Crystal structure of aquadibromo(2,4,6-tri-2-pyridyl-1,3,5-triazine)manganese(II) monohydrate, $Mn(H_2O)Br_2(C_{18}H_{12}N_6) \cdot H_2O$

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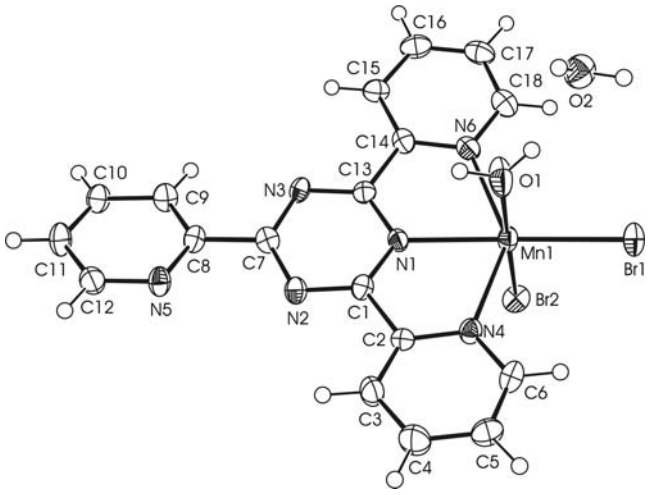

Abstract

$C_{18}H_{16}Br_2MnN_6O_2$, monoclinic, $P2_1/n$ (no. 14), a = 8.7713(4) Å, b = 11.9086(5) Å, c = 20.0404(9) Å, β = 97.333(1)°, V = 2076.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.040, $wR_{ref}(F^2)$ = 0.103, T = 200 K.

Source of material

To a solution of $MnBr_2 \cdot 4H_2O$ (0.2868 g, 1.00 mmol) in MeOH (30 ml) was added 2,4,6-tri-2-pyridyl-1,3,5-triazine (tptz, 0.1561 g, 0.50 mmol) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration and washed with MeOH and dried under vacuum, to give an orange powder (0.1065 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a CH_3CN 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 H atoms of the water molecules were located from difference Fourier maps then allowed to ride on their parent O atoms in the final cycles of refinement with d(O—H) = 0.84 Å and U_{iso}(H) = 1.5 U_{eq}(O). The highest peak (1.13 e·Å^{-3}) and the deepest hole (–0.93 e·Å^{-3}) in the difference Fourier map are located 0.92 Å and 0.80 Å from the atoms Br2 and Br1, respectively.

Discussion

The crystal structure of the title compound consists of the neutral Mn(II) complex $[Mn(H_2O)Br_2(tptz)]$ and a solvent water molecule. The previously reported analogous chloro complex $[MnCl_2(tptz)]$ crystallizes in the triclinic space group $P\bar{1}$ and the Mn(II) ion is five-coordinated in an approximately square-pyramidal manner by three N atoms and two Cl atoms [1].

In the title complex, however, the central Mn(II) ion is six-coordinated in a distorted octahedral manner by three N atoms of the tridentate tptz ligand, two Br atoms and one O atom from the water ligand. The tight N–Mn–N chelating angles (∠N1–Mn1–N4 = 70.4(1)° and ∠N1–Mn1–N6 = 70.5(1)°) and the Br-Br repelling (∠Br1–Mn1–Br2 = 97.48(2)°) contribute to the distortion of the ocataheron. The apical N1–Mn1–Br1, O1–Mn1–Br2 and N4–Mn1–N6 bond angles are 165.48(9)°, 176.1(1)° and 140.6(1)°, respectively. Because of the different *trans* effects of the N and O atoms, the Mn1—Br1 bond *trans* to the N1 atom (2.5623(7) Å) is somewhat shorter than the Mn1—Br2 bond *trans* to the O1 atom (2.6316(8) Å). The Mn—$N_{pyridyl}$ bonds (2.315(4) and 2.323(3) Å) are slightly longer than the Mn—$N_{triazine}$ bond (2.223(3) Å).

In the crystal structure, the two pyridyl rings coordinating the Mn atom are located approximately parallel to their carrier triazine ring, making dihedral angles of 3.9(2)° and 6.8(3)°. The dihedral angle between the uncoordinated pyridyl ring and triazine ring is 13.4(2)°. The complex displays numerous intermolecular π-π interactions between the six-membered rings. The centroid-centroid distance Cg1 (the centroid of ring N5-C12) - Cg1^{i} (symmetry code i: –x,–y,–z) is 3.591(2) Å, the ring planes are parallel and shifted by 1.209 Å. There are also intermolecular hydrogen bonds between the water molecules and H-acceptor atoms with d(O···O) = 2.724(5) Å, d(O···N) = 2.891(5) Å and d(O···Br) = 3.217(3) - 3.460(3) Å.

Table 1. Data collection and handling.

Crystal:	orange block, size 0.22 × 0.22 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	45.12 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14935, 5094
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3450
$N(param)_{refined}$:	262
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-III [3], PLATON [4]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.1675	0.4694	0.2955	0.067
H(1B)	4*e*	0.1863	0.3820	0.2478	0.067

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	4*e*	0.6175	0.2124	0.1380	0.043
H(4)	4*e*	0.8384	0.2524	0.2137	0.051
H(5)	4*e*	0.8455	0.4174	0.2778	0.044
H(6)	4*e*	0.6366	0.5369	0.2643	0.037
H(9)	4*e*	–0.0264	0.1838	–0.0577	0.035
H(10)	4*e*	–0.0582	0.0222	–0.1260	0.036
H(11)	4*e*	0.1245	–0.1216	–0.1095	0.041

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(12)	4*e*	0.3363	–0.0990	–0.0291	0.036
H(15)	4*e*	–0.1853	0.3992	0.0271	0.032
H(16)	4*e*	–0.3707	0.5323	0.0496	0.040
H(17)	4*e*	–0.2994	0.6792	0.1239	0.041
H(18)	4*e*	–0.0482	0.6919	0.1744	0.038
H(2A)	4*e*	0.0871	0.5176	0.4017	0.057
H(2B)	4*e*	0.0648	0.4090	0.3855	0.057

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*	0.28502(8)	0.55913(5)	0.18453(3)	0.0257(3)	0.0176(3)	0.0238(3)	0.0000(3)	0.0004(3)	–0.0038(3)
Br(1)	4*e*	0.34725(5)	0.69089(3)	0.28541(2)	0.0430(3)	0.0195(2)	0.0250(2)	–0.0005(2)	0.0006(2)	–0.0044(2)
Br(2)	4*e*	0.36179(5)	0.69653(4)	0.09152(2)	0.0337(3)	0.0309(3)	0.0296(2)	–0.0021(2)	0.0014(2)	0.0056(2)
O(1)	4*e*	0.2044(4)	0.4483(3)	0.2609(2)	0.078(3)	0.025(2)	0.035(2)	–0.014(2)	0.023(2)	–0.008(2)
N(1)	4*e*	0.2491(4)	0.4117(3)	0.1164(2)	0.021(2)	0.019(2)	0.021(2)	0.002(1)	0.002(1)	–0.003(1)
N(2)	4*e*	0.3444(4)	0.2447(3)	0.0734(2)	0.030(2)	0.023(2)	0.017(2)	–0.000(2)	0.001(2)	–0.001(1)
N(3)	4*e*	0.0846(4)	0.3019(3)	0.0408(2)	0.025(2)	0.021(2)	0.018(2)	–0.003(2)	–0.003(1)	–0.001(1)
N(4)	4*e*	0.5064(4)	0.4500(3)	0.1950(2)	0.024(2)	0.022(2)	0.022(2)	0.001(2)	–0.002(1)	–0.001(2)
N(5)	4*e*	0.2857(4)	0.0513(3)	0.0033(2)	0.034(2)	0.023(2)	0.020(2)	0.001(2)	–0.003(2)	–0.003(2)
N(6)	4*e*	0.0327(4)	0.5563(3)	0.1337(2)	0.028(2)	0.023(2)	0.027(2)	0.002(2)	0.008(2)	0.001(2)
C(1)	4*e*	0.3589(5)	0.3350(3)	0.1129(2)	0.026(2)	0.021(2)	0.019(2)	–0.002(2)	0.001(2)	0.001(2)
C(2)	4*e*	0.5049(5)	0.3553(4)	0.1582(2)	0.019(2)	0.027(2)	0.026(2)	–0.000(2)	0.004(2)	–0.005(2)
C(3)	4*e*	0.6240(5)	0.2793(4)	0.1641(2)	0.030(3)	0.032(3)	0.044(3)	0.007(2)	–0.005(2)	–0.015(2)
C(4)	4*e*	0.7535(6)	0.3026(4)	0.2089(3)	0.031(3)	0.044(3)	0.050(3)	0.012(2)	–0.004(2)	–0.009(2)
C(5)	4*e*	0.7579(5)	0.3997(4)	0.2466(2)	0.022(2)	0.045(3)	0.038(3)	0.006(2)	–0.011(2)	–0.003(2)
C(6)	4*e*	0.6330(5)	0.4702(4)	0.2381(2)	0.036(3)	0.027(2)	0.028(2)	–0.006(2)	–0.003(2)	–0.004(2)
C(7)	4*e*	0.2051(5)	0.2323(3)	0.0384(2)	0.028(2)	0.019(2)	0.016(2)	0.003(2)	0.002(2)	0.006(2)
C(8)	4*e*	0.1781(5)	0.1326(3)	–0.0062(2)	0.031(2)	0.021(2)	0.016(2)	–0.004(2)	0.001(2)	0.001(2)
C(9)	4*e*	0.0477(5)	0.1252(4)	–0.0530(2)	0.033(3)	0.027(2)	0.026(2)	0.002(2)	–0.001(2)	–0.000(2)
C(10)	4*e*	0.0285(5)	0.0295(4)	–0.0927(2)	0.034(3)	0.035(3)	0.021(2)	–0.004(2)	–0.003(2)	–0.009(2)
C(11)	4*e*	0.1364(6)	–0.0549(4)	–0.0834(2)	0.045(3)	0.031(2)	0.025(2)	–0.002(2)	0.000(2)	–0.012(2)
C(12)	4*e*	0.2622(5)	–0.0405(4)	–0.0352(2)	0.032(3)	0.028(2)	0.031(2)	0.002(2)	0.004(2)	–0.003(2)
C(13)	4*e*	0.1128(5)	0.3907(3)	0.0809(2)	0.023(2)	0.020(2)	0.020(2)	–0.002(2)	0.005(2)	0.003(2)
C(14)	4*e*	–0.0106(5)	0.4712(3)	0.0903(2)	0.030(2)	0.020(2)	0.022(2)	0.001(2)	0.006(2)	0.002(2)
C(15)	4*e*	–0.1590(5)	0.4593(4)	0.0575(2)	0.022(2)	0.037(3)	0.019(2)	0.000(2)	–0.000(2)	0.002(2)
C(16)	4*e*	–0.2678(5)	0.5382(4)	0.0707(2)	0.022(2)	0.041(3)	0.036(3)	0.002(2)	0.000(2)	0.009(2)
C(17)	4*e*	–0.2260(5)	0.6247(4)	0.1145(2)	0.027(3)	0.036(3)	0.042(3)	0.009(2)	0.009(2)	0.004(2)
C(18)	4*e*	–0.0762(5)	0.6313(4)	0.1445(2)	0.036(3)	0.029(2)	0.030(3)	0.006(2)	0.008(2)	0.001(2)
O(2)	4*e*	0.0524(4)	0.4745(3)	0.3702(2)	0.041(2)	0.044(2)	0.029(2)	–0.004(2)	0.001(2)	–0.000(2)

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