Synthesis and magnetism of chromium(II) methylphosphonate, $\mathrm{Cr^{II}(MePO_3)\cdot H_2O}$: a new weak ferromagnet

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A new chromium(II) phosphonate, $\mathrm{Cr^{II}(MePO_3)\cdot H_2O}$, is prepared and characterised; magnetic measurements in the temperature range 100–300 K show a typical Curie–Weiss behaviour with a Curie constant of 2.90(5) emu K mol^{-1} and a negative Weiss constant θ of −226(6) K; the thermal variation of the magnetic susceptibility below 60 K depends upon the cooling mode (z.f.c. = zero-field cooled and f.c. = field cooled); the compound is a canted antiferromagnet with the ordering temperature T_N at 35.8(3) K.

Phosphonate salts of transition-metal ions, $\mathrm{M^{II}(RPO_3)\cdot H_2O}$[1] (M = divalent metal ion, R = alkyl) are interesting materials because they can be used as ionic exchangers,[2] catalysts[3] and hosts in intercalation compounds.[4,5] They crystallise mainly in a layered structure, composed of metal ions and the phosphonate oxygen atoms lying in puckered sheets. The pendent organic R groups lie in the interlamellar space, and two organic layers having van der Waals contacts, are interspersed with the inorganic layers. The bonding requirements of the metal ion determine the atomic arrangement within these layers. Manganese(II) and iron(II) are six-coordinate,[6,7] with five coordination sites occupied by phosphonate oxygens and the sixth by a coordinated water oxygen. The copper(II) ion in $\mathrm{Cu^{II}(MePO_3)\cdot H_2O}$ is five-coordinate, and has a distorted tetragonal-pyramidal geometry. The base of the pyramid consists of three phosphonate oxygens and a coordinated water molecule. The three oxygens of the phosphonate groups are all bonded to Cu atoms with two of them bridging copper atoms.[8,9] Cooperative magnetism has been previously observed in transition-metal ion phosphonates. For example, $\mathrm{Cu^{II}(C_nH_{2n+1}PO_3)\cdot H_2O}$ are one-dimensional antiferromagnetic systems,[8,9] while $\mathrm{Mn^{II}(C_nH_{2n+1}PO_3)\cdot H_2O}$[6] and $\mathrm{Fe^{II}(EtPO_3)\cdot H_2O}$[7] are weak ferromagnets but, as yet, no true ferromagnets have been obtained. With the aim of finding new insulators which might order ferromagnetically,[10] we have synthesised and studied the magnetic properties of a new chromium(II) phosphonate compound, $\mathrm{Cr^{II}(MePO_3)\cdot H_2O}$.

All reactions were carried out under an inert atmosphere using usual Schlenck techniques. Water for HPLC was purged with N_2 prior to use. $\mathrm{Cr^{II}(MePO_3)\cdot H_2O}$ was prepared by mixing filtered aqueous solutions of methylphosphonic acid and $\mathrm{CrCl_2}$ in the presence of urea. The resulting blue solution was kept at 70 °C in an oil bath for a few days. The light-blue microcrystalline precipitate that formed was filtered off under nitrogen, washed several times with degassed water and then dried under vacuum; the compound slowly decomposes in air. Thermogravimetric analysis (TGA) shows a two-stage loss, with the first step at 145 °C (5.9%) and the second at 204 °C (8.9%), representing the loss of water. This indicates the water content in the formula unit corresponds approximately to one molecule and that this molecule is coordinated to the chromium atoms in two different sites. The IR spectrum is similar to that of $\mathrm{Cu^{II}(MePO_3)\cdot H_2O}$[4c] and is shown in Fig. 1. It features a broad and intense band centred at *ca.* 3300 cm^{-1} typical of coordinated water, as well as bands at 1600 and 800 cm^{-1} and four bands due to $\mathrm{PO_3}$ group vibrations in the range 1200–970 cm^{-1}. Elemental analyses and the IR spectrum are consistent with the proposed formula.† The diffuse reflectance electronic spectrum displays a very broad band with two maxima at 11300 and at 15550 cm^{-1}, a shoulder at 29600 cm^{-1} and an intense peak at 39060 cm^{-1}. All the observed X-ray powder diffraction peaks could be indexed on a hexagonal unit cell of dimensions similar to those observed in a recently reported β-$\mathrm{Cu(MePO_3)\cdot H_2O}$ phase.[8] The latter crystallises in the rhombohedral space group $R\bar{3}$, in an unusual tubular zeolite-like structure. Thus, we find for $\mathrm{Cr^{II}(MePO_3)\cdot H_2O}$ $a = b = 16.3 \pm 0.4$ Å, $c = 7.2 \pm 0.5$ Å and $\gamma = 120°$.‡ Static magnetic susceptibility measurements were made on two samples of different preparations and in fields of 10 and 50 mT from 5 to 300 K by using a Quantum Design MPMS5 SQUID magnetometer and the data were corrected for the core diamagnetism. The microcrystalline sample was zero-field cooled (z.f.c.) to 5 K and the magnetization measured on heating the sample to room temperature in an applied field of 50 mT. The temperature dependence of the inverse of the z.f.c. molar magnetic susceptibility is shown in Fig. 2. Above 100 K the plot is linear, the Curie constant C being 2.89(5) emu K mol^{-1}, corresponding to an effective magnetic moment of 4.82 μ_B and consistent with the presence of $\mathrm{Cr^{II}}$ in a d^4 high-spin configuration. The large negative value of Weiss constant $\theta = -226(6)$ K, as fitted to the high-temperature susceptibility data using the relation $\chi = N\mu_{eff}^2/3k_B(T - \theta)$, indicates strong antiferromagnetic near-neighbour exchange between the adjacent chromium(II) ions. Below 100 K the magnetic susceptibility increases until a peak at 34 K is observed [Fig. 3(*a*)]. This peak can be ascribed to a three-

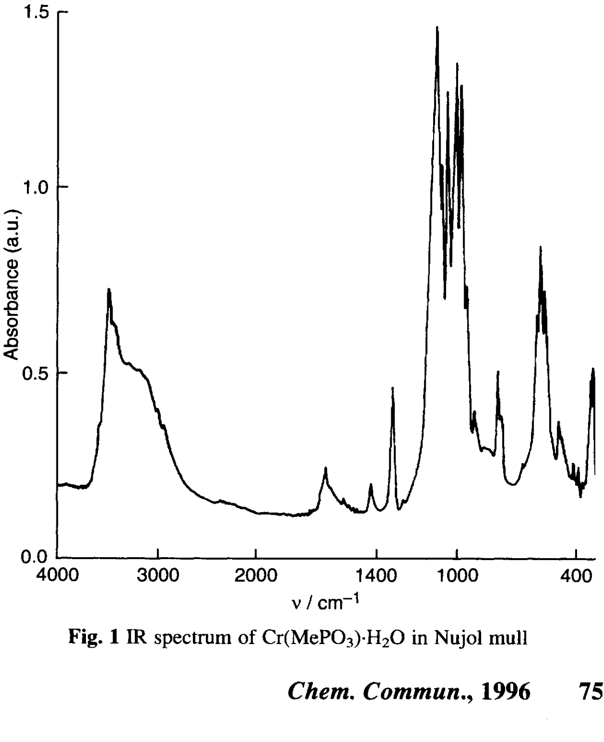

Fig. 1 IR spectrum of $\mathrm{Cr(MePO_3)\cdot H_2O}$ in Nujol mull

dimensional antiferromagnetic ordering. To obtain a better estimate of the critical temperature, T_N, the experiment was repeated in a lower applied field, *i.e.* 10 mT, and the temperature increased in steps of 0.3 K in the temperature range 25–45 K. The sharpness of the peak increases as well as the susceptibility values (χ_{max} = 2.96 emu mol^{-1}). The value of T_N was found to be 35.8(3) K and the width of the transition was 4 K.§ In a subsequent experiment, the sample heated in the paramagnetic region was field cooled, f.c., (under a field of 4 T) and a plot of χ *vs.* T in the temperature range 5–60 K measured at an applied field of 40 mT is shown in Fig. 3(*b*). A steady decrease of the susceptibility from the value at 5 K is observed. At lower temperatures a magnetic hysteresis is observed on comparing the two curves for the z.f.c. and f.c. modes. The isothermal magnetization at 5 K, well below T_N, performed on a z.f.c. sample increases slowly up to a threshold field, H_T, of 50 mT, where it rises and it reaches a maximum value of 1400 emu G mol^{-1} at 4 T. Hysteresis phenomena disappear at temperatures above T_N. At temperatures well above the critical temperature, *i.e.* at 80 K, the isothermal magnetization *vs.* field plot is linear, and the C and θ values obtained by the fit were found to be 2.90(5) emu K mol^{-1} and −226(5) K, thus confirming the high-spin d^4 electronic configuration for the metal ion. Attempts to grow single crystals of $Cr(MePO_3)_2{\cdot}H_2O$ are in progress.

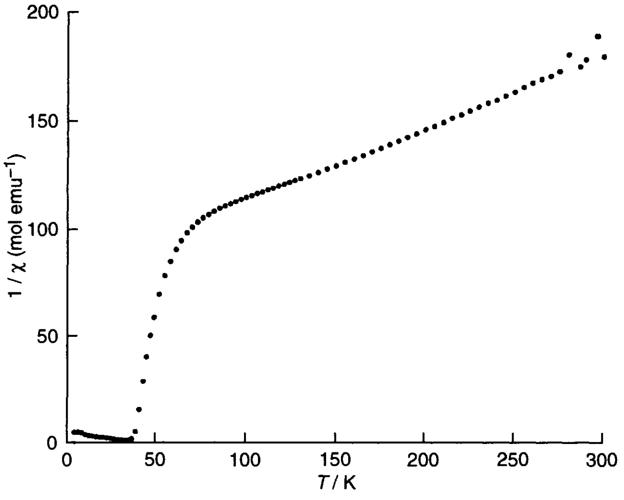

Fig. 2 1/χ *vs.* T plot for polycrystalline $Cr(MePO_3){\cdot}H_2O$

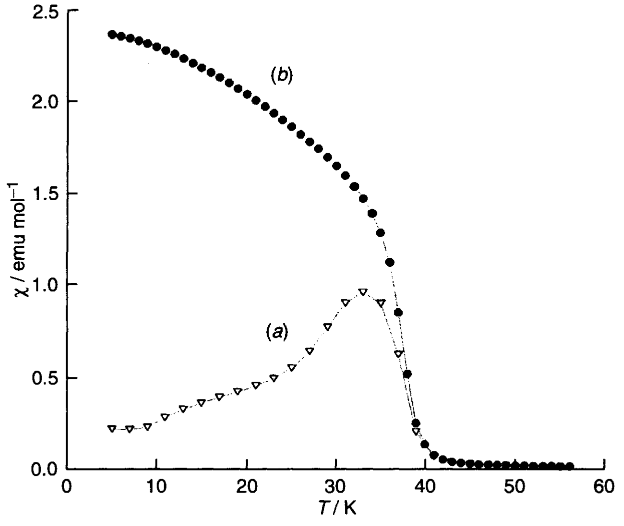

Fig. 3 Temperature dependence of (*a*) zero-field cooled and (*b*) field cooled susceptibility of $Cr(MePO_3){\cdot}H_2O$ in the temperature range 5–60 K

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Footnotes

† Elemental analyses were performed by Malissa and Reuter Gmbh, Lindlar, Germany on two different samples and the results were averaged. Oxygen analyses were not possible owing to the presence of Cr and P. Calc. for CH_5CrO_4P: C, 7.32; H, 3.07; P, 18.88; Cr, 31.70; Found: C, 6.22; H, 2.67; P, 17.23; Cr, 31.94. The Cr : P : C ratios are consistent with the formula proposed.

‡ X-Ray powder diffraction profiles were recorded on a Seifert XRD-3000 diffractometer, with a curved graphite-single crystal monochromator [λ(Cu-Kα) = 1.542 Å] and a position sensitive detector operating in constant scan mode of 0.5° min^{-1} over the range $3 < 2\theta < 80°$. The sample was mounted on a flat plate under a Mylar sheet in an N_2-filled dry box. The diffractometer zero point was determined from an external Si standard. The X-ray spectra were found to reproducible for the two samples studied, although the degree of crystallinity differed.

§ The width of the transition is estimated from the difference between the temperatures corresponding to 10 and 90% of the value of χ_{max} taken above and below T_N, respectively.

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