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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.035
wR factor = 0.093
Data-to-parameter ratio = 9.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A one-dimensional double-wavelike chain
coordination polymer: *catena*-poly[[diaqua-
manganese(II)]- μ -(2,2'-bipyridyl-3,3'-dicar-
boxylato- $\kappa^4 N, N': O, O'$)]The asymmetric unit of the title polymer, $[\text{Mn}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$, consists of an Mn^{II} ion, which lies on a twofold axis, one half of a 2,2'-bipyridine-3,3'-dicarboxylate dianion and a coordinated water molecule. The one-dimensional chains extend into two-dimensional sheets *via* $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions. The crystal packing of the two-dimensional sheets appears to be dominated by aromatic π - π interactions.

Received 29 April 2003

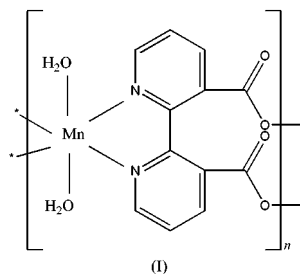
Accepted 6 May 2003

Online 16 May 2003

Comment

In recent years, the design and synthesis of new coordination polymers from transition metal ions and multidentate organic ligands have attracted great interest, owing to their intriguing molecular topologies and potential applications as functional materials (Batten & Robson, 1998; Hagrman *et al.*, 1999). The main and essential task of this domain is to render polymer structure controllable and predictable (Moulton & Zaworotko, 2001). Researchers can then develop synthetic strategies to influence the arrangement of coordination polymers in the crystalline state (Yaghi *et al.*, 1998; Batten, 2001). Before carrying out further studies on more complicated systems, it is useful for researchers to initially model and investigate simple systems. Therefore, it is useful to investigate one-dimensional chain-like structures, which are the simplest topological type of coordination polymers.

In general, rigid linear multidentate ligands, such as 1,4-benzenedicarboxylic acid and 4,4'-bipyridine, can be used as rod-like molecules to connect metal centers to construct an infinite structure. When these types of ligands coordinate to a metal ion, distortion of the ligand molecule can often occur and the ligand geometry changes. The resulting twist can make the ligand molecule behave as an efficient linker molecule, even when it is normally not considered one, as in the case of 2,2'-bipyridine derivatives and binaphthyl compounds.

Here we present the structure of a novel one-dimensional
coordination polymer, $[\text{Mn}(2,2'\text{-bipyridine-3,3'}\text{-dicarboxyl-}$

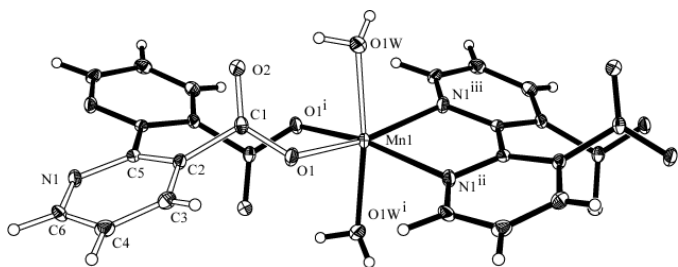


Figure 1

View of part of the one-dimensional polymeric chain structure of (I), with the asymmetric unit shown using open bonds. The displacement ellipsoids are drawn at the 30% probability level [symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 1 + y, \frac{1}{2} - z$].

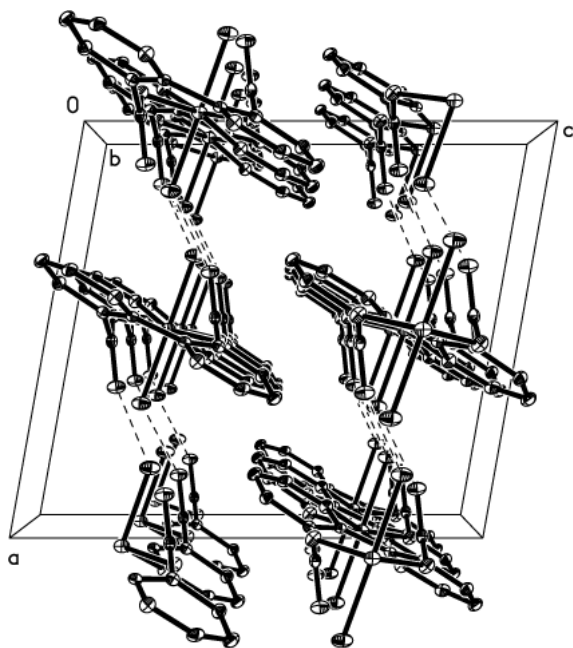


Figure 2

The molecular packing of (I), viewed along the *b* axis, showing the one-dimensional chains which are connected by hydrogen bonds to form the two-dimensional sheet structure. Dashed lines indicate the hydrogen-bonding interactions. Ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

ato)(H₂O)₂]_n, (I). The asymmetric unit of the coordination polymer consists of an Mn^{II} ion (on a twofold axis), a half of a 2,2'-bipyridine-3,3'-dicarboxylate and a coordinated water molecule. The coordination geometry of the Mn^{II} ion is that of a distorted octahedron, in which the equatorial positions are occupied by two O atoms, O1 and O1ⁱ [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$], from two carboxyl groups and two N atoms, N1ⁱⁱ and N1ⁱⁱⁱ [symmetry codes: (ii) $x, 1 + y, z$; (iii) $1 - x, 1 + y, \frac{1}{2} - z$], from 2,2'-bipyridine [Mn1–O1 = 2.157 (2) Å and Mn1–N1ⁱⁱ = 2.241 (3) Å]. The axial sites are occupied by two water molecules [O1Wⁱ–Mn–O1W = 172.52 (16)° and Mn1–O1W = 2.210 (2) Å]. Two carboxyl groups coordinate to Mn1 in monodentate mode and the two uncoordinated O atoms from the carboxyl groups are located *trans* to each other. The 2,2'-bipyridine unit chelates the Mn ion as a

bidentate ligand. In the bipyridyl ligand, the two pyridyl rings are not coplanar, but are twisted with a dihedral angle of 26.15 (1)°, and the carboxyl group is twisted from the pyridyl plane with a dihedral angle of 54.24 (3)°. The carboxyl groups and 2,2'-bipyridine units connect the Mn ions alternately to form a one-dimensional double-wavelike chain along the *b*-axis direction. The three-dimensional packing arrangement of the double-wavelike chains in the crystal structure is such that one chain runs in a carboxylate–Mn–bipyridine–Mn–carboxylate order along the *b*-axis direction, while another runs in the reverse order. Similar chains are connected by O–H···O hydrogen bonds, with a distance of 1.97 (6)° for H1WB···O2($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), to form extended two-dimensional sheets whose projection plane is on the *ab* plane, and a short intramolecular O–H···O hydrogen bond with a distance of 1.89 Å for H1WA···O2, controls, to some extent, the conformation of the one-dimensional chain. In the crystal structure, the packing of the two-dimensional sheets appears to be controlled by aromatic π – π interactions between two pyridine rings, with a centroid–centroid distance of 3.59 Å (Janiak, 2000).

Experimental

Mn(OAc)₂·4H₂O (127.3 mg, 0.52 mmol), 2,2'-bipyridine-3,3'-dicarboxylic acid (122.8 mg, 0.50 mmol), and pyridine (0.2 ml) were dissolved in a mixture of 7 ml water and 4 ml ethanol. The mixture was placed in a Teflon-lined stainless steel vessel (25 ml). The vessel was sealed and heated at 403 K for 72 h and then cooled to room temperature. Large yellow block-shaped crystals were collected by filtration, followed by washing with water and ethanol, in *ca* 72% yield.

Crystal data

[Mn(C₁₂H₆N₂O₄)(H₂O)₂]
M_r = 333.16
 Monoclinic, *C*2/*c*
a = 11.617 (2) Å
b = 8.030 (2) Å
c = 12.961 (3) Å
 β = 100.17 (3)°
V = 1190.1 (5) Å³
Z = 4

D_x = 1.859 Mg m^{−3}
 Mo K α radiation
 Cell parameters from 25 reflections
 θ = 2.3–14.0°
 μ = 1.14 mm^{−1}
T = 293 (2) K
 Block, yellow
 0.40 × 0.30 × 0.30 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: ψ scan (XCAD4; Harms & Wocadlo, 1995)
T_{min} = 0.670, *T_{max}* = 0.710
 1103 measured reflections
 1051 independent reflections

895 reflections with *I* > 2 σ (*I*)
R_{int} = 0.017
 θ_{max} = 25.0°
h = 0 → 13
k = 0 → 9
l = −15 → 15
 3 standard reflections every 200 reflections
 intensity decay: 1.0%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.035
wR(*F*²) = 0.093
S = 1.01
 1051 reflections
 116 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 6.4486P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.38 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mn1—O1	2.157 (2)	Mn1—N1 ⁱⁱ	2.241 (3)
Mn1—O1W	2.210 (3)		
O1 ⁱ —Mn1—O1	87.88 (13)	O1W ⁱ —Mn1—N1 ⁱⁱ	82.48 (11)
O1—Mn1—O1W ⁱ	91.72 (11)	O1W—Mn1—N1 ⁱⁱ	103.66 (11)
O1—Mn1—O1W	82.88 (11)	N1 ⁱⁱ —Mn1—N1 ⁱⁱⁱ	72.34 (14)
O1W ⁱ —Mn1—O1W	172.52 (16)	C1—O1—Mn1	119.4 (2)
O1 ⁱ —Mn1—N1 ⁱⁱ	162.52 (10)	C6—N1—Mn1 ^{iv}	120.7 (2)
O1—Mn1—N1 ⁱⁱ	102.05 (9)	C5—N1—Mn1 ^{iv}	117.7 (2)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WB \cdots O2 ^v	0.78 (5)	1.97 (6)	2.723 (4)	163 (5)
O1W—H1WA \cdots O2	0.87 (5)	1.89 (5)	2.680 (4)	151 (4)

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

H atoms were located in a difference Fourier map and refined independently with isotropic displacement parameters. The C—H distances ranged from 0.84 (4) to 0.99 (4) Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

This work was funded by a State Key Project for Fundamental Research of the National Natural Science Foundation of China.

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