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$Mn_3(OAc)_6 \cdot CH_3CN$: a porous dehydrated manganese(II) acetate

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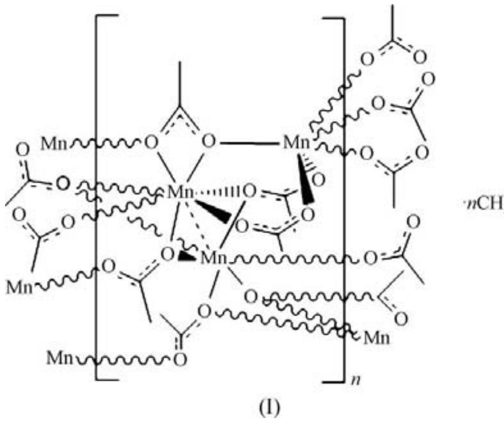
The crystal structure of a new form of dehydrated manganese(II) acetate, poly[[hexa-μ_3-acetato-trimanganese(II)] acetonitrile solvate], $\{[Mn_3(CH_3COO)_6]\cdot CH_3CN\}_n$, (I), reveals a three-dimensional polymeric structure based on an $\{Mn_3\}$ trimer. The $\{Mn_3\}$ asymmetric unit contains three crystallographically independent Mn positions, comprising a seven-coordinate center sharing a mirror plane with a six-coordinate center, and another six-coordinate atom located on an inversion center. Two of the four crystallographically independent acetate (OAc) ligands, as well as the acetonitrile solvent molecule, are also located on the mirror plane. The Mn atoms are connected by a mixture of Mn—O—Mn and Mn—OCO—Mn bridging modes, giving rise to face- and corner-sharing interactions between manganese polyhedra within the trimers, and edge- and corner-sharing connections between the trimers. The network contains substantial pores which are tightly filled by crystallographically located acetonitrile molecules. This structure represents the first porous structurally characterized phase of anhydrous manganese(II) acetate and as such it is compared with the closely related densely packed anhydrous manganese(II) acetate phase, solvent-free β-$Mn(OAc)_2$.

Comment

Coordination networks constructed from rigid bis-carboxylate or amine ligand linkers, such as terephthalic acid (Li *et al.*, 1999) or 4,4-dipyridyl (Zaworotko, 2000), have attracted much attention in recent years. In such substances, changing the length of the linker ligand allows adjustment of structural properties such as pore size (Zaworotko, 2000; Yaghi *et al.*, 2003). However, simple mono-carboxylates, such as formate or acetate (OAc), are also able to generate complex extended structures due to the many accessible carboxylate bridging coordination modes (Viertelhaus *et al.*, 2003; Martin & Hess, 1996). Such structures more closely resemble metal oxides such as zeolites, as the small size of the ligands obliges the metal ions to play a structural role in the linkers as well as the nodes. The resulting short metal–metal distances can lead to interesting magnetic behaviour, driving investigation of a number of stable porous formate networks based on divalent metal ions (Wang, Zhang, Fujiwara *et al.*, 2004; Wang, Zhang, Otsuka *et al.*, 2004; Wang *et al.*, 2005; Viertelhaus *et al.*, 2005; Rood *et al.*, 2006). Such formate-based materials can accommodate a range of guests and have potential as porous magnets (Wang, Zhang, Fujiwara *et al.*, 2004; Dybtsev *et al.*, 2004). However, anhydrous acetate-based frameworks have received less attention to date.

Our recent investigation of the coordination chemistry of the novel chiral ethanolamine ligand, (*S*)-*N*-phenylethyldiethanolamine [(*S*)-H_2PEDEA], has resulted in the serendipitous isolation of a new anhydrous manganese(II) acetate coordination framework, *viz.* $\{[Mn_3(OAc)_6]\cdot CH_3CN\}_n$, (I), which crystallizes in the space group *Pnma*. Compound (I) is the first structurally characterized porous anhydrous manganese(II) acetate phase, and was isolated as a minor product from the attempted reaction of the well known manganese(III) trimer $[Mn_3O(OAc)_6(py)_3]ClO_4$ (py is pyridine; Vincent *et al.*, 1987) with (*S*)-H_2PEDEA in acetonitrile–methanol. In this way, reduction from Mn^{III} to Mn^{II} occurs due to reaction with the alcohol groups provided by the solvent and (*S*)-H_2PEDEA. Accommodation of acetonitrile molecules within the resulting framework leads to a porous structure with a substantially increased unit-cell volume (by *ca* 9%) in comparison with the previously published densely packed β-$Mn(OAc)_2$ (Martin & Hess, 1996) and γ-$Mn(OAc)_2$ (Yang *et al.*, 2005).



(I)

The three-dimensional network formed by compound (I) is based on assembly of an $\{Mn_3\}$ asymmetric unit, consisting of a central seven-coordinate Mn centre (Mn1) and two six-coordinate Mn atoms (Mn2 and Mn3), four crystallographically independent acetate ligands, and an acetonitrile molecule (Fig. 1). Two of the Mn atoms (Mn1 and Mn2), two acetate ligands (those containing atoms C1 and C3) and the acetonitrile molecule are located on a mirror plane, while atom Mn3 sits on an inversion center. The C1 acetate ligand is bisected by the mirror, so that only atoms C1 and C2 sit on the mirror plane and atom O7^i [symmetry code: (i) $x, \frac{1}{2} - y, z$] is generated by mirror symmetry from atom O7. In the C3 acetate ligand, all four atoms are located on the mirror plane.

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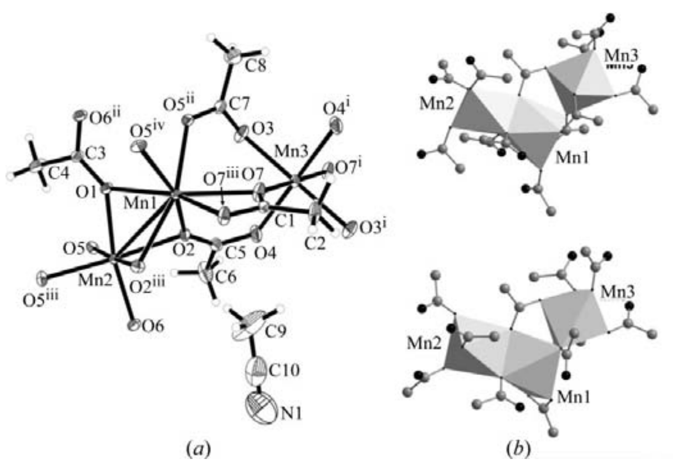

Figure 1
(*a*) The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{3}{2} - z$; (iii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (iv) $-x, -y, -z + 1$.] (*b*) Polyhedral representation of the $\{Mn_3\}$ units in (I) (top) and β-Mn(OAc)$_2$ (bottom), showing the connectivity of the three Mn atoms.

The four crystallographically independent acetate ligands show two different μ_3 coordination modes. The C3, C5 and C7 acetates all have one O atom [O1, O2 and O5^{iii}, respectively; symmetry code: (iii) $x - \frac{1}{2}, y, \frac{3}{2} - z$] acting as a monoatomic bridge between two Mn sites, with the other connecting to a third Mn atom. For the C1 acetate, both O atoms (O7 and symmetry-related O7^{i}) act as monoatomic bridges coordinating to atom Mn1, so that atoms O7 and O7^{i}, respectively, link atom Mn1 to atom Mn3 and symmetry-related atom Mn3^{v} (Fig. 4) [symmetry code: (v) $-x, y + \frac{1}{2}, 1 - z$]. The overall result is that the Mn centres are connected through a mixture of Mn—O—Mn and Mn—OCO—Mn bridges, whereby atoms Mn1 and Mn2 are connected by three Mn—O—Mn bridges (*e.g.* face-sharing polyhedra), and atom Mn1 connects to atom Mn3 by a single Mn—O—Mn bridge supported by two Mn—OCO—Mn linkages (corner-sharing polyhedra). The Mn1$\cdots$Mn2 face-sharing connection results in a short Mn$\cdots$Mn contact of 3.170 (1) Å that may indicate a weak metal–metal interaction. This contrasts with the $\{Mn_3\}$ unit observed in β-Mn(OAc)$_2$ [Martin & Hess, 1996; Cambridge Structural Database (Allen, 2002) refcode QQQFUV02], which exhibits one face-sharing and one edge-sharing interaction between the Mn centers (Fig. 1). However, both β-Mn(OAc)$_2$ and compound (I) show the same overall level of condensation, as the four connections to other trimers comprise exclusively corner-sharing interactions in β-Mn(OAc)$_2$, but two edge-sharing and two corner-sharing interactions in compound (I). The structure of γ-Mn(OAc)$_2$ (Yang *et al.*, 2005) is essentially the same as that of β-Mn(OAc)$_2$. However, the presence of disorder in the acetate bridging ligands merges the Mn2 and Mn3 sites into one position. This results in an inversion center at the seven-coordinate Mn1 atom and a higher symmetry space group ($P4_12_12$, compared with $P2_12_12_1$ for the β phase).

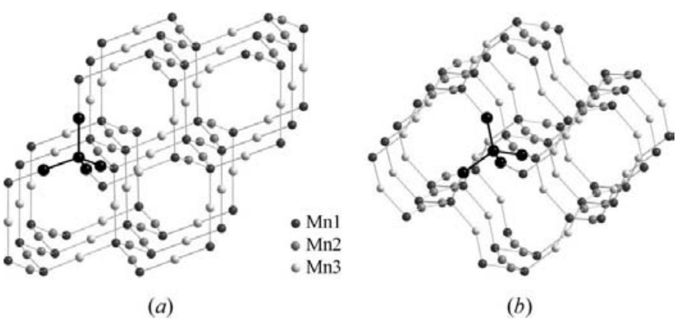

Figure 2
Diamondoid networks of Mn atoms in (*a*) compound (I) and (*b*) β-Mn(OAc)$_2$. In each network, one tetrahedral $\{Mn_5\}$ unit has been highlighted in black and shown with larger spheres.

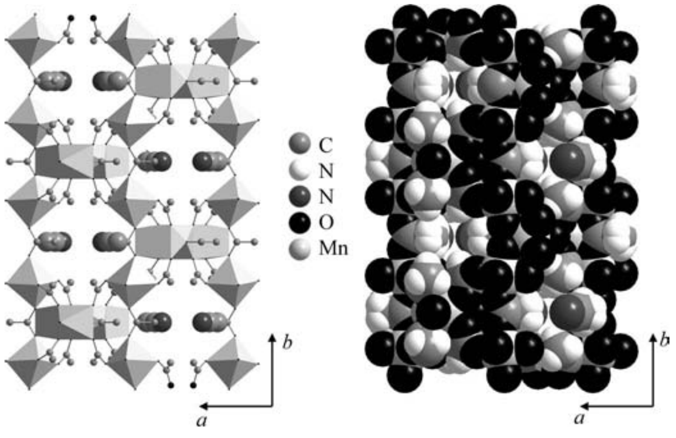

Figure 3
The crystal packing in compound (I), viewed along the crystallographic *a* axis. (*a*) Mn atoms are represented as polyhedra and the acetonitrile molecules located within the pores are highlighted with larger spheres. (*b*) A space-filling representation, illustrating the tight filling of the pores by acetonitrile.

The simplest way of describing the network formed by compound (I) is as a diamondoid net of Mn centres (Fig. 2). Seven-coordinate atom Mn1 forms a tetrahedral node by connecting to four other Mn1 centers *via* two Mn2 and two Mn3 atoms, which combined with the acetate ligands act as linkers. As such, atom Mn1 sits at the center of an $\{Mn_5\}$ tetrahedral unit with vertices described by two Mn2 and two Mn3 atoms (Figs. 2 and 4). This arrangement results in wavy chains of Mn1 and Mn2 atoms propagating parallel to the crystallographic *a* axis, formed by face-sharing intra-trimer and edge-sharing inter-trimer Mn1$\cdots$Mn2 interactions. The chains are connected to form a three-dimensional network by the corner-sharing links provided by atom Mn3 between the Mn1 nodes, leading to pores which run along the crystallographic *a* axis which are occupied by the crystallographically located acetonitrile guests (one per $\{Mn_3\}$ formula unit; Fig. 3). Tight binding of the acetonitrile guest molecules is indicated by the zero solvent-accessible void space calculated by *PLATON* (Spek, 2009), and is illustrated by the space-filling diagram on the right-hand side of Fig. 3.

Note that the chiral literature compound β-Mn(OAc)$_2$ (space group $P2_12_12_1$; Martin & Hess, 1996) is also based on a

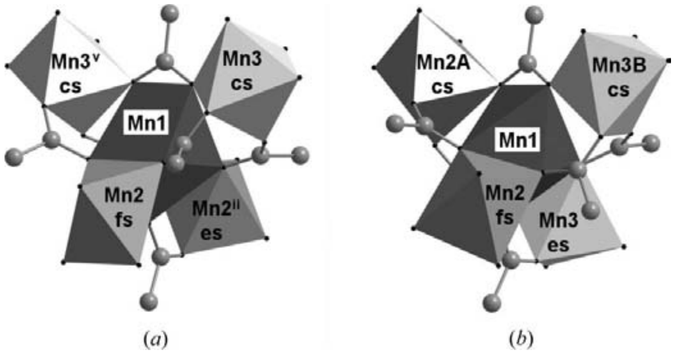

Figure 4
(*a*) The symmetrical tetrahedral {Mn_5} units in compound (I). (*b*) The chiral tetrahedral {Mn_5} unit in β-$Mn(OAc)_2$. Abbreviations denote corner-sharing (cs), edge-sharing (es) and face-sharing (fs) polyhedra. [Symmetry codes: (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (v) $-x, y + \frac{1}{2}, 1 - z$; (A) $x + \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (B) $-x, y + \frac{1}{2}, \frac{3}{2} - z$.]

diamondoid arrangement of Mn centers (Fig. 2). However, breaking the structure down again into chains of Mn1 and Mn2 connected by Mn3 atoms reveals that the nature of the intra- and interchain connections is different from that of compound (I). The Mn1···Mn2 chains in β-$Mn(OAc)_2$ contain alternating face- and corner-sharing connections [rather than the face- and edge-sharing connections seen in compound (I)], and the Mn3 linkers connect to the chains through alternating edge- and corner-sharing connections [compared with exclusively corner-sharing in compound (I)]. As a result, the β-$Mn(OAc)_2$ network is less regular (as reflected in the chiral space group). This distortion probably occurs because it is 'collapsed' compared with compound (I), filling the space left by the absent acetonitrile molecules. The chirality of β-$Mn(OAc)_2$, observed in the helical axes described by Martin & Hess (1996), is also manifested in the subtly contrasting connectivity around the Mn1 node positions compared with compound (I) (Fig. 4). In compound (I), atom Mn1 and the two Mn2 atoms sit on a mirror plane between two crystallographically identical Mn3 positions (Fig. 4). In β-$Mn(OAc)_2$, the equivalent Mn1 position is effectively a chiral center, as all four combinations of connection mode (face-, edge- or corner-sharing) and linked atom (*e.g.* Mn2 or Mn3 sites) are different.

Experimental

$[Mn_3(OAc)_6(py)_3]ClO_4$ was synthesized according to a published procedure (Vincent *et al.*, 1987). (*S*)-H_2PEDEA was synthesized by reacting (*S*)-*N*-phenylethylamine with ethylene oxide in ethanol. Full details will be published elsewhere. All other reagents were obtained commercially as ACS reagent grade and used as supplied. IR spectra were recorded on a Bruker TENSOR 27 spectrometer.

(*S*)-H_2PEDEA (0.078 g, 0.373 mmol) in methanol (3 ml) was added to a solution of $[Mn_3(OAc)_6(py)_3]ClO_4$ (0.27 g, 0.310 mmol) in acetonitrile (7 ml). The resulting dark-brown mixture was stirred for 16 h at room temperature before filtration. Slow evaporation of the solvent produced a dark-brown microcrystalline solid (0.092 g). The X-ray powder pattern of this material matched neither compound (I) nor β/γ-$Mn(OAc)_2$. However, elemental analysis on the dried material indicated that it was a form of manganese(II) acetate. Further evaporation produced a small quantity of pale-yellow single-crystal X-ray diffraction quality crystals of compound (I). FT–IR (KBr disc, ν, cm^{-1}): 3386 (*s*), 2936 (*w*), 2255 (*w*), 1577 (*v*), 1418 (*v*), 1344 (*s*), 1049 (*m*), 1026 (*m*), 940 (*w*), 660 (*s*), 615 (*m*), 502 (*w*).

Crystal data

$[Mn_3(C_2H_3O_2)_6]\cdot C_2H_3N$
$M_r = 560.14$
Orthorhombic, *Pnma*
$a = 10.788\ (2)$ Å
$b = 12.702\ (2)$ Å
$c = 15.784\ (3)$ Å
$V = 2163.0\ (7)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.78\ mm^{-1}$
$T = 193$ K
0.15 × 0.08 × 0.05 mm

Data collection

Bruker CCD-1000 area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.692$, $T_{max} = 0.915$
18714 measured reflections
2763 independent reflections
2307 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.071$
$S = 1.09$
2763 reflections
159 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—O1	2.3004 (18)	Mn2—O2^{i}	2.2135 (13)
Mn1—O2	2.2871 (14)	Mn2—O5	2.1711 (13)
Mn1—O2^{i}	2.2871 (14)	Mn2—O5^{i}	2.1710 (13)
Mn1—O5^{ii}	2.2514 (13)	Mn2—O6	2.0983 (19)
Mn1—O5^{iii}	2.2514 (14)	Mn3—O3	2.1509 (14)
Mn1—O7	2.3215 (14)	Mn3—O3^{iv}	2.1510 (14)
Mn1—O7^{i}	2.3215 (14)	Mn3—O4	2.1273 (16)
Mn1—Mn2	3.1697 (7)	Mn3—O4^{iv}	2.1273 (16)
Mn2—O1	2.1737 (19)	Mn3—O7	2.1374 (14)
Mn2—O2	2.2134 (13)	Mn3—O7^{iv}	2.1373 (14)

Symmetry codes: (i) $x, -y + \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (iv) $-x, -y, -z + 1$.

All H atoms were placed in geometrically idealized positions. For the acetate ligands and acetonitrile solvent molecules the H atoms were constrained to ride and rotate on their parent atoms, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$. The relatively large $U_{eq}(max)/U_{eq}(min)$ for carbon on the acetate framework and the acetonitrile solvent molecules is a consequence of slight thermal disorder on the terminal methyl positions.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EG3016). Services for accessing these data are described at the back of the journal.

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