Data collection

Enraf–Nonius CAD-4-Turbo four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.373$, $T_{\max} = 0.448$
4011 measured reflections
2858 independent reflections
2455 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 24.98°$
$h = -1 \rightarrow 9$
$k = -2 \rightarrow 19$
$l = -14 \rightarrow 14$
3 standard reflections every 200 reflections intensity decay: 4.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.059$
$S = 0.934$
2858 reflections
200 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 6.4085P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.042$ e Å^{-3}
$\Delta\rho_{\min} = -1.029$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Os—F1	1.989 (3)	Os—N2	2.063 (4)
Os—F2	1.989 (3)	Os—N1	2.099 (4)
Os—N3	2.058 (4)	Os—Cl	2.3681 (15)
F1—Os—F2	176.55 (11)	N3—Os—N1	92.35 (15)
F1—Os—N3	89.01 (14)	N2—Os—N1	178.66 (14)
F2—Os—N3	87.67 (14)	F1—Os—Cl	92.71 (9)
F1—Os—N2	89.80 (14)	F2—Os—Cl	90.56 (10)
F2—Os—N2	89.07 (14)	N3—Os—Cl	176.44 (11)
N3—Os—N2	86.44 (15)	N2—Os—Cl	90.45 (11)
F1—Os—N1	90.75 (13)	N1—Os—Cl	90.74 (11)
F2—Os—N1	90.31 (13)		

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1992). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *DIAMOND* (Bergerhoff, 1995). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1051). Services for accessing these data are described at the back of the journal.

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{4,4′-Dimethyl-6,6′-bis(morpholinomethyl)-2,2′-[1,3-propanediylbis(nitrilomethylidene)]diphenolato-*O*,*N*,*N*′,*O*′}manganese(II) diperchlorate monohydrate

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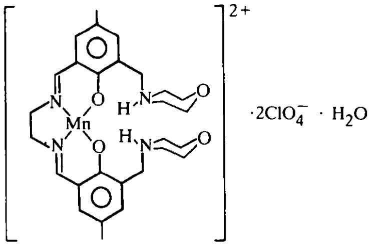
Abstract

In the title compound, $[Mn(C_{28}H_{36}N_4O_4)](ClO_4)_2 \cdot H_2O$, the morpholine rings adopt chair conformations. The geometry around the Mn$^{\rm II}$ ion is slightly distorted square planar. The dihedral angle between the N/Mn/N and O/Mn/O planes is 10.1 (1)°. In addition to van der Waals interactions, the molecules are stabilized by N—H···O and C—H···O hydrogen bonds.

Comment

The main line of defence in mammalian organisms for controlling extra- and intracellular superoxide radical anions is the series of Cu-, Zn-, Mn- and Fe-containing superoxide dismutase enzymes. A stable non-toxic and low molecular weight mononuclear manganese(II) or manganese(III) complex that catalyses the dismutation of a superoxide anion might be a suitable alternative for superoxide dismutase in clinical applications (Wada *et al.*, 1994), with the desirable qualities of low cost, cell permeability and non-immunogenicity (Faulkner *et al.*, 1994). Thus, we have attempted to develop a manganese-based mononuclear complex, because these are better model compounds for metalloenzymes; compared with copper(II) and iron(III) complexes in different ligand environments, many of the manganese(II) and manganese(III) complexes are known to exhibit superoxide dismutase-type activity (Riley & Weiss, 1994). We describe here the structure of the title mononuclear manganese complex, (I).



(I)

A *ZORTEP* (Zsolnai, 1997) representation of (I) is shown in Fig. 1. Selected geometric parameters are given in Table 1 and hydrogen-bonding details are given in Table 2. There are two perchlorate ions in the lattice in order to neutralize the two positive charges of the complex.

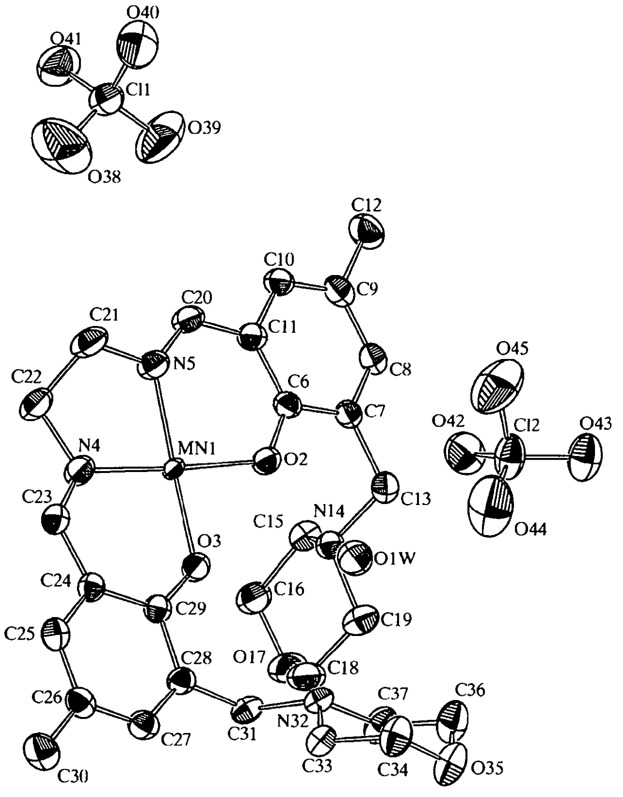


Fig. 1. The molecular structure of the title complex, with 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have been omitted for clarity.

In complex (I), the ligand is a side-off type, where the Mn^{II} ion is encircled by four donating centres in equatorial planes. The phenoxy O2 and O3 atoms and the amine N4 and N5 atoms are coordinated to the Mn^{II} ion at distances of 1.918 (3), 1.924 (3), 1.927 (4) and 1.950 (4) Å, respectively. There is a slight distortion of the coordination plane around the Mn^{II} ion which can be quantified by the dihedral angle between the N5/Mn1/N4 and O2/Mn1/O3 planes [10.1 (1)°]. The fifth coordination site is occupied by the perchlorate O39($1-x$, $2-y$, $-z$) atom at the axial position, with an Mn1···O39($1-x$, $2-y$, $-z$) distance of 2.775 (6) Å. This may be the reason for the slight distortion of the square basal plane. The N14 and N32 atoms of the two morpholine rings are protonated, as shown by the degree of pyramidalization: N14 deviates from the C13/C15/C19 plane by 0.456 (4) Å and N32 deviates from the C31/C33/C37 plane by 0.474 (4) Å. These two positive charges are stabilized by two lattice perchlorate anions.

The two morpholine rings adopt chair conformations. The best planes through the C atoms of these morpholine rings make dihedral angles of 84.0 (1) and 48.7 (2)° with the phenyl rings to which they are attached.

In complex (I), several intramolecular (N—H···O) and intermolecular (C—H···O) hydrogen bonds occur. It is well known that the stabilization energy of a hydrogen bond is much greater than that of typical van der Waals interactions (Brock & Dunitz, 1994). Thus, intermolecular hydrogen bonds are favoured during the process of crystallization. There is one water molecule per complex, which is involved in an N—H···O hydrogen bond between N32 and O1*W*.

Experimental

To a solution of 4,4′-dimethyl-6,6′-bis(morpholinomethyl)-2,2′-[1,3-propanediylbis(nitrilomethylidene)]diphenol (2.24 g, 0.0045 mol) and NaOH (0.36 g, 0.018 mol) in MeOH (30 ml) was added a solution of Mn(ClO$_4$)$_2$ (1.64 g, 0.0045 mol) in MeOH and the resulting solution was refluxed for 2 h. The solvent was evaporated and the product was separated by filtration, washed with MeOH and dried. Crystals of (I) were obtained by recrystallization from a dimethylformamide/EtOH mixture (yield 60%).

Crystal data

$[Mn(C_{28}H_{36}N_4O_4)](ClO_4)_2\cdot H_2O$
$M_r = 764.46$
Triclinic
$P\bar{1}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 1.33$–$33.19°$

$a = 8.9162\,(1)$ Å
$b = 9.6764\,(1)$ Å
$c = 20.0766\,(1)$ Å
$\alpha = 78.536\,(1)^\circ$
$\beta = 81.520\,(1)^\circ$
$\gamma = 83.922\,(1)^\circ$
$V = 1673.79\,(3)$ Å^3
$Z = 2$
$D_x = 1.517$ Mg m^{-3}
D_m not measured

$\mu = 0.624$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
$0.42 \times 0.24 \times 0.18$ mm
Dark brown

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.780$, $T_{max} = 0.896$
9910 measured reflections
6440 independent reflections

5610 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 26^\circ$
$h = -10 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 24$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.207$
$S = 1.090$
6440 reflections
462 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1169P)^2 + 2.3590P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.250$ e Å^{-3}
$\Delta\rho_{min} = -0.804$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.026 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn1—O2	1.918 (3)	O2—C6	1.341 (5)
Mn1—O3	1.924 (3)	O3—C29	1.315 (5)
Mn1—N4	1.927 (4)	N4—C23	1.291 (6)
Mn1—N5	1.950 (4)	N5—C20	1.284 (6)
O2—Mn1—O3	90.19 (12)	O2—Mn1—N5	93.24 (14)
O2—Mn1—N4	176.59 (14)	O3—Mn1—N5	169.36 (15)
O3—Mn1—N4	93.13 (14)	N4—Mn1—N5	83.36 (16)
O3—Mn1—O2—C6	172.1 (3)	O2—Mn1—O3—C29	171.9 (3)
N4—Mn1—O2—C6	−20 (3)	N4—Mn1—O3—C29	−7.4 (3)
N5—Mn1—O2—C6	−18.0 (3)	N5—Mn1—O3—C29	62.9 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N32—H32···O1W	0.91	2.01	2.782 (6)	141
N14—H14···O2	0.91	2.15	2.818 (4)	129
C33—H33B···O17^i	0.97	2.47	3.130 (6)	125

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

Most of the H atoms were fixed geometrically. The remainder (H10, H18*A*, H18*B*, H20, H25, H31*A* and H31*B*) were located from difference Fourier maps and refined. The H atoms of the water molecule were not located.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ZORTEP* (Zsolnai, 1997). Software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983, 1995).

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Dichloro(ethylenediaminetetraacetic acid)-palladium(II) hexahydrate

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Abstract

In the title compound, $[PdCl_2(C_{10}H_{16}N_2O_8)]{\cdot}6H_2O$, the Pd^{II} atom has a square-planar environment made up of two chloride anions and the two N atoms of ethylenediaminetetraacetic acid (edta), with the four carboxylic