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catena-Poly[4,4′-bipyridinium [[diaquadisulfatomanganate(II)]-μ-4,4′-bipyridine-$\kappa^2N:N'$] dihydrate]

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.092
Data-to-parameter ratio = 11.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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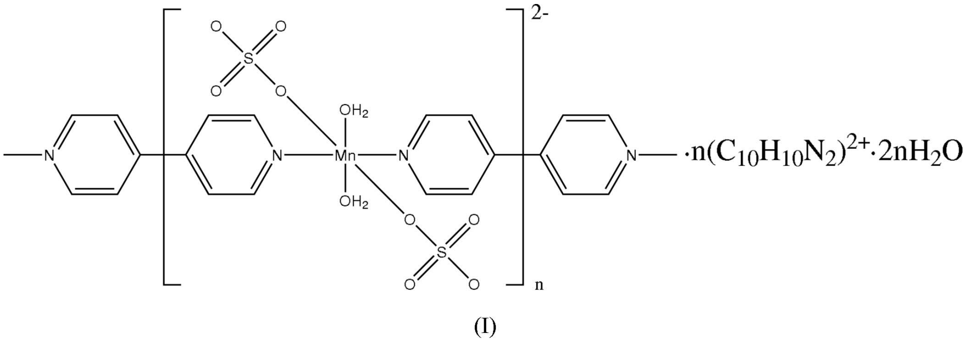
The title complex, $\{(C_{10}H_{10}N_2)[Mn(SO_4)_2(C_{10}H_8N_2)(H_2O)_2]\cdot 2H_2O\}_n$, consists of an anionic one-dimensional chain, diprotonated 4,4′-bipyridine cations and uncoordinated water molecules. In the anionic chain, the Mn atom lies on a center of inversion in an octahedral geometry. Hydrogen bonds link the chains into a three-dimensional architecture.

Comment

Recently, a great number of transition metal complexes with 4,4′-bipyridine (4,4′-bipy) and sulfate have been reported; they produce many interesting architectures, such as one-dimensional (Norquist *et al.*, 2003), two-dimensional (Huang *et al.*, 1998) and three-dimensional (Huang *et al.*, 1999; Hou *et al.*, 2001; Xu *et al.*, 2003) polymers or cation–anion complexes (Li *et al.*, 2004). In these complexes, the sulfate can exist as a bridging (Tong *et al.*, 2000) or monodentate (Kondo *et al.*, 1999) ligand, or an uncoordinated anion (Li *et al.*, 2004). 4,4′-Bipy also can act as a bridging ligand (Hagrman *et al.*, 1998) or a proton acceptor (Noro *et al.*, 1999). We present here a manganese complex, (I), with monodentate SO_4^{2-} and doubly protonated 4,4′-bipy ligands.



(I)

The title complex consists of an anionic $\{[Mn(SO_4)_2(4,4'\text{-bipy})(H_2O)_2]^{2-}\}_n$ chain, 4,4′-bipyridinium cations and uncoordinated water molecules (Fig. 1 and Table 1). In the anionic chain (Fig. 2), each Mn atom, sitting on a special position of $\overline{1}$ site symmetry, adopts an octahedral geometry defined by two N donors from two 4,4′-bipy ligands, two O atoms from two sulfate anions, and two O atoms from two water molecules. Each sulfate acts as a monodentate ligand and this is the first example of an anionic chain with monodentate SO_4^{2-} in the system M^{2+}–SO_4^{2-}–4,4′-bipy; the Mn···Mn separation is 11.7768 (10) Å. The one-dimensional chains are hold together by hydrogen-bondng interactions to give a three-dimensional network through three kinds of donors, O6, O5, and N2 (Table 2). The 4,4′-bipyridinium cation with the neighboring

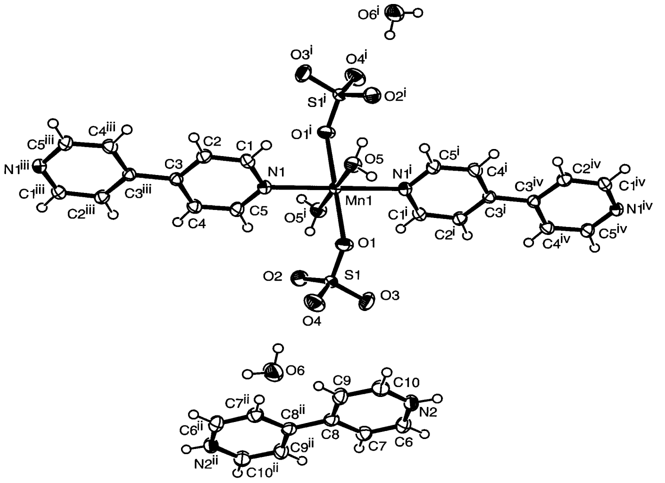


Figure 1
A view of a segment of (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $2 - x, 2 - y, 2 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $2 - x, 3 - y, 1 - z$; (iv) $x, -1 + y, 1 + z$.]

4,4′-bipy in the one-dimensional chain forms π–π interactions with a distance of about 3.47 Å and a dihedral angle of 5.41 (6)°. Therefore, in the crystal packing, hydrogen bonds and π–π interactions enhance the stability of the structure.

Experimental

A mixture of $MnSO_4 \cdot H_2O$ (0.085 g, 0.50 mmol) and 5-sulfosalicylic acid dihydrate (0.125 g, 0.49 mmol) in water (15 ml) was added to a previously prepared solution of 4,4′-bipyridine (0.078 g, 0.50 mmol) in dimethylformamide (10 ml) under stirring. The resulting solution was set aside and the solvents allowed to evaporate. After two weeks, pale-yellow needle-shaped crystals of (I) were obtained and collected by suction filtration.

Crystal data

$(C_{10}H_{10}N_2)[Mn(SO_4)_2(C_{10}H_8N_2)(H_2O)_2] \cdot 2H_2O$
$M_r = 633.51$
Triclinic, $P\overline{1}$
$a = 6.9619\ (8)$ Å
$b = 9.3723\ (11)$ Å
$c = 9.9791\ (11)$ Å
$\alpha = 74.900\ (2)^\circ$
$\beta = 89.418\ (2)^\circ$
$\gamma = 78.241\ (2)^\circ$
$V = 614.82\ (12)$ Å^3
$Z = 1$
$D_x = 1.711$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3372 reflections
$\theta = 2.3$–28.1°
$\mu = 0.78$ mm^{-1}
$T = 295\ (2)$ K
Needle, pale yellow
0.43 × 0.17 × 0.15 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{min} = 0.730$, $T_{max} = 0.892$
4433 measured reflections
2144 independent reflections
2101 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 25.0^\circ$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.092$
$S = 1.17$
2144 reflections
193 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.605P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

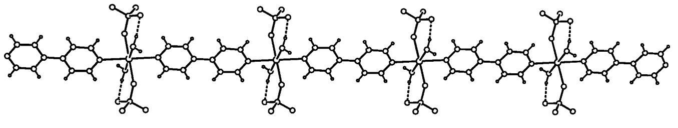


Figure 2
A view of the anionic chain in (I). Hydrogen bonds are shown as dashed lines.

Table 1
Selected geometric parameters (Å, °).

Mn1—O1	2.1453 (17)	S1—O2	1.4629 (19)
Mn1—O5	2.2117 (18)	S1—O3	1.471 (2)
Mn1—N1	2.334 (2)	S1—O4	1.469 (2)
S1—O1	1.4776 (18)		
O1^{i}—Mn1—O1	180	N1^{i}—Mn1—N1	180
O1—Mn1—O5^{i}	86.85 (7)	O2—S1—O4	110.94 (12)
O1—Mn1—O5	93.15 (7)	O2—S1—O3	109.11 (12)
O5^{i}—Mn1—O5	180	O4—S1—O3	108.75 (14)
O1—Mn1—N1^{i}	86.17 (7)	O2—S1—O1	110.66 (11)
O5—Mn1—N1^{i}	89.78 (7)	O4—S1—O1	108.30 (12)
O1—Mn1—N1	93.83 (7)	O3—S1—O1	109.04 (11)
O5—Mn1—N1	90.22 (7)		

Symmetry code: (i) $-x + 2, -y + 2, -z + 2$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6A···O4	0.86 (3)	1.98 (3)	2.792 (3)	156 (3)
O5—H5A···O4^{v}	0.85 (1)	1.92 (1)	2.762 (3)	174 (3)
O5—H5B···O2^{i}	0.85 (3)	2.01 (2)	2.809 (3)	156 (3)
O6—H6B···O2^{vi}	0.86 (1)	2.12 (1)	2.952 (3)	164 (3)
N2—H2A···O3^{vii}	0.90 (1)	1.69 (1)	2.584 (3)	172 (3)

Symmetry codes: (i) $-x + 2, -y + 2, -z + 2$; (v) $-x + 1, -y + 2, -z + 2$; (vi) $-x + 1, -y + 2, -z + 1$; (vii) $-x + 1, -y + 1, -z + 2$.

H atoms on C atoms were positioned geometrically and were included in the refinement in the riding-model approximation, with C—H = 0.93 Å and $U_{eq}(H) = 1.2U_{eq}(C)$. H atoms on N and O atoms were located in a difference Fourier map and were refined with distance restraints of O—H = 0.85 (1) Å and N—H = 0.90 (1) Å, and with a fixed isotropic displacement parameter of $U_{iso}(H) = 0.05$ Å^2.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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