



Preparation, structures and properties of manganese complexes containing amine–(amido or amidato)–phenolato type ligands



Ryoji Mitsuhashi^{a,b}, Rina Ogawa^a, Ryuta Ishikawa^c, Takayoshi Suzuki^{a,d,*}, Yukinari Sunatsuki^a, Satoshi Kawata^c

^a Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan

^b Department of Applied Chemistry for Environment, School of Science and Technology, Kwansai Gakuin University, Sanda, Hyogo 669-1337, Japan

^c Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814-0180, Japan

^d Photosynthesis Research Center, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan

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ABSTRACT

Complexation of 2-hydroxy-*N*-(*n*-aminoalkyl)benzamides, where *n*-aminoalkyl substituents are 2-amino-2-methylpropyl ($H_2L^{Me_2}$), (*R*)-2-aminopropyl $\{(R)-H_2L^{Me}\}$ and 3-aminopropyl (H_2L3), with manganese(II) chloride or perchlorate were examined. With the 2-aminopropyl derivatives, dinuclear methoxido-bridged manganese(III) complexes bearing the dianionic ligands, $\{[Mn(L^{Me_2} \text{ or } (R)-L^{Me})_2(MeOH)]_2(\mu-O)_2\}$ (**2** or **4**), were isolated and their crystal structures were determined. There was a weak antiferromagnetic interaction between two axially distorted Mn^{III} centers in **2**. Also, with the ligand of $(L^{Me_2})^{2-}$ a mononuclear manganese(IV) complex, $[Mn(L^{Me_2})_2] \cdot DMF$ (**3-DMF**) was obtained. In the crystal of **3-DMF** a heterochiral dimerization via the intermolecular double hydrogen-bonds was observed. In the case of reactions with H_2L3 , mononuclear manganese(III) complexes, $[Mn(H_2L3')_2Cl_2]Cl$ (**6**) and $[Mn(H_2L3')_2(MeOH)_2]Cl_2(ClO_4)$ (**7**), were afforded, where the ligand (H_2L3') has a phenolate–amide–ammonium type zwitterionic form of H_2L3 and coordinates to a Mn^{III} center via the phenolato-*O* and amide-*O* atoms to form a six-membered chelate ring. Furthermore, a tetranuclear Mn^{II}₂Mn^{III}₂ double incomplete-cubane type cluster compound, $[Mn_4(HL3)_2Cl_2(OMe)_6(MeOH)_2] \cdot 4MeOH$ (**5a-4MeOH**) was revealed by the single-crystal X-ray diffraction study, although the bulk crystals (**5**) obtained from the reaction mixture showed a different PXRD pattern. The elemental analysis of the bulk crystals of **5** suggested that they consist of the same tetranuclear clusters. It is interesting that the bulk crystals of **5** were highly efflorescent, and it was suggested that their coordinated MeO[−] and MeOH ligands were easily substituted by OH[−] and H₂O, respectively, in atmospheric air. This conversion changed their magnetic behaviors drastically.

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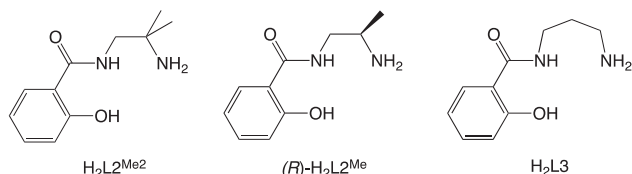
1. Introduction

Multinuclear and high-valent manganese complexes are currently attractive synthetic targets, because such complexes or clusters often exist in active sites of biological metalloenzymes [1–9]. For example, a number of chemists worldwide are challenging to prepare the Mn₄CaO₅ cluster which was found in the active site of oxygen evolving complex (OEC) of photosystem II (PSII) [10–12]. In addition, mixed-valent manganese clusters are another topical motif because of their behaviors of single-molecule magnets [13–15]. In order to prepare such multi-valent and/or

multinuclear manganese clusters, a variety of ligands are designed. In particular, multidentate Schiff bases containing amine or hydroxyl subunits are utilized successfully [16–23]. We are focusing on similar amidate (i.e., deprotonated amide)-containing ligands, because the amidates can coordinate via both the *N* and *O* atoms, dependent on the substituent groups. Also, because the amidate-*N* or -*O* donor has a strong σ - and π -donicity, it can stabilize a high-valent state of the coordinated metal ions [24–28]. However, synthetic studies of manganese complexes with amidate-containing ligands are relatively rare. Tuchagues et al. reported bis(2-hydroxybenzamide)-bridged dinuclear Mn^{III} complexes [24]. In a previous paper, we have reported the syntheses, crystal structures and spectroscopic properties of cobalt(III) complexes with a series of amine–amidato–phenolato type tridentate ligands [28]. In this study, complexation of 2-hydroxy-*N*-(*n*-aminoalkyl)

* Corresponding author at: Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan.

E-mail address: suzuki@okayama-u.ac.jp (T. Suzuki).



Scheme 1. Ligand precursors used in this study and their abbreviations.

benzamides (**Scheme 1**), where *n*-aminoalkyl substituents are 2-amino-2-methylpropyl ($H_2L_2^{Me_2}$), (*R*)-2-aminopropyl $\{(R)-H_2L_2^{Me}\}$ and 3-aminopropyl (H_2L_3), with manganese(II) chloride or perchlorate were examined, and the structures and magnetic properties of the resulting complexes were reported.

2. Results and discussion

2.1. Preparation and structural characterization of manganese complexes with $H_2L_2^{Me_2}$

A reaction of $MnCl_2 \cdot 4H_2O$ and $H_2L_2^{Me_2}$ in methanol in the presence of two equivalent amounts of NEt_3 gave a formation of greenish brown precipitate (**1**) (**Scheme 2**). Elemental analysis of **1** (Found: C, 43.77; H, 5.93; N, 8.61%) indicated that its composition was $MnCl(L_2^{Me_2})(MeOH)$ (Calc. for $C_{12}H_{18}ClMnN_2O_3$: C, 43.85; H, 5.52; N, 8.52), which suggested the oxidation of the Mn center to Mn^{III} during the reaction. Even if excess amounts of $H_2L_2^{Me_2}$ and NEt_3 were employed in the reaction, the same product was precipitated, owing probably to a poor solubility of **1** in methanol. The molecular structure of **1** could not be determined, because it was hardly soluble in common organic solvents, except for *N,N*-dimethylformamide (DMF).

From a solution of **1** in DMF the Mn^{III} complex was attempted to be recrystallized by slow diffusion of layered methanol, and brown block-shaped crystals were deposited after a week. X-ray analysis (**Table S1**) of these crystals revealed that they consisted of a methoxido-bridged Mn^{III} dinuclear complex (**2**) containing a doubly deprotonated amine–amidato–phenolato type ligand, $(L_2^{Me_2})^{2-}$. The dinuclear unit has a crystallographically imposed center of symmetry, and there are two halves of such dinuclear complexes in the asymmetric unit of triclinic crystal lattice

with a space group $P\bar{1}$. There are no remarkable structural differences between two crystallographically independent $\{[Mn(L_2^{Me_2})(MeOH)]_2(\mu-O_2Me)_2\}$ molecules, and the molecular structure of one of the two dimers in **2** is depicted in **Fig. 1**. The ligand, $(L_2^{Me_2})^{2-}$, acts as a tridentate ligand via the phenolato-O, amidato-N, and amine-N atoms and coordinates to a Mn^{III} center in a meridional configuration. Two mutually *cis*-positioned methoxido ligands bridge two Mn centers to form a planar Mn_2O_2 core; however, this core is rhomboidal as the $Mn1-O3^*$ ($Mn2-O7^*$) bond is significantly longer than the $Mn1-O3$ ($Mn2-O7$) bond (see **Table S2**). The $Mn1-O4$ ($Mn2-O8$) bond of MeOH ligand is further long, which might result from the Jahn–Teller effect of high-spin Mn^{III} ion. The OH group of coordinating methanol molecule and the *cis*-positioned amino ($-NH_2$) group of $(L_2^{Me_2})^{2-}$ are hydrogen-bonded to the amidato-O atom of the neighboring molecule

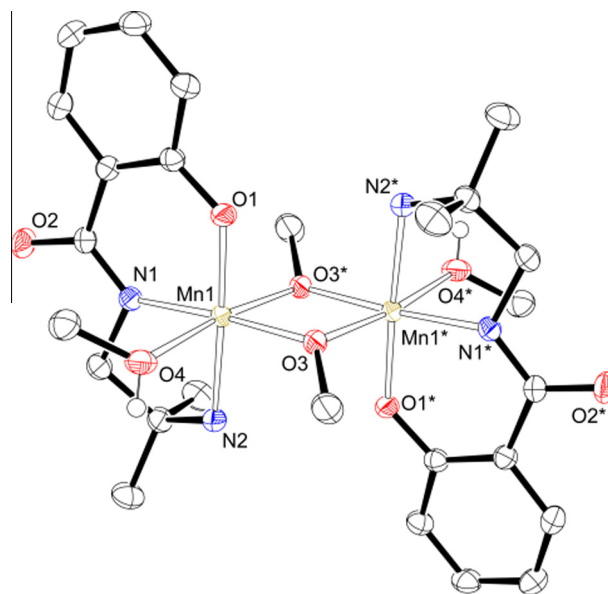
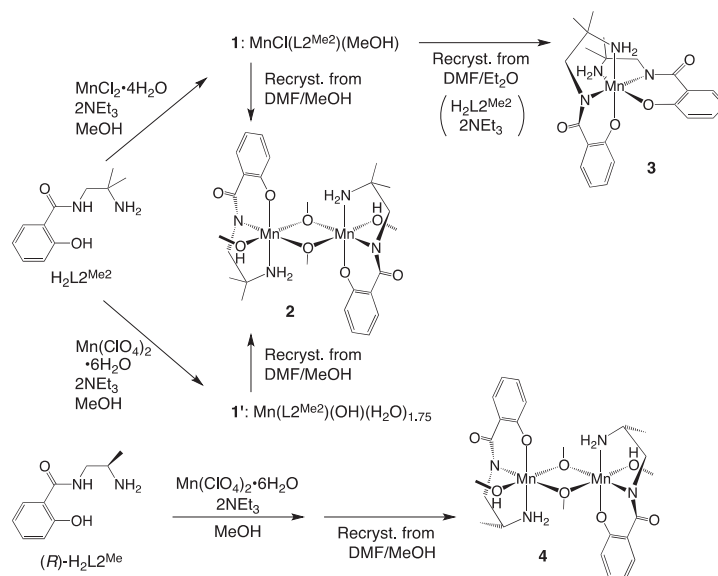


Fig. 1. An ORTEP (50% probability level, H-atoms omitted except for the hydroxo-H of the MeOH) of one of two crystallographically independent $\{[Mn(L_2^{Me_2})(MeOH)]_2(\mu-O_2Me)_2\}$ molecules in **2**.



Scheme 2. Preparation of manganese complexes with $H_2L_2^{Me_2}$ or (*R*)- $H_2L_2^{Me}$.

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