

[2-(2-Pyridyl)-1*H*-benzimidazole- κ^2N^2,N^3]bis(*p*-toluate- κ^2O,O')-manganese(II)

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Received 3 October 2007

Accepted 31 October 2007

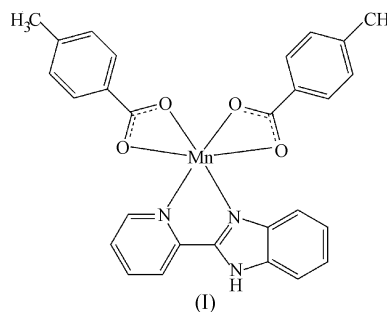
Online 30 November 2007

In the title compound, $[\text{Mn}(\text{C}_8\text{H}_7\text{O}_2)_2(\text{C}_{12}\text{H}_9\text{N}_3)]$, the manganese(II) centre is surrounded by three bidentate chelating ligands, namely, one 2-(2-pyridyl)benzimidazole ligand [$\text{Mn}-\text{N} = 2.1954(13)$ and $2.2595(14)$ Å] and two *p*-toluate ligands [$\text{Mn}-\text{O} = 2.1559(13)$ – $2.2748(14)$ Å]. It displays a severely distorted octahedral geometry, with *cis* angles ranging from $58.87(4)$ to $106.49(5)^\circ$. Intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds between the *p*-toluate ligands link the molecules into infinite chains, and every two neighbouring chains are further coupled by $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds between the 2-(2-pyridyl)benzimidazole and *p*-toluate ligands, leading to an infinite ribbon-like double-chain packing mode. The complete solid-state structure can be described as a three-dimensional supramolecular framework, stabilized by these intermolecular hydrogen-bonding interactions and possible $\text{C}-\text{H}\cdots\pi$ interactions, as well as stacking interactions involving the 2-(2-pyridyl)benzimidazole ligands.

Comment

Low molecular weight manganese carboxylate species play an important role at the active sites of various redox-based enzymes (Weighardt, 1989). Mn superoxide dismutase, Mn peroxidase and Mn dioxygenase are each believed to contain a mononuclear Mn site, which participates in the redox changes of biological systems (Law *et al.*, 1999). X-ray crystallography reveals that the peripheral ligation around the Mn centre in these enzymes includes both carboxylate groups in various binding modes and the imidazole rings from various amino acid residues (Pecoraro & Butler, 1986), suggesting that changes in the carboxylate binding mode may be important to the action of these enzymes (Rardin *et al.*, 1991). Carboxyl- and imidazole-containing molecules are often employed to prepare simple models for the active sites of these enzymes. Understanding the structural effects of imidazole ligation to the Mn centre and the different carboxylate binding modes in these models will undoubtedly be helpful in gaining insight

into the structural aspects that may influence the mechanism of action of the enzyme active sites. As far as we are aware, for the great majority of six-coordinate Mn complexes with carboxylate ligation, the number of carboxylate ligands acting as a chelating ligand usually remains low so as to avoid (or reduce) the strain from small-angle chelation (the chelation angle is usually less than 60°), and thus far reports of mononuclear complexes with more than two carboxylate ligands chelating an octahedral Mn centre have been rare (Jha & Mishra, 1986; Chai *et al.*, 2004; Moubaraki *et al.*, 2003). In the present paper, we report the structure of the title compound, (I), which is a rare example of a mononuclear manganese complex with three chelating ligands, including a pair of chelating carboxylate ligands and a third chelating imidazole-containing ligand, simultaneously in the coordination environment. A mononuclear seven-coordinate Mn^{II} complex with a similar chelating ligand situation has recently been reported (Viossat *et al.*, 2003).



Compound (I) consists of neutral $[\text{Mn}(\text{ptl})_2(\text{pybim})]$ monomers [ptl is *p*-toluate and pybim is 2-(2-pyridyl)benzimidazole] lying in a crystallographic general position. The Mn^{II} atom is coordinated to one bidentate chelating pybim ligand *via* atoms N1 and N2, and to a pair of anionic bidentate chelating ptl ligands *via* atoms O1, O2, O3 and O4, as shown in Fig. 1. The complex displays a highly distorted octahedral

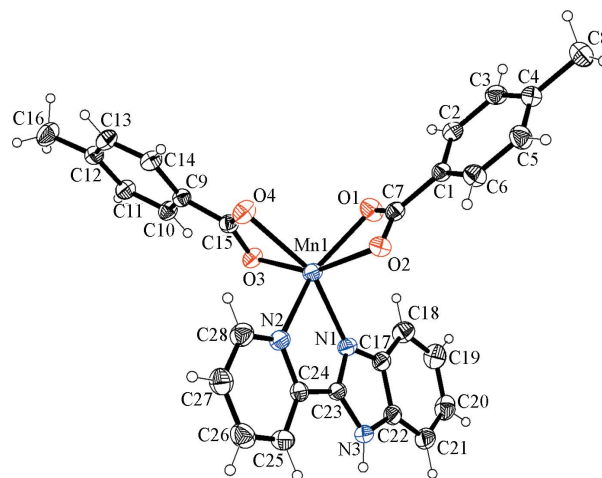


Figure 1

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.

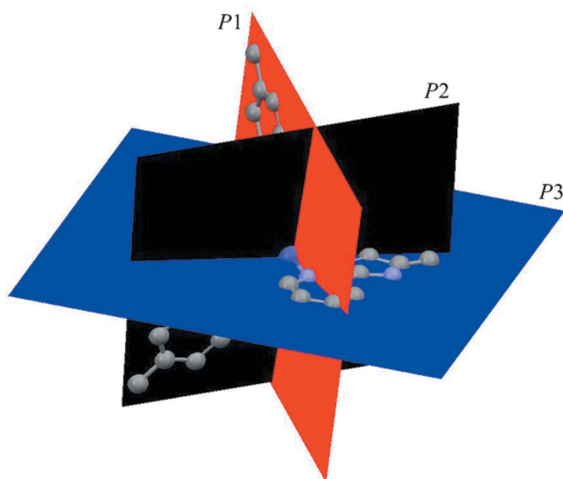


Figure 2

A view of (I), showing the coplanarity of the central metal atom with each of the ligands and the approximately perpendicular interpenetration of the mean planes.

geometry around the Mn centre (Table 1), in which three O atoms (O1, O2 and O3) of the tpl ligands and one pyridyl N atom (N2) of the pybim ligand define the equatorial plane, with atom Mn1 displaced from the least-squares O1–O3/N2 plane by 0.163 (2) Å. Imidazole atom N1 of the pybim ligand and atom O4 of the tpl ligand complete the distorted octahedron through coordination in the axial positions, with an N1–Mn1–O4 angle of 155.83 (5)°.

The Mn–N distances and N–Mn–N pybim chelate angle (Table 1) are comparable to those observed in the only reported pybim-containing Mn^{II} complex, viz. [Mn₃(AcO)₆(pybim)₂] [Ac is acetyl; 2.197 (2) and 2.394 (2) Å, and 72.72 (6)°, respectively; Tangoulis *et al.*, 1996]. The Mn–N(imidazole) distance in both compounds, perceptibly shorter than the Mn–N(pyridine) distance, indicates that the imidazole N atom of the pybim ligand is a stronger donor, since the benzene group in the *ortho* position enhances the electron density on this N atom. The Mn–O distances and O–Mn–O carboxylate chelate angles are as expected for Mn^{II} complexes with a similar coordination environment (Chai *et al.*, 2004; Moubaraki *et al.*, 2003; Viossat *et al.*, 2003; Baumeister & Hartung 1997; Jha & Mishra, 1986).

The two chelate ring planes formed by the ptl ligands, viz. O1/C7/O2/Mn1 and O3/C15/O4/Mn1, with a maximum out-of-plane deviation of 0.027 (1) Å for atom C7, are each almost coplanar with the respective attached methylphenyl planes [C1–C6/C8 and C9–C14/C16, respectively], as indicated by the small dihedral angles of 7.9 (6) and 3.4 (1)°, respectively. The pybim ligand and the pybim chelate ring (N1/C23/C24/N2/Mn1) are each reasonably planar, with a maximum out-of-plane deviation of 0.096 (6) Å for atom H28A and a very small dihedral angle of 3.3 (1)° observed between them, suggesting that the pybim plane can be extended to involve atom Mn1. The three Mn1-containing mean planes, denoted P1 (C1–C8/O1/O2/Mn1), P2 (C9–C16/O3/O4/Mn1) and P3 (C17–C28/N1–N3/Mn1), with maximum out-of-plane deviations of 0.137 (6) Å for atom O1, 0.062 (1) Å for C10 and 0.085 (9) Å for Mn1, respectively, make P1/P2, P3/P1 and P3/P2 dihedral angles of 87.2 (2), 83.8 (6) and 71.0 (4)°, respectively, indicating the approximate perpendicularity of these planes to one another (Fig. 2).

The high-spin d^5 Mn²⁺ ion usually favours the formation of the octahedral d^2sp^3 hybrid orbital, with *cis* angles equal to 90°. The chelating carboxylate group usually gives a narrow bite of less than 60° at the central Mn atom, thus resulting in the distortion of the coordination environment, and the higher the number of chelating carboxylate groups, the more distorted the central metal coordination environment and the more unstable the complex in keeping an octahedral coordination. Thus far, mononuclear Mn complexes with more than two chelating carboxylate groups have therefore rarely been encountered. The strong distortion deviating from an ideal Mn octahedron in (I), with the *cis* angles subtended at the Mn atom ranging from 58.87 (4) to 106.49 (5)°, is obviously due to the triple narrow bite of the three chelating ligands. The title compound provides a rare example of a six-coordinate Mn compound with an added *N,N'*-chelating ligand besides two chelating carboxylate ligations, though several similar complexes are found to

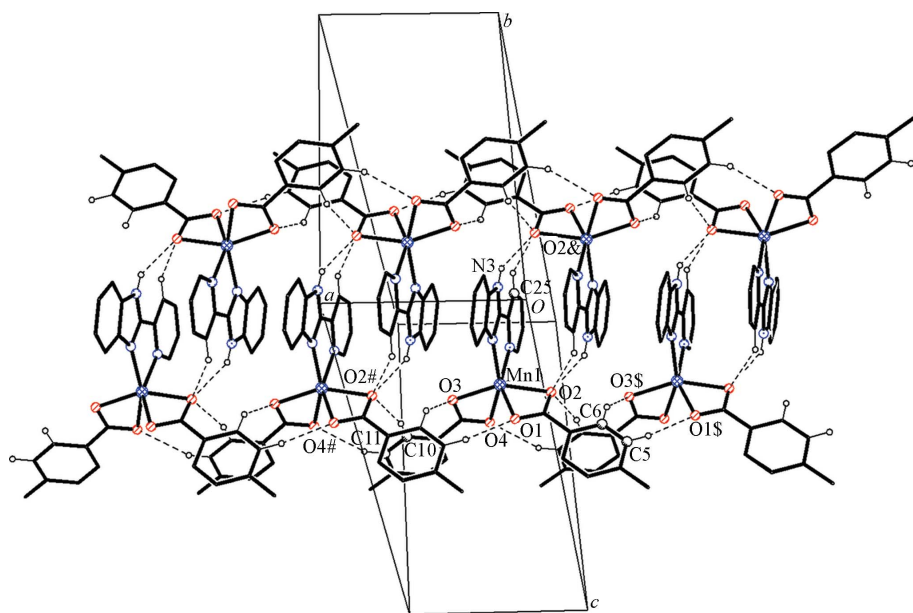


Figure 3

A packing diagram for (I), showing part of the one-dimensional hydrogen-bonded ribbon-shaped double-chain network. Atoms labelled with a dollar sign (\$), a hash (#) or an ampersand (&) are at the symmetry positions ($x - 1, y, z$), ($x + 1, y, z$) and ($-x, -y + 1, -z + 1$), respectively. H atoms not involved in the hydrogen bonding have been omitted.

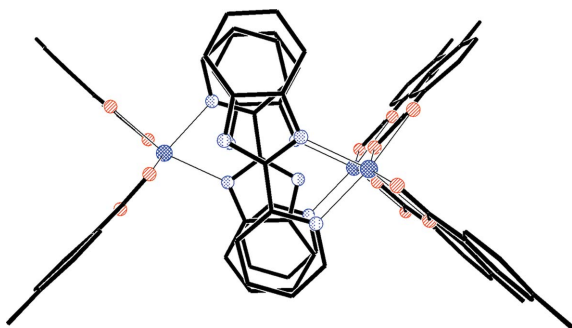


Figure 4
A view of the partial π - π stacking interactions between the pyridine rings of the pybim ligands in (I).

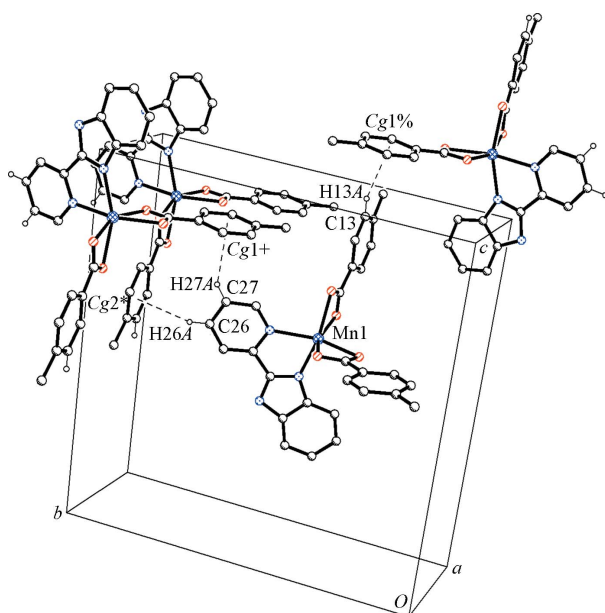


Figure 5
A partial packing diagram of (I), showing the three symmetry-independent C-H... π interactions. The π -ring centroids (Cg1 and Cg2) labelled with a percent sign (%), an asterisk (*) or a plus sign (+) are at the symmetry positions $(1+x, \frac{1}{2}-y, \frac{1}{2}+z)$, $(1-x, -\frac{1}{2}+y, \frac{1}{2}-z)$ and $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$, respectively. Cg1 denotes the centroid of the C1-C6 ring and Cg2 denotes the centroid of the C9-C14 ring. H atoms not involved in C-H... π interactions have been omitted.

have two added monodentate ligands in a more regular octahedral Mn coordination (Jha & Mishra, 1986; Chai *et al.*, 2004; Moubaraki *et al.*, 2003). Two seven-coordinate complexes with a di- or mononuclear Mn centre have also been previously reported to possess a similar chelating ligand set, in which the central Mn coordination environments are approximately described as distorted capped octahedra (Viostat *et al.*, 2003; Baumeister & Hartung, 1997).

As listed in Table 2, one normal intermolecular N-H...O hydrogen bond and five nonclassical intermolecular C-H...O hydrogen bonds are observed in the crystal structure. Four benzene C atoms (C5, C6, C10 and C11) in one molecule donate their H atoms to the carboxyl O atoms (O1, O3, O2 and O4, respectively) of two symmetry-related molecules to

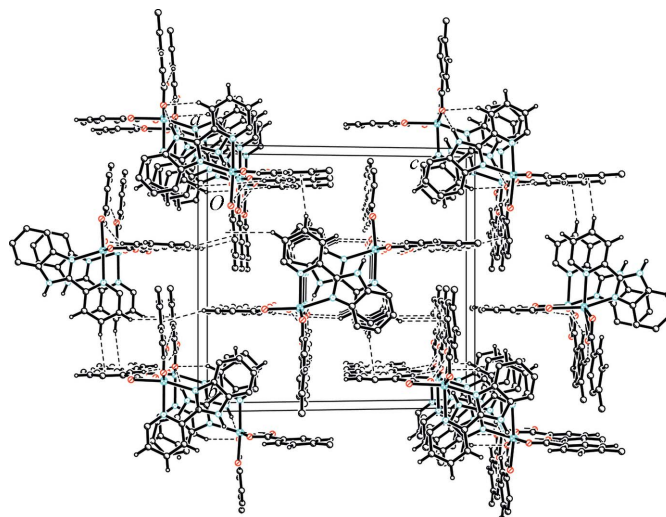


Figure 6
A partial packing diagram of (I), showing the formation of the three-dimensional supramolecular framework. Hydrogen-bonding and C-H... π interactions are depicted as dashed lines. H atoms not involved in the intermolecular interactions have been omitted for clarity.

generate infinite one-dimensional chains with the pybim ligands located at the same side of the chain (Fig. 3). Two molecules of neighbouring chains are further coupled *via* an N3-H3B...O2ⁱ [symmetry code: (i) $-x, -y+1, -z+1$] hydrogen bond and a fifth weak C25-H25A...O2ⁱ hydrogen bond to generate a centrosymmetric dimer (Fig. 3), thus resulting in the formation of an infinite hydrogen-bonded ribbon-shaped double-chain network (Fig. 3). All the pybim ligands are located within the region of the hydrogen-bonded ribbon network, in which a normal and a weaker π - π stacking interaction (3.4 Å; Bondi, 1964) between inversion-related pybim ligands are observed (Fig. 4), with perpendicular pybim plane separations of 3.498 (4) and 3.669 (7) Å, respectively.

Three C-H... π interactions, with H...Cg distances of less than 3 Å (Cg is the centroid of the π ring) and γ less than 30° (γ is the angle formed by the H...Cg vector and the normal to the π -ring plane) (Spek, 2003) are also observed within the structure of (I) (Table 2). These C-H... π interactions link the monomer to adjacent symmetry-related monomers (Fig. 5) and complete an overall three-dimensional supramolecular network (Fig. 6). These intermolecular interactions together with numerous other van der Waals contacts ensure the solid-state crystalline cohesion of the title compound.

Experimental

2-(2-Pyridyl)benzimidazole (1 mmol) dissolved in ethanol (15 ml) was added dropwise to an ethanol-dimethylformamide solution (30 ml, *ca* 1:1 *v/v*) containing manganese *p*-toluate tetrahydrate (1 mmol), with continuous stirring. The mixture was refluxed for 1 h and then filtered. The yellow filtrate was allowed to stand undisturbed for several weeks at room temperature, during which time yellow crystals of (I) suitable for X-ray diffraction analysis were deposited. Analysis calculated for $C_{28}H_{23}MnN_3O_4$: C 64.62, H 4.45, N 8.07%; found C 64.47, H 4.55, N 8.11%. FT-IR (KBr, cm^{-1}): 3066 (*m*),

2922 (*w*), 1618 (*s*), 1587 (*s*), 1520 (*vs*), 1412 (*vs*), 1311 (*m*), 1299 (*m*), 1194 (*m*), 1058 (*w*), 980 (*m*), 863 (*s*), 787 (*m*), 774 (*s*), 746 (*s*), 622 (*s*), 544 (*w*), 486 (*w*).

Crystal data

[Mn(C₈H₇O₂)₂(C₁₂H₉N₃)]
 $M_r = 520.43$
 Monoclinic, $P2_1/c$
 $a = 7.582$ (2) Å
 $b = 17.482$ (5) Å
 $c = 18.731$ (5) Å
 $\beta = 100.368$ (4)°
 $V = 2442.3$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.58$ mm⁻¹
 $T = 295$ (2) K
 $0.46 \times 0.42 \times 0.20$ mm

Data collection

Rigaku Mercury CCD
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.760$, $T_{\max} = 0.890$
 18797 measured reflections
 5561 independent reflections
 4584 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.105$
 $S = 1.00$
 5561 reflections
 331 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.30$ e Å⁻³

H atoms on phenyl/pyridyl rings and methyl groups were placed in calculated positions, with C—H distances of 0.93 and 0.96 Å, respectively, and were included in the final cycles of refinement as riding [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{C})$, respectively]. The H atom on the imidazole N atom was located from difference maps and refined isotropically.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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* and *PLATON* (Spek, 2003).

This work was supported by the NNSFC (grant Nos. 20471061 and 20633020) and the Fujian Province Youth Foundation (grant No. 2005 J059).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3169). Services for accessing these data are described at the back of the journal.

Table 1

Selected geometric parameters (Å, °).

Mn1—O3	2.1559 (13)	Mn1—O2	2.2370 (13)
Mn1—N1	2.1954 (13)	Mn1—N2	2.2595 (14)
Mn1—O1	2.2268 (13)	Mn1—O4	2.2748 (14)
O3—Mn1—N1	102.06 (5)	O1—Mn1—N2	152.00 (5)
O3—Mn1—O1	101.12 (4)	O2—Mn1—N2	93.35 (5)
N1—Mn1—O1	104.44 (5)	O3—Mn1—O4	59.32 (4)
O3—Mn1—O2	154.21 (4)	N1—Mn1—O4	155.83 (5)
N1—Mn1—O2	98.99 (4)	O1—Mn1—O4	94.87 (5)
O1—Mn1—O2	58.87 (4)	O2—Mn1—O4	103.43 (4)
O3—Mn1—N2	106.49 (5)	N2—Mn1—O4	95.17 (5)
N1—Mn1—N2	74.45 (5)		

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are defined in the caption to Fig. 5.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3B $\cdots$ O2 ⁱ	0.88 (2)	2.18 (2)	2.9882 (19)	153.3 (18)
C5—H5A $\cdots$ O1 ⁱⁱ	0.93	2.57	3.442 (2)	157
C6—H6A $\cdots$ O3 ⁱⁱ	0.93	2.42	3.196 (2)	141
C10—H10A $\cdots$ O2 ⁱⁱⁱ	0.93	2.44	3.345 (2)	166
C11—H11A $\cdots$ O4 ⁱⁱⁱ	0.93	2.54	3.426 (2)	158
C25—H25A $\cdots$ O2 ⁱ	0.93	2.55	3.351 (2)	145
C13—H13A $\cdots$ Cg1 ^{iv}	0.93	2.90	3.794 (1)	163
C26—H26A $\cdots$ Cg2 ^v	0.93	2.79	3.654 (3)	155
C27—H27A $\cdots$ Cg1 ^{vi}	0.93	2.91	3.712 (1)	145

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

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