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Crystal structure of octaaqua(μ_2-2,2′-bipyrimidine)dimanganese(II) bis(sulfate) — water (1:2), $[Mn_2(H_2O)_8(C_8H_6N_4)][(SO_4)_2] \cdot 2H_2O$

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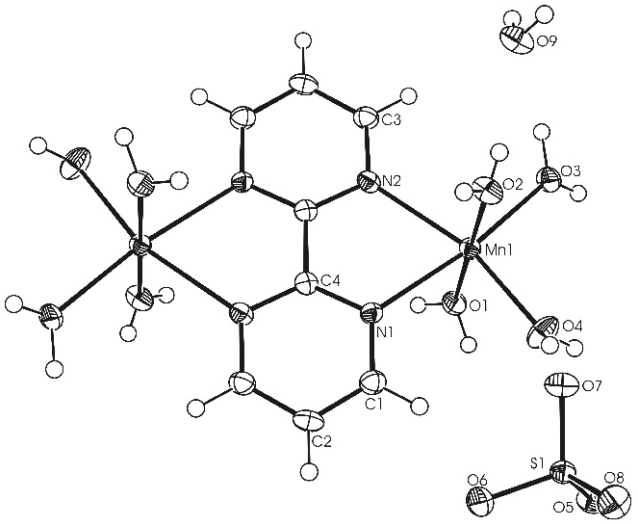

Abstract

$C_8H_{26}Mn_2N_4O_{18}S_2$, monoclinic, $P12_1/c1$ (no. 14), a = 8.1522(5) Å, b = 11.6765(7) Å, c = 11.9942(7) Å, β = 91.667(1)°, V = 1141.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.104, T = 200 K.

Source of material

$MnSO_4 \cdot H_2O$ (0.1688 g, 0.999 mmol) and 2,2′-bipyrimidine (bpym; 0.1587 g, 1.003 mmol) in H_2O (20 ml) were refluxed for 1 h. After evaporation of the solvent, the residue was washed with ether and dried at 50 °C, to give a light yellow powder (0.3152 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a water solution at 50 °C.

Experimental details

The H atoms of the bipyrimidine ring were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C). The H atoms of the water ligands and solvent molecules were located from Fourier difference maps and refined isotropically: d(O—H) = 0.72(4) Å - 0.99(4) Å. The highest peak (0.50 eÅ^{-3}) and the deepest hole (–0.54 eÅ^{-3}) in the difference Fourier map are located 1.71 Å and 0.71 Å from the atoms H2A and S1, respectively.

Discussion

The asymmetric unit of the title crystal structure contains one half of an Mn(II) cationic complex, an SO_4^{2-} anion and a water solvent molecule. The centroid of the complex is located at a center of inversion. Each two Mn(II) ions are bridged by a bis-chelating 2,2′-bipyrimidine ligand to form a dinuclear Mn(II) complex. Each Mn atom is six-coordinated in a considerably distorted octahedral manner by two N atoms of the bridging bpym ligand and four O atoms from four water molecules. In the previously reported crystal structures of the analogous dinuclear Mn(II) complex $[Mn_2(SO_4)_2(H_2O)_6(bpym)]$, an SO_4^{2-} anion coordinates the Mn(II) ion as a monodentate ligand via one O atom, and thus each Mn atom is coordinated by two N atoms from bpym and four O atoms from one sulfato ligand and three water molecules [1,2]. The main contribution to the distortion of the ocatahedron is made by the tight chelate angle ∠N1–Mn1–N2 = 71.82(8)°, which results in non-linear *trans* axes (∠N1–Mn1–O3 = 172.02(8)° and ∠N2–Mn1–O4 = 162.25(9)°). The apical O1–Mn1–O2 bonds are almost linear with the bond angle of 179.49(9)°. The distances d(Mn—N) and d(Mn—O) are roughly equivalent: d(Mn1—N1/N2) = 2.295(2) Å and 2.307(2) Å, respectively, d(Mn1—O1/O2/O3/O4) = 2.130(2) - 2.186(2) Å). The shape of the sulfate anion is nearly tetrahedral with the O–S–O bond angles of 107.8(1)° - 110.7(1)°, and the almost equal d(S—O) = 1.460(2) - 1.491(2) Å.

In the crystal structure, the complex, the anions and the solvent molecules are linked by O–H···O hydrogen bonds with d(O···O) = 2.706(3) - 2.818(3) Å, forming a three-dimensional network. In addition, several intermolecular π–π interactions between pyrimidine rings are present. The distance between Cg1 (the centroid of ring N1–C4) and Cg1^{i} (symmetry code i: 2–x,–y,1–z) is 5.589(2) Å, and the ring planes are parallel and shifted by 4.611 Å.

Table 1. Data collection and handling.

Crystal:	light yellow block size 0.14 × 0.21 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.80 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8031, 2765
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2091
$N(param)_{refined}$:	194
Programs:	SHELXS-97, SHELXL-97 [3], ORTEP-3 [4], PLATON [5]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.242(5)	–0.111(3)	0.299(3)	0.03(1)
H(1B)	4*e*	0.251(6)	–0.093(4)	0.196(4)	0.08(2)
H(2A)	4*e*	0.474(5)	0.301(3)	0.380(3)	0.04(1)

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(2B)	4*e*	0.322(5)	0.312(3)	0.377(3)	0.04(1)
H(3A)	4*e*	0.005(4)	0.167(3)	0.230(3)	0.020(9)
H(3B)	4*e*	–0.021(5)	0.196(3)	0.339(4)	0.07(1)
H(4A)	4*e*	0.461(5)	0.178(3)	0.129(3)	0.05(1)
H(4B)	4*e*	0.330(5)	0.121(3)	0.086(4)	0.05(1)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.6682	0.0338	0.2148	0.026
H(2)	4*e*	0.9039	–0.0617	0.2769	0.028
H(3)	4*e*	0.0777	0.1180	0.5361	0.026
H(9A)	4*e*	0.164(5)	0.477(4)	0.462(4)	0.05(1)
H(9B)	4*e*	0.099(5)	0.393(3)	0.493(4)	0.04(1)

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(1)	4*e*	0.30433(5)	0.10957(3)	0.30717(3)	0.0169(2)	0.0179(2)	0.0176(2)	0.0010(2)	0.0013(2)	0.0010(2)
O(1)	4*e*	0.2237(3)	–0.0624(2)	0.2588(2)	0.027(1)	0.018(1)	0.025(1)	0.0017(9)	0.0006(9)	–0.001(1)
O(2)	4*e*	0.3846(3)	0.2780(2)	0.3533(2)	0.020(1)	0.021(1)	0.035(1)	0.0004(9)	–0.002(1)	–0.005(1)
O(3)	4*e*	0.0605(2)	0.1797(2)	0.2820(2)	0.015(1)	0.031(1)	0.025(1)	0.0040(9)	–0.0041(9)	–0.003(1)
O(4)	4*e*	0.3882(3)	0.1392(2)	0.1431(2)	0.028(1)	0.045(1)	0.020(1)	–0.014(1)	0.004(1)	0.003(1)
N(1)	4*e*	0.5515(3)	0.0281(2)	0.3581(2)	0.016(1)	0.019(1)	0.016(1)	0.0004(9)	0.0018(8)	–0.0001(9)
N(2)	4*e*	0.2972(3)	0.0614(2)	0.4935(2)	0.017(1)	0.019(1)	0.022(1)	0.0021(9)	0.0024(9)	0.001(1)
C(1)	4*e*	0.6770(3)	0.0085(2)	0.2900(2)	0.022(1)	0.022(1)	0.021(1)	–0.001(1)	0.004(1)	0.001(1)
C(2)	4*e*	0.8168(3)	–0.0469(2)	0.3259(3)	0.018(1)	0.025(1)	0.029(2)	0.001(1)	0.008(1)	–0.004(1)
C(3)	4*e*	0.1741(3)	0.0804(2)	0.5636(2)	0.018(1)	0.025(1)	0.023(2)	0.002(1)	0.002(1)	–0.002(1)
C(4)	4*e*	0.5707(3)	–0.0089(2)	0.4627(2)	0.019(1)	0.012(1)	0.019(1)	–0.002(1)	0.002(1)	0.000(1)
S(1)	4*e*	0.76934(8)	0.21735(6)	0.01718(6)	0.0154(3)	0.0181(3)	0.0188(4)	–0.0004(3)	0.0026(2)	–0.0007(3)
O(5)	4*e*	0.6716(2)	0.1426(2)	–0.0579(2)	0.022(1)	0.025(1)	0.027(1)	0.0001(8)	–0.0001(8)	–0.0069(9)
O(6)	4*e*	0.8920(2)	0.1443(2)	0.0784(2)	0.023(1)	0.036(1)	0.025(1)	0.0069(9)	–0.0036(8)	–0.0002(9)
O(7)	4*e*	0.6597(2)	0.2709(2)	0.0977(2)	0.023(1)	0.023(1)	0.029(1)	–0.0020(8)	0.0066(8)	–0.0063(9)
O(8)	4*e*	0.8534(2)	0.3054(2)	–0.0459(2)	0.027(1)	0.026(1)	0.032(1)	–0.0064(9)	0.0049(9)	0.005(1)
O(9)	4*e*	0.1749(3)	0.4121(2)	0.4677(2)	0.026(1)	0.021(1)	0.042(1)	0.002(1)	0.008(1)	–0.001(1)

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References

1. De Munno, G.; Ruiz, R.; Lloret, F.; Faus, J.; Sessoli, R.; Julve, M.: Oxalate and 2,2′-Bipyrimidine as Useful Tools in Designing Layered Compounds. Inorg. Chem. **34** (1995) 408-411.
2. Hong, D. M.; Chu, Y. Y.; Wei, H. H.: Structure and magnetic properties of 2,2′-bipyrimidine-(bpym)-bridged binuclear Mn(II) complex: $[Mn_2(H_2O)_6(bpym)(SO_4)_2]$. Polyhedron **15** (1996) 447-452.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
4. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.
5. Spek, A. L.: Single-crystal structure validation with the program PLATON. J. Appl. Crystallogr. **36** (2003) 7-13.