metal-organic compounds

Diaqua(2,2′-bipyridine)malonato-manganese(II)

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In the crystal structure of the title compound, $[Mn(C_3H_2O_4)(C_{10}H_8N_2)(H_2O)_2]$, the Mn^{II} atom demonstrates a distorted octahedral geometry, being coordinated by two N atoms of a 2,2′-bipyridine ligand, two O atoms from the carboxylate groups of the chelating malonate dianion and two O atoms of two *cis* water molecules. The complex molecules are linked to form a three-dimensional supramolecular array by both hydrogen-bonding interactions between coordinated water and the carboxylate groups of neighboring molecules and aromatic π–π-stacking interactions of the bipyridine rings.

Comment

In recent years, extensive research has been carried out on 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). The malonate dianion may act as a bidentate or tridentate bridging ligands to form various structural topologies (Filippova *et al.*, 2000; Li *et al.*, 1997; Lightfoot & Snedden, 1999). To the best of our knowledge, there are only five reports on the structures of manganese(II) complexes with malonate (mal), *viz.* $[Mn(mal)(H_2O)_2]$ (Lis & Matuszewski, 1979), $[Mn(mal)(phen)_2]$ (phen is 1,10-phenanthroline; Wang *et al.*, 2000), $[Mn_3(mal)_4(H_2O)_6]$ (Wei *et al.*, 1996), $[CaMn(mal)_2(H_2O)_4]$ (de Muro *et al.*, 2000) and $[MnCu(mal)_2(H_2O)_4]$ (Ruiz-Perez *et al.*, 2000). Both $[Mn(mal)(H_2O)_2]$ and $[Mn(mal)(phen)_2]$ are mononuclear structures in which malonate acts as a chelating ligand; the other three structures were found to be polymeric, with the malonate ligands serving as *syn–anti* bridges. We report here the preparation and crystal structure of the title Mn^{II} complex, diaqua(2,2′-bipyridine)-malonatomanganese(II), (I), with a chelating malonate ligand.

The molecular structure of (I) is shown in Fig. 1. The title complex exists as discrete monomers. A malonate dianion chelates the Mn^{II} atom through two O atoms from different carboxylate groups. The Mn^{II} atom are also coordinated by two 2,2′-bipyridine N atoms and two O atoms of two *cis* water

molecules. The Mn site exhibits a distorted octahedral coordination sphere with the bond angles ranging from 161.39 (7) to 176.94 (7)° for *trans* angles and from 72.22 (7) to 104.64 (7)° for the other angles (Table 1). The Mn—O(carboxylate) bond

(I)
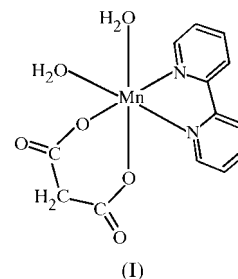
distances are 2.1215 (17) and 2.1667 (16) Å, which are comparable with those reported for $[Mn(mal)(phen)_2]$ (Wang *et al.*, 2000). The Mn—O(water) distances of 2.1595 (19) and 2.1757 (19) Å are comparable with those found in $[Mn_2(mal)_4(H_2O)_6]$ (Wei *et al.*, 1996). The Mn—N bond
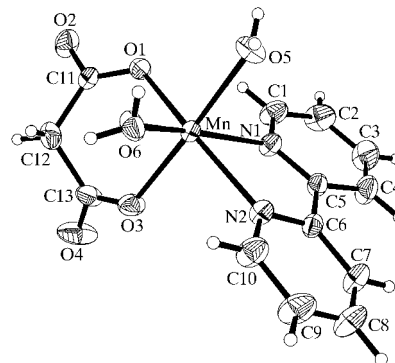
Figure 1
The molecular structure of (I), showing ellipsoids at the 35% probability level.
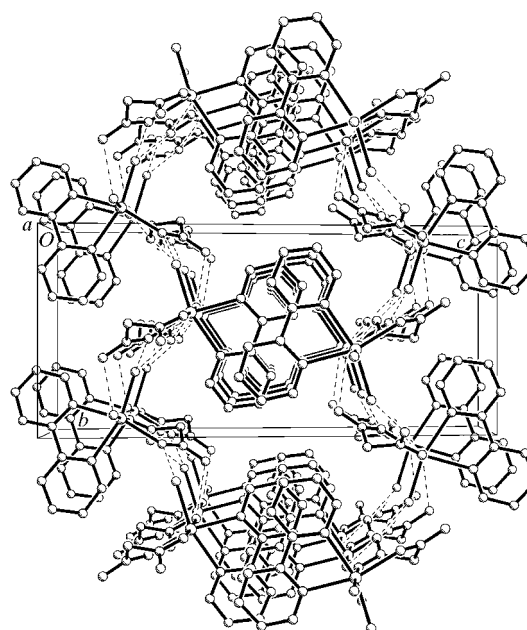
Figure 2
The molecular packing diagram of (I), with hydrogen bonds shown as dashed lines.

lengths are in good agreement with the corresponding bond lengths found in a previously reported complex (McCann *et al.*, 1998). The six-membered malonate chelate ring has a boat configuration and the stability of this ring is the reason that malonate coordinates only to one metal atom and does not act as a bridge between metal atoms.

Both hydrogen-bonding and π–π-stacking interactions play an important role in constructing the three-dimensional supramolecular structure. As shown in Fig. 2, complex molecules are linked to each other through hydrogen bonds between coordinated water molecules and the carboxylate groups of neighboring molecules to form layers in the crystal (Table 2). Neighboring layers are linked to each other through π–π-stacking interactions between the 2,2'-bipyridine rings of adjacent molecules, with face-to-face separations of *ca* 3.62 and 3.95 Å.

Experimental

An ethanol solution (10 ml) of 2,2'-bipyridine (0.156 g, 1 mmol) was added slowly to an aqueous solution (10 ml) of MnCl$_2$·4H$_2$O (0.198 g, 1 mmol) with continuous stirring and refluxing. A large amount of precipitate was produced. An aqueous solution (10 ml) of malonic acid (0.116 g, 1 mmol), neutralized with an aqueous solution of NaOH (0.080 g, 2 mmol), was added slowly to the above reaction mixture with continuous stirring and refluxing until the precipitate had dissolved. After half an hour, the reaction mixture was cooled to room temperature and filtered. Yellow single crystals were obtained from the filtrate after a week. Crystals of the title complex suitable for X-ray analysis were obtained by slow evaporation from an ethanol solution.

Crystal data

[Mn(C$_3$H$_2$O$_4$)(C$_{10}$H$_8$N$_2$)(H$_2$O)$_2$]	$D_x = 1.547$ Mg m^{-3}
$M_r = 349.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 26
$a = 7.834$ (2) Å	reflections
$b = 9.408$ (2) Å	$\theta = 3.7$–$14.8°$
$c = 20.532$ (4) Å	$\mu = 0.91$ mm^{-1}
$\beta = 97.75$ (2)°	$T = 296$ (2) K
$V = 1499.4$ (6) Å^3	Prism, yellow
$Z = 4$	$0.50 \times 0.42 \times 0.38$ mm

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.010$
ω scans	$\theta_{max} = 25.0°$
Absorption correction: empirical	$h = 0 \rightarrow 9$
(North *et al.*, 1968)	$k = 0 \rightarrow 11$
$T_{min} = 0.843$, $T_{max} = 0.996$	$l = -24 \rightarrow 24$
3153 measured reflections	3 standard reflections
2647 independent reflections	every 97 reflections
2210 reflections with $I > 2\sigma(I)$	intensity decay: 2.6%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 0.4939P]$
$wR(F^2) = 0.080$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2647 reflections	$\Delta\rho_{max} = 0.57$ e Å^{-3}
216 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
H atoms treated by a mixture of	Extinction correction: *SHELXL*97
independent and constrained	Extinction coefficient: 0.0055 (8)
refinement	

All the water H atoms were located in a difference Fourier map and the remaining H atoms were fixed geometrically and allowed to ride on their parent atoms (C—H = 0.93 or 0.97 Å).

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.1667 (16)	Mn—N2	2.2751 (19)
Mn—O3	2.1215 (17)	O1—C11	1.267 (3)
Mn—O5	2.1595 (19)	O2—C11	1.235 (3)
Mn—O6	2.1757 (19)	O3—C13	1.237 (3)
Mn—N1	2.2877 (19)	O4—C13	1.255 (3)
O1—Mn—O3	85.70 (6)	O5—Mn—N2	92.09 (8)
O1—Mn—O5	93.85 (7)	O6—Mn—N2	91.74 (7)
O1—Mn—O6	104.64 (7)	O1—Mn—N1	92.24 (7)
O3—Mn—O5	176.94 (7)	O3—Mn—N1	95.95 (7)
O3—Mn—O6	93.13 (7)	O5—Mn—N1	87.10 (7)
O5—Mn—O6	84.04 (7)	O6—Mn—N1	161.39 (7)
O1—Mn—N2	163.06 (7)	N1—Mn—N2	72.22 (7)
O3—Mn—N2	89.17 (7)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H5A$\cdots$O2^i	0.81 (2)	1.88 (2)	2.692 (3)	178 (2)
O5—H5B$\cdots$O4^{ii}	0.81 (3)	1.88 (3)	2.688 (3)	177 (3)
O6—H6A$\cdots$O2^{iii}	0.82 (3)	1.82 (3)	2.626 (3)	171 (3)
O6—H6B$\cdots$O4^i	0.82 (2)	2.00 (2)	2.816 (3)	179 (3)

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

Data collection: *XSCANS User's Manual* (Siemens, 1991); cell refinement: *XSCANS User's Manual*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990*a*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*b*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*.

References

Devereux, M., McCann, M., Leon, V., Geraghty, M., McKee, V. & Wikaira, J. (2000). *Polyhedron*, **19**, 1205–1211.
Filippova, Z. G., Kravtsov, V. Kh. & Gdanec, M. (2000). *Russ. J. Coord. Chem.* **26**, 809–816.
Li, L., Liao, D. & Jiang, Z. (2002). *Inorg. Chem.* **41**, 421–424.
Li, J., Zeng, H., Chen, J., Wang, Q. & Wu, X. (1997). *Chem. Commun.* pp. 1213–1214.
Lightfoot, P. & Snedden, A. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3549–3551.
Lis, T. & Matuszewski, J. (1979). *Acta Cryst.* B**35**, 2212–2214.
McCann, S., McCann, M., Casey, M. T., Jackman, M., Devereux, M. & McKee, V. (1998). *Inorg. Chim. Acta*, **279**, 24–29.
Muro, I. G. de, Insausti, M., Lezama, L., Urtiaga, M. K., Arriortua, M. I. & Rojo, T. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3360–3364.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ruiz-Perez, C., Sanchiz, J., Hernandez-Molina, M., Lloret, F. & Julve, M. (2000). *Inorg. Chim. Acta*, **298**, 202–208.
Sheldrick, G. M. (1990*a*). *SHELXTL-Plus.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1990*b*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. Release 97-2. University of Göttingen, Germany.
Shi, Z., Zhang, L., Gao, S., Yang, G., Hua, J., Gao, L. & Feng, S. (2000). *Inorg. Chem.* **39**, 1990–1993.
Siemens (1991). *XSCANS User's Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wang, Z., Zhou, X., Yu, W. & Fu, Y. (2000). *Z. Kristallogr.* **215**, 423–424.
Wei, Y., Zhang, S., Shao, M., Liu, Q. & Tang, Y. (1996). *Polyhedron*, pp. 4303–4305.