Ferromagnetic Tetrahalogenochromates(II) containing Mixed Halides (Cl and Br)†

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Tetrahalogenochromates(II) containing mixed halides, $[NRH_3]_2[CrCl_xBr_{4-x}]$ (R = Me, Et, Pr^n, Bu^n, or n-C_8H_{17}), exhibit similar ferromagnetic behaviour to the homoleptic tetrahalogenochromates(II). Broad spin-allowed *d–d* absorption bands at *ca.* 10 900 cm^{-1} in their reflectance spectra indicate tetragonal six-co-ordination of chromium(II) and hence polymeric structures; the reflectance spectra also contain very sharp absorption bands at *ca.* 15 900 and 18 700 cm^{-1} assigned to spin-forbidden *d–d* transitions intensified by the magnetic coupling. Far-i.r. absorption bands near 290 and 245 cm^{-1} are assigned to ν(Cr–Cl) and ν(Cr–Br) vibrations respectively.

Tetrachlorochromates(II) and tetrabromochromates(II) containing monoalkylammonium cations, $[NRH_3]_2[CrCl_4]$ (R = Me, Et, Pr^n, n-C_5H_{11}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, Ph, *o*-MeC_6H_4, or CH_2Ph)[1–5] and $[NRH_3]_2[CrBr_4]$ (R = Me, Et, Pr^n, n-C_5H_{11}, n-C_8H_{17}, or n-$C_{12}H_{25}$),[6] have been found to exhibit ferromagnetic behaviour, which is still rare amongst transition-metal complexes.[7] Corresponding tetrahalogenochromates(II) containing mixed halides (chloride and bromide) (Table 1) have now been found to exhibit the same unusual behaviour. Except for the recently reported rubidium salts, $Rb_2[CrCl_3Br]$, $Rb_2[CrCl_2Br_2]$, and $Rb_2[CrCl_2I_2]$,[8] these are the first mixed halides of chromium(II) to be obtained, although such compounds are well known for transition metals such as copper(II).[9]

Results and Discussion

Magnetic and Spectroscopic Properties.—The mixed halides exhibit typical ferromagnetic behaviour: magnetic moments ($\mu_{eff.}$) greater than the spin-only value (4.90 B.M.) at room temperature, which increase considerably as the temperature is lowered; and Curie–Weiss law behaviour with positive intercepts on the temperature axis, as found earlier for this class of complex.[1–8] From, for example, the magnetic moments of the monobutylammonium salts (Table 1), the magnetic behaviour of the mixed halides is found to be closer to that of the $[CrCl_4]^{2-}$ salts than of the $[CrBr_4]^{2-}$ salts. This appears to be due to chloride rather than bromide bridges (see below).

Like other tetrachlorochromates(II), the far-i.r. spectrum of $[NBu^nH_3]_2[CrCl_4]$ has a strong absorption band near 300 cm^{-1} (Table 2) which can be assigned to Cr–Cl stretching vibrations. As expected, the analogous bromide has a band at lower wavenumber (242 cm^{-1}) in the region where other tetrabromochromates(II) absorb.[6] The mixed halides absorb in both regions, but the Cr–Cl band is much the more intense. The diffuse reflectance spectra (Table 2) of the mixed halides contain, near 10 900 cm^{-1}, a broad, asymmetric band which is characteristic of tetragonally distorted, six-co-ordinate chromium(II) and can be assigned to the overlapping spin-allowed transitions $^5B_{1g} \longrightarrow (^5A_{1g}, {}^5B_{2g}$, and $^5E_g)$. This value is between the values for analogous chlorides (*ca.* 11 000 cm^{-1}) and bromides (*ca.* 10 500 cm^{-1}), although the breadth of the bands prevents accurate comparison. There are also two narrow bands of unusual intensity near 18 700 and 15 900 cm^{-1} which are characteristic of ferromagnetic tetrahalogenochromates(II). These bands have been assigned to quintet–triplet transitions which have gained intensity through magnetic coupling.[3,4,7,8]

Structures.—Single-crystal *X*-ray investigations have shown that the ferromagnetic complexes $[H_3N(CH_2)_3NH_3][CrCl_4]$,[10] $[H_3dien][CrCl_4]Cl$ (dien = diethylenetriamine),[11] $[NMeH_3]_2[CrCl_4]$,[4] and $[NEtH_3]_2[CrCl_4]$[12] contain infinite sheets of $[CrCl_4]^{2-}$ units bridged by approximately linear Cr–Cl–Cr bonds to give tetragonally elongated, six-co-ordinate chromium(II). The magnetic behaviour and the reflectance spectra suggest similar structures for the mixed halides, and this has been confirmed by a structural investigation[12] of $[NEtH_3]_2[CrCl_{2.9}Br_{1.1}]$, which is isomorphous with $[NEtH_3]_2[CrCl_4]$. In the mixed halide there are linear chloride bridges, but the bromide ions are in terminal positions. Since magnetic interaction is transmitted *via* the bridging atom this would explain why the magnetic behaviour of this and the other mixed halides is closer to that of the tetrachlorochromates(II) rather than of the tetrabromochromates(II). The spectroscopic properties are intermediate because they reflect the average environment of the Cr^{2+} ion.

The greater propensity of chloride to form bridges and its greater donor ability have presumably biased the preparation of crystals containing a higher proportion of chloride, although equimolar quantities of each halide were used in the preparations. No investigations of the effect of varying the $Br^-:Cl^-$ molar ratio on the composition of the products have been carried out.

Experimental

The mixed halides were prepared under nitrogen from anhydrous chromium(II) bromide or chloride and the alkylammonium chloride or bromide in 1:2 molar ratios in glacial acetic acid. They are all hygroscopic and air sensitive. Measurements were carried out as before.[1]

$[NMeH_3]_2[CrCl_{2.3}Br_{1.7}]$.—Anhydrous chromium(II) bromide (2.74 g) was dissolved in hot glacial acetic acid (50 cm^3) to give a green solution. To this was added methylammonium chloride (1.69 g) dissolved in warm glacial acetic acid (50 cm^3). The halide separated as pale yellow plates. The reaction mixture was refluxed for 10 min but the crystals did not redissolve. They

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† *Non-S.I. unit employed:* B.M. ≈ 9.27 × 10^{-24} A m^2.

Table 1. Analytical data and magnetic properties

		Analyses^a (%)					Magnetic properties		
Compound	Colour	C	H	N	Cr	T/K	$\mu_{eff.}{}^b$/B.M.	θ^b/°	$10^6\chi_D{}^c$/cm^3 mol^{-1}
$[NMeH_3]_2[CrCl_{2.3}Br_{1.7}]$	Pale yellow	7.2	3.5	8.4	15.9	295	5.72	−94	165
		(7.2)	(3.6)	(8.4)	(15.6)	90	11.9		
$[NEtH_3]_2[CrCl_{2.6}Br_{1.4}]$	Pale yellow	13.9	4.5	7.8	14.8	295	5.50	−83	185
		(13.8)	(4.6)	(8.0)	(14.9)	90	10.2		
$[NEtH_3]_2[CrCl_{2.9}Br_{1.1}]$	Pale yellow	14.5	4.7	8.0	15.7	295	5.48	−83	180
		(14.4)	(4.8)	(8.4)	(15.5)	90	9.43		
$[NPr^nH_3]_2[CrCl_{2.6}Br_{1.4}]$	Pale yellow	19.0	5.2	7.2	14.1	295			
		(19.2)	(5.4)	(7.4)	(13.8)	90			
$[NPr^nH_3]_2[CrCl_{2.2}Br_{1.8}]$	Pale yellow	18.4	5.2	7.0	13.4	295	5.55	−84	210
		(18.3)	(5.1)	(7.1)	(13.2)	90	10.0		
$[NBu^nH_3]_2[CrCl_4]$	Silver	28.9	6.8	7.8		295	5.60	−63	215
		(28.1)	(7.1)	(8.2)		90	9.11		
$[NBu^nH_3]_2[CrCl_{2.6}Br_{1.4}]$	Pale yellow	23.7	6.1	6.5	13.2	295	5.66	−69	230
		(23.8)	(6.0)	(6.9)	(12.9)	90	9.47		
$[NBu^nH_3]_2[CrBr_4]$	Golden yellow	18.8	4.7	5.3	10.4	295	5.95	−85	260
		(18.5)	(4.7)	(5.4)	(10.0)	90	12.5		
$[N(C_8H_{17})H_3]_2[CrCl_{2.2}Br_{1.8}]$	Yellow-brown	36.1	7.7	5.0	9.4	295	5.52	−70	340
		(36.0)	(7.6)	(5.2)	(9.7)	90	9.73		

[a] Calculated values in parentheses. For several of the mixed halides less satisfactory but reasonable agreement between calculated and experimental values is obtained by assuming integral values for halide content, *e.g.* calculated for $[NMeH_3]_2[CrCl_2Br_2]$: C, 6.9; H, 3.5; Cr, 15.0; N, 8.1%. However, since the anions are polymerised the formulae which fit best are given. [b] Calculated from $\mu_{eff.} = 2.828(\chi_{Cr}T)^{\frac{1}{2}}$ and the Curie–Weiss law, $\chi_{Cr}{}^{-1} \propto (T + \theta)$; θ values from least-squares extrapolation of higher-temperature linear part of curve. [c] Diamagnetic correction.

Table 2. Diffuse reflectance and far-i.r. spectral data

	Reflectance/cm^{-1}				Far-i.r./cm^{-1}	
Compound					ν(Cr–Cl)	ν(Cr–Br)
$[NMeH_3]_2[CrCl_{2.3}Br_{1.7}]$	18 600	17 500	15 900	10 800vbr	305vs,vbr	250w
$[NEtH_3]_2[CrCl_{2.6}Br_{1.4}]$	18 700	17 500	15 900	10 900	290vs,vbr	250 (sh)
$[NEtH_3]_2[CrCl_{2.9}Br_{1.1}]$	18 700	17 600	15 900	11 100	280vs,vbr	250 (sh)
$[NPr^nH_3]_2[CrCl_{2.6}Br_{1.4}]$	18 700		15 950	11 100	290s,vbr	240 (sh)
$[NPr^nH_3]_2[CrCl_{2.2}Br_{1.8}]$	18 700	17 500	15 950	10 900	290vs,vbr	250 (sh)
$[NBu^nH_3]_2[CrCl_4]$					300vs,vbr	
$[NBu^nH_3]_2[CrCl_{2.6}Br_{1.4}]$	18 600	17 500	15 900	10 900	290vs,vbr	245 (sh)
$[NBu^nH_3]_2[CrBr_4]$	18 450	17 500	15 800	10 800		242s
$[N(C_8H_{17})H_3]_2[CrCl_{2.2}Br_{1.8}]$	18 600	17 500	15 900	10 900	290m,vbr	225m

were filtered off, washed with acetic acid and then acetone, and dried by pumping for 12 h.

Pale yellow plates of the ethylammonium salt $[NEtH_3]_2$-$[CrCl_{2.6}Br_{1.4}]$ were prepared similarly from anhydrous chromium(II) chloride and ethylammonium bromide. When the conditions were varied, in that the ethylammonium bromide was extracted by hot glacial acetic acid into a solution of chromium(II) bromide in acetic acid, pale yellow plates of $[NEtH_3]_2[CrCl_{2.9}Br_{1.1}]$ were obtained. No crystals separated from ethanolic solutions of the constituents.

The n-propylammonium salt $[NPr^nH_3]_2[CrCl_{2.2}Br_{1.8}]$ was obtained as pale yellow plates similarly to the methylammonium salt, from chromium(II) chloride and n-propylammonium bromide. When the alkylammonium bromide was extracted by refluxing glacial acetic acid into a chromium(II) chloride solution a product analysing as $[NPr^nH_3]_2[CrCl_{2.6}Br_{1.4}]$ was obtained.

In the preparation of $[NBu^nH_3]_2[CrCl_{2.6}Br_{1.4}]$ a solution of n-butylammonium bromide (2.87 g) in glacial acetic acid (30 cm^3) was added to a hot solution of anhydrous chromium(II) chloride (1.16 g) in glacial acetic acid (50 cm^3). The pale yellow plates which separated immediately were redissolved by heating and the solution allowed to cool. The crystals were filtered off, washed with acetic acid, and dried in vacuum for 15 h.

The n-octylammonium salt $[N(C_8H_{17})H_3]_2[CrCl_{2.2}Br_{1.8}]$ was prepared by extraction of n-octylammonium bromide (6.2 g) into a hot solution of anhydrous $CrCl_2$ (1.8 g) in glacial acetic acid (75 cm^3). The crystals were washed with glacial acetic acid and dried for 10 h at the pump.

$[NBu^nH_3]_2[CrCl_4]$.—To prepare the monobutylammonium tetrachlorochromate(II), the amine hydrochloride (5.12 g) in ethanol (60 cm^3) was added slowly to an ethanolic solution of $CrCl_2 \cdot 4H_2O$ (4.56 g, 50 cm^3). The white crystals were filtered off, washed with methylated spirits, and dried at the pump. The corresponding bromide $[NBu^nH_3]_2[CrBr_4]$ was prepared by extraction of the amine hydrobromide (4.81 g) into hot glacial acetic acid (200 cm^3) containing anhydrous $CrBr_2$ (3.31 g). Golden yellow plates separated on slow cooling; these were filtered off, washed with acetic acid, and dried in vacuum.

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