot H_2O$	24.7	2.9	5.8	–	violet
	25.0	2.8	5.7	–	
$Ni(po)Br_2 \cdot H_2O$	18.1	2.1	4.2	–	brown
	18.3	2.3	4.2	–	

*New complexes.

Mode of Coordination by Hapo

This ligand has an N-oxide group and an amino-group and so it might be a bidentate ligand, or a unidentate O or N ligand. As discussed below, we consider that the complexes of the type $[M(Hapo)_6]X_2$ (X = ClO_4, BF_4, NO_3) contain unidentate O-bonded Hapo, because the complexes are ionic and six-coordinate and have electronic spectra similar to those for related 6:1 complexes with pyridine N-oxides [1]. Ligand infrared spectra are shown in Table II. The $[M(Hapo)_6]X_2$ complexes have N-oxide ν(NO) frequencies in the usual region for pyridine N-

TABLE II. Ligand Infrared Spectra (cm^{-1}).[a]

Compound	$\nu(NH_2)$	$\nu(CN)$	$\nu(NO)$
Hapo[b] ($CHCl_3$ solution)	3500, 3360	1340, 1255sh	
Hapo	[c]	1352m, 1255vw	1198vs
$Cu(apo)_2$	3307s (ν(NH))	1372m, 1302vs	1178vs
$Cu(Hapo)Cl_2$	[c]	1385w, 1280vs	1198vs
$Cu(Hapo)_2Cl_2 \cdot H_2O$	[c]	1379m, 1275s	1202vs
$Cu(Hapo)_2Br_2O \cdot C_2H_5OH$	[c]	1379m, 1275s	1199vs
$Cu(Hapo)_4(BF_4)_2$	3485vs, 3373vs	1372m, 1280m	1203vs
$Cu(Hapo)_2(NO_3)_2$	3445vs, 3338vs	1372w[d]	1198vs
$Ni(Hapo)Cl_2 \cdot H_2O$	[c]	1380m, 1282m, 1269m	1196vs
$Ni(Hapo)_2Br_2$	3378m, 3260m	1370m, 1274s, 1263m, 1243m	1211vs, 1191vs
$[Ni(Hapo)_6](BF_4)_2 \cdot 2H_2O$	3425s[e]	1368m, 1264w	1208vs, 1197vs
$[Ni(Hapo)_6](NO_3)_2 \cdot H_2O$	3340s[e]	1268w[d]	1208vs, 1195vs
$[Ni(Hapo)_6](ClO_4)_2$	3402s[e]	1367s, 1267w	1203vs, 1193s
$Co(Hapo)Cl_2 \cdot C_2H_5OH$	*ca.* 3530sb,[e]	1374w, 1278sb	1193vs
$Co(Hapo)_2Br_2 \cdot C_2H_5OH$	[c]	1363w, 1272sb	1208vs, 1197vs, 1182vs
$Co(Hapo)_2Br_2 \cdot H_2O$	[c]	1370m, 1272s	1210vs, 1199vs, 1187vs
$[Co(Hapo)_6](NO_3)_2 \cdot H_2O$	3345s,[c,e]	1270w[d]	1211vs, 1197vs
$[Co(Hapo)_6](ClO_4)_2$	3400s[e]	1359m, 1262w	1208vs, 1194vs
$[Mn(Hapo)_6](ClO_4)_2$	[c]	1360m, 1265w	1202vsb
$Cr(Hapo)_4Cl_3 \cdot H_2O$	3320s[e]	1365m, 1268m	1193vs
$Fe(Hapo)_4Cl_3$	3320se	1363m, 1272mb	1198vs

[a] Mull spectra, unless otherwise indicated. [b] From reference 23. [c] Broad, ill-defined absorptions. [d] Masked by anion absorption. [e] Complex absorption occurs in the range 3300–3100 cm^{-1}, making it difficult to identify $\nu_{sym}(NH_2)$.

oxide complexes [1]. The other Hapo complexes also have ν(NO) frequencies in this region and so N-oxide coordination is proposed for all the Hapo complexes.

The ν(NO) value (1192 cm^{-1}) for uncoordinated Hapo is lower than usual for a pyridine N-oxide ligand [1], and is similar to the values in the complexes. The low ν(NO) frequency in the free ligand is probably caused by hydrogen bonding between the N-oxide and amino-groups. Complex formation normally lowers ν(NO) in pyridine N-oxides, but with Hapo it would also break down hydrogen bonding and simultaneously tend to increase ν(NO) [1]. These two effects appear to approximately cancel out with Hapo, leading to no marked change in ν(NO) upon N-oxide coordination. With N-alkyl and N,N-dialkyl substituted derivatives of Hapo, hydrogen bonding should be reduced or eliminated. In keeping with this West *et al.* find that such ligands have more normal ν(NO) values (1206–1220 cm^{-1}) which decrease, upon N-oxide coordination, to give values (1178–1212 cm^{-1}) similar to those for our Hapo complexes [9–18].

We now consider whether amine coordination, as well as N-oxide coordination, occurs in any of the complexes. Coordination by aromatic amines generally leads to characteristic changes in i.r. spectra. With, for example, anilines and *o*-phenylenediamine, the $\nu(NH_2)$, $\delta(NH_2)$ and ν(CN) frequencies of the amino-group all decrease upon coordination [20–22]. Some complexes of *o*-phenylenediamine contain unidentate ligand. In this case, $\nu(NH_2)$ and ν(CN) frequencies corresponding to coordinated NH_2 groups are observed, with additional bands associated with the uncoordinated NH_2 group, at frequencies similar to or greater than the free ligand values [21, 22].

Accurate $\nu(NH_2)$ frequencies could not be obtained for all the Hapo complexes because the bands were sometimes broad and ill-defined. This is probably a result of hydrogen bonding. Some complexes exhibited two sharp bands, assigned to the asymmetric and symmetric $\nu(NH_2)$ vibrations. In other cases $\nu(NH_2)_{asy}$ was well defined, but several absorptions occurred at slightly lower frequencies, obscuring $\nu(NH_2)_{sym}$. The highest frequency band for the $[M(Hapo)_6]X_2$ complexes occurs in the range 3400–3340 cm^{-1}. A $\nu(NH_2)$ band in this region is, therefore, consistent with an uncoordinated NH_2 group, since the $[M(Hapo)_6]X_2$ complexes are considered to contain unidentate N-oxide-bonded

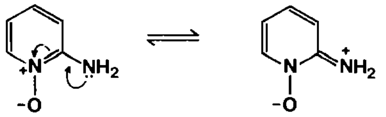
TABLE III. Magnetic Data.

Compound	μ_{eff} (B.M.)		θ (K)[a]
	298 °K	89 °K	
$Cu(apo)_2$	1.83	1.78	−2
$Cu(Hapo)Cl_2$	1.00	b	–
$Cu(Hapo)_2Cl_2 \cdot H_2O$	0.99	b	–
$Cu(Hapo)_2Br_2 0.5C_2H_5OH$	0.73	b	–
$Cu(Hapo)_2(NO_3)_2$	1.92	1.85	−8
$Cu(Hapo)_4(BF_4)_2$	1.94	1.90	−1
$Ni(Hapo)Cl_2 \cdot H_2O$	3.11	2.91	−17
$Ni(Hapo)_2Br_2$	2.97	2.15	−115[c]
$[Ni(Hapo)_6](NO_3)_2 \cdot H_2O$	3.44	3.30	−6
$[Ni(Hapo)_6](BF_4)_2 \cdot 2H_2O$	3.42	3.44	+2
$[Ni(Hapo)_6](ClO_4)_2$	3.23	–	–
$Co(Hapo)Cl_2 \cdot C_2H_5OH$	4.84	4.58	−14
$Co(Hapo)_2Br_2 \cdot H_2O$	4.91	4.64	−15
$Co(Hapo)_2Br_2 \cdot C_2H_5OH$	4.67	3.28	−90[c]
$[Co(Hapo)_6](NO_3)_2 \cdot H_2O$	5.25	4.89	−18
$[Co(Hapo)_6](ClO_4)_2$	5.17	–	–
$[Mn(Hapo)_6](ClO_4)_2$	5.93	–	–
$Cr(Hapo)_4Cl_3 \cdot H_2O$	3.90	3.93	+1
$Fe(Hapo)_4Cl_3$	5.85	5.97	+5

[a] Corresponds to θ in $\chi_A = C/(T - \theta)$. [b] Magnetic data at low temperature are not given for these strongly antiferromagnetic compounds, because of the considerable errors associated with measuring the low susceptibilities. [c] Deviates from linearity at low temperatures.

Hapo, as discussed later. Where $\nu(NH_2)$ bands are well-defined in our other Hapo complexes, the highest frequency band is in, or close to, the above range, suggesting that ligands with uncoordinated NH_2 groups are present in each case.

The $\delta(NH_2)$ mode for Hapo, in chloroform solution, was assigned by Katritzky *et al.* to a shoulder at 1592 cm^{-1}, with strong ring bands occurring at 1640 cm^{-1} and 1577 cm^{-1} [23, 24]. We were not able to definitely assign $\delta(NH_2)$ in our complexes. Katritzky and Jones have assigned the $\nu(CN)$ mode for Hapo (chloroform solution) to bands at 1340 cm^{-1} and 1255 (sh) cm^{-1}, respectively [23]. In the Hapo complexes these bands are *ca.* 10–30 cm^{-1} higher in frequency (in some cases they are slightly split). The frequency shifts indicate unidentate N-oxide coordination, which increases the contribution from canonical form (III). With the complex $Ni(Hapo)_2Br_2$, however, an additional band occurs at 1243 cm^{-1}. This is below the free ligand value and could be due to a coordinated NH_2 group. The complex might, therefore, contain one unidentate and one bidentate Hapo molecule.

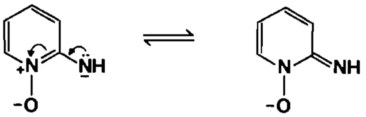


II III

Coordination by anilines produces a strong new band in the range 1185–1010 cm^{-1}, assigned to the NH_2 wagging mode of the coordinated amino-group [20]. With most of the Hapo complexes, no such absorption occurs. With $Ni(Hapo)_2Br_2$, however, a strong band occurs at 1038 cm^{-1}, in addition to the usual ligand bands found in the other complexes. This suggests that at least one bidentate Hapo molecule is present, in keeping with the conclusion from $\nu(CN)$ frequencies. Some additional broad absorption occurs for $Cu(Hapo)Cl_2$ at *ca.* 1050 cm^{-1}, so bidentate ligand may also be present, although there is no support for this from $\nu(CN)$ frequencies.

We stress that the above conclusions based on i.r. data are tentative, because we have no complex definitely containing bidentate Hapo, which could be used to check the validity of our bonding criteria.

The complex $Cu(apo)_2$ contains deprotonated ligand and its i.r. spectrum is difficult to interpret because no spectroscopic information is available about the free deprotonated ligand. The $\nu(CN)$ frequencies are above the values for Hapo. This is reasonable since canonical form (V), with C=N character, is probably important.



(IV) (V)

A single $\nu(N-H)$ band occurs at 3307 cm^{-1}. A similar $\nu(NH)$ band occurs at 3300 cm^{-1} in the complexes $Ni(NHC_6H_4NH)_2$ and $Ni(NHC_6H_4S)_2$ (of deprotonated *o*-phenylenediamine and *o*-aminobenzenethiol) which contain coordinated NH groups [25]. N-coordination is likely, therefore, for $Cu(apo)_2$. The $\nu(NO)$ frequency (1178 cm^{-1}) is below the value for Hapo and in the region for N-oxide complexes [1], and so bidentate coordination probably occurs.

Complexes of Copper(II)

The magnetic properties of the complexes are given in Table III. Reflectance spectra are listed in Table IV. Infrared spectra of anions are given in Table V. The low temperature magnetism of $Cu(apo)_2$ suggests that strong magnetic interaction is absent. The complex has bands at 13,500 and 18,000 cm^{-1} in its reflectance spectrum. Some square-planar CuN_2O_2 complexes, of Schiff bases and aminoacids, have spectra with bands in the regions

TABLE IV. Diffuse Reflectance Spectra.[a]

Compound	Temperature (K)	Absorption Maxima (cm^{-1} × 10^{-3})
$Cu(apo)_2$	298	13.5; 18.0
$Cu(Hapo)Cl_2$	298	12.6
$Cu(Hapo)_2Cl_2 \cdot H_2O$	298	12.0
$Cu(Hapo)_2Br_2 \cdot 0.5C_2H_5OH$	298	11.2
$Cu(Hapo)_2(NO_3)_2$	298	14.2
$Cu(Hapo)_4(BF_4)_2$	298	14.4sh, 16.0
$Ni(Hapo)Cl_2 \cdot H_2O$	298	7.5; 12.5; 19.8sh, 22.8
$Ni(Hapo)_2Br_2$	298	7.6sh, 8.6; 13.4; 19.5sh, *ca.* 22.5sh
$[Ni(Hapo)_6](NO_3)_2 \cdot H_2O$	298	7.7; 13.0sh; 15.5sh, 22.8sh
$[Ni(Hapo)_6](BF_4)_2 \cdot 2H_2O$	298	7.7; 13.0; 18.5sh, 22.7
$[Ni(Hapo)_6](ClO_4)_2$	298	7.7; 13.0sh, 13.8sh; 19.0sh, 22.5
	83	8.0, 13.0sh, 14.0; 19.2sh, 22.7
$Co(Hapo)Cl_2 \cdot C_2H_5OH$	298	7.5; 18.1
	83	6.7, 8.1; 17.9, 19.3sh, 20.8sh
$Co(Hapo)_2Br_2 \cdot C_2H_5OH$	298	6.5, 7.4sh; 10.6; 15.0sh, 17.3sh, 18.0, 19.5sh
	83	6.5, 7.5sh; 11.0; 14.6sh, 18.3
$Co(Hapo)_2Br_2 \cdot H_2O$	298	6.7; 17.3, 18.7sh; 21.0sh
$[Co(Hapo)_6](NO_3)_2 \cdot H_2O$	298	7.7; 14.0sh, 18.2
$[Co(Hapo)_6](ClO_4)_2$	298	6.8, 7.6; 14.2sh, 18.1
	83	6.6, 7.8; 15.0sh, 18.5
$Cr(Hapo)_4Cl_3 \cdot H_2O$	298	13.3; 17.7sh, 20.4
$Fe(Hapo)_4Cl_3$	298	8.8

[a] Strong charge transfer/ligand absorption commences above *ca.* 20,000 cm^{-1}.

TABLE V. Infrared Spectra of Anions in Complexes.

Complex	Anion Absorptions (cm^{-1})		
	ν_3		
$[Co(Hapo)_6](ClO_4)_2$	1097vsb		
$[Ni(Hapo)_6](ClO_4)_2$	1098vsb		
$[Mn(Hapo)_6](ClO_4)_2$	1078vsb		
	ν_3	ν_4	
$Cu(Hapo)_4(BF_4)_2$	1065vsb	521w	
$[Ni(Hapo)_6](BF_4)_2 \cdot 2H_2O$	1065vsb	518w	
	ν_3	ν_2	ν_1
$[Ni(Hapo)_6](NO_3)_2 \cdot H_2O$	1363vs	828m	–
$[Co(Hapo)_6](NO_3)_2 \cdot H_2O$	1363vsb	828m	–
$Cu(Hapo)_2(NO_3)_2$	1492vs, 1282vs	805m	1015[a]

[a] Superimposed on ligand abosrption.

ca. 15–17,000 cm^{-1} and *ca.* 18,500–21,000 cm^{-1}, with the latter region sometimes obscured by ligand or charge transfer absorption [26–29]. A square-planar structure is, therefore, possible for $Cu(apo)_2$ and the rather lower frequencies in its spectrum may be a function of the ligand. Alternatively, weak axial interaction or a small tetrahedral distortion could occur, since they would lead to lower band frequencies [29–31].

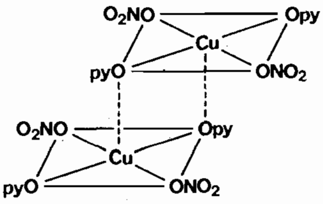
The i.r. spectrum of $[Cu(Hapo)_4](BF_4)_2$ shows that the anion is uncoordinated. The reflectance spectrum has a band at 16,000 cm^{-1} and a shoulder at 14,600 cm^{-1}. The complexes $[Cu(po)_4]X_2$ (po = pyridine N-oxide, X = BF_4, ClO_4) have square-planar, ionic structures and similar structures have been proposed for complexes with substituted pyridine N-oxides [32–35]. The reflectance spectrum of $[Cu(po)_4](ClO_4)_2$ has maxima at 14,700 and 13,700 (sh) cm^{-1} and the analogous complexes with 2,6-lutidine N-oxide and 2,4,6-collidine N-oxide absorb at *ca.* 15,500 and 15,700 cm^{-1}, respectively [34–36]. These spectra are fairly similar to that of $[Cu(Hapo)_4](BF_4)_2$, so the complex is probably square-planar.

The i.r. spectrum of $Cu(Hapo)_2(NO_3)_2$ shows that coordinated nitrate groups are present. The ν_3 (asymmetric stretching) band of ionic nitrate splits when nitrate coordination occurs. The extent of splitting is usually greater for bidentate nitrate than for unidentate nitrate, with complexes of similar type [37]. For some complexes of nickel(II) and copper-

TABLE VI. Major Lines in X-ray Powder Diffraction Spectra (d-Spacings (Å)).

[Mn(Hapo)$_6$] (ClO$_4$)$_2$	[Co(Hapo)$_6$] (ClO$_4$)$_2$	[Ni(Hapo)$_6$] (ClO$_4$)$_2$	[Ni(Hapo)$_6$] (BF$_4$)$_2$·2H$_2$O
9.60s	9.60s	9.60s	9.60s
7.50w	7.51s	7.51s	7.46s
6.24vs	6.28vs	6.28vs	6.24vs
5.23w	5.23w	5.23vw	5.21vw
4.65s	4.65vs	4.65s	4.63vs
4.02vs	4.02vs	4.02vs	4.01vs
3.93vw	3.92w	3.92m	3.88w
3.81w	3.83m	3.83m	3.81s
3.61vw	3.62vw	3.62vw	–
3.21w	3.22w	3.22w	3.20vw
[Co(Hapo)$_6$] (NO$_3$)$_2$·H$_2$O	[Ni(Hapo)$_6$] (NO$_3$)$_2$·H$_2$O	Cr(Hapo)$_4$Cl$_3$·H$_2$O	Fe(Hapo)$_4$Cl$_3$
9.40vs	9.40vs	8.29s	8.36s
7.25m	7.25m	8.15s	8.22s
6.20m	6.20m	7.73s	7.79s
4.55s	4.55s	7.35vs	7.46vs
3.99vs	3.98s	5.72w	5.79w
3.76s	3.75s	4.45m	4.51m
3.22vw	3.21vw	4.22w	4.28w
3.15vw	3.15vw	4.09w	4.12w
2.95w	2.94w	4.02w	4.08w
2.86m	2.86m	3.91m	3.93m
Co(po)Cl$_2$·H$_2$O	Ni(po)Cl$_2$·H$_2$O	Ni(po)Br$_2$·H$_2$O	Cu(po)Cl$_2$
8.78vs	8.78vs	8.85vs	7.79vs
6.64vs	6.64s	7.00m	6.72m
5.98vs	5.96vs	6.24s	5.54vw
4.82w	4.82w	4.01w	4.80vw
4.63vw	4.65w	3.58w	4.08m
4.43w	4.41m	3.15m	
3.38m	3.36w	3.12m	
3.11w	3.09m	3.04w	
3.00s	3.00m	2.99w	
2.93vw	2.90vw	2.80w	

(II), the ν_3 splittings are 102–125 cm^{-1} for unidentate nitrate, and 180–235 cm^{-1} for bidentate nitrate [38]. Bridging nitrate gives similar spectra to bidentate nitrate [37]. For Cu(Hapo)$_2$(NO$_3$)$_2$, the ν_3 splitting is 210 cm^{-1}, and so West proposed a dimeric structure, with bridging and bidentate nitrates [19]. E.s.r. measurements supported a dimer structure [19]. However, [Cu(po)$_2$(NO$_3$)$_2$]$_2$ has the N-oxide-bridged structure (VI) with unidentate nitrate, and the nitrate bands occur at 1480 and 1290 cm^{-1}, very similar to those for Cu(Hapo)$_2$(NO$_3$)$_2$ [39, 40]. Furthermore, the reflectance spectrum of [Cu(po)$_2$(NO$_3$)$_2$]$_2$ (13,900 cm^{-1}; 11,800 sh cm^{-1}) [39] is similar to that for the Hapo complex (14,200 cm^{-1}). The dimeric structure (VI) appears possible, therefore, for Cu(Hapo)$_2$(NO$_3$)$_2$. The magnetic moment of Cu(Hapo)$_2$(NO$_3$)$_2$ decreases slightly with decreasing temperature, possibly because of weak antiferromagnetism (Table III). The complex [Cu(po)$_2$(NO$_3$)$_2$]$_2$ is weakly ferromagnetic, however, studies have shown that the magnetic interaction in analogous complexes with substituted pyridine N-oxides is dependent on the ring substituent [41]. Weak magnetic interaction is commonly found [42] for 'out of plane' bridging as in (VI).



VI

The complexes of Hapo with copper halides have subnormal magnetic moments. This indicates N-oxide

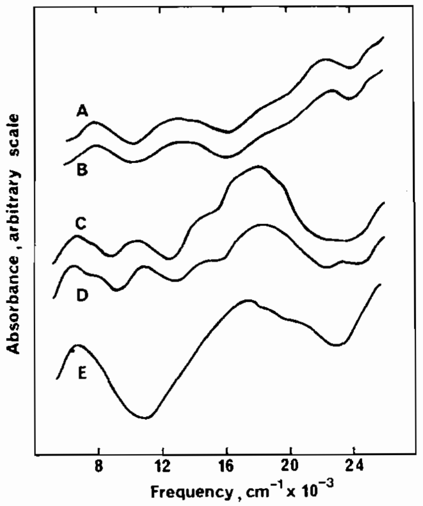


Fig. 1. Diffuse reflectance spectra. $[Ni(Hapo)_6](ClO_4)_2$: at room temperature (A) and liquid nitrogen temperature (B); $Co(Hapo)_2Br_2 \cdot C_2H_5OH$: at room temperature (C) and liquid nitrogen temperature (D); $Co(Hapo)_2Br_2 \cdot H_2O$ at room temperature (E).

TABLE VII. Magnetic Data for $Ni(Hapo)_2Br_2$ and $Co(Hapo)_2Br_2 \cdot C_2H_5OH$.

$Ni(Hapo)_2Br_2$			$Co(Hapo)_2Br_2 \cdot C_2H_5OH$		
T (°K)	$10^6\ \chi_A$ (cgsu)	μ_{eff} (B.M.)	T (°K)	$10^6\ \chi_A$ (cgsu)	μ_{eff} (B.M.)
298	3655	2.97	298	9045	4.67
275	3890	2.94	275	9665	4.63
255	4110	2.91	255	10195	4.57
235	4310	2.86	235	10785	4.52
215	4600	2.83	215	11440	4.46
196	4820	2.76	196	12165	4.38
176	5155	2.71	176	12920	4.28
151	5515	2.59	156	13660	4.15
127	5965	2.47	137	14380	3.99
104	6280	2.29	118	14900	3.76
89	6420	2.15	108	15065	3.63
			99	15110	3.47
			89	14975	3.28

bridged, probably dimeric, structures and many examples are known with pyridine N-oxide ligands [1].

[M(Hapo)$_6$] X$_2$ Complexes

I.r. spectra (Table V) show that the anions (ClO_4, BF_4 and NO_3) are uncoordinated in these complexes. The reflectance spectra of the cobalt(II) and nickel(II) complexes (Table IV, Fig. 1) are in the region for MO_6 complexes, and are very similar to the spectra for complexes with other 2-substituted N-oxides, such as 2-picoline N-oxide and 2-ethylpyridine N-oxide [43, 44]. This strongly supports unidentate O-bonding by Hapo.

X-ray powder patterns, shown in Table VI, confirm $[MO_6]X_2$ structures for all the hexakis complexes, in that the patterns for the Ni^{II}, Co^{II} and Mn^{II} perchlorate complexes, and for the Ni^{II} tetrafluoroborate, are almost identical. The X-ray powder patterns for the Ni^{II} and Co^{II} nitrate complexes are also identical.

The electronic spectra of the nickel(II) complexes indicate a regular octahedral chromophore. Bands are present at *ca.* 8000 and 13,000 cm^{-1}, assigned to the ν_1 ($^3T_{2g} \leftarrow {}^3A_{2g}$) and ν_2($^3T_{1g} \leftarrow {}^3A_{2g}$) transitions of octahedral nickel(II). No low symmetry components of ν_1 are present, and the ν_2/ν_1 ratios of *ca.* 1.7 are normal for undistorted complexes. The ν_3 ($^3T_{1g}(P) \leftarrow {}^3A_{2g}$) region is obscured by a charge transfer band [43], and so we cannot compare observed and calculated ν_3 values. Components of ν_2 are present with $[Ni(Hapo)_6](ClO_4)_2$. This often happens with NiO_6 systems and is attributed to singlet–triplet mixing [45]. The regular octahedral NiO_6 entity in the nickel complexes is in agreement with the results of X-ray structure work, which shows that regular MO_6 units are present in [M(pyridine N-oxide)$_6$]X_2 complexes [46]. The X-ray work shows that the MON bonds are bent, and so the overall symmetry of the complex ions is S_6 rather than O_h [46]. This should produce two i.r. active ν(NO) vibrations. Such a splitting of ν(NO) is not present in $[M(po)_6]^{2+}$ complexes, according to recent studies [47], but it does appear to occur with hexakis complexes of some substituted pyridine N-oxides [35, 43, 48]. We observe a clear splitting of ν(NO) with all the $[M(Hapo)_6]X_2$ complexes, except for the manganese compound.

Complexes of Nickel(II) and Cobalt(II) Halides with 2-Aminopyridine N-Oxide and Pyridine N-Oxide

We now discuss nickel(II) and cobalt(II) complexes of Hapo, and some related complexes with pyridine N-oxide which have not been fully characterised.

The complexes $Ni(Hapo)_2Br_2$ and $Co(Hapo)_2Br_2 \cdot C_2H_5OH$ are strongly antiferromagnetic (see Table VII). They most likely have N-oxide-bridged structures, because halide-bridged structures of the type $ML_2(halide)_2$ (M = Ni, Co) do not generally produce strong antiferromagnetism [49, 50].

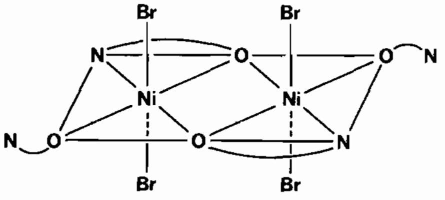
The magnetic data for $Ni(Hapo)_2Br_2$ have been compared with data predicted from various models using a least-squares procedure, and the results are shown in Table VIII. The best fit was obtained with the dinuclear model, although some other models also gave reasonable fits. The reflectance spectrum of the complex indicates a somewhat distorted six-

TABLE VIII. Best-Fits of Magnetic Data of $Ni(Hapo)_2Br_2$.[a]

Model	Reference[b]	g	J (cm^{-1})	$\Sigma[(\chi_{obs} - \chi_{calc})T]^2$	$\left\{\frac{\Sigma(\chi_{obs} - \chi_{calc})^2}{\Sigma(\chi_{obs})^2}\right\}^{1/2}$	S.E.[c]
Dimer	51	2.25	−27.9	0.14×10^{-3}	0.004	0.006
Linear trimer	52	2.36	−31.5	3.21×10^{-3}	0.032	0.034
Equilateral triangle	52	2.39	−23.6	1.86×10^{-3}	0.022	0.024
Regular tetrahedron	53	2.42	−17.9	1.64×10^{-3}	0.019	0.022
Heisenberg linear polymer	54	2.35	−21.9	0.57×10^{-3}	0.010	0.012

[a] Best fits were obtained using a least-squares procedure which minimised $\Sigma[(\chi_{obs} - \chi_{calc})T]^2$. [b] References to the susceptibility equations. The temperature independent paramagnetism was taken as 200×10^{-6} cgsu. [c] S.E. is the standard error expression $\{\Sigma[\mu_{eff}(obs) - \mu_{eff}(calc)]^2/(NP - K)\}^{1/2}$, where K is the number of parameters used to fit the NP data points (Ginsberg *et al., Inorg. Chem., 11,* 2884 (1972)).

coordinate structure, since a shoulder is present at 7,600 cm^{-1} on the $^3T_{1g} \leftarrow {}^3A_{2g}$ transition. The ligand i.r. data suggest the presence of some bidentate ligand, and a simple dinuclear structure incorporating this is shown in (VII). We are only aware of one antiferromagnetic nickel(II) complex with a simple pyridine N-oxide ligand, namely the violet compound $Ni(po)_2Br_2$, for which a dinuclear N-oxide-bridged structure was proposed [55].



(VII)

The reflectance spectrum (Table IV, Fig. 1) of the antiferromagnetic complex $Co(Hapo)_2Br_2 \cdot C_2H_5OH$ contains a band at *ca.* 10,600 cm^{-1} and this excludes a regular tetrahedral or octahedral structure [45]. Such a band is found with distorted tetrahedral or five-coordinate cobalt(II) complexes. The main band at *ca.* 18,000 cm^{-1} is too high in frequency for a distorted tetrahedral system (CoO_2Br_2 and CoN_2Br_2 systems have main bands at 15–16,000 cm^{-1} [56, 57]) but the band is acceptable for a five-coordinate structure [58, 59]. The treatment of the magnetic properties of polynuclear cobalt(II) complexes, with orbitally degenerate ground states, is very complex, so we consider that an attempt to compare the magnetic data to that derived from various models is not justified.

When blue $Co(Hapo)_2Br_2 \cdot C_2H_5OH$ is exposed to the atmosphere it is converted to mauve $Co(Hapo)_2Br_2 \cdot H_2O$. The latter compound is magnetically dilute and its reflectance spectrum (Table IV, Fig. 1) indicates a six-coordinate structure. The compound is most likely bromide-bridged.

We now consider the 1:1 solvated complexes $Ni(Hapo)Cl_2 \cdot H_2O$ and $Co(Hapo)Cl_2 \cdot C_2H_5OH$. With simple pyridine N-oxide ligands, the 1:1 copper(II) halide complexes are N-oxide bridged, and strongly antiferromagnetic [1]. The 1:1 nickel(II) and cobalt(II) halide complexes (solvated and unsolvated), with simple pyridine N-oxides, appear to be halide-bridged, on the basis of far-infrared spectra [60, 61]. In keeping with this, low temperature magnetic measurements on $Ni(pyridine\ N\text{-}oxide)Cl_2$ show no evidence of magnetic interaction [60]. The pyridine N-oxide complexes $M(po)Hal_2 \cdot H_2O$ (M = Ni, Co) have not been fully characterised, so we first discuss some additional measurements on these compounds, as a background to the related Hapo complexes.

The reflectance spectra of $Ni(po)Cl_2 \cdot H_2O$ and $Ni(po)Br_2 \cdot H_2O$ are typical of six-coordinate nickel(II) and the ν_2/ν_1 ratios (*ca.* 1.67) indicate no marked distortion. This is confirmed by spectra at liquid nitrogen temperatures, which show no evidence of band asymmetry or splitting and a similar result is found for $Co(po)Cl_2 \cdot H_2O$. The X-ray powder patterns of $Ni(po)Cl_2 \cdot H_2O$ and $Co(po)Cl_2 \cdot H_2O$ are very similar to each other, but quite different from that of N-oxide bridged $Cu(po)Cl_2$ (Table VI). The magnetic properties of the nickel and cobalt complexes, down to liquid nitrogen temperature, show no significant magnetic interaction in present, so halide-bridged, rather than N-oxide-bridged, structures are proposed.

The Hapo complexes $Ni(Hapo)Cl_2 \cdot H_2O$ and $Co(Hapo)Cl_2 \cdot C_2H_5OH$ have visible spectra and magnetic properties very similar to those of the solvated po complexes, and so similar halide-bridged structures are likely.

Chromium(III) and Iron(III) Complexes

The complexes $Cr(Hapo)_4Cl_3 \cdot H_2O$ and $Fe(Hapo)_4Cl_3$ are magnetically dilute. The reflectance spectrum of $Cr(Hapo)_4Cl_3 \cdot H_2O$ indicates the presence of strong tetragonal distortion, since the $\nu_1(^4T_{2g} \leftarrow {}^4A_{2g})$ transition of octahedral chromium(III) is markedly split [45]. The spectrum is generally similar to spectra of the complexes *trans*-$[CrL_2X_2](ClO_4)$ (L = *o*-phenylenebisdimethylarsine, X = Cl or Br) but with bands shifted to lower frequency by about 3000 cm^{-1} [62]. The structure *trans*-$[Cr(Hapo)_4Cl_2]Cl \cdot H_2O$ is most likely, with a *trans*-CrO_4Cl_2 chromophore.

The X-ray powder pattern (Table VI) of the $Fe(Hapo)_4Cl_3$ complex is very similar to that of $[Cr(Hapo)_4Cl_2]Cl \cdot H_2O$, indicating that the complexes are isostructural. The H_2O molecule in the chromium complex presumably occupies a lattice site, without markedly influencing the overall structure.

Coordination by Hapo and Substituted Derivatives

West *et al.* have studied many complexes with N-alkyl derivatives of Hapo [9–18]. We now compare the structures of West's complexes with the structures of analogous Hapo complexes.

The West complexes $[CuL_4](BF_4)_2$ and $[CoL_6](ClO_4)_2$ are similar to the corresponding Hapo complexes and contain O-donor ligand [9–14]. West finds that his complexes of the type $CuL_2(NO_3)_2$ with 2-ethyl- and 2-n-propyl-aminopyridine N-oxide are monomeric with one or two bidentate nitrates and O-donor ligand [12, 13]. West's complex with 2-isopropylaminopyridine N-oxide is dimeric, probably with bridging nitrate and O, N and O-donor ligand [14]. We assign a dimeric structure to $Cu(Hapo)_2(NO_3)_2$, however, with bridging O-donor ligand and unidentate nitrate.

West finds that his halide complexes $CuLX_2$ and CuL_2X_2 are monomeric with bidentate O,N ligands [10, 12–14, 16, 17]. West excludes dimer structures because transitions corresponding to M = 2 are absent from esr spectra. In contrast, we consider that the copper halide complexes with Hapo are dimers, containing bridging O-donor ligand, on the basis of the low magnetic moments of the complexes.

In general, Hapo is almost always a unidentate O-donor, the N-alkyl derivatives are either unidentate or bidentate and the N,N-dialkyl ligands are almost exclusively bidentate. Some structural assignments with these ligands are rather tentative, and we intend to carry out X-ray structure analyses in the Hapo system.

Experimental

The ligand Hapo was prepared from 2-aminopyridine [63]. All metal complexes were dried *in vacuo* over phosphorus pentoxide.

$Cu(apo)_2$

A solution of Hapo (1.0 g) in boiling ethanol (20 ml) was added to a boiling solution of copper(II) acetate monohydrate (1.3 g) in ethanol (40 ml). A green powder was deposited.

$Cu(Hapo)Cl_2$

A solution of Hapo (1.0 g) in warm ethanol (30 ml) was slowly added to a boiling solution of copper(II) chloride dihydrate (2.5 g) in ethanol (40 ml). A red-brown precipitate formed, this redissolved as the solution was boiled. A brown powder later precipitated form the cooled solution.

$Cu(Hapo)_2Cl_2 \cdot H_2O$

Warm solutions (60 ml) of copper(II) chloride dihydrate (0.85 g) and Hapo in ethanol were mixed with vigorous stirring. The precipitate which formed was immediately filtered off.

$Cu(Hapo)_2Br_2 0.5C_2H_5OH$

A solution of anhydrous copper(II) bromide (0.60 g) in boiling methanol (35 ml) was treated with a boiling solution of Hapo (1.2 g) in ethanol (60 ml) and the mixture was warmed for 15 min. After standing overnight, the solution deposited a red brown powder.

$Cu(Hapo)_2(NO_3)_2$

A solution of Hapo (1.1 g) in boiling ethanol (40 ml) and 2,2-dimethoxypropane (6 ml) was combined with a solution of copper(II) nitrate trihydrate (1.20 g) in warm ethanol (20 ml) and dimethoxypropane (6 ml). The solution was warmed for 10 min and left to stand, whereupon a green powder was deposited.

$Cu(Hapo)_4(BF_4)_2$

This complex was prepared analogously to $Cu(Hapo)_2(NO_3)_2$ using: hydrated copper tetrafluoroborate (1.7 g), ethanol (20 ml), dimethoxypropane (6 ml); Hapo (1.0 g), ethanol (25 ml) and dimethoxypropane (6 ml).

$Ni(Hapo)Cl_2 \cdot H_2O$

A solution of nickel(II) chloride hexahydrate (1.36 g) in ethanol (30 ml) was added to a boiling ethanol solution (25 ml) of Hapo (1.3 g). The complex was deposited after a few minutes.

$Ni(Hapo)_2Br_2$

A boiling solution of Hapo (1.0 g) in ethanol (30 ml) was added to a boiling solution of nickel(II) bromide trihydrate (1.2 g) in ethanol (35 ml) and 2,2-dimethoxypropane (8 ml). The complex was deposited after a few minutes.

$Co(Hapo)Cl_2 \cdot C_2H_5OH$

A warm solution of cobalt(II) chloride hexahydrate (1.56 g) in ethanol (30 ml) and dimethoxypropane (10 ml) was added to a warm ethanol solution (20 ml) of Hapo (1.0 g). The solution was boiled for several minutes and, on cooling, deposited the complex.

$Co(Hapo)_2Br_2 \cdot C_2H_5OH$

A warm solution of hydrated cobalt(II) bromide (2.0 g) in ethanol (35 ml) and dimethoxypropane (5 ml) was added to a warm solution of Hapo (1.0 g) in ethanol (20 ml). The solution was concentrated to 30 ml and filtered. After several hours the complex was deposited.

$Co(Hapo)_2Br_2 \cdot H_2O$

Powdered $Co(Hapo)_2Br_2 \cdot C_2H_5OH$ was exposed to the atmosphere. The blue powder changed to mauve after several days.

$Fe(Hapo)_4Cl_3$

A warm solution of anhydrous ferric chloride (1.1 g) in ethanol (30 ml) was added to a warm solution of Hapo (1.0 g) in alcohol (25 ml). The resulting blue solution was evaporated on a hot plate until the complex began to deposit.

$Co(Hapo)_4Cl_3 \cdot H_2O$

The complex was prepared analogously to $Fe(Hapo)_4Cl_3$ using the following quantities: chromium(III) chloride hexahydrate 1.7 g, ethanol 25 ml, 2,2-dimethoxypropane 5 ml, Hapo 1.0 g and ethanol 25 ml.

Hexakis Complexes

A solution of Hapo (1.3 g) in warm ethanol (30 ml) and 2,2-dimethoxypropane (5 ml) was added to a boiling solution of the appropriate metal salt (1.2 g) in ethanol (35 ml) and 2,2-dimethoxypropane (10 ml). The complexes were obtained immediately, or after concentration of the solutions to 30 ml and leaving to stand in a desiccator over phosphorus pentoxide.

Analyses and Physical Measurements

These were as previously described [4].

References

1 N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, *Coord. Chem. Rev., 11,* 93 (1973).

2 A. E. Landers and D. J. Phillips, *Inorg. Chim. Acta, 25,* L39 (1977).

3 A. E. Landers and D. J. Phillips, *Abstr. of 9th Conference of the RACI Division of Coord. and Metal-Org. Chemistry* (Sydney, 1980) 89.

4 A. E. Landers and D. J. Phillips, *Inorg. Chim. Acta, 51,* 109 (1981).

5 A. E. Landers and D. J. Phillips, *Inorg. Chim. Acta, 59,* 41 (1982).

6 A. E. Landers and D. J. Phillips, *Inorg. Chim. Acta, 59,* 125 (1982).

7 H. Sigel and H. Brintzinger, *Helv. Chim. Acta, 46,* 701 (1963).

8 H. Sigel and H. Brintzinger, *Helv. Chim. Acta, 46,* 712 (1963).

9 R. E. Kohrman, P. G. Phadtare and D. X. West, *J. Inorg. Nucl. Chem., 37,* 301 (1975).

10 D. X. West and W-H. Wang, *J. Inorg. Nucl. Chem., 41,* 1719 (1979).

11 D. X. West and S. H. Hulslander, *J. Inorg. Nucl. Chem., 43,* 2713 (1981).

12 D. X. West and W-H. Wang, *J. Inorg. Nucl. Chem., 42,* 1656 (1980).

13 D. X. West and K. Duffield, *J. Inorg. Nucl. Chem., 43,* 1517 (1981).

14 D. X. West and J. B. Sedgwick, *J. Inorg. Nucl. Chem., 43,* 2307 (1981).

15 R. E. Khorman, P. G. Phadtare and D. X. West, *J. Inorg. Nucl. Chem., 37,* 1296 (1975).

16 D. X. West and W-H. Wang, *J. Inorg. Nucl. Chem., 42,* 985 (1980).

17 D. X. West and W-H. Wang, *J. Inorg. Nucl. Chem., 43,* 1511 (1981).

18 D. X. West and T. J. O'Grady, *J. Inorg. Nucl. Chem., 43,* 2725 (1981).

19 D. X. West, *J. Inorg. Nucl. Chem., 43,* 3169 (1981).

20 M. A. J. Jungbauer and C. Curran, *Spectrochim. Acta, 21,* 641 (1965).

21 D. R. Marks, D. J. Phillips and J. P. Redfern, *J. Chem. Soc. (A),* 1464 (1967).

22 D. R. Marks, D. J. Phillips and J. P. Redfern, *J. Chem. Soc. (A),* 2013 (1968).

23 A. R. Katritzky and R. A. Jones, *J. Chem. Soc.,* 3674 (1959).

24 A. R. Katritzky and A. R. Hands, *J. Chem. Soc.,* 2195 (1958).

25 L. F. Larkworthy, J. M. Murphy and D. J. Phillips, *Inorg. Chem., 7,* 1436 (1968).

26 R. J. Dudley, R. J. Fereday, B. J. Hathaway and P. G. Hodgson, *J. Chem. Soc. Dalton,* 1341 (1972).

27 C. P. Nash and L. P. Schaeffer, *J. Am. Chem. Soc., 91,* 1319 (1969).

28 G. A. Barclay and F. S. Stephens, *J. Chem. Soc.,* 2027 (1963).

29 D. P. Graddon and L. Munday, *J. Inorg. Nucl. Chem., 23,* 231 (1961).

30 H. Yokoi, M. Sai, T. Isobe and S. Ohsawa, *Bull. Chem. Soc. Japan, 45,* 2189 (1972).

31 J. I. Bullock, R. J. Hobson and D. C. Povey, *J. Chem. Soc. Dalton,* 2037 (1974).

32 J. D. Lee, D. S. Brown and B. G. A. Melsom, *Acta Cryst., B25,* 1378 (1969).

33 J. D. Lee, D. S. Brown and B. G. A. Melsom, *Acta Cryst., B25,* 1595 (1969).

34 N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3,* 415 (1969).

35 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7,* 1835 (1968).

36 R. Whyman, W. E. Hatfield and J. S. Paschal, *Inorg. Chim. Acta, 1,* 113 (1967).

37 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', 3rd ed., pp. 244–6, Wiley, New York, 1978.

38 N. F. Curtis and Y. M. Curtis, *Inorg. Chem., 4,* 804 (1965).

39 R. L. Carlin and M. J. Baker, *J. Chem. Soc.,* 5008 (1964).

40 S. Scavnicar and B. Matkovic, *Acta Cryst.*, *B25*, 2046 (1969).
41 K. T. McGregor, J. A. Barnes and W. E. Hatfield, *J. Am. Chem. Soc.*, *95*, 7993 (1973).
42 M. D. Glick and R. L. Lintvedt, *Prog. Inorg. Chem.*, *21*, 233 (1976).
43 G. Schmauss and H. Specker, *Z. Anorg. Chem.*, *364*, 1 (1969).
44 J. H. Nelson and R. O. Ragsdale, *Inorg. Chim. Acta*, *2*, 439 (1968).
45 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam (1968).
46 T. J. Bergendahl and J. S. Wood, *Inorg. Chem.*, *14*, 338 (1975).
47 A. T. Hutton and D. A. Thornton, *J. Mol. Struct.*, *39*, 33 (1977).
48 L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta*, *3*, 473 (1969).
49 Landolt-Bornstein, New Series Group II, Volume 2, 'Magnetic Properties of Coordination and Organometallic Transition Metal Compounds', by E. König, Springer, Berlin (1966).
50 B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, *6*, 37 (1964).
51 A. Earnshaw, 'Introduction to Magnetochemistry', Academic Press, London (1968).
52 A. P. Ginsberg, R. L. Martin and R. C. Sherwood, *Inorg. Chem.*, *7*, 932 (1968).
53 J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin and R. C. Sherwood, *Inorg. Chem.*, *10*, 240 (1971).
54 M. E. Fisher, *Am. J. Phys.*, *32*, 343 (1964).
55 S. V. Nipankar, V. R. Marathe and C. R. Kanekar, *Ind. J. Chem.*, *10*, 649 (1972).
56 D. W. Herlocker, *Inorg. Chim. Acta*, *6*, 211 (1972).
57 L. Sacconi, I. Bertini and F. Mani, *Inorg. Chem.*, *6*, 262 (1967).
58 M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, *5*, 45 (1966).
59 M. Ciampolini and N. Nardi, *Inorg. Chem.*, *6*, 445 (1967).
61 N. M. Karayannis, C. M. Paleos, L. L. Pytlewski and M. M. Labes, *Inorg. Chem.*, *8*, 2559 (1969).
61 D. H. Brown, D. Kenyon and D. W. A. Sharp, *J. Chem. Soc. (A)*, 1474 (1969).
62 J. R. Perumareddi, *Coord. Chem. Rev.*, *4*, 73 (1969).
63 J. Delarge and L. Thunus, *Farmaco Ed. Sci.*, *21*, 846 (1966).