Aqua(3-carboxylatophenoxyacetato-κO)-bis(1,10-phenanthroline-$\kappa^2 N,N'$)manganese(II) tetrahydrate

Shan Gao[a] and Seik Weng Ng[b]*

[a]College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

The dicarboxylate ligand in the title compound, $[Mn(C_9H_6O_5)(C_{12}H_8N_2)_2(H_2O)]\cdot 4H_2O$, coordinates in a monodentate manner to the Mn^{II} atom through the carboxylate group on the benzene ring. The two O atoms in the octahedral configuration around the Mn^{II} atom are *cis* to each other. Extensive hydrogen bonding leads to a three-dimensional network.

Comment

The carboxyphenoxyacetate ligand is a multidentate ligand with both rigid and flexible parts. As part of an investigation of carboxyphenoxyacetate complexes, we present here the crystal structure of the title Mn^{II} complex, (I).
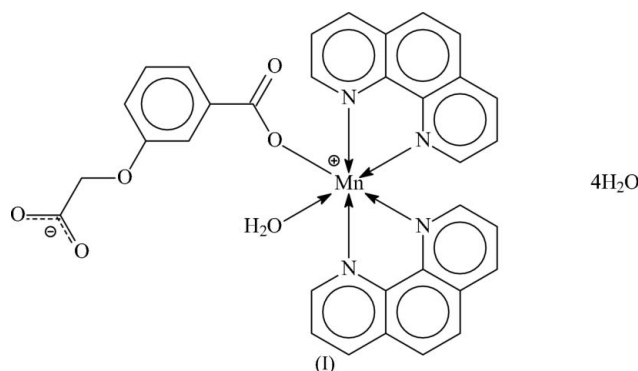
The molecular structure of (I) is shown in Fig. 1. The bis-(phenanthroline)-chelated Mn^{II} complex of 3-carboxylphenoxyacetate exists as a monoaqua-coordinated tetrahydrate. The octahedral coordination geometry around the Mn^{II} atom is similar to that in the bis(phenanthroline)-chelated Mn^{II} complex with 4-carboxyphenoxyacetate (Huo *et al.*, 2005). The 3-carboxylphenoxyacetate dianion coordinates in a monodentate fashion to the Mn^{II} atom through the carboxylate group on the benzene ring. The carboxylate group of the oxyacetate arm does not coordinate, but it engages in hydrogen-bonding interactions (Table 2). The two coordinated O atoms are *cis* to each other. The coordinated bond distances and angles are normal compared with those for reported related structures. Extensive hydrogen bonds (Table 2) lead to a three-dimensional network.

Experimental

Manganese dichloride hexahydrate (0.47 g, 2 mmol), 1,10-phenanthroline (0.80 g, 4 mmol) and 3-carboxyphenoxyacetic acid (0.39 g, 2 mmol) were dissolved in a small volume of hot water. The clear solution was set aside for several days to obtain yellow prismatic

crystals of (I). Analysis calculated for $C_{33}H_{32}MnN_4O_{10}$: C 56.64, H 4.61, N 8.01%; found: C 56.67, H 4.59, N 7.99%.

Crystal data

$[Mn(C_9H_6O_5)(C_{12}H_8N_2)_2$-$(H_2O)]\cdot 4H_2O$
$M_r = 699.57$
Triclinic, $P\overline{1}$
$a = 8.123$ (2) Å
$b = 14.134$ (3) Å
$c = 15.655$ (3) Å
$\alpha = 110.51$ (3)°
$\beta = 90.95$ (3)°
$\gamma = 104.70$ (3)°
$V = 1617.3$ (8) Å^3

$Z = 2$
$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14540
   reflections
$\theta = 3.1–27.5°$
$\mu = 0.47$ mm^{-1}
$T = 295$ (2) K
Block, yellow
$0.38 \times 0.26 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID IP
   diffractometer
ω scans
Absorption correction: multi-scan
   (*ABSCOR*; Higashi, 1995)
   $T_{min} = 0.629$, $T_{max} = 0.911$
12644 measured reflections

5673 independent reflections
3748 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 25.0°$
$h = -8 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.066$
$wR(F^2) = 0.184$
$S = 1.02$
5673 reflections
470 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1002P)^2 + 0.5697P]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.099 (3)	Mn1—N2	2.269 (3)
Mn1—O1w	2.177 (3)	Mn1—N3	2.284 (4)
Mn1—N1	2.268 (3)	Mn1—N4	2.267 (4)
O1—Mn1—O1w	86.5 (1)	O1w—Mn1—N4	87.5 (1)
O1—Mn1—N1	104.3 (1)	N1—Mn1—N2	73.4 (1)
O1—Mn1—N2	87.4 (1)	N1—Mn1—N3	159.7 (1)
O1—Mn1—N3	90.4 (1)	N1—Mn1—N4	93.8 (1)
O1—Mn1—N4	161.3 (1)	N2—Mn1—N3	93.7 (1)
O1w—Mn1—N1	93.9 (1)	N2—Mn1—N4	102.6 (1)
O1w—Mn1—N2	164.1 (1)	N3—Mn1—N4	73.5 (1)
O1w—Mn1—N3	101.1 (1)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1w—H1w1$\cdots$O2w	0.85	1.96	2.712 (7)	147
O1w—H1w2$\cdots$O2	0.85	1.91	2.638 (5)	143
O2w—H2w1$\cdots$O3w	0.88	2.19	2.83 (1)	129
O3w—H3w1$\cdots$O4^i	0.90	1.82	2.23 (2)	105
O4w—H4w1$\cdots$O4	0.87	1.64	2.39 (2)	144
O5w—H5w1$\cdots$O5′	0.86	1.80	2.62 (2)	159

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

The C-bound H atoms were positioned geometrically (C—H = 0.93 or 0.97 Å) and were included in the refinement in the riding-model
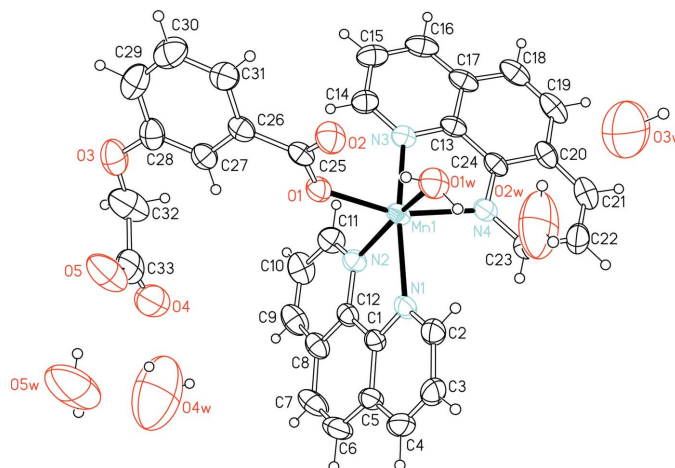

Figure 1
ORTEPII plot of (I). Displacement ellipsoids are drawn at the 30% probability level, and H atoms are drawn as spheres of arbitrary radii. The minor disordered component has been omitted for clarity.

approximation, with $U_{iso}(H)$ set to 1.2 times $U_{eq}(C)$. The H atoms of the water molecules were placed at chemically sensible positions on the basis of hydrogen bonds but they were not refined; their displacement parameters were similarly tied. The water molecules were restrained to behave in an approximately isotropic manner. All H$\cdots$H contacts exceed 2 Å. The oxyacetate arm of the dianion is disordered over two positions; the occupancy factors refined to 0.44 (1) and 0.56 (1). A number of restraints were imposed. The O3—C32 and O3–C-32′ distances were restrained to within 0.01 Å of each other, as were the C32—C33 and C32′—C33′ pair. The four C—O distances of the –CO$_2$ portion were also restrained in this manner; owing to this restraint, the electrons in the portion are assumed to be delocalized. The vibrations of the disordered atoms were restrained to behave in a nearly isotropic fashion.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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