Bis(monoalkylammonium) Tetrachlorochromates(II): a new Series of Two-dimensional Ionic Ferromagnets

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Summary The compounds $(RNH_2)_2CrCl_4$ (R = Me, Et, C_8H_{15}, or $C_{10}H_{21}$) have been prepared and characterized; their magnetic and optical behaviour is compared to that of the transparent ferromagnets A_2CrCl_4 (A = K, Rb, or Cs).

FOR both scientific and technological reasons there has been much interest in recent years in ionic transition metal compounds which order ferromagnetically, and at the same time are transparent to visible light. Such a combination of properties is rare, but by a combination of optical[1] and magnetic measurements[2] and elastic[3] and inelastic[4] neutron scattering we have recently shown that the compounds A_2CrCl_4 (A = K, Rb, or Cs) belong to this select group. Their structures are analogous to that of K_2NiF_4, a layer lattice, and it would therefore be of interest to examine the effect on the magnetic and optical properties of varying the interlayer separation by substituting larger cations. We now report the preparation and characterisation of the new series of compounds $(RNH_3)_2CrCl_4$ (R = Me, Et, C_8H_{15}, or $C_{10}H_{21}$), together with magnetic and optical evidence that, like A_2CrCl_4, they contain ferromagnetically coupled layers of Cr^{II} ions. The monomethylammonium salt orders as a three-dimensional ferromagnet in the region of 60 K.

All the compounds were prepared by mixing stoicheiometric quantities of the appropriate monoalkylammonium chloride in ethanolic solution to an ethanolic solution of $CrCl_2$, prepared by bubbling HCl gas through ethanol containing 'Specpure' chromium powder.[5] Crystals in the form of thin, very pale, green flat plates large enough for optical spectroscopy were obtained by slow recrystallization from the same solvent. Satisfactory analyses (within ± 1% error for all elements) were obtained in all cases. Even in crystalline form the compounds are extremely unstable to air and moisture and must be prepared from well dried starting materials and handled exclusively under dry oxygen-free nitrogen.

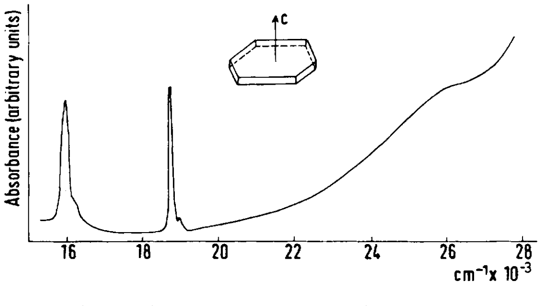

FIGURE. Visible absorption spectrum of a crystal of $(MeNH_3)_2$-$CrCl_4$ at 20 (------) and 130 K (————).

X-Ray powder diffraction patterns confirm that at room temperature the compounds are isomorphous with the corresponding Mn^{II}[6] and Fe^{II}[7] salts [orthorhombic: *Abma*: (D^{18}_{2h})]. The latter, which have been extensively studied,[8] contain antiferromagnetic layers. The room temperature unit-cell parameters of the two simplest compounds are: (a) R = Me; a = 7·43, b = 7·27, c = 18·89 Å; (b) R = Et; a = 7·59, b = 7·36, c = 21·41 Å. The space group and unit-cell parameters of the monomethylammonium compound were also confirmed by single crystal precession photography. In addition, we have made a preliminary study of the crystal and magnetic structure of a deuteriated sample of the monomethylammonium salt at low temperature by powder neutron diffraction.[9] At 87 and 4·2 K the diffraction profiles can be indexed as monoclinic (a = 7·19, b = 7·43, c = 18·80 Å, β = 90·8° at 87 K; and a = 7·16, b = 7·42, c = 18·82 Å, β 90·9° at 4·2 K). An analogous phase change between room temperature and 4·2 K has also been observed in the corresponding Mn^{II} compound.[6] Most significant is the fact that no peaks which can be ascribed to pure magnetic scattering are found in the 4·2 K neutron diffraction profile. Thus at 4·2 K the compound is either ferromagnetically ordered, so that the crystallographic and magnetic unit cells coincide, or it is still above its ordering temperature. However, magnetic susceptibility measurements on a powdered sample of the monomethylammonium salt between 77 and 150 K gave a large positive value (+ 60 K) for the Weiss constant, indicating three-dimensional ferromagnetic ordering. For comparison, Rb_2CrCl_4, with a Weiss constant of +82 K, has a ferromagnetic Curie temperature of 63 K.[3]

Further evidence that the compounds order ferromagnetically comes from the striking temperature dependence of their visible absorption spectra. We previously[1,10] showed that in transition metal compounds in which ferromagnetic exchange interactions dominate, the spin-forbidden ligand field transitions lose their intensity rapidly below the ordering temperature because electronic excitations (excitons) which lower the overall spin projection of the crystal (*e.g.*, quintet-to-triplet) gain intensity only if combined with annihilation of a thermally populated magnon. In the A_2CrCl_4 series this behaviour is shown by two particularly narrow quintet–triplet absorption bands near 530 and 640 nm, which have intensities at low temperatures quite closely proportional to T^2, a result which can be rationalised by taking into account the spin–wave dispersion spectrum of a predominantly two-dimensional easy-plane ferromagnet.[10,11] The Figure shows the visible absorption spectrum of $(MeNH_3)_2CrCl_4$ at two different temperatures, with the incident light propagating along the c-axis. Not only are narrow bands found at frequencies very close to those in the A_2CrCl_4 salts, but their behaviour on increasing the temperature is also similar. Comparable behaviour has also been found in other members of the monoalkylammonium series, suggesting that they all order ferromagnetically.

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