Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(μ-4-carboxy-2-sulfonatobenzoato)bis[aqua(2,2′-bipyridyl)manganese(II)]

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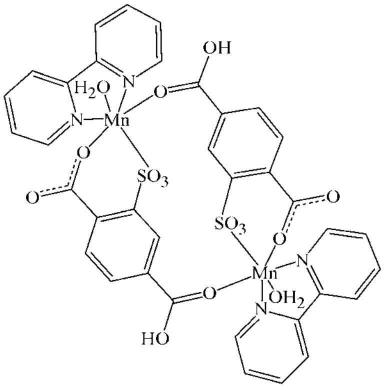
Received 11 August 2007
Accepted 15 August 2007
Online 22 September 2007

In the title compound, $[Mn_2(C_8H_4O_7S)_2(C_{10}H_8N_2)_2(H_2O)_2]$, pairs of hexacoordinated manganese(II) centres are bridged by 2-sulfonatoterephthalate(2−) anions to form cyclic centrosymmetric dimers, which are linked into sheets by O—H···O hydrogen bonds.

Comment

The rational design and synthesis of metal–organic frameworks have recently received extensive attention owing to their potential applications in catalysis, chemical separation and gas storage (Chae *et al.*, 2004; Eddaoudi *et al.*, 2002; Rosi *et al.*, 2003; Rowsell *et al.*, 2004; Seo *et al.*, 2000; Jesse & Yaghi, 2005). Multidentate *O*/*N*-donor ligands containing rigid frameworks, such as polycarboxylates, polybipyridines or their derivatives, and mixed polycarboxylate and polybipyridine ligands, have been employed to construct metal coordination frameworks (Rosi *et al.*, 2005; Zhang *et al.*, 2003; Wen *et al.*, 2007; Sun *et al.*, 2001, 2003). Among such ligands, rod-like multidentate bridging ligands, such as terephthalate (tp), are known to form one-, two- and three-dimensional coordination networks.

The coordination chemistry of the deprotonated forms of H_2tp with up to four potential O-atom donors, which can adopt different coordination modes in different chemical environments, has been widely investigated. Terephthalate anions can act as bridging ligands, forming short bridges by use of just one carboxylate unit or long bridges by use of both carboxylate groups. 2-Sulfoterephthalic acid (H_3STP) has been little explored (Horike, Matsuda, Tanaka, Matsubara *et al.*, 2006; Horike, Matsuda, Tanaka, Mizuno *et al.*, 2006). However, the sulfonate group shows interesting functional properties owing to flexible coordination modes caused by weak interactions between metal centres and the sulfonate group (Cote & Shimizu, 2003). By introduction of a soft sulfonate group into rigid multicarboxylate ligands, coordination complexes with diverse structural frameworks can be expected. We report here the synthesis and crystal structure of the title compound, (I), which exemplifies this type of coordination.



(I)

The asymmetric unit of (I) consists of one Mn^{II} ion, one 2,2′-bipyridine molecule, one $HSTP^{2-}$ anion and one water molecule (Fig. 1). The six-coordinate metal centre is located on a general position, and the N_2O_4 chromophore about the Mn centre involves the two pyridine N atoms of a 2,2′-bipyridine molecule and two *cis* carboxylate O atoms from two symmetry-related $HSTP^{2-}$ ligands at the equatorial sites; the axial positions are occupied by a water molecule and a sulfonate O atom. The Mn—N distances (Table 1) are in agreement with values observed previously (Ma *et al.*, 2004). The Mn—O distances are similar to those documented elsewhere (Chen *et al.*, 2003). The C—O distances are consistent with the location of the H atoms deduced from difference maps, which indicate that the $HSTP^{2-}$ ligand carries a charge of −2, so satisfying the charge-balance requirement. The angles subtended at Mn by *cis* pairs of ligating atoms cover the range 80.75 (10)–108.28 (9)°, and the angles subtended by the *trans* pairs are in the range 156.51 (8)–167.23 (9)°, indicating that the MnN_2O_4 unit is distorted from regular octahedral geometry.

The two symmetry-related $HSTP^{2-}$ ligands in (I) act as bridging ligands, forming long bridges that link metal centres to generate a dimeric unit containing a 16-membered ring. Although some examples of H-shaped dimeric units or pseudo-honeycomb coordination nets constructed by tp or 5-sulfoisophthalate ligands have been reported (Cano *et al.*,

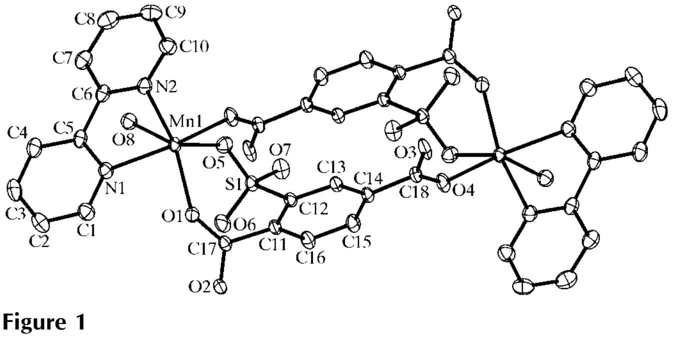


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. All H atoms have been omitted for clarity.

DOI: 10.1107/S0108270107040498

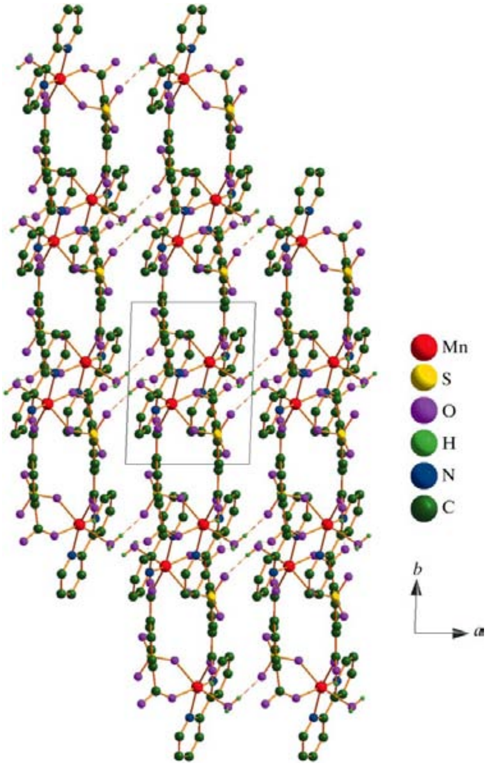


Figure 2
The extended structure of (I), viewed down [001], with hydrogen bonds shown as dashed lines. C-bound H atoms have been omitted for clarity.

1997; Chen *et al.*, 2003; Kulynych & Shimizu, 2002), the pattern found here for (I) has not been reported previously. The sulfonate groups of $HSTP^{2-}$ adopt an *O*-monodentate mode, coordinated to metal centres, similar to that of the Cu derivative (Kulynych & Shimizu, 2002) but different from that of the Cd derivative (Horike, Matsuda, Tanaka, Matsubara *et al.*, 2006; Horike, Matsuda, Tanaka, Mizuno *et al.*, 2006). The sulfonate O atom and *cis* carboxylate O atom coordinated to the metal centre form a seven-membered chelate ring. The carboxylate group acts as a bis-monodentate ligand toward two metal centres. The whole $HSTP^{2-}$ ligand adopts a μ_2 mode bridging two metal centres. The dihedral angle between the mean plane of the benzene ring and the plane of the carboxylate group is 57.0°, while the protonated carboxylate group and the aromatic ring are coplanar. The rings of the 2,2′-bipyridine ligand are also twisted by 10.55°. Three types of hydrogen bonds are observed (Table 2), and these link the dimers into sheets parallel to (001) (Fig. 2).

Experimental

A mixture of H_3STP (0.025 g, 0.1 mmol), $MnCl_2$ (0.013 g, 0.1 mmol), 2,2′-bipyridine (0.016 g, 0.1 mmol) and water (7 ml) was stirred for about 30 min. The pH of the resulting solution was adjusted to 7.0 using aqueous sodium hydroxide solution (0.1 mol dm^{-3}), and then sealed in a Teflon-lined stainless steel autoclave and heated to 393 K for 3 d. The autoclave was then allowed to cool to ambient temperature. Compound (I) was obtained as yellow block-shaped crystals, recovered by vacuum filtration and dried in air (yield *ca* 82%).

Crystal data

$[Mn_2(C_8H_4O_7S)_2(C_{10}H_8N_2)_2(H_2O)_2]$
$M_r = 946.62$
Triclinic, $P\overline{1}$
$a = 7.317$ (7) Å
$b = 9.604$ (3) Å
$c = 12.799$ (5) Å
$\alpha = 88.47$ (3)°
$\beta = 86.06$ (5)°
$\gamma = 87.74$ (5)°
$V = 896.4$ (10) Å^3
$Z = 1$
Cu $K\alpha$ radiation
$\mu = 7.58$ mm^{-1}
$T = 293$ (2) K
0.30 × 0.25 × 0.20 mm

Data collection

Oxford Diffraction four-circle diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
$T_{min} = 0.163$, $T_{max} = 0.220$
7219 measured reflections
3189 independent reflections
2685 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.105$
$S = 1.09$
3189 reflections
273 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.108 (2)	Mn1—N1	2.257 (2)
Mn1—O4^i	2.163 (2)	O1—C17	1.237 (4)
Mn1—O5	2.179 (3)	O2—C17	1.250 (3)
Mn1—O8	2.226 (3)	O3—C18	1.281 (3)
Mn1—N2	2.232 (3)	O4—C18	1.225 (3)
O1—Mn1—O4^i	92.90 (9)	O5—Mn1—N2	80.75 (10)
O1—Mn1—O5	90.57 (9)	O8—Mn1—N2	87.89 (10)
O4^i—Mn1—O5	87.09 (9)	O1—Mn1—N1	88.62 (9)
O1—Mn1—O8	104.73 (9)	O4^i—Mn1—N1	167.23 (9)
O4^i—Mn1—O8	84.08 (9)	O5—Mn1—N1	105.59 (9)
O5—Mn1—O8	162.66 (8)	O8—Mn1—N1	83.27 (9)
O1—Mn1—N2	156.51 (8)	N2—Mn1—N1	73.02 (9)
O4^i—Mn1—N2	108.28 (9)		

Symmetry code: (i) $-x+1, -y, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3$A\cdots$O2^{ii}	0.82	1.69	2.483 (4)	163
O8—H81$\cdots$O6^{iii}	0.82	1.91	2.735 (4)	175
O8—H82$\cdots$O2^{iv}	0.83	1.96	2.743 (4)	158

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

The C-bound H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with U_{iso}(H) values of $1.2U_{eq}$(C). The O-bound H atoms were located in difference maps and refined as riding in their as-found relative positions, with U_{iso}(H) values set at $1.2U_{eq}(O_{aqua})$ or $1.5U_{eq}(O_{OH})$, giving O—H distances of 0.82–0.83 Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

The authors thank Henan Institute of Science and Technology for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3138). Services for accessing these data are described at the back of the journal.

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