

A one-dimensional chain structure based on unusual tetranuclear manganese(II) clusters

Guang-Bo Che,* Jian Wang, Chun-Bo Liu, Xiu-Ying Li and Bo Liu

College of Chemistry, Jilin Normal University, Siping 136000, People's Republic of China

Correspondence e-mail: guangbochejl@yahoo.com

Received 21 September 2008

Accepted 26 September 2008

Online 4 October 2008

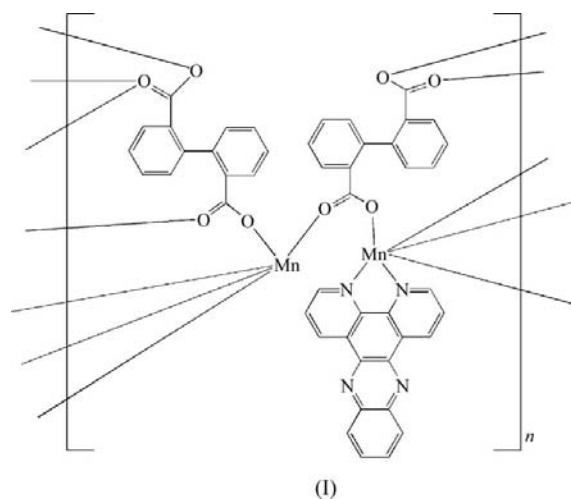
The title coordination polymer, poly[bis(μ_4 -biphenyl-2,2'-dicarboxylato)(dipyrido[3,2-*a*:2',3'-*c*]phenazine)manganese(II)], $[\text{Mn}_2(\text{C}_{14}\text{H}_8\text{O}_4)_2(\text{C}_{18}\text{H}_{10}\text{N}_4)]_n$, was obtained through the reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, biphenyl-2,2'-dicarboxylic acid (H_2dpdc) and dipyrido[3,2-*a*:2',3'-*c*]phenazine (*L*) under hydrothermal conditions. The asymmetric unit contains two crystallographically unique Mn^{II} ions, one unique *L* ligand and two unique dpdc ligands. One Mn ion is six-coordinated by four O atoms from three different dpdc ligands and two N atoms from one *L* ligand, adopting a distorted octahedral coordination geometry. The distortions from ideal octahedral geometry are largely due to the presence of chelating ligands and the resulting acute N–Mn–N and O–Mn–O angles. The second Mn ion is coordinated in a distorted trigonal bipyramidal fashion by five O atoms from four distinct dpdc ligands. Four Mn^{II} ions are bridged by the carboxylate groups of the dpdc ligands to form an unusual tetranuclear Mn^{II} cluster. Clusters are further connected by the aromatic backbone of the dicarboxylate ligands, forming a one-dimensional chain structure along the *b* axis. The title compound is the first example of a chain structure based on a tetranuclear Mn^{II} cluster.

Comment

The metal–organic coordination architectures formed with transition metal ions and organic ligands have been a promising topic for many years owing to their intriguing structures and potential applications in the fields of catalysis, separation, gas storage, molecular recognition, magnetic devices and nonlinear optical materials (Eddaoudi *et al.*, 2001; Batten & Robson, 1998; Yang *et al.*, 2008). In this regard, chain structures have received much attention in coordination chemistry and materials chemistry (Lehn, 1990; Li *et al.*, 2002; Chen & Liu, 2002; Yang, Li *et al.*, 2007). An appropriate flexible bidentate organic acid bridge could be useful in the

formation of chains in the presence of secondary ligands, such as 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) (Qi *et al.*, 2003). The N atoms from the secondary ligand may occupy two coordination positions of the metal ions. The remainder of the coordination positions are available for other carboxylate ligands to allow the formation of a chain.

The use of aromatic carboxylic acids in the syntheses of chain coordination polymers has aroused enormous interest owing to their versatile coordination modes and varieties of structural conformations (Chen & Liu, 2002; Zhang *et al.*, 2003; Fan *et al.*, 2002). So far, aromatic multicarboxylate ligands, such as benzene-1,2-dicarboxylic acid, benzene-1,3-dicarboxylic acid and benzene-1,4-dicarboxylic acid, have been widely used to construct chain structures with interesting properties (Chen & Liu, 2002). In this regard, biphenyl-2,2'-dicarboxylic acid (H_2dpdc) is also a good ligand in coordination chemistry because of its strong coordination ability and versatile coordination modes, so much attention has been paid to it in recent decades. On the other hand, the phen molecule, as one type of important organic ligand, has been widely utilized in the construction of chain structure complexes. An important derivative of phen, dipyrido[3,2-*a*:2',3'-*c*]phenazine (*L*) has been widely used to synthesize various Ru^{II} complexes in order to recognize the secondary structure of DNA (Wu *et al.*, 1997). However, chain coordination polymers based on the ligand *L* have rarely been documented. In the present study, we selected H_2dpdc as a linker and *L* as a secondary chelating ligand, forming a new chain coordination polymer, $[\text{Mn}_2(\text{dpdc})_2(\text{L})]$, (I), based on unusual tetranuclear Mn^{II} clusters.



Selected bond lengths and angles for (I) are given in Table 1. As shown in Fig. 1, the asymmetric unit of (I) contains two crystallographically unique Mn^{II} ions, one unique *L* ligand and two unique dpdc ligands. Mn1 is six-coordinated by four O atoms [O1, O3ⁱ, O7ⁱⁱ and O8ⁱⁱ; symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $-x, -y + 1, -z + 1$] from three different dpdc ligands, and two N atoms (N1 and N2) from one *L* ligand, adopting a distorted octahedral coordination geometry. The distortions from ideal octahedral geometry are largely due to

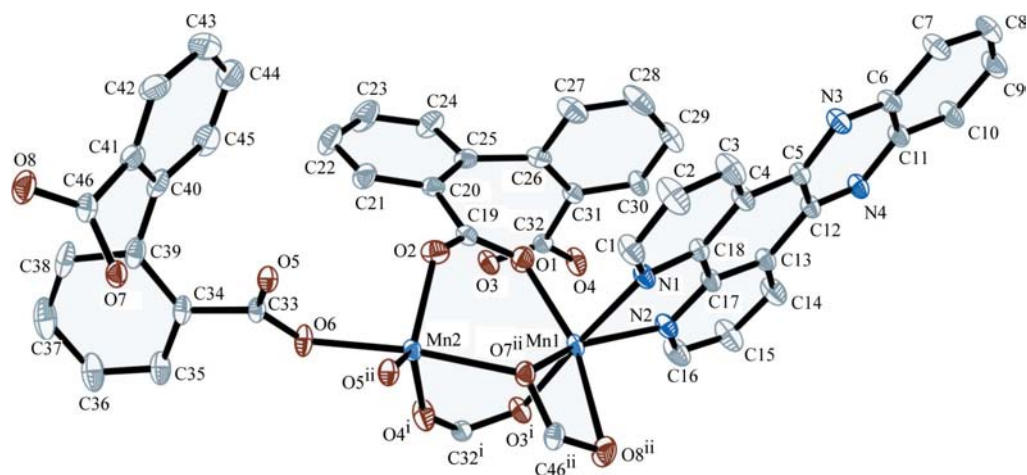


Figure 1

A view of the local coordination of the Mn^{II} atoms in (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $-x, -y + 1, -z + 1$.]

the presence of chelating ligands and the resulting acute $\text{N1}-\text{Mn1}-\text{N2}$ and $\text{O7}^{\text{ii}}-\text{Mn1}-\text{O8}^{\text{ii}}$ angles. Mn2 is coordinated in a distorted trigonal bipyramidal fashion by five O atoms (O2 , O6 , O4^{i} , O5^{ii} , O7^{ii}) from four distinct dpdc ligands. The axial sites are occupied by O6 and O7^{ii} and the $\text{O6}-\text{Mn2}-\text{O7}^{\text{ii}}$ angle is $172.21(10)^\circ$; the other six angles involving these two donors lie in the range $83.90(11)$ – $92.53(12)^\circ$. The main distortions from ideal trigonal bipyramidal geometry occur in the equatorial plane, where the angles vary between $103.87(12)$ and $132.03(12)^\circ$. Mn2 lies only $0.0348(4)$ Å out of the equatorial plane defined by O2 , O4^{i} and O5^{ii} . The average $\text{Mn}-\text{O}$ and $\text{Mn}-\text{N}$ distances in (I) are comparable to those observed for $[\text{Mn}(\text{bza})_2(\text{ppz})_2]$ [Hbza is benzoic acid and ppz is 3-(2-pyridyl)pyrazole; Zou *et al.*, 2005]. Two coordination modes for the dpdc ligands in (I) have been found: one is bis-bidentate, and the second is bidentate/monodentate–bidentate. In these modes, an unusual tetranuclear Mn^{II} cluster is formed, where four Mn^{II} ions are bridged by the carboxylate groups of the dpdc ligands to form a discrete rod (Fig. 2). Each cluster lies across an inversion center, with the Mn2 ions in the middle and the Mn1 ions on the ends of the rod. Thus, each tetranuclear metal cluster is surrounded by eight organic ligands: six bridging dpdc and two chelating *L* ligands. To the best of our knowledge, the rod-like tetranuclear Mn^{II} cluster containing the bpy-like chelating ligand *L* has not been reported so far, although other noncoplanar tetranuclear Cd^{II} clusters, including bpy-like chelating ligands, have been reported (Wang *et al.*, 2007).

In the structure of (I), the tetranuclear Mn^{II} –carboxylate clusters act as rod-shaped secondary building units, which are connected together by the aromatic backbone of the dicarboxylate ligands, forming a one-dimensional chain structure along the *b* axis (Fig. 3). These chains are decorated with *L* ligands alternately on two sides. It is noteworthy that the structure of (I) presented here is clearly different from that reported for $[\text{Pb}(\text{dpdc})(\text{L})]$ (Yang, Ma *et al.*, 2007). This reported compound features a helical chain structure based on mononuclear lead(II) centers, which are connected by strong

π – π interactions to result in a three-dimensional supramolecular architecture.

In summary, over the past decade, chain structures have received much attention in coordination chemistry and materials chemistry because of their importance in areas such as optical devices, enantiomer separation, chiral synthesis, ligand exchange and selective catalysis (Chen & Liu, 2002). Consequently, many chain complexes have been generated by

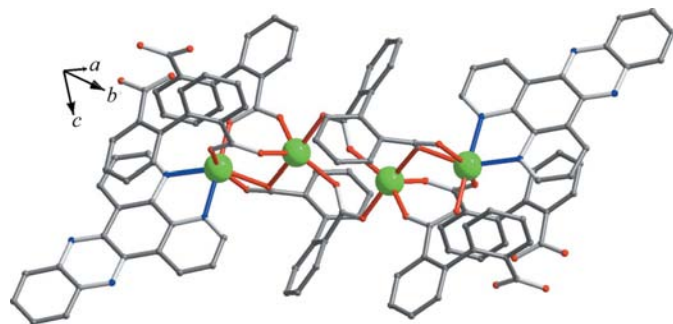


Figure 2

A view of the tetranuclear Mn^{II} cluster of (I).

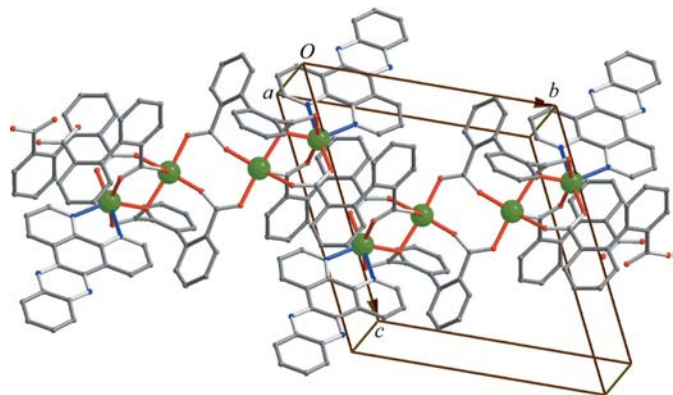


Figure 3

A view of the one-dimensional chain structure of (I), based on tetranuclear Mn^{II} clusters.

self-assembly processes. However, the reported chain complexes constructed from dicarboxylate and hetero-aromatic N-donor chelating ligands are mainly based on mononuclear metal centers. To the best of our knowledge, (I), constructed from the dicarboxylate anion and a phen derivative, is the first one-dimensional chain structure based on tetranuclear Mn^{II} clusters.

Experimental

MnCl₂·4H₂O (0.090 g, 0.5 mmol), H₂dpdc (0.062 g, 0.5 mmol) and L (0.145 g, 0.5 mmol) were dissolved in distilled water (14 ml), and triethylamine was added until the pH value of the system was adjusted to about 5.5. The resulting solution was stirred for about 1 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 413 K for 3 d under autogenous pressure. The reaction system was then cooled slowly to room temperature. Pale-yellow block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 44%, based on Mn). The compound once formed is insoluble in most solvents, including water.

Crystal data

[Mn ₂ (C ₁₄ H ₈ O ₄) ₂ (C ₁₈ H ₁₀ N ₄)]	$\gamma = 82.24 (3)^\circ$
$M_r = 872.59$	$V = 1917.6 (9) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 11.993 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 13.516 (3) \text{ \AA}$	$\mu = 0.72 \text{ mm}^{-1}$
$c = 14.196 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\alpha = 62.13 (3)^\circ$	$0.31 \times 0.24 \times 0.21 \text{ mm}$
$\beta = 70.55 (2)^\circ$	

Data collection

Rigaku R-Axis RAPID diffractometer	18726 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	8667 independent reflections
$T_{\min} = 0.794, T_{\max} = 0.856$	5367 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$	541 parameters
$wR(F^2) = 0.142$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.49 \text{ e \AA}^{-3}$
8667 reflections	$\Delta\rho_{\text{min}} = -0.37 \text{ e \AA}^{-3}$

All H atoms were positioned geometrically (C–H = 0.93 Å) and refined as riding, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{carrier})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Table 1

Selected geometric parameters (Å, °).

Mn1–N1	2.236 (3)	Mn2–O5 ⁱⁱ	2.093 (2)
Mn1–N2	2.215 (3)	Mn2–O6	2.124 (3)
Mn1–O1	2.078 (3)	Mn1–O7 ⁱⁱ	2.183 (2)
Mn2–O2	2.072 (3)	Mn2–O7 ⁱⁱ	2.191 (3)
Mn1–O3 ⁱ	2.095 (3)	Mn1–O8 ⁱⁱ	2.422 (3)
Mn2–O4 ⁱ	2.090 (3)		
O1–Mn1–O3 ⁱ	94.57 (11)	N2–Mn1–O8 ⁱⁱ	103.65 (11)
O1–Mn1–O7 ⁱⁱ	102.47 (10)	N1–Mn1–O8 ⁱⁱ	94.43 (11)
O3 ⁱ –Mn1–O7 ⁱⁱ	96.67 (10)	O2–Mn2–O4 ⁱ	103.87 (12)
O1–Mn1–N2	97.39 (12)	O2–Mn2–O5 ⁱⁱ	123.95 (10)
O3 ⁱ –Mn1–N2	103.28 (11)	O4 ⁱ –Mn2–O5 ⁱⁱ	132.03 (12)
O7 ⁱⁱ –Mn1–N2	150.51 (10)	O2–Mn2–O6	92.53 (12)
O1–Mn1–N1	88.13 (12)	O4 ⁱ –Mn2–O6	88.76 (11)
O3 ⁱ –Mn1–N1	176.37 (11)	O5 ⁱⁱ –Mn2–O6	92.47 (9)
O7 ⁱⁱ –Mn1–N1	85.08 (10)	O2–Mn2–O7 ⁱⁱ	91.76 (11)
N2–Mn1–N1	73.93 (11)	O4 ⁱ –Mn2–O7 ⁱⁱ	83.90 (11)
O1–Mn1–O8 ⁱⁱ	158.69 (10)	O5 ⁱⁱ –Mn2–O7 ⁱⁱ	90.52 (9)
O3 ⁱ –Mn1–O8 ⁱⁱ	83.93 (11)	O6–Mn2–O7 ⁱⁱ	172.21 (10)
O7 ⁱⁱ –Mn1–O8 ⁱⁱ	56.84 (9)		

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

The authors thank Jilin Normal University for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3265). Services for accessing these data are described at the back of the journal.

References

- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
- Chen, X. M. & Liu, G. F. (2002). *Chem. Eur. J.* **8**, 4811–4817.
- Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reinecke, T. M., O’Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
- Fan, J., Sun, W. Y., Okamura, T., Xie, J., Tang, W. X. & Ueyama, N. (2002). *New J. Chem.* **2**, 199–201.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Lehn, J. M. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 1304–1305.
- Li, Y. G., Zhang, H., Wang, E., Hao, N., Hu, C., Yu, Y. & Hall, D. (2002). *New J. Chem.* **26**, 1619–1623.
- Qi, Y., Wang, Y., Hu, C., Cao, M., Mao, L. & Wang, E. (2003). *Inorg. Chem.* **42**, 8519–8523.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Wang, X.-L., Bi, Y.-F., Lin, H.-Y. & Liu, G.-C. (2007). *Cryst. Growth Des.* **7**, 1086–1091.
- Wu, J.-Z., Li, L., Zeng, T.-X., Ji, L.-N., Zhou, J.-Y., Luo, T. & Li, R.-H. (1997). *Polyhedron*, **16**, 103–107.
- Yang, J., Li, G.-D., Cao, J.-J., Yue, Q., Li, G.-H. & Chen, J.-S. (2007). *Chem. Eur. J.* **13**, 3248–3261.
- Yang, J., Ma, J.-F., Batten, S. R. & Su, Z.-M. (2008). *Chem. Commun.* pp. 2233–2235.
- Yang, J., Ma, J.-F., Liu, Y.-Y., Ma, J.-C. & Batten, S. R. (2007). *Inorg. Chem.* **46**, 6542–6555.
- Zhang, X. M., Tong, M. L., Gong, M. L. & Chen, X. M. (2003). *Eur. J. Inorg. Chem.* **2003**, 138–142.
- Zou, R.-Q., Liu, C.-S., Shi, X.-S., Bu, X.-H. & Ribas, J. (2005). *CrystEngComm*, **7**, 722–727.