Chromium(II) Chemistry. Part IX.[1] Ferromagnetic and Antiferromagnetic Chlorochromates(II)

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The new chromium(II) complex chlorides $M_2[CrCl_4(OH_2)_2]$ [M = NH_4, Hpy (pyridinium), Rb, or Cs] are magnetically dilute, high-spin compounds with reflectance spectra of the type expected for tetragonally distorted octahedral anions $[CrCl_4(OH_2)_2]^{2-}$. Several compounds are isomorphous with their copper(II) analogues of known structure. Thermal dehydration gives compounds $M_2[CrCl_4]$ (M = NH_4, Rb, or Cs), which are ferromagnetic as is $K_2[CrCl_4]$ obtained from a hydrate too unstable to be completely characterized. The reflectance spectra again indicate tetragonal six-co-ordination, and hence the anhydrous compounds have polymeric structures which permit the ferromagnetic interaction through 180° coupling. Unusually intense spin-forbidden absorptions are found in the reflectance spectra of these compounds. The complex $Cs[CrCl_3(OH_2)_2]$ is weakly antiferromagnetic and presumably has a similar structure to $Li[CuCl_3(OH_2)_2]$. Chloride-bridged structures in $[Hpy]_2[CrCl_4]$ and $M[CrCl_3]$ (M = Hpy, Me_4N, or Cs) produce antiferromagnetic behaviour which leads to slight intensification of the spin-forbidden bands.

EARLIER workers[2] reported that from a mixture of hexamine ($C_6H_{12}N_4$), concentrated hydrochloric acid, and a transition-metal chloride MCl_2, the chromium(II) compound, $CrCl_2 \cdot 2HCl \cdot (C_6H_{12}N_4) \cdot 2OH_2$, can be isolated. Attempts to prepare this compound, which is the first example of a complex Cr^{II} chloride not studied in melts,[3,4] were unsuccessful, probably due to the decomposition of hexamine in concentrated HCl. However, from mixtures of hydrated chromium(II) chloride and an alkali metal, ammonium, or substituted ammonium chloride several hydrated Cr^{II} complex chlorides have been isolated[5] (Table 1). These have been thermally dehydrated to complex chlorides in which, according to the stoicheiometry and the nature of the cation, ferromagnetic or antiferromagnetic interactions occur. Compounds in which ferromagnetic interactions occur are

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[1] Part VIII, L. F. Larkworthy, K. C. Patel, and J. K. Trigg, *J. Chem. Soc.* (*A*), 1971, 2766.

[2] G. A. Barbieri and A. Tettamanzi, *Atti. Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1932, **15**, 877.

[3] H. J. Seifert and K. Klatyk, *Z. anorg. Chem.*, 1964, **334**, 113; R. Gut and R. Gnehur, *Chimica e Industria*, 1962, **16**, 289; S. N. Shkol'nikov and A. M. Volkov, *Izvest. Vyss. Uchebn. Zavedenii, Tsvetn. Met*, 1964, **7**, 82.

[4] D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, 1963, **6**, 23.

[5] L. F. Larkworthy and J. K. Trigg, *Chem. Comm.*, 1970, 1221.

still comparatively uncommon.[6,7] During the present work the preparation of some of these compounds by the addition of the metal or ammonium acetate to a solution of chromium(II) acetate in a mixture of acetyl chloride and glacial acetic acid was reported,[8] but no magnetic or reflectance measurements were carried out. Recently, investigations [9,10] of the magnetic, spectroscopic, and neutron-diffraction[11] properties at liquid-helium temperature and above of the anhydrous chlorides $M_2[CrCl_4]$ (M = K, Rb, or Cs) obtained from the melt have been described.

EXPERIMENTAL

The hydrated complex chlorides were obtained under nitrogen from aqueous solutions containing stoicheiometric quantities of $CrCl_2{\cdot}4OH_2$ [12] and the appropriate chloride. The preparations of the caesium tetrachlorochromates(II) are described below. Since minor variations in experimental conditions can give chlorides of differing stoicheiometry, brief details for the other compounds are given below or in footnotes in Table 1.

TABLE 1

Analyses and some preparative details

Compound	Colour	(Analyses [a]/%) Cr	Cl	H_2O	C	H	N
$[NH_4]_2[CrCl_4(OH_2)_2]$ [b]	Light blue	19.9 (19.6)	53.3 (53.3)	13.5 (13.6)		4.2 (4.6)	10.2 (10.5)
$[Hpy]_2[CrCl_4(OH_2)_2]$ [c]	Light green	13.5 (13.3)	36.2 (36.4)		30.7 (30.8)	4.1 (4.1)	7.2 (7.2)
$Rb_2[CrCl_4(OH_2)_2]$ [b,d]	Light blue	13.1 (13.0)	35.4 (35.4)	9.3 (9.0)			
$Rb_2[CrCl_4(OH_2)_2]$ [b,d]	Green	13.1 (13.0)	35.4 (35.4)	8.9 (9.0)			
$Cs_2[CrCl_4(OH_2)_2]$ [d]	Light blue	10.5 (10.5) 10.8 [e]	28.5 (28.6) 28.5 [e]	7.2 (7.3)			
$Cs[CrCl_3(OH_2)_2]$ [b]	Off-white	16.2 (15.9)	32.5 (32.5)	10.8 (11.0)			
$[NH_4]_2[CrCl_4]$ [d]	Yellow–brown	22.9 (22.6)	61.6 (61.7)				
$K_2[CrCl_4]$ [d]	Yellow–green	19.2 (19.1)	51.8 (52.1)				
$[Hpy]_2[CrCl_4]$	Yellow	15.3 (14.7)	40.3 (40.1)		32.8 (33.9)	3.5 (3.4)	7.8 (7.9)
$[Hpy][CrCl_3]$	Yellow	22.4 (21.8)	44.2 (43.5)		25.4 (25.2)	2.5 (2.5)	6.0 (5.9)
$Rb_2[CrCl_4]$	Chocolate	14.3 (14.3)	38.4 (38.9)				
$Cs_2[CrCl_4]$ [d]	Brown	11.6 (11.3) 11.6 [f]	30.8 (30.9) 30.8 [f]				

[a] Calculated values are given in parentheses. [b] Isolated from solutions of constituents in concentrated HCl. [c] Isolated from ethanol. [d] See Experimental section for preparative details. [e] Sample reprepared from $Cs_2[CrCl_4]$. [f] Obtained from a mixture of acetyl chloride and acetic acid.

Dicaesium Diaquatetrachlorochromate(II), $Cs_2[CrCl_4(OH_2)_2]$.—The solution obtained when caesium chloride (9.12 g) was added to $CrCl_2{\cdot}4OH_2$ (5.28 g) in water (20 cm^3) was concentrated to *ca.* 3 cm^3 and shaken with acetone (75 cm^3). The resulting blue crystals were filtered off, washed with acetone, dried by continuous pumping, and preserved in sealed glass tubes. In air the crystals soon become pink. Acetone was used to wash the other hydrates, but was not needed to crystallize them from the concentrated hydrochloric acid in which they were prepared.

Dicaesium Tetrachlorochromate(II), $Cs_2[CrCl_4]$.—The hydrated compound prepared as above was filtered off on a sintered-glass filter under nitrogen. The compound on the sinter was preserved from aerial oxidation by taps above and below the sinter, and a pig was attached above. When the hydrate had been washed with acetone the glass tube below the sinter was sealed off above the tap, the sinter immersed in a bath at 140 °C, and the compound dehydrated by pumping on it continuously for *ca.* 7 h. The brown compound obtained was then shaken from the sinter into the pig and sealed off in the glass tube. It is stable to dry air as are the anhydrous compounds generally. The dihydrates had i.r. absorptions at *ca.* 3 300 and 1 620 cm^{-1} due to water which were absent from the spectra of the anhydrous compounds. The water content was confirmed by thermogravimetric analysis. A sample of this compound, prepared by Hardt and Streit's method [8] from acetyl chloride in glacial acetic acid but starting from Cr^{II} chloride instead of the acetate, was identical with the compound obtained by dehydration.

In the preparation of $[NH_4]_2[CrCl_4]$ the dihydrate was heated at 130 °C because at 150 °C a white solid, presumably ammonium chloride, condensed on the cooler walls of the apparatus and a mixture of yellow-brown and yellow material remained. To prepare $[Hpy]_2[CrCl_4]$ the dihydrate was heated at 40 °C *in vacuo* over P_4O_{10} for 1 week with the whole apparatus in a drying cabinet to prevent condensation of [Hpy]Cl on colder parts of the apparatus (Hpy = pyridinium). Heating under continuous pumping at 80 °C for *ca.* 15 h gave $[Hpy][CrCl_3]$. Although 2 : 1 or even greater ratios of $[Me_4N]Cl$ to $CrCl_2{\cdot}4OH_2$ were used in ethanol and in acetic acid, only $[Me_4N][CrCl_3]$ was obtained.

Potassium and Lithium Systems.—When a blue aqueous solution containing a 2 : 1 molar ratio of potassium and chromium(II) chlorides was concentrated to a small volume and then shaken with acetone blue crystals separated. These were filtered off and dried *in vacuo*, and a blue free-running substance, presumably the dihydrate, was obtained, but after 24 h water appeared on the sides of the sealed containers and after 1 week a white solid could be seen. The magnetic moment of a freshly prepared specimen, calculated assuming a dihydrate, was 4.6 B.M.,* invariant with temperature, and the reflectance spectrum resembled those of the other dihydrates (Table 2), but no analyses were

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* 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2, 1 oersted = $(10^{-5}\ \text{N})^{\frac{1}{2}}$ cm^{-1}.

[6] D. H. Martin, 'Magnetism in Solids,' Iliffe Books Ltd., London, 1967, p. 35.

[7] F. E. Mabbs and D. J. Machin, 'Magnetism and Transition Metal Complexes,' Chapman and Hall, London, 1973, p. 9.

[8] H. D. Hardt and G. Streit, *Z. anorg. Chem.*, 1970, **373**, 97.

[9] D. H. Leech and D. J. Machin, *J.C.S. Chem. Comm.*, 1974, 866.

[10] P. Day, A. K. Gregson, and D. H. Leech, *Phys. Rev. Letters*, 1973, **30**, 19.

[11] M. T. Hutchings, A. K. Gregson, P. Day, and D. H. Leech, *Solid State Comm.*, 1974, **15**, 313.

[12] A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *J. Chem. Soc.*, 1965, 3267.

obtained. Dehydration gave yellow-green $K_2[CrCl_4]$ with satisfactory analyses. Attempts to obtain lithium salts were unsuccessful.

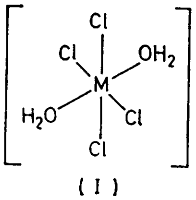
Solutions of Chromium(II) *Chloride in Concentrated Hydrochloric Acid.*—The erratic production of a green solution when $CrCl_2{\cdot}4OH_2$ was dissolved in concentrated HCl was first thought to be due to oxidation, but this was not so since its spectrum had peaks at 11 800 and 5 600 cm^{-1} which on deliberate aerial oxidation were replaced by much more intense peaks at 22 000 and 14 900 cm^{-1}, and on dilution with water the spectrum of the hydrated Cr^{II} ion [12] was obtained. This behaviour, and the resemblance of the solution spectrum to the reflectance spectra of the complex chlorides (Table 2), shows that the green colour was due to chloro-complexes. Dilute solutions of $CrCl_2{\cdot}4OH_2$ in concentrated HCl are green, but concentrated solutions are blue. A green form of $Rb_2[CrCl_4(OH_2)_2]$ was isolated by addition of RbCl in concentrated HCl to the former, and a blue form similarly from the latter. There were very minor differences in reflectance spectra in the 20 000 cm^{-1} region, but both forms had magnetic properties and powder photographs identical within experimental error and gave ferromagnetic $Rb_2[CrCl_4]$ on dehydration.

Analyses and Physical Measurements.—Analyses and magnetic and spectroscopic measurements were carried out as before.[1] *X*-Ray powder photographs were recorded on a Philips PW 1024/00 camera of radius 114.6 mm with copper K_α radiation and a nickel filter. Air-sensitive samples were preserved in sealed Lindemann capillaries. Thermogravimetric analyses were carried out under nitrogen on a Stanton automatic thermorecording balance.

No field-dependence of magnetic moment was detected at room or liquid-nitrogen temperatures. Field strengths used ranged from *ca.* 1 500 to 4 500 Oe. Most measurements on the ferromagnetic compounds were carried out at *ca.* 2 000 Oe because higher fields caused the tube to stick to the side of the cryostat, especially at low temperatures. Field-dependence studies at liquid-nitrogen temperatures were carried out in a sample in a thick-walled Pyrex tube of *ca.* 2 mm internal diameter.

RESULTS AND DISCUSSION

Magnetic Behaviour.—The dihydrated complex chlorides containing 2 : 1 ratios of MCl to $CrCl_2$ have effective magnetic moments $\mu_{eff.}$ (Table 2) close to the spin-only value (4.90 B.M.) at all temperatures studied; they obeyed the Curie law (Weiss constant θ ≈ 0 °) and are therefore [12] magnetically dilute and high spin. This is consistent with discrete anionic structures, (I). The 1 : 1 compound $Cs[CrCl_3(OH_2)_2]$ has a magnetic moment below the spin-only value which was reduced further as the temperature was decreased due to antiferromagnetic interactions. Its magnetic behaviour can be reproduced by substitution of $J = -3.0$ cm^{-1} and $g = 1.93$ in the expression [13] for a binuclear compound with



(I)

TABLE 2

Magnetic properties and reflectance spectra

Compound	T/K	$\mu_{eff.}$ ^{a}/ B.M.	θ ^{a}/°	10^6 Diamagnetic correction/ c.g.s. units	Reflectance spectra/cm^{-1}							
$[NH_4]_2[CrCl_4(OH_2)_2]$	295	4.80	5	−133		18 800w (sh)		16 800w (sh)		12 900s		10 000m (sh)
	90	4.70				18 900w (sh)		16 900w (sh)		13 500s		10 400m (sh)
$[Hpy]_2[CrCl_4(OH_2)_2]$	295	4.67	−1	−217		19 100vw		17 500w (sh)		13 300s		10 850 (sh)
	90	4.64				19 050vw		17 500w (sh)		13 600s		11 100m
$K_2[CrCl_4(OH_2)_2]$ ^{b}	295	4.63	0	−136						13 000s		10 000 (sh)
	90	4.63								13 400s		9 800m
$Rb_2[CrCl_4(OH_2)_2]$	295	4.89	0	−151		18 900vw (sh)		17 000w (sh)		12 900s		9 500m (sh)
(light blue)	90	4.91				19 000vw (sh)		17 000w (sh)		13 600s		11 000m
	295	4.84	−1	−151		19 900wvb		16 800w (sh)		13 000s		9 600 (sh)
(green)	90	4.84				20 200wvb		17 000w (sh)		13 200s		10 800m (sh)
$Cs_2[CrCl_4(OH_2)_2]$	295	4.87	0	−176						12 900svb		
		(4.90) ^{c}										
	90	4.87	(0) ^{c}		22 500vw		18 900vw (sh)	17 200vw (sh)		13 100svb		
		(4.90) ^{c}										
$Cs[CrCl_3(OH_2)_2]$	295	4.61	24	−134	23 400w	19 100w	18 200w	16 800w	16 000w	12 300s		6 600m
	90	4.25			23 400w	19 100w	18 200w	16 800w	16 000w	12 400s	11 500w (sh)	7 000m
$[NH_4]_2[CrCl_4]$	295	5.70	−73	−107	23 000w		18 600 ^{d}	17 400 (sh)	15 800 ^{d}	11 000s		8 000m (sh)
	90	9.93					18 600 ^{d}	17 600 (sh)	15 800 ^{d}	11 200s		8 000m (sh)
$K_2[CrCl_4]$	295	5.32	−72	−110	22 600w (sh)		18 700 ^{d}	17 500w	15 900 ^{d}	11 000s		7 700m (sh)
	90	8.90			22 500wb	19 800vw (sh)	18 700 ^{d}	17 600w	15 900 ^{d}	11 400s	9 800 (sh)	7 700m
$Rb_2[CrCl_4]$	295	5.85	−82	−125	22 500w (sh)		18 700 ^{d}	17 700w (sh)	15 900 ^{d}	10 900s		7 600m (sh)
	90	11.3			22 700wb		18 700 ^{d}	17 700w (sh)	15 900 ^{d}	11 200s		7 400m
$Cs_2[CrCl_4]$	295	5.79	−82	−150			18 700 ^{d}		15 900 ^{d}	11 000s		7 500m (sh)
		(5.59) ^{e}	−86) ^{e}									
	90	11.6			21 000vb ^{f}		18 700 ^{d}		15 900 ^{d}	11 200s	10 500 (sh)	8 000m (sh)
		(11.35) ^{e}										
$[Hpy]_2[CrCl_4]$	295	4.28	77	−191			18 600w	17 600w ^{g}	15 700w	11 000s		8 000m (sh)
	90	3.55					18 600w	17 500w ^{g}	15 800w	11 300s		8 000m (sh)
$[Me_4N][CrCl_3]$	295	3.81 ^{h}		−135	22 600w	20 900w	18 700w	17 600w ^{g}	16 050w	10 300s		7 500m (sh)
	90	2.46			22 700w	21 000 (sh)	18 800w	17 600w ^{g}	16 000w	11 000s		8 000m (sh)
$Cs[CrCl_3]$	295	3.30		−95	23 000w		18 100wb		15 800w	11 200s		5 900m
	90	1.95					18 600w	17 500m	15 800w	11 500s	10 800 (sh)	5 900m
$[Hpy][CrCl_3]$	295	4.44		−119			18 600w	17 400w ^{g}	15 700w	10 800s		7 000 (sh)
	90	3.05				21 000 (sh)	18 600w	17 500w ^{g}	15 800w	11 200s		7 500m (sh)

[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] No analyses, and degree of hydration uncertain (see Experimental section). [c] Re-obtained from ferromagnetic $Cs_2[CrCl_4]$. [d] Unusually intense, narrow, spin-forbidden bands. [e] Prepared from acetyl chloride and glacial acetic acid; the reflectance spectrum was almost identical with that given above for the product from the dihydrate. [f] Spin-forbidden bands seem, at liquid–nitrogen temperature, to be superimposed on this very broad band or shoulder centred at *ca.* 21 000 cm^{-1}. [g] Additional shoulders at 16 900 cm^{-1}. [h] Néel point at 104 K.

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[13] A. Earnshaw, 'Introduction to Magnetochemistry,' Academic Press, London, 1968.

$S = 2$. The related copper(II) compound Li[$CuCl_3$-$(OH_2)_2$] has a structure in which binuclear $Cu_2Cl_2(OH_2)_2$ units, formed by symmetrical chloride bridges, are weakly linked by further chloride bridges to form chains.[14]

The anhydrous compounds M_2[$CrCl_4$], except [Hpy]$_2$-[$CrCl_4$], have magnetic moments which are much greater than the spin-only value at room temperature, and increased still further as the temperature decreased (Table 2 and Figure 1). This is ferromagnetic behaviour. At the lowest temperatures available the atomic susceptibility, χ_a, and $\mu_{eff.}$ still increased very sharply as the temperature was lowered so that the Curie point lies below 85 K. The ferromagnetic compounds gave graphs of reciprocal susceptibility, χ_a^{-1}, against absolute temperature which were non-linear below *ca.* 150 K (Figure 1). The θ values (Table 2) were obtained by least-squares extrapolation of the upper linear portion. Impurities cannot be responsible for the ferromagnetic behaviour because (*a*) the compounds were formed by dehydration of the normally paramagnetic dihydrates in all-glass apparatus, (*b*) duplicate preparations gave reproducible moments, (*c*) reformation of Cs_2[$CrCl_4$-$(OH_2)_2$] from Cs_2[$CrCl_4$] destroyed the ferromagnetism by breaking up the polymeric structure (see below), (*d*) a variety of compounds behave similarly, and (*e*) Cs_2[$CrCl_4$] was ferromagnetic whether prepared from the dihydrate or isolated from a mixture of glacial acetic acid and acetyl chloride. It has also been shown recently that K_2[$CrCl_4$] prepared from the melt[9] is ferromagnetic. Extrapolation of the upper linear portion of the reciprocal susceptibility against temperature curve gave a Weiss constant of −67 ° with which our value of −72 ° is in good agreement. For Cs_2[$CrCl_4$] our θ values of −82 or −86 ° (Table 2) agree reasonably with the value of −76 ° for a preparation from the melt. Magnetization experiments have confirmed[10] that K_2[$CrCl_4$] becomes ferromagnetic below 65 K. It is also possible to reproduce the magnetic data theoretically in terms of a Heisenberg ferromagnet assuming a square lattice with $S = 2$ and an exchange integral of 5.0 cm.$^{-1}$ Further analysis[15] of the ferromagnetic behaviour of these compounds is being carried out, and recently reported neutron-diffraction studies[11] have further confirmed the ferromagnetic alignment of the spins.

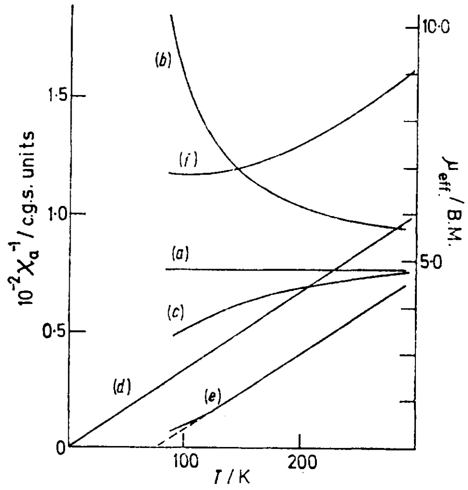

FIGURE 1 Variation with absolute temperature of effective magnetic moments, $\mu_{eff.}$, of (*a*) Rb_2[$CrCl_4(OH_2)_2$], (*b*) [NH_4]$_2$-[$CrCl_4$], and (*c*) [Me_4N][$CrCl_3$]. Curves (*d*), (*e*), and (*f*) show the variation of the corresponding molar susceptibilities, $10^{-2}\chi_a^{-1}$

The compound [Hpy]$_2$[$CrCl_4$] and all those of general formula M[$CrCl_3$] have magnetic moments well below the spin-only value at room temperature which decreased further with decreasing temperature. In general, reciprocal susceptibility against absolute temperature plots either curved upwards at low temperature or if linear had large θ values; the magnetic behaviour of these compounds is therefore antiferromagnetic. Recently, it has been found[9] for Cs[$CrCl_3$] that substitution of values of J and g within the ranges −25.0 to −26.5 cm^{-1} and 1.94—1.98 respectively in the expression[16] for a one-dimensional array of spins reasonably replicated the magnetic data. Our data for Cs[$CrCl_3$] differ somewhat,* possibly because, unlike the preparation from the melt,[9] the sample was not crystallized but obtained by dehydration and its amorphous nature could have affected the results. Similarly, although the magnetic behaviour of [Hpy][$CrCl_3$] was similar, the magnetic data were not reproducible between duplicate preparations with satisfactory analyses. The compound [Me_4N][$CrCl_3$] has a Néel point at 104 K and its magnetic data can be fitted approximately to the one-dimensional expression with $J = -12.5$ cm^{-1} and $g = 2.02$. The data for [Hpy]$_2$-[$CrCl_4$] follow the expression[9] for a two-dimensional antiferromagnet with $J = -6.5$ cm^{-1} and $g = 1.97$.

Electronic Spectra.—One spin-allowed *d-d* transition is expected in the visible spectra of octahedral high-spin Cr^{II} compounds. However, even when six identical donor atoms are present[17] the spectra of Cr^{II} compounds consist of a main band, usually of greater intensity, and a weaker band or shoulder (the so-called distortion band) at lower frequency, because of tetragonal distortion arising from the $t_{2g}^3e_g^1$ configuration. The main band is ascribed in D_{4h} symmetry to superimposed $^5B_{1g}\rightarrow{}^5B_{2g}$ and $^5B_{1g}\rightarrow{}^5E_g$ transitions, and the distortion band to the $^5B_{1g}\rightarrow{}^5A_{1g}$ transition. The reflectance spectra (Table 2 and Figure 2) of the complex chlorides followed the usual pattern for tetragonal six-co-ordinate Cr^{II} with main bands at 12 000—13 000 cm^{-1} (dihydrates) or *ca.* 11 000 cm^{-1} (anhydrous compounds), and shoulders or less-intense bands at lower frequencies.

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* These data, together with those of *X*-ray-diffraction measurements, are to be found in Supplementary Publication No. SUP 21419 (8 pp.). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[14] P. H. Vossos, L. D. Jennings, and R. E. Rundle, *J. Chem. Phys.*, 1960, **32**, 1590.

[15] P. Day and D. J. Machin, personal communication.

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

[17] A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc.* (*A*), 1969, 1339, 2276.

The *X*-ray powder patterns of $[NH_4]_2[CrCl_4(OH_2)_2]$ and $Rb_2[CrCl_4(OH_2)_2]$ and the analogous Cu^{II} compounds were almost identical. Thus the complex anions in the hydrated 2 : 1 compounds have structures (I) as in $[NH_4]_2[CuCl_4(OH_2)_2]$ in which[18] *trans*-chloride ions are held by long bonds (*ca.* 3.1 Å) to the metal. Chloride-bridged tetragonal structures are ascribed to the anhydrous compounds $M_2[CrCl_4]$. If co-ordinated ions replace water molecules in structure (I) this accounts for the movement of the main band to lower frequency on dehydration. Presumably because they were prepared by dehydration of the solid dihydrates, the anhydrous chlorides gave poor powder patterns. A crystalline sample of $Cs_2[CrCl_4]$ prepared from acetyl chloride and glacial acetic acid gave a clear pattern and the *d* spacings calculated from this agreed well with those reported earlier.[3] A possible structure for $Cs[CrCl_3(OH_2)_2]$ has been suggested above. The anhydrous complexes M$[CrCl_3]$ are likely to have the anionic chain structures reported for $Cs[CrCl_3]$ and $Cs[CrBr_3]$[19] with which the magnetic behaviour of the chlorides is compatible.

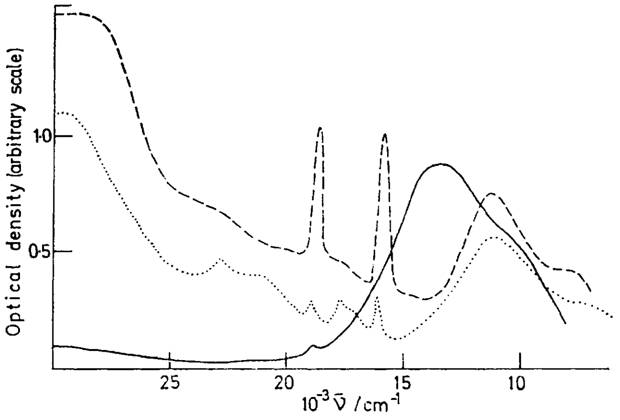

FIGURE 2 Reflectance spectra of $[NH_4]_2[CrCl_4(OH_2)_2]$ (——), $[Me_4N][CrCl_3]$ (· · · ·), and $[NH_4]_2[CrCl_4]$ (— — —)

The reflectance spectra of the Cr^{II} compounds were rich in spin-forbidden bands. For example, $Cs_2[CrCl_4(OH_2)_2]$ and $Cs[CrCl_3(OH_2)_2]$ showed several weak absorptions between 15 500 and 24 000 cm^{-1}. All these bands disappeared on deliberate oxidation so that none can be due to traces of Cr^{III}. The Tanabe–Sugano diagram for high-spin Cr^{II} shows many triplet levels which could account for these absorptions. The single-crystal spectrum of $Cs[CrCl_3]$ has[19] been reported, with which the powder reflectance spectrum reported here is in moderate agreement. Since the crystal structure shows no evidence of a static Jahn–Teller distortion, *i.e.* there should be no splitting of the E_g level, the lowest-energy band (*ca.* 6 000 cm^{-1}) is assigned[19] to the $^5E_g \rightarrow {}^3T_{1g}(H)$ transition and that at 11 500 cm^{-1} to the $^5E_g \rightarrow {}^5T_{2g}$ transition whereas we have assigned these to the $^5B_{1g} \rightarrow {}^5A_{2g}$ and superimposed $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$ transitions. If $10Dq$ is assumed to be *ca.* 11 000 cm^{-1} for chloride and $B = 830$ cm^{-1} for Cr^{II}, the Tanabe–Sugano diagram suggests that the $^5E_g \rightarrow {}^3T_{1g}(H)$ transition is at higher energy.

The ferromagnetic compounds exhibited two bands, which were unusually sharp and intense compared with the spin-allowed absorptions, at *ca.* 15 900 and 18 700 cm^{-1}, superimposed on weaker broader absorption in the 17 000—19 000 cm^{-1} region, and the separation between the two bands suggests that they are due to spin-forbidden transitions to the $^3E_g(^3H)$ and $^3A_{1g}(^3G)$ terms which have gained unusual intensity due to the magnetic coupling. Spectra of the antiferromagnetic chlorides showed more intense spin-forbidden bands than the dihydrates, but these were much weaker than in the ferromagnetic compounds. It has also been found that similarly prominent bands occur[20] in the reflectance spectrum of the ferromagnetic compound $Cs_2[CrBr_4]$, but not in spectra of other bromides which are antiferromagnetic or normally paramagnetic. Although the compound $K[CrF_3]$ was magnetically normal[21] down to liquid-nitrogen temperature, the lower limit of the measurements, similar intense bands were found in its reflectance spectrum, and neutron-diffraction investigations[22] indicated antiferromagnetic alignment between ferromagnetic layers at 4.2 K.

At liquid-nitrogen temperature little change occurred in the spectra of the ferromagnetic chlorides, but recent investigations[10] of $K_2[CrCl_4]$ showed that at 4.2 K the spin-forbidden bands almost disappeared, and it is believed that the high intensity of these bands arises from an exchange-induced dipole mechanism. The details of the mechanism vary according to whether the magnetic coupling is ferromagnetic or antiferromagnetic, and this leads to different intensities and temperature dependence of intensity.

Magnetic Behaviour and Structure.—Presumably because of lack of data, there has been little discussion of magnetic interaction in Cr^{II} compounds. The many paths permitting parallel (ferromagnetic interaction) or antiparallel (antiferromagnetic interaction) coupling in 180° high-spin d^4 systems have been described[23] for the situation where two planar $[CrX_4]^{2-}$ units share a corner, and it has been concluded that the net result is likely to be antiferromagnetic coupling, in contradiction of the results now available. The compound $Cs_2[CrCl_4]$ has very recently[11] been reported to have a tetragonally compressed octahedron of chloride ions about the metal ion: Cr–Cl (axial) 2.399 Å and Cr–Cl (equatorial) 2.609 Å. Since it has the $K_2[NiF_4]$ structure,[24] this implies that the magnetic coupling is transmitted *via* the long linear Cr–Cl–Cr axes. The long metal–chloride

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distance could lead to a dampening of the antiferromagnetic compared with the ferromagnetic interaction. The only chloride of 2 : 1 stoicheiometry which exhibits antiferromagnetism so far obtained is $[Hpy]_2[CrCl_4]$. No structural data are available for this compound, the corresponding Cu^{II} compound does not seem to have been reported, and attempts to obtain crystals of $[Hpy]_2[CrCl_4]$ from glacial acetic acid with or without acetyl chloride gave $[Hpy][CrCl_3]$. It is possible that the presence of the pyridinium cation reduces the Cr–Cl–Cr angle and/or the tetragonal distortion and favours the antiferromagnetic interaction. The angle must be important since 1 : 1 compounds, *e.g.* $Cs[CrCl_3]$, have linear-chain structures[19] in which the Cr–Cl–Cr bridge angles are much closer to 90 than 180° and their antiferromagnetism agrees with the predictions.[23] Direct interaction may also be more important in the 1 : 1 compounds where the chromium atoms are much closer together. The nature of the bridging atom is also important since most bromides $M_2[CrBr_4]$ are antiferromagnetic except $Cs_2[CrBr_4]$[20] and $[EtH_3N]_2[CrBr_4]$ which are ferromagnetic.

Tetrahedral Chromium(II).—An absorption band of a molten KCl–LiCl eutectic containing $CrCl_2$ at 9 800 cm^{-1} (ε 45 l mol^{-1} cm^{-1}) has been assigned[4] to a very distorted $[CrCl_4]^{2-}$ ion. However, the anhydrous double chlorides (Table 2) of either stoicheiometry, which are polymeric and distorted six co-ordinate, have absorption bands at room temperature at *ca.* 11 000 and 6 000—8 000 cm^{-1}. Therefore, the 9 800 cm^{-1} band seems more likely to be due to six-co-ordinate and polymeric species still present in the molten eutectic, the somewhat different frequency being due to the different temperatures of the measurements.

Others have found it impossible to isolate complexes of the type $[Et_4N]_2[CrX_4]$ from acetonitrile[25] or from tetrahydrofuran[26] or other solvents in attempts to obtain tetrahedral Cr^{II}, and likewise we were unable to isolate any salts of the $[Et_4N]^+$ ion from glacial acetic acid, ethanol, or aqueous HCl. Such compounds, like the closely related compounds in Table 1, are expected to be polymeric and tetragonal, rather than distorted tetrahedral.[26] In its failure readily to form distorted tetrahedral anions of the type $[CrX_4]^{2-}$, high-spin Cr^{II} differs from Cu^{II} and this is exceptional. Two compounds, $CrBr_2{\cdot}2POPh_3$ and $CrI_2{\cdot}2POPh_3$ are believed[26] to contain tetrahedral Cr^{II}, and tetrahedral Cr^{II} ions are believed[25] to exist in acetonitrile solutions containing chromium(II) bromide and an excess of halide ion, but the evidence is not extensive.

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