

Bis(μ -6-hydroxypicolinato)- μ -oxo-bis[dipyridinemanganese(III)] monohydrate

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Received 6 May 2004

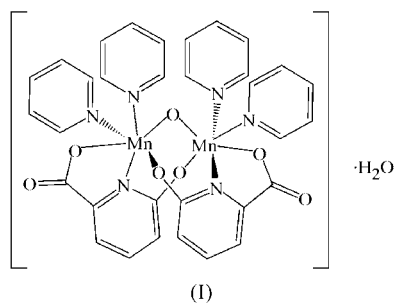
Accepted 24 May 2004

Online 22 June 2004

The title compound, $[\text{Mn}_2(\mu\text{-O})(\text{C}_6\text{H}_3\text{NO}_3)_2(\text{C}_5\text{H}_5\text{N})_4]\cdot\text{H}_2\text{O}$, was isolated from the reaction of 2,6-pyridinedicarboxylic acid with $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ in pyridine. The dimanganese complex has twofold symmetry; the Mn^{III} atoms are bridged by one oxo and two amidate ligands and show compressed octahedral Jahn–Teller distortion. The molecular packing comprises a three-dimensional structure constructed by means of extensive intermolecular interactions, including three kinds of hydrogen bonds and π – π interactions.

Comment

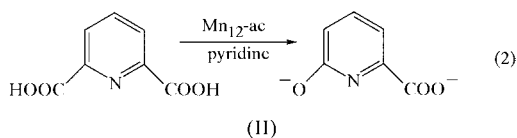
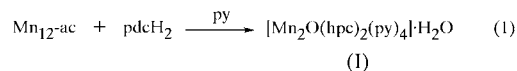
The discovery of the role of manganese at the active sites in various enzymatic systems has given considerable impetus to research in the field of polynuclear complexes of manganese. The manganese catalase in *Lactobacillus platarum* has been shown to contain a dimanganese unit with $[\text{Mn}_2^{\text{III}}(\mu\text{-oxo})(\mu\text{-carboxylato})_2]$ cores (Fronko *et al.*, 1988). Several Mn complexes containing the $[\text{Mn}_2(\mu\text{-O})]^{4+}$ core have been



reported so far (Sheats *et al.*, 1987; Wieghardt *et al.*, 1988; Wu *et al.*, 1990; Hotzelmann *et al.*, 1992; Vincent *et al.*, 1993; Gultneh *et al.*, 1995; Canada-Vilalta *et al.*, 2004). The two Mn ions in those complexes are bridged by oxo and dicarboxylate ligands, and the six-coordination around each Mn ion is completed by ligands such as water, CH_3CN and bipyridine (py). We report here the crystal structure of the title

compound, $[\text{Mn}_2(\mu\text{-O})(\text{hpc})_2(\text{py})_4]\cdot\text{H}_2\text{O}$, (I), containing an $[\text{Mn}_2^{\text{III}}(\mu\text{-O})]^{4+}$ core bridged by a 6-hydroxypicolinate ion (hpc^{2-}).

Complex (I) was obtained during the course of our attempt to synthesize new multinuclear manganese complexes using 2,6-pyridinedicarboxylic acid (pdcH₂) and $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ (abbreviated to $\text{Mn}_{12}\text{-ac}$) in pyridine (see equation 1). In this reaction, the pdcH₂ ligand could not replace the acetate ions of $\text{Mn}_{12}\text{-ac}$ but was oxidized to hpc^{2-} (see equation 2). A possible mechanism may be oxidation of pdcH₂ followed by removal of carbon dioxide.



Complex (I) consists of two hpc^{2-} ions, four pyridine rings and two Mn^{III} ions bridged by an oxo ion (Fig. 1 and Table 1). Each Mn ion is coordinated by two hpc^{2-} ions in bridging and chelating fashions, so that the molecule has a twofold axis perpendicular to the line connecting the two Mn^{III} ions and passing through the μ -oxo ion. The N1/C1/O1 amidate group of each hpc^{2-} ion bridges the two Mn^{III} ions, while the N1/C5/C6/O2 carboxypyridine group chelates to an Mn^{III} ion to form a five-membered ring. Coordination of two pyridine rings completes a distorted octahedral six-coordination around each Mn ion.

The Mn ions exhibit a marked Jahn–Teller (J–T) distortion, as expected for a high-spin d^4 Mn^{III} ion (Cotton *et al.*, 1999). The Mn1–O2 and Mn1–O4 bond distances [1.939 (2) and 1.789 (1) Å, respectively] are the shortest among the six Mn–N and Mn–O bonds, and the other four are all longer than 2.00 Å, indicating a compression type of J–T distortion.

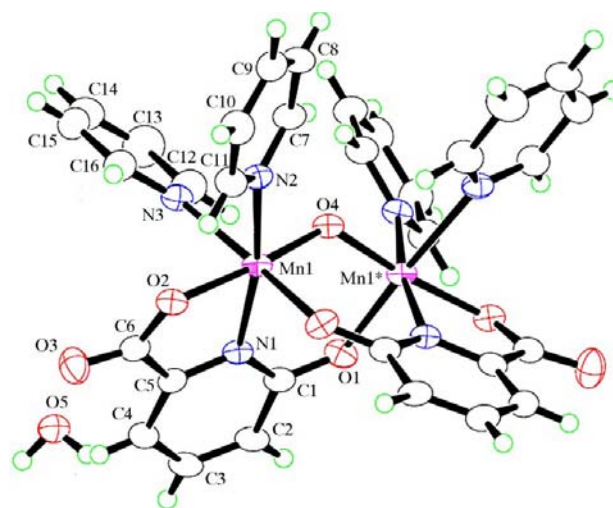


Figure 1
The molecular structure of (I), with the atom-numbering scheme, showing 50% probability displacement ellipsoids. The atom labelled with an asterisk (*) is at the symmetry position $(1-x, y, \frac{1}{2}-z)$.

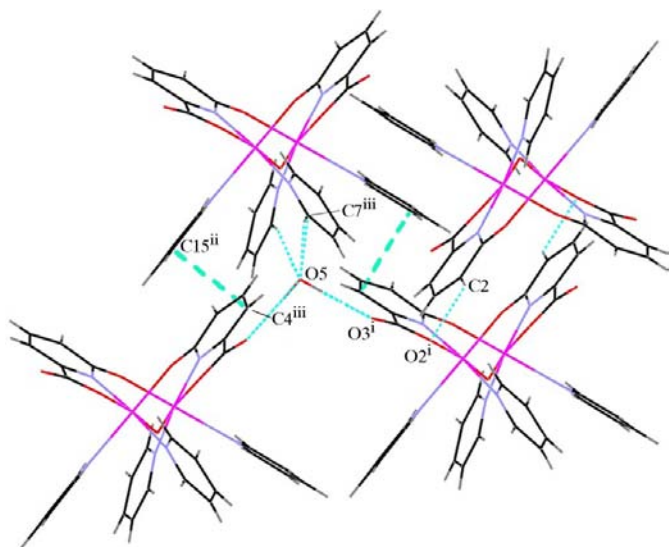


Figure 2
The molecular packing, showing intermolecular π - π interactions (dashed lines) and hydrogen bonds (dotted lines). [Symmetry codes: (i) $x, -y, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$; (iii) $2 - x, -y, 1 - z$.]

Among nine complexes with a similar $[\text{Mn}_2(\mu\text{-O})]^{4+}$ core structure, three show compressed J-T distortion; two of them (Wieghardt *et al.*, 1985; Sheats *et al.*, 1987) have tridentate capping ligands, such as Me_3TACN (Me_3TACN is N,N',N'' -trimethyl-1,4,7-triazacyclononane) or $\text{HB}(\text{pz})_3$ [$\text{HB}(\text{pz})_3$ is hydrotris(1-pyrazolyl)borate], and the other example (Vincent *et al.*, 1993) has a strong coordination with an N_3^- ligand. In (I), the effect of the tridentate hpc^{2-} ion together with the strong coordination of the μ -oxo ligand probably induces the compressed J-T distortion. The $\text{Mn1}-\text{N1}(\text{hpc}^{2-})$ distance [2.094 (2) Å] is shorter than the $\text{Mn1}-\text{N2}/\text{N3}(\text{py})$ bonds [2.169 (2) and 2.325 (2) Å], which is also attributable to the effect of the tridentate nature of the hpc^{2-} ion. The $\text{Mn1}\cdots\text{Mn1}^{\text{iv}}$ [symmetry code: (iv) $1 - x, y, \frac{1}{2} - z$] distance is 3.172 (1) Å, which is longer than the distances reported so far (3.14–3.16 Å) for complexes with the similar $[\text{Mn}_2(\mu\text{-O})]^{4+}$ core structure. This difference is due to the larger $\text{Mn}-\text{O}-\text{Mn}^{\text{iv}}$ angle [125.0 (1)°] in (I).

The molecular packing is shown in Fig. 2. Water atom O5 lies on a twofold axis. Each complex molecule is connected to neighboring molecules *via* π - π interactions and hydrogen bonds (Table 2), resulting in a three-dimensional structure. The shortest $\text{C}\cdots\text{C}$ distance between the pyridine and hpc^{2-} groups of neighboring complex molecules is 3.292 (4) Å for $\text{C4}\cdots\text{C15}(\frac{3}{2}-x, y - \frac{1}{2}, \frac{1}{2} - z)$, indicating a strong π - π interaction. The dihedral angle between these two planes is 17.28 (10)°. The absence of any counter-ions in (I) enables such intermolecular interactions.

Experimental

$\text{Mn}_{12}\text{-ac}$ was prepared according to a literature method (Lis, 1980). To a solution of $\text{Mn}_{12}\text{-ac}$ (0.05 mmol) in pyridine (10 ml) was added pdCH_2 (0.4 mmol). After stirring for 30 min, the mixture was filtered and the dark-brown filtrate was left to stand, allowing slow

evaporation of the solvent at room temperature. Brown block-shaped crystals of (I) suitable for X-ray analysis were obtained after four weeks. IR (KBr pellet, cm^{-1}): 3198 (*b*), 3087 (*m*), 2923 (*m*), 1654 (*m*), 1632 (*m*), 1592 (*s*), 1570 (*m*), 1435 (*m*), 1396 (*m*), 1371 (*m*), 1278 (*w*), 1193 (*w*), 1015 (*w*), 910 (*w*), 785 (*w*), 720 (*m*), 699 (*w*), 661 (*w*).

Crystal data

$[\text{Mn}_2\text{O}(\text{C}_6\text{H}_3\text{NO}_3)_2(\text{C}_5\text{H}_5\text{N})_4]\cdot\text{H}_2\text{O}$	Mo $K\alpha$ radiation
$M_r = 734.48$	Cell parameters from 4653 reflections
Monoclinic, $C2/c$	$\theta = 3.1\text{--}27.5^\circ$
$a = 13.606$ (8) Å	$\mu = 0.88$ mm^{-1}
$b = 16.379$ (9) Å	$T = 150.2$ K
$c = 14.289$ (9) Å	Block, brown
$\beta = 104.118$ (7)°	$0.20 \times 0.15 \times 0.15$ mm
$V = 3088$ (3) Å ³	
$Z = 4$	
$D_x = 1.580$ Mg m^{-3}	

Data collection

Rigaku/MSC Mercury CCD diffractometer	3512 independent reflections
ω scans	3144 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Jacobson, 1998)	$R_{\text{int}} = 0.034$
$T_{\text{min}} = 0.764, T_{\text{max}} = 0.876$	$\theta_{\text{max}} = 27.5^\circ$
11 903 measured reflections	$h = -13 \rightarrow 17$
	$k = -18 \rightarrow 21$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 5.1887P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.40$ e Å ⁻³
3144 reflections	$\Delta\rho_{\text{min}} = -0.46$ e Å ⁻³
260 parameters	
Only coordinates of H atoms refined	

Table 1

Selected geometric parameters (Å, °).

$\text{Mn1}-\text{Mn1}^{\text{iv}}$	3.172 (1)	$\text{Mn1}-\text{N1}$	2.094 (2)
$\text{Mn1}-\text{O1}^{\text{iv}}$	2.083 (2)	$\text{Mn1}-\text{N2}$	2.169 (2)
$\text{Mn1}-\text{O2}$	1.939 (2)	$\text{Mn1}-\text{N3}$	2.325 (2)
$\text{Mn1}-\text{O4}$	1.789 (1)		
$\text{O1}^{\text{iv}}-\text{Mn1}-\text{O2}$	90.95 (8)	$\text{O2}-\text{Mn1}-\text{N3}$	84.24 (8)
$\text{O1}^{\text{iv}}-\text{Mn1}-\text{O4}$	96.18 (8)	$\text{O4}-\text{Mn1}-\text{N1}$	97.59 (7)
$\text{O1}^{\text{iv}}-\text{Mn1}-\text{N1}$	93.10 (7)	$\text{O4}-\text{Mn1}-\text{N2}$	91.55 (8)
$\text{O1}^{\text{iv}}-\text{Mn1}-\text{N2}$	90.41 (7)	$\text{O4}-\text{Mn1}-\text{N3}$	88.71 (8)
$\text{O1}^{\text{iv}}-\text{Mn1}-\text{N3}$	173.97 (8)	$\text{N1}-\text{Mn1}-\text{N2}$	169.78 (9)
$\text{O2}-\text{Mn1}-\text{O4}$	172.80 (6)	$\text{N1}-\text{Mn1}-\text{N3}$	89.75 (7)
$\text{O2}-\text{Mn1}-\text{N1}$	80.98 (8)	$\text{N2}-\text{Mn1}-\text{N3}$	85.91 (7)
$\text{O2}-\text{Mn1}-\text{N2}$	89.37 (8)	$\text{Mn1}-\text{O4}-\text{Mn1}^{\text{iv}}$	125.0 (1)

Symmetry code: (iv) $1 - x, y, \frac{1}{2} - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O5}-\text{H14}\cdots\text{O3}^{\text{iii}}$	0.87 (2)	1.88 (2)	2.748 (3)	178 (1)
$\text{C2}-\text{H1}\cdots\text{O2}^{\text{i}}$	0.96 (3)	2.63 (2)	3.340 (3)	131 (2)
$\text{C7}-\text{H4}\cdots\text{O5}^{\text{v}}$	0.92 (3)	2.38 (2)	3.137 (3)	140 (2)

Symmetry codes: (i) $x, -y, z + \frac{1}{2}$; (iii) $2 - x, -y, 1 - z$; (v) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.

H atoms were located from difference density maps and their coordinates were refined, with $U_{\text{iso}}(\text{H}) = 0.0146$ Å². The C-H and O-H bond lengths are 0.80 (3)–1.00 (3) and 0.87 (2) Å, respectively.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *MERCURY* (Version 1.2.1; Bruno *et al.*, 2002); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1180). Services for accessing these data are described at the back of the journal.

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