

Poly[[bis(pyridin-3-ol)manganese(II)]-
di- μ -pyridin-3-olato]

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Received 4 January 2005

Accepted 11 January 2005

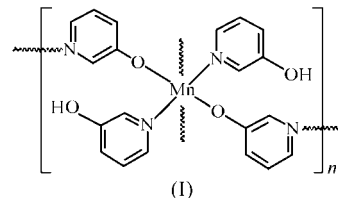
Online 19 February 2005

In the title complex, $[\text{Mn}(\text{C}_5\text{H}_4\text{NO})_2(\text{C}_5\text{H}_5\text{NO})_2]_n$ or $[\text{Mn}(\mu\text{-3-PyO})_2(3\text{-PyOH})_2]_n$ (3-PyO⁻ is the pyridin-3-olate anion and 3-PyOH is pyridin-3-ol), the Mn^{II} atom lies on an inversion centre and has octahedral geometry, defined by two N atoms and two deprotonated exocyclic O atoms of symmetry-related pyridin-3-olate ligands [$\text{Mn}-\text{N} = 2.3559$ (14) Å and $\text{Mn}-\text{O} = 2.1703$ (11) Å], as well as two N atoms of terminal 3-PyOH ligands [$\text{Mn}-\text{N} = 2.3482$ (13) Å]. The Mn^{II} atoms are bridged by the deprotonated pyridin-3-olate anion into a layer structure, generating sheets in the (101) plane. These sheets are linked by O—H...O hydrogen bonds. There are also $\pi-\pi$ and C—H... π interactions in the crystal structure.

Comment

Molecular self-assembly of coordination architecture has been a rapidly developing research area within supramolecular chemistry in recent years (Liu *et al.*, 2003). The choice of ligand is an important factor since it greatly influences the structure of the coordination architecture and the functionality of the complex formed. Bifunctional hydroxypyridine (PyOH) molecules, including the 2-PyOH, 3-PyOH and 4-PyOH isomers, are good candidates for the construction of supramolecular systems which are not only capable of binding to metal centres but can also form regular hydrogen bonds by functioning as both hydrogen-bond donors and acceptors (Breeze & Wang, 1993). Among the isomers of PyOH molecules, 2- or 4-PyOH exhibit tautomerization to their pyridone isomers, *viz.* 2- or 4-pyridone (Yang & Craven, 1998; Wheeler & Ammon, 1974; Trikoupi *et al.*, 2002). For example, 4-PyOH would be expected to coordinate, if at all, through the pyridone O atom, which has only weak donor properties because the N atom is protonated (Gao *et al.*, 2004; Lu *et al.*, 2004), whereas 3-PyOH does not have the corresponding tautomeric form, *viz.* '3-pyridone', and so is a true hydroxypyridine (Flakus *et al.*, 2003). Therefore, 3-PyOH is able to construct high-dimensional coordination polymers, in contrast with 2- or 4-PyOH. To date, only two such extended structures of Cu^{II} coordination polymers by means of covalent bonds have been

reported, namely $[\text{Cu}(3\text{-PyO-N,O})_2(3\text{-PyOH})(\text{H}_2\text{O})]_n$ (chain; Castillo *et al.*, 2000) and $[\text{Cu}(3\text{-PyOH})_2(\text{O}_2\text{CCF}_3)_2]_n$ (layer; Kawata *et al.*, 1997). As a contribution to this study, we report here the structure of the title novel two-dimensional manganese(II) coordination polymer, $[\text{Mn}(\mu\text{-3-PyO-N,O})_2(3\text{-PyOH})_2]_n$ (I).



As shown in Fig. 1, the asymmetric unit of (I) is composed of one Mn^{II} atom, one neutral 3-PyOH molecule and one deprotonated pyridin-3-onate anion. The Mn^{II} atom lies on an inversion centre [chosen for convenience to be at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$] and is six-coordinated by two N atoms and two deprotonated exocyclic O atoms of symmetry-related pyridin-3-olate ligands, as well as by two N atoms of the terminal 3-PyOH molecules. The Mn1—N1 bond is slightly shorter than the Mn1—N2ⁱ(3-PyO⁻) bond (Table 1) and the Mn1—O2ⁱⁱ bond is shorter than the Mn—N bonds.

Compound (I) has a two-dimensional layer structure (Figs. 2a and 2b) with sheets in the (101) plane; the shortest Mn...Mn separation is 7.4156 (15) Å [*e.g.* between Mn1 at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and (0, 0, 0)]. In contrast, in the reported one-dimensional copper(II) polymer $[\text{Cu}(3\text{-PyO-N,O})_2(3\text{-PyOH})(\text{H}_2\text{O})]_n$ (Castillo *et al.*, 2000), the Cu^{II} atoms are bridged by the deprotonated pyridin-3-olate anion, producing a one-dimensional chain with a Cu...Cu separation of 7.03 Å, while

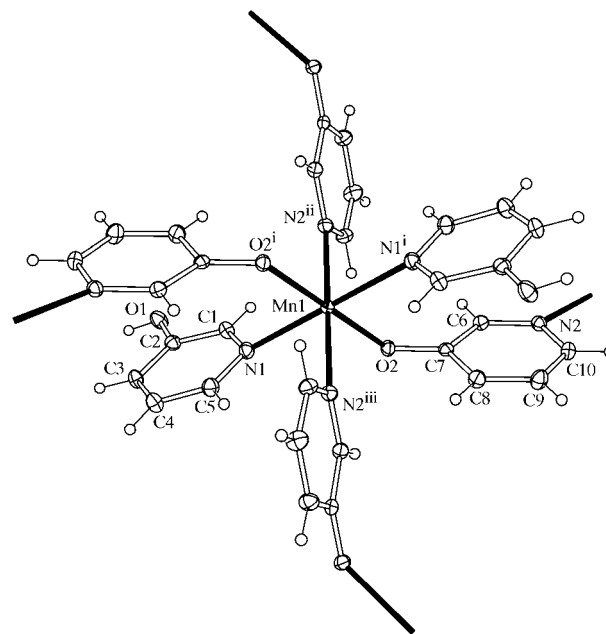


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $\frac{3}{2}-x, y+\frac{1}{2}, \frac{3}{2}-z$.]

in the reported two-dimensional copper(II) polymer [Cu(3-PyOH)₂(O₂CCF₃)₂]_n (Kawata *et al.*, 1997), the Cu centres are linked by neutral 3-hydroxypyridine ligands, with a shortest Cu...Cu separation of 7.23 Å.

The sheets of (I) are linked by O—H...O hydrogen bonds (Table 2) between the neutral 3-PyOH hydroxy group (O1—H1) and a screw-axis-related deprotonated phenolate O2 atom. In addition to these strong hydrogen bonds, there are also π–π interactions between the neutral and symmetry-related deprotonated 3-PyOH ligands. The centroid–centroid separation between the N1/C1–C5 ring at (x, y, z) and the N2/C6–C10 ring at (1 – x, 1 – y, 1 – z) is 3.631 Å, with an interplanar angle of 19.25°. There is also a C—H...π interaction, *viz.* C5—H5...Cg2 (Table 2), where Cg2 is the centroid of the N2/C6–C10 ring at (x – ½, ½ – y, z – ½).

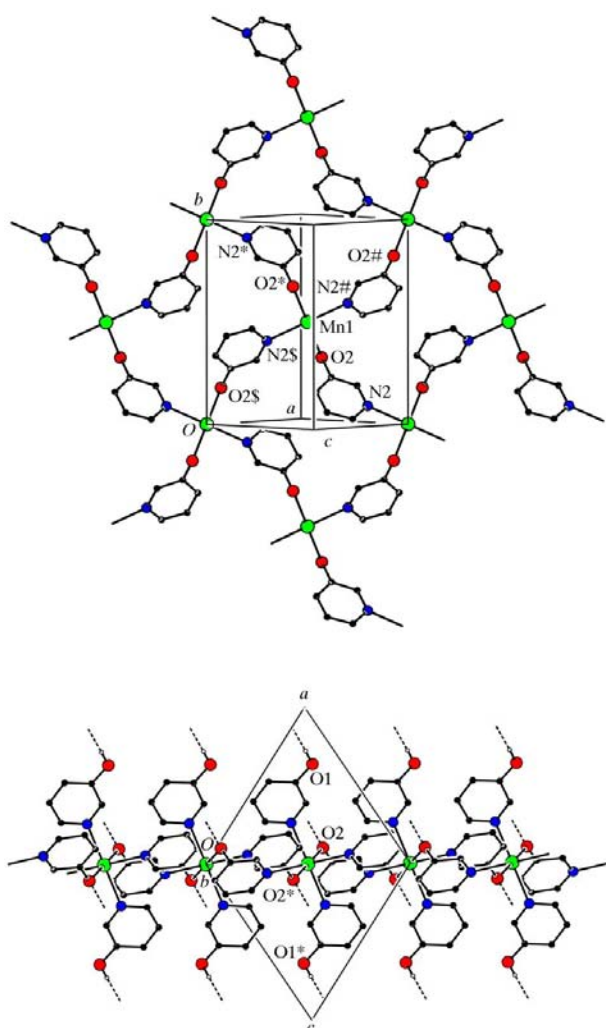


Figure 2
(a) A view of the two-dimensional framework of (I) in the (101) plane. The terminal 3-PyOH ligands and H atoms have been omitted for clarity. Atoms marked with an asterisk (*), hash (#) or dollar (\$) symbol are at the symmetry positions (1 – x, 1 – y, 1 – z), (½ – x, ½ + y, ½ – z) and (x – ½, ½ – y, z – ½), respectively. (b) An edge-on view of the two-dimensional sheet structure of (I), with the terminal 3-PyOH ligands included and showing the directions of the hydrogen bonds. Atoms marked with an asterisk (*) are at the symmetry position (1 – x, 1 – y, 1 – z).

Experimental

Complex (I) was synthesized by the addition of manganese diacetate tetrahydrate (10 mmol) to an aqueous solution of 3-hydroxypyridine (20 mmol). The solution was then allowed to evaporate at room temperature, and yellow crystals were obtained after several days. Analysis calculated for C₂₀H₁₈MnN₄O₄: C 55.44, H 4.19, N 12.93%; found: C 55.47, H 4.25, N 12.95%.

Crystal data

[Mn(C₅H₄NO)₂(C₅H₅NO)₂]
M_r = 433.32
Monoclinic, P2₁/n
a = 9.4512 (19) Å
b = 10.583 (2) Å
c = 9.5998 (19) Å
β = 113.90 (3)°
V = 877.9 (4) Å³
Z = 2

D_x = 1.639 Mg m⁻³
Mo Kα radiation
Cell parameters from 7874 reflections
θ = 3.0–27.5°
μ = 0.79 mm⁻¹
T = 296 (2) K
Prism, yellow
0.36 × 0.24 × 0.18 mm

Data collection

Rigaku R-Axis RAPID diffractometer
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
T_{min} = 0.764, T_{max} = 0.871
8483 measured reflections

2012 independent reflections
1870 reflections with I > 2σ(I)
R_{int} = 0.019
θ_{max} = 27.5°
h = -12 → 12
k = -13 → 13
l = -12 → 12

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.029
wR(F²) = 0.095
S = 1.04
2012 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F_o²) + (0.0688P)² + 0.2628P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.43 e Å⁻³
Δρ_{min} = -0.25 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Mn1–N1	2.3482 (13)	Mn1–O2 ⁱⁱ	2.1703 (11)
Mn1–N2 ⁱ	2.3559 (14)		
N1–Mn1–N2 ⁱ	91.98 (5)	O2–Mn1–N2 ⁱⁱⁱ	92.18 (4)
O2–Mn1–N1 ⁱⁱ	88.72 (4)		

Symmetry codes: (i) ½ – x, y + ½, ½ – z; (ii) 1 – x, 1 – y, 1 – z; (iii) x – ½, ½ – y, z – ½.

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

Cg2 is the centroid of the N2/C6–C10 ring.

D–H...A	D–H	H...A	D...A	D–H...A
O1–H11...O2 ^{iv}	0.85 (3)	1.78 (3)	2.621 (3)	176 (2)
C5–H5...Cg2 ⁱⁱⁱ	0.93	2.91	3.773 (2)	155

Symmetry codes: (iii) x – ½, ½ – y, z – ½; (iv) ½ – x, y + ½, ½ – z.

H atoms attached to C atoms were placed in calculated positions [C–H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)] using the riding-model approximation. Hydroxy atom H1 was located in a difference map and refined with an O–H distance restraint of 0.85 (1) Å and with U_{iso}(H) = 1.5U_{eq}(O).

Data collection: RAPID-AUTO (Rigaku, 1998); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MS, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick,

1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP II* (Johnson, 1976) and *PLATON* (Spek 2003); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Natural Science Foundation of China (grant No. 20101003), the Outstanding Teacher Foundation of Heilongjiang Province (grant No. 1054 G036) and Heilongjiang University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1807). Services for accessing these data are described at the back of the journal.

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