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catena-Poly[[(2,2′-bipyridine-κ^2N,N')manganese(II)]-di-μ-bromido]

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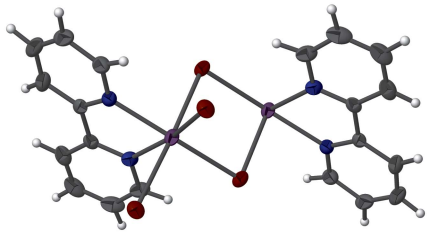
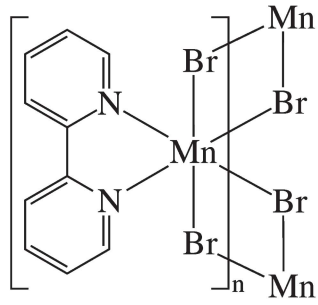
Structural data: full structural data are available from iucrdata.iucr.org

In the polymeric title complex, $[MnBr_2(C_{10}H_8N_2)]_n$, the Mn^{II} ion, situated on a twofold axis of symmetry, is six-coordinated in a distorted octahedral coordination geometry defined by two N atoms from the chelating 2,2′-bipyridine ligand and four bridging Br^- anions. The crystal reveals a one-dimensional Br-bridged chain along the *c*-axis direction with a zigzag topology. In the crystals, contacts between chains include π–π interactions between pyridyl rings [inter-centroid separation = 4.082 (1) Å]

3D view



Chemical scheme



Structure description

With reference to the title complex, $[MnBr_2(bipy)]_n$ (bipy = 2,2′-bipyridine), the crystal structures of related Mn^{II} complexes, namely $[MnCl_2(bipy)]_n$ (Lubben *et al.*, 1995) and $[MnBr_2(bipy)_2]$ (Hwang & Ha, 2007) have been determined previously.

In the title complex, the central Mn^{II} cation is six-coordinated within a distorted octahedral coordination geometry defined by two N atoms from chelating bipy ligand and four bridging Br^- anions (Fig. 1). The maximum deviation from the ideal octahedral angles is seen in the N1—Mn—N1^{i} chelate angle of 73.08 (7)°; symmetry operation (i): $-x, y, -z+\frac{1}{2}$. The Mn ions are bridged by four bromido ligands to form a zigzag chain (glide symmetry) structure along the *c*-axis direction so the asymmetric unit of the polymer contains one half of the repeat unit, *i.e.* $MnBr_2(bipy)$; the Mn^{II} cation is situated on a twofold axis of symmetry. The Mn—Br bond lengths are somewhat different: the Mn—Br(*trans* to Br) distance of 2.7975 (2) Å is longer than the Mn—Br(*trans* to N) distance of 2.6373 (3) Å. The distance between adjacent Mn atoms is relatively short with the separation being 3.9656 (3) Å. The complex molecules are stacked in columns along the *a* axis (Fig. 2). In the columns, several intermolecular π–π interactions between adjacent pyridine rings are present. The closest contact involves *Cg*1 (the centroid of ring

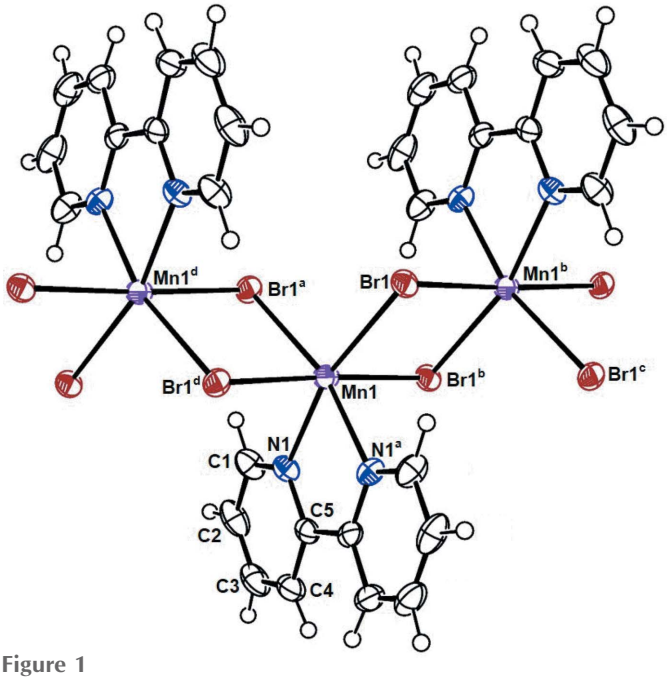


Figure 1
Part of the coordination polymer formed by the title complex showing the atom labelling and displacement ellipsoids drawn at the 50% probability level for non-H atoms. Symmetry codes: (*a*) $-x, y, -z+\frac{1}{2}$; (*b*) $-x, -y, -z$; (*c*) $x, -y, z-\frac{1}{2}$; (*d*) $x, -y, z+\frac{1}{2}$.

N1,C1–C5) and *Cg*1^{ii} [symmetry code: (ii) $x, -y+1, z+\frac{1}{2}$], the centroid–centroid distance is 4.082 (1) Å and the dihedral angle between the ring planes is 8.79 (9)°.

Synthesis and crystallization

To a solution of $[MnBr_2(bipy)_2]$ (0.2713 g, 0.515 mmol) in 2-methoxyethanol (30 ml) was added $MnBr_2{\cdot}4H_2O$ (0.1491 g, 0.520 mmol), followed by reflux for 2 h. After cooling, the formed precipitate was separated by filtration, washed with ethanol and ether, and dried at 323 K, to give a pale-yellow powder (0.2671 g). Pale-yellow crystals of the product suitable for X-ray analysis were obtained by slow evaporation from its 2-methoxyethanol solution at room temperature.

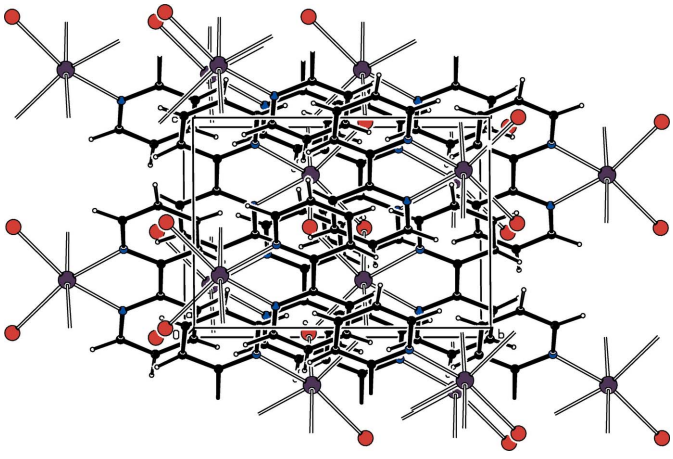


Figure 2
The packing in the crystal of the title complex, viewed approximately along the *a* axis.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[MnBr_2(C_{10}H_8N_2)]$
M_r	370.94
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	223
a, *b*, *c* (Å)	17.3039 (9), 9.5255 (5), 7.1852 (3)
β (°)	109.0347 (15)
V (Å^3)	1119.57 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	8.28
Crystal size (mm)	0.29 × 0.14 × 0.05
Data collection	
Diffractometer	PHOTON 100 CMOS detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.373, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14090, 1068, 1037
R_{int}	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.034, 1.11
No. of reflections	1068
No. of parameters	85
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.23

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2014/7* (Sheldrick, 2015*a*), *SHELXL2014/7* (Sheldrick, 2015*b*) and *ORTEP-3 for Windows* (Farrugia, 2012).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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References

Bruker (2016). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
Hwang, I.-C. & Ha, K. (2007). *Z. Krist. New Cryst. Struct.* **222**, 209–210.
Lubben, M., Meetsma, A. & Feringa, B. L. (1995). *Inorg. Chim. Acta*, **230**, 169–172.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

IUCrData (2021). **6**, x210083 [https://doi.org/10.1107/S2414314621000833]

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Crystal data

$[MnBr_2(C_{10}H_8N_2)]$
M_r = 370.94
Monoclinic, $C2/c$
a = 17.3039 (9) Å
b = 9.5255 (5) Å
c = 7.1852 (3) Å
β = 109.0347 (15)°
V = 1119.57 (10) Å^3
Z = 4
$F(000)$ = 708
D_x = 2.201 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9930 reflections
θ = 3.6–26.0°
μ = 8.28 mm^{-1}
T = 223 K
Block, pale yellow
0.29 × 0.14 × 0.05 mm

Data collection

PHOTON 100 CMOS detector diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.373, T_{max} = 0.745
14090 measured reflections
1068 independent reflections
1037 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 26.0°, θ_{min} = 3.6°
h = −21→21
k = −11→11
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.013
$wR(F^2)$ = 0.034
S = 1.11
1068 reflections
85 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0095P)^2 + 1.0722P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All H atoms were located from Fourier difference maps and refined isotropically; C—H = 0.93 (2)–0.97 (2) Å.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.0000	0.08813 (3)	0.2500	0.02456 (9)
Br1	−0.09377 (2)	−0.09461 (2)	0.00183 (2)	0.02780 (8)
N1	0.07232 (8)	0.27734 (14)	0.39308 (19)	0.0259 (3)
C1	0.14754 (10)	0.2716 (2)	0.5270 (3)	0.0339 (4)
C2	0.19474 (12)	0.3903 (2)	0.5944 (3)	0.0411 (4)
C3	0.16249 (12)	0.5191 (2)	0.5240 (3)	0.0416 (4)
C4	0.08538 (12)	0.52703 (19)	0.3900 (3)	0.0354 (4)
C5	0.04134 (10)	0.40425 (15)	0.3247 (2)	0.0251 (3)
H1	0.1647 (13)	0.178 (3)	0.573 (3)	0.046 (6)*
H2	0.2483 (15)	0.379 (2)	0.692 (3)	0.043 (6)*
H3	0.1942 (17)	0.599 (2)	0.561 (4)	0.053 (7)*
H4	0.0607 (15)	0.612 (2)	0.333 (4)	0.049 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.02373 (17)	0.02100 (17)	0.02314 (17)	0.000	−0.00031 (13)	0.000
Br1	0.02714 (10)	0.02824 (11)	0.02510 (10)	−0.00752 (6)	0.00451 (7)	−0.00407 (5)
N1	0.0229 (6)	0.0269 (7)	0.0271 (6)	−0.0011 (5)	0.0070 (5)	−0.0057 (5)
C1	0.0246 (8)	0.0390 (10)	0.0346 (9)	0.0008 (7)	0.0047 (7)	−0.0101 (7)
C2	0.0284 (9)	0.0578 (12)	0.0360 (10)	−0.0106 (8)	0.0091 (8)	−0.0203 (8)
C3	0.0470 (10)	0.0427 (11)	0.0395 (10)	−0.0210 (9)	0.0203 (8)	−0.0179 (8)
C4	0.0487 (10)	0.0276 (9)	0.0365 (9)	−0.0090 (8)	0.0227 (8)	−0.0072 (7)
C5	0.0299 (8)	0.0251 (8)	0.0262 (8)	−0.0030 (6)	0.0173 (7)	−0.0040 (6)

Geometric parameters (Å, º)

Mn1—N1^{i}	2.2433 (13)	C1—C2	1.386 (3)
Mn1—N1	2.2433 (13)	C1—H1	0.97 (2)
Mn1—Br1^{i}	2.6373 (3)	C2—C3	1.375 (3)
Mn1—Br1	2.6373 (3)	C2—H2	0.97 (2)
Mn1—Br1^{ii}	2.7975 (2)	C3—C4	1.369 (3)
Mn1—Br1^{iii}	2.7975 (2)	C3—H3	0.93 (2)
Br1—Mn1^{ii}	2.7975 (2)	C4—C5	1.391 (2)
N1—C1	1.344 (2)	C4—H4	0.95 (2)
N1—C5	1.348 (2)	C5—C5^{i}	1.482 (3)
N1^{i}—Mn1—N1	73.08 (7)	C1—N1—Mn1	124.10 (11)
N1^{i}—Mn1—Br1^{i}	165.56 (4)	C5—N1—Mn1	117.21 (10)
N1—Mn1—Br1^{i}	95.29 (3)	N1—C1—C2	122.67 (18)
N1^{i}—Mn1—Br1	95.29 (3)	N1—C1—H1	113.6 (13)
N1—Mn1—Br1	165.56 (4)	C2—C1—H1	123.7 (13)
Br1^{i}—Mn1—Br1	97.395 (13)	C3—C2—C1	118.50 (18)
N1^{i}—Mn1—Br1^{ii}	92.32 (3)	C3—C2—H2	122.7 (13)
N1—Mn1—Br1^{ii}	85.65 (3)	C1—C2—H2	118.8 (13)

Br1^{i}—Mn1—Br1^{ii}	95.344 (7)	C4—C3—C2	119.58 (17)
Br1—Mn1—Br1^{ii}	86.331 (6)	C4—C3—H3	120.3 (16)
N1^{i}—Mn1—Br1^{iii}	85.65 (3)	C2—C3—H3	120.0 (16)
N1—Mn1—Br1^{iii}	92.31 (3)	C3—C4—C5	119.46 (18)
Br1^{i}—Mn1—Br1^{iii}	86.331 (6)	C3—C4—H4	123.3 (15)
Br1—Mn1—Br1^{iii}	95.344 (7)	C5—C4—H4	117.1 (15)
Br1^{ii}—Mn1—Br1^{iii}	177.470 (13)	N1—C5—C4	121.44 (16)
Mn1—Br1—Mn1^{ii}	93.669 (6)	N1—C5—C5^{i}	116.04 (9)
C1—N1—C5	118.32 (14)	C4—C5—C5^{i}	122.51 (11)
C5—N1—C1—C2	−1.2 (2)	Mn1—N1—C5—C4	−173.49 (11)
Mn1—N1—C1—C2	171.71 (13)	C1—N1—C5—C5^{i}	179.20 (16)
N1—C1—C2—C3	1.3 (3)	Mn1—N1—C5—C5^{i}	5.8 (2)
C1—C2—C3—C4	−0.1 (3)	C3—C4—C5—N1	1.2 (2)
C2—C3—C4—C5	−1.1 (3)	C3—C4—C5—C5^{i}	−178.03 (18)
C1—N1—C5—C4	−0.1 (2)		

Symmetry codes: (i) $-x$, y, $-z+1/2$; (ii) $-x$, $-y$, $-z$; (iii) x, $-y$, $z+1/2$.