C(4)	0.4892 (6)	−0.0056 (6)	0.3259 (3)	5.75 (22)
C(5)	0.5735 (6)	0.0796 (7)	0.3077 (3)	6.84 (27)
C(6)	0.5326 (6)	0.1998 (8)	0.2936 (3)	7.06 (26)
C(7)	0.4039 (5)	0.2301 (5)	0.2984 (3)	4.35 (18)
C(8)	−0.0861 (5)	0.0653 (6)	0.1651 (3)	4.58 (21)
C(9)	−0.1497 (5)	0.1260 (6)	0.0991 (3)	4.64 (20)
C(10)	−0.2685 (6)	0.1893 (6)	0.0966 (3)	5.65 (20)
C(11)	−0.3243 (7)	0.2487 (6)	0.0377 (4)	8.17 (28)
C(12)	−0.2621 (8)	0.2485 (7)	−0.0178 (4)	9.21 (29)
C(13)	−0.1415 (8)	0.1841 (7)	−0.0180 (3)	8.89 (30)
C(14)	−0.0889 (6)	0.1241 (7)	0.0429 (3)	5.91 (22)
C(15)	0.2685 (5)	0.0601 (5)	0.1526 (3)	4.23 (18)
C(16)	0.3511 (6)	0.0331 (6)	0.1042 (3)	5.04 (22)
C(17)	0.3611 (5)	0.1192 (6)	0.0536 (3)	5.41 (20)
C(18)	0.2901 (5)	0.2296 (5)	0.0510 (3)	4.30 (20)
C(19)	0.2966 (6)	0.3230 (6)	0.0002 (3)	6.06 (23)
C(20)	0.2284 (7)	0.4281 (6)	0.0031 (3)	6.65 (25)
C(21)	0.1511 (6)	0.4507 (6)	0.0537 (3)	5.61 (22)
C(22)	0.1436 (5)	0.3635 (5)	0.1046 (3)	4.04 (19)
C(23)	0.2127 (5)	0.2554 (5)	0.1032 (2)	3.69 (17)

Table 2. *Geometric parameters* (Å, °)

Sn(1)—S(1)	2.386 (2)	Sn(1)—C(1)	2.139 (5)
Sn(1)—N(1)	2.367 (4)	Sn(1)—C(8)	2.133 (6)
Sn(1)—Cl(1)	2.475 (5)		
S(1)—Sn(1)—N(1)	78.7 (1)	S(1)—Sn(1)—Cl(1)	87.5 (1)
C(1)—Sn(1)—C(8)	131.9 (2)	C(1)—Sn(1)—S(1)	114.7 (2)
C(1)—Sn(1)—Cl(1)	90.2 (2)	C(1)—Sn(1)—N(1)	95.7 (2)
C(8)—Sn(1)—S(1)	113.2 (2)	C(8)—Sn(1)—Cl(1)	95.3 (2)
C(8)—Sn(1)—N(1)	90.0 (2)	Cl(1)—Sn(1)—N(1)	166.2 (1)

Data reduction was performed with the program *XP*2$_1$ (Pavelčik, 1987). The structure was solved by the Patterson method and refinement was on *F* by block-diagonal least squares. H atoms were located at calculated positions; their coordinates and thermal parameters were fixed. Calculations were performed with a local version of the *NRC* (Ahmed, Hall, Pippy & Huber, 1973) system and *PARST* (Nardelli, 1984).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71214 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1027]

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Facile Synthesis and Structure of the Mn^{IV}–Mn^{IV} Dinuclear Complex [Mn(salpn)O]$_2$(DMSO)$_2$ [salpnH$_2$ = *N*,*N*′-bis(salicylidene)-1,3-diaminopropane]

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Abstract

The Mn^{IV} dimer [Mn(salpn)O]$_2$, di-μ-oxo-bis({2,2′-[1,3-propanediylbis(nitrilomethylidyne)]diphenolato-*N*,*N*′,*O*,*O*′}manganese(IV)), has been produced as the DMSO adduct by the facile air oxidation of the complex {[Mn^{III}(salpn)(H$_2$O)](ClO$_4$)}$_2$ in DMSO, giving dark-green crystals. Both Mn atoms are in approximately octahedral environments made up of the tetradentate Schiff base salpn and two μ-oxo O atoms, which are both *cis* [Mn—O 1.804 (5) and Mn—O′ 1.832 (5) Å].

Comment

Manganese plays a vital role in a number of metalloproteins (Dismukes, 1986). Of these metalloproteins the most important is undoubtedly the dioxygen envolving complex (OEC) of photosystem II (PSII) found in green plants (Dismukes, 1986; Pecoraro, 1988). It is now well established that in PSII four Mn atoms are essential for high rates of dioxygen evolution, although the precise configuration of the active site is still not known (Pecoraro, 1988). Extended X-ray absorption fine structure (EXAFS) studies of the OEC shows that there is at least one, and possibly two short Mn···Mn distances of ~2.7 Å (George, Prince & Cramer, 1989). A number of model complexes have been synthesized, with mononuclear Mn (Dutta, Basu & Chakravorty 1991), dinuclear Mn (Ashmawy, McAuliffe, Parish & Tames, 1985; Wieghardt *et al.*, 1986; Bonadies *et al.*, 1989) and higher nuclearity Mn (Perlepes, Huffman & Christou, 1991). Our own studies have centred on

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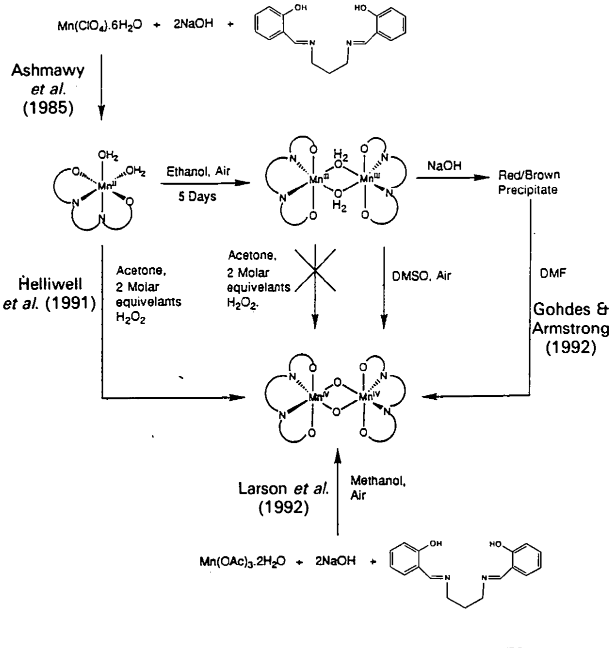
the use of potentially tetradentate Schiff base ligands with an N_2O_2-donor set. By employing the salpnH_2 ligand [salpnH_2 = *N*,*N*′-bis(salicylidene)-1,3-diaminopropane] and the weakly coordinating perchlorate counterion we were able to produce molecular O from the dimeric species {[Mn(salpn)(H_2O)](ClO_4)}$_2$ (Ashmawy *et al.*, 1985). In a recent attempt to crystallize this compound (Gohdes & Armstrong, 1992), the compound [Mn(salpn)(EtOH)$_2$]ClO_4 was isolated, and presented as a monomer. However, the Mn···Mn separation of 5.288 Å is very similar to the Mn···Mn separation of 5.21 Å in the complex [Mn(salpn)$_2$(EtOH)$_3H_2O$](BPh_4)$_2$ (Ashmawy, Beagley, McAuliffe, Parish & Pritchard, 1990), a species we characterized as a dimer held together by a vast array of hydrogen bonds. [Mn(salpn)(EtOH)$_2$]ClO_4 was then converted to [Mn(salpn)O]$_2$ (as the *N*,*N*-dimethylformamide solvate) by air oxidation in basic methanol (Gohdes & Armstrong, 1992), as depicted below. This dimeric compound was also concurrently isolated from the reaction of manganese(III) acetate in basic methanol with salpnH_2 (Larson, Lah, Li, Bonadies & Pecoraro, 1992), also depicted below. These studies closely follow our own and we have isolated [Mn(salpn)O]$_2$ from a reaction in *N*,*N*-dimethylformamide (DMF) (Helliwell, McGlynn, McAuliffe & Pritchard, 1991), and also from a more surprising reaction in dimethyl sulfoxide (DMSO):



The assignment of oxidation state Mn^{IV} in the [Mn(salpn)O]$_2$(DMSO)$_2$ complex has been made on the basis of comparisons of bond lengths and angles with the previously reported DMF solvates (Gohdes & Armstrong, 1992; Larson *et al.*, 1992). The DMSO solvate is essentially identical to the DMF solvates, with an Mn···Mn separation of 2.736 (2) Å and a crystallographically imposed inversion centre. The isolation of [Mn(salpn)O]$_2$(DMSO)$_2$ by the route shown in the scheme above is somewhat surprising as exposure of the compound {[Mn(salpn)(H_2O)]ClO_4}$_2$ to 2 molar equivalents of H_2O_2 in acetone does not appear to facilitate oxidation. However, merely dissolving the Mn^{III} complex in dimethyl sulfoxide and allowing the solution to stand in air yielded crystals of [Mn(salpn)O]$_2$(DMSO)$_2$, with structure as shown in Fig. 1. It might be concluded from these observations that dissolution of {[Mn(salpn)(H_2O)]ClO_4}$_2$ in DMSO is followed by solvolysis, altering the redox potential of Mn^{III} and allowing oxidation to Mn^{IV}.

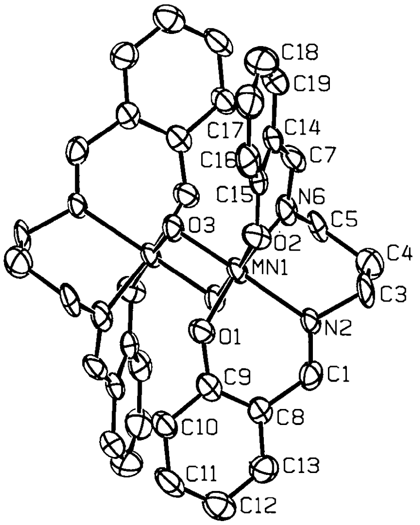


Fig. 1. The title compound drawn using *ORTEP*II (Johnson, 1976) with DMSO solvate molecules omitted for clarity.

Experimental

Crystal data

$[Mn_2(C_{17}H_{16}N_2O_2)_2O_2]$-$.2(C_2H_6OS)$
M_r = 858.78
Monoclinic
$P2_1/c$
a = 10.584 (4) Å
b = 10.264 (4) Å
c = 18.064 (6) Å
β = 101.14 (3)°
V = 1925 (1) Å^3
Z = 2
D_x = 1.481 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 7.4–11.7°
μ = 0.788 mm^{-1}
T = 296 K
Block
0.25 × 0.20 × 0.10 mm
Dark green
Crystal source: inorganic preparation

Data collection

Rigaku AFC-6*S* diffractometer

$R_{\rm int}$ = 0.052
$\theta_{\rm max}$ = 25.05°

$\omega/2\theta$ scans
Absorption correction: refined from ΔF
$T_{\min} = 0.96$, $T_{\max} = 1.03$
3716 measured reflections
3508 independent reflections
2021 observed reflections [$I > 4\sigma(I)$]

$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -21 \rightarrow 20$
3 standard reflections monitored every 150 reflections intensity variation: -5%

Refinement

Refinement on F
Final $R = 0.063$
$wR = 0.079$
$S = 2.88$
2021 reflections
244 parameters
H-atom parameters not refined; placed at idealized positions

$w = 1/[\sigma^2(F_o) + 0.003F_o^2]$
$(\Delta/\sigma)_{\max} < 0.01$
$\Delta\rho_{\max} = 0.54$ e Å^{-3}
$\Delta\rho_{\min} = -0.44$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\text{eq}} = \frac{8\pi^2}{3}\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mn(1)	0.5073 (1)	0.1198 (1)	0.46786 (6)	2.41 (4)
O(1)	0.5524 (5)	0.0587 (4)	0.3769 (4)	2.9 (2)
O(2)	0.6423 (5)	0.2490 (4)	0.4713 (3)	3.0 (2)
O(3)	0.6116 (5)	0.0087 (4)	0.5287 (2)	2.5 (2)
N(2)	0.3681 (6)	0.2337 (5)	0.4030 (3)	2.4 (3)
N(6)	0.4572 (7)	0.2136 (5)	0.5552 (3)	2.8 (3)
C(1)	0.3147 (8)	0.2071 (7)	0.3362 (4)	3.0 (3)
C(3)	0.327 (1)	0.3518 (7)	0.4388 (5)	3.8 (4)
C(4)	0.254 (1)	0.3157 (9)	0.4993 (5)	4.4 (4)
C(5)	0.3231 (8)	0.2169 (7)	0.5578 (4)	3.1 (3)
C(7)	0.538 (1)	0.2750 (7)	0.6059 (4)	3.3 (4)
C(8)	0.3525 (8)	0.0990 (6)	0.2920 (4)	2.6 (3)
C(9)	0.4682 (8)	0.0324 (7)	0.3141 (4)	2.7 (3)
C(10)	0.5034 (9)	−0.0610 (7)	0.2644 (4)	3.5 (4)
C(11)	0.416 (1)	−0.0938 (8)	0.1997 (4)	4.0 (4)
C(12)	0.300 (1)	−0.0317 (8)	0.1788 (4)	3.8 (4)
C(13)	0.2717 (8)	0.0658 (7)	0.2248 (4)	3.5 (4)
C(14)	0.6712 (8)	0.3005 (6)	0.6034 (4)	3.1 (3)
C(15)	0.7133 (8)	0.2914 (6)	0.5333 (4)	3.1 (3)
C(16)	0.8379 (8)	0.3370 (7)	0.5317 (5)	3.4 (4)
C(17)	0.9164 (8)	0.3820 (8)	0.5966 (6)	4.1 (4)
C(18)	0.877 (1)	0.3870 (9)	0.6637 (5)	4.6 (4)
C(19)	0.754 (1)	0.3510 (8)	0.6664 (5)	3.9 (4)
S(1)	0.9326 (3)	0.5705 (2)	0.8794 (1)	4.6 (1)
O(4)	0.8652 (7)	0.6169 (6)	0.8050 (4)	6.5 (4)
C(20)	1.090 (1)	0.527 (1)	0.8701 (6)	5.0 (5)
C(21)	0.873 (1)	0.412 (1)	0.8911 (6)	6.1 (6)

Table 2. *Geometric parameters* (Å, °)

Mn(1)—Mn(1$^{\text{i}}$)	2.736 (2)	Mn(1)—O(3$^{\text{i}}$)	1.832 (5)
Mn(1)—O(1)	1.904 (5)	Mn(1)—N(2)	2.060 (6)
Mn(1)—O(2)	1.942 (5)	Mn(1)—N(6)	2.006 (6)
Mn(1)—O(3)	1.804 (5)		
O(1)—Mn(1)—O(2)	87.0 (2)	O(2)—Mn(1)—O(3$^{\text{i}}$)	175.2 (2)
O(1)—Mn(1)—O(3)	95.2 (2)	O(3)—Mn(1)—O(3$^{\text{i}}$)	82.4 (2)
O(1)—Mn(1)—O(3$^{\text{i}}$)	94.7 (2)	Mn(1)—O(3)—Mn(1$^{\text{i}}$)	97.6 (2)
O(1)—Mn(1)—N(2)	88.1 (2)	Mn(1)—N(6)—C(5)	116.9 (5)
O(1)—Mn(1)—N(6)	170.3 (2)	Mn(1)—N(6)—C(7)	123.5 (6)
O(2)—Mn(1)—O(3)	93.0 (2)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

The ligand salpnH$_2$ [*N*,*N'*-bis(salicylidene)-1,3-diaminopropane] was prepared as previously reported (Ashmawy *et al.*, 1985). The deep-green complex $\{[\text{Mn}^{\text{III}}(\text{salpn})(\text{H}_2\text{O})]\text{ClO}_4\}_2$ was prepared and isolated as previously reported (Ashmawy *et al.*, 1985). Recrystallization from dimethyl sulfoxide in air yielded crystals of $[\text{Mn}(\text{salpn})\text{O}]_2(\text{DMSO})_2$. ω scans of several intense reflections made prior to data collection had an average width at half-height of 0.48° with take-off angle 6.0°. Scans of $(1.84 + 0.30\tan\theta)°$ were made at a speed of 2.0° min^{-1} (in ω). The weak reflections [$I < 10.00\sigma(I)$] were rescanned (maximum of three rescans) and the counts accumulated to assure good counting statistics. The structure was solved by direct methods (Gilmore, 1984; Beurskens, 1984). The non-H atoms were refined anisotropically. H atoms were included in the structure-factor calculations at idealized positions (C—H = 0.95 Å), and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. Refinement was by full-matrix least-squares methods. High R and S values are linked to the occurrence of many weak reflections, particularly at high 2θ values.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond distances and angles involving H atoms, torsion angles and intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55938 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1030]

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