β-$Mn(O_2CMe)_2$: solvothermal synthesis and crystal structure of an unprecedented three-dimensional manganese(II) network

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Crystalline anhydrous bis(acetato)manganese(II) is isolated from superheated acetonitrile under autogeneous pressure; the single-crystal X-ray structure reveals a covalently linked three-dimensional network with six- and seven-coordinate manganese(II) centres.

The linking of high-spin metal centres into large clusters and extended solids is of considerable interest for the molecular design of magnetic materials.[1] The synthesis of large clusters of manganese carboxylates has proven a successful means of preparing molecules with high-spin ground states because of the four and five unpaired electrons provided by the manganese-(III) and -(II) ions, respectively. Recently clusters with up to eighteen Mn centres,[2] and clusters which possess very high ground states of $S > 12$, have been reported.[3] Interestingly, because Mn^{II} is quite oxophilic, many of these materials contain both Mn^{III} and Mn^{II} centres. As a result, the chemistry of materials containing exclusively Mn^{II} is less extensively developed.

Complexes of manganese(II) are known to form with a large number of anionic ligands, though a majority of these complexes also contain coordinated water or waters of hydration. Although anhydrous $Mn(O_2CMe)_2$ has been reported previously,[4] until this report, structural details remained elusive. In our efforts to link Mn^{II} centres into extended lattices, we have discovered that in fact at least two polymorphs of $Mn(O_2CMe)_2$ exist. Powder X-ray diffraction studies indicate that previously reported syntheses yield what we have described as α-$Mn(O_2CMe)_2$,† although the crystal structure of this material is not yet known. However, single crystals of β-$Mn(O_2CMe)_2$, suitable for an X-ray structural determination, were grown from superheated acetonitrile. Such solvothermal syntheses provide a useful route to a variety of novel anhydrous Mn^{II} materials.

Structurally characterized examples of extended solids of manganese carboxylates include several one-dimensional chain and two-dimensional layer structures which exhibit a variety of interesting magnetic properties. However, based on a search of the Cambridge Structural Database (CSD), only six examples of three-dimensional network structures are known, and all of these frameworks are constructed from bifunctional acids as ligands.[5–10] Further, crystal structures of the anhydrous homoleptic acetates of 3d metals have only been reported (in CSD) for Sc, Cr, Co(K), Cu and Zn, and of these only $\{Zn(O_2CMe)_2\}_n$ forms a three-dimensional network.[11] We here report the synthesis and single-crystal structure of β-$Mn(O_2CMe)_2$, the first structurally characterized example of an anhydrous manganese biscarboxylate, and the first manganese carboxylate with a three-dimensional network structure in which simple carboxylate ligands form the lattice.

Single crystals of β-$Mn(O_2CMe)_2$ were first observed as a byproduct from the reaction of $[Mn_3O(O_2CMe)_6(py)_3]$ and terephthalic acid in acetonitrile at 150 °C under autogeneous pressure. Large colourless octahedral crystals of β-$Mn(O_2CMe)_2$ (*ca.* 10% yield) were separated from a dark green amorphous phase. Subsequent efforts to obtain a quantitative yield by dehydrating $Mn(O_2CMe)_2 \cdot 4H_2O$ at 110 °C under dynamic vacuum for 12 h[4a] yielded a second phase, α-$Mn(O_2CMe)_2$, which is readily differentiated from the β-phase by X-ray powder diffraction. However, the IR spectra and elemental analyses of α- and β-$Mn(O_2CMe)_2$ are essentially indistinguishable. Dehydrating a sample of $Mn(O_2CMe)_2 \cdot 4H_2O$ in superheated acetonitrile§ yields a mixture of α- and β-$Mn(O_2CMe)_2$.‡ Long reaction times (of the order of weeks) favour the synthesis and crystal formation of β-$Mn(O_2CMe)_2$.

The structure of $Mn(O_2CMe)_2$ consists of a complex three-dimensional network constructed from a trimer of acetate bridged Mn(II) centres (Fig. 1).¶ Visualization of the trimer in the context of the framework structure is simplified by a polyhedral representation [Fig. 1(*b*)]. The seven-coordinate Mn(1) polyhedron shares one face with the distorted octahedron around Mn(2), and an edge with the distorted octahedron around

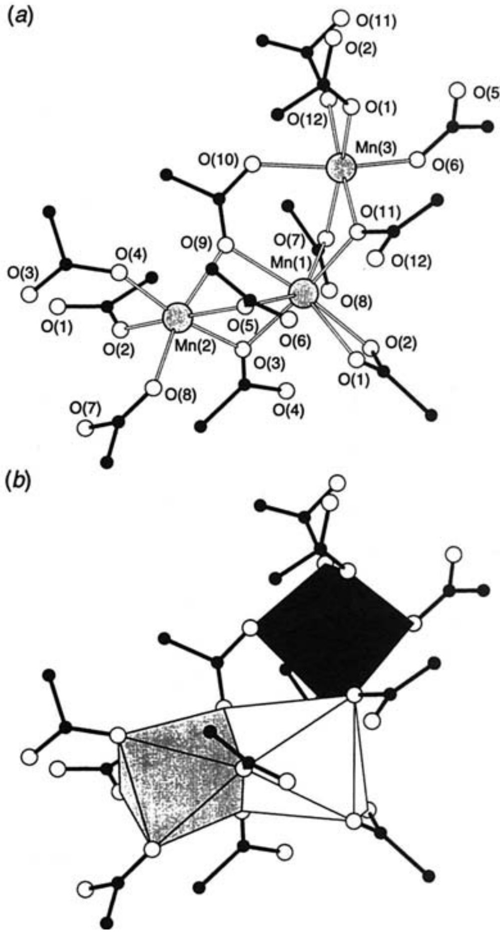


Fig. 1 (*a*) Ball and stick and (*b*) polyhedral representation of the manganese acetate trimer of β-$Mn(O_2CMe)_2$ showing the atom numbering scheme. Significant distances (Å) include: Mn(1)–O(1) 2.357(5), Mn(1)–O(2) 2.377(5), Mn(1)–O(3) 2.192(5), Mn(1)–O(5) 2.308(4), Mn(1)–O(7) 2.288(4), Mn(1)–O(9) 2.312(5), Mn(1)–O(11) 2.164(2), Mn(2)–O(2) 2.142(5), Mn(2)–O(3) 2.249(5), Mn(2)–O(4) 2.109(5), Mn(2)–O(5) 2.188(4), Mn(2)–O(8) 2.116(5), Mn(2)–O(9) 2.242(5), Mn(3)–O(1) 2.171(5), Mn(3)–O(6) 2.104(5), Mn(3)–O(7) 2.219(4), Mn(3)–O(10) 2.134(5), Mn(3)–O(11) 2.236(4), Mn(3)–O(12) 2.180(5).

Mn(3). The trimers are linked along *a* by corner-sharing Mn(1) and Mn(2) polyhedra through O(2) and along *b* by corner-sharing Mn(1) and Mn(3) polyhedra through O(1) (Fig. 2). Similar corner sharing of the trimers through O(1) and O(2) create two types of helical connectivity around the 2_1 axes running along *c*. The polyhedral connectivity of the two helices can be represented as -(3-1-2)-1- (3-1-2)-1- and -(3-1)-(2-1)-(2-1)-, respectively, in which the polyhedra common to one trimer are in parentheses. (The latter helix creates a pseudo-4_1 axis of symmetry.) The two types of helices turn in opposite senses.

The structure of manganese acetate tetrahydrate[12] can also be described as a condensation of manganese trimers, but, into a two-dimensional layer. However, the waters of hydration form a less condensed hydrate trimer that can be described as three corner-sharing octahedra; a connectivity which is similar to the inter-trimer linkage in β-$Mn(O_2CMe)_2$.

With only two acetate ligands per manganese atom in β-$Mn(O_2CMe)_2$, extensive ligand bridging is required in order to fill the coordination sphere of the manganese cations. Two generalized acetate coordination geometries, **I** and **II**, are observed. The oxygen atoms of the five type **I** acetates that bridge two Mn centres form the primary backbone of the trimer. The triply bridged Mn(1)···Mn(2) contact is separated by 3.202(1) Å and the double bridged Mn(1)···Mn(3) distance is 3.373(1) Å. The oxygens of the type **II** acetate join three trimers, and, together with the terminal oxygen atoms of the type **I** acetates, link the trimers into a three-dimensional network, with inter-trimer contacts Mn(1)···Mn(2) 3.816(1) Å and Mn(1)···Mn(3) 3.887(1) Å.

It is interesting to note that the shortest Mn–O distances (caption of Fig. 2) are to the non-bridged oxygens of the type **I** acetate ligands (2.14 Å av.). However, one of the Mn–O distances to the bridging oxygens of the type **I** acetate ligands is nearly as short (2.19 Å av.). The strongest influence on the Mn–O bond distances appears to be the seven- *vs.* six-coordination of the central manganese [Mn(1), CN = 7, Mn–O 2.28 Å av.; Mn(2), CN = 6, Mn–O 2.17 Å av.; Mn(3), CN = 6, Mn–O 2.17 Å av.].

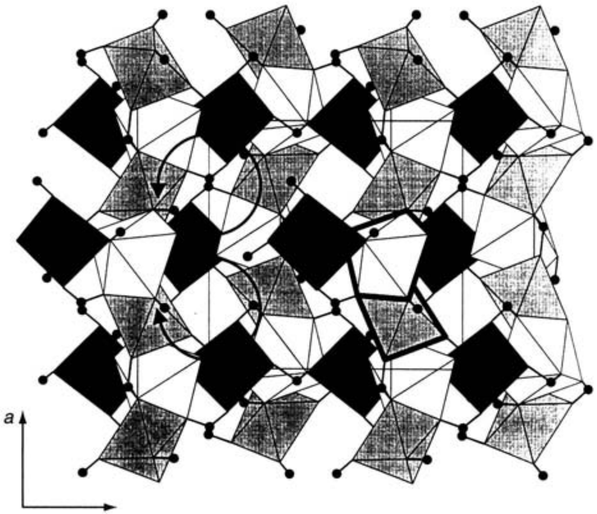
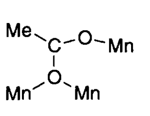


Fig. 2 View of the β-$Mn(O_2CMe)_2$ network looking down *c* showing the trimer connectivity and rotation of the network helices. Methyl carbons have been eliminated for clarity.



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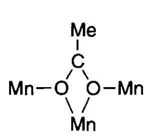

II

Room-temperature magnetic susceptibility measurements indicate a moment of 6.0 μ_B, consistent with isolated $S = 5/2$ centres. We are currently investigating the temperature dependence of the magnetic susceptibility of $Mn(O_2CMe)_2$ in which an antiferromagnetic ordering is observed at 15 K.

This work was supported by a grant from the National Science Foundation (DMR 9501370), an NSF Research Experience for Undergraduates supplement, and North Carolina State University.

Footnotes

† A powder pattern of a sample of commercial anhydrous manganese acetate from Aldrich showed it to be α-$Mn(O_2CMe)_2$.

‡ *Synthesis*: a 300 mg sample of $Mn(O_2CMe)_2 \cdot 4H_2O$ was placed into a thick walled fused silica ampoule into which 3 ml of acetonitrile was then added (60% full). The reaction mixture was frozen in liquid N_2, evacuated, and flame sealed. The reaction vessel was then placed into a furnace at 150 °C. Reaction times of 2 to 3 days to $2\frac{1}{2}$ weeks yielded a mixture of the α and β phases, whereas a reaction run for six weeks yielded a nearly quantitative preparation of β-$Mn(O_2CMe)_2$. Elemental analysis. Calc. for $MnC_4H_6O_4$: C, 27.76; H, 3.50; N, 0.00. Found: C, 27.42; H, 3.45; N, 0.00%.

§ Under solvothermal conditions at 150 °C the following reaction occurs.

$$MeCN + 2\,H_2O \rightarrow MeCO_2H + NH_3$$

¶ *Crystal data* for $Mn(O_2CMe)_2$: $C_{12}H_{18}Mn_3O_{12}$, $M = 519.1$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 11.3001(9)$, $b = 11.5329(9)$, $c = 15.272(1)$ Å, $U = 1990.3(3)$ Å^3, $Z = 4$, $D_c = 1.732$ g cm^{-3}, μ(Mo-Kα) = 18.6 cm^{-1}, Mo-Kα radiation (0.710 73 Å). Intensity data for *h*, *k*, *l*, were collected by the ω-scan method to the limit of θ < 30°. The final refinement was carried out by full-matrix least squares on 2108 independent reflections [$I > 2.5\sigma(I)$]. All non-hydrogen atoms were refined anisotropically. The structure was refined to $R = 0.043$ and $R_w = 0.045$. The absolute configuration of this structure was refined with a Rogers parameter of 1.21(8). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic 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 182/238.

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Received, 6th June 1996; Com. 6/03969C