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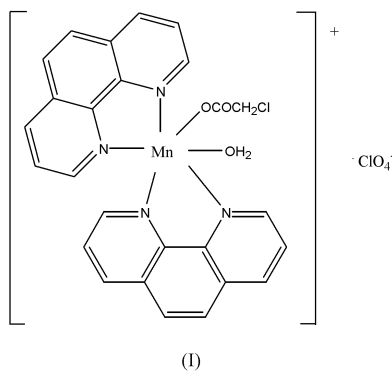
Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.055
 wR factor = 0.161
Data-to-parameter ratio = 12.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Aqua(chloroacetato)bis(1,10-phenanthroline-*N,N'*)-
manganese(II) perchlorateReceived 30 May 2002
Accepted 18 June 2002
Online 29 June 2002

The crystal structure of the title compound, $[\text{Mn}(\text{ClCH}_2\text{COO})(\text{phen})_2(\text{H}_2\text{O})]\text{ClO}_4$ (phen is 1,10-phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$), contains monomeric $[\text{Mn}(\text{ClCH}_2\text{COO})(\text{phen})_2(\text{H}_2\text{O})]^+$ cations and perchlorate anions. The manganese ion is coordinated by two chelating phen ligands [$\text{Mn}-\text{N}$ 2.243 (3)–2.375 (4) Å], one water molecule [$\text{Mn}-\text{O}$ 2.182 (3) Å] and a chloroacetate ligand [$\text{Mn}-\text{O}$ 2.119 (3) Å] in a distorted octahedral geometry. Consolidation of the crystal structure is achieved by $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions between the coordinated water molecules and the uncoordinated O atom of the chloroacetate ligand.

Comment

Presently, there is considerable interest in preparing and characterizing biomimetic manganoenzyme complexes in order that the mode of action of natural catalases can be established (Wiegardt, 1989), especially in the oxygen evolving center (OEC) of photosystem II (PSII) in green plants. It is thought that the coordination environment of Mn in the OEC contains O,N-donors and the binding of water to the Mn site may be important for the oxidation of water to yield dioxygen. In recent years, manganese–phen complexes have been extensively studied as model compounds for simulating the OEC in PSII (Manchanda *et al.*, 1994). The complexing behavior of phen with the Mn ion gives rise to a wide variety of Mn–phen coordination complexes, in which most of the mononuclear manganese complexes contain the $[\text{Mn}(\text{phen})_2]^{2+}$ core. We have undertaken the synthesis and structural characterization of Mn–phen compounds containing various carboxylates (Ma *et al.*, 2001). In this paper, we report the synthesis and crystal structure of a mononuclear manganese compound $[\text{Mn}(\text{ClCH}_2\text{COO})(\text{phen})_2(\text{H}_2\text{O})]\text{ClO}_4$, (I).



The crystal structure of (I) consists of discrete $[\text{Mn}(\text{ClCH}_2\text{COO})(\text{phen})_2(\text{H}_2\text{O})]^+$ cations and perchlorate anions. As illustrated in Fig. 1, the Mn^{II} ion is located in a severely distorted octahedral environment containing four N

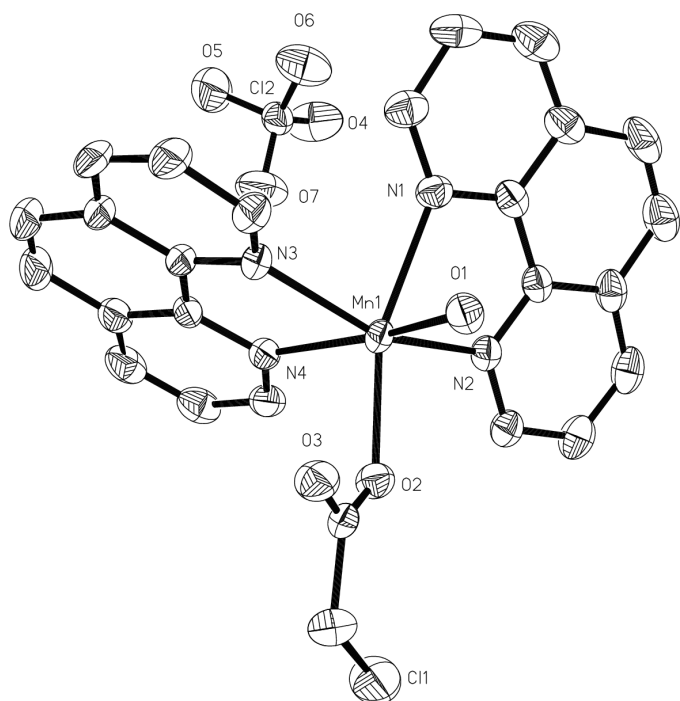


Figure 1
ORTEP (Johnson, 1976) drawing of the structure of $[\text{Mn}(\text{ClCH}_2\text{COO})(\text{phen})_2(\text{H}_2\text{O})]\text{ClO}_4$, showing 30% probability displacement ellipsoids.

atoms from a pair of *cis*-related chelating phen ligands, and two O atoms, one from a monodentate chloroacetate ligand [$\text{Mn1}-\text{O2}$ 2.119 (3) Å] and the other from a water molecule [$\text{Mn1}-\text{O1}$ 2.182 (3) Å]. Each phen ligand forms a near-perfect plane, the largest deviation from the least-squares planes being 0.024 (1) Å; the two phen planes are inclined at 69.6° to each other. The Mn–N bonds have lengths ranging from 2.243 (3) to 2.375 (4) Å, while the Mn–O bonds have lengths of 2.182 (3) and 2.119 (3) Å. The phen ligand exhibits its usual N···N distances [$\text{N1}\cdots\text{N2}$ 2.700 (3) Å and $\text{N3}\cdots\text{N4}$ 2.692 (3) Å] and acute bite angles [$\text{N1}-\text{Mn}-\text{N2}$ 71.38 (13)° and $\text{N3}-\text{Mn}-\text{N4}$ 73.13 (13)°]. These values are very close to those found in $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ (McCann *et al.*, 1998), $[\text{Mn}(\text{phen})_2(\text{NCS})_2]$ (Holleman *et al.*, 1994) and $[\text{Mn}(\text{phen})_2(\text{N}_3)_2]$ (Shen *et al.*, 1999), in which pairs of phenanthroline ligands are also *cis*-related.

There are strong hydrogen-bonding interactions between the coordinated water and uncoordinated oxygen of the chloroacetate ligand [$\text{O3}\cdots\text{O1}$ 2.753 (5) Å], resulting in a dimeric structure, as shown in Fig. 2. It is believed that these hydrogen-bond interactions play an important role in the consolidation of the crystal structure.

Experimental

A mixture of $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (0.49 g, 2.0 mmol), NaOH (0.08 g, 2.0 mmol), $\text{NaClO}_4\cdot \text{H}_2\text{O}$ (0.28 g, 2.0 mmol), 1,10-phenanthroline (0.40 g, 2.0 mmol) and ClCH_2COOH (0.19 g, 2.0 mmol) in 20 ml of $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (15:5) was stirred for 5 h. After filtration, the filtrate was allowed to stand for 40 d, depositing yellow-green crystals of (I).

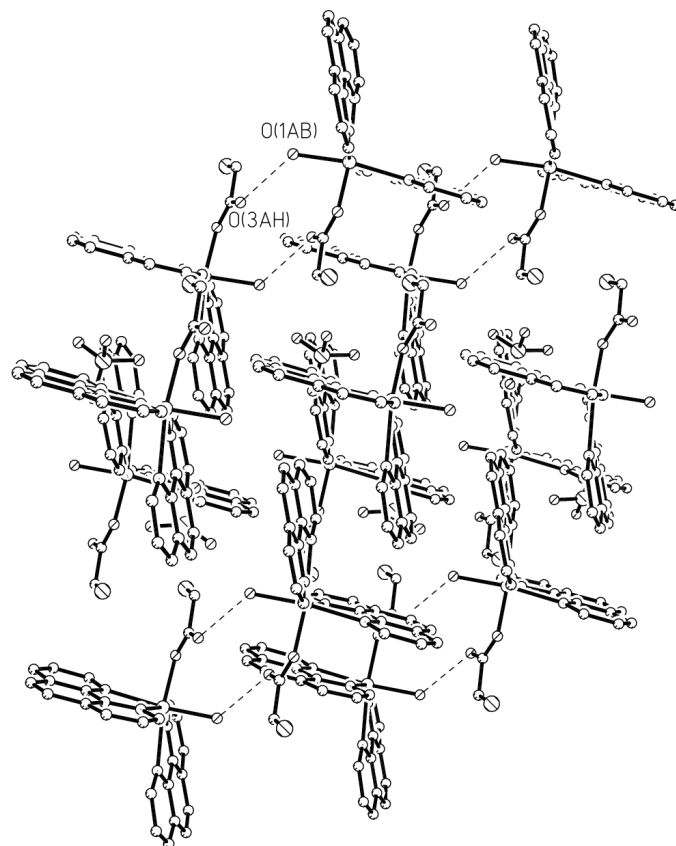


Figure 2
ORTEP (Johnson, 1976) packing diagram of the title compound.

Crystal data

$[\text{Mn}(\text{C}_2\text{H}_2\text{ClO}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2\cdot (\text{H}_2\text{O})]\text{ClO}_4$
 $M_r = 626.30$
 Triclinic, $P\bar{1}$
 $a = 9.4884$ (4) Å
 $b = 9.6935$ (5) Å
 $c = 15.2244$ (8) Å
 $\alpha = 74.715$ (2)°
 $\beta = 78.456$ (1)°
 $\gamma = 73.955$ (1)°
 $V = 1285.84$ (11) Å³

$Z = 2$
 $D_x = 1.618$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3298 reflections
 $\theta = 1.4-25.1^\circ$
 $\mu = 0.78$ mm⁻¹
 $T = 293$ (2) K
 Block, yellow-green
 $0.70 \times 0.24 \times 0.20$ mm

Data collection

Siemens SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.615$, $T_{\max} = 0.856$
 6697 measured reflections

4509 independent reflections
 3229 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 25.1^\circ$
 $h = -11 \rightarrow 11$
 $k = -11 \rightarrow 7$
 $l = -16 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.161$
 $S = 1.05$
 4509 reflections
 369 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.60$ e Å⁻³
 $\Delta\rho_{\min} = -0.73$ e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Mn—O2	2.119 (3)	Mn—N2	2.248 (3)
Mn—O1	2.182 (3)	Mn—N4	2.275 (3)
Mn—N3	2.243 (3)	Mn—N1	2.375 (4)
O2—Mn—O1	94.08 (13)	N3—Mn—N4	73.13 (13)
O2—Mn—N3	113.93 (12)	N2—Mn—N4	96.59 (13)
O1—Mn—N3	91.41 (13)	O2—Mn—N1	159.23 (13)
O2—Mn—N2	88.77 (13)	O1—Mn—N1	83.81 (13)
O1—Mn—N2	100.51 (13)	N3—Mn—N1	86.81 (13)
N3—Mn—N2	153.65 (13)	N2—Mn—N1	71.41 (13)
O2—Mn—N4	85.87 (12)	N4—Mn—N1	102.14 (12)
O1—Mn—N4	162.90 (13)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1B \cdots O3 ⁱ	0.89 (5)	1.87 (6)	2.753 (5)	170 (5)

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

H atoms bonded to carbon were placed at calculated positions, and refined with isotropic displacement parameters, using a riding model. H atoms associated with the water molecules were located from difference maps and refined freely. The crystal used was rather large, since smaller crystals resulted in very weak intensities.

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

This work was supported by The State Key Basic Research and Development Plan (G1998010100) and NNSFC (Nos. 29733090 and 29973047).

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