

Bis[μ_3 -1,8-bis(triisopropylsilylamido)-naphthalene]bis(tetrahydrofuran)-di- μ_3 -oxido-dimanganese(III)disodium

Alexander J. Blake,* Naomi A. Harris, Deborah L. Kays,* William Lewis and Graeme J. Moxey

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, England
Correspondence e-mail: a.j.blake@nottingham.ac.uk, deborah.kays@nottingham.ac.uk

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The solid-state structure of the title compound, $[\text{Na}_2\text{Mn}_2(\text{C}_{32}\text{H}_{56}\text{N}_2\text{OSi}_2)_2\text{O}_2]$ or $[\text{1,8-C}_{10}\text{H}_6(\text{NSi}^i\text{Pr}_3)_2\text{Mn}(\mu_3\text{-O})\text{Na}(\text{THF})_2]$, which lies across a crystallographic twofold axis, exhibits a central $[\text{Mn}_2\text{O}_2\text{Na}_2]^{4+}$ core, with two oxide groups, each triply bridging between the two Mn^{III} ions and an Na^+ ion. Additional coordination is provided to each Mn^{III} centre by a $\text{1,8-C}_{10}\text{H}_6(\text{NSi}^i\text{Pr}_3)_2$ [1,8-bis(triisopropylsilylamido)naphthalene] ligand and to the Na^+ centres by a tetrahydrofuran molecule. The presence of an additional $\text{Na}^+\cdots\text{H}-\text{C}$ agostic interaction potentially contributes to the distortion around the bridging oxide group.

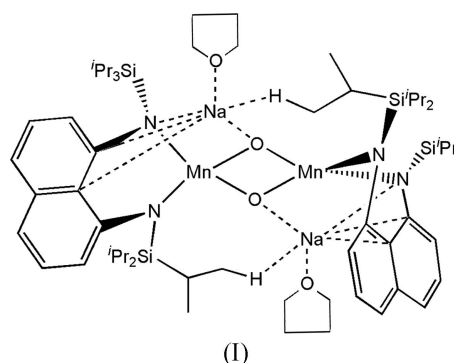
Comment

Polynuclear transition metal complexes containing oxygen-based bridging ligands are of significant interest as models for bioinorganic systems (Vincent *et al.*, 1989; Christou, 1989; Libby *et al.*, 1991; Wang *et al.*, 1991). In the case of manganese, complexes such as $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CR})_x\text{L}_n]^y$ ($x = 6$ or 7 ; $y = -1, 0$ or 1) have been used to model the photosynthetic water oxidation centre (WOC) within green plants and cyanobacteria. In this paper, we describe the crystallographic characterization of the title compound, $[\text{1,8-C}_{10}\text{H}_6(\text{NSi}^i\text{Pr}_3)_2\text{Mn}(\mu_3\text{-O})\text{Na}(\text{THF})_2]$ (THF is tetrahydrofuran), (I), which features a central $[\text{Mn}_2\text{O}_2\text{Na}_2]^{4+}$ core.

The crystal structure of (I) is shown in Fig. 1, and important bond distances and angles are shown in Table 1. The complex lies across a crystallographic twofold axis and consists of a central $[\text{Mn}_2\text{O}_2\text{Na}_2]^{4+}$ core, with two oxide groups, each triply bridging between the two Mn^{III} ions and an Na^+ ion. Additional coordination to each Mn^{III} centre is provided by a $\text{1,8-C}_{10}\text{H}_6(\text{NSi}^i\text{Pr}_3)_2$ ligand and to the Na^+ centres by a THF molecule.

The Mn^{III} centres in (I) are each coordinated by two amide N atoms and two bridging oxides in a tetrahedrally distorted

square-planar environment where the mean tetrahedral distortion, defined as the mean of the absolute deviations of the ligand atoms from the MnN_2O_2 least-squares mean plane, is 0.49 (5) Å. The $\text{N1}-\text{Mn1}-\text{N2}$ angle is wider than that in $\text{1,8-C}_{10}\text{H}_6(\text{NSi}^i\text{Pr}_3)_2\text{Li}(\text{THF})\text{MnCl}(\text{THF})$, (II) [85.83 (7)°; Blake *et al.*, 2009], presumably in part a reflection of the different coordination environments of the metal cations in these two complexes. The $\text{Mn}-\text{N}$ distances in (I) are significantly shorter than that in (II) [2.1093 (17) Å], due to the smaller ionic radius of Mn^{III} compared with Mn^{II} (Shannon & Prewitt, 1969, 1970). In (I), the Mn^{III} centre lies 1.150 (3) Å out of the N1/C1/C10/C9/N2 plane of the ligand, which exhibits a significant twisting of the framework; the amide N atoms are significantly distorted from the naphthalene plane [the $\text{N}\cdots$ naphthalene plane distances are 0.460 (5) and -0.518 (5) Å for atoms N1 and N2, respectively].



The Mn_2O_2 moiety deviates somewhat from planarity, the angle between the $\text{O1}-\text{Mn1}-\text{O1}^i$ and $\text{O1}-\text{Mn1}^i-\text{O1}^i$

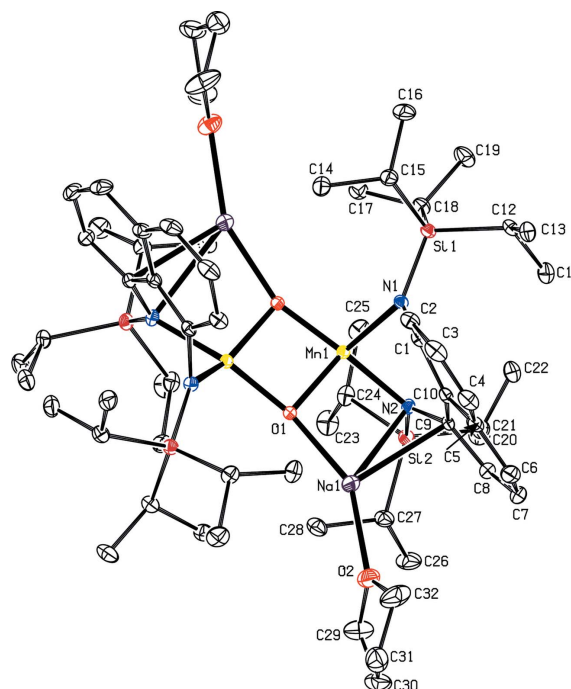
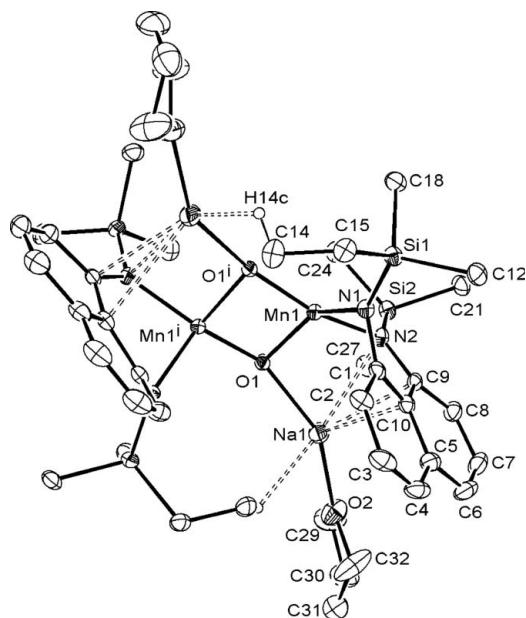


Figure 1
A view of (I), showing the atom-numbering scheme for the reference asymmetric unit. Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity.

**Figure 2**

A view of (I), indicating the full coordination around Na1. Displacement ellipsoids are drawn at the 30% probability level. For clarity, atoms C11, C13, C16, C17 and C19 of the isopropyl groups on Si1, and atoms C20, C22, C23, C25, C26 and C28 of the isopropyl groups on Si2 have been omitted, and only those H atoms involved in agostic interactions are shown. The interactions between Na1 and atoms C9, C10, N2 and H14C are shown as dashed lines. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.]

planes being $12.10(4)^\circ$ [symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$]. The $\text{Mn1} \cdots \text{Mn1}^i$ distance in (I) is longer than that found in $[\text{HC}(\text{CMeNDipp})_2\text{Mn}(\mu\text{-O})_2]$, (III) [2.659 (1) Å; Dipp is 2,6-diisopropylphenyl; Chai *et al.*, 2005], but shorter than that for the central Mn_2O_2 core in $(\text{Bu}_4\text{N})[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9\text{H}_2\text{O}]$, (IV) [2.816 (4) Å; Wang *et al.*, 1991]. The Mn—O distances in (I) are slightly shorter than the analogous values for (IV) [1.900 (11), 1.905 (11), 1.913 (10) and 1.909 (10) Å]. Both these complexes feature μ_3 -bridging oxides, *viz.* between two Mn^{III} centres and one Na^+ centre in the case of (I), and between three Mn^{III} centres in the case of (IV).

The Na—O distances in (I) (Table 1) reflect the differing coordination environments around each O atom. The Na1—O1 distance is somewhat shorter than that found in other triply-bridged complexes, *e.g.* $[\text{Ph}_2\text{SiO}]_8[\text{AlO}_2\text{Na}]_4 \cdot 5\text{THF}$, which has these distances in the range 2.204 (5)–2.392 (6) Å (Veith *et al.*, 2007). These differences are presumably a consequence of the differing coordination environments in these two complexes. The Na1—O2 distance in (I) is significantly longer than the Na1—O1 distance, but it lies within the range of other Na—THF interactions in the literature (Allen, 2002) and is very similar to analogous Na—O distances in other complexes, such as $[(\text{THF})_3\text{Na}][(\text{N}_2)\text{Mo}\{\text{N}(\text{Ad})\text{C}_6\text{H}_3\text{-2,6-Me}_2\}_3]$ [2.254 (10) Å; Peters *et al.*, 1999] and $\text{Na}_2\text{Ga}_4(\text{Si}^i\text{Bu}_3)_4 \cdot 2\text{THF}$ [2.252 (3) Å; Wiberg *et al.*, 2002]. The geometry around atom O1 is highly distorted trigonal pyramidal [$\text{Na1}-\text{O1}-\text{Mn1}^i = 156.41(14)^\circ$], with atom O1 lying 0.286 (2) Å out of the plane defined by atoms Mn1, Mn1ⁱ and Na1.

In addition to the coordination by the triply bridging oxide ligand and the THF molecule, the Na^+ centre interacts significantly with atoms C9, C10 and N2 of the 1,8-bis(triisopropylsilylamido)naphthalene ligand (Table 1 and Fig. 2). Finally, there is an additional agostic interaction with atom H14C [$\text{Na1} \cdots \text{H14C}^i = 2.41$ Å, $\text{Na1} \cdots \text{C14}^i = 2.994(4)$ Å and $\text{Na1} \cdots \text{H14C}^i - \text{C14}^i = 118^\circ$], which potentially contributes to the distortion around the bridging oxide.

The dimer of (I) features possible C—H \cdots O interactions (Table 2). However, as these involve bridging O atoms, are quite long and involve unactivated methyl H atoms, they may not be significant in themselves but a result of steric crowding. One methyl H atom is also implicated in a possible intramolecular C—H \cdots π interaction with the ring C1—C5/C10 (Table 2). There are no specific directional intermolecular interactions.

Experimental

A solution of 1,8- $\text{C}_{10}\text{H}_6(\text{NSi}^i\text{Pr}_3)_2\text{Li}(\text{THF})\text{MnCl}(\text{THF})$ (0.075 g, 0.11 mmol; Blake *et al.*, 2009) in toluene (10 ml) was added to a stirred slurry of NaO^tBu (0.010 g, 0.11 mmol) in toluene (10 ml) and the mixture stirred at room temperature for 24 h. Removal of volatiles *in vacuo* gave a brown solid, which was extracted with hexanes (10 ml). The solution was filtered and concentrated to *ca* 5 ml, which yielded brown crystals of (I) after storage at 238 K.

Crystal data

$[\text{Na}_2\text{Mn}_2(\text{C}_{32}\text{H}_{56}\text{N}_2\text{OSi}_2)_2\text{O}_2]$	$V = 6938.0(10)$ Å ³
$M_r = 1269.80$	$Z = 4$
Orthorhombic, <i>Pbcn</i>	Mo $K\alpha$ radiation
$a = 25.209(2)$ Å	$\mu = 0.49$ mm ⁻¹
$b = 17.6946(15)$ Å	$T = 150$ K
$c = 15.5541(13)$ Å	$0.27 \times 0.27 \times 0.07$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	34383 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	6173 independent reflections
$T_{\min} = 0.652$, $T_{\max} = 0.746$	5327 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$	10 restraints
$wR(F^2) = 0.155$	H-atom parameters constrained
$S = 1.21$	$\Delta\rho_{\text{max}} = 0.59$ e Å ⁻³
6173 reflections	$\Delta\rho_{\text{min}} = -0.35$ e Å ⁻³
373 parameters	

Table 1

Selected geometric parameters (Å, °).

Mn1—O1 ⁱ	1.853 (2)	Na1—O1	2.201 (3)
Mn1—O1	1.876 (2)	Na1—O2	2.254 (4)
Mn1—N1	1.949 (3)	Na1—C9	2.665 (4)
Mn1—N2	1.999 (3)	Na1—N2	2.706 (4)
Mn1—C1	2.608 (4)	Na1—C14 ⁱ	2.994 (4)
Mn1—Mn1 ⁱ	2.7037 (10)	Na1—C10	3.010 (4)
N1—Mn1—N2	89.78 (12)	Mn1 ⁱ —O1—Na1	156.41 (14)
Mn1 ⁱ —O1—Mn1	92.96 (10)	Mn1—O1—Na1	101.25 (11)

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

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1–C5/C10 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C17–H17B \cdots O1 ⁱ	0.98	2.44	3.401 (5)	167
C28–H28B \cdots O1	0.98	2.52	3.475 (5)	165
C13–H13A \cdots Cg1	0.98	2.83	3.714 (5)	150

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

The intensity of the diffraction falls off very steeply above $ca\ 2\theta = 50^\circ$, and accordingly a cut-off was applied at $2\theta = 50.2^\circ$. This feature appeared consistent throughout the frame set, suggesting that no changes occurred to the crystal during data collection.

Methyl H atoms were located in circular difference Fourier syntheses and thereafter refined as part of a rigid rotating group, with $C-H = 0.98\ \text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The remaining H atoms were placed geometrically and refined with aromatic $C-H = 0.95\ \text{\AA}$, methylene $C-H = 0.99\ \text{\AA}$ and methine $C-H = 1.00\ \text{\AA}$, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Rigid-bond restraints (Sheldrick, 2008), with effective standard deviations of $0.01\ \text{\AA}^2$ for 1,2-atom pairs and $0.001\ \text{\AA}^2$ for 1,3-atom pairs, were applied to the anisotropic displacement parameters of the THF atoms (O2/C29–C32). Eight reflections were excluded from the refinement, primarily because they were at least partially occluded by the backstop.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE* and *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3151). Services for accessing these data are described at the back of the journal.

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