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Key indicators

Single-crystal X-ray study
 T = 150 K
 Mean $\sigma(C-C)$ = 0.003 Å
 R factor = 0.040
 wR factor = 0.131
 Data-to-parameter ratio = 17.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

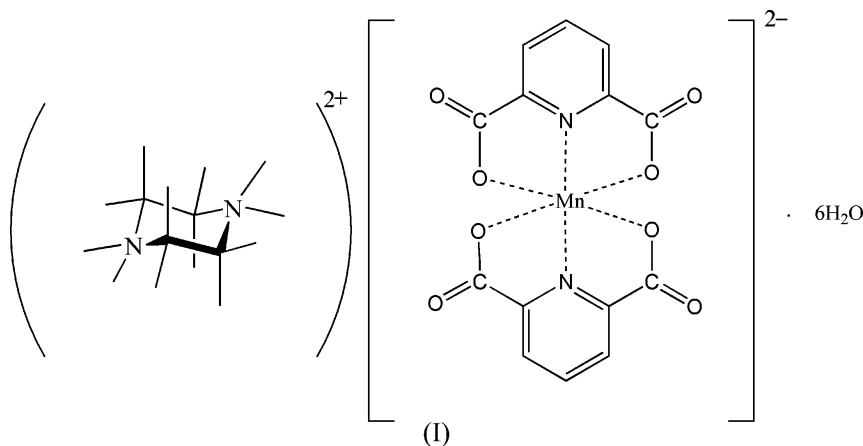
Piperazinediium bis(pyridine-2,6-dicarboxylato)-manganate(II) hexahydrate

The reaction of manganese(II) nitrate with the proton-transfer compound piperazinediium pyridine-2,6-dicarboxylate, or (pipzH₂)(pydc), in aqueous solution leads to the formation of the title compound, (C₄H₁₂N₂)[Mn(C₇H₃NO₄)₂].6H₂O. The anion is a six-coordinate complex with a distorted octahedral geometry around the central atom. In the crystal structure, intra- and intermolecular O—H...O and N—H...O hydrogen bonds connect the various components into a supramolecular structure.

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Comment

There are several studies on proton transfer between a carboxylic acid and a heterocyclic amine. Continuing our research on proton-transfer systems, we have now found a synthetic route to combine a carboxylic acid with an amine and produce water-soluble self-associating ion-pair systems, which can react with metal ions and result in different complexes (Aghabozorg, Ghadermazi & Ramezanipour, 2006; Soleimannejad *et al.*, 2005; Moghimi, Aghabozorg *et al.*, 2005; Moghimi *et al.*, 2002; Aghabozorg, Akbari & Ramezanipour, 2005; Moghimi *et al.*, 2003). The resulting compounds, with some remaining sites as electron donors, can coordinate to many metal ions (Aghabozorg, Nakhjavan *et al.*, 2006; Aghabozorg, Ghadermazi *et al.*, 2006; Sheshmani *et al.*, 2006; Moghimi, Sheshmani *et al.*, 2005; Moghimi, Sharif *et al.*, 2005; Aghabozorg, Moghimi *et al.*, 2005; Aghabozorg, Dalir Kheirollahi *et al.*, 2005; Moghimi, Alizadeh *et al.*, 2005; Ramezanipour *et al.*, 2005). We report here the crystal structure of the title compound, (I).



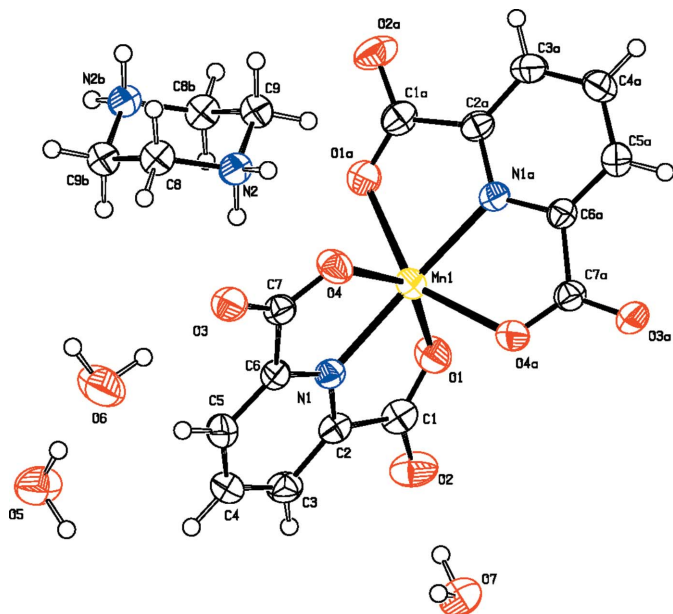


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry codes: (a) $1 - x, y, \frac{1}{2} - z$, (b) $1 - x, 2 - y, -z$].

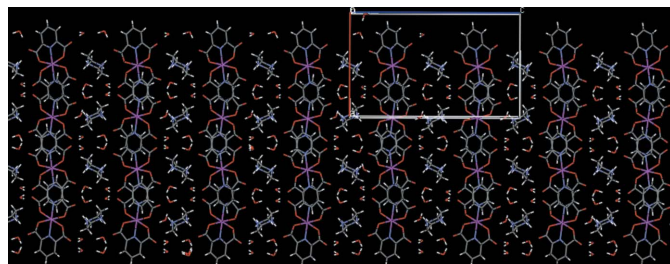


Figure 2

A layered packing diagram of (I). The space between the two layers of $[\text{Mn}(\text{pydc})_2]^{2-}$ fragments is filled with a layer of $(\text{pipzH}_2)^{2+}$ cations and water molecules.

bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The piperazine ring is not planar, having a total puckering amplitude, Q_T , of 1.518 (3) Å and a chair conformation [$\varphi = 0.00$ (3)° and $\theta = 0.00$ (3)°] (Cremer & Pople, 1975). The Mn^{II} atom is six-coordinated by two pyridine-2,6-dicarboxylate, or $(\text{pydc})^{2-}$, groups, *i.e.* each $(\text{pydc})^{2-}$ is coordinated through one pyridine N atom and two carboxylate O atoms (Table 1). Atoms N1 and N1ⁱ of the two $(\text{pydc})^{2-}$ fragments occupy the axial positions, while atoms O2, O2ⁱ, O3 and O3ⁱ form the equatorial plane [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$].

The N1–Mn–N1ⁱ [173.44 (9)°] angle deviates from linearity. Therefore, the coordination around Mn^{II} is distorted octahedral. There are three uncoordinated water molecules, and one half piperazinium ion as counter-ion, in the asymmetric unit, with some hydrogen bonds to water molecules and coordinated COO^- groups of $(\text{pydc})^{2-}$ fragments.

In the crystal structure, the spaces between two layers of $[\text{Mn}(\text{pydc})_2]^{2-}$ fragments are filled with layers of $(\text{pipzH}_2)^{2+}$ cations and water molecules (Fig. 2). Intra- and intermolecular

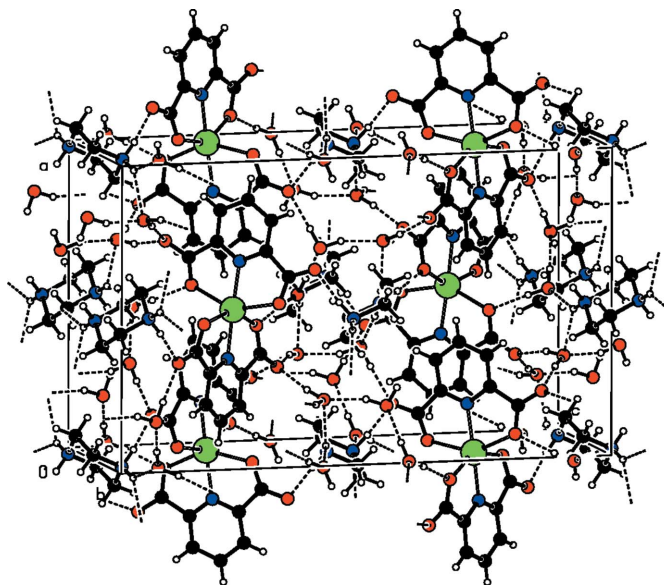


Figure 3

A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

N–H...O and O–H...O hydrogen bonds (Table 2) seem to be effective in the stabilization of the crystal structure, resulting in the formation of a supramolecular structure (Fig. 3).

Experimental

A solution of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (143 mg, 0.5 mmol) in water (20 ml) was added to an aqueous solution of $(\text{pipzH}_2)(\text{pydc})$ (253 mg, 1.0 mmol, 20 ml) in a 1:2 molar ratio. Yellow crystals of (I) were obtained after a few days at room temperature.

Crystal data

$(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Mn}(\text{C}_7\text{H}_3\text{NO}_4)_2] \cdot 6\text{H}_2\text{O}$	$Z = 4$
$M_r = 581.40$	$D_x = 1.523 \text{ Mg m}^{-3}$
Orthorhombic, <i>Pbcn</i>	Mo $K\alpha$ radiation
$a = 13.553$ (3) Å	$\mu = 0.60 \text{ mm}^{-1}$
$b = 8.4219$ (19) Å	$T = 150$ (2) K
$c = 22.215$ (5) Å	Block, yellow
$V = 2535.7$ (10) Å ³	$0.36 \times 0.35 \times 0.25 \text{ mm}$

Data collection

Bruker SMART 1000	20178 measured reflections
diffractometer	2902 independent reflections
ω scans	2003 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.040$
SADABS (Sheldrick, 1998)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.814, T_{\text{max}} = 0.865$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0874P)^2 + 0.3048P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.94$	$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
2902 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
168 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Mn1–N1	2.1640 (19)	O2–C1	1.254 (3)
Mn1–O4	2.2458 (16)	O3–C7	1.253 (3)
Mn1–O1	2.2484 (16)	O4–C7	1.255 (3)
O1–C1	1.258 (3)		
N1–Mn1–N1 ⁱ	173.44 (9)	O1 ⁱ –Mn1–O1	102.52 (9)
N1–Mn1–O4 ⁱ	103.44 (6)	O2–C1–O1	126.3 (2)
N1–Mn1–O4	72.28 (6)	O2–C1–C2	116.9 (2)
O4 ⁱ –Mn1–O4	102.24 (9)	O1–C1–C2	116.77 (19)
N1–Mn1–O1 ⁱ	111.94 (6)	O3–C7–O4	125.5 (2)
O4–Mn1–O1 ⁱ	88.30 (6)	O3–C7–C6	117.95 (19)
N1–Mn1–O1	72.42 (6)	O4–C7–C6	116.54 (18)
O4–Mn1–O1	144.61 (6)		
O1 ⁱ –Mn1–O1–C1	–120.40 (18)	O1 ⁱ –Mn1–O4–C7	108.16 (16)
O4 ⁱ –Mn1–O1–C1	93.61 (17)	O4 ⁱ –Mn1–O4–C7	–105.93 (17)

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

Table 2

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>
N2–H2 <i>B</i> ...O3	0.95	1.78	2.725 (2)	174
N2–H2 <i>A</i> ...O5 ⁱⁱ	0.95	2.06	2.826 (3)	137
N2–H2 <i>A</i> ...O7 ⁱⁱⁱ	0.95	2.23	2.944 (2)	131
O5–H5 <i>A</i> ...O1 ^{iv}	0.95	1.95	2.895 (3)	174
O5–H5 <i>B</i> ...O6	0.95	1.88	2.830 (3)	176
O6–H6 <i>A</i> ...O3	0.95	1.88	2.833 (3)	177
O6–H6 <i>B</i> ...O7 ^v	0.95	1.84	2.761 (3)	162
O7–H7 <i>A</i> ...O2	0.95	1.85	2.797 (2)	174
O7–H7 <i>B</i> ...O2 ⁱⁱ	0.95	1.81	2.733 (2)	164

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

H atoms were positioned geometrically, with O–H = 0.95 Å (for OH₂), N–H = 0.95 Å (for NH₂) and C–H = 0.95 Å for aromatic and methylene H atoms, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT-Plus (Bruker, 1998); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics:

SHELXTL (Sheldrick, 1998); software used to prepare material for publication: SHELXTL.

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