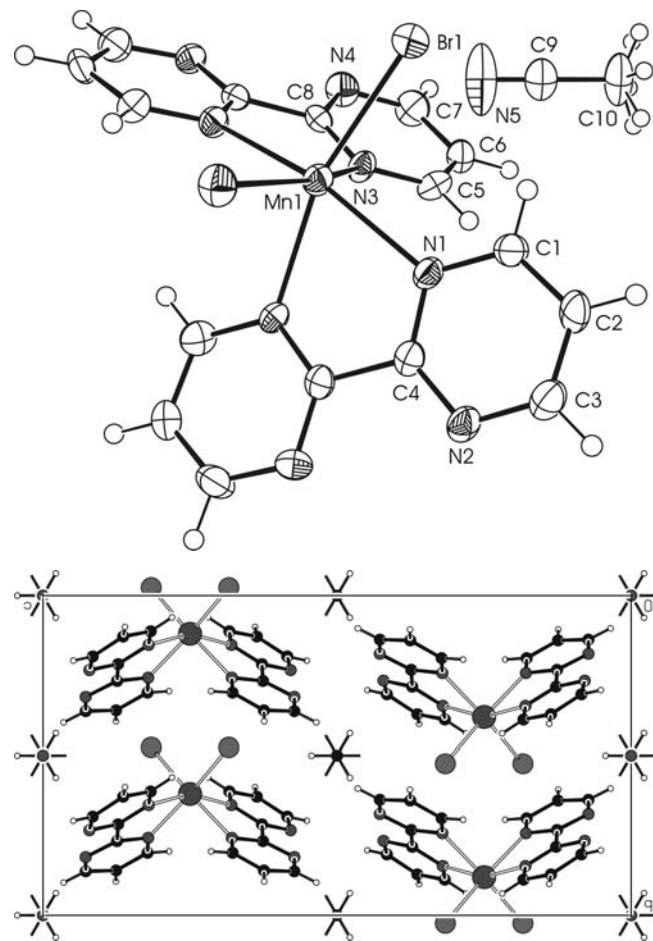


Crystal structure of dibromobis(2,2'-bipyrimidine- κ^2N,N')manganese(II) — acetonitrile (1:1), $\text{MnBr}_2(\text{C}_8\text{H}_6\text{N}_4)_2 \cdot \text{CH}_3\text{CN}$

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Abstract

$\text{C}_{18}\text{H}_{15}\text{Br}_2\text{MnN}_9$, orthorhombic, $C222_1$ (no. 20), $a = 8.576(1) \text{ \AA}$, $b = 11.554(2) \text{ \AA}$, $c = 21.213(3) \text{ \AA}$, $V = 2101.9 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.045$, $wR_{\text{ref}}(F^2) = 0.093$, $T = 200 \text{ K}$.

Source of material

To a solution of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ (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 CH_3CN solution.

Experimental details

Hydrogen atoms were positioned geometrically and allowed to ride on their parent atoms with $d(\text{C}—\text{H}) = 0.95 \text{ \AA}$ (CH) or $0.98 \text{ \AA}$ (CH_3) and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C}_{\text{methyl}})$. The methyl group of the acetonitrile solvent molecule appears to be disordered. Its H atoms were modelled as disordered over two sites rotated by 60° from one another, with an occupancy ratio of 0.5 : 0.5. The highest peak ($0.73 \text{ e} \cdot \text{\AA}^{-3}$) and the deepest hole ($-0.65 \text{ e} \cdot \text{\AA}^{-3}$) in the difference Fourier map are located $2.07 \text{ \AA}$ and $1.71 \text{ \AA}$ from the atom Br1, respectively. Because the Flack parameter is 0.02(2) in the final cycles of refinement, the absolute crystal structure can be regarded as correct.

Discussion

The asymmetric unit of the title crystal structure contains one half of a neutral Mn(II) complex and one half of an acetonitrile solvent molecule. In the complex, the Mn(II) ion is six-coordinated in a distorted octahedral manner by four N atoms of the two bidentate 2,2'-bipyrimidine ligands and two Br^- anions (figure, top). The complex is located on a two-fold rotation axis running in the [010] direction and passing through the Mn1 atom. The acetonitrile is disposed about a two-fold rotation axis along [100] and passing through the N5, C9 and C10 atoms; thus the methyl H atoms are disordered over two sites (figure, bottom). The tight N–Mn–N chelating angle ($\angle \text{N1–Mn1–N3}^i = 71.0(2)^\circ$; symmetry code i: $-x, y, 1/2 - z$) and the Br–Br repelling ($\angle \text{Br1–Mn1–Br1}^i = 100.00(5)^\circ$) contribute the distortion of the octahedron. The apical N3–Mn1–Br1ⁱ and N1–Mn1–N1ⁱ bond angles are $164.1(1)^\circ$ and $159.7(2)^\circ$, respectively. The Mn–N bond lengths are almost equivalent ($2.294(4) \text{ \AA}$ and $2.297(5) \text{ \AA}$). The dihedral angle between the least-squares planes of the two bpym ligands is $62.37(7)^\circ$.

In the crystal structure, the complexes are stacked in columns along [100]. When viewed down the c axis, the successive complexes are stacked in the opposite manner (figure, bottom). In the columns, inter- and intramolecular π – π interactions between adjacent pyrimidine rings are present. The shortest distance between Cg1 (the centroid of ring N1–C4) and Cg2ⁱⁱ (ring N3–C8, symmetry code ii: $1/2 - x, 1/2 + y, 1/2 - z$) is $4.207(3) \text{ \AA}$, and the dihedral angle between the ring planes is $8.0(3)^\circ$. In addition, there are inter- and intra-molecular hydrogen bonds with $d(\text{C1–H1} \cdots \text{Br1}) = 3.565(6) \text{ \AA}$, $\angle \text{C1–H1} \cdots \text{Br1} = 127.4^\circ$; $d(\text{C–H6} \cdots \text{Br1}) = 3.786(6) \text{ \AA}$, $\angle \text{C6–H6} \cdots \text{Br1} = 153.2^\circ$; $d(\text{C7–H7} \cdots \text{N5}) = 3.25(1) \text{ \AA}$, $\angle \text{C7–H7} \cdots \text{N5} = 137.5^\circ$ and $d(\text{C10–H10C} \cdots \text{N2}) = 3.507(5) \text{ \AA}$, $\angle \text{C10–H10C} \cdots \text{N2} = 149.9^\circ$.

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Table 1. Data collection and handling.

Crystal:	yellow block, size 0.09 × 0.10 × 0.16 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ :	44.56 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART 1000 CCD, φ/ω
$2\theta_{\max}$:	56.6°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	7816, 2606
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1772
$N(\text{param})_{\text{refined}}$:	138
Programs:	SHELXS-97, SHELXL-97 [1], ORTEP-III [2], PLATON [3]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	8c		0.3711	0.4319	0.2807	0.034
H(2)	8c		0.5521	0.4017	0.3606	0.040
H(3)	8c		0.4739	0.2961	0.4484	0.043
H(5)	8c		0.2865	0.2003	0.2142	0.036
H(6)	8c		0.3807	0.1061	0.1239	0.039
H(7)	8c		0.2233	0.1026	0.0352	0.044
H(10A)	8c	0.50	0.7985	0.0000	0.0436	0.090
H(10B)	8c	0.50	0.7985	0.0693	−0.0218	0.090
H(10C)	8c	0.50	0.7985	−0.0693	−0.0218	0.090

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Br(1)	8c	0.16608(7)	0.52524(5)	0.18405(3)	0.0334(3)	0.0372(3)	0.0334(3)	−0.0014(3)	0.0009(3)	0.0059(3)
Mn(1)	4b	0	0.3803(1)	¼	0.0236(7)	0.0310(7)	0.0224(7)	0	−0.0026(6)	0
N(1)	8c	0.1976(5)	0.3453(4)	0.3204(2)	0.022(3)	0.031(2)	0.023(3)	0.002(2)	−0.004(2)	0.000(2)
N(2)	8c	0.2575(6)	0.2664(5)	0.4211(2)	0.027(3)	0.043(3)	0.021(3)	0.001(2)	−0.005(2)	−0.004(2)
N(3)	8c	0.0808(5)	0.2429(4)	0.1789(3)	0.022(3)	0.033(3)	0.022(3)	0.001(2)	−0.007(2)	−0.002(2)
N(4)	8c	0.0422(6)	0.1825(5)	0.0726(2)	0.035(3)	0.045(3)	0.022(3)	0.000(3)	0.002(2)	−0.006(2)
C(1)	8c	0.3421(7)	0.3884(4)	0.3168(3)	0.029(3)	0.028(3)	0.027(3)	−0.003(3)	−0.002(4)	0.002(3)
C(2)	8c	0.4493(7)	0.3716(5)	0.3636(3)	0.020(3)	0.046(4)	0.033(4)	0.007(3)	0.004(3)	−0.006(3)
C(3)	8c	0.4014(7)	0.3093(6)	0.4153(3)	0.032(4)	0.045(4)	0.031(4)	0.005(3)	−0.006(3)	−0.003(3)
C(4)	8c	0.1635(7)	0.2855(4)	0.3723(3)	0.023(3)	0.030(3)	0.023(3)	0.004(3)	−0.001(3)	−0.006(2)
C(5)	8c	0.2228(7)	0.1958(5)	0.1777(3)	0.034(3)	0.028(3)	0.028(4)	0.005(3)	−0.007(3)	0.004(3)
C(6)	8c	0.2801(7)	0.1405(5)	0.1244(3)	0.023(3)	0.035(4)	0.039(4)	0.001(3)	0.001(3)	0.003(3)
C(7)	8c	0.1855(8)	0.1378(5)	0.0727(3)	0.037(4)	0.043(4)	0.030(4)	0.008(3)	0.006(3)	−0.006(3)
C(8)	8c	−0.0035(7)	0.2325(4)	0.1260(3)	0.022(3)	0.023(3)	0.027(3)	−0.006(3)	0.002(3)	0.004(2)
N(5)	4a	0.463(1)	0	0	0.033(6)	0.11(1)	0.14(1)	0	0	−0.065(8)
C(9)	4a	0.592(1)	0	0	0.037(6)	0.056(8)	0.043(7)	0	0	−0.015(5)
C(10)	4a	0.760(1)	0	0	0.028(5)	0.09(1)	0.059(8)	0	0	−0.028(7)

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