

## Complexes of Chromium(II) Halides with Methylpyridines

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The chromium(II) complexes  $\text{Cr}(\text{mepy})_4\text{X}_2$  and  $\text{Cr}(\text{mepy})_2(\text{H}_2\text{O})_2\text{I}_2$ , where mepy is 3- or 4-methylpyridine and X is Cl, Br, or I, are high-spin with essentially temperature-independent magnetic moments of approximately 4.8 BM. Reflectance spectra indicate six-coordination, with trans-structures for the complexes  $\text{Cr}(\text{mepy})_4\text{X}_2$ , the tetragonal distortion increasing in the order  $\text{Cl} < \text{Br} < \text{I}$ . The complexes  $\text{Cr}(\text{mepy})_2\text{X}_2$ , where X is Cl or Br, have been assigned halide-bridged structures because their magnetic moments decreased considerably as the temperature was lowered, and their reflectance spectra show that the metal ion is six-coordinate. From the far infrared spectra of  $\text{Cr}(\text{mepy})_2\text{Cl}_2$  and  $\text{Cr}(\text{mepy})_2\text{Br}_2$  it appears that stretching vibrations of short Cr–Cl bonds occur

well above  $300\text{ cm}^{-1}$ , and Cr–N and short Cr–Br stretching vibrations overlap in the region of  $280\text{ cm}^{-1}$ . The spectra of  $\text{Cr}(\text{mepy})_4\text{X}_2$  contain strong bands near  $290\text{ cm}^{-1}$  which are assigned to metal–nitrogen stretching vibrations. There are no halogen-dependent bands above  $200\text{ cm}^{-1}$ . It is therefore believed that only long Cr–X bonds are present.

### Introduction

The complexes formed by pyridine and substituted pyridines with the bivalent metals of the first transition series from manganese through copper have been extensively investigated, but only a few com-

TABLE I. Analytical Data.

Compound	C <sup>a</sup>	H	N	Cr	X <sup>b</sup>
$\text{Cr}(\text{3-mepy})_2\text{Cl}_2$ pale green	45.6 (46.6)	4.4 (4.5)	9.1 (9.1)	17.25 (16.8)	23.4 (23.0)
$\text{Cr}(\text{3-mepy})_2\text{Br}_2$ pale green	36.8 (36.2)	3.7 (3.5)	7.2 (7.0)	13.2 (13.1)	39.7 (40.2)
$\text{Cr}(\text{3-mepy})_2(\text{H}_2\text{O})_2\text{I}_2$ green	27.7 (27.3)	3.0 (3.4)	5.2 (5.3)	10.0 (9.85)	47.8 (48.1)
$\text{Cr}(\text{3-mepy})_4\text{Cl}_2$ brown	54.0 (58.2)	5.7 (5.7)	10.5 (11.3)	11.1 (10.5)	14.85 (14.3)
$\text{Cr}(\text{3-mepy})_4\text{Br}_2$ golden-brown	48.9 (49.3)	4.9 (4.8)	9.4 (9.6)	9.0 (8.9)	27.7 (27.4)
$\text{Cr}(\text{3-mepy})_4\text{I}_2$ olive-brown	41.3 (42.5)	4.3 (4.1)	8.2 (8.3)	7.9 (7.7)	36.8 (37.5)
$\text{Cr}(\text{4-mepy})_2\text{Cl}_2$ blue-green	46.0 (46.6)	5.0 (4.5)	8.8 (9.1)	17.05 (16.8)	22.5 (23.0)
$\text{Cr}(\text{4-mepy})_2\text{Br}_2$ pale green	36.1 (36.2)	3.7 (3.5)	7.0 (7.0)	13.2 (13.1)	39.6 (40.2)
$\text{Cr}(\text{4-mepy})_2(\text{H}_2\text{O})_2\text{I}_2$ green	27.4 (27.3)	4.0 (3.4)	4.9 (5.3)	10.0 (9.85)	48.3 (48.1)
$\text{Cr}(\text{4-mepy})_4\text{Cl}_2$ yellow-brown	58.1 (58.2)	5.6 (5.7)	11.2 (11.3)	10.7 (10.5)	14.5 (14.3)
$\text{Cr}(\text{4-mepy})_4\text{Br}_2$ olive-yellow	49.9 (49.3)	5.5 (4.8)	9.8 (9.6)	9.0 (8.9)	27.5 (27.4)
$\text{Cr}(\text{4-mepy})_4\text{I}_2$ olive-yellow	42.1 (42.5)	4.1 (4.1)	8.3 (8.3)	7.8 (7.7)	36.9 (37.5)

<sup>a</sup>Calculated values are given in parentheses. <sup>b</sup>Halide analyses.

TABLE II. Magnetic Data and Reflectance Spectra.

	$\mu_{\text{eff}}^{\text{a}}$ /B.M.		$\theta^{\text{b}}$ /°	$\chi_{\text{L}}^{\text{c}}$	Reflectance Spectra <sup>d</sup> /cm <sup>-1</sup>	
	300K	86K			$\nu_2$	$\nu_1$
Cr(3-mepy) <sub>4</sub> Cl <sub>2</sub>	4.79	4.74	2	292	—	9800
Cr(3-mepy) <sub>4</sub> Br <sub>2</sub>	4.90	4.79	5	314	17000sh <sup>e</sup>	10800
Cr(3-mepy) <sub>4</sub> I <sub>2</sub>	4.86	4.87	0	372	17500sh	11800
Cr(4-mepy) <sub>4</sub> Cl <sub>2</sub>	4.79	4.89	-4	292	17000sh	9700
Cr(4-mepy) <sub>4</sub> Br <sub>2</sub>	4.93	4.86	3	314	17000s	10800m
Cr(4-mepy) <sub>4</sub> I <sub>2</sub>	4.90	4.80	5	372	17500sh	12000
Cr(3-mepy) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> I <sub>2</sub>	4.88	4.80	4	250	16600s	11400m
Cr(4-mepy) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> I <sub>2</sub>	4.87	4.79	5	250	16500s	11800m
Cr(3-mepy) <sub>2</sub> Cl <sub>2</sub>	4.62	4.01	46	169	14500	11300sh
Cr(3-mepy) <sub>2</sub> Br <sub>2</sub>	4.76	4.16	42	192	14200s	11000m
Cr(4-mepy) <sub>2</sub> Cl <sub>2</sub>	4.70	4.09	45	169	14600s	11700sh
Cr(4-mepy) <sub>2</sub> Br <sub>2</sub>	4.60	4.03	41	192	14200s	11500sh

<sup>a</sup>Calculated from  $\mu_{\text{eff}} = 2.828 (\chi_{\text{A}}T)^{1/2}$ . <sup>b</sup>Curie-Weiss law taken as  $\chi_{\text{A}}^{-1} \propto (T + \theta)$ , and  $\theta$  calculated by least squares extrapolation. <sup>c</sup> $10^{-6} \chi_{\text{L}}$  is the diamagnetic correction (c.g.s.u.). <sup>d</sup>Only spectra at liquid nitrogen temperature are reported as these were better resolved. <sup>e</sup>For the tetrakis(amine) complexes  $\nu_2$  was a shoulder on much more intense charge transfer absorption rising to higher frequency and was not detectable for Cr(3-mepy)<sub>4</sub>Cl<sub>2</sub>.

plexes of pyridine with bivalent chromium have been studied [1-3]. The preparation and properties of complexes of various stoichiometries (Table I) formed by chromium(II) halides with 3- and 4-methylpyridine (3-mepy and 4-mepy) are reported in this paper.

### Experimental

All operations were carried out under nitrogen or in vacuum because of the sensitivity of the complexes to oxygen.

The bis(amine) complexes were generally prepared by the addition of a stoichiometric amount of the methylpyridine in acetone to a solution of the appropriate hydrated chromium(II) halide [4] in ethanol. The complexes separated immediately, but, except for Cr(3-mepy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>I<sub>2</sub> and Cr(4-mepy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>I<sub>2</sub>, they were sometimes hydrated to variable extents. This led to uncertainty about the coordination of water so the chloro- and bromo-complexes were dehydrated by recrystallization from dimethylformamide. The crystals were washed with acetone or ethanol and dried by direct pumping for several hours.

To isolate the tetrakis(amine) complexes addition of an excess of the methylpyridine to the chromium(II) halide was necessary. From the colour changes it was apparent that the bis(amine) complexes were first formed, and these were converted into the tetrakis-complexes on the addition of further ligand. It was difficult to isolate the brown complex Cr(3-mepy)<sub>4</sub>Cl<sub>2</sub> because even when a cold, ethanolic solution of the halide was added to cold, neat 3-methylpyridine, the brown crystals first obtained became pale green as Cr(3-mepy)<sub>2</sub>Cl<sub>2</sub> formed on warming up

to room temperature. The green solid was filtered off, the filtrate discarded, and the solid boiled with further 3-methylpyridine until it dissolved completely. The solution was chilled in liquid nitrogen and the brown tetrakis(amine) complex, which precipitated immediately, was filtered off as quickly as possible and dried without washing as this formed the bis(amine) complex. The poor analyses (Table I), however, show that the product was still contaminated with the bis-complex. The other chloro- and bromo-tetrakis(amine) complexes were obtained without difficulty and re-crystallized from dimethylformamide, although it was necessary to wash then with ethanol or acetone containing a little methylpyridine to prevent loss of coordinated amine. The iodo-tetrakis(amine) complexes were much more soluble in dimethylformamide and were re-crystallized from concentrated solutions to which ligand was added, or to which ethanol or acetone containing ligand was added. Attempts to isolate chromium(II) complexes of 2-methylpyridine produced blue substances which could not be characterised.

The methylpyridines were re-distilled before use. Dimethylformamide was dried over barium oxide and distilled under reduced pressure of nitrogen. It was stored under nitrogen. To determine the chromium content the complexes were boiled with dilute nitric acid until a deep green solution was obtained. Then ammonia was added to precipitate the hydrated oxide which was ignited to Cr<sub>2</sub>O<sub>3</sub>. Halides were determined gravimetrically as the silver halide in the filtrate.

Diffuse reflectance spectra were recorded at room and liquid nitrogen temperatures with a Unicam SP 700C spectrophotometer. The complexes were sealed in cells to prevent aerial oxidation, and lithium

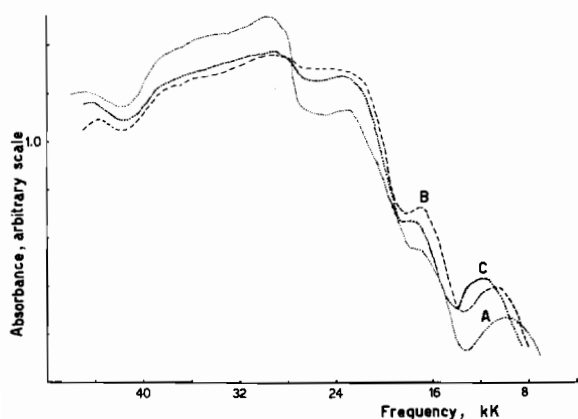


Figure 1. Reflectance spectra at liquid nitrogen temperature of A,  $\text{Cr}(4\text{-mepy})_4\text{Cl}_2$ , B,  $\text{Cr}(4\text{-mepy})_4\text{Br}_2$ , and C,  $\text{Cr}(4\text{-mepy})_4\text{I}_2$ .

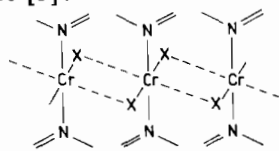
fluoride was used as a reference. Magnetic measurements were made using a Newport Instruments Ltd. Gouy balance over the temperature range 85–300 K. The samples were sealed under vacuum in glass tubes. Infrared spectra ( $4000\text{--}250\text{ cm}^{-1}$ ) of nujol mulls between KBr or polythene discs were recorded on a Perkin Elmer 457 spectrophotometer. Far infrared spectra ( $500\text{--}50\text{ cm}^{-1}$ ) of nujol mulls between polythene discs were recorded on a RIIC Interferometer FS 720. The mulls were prepared in a nitrogen bag.

## Results and Discussion

### Magnetic Behaviour

The complexes of the types  $\text{Cr}(\text{mepy})_4\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ) and  $\text{Cr}(\text{mepy})_2(\text{H}_2\text{O})_2\text{I}_2$  have effective magnetic moments  $\mu_{\text{eff}}$  near 4.8 B.M. (Table II) which show negligible variation with temperature as expected for magnetically-dilute, chromium(II) compounds with a high-spin  $3d^4$  configuration. The absence of magnetic interaction indicates that these are six-coordinate monomers, and therefore that in the iodides the water molecules are coordinated.

The complexes  $\text{Cr}(\text{mepy})_2\text{X}_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) have temperature-dependent magnetic moments, and they obey the Curie–Weiss law with large Weiss constants  $\theta$  (Table II). This antiferromagnetic interaction indicates that they have the halide-bridged, linear polymeric structure (I) found for many pyridine and substituted pyridine complexes of this general type [5].



I

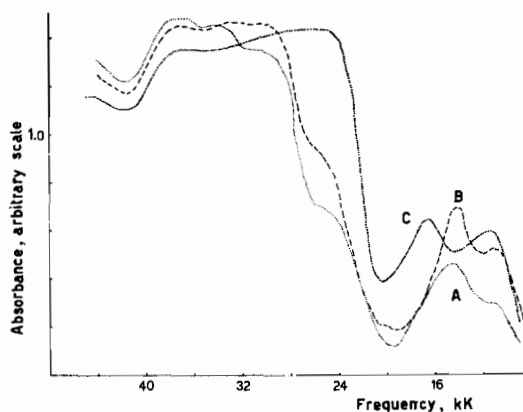


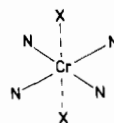
Figure 2. Reflectance spectra at liquid nitrogen temperature of A,  $\text{Cr}(3\text{-mepy})_2\text{Cl}_2$ , B,  $\text{Cr}(3\text{-mepy})_2\text{Br}_2$ , and C,  $\text{Cr}(3\text{-mepy})_2(\text{OH}_2)_2\text{I}_2$ .

Pyridine forms complexes of the same types as the methyl pyridines with chromium(II) halides and their magnetic behaviour [3] is similar.

### Electronic Spectra

The diffuse reflectance spectra of the complexes have intense charge transfer or intra-ligand absorptions above  $20000\text{ cm}^{-1}$  (Table II and Figures 1 and 2), and much weaker bands, assigned to d–d transitions, at lower frequencies. High-spin chromium(II) in an octahedral crystal field is expected to have one spin-allowed d–d transition ( ${}^5E_g \rightarrow {}^5T_{2g}$ ), but even with six identical donor atoms two absorption bands are found because the large tetragonal elongation usually associated with the high-spin  $d^4$  configuration splits the  $E_g$  (into  $B_{1g}$  and  $A_{1g}$ ) and  $T_{2g}$  (into  $B_{2g}$  and  $E_g$ ) terms. Three spin-allowed transitions are then possible:  ${}^5B_{1g} \rightarrow {}^5A_{1g}$ ,  ${}^5B_{1g} \rightarrow {}^5B_{2g}$ , and  ${}^5B_{1g} \rightarrow {}^5E_g$  ( $D_{4h}$  symmetry), but only two bands are generally found because the splitting of the T term is much less sensitive to distortion. The d–d spectra of the methylpyridine complexes follow the usual pattern. The lower frequency, weaker absorption is assigned to the  ${}^5B_{1g} \rightarrow {}^5A_{1g}$  transition (the distortion band), and the higher frequency absorption to superimposed  ${}^5B_{1g} \rightarrow {}^5B_{2g}$ ,  ${}^5E_g$  transitions (the main band). These bands are labelled  $\nu_1$  and  $\nu_2$  in Table II.

The complexes  $\text{Cr}(\text{mepy})_4\text{X}_2$  have  $\nu_1$  bands which clearly increase in frequency with X in the order  $\text{Cl} < \text{Br} < \text{I}$ . This indicates that the tetrakis(amine) complexes have approximately  $D_{4h}$  *trans*-octahedral structures (II) with halide ions coordinated along the tetra-



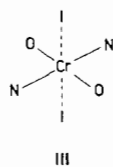
II

TABLE III. Far Infrared Spectra of Bis(mepy) Complexes.

Cr(3-mepy) <sub>2</sub> Cl <sub>2</sub>	Cr(3-mepy) <sub>2</sub> Br <sub>2</sub>	Cr(4-mepy) <sub>2</sub> Cl <sub>2</sub>	Cr(4-mepy) <sub>2</sub> Br <sub>2</sub>	Cr(3-mepy) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> I <sub>2</sub>	Cr(4-mepy) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> I <sub>2</sub>
358w	356w	336m	336w		
320vs $\nu(\text{Cr-Cl})$		332vs $\nu(\text{Cr-Cl})$			
282s $\nu(\text{Cr-N})$	282m $\nu(\text{Cr-N})$	280s $\nu(\text{Cr-N})$	296s $\nu(\text{Cr-Br})$	283sh $\nu(\text{Cr-N})$	275s, b $\nu(\text{Cr-N})$
	272vs $\nu(\text{Cr-Br})$	268m	271m $\nu(\text{Cr-N})$	278vs $\nu(\text{Cr-N})$	
234w	230w		251m	226w	212m
186s, br $\delta(\text{N-Cr-N})$	184s $\delta(\text{N-Cr-N})$	196s $\delta(\text{N-Cr-N})$	186s $\delta(\text{N-Cr-N})$	205m	198m
	176sh			180vs	
160m		158s		169s	
	126m		123m		151s, vb
100vs				94vs	95s

gonal axis so that ligand inequivalence increases the degree of distortion in the same order. Similar behaviour was found in other cases [6] where the chromium(II) complexes are of the type  $\text{CrN}_4\text{X}_2$ . The  $\nu_2$  bands are obscured [ $\text{Cr}(\text{3-mepy})_4\text{Cl}_2$ ], or appear as shoulders on the side of more intense charge transfer absorptions. Far infrared investigations confirm the structure as these complexes have no absorption bands which can be assigned to short Cr-X vibrations (see below).

The complexes  $\text{Cr}(\text{mepy})_2(\text{H}_2\text{O})_2\text{I}_2$  have clearly-resolved  $\nu_2$  bands at lower frequency as would be expected from the weaker field of  $\text{H}_2\text{O}$  compared with methylpyridine. As the distortion bands  $\nu_1$  are only a little lower in frequency than for the complexes  $\text{Cr}(\text{mepy})_4\text{I}_2$ , and the main bands  $\nu_2$  are between the values for  $\text{Cr}(\text{mepy})_4\text{X}_2$  and  $\text{Cr}(\text{mepy})_2\text{-X}_2$ , it is suggested that in the hydrates the iodide ions lie along the tetragonal axis with *trans*-ligands in the plane (III) to reduce steric effects, but this is not certain.



The formal symmetry of the chromium ion in these complexes, whichever structure is adopted, is lower than  $D_{4h}$ , but splitting of the excited E term, which would be expected, is not detectable in the spectra although there is some asymmetry on the high-frequency side of  $\nu_1$ .

The  $\nu_1$  and  $\nu_2$  bands are clearly visible in the spectra of the complexes  $\text{Cr}(\text{mepy})_2\text{X}_2$ . Halide-bridged structures analogous to (I) have been reported for many pyridine (py) and substituted pyridine complexes of bivalent transition metals, but copper(II) complexes have two different Cu-Cl bond lengths; for example, in  $\text{Cu}(\text{py})_2\text{Cl}_2$ , these are 2.298 and

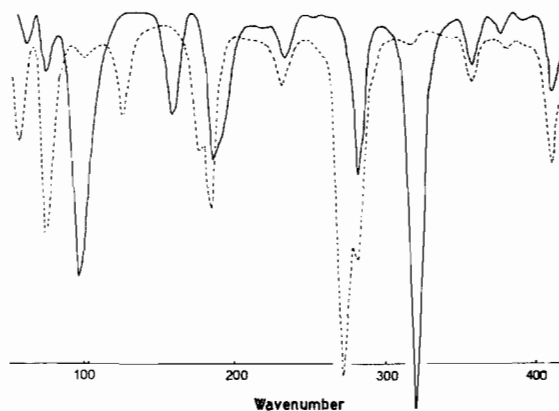


Figure 3. Far infrared spectra of  $\text{Cr}(\text{3-mepy})_2\text{Cl}_2$  (—) and  $\text{Cr}(\text{3-mepy})_2\text{Br}_2$  (-----).

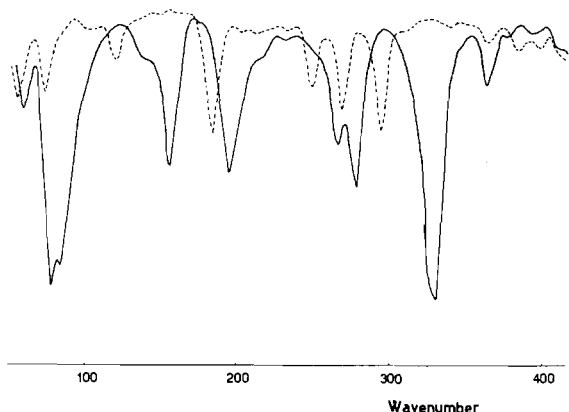
3.026 Å [5a]. Since  $\text{Cu}(\text{py})_2\text{Cl}_2$  and  $\text{Cr}(\text{py})_2\text{Cl}_2$  [1, 2], (and  $\text{Cu}(\text{py})_2\text{Br}_2$  and  $\text{Cr}(\text{py})_2\text{Br}_2$ ) are isomorphous it is likely that the complexes  $\text{Cr}(\text{mepy})_2\text{-X}_2$  have two types of Cr-Cl bond. The symmetry of the metal ion is approximately  $C_{2h}$  and splitting of the excited E term would be expected but was not detected. The  $\nu_2$  absorption is at higher frequency in the chlorides because of the greater ligand field of chloride compared with bromide. The failure of iodide ion to form bridged complexes readily is presumably due to its greater size and polarizability compared with chloride and bromide.

#### Far Infrared Spectra

Very few metal-ligand stretching vibrations have been reported for chromium(II) complexes. Clark and Williams [7] investigated the polymeric halide-bridged complex  $\text{Cr}(\text{py})_2\text{Cl}_2$  to  $200\text{ cm}^{-1}$  and assigned a band at  $219\text{ cm}^{-1}$  to  $\nu(\text{Cr-N})$  and bands at  $328\text{ cm}^{-1}$  and  $303\text{ cm}^{-1}$  to  $\nu(\text{Cr-Cl})$ . Recently [8], the spectrum of  $\text{Cr}(\text{py})_2\text{Cl}_2$  has been re-recorded from 400 to  $200\text{ cm}^{-1}$  and absorption bands found at rather different frequencies: 322vs, 281s, and 215s  $\text{cm}^{-1}$ . The band at  $322\text{ cm}^{-1}$  can be assigned to  $\nu(\text{Cr-}$

TABLE IV. Far Infrared Spectra of Tetrakis(mepy) Complexes.

Cr(3-mepy) <sub>4</sub> Cl <sub>2</sub>	Cr(3-mepy) <sub>4</sub> Br <sub>2</sub>	Cr(3-mepy) <sub>4</sub> I <sub>2</sub>	Cr(4-mepy) <sub>4</sub> Cl <sub>2</sub>	Cr(4-mepy) <sub>4</sub> Br <sub>2</sub>	Cr(4-mepy) <sub>4</sub> I <sub>2</sub>
335w		330w			
322m			332w		
295m $\nu(\text{Cr-N})$	286s $\nu(\text{Cr-N})$	292s $\nu(\text{Cr-N})$	298s $\nu(\text{Cr-N})$	296s $\nu(\text{Cr-N})$	298s $\nu(\text{Cr-N})$
280s $\nu(\text{Cr-N})$		266w			258wsh
			246m	244m	246m
222m	223m	226m			
212m $\delta(\text{N-Cr-N})$	208sh				
	204s $\delta(\text{N-Cr-N})$	202s $\delta(\text{N-Cr-N})$	202m $\delta(\text{N-Cr-N})$	199m $\delta(\text{N-Cr-N})$	192m $\delta(\text{N-Cr-N})$
		189m		180w	
172s		172w			
	166m		164m	160w	163w
146s } $\nu(\text{Cr-Cl})$		140w	142m, sh		
136s } ?			136s } $\nu(\text{Cr-Cl})$		
116s			122s } ?	120wsh	
100w, sh	108m, sh		107m	102m	106w
	98vs			95m	90m

Figure 4. Far infrared spectra of Cr(4-mepy)<sub>2</sub>Cl<sub>2</sub> (—) and Cr(4-mepy)<sub>2</sub>Br<sub>2</sub> (-----).

Cl) since it is absent from the spectrum of Cr(py)<sub>2</sub>-Br<sub>2</sub> which, in this range, has an intense, broad, and asymmetric band at 272 cm<sup>-1</sup>, and strong absorption rising to a maximum at 200 cm<sup>-1</sup>, the limit of the presently available instrument (Perkin Elmer 557). This suggests that  $\nu(\text{Cr-N})$  is at 281 cm<sup>-1</sup> in the chloride, the absorption at 272 cm<sup>-1</sup> for the bromide contains superimposed  $\nu(\text{Cr-N})$  and  $\nu(\text{Cr-Br})$  absorptions, and the band near 200 cm<sup>-1</sup> corresponds to  $\delta(\text{N-Cr-N})$ . Far infrared investigations (Table III, 400–70 cm<sup>-1</sup>) of the complexes Cr(mepy)<sub>2</sub>X<sub>2</sub> confirm these assignments. The  $\nu(\text{Cr-Cl})$  vibrations are clearly at 320 (3-mepy) and 332 cm<sup>-1</sup> (4-mepy), and  $\nu(\text{Cr-N})$  vibrations near 280 cm<sup>-1</sup> (Figures 3 and 4). Again there is overlapping of  $\nu(\text{Cr-N})$  and  $\nu(\text{Cr-Br})$  vibrations so that the correct assignments could be the reverse of those given in Table III. For the

complexes M(py<sub>2</sub>)Cl<sub>2</sub>, M = Mn, Fe, Co, Ni or Cu,  $\nu(\text{M-N})$  rises from approximately 220 cm<sup>-1</sup> (Mn) to approximately 270 cm<sup>-1</sup> (Cu) as the M–N bond increases in strength [9]. Since the  $\nu(\text{Cr-N})$  values are slightly higher than those reported for copper(II) it is likely that if similar complexes could be prepared for the first half of the transition series the  $\nu(\text{M-N})$  values would reach a maximum at chromium.

One infrared active  $\nu(\text{Cr-N})$  vibration, but two  $\nu(\text{Cr-Br})$  vibrations are expected [10] for polymeric octahedral structures (I). There are bands at 160 and 100 cm<sup>-1</sup> [Cr(3-mepy)<sub>2</sub>Cl<sub>2</sub>], and 158 and 80 cm<sup>-1</sup> [Cr(4-mepy)<sub>2</sub>Cl<sub>2</sub>] which are absent from the spectra of the corresponding bromides. Their spectra, however, contain additional bands at 126 cm<sup>-1</sup> [Cr(3-mepy)<sub>2</sub>Br<sub>2</sub>] and 123 cm<sup>-1</sup> [Cr(4-mepy)<sub>2</sub>Br<sub>2</sub>]. These halogen-dependent bands could correspond to long Cr–Cl stretching vibrations or deformations of the short Cl–Cr–Cl system. Support for these suggestions comes from investigations of other chlorochromium(II) systems. Complexes such as Cs<sub>2</sub>[CrCl<sub>4</sub>(OH<sub>2</sub>)<sub>2</sub>] have absorptions near 325 cm<sup>-1</sup> which have been assigned to short Cr–Cl stretching vibrations [11]. The complex Cs<sub>2</sub>CrCl<sub>4</sub>, which contains planar CrCl<sub>4</sub><sup>2-</sup> units linked to similar units by long Cr–Cl bonds to complete tetragonally-distorted octahedra around the metal ion, has been investigated [11] to 70 cm<sup>-1</sup> and absorptions near 300 cm<sup>-1</sup> are assigned to short Cr–Cl stretching vibrations, while a complex series of bands near 150 cm<sup>-1</sup> may be due to the deformation vibrations of the short metal-chloride bonds and/or the stretching vibrations of the long bonds.

Halogen-independent bands in all four spectra near 190 cm<sup>-1</sup> are assigned to N–Cr–N deformation vibrations.

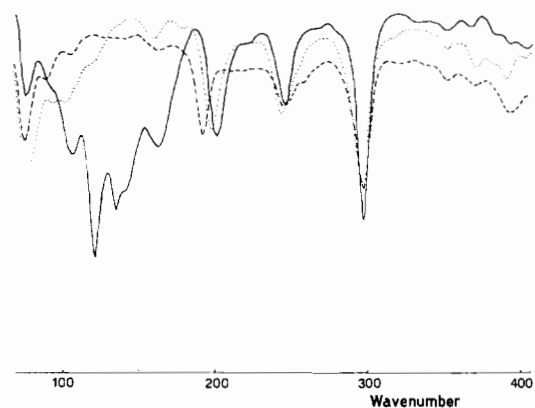


Figure 5. Far infrared spectra of  $\text{Cr(4-mepy)}_4\text{Cl}_2$  (—),  $\text{Cr(4-mepy)}_4\text{Br}_2$  (·····), and  $\text{Cr(4-mepy)}_4\text{I}_2$  (-----).

The far infrared spectra of the complexes  $\text{Cr(4-mepy)}_4\text{Br}_2$  and  $\text{Cr(4-mepy)}_4\text{I}_2$  do not differ significantly over the range investigated, and the spectrum of  $\text{Cr(4-mepy)}_4\text{Cl}_2$  differs only in that there are strong absorptions at 136 and 122  $\text{cm}^{-1}$  (Table IV and Figure 5). These halogen-sensitive bands are at much lower frequency than the  $\nu(\text{Cr}-\text{Cl})$  absorptions in the complexes  $\text{Cr(mepy)}_2\text{Cl}_2$  and this suggests that "long"  $\text{Cr}-\text{Cl}$  bonds are present in  $\text{Cr(4-mepy)}_4\text{Cl}_2$  i.e. the chloride ions are coordinated along the tetragonal axis as assumed from the reflectance spectra. The long-bond  $\nu(\text{Cr}-\text{Br})$  and  $\nu(\text{Cr}-\text{I})$  absorptions are presumably below the instrumental range. The  $\nu(\text{Cr}-\text{N})$  vibrations are just below 300  $\text{cm}^{-1}$ .

The spectra of the complexes  $\text{Cr(3-mepy)}_4\text{X}_2$  show the same general features but are more complicated. The band of the chloride at 322  $\text{cm}^{-1}$  is too weak to be a  $\nu(\text{Cr}-\text{Cl})$  vibration and long-bonded vibrations occur at 136 and 146  $\text{cm}^{-1}$  (these absorptions are absent from the spectra of the bromide and iodide), and the  $\nu(\text{Cr}-\text{N})$  vibration is split. It is also possible that the intense band at 98  $\text{cm}^{-1}$  in the

spectrum of  $\text{Cr(3-mepy)}_4\text{Br}_2$  arises from a long-bonded  $\nu(\text{Cr}-\text{Br})$  vibration as the chloride and iodide absorb weakly at this wavenumber.

The complexes  $\text{Cr(3-mepy)}_2(\text{OH}_2)_2\text{I}_2$  and  $\text{Cr(4-mepy)}_2(\text{OH}_2)_2\text{I}_2$  have similar spectra (Table III) in which strong absorptions at approximately 275  $\text{cm}^{-1}$  are assigned to  $\nu(\text{Cr}-\text{N})$  vibrations.

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