

Aquabenzotobis(1,10-phenanthroline- κ^2N,N')manganese(II) perchlorate dimethylformamide solvateXiaofeng Zhang, Cheng Fan,
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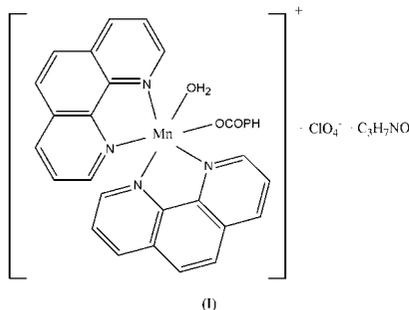
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(C-C) = 0.007$ Å
 R factor = 0.060
 wR factor = 0.153
Data-to-parameter ratio = 12.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the title compound, $[\text{Mn}(\text{PhCOO})(\text{phen})_2(\text{H}_2\text{O})](\text{ClO}_4)\cdot\text{dmf}$ (PhCOO is benzoate, $\text{C}_7\text{H}_5\text{O}_2$, phen is 1,10-phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$, and dmf is dimethylformamide, $\text{C}_3\text{H}_7\text{NO}$), contains a monomeric $[\text{Mn}(\text{PhCOO})(\text{phen})_2(\text{H}_2\text{O})]^+$ cation, a perchlorate anion and a dimethylformamide solvent molecule. The Mn^{2+} ion is coordinated by four N atoms from two phenanthroline ligands [$\text{Mn}-\text{N} = 2.261(3)\text{--}2.303(3)$ Å] and two O atoms from one aqua ligand [$\text{Mn}-\text{O} = 2.156(3)$ Å] and a benzoate ligand [$\text{Mn}-\text{O} = 2.124(3)$ Å], forming a distorted octahedral environment. Perchlorate and dmf are present outside the cation as anion and solvent molecule, respectively. There is an $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interaction between one of the ligated water molecules and the dmf molecule.

Comment

One of the most important processes in nature occurs in the oxygen evolving complex (OEC) of photosystem II in green plants (Wieghardt, 1989). Manganese ions are the essential components in the active center of the PSII. The coordination sphere of the manganese is believed to be composed of O and N donors from available amino acid side chains (Wieghardt, 1989). In recent years, we have used phen and carboxylic acids to synthesize a series of manganese-phen-carboxylic acid complexes, of which there are some mononuclear complexes, such as $\{[\text{Mn}(\text{phen})_2(\text{OAc})(\text{H}_2\text{O})]\text{ClO}_4\}_2\cdot\text{H}_2\text{O}$ (Zhang, Huang *et al.*, 2002) and $[\text{Mn}(\text{phen})_2(\text{ClCH}_2\text{COO})(\text{H}_2\text{O})]\text{ClO}_4$ (Zhang, Chen *et al.*, 2002). In this paper, we report the synthesis and crystal structure of a similar mononuclear manganese compound, *viz.* $[\text{Mn}(\text{PhCOO})(\text{phen})_2(\text{H}_2\text{O})]\text{ClO}_4\cdot\text{dmf}$, (I).



The crystal structure of (I) consists of a discrete $[\text{Mn}(\text{PhCOO})(\text{phen})_2(\text{H}_2\text{O})]^+$ cation, a perchlorate anion and a dmf solvent molecule. As illustrated in Fig. 1, the Mn^{II} atom is located in a distorted octahedral environment, with three

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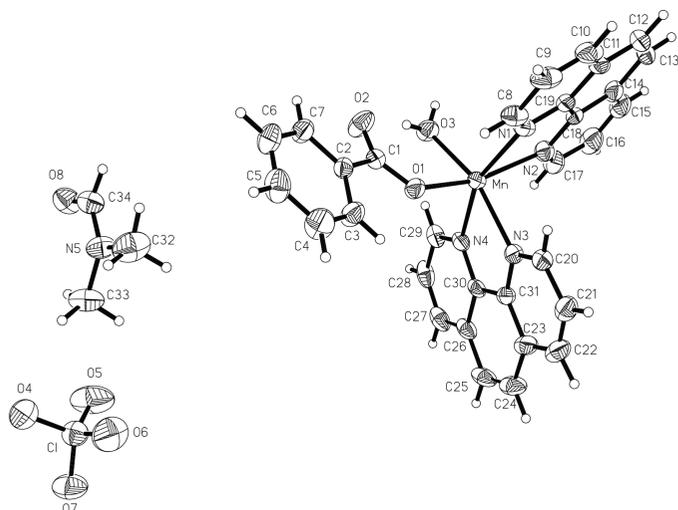


Figure 1
View of the structure of (I), showing 30% probability displacement ellipsoids and the atomic numbering scheme.

trans angles in the range 158.51 (12)–163.23 (11)°. It is coordinated by four N atoms from a pair of *cis*-related chelating phenanthroline ligands and two O atoms from a monodentate benzoate ligand [Mn–O1 = 2.124 (3) Å] and a water molecule [Mn–O3 = 2.156 (3) Å]. The equatorial plane is formed by atoms O1, N1, N2 and N4, with the largest deviation from the mean plane being 0.176 Å, and the Mn atom is 0.0826 (13) Å out of this plane. The axial positions are occupied by the fourth phen N atom and a water O atom.

Each phenanthroline ligand is essentially planar, with mean deviations of 0.028 and 0.039 Å, and the planes are inclined at 76.45 (8)° with respect to one another. The Mn–N bond lengths are in the range 2.261 (3)–2.303 (3) Å, while the Mn–O bond lengths are 2.124 (3) and 2.156 (3) Å. It should be noted that the Mn–N bond lengths *trans* to benzoate and aqua O atoms are 2.303 (3) and 2.261 (3) Å, respectively, showing the stronger *trans* influence of benzoate over water. The phenanthroline ligands exhibit the usual acute N···N bite distances [N1···N2 2.7019 (13) Å and N3···N4 2.7092 (16) Å] and N–Mn–N angles [N1–Mn1–N2 72.40 (12)° and N3–Mn1–N4 73.32 (12)°]. These values are close to those observed in {[Mn(phen)₂(OAc)(H₂O)]ClO₄}₂·H₂O (Zhang, Huang *et al.*, 2002) and [Mn(phen)₂(ClCH₂COO)(H₂O)]ClO₄ (Zhang, Chen *et al.*, 2002). In addition, a strong hydrogen-bonding interaction is observed between the ligated water molecule and the dmf solvent molecule (Table 2).

Experimental

Mn(O₂CPh)₂·2H₂O (0.63 g, 2 mmol) was added to a solution of 2,5-pyridinedicarboxylic acid (0.33 g, 2 mmol) and KOH (0.23 g, 4 mmol) in 30 ml of CH₃OH/H₂O (*v/v* 1:2); the resulting solution was stirred for 30 min at room temperature. Then phenanthroline (0.40 g, 2 mmol) and NaClO₄·H₂O (0.28 g, 2 mmol) were added and the resulting solution was stirred at room temperature for 12 h. After filtration, the collected precipitate was dissolved in 15 ml of dmf/CH₂Cl₂ (*v/v* 1:1), the resulting filtrate was kept at room temperature for several weeks, and yellow crystals of (I) were obtained.

Crystal data

[Mn(C₇H₅O₂)(C₁₂H₈N₂)₂(H₂O)]·
(ClO₄)·C₃H₇NO
M_r = 727.02
Monoclinic, *P*2₁/*c*
a = 12.1787 (4) Å
b = 16.0320 (5) Å
c = 17.3628 (5) Å
β = 105.223 (1)°
V = 3271.11 (18) Å³
Z = 4

D_x = 1.476 Mg m^{−3}
Mo *Kα* radiation
Cell parameters from 5235
reflections
θ = 1.8–25.0°
μ = 0.55 mm^{−1}
T = 293 (2) K
Block, yellow
0.34 × 0.28 × 0.16 mm

Data collection

Siemens SMART CCD
diffractometer
ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
T_{min} = 0.700, *T_{max}* = 0.916
9876 measured reflections

5671 independent reflections
4440 reflections with *I* > 2σ(*I*)
R_{int} = 0.030
θ_{max} = 25.0°
h = −14 → 13
k = −18 → 17
l = −20 → 10

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.061
wR(*F*²) = 0.153
S = 1.13
5671 reflections
450 parameters
H atoms treated by a mixture of
independent and constrained
refinement

w = 1/[σ²(*F_o*²) + (0.0479*P*)²
+ 5.0132*P*]
where *P* = (*F_o*² + 2*F_c*²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.34 e Å^{−3}
Δρ_{min} = −0.43 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Mn–O1	2.124 (3)	Mn–N1	2.272 (3)
Mn–O3	2.156 (3)	Mn–N4	2.275 (3)
Mn–N3	2.261 (3)	Mn–N2	2.303 (3)
O1–Mn–O3	86.56 (12)	N3–Mn–N4	73.32 (12)
O1–Mn–N3	89.71 (11)	N1–Mn–N4	158.51 (12)
O3–Mn–N3	161.90 (12)	O1–Mn–N2	163.23 (11)
O1–Mn–N1	92.24 (12)	O3–Mn–N2	90.95 (12)
O3–Mn–N1	105.13 (12)	N3–Mn–N2	97.51 (11)
N3–Mn–N1	92.70 (12)	N1–Mn–N2	72.40 (12)
O1–Mn–N4	103.67 (11)	N4–Mn–N2	92.92 (11)
O3–Mn–N4	90.36 (13)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O3–H3 <i>D</i> ···O8 ⁱ	0.838 (19)	1.86 (2)	2.684 (4)	168 (5)

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

H atoms bonded to carbon were placed at calculated positions, with isotropic displacement parameters, riding on their carrier atoms. Water H atoms were located from difference maps and refined freely. The O–H bond lengths are 0.838 (19) and 0.85 (2) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *SAINT* and *SHELXTL*. Versions 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wieghardt, K. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 1153–1172.
Wieghardt, K., Bossek, U., Nuber, B., Weiss, J., Bonvoisin, J., Corbela, M., Vitols, S. E. & Girerd, J. J. (1989). *J. Am. Chem. Soc.* **110**, 7398–7411.
Zhang, X.-F., Chen, F., Wang, W.-G., Chen, C.-N. & Liu, Q.-T. (2002) *Acta Cryst.* **E58**, m360–m362.
Zhang, X.-F., Huang, D.-G., Chen, F., Chen, C. N. & Liu, Q. T. (2002). *Chin. J. Struct. Chem.* Submitted.