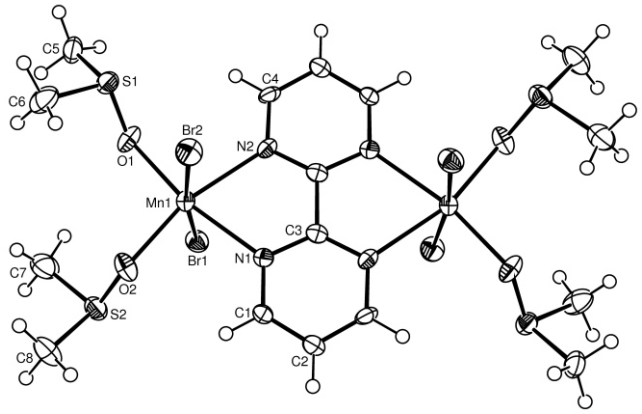
Crystal structure of (μ_2-2,2′-bipyrimidine)-tetrabromo-tetrakis-(dimethyl sulfoxide-κO)dimanganese(II), $Mn_2Br_4(C_8H_6N_4)(C_2H_6SO)_4$

Kwang Ha*

Chonnam National University, School of Applied Chemical Engineering, Research Institute of Catalysis, Gwangju 500-757, Republic of Korea

Received April 6, 2011, accepted and available on-line August 25, 2011; CCDC no. 1267/3502



Abstract

$C_{16}H_{30}Br_4Mn_2N_4O_4S_4$, monoclinic, $P12_1/c1$ (no. 14), a = 6.6356(4) Å, b = 13.1058(8) Å, c = 18.255(1) Å, β = 98.638(1)°, V = 1569.6 Å^3, Z = 2, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.105, T = 200 K.

Source of material

To a solution of $MnBr_2 \cdot 4H_2O$ (0.2867 g, 1.000 mmol) in EtOH (30 ml) was added 2,2′-bipyrimidine (bpym; 0.1584 g, 1.002 mmol) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration, washed with EtOH and dried at 50 °C, to give a yellow powder (0.3441 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a dimethyl sulfoxide (DMSO) solution at 90 °C.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 $U_{eq}(C_{methyl})$. The highest peak (0.87 e Å^{-3}) and the deepest hole (–1.11 e Å^{-3}) in the difference Fourier map are located 1.08 Å and 0.89 Å from the atoms O2 and Br1, respectively.

Discussion

Single crystals of the title complex $[Mn_2Br_4(bpym)(DMSO)_4]$ were unexpectedly obtained during crystallization from a DMSO solution of the reaction product prepared by the reaction of $MnBr_2 \cdot 4H_2O$ and bpym. In the title crystal structure, the two Mn(II) ions are bridged by a 2,2′-bipyrimidine ligand acting as a bis-chelating ligand to form a dinuclear Mn(II) complex. The centroid of the complex is located on an inversion center, and therefore, the asymmetric unit contains one half of the complex and the two pyrimidine rings are exactly parallel. Each Mn atom is six-coordinated in a considerably distorted octahedral manner by two N atoms of the bridging bpym ligand, two Br^- anions and two O atoms from two distinct DMSO molecules. The Br atoms are in *trans* conformation with respect to each other (∠Br1–Mn1–Br2 = 172.21(4)°). The main contribution to the distortion is the tight N1–Mn1–N2 chelating angle of 72.3(2)°, which results in non-linear *trans* arrangement of the N1–Mn1–O1 and N2–Mn1–O2 bonds (∠N1–Mn1–O1 = 167.4(2)° and ∠N2–Mn1–O2 = 163.9(2)°). The bond lengths Mn—Br, Mn—O and Mn—N are almost equal, with d(Mn—Br) = 2.708(1) Å and 2.688(1) Å, d(Mn—O) = 2.106(4) Å and 2.108(4) Å, and d(Mn—N) = 2.281(4) Å and 2.295(5) Å, respectively. The molecules are stacked in columns along [100]. In the columns, several intermolecular π–π interactions between adjacent pyrimidine rings are present. For Cg1 (the centroid of ring N2–C4) and Cg1^i (symmetry code i: 2–x,1–y,1–z), the centroid-centroid distance is 3.682(3) Å, the planes are parallel and shifted by 1.680 Å. There are also intramolecular C–H···Br hydrogen bonds with d(C···Br) = 3.603(5) Å.

Table 1. Data collection and handling.

Crystal:	yellow rod, size 0.08 × 0.13 × 0.14 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	61.90 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, $\varphi\backslash\omega$
$2\theta_{max}$:	56.54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11417, 3880
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2242
$N(param)_{refined}$:	158
Programs:	SHELXS-97, SHELXL-97 [1], ORTEP-3 [2]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.0950	0.3023	0.5056	0.029
H(2)	4*e*	–0.0313	0.3995	0.5952	0.032
H(4)	4*e*	0.8680	0.4474	0.3675	0.029
H(5A)	4*e*	1.0051	0.2383	0.2628	0.054
H(5B)	4*e*	0.9100	0.2440	0.1770	0.054
H(5C)	4*e*	0.8585	0.1491	0.2262	0.054
H(6A)	4*e*	0.4897	0.1497	0.2011	0.067
H(6B)	4*e*	0.4928	0.2356	0.1390	0.067
H(6C)	4*e*	0.3436	0.2471	0.1997	0.067
H(7A)	4*e*	0.3530	0.0179	0.3231	0.072
H(7B)	4*e*	0.4294	–0.0505	0.3945	0.072
H(7C)	4*e*	0.5491	0.0518	0.3799	0.072
H(8A)	4*e*	–0.0915	0.0716	0.4106	0.067
H(8B)	4*e*	0.0172	–0.0375	0.4117	0.067
H(8C)	4*e*	–0.0016	0.0322	0.3391	0.067

* e-mail: hakwang@chonnam.ac.kr

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}
Br(1)	4*e*	0.70513(9)	0.21274(5)	0.51350(3)	0.0322(3)	0.0304(4)	0.0294(3)	–0.0032(3)	0.0012(3)	0.0030(3)
Br(2)	4*e*	0.24945(9)	0.43160(5)	0.30034(3)	0.0371(3)	0.0313(4)	0.0344(4)	0.0052(3)	0.0033(3)	0.0035(3)
Mn(1)	4*e*	0.4666(1)	0.31075(6)	0.40197(5)	0.0278(5)	0.0208(5)	0.0239(5)	–0.0017(4)	0.0061(4)	–0.0033(4)
S(1)	4*e*	0.6707(2)	0.2892(1)	0.24964(8)	0.0371(8)	0.0285(9)	0.0252(8)	0.0018(7)	0.0091(7)	–0.0010(7)
S(2)	4*e*	0.2557(2)	0.0901(1)	0.42710(9)	0.0338(8)	0.0277(9)	0.0335(9)	–0.0080(7)	0.0026(7)	–0.0002(7)
O(1)	4*e*	0.6538(6)	0.2543(3)	0.3277(2)	0.041(2)	0.042(3)	0.022(2)	0.009(2)	0.009(2)	–0.007(2)
O(2)	4*e*	0.2405(6)	0.1965(3)	0.3928(2)	0.034(2)	0.021(2)	0.045(3)	–0.003(2)	–0.001(2)	–0.001(2)
N(1)	4*e*	0.3240(6)	0.3942(3)	0.4911(2)	0.024(2)	0.021(3)	0.023(3)	–0.001(2)	0.007(2)	0.000(2)
N(2)	4*e*	0.6548(6)	0.4554(3)	0.4332(2)	0.025(2)	0.025(3)	0.018(2)	0.003(2)	0.007(2)	–0.002(2)
C(1)	4*e*	0.1603(8)	0.3647(4)	0.5214(3)	0.033(3)	0.016(3)	0.024(3)	–0.002(3)	0.008(3)	0.003(2)
C(2)	4*e*	0.0841(8)	0.4216(4)	0.5744(3)	0.027(3)	0.024(3)	0.029(3)	–0.006(3)	0.006(3)	0.001(3)
C(3)	4*e*	0.4087(7)	0.4839(4)	0.5167(3)	0.019(3)	0.021(3)	0.023(3)	0.001(3)	0.002(2)	0.005(2)
C(4)	4*e*	0.8184(8)	0.4880(4)	0.4040(3)	0.027(3)	0.026(3)	0.022(3)	0.005(3)	0.015(2)	0.003(3)
C(5)	4*e*	0.8850(8)	0.2227(5)	0.2263(3)	0.036(3)	0.038(4)	0.035(4)	–0.005(3)	0.009(3)	–0.016(3)
C(6)	4*e*	0.4777(9)	0.2230(6)	0.1908(3)	0.039(4)	0.070(5)	0.024(3)	–0.006(4)	0.004(3)	–0.006(3)
C(7)	4*e*	0.415(1)	0.0194(5)	0.3753(4)	0.056(4)	0.031(4)	0.062(5)	–0.005(4)	0.023(4)	0.003(4)
C(8)	4*e*	0.0185(9)	0.0327(5)	0.3934(4)	0.036(4)	0.033(4)	0.063(5)	–0.013(3)	0.003(3)	–0.001(4)

Acknowledgment. This work was supported by Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant no. 2010-0029626).

References

1. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
2. Farrugia, L. J.: ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI) J. Appl. Crystallogr. **30** (1997) 565.