

**(6-Oxido-2-oxo-1,2-dihydro-
pyrimidine-5-carboxylato- κ^2O^5,O^6)-
bis[2-(2-pyridyl)-1H-benzimidazole-
 κ^2N^2,N^3]manganese(II) monohydrate**Cheng-Bing Ma, Hui Chen, Ming-Qiang Hu and
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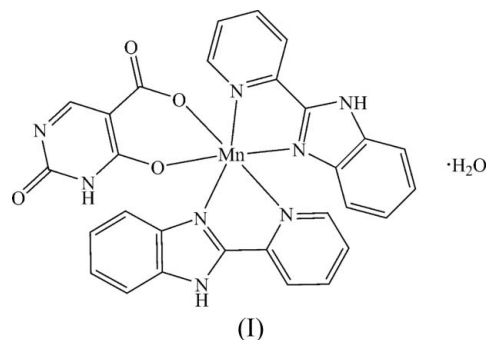
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In the title compound, $[\text{Mn}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{C}_{12}\text{H}_9\text{N}_3)_2]\cdot\text{H}_2\text{O}$, the Mn^{II} centre is surrounded by three bidentate chelating ligands, namely, one 6-oxido-2-oxo-1,2-dihydropyrimidine-5-carboxylate (or uracil-5-carboxylate, Huca^{2-}) ligand [$\text{Mn}-\text{O} = 2.136(2)$ and $2.156(3)$ Å] and two 2-(2-pyridyl)-1H-benzimidazole (Hpybim) ligands [$\text{Mn}-\text{N} = 2.213(3)$ – $2.331(3)$ Å], and it displays a severely distorted octahedral geometry, with *cis* angles ranging from $73.05(10)$ to $105.77(10)^\circ$. Inter-molecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds both between the Hpybim and the Huca^{2-} ligands and between the Huca^{2-} ligands link the molecules into infinite chains. The lattice water molecule acts as a hydrogen-bond donor to form double $\text{O}\cdots\text{H}-\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with the Huca^{2-} O atoms, crosslinking the chains to afford an infinite two-dimensional sheet; a third hydrogen bond ($\text{N}-\text{H}\cdots\text{O}$) formed by the water molecule as a hydrogen-bond acceptor and a Hpybim N atom further links these sheets to yield a three-dimensional supramolecular framework. Possible partial $\pi-\pi$ stacking interactions involving the Hpybim rings are also observed in the crystal structure.

Comment

Manganese-containing small molecular species have been found to play an important role at the active sites of several redox-based enzymes (Weighardt, 1989). The peripheral ligation around the Mn centre(s) in these enzymes is believed to include both the carboxy and/or phenol hydroxy groups and the imidazole ring from various amino acid residues, affording a predominant N/O coordination sphere (Pecoraro & Butler, 1986). Simple carboxylate-, phenoxide- and imidazole-containing molecules are often used in place of the peptide side chains in preparing molecular models of the active sites of these enzymes. Uracil-5-carboxylic acid (H_3uca) (also named

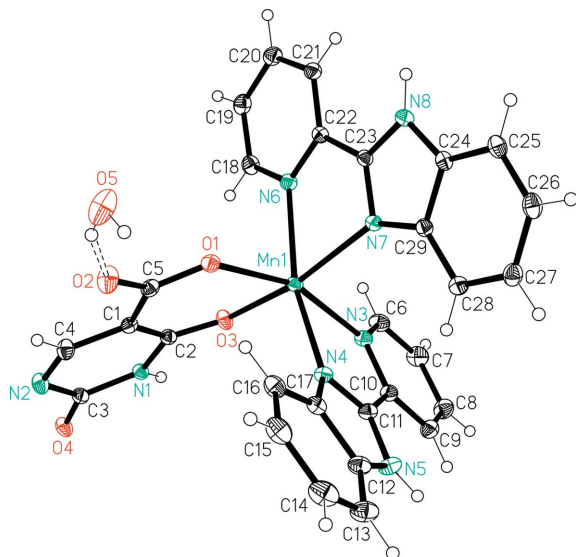
2,4-dihydropyrimidine-5-carboxylic acid), which possesses a biologically important pyrimidine heterocycle bearing both one carboxy group and two hydroxy groups, could display diverse coordination modes to metal ions through the carboxy O atoms, the hydroxy O atoms and the pyrimidine N atoms, either independently or simultaneously.



As part of our study of manganese biochemistry, we have investigated manganese complexation by uracil-5-carboxylic acid. α,α' -Diimine molecules strongly favouring bidentate chelation coordination, such as 2,2'-bipyridine and 2-(2-pyridyl)-1H-benzimidazole (Hpybim), are introduced to prevent the formation of uracil-5-carboxylic acid-bridging manganese polymeric complexes, and thus small molecular manganese compounds are expected. In the present work, the reaction of disodium uracil-5-carboxylic acid with manganese acetate in the presence of Hpybim affords pale-yellow crystals of the title compound, (I), which represents a rare example of a mononuclear six-coordinate transition metal complex with mixed ligands including uracil-5-carboxylic acid, though several eight-coordinate lanthanide complexes with a similar mixed-ligand system have been reported recently (Xiong *et al.*, 2008; Sun & Jin, 2004; Xing *et al.*, 2008; Liu *et al.*, 2009).

Compound (I) consists of one neutral $[\text{Mn}(\text{Huca})(\text{Hpybim})_2]$ monomer and one solvent water molecule, all in general positions in the asymmetric unit. The Mn^{II} atom is surrounded by three bidentate chelating ligands, coordinated *via* four N atoms (N3, N4, N6 and N7) from a pair of neutral Hpybim ligands, and *via* two O atoms (O1 and O3) from one dianionic Huca^{2-} ligand, as shown in Fig. 1. The complex displays a severely distorted octahedral geometry around the Mn centre (Table 1), in which three N atoms (N4, N6 and N7) of the Hpybim ligands and the phenolate O atom (O3) of the Huca^{2-} ligand define a best octahedral equatorial plane [the mean out-of-plane deviation is $0.027(5)$ Å and the maximum out-of-plane deviation of $0.030(7)$ Å is for atom N7], with the Mn atom displaced from the plane by $0.053(5)$ Å. The pyridyl N atom (N3) of the Hpybim ligand and one carboxylate O atom (O1) of the Huca^{2-} ligand complete the distorted octahedron through coordination in the axial positions, with an $\text{O1}-\text{Mn1}-\text{N3}$ angle of $160.52(9)^\circ$.

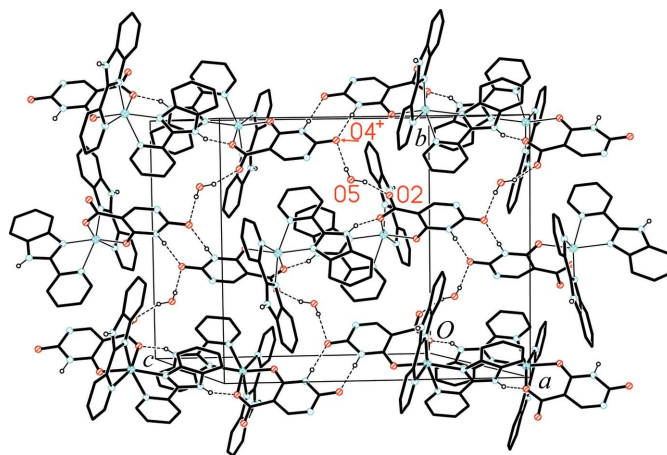
The high-spin d^5 Mn^{2+} ion favours the formation of octahedral d^2sp^3 hybrid orbitals, with *cis* angles of 90° . The rigid chelating Hpybim ligand usually gives a narrow bite of less than 75° at a central Mn atom. The strong distortion from an ideal Mn octahedron in (I), with the *cis* angles ranging from


Figure 1

A view of the molecule of (I), showing the atom-labelling scheme and 20% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

73.05 (10) to 105.77 (10)°, is obviously due to the double chelation of the two Hpybim ligands. The average Mn–N distance [2.28 (5) Å] and the N–Mn–N chelate angles [74.34 (11) and 73.05 (10)°] are comparable with those observed in the reported pybim-containing monomeric Mn^{II} complex [Mn(ptl)₂(Hpybim)] [ptl is *p*-toluate; 2.2274 (19) Å and 74.45 (5)°, respectively; Ma *et al.*, 2007] and, as expected, the Mn–N(imidazole) distances in (I) are shorter than the Mn–N(pyridine) distances, since the benzene group in the *ortho* position enhances the electron density on the imidazole N atom. Two Hpybim ligands are each reasonably planar, with maximum out-of-plane deviations of 0.107 (2) and 0.146 (3) Å for atoms H14A and H27A, respectively. A very small dihedral angle of 4.2 (1)° is observed between the N3-containing Hpybim ligand plane and the chelate plane N3/N4/Mn1. However, the other Hpybim ligand makes a larger dihedral angle [16.9 (1)°] with its chelate plane N6/N7/Mn1.

The Huca²⁻ dianion in (I) acts as a bidentate ligand to chelate to the Mn atom through one carboxylate O atom and the phenolate O atom; the second carboxylate O atom and the carbonyl O atom in the 2-position, as well as the two pyrimidine N atoms, are uncoordinated. Difference-map plots unequivocally located the lone ring H atom as being bonded to N1, between atoms O3 and O4. The position of the protonated N atom differs from that found in [Mn(Huca)(H₂O)₂]_n (Chen *et al.*, 2007), where the H atom is clearly established as being bonded to the other ring N atom. The Mn–O distances (Table 1) and the O3–Mn–O1 chelate angle of 84.07 (9)° are comparable to those observed in [Mn(H₂uca)₂] (Maistralis *et al.*, 1991) and [Mn(Huca)(H₂O)₂]_n (Chen *et al.*, 2007). The Huca²⁻ ligand is also reasonably planar, with a maximum out-of-plane deviation of 0.101 (5) Å for atom O4. The ligand plane is folded with respect to the O1/O3/Mn1 chelate plane, at an angle of 16.0 (1)°.


Figure 2

A packing diagram for (I), showing part of the two-dimensional hydrogen-bonded network derived from the crosslinkage of the one-dimensional chains hydrogen-bonded via O5–H5A···O2 and O5–H5B···O4. The atom labelled with a plus sign (+) is at the symmetry position $(x, -y + \frac{1}{2}, z + \frac{1}{2})$.

As shown in Fig. 2, with details in Table 2, extensive intermolecular hydrogen bonding produces a three-dimensional hydrogen-bonded framework. The uncoordinated imidazole N8–H8 group of the Hpybim ligand donates the H atom to carboxylate atom O1 of the molecule related by the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (see Fig. S1 in the *Supplementary material*). Similarly, the protonated N1–H1 group of the Huca²⁻ ligand donates atom H1 to uncoordinated carbonyl atom O4 of the molecule related by the inversion centre at $(\frac{1}{2}, \frac{1}{2}, 0)$ to yield a one-dimensional chain extending in the *c* direction (Fig. S2 in the *Supplementary material*). The lattice water molecule (O5) connects to three [Mn(Huca)(Hpybim)₂] monomers (Table 2, and Fig. S3 in the *Supplementary material*), to complete the three-dimensional hydrogen-bonded framework. There are, in addition, two types of partial π – π stacking interactions between inversion-related pybim ligands. The centroid–centroid separations are 3.705 (3) Å between the N3/C6–C10 rings at (x, y, z) and $(-x, 1 - y, -z)$, and 3.797 (3) Å between the N6/C18–C22 ring at (x, y, z) and the C24–C29 ring at $(1 - x, 1 - y, 1 - z)$.

Experimental

To a hot water–dimethylformamide (15 ml, *ca* 2:1 *v/v*) solution containing uracil-5-carboxylic acid (0.5 mmol), sodium hydroxide (1.0 mmol) and 2-(2-pyridyl)-1*H*-benzimidazole (1.0 mmol), solid manganese acetate tetrahydrate (0.5 mmol) was added in portions with continuous stirring. The mixture was refluxed for 30 min and then filtered to remove the precipitate. The light-yellow filtrate was allowed to stand undisturbed for approximately one month at room temperature, during which time pale-yellow crystals of (I) suitable for X-ray diffraction analysis were deposited in *ca* 30% yield. Analysis calculated for C₂₉H₂₂MnN₈O₅: C 56.41, H 3.59, N 18.15%; found C 56.50, H 3.51, N 18.24%. FT–IR (KBr, cm⁻¹): 3467 (*vs, br*), 2022 (*w*), 1622 (*vs*), 1538 (*m*), 1455 (*w*), 1441 (*w*), 1385 (*s*), 1320 (*w*), 1300 (*s*), 1231 (*w*), 1208 (*w*), 1183 (*w*), 1150 (*w*), 1050 (*w*), 994 (*w*), 976 (*w*), 898 (*w*), 849 (*w*), 811 (*m*), 751 (*s*), 647 (*s*), 582 (*w*), 501 (*m*), 431 (*w*), 406 (*w*).

Crystal data

$[\text{Mn}(\text{C}_5\text{H}_2\text{N}_2\text{O}_4)(\text{C}_{12}\text{H}_9\text{N}_3)_2]\cdot\text{H}_2\text{O}$	$V = 2720 (3) \text{ \AA}^3$
$M_r = 617.49$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.915 (6) \text{ \AA}$	$\mu = 0.54 \text{ mm}^{-1}$
$b = 15.42 (1) \text{ \AA}$	$T = 293 \text{ K}$
$c = 17.972 (12) \text{ \AA}$	$0.20 \times 0.12 \times 0.05 \text{ mm}$
$\beta = 115.945 (2)^\circ$	

Data collection

Rigaku Mercury CCD diffractometer	20068 measured reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)	6139 independent reflections
$T_{\min} = 0.910$, $T_{\max} = 0.981$	4436 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$	388 parameters
$wR(F^2) = 0.182$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
6139 reflections	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

The aromatic H atoms were placed in calculated positions, with C—H distances of 0.93 Å and N—H distances of 0.86 Å, and treated as riding atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or N})$]. The locations of the water H atoms were not well defined in difference maps; the O—H distances were normalized at 0.85 Å and then allowed for as riding atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *CrystalClear* (Rigaku/MS, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Table 1

Selected bond lengths (Å).

Mn1—O3	2.136 (2)	Mn1—N7	2.256 (3)
Mn1—O1	2.156 (3)	Mn1—N3	2.319 (3)
Mn1—N4	2.213 (3)	Mn1—N6	2.331 (3)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O4 ⁱ	0.86	2.00	2.830 (4)	160
N5—H5 \cdots O5 ⁱⁱ	0.86	1.89	2.722 (4)	162
N8—H8A \cdots O1 ⁱⁱⁱ	0.86	1.98	2.793 (4)	158
O5—H5A \cdots O2	0.85	1.88	2.675 (4)	154
O5—H5B \cdots O4 ^{iv}	0.85	2.12	2.959 (4)	169

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3213). Services for accessing these data are described at the back of the journal.

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