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Tetraaqua(1,10-phenanthroline-κ^2N,N')manganese(II) sulfate dihydrate

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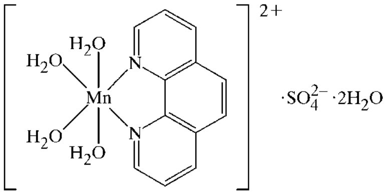
The title compound, $[Mn(C_{12}H_8N_2)(H_2O)_4]SO_4·2H_2O$, was obtained unexpectedly as a by-product from the reaction of sodium maleate, 1,10-phenanthroline (phen) and manganese sulfate tetrahydrate. The Mn atom is coordinated by the two N atoms of the phen ligand and four water O atoms in a highly distorted octahedral geometry, with Mn—O distances in the range 2.155 (2)–2.203 (2) Å and Mn—N distances of 2.254 (2) and 2.272 (3) Å. Extensive hydrogen-bonding interactions involving the water molecules and sulfate anions, and stacking interactions involving the phen rings, are observed in the crystal structure.

Comment

It has been well established that manganese is one of the trace elements in biosystems and that it plays an important role in the active sites of various redox-based enzymes (Weighardt, 1989). In addition to the best known oxygen-evolving complex (OEC), which is believed to contain a tetranuclear manganese cluster catalyzing the oxidation of water to yield dioxygen during photosynthesis (Debus, 1992), there are three manganese enzymes containing a mononuclear manganese site, *viz.* superoxide dismutase, peroxidase and dioxygenase, which participate in redox changes in biological systems (Law *et al.*, 1999). Carboxylate-bridged complexes containing 1,10-phenanthroline (phen) or bipyridine (bpy) are often employed to mimic the function and structure of these active sites built on the knowledge that the Mn centers in these enzymes are predominately coordinated by *N*,*O*-donors from available amino acid side chains (Pecoraro & Butler, 1986). With the initial intention of preparing a maleate-bridged poly-manganese complex, we obtained the title compound, (I), unexpectedly. Compound (I) represents a new example of mononuclear manganese, with only one phen ligand and with sulfate as counter-ion, though a similar complex, $[Mn(C_{12}H_8N_2)(H_2O)_3(SO_4)]$ has been reported (Zheng *et al.*, 2000).



(I)

The title compound (Fig. 1) consists of a discrete non-centrosymmetric $[Mn(phen)(H_2O)_4]^{2+}$ unit, a sulfate anion and two solvate water molecules. The Mn atom displays a distorted octahedral environment (Table 1). The two phen N atoms and two water O atoms (O1 and O3) define one octahedral equatorial plane, with a maximum deviation of 0.181 (4) Å for atom N1, with the Mn atom lying 0.015 (5) Å out of the plane. The O atoms of the remaining two water molecules complete the octahedron through coordination in the axial positions. The phen rings are nearly planar, with a mean atomic deviation of 0.022 (1) Å. A small dihedral angle of 9.40 (1)° was found between phen and the above-mentioned equatorial planes, indicating that the phen plane can be extended to involve atoms O1 and O3. The mean Mn—N bond length [2.263 (4) Å] is in agreement with that reported in other Mn–phen complexes, *e.g.* $[Mn(phen)_2Cl(H_2O)]^+$ [2.270 (1) Å; Ma *et al.*, 2001], but longer than that found in the nickel analog [2.069 (2) Å; Cherni *et al.*, 1999], due to the larger radius of the Mn^{II} ion. The angle that is most distorted from the ideal value of 180° is O3—Mn—N2 of 161.76 (10)°, and the phen N1—Mn—N2 chelate angle of 73.33 (10)° is as expected for a manganese complex (Drew *et al.*, 1989; McCann *et al.*, 1997; Ramalakshmi *et al.*, 1999; Wang *et al.*, 2000; Deng *et al.*, 2000). The bond distances and angles in the phen ligand are consistent with those in the free base (Nishigaki *et al.*, 1978), and the S—O bond distances [1.464 (2)–1.478 (2) Å] and O—S—O angles [109.0 (1)–109.8 (1)°] approximate to the respective values of an ideal tetrahedral S-atom environment.

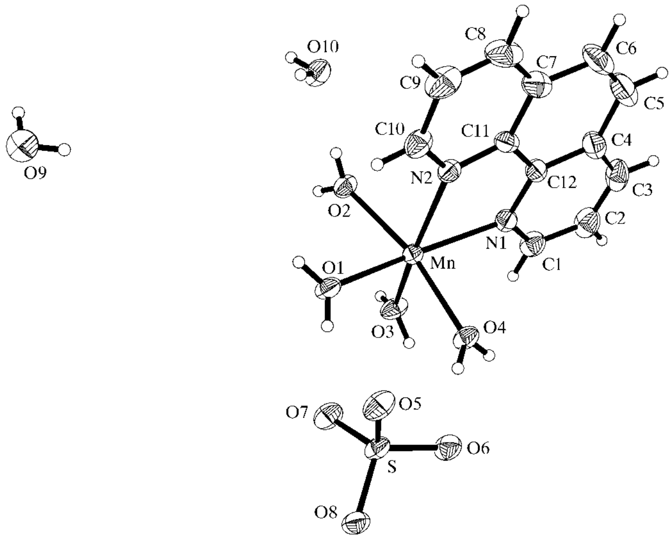


Figure 1
Displacement-ellipsoid drawing of the title compound, with the atomic labeling scheme and 30% probability displacement ellipsoids.

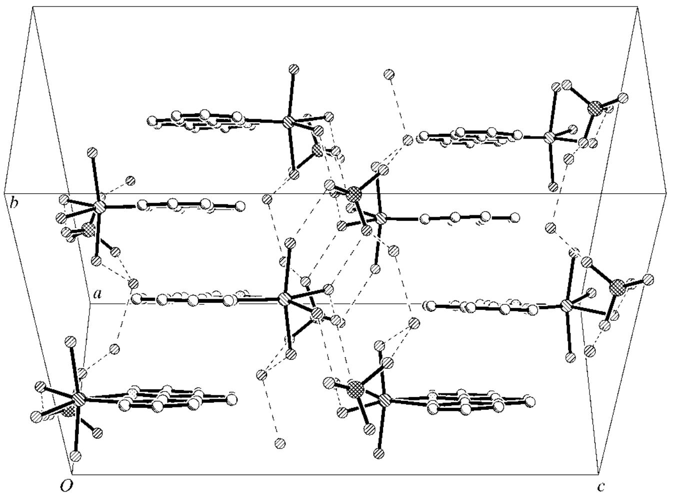


Figure 2
Packing diagram of the title compound, showing the complex hydrogen-bonding and π–π-stacking interactions. Hydrogen bonds are depicted by dashed lines.

As shown in Fig. 2, extensive intermolecular hydrogen bonds link $[Mn(phen)(H_2O)_4]^{2+}$ cations to uncoordinated water molecules and sulfate anions (Table 2), creating a three-dimensional suspended ladder-like framework. Additionally, there is a π–π-stacking interaction between phen ligands, which are arranged in an alternate head-to-tail manner, resulting in a ring separation of 3.561 (1) Å, which is close to the sum of the van der Waals radii of two C atoms (Bondi, 1964). The two types of interaction produce the special solid-state crystal structure seen in (I) and promote the stabilization of the structure.

Experimental

To an aqueous ethanol solution (30 ml, *ca* 1:1, *v*/*v*) containing $MnSO_4{\cdot}4H_2O$ (2 mmol) and sodium maleate (2 mmol), 1,10-phenanthroline (4 mmol) was added slowly with continuous stirring. The resulting suspension was refluxed for 8 h and then filtered. The red filtrate was maintained at room temperature for 25 d, after which time, colorless crystals of the title compound suitable for X-ray diffraction analysis were obtained.

Crystal data

$[Mn(C_{12}H_8N_2)(H_2O)_4]SO_4{\cdot}2H_2O$
$M_r = 439.30$
Orthorhombic, *Pbca*
$a = 8.8713$ (2) Å
$b = 18.5116$ (1) Å
$c = 22.1042$ (5) Å
$V = 3630.00$ (12) Å^3
$Z = 8$
$D_x = 1.608$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5079 reflections
$\theta = 1.8$–25.1°
$\mu = 0.90$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.57 × 0.44 × 0.37 mm

Data collection

Siemens CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.526$, $T_{max} = 0.718$
11 327 measured reflections
3190 independent reflections
2293 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 25.1°$
$h = -10 \rightarrow 10$
$k = -22 \rightarrow 20$
$l = -19 \rightarrow 26$

Table 1
Selected geometric parameters (Å, °).

Mn—O3	2.155 (2)	Mn—O1	2.203 (2)
Mn—O4	2.159 (2)	Mn—N2	2.254 (2)
Mn—O2	2.184 (2)	Mn—N1	2.272 (3)
O3—Mn—O4	87.74 (9)	O2—Mn—N2	86.68 (9)
O3—Mn—O2	86.73 (10)	O1—Mn—N2	98.33 (9)
O4—Mn—O2	168.42 (9)	O3—Mn—N1	91.67 (10)
O3—Mn—O1	97.90 (10)	O4—Mn—N1	87.24 (9)
O4—Mn—O1	86.43 (9)	O2—Mn—N1	103.08 (9)
O2—Mn—O1	84.26 (9)	O1—Mn—N1	168.30 (10)
O3—Mn—N2	161.76 (10)	N2—Mn—N1	73.33 (10)
O4—Mn—N2	101.51 (9)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···O7	0.85 (3)	1.85 (3)	2.692 (3)	172 (3)
O2—H2*C*···O10	0.83 (3)	1.85 (3)	2.678 (3)	175 (3)
O4—H4*B*···O6	0.84 (3)	1.94 (3)	2.773 (4)	173 (3)
O1—H1*C*···O5^{i}	0.90 (4)	1.80 (4)	2.687 (3)	171 (4)
O2—H2*B*···O1^{ii}	0.82 (3)	2.18 (3)	3.000 (4)	177 (3)
O3—H3*C*···O5^{iii}	0.84 (2)	1.90 (2)	2.736 (4)	171 (2)
O3—H3*B*···O6^{iv}	0.83 (2)	1.96 (2)	2.797 (3)	176 (2)
O4—H4*A*···O8^{iv}	0.82 (3)	1.86 (3)	2.677 (3)	175 (3)
O9—H9*B*···O6^{i}	0.83 (4)	2.08 (4)	2.855 (4)	156 (4)
O9—H9*C*···O7^{v}	0.84 (4)	2.06 (4)	2.901 (4)	178 (4)
O10—H10*B*···O8^{i}	0.83 (3)	2.02 (3)	2.849 (4)	173 (3)
O10—H10*C*···O9^{vi}	0.84 (3)	1.93 (3)	2.756 (4)	169 (3)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.097$
$S = 1.04$
3190 reflections
284 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 1.5395P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0031 (3)

H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.93 Å, and treated as riding atoms. Water H atoms were located from difference maps and refined isotropically; 11 O—H distances involving the water molecules were restrained to be 0.85 (2) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: NA1575). Services for accessing these data are described at the back of the journal.

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