Chromium(II) Chemistry. Part 15.[1] Synthesis and Magnetic Properties of Piperazinium, Hydrazinium, and Monoaryl and Other Substituted Ammonium Tetrachlorochromates†

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The complex chlorides $M_2[CrCl_4(OH_2)_2]$ [$M = \frac{1}{2}H_2$pipz (pipz = piperazine) or $NPhH_3$] are magnetically dilute, high-spin chromium(II) compounds. On thermal dehydration antiferromagnetic [H_2pipz][$CrCl_4$] and ferromagnetic $[NPhH_3]_2[CrCl_4]$ are obtained. The latter was also prepared from a mixture of glacial acetic acid and acetyl chloride, as was $[NH_4]_2[CrCl_4]$, previously obtained by thermal dehydration. The complexes $[N(o\text{-}CH_3C_6H_4)H_3]_2[CrCl_4]$ and $[H_3N(CH_2)_3NH_3][CrCl_4]$ exhibit ferromagnetic behaviour, but $[NEt_3H]_2[CrCl_4]$ and $[N_2H_6]_2[CrCl_6]$ are antiferromagnetic. The reflectance spectra of the anhydrous tetrachlorochromates indicate tetragonal six-co-ordination and hence polymeric structures. The magnetic susceptibility data for the ferromagnetic complexes from room to liquid-nitrogen temperature have been fitted to a high-temperature series expansion formula for a sheet ferromagnet giving *J ca.* 6.5 cm^{-1} and *g ca.* 1.94.

Complex chlorides of bivalent chromium of the type $M_2[CrCl_4]$ where M = K, Rb, Cs,[2-4] NH_4,[2] or RNH_3 (R = alkyl)[5-7] have been shown to be ferromagnetic. Salts of multiply-charged linear cations, *e.g.* [H_3dien][$CrCl_4$]Cl (dien = diethylenetriamine), also exhibit[7] this behaviour, although $[NMe_2H_2]_2[CrCl_4]$[7] and [Hpy]$_2$[$CrCl_4$][2] (py = pyridine) are antiferromagnetic. Chlorochromate(II) salts of further types of substituted ammonium cation have been synthesised in a search for more complexes possessing unusual magnetic properties.

Results and Discussion

The dihydrates [H_2pipz][$CrCl_4(OH_2)_2$] and $[NPhH_3]_2[CrCl_4(OH_2)_2]$ obey the Curie law down to liquid-nitrogen temperature with effective magnetic moments (μ_{eff}) temperature-independent and close to the spin-only value of 4.90 B.M. (Table 1) as expected for high-spin magnetically dilute chromium(II) complexes ($3d^4$). The anhydrous complexes $[N(o\text{-}CH_3C_6H_4)H_3]_2[CrCl_4]$, $[NPhH_3]_2[CrCl_4]$, and $[H_3N(CH_2)_3NH_3][CrCl_4]$ obey the Curie–Weiss law with positive intercepts on the temperature axis and values of μ_{eff} which are well above the spin-only value and increase further as the temperature is lowered (Table 1 and Figure). These are therefore ferromagnetic compounds. The salts [H_2pipz][$CrCl_4$], $[N_2H_6]_2[CrCl_6]$, and $[NEt_3H]_2[CrCl_4]$, on the other hand, show antiferromagnetic behaviour, with effective moments which decrease as the temperature is lowered; they follow the Curie–Weiss law with negative intercepts on the temperature axis.

The diffuse reflectance spectra (Table 2) generally contain, near 12 000 cm^{-1}, one broad band which is asymmetric or with a shoulder to lower wavenumber. This is typical of six-co-ordinate chromium(II). The main band in the spectra of [H_2pipz][$CrCl_4(OH_2)_2$] and $[NPhH_3]_2[CrCl_4(OH_2)_2]$ is at the same wavenumber (*ca.* 13 000 cm^{-1}) as the bands in the spectra[2] of $A_2[CrCl_4(OH_2)_2]$ (A = NH_4, Rb, Cs, or Hpy). These are isomorphous with the corresponding copper(II) compounds, which contain *trans*-octahedral anions with two short and two long metal–halide bonds. The same structure for the dihydrates would explain their normal paramagnetic behaviour.

Six-co-ordination in the anhydrous tetrachlorochromates(II) implies the presence of chloride bridges, and this is consistent with the ferro- or antiferro-magnetic behaviour found for these complexes. Single-crystal *X*-ray investigations[8] have recently shown that $[H_3N(CH_2)_2NH_3][CrCl_4]$ contains infinite sheets of $[CrCl_4]^{2-}$ units bridged by approximately linear Cr–Cl–Cr bonds, well separated by the doubly charged cations. Similar structures have been reported for a few ferromagnetic chlorochromates(II)[4,9,10] and are well known for analogous copper(II) complexes.

X-Ray powder photographs show that anilinium tetrachlorochromate(II) is isomorphous with the corresponding copper(II) compound. The latter also has the chloride-bridged sheet structure,[11] the Cu–Cl $\cdots$ Cu bond angle being 164.4° and the Cu–Cu distance 5.21 Å.

The ferromagnetic behaviour of $[H_3N(CH_2)_3NH_3][CrCl_4]$, $[NPhH_3]_2[CrCl_4]$, and $[N(o\text{-}CH_3C_6H_4)H_3]_2[CrCl_4]$ is reasonably well reproduced by substitution of the values of *J* and *g* given in Table 3 in the high-temperature series expansion equation (i)[4,12] (where the symbols have their usual meanings and $x = J/kT$) for a sheet ferromagnet with $S = 2$. Examples of fits are given in the Figure. For high-spin

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

chromium(II), *g* values a little below 2.00 are expected. The values of *g* for $[NPhH_3]_2[CrCl_4]$ and $[H_3N(CH_2)_3NH_3][CrCl_4]$, which gave the best fit of the data (Table 3), are somewhat below 2.00. However, as can be seen from the Figure, values of $J = 7.1$ cm^{-1} and $g = 1.96$ for $[H_3N(CH_2)_3NH_3][CrCl_4]$ give only a slightly less satisfactory fit so that the magnetic data cannot be used to fix *J* and *g* precisely.

The values of the magnetic parameters are similar to those reported[4,6,7] for other tetrachlorochromates(II).

The reflectance spectra of the ferromagnetic complexes contain two narrow bands of unusual intensity near 18 600 and 15 800 cm^{-1}. Similar bands have been found at almost identical frequencies in the spectra of ferromagnetic tetrahalogenochromates(II) generally and have been assigned to quintet–triplet transitions to the levels $^3E_g(^3H)$ and $^3A_{1g}(^3G)$ intensified by the magnetic coupling.

It is considered[13] that parameters such as metal–metal separation, *d*-electron configuration, size and polarisability of bridging atom or group, bridging angle, and planarity of the bridging system are important in determining whether the

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† *Non-S.I. unit employed:* 1 B.M. ≃ 9.27×10^{-24} J T^{-1}.

Table 1. Analytical data and magnetic properties

Compound	Colour	Analyses [a] (%)						Magnetic properties		
		Cr	Cl	C	H	N	T/K	μ_{eff} [b]/ B.M.	θ [b]/°	$10^6 \chi_D$ [c]/ cm^3 mol^{-1}
$[H_2pipz][CrCl_4(OH_2)_2]$	Light blue	16.15	44.7	15.1	5.1	8.9	295	4.84	−1	−193
		(16.35)	(44.6)	(15.1)	(5.0)	(8.8)	90	4.87		
$[H_2pipz][CrCl_4]$	Light grey	18.4	50.6	16.5	4.3	10.1	295	4.44	82	−167
		(18.4)	(50.3)	(17.0)	(4.3)	(9.9)	90	3.63		
$[NPhH_3]_2[CrCl_4(OH_2)_2]$	Light blue	12.4	33.6	34.3	4.7	6.6	295	4.79	−2	−250
		(12.4)	(33.9)	(34.5)	(4.8)	(6.7)	90	4.84		
$[NPhH_3]_2[CrCl_4]$	Grey [d]	13.7 [d]	37.5	37.2	4.0	7.2	295	5.31 [d] 5.06 [e]	−56 [d]	−224
	Pinkish brown [e]	13.4 [e]	36.95	37.3	4.1	7.0	90	7.63 [d] 7.39 [e]	−56 [e]	
		(13.6)	(37.1)	(37.7)	(4.2)	(7.3)				
$[N(o\text{-}CH_3C_6H_4)H_3][CrCl_4]$	White	12.7	34.2	41.3	5.2	6.0	295	5.52	−64	−248
		(12.7)	(34.6)	(41.0)	(4.9)	(6.8)	90	8.25		
$[NEt_3H]_2[CrCl_4]$	Off-white	13.1	35.9	35.9	8.25	7.3	295	4.55	29	−270
		(13.1)	(35.6)	(36.2)	(8.0)	(7.0)	90	4.15		
$[N_2H_6]_2[CrCl_6]$	Green	16.0	64.4	—	3.0	16.45	295	4.72	74	−195
		(15.6)	(63.9)		(3.6)	(16.8)	90	3.91		
$[H_3N(CH_2)_3NH_3][CrCl_4]$	Yellow-green	19.4	52.5	13.2	4.7	10.3	295	5.52	−67	−157
		(19.3)	(52.6)	(13.3)	(4.4)	(10.4)	90	8.63		
$[NH_4]_2[CrCl_4]$	Greyish brown	23.1	61.1	—	3.1	10.9				
		(22.6)	(61.7)		(3.5)	(12.2)				

[a] Calculated values in parentheses. [b] Calculated from $\mu_{eff} = 2.828 (\chi_A T)^{\frac{1}{2}}$ and the Curie–Weiss law, $\chi_A^{-1} (T + \theta)$. [c] Diamagnetic correction. [d] Obtained by thermal dehydration of dihydrate. [e] Crystallised from glacial acetic acid–acetyl chloride.

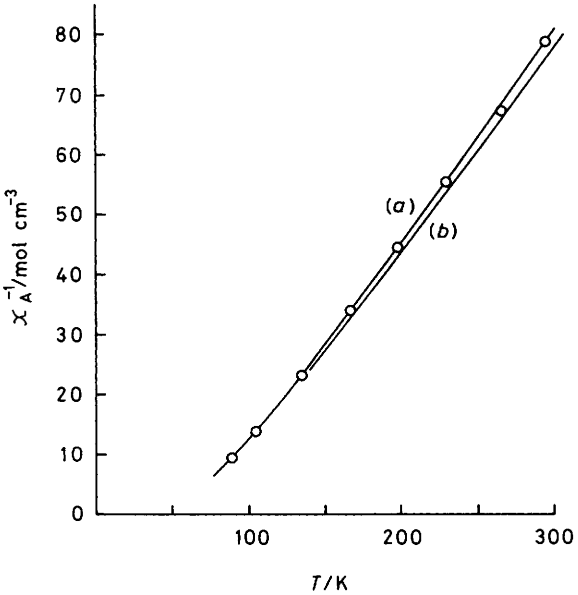

Figure. Variation with temperature of experimental reciprocal molar susceptibility of $[H_3N(CH_2)_3NH_3][CrCl_4]$; lines calculated by substitution in equation (i) of (a) $J = 7.4$ cm^{-1} and $g = 1.91$ and (b) $J = 7.1$ cm^{-1} and $g = 1.96$

magnetic interaction will be ferromagnetic or antiferromagnetic. The local environments of the metal ions are very similar in the few ferromagnetic chromium(II) complexes {$Rb_2[CrCl_4]$,[10] $[H_3dien][CrCl_4]Cl$,[9] and $[H_3N(CH_2)_3NH_3][CrCl_4]$ [8]} for which structural data are available. They all have layer structures, the bridges are approximately linear (for the three complexes, the Cr • • • Cl–Cr angles are 180, 162.3, and 165.3°, respectively), the direct Cr–Cr separations are in the range 5.05—5.25 Å, and the distortion axes alternate at 90°. This co-operative Jahn–Teller distortion [14] permits super-exchange *via* bridging chloride anions between a half-filled d_{z^2} orbital on one chromium ion and an empty $d_{x^2-y^2}$ orbital of a neighbour. With the high spin d^4 configuration ferromagnetic interaction is expected through linear $3d^4$-anion-$3d^4$ interactions as has now been found in a large number of complex halides of chromium(II), although extensive structural data are lacking.

Their reflectance spectra and magnetic behaviour suggest that the antiferromagnetic compounds have chloride-bridged structures, but no details are known. The powder photograph of $[NEt_3H]_2[CrCl_4]$ bears no resemblance to that of $[NEt_3H]_2[CuCl_4]$. This is perhaps not surprising since the copper(II) complex contains [15] discrete distorted tetrahedral anions. The only antiferromagnetic tetrahalogenochromate(II) of known structure [8] is $[NMe_2H_2]_2[CrCl_4]$ and this does not have a layer structure but contains isolated $[Cr_3Cl_{12}]^{6-}$ units. The antiferromagnetism of $[N_2H_6]_2[CrCl_6]$ suggests that its lattice does not contain isolated $[CrCl_6]^{4-}$ units, since this would lead to magnetically dilute behaviour, but contains ionic chloride and halide bridged complex anions.

Experimental

The complexes turn green after brief exposure to the atmosphere; they were prepared and handled under nitrogen, generally in all-glass apparatus. In some of the later experiments solids were transferred under nitrogen in a glove box with a gas recirculation and purification system obtained from Faircrest Engineering Ltd., Croydon.

The amine hydrochlorides were crystallised from cold concentrated solutions prepared by the addition of hydrochloric acid to an aqueous solution containing an equimolar quantity of amine.

The infrared spectra of the complexes contain bands near 300 cm^{-1} which can be assigned to ν(Cr–Cl) vibrations.

Piperazinium Diaquatetrachlorochromate(II).—Chromium(II) chloride tetrahydrate (6.75 g) was dissolved in 12 mol dm^{-3}

Table 2. Diffuse reflectance spectra

Compound	T/K	$\nu_{max.}$/cm^{-1}					
$[H_2pipz][CrCl_4(OH_2)_2]$	RT [a]		18 900vw (sh)	17 000w (sh)		13 000s, vbr	10 000m (sh)
	LT		19 000vw (sh)	16 800m (sh)		13 500s, vbr	10 300m
$[H_2pipz][CrCl_4]$	RT		18 700vw	17 600vw	15 800w	11 200s, vbr	
	LT		18 800vw	17 700vw	15 900w	11 600s, br	10 000m (sh)
$[NPhH_3]_2[CrCl_4(OH_2)_2]$	RT	21 300w				12 700s, br	10 000m (sh)
$[NPhH_3]_2[CrCl_4]$	RT	20 500vw	18 550 [b]	17 400vw [d]	15 750 [b]	11 400s, vbr	8 600m (sh)
	LT	20 600vw	18 600 [b]	17 600vw [d]	15 700 [b]	11 750s, vbr	9 000m (sh)
			18 800 (sh)				
$[N(o\text{-}CH_3C_6H_4)H_3]_2[CrCl_4]$	RT	20 600vw	18 550 [b]	16 800vw, br	15 750 [b]	11 650s, vbr	9 500m (sh)
$[NEt_3H]_2[CrCl_4]$	RT	20 800m, vbr				12 500s, vbr	9 500m (sh)
$[N_2H_6]_2[CrCl_6]$ [c]	RT	20 800vw	18 600vw	17 400vw [d]	15 800w	10 800s, vbr	7 500m (sh)
	LT	20 900vw	18 700vw	17 500vw [d]	15 800w	10 900s, vbr	8 200 (sh)
$[H_3N(CH_2)_3NH_3][CrCl_4]$	RT	20 500vw	18 600 [b]	17 500vw [d]	15 800 [b]		
	LT	20 600vw	18 600 [b]	17 600vw [d]	15 900 [b]	11 500s, vbr	9 000m (sh)
					13 800w (sh)		
$[NH_4]_2[CrCl_4]$	RT		18 550 [b]	17 700	15 800 [b]	11 100s, vbr	8 300m (sh)

[a] RT = Room Temperature, LT = liquid-nitrogen temperature. [b] Unusually intense and sharp spin-forbidden band. [c] This complex also contains a band at 22 600vw cm^{-1} at both RT and LT. [d] Also very weak absorptions at *ca.* 17 000 cm^{-1}.

Table 3. Temperature variation of molar susceptibilities and exchange integrals (J) of the ferromagnetic tetrachlorochromates(II)

$[N(o\text{-}CH_3C_6H_4)H_3]_2[CrCl_4]$		$[H_3N(CH_2)_3NH_3][CrCl_4]$		$[NPhH_3]_2[CrCl_4]$	
$10^6\ \chi_A$/cm^3 mol^{-1}	T/K	$10^6\ \chi_A$/cm^3 mol^{-1}	T/K	$10^6\ \chi_A$/cm^3 mol^{-1}	T/K
12 410	295.5	12 690	295.4	11 710	295.5
14 810	265.4	14 910	265.5	13 620	265.3
18 380	229.5	18 090	229.5	16 500	229.5
22 820	197.4	22 440	197.4	20 090	197.4
29 810	166.5	29 430	166.5	25 820	166.5
42 530	135.3	43 100	135.3	36 340	135.3
70 870	104.0	71 550	104.0	59 880	104.0
96 980	89.5	105 900	89.5	81 570	89.5
J = 6.6 cm^{-1}, g = 1.99		J = 7.4 cm^{-1}, g = 1.91		J = 6.3 cm^{-1}, g = 1.89	

hydrochloric acid (110 cm^3) by heating. To the solution was added a solution of piperazinium chloride (9.64 g) in 12 mol dm^{-3} hydrochloric acid (120 cm^3). The mixture was cooled in ice with shaking and then left for a few minutes; light blue crystals separated from the light green solution. The crystals were filtered off, washed with concentrated hydrochloric acid and then acetone, and dried for 4 h under vacuum.

Piperazinium Tetrachlorochromate(II).—The hydrated compound was prepared as above, filtered off, and washed with hydrochloric acid (12 mol dm^{-3}) and then acetone. After drying for 7 h at 120 °C under vacuum, a light grey compound was obtained.

Bis(*ammonium*) *Tetrachlorochromate*(II).—Ammonium tetrachlorochromate(II) was earlier[2] prepared by thermal dehydration of $[NH_4]_2[CrCl_4(OH_2)_2]$. Extraction of ammonium chloride (2.37 g) into a solution of chromium(II) chloride (4.32 g) in glacial acetic acid (200 cm^3) as for *o*-methylanilinium tetrachlorochromate(II) (below) gave a mixture of purple and bluish materials. On heating with acetyl chloride (20 cm^3), the brown ammonium salt was obtained; this was dried similarly to the *o*-methylanilinium compound. Heating the dihydrate with acetyl chloride did not give the anhydrous complex.

Bis(*anilinium*) *-Diaquatetrachlorochromate*(II) *and -Tetrachlorochromate*(II).—Chromium(II) chloride tetrahydrate (4.78 g) was dissolved in 12 mol dm^{-3} hydrochloric acid (30 cm^3) by heating. To the solution was added a solution of anilinium chloride (5.16 g) in 12 mol dm^{-3} hydrochloric acid (25 cm^3) The mixture was shaken while being cooled in ice and then left for a few minutes; light blue crystals separated from the light green solution. The crystals were filtered off, washed with concentrated hydrochloric acid and acetone, and then kept under vacuum (pump) for 4 h at room temperature to give the diaqua complex, and for a further 6 h at 120 °C to give the grey anhydrous complex.

The anhydrous complex was also prepared by warming the dihydrate (4.00 g) with an excess of acetyl chloride (50 cm^3). The blue colour of the dihydrate became pinkish brown after about 0.5 h, and analysis of the product indicated a monohydrate. Extended treatment with acetyl chloride produced the anhydrous complex.

Bis(o-*methylanilinium*) *Tetrachlorochromate*(II).—*o*-Methylanilinium chloride (6.60 g) was extracted into a boiling solution of chromium(II) chloride tetrahydrate (4.51 g) in glacial acetic acid (200 cm^3). White crystals were obtained on cooling; these were filtered off, washed with glacial acetic acid, and dried by pumping for 10 h at room temperature.

Trimethylenediammonium Tetrachlorochromate(II).—Chromium(II) chloride tetrahydrate (5.35 g) was dissolved in 12 mol dm^{-3} hydrochloric acid (100 cm^3) by heating. To the solution was added a solution of trimethylenediammonium chloride (4.03 g) in 12 mol dm^{-3} hydrochloric acid (30 cm^3). The mixture was cooled in ice with shaking and then left for a few minutes; yellow-green crystals separated from the light green solution. The crystals were filtered off, washed with concentrated hydrochloric acid and acetone, and then dried for 4 h under vacuum.

Bis(triethylammonium) Tetrachlorochromate(II).—Chromium(II) chloride tetrahydrate (6.75 g), dissolved in ethanol (30 cm^3), was added to a solution of triethylammonium chloride (9.52 g) in ethanol (50 cm^3). The blue solution was concentrated until 25 cm^3 remained. 2,2-Dimethoxypropane (50 cm^3) was added with shaking, and off-white crystals separated immediately from the light green solution. The crystals were filtered off, washed with ethanol containing a small amount of 2,2-dimethoxypropane, and dried under vacuum for 6 h.

Bis(hydrazinium) Hexachlorochromate(II).—This compound was prepared by extraction of hydrazinium dichloride (4.09 g) into a hot solution of chromium(II) chloride (4.87 g) in glacial acetic acid (200 cm^3). The light green crystals obtained on cooling were filtered off, washed with glacial acetic acid, and dried for 10 h under vacuum.

Analyses and Physical Measurements.—To determine chromium, the compound was dissolved in water, a little nitric acid was added, and the mixture was boiled until a deep green solution was obtained. Concentrated ammonia was then added until the solution was alkaline to Methyl Red, to precipitate chromium hydroxide. This was filtered off and ignited to give Cr_2O_3. Chloride was determined gravimetrically as AgCl in the filtrate from the chromium determination.

Magnetic measurements were carried out by the Gouy method from room to liquid-nitrogen temperature on samples sealed *in vacuo* in Pyrex tubes. The apparatus was supplied by Newport Instruments, Newport Pagnell, Bucks. The field was calibrated with $Hg[Co(NCS)_4]$. Diffuse reflectance spectra were recorded on a Unicam SP 700C or Beckman Acta MIV spectrophotometer provided with reflectance attachment. The samples were sealed in silica cells under vacuum. I.r. spectra were recorded with a Perkin-Elmer 577 spectrophotometer. The Nujol mulls (KBr or Polythene plates) were made up in a glove bag under nitrogen. *X*-Ray powder photographs were taken with a Philips Debye–Scherrer camera of radius 114.6 mm, and Ni-filtered, Cu-K_α radiation. The samples were sealed in Lindemann glass capillaries.

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