

catena-Poly[[chlorodipyridine-manganese(II)]- μ_3 -6-oxo-1,6-dihydropyridine-2-carboxylato]

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Received 16 November 2004

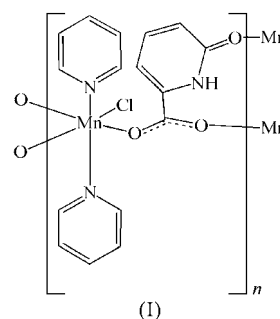
Accepted 24 January 2005

Online 28 February 2005

The title one-dimensional chain polymer complex, $[\text{Mn}(\text{C}_6\text{H}_4\text{NO}_3)\text{Cl}(\text{C}_6\text{H}_5\text{N})_2]_n$, was isolated from the reaction of MnCl_2 with 6-oxo-1,6-dihydropyridine-2-carboxylic acid (HpicOH) in pyridine. The asymmetric unit contains one $[\text{Mn}(\text{HPicO})\text{Cl}(\text{py})_2]$ moiety (py is pyridine), with the $(\text{HPicO})^-$ ligand acting in a tridentate manner *via* the two carboxylate O atoms and the pyridone O atom. The operation of inversion centres generates eight- and 14-membered rings and, in conjunction with an *a*-axis translation, leads to an infinite chain extending along $[100]$. The $\text{Mn}\cdots\text{Mn}$ separations in this chain are 5.1069 (6) and 7.1869 (6) Å. The Mn^{II} atom has a distorted octahedral coordination, with *trans*-axial pyridine ligands and with three O atoms and the Cl atom in the equatorial plane. The conformation of the 14-membered ring is stabilized by pairs of inversion-related $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.

Comment

Manganese is a special metal with a number of oxidation states (II–IV) under normal conditions, which results in many properties in naturally occurring processes and in magnetism, examples being the photosynthetic water-oxidizing complex (WOC) of green plants and cyanobacteria containing an Mn_4 unit (Law *et al.*, 1998; Yocum *et al.*, 1999), and the single-molecule magnets represented by Mn_{12} complexes, with slow-relaxation



magnetization and quantum tunnelling of magnetization (Sessoli *et al.*, 1993; Thomas *et al.*, 1996). Bridging carboxylates, which are a common feature of these complexes, are interesting ligands, both because of their ability to assume a large range of coordination modes and because of their biological relevance (Christou *et al.*, 1989; Wiegardt, 1989; Rardin *et al.*, 1991; Akhriff *et al.*, 1999). Low-dimensional extended structures (one-dimensional, chain-like) have attracted particular interest due to their specific structural features and unusual non-linear optical and magnetic properties (Chen *et al.*, 1993; Cox *et al.*, 1998; Monfort *et al.*, 2000; Matouzenko *et al.*, 2003). 2-Pyridone derivatives have been extensively studied since they cause base mispairing and enzymatic reactions related to bifunctional catalysis (Beak *et al.*, 1976), and show excellent pharmacodynamic properties, justifying the view that this is a very promising new class of totally synthetic antibacterial agents (Li *et al.*, 2000). In

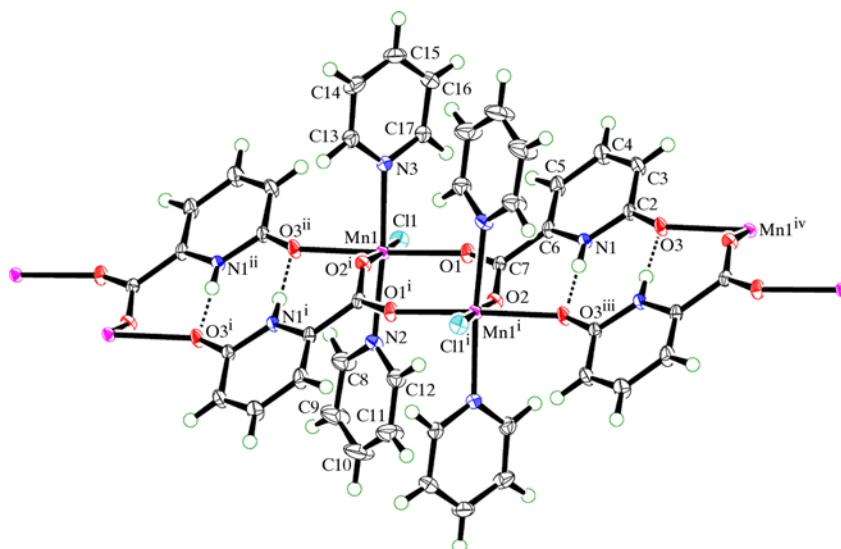


Figure 1

The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids, together with the $\text{N1}-\text{H1}\cdots\text{O3}$ hydrogen bonds. For clarity, the pyridine ligands are not shown. [Symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 + x, y, z$; (iii) $-x, -y, -z$; (iv) $x - 1, y, z$.]

contrast with organic compounds with 2-pyridone, only a few structures are known of coordination complexes with 2-pyridone ligands. Although 2-oxo-1,2-dihydropyridine-6-carboxylic acid (HpicOH) is a simple 2-pyridone derivative, only three dimer complexes have been reported to date, *viz.* with Re^{2+} (Chattopadhyay *et al.*, 2003), Gd^{3+} (Soares-Santos *et al.*, 2003) and Mn^{3+} ions (Bian *et al.*, 2004). We report here the title novel one-dimensional manganese(II) chain polymer complex, $[\text{MnCl}(\text{py})_2(\text{HpicO})]_n$ (py is pyridine), (I).

The asymmetric unit of (I) contains one $[\text{MnCl}(\text{py})_2(\text{HpicO})]$ moiety (Fig. 1). Each $(\text{HpicO})^-$ ligand acts in a tridentate manner *via* the two carboxylate O atoms and the pyridone O atom. The operation of the inversion centres at $(\frac{1}{2}, 0, 0)$ and $(0, 0, 0)$ generates eight- and 14-membered rings and, in conjunction with an *a*-axis translation, leads to an infinite chain extending along $[100]$. The $\text{Mn} \cdots \text{Mn}$ separations in this chain are 5.1069 (6) and 7.1869 (6) Å. The unique Mn^{II} atom (Fig. 1) has distorted octahedral coordination, with *trans*-axial pyridine ligands and with three O atoms and the Cl atom in the equatorial plane (see Table 1 for selected geometric details). The conformation of the 14-membered ring is stabilized by pairs of inversion-related $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 2).

In the crystal structure of (I), surprisingly, there are no significant $\pi-\pi$ interactions, but the $[100]$ chains are linked to form sheets in the (001) plane by a series of inversion-related $\text{C}-\text{H} \cdots \text{Cl}$ contacts (Table 2) centred about inversion centres at $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(1, \frac{1}{2}, 0)$, *etc.*, as shown in Fig. 2.

The observed temperature dependence of the magnetic susceptibility showed a monotonic increase of $\chi_M T$ from 2 to 300 K, indicating antiferromagnetic interaction between Mn^{II} ions. Although the magnetic properties of the double-chain

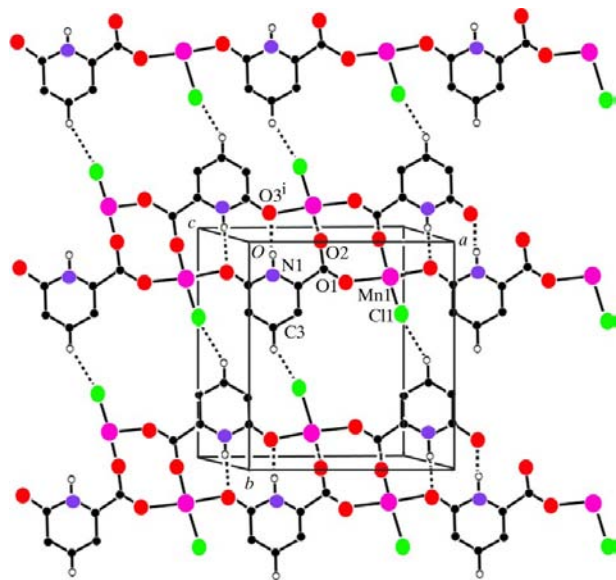


Figure 2

The two-dimensional molecular packing in (I) *via* $\text{C}-\text{H} \cdots \text{Cl}$ contacts between chains. [Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, 1-y, -z$.]

compound (I) should be analyzed using the alternating chain model (Fisher, 1964), we could not obtain a quantitative analysis due to inevitable contamination of (I) with impurities.

Experimental

To a solution of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ (65.0 mg, 0.4 mol) in pyridine (10 ml) was added HpicOH (55.8 mg, 0.4 mmol). The resulting green-brown solution was stirred for 6–7 h and hexane was added slowly. Colourless block-shaped crystals of (I) suitable for X-ray analysis were obtained after two weeks. Selected IR data (KBr pellet, ν , cm^{-1}): 3337 (*b*), 3104 (*w*), 3061 (*m*), 3039 (*w*), 3002 (*m*), 1602 (*s*), 1490 (*m*), 1446 (*s*), 1364 (*w*), 1221 (*m*), 1154 (*w*), 1081 (*m*), 1038 (*m*), 1008 (*m*), 754 (*s*), 694 (*s*), 629 (*m*), 421 (*m*).

Crystal data

$[\text{Mn}(\text{C}_6\text{H}_4\text{NO}_3)\text{Cl}(\text{C}_6\text{H}_5\text{N})_2]$
 $M_r = 386.70$
 Monoclinic, $P2_1/c$
 $a = 9.9034$ (10) Å
 $b = 10.9374$ (9) Å
 $c = 16.408$ (2) Å
 $\beta = 102.252$ (5)°
 $V = 1736.7$ (3) Å³
 $Z = 4$

$D_x = 1.479$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5361 reflections
 $\theta = 3.2-27.5^\circ$
 $\mu = 0.93$ mm⁻¹
 $T = 150.2$ K
 Prism, colourless
 $0.20 \times 0.10 \times 0.10$ mm

Data collection

Rigaku/MSC Mercury CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*REQAB*; Jacobson, 1998)
 $T_{\text{min}} = 0.823$, $T_{\text{max}} = 0.911$
 13 156 measured reflections

3925 independent reflections
 3530 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -13 \rightarrow 14$
 $l = -21 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.062$
 $S = 1.10$
 3530 reflections
 217 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 0.9672P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.33$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mn1—Cl1	2.4534 (4)	Mn1—N2	2.2629 (13)
Mn1—O1	2.1568 (11)	Mn1—N3	2.2790 (13)
Mn1—O2 ⁱ	2.2085 (10)	O3—C1	1.2704 (18)
Mn1—O3 ⁱⁱ	2.2212 (11)		
Cl1—Mn1—O2 ⁱ	176.73 (4)	N2—Mn1—N3	173.93 (5)
O1—Mn1—O3 ⁱⁱ	172.14 (4)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N1}-\text{H1} \cdots \text{O3}^{\text{iii}}$	0.83	2.01	2.8188 (15)	164
$\text{C3}-\text{H3} \cdots \text{Cl1}^{\text{iv}}$	0.95	2.72	3.5640 (17)	149

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

All H atoms were clearly revealed in difference maps and were subsequently allowed for in the correct sites as riding atoms in the

final refinement cycles, with C—H = 0.95 Å, N—H = 0.83 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *CrystalClear* (Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1797). Services for accessing these data are described at the back of the journal.

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