Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Di-μ-oxido-bis{[1,3-bis(tetramethylguanidino)propane-κ^2N,N']bromidomanganese(III)}

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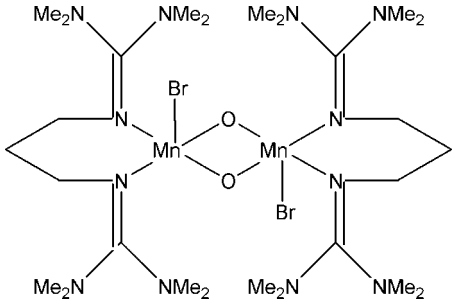
Received 4 July 2007; accepted 5 July 2007

Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.037; wR factor = 0.098; data-to-parameter ratio = 21.3.

The title compound, $[Mn_2Br_2O_2(C_{13}H_{30}N_6)_2]$, is the first crystallographically characterized $Mn^{III}_2(\mu\text{-}O)_2$ complex with a bidentate imine ligand . The molecule lies on a crystallographic inversion centre and shows distorted square-pyramidal coordination of the Mn atoms by two guanidine N atoms, the two bridging O atoms and a terminal Br ligand. The crystal structure involves an intermolecular C—H···Br hydrogen bond.

Related literature

For related literature, see: Allen (2002); Ferreira *et al.* (2004); Glerup *et al.* (1994); Goodson & Hodgson (1989); Goodson *et al.* (1990); Harmjanz (1997); Heuwing (2004); Kitajima *et al.* (1991); Mukhopadhyay *et al.* (2004); Pohl *et al.* (2000); Schneider (2000); Waden (1999); Wu *et al.* (2004).



Experimental

Crystal data

$[Mn_2Br_2O_2(C_{13}H_{30}N_6)_2]$
M_r = 842.56
Monoclinic, $C2/c$
a = 19.592 (4) Å
b = 9.2077 (17) Å
c = 19.767 (4) Å
β = 90.03 (1)°
V = 3566.0 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.99 mm^{-1}
T = 120 (2) K
0.43 × 0.40 × 0.38 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.290, T_{max} = 0.322
16870 measured reflections
4242 independent reflections
3584 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.098
S = 1.03
4242 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—Mn1	2.7391 (6)	N1—C1	1.301 (3)
Mn1—O1	1.8188 (18)	N2—C1	1.362 (3)
Mn1—O1^{i}	1.8235 (18)	N3—C1	1.357 (3)
Mn1—N1	2.080 (2)	N4—C9	1.311 (3)
Mn1—N4	2.080 (2)	N5—C9	1.346 (4)
Mn1···Mn1^{i}	2.7068 (9)	N6—C9	1.363 (3)

O1—Mn1—O1^{i}	84.00 (8)	O1—Mn1—Br1	99.81 (6)
O1—Mn1—N1	167.18 (8)	O1^{i}—Mn1—Br1	101.45 (6)
O1^{i}—Mn1—N1	91.89 (8)	N1—Mn1—Br1	92.90 (6)
O1—Mn1—N4	93.15 (8)	N4—Mn1—Br1	90.56 (6)
O1^{i}—Mn1—N4	167.96 (8)	Mn1—O1—Mn1^{i}	96.00 (8)
N1—Mn1—N4	88.36 (9)		

Symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11*C*···Br1^{ii}	0.98	2.89	3.754 (3)	148

Symmetry code: (ii) $x, y+1, z$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

AN thanks the University of Paderborn for granting a fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2430).

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supplementary materials

Acta Cryst. (2007). E**63**, m2099-m2100 [**doi:10.1107/S1600536807032801**]

Di-μ-oxido-bis{[1,3-bis(tetramethylguanidino)propane-κ^2N,N']bromidomanganese(III)}

A. Neuba, O. Seewald, U. Flörke and G. Henkel

Comment

Since evidence was found that an oxo-bridged manganese cluster participates significantly in the water oxidation process of photosystem II the research and synthesis of oxo-complexes, which contain manganese atoms in high oxidation states of +III or +IV, have become of considerable interest in bioinorganic chemistry (Mukhopadhyay *et al.*, 2004). Recently, a heterocuban oxo-bridged manganese cluster was probably identify as the oxgen-evolving center (OEC) which catalyzes one of the most thermodynamically demanding reactions in biology: the photoinduced oxidation of water (Ferreira *et al.*, 2004). As well the occurrence of manganese hydroxo- and oxo-complexes in the active centres of superoxiddismutases or katalases and the attempt to understand the catalytic processes in these metalloproteins create a need for small biological relevant modell complexes (Wu *et al.*, 2004). In search of bifunctional ligands able to stabilize unusually high metal oxidation states, we have extended our studies to guanidyl-type systems with N-donor functions. The first derivative, the ligand bis(tetramethylguanidino)propylene (btmgp) and its complexes with copper, iron, nickel, lithium, palladium and cobalt have recently been investigated (Harmjanz, 1997; Waden, 1999; Pohl *et al.*, 2000; Schneider, 2000; Heuwing, 2004).

We have now examined the reaction behaviour of the complex [$MnBr_2$(btmgp)] (II) containing the ligand bis(tetramethylguanidino)propylene (btmgp), towards molecular oxygen which leads to the title complex (I) with distorted square pyramidal coordination of the manganese atoms (Figure 1). There are many examples of bis(µ-oxo)-dimanganese complexes of Mn(III,IV) and Mn(IV,IV) species. However, dimanganese(III,III) species are rare, only a few examples are noted in literature and no compound with a $Mn^{III}{}_2O_2$ core, a bidentate imin-donor ligand and two terminal co-ligands is found in the CSD (Allen, 2002) to date.

There are only few examples of the dimanganese(III,III) species with tetradentate N-donor ligands and octahedrally coordinated manganese centres. The geometric centre of (I) lies on a crystallographic inversion centre and the resulting Mn_2O_2 core is thus strictly planar. The distance of the Mn atom to the N_2O_2 plane is 0.207 (1) Å and the nonbonding Mn–Mn distance is 2.7068 (9) Å. The Mn–O and Mn–N bond lengths (Table 1) are comparable with those from other characterized $Mn^{III}{}_2O_2$ complexes that range from 1.787 (6) to 1.863 (8) and 2.084 (6) to 2.468 (10) Å, respectively (Goodson & Hodgson, 1989; Goodson *et al.*, 1990; Kitajima *et al.*, 1991; Glerup *et al.*, 1994). Cell packing (Figure 2) exhibits C–H···Br intermolecular hydrogen bonds (see table) that link molecules to endless chains along [010].

Experimental

The synthesis of the btmgp-ligand is described in the literature (Pohl *et al.*, 2000). (II): the reaction of $MnBr_2$ (215 mg, 1 mmol) in 10 ml *ABS*. MeCN with btmgp (297 mg, 1.1 mmol) leads to a suspension with a white precipitate. After 30 min at reflux the blear solution had been filtered. By cooling down slowly, colourless crystals of (II) were be obtained. (I): slow diffusion of air to the mother liquor of (II) leads after several weeks to few dark red crystals of (I) suitable for X-ray diffraction.

Refinement

Hydrogen atoms located from difference Fourier maps were refined at idealized positions riding on the carbon atoms with isotropic displacement parameters U_{iso}(H) = 1.2U(Ceq) or 1.5U(CH_3). All CH_3 hydrogen atoms were allowed to rotate but not to tip.

Figures

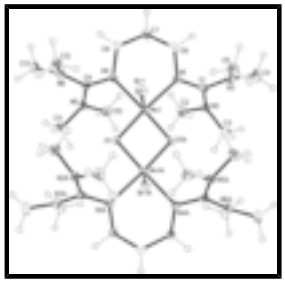

Fig. 1. Molecular structure of I. Displacement ellipsoids are drawn at the 50% probability level.

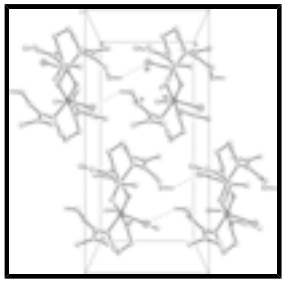

Fig. 2. Crystal packing of the title compound viewed along [001] with hydrogen bond indicated as dashed lines. H-atoms not involved are omitted.

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Crystal data

$[Mn_2Br_2O_2(C_{13}H_{30}N_6)_2]$	F_{000} = 1744
M_r = 842.56	D_x = 1.569 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 4977 reflections
a = 19.592 (4) Å	θ = 2.3–28.1º
b = 9.2077 (17) Å	μ = 2.99 mm^{-1}
c = 19.767 (4) Å	*T* = 120 (2) K
β = 90.03 (1)º	Block, red
V = 3566.0 (11) Å^3	0.43 × 0.40 × 0.38 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	4242 independent reflections
Radiation source: sealed tube	3584 reflections with $I > 2\sigma(I)$

Monochromator: graphite	R_{int} = 0.038
T = 120(2) K	θ_{max} = 27.9º
φ and ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	h = −25→24
T_{min} = 0.290, T_{max} = 0.322	k = −12→12
16870 measured reflections	l = −26→25

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.037	H-atom parameters constrained
$wR(F^2)$ = 0.098	$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 4.3912P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max}$ = 0.001
4242 reflections	$\Delta\rho_{max}$ = 0.85 e Å^{-3}
199 parameters	$\Delta\rho_{min}$ = −0.43 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}
Br1	0.144709 (14)	0.50925 (3)	0.428308 (14)	0.02284 (10)
Mn1	0.181051 (19)	0.74639 (4)	0.503835 (19)	0.01510 (11)
O1	0.24607 (9)	0.82399 (19)	0.44903 (9)	0.0175 (4)
N1	0.11406 (11)	0.6931 (2)	0.58156 (11)	0.0176 (4)
N2	0.17932 (12)	0.7459 (2)	0.67596 (11)	0.0202 (5)
N3	0.11891 (13)	0.5314 (2)	0.67283 (12)	0.0225 (5)
N4	0.10314 (11)	0.8676 (2)	0.45995 (11)	0.0179 (4)
N5	0.15979 (11)	1.0805 (2)	0.43426 (11)	0.0198 (5)
N6	0.08802 (13)	0.9809 (2)	0.35454 (12)	0.0227 (5)
C1	0.13683 (13)	0.6562 (3)	0.64095 (13)	0.0186 (5)
C2	0.18411 (16)	0.8976 (3)	0.65726 (14)	0.0257 (6)

H2A	0.1415	0.9282	0.6356	0.038*
H2B	0.2221	0.9110	0.6257	0.038*
H2C	0.1920	0.9563	0.6979	0.038*
C3	0.24051 (15)	0.6906 (3)	0.70875 (15)	0.0287 (6)
H3A	0.2340	0.5880	0.7202	0.043*
H3B	0.2493	0.7461	0.7502	0.043*
H3C	0.2795	0.7005	0.6780	0.043*
C4	0.11317 (19)	0.5181 (3)	0.74572 (15)	0.0316 (7)
H4A	0.1244	0.6113	0.7669	0.047*
H4B	0.1449	0.4434	0.7619	0.047*
H4C	0.0664	0.4906	0.7576	0.047*
C5	0.10379 (16)	0.4014 (3)	0.63481 (15)	0.0277 (6)
H5A	0.1090	0.4211	0.5864	0.042*
H5B	0.0568	0.3709	0.6440	0.042*
H5C	0.1353	0.3239	0.6482	0.042*
C6	0.04418 (13)	0.6489 (3)	0.56308 (14)	0.0204 (5)
H6A	0.0186	0.6224	0.6044	0.025*
H6B	0.0460	0.5624	0.5334	0.025*
C7	0.00763 (13)	0.7711 (3)	0.52682 (14)	0.0218 (5)
H7A	−0.0414	0.7461	0.5232	0.026*
H7B	0.0113	0.8603	0.5546	0.026*
C8	0.03464 (13)	0.8032 (3)	0.45688 (14)	0.0202 (5)
H8A	0.0364	0.7122	0.4303	0.024*
H8B	0.0033	0.8711	0.4336	0.024*
C9	0.11696 (13)	0.9723 (3)	0.41713 (14)	0.0180 (5)
C10	0.17422 (15)	1.1128 (3)	0.50419 (14)	0.0236 (6)
H10A	0.1381	1.0723	0.5328	0.035*
H10B	0.1763	1.2182	0.5105	0.035*
H10C	0.2181	1.0696	0.5169	0.035*
C11	0.21030 (15)	1.1363 (3)	0.38758 (15)	0.0261 (6)
H11A	0.1973	1.1105	0.3412	0.039*
H11B	0.2549	1.0938	0.3981	0.039*
H11C	0.2128	1.2422	0.3918	0.039*
C12	0.07306 (16)	0.8521 (3)	0.31598 (15)	0.0286 (6)
H12A	0.0875	0.7662	0.3415	0.043*
H12B	0.0977	0.8556	0.2729	0.043*
H12C	0.0239	0.8469	0.3073	0.043*
C13	0.06961 (17)	1.1172 (3)	0.32315 (15)	0.0292 (6)
H13A	0.0822	1.1976	0.3531	0.044*
H13B	0.0203	1.1193	0.3150	0.044*
H13C	0.0938	1.1271	0.2800	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02406 (16)	0.01950 (14)	0.02495 (16)	−0.00028 (10)	0.00025 (11)	−0.00428 (10)
Mn1	0.01504 (19)	0.01594 (19)	0.01433 (19)	0.00004 (14)	0.00055 (14)	0.00107 (14)
O1	0.0163 (9)	0.0198 (9)	0.0163 (9)	0.0007 (7)	0.0000 (7)	0.0034 (7)

N1	0.0159 (11)	0.0200 (10)	0.0171 (10)	−0.0006 (8)	0.0028 (8)	0.0006 (8)
N2	0.0225 (11)	0.0224 (11)	0.0157 (10)	−0.0013 (9)	0.0004 (9)	−0.0004 (8)
N3	0.0287 (13)	0.0214 (11)	0.0174 (11)	−0.0018 (10)	0.0021 (9)	0.0028 (9)
N4	0.0151 (10)	0.0185 (10)	0.0201 (11)	0.0002 (8)	−0.0001 (8)	0.0013 (8)
N5	0.0203 (11)	0.0189 (11)	0.0203 (11)	0.0020 (9)	0.0035 (9)	0.0007 (9)
N6	0.0278 (13)	0.0217 (11)	0.0187 (11)	0.0025 (9)	−0.0007 (10)	0.0020 (9)
C1	0.0183 (13)	0.0201 (12)	0.0175 (12)	0.0029 (10)	0.0036 (10)	−0.0023 (10)
C2	0.0319 (16)	0.0221 (13)	0.0230 (14)	−0.0041 (11)	0.0011 (12)	−0.0019 (11)
C3	0.0268 (15)	0.0368 (16)	0.0225 (14)	0.0046 (12)	−0.0032 (12)	−0.0050 (12)
C4	0.0430 (19)	0.0316 (16)	0.0201 (14)	−0.0015 (13)	0.0040 (13)	0.0070 (12)
C5	0.0302 (16)	0.0219 (13)	0.0311 (16)	−0.0022 (11)	−0.0009 (13)	−0.0001 (12)
C6	0.0155 (12)	0.0227 (13)	0.0231 (13)	−0.0028 (10)	0.0023 (10)	0.0036 (10)
C7	0.0153 (12)	0.0235 (13)	0.0265 (14)	0.0004 (10)	0.0000 (10)	0.0023 (11)
C8	0.0163 (12)	0.0221 (13)	0.0222 (13)	−0.0008 (10)	−0.0026 (10)	0.0018 (10)
C9	0.0144 (12)	0.0194 (12)	0.0202 (13)	0.0050 (10)	−0.0003 (10)	−0.0011 (10)
C10	0.0251 (14)	0.0191 (13)	0.0266 (14)	−0.0009 (11)	−0.0027 (11)	−0.0020 (11)
C11	0.0260 (15)	0.0211 (13)	0.0313 (15)	−0.0038 (11)	0.0087 (12)	−0.0013 (11)
C12	0.0333 (16)	0.0311 (15)	0.0214 (14)	−0.0048 (12)	−0.0018 (12)	−0.0014 (12)
C13	0.0375 (17)	0.0315 (15)	0.0187 (13)	0.0051 (13)	0.0008 (12)	0.0081 (11)

Geometric parameters (Å, °)

Br1—Mn1	2.7391 (6)	C3—H3C	0.9800
Mn1—O1	1.8188 (18)	C4—H4A	0.9800
Mn1—O1^{i}	1.8235 (18)	C4—H4B	0.9800
Mn1—N1	2.080 (2)	C4—H4C	0.9800
Mn1—N4	2.080 (2)	C5—H5A	0.9800
Mn1—Mn1^{i}	2.7068 (9)	C5—H5B	0.9800
O1—Mn1^{i}	1.8236 (18)	C5—H5C	0.9800
N1—C1	1.301 (3)	C6—C7	1.514 (4)
N1—C6	1.474 (3)	C6—H6A	0.9900
N2—C1	1.362 (3)	C6—H6B	0.9900
N2—C2	1.448 (3)	C7—C8	1.510 (4)
N2—C3	1.455 (4)	C7—H7A	0.9900
N3—C1	1.357 (3)	C7—H7B	0.9900
N3—C5	1.444 (4)	C8—H8A	0.9900
N3—C4	1.450 (4)	C8—H8B	0.9900
N4—C9	1.311 (3)	C10—H10A	0.9800
N4—C8	1.468 (3)	C10—H10B	0.9800
N5—C9	1.346 (4)	C10—H10C	0.9800
N5—C10	1.442 (3)	C11—H11A	0.9800
N5—C11	1.447 (3)	C11—H11B	0.9800
N6—C9	1.363 (3)	C11—H11C	0.9800
N6—C12	1.440 (4)	C12—H12A	0.9800
N6—C13	1.445 (4)	C12—H12B	0.9800
C2—H2A	0.9800	C12—H12C	0.9800
C2—H2B	0.9800	C13—H13A	0.9800
C2—H2C	0.9800	C13—H13B	0.9800

C3—H3A	0.9800	C13—H13C	0.9800
C3—H3B	0.9800		
O1—Mn1—O1^{i}	84.00 (8)	N3—C5—H5B	109.5
O1—Mn1—N1	167.18 (8)	H5A—C5—H5B	109.5
O1^{i}—Mn1—N1	91.89 (8)	N3—C5—H5C	109.5
O1—Mn1—N4	93.15 (8)	H5A—C5—H5C	109.5
O1^{i}—Mn1—N4	167.96 (8)	H5B—C5—H5C	109.5
N1—Mn1—N4	88.36 (9)	N1—C6—C7	110.6 (2)
O1—Mn1—Br1	99.81 (6)	N1—C6—H6A	109.5
O1^{i}—Mn1—Br1	101.45 (6)	C7—C6—H6A	109.5
N1—Mn1—Br1	92.90 (6)	N1—C6—H6B	109.5
N4—Mn1—Br1	90.56 (6)	C7—C6—H6B	109.5
Mn1—O1—Mn1^{i}	96.00 (8)	H6A—C6—H6B	108.1
C1—N1—C6	118.0 (2)	C8—C7—C6	114.4 (2)
C1—N1—Mn1	120.79 (18)	C8—C7—H7A	108.7
C6—N1—Mn1	117.94 (17)	C6—C7—H7A	108.7
C1—N2—C2	119.7 (2)	C8—C7—H7B	108.7
C1—N2—C3	121.2 (2)	C6—C7—H7B	108.7
C2—N2—C3	113.4 (2)	H7A—C7—H7B	107.6
C1—N3—C5	120.9 (2)	N4—C8—C7	111.2 (2)
C1—N3—C4	123.6 (2)	N4—C8—H8A	109.4
C5—N3—C4	115.5 (2)	C7—C8—H8A	109.4
C9—N4—C8	117.3 (2)	N4—C8—H8B	109.4
C9—N4—Mn1	120.79 (18)	C7—C8—H8B	109.4
C8—N4—Mn1	118.13 (16)	H8A—C8—H8B	108.0
C9—N5—C10	121.0 (2)	N4—C9—N5	120.7 (2)
C9—N5—C11	121.9 (2)	N4—C9—N6	122.9 (2)
C10—N5—C11	113.9 (2)	N5—C9—N6	116.4 (2)
C9—N6—C12	121.1 (2)	N5—C10—H10A	109.5
C9—N6—C13	123.0 (2)	N5—C10—H10B	109.5
C12—N6—C13	115.9 (2)	H10A—C10—H10B	109.5
N1—C1—N3	123.5 (2)	N5—C10—H10C	109.5
N1—C1—N2	120.6 (2)	H10A—C10—H10C	109.5
N3—C1—N2	115.8 (2)	H10B—C10—H10C	109.5
N2—C2—H2A	109.5	N5—C11—H11A	109.5
N2—C2—H2B	109.5	N5—C11—H11B	109.5
H2A—C2—H2B	109.5	H11A—C11—H11B	109.5
N2—C2—H2C	109.5	N5—C11—H11C	109.5
H2A—C2—H2C	109.5	H11A—C11—H11C	109.5
H2B—C2—H2C	109.5	H11B—C11—H11C	109.5
N2—C3—H3A	109.5	N6—C12—H12A	109.5
N2—C3—H3B	109.5	N6—C12—H12B	109.5
H3A—C3—H3B	109.5	H12A—C12—H12B	109.5
N2—C3—H3C	109.5	N6—C12—H12C	109.5
H3A—C3—H3C	109.5	H12A—C12—H12C	109.5
H3B—C3—H3C	109.5	H12B—C12—H12C	109.5
N3—C4—H4A	109.5	N6—C13—H13A	109.5
N3—C4—H4B	109.5	N6—C13—H13B	109.5

H4A—C4—H4B	109.5	H13A—C13—H13B	109.5
N3—C4—H4C	109.5	N6—C13—H13C	109.5
H4A—C4—H4C	109.5	H13A—C13—H13C	109.5
H4B—C4—H4C	109.5	H13B—C13—H13C	109.5
N3—C5—H5A	109.5		
O1^{i}—Mn1—O1—Mn1^{i}	0.0	C4—N3—C1—N1	−147.6 (3)
N1—Mn1—O1—Mn1^{i}	71.8 (4)	C5—N3—C1—N2	−150.0 (3)
N4—Mn1—O1—Mn1^{i}	168.26 (9)	C4—N3—C1—N2	30.3 (4)
Br1—Mn1—O1—Mn1^{i}	−100.62 (7)	C2—N2—C1—N1	17.6 (4)
O1—Mn1—N1—C1	−58.7 (5)	C3—N2—C1—N1	−134.1 (3)
O1^{i}—Mn1—N1—C1	12.3 (2)	C2—N2—C1—N3	−160.4 (2)
N4—Mn1—N1—C1	−155.7 (2)	C3—N2—C1—N3	48.0 (3)
Br1—Mn1—N1—C1	113.8 (2)	C1—N1—C6—C7	138.4 (2)
O1—Mn1—N1—C6	142.1 (3)	Mn1—N1—C6—C7	−61.8 (3)
O1^{i}—Mn1—N1—C6	−146.92 (18)	N1—C6—C7—C8	69.5 (3)
N4—Mn1—N1—C6	45.12 (18)	C9—N4—C8—C7	−140.8 (2)
Br1—Mn1—N1—C6	−45.36 (18)	Mn1—N4—C8—C7	60.9 (3)
O1—Mn1—N4—C9	−9.4 (2)	C6—C7—C8—N4	−69.2 (3)
O1^{i}—Mn1—N4—C9	66.5 (5)	C8—N4—C9—N5	147.5 (2)
N1—Mn1—N4—C9	157.9 (2)	Mn1—N4—C9—N5	−54.7 (3)
Br1—Mn1—N4—C9	−109.2 (2)	C8—N4—C9—N6	−30.5 (4)
O1—Mn1—N4—C8	148.21 (19)	Mn1—N4—C9—N6	127.3 (2)
O1^{i}—Mn1—N4—C8	−135.9 (4)	C10—N5—C9—N4	−20.4 (4)
N1—Mn1—N4—C8	−44.54 (19)	C11—N5—C9—N4	138.2 (3)
Br1—Mn1—N4—C8	48.34 (18)	C10—N5—C9—N6	157.8 (2)
C6—N1—C1—N3	32.9 (4)	C11—N5—C9—N6	−43.7 (4)
Mn1—N1—C1—N3	−126.3 (2)	C12—N6—C9—N4	−35.3 (4)
C6—N1—C1—N2	−144.9 (2)	C13—N6—C9—N4	143.8 (3)
Mn1—N1—C1—N2	55.9 (3)	C12—N6—C9—N5	146.6 (3)
C5—N3—C1—N1	32.1 (4)	C13—N6—C9—N5	−34.3 (4)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11C···Br1^{ii}	0.98	2.89	3.754 (3)	148

Symmetry codes: (ii) *x*, *y*+1, *z*.

Fig. 1

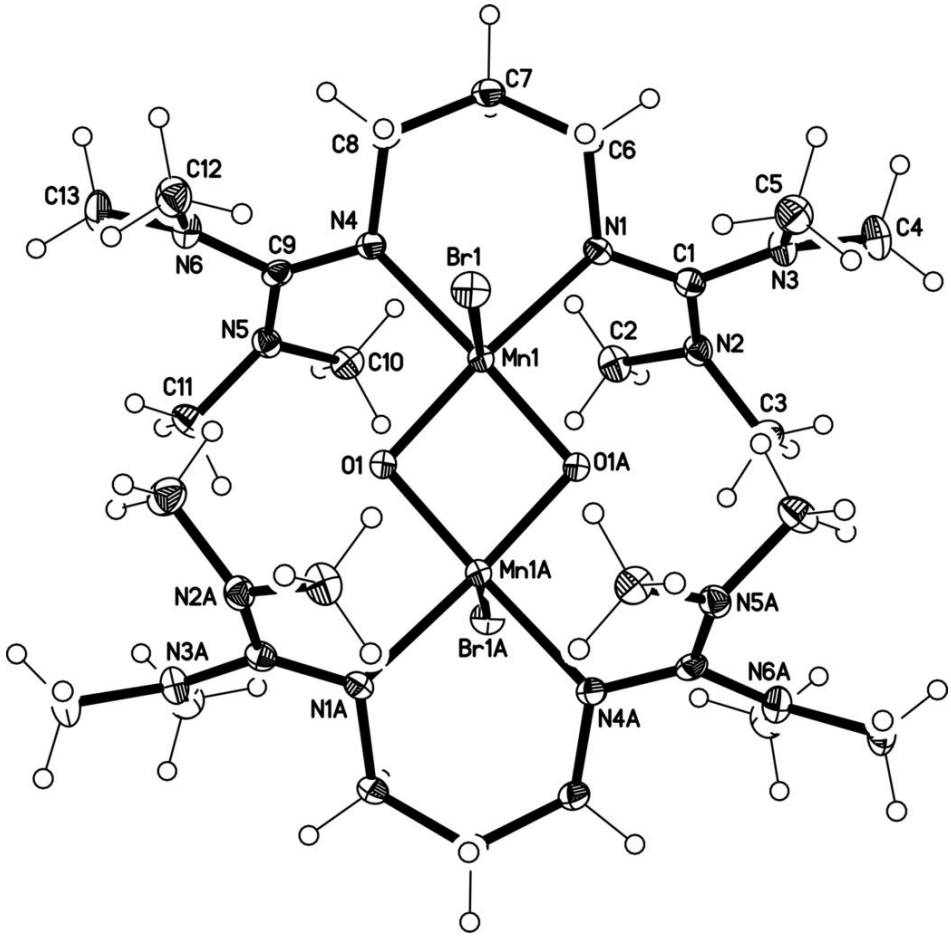
C7
C8
C6
C12
C13
C5
N4
N1
C4
C9
N6
Br1
C1
N3
N5
C2
N2
C10
Mn1
C11
C3
O1
O1A
Mn1A
N2A
N5A
Br1A
N3A
N6A
N1A
N4A

Fig. 2