Efficient Formation of Homo and Hetero Metal Clusters by Triangular Trisaloph Ligand as a Partial Template

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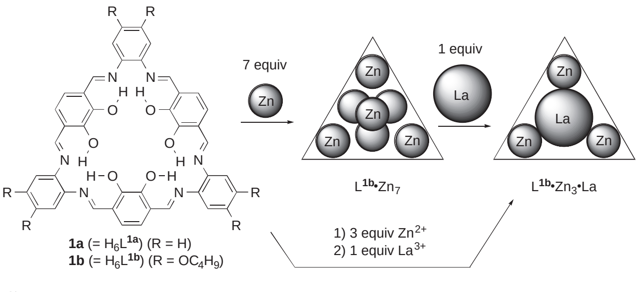
Homo metal cluster containing seven Zn atoms was efficiently synthesized in high yield via a template effect of a trisaloph ligand and characterized by NMR, MS, X-ray crystallography, etc. The homo cluster can be converted quantitatively to $Zn_3 \cdot La$ hetero metal cluster.

Template synthesis[1] is considerably useful for macrocyclization, specific coupling, and self-replication.[2] Conformation of molecules engaged in the reactions is significantly frozen by the template.

Metal clusters containing organic ligands exhibit various functions and properties such as catalytic activity, ferromagnetism, etc.[3] Simple reactions of metal ions with suitable ligands yield these metal clusters, although structures of the clusters are often unpredictable. Regulation of the cluster size and the number of the metal ions in the clusters has been very difficult, but this regulation is necessary to obtain sophisticated materials. Usual template strategy seems useless for the cluster synthesis because a large cluster would require a much larger template, which is hard to prepare. To design interacting sites of the template with certain sites of the metal atoms in the cluster would be very difficult.

We, however, conceived the idea that combination of templating and spontaneous assembling of chemical species may lead to desired, well-organized clusters. In this strategy, a relatively large template binds and arranges several metal ions to give a metal assembled field, which initiates spontaneous assembling of more metal ions to give the final template-assisted cluster.

We reported the first synthesis and X-ray characterization of the parent trisaloph **1a** (H_6L^{1a})[4] and analogues[5] because versatile functions of these compounds were expected. The central cavity in **1** provides three metal-binding sites, and the metal complexes would possess a recognition site for additional metal via the negatively charged phenolate groups. Here, we describe efficient partial-template syntheses of metal clusters consisting several metal atoms (seven Zn,[6] seven Mn, and six Ni atoms) by using triangular trisaloph template **1b** (H_6L^{1b}). Interestingly, the Zn cluster, $L^{1b} \cdot Zn_7$, is easily converted to hetero metal cluster $L^{1b} \cdot Zn_3 \cdot La$. These types of hetero clusters are expected to provide various functions.[7] This new strategy will open a novel way to design and synthesize a family of highly organized metal clusters (Scheme 1).



Scheme 1. Formation of homo and hetero metal clusters by **1**.

Trisaloph ligand **1b** was prepared in 94% yield by treatment of 2,3-dihydroxybenzene-1,4-dicarbaldehyde with 4,5-dibutoxybenzene-1,2-diamine in $CHCl_3$–CH_3CN (1:1) at room temperature. **1b** reacted with $Zn(OAc)_2 \cdot 2H_2O$ very readily at room temperature to give **1b**•Zn complexes. A red solution of **1b** in $CHCl_3$ immediately turned to a deeper red solution by the addition of 3 equiv of $Zn(OAc)_2 \cdot 2H_2O$ in CH_3OH and then to a paler solution by more Zn. In the absorption spectra of **1b**, bathochromic shift (to 417 nm) of λ_{max} at 403 nm of free **1b** occurred up to 3 equiv of Zn. More Zn caused increase of the absorption of λ_{max} at 417 nm without change of the wavelength. During the titration experiment no isosbestic points were observed. These facts indicate that intermediary oligo–Zn complexes were formed. ^{1}H NMR titration for the complexation in $CDCl_3$–CD_3OD (9:1) clearly showed the formation of the Zn complexes as shown in Figure 1b. Although very broad signals were observed in the presence of 3 equiv of Zn, a simple and sharp spectrum was obtained in the presence of 7 equiv of Zn, suggesting formation of a homo Zn_7 complex ($L^{1b} \cdot Zn_7$). Noteworthy is that the $-OCH_2-$ protons appeared as an ABX pattern. ESI mass spectrum (1909.0: $[L^{1b} \cdot Zn_7O(OAc)_5]^+$, 925.0: $[L^{1b} \cdot Zn_7O(OAc)_4]^{2+}$) also supported the formation of the $L^{1b} \cdot Zn_7$ complex bearing one oxygen atom in the cluster structure. The pure complex $L^{1b} \cdot Zn_7$ was easily obtained in 98% by reaction of **1b** in $CHCl_3$ and 7 equiv of $Zn(OAc)_2 \cdot 2H_2O$ in MeOH for 1 h at room temperature. Elemental analysis strongly suggested that the complex has seven Zn atoms, six acetate groups and one oxygen atom in the cluster. ^{1}H and ^{13}C NMR spectra of the pure $L^{1b} \cdot Zn_7$ in $CDCl_3$ indicate C_{3v} symmetry of $L^{1b} \cdot Zn_7$ bearing two kinds of acetate groups (Figure 1a). Reddish orange

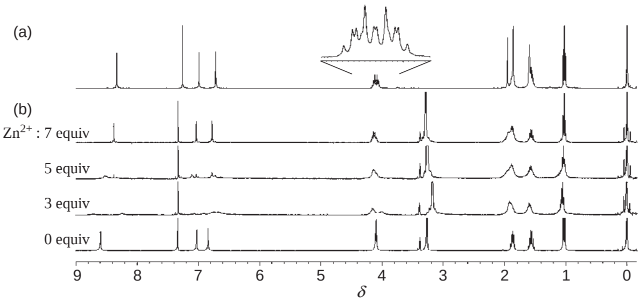


Figure 1. (a) ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of $L^{1b} \cdot Zn_7(O)(OAc)_6$, (b) ^{1}H NMR spectra (400 MHz, $CDCl_3$–CD_3OD (9:1)) of **1b** in the presence of $Zn(OAc)_2 \cdot 2H_2O$.

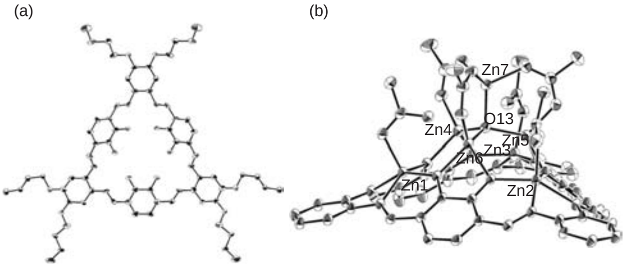


Figure 2. X-ray structures of (a) **1b** and (b) $L^{1b}\cdot Zn_7(O)(OAc)_6$. The ^{n}BuO groups are omitted for clarity.

single crystals were furnished by recrystallization from THF–AcOEt.

The crystal structure of the heptanuclear complex $L^{1b}\cdot Zn_7$ was determined by X-ray crystallography (Figure 2b).[8,9] L^{1b} adopts a bowl-shaped conformation, which is considerably deformed from the planer structure of the free ligand **1b** (Figure 2a).[8,9] Three of the seven zinc atoms (Zn1, Zn2, and Zn3) sit in the N_2O_2 sites of L^{1b}. In addition, L^{1b} acts as a cyclic tris(catechol) ligand. Each catecholato moiety coordinates to a Zn atom (Zn4, Zn5, and Zn6). In the center of the complex, there is an oxygen atom (μ_4-oxo, O13) coordinating to the three zinc atoms (Zn4, Zn5, and Zn6) at the catecholate moieties and the seventh one (Zn7). Thus, a $Zn_4(\mu_4\text{-}O)$ tetrahedral core[10] is formed on the convex part of the bowl-shaped structure. It is noteworthy that all the six acetato ligands present on the convex side of the bowl nicely enclose the $Zn_4(\mu_4\text{-}O)$ tetrahedral core.

We also employed other metal ions to produce such metal clusters. Mn cluster with **1b** was also prepared in 97% yield by the treatment of **1b** with 7 equiv of $Mn(OAc)_2\cdot 4H_2O$ at room temperature. Elemental analysis and ESI MS strongly supported a similar molecular constitution of the Mn_7 cluster to that of $L^{1b}\cdot Zn_7$. In case of Ni, however, ESI mass spectrometry implied that excess $Ni(OAc)_2\cdot 4H_2O$ caused formation of Ni_6 cluster instead of Ni_7 one.

Very interestingly, the $L^{1b}\cdot Zn_7$ cluster can be smoothly converted to a heteronuclear metal cluster[11] at room temperature. New signals in ^{1}H NMR spectrum of $L^{1b}\cdot Zn_7$ ($CDCl_3$–CD_3OD (9:1)) appeared on addition of 1 equiv of $La(OAc)_3\cdot 1.5H_2O$ to a solution of $L^{1b}\cdot Zn_7$. The integrals of the resonances suggest that $L^{1b}\cdot Zn_7$ changed quantitatively to the new complex. Peaks (767.1: $[L^{1b}\cdot Zn_3\cdot La(OAc)]^{2+}$) in ESI mass spectra of the mixture are assigned to $L^{1b}\cdot Zn_3\cdot La$ as a hetero metal cluster. It is worthwhile to point out that intense signals in the mass spectrum were observed for the dimer of $L^{1b}\cdot Zn_3\cdot La$ (1594.2: $[(L^{1b}\cdot Zn_3\cdot La)_2(OAc)_4]^{2+}$, 1043.1: $[(L^{1b}\cdot Zn_3\cdot La)_2(OAc)_3]^{3+}$) and weak signals for trimer and tetramer. Smaller peaks which can be ascribed to other oligomers appeared concomitantly. This oligomerization, which is fascinating in respect of supramolecular chemistry, is presumably due to more planar structure of the hetero cluster than that of $L^{1b}\cdot Zn_7$. In contrast, ^{1}H NMR spectroscopy indicated that a mixture of **1b** and Zn (3 equiv) smoothly and quantitatively changed into $L^{1b}\cdot Zn_3\cdot La$ by the addition of 1 equiv of La (Figure 3). Mixing of **1b** with $Zn(OAc)_2\cdot 2H_2O$ (3 equiv) and $La(OAc)_3\cdot 1.5H_2O$ (1 equiv) in $CHCl_3$–CH_3OH–H_2O at room temperature immediately produced $L^{1b}\cdot Zn_3\cdot La$, which was obtained as dark red crystals in 91% yield by reprecipitation. Elemental analysis confirmed the formation of $L^{1b}\cdot Zn_3\cdot La$.

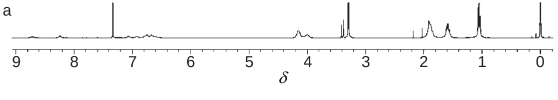


Figure 3. ^{1}H NMR spectra (400 MHz, $CDCl_3$–CD_3OD (9:1)) of **1b** in the presence of Zn^{2+} (3 equiv) and La^{3+} (a, 0 equiv; b, 1 equiv).

We also examined exchange of the acetato ligands in $L^{1b}\cdot Zn_7$ by other carboxylic acids. ^{1}H NMR and ESI mass spectroscopy indicated that all the acetate groups bound to the Zn atoms in $L^{1b}\cdot Zn_7$ were completely replaced by the addition of excess amount of propionic acids. This ligand exchange is interesting and probably useful to construct organic–inorganic supramolecular architectures containing metal clusters on the partial template molecule **1**.

We are now investigating detailed structures and properties of Mn and Ni homo metal clusters and various hetero metal clusters with **1**.

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