

Cooperative formation and functions of multimetal supramolecular systems*

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Abstract: Multimetal complexes provide a variety of interesting structures, unique properties, and functions. Such sophisticated functions are often produced by synergistic and cooperative interactions among the metal ions accumulated in the restricted small area of the multimetal systems. We describe novel three strategies (i.e., macrocyclic, C-shape, and multimetal template) for the preparation of the multimetal supramolecular systems by the cooperative metal binding of a multi-Schiff-base and multi-oxime ligands, and their characteristic structures and functions. The three approaches are versatile and effective because the employed coordination reactions smoothly and quickly proceeded under mild conditions to quantitatively form the desired coordination structures. The multimetal supramolecular systems obtained here exhibit the synergistic and cooperative functions for ion recognition, magnetic properties, helicity control, and modulation of reaction selectivity. These types of multimetal complexes could be developed for a cascade functional supramolecular system that shows highly synergistic properties, integrated multifunctions, and function amplification.

Keywords: coordination chemistry; imines; metal complexes; molecular recognition; supramolecular chemistry.

INTRODUCTION

Multimetal complexes provide a variety of interesting structures such as metallamacrocycles [1], metal-lacryptands [2], metallahelicates [3], etc., and unique properties and functions such as guest recognition [4], photophysical behaviors [5], magnetic properties [6], redox activity [7], catalytic activity [8], etc. Many of them cannot be achieved by discrete single-metal complexes because such sophisticated functions are often produced by synergistic and cooperative interactions among the metal ions accumulated in the restricted small area of the multimetal systems. However, it is difficult to obtain the multimetal complexes in high yields especially in the case of metal cluster complexes containing three or more metal ions. Thus, we have developed new strategies and methods for the cooperative high-yield synthesis of the multimetal complexes based on a supramolecular approach in a cooperative fashion [1f].

We describe our new strategies for the preparation of the multimetal supramolecular systems by the cooperative metal binding of a multi-Schiff-base and multi-oxime ligands, and their characteristic structures and functions.

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METAL COMPLEXATION OF SALEN AND ITS ANALOGS

Salen and its derivatives are well known ligands to various metal ions, and many types of their metal complexes have been reported. Some of the salen complexes exhibit interesting catalytic activities for organic reactions [9], magnetic properties [10], optical properties [11], etc. We noticed that a significant binding affinity to another metal ion is an additional important feature of these complexes [12]. In other words, the salen complexes are considered to be a metallo-ligand due to the chelate coordination by the negatively charged oxygen atoms of the complexes to form the corresponding multimetal complexes. The enhancement of the negative charge of the oxygens upon the complexation is also supported by our preliminary density functional theory (DFT) calculations (Fig. 1).

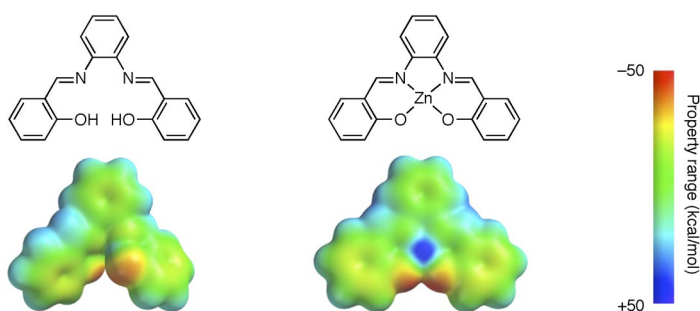


Fig. 1 Electrostatic potential map of salen-Zn complex.

Various multimetal complexes based on the simple salen derivatives have been reported [12]. Furthermore, the binding properties of the salen analog complexes were also applied to supramolecular chemistry, in which the oxime functionality as well as salens are incorporated into a crown ether framework [13]. It is noteworthy that the cationic metal ions locate in close proximity to the multimetal systems. It would seem that the synthetic yield is low due to the electrostatic repulsion between the metal ions, although the overall charge of the metal complex is neutral. However, this repulsion does not affect the multimetal complexes because the complexation of the salen analogs gives rise to the polarization of the ligands to enhance the binding affinity. We were convinced that this phenomenon could be applied to the synthesis of more complicated multimetal complexes.

In this account, we introduce our three strategic molecular designs for preparing multimetal complexes. An initial organic ligand binds to a metal ion to give the corresponding metal complex, and then the successive complexation with a different metal ion affords the desired final multimetal supramolecular complex.

MACROCYCLIC STRATEGY FOR SYNTHESIS OF MULTIMETAL COMPLEXES

Even though the two oxygen atoms of the salen complexes can coordinate to a metal ion, the yields of the complexation with another metal ion are not always high because of the insufficient chelate effect on the complexation. Hence, we designed a macrocyclic framework to increase the metal binding strength due to a macrocyclic effect that is caused by the cyclic arrangement of the negatively charged oxygen atoms. The basic macrocyclic structure is illustrated in Fig. 2. We expected that the complexation of the macrocyclic ligand with 3 equiv of a suitable metal ion should produce a binding cavity for another metal ion. A successive metal complexation should give the homo- and heteronuclear metal complexes.

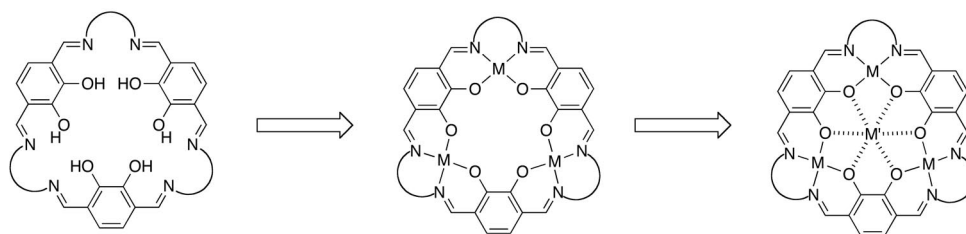
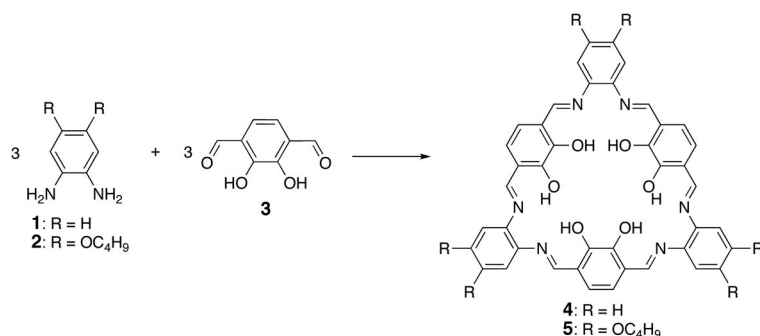


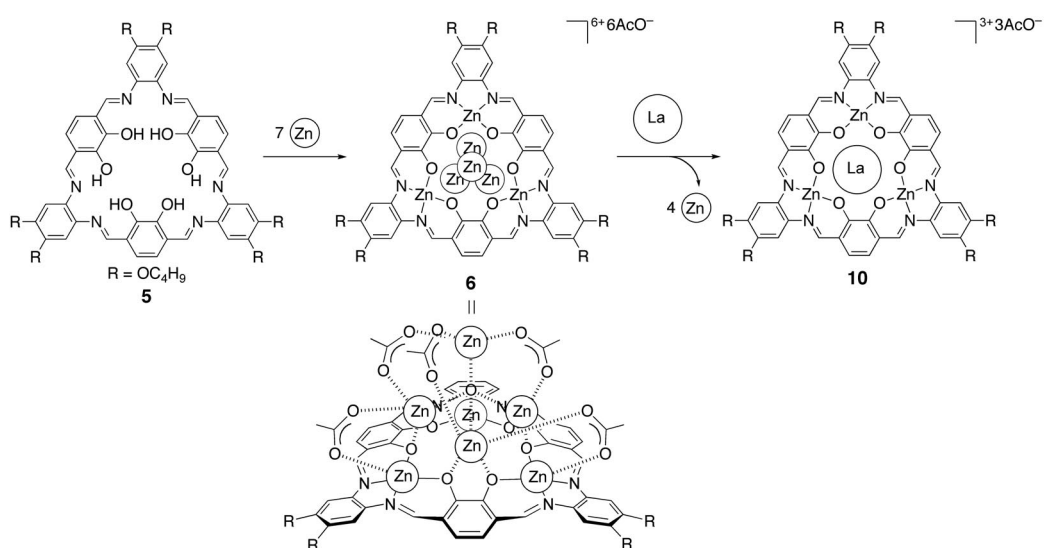
Fig. 2 Basic macrocyclic framework of trisaloph analogs.

We reported the first synthesis and structure of the basic trisaloph **4** as a precursor ligand for the multimetal complexes by the simple condensation reaction of a diamine **1** and dialdehyde **3** (Scheme 1) [14]. The product **4** was obtained as single crystals in 91 % yield. As we expected, the trisaloph **4** has a triangular structure with a cavity structurally similar to that of crown ethers.

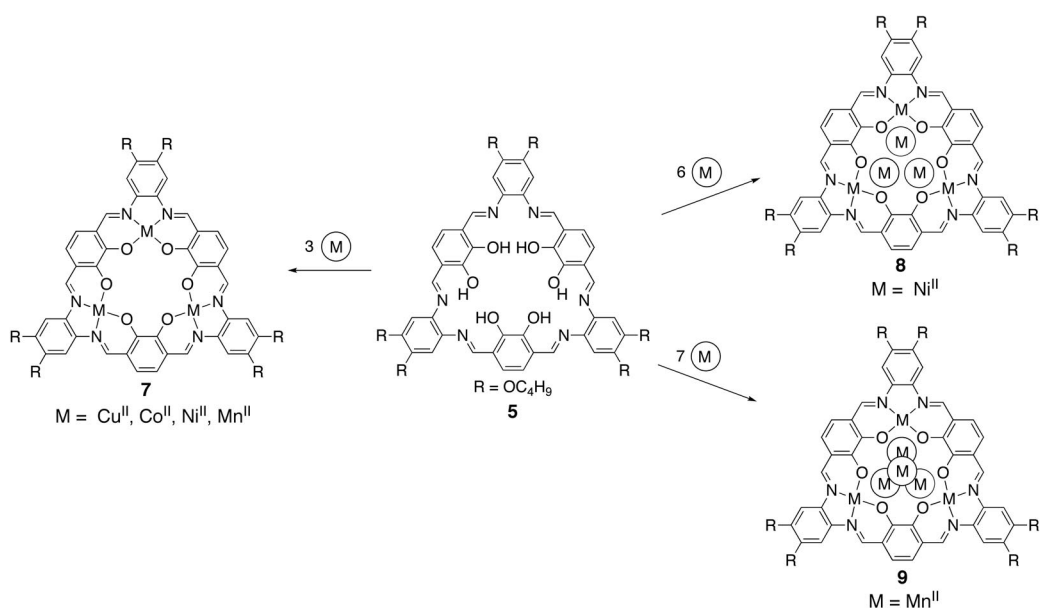


Scheme 1 Synthesis of trisaloph ligands.

The treatment of trisaloph **5** with $\text{Zn}(\text{OAc})_2$ quantitatively gave a red heptanuclear Zn complex **6** (Scheme 2), although we first expected the formation of the tri- and tetranuclear complexes [15]. ^1H NMR titration of the Zn complexation suggested that a 7:1 complexation took place. In addition, the electrospray ionization-mass spectrometry (ESI-MS) and elemental analysis strongly supported the Zn_7 complex formation. Finally, an X-ray crystallographic analysis of the complex revealed that three Zn ions locate at each N_2O_2 site in a fashion similar to that of a simple saloph-Zn complex, three more Zn ions are bound by the catechol moieties of the ligand **5**, and the final Zn ion sits on the top of the central oxygen atom that is surrounded by the latter three Zn ions. The heptanuclear Zn cluster core is stabilized by coordination of the six acetate anions. This is one of the reasons why the Zn_7 complex **6** is quantitatively formed. We named this preparative method “partial template synthesis” because the triangular ligand **5** provides only a base necessary for the initial complexation with the Zn ions and then the three-dimensional cluster complex is spontaneously produced. The nuclearity of the mono-metal cluster complexes strongly depends on the metal ions. The trinuclear complexes **7** are obtained in high yields with Cu, Co, Ni, and Mn, a hexanuclear complex **8** in Ni, and heptanuclear complexes in Zn and Mn (Scheme 3) [16]. Interestingly, a heteronuclear cluster complex **10a** is quantitatively synthesized just by treatment of the Zn_7 complex **6** with 1 equiv of La at room temperature (Scheme 2) [15b]. A preliminary X-ray diffraction analysis showed that the heteronuclear complex is more planar than the Zn_7 complex **6**, which has a convex geometry.

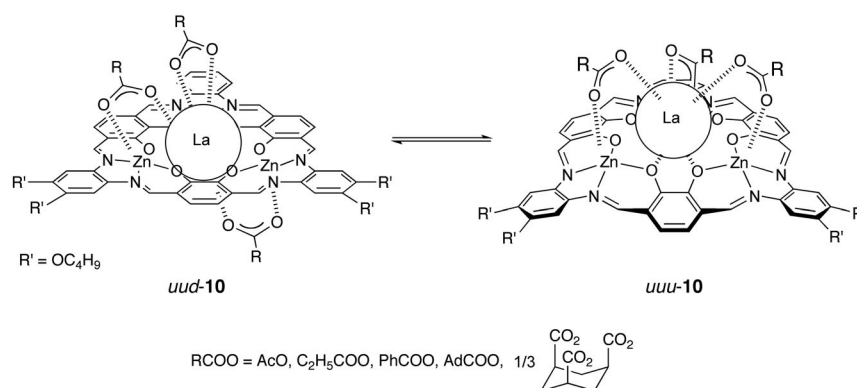


Scheme 2 Formation of homo- and heteronuclear trisaloph complexes.



Scheme 3 Nuclearity of trisaloph homo-multinuclear complexes.

There are two isomers of the Zn_3La trisaloph complex **10a** in $\text{DMSO-}d_6$ based on the different coordination modes of the acetato ligands; i.e., the *uuu*-isomer with the three acetato ligands on the upper side and the *uud*-isomer with two on the upper side and one on the underside (Scheme 4) [17]. The trisaloph heteronuclear complex bearing three triflates **10b** was synthesized by the reaction with $\text{La}(\text{OTf})_3$ according to a synthetic procedure similar to that for **10a** (Fig. 3). The triflate anions of **10b** are easily exchanged by the addition of other anions. The heteronuclear complexes **10** bearing various carboxylates were prepared in situ (Scheme 4), and the ratio of the two isomers was determined by the ^1H NMR spectra. Only 1,3,5-cyclohexanetricarboxylate resulted in the discrete formation of the



Scheme 4 Two anion ligation modes in trisaloph complex **10**.

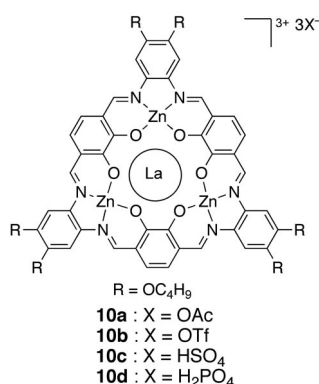


Fig. 3 Trisaloph heteronuclear complexes bearing various counter anions.

uuu-isomer probably due to the C_3 symmetric structure of the anion. The complexation with the other carboxylate gave mixtures of the two isomers or unidentified compounds.

Complexes **10c** and **10d** were isolated by a similar anion-exchange method. The formation of **10d** is noteworthy because the reaction of the mononuclear saloph·Zn complex with $H_2PO_4^-$ dissociated the complex to give the free ligand. The ratio of the two isomers of **10c** in solution was determined to be 2:1, while the ratio of **10a** was 1:1. On the other hand, the phosphate complex **10d** was suggested to exist as only one discrete isomer, a C_3 symmetric *uuu*-**10d**. The DFT calculation revealed three intramolecular hydrogen bonds between three H_2PO_4 anions assembled on *uuu*-**10d** (a model compound without side-chains), and a large stabilization energy ($-\Delta E$) for *uuu*-**10d** compared to that of *uud*-**10d** (Fig. 4) [18]. On the contrary, the $\Delta\Delta E$ for the two isomers of the **10a** without any hydrogen bond is much smaller. The ion peaks assigned to the dimeric species were observed in matrix-assisted laser desorption/ionization with time-of-flight mass spectrometry (MALDI-TOF MS). The DFT-calculated structures of the dimer and trimer of *uuu*-**10d** are linearly stacked trisaloph complexes through intermolecular hydrogen bonding, indicating that the infinite one-dimensional aggregation of *uuu*-**10d** can be formed with an interaction energy for each stacking (Fig. 4). This result rationalizes the formation of a fibril assembly of *uuu*-**10d** in aqueous media (vide infra).

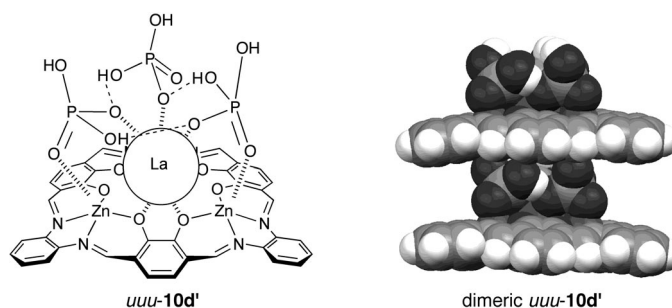
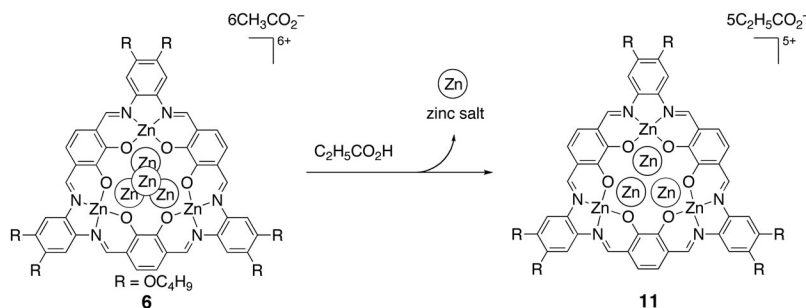


Fig. 4 DFT-calculated structures of **10'd** and its dimer.

The nuclearity of the multinuclear Zn complexes of the trisaloph ligands also depends on the counter anions. The hexanuclear cluster complex **11** was obtained as the sole product from **5** and excess $\text{Zn}(\text{C}_2\text{H}_5\text{CO}_2)_2$, while the reaction of **5** with 7 equiv of $\text{Zn}(\text{OAc})_2$ quantitatively afforded the heptanuclear complex **6** in solution [19]. This significant counter anion effect on the cluster formation is probably due to the difference in the steric repulsion between the anionic ligands of the clusters because the six anions on the heptanuclear complex are closely located. The anion effect on the nuclearity encouraged us to examine the structural control of the zinc cluster by the anion-exchange reaction. The reaction of **6** with an excess of $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ and successive recrystallization yielded **11** (Scheme 5). This fact demonstrates that one zinc atom of **6** is removed just by the anion-exchange reaction. Namely, the nuclearity of the clusters is easily controlled by utilizing the subtle difference in the anion structure.



Scheme 5 Nuclearity control of trisaloph multinuclear Zn complex by anion exchange.

When a suitable combination of metal ions is employed in the multimetal systems, the obtained heteronuclear complexes show unique magnetic properties. For example, a Zn_3Er complex **12** based on the macrocyclic Schiff-base scaffold has characteristic magnetic properties, i.e., single-molecule magnetic (SMM) behavior (Fig. 5) [20]. Similar heterotetranuclear complexes **13** and **14** were also prepared to work as an SMM [21].

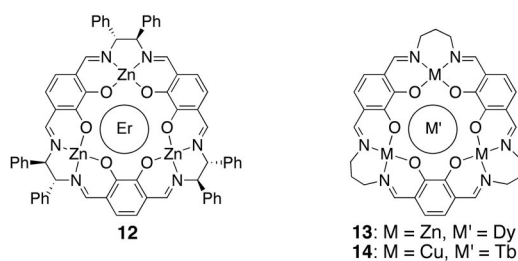
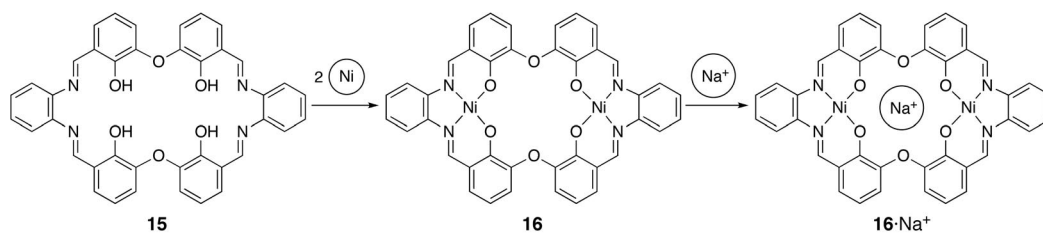


Fig. 5 SMMs based on scaffold of trisaloph analogs.

Alkali metal ions are captured in the cavity of the Ni complex **16** that is obtained from the reaction of the bisalen ligand **15** with two Ni ions (Scheme 6) [22]. The Ni complex **16** shows a much higher (>6000-fold) affinity to Na^+ than the metal-free host **15**. On the other hand, the trinuclear Ni complex was not formed in the presence of an excess amount of Ni. Complexation of the Ni complex **16** with larger alkali metal ions (K, Rb, and Cs) produces one-dimensional oligomeric assemblies of the complexes.



Scheme 6 Ion recognition of dinuclear Ni complex **16**.

The larger macrocyclic bisN₂O₂ complexes with Cu and Ni recognize a Ba^{2+} ion in an intramolecular sandwich-like fashion (Fig. 6) [23].

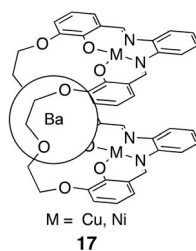
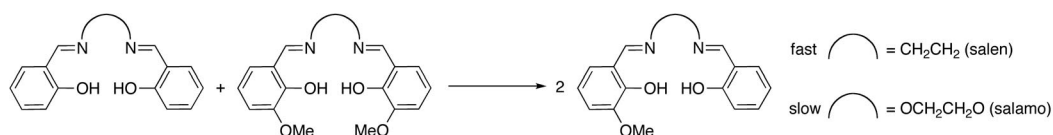


Fig. 6 Ba^{2+} binding by **17**.

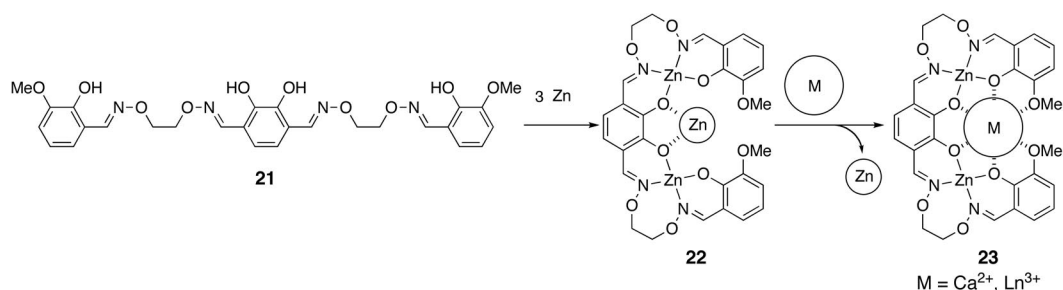
Meso-scale molecular assemblies can be generated using a metal-free trisaloph derivative **18a** in the presence of alkali metal ions (Fig. 7) [24]. We designed a trisaloph ligand **18b** bearing an adamantane unit at each terminal of the side-chains in the triangular ligand to increase the solubility in common organic solvents [18]. It is noteworthy to point out that **18b** can be dissolved in an aqueous media by the addition of β -cyclodextrin because an adamantane is an excellent guest for cyclodextrins. Interestingly, the complexation with β -cyclodextrin in aqueous media resulted in the aggregate formation of **19**, which was confirmed by a dynamic light-scattering (DLS) experiment and scanning electron

For preparation of the oligosalen derivatives for multimetal complexes, one of the serious issues is their low solubility in various solvents. One more disadvantage of the oligosalens is their relatively high reactivity toward a disproportionation reaction. Even if a pure linear salen oligomer was obtained, the disproportionation reaction would change it to a complex mixture. In sharp contrast, we found that 1,2-bis(salicylideneaminoxy)ethane (H_2 salamo), which has an oxime functionality instead of a Schiff base, resists the disproportionation [25]. In fact, a cross-over experiment indicated that the half-life of the disproportionation of H_2 salamo is greater than 23000 times longer than that of the corresponding salen (Scheme 7). In addition, the salamo ligands solve the solubility problem. We prepared many oligosalamo derivatives, which are soluble in the usual organic solvents probably due to their less planar and more flexible structures than the salen derivatives.



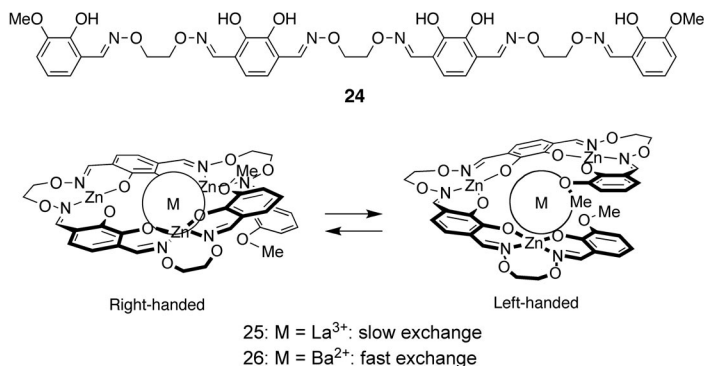
Scheme 7 Disproportionation reaction of H_2 salamo and H_2 salen.

A bissalamo **21** was designed and synthesized for the synergistic formation of the trinuclear metal complexes (Scheme 8) [26]. The complexation reaction of **21** with Zn very cooperatively proceeded to give **22** quantitatively. During the 1H NMR titration for the Zn complexation, only the signals of the free ligand **21** and the Zn_3 complex **22** appeared, while signals of the intermediate complexes, mononuclear and dinuclear Zn complexes, were not observed. Heterotrinuclear complexes can be quantitatively prepared just by the addition of a suitable metal ion such as lanthanides and Ca^{2+} to a solution of **22** at room temperature. These results clearly indicated that the central C-shaped site works as an excellent recognition site for the metal ions. The X-ray crystallographic structure reveals that only two oxygen atoms in the C-shaped site coordinate to the central Zn ion, although the other two Zn ions are strongly captured in the N_2O_2 sites. This is the reason why only the central Zn ion is replaced by the other metal ions. Lanthanide ions and Ca^{2+} show very strong affinity to the central site, but the affinity of Sr^{2+} and Ba^{2+} is moderate. On the other hand, no transmetalation reaction occurs in the case of alkali metal ions and Mg^{2+} . The selectivity coefficient for Ca^{2+}/Mg^{2+} is more than 100000, which is comparable or greater than those of the famous Ca^{2+} binders, BAPTA and Quin2 [27]. Thus, we believe that the complex **22** could be potentially used for Ca^{2+} ion sensing in living cells. All the obtained X-ray structures of the heteronuclear complexes are helical. As a larger central metal ion is employed, the winding angle of the helices decreases.



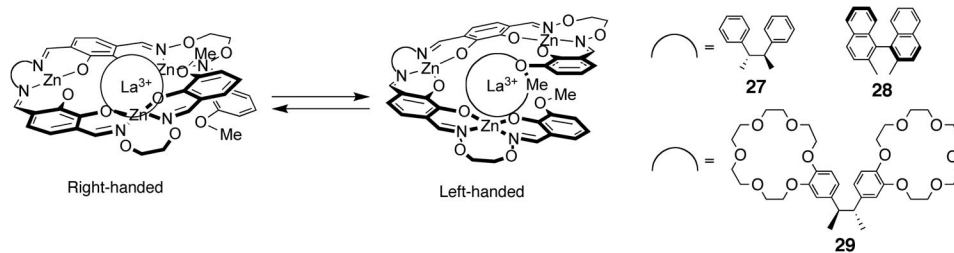
Scheme 8 Synthesis of homo- and heteronuclear complexes from bissalamo **21**.

For tetranuclear metal systems, we synthesized trisalamo **24** [28]. However, the reaction of trisalamo **24** with Zn^{2+} affords a complex mixture. The ESI-MS indicates that the mixture contains the tetranuclear complex but we did not obtain the pure compound. When we added 1 equiv of La^{3+} and Ba^{2+} to a solution of the mixture, sharp ^1H NMR spectra, which are assigned to single species, **25** and **26**, were obtained. The terminal benzene rings stack on each other to stabilize the helical structure in the solid state and also in a solution (Scheme 9).



Scheme 9 Formation of helical heteronuclear complexes from trisalamo **24**.

The ratio of helical isomers of such multimetal complexes can be controlled by introducing a chiral auxiliary into the central part of a multidentate salamo ligand (Scheme 10) [29]. The ratio of the M to P isomers is ca. 100 % for a 1,1'-binaphthyl unit [30]. A 1,2-diphenylethylene linker yielded a mixture of M and P with a ratio of 71:29 in solution. In the solid state, however, only the pure M helical complex **27** is involved. Moreover, the helical complexes are arranged in a helical fashion in the single crystals to form a superhelix.



Scheme 10 Helical isomers of heteronuclear complexes of salamo derivatives.

Recently, we reported the helicity control of the multimetal complexes on the basis of leverage motion by utilizing host-guest interactions. Dr. S. Akine, a colleague in our group, designed the novel complex **29** in line with this concept (Scheme 10) [31]. We also reported many complexes bearing interesting functions on the basis of the C-shape strategy. For instance, a Cu_2Gd complex **30** exhibits ferromagnetic interactions among the metal ions at low temperature (Fig. 9) [32]. The stereochemistry of olefin metathesis reactions of **31** can be well controlled by the multimetalation (Scheme 11) [33]. Only the *cis* isomer (*cis*-**33**) is obtained in the presence of Zn and Ca, but the *trans* isomer (*trans*-**33**) is predominantly produced (*cis*-**33**:*trans*-**33** = 7:93) without metal ions.

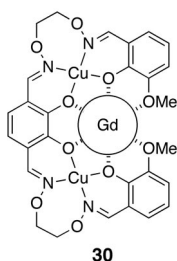
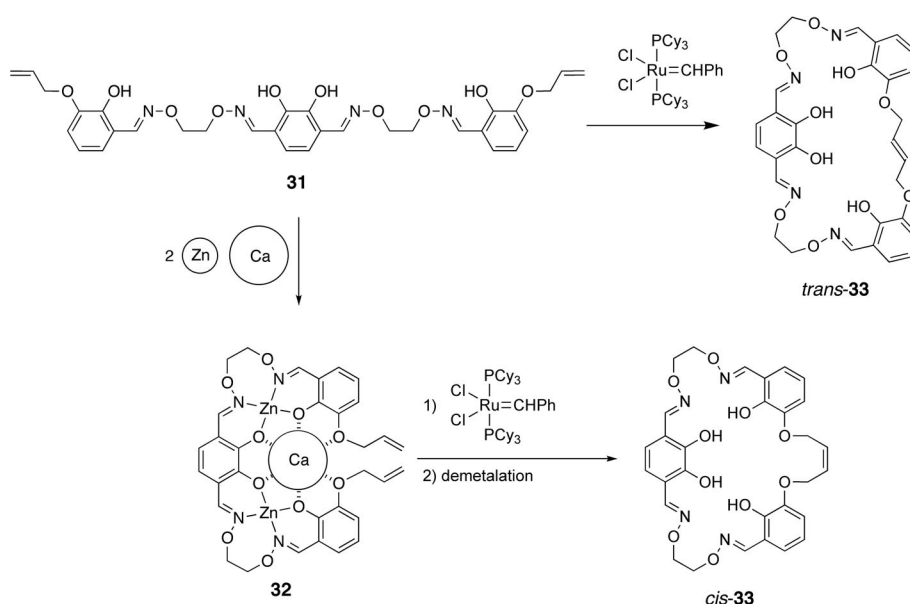


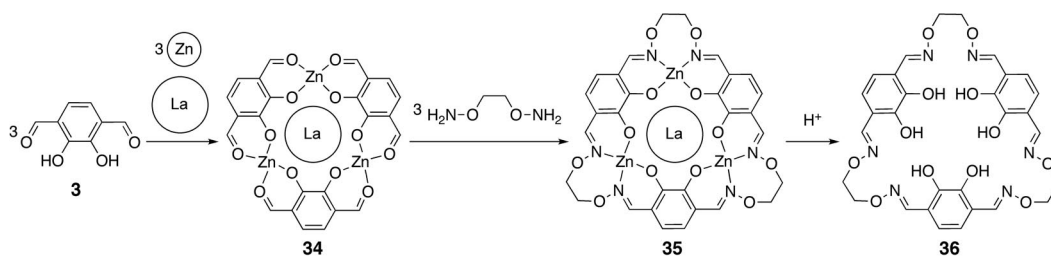
Fig. 9 Cu₂Gd complex **30**.



Scheme 11 Metal ion effect on olefin metathesis of **31**.

MULTIMETAL TEMPLATE STRATEGY FOR MACROCYCLIC MULTIMETAL COMPLEXES

The template synthesis for macrocyclic compounds often utilizes one template species to create a pre-organized structure that is appropriate for the successive ring-closing reaction. Multiple metal ions should be necessary for the effective one-pot synthesis of macrocyclic multimetal complexes from their organic components and metal ions, although such a multimetal template seemed to be very difficult. However, the trisalamo Zn₃La complex **35** was synthesized in a one-pot with a high yield by this efficient template method (Scheme 12) [34]. After demetalation of the complex by the treatment of hydrochloric acid, the metal-free macrocyclic ligand **36** was obtained in 94 % overall yield from the starting materials. On the other hand, the yield of **36** is only 15 % without Zn and La. A structural similarity between an intermediary tetranuclear complex **34** and the macrocyclic complex **35** was observed by X-ray crystallography. Therefore, the final cyclization reaction with 1,2-bis(aminooxy)ethane proceeded very smoothly without any significant strains.



Scheme 12 Multimetal template synthesis of macrocyclic trisalamo **36**.

The Er-based SMM, Zn_3Er **12**, was also obtained in high yield according to the multimetal method. This template strategy is also applied to the preparation of the homo-heptanuclear Zn complex, **6** (87 %) by the one-pot reaction of the diamine **2** and dialdehyde **3** in the presence of Zn. The multi-template method will probably open a new way to synthesize much larger nano- and meso-scale multimetal complexes.

CONCLUSION

The three approaches for the construction of the multimetal supramolecular systems described here are versatile and effective because the employed coordination reactions smoothly and quickly proceeded under mild conditions leading to the quantitative formation of the desired coordination structures. The accumulation of the several metal ions in the restricted area of the molecule results in the synergistic and cooperative functions for ion recognition, magnetic properties, helicity control, and modulation of reaction selectivity. In general, the cooperative functions should be important for multiple-function molecular systems, which are useful not only to downsize molecular devices, but also to make intelligent materials responding to external stimuli. We are also convinced that the multimetal complexes could be developed for a cascade functional supramolecular system, in which several independent multimetal complexes with a different cooperative function are assembled and then communicate with each other to exhibit highly synergistic properties and/or function amplification from the nano-scale level to the human-scale.

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