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A one-dimensional coordination polymer of manganese(II) with *N*-(2-hydroxyethyl)iminodiacetate: {[Mn(Hheidi)(H₂O)]·H₂O}_n

YE-QI LIU, YONG-GE WEI, QUN LIU, SHI-WEI ZHANG*
AND MEI-CHENG SHAO

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

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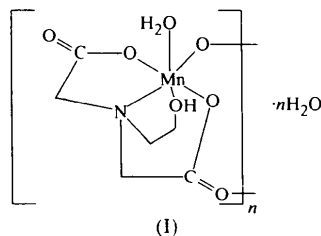
Abstract

The one-dimensional polymer *catena*-poly[[aqua-manganese(II)- μ -[*N*-(2-hydroxyethyl)iminodiacetato]-*O*¹, *O*², *O*^N, *N*:*O*¹] hydrate], {[Mn^{II}(Hheidi)(H₂O)]·H₂O}_n [Hheidi is *N*-(2-hydroxyethyl)iminodiacetate, C₆H₉NO₅], was synthesized in aqueous solution. The polymeric [Mn^{II}(Hheidi)(H₂O)] segment is totally chiral and is connected into a three-dimensional structure by hydrogen bonds.

Comment

The magnetochemistry of manganese has been a very active field of study in recent years. Several extraordinary magnetic properties such as the quantum tunneling of magnetization and the very large coercive force in molecular ferromagnets have been discovered respectively in the manganese-oxo clusters Mn₁₂ (Friedman *et al.*, 1996; Wei *et al.*, 1997; Aubin *et al.*, 1997) and Mn₃ (Zhang *et al.*, 1996). In addition, many

molecular magnets based on polymeric manganese-containing compounds have been synthesized and characterized, for example, MnCu(pbaOH)(H₂O)₃ [pbaOH is 2-hydroxy-1,3-propylenebis(oxamato)] (Kahn *et al.*, 1988), [Mn(L)₂(N₃)₂]_n (*L* is 3-ethylpyridine or 2-hydroxypyridine) (Escuer *et al.*, 1998). In this paper, we report the single-crystal structure of another novel one-dimensional polymeric compound, *i.e.* the manganese complex of the *N*-(2-hydroxyethyl)iminodiacetate ligand, {[Mn(Hheidi)(H₂O)]·H₂O}_n, (I), which has a well defined chiral chain in the crystal.



As shown in Fig. 1, the single-crystal X-ray diffraction analysis reveals that the Mn atoms in the crystal all have slightly distorted octahedral environments. The coordination sphere of one Mn atom is completed by atoms O2, O3, O5 (which is disordered over two positions, O5*a* and O5*b*, in the crystal), the N atom from one *N*-(2-hydroxyethyl)iminodiacetate ligand, the O6 atom from a water molecule and the O1ⁱ atom from another *N*-(2-hydroxyethyl)iminodiacetate ligand which bridges to another Mn atom [symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$]. Although the crystals are brown, the charge equilibrium necessitates that the valency of the Mn atom is equal to 2, which is also in accordance with the 'bond-valence-sum' analysis (Brown, 1981) for

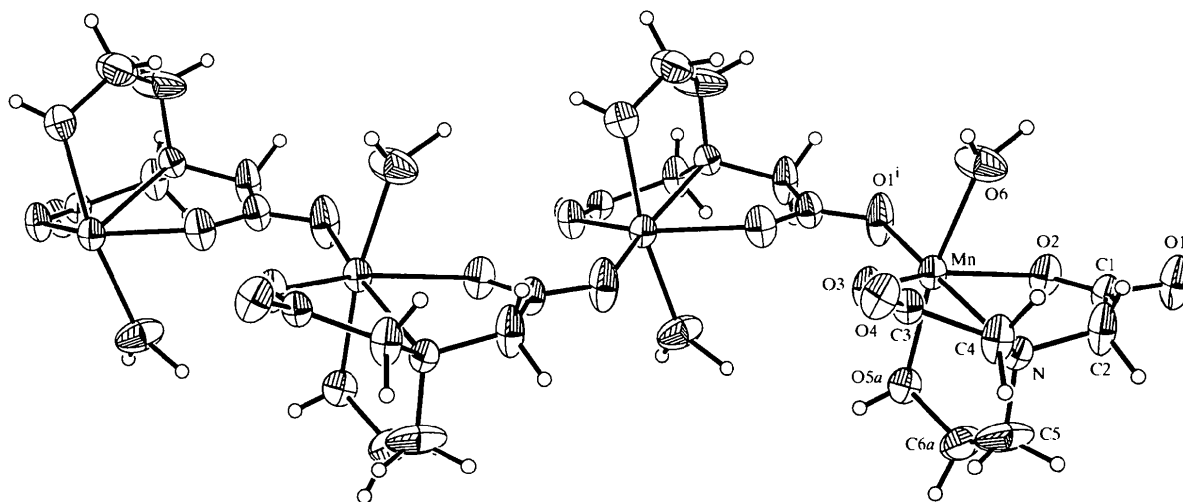


Fig. 1. The structure of the title polymer with the atom-numbering scheme (50% probability ellipsoids). [Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$]

the Mn atom. It is interesting that Mn atoms in the crystal are bridged by one carboxylate group and form one-dimensional zigzag chains, which are linked by hydrogen bonds to the water molecules of crystallization to complete the three-dimensional structure in the crystal (Fig. 2). Since it crystallizes in chiral space group $P2_12_12_1$, the resultant one-dimensional chain-like polymer is also chiral. Every chiral chain is made up of two columns of Mn atoms, which are parallel to each other and lie in the same plane. Unfortunately, because the bridging carboxylate groups (atoms O1a, O2 and C1) in a chain are almost in the plane formed by the two parallel columns of Mn atoms in the same chain, the chiral chain is not helical. However, this kind of chain structure shows π electrons delocalized over the whole chain, which may result in some special electrical and magnetic properties, such as enhanced anti-ferromagnetic interactions between metal centers, which have been observed in two similar polymeric complexes of manganese with the bicine [or *N,N*-bis(2-hydroxyethyl)glycine] ligand (Sun *et al.*, 1997, 1998).

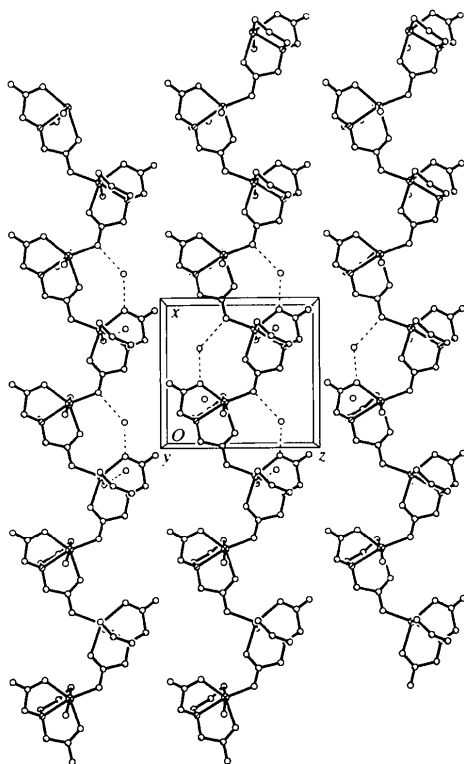


Fig. 2. The packing of the title compound in the unit cell (view along the direction parallel to the *b* axis). Hydrogen bonds are indicated by broken lines. Mn atoms are criss-crossed, O atoms are dotted, N atoms are striped and C atoms are ticked on one side.

Experimental

For the preparation of (I), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1.00 g, 5.00 mmol) and H_3heidi (0.442 g, 2.5 mmol) were dissolved in water

(20 ml) and stirred for 30 min, whereupon triethylamine (0.9 ml) was added dropwise to the resulting colorless solution. On stirring, this solution became progressively browner. After 2 h, it was filtered and evaporated. After about one week, grey-brown crystals had been deposited in about 40% yield. The chemicals used were all of analytical purity and were used without purification.

Crystal data

$[\text{Mn}(\text{C}_6\text{H}_9\text{NO}_5)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$
 $M_r = 266.11$
 Orthorhombic
 $P2_12_12_1$
 $a = 9.782(2) \text{ \AA}$
 $b = 10.283(2) \text{ \AA}$
 $c = 10.497(2) \text{ \AA}$
 $V = 1055.9(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.674 \text{ Mg m}^{-3}$
 $D_m = 1.68(2) \text{ Mg m}^{-3}$
 D_m measured by flotation in $\text{CH}_2\text{Cl}_2/\text{C}_3\text{H}_6\text{Br}_2$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 5.0\text{--}12.5^\circ$
 $\mu = 1.267 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Tetrahedral block
 $0.5 \times 0.5 \times 0.5 \text{ mm}$
 Light brown

Data collection

Rigaku AFC-6S diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (Coppens *et al.*, 1965)
 $T_{\min} = 0.417$, $T_{\max} = 0.531$
 1214 measured reflections
 1214 independent reflections

1164 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 25.99^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 12$
 $l = 0 \rightarrow 12$
 3 standard reflections every 200 reflections
 intensity decay: 3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.106$
 $S = 1.031$
 1208 reflections
 175 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0811P)^2 + 0.2520P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
 $\Delta\rho_{\max} = 0.540 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.012 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = 0.01 (4)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Mn—O1'	2.093 (3)	Mn—O2	2.192 (3)
Mn—O5a	2.14 (2)	Mn—O5b	2.248 (12)
Mn—O3	2.151 (3)	Mn—N	2.330 (3)
Mn—O6	2.175 (3)		
O1'—Mn—O5a	89.8 (5)	O1'—Mn—O5b	99.3 (3)
O1'—Mn—O3	120.28 (11)	O3—Mn—O5b	85.7 (3)
O5a—Mn—O3	96.6 (5)	O6—Mn—O5b	163.2 (3)
O1'—Mn—O6	97.5 (2)	O2—Mn—O5b	96.5 (4)
O5a—Mn—O6	170.6 (5)	O1'—Mn—N	163.60 (12)
O3—Mn—O6	84.87 (12)	O5a—Mn—N	81.6 (5)
O1'—Mn—O2	91.76 (10)	O3—Mn—N	74.80 (10)
O5a—Mn—O2	89.8 (5)	O6—Mn—N	89.89 (13)
O3—Mn—O2	147.20 (9)	O2—Mn—N	74.40 (10)
O6—Mn—O2	84.07 (13)	O5b—Mn—N	74.2 (3)

Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.

The H atoms of the OH groups were found in the difference syntheses and all their parameters were refined. However, the H atoms of the CH groups were located in suitable geometric positions calculated using *SHELXL93* (Sheldrick, 1993), and were refined using a riding model with U_{iso} fixed at 0.08 \AA^2 .

During the refinement, two peaks with large residual electron density were found near the C6 and O5 sites, which were then further refined as split atom sites C6a/C6b and O5a/O5b, respectively. The occupancies of the C6a and C6b sites were then constrained to a sum of 1.0, while the occupancies of the O5a and O5b sites were constrained to be the same as those of the C6a and C6b sites, respectively. The displacement parameters of the above-mentioned atom sites were all left unconstrained however. Attempts to refine the structure with a single strongly anisotropic C6 site were unsuccessful and resulted in very odd displacements. Indeed, the present split sites have more realistic geometric positions: the bond distances C5—C6a 1.53 (2), C5—C6b 1.42 (1), C6a—O5a 1.42 (2) and C6b—O5b 1.41 (1) Å, and the bond angles N—C5—C6a 114.9 (6), N—C5—C6b 116.0 (5), C5—C6a—O5a 119.2 (12) and C5—C6b—O5b 107.8 (7)° are more comparable with those of similar compounds (Sun *et al.*, 1997, 1998). It seems that this kind of disorder, which originates from the one-dimensional zigzag chiral chain, is incompatible with the crystallographic 2₁ symmetry along the *b* axis or the thermal motion of the hydroxyethyl group in the ligand.

Full-matrix least-squares refinement using anomalous dispersion factors for all non-H atoms resulted in an *R* factor of 0.039 for the present absolute structure and 0.05 for the other enantiomorph. Consequently, the absolute configuration of the compound has been assigned as *R*. The Flack parameter (Flack, 1983) also confirmed this assignment.

In the final cycles of refinement, seven reflections were omitted because of their large $(F_o^2 - F_c^2)/s.u.$ ratios. In the final electron-density difference map, the minimum of $-1.012 \text{ e \AA}^{-3}$ and maximum of 0.54 e \AA^{-3} were near the Mn atom at distances of 1.0 and 0.80 Å, respectively.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1994). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1217). Services for accessing these data are described at the back of the journal.

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5-(8,8-Dicyanoheptafulven-3-yl)-2-hydroxy-1,3-xylyl-18-crown-5 potassium salt monohydrate†

SHINYA MATSUMOTO,^a KANAME YUMURA,^b HIROYUKI OTANI^b AND JIN MIZUGUCHI^a

^aDepartment of Applied Physics, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan, and ^bDepartment of Chemistry, Faculty of Education and Human Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan. E-mail: mizuj@ed.ynu.ac.jp

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Abstract

The title compound, [K(C₂₆H₂₇N₂O₆)]·H₂O, is a potassium salt of the crown ether dye composed of 8,8-dicyanoheptafulvene and a crown ether having a phen-

† Systematic name: potassium 19-(8,8-dicyanoheptafulven-3-yl)bicyclo-[15.3.1][3.6.9.12.15]pentaoxahenicoso-1(20),17(21),18-trien-21-olate monohydrate.