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Redetermination of the mixed-valence hexanuclear manganese oxide complex di-μ_4-oxo-tetra-μ_3-pivalato-hexa-μ_2-pivalato-tetrakis(pivalic acid)dimanganese(III)-tetramanganese(II) at 100 K

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Key indicators

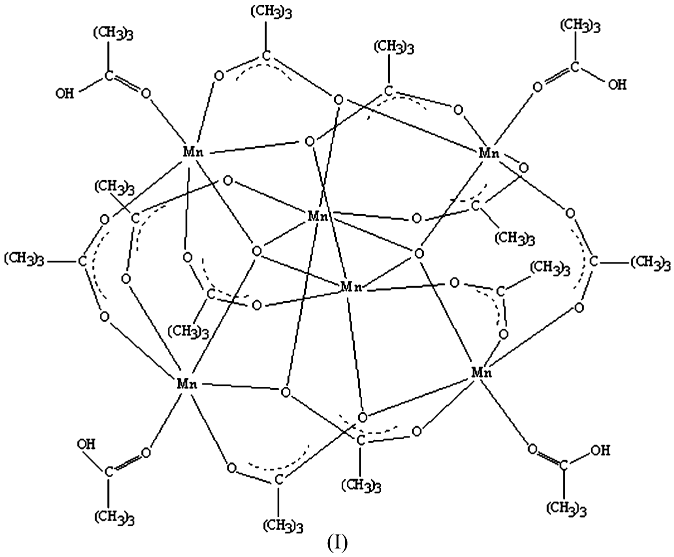
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.009 Å
R factor = 0.062
wR factor = 0.164
Data-to-parameter ratio = 16.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, $[Mn_6(C_4H_9O_2)_{10}O_2(C_4H_{10}O_2)_4]$, has been redetermined at 100 K. The improved precision of the structure determination allowed the determination of the positions of the Mn^{III} atoms in the Mn_6O_2 core. The $Mn^{III}\cdots Mn^{III}$ distance of 2.744 (3) Å is significantly shorter than the remaining $Mn^{II}\cdots Mn^{III}$ distances [3.106 (3)–3.137 (3) Å].

Comment

High nuclearity oxide-bridged Mn complexes are of considerable interest, due to antiferromagnetic coupling and electron delocalization in mixed-valence clusters. This has became a multidisciplinary area of study, currently involving biochemical processes, preparation of molecular ferromagnets and coordination chemistry building blocks (Dismukes, 1986; Cannon & White, 1988; Miller *et al.*, 1988; Schake *et al.*, 1989; Jayasooriya *et al.*,1989; Wu *et al.*, 1998).



(I)

This paper reports a 100 K redetermination of the crystal structure of a very interesting mixed-valence hexanuclear manganese complex, (I), which has been previously prepared and characterized by Baikie *et al.* (1986). Their room-temperature structure was of low precision due to disorder of the terminal *tert*-butyl groups. Additionally, almost at the same time, Gerbeleu *et al.* (1987) reported a low-precision crystal structure of the same polynuclear Mn complex. However, they did not consider this compound as a mixed-valence Mn compound, but as a coordination compound of Mn^{III}, with all

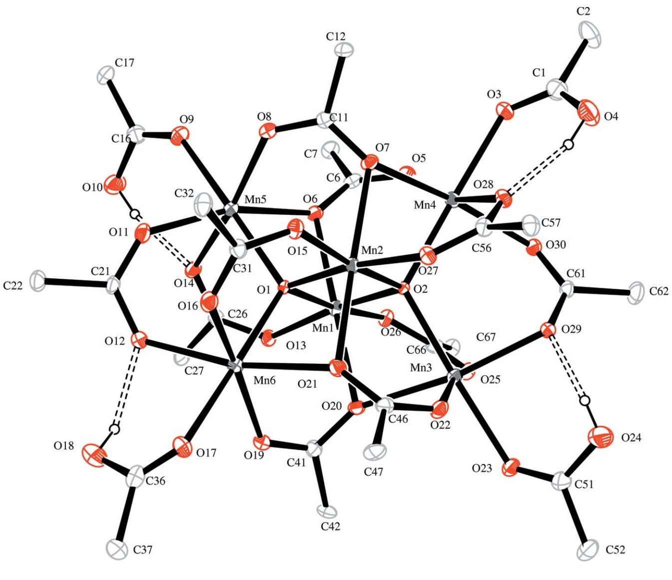


Figure 1
The molecular structure and atom-labelling scheme for (I). Displacement ellipsoids are drawn at the 20% probability level. *tert*-Butyl methyl groups and H atoms, except those of the undeprotonated acid ligands, have been omitted for clarity. Open dashed lines indicate hydrogen bonds.

pivalic acid ligands deprotonated. Whereas Baikie *et al.* (1986) indicated the most important features of (I), they could only point to inner metal centres in the $[Mn_6O_2]^{10+}$ cluster as possible sites of Mn^{III} atoms, because their room-temperature data did not provide sufficient support for distinction between Mn^{II} and Mn^{III} atoms.

Our results show that, in compound (I), the six Mn atoms are six-coordinate and possess distorted octahedral geometry. Analysis of the Mn$\cdots$Mn and Mn—O distances clearly points to Mn1 and Mn2 as the metal centres with the higher oxidation state. At 100 K, the Mn1$\cdots$Mn2 distance of 2.744 (3) Å is significantly shorter than the other Mn$\cdots$Mn distances [3.106 (3)–3.137 (3) Å] within the Mn_6O_2 cluster. For the room-temperature structure (Baikie *et al.*, 1986), the Mn1$\cdots$Mn2 contact was 2.949 Å, and the other Mn$\cdots$Mn distances were within the range 3.064–3.152 Å. The Mn—O distances between atoms Mn1, Mn2 and O1, O2, with a mean value of 1.864 (4) Å, are significantly shorter than the distances of atoms Mn3, Mn4, Mn5 and Mn6 to atoms O1 and O2 [mean value 2.159 (4) Å], which is in agreement with the higher oxidation state of the former Mn atoms. The Mn^{III} atoms show a typical Jahn–Teller distortion, with four shorter and two longer Mn—O bonds. The long pair form a long axis in a pseudo-octahedral coordination (Schake *et al.*, 1989).

The terminal ligands are identified as pivalic acid. The O—H groups of these ligands are involved in intramolecular hydrogen bonds (Table 2).

Experimental

Manganese(II) chloride ($MnCl_2\cdot4H_2O$, 8.8 g, 44 mmol) and potassium permanganate ($KMnO_4$, 0.82 g, 5.2 mmol) were placed in a flask, and then pyridine (40 ml), pivalic acid (60 ml) and distilled water (20 ml) were added. The mixture was heated at 333 K with stirring for 4 h, left to cool and filtered. The two layers which formed were separated and the black organic layer was left to evaporate at 313 K. After several days, large red–brown crystals of (I) were collected, together with a black powder. The crystals were separated, rinsed with water and dried in air.

Crystal data

$[Mn_6(C_4H_9O_2)_{10}O_2(C_4H_{10}O_2)_4]$
$M_r = 1781.39$
Orthorhombic, *Pbca*
$a = 26.4265$ (5) Å
$b = 24.8578$ (5) Å
$c = 28.1714$ (7) Å
$V = 18505.9$ (7) Å^3
$Z = 8$
$D_x = 1.279$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.86$ mm^{-1}
$T = 100$ (2) K
Prism, red-brown
0.58 × 0.51 × 0.44 mm

Data collection

Stoe IPDS2 diffractometer
Rotation method scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
$T_{min} = 0.612$, $T_{max} = 0.684$
16317 measured reflections
16156 independent reflections
9653 reflections with $I > 2\sigma(I)$
$R_{int} = 0.112$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.164$
$S = 0.95$
16156 reflections
1013 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1086P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.98$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: none

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	1.846 (4)	Mn2—O21	2.222 (5)
Mn1—O2	1.877 (4)	Mn2—O7	2.249 (4)
Mn1—O13	1.956 (4)	Mn3—O2	2.151 (4)
Mn1—O26	1.985 (4)	Mn3—O23	2.242 (4)
Mn1—O20	2.229 (4)	Mn4—O2	2.171 (3)
Mn1—O6	2.246 (4)	Mn4—O3	2.207 (4)
Mn1—Mn2	2.744 (3)	Mn5—O1	2.155 (4)
Mn2—O1	1.886 (4)	Mn5—O9	2.204 (4)
Mn2—O2	1.845 (4)	Mn6—O1	2.159 (4)
Mn2—O15	2.001 (4)	Mn6—O17	2.216 (4)
Mn2—O27	1.959 (4)		
O1—Mn1—O2	85.20 (16)	O2—Mn1—Mn2	42.04 (11)
O13—Mn1—O26	85.95 (17)	O1—Mn2—O2	85.06 (17)
O1—Mn1—O20	99.50 (17)	O1—Mn2—O21	84.64 (16)
O2—Mn1—O20	85.44 (17)	O2—Mn2—O7	86.54 (16)
O1—Mn1—O6	85.62 (17)	Mn5—O1—Mn6	120.64 (15)
O2—Mn1—O6	97.97 (17)	Mn3—O2—Mn4	120.65 (16)
O1—Mn1—Mn2	43.23 (12)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O28	0.82	1.80	2.602 (6)	164
O10—H10$\cdots$O14	0.82	1.85	2.661 (6)	168
O18—H18$\cdots$O12	0.82	1.90	2.606 (6)	144
O24—H24$\cdots$O29	0.82	1.78	2.582 (6)	166

Acta Cryst. (2006). E**62**, m1442–m1444 Poyraz *et al.* • $[Mn_6(C_4H_9O_2)_{10}O_2(C_4H_{10}O_2)_4]$ **m1443**

Some *tert*-butyl groups showed high displacement parameters, but no reasonable model of disorder could be obtained. H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with O—H = 0.82 Å and C—H = 0.96 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,O), or 1.5$U_{\rm eq}$(C) for methyl atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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