Crystal structure of dibromobis(1-(2-pyridylmethyl)-2-(2-pyridyl)benzimidazole)manganese(II) — acetonitrile (1:1), $MnBr_2(C_{18}H_{14}N_4)_2 \cdot CH_3CN$

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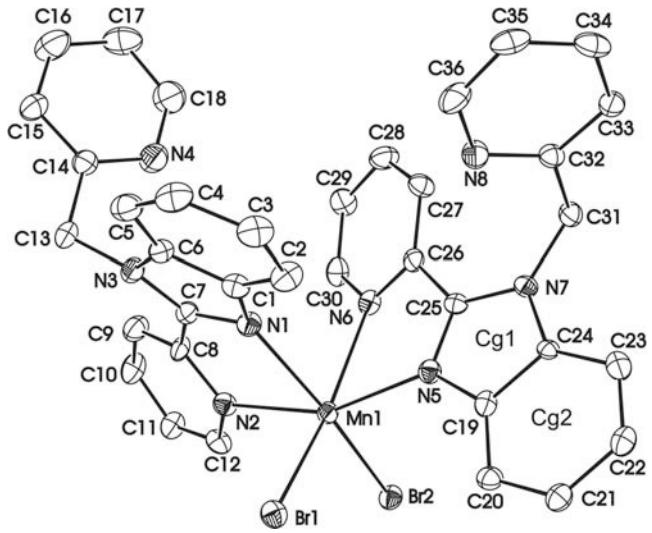

Abstract

$C_{38}H_{31}Br_2MnN_9$, triclinic, $P\bar{1}$ (no. 2), a = 9.610(1) Å, b = 12.019(2) Å, c = 17.771(2) Å, α = 107.096(3)°, β = 96.468(3)°, γ = 107.982(3)°, V = 1818.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.061, $wR_{ref}(F^2)$ = 0.153, T = 200 K.

Source of material

1-(2-Pyridylmethyl)-2-(2-pyridyl)benzimidazole, $C_{18}H_{14}N_4$, was synthesized by reacting 1,2-diaminobenzene and 2-pyridinecarboxaldehyde according to the literature procedure [1]. A solution of $MnBr_2$ (0.30 g, 1.40 mmol) and 1-(2-pyridylmethyl)-2-(2-pyridyl)benzimidazole (0.40 g, 1.40 mmol) in EtOH (10 ml) was stirred for 1 h at room temparature. The formed precipitate was separated by filtration and washed with acetone and dried in vacuo, to give a yellow powder (0.23 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their respective carrier atoms [d(C—H) = 0.95 Å (CH), 0.99 Å (CH_2) or 0.98 Å (CH_3) and U_{iso}(H) = 1.2 U_{eq}(CH and CH_2) or 1.5 U_{eq}(CH_3)].

Discussion

The crystal structure of the title compound consists of neutral complex [$MnBr_2(C_{18}H_{14}N_4)_2$] and an acetonitrile solvent molecule. Mn(II) ion is six-coordinated in a distorted octahedral manner by four N atoms from two chelate 1-(2-pyridylmethyl)-2-(2-pyridyl)benzimidazole (pmpb) ligands and two Br atoms. In the previously reported crystal structure of dinuclear Cu(I) complex [Cu(pmpb)(CH_3CN)]$_2$(BF_4)$_2$ [1], the pmpb acted as a chelating and bridging tridentate ligand, whereas the ligand in the title complex chelates the Mn(II) ion to form a five-membered chelate ring through the α-diimine coordination setting involving the benzimidazole imine N atom and the 2-(2-pyridyl) group. The Br atoms are in *cis* conformation with respect to each other. The main contributions to the distortion are the tight N–Mn–N chelate angles (70.7(2)° and 71.1(2)°), which result in non-linear *trans* axes (∠Br1–Mn1–N6 = 163.1(1)°, ∠Br2–Mn1–N1 = 162.9(1)° and ∠N2–Mn1–N5 = 156.7(2)°). While the two Mn—Br bond lengths are nearly equivalent (2.616(1) Å and 2.648(1) Å), the two Mn—$N_{imidazole}$ bonds (2.211(5) and 2.295(5) Å) are somewhat shorter than the two Mn—$N_{pyridine}$ bonds (2.350(6) and 2.451(6) Å). The complex displays numerous intra- and intermolecular π-π interactions between the imidazole and six-membered rings. The shortest distance between Cg1 (the centroid of imidazole ring N5-C25) and Cg2^i (ring C19-C24; symmetry code i: $-x$,1$-y$,$-z$) is 3.973(4) Å, and the dihedral angle between the ring planes is 0.8(3)°. In addition, there are weak intra- and intermolecular C–H···Br hydrogen bonds with d(C···Br) = 3.536(7) - 3.723(7) Å.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.11 × 0.13 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	26.01 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{max}$:	52.14°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11226, 7065
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4182
$N(param)_{refined}$:	452
Programs:	SHELXS-97 [2], SHELXL-97 [3], ORTEP [4], PLATON [5]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.0939	0.7120	0.3120	0.058
H(3)	2*i*	–0.0180	0.7083	0.4223	0.064
H(4)	2*i*	0.1260	0.7744	0.5531	0.064
H(5)	2*i*	0.3891	0.8422	0.5791	0.063
H(9)	2*i*	0.8475	0.8686	0.4187	0.062

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(10)	2*i*	1.0438	0.9459	0.3580	0.064
H(11)	2*i*	0.9915	1.0038	0.2458	0.053
H(12)	2*i*	0.7407	0.9642	0.1911	0.049
H(13A)	2*i*	0.6502	0.9141	0.5734	0.057
H(13B)	2*i*	0.7651	0.9328	0.5157	0.057
H(15)	2*i*	0.7786	0.8045	0.6401	0.074
H(16)	2*i*	0.8015	0.6162	0.6361	0.097
H(17)	2*i*	0.7349	0.4541	0.5086	0.095
H(18)	2*i*	0.6449	0.4899	0.3944	0.092
H(20)	2*i*	0.0554	0.8497	0.1252	0.044
H(21)	2*i*	–0.1943	0.7986	0.0600	0.047
H(22)	2*i*	–0.3623	0.5933	0.0106	0.049
H(23)	2*i*	–0.2938	0.4306	0.0280	0.049

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(27)	2*i*	0.1759	0.3532	0.1858	0.050
H(28)	2*i*	0.3997	0.3184	0.2205	0.066
H(29)	2*i*	0.6306	0.4640	0.2218	0.061
H(30)	2*i*	0.6328	0.6439	0.1974	0.053
H(31A)	2*i*	0.0098	0.2984	0.0856	0.045
H(31B)	2*i*	–0.1447	0.2973	0.0401	0.045
H(33)	2*i*	–0.3167	0.1582	0.0919	0.049
H(34)	2*i*	–0.4218	0.1302	0.2025	0.061
H(35)	2*i*	–0.2974	0.2738	0.3337	0.066
H(36)	2*i*	–0.0806	0.4377	0.3505	0.068
H(37A)	2*i*	0.3066	0.0146	0.0819	0.094
H(37B)	2*i*	0.3322	0.1340	0.0550	0.094
H(37C)	2*i*	0.2163	0.0003	–0.0039	0.094

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*	0.3966(1)	0.81491(9)	0.20335(5)	0.0268(5)	0.0338(6)	0.0320(5)	0.0036(4)	0.0038(4)	0.0140(4)
Br(1)	2*i*	0.32905(7)	1.01681(7)	0.26022(4)	0.0364(4)	0.0420(5)	0.0444(4)	0.0106(3)	0.0117(3)	0.0146(3)
Br(2)	2*i*	0.46459(7)	0.83518(7)	0.06832(4)	0.0380(4)	0.0484(5)	0.0350(4)	0.0086(3)	0.0096(3)	0.0191(3)
N(1)	2*i*	0.4088(6)	0.7984(5)	0.3291(3)	0.033(3)	0.042(4)	0.036(3)	0.009(3)	0.011(3)	0.017(3)
N(2)	2*i*	0.6500(5)	0.9000(5)	0.2721(3)	0.029(3)	0.036(3)	0.046(3)	0.009(3)	0.008(3)	0.015(3)
N(3)	2*i*	0.5474(6)	0.8542(5)	0.4555(3)	0.040(3)	0.044(4)	0.033(3)	0.011(3)	0.004(3)	0.015(3)
N(4)	2*i*	0.6539(7)	0.6632(7)	0.4467(4)	0.076(5)	0.061(5)	0.051(4)	0.032(4)	0.011(3)	0.018(3)
N(5)	2*i*	0.1689(5)	0.6714(5)	0.1522(3)	0.034(3)	0.036(4)	0.032(3)	0.012(3)	0.008(2)	0.011(2)
N(6)	2*i*	0.4138(6)	0.6083(5)	0.1774(3)	0.039(3)	0.044(4)	0.033(3)	0.015(3)	0.006(3)	0.012(3)
N(7)	2*i*	0.0037(5)	0.4725(5)	0.1055(3)	0.029(3)	0.031(3)	0.035(3)	0.007(2)	0.011(2)	0.015(2)
N(8)	2*i*	–0.0663(6)	0.3999(5)	0.2356(3)	0.041(3)	0.051(4)	0.037(3)	0.005(3)	0.012(3)	0.016(3)
C(1)	2*i*	0.3132(7)	0.7832(6)	0.3812(4)	0.040(4)	0.038(4)	0.044(4)	0.016(3)	0.017(3)	0.017(3)
C(2)	2*i*	0.1530(7)	0.7388(7)	0.3650(4)	0.038(4)	0.065(5)	0.051(5)	0.021(4)	0.019(3)	0.029(4)
C(3)	2*i*	0.0883(8)	0.7369(7)	0.4307(5)	0.038(4)	0.066(6)	0.069(6)	0.022(4)	0.024(4)	0.034(4)
C(4)	2*i*	0.1754(9)	0.7760(7)	0.5099(5)	0.061(5)	0.067(6)	0.055(5)	0.034(4)	0.035(4)	0.033(4)
C(5)	2*i*	0.3307(9)	0.8166(7)	0.5261(4)	0.068(5)	0.052(5)	0.048(5)	0.027(4)	0.021(4)	0.024(4)
C(6)	2*i*	0.3963(7)	0.8178(6)	0.4603(4)	0.045(4)	0.036(4)	0.035(4)	0.014(3)	0.009(3)	0.015(3)
C(7)	2*i*	0.5486(7)	0.8405(6)	0.3755(4)	0.035(4)	0.036(4)	0.032(4)	0.010(3)	0.006(3)	0.013(3)
C(8)	2*i*	0.6821(7)	0.8786(6)	0.3411(4)	0.030(4)	0.049(5)	0.026(4)	0.009(3)	–0.001(3)	0.013(3)
C(9)	2*i*	0.8274(8)	0.8910(7)	0.3728(4)	0.045(4)	0.062(6)	0.048(5)	0.015(4)	0.003(4)	0.025(4)
C(10)	2*i*	0.9442(7)	0.9368(7)	0.3365(4)	0.026(4)	0.081(6)	0.049(5)	0.016(4)	0.004(3)	0.021(4)
C(11)	2*i*	0.9137(7)	0.9683(7)	0.2697(4)	0.025(4)	0.062(5)	0.045(4)	0.011(3)	0.011(3)	0.021(4)
C(12)	2*i*	0.7639(7)	0.9461(6)	0.2385(4)	0.032(4)	0.039(4)	0.050(4)	0.002(3)	0.021(3)	0.018(3)
C(13)	2*i*	0.6711(8)	0.8745(7)	0.5208(4)	0.056(5)	0.051(5)	0.030(4)	0.018(4)	0.001(3)	0.013(3)
C(14)	2*i*	0.6942(8)	0.7533(7)	0.5201(4)	0.058(5)	0.044(5)	0.038(4)	0.017(4)	0.014(4)	0.015(3)
C(15)	2*i*	0.7502(9)	0.7377(8)	0.5900(5)	0.081(6)	0.059(6)	0.048(5)	0.030(5)	0.002(4)	0.023(4)
C(16)	2*i*	0.765(1)	0.628(1)	0.5880(6)	0.107(8)	0.096(8)	0.068(7)	0.059(7)	0.022(6)	0.043(6)
C(17)	2*i*	0.725(1)	0.5321(9)	0.5131(6)	0.098(7)	0.074(7)	0.101(8)	0.056(6)	0.038(6)	0.050(6)
C(18)	2*i*	0.671(1)	0.5549(9)	0.4453(6)	0.100(7)	0.067(7)	0.068(6)	0.041(6)	0.024(5)	0.018(5)
C(19)	2*i*	0.0307(6)	0.6695(6)	0.1163(4)	0.024(3)	0.043(4)	0.028(3)	0.006(3)	0.008(3)	0.014(3)
C(20)	2*i*	–0.0133(7)	0.7660(6)	0.1062(4)	0.036(4)	0.037(4)	0.039(4)	0.011(3)	0.011(3)	0.019(3)
C(21)	2*i*	–0.1614(7)	0.7347(7)	0.0671(4)	0.035(4)	0.047(5)	0.038(4)	0.017(3)	0.008(3)	0.017(3)
C(22)	2*i*	–0.2629(7)	0.6108(7)	0.0379(4)	0.032(4)	0.053(5)	0.036(4)	0.015(4)	0.004(3)	0.015(3)
C(23)	2*i*	–0.2238(7)	0.5139(7)	0.0472(4)	0.039(4)	0.041(5)	0.034(4)	0.006(3)	0.011(3)	0.009(3)
C(24)	2*i*	–0.0744(6)	0.5450(5)	0.0869(3)	0.025(3)	0.027(4)	0.029(3)	0.007(3)	0.009(3)	0.014(3)
C(25)	2*i*	0.1495(6)	0.5524(6)	0.1439(3)	0.031(3)	0.032(4)	0.029(3)	0.012(3)	0.014(3)	0.014(3)
C(26)	2*i*	0.2800(7)	0.5209(6)	0.1720(3)	0.038(4)	0.036(4)	0.022(3)	0.008(3)	0.008(3)	0.008(3)
C(27)	2*i*	0.2706(7)	0.4118(6)	0.1883(4)	0.035(4)	0.038(4)	0.053(5)	0.009(3)	0.013(3)	0.019(3)
C(28)	2*i*	0.4030(8)	0.3909(7)	0.2084(4)	0.063(5)	0.054(5)	0.062(5)	0.029(4)	0.011(4)	0.032(4)
C(29)	2*i*	0.5394(8)	0.4775(7)	0.2104(4)	0.044(4)	0.047(5)	0.063(5)	0.025(4)	0.009(4)	0.015(4)
C(30)	2*i*	0.5391(7)	0.5843(7)	0.1951(4)	0.033(4)	0.051(5)	0.043(4)	0.018(4)	0.006(3)	0.007(3)
C(31)	2*i*	–0.0670(7)	0.3376(6)	0.0912(4)	0.041(4)	0.036(4)	0.030(4)	0.009(3)	0.009(3)	0.009(3)
C(32)	2*i*	–0.1387(7)	0.3172(6)	0.1609(4)	0.032(3)	0.036(4)	0.039(4)	0.011(3)	0.011(3)	0.016(3)
C(33)	2*i*	–0.2702(7)	0.2149(6)	0.1454(4)	0.036(4)	0.046(5)	0.039(4)	0.007(3)	0.007(3)	0.020(3)
C(34)	2*i*	–0.3317(8)	0.1982(7)	0.2107(5)	0.043(4)	0.048(5)	0.076(6)	0.016(4)	0.027(4)	0.038(4)
C(35)	2*i*	–0.2584(9)	0.2831(8)	0.2882(5)	0.062(5)	0.074(6)	0.059(5)	0.035(5)	0.034(4)	0.048(5)
C(36)	2*i*	–0.1292(9)	0.3803(8)	0.2974(4)	0.066(5)	0.075(6)	0.036(4)	0.025(5)	0.016(4)	0.027(4)
N(9)	2*i*	0.0345(9)	0.0965(7)	0.1175(5)	0.100(6)	0.084(6)	0.097(6)	0.061(5)	0.048(5)	0.048(5)
C(37)	2*i*	0.2581(9)	0.0552(8)	0.0526(5)	0.065(5)	0.084(7)	0.066(5)	0.041(5)	0.038(4)	0.042(5)
C(38)	2*i*	0.136(1)	0.0803(7)	0.0903(5)	0.078(6)	0.044(5)	0.060(5)	0.019(5)	0.008(5)	0.029(4)

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