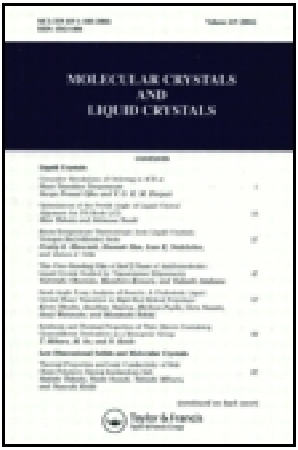

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Molecular Magnetism in Manganese Dicyanamide Extended Network Structures

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Molecular Magnetism in Manganese Dicyanamide Extended Network Structures

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Dicyanamide, dca$^-$ ($N(CN)_2^-$), forms an extended rutile-like single net in the binary complex, $Mn^{II}(dca)_2$, in which dca groups bridge the Mn^{II} ions via the nitrile and amide nitrogen atoms. A trihydrate, which forms in the synthesis, displays an unusual structure consisting of square channels, formed by sheets of $Mn(dca)_2(H_2O)_2$, into which are inserted linear chains of $Mn(dca)_2(H_2O)_2$. Clathrated water molecules form H-bonded networks with the coordinated water and dca species. This trihydrate displays weak antiferromagnetic coupling between the high-spin Mn(II) ions without long-range ordering. $Mn(dca)_2$also displays weak antiferromagnetic coupling, but with an unusual magnetic phase transition being noted at $T_c = 16K$, particularly in low applied-fields. Dehydration of $Mn(dca)_2{\bullet}3H_2O$ yields $Mn(dca)_2$ with the same magnetic transition at 16K.

Keywords: molecular magnetism; dicyanamide; manganese; crystal structure; coordination polymer

INTRODUCTION

Molecule-based magnetic materials normally, but not always, require covalent-bridging in three dimensions between different spin-centres, such as different d-block metal ions, different redox states of the same ion or metal-ion and organic radical, in order to display spontaneous magnetization.[1-2] Recently, we have communicated new examples of homometallic ferromagnets containing dicyanamide bridging moieties in complexes of type $M(dca)_2$, where $dca^- = N(CN)_2^-$ and $M = Co^{II}$ ($T_c = 9K$) and Ni^{II} ($T_c = 20K$).[3] These metal complexes are isostructural with the crystallographically characterized $Cu^{II}(dca)_2$ complex, which is very weakly antiferromagnetically coupled and not ordered. A rutile-like single net structure is adopted which involves bridging via both the amide N donor and the nitrile N donor atoms. The precise origin of ferromagnetism was not obvious and so we are extending the range of the M^{II} ion in order to make broader comparisons between d^n configurations. Here we describe the structural and magnetic properties of $Mn^{II}(dca)_2$ and of a hydrated species, $Mn^{II}(dca)_2.3H_2O$.

PREPARATIONS, CHARACTERIZATION AND CRYSTALLOGRAPHY

The complexes $Mn(dca)_2$ and $Mn(dca)_2.3H_2O$ both crystallize out of concentrated aqueous solutions containing predissolved $Mn(ClO_4)_2.6H_2O$ and sodium dicyanamide mixed in a 1:2 mole ratio. The colourless crystals can be readily identified by their morphologies, $Mn(dca)_2$ being triangular prismatic and $Mn(dca)_2.3H_2O$ cubic in appearance. The crystals were separated by hand for physical measurements and checked by powder X-ray diffraction and/or unit cell determination. It is possible to obtain solely $Mn(dca)_2.3H_2O$ by redissolving the mixture of crystals and allowing slow evaporation. The method used to get $Mn(dca)_2$ alone is to mix solid $Mn(ClO_4).6H_2O$ and solid Na(dca), then add the minimum of water. The product precipitates rapidly with heating and is washed free of any starting material with ethanol and checked by powder diffraction. The two compounds were identified by I.R. spectroscopy, their ν (C≡N) and ν (C–N) bands being in different positions. Microanalytical data were satisfactory in both cases. $Mn(dca)_2.3H_2O$ was carefully dehydrated by heating *in vacuo* at 100°C for 5 hr.

Crystal structures at 123K were determined using an Enraf KappaCCD area-detector diffractometer: $Mn(dca)_2$: Orthorhombic, *Pnnm* (No. 58), a = 7.2723(3) Å, b = 6.1126(3) Å, c = 7.5563(4) Å, U = 335.90(3) Å^3, $Z = 2$, $R_1 = 0.0249$ ($I_o > 2\sigma(I_o)$), $wR_2 = 0.0645$ (all data); $Mn(dca)_2.3H_2O$: Monoclinic, $P2_1/n$ (No. 14), a = 7.3165(2) Å, b = 11.6229(5) Å, c = 11.3590(5) Å, β = 103.241(5)°, U = 940.28(6) Å^3, $Z = 4$, $R_1 = 0.0313$ ($I_o > 2\sigma(I_o)$), $wR_2 = 0.0992$ (all data).

Magnetic measurements were made using a Quantum Design MPMS 5 Squid magnetometer.

DESCRIPTION OF CRYSTAL STRUCTURES

The crystal structure of $Mn(dca)_2$ is composed of a polymeric network (Figure 1). All metal atoms and all dca ligands are equivalent - in fact, there are only four crystallographically unique atoms (Mn, N1, C1 and N2). Each Mn cation is coordinated to six dca ligands, and each dca ligand is coordinated to three Mn cations, through both the nitrile nitrogens (Mn-N1 = 2.189(1) Å) and the amido nitrogens (Mn-N2 = 2.290(2) Å). The topology of the polymeric coordination network formed is that of rutile, with 6-connecting centres (metal atoms) and three connecting centres (dca ligands) in the ratio of 1:2. Rutile is becoming an increasingly important and prevalent 3,6-connected net in crystal engineering.[3-5]

The structure is isomorphous with the related compounds $M(dca)_2$, M = Co, Ni, Cu.[3] While the structure of $Cu(dca)_2$ shows appreciable Jahn-Teller distortion, the metal-nitrogen distances in $Mn(dca)_2$ are comparable. As with $Cu(dca)_2$,[3] there are considerable distortions in the $Mn(dca)_2$

network, possibly due to π-π interactions between pairs of dca ligands across the square channels (closest contacts being C1-C1 = 3.493 Å, N2-N2 = 3.670 Å).

The structure of $Mn(dca)_2.3H_2O$ is very different. and contains square-grid sheets of composition $Mn(dca)_2(H_2O)_2$. These sheets stack in a fashion that results in square channels running through the structure. These channels are occupied by polymeric linear chains which have an identical composition to the sheets (Figure 2).

Each of the octahedral Mn atoms in the sheets (all of which are equivalent) are coordinated to four dca ligands via the nitrile nitrogens only (Mn1-N1 = 2.202(2)Å, Mn1-N2 = 2.179(2)Å) and two *trans* water ligands (Mn1-O1 = 2.227(2)Å). Each dca (all of which are also equivalent within the sheets) consequently acts as a 2-connecting bridge, with each Mn connected via dca bridges to four separate Mn neighbours.

Within the chains all Mn atoms, all dca ligands and all water ligands are also equivalent. As for the sheets, the Mn atoms in the chains are coordinated to four dca ligands via the nitrile nitrogens only (Mn2-N4 = 2.184(2)Å, Mn2-N5 = 2.201(2)Å) and two *trans* water ligands (Mn2-O2 = 2.223(2)Å). While the dca ligands again act as 2-connecting bridges, this time the dca ligands connect each Mn atom to only *two* neighbouring Mn atoms, via two '$Mn(dca)_2Mn$' bridges. This is possible due to the bent nature of the dca bridge.

The structure also contains clathrated water molecules (O3), which participate in polymeric hydrogen-bonded networks (Figure 2). These networks (again, all of which are equivalent) have a sheet topology, and are found between any pairs of adjacent $Mn(dca)_2(H_2O)_2$ sheets. They involve the water molecules and dca ligands (via the uncoordinated amido nitrogens) belonging to both the chains and the sheets, and the intercalated water.

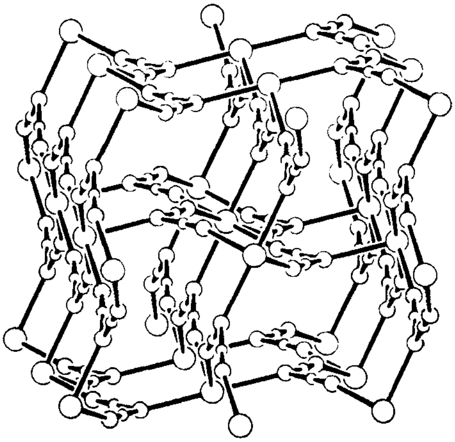

FIGURE 1 The rutile-like structure of $Mn(dca)_2$. The circles represent in order of decreasing size Mn, N and C.

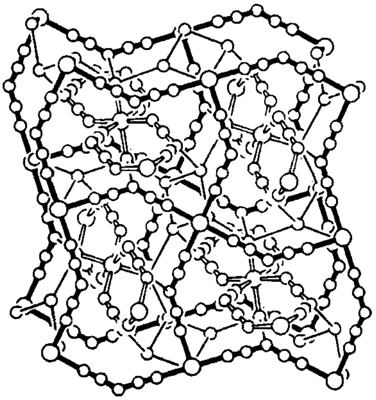

FIGURE 2 The structure of $Mn(dca)_2.3H_2O$, containing $Mn(dca)_2(H_2O)_2$ sheets penetrated by $Mn(dca)_2(H_2O)_2$ chains. Also shown is the sheet-like hydrogen-bonded network between adjacent $Mn(dca)_2(H_2O)_2$ sheets. For clarity, only the water molecules involved in the hydrogen-bonded network between the two $Mn(dca)_2(H_2O)_2$ sheets shown are included in the figure.

MAGNETISM

$Mn(dca)_2$

Two samples were studied and were made by the two methods given in the Preparation section. They were analytically pure and showed X-ray diffractograms predicted from the crystal structure. They showed the same magnetic properties.

The χT vs. T data are given in Figure 3 for values of the applied magnetic field listed. The 10,000 Oe data are the same as those at 5,000 Oe. In the 10,000 Oe field, the χT value at 300 K of 4.073 $cm^3mol^{-1}K$ (μ_{eff} = 5.71 μ_B per Mn^{II}) decreases gradually, by only a small amount down to *ca.* 50 K, then a little more steeply reaching 0.507 $cm^3mol^{-1}K$ (2.01 μ_B) at 4.5 K. Such behaviour is generally indicative of weak antiferromagnetic coupling occurring, perhaps influenced to a minor degree by zero-field splitting of the high-spin d^5 ions. The corresponding χ vs. T curve is Curie-Weiss like in shape with an inflection evident at ca. 16K and a levelling off in χ below ca. 6K. Above 20K, θ = -32K and C = 4.22 $cm^3K\ mol^{-1}$. At lower field values, an abrupt break occurs in χT at T=16 K being particularly steep in the 20 Oe field where it reaches a maximum in χT of 35.46 $cm^3mol^{-1}K$ at T=12 K (16.84 μ_B) prior to decreasing quite rapidly down to 4 K. The minimum value of χT prior to the abrupt increase is 1.338 $cm^3mol^{-1}K$ (3.27 μ_B).

This abrupt increase below 16 K is indicative of the onset of magnetic ordering. To confirm the occurrence of a magnetic phase transition, magnetization *vs* T behaviour was measured under a field of 5 Oe and is given in Figure 4. As the temperature is lowered, the FCM (field cooled magnetization) shows a rapid increase below 16 K and continues to increase more gradually whilst the temperature is lowered to 4.5 K, with an upward discontinuity at 6.5 K, the latter observable in fields of up to 100 Oe. On turning off the field, and increasing the temperature the remanent magnetization (RM) follows the FCM curve. Despite the extreme sensitivity of magnetization to tiny fields, the ZFCM values appear to be very small in size and constant below T_c, and zero above T_c. An hysteresis loop, measured at 5 K, yields a remanent magnetization of 63 cm^3mol^{-1} Oe and coercive

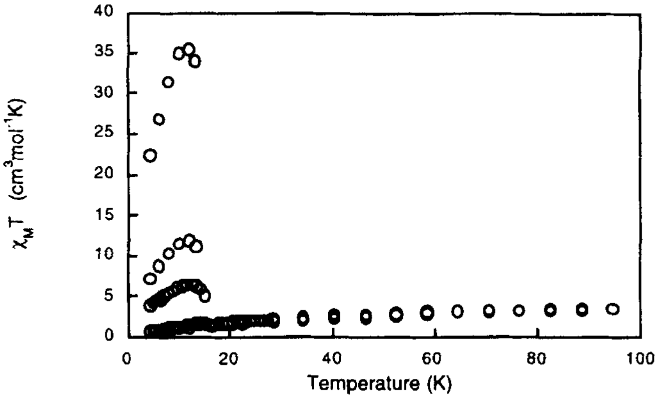

FIGURE 3 Temperature dependence of χT for Mn(dca)$_2$. Applied-field values, from top to bottom (below 16K), 20, 50, 100, 1000 and 5000 Oe.

field of 263 Oe.

High-field magnetisation data (0.1T to 5T) measured between 4 and 20K show a linear dependence of M on H with a low value of M, for instance, of 0.88 Nμ_B observed under H = 5T at 4.5K. Such behaviour is indicative of antiferromagnetic coupling with no evidence for saturation, at least in this field regime.

Mn(dca)$_2$.3H$_2$O

The magnetic susceptibility data obtained in a field of 1T show a Curie-Weiss like temperature dependence (θ = -4.1 K) with a χT value at 300 K of 4.31 cm^{3}mol^{-1}K (μ_{eff} = 5.87 μ_B). Between 300 and 4.2 K the χT data are generally reminiscent of a zero-field split d^5 (high-spin) system, perhaps combined with very weak antiferromagnetic coupling. Thus χT remains

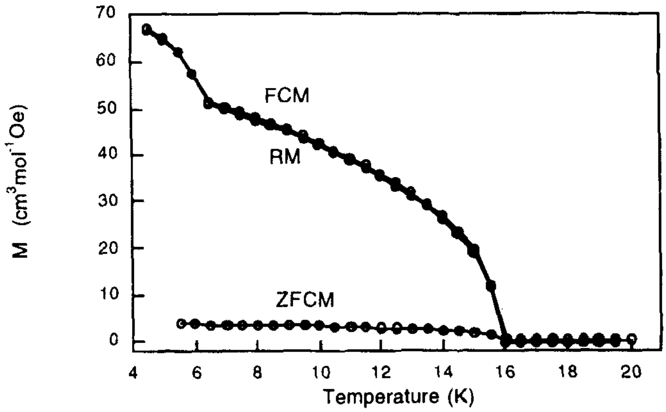

FIGURE 4 Temperature dependence of magnetization for Mn(dca)$_2$ in an applied field of 5 Oe.

constant down to *ca.* 50 K before decreasing rapidly towards 2.23 cm^{3}mol^{-1} K (4.22 μ_B) at 4.5 K. There is no evidence for long-range magnetic ordering in Mn(dca)$_2$.3H$_2$O when magnetization measurements are made under small applied fields. This undoubtedly relates to the structural details inherent in this hydrated species when compared to the parent Mn(dca)$_2$. In particular, it does not contain the N(amide)-Mn links which, presumably, provide key pathways required for 3-D ordering. However, see below for other possibilities. As in other interpenetrating network systems such as Mn(dca)$_2$(pyrazine)[6] or Mn(tcm)$_2$,[3,7] where tcm = tricyanomethanide, very weak antiferromagnetic coupling is noted without magnetic ordering occurring. The H–bonded water interactions also do not transmit strong interactions in this trihydrate.

Dehydrated sample obtained from $Mn(dca)_2.3H_2O$

This sample shows the XRD powder pattern of $Mn(dca)_2$ and also displays the same magnetic behaviour, including T_C at 16 K. Clearly the structure of Figure 2 transforms back in to the rutile-like lattice shown in Figure 1.

COMPARISONS TO OTHER M^{II} $(dca)_2$ COMPOUNDS AND POSSIBLE ORIGIN OF LONG-RANGE ORDER IN $Mn(dca)_2$

In fields of 1T, $Co(dca)_2$ and $Ni(dca)_2$ show ferromagnetic coupling[3] whilst $Cu(dca)_2$ and $Mn(dca)_2$ show weak antiferromagnetic coupling. High-field magnetization data taken at 5K for the Co and Ni compounds show M_{sat} values, and line shapes, typical of ferromagnetic coupling of spins. Long-range ferromagnetic ordering is confirmed by the FCM and ZFCM behaviour noted in very low fields. In contrast, $Mn(dca)_2$ shows a linear dependence of high-field magnetization, typical of antiferromagnetic coupling. It also shows a sharp magnetic phase transition to an ordered state below 16K. The shape of the χT vs T curves in low applied-fields is reminiscent of ferrimagnetic ordering, but a M_{sat} value is not obtained in fields of up to 5T.

There are, therefore, many fascinating puzzles to be answered. First, how, if at all, is it possible to have ferrimagnetic ordering in a molecular system which has structurally identical Mn^{II} sites, all with spins of $S = 5/2$? The low-field χT vs T plots are very similar in shape to those of the 2D-sheet complex $[Mn(4CN\text{-}py)_2(N_3)_2]_n$ [8] and rather similar to those of a layered $\{Mn^{III}\ (S = 2)\ Fe^{III}\ (S = 1/2)\}$ cyano-bridged ferrimagnet,[9] and those of a spin canted antiferromagnet (weak ferromagnet) the oxalato-bridged $\{(Mn^{II}\ (S = 5/2)\ Fe^{III}\ (S = 5/2)\ (C_2O_4)_3)^-\}$.[10] In all of these materials it is possible to assign different spins on the metal sites or different symmetries and/or different single ion anisotropies for identical spins. None of these features are apparent in $Mn(dca)_2$ at least from the structural data obtained at 123K. We need to check for a structural phase transitions occurring at very low temperatures. Low temperature neutron diffraction studies are also planned in order to deduce the magnetic structure of all the $M(dca)_2$ compounds.

It is possible that traces of an extrinsic impurity is responsible for the magnetic phase transition occurring in Mn(dca)$_2$ at 16K. However, this is ruled out by being able to dehydrate the non-ordered Mn(dca)$_2$.3H$_2$O, and form the ordered Mn(dca)$_2$.

A second puzzle is why the magnetic features of members of the isostructural M(dca)$_2$ series are so different to each other not only in the long-range ordered state but also above T_c. There are no obvious correlations between the sign of exchange and the symmetry of the magnetic orbitals, the single-ion orbital degeneracy or spin-polarization via dca. All such arguments are based of course, on conventional molecular energy level approaches which might not apply to 3D network crystals.

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