Preparation and Magnetic Properties of some Alkali-metal Salts of Chlorochromate(II) and Chlorochromate(III) Anions

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The preparation from melts of the chromium(II) compounds $ACrCl_3$ and A_2CrCl_4 (A = K or Cs) and two chromium(III) compounds K_3CrCl_6 and $K_3Cr_2Cl_9$ are reported. The compounds $ACrCl_3$ species are antiferromagnetic while the A_2CrCl_4 species are ferromagnetic and are examples of ferromagnets which are transparent in much of the visible region of the spectrum. The magnetic properties of the chromium(II) compounds are analysed on the basis of one- or two-dimensional nearest-neighbour Heisenberg models. $K_3Cr_2Cl_9$ Shows evidence of antiferromagnetic exchange. Electronic spectra of some of the compounds are briefly described. Attempts to prepare analogous titanium(II) and vanadium(II) complexes were unsuccessful.

THERE is considerable interest in the production of optically transparent ferromagnets, especially since they offer means of modulating laser beams for a wide range of applications from speech transmission to oscilloscope displays. We have investigated the preparation of alkali-metal salts of chloroferrate(II) complexes as part of our studies of such compounds. It is necessary to use simple counter-ions since they will make more probable the formation of the polymeric structures required. Since these salts cannot be precipitated from solution, we have prepared them from suitable melts using the methods described before.[1]

We report here the preparation of the compounds $ACrCl_3$ and A_2CrCl_4 (A = K or Cs), K_3CrCl_6, and $K_3Cr_2Cl_9$. Magnetic susceptibilities of the chromium(II) compounds are interpreted using a nearest-neighbour Heisenberg coupling model. The compounds $ACrCl_3$ are shown to be antiferromagnetic while ferromagnetic ordering is observed in the A_2CrC_4 compounds. Electronic spectra are discussed briefly since analyses of the spectra of single crystals of K_2CrCl_4 [2] and $CsCrCl_3$ [3] have been published. $K_3Cr_2Cl_9$ Shows some evidence of magnetic interactions.

Preparation of Compounds.—Both of the methods used [1] for the preparation of iron(II) compounds were employed in the preparation of their chromium(II) analogues. In the first, stoicheiometric amounts of $CrCl_2$ and alkali-metal chloride were melted together, the $CrCl_2$ being obtained by reduction of resublimed $CrCl_3$ in a mixture of hydrogen and hydrogen chloride at *ca.* 500 °C. The potassium compounds were also prepared by the second method, which involves reducing stoicheiometric melts of $CrCl_3$ and KCl with high-purity chromium. The compounds resulting from this reduction contained some impurities, judged by their colours, but, unlike the iron complexes, the impurities were not ferromagnetic and did not interfere in magnetic measurements. Chromium(III) complexes were prepared from stoicheiometric melts of the alkali-metal chloride and resublimed chromium(III) chloride.

Phase studies [4,5] show that $KCrCl_3$ and K_2CrCl_4 melt congruently at 494 and 478 °C respectively, $CsCrC_3$

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[1] D. H. Leech and D. J. Machin, *J. Inorg. Nuclear Chem.*, 1975, in the press.

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

[3] G. L. McPherson, G. L. Kistenmacher, J. B. Folkers, and G. D. Stucky, *J. Chem. Phys.*, 1972, **57**, 3771.

[4] H. J. Seifert and K. Klatyk, *Naturwiss.*, 1962, **49**, 539.

[5] H. J. Seifert and K. Klatyk, *Z. anorg. Chem.*, 1964, **334**, 113.

melts congruently at 709 °C, but Cs_2CrCl_4 melts incongruently at 563 °C. Special care was taken with the last compound to minimise the amounts of impurities, by slow cooling from well above the melting point. Analytical data are given in Table 1. Phase studies[6] suggest that it should be possible to prepare the analogous titanium(II) and vanadium(II) complexes from melts since the compounds $ATiCl_3$, $AVCl_3$, and A_2TiCl_4 (A = K or Cs) all melt congruently or incongruently in the range 640—1 100 °C. Attempts to prepare K_2TiCl_4 and $KVCl_3$ by reduction of stoicheiometric quantities of $TiCl_3$ or VCl_3 with the metal in molten KCl lead to only partial reaction. Two reasons for this can be suggested. First, the reactions are exothermic, and at the higher temperatures required [compared with the chromium(II) analogues] the reaction will not be favoured. Secondly, also as a result of higher reaction temperatures, considerable amounts of the trihalides sublime from the reaction mixture and also tend to attack the silica reaction tubes. We have thus been unable to prepare these compounds.

TABLE 1

Analytical data

		Analyses (%)			
		Calc.		Found	
Compound	M.p. (t/°C)	Cr	Cl	Cr	Cl
$KCrCl_3$	494	26.3	53.9	26.0	53.6
K_2CrCl_4	478	19.1	52.1	19.5	52.3
$CsCrCl_3$	709	17.9	36.5	18.2	36.7
Cs_2CrCl_4	563 *	11.3	30.8	11.1	30.3
K_3CrCl_6	850	13.6	55.7	13.8	55.0
$K_3Cr_2Cl_9$	813	19.2	59.0	19.7	58.6

* Incongruent m.p.

Magnetic Properties.—All the compounds studied are such that magnetic interactions will occur in one, or two, dimensions. The magnetic properties of these systems can be described[7] by either a Heisenberg, or Ising, spin Hamiltonian. For a system of N magnetic ions in an applied field H, these may be combined in the form

$$H_{\text{op}} = \sum_{i=1}^{N} \sum_{j=1}^{N} \{J^{\parallel}{}_{ij}\, S^{z}{}_{i}S^{z}{}_{j} + J^{\perp}{}_{ij}\,(S^{x}{}_{i} \,.\, S^{x}{}_{j} + S^{y}{}_{i} \,.\, S^{y}{}_{j})\} - g\beta \sum_{i=1}^{N} H \,.\, S_i \qquad (1)$$

where $S^{x}{}_{i}$ *etc.* are the components of the spin-vector S_i of the i th ion. The case $J^{\perp}{}_{ij} = 0$ corresponds to pure Ising coupling while $J^{\perp}{}_{ij} = J^{\parallel}{}_{ij}$ corresponds to a spatially isotropic Heisenberg coupling. We have used a nearest-neighbour Heisenberg model to calculate susceptibilities with a Hamiltonian of the form (2) where J

$$H_{\text{op}} = -2J \sum_{(ij)} S_i \,.\, S_j - g\beta \sum_{i=1}^{N} H \,.\, S_i \qquad (2)$$

is the exchange energy constant for nearest neighbour interactions between sites (ij). J Is positive for a ferromagnetic coupling. Equation (2) can be simplified by introducing a new vector $Y_i = S_i/[S(S+1)]^{\frac{1}{2}}$ and putting $J = JS(S+1)$ and $g = g[S(S+1)]^{\frac{1}{2}}$ when

$$H_{\text{op}} = -2J \sum_{(ij)} T_i \,.\, T_j - g\beta \sum_{i=1}^{N} H \,.\, T_i \qquad (3)$$

which is the Hamiltonian for the classical, or $S = \infty$, Heisenberg model.[8]

(a) *Chromium*(II) *Compounds*.—(i) $CsCrCl_3$. The crystal structure of this compound has been the subject of some debate,[4,9] but the most recent work[3] shows that the structure is very similar to that of $CsNiCl_3$, consisting of linear chains of octahedra sharing opposite faces. Previous workers have reported that the susceptibility obeys a Curie–Weiss law[10] with $\theta = 328$ K while calculations based on a chain of ten interacting centres[11] gave $J = -35$ $\boldsymbol{k}$ when $S = 2$ and $g = 2$. Our measurements (see Table 2) show that at room temperature, $\mu_{\text{eff.}}$ is 3.41 B.M., well below the spin-only value of 4.9 B.M.; moreover, there is a broad maximum in the susceptibility near 140 K, suggesting antiferromagnetic behaviour. The temperature dependence is shown in Figure 1.

TABLE 2

Summary of magnetic properties

				Parameters which give best fit	
Compound	$\mu_{\text{eff.}}$ (B.M.) at 290 K	θ/K	Range *	J †	g
$CsCrCl_3$	3.41			−25.0 to −26.5	1.94 to 1.98
$KCrCl_3$	4.56	45	80	−5.0 to −4.0	1.98 to 1.96
Cs_2CrCl_4	5.52	−77	120	5.25 to 6.00	2.00
K_2CrCl_4	5.55	−68	100	4.75 to 5.25	2.00 [a]
				4.83	2.00 [b]

* A Curie–Weiss law is obeyed between this temperature and 300 K. † As multiples of the Boltzmann constant, $\boldsymbol{k}$ (*ca.* 1.38×10^{-23} J K^{-1}).

[a] Rushbrooke and Wood's treatment. [b] Stanley's treatment.

Fisher[12] has shown that, in the limit of infinite spin, the problem of a linear chain of spins interacting with a nearest-neighbour isotropic Heisenberg Hamiltonian can be solved exactly. Smith and Friedberg[13] used this approach to analyse their data on $CsMnCl_3{\cdot}2H_2O$. Following these authors, the susceptibility of $CsCrCl_3$ may be written as

$$\chi_{(N)}(T) = \frac{Ng^2\beta^2 S(S+1)}{3\boldsymbol{k}T} \cdot \frac{1 + u(K)}{1 - u(K)} \qquad (4)$$

where $K = 2JS(S+1)/\boldsymbol{k}T$ and $u(K) = \coth K - 1/K$.

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[6] P. Ehrlich and H. Kühnl, *Z. anorg. Chem.*, 1957, **292**, 146; Hsi-Ch'ang Li and D. M. Chizhikov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Tekh. Nauk, Met. i. Toplivo*, 1961, **5**, 22; P. Ehrlich and R. Schmitt, *Z. anorg. Chem.*, 1961, **308**, 91; H. J. Seifert and P. Erhlich, *ibid.*, 1959, **302**, 284.

[7] D. H. Martin, 'Magnetism in Solids,' Ilife, London, 1967.

[8] R. L. Stephenson and P. J. Wood, *Phys. Rev.*, 1968, **173**, 475.

[9] E. Iberson, R. Gut, and D. M. Gruen, *J. Phys. Chem.*, 1962, **66**, 65.

[10] D. J. W. Ijdo, Ph.D. Thesis, University of Leiden, 1960.

[11] L. F. Larkworthy and J. K. Trigg, *Chem. Comm.*, 1970, 1221.

[12] M. E. Fisher, *Amer. J. Phys.*, 1964, **32**, 343.

[13] T. Smith and S. A. Friedberg, *Phys. Rev.*, 1968, **176**, 660.

Calculations from equation (4) with $S = 2$, $g = 2.00$, and varying J generally reproduce the trend of the data well but the predicted maxima are too high. Since there is no reason to suppose $g = 2.00$ to be correct, if this parameter is also allowed to vary a better fit to the experimental data is obtained. Representative curves are shown in Figure 1. The range of parameters for which agreement is good is $J = -25.0$ to -26.5 $\boldsymbol{k}$ and $g = 1.94$ to 1.98, confirming the antiferromagnetic nature of the exchange.

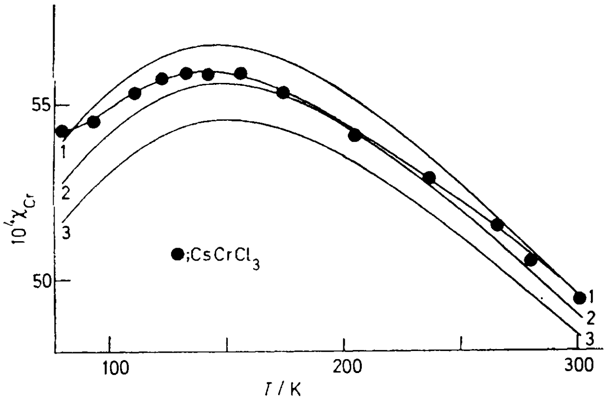

FIGURE 1 Fisher's expression for the classical Heisenberg chain, fitted to the CsCrCl$_3$ data, assuming $S = 2$ and $g = 1.96$. Susceptibilities are in c.g.s. units. Curve 1, $J = 25.5$ $\boldsymbol{k}$; curve 2, $J = 26.0$ $\boldsymbol{k}$; curve 3, $J = 26.5$ $\boldsymbol{k}$

(ii) KCrCl$_3$. The structure of this compound is not known, but is not the same[5] as that of CsCrCl$_3$. Samples of this compound prepared by either of the methods outlined above had essentially the same magnetic properties both as regards the values of $\mu_{\text{eff.}}$ and the temperature dependence of their susceptibilities. Any impurities resulting from the KCl/CrCl$_3$/Cr preparation do not make significant contributions to the magnetic properties.

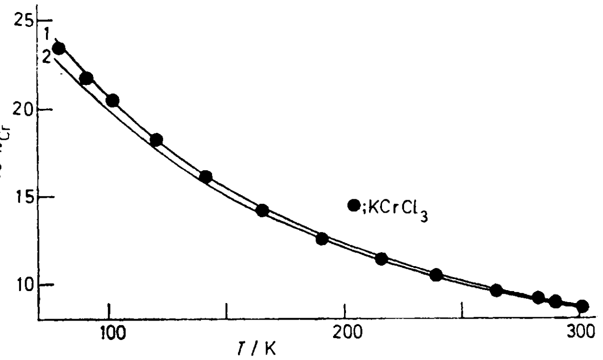

FIGURE 2 Fisher's expression for the classical Heisenberg chain, fitted to data on KCrCl$_3$, assuming $S = 2$ and $g = 1.98$. Susceptibilities are in c.g.s. units. Curve 1, $J = -4.5$ $\boldsymbol{k}$; curve 2, $J = -5.0$ $\boldsymbol{k}$

The value of $\mu_{\text{eff.}}$ (4.56 B.M. at 290 K) is again less than the spin-only value. The susceptibility obeys a Curie–Weiss law over the temperature range studied with $\theta = 45$ K. Thus, unlike the caesium analogue, there is no maximum in the susceptibility and any antiferromagnetic interaction is weaker, as expected from the smaller θ-value and larger $\mu_{\text{eff.}}$. It is reasonable to suggest that the compound is antiferromagnetic since a non-interacting d^4 system will obey a Curie law, the ground term in O_h symmetry being ^5E_g. By making the further reasonable assumption that the structure is such that the magnetic interaction is one dimensional, the treatment outlined above reproduces our data for $S = 2$, J between -5.0 and -4.0 $\boldsymbol{k}$, and g between 1.98 and 1.96. These data are shown in Figure 2 for $g = 1.98$. A maximum in the susceptibility is predicted between 25 and 30 K, outside the range of temperatures available to us. As expected the values of J are much less than those deduced for CsCrCl$_3$.

(iii) Cs$_2$CrCl$_4$. This compound has the K$_2$NiF$_4$ structure.[5,10] The magnetic interactions are therefore two dimensional since the structure is composed of layers of octahedra sharing corners. Ijdo[10] has reported that Cs$_2$CrCl$_4$ obeys a Curie–Weiss law with $\theta = -108$ K, while one report gives a Curie temperature[14] of 70 K and $\theta = 90$ and another[11] gives $\mu_{\text{eff.}} = 5.78$ and 11.6 B.M. at 300 and 80 K respectively. Not surprisingly, attempts to fit this latter data to an interacting dimer model are unsuccessful.

A preliminary account of our studies of the magnetic properties of Cs$_2$CrCl$_4$ and K$_2$CrCl$_4$ has recently been published.[15] We find that $\mu_{\text{eff.}}$ is 5.52 B.M. at 290 K, and a Curie–Weiss law is obeyed above ~120 K with $\theta = 77$ K. Thus although most compounds with the K$_2$NiF$_4$ structure are antiferromagnets, Cs$_2$CrCl$_4$ behaves as a ferromagnet. Below 120 K, the inverse susceptibility deviates upwards from the Curie–Weiss law plot. Most theories of magnetism predict that

$$1/\chi \propto (T - T_c)^{\gamma}$$

where T_c is the Curie temperature. Well above T_c, $\gamma \rightarrow 1$, *i.e.* a Curie–Weiss law is obeyed. Stanley and Kaplan[16] have shown that for some two-dimensional systems as $T \rightarrow T_c$

$$\gamma^{(2)}(S) = 2.5 + 0.67/S^2 \text{ if } S > \tfrac{1}{2}$$

If this is the case, χ_{Cr}^{-1} should vary in exactly the manner which we observe. Rushbrooke and Wood[17] have calculated susceptibilities out to sixth-order terms for arbitrary spin and a wide range of lattice structures. The expression relevant to Cs$_2$CrCl$_4$ is

$$\frac{Ng^2\beta^2}{\chi J}\cdot\frac{1}{\theta} = \frac{3}{S(S+1)}\sum_{n=0}^{\infty}\frac{b_n}{\theta^n} \qquad (5)$$

where $\theta = \boldsymbol{k}T/J$ and the coefficients b_n are given in general forms applicable to any value of S and any

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[14] P. F. Bongers, personal communication.

[15] D. H. Leech and D. J. Machin, *J.C.S. Chem. Comm.*, 1974, 866.

[16] H. E. Stanley and T. A. Kaplan, *J. Appl. Phys.*, 1967, **38**, 975.

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

lattice. This approach has been applied by Lines [18] to plane square antiferromagnetic systems, and rearranges (5) to

$$\frac{Ng^2\beta^2}{\chi J} = 3\theta + \sum_{n=1}^{\infty} \frac{C_n}{\theta^{n-1}} \qquad (6)$$

where θ is now $kT/JS(S+1)$ and coefficients C_1 to C_6 are listed for different values of S. We have applied Lines approach to Cs_2CrCl_4 using the values of C_n listed for $S = 2$ and replacing C_n by $(-1)^n C_n$ since ours is a ferromagnetic problem; however, no single value of J reproduces the data over the whole temperature range. The fit can be improved by adopting the procedure of Rushbrooke and Wood who argue that if the observed value of the saturation moment is less than the spin only value, the value of S in equation (5) [and (6)] should be scaled by the ratio $\mu_{obs}/\mu_{s.o.}$. The saturation magnetisation of Cs_2CrCl_4 corresponds to 3.8 magnetic electrons.[14] Scaling equation (6) by the factor 3.8/4.0 gives the somewhat more satisfactory fit to the observed data as is shown in Figure 3. The range of J in which the fit to the experimental data is acceptable is 5.25 to 6.00 k.

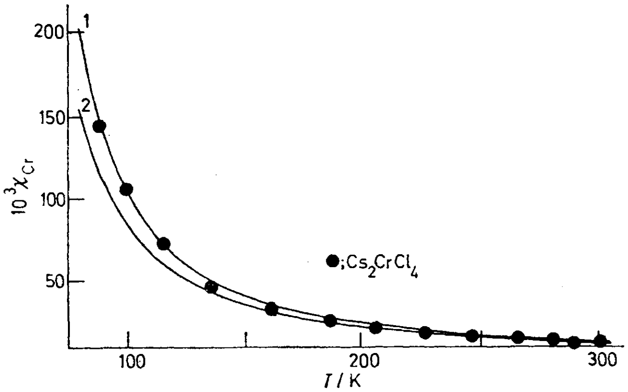

FIGURE 3 Rushbrooke and Wood's series expansion for the $S = 2$ Heisenberg plane square net, scaled according to $n_B = 3.8\beta$ and fitted to the Cs_2CrCl_4 data. Susceptibilities are in c.g.s. units. Curve 1, $J = 6.00\ k$; curve 2, $J = 5.25\ k$

It is of some interest to consider methods for predicting transition temperatures in these systems. The two-dimensional isotropic Heisenberg system is not ordered except at zero temperature. Thus, if the transition predicted by Stanley and Kaplan [19] is real it would have to be to a new type of low-temperature phase which would have long range correlations but no true long-range order. The new transition temperature, $T_c^{(2)}$ would then be

$$kT_c^{(2)} = (J/5)\,(Z-1)\,[2S(S+1)-1] \qquad (7)$$

for $S > \frac{1}{2}$. Z Is the co-ordination number of the lattice. This estimate has since been revised downwards.[20] However, Lines [21] has shown that this Heisenberg model is very sensitive to anisotropy and/or interlayer exchange forces, even very small perturbations raising the value of T_c from 0 K to

$$kT_c = (2J/3)2S(S+1)$$

and in this case $T_c^{(2)}$ will only be observed if $T_c < T_c^{(2)}$.

In spite of the above, the Néel temperatures of a number of plane square antiferromagnets are rather well reproduced [22] by equation (7). Applying this to Cs_2CrCl_4, a value of J of 5.6 k predicts a transition temperature of only 37 K, whereas Bongers [14] reports $T_c = 70$ K and Day *et al.*[23] found that $T_c = 58$ K. These are somewhat closer to the molecular field value $\theta = 77$ K. Neutron diffraction studies [24] show that this is a transition to a ferromagnetic phase, and also that only small amounts of $CsCrCl_3$ are present in the incongruently melting material.

(iv) K_2CrCl_4. Preparations by both methods had essentially the same magnetic properties. The crystal structure is close [5,25] to that of K_2NiF_4 so that the treatment applied to Cs_2CrCl_4 is appropriate. For our preparation $\mu_{eff.}$ is 5.55 B.M. at 291 K and a Curie–Weiss law is obeyed down to *ca.* 100 K with $\theta = -68$ K. Previous measurements gave a lower $\mu_{eff.}$ (5.34 B.M.) on material obtained by dehydrating the dihydrate.[11] Bongers [14] reports $\theta = -84$ K. Our data are reproduced satisfactorily by Rushbrooke and Wood's treatment,[17] see Figure 4, the range of values of J being 4.75 to 5.25 k. These data have also been compared with the results of Stanley [20] who has calculated the coefficients a_l for $l = 1$—9 in the following expression for the zero field susceptibility of an $S = \infty$ Heisenberg system:

$$\chi/\chi\text{Curie} = 1 + \sum_{l=1}^{\infty} a_l\,(J/kT)^l \qquad (8)$$

Our data are rather well reproduced by the single value $J = 4.83\ k$ (see Figure 4). This falls within the range predicted by the Rushbrooke and Wood treatment. No significance attaches to the unique value of J obtained since, although Stanley's calculations are to higher order, the approximation of infinite spin is not satisfied by $S = 2$.

(b) *Chromium*(III) *Compounds*.—We have only studied K_3CrCl_3 and $K_3Cr_2Cl_9$. Both compounds are essentially octahedral, thus in non-interacting systems $\mu_{eff.}$ for the $^3A_{2g}$ ground term will be the spin-only value and a Curie law will be obeyed.[26]

(i) K_2CrCl_6. Our results are essentially the same as those of Hatfield,[27] $\mu_{eff.}$ being 3.90 B.M. at 291 K, the susceptibility following a Curie–Weiss law with a very

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

[19] H. E. Stanley and T. A. Kaplan, *Phys. Rev. Letters*, 1966, **17**, 913.

[20] H. E. Stanley, *Phys. Rev.*, 1967, **158**, 546.

[21] M. E. Lines, *Phys. Rev.*, 1967, **164**, 736.

[22] R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, *Phys. Rev.* (*B*), 1970, **1**, 2211.

[23] A. K. Gregson, P. Day, D. H. Leech, M. Fair, and W. E. Gardner; quoted in reference 24.

[24] M. T. Hutchings, A. K. Gregson, P. Day, and D. H. Leech, *Solid State Comm.*, 1974, **15**, 313.

[25] T. S. Cameron, quoted in ref. 2.

[26] F. E. Mabbs and D. J. Machin, ' Magnetism and Transition Metal Complexes,' Chapman and Hall, London, 1973.

[27] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Amer. Chem. Soc.*, 1963, **85**, 265.

small $\theta = 2$ K; details are in Table 3. It is clearly unlikely that there will be magnetic interactions in this compound except in long range Cr–Cl · · · Cl–Cr chains.

(ii) $K_3Cr_2Cl_9$. This compound is isostructural [28] with $Cs_3Cr_2Cl_9$ and thus contains dimeric units formed from two octahedra sharing a face. The structure is interesting in that the chromium atoms are displaced from the centres of the octahedra, increasing the Cr–Cr separation to 3.12 Å, in contrast with the tungsten analogue where the metal atoms move closer together to 2.41 Å compared to the W–W separation of 2.74 Å in the metal. The exchange interactions in the dimer are thus of considerable interest.

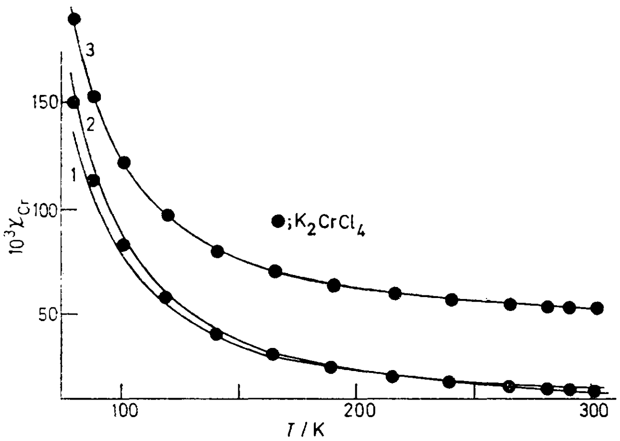

FIGURE 4 Data on K_2CrCl_4 fitted to Rushbrooke and Wood's series expansion for the $S = 2$ Heisenberg plane square net (curves 1 and 2), and to Stanley's series expansion for the classical Heisenberg plane square net scaled according to $S = 2$, and $J = 4.83$ $\boldsymbol{k}$ (curve 3). Susceptibilities are in c.g.s. units. Curve 3 is displaced upwards by 50 units. Curve 1, $J = 4.75$ $\boldsymbol{k}$; curve 2, $J = 5.25$ $\boldsymbol{k}$; curve 3, $J = 4.83$ $\boldsymbol{k}$

Our measurements on $K_3Cr_2Cl_9$ which are detailed in Table 3 show that $\mu_{eff.}$ is 3.59 B.M. at 291 K. A Curie-Weiss law is obeyed with only small deviations below 100 K. The value of θ is 89 K. Thus there are substantial interactions despite the large Cr–Cr distance. We disagree with a previous report [28] in that $\mu_{eff.}$ is given as 3.77 B.M. at 300 K, but agree on the value of θ. Wentworth's value for $\mu_{eff.}$ seems rather high when θ is so large. We have not attempted to fit this data to calculations for a dimer model, but this has been done [29] for the tetraethyl ammonium salt for which $J = -5$ $\boldsymbol{k}$, the value of θ being 12 K. Wentworth [28] reports $J = -4$ cm^{-1} for the tetra-n-butylammonium salt. There are considerable differences between the magnetic properties of the salts $M_3Cr_2Cl_9$. These are summarised in Table 4. Wentworth ascribes these changes to variation in long-range ordering in the lattice, brought about by changes in cation size *e.g.* in the isostructural series M = K, Rb, and Cs. This seems unlikely to us since there is still significant interaction in the alkylammonium salts. The cause is more probably changes in the ground state of the chromium atoms resulting from second-order perturbations of the crystal field by the cations. Studies of this effect might be rewarding in terms of our understanding of interactions in dimers.

TABLE 3

Magnetic susceptibilities (in c.g.s. units) of K_3CrCl_6 and $K_3Cr_2Cl_9$.

K_3CrCl_6		$K_3Cr_2Cl_9$	
T/K	$10^6\chi_{Cr}$	T/K	$10^6\chi_{Cr}$
304.0	6 260	302.8	5 360
296.0	6 420	288.3	5 590
287.3	6 630	279.3	5 720
278.0	6 810	265.0	5 940
264.5	7 090	240.0	6 390
239.5	7 780	214.3	6 900
214.8	8 650	189.8	7 520
186.8	9 900	165.0	8 290
161.8	11 500	140.8	9 220
140.0	13 300	119.8	10 100
115.8	16 100	103.3	10 900
95.0	19 300	90.0	11 500
85.0	21 300	78.5	12 100

TABLE 4

Magnetic properties of compounds $M_3Cr_2Cl_9$

Compound	$\mu_{eff.}$/B.M.	θ/K
$K_3Cr_2Cl_9$	3.59	89 [a]
$Rb_3Cr_2Cl_9$	3.77	61 [b]
$Cs_3Cr_2Cl_9$	3.76	38 [b]
$Et_4N_3Cr_2Cl_9$	3.94	12 [c]
$Bu_4N_3Cr_2Cl_9$	3.91	12 [b]

[a] This work, ref. 28 reports $\mu_{eff.} = 3.77$ B.M. [b] Ref. 28. [c] Ref. 29.

Electronic Spectra.—Since the completion of this work detailed investigations of the spectra of single crystals of $CsCrCl_3$ and of K_2CrCl_4 have been published; [3,2] our results will, therefore, not be discussed in detail. Our measurements were made on powdered samples by the diffuse-reflectance method.

In an octahedral crystal field there is only one spin-allowed transition, $^5E_g \rightarrow {}^5T_{2g}$, but a large number of possible transitions to triplet and singlet levels.

$CsCrCl_3$. The spectrum of a single crystal has been studied by Stucky *et al.*[3] Our diffuse-reflectance spectrum is poorly resolved in the visible region so that we are unable to confirm the presence of the 19 000—22 000 cm^{-1} band assigned to a simultaneous excitation of a magnetically coupled pair of atoms. Otherwise we observe an exactly identical spectrum.

Cs_2CrCl_4. A detailed analysis of the spectrum of K_2CrCl_4 has been published by Day, Gregson, and Leech.[2] It consists of three broad bands in the region 8 000—14 000 cm^{-1}, assigned to transitions to low symmetry components of ^5D, and two sharp bands at 15 900 and 18 700 cm^{-1} which are transitions to triplet states. The intensity of these spin-forbidden bands is enhanced as a result of magnetic exchange.[30] These compounds are of special interest because the visible

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[28] R. Saillant and R. D. Wentworth, *Inorg. Chem.*, 1968, **7**, 1606.

[29] A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 1961, 396.

[30] V. V. Druzhinin, R. V. Pisarev, and G. A. Karamipherka, *Soviet Phys., Solid State*, 1971, **12**, 1789.

region is essentially clear, apart from these two sharp bands.

The diffuse-reflectance spectrum of the caesium salt is almost identical to that of the potassium salt, consisting of a broad unresolved band centred at 11 000 cm^{-1} with two sharp bands at 15 700 and 18 500 cm^{-1}. The latter band has small shoulders at *ca.* 18 100 and 18 900 cm^{-1} which are not observed in the potassium salt. This compound is thus also of technical interest although it will be much more difficult to obtain single crystals because it melts incongruently. The spin-forbidden bands of Cs_2CrCl_4 are more intense than in $CsCrCl_3$ as would be expected if this arises from magnetic exchange, since these effects are greater in Cs_2CrCl_4.

K_3CrCl_6 *and* $K_3Cr_2Cl_9$. The spectra of $CrCl_6^{3-}$ species are well known and we observe the expected bands. In the case of $K_3Cr_2Cl_9$, we observe two bands: at 13 100 cm^{-1} ($^4A_2 \longrightarrow {}^4T_2$) and 13 400 cm^{-1} [$^4A_2 \longrightarrow {}^4T_1$ (F)]. These are rather higher energies than those previously observed for other salts of the $[Cr_2Cl_9]^{3-}$ ion (see *e.g.* ref. 28), but are still lower than the energies of bands observed in K_3CrCl_6.

EXPERIMENTAL

All compounds were prepared in silica apparatus using methods described previously (see ref. 1 and references therein). Analyses were by conventional techniques.

Magnetic susceptibilities were measured using conventional Guoy apparatus calibrated with nickel chloride solution. The Curie–Weiss law was used in the form $\chi = C/(T + \theta)$ and magnetic moments were calculated from the expression $\mu_{eff.} = 2.828(\chi_{Cr}.T)^{\frac{1}{2}}$ B.M. Susceptibilities are in c.g.s. units.

Diffuse-reflectance spectra were recorded with a Beckman DK2A spectrometer using MgO as reference reflector. Samples were prepared in a dry box and protected from the air with silica cover-slips sealed with grease.

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