The Crystal Structures of Propane-1,3-diammonium Tetrachlorochromate(II), a Sheet Ferromagnet, and Bis(dimethylammonium) Tetrachlorochromate(II), an Antiferromagnetic Compound Containing Isolated $[Cr_3Cl_{12}]^{6-}$ Units

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Summary *X*-Ray crystallographic studies have shown that the ferromagnetic complex propane-1,3-diammonium tetrachlorochromate(II) contains layers of chlorine-bridged $[CrCl_4]^{2-}$ units, but antiferromagnetic bis(dimethylammonium) tetrachlorochromate(II) contains isolated chlorine-bridged anions $[Cr_3Cl_{12}]^{6-}$ in which the metal atoms are arranged linearly.

CHLOROCHROMATES(II) of the type $M_2[CrCl_4]$ (M = K, Rb, Cs,[1-3] NH_4,[3] or NRH_3 where R = Me, Et,[4,5] C_8H_{17}, or $C_{10}H_{21}$[5]) are unusual in that they are ferromagnetic compounds as are[4] $[H_2en][CrCl_4]$, $[H_3dien][CrCl_4]Cl$, and $[H_4trien][CrCl_4]Cl_2$ (en = ethylenediamine, dien = diethylenetriamine, and trien = triethylenetetramine), but other tetrachlorochromates(II), $[Hpy]_2[CrCl_4]$[3] and $[NMe_2H_2][CrCl_4]$[4] (py = pyridine), exhibit antiferromagnetic behaviour. The new complex propane-1,3-diammonium tetrachlorochromate(II) $[H_3N(CH_2)_3NH_3][CrCl_4]$, for which satisfactory analyses were obtained, is also ferromagnetic: it has an effective magnetic moment, μ_{eff}, of 5·52 B.M. (for high-spin Cr^{II}, $S = 2$, $\mu_{s.o.} = 4{\cdot}90$ B.M.) at 295 K which increased to 8·63 B.M. at 90 K, and the Weiss constant θ is $-67°$ $[\chi_A^{-1} \propto (T + \theta)]$. The temperature variation of susceptibility (80—300 K) can be fitted to the Lines series expansion formula[6] for a layer structure, modified[1] to take account of the ferromagnetic nature of the exchange, with $J = 7{\cdot}4\ cm^{-1}$ and $g = 1{\cdot}91$, g being a little low for high-spin chromium(II) for which values closer to 2·00 are expected. The structure consists (Figure 1) of layers of chlorine-bridged $[CrCl_4]$ units at $y = 0$ and $y = \frac{1}{2}$. The propane-1,3-diammonium cations lie between the layers, which are about 9·3 Å apart, with the central carbon atom on the crystallographic mirror plane at $y = \frac{1}{4}$. The square-planar $[CrCl_4]$ units occupy centrosymmetric sites, and chlorine bridges to adjacent $[CrCl_4]$ units complete a tetragonally elongated octahedron around each chromium ion. Each bridging chlorine atom lies closer (2·39 Å) to one chromium atom than the other (2·87 Å). The bridging angle (165·3°) and the Cr–Cr separation (5·22 Å) are close to the values[7] in $[H_3dien][CrCl_4]Cl$ (5·13 Å and 162·3°) and the tetragonal

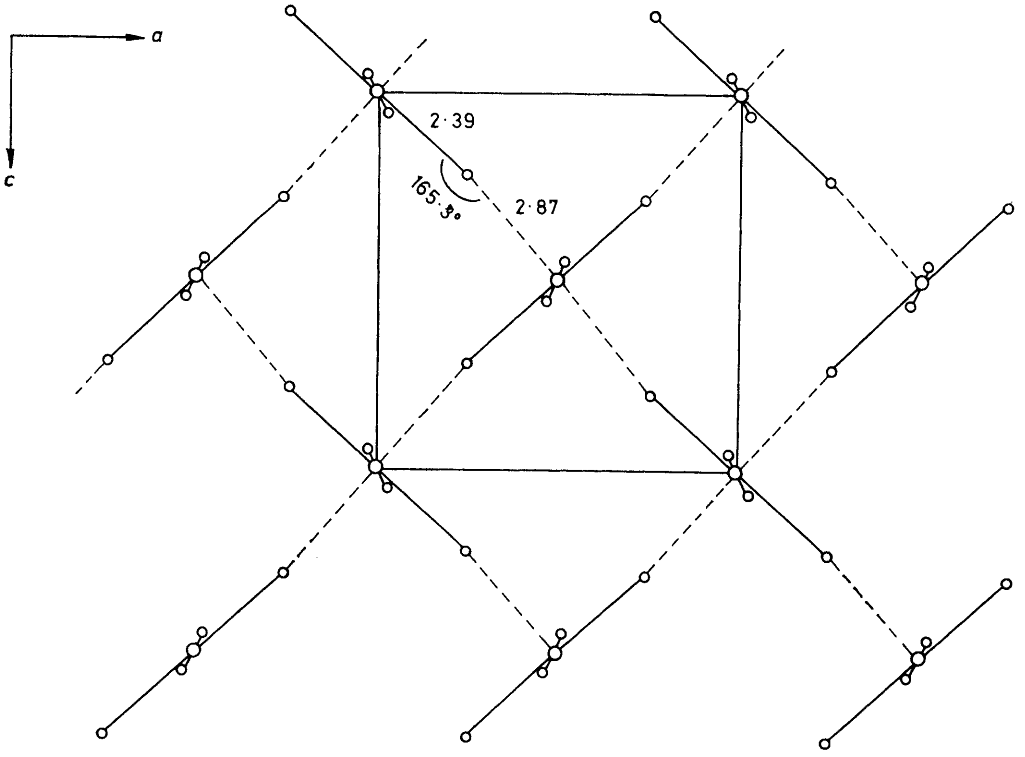

FIGURE 1. The packing of the anions in propane-1,3-di-ammonium tetrachlorochromate(II), viewed along the *b* axis.

axes lie alternately along [101] and [$\bar{1}$01] unit cell directions. This type of co-operative Jahn–Teller distortion has been reported recently for Rb_2CrCl_4 and is[8,9] the basis of the ferromagnetism.

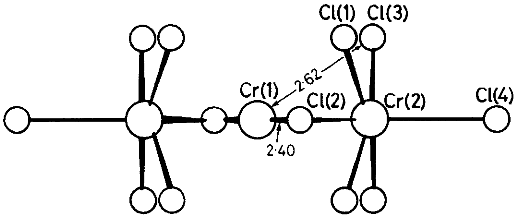

FIGURE 2. The trimeric anion of bis(dimethylammonium) tetrachlorochromate(II).

Antiferromagnetic bis(dimethylammonium) tetrachlorochromate(II) has a very different structure (Figure 2). It contains isolated $[Cr_3Cl_{12}]^{6-}$ units in which the chromium atoms are arranged linearly. The central metal atom Cr(1) lies on a centre of symmetry and is bridged by three chlorine atoms to each terminal metal atom; two chlorine atoms are much closer (2·40 Å) than the other four (2·62 Å). The angles subtended by adjacent Cr(1)–Cl bonds at Cr(1) differ by several degrees from right angles, but Cr(1) can be considered surrounded by a tetragonally flattened octahedron of chlorine atoms. The terminal chromium atoms, however, form four short and two long Cr–Cl bonds although there are large angular distortions from a tetragonally elongated octahedral geometry. The presence of the two types of Jahn–Teller distortion within the same anion is unique. Many chlorocuprates(II), which are also subject to Jahn–Teller distortion, are known,[19] but $[Cu_3Cl_{14}]^{8-}$, the only discrete trinuclear anion among this class of complexes, has a different structure.[11]

Values of μ_{eff} for linear chains of three interacting spins with $S = 2$ have been calculated[12] as a function of temperature. The magnetic behaviour of $[NMe_2H_2]_2[CrCl_4]$ can be fitted to the calculated data if it is assumed that $J = -8{\cdot}0$ cm^{-1} and $g = 2{\cdot}00$.

Yellow-green plates of propane-1,3-diammonium tetrachlorochromate(II) were isolated under nitrogen from stoicheiometric quantities of chromium(II) chloride tetrahydrate and the diammonium chloride in concentrated hydrochloric acid. The single crystals, which were sealed in Lindemann glass capillaries, are orthorhombic ($C_3H_{12}Cl_4CrN_2$, $a = 7{\cdot}235$, $b = 18{\cdot}535$, $c = 7{\cdot}517$ Å, space group $Pnma$, $Z = 4$). The structure was solved by the heavy-atom method and refined by isotropic full-matrix least-squares to $R = 0{\cdot}19$ for 794 (89%) observed reflexions. The rather high R factor is probably due to high absorption of chromium for the copper radiation used and very anisotropic crystal shape.†

Pale yellow-green prisms of bis(dimethylammonium) tetrachlorochromate(II), crystallised by the addition of 2,2-dimethoxypropane to a concentrated ethanolic solution of the constituent halides, were handled as above. The crystals are orthorhombic ($C_4H_{16}Cl_4CrN_2$) ($a = 12{\cdot}842$, $b = 19{\cdot}185$, $c = 7{\cdot}431$ Å, space group $Pnnm$, $Z = 6$). The structure was solved as above to $R = 0{\cdot}076$ (anisotropic refinement) for 1441 (85%) observed reflexions.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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