

catena-Poly[[diaquamanganese(II)]- μ -pyridine-2,4,6-tricarboxylato- $\kappa^5N,O^2,O^6:O^4,O^4'$]

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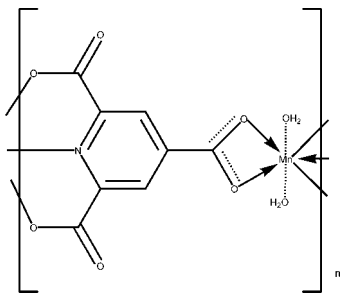
Received 7 November 2007; accepted 12 November 2007

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.003$ Å;
R factor = 0.030; wR factor = 0.089; data-to-parameter ratio = 13.8.

In the title compound, $[Mn(C_8H_2NO_6)(H_2O)_2]_n$, each pyridine-2,4,6-tricarboxylate (tpc) ligand bridges two Mn^{II} ions with the formation of polymeric chains located on a twofold rotation axis. Each Mn^{II} ion is coordinated by two O and one N atoms from one tpc ligand, two O atoms from another ligand and two water molecules in a distorted pentagonal-bipyramidal geometry. The Mn–N [2.243 (2) Å] and Mn–O [2.206 (2)–2.3123 (16) Å] bond lengths are normal. The coordinated water molecules link neighbouring polymeric chains *via* O–H...O hydrogen bonds into a two-dimensional framework parallel to the *bc* plane.

Related literature

For the structures and potential applications of inorganic-organic hybrid coordination polymers, see: Evans & Lin (2002); Gao *et al.* (2005); Kil & Myunghyun (2000). For the structures and properties of compounds containing pyridine-2,4,6-tricarboxylic acid, see: Mehmet *et al.* (2006); Moulton & Zaworotko (2001); Sujit *et al.* (2004); Syper *et al.* (1980).



Experimental

Crystal data

$[Mn(C_8H_2NO_6)(H_2O)_2]$
 $M_r = 299.08$
Monoclinic, $C2/c$
 $a = 11.406$ (2) Å
 $b = 9.1463$ (18) Å
 $c = 10.155$ (2) Å
 $\beta = 107.76$ (3)°

$V = 1008.9$ (3) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.35$ mm⁻¹
 $T = 293$ (2) K
 $0.15 \times 0.05 \times 0.05$ mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{min} = 0.874$, $T_{max} = 1.000$
(expected range = 0.817–0.935)

5072 measured reflections
1155 independent reflections
1109 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.089$
 $S = 1.01$
1155 reflections

84 parameters
H-atom parameters constrained
 $\Delta\rho_{max} = 0.45$ e Å⁻³
 $\Delta\rho_{min} = -0.49$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1W–H1WB...O3 ⁱ	0.96	2.02	2.853 (2)	144
O1W–H1WC...O1 ⁱⁱ	0.96	2.18	2.858 (2)	127
O1W–H1WC...O4 ⁱⁱⁱ	0.96	2.18	3.000 (2)	142

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*.

HJX acknowledges a Start-up Grant from Southeast University, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2352).

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supplementary materials

Acta Cryst. (2008). E64, m35 [doi:10.1107/S1600536807058102]

***catena*-Poly[[diaquamanganese(II)]- μ -pyridine-2,4,6-tricarboxylato- $\kappa^5N,O^2,O^6:O^4,O^4'$]**

D.-W. Fu and H.-J. Xu

Comment

The construction of inorganic-organic hybrid coordination polymers has been a field of rapid growth in supramolecular and material chemistry because of the formation of fascinating structures and their potential application such as ion-exchange, adsorption, catalytic, fluorescence and magnetic materials (Moulton *et al.*, 2001; Evans *et al.*, 2002; Kil *et al.*, 2000). Pyridine-2, 4, 6-tricarboxylic acid (H₃tpc) is a good building unit for constructing MOFs due to the existence of both N and O atoms in the ligands, which are used along with bridging ligand to bind metal centres, which can link 3 d, 4f, and 3 d-4f metal ions. However, there are only several of reports on the infinite one-dimensional, two-dimensional and three-dimensional coordination solids assembled by H₃tpc (Gao *et al.*, 2005); Mehmet *et al.*, 2006); Sujit *et al.*, 2004). In this paper, we report the crystal structure of the title compound prepared from MnCl₂.4H₂O and pyridine-2, 4, 6-tricarboxylic acid.

In (I) (Fig. 1), each metal ion is heptacoordinated and exhibits a distorted pentagonal bipyramidal geometry, in which the tpc³⁻ ligand is bonded equatorially through the pyridine-2, 4, 6-tricarboxylic acid (NO₄ donor set), while two water molecules occupy the axial sites. Each carboxylic acid group at the 2, 6-position of the tpcH₃ ligand is only bound to one metal ion and the carboxylic groups at the 4-position adopt chelate mode. The coordinated water molecules link two neighboring one-dimensional chains by the intermolecular hydrogen bonds to form two-dimensional framework (Fig.2).

Experimental

The ligand, tpcH₃, was synthesized according to the reported literature (Syper *et al.*, 1980). A mixture of tpcH₃ (25 mg, 0.12 mmol), MnCl₂.4H₂O (45 mg, 0.22 mmol), five drops of EtOH, a few drops of water and two drops of hydrochloric acid sealed in a glass tube was kept at 160 °C. Yellow crystals suitable for X-ray analysis were obtained after 4 days.

Refinement

All H atoms were geometrically positioned (O—H 0.96 Å, C—H 0.93 Å) and were allowed to ride on the parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{O})$.

Figures

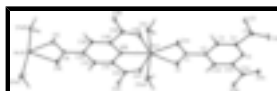


Fig. 1. A portion of polymeric chain in (I), showing the atomic numbering scheme and displacement ellipsoids drawn at the 30% probability level [symmetry codes: (A) $-x, y, 1/2 - z$; (B) $x, y + 1, z$; (C) $-x, y + 1, 1/2 - z$].

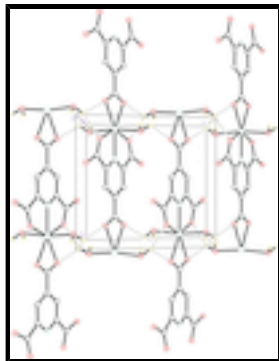


Fig. 2. A portion of the crystal packing viewed along the a axis. Dashed lines denote O—H \cdots O hydrogen bonds. H atoms were omitted for clarity.

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Crystal data

[Mn(C₈H₂NO₆)(H₂O)₂]

$M_r = 299.08$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 11.406\ (2)\ \text{\AA}$

$b = 9.1463\ (18)\ \text{\AA}$

$c = 10.155\ (2)\ \text{\AA}$

$\beta = 107.76\ (3)^\circ$

$V = 1008.9\ (3)\ \text{\AA}^3$

$Z = 4$

$F(000) = 600$

$D_x = 1.969\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5380 reflections

$\theta = 3.2\text{--}27.5^\circ$

$\mu = 1.35\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.15 \times 0.05 \times 0.05\ \text{mm}$

Data collection

Rigaku Mercury2
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: $13.6612\ \text{pixels mm}^{-1}$
 ω scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)

$T_{\min} = 0.874$, $T_{\max} = 1.000$

5072 measured reflections

1155 independent reflections

1109 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -14 \rightarrow 14$

$k = -11 \rightarrow 11$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.089$

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 2.4P]$
1155 reflections	where $P = (F_o^2 + 2F_c^2)/3$
84 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Mn1	0.0000	0.57159 (4)	0.2500	0.02459 (17)
O1	-0.06002 (17)	0.34882 (16)	0.31586 (18)	0.0349 (4)
O1W	-0.14376 (17)	0.58998 (18)	0.04818 (18)	0.0365 (4)
H1WB	-0.2176	0.5432	0.0532	0.055*
H1WC	-0.1160	0.5432	-0.0215	0.055*
O3	0.20027 (14)	-0.15346 (16)	0.04948 (16)	0.0281 (3)
O4	0.13754 (15)	-0.34426 (15)	0.14530 (17)	0.0291 (4)
N1	0.0000	-0.1832 (2)	0.2500	0.0195 (5)
C1	0.0000	0.2830 (3)	0.2500	0.0239 (6)
C2	0.0000	0.1182 (3)	0.2500	0.0192 (5)
C3	0.07379 (18)	0.0412 (2)	0.1868 (2)	0.0201 (4)
H3A	0.1239	0.0901	0.1441	0.024*
C4	0.07040 (17)	-0.1104 (2)	0.18927 (19)	0.0187 (4)
C5	0.14191 (18)	-0.2120 (2)	0.1247 (2)	0.0206 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0370 (3)	0.0115 (2)	0.0320 (3)	0.000	0.0205 (2)	0.000
O1	0.0548 (10)	0.0144 (7)	0.0455 (9)	0.0032 (6)	0.0302 (8)	-0.0026 (6)
O1W	0.0445 (10)	0.0296 (8)	0.0384 (9)	-0.0064 (7)	0.0174 (8)	-0.0046 (7)
O3	0.0368 (8)	0.0203 (7)	0.0383 (8)	-0.0020 (6)	0.0280 (7)	-0.0003 (6)
O4	0.0412 (8)	0.0149 (7)	0.0425 (9)	0.0005 (6)	0.0293 (7)	-0.0012 (6)
N1	0.0271 (11)	0.0121 (10)	0.0246 (11)	0.000	0.0159 (9)	0.000
C1	0.0344 (15)	0.0116 (12)	0.0267 (13)	0.000	0.0111 (11)	0.000
C2	0.0263 (13)	0.0115 (11)	0.0219 (12)	0.000	0.0104 (10)	0.000

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C3	0.0262 (9)	0.0144 (8)	0.0245 (9)	-0.0017 (7)	0.0151 (8)	0.0001 (7)
C4	0.0237 (9)	0.0148 (9)	0.0217 (9)	0.0001 (7)	0.0130 (7)	-0.0009 (7)
C5	0.0243 (9)	0.0169 (9)	0.0247 (9)	0.0001 (7)	0.0138 (7)	-0.0029 (7)

Geometric parameters (\AA , $^\circ$)

Mn1—O1W ⁱ	2.206 (2)	O4—Mn1 ^{iv}	2.2807 (15)
Mn1—O1W	2.206 (2)	N1—C4 ⁱ	1.331 (2)
Mn1—N1 ⁱⁱ	2.243 (2)	N1—C4	1.331 (2)
Mn1—O4 ⁱⁱⁱ	2.2807 (15)	N1—Mn1 ^{iv}	2.243 (2)
Mn1—O4 ⁱⁱ	2.2807 (15)	C1—O1 ⁱ	1.248 (2)
Mn1—O1	2.3123 (16)	C1—C2	1.507 (4)
Mn1—O1 ⁱ	2.3123 (16)	C2—C3 ⁱ	1.395 (2)
O1—C1	1.248 (2)	C2—C3	1.395 (2)
O1W—H1WB	0.9600	C3—C4	1.387 (3)
O1W—H1WC	0.9600	C3—H3A	0.9300
O3—C5	1.274 (2)	C4—C5	1.511 (2)
O4—C5	1.232 (2)		
O1W ⁱ —Mn1—O1W	171.25 (9)	Mn1—O1W—H1WB	109.4
O1W ⁱ —Mn1—N1 ⁱⁱ	85.63 (4)	Mn1—O1W—H1WC	109.4
O1W—Mn1—N1 ⁱⁱ	85.63 (4)	H1WB—O1W—H1WC	109.5
O1W ⁱ —Mn1—O4 ⁱⁱⁱ	87.89 (7)	C5—O4—Mn1 ^{iv}	118.68 (12)
O1W—Mn1—O4 ⁱⁱⁱ	89.16 (7)	C4 ⁱ —N1—C4	119.9 (2)
N1 ⁱⁱ —Mn1—O4 ⁱⁱⁱ	70.28 (4)	C4 ⁱ —N1—Mn1 ^{iv}	120.03 (11)
O1W ⁱ —Mn1—O4 ⁱⁱ	89.16 (7)	C4—N1—Mn1 ^{iv}	120.03 (11)
O1W—Mn1—O4 ⁱⁱ	87.89 (7)	O1—C1—O1 ⁱ	122.3 (3)
N1 ⁱⁱ —Mn1—O4 ⁱⁱ	70.28 (4)	O1—C1—C2	118.85 (13)
O4 ⁱⁱⁱ —Mn1—O4 ⁱⁱ	140.55 (7)	O1 ⁱ —C1—C2	118.85 (13)
O1W ⁱ —Mn1—O1	90.01 (6)	C3 ⁱ —C2—C3	119.3 (2)
O1W—Mn1—O1	97.71 (6)	C3 ⁱ —C2—C1	120.33 (12)
N1 ⁱⁱ —Mn1—O1	151.78 (4)	C3—C2—C1	120.33 (12)
O4 ⁱⁱⁱ —Mn1—O1	81.72 (5)	C4—C3—C2	118.18 (17)
O4 ⁱⁱ —Mn1—O1	137.62 (5)	C4—C3—H3A	120.9
O1W ⁱ —Mn1—O1 ⁱ	97.71 (6)	C2—C3—H3A	120.9
O1W—Mn1—O1 ⁱ	90.01 (6)	N1—C4—C3	122.19 (17)
N1 ⁱⁱ —Mn1—O1 ⁱ	151.78 (4)	N1—C4—C5	112.04 (16)
O4 ⁱⁱⁱ —Mn1—O1 ⁱ	137.62 (5)	C3—C4—C5	125.77 (16)
O4 ⁱⁱ —Mn1—O1 ⁱ	81.72 (5)	O4—C5—O3	124.75 (17)
O1—Mn1—O1 ⁱ	56.44 (8)	O4—C5—C4	118.36 (17)
C1—O1—Mn1	90.64 (14)	O3—C5—C4	116.86 (16)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1W—H1WB···O3 ^v	0.96	2.02	2.853 (2)	144
O1W—H1WC···O1 ^{vi}	0.96	2.18	2.858 (2)	127
O1W—H1WC···O4 ^{vii}	0.96	2.18	3.000 (2)	142

Symmetry codes: (v) $x-1/2, y+1/2, z$; (vi) $x, -y+1, z-1/2$; (vii) $-x, -y, -z$.

Fig. 1

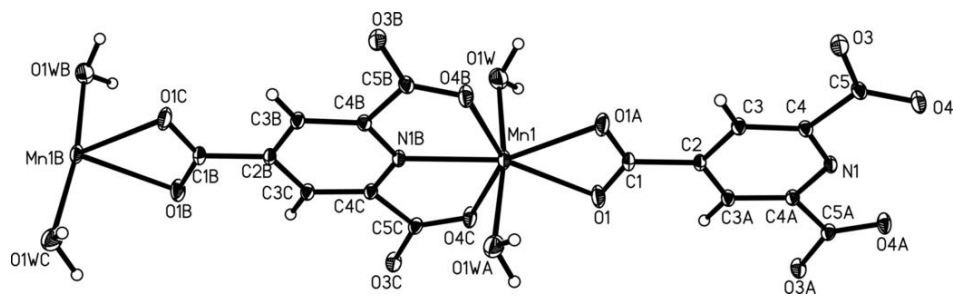


Fig. 2

