μ_3-Oxo-hexa-μ_2-pivalato-(pivalic acid-κO)-bis(pyridine-κN)trimanganese(III,III,II)

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The asymmetric unit of the title compound, [Mn₃(C₅H₉O₂)₆O(C₅H₅N)₂(C₅H₁₀O₂)], comprises two independent and similar [Mn^{III}₂Mn^{II}O{(CH₃)₃CCO₂}₆(py)₂(CH₃)₃CCOOH] (py = pyridine) molecules each with an Mn₃(μ_3-O) core. In each molecule, the Mn atoms have octahedral geometry with two coordinated pyridines bonded to two Mn^{III} and a terminal pivalic acid coordinated to the Mn^{II} atom.

Comment

Oxo-centered triangular Mn complexes, Mn₃(μ_3-O), have been considered as effective models for studying M–M interactions in mixed-metal clusters, and electron delocalization in mixed-valence clusters. A wide variety of mixed-metal combinations and mixed-valency combinations have been reported (Cannon & White, 1988; Jayasooriya *et al.*, 1989; Wu *et al.*, 1998). In the Mn₃(μ_3-O) systems, the geometry of the central core remains relatively constant throughout the series and is often close to having threefold symmetry with a planar M_3O unit (Wu *et al.*, 1998).

(I)
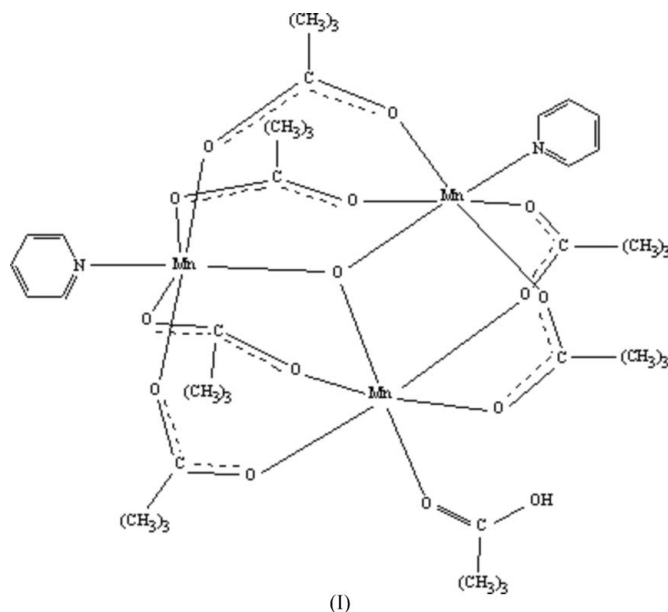
In (I), the three Mn atoms form a regular triangular geometry and are linked by a central μ_3-O atom (Fig. 1). The asymmetric unit consists of two independent and similar molecules (A and B), [Mn^{III}₂Mn^{II}O{(CH₃)₃CCO₂}₆(py)₂(CH₃)₃CCO-
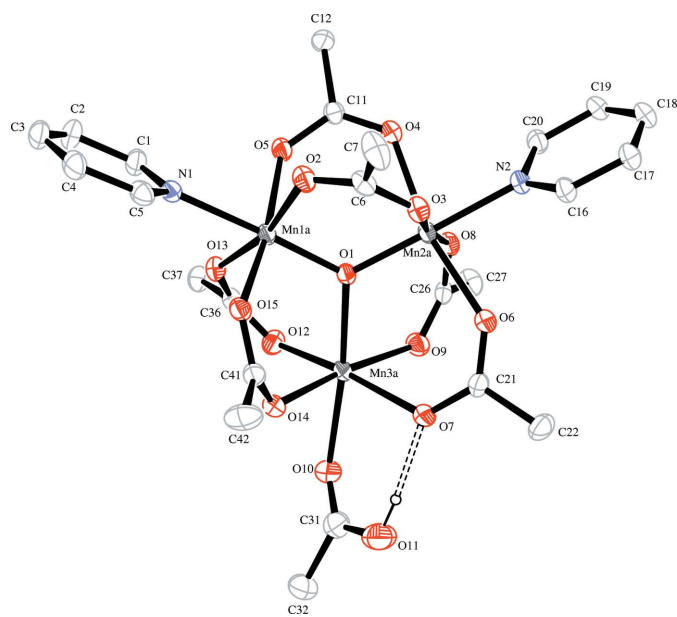
Figure 1
The molecular structure and atomic labelling scheme of molecule A in (I). Displacement ellipsoids are drawn at the 20% probability level. The *tert*-butyl methyl groups and H atoms, except for those of the pivalic acid ligands, have been omitted for clarity and open dashed lines indicate hydrogen bonds.

OH]. The Mn atoms in both molecules have two different types of Mn—(μ_3-O) bond lengths (Table 1). The Mn$_3$ triangle is isosceles and clearly indicates that one Mn atom differs from the other two. This is most logically interpreted in terms of identifying Mn3A and Mn3B as having different oxidation states from the other Mn atoms. This asymmetry is most noticeable in the Mn$_3$O central core, with longer Mn3A—O1 and Mn3B—O16 distances.

The planes of the coordinated pyridines are almost orthogonal to the central Mn$_3$O core. The Mn—N bond lengths in A and B are quite similar and in the range 2.081 (3) to 2.094 (4) Å: these bond lengths agree with Mn^{III}—N for related Mn$_3$(μ_3-O) complexes [2.061 (10)–2.280 (7) Å; Baikie *et al.*, 1978; Baikie *et al.*, 1980; Vincent *et al.*, 1987; Wu *et al.*, 1998]. Other selected bond lengths and angles agree well with the literature values (see previous references).

In both molecules, the Mn^{III} atoms show a typical Jahn–Teller distortion, with two longer and two shorter Mn—O bonds. The long pair form a long axis in a pseudo-octahedral coordination (Wu *et al.*, 1998). The crystal structure is stabilized by intermolecular O—H⋯O hydrogen bonds involving the H atoms of terminal pivalic acid groups and O atoms of the pivalate groups (Table 2).

Experimental

A mixture of molten pivalic acid (60 ml), pyridine (40 ml) and water (20 ml) was added to a mixture of ground MnCl$_2$·4H$_2$O (8.8 g, 44 mmol) and finely ground KMnO$_4$ (0.81 g, 5.2 mmol) in a 250 ml conical flask. The mixture was heated at 323–333 K with stirring and

then the mixture was left to cool and filtered. Two layers in the flask were separated and after several days black crystals from the organic layer were collected, washed thoroughly with water and dried in air.

Crystal data

[Mn$_3$(C$_5$H$_9$O$_2$)$_6$O(C$_5$H$_5$N)$_2$-(C$_5$H$_{10}$O$_2$)]	$V = 11308.5$ (5) Å^3
$M_r = 1047.88$	$Z = 8$
Monoclinic, $P2_1/c$	$D_x = 1.231$ Mg m^{-3}
$a = 27.1668$ (7) Å	Mo $K\alpha$ radiation
$b = 19.3139$ (4) Å	$\mu = 0.72$ mm^{-1}
$c = 22.8444$ (5) Å	$T = 150$ (2) K
$\beta = 109.361$ (2)°	Prism, black
	$0.52 \times 0.32 \times 0.22$ mm

Data collection

Stoe IPDS-2 diffractometer	20095 measured reflections
Rotation method scans	19951 independent reflections
Absorption correction: integration	12017 reflections with $I > 2\sigma(I)$
(*X-RED32*; Stoe & Cie, 2002)	$R_{int} = 0.110$
$T_{min} = 0.759$, $T_{max} = 0.854$	$\theta_{max} = 25.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	$(\Delta/\sigma)_{max} = 0.024$
$S = 1.05$	$\Delta\rho_{max} = 0.62$ e Å^{-3}
19951 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}
1220 parameters	Extinction correction: *SHELXL97*
H-atom parameters constrained	Extinction coefficient: none

Table 1
Selected geometric parameters (Å, °).

Mn1A—O1	1.810 (3)	Mn1B—O16	1.818 (3)
Mn1A—O2	2.140 (3)	Mn1B—O17	2.198 (3)
Mn1A—O5	2.004 (3)	Mn1B—O19	1.967 (3)
Mn1A—O13	2.076 (3)	Mn1B—O28	1.962 (3)
Mn1A—O15	2.008 (3)	Mn1B—O30	2.119 (3)
Mn2A—O1	1.814 (3)	Mn2B—O16	1.816 (3)
Mn2A—O3	1.978 (3)	Mn2B—O18	1.966 (3)
Mn2A—O4	2.167 (3)	Mn2B—O20	2.162 (3)
Mn2A—O6	2.145 (3)	Mn2B—O21	1.960 (3)
Mn2A—O8	1.960 (3)	Mn2B—O23	2.174 (3)
Mn3A—O1	2.124 (3)	Mn3B—O16	2.109 (3)
Mn3A—O7	2.207 (3)	Mn3B—O22	2.133 (3)
Mn3A—O9	2.130 (3)	Mn3B—O24	2.221 (3)
Mn3A—O10	2.224 (4)	Mn3B—O25	2.251 (3)
Mn3A—O12	2.129 (4)	Mn3B—O27	2.177 (3)
Mn3A—O14	2.169 (3)	Mn3B—O29	2.131 (3)
O1—Mn1A—N1	177.67 (13)	O16—Mn1B—N3	178.90 (14)
O1—Mn2A—N2	178.47 (15)	O16—Mn2B—N4	176.27 (14)
Mn1A—O1—Mn2A	122.36 (15)	Mn1B—O16—Mn2B	124.60 (15)
Mn1A—O1—Mn3A	118.09 (14)	Mn1B—O16—Mn3B	115.50 (13)
Mn2A—O1—Mn3A	119.55 (14)	Mn2B—O16—Mn3B	119.88 (14)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O11—H11⋯O7	0.84	1.77	2.605 (5)	172
O26—H26⋯O24	0.84	1.73	2.560 (4)	170

Ten *tert*-butyl groups are disordered, giving unrealistically anisotropic displacement parameters and bond lengths. The refinement was performed with soft restraints for the split C atom sites, leading to

satisfactory refinement results. For the disordered *tert*-butyl groups the C—CH$_3$ distances were constrained to 1.52 (2) Å. Fixed occupancy factors of 0.5 were applied for both positions initially as it was possible to obtain reasonable refined values for related pairs: these were subsequently allowed to vary but constrained to sum to unit occupancy. All non-H atoms, except for the disordered C atoms, were assigned anisotropic displacement parameters. The H atoms were placed in idealized positions and refined using a riding model, with distances in the range 0.84–0.98 Å and U_{iso}(H) = 1.2U_{eq}(C,O) or 1.5U_{eq}(methyl C).

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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