Engineering coordination architecture by hydrothermal synthesis; preparation, X-ray crystal structure and magnetic behaviour of the coordination solid $[Mn_3\{C_6H_3(CO_2)_3\text{-}1,3,5\}_2]$

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The hydrothermal reaction of manganese dichloride with the potassium salt of benzene-1,3,5-tricarboxylic acid at 220 °C gives $[Mn_3\{C_6H_3(CO_2)_3\text{-}1,3,5\}_2]$ which exhibits two pathways for antiferromagnetic coupling.

Hydrothermal synthesis is a common technique for the preparation of oxides with extended structures such as zeolites[1] and metal phosphates.[2] Recently, many interesting compounds have been synthesised by this technique using organic substituted phosphonic acids.[3] These have demonstrated the way in which product structures can be affected by the shape of the substituent. Similar effects are also important in the construction of framework solids based on either metal–ligand interactions[4] or on hydrogen bonding,[5] for example the structure of $Cd(CN)_2$ may be manipulated by the inclusion of various templates with different geometries.[4] The use of templates to influence the morphology of crystalline deposits is especially well developed in biology where through the process of biomineralisation organisms are able to engineer crystals for specific functions.[6]

Ourselves[7] and others[8] have recently shown that new coordination solids with three-dimensional structures can be prepared using solvothermal synthesis. In order to investigate the types of magnetic behaviour possible in these networks we have extended our studies to benzene-1,3,5-tricarboxylic acid (trimesic acid) which has recently been used as a structural component in an interesting network formed under ambient conditions.[9] Trimesic acid may facilitate the transmission of magnetic information *via* superexchange pathways and π-stacking interactions. Many unusual manganese complexes containing carboxylate ligands have recently been synthesised using more conventional conditions[10] and comparison with these can provide some indication of the difference that the high-temperature conditions make to the nature of the products.

Reaction of manganese dichloride (0.25 g, 2 mmol) with an excess of benzene-1,3,5-tricarboxylic acid (trimesic acid) (0.835 g, 3 mmol) and KOH (0.669 g, 12 mmol) in aqueous solution at 220 °C for 3 days followed by cooling to room temperature over 4 hours gave **1** in 88% yield as pink crystals for which a satisfactory microanalysis was obtained. Compound **1** crystallises[†] in the space group $R\bar{3}$ and has a structure consisting of Mn^{II} ions and the trianion of trimesic acid in a 3 : 2 ratio producing a neutral framework. The structure reveals an underlying threefold symmetry (Fig. 1) already present in the ligand such that the asymmetric unit corresponds to a third of the ligand with 1/3 of Mn(1) and 1/6 of Mn(2). The carboxylate function displays both a bridging and a terminal coordinating rôle.

The basic structural feature is a linear Mn_3 unit lying along the *c* axis. All of the manganese atoms have approximately octahedral geometry (Fig. 2). The central manganese atom lies on a $\bar{3}$ site and is bridged to the two outer metals (which are crystallographically equivalent to each other and lie on the threefold axis) *via* oxygens from six different trimesic acid trianions. The Mn···Mn distance is 3.01 Å and the Mn–O(2)–Mn angle (all six are crystallographically equivalent) is 88.8°. The aromatic ring lies in the *ab* plane orthogonal to the trimers with

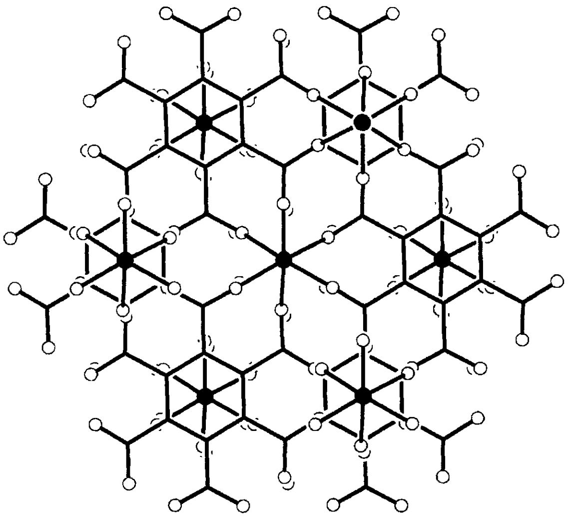

Fig. 1 View down the *c* axis showing a central trimanganese unit and its six nearest neighbours

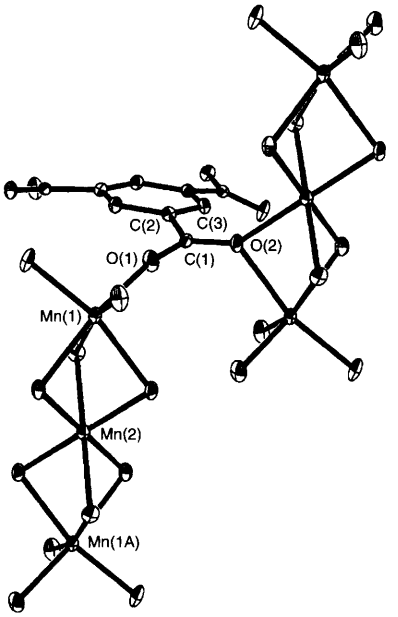

Fig. 2 View of two adjacent trimanganese units showing the atom numbering scheme. Selected bond lengths (Å): Mn(1)–O(1) 2.084(2), Mn(1)–O(2) 2.267(2), Mn(2)–O(2) 2.161(2), O(1)–C(1) 1.234(4), O(2)–C(1) 1.279(3), C(1)–C(2) 1.503(4), C(2)–C(3) 1.391(4), C(2)–C(3a) 1.398(4), Mn(1)···Mn(2) 3.099(1).

its centre on the *c* axis; however, the carboxylate units are twisted slightly out of the plane. The two oxygen atoms in the carboxylate perform different functions within the lattice: O(2) bridges between Mn(1) (2.27 Å) and Mn(2) (2.16 Å) of one trimer whilst O(1) coordinates in a terminal fashion to Mn(1) (2.08 Å) of an adjacent trimer. Hence each carboxylate bridges between two trimers and each trianion is therefore coordinated to six trimers. Each trimer has six nearest neighbours, three below and three above with a shortest inter-trimer distance between Mn atoms of 5.01 Å. The structure has some features in common with $[Mn(O_2CMe)_2(H_2O)_4]$ which is also based on linear Mn_3 units and in which some of the acetate ligands act as bridges within and between trimers.[11]

Looking down the *c* axis the structure can be seen to consist of alternating trimers and pairs of ligand trianions. The two ligands are parallel but staggered so that the C(2) type atoms of one ring (those with carboxylate substituents) lie directly above the unsubstituted C(3) atoms. The separation between the rings is 3.39 Å, close to the interlayer distance in graphite of 3.35 Å.[12] The distance between Mn(1) and the centroid of the ring above it is 4.53 Å. The Mn···Mn distance is significantly smaller than that observed in other manganese(II) complexes with carboxylate bridges (3.0 *vs.* typically 3.4–3.7 Å)[9] and this may be a consequence of the efficient parallel packing of ligands. The tight packing in this compound is also illustrated by the unusually small value of 12.2 $Å^3$ calculated for the average non-hydrogen atomic volume. This suggests that hydrothermal methods may generate coordination solids with significantly higher densities than those of products prepared under ambient conditions.

The magnetic susceptibility (χ_m)[‡] of **1** increases down to 5 K where a local maximum is observed, indicating antiferromagnetic coupling. At room temperature the observed moment per trimer of 10.26 μ_B is typical for three non-interacting $S = 5/2$ centres. At lower temperatures the value falls steadily to 2.88 μ_B at 4 K. The behaviour could not be modelled[13] successfully using the treatment described for $[Mn_3(O_2CMe)_6(bipy)_2]$ which contains isolated linear Mn_3 trimers and where only intra-trimer interactions were considered.[14] Inclusion of an inter-trimer interaction led to a more satisfactory fit. The procedure neglects the Mn(1)···Mn(1a) intra-trimer interaction which is likely to be smaller than the inter-trimer Mn(1)···Mn(1b) interaction as the distance is greater (6.02 *vs.* 5.01 Å) and the inter-trimer interaction has a more direct superexchange path *via* a carboxylate group. A good fit was achieved with $J = -10.08(10)$, $J' = -0.52(5)$ cm^{-1} and $g = 2.15$. The intra-trimer exchange parameter is larger than that obtained for $[Mn_3(O_2CMe)_6(bipy)_2]$. Although no magneto-structural correlations have yet been reported for manganese complexes[15] it is tempting to equate this stronger interaction with the shorter Mn···Mn contact in **1**.

The structural complexity and high density of the title compound compared to other manganese carboxylates prepared by traditional methods illustrates the potential of hydrothermal synthesis as a technique for the synthesis of coordination compounds. The symmetry of the ligand has a profound effect on the symmetry of the product as observed previously in crystal engineering, therefore it should be possible to prepare complexes related to **1** by using other rigid carboxylates with different symmetries.

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Footnotes

[†] *Crystal data* for $C_{18}H_6Mn_3O_{12}$: $M = 579.05$, rhombohedral, space group $R\bar{3}$, $a = 8.685(1)$, $c = 18.491(4)$ Å, $U = 1207.9(3)$ Å^3, $Z = 3$, $D_c = 2.388$ g cm^{-3}, μ(Mo-Kα) = 2.4 mm^{-1}, $F(000) = 855$, 477 unique reflections were collected of which 466 had $F > 4\sigma(F)$, $5 < 2\theta < 50°$ graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction applied using Texsan software (Molecular Structure Corporation, The Woodlands, TX, 1992), min./max. transmission factors 0.9153/1.000, pink rhomb, 0.35 × 0.35 × 0.40 mm, ω–2θ scans, $T = 293$ K. A correction for Lorentz and polarisation factors was applied and the structure was solved by direct methods (SHELXTL-plus, Siemens Inc., Madison, WI), the hydrogen atom was placed on an idealised position and was refined isotropically, all other atoms were refined anisotropically using full-matrix least squares on $|F^2|$ using SHELX-93 software (G. M. Sheldrick, University of Göttingen, 1993). 51 parameters refined, $R1 = 0.0294$, $wR2 = 0.0928$, $S = 1.503$, maximum residual electron density (1 hole) = 0.561 (−0.803) e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/13.

[‡] The magnetic properties of **1** have been studied in the range 2–300 K in a field of 1 kG. The magnetic susceptibility is given by equations (1) and (2), where z = number of nearest neighbours (six); J = intra-trimer interaction parameter between Mn(1) and Mn(2); J' = inter-trimer interaction, S_x = spin for manganese centre Mn(x).

$$\chi_m = Ng^2\beta^2 F(J,T)/[3kT - zJ' F(J,T)] \tag{1}$$

$$F(J,T) = \frac{\sum\limits_{S'=0}^{S'=2S_1}\sum\limits_{S=|S'-S_2|}^{S'=S'+S_2} S(S+1)(2S+1)\exp[-J[S(S+1)-S'(S'+1)]/2kT]}{\sum\limits_{S'=0}^{S'=2S_1}\sum\limits_{S=|S'-S_2|}^{S'=S'+S_2} (2S+1)\exp[-J[S(S+1)-S'(S'+1)]/2kT]} \tag{2}$$

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