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Sodium [1,2-bis(2-methyl-2-oxopropanamido)-benzene](tetrahydrofuran)manganese(III) methanol solvate

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The Mn^{III} complex in the title compound, Na[Mn($C_{14}H_{16}N_2O_4$)(C_4H_8O)]·CH_3OH, is an important intermediate in the synthesis of some interesting Mn^{V} compounds. The Mn^{III} atom is a paramagnetic (d^4) species in an elongated square-pyramidal (O_2N_2O) coordination belonging to point group C_s.

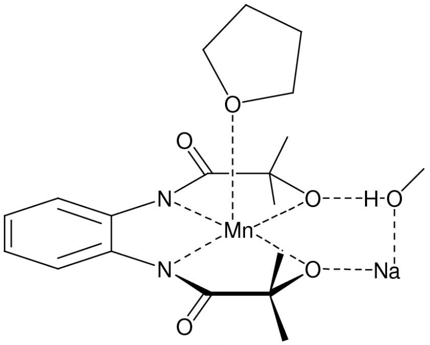
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.036
wR factor = 0.082
Data-to-parameter ratio = 14.7

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

Comment

The title Mn^{III} complex, (I), is an intermediate product formed during the synthesis of an Mn^{V}–oxo complex (Collins & Gordon-Wylie, 1989). The Mn^{III}–oxo complex is of interest as a mimic of the proposed highly reactive intermediate in salen–manganese-catalysed epoxidation reactions.



(I)

The title compound, (I), is paramagnetic and showed a typical Mn^{III} EPR (electron paramagnetic resonance) signal in

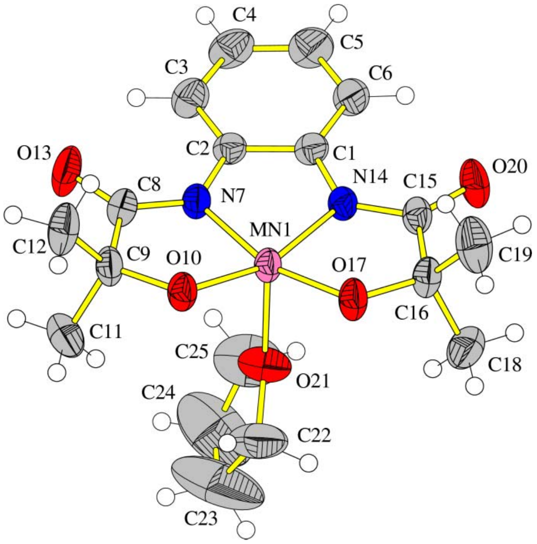


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

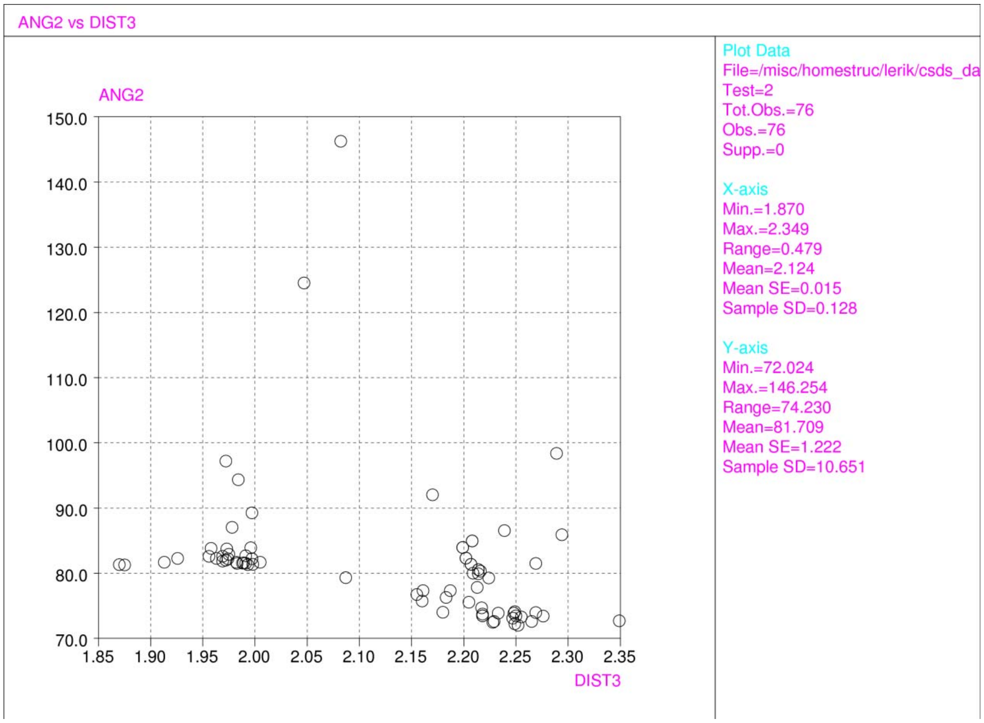


Figure 2
Scatterplot of the bite angle N—Mn—N *versus* the distance N—Mn for 76 fragments found in the CSD (Allen, 2002) with similar coordination geometry to the title compound.

parallel mode EPR (Campbell *et al.*, 1999; 2001). The UV–vis spectrum showed a major peak at 388 nm with an extinction coefficient of 442 M^{-1} cm^{-1}. The oxidation state of the Mn^{III} atom fits well with bond-valence calculations (Brown & Altermatt, 1985). The elongated square-pyramidal coordination around the Mn atom is described by four close ligand atoms (N7, N14, O10 and O17) and a fifth more distant atom (O21) from the weakly coordinated tetrahydrofuran (THF) solvent molecule. These five closest lying ligand atoms of the first coordination sphere around the Mn atom belong to the point group C_s (Fig. 1).

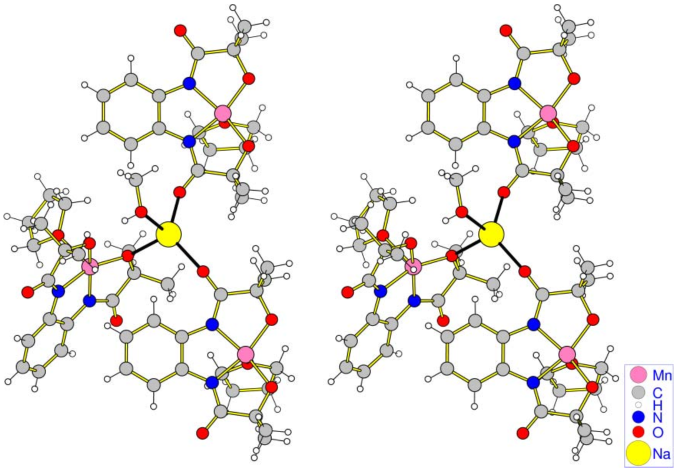


Figure 3
Stereoview of the environment around the sodium ion. Both carbonyl O atoms and one of the deprotonated hydroxyl O atoms of the title complex coordinate to the sodium ion.

In the Cambridge Structural Database (CSD; Version 5.26; Allen, 2002), there are 76 fragments containing Mn with N_2O_3 coordination. A scatterplot of the bite-angle N—Mn—N *versus* the distance Mn—N is shown in Fig. 2. Clearly, only two fragments, both occurring in CSD entry LEZZAR (MacDonnel *et al.*, 1994), resemble the title compound regarding these two parameters. The four closest ligand atoms (N7, N14, O10 and O17) form a plane with an r.m.s. deviation of 0.027 (2) Å and with the Mn atom displaced 0.238 (2) Å from this plane in the direction of atom O21 in the apically coordinated THF molecule. Another plane defined by C1–C6/N7/N14 with an r.m.s. deviation of 0.018 (3) Å is inclined by 7.5 (1)° to the previous plane. The Mn atom is displaced 0.054 (3) Å from the latter plane. The Na$^+$ ion is coordinated by three different molecules of the Mn complex and by a methanol molecule in a distorted tetrahedral configuration (Fig. 3). Both carbonyl O atoms of each Mn^{III} complex coordinate to the Na$^+$ ions. The hydroxyl group of the methanol molecule also forms a hydrogen bond to one of the deprotonated hydroxyl O atoms in the Mn complex. In addition to this conventional O—H$\cdots$O hydrogen bond, there are several weak C—H$\cdots\pi$ interactions stabilizing the structure. No solvent-accessible voids exist in the structure, as calculated with *PLATON* (Spek, 2003).

Experimental

The ligand was synthesized according to literature procedures (Anson *et al.*, 1987) and the complex was synthesized by a modified

m1170 Berggren *et al.* • Na[Mn($C_{14}H_{16}N_2O_4$)(C_4H_8O)]·CH_4O *Acta Cryst.* (2005). E**61**, m1169–m1171

procedure (Hsieh & Pecoraro, 2002). The ligand (280 mg, 1 mmol) was dissolved in a solution of MeONa (243 mg, 4.1 mmol) in freshly distilled MeOH (8 ml). The solution was left to stir for 1 h before anhydrous $MnCl_2$ (126 mg, 1 mmol) was added. The reaction mixture was refluxed overnight. The white precipitate which formed was removed by centrifugation and the dark-red filtrate was evaporated to dryness under reduced pressure. The product was extracted from the solid residue using 2-propanol. The solvent was removed under reduced pressure to give the desired product as a red–brown solid. Red–brown X-ray quality crystals were grown by diffusion of THF into a methanol solution of the complex.

Crystal data

$Na[Mn(C_{14}H_{16}N_2O_4)(C_4H_8O)]\cdot CH_4O$
$M_r = 458.33$
Tetragonal, $P4_3$
$a = 10.8281\ (19)$ Å
$c = 19.043\ (4)$ Å
$V = 2232.8\ (7)$ Å^3
$Z = 4$
$D_x = 1.364$ Mg m$^{-3$}
Mo *Kα* radiation
Cell parameters from 970 reflections
$\theta = 2.1–25.2°$
$\mu = 0.65$ mm^{-1}
$T = 293\ (2)$ K
Elongated octahedron, red–brown
0.62 × 0.20 × 0.17 mm

Data collection

Stoe IPDS diffractometer
Area-detector φ scans
Absorption correction: numerical (*X-RED* in *IPDS Software*; Stoe & Cie, 1997)
$T_{min} = 0.666$, $T_{max} = 0.898$
12516 measured reflections
3949 independent reflections
3340 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 25.9°$
$h = -13 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -23 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.082$
$S = 0.98$
3949 reflections
268 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}
Absolute structure: Flack (1983), 1710 Friedel pairs
Flack parameter = −0.036 (17)

Table 1
Selected geometric parameters (Å, °).

Mn1—O17	1.857 (2)	Na26—O10	2.298 (3)
Mn1—O10	1.864 (2)	Na26—O13^{i}	2.220 (2)
Mn1—N7	1.906 (3)	Na26—O20^{ii}	2.278 (2)
Mn1—N14	1.924 (2)	Na26—O27	2.296 (3)
Mn1—O21	2.223 (3)		
O17—Mn1—O10	104.68 (10)	N7—Mn1—N14	82.34 (10)
O17—Mn1—N7	162.61 (10)	O17—Mn1—O21	96.04 (11)
O10—Mn1—N7	84.91 (10)	O10—Mn1—O21	98.48 (10)
O17—Mn1—N14	84.39 (10)	N7—Mn1—O21	96.84 (11)
O10—Mn1—N14	160.43 (10)	N14—Mn1—O21	97.74 (11)

Symmetry codes: (i) $1 - y, x, z - \frac{1}{4}$; (ii) $2 - y, x, z - \frac{1}{4}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O27—H27···O17	0.82	1.82	2.633 (4)	174

H atoms attached to carbon were positioned geometrically and refined as riding, with distance constraints and displacement parameter constraints as follows: methyl C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$; methylene C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$; aromatic C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The OH group of the methanol molecule was allowed to rotate about the C—O axis, with a fixed O—H distance of 0.82 Å and an ideal tetrahedral angle at O. The coordinated THF molecule shows large anisotropic displacement parameters, especially for the two C atoms most distant from the coordinating O atom (O21). This is related to the weak coordination of the THF molecule in the present case and the lack of significant intermolecular interactions for this ligand. The unusually short bond C23—C24 can also be related to the large anisotropic displacement parameters of these atoms.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97*.

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Acta Cryst. (2005). E**61**, m1169–m1171 Berggren *et al.* • $Na[Mn(C_{14}H_{16}N_2O_4)(C_4H_8O)]\cdot CH_4O$ **m1171**