Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

catena-Poly[[[dibromidomanganese(II)]-μ-2,2′-bipyrimidine-$\kappa^4N^1,N^{1'}:N^3,N^{3'}$]-dihydrate]

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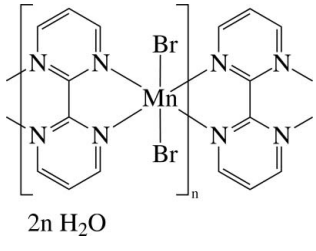
Received 9 November 2011; accepted 21 November 2011

Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.006 Å; R factor = 0.033; wR factor = 0.097; data-to-parameter ratio = 19.5.

The asymmetric unit of the title compound, $\{[MnBr_2(C_8H_6N_4)]\cdot 2H_2O\}_n$, contains one half of a repeat unit of the neutral linear coordination polymer and a solvent water molecule, with the Mn^{II} ion on a crystallographic twofold axis. In the polymer, inversion-related Mn^{II} ions are bridged by the bis-chelating 2,2′-bipyrimidine (bpym) ligands, thereby forming a chain structure along the *c*-axis direction, and are six-coordinated in a distorted *cis*-N_4Br_2 octahedral environment by four N atoms of twofold-related bpym ligands and twofold-related bromide anions. In the crystal, the complex polymers and solvent water molecules are linked by intermolecular O—H···Br and C—H···O hydrogen bonds, forming a two-dimensional layered structure extending parallel to the *ac* plane.

Related literature

For the crystal structure of the chlorido Mn^{II} complex polymer $[MnCl_2(bpym)]_n.2nH_2O$, which is isotypic to the title compound, see: Armentano *et al.* (2003).



Experimental

Crystal data

$[MnBr_2(C_8H_6N_4)]\cdot 2H_2O$ M_r = 408.96
Monoclinic, $C2/c$
a = 17.950 (9) Å
b = 8.263 (4) Å
c = 10.188 (5) Å
β = 123.888 (8)°
V = 1254.4 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 7.42 mm^{-1}
T = 200 K
0.30 × 0.17 × 0.16 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.668, T_{max} = 1.000
4360 measured reflections
1524 independent reflections
1207 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.097
S = 1.14
1524 reflections
78 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn1—N1	2.300 (3)	Mn1—Br1	2.6094 (10)
Mn1—N2	2.322 (3)		
N1—Mn1—N2	71.21 (11)	Br1^{i}—Mn1—Br1	97.93 (5)

Symmetry code: (i) $-x, y, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···Br1^{ii}	0.84	2.57	3.356 (3)	156
O1—H1B···Br1^{iii}	0.84	2.61	3.394 (4)	157
C2—H2···O1^{iv}	0.95	2.45	3.364 (5)	161

Symmetry codes: (ii) $-x, y, -z+\frac{1}{2}$; (iii) $-x, -y+1, -z+1$; (iv) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

This study was supported financially by Chonnam National University, 2010.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2362).

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supporting information

Acta Cryst. (2011). E**67**, m1848 [https://doi.org/10.1107/S1600536811049919]

catena-Poly[[[dibromidomanganese(II)]-μ-2,2′-bipyrimidine-$\kappa^4N^1,N^{1'}:N^3,N^{3'}$]dihydrate]

Kwang Ha

S1. Comment

The title compound, $[MnBr_2(bpym)]_n.2nH_2O$ (bpym = 2,2′-bipyrimidine, $C_8H_6N_4$), consists of a neutral complex polymer and solvent water molecules. The compound is isomorphous with the chloro analogue $[MnCl_2(bpym)]_n.2nH_2O$ (Armentano *et al.*, 2003).

The asymmetric unit contains one half of a repeat unit of the polymer and a water molecule (Fig. 1). In the polymer, the symmetry related Mn^{II} ions are bridged by the bis(chelating) bpym ligands, thereby forming a chain structure along the *c* axis, and are six-coordinated in a distorted *cis*-N_4Br_2 octahedral environment by four N atoms of the two different bpym ligands and two bromide anions. The Br atoms are *cis* with respect to each other. The main contributions to the distortion are the tight N—Mn—N chelate angle and the Br—Br repelling (<N1—Mn1—N2 = 71.21 (11)° and <Br1—Mn1—Br1^a = 97.93 (5)°; symmetry code a: -*x*, *y*, 3/2 - *z*), which result in non-linear *trans* axes (<N1—Mn1—N1^a = 153.49 (16)° and <N2—Mn1—Br1^a = 165.13 (7)°). The Mn—N bond lengths are almost equivalent (Table 1). In the crystal structure, the complex polymers and solvent water molecules are linked by intermolecular O—H···Br and C—H···O hydrogen bonds, forming a two-dimensional layer structure extending parallel to *ac* plane (Fig. 2, Table 2). The chains are stacked along the *b* axis. The shortest ring centroid-centroid distance is 5.337 (3) Å.

S2. Experimental

To a solution of $MnBr_2.4H_2O$ (0.2867 g, 1.000 mmol) in EtOH (30 ml) was added 2,2′-bipyrimidine (0.1584 g, 1.002 mmol) and stirred for 3 h at room temperature. The 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 analysis were obtained by slow evaporation from a methanol solution.

S3. Refinement

Carbon-bound H atoms were positioned geometrically and allowed to ride on their respective parent atoms [C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C)]. The H atoms of the solvent water molecule were located in a difference Fourier map then allowed to ride on their parent O atom in the final cycles of refinement with O—H = 0.84 Å and U_{iso}(H) = 1.5 U_{eq}(O). The highest peak (0.92 e Å^{-3}) and the deepest hole (-0.75 e Å^{-3}) in the difference Fourier map are located 1.26 Å and 0.96 Å from the atoms H1B and Br1, respectively.

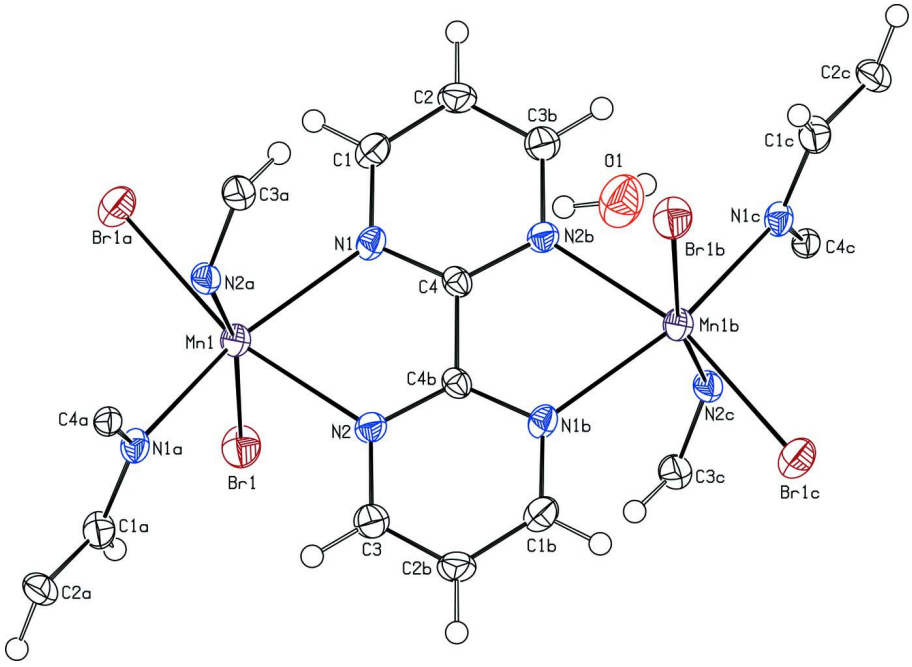

Figure 1

A fragment structure of the title compound, with displacement ellipsoids drawn at the 50% probability level for non-H atoms [symmetry codes: (*a*) -*x*, *y*, 3/2 - *z*, (*b*) -*x*, -*y*, 1 - *z*, (*c*) *x*, -*y*, -1/2 + *z*].

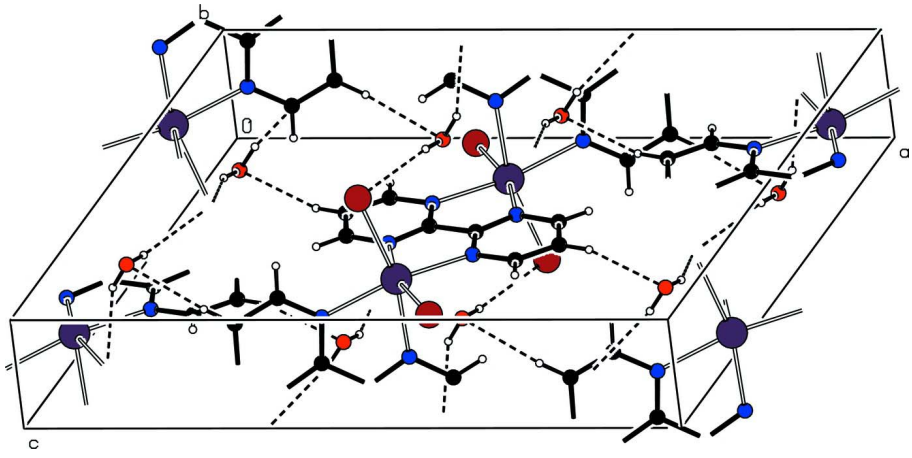

Figure 2

View of the unit-cell contents of the title compound. Hydrogen-bond interactions are drawn with dashed lines.

***catena*-Poly[[[dibromidomanganese(II)]-*μ*-2,2′-bipyrimidine- $\kappa^4N^1,N^{1'}:N^3,N^{3'}$]dihydrate]**

Crystal data

$[MnBr_2(C_8H_6N_4)]\cdot 2H_2O$
M_r = 408.96
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 17.950 (9) Å
b = 8.263 (4) Å
c = 10.188 (5) Å
β = 123.888 (8)°
V = 1254.4 (10) Å^3
Z = 4
F(000) = 788
D_x = 2.165 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2416 reflections

θ = 2.4–28.3°
μ = 7.42 mm^{-1}
T = 200 K

Stick, yellow
0.30 × 0.17 × 0.16 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.668, T_{max} = 1.000

4360 measured reflections
1524 independent reflections
1207 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 28.3°, θ_{min} = 2.7°
h = −23→23
k = −11→8
l = −13→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.097
S = 1.14
1524 reflections
78 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Mn1	0.0000	0.20755 (10)	0.7500	0.0207 (2)
Br1	−0.11908 (3)	0.41487 (5)	0.54940 (5)	0.03063 (17)
N1	0.07975 (19)	0.1437 (4)	0.6421 (3)	0.0197 (6)
N2	−0.07926 (19)	0.0143 (4)	0.5541 (3)	0.0200 (6)
C1	0.1597 (2)	0.2064 (5)	0.6848 (4)	0.0243 (8)
H1	0.1869	0.2857	0.7660	0.029*
C2	0.2028 (2)	0.1594 (5)	0.6146 (4)	0.0272 (9)
H2	0.2598	0.2025	0.6478	0.033*
C3	−0.1606 (2)	−0.0473 (5)	0.5058 (5)	0.0254 (8)
H3	−0.1892	−0.0125	0.5561	0.030*
C4	0.0437 (2)	0.0356 (4)	0.5240 (4)	0.0177 (7)
O1	0.0770 (2)	0.2654 (4)	0.2093 (4)	0.0470 (8)
H1A	0.0833	0.3297	0.1523	0.070*

H1B	0.0717	0.3369	0.2623	0.070*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0210 (4)	0.0249 (5)	0.0165 (4)	0.000	0.0106 (3)	0.000
Br1	0.0324 (3)	0.0312 (3)	0.0244 (3)	0.00758 (15)	0.0134 (2)	0.00491 (15)
N1	0.0224 (15)	0.0209 (17)	0.0148 (15)	−0.0028 (12)	0.0097 (13)	−0.0009 (12)
N2	0.0187 (14)	0.0245 (18)	0.0166 (15)	−0.0033 (12)	0.0097 (13)	−0.0003 (12)
C1	0.0251 (19)	0.027 (2)	0.0189 (19)	−0.0074 (15)	0.0110 (16)	−0.0016 (14)
C2	0.0195 (18)	0.039 (3)	0.025 (2)	−0.0068 (16)	0.0131 (17)	−0.0006 (17)
C3	0.0231 (19)	0.032 (2)	0.022 (2)	−0.0018 (16)	0.0130 (17)	0.0006 (16)
C4	0.0180 (17)	0.0193 (19)	0.0172 (17)	0.0038 (13)	0.0107 (15)	0.0028 (13)
O1	0.058 (2)	0.045 (2)	0.041 (2)	−0.0146 (16)	0.0301 (18)	−0.0070 (15)

Geometric parameters (Å, º)

Mn1—N1	2.300 (3)	C1—C2	1.371 (5)
Mn1—N1^{i}	2.300 (3)	C1—H1	0.9500
Mn1—N2	2.322 (3)	C2—C3^{ii}	1.379 (5)
Mn1—N2^{i}	2.322 (3)	C2—H2	0.9500
Mn1—Br1^{i}	2.6094 (10)	C3—C2^{ii}	1.379 (5)
Mn1—Br1	2.6094 (10)	C3—H3	0.9500
N1—C4	1.340 (5)	C4—N2^{ii}	1.333 (4)
N1—C1	1.349 (4)	C4—C4^{ii}	1.481 (7)
N2—C4^{ii}	1.333 (4)	O1—H1A	0.8400
N2—C3	1.353 (5)	O1—H1B	0.8400
N1—Mn1—N1^{i}	153.49 (16)	C1—N1—Mn1	126.2 (2)
N1—Mn1—N2	71.21 (11)	C4^{ii}—N2—C3	116.4 (3)
N1^{i}—Mn1—N2	90.38 (11)	C4^{ii}—N2—Mn1	117.3 (2)
N1—Mn1—N2^{i}	90.38 (11)	C3—N2—Mn1	126.2 (2)
N1^{i}—Mn1—N2^{i}	71.21 (11)	N1—C1—C2	122.1 (4)
N2—Mn1—N2^{i}	93.08 (16)	N1—C1—H1	119.0
N1—Mn1—Br1^{i}	93.93 (8)	C2—C1—H1	119.0
N1^{i}—Mn1—Br1^{i}	103.45 (8)	C1—C2—C3^{ii}	117.7 (3)
N2—Mn1—Br1^{i}	165.13 (7)	C1—C2—H2	121.2
N2^{i}—Mn1—Br1^{i}	86.37 (8)	C3^{ii}—C2—H2	121.2
N1—Mn1—Br1	103.45 (8)	N2—C3—C2^{ii}	121.5 (3)
N1^{i}—Mn1—Br1	93.93 (8)	N2—C3—H3	119.2
N2—Mn1—Br1	86.37 (8)	C2^{ii}—C3—H3	119.2
N2^{i}—Mn1—Br1	165.13 (7)	N2^{ii}—C4—N1	126.2 (3)
Br1^{i}—Mn1—Br1	97.93 (5)	N2^{ii}—C4—C4^{ii}	116.9 (4)
C4—N1—C1	116.1 (3)	N1—C4—C4^{ii}	116.9 (4)
C4—N1—Mn1	117.7 (2)	H1A—O1—H1B	96.1
N1^{i}—Mn1—N1—C4	49.5 (3)	N1—Mn1—N2—C3	−177.7 (3)
N2—Mn1—N1—C4	1.3 (3)	N1^{i}—Mn1—N2—C3	21.8 (3)

N2^{i}—Mn1—N1—C4	94.4 (3)	N2^{i}—Mn1—N2—C3	93.0 (3)
Br1^{i}—Mn1—N1—C4	−179.2 (3)	Br1^{i}—Mn1—N2—C3	−179.6 (2)
Br1—Mn1—N1—C4	−80.1 (3)	Br1—Mn1—N2—C3	−72.1 (3)
N1^{i}—Mn1—N1—C1	−131.5 (3)	C4—N1—C1—C2	−1.7 (6)
N2—Mn1—N1—C1	−179.7 (3)	Mn1—N1—C1—C2	179.2 (3)
N2^{i}—Mn1—N1—C1	−86.5 (3)	N1—C1—C2—C3^{ii}	1.7 (6)
Br1^{i}—Mn1—N1—C1	−0.2 (3)	C4^{ii}—N2—C3—C2^{ii}	1.9 (5)
Br1—Mn1—N1—C1	99.0 (3)	Mn1—N2—C3—C2^{ii}	178.5 (3)
N1—Mn1—N2—C4^{ii}	−1.1 (2)	C1—N1—C4—N2^{ii}	−0.2 (6)
N1^{i}—Mn1—N2—C4^{ii}	−161.7 (3)	Mn1—N1—C4—N2^{ii}	179.0 (3)
N2^{i}—Mn1—N2—C4^{ii}	−90.5 (3)	C1—N1—C4—C4^{ii}	179.5 (4)
Br1^{i}—Mn1—N2—C4^{ii}	−3.0 (5)	Mn1—N1—C4—C4^{ii}	−1.3 (5)
Br1—Mn1—N2—C4^{ii}	104.4 (3)		

Symmetry codes: (i) −*x*, *y*, −*z*+3/2; (ii) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···Br1^{iii}	0.84	2.57	3.356 (3)	156
O1—H1*B*···Br1^{iv}	0.84	2.61	3.394 (4)	157
C2—H2···O1^{v}	0.95	2.45	3.364 (5)	161

Symmetry codes: (iii) −*x*, *y*, −*z*+1/2; (iv) −*x*, −*y*+1, −*z*+1; (v) −*x*+1/2, −*y*+1/2, −*z*+1.