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catena-Poly[[aqua(2,2′-bipyridine-κ^2N,N')manganese(II)]-μ-terephthalato-κ^3O,O':O'']

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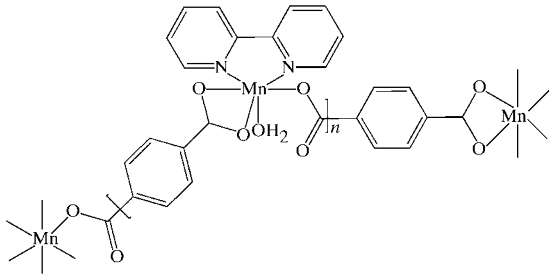
The title complex, $[\mathrm{Mn}(\mathrm{C_8H_4O_4})(\mathrm{C_{10}H_8N_2})(\mathrm{H_2O})]_n$, takes the form of a zigzag chain, with the terephthalate dianion (tp) acting as a tridentate ligand. The $\mathrm{Mn^{II}}$ center is surrounded by two tp ligands, one water molecule and one 2,2′-bipyridine (bipy) ligand and exhibits a severely distorted octahedral coordination environment, with *cis* angles ranging from 57.31 (8) to 123.97 (11)°. The complete solid-state structure can be described as a three-dimensional supramolecular framework stabilized by hydrogen-bonding interactions involving the coordinated water molecule and the carboxy O atoms of the tp ligands, and by π–π stacking interactions involving the bipy rings and the benzene ring of the tp ligand.

Comment

Owing to the great variety of intriguing structural topologies (Zaworotko, 1994) and potential applications in such fields as catalysis (Fujita *et al.*, 1994) and molecular magnetism (Miller & Epstein, 1994), the crystal engineering of supramolecular architectures organized by coordinate covalent bonds and/or supramolecular contacts, such as hydrogen bonds and π–π interactions, has been investigated actively. A commonly used strategy for obtaining such systems is to select appropriate bridging ligands with versatile bonding modes, in order to bind more than one metal ion, and with the ability to form hydrogen bonds. Aromatic chelating ligands, such as 2,2′-bipyridine (bipy) and 1,10-phenanthroline, are often introduced as ancillary ligands, with the hope of providing potential supramolecular recognition sites for π–π stacking interactions.

Terephthalate (tp) is an appropriate bridging ligand for mediating magnetic exchange interactions between paramagnetic metal centers over a limited distance (about 11 Å; Bürger *et al.*, 1995). Its versatile binding ability has been manifested by the formation of one mononuclear (Xiang *et al.*, 1998), one dinuclear (Cano *et al.*, 1997), three one-dimensional (Hong & Do, 1997; Li *et al.*, 2002; Yang Bian *et al.*, 2003) and four three-dimensional (Cano *et al.*, 1994; Hong & Do, 1997; Sun *et al.*, 2001; Kaduk, 2002; Ma, Chen, Liu *et al.*, 2003) manganese(II)–terephthalate complexes, and various bonding modes, including monodentate, bidentate and tetradentate for the tp ligands, have been observed in these complexes. In the present paper, we report the single-crystal structure of a new polymeric $\mathrm{Mn^{II}}$–terephthalate complex, (I), in which the tp dianion acts as a tridentate bridging ligand, a rare coordination mode that has not been reported previously in manganese–terephthalate complexes.



(I)

Compound (I) consists of infinite one-dimensional chains in which successive $\mathrm{Mn^{II}}$ atoms are bridged by one tp ligand, as shown in Fig. 1. Each $\mathrm{Mn^{II}}$ atom has a severely distorted six-coordinate geometry (Table 1), with the three *trans* angles [147.16 (10), 158.43 (11) and 143.66 (10)°] deviating significantly from the ideal value of 180°. The Mn atom is coordinated by three carboxy O atoms [Mn—O = 2.098 (2)–2.281 (2) Å] from two tp ligands, one water O atom [Mn—O5 = 2.160 (3) Å] and two pyridyl N atoms [Mn—N = 2.235 (3) and 2.260 (3) Å] from the chelating bipy ligand. The Mn—N and $\mathrm{Mn—O_{carboxy}}$ bond lengths are similar to those found for another ternary Mn–tp–bipy polymeric complex, $[\mathrm{Mn_2(tp)(bipy)_2}]_n(\mathrm{ClO_4})_{2n}$ (Cano *et al.*, 1994). The $\mathrm{Mn—O_{water}}$ distance is comparable to those in other $\mathrm{Mn^{II}}$–water complexes (Okabe & Koizumi, 1997; Hao *et al.*, 2000; Ma *et al.*, 2002; Ma, Chen, Chen & Liu, 2003; Schlueter & Geiser, 2003). The main distortion from ideal octahedral geometry is caused by the double chelation by the rigid bipy ligand and the chelating carboxylate group of the tp ligand. The N1—Mn—N2 bipy chelate angle [72.56 (11)°] is in agreement with those in other bipy-containing $\mathrm{Mn^{II}}$ complexes (Baumeister & Hartung, 1997; Zhang *et al.*, 2002; Shen, 2003). The O1—Mn—O2 carboxy chelate angle [57.31 (8)°] is very similar to that in $[\mathrm{Mn(tp)(4,4'\text{-}bipy)}]_n$ [57.07 (11)°; Ma, Chen, Liu *et al.*, 2003] but significantly larger than that in $[\mathrm{Mn_2(tp)(dca)_2(terpy)_2(MeOH)_2}]_n$ [52.94 (10)°; Escuer *et al.*, 2002].

Each tp dianion acts as a tridentate bridging ligand, joining two Mn atoms in a head-to-tail fashion; one of the carboxylate groups chelates one Mn atom, while the other binds the second Mn atom in a monodentate fashion. The present work is the first time that this tridentate μ_2 bridging mode has been observed for the tp ligand in Mn complexes, and to date this mode has been encountered in just one five-coordinate copper(II) complex (Yang, Zeng *et al.*, 2003). The two tp

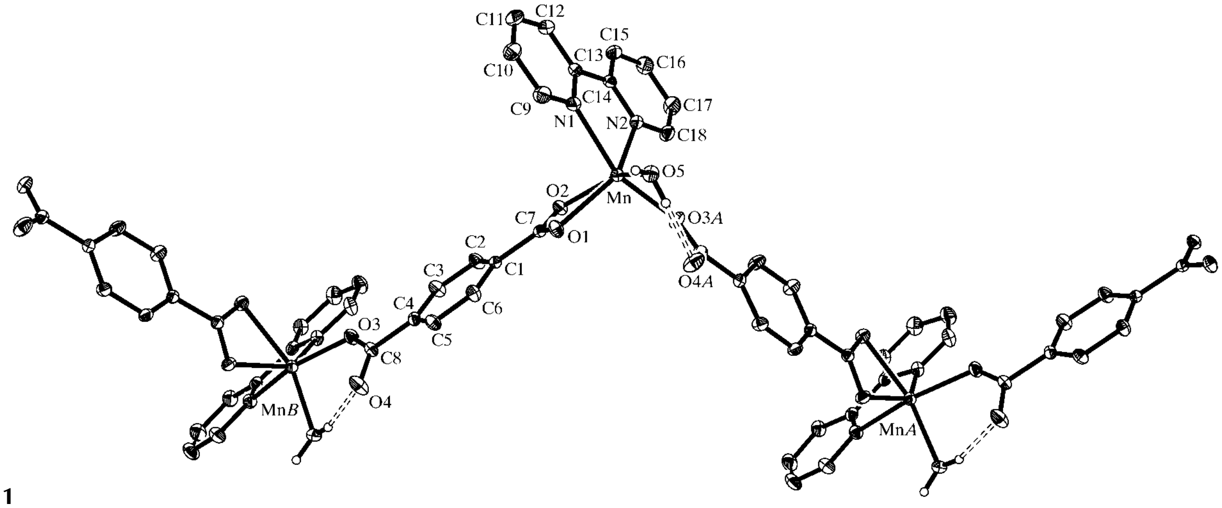
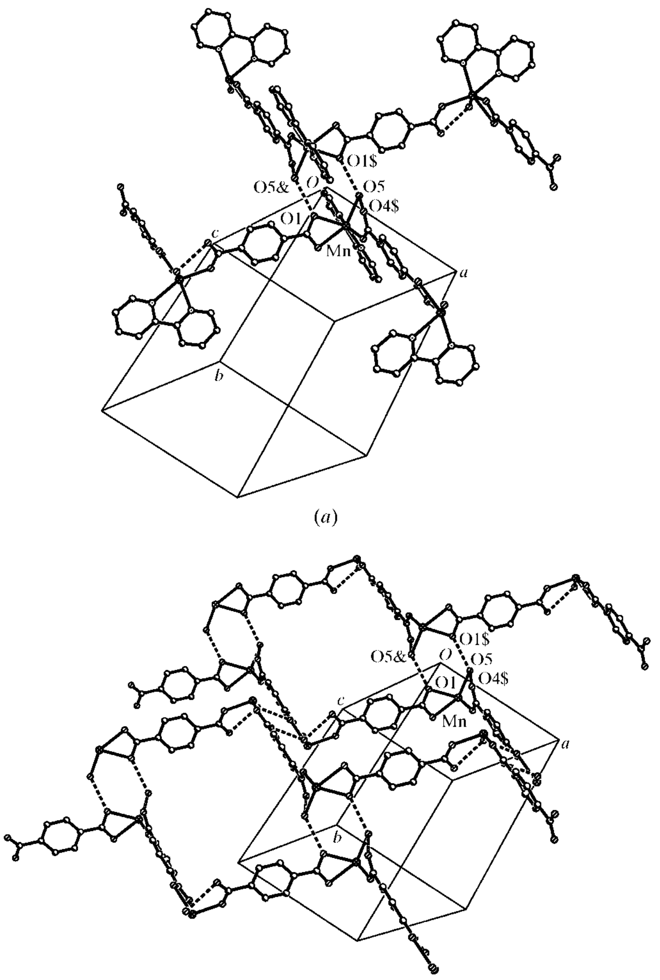


Figure 1
A view of part of the polymeric chain of (I), showing the atom-labelling scheme and displacement ellipsoids at the 30% probability level. Atoms marked with the suffixes *A* and *B* are at the symmetry positions $(1 - x, \frac{1}{2} - y, z - \frac{1}{2})$ and $(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$, respectively. Intrachain hydrogen bonds are depicted as double dashed lines.



(*a*)

(*b*)

Figure 2
The crystal packing of (I), showing (*a*) the antiparallel relationship of neighboring chains and the interchain hydrogen-bonding crosslinkage, and (*b*) part of the two-dimensional hydrogen-bonded network. Bipy ligands and H atoms have been omitted for clarity. Atoms labelled with an ampersand (&) or dollar sign ($) are at the symmetry positions $(-x, -y, -z)$ and $(x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2})$, respectively.

ligands coordinated to a given Mn center are *cis* to one another, resulting in a one-dimensional zigzag chain. The Mn···Mn···Mn angle formed by three successive Mn ions is 104.01 (2)° and successive bipy moieties are oriented at an angle of 89.5 (8)° to one another. The intrachain Mn···Mn separation is 11.132 (2) Å and the closest interchain contact is 5.642 (2) Å. Neighboring chains are arranged in an antiparallel fashion (Fig. 2*a*).

The neighboring zigzag chains are crosslinked by O5—H5*B*···O1$(-x, -y, -z)$ hydrogen bonds, formed by the coordinated water molecule and one of the chelating carboxy O atoms of a symmetry-related chain (Table 2), thus resulting in the formation of a two-dimensional hydrogen-bonded pleated sheet, as shown in Fig. 2(*b*). The second water H atom is donated to form an intrachain O5—H5*C*···O4$(x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2})$ hydrogen bond with the uncoordinated carboxy O atom. These two-dimensional hydrogen-bonded sheets are further packed into a three-dimensional herring-bone-like supramolecular network *via* two kinds of π–π stacking interactions, namely one type between the bipy ligands and one between the phenyl ring of the tp ligand and the bipy ligand, with perpendicular ring separations of 3.459 (8) and 3.542 (9) Å, respectively.

Experimental

A mixture of $Mn(NO_3)_2\cdot6H_2O$ (1 mmol, 0.28 g), dipotassium terephthalate (1 mmol, 0.24 g) and 2,2′-bipyridine (1 mmol, 0.16 g) in methanol–water (1:2 *v*/*v*, 15 ml) was heated at 413 K for 4 d under autogenous pressure in a 25 ml sealed Teflon-lined stainless steel vessel, and then cooled to room temperature over a period of 5 h, yielding yellow crystals of (I). Analysis calculated for $C_{18}H_{14}MnN_2O_5$: C 54.98, H 3.59, N 7.12%; found: C 54.92, H 3.61, N 7.08%. FT–IR (KBr, cm^{-1}): 3205 (*br*, *s*), 1605 (*s*), 1577 (*vs*), 1531 (*m*), 1505 (*m*), 1475 (*m*), 1439 (*s*), 1379 (*vs*), 1313 (*m*), 1247 (*w*), 1151 (*m*), 1089 (*w*), 1050 (*m*), 1019 (*m*), 882 (*w*), 864 (*w*), 806 (*m*), 760 (*s*), 750 (*s*), 670 (*m*), 650 (*m*), 628 (*m*), 569 (*w*), 525 (*m*), 413 (*m*).

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Crystal data

$[Mn(C_8H_4O_4)(C_{10}H_8N_2)(H_2O)]$
$M_r = 393.25$
Monoclinic, $P2_1/n$
$a = 9.8637$ (2) Å
$b = 16.3316$ (5) Å
$c = 11.3110$ (1) Å
$\beta = 111.726$ (2)°
$V = 1692.66$ (6) Å^3
$Z = 4$

$D_x = 1.543$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2431 reflections
$\theta = 2.3$–25.0°
$\mu = 0.81$ mm^{-1}
$T = 293$ (2) K
Block, pale yellow
0.54 × 0.53 × 0.30 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.626$, $T_{\max} = 0.784$
5399 measured reflections

2973 independent reflections
2230 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 25.0°$
$h = -9 \rightarrow 11$
$k = -12 \rightarrow 19$
$l = -13 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.150$
$S = 1.03$
2973 reflections
243 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—O3$^{\rm i}$	2.098 (2)	Mn—N1	2.260 (3)
Mn—O5	2.160 (3)	Mn—O2	2.271 (2)
Mn—N2	2.235 (3)	Mn—O1	2.281 (2)
O3$^{\rm i}$—Mn—O5	86.79 (10)	N2—Mn—O2	88.63 (10)
O3$^{\rm i}$—Mn—N2	90.04 (10)	N1—Mn—O2	94.26 (10)
O5—Mn—N2	123.97 (11)	O3$^{\rm i}$—Mn—O1	105.72 (9)
O3$^{\rm i}$—Mn—N1	158.43 (11)	O5—Mn—O1	90.04 (10)
O5—Mn—N1	92.42 (11)	N2—Mn—O1	143.66 (10)
N2—Mn—N1	72.56 (11)	N1—Mn—O1	95.83 (10)
O3$^{\rm i}$—Mn—O2	98.05 (10)	O2—Mn—O1	57.31 (8)
O5—Mn—O2	147.16 (10)		

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5B···O1$^{\rm ii}$	0.86 (2)	1.86 (2)	2.718 (4)	172 (5)
O5—H5C···O4$^{\rm i}$	0.85 (2)	1.87 (3)	2.672 (4)	157 (5)

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

Water H atoms were located from difference maps and included in the refinement with a DFIX restraint of 0.85 (2) Å. Aromatic H atoms were placed in calculated positions and treated as riding (C—H = 0.93 Å).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SHELXTL* (Siemens, 1994) and *SAINT*; program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1056). Services for accessing these data are described at the back of the journal.

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