

Poly[[diaqua(*N,N*-dimethylformamide- κ O)manganese(II)]- μ_3 -sulfato]

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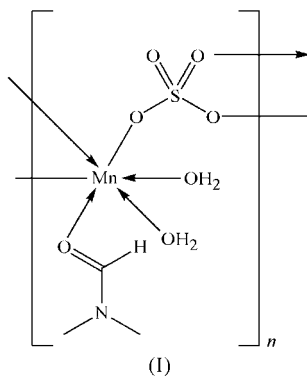
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In the title complex, $[\text{Mn}(\text{SO}_4)(\text{C}_3\text{H}_7\text{NO})(\text{H}_2\text{O})_2]_n$, each Mn^{II} ion has a distorted octahedral geometry formed by three O atoms of three different sulfate groups, one O atom of a dimethylformamide ligand and two water molecules. The sulfate groups act as tridentate bridging ligands connecting the Mn^{II} ions into a two-dimensional layer structure which can be regarded as a 4.8^2 network.

Comment

Inorganic open-framework structures involving aluminosilicates (Breck, 1974), silicates (Breck, 1974), phosphates (Cheetham *et al.*, 1999) and carboxylates (Guillou *et al.*, 2002), which include not only three-dimensional structures with channels but also structures with two-dimensional layers and one-dimensional chains (Rao *et al.*, 2001), have been widely investigated in the past few years. Recently, there has been growing interest in the study of open-framework architectures containing oxoanions of sulfur and selenium (Choudhury *et al.*, 2002, and references therein). To date, several layered sulfates of iron (Paul, Choudhury, Sampathkumaran *et al.*, 2002),



nickel (Behera *et al.*, 2004) and cadmium (Paul, Choudhury & Rao, 2002) have been reported, but among the transition metal sulfates, layered manganese sulfates have not been synthesized. In this article, we report the synthesis and struc-

ture of the title compound, $[\text{Mn}(\text{SO}_4)(\text{DMF})(\text{H}_2\text{O})_2]_n$ (DMF is dimethylformamide), (I), which was obtained by accident in the reaction of 2-(2-hydroxy-3-methoxybenzylidene)-*N*-phenylhydrazinecarbothioamide and $\text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ in MeOH–DMF solution.

The molecular structure of complex (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The asymmetric unit consists of one Mn^{II} ion, one DMF ligand, one sulfate ion and two coordinated water molecules. The coordinated O1W water molecule forms intramolecular hydrogen bonds with O atoms of the sulfate group. Each Mn^{II} ion displays a slightly distorted octahedral geometry involving three O atoms of three different sulfate groups, one O atom of the DMF ligand and two water molecules. The equatorial plane is defined by atoms O1W, O1, O2ⁱ and O3ⁱ [the deviation from the mean plane is 0.06 (3) Å and the displacement of the Mn^{II} atom from this plane is 0.119 (3) Å; symmetry code: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$], while the axial positions are occupied by atoms O2W and O5. The average Mn–O(water) distance is somewhat longer than that of Mn–O(sulfate), while the Mn–O(DMF) distance is the shortest.

In the previously reported layered transition metal sulfates, the sulfate groups have two kinds of coordination modes, namely tridentate bridging for Fe, tetradentate bridging for Cd and both for Ni. In (I), the sulfate groups only act as tridentate bridging ligands connecting the Mn^{II} ions into a two-dimensional inorganic layer structure. By treating the Mn centre and S atoms of the μ_3 -sulfate groups as nodes and connecting the nodes according to the connectivity, the two-dimensional structure is comprised of an octagonal and rhombic mesh with a three-connected 4.8^2 topology (Fig. 2*a*). The diagonals of the distorted rhombic windows are about 4.385 (2) and 5.247 (2) Å, while the dimensions of the distorted octagonal windows, estimated from the maximum distances between opposite vertices, are about 9.743 (2) and 11.01 (2) Å. Therefore, the inorganic layer is built up of eight-membered rings

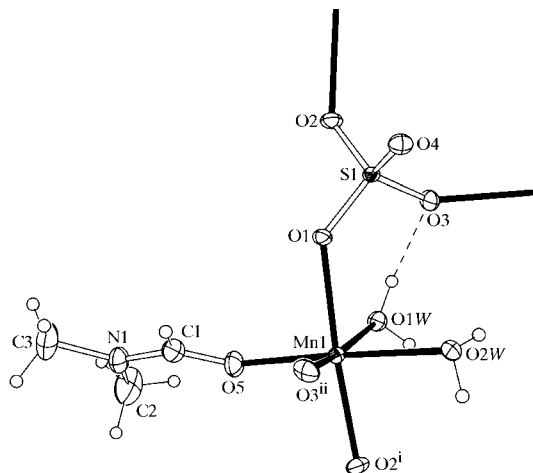


Figure 1
ORTEP plot (Johnson, 1976) of the title complex, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The hydrogen bond is denoted by a dashed line.

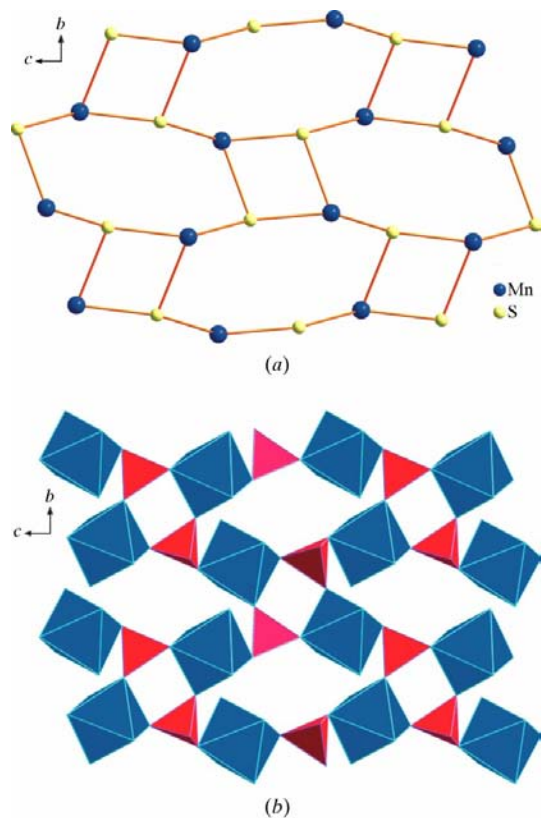


Figure 2
(a) The layer structure of 4.8^2 topology and (b) a polyhedral representation of the inorganic layer in (I) in the bc plane.

formed by two MnO_6 octahedra and two SO_4 tetrahedra, and 16-membered rings formed by four MnO_6 octahedra and four SO_4 tetrahedra linked through shared vertices (Fig. 2b). Such layers are further held together by van der Waals interactions to form eight- and 16-membered channels along the a axis, in which the 16-membered channels are filled by the DMF molecules and coordinated water molecules which interact with the framework O atoms through strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2).

Experimental

A methanol solution (10 ml) containing manganese sulfate hexahydrate (0.130 g, 0.5 mmol) was added to a dimethylformamide solution (5 ml) of 2-(2-hydroxy-3-methoxybenzylidene)-*N*-phenylhydrazinecarbothioamide (0.15 g, 0.5 mmol). The final solution was allowed to evaporate at room temperature, and colourless prismatic crystals of (I) were separated from the filtered solution after several weeks. Analysis calculated for $\text{C}_3\text{H}_{11}\text{MnNO}_7\text{S}$: C 13.85, H 4.26, N 5.38%; found: C 13.76, H 4.33, N 5.44%.

Crystal data

$[\text{Mn}(\text{SO}_4)(\text{C}_3\text{H}_7\text{NO})(\text{H}_2\text{O})_2]$	$V = 963.0 (4) \text{ \AA}^3$
$M_r = 260.13$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.890 (2) \text{ \AA}$	$\mu = 1.60 \text{ mm}^{-1}$
$b = 7.7642 (16) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 12.272 (3) \text{ \AA}$	$0.36 \times 0.28 \times 0.19 \text{ mm}$
$\beta = 111.87 (3)^\circ$	

Data collection

Rigaku R-Axis RAPID diffractometer	9196 measured reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	2201 independent reflections
$T_{\min} = 0.593, T_{\max} = 0.731$	2117 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.055$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
$S = 1.08$	$\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$
2201 reflections	
132 parameters	
6 restraints	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Mn1—O1W	2.2261 (11)	Mn1—O2 ⁱ	2.1450 (13)
Mn1—O2W	2.2322 (11)	Mn1—O3 ⁱⁱ	2.1605 (10)
Mn1—O1	2.2185 (13)	Mn1—O5	2.1271 (11)
O5—Mn1—O3 ⁱⁱ	98.26 (4)	O3 ⁱⁱ —Mn1—O1W	166.43 (4)
O2 ⁱ —Mn1—O3 ⁱⁱ	97.30 (4)	O1—Mn1—O1W	83.96 (4)
O2 ⁱ —Mn1—O1	175.27 (4)	O5—Mn1—O2W	177.55 (4)
O3 ⁱⁱ —Mn1—O1	85.96 (4)	O3 ⁱⁱ —Mn1—O2W	82.44 (4)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2

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

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1W—H1W1 \cdots O4 ⁱⁱⁱ	0.849 (9)	1.922 (15)	2.7591 (16)	168.3 (16)
O1W—H1W2 \cdots O3	0.848 (9)	2.024 (11)	2.8164 (16)	155.3 (18)
O2W—H2W1 \cdots O4 ⁱ	0.851 (9)	1.939 (11)	2.7599 (18)	161.7 (19)
O2W—H2W2 \cdots O1 ⁱⁱⁱ	0.838 (9)	1.948 (9)	2.7851 (14)	175.8 (17)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

Carbon-bound H atoms were placed in calculated positions, with $\text{C}-\text{H} = 0.93 \text{ \AA}$, and were refined in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the water molecules were located in a difference Fourier map and refined with $\text{O}-\text{H}$ and $\text{H}\cdots\text{H}$ distance restraints of 0.85 (1) and 1.39 (1) \AA , respectively, 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/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); 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: SQ3072). Services for accessing these data are described at the back of the journal.

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