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A two-dimensional manganese(II) coordination polymer: poly[[diaqua-manganese(II)]-μ-4,4-bipyridine-κ^2N:N'-μ-(p-phenylenedioxy-diacetato)-κ^2O:O']

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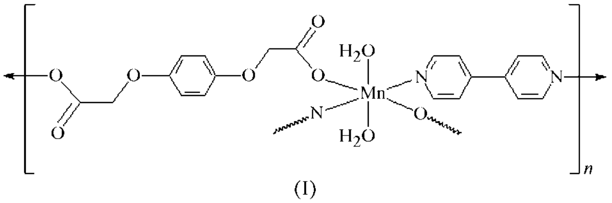
In the title two-dimensional coordination polymer, [Mn(1,4-BDOA)(4,4-bipy)(H_2O)$_2$]$_n$ [1,4-BDOA^{2-} is the p-phenylenedioxydiacetate dianion ($C_{10}H_8O_6$) and 4,4-bipy is 4,4-bipyridine ($C_{10}H_8N_2$)], each Mn^{II} atom displays octahedral coordination by two O atoms of the 1,4-BDOA^{2-} groups, two N atoms of the 4,4-bipy ligands and two solvent water molecules. The Mn^{II} atom, 4,4-bipy ligand and 1,4-BDOA^{2-} group occupy different inversion centres. Adjacent Mn^{II} atoms are bridged by 1,4-BDOA^{2-} groups and 4,4-bipy ligands, forming a two-dimensional network with Mn$\cdots$Mn separations of 11.592 (2) and 11.699 (2) Å. Hydrogen bonds from a water O—H group link the layers in the third dimension.

Comment

The construction of coordination polymers and networks by the self-assembly of organic ligands and transition metal ions is a rapidly growing area of research (Xia *et al.*, 2004). The considerable interest is fuelled by their impact on basic structural chemistry and also by their possible applications in a number of fields. The general strategy for designing a coordination polymer relies on the use of multidentate N- or O-donor ligands that have the capacity to bridge metal centres (Li *et al.*, 2003). Among such N-donor ligands, the rigid 4,4-bipyridine (4,4-bipy) molecule and its related species are often chosen to construct coordination polymers, and usually act as a linear bridge between metal centres (Sun *et al.*, 2004). It is found that the introduction of an O-donor ligand, such as polycarboxylate, into the N-donor system can alter the structural and functional properties of coordination polymers. Although the structures of a few corresponding polymers have been reported (Lightfoot & Snedden, 1999; Lu *et al.*, 1999; Zheng *et al.*, 1999), the architecture of coordination polymers formed from mixed multi-ligands is still a challenge to chemists, because prediction of the compositions or structures of the products is difficult.



(I)

The versatile polycarboxylates, such as benzene-1,4-dioxyacetic acid (p-phenylenedioxydiacetic acid, 1,4-BDOAH$_2$), have been widely used in the construction of high-dimensional porous materials, on the basis of their high symmetry and the varied carboxylate coordination modes. However, the coordination chemistry and structural properties of the flexible 1,4-

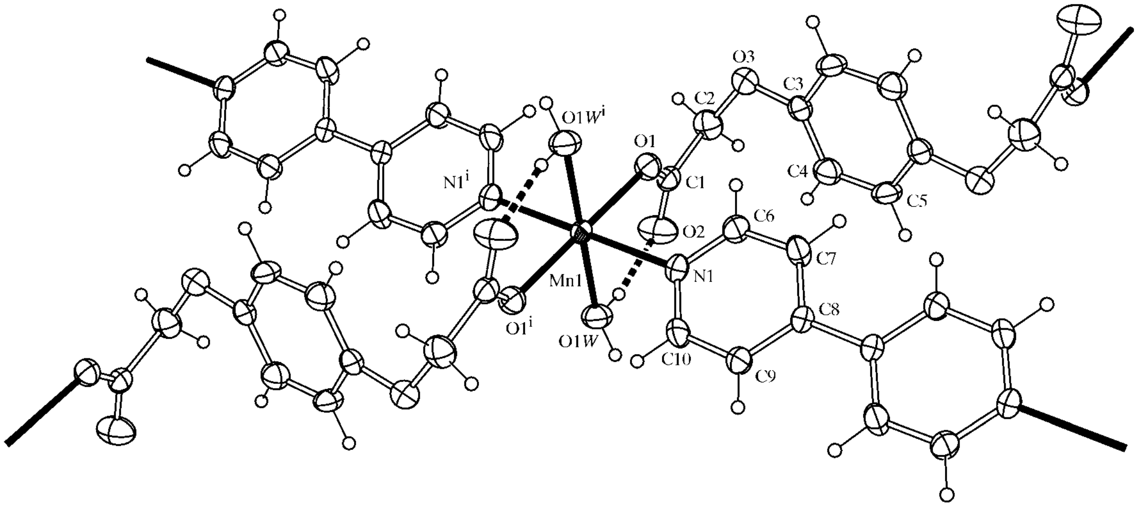


Figure 1
A view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

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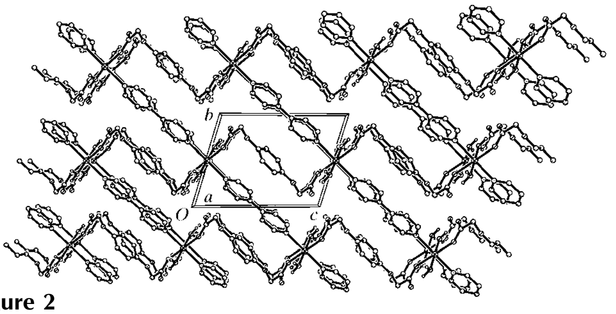

Figure 2
The two-dimensional layer structure of (I), viewed along the *a* axis.

$BDOAH_2$ molecule itself have received little attention to date. Recently, we have reported some Co^{II} and Cu^{II} one-dimensional coordination polymers using this ligand, in which the 1,4-$BDOA^{2-}$ dianion acts as a bi- or tridentate bridging ligand with N-heterocyclic co-ligands (Gao *et al.*, 2004*a*,*b*). In this paper, we report the structure of the title novel two-dimensional manganese(II) coordination polymer, $[Mn(1,4\text{-}BDOA)(4,4\text{-}bipy)(H_2O)_2]_n$, (I), obtained by the hydrothermal reaction of $MnCl_2\cdot6H_2O$, 4,4-bipy and 1,4-$BDOAH_2$.

As illustrated in Fig. 1, complex (I) consists of an Mn^{II} cation, one 1,4-$BDOA^{2-}$ dianion, one 4,4-bipy ligand and two coordinated water molecules, whereby the Mn^{II} atom, 4,4-bipy ligand and 1,4-$BDOA^{2-}$ group occupy three different inversion centres. The local coordination environment around the Mn^{II} atom can be described as approximately octahedral, involving two N atoms of the 4,4-bipy ligands, two monodentate carboxyl O atoms of the 1,4-$BDOA^{2-}$ groups and two solvent water molecules [Mn1—O1*W* = 2.212 (2) Å]. The Mn—O1(carboxylate) bond length [2.163 (2) Å] is somewhat shorter than Mn—N1 bond distance [2.292 (2) Å]

It is worth noting that the C1—O1 bond [1.266 (4) Å] is slightly longer than C1—O2 [1.245 (4) Å], consistent with the monodentate coordination mode of carboxyl groups. The 1,4-$BDOA^{2-}$ ligands are not planar: the C3—O3—C2—C1 torsion angle is 68.3 (4)°. The dihedral angle between the benzene ring and the 4,4-bipy ligand is 53.8 (3)°.

Both 4,4-bipy and 1,4-$BDOA^{2-}$ act as bidentate bridging ligands linking Mn metal centres, leading to the formation of a two-dimensional coordination polymer (Fig. 2). Each 1,4-$BDOA^{2-}$ ligand behaves as a bis-monodentate ligand, bridging two adjacent Mn^{II} atoms through its carboxyl O atoms to produce a zigzag chain parallel to the *c* axis, with an intrachain Mn···Mn separation of 11.592 (2) Å. This is somewhat longer than in Mn–terephthalate complexes. To the best of our knowledge, few six-coordinate Mn^{II} polymers based on the terephthalate ligand (tp) have been structurally characterized to date (Yang *et al.*, 2003; Hong & Do, 1997; Tan *et al.*, 1997; Cano *et al.*, 1997). In these complexes, the intrachain Mn···Mn separations vary from 9.655 Å in $[Mn(5\text{-methylpyrazole})_2(tp)]_n$ (Hong & Do, 1997) to the longest distance of 11.457 Å in $[Mn_2(phen)_4(H_2O)_2(tp)]ClO_4$ (Cano *et al.*, 1997).

Neighbouring chains in (I) are further connected by the N atoms of the bis-monodentate bridging 4,4-bipy ligand, generating a two-dimensional layer architecture parallel to the crystallographic *bc* plane, with an Mn···Mn separation of 11.699 (2) Å. The shortest interlayer Mn···Mn separation in (I) is 10.672 (2) Å.

The coordinated water molecules form hydrogen bonds with carboxyl O atoms. Of the two independent hydrogen bonds (Table 2), one is intramolecular and the other interlayer. The latter extends the two-dimensional layers into the third dimension.

Experimental

Benzene-1,4-dioxyacetic acid (1,4-$BDOAH_2$) was prepared following the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci (1990). $MnCl_2\cdot6H_2O$ (4.68 g, 20 mmol), 4,4-bipy (3.12 g, 20 mmol) and 1,4-$BDOAH_2$ (4.52 g, 20 mmol) were dissolved in a 4:1 ethanol–water solution, and the pH was adjusted to 7 with 0.1 *M* NaOH. The mixture was sealed in a 25 ml Teflon-lined stainless steel bomb and held at 423 K for 5 d. The bomb was then allowed to cool naturally to room temperature. Pale-yellow crystals of (I) separated from the filtered solution after several days. Analysis calculated for $C_{20}H_{20}MnN_2O_8$: C 50.97, H 4.28, N 5.94%; found: C 51.06, H 4.34, N 5.88%.

Crystal data

$[Mn(C_{10}H_8O_6)(C_{10}H_8N_2)(H_2O)_2]$
$M_r = 471.32$
Triclinic, $P\overline{1}$
$a = 5.783$ (2) Å
$b = 8.229$ (2) Å
$c = 10.827$ (3) Å
$\alpha = 105.65$ (3)°
$\beta = 97.48$ (3)°
$\gamma = 97.689$ (9)°
$V = 484.2$ (3) Å^3
$Z = 1$
$D_x = 1.617$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3999 reflections
$\theta = 3.7$–27.5°
$\mu = 0.74$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.29 × 0.23 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.815$, $T_{max} = 0.885$
4561 measured reflections
2181 independent reflections
1527 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 27.5°$
$h = -7 \rightarrow 7$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.107$
$S = 1.03$
2181 reflections
148 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.0764P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N1	2.292 (2)	O1—C1	1.266 (4)
Mn1—O1	2.163 (2)	O2—C1	1.245 (4)
Mn1—O1*W*	2.212 (2)		
O1—Mn1—O1*W*	91.18 (9)	O1—C1—C2	116.8 (3)
O1*W*—Mn1—N1	91.16 (9)	O2—C1—C2	117.2 (3)

C-atom bonded H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and were refined in

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O1^{ii}	0.85 (3)	2.12 (2)	2.903 (3)	152 (3)
O1W—H1W2···O2	0.85 (3)	1.80 (3)	2.630 (3)	164 (3)

Symmetry code: (ii) $x - 1, y, z$.

the riding-model approximation. Water H atoms were located in a difference map and refined, with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(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*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1660). Services for accessing these data are described at the back of the journal.

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