Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Poly[*trans*-diaquamanganese(II)-μ-(3-pyridinecarboxylato-*N*:*O*)-μ-(3-pyridinecarboxylato-*O*:*N*)]

Xiang Hao, Yong-Ge Wei, Qun Liu and Shi-Wei Zhang*

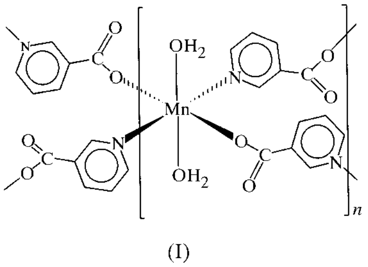
Department of Chemistry, Peking University, Beijing 100871, People's Republic of China
Correspondence e-mail: zsw@ipc.pku.edu.cn

Received 29 September 1999
Accepted 26 November 1999

The title complex, $[\mathrm{Mn^{II}(nic)_2(H_2O)_2}]_n$ [nic is 3-pyridinecarboxylate (also called nicotinate), $\mathrm{C_6H_4NO_2}^-$], has a two-dimensional layer structure with the unique Mn atom on an inversion centre. In each layer, all nicotinate ligands are coordinated to Mn atoms in a bridging/bidentate mode, thus linking the $\{\mathrm{Mn^{II}(nic)_2(H_2O)_2}\}$ monomeric units together to form a dative-bond-based layered polymer. The intra-layer hydrogen bonds involving all water molecules and the carboxylate groups may play an auxiliary part in stabilizing the layer. The layers are arranged in an ordered manner along the *a* axis through van der Waals forces so as to complete the solid-state structure of the crystal.

Comment

In recent years, polymer-based materials have received much attention owing to their novel magnetic properties (Manriquez *et al.*, 1991; Mallah *et al.*, 1993). The main preparation strategy adopted by most inorganic chemists is to assemble metal ions with multidentate ligands to form molecular-based inorganic polymers (Kahn, 1987, and references therein). These inorganic and organic hybrid materials, classified as Type II MMC (macromolecular metal complexes) according to Ciardelli, Tsuchida & Wöhrle's scheme, may exhibit properties of multifunctionality and processability (Ciardelli *et al.*, 1996). Following the strategy above, we have succeeded in isolating three crystals of Type II MMC: $\{[\mathrm{Mn(Hheidi)(H_2O)}]\cdot\mathrm{H_2O}\}_n$ [Hheidi is *N*-(2-hydroxyethyl)-iminodiacetate] (Liu *et al.*, 1999), $[\mathrm{Mn(pyz)_2(SCN)_2}]_n$ and $[\mathrm{Fe(pyz)_2(SCN)_2}]_n$ (pyz is pyrazine) (Wei *et al.*, 2000). Variable-temperature magnetic susceptibility studies revealed that the third complex could exhibit magnetic ordering phase transition at 7.7 K. In this paper, we report another polymeric complex of Type II MMC, *i.e.* $[\mathrm{Mn(nic)_2(H_2O)_2}]_n$, (I).



(I)

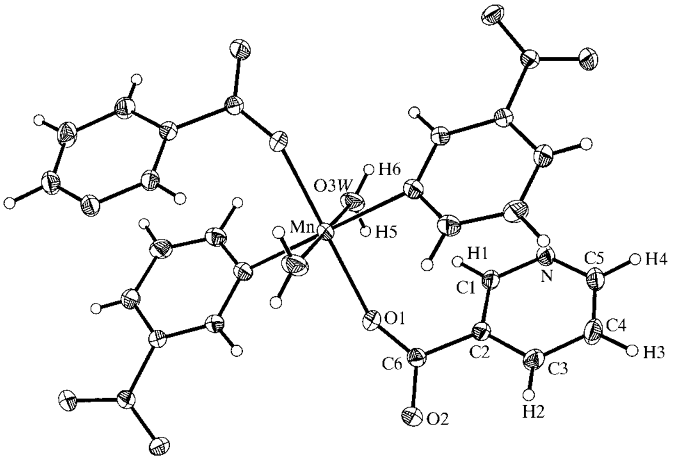


Figure 1
The structure of the monomeric unit of the title polymer with the atom-numbering scheme (50% probability ellipsoids).

As shown in Fig. 1, the Mn atom resides on the centre of symmetry of the octahedron and is coordinated by two N atoms of the pyridine rings, two O atoms of the carboxylate groups and two O atoms of the water molecules; all of the corresponding pairs of ligand atoms lie in *trans* positions and

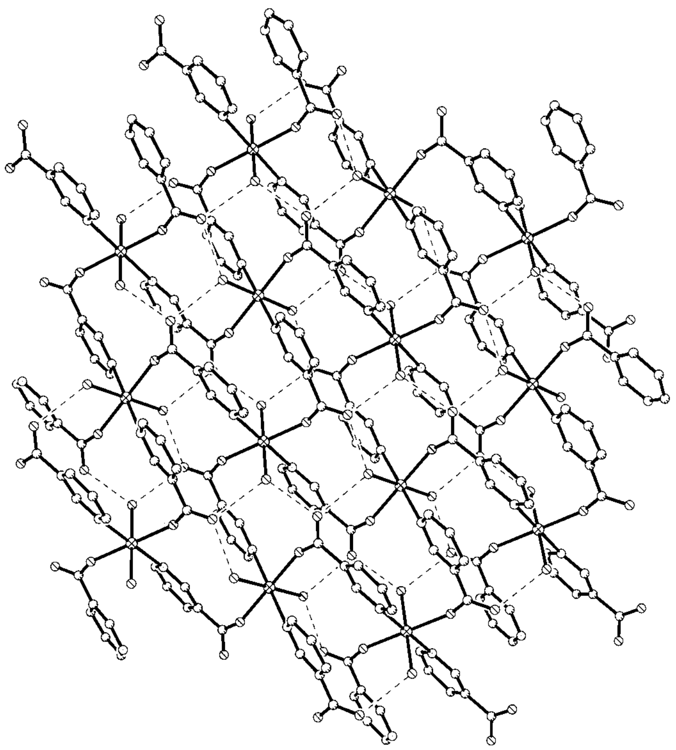


Figure 2
The structure of one layer of the title polymer. Hydrogen bonds are indicated by broken lines and H atoms have been omitted for clarity. Mn atoms are criss-crossed, O atoms are striped, N atoms are dotted and C atoms are ticked on one side.

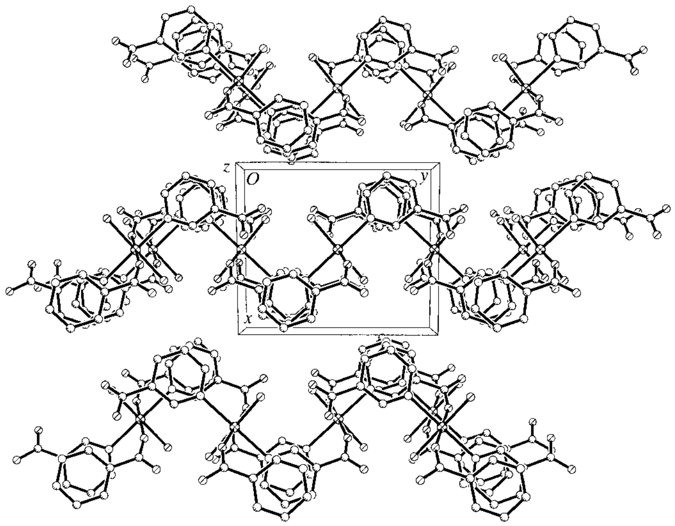


Figure 3
Packing diagram of the title polymer in the unit cell (view along the *z* axis). The atom labelling is as in Fig. 2.

the two ligands of each pair are related by the centre of symmetry. According to the bond-valence theory (Brown, 1981), the sum of the bond valences around Mn is equal to 1.998, which is in good agreement with the valence of the Mn^{2+} ion. As shown in Table 1, 12 of the 15 bond angles around the Mn atom are slightly distorted from the ideal octahedral values of 90°.

In the polymeric layer (see Fig. 2), each nicotinate ligand connects two Mn atoms through one O atom of its carboxylate group and the N atom of its pyridine ring, *i.e.* the coordination mode of the nicotinate ligand is bridging/bidentate. Acting as adhesives, the nicotinate ligands link the $\{Mn(nic)_2(H_2O)_2\}$ monomeric units together to form an extended dative-bond-based layer. All water molecules and the uncoordinated O atoms of the carboxylate groups participate in constituting the intra-layer hydrogen bonds which may play an auxiliary part in stabilizing the layer [$O3W—H6\cdots O2^{iv}$ 2.695 (2) Å and 176 (3)°; $O3W—H5\cdots O2^{v}$ 2.809 (2) Å and 174 (3)°; symmetry codes: (iv) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $1 - x, 1 - y, 1 - z$]. If all ligands are omitted from the layer for clarity, an Mn-only layer will be obtained and it can be seen that this layer is just the *yz* plane, *viz bc* plane in monoclinic system (see Fig. 3). Moreover, all Mn atoms of this layer are related by the 2_1 screw axes (parallel to the *b* axis, and $z = \frac{1}{4}$) and *c* glide planes (perpendicular to the *b* axis, and $y = \frac{1}{4}$). The shortest distance between two Mn atoms of this layer is 6.223 (1) Å. The perpendicular and Mn···Mn distances between two adjacent Mn-only layers are 8.597 (2) Å and 8.730 (2) Å, respectively. Fig. 3 is a packing diagram of the unit cell for (I). As it shows, the layers are arranged in an orderly manner along the *a* axis (*x* in Fig. 3) through van der Waals forces so as to complete the solid-state structure of the crystal.

It is interesting to compare the two related manganese(II) pyridinecarboxylates when the carboxylate group is in the *ortho* position (Okabe & Koizumi, 1998) and the *meta* position [the title complex, (I)]. In the former situation, each 2-pyridinecarboxylate ligand is coordinated to the Mn atom in the chelating mode, thus giving rise to the simple mononuclear complex, whereas in the latter situation, the coordination mode of the 3-pyridinecarboxylate ligand is bridging/bidentate, leading to the two-dimensional layer structure.

Experimental

A solution of $MnSO_4{\cdot}H_2O$ (0.17 g, 1.0 mmol) dissolved in distilled water (5 ml) was layered in a culture tube with a solution of nicotinic acid (0.12 g, 1.0 mmol) and KOH (56 mg, 1.0 mmol) dissolved in distilled water (3 ml) and ethanol (2 ml). After a month's diffusion, colourless lamellar crystals were precipitated in 29% yield (based on Mn). The chemicals used were all of analytical purity and obtained from commercial sources.

Crystal data

$[Mn(C_6H_4NO_2)_2(H_2O)_2]$
$M_r = 335.18$
Monoclinic, $P2_1/c$
$a = 8.730$ (2) Å
$b = 10.189$ (2) Å
$c = 7.1470$ (10) Å
$\beta = 100.02$ (3)°
$V = 626.0$ (2) Å^3
$Z = 2$
$D_x = 1.778$ Mg m^{-3}
$D_m = 1.780$ (3) Mg m^{-3}
D_m measured by flotation in CCl_4/ $C_2H_4Br_2$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.0$–12.5°
$\mu = 1.086$ mm^{-1}
$T = 293$ (2) K
Lamellar, colourless
0.70 × 0.30 × 0.15 mm

Data collection

AFC-6*S* diffractometer
2θ scans
Absorption correction: ψ scan (Coppens *et al.*, 1965)
$T_{min} = 0.630$, $T_{max} = 0.850$
1961 measured reflections
1826 independent reflections
$R_{int} = 0.026$
$\theta_{max} = 29.99$°
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 0$
$l = 0 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.108$
$S = 1.065$
1826 reflections
122 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0619P)^2 + 0.1001P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.071 (6)

All H atoms were refined and C—H distances were in the range 0.88 (3)–0.97 (3) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine

Table 1
Selected geometric parameters (Å, °).

Mn—O1	2.1617 (14)	$Mn—N^{i}$	2.2876 (16)
Mn—O3*W*	2.1830 (15)		
O1—Mn—O3*W*	91.58 (6)	$O3W—Mn—N^{i}$	94.61 (6)
$O1^{ii}—Mn—O3W$	88.42 (6)	$O3W^{ii}—Mn—N^{i}$	85.39 (6)
$O1—Mn—N^{i}$	91.35 (6)	$O3W—Mn—N^{iii}$	85.39 (6)
$O1^{ii}—Mn—N^{i}$	88.65 (6)		

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

structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Siemens, 1990); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

This work was supported by grants (Nos. 29871003 and 29733080) from the National Natural Science Foundation of the People's Republic of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1271). Services for accessing these data are described at the back of the journal.

References

Brown, I. D. (1981). *Structure and Bonding in Crystals*, Vol. 2, ch. 14, pp. 1–30. New York: Academic Press.

Ciardelli, F., Tsuchida, E. & Wöhrle, D. (1996). Editors. *Macromolecule–Metal Complexes*, pp. 1–4. Berlin: Springer-Verlag.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Kahn, O. (1987). *Struct. Bonding* (*Berlin*), pp. 68 and 89.

Liu, Y.-Q., Wei, Y.-G., Liu, Q., Zhang, S.-W. & Shao, M.-C. (1999). *Acta Cryst.* C**55**, 534–536.

Mallah, T., Thiébaut, S., Verdaguer, M. & Veillet, P. (1993). *Science*, **262**, 1554–1557.

Manriquez, J. M., Yee, G. T., Mclean, R. S., Epstein, A. J. & Miller, J. S. (1991). *Science*, **252**, 1415–1417.

Molecular Structure Corporation (1994). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1997). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Okabe, N. & Koizumi, M. (1998). *Acta Cryst.* C**54**, 288–290.

Sheldrick, G. M. (1997*a*). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Siemens (1990). *XP*. Version 4.2 for MSDOS. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Wei, Y.-G., Liu, Q. & Zhang, S.-W. (2000). In preparation.