

Aqua(dipicolinato- κ^3O,N,O')(1*H*-imidazole- κN^3)(1,10-phenanthroline-*N,N'*)manganese(II)

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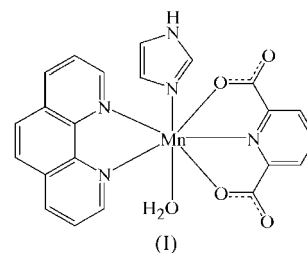
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In the title compound, $[\text{Mn}(\text{C}_7\text{H}_3\text{NO}_4)(\text{C}_3\text{H}_4\text{N}_2)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$, the Mn^{II} centre is surrounded by one bidentate phenanthroline ligand [$\text{Mn}-\text{N} = 2.383(3)$ and $2.421(3)$ Å], one tridentate dipicolinate ligand [$\text{Mn}-\text{N} = 2.300(3)$ Å, and $\text{Mn}-\text{O} = 2.300(2)$ and $2.357(2)$ Å], one monodentate imidazole ligand [$\text{Mn}-\text{N} = 2.238(3)$ Å] and one water molecule [$\text{Mn}-\text{O} = 2.157(3)$ Å]. It displays a distorted pentagonal-bipyramidal geometry, with neighbouring angles within the equatorial plane ranging from $68.05(9)$ to $77.48(10)^\circ$. Intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules into infinite chains. The chains are crosslinked by hydrogen bonds involving the carboxyl O atoms of the dipicolinate ligand and the protonated imidazole N atom, leading to an infinite two-dimensional network sheet packing mode. The complete solid-state structure can be described as a three-dimensional supramolecular framework, stabilized by these intermolecular hydrogen-bonding interactions and $\pi-\pi$ stacking interactions involving the phenanthroline rings.

Comment

Manganese-containing small molecular compounds play an important role in the active sites of various redox-based enzymes (Weighardt, 1989). In addition to the best known oxygen-evolving complex, which is believed to contain a tetranuclear manganese cluster catalyzing the oxidation of water to yield O_2 during photosynthesis (Debus, 1992), there are three enzymes containing a mononuclear Mn site, *viz.* superoxide dismutase, peroxidase and dioxygenase, which participate in the redox changes of biological systems (Law *et al.*, 1999). On the basis of the knowledge that the coordination environment of the Mn centres in these enzymes is dominated by *N,O*-donors from available amino acid residues (Pecoraro & Butler, 1986), *N,O*-containing ligands are often employed to prepare model compounds for the better understanding of their exact nature and mechanism of action. In the course of our study on manganese biochemistry, we have selected

dipicolinic acid as the primary ligand, in combination with some *N*-donor ancillary ligands, such as imidazole and α,α' -diimine, to react with Mn^{2+} salts. Dipicolinates often ligate to transition metals *via* carboxylate bridges between metal centres, forming extended polymeric complexes. We have utilized some α,α' -diimines, such as 2,2'-bipyridine, which strongly favour bidentate chelation coordination, to cleave the carboxylate bridges of manganese dipicolinate polymeric complexes, and successfully isolated a trinuclear and a mononuclear oligomer as model compounds (Ma *et al.*, 2003). In the present work, reaction of disodium dipicolinate and 1,10-phenanthroline with manganese acetate in the presence of imidazole led to the isolation of yellow crystals of the title compound, (I), which represents a new interesting example of a mononuclear manganese complex with four peripheral ligands.



Compound (I) (Fig. 1) consists of neutral $[\text{Mn}(\text{dpc})(\text{Him})(\text{phen})(\text{H}_2\text{O})]$ monomers (dpc is dipicolinate, Him is imidazole and phen is 1,10-phenanthroline), lying in a crystallographic general position. The coordination environment around the Mn^{II} ion is a distorted pentagonal bipyramid, where two O atoms (O1 and O3) and one N atom (N1) from the tridentate dipicolinate ligand and two N atoms (N2 and N3) from the bidentate chelating phenanthroline ligand define the pentagonal equatorial plane, with atom Mn1 lying $0.019(3)$ Å out of the plane. The phen ligand is reasonably planar, with a mean deviation of $0.030(9)$ Å, and bond distances and angles are consistent with those in the free base (Nishigaki *et al.*, 1978). All atoms in the dpc ligand are also nearly coplanar, with a maximum deviation of $0.160(1)$ Å for

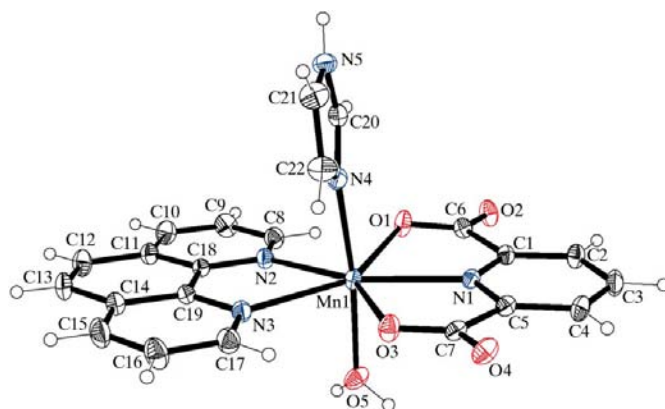


Figure 1
A view of the molecule of (I), showing the atomic labelling scheme and 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

atom O4. A very small dihedral angle of $3.00(1)^\circ$ was observed between the phen and pdc ligand planes, indicating that the pdc plane can be extended to involve atoms N2 and N3 (the phen and pdc ligands are nearly coplanar). The water O atom (O5) and one imidazole N atom (N4) complete the pentagonal bipyramid through coordination in the axial positions, with an $O5-Mn1-N4$ angle of $170.22(12)^\circ$.

The high-spin d^5 Mn^{2+} ion usually favours the formation of the octahedral d^2sp^3 hybrid orbital instead of the pentagonal-bipyramidal coordination involving the d^3sp^3 hybrid orbital. Several seven-coordinate Mn^{II} complexes are observed with a quinquedentate ligand, such as 15-crown-5 (Reid *et al.*, 1999; Lin *et al.*, 2006), which serves to define a pentagonal plane on the equator and leaves two axial positions open for further coordination to give a regular pentagonal bipyramid. The combination of nearly coplanar phen and pdc ligands [the mean deviation is just $0.095(1)^\circ$] in (I) perfectly functions as a

pseudo-quinquedentate ligand, thus giving a new rare example of a pentagonal bipyramid. However, the pentagonal-bipyramidal geometry is very distorted (Table 1). This is mainly caused by the double chelation by the two rigid planar ligands, *i.e.* phen and pdc.

The $Mn-N(\text{phen})$, $Mn-O(\text{pdc})$, $Mn-N(\text{pdc})$ and $Mn-O(\text{water})$ bond lengths in (I) are all somewhat longer than those found in the six-coordinate $[Mn(\text{pdc})(\text{phen})(\text{H}_2\text{O})]$ complex reported previously (Ma *et al.*, 2002). This may be because of the larger steric strain of (I) with the presence of more ligands. The $Mn-N(\text{Him})$ distance of $2.238(3) \text{ \AA}$ is in agreement with distances reported in another seven-coordinate complex, *viz.* $[Mn(\text{pdc})(\text{Him})_2(\text{bipy})]\cdot\text{H}_2\text{O}$ [$2.248(5)$ and $2.240(5) \text{ \AA}$; Ma *et al.*, 2003].

As listed in Table 2, three intermolecular hydrogen bonds are observed in the crystal structure. The coordinated water molecule (O5) donates its H atoms to two uncoordinated

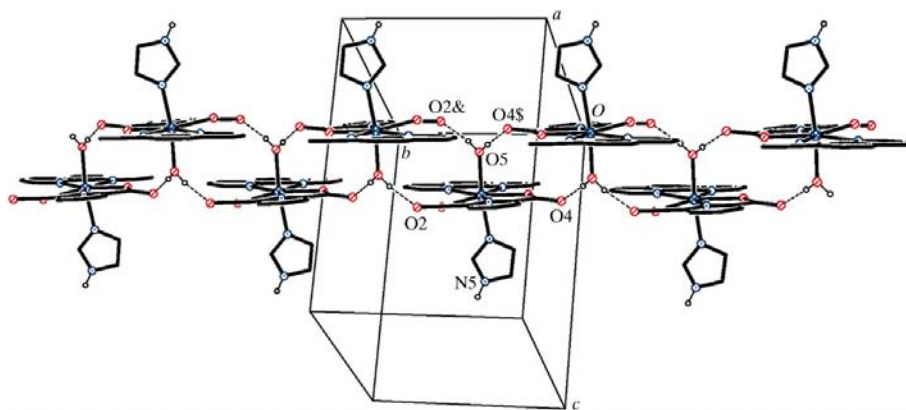


Figure 2

A packing diagram for (I), showing part of the one-dimensional hydrogen-bonded network. Atoms labelled with a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(-x + 2, -y, -z + 1)$ and $(-x + 2, -y + 1, -z + 1)$, respectively.

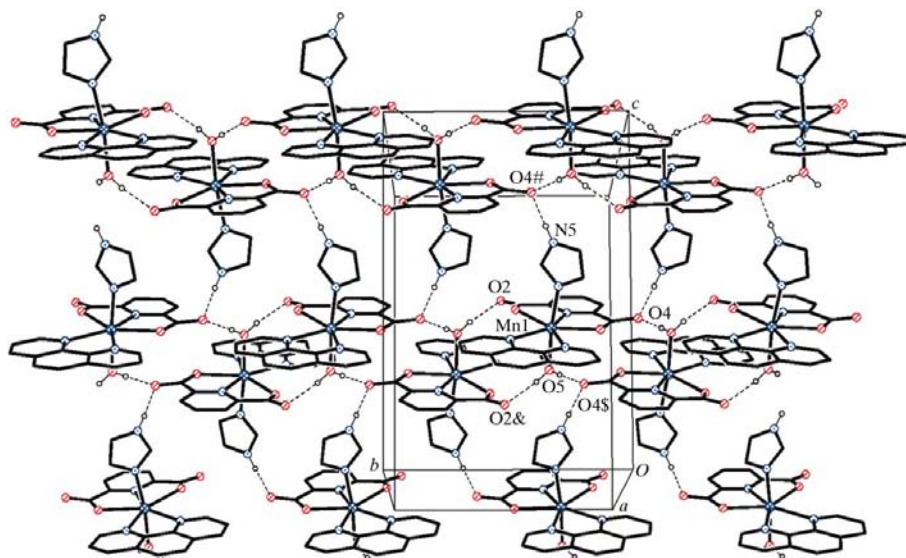
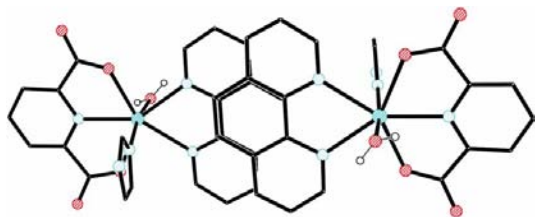
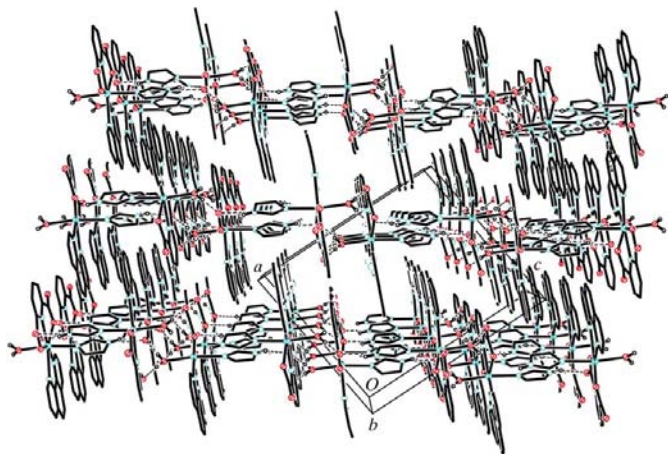


Figure 3

A packing diagram for (I), showing part of the two-dimensional hydrogen-bonded network derived from crosslinkage of the one-dimensional chains *via* $N5-H5A \cdots O4\#$ hydrogen bonds. Atoms labelled with a dollar sign (\$), an ampersand (&) or a hash (#) are at the symmetry positions $(-x + 2, -y, -z + 1)$, $(-x + 2, -y + 1, -z + 1)$ and $(-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2})$, respectively.


Figure 4

A view of the π - π stacking interactions in (I), showing a significant overlap between the C11–C14/C19/C18 benzene ring of the phen ligand with the parallel ring at the symmetry position ($-x + 1, -y + 1, -z + 1$).


Figure 5

A partial packing diagram of (I), showing the formation of the three-dimensional supramolecular framework. Hydrogen bonds are depicted as dashed lines.

carboxyl O atoms (O2 and O4) of symmetry-related molecules to generate infinite one-dimensional chains with the Him ligands located on both sides of the chain (Fig. 2). Neighbouring chains are further crosslinked by N5–H5A...O4($-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$) hydrogen bonds, formed by the protonated imidazole N atom and the carboxy O atom of a symmetry-related chain, thus resulting in the formation of an infinite two-dimensional hydrogen-bonded network sheet with the phen ligands located above and below the sheet, as shown in Fig. 3. These two-dimensional hydrogen-bonded sheets are further packed into an overall three-dimensional supramolecular framework *via* partial π - π stacking interactions between the phen ligands (Figs. 4 and 5), with perpendicular ring separations of 3.447 (1) Å between the closest benzene rings (C11–C14/C19/C18), which are comparable to the sum of the van der Waals contact radii for two C atoms (3.4 Å; Bondi, 1964). These intermolecular interactions together with other van der Waals interactions stabilize the whole solid-state structure of the title compound.

Experimental

Dipicolinic acid (1 mmol), dissolved in water (15 ml), was neutralized with sodium hydroxide (2 mmol) and added in portions to a hot methanol (15 ml) solution containing manganese acetate tetrahydrate (1 mmol), 1,10-phenanthroline (1 mmol) and imidazole (1 mmol) with continuous stirring. The mixture was refluxed for 1 h and then filtered. The yellow filtrate was allowed to stand undisturbed

for about one week at room temperature, during which time yellow crystals of (I) suitable for X-ray diffraction analysis were deposited. Analysis calculated for $C_{22}H_{17}MnN_5O_5$: C 54.33, H 3.52, N 14.40%; found C 54.42, H 3.55, N 14.44%. FT-IR (KBr, cm^{-1}): 3262 (s), 2923 (m), 2844 (m), 1611 (vs), 1587 (s), 1512 (w), 1496 (m), 1465 (w), 1440 (s), 1380 (vs), 1346 (m), 1282 (s), 1205 (w), 1178 (w), 1143 (w), 1101 (m), 1075 (m), 1046 (w), 1016 (w), 944 (m), 920 (w), 884 (w), 850 (s), 775 (s), 698 (w), 666 (s), 628 (w), 525 (w), 474 (m), 435 (m), 417 (w).

Crystal data

$[Mn(C_7H_3NO_4)(C_3H_4N_2)(C_{12}H_8N_2)(H_2O)]$	$\beta = 97.151 (1)^\circ$
$M_r = 486.35$	$V = 2058.19 (9) \text{ \AA}^3$
Monoclinic, $P2_1/n$	$Z = 4$
$a = 12.9514 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.4900 (2) \text{ \AA}$	$\mu = 0.69 \text{ mm}^{-1}$
$c = 15.2681 (5) \text{ \AA}$	$T = 295 (2) \text{ K}$
	$0.49 \times 0.42 \times 0.40 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	7067 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3631 independent reflections
$T_{min} = 0.720, T_{max} = 0.765$	2703 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.128$	$\Delta\rho_{max} = 0.35 \text{ e \AA}^{-3}$
$S = 1.00$	$\Delta\rho_{min} = -0.39 \text{ e \AA}^{-3}$
3631 reflections	
306 parameters	
2 restraints	

Table 1

Selected geometric parameters (Å, °).

Mn1–O5	2.157 (3)	Mn1–O3	2.357 (2)
Mn1–N4	2.238 (3)	Mn1–N2	2.383 (3)
Mn1–O1	2.300 (2)	Mn1–N3	2.421 (3)
Mn1–N1	2.300 (3)		
O5–Mn1–N4	170.22 (12)	N4–Mn1–N2	94.26 (10)
O5–Mn1–O1	98.30 (11)	O1–Mn1–N2	77.33 (9)
N4–Mn1–O1	91.32 (11)	N1–Mn1–N2	145.10 (10)
O5–Mn1–N1	90.82 (11)	O3–Mn1–N2	146.54 (10)
N4–Mn1–N1	94.31 (10)	O5–Mn1–N3	87.65 (11)
O1–Mn1–N1	68.70 (9)	N4–Mn1–N3	83.40 (10)
O5–Mn1–O3	89.72 (10)	O1–Mn1–N3	145.54 (10)
N4–Mn1–O3	84.51 (10)	N1–Mn1–N3	145.50 (10)
O1–Mn1–O3	136.06 (9)	O3–Mn1–N3	77.48 (10)
N1–Mn1–O3	68.05 (9)	N2–Mn1–N3	69.19 (10)
O5–Mn1–N2	86.21 (10)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5–H5A...O4 ⁱ	0.86	1.91	2.745 (4)	162
O5–H5B...O4 ⁱⁱ	0.84 (2)	1.87 (2)	2.711 (4)	177 (4)
O5–H5C...O2 ⁱⁱⁱ	0.84 (2)	1.88 (2)	2.716 (4)	171 (5)

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

Water H atoms were located from difference maps and refined with a DFIX (Sheldrick, 1997) restraint of 0.85 (2) Å applied to the O–H distances. Aromatic H atoms were placed in calculated positions, with C–H distances of 0.93 Å and an N–H distance of 0.86 Å, and treated as riding atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1994); data reduction: *XPREP* (Siemens, 1994); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3161). Services for accessing these data are described at the back of the journal.

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