

(Acetylacetonato)bis(1,10'-phenanthroline-*N,N'*)-manganese(II) perchlorate

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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$

R factor = 0.064

wR factor = 0.191

Data-to-parameter ratio = 13.3

For 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, $[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{ClO}_4)$, contains a monomeric $[\text{Mn}(\text{phen})_2(\text{acac})]^+$ cation and a perchlorate anion [phen is 1,10'-phenanthroline ($\text{C}_{12}\text{H}_8\text{N}_2$) and acac is acetylacetonate ($\text{C}_5\text{H}_7\text{O}_2$)]. The Mn^{II} ion is coordinated by four N atoms from the phen ligands [$\text{Mn}-\text{N}$ 2.253 (4)–2.322 (4) Å] and two O atoms of the acac ligand [$\text{Mn}-\text{O}$ 2.116 (3) and 2.124 (3) Å] in chelating mode, forming a distorted octahedral geometry.

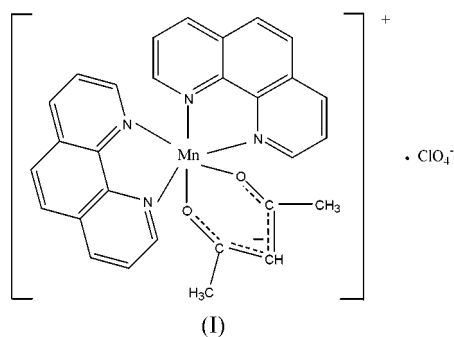
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Comment

Considerable attention has been focused on the bioinorganic chemistry of Mn and, in particular, on multinuclear Mn metalloenzymes, such as the tetra-Mn in the oxygen-evolving centre (OEC) of photosystem II (PSII) in green plants (Wiegardt, 1989). It is thought that the coordination environment of the Mn in OEC consists essentially of the ligands with O and N donor atoms, and the binding of water to the Mn site may be important for the oxidation of water for the evolution of dioxygen. In recent years, Mn–phen (phen is 1,10'-phenanthroline) complexes have been extensively studied as model compounds for simulating OEC in PSII (Manchanda *et al.*, 1994). In a reaction system containing phen, $\text{Mn}(\text{acac})_3$ (acac is acetylacetonate) and dicarboxylic acid, we isolated the title complex, $[\text{Mn}(\text{phen})_2(\text{acac})]\text{ClO}_4$, (I), which contains three different chelating ligands in the cation. Here, we describe its synthesis and crystal structure.



The crystal structure of (I) is composed of a monomeric $[\text{Mn}(\text{phen})_2(\text{acac})]^+$ cation and one perchlorate anion, as illustrated in Fig. 1. It is noted that all three ligands coordinate to the Mn^{II} ion in chelating mode, leading to a serious distortion from the octahedral configuration, with chelating angles of $73.85(14)$ and $72.66(14)^\circ$ for $\text{N}-\text{Mn}-\text{N}$ and $85.13(13)^\circ$ for $\text{O}-\text{Mn}-\text{O}$.

In addition to $[\text{Mn}(\text{phen})_3]^{2+}$ complexes having three phen chelating ligands (Drew *et al.*, 1989), only two examples of an Mn–phen complex containing three different chelating ligands

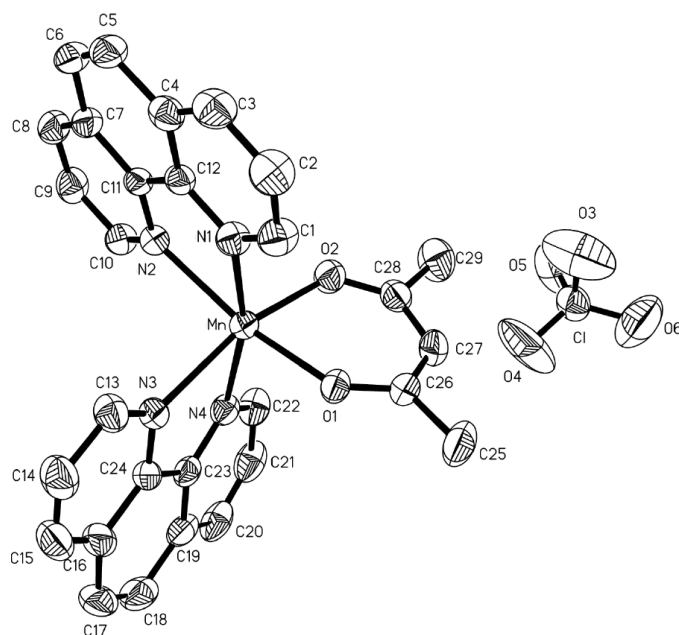


Figure 1
The structure of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

were found in the literature, namely $[\text{Mn}(\text{phen})(\text{acac})_2]$ (Stephens, 1977) and $[\text{Mn}(\text{phen})_2\{\text{CH}_2(\text{COO})_2\}]$ (Wang *et al.*, 2000)

All the atoms in the phen ligands of (I), including the Mn^{II} ion, form a perfect plane, the largest deviation from the least-squares plane being 0.0148 \AA , and the phen planes are inclined at 83.4° with respect to each other. The acac ligand is also planar and the Mn^{II} atom lies 0.2 \AA from the acac plane.

The Mn–N bond lengths in (I) are in the range $2.253(4)$ – $2.322(4) \text{ \AA}$, and the Mn–O bond lengths are in the range $2.116(3)$ – $2.124(3) \text{ \AA}$. The phenanthroline exhibits its usual acute $\text{N}\cdots\text{N}$ bite distances [$\text{N}1\cdots\text{N}2$ $2.723(3)$ and $\text{N}3\cdots\text{N}4$ $2.720(3) \text{ \AA}$], and the N–Mn–N angles 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).

The packing diagram for (I) seems to show weak $\pi\cdots\pi$ stacking of pairs of phen planes between neighbouring $[\text{Mn}(\text{phen})_2(\text{acac})]^+$ cations, with the characteristic interplanar distance of 3.6 \AA , slightly larger than the sum of the van der Waals radii of the two C atoms.

Experimental

A mixture of 2,5-pyridinedicarboxylic acid (0.32 g, 2.5 mmol) and KOH (0.28 g, 5 mmol) was dissolved in MeOH–H₂O (20 ml; 1:1 v/v). To the resulting turbid solution, $\text{Mn}(\text{acac})_3$ (0.70 g, 2.0 mmol) was added and the solution stirred for 30 min at room temperature. After addition of phen (0.4 g, 2 mmol) and $\text{NaClO}_4\cdot 4\text{H}_2\text{O}$ (0.28 g, 2.0 mmol) and stirring for 2 h, the reaction solution was filtered. The filtrate was allowed to stand at room temperature for two weeks to deposit orange crystals of (I).

Crystal data

$[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{ClO}_4)$
 $M_r = 613.90$
 Monoclinic, $C2/c$
 $a = 33.3452(4) \text{ \AA}$
 $b = 10.5753(1) \text{ \AA}$
 $c = 17.1597(3) \text{ \AA}$
 $\beta = 110.05^\circ$
 $V = 5684.35(13) \text{ \AA}^3$
 $Z = 8$

$D_x = 1.435 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 4315 reflections
 $\theta = 2.3$ – 25.0°
 $\mu = 0.61 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, orange
 $0.40 \times 0.38 \times 0.26 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.593$, $T_{\text{max}} = 0.854$
 10 092 measured reflections

4933 independent reflections
 3118 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\text{max}} = 25^\circ$
 $h = -39 \rightarrow 33$
 $k = -8 \rightarrow 12$
 $l = -16 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.191$
 $S = 1.03$
 4933 reflections
 370 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.86 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Mn–O2	2.116 (3)	Mn–N4	2.269 (4)
Mn–O1	2.124 (3)	Mn–N2	2.279 (4)
Mn–N1	2.253 (4)	Mn–N3	2.322 (4)
O2–Mn–O1	85.13 (13)	N1–Mn–N2	73.85 (14)
O2–Mn–N1	101.99 (14)	N4–Mn–N2	98.96 (13)
O1–Mn–N1	91.43 (14)	O2–Mn–N3	162.22 (14)
O2–Mn–N4	90.79 (14)	O1–Mn–N3	90.06 (13)
O1–Mn–N4	95.94 (13)	N1–Mn–N3	95.22 (14)
N1–Mn–N4	165.76 (14)	N4–Mn–N3	72.66 (14)
O2–Mn–N2	95.38 (13)	N2–Mn–N3	93.65 (13)
O1–Mn–N2	165.08 (13)		

The structure was solved by direct methods and subsequent difference Fourier syntheses. H atoms bonded to C atoms were placed at calculated positions, with isotropic displacement parameters riding on those of their carrier atoms.

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; software used to prepare material for publication: SHELXTL.

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