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**Title:** Poly[[myy-N,N'-bis(2-hydroxyethyl)-N,N,N',N'-tetramethylpropane-1,3-diaminium-kappa2O:O']tetra-myy-bromido-dibromidodimanganese(II)]

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# Poly[[ $\mu$ -*N,N'*-bis(2-hydroxyethyl)-*N,N,N',N'*-tetramethylpropane-1,3-diaminium- $\kappa^2$ O:O']tetra- $\mu$ -bromido-dibromidodimanganese(II)]

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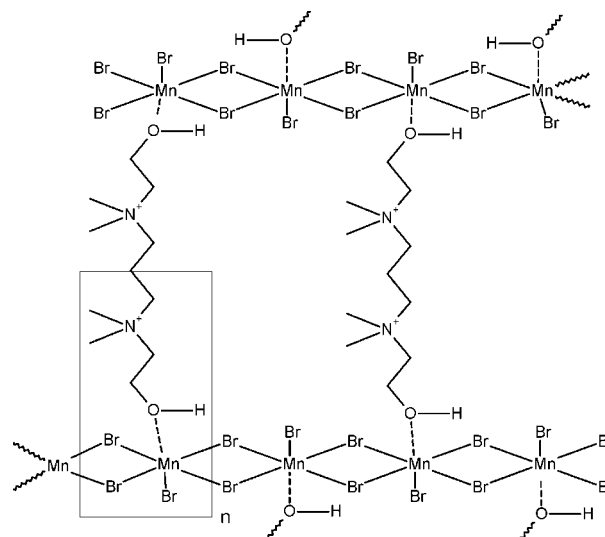
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Key indicators: single-crystal X-ray study;  $T = 123$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.021;  $wR$  factor = 0.047; data-to-parameter ratio = 17.7.

The asymmetric unit of the title three-dimensional coordination polymer,  $[\text{Mn}_2\text{Br}_6(\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_2)]_n$ , consists of one  $\text{Mn}^{\text{II}}$  cation, half of a dicationic *N,N'*-bis(2-hydroxyethyl)-*N,N,N',N'*-tetramethylpropane-1,3-diaminium ligand (*L*) (the other half being generated by a twofold rotation axis), and three bromide ions. The  $\text{Mn}^{\text{II}}$  cation is coordinated by a single *L* ligand *via* the hydroxy O atom and by five bromide ions, resulting in a distorted octahedral  $\text{MnBr}_5\text{O}$  coordination geometry. Four of the bromide ions are bridging to two adjacent  $\text{Mn}^{\text{II}}$  atoms, thereby forming polymeric chains along the *a* and *b* axes. The *L* units act as links between neighbouring  $\text{Mn}-(\mu\text{-Br})_2\text{-Mn}$  chains, also forming a polymeric continuum along the *c* axis, which completes the formation of a three-dimensional network. Classical O—H...Br hydrogen bonds are present. The distance between adjacent  $\text{Mn}^{\text{II}}$  atoms is 4.022 (1) Å.

## Related literature

For related structures of  $M^{\text{II}}$  transition metal halide one-dimensional coordination polymers, see: Han *et al.* (2012); Englert & Schiffrers (2006). For two-dimensional networks, see: Hu & Englert (2006); Turgunov *et al.* (2011). For properties of metal halides, see: Hitchcock *et al.* (2003); Wang *et al.* (2011). For ligand conformations, see: Kärnä *et al.* (2010).



## Experimental

### Crystal data

$[\text{Mn}_2\text{Br}_6(\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_2)]$   
 $M_r = 809.69$   
Tetragonal,  $P4_32_12$   
 $a = 8.0163$  (4) Å  
 $c = 35.3103$  (18) Å  
 $V = 2269.1$  (2) Å<sup>3</sup>

$Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 11.69$  mm<sup>-1</sup>  
 $T = 123$  K  
 $0.25 \times 0.25 \times 0.20$  mm

### Data collection

Bruker–NoniusKappa APEXII diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)  
 $T_{\min} = 0.440$ ,  $T_{\max} = 0.746$

5076 measured reflections  
1966 independent reflections  
1856 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$   
 $wR(F^2) = 0.047$   
 $S = 1.02$   
1966 reflections  
111 parameters  
1 restraint

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\max} = 0.36$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.41$  e Å<sup>-3</sup>  
Absolute structure: Flack (1983), 690 Friedel pairs  
Flack parameter: 0.048 (14)

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...Br3 <sup>i</sup>	0.75 (2)	2.49 (2)	3.232 (3)	175 (5)

Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{5}{2}, -z + \frac{1}{4}$ .

Data collection: COLLECT (Bruker, 2008); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008b); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008b); molecular graphics: Mercury (Macrae *et al.*, 2008); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2604).

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## References

- Bruker (2008). *COLLECT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Englert, U. & Schiffrers, S. (2006). *Acta Cryst. E* **62**, m295–m296.
- Flack, H. D. (1983). *Acta Cryst. A* **39**, 876–881.
- Han, S., Liu, X.-Y., Cai, Z.-F. Z.-P., Yin, W.-T., Xie, X.-D., Zhou, J.-R., Yang, L.-M. & Ni, C.-L. (2012). *Inorg. Chem. Commun.* **24**, 91–94.
- Hitchcock, P. B., Lee, T. H. & Leigh, G. J. (2003). *Dalton Trans.* pp. 2276–2279.
- Hu, C. & Englert, U. (2006). *Angew. Chem. Int. Ed. Engl.* **45**, 3457–3459.
- Kärnä, M., Lahtinen, M., Hakkarainen, P.-L. & Valkonen, J. (2010). *Aust. J. Chem.* **63**, 1122–1137.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (2008a). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008b). *Acta Cryst. A* **64**, 112–122.
- Turgunov, K. K., Wang, Y., Englert, U. & Shakhidoyatov, K. M. (2011). *Acta Cryst. E* **67**, m953–m954.
- Wang, Y.-Q., Sun, Q., Yue, Q., Cheng, A.-L., Song, Y. & Gao, E.-Q. (2011). *Dalton Trans.* **40**, 10966–10974.

## supporting information

*Acta Cryst.* (2012). E68, m1453–m1454 [doi:10.1107/S1600536812044765]

## Poly[[ $\mu$ -*N,N'*-bis(2-hydroxyethyl)-*N,N,N',N'*-tetramethylpropane-1,3-diaminium- $\kappa^2$ O:O']tetra- $\mu$ -bromido-dibromidodimanganese(II)]

Heikki Rinta, Anssi Peuronen and Manu Lahtinen

### S1. Comment

Solid state chemistry of metal halides has been widely studied in order to improve various magnetic and non-linear optical applications. In the crystal structure of the type  $MX_4L_2$ , the bridging qualities of the halide anions and the coordination properties of the organic ligands result in various polymeric structures. For example, one-dimensional  $M-(\mu-X)_2-M$  bridged chains with low-dimensional arrangement have more suitable magnetic properties than classic structures of layered metal halide salts (Han *et al.* 2012; Wang *et al.* 2011 and Hitchcock *et al.* 2003).

The title compound,  $[\text{Mn}^{\text{II}}(\mu\text{-Br})_2\mu\text{-(C}_{11}\text{H}_{28}\text{N}_2\text{O}_2)\text{Br}]_n$ , crystallizes in a tetragonal  $P4_32_12$  crystal system showing one  $\text{Mn}^{\text{II}}$  cation, half of a dicationic  $[\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_2]^{2+}$  ligand (*L*) and three bromide anions in an asymmetric unit (Fig. 1). In this three-dimensional polymer each  $\text{Mn}^{\text{II}}$  cation is coordinated by four bridging bromo anions in the equatorial plane. A single terminal bromo anion and a ligand are located in the axial positions of the distorted octahedron showing axial  $\text{Br3-Mn1-O1}$  angle of  $174.03(8)^\circ$ . The three-dimensional network structure comprises two alternating crossed  $\text{Mn}-(\mu\text{-Br})_2\text{-Mn}$  chains (*a*- and *b*-axes) and an undulated  $\text{L-Mn}-(\mu\text{-Br})_2\text{-Mn-L}$  chain (*c*-axis). Distances between parallel  $\text{Mn}-(\mu\text{-Br})_2\text{-Mn}$  chains (planes through Mn -centres) are about 17.656 Å and between anti-parallel chains 8.7825 Å. This allows a formation of a structure model having alternating organic cation and a metal halide layers along *c*-axis (Figures 2 & 3).

In  $\text{Mn}^{\text{II}}$  cation coordination environment, the terminal Br<sup>−</sup> anion fulfills the coordination of the  $\text{Mn}^{\text{II}}$  cation to octahedral  $\text{MnBr}_5\text{O}$ . The metal–metal distance along the resulting chain of octahedra is 4.022 (1) Å. All the equatorial  $\text{Mn-Br}$  bridge bond distances are almost identical but still somewhat longer than the axial  $\text{Mn1-Br3}$  bond. The bridging bromides and the adjacent Mn -centers form folded square-planar geometry, showing nearly orthogonal contact angle of  $94.05(2)^\circ$  via  $\text{Mn4-Br2-Mn4}$  atoms, and torsion angle of  $12.82(2)^\circ$  through  $\text{Mn4-Br2-Mn4-Br1}$  atoms.

In the structure, the ligands are in S-shaped conformation between the anti-parallel  $\text{Mn}-(\mu\text{-Br})_2\text{-Mn}$  chains (Fig. 4). It seems that S-conformation is an ideal conformation for this type of relatively flexible ditopic ligand (Kärnä *et al.* 2010). The torsion angle  $\text{C2-N4-N4-C2}$  is  $156.70^\circ$ . Similar cation conformations are found in ion pair structures  $[\text{Zn}^{\text{II}}\text{Br}_4(\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_2)]$  and  $(\text{C}_{11}\text{H}_{28}\text{N}_2\text{O}_2)\text{Br}_2\text{H}_2\text{O}$ .

Classical  $\text{Br3}\cdots\text{H-O1}$  hydrogen bonds are present in the  $\text{Mn}^{\text{II}}$  cation coordination environment between the terminal Br<sup>−</sup> anions of  $\text{Mn}^{\text{II}}$  cation and the hydroxyl group of the neighboring metal center (Fig. 5). Hence, it seems likely that in the parent complex the hydrogen bonding steers the oxygen's coordination to the  $\text{Mn}^{\text{II}}$  cation. Weak interactions between O1 and halide bridge on the other side of Br1 and Br2 leads to distortions of chains torsion angle. The angle between the  $\text{Mn1-Br1-Br2}$  and  $\text{Mn1-Br1-Br2}$  planes is  $162.6^\circ$ . For this reason,  $\text{Mn}-(\mu\text{-Br})_2\text{-Mn}$  chains zigzag-conformation (Fig. 6).

## S2. Experimental

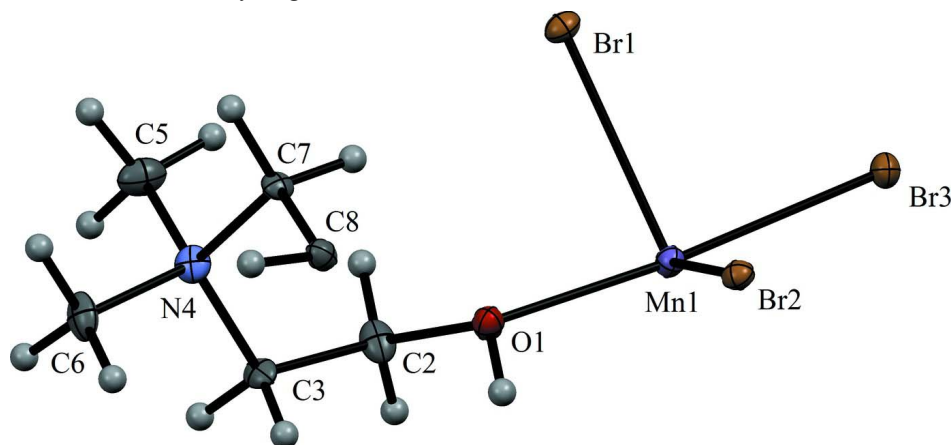
The single crystals of the title compound were obtained in the following two steps: First, dicationic bromide salt, as the precursor, was synthesized in 30 ml of acetone by reacting 2.20 ml (13.15 mmol) of TMPDA,  $C_7H_{18}N_2$ , and 2.16 ml (28.93 mmol) of 2-bromo-1-ethanol,  $C_2H_5BrO$ , for 48 h at 60 °C in a sealed flask. After removing the solvent, the white precipitation was washed by acetone and dried in *vacuo* (yield 71.6%; 3.58 g).

$^1H$ -NMR (DMSO, 250 MHz, p.p.m.): 2.08–2.32 (2H, m,  $CH_2-CH_2-CH_2$ ), 3.16 (12H, s,  $N-CH_3$ ), 3.31 (2H, s,  $H_2O$ ), 3.37–3.43 (4H, t,  $HO-CH_2-CH_2-N$ ), 3.48–3.52 (4H, t,  $N-CH_2-CH_2-CH_2-N$ ), 3.84 (4H, s,  $CH_2-OH$ ), 5.29–5.33 (2H, t, OH)

Second, the precursor salt and the dried  $MnBr_2 \cdot 4H_2O$  (molar ratio ~1:1.5) were dissolved separately in minimum volume of warm methanol before combining the solutions. The title compound was synthesized in an open flask by metathesis reaction of the two aforementioned salts. The combined solution was stirred for about 1 h at 40 °C after which it was slowly cooled to RT and methanol was allowed to evaporate slowly. After several days, purple crystals suitable for X-ray analysis were formed.

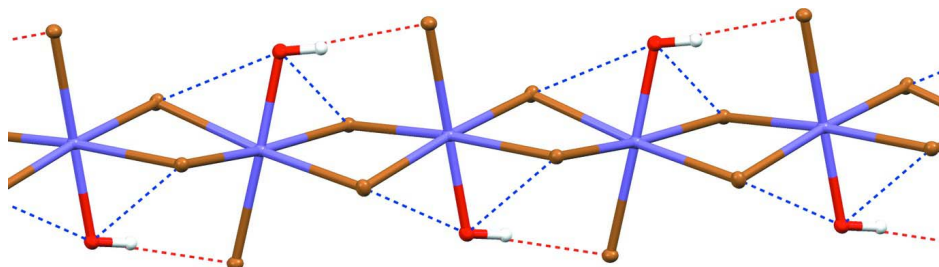
## S3. Refinement

Hydrogen atoms (except of a hydroxyl hydrogen atom that was taken from the electron density map) were calculated to their positions as riding atoms (C host) using isotropic displacement parameters that were fixed to be 1.2 or 1.5 times larger than those of the attached non-hydrogen atom.



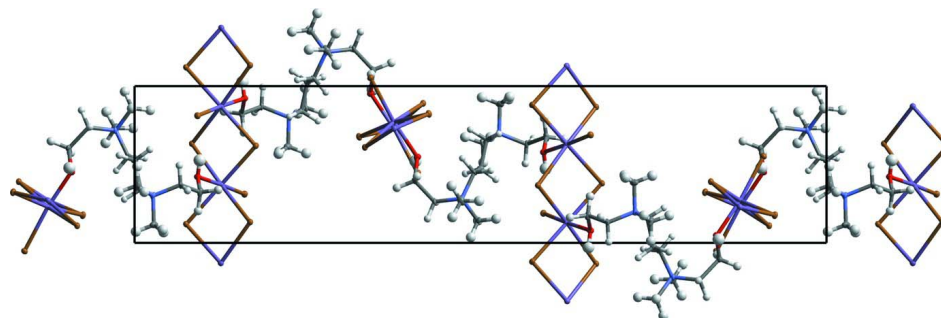
**Figure 1**

Asymmetric unit and labeling scheme of the title compound. Ellipsoids are presented at the 50% probability level.

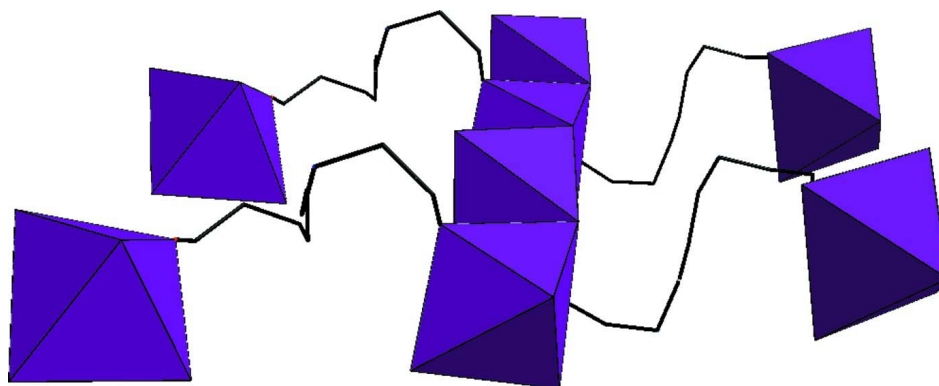


**Figure 2**

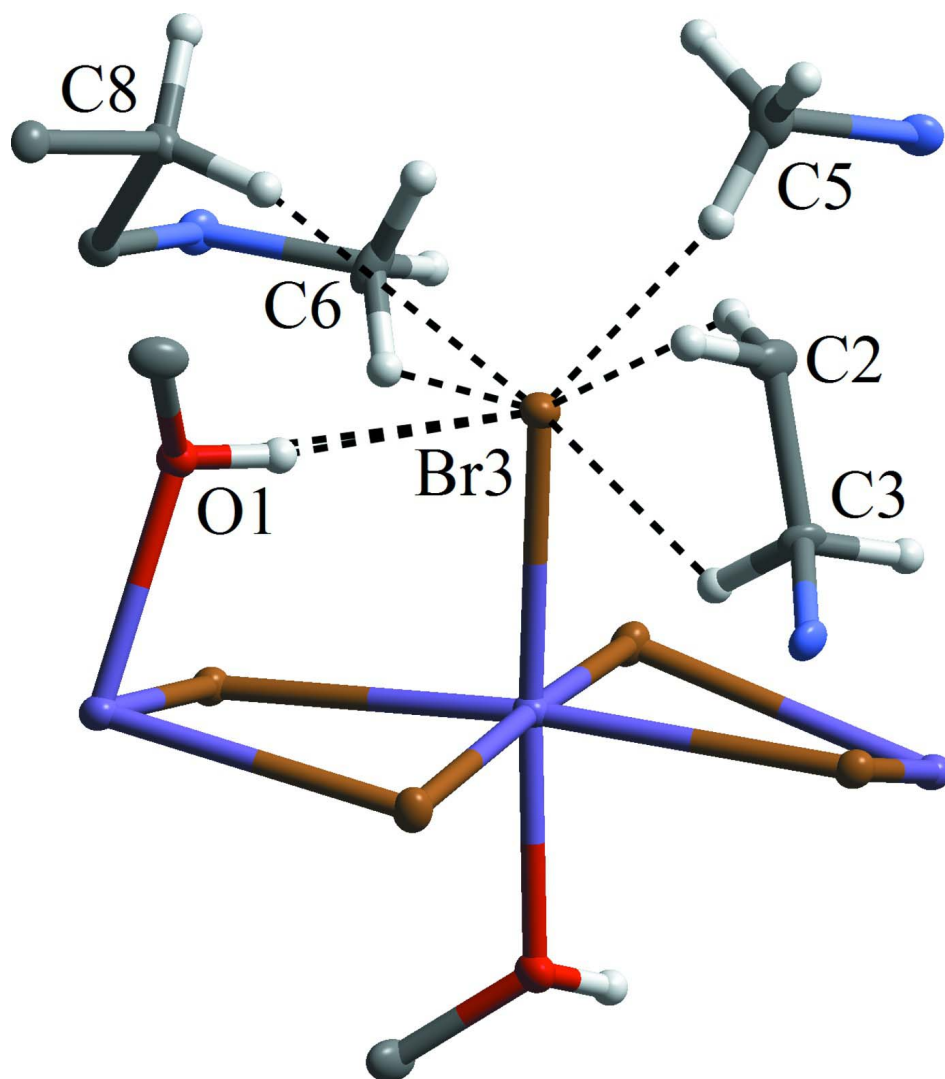
The one-dimensional linear chain with  $(\mu-Br)_2$  bridges,  $Mn \cdots Mn$  contact with a distance of 4.022 (1) Å and hydrogen bonding scheme.

**Figure 3**

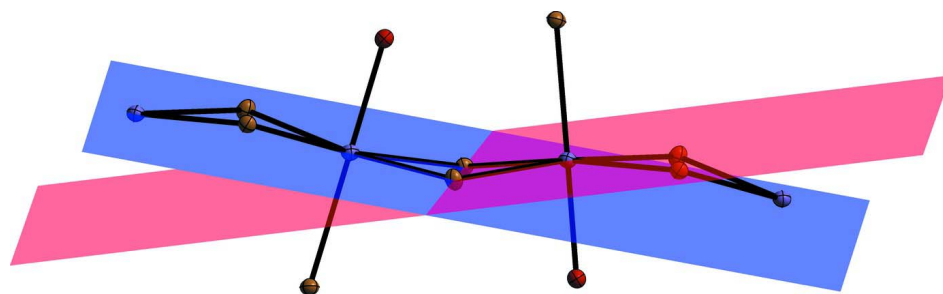
Undulated network formed by the *L* ligands connecting the alternating crossed Mn-( $\mu$ -Br)<sub>2</sub>—Mn chains, viewed along *b*-axis.

**Figure 4**

S-shaped conformation of the ligands (only ligand backbone showed) between the anti-parallel Mn-( $\mu$ -Br)<sub>2</sub>—Mn slightly distorted octahedron chains.

**Figure 5**

The structure is stabilized by weak intermolecular interactions between Br3 and nearby ligands.

**Figure 6**

Zigzag tilting of the adjacent MnBr<sub>5</sub>O octahedra.

**Poly[[ $\mu$ -*N,N'*-bis(2-hydroxyethyl)-*N,N,N',N'*-tetramethyl]propane-1,3-diaminium- $\kappa^2$ O:O']tetra- $\mu$ -bromido-dibromidodimanganese(II)]**

*Crystal data*

[Mn<sub>2</sub>Br<sub>6</sub>(C<sub>11</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>)]

$M_r = 809.69$

Tetragonal,  $P4_32_12$

Hall symbol: P 4nw 2abw

$a = 8.0163$  (4) Å

$c = 35.3103$  (18) Å

$V = 2269.1$  (2) Å<sup>3</sup>

$Z = 4$

$F(000) = 1536$

$D_x = 2.370$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1871 reflections

$\theta = 0.4$ – $27.9^\circ$

$\mu = 11.69$  mm<sup>-1</sup>

$T = 123$  K

Block, violet

$0.25 \times 0.25 \times 0.20$  mm

*Data collection*

Bruker–NoniusKappa APEXII  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2008a)

$T_{\min} = 0.440$ ,  $T_{\max} = 0.746$

5076 measured reflections

1966 independent reflections

1856 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.8^\circ$

$h = -9 \rightarrow 9$

$k = -4 \rightarrow 9$

$l = -22 \rightarrow 41$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.047$

$S = 1.02$

1966 reflections

111 parameters

1 restraint

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.36$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.41$  e Å<sup>-3</sup>

Absolute structure: Flack (1983), 690 Friedel  
pairs

Absolute structure parameter: 0.048 (14)

*Special details*

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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  $F^2 > 2\sigma(F^2)$  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<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C2	0.8227 (5)	0.8960 (5)	0.15487 (11)	0.0158 (9)	
H2A	0.8379	0.8507	0.1290	0.019*	



H2B	0.7031	0.9236	0.1580	0.019*	
C3	0.8705 (5)	0.7633 (5)	0.18350 (10)	0.0143 (9)	
H3A	0.8340	0.6538	0.1735	0.017*	
H3B	0.9937	0.7605	0.1853	0.017*	
C5	0.6146 (5)	0.7687 (6)	0.22206 (11)	0.0197 (10)	
H5A	0.5825	0.6644	0.2095	0.030*	
H5B	0.5680	0.8634	0.2081	0.030*	
H5C	0.5713	0.7693	0.2480	0.030*	
C6	0.8652 (5)	0.6412 (5)	0.24628 (11)	0.0172 (10)	
H6A	0.8250	0.6531	0.2724	0.026*	
H6B	0.9874	0.6423	0.2461	0.026*	
H6C	0.8250	0.5356	0.2357	0.026*	
C7	0.8412 (5)	0.9495 (5)	0.24099 (11)	0.0116 (9)	
H7A	0.7764	0.9603	0.2647	0.014*	
H7B	0.8049	1.0396	0.2237	0.014*	
C8	1.0268 (5)	0.9732 (5)	0.2500	0.0140 (13)	
H8A	1.0594	0.9039	0.2720	0.017*	0.50
H8B	1.0961	0.9406	0.2280	0.017*	0.50
N4	0.8013 (4)	0.7825 (4)	0.22294 (9)	0.0130 (8)	
O1	0.9205 (3)	1.0470 (4)	0.15874 (8)	0.0140 (6)	
Br1	0.61915 (5)	1.32320 (5)	0.175357 (11)	0.01348 (10)	
Br2	1.13256 (5)	1.39037 (5)	0.167113 (10)	0.01205 (10)	
Br3	0.81111 (5)	1.55274 (5)	0.090982 (11)	0.01279 (11)	
Mn1	0.87136 (8)	1.27065 (7)	0.124710 (17)	0.01152 (14)	
H1	1.010 (3)	1.021 (5)	0.1575 (13)	0.017*	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C2	0.024 (2)	0.0120 (19)	0.011 (2)	−0.004 (2)	−0.003 (2)	−0.0030 (18)
C3	0.021 (2)	0.014 (2)	0.009 (2)	0.001 (2)	0.0015 (19)	0.0001 (17)
C5	0.013 (2)	0.025 (2)	0.021 (2)	−0.001 (2)	0.001 (2)	−0.006 (2)
C6	0.023 (2)	0.013 (2)	0.015 (2)	−0.0018 (19)	−0.0049 (19)	0.0016 (18)
C7	0.015 (2)	0.0074 (18)	0.012 (2)	−0.0020 (19)	−0.0027 (18)	−0.0025 (17)
C8	0.0114 (19)	0.0114 (19)	0.019 (3)	0.002 (3)	0.0015 (19)	0.0015 (19)
N4	0.0139 (16)	0.0157 (17)	0.0094 (17)	0.0011 (16)	−0.0017 (14)	0.0004 (15)
O1	0.0105 (14)	0.0137 (14)	0.0178 (15)	0.0010 (13)	0.0016 (14)	0.0026 (14)
Br1	0.01241 (19)	0.0168 (2)	0.01122 (19)	−0.00105 (19)	0.00124 (18)	−0.00200 (18)
Br2	0.01210 (19)	0.01371 (19)	0.01035 (19)	0.00068 (18)	0.00073 (16)	0.00004 (17)
Br3	0.01400 (19)	0.01200 (19)	0.0124 (2)	−0.00096 (19)	−0.00056 (18)	0.00178 (17)
Mn1	0.0117 (3)	0.0115 (3)	0.0113 (3)	−0.0001 (3)	0.0003 (3)	0.0014 (3)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

C2—O1	1.449 (5)	C7—C8	1.533 (5)
C2—C3	1.517 (5)	C7—H7A	0.9900
C2—H2A	0.9900	C7—H7B	0.9900
C2—H2B	0.9900	C8—C7 <sup>i</sup>	1.533 (5)

C3—N4	1.507 (4)	C8—H8A	0.9900
C3—H3A	0.9900	C8—H8B	0.9900
C3—H3B	0.9900	O1—Mn1	2.194 (3)
C5—N4	1.501 (5)	O1—H1	0.748 (19)
C5—H5A	0.9800	Br1—Mn1	2.7319 (7)
C5—H5B	0.9800	Br1—Mn1 <sup>ii</sup>	2.7635 (7)
C5—H5C	0.9800	Br2—Mn1 <sup>iii</sup>	2.7407 (7)
C6—N4	1.491 (5)	Br2—Mn1	2.7472 (8)
C6—H6A	0.9800	Br3—Mn1	2.6010 (7)
C6—H6B	0.9800	Mn1—Br2 <sup>ii</sup>	2.7407 (7)
C6—H6C	0.9800	Mn1—Br1 <sup>iii</sup>	2.7635 (7)
C7—N4	1.517 (5)		
O1—C2—C3	112.7 (3)	C7 <sup>i</sup> —C8—H8A	110.4
O1—C2—H2A	109.0	C7—C8—H8A	110.4
C3—C2—H2A	109.0	C7 <sup>i</sup> —C8—H8B	110.4
O1—C2—H2B	109.0	C7—C8—H8B	110.4
C3—C2—H2B	109.0	H8A—C8—H8B	108.6
H2A—C2—H2B	107.8	C6—N4—C5	107.3 (3)
N4—C3—C2	116.8 (3)	C6—N4—C3	107.9 (3)
N4—C3—H3A	108.1	C5—N4—C3	109.9 (3)
C2—C3—H3A	108.1	C6—N4—C7	111.4 (3)
N4—C3—H3B	108.1	C5—N4—C7	106.5 (3)
C2—C3—H3B	108.1	C3—N4—C7	113.6 (3)
H3A—C3—H3B	107.3	C2—O1—Mn1	122.3 (2)
N4—C5—H5A	109.5	C2—O1—H1	106 (4)
N4—C5—H5B	109.5	Mn1—O1—H1	112 (4)
H5A—C5—H5B	109.5	Mn1—Br1—Mn1 <sup>ii</sup>	94.082 (12)
N4—C5—H5C	109.5	Mn1 <sup>iii</sup> —Br2—Mn1	94.254 (12)
H5A—C5—H5C	109.5	O1—Mn1—Br3	174.03 (8)
H5B—C5—H5C	109.5	O1—Mn1—Br1	84.28 (8)
N4—C6—H6A	109.5	Br3—Mn1—Br1	91.62 (2)
N4—C6—H6B	109.5	O1—Mn1—Br2 <sup>ii</sup>	92.05 (8)
H6A—C6—H6B	109.5	Br3—Mn1—Br2 <sup>ii</sup>	91.89 (2)
N4—C6—H6C	109.5	Br1—Mn1—Br2 <sup>ii</sup>	84.75 (2)
H6A—C6—H6C	109.5	O1—Mn1—Br2	81.38 (8)
H6B—C6—H6C	109.5	Br3—Mn1—Br2	95.01 (2)
N4—C7—C8	113.7 (3)	Br1—Mn1—Br2	98.83 (2)
N4—C7—H7A	108.8	Br2 <sup>ii</sup> —Mn1—Br2	172.12 (3)
C8—C7—H7A	108.8	O1—Mn1—Br1 <sup>iii</sup>	89.94 (8)
N4—C7—H7B	108.8	Br3—Mn1—Br1 <sup>iii</sup>	94.43 (2)
C8—C7—H7B	108.8	Br1—Mn1—Br1 <sup>iii</sup>	173.07 (2)
H7A—C7—H7B	107.7	Br2 <sup>ii</sup> —Mn1—Br1 <sup>iii</sup>	91.67 (2)
C7 <sup>i</sup> —C8—C7	106.5 (4)	Br2—Mn1—Br1 <sup>iii</sup>	84.03 (2)
O1—C2—C3—N4	79.7 (4)	C2—O1—Mn1—Br2	179.1 (3)
N4—C7—C8—C7 <sup>i</sup>	167.0 (4)	C2—O1—Mn1—Br1 <sup>iii</sup>	−96.9 (3)
C2—C3—N4—C6	−179.3 (3)	Mn1 <sup>ii</sup> —Br1—Mn1—O1	−105.44 (8)

C2—C3—N4—C5	64.0 (5)	Mn1 <sup>ii</sup> —Br1—Mn1—Br3	78.92 (2)
C2—C3—N4—C7	−55.2 (5)	Mn1 <sup>ii</sup> —Br1—Mn1—Br2 <sup>ii</sup>	−12.838 (12)
C8—C7—N4—C6	54.1 (4)	Mn1 <sup>ii</sup> —Br1—Mn1—Br2	174.24 (3)
C8—C7—N4—C5	170.8 (3)	Mn1 <sup>iii</sup> —Br2—Mn1—O1	78.06 (8)
C8—C7—N4—C3	−68.1 (4)	Mn1 <sup>iii</sup> —Br2—Mn1—Br3	−106.73 (2)
C3—C2—O1—Mn1	−175.3 (2)	Mn1 <sup>iii</sup> —Br2—Mn1—Br1	160.85 (3)
C2—O1—Mn1—Br1	79.3 (3)	Mn1 <sup>iii</sup> —Br2—Mn1—Br1 <sup>iii</sup>	−12.785 (11)
C2—O1—Mn1—Br2 <sup>ii</sup>	−5.2 (3)		

Symmetry codes: (i)  $-y+2, -x+2, -z+1/2$ ; (ii)  $x-1/2, -y+5/2, -z+1/4$ ; (iii)  $x+1/2, -y+5/2, -z+1/4$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ Br3 <sup>iii</sup>	0.75 (2)	2.49 (2)	3.232 (3)	175 (5)

Symmetry code: (iii)  $x+1/2, -y+5/2, -z+1/4$ .