Crystal structure of tetraaqua-(1,10-phenanthroline-*N*,*N*')manganese(II) sulfate dihydrate, $[Mn(H_2O)_4(phen)]SO_4 \cdot 2H_2O$

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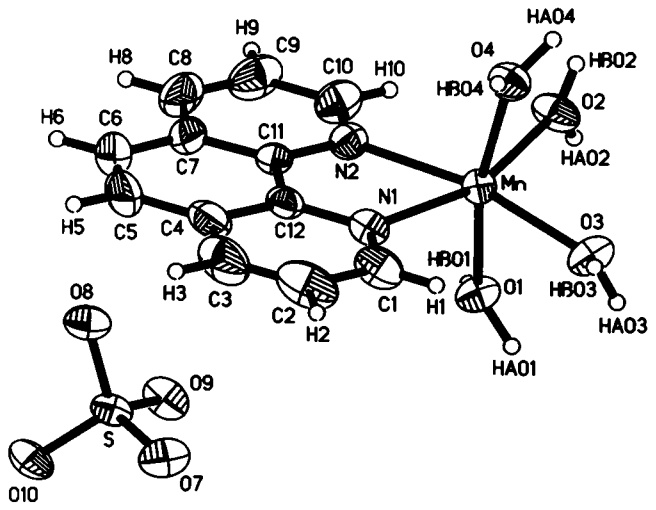

Abstract

$C_{12}H_{20}MnN_2O_{10}S$, orthorhombic, *Pbca* (No. 61), $a = 8.877(2)$ Å, $b = 18.509(1)$ Å, $c = 22.087(2)$ Å, $V = 3629.0$ Å^3, $Z = 8$, $R_{gt}(F) = 0.034$, $wR_{ref}(F^2) = 0.088$, $T = 293$ K.

Source of material

Yellow crystals of the title compound were grown by the reaction of $MnSO_4 \cdot H_2O$ (0.100 g, 0.592 mmol), phenanthroline monohydrate (0.117 g, 0.592 mmol) and suberic acid (0.103 g, 0.592 mmol) dissolved in 25 ml CH_3CH_2OH/H_2O (1:1 v/v), followed by slow evaporation of the solvent at room temperature. Repeated experiments showed that the presence of suberic acid is essential for the crystal growth.

Discussion

The crystal structure of the title compound consists of $[Mn(H_2O)_4(phen)]^{2+}$ complex cations, SO_4^{2-} anions and crystal H_2O molecules. In the complex cations, the Mn atoms are octahedrally coordinated by four O atoms and two N atoms, which belong to four water molecules and one bidentate chelating phenanthroline ligands, respectively. The octahedral coordination around the central Mn atom is substantially distorted with d(Mn—N) = 2.255 Å, 2.274 Å and d(Mn—O) = 2.153 Å – 2.202 Å. Based on the π-π stacking interactions between the chelating phenanthroline ligands with the mean spacings of 3.51 Å, the complex cations are assembled into 1D columns parallel to [100]. Through the hydrogen bonds, the resultant columns are held together by the SO_4^{2-} anions and H_2O molecules, leading to a 3D framework with tunnels parallel to [100]. The chelating phenanthroline ligands exhibit nearly perfect planarity. The tetrahedral SO_4^{2-} anions display a slight deviation with d(S—O) = 1.468 Å – 1.482 Å and ∠O–S–O = 109.1° – 109.7°. The present $[Mn(H_2O)_4(phen)]^{2+}$ complex cations can be viewed as resulting from a substitution of H_2O molecule for the sulfato ligand in the previously reported $Mn(phen)(H_2O)_3SO_4$ [1].

Table 1. Data collection and handling.

Crystal:	yellow thin plate, size 0.033 × 0.178 × 0.189 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.96 cm^{-1}
Diffractometer, scan mode:	Bruker P4, θ/2θ
$2\theta_{max}$:	55.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5204, 4161
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3226
$N(param)_{refined}$:	237
Programs:	SHELXS-97 [2], SHELXL-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8*c*	0.3621	–0.0427	0.3769	0.076(3)
H(2)	8*c*	0.4456	–0.1039	0.2912	0.076
H(3)	8*c*	0.3716	–0.0645	0.1975	0.076
H(5)	8*c*	0.2286	0.0275	0.1337	0.076
H(6)	8*c*	0.0779	0.1244	0.1287	0.076
H(8)	8*c*	–0.0715	0.2219	0.1827	0.076
H(9)	8*c*	–0.1531	0.2711	0.2720	0.076
H(10)	8*c*	–0.0774	0.2195	0.3626	0.076
HA(O1)	8*c*	0.3674	0.1877	0.4500	0.05
HB(O1)	8*c*	0.2494	0.2212	0.4216	0.05
HA(O2)	8*c*	0.0004	0.1856	0.4865	0.05
HB(O2)	8*c*	–0.1082	0.1364	0.4816	0.05
HA(O3)	8*c*	0.3330	0.0576	0.5091	0.05
HB(O3)	8*c*	0.2985	–0.0040	0.4875	0.05
HA(O4)	8*c*	–0.0862	–0.0180	0.4518	0.05
HB(O4)	8*c*	0.0074	–0.0455	0.4134	0.05
HA(O5)	8*c*	1.0196	0.1585	0.6207	0.05
HB(O5)	8*c*	0.8727	0.1535	0.6125	0.05
HA(O6)	8*c*	0.7798	0.3238	0.4198	0.05
HB(O6)	8*c*	0.6814	0.2664	0.4352	0.05

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	8*c*	0.13405(4)	0.08801(2)	0.41478(1)	0.0332(2)	0.0259(2)	0.0305(2)	0.0008(1)	0.0008(1)	–0.0009(1)
S	8*c*	0.08865(6)	0.15594(2)	–0.03211(2)	0.0269(2)	0.0221(2)	0.0464(3)	–0.0001(2)	0.0057(2)	0.0008(2)
N(1)	8*c*	0.2395(2)	0.02932(9)	0.33599(8)	0.0349(9)	0.0331(9)	0.041(1)	–0.0013(8)	0.0058(8)	–0.0014(8)
N(2)	8*c*	0.0463(2)	0.14232(9)	0.32940(8)	0.036(1)	0.0361(9)	0.0381(9)	–0.0007(8)	–0.0024(8)	0.0016(8)
C(1)	8*c*	0.3307(3)	–0.0269(1)	0.3390(1)	0.047(1)	0.039(1)	0.062(2)	0.005(1)	0.014(1)	–0.002(1)
C(2)	8*c*	0.3825(4)	–0.0640(2)	0.2874(2)	0.057(2)	0.049(1)	0.099(3)	0.009(1)	0.028(2)	–0.014(2)
C(3)	8*c*	0.3385(4)	–0.0405(2)	0.2320(2)	0.066(2)	0.078(2)	0.064(2)	–0.007(2)	0.027(2)	–0.031(2)
C(4)	8*c*	0.2444(3)	0.0194(2)	0.2263(1)	0.040(1)	0.068(2)	0.047(1)	–0.016(1)	0.015(1)	–0.016(1)
C(5)	8*c*	0.1961(4)	0.0491(2)	0.1695(1)	0.062(2)	0.117(3)	0.034(1)	–0.021(2)	0.014(1)	–0.016(2)
C(6)	8*c*	0.1062(4)	0.1066(2)	0.1664(1)	0.059(2)	0.115(3)	0.035(1)	–0.024(2)	–0.001(1)	0.005(2)
C(7)	8*c*	0.0527(3)	0.1412(2)	0.2197(1)	0.045(1)	0.073(2)	0.038(1)	–0.021(1)	–0.007(1)	0.012(1)
C(8)	8*c*	–0.0418(3)	0.2017(2)	0.2193(1)	0.058(2)	0.073(2)	0.058(2)	–0.013(2)	–0.020(1)	0.030(2)
C(9)	8*c*	–0.0902(3)	0.2309(2)	0.2720(2)	0.056(2)	0.053(2)	0.080(2)	0.002(1)	–0.022(2)	0.018(2)
C(10)	8*c*	–0.0435(3)	0.1993(1)	0.3265(1)	0.049(2)	0.042(1)	0.058(2)	0.006(1)	–0.009(1)	0.004(1)
C(11)	8*c*	0.0959(2)	0.1133(1)	0.2767(1)	0.030(1)	0.046(1)	0.036(1)	–0.0134(9)	–0.0009(9)	0.0039(9)
C(12)	8*c*	0.1950(2)	0.0523(1)	0.2802(1)	0.031(1)	0.046(1)	0.036(1)	–0.013(1)	0.0059(9)	–0.006(1)
O(1)	8*c*	0.2843(2)	0.17902(7)	0.42486(7)	0.0356(8)	0.0272(7)	0.0511(9)	–0.0001(6)	–0.0083(7)	–0.0016(6)
O(2)	8*c*	–0.0252(2)	0.14582(8)	0.47005(8)	0.0394(8)	0.0366(8)	0.057(1)	–0.0051(7)	0.0157(8)	–0.0141(7)
O(3)	8*c*	0.2634(2)	0.03698(7)	0.48832(7)	0.0436(9)	0.0262(7)	0.0536(9)	0.0010(6)	–0.0157(8)	–0.0012(6)
O(4)	8*c*	–0.0139(2)	–0.00548(8)	0.42461(7)	0.0403(8)	0.0330(7)	0.0472(9)	–0.0063(7)	0.0038(7)	–0.0022(7)
O(5)	8*c*	0.9455(2)	0.13044(8)	0.63007(8)	0.0445(9)	0.0393(8)	0.061(1)	–0.0001(7)	–0.0105(8)	0.0038(8)
O(6)	8*c*	0.7044(2)	0.2963(1)	0.40312(9)	0.047(1)	0.063(1)	0.064(1)	0.0009(9)	–0.0023(9)	0.0000(9)
O(7)	8*c*	0.1872(2)	0.10551(8)	0.00081(8)	0.0417(9)	0.0288(7)	0.070(1)	0.0034(7)	–0.0080(8)	0.0039(7)
O(8)	8*c*	–0.0448(2)	0.11719(9)	–0.05448(8)	0.0344(8)	0.0428(8)	0.059(1)	–0.0090(7)	0.0009(8)	0.0006(8)
O(9)	8*c*	0.0402(2)	0.21419(8)	0.00958(8)	0.0473(9)	0.0283(7)	0.0548(9)	0.0025(7)	0.0138(8)	–0.0036(7)
O(10)	8*c*	0.1710(2)	0.18756(8)	–0.08327(7)	0.0454(9)	0.0322(7)	0.0525(9)	–0.0069(7)	0.0172(8)	–0.0013(7)

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