Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Pentaaqua-1κ^2O,2κ^3O-bis(2,2′-bipyridine)-1κ^2N,N';2κ^2N,N'-μ-biphenyl-2,2′-dicarboxylato-1:2κ^2O:O'-biphenyl-2,2′-dicarboxylato-1κO-dimanganese(II) tetrahydrate

Lin Du, Rui-Bing Fang and Qi-Hua Zhao*

Department of Chemistry, Key Laboratory of Medicinal Chemistry for Natural Resources, Ministry of Education, Yunnan University, Kunming 650091, People's Republic of China

Correspondence e-mail: qhzhao@ynu.edu.cn

Received 6 March 2007
Accepted 17 April 2007

The title compound, $[Mn_2(C_{14}H_8O_4)_2(C_{10}H_8N_2)_2(H_2O)_5]\cdot 4H_2O$, has been obtained under hydrothermal conditions. In the asymmetric unit, there are two crystallographically distinct Mn^{II} ions, bridged by a dpa^{2-} ligand (H_2dpa = diphenic acid), which are sixfold coordinated by four O atoms and two N atoms. The O atoms coordinated to one Mn atom are from three water molecules and one dpa^{2-} ligand, while those coordinated to the other Mn atom are from two water molecules and two dpa^{2-} ligands. In the crystal structure, centrosymmetric dimers are formed *via* a pair of intermolecular O—H···O hydrogen bonds.

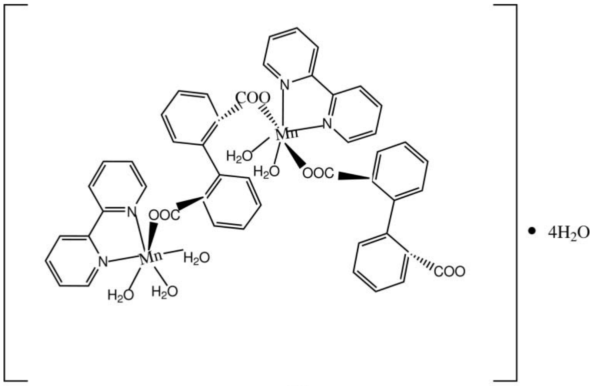
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.074
wR factor = 0.209
Data-to-parameter ratio = 17.7

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

Comment

The selection of multi-functional organic ligands containing appropriate coordination sites linked by a spacer with specific relative orientation is crucial for the construction of desirable frameworks (Wang *et al.*, 2005; Biradha & Fujita, 2002). Diphenic acid (H_2dpa) is an excellent aromatic dicarboxylate ligand and possesses several interesting structural characteristics (Wang *et al.*, 2005; Wang, Hong *et al.*, 2003; Wang, Zheng *et al.*, 2003). A number of transition metal and rare earth coordination polymers with H_2dpa as a bridging ligand have been reported, for example $[Mn_2(dpa)_2(phen)]_n$ (Ren *et al.*, 2005), $[M_2(O_2CC_{12}H_8CO_2)_2(H_2O)_8]$, where M = Co or Ni (Rueff *et al.*, 2002), and $[M(dpa)_{1.5}(H_2O)]\cdot 0.5DMF$, where M = Tb, Ho, Er or Y (Guo *et al.*, 2005). Introducing H_2dpa as a functional ligand in order to obtain some extended structures, we report here the synthesis and characterization of a new binuclear manganese(II) complex, (I), with both diphenate and bipyridyl ligands.



(I)

As illustrated in Fig. 1, the asymmetric unit of compound (I) contains two independent Mn^{II} ions, both of which adopt a distorted octahedral coordination. Selected bond distances

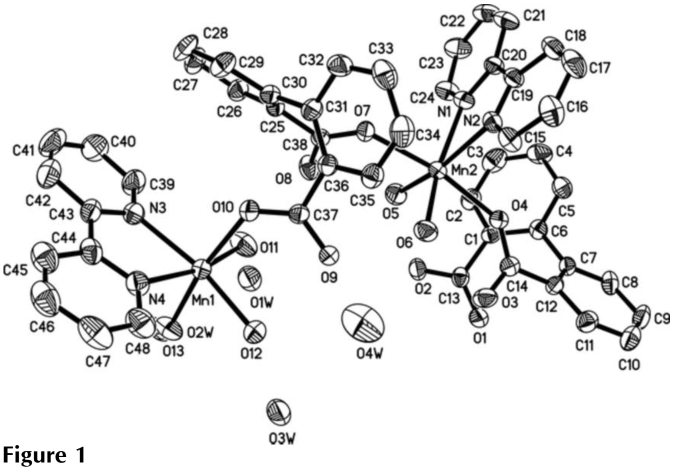


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity.

and angles are given in Table 1. The coordination environment around atom Mn1 consists of four O atoms from one diphenate anion (O10) and three coordinated water molecules (O11, O12 and O13), and two N atoms (N1, N2) from a 2,2′-bipy ligand. The Mn2 center is also eight-coordinate, being surrounded by four O atoms, from two diphenate anions (O7, O4) and two coordinated water molecules (O5, O6), and two N atoms (N3, N4) from a second 2,2′-bipy ligand. The Mn2—O bond distances are slightly shorter than the Mn1—O distances, while the Mn2—N bond distances are slightly longer than the Mn1—N distances (Table 1). Atoms Mn1 and Mn2 are separated by a distance of 6.644 (2) Å.

The benzene rings of the dpa^{2-} ligands are not coplanar due to the steric hindrance of the 2,2′-positioned carboxylate groups in the coordination process (Wang, Hong *et al.*, 2003; Wang, Zheng *et al.*, 2003). In the dpa^{2-} ligand bridging the two Mn ions, the dihedral angle between benzene rings C1–C6 and C7–C12 is 57.96 (15)°. In the dpa^{2-} ligand coordinated to the Mn2 ion, the dihedral angle between benzene rings C25–C30 and C31–C36 is 61.73 (19)°. The pyridine rings of the two 2,2′-bipy ligands are nearly coplanar; the dihedral angle between pyridine rings C15–C19/N1 and C20–C24/N2 is 6.4 (2)°, and that between rings C39–C43/N3 and C44–C48/N4 is 5.5 (3)°.

In the crystal structure, centrosymmetric dimers are formed via an intermolecular O—H⋯O hydrogen bond (O13—H13*A*⋯O1^{i}). There are also a number of intra- and intermolecular O—H⋯O hydrogen bonds involving the coordinated and non-coordinated water molecules and the carboxylate groups (Table 2). The crystal packing of complex (I), viewed down the *a* axis, is shown in Fig. 2.

Experimental

Compound (I) was synthesized hydrothermally from $Mn(CH_3COO)_2{\cdot}6H_2O$, diphenic acid and distilled water (molar ratio: 1:1:10). The resulting mixture was stirred for ca 1 h at room temperature, sealed in a 25 ml Teflon-lined stainless steel autoclave and heated at 423 K for 3 d. After the reaction system had been cooled gradually to room temperature, insoluble products were filtered off. The filtrate was left to evaporate slowly at room temperature. After about 30 d, pink crystals of complex (I) were obtained.

Crystal data

$[Mn_2(C_{14}H_8O_4)_2(C_{10}H_8N_2)_2(H_2O)_5]{\cdot}4H_2O$
$M_r = 1064.80$
Triclinic, $P\overline{1}$
$a = 10.014\ (3)$ Å
$b = 13.167\ (5)$ Å
$c = 20.051\ (6)$ Å
$\alpha = 79.50\ (2)^\circ$
$\beta = 75.92\ (2)^\circ$
$\gamma = 86.08\ (2)^\circ$
$V = 2520.6\ (15)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.58$ mm^{-1}
$T = 293\ (2)$ K
0.34 × 0.29 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.823$, $T_{max} = 0.904$
16503 measured reflections
11306 independent reflections
5019 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.074$
$wR(F^2) = 0.209$
$S = 1.00$
11306 reflections
640 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O11	2.158 (4)	Mn2—O5	2.132 (3)
Mn1—O12	2.177 (3)	Mn2—O6	2.158 (3)
Mn1—O13	2.178 (4)	Mn2—O4	2.168 (3)
Mn1—O10	2.193 (3)	Mn2—O7	2.190 (3)
Mn1—N4	2.239 (5)	Mn2—N2	2.274 (4)
Mn1—N3	2.241 (4)	Mn2—N1	2.278 (4)
O11—Mn1—O12	101.70 (17)	O5—Mn2—O6	105.44 (14)
O11—Mn1—O13	85.11 (15)	O5—Mn2—O4	88.27 (13)
O12—Mn1—O13	87.15 (14)	O6—Mn2—O4	83.25 (12)
O11—Mn1—O10	88.53 (14)	O5—Mn2—O7	86.02 (13)
O12—Mn1—O10	86.95 (13)	O6—Mn2—O7	90.25 (13)
O13—Mn1—O10	170.28 (14)	O4—Mn2—O7	169.91 (12)
O11—Mn1—N4	166.21 (17)	O5—Mn2—N2	162.25 (15)
O12—Mn1—N4	92.01 (16)	O6—Mn2—N2	92.28 (14)
O13—Mn1—N4	94.16 (16)	O4—Mn2—N2	92.94 (13)
O10—Mn1—N4	93.77 (15)	O7—Mn2—N2	95.03 (13)
O11—Mn1—N3	93.34 (17)	O5—Mn2—N1	91.42 (15)
O12—Mn1—N3	164.90 (16)	O6—Mn2—N1	163.12 (15)
O13—Mn1—N3	92.83 (15)	O4—Mn2—N1	96.88 (14)
O10—Mn1—N3	94.88 (14)	O7—Mn2—N1	91.58 (13)
N4—Mn1—N3	72.92 (17)	N2—Mn2—N1	70.85 (15)

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1*W*—H1*WA*⋯O3*W*^{i}	0.85	2.34	2.837 (6)	118
O1*W*—H1*WB*⋯O2*W*	0.85	2.35	2.806 (6)	114
O2*W*—H2*WA*⋯O12^{i}	0.85	2.48	2.755 (6)	100
O2*W*—H2*WB*⋯O4*W*^{i}	0.85	2.47	3.222 (9)	147
O3*W*—H3*WA*⋯O1*W*^{ii}	0.85	2.57	2.917 (6)	106
O3*W*—H3*WA*⋯O13^{i}	0.85	2.55	2.838 (6)	101
O5—H5*C*⋯O2	0.85	2.29	2.646 (5)	106
O3*W*—H3*WB*⋯O1*W*^{i}	0.85	2.16	2.837 (6)	136

m1440 Du *et al.* • $[Mn_2(C_{14}H_8O_4)_2(C_{10}H_8N_2)_2(H_2O)_5]{\cdot}4H_2O$ *Acta Cryst.* (2007). E**63**, m1439–m1441

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*B*···O4*W*	0.85	2.52	3.326 (9)	158
O6—H6*B*···O9	0.85	2.26	2.674 (5)	110
O4*W*—H4*WB*···O2*W*	0.85	2.04	2.788 (9)	146
O12—H12*B*···O2*W*^{i}	0.85	2.32	2.755 (6)	112
O13—H13*A*···O1^{i}	0.85	1.92	2.613 (5)	138
O13—H13*B*···O3*W*^{i}	0.85	2.16	2.838 (6)	136

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

The water H atoms were located in a different Fourier map and refined using a riding model with a distance constraint of 0.85 Å. H atoms on all C atoms were included in calculated positions and constrained to an ideal geometry, with C—H = 0.93 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

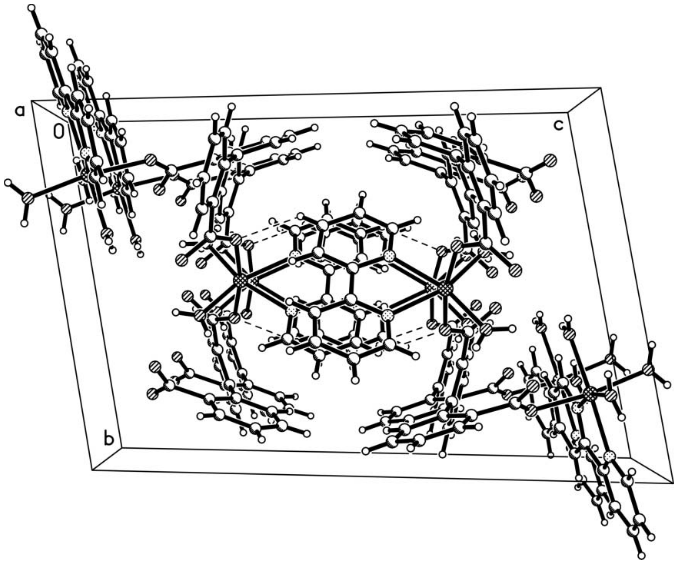


Figure 2
The packing of (I), viewed along the *a*-axis direction, showing the centrosymmetric dimer formation (dashed lines).

References

Biradha, K. & Fujita, M. (2002). *Angew. Chem. Int. Ed.* **41**, 3392–3395.

Bruker (2002). *SMART* (Version 5.628) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Guo, X. D., Zhu, G. S., Fang, Q. R., Xue, M., Tian, G., Sun, J. Y., Li, X. T. & Qiu, S. L. (2005). *Inorg. Chem.* **44**, 3850–3855.

Ren, Y. W., Dang, L. L., Li, J., Gao, W. W. & Zhang, F. X. (2005). *J. Struct. Chem.* **46**, 352–357.

Rueff, J. M., Pillet, S., Claiser, N., Bonaventure, G., Souhassou, M. & Rabu, P. (2002). *Eur. J. Inorg. Chem.* pp. 895–900.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*a*). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Wang, R. H., Hong, M. C., Luo, J. H., Cao, R. & Weng, J. B. (2003). *Chem. Commun.* pp. 1018–1019.

Wang, R., Zhou, Y. F., Sun, Y. Q., Yuan, D. Q., Han, L., Lou, B. Y., Wu, B. & Hong, M. C. (2005). *Cryst. Growth Des.* **5**, 251–256.

Wang, Y. B., Zheng, X. J., Zhuang, W. J. & Jin, L. P. (2003). *Eur. J. Inorg. Chem.* pp. 1355–1360.

Acta Cryst. (2007). E**63**, m1439–m1441 Du *et al.* • $[\mathrm{Mn_2(C_{14}H_8O_4)_2(C_{10}H_8N_2)_2(H_2O)_5}]\cdot\mathrm{4H_2O}$ **m1441**