Chromium(II) Chemistry. Part 14.[1] Ferromagnetic and Antiferromagnetic Tetrabromochromates(II)

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

The dihydrated chromium(II) complex bromides $M_2[CrBr_4(OH_2)_2]$, where M = Cs, Rb, NH_4, or Hpy (py = pyridine), are magnetically dilute, high-spin compounds. The ammonium salt is isomorphous with the analogous copper(II) bromide which is known to contain *trans*-$[CuBr_4(OH_2)_2]^{2-}$ anions with two short and two long Cu–Br bonds. The piperazinium salts $[H_2pipz]_2[CrBr_6]\cdot 2H_2O$ and $[H_2pipz]_2[CrBr_6]$, and the guanidinium salt $[C(NH_2)_3]_2[CrBr_4]\cdot 2MeCO_2H$, are also magnetically dilute. Their reflectance spectra are as expected for tetragonally distorted octahedral anions. Thermal dehydration gives the compounds $M_2[CrBr_4]$, where M = Cs, Rb, NH_4, $NPhH_3$, or Hpy, but the monoalkylammonium salts $[NRH_3]_2[CrBr_4]$, where R = Me, Et, Pr^n, Bu^n, n-C_5H_{11}, n-C_8H_{17}, or n-$C_{12}H_{25}$, $[NMe_2H_2]_2[CrBr_4]$, and $[C(NH_2)_3]_2[CrBr_4]\cdot 2MeCO_2H$ have been crystallised from glacial acetic acid, and $[NEt_4]_2[CrBr_4]$ from mixed organic solvents. Ferromagnetic behaviour is exhibited by $Cs_2[CrBr_4]$ and the monoalkylammonium salts, but the other tetrabromochromates(II) are antiferromagnetic. The reflectance spectra indicate tetragonal six-co-ordination of Cr^{II} and hence polymeric structures. Like the analogous tetrachlorochromates(II), the magnetic data for the ferromagnetic tetrabromochromates from liquid-nitrogen to room temperature can be reproduced by the high-temperature series-expansion formula for a sheet ferromagnet with $S = 2$, and $J_{Br} > J_{Cl}$. The reflectance spectra contain very sharp bands at *ca*. 15 600 and 18 400 cm^{-1} assigned to spin-forbidden transitions intensified by magnetic coupling. The magnetic behaviour of the antiferromagnetic complexes is reproduced by the high-temperature series-expansion formula with appropriate changes of sign. The stretching vibrations of the short Cr–Br bonds occur near 250 cm^{-1}.

RECENT investigations have shown that chlorochromates(II) of the type $M_2[CrCl_4]$ (M = K, Rb, Cs, NH_4,[2-5] or NRH_3,[4,6,7] where R = Me, Et, C_8H_{17}, or $C_{10}H_{21}$) are ferromagnetic, as are[6] $[H_2en][CrCl_4]$, $[H_3dien][CrCl_4]Cl$, and $[H_4trien][CrCl_4]Cl_2$ (en = ethylenediamine, dien = diethylenetriamine, and trien = triethylenetetraamine). These complexes are also unusual in that their solid-state spectra show well resolved and comparatively intense spin-forbidden absorptions near 15 800 and 18 700 cm^{-1}. These bands lose their intensity through ferromagnetic ordering on cooling to 4.2 K.[4,7] Other tetrachlorochromates(II), $[Hpy]_2[CrCl_4]$[3] (py = pyridine) and $[NMe_2H_2]_2[CrCl_4]$,[6] and all those of the general formula $M[CrCl_3]$, M = Hpy, NMe_4,[3] K, Cs,[5] or NMe_2H_2,[6] show antiferromagnetic behaviour. In a search for further complexes with unusual magnetic properties, tetrabromochromate(II) salts of a variety of alkali-metal and organic cations have been synthesised (Table 1). Preliminary accounts[8] of some of this work have been given.

EXPERIMENTAL

The hydrated complex bromides, except the pyridinium salt, were obtained under nitrogen from solutions in concentrated hydrobromic acid of stoicheiometric quantities of[9] $CrBr_2\cdot 6H_2O$ and the appropriate bromide. The preparations of the caesium, piperazinium, and pyridinium salts are described below.

Dicaesium Diaquatetrabromochromate(II).—Chromium(II) bromide hexahydrate (7.43 g) was dissolved by heating in 12 mol dm^{-3} hydrobromic acid (20 cm^3). The blue solution was added slowly with shaking to a cold solution of caesium bromide (9.88 g) in the same solvent (35 cm^3). Light blue crystals quickly appeared. These were filtered off, washed with acetone, dried by continuous pumping, and sealed in glass tubes under vacuum.

The piperazinium salt, $[H_2pipz]_2[CrBr_6]\cdot 2H_2O$, was obtained as light blue *crystals* from a mixture of hot solutions in 12 mol dm^{-3} hydrobromic acid of the reactants in 1 : 1 mol ratio. The stoicheiometry is unexpected in view of the reactant ratio. It was necessary to heat to dissolve the piperazinium bromide. The crystals were washed with concentrated hydrobromic acid and then acetone.

Dipyridinium Diaquatetrabromochromate(II).—Chromium(II) bromide hexahydrate (1.96 g), dissolved in ethanol (15 cm^3), was added to a solution of pyridinium bromide in ethanol (1.92 g, 10 cm^3). The pale green solution was concentrated *in vacuo* until a few crystals appeared. The whole was shaken with ethyl acetate and the light green crystals which separated in bulk were filtered off, washed with ethyl acetate, and dried by continuous pumping for 15 h.

The anhydrous complexes were prepared by thermal dehydration[3] of the dihydrates *in vacuo* over many hours, or directly by crystallisation from glacial acetic acid or ethanol. The temperatures used in dehydration were: $Cs_2[CrBr_4]$, 130; $Rb_2[CrBr_4]$, 150; $[NH_4]_2[CrBr_4]$, 150 (in this preparation a white film, presumably a trace of ammonium bromide, appeared above the bulk of the solid, but the analyses were satisfactory); $[NPhH_3]_2[CrBr_4]$, 120; $[H_2pipz]_2[CrBr_6]$, 120 °C. To prepare $[Hpy]_2[CrBr_4]$ the dihydrate was heated at *ca*. 70 °C *in vacuo* over P_4O_{10} for 1 week with the whole apparatus in a drying cabinet to prevent condensation of [Hpy]Br on colder parts of the apparatus.

The following *monoalkylammonium* salts were prepared by extraction of a stoicheiometric amount of the substituted ammonium bromide into a hot solution of anhydrous chromium(II) bromide in glacial acetic acid: $[NRH_3]_2[CrBr_4]$, where R = Me, Et, Pr^n, Bu^n, n-C_5H_{11} (n-pentyl), n-C_8H_{17} (n-octyl), or n-$C_{12}H_{25}$ (n-dodecyl) The complexes were filtered off, washed with glacial acetic acid, and dried by continuous pumping for several hours at room temperature followed by several hours at *ca*. 120 °C. The *dimethylammonium* salt $[NMe_2H_2]_2[CrBr_4]$ was similarly prepared, but was dried at room temperature for 15 h as was guanidinium tetrabromochromate(II)–diacetic acid $[C(NH_2)_3]_2$-

$[CrBr_4]\cdot 2MeCO_2H$. This *compound* smells of acetic acid, and forms fine needles which are being investigated by single-crystal *X*-ray methods.

There were only a few faint lines in the powder photographs of $Cs_2[CrBr_4]$ (ferromagnetic) and $Rb_2[CrBr_4]$ (antiferromagnetic) prepared by thermal dehydration. Microcrystalline samples of $Cs_2[CrBr_4]$ were obtained by extraction of caesium bromide into anhydrous chromium(II) bromide dissolved in boiling glacial acetic acid, or by the reverse procedure. However, these samples were antiferromagnetic (μ = 3.42 B.M.* at 295 K and 2.19 B.M. at 90 K) and did not show the sharp bands found in the reflectance spectrum of ferromagnetic $Cs_2[CrBr_4]$. This behaviour will be further investigated.

The anhydrous chromium(II) bromide was prepared by thermal dehydration of the hexahydrate under continuous pumping. To prevent hydrolysis the temperature was raised in 20 °C stages at 1 h intervals from room temperature to 120 °C. The complex $[NEtH_3]_2[CrBr_4]$ was also prepared successfully from $CrBr_2\cdot 6H_2O$ in glacial acetic acid.

To obtain the tetraethylammonium *salt*, $[NEt_4]_2[CrBr_4]$, 2,2-dimethoxypropane was added to a blue ethanolic solution of $CrBr_2\cdot 6H_2O$ and $[NEt_4]Br$ in 1 : 2 mol ratio. The mixture was boiled for 15 min and the light green solution was concentrated to a small volume. Ethyl acetate was added and the mixture shaken and cooled. The greenish white crystals which separated were filtered off, washed with ethyl acetate, and dried at 110 °C for several hours.

TABLE 1

Analytical data and magnetic properties

		Analyses (%) [a]						Magnetic properties			
Compound	Colour	Cr	Br	H_2O	C	H	N	*T*/K	$\mu_{eff.}$ [b]/ B.M.	θ [b]/°	Dia-magnetic [c] correction/ c.g.s units $\times 10^6$
$Cs_2[CrBr_4(OH_2)_2]$ [d]	Light blue	7.90	47.5	5.30				295	4.85	0	−234
		(7.70)	(47.5)	(5.30)				90	4.89		
$Cs_2[CrBr_4]$	Dark green	8.35	50.2					295	5.00	−44	−208
		(8.15)	(50.1)					90	7.20		
$Rb_2[CrBr_4(OH_2)_2]$ [d]	Light blue	9.00	55.3	6.10				295	4.88	0	−209
		(9.00)	(55.2)	(6.20)				90	4.90		
$Rb_2[CrBr_4]$	Dark green	9.75	58.8					295	4.17	82	−183
		(9.55)	(58.9)					90	3.45		
$[NH_4]_2[CrBr_4(OH_2)_2]$ [d]	Light turquoise	11.8	71.9	8.15		2.75	6.55	295	4.85	0	−191
		(11.7)	(72.0)	(8.10)		(2.70)	(6.30)	90	4.89		
$[NH_4]_2[CrBr_4]$	Orange-brown	12.3	78.3			2.15	6.60	295	4.17	94	−165
		(12.7)	(78.5)			(1.95)	(6.85)	90	3.36		
$[Hpy]_2[CrBr_4(OH_2)_2]$ [d]	Light green	9.15	56.0		20.9	2.60	4.65	295	4.75	−4	−257
		(9.15)	(56.3)		(21.1)	(2.80)	(4.95)	90	4.83		
$[Hpy]_2[CrBr_4]$	Yellow	10.1	60.1		21.6	2.40	5.00	295	4.35	60	−231
		(9.75)	(60.15)		(22.55)	(2.25)	(5.30)	90	3.70		
$[H_2pipz]_2[CrBr_6]\cdot 2H_2O$ [d]	Light blue	7.00	64.5		12.8	3.50	7.45	295	4.92	0	−324
		(6.95)	(64.1)		(12.8)	(4.30)	(7.50)	90	4.92		
$[H_2pipz]_2[CrBr_6]$	Light green	7.60	67.4		13.0	3.70	8.15	295	4.75	4	−288
		(7.30)	(67.4)		(13.5)	(3.95)	(7.90)	90	4.68		
$[C(NH_2)_3]_2[CrBr_4]\cdot 2MeCO_2H$ [e]	Light green	8.20	52.6		11.5	3.50	14.4	295	4.90	1	−284
		(8.50)	(52.25)		(11.8)	(3.30)	(13.8)	90	4.86		
$[NPhH_3]_2[CrBr_4]$	Yellow	9.40	57.2		25.3	3.00	4.90	295	4.56	35	−269
		(9.30)	(57.1)		(25.7)	(2.85)	(5.00)	90	4.18		
$[NMeH_3]_2[CrBr_4]$	Greenish yellow	11.6	73.0		5.80	2.95	6.45	295	6.27	−100	−196
		(11.9)	(73.3)		(5.50)	(2.75)	(6.40)	90	16.3		
$[NMe_2H_2]_2[CrBr_4]$	Light green	11.4	68.9		10.45	3.60	5.75	295	4.48	70	−220
		(11.2)	(68.6)		(10.35)	(3.45)	(6.05)	90	3.73		
$[NEtH_3]_2[CrBr_4]$	Off white	8.65	51.55		29.9	6.60	4.40	295	5.94	−87	−212
		(8.20)	(50.6)		(30.4)	(6.35)	(4.45)	90	13.1		
$[NEt_4]_2[CrBr_4]$	Olive-yellow	11.1	69.0		10.6	3.75	6.20	295	4.58	88	−363
		(11.2)	(69.0)		(10.3)	(3.45)	(6.05)	90	3.72		
$[NPr^nH_3]_2[CrBr_4]$	Greenish yellow	10.8	65.25		14.7	4.45	5.65	295	5.75	−87	−244
		(10.6)	(65.1)		(14.6)	(4.05)	(5.70)	90	13.3		
$[N(C_5H_{11})H_3]_2[CrBr_4]$	Greenish yellow	9.60	58.6		21.8	5.45	5.00	295	5.74	−91	−291
		(9.50)	(58.3)		(21.95)	(5.10)	(5.10)	90	13.5		
$[N(C_8H_{17})H_3]_2[CrBr_4]$	Greenish yellow	8.45	51.0		30.1	6.85	4.40	295	5.77	−89	−362
		(8.25)	(50.6)		(30.4)	(6.35)	(4.45)	90	12.8		
$[N(C_{12}H_{25})H_3]_2[CrBr_4]$	Greenish yellow	7.20	42.7		39.1	7.50	3.70	295	5.67	−95	−457
		(7.00)	(43.0)		(38.8)	(7.55)	(3.80)	90	14.3		

[a] Calculated values in parentheses. [b] Calculated from $\mu_{eff.} = 2.828(\chi_A T)^{\frac{1}{2}}$ and the Curie–Weiss law, $\chi_A^{-1} \propto (T + \theta)$. [c] Susceptibility also corrected for temperature-independent paramagnetism by subtraction of 100×10^{-6} c.g.s. units. [d] Water absorptions were found at *ca.* 3 300 and 1 635 cm^{-1}. [e] Un-ionised CO_2H absorptions at 1 715 and 1 290 cm^{-1}.

Other Preparative Investigations.—Attempts to prepare tetrabromochromate(II) salts of the ethylenediammonium and diethylenetriammonium cations from solutions of the ammonium bromide and $CrBr_2\cdot 6H_2O$ in concentrated hydrobromic acid or glacial acetic acid did not give products with satisfactory analyses. A *p*-methylanilinium salt could also not be obtained from concentrated hydrobromic acid. The corresponding chlorides have, however, been

---

* Throughout this paper: 1 B.M. ≈ 0.927×10^{-23} A m^2.

isolated[6] by similar procedures. Although chromium metal will dissolve in tetrahydrofuran or ethanol through which hydrogen chloride is passed at room temperature, it would not react with hydrogen bromide under the same conditions.

The copper(II) complexes $[NH_4]_2[CuBr_4(OH_2)_2]$ and $[NEtH_3]_2[CuBr_4]$, required for *X*-ray powder photographs, were prepared as before.[10] They gave satisfactory metal analyses.

Analyses and Physical Measurements.—These were carried out as in previous Parts except that some electronic spectra were recorded on a Beckman Acta MIV recording spectrophotometer provided with a reflectance attachment.

TABLE 2

Reflectance spectra

Compound	T/K [a]	$\nu_{max.}$/cm^{-1}						
$Cs_2[CrBr_4(OH_2)_2]$	RT	24 600vw	22 300vw	20 100wbr	18 700w		12 400s,vbr	
	LT	24 600vw	22 100vw	20 300wbr	18 800w		12 600s,vbr	
$Cs_2[CrBr_4]$	RT			18 350 [b]	16 950m,br	15 600 [b]	9 100s,br	5 600(sh)
	LT			18 400 [b]	16 600m,br	15 600 [b]	9 300s,br	6 000m
$Rb_2[CrBr_4(OH_2)_2]$	RT		22 000vw	20 800w	18 800w		12 400s,vbr	
	LT		22 100vw	20 950w	18 850w		12 800s,vbr	10 000m(sh)
$Rb_2[CrBr_4]$	RT				16 850m	15 600w(sh)	9 100s,br	5 200m
	LT			19 700vw	16 800m	15 600w(sh)	9 300s,br	6 000m
$[NH_4]_2[CrBr_4(OH_2)_2]$	RT	24 800vw	22 000w(sh)	21 200wbr	18 900w		12 500s,vbr	
	LT	24 800vw	22 100w(sh)	21 300wbr	18 900w		13 100s,br	10 000m
$[NH_4]_2[CrBr_4]$	RT		20 300m(sh)			15 600w	9 600s,vbr	6 200w
	LT	22 200vw	20 400m	18 300w	17 400w	15 800w	10 000s,vbr	6 200w
$[Hpy]_2[CrBr_4(OH_2)_2]$	RT						12 850s	10 100(sh)
	LT					15 900vw	13 100s	10 200m
$[Hpy]_2[CrBr_4]$	RT					15 600w	9 800s,vbr	
	LT			18 400w(sh)	17 400w	15 700w	10 000s,vbr	
$[H_2pipz]_2[CrBr_6]\cdot 2H_2O$	RT	22 600w	22 000w(sh)	18 600vw	17 900vw	16 700w(sh)	11 200s,vbr	
$[H_2pipz]_2[CrBr_6]$	RT				18 000vw	16 800w	10 200s,vbr	
$[C(NH_2)_3]_2[CrBr_4]\cdot 2MeCO_2H$	RT					16 900vw	11 600s,vbr	7 000m
$[NPhH_3]_2[CrBr_4]$	RT	20 600w(sh)	18 300 [b]	17 400vw [c]	15 600 [b]	13 400w(sh)	10 000s,vbr	7 000(sh)
	LT	20 600w(sh)	18 300 [b]	17 400vw [c]	15 600 [b]	13 400w(sh)	10 200s,vbr	7 400(sh)
$[NMeH_3]_2[CrBr_4]$	RT	20 100w(sh)	18 400 [b]	17 400vw [c]	15 750 [b]	14 100w	10 500s,vbr	
$[NMe_2H_2]_2[CrBr_4]$	RT				16 900w		11 700s,vbr	8 300(sh)
$[NEtH_3]_2[CrBr_4]$	RT	19 850w(sh)	18 200 [b]	17 250w	15 500 [b]	14 200w	10 350s,vbr	
	LT	19 950w(sh)	18 300 [b]	17 300w	15 600 [b]	14 300w	10 700s,vbr	9 400m(sh)
$[NEt_4]_2[CrBr_4]$	RT		18 500vw	17 500vw	15 800vw		9 800s,vbr	6 750w
	LT		18 500vw	17 500vw	15 850vw		10 000s,vbr	6 800w
$[NPr^nH_3]_2[CrBr_4]$	RT	20 000vw (sh)	18 400 [b]	17 500vw [c]	15 700 [b]	14 200vw	10 600s,vbr	8 000(sh)
$[N(C_5H_{11})H_3]_2[CrBr_4]$	RT	20 000vw (sh)	18 400 [b]	17 400vw [c]	15 700 [b]	14 400vw (sh)	10 500s, vbr [d]	
$[N(C_8H_{17})H_3]_2[CrBr_4]$	RT	19 800vw	18 400 [b]	17 400vw [c]	15 750 [b]	14 500vw (sh)	10 750s, vbr [d]	
$[N(C_{12}H_{25})H_3]_2[CrBr_4]$	RT	20 000w(sh)	18 400 [b]	17 200vw	15 800 [b]	14 200vw	10 800s, vbr [d]	

[a] RT — Room temperature, LT = liquid-nitrogen temperature. [b] Unusually intense and sharp spin-forbidden band. [c] Also very weak absorptions at *ca.* 17 000 cm^{-1}. [d] Asymmetric to low frequencies.

RESULTS AND DISCUSSION

Dihydrates.—The dihydrates $M_2[CrBr_4(OH_2)_2]$, where M = Rb, Cs, NH_4, or Hpy, are similar to the analogous chlorides.[3] Their magnetic behaviour was straightforward: the magnetic moments, $\mu_{eff.}$, were found (Table 1) to be close to the spin-only value for high-spin Cr^{II} (4.90 B.M.), and essentially independent of temperature. The reflectance spectra (Table 2), except that of the caesium salt, contained one band near 12 500 cm^{-1}, assigned to superimposed $^5B_{1g} \longrightarrow {}^5E_g$ and $^5B_{1g} \longrightarrow {}^5B_{2g}$ transitions (the main band), and another band near 10 000 cm^{-1}, usually resolved only at liquid-nitrogen temperature, assigned to the $^5B_{1g} \longrightarrow {}^5A_{1g}$ transition. The very broad and asymmetric band at about 12 400 cm^{-1} in the spectrum of $Cs_2[CrBr_4(OH_2)_2]$ presumably contains all three transitions under its envelope. The transition $^5B_{1g} \longrightarrow {}^5B_{2g}$ (and thus approximately the position of the main band) corresponds to Δ, and, as expected, the main band of the bromides is at lower frequency than in the spectra of the chlorides (*ca.* 13 000 cm^{-1}).[3]

The *X*-ray powder patterns of the ammonium, rubidium, and caesium diaquatetrachlorochromates(II) and diaquatetrabromochromates(II) can be indexed in terms of tetragonal unit cells, the dimensions of which are given in Table 3. In general, the chromium(II) compounds are isomorphous with the corresponding copper(II) compounds which contain[10] *trans*-octahedral anions $[CuX_4(OH_2)_2]^{2-}$ with two short and two long metal–halide bonds: *e.g.* in[11] $K_2[CuCl_4(OH_2)_2]$, r(Cu–Cl) = 2.285 and 2.895, r(Cu–O) = 1.971 Å; and in[12] $[NH_4]_2[CuBr_4(OH_2)_2]$, r(Cu–Br) = 2.46 and 3.14, r(Cu–O) =

TABLE 3

Unit-cell dimensions of tetragonal dihydrates

Compound	a/Å	c/Å	c/a
$Cs_2[CrCl_4(OH_2)_2]$	7.85	8.28	1.05
$Cs_2[CrBr_4(OH_2)_2]$	8.22	8.50	1.03
$Rb_2[CrCl_4(OH_2)_2]$	7.56	8.06	1.07
$Rb_2[CrBr_4(OH_2)_2]$	7.95	8.31	1.05
$[NH_4]_2[CrCl_4(OH_2)_2]$	7.60	7.93	1.04
$[NH_4]_2[CrBr_4(OH_2)_2]$	7.97	8.24	1.03

2.20 Å. Thus the chromium(II) compounds can be assigned very similar structures.

The salts of the piperazinium dication, $[H_2pipz]_2[CrBr_6]\cdot 2H_2O$ and $[H_2pipz]_2[CrBr_6]$, and the guanidinium salt $[C(NH_2)_3]_2[CrBr_4]\cdot 2MeCO_2H$, are high spin, and their magnetic moments are essentially independent of temperature so it is unlikely that bridging bromide is present (see below). The reflectance spectrum of the acetic acid adduct contains a broad band at 11 600 cm^{-1} at slightly lower frequency than the main band (*ca.* 12 400 cm^{-1}) of $M_2[CrBr_4(OH_2)_2]$; thus the acetic acid may be co-ordinated. The guanidinium cation is also a potential ligand. Both piperazinium salts have a very broad band near 11 000 cm^{-1} in their reflectance spectra which presumably arises from superimposition of the three spin-allowed *d–d* transitions. It is possible that the dihydrate should be formulated $[H_2pipz]_2[CrBr_4(OH_2)_2]Br_2$, but this would be expected to give a reflectance band near 12 400 cm^{-1}.

Anhydrates.—The anhydrous alkali-metal, ammonium, and pyridinium tetrabromochromates(II) were [8b] obtained by thermal dehydration of the dihydrates, but non-aqueous solvent procedures, as described in the Experimental section, are generally preferable.

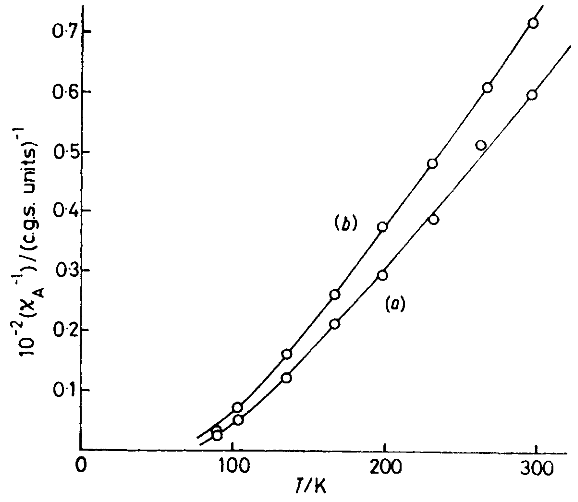

FIGURE 1 Variation with temperature of experimental reciprocal molar susceptibilities of ferromagnetic $[NMeH_3]_2[CrBr_4]$ (*a*) and $[N(C_5H_{11})H_3]_2[CrBr_4]$ (*b*). Lines are calculated by substitution of *J* and *g* values from Table 4 in equation (1)

The tetrabromochromates(II) of Cs and NRH_3, where R = Me, Et, Pr^n, $n\text{-}C_5H_{11}$, $n\text{-}C_8H_{17}$, or $n\text{-}C_{12}H_{25}$, show ferromagnetic behaviour, with magnetic moments well above the spin-only value at room temperature which increased markedly as the temperature was lowered (Tables 1 and 4). Plots of the reciprocal susceptibility, χ_A^{-1}, *versus* temperature for $[NMeH_3]_2[CrBr_4]$ and $[N(C_5H_{11})H_3]_2[CrBr_4]$ are given in Figure 1 as typical examples. The Curie–Weiss law is obeyed above *ca.* 150 K, with positive intercepts on the temperature axis (Weiss constants θ in the range −40 to −100°); below this temperature (*ca.* 220 K for $[NMeH_3]_2[CrBr_4]$) the χ_A^{-1} *versus* T curves show considerable upward curvature. The Curie temperatures T_C apparently lie just below the limit of our measurements.

Although little detailed structural information has been reported, the ferromagnetic chlorochromates(II) are known to contain sheets of bridged $[CrCl_4]^{2-}$ units well separated by the alkylammonium ions [4,6,7,13] or double layers [2,4] of the alkali-metal chloride. Such structures are well established for the salts $[NRH_3]_2[MCl_4]$, where M = Cu, Fe, or Mn, which are frequently isomorphous [3,7] with the chromium(II) analogues. The *X*-ray powder photographs of $[NEtH_3]_2[CuBr_4]$ and $[NEtH_3]_2[CrBr_4]$ are very similar, and although single-crystal data are not yet available these complexes would be expected to have sheet structures like their chloro-analogues. The ferromagnetic behaviour over the range 85—300 K is reasonably well reproduced by substitution of the values of J and g given in Table 5 in the high-temperature series expansion [14] (1) (where the symbols have their usual meanings and $x = J/kT$) for a sheet ferromagnet with $S = 2$. Examples of the fits are given in Figure 1.

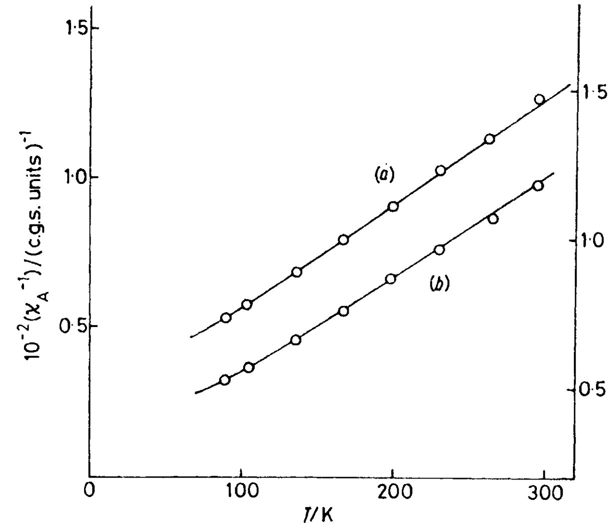

FIGURE 2 Variation with temperature of experimental reciprocal molar susceptibilities of antiferromagnetic $[Hpy]_2[CrBr_4]$ (*a*) and $[NMe_2H_2]_2[CrBr_4]$ (*b*). Lines are calculated by substitution of *J* and *g* values from Table 4 in equation (1) with all signs positive. Right-hand scale applies to (*b*)

$$Ng\beta^2/\chi = kT/2 + J(-4 + 9x - 9.072x^2 + 55.728x^3 - 160.704x^4 + 116.640x^5) \quad (1)$$

The values of J for the bromochromates(II), except $Cs_2[CrBr_4]$, are somewhat larger than those (9 cm^{-1} or less) for the related chlorochromates(II).[6,7] There is some discrepancy between the reported values of J and g for $[NMeH_3]_2[CrCl_4]$ and $[NEtH_3]_2[CrCl_4]$, and although the room-temperature moments of $[NMeH_3]_2[CrCl_4]$ agree well (5.62 [7] and 5.57 [6] B.M.), the values for $[NEtH_3]_2[CrCl_4]$(4.98 [7] and 6.08 [6] B.M.) do not. The discrepancies in J and g may be partly due to one set [7] of parameters being obtained from measurements over the range 50—150 K and the other set [6] over the range 90—300 K. There are also considerable experimental difficulties in handling these air-sensitive complexes.

TABLE 4

Variation of corrected molar susceptibilities of anhydrous tetrabromochromates(II) with absolute temperature

$10^6\chi_A$/ c.g.s. units	T/K	$10^6\chi_A$/ c.g.s. units	T/K
$[NMeH_3]_2[CrBr_4]$		$[NEtH_3]_2[CrBr_4]$	
16 590	295.0	15 030	291.5
19 400	262.6	17 360	262.6
25 510	230.3	21 350	230.4
33 460	198.4	27 920	198.6
47 140	166.4	39 930	166.4
80 990	135.2	60 010	135.4
192 400	103.4	131 600	103.6
371 000	89.5	239 300	89.5
$[NPr^nH_3]_2[CrBr_4]$		$[N(C_5H_{11})H_3]_2[CrBr_4]$	
13 890	295.5	13 860	295.5
16 530	265.5	16 320	265.5
20 770	229.5	20 640	229.5
26 570	197.3	26 470	197.4
36 390	166.4	38 060	166.5
62 460	135.3	62 450	135.2
136 400	104.0	141 800	104.0
246 200	89.5	257 200	89.5
$[N(C_8H_{17})H_3]_2[CrBr_4]$		$[N(C_{12}H_{25})H_3]_2[CrBr_4]$	
14 010	295.5	13 540	295.5
16 920	265.5	16 250	265.5
20 970	229.5	20 040	229.5
27 080	197.4	26 670	197.4
37 580	166.5	38 550	166.5
61 500	135.3	65 600	135.3
133 300	104.0	180 900	104.0
228 900	89.5	287 700	89.5
$Cs_2[CrBr_4]$		$[NH_4]_2[CrBr_4]$	
10 500	295.1	7 275	295.1
11 975	262.4	7 952	262.6
13 970	230.1	8 714	230.0
16 740	198.3	9 649	198.2
21 100	166.2	10 750	166.2
28 950	135.4	12 240	135.4
48 510	103.3	14 450	103.4
72 430	89.1	15 730	89.1
$Rb_2[CrBr_4]$		$[Hpy]_2[CrBr_4]$	
7 250	293.3	7 918	294.8
7 909	262.3	8 828	262.4
8 686	230.1	9 705	230.3
9 608	198.4	11 000	198.3
10 800	166.4	12 560	166.5
12 300	135.2	14 620	135.3
14 620	103.3	17 350	103.3
16 510	89.4	19 040	89.4
$[NPhH_3]_2[CrBr_4]$		$[NMe_2H_2]_2[CrBr_4]$	
8 732	295.5	8 351	295.5
9 663	265.4	9 230	265.5
10 950	229.5	10 270	229.5
11 970	197.4	11 420	197.4
14 090	166.5	13 120	166.4
16 790	135.3	15 140	135.2
21 010	104.0	17 740	104.0
24 340	89.5	19 160	89.5
$[NEt_4]_2[CrBr_4]$			
8 802	295.3		
9 637	262.5		
10 790	230.4		
12 160	198.3		
13 610	166.3		
14 800	135.2		
18 020	103.3		
19 270	89.4		

However from the limited number of complexes so far investigated it seems that bromide can transmit stronger ferromagnetic coupling than chloride. Irrespective of J values, this is also indicated by the generally higher magnetic moments and larger θ values (ignoring sign) of the bromides. The corresponding tetrabromocuprates(II) have [15] higher Curie temperatures and larger J values than the tetrachlorocuprates(II).

Many of the tetrabromochromates(II), *i.e.* the Rb, NH_4, Hpy, $C(NH_2)_3$, $NPhH_3$, NEt_4, and NMe_2H_2 salts, exhibit antiferromagnetic behaviour. Their magnetic moments are well below the spin-only value, and decreased still further as the temperature was lowered. In general these complexes obeyed the Curie–Weiss law with large negative intercepts (θ positive) on the temperature axis (Table 1). The magnetic behaviour can be reproduced (Figure 2) by substitution of the J and g values in Table 5 into equation (1) with all signs positive as is appropriate [14] for a sheet antiferromagnet.

TABLE 5

Exchange integrals of tetrabromochromates(II)

Complex	J/cm^{-1}	g
(*a*) Ferromagnetic		
$Cs_2[CrBr_4]$	3.0	1.92
$[NMeH_3]_2[CrBr_4]$	11.6	1.98
$[NEtH_3]_2[CrBr_4]$	10.0	1.94
$[NPr^nH_3]_2[CrBr_4]$	10.4	1.87
$[N(C_5H_{11})H_3]_2[CrBr_4]$	10.7	1.85
$[N(C_8H_{17})H_3]_2[CrBr_4]$	10.3	1.89
$[N(C_{12}H_{25})H_3]_2[CrBr_4]$	9.8	1.98
(*b*) Antiferromagnetic		
$Rb_2[CrBr_4]$	−5.60	1.88
$[NH_4]_2[CrBr_4]$	−5.90	1.89
$[Hpy]_2[CrBr_4]$	−4.23	1.92
$[NPhH_3]_2[CrBr_4]$	−2.51	1.94
$[NMe_2H_2]_2[CrBr_4]$	−4.70	1.98
$[NEt_4]_2[CrBr_4]$	−4.86	2.03

Electronic Spectra.—In their reflectance spectra (Table 2) the tetrabromochromates(II), whether ferromagnetic or antiferromagnetic, have a very broad band near 10 500 cm^{-1}, asymmetric, or with a shoulder, to lower frequencies. This is characteristic of tetragonally distorted, six-co-ordinate Cr^{II}, and confirms that the $[CrBr_4]^{2-}$ units are polymerised. The band is assigned to the overlapping transitions $^5B_{1g} \longrightarrow (^5A_{1g}, {}^5B_{2g}$, and $^5E_g)$, and it is at lower frequency than for the corresponding chlorides (*ca.* 11 000 cm^{-1}),[6] as would be expected from the weaker field of bromide.

The spectra of all the complexes, including the dihydrates, contain many weak bands to higher frequency than the broad, spin-allowed absorptions. These bands can be assigned to spin-forbidden transitions, but in the spectra of the ferromagnetic complexes two narrow bands of unusual intensity are present near 18 400 and 15 600 cm^{-1} (Figure 3). Similar bands, occurring at almost identical frequencies in the spectra of the ferromagnetic tetrachlorochromates(II), have been assigned [4,7,16] to the quintet–triplet transitions to the levels $^3E_g(^3H)$ and $^3A_{1g}(^3G)$. Transitions to these levels should be independent of ligand-field strength and the spectra of the tetrabromochromates(II) show that this is true. The slightly lower frequencies of transitions in the spectra of the bromides can be ascribed to the greater nephelauxetic effect of bromide.

On cooling to liquid-nitrogen temperature the sharp bands of the ferromagnetic chlorochromates show little variation of intensity, but below T_C their intensities diminish remarkably until at 4.2 K they all but disappear.[4,7,16] The intensities increase with T_C almost up to T_C (*ca.* 60 K), and become constant just above T_C. The spin-forbidden transitions gain intensity as the temperature increases because increasing thermal energy produces population of higher energy magnetic levels in which some of the spins are reversed. Then, when the spin-forbidden transition takes place on one chromium(II) ion ($\Delta S = -1$), an adjacent chromium(II) ion drops to a lower magnetic level ($\Delta S = +1$), so that the net spin change is zero.

The tetrabromochromates(II) would be expected to behave similarly. Figure 3 shows that the spin-forbidden bands at 18 200 and 15 500 cm^{-1} in the spectrum of $[NEtH_3]_2[CrBr_4]$ are still prominent at liquid-nitrogen temperature, but they were less intense than at room temperature. The methylammonium salt behaved similarly. Since the intensities of the corresponding bands of the chlorochromates(II) become constant just above the Curie point it appears that T_C for these compounds is just below liquid-nitrogen temperature.

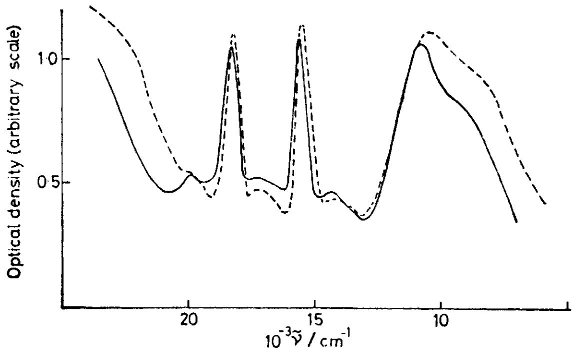

FIGURE 3 Reflectance spectrum of $[NEtH_3]_2[CrBr_4]$ at liquid-nitrogen temperature (——) and room temperature (— — —)

Previously reported solid-state spectra of antiferromagnetic tetrachloro- and trichloro-chromates(II) do not contain these unusually intense spin-forbidden transitions, but they are in the spectrum of antiferromagnetic $[NPhH_3]_2[CrBr_4]$. Relatively intense spin-forbidden transitions have been found in CrI_2,[4] $K[CrF_3]$, and $[NH_4][CrF_3]$,[17] and MnF_3,[18] none of which is ferromagnetic.

TABLE 6

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

Compound			ν(Cr–Br)[a]	
$Cs_2[CrBr_4]$	470m	430(sh)	250vs, vbr	
$Rb_2[CrBr_4(OH_2)_2]$	450 (sh) [b]		270s	220s [c]
$[H_2pipz]_2[CrBr_6]\cdot 2H_2O$	460w [b]	420vw	270m, 245m	225w [c]
$[H_2pipz]_2[CrBr_6]$	450m		260s	
$[H_2pipz]Br_2$		320m,br	250vs, vbr	
$[C(NH_2)_3]_2[CrBr_4]\cdot 2MeCO_2H$				225w
$[NPhH_3]_2[CrBr_4]$	465s	385m,br	250m, 240s	
$[NPhH_3]Br$		387s	250s,vbr	
$[NMeH_3]_2[CrBr_4]$	470vw		250s,vbr	
$[NMe_2H_2]_2[CrBr_4]$			240w	225m
$[NEtH_3]_2[CrBr_4]$	470m		240s,vbr	
$[NEt_4]_2[CrBr_4]$	470w	430w	250m, 235s	
$[NPr^nH_3]_2[CrBr_4]$		400w	250m, 235s	
$[N(C_5H_{11})H_3]_2[CrBr_4]$			245m, 235 (sh)	
$[N(C_5H_{11})H_3]Br$				220w
$[N(C_8H_{17})H_3]_2[CrBr_4]$			240 (sh), 230m	
$[N(C_{12}H_{25})H_3]_2[CrBr_4]$			240m, 230m	205w
$[N(C_{12}H_{25})H_3]Br$				210m

[a] Where bands of substituted ammonium chloride are not given there was no significant absorption in the region concerned. [b] ν(Cr–O). [c] δ(O–Cr–O).

Other Investigations.—The spectra of ethanolic solutions of $[N(C_5H_{11})H_3]_2[CrBr_4]$ and $[N(C_{12}H_{25})H_3]_2[CrBr_4]$ contained a broad band at 12 100 cm^{-1} (ε *ca.* 27 cm^2 mol^{-1}) assigned to overlapping spin-allowed *d–d* transitions. There was also a weak band at 21 400 cm^{-1} which arose from a trace of chromium(III) impurity since its intensity increased approximately nine-fold on deliberate aerial oxidation. A band also appeared at 15 700 cm^{-1}, and that at 12 100 cm^{-1} disappeared. As expected, destruction of the polymeric structure on dissolution caused the disappearance of the spin-forbidden absorptions.

The spin-allowed absorptions at 12 100 cm^{-1} are at higher wavenumber than in the reflectance spectra of the $[CrBr_4]^{2-}$ salts and close to the values for the $[CrBr_4(OH_2)_2]^{2-}$ salts, suggesting that solvated $[CrBr_4]^{2-}$ units are present in solution. The complexes $[N(C_5H_{11})H_3]_2[CrBr_4]$ and $[N(C_{12}H_{25})H_3]_2[CrBr_4]$ have molar conductances in 0.001 mol dm^{-3} ethanolic solution of 104 and 95 ohm^{-1} cm^2 mol^{-1} respectively. These values are somewhat higher than the range (70—90 ohm^{-1} cm^2 mol^{-1}) for [19] 1 : 2 electrolytes, suggesting that some slight dissociation of the $[CrBr_4]^{2-}$ units may have occurred. The low absorption coefficients exclude the presence of tetrahedral anions.

The i.r. spectra of the $[CrBr_4]^{2-}$ salts contain weak or no absorptions in the range 285—320 cm^{-1}, where the $[CrCl_4]^{2-}$ salts exhibit strong bands [6] assigned to ν(Cr–Cl) stretching vibrations. [In Table 4 of ref. 6 the ν(Cr–Cl) symbol should have been bracketed above the second and third columns of frequencies only.] Instead, the $[CrBr_4]^{2-}$ salts absorb (Table 6) in the range 220—270 cm^{-1}, *i.e.* at about four fifths of the value of ν(Cr–Cl), as would be expected for ν(Cr–Br) vibrations. Although square-planar $[CrX_4]^{2-}$ units are expected to have one i.r.-active ν(Cr–X) mode, two bands are found for the chlorides and the bromides. This is presumably because the $[CrX_4]^{2-}$ units are not isolated but weakly bridged in the solid state.

We thank the Government of Pakistan for a scholarship to (M. A. B.).

[0/634 *Received, 29th April*, 1980]

REFERENCES

[1] Part 13, L. F. Larkworthy, A. J. Roberts, B. J. Tucker, and A. Yavari, *J.C.S. Dalton*, 1980, 262.

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

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

[4] P. Day, *Accounts Chem. Res.*, 1979, **12**, 236.

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

[6] L. F. Larkworthy and A. Yavari, *J.C.S. Dalton*, 1978, 1236.

[7] C. Bellitto and P. Day, *J.C.S. Dalton*, 1978, 1207.

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

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

[10] R. Colton and J. H. Canterford, ' Halides of the First Row Transition Metals,' Wiley–Interscience, London, 1969, p. 545.

[11] R. Chidambaram, Q. O. Navarro, A. Garcia, K. Linggoatmodjo, L. Shi-Chien, and Il-Hwan Suh, *Acta Cryst.*, 1970, **B26**, 827.

[12] A. Silberstein, *Compt. rend.*, 1936, **202**, 1196.

[13] M. A. Babar, M. F. C. Ladd, L. F. Larkworthy, G. P. Newell, and D. C. Povey, *J. Cryst. Mol. Struct.*, 1978, **8**, 43.

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

[15] L. J. de Jongh and A. R. Miedema, *Adv. Phys.*, 1974, **23**, 1.

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

[17] A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *J. Chem. Soc.* (*A*), 1966, 363.

[18] R. J. H. Clark, *J. Chem. Soc.*, 1964, 417.

[19] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 110.