

## *catena*-Poly[[tetraaquamanganese(II)]- $\mu$ -4-(carboxylatomethylsulfanyl)-phenoxyacetato]

Hong Su, Yun-Long Feng\* and Yi-Hang Wen

Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Institute of Physical Chemistry, Zhejiang Normal University, Jinhua, Zhejiang 321004, People's Republic of China

Correspondence e-mail: sky37@zjnu.cn

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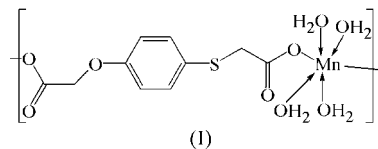
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The title compound,  $[\text{Mn}(\text{C}_{10}\text{H}_8\text{O}_5\text{S})(\text{H}_2\text{O})_4]_n$ , a one-dimensional manganese(II) complex comprising helical chains bridged by 4-(carboxylatomethylsulfanyl)phenoxyacetate ligands has been characterized by single-crystal X-ray diffraction analysis. Hydrogen-bonding interactions between adjacent chains extend the complex into a three-dimensional supramolecular architecture.

### Comment

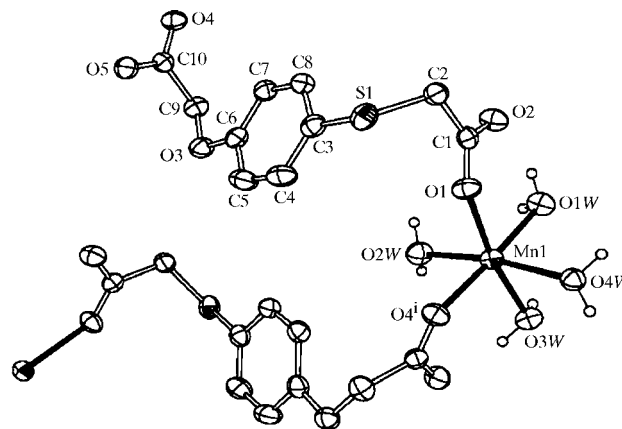
The crystal engineering and synthesis of discrete metallo-helicates and infinite metal-containing helical coordination polymers have received much attention from chemists, because helicity is an essential feature of living systems and is important in advanced materials, such as optical devices, enantiomer separation, chiral synthesis, ligand exchange and selective catalysis (Chen & Suslick, 1993; Woods *et al.*, 1996; Piquet *et al.*, 1997; Qi *et al.*, 2003). Most of the recent studies in this area have been involved with the construction of compounds from  $d^{10}$  transition metal ions and functional ligands (Psillakes *et al.*, 1997; Tong *et al.*, 1998; Nomiya *et al.*, 2000). In this context, the fine-tuning of organic ligands and the careful selection of metal ions are especially crucial to the construction of desirable helical frameworks (Nishida *et al.*, 2001; Gao *et al.*, 2003; Barnett & Champness, 2003). We are interested in the solid-state coordination chemistry of 4-(carboxylatomethylsulfanyl)phenoxyacetic acid ( $p$ -CMPT $\text{H}_2$ ), which remains largely unexplored. Although this is a rather simple molecule, it has the potential for coordinative interaction and hydrogen bonding. Firstly, it has two carboxyl groups, one ether O atom and one thioether S atom, which induce multiple coordination modes with transition metal ions. Secondly, it can act not only as a hydrogen-bond donor but also as hydrogen-bond acceptor, owing to the existence of deprotonated and/or protonated carboxyl groups. Therefore, it is regarded as an excellent candidate for the construction of

different kinds of coordination polymers, including infinite one-dimensional chain compounds, two-dimensional layer compounds and three-dimensional netlike compounds (Gao, Huo *et al.*, 2005; Gao, Su *et al.*, 2005). We report here the title novel one-dimensional manganese(II) complex, (I), comprising helical chains bridged by 4-(carboxylatomethylsulfanyl)phenoxyacetate ( $p$ -CMPT $^{2-}$ ).



The present X-ray diffraction analysis shows that complex (I) possesses a one-dimensional single helical structure. The fundamental unit of the crystal structure is illustrated in Fig. 1. Each  $\text{Mn}^{\text{II}}$  ion is six-coordinated in a distorted octahedral geometry. Its equatorial plane is defined by atoms O1, O1W, O3W and O4 $^{\dagger}$  [symmetry code: (i)  $-x + 1, y - \frac{1}{2}, -z + 1$ ], with an r.m.s. deviation of 0.075 (2) Å; the deviation of the  $\text{Mn}^{\text{II}}$  atom from this plane is 0.0116 (2) Å. The axial positions are occupied by atoms O2W and O4W, with an angle of 170.53 (6)°. It is interesting to note that each  $p$ -CMPT $^{2-}$  ligand, serves as a bridging ligand to link two  $\text{Mn}^{\text{II}}$  atoms, forming a single-strand helical coordination polymer. Both carboxylate anions in one  $p$ -CMPT $^{2-}$  ligand are mono-coordinated to the adjacent metal atom, with Mn–O distances of 2.1599 (15) and 2.1528 (16) Å (Fig. 2). In this way, each  $p$ -CMPT $^{2-}$  acts as a bidentate group linking two metal atoms and yields a half-turn unit of the helical structure. The distance between neighbouring Mn atoms is 11.377 Å. Extension of the structure in one dimension along the  $b$  axis gives a one-dimensional helical Mn– $p$ -CMPT $^{2-}$  network (Fig. 2), resulting from the unique coordination feature of the  $p$ -CMPT $^{2-}$  ligands. Each helical cycle contains three Mn atoms and two bridging  $p$ -CMPT $^{2-}$  ligands.

The structure of (I) also contains intermolecular hydrogen bonds, which are formed between the free water molecules



**Figure 1**  
A view of the title compound showing the atom-numbering scheme. Non-water H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i)  $1 - x, y - \frac{1}{2}, 1 - z$ .]

and uncoordinated carboxylate O atoms [ $O\cdots O = 2.676(2)$  and  $2.744(2)$  Å], resulting in a two-dimensional layer structure parallel to the  $bc$  plane. Adjacent two-dimensional layers form a three-dimensional framework linked by further intermolecular hydrogen bonds formed between the water molecules, coordinated carboxylate O atoms and water molecules of an adjacent layer [ $O\cdots O = 2.972(3)$  and  $2.878(2)$  Å] (Fig. 3).

In summary, employing the flexibility and unique coordination feature of  $p$ -CMPT<sup>2-</sup>, we have successfully prepared a one-dimensional chain coordination polymer consisting of helical chains bridged by  $p$ -CMPT<sup>2-</sup>. Knowledge of the

chemistry of well defined helical coordination polymers is necessary for the understanding of the detection and amplification of chirality. There is increasing interest in dynamic helical coordination polymers (Yamada *et al.*, 2004; Matsuda *et al.*, 2004), the most important feature of which is high sensitivity to a chiral environment, and therefore such systems might provide the basis to construct a novel chirality-sensing probe. This work has demonstrated that extended structural motifs can be constructed through  $p$ -CMPT<sup>2-</sup> ligands bridging neutral one-dimensional helical chains.

## Experimental

4-(Carboxymethylsulfanyl)phenoxyacetic acid was prepared following the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci (1990).  $MnCl_2 \cdot 6H_2O$  (0.099 g, 0.5 mmol) and 4-(carboxymethylsulfanyl)phenoxyacetic acid (0.224 g, 1 mmol) were dissolved separately in water (25 ml) and the two solutions mixed slowly with stirring for about 15 min at room temperature. The pH was adjusted to 6 with 0.1 M sodium hydroxide. Colourless crystals of (I) separated from the filtered solution after several days (yield *ca* 56%). Elemental analysis calculated for  $C_{10}H_{16}MnO_9S$ : C 32.70, H 4.39%; found: C 33.02, H 4.41%.

### Crystal data

|                               |   |
|-------------------------------|---|
| $[Mn(C_{10}H_8O_5S)(H_2O)_4]$ | $Z = 2$                                   |
| $M_r = 367.24$                | $D_x = 1.724 \text{ Mg m}^{-3}$           |
| Monoclinic, $P2_1$            | Mo $K\alpha$ radiation                    |
| $a = 5.0977(10)$ Å            | $\mu = 1.12 \text{ mm}^{-1}$              |
| $b = 11.444(2)$ Å             | $T = 295(2)$ K                            |
| $c = 12.183(2)$ Å             | Prism, colourless                         |
| $\beta = 95.58(3)^\circ$      | $0.37 \times 0.25 \times 0.16 \text{ mm}$ |
| $V = 707.4(2)$ Å <sup>3</sup> |   |

**Table 1**

Selected geometric parameters (Å, °).

|                          |             |                          |             |
|--------------------------|-------------|--------------------------|-------------|
| Mn1—O4 <sup>i</sup>      | 2.1528 (16) | Mn1—O4W                  | 2.2164 (14) |
| Mn1—O1                   | 2.1599 (15) | Mn1—O1W                  | 2.2185 (15) |
| Mn1—O3W                  | 2.1881 (15) | Mn1—O2W                  | 2.2435 (17) |
| O4 <sup>i</sup> —Mn1—O1  | 91.66 (5)   | O1—Mn1—O1W               | 87.54 (6)   |
| O4 <sup>i</sup> —Mn1—O3W | 96.94 (6)   | O3W—Mn1—O1W              | 84.11 (6)   |
| O1—Mn1—O3W               | 170.43 (6)  | O4W—Mn1—O1W              | 95.27 (6)   |
| O4 <sup>i</sup> —Mn1—O4W | 87.97 (6)   | O4 <sup>i</sup> —Mn1—O2W | 89.43 (6)   |
| O1—Mn1—O4W               | 91.00 (6)   | O1—Mn1—O2W               | 98.19 (6)   |
| O3W—Mn1—O4W              | 85.13 (6)   | O3W—Mn1—O2W              | 86.15 (6)   |
| O4 <sup>i</sup> —Mn1—O1W | 176.68 (7)  | O4W—Mn1—O2W              | 170.53 (6)  |

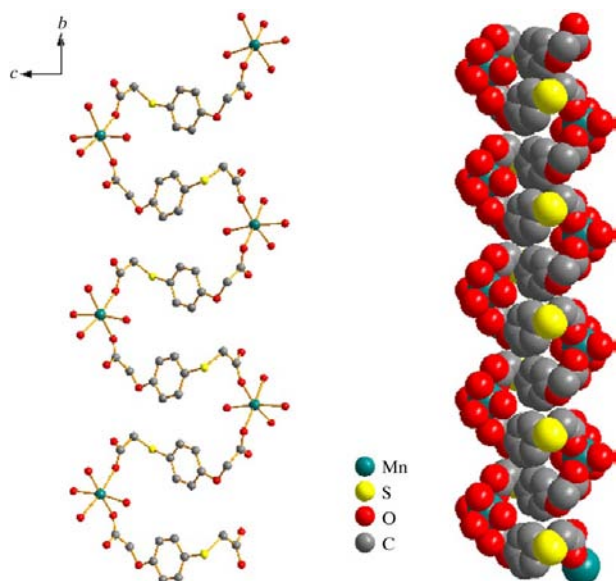
Symmetry code: (i)  $-x + 1, y - \frac{1}{2}, -z + 1$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

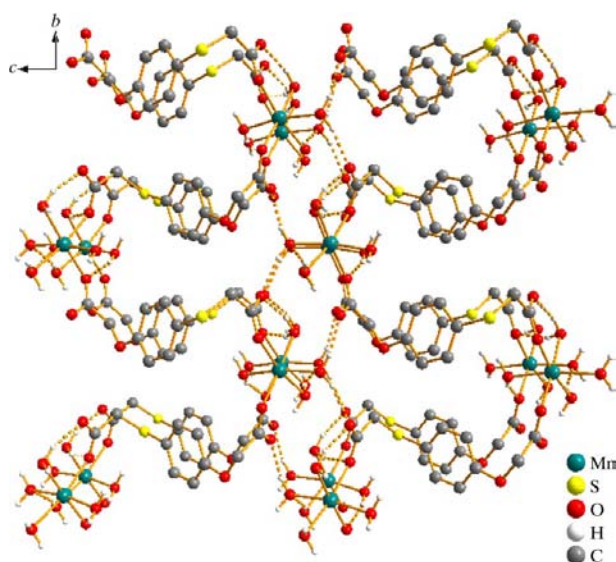
| $D-H\cdots A$                              | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--|----------|-------------|-------------|---------------|
| O1W—H10 <sup>i</sup> ···O1 <sup>ii</sup>   | 0.85 (3) | 2.15 (3)    | 2.972 (3)   | 163 (2)       |
| O1W—H11 <sup>i</sup> ···O2                 | 0.86 (2) | 1.83 (3)    | 2.651 (2)   | 161 (3)       |
| O2W—H12 <sup>i</sup> ···O4 <sup>iii</sup>  | 0.85 (2) | 2.08 (3)    | 2.896 (2)   | 162 (3)       |
| O2W—H13 <sup>i</sup> ···S1 <sup>ii</sup>   | 0.85 (2) | 2.47 (3)    | 3.316 (2)   | 175 (3)       |
| O3W—H14 <sup>i</sup> ···O5 <sup>i</sup>    | 0.85 (2) | 1.97 (3)    | 2.709 (2)   | 145 (2)       |
| O3W—H15 <sup>i</sup> ···O4W <sup>iii</sup> | 0.84 (2) | 2.08 (3)    | 2.878 (2)   | 159 (2)       |
| O4W—H16 <sup>i</sup> ···O5 <sup>iv</sup>   | 0.85 (2) | 1.85 (2)    | 2.676 (2)   | 164 (2)       |
| O4W—H17 <sup>i</sup> ···O2 <sup>v</sup>    | 0.85 (2) | 1.93 (3)    | 2.744 (2)   | 162 (2)       |

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



**Figure 2**

Ball-and-stick (left) and space-filling (right) plots of (I), showing the one-dimensional helical Mn- $p$ -CMPT<sup>2-</sup> network along the  $b$  axis. H atoms have been omitted.



**Figure 3**

A packing diagram for (I). Hydrogen bonds are depicted as dashed lines.

## Data collection

|   |  |
|---|--|
| Rigaku R-AXIS RAPID diffractometer                        | 6919 measured reflections              |
| $\omega$ scans  | 3164 independent reflections           |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | 2967 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.709$ , $T_{\max} = 0.840$                   | $R_{\text{int}} = 0.024$               |
|   | $\theta_{\max} = 27.5^\circ$           |

## Refinement

|  |  |
|--|--|
| Refinement on $F^2$  | $w = 1/[\sigma^2(F_o^2) + (0.0264P)^2]$                |
| $R[F^2 > 2\sigma(F^2)] = 0.025$  | where $P = (F_o^2 + 2F_c^2)/3$                         |
| $wR(F^2) = 0.054$  | $(\Delta/\sigma)_{\max} = 0.001$                       |
| $S = 1.04$   | $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$  |
| 3164 reflections   | $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$ |
| 214 parameters   | Absolute structure: Flack (1983),                      |
| H atoms treated by a mixture of independent and constrained refinement | with 1457 Friedel pairs                                |
|  | Flack parameter: 0.004 (11)                            |

C-bound H atoms were placed in calculated positions, with C—H = 0.93 (aromatic) or 0.97 Å (aliphatic) and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and treated using the riding-model approximation. The H atoms of the water molecules were located in a difference Fourier map and refined with O—H distance restraints of 0.85 (1) Å and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TY1014). Services for accessing these data are described at the back of the journal.

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