

## A three-dimensional homochiral metal-organic framework constructed from manganese(II) with *S*-carboxymethyl-*N*-(*p*-tosyl)-*L*-cysteine and 4,4'-bipyridine

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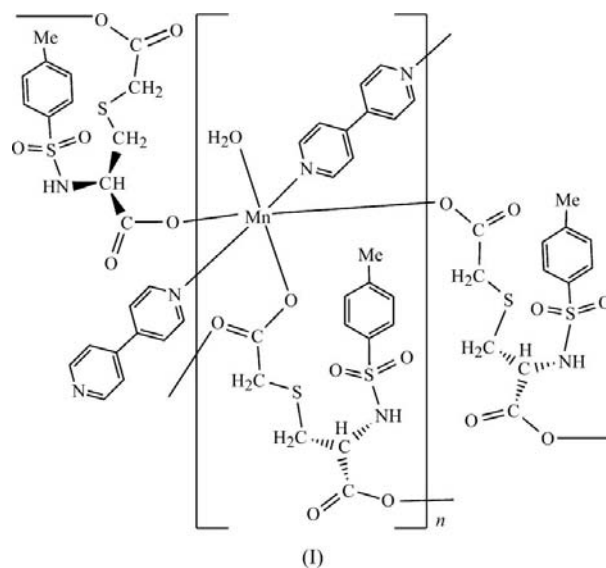
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In the chiral polymeric title compound, poly[aqua(4,4'-bipyridine)[ $\mu_3$ -*S*-carboxylatomethyl-*N*-(*p*-tosyl)-*L*-cysteinato]-manganese(II)],  $[\text{Mn}(\text{C}_{12}\text{H}_{13}\text{NO}_6\text{S}_2)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]_n$ , the  $\text{Mn}^{\text{II}}$  ion is coordinated in a distorted octahedral geometry by one water molecule, three carboxylate O atoms from three *S*-carboxylatomethyl-*N*-(*p*-tosyl)-*L*-cysteinate (Ts-cmc) ligands and two N atoms from two 4,4'-bipyridine molecules. Each Ts-cmc ligand behaves as a chiral  $\mu_3$ -linker connecting three  $\text{Mn}^{\text{II}}$  ions. The two-dimensional frameworks thus formed are further connected by 4,4'-bipyridine ligands into a three-dimensional homochiral metal-organic framework. This is a rare case of a homochiral metal-organic framework with a flexible chiral ligand as linker, and this result demonstrates the important role of noncovalent interactions in stabilizing such assemblies.

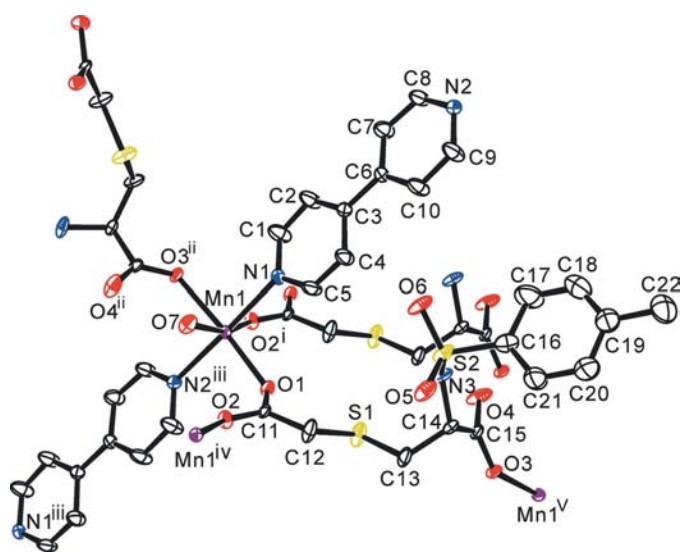
### Comment

Homochiral metal-organic frameworks (MOFs) have attracted much attention owing to their interesting topological structures and their potential applications, such as chiral separation and asymmetric heterogeneous catalysis (Seo *et al.*, 2000; Bradshaw *et al.*, 2004; Kesanli & Lin 2003; Wu *et al.*, 2005; Wu & Lin, 2007). However, the control of chirality in MOFs is still a great challenge. One strategy for the preparation of homochiral MOFs is to select appropriate enantiopure ligands as the chiral linkers. The most often used chiral organic linkers are rigid organic ligands, such as rigid dicarboxylates (Cui *et al.*, 2002; Tanaka *et al.*, 2008). The use of flexible chiral ligands as linkers is rare, since the structures formed by this type of ligand are not easy to predesign and control (Gordon & Harrison, 2004). In this work, we investigate the structure of a chiral MOF constructed from a flexible chiral linker, *S*-carboxylatomethyl-*N*-(*p*-tosyl)-*L*-cysteinate (Ts-cmc), together with an achiral linker, 4,4'-bipyridine (4,4'-bipy). We

report here the structure of  $[\text{Mn}(\text{Ts-cmc})(4,4'\text{-bipy})(\text{H}_2\text{O})]_n$ , (I), which exhibits a homochiral three-dimensional metal-organic framework.



Complex (I) crystallizes in the chiral space group  $P2_1$ . The  $\text{Mn}^{\text{II}}$  ion is six-coordinated in a distorted octahedral geometry by one water molecule, two carboxylate O atoms from the carboxymethyl groups of two Ts-cmc ligands, another carboxylate O atom from the *L*-cysteine unit of another Ts-cmc ligand and two N atoms from two 4,4'-bipyridine molecules (Fig. 1). The Mn—O and Mn—N bond lengths (Table 1) are comparable to the corresponding distances reported for  $\text{Mn}^{\text{II}}$  compounds bearing *N*-tosyl-amino acid ligands (Chen *et al.*, 2005; Liang *et al.*, 2004; Brückner *et al.*, 1993). The bond

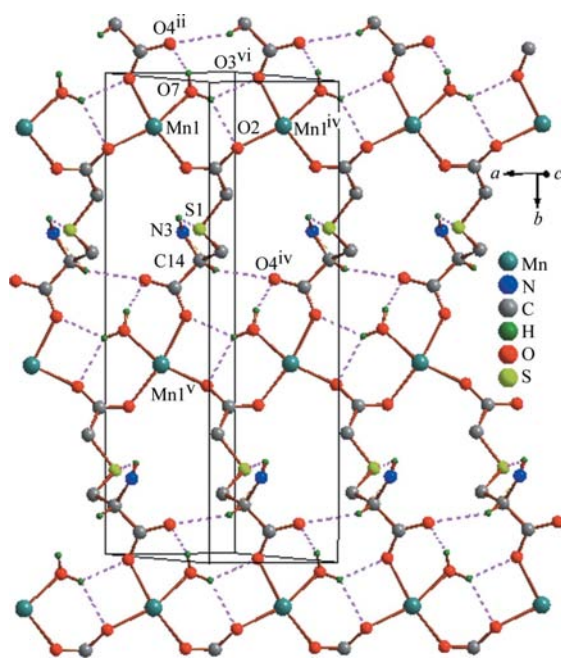


**Figure 1**  
A view of compound (I), showing the atom-labeling scheme and 30% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $-x + 2, y - \frac{1}{2}, -z + 1$ ; (iii)  $x, y, z + 1$ ; (iv)  $x - 1, y, z$ ; (v)  $-x + 2, y + \frac{1}{2}, -z + 1$ .]

angles in Table 1 reveal some degree of distortion in the octahedral coordination geometry.

The carboxylatomethyl carboxylate groups of Ts-cmc adopt a *syn-anti*  $\mu_2$ -bridging mode connecting adjacent  $\text{Mn}^{\text{II}}$  ions into one-dimensional chains along the *a* axis, with an  $\text{Mn1} \cdots \text{Mn1}^{\text{iv}}$  [symmetry code: (iv)  $x - 1, y, z$ ] distance of 5.382 (4) Å within the chain. The carboxylate groups from the L-cysteine fragments of Ts-cmc in each chain coordinate to the  $\text{Mn}^{\text{II}}$  ions from adjacent chains in a monodentate mode, forming a two-dimensional sheet parallel to the *ab* plane with an interchain  $\text{Mn1} \cdots \text{Mn1}^{\text{v}}$  distance of 10.230 (7) Å [symmetry code: (v)  $-x + 2, y + \frac{1}{2}, -z + 1$ ] (Fig. 2). Therefore, the two carboxylate groups of the Ts-cmc ligand exhibit different coordination modes, *viz.* *syn-anti*  $\mu_2$ -bridging and monodentate. Each Ts-cmc ligand in (I) thus acts as a  $\mu_3, \eta^3$ -bridge connecting three  $\text{Mn}^{\text{II}}$  ions. This is very different from the reported connecting modes of *S*-carboxymethyl-L-cysteine (Wang *et al.*, 2005). Notably, the amine group of Ts-cmc forms a hydrogen bond with the S atom in the same ligand ( $\text{N3} \cdots \text{S1}$ ; Table 2 and Fig. 2), giving a hydrogen-bonded ring motif with graph-set notation  $S(5)$  (Bernstein *et al.*, 1995). In addition to another three classical hydrogen bonds [ $\text{O7} \cdots \text{H7A} \cdots \text{O2}$ ,  $\text{O7} \cdots \text{H7A} \cdots \text{O3}^{\text{vi}}$  and  $\text{O7} \cdots \text{H7B} \cdots \text{O4}^{\text{ii}}$ ; symmetry codes: (ii)  $-x + 2, y - \frac{1}{2}, -z + 1$ ; (vi)  $-x + 1, y - \frac{1}{2}, -z + 1$ ], a nonclassical hydrogen bond is also present ( $\text{C14} \cdots \text{H14} \cdots \text{O4}^{\text{iv}}$ ; Table 2 and Fig. 2). The propagation of the  $\text{O7} \cdots \text{H7A} \cdots \text{O3}^{\text{vi}}$ ,  $\text{O7} \cdots \text{H7B} \cdots \text{O4}^{\text{ii}}$  and  $\text{C14} \cdots \text{H14} \cdots \text{O4}^{\text{iv}}$  hydrogen bonds affords a complex fused-ring hydrogen-bonding system (Fig. 2), further stabilizing the two-dimensional sheet.

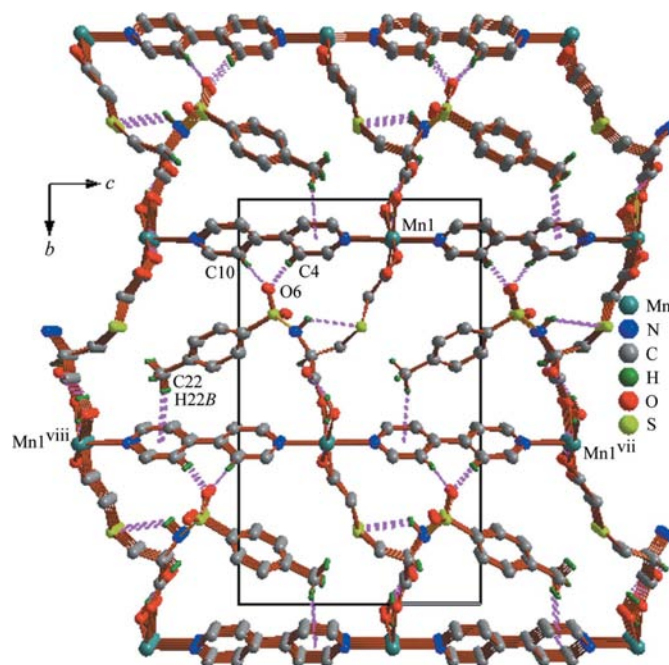
Neighboring two-dimensional sheets are bridged by coordinated 4,4'-bipy ligands, which bind to  $\text{Mn}^{\text{II}}$  centers from



**Figure 2**

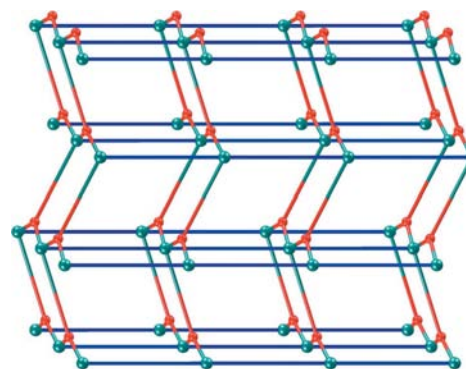
The two-dimensional network in (I), with *p*-tosyl groups and H atoms not involved in hydrogen bonding omitted for clarity. [Symmetry codes: (ii)  $-x + 2, y - \frac{1}{2}, -z + 1$ ; (iv)  $x - 1, y, z$ ; (v)  $-x + 2, y + \frac{1}{2}, -z + 1$ ; (vi)  $-x + 1, y - \frac{1}{2}, -z + 1$ .]

adjacent sheets, forming a homochiral three-dimensional metal-organic framework as depicted in Fig. 3. It has a grid size of 13.126 (7) × 17.618 (10) Å defined by the diagonal  $\text{Mn1} \cdots \text{Mn1}^{\text{vii}}$  and  $\text{Mn1} \cdots \text{Mn1}^{\text{viii}}$  distances [symmetry codes: (vii)  $-x + 2, y + \frac{1}{2}, -z + 2$ ; (viii)  $-x + 2, y + \frac{1}{2}, -z$ ]. From a topological viewpoint, the Ts-cmc ligands act as 3-connecting nodes linking three  $\text{Mn}^{\text{II}}$  ions, and the  $\text{Mn}^{\text{II}}$  ions act as 5-connecting nodes linking three Ts-cmc ligands and two 4,4'-bipy ligands. The overall 3,5-connected three-dimensional network is shown in Fig. 4 and has the Schläfli symbol  $(6^3)(6^9.8)$ . The *p*-tosyl group, a part of the Ts-cmc ligand, interacts with the three-dimensional framework further *via* the formation of  $\text{C} \cdots \text{H} \cdots \pi$  interactions and hydrogen bonds (Fig. 3). Sulfonyl atom O6 participates in two hydrogen bonds with H atoms from the 4,4'-bipy ligand in the same asymmetric unit ( $\text{C4} \cdots \text{H4} \cdots \text{O6}$  and  $\text{C10} \cdots \text{H10} \cdots \text{O6}$ ; Table 2). This gives



**Figure 3**

The three-dimensional metal-organic framework in (I). [Symmetry codes: (vii)  $-x + 2, y + \frac{1}{2}, -z + 2$ ; (viii)  $-x + 2, y + \frac{1}{2}, -z$ .]



**Figure 4**

A schematic representation of the three-dimensional 3,5-connected topology of (I). (In the electronic version of the paper, teal-colored spheres represent the Mn nodes, red spheres represent the Ts-cmc ligands and blue lines represent the 4,4'-bipy ligands.)

a hydrogen-bonded ring motif with graph-set notation  $R_2^1(7)$  (Bernstein *et al.*, 1995). The methyl group of the tosyl fragment forms a  $C22-H22B \cdots \pi$  interaction with the  $C1-C5/N1$  pyridyl ring at  $(1-x, \frac{1}{2}+y, -z)$ , with a  $H22B \cdots Cg$  distance of 2.75 Å, a  $C22 \cdots Cg$  distance of 3.695 (16) Å and a  $C22-H22B \cdots Cg$  angle of 169°, where  $Cg$  denotes the centroid of the pyridyl ring. All of the noncovalent interactions involved in this structure play a vital role in the stabilization of the three-dimensional framework – a construct known to be difficult to stabilize when the linker is flexible as in this case.

### Experimental

A mixture of *S*-carboxymethyl-*N*-*p*-tosyl-L-cysteine (0.0667 g, 0.2 mmol), prepared according to the literature method of Chen *et al.* (2009), 4,4'-bipyridine (0.0312 g, 0.2 mmol),  $Mn(CH_3COO)_2 \cdot 4H_2O$  (0.0490 g, 0.2 mmol) and water (8 ml) was sealed in a 23 ml Teflon-lined autoclave, heated at 353 K for 6 d and cooled over a period of 48 h. Yellow crystals of (I) were collected in a yield of 63% (0.0706 g). Analysis found: C 46.85, H 4.02, N 7.28, S 11.12%;  $C_{22}H_{23}MnN_3O_7S_2$  requires: C 47.14, H 4.14, N 7.50, S 11.44%.

#### Crystal data

$[Mn(C_{12}H_{13}NO_6S_2)(C_{10}H_8N_2) \cdot (H_2O)]$	$\beta = 96.771 (9)^\circ$
$M_r = 560.49$	$V = 1210.6 (15) \text{ \AA}^3$
Monoclinic, $P2_1$	$Z = 2$
$a = 5.382 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 19.375 (14) \text{ \AA}$	$\mu = 0.77 \text{ mm}^{-1}$
$c = 11.691 (9) \text{ \AA}$	$T = 298 (2) \text{ K}$
	$0.30 \times 0.12 \times 0.09 \text{ mm}$

#### Data collection

Bruker SMART CCD area-detector diffractometer	6227 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Bruker, 1998)	3179 independent reflections
$T_{\min} = 0.803, T_{\max} = 0.934$	2615 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.053$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	H-atom parameters constrained
$wR(F^2) = 0.163$	$\Delta\rho_{\text{max}} = 1.15 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.51 \text{ e \AA}^{-3}$
3179 reflections	Absolute structure: Flack (1983),
317 parameters	983 Friedel pairs
1 restraint	Flack parameter: $-0.02 (4)$

**Table 1**

Selected geometric parameters (Å, °).

Mn1–O7	2.157 (6)	Mn1–O3 <sup>ii</sup>	2.239 (5)
Mn1–O2 <sup>i</sup>	2.164 (5)	Mn1–N2 <sup>iii</sup>	2.278 (5)
Mn1–O1	2.193 (5)	Mn1–N1	2.304 (5)
O7–Mn1–O2 <sup>i</sup>	163.6 (2)	O1–Mn1–N2 <sup>iii</sup>	93.0 (2)
O7–Mn1–O1	89.2 (2)	O3 <sup>ii</sup> –Mn1–N2 <sup>iii</sup>	87.5 (2)
O2 <sup>i</sup> –Mn1–O1	106.6 (2)	O7–Mn1–N1	87.6 (2)
O7–Mn1–O3 <sup>ii</sup>	80.0 (2)	O2 <sup>i</sup> –Mn1–N1	88.0 (2)
O2 <sup>i</sup> –Mn1–O3 <sup>ii</sup>	84.2 (2)	O1–Mn1–N1	89.9 (2)
O1–Mn1–O3 <sup>ii</sup>	169.21 (19)	O3 <sup>ii</sup> –Mn1–N1	90.1 (2)
O7–Mn1–N2 <sup>iii</sup>	95.3 (2)	N2 <sup>iii</sup> –Mn1–N1	175.8 (2)
O2 <sup>i</sup> –Mn1–N2 <sup>iii</sup>	88.4 (2)		

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

H atoms of amine groups and water molecules were located in a difference Fourier map and allowed for riding on their parent

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C14–H14 $\cdots$ O4 <sup>iv</sup>	0.98	2.46	3.243 (9)	137
C4–H4 $\cdots$ O6	0.93	2.29	3.213 (11)	171
C10–H10 $\cdots$ O6	0.93	2.50	3.426 (11)	177
N3–H3 $\cdots$ S1	0.90	2.58	3.156 (8)	122
O7–H7A $\cdots$ O2	0.85	2.23	2.928 (8)	139
O7–H7B $\cdots$ O4 <sup>ii</sup>	0.86	1.85	2.662 (9)	158
O7–H7A $\cdots$ O3 <sup>vi</sup>	0.85	2.13	2.780 (7)	132

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

atoms [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$  and  $1.2U_{\text{eq}}(\text{N})$ ]. Other H atoms were placed at calculated positions ( $C-H = 0.93-0.98 \text{ \AA}$ ) and were included in the refinement in the riding-model approximation, with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$  [ $1.5U_{\text{eq}}(\text{C})$  for methyl H atoms]. The highest difference peak is located 1.10 Å from atom Mn1.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT* and *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3174). Services for accessing these data are described at the back of the journal.

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