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A low-temperature neutron diffraction study of Mn_{12}-acetate

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In the low-temperature region, where the dodecanuclear mixed-valence manganese carboxylate hexadecaacetatotetra-aquadodecaoxododecamanganese bis(acetic acid) tetrahydrate, $[Mn_{12}O_{12}(C_2D_3O_2)_{16}(H_2O)_4]\cdot 2C_2HD_3O_2\cdot 4H_2O$, displays unusual magnetic properties, its structure is similar to that previously determined at room temperature [Lis (1980). *Acta Cryst.* B**36**, 2042–2046], differing only by a small change in the configuration of one of the coordinated acetate groups, related to the formation of additional hydrogen bonds, and by the orientation of the methyl groups. Since most of the magnetization density of this system resides on the Mn atoms, the consequences of these rearrangements for the magnetic properties of the compound are small.

Comment

The title dodecanuclear mixed-valence manganese carboxylate complex, commonly known as Mn_{12}, Mn_{12}-Ac or Mn_{12}-acetate, was first prepared and its crystal structure characterized at room temperature (RT) using X-ray diffraction by Lis (1980). This molecule has subsequently attracted substantial attention from both the physics and chemistry communities, because of its unusual low-temperature (LT) magnetic properties (Chudnovsky & Tejada, 1998; Chudnovsky, 1996; Schwarzschild, 1997). It exhibits anomalous hysteresis loops with steps at certain critical fields at integer multiples of 0.46 T. These field steps provide clear evidence of a quantum process, and Mn_{12} is a model system for the study of tunnelling of the magnetization (from up to down and *vice versa*). This is of interest for two reasons: firstly, because this is a direct manifestation of quantum physics in a macroscopic observable, just as in the Josephson effect or the quantum Hall effect, and secondly, because of technological interest in possible quantum demagnetization of magnetic memories. At a minimum, high-spin magnetic molecules like Mn_{12} are ideal magnetic nanoparticles, in which a direct connection can be made between microscopic intramolecular magnetic interactions and mesoscopic physics. Some headway has been made towards understanding the magnetic energy-level scheme and intramolecular interactions, both by means of inelastic neutron scattering (Hennion *et al.*, 1997; Zhong *et al.*, 1999; Mirebeau *et al.*, 1999) and electron paramagnetic resonance (Barra *et al.*, 1997; Hill *et al.*, 1998).

Recently, we have determined the internal magnetic structure of this molecule at LT using polarized neutron diffraction techniques (Robinson *et al.*, 2000). In these studies, it became clear that the structure reported by Lis (1980) was not in agreement with the neutron nuclear scattering factors. The present study was undertaken in order to provide a crystal structure for Mn_{12} at LT, to explain how this structure differs from that found at RT, to assess the consequences of these rearrangements on its magnetic properties and for the correct interpretation of the polarized neutron diffraction experiments. Our results are in agreement with the qualitative conclusions of Mirebeau *et al.* (1999) and indicate that the differences are small, related to changes in hydrogen bonding, and are unlikely to influence the magnetization density significantly.

In the LT structure of Mn_{12}, a water molecule coordinates directly with atom Mn3 through its O12 atom, and donates

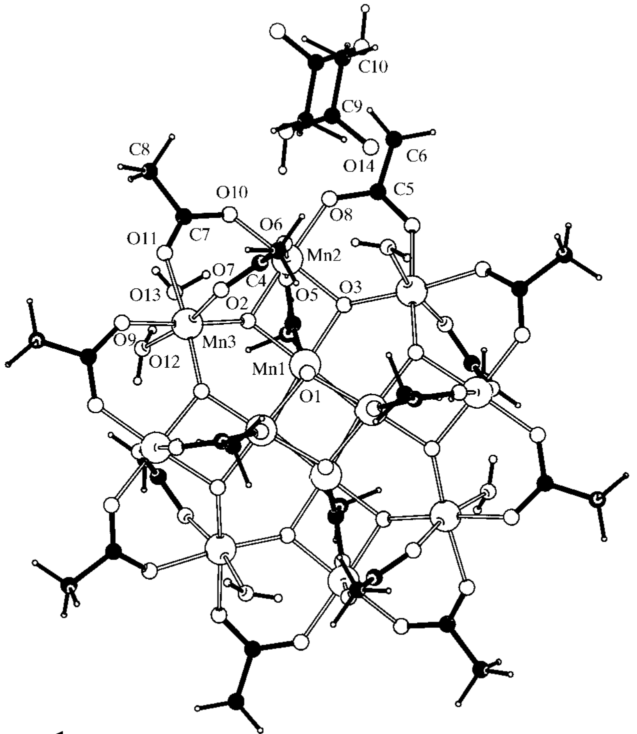

Figure 1
The molecular structure of Mn_{12} at 20 K, projected onto the tetragonal basal plane ([001] direction). H, D, C, O and Mn atoms are represented by spheres of increasing radius. Only C, O and Mn atoms in the asymmetric unit have been labeled, for clarity. One half-occupancy acetic acid molecule is shown superimposed on a symmetry-related half-occupancy acetic acid molecule at the same position.

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hydrogen bonds to the O6 group of the C4 carboxylate ligand (H3) and to the O13 atom of the second water molecule (H1). At RT, there are no further hydrogen-bonding interactions. At LT, there is a more extensive hydrogen-bonding network which slightly displaces Mn3 and its ligands. The orientation of the solvent acetic acid molecule at LT permits the acid O17 atom to form a second hydrogen bond to the O6 atom, *via* atom H4, in one of its two symmetry-related half-occupied positions. Despite the fact that this H-atom position has at most half occupancy, the geometry of this bond is good. The second water molecule donates H2 to the O5 group of the C2 carboxylate ligand and H4 to three possible acceptors, *i.e.* atoms O7, O9 and O11 of carboxylate ligands C4, C6 and C8. The four-centred hydrogen-bond arrangement has two major components between O13 and O7, and between O13 and O11, and a minor component between O13 and O9.

Although nominally deuterated, the crystal used in this work has undergone back substitution of H for D, presumably due to exposure to the atmosphere during crystal mounting and handling, resulting in the water and acetic acid H1–H5 atoms being H rather than D. Our measured mosaic value of 0.4° FWHM (full width at half maximum) is consistent with, if slightly smaller than, the value recently quoted by Bellessa *et al.* (1999), and the fact that it is much greater than 0.01° gives support to the analysis in their article.

Experimental

Nominally fully deuterated crystals of Mn_{12} were prepared from their perdeuterated components as previously described by Sessoli *et al.* (1993). A needle-shaped crystal (50 mg in mass) was mounted on the D9 four-circle diffractometer at the Institut Laue Langevin and the temperature lowered to 20 K at a rate of 2 K min^{-1} using a Displex cooling device.

Crystal data

$[Mn_{12}O_{12}(C_2D_3O_2)_{16}(H_2O)_4]\cdot$-
$2C_2HD_3O_2\cdot4H_2O$
$M_r = 2115.26$
Tetragonal, $I\bar{4}$
$a = 17.123\ (8)$ Å
$c = 12.255\ (6)$ Å
$V = 3593\ (3)$ Å^3
$Z = 2$
$D_x = 1.867$ Mg m^{-3}

Neutron radiation
$\lambda = 0.84050$ Å
Cell parameters from 1727 reflections
$\theta = 4.4–31.0°$
$\mu = 0.09$ mm^{-1}
$T = 20\ (2)$ K
Needle, red–black
2 × 2 × 6 mm

Data collection

D9 four-circle diffractometer
Equatorial geometry
1727 measured reflections
1727 independent reflections
1600 reflections with $I > 2\sigma(I)$
$\theta_{max} = 31°$

$h = 0 \rightarrow 20$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 14$
5 standard reflections
every 10 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.209$
$S = 1.57$
1727 reflections
423 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 128.3191P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 3.24 \times 10^{-11}$ cm Å^{-3}
$\Delta\rho_{min} = -1.65 \times 10^{-11}$ cm Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H1···O13	0.98 (2)	1.76 (2)	2.741 (13)	174 (2)
O12—H3···O6^{i}	0.85 (4)	1.87 (3)	2.706 (13)	167 (3)
O13—H2···O5	0.94 (3)	2.13 (3)	2.974 (11)	149 (2)
O13—H4···O7^{ii}	0.84 (5)	2.32 (4)	3.089 (12)	151 (3)
O13—H4···O11^{ii}	0.84 (5)	2.43 (4)	3.086 (12)	135 (3)
O13—H4···O9^{ii}	0.84 (5)	2.64 (4)	3.205 (11)	125 (3)
O17—H5···O6	1.01 (5)	1.90 (4)	2.89 (3)	169 (4)

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

Integrated intensities were extracted from the data recorded by the D9 position-sensitive detector (psd), using custom-designed software, and these were corrected for absorption and Lorentz effects. It was found that all labile D-atom positions were occupied by H atoms. All atoms of the central $Mn_{12}O_{12}$ core of the molecule, the 16 carboxylate ligands, an additional solvent acetic acid molecule, an acid H atom and two water molecules were refined. H-atom parameters were restrained so that they approximated to isotropic behaviour, although the corresponding U_{iso} values were free to vary. Atoms closer than 1.7 Å were restrained to have the same anisotropic displacement parameters. H and non-H atoms were restrained in the same way. This approach was used because there were an insufficient number of reflections for unrestrained refinement.

Data collection: ILL program *MAD*; cell refinement: ILL program *RAFD*9; data reduction: ILL program *RETREAT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1327). Services for accessing these data are described at the back of the journal.

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