Chromium(II) Chemistry. Part 12.[1] Further Examples of Ferromagnetic Chlorochromates(II)

By **Leslie F. Larkworthy** * and **Ahmad Yavari**, The Joseph Kenyon Laboratory, University of Surrey, Guildford GU2 5XH

The chlorochromates(II) $[NMeH_3]_2[CrCl_4]$, $[NEtH_3]_2[CrCl_4]$, $[H_2en][CrCl_4]$, $[H_3dien][CrCl_4]Cl$, and $[H_4trien][CrCl_4]Cl_2$ (en, dien, and trien are ethylenediamine, 3-azapentane-1,5-diamine, and 3,6-diazaoctane-1,8-diamine respectively) are ferromagnetic whereas $[NMe_2H_2]_2[CrCl_4]$ and $[NMe_2H_2][CrCl_3]$ are antiferromagnetic. The ferromagnetic complexes are isomorphous with the corresponding copper(II) complexes. These are known to contain two-dimensional networks of planar $[CuCl_4]^{2-}$ units bridged by chloride ions of adjacent units so that the metal ions occupy tetragonally elongated octahedra. The magnetic behaviour of the ferromagnetic chromium(II) complexes from room to liquid-nitrogen temperature is reasonably represented by the high-temperature series-expansion formula for a sheet ferromagnet. The reflectance spectra of all the complexes are characteristic of six-co-ordinate Cr^{II}, and, in the case of the ferromagnetic complexes, contain very sharp bands at *ca.* 15 800 and 18 700 cm^{-1} assigned to spin-forbidden bands intensified by magnetic coupling. Absorption bands in the far-i.r. spectra near 300 cm^{-1} are assigned to Cr–Cl stretching vibrations within the planar $[CrCl_4]^{2-}$ units.

CHLOROCHROMATES(II) of the type $M_2[CrCl_4]$ (M = K, Rb, Cs,[2-4] or NH_4 [2]) have been shown to be ferromagnetic. These complexes were obtained from the melt (M = K, Rb, or Cs),[3,4] or by thermal dehydration [2] of $M_2[CrCl_4(OH_2)_2]$. The complex $[Hpy]_2[CrCl_4]$ was found [2] to be antiferromagnetic as were all the chlorochromates(II) of general formula $M[CrCl_3]$ [M = Hpy (pyridinium), K, or Cs [2,3]]. The use of non-aqueous solvents such as ethanol and glacial acetic acid has now permitted the direct isolation of crystalline, anhydrous, substituted-ammonium chlorochromates(II). This provides a much more versatile preparative procedure and further complexes exhibiting unusual magnetic behaviour have been obtained. The ferromagnetic complexes (Table 1) are $[NMeH_3]_2[CrCl_4]$, $[NEtH_3]_2[CrCl_4]$, $[H_2en][CrCl_4]$, $[H_3dien][CrCl_5]$, and $[H_4trien][CrCl_6]$ (en = ethylenediamine, dien = 3-azapentane-1,5-diamine, and trien = 3,6-diazaoctane-1,8-diamine), and the antiferromagnetic complexes are $[NMe_2H_2]_2[CrCl_4]$ and $[NMe_2H_2][CrCl_3]$. A preliminary account of some of this work has been given,[5] and Bellitto and Day [6] have recently obtained the ferromagnetic complexes $[NRH_3][CrCl_4]$ (R = Me, Et, C_8H_{17}, or $C_{10}H_{21}$) by other non-aqueous procedures. It is now known that the complex bromides $[NMeH_3]_2[CrBr_4]$ and $[NEtH_3]_2[CrBr_4]$ [7a] as well as $Cs_2[CrBr_4]$ [7b] are ferromagnetic.

TABLE 1

Analyses

Complex	Colour	Analysis (%) *				
		Cr	Cl	C	H	N
$[NEtH_3]_2[CrCl_4]$	Silver	18.2 (18.2)	49.5 (49.65)	16.7 (16.8)	5.95 (5.6)	10.15 (9.8)
$[H_2en][CrCl_4]$	Grey-green	20.0 (20.3)	55.3 (55.5)	9.1 (9.4)	4.0 (3.9)	10.6 (10.9)
$[H_3dien][CrCl_5]$	Greenish grey	15.1 (15.5)	52.9 (52.9)	14.45 (14.3)	5.0 (4.8)	12.8 (12.5)
$[H_4trien][CrCl_6]$	Off-white	12.9 (12.5)	50.8 (51.3)	17.1 (17.3)	5.5 (5.3)	13.2 (13.5)
$[NMeH_3]_2[CrCl_4]$	Greyish yellow	19.8 (20.15)	54.7 (55.0)	9.4 (9.3)	4.85 (4.65)	11.1 (10.85)
$[NMe_2H_2]_2[CrCl_4]$	Off-white	18.1 (18.2)	49.7 (49.65)	16.5 (16.8)	5.9 (5.6)	9.9 (9.8)
$[NMe_2H_2][CrCl_3]$	Greyish yellow	25.75 (25.4)	51.8 (52.1)	11.7 (11.7)	4.4 (3.9)	6.8 (6.8)

* Calculated values are given in parentheses.

EXPERIMENTAL

All the preparations and measurements were carried out under nitrogen.

Ethylammonium Tetrachlorochromate(II).—Chromium(II) chloride tetrahydrate (6.44 g), dissolved in ethanol (50 cm^3),

---

[1] Part 11, A. Earnshaw, L. F. Larkworthy, K. C. Patel, and B. J. Tucker, *J.C.S. Dalton*, 1977, 2209.

[2] L. F. Larkworthy, J. K. Trigg, and A. Yavari, *J.C.S. Dalton*, 1975, 1879.

[3] D. H. Leech and D. J. Machin, *J.C.S. Dalton*, 1975, 1609.

[4] A. K. Gregson, P. Day, W. E. Gardner, D. H. Leech, and M. J. Fair, *J.C.S. Dalton*, 1975, 1306.

[5] L. F. Larkworthy and A. Yavari, *Inorg. Chim. Acta*, 1976, **20**, L9.

[6] C. Bellitto and P. Day, *J.C.S. Chem. Comm.*, 1976, 870.

[7] L. F. Larkworthy and A. Yavari, *J.C.S. Chem. Comm.*, (*a*) 1977, 172; (*b*) 1973, 632.

was added with shaking to a solution of ethylammonium chloride (5.38 g) in ethanol (80 cm^3). The yellow-green crystals, which separated immediately, were filtered off, washed with ethanol, and dried for 6 h by continuous pumping. A silver complex was obtained which is hygroscopic and air-sensitive, turning green on exposure to air, but it does not seem absolutely necessary [6] to use specially dried starting materials in this preparation.

Methylammonium tetrachlorochromate(II) was obtained similarly. In the preparation of dimethylammonium tetrachlorochromate(II) it was necessary to concentrate the ethanolic solution of the reactants and add 2,2-dimethoxypropane to remove water and cause crystallisation of the off-white *complex*. In air the complex turned green in less than 30 min; in a desiccator over calcium chloride it soon became pink, presumably because a different reaction occurred in dry air.

Dimethylammonium Trichlorochromate(II).—Chromium(II) chloride tetrahydrate (3.67 g) was dissolved in hot glacial acetic acid (250 cm^3), and the solution was added to an excess of dimethylammonium chloride (15 g) dissolved in glacial acetic acid (25 cm^3). Pale olive-green *crystals* separated immediately from the pale green solution. They were filtered off, washed with glacial acetic acid, and dried.

Ethylenediammonium Tetrachlorochromate(II).—To $CrCl_2\cdot 4H_2O$ (4.55 g), dissolved by heating in concentrated hydrochloric acid (40 cm^3), was added a solution of ethylenediammonium chloride (3.06 g) in concentrated HCl (100 cm^3). The mixture was shaken, cooled in ice, and then allowed to stand for a few minutes; yellow-green *crystals* separated from a pale blue solution. The crystals were filtered off, washed with concentrated HCl, and then acetone, and dried.

3,6-*Diazoniaoctane*-1,8-*diammonium hexachlorochromate*-(II) was obtained similarly, but 3-*azoniapentane*-1,5-*diammonium pentachlorochromate*(II) did not crystallise until hydrogen chloride was passed through the blue solution of the constituents in concentrated HCl for *ca.* 1 min. The solution turned green and greyish green crystals separated. Both complexes were washed with concentrated HCl and then ethanol.

The corresponding copper(II) complexes were prepared as in the literature [8-10] amd their purity checked by metal and sometimes chloride analyses. Analyses and physical measurements were carried out as in previous Parts of this series except that i.r. spectra were recorded on a Perkin-Elmer 577 spectrophotometer over the range 200—4 000 cm^{-1}. The mulls were prepared from deoxygenated Nujol in a glove-bag flushed with nitrogen.

RESULTS AND DISCUSSION

Magnetic Behaviour and X-Ray Powder Data.—The effective magnetic moments (Table 2) of the tetrachlorochromates, except $[NMe_2H_2]_2[CrCl_4]$, were found to be much greater than the spin-only value (4.90 B.M.) * for high-spin Cr^{II} even at room temperature, and at liquid-nitrogen temperature they increased still further. Plots of reciprocal susceptibility, χ_A^{-1}, against absolute temperature were linear down to liquid-nitrogen temperature except for $[NEtH_3]_2[CrCl_4]$ and $[NMeH_3]_2[CrCl_4]$ which showed slight upward curvature $<$ *ca.* 120 K. Least-squares extrapolation of the linear portions gave θ values (Table 2, footnote *a*) of −50 to −75°. This behaviour is very like that of the previously reported ferromagnetic complexes.[2-4] Curie points presumably lie at *ca.* 60 K below the limit of our measurements.

TABLE 2

Magnetic properties and reflectance spectra

Complex	T/K	$\mu_{eff.}{}^a$/B.M.	$\theta\,^a$/°	10^6 Diamagnetic correction/ c.g.s. units	Reflectance spectra (cm^{-1})								
$[NEtH_3]_2[CrCl_4]$	295	6.08	−73	−168		20 400vw	18 800(sh)	18 600 ^{b}	17 600vw	15 800 ^{b}	11 250s,vb	9 700(sh)	
	90	10.12			25, 400m,b	20 600vw	18 800w	18 650 ^{b}	17 600vw	15 800 ^{b}	11 550s	9 900(sh)	8 300(sh)
$[H_2en][CrCl_4]$	295	5.11	−64	−139		20 650(sh)		18 550 ^{b}	17 350w	15 700 ^{b}	11 350s,vb		8 000(sh)
	90	8.10				20 700w		18 600 ^{b}	17 500w	15 700 ^{b}	11 500s,b		8 400m
$[H_3dien][CrCl_5]$	295	5.36	−63	−193		20 500vw		18 520 ^{b}	17 350w	15 700 ^{b}	11 200s,vb		8 000(sh)
	90	8.29			24 300m(sh)	20 700vw		18 550 ^{b}	17 500w	15 700 ^{b}	11 500s,b	9 800(sh)	8 000m
$[H_4trien][CrCl_6]$	295	5.33	−52	−246	22 400vw		18 700(sh)	18 550 ^{b}	17 400vw	15 780 ^{b}	11 300s,vb		
	90	7.35			23 000w		18 700(sh)	18 550 ^{b}	17 450vw	15 750 ^{b}	11 350s,vb	9 900(sh)	8 500(sh)
$[NMeH_3]_2[CrCl_4]$	295	5.57	−74	−144		20 500(sh)	18 800(sh)	18 650 ^{b}	17 550w	15 820 ^{b}	11 150s,vb		
	90	9.16			25 500(sh)	20 700w	18 900(sh)	18 720 ^{b}	17 600w	15 900 ^{b}	11 500s,b	10 100(sh)	8 700(sh)
$[NMe_2H_2]_2[CrCl_4]$	295	4.39	84	−168	22 600vw	20 600vw	18 500w	17 500w	17 000(sh)	15 750 ^{c}	10 500s,vb	7 500(sh)	
	90	3.69			22 650vw	20 650vw	18 500w	17 550w	17 100(sh)	15 800 ^{c}	10 800s,b	8 000m	
$[NMe_2H_2][CrCl_3]$	295	3.80		−107	22 850w	21 200(sh)	18 700w	17 600 ^{c}	16 900(sh)	15 900 ^{c}	10 980s,vb	7 700(sh)	
	90	2.46			22 850w	21 200(sh)	18 700w	17 650 ^{c}	16 900(sh)	15 950 ^{c}	11 250s,b	7 500m	

[a] Calculated from $\mu_{eff.} = 2.828(\chi_A T)^{\frac{1}{2}}$ and the Curie–Weiss law, $\chi_A^{-1} \propto (T + \theta)$. [b] Unusually intense and sharp spin-forbidden bands. [c] Medium-intense spin-forbidden bands.

X-Ray powder data [5] show that $[H_3dien][CrCl_5]$ is isomorphous with the corresponding copper(II) complex $[H_3dien][CuCl_4]Cl$. The latter has a structure,[11] refined recently,[12] which contains square-planar $[CuCl_4]^{2-}$ units in which the Cu–Cl distances are almost equal (*ca.* 2.3 Å) and discrete chloride anions and amine cations. Additional chlorides from neighbouring $[CuCl_4]^{2-}$ units complete an elongated octahedron about each copper ion and give a two-dimensional infinite network of $[CuCl_4]^{2-}$ units linked with very approximately linear Cu–Cl $\cdots$ Cu bridges (bridging angle 166.5°, ref. 11; 164.50°, ref. 12), the Cu–Cu distance being 5.108 Å. The networks are well separated by intervening amine cations and chloride ions. Single-crystal studies [13] of $[H_3dien][CrCl_5]$ and related complexes are in progress.

The complexes $[NMeH_3]_2[CuCl_4]$, $[NEtH_3]_2[CuCl_4]$,[8,14]

---

* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

[8] R. D. Willett, *J. Chem. Phys.*, 1964, **41**, 2243.

[9] M. Mori and S. Fujiwara, *Bull. Chem. Soc. Japan*, 1963, **36**, 1636.

[10] H. Remy and G. Laves, *Chem. Ber.*, 1933, 401.

[11] B. Zaslow and G. Ferguson, *Chem. Comm.*, 1967, 822; G. Ferguson and B. Zaslow, *Acta Cryst.*, 1971, **B27**, 849.

[12] T. J. Greenough and M. F. C. Ladd, *Acta Cryst.*, 1977, **B33**, 1266.

[13] M. F. C. Ladd and D. C. Povey, personal communication.

[14] J. P. Steadman and R. D. Willett, *Inorg. Chim. Acta*, 1970, **4**, 367.

and $[H_2en][CuCl_4]$ [15] have essentially the same structure with substituted ammonium ions separating the sheets of square-planar $[CuCl_4]^{2-}$ anions linked axially by long Cu–Cl bonds in which the Cu–Cu separation is again *ca.* 5.1 Å. Since *X*-ray powder data * show that the complexes of Cu^{II} and Cr^{II} are isomorphous the latter can also be assigned sheet structures. Presumably, the ferromagnetic interaction in the chromium(II) complexes is transmitted along the tetragonal axes *via* unsymmetrical, approximately linear, Cr–Cl • • • Cr bridges in which the separation of the chromium(II) ions is *ca.* 5.1 Å. The salt $Cs_2[CrCl_4]$, with which most investigations [4] have so far been carried out, has the $K_2[NiF_4]$ structure in which two-dimensional networks of planar $[CrCl_4]^{2-}$ units, bridged by four linear Cr–Cl–Cr bonds, are separated by double layers of caesium and chloride ions. The six-fold co-ordination of the chromium(II) ion is completed by axial (non-bridging) chloride ions within the CsCl layers 2.399 Å away, but the planar Cr–Cl bond lengths are all 2.609 Å, *i.e.* the octahedron is compressed along its four-fold axis; the magnetic interaction is presumably not transmitted along this tetragonal axis, because non-bridging chloride ions lie along it, but along the symmetrical Cr–Cl–Cr bridges in which the Cr–Cr separation is 5.2 Å, very close to that in the substituted-ammonium salts. Further structural investigation is necessary, but it seems that the magnitude of the metal-ion separation is critical for the development of ferromagnetic interaction.

The structures of the isomorphous complexes $[H_4trien][CuCl_6]$ and $[H_4trien][CrCl_6]$ are not known, but since the chromium(II) complex has similar magnetic and spectroscopic properties to $[H_3dien][CrCl_4]Cl$ it is likely that both should be formulated as $[H_4trien][MCl_4]Cl_2$.

The magnetic behaviour of the complexes $[NMeH_3]_2[CrCl_4]$, $[H_3dien][CrCl_5]$, and $[H_4trien][CrCl_6]$ over the range 85—300 K is well reproduced by substitution of the values of *J* (the nearest-neighbour exchange integral) and *g* given in Table 3 in the high-temperature series-expansion formula [16] (1) ($x = J/kT$) for a sheet ferromagnet. When *g* values close to (and generally a little below) the value of 2.00 expected for high-spin chromium(II) complexes are chosen the fits are satisfactory, although they are less satisfactory for $[NEtH_3]_2[CrCl_4]$ and $[H_2en][CrCl_4]$ than for the other complexes (Figure 1).

TABLE 3

Exchange integrals (*J*) of chlorochromates(II)

Complex	J/cm^{-1}	g
(*a*) ferromagnetic		
$[NMeH_3]_2[CrCl_4]$	7.51	1.94
$[NEtH_3]_2[CrCl_4]$	9.24	2.01
$[H_2en][CrCl_4]$	4.92	1.94
$[H_3dien][CrCl_5]$	6.16	1.94
$[H_4trien][CrCl_6]$	5.41	1.94
(*b*) Antiferromagnetic		
$[NMe_2H_2]_2[CrCl_4]$	−5.80	2.00
$[NMe_2H_2][CrCl_3]$	−11.1	1.90

$$Ng\beta^2/\chi = (kT/2) + J(-4 + 9x - 9.072x^2 + 55.728x^3 - 160.704x^4 + 116.64x^5) \quad (1)$$

The complex $[NMe_2H_2]_2[CrCl_4]$ has magnetic moments well below the spin-only value over the temperature range studied, and $\theta = 84°$. It is therefore antiferromagnetic, like $[Hpy]_2[CrCl_4]$,[2] although the stoicheiometry is the same as that of the ferromagnetic complexes. The antiferromagnetic behaviour of $[NMe_2H_2]_2[CrCl_4]$ can be approximately represented by substitution of the *J* and *g* values in Table 3 in expression (1) after changing the signs of the coefficients appropriately.[16] There is no crystallographic evidence that this complex has a sheet structure although the antiferromagnetic behaviour and the reflectance spectra (see below) show that the anions must be polymerised. It is unfortunate that powder data show this and the corresponding copper(II) complex [10] not to be isomorphous because if they were single-crystal investigations of the latter air-stable complex might have given more information on the relation of magnetic behaviour to structure.

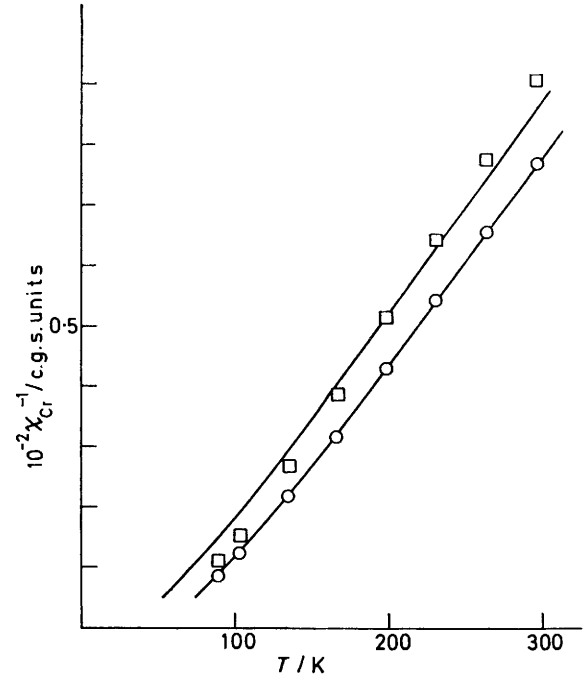

FIGURE 1 Comparison of variation with temperature of calculated (—) and experimental reciprocal molar susceptibilities for $[NMeH_3]_2[CrCl_4]$ (○) and $[H_2en][CrCl_4]$ (□)

The complex $[NMe_2H_2][CrCl_3]$ is also antiferromagnetic and presumably has a linear-chain structure [17] like $Cs[CrCl_3]$. Powder data show that it is not isomorphous with the analogous copper(II) complex.[18] However,

---

* These and the detailed magnetic data are to be found in Supplementary Publication No. SUP 22282 (13 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[15] G. B. Birrell and B. Zaslow, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1751.

[16] M. E. Lines, *J. Phys. and Chem. Solids*, 1970, **31**, 101.

[17] Ting-i Li and G. D. Stucky, *Acta Cryst.*, 1973, **B29**, 1529.

[18] R. D. Willett, *J. Chem. Phys.*, 1966, **44**, 39.

the magnetic data could be fitted only poorly using the one-dimensional expression given by Smith and Friedberg [19] even when a low value of g was assumed (Table 3), although reasonable fits were obtained [3] for Cs[CrCl$_3$].

Electronic Spectra.—The reflectance spectra (Table 2) indicate that in all the complexes the anions are polymerised because the reflectance spectra are typical [2] of six-co-ordinate Cr^{II}. The more intense band near 11 000 cm^{-1} is assigned to superimposed $^5B_{1g}\rightarrow{}^5B_{2g}$ and $^5B_{1g}\rightarrow{}^5E_g$ transitions (D_{4h} ligand field) and the weaker band in the region of 8 000 cm^{-1} to the $^5B_{1g}\rightarrow{}^5A_{1g}$ transition. The weak shoulder apparent in some spectra near 10 000 cm^{-1} may be due to a resolved $^5B_{1g}\rightarrow{}^5B_{2g}$ transition.

The unusually intense and sharp bands at *ca.* 15 800 and 18 700 cm^{-1} in the spectra of the ferromagnetic complexes were also found in the spectra of the ferromagnetic alkali-metal tetrachlorochromates(II), and were assigned to spin-forbidden transitions to the $^3E_g(^3H)$ and $^3A_{1g}(^3G)$ terms intensified through the magnetic coupling. It has recently been demonstrated [6] that these bands in the spectrum of [NMeH$_3$]$_2$[CrCl$_4$] lose their intensity at 20 K, which is well below the Curie temperature (expected to be *ca.* 60 K), because at this temperature there is insufficient population of the higher-energy spin levels for the intensity-enhancing mechanism to operate. There was little diminution of intensity on cooling to liquid-nitrogen temperature, the limit of our measurements. The presence of these intense bands appears to be characteristic of chromium(II) complexes which order ferromagnetically. In the reflectance spectra, the spin-forbidden bands and the ligand-field transitions were of similar intensity, but the spectrum of [NEtH$_3$]$_2$[CrCl$_4$] dissolved in ethanol exhibited only the ligand-field transitions as a broad asymmetric band at 12 100 cm^{-1}, presumably because of the destruction of the polymeric structure on dissolution.

TABLE 4

Far i.r. spectra (200—500 cm^{-1}) of chromium(II) complex chlorides

Compound	ν(Cr–Cl) [a]							
Cs$_2$[CrCl$_4$] [b]		312s	294m					
Cs$_2$[CrCl$_4$] [b,c]		312s	292vs		168(sh)	158s	152vs,	144m
			288s		114w	102m	76s	
[NMeH$_3$]$_2$[CrCl$_4$] [d]		303m						
[NEtH$_3$]$_2$[CrCl$_4$]	410m	315(sh)	293s					
[NEtH$_3$]Cl				262w				
[H$_2$en][CrCl$_4$]		318(sh)	300s,vb					
[H$_2$en]Cl$_2$	339m			250m				
[H$_3$dien][CrCl$_5$]	345(sh)	305s		267m	208m			
[H$_3$dien]Cl$_3$	353w	294s			*ca.* 200m			
[H$_4$trien][CrCl$_6$]		310s		275(sh)	*ca.* 200m			
[H$_4$trien]Cl$_4$	400w		298m		*ca.* 200m			
[NMe$_4$][CrCl$_3$] [e]		299s		255(sh)				
[NMe$_2$H$_2$][CrCl$_3$]		308s		251m				
Cs$_2$[CrCl$_4$(OH$_2$)$_2$] [e]	450m [f]	335s		236m [g]				
Rb$_2$[CrCl$_4$(OH$_2$)$_2$] [e]	446m [f]	325s		237w [g]				
[NH$_4$]$_2$[CrCl$_4$(OH$_2$)$_2$] [e]	458m [f]	325s		243w [g]				

[a] Broad bands in this region. [b] Ref. 2, crystalline sample obtained from acetyl chloride–glacial acetic acid; samples obtained by thermal dehydration of dihydrates did not mull well and no spectra were obtained. [c] Recorded on an RIIC FS 720 interferometer over the range 50—400 cm^{-1} at liquid-nitrogen temperature. [d] Where bands of corresponding substituted-ammonium chloride are not given there was no significant absorption in the region concerned. [e] Ref. 2. [f] ν(Cr–O). [g] δ(O–Cr–O).

The reflectance spectra of the antiferromagnetic complexes contain a series of clearly present, but much less intense, spin-forbidden bands. The Tanabe–Sugano diagram indicates that the high-spin d^4 configuration leads to many spin-forbidden transitions. In other chromium complexes these are usually obscured by the spin-allowed bands because ligands stronger than chloride are present.

Infrared Spectra.—The i.r. spectra in the fingerprint region confirm the presence of the organic cations, or water in the case of M$_2$[CrCl$_4$(OH$_2$)$_2$] (M = Rb, Cs, or NH$_4$), which were prepared earlier [2] but i.r. spectra were not reported. The rubidium and ammonium salts were found [2] to be isomorphous with the corresponding copper(II) complexes. The same is probably true for the caesium salts although this was not checked because of difficulties with Cs$_2$[CuCl$_4$(OH$_2$)$_2$] which readily decomposed to Cs$_2$[CuCl$_4$]. The anions [CuCl$_4$(OH$_2$)$_2$]$^{2-}$ have *trans* structures with Cu–O bond lengths of *ca.* 2.55 Å, and ' short ' and ' long ' Cu–Cl bond lengths of *ca.* 2.3 and 3.0 Å respectively.[20] The isomorphous chromium(II) complexes therefore also contain short and long Cr–Cl bonds. In the spectra of the chromium(II) hydrates (Table 4) the bands at *ca.* 450 and 240 cm^{-1} are assigned to ν(Cr–O) and δ(Cr–O) vibrations. The strong band at 325 or 335 cm^{-1} is assigned to a short ν(Cr–Cl) vibration. These frequencies are similar to those assigned [21] to short Cu–Cl stretching vibrations from studies of polarised i.r. spectra of crystals of the complexes A$_2$[CuCl$_4$(OH$_2$)$_2$] (A = ammonium or alkali-metal cation). Absorptions due to stretching vibrations of the long Cr–Cl bonds and deformations of the short Cr–Cl bonds are presumably to be expected in the 130—180

---

[19] T. Smith and S. A. Friedberg, *Phys. Rev.*, 1968, **176**, 660.

[20] R. Colton and J. H. Canterford, ' Halides of the First Row Transition Metals,' Wiley–Interscience, London, 1969, p. 535.

[21] J. T. R. Dunsmuir and A. P. Lane, *J. Chem. Soc. (A)*, 1971, 2724; D. M. Adams and P. J. Lock, *ibid.*, 1967, 620; 1971, 2801.

cm^{-1} region where they are found for the copper(II) complexes.

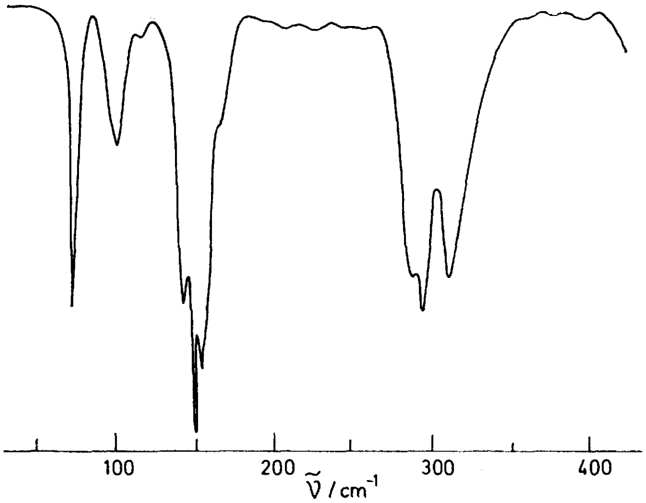

FIGURE 2 Far-i.r. spectrum of $Cs_2[CrCl_4]$

Except through what can reasonably be considered counter-ion absorptions, the anhydrous chlorochromates do not absorb significantly in regions of the Cr–O vibrations of the aqua-complexes. However, medium-to-strong absorptions occurring in the range 285—320 cm^{-1} just below the values in the spectra of the aqua-complexes are assigned to short Cr–Cl stretching vibrations within the planar $CrCl_4$ units. A square-planar $CrCl_4$ unit is expected to have one i.r.-active ν(Cr–Cl) mode. However, in this region either a very broad band (sometimes complicated by absorption of the counter ions) or, more generally, two bands are found. The splitting probably arises because the $CrCl_4$ units are not isolated: there are two terminal Cr–Cl bonds, and two in which chloride bridges to other units.

The spectrum of a crystalline sample of $Cs_2[CrCl_4]$ was recorded down to 50 cm^{-1} (Figure 2). Besides absorptions assigned to short Cr–Cl stretching vibrations near 300 cm^{-1}, there is intense complex absorption centred at 152 cm^{-1}. By analogy with the far-i.r. spectra [21] of $A_2[CuCl_4(OH_2)_2]$, this complex absorption is assigned to overlapping long-bonded Cr–Cl stretching and short-bonded Cr–Cl deformation vibrations.

We thank the Ministry of Science and Higher Education of Iran for the award of a scholarship (to A. Y.).

[7/1810 *Received, 14th October, 1977*]