Crystal structure of dibromobis(2-pyridinealdoxime-κ^2N,N')-manganese(II), $MnBr_2(C_6H_6N_2O)_2$

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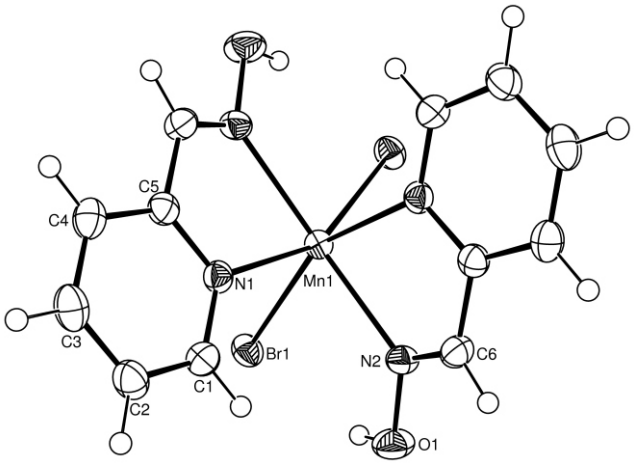

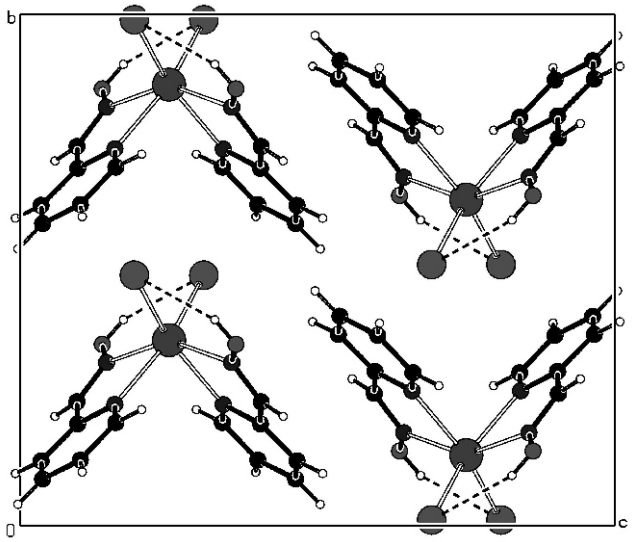

Abstract

$C_{12}H_{12}Br_2MnN_4O_2$, monoclinic, *C*12/*c*1 (no. 15), a = 7.7491(4) Å, b = 12.9943(7) Å, c = 15.3876(8) Å, β = 100.613(1)°, V = 1522.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.061, T = 200 K.

Source of material

To a solution of $MnBr_2 \cdot 4H_2O$ (0.2862 g, 0.998 mmol) in EtOH (20 ml) was added *syn*-2-pyridinealdoxime (0.3669 g, 3.004 mmol) and stirred for 3 h at room temperature. The formed precipitate was separated by filtration, washed with ether, and dried at 50 °C, to give a yellow powder (0.4116 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a 2-butanone solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with d(C—H) = 0.95 Å (CH) and U_{iso}(H) = 1.2 U_{eq}(C). The hydroxy H atom was located from Fourier difference maps and refined isotropically: d(O—H) = 0.82(3) Å. The highest peak (0.72 e Å^{-3}) and the deepest hole (–0.46 e Å^{-3}) in the difference Fourier map are located 1.18 Å and 1.43 Å from the atoms O1 and H1, respectively.

Discussion

The asymmetric unit of the title crystal structure contains one half of a neutral Mn(II) complex. The compound crystallized in the monoclinic space group *C*2/*c*, whereas the previously reported analogous chloro complex with two water solvent molecules $[MnCl_2(C_6H_6N_2O)_2] \cdot 2H_2O$ crystallized in the space group $P2_1/c$ [1]. The central Mn(II) ion has a considerably distorted octahedral coordination defined by four N atoms of the two chelating 2-pyridinealdoxime ligands and two Br^- anions (figure, top). The complex is disposed about a twofold rotation axis running in the [010] direction and passing through the Mn1 atom (figure, bottom). The tight N–Mn–N chelating angle (∠N1–Mn1–N2^i = 70.34(8)°; symmetry code i: 1–x,y,½–z) and the Br–Br repelling (∠Br1–Mn1–Br1^i = 101.80(2)°) contribute to the distortion of the ocataheron. The apical N1–Mn1–Br1^i and N2–Mn1–N2^i bond angles are 155.29(6)° and 151.4(1)°, respectively. The Mn—N(pyridine) and Mn—N(oxime) bond lengths are nearly equivalent with d(Mn—$N_{pyridine}$) = 2.301(2) Å and d(Mn—N_{oxime}) = 2.312(2) Å, and the dihedral angle between the least-squares planes of the pyridyl rings is 86.06(7)°. In the crystal structure, the complexes are stacked in columns along [100]. When viewed down [001], the successive complexes are stacked in the opposite manner. In the columns, intermolecular π–π interactions between adjacent pyridine rings are present. For Cg1 (the centroid of ring N1-C5) and Cg1^{ii} (symmetry code ii: ½–x,½–y,–z), the centroid-centroid distance is 3.722(2) Å, the planes are parallel and shifted by 1.373 Å. In addition, the complex reveals intramolecular O–H···Br hydrogen bonding between the hydroxy O atom and the Br atom with d(O1–H1O···Br1) = 3.295(2) Å forming a nearly planar five-membered ring.

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Table 1. Data collection and handling.

Crystal:	yellow block, size 0.15 × 0.21 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	61.22 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	56.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5348, 1827
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1467
$N(param)_{refined}$:	100
Programs:	SHELXS-97, SHELXL-97 [2], ORTEP-3 [3]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1O)	8*f*	0.159(4)	0.098(3)	0.327(2)	0.05(1)
H(1)	8*f*	0.1350	0.2733	0.2040	0.034
H(2)	8*f*	–0.0015	0.3957	0.1039	0.038
H(3)	8*f*	0.1460	0.4589	–0.0044	0.040
H(4)	8*f*	0.4311	0.3986	–0.0084	0.035
H(6)	8*f*	0.3118	0.2866	0.4419	0.033

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*	½	0.13747(4)	¼	0.0216(3)	0.0244(3)	0.0215(3)	0	0.0035(2)	0
Br(1)	8*f*	0.24254(4)	0.01044(2)	0.19169(2)	0.0275(2)	0.0291(2)	0.0306(2)	–0.0044(1)	0.0007(1)	–0.0001(1)
N(1)	8*f*	0.3568(3)	0.2632(2)	0.1589(1)	0.024(1)	0.024(1)	0.020(1)	0.0002(9)	0.0026(9)	–0.0019(9)
N(2)	8*f*	0.3353(3)	0.1815(2)	0.3554(2)	0.021(1)	0.033(1)	0.027(1)	–0.0018(9)	0.0057(9)	0.003(1)
O(1)	8*f*	0.1690(3)	0.1455(2)	0.3624(2)	0.028(1)	0.043(1)	0.046(1)	–0.0094(9)	0.015(1)	–0.005(1)
C(1)	8*f*	0.1959(4)	0.2990(2)	0.1603(2)	0.027(1)	0.034(2)	0.025(2)	0.001(1)	0.006(1)	–0.003(1)
C(2)	8*f*	0.1132(4)	0.3720(2)	0.1007(2)	0.030(2)	0.035(2)	0.029(2)	0.009(1)	0.001(1)	–0.002(1)
C(3)	8*f*	0.2000(4)	0.4094(2)	0.0373(2)	0.041(2)	0.029(2)	0.029(2)	0.006(1)	–0.002(1)	0.003(1)
C(4)	8*f*	0.3681(4)	0.3737(2)	0.0347(2)	0.037(2)	0.027(1)	0.024(2)	–0.002(1)	0.003(1)	0.003(1)
C(5)	8*f*	0.4412(3)	0.3012(2)	0.0964(2)	0.024(1)	0.023(1)	0.023(2)	–0.003(1)	0.003(1)	–0.002(1)
C(6)	8*f*	0.3853(3)	0.2582(2)	0.4050(2)	0.028(2)	0.031(1)	0.026(2)	0.002(1)	0.008(1)	–0.001(1)

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