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Key indicators

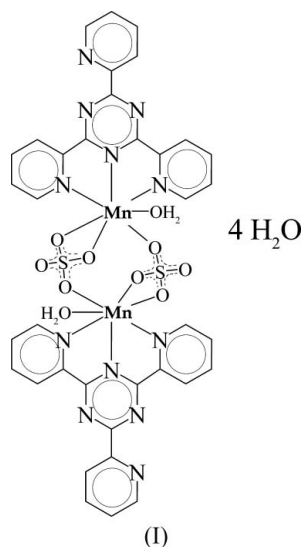
Single-crystal X-ray study
 $T = 291\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.008\text{ \AA}$
 R factor = 0.066
 wR factor = 0.109
Data-to-parameter ratio = 12.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Di- μ -sulfato- $\kappa^3\text{O},\text{O}':\text{O}'';\kappa^3\text{O},\text{O}':\text{O}''$ -bis[aqua-[2,4,6-tris(2-pyridyl)-1,3,5-triazine- $\kappa^3\text{N}^1,\text{N}^2,\text{N}^6$]-manganese(II)] tetrahydrate

The title compound, $[\text{Mn}_2(\text{SO}_4)_2(\text{C}_{16}\text{H}_{12}\text{N}_6)_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$, crystallizes as dimers built up around inversion centers. The Mn cation is seven-coordinated in the form of a pentagonal bipyramid, with three sulfate O atoms involved in its coordination (two equatorial and one axial). The sulfate species also bridge to the second Mn cation. The other three equatorial sites are occupied by N atoms from the tridentate 2,4,6-tris(2-pyridyl)-1,3,5-triazine ligand and the remaining axial site by a water molecule. This compound is isostructural with the previously reported Cd analog.

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Comment

In the past few years we have reported a number of thiosulfate and sulfite complexes obtained by decomposition of less common sulfur oxoanions such as dithionite and pyrosulfite. The important aspect is the instability of these anions in aqueous solutions (Remy, 1956), which, when interacting with transition metal ions and organic ligands, can produce a wide variety of transformation products. The high instability, which makes the chemistry of these anions so difficult, makes them attractive as precursors. Some previously unintentional outcomes (Harvey *et al.*, 2004) suggested, and further rational synthesis confirmed (Díaz de Vivar *et al.*, 2004), that the method could be an alternative route for the preparation of thiosulfate or sulfite complexes where direct synthesis had previously proven unsuccessful.



In spite of the achievements of the method in generating interesting structures, the fascinating reactions it promotes have usually remained far beyond the chemist's control and

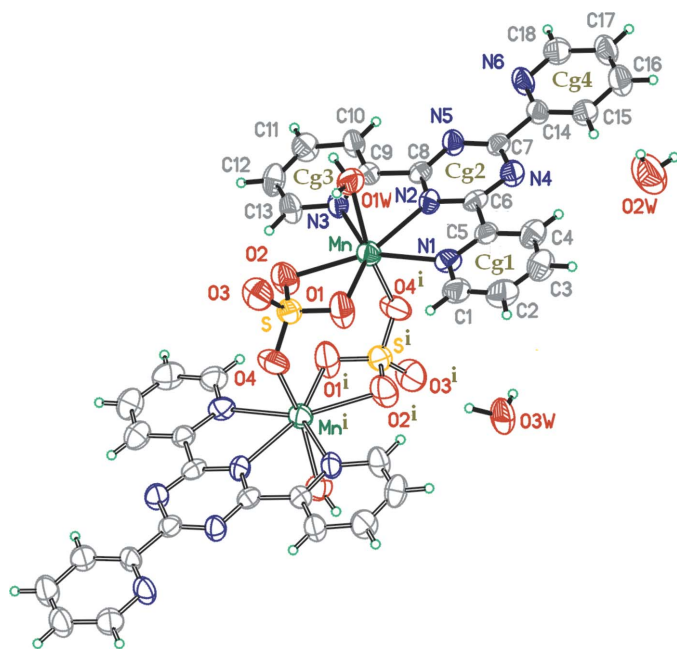


Figure 1
View of (I), showing 50% displacement ellipsoids. [Symmetry code: (i) $-x, -y, -z$.]

their outcomes have been, more often than not, mainly determined by chance. An example of this assertion is presented here, *viz.* the title compound, $[\text{Mn}(\text{SO}_4)(\text{C}_{16}\text{H}_{12}\text{N}_6)(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, (I), a manganese sulfate complex serendipitously obtained when aiming for the thiosulfate analog.

Compound (I) is a dimeric centrosymmetric species isostructural to the Cd analog obtained by a conventional synthesis starting from a sulfate salt (Harvey *et al.*, 2003). Compound (I) displays a seven-coordinate environment around the Mn ion, with three N atoms from a tridentate 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tpt) molecule, one O atom from a water molecule and three further O atoms from each of two symmetry-related sulfate ions, each one of which binds to two metal centers, thus generating the dimeric structure (Fig. 1).

The coordination polyhedron about Mn can be described as a distorted pentagonal bipyramid, with the equatorial plane formed by atoms N1, N2, N3, O1 and O2 [maximum deviation from the mean plane = 0.04 (1) Å for N2] and equatorial angles subtended at the Mn site ranging from 60.49 (11) to 85.09 (12)° (ideal 72°). The axial sites are occupied by O1W and O4ⁱ [symmetry code: (i) $-x, -y, -z$] and they subtend an angle of 167.75 (12)° at the metal.

The S—O distances in the sulfate group are all similar (Table 1), suggesting double-bond delocalization. The mean value [1.461 (9) Å] is similar to that reported for the free anion; a search in the November 2004 version of the Cambridge Structural Database (CSD; Allen, 2002) gave a mean value of 1.472 (8) Å for 118 structures with $R < 0.05$.

The tpt anion is almost planar and acts as a tridentate species, with its central Mn—N bond [2.257 (3) Å] being significantly shorter than the lateral ones [2.376 (4) and 2.378 (4) Å]. The ligand does not show any abnormal features,

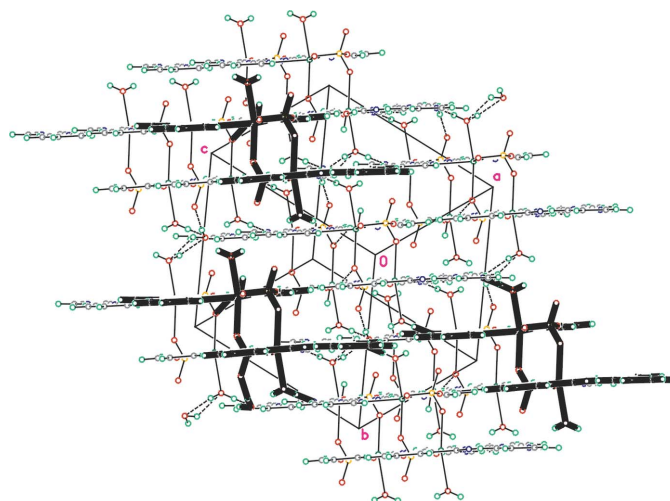


Figure 2
Packing view of (I) along the planes, which are seen as horizontal lines. Selected dimers are drawn in heavy full lines so as to distinguish them from the background. Hydrogen bonds are shown as dashed lines.

with its three bound rings being almost coplanar: the atoms deviate, on average, from an ideal plane by less than 0.02 (1) Å. The terminal pyridyl ring deviates from planarity by less than 0.01 (1) Å and the dihedral angle it makes with the metal-bonded ring system is 3.6 (1)°.

As a result of the dimers being located around an inversion center, their planar tpt molecules are parallel to each other. Crystal symmetry preserves the orientation of the dimeric units, which stack in sets of parallel planes, alternately sharing one of the two layers in the double molecular units. This disposition (Fig. 2) results in a set of interleaved planar arrays at a nearly graphitic (*ca.* 3.6 Å) distance from one another. Thus, the molecules of (I) are linked by π – π interactions between aromatic rings (Table 3) as well as an extensive hydrogen-bonding network, having all the available water molecules as donors and some water O atoms, tpt N atoms and some sulfate O atoms as acceptors (Table 2).

Experimental

A 96% ethanol solution of 2,2′-dipyridylamine was diffused into an aqueous solution containing $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, sodium dithionite and potassium pyrosulfite (1:1:2 molar ratio). After two weeks a few colorless prisms of (I) suitable for X-ray analysis were obtained.

Crystal data

$[\text{Mn}_2(\text{SO}_4)_2(\text{C}_{16}\text{H}_{12}\text{N}_6)_2 \cdot (\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$
 $M_r = 1034.77$
 Triclinic, $P\bar{1}$
 $a = 8.8737$ (16) Å
 $b = 10.5634$ (19) Å
 $c = 12.587$ (2) Å
 $\alpha = 103.566$ (3)°
 $\beta = 97.981$ (3)°
 $\gamma = 110.409$ (3)°
 $V = 1042.9$ (3) Å³

$Z = 1$
 $D_x = 1.648$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1017 reflections
 $\theta = 5.1$ – 43.9 °
 $\mu = 0.79$ mm⁻¹
 $T = 291$ (2) K
 Prism, colorless
 $0.22 \times 0.16 \times 0.14$ mm

Data collection

Bruker SMART CCD diffractometer	4041 independent reflections
φ and ω scans	2775 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$R_{\text{int}} = 0.058$
$T_{\text{min}} = 0.846$, $T_{\text{max}} = 0.898$	$\theta_{\text{max}} = 26.0^\circ$
8696 measured reflections	$h = -10 \rightarrow 10$
	$k = -13 \rightarrow 12$
	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 2.08P]$
$R[F^2 > 2\sigma(F^2)] = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} = 0.026$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.46 \text{ e } \text{\AA}^{-3}$
4041 reflections	$\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{\AA}^{-3}$
319 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected interatomic distances (\AA).

Mn—O4 ⁱ	2.148 (3)	Mn—N3	2.378 (4)
Mn—N2	2.257 (3)	S—O3	1.450 (3)
Mn—O1W	2.262 (3)	S—O2	1.457 (3)
Mn—O2	2.297 (3)	S—O4	1.463 (3)
Mn—O1	2.298 (3)	S—O1	1.473 (3)
Mn—N1	2.376 (4)		

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3W—H3WA \cdots O3 ⁱ	0.83 (4)	2.04 (3)	2.811 (5)	155 (4)
O3W—H3WB \cdots O3 ⁱⁱ	0.83 (4)	2.01 (2)	2.833 (5)	169 (4)
O2W—H2WB \cdots O4 ⁱⁱⁱ	0.83 (4)	2.43 (2)	3.052 (6)	132 (4)
O2W—H2WA \cdots O3 ⁱⁱⁱ	0.83 (4)	2.46 (2)	3.130 (5)	139 (4)
O1W—H1WA \cdots N6 ^{iv}	0.83 (4)	2.08 (2)	2.867 (5)	158 (4)
O1W—H1WB \cdots O3W ^v	0.83 (4)	1.98 (2)	2.785 (5)	162 (4)

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

Table 3

 π - π contacts for (I).

Group 1 \cdots group 2	cpd (\AA)	ccd (\AA)	sa ($^\circ$)
Cg1 \cdots Cg3 ^{vi}	3.628 (3)	3.36 (2)	22.2 (10)
Cg1 \cdots Cg4 ^{vii}	3.593 (3)	3.34 (4)	21.4 (17)
Cg2 \cdots Cg3 ^{iv}	3.694 (3)	3.34 (3)	25.4 (9)

cpd: (average) centroid-to-plane distance; ccd: centroid-to-centroid distance; sa: slippage angle (average angle between the intercentroid vector and one plane normal). For symmetry codes, see Table 2. Cg1–Cg4 are the centroids of the rings as defined in Fig. 1.

H atoms attached to C atoms were placed at calculated positions (C—H = 0.93 \AA) and refined as riding. H atoms of water molecules were located in difference maps and refined with restrained O—H distances of 0.85 (2) \AA . The constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$ was applied in all cases.

Data collection: SMART-NT (Bruker, 2001); cell refinement: SAINT-NT (Bruker, 2000); data reduction: SAINT-NT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL/PC (Sheldrick, 1994); software used to prepare material for publication: SHELXL97.

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