Synthesis and Magnetism of Mixed Valency [N(n-C_4H_9)$_4$ or P(C_6H_5)$_4$]$Cr^{II}Cr^{III}(C_2O_4)_3$

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Mixed valency compounds $ACr^{II}Cr^{III}(C_2O_4)_3$ [A = N(n-C_4H_9)$_4$, P(C_6H_5)$_4$] have been synthesised and characterised structurally and magnetically, the structures consisting of hexagonal layers of Cr bridged by $C_2O_4^{2-}$; although short range antiferromagnetic correlations are observed below 100 K no transition to a long range ordered state is observed above 2 K.

The last few years have seen an intensive search for novel magnetic materials built from molecular units consisting of transition metal coordination complexes.[1] In the quest for higher ordering temperatures a dramatic recent development was the synthesis of mixed valency $Cr^{II}Cr^{III}$ hexacyano-compounds with T_c's much higher than those obtained with other combinations of M^{II} and M^{III}, indeed approaching room temperature.[2] Such systems are reminiscent of the ferromagnetic ternary Cr^{II} halides with the layer perovskite structure first prepared and studied by us in the 1970s.[3,4] In parallel further bimetallic $M^{II}M^{III}$ ferro- and ferri-magnets have been reported, in which the ambidentate ligand bridging between the metal ions is oxalate.[5–8] We have therefore synthesised and characterised two compounds $ACr^{II}Cr^{III}(C_2O_4)_3$ and examined their bulk magnetic properties. In startling contrast to the hexacyano-compound, we found that in neither oxalate is there any transition to a long range ordered state above 2 K although deviation from Curie–Weiss behaviour is observed below 100 K.

The compounds were prepared from stoichiometric quantities of $K_3Cr(C_2O_4)_3{\cdot}3H_2O$, $CrCl_2$ and either N(n-C_4H_9)$_4$Br or P(C_6H_5)$_4$Br following two procedures. In the case of the N(n-C_4H_9)$_4$ salt, Cr^{III} and Cr^{II} solutions were prepared separately in oxygen-free water before mixing and adding an aqueous solution of the organic template cation. The resulting grey green precipitate was allowed to settle, washed with deoxygenated water, filtered under N_2 and dried. To prepare the P(C_6H_5)$_4$ salt the three reactants were weighed dry into a Youngs Schlenk tube in a glove box and sufficient deoxygenated water was added to dissolve them completely on shaking. The light green precipitate that formed over 30 min was filtered under N_2, washed with water and acetone and dried under N_2. Elemental analyses of both salts agree with the formulae proposed.

X-Ray powder diffraction profiles were recorded on a Siemens D500 diffractometer (Cu-Kα radiation), operating in reflection geometry. The samples were mounted under Mylar sheets in a N_2-filled glove box. All the observed diffraction peaks from both samples could be indexed on a hexagonal cell of dimensions very similar to those found earlier in other $AM^{II}M^{III}(C_2O_4)_3$ compounds with the same A. Thus for the N(n-C_4H_9)$_4$ compound we find a_0 = 9.74(1), c_0 = 54.2(2) Å from refinement of 11 major reflections. This is to be compared with a_0 = 9.414(5), c_0 = 53.662(6) Å found for the corresponding $Mn^{II}Cr^{III}$ compound by single crystal diffraction.[7] Similarly, for the P(C_6H_5)$_4$ compound a_0 = 9.70(3), c_0 = 57.5(3) Å from 8 major reflections, compared with a_0 = 9.391(3), c_0 = 57.28(2) Å from the single crystal diffraction of the $Mn^{II}Cr^{III}$ analogue.[8] The structures of both $Mn^{II}Cr^{III}$ compounds consist of hexagonal honeycomb sheets of alternating Mn^{II} and Cr^{III} bridged by bidentate $C_2O_4^{2-}$ in such a way that each metal ion has trigonally distorted octahedral coordination, while the organic cations occupy sites between the sheets. The similarity between the cell constants of the $Cr^{II}Cr^{III}$ and $Mn^{II}Cr^{III}$ compounds confirms that the former have closely related layer structures. It is interesting that for both A, the cell constants of the $Cr^{II}Cr^{III}$ compound are slightly larger than $Mn^{II}Cr^{III}$.

Magnetic susceptibility measurements were made in fields of 10 and 50 mT from 300–2 K using a Quantum Design MPMS7 SQUID magnetometer and corrected for core diamagnetism and that for the sample capsule. Above 150 K the Curie–Weiss law was well obeyed (Fig. 1), the Curie constants C being 5.7(5) and 5.5(1) emu K mol^{-1} for A = N(n-C_4H_9)$_4$ and P(C_6H_5)$_4$ respectively. The ground state of six-coordinate Cr^{III} (d^3) is orbitally non-degenerate but six coordinate high spin Cr^{II} (d^4) is expected to be subject to a Jahn–Teller distortion. If we assume that such a distortion is present and the degeneracy is thereby lifted, C is calculated as 4.875 emu K mol^{-1} assuming g = 2, in good agreement with the observed value, allowing for an orbital contribution from Cr^{II} with a ^5E ground state. The Weiss constants fitted to the high temperature (300–150 K) susceptibility data are −12.7(5) K and −7.0(5) K for the N(n-C_4H_9)$_4$ and P(C_6H_5)$_4$ salts respectively, suggesting antiferromagnetic near neighbour exchange. Fig. 2 shows the product χT *vs.* temperature for both compounds. Progressive negative deviation from Curie–Weiss behaviour is clearly visible below about

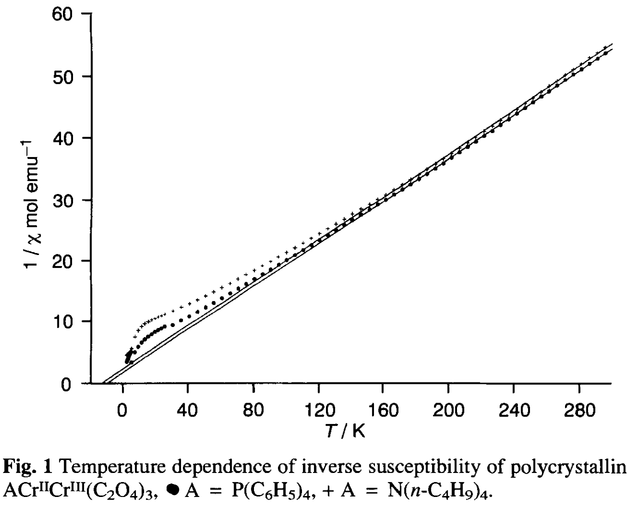

Fig. 1 Temperature dependence of inverse susceptibility of polycrystalline $ACr^{II}Cr^{III}(C_2O_4)_3$, ● A = P($C_6H_5$)$_4$, + A = N($n$-$C_4H_9$)$_4$.

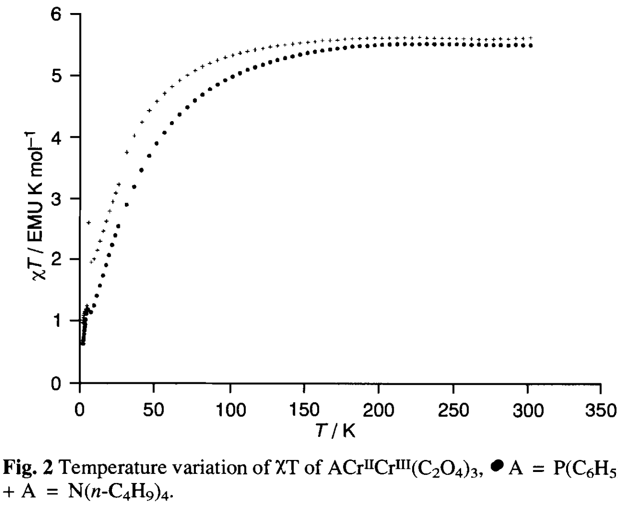

Fig. 2 Temperature variation of χT of $ACr^{II}Cr^{III}(C_2O_4)_3$, ● A = P($C_6H_5$)$_4$, + A = N($n$-$C_4H_9$)$_4$.

150 K again indicating antiferromagnetic short range spin correlations. However, χT continues to fall monotonically down to 2 K with only a small maximum in both compounds between 2 and 4 K. Furthermore, the magnetisation isotherm at 5 K only deviates slightly from linearity above 2 T.

The bulk magnetic behaviour of $ACr^{II}Cr^{II}(C_2O_4)_3$ contrasts strongly with that of $Cr_3{}^{II}[Cr^{III}(CN)_6]_2 10H_2O$,[2] which orders three-dimensionally at 240 K, the highest temperature recorded till now for any magnetic material in which the exchange interaction is propagated by a polyatomic ligand. Given that the magnetic ions, oxidation states and coordination numbers are the same, the difference in T_c is striking. Both in the cyanides and the oxalates the near neighbour exchange is antiferromagnetic, but the lattice connectivity is different: in the former, three-dimensional near cubic and in the latter, two-dimensional hexagonal. Further, the Jahn–Teller distortion around the Cr^{II} in the cyanide series is tetragonal while in the oxalates the structure requires that it be trigonal. In neither series has cooperative Jahn–Teller ordering yet been detected so in both the effect (if any) of structural disorder on the magnetic properties remains to be determined. For that, single crystals will be required.

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