Crystal structure of di(μ_2-bromo)-dibromo-bis(2,3,5,6-tetra-2-pyridylpyrazine)dimanganese(II) — nitromethane (1:2), $[MnBr_2(C_{24}H_{16}N_6)]_2 \cdot 2CH_3NO_2$

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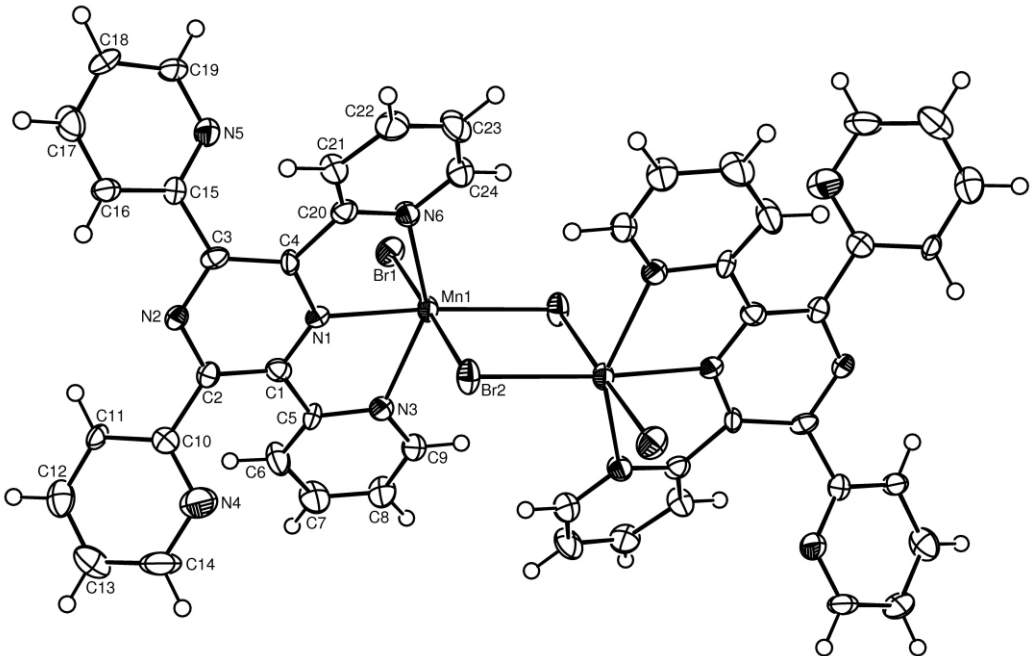
Received April 27, 2011, accepted and available on-line August 31, 2011; CCDC no. 1267/3550



Abstract

$C_{50}H_{38}Br_4Mn_2N_{14}O_4$, triclinic, $P\bar{1}$ (no. 2), a = 9.4490(6) Å, b = 10.4294(7) Å, c = 13.759(1) Å, α = 72.754(2)°, β = 79.541(2)°, γ = 82.421(2)°, V = 1269.0 Å^3, Z = 1, $R_{gt}(F)$ = 0.053, $wR_{ref}(F^2)$ = 0.133, T = 200 K.

Source of material

2,3,5,6-Tetra-2-pyridylpyrazine (tppz; 0.1874 g, 0.482 mmol) was added to a solution of $MnBr_2 \cdot 4H_2O$ (0.2771 g, 0.966 mmol) in EtOH (30 ml). The mixture was 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 (0.2777 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3NO_2 solution.

Experimental details

Hydrogen atoms 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 solvent molecule CH_3NO_2 displayed relatively large displacement factors and low electron density peaks so that the molecule appears to be highly disordered. The atoms O2, O3, N7, N8, C25 and C26 were modelled isotropically around the O1 atom as disordered over two sites with a site occupancy factor of 0.5. The H atoms of the solvent molecule could neither be located from Fourier difference maps nor added geometrically. The highest peak (0.86 e Å^{-3}) and the deepest hole (–0.66 e Å^{-3}) in the difference Fourier map are located 1.21 Å and 0.84 Å from the atoms Br1 and Br2, respectively.

Discussion

The asymmetric unit of the title crystal structure contains one half of a neutral dinuclear Mn(II) complex and a nitromethane solvent molecule. The structure of the complex is similar to that of the previously reported analogous chloro complex $[Mn_2Cl_4(tppz)_2]$ [1], however, owing to the crystallization solvent molecule the unit cell parameters are quite different. In the complex, the two Mn(II) ions are bridged by the two Br anionic ligands to form a dinuclear complex, and a center of inversion is located at the centroid of the complex. Each Mn atom is six-coordinated in a considerably distorted octahedral manner by three N atoms of the tridentate tppz ligand, two bridging Br^- ligands and a Br^- anion. The main contributions to the distortion are the tight chelating angles (∠N1–Mn1–N3 = 71.2(2)° and ∠N1–Mn1–N6 = 71.8(2)°) and the Br bridging, which results in non-linear *trans* arrangement of the N3–Mn1–N6 and N1–Mn1–Br2^i (symmetry code i: $-x,1-y,1-z$) bonds (∠N3–Mn1–N6 = 142.8(2)° and ∠N1–Mn1–Br2^i = 170.3(1)°), whereas the Br1–Mn1–Br2 bond is almost linear (∠Br1–Mn1–Br2 = 178.51(4)°). The three Mn—N bond lengths are roughly equivalent (d(Mn—$N_{pyrazine}$) =

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2.249(5) Å; d(Mn–$N_{pyridyl}$) = 2.266(5) and 2.265(5)Å). Contrarily, the three Mn—Br bond lengths are somewhat different. The bridging bond (d(Mn1—Br2) = 2.831(1) Å) is slightly longer than the other Mn—Br bonds (d(Mn1—Br1) = 2.593(1) Å and d(Mn1—$Br2^{i}_{bridging}$) = 2.592(1) Å. The distance between the Mn atoms is relatively short with 4.012(1) Å.

In the crystal structure, the pyrazine ring is fairly distorted; the maximum deviation is 0.107(4) Å for C1 atom from the least-squares plane of the ring. The dihedral angles between the nearly planar pyridyl rings and the least-squares plane of their carrier pyrazine rings are 21.4(3)°, 39.1(2)°, 31.6(3)° and 29.3(3)°, respectively. The complex displays numerous inter- and intramolecular π–π interactions between the pyridyl rings. The shortest distance between Cg1 (the centroid of ring N4-C14) and $Cg2^{ii}$ (ring N5-C19, symmetry code ii: $-x$,1$-y$,$-z$) is 4.761(4) Å, and the dihedral angle between the ring planes is 43.1(3)°.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.06 × 0.12 × 0.19 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	37.07 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	51.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7972, 4897
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3156
$N(param)_{refined}$:	326
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-3 [3], PLATON [4]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(6)	2*i*		0.5638	0.3663	0.1908	0.042
H(7)	2*i*		0.7035	0.2992	0.3255	0.047
H(8)	2*i*		0.5987	0.3203	0.4873	0.040
H(9)	2*i*		0.3648	0.4162	0.5100	0.034
H(11)	2*i*		0.4664	0.4152	–0.0659	0.026
H(12)	2*i*		0.6276	0.2354	–0.0939	0.044
H(13)	2*i*		0.6451	0.0364	0.0359	0.053
H(14)	2*i*		0.4916	0.0131	0.1910	0.064
H(16)	2*i*		0.1020	0.5932	–0.1396	0.030
H(17)	2*i*		0.0156	0.7626	–0.2762	0.045
H(18)	2*i*		–0.0562	0.9790	–0.2552	0.047
H(19)	2*i*		–0.0430	1.0161	–0.0986	0.044
H(21)	2*i*		–0.1841	0.6807	0.0895	0.032
H(22)	2*i*		–0.39520	0.76750	0.17750	0.0420
H(23)	2*i*		–0.38080	0.83140	0.32420	0.0440
H(24)	2*i*		–0.16430	0.78510	0.39070	0.0390
O(1)	2*i*		0.255(1)	0.082(1)	0.417(1)	0.185(5)
O(2)	2*i*	0.50	0.353(2)	0.009(2)	0.561(2)	0.150(7)
O(3)	2*i*	0.50	0.197(3)	–0.028(2)	0.558(2)	0.175(9)
N(7)	2*i*	0.50	0.127(3)	0.008(2)	0.490(2)	0.118(7)
N(8)	2*i*	0.50	0.382(3)	0.029(2)	0.462(2)	0.114(7)
C(25)	2*i*	0.50	0.502(3)	–0.004(2)	0.425(2)	0.094(7)
C(26)	2*i*	0.50	0.018(3)	0.014(3)	0.446(2)	0.118(9)

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)	2*i*	0.1287(1)	0.5948(1)	0.37317(7)	0.0202(5)	0.0279(5)	0.0166(5)	–0.0002(4)	–0.0020(4)	–0.0075(4)
Br(1)	2*i*	0.29812(7)	0.78878(7)	0.30581(5)	0.0305(4)	0.0335(4)	0.0311(4)	–0.0087(3)	–0.0024(3)	–0.0045(3)
Br(2)	2*i*	–0.05527(7)	0.38197(7)	0.44154(5)	0.0338(4)	0.0370(4)	0.0216(4)	–0.0119(3)	0.0024(3)	–0.0140(3)
N(1)	2*i*	0.1666(5)	0.5470(5)	0.2210(4)	0.023(3)	0.019(3)	0.018(3)	0.001(2)	–0.006(2)	–0.002(2)
N(2)	2*i*	0.2261(5)	0.5129(5)	0.0287(4)	0.021(3)	0.019(3)	0.017(3)	–0.005(2)	–0.001(2)	–0.002(2)
N(3)	2*i*	0.3229(5)	0.4426(5)	0.3696(4)	0.027(3)	0.022(3)	0.022(3)	–0.001(2)	–0.004(2)	–0.006(2)
N(4)	2*i*	0.3950(7)	0.2011(6)	0.1576(5)	0.049(4)	0.039(4)	0.047(4)	0.003(3)	–0.003(3)	–0.001(3)
N(5)	2*i*	0.0345(6)	0.8342(5)	–0.0289(4)	0.043(3)	0.026(3)	0.022(3)	0.000(3)	–0.004(3)	–0.008(3)
N(6)	2*i*	–0.0503(5)	0.7066(5)	0.2833(4)	0.022(3)	0.029(3)	0.022(3)	0.004(2)	–0.007(2)	–0.009(3)
C(1)	2*i*	0.2814(6)	0.4667(6)	0.1987(5)	0.022(3)	0.018(3)	0.026(4)	–0.003(3)	–0.001(3)	–0.005(3)
C(2)	2*i*	0.2962(6)	0.4347(6)	0.1031(5)	0.021(3)	0.023(3)	0.018(3)	–0.005(3)	–0.001(3)	–0.004(3)
C(3)	2*i*	0.1245(6)	0.6100(6)	0.0476(5)	0.030(3)	0.013(3)	0.023(4)	–0.005(3)	–0.010(3)	–0.002(3)
C(4)	2*i*	0.0809(6)	0.6130(6)	0.1511(5)	0.023(3)	0.021(3)	0.014(3)	–0.004(3)	0.005(3)	–0.005(3)
C(5)	2*i*	0.3813(6)	0.4219(6)	0.2769(4)	0.019(3)	0.028(4)	0.011(3)	–0.005(3)	–0.001(3)	–0.004(3)
C(6)	2*i*	0.5230(7)	0.3734(7)	0.2576(5)	0.026(4)	0.052(5)	0.030(4)	0.006(3)	–0.002(3)	–0.021(4)
C(7)	2*i*	0.6060(7)	0.3347(8)	0.3370(6)	0.025(4)	0.056(5)	0.041(5)	0.011(3)	–0.013(4)	–0.019(4)
C(8)	2*i*	0.5452(7)	0.3486(7)	0.4313(5)	0.024(4)	0.050(5)	0.028(4)	0.005(3)	–0.014(3)	–0.012(4)
C(9)	2*i*	0.4051(7)	0.4043(6)	0.4444(5)	0.035(4)	0.030(4)	0.022(4)	0.000(3)	–0.006(3)	–0.010(3)
C(10)	2*i*	0.3919(6)	0.3184(6)	0.0807(5)	0.019(3)	0.026(4)	0.027(4)	–0.001(3)	–0.007(3)	–0.009(3)
C(11)	2*i*	0.4739(6)	0.3332(6)	–0.0127(5)	0.020(3)	0.026(4)	0.014(3)	–0.003(3)	0.002(3)	0.001(3)
C(12)	2*i*	0.5683(7)	0.2266(8)	–0.0290(6)	0.029(4)	0.056(5)	0.030(4)	–0.004(4)	–0.007(3)	–0.017(4)
C(13)	2*i*	0.5778(8)	0.1088(8)	0.0467(7)	0.034(4)	0.040(5)	0.060(6)	0.005(4)	0.001(4)	–0.024(4)
C(14)	2*i*	0.4885(8)	0.0964(8)	0.1389(7)	0.053(5)	0.025(4)	0.061(6)	0.012(4)	0.004(5)	0.005(4)
C(15)	2*i*	0.0728(6)	0.7117(6)	–0.0418(5)	0.026(3)	0.026(4)	0.018(3)	–0.002(3)	–0.002(3)	–0.007(3)
C(16)	2*i*	0.0703(6)	0.6809(6)	–0.1328(5)	0.025(3)	0.020(3)	0.026(4)	0.000(3)	–0.004(3)	–0.002(3)
C(17)	2*i*	0.0205(7)	0.7809(7)	–0.2133(6)	0.040(4)	0.045(5)	0.035(4)	0.000(4)	–0.010(4)	–0.022(4)
C(18)	2*i*	–0.0221(7)	0.9082(7)	–0.2011(5)	0.049(5)	0.038(4)	0.024(4)	0.013(4)	–0.019(4)	0.001(3)
C(19)	2*i*	–0.0132(8)	0.9291(7)	–0.1073(5)	0.061(5)	0.018(4)	0.028(4)	0.010(3)	–0.011(4)	–0.005(3)
C(20)	2*i*	–0.0562(6)	0.6797(6)	0.1939(5)	0.028(3)	0.017(3)	0.022(4)	–0.005(3)	–0.004(3)	–0.003(3)
C(21)	2*i*	–0.1820(6)	0.7016(7)	0.1519(5)	0.017(3)	0.042(4)	0.028(4)	0.006(3)	–0.013(3)	–0.016(3)
C(22)	2*i*	–0.3061(7)	0.7551(7)	0.2031(6)	0.021(3)	0.045(5)	0.036(4)	0.007(3)	–0.010(3)	–0.006(4)
C(23)	2*i*	–0.2987(7)	0.7898(7)	0.2907(6)	0.021(4)	0.047(5)	0.040(5)	0.009(3)	–0.002(3)	–0.017(4)
C(24)	2*i*	–0.1691(7)	0.7629(7)	0.3293(5)	0.040(4)	0.032(4)	0.027(4)	–0.001(3)	–0.003(3)	–0.012(3)

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).

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