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Diaqua(cyclohexane-1,1-diacetato-κ^2O,O')-(phenanthroline-κ^2N,N')manganese(**II**) trihydrate

Liang Shen,[a]* Li-Cheng Yan,[a] Zhi-Min Jin[b] and Yi-Jian Zhang[a]

[a]Department of Chemistry, Hangzhou Teachers' College, Hangzhou, People's Republic of China, and [b]College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou, People's Republic of China

Correspondence e-mail: shenchem@sina.com

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Key indicators

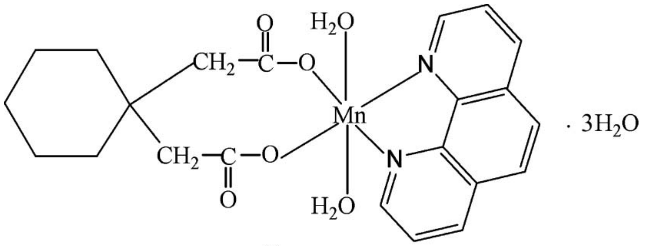
Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.075
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title compound, $[Mn(C_{10}H_{14}O_4)(C_{12}H_8N_2)(H_2O)_2]\cdot 3H_2O$, the Mn^{II} atom is in a distorted octahedral geometry, being coordinated by two N atoms of one 1,10-phenanthroline ligand, two O atoms from two carboxylate groups of the chelating cyclohexane-1,1′-diacetate dianion and two O atoms of two *trans* water molecules. The complex molecules are linked to form a three-dimensional network by hydrogen-bonding interactions between coordinated water molecules, non-coordinated water molecules and carboxylate groups of neighbouring molecules, and by aromatic π–π stacking interactions of the phenthroline rings.

Comment

In recent years, considerable research effort has been put into one-, two- and three-dimensional manganese(II) complexes with dicarboxylate ligands which have potential applications in molecular-based magnets, catalysis and supramolecular chemistry (Li *et al.*, 2002; Devereux *et al.*, 2000; Shi *et al.*, 2000). Cyclohexane-1,1′-diacetic acid (CDA) has been studied as a dielectric material, as well as an intermediate of pharmaceuticals. As a dicarboxylate, the cyclohexane-1,1′-diacetate dianion may act as a bidentate chelating ligand. To our knowledge, there is one report of the crystal structure of cyclohexane-1,1′-diacetic acid (Vanek et al., 1998), but no reports about the structures of transition metal complexes with cyclohexane-1,1′-diacetate. We report here the preparation and crystal structure of the title Mn^{II} complex, (I), with the chelating CDA ligand.



(I)

The molecular structure of (I) is shown in Fig. 1. The title complex exists as discrete monomers. A cyclohexane-1,1′-diacetate dianion chelates a Mn^{II} atom by two O atoms from different carboxylate groups. The Mn^{II} atom is also coordinated by two N atoms of one 1,10-phenanthroline ligand and two O atoms of two *trans* water molecules. The Mn site exhibits a distorted octahedral coordination, with bond angles ranging from 163.41 (5) to 177.46 (5)° for *trans* angles, and from 72.99 (5) to 103.27 (5)° for others (Table 1). The Mn—O(carboxylate) bond distances are 2.105 (1) and 2.101 (2) Å,

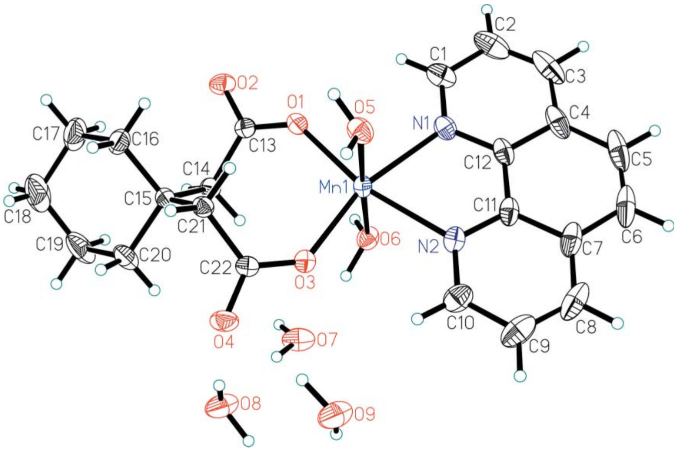


Figure 1
The molecular structure of (I), showing 35% probability displacement ellipsoids and the atom-numbering scheme.

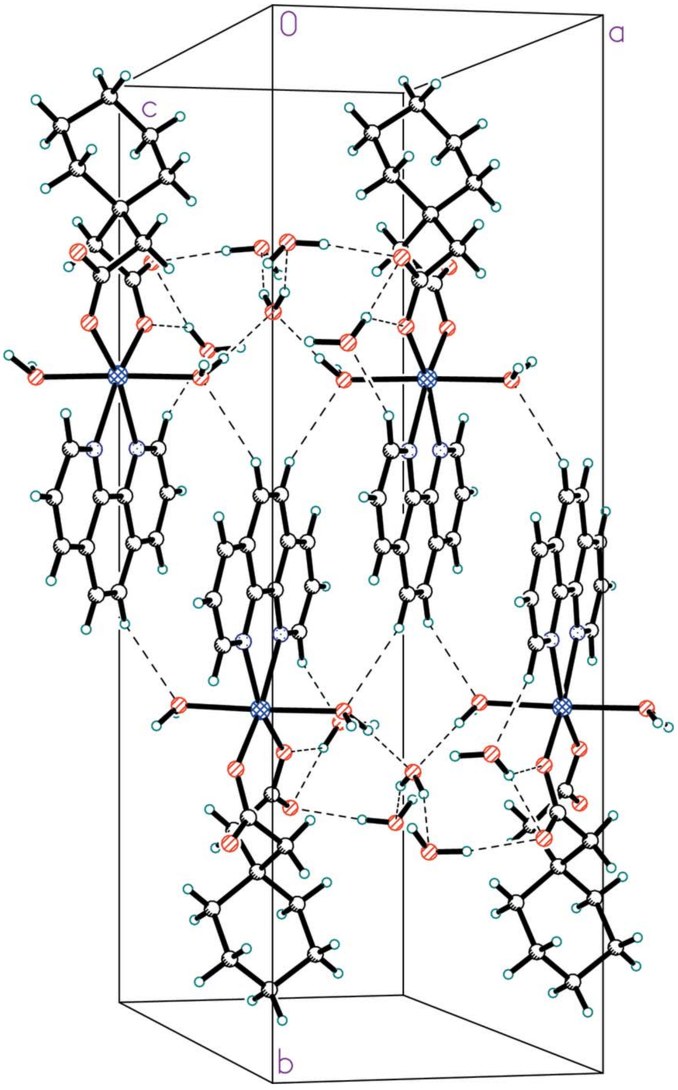


Figure 2
Part of the molecular packing of (I), showing the O—H$\cdots$O hydrogen bonds (dashed lines) and the stacking of phenanthroline rings.

which are comparable with those in [Mn(maleate)(1,10-phenanthroline)$_2$] (Wang *et al.*, 2000). The Mn—O(water) distances of 2.224 (2) and 2.207 (2) Å are also comparable with those in [Mn(maleate)(H$_2$O)$_4$] (Shen, 2003). The Mn—N bond lengths are in good agreement with the corresponding ones found in [Mn(1,10-phenanthroline)$_2$Cl$_2$] (McCann et al., 1998).

Hydrogen-bonding interactions (Table 2) play an important role in the solid-state structure of (I). As shown in Fig. 2, complex molecules link to each other through hydrogen bonds involving coordinated water molecules, carboxylate groups and non-coordinated water molecules, forming a three-dimensional network. In addition, the structure is stablized by π–π interactions between phenanthroline rings. These π–π interactions are evident from the centroid–centroid distance of 3.578 (2) Å between the C11-benzene ring and the N2-pyridyl ring at ($-x$, $1 - y$, $1 - z$), 3.717 (2) Å between the C11-benzene ring and the N2-pyridyl ring at ($1 - x$, $1 - y$, $1 - z$), and 3.871 (2) Å between the C11-benzene ring and its symmetric equivalent at ($1 - x$, $1 - y$, $1 - z$).

Experimental

An ethanol solution (10 ml) containing 1,10-phenanthroline (0.180 g, 1 mmol) was added slowly to an aqueous solution (10 ml) containing MnCl$_2$·4H$_2$O (0.198 g, 1 mmol) with continuous stirring and refluxing. A copious precipitate was produced. An aqueous solution (10 ml) containing cyclohexane-1,1-diacetic acid (0.200 g, 1 mmol) neutralized with an aqueous solution containing NaOH (0.080 g, 2 mmol) was slowly added to the above reaction mixture with continuous stirring and refluxing until the precipitate had dissolved. After 30 min, the reaction mixture was cooled to room temperature and filtered. Yellow single crystals of the title complex were obtained after a week.

Crystal data

[Mn(C$_{12}$H$_8$N$_2$)(C$_{10}$H$_{14}$O$_4$)(H$_2$O)$_2$]·3H$_2$O
M_r = 523.44
Monoclinic, $P2_1/c$
a = 7.8763 (3) Å
b = 25.0242 (7) Å
c = 12.7232 (3) Å
β = 101.275 (1)°
V = 2459.3 (1) Å^3
Z = 4
D_x = 1.414 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14069 reflections
θ = 2.3–27.4°
μ = 0.59 mm^{-1}
T = 297 (1) K
Block, yellow
0.21 × 0.18 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min}$ = 0.801, $T_{\max}$ = 0.905
23941 measured reflections
5611 independent reflections
3284 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int}$ = 0.045
$\theta_{\max}$ = 27.5°
$h = -10 \rightarrow 10$
$k = -32 \rightarrow 32$
$l = -14 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.075
S = 1.02
5611 reflections
308 parameters
H-atom parameters constrained
$w = 1/[0.0003F_o^2 + \sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.45 e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 11.4 (7)

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Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.101 (1)	Mn1—O6	2.224 (2)
Mn1—O3	2.105 (1)	Mn1—N1	2.285 (2)
Mn1—O5	2.207 (2)	Mn1—N2	2.278 (2)
O3—Mn1—O1	103.27 (5)	N2—Mn1—O3	93.20 (5)
O5—Mn1—O1	87.70 (5)	O6—Mn1—O5	177.46 (5)
O6—Mn1—O1	91.86 (5)	N1—Mn1—O5	86.90 (6)
N1—Mn1—O1	90.53 (5)	N2—Mn1—O5	89.48 (6)
N2—Mn1—O1	163.41 (5)	N1—Mn1—O6	90.60 (6)
O5—Mn1—O3	93.19 (5)	N2—Mn1—O6	90.23 (6)
O6—Mn1—O3	89.35 (5)	N2—Mn1—N1	72.99 (5)
N1—Mn1—O3	166.19 (5)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H23···O7	0.96	1.82	2.776 (2)	175
O5—H24···O2^{i}	0.93	1.77	2.671 (2)	163
O6—H25···O4^{ii}	0.90	1.88	2.744 (2)	162
O6—H26···O7^{iii}	0.94	1.85	2.769 (2)	165
O7—H27···O9^{i}	0.90	1.96	2.831 (2)	163
O7—H28···O8	0.85	1.90	2.748 (2)	170
O8—H29···O3^{iv}	0.89	2.44	3.201 (2)	144
O8—H29···O4^{iv}	0.89	2.13	2.970 (2)	157
O8—H30···O2	0.93	1.92	2.812 (2)	158
O9—H31···O4^{iv}	0.95	1.95	2.879 (2)	163
O9—H32···O1	0.99	2.52	3.318 (2)	138
O9—H32···O2	0.99	1.94	2.909 (2)	165

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

The H atoms of the water molecules were located in a difference Fourier map and they were allowed to ride on their parent atoms with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom). The other H atoms were placed in idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93 (aromatic) and 0.97 Å (methylene), and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999; program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Devereux, M., McCann, M., Leon, V., Geraghty, M., Mckec, V. & Wikaira, J. (2000). *Polyhedron*, **19**, 1205–1211.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall and C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Li, L., Liao, D. & Jiang, Z. (2002). *Inorg. Chem.* **41**, 421–424.

McCann, S., McCann, M., Casey, M. T., Jackman, M., Devereux, M. & McKee, V. (1998). *Inorg. Chim. Acta*, **279**, 24–29.

Rigaku (1998). *PROCESS-AUTO.* Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo, Japan.

Rigaku/MSC (2004). *CrystalStructure.* Version 3.6.0. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Shen, L. (2003). *Acta Cryst.* C**59**, m128–m129.

Shi, Z., Zhang, L., Gao, S., Yang, G., Hua, J., Gao, L. & Feng, S. (2000). *Inorg. Chem.* **39**, 1990–1993.

Vanek, P., Zikmund, Z., Kroupa, J., Pronin, A., Kamba, S. & Petzelt, J. (1998). *Solid State Commun.* **105**, 439–443.

Wang, Z., Zhou, X., Yu, W. & Fu, Y. (2000). *Z. Kristallogr.* **215**, 423–424.

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