

# Multi-metal complexation and partially templated synthesis of metal clusters by using triangular trisaloph ligands

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**Abstract**—On the basis of the concept of partial template, triangular trisaloph ligands **2a** and **2b** reacted with excess Zn<sup>II</sup> to give heptanuclear Zn clusters with a similar geometry. The Zn complex of **2c**, which was difficult to be prepared according to a previous procedure, was synthesized in high yield in a one-pot fashion. Various multi-nuclear complexes of **2a** with Mn, Co, Ni, and Cu were also produced, although the trinuclear Mn<sup>II</sup> and Co<sup>II</sup> complexes were smoothly oxidized to the Mn<sup>III</sup> and Co<sup>III</sup> complexes.

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## 1. Introduction

Template syntheses<sup>1</sup> have been frequently employed for macro-cyclization, specific coupling, and self-replication.<sup>2</sup> The template assembles and orients reactants and/or intermediates of the reactions to afford the desired product. Conformation of the molecules, which are engaged in the reaction is significantly frozen by the template to reduce entropic loss in the transition state. Consequently, the reaction is forced to proceed along the pathway to the product.

Multi-metal complexes and metal clusters exhibit various functions and properties such as catalytic activity, ferromagnetism, etc.<sup>3</sup> In particular, the clusters are usually prepared by simply mixing the metal ions and suitable ligands, but the cluster structure is often unpredictable. Regulation of the cluster size and the number of the metal ions in the cluster have been difficult. The size regulation, however, is necessary to obtain sophisticated materials because functions of the clusters depend on the size and the number of the metals. For the cluster synthesis, usual template strategy seems to be laborious, since a large cluster would require a much larger template, which is hard to prepare. In addition, to design metal-interacting sites of the template would be very difficult because appropriate placement of the sites for cluster formation is also inevitable for the template synthesis.

We, however, conceived the idea that combination of a template and spontaneous assembling of metals may lead to desired and well-organized clusters. Similar phenomena occur in protein folding assisted by molecular chaperons. In this strategy a relatively large template captures and arranges some metal ions to produce a metal assembled field, which initiates spontaneous assembling of more metal ions to give the final template-assisted clusters. Furthermore, this way would be applicable to preparation of functional multi-metal complexes.

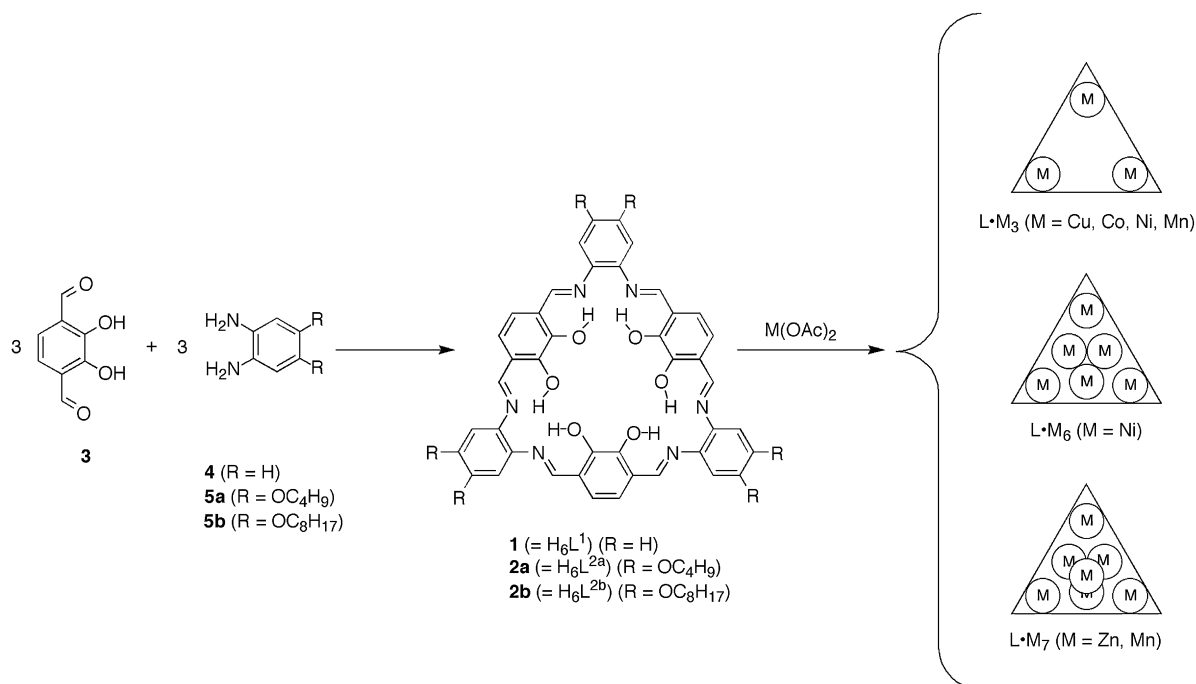
We reported the first synthesis and X-ray characterization of the parent trisaloph **1** (H<sub>6</sub>L<sup>1</sup>)<sup>4</sup> and analogues<sup>5</sup> because versatile functions of these compounds were expected. The central cavity in **1** provides three metal binding sites (Scheme 1) and the metal complexes would possess a recognition site for additional metal via the negatively charged phenolate groups. We preliminarily reported preparation and characterization of a heptanuclear Zn cluster<sup>6</sup> on the basis of the concept of the partial template. Here we describe metal binding properties of trisaloph ligands **2** toward Zn, Mn, Co, Ni, and Cu, and convenient synthesis of multi-homometal complexes by using **2**. We have also found one-pot and high-yield formation of the trisaloph-containing metal cluster from the metal ions and starting materials for the preparation of the ligands.

## 2. Results and discussion

Ligand **2b** was prepared in 87% yield by the reaction of **3** with **5b** at room temperature according to a procedure similar to that for **2a**. Compounds **2a** and **2b** reacted with

*Keywords:* Multi-metal complex; Template synthesis; Metal clusters; Saloph ligand.

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Scheme 1.

$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  very readily at room temperature to afford dark red Zn complexes. Red solutions of **2a** and **2b** in  $\text{CHCl}_3$  turned deeper by the addition of 3 equiv of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in  $\text{CH}_3\text{OH}$  and then to paler solutions by more Zn. Significant UV–vis spectral changes ( $\text{CHCl}_3$ – $\text{MeOH}=1:1$ ) of the solutions were observed upon the complexation (Fig. 1). Up to 3 equiv of  $\text{Zn}^{\text{II}}$ ,  $\lambda_{\text{max}}$  of **2a** at 403 nm shifted to 417 nm (for **2b**, 397 nm to 417 nm). Over 3 equiv of  $\text{Zn}^{\text{II}}$  bathochromic shift did not occur but the absorption increased until 6–7 equiv of  $\text{Zn}^{\text{II}}$ . These results indicate the initial formation of the trinuclear Zn complexes of **2a** and **2b** and successive complexation with more  $\text{Zn}^{\text{II}}$ . In the ESI mass spectroscopy, signals which are assigned to the trinuclear complexes were detected in the presence of 3 equiv of  $\text{Zn}^{\text{II}}$  but no signals for higher multi-nuclear complexes of **2a** (Table 1) and **2b**. In contrast, intense signals for the hexa- and heptanuclear complexes (Table 1, 864.0:  $[\text{L}^{2a} \cdot \text{Zn}_6(\text{OH})(\text{OAc})_3]^{2+}$ , 555.7:  $[\text{L}^{2a} \cdot \text{Zn}_6(\text{OH})(\text{OAc})_2]^{3+}$ ,

1909.0:  $[\text{L}^{2a} \cdot \text{Zn}_7\text{O}(\text{OAc})_5]^+$ , 926.0:  $[\text{L}^{2a} \cdot \text{Zn}_7\text{O}(\text{OAc})_4]^{2+}$ ) appeared in the presence of 10 equiv of  $\text{Zn}^{\text{II}}$ , although incorporation of one oxygen atom in the cluster structure was suggested. Thus, the UV–vis titration and ESI-MS examination implied formation of the hexa- and heptanuclear Zn complexes of **2a** and **2b**. In **2a** and **2b**, similar spectral changes in  $^1\text{H}$  NMR in  $\text{CDCl}_3$ – $\text{CD}_3\text{OD}$  (9:1) were observed upon complexation with  $\text{Zn}^{\text{II}}$  (Fig. 2 for **2b**). Very broad resonances of **2a** and **2b** in the presence of 3 equiv of  $\text{Zn}^{\text{II}}$  did not elucidate the complex structure, but the simple and sharp spectra in the presence of 7 equiv of Zn suggested the formation of homo  $\text{Zn}_7$  complexes (Fig. 2). As seen in **2a**, the  $-\text{OCH}_2-$  protons of **2b** appeared as an  $\text{ABX}_2$  pattern.

The  $\text{Zn}_7$  complexes of **2a** and **2b** were synthesized in 91% and 71% yield by reaction of **2a** and **2b** in  $\text{CHCl}_3$  with 7 equiv of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in  $\text{MeOH}$  for 1 h and 15 min, respectively, at room temperature. Elemental analysis showed that the complexes have seven Zn atoms, six acetate groups, and one oxygen atom in the heptanuclear complexes.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{L}^{2a} \cdot \text{Zn}_7$  and  $\text{L}^{2b} \cdot \text{Zn}_7$  in  $\text{CDCl}_3$  also indicate that the complexes have two kinds of acetate groups ( $^1\text{H}$  NMR: 1.86 and 1.95 ppm for both complexes,  $^{13}\text{C}$  NMR: 21.7, 178.9, and 23.5, 180.2 ppm for  $\text{L}^{2a} \cdot \text{Zn}_7$  and  $\text{L}^{2b} \cdot \text{Zn}_7$ , respectively). The NMR data obtained here indicate  $C_{3v}$  symmetry of  $\text{L}^{2a} \cdot \text{Zn}_7$  and  $\text{L}^{2b} \cdot \text{Zn}_7$  bearing two kinds of acetate groups. X-ray crystallographic analysis of  $\text{L}^{2a} \cdot \text{Zn}_7$  clearly elucidated the above spectroscopic behavior (Fig. 3).<sup>6b</sup> Upon complexation a bowl-shaped structure is formed because the coordination to the Zn ions deforms the original plane of  $\text{L}^{2a}$ . It is noteworthy that all the six acetate ligands present on the convex side of the bowl nicely enclose the  $\text{Zn}_4(\mu_4\text{-O})$  tetrahedral core. Although the X-ray structure of  $\text{L}^{2b} \cdot \text{Zn}_7$  was not figured out, the spectral

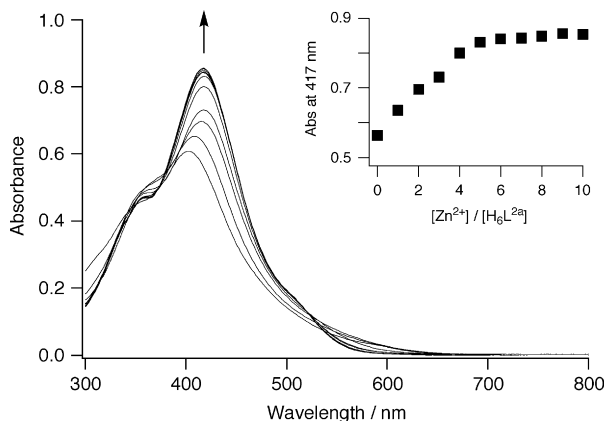


Figure 1. UV–vis spectral changes of ligand **2a** in  $\text{CHCl}_3$ – $\text{CH}_3\text{OH}$  (1:1) upon addition of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .  $[\mathbf{2a}] = 1.0 \times 10^{-5}$  M.

**Table 1.** Oligonuclear complexes of **2a** detected by ESI mass measurements

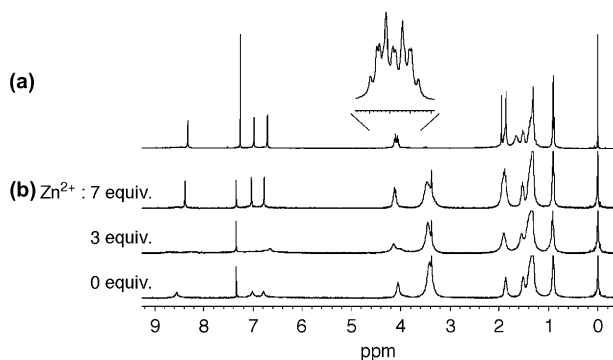
Metal salt	Mass peaks ( <i>m/z</i> )			
	In the presence of 3 equiv		In the presence of 10 equiv	
Zn(OAc) <sub>2</sub>	680.1	[L <sup>2a</sup> ·Zn <sub>3</sub> <sup>II</sup> ·NaH] <sup>2+</sup>	555.7	[L <sup>2a</sup> ·Zn <sub>6</sub> <sup>II</sup> (OH)(OAc) <sub>2</sub> ] <sup>3+</sup>
	688.1	[L <sup>2a</sup> ·Zn <sub>3</sub> <sup>II</sup> ·Ca] <sup>2+</sup>	772.1	[L <sup>2a</sup> ·Zn <sub>5</sub> <sup>II</sup> (OH)(OAc)] <sup>2+</sup>
	701.1	[L <sup>2a</sup> ·Zn <sub>4</sub> <sup>II</sup> ] <sup>2+</sup>	864.0	[L <sup>2a</sup> ·Zn <sub>6</sub> <sup>II</sup> (OH)(OAc) <sub>3</sub> ] <sup>2+</sup>
	1359.2	[(L <sup>2a</sup> ·Zn <sub>3</sub> <sup>II</sup> ·Na) <sub>3</sub> ] <sup>3+</sup>	926.0	[L <sup>2a</sup> ·Zn <sub>7</sub> <sup>II</sup> (O)(OAc) <sub>4</sub> ] <sup>2+</sup>
			1909.0	[L <sup>2a</sup> ·Zn <sub>7</sub> <sup>II</sup> (O)(OAc) <sub>5</sub> ] <sup>+</sup>
Mn(OAc) <sub>2</sub>	435.1	[L <sup>2a</sup> ·Mn <sub>3</sub> <sup>III</sup> ] <sup>3+</sup>	539.7	[L <sup>2a</sup> ·Mn <sub>6</sub> <sup>II</sup> (OCH <sub>3</sub> )(OAc) <sub>2</sub> ] <sup>3+</sup>
	462.4	[L <sup>2a</sup> ·Mn <sub>3</sub> <sup>III</sup> ·Na(OAc)] <sup>3+</sup>	545.7	[L <sup>2a</sup> ·Mn <sub>6</sub> <sup>II</sup> (OCH <sub>3</sub> )(OAc) <sub>2</sub> (H <sub>2</sub> O)] <sup>3+</sup>
	682.1	[L <sup>2a</sup> ·Mn <sub>3</sub> <sup>III</sup> ·(OAc)] <sup>2+</sup>	550.1	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OCH <sub>3</sub> ) <sub>2</sub> (OAc) <sub>2</sub> ] <sup>3+</sup>
	709.1	[L <sup>2a</sup> ·Mn <sub>3</sub> <sup>III</sup> ·Na(OAc)(OCH <sub>3</sub> )] <sup>2+</sup>	565.4	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OCH <sub>3</sub> )(OAc) <sub>3</sub> (H <sub>2</sub> O)] <sup>3+</sup>
	723.1	[L <sup>2a</sup> ·Mn <sub>3</sub> <sup>III</sup> ·Na(OAc) <sub>2</sub> ] <sup>2+</sup>	819.6	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OH) <sub>3</sub> (OAc) <sub>2</sub> ] <sup>2+</sup>
			826.6	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OH) <sub>2</sub> (OCH <sub>3</sub> )(OAc) <sub>2</sub> ] <sup>2+</sup>
			833.6	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OH)(OCH <sub>3</sub> ) <sub>2</sub> (OAc) <sub>2</sub> ] <sup>2+</sup>
			840.6	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OH) <sub>2</sub> (OAc) <sub>3</sub> ] <sup>2+</sup>
			847.6	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OH)(OCH <sub>3</sub> )(OAc) <sub>3</sub> ] <sup>2+</sup>
			861.6	[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>5</sub> <sup>II</sup> (OH)(OAc) <sub>4</sub> ] <sup>2+</sup>
918.1			[L <sup>2a</sup> ·Mn <sup>III</sup> Mn <sub>6</sub> <sup>II</sup> (O)(OAc) <sub>5</sub> ] <sup>2+</sup>	
1723.2			[L <sup>2a</sup> ·Mn <sub>6</sub> <sup>II</sup> (OH)(OAc) <sub>4</sub> ] <sup>+</sup>	
Ni(OAc) <sub>2</sub>	1339.8	[(L <sup>2a</sup> ·Ni <sub>3</sub> <sup>II</sup> ·Na) <sub>2</sub> ] <sup>2+</sup>	822.1	[L <sup>2a</sup> ·Ni <sub>6</sub> <sup>II</sup> (OH) <sub>2</sub> (OAc) <sub>2</sub> ] <sup>2+</sup>
			1339.8	[(L <sup>2a</sup> ·Ni <sub>3</sub> <sup>II</sup> ·Na) <sub>2</sub> ] <sup>2+</sup>
Cu(OAc) <sub>2</sub>	685.7	[L <sup>2a</sup> ·Cu <sub>3</sub> <sup>II</sup> ·Ca] <sup>2+</sup>	1354.4	[(L <sup>2a</sup> ·Cu <sub>3</sub> <sup>II</sup> ·Na) <sub>2</sub> ] <sup>2+</sup>
	908.6	[(L <sup>2a</sup> ·Cu <sub>3</sub> <sup>II</sup> ) <sub>2</sub> ·CaNa] <sup>3+</sup>		
	1354.4	[L <sup>2a</sup> ·Cu <sub>3</sub> <sup>II</sup> ·Na] <sup>+</sup> [(L <sup>2a</sup> ·Cu <sub>3</sub> <sup>II</sup> ·Na) <sub>2</sub> ] <sup>2+</sup>		
Co(OAc) <sub>2</sub>	446.7	[L <sup>2a</sup> ·Co <sub>2</sub> <sup>III</sup> Co <sup>II</sup> Na] <sup>3+</sup>	446.7	[L <sup>2a</sup> ·Co <sub>2</sub> <sup>III</sup> Co <sup>II</sup> ·Na] <sup>3+</sup>
	466.4	[L <sup>2a</sup> ·Co <sub>3</sub> <sup>III</sup> ·Na(OAc)] <sup>3+</sup>	466.4	[L <sup>2a</sup> ·Co <sub>3</sub> <sup>III</sup> ·Na(OAc)] <sup>3+</sup>
	670.1	[L <sup>2a</sup> ·Co <sup>III</sup> Co <sub>2</sub> <sup>II</sup> Na] <sup>2+</sup>	670.1	[L <sup>2a</sup> ·Co <sup>III</sup> Co <sub>2</sub> <sup>II</sup> ·Na] <sup>2+</sup>
	1340.3	[L <sup>2a</sup> ·Co <sub>3</sub> <sup>III</sup> Na] <sup>+</sup>	699.7	[L <sup>2a</sup> ·Co <sub>2</sub> <sup>III</sup> Co <sup>II</sup> ·Na(OAc)] <sup>2+</sup>
			729.2	[L <sup>2a</sup> ·Co <sub>3</sub> <sup>III</sup> ·Na(OAc) <sub>2</sub> ] <sup>2+</sup>
		1340.3	[L <sup>2a</sup> ·Co <sub>3</sub> <sup>III</sup> ·Na] <sup>+</sup>	
		1399.3	[L <sup>2a</sup> ·Co <sup>III</sup> Co <sub>2</sub> <sup>II</sup> ·Na(OAc)] <sup>+</sup>	

similarity observed in L<sup>2b</sup>·Zn<sub>7</sub> strongly supports that L<sup>2b</sup>·Zn<sub>7</sub> has nearly the same structure as that of L<sup>2a</sup>·Zn<sub>7</sub>.

Compared to **2a** and **2b**, **2c** bearing longer dodecyloxy chains was prepared in much lower yield,<sup>5c</sup> although we also examined various reaction conditions for the cyclization of dialdehyde **3** and catechol derivative **5c**. Surprisingly, L<sup>2c</sup>·Zn<sub>7</sub> was successfully obtained in high yield in a one-pot fashion. When Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, **3**, and **5c** were mixed in the ratio of 7:3:3, L<sup>2c</sup>·Zn<sub>7</sub> was obtained in 87% yield (Scheme 2). In a similar way, L<sup>2a</sup>·Zn<sub>7</sub> was prepared in 80%. High dilution

condition was not necessary for this one-pot reaction. This metal-assisted procedure may be applicable to many other analogues with other kinds of side chains.

Compound **2a** also readily reacts with Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O to give multi-nuclear complexes. UV–vis spectroscopy supported that a trinuclear Mn complex of **2a** was initially formed in the presence of 3 equiv of Mn<sup>II</sup>. The absorbance of λ<sub>max</sub> at 403 nm decreased with ca. 3 equiv. and then increased with a bathochromic shift. When a small amount of O<sub>2</sub> was contained, the spectral change indicated formation of an oligo-Mn complex but the change was complicated due to autooxidation of Mn<sup>II</sup> to Mn<sup>III</sup>. Under aerobic conditions the spectrum of **2a** in the presence of 3 equiv of Mn<sup>II</sup> smoothly changed with significant increase of absorption in the region of longer wavelength (450–650 nm) indicating oxidation of Mn<sup>II</sup> to Mn<sup>III</sup>. The spectra of the Mn complex after complete oxidation are shown in Figure 4. Parent saloph–Mn<sup>II</sup> is rapidly oxidized to the corresponding Mn<sup>III</sup> complex, which has characteristic absorption at longer wavelength than the Mn<sup>II</sup> species.<sup>7</sup> Under anaerobic conditions the spectrum of **2a** in the presence of 3 equiv of Mn<sup>II</sup> did not change, but addition of O<sub>2</sub> into the solution resulted in nearly the same spectrum as that observed under aerobic conditions. On the other hand, only very small change was observed in the spectrum obtained in the presence of 10 equiv of Mn<sup>II</sup>, even if the mixture of **2a** and Mn<sup>II</sup> was allowed to stand overnight under aerobic conditions. The ESI



**Figure 2.** (a) <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of L<sup>2b</sup>·Zn<sub>7</sub>(O)(OAc)<sub>6</sub>, (b) <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>–CD<sub>3</sub>OD (9:1)) of **2b** in the presence of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O.

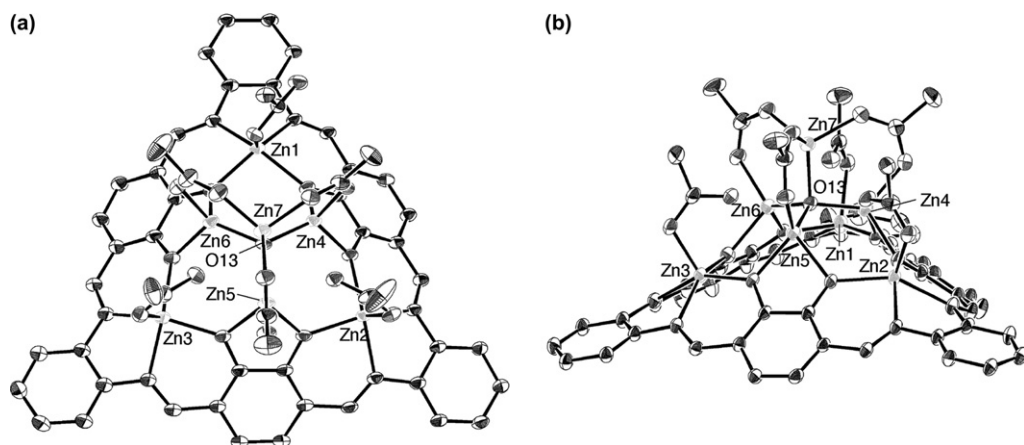
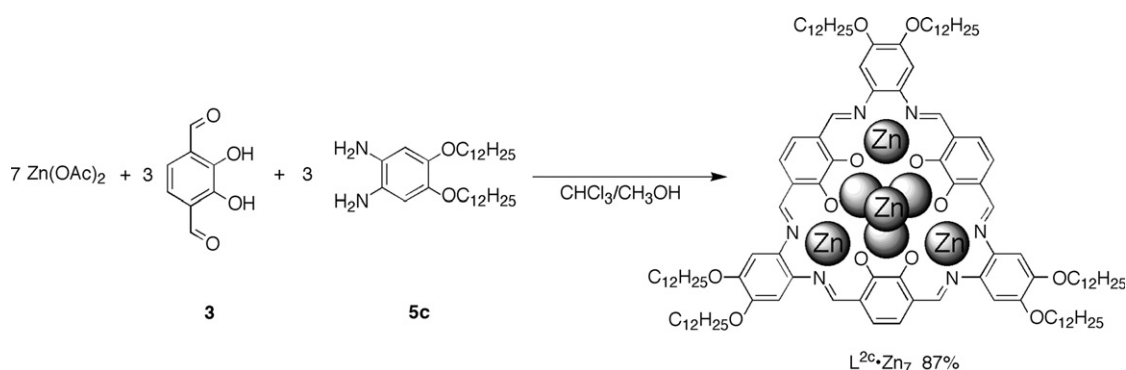


Figure 3. (a) Top and (b) side view of X-ray structure of  $L^{2a} \cdot Zn_7(O)(OAc)_6$ . The  $t$ BuO groups are omitted for clarity.



Scheme 2.

mass spectrum of **2a** in the presence of 3 equiv of  $Mn^{II}$  showed peaks ascribed to a trinuclear species [ $L^{2a} \cdot Mn_3$ ] but no peaks for higher oligo-Mn complexes (Table 1). The mass spectrum indicated that all the Mn atoms in the [ $L^{2a} \cdot Mn_3$ ] are trivalent. Divalent manganese in the saloph moiety was readily oxidized during the measurement by air from divalent to trivalent. In the presence of 10 equiv of  $Mn^{II}$ , however, hexa- and heptanuclear  $Mn^{II}$  complexes were detected in the mass spectrum, though partially oxidized species also existed (Table 1). Elemental analysis of the isolated heptanuclear  $Mn^{II}$  complex confirmed the stability

against air oxidation. Hence, the heptanuclear structure considerably enhances stability of the saloph- $Mn^{II}$  units in  $L^{2a} \cdot Mn_3$  against autooxidation.

ESI mass spectroscopic study indicated that  $Ni(OAc)_2 \cdot 4H_2O$  converted **2a** to the corresponding hexa-metal complexes but the heptanuclear Ni complex was not formed even by the addition of excess  $Ni^{II}$  (Table 1). In the presence of 3 equiv of  $Ni^{II}$  signals for the trinuclear Ni complex were observed (Table 1, 1339.8: [ $L^{2a} \cdot Ni_3Na_2$ ] $^{2+}$ ). The UV-vis spectra of the parent  $Ni^{II}$ (saloph) complex show strong absorption of  $\lambda_{max}$  at 480 nm.<sup>8</sup> However, the Ni complex of **2a** showed no characteristic absorption around the region. This implies that the  $Ni^{II}$ (saloph) units in **2a** are nonplanar. In addition, the isolated Ni complex was found to be paramagnetic because no NMR signals were detected in the expected region of the  $^1H$  NMR spectrum.

In contrast to Zn, Mn, and Ni, the corresponding trinuclear complexes of **2a** were obtained by the reaction with Cu and Co. The higher oligo-metal complexes were not formed even in the presence of excess amount of the metals. In the case of Cu, the absorption at 403 nm decreased but absorptions at 388 and 426 nm increased upon addition of up to 3 equiv of  $Cu^{II}$  (Fig. 5). The mole ratio method suggested the formation of  $L^{2a} \cdot Cu_3$ . However, no isosbestic point was observed in the titration experiment. Hence,  $Cu^{II}$  was introduced in a stepwise fashion to give the trinuclear complex. ESI mass and elemental analysis also supported the predominant formation of  $L^{2a} \cdot Cu_3$  (Table 1).

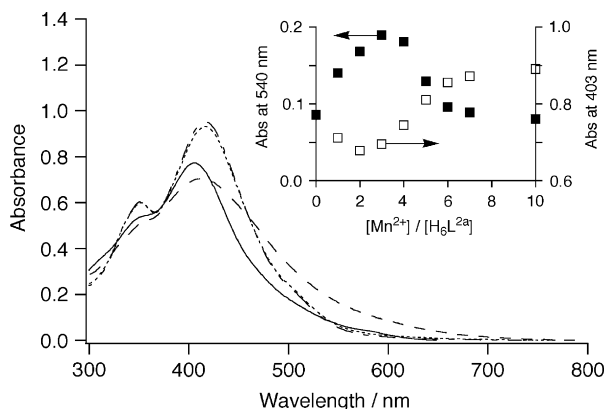
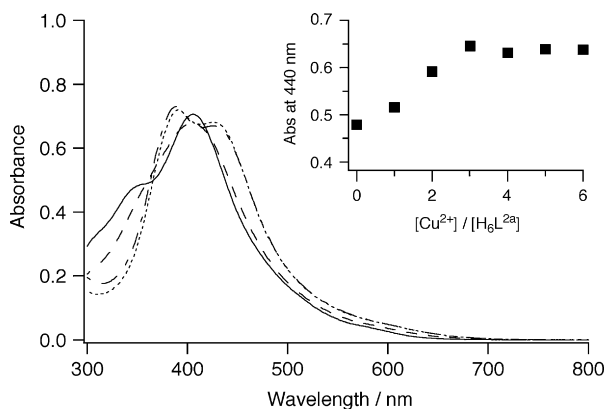
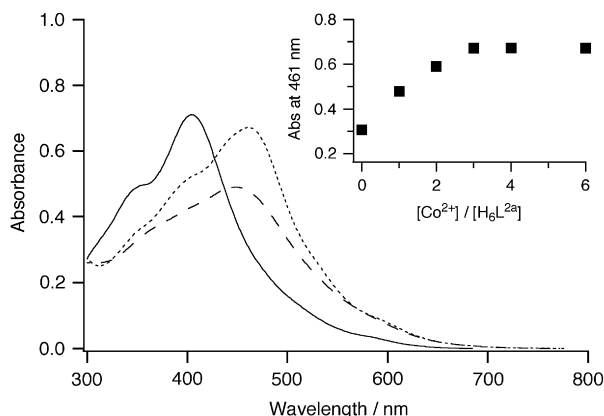


Figure 4. UV-vis spectral changes of ligand **2a** in  $CHCl_3$ - $CH_3OH$  (1:1) upon addition of  $Mn(OAc)_2 \cdot 4H_2O$ . [**2a**] $=1.0 \times 10^{-5}$  M. [ $Mn^{2+}$ ]/[**2a**] $=0$  (—), 3.0 (— — —), 7.0 (---), and 10 (— · —). Spectra were recorded after complete oxidation under aerobic condition.



**Figure 5.** UV-vis spectral changes of ligand **2a** in  $\text{CHCl}_3\text{-CH}_3\text{OH}$  (1:1) upon addition of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ .  $[\mathbf{2a}] = 1.0 \times 10^{-5}$  M.  $[\text{Cu}^{2+}]/[\mathbf{2a}] = 0$  (—), 1.0 (— — —), 3.0 (---), and 6.0 (— · —).

In the case of  $\text{Co}^{\text{II}}$  complex, a trinuclear Co complex of **2a** was formed by the addition of excess  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ . Absorptions at 403 nm and at ca. 450 nm decreased and increased, respectively, upon addition of 3 equiv of  $\text{Co}^{\text{II}}$ . As seen in  $\text{Mn}^{\text{II}}$ , autooxidation of the complex took place to give the corresponding  $\text{Co}^{\text{III}}$  complex. Under aerobic conditions, the UV-vis titration clearly showed formation of  $\text{L}^{2a} \cdot \text{Co}_3$ , which has a characteristic absorption at 460 nm after complete oxidation with air (Fig. 6). The UV-vis spectrum of the parent  $\text{Co}^{\text{II}}(\text{saloph})$  complex has a CT absorption band at 388 nm while the  $\text{Co}^{\text{III}}(\text{saloph})$  complex has a CT absorption band in the region of 440–470 nm.<sup>9</sup> The UV-vis spectrum of the Co complex of **2a** in degassed solvent has an absorption band at 380–390 nm as observed in that of the  $\text{Co}^{\text{II}}(\text{saloph})$  complex. The rate of oxidation is much slower than that for the trinuclear Mn complex. The difference in the reactivity was in good accordance with the stability difference between the saloph Mn and Co complexes against air oxidation. When the solutions used under the anaerobic condition were exposed to air, the absorption spectra changed to those obtained under the aerobic condition. Formation of the oxidized complex was also supported by ESI-MS and elemental analysis (Table 1).



**Figure 6.** UV-vis spectral changes of ligand **2a** in  $\text{CHCl}_3\text{-CH}_3\text{OH}$  (1:1) upon addition of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ .  $[\mathbf{2a}] = 1.0 \times 10^{-5}$  M.  $[\text{Co}^{2+}]/[\mathbf{2a}] = 0$  (—), 1.0 (— — —), 6.0 (---). Spectra were recorded after complete oxidation under aerobic condition.

### 3. Conclusion

On the basis of the concept of partial template, triangular trisaloph ligands **2a** and **2b** reacted with excess  $\text{Zn}^{\text{II}}$  to give the corresponding heptanuclear Zn complexes with a similar geometry. Interestingly, the Zn complex of **2c**, which was difficult to be prepared according to a previous procedure, was synthesized in high yield in a one-pot fashion. In the case of Mn and Ni complexes, various multi-nuclear complexes of **2a** were also readily obtained, although the trinuclear  $\text{Mn}^{\text{II}}$  complex was rapidly oxidized to the corresponding  $\text{Mn}^{\text{III}}$  complex. In contrast, Cu and Co afforded trinuclear complexes even in the presence of excess amount of the metals. The  $\text{Co}^{\text{II}}$  complex was easily oxidized by air but was less sensitive to the autooxidation than the  $\text{Mn}^{\text{II}}$  complex. The formation of various kinds of multi-nuclear complexes by using the triangular trisaloph ligands would be utilized to produce new functional metal clusters such as a host molecule, molecular catalyst for organic reactions, metallo-liquid crystals, and nonlinear optical materials. We believe that the concept of a partial template will be developed to construct not only metal clusters but also sophisticated organic-inorganic-hybrid supramolecules.

### 4. Experimental

#### 4.1. General experimental procedures

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker ARX400 (400 and 100 MHz) spectrometer. Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar Pulsar *i* spectrometer. UV-vis spectra were recorded on a JASCO Ubest V-560 and a JASCO V-660 spectrophotometer. 2,3-Dihydroxybenzene-1,4-dicarbaldehyde (**3**),<sup>10</sup> 1,2-bis(dodecyloxy)-4,5-diaminobenzene (**5c**),<sup>11</sup> and  $\text{L}^{2a} \cdot \text{Zn}_7$ <sup>6b</sup> were prepared as previously reported.

#### 4.2. Synthesis of oligonuclear complexes

**4.2.1.  $\text{L}^{2b} \cdot \text{Zn}_7$ .** To a solution of  $\text{H}_6\text{L}^{2b}$  (34.7 mg, 0.023 mmol) in  $\text{CHCl}_3$  (2 mL) was added a solution of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (36.0 mg, 0.162 mmol) in MeOH (2 mL). After 15 min, the solvent was removed by evaporation and the residue was reprecipitated from  $\text{CHCl}_3/\text{MeCN}$  to give reddish orange crystals, which were collected by filtration and dried in vacuo. Yield: 71% (38.0 mg, 0.016 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.90 (t,  $J = 6.6$  Hz, 18H), 1.23–1.45 (m, 48H), 1.45–1.57 (m, 12H), 1.81–1.93 (m, 12H), 4.03–4.16 (m, 12H), 6.71 (s, 6H), 6.98 (s, 6H), 8.33 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.14, 22.71, 26.08, 29.26, 29.31, 29.38, 31.85, 69.73, 101.98, 119.28, 120.80, 134.17, 150.26, 158.67, 161.89. Anal. Calcd for  $[\text{L}^{2b} \cdot \text{Zn}_7(\text{O})(\text{OAc})_6] \cdot \text{CHCl}_3 \cdot \text{H}_2\text{O}$ : C, 50.63; H, 5.82; N, 3.44. Found C, 50.59; H, 5.97; N, 3.46.

**4.2.2.  $\text{L}^{2a} \cdot \text{Mn}_7$ .** To a solution of  $\text{H}_6\text{L}^{2a}$  (14.65 mg, 0.013 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added a solution of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (21.85 mg, 0.089 mmol) in MeOH (10 mL) and the mixture was stirred for few minutes. The solvent was removed by evaporation and the residue was reprecipitated from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  to give black crystals, which were collected by filtration and dried in vacuo. Yield: 97% (24.2 mg, 0.012 mmol). Anal. Calcd for

[L<sup>2a</sup>Mn<sub>7</sub>(O)(OAc)<sub>6</sub>]·4H<sub>2</sub>O: C, 47.60; H, 5.02; N, 4.27. Found: C, 47.75; H, 4.97; N, 4.01.

**4.2.3. L<sup>2a</sup>·Co<sub>3</sub>.** To a solution of H<sub>6</sub>L<sup>2a</sup> (16.2 mg, 0.014 mmol) in CHCl<sub>3</sub> (2 mL) was added a solution of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (10.5 mg, 0.042 mmol) in MeOH (2 mL). After a few minutes, the solvent was removed by evaporation and the residue was reprecipitated from CHCl<sub>3</sub>/MeCN to give black powder, which was collected by filtration and dried in vacuo. Yield: 70% (15.0 mg, 0.0098 mmol). Anal. Calcd for [L<sup>2a</sup>·Co<sub>3</sub>(OAc)<sub>3</sub>]·2H<sub>2</sub>O: C, 56.47; H, 5.60; N, 5.49. Found: C, 56.47; H, 5.76; N, 5.44.

**4.2.4. L<sup>2a</sup>·Cu<sub>3</sub>.** The compound was synthesized following the procedure described in Section 4.2.3 using Cu(OAc)<sub>2</sub>·H<sub>2</sub>O. Yield: 80%. Anal. Calcd for [L<sup>2a</sup>·Cu<sub>3</sub>]·CHCl<sub>3</sub>·H<sub>2</sub>O: C, 54.77; H, 5.14; N, 5.72. Found: C, 54.32; H, 5.20; N, 5.98.

**4.2.5. L<sup>2a</sup>·Ni<sub>3</sub>.** The compound was synthesized following the procedure described in Section 4.2.3 using Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O. Yield: 78%. Anal. Calcd for [L<sup>2a</sup>·Ni<sub>3</sub>]·CHCl<sub>3</sub>·H<sub>2</sub>O: C, 55.32; H, 5.20; N, 5.78. Found: C, 55.74; H, 5.60; N, 5.31.

### 4.3. One-pot synthesis of L<sup>2c</sup>·Zn<sub>7</sub>

To a solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (96 mg, 0.43 mmol) in degassed MeOH (5 mL) was added **3** (30 mg, 0.182 mmol). A solution of **5c** (87 mg, 0.182 mmol) in degassed CHCl<sub>3</sub> (5 mL) was then added to the mixture, which was stirred for 8 h at room temperature. The solvent was removed by evaporation and the residue was reprecipitated from CHCl<sub>3</sub>/MeCN to give reddish orange crystals, which were collected by filtration and dried in vacuo. Yield: 87% (104 mg, 0.053 mmol). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.88 (t, *J*=6.9 Hz, 18H), 1.20–1.44 (m, 96H), 1.47–1.57 (m, 12H), 1.84–1.92 (m, 12H), 4.01–4.17 (m, 12H), 6.71 (s, 6H), 6.98 (s, 6H), 8.32 (s, 6H). Anal. Calcd for [L<sup>2c</sup>·Zn<sub>7</sub>(O)(OAc)<sub>6</sub>]·5H<sub>2</sub>O: C, 55.38; H, 7.23; N, 3.08. Found: C, 55.27; H, 7.16; N, 3.17.

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### Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.02.046.

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