

## A mixed-valence manganese(III)–manganese(IV) di- $\mu$ -oxo complex, [(cyclam)MnO]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)

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Received 17 May 2001

Accepted 25 May 2001

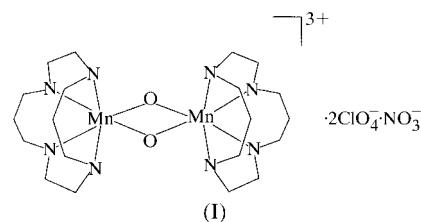
The title dinuclear di- $\mu$ -oxo-bis[(1,4,8,11-tetraazacyclotetradecane- $\kappa^4$ N)manganese(III,IV)] diperchlorate nitrate complex, [Mn<sub>2</sub>O<sub>2</sub>(C<sub>10</sub>H<sub>24</sub>N<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>) or [(cyclam)MnO]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>), was self-assembled by the reaction of Mn<sup>2+</sup> with 1,4,8,11-tetraazacyclotetradecane in aqueous media. The structure of this compound consists of a centrosymmetric binuclear [(cyclam)MnO]<sup>3+</sup> unit, two perchlorate anions and one nitrate anion. While the low-temperature electron paramagnetic resonance spectra show a typical 16-line signal for a di- $\mu$ -oxo Mn<sup>III</sup>/Mn<sup>IV</sup> dimer, the magnetic susceptibility studies also confirm a characteristic antiferromagnetic coupling between the electronic spins of the Mn<sup>IV</sup> and Mn<sup>III</sup> ions.

### Comment

The tetranuclear manganese center in photosystem II (PSII) in green plants has been shown to play an essential role in the oxidation of water to molecular oxygen (Sauer, 1980). Recent electron paramagnetic resonance (EPR) studies of the S<sub>2</sub> state in PSII suggested that the S<sub>2</sub> state exhibits an unusual 16-line EPR spectrum, which is in the mixed balance state of manganese(III) and manganese(IV) ions, and consists of two dinuclear di- $\mu$ -oxo-dimanganese cores, 2[Mn<sub>2</sub>(O)<sub>2</sub>] (Paula *et al.*, 1986; Brudvig *et al.*, 1986). In addition, EXAFS studies indicated that the N and/or O atoms act as terminal ligands around the [Mn<sub>2</sub>(O)<sub>2</sub>] core (Cole *et al.*, 1987; Yachandra *et al.*, 1987). Recently, several di- $\mu$ -oxo-dimanganese(III,IV) complexes with a terminal N<sub>4</sub> donor set have been reported as model complexes for the S<sub>2</sub> state (Cooper *et al.*, 1978; Stebler

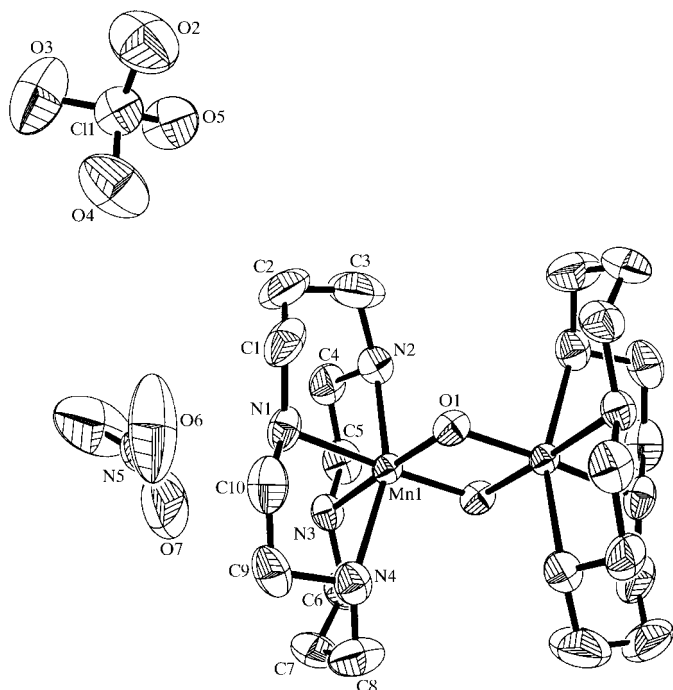
*et al.*, 1986; Collins *et al.*, 1987; Towle *et al.*, 1988; Suzuki *et al.*, 1988; Hagen *et al.*, 1988; Sheat *et al.*, 1987). Interest in complexes of this general type stems more from their potential use as two-electron oxidation electrocatalysts. Gilbert *et al.* (1998) have electrochemically oxidized alcohols and ethers in the presence of both the bpy and phen complexes (bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline), and Brewer *et al.* (1989) have shown that the bpy complex oxidizes water in the presence of a chemical oxidant such as the cerium(IV) ion. Consequently, various synthetic efforts have been made to obtain di- $\mu$ -oxo-dimanganese compounds with the desired electrochemical properties in the expectation of producing useful catalytic complexes. However, most of the synthetic methods involve the oxidation of Mn<sup>II</sup> precursors using persulfate, permanganate, hydrogen peroxide or dioxygen (Bruckner *et al.*, 1998; Sam *et al.*, 1994; Kim *et al.*, 1997; Feichtinger *et al.*, 1997). We report here a new mixed-valence Mn<sup>III</sup>–Mn<sup>IV</sup> di- $\mu$ -oxo compound, *viz.* [(cyclam)MnO]<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>NO<sub>3</sub>, (I), obtained through self-assembly from aqueous solution.

The structure of the title compound, (I), consists of an apparently centrosymmetric binuclear [(cyclam)MnO]<sup>3+</sup> unit, two perchlorate anions and one nitrate anion. The geometry about each manganese center is a slightly distorted octahedron, the ligating atoms being two *cis* oxo-bridges and four N atoms from the cyclam ligand. Referring to Table 1, the *trans* angles at Mn fall in the range 158.6 (1)–174.3 (1)°, with the greatest deviation from linearity occurring at the intra-ligand N4–Mn–N2 angle defined by the two axial N atoms. The four chelating N–Mn–N angles fall in the range 80.2 (1)–85.7 (1)°, with an average value of 82.2 (3)°. The Mn...Mn separation of 2.7398 (7) Å is comparable with the values for other di- $\mu$ -oxo-dimanganese complexes. The Mn–O–Mn bond angle is slightly larger than other reported values, which range from 94.0 to 96.6°. The presence of the crystallographic inversion center in the middle of the dimer causes the two manganese centers to be crystallographically equivalent. While this could indicate that the two manganese centers are chemically equivalent, and that the complex is delocalized, it could also be due to a static disorder resulting from the crystallographic superposition of an equal number of Mn<sup>III</sup>–Mn<sup>IV</sup> and Mn<sup>IV</sup>–Mn<sup>III</sup> cations, or from a dynamic disorder due to rapid (on the crystallographic time scale) electron transfer



between the two manganese centers. Burgi and co-workers (Stebler *et al.*, 1986) noted an analogous crystallographic symmetry in the phen complex, where the dimer has apparent C<sub>2</sub> symmetry leading to crystallographically equivalent manganese centers, and their excellent and detailed analysis need not be repeated here. The EPR spectrum at 110 K exhibits a 16-line pattern centered near *g* = 2.0, which is

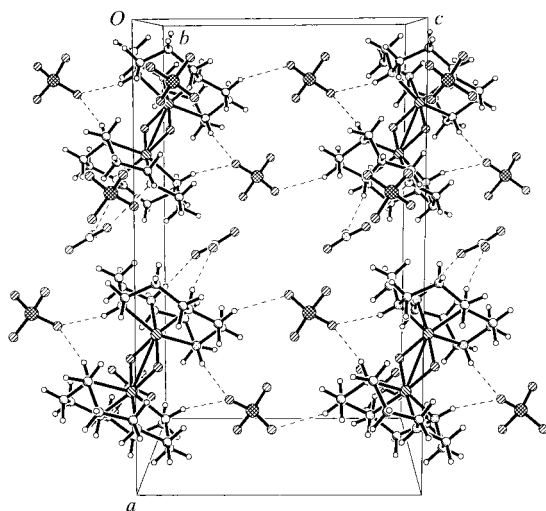
expected for an antiferromagnetically coupled  $\text{Mn}^{\text{III,IV}}$  dimer with a spin state of  $\frac{1}{2}$  where two manganese ions are not equivalent. Magnetic susceptibility shows a characteristic antiferromagnetic interaction between  $\text{Mn}^{\text{IV}}$  and  $\text{Mn}^{\text{III}}$  ions.



**Figure 1**  
The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Hence, we conclude that the complex is in a trapped mixed-valence state.

The packing diagram of (I) in the unit cell viewed down the  $b$  axis is shown in Fig. 2. There are intermolecular and intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, and weak  $\text{C}-\text{H}\cdots\text{O}$  interactions (Table 2).



**Figure 2**  
Packing diagram of (I) in the unit cell viewed down the  $b$  axis.

## Experimental

The title complex was prepared by adding a solution of  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.574 g, 2.0 mmol) in water (8 ml) to a solution of cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) (0.42 g, 2.1 mmol) in  $\text{CH}_3\text{OH}$  (10 ml). The solution changed color quickly from colorless to red-brown and lastly to dark blue. To the resultant dark-blue solution was added a solution of  $\text{NaClO}_4$  (0.37 g, 3.0 mmol) in water (5 ml). The solution was left to stand undisturbed for one day and plate-like dark-green crystals suitable for X-ray analysis appeared. The crystals were stable in the air. Analysis calculated for  $\text{C}_{20}\text{H}_{48}\text{Cl}_2\text{Mn}_2\text{N}_9\text{O}_{13}$ : Mn 13.72, C 29.92, H 5.99, N 15.71%; found: Mn 14.00, C 29.65, H 5.78, N 15.47%.

### Crystal data

$[\text{Mn}_2\text{O}_2(\text{C}_{10}\text{H}_{24}\text{N}_4)_2](\text{ClO}_4)_2(\text{NO}_3)$   
 $M_r = 803.45$   
 Monoclinic,  $C2/c$   
 $a = 19.9616$  (4) Å  
 $b = 13.8047$  (4) Å  
 $c = 12.1531$  (3) Å  
 $\beta = 90.508$  (1)°  
 $V = 3348.8$  (1) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.594$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8192 reflections  
 $\theta = 2.5$ – $38.6^\circ$   
 $\mu = 0.99$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Plate, black  
 $0.38 \times 0.36 \times 0.12$  mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.706$ ,  $T_{\text{max}} = 0.891$   
 11565 measured reflections

3823 independent reflections  
 3292 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -25 \rightarrow 25$   
 $k = -17 \rightarrow 17$   
 $l = -11 \rightarrow 15$

**Table 1**

Selected geometric parameters (Å, °).

Mn1—O1 <sup>i</sup>	1.8263 (19)	Mn1—N2	2.185 (3)
Mn1—O1	1.8291 (18)	Mn1—N4	2.217 (3)
Mn1—N1	2.114 (2)	Mn1—Mn1 <sup>i</sup>	2.7398 (9)
Mn1—N3	2.125 (2)		
O1 <sup>i</sup> —Mn1—O1	82.90 (8)	N1—Mn1—N2	85.69 (10)
O1 <sup>i</sup> —Mn1—N1	173.95 (9)	N3—Mn1—N2	80.24 (10)
O1—Mn1—N1	91.07 (9)	O1 <sup>i</sup> —Mn1—N4	99.97 (9)
O1 <sup>i</sup> —Mn1—N3	91.74 (9)	O1—Mn1—N4	98.00 (9)
O1—Mn1—N3	174.34 (9)	N1—Mn1—N4	80.37 (10)
N1—Mn1—N3	94.30 (9)	N3—Mn1—N4	84.70 (10)
O1 <sup>i</sup> —Mn1—N2	95.60 (9)	N2—Mn1—N4	158.61 (10)
O1—Mn1—N2	98.40 (10)	Mn1 <sup>i</sup> —O1—Mn1	97.10 (8)

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
N1—H11N <sup>i</sup> ⋯O6	0.92	2.0052	2.912 (7)	168
N2—H12N <sup>i</sup> ⋯O5 <sup>i</sup>	0.91	2.1055	2.980 (5)	161
N3—H13N <sup>i</sup> ⋯O7	0.93	2.1148	3.008 (5)	160
N4—H14N <sup>i</sup> ⋯O5 <sup>ii</sup>	0.92	2.1977	3.087 (4)	163
C1—H1A <sup>i</sup> ⋯O1	0.97	2.5931	3.118 (4)	114
C2—H2B <sup>i</sup> ⋯O5	0.97	2.5918	3.419 (5)	143
C5—H5A <sup>i</sup> ⋯O4 <sup>iii</sup>	0.97	2.5203	3.394 (5)	150

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

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.150$   
 $S = 1.07$   
 3823 reflections  
 209 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0856P)^2 + 5.1838P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.80 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$

After checking their presence in the difference map, all H atoms were geometrically fixed and allowed to ride on their attached atoms with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  for the attached atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1996); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

This work was funded by the State Key Project of Fundamental Research, the National Natural Science Foundation of China (NSF 29823001), and the Malaysian Government and Universiti Sains Malaysia research grant R&D No. 305/PFIZIK/610942.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1485). Services for accessing these data are described at the back of the journal.

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