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Bis[aquachlorobis(1,10-phenanthroline)-manganese(II)] benzene-1,4-dioxyacetate dihydrate

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The title complex, $[MnCl(phen)_2(H_2O)]_2(1,4\text{-BDOA})\cdot 2H_2O$ [1,4-BDOA = benzene-1,4-dioxyacetate ($C_{10}H_8O_6$) and phen = 1,10-phenanthroline ($C_{12}H_8N_2$)], consists of $[MnCl(phen)_2(H_2O)]^+$ cations, a benzene-1,4-dioxyacetate dianionsand water molecules. In the cation, the Mn atom is six-coordinate with an octahedral geometry comprising four N atoms from two phen ligands, one Cl and one water molecule. The benzene-1,4-dioxyacetate dianion lies on an inversion center. Intermolecular hydrogen bonds and π–π stacking interactions form the supramolecular network structure.

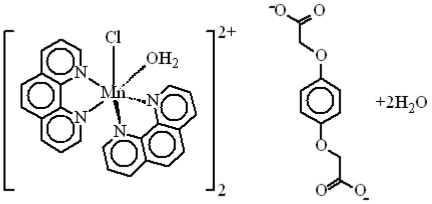
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.039
wR factor = 0.098
Data-to-parameter ratio = 14.6

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

Comment

There is interest in metal complexes of aromatic carboxylic acids that act as bridging ligands, such as isophthalic acid and benzenetetracarboxylic acid (Gomez-Lor *et al.*, 2002; Yang *et al.*, 2003). Phenylenedioxydiacetic acids, biologically active compounds that are widely used in agriculture, are a family of flexible multidentate ligands of versatile binding modes. To the best of our knowledge, investigations of the complexes of phenylenedioxydiacetic acids have mainly focused on the sodium, calcium, zinc, manganese, nickel, cobalt and copper salts of benzene-1,2-dioxyacetic acid (1,2-BDOA) (Smith *et al.*, 1987, 1991; McCann *et al.*, 1994), and there is little information on complexes of the 1,4-BDOA analog. The reaction of disodium benzene-1,4-dioxyacetate and 1,10-phenanroline with manganese(II) chloride hexahydrate occasionally yielded a manganese(II) complex, $[Mn(chloride)(1,10\text{-phenanroline})_2(H_2O)]_2(1,4\text{-BDOA})\cdot 2H_2O$, (I), whose crystal structure is reported here.



(I)

The asymmetric unit of (I) consists of the mononuclear $[MnCl(phen)_2(H_2O)]^+$ cation, half of a benzene-1,4-dioxyacetate dianion, and an uncoordinated water molecule (Fig. 1). The Mn^{II} ion is coordinated by four N atoms of two phen ligands, one Cl anion and one water molecule to form a distorted octahedral coordination geometry. The Mn—N bond lengths range from 2.242 (2) to 2.338 (2) Å. The benzene-1,4-dioxyacetate dianion lies on a special position of $\overline{1}$ site symmetry; the oxyacetate substituents and the benzene ring are almost coplanar [C25—C26—O3—C27 = 2.3 (4)°]. The phen ligands are bonded to the Mn^{II} atom in a *cis* mode, being nearly perpendicular to each other [dihedral angle = 86.6 (5)°]. The water molecules form O—H···O and O—H···Cl hydrogen bonds with carboxylate O atoms of adjacent 1,4-BDOA and Cl^- units (Fig. 2), resulting in a one-dimensional chain. There are π–π stacking interactions between adjacent phen ligands at 3.68 (4) and 3.88 (4) Å. Such π–π interactions and hydrogen bonds lead to a supramolecular three-dimensional network structure.

Experimental

The title complex was prepared by the addition of phen (3.98 g, 20 mmol) and $MnCl_2 \cdot 6H_2O$ (4.68 g, 20 mmol) to an aqueous solution of disodium benzene-1,4-dioxyacetate (5.40 g, 20 mmol). Colorless single crystals were obtained from the filtered solution after several days.

Crystal data

$[MnCl(C_{12}H_8N_2)_2(H_2O)]_2$-$(C_{10}H_8O_6) \cdot 2H_2O$
$M_r = 1197.82$
Triclinic, $P\bar{1}$
$a = 10.030\ (2)$ Å
$b = 12.078\ (2)$ Å
$c = 12.858\ (3)$ Å
$\alpha = 62.13\ (3)°$
$\beta = 84.36\ (3)°$
$\gamma = 73.23\ (3)°$
$V = 1317.1\ (6)$ Å^3
$Z = 1$
$D_x = 1.510$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12078 reflections
$\theta = 3.2$–$26.7°$
$\mu = 0.65$ mm^{-1}
$T = 293\ (2)$ K
Prism, colorless
0.32 × 0.27 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.819$, $T_{max} = 0.892$
12055 measured reflections
5546 independent reflections
4318 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.8°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 15$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.099$
$S = 1.01$
5546 reflections
381 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2 + 0.3788P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—Cl1	2.426 (1)	Mn1—N2	2.326 (2)
Mn1—O1*W*	2.169 (2)	Mn1—N3	2.242 (2)
Mn1—N1	2.261 (2)	Mn1—N4	2.338 (2)
O1*W*—Mn1—Cl1	93.84 (5)	N2—Mn1—Cl1	169.42 (5)
O1*W*—Mn1—N1	98.75 (7)	N2—Mn1—N4	86.77 (7)
O1*W*—Mn1—N2	83.90 (7)	N3—Mn1—Cl1	99.53 (5)
O1W—Mn1—N3	96.23 (7)	N3—Mn1—N1	156.31 (7)
O1*W*—Mn1—N4	165.48 (6)	N3—Mn1—N2	91.00 (7)
N1—Mn1—Cl1	97.68 (6)	N3—Mn1—N4	72.80 (7)
N1—Mn1—N2	72.55 (7)	N4—Mn1—Cl1	97.30 (5)
N1—Mn1—N4	88.98 (7)		

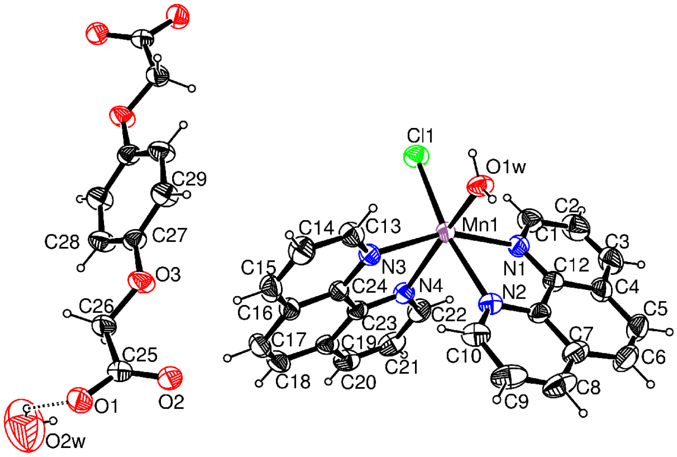


Figure 1
ORTEP-3 (Farrugia, 1997) plot of the asymmetric unit of the title compound, together with the other half of the dianion generated by inversion symmetry. Displacement ellipsoids are drawn at the 30% probability level.

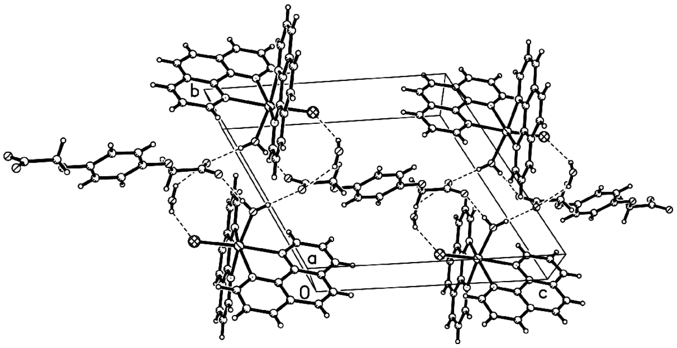


Figure 2
The hydrogen-bonded chain structure in (I).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H30*B*···O1^{i}	0.83 (2)	1.93 (2)	2.767 (2)	175 (3)
O1*W*—H30*A*···O2^{ii}	0.83 (2)	1.92 (2)	2.750 (2)	177 (3)
O2*W*—H31*A*···Cl1^{iii}	0.85 (6)	2.58 (4)	3.352 (4)	152 (7)
O2*W*—H31*B*···O1	0.84 (5)	2.29 (5)	3.012 (5)	143 (7)

Symmetry codes: (i) $1-x, 1-y, -z$; (ii) $x-1, y, z$; (iii) $1+x, y, z$.

The H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and $U_{iso}(H) = 1.2U_{eq}$(parent C-atom) and were included in the refinement in the riding model approximation. The O—H distance was restrained to 0.85 (1) Å; $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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m114 Shan Gao *et al.* • $[MnCl(C_{12}H_8N_2)_2(H_2O)]_2(C_{10}H_8O_6) \cdot 2H_2O$ *Acta Cryst.* (2004). E**60**, m113–m115

References

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

Gomez-Lor, B., Gutiérrez-Puebla, E., Iglesias, M., Monge, M. A., Ruiz-Valero, C. & Snejko, N. (2002). *Inorg. Chem.* **41**, 2429–2432.

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

McCann, M., Devereux, M., Cardin, C. & Convery, M. (1994). *Polyhedron*, **13**, 221–226.

Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Smith, G., Bott, R. C., Sagatys, D. S. & Kennard, C. H. L. (1991). *Polyhedron*, **10**, 1565–1568.

Smith, G., O'Reilly, E. J. & Kennard, C. H. L. (1987). *Polyhedron*, **6**, 871–879.

Yang, S.-Y., Long, L.-P., Hung, R.-B., Zheng, L.-S. & Ng, S. W. (2003). *Acta Cryst.* E**59**, m921–m923.

Acta Cryst. (2004). E**60**, m113–m115 Shan Gao *et al.* • $[MnCl(C_{12}H_8N_2)_2(H_2O)]_2(C_{10}H_8O_6)\cdot 2H_2O$ **m115**