

Takashiro Akitsu,\* Yui  
Takeuchi and Yasuaki EinagaDepartment of Chemistry, Faculty of Science  
and Technology, Keio University, 3-14-1  
Hiyoshi, Kohoku-ku, Yokohama 223-8522,  
JapanCorrespondence e-mail:  
akitsu@chem.keio.ac.jp

## Key indicators

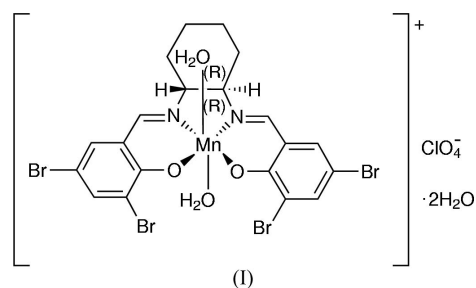
Single-crystal X-ray study  
 $T = 297$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.016$  Å  
H-atom completeness 67%  
 $R$  factor = 0.042  
 $wR$  factor = 0.122  
Data-to-parameter ratio = 10.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Diaqua[(1*R*,2*R*)-*N,N'*-bis(3,5-dibromosalicylidene)-  
cyclohexane-1,2-diamine- $\kappa^4\text{O},\text{N},\text{N}',\text{O}'$ ]manganese(III)  
perchlorate dihydrateThe crystal structure of the title compound,  $[\text{Mn}(\text{C}_{20}\text{H}_{16}\text{Br}_4\text{N}_2\text{O}_2)(\text{H}_2\text{O})_2](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$ , has been determined. The mononuclear complex affords an elongated octahedral  $\text{MnN}_2\text{O}_4$  coordination geometry with the four donor atoms of the tetradentate chiral Schiff base in the equatorial plane and with two aqua ligands in axial positions with  $\text{Mn}-\text{O} = 2.278$  (9) and 2.269 (10) Å.

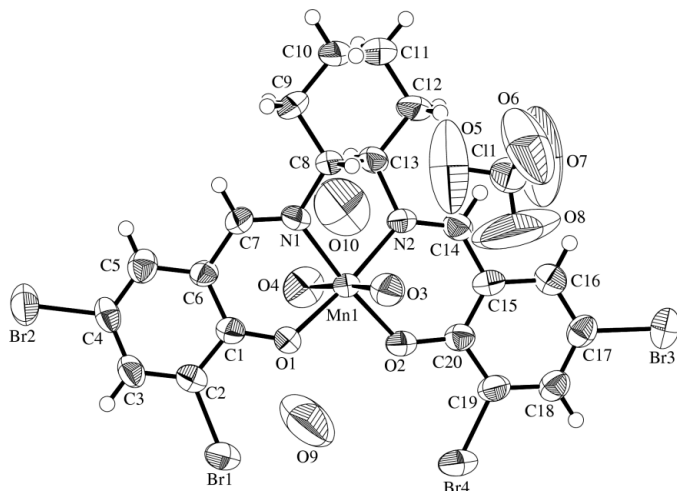
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## Comment

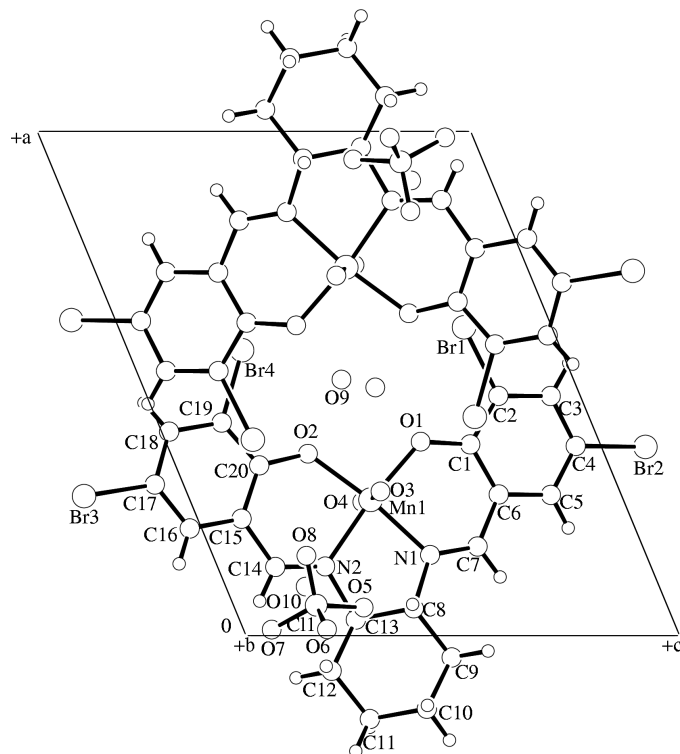
Photo- and magnetic functional materials derived from transition metal complexes have been studied widely (Sato 2003; Sato *et al.*, 2003). Hence it is important to examine complexes exhibiting structural changes which accompany changes of spin or valence states. Theoretically, it has been shown that the  $^5D$  ground state may split into  $^5T_{2g}$  and  $^5E_g$  terms, and Jahn–Teller distortion removes the orbital degeneracy of the  $^5E_g$  ground state to give the singlet  $^5A_{1g}$  or  $^5B_{1g}$  states (Kennedy & Murray, 1985). Axial elongation results in removing the spin degeneracy of the  $^5B_{1g}$  level lying lowest with negative zero-field splitting,  $D$ , by spin-orbit coupling, whereas axial compression, which is rare, leads to  $^5A_{1g}$  with positive  $D$ . It has been reported that some high-spin  $\text{Mn}^{\text{III}}$  complexes exhibit ferromagnetism, or they are suitable building blocks for single molecular magnets (Miyasaka *et al.*, 2002). Furthermore, chiral Schiff base  $\text{Mn}^{\text{III}}$  complexes are employed for Kochi–Jacobsen–Katsuki enantioselective oxidation (Korendovych & Rybak-Akimova, 2004; Martínez *et al.*, 2002; Reger & Janda, 2000; Khavrutskii *et al.*, 2003*a,b*) and models of metalloproteins in photosystem II (Ashmawy *et al.*, 1985; Aurangzeb *et al.*, 1994; Bermejo *et al.*, 1996). Recently, we reported the first chiral trinuclear cluster complex having an  $\text{Mn}^{\text{III}}-\text{NC}-\text{Ni}^{\text{II}}-\text{CN}-\text{Mn}^{\text{III}}$  unit (Akitsu *et al.*, 2005). We report here the crystal structure of the title compound, (I), which is a mononuclear chiral Schiff base  $\text{Mn}^{\text{III}}$  complex having elongated axial  $\text{Mn}-\text{O}$  bonds to two aqua ligands.Complex (I) adopts an axially elongated octahedral  $\text{MnN}_2\text{O}_4$  coordination geometry with the four donor atoms of



**Figure 1**

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms were not located on water molecules.

the tetradentate Schiff base forming the equatorial plane and two aqua ligands occupying the axial sites (Fig. 1). The displacement of Mn1 from the O1/N1/N2/O2 least-squares plane towards the axial O3 atom is 0.0117 (5) Å. The  $T$  value, which measures the degree of tetragonal distortion of the  $MnN_2O_4$  chromophore, is 0.876, where  $T = R_S/R_L$ , the ratio of equatorial and axial mean bond lengths undergoing the Jahn–Teller effect (Hathaway & Billing, 1970). The effective magnetic moment and diffuse reflectance spectrum also support a  ${}^5B_{1g}$  ground state for the high-spin  $Mn^{III}$  ion with  $S = 2$ . The chiral (1*R*,2*R*)-1,2-diaminocyclohexane group adopts a  $\lambda$  configuration, with torsion angle N1–C8–C13–N2 = 47 (1)°, and adopts a chair conformation. Comparison of the geometric parameters for (I) with those of analogous complexes, both chiral (Nishikori *et al.*, 1999, 2000; Lenoble *et al.*, 1998; Pospisil *et al.*, 1996) and achiral (Oki & Hodgson, 1990), does not reveal any significant differences. The overall molecular structure of planar (I) is a stepped conformation, and the dihedral angle between the least-squares planes of the benzene rings of the ligands (C1–C6 and C15–C20) is 7.0 (4)°. The angles between the O1/N1/N2/O2 and C1–C6 planes and between the O1/N1/N2/O2 and C15–C20 planes are 163.0 (3) and 165.8 (3)°, respectively. Moreover, the angles between the O1/N1/N2/O2 and N1/C7/C1/C6/O1 planes, between the O1/N1/N2/O2 and N2/C14/C15/C20/O2 planes, and between the N1/C7/C1/C6/O1 and N2/C14/C15/C20/O2 planes are 162.2 (4), 165.4 (4) and 176.8 (4)°, respectively. In the crystal structure of (I) (Fig. 2), the axial water ligands and solvent water molecules are expected to form hydrogen bonds. On geometrical grounds, the following hydrogen bonds are likely: O3...O5 = 3.21 (2) Å, O3...O8 = 3.37 (3) Å, O3...O9<sup>i</sup> = 2.80 (1) Å, O4...O9 = 3.02 (1) Å, O4...O10 = 2.68 (1) Å, O10...O6<sup>ii</sup> = 2.93 (2) Å and O10...O7<sup>iii</sup> = 2.82 (2) Å [symmetry codes: (i)  $1 - x, \frac{1}{2} - y, 1 - z$ ; (ii)  $x, 1 - y, z$ ; (iii)  $-x, -\frac{1}{2} - y, -z$ ]. However, it should be noted that it was not possible to locate the positions of the H atoms in these water molecules.



**Figure 2**

The molecular packing diagram of (I), viewed down the crystallographic  $b$  axis.

## Experimental

Reaction of 3,5-dibromosalicylaldehyde (0.14 g, 0.50 mmol) and (1*R*,2*R*)-(-)-1,2-diaminocyclohexane (0.029 g, 0.25 mmol) in methanol (30 ml) with manganese(III) acetate dihydrate (0.069 g, 0.26 mmol) at 298 K for 5 h gave rise to a brown solution. After adding sodium perchlorate hydrate (0.085 g, 0.60 mmol), the solution was stirred at 298 K for 18 h. **[Caution!]** In general perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care. Brown microcrystals of a precursor complex,  $[Mn(C_{20}H_{16}Br_4N_2O_2)(H_2O)_2](MeOH)](ClO_4)$ , were obtained from the filtrate. Analysis found: C 29.8, H2.83, N3.28%; calculated for  $C_{20}H_{24}Br_4ClMnN_2O_{10}$ : C 30.0, H2.46, N3.33%. IR (KBr): 1619  $cm^{-1}$  (C=N); m.p. 598 K (decomposition); effective magnetic moment 4.62 BM at 295 K. UV–vis (diffuse reflectance spectra,  $cm^{-1}$ ): 15400 (*sh, d-d*), 20000 (*sh, d-d*), 22000 (*sh,  $\pi-\pi^*$* ). Brown crystals of (I) suitable for X-ray analysis were obtained from an aqueous methanol (95% purity) solution at 298 K over a period of several days. Unfortunately, single crystals of (I) (with axial aqua ligands and uncoordinated water molecules) could not be obtained reproducibly. Analytical and spectroscopic characterization of (I) could not therefore be carried out.

### Crystal data

$[Mn(C_{20}H_{16}Br_4N_2O_2)(H_2O)_2] \cdot (ClO_4) \cdot 2H_2O$   
 $M_r = 854.34$   
 Monoclinic,  $P2_1$   
 $a = 13.270$  (5) Å  
 $b = 11.612$  (5) Å  
 $c = 10.530$  (6) Å  
 $\beta = 112.48$  (3)°  
 $V = 1499.3$  (13) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.893$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 10.0$ – $11.5$ °  
 $\mu = 5.91$  mm<sup>-1</sup>  
 $T = 297$  (2) K  
 Prism, brown  
 $0.60 \times 0.30 \times 0.20$  mm

Data collection

Rigaku AFC-7R diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction:  $\psi$  scans  
 (North *et al.*, 1968)  
 $T_{\min} = 0.246$ ,  $T_{\max} = 0.307$   
 3620 measured reflections  
 3620 independent reflections  
 2220 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.000$   
 $\theta_{\text{max}} = 27.6^\circ$   
 $h = 0 \rightarrow 17$   
 $k = 0 \rightarrow 15$   
 $l = -13 \rightarrow 12$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 1.5%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.122$   
 $S = 1.01$   
 3620 reflections  
 344 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0574P)^2 + 1.5653P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.57 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.48 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0006 (6)  
 Absolute structure: Flack (1983), no  
 Friedel pairs  
 Flack parameter: 0.02 (2)

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Mn1—O1	1.884 (6)	Mn1—N2	1.981 (8)
Mn1—O2	1.893 (6)	Mn1—O4	2.269 (10)
Mn1—N1	1.975 (8)	Mn1—O3	2.278 (9)
O1—Mn1—O2	94.8 (3)	N1—Mn1—O4	90.1 (4)
O1—Mn1—N1	91.7 (3)	N2—Mn1—O4	93.8 (4)
O2—Mn1—N1	173.4 (3)	O1—Mn1—O3	91.1 (3)
O1—Mn1—N2	173.5 (3)	O2—Mn1—O3	88.8 (3)
O2—Mn1—N2	91.6 (3)	N1—Mn1—O3	91.8 (4)
N1—Mn1—N2	81.8 (3)	N2—Mn1—O3	89.8 (3)
O1—Mn1—O4	85.5 (4)	O4—Mn1—O3	176.2 (3)
O2—Mn1—O4	89.7 (4)		
N1—C8—C13—N2	−47 (1)		

H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.93–0.98  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and included in the final cycles of refinement using riding-model constraints. H atoms of the aqua ligands and solvents were not included, since they could not be observed in difference Fourier maps, nor located uniquely by considering hydrogen-bonding features.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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