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# Anion-Controlled Assembly of Four Manganese Ions: Structural, Magnetic, and Electrochemical Properties of Tetramanganese Complexes Stabilized by Xanthene-Bridged Schiff Base Ligands

Masakazu Hirotsu,*[†] Yuu Shimizu,[†] Naoto Kuwamura,[†,‡] Rika Tanaka,[§] Isamu Kinoshita,[†,‡,#] Ryoichi Takada,[†] Yoshio Teki,[†] and Hideki Hashimoto[†,‡,#]

[†]Graduate School of Science, [§]Graduate School of Engineering, and [#]The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

[‡]CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Ⓢ *Supporting Information*

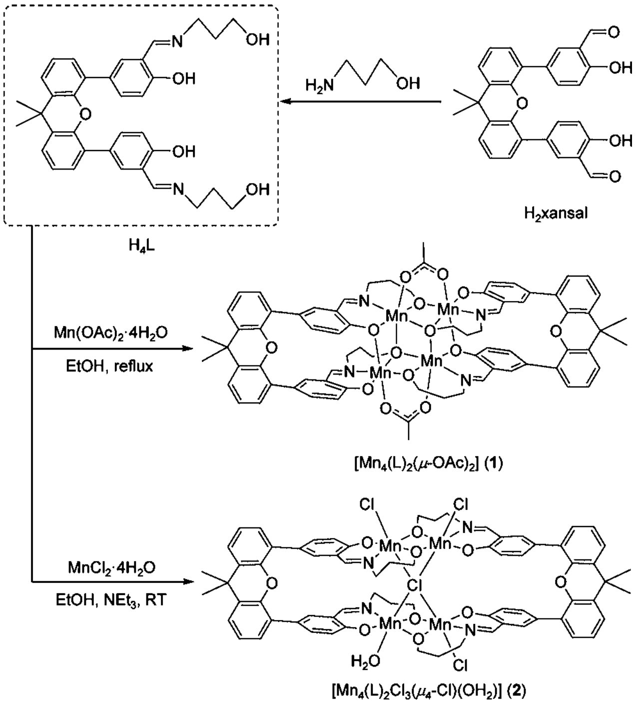
**ABSTRACT:** The reaction of manganese(II) acetate with a xanthene-bridged bis[3-(salicylideneamino)-1-propanol] ligand, $H_4L$, afforded the tetramanganese(II,II,III,III) complex $[Mn_4(L)_2(\mu\text{-OAc})_2]$, which has an incomplete double-cubane structure. The corresponding reaction using manganese(II) chloride in the presence of a base gave the tetramanganese(III,III,III,III) complex $[Mn_4(L)_2Cl_3(\mu_4\text{-Cl})(OH_2)]$, in which four Mn ions are bridged by a $Cl^-$ ion. A pair of L ligands has a propensity to incorporate four Mn ions, the arrangement and oxidation states of which are dependent on the coexistent anions.

Photosynthetic water oxidation is catalyzed by the oxygen-evolving complex (OEC) containing a manganese cluster in photosystem II (PSII). X-ray diffraction studies of PSII revealed that the active site of the OEC has a cubane-like $Mn_3CaO_n$ core bridged to a fourth Mn atom.[1,2] The coexistence of $Cl^-$ ions around the $Mn_4Ca$ cluster plays an important role in water oxidation.[2a] Recently, the crystal structure of PSII was solved at a resolution of 1.9 Å, and the structure of the $Mn_4CaO_5$ cluster with the coordinated amino acid residues was clearly presented.[2b] On the other hand, artificial water oxidation catalysts have been developed using complexes of ruthenium, manganese, and some other transition metals.[3−7] However, it is still important to clarify the mechanisms of water oxidation in PSII by using biomimetic manganese complexes similar to the active site of the OEC.[8]

A variety of tetranuclear manganese clusters were synthesized to model the OEC active site, and their structural, spectroscopic, and magnetic properties were investigated.[8,9g] Furthermore, several manganese−calcium complexes were developed to elucidate the role of $Ca^{2+}$ in the $Mn_4Ca$ cluster.[9,10] Agapie et al. recently reported that a discrete $[Mn_3CaO_4]^{6+}$ core is synthesized on a trinucleating ligand with three N,N,O-tridentate arms.[10] Tetramanganese complexes with an incomplete double-cubane structure of $Mn_4O_6$ are potential starting materials for the model of the OEC active site.[11] The defective site could be occupied by a $Ca^{2+}$ ion to form a $Mn_3CaO_4$ cubane structure binding a fourth Mn ion.

We recently designed 5,5′-(9,9-dimethylxanthene-4,5-diyl)-bis(salicylaldehyde) ($H_2$xansal; Scheme 1) to develop bimetallic Schiff base complex catalysts.[12] The xansal-based Schiff base ligands secure two Mn ions in close proximity. This bimetallic platform is applicable to the tetrametallic one by dimerization. Here we report the synthesis of $Mn_4$ complexes by using a new ligand derived from $H_2$xansal and 3-amino-1-propanol ($H_4L$; Scheme 1). The $Mn_4$ core structures are dependent on the coexistent anions, and the incomplete double-cubane structure was obtained in the presence of acetate anions.

Scheme 1



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The treatment of $H_4L$ with 2 equiv of $Mn(OAc)_2{\cdot}4H_2O$ under reflux in ethanol afforded a moss-green powder. Brown crystals of $[Mn_4(L)_2(\mu\text{-}OAc)_2]$ (**1**), which were suitable for X-ray analysis, were obtained in 36% yield by layering 2-propanol onto a dichloromethane solution of the powder.

The dimeric structure of **1** has a crystallographic inversion center (Figure 1). Four Mn ions are encapsulated by two L and two acetate ligands, and each Mn center is in the O,N,O-tridentate Schiff base. The two $Mn_2(L)$ units are bridged by four alkoxide O atoms and two acetate ions to give the tetranuclear structure of **1**. Two Mn ions in a $Mn_2(L)$ unit are also bridged through a phenolate and an alkoxide O atom to form an incomplete double-cubane structure of $Mn_4O_6$, where Mn1, Mn1*, O4, and O4* are shared by two incomplete cubes. In the equatorial Schiff base plane, bond lengths around Mn1 [Mn1−O1, 2.073(3); Mn1−O2, 2.124(3); Mn1−O4*, 2.234(3); Mn1−N1, 2.202(3) Å] are longer than the corresponding bond lengths around Mn2 [Mn2−O3, 1.868(3); Mn2−O4, 1.947(3); Mn2−O2*, 1.907(3); Mn2−N2, 2.023(3) Å]. In contrast to this, the Mn2−O7* distance of 2.207(3) Å is larger than the Mn1−O6 distance of 2.166(3) Å, which arises from the Jahn−Teller distortion of the $Mn^{3+}$ ion. Therefore, the oxidation states of Mn1 and Mn2 are $Mn^{II}$ and $Mn^{III}$, respectively.

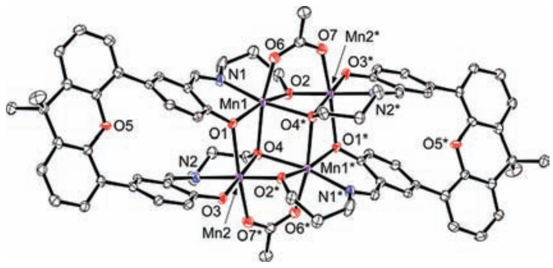

**Figure 1.** ORTEP drawing of **1** with thermal ellipsoids at the 50% probability level. H atoms are omitted for clarity.

Temperature-dependent magnetic susceptibility measurements of **1** were performed in the temperature range 1.7—300 K (Figure S1 in the Supporting Information, SI). The Curie−Weiss law fitting gives $C = 13.71$ cm$^3$ K mol$^{-1}$ and $\theta = -8.9$ K, which indicates weak antiferromagnetic exchange interactions of the mixed-valence $Mn^{II}{}_2Mn^{III}{}_2$ complex. Similar features are observed in $Mn^{III}Mn^{II}Mn^{III}$ complexes containing phenolato, carboxylato, and alkoxo bridges.[13]

To elucidate the effect of the bridging acetate ligands on dimerization, we carried out the reaction of $H_4L$ with 2 equiv of $MnCl_2{\cdot}4H_2O$ in the presence of triethylamine in ethanol under ambient conditions. Dark-brown crystals of $[Mn_4(L)_2Cl_3(\mu_4\text{-}Cl)(OH_2)]$ (**2**) were obtained in 67% yield, and the elemental analysis suggested that one L ligand holds two Mn ions.

A single-crystal X-ray structure analysis of **2** confirmed the dimeric structure consisting of two $Mn_2(L)$ units, in which two Mn atoms are related by a crystallographic $C_2$ axis through Cl3, O6, and O7 (Figure 2). Three of four $Cl^-$ ions are bound to Mn ions as terminal ligands. The central $Cl^-$ ion acts as a bridging ligand connecting four Mn ions. The Mn−Cl(bridging) bond distances are 2.7355(16) and 2.9374(15) Å, which are significantly larger than the Mn−Cl(terminal) distances [2.582(6) and 2.4572(18) Å]. The $Mn_4(L)_2$ macrocycle in **2** shows a helical structure accommodating a $Cl^-$ ion (Figure 2b). This is different from the $C_i$ symmetric structure of **1**, which suggests flexibility of L. The coordination bonds in the Schiff base planes around Mn1 and Mn2 in **2** are similar to those around $Mn^{III}$ ions in **1** and related $Mn^{III}$ complexes.[14] Thus, we deduced that **2** is a $Mn^{III}{}_4$ complex. Magnetic susceptibility data of **2** were analyzed using a model including two dominant interaction pathways, $J$ and $\theta_1$ (Figure S1 in the SI): $J$ denotes the interactions between two $Mn^{III}$ ions bridged by alkoxide O atoms, and $\theta_1$ denotes the intramolecular interaction between the two alkoxo-bridged $Mn^{III}{}_2$ units, which are connected by a $Cl^-$ ion. The parameters were optimized to $J = -24.3$ K ($-16.9$ cm$^{-1}$), and $\theta_1 = -39.9$ K, which show the antiferromagnetic interactions. The $J$ value is similar to that observed for the $Mn^{III}{}_2$ complex of 3-(salicylideneamino)-1-propanol ($H_2L'$), $[Mn_2(L')_2Cl_2(OH_2)_2]$ ($-16.0$ cm$^{-1}$).[14a]

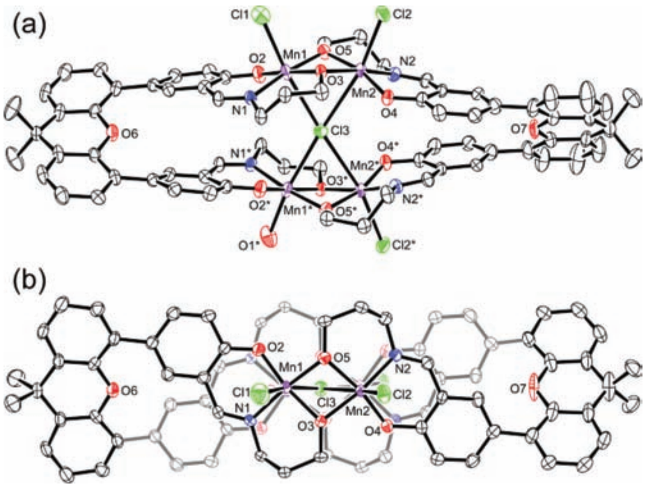

**Figure 2.** ORTEP drawings of **2** with thermal ellipsoids at the 50% probability level: (a) Side and (b) top views. H atoms are omitted for clarity. The Cl1 and O1 atoms are disordered over two positions related by a $C_2$ axis, with equal site occupancy factors.

It is notable that all Mn centers of **2** are in the trivalent state, while **1** has a $Mn^{II}{}_2Mn^{III}{}_2$ mixed-valence state. The reactions of $H_2L'$ with $Mn(OAc)_2{\cdot}4H_2O$ or $MnCl_2{\cdot}4H_2O$ give $Mn^{III}{}_2$ complexes $[Mn_2(L')_2(OAc)_2]$ and $[Mn_2(L')_2Cl_2(CH_3OH)_2]$, respectively.[14] Therefore, the mixed-valence state of **1** stems from the incomplete double-cubane structure directed by the L and acetate ligands.

The electrochemical behavior of **1** and **2** was studied by cyclic voltammetry in $CH_2Cl_2$. Complex **1** exhibits two overlapped one-electron couples at −1.08 V and two quasi-reversible couples at −0.24 and 0.17 V [$E_{1/2}$ vs $E^{\circ\prime}(Fc^{+/0})$; Figure 3]. These couples were assigned to $Mn^{III}{}_2Mn^{II}{}_2/Mn^{II}{}_4$, $Mn^{III}{}_3Mn^{II}/Mn^{III}{}_2Mn^{II}{}_2$, and $Mn^{III}{}_4/Mn^{III}{}_3Mn^{II}$, respectively (see the SI). This suggests that the tetranuclear core structure of **1** is retained in $CH_2Cl_2$. It should be noted that the four Mn ions are bridged by two xanthene backbones as well as six O-donor atoms and two acetate ligands. Complex **2** shows irreversible reduction waves in the range of −1.1 to −0.3 V vs $E^{\circ\prime}(Fc^{+/0})$, which are attributable to the reduction from $Mn^{III}{}_4$ to $Mn^{II}{}_4$ (Figure S3 in the SI).

The electrospray ionization (ESI) mass spectrum of **2** in acetonitrile exhibits the signals for tetrametallic $[Mn_4(L)_2Cl_2]^{2+}$ and $[Mn_4(L)_2Cl_3]^+$ at $m/z$ 705 and 1447, respectively (Figure S7 in the SI). On the other hand, a methanol solution of **2** shows the signal for bimetallic $[Mn_2(L)(OCH_3)]^+$ ($m/z$ 701), suggesting dissociation of the chloride ligands, followed by monomerization (Figure S10 in the SI). The absorption

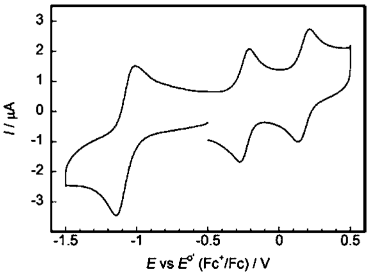

**Figure 3.** Cyclic voltammogram of **1** ($1 \times 10^{-4}$ M) in $CH_2Cl_2$ containing 0.1 M $Bu_4NPF_6$: scan rate, 100 mV $s^{-1}$; working electrode, glassy carbon; auxiliary electrode, platinum wire; reference electrode, Ag/$Ag^+$. Potentials are versus ferrocenium/ferrocene ($Fc^+$/Fc).

spectrum of **2** in methanol gradually changed (Figure S5 in the SI), and the ESI mass spectrum showed new signals of $[Mn_2(L_2H_2)]^+$ and $[Mn_2(L_2H_3)]^+$ (Figure S11 in the SI), which were also observed for a methanol solution of **1** (Figures S8 and S9 in the SI). Thus, **1** and **2** are not stable in methanol.

In conclusion, the xansal-based Schiff base ligand studied here has a propensity to incorporate four Mn ions by dimerization. The structures and oxidation states of the $Mn_4$ core are controlled by the coexistent anions. Acetate ions are effective to construct an incomplete double-cubane structure, but $Cl^-$ ions are not. The synthesis of the OEC model in this tetrametallic platform is currently under investigation, including the introduction of oxo bridges and $Ca^{2+}$ to **1**.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Text, tables, figures, and CIF files giving experimental details and crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: mhiro@sci.osaka-cu.ac.jp.

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