

# Novel ion recognition systems based on cyclic and acyclic oligo(salen)-type ligands

Shigehisa Akine

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**Abstract** This review describes the design of novel ion recognition systems based on salen ( $H_2salen = N,N'$ -disalicylideneethylenediamine) or related ligands. The phenoxo groups of the salen-based metallohosts play an important role in the ion recognition because the phenoxo groups can further coordinate to metal ions in a bridging fashion. In particular, the integration of two or more salen-type coordination sites in a cyclic fashion is effective for the construction of the metallohosts. They show unique multi-metal complexation behavior and binding selectivities due to the phenoxo-bridged structures. The peripheral salen-type sites are suitable for binding to d-block transition metal ions and the central  $O_6$  (or larger) site is for the group 1–3 metals. Acyclic oligo(salen) molecules are also effective for obtaining metallohosts. The metalation of a bis(salen)-type ligand with d-block metals leads to a trinuclear complex with a C-shaped structure, which can selectively recognize  $Ca^{2+}$  and lanthanide(III) ions via a unique metal exchange process. The longer oligo(salen) ligands form a helical structure when they recognize the  $La^{3+}$  or  $Ba^{2+}$  ion in the presence of the zinc(II) ion. The helix inversion behavior of the helical metal complexes due to the labile character of the coordination bonds is successfully utilized for the dynamic helicity control. The transformation of the acyclic ligand into cyclic ones via olefin metathesis significantly changes the binding selectivity.

**Keywords** Salen · Transition metal complex · Crown ether · Ion recognition · Helical structure

S. Akine (✉)

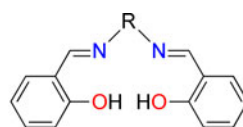
Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan  
e-mail: akine@chem.tsukuba.ac.jp

## Abbreviations

salen	$N,N'$ -disalicylideneethylenediamine dianion
saltn	$N,N'$ -disalicylidene-1,3-diaminopropane dianion
salbn	$N,N'$ -disalicylidene-1,4-diaminobutane dianion
saloph	$N,N'$ -disalicylidene- <i>o</i> -phenylenediamine dianion
salamo	1,2-Bis(salicylideneaminoxy)ethane dianion

## Introduction

The salen [1, 2] ligand and its analogues (Chart 1) are versatile and important compounds that have been widely used in coordination chemistry. The salen-type ligands are easily prepared by the condensation of the appropriate salicylaldehyde derivative with diamines. The imine  $C=N$  bond formation proceeds quite smoothly by gently heating a solution of the two compounds. Chemical modification of the aldehyde or diamine leads to various kinds of



salen-type ligands

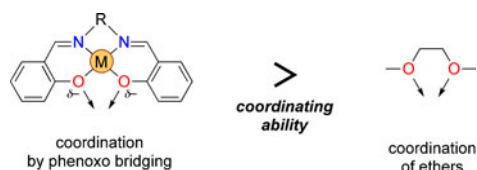
$H_2salen$  ( $R = CH_2CH_2$ )  
 $H_2saltn$  ( $R = CH_2CH_2CH_2$ )  
 $H_2salbn$  ( $R = CH_2CH_2CH_2CH_2$ )  
 $H_2saloph$  ( $R = o-C_6H_4$ )  
 $H_2salamo$  ( $R = OCH_2CH_2O$ )



metal complexes of salen-type ligands

$M = Ni^{II}, Cu^{II}, Co^{II}$ , etc.  
(square planar)  
 $M = Zn^{II}, Fe^{III}, Mn^{III}, Cr^{III}$ , etc.  
(penta- or hexacoordinate)

**Chart 1** Salen and related ligands and their complexes. The additional ligand X is omitted in the following charts and schemes

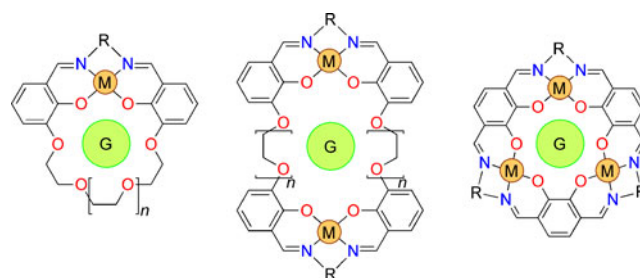


**Scheme 1** Coordinating ability of  $[M(\text{salen})]$  complexes through phenoxo bridging

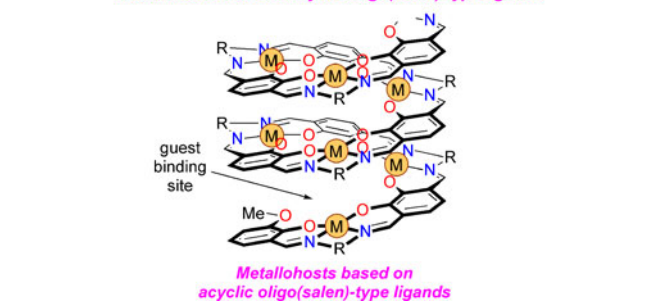
functionalized salen ligands, which can be used for the synthesis of functional metal complexes. In general, the salen-type ligands coordinate to a transition or typical metal ion as a doubly deprotonated form in a tetradentate fashion. For example, the complexation with nickel(II) [3], copper(II) [3], cobalt(II) [4], etc., affords the square planar complexes, while complexation with zinc(II) [5], iron(III) [6, 7], manganese(III) [8], chromium(III) [9], titanium(IV) [10], etc., yields the penta- or hexacoordinate complexes with additional neutral or anionic ligand(s). A number of salen metal complexes have already been developed to study their structures, reactivities or the fundamental physical properties such as optical or magnetic properties. In addition, there are many functional salen metal complexes; for example, some of the salen–metal complexes show a catalytic activity in organic reactions [11–13] such as epoxidation, act as a model of the catalytic centers of metalloenzymes [14, 15], exhibit nonlinear optical properties [16, 17] or behave as a metallomesogen [18]. The use of the salen complexes as a constituent of supramolecules has currently attracted much attention [19–23].

One of the important features of the metal complexes with salen-type ligands is that these complexes can further be used as a constituent of the oligometallic complexes [24–26]. Although the parent salen ligand and its analogues form a mononuclear complex  $[M(\text{salen})]$  with various kinds of metal ions, they also form oligometallic complexes in which the  $[M(\text{salen})]$  complex further coordinates to other metal ions. In such a case, the phenoxo groups of the salen ligand play a key role in the formation of the oligometallic structures by bridging two or more metal ions in a  $\mu_2$  fashion. This *coordinating ability* of the  $[M(\text{salen})]$  units may be utilized as a cation recognition phenomenon. The two phenoxo groups of the  $[M(\text{salen})]$  complexes can coordinate to other metal ions in a bidentate fashion in a manner similar to glycol ether, but the coordination ability to the metal ions is much higher (Scheme 1; for details, see below). However, a more sophisticated molecular design is needed to realize the strong and highly selective ion recognition by taking advantage of this *coordinating ability* of the  $[M(\text{salen})]$  complexes to metal ions.

It is well known that simultaneous and synergistic non-covalent interactions result in strong and specific host–guest binding phenomena, even if the individual



**Chart 2** Design of cyclic and acyclic oligo(salen) metallohosts for ion recognition



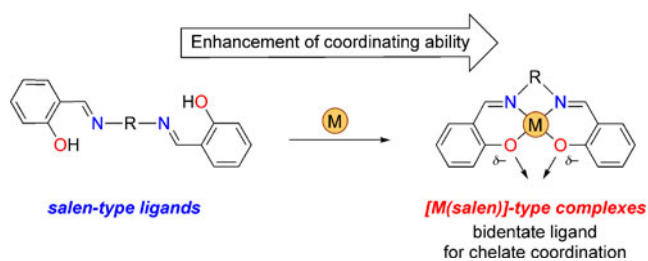
**Chart 2** Design of cyclic and acyclic oligo(salen) metallohosts for ion recognition

interactions are weak [27]. In this context, the incorporation of a  $[M(\text{salen})]$  moiety into a cyclic skeleton or the accumulation of multiple  $[M(\text{salen})]$  units in a preorganized fashion would effectively develop a novel metal-containing ionophore (Chart 2). Such a metal-containing ionophore is expected to show an interplay between the guest species and the metal complex moieties, leading to various kinds of functional host–guest systems [28–41]. Since the d-block metal complex moieties in these metallohosts would basically retain its intrinsic chemical reactivity or physical properties, they are expected to behave as a guest-responding functional molecule whose reactivity or properties can change upon the guest binding. On the other hand, the guest binding would be regulated by the chemical or electrochemical tuning of the metal in the metallohosts.

In this review, the design, synthesis, and complexation behavior of cyclic and acyclic ligands containing one or more salen-type coordination sites (Chart 2) are described. Novel guest recognition systems based on a metal exchange and the unique selectivity regarding their ion recognition behavior are outlined.

### Salen complexes as a ligand

As already described, mononuclear salen-metal complexes can coordinate to another metal ion through the negatively-charged phenoxo oxygen donors. For designing salen-containing host molecules, it is important to understand the nature of the *coordinating ability* of the  $[M(\text{salen})]$  complexes. In this section, the coordinating behavior of

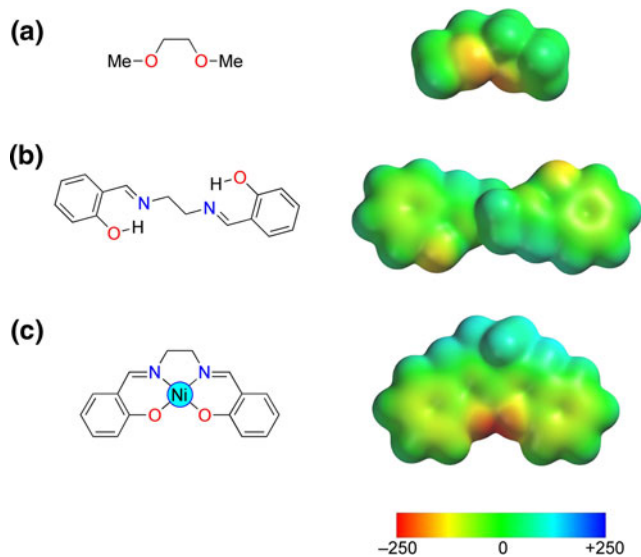


**Scheme 2** Coordinating behavior of  $[M(\text{salen})]$  complexes toward a hard metal ion

$[M(\text{salen})]$  complexes of mono(salen)-type ligands is briefly summarized.

When the salen-type ligands form a metal complex, four coordination bonds are newly formed and the two phenoxo oxygen atoms are fixed in a structure suitable for the bidentate chelate coordination to another metal ion (Scheme 2). At the same time, their two phenolic O–H oxygen atoms are converted into more polarized O–M phenoxo oxygen atoms. The electrostatic potential surface obtained by DFT calculation showed that the negative charge of  $[\text{Ni}^{\text{II}}\text{salen}]$  complex is mainly distributed on the phenoxo oxygen atoms (Fig. 1). The surface around the phenoxo groups is more negative than those around the phenol groups of the  $\text{H}_2\text{salen}$  or the ether groups of glycol ether. Due to the increased negative charges of the phenoxo groups as well as the structural change, the  $[M(\text{salen})]$ -type complexes are more likely to coordinate to another metal ion in a bidentate fashion.

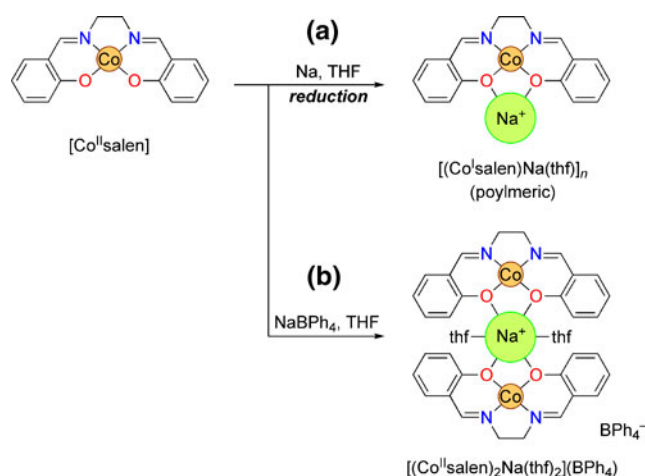
Representative examples of the adduct complexes are the alkali metal adducts of the  $[M(\text{salen})]$  ( $M = \text{Co}, \text{Cu}$ ,



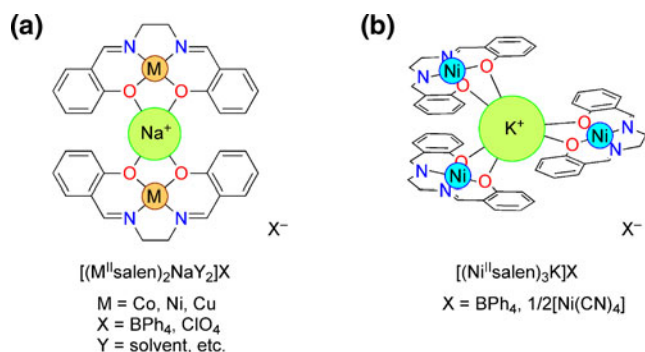
**Fig. 1** Electrostatic potential surface of **a** glyme in a *gauche* conformation, **b**  $\text{H}_2\text{salen}$ , and **c**  $[\text{Ni}^{\text{II}}\text{salen}]$  obtained by DFT calculations (B3LYP/6-31G\*\*) using SPARTAN program

Ni) complexes. The reduction of the  $[\text{Co}^{\text{II}}\text{salen}]$  complex with elemental sodium afforded a dinuclear complex  $[(\text{Co}^{\text{I}}\text{salen})\text{Na}]$  in which the anionic  $[\text{Co}^{\text{I}}\text{salen}]^-$  unit coordinates to  $\text{Na}^+$  [42–45] (Scheme 3a). The corresponding complexes with  $\text{Li}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$  were also isolated using a similar procedure. In contrast, the reaction of  $[\text{Co}^{\text{II}}\text{salen}]$  with a sodium salt ( $\text{NaBPh}_4$ ) afforded a trinuclear complex  $[(\text{Co}^{\text{II}}\text{salen})_2\text{Na}(\text{thf})_2](\text{BPh}_4)$  in which two neutral  $[\text{Co}^{\text{II}}\text{salen}]$  units coordinate to  $\text{Na}^+$  [46, 47] (Scheme 3b). In both of these complexes, the phenoxo groups of the  $[\text{Co}(\text{salen})]$  ( $\text{Co} = \text{Co}^{\text{I}}$  or  $\text{Co}^{\text{II}}$ ) units coordinate to  $\text{Na}^+$  in a bidentate fashion.

Similarly, the  $[M^{\text{II}}\text{salen}]$  ( $M = \text{Cu}$  [48–50],  $\text{Ni}$  [51, 52]) complexes coordinate to a  $\text{Na}^+$  ion to give trinuclear complexes  $[(M^{\text{II}}\text{salen})_2\text{Na}]^+$  (Chart 3a). The reaction of  $[M^{\text{II}}\text{salen}]$  ( $M = \text{Ni}, \text{Cu}, \text{Co}$ ) with a smaller  $\text{Li}^+$  ion afforded 1:1 adducts  $(M^{\text{II}}\text{salen})\text{LiX}$  ( $M = \text{Cu}$  [46],  $\text{Co}$  [46],  $\text{Ni}$  [53]), while the larger  $\text{K}^+$  ion can accommodate three  $[\text{Ni}^{\text{II}}\text{salen}]$  units to give a tetranuclear complex  $[(\text{Ni}^{\text{II}}\text{salen})_3\text{K}]^+$  [51, 54] (Chart 3b). Thus, the structure of



**Scheme 3** Bimetallic complexes of salen ligand with cobalt and sodium ions

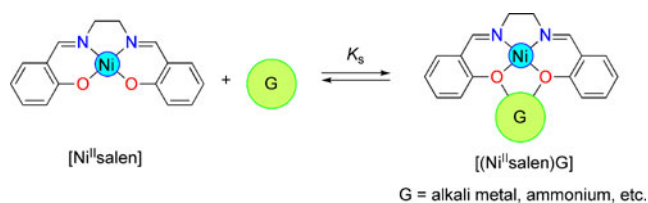


**Chart 3**  $[M^{\text{II}}\text{salen}]$  complexes as ligands for alkali metal ions ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ )

**Table 1** Stability constants ( $K_s$ ) of the complexes between  $[\text{Ni}^{\text{II}}\text{salen}]$  and cations

Guest	$K_s$
NaBPh <sub>4</sub>	98
KBPh <sub>4</sub>	13
CsBPh <sub>4</sub>	~5
NH <sub>4</sub> BPh <sub>4</sub>	50
EtNH <sub>3</sub> BPh <sub>4</sub>	20
Et <sub>2</sub> NH <sub>2</sub> BPh <sub>4</sub>	6.3
Et <sub>3</sub> NHBPh <sub>4</sub>	1.3
NEt <sub>4</sub> BPh <sub>4</sub>	~2

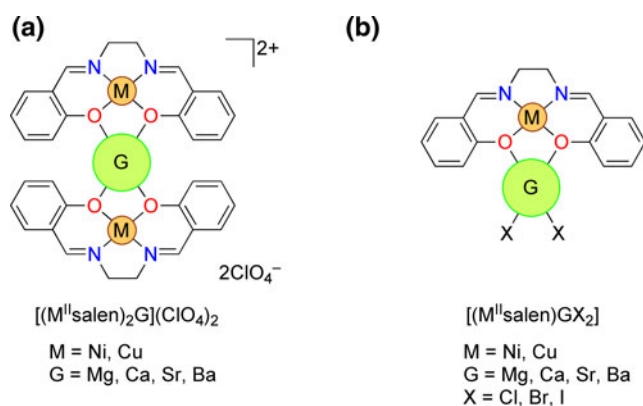
Determined by spectrophotometric titration at 25 °C in acetonitrile (data cited from Refs. [55, 56])

**Scheme 4** Equilibrium for the complexation of  $[\text{Ni}^{\text{II}}\text{salen}]$  with alkali metal or ammonium guests

the adduct complexes depends on the ionic radius of the alkali metal ions.

The binding of the nickel(II) complex  $[\text{Ni}^{\text{II}}\text{salen}]$  toward alkali metal ions in solution was investigated by spectrophotometric titrations (Scheme 4; Table 1) [55]. The stability constants of  $[\text{Ni}^{\text{II}}\text{salen}]$  with alkali metal and ammonium ions are in the order of  $\text{Na}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Cs}^+ > \text{NEt}_4^+$ , clearly showing the  $\text{Na}^+$  selectivity. The  $[\text{Ni}^{\text{II}}\text{salen}]$  also forms an adduct complex with alkylammonium salts with the stability constant order of  $\text{NH}_4^+ > \text{EtNH}_3^+ > \text{Et}_2\text{NH}_2^+ > \text{Et}_3\text{NH}^+$  [56].

The mononuclear  $[\text{M}^{\text{II}}\text{salen}]$  ( $M = \text{Ni}, \text{Cu}$ ) complexes can also coordinate to alkaline earth metal ions. Trinuclear complexes  $[(\text{M}^{\text{II}}\text{salen})_2\text{G}](\text{ClO}_4)_2$  (Chart 4a) were obtained by the complexation of  $[\text{M}^{\text{II}}\text{salen}]$  with  $\text{G}(\text{ClO}_4)_2$  ( $M = \text{Cu}$  [50, 57],  $\text{Ni}$  [58];  $G = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$ ). In the X-ray crystal structure of  $[(\text{Ni}^{\text{II}}\text{salen})_2\text{Ba}](\text{ClO}_4)_2$ , the two

**Chart 4** Structures of  $[\text{M}^{\text{II}}\text{salen}]$  adducts to alkaline earth metal ions**Table 2** Stability constants ( $\log K_1, \log K_2$ ) for  $[(\text{Ni}^{\text{II}}\text{L})_2\text{G}]$  adducts

Guest	$[\text{Ni}^{\text{II}}\text{L}]$		
	$[\text{Ni}^{\text{II}}\text{saloph}]$	$[\text{Ni}^{\text{II}}\text{salen}]$	$[\text{Ni}^{\text{II}}\text{saltn}]$
$\text{Mg}(\text{ClO}_4)_2$	2.8, 4.9	~6.0, ~5.1	Too large
$\text{Ca}(\text{ClO}_4)_2$	3.0, 4.21	3.8, 4.08	Too large
$\text{Sr}(\text{ClO}_4)_2$	2.49, 4.08	3.13, 3.72	Too large
$\text{Ba}(\text{ClO}_4)_2$	2.45, 4.05	3.09, 3.53	3.68, 3.59

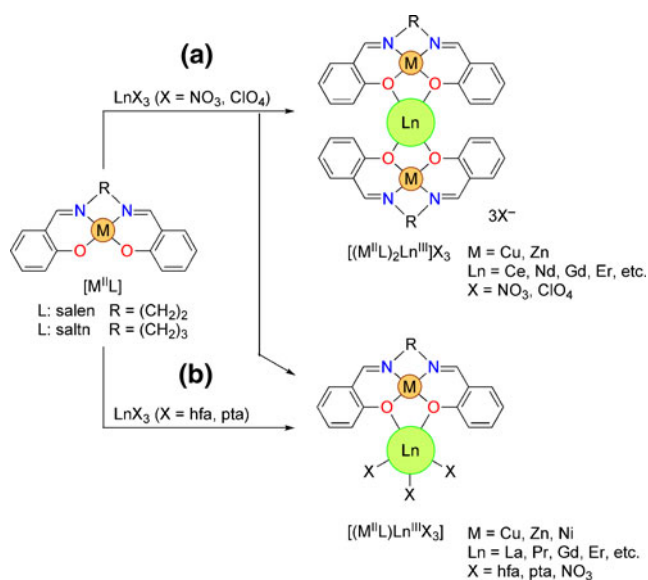
Determined by spectrophotometric titration at 25 °C in acetonitrile (data cited from Ref. [58])

**Scheme 5** Equilibria for the complexation between  $[\text{Ni}^{\text{II}}\text{salen}]$  and alkaline earth metal ions

$[\text{Ni}^{\text{II}}\text{salen}]$  units coordinate to a  $\text{Ba}^{2+}$  ion. However, the formation of two kinds of heteronuclear complexes,  $[(\text{Ni}^{\text{II}}\text{salen})\text{G}]^{2+}$ , then  $[(\text{Ni}^{\text{II}}\text{salen})_2\text{G}]^{2+}$  in solution has been proposed from a spectrophotometric titration study (Scheme 5; Table 2) [58]. Compared to the binding to alkali metal ions, the binding of  $[\text{Ni}^{\text{II}}\text{salen}]$  with divalent alkaline earth metal ions is significantly strong. The stability constants for the complexation with alkali and alkaline earth metal ions increase with the increasing charge density, probably because  $[\text{Ni}^{\text{II}}\text{salen}]$  has no pre-organized cavity for size selective complexation [58]. This indicates that the interaction between  $[\text{Ni}^{\text{II}}\text{salen}]$  and alkaline earth metal ions is mainly governed by the electrostatic term. It is also noteworthy that the stability constants of the three nickel(II) complexes listed in Table 2 are in the order of  $[\text{Ni}^{\text{II}}\text{saltn}] > [\text{Ni}^{\text{II}}\text{salen}] > [\text{Ni}^{\text{II}}\text{saloph}]$ . The flexibility of the linker between two  $\text{sp}^2$  nitrogen donors is suggested to affect the binding strength. Whereas the reaction of  $[\text{Ni}^{\text{II}}\text{salen}]$  with perchlorate salts,  $\text{G}(\text{ClO}_4)_2$ , gave trinuclear species  $[(\text{Ni}^{\text{II}}\text{salen})_2\text{G}](\text{ClO}_4)_2$ , the reaction of  $[\text{M}^{\text{II}}\text{salen}]$  ( $M = \text{Cu}, \text{Ni}$ ) with alkaline earth halide salts,  $\text{GX}_2$  ( $G = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ;  $X = \text{Cl}, \text{Br}, \text{I}$ ), afforded a series of 1:1 adduct complexes  $[(\text{M}^{\text{II}}\text{salen})\text{GX}_2]$  [59] (Chart 4b). Thus, the counter anion significantly influences the stoichiometry and structure of the adduct complexes.

The  $[\text{M}^{\text{II}}\text{salen}]$ -type d-block transition metal complexes also form stable adducts with f-block lanthanide(III) ions [60–62]. In particular, the magnetic interactions in  $\text{Cu}^{\text{II}}/\text{Gd}^{\text{III}}$  and related 3d/4f heterometallic systems are of great interest. The ferromagnetic interactions between copper(II) and gadolinium(III) were first found in  $[(\text{Cu}^{\text{II}}\text{salen})_2\text{Gd}^{\text{III}}](\text{ClO}_4)_3$  and  $[(\text{Cu}^{\text{II}}\text{saltn})\text{Gd}^{\text{III}}(\text{NO}_3)_3]$ , etc. [63, 64], which were synthesized by the reaction of the



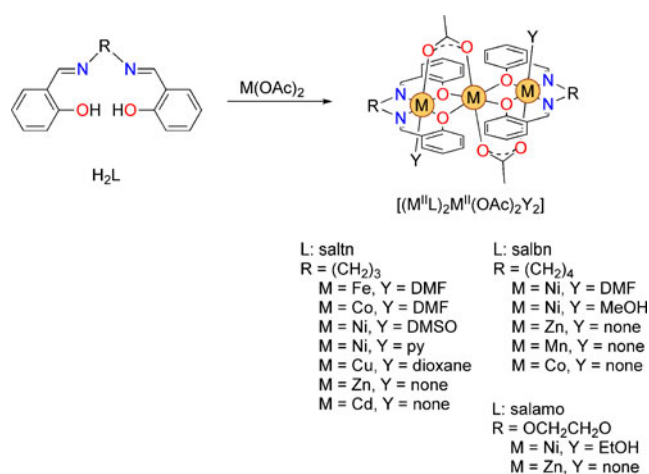


**Scheme 6** Heteronuclear 3d/4f complexes derived from salen-type ligands

mononuclear  $[\text{Cu}^{\text{II}}\text{L}]$  ( $L = \text{salen, saltn}$ ) with  $\text{GdX}_3$  ( $X = \text{ClO}_4, \text{NO}_3$ ) salts (Scheme 6). Using a similar procedure, several copper(II)–lanthanide(III) [65, 66] or zinc(II)–lanthanide(III) [67–69] heterodinuclear complexes were synthesized to study their physical properties. Depending on the reaction conditions, dinuclear  $[(\text{M}^{\text{II}}\text{L})\text{LnX}_3]$  complexes and trinuclear  $[(\text{M}^{\text{II}}\text{L})_2\text{Ln}^{\text{III}}\text{X}_3]$  complexes were obtained ( $L = \text{salen-type ligand}$ ) (Scheme 6a). An ESI–MS study showed that an equimolar mixture of  $[\text{Ni}^{\text{II}}\text{salen}]$  and  $\text{Ln}(\text{NO}_3)_3$  in methanol contains both the  $\text{NiLn}$  and  $\text{Ni}_2\text{Ln}$  species and that the formation of dinuclear  $\text{NiLn}$  species is more favored when the smaller lanthanide is used [70].

On the other hand, the reaction of  $[\text{M}^{\text{II}}\text{salen}]$  ( $M = \text{Cu, Ni}$ ) complexes with lanthanide(III) diketonato complexes  $[\text{LnX}_3]$  ( $X = \text{hfa, pta}$ ) mostly afforded dinuclear 3d/4f complexes  $[(\text{M}^{\text{II}}\text{salen})\text{LnX}_3]$  [71–74] ( $\text{hfa} = 1,1,1,5,5,5$ -hexafluoropentane-2,4-dionate,  $\text{pta} = 1,1,1$ -trifluoro-5,5-dimethylhexane-2,4-dionate) (Scheme 6b), whose magnetic and thermal properties were studied. The corresponding zinc(II)–lanthanide(III) complex  $[(\text{Zn}^{\text{II}}\text{saltn})\text{Eu}(\text{pta})_3]$  was also prepared and its luminescence due to the f–f transition of europium(III) was observed. The stability constant for the formation of  $[(\text{Zn}^{\text{II}}\text{saltn})\text{Eu}(\text{pta})_3]$  from  $[\text{Zn}^{\text{II}}\text{saltn}]$  and  $[\text{Eu}(\text{pta})_3]$  is  $\log \beta = 4.13$  in chloroform, which is significantly higher than that for the  $\text{H}_2\text{saltn}[\text{Eu}(\text{pta})_3]$  system ( $\log \beta = 2.95$ ) [75]. This indicates that the conversion of  $\text{H}_2\text{saltn}$  into  $[\text{Zn}^{\text{II}}\text{saltn}]$  significantly enhances the binding ability to the  $\text{Eu}^{3+}$  ion.

The mononuclear  $[\text{M}^{\text{II}}\text{salen}]$  complexes can coordinate not only to the group 1–3 metals but also to d-block transition metals. The reaction of  $[\text{M}^{\text{II}}\text{salen}]$ -type complexes

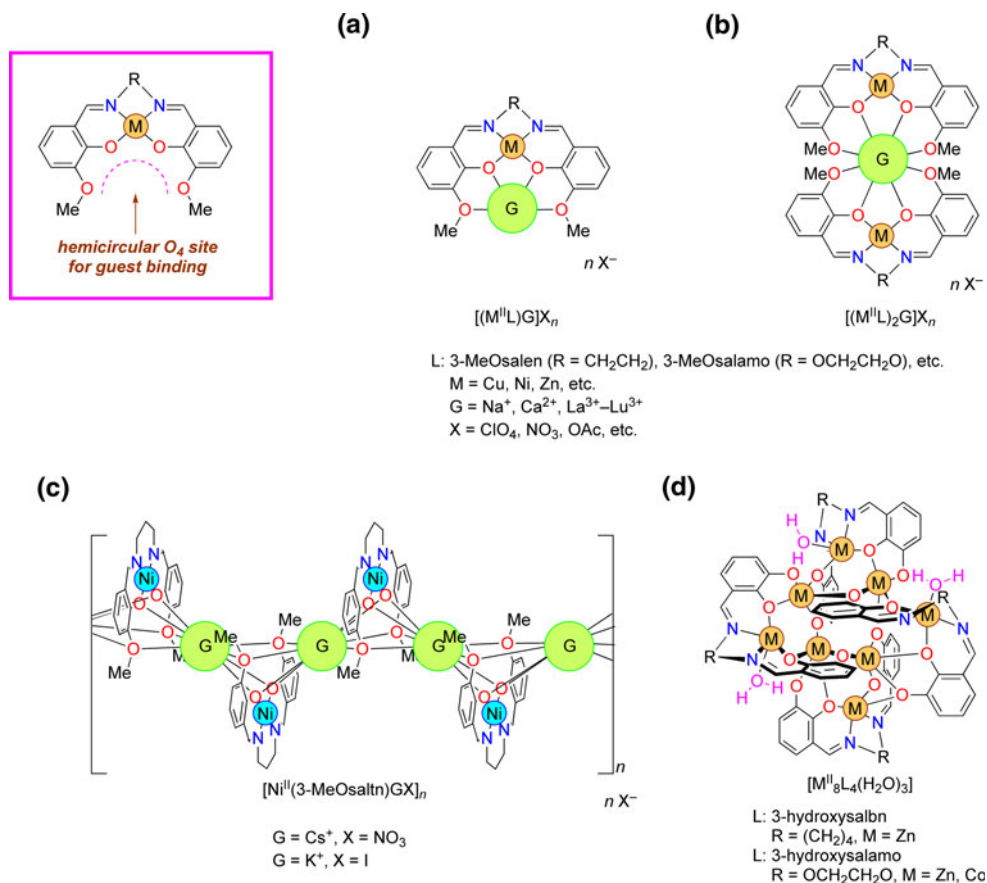


**Scheme 7** Formation of trinuclear complexes by the reaction of salen-type ligands with a transition metal acetate

with transition metal salts afforded various kinds of adduct complexes [50, 57, 76–81]. In some cases, homotrimeric complexes  $[(\text{M}^{\text{II}}\text{L})_2\text{M}^{\text{II}}(\text{OAc})_2\text{Y}_2]$  were directly obtained by the reaction of the salen-type ligands  $\text{H}_2\text{L}$  with metal acetate,  $\text{M}(\text{OAc})_2$  ( $M = \text{divalent d-block metals}$ ) (Scheme 7) [82–93]. Ligands with a longer N–N bridge, such as saltn, salbn, and salamo, are likely to form this type of trinuclear structures when complexed with cobalt(II), zinc(II), manganese(II), etc. In these complexes, the two  $[\text{M}^{\text{II}}\text{L}]$  units are bound together by the third  $\text{M}^{\text{II}}$  ion via  $\mu$ -phenoxo bridges as well as the  $\mu$ -acetato ligands. Heterotrimeric analogues  $[(\text{M}^{\text{II}}\text{L})_2\text{M}^{\text{II}}(\text{OAc})_2]$  ( $M \neq M'$ ) with a similar structure have also been prepared [94–99]. On the other hand, the complexation of the salen-type ligands with lanthanide(III) ions instead of d-block metal ions afforded several kinds of oligometallic complexes or coordination polymers [100, 101].

When the salen-type ligands have methoxy groups at the 3,3'-positions, these groups take part in the coordination [89, 102]. The methoxy groups improve the *coordinating ability* of the  $[\text{M}^{\text{II}}\text{salen}]$ -type unit by changing the bidentate bis(phenoxo)  $\text{O}_2$  chelate site into a hemicircular  $\text{O}_4$  binding site (Chart 5). The  $\text{O}_4$  donor set consisting of two phenoxo and two methoxy groups is particularly suitable for the tetradentate chelate coordination to larger cations such as the group 1–3 metals. Using these kinds of ligands, a large number of heterometallic  $[\text{M}^{\text{II}}(3\text{-MeOsalen})\text{Ln}]$ -type complexes can be synthesized (Chart 5a). In particular,  $\text{Cu}^{\text{II}}/\text{Gd}^{\text{III}}$  and related 3d/4f heterodinuclear complexes [103–119] are of interest because of their magnetic exchange interactions. This basic idea has also been applied to the synthesis of the  $\text{Zn}^{\text{II}}/\text{Ln}^{\text{III}}$  heterodinuclear complexes that exhibit a visible ( $\text{Ln} = \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Tb}^{3+}$ , etc.) or near IR ( $\text{Ln} = \text{Nd}^{3+}, \text{Yb}^{3+}$ , etc.) luminescence [120–126]. An ESI–MS study clearly showed that the

**Chart 5** 3-MeOsalen-type ligands for **a** dinuclear complexes, **b** trinuclear complexes, and **c** coordination polymers. **d** Octanuclear clusters obtained from 3-hydroxysalbn or 3-hydroxysalamo ligand



interaction of  $[Ni^{II}(3-MeOsalen)]$  with  $Ln^{3+}$  ( $=La^{3+}$ ,  $Eu^{3+}$ ,  $Lu^{3+}$ ) is stronger than that of  $[Ni^{II}salen]$  [70]. This result indicates that the methoxy groups improve the *coordinating ability* of the  $[M^{II}salen]$  unit.

Trinuclear  $[(M^{II}(3-MeOsalen))_2Ln]$ -type complexes (M = Ni, Cu [127], Zn [128–131]) were also synthesized from the 3-MeOsalen-type ligands (Chart 5b). In these complexes, the lanthanide(III) ion is almost completely surrounded by two sets of the tetradentate O<sub>4</sub> donor sets. The formation ratio of the dinuclear  $ZnLn$  and trinuclear  $Zn_2Ln$  complexes for the  $[Zn^{II}(3-MeOsalamo)]-Ln(NO_3)_3$  system depends on the ionic radius of the lanthanide(III) ions [126, 132]. Larger lanthanide(III) ions, such as  $La^{3+}$ , can accommodate two  $[Zn^{II}(3-MeOsalamo)]$  units to give a  $Zn_2Ln$  complex, whereas the smaller lanthanide(III) ions ( $Sm^{3+}-Lu^{3+}$ ) can interact with only one  $[Zn^{II}(3-MeOsalamo)]$  unit to give a dinuclear  $ZnLn$  complex.

In addition to the above-mentioned rare earth metal complexes, the  $[M^{II}(3-MeOsalen)]$ -type units can form various kinds of heteronuclear complexes containing alkali [46, 133–136] or alkaline earth metals [137]. The reaction of the  $[M^{II}(3-MeOsalen)]$  complexes with these metal ions gave a stable 1:1 adduct  $[(M^{II}(3-MeOsalen))G]X_n$  or 2:1 trinuclear complex  $[(M^{II}(3-MeOsalen))_2G]X_n$ , depending on the ionic radius of G and the counter anions (Chart 5a,

b). The  $[M^{II}(3-MeOsaln)]$ -alkali metal systems have also been used to synthesize coordination polymers in which the alkali metal ions are infinitely connected by the phenoxo groups of the  $[M^{II}(3-MeOsaln)]$  bridges (for example, see Chart 5c) [133, 138–140]. When the d-block metal ions are absent, oligometallic complexes containing several lanthanide(III) ions were formed upon the complexation of the 3-MeOsalen-type ligands with the lanthanide(III) salt [141, 142].

The introduction of hydroxy groups at the 3,3'-positions significantly changes the complexation behavior. The 3-hydroxysalbn [143, 144] and 3-hydroxysalamo [145] ligands formed an interesting octanuclear cluster structure upon complexation with zinc(II) or cobalt(II) acetate (Chart 5d). The ligand has two catecholato coordination sites in addition to the N<sub>2</sub>O<sub>2</sub> chelate site. The catecholato-type coordination significantly affects the *coordinating behavior* of the  $[M^{II}salen]$ -type complexes, leading to a unique oligometallic structure.

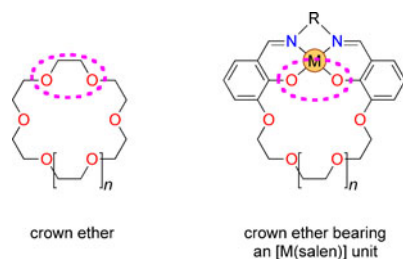
Therefore, mononuclear  $[M(salen)]$ -type complexes behave as a ligand to the group 1–3 and transition metals to give the *adduct* complexes. Some of them are stable enough to be isolated as crystalline hetero- or homo-multimetallic complexes. In all the complexes, the bridging of the phenoxo moieties plays an important role in the

formation of the oligometallic structures. The binding study with guest cations in solution clearly demonstrated that the *coordinating ability* is mainly governed by the electrostatic interaction between the phenoxo groups and the guest cation. This *coordinating ability* of these mono(salen)-type complexes should be taken into account for understanding the guest-binding behavior of the macrocyclic salen and acyclic oligo(salen) derivatives described in this review.

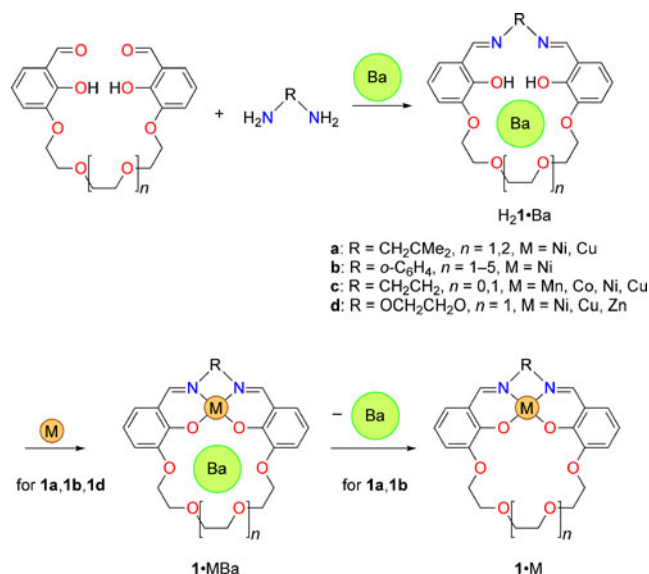
### Salen-containing macrocycles and their ion recognition ability

A crown ether is one of the most important host molecules that can bind alkali metal ions [27]. In many cases, each of the oxygen atoms coordinates to the guest metal ion in a convergent fashion. If the two neighboring oxygen atoms, the  $-\text{OCH}_2\text{CH}_2\text{O}-$  fragment, are replaced by an  $[\text{M}(\text{salen})]$  unit, a stronger guest binding is expected due to the negative charge of the two neighboring phenoxo oxygen atoms (Chart 6).

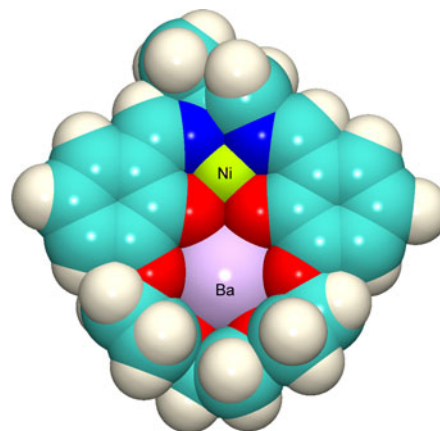
In fact, crown ethers in which one of the  $-\text{OCH}_2\text{CH}_2\text{O}-$  fragments is replaced with an  $[\text{M}(\text{salen})]$  unit was first developed by D. N. Reinhoudt [146–151]. This class of complexes  $1\cdot\text{M}$  ( $\text{M} = \text{Ni}, \text{Cu}, \text{Zn}$ ) was synthesized by cyclization of a dialdehyde and a diamine in the presence of a barium salt followed by the complexation with a d-block metal and removal of the template  $\text{Ba}^{2+}$  ion (Scheme 8). The heterometallic dinuclear complexes  $1\cdot\text{MBa}$  contain a d-block metal ion such as nickel(II), copper(II), or zinc(II) in the *soft* salen-type binding site and a  $\text{Ba}^{2+}$  and  $\text{Cs}^+$  ion as the template in the *hard* crown ether cavity (Fig. 2). Although no stability constants in solution have been reported, the host–guest complexes  $\text{H}_21\cdot\text{Ba}$  and  $1\cdot\text{MBa}$  are stable enough to be isolated as crystals. The electrochemical properties due to the d-block metals are affected by the presence or absence of the template  $\text{Ba}^{2+}$  ion. To date, several analogous ligands have been synthesized to obtain the heterodinuclear complexes containing  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{La}^{3+}$ , etc. [152–157]. Some of the compounds showed a catalytic activity in organic reactions [158–161]



**Chart 6** Design of crown ethers bearing an  $[\text{M}(\text{salen})]$  unit



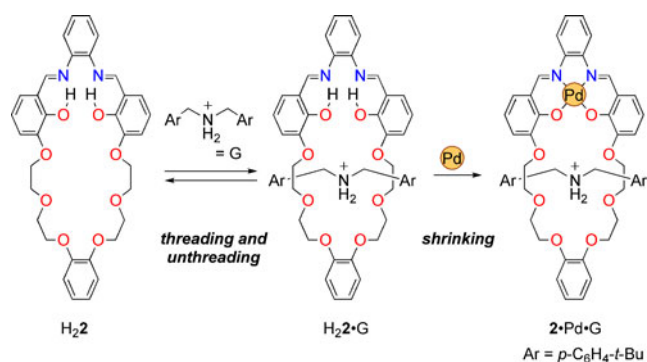
**Scheme 8** Synthesis of  $[\text{M}^{\text{II}}(\text{salen})]$ -containing crown ethers  $1\cdot\text{M}$



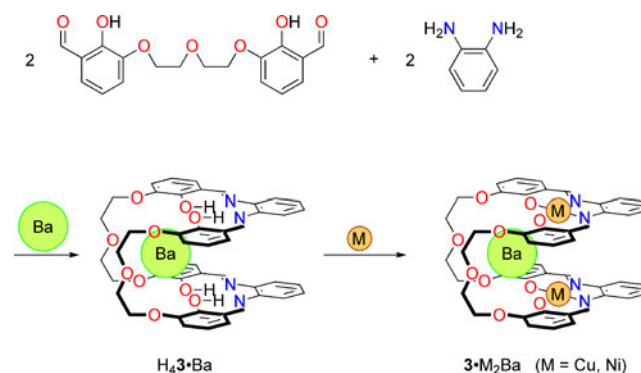
**Fig. 2** X-ray crystal structure of  $1\cdot\text{NiBa}$  reported by D. N. Reinhoudt et al. The counter anions and solvent molecules are omitted

or act as SOD/catalase mimetics [162]. These macrocycles are regarded as a kind of compartmental ligand [163–167] that has two coordination sites separated by two phenoxo oxygen atoms. Salen-containing macrocyclic compounds having a binaphthocrown ether [168, 169], spherand [148, 170], calixcrown [171], cyclic amide [172–174], and SCS-pincer ligand [175] have also been designed for the recognition of guest species including organic molecules.

One of the important features of the macrocycles containing a salen-type coordination site is that the metalation of the salen moiety makes the macrocycle more rigid. The four coordination bonds that are newly formed make the effective size of the cavity smaller. This shrinkage of a macrocycle by metalation was used to *lock* a rotaxane structure (Scheme 9) [176, 177]. A saloph-crown ether  $\text{H}_22$



**Scheme 9** Rotaxane synthesis using the threading followed by shrinking protocol based on saloph-crown ether  $H_2$

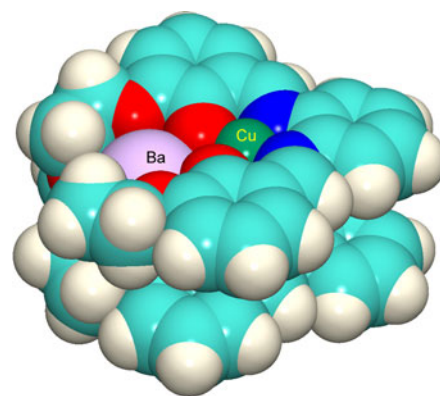


**Scheme 10** Synthesis of metal complexes of bis(saloph) crown ether  $H_43$  using  $Ba^{2+}$  ion as a template

formed a host–guest complex  $H_2 \cdot G$  with a dialkylammonium salt ( $G$ ) having a pseudorotaxane structure. This pseudorotaxane  $H_2 \cdot G$  existed as an equilibrated mixture of separate entities and the complexed form. However, when palladium(II) was added to the mixture, the pseudorotaxane  $H_2 \cdot G$  was converted into a rotaxane  $2 \cdot Pd \cdot G$  which can no longer dissociate into the constituents. This method, *threading followed by shrinking*, can be a new protocol for rotaxane synthesis in which the shrinking retards the equilibrium at the final stage. Another protocol for the rotaxane synthesis utilizes the modulation of the C=N bond recombination kinetics by complexation at the salen site [178]. The threading of the axle occurs in the absence of metal ions due to the C=N bond recombination, but the complexation with nickel(II) locks the threading/unthreading to give the rotaxane structure.

Crown ethers containing two  $[M(\text{salen})]$  units have also been designed. A macrocycle  $H_43 \cdot Ba$  was synthesized from the dialdehyde and diamine in the presence of  $Ba^{2+}$  as a template (Scheme 10) [179, 180]. The obtained host–guest complex  $H_43 \cdot Ba$  is stable enough to be isolated as crystals. This high stability is closely related to the template effect during the macrocyclization.  $Cs^+$  was also effective as a template for the  $[2 + 2]$  macrocyclization. The mononuclear barium complex  $H_43 \cdot Ba$  was easily converted into the corresponding heterodinuclear complexes  $3 \cdot M_2Ba$  ( $M = Cu, Ni, Zn$ ), some of which were identified by X-ray crystallography. In the crystal structure of  $3 \cdot M_2Ba$  ( $M = H_2, Cu, Ni$ ), all ten oxygen atoms (four phenolic and six ether oxygen atoms) coordinate to the  $Ba^{2+}$  ion so that the macrocyclic framework completely surrounds the  $Ba^{2+}$  ion (Fig. 3). A similar bis(salen) ligand formed a  $Zn_2Ba$  heterotrimeric complex, which can recognize amine derivatives [181].

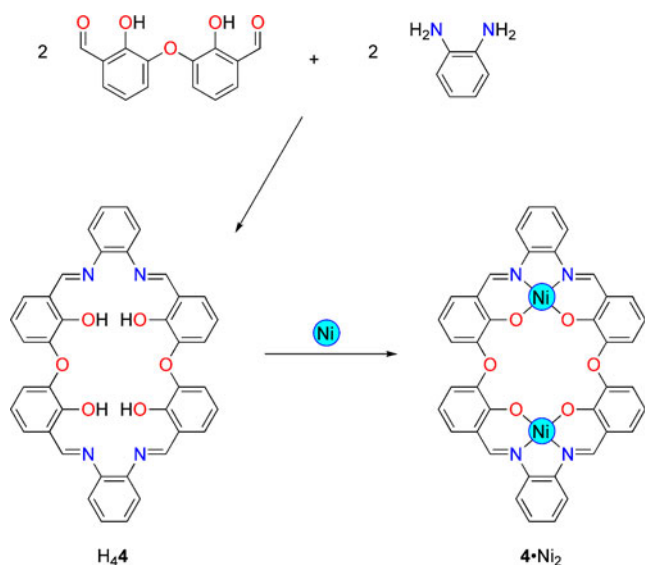
A smaller bis(salen)-type crown ether  $H_44$ , which has a cavity similar to 18-crown-6, was also synthesized [182]. In contrast to the above mentioned larger derivative  $H_43$ , a template metal was not required for the synthesis. The



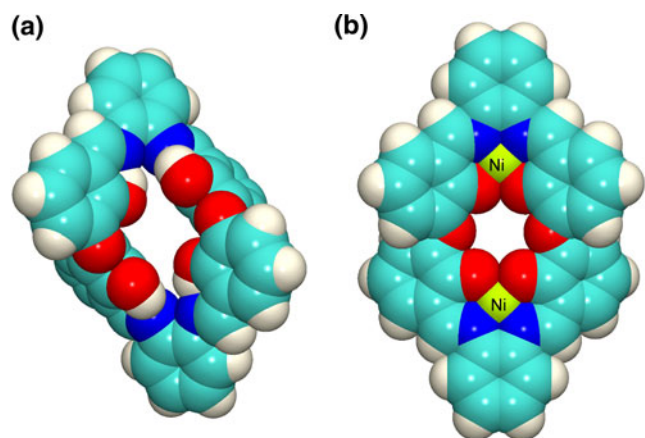
**Fig. 3** X-ray crystal structure of  $3 \cdot Cu_2Ba$  reported by D. N. Reinhoudt et al. The counter anions and solvent molecules are omitted

reaction of a diformyl diphenyl ether derivative with *o*-phenylenediamine gave the  $[2 + 2]$  cyclic product  $H_44$  in high yield without using the metal salt as a template (Scheme 11). However, this ligand  $H_44$  in its uncomplexed form did not show any noticeable binding affinity toward alkali metal ions ( $Na^+, K^+, Rb^+, Cs^+$ ). This poor binding affinity is reasonably explained by the properties of the oxygen donor atoms; both of the phenol oxygen atoms and biaryl ether oxygen atoms have a lower coordination ability to metal ions than the dialkyl ethers or alkyl aryl ethers. Furthermore, its non-planar structure, in which not all the phenolic oxygen atoms are directed inwardly to the cavity (Fig. 4a), is also responsible for the poor binding affinity. However, the conversion of the ligand  $H_44$  into the corresponding dinickel(II) complex  $4 \cdot Ni_2$  significantly changed the binding behavior due to the newly formed eight coordination bonds. The X-ray crystallographic analysis revealed that the dinuclear complex  $4 \cdot Ni_2$  adopted a planar structure. All six oxygen atoms are directed inwardly to the cavity and make a hexagonal array, which approximates an 18-crown-6 (Fig. 4b). Thus, the oxygen donor atoms of  $4 \cdot Ni_2$  are well preorganized for ion recognition.

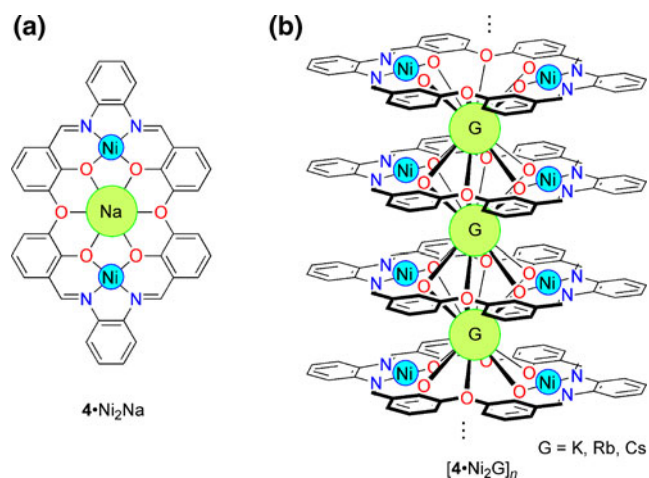




**Scheme 11** Synthesis of bis(saloph) macrocycle  $H_44$  and its metal complex  $4 \cdot Ni_2$



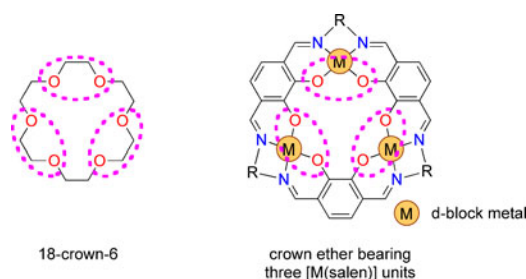
A spectroscopic study showed that the metallohost,  $4 \cdot Ni_2$ , very strongly binds a  $Na^+$  ion in DMSO to afford the 1:1 metallohost–guest complex,  $4 \cdot Ni_2Na$  (Chart 7a). The binding affinity is significantly enhanced in an off/on fashion by the conversion from the bis(saloph) ligand  $H_44$  to the nickel(II) complex  $4 \cdot Ni_2$ . The enhancement of the binding affinity was also observed for  $K^+$ ,  $Rb^+$ , and  $Cs^+$ . In these cases, however, the complexation afforded several kinds of oligomeric species, such as 2:1, 3:2, 4:3 (ligand/metal) complexes, as well as the 1:1 complex. Since the parent 18-crown-6 ether can form a 2:1 or 3:2 sandwich complex with a larger alkali metals, such as  $Rb^+$  and  $Cs^+$  [183], the oligomeric complexes of  $4 \cdot Ni_2$  should adopt a sandwich or club sandwich structure, in which two or more flat molecules of  $4 \cdot Ni_2$  are held together by the guest metal ions (Chart 7b). The phenoxo oxygen atoms also contribute



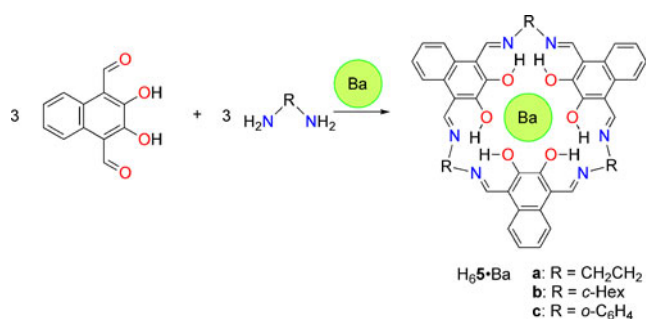
**Chart 7** Proposed structures of metallohost–guest complexes of  $4 \cdot Ni_2$  with alkali metal ions

to the O–G–O bridged structure as seen in the  $H_2(3\text{-MeOsalt})$  coordination polymers (see Chart 5c) [133]. Consequently, the conversion of the macrocycle  $H_44$  into the planar metallohost  $4 \cdot Ni_2$  not only enhances the guest binding affinity, but also induces the metal-assisted assembly with the stacking structures. This complexation at the saloph sites makes the molecular structure more rigid and planar, thus favorable for the aggregate formation.

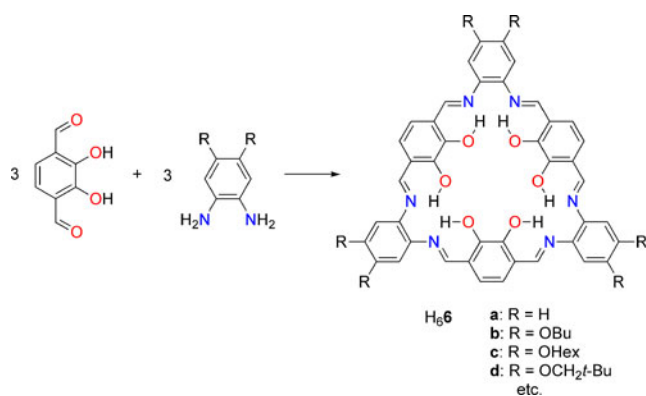
When all the three  $-OCH_2CH_2O-$  fragments of the 18-crown-6 are replaced by three  $[M(\text{salen})]$  units, the cavity is surrounded by six negatively-charged phenoxo oxygen atoms (Chart 8). An extremely high binding affinity toward hard metal ions is expected due to the negatively charged phenoxo groups integrated in a cyclic fashion, as predicted from the examples of metallacrown ethers having peripheral coordination sites for d-block metals and a central cavity [184, 185]. A useful building block for the tris(salen) macrocycles is 2,3-dihydroxybenzene-1,4-dicarbaldehyde, from which various kinds of tris(salen)-type macrocyclic ligands can be prepared. The first tris(salen)-type macrocycles  $H_65\text{-Ba}$  were synthesized in  $\sim 70\%$  yield by the reaction of 2,3-dihydroxynaphthalene-



**Chart 8** Design of metallohosts derived from tris(salen)-type macrocyclic ligands



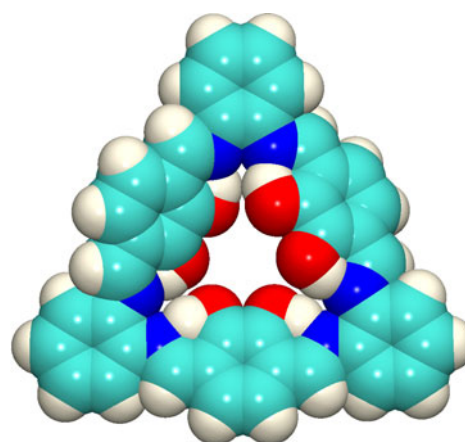
**Scheme 12** Synthesis of tris(salen)-type macrocyclic complexes  $H_65 \cdot Ba$  using  $Ba^{2+}$  ion as a template



**Scheme 13** Non-template synthesis of tris(saloph) macrocyclic ligands  $H_66$

1,4-dicarbalddehyde with a series of diamines in the presence of a barium salt as the template (Scheme 12) [186]. The [3 + 3] macrocyclization of the dialdehyde with the diamines efficiently took place, while the [4 + 4] macrocycle was obtained when propane-1,3-diamine was used. However, the ion recognition ability of these macrocycles was not reported.

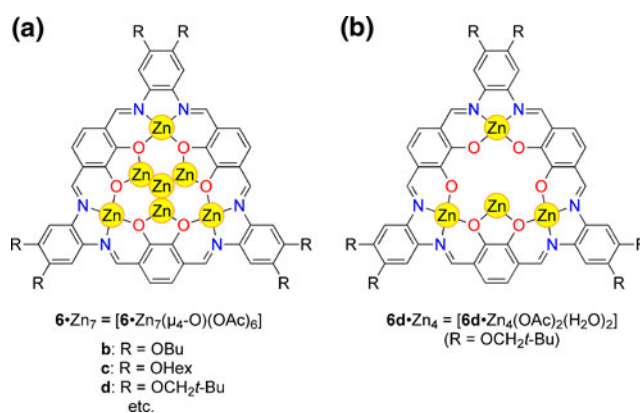
This type of macrocycle was also synthesized without using the template ion. The reaction of 2,3-dihydroxybenzene-1,4-dicarbaldehyde with *o*-phenylenediamine almost quantitatively afforded the [3 + 3] macrocycle  $H_66a$  (Scheme 13) [187]. The reason for the highly efficient cyclization can be explained by the following kinetic and thermodynamic aspects. During the final stage of the [3 + 3] cyclization, the intramolecular O–H...N hydrogen bonds as well as the rigid phenylene framework make the amino and formyl groups close to each other so that the cyclization is kinetically favored. Furthermore, the less strained [3 + 3] macrocycle is predominantly formed as the result of the thermodynamic equilibration due to the dynamic feature of the C=N bonds [188], even if acyclic oligomers or macrocycles with different sizes are initially formed. The low solubility of the [3 + 3] macrocycle  $H_66a$  may also contribute to the efficient formation. In the crystal



**Fig. 5** X-ray crystal structure of tris(saloph) macrocycle  $H_66a$

structure, the tris(saloph)  $H_66a$  adopts an almost planar structure in which the six phenolic oxygen atoms are directed inwardly (Fig. 5). The larger macrocyclic tris(saloph) ligands were also synthesized using a similar non-template procedure [189–193].

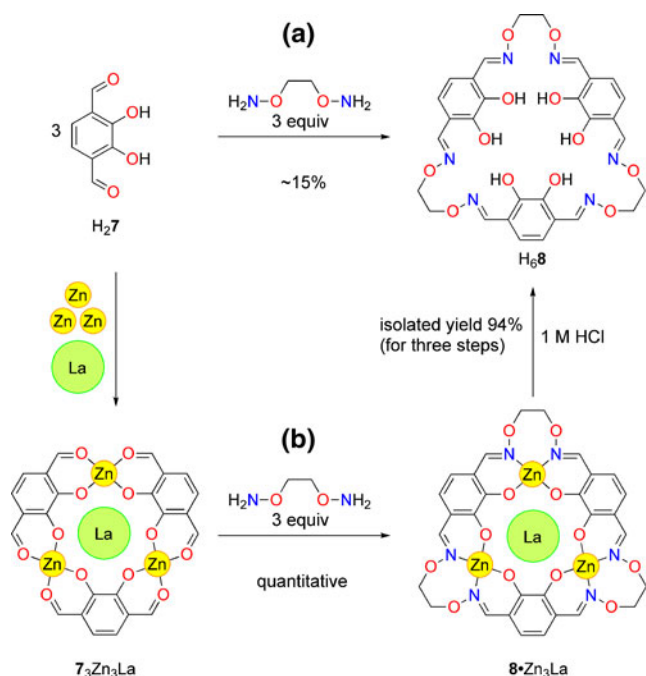
The metal complexation behavior was investigated for more soluble analogues [194–202] such as  $H_66b$ – $H_66d$  having alkoxy groups. The ligand  $H_66c$  binds alkali metal ions  $G$  ( $=Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ) in the central  $O_6$  site to give the host–guest complexes  $H_66c \cdot G$ , which form a tubular aggregate in solution [194]. On the other hand, the metalation of the three peripheral saloph sites with d-block transition metals led to somewhat unexpected results [197–202]. The complexation of  $H_66$  with an excess amount of zinc(II) acetate almost quantitatively afforded the heptanuclear complex  $6 \cdot Zn_7$ , in which three zinc(II) ions are in the saloph coordination sites and a tetrahedral  $Zn_4(\mu_4-O)$  unit is in the central  $O_6$  cavity (Chart 9a) [197, 198]. Although the macrocycle  $H_66$  has three saloph sites, the



**Chart 9** Oligometallic complexes obtained by the reaction of  $H_66$  with zinc(II) acetate. In the structural formulae, the counter anions and solvent molecules coordinating to the metal ions are omitted for clarity

trinuclear complex with a vacant  $O_6$  cavity was difficult to be isolated in its discrete form because of the aggregation [198]. Upon the reaction with 4 equiv of zinc(II), a tetranuclear complex  $6 \cdot Zn_4$ , which has the fourth zinc(II) in the  $O_6$  cavity, was obtained (Chart 9b) [202]. The complexation with zinc(II) in the central  $O_6$  cavity is ascribed to the accumulated phenoxo groups inwardly directed, which can coordinate to the zinc(II) ions in a catecholato fashion. In fact, the zinc(II) ions in the  $O_6$  cavity of the hepta- or tetranuclear complexes  $6 \cdot Zn_7$  and  $6 \cdot Zn_4$  are always coordinated by the macrocyclic moiety in a catecholato fashion. A related catecholato-type coordination was also observed for the octanuclear zinc(II) complexes of the hydroxy-substituted mono(salen)-type ligands (3-hydroxysalbn or 3-hydroxysalamo) as described above (see Chart 5d) [143–145].

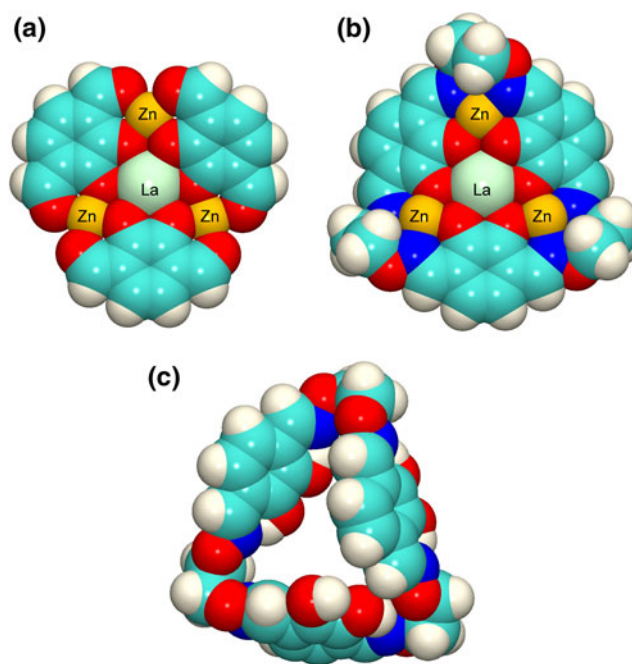
In contrast to the Schiff base macrocycles  $H_66$ , the macrocyclization reaction of the 2,3-dihydroxybenzene-1,4-dicarbaldehyde ( $H_27$ ) with 1,2-bis(aminoxy)ethane afforded the [3 + 3] macrocyclic oxime ligand  $H_68$  in low yield ( $\sim 15\%$ ) [203] (Scheme 14a). The low efficiency of the macrocyclization is attributed to the inertness of the oxime functionality compared to the imine analogues [204, 205]. While the imines undergo C=N bond recombination in solution, the oximes do not undergo such a reaction under the typical conditions [206]. Consequently, the equilibration to the most thermodynamically stable macrocycle does not occur. The GPC analysis of the cyclization products indicated the formation of various kinds of cyclic and acyclic oligomers.



**Scheme 14** Oligometallic template synthesis for macrocyclic tris(salamo) ligand  $H_68$

Noteworthy is the fact that the efficiency of the [3 + 3] cyclization reaction is dramatically improved when zinc(II) and lanthanum(III) ions are present. After the demetalation with dilute hydrochloric acid, the free macrocyclic oxime ligand  $H_68$  was isolated in 94% yield based on the starting dialdehyde  $H_27$  (Scheme 14b). Apparently, the zinc(II) and lanthanum(III) ions act as a template for the cyclization. Such a significant *oligometallic template* effect, in which multiple metal ions simultaneously act as the template for the cyclization, is quite rare [207–212]. In particular, this is the first example of the *hetero-oligometallic template* effect where different kinds of metal ions simultaneously act as the template.

The highly efficient macrocyclization by the *oligometallic template* can be explained by an important intermediate, the  $Zn_3La$  tetranuclear complex of the dialdehyde  $H_27$ . This discrete complex,  $7_3Zn_3La$ , was quantitatively formed when the dialdehyde,  $H_27$ , was mixed with zinc(II) (1 equiv) and lanthanum(III) (1/3 equiv). In the X-ray crystal structure of  $7_3Zn_3La$ , the salicylaldehyde moieties of the dialdehyde  $H_27$  coordinate to the  $Zn^{2+}$  ions at the periphery and the catechol moiety to the  $La^{3+}$  ion at the center (Fig. 6a), as seen in the related self-assembled metallacrowns [213, 214]. The reaction of this tetranuclear complex,  $7_3Zn_3La$ , with 3 equiv of 1,2-bis(aminoxy)ethane almost quantitatively took place to afford the corresponding macrocyclic complex,  $8 \cdot Zn_3La$ . The X-ray structure of the resulting complex,  $8 \cdot Zn_3La$  (Fig. 6b), is



**Fig. 6** X-ray structures of **a**  $7_3Zn_3La$ , **b**  $8 \cdot Zn_3La$ , and **c**  $H_68$ , showing the structural similarity of  $7_3Zn_3La$  and  $8 \cdot Zn_3La$ . The counter anions and solvent molecules are omitted. Reprinted with permission from Ref. [203]



remarkably similar to the initial tetranuclear complex  $7_3Zn_3La$ . This indicates that the macrocyclization requires very little structural change in the dialdehyde moieties because of coordination to the  $Zn_3La$  tetranuclear core. The almost complete conversion is ascribed to the seven-membered ring-closure, which presumably more easily takes place than the 36-membered ring closure in the absence of the template metals. Furthermore, the free macrocyclic ligand  $H_6\mathbf{8}$  (Fig. 6c) was obtained by demetalation with dilute hydrochloric acid because of the high chemical stability of the oxime functionality under the acidic hydrolytic conditions.

The  $H_6\mathbf{8}$  ligand formed two types of hexanuclear complexes,  $8_2Zn_6$  then  $8\cdot Zn_6$ , upon complexation with zinc(II) (Scheme 15a, b) [215]. It is noteworthy that each of the complexation steps very efficiently took place. When less than 3 equiv of zinc(II) were present, only the first complex  $8_2Zn_6$  was observed. As seen in the imine analogue  $H_6\mathbf{6}$ , the formation of the trinuclear species  $8\cdot Zn_3$  with a vacant  $O_6$  cavity is unfavorable. The unique unsymmetrical dimeric structure formulated as  $[8\cdot Zn_3]_2\text{-}Zn_2\text{-}[H_2\mathbf{8}\cdot Zn]$  is clearly demonstrated by the X-ray crystallography as well as the MS and NMR studies. Contrary to the corresponding imine analogues  $H_6\mathbf{6}$  that formed an oligomeric mixture of  $6\cdot Zn_3$ , the oxime macrocycle,  $H_6\mathbf{8}$ , exclusively gave the unsymmetrical dimer  $8_2Zn_6$ . When more than 3 equiv of zinc(II) are added, the second hexanuclear complex  $8\cdot Zn_6$  begins to form. This complex  $8\cdot Zn_6$  has a monomeric structure in which a  $Zn_3(\mu_3\text{-OH})$  unit occupies the central

$O_6$  cavity of the trimetalated ligand,  $8\cdot Zn_3$ . Consequently, the ligand  $H_6\mathbf{8}$  undergoes an apparent two-step conversion to  $8_2Zn_6$ , then  $8\cdot Zn_6$ . This is in stark contrast to the complexation behavior of the imine analogues  $H_6\mathbf{6}$ , which forms a 1:4 complex, then a 1:7 complex.

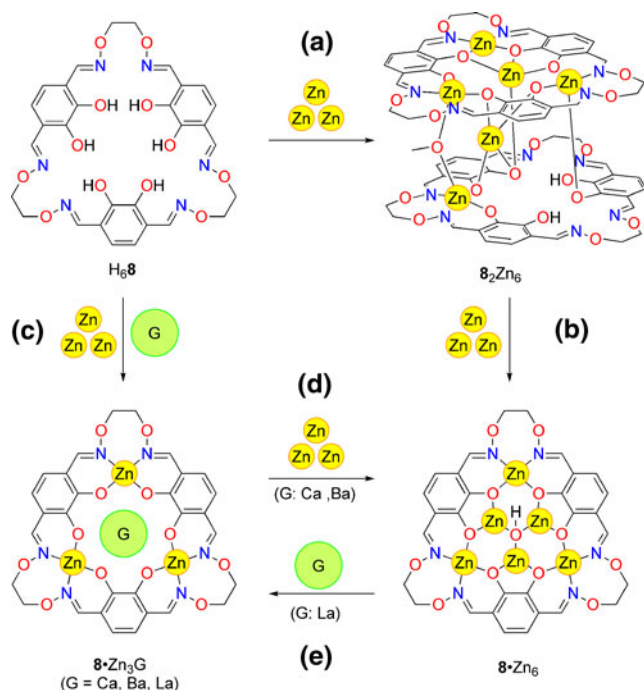
Although the  $8\cdot Zn_3$  with a vacant  $O_6$  site is difficult to prepare, the ligand  $H_6\mathbf{8}$  can recognize a guest metal ion in the presence of three equiv of zinc(II) ions. When the ligand  $H_6\mathbf{8}$  was reacted with 3 equiv of zinc(II) and 1 equiv of the guest ion  $G$  ( $=Ca^{2+}$ ,  $Ba^{2+}$ ,  $La^{3+}$ , etc.), the metallohost–guest complex  $8\cdot Zn_3G$  was quantitatively formed (Scheme 15c). This should be driven by the thermodynamic equilibration, because the different nature of the peripheral  $N_2O_2$  sites and the central  $O_6$  cavity is particularly suitable for the site-selective metalation with two different metal sources. However, the heterometallic complexes,  $8\cdot Zn_3Ca$  and  $8\cdot Zn_3Ba$ , were completely converted into the homometallic complex,  $8\cdot Zn_6$ , when an additional 3 equiv of zinc(II) ions were present (Scheme 15d). On the other hand, the homometallic  $8\cdot Zn_6$  was quantitatively converted into  $8\cdot Zn_3La$  when 1 equiv of  $La^{3+}$  was added (Scheme 15e). As a result, the apparent binding affinity in the central  $O_6$  site is in the order of  $Ca^{2+}$ ,  $Ba^{2+} < Zn_3(\mu_3\text{-OH}) < La^{3+}$ .

The relatively rigid framework of the metalated tris(salen)-type macrocycle is also useful to design a ligand field for the metal ion in the central  $O_6$  cavity. It is usually difficult to precisely design a ligand field of the group 1–3 metals because of the flexible coordination geometry. However, the six phenoxo oxygen atoms of the macrocyclic systems are arranged in a cyclic fashion around the guest metal  $G$ . This structural constraint leads to an easy-axis magnetic anisotropy for lanthanide(III), resulting in an SMM (single-molecule magnet) behavior as predicted from the coordination environment [216, 217].

Consequently, the integrated salen moieties provide a unique environment for the homo- and heterometallic complexes. The complexation at the peripheral salen-type coordination sites of the bis- or tris(salen) macrocycles with d-block metal ions makes a cavity surrounded by multiple phenoxo groups, in which subsequent complexation with the group 1–3 metals or d-block is significantly enhanced. This unique multi-metal complexation behavior probably results from both the macrocyclic effect and the *coordinating ability* of the  $[M^II\text{salen}]$  units due to the negative charges.

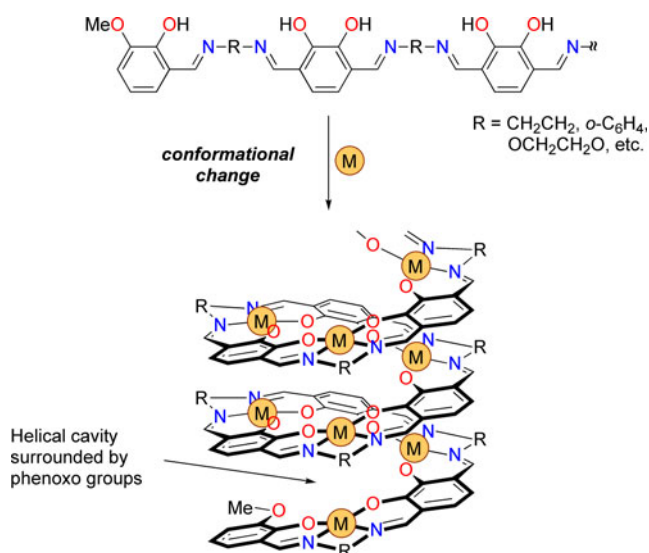
### Linear oligo(salen) ligands for helical metallohost–guest complexes

In the design of oligo(salen) host molecules, the salen-type coordination sites need to be arranged in such a way that all



**Scheme 15** Summary of the oligometal complexation of tris(salamo) macrocyclic ligand  $H_6\mathbf{8}$

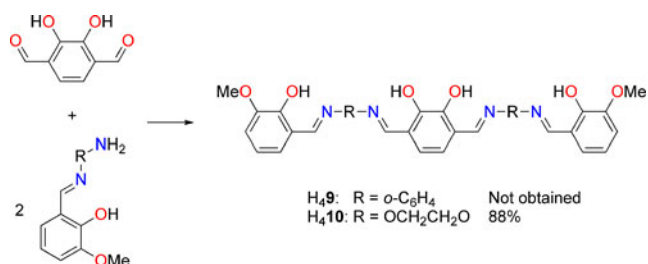




**Scheme 16** Design of acyclic oligo(salen)-type ligands for helical metallohost-guest complexes

the phenoxo moieties are oriented to the guest recognition site. If this requirement is satisfied, acyclic oligo(salen) molecules are also expected to act as an ion recognition system. One of the candidates is a series of acyclic oligo(salen) ligands in which the neighboring salen-type ligands share one benzene ring (Scheme 16). When the salen-type coordination sites of this ligand are metalated, the oxygen atoms of the neighboring two salen units are forced to orient to the recognition site in a convergent fashion. This will change the conformation of the bis(salen) ligand into a C-shaped structure and that of the tris(salen) or longer analogues into a helical one. The C-shaped or helical metallohosts are expected to bind a guest ion in the cavity surrounded by the phenoxo groups. Their physical properties as a fragment of helical salen polymers [218–220] or their dynamic behavior as a salen-containing foldamer [221–223] are also of interest.

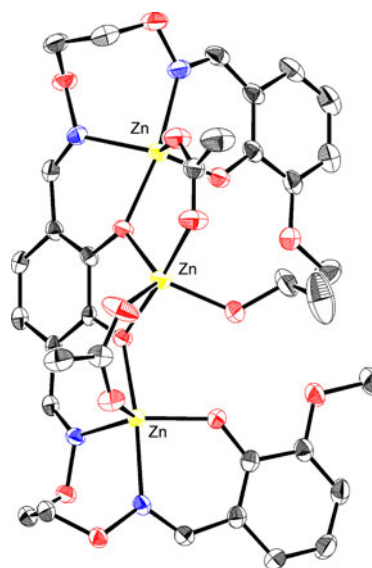
The first acyclic bis(salen)-type ligand based on the above mentioned concept is the tetraoxime ligand **H<sub>4</sub>10** [224] (Scheme 17). The oxime functionality was indispensable for this study. The synthesis of the imine analogues was unsuccessful due to the labile character of the



**Scheme 17** Synthesis of acyclic bis(salen)-type ligands **H<sub>4</sub>9** and **H<sub>4</sub>10**

imine C=N bonds [225]. For example, the reaction of the monoimine derivative with the dialdehyde yielded the cyclic tris(saloph) **H<sub>6</sub>6a** (see Scheme 13) instead of the desired acyclic bis(saloph) **H<sub>4</sub>9**. The low solubility of the cyclic tris(saloph) **H<sub>6</sub>6a** presumably shifted the equilibrium to the macrocycle. Thus, an imine group is not suitable as a constituent of the acyclic bis(salen)-type ligands. In contrast, the oxime analogue, salamo [204, 205], is highly stable under conditions in which the imine analogues suffer from C=N recombination. The synthetic intermediate monooxime and the target tetraoxime ligand **H<sub>4</sub>10** are sufficiently stable to resist such a C=N bond recombination.

Since the bis(salamo) ligand **H<sub>4</sub>10** has two salamo coordination moieties for d-block metals, the ligand **H<sub>4</sub>10** is expected to form a dinuclear metallohost. However, contrary to expectation, the bis(salamo) ligand **H<sub>4</sub>10** quantitatively afforded a trinuclear zinc(II) complex **10**·Zn<sub>3</sub>, which was identified by mass spectrometry and X-ray crystallography (Fig. 7) [224, 225]. All the added zinc(II) ions were used for the formation of the trinuclear complex **10**·Zn<sub>3</sub>. When 2 equiv of zinc(II) acetate were present, 2/3 of the **H<sub>4</sub>10** was converted into **10**·Zn<sub>3</sub> and the remaining 1/3 was unchanged. During the complexation, no other complexes with a different stoichiometry, such as 1:1 and 1:2, were observed. The favored formation of the trinuclear complex **10**·Zn<sub>3</sub> can be explained by a chelate cooperativity [226], in which bridging coordination of the acetato and phenoxo ligands play an important role (Fig. 7). In the crystal structure, two of the three zinc(II) ions are located at the salamo moieties as expected, while the third one is in the central O<sub>6</sub> site. Two  $\mu$ -acetato ligands



**Fig. 7** X-ray crystal structure of **10**·Zn<sub>3</sub>. The hydrogen atoms are omitted for clarity

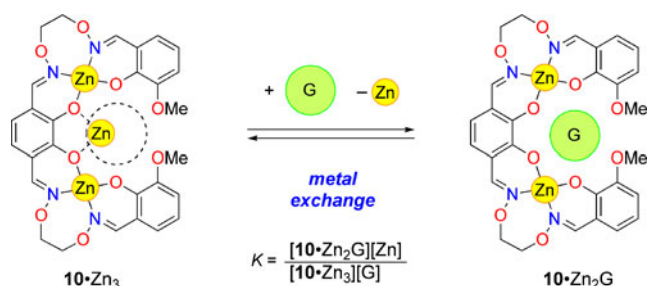
coordinate to the zinc(II) trinuclear core. Although the central zinc(II) ion occupies the  $O_6$  cavity, four of the six oxygen donor atoms (two phenoxo and two methoxy oxygen atoms) do not coordinate to the central zinc(II) ion, e.g., the zinc(II) ion seems to be too small to fit. Therefore, the  $O_6$  site is expected to bind a larger group 1–3 metal ion with concomitant release of the initially bound zinc(II).

However, the metal exchange with alkali metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) or  $\text{Mg}^{2+}$  did not proceed at all, although the six oxygen atoms of the  $\mathbf{10}\cdot\text{Zn}_2$  unit are arranged like a crown ether. On the other hand, the metal exchange took place when a guest metal G ( $=\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , or  $\text{Ba}^{2+}$ ) was added (Scheme 18) [224, 227, 228]. The formation of the heterotrimeric complexes  $\mathbf{10}\cdot\text{Zn}_2\text{G}$  was evidenced by the mass spectrometry and X-ray crystallography. While there have been a few reports on hetero- to homometallic or hetero- to heterometallic transmetalation [229–231], the formation of the  $\mathbf{10}\cdot\text{Zn}_2\text{G}$  from  $\mathbf{10}\cdot\text{Zn}_3$  is the first example of the homo- to heterometallic transformation and also the first ion recognition system based on the principle of metal exchange. The selectivity for the metal exchange is in the order of  $\text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} \gg \text{Mg}^{2+}$ , clearly showing the  $\text{Ca}^{2+}$ -selectivity (Table 3). The  $\text{Ca}^{2+}/\text{Mg}^{2+}$  selectivity, which is biologically important, is estimated to be  $>10^5$ , being comparable to those of the excellent  $\text{Ca}^{2+}$  receptors or sensors, such as BAPTA [232] (selectivity coefficients, 5.20), Quin2 (4.4) [232], and K23E1 (5.0) [233]. Thus, among the biologically important metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ), the trinuclear complex

**Table 3** Equilibrium constants for metal exchange of trinuclear complex  $\mathbf{10}\cdot\text{Zn}_3$

Group 1		Group 2		Group 3	
$\text{Na}^+$	<0.001	$\text{Mg}^{2+}$	<0.001	$\text{Sc}^{3+}$	>1000
$\text{K}^+$	<0.001	$\text{Ca}^{2+}$	32	$\text{Y}^{3+}$	>1000
$\text{Rb}^+$	<0.001	$\text{Sr}^{2+}$	3.9	$\text{La}^{3+}$	>1000
$\text{Cs}^+$	<0.001	$\text{Ba}^{2+}$	0.16	$\text{Lu}^{3+}$	>1000

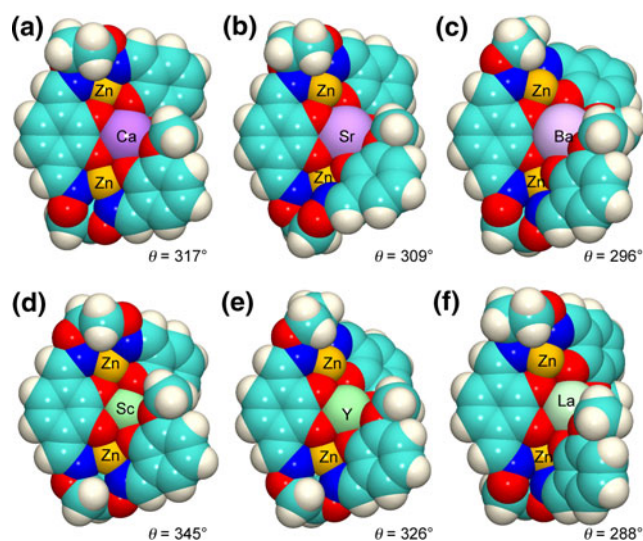
Determined by  $^1\text{H}$  NMR titration in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (1:1) (data cited from Ref. [228])



**Scheme 18** Ion recognition based on metal exchange of trinuclear complex  $\mathbf{10}\cdot\text{Zn}_3$ . The counter anions are not included for simplicity in the determination of the equilibrium constants

$\mathbf{10}\cdot\text{Zn}_3$  exclusively recognized  $\text{Ca}^{2+}$ . When rare earth metal ions ( $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ – $\text{Lu}^{3+}$ ) were used as the guest, the metal exchange of the  $\mathbf{10}\cdot\text{Zn}_3$  quantitatively occurred (Table 3). The equilibrium constants are estimated to be  $>1000$  in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (1:1). The difference in the ionic sizes of these rare earth metal ions did not affect the quantitative metal exchange. As a result, this trinuclear complex  $\mathbf{10}\cdot\text{Zn}_3$  discriminates the charge of the guest metals. This trend is basically derived from the intrinsic properties of the  $[\text{M}^{\text{II}}\text{salen}]$ -type complex (see Tables 1, 2), whose interaction with the group 1,2 metals is mainly governed by an electrostatic interaction [58]. However, the trinuclear complex  $\mathbf{10}\cdot\text{Zn}_3$  showed a significant  $\text{Ca}^{2+}$ -selectivity among the alkaline earth metal ions. This size-selectivity can be ascribed to the preorganization effect, in which all of the six oxygen donor atoms participate in the coordination to the guest ion (see below). When sulfur-containing salamo [92, 234] moieties were introduced instead of the  $\text{N}_2\text{O}_2$  salamo coordination sites, the dipalladium(II) metallohost showed an  $\text{Ag}^+$ -selectivity in the binding in the central  $\text{S}_2\text{O}_4$  recognition site [235].

The X-ray crystallographic analysis revealed that the heterotrimeric metallohost–guest complexes  $\mathbf{10}\cdot\text{Zn}_2\text{G}$  adopt a single-helical structure in which the acyclic bis(salamo) ligand  $\mathbf{10}$  winds around the central metal ion G (Fig. 8) [228]. All of the oxygen donors of the  $O_6$  site including the methoxy groups effectively surround the central guest metal ion. This size fit should be the reason for stabilization of the heterotrimeric complex  $\mathbf{10}\cdot\text{Zn}_2\text{G}$  to shift the metal exchange equilibrium. Among the three complexes with alkaline earth metals ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ),

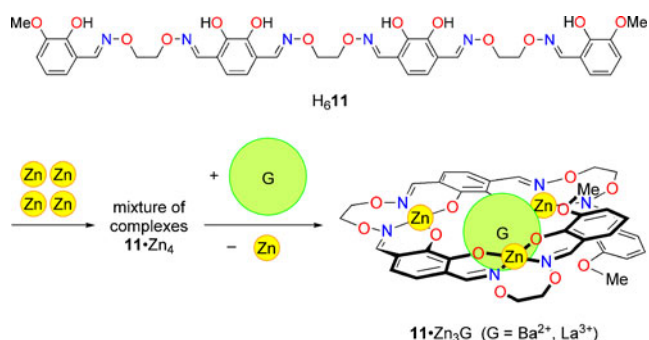


**Fig. 8** X-ray crystal structures of  $\mathbf{10}\cdot\text{Zn}_2\text{G}$  ( $\text{G} = \text{Ca}^{2+}$  (a),  $\text{Sr}^{2+}$  (b),  $\text{Ba}^{2+}$  (c),  $\text{Sc}^{3+}$  (d),  $\text{Y}^{3+}$  (e),  $\text{La}^{3+}$  (f)). The counter anions and solvent molecules are omitted. The winding angles ( $\theta$ ) of the helices are also indicated. Reprinted with permission from Ref. [228]

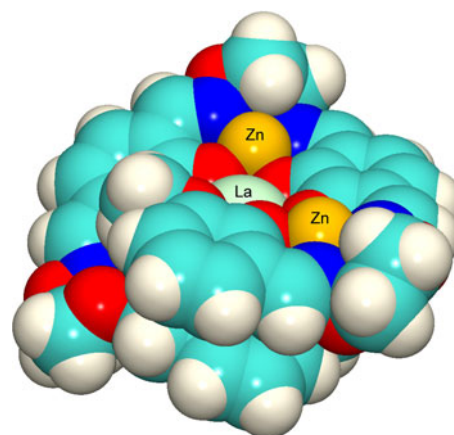
the winding angle of the  $10 \cdot \text{Zn}_2\text{Ba}$  is the smallest ( $296^\circ$ ) and that of the  $10 \cdot \text{Zn}_2\text{Ca}$  is the largest ( $317^\circ$ ) (Fig. 8a–c). The  $\text{Ca}^{2+}$ -selectivity can probably be ascribed to the smallest strain of the oligooxime moiety in  $10 \cdot \text{Zn}_2\text{G}$  among the four alkaline earth metal ions ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ). A similar trend was observed for the rare earth metal complexes ( $345^\circ$  for  $10 \cdot \text{Zn}_2\text{Sc}$ ,  $326^\circ$  for  $10 \cdot \text{Zn}_2\text{Y}$ , and  $288^\circ$  for  $10 \cdot \text{Zn}_2\text{La}$ ) (Fig. 8d–f). Thus, the ligand moiety changes its winding angle to accommodate the guest metal ion, which is known as the induced fit mechanism. The winding angle can be set at various values by choosing the guest cation G. Accordingly, the helical complexes  $10 \cdot \text{Zn}_2\text{G}$  are regarded as a *tunable* molecular spring or coil, whose winding angles can be modulated by changing the central guest ion G.

A longer derivative, tris(salamo) ligand  $\text{H}_6\mathbf{11}$ , was expected to form a single-helical metallohost upon the complexation with zinc(II) ions. However, the complexation of the ligand  $\text{H}_6\mathbf{11}$  with zinc(II) afforded a mixture of  $11 \cdot \text{Zn}_4$  isomers. Probably, the central zinc(II) ion is not tightly fixed in the cavity, because the trinuclear  $11 \cdot \text{Zn}_3$  unit has a cavity too large to fit a small zinc(II) ion. However, this mixture was converted into a discrete metallohost–guest complex  $11 \cdot \text{Zn}_3\text{G}$  when reacted with a guest metal G ( $=\text{Ba}^{2+}$  or  $\text{La}^{3+}$ ) (Scheme 19). This indicates that the metal exchange efficiently took place. Since other cations, such as  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , did not cause such a convergence to one species, the tetranuclear  $11 \cdot \text{Zn}_4$  mixture acts as a metalloreceptor that shows selectivity toward large cations such as  $\text{Ba}^{2+}$  and  $\text{La}^{3+}$  ions [227]. The complex  $11 \cdot \text{Zn}_3\text{La}$  has a single-helical structure in which the three salamo sites are occupied by zinc(II) ions (Fig. 9). The resulting six phenoxo oxygen atoms and the two terminal methoxy groups nicely surround the  $\text{La}^{3+}$  ion in the cavity. The helix winding angle of the tris(salamo) moiety in  $11 \cdot \text{Zn}_3\text{La}$  from one methoxy group to the other is about  $421^\circ$ , which corresponds to a 1.2 turn helix [236].

The extended analogues, tetrakis- and pentakis(salamo) ligands ( $\text{H}_8\mathbf{12}$ ,  $\text{H}_{10}\mathbf{13}$ ), were also prepared [237] to obtain helices with a greater number of winding turns. The

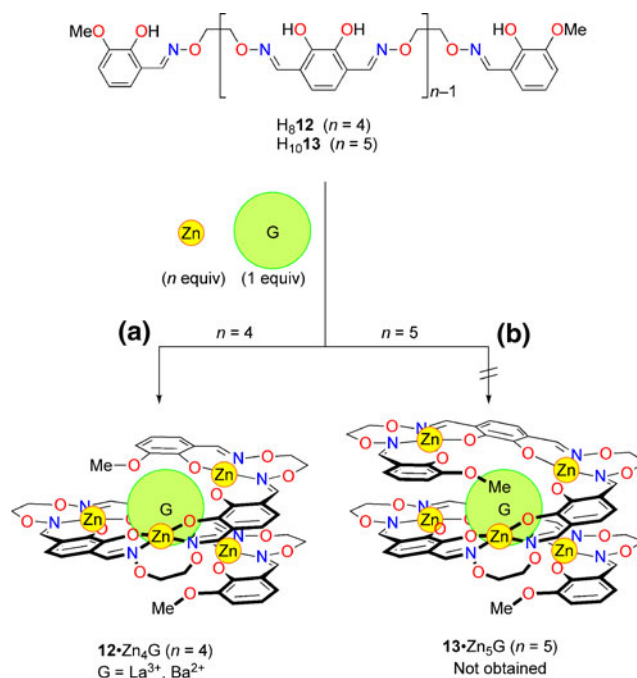


**Scheme 19** Ion recognition of  $\text{Ba}^{2+}$  and  $\text{La}^{3+}$  by acyclic tris(salamo) ligand  $\text{H}_6\mathbf{11}$  in the presence of zinc(II) ions



**Fig. 9** X-ray crystal structure of  $11 \cdot \text{Zn}_3\text{La}$ . The counter anions and solvent molecules are omitted. Reprinted with permission from Ref. [236]

complexation of the tetrakis(salamo) ligand  $\text{H}_8\mathbf{12}$  with zinc(II) acetate in the presence of a  $\text{La}^{3+}$  or  $\text{Ba}^{2+}$  ion gave a discrete metallohost–guest complex,  $12 \cdot \text{Zn}_4\text{G}$  ( $\text{G} = \text{La}^{3+}$ ,  $\text{Ba}^{2+}$ ) (Scheme 20a), while other metals with a smaller size ( $\text{Lu}^{3+}$ ,  $\text{Ca}^{2+}$ , etc.) did not lead to such a discrete species. The  $^1\text{H}$  NMR spectral study showed that the pentanuclear complex  $12 \cdot \text{Zn}_4\text{La}$  adopts a single-helical structure in which the  $n$ th benzene ring approximately lies on the  $(n + 3)$ th benzene ring. Such a complexation behavior of the tetrakis(salamo) ligand  $\text{H}_8\mathbf{12}$  is generally similar to that of the shorter analogue, the tris(salamo)



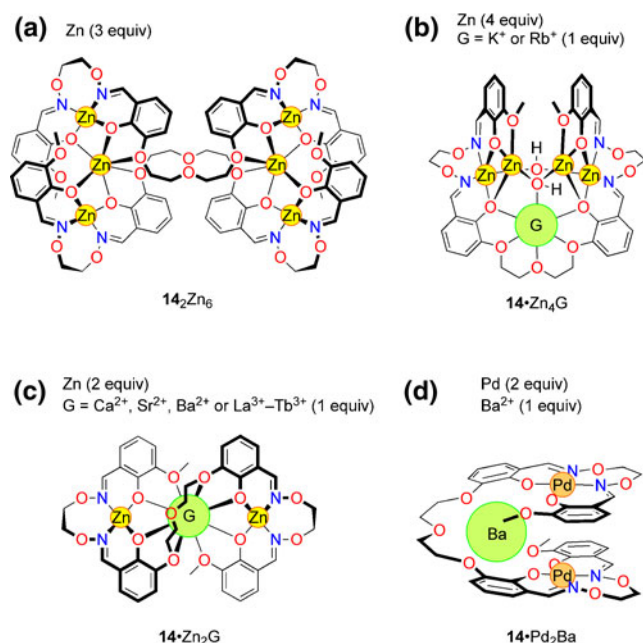
**Scheme 20** Oligometal complexation of longer acyclic oligo(salamo) ligands  $\text{H}_8\mathbf{12}$ ,  $\text{H}_{10}\mathbf{13}$  with zinc(II) and guest metal ions



ligand **H<sub>6</sub>11**. On the other hand, the complexation of the longer analogue, the pentakis(salamo) ligand **H<sub>10</sub>13**, with zinc(II) and lanthanum(III) did not give a single discrete species (Scheme 20b). The **13**-Zn<sub>5</sub> structure was presumably formed upon the complexation, but the helical recognition site might have too many phenoxo oxygen atoms for a La<sup>3+</sup> ion. Consequently, there should be a limit in the chain lengths of the acyclic oligo(salamo) ligands that can form a discrete Zn<sub>n</sub>La helical complex upon the complexation with zinc(II) and lanthanum(III) ions.

An alternative way of connecting multiple salamo units is to use a flexible linker. A bis(salamo) ligand **H<sub>4</sub>14** in which the two salamo sites are connected with a diethyleneoxy linker was synthesized [238]. The conformational flexibility allows the molecule to adopt a variety of folded structures. The salamo sites can form a complex with d-block metals and the oxygen donor set consisting of diethylene glycol and phenoxo groups can coordinate to the group 1–3 metals.

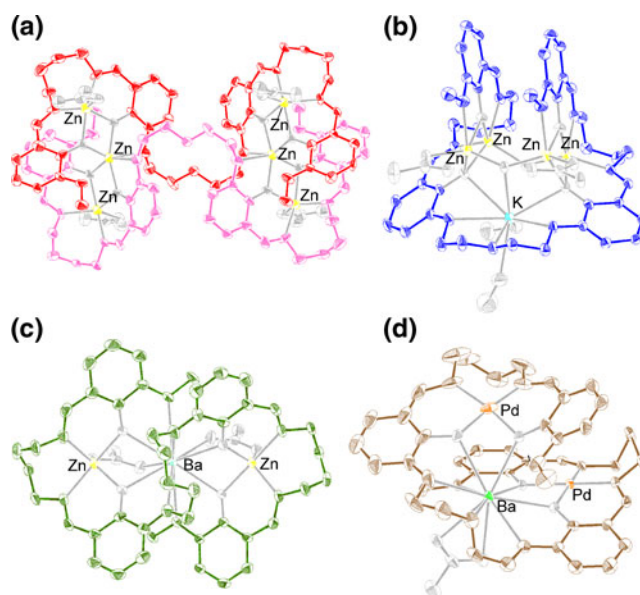
The complexation of the ligand **H<sub>4</sub>14** with 3 equiv of zinc(II) acetate afforded a crystalline hexanuclear complex **14**<sub>2</sub>Zn<sub>6</sub> (Scheme 21a). The complex has two



**Scheme 21** Summary of oligometal complexation behavior of diethylene glycol-linked bis(salamo) ligand **H<sub>4</sub>14**

[(Zn<sup>II</sup>salamo)<sub>2</sub>Zn<sup>II</sup>] trinuclear cores doubly connected by the diethylene glycol linker. The structure of each [(Zn<sup>II</sup>salamo)<sub>2</sub>Zn<sup>II</sup>] fragment is quite similar to that of [(Zn<sup>II</sup>(3-MeOsalamo))<sub>2</sub>Zn<sup>II</sup>(OAc)<sub>2</sub>] [89]. The two [(Zn<sup>II</sup>salamo)<sub>2</sub>Zn<sup>II</sup>] cores are related by a crystallographic inversion center. Thus, the complex **14**<sub>2</sub>Zn<sub>6</sub> has an achiral meso double helical structure (Fig. 10a). When the complexation with zinc(II) was carried out in the presence of an alkali metal ion (K<sup>+</sup> or Rb<sup>+</sup>), a monomeric heterometal pentanuclear complex **14**•Zn<sub>4</sub>G (G = K<sup>+</sup>, Rb<sup>+</sup>) was obtained (Scheme 21b). The two salamo sites form a tetranuclear [(Zn<sup>II</sup>salamo)<sub>2</sub>Zn<sup>II</sup>(μ-OH)<sub>2</sub>] core containing two bridging hydroxo groups. Furthermore, five oxygen donor atoms including diethylene glycol and phenoxo groups form a cyclic array to surround the K<sup>+</sup> or Rb<sup>+</sup> ion. In these complexes, the ligand **14** adopts a folded Ω-shaped structure in which two terminal benzene rings are stacked on top of each other at a distance of 3.4 Å (Fig. 10b).

The complexation of the ligand **H<sub>4</sub>14** with zinc(II) and alkaline earth metal ions afforded a trinuclear complex **14**•Zn<sub>2</sub>G (G = Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) (Scheme 21c). The two [Zn<sup>II</sup>salamo] units coordinate to one alkaline earth metal ion (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) and the ligand **14** makes an S-shaped helical structure in which the two salamo arms are helically radiated from the diethylene glycol linker (Fig. 10c). Complexation of the ligand **H<sub>4</sub>14** with zinc(II) and lanthanides(III) also gave a trinuclear complex **14**•Zn<sub>2</sub>Ln (Ln = La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>) with a similar S-shaped helical structure. Some of these lanthanide(III) complexes exhibited a visible or near infrared luminescence. While the **14**•Zn<sub>2</sub>La showed a relatively



**Fig. 10** Crystal structures of **a** **14**<sub>2</sub>Zn<sub>6</sub>, **b** **14**•Zn<sub>4</sub>K, **c** **14**•Zn<sub>2</sub>Ba, and **d** **14**•Pd<sub>2</sub>Ba Reprinted with permission from Ref. [238]



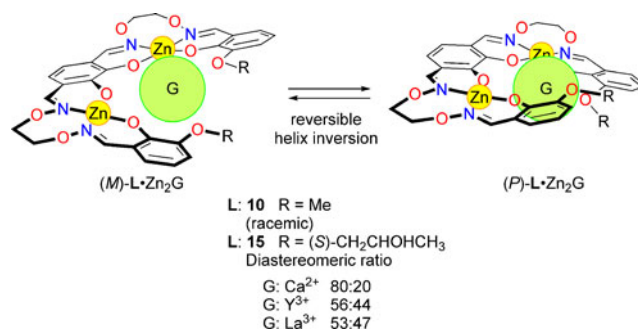
intense ligand-centered emission at 477 nm (quantum yield 2.3%),  $14\cdot\text{Zn}_2\text{Sm}$  and  $14\cdot\text{Zn}_2\text{Nd}$  showed an f–f emission in the visible and near infrared regions, respectively. The energy transfer from the  $14\cdot\text{Zn}_2$  moiety to the lanthanide(III) ion efficiently occurs. This significantly contrasts with the single-helical complexes  $10\cdot\text{Zn}_2\text{Ln}$  ( $\text{Ln} = \text{La}^{3+}$ – $\text{Lu}^{3+}$ ), which did not exhibit a lanthanide(III) luminescence in the visible region [239]. The weaker emission of  $10\cdot\text{Zn}_2\text{Ln}$  can be explained by the lower energy level of the excited state due to the terephthalaldehyde moiety, which is not sufficient for the efficient energy transfer to the lanthanide(III) ion such as  $\text{Sm}^{3+}$ .

In addition to the group 1–3 metal ions, the d-block metals significantly affect the folding structure of **14**. Upon the complexation with palladium(II) as the d-block metal in the presence of  $\text{Ba}^{2+}$  ion, a heterometal trinuclear complex  $14\cdot\text{Pd}_2\text{Ba}$  was obtained (Scheme 21d). The X-ray crystallographic analysis revealed that the two square planar palladium(II) ions are at the salamo coordination sites and that the  $\text{Ba}^{2+}$  ion is in the helical cavity surrounded by nine oxygen donors coming from the methoxy, phenoxo, and the diethylene glycol unit (Fig. 10d). Thus, the ligand **14** winds around the  $\text{Ba}^{2+}$  ion to make a single helix with more than one-turn (winding angle:  $438^\circ$ ).

If there is a difference in the binding strengths to these metal ions, the metal exchange may take place with the conversion of the folding structures. From the metal exchange experiments, the affinity order was found to be  $\text{Zn}^{2+} < \text{Ba}^{2+} \sim \text{La}^{3+}$  (in the  $\text{O}_9$  site) and  $\text{Zn}^{2+} < \text{Pd}^{2+}$  (in the  $\text{N}_2\text{O}_2$  site). This affinity difference allows a multi-step conversion among these folded structures; for example, from the meso double helical  $14_2\text{Zn}_6$  to the S-shaped helical  $14\cdot\text{Zn}_2\text{Ba}$  and then to the single helical  $14\cdot\text{Pd}_2\text{Ba}$ .

### Dynamic behavior and helicity control of helical metallohost–guest complexes

As described above, the acyclic oligo(salamo) ligands form a helical structure by the complexation with both d-block metals such as zinc(II) and hard guest ions such as the group 1–3 metals. There has been reported a number of metal-containing helical structures such as metal helicates [240–242], and one of the significant features of these complexes is the lability in coordination bonds. Consequently, dynamic structural changes of these helical oligo(salamo) complexes will take place via equilibration to give the most thermodynamically stable structure. In particular, dynamic helix inversion between the right- and left-handed forms is of interest because some of the important physical properties depend on the helical handedness.



**Scheme 22** Helix inversion of helical complexes  $15\cdot\text{Zn}_2\text{G}$  between right- and left-handed forms

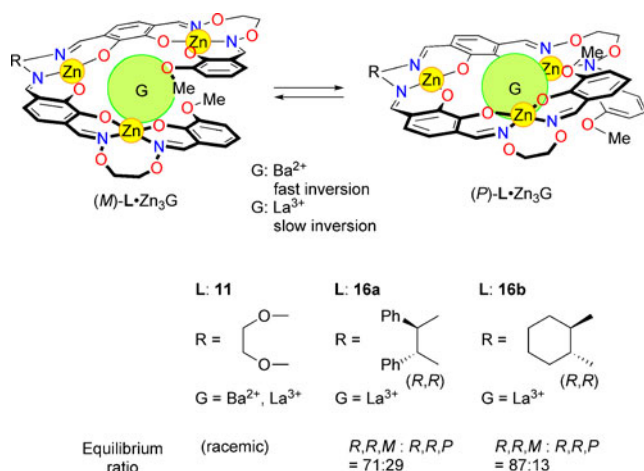
The helix inversion rates for the above mentioned helical oligo(salamo) metal complexes were investigated from the NMR spectral feature. The trinuclear complexes  $10\cdot\text{Zn}_2\text{G}$  ( $\text{G} = \text{Ca}^{2+}$ , lanthanide) obtained from the bis(salamo) ligand **H<sub>4</sub>10** described above undergo a fast helix inversion (Scheme 22) on the NMR timescale in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (1:1). This is evident from the fact that the diastereotopic protons of the  $\text{OCH}_2\text{CH}_2\text{O}$  moieties are observed as two equivalent signals [227]. The bis(salamo) ligand **H<sub>4</sub>10** has no chiral group so that the corresponding helical complexes  $10\cdot\text{Zn}_2\text{G}$  are racemic unless they are under chiral conditions. However, if an additional chiral auxiliary is introduced into an interconvertible enantiomer pair, the two isomers are no longer a pair of enantiomers, but diastereomers, whose equilibrium ratio in solution is not necessarily 1:1. Such a dynamic helicity control is one of the important features of the interconvertible helical metal complexes.

As the chiral auxiliary, the (S)-2-hydroxypropyl group, which can be derived from ethyl lactate, was introduced in the bis(salamo) scaffold. The helical heterotrimeric complexes  $15\cdot\text{Zn}_2\text{G}$  ( $\text{G} = \text{La}^{3+}$ ,  $\text{Ca}^{2+}$ , etc.) were prepared by the complexation of the ligand **H<sub>4</sub>15** with zinc(II) and appropriate guest ions [243], in a manner similar to the achiral analogues  $10\cdot\text{Zn}_2\text{G}$ . A <sup>1</sup>H NMR spectroscopic study showed that the trinuclear complexes  $15\cdot\text{Zn}_2\text{G}$  undergo a fast helix inversion (Scheme 22) in  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (1:1) at 293 K as observed for the achiral methoxy analogues  $10\cdot\text{Zn}_2\text{G}$ . However, the low-temperature NMR study clearly indicated the existence of two diastereomers, which can be assigned to the right- and left-handed helices. The diastereomeric ratio of  $15\cdot\text{Zn}_2\text{Ca}$  at 223 K is 80:20, demonstrating that one of the two isomers preferentially exists. The  $\Delta G^\ddagger$  for the interconversion is estimated to be approximately 52 kJ/mol from the coalescence temperature. Since the diastereomeric ratios for the  $15\cdot\text{Zn}_2\text{Y}$  and  $15\cdot\text{Zn}_2\text{La}$  at 223 K are 56:44 and 53:47, respectively,  $\text{Ca}^{2+}$  is the most effective for the helicity control among the  $\text{Ca}^{2+}$ ,  $\text{Y}^{3+}$ , and  $\text{La}^{3+}$  ions.

In general, helix inversion less likely takes place when the helix winds more tightly or the helical turn increases. For examples, [5]helicene having a rigid helical structure easily undergoes helix inversion, but [6]helicene does not unless at a higher temperature [244–246]. In the case of the helical oligo(salamo) metal complexes, the intrinsic labile characters of the coordination bonds as well as the structural features may affect the helix inversion kinetics.

As described above, the tris(salamo) tetranuclear complexes **11**·Zn<sub>3</sub>G have a helical structure with a winding of more than one-turn, in which the two terminal benzene rings stack parallel on top of each other. Considering this structural feature, the helix inversion requires cleavage of some of the coordination bonds. The <sup>1</sup>H NMR spectroscopy showed that the barium complex **11**·Zn<sub>3</sub>Ba undergoes helix inversion on the NMR timescale in CDCl<sub>3</sub>/CD<sub>3</sub>OD (1:1) [236], but that the helix inversion of **11**·Zn<sub>3</sub>La is very slow even at 353 K in the same solvent (Scheme 23). Consequently, the helix inversion rate of **11**·Zn<sub>3</sub>G can be easily tuned by replacing the guest metal ion. This helix inversion rate of **11**·Zn<sub>3</sub>G is much slower than that of the shorter analogue, the trinuclear complex **10**·Zn<sub>2</sub>G. Therefore, the helix inversion rate mostly depends on the helix winding (ligand chain length) and on the intrinsic lability of the guest metal (La<sup>3+</sup>, Ba<sup>2+</sup>, etc.).

The helicity control for the tris(salamo) helical complexes have also been investigated using a chiral salen unit as the chiral auxiliary. This is based on the fact that [M(salen)] complexes having chiral groups can effectively induce a chiral distortion for excellent enantioselective catalytic organic reactions [11–13]. These kinds of chiral salen units were introduced in place of the salamo unit in the middle of the acyclic tris(salamo) framework, taking into consideration the reactivities of the imine and oxime C=N bonds. The ligands H<sub>6</sub>**16a,b** were synthesized by the

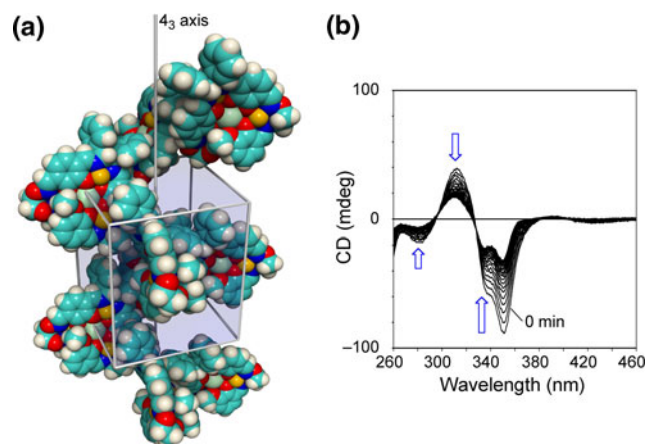


**Scheme 23** Helix inversion and helicity control of tris(salamo) complexes **11**·Zn<sub>3</sub>G (G = Ba<sup>2+</sup>, La<sup>3+</sup>)

reaction of a mono-formyl salamo derivative with commercially available chiral diamines. The helical complexes **16a**·Zn<sub>3</sub>La and **16b**·Zn<sub>3</sub>La were prepared by the complexation of the ligands H<sub>6</sub>**16a,b** with zinc(II) and lanthanum(III). The <sup>1</sup>H NMR studies indicated the formation of two diastereomers (71:29 for diphenylethylene derivative **16a**·Zn<sub>3</sub>La [247], 87:13 for cyclohexane derivative **16b**·Zn<sub>3</sub>La [248]) in CDCl<sub>3</sub>/CD<sub>3</sub>OD (1:1) (Scheme 23). The chiral auxiliaries of H<sub>6</sub>**16a,b** are effective in making a difference in the thermodynamic stability of the two diastereomers and to obtain one of the isomers predominantly in solution.

In general, crystallization is a useful way to obtain one of the diastereomers in a pure form [249]. In the case of **16a**·Zn<sub>3</sub>La having an (R,R)-diphenylethylene moiety, the pure left-handed isomer ((R,R,M) isomer) was isolated as crystals (Fig. 11a) from the 71:29 diastereomeric mixture [247]. This is reasonably explained by the assumption that the minor (R,R,P) isomer isomerized to the major (R,R,M) isomer maintaining the equilibrium in the mother liquor during the crystallization. This would be more probable than the major (R,R,M) isomer simply being crystallized without an equilibrium shift in the mother liquor. In fact, the equilibrium shift from 100:0 to the initial ratio 71:29 was observed upon dissolution of the obtained pure (R,R,M) isomer (Fig. 11b). This result clearly indicates that the complex **16a**·Zn<sub>3</sub>La undergoes a helix inversion in solution. From the NMR and CD spectral changes, the half-life of the isomerization was spectroscopically determined to be approximately 44 min at 295 K.

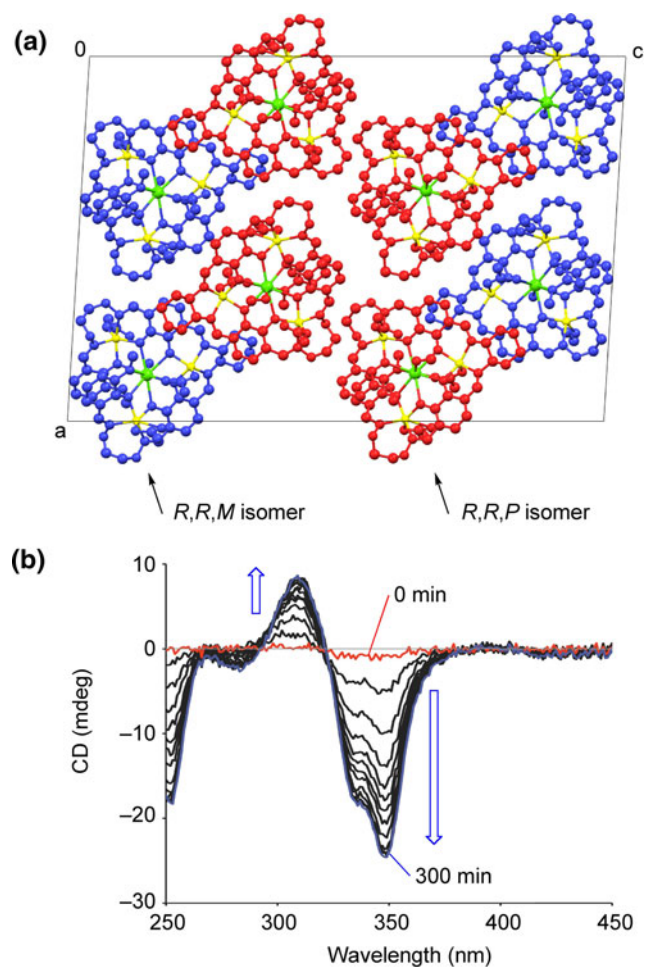
The complex **16a**·Zn<sub>3</sub>La crystallizes in the tetragonal system, space group *P*4<sub>3</sub>, which has a left-handed four-fold screw axis along the *c* axis. As a result, a left-handed



**Fig. 11** a Superhelical structure formed in the crystal of **16a**·Zn<sub>3</sub>La; b CD spectral changes of **16a**·Zn<sub>3</sub>La in solution after dissolving of the crystal in chloroform/methanol (1:1). Reprinted with permission from Ref. [247]

helical array of the left-handed helical complex is formed. This structure approximates a coiled-coil structure—a supramolecular superhelix—in the crystal lattice (Fig. 11a) [247]. Such a hierarchical *helix of helix* structure is found in biomolecules, such as supercoiled DNAs [250], coiled coil structures of proteins [251], or in synthetic helical polymers with a higher-ordered morphology [252, 253]. To the best of our knowledge, this is the first example of a coiled-coil structure formed by the folding and assembly of artificial flexible acyclic molecules.

In contrast to the diphenylethylene helical complex **16a**·Zn<sub>3</sub>La, crystallization of the tetranuclear complex **16b**·Zn<sub>3</sub>La having a cyclohexanediamine moiety did not lead to isolation of one of the isomers. Instead, it crystallized as a mixture of the right- and left-handed isomers in a 1:1 ratio, and therefore the diastereomeric excess (87:13, de 74%) completely disappeared (de 0%) (Fig. 12a) [248]. In the crystal structure, the right- and left-handed isomers



**Fig. 12** **a** Quasiracemate structure of the crystal of  $(R,R)$ -**16b**·Zn<sub>3</sub>La; **b** CD spectral changes of  $(R,R)$ -**16b**·Zn<sub>3</sub>La in solution after dissolving of the crystal in chloroform/methanol (1:1). Reprinted with permission from Ref. [248]

are almost mirror images of each other except for the  $R,R$ -cyclohexanediamine moiety. The packing of this crystal resembles the centrosymmetric space group  $C2/c$ , but the unit cell lacks the formal center of symmetry due to the chiral  $R,R$ -cyclohexanediamine moiety. Such a crystal consisting of a 1:1 mixture of two diastereomers being almost mirror images of each other is called a quasiracemate crystal [249]. Relatively fewer helical compounds or complexes are known to form such a quasiracemate crystal [254–260]. One of the important aspects of the complex **16b**·Zn<sub>3</sub>La is that the diastereomeric ratio in solution ( $R,R,M$  isomer :  $R,R,P$  isomer = 87:13; de = 74%) is significantly different from that in the crystal (50:50; de = 0%). When the quasiracemate crystals of **16b**·Zn<sub>3</sub>La are dissolved in chloroform/methanol (1:1), the diastereomeric ratio changed from 50:50 to the initial ratio 87:13, which corresponds to the de increase from 0 to 74% (Fig. 12b) [248]. Therefore, this phenomenon can be regarded as spontaneous enrichment of the left-handed helix from a *racemic* 1:1 mixture when we focus only on the helical chirality.

Whereas the true racemate crystals will not undergo the spontaneous enrichment of one of the enantiomers upon dissolution, the quasiracemate crystals generally undergo such an enrichment because the two isomers are diastereomers. However, it has been difficult to develop a system in which a crystalline 1:1 mixture changes into a single isomer by dissolution. There are two conflicting requirements; i.e., the small chiral auxiliary must effectively control the helical chirality in solution but behave like an achiral group during crystallization. The cyclohexane moiety of **16b**·Zn<sub>3</sub>La worked well as a chiral group to stabilize one of the isomers in solution. Nevertheless, this cyclohexane group behaved like an achiral group during the crystallization to give quasiracemate crystals. In general, an enantiomer pair tends to crystallize as a racemate that is generally more tightly packed; this is known as an empirical rule, i.e., Wallach's rule [261, 262]. In the case of **16b**·Zn<sub>3</sub>La, the two isomers, which are no longer an enantiomer pair, can form quasiracemate crystals approximately according to the Wallach's rule, probably because the cyclohexane moiety is relatively small for the overall helical shape of the molecule.

### New ligands by ring-closing olefin metathesis

As described above, cyclic and acyclic oligo(salamo) ligands exhibited the characteristic complexation behavior such as oligometal complexation and site-selective metal exchange. In general, the difference between the acyclic and cyclic ligands (or hosts) in the coordination behavior mainly arises from the preorganization of the coordinating

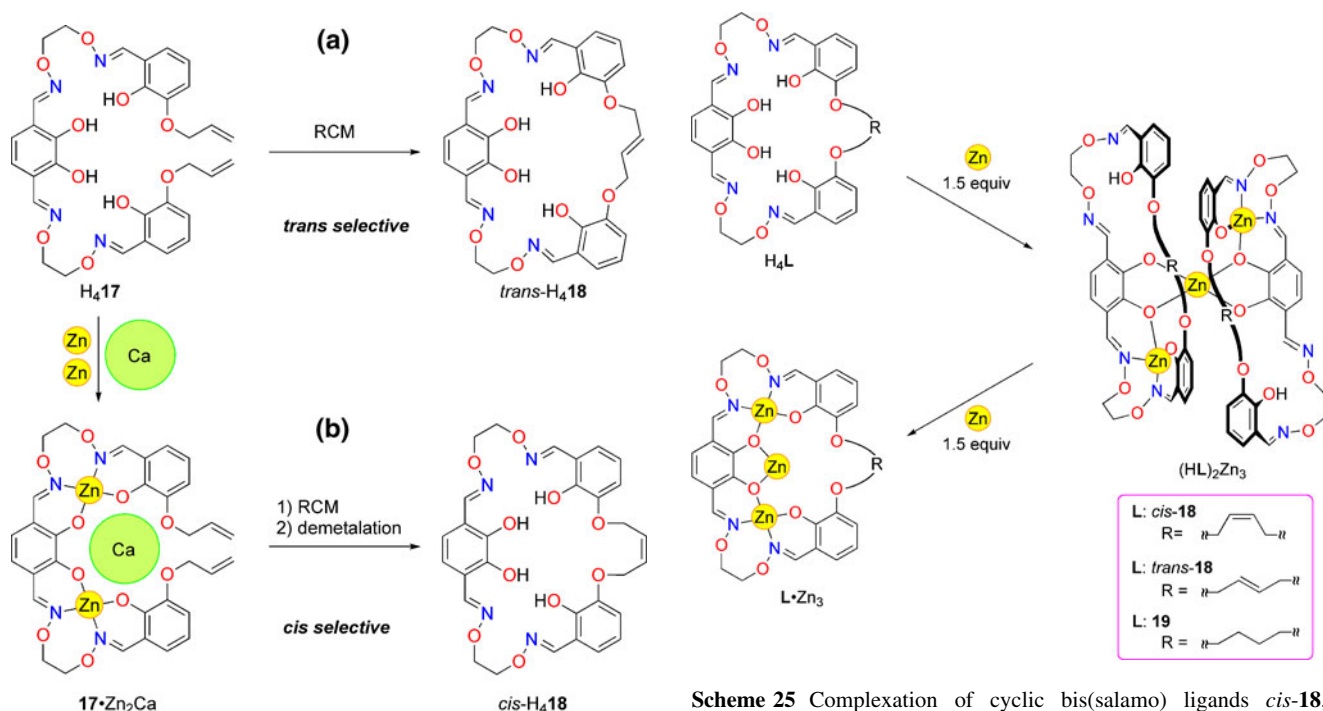


atoms for the metal ions (macrocyclic effect). The stronger binding affinity and higher selectivity are usually achieved by taking advantage of the macrocyclic framework suitable for the guest species. Therefore, conversion from an acyclic structure to cyclic ones is expected to significantly change the metal complexation ability and selectivity of the oligo(salamo) ligands. Ring closing olefin metathesis (RCM) catalyzed by Ru complexes [263] is used as the key method for the conversion.

An acyclic bis(salamo) ligand **H<sub>4</sub>17** bearing two terminal allyl groups was designed and synthesized for this purpose [264]. Ring-closing metathesis of the two terminal olefins produced a macrocycle **H<sub>4</sub>18** with a cis or trans olefinic moiety. In this conversion, it is important to selectively obtain the cis and trans isomers of the olefinic macrocycle **H<sub>4</sub>18**. The ring-closing olefin metathesis of the free ligand **H<sub>4</sub>17** afforded the macrocycle *trans*-**H<sub>4</sub>18** as the major product (cis/trans = 7:93) (Scheme 24a). The corresponding metal complexes **17**·Zn<sub>2</sub>G also underwent the ring-closing olefin metathesis and the cyclic product **H<sub>4</sub>18** was obtained after demetalation. It is reported that the use of a template metal changes the cis/trans selectivity in the crown ether synthesis based on the olefin metathesis [265]. The cis/trans ratio of the **H<sub>4</sub>18** also significantly depends on the combination of the metal ions. Whereas the reaction of **17**·Zn<sub>3</sub> or **17**·Zn<sub>2</sub>Ba afforded the trans isomer as the major product (cis/trans = 32:68 and 24:76), the reaction of **17**·Zn<sub>2</sub>Ca exclusively gave the

*cis* cyclic product *cis*-**H<sub>4</sub>18** (Scheme 24b). The Zn<sub>2</sub>Ca trimetallic core as an *oligometallic template* tightly fixes the allyl groups so that the macrocyclization produces a seven-membered metallacycle. However, the reaction of **17**·Zn<sub>2</sub>La gave only the *cis*-**H<sub>4</sub>18** as a cyclic product in low yield (5%) due to the side reactions. As a result, the olefin metathesis reactions of the free **H<sub>4</sub>17** and its complex **17**·Zn<sub>2</sub>Ca are effective for obtaining the trans and cis isomers, respectively. The saturated ligand **H<sub>4</sub>19** was prepared by the hydrogenation of *trans*-**H<sub>4</sub>18** using a Pd/C catalyst. Olefin metathesis was also used to obtain related macrocyclic tetrakis(salen) ligands via [2 + 2] macrocyclization [266].

The obtained cyclic ligands *cis*-**H<sub>4</sub>18**, *trans*-**H<sub>4</sub>18**, and **H<sub>4</sub>19** also have two peripheral salamo coordination sites and the central O<sub>6</sub> cavity as seen in the acyclic analogue **H<sub>4</sub>10** having methoxy groups. The structural differences in the organic moieties of these ligands lead to a different complexation behavior in the O<sub>6</sub> site. The complexation of the **H<sub>4</sub>L** ligands (**L** = **17**, *cis*-**18**, *trans*-**18**, **19**) with zinc(II) acetate (3 equiv) yielded the trinuclear complexes **L**·Zn<sub>3</sub> [267]. Contrary to the cooperative formation of **17**·Zn<sub>3</sub> from the acyclic ligand **H<sub>4</sub>17**, the complexation of the macrocyclic ligands **H<sub>4</sub>L** (**L** = *cis*-**18**, *trans*-**18**, **19**) showed a two-step feature, first giving the 2:3 complex (HL)<sub>2</sub>Zn<sub>3</sub> and then the 1:3 complex **L**·Zn<sub>3</sub> (Scheme 25). The structure of the 2:3 complex (HL)<sub>2</sub>Zn<sub>3</sub> (**L** = *trans*-**18**, **19**) consisting of two molecules of the triply deprotonated



**Scheme 24** Selective synthesis of cis and trans isomers of cyclic ligand **H<sub>4</sub>18** using the oligometallic template strategy

**Scheme 25** Complexation of cyclic bis(salamo) ligands *cis*-**18**, *trans*-**18**, and **19** leading to (HL)<sub>2</sub>Zn<sub>3</sub> and **L**·Zn<sub>3</sub> complexes. In the structural formulae, the counter anions and solvent molecules coordinating to the metal ions are omitted for clarity



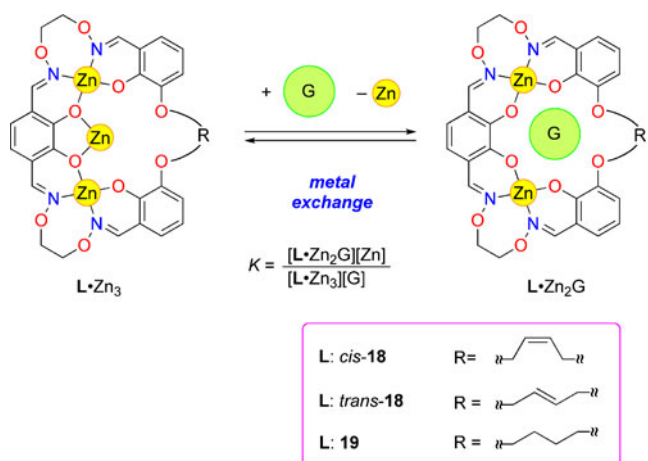
ligand (HL)<sup>3-</sup> and three zinc(II) ions was determined by X-ray crystallographic analyses and spectroscopic studies. In the crystal structure, the two (HL)Zn units are held together by the third zinc(II) ion via the coordination of the catecholato moiety of each (HL)Zn unit. The structures of the three 1:3 complexes **L**·Zn<sub>3</sub> (**L** = *cis*-**18**, *trans*-**18**, **19**) are similar to each other.

The guest ion recognition behavior of the four trinuclear complexes **L**·Zn<sub>3</sub> (**L** = **17**, *cis*-**18**, *trans*-**18**, **19**) based on a metal exchange was studied to clarify the ring effects and the structural effects of the linking olefinic moiety (Scheme 26; Table 4). As expected, four complexes **L**·Zn<sub>3</sub> (**L** = **17**, *cis*-**18**, *trans*-**18**, **19**) showed a different binding behavior in the recognition of alkaline earth metal ions. The acyclic derivative **17**·Zn<sub>3</sub> showed a Ca<sup>2+</sup>-selectivity, as observed for the methoxy derivative **10**·Zn<sub>3</sub>. The *cis*-**18**·Zn<sub>3</sub> also strongly binds Ca<sup>2+</sup>, indicating that the macrocycle *cis*-**18** remembers the best metal combination for the *oligometallic template* used in the macrocyclization. The X-ray crystallographic analysis of *cis*-**18**·Zn<sub>2</sub>Ca showed that the six oxygen atoms of the *cis*-**18** ligand

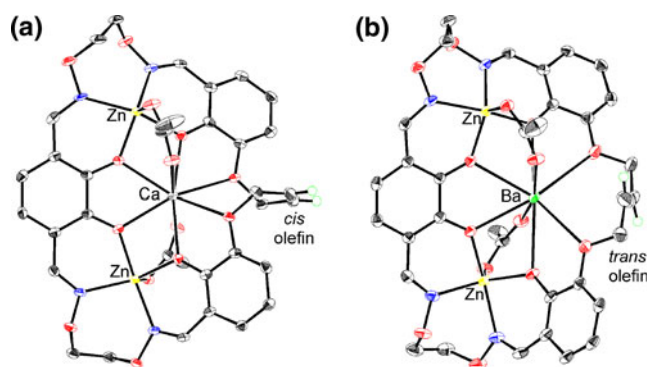
**Table 4** Equilibrium constants for the metal exchange of trinuclear complexes **L**·Zn<sub>3</sub>

Guest	Trinuclear complex			
	<b>17</b> ·Zn <sub>3</sub>	<i>cis</i> - <b>18</b> ·Zn <sub>3</sub>	<i>trans</i> - <b>18</b> ·Zn <sub>3</sub>	<b>19</b> ·Zn <sub>3</sub>
La(NO <sub>3</sub> ) <sub>3</sub>	>1000	>1000	>1000	>1000
Mg(OAc) <sub>2</sub>	1.2	0.011	0.19	0.015
Ca(OAc) <sub>2</sub>	100	>1000	0.20	400
Ba(OAc) <sub>2</sub>	7	>1000	60	600

Determined by <sup>1</sup>H NMR titration in CDCl<sub>3</sub>/CD<sub>3</sub>OD (1:1) (data cited from Ref. [267])



**Scheme 26** Ion recognition of trinuclear complexes **L**·Zn<sub>3</sub> based on metal exchange. The counter anions are not included for simplicity in the determination of equilibrium constants



**Fig. 13** X-ray crystal structures of *cis*-**18**·Zn<sub>2</sub>Ca and *trans*-**18**·Zn<sub>2</sub>Ba

effectively coordinate to Ca<sup>2+</sup> in the O<sub>6</sub> cavity (Fig. 13a). The structural feature is very similar to that of the acyclic **17**·Zn<sub>2</sub>Ca except for the terminal olefin moieties, confirming again that the Zn<sub>2</sub>Ca oligometallic template can fix the two allyl groups at positions suitable for the ring-closing olefin metathesis. The metal exchange of *cis*-**18**·Zn<sub>3</sub> with Ba<sup>2+</sup> also quantitatively took place, but the exchange with Mg<sup>2+</sup> did not efficiently proceed. Consequently, the Ca<sup>2+</sup>/Mg<sup>2+</sup> or Ba<sup>2+</sup>/Mg<sup>2+</sup> selectivity significantly increased by the conversion of **17** to *cis*-**18**. On the contrary, *trans*-**18**·Zn<sub>3</sub> binds Ba<sup>2+</sup> much stronger than Ca<sup>2+</sup> or Mg<sup>2+</sup>. The Ca<sup>2+</sup>/Ba<sup>2+</sup> selectivity is reversed from 13 to 1/300 by the conversion of the acyclic **17** to the *trans*-**18**. The restricted conformation of the ligand *trans*-**18** with a longer trans-olefin linkage makes the cavity large enough to surround the larger Ba<sup>2+</sup> ion (Fig. 13b). The binding behavior of the saturated analogue **19**·Zn<sub>3</sub> was similar to that of *cis*-**18**·Zn<sub>3</sub>. The flexible tetramethylene linker changes its conformation to suitably accommodate the guest. As a result, significant size selectivities are observed in the ion recognition of *cis*-**18**·Zn<sub>3</sub>, *trans*-**18**·Zn<sub>3</sub>, and **19**·Zn<sub>3</sub> based on the metal exchange when alkaline earth metal ions are used as the guest. On the other hand, when La<sup>3+</sup> was used as the guest, the metal exchange quantitatively occurred irrespective of the ligand structure. This is probably because the ion recognition based on the metal exchange is mainly governed by the electrostatic interaction between the guest metal and phenoxo oxygen atoms. This electrostatic interaction with the trivalent La<sup>3+</sup> is strong enough to replace the divalent Zn<sup>2+</sup> regardless of the structural difference in the three macrocycles.

## Conclusion

Various kinds of salen-containing host molecules were designed for the development of new ion recognition systems. This molecular design is based on the *coordinating ability* of the [M(salen)] units, which are suitable for

chelate coordination to the group 1–3 metal ions. In particular, the integration of two or more salen-type coordination sites in a cyclic fashion is effective for the construction of the metallohosts. They showed a unique multi-metal complexation behavior due to the phenoxo-bridged structures. The peripheral salen-type coordination sites are suitable for binding to d-block transition metal ions, and the central O<sub>6</sub> (or larger) cavity is for the group 1–3 metals. Acyclic oligo(salen) molecules are also useful for the oligometal complexation. The metalation of the bis(salamo) ligand with zinc(II) afforded a trinuclear complex with a C-shaped structure, which can selectively recognize Ca<sup>2+</sup> and lanthanide(III) ions via a unique metal exchange process. The longer oligo(salamo) ligands gave helical metal complexes when they formed a complex with the La<sup>3+</sup> or Ba<sup>2+</sup> ion in the presence of zinc(II) ions. The helix inversion behavior of the helical metal complexes due to the labile character of the coordination bonds has been successfully utilized for the dynamic helicity control. The transformation of the acyclic ligand bearing allyl groups into cyclic ones via olefin metathesis significantly changed the binding selectivity.

The integration of two or more salen-type coordination sites in a cyclic or helical arrangement is particularly effective for the oligometal complexation systems. The transformation of the oligo(salen)-type ligands into metalocyclic or metallohelical structures using the oligometal complexation will also be useful to achieve sophisticated functions, which originate from the intrinsic properties of the salen-metal complexes and from the integration of multiple metal complex units in close proximity.

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