Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Poly[manganese(II)-μ_2-benzidine-κ^2N:N'-μ_3-biphenyl-2,2′-dicarboxylato-κ^4O:O',O'':O''']

Min Jiang,[a,b] Jun Li[b]* and Feng-Xing Zhang[a]

[a]Department of Chemistry, Northwest University, Xi'an, Shaanxi 710069, People's Republic of China, and [b]Department of Chemistry, Shaaxi University of Technology, Hanzhong, Shaanxi 723000, People's Republic of China
Correspondence e-mail: junli@nwu.edu.cn

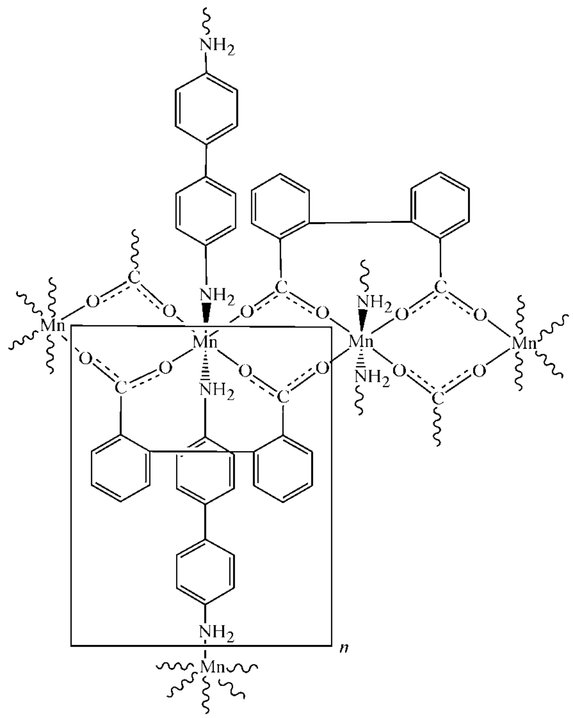
Received 17 February 2004
Accepted 11 August 2004
Online 18 September 2004

The title compound, $[Mn(C_{14}H_8O_4)(C_{12}H_{12}N_2)]_n$, with a novel three-dimensional framework, has been prepared by a hydrothermal reaction at 433 K. Each Mn atom lies on a twofold axis in a slightly distorted octahedral geometry, coordinated by two N atoms from two benzidine ligands and four O atoms from three symmetry-related biphenyl-2,2′-dicarboxylate (bpdc) ligands. The benzidine ligands lie about inversion centres and the bpdc ligands about twofold axes. Each bpdc ligand is bonded to three Mn ions to form a continuous chain of metal ions. The bpdc ligands are accommodated in a series of distorted holes resembling hexagonal prisms.

Comment

The design and syntheses of multidimensional coordination polymers constitute an attractive area of research because of their intriguing structural diversity and potential applications in functional materials (Moulton & Zaworotko, 2001). Coordination polymers are built by the rational selection of metal ions and the use of structurally interesting ligands with specific functionality to construct metal-organic frameworks. 2,2′-Diphenyldicarboxylic acid (H_2bpdc) is useful as a building block for the construction of coordination polymers, and a few coordination polymers using biphenyl-2,2′-dicarboxylate (bpdc) as a bridging ligand have been reported (Speier *et al.*, 2001; Rueff *et al.*, 2002; Wang *et al.*, 2002, 2003, 2003*a*,*b*; Kumagai *et al.*, 2002; Thirumurugan *et al.*, 2003). We report here a novel three-dimensional manganese polymer, $[Mn(C_{14}H_8O_4)(C_{12}H_{12}N_2)]_n$, (I), constructed from bpdc and benzidine.

The coordination environment of the Mn^{II} ion is shown in Fig. 1 and the geometry is listed in Table 1. Atom Mn1, which lies on a crystallographic twofold axis, is coordinated to three symmetrically related bpdc ligands *via* atoms O2(x, $1-y$, $\frac{1}{2}+z$) and O2($-x$, $1-y$, $-z$) of two bpdc ligands related by the twofold axis, and atoms O1 and O1($-x$, y, $\frac{1}{2}-z$) of one bpdc ligand, which itself lies on the twofold axis through atom Mn1. The axial coordination sites of the resulting octahedral environment of atom Mn1 are occupied by N atoms of the benzidine moiety, which itself lies astride a centre of symmetry.



(I)

This configuration results in columns (or chains) of linked Mn^{II} ions coordinated to an approximately square array of O atoms, as shown in Fig. 2 and end-on in Fig. 3. The benzidine ligands link adjacent columns but bind to different columns alternately along the chain, thus producing a three-dimensional network structure in which every Mn^{II} column is linked to four adjacent columns. The Mn^{II}–benzidine links can be thought of as forming a network of distorted hexagonal holes in which the phenyl rings of the bpdc ligands are contained along the b direction (Fig. 3).

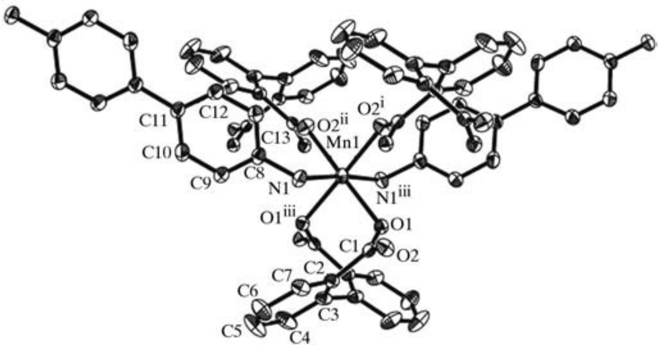


Figure 1
The coordination environment of the Mn^{II} ions, with displacement ellipsoids shown at the 30% probability level. All H atoms have been omitted for clarity. The crystallographic twofold axis is vertical. [Symmetry codes: (i) x, $1-y$, $\frac{1}{2}+z$; (ii) $-x$, $1-y$, $-z$; (iii) $-x$, y, $\frac{1}{2}-z$.]

DOI: 10.1107/S0108270104020050

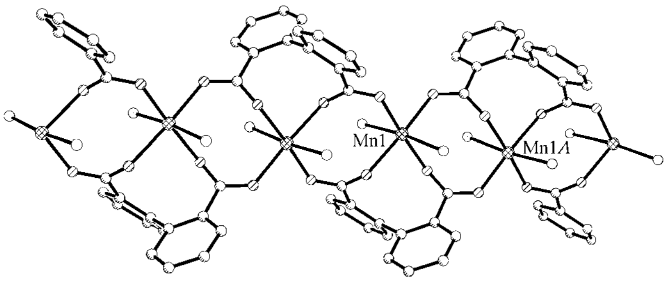


Figure 2
A segment of the Mn-containing columns, viewed from the side, approximately down *a*. Atoms Mn1 and Mn1*A* are separated by *c*/2. All H atoms and the benzidine ligands, except for the coordinated N atoms (dotted), have been omitted for clarity.

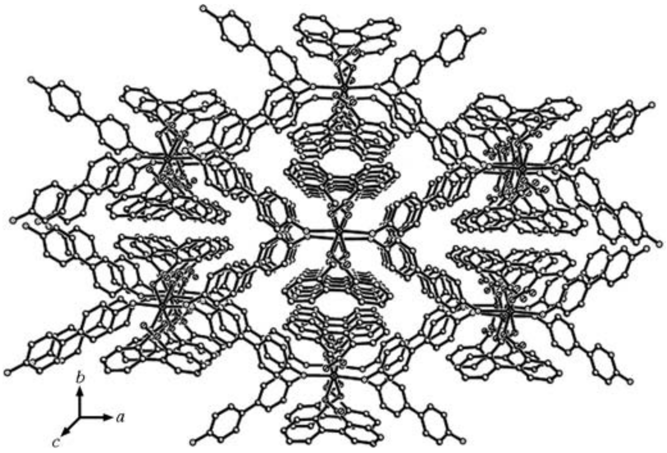


Figure 3
A view of the three-dimensional framework along the *c* axis. The columns of coordinated Mn ions of Fig. 2 are seen end-on, with the bpdc ligands extending in the *b* direction. All H atoms have been omitted for clarity.

The bpdc group acts as a tetradentate μ_3-bridging ligand, linking three Mn atoms (Fig. 2). Each bpdc ligand is in a twisted mode, and the dihedral angle between the planes of the two benzene ring is 68.53 (7)°. The two benzene rings are coplanar in the centrosymmetric benzidine ligands, but the two benzidine ligands that are linked to the same Mn atom are not in parallel planes. This mode of μ_3 binding is found for one of the bpdc ligands in seven, apparently isostructural, complexes of Nd, Dy and Y (Thirumurugan *et al.*, 2003), and La, Pr, Eu and Tb (Wang *et al.*, 2003*a*), but in these structures a second crystallographically distinct bpdc ligand binds in a different way. The continuous μ_3 mode of binding of bpdc ligands to produce the tertiary structure found in (I) (Fig. 2) is unique according to the Cambridge Structural Database (Version 5.25 of July 2004; Allen, 2002).

Only one of the H atoms attached to atom N1 appears to take part in hydrogen bonding (Table 2).

Experimental

All reagents were of AR grade and were used without further purification. A mixture of 2,2′-diphenic acid (0.242 g, 1 mmol), benzidine (0.184 g, 1 mmol) and $MnCl_2$ (0.170 g, 1 mmol) with H_2O (15 ml) was placed in a Teflon-lined stainless steel vessel, heated to 333 K and maintained at that temperature for 96 h, and then cooled slowly to room temperature. The resulting deep-orange crystals were collected by filtration and washed with water (yield 80%). Interestingly, although we changed the ratio of the mixture to 1:2:1 and 1:2:2, we still obtained the same deep-orange crystals.

Crystal data

$[Mn(C_{14}H_8O_4)(C_{12}H_{12}N_2)]$
$M_r = 479.38$
Monoclinic, $C2/c$
$a = 24.309\ (10)$ Å
$b = 10.161\ (4)$ Å
$c = 9.326\ (4)$ Å
$\beta = 100.677\ (7)°$
$V = 2263.7\ (16)$ Å^3
$Z = 4$
$D_x = 1.407$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1010 reflections
$\theta = 2.2–21.8°$
$\mu = 0.62$ mm^{-1}
$T = 293\ (2)$ K
Needle, dark orange
0.42 × 0.28 × 0.23 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.781$, $T_{max} = 0.871$
5868 measured reflections
2005 independent reflections
1313 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 25.0°$
$h = -23 \rightarrow 28$
$k = -12 \rightarrow 11$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.083$
$S = 0.87$
2005 reflections
150 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

$Mn1-O2^{i}$	2.1214 (19)	N1—C8	1.426 (3)
Mn1—O1	2.2066 (18)	O1—C1	1.271 (3)
Mn1—N1	2.320 (2)	O2—C1	1.251 (3)
$O2^{i}-Mn1-O2^{ii}$	86.23 (11)	$O2^{i}-Mn1-N1$	91.73 (7)
$O2^{i}-Mn1-O1$	176.45 (7)	$O2^{ii}-Mn1-N1$	92.22 (8)
$O2^{ii}-Mn1-O1$	91.55 (7)	O1—Mn1—N1	85.58 (7)
$O1-Mn1-O1^{iii}$	90.81 (9)	$N1^{iii}-Mn1-N1$	174.58 (11)
$O1-Mn1-N1^{iii}$	90.61 (7)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
$N1-H1B\cdots O1^{ii}$	0.90	2.24	2.990 (3)	140

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

H atoms attached to C atoms were treated as riding, with C—H distances of 0.93 Å, N—H distances of 0.90 Å and U_{iso}(H) values of $1.5U_{eq}$(C,N).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 2000); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 2000); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*/*PC*.

The authors sincerely thank the National Natural Science Foundation of China and the Provincial Natural Foundation of Shaanxi for support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1439). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bruker (2000). *SMART* (Version 5.0) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Kumagai, H., Inoue, K. & Kurmoo, M. (2002). *Bull. Chem. Soc. Jpn*, **75**, 1283–1289.

Moulton, B. & Zaworotko, M. (2001). *Chem. Rev.* **101**, 1629–1658.

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

Sheldrick, G. M. (1999). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2000). *SHELXS*97, *SHELXL*97 and *SADABS*. University of Göttingen, Germany.

Speier, G., Tyeklar, Z., Toth, P., Speier, E., Tisza, S., Rockenbauer, A., Whalen, A. M., Alkire, N. & Pierpont, A. G. (2001). *Inorg. Chem.* **40**, 5653–5659.

Thirumurugan, A., Pati, S. K., Green, M. A. & Natarajan, S. (2003). *J. Mater. Chem.* **13**, 2937–2941.

Wang, R.-H., Hong, M.-C., Luo, J.-H., Cao, R. & Weng, J.-B. (2002). *Eur. J. Inorg. Chem.* pp. 2082–2085.

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

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

Wang, Y.-B., Zheng, X.-J., Zhuang, W.-J. & Jin, L.-P. (2003*b*). *Eur. J. Inorg. Chem.* pp. 3572–3582.