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Bis(benzimidazolium) diaquabis(pyridine-2,4-dicarboxylato-κ^2N,O)manganese(II) dihydrate

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The asymmetric unit of the title compound, $(C_7H_7N_2)_2[Mn(C_7H_3O_4N)_2(H_2O)_2]\cdot 2H_2O$, contains one half-anion, one cation and one uncoordinated water molecule. The Mn^{II} atom, lying on a centre of symmetry, is coordinated in a distorted octahedral arrangement by two O atoms and two N atoms of two pyridine-2,4-dicarboxylate and two O atoms of two aqua ligands. In the crystal structure, intermolecular O—H⋯O and N—H⋯O hydrogen bonds and π–π interactions link the molecules into a three-dimensional supramolecular framework.

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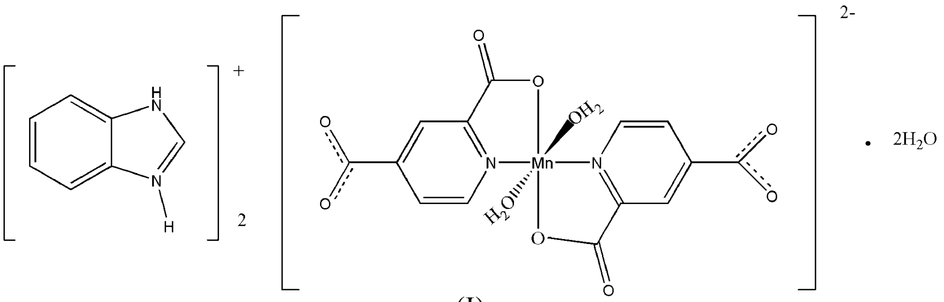
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.129
Data-to-parameter ratio = 14.5

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

Comment

Utilizing hydrogen-bonding and other noncovalent interactions has proven to be a commonly used strategy in constructing supramolecular frameworks, owing to their relative strength, directionality and biological relevance (Fyfe & Stoddart, 1999; Roesky & Andruh, 2003). We here report the crystal structure of the title compound, (I).



(I)

In the structure of (I) (Fig. 1), the bond lengths and angles (Table 1) are generally within normal ranges (Allen *et al.*, 1987). The formula unit consists of one monomeric $[Mn(pdc)_2(H_2O)_2]^{2-}$ (where pdc is pyridine-2,4-dicarboxylate) anion, two protonated benzimidazole cations and two

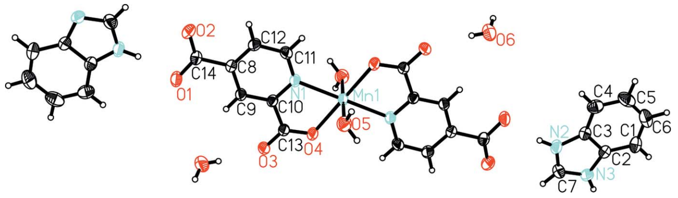


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator $(1 - x, 1 - y, 2 - z)$.

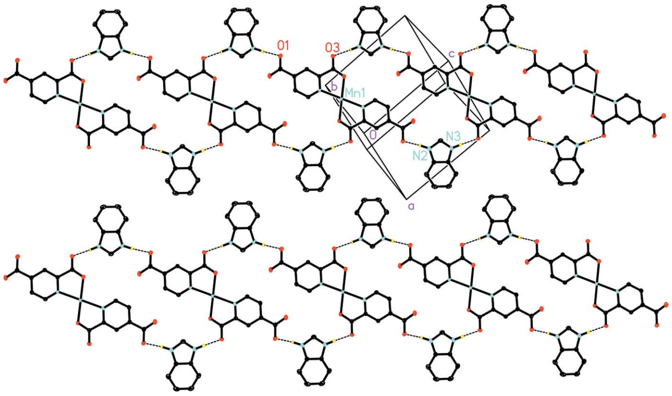


Figure 2
Ribbons in one layer; H atoms on C atoms and water molecules have been omitted for clarity. Dashed lines indicate hydrogen bonds.

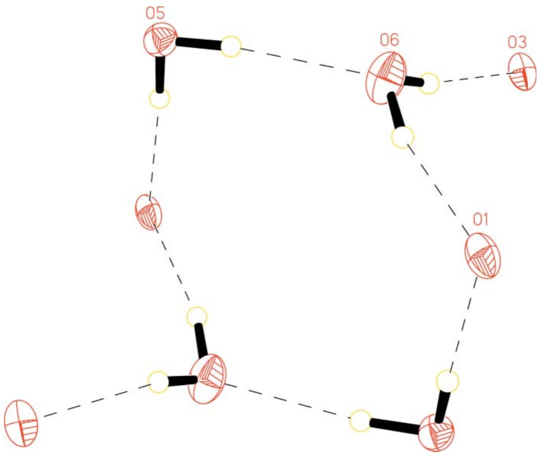


Figure 3
The armchair O_8 configuration isolated from the three-dimensional network of (I).

water molecules. The asymmetric unit contains one half-anion, one cation and one water molecule.

The Mn atom, lying on a centre of symmetry, is coordinated by two O and two N atoms from two chelating pdc ligands, and two O atoms from two aqua ligands, forming a distorted octahedral geometry. This kind of coordination mode of the pdc ligand has been reported in other transition metal pdc complexes (Noro *et al.*, 2002, 2005). The octahedral environment of the the Mn centre is highly distorted, owing to the *N*,*O*-chelation of the rigid pdc ligand (Table 1), with the *cis* angles [75.73 (7)–104.26 (07)°] deviating significantly from the ideal value of 90°.

As shown in Fig. 2, Mn^{II} complex anions and protonated benzimidazole molecules are linked into ribbons by intermolecular $N—H\cdots O$ hydrogen bonds (Table 2), and the ribbons within one layer do not interact each other. However, one ribbon is linked to the ribbons in the layers above and below, by pairs of intermolecular $O—H\cdots O$ hydrogen bonds (Table 2). As shown in Fig. 3, the four O atoms ($O1^{i}$, $O3^{i}$, O5 and O6) and the symmetry-related atoms ($O1^{ii}$, $O3^{ii}$, $O5^{iii}$ and $O6^{iii}$) [symmetry codes (i) $1 + x, y, z$; (ii) $1 - x, 2 - y, 2 - z$; (iii) $-x, -y, -z$] constitute an armchair O_8 configuration. In the armchair O_8 configuration, two water dimers are linked by two carboxylate O atoms (O1 and $O1^{i}$) to constitute a chair conformation. The armchair units link layers, with the help of π–π interactions [as a result of the pyridine and benzimidazole rings in one layer not being strictly coplanar, there are three different types of π–π interactions: the face-to-face distance between benzimidazole rings is 3.304 (4) Å (symmetry code: $1 - x, y - 1, 1 - z$), between benzimidazole and pyridine rings is 3.369 (8) Å (symmetry code: $-x, -y, -z$), and between pyridine rings is 3.517 (2) Å [symmetry codes: ($-x, -y, -z$) and ($2 + x, y, z$)], resulting in a three-dimensional supramolecular structure, as shown in Fig. 4. Fig. 5 shows a packing diagram of (I) viewed along the *a* axis.

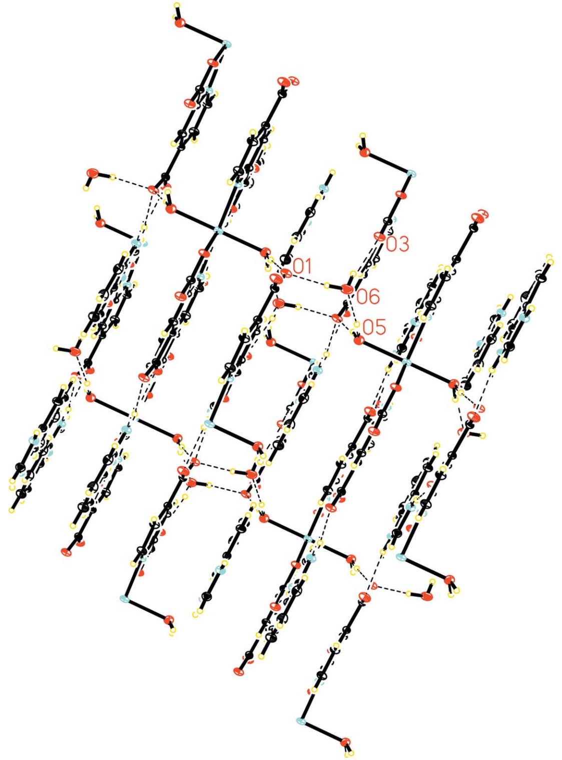


Figure 4
The layers linked by the armchair O_8 configuration.

Experimental

A mixture of $Mn(OAc)_2$ (245 mg, 1 mmol), H_2pdc (168 mg, 1 mmol), NaOH (80 mg, 2 mmol) and benzimidazole (236 mg, 2 mmol) in methanol–water (2:1 *v*/*v*, 15 ml) was heated at 428 K for 4 d, under autogenous pressure in a sealed Teflon-lined stainless steel vessel (20 ml), and then cooled to room temperature over a period of 2 h, yielding yellow crystals of compound (I) suitable for X-ray diffraction analysis.

Crystal data

$(C_7H_7N_2)_2[Mn(C_7H_3O_4N)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 695.50$
Triclinic, $P\overline{1}$
$a = 8.4882\ (18)$ Å
$b = 9.0617\ (19)$ Å
$c = 10.7716\ (19)$ Å
$\alpha = 96.539\ (6)^\circ$
$\beta = 101.032\ (6)^\circ$
$\gamma = 111.508\ (5)^\circ$
$V = 741.1\ (3)$ Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.52$ mm^{-1}
$T = 294\ (2)$ K
0.25 × 0.20 × 0.10 mm

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Data collection

Bruker P4 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.882$, $T_{\max} = 0.949$
5758 measured reflections
3336 independent reflections
2518 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
Standard reflections: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.129$
$S = 1.01$
3336 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O4	2.1534 (17)	C13—O4	1.263 (3)
Mn1—N1	2.235 (2)	C14—O2	1.232 (3)
Mn1—O5	2.243 (2)	C14—O1	1.281 (3)
C13—O3	1.255 (3)		
O4—Mn1—N1	75.73 (7)	N1—Mn1—O5	90.88 (8)
O4—Mn1—O5	91.45 (8)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1$^{\rm i}$	0.86	1.86	2.705 (3)	167
N3—H1*A*···O3$^{\rm iv}$	0.86	1.86	2.713 (3)	174
O5—H5*C*···O1$^{\rm i}$	0.93 (4)	1.83 (4)	2.751 (3)	174 (3)
O5—H5*B*···O6	0.87 (4)	1.90 (4)	2.767 (4)	173 (4)
O6—H6*B*···O3$^{\rm i}$	0.74 (5)	2.07 (5)	2.797 (3)	169 (5)
O6—H6*C*···O1$^{\rm ii}$	0.90 (5)	2.04 (5)	2.927 (4)	168 (4)

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

H atoms of water molecules were located in difference syntheses and refined isotropically [O—H = 0.74 (5)–0.93 (4) Å and $U_{\rm iso}$(H) = 0.070 (12)–0.103 (18) Å^2]. The remaining H atoms were positioned geometrically with N—H = 0.86 Å and C—H = 0.93 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N).

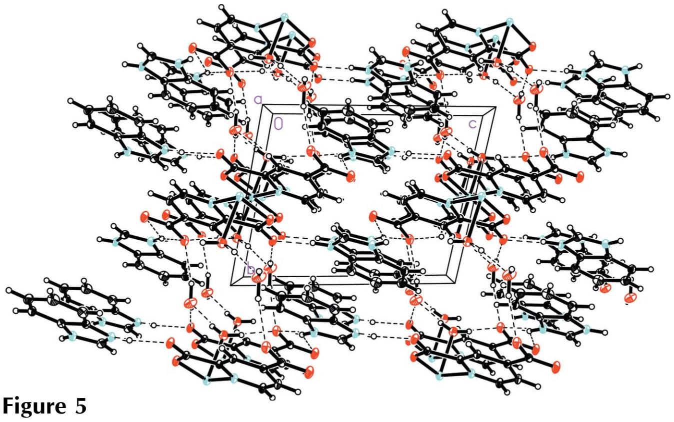

Figure 5
A packing diagram of (I) viewed down the *a* axis. Dashed lines indicate hydrogen bonds.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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