metal-organic compounds

Disorder effects in Mn$_{12}$–acetate at 83 K

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The structure of hexadeca-μ-acetato-tetraaquadodeca-μ_3-oxo-dodecamanganese bis(acetic acid) tetrahydrate, [Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$]·2CH$_3$COOH·4H$_2$O, known as Mn$_{12}$–acetate, has been determined at 83 (2) K by X-ray diffraction methods. The fourfold (S_4) molecular symmetry is disrupted by a strong hydrogen-bonding interaction with the disordered acetic acid molecule of solvation, which displaces one of the acetate ligands in the cluster. Up to six Mn$_{12}$ isomers are potentially present in the crystal lattice, which differ in the number and arrangement of hydrogen-bonded acetic acid molecules. These results considerably improve the structural information available on this molecular nanomagnet, which was first synthesized and characterized by Lis [*Acta Cryst.* (1980), B**36**, 2042–2046].

Comment

The compound [Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$]·4H$_2$O·2CH$_3$COOH, known as Mn$_{12}$–acetate, (I), is the prototype of a class of magnetic materials referred to as 'single-molecule magnets' (Sessoli *et al.*, 1993). The acronym reflects the exceedingly slow relaxation of the magnetization at low temperature (LT), which is reminiscent of bulk magnets. In (I), however, the slow magnetic relaxation has a purely molecular origin, as established by measurements in solution (Cheesman *et al.*, 1997) and in polymer films (Eppley *et al.*, 1995). It arises from the huge easy-axis magnetic anisotropy in the ground spin state ($S = 10$), and from the energy barrier (60 K) to be overcome for the reversal of the magnetization. In addition, due to the intrinsic quantum nature of the system, underbarrier tunnelling processes are possible, which lead to characteristic steps in the hysteresis loops at LT (Friedman *et al.*, 1996).

Compound (I) was first synthesized and structurally characterized by room temperature (RT) methods in 1980 (Lis, 1980). The crystal lattice (tetragonal space group $I\bar{4}$) comprises [Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$] cluster units which

(I)
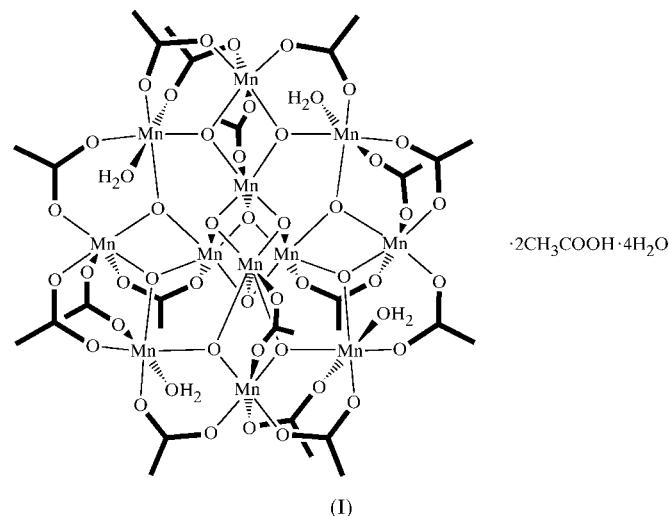
develop around $\bar{4}$ axes. These units feature a central cubane-like tetramanganese(IV)–oxo moiety linked to eight peripheral manganese(III) centres by eight μ_3-O and four μ-acetate ligands. Twelve additional μ-acetates and four water ligands complete the Jahn–Teller distorted coordination sphere of the manganese(III) ions (Lis, 1980).
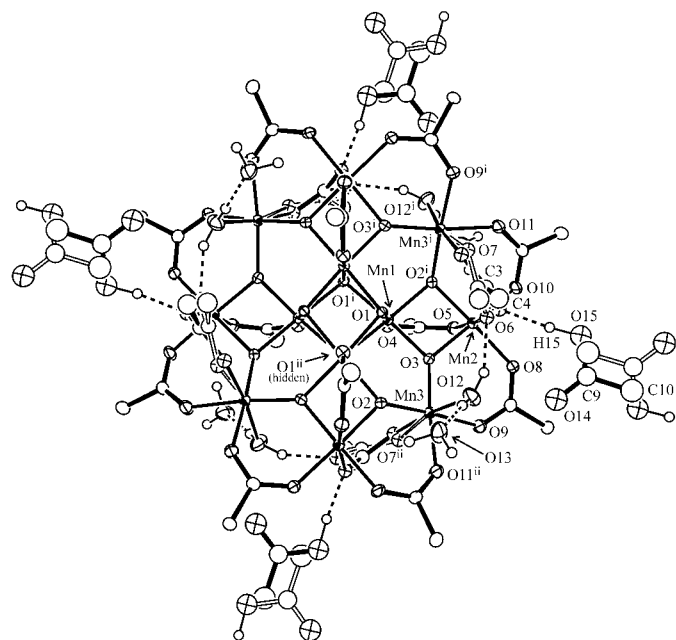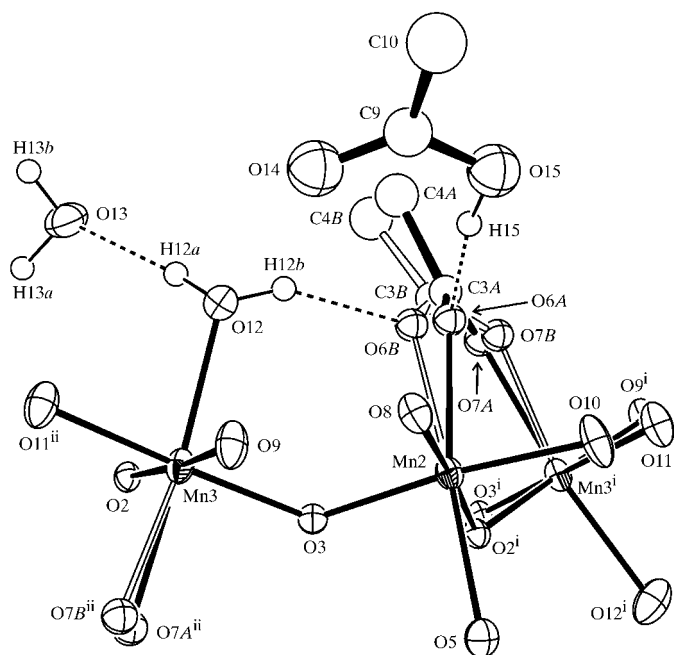

Figure 1
The molecular structure of (I) at 83 (2) K. The two positions occupied by the acetic acid molecule and by the O6/O7/C3/C4 acetate ligand are differentiated using solid and open bonds. For clarity, only the H atoms of the acetic acid and water molecules are shown (small spheres). The network of hydrogen bonds is indicated by dashed lines (the symmetry codes are as in Table 1). Displacement ellipsoids are at the 50% probability level.

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Figure 2
The coordination environment of atoms Mn2 and Mn3. Displacement ellipsoids are at the 50% probability level (the symmetry codes are as in Table 1).

The relationship between tunnelling and molecular symmetry in (I) has recently become the focus of considerable interest, because the selection rules imposed by the S_4 crystallographic symmetry are not obeyed. For this reason, symmetry-breaking effects arising from crystal dislocations have been suggested (Mertes *et al.*, 2001). Close examination of the structural data, however, suggests a possible mechanism for symmetry lowering at the molecular level. Each cluster is in fact surrounded by four water and two acetic acid molecules of solvation. The latter are located between adjacent Mn_{12} units in the *ab* plane and are disordered over two partially overlapping positions related by a twofold axis parallel to **c**. As confirmed by a very recent neutron diffraction study at LT (Langan *et al.*, 2001), one of the acetate ligands (O6/O7/C3/C4) is involved in a strong hydrogen-bonding interaction with the disordered acetic acid molecule. Indeed, atom O6 and the neighbouring methyl C4 atom exhibit unusually large displacement parameters at RT compared with the remaining acetate ligands (Lis, 1980), possibly reflecting unresolved disorder.

To investigate this issue in more detail, we collected a new set of X-ray diffraction data at 83 (2) K. Preliminary structure refinement showed abnormal elongation of the displacement ellipsoids of atoms O6, C4 and, to a lesser extent, O7 and C3. We thus modelled the O6/O7/C3/C4 acetate ligand over two positions, *A* and *B* (Figs. 1 and 2). The resulting hydrogen-bonding geometry between atoms O15 and O6*A* [O15···O6*A* 2.687 (7) Å, H15···O6*A* 1.68 Å and O15—H15···O6*A* 169°] compares extremely well with that found in solid acetic acid at the same temperature (O···O′ 2.62 Å, H···O′ 1.63 Å and O—H···O′ 165°; Nahringbauer, 1970).

Notably, the coordination geometry of atoms Mn2 and Mn3 undergoes significant distortion upon hydrogen bonding, the Mn2—O6 and Mn3—O7 distances varying by −0.09 and 0.05 Å, respectively. Angular distortions are also meaningful, with O6*A*—Mn2—O6*B* = 14.10 (14)° and O7*A*—Mn3^i—O7*B* = 6.8 (3)°.

These results definitely show that the disorder of the acetic acid molecule is supramolecularly transmitted to the Mn_{12} units *via* a strong hydrogen-bonding interaction. Since the number (*n*) of hydrogen-bonded acetic acid molecules which surround each Mn_{12} unit can, in principle, range from 0 to 4, up to six isomeric forms of the cluster can be envisaged. Two of them (*n* = 0 and 4) retain S_4 point-group symmetry, while the remaining isomers have either C_2 (*n* = 2, 'trans') or C_1 (*n* = 1, 2, 'cis', and 3) symmetry. Ordered layers of alternating *n* = 0 and 4 isomers would clearly preserve S_4 molecular symmetry, at the same time leading to doubled unit-cell vectors in the *ab* plane. Careful inspection of the diffraction pattern using a CCD device gave no hint as to the presence of a supercell, thus excluding an ordered structure in the *ab* plane. Non-axial isomers must then be present in the lattice, which provides a possible explanation for the intriguing tunnelling behavior of (I) (Cornia *et al.*, 2002).

Experimental

Compound (I) was synthesized as described by Lis (1980). Crystals were obtained by layering acetone over the CH_3COOH/H_2O reaction mixture

Crystal data

$[Mn_{12}O_{12}(C_2H_3O_2)_{16}(H_2O)_4]$·· $2C_2H_4O_2$·$4H_2O$	Mo $K\alpha$ radiation
$M_r = 2060.22$	Cell parameters from 70 298
Tetragonal, $I\bar{4}$	reflections
$a = 17.1668$ (3) Å	$\theta = 1.0–27.5°$
$c = 12.2545$ (3) Å	$\mu = 2.13$ mm^{-1}
$V = 3611.39$ (13) Å^3	$T = 83$ (2) K
$Z = 2$	Parallelepiped, black
$D_x = 1.895$ Mg m^{-3}	$0.18 \times 0.12 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	4151 independent reflections
	3980 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.053$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$\theta_{max} = 27.5°$
	$h = -22 \rightarrow 22$
$T_{min} = 0.718$, $T_{max} = 0.849$	$k = -22 \rightarrow 22$
24 331 measured reflections	$l = -15 \rightarrow 15$

Table 1
Selected interatomic distances (Å).

Mn1—O3	1.8611 (18)	Mn2—O6*A*	2.137 (5)
Mn1—O2^i	1.8804 (18)	Mn2—O6*B*	2.227 (4)
Mn1—O1	1.902 (2)	Mn2—O5	2.231 (2)
Mn1—O1^{ii}	1.9154 (18)	Mn3—O2	1.8923 (19)
Mn1—O1^i	1.9206 (17)	Mn3—O3	1.8977 (18)
Mn1—O4	1.918 (2)	Mn3—O9	1.964 (2)
Mn2—O3	1.8818 (18)	Mn3—O11^{ii}	1.993 (2)
Mn2—O2^i	1.8975 (19)	Mn3—O7*A*^{ii}	2.161 (7)
Mn2—O8	1.938 (2)	Mn3—O7*B*^{ii}	2.114 (6)
Mn2—O10	1.940 (2)	Mn3—O12	2.177 (2)

Symmetry codes: (i) $y, -x, -z$; (ii) $-y, x, -z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.073$
$S = 1.13$
4151 reflections
235 parameters
H atoms treated by a mixture of
    independent and constrained
    refinement
$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 2.6570P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: *SHELXL*97
    (Sheldrick, 1997)
Extinction coefficient: 0.00236 (18)
Absolute structure: Flack (1983),
    1975 Friedel pairs
Flack parameter = 0.102 (16)

Table 2
Hydrogen-bonding geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O12—H12$a$$\cdots$O13	0.85 (4)	1.88 (5)	2.722 (4)	172 (4)
O12—H12$b$$\cdots$O6$A$	0.84 (3)	2.23 (3)	3.016 (6)	156 (2)
O12—H12$b$$\cdots$O6$B$	0.84 (3)	1.85 (3)	2.613 (5)	150 (2)
O13—H13$a$$\cdots$O5^i	0.94	2.14	2.984 (3)	149
O13—H13$b$$\cdots$O7$A^{ii}$	0.84	2.49	3.244 (7)	151
O13—H13$b$$\cdots$O7$B^{ii}$	0.84	2.24	3.001 (6)	152
O13—H13$b$$\cdots$O11^{ii}	0.84	2.46	3.114 (3)	135
O13—H13$b$$\cdots$O9^{iii}	0.84	2.66	3.214 (3)	125
O15—H15$\cdots$O6A	1.02	1.68	2.687 (7)	169

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

The space-group assignment based on RT data ($I\bar{4}$) was confirmed at 83 (2) K by the Laue symmetry of the diffraction pattern, the systematic absences and the successful solution and refinement of the structure. An anisotropic model including all non-H atoms in the cluster, along with the crystallization water molecule, was used to determine the correct absolute structure. The R_1 and Flack parameters (Flack, 1983) were 0.0592 and 0.11 (3), respectively, compared with 0.0638 and 0.87 (4), respectively, for the inverted structure ($x' = x, y' = y, z' = -z$). A rigid-group refinement with isotropic displacement parameters, based on the molecular structure of acetic acid at the same temperature (Nahringbauer, 1970), was used for the disordered acetic acid of solvation. The two components (*A* and *B*) of the disordered acetate ligand were restrained to have the same geometry as O8/O9/C5/C6. The same isotropic displacement parameters were assigned to corresponding atoms in the two fragments, *A* and *B*. The final site-occupancy factors were 0.457 (7) and 0.543 (7) for *A* and *B*, respectively. The H atoms of the coordinated water molecule (O12) were located in difference Fourier maps and were refined isotropically with restrained O—H distances, while those of the extra-cluster water molecule (O13) were set in positions determined by neutron diffraction (Langan *et al.*, 2001). The H atoms in

the methyl groups were treated as riding in the tetrahedral approximation, with torsion-angle refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1192). Services for accessing these data are described at the back of the journal.

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