

Quan-Zheng Zhang and
Can-Zhong Lu*State Key Laboratory of Structural Chemistry,
Fujian Institute of Research on the Structure of
Matter, Chinese Academy of Sciences, Fuzhou,
Fujian, 350002, People's R. epublic of China

Correspondence e-mail: zclu@ms.fjirsm.ac.cn

Key indicators

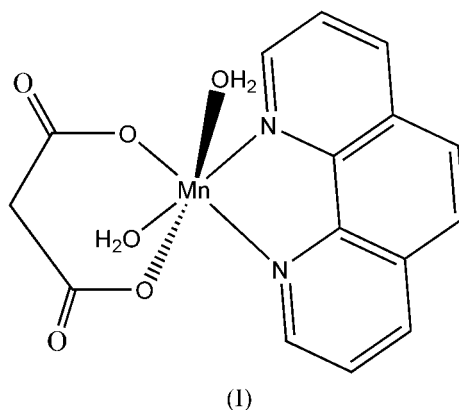
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.026
 wR factor = 0.071
Data-to-parameter ratio = 12.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*cis*-Diaquamalonato(1,10-phenanthroline)-
manganese(II)

In the title complex, $[\text{Mn}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]$, the Mn^{II} atom displays a distorted octahedral geometry, being coordinated by two N atoms of a 1,10-phenanthroline ligand, two O atoms from the carboxylate groups of the chelating malonate dianion and two O atoms of *cis* water molecules. The complex molecules are linked to form a three-dimensional supramolecular array *via* $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and $\pi-\pi$ interactions.

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Comment

As an important dicarboxylate ligand, malonate has been extensively used for the preparation of transition metal complexes. In numerous such complexes, the malonate dianion generally exhibits bidentate, tridentate or tetradentate coordination modes. Although many complexes containing mixed malonate and nitrogen-donor ligands have been synthesized and characterized, complexes containing mixed malonate (mal) and 1,10-phenanthroline (phen) ligands have been reported less often. To the best of our knowledge, there are only three reports on the structures of metal complexes with malonate and 1,10-phenanthroline ligands, *viz.* $[\text{Cu}(\text{mal})(\text{phen})(\text{H}_2\text{O})]\cdot 1.5\text{H}_2\text{O}$ (Kwik *et al.*, 1986), $[\text{Mn}(\text{mal})(\text{phen})_2(\text{EtOH})]$ (Zhang *et al.*, 2000) and $[\text{Mn}_2\text{Cl}(\text{mal})(\text{phen})_3(\text{H}_2\text{O})]\text{Cl}$ (Sain *et al.*, 2003). We report here the preparation and crystal structure of the title compound, (I).



The molecular structure of (I) is shown in Fig. 1, displaying a structure similar to that of the reported complex $[\text{Mn}(\text{mal})(\text{bipy})(\text{H}_2\text{O})_2]$ (bipy is 2,2'-bipyridine; Sain *et al.*, 2003), (II). The malonate dianion reveals a bidentate coordination mode, connecting to the Mn atom through two O atoms from different carboxylate groups. The dihedral angle between the planes O1/C1/O2 and O3/C3/O4 is $54.4(4)^\circ$. The Mn atom is also chelated by two N atoms of the phen ligand

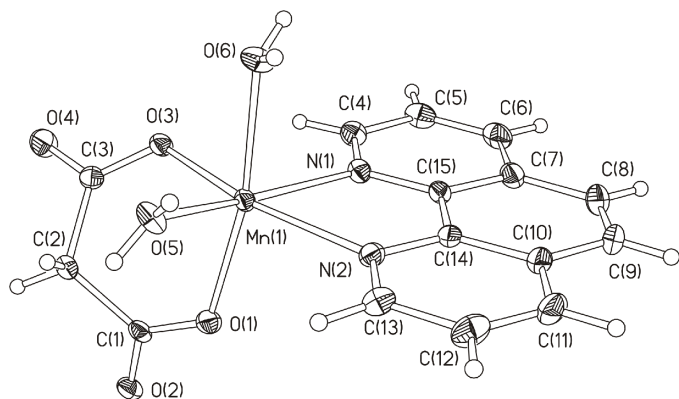


Figure 1
The molecular structure of (I), showing displacement ellipsoids drawn at the 30% probability level.

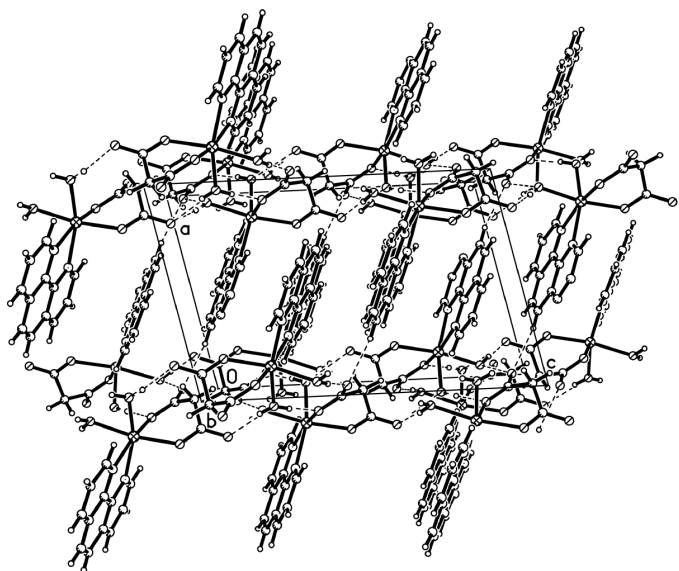


Figure 2
The crystal structure of (I), viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

and two O atoms of *cis* water molecules. The Mn center exhibits a distorted octahedral coordination geometry with the bond angles in the range 162.62 (4)–169.19 (4)° for *trans* angles and 73.65 (5)–102.87 (5)° for *cis* angles (Table 1).

As shown in Fig. 2, the molecular packing of (I) exhibits a three-dimensional supramolecular structure similar to that of (II). Both hydrogen-bonding (Table 2) and π - π stacking interactions play an important role in constructing the three-dimensional structure. The complex molecules are linked to one another through hydrogen bonding between the coordinated water molecules and the carboxyl O atoms to form layers. Neighboring layers are further linked together through π - π stacking interactions between the phen rings of adjacent molecules, with a face-to-face separation of *ca* 3.53 Å.

Experimental

An ethanol solution (8 ml) of 1,10-phenanthroline (1.2 mmol) was added slowly to an aqueous solution (10 ml) of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$

(1 mmol) with continuous stirring. An aqueous solution (10 ml) of malonic acid (1.5 mmol), adjusted to a pH of about 5 with an aqueous NaOH solution (1 *N*), was then added slowly to the above reaction mixture with continuous stirring. After half an hour, the reaction mixture was allowed to stand at room temperature undisturbed for two weeks, resulting in yellow crystals of (I) (yield 57%).

Crystal data

$[\text{Mn}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]$
 $M_r = 373.22$
 Monoclinic, $P2_1/c$
 $a = 9.978$ (5) Å
 $b = 9.918$ (4) Å
 $c = 15.426$ (7) Å
 $\beta = 102.310$ (7)°
 $V = 1491.6$ (11) Å³
 $Z = 4$

$D_x = 1.662$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5579 reflections
 $\theta = 2.1$ – 27.5°
 $\mu = 0.92$ mm⁻¹
 $T = 293$ (2) K
 Prism, yellow
 $0.31 \times 0.19 \times 0.11$ mm

Data collection

Bruker SMART CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.812$, $T_{\text{max}} = 0.904$
 11205 measured reflections

3410 independent reflections
 3244 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -12 \rightarrow 11$
 $k = -11 \rightarrow 12$
 $l = -20 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.071$
 $S = 1.08$
 3410 reflections
 274 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 0.4812P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.061$
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³
 Extinction correction: SHELXL
 Extinction coefficient: 0.0029 (11)

Table 1

Selected geometric parameters (Å, °).

Mn1—O3	2.1462 (12)	Mn1—O6	2.2010 (13)
Mn1—O1	2.1512 (13)	Mn1—N1	2.2652 (14)
Mn1—O5	2.1799 (12)	Mn1—N2	2.2798 (13)
O3—Mn1—O1	84.88 (4)	O5—Mn1—N1	162.62 (4)
O3—Mn1—O5	102.87 (5)	O6—Mn1—N1	87.68 (5)
O1—Mn1—O5	94.44 (4)	O3—Mn1—N2	164.00 (4)
O3—Mn1—O6	85.87 (4)	O1—Mn1—N2	96.27 (4)
O1—Mn1—O6	169.19 (4)	O5—Mn1—N2	92.97 (5)
O5—Mn1—O6	82.19 (4)	O6—Mn1—N2	94.17 (5)
O3—Mn1—N1	90.38 (4)	N1—Mn1—N2	73.65 (5)
O1—Mn1—N1	97.95 (5)		

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>
O5—H5A...O2 ⁱ	0.81 (2)	1.95 (2)	2.7529 (16)	172 (2)
O5—H5B...O3 ⁱⁱ	0.88 (2)	1.83 (2)	2.7140 (16)	174 (2)
O6—H6A...O4 ⁱⁱ	0.84 (2)	1.81 (2)	2.6397 (17)	173 (2)
O6—H6B...O2 ⁱⁱⁱ	0.84 (2)	2.02 (2)	2.8519 (17)	171 (2)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

All H atoms were located in difference Fourier maps and refined isotropically. The C—H and O—H bond lengths are 0.90 (2)–1.00 (2) and 0.81 (2)–0.88 (2) Å, respectively.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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