Crystal structure of *trans*-triaqua(1,10-phenanthroline-*N,N'*)sulfato-manganese(II), $\text{Mn}(\text{H}_2\text{O})_3(\text{C}_{12}\text{H}_8\text{N}_2)\text{SO}_4$

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Abstract

$\text{C}_{12}\text{H}_{14}\text{MnN}_2\text{O}_7\text{S}$, monoclinic, $P12_1/c1$ (No. 14), $a = 12.020(1) \text{ \AA}$, $b = 10.082(1) \text{ \AA}$, $c = 13.847(1) \text{ \AA}$, $\beta = 111.88(1)^\circ$, $V = 1557.2 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.032$, $wR_{\text{ref}}(F^2) = 0.087$, $T = 293 \text{ K}$.

Source of material

10.0 ml CH_3OH was added to an aqueous solution of 0.23 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (1.36 mmol) dissolved in 10.0 ml H_2O , producing a colorless solution, to which 0.26 g (1.31 mmol) 1,10-phenanthroline monohydrate was added under continuous stirring. The mixture was then further stirred, yielding pale yellow precipitate. After filtration, the yellowish filtrate was allowed to stand at room temperature. Slow evaporation afforded a mixture of yellow crystals and colorless plate-like crystals. The X-ray crystal structure determinations showed that the former ones are from the title compound *trans*- $\text{Mn}(\text{H}_2\text{O})_3(\text{phen})\text{SO}_4$ and the later ones belong to the *cis*- $\text{Mn}(\text{H}_2\text{O})_3(\text{phen})\text{SO}_4$ isomer [1].

Discussion

The crystal structure of the title compound is built up by the *trans*- $[\text{Mn}(\text{H}_2\text{O})_3(\text{phen})\text{SO}_4]$ complex molecules, within which the Mn atoms are each surrounded by two N and four O atoms from one phen ligand, one sulfato ligand and three H_2O molecules to complete distorted octahedra with two water O atoms at the *trans* positions ($d(\text{Mn}—\text{O}) = 2.128(2) \text{ \AA} - 2.208(2) \text{ \AA}$, $d(\text{Mn}—\text{N}) = 2.262(2) \text{ \AA} - 2.285(2) \text{ \AA}$). The *trans*- $[\text{Mn}(\text{H}_2\text{O})_3(\text{phen})\text{SO}_4]$ complex molecule display one strong intramolecular hydrogen bond with $d(\text{O}(6)—\text{H} \cdots \text{O}(2)) = 2.713 \text{ \AA}$ and $\angle \text{O}(6)—\text{H} \cdots \text{O}(2) = 165^\circ$. Through the intermolecular hydrogen bonds present be-

tween the water O atom and the non-coordinating sulfato O atom ($d(\text{O}—\text{H} \cdots \text{O}) = 2.714 \text{ \AA} - 2.798 \text{ \AA}$ and $\angle \text{O}—\text{H} \cdots \text{O} = 167^\circ - 176^\circ$), the *trans*- $[\text{Mn}(\text{H}_2\text{O})_3(\text{phen})\text{SO}_4]$ complex molecules are assembled into 2D layers parallel to (001) with the chelating phen ligands distributed on both sides. Interdigitation of the phen ligands of the neighboring layers satisfies well the requirement of the significant intermolecular π - π stacking interactions, in which the quinoline fragments of the phen ligands are partially engaged with a mean interplanar distance of 3.42 $\text{\AA}$. The sulfato group exhibits considerable deviation from a T_d symmetry on the basis of the S—O bond distances varying over the range 1.452 $\text{\AA} - 1.488 \text{ \AA}$ and the O—S—O bond angles of $109.0^\circ - 110.4^\circ$. Except the S—O bond to the coordinating O(1) atom, the remaining S—O bond length increases with the number of the hydrogen bonds to the sulfato O atom.

Table 1. Data collection and handling.

Crystal:	yellow block, size $0.222 \times 0.289 \times 0.578 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71073 \text{ \AA}$)
μ :	10.19 cm^{-1}
Diffractionmeter, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{\text{max}}$:	55°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4540, 3574
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3021
$N(\text{param})_{\text{refined}}$:	265
Programs:	SHELXS-97 [2], SHELXL-97 [3]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.682(3)	0.386(3)	0.117(3)	0.08(1)
H(2)	4e	0.480(3)	0.396(4)	0.099(3)	0.11(1)
H(3)	4e	0.349(3)	0.249(3)	-0.019(3)	0.068(9)
H(5)	4e	0.313(3)	0.074(3)	-0.146(3)	0.08(1)
H(6)	4e	0.379(3)	-0.080(4)	-0.244(3)	0.09(1)
H(8)	4e	0.555(3)	-0.166(4)	-0.275(3)	0.10(1)
H(9)	4e	0.756(3)	-0.155(3)	-0.243(3)	0.08(1)
H(10)	4e	0.878(3)	0.003(3)	-0.127(2)	0.065(8)
HA(O5)	4e	0.952(3)	0.441(3)	0.146(2)	0.056(8)
HB(O5)	4e	0.983(3)	0.349(3)	0.212(2)	0.066(9)
HA(O6)	4e	0.811(3)	0.494(3)	-0.053(2)	0.067(9)
HB(O6)	4e	0.858(3)	0.417(3)	-0.106(2)	0.057(8)
HA(O7)	4e	0.934(3)	0.100(3)	0.205(3)	0.069(9)
HB(O7)	4e	0.906(2)	0.004(3)	0.132(2)	0.056(8)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mn	4e	0.85917(2)	0.23587(3)	0.02227(2)	0.0276(2)	0.0253(2)	0.0310(2)	−0.0028(1)	0.0089(1)	−0.0001(1)
N(1)	4e	0.6676(2)	0.2468(2)	0.0181(2)	0.0380(9)	0.0344(9)	0.047(1)	0.0005(7)	0.0212(8)	−0.0025(7)
N(2)	4e	0.7528(2)	0.0792(2)	−0.0917(1)	0.0316(8)	0.0323(8)	0.0344(8)	−0.0007(7)	0.0111(7)	−0.0023(7)
C(1)	4e	0.6260(3)	0.3290(3)	0.0713(2)	0.062(2)	0.048(1)	0.071(2)	0.004(1)	0.040(1)	−0.011(1)
C(2)	4e	0.5055(3)	0.3338(3)	0.0594(3)	0.071(2)	0.063(2)	0.090(2)	0.020(2)	0.054(2)	0.004(2)
C(3)	4e	0.4264(3)	0.2497(3)	−0.0081(3)	0.043(1)	0.075(2)	0.083(2)	0.022(1)	0.039(2)	0.031(2)
C(4)	4e	0.4660(2)	0.1601(2)	−0.0657(2)	0.030(1)	0.054(1)	0.053(1)	0.0050(9)	0.0150(9)	0.024(1)
C(5)	4e	0.3889(2)	0.0697(3)	−0.1396(2)	0.027(1)	0.076(2)	0.065(2)	−0.008(1)	0.006(1)	0.025(2)
C(6)	4e	0.4301(2)	−0.0131(3)	−0.1929(2)	0.043(1)	0.073(2)	0.051(1)	−0.025(1)	−0.005(1)	0.006(1)
C(7)	4e	0.5553(2)	−0.0162(2)	−0.1778(2)	0.047(1)	0.048(1)	0.035(1)	−0.015(1)	0.0025(9)	0.001(1)
C(8)	4e	0.6047(3)	−0.1043(3)	−0.2285(2)	0.077(2)	0.057(2)	0.052(2)	−0.025(2)	0.014(1)	−0.023(1)
C(9)	4e	0.7239(3)	−0.1012(3)	−0.2112(2)	0.083(2)	0.052(2)	0.057(2)	−0.003(1)	0.029(2)	−0.022(1)
C(10)	4e	0.7954(2)	−0.0065(2)	−0.1414(2)	0.047(1)	0.042(1)	0.047(1)	0.002(1)	0.019(1)	−0.009(1)
C(11)	4e	0.6341(2)	0.0735(2)	−0.1078(2)	0.0305(9)	0.0320(9)	0.0309(9)	−0.0044(7)	0.0064(7)	0.0047(7)
C(12)	4e	0.5891(2)	0.1631(2)	−0.0499(2)	0.0270(9)	0.034(1)	0.038(1)	0.0010(8)	0.0118(8)	0.0115(8)
S	4e	1.06905(4)	0.28041(4)	−0.08316(4)	0.0308(2)	0.0216(2)	0.0340(2)	−0.0006(2)	0.0143(2)	−0.0013(2)
O(1)	4e	1.0063(1)	0.2094(2)	−0.0260(1)	0.0398(8)	0.0458(9)	0.060(1)	0.0116(7)	0.0276(7)	0.0246(8)
O(2)	4e	0.9870(1)	0.3815(2)	−0.1516(1)	0.0526(9)	0.0315(7)	0.0422(8)	0.0117(6)	0.0222(7)	0.0105(6)
O(3)	4e	1.1030(1)	0.1853(1)	−0.1479(1)	0.0526(9)	0.0285(7)	0.0444(8)	0.0033(6)	0.0200(7)	−0.0082(6)
O(4)	4e	1.1753(1)	0.3457(2)	−0.0112(2)	0.0343(8)	0.052(1)	0.074(1)	−0.0068(7)	0.0155(8)	−0.0298(9)
O(5)	4e	0.9291(2)	0.3663(2)	0.1552(1)	0.075(1)	0.0276(8)	0.0365(8)	−0.0144(8)	0.0004(8)	0.0008(7)
O(6)	4e	0.8076(1)	0.4124(2)	−0.0792(1)	0.0383(8)	0.0312(8)	0.0404(8)	0.0043(6)	0.0142(7)	0.0036(6)
O(7)	4e	0.9144(2)	0.0834(2)	0.1395(1)	0.079(1)	0.0234(7)	0.0331(8)	−0.0014(7)	0.0158(8)	0.0014(6)

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