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Key indicators

Single-crystal X-ray study

$T = 150$ K

Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å

Disorder in main residue

R factor = 0.057

wR factor = 0.135

Data-to-parameter ratio = 16.5

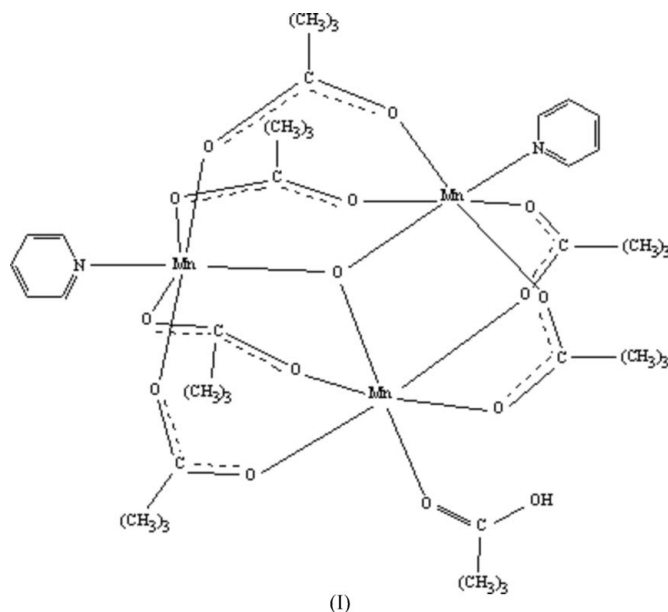
For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

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

The asymmetric unit of the title compound, $[\text{Mn}_3(\text{C}_5\text{H}_9\text{O}_2)_6\text{O}(\text{C}_5\text{H}_5\text{N})_2(\text{C}_5\text{H}_{10}\text{O}_2)]$, comprises two independent and similar $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}\text{O}\{(\text{CH}_3)_3\text{CCO}_2\}_6(\text{py})_2(\text{CH}_3)_3\text{CCOOH}]$ (py = pyridine) molecules each with an $\text{Mn}_3(\mu_3\text{-O})$ 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, $\text{Mn}_3(\mu_3\text{-O})$, 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 $\text{Mn}_3(\mu_3\text{-O})$ systems, the geometry of the central core remains relatively constant throughout the series and is often close to having threefold symmetry with a planar $M_3\text{O}$ unit (Wu *et al.*, 1998).



In (I), the three Mn atoms form a regular triangular geometry and are linked by a central $\mu_3\text{-O}$ atom (Fig. 1). The asymmetric unit consists of two independent and similar molecules (A and B), $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}\text{O}\{(\text{CH}_3)_3\text{CCO}_2\}_6(\text{py})_2(\text{CH}_3)_3\text{CCO}-$

Received 27 September 2006

Accepted 13 November 2006

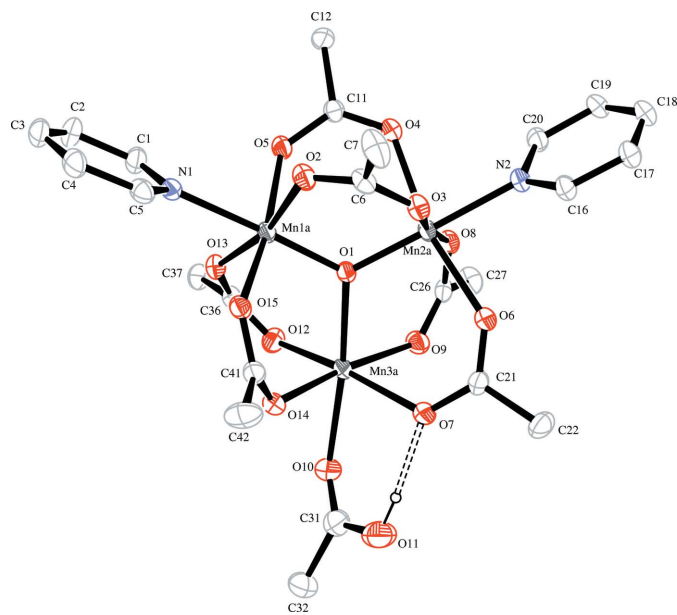


Figure 1
The molecular structure and atomic labelling scheme of molecule *A* in (I). Displacement ellipsoids are drawn at the 20% probability level. The *tert*-butyl methyl groups and H atoms, except for those of the pivalic acid ligands, have been omitted for clarity and open dashed lines indicate hydrogen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

OH]. The Mn atoms in both molecules have two different types of Mn—(μ_3 -O) bond lengths (Table 1). The Mn₃ 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 Mn₃O central core, with longer Mn3A—O1 and Mn3B—O16 distances.

The planes of the coordinated pyridines are almost orthogonal to the central Mn₃O 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 Mn₃(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 MnCl₂·4H₂O (8.8 g, 44 mmol) and finely ground KMnO₄ (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

[Mn₃(C₅H₉O₂)₆O(C₅H₅N)₂·
(C₅H₁₀O₂)]
M_r = 1047.88
Monoclinic, *P*2₁/*c*
a = 27.1668 (7) Å
b = 19.3139 (4) Å
c = 22.8444 (5) Å
 β = 109.361 (2)°

V = 11308.5 (5) Å³
Z = 8
D_x = 1.231 Mg m⁻³
Mo *K*α radiation
 μ = 0.72 mm⁻¹
T = 150 (2) K
Prism, black
0.52 × 0.32 × 0.22 mm

Data collection

Stoe IPDS-2 diffractometer
Rotation method scans
Absorption correction: integration
(*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.759, *T_{max}* = 0.854

20095 measured reflections
19951 independent reflections
12017 reflections with *I* > 2σ(*I*)
R_{int} = 0.110
 θ_{\max} = 25.1°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.057
wR(*F*²) = 0.123
S = 1.05
19951 reflections
1220 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δσ)_{max} = 0.024
Δρ_{max} = 0.62 e Å⁻³
Δρ_{min} = -0.41 e Å⁻³
Extinction correction: *SHELXL97*
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, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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–CH₃ 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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{O})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

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*.

The authors acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for use of the Stoe IPDS2 diffractometer purchased under grant F.279 of the University

Research Fund and also thank Gazi University Scientific Research Unit (BAP-04/2004–12) for financial support for this study.

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