Poly[[(1,10-phenanthroline)(*μ₃*-pyridine-2,3-dicarboxylato)manganese(II)] monohydrate]

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The title complex, $\{[Mn(C_7H_3NO_4)(C_{12}H_8N_2)]\cdot H_2O\}_n$, conventionally abbreviated to $\{[Mn(2,3\text{-pddc})(phen)]\cdot H_2O\}_n$ (phen is 1,10-phenanthroline and 2,3-pddc is 2,3-pyridine-dicarboxylate), has been synthesized under hydrothermal conditions. In the complex, the Mn atom is coordinated by three O atoms of three symmetry-equivalent 2,3-pddc molecules. The complex thus extends in two dimensions, resulting in the formation of a two-dimensional network structure. The complex is further assembled into a three-dimensional network by π–π stacking interactions involving the phen ligands.

## Comment

The hydrothermal method has become a promising technique for the preparation of novel organic–inorganic hybrid materials (Tong *et al.*, 2003). 2,3-Pyridinedicarboxylate (2,3–pddc) can act as a chelating bidentate ligand through the N atom and one O atom of the carboxylate group in the *ortho* position, the second carboxylate group remaining uncoordinated (Okabe *et al.*, 1996; Suga & Okabz, 1996; Sengupta *et al.*, 2001). We report here the structure of the title complex, (I), in which both carboxylate groups take part in the coordination with the Mn atoms.

(I)
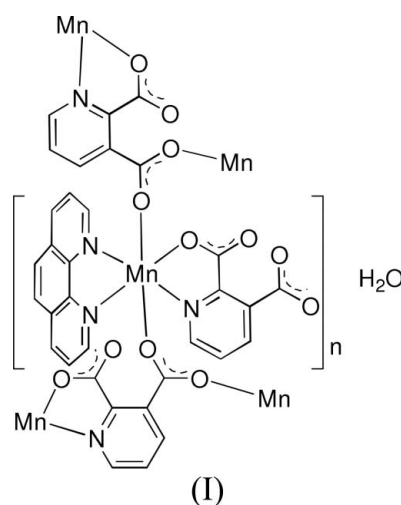
The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The asymmetric unit consists of an Mn atom, one 2,3-pddc group, one phen ligand (phen is 1,10-phenanthroline) and one water molecule. The coordination around the Mn atom is square bipyramidal (distorted octahedral). The equatorial belt is formed by two N atoms (N1 and N3) and two O atoms (O2
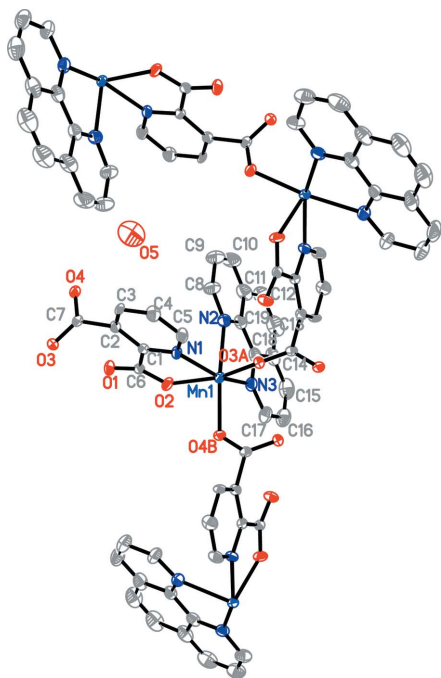
Figure 1
Complex (I), with the atomic numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity. Suffixes A and B correspond to symmetry codes i and ii in Table 1.
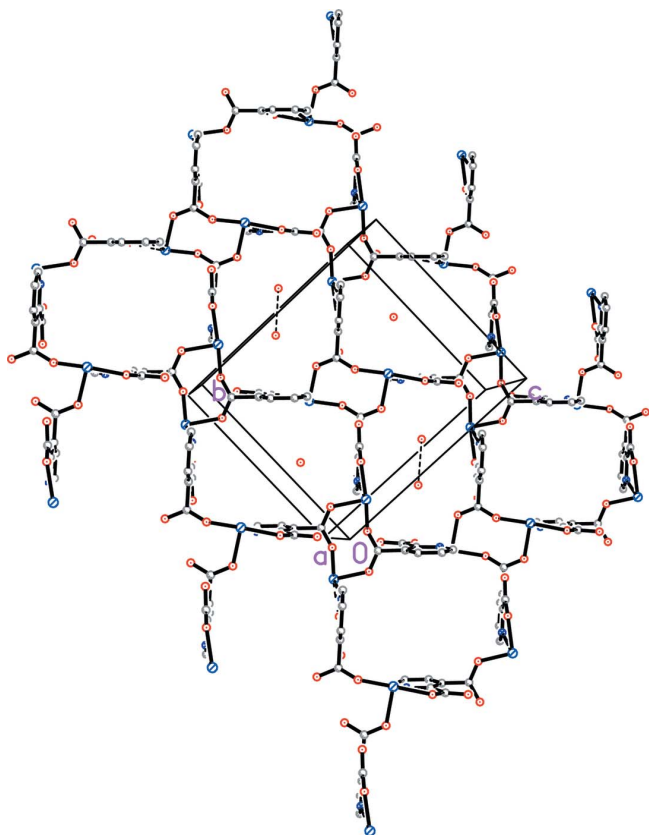
Figure 2
A view along the *a* axis of the network structure of complex (I). The phen groups and H atoms have been omitted for clarity.
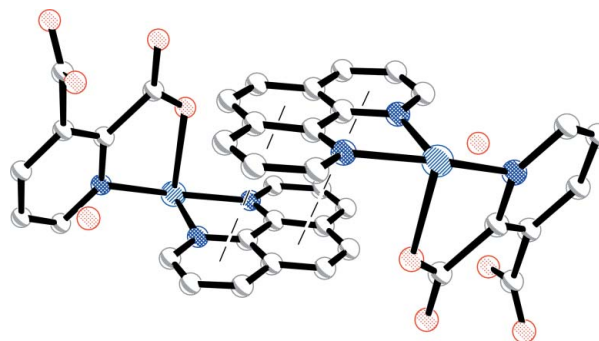
Figure 3
A view of the π–π stacking interactions (dashed lines) of the phen groups in complex (I). H atoms have been omitted.

and $O3^i$), and the axial positions are occupied by one N atom (N2) and one O atom ($O4^{ii}$) (symmetry codes are as in Table 1). The Mn—O and Mn—N bond lengths fall in the ranges 2.108 (3)–2.145 (3) and 2.228 (4)–2.335 (4) Å, respectively. They are consistent with the corresponding distances in complexes $[H_3O]_{2x}[Mn(pyrazinedicarboxylate)_2]_x$ (Mao *et al.*, 1996), $[Mn(pyrazinedicarboxylate)(H_2O)\cdot 2H_2O]$ (Zou *et al.*, 1999) and $[Mn_2(pyridinedicarboxylate)_2(H_2O)_3]_n\cdot 2nH_2O$ (Li & Li, 2004).

In complex (I), the Mn atom is coordinated by three different O atoms of three symmetry-equivalent 2,3-pddc ligands, so the complex is extended in two dimensions, resulting in the formation of a two-dimensional supramolecular complex (Fig. 2). The complex is further assembled into a three-dimensional network by π–π stacking interactions. One pyridyl ring and the central benzene ring of a symmetry-related phen molecule at $(2 - x, 2 - y, 1 - z)$ take part in π–π stacking interactions, as illustrated in Fig. 3; the distance between their centroids is 3.884 (4) Å. The distance between the centroid of the pyridyl ring and the plane of the benzene ring is 3.760 Å and the slip angle (θ) is *ca* 14.9°. The centroid–centroid distance of the two six-membered rings is much shorter than that reported previously for the stacking of naphthalene groups [4.6 Å (Onoue *et al.*, 1997) and 4.83 Å (Ortholand *et al.*, 1989)]. This indicates that the π–π stacking interactions in the complex are strong, and it is these interactions that stabilize the three-dimensional network in the crystal structure.

Experimental

In a typical hydrothermal synthesis, a mixture of $MnCl_2\cdot 4H_2O$ (99.0 mg, 0.5 mmol), 2,3-pyridinedicarboxylic acid (84.1 mg, 0.5 mmol), phen (99.1 mg, 0.5 mmol), NaOH (80.0 mg, 2.0 mmol) and water (30.0 ml) in a molar ratio of approximately 1:1:1:4:3333 was sealed in a 50 ml stainless steel reactor with a Teflon liner and heated to 447 K for 4 d and then slowly cooled to room temperature. Yellow rod-like crystals of complex (I) were obtained with a yield of 60% (based on Mn). m.p. > 573 K. Elemental analysis calculated for $C_{19}H_{13}MnN_3O_5$: C 54.56, H 3.13, N 10.05%; found: C 54.37, H 3.08, N 10.23%. Selected FT–IR (KBr, cm^{-1}): ν 3383 (*s*, *br*), 1657 (*s*), 1563 (*vs*), 1513 (*m*), 1423 (*s*), 1383 (*s*), 1351 (*m*), 1115 (*s*), 1064 (*m*), 854 (*s*), 836 (*vs*), 729 (*m*), 653 (*m*), 439 (*m*).

$[Mn(C_7H_3NO_4)(C_{12}H_8N_2)]\cdot H_2O$
$M_r = 418.26$
Monoclinic, $P2_1/n$
$a = 11.649$ (4) Å
$b = 11.774$ (4) Å
$c = 13.292$ (4) Å
$\beta = 109.939$ (5)°
$V = 1713.6$ (9) Å^3
$Z = 4$

$D_x = 1.621$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1897
 reflections
$\theta = 2.4–23.9°$
$\mu = 0.81$ mm^{-1}
$T = 298$ (2) K
Rod, yellow
$0.38 \times 0.35 \times 0.29$ mm

Data collection

Siemens SMART CCD area-
 detector diffractometer
φ and ω scans
Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.748$, $T_{max} = 0.799$
10888 measured reflections

4136 independent reflections
2336 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 28.4°$
$h = -15 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.196$
$S = 1.00$
4136 reflections
259 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
$w = 1/[\sigma^2(F_o^2) + (0.1091P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O3^i	2.108 (3)	Mn1—N3	2.228 (4)
Mn1—O2	2.134 (3)	Mn1—N1	2.292 (3)
Mn1—O4^{ii}	2.145 (3)	Mn1—N2	2.335 (4)
O3^i—Mn1—O4^{ii}	95.12 (11)	O4^{ii}—Mn1—N1	103.78 (12)
O2—Mn1—O4^{ii}	88.98 (11)	O3^i—Mn1—N2	91.69 (13)
O3^i—Mn1—N3	105.21 (13)	O2—Mn1—N2	89.23 (12)
O2—Mn1—N3	96.45 (12)	O4^{ii}—Mn1—N2	166.30 (13)
O4^{ii}—Mn1—N3	94.07 (13)	N3—Mn1—N2	72.64 (14)
O3^i—Mn1—N1	84.32 (11)	N1—Mn1—N2	88.69 (13)
O2—Mn1—N1	73.30 (11)		

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

The C-bound H atoms were included in calculated positions and refined as riding atoms, with C—H = 0.93 Å and U_{iso}(H) = $1.2U_{eq}$(parent C atom). The water H atoms were located in a difference Fourier synthesis and refined isotropically [O—H = 0.887 (18) and 0.909 (18) Å].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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