Inorganica Chimica Acta, 36 (1979) 223–228
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Chromium(II) Complexes with Halogen-Substituted Pyridines

M. M. KHAMAR, L. F. LARKWORTHY
Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, U.K.

and D. J. PHILLIPS
School of Chemistry, University of New South Wales, Kensington, N.S.W., 2033, Australia

Received February 9, 1979

Complexes of chromium(II) halides with 3-chloro-, 3-bromo-, 3-iodo-, and 3,5-dichloro-pyridine of the types $Cr(pyridine)_2X_2$, $X = Cl, Br, I$, *and* $Cr(pyridine)_2(H_2O)_2I_2$ *have been isolated. The former compounds are apparently polymeric and antiferromagnetic and the latter monomeric with temperature-independent magnetic moments. One tetrakis(amine) complex,* $Cr(3,5\text{-dichloropyridine})_4I_2$, *has been obtained. Far infrared investigations confirm that 'short' bond Cr–Cl stretching vibrations of the bis(amine) complexes occur near 320 cm*$^{-1}$*, and Cr–Br and Cr–I stretching vibrations at approximately 260 cm*$^{-1}$ *and 240 cm*$^{-1}$ *respectively.*

Introduction

Complexes of pyridine and substituted pyridines with many metal ions of the first transition series have been widely investigated [1a]. With chromium(II), however, only pyridine [2] and methylpyridine [3] complexes, have been previously reported. We present a magnetic and spectroscopic investigation of a series of chromium(II) complexes with halogen-substituted pyridines.

Results and Discussion

The complexes isolated fall into three classes, a) $Cr(3\text{-}Xpy)_2Hal_2$; b) $Cr(3\text{-}Xpy)_2(H_2O)_2I_2$, and (c) $Cr(3,5\text{-}Clpy)_4I_2$ (see Table I, 3-Xpy is 3-chloro-, 3-bromo-, or 3-iodo-substituted pyridine, 3,5-Clpy is 3,5-dichloropyridine, and Hal is Cl, Br, or I). The first class of compound has not previously been reported as the iodide.

Complexes of the type $M(py)_2Cl_2$ and $M(py)_2Br_2$ with copper(II) and chromium(II) have rhombically-distorted, halogen-bridged structures, with two different types of M–Hal bond lengths. For example, $Cu(py)_2Cl_2$ has Cu–Cl bond lengths of 2.298 and 3.026 Å, and the Cu–N bond length is 2.004 Å. Similar structures would be expected for our complexes of the type $Cr(X\text{-}py)_2Hal_2$.

Magnetic properties support halogen-bridging. The $Cr(X\text{-}py)_2Hal_2$ complexes differ from those in groups b) and c) in that the room temperature magnetic moments are depressed below the spin-only value (4.90 B.M.) for four unpaired electrons, and further reductions in μ_{eff} occur on cooling (Table II). The compounds obey the Curie–Weiss law with large θ values in the range 20° to 60°. This magnetic behaviour is consistent with antiferromagnetic interaction made possible through halogen-bridging. Bridging iodide is uncommon, presumably because of the greater size and polarizability of this halide. With nickel(II), for example, $Ni(py)_2I_2$ is tetrahedral [1b] although the bromide and chloride are polymeric. Although copper(II) and high-spin chromium(II) frequently form similar compounds, iodo-complexes with pyridines do not seem to have been described for copper(II), presumably because of its oxidising ability.

The visible spectra of the $Cr(X\text{-}py)_2Hal_2$ complexes have intense charge transfer absorptions above 20,000 cm^{-1}, and less intense bands (Table I), assigned to d–d transitions, occur at lower energies. The d–d absorptions are similar to those reported [2b, 3] for other $Cr(py)_2Hal_2$ complexes.

Four d–d transitions are expected [5b] with rhombically distorted chromium(II). There is firstly the $^5B_g \rightarrow {}^5A_g$ transition between the split components of the ^5E_g ground term (O_h symmetry). All the $Cr(X\text{-}py)_2Hal_2$ complexes exhibit, near to 10,000 cm^{-1}, a shoulder or band which is assigned to this transition. The other transitions are to the three components of the split $^5T_{2g}$ level. The main d–d band near 14,000 cm^{-1} is assigned to these transitions superimposed. Slight asymmetry is found in this band with some complexes, and there is some indication of three components in the spectra of $Cr(3\text{-}Brpy)_2Cl_2$ and $Cr(3\text{-}Ipy)_2X_2$ from the presence of not very obvious shoulders near 12000 cm^{-1}.

TABLE I. Analytical Data and Reflectance Spectra.

Complex	Analyses (%)						Reflectance Spectra/cm^{-1}				
		C	H	N	Cr	Hal					
$Cr(3\text{-}Clpy)_2Cl_2$	Calc.	34.3	2.3	8.0	14.9	20.25	RT		14000s		10700sh
	Found	34.1	2.3	7.8	15.0	20.5	LT		14300s		10700m
$Cr(3\text{-}Clpy)_2Br_2$	Calc.	27.35	1.8	6.4	11.8	36.4	RT		13400s		10000sh
	Found	27.2	2.0	6.1	12.1	36.8	LT		13800s		10100m
$Cr(3\text{-}Clpy)_2(H_2O)_2I_2$	Calc.	21.1	2.1	4.9	9.1	44.6	RT	16000s		12000m	10600sh
	Found	21.0	2.0	5.1	9.35	45.4	LT	16500s		12000m	10700sh
$Cr(3\text{-}Brpy)_2Cl_2$	Calc.	27.4	1.8	6.4	11.85	16.15	RT		1400s,vb		10400sh
	Found	28.0	1.8	6.3	11.95	16.3	LT		14200m	12150sh	10400sh
$Cr(3\text{-}Brpy)_2Br_2$	Calc.	22.75	1.5	5.3	9.85	30.3	RT		13500s		10300sh
	Found	22.8	1.7	5.1	10.1	30.6	LT		13900s		10400m
$Cr(3\text{-}Brpy)_2I_2$	Calc.	19.3	1.3	4.5	8.4	40.8	RT		13100vs		10700sh
	Found	19.3	1.3	4.4	8.6	41.7	LT		13500vs		10600m
$Cr(3\text{-}Brpy)_2(H_2O)_2I_2$	Calc.	18.25	1.8	4.3	7.9	38.6	RT	15700s		12000m	10600sh
	Found	18.1	1.9	4.2	8.1	38.5	LT	16300s		12000m	10700sh
$Cr(3\text{-}Ipy)_2Cl_2$	Calc.	22.5	1.5	5.3	9.8	13.3	RT		14000s	12400sh	10500sh
	Found	22.55	1.5	5.25	9.9	13.6	LT		14500s	12600sh	10900sh
$Cr(3\text{-}Ipy)_2Br_2$	Calc.	19.3	1.3	4.5	8.4	25.7	RT		13600sh	11900sh	10400sh
	Found	19.6	1.4	4.4	8.6	26.3	LT		14100s	12000sh	10400sh
$Cr(3\text{-}Ipy)_2I_2$	Calc.	16.8	1.1	3.9	7.3	35.5	RT		13250vs		11000sh
	Found	16.75	1.1	3.75	7.5	36.2	LT		13600vs	12100sh	11000sh
$Cr(3,5\text{-}Clpy)_2Cl_2$	Calc.	28.7	1.4	6.7	12.4	16.9	RT		13400s		10000sh
	Found	28.3	1.75	6.35	12.6	17.2	LT		13750s		9600m
$Cr(3,5\text{-}Clpy)_2Br_2$	Calc.	23.65	1.2	5.5	10.2	31.5	RT		13400s		9800sh
	Found	23.5	1.5	5.2	10.4	32.0	LT		13600s		9300m
$Cr(3,5\text{-}Clpy)_2I_2$	Calc.	19.95	1.0	4.65	8.6	42.2	RT		13000s		9200m
	Found	20.1	1.2	4.3	8.8	42.3	LT		13200s		8800m
$Cr(3,5\text{-}Clpy)_4I_2$	Calc.	26.7	1.35	6.2	5.8	28.3	RT	15000s,sh			
	Found	26.3	1.45	5.7	5.95	28.1	LT	15200s,sh			7000m

TABLE II. Magnetic and Preparative Data for the Complexes.

Complex	Colour	μ_{eff}[a] (B.M.)		θ[b] (°)	Preparative[c] Method
		295 K	90 K		
$Cr(3\text{-}Clpy)_2Cl_2$	light green	4.08	3.65	37	E
$Cr(3\text{-}Clpy)_2Br_2$	green	4.51	3.93	48	E
$Cr(3\text{-}Clpy)_2(H_2O)_2I_2$	olive green	4.80	4.85	–3	C
$Cr(3\text{-}Brpy)_2Cl_2$	light green	4.59	4.10	37	E
$Cr(3\text{-}Brpy)_2Br_2$	dark green	4.59	4.11	37	E
$Cr(3\text{-}Brpy)_2I_2$	green	4.61	4.13	36	D
$Cr(3\text{-}Brpy)_2(H_2O)_2I_2$	olive green	4.83	4.78	2	C
$Cr(3\text{-}Ipy)_2Cl_2$	light green	4.64	4.30	22	E
$Cr(3\text{-}Ipy)_2Br_2$	bluish green	4.69	4.30	27	E
$Cr(3\text{-}Ipy)_2I_2$	green	4.60	4.27	22	C
$Cr(3,5\text{-}Clpy)_2Cl_2$	light yellow	4.71	4.06	53	E

(continued on facing page)

TABLE II. *(continued)*

Complex	Colour	μ_{eff}^{a} (B.M.)		θ^b (°)	Preparative^c Method
		295 K	90 K		
$Cr(3,5\text{-}Clpy)_2Br_2$	yellow	4.67	4.00	57	E
$Cr(3,5\text{-}Clpy)_2I_2$	dark yellow	4.69	4.33	24	A
$Cr(3,5\text{-}Clpy)_4I_2$	dark red	4.82	4.63	11	B

^{a}Calculated from $\mu_{eff} = 2.828\ (\chi_A T)^{1/2}$. ^{b}Curie–Weiss law taken as $\chi_A^{-1} \alpha (T + \theta)$, and θ calculated by a least squares extrapolation. ^{c}The significance of these symbols is given in the experimental section.

The energies of the transitions to the components of the $^5T_{2g}$ term are related to the average 10Dq value for each complex. In line with this, the energies decrease in the order mepy [3] > py [2b] > 3X-py > 3,5-Cl for complexes with the same halide, of the type $Cr(py)_2Hal_2$. This order is that expected for the 10Dq values of the pyridine ligands.

The energy of the $^5B_g \rightarrow {}^5A_g$ transition is related to the distortion produced by the Jahn–Teller effect, and to that produced by the difference in the 10Dq values of the pyridine and halide ligands. This distortion should therefore decrease as the 10Dq values of the pyridines decrease. In keeping with this, the energies of this band are mainly in the same order as that given above for the 10Dq values of the pyridine ligands.

The complexes $Cr(X\text{-}py)_2(H_2O)_2I_2$ (X-py = 3-chloro and 3-bromo-pyridine), in contrast to the complexes $Cr(X\text{-}py)_2Hal_2$, are magnetically dilute. They obey the Curie law, with magnetic moments independent of temperature and near to the spin-only value. This suggests that halogen-bridging is absent and we assume that the complexes are monomeric and six-coordinate.

The electronic spectra show evidence of reduced symmetry compared to the $Cr(X\text{-}py)_2Hal_2$ complexes because three d–d absorptions are detected at approximately 16,000, 12,000 and 10,800 cm^{-1}. We assign the lowest energy absorption to the transition between the components of the split ^5E_g term and the other absorptions to transitions to components of the $^5T_{2g}$ term.

The complex $Cr(3,5\text{-}Clpy)_4I_2$ has a magnetic moment of 4.8 B.M. at room temperature near the spin-only value for high-spin chromium(II), and a six co-ordinate *trans* structure, with terminal iodides, seems likely, similar to that found for other [M(pyridine)$_4$(Hal)$_2$] complexes [2–5]. The θ value of 11° is, however, larger than commonly found for magnetically-dilute chromium(II) compounds. In its visible spectrum a clear d–d band is found at 7000 cm^{-1} and this is assigned to the transition between the components of the ^5E_g term. Other d–d transitions appear as a shoulder at 15000 cm^{-1}, partly masked by a low energy, high intensity absorption which we assume to be charge transfer in origin. The spectra of the corresponding pyridine [2b] and methylpyridine [3] complexes are similar but with the distortion band at higher frequency because of the stronger fields of these ligands.

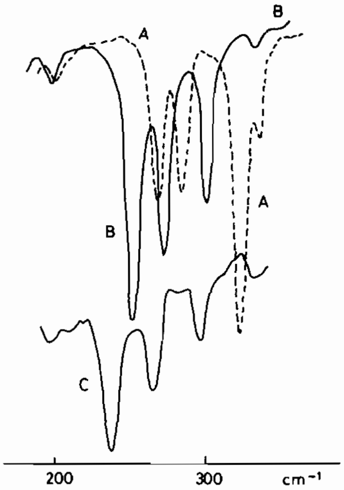

Fig. 1. Far infrared spectra of A, $Cr(3\text{-}Brpy)_2Cl_2$; B, $Cr(3\text{-}Brpy)_2Br_2$; and C, $Cr(3\text{-}Brpy)_2I_2$.

All the bis-ligand complexes show intense absorption above 20,000 cm^{-1}, which we assume to be intra-ligand or charge transfer in origin. The free pyridine ligands absorb in the range 35,000 to 39,000 cm^{-1}, and absorption in this region in the complexes may also be intra-ligand in character. The additional absorption in the region 20,000 to 30,000 cm^{-1} is probably of charge transfer type. Relatively low-energy metal to ligand charge transfer absorption is possible for complexes of readily oxidisable metals with ligands containing empty antibonding π-orbitals [5]. The absorptions in the 20,000–30,000 cm^{-1} region are not markedly halogen-dependent, and we therefore assign them to metal-to-pyridine charge transfer transitions, possibly of $e_g \rightarrow \pi^*$ type. Similar low energy absorptions have been reported for vanadium(II)–pyridine complexes [7] and chromium(II)–methylpyridine [3] complexes.

TABLE III. Far-infrared Spectra (cm^{-1}).[a]

3-Clpy	Cr(3-Clpy)$_2$Cl$_2$	Cr(3-Clpy)$_2$Br$_2$	Cr(3-Clpy)$_2$(H$_2$O)$_2$I$_2$	
402s	412m	412m	416m	
	336vs	330m	324m	
	310vs ν(Cr–Cl)			
292s,vb		300w		
	272s ν(Cr–N)	274vs ν(Cr–N)	270s ν(Cr–N)	
		260vs ν(Cr–Br)		
232w				
195m,b	212w,b	212w,b	212w	
			196m	
	177vs δ(Cr–N)	178m δ(Cr–N)	184m δ(Cr–N)	
	δ(Cr–Cl)	164s	160vs	
	150m ν(Cr–Cl)[b]	121m		
	108vs		100m	
3-Brpy	Cr(3-Brpy)$_2$Cl$_2$	Cr(3-Brpy)$_2$Br$_2$	Cr(3-Brpy)$_2$I$_2$	Cr(3-Brpy)$_2$(H$_2$O)$_2$I$_2$
410m	408m	408m	408m	408m
	336w	332w	330w	332w
320w	324vs ν(Cr–Cl)			
	285m	300m	294m	290m
	268m ν(Cr–N)	272m ν(Cr–N)	264m ν(Cr–N)	265vs ν(Cr–N)
		252s ν(Cr–Br)		
			238s ν(Cr–I)	236w
				218w
	200w	198w		210w
	180w			
	168m δ(Cr–N)	176m δ(Cr–N)	170m δ(Cr–N)	179vs,b δ(Cr–N)
	δ(Cr–Cl)	150m	143m	136s
	138m ν(Cr–Cl)[b]			
	98s	110m	94w	96vs
3-Ipy	Cr(3-Ipy)$_2$Cl$_2$	Cr(3-Ipy)$_2$Br$_2$	Cr(3-Ipy)$_2$I$_2$	
394m	410s	406s	408s	
	324vs,b ν(Cr–Cl)			
290w	300s	300s	296s	
		282vs ν(Cr–Br)		
262m	260s ν(Cr–N)	258m ν(Cr–N)	272s ν(Cr–N)	
234w[a]		246vs	254m	
			234vs ν(Cr–I)	
	188w	184w	182w	
	178m δ(Cr–N)	172m		
	162s δ(Cr–Cl)		164m	
	132m ν(Cr–Cl)[b]	146s δ(Cr–N)	138s δ(Cr–N)	
	94vs	104s	91m	
3,5-Clpy	Cr(3,5-Clpy)$_2$Cl$_2$	Cr(3,5-Clpy)$_2$Br$_2$	Cr(3,5-Clpy)$_2$I$_2$	Cr(3,5-Clpy)$_4$I$_2$
392vs	396s	396m	396s	390vs
	324vs ν(Cr–Cl)			
	272s ν(Cr–N)	272vs, b ν(Cr–N)	262s ν(Cr–N)	270vs ν(Cr–N)
		ν(Cr–Br)		
			250vs,b ν(Cr–I)	
196vs,b	202s			202s
	196sh	194m	190vs	190vs

(continued on facing page)

TABLE III. *(continued)*

164s,vb	δ(Cr–N)	158w	δ(Cr–N)	154s	δ(Cr–N)	170m	δ(Cr–N)
	δ(Cr–Cl)	146m		130vs,b		114m	
140m	ν(Cr–Cl)^b						
112vs,b		104w		88m		86s	

^{a}Many weak absorptions at lower frequency. ^{b}Deformations of long Cr–Cl bonds.

Far Infrared Spectra

From the spectra of the bis(pyridine) complexes (Table III) it is apparent that the strong absorptions near 320 cm^{-1} in the spectra of the chlorides can be assigned to stretching vibrations of the short Cr–Cl bands; no halogen-dependent bands appear in this region with the bromo- and iodo-complexes (Fig. 1). In all spectra there are very strong absorptions near 260 cm^{-1} which are assigned to ν(Cr–N) vibrations. The bromo-complexes exhibit additional bands in this region which are assigned to ν(Cr–Br) vibrations; in one case {Cr(3,5-Clpy)$_2$Br$_2$} the ν(Cr–N) and ν(Cr–Br) absorptions appear to coincide, and in others it is uncertain which absorption is which. These assignments are similar to those reported recently [3] for the analogous complexes, Cr(mepy)$_2$Hal$_2$, Hal = Cl or Br, except that the ν(Cr–N) absorptions are generally at lower frequency for the halo-pyridine complexes as might be expected because of the larger mass of the ligand. Deformation vibrations of the (Cl–Cr–Cl) and (N–Cr–N) units and stretching vibrations of the long Cr–Cl bands are expected in the 150 cm^{-1} region, and tentative assignments have been given.

The iodo-complexes Cr(X-py)$_2$I$_2$ are the first of this stoicheiometry to be investigated, and comparison with the chloride and bromide spectra suggests that ν(Cr–I) vibrations occur near 240 cm^{-1}. The larger size of iodide and its reluctance to form bridges could have produced tetrahedral structures for the iodo-complexes. However, a structural change at iodide in the series Cr(X-py)$_2$Hal$_2$ would be expected to bring ν(Cr–I) above ν(Cr–Br). The antiferromagnetic behaviour of the iodides indicates a polymeric structure, and tetrahedral monomeric chromium(II) complexes should have greater than spin-only magnetic moments through a first order orbital contribution. Additionally, solution spectra of Cr(3-Ipy)$_2$I$_2$ (ethanol) and Cr(3,5-Clpy)$_2$I$_2$ (ethanol and chloroform) differed from the reflectance spectra indicating solvolysis, and the extinction coefficients of the d–d transitions ($\epsilon \cong 30$ l dm^3 mol^{-1} cm^{-1} for bands near 14000 cm^{-1}) were not large enough to suggest tetrahedral coordination.

The absence of intense absorptions near 240 cm^{-1} from the spectra of the complexes Cr(X-py)$_2$(H$_2$O)$_2$I$_2$ and Cr(3,5-Clpy)$_4$I$_2$ suggests that the iodide is held by 'long' bands to the metal ion. The corresponding methylpyridine complexes gave similar spectra [3].

Experimental

Preparations

These were performed under nitrogen using deoxygenated solvents. Analyses are given in Table I. The complexes which were obtained by methods analogous to method E, given below, are indicated in Table II. The chlorides and bromides were obtained from concentrated ethanolic solutions of their constituents, but the iodides, being highly soluble in ethanol, were isolated from solutions in acetone.

A) Cr(3,5-dichloropyridine)$_2$I$_2$

An alcoholic solution (30 cm^3) of 3,5-dichloropyridine (2.7 g) was added to an alcohol solution (25 cm^3) of CrI$_2$·5H$_2$O (3.6 g). The bluish-green solution was evaporated to dryness giving a dark red precipitate of the tetrakis(amine) complex Cr(3,5-Clpy)$_4$I$_2$ (see B). This compound was suspended for 2.5 h in acetone at about 60 °C to remove two of the pyridine molecules. The yellowish orange product was filtered off, washed with acetone and pumped dry for 5 h.

B) Cr(3,5-dichloropyridine)$_4$I$_2$

A cold ethanolic solution (20 cm^3) of 3,5-dichloropyridine (6.8 g) was added to a cold ethanolic solution (30 cm^3) of CrI$_2$·5H$_2$O (4.5 g). After a few hours at room temperature, dark red crystals separated. These were filtered off, washed with ethanol and pumped dry for 4 h.

C) Cr(3-chloropyridine)$_2$(H$_2$O)$_2$I$_2$, Cr(3-bromopyridine)$_2$(H$_2$O)$_2$I$_2$, and Cr(3-iodopyridine)$_2$I$_2$

A solution of 3-chloropyridine (3.1 g) in acetone (20 cm^3) was added to a solution of CrI$_2$·5H$_2$O (5.4 g) in acetone (30 cm^3). The resulting dark green precipitate was filtered off, washed with acetone and pumped dry for 4 h.

The preparations of Cr(3-bromopyridine)$_2$(H$_2$O)$_2$I$_2$ and Cr(3-iodopyridine)$_2$I$_2$ were analogous to that of Cr(3-chloropyridine)$_2$(H$_2$O)$_2$I$_2$.

D) Cr(3-bromopyridine)$_2$I$_2$

Because iodide bridges less readily than chloride or bromide, iodo-complexes containing two pyridine molecules tend to complete an octahedral structure by coordination of two water molecules as in $Cr(3\text{-}Clpy)_2(H_2O)_2I_2$ and $Cr(3\text{-}Brpy)_2(H_2O)_2I_2$. To prepare the anhydrous compound $Cr(3\text{-}Brpy)_2I_2$, the amine was dissolved in 2,2-dimethoxypropane and a solution of hydrated chromium(II) iodide in acetone added. A pale green precipitate separated, and the suspension was boiled for some minutes to ensure complete reaction of the water of hydration with the dimethoxypropane. The solid was then filtered off, washed with acetone, and dried. This procedure was not successful with $Cr(3\text{-}Clpy)_2(H_2O)_2I_2$.

E) Other Complexes

The preparation of the remaining complexes (marked E in Table I), were all analogous to that of $Cr(3\text{-chloropyridine})_2Cl_2$ which follows.

An alcoholic solution (50 cm^3) of 3-chloropyridine (5.9 g) was added to an alcoholic solution (30 cm^3) of $CrCl_2 \cdot 4H_2O$ (5.0 g). The resulting green precipitate was filtered off, washed with absolute ethanol and dried under continuous pumping for 4 h.

Several attempts were made to prepare tetrakis(amine) compounds of 3-chloro-, 3-bromo-, and 3-iodo-pyridines with chromium(II) iodide. The first two formed yellow solutions with an excess of ligand when well cooled in liquid nitrogen, but at ordinary temperature the solutions became green as the bis(amine) compound formed. When the yellow solids were filtered off rapidly the green compounds formed on the sinter. 3-Iodopyridine forms a brown, presumably tetrakis(pyridine) compound, but the analyses were poor.

Physical measurements were carried out as before [7].

References

1 (a) R. Colton and J. H. Canterford, 'Halides of the First Row Transition Elements', Wiley–Interscience, London, (1969).
(b) ibid p. 440.
2 (a) A. Earnshaw, L. F. Larkworthy and K. S. Patel, *Chemy. Ind.*, 1521 (1965);
(b) D. G. Holah and J. P. Fackler, *Inorg. Chem.*, *4*, 1112 (1965).
3 M. M. Khamar, L. F. Larkworthy and M. H. O. Nelson-Richardson, *Inorg. Chim. Acta, 28,* 245 (1978).
4 B. Morosin, *Acta Cryst., B31,* 632 (1975).
5 A. B. P. Lever, 'Inorganic Electronic Spectroscopy', Elsevier, Amsterdam, 1968; (a) p. 229; (b) p. 287.
6 A. F. Wells, 'Structural Inorganic Chemistry', Oxford, 1962, 3rd Edition, p. 915.
7 M. M. Khamar, L. F. Larkworthy, K. C. Patel, D. J. Phillips and G. Beech, *Aust. J. Chem., 27,* 41 (1974).