Preparation, Characterization, and Magnetic Properties of Organic-intercalated Two-dimensional Ionic Ferromagnets $(C_nH_{2n+1}NH_3)_2CrCl_4$ (n = 3, 5, or 12)

By **Martin J. Stead** and **Peter Day**,* Oxford University, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The title compounds have been prepared and characterized by chemical analysis and powder X-ray diffraction. Spacing between the planes of chromium(II) ions increases from 12.35 to 17.81 to 31.05 Å as n increases from 3 to 5 to 12 but the spacing between Cr^{II} within the planes remains almost constant. Magnetic susceptibility data in the range 60—140 K have been fitted to a high-temperature series expansion for a square two-dimensional lattice to give $J = 6.5 \pm 0.2$ cm^{-1} ($\mathcal{H} = -JS_iS_j$) and $g = 1.95$ for all three compounds. Low-temperature magnetization measurements show that all the salts order ferromagnetically in the region 50 ± 10 K although the transition is broadened by the applied magnetic field. The effective magnetic moments of 5.04—5.35 μ_B at 140 K remain higher than the spin-only value of 4.90 μ_B because of persisting short-range order.

THERE has been a great deal of interest in recent years in compounds whose co-operative magnetic behaviour approximates to one- or two-dimensional.[1] Prominent among the latter are the so called layer perovskite halide salts with general formula $(RNH_3)_2MX_4$, where R is an organic group, M is a bivalent $3d$ ion or Cd, and X a halogen.[2] In these compounds, whose structures are roughly based on the tetragonal K_2NiF_4 lattice, layers of corner-sharing MX_6 octahedra are separated by RNH_3^+ which, if R is a long-chain alkyl group, have their long axes pointing away from the layers.[3] The manganese [4] and iron [5] salts have antiferromagnetic near-neighbour exchange while the copper ones are ferromagnetic.[6] We have shown that the chromium salts with R = CH_3 or CH_3CH_2 are also ferromagnetic, with T_c much higher than in the corresponding copper examples.[7] These salts have the added interest that their visible absorption spectra are dominated by sharp well resolved spin-forbidden ligand-field bands, whose intensities are a very sensitive measure of the ferromagnetic spin correlations.[8] Salts of the type $(C_nH_{2n+1}NH_3)_2MCl_4$ with M = Mn have been reported with up to n = 12 or 16 [9] and with M = Cd, up to n = 10.[3] In this paper we report the preparation and characterization of chromium salts with a wider range of n than hitherto and magnetic measurements at temperatures well above and below their three-dimensional ordering temperatures.

EXPERIMENTAL

Preparation.—The compounds were prepared by the method reported earlier.[7] They are extremely sensitive to oxidation and all solvents, *etc.* must be rigorously oxygen-free. All manipulations were carried out by Schlenk techniques under O_2-free nitrogen. Alkylamines were from B.D.H. and Aldrich, and the starting solution of Cr^{II} in ethanol was obtained by dissolving Koch-Light 99.99% Cr metal using Air Products HCl gas.

X-*Ray Powder Diffraction*.—Samples were sealed under nitrogen in tubes and diffraction patterns obtained with a Philips PW 1024 camera (nickel-filtered Cu-K_α radiation).

Magnetic Susceptibility.—Samples (*ca*. 4 mg) were loaded in a dry-box into ' Rislan ' spheres which were glued to quartz fibres and suspended from a Sartorius microbalance in an Oxford Instruments Faraday balance. The latter had a vertical superconducting solenoid capable of producing fields up to 4.8 T, and the sample was surrounded by helium exchange gas, whose temperature was controlled by a Harwell temperature controller from 4.2 to 140 K. Temperature was measured with a previously calibrated Au, 0.03 atomic % Fe *versus* chromel thermocouple, with its cold junction in the liquid-helium bath.

RESULTS

Chemical Analysis.—Elemental analysis results are listed in Table 1. In addition, solid samples were checked for chromium(III) content by dissolving small quantities in deoxygenated spectroscopic grade ethanol in a glove-box, sealing the solution in a 1-cm spectrophotometer cell, and recording the visible absorption spectrum. Oxygen was then bubbled through and the spectrum remeasured. Chromium(III) in ethanol has a broad band at 465 nm while Cr^{II} has no absorption at this wavelength. Upper limits of Cr^{III} were *ca*. 3%.

TABLE 1

Elemental analyses (%) * of $(C_nH_{2n+1}NH_3)_2CrCl_4$

	n = 3	n = 5	n = 12
C	22.2 (22.9)	30.9 (32.4)	51.5 (50.9)
H	6.75 (6.35)	8.50 (7.55)	11.2 (9.9)
N	8.90 (8.90)	7.20 (7.55)	5.05 (4.95)
Cl	45.1 (45.2)	37.4 (38.3)	25.5 (25.1)
Cr	16.4 (16.6)	12.9 (14.0)	8.30 (9.20)

* Calculated values are given in parentheses.

Unit-cell Parameters.—In common with the methyl- and ethyl-ammonium salts [7] the powder X-ray diffraction photographs were indexed in the orthorhombic space group *Cmca* (D_{2h}^{18}) and least-squares fitted to extract values of the unit-cell parameters. These are listed in Table 2, with the literature values for the corresponding copper salts, including the C_1 and C_2 examples, for comparison. In all the compounds a_0 and b_0 are almost invariant, suggesting that the principal intralayer dimensions are independent of the length of the alkyl chain. On the other hand, c_0 increases

TABLE 2

Unit-cell parameters (Å) of $(C_nH_{2n+1}NH_3)_2MCl_4$ (M = Cr or Cu)

	n	1	2	3	5	12
Cr	a_0	7.43 [a]	7.59 [a]	7.61 [b]	7.47 [b]	7.45 [b]
	b_0	7.27	7.36	7.36	7.37	7.20
	c_0	18.89	21.41	24.71	35.62	62.1
Cu	a_0	7.54 [c]	7.47 [c]	7.65 [c]	7.51 [c]	
	b_0	7.30	7.35	7.33	7.38	
	c_0	18.55	21.18	24.66	34.81	

[a] Ref. 7. [b] Present work. [c] L. J. de Jongh, A. C. Botherman, F. R. deBoer, and A. R. Miedema, *J. Appl. Phys.*, 1969, **40**, 1363.

rapidly, and is always slightly bigger in each chromium compound than in the corresponding copper compound.

High-temperature Susceptibility.—Figure 1 shows the inverse molar susceptibility of each compound as a function of temperature from 140 to 60 K. Above *ca.* 70 K the Curie–Weiss law is obeyed, with values of the Weiss constant, θ, equal to 56, 57, and 57 K for $n = 3$, 5, and 12 respectively. After a correction for diamagnetism of the samples and holder, and for temperature-independent paramagnetism, the effective magnetic moments of the three compounds calculated from $\mu = 2.83\chi_m^{\frac{1}{2}}(T - \theta)^{\frac{1}{2}}$ were respectively 5.04, 5.04, and 5.35 μ_B, slightly above the values found for magnetically dilute chromium(II) compounds, *e.g.* 4.98 μ_B for $Rb_2CrCl_4(H_2O)_2$.[10]

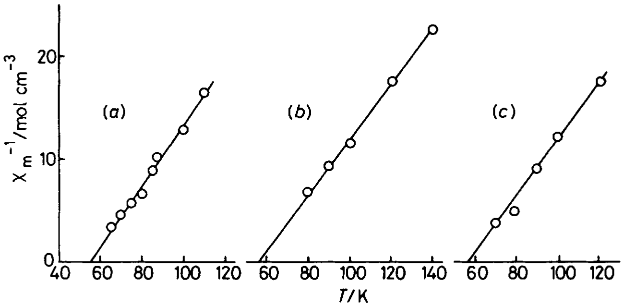

FIGURE 1 Curie–Weiss behaviour of the susceptibility of $(C_nH_{2n+1}NH_3)_2CrCl_4$; (*a*) $n = 3$, (*b*) $n = 5$, (*c*) $n = 12$

The high-temperature susceptibilities were also fitted to the series expansion of Rushbrooke and Wood,[11] modified by Lines,[12] for a quadratic layer Heisenberg ferromagnet. Writing the exchange Hamiltonian as equation (1) with the

$$\mathscr{H} = -\Sigma J S_i S_j \tag{1}$$

summation covering all pairs of near-neighbour ions i,j the susceptibility, χ, is given by equation (2) where $x = kT/JS(S + 1)$ and the C_n are functions of the spin S. For an $S = 2$ ferromagnet equation (2) becomes equation (3) where $y = J/kT$.

$$Ng^2\mu_B{}^2/\chi J = 3x + \sum_{n=1}^{\infty} (C_n/x^{n-1}) \tag{2}$$

$$Ng^2\mu_B{}^2/\chi = \tfrac{1}{2}kT + J(-4 + 9y - 9.07y^2 + 55.73y^3 + 160.7y^4 + 116.6y^5 + \ldots) \tag{3}$$

In Figure 2 the experimental data for all three compounds are plotted together and superimposed on a curve calculated from equation (3) with $J = 6.5$ cm^{-1} and $g = 1.95$. For a high-spin octahedral $3d^4$ compound g is expected to be a little below 2.00. It is clear that the behaviour of all three compounds at temperatures well above T_c can be described by a common curve.

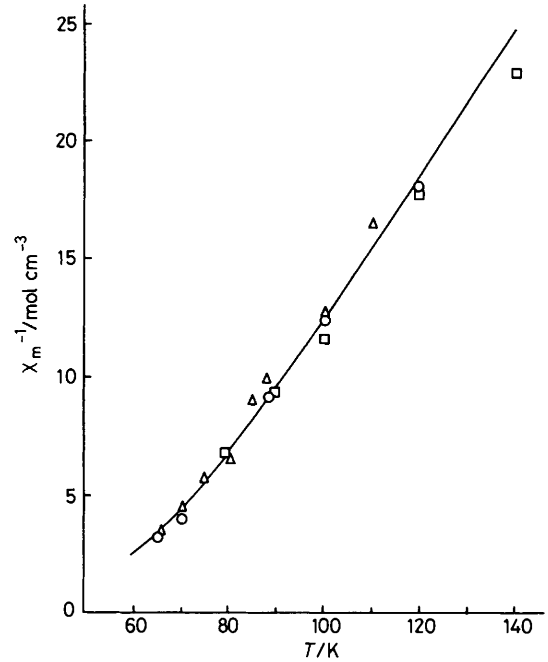

FIGURE 2 Inverse molar susceptibility of $(C_nH_{2n+1}NH_3)_2CrCl_4$; $n = 3$ (△), $n = 5$ (□), $n = 12$ (○). Full line is equation (3) with $J = 6.5$ cm^{-1} and $g = 1.95$

Low-temperature Magnetization.—Figure 3 shows magnetization curves for the three compounds as a function of temperature down to 4.2 K. The measurements on the C_3 and C_{12} compounds were made at an applied field of 1.26 T but the C_5 results were obtained at 2.53 T. In the latter case the greater rounding of the transition brought about by the higher field is clearly apparent. In the absence of measurements at very low fields, any estimates of the spontaneous ordering temperatures must remain very approximate. For all three compounds, however, the points of inflexion in the magnetization curves are near 50 K, suggesting that T_c lies in this region.

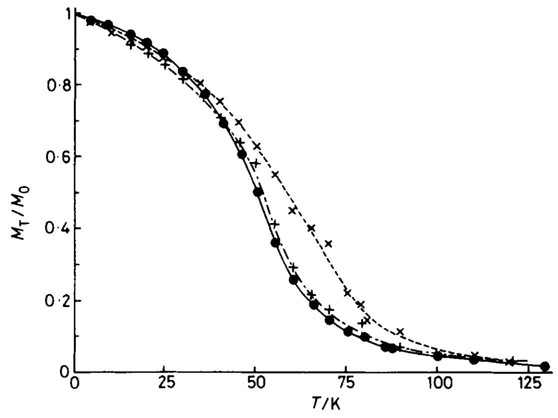

FIGURE 3 Magnetization of $(C_nH_{2n+1}NH_3)_2CrCl_4$; $n = 3$ (●), $n = 5$ (×), $n = 12$ (+)

In the methyl- and ethyl-ammonium tetrachlorochromates,[7] as well as in Rb_2CrCl_4,[13] the temperature variation of the magnetization is described quite well by a power law, equation (4). In Figure 4 the same law is applied to the

$$1 - (M_T/M_0) = CT^{\gamma} \qquad (4)$$

propyl-, pentyl-, and dodecyl-ammonium salts. The dashed line in this Figure represents $\gamma = 1.5$, which is quite a good approximation to the behaviour of all three salts.

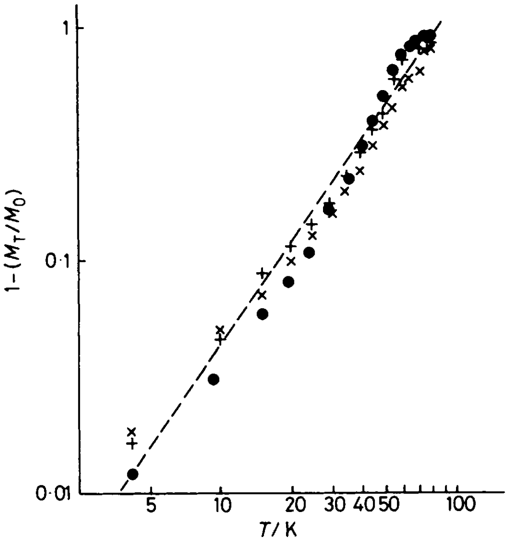

FIGURE 4 Power-law dependence of magnetization on temperature; key as in Figure 3

DISCUSSION

In all the organic-intercalated layer perovskite halide salts whose structures have been determined so far the metal ions lie on a square-planar lattice, each surrounded by six halide ions. Lengthening the alkyl chain R in the RNH_3^+ cation has a negligible effect on the geometry of the metal halide layers, but merely increases the spacing between them. The unit-cell parameters in Table 2 show that this generalization applies equally to the new chromium compounds. In the manganese, iron, and cadmium salts the metal ion co-ordination is almost octahedral but in the chromium and copper ones a strong static Jahn–Teller distortion is anticipated.

Crystal structures are available for several copper(II) and chromium(II) compounds with layer perovskite structures, so some useful comparisons can be made. In every case the basic form of the Jahn–Teller distortion consists of a tetragonal elongation of the octahedra, alternately along [100] and [010] of the original K_2NiF_4-like unit cell. The two copper(II) salts have quite similar Cu–Cl bond lengths, as follows: $(C_2H_5NH_3)_2CuCl_4$ [14] 2.975, 2.285, 2.277; $(C_3H_7NH_3)_2CuCl_4$ [15] 3.04, 2.29, 2.29 Å; where the first and second figures relate to the basal plane, and the third to the bond parallel to the long axis of the orthorhombic unit cell. The Cr–Cl bond lengths in the three tetrachlorochromate(II) salts span a somewhat wider range, especially in the longest bond: Rb_2CrCl_4 [16] 2.700, 2.379, 2.357 (77 K); $[H_3N(CH_2)_3NH_3]CrCl_4$ [17] 2.87, 2.39, 2.39; $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]CrCl_4(Cl)$[18] 2.79, 2.39, 2.41 Å. Furthermore, the axial Cr–Cl bonds are always *ca.* 0.1 Å longer than the corresponding Cu–Cl bonds. If this were the sole difference between the crystal structures of the chromium(II) and copper(II) salts with the same RNH_3^+ cation one would expect the c_0 parameters of corresponding salts in Table 2 to differ always by the same amount. Taking into account the experimental error, the difference throughout is, in fact, somewhat larger, suggesting that the variation in the metal–chlorine bond length brings about small changes in the hydrogen bonding of the cation to the inorganic layer, which in turn cause slight shifts in the angle between the C–N bond and the crystallographic *c* axis. More precise comment must await further crystallographic studies.

In the chromium(II), as in the copper(II), layer perovskite salts the co-operative Jahn–Teller ordering is crucial in determining the sign of the near-neighbour exchange constant. Since the principal axes of elongation in neighbouring MCl_6 groups are nearly orthogonal to one another the principal super-exchange pathway lies between a filled z^2 and a half-filled $x^2 - y^2$ orbital in the d^9 compounds, and a half-filled z^2 and an empty $x^2 - y^2$ in the d^4. Both are expected [19] to lead to ferromagnetic exchange, as observed.

The exchange constant of 6.5 ± 0.2 cm^{-1} derived from the high-temperature series expansion is marginally lower than the values obtained earlier [7] for the methyl- (9 cm^{-1}) and ethyl-ammonium salts (7 cm^{-1}) and, taken in conjunction with the more precise figure of 10.7 ± 0.1 cm^{-1} measured [20] by inelastic neutron scattering for Rb_2CrCl_4, suggests a small systematic variation with increasing size of the cation. This is more likely to result from small changes in the Cr–Cl · · · Cr bond angles within the basal plane to accommodate slight shifts in the H-bond angles than a consequence of increasing separation between the layers. Thus in Rb_2CrCl_4 the Cr–Cl · · · Cr angle is exactly 180°, while in the diethylenetriammonium salt, for example, it is reduced to 162°.[18] Any departure from 180° destroys the orthogonality of the $x^2 - y^2$ orbitals on adjacent centres, and introduces an antiferromagnetic component into the exchange, as demonstrated very nicely by Hatfield and co-workers [21] for a series of copper(II) dimeric complexes.

The magnetization behaviour of all three compounds at low temperature is very similar and, given that the interlayer spacing increases from 10.78 and 11.93 Å in the methyl- and ethyl-ammonium salts to 12.35, 17.81, and 31.05 Å in those studied here, reinforces the conclusion that the magnetic behaviour of organic-intercalated layer salts is essentially independent of the interlayer separation. Characteristic, too, of the two-dimensional nature of the exchange is the way in which the magnetization obeys the power law of equation (4). The celebrated Bloch $T^{3/2}$ law [22] only applies to isotropic ferromagnets up to about two tenths of T_c,[23] but a two-dimensional ferromagnet has a spin–wave dispersion relation which is almost flat in the direction perpendicular to the layers. Consequently a very high density of spin–wave modes can exist at low energy close to the

Brillouin zone centre, accommodating a relatively high thermal population of spin-waves without appreciable interactions between them.

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REFERENCES

[1] See, for example, L. J. de Jongh and A. R. Miedema, *Adv. Phys.*, 1974, **23**, 1; R. D. Willett, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 111.

[2] H. Arend, W. Huber, F. H. Mischgofsky, and G. K. Richter-van Leeuwen, *J. Cryst. Growth*, 1978, **43**, 213.

[3] R. Blinc, M. I. Burgar, V. Rutar, B. Zeks, R. Kind, H. Arend, and G. Chapuis, *Phys. Rev. Lett.*, 1979, **43**, 1679.

[4] W. D. Van Amstel and L. J. de Jongh, *Solid State Commun.*, 1972, **11**, 1423.

[5] F. M. Mostafa and R. D. Willett, *Phys. Rev.. B*, 1971, **3**, 2213.

[6] L. J. de Jongh and W. D. Van Amstel, *J. Phys. (Paris), Colloq.*, 1971, **1 C1**, 880.

[7] C. Bellitto and P. Day, *J. Chem. Soc., Chem. Commun.*, 1976, 870; *J. Chem. Soc., Dalton Trans.*, 1978, 1207.

[8] C. Bellitto, M. J. Fair, T. E. Wood, and P. Day, *J. Phys. C*, 1980, **13**, L627.

[9] V. Salerno, A. Grieco, and M. Vacatello, *J. Phys. Chem.*, 1976, **80**, 2444.

[10] L. F. Larkworthy and J. K. Trigg, *Chem. Commun.*, 1970, 1221.

[11] G. S. Rushbrooke and P. J. Wood, *Mol. Phys.*, 1958, **1**, 257.

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

[13] A. K. Gregson, P. Day, D. H. Leech, M. J. Fair, and W. E. Gardner, *J. Chem. Soc., Dalton Trans.*, 1975, 1306.

[14] J. P. Steadman and R. D. Willett, *Inorg. Chim. Acta*, 1970, **4**, 367.

[15] P. Barendregt and H. Schenk, *Physica*, 1970, **49**, 465.

[16] P. Day, M. J. Hutchings, E. Janke, and P. J. Walker, *J. Chem. Soc., Chem. Commun.*, 1979, 711.

[17] M. A. Babar, M. F. C. Ladd, L. F. Larkworthy, D. C. Povey, K. J. Proctor, and L. J. Summers, *J. Chem. Soc., Chem. Commun.*, 1981, 1046.

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

[19] J. B. Goodenough, 'Magnetism and the Chemical Bond,' Interscience, New York, 1963, p. 222.

[20] M. T. Hutchings, M. J. Fair, P. Day, and P. J. Walker, *J. Phys. C*, 1976, **9**, L55.

[21] V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.

[22] F. Bloch, *Z. Physik*, 1931, **61**, 206.

[23] C. Kittel, 'Introduction to Solid State Physics,' 4th edn., Wiley, New York, 1971, p. 535.