Accounts

Aggregation of Octahedral Thiolato Complexes by Forming Sulfur-Bridged Structures with Transition Metal Ions

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The main developments in rational construction of chiral metallo-aggregates based on octahedral metal complexes with 2-aminoethanethiolate (aet) or L-cysteinate (L-cys), as well as their functionality as an S-donating chiral metalloligand, are reviewed in this paper. The reactions of the tris(thiolato)-type *fac*(*S*)-$[M(aet\ or\ L\text{-}cys\text{-}N,S)_3]^{0\ or\ 3-}$ ($M = Co^{III}$, Rh^{III}, Ir^{III}) with transition metal ions gave a variety of S-bridged metallo-aggregates, the structures and chiral properties of which are highly dependent on the nature of the reacting metal ions. The aggregation of the bis(thiolato)-type *cis*(*S*)-$[Co(aet)_2(en)]^{2+}$ was also performed through the replacement of a Ni^{II} ion in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ by other transition metal ions. While aggregation of these tris(thiolato)- and bis(thiolato)-types of octahedral units commonly produced discrete S-bridged polynuclear structures, one-dimensional and two-dimensional extended polymeric structures, besides a discrete trinuclear structure, were constructed by the reactions of the mono(thiolato)-type $[Co(aet\ or\ L\text{-}cys\text{-}N,S)(en)_2]^{2+\ or\ +}$ with silver(I) ion, because of the adoption of μ_3-thiolato bridging mode and/or the coordination ability of the free carboxylate group.

Recently, there has been an upsurge of interest in the chemistry of coordinated thiolato groups, because of the importance of this species in a variety of systems ranging from inorganic to organic and biological chemistry. One of the most attractive properties of thiolato groups bound to a transition metal center is their relatively high Lewis basicity, which leads to derivatives modified at sulfur atoms, such as coordinated sulfenato, sulfinato, thioether, and disulfide groups.[1–7] In addition, it has been recognized that coordinated thiolato groups have an affinity for transition metal ions to form S-bridged polynuclear structures, owing to their high Lewis basicity.[8–21] Thus, transition metal complexes containing thiolato donor groups could function as a metalloligand to a second metal center through S atoms. The use of thiolato metal complexes as an S-donating metalloligand would be of great interest with respect to the rational construction of well-organized S-bridged polynuclear structures by a systematic variation and combination of metal ions with different oxidation states and coordination geometries. In particular, it is of the author's special interest to employ octahedral thiolato metal complexes with simple aliphatic thiolate ligands as metalloligands, which are expected to create a variety of chiral metallo-aggregates by the control of their stereoisomerism.

The ligating ability of thiolato groups in an octahedral metal complex was initially suggested by Busch et al. in 1962. They prepared S-bridged trinuclear complexes with 2-aminoethanethiolate (aet), $[Co^{III}\{Co(aet)_3\}_2]^{3+}$ and $[Ni^{II}\{Co(aet)_3\}_2]^{2+}$, from the reactions of *fac*(*S*)-$[Co(aet)_3]$ with Co^{III} or Ni^{II}.[8a] The subsequent structural studies demonstrated that these complexes have a linear-type S-bridged trinuclear structure, in which the central metal ion is coordinated by 6 S atoms from two terminal *fac*(*S*)-$[Co(aet)_3]$ units.[22] The investigations of the linear-type S-bridged trinuclear structure were extended by several research groups to include other metal ions such as Fe^{III}, Ru^{III}, and Os^{III} at the center of the trinuclear structure.[8c–f] The author's group has shown that not only *fac*(*S*)-$[Co(aet)_3]$ but also a series of thiolato complexes with three aet or L-cys ligands, *fac*(*S*)-$[Co(L\text{-}cys\text{-}N,S)_3]^{3-}$, *fac*(*S*)-$[Rh(aet\ or\ L\text{-}cys\text{-}N,S)_3]^{0\ or\ 3-}$, and *fac*(*S*)-$[Ir(aet\ or\ L\text{-}cys\text{-}N,S)_3]^{0\ or\ 3-}$ (L-cys = L-cysteinate), construct the linear-type S-bridged trinuclear structure by the reactions with Fe^{III}, Co^{III}, and Ni^{II}.[9] From these investigations, it was evidenced that the tris(thiolato)-type *fac*(*S*)-$[M(aet\ or\ L\text{-}cys\text{-}N,S)_3]^{0\ or\ 3-}$ acts as an effective tridentate-*S*,*S*,*S* metalloligand toward transition metal ions, which prefer to take an octahedral coordination geometry. It has been noticed that *fac*(*S*)-$[Co(aet)_3]$ reacts also with metal ions such as Zn^{II} and Cd^{II}, which prefer to take a tetrahedral geometry, and the reaction products have long been presumed to have linear-type S-bridged structures.[8b,d] However, this presumption turned out to be incorrect with the discovery of cage-type S-bridged polynuclear complexes, $[Zn_3(OH)\{M(aet)_3\}_4]^{5+}$ and $[Zn_4O\{M(aet)_3\}_4]^{6+}$, which are formed from *fac*(*S*)-$[M(aet)_3]$ ($M = Co^{III}$, Rh^{III}, Ir^{III}) and tetrahedral Zn^{II} in water.[11a–f] In addition, it has been shown that other types of S-bridged polynuclear structures can be constructed by using metal ions, which prefer to take a linear or a square-planar co-

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ordination geometry.[12,13] Thus, the S-bridged polynuclear structures and the aggregation modes of the octahedral *fac*(*S*)-[M(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ units were found to be highly dependent on the nature of the reacting metal ions.

The ligating ability of coordinated thiolato groups toward transition metal ions such as Cu^{I}, Ag^{I}, and Hg^{II} has also been noticed in the 1970s for mono(thiolato)-type cobalt(III) complexes, $[Co(aet)(en)_2]^{2+}$ and $[Co(tga)(en)_2]^{+}$ (tga = mercaptoacetate). That is, Lane et al. showed that $[Co(aet)(en)_2]^{2+}$ and $[Co(tga)(en)_2]^{+}$ form strong adducts with Cu^{I}, one of which was characterized to be an S-bridged tetranuclear complex, $[Cu_2(CH_3CN)_4\{Co(aet)_2\}_2]^{6+}$.[14a] Heeg et al. reported that $[Co(aet)(en)_2]^{2+}$ and $[Co(tga)(en)_2]^{+}$ readily form 1:1 and 2:1 adducts with Ag^{I} or Hg^{II} in water, although only the 2:1 adducts with Ag^{I} have been characterized to have an S-bridged Co^{III}Ag^{I}Co^{III} trinuclear structure in [Ag{Co(aet or tga)(en)$_2$}$_2$]$^{5+\text{ or }3+}$.[14b,c] No further reports concerning these adducts have appeared for a long time, despite intensive interest concerning the structures and chiral properties of S-bridged polynuclear complexes constructed by the aggregation of thiolato metal complexes. Recently, the author's group has shown that the 1:1 adduct of $[Co(aet)(en)_2]^{2+}$ and $AgNO_3$ is an S-bridged (Co^{III}Ag^{I})$_n$ polymeric complex having a one-dimensional zigzag infinite chain structure, which exhibits unique chiral behavior.[14d,g] Furthermore, the use of Λ_L- or Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^{+}$, instead of $[Co(aet)(en)_2]^{2+}$, was found to result in the creation of fascinating chiral supramolecular structures, which are markedly dependent on the Λ_L and Δ_L diastereomers.[14e]

In contrast to the case for the tris(thiolato)- and mono(thiolato)-type complexes, the aggregation of the bis(thiolato)-type complexes by utilizing the ligating ability of coordinated thiolato groups has not been studied until recently. This was mainly because of the great difficulty in isolating this type of mononuclear species.[23] During the course of the investigation of S-bridged aggregates based on square-planar [M(aet)$_2$] (M = Ni^{II}, Pd^{II}) units,[16] the author's group serendipitously found that an S-bridged Co^{III}Ni^{II}Co^{III} trinuclear complex containing two *cis*(*S*)-[Co(aet)$_2$(en)]$^{+}$ units, [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$, could be readily prepared by the facile reaction of $[CoCl_2(en)_2]^{+}$ with [Ni(aet)$_2$].[17a] It has been noticed that the Ni–S bonds in [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ are relatively unstable in water to afford mononuclear *cis*(*S*)-[Co(aet)$_2$(en)]$^{+}$ species,[17b] which allows the use of this trinuclear complex as the starting material for the construction of S-bridged metallo-aggregates, instead of the mononuclear *cis*(*S*)-[Co(aet)$_2$(en)]$^{+}$. Thus, considerable progress has also been made in the chemistry of S-bridged polynuclear structures composed of the bis(thiolato)-type octahedral units through the replacement of the central Ni^{II} ion in [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ by other transition metal ions.[17c–g] In addition, recent findings on the ligating ability of the thiolato groups in the bis(thiolato)-type [Co(D-pen-*N*,*O*,*S*)$_2$]$^{-}$ (D-pen = D-penicillaminate) also contribute to the advance in the construction of the chiral S-bridged metallo-aggregates.[17g,18]

In this account, the author wishes to review the formation, structures, and properties of S-bridged metallo-aggregates based on the mono(thiolato)-, bis(thiolato)-, and tris(thiolato)-types of octahedral complex-units (Chart 1), which function as S-donating metalloligands toward various transition metal ions, emphasizing how a large variety of S-bridged metallo-aggregates can be constructed and how their structures and properties are controlled by the nature of S-donating metalloligands and reacting metal ions, as well as the reaction conditions employed.

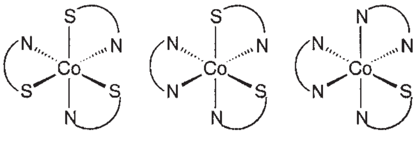
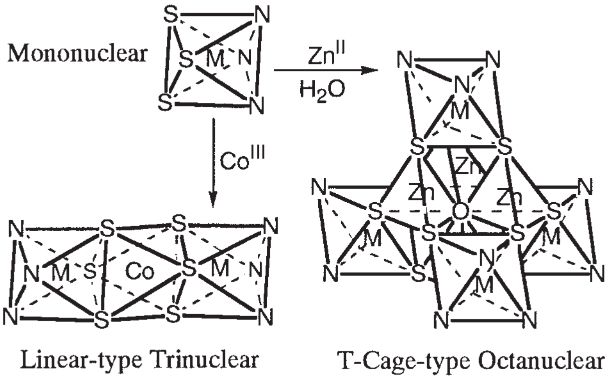

Tris(thiolato) Bis(thiolato) Mono(thiolato)

Chart 1.



Scheme 1.

1. Tris(thiolato)-Type System

1.1 Aggregation of *fac*(*S*)-[M(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ by Octahedral-Type Metal Ions. The reactions of *fac*(*S*)-[M(aet)$_3$] (M = Rh^{III},[24a] Ir^{III}) with $[CoCl(NH_3)_5]^{2+}$ in water produced linear-type S-bridged MCo^{III}M trinuclear complexes, [Co^{III}{M(aet)$_3$}$_2$]$^{3+}$,[9e,g] like the reaction of *fac*(*S*)-[Co(aet)$_3$] with $[CoX(NH_3)_5]^{2+}$ (X = Cl, Br) (Scheme 1).[8a] In these trinuclear structures, the central Co^{III} ion is coordinated by 6 S atoms from two terminal octahedral *fac*(*S*)-[M(aet)$_3$] units, indicating the availability of *fac*(*S*)-[M(aet)$_3$] as a tridentate-*S*,*S*,*S* metalloligand. Of three possible binding modes (Fig. 1), *fac*(*S*)-[M(aet)$_3$] adopts the chelating mode in the MCo^{III}M trinuclear structures. When *fac*(*S*)-[M(aet)$_3$] (M = Rh^{III}, Ir^{III}) were reacted with Co^{2+} in water, S-bridged MCo^{II}M trinuclear complexes, [Co^{II}{M(aet)$_3$}$_2$]$^{2+}$, which are readily converted to [Co^{III}{M(aet)$_3$}$_2$]$^{3+}$ by the H_2O_2 or air oxidation, were formed.[9e,g] It has been shown that a similar reaction of *fac*(*S*)-[Co(aet)$_3$] with Co^{2+} immediately produces [Co^{III}{Co(aet)$_3$}$_2$]$^{3+}$, while the intermediate [Co^{II}{Co(aet)$_3$}$_2$]$^{2+}$ has not been detected.[8a,9d] Thus, it is seen that the *fac*(*S*)-[M(aet)$_3$] (M = Rh^{III}, Ir^{III}) units stabilize the central Co^{II} oxidation state, compared with the *fac*(*S*)-[Co(aet)$_3$] unit.

For [Co^{III}{M(aet)$_3$}$_2$]$^{3+}$ (M = Rh^{III}, Ir^{III}), both the *meso* ($\Delta\Lambda$) and *racemic* ($\Delta\Delta/\Lambda\Lambda$) forms were produced,[9e,g] as in the case for [Co^{III}{Co(aet)$_3$}$_2$]$^{3+}$,[8b] and these were successfully separated and optically resolved by fractional crystallization and/or SP-Sephadex C-25 column chromatography. The crystal structures of $\Delta\Lambda$-[Co^{III}{Rh(aet)$_3$}$_2$](NO$_3$)$_3$ and $\Delta\Lambda$-[Co^{III}{Ir(aet)$_3$}$_2$](NO$_3$)$_3$ were determined by X-ray analyses; the structure of the latter complex is depicted in Fig. 2.[9e,g] In

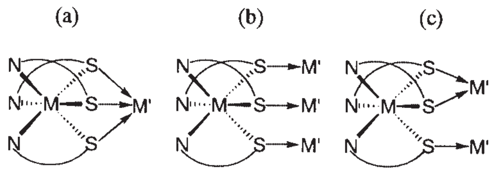


Fig. 1. Three binding modes, chelating (a), bridging (b), and chelate-bridging (c), possible for the *fac*(*S*)-[M(didentate-*N*,*S*)$_3$]-type metalloligand.

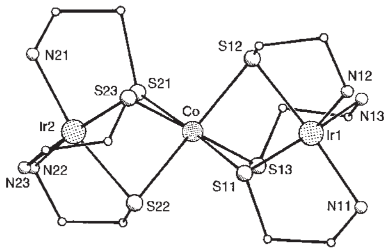


Fig. 2. Crystal structure of $\Delta\Lambda$-[Co{Ir(aet)$_3$}$_2$]$^{3+}$. Hydrogen atoms are omitted for clarity.

these trinuclear structures, two *fac*(*S*)-[M(aet)$_3$] octahedral units are linked by a central Co$^{\rm III}$ ion such that three metals are arranged to be linear with two identical M–Co distances. The coordination geometry of the central Co$^{\rm III}$ ion is trigonally distorted from a regular octahedron, having acute S–Co–S bite angles (Table 1). The overall structures of $\Delta\Lambda$-[Co$^{\rm III}${M(aet)$_3$}$_2$]$^{3+}$ (M = Rh$^{\rm III}$, Ir$^{\rm III}$) are similar to that of the corresponding S-bridged Co$^{\rm III}$Co$^{\rm III}$Co$^{\rm III}$ complex, $\Delta\Lambda$-[Co$^{\rm III}${Co(aet)$_3$}$_2$]$^{3+}$ (Table 1).[22a] However, the Co–S distances in $\Delta\Lambda$-[Co$^{\rm III}${M(aet)$_3$}$_2$]$^{3+}$ are longer than the corresponding Co–S ones in $\Delta\Lambda$-[Co$^{\rm III}${Co(aet)$_3$}$_2$]$^{3+}$, which indicates that the S atoms of the *fac*(*S*)-[M(aet)$_3$] units (M = Rh$^{\rm III}$, Ir$^{\rm III}$) bind to the central Co$^{\rm III}$ ion more weakly than do the S atoms of the *fac*(*S*)-[Co(aet)$_3$] units. The averaged M–N distances in [Co$^{\rm III}${M(aet)$_3$}$_2$]$^{3+}$ are ca. 0.12 Å longer than the Co–N one in [Co$^{\rm III}${Co(aet)$_3$}$_2$]$^{3+}$, as is expected from the difference in covalent radii between Co$^{\rm III}$ and M = Rh$^{\rm III}$, Ir$^{\rm III}$ ions.[25] On the other hand, the averaged M–S distances are only ca. 0.07 Å longer than the corresponding Co–S one in [Co$^{\rm III}${Co(aet)$_3$}$_2$]$^{3+}$. These structural parameters suggest that the M–S bonds in the *fac*(*S*)-[M(aet)$_3$] (M = Rh$^{\rm III}$, Ir$^{\rm III}$) units are stronger than the Co–S bonds in the *fac*(*S*)-[Co(aet)$_3$] units, which results in the weaker binding to the central Co$^{\rm III}$ ion. The Ir–S bonds would be stronger than the Rh–S bonds, taking account of the fact that the *meso–racemic* isomerization resulting from the cleavage of the Co–S bonds has been recognized only for [Co$^{\rm III}${Ir(aet)$_3$}$_2$]$^{3+}$ in methanol–H$_2$O and ethanol–H$_2$O.[9g]

The electrochemical data for the *racemic* [Co$^{\rm III}${M(aet)$_3$}$_2$](NO$_3$)$_3$ (M = Co$^{\rm III}$, Rh$^{\rm III}$, Ir$^{\rm III}$) in 0.1 mol dm^{-3} aqueous NaNO$_3$ are summarized in Table 2.[9e,g] The cyclic voltammogram of [Co$^{\rm III}${Ir(aet)$_3$}$_2$]$^{3+}$ displayed almost reversible redox couples at $E_{1/2} = -0.23$ V and $+0.73$ V in the potential region of -1.1 V to $+1.1$ V (vs Ag/AgCl). The redox couple at $E_{1/2} = -0.23$ V, assigned as the one-electron process due to the central Co$^{\rm III/II}$, is 0.13 V more positive than that for [Co$^{\rm III}${Rh(aet)$_3$}$_2$]$^{3+}$ and 0.43 V more positive than that for [Co$^{\rm III}${Co(aet)$_3$}$_2$]$^{3+}$, indicating that the terminal *fac*(*S*)-[M(aet)$_3$] units make it easier to reduce the central Co$^{\rm III}$ to Co$^{\rm II}$ in the order M = Ir$^{\rm III}$ > Rh$^{\rm III}$ > Co$^{\rm III}$. This can be ascribed to the electron donating ability of the thiolato groups in the *fac*(*S*)-[Co(aet)$_3$] units, which decreases in the order M = Co$^{\rm III}$ > Rh$^{\rm III}$ > Ir$^{\rm III}$. On the other hand, the redox couple at $E_{1/2} = +0.73$ V involving the terminal Ir$^{\rm IV/III}$ process is 0.28 V more negative than the Rh$^{\rm IV/III}$ process for [Co$^{\rm III}${Rh(aet)$_3$}$_2$]$^{3+}$. For [Co$^{\rm III}${Co(aet)$_3$}$_2$]$^{3+}$, no redox couple is observed in the positive potential region up to $+1.1$ V, while a one-electron redox process due to the terminal Co$^{\rm III/II}$ occurs at $E_{1/2} = -0.84$ V. Thus, it is considered that the *fac*(*S*)-[M(aet)$_3$] units are oxidized more easily in the order M = Ir$^{\rm III}$ > Rh$^{\rm III}$ > Co$^{\rm III}$.

The linear-type S-bridged trinuclear complexes with L-cys ligands, [Co$^{\rm III}${M(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, in which two *fac*(*S*)-[M(L-cys-*N*,*S*)$_3$]$^{3-}$ units are linked by a central Co$^{\rm III}$ ion, were also produced by the reactions of $\Delta_{\rm LLL}$-*fac*(*S*)-[M(L-cys-*N*,*S*)$_3$]$^{3-}$ (M = Co$^{\rm III}$,[24b] Rh$^{\rm III}$, Ir$^{\rm III}$) with [CoCl(NH$_3$)$_5$]$^{2+}$ or Co^{2+},[9a,b,e,g] although the reactions with Co^{2+} for M = Rh$^{\rm III}$, Ir$^{\rm III}$ required the air or H$_2$O$_2$ oxidation as was true in the case of the corresponding aet complexes. This result clearly indicates that $\Delta_{\rm LLL}$-*fac*(*S*)-[M(L-cys-*N*,*S*)$_3$]$^{3-}$ functions as an effective tri-

Table 1. Selected Bond Distances (Å) and Angles (deg) (Averaged) for $\Delta\Lambda$-[Co{M(aet)$_3$}$_2$]$^{3+}$ (M = Co$^{\rm III}$, Rh$^{\rm III}$, Ir$^{\rm III}$)

	[Co{Co(aet)$_3$}$_2$]$^{3+}$	[Co{Rh(aet)$_3$}$_2$]$^{3+}$	[Co{Ir(aet)$_3$}$_2$]$^{3+}$
M–S	2.238(7)	2.307(2)	2.307(2)
M–N	1.996(8)	2.122(7)	2.120(8)
Co–S	2.262(11)	2.291(2)	2.297(2)
M···Co	2.857(1)	2.910(1)	2.906(1)
S–Co–S	83.5(9)	84.58(7)	84.7(1)

Table 2. Electrochemical Data ($E_{1/2} = (E_{\rm pc} + E_{\rm pa})/2$ in V vs Ag/AgCl) for $\Delta\Delta/\Lambda\Lambda$-[Co{M(aet)$_3$}$_2$]$^{3+}$ (M = Co$^{\rm III}$, Rh$^{\rm III}$, Ir$^{\rm III}$)

	M$^{\rm IV/III}$Co$^{\rm III}$M$^{\rm III}$	M$^{\rm III}$Co$^{\rm III/II}$M$^{\rm III}$	M$^{\rm III}$Co$^{\rm II}$M$^{\rm III/II}$
[Co{Ir(aet)$_3$}$_2$]$^{3+}$	+0.73	−0.23	
[Co{Rh(aet)$_3$}$_2$]$^{3+}$	+1.01	−0.36	
[Co{Co(aet)$_3$}$_2$]$^{3+}$		−0.66	−0.84

At 22 °C in 0.1 mol dm^{-3} aqueous NaNO$_3$ at a glassy-carbon electrode with scan rate 100 mV s^{-1}.

dentate-*S*,*S*,*S* metalloligand. As expected, the reactions with $[\mathrm{CoCl(NH_3)_5}]^{2+}$ formed only the $\Delta_{\rm LLL}\Delta_{\rm LLL}$ isomer, retaining the chiral configuration of the starting $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{M}(\text{L-cys-}N,S)_3]^{3-}$. However, the configurational inversion, which gives the $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ and $\Delta_{\rm LLL}\Lambda_{\rm LLL}$ isomers, was recognized for the reaction of $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ with Co^{2+} at room temperature.[9a,b] In particular, the reaction with excess Co^{2+} produced only the inverted $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomer. This can be ascribed to the dissociation followed by the rearrangement of L-cys ligands in $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ to take the $\Lambda_{\rm LLL}$ configuration, which is induced by the formation of an S-bridged structure with $\mathrm{Co^{II}}$. Molecular model examinations revealed that effective intramolecular hydrogen bonds are formed between coordinated amine groups and free carboxylate groups for the $\Delta_{\rm LLL}$ configurational *fac*(*S*)-$[\mathrm{Rh}(\text{L-cys-}N,S)_3]^{3-}$ unit in the S-bridged trinuclear structure.[9b,d] The $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ and $\Delta_{\rm LLL}\Lambda_{\rm LLL}$ isomers, besides the $\Delta_{\rm LLL}\Delta_{\rm LLL}$ one, were also formed for $[\mathrm{Co^{III}}\{\mathrm{Rh}(\text{L-cys-}N,S)_3\}_2]^{3-}$, when the reaction solution of $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Rh}(\text{L-cys-}N,S)_3]^{3-}$ and Co^{2+} was heated at 95 °C for 1 h, followed by the air oxidation.[9e] On the other hand, the formation of the $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ and $\Delta_{\rm LLL}\Lambda_{\rm LLL}$ isomers was not detected for $[\mathrm{Co^{III}}\{\mathrm{Ir}(\text{L-cys-}N,S)_3\}_2]^{3-}$, even when the reaction solution of $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Ir}(\text{L-cys-}N,S)_3]^{3-}$ and Co^{2+} was heated at 95 °C for one day.[9g] From these results, it is considered that the robustness of $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{M}(\text{L-cys-}N,S)_3]^{3-}$ decreases in the order $\mathrm{M} = \mathrm{Ir^{III}} > \mathrm{Rh^{III}} > \mathrm{Co^{III}}$. The configurational inversion of the $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ has also been found for the reaction with $\mathrm{Fe^{II}}$, which produced a linear-type S-bridged trinuclear $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$- and $\Delta_{\rm LLL}\Lambda_{\rm LLL}$-$[\mathrm{Fe^{III}}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$, while the reaction with $\mathrm{Fe^{III}}$ proceeded with retention of the chiral configuration to give $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\mathrm{Fe^{III}}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$.[9c]

The electronic absorption spectra of $[\mathrm{Co^{III}}\{\mathrm{M(aet)_3}\}_2]^{3+}$ and $[\mathrm{Co^{III}}\{\mathrm{M}(\text{L-cys-}N,S)_3\}_2]^{3-}$ exhibit characteristic intense absorption bands in the visible and near-UV regions of (16–32) × 10^3 cm^{-1} (Fig. 3).[9] These intense bands are obviously assigned as arising at least in part from the central $\mathrm{Co^{III}S_6}$ chromophore, taking account of the absorption spectral behavior of the mononuclear *fac*(*S*)-$[\mathrm{M(aet)_3}]$ and *fac*(*S*)-$[\mathrm{M}(\text{L-cys-}N,S)_3]^{3-}$, which gives no intense band in the corresponding region (Fig. 4). It is noticed that the intense visible bands (ca. 16 × 10^3 and 23 × 10^3 cm^{-1}) for the $\mathrm{Ir^{III}Co^{III}Ir^{III}}$ trinuclear complexes are located at lower energy than those for the $\mathrm{Rh^{III}Co^{III}Rh^{III}}$ complexes. This seems to reflect the electron donating ability of the thiolato groups in *fac*(*S*)-$[\mathrm{Ir}(\text{aet or L-cys-}N,S)_3]^{0\text{ or }3-}$, which is weaker than that in *fac*(*S*)-$[\mathrm{Rh}(\text{aet or L-cys-}N,S)_3]^{0\text{ or }3-}$.

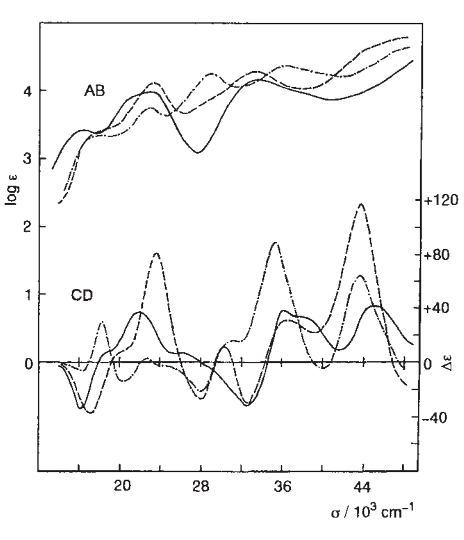


Fig. 3. Electronic absorption and CD spectra of ΔΔ-$[\mathrm{Co\{Co(aet)_3\}_2}]^{3+}$ (-•-), ΔΔ-$[\mathrm{Rh\{Co(aet)_3\}_2}]^{3+}$ (- - -), and ΔΔ-$[\mathrm{Ir\{Co(aet)_3\}_2}]^{3+}$ (—) in $\mathrm{H_2O}$.

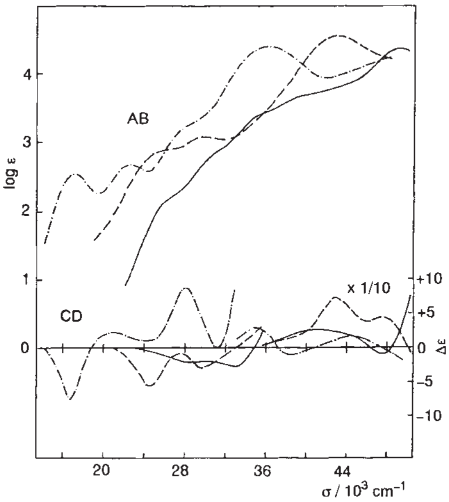


Fig. 4. Electronic absorption and CD spectra of $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ (-•-), $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Rh}(\text{L-cys-}N,S)_3]^{3-}$ (- - -), and $\Delta_{\rm LLL}$-*fac*(*S*)-$[\mathrm{Ir}(\text{L-cys-}N,S)_3]^{3-}$ (—) in $\mathrm{H_2O}$.

The reactions of *fac*(*S*)-$[\mathrm{M(aet)_3}]$ or *fac*(*S*)-$[\mathrm{M}(\text{L-cys-}N,S)_3]^{3-}$ ($\mathrm{M} = \mathrm{Co^{III}}, \mathrm{Rh^{III}}$) with Ni^{2+} also produced S-bridged trinuclear complexes, $[\mathrm{Ni^{II}}\{\mathrm{M(aet)_3}\}_2]^{2+}$ and $[\mathrm{Ni^{II}}\{\mathrm{M}(\text{L-cys-}N,S)_3\}_2]^{4-}$.[9c,h] X-ray analyses of ΔΔ/ΛΛ-$[\mathrm{Ni^{II}\{Co(aet)_3\}_2}]\mathrm{Cl_2}$ and ΔΔ/ΛΛ-$[\mathrm{Ni^{II}\{Rh(aet)_3\}_2}](\mathrm{NO_3})_2$ established that the central $\mathrm{Ni^{II}}$ ion is octahedrally coordinated by six thiolato S atoms from the two *fac*(*S*)-$[\mathrm{M(aet)_3}]$ units.[9h,22b] Since $\mathrm{Ni^{II}}$ ion possibly takes octahedral, square-planar, and tetrahedral coordination geometries, the formation of the linear-type $\mathrm{MNi^{II}M}$ structure seems to indicate that *fac*(*S*)-$[\mathrm{M}(\text{aet or L-cys-}N,S)_3]^{0\text{ or }3-}$ preferably act as a chelating tridentate-*S*,*S*,*S* ligand so as to accommodate a reacting metal ion in an $\mathrm{S_6}$ coordination environment. Consistent with this, a number of linear-type S-bridged trinuclear complexes, $[\mathrm{M'\{Rh(aet)_3\}_2}]^{3+}$ and $[\mathrm{M'\{Ir(aet)_3\}_2}]^{3+}$, have also been prepared for other transition metal ions $\mathrm{M'} = \mathrm{V^{III}}, \mathrm{Cr^{III}}, \mathrm{Fe^{III}}, \mathrm{Mo^{III}}, \mathrm{Re^{III}}$.[10]

1.2 Aggregation of *fac*(*S*)-$[\mathrm{M(aet)_3}]$ by Tetrahedral-Type Metal Ions. Unlike the reactions with octahedral-type metal ions, the reactions of *fac*(*S*)-$[\mathrm{M(aet)_3}]$ ($\mathrm{M} = \mathrm{Co^{III}}, \mathrm{Rh^{III}}, \mathrm{Ir^{III}}$) with Zn^{2+} in water, which prefers to take a tetrahedral coordination geometry, produced *T*-symmetrical cage-type octanuclear complexes with a "complete" $[\mathrm{Zn_4O}]^{6+}$ core, $[\mathrm{Zn_4O\{M(aet)_3\}_4}]^{6+}$, by way of precursory cage-type heptanuclear complexes with a "defective" $[\mathrm{Zn_3(OH)}]^{5+}$ core, $[\mathrm{Zn_3(OH)\{M(aet)_3\}_4}]^{5+}$ (Scheme 1).[11a–f] The T-cage-type octanuclear complexes with a "complete" $[\mathrm{Zn_4O}]^{6+}$ core were effectively prepared by the reactions with a mixture of Zn^{2+} and ZnO in water. Since the reaction solutions of *fac*(*S*)-$[\mathrm{M(aet)_3}]$ and Zn^{2+} turned from neutral to acidic, it is likely that the cen-

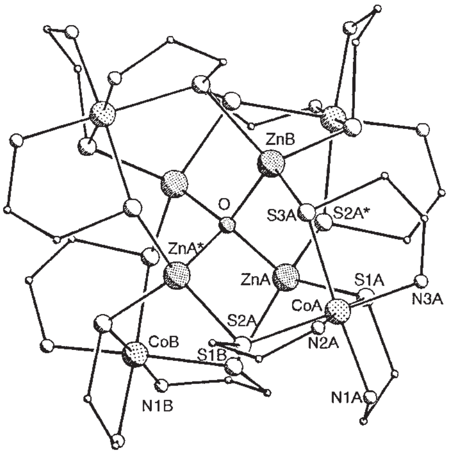


Fig. 5. Crystal structure of spontaneously resolved ΛΛΛΛ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$. Hydrogen atoms are omitted for clarity.

tral oxide ion in the octanuclear structure comes from water, liberating hydrogen ions in solution. The stability of the T-cage-type structure with a "complete" $[Zn_4O]^{6+}$ core, together with the strong affinity of Zn^{II} toward oxygen atom, may be a significant factor of pulling hydrogen ions off water, which is promoted by adding the potentially strong base of ZnO.

The structure of the representative T-cage-type octanuclear complex, $[Zn_4O\{Co(aet)_3\}_4]Br_6$,[11c] is shown in Fig. 5. In this $Co^{III}{}_4Zn^{II}{}_4$ octanuclear structure, four Zn^{II} ions are bound to a central oxide ion in a tetrahedral geometry, and to this tetrahedral $[Zn^{II}{}_4O]^{6+}$ core four *fac*(*S*)-$[Co(aet)_3]$ units are bound in a tetrahedral arrangement (average Zn–S = 2.343(3) Å, Zn–O = 1.948(12) Å, S–Zn–S = 111.7(1)°, S–Zn–O = 107.2(3)°). The *T*-symmetrical structure is understood by four C_3 axes passing through the Co, O, and Zn atoms. Each Zn^{II} ion takes an approximately tetrahedral geometry, coordinated by three S atoms from three different *fac*(*S*)-$[Co(aet)_3]$ units and an O atom at the center of the octanuclear structure. Each *fac*(*S*)-$[Co(aet)_3]$ unit is bound to three different Zn^{II} ions through sulfur-bridges; this bridging binding mode (Fig. 1b) is distinct from the binding mode for the linear-type trinuclear structure. Notably, all four *fac*(*S*)-$[Co(aet)_3]$ units, as well as all 12 bridging S atoms, take the unified chirality to form only the ΔΔΔΔ and ΛΛΛΛ isomers. Furthermore, the bromide salt of $[Zn_4O\{Co(aet)_3\}_4]^{+}$ crystallized in a chiral space group $P2_13$, indicating the occurrence of spontaneous resolution upon crystallization. The crystal used for X-ray analysis, which showed a positive CD value at 580 nm, was determined to contain the ΛΛΛΛ isomer.[11c]

Figure 6 illustrates the absorption and CD spectra of the ΔΔΔΔ isomer of $[Zn_4O\{Co(aet)_3\}_4]^{6+}$,[11c] together with those of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$. The $Co^{III}{}_4Zn^{II}{}_4$ octanuclear complex exhibits two d–d bands (ca. 18 × 10^3 and 24 × 10^3 cm^{-1}) and two intense sulfur-to-cobalt charge transfer (CT) bands (ca. 30 × 10^3 and 38 × 10^3 cm^{-1}) in the near-UV region. This absorption spectral feature is similar to that of *fac*(*S*)-[Co(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$; furthermore, the absorption curve coincides with that of 4 mol of *fac*(*S*)-[Co(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ over the whole region. This implies that the absorption spectrum of the $Co^{III}{}_4Zn^{II}{}_4$ octanuclear complex is dominated by the *fac*(*S*)-$[Co(aet)_3]$ units, that is, the electronic state of the coordinated thiolato groups in *fac*(*S*)-$[Co(aet)_3]$ is little affected by bridging with Zn^{II}. Two kinds of CD contribution are expected for ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$: one from four Δ-*fac*(*S*)-$[Co(aet)_3]$ units and the other from 12 *S* configurational S atoms. The CD spectrum of ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$ is quite similar to that of 4 mol of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ in the region of (16–39) × 10^3 cm^{-1}. This good agreement suggests that the CD contribution due to asymmetric S atoms is minor in this region. In the sulfur-to-cobalt CT region of (32–40) × 10^3 cm^{-1}, however, the CD bands of ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$ are reversed in sign, compared with those of 4 mol of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$. Taking into consideration that the vicinal CD contribution due to L-cys-*N*,*S* ligands is relatively small,[9c] it is reasonable to assume that the bridging S atoms contribute dominantly to the CD spectra in this region.

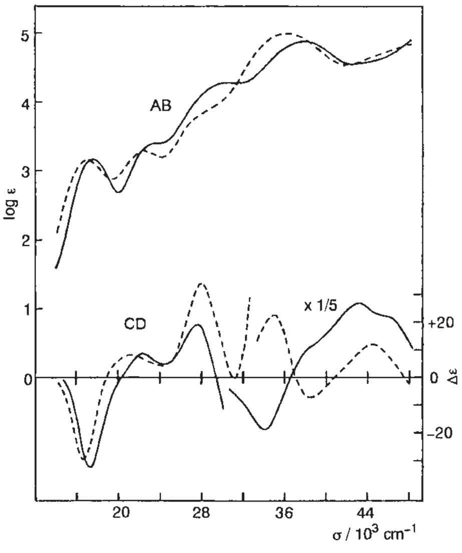


Fig. 6. Electronic absorption and CD spectra of ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$ (—) and Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ (×4) (- - -) in H_2O.

The cyclic voltammogram of $[Zn_4O\{Co(aet)_3\}_4]^{6+}$ displayed four consecutive reduction waves ($E_{pc} = -0.44$, -0.56, -0.69, and -0.87 V) and coupled oxidation waves ($E_{pa} = -0.36, -0.48, -0.61$, and -0.79 V) in the negative potential region (Fig. 7).[11c] Since no redox reaction occurred under the same conditions for $[Zn_4O\{Rh(aet)_3\}_4]^{6+}$ and $[Zn_4O\{Ir(aet)_3\}_4]^{6+}$, the characteristic redox processes can be assigned as the stepwise reactions as follows:

$$[Co^{III}{}_4Zn^{II}{}_4]^{6+} \rightleftarrows [Co^{III}{}_3Co^{II}Zn^{II}{}_4]^{5+} \rightleftarrows [Co^{III}{}_2Co^{II}{}_2Zn^{II}{}_4]^{4+} \rightleftarrows [Co^{III}Co^{II}{}_3Zn^{II}{}_4]^{3+} \rightleftarrows [Co^{II}{}_4Zn^{II}{}_4]^{2+}$$

Since similar redox behavior has been observed for the T-cage-type $Co^{III}{}_4Hg^{II}{}_4$ octanuclear complex, $[Hg_4O\{Co(aet)_3\}_4]^{6+}$ (vide infra), the presence of four consecutive redox couples may be used for the assignment of the cage-type S-bridged structures composed of four *fac*(*S*)-$[Co(aet)_3]$ units.

While the T-cage-type S-bridged octanuclear complexes with a "complete" $[Zn_4O]^{6+}$ core are fairly stable in water, the cage-type heptanuclear complexes with a "defective" $[Zn_3(OH)]^{5+}$ core showed drastic CD spectral changes with

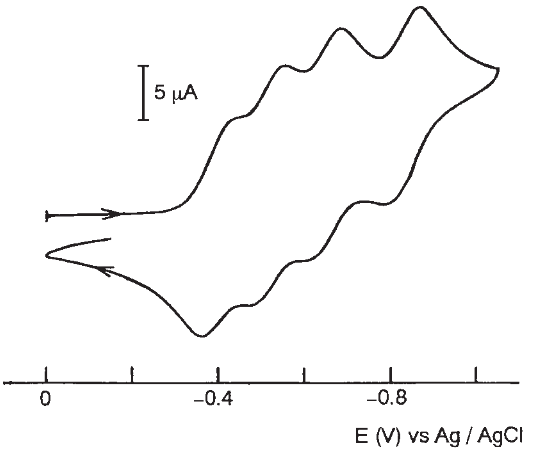


Fig. 7. Cyclic voltammogram of 1.0 mmol dm^{-3} [Zn_4O-{$Co(aet)_3$}$_4$]$^{6+}$ in 0.1 mmol dm^{-3} aqueous solution of $NaNO_3$. The scan rate is 50 mV s^{-1}.

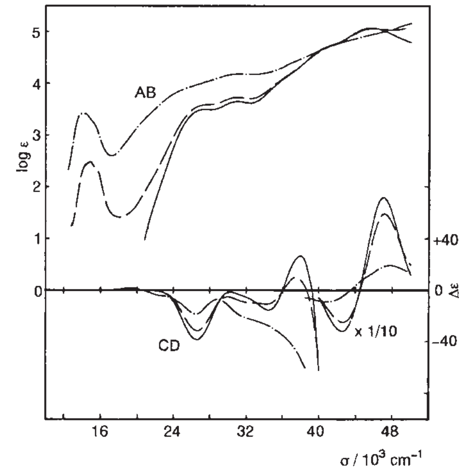
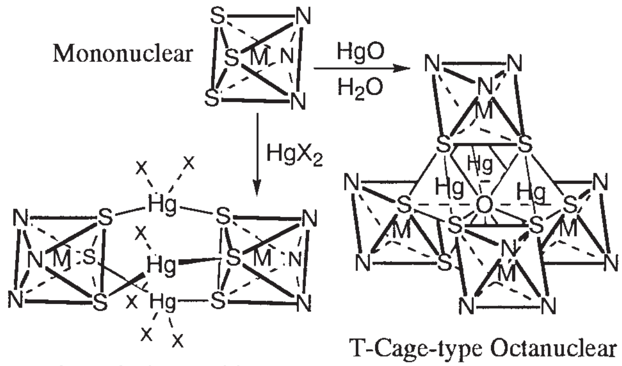


Fig. 8. Electronic absorption and CD spectra of ΔΔΔΔ-[Co_4O{$Rh(aet)_3$}$_4$]$^{6+}$ (-•-), ΔΔΔΔ-[$Zn_{3.7}Co_{0.3}O${$Rh(aet)_3$}$_4$]$^{6+}$ (- - -), and ΔΔΔΔ-[Zn_4O{$Rh(aet)_3$}$_4$]$^{6+}$ (—) in H_2O.

time in water, because of the cleavage of Zn–S bonds.[11a,e] Thanks to this property, the heptanuclear structure in [$Zn_3(OH)${$Rh(aet)_3$}$_4$]$^{5+}$ was converted to the linear-type trinuclear structure in [Co{$Rh(aet)_3$}$_2$]$^{3+}$ by the reaction with [$CoCl(NH_3)_5$]$^{2+}$ in water.[11e] On the other hand, the conversion of the linear-type trinuclear structure to the cage-type octanuclear structure was achieved by the reactions of [Co{$M(aet)_3$}$_2$]$^{3+}$ (M = Rh^{III}, Ir^{III}) with Zn powder in water, followed by the addition of Zn^{2+}.[11b,d,f] The plasma emission spectral analyses of the reaction products pointed out the presence of Co and Zn atoms, and the absorption spectrum of each product exhibited an extra absorption band centered at ca. 14.8 × 10^3 cm^{-1}, which is characteristic of tetrahedral Co^{II} chromophore (Fig. 8). From these results, along with the X-ray structural analyses, we concluded that, in the course of the conversion reactions of [Co{$M(aet)_3$}$_2$]$^{3+}$ with a mixture of Zn and Zn^{2+}, Co^{II} is partially trapped in place of Zn^{II} in the T-cage-type octanuclear structure to form [$Zn^{II}_{4-x}Co^{II}_xO$]$^{6+}$ core ($x = 0.3$ for M = Rh^{III}, $x = 1.2$ for M = Ir^{III}).

Encouraged by this result, we also attempted the syntheses of T-cage-type octanuclear complexes with a "complete" [Co^{II}_4O]$^{6+}$ core, [Co_4O{$M(aet)_3$}$_4$]$^{6+}$. The reactions of *fac*(*S*)-[$M(aet)_3$] (M = Rh^{III}, Ir^{III}) with a mixture of CoO and Co^{2+} in water produced dark-green products, which showed a characteristic intense absorption band at ca. 14.2 × 10^3 cm^{-1} (Fig. 8). These products were assigned as T-cage-type $M_4Co^{II}_4$ octanuclear complexes, [Co_4O{$M(aet)_3$}$_4$]$^{6+}$ (M = Rh^{III}, Ir^{III}), by single-crystal X-ray analyses, as well as the plasma emission and elemental analyses.[11f,g] While [Zn_4O{$M(aet)_3$}$_4$]$^{6+}$ (M = Rh^{III}, Ir^{III}) in 0.1 mol dm^{-3} aqueous $NaNO_3$ were electrochemically inactive in the potential region of −1.0 V to +1.0 V (vs Ag/AgCl), the cyclic voltammograms for [Co_4O{$M(aet)_3$}$_4$]$^{6+}$ yielded one reversible redox couple assigned to [Co_4O]$^{6+}$/[Co_4O]$^{5+}$ in a rather negative potential region ($E_{1/2} = -0.84$ V for M = Rh^{III}, −0.97 V for M = Ir^{III}). Since no redox reaction occurred in a positive potential region up to +0.8 V, one may conclude that the tetrahedral Co^{II} state is fairly stabilized in the T-cage-type $M_4Co^{II}_4$ octanuclear structure.

The formation of the cage-type heptanuclear and octanuclear complexes with tetrahedral Zn^{II} and/or Co^{II} ions suggested that similar cage-type structures are formed from *fac*(*S*)-[$M(aet)_3$] and other metal ions, which can adopt a tetrahedral coordination geometry. Indeed, the reaction of *fac*(*S*)-[$Rh(aet)_3$] with Cd^{2+} in water produced a cage-type $Rh^{III}_4Cd^{II}_3$ heptanuclear complex with a "defective" [$Cd_3(OH)$]$^{5+}$ core, [$Cd_3(OH)$-{$Rh(aet)_3$}$_4$]$^{5+}$, the structure of which was determined by X-ray analysis.[11h] The corresponding T-cage-type $Rh^{III}_4Cd^{II}_4$ octanuclear complex with a "complete" [Cd_4O]$^{6+}$ core, [Cd_4O{$Rh(aet)_3$}$_4$]$^{6+}$, was also obtained by the reaction of *fac*(*S*)-[$Rh(aet)_3$] with a mixture of CdO and Cd^{2+}.[11h] It was found that [Cd_4O{$Rh(aet)_3$}$_4$]$^{6+}$ is not stable in water. Attempts to resolve a pair of enantiomers (ΔΔΔΔ/ΛΛΛΛ) with the use of [Sb_2(*R*,*R*-tartrato)$_2$]$^{2-}$ in water resulted in the formation of optically active [$Cd_3(OH)${$Rh(aet)_3$}$_4$]$^{5+}$. This is in contrast to the fact that [Zn_4O{$Rh(aet)_3$}$_4$]$^{6+}$ is very stable in water and can be formed by allowing an aqueous solution of [$Zn_3(OH)${$Rh(aet)_3$}$_4$]$^{5+}$ to stand.[11d] The T-cage-type $M_4Hg^{II}_4$ octanuclear complexes involving tetrahedral Hg^{II} ions, [Hg_4O{$M(aet)_3$}$_4$]$^{6+}$, have also been produced by the reactions of *fac*(*S*)-[$M(aet)_3$] (M = Co^{III}, Rh^{III}) with HgO in water (Scheme 2).[11i] It was found that the $M_4Hg^{II}_4$ octanuclear complexes are stable in water, which could be ascribed to the strong



Scheme 2.

Hg–S bonds. In addition, the T-cage-type $Cr^{III}{}_4Zn^{II}{}_4$ complex composed of four *fac*(*S*)-[Cr(aet)$_3$] units, $[Zn_4O\{Cr(aet)_3\}_4]^{6+}$, has been prepared from *fac*(*S*)-[Cr(aet)$_3$] and Zn^{2+} in water.[19b] In this $Cr^{III}{}_4Zn^{II}{}_4$ octanuclear complex, the intramolecular magnetic exchange interaction is very small ($J = -0.17$ cm^{-1}), reflecting the large separation among four Cr^{III} ions (average 6.755(4) Å) in the T-cage-type octanuclear structure.

Here, it should be noted that only a pair of enantiomers, ΔΔΔΔ and ΛΛΛΛ, in which the chiral configurations of all four *fac*(*S*)-[M(aet)$_3$] units and all 12 bridging S atoms are unified, were commonly formed for a series of cage-type heptanuclear and octanuclear complexes.[11,19b] Molecular model examinations indicated that there exist significant nonbonding interactions of the aet chelate rings among the *fac*(*S*)-[M(aet)$_3$] units when the absolute configurations of the four *fac*(*S*)-[M(aet)$_3$] units are not uniform. The ΔΔΔΔ and ΛΛΛΛ isomers for all the cage-type complexes were successfully optically resolved; furthermore, the chloride, bromide, and nitrate salts of the T-cage-type octanuclear complexes, $[Zn_4O\{M(aet)_3\}_4]^{6+}$ (M = Cr^{III}, Co^{III}, Rh^{III}, Ir^{III}), $[Zn_{4-x}Co_xO\{M(aet)_3\}_4]^{6+}$ (M = Rh^{III}, Ir^{III}), and $[Co_4O\{M(aet)_3\}_4]^{6+}$ (M = Rh^{III}, Ir^{III}), were found to be subjected to spontaneous resolution to afford optically active crystals.[11,19b] Thus, by the use of tetrahedral-type bridging metal ions, optically active metallo-aggregates containing a total of 16 chiral centers are available from the *fac*(*S*)-[M(aet)$_3$] (M = Cr^{III}, Co^{III}, Rh^{III}, Ir^{III}) molecules that are unable to be optically resolved because of their poor solubility in any solvent.

1.3 Aggregation of *fac*(*S*)-[M(aet)$_3$] by Linear-Type Metal Ions.

Though the reactions of *fac*(*S*)-[M(aet)$_3$] (M = Co^{III}, Rh^{III}) with HgO in water gave the T-cage-type $M_4Hg^{II}{}_4$ octanuclear complexes, $[Hg_4O\{M(aet)_3\}_4]^{6+}$,[11i] the corresponding reactions of *fac*(*S*)-[Rh(aet)$_3$] with HgX$_2$ (X = Cl, NO$_3$) produced $Rh^{III}{}_2Hg^{II}{}_3$ pentanuclear complexes, $[Hg_3Cl_6\{Rh(aet)_3\}_2]$ and $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2]^{2+}$, in which five metals form a trigonal-bipyramid (Scheme 2).[12a,b] The molecular structures of $[Hg_3Cl_6\{Rh(aet)_3\}_2]$ and $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2](NO_3)_2$, determined by X-ray analyses, revealed that each Hg^{II} ion has a significantly distorted tetrahedral geometry with expanded S–Hg–S angles (average S–Hg–S = 147.6(1)° for X = Cl, 161.0(2)° for X = NO$_3$), coordinated by two thiolato S atoms from two terminal *fac*(*S*)-[Rh(aet)$_3$] units, together with two Cl or O atoms.[12a,b] In this pentanuclear structure, each *fac*(*S*)-[Rh(aet)$_3$] unit is bound with three different Hg^{II} ions (average Hg–S = 2.443(4) Å for X = Cl, 2.388(5) Å for X = NO$_3$), and the two *fac*(*S*)-[Rh(aet)$_3$] units have the same chiral configuration to give only the *racemic* (ΔΔ/ΛΛ) form. The binding mode (Fig. 1b) and the chiral behavior of the two *fac*(*S*)-[Rh(aet)$_3$] units in this pentanuclear structure are markedly distinct from those of the two units in the linear-type trinuclear structure. Furthermore, the $Rh^{III}{}_2Hg^{III}{}_3$ pentanuclear complexes possess a helical chirality due to three S–Hg–S linkages, besides the configurational chiralities of *fac*(*S*)-[Rh(aet)$_3$] units and bridging S atoms. The same stereochemical behavior has been observed for the corresponding $Co^{III}{}_2Hg^{III}{}_3$ pentanuclear complex, $[Hg_3(NO_3)_4\{Co(aet)_3\}_2]^{2+}$, which was prepared from *fac*(*S*)-[Co(aet)$_3$] and Hg(NO$_3$)$_2$ in water.[12b]

Analogous S-bridged pentanuclear complexes, $[Ag_3\{M(aet)_3\}_2]^{3+}$ (M = Co^{III}, Rh^{III}, Ir^{III}, Cr^{III}), which also give the *racemic* (ΔΔ/ΛΛ) form, were produced by the 2:3 reactions of *fac*(*S*)-[M(aet)$_3$] with Ag$^+$ in water.[12c–f] X-ray analyses of the $M_2Ag^{I}{}_3$ complexes indicated that each Ag^I ion has an almost linear geometry coordinated by two thiolato S atoms from two terminal *fac*(*S*)-[M(aet)$_3$] units; the structure of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ is shown in Fig. 9. The Ag···Ag distances (ca. 3.0–3.3 Å) in $[Ag_3\{M(aet)_3\}_2]^{3+}$ are much smaller than the Hg···Hg distances (3.6–3.9 Å) found in $[Hg_3Cl_6\{Rh(aet)_3\}_2]$ or $[Hg_3(NO_3)_4\{Rh(aet)_3\}_2]^{2+}$, which is suggestive of the presence of Ag···Ag bonding interactions in the S-bridged $M_2Ag^{I}{}_3$ pentanuclear structure. Interestingly, the addition of excess NaCl to an aqueous solution of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ did not cause any precipitation of AgCl,[12e] which may support the presence of Ag···Ag interactions. On the other hand, the reaction of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ with Co^{2+} in the presence of I$^-$ gave $[Co\{Co(aet)_3\}_2]^{3+}$, indicating that the two-coordinate Ag^I ions in this complex are reactive toward I$^-$ ions.[12e] It was recognized that the Ag^I ions in the $M_2Ag^{I}{}_3$ pentanuclear structure are also reactive toward the thiolato S atoms of the mononuclear *fac*(*S*)-[M(aet)$_3$]. That is, the addition of 0.5 mol equiv of *fac*(*S*)-[Rh(aet)$_3$] to the yellow aqueous solution of $[Ag_3\{Rh(aet)_3\}_2]^{3+}$ produced a dark red solution in a few minutes, from which an S-bridged nonanuclear complex, $[Ag_5\{Rh(aet)_3\}_4]^{5+}$, was isolated in a high yield.[12d] As shown in Fig. 10, in this $Rh^{III}{}_4Ag^{I}{}_5$ nonanuclear structure, each of the four Ag^I ions (Ag1–Ag4) is situated in a distorted trigonal-planar environment coordinated by three thiolato S atoms from

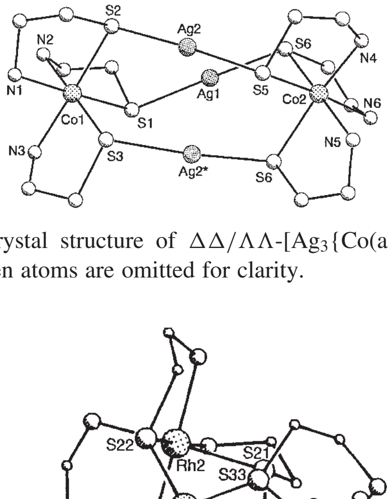


Fig. 9. Crystal structure of ΔΔ/ΛΛ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$. Hydrogen atoms are omitted for clarity.

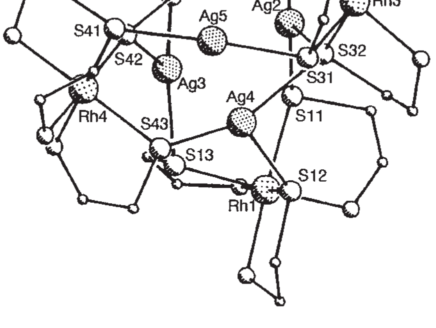


Fig. 10. Crystal structure of ΔΔΛΛ-$[Ag_5\{Rh(aet)_3\}_4]^{5+}$. Hydrogen atoms are omitted for clarity.

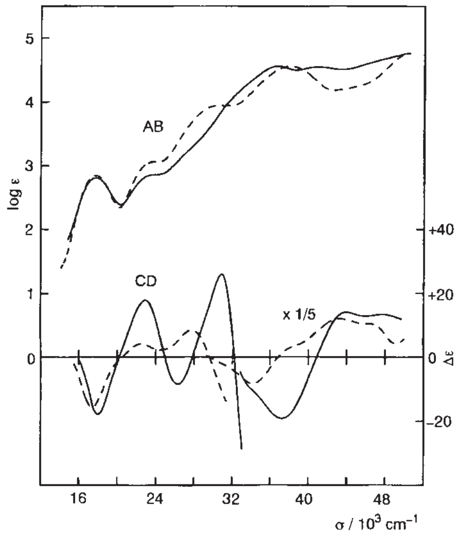


Fig. 11. Electronic absorption and CD spectra of ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ (—) and ΔΔΔΔ-$[Zn_4O\{Rh(aet)_3\}_4]^{6+}$ (×0.5) (- - -) in H_2O.

three different *fac*(*S*)-[M(aet)$_3$] units, while the remaining Ag^I ion (Ag5) is linearly coordinated by two S atoms from two *fac*(*S*)-[M(aet)$_3$] units. When an aqueous solution of $[Ag_5\{Rh(aet)_3\}_4]^{5+}$ was treated with 1 molar equiv of Ag^+, $[Ag_3\{Rh(aet)_3\}_2]^{3+}$ was immediately reproduced, indicating the facile interconversion between the $Rh^{III}{}_2Ag^I{}_3$ pentanuclear and the $Rh^{III}{}_4Ag^I{}_5$ nonanuclear S-bridged structures.[12d]

The S-bridged $M_2Ag^I{}_3$ (M = Co^{III}, Rh^{III}, Ir^{III}) pentanuclear complexes were optically resolved into the ΔΔ and ΛΛ isomers by fractional crystallization and/or SP-Sephadex C-25 column chromatography.[12c–e] Figure 11 compares the absorption and CD spectra of the ΔΔ isomer of $[Ag_3\{Co(aet)_3\}_2]^{3+}$ with those of 0.5 mol of ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$. The former ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ possesses a chirality due to left-handed triple helical structure besides two Δ configurational *fac*(*S*)-[Co(aet)$_3$] units and 6 *S* configurational bridging S atoms, while the latter ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$ has chiralities due to four Δ configurational *fac*(*S*)-[Co(aet)$_3$] units and 12 *S* configurational S atoms. Thus, it is assumed that the CD spectral difference between ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ and 0.5 mol of ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$ can be ascribed to the presence of the left-handed triple helical chirality in ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$. In the first d–d absorption band region of ca. (16–20) × 10^3 cm^{-1}, the CD spectrum of ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ resembles that of 0.5 mol of ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$, suggesting that the CD contribution due to the helical chirality is relatively small in this region. On the other hand, in the region of the second d–d and the sulfur-to-cobalt CT bands (ca. (20–40) × 10^3 cm^{-1}), the CD intensity of each band for ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ is much larger than that for 0.5 mol of ΔΔΔΔ-$[Zn_4O\{Co(aet)_3\}_4]^{6+}$. This CD spectral deviation suggests that the left-handed triple helical chirality in ΔΔ-$[Ag_3\{Co(aet)_3\}_2]^{3+}$ contributes considerably to the CD spectrum in this region.

The corresponding $M_2Au^I{}_3$ pentanuclear complexes, ΔΔ/ΛΛ-$[Au_3\{M(aet)_3\}_2]^{3+}$ (M = Co^{III}, Rh^{III}), in which two *fac*(*S*)-[M(aet)$_3$] units are linked by three linear Au^I ions, have also been prepared by the reactions of *fac*(*S*)-[M(aet)$_3$] with $[Au^{III}Cl_4]^-$ in water, accompanied by the spontaneous reduction of Au^{III} to Au^I.[12g] X-ray analysis of $[Au_3\{Rh(aet)_3\}_2]^{3+}$ revealed that the intramolecular Au···Au distances are in the range of ca. 3.04–3.16 Å, suggestive of the presence of bonding interactions between three linking Au^I ions.[26] Furthermore, it was shown that the two $Rh^{III}{}_2Au^I{}_3$ complex-cations are connected through a weak Au···Au interaction (3.311(3) Å), forming a dimer of the pentanuclear structure in crystal.

1.4 Aggregation of *fac*(*S*)-[M(aet)$_3$] by Planar-Type Metal Ions. It is well known that Cu^{II} is the representative metal ion that prefers to adopt a square-planar coordination geometry. When *fac*(*S*)-[M(aet)$_3$] (M = Rh^{III}, Ir^{III}) were reacted with Cu^{2+} in a 1:1 ratio in water at room temperature, cage-type $M_4Cu^I{}_4$ octanuclear complexes with a C_2 symmetry, $[Cu^I{}_4\{M(aet)_3\}_2\{M_2(aet)_4(cysta)\}]^{6+}$ (cysta = cystamine), were produced. X-ray analysis of $[Cu^I{}_4\{Rh(aet)_3\}_2\{Rh_2(aet)_4(cysta)\}](NO_3)_6$ revealed the presence of four Cu^I ions and four *fac*(*S*)-[Rh(N)$_3$(S)$_3$] units in the S-bridged octanuclear structure.[13a] As shown in Fig. 12a, each Cu^I ion is situated in an approximately trigonal-planar environment (average S–Cu–S = 118.7(2)°, Cu–S = 2.268(4) Å), coordinated by three thiolato S atoms from three different *fac*(*S*)-[Rh(N)$_3$(S)$_3$] units. The three S atoms in each of the Rh1 and Rh2 units have a normal μ_2-thiolato structure, binding with three different Rh^{III} atoms.

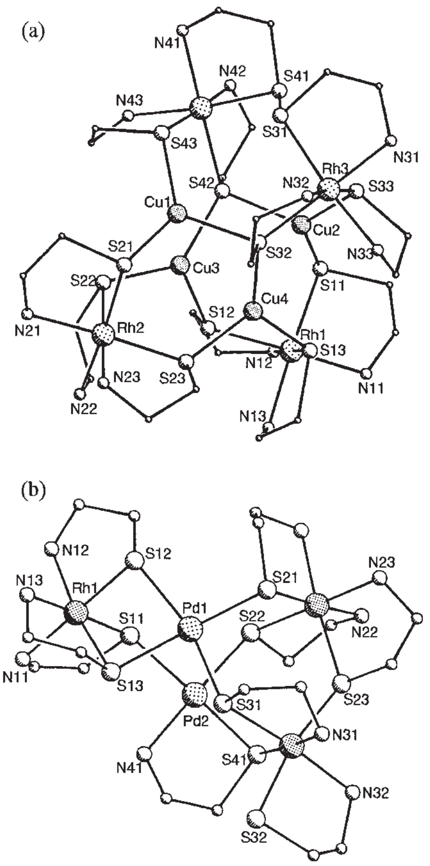


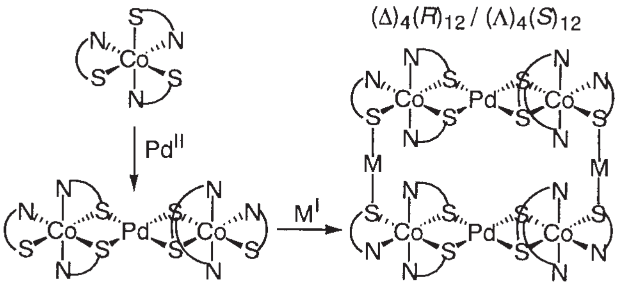
Fig. 12. Crystal structures of ΔΔΛΛ-$[Cu_4\{Rh(aet)_3\}_2\{Rh_2(aet)_4(cysta)\}]^{6+}$ (a) and spontaneously resolved ΔΛΔ-$[Pd\{Pd(aet)\}\{Rh(aet)_2\}\{Rh(aet)_3\}_2]^{4+}$ (b). Hydrogen atoms are omitted for clarity.

On the other hand, three different types of S atoms, μ_2- and μ_3-thiolato and disulfide (S–S = 2.142(5) Å), exist in the Rh3 and Rh4 units. Thus, it was shown that four Cu^{II} ions are transformed to four Cu^{I} ions, accompanied by the formation of a disulfide bond between two *fac*(*S*)-[Rh(aet)$_3$] units in the course of the formation of C_2-cage-type octanuclear structure. Since no reducing agents such as free thiols were used in the reactions, it is probable that the reduction of Cu^{II} to Cu^{I} occurred spontaneously, owing mainly to the valence specificity of the trigonal-planar copper geometry, which is constrained in the C_2-cage-type octanuclear structure.

None of the S-bridged polynuclear complexes were isolated from similar 1:1 reactions of *fac*(*S*)-[M(aet)$_3$] (M = Rh^{III}, Ir^{III}) with Pd^{II} at room temperature, which takes a rigid square-planar geometry. When the reaction solution of *fac*(*S*)-[Rh(aet)$_3$] and $[PdCl_4]^{2-}$ was heated at 70 °C for 2 h, however, a novel S-bridged $Rh^{III}{}_3Pd^{II}{}_2$ pentanuclear complex, $[Pd\{Pd(aet)\}\{Rh(aet)_2\}\{Rh(aet)_3\}_2]^{4+}$, in which three Rh^{III} octahedrons are linked by two square-planar Pd^{II} ions, was obtained.[13b,c] X-ray analysis indicated that one of the three octahedral Rh^{III} centers is chelated by two aet ligands and the remaining coordination sites are occupied by two S atoms from two aet ligands that chelate to the adjacent Rh^{III} and Pd^{II} centers (Fig. 12b). This implies that the didentate-*N*,*S* ligand aet transferred from Rh^{III} to Pd^{II} coordination sphere, while the square-planar geometry of Pd^{II}, as well as the octahedral geometry of Rh^{III}, was retained. It should be noted that each of the two *fac*(*S*)-[Rh(aet)$_3$] units in the $Rh^{III}{}_3Pd^{II}{}_2$ pentanuclear structure are bound to two Pd^{II} ions, and this chelate-bridging binding mode has not been found in the other S-bridged polynuclear structures described above. The corresponding $Ir^{III}{}_3Pd^{II}{}_2$ pentanuclear complex, $[Pd\{Pd(aet)\}\{Ir(aet)_2\}\{Ir(aet)_3\}_2]^{4+}$, has also been prepared from *fac*(*S*)-[Ir(aet)$_3$] and $[PdCl_4]^{2-}$ by a similar procedure, but under more severe reaction conditions (80 °C for 3 days).[13c]

A similar but more pronounced chelate-transfer of aet was recognized for the reaction of *fac*(*S*)-[Co(aet)$_3$] with $[PdCl_4]^{2-}$ in water (35 °C for 3 days).[13c] That is, the predominant reaction product was found to be an S-bridged $Co^{III}{}_2Pd^{II}{}_3$ pentanuclear complex, $[Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2]^{4+}$, in which one *cis*(*S*)-[Pd(aet)$_2$] and two *fac*(*S*)-[Co(aet)$_3$] units are linked by two square-planar Pd^{II} ions. The presence of the *cis*(*S*)-[Pd(aet)$_2$] unit in this pentanuclear complex clearly indicates that the ligand aet easily transferred from Co^{III} to Pd^{II} coordination sphere in the course of the reaction. The binding mode of the two *fac*(*S*)-[Co(aet)$_3$] units toward two Pd^{II} ions in $[Pd_2\{Pd(aet)_2\}\{Co(aet)_3\}_2]^{4+}$ is the same as that of the *fac*(*S*)-[M(aet)$_3$] (M = Rh^{III}, Ir^{III}) units in $[Pd\{Pd(aet)\}\{M(aet)_2\}\{M(aet)_3\}_2]^{4+}$, occupying six of eight coordination sites of the two square-planar Pd^{II} ions.

When the reaction of *fac*(*S*)-[Co(aet)$_3$] with $[PdCl_4]^{2-}$ was carried out in a 2:1 ratio under moderate conditions (30 °C for 6 h), a linear-type S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex, $[Pd\{Co(aet)_3\}_2]^{2+}$ was produced.[13d] Remarkably, in $[Pd\{Co(aet)_3\}_2]^{2+}$ the two [Co(aet)$_3$] units take an unprecedented *mer*(*S*) geometry. Moreover, one of three thiolato S atoms of each *mer*(*S*)-[Co(aet)$_3$] unit does not participate in the formation of the S-bridged trinuclear structure. This suggests that $[Pd\{Co(aet)_3\}_2]^{2+}$ can be used as a new class of S-donating polynuclear-metalloligand. Indeed, it was found that $[Pd\{Co(aet)_3\}_2]^{2+}$ readily reacts with M^{I} = Ag^{I}, Au^{I} to afford cyclic $Co^{III}{}_4Pd^{II}{}_2M^{I}{}_2$ octanuclear complexes, $[M^{I}{}_2\{Pd^{II}[Co^{III}(aet)_3]_2\}_2]^{6+}$. These were the first examples of chiral metallacycles consisting of three kinds of metal ions with different oxidation states and coordination geometries; octahedral Co^{III}, square-planar Pd^{II}, and linear Ag^{I} or Au^{I} ions (Scheme 3).[13d]



Scheme 3.

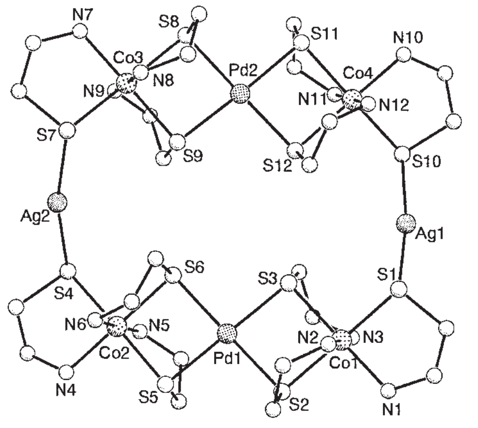
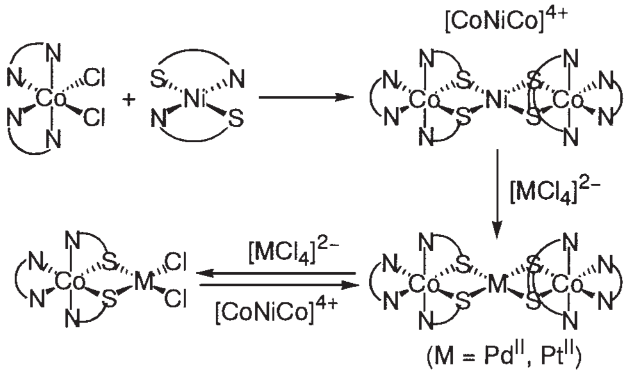


Fig. 13. Crystal structure of ΔΔΔΔ/ΛΛΛΛ-$[Ag_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$. Hydrogen atoms are omitted for clarity.

The structures of $[Au_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ and $[Ag_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ were established by X-ray analyses; the latter complex is depicted in Fig. 13.[13d] In the octanuclear structure, two of three thiolato S atoms of each *mer*(*S*)-[Co(aet)$_3$] unit are bound to one Pd^{II} ion to form a linear-type S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear moiety, $[Pd\{Co(aet)_3\}_2]^{2+}$. The two trinuclear moieties are connected with each other by two S–M^{I}–S linkages, completing a cyclic $Co^{III}{}_4Pd^{II}{}_2M^{I}{}_2$ octanuclear structure. The overall structures of $[Ag_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ and $[Au_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ are similar to each other. However, the S–Ag–S angles (average 168.2(1)°) in $[Ag_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ are considerably deviated from 180° compared to the S–Au–S angles (178.85(7)°) in $[Au_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$; furthermore, the averaged Ag–S distance (2.373(3) Å) is ca. 0.09 Å longer than the averaged Au–S distance (2.285(2) Å). When an aqueous solution of $[Ag_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ was treated with $[Au^{I}Cl\{S(CH_2CH_2OH)_2\}]$ at room temperature, Ag^{I} ions in $[Ag_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ were replaced by Au^{I} ions to produce $[Au_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$. These results imply that the $Co^{III}{}_4Pd^{II}{}_2Ag^{I}{}_2$ octanuclear metallacycle is more flexible than the $Co^{III}{}_4Pd^{II}{}_2Au^{I}{}_2$ one. In $[M^{I}{}_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ (M^{I} = Au^{I}, Ag^{I}), either the Δ or Λ configurational *mer*(*S*)-[Co(aet)$_3$] unit is selectively incorporated to give only the ΔΔΔΔ and ΛΛΛΛ isomers. In addition, all 12 asymmetric bridging S atoms are unified to have the *R* configuration for the ΔΔΔΔ and the *S* configuration for the ΛΛΛΛ isomer. Thus, the cyclic octanuclear structure in $[M^{I}_2\{Pd[Co(aet)_3]_2\}_2]^{6+}$ discriminates the chiral configurations of the Co^{III} and bridging S chiral centers to afford only a pair of enantiomers: $(\Delta)_4(R)_{12}$ and $(\Lambda)_4(S)_{12}$. Since the $(\Delta)_4(R)_{12}$ and $(\Lambda)_4(S)_{12}$ isomers were successfully optically resolved, it was shown that optically active metallacycles having a total of 16 chiral centers are obtained by the stepwise reactions of *fac*(*S*)-$[Co(aet)_3]$ with square-planar Pd^{II} and linear Au^{I} or Ag^{I}.

2. Bis(thiolato)-Type System

2.1 Aggregation of *cis*(*S*)-$[Co(aet)_2(en)]^+$ by M = Ni^{II}, Pd^{II}, Pt^{II}. As part of investigations into the binding ability of *cis*(*S*)-[M(thiolato-*S*)$_2$(amine-*N*)$_2$]-type metalloligands, the reaction of $[CoCl_2(en)_2]^+$ with $[Ni(aet)_2]$ was carried out in water, expecting the formation of an S-bridged $Co^{III}Ni^{II}$ dinuclear complex, $[Co\{Ni(aet)_2\}(en)_2]^{3+}$. However, this reaction led to the isolation of the first example of an S-bridged trinuclear complex composed of octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ units, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, in which the didentate-*N*,*S* ligand aet does not chelate to Ni^{II} but to Co^{III} (Scheme 4).[17a,b] This result obviously implies that the ligand aet readily transfers from the Ni^{II} to the Co^{III} coordination sphere. Figure 14 shows the molecular structure of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, which was determined by X-ray analysis. The Ni^{II} ion is coordinated by four thiolato S atoms from two terminal *cis*(*S*)-$[Co(aet)_2(en)]^+$ units (average Ni–S = 2.204(1) Å), forming the linear-type S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear structure. The central $Ni^{II}S_4$ sphere is largely distorted from square-planar to tetrahedral geometry, in which the two NiS_2 planes intersect to form a dihedral angle of 16.2°. Considering two chiral configurations, Δ and Λ, and two geometries, C_1-*cis*(*S*) and C_2-*cis*(*S*) (Chart 2), for the two *cis*(*S*)-$[Co(aet)_2(en)]^+$ units, a total of 10 isomers are possible for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$. However, it was found that only a pair of enantiomers, ΔΔ-C_2C_2 and ΛΛ-C_2C_2, are formed for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$.[17b] This is in contrast to the fact that both the *meso* (ΔΛ) and *racemic* (ΔΔ/ΛΛ) forms were produced for the linear-type S-bridged trinuclear complexes composed of the two *fac*(*S*)-$[Co(aet)_3]$ units, $[M\{Co(aet)_3\}_2]^{3+}$, as described in Section 1.1. It was noticed that $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ undergoes absorption and CD spectral changes with time in a dilute aqueous solution.[17b] That is, the characteristic absorption bands at 361 and 240 nm decreased with time and the absorption spectrum after 24 h was very similar to that observed for the mononuclear *cis*(*S*)-[Co(thiolato-*S*)$_2$(amine-*N*)$_4$]$^+$-type complexes, giving one intense absorption band with two components at around 275 nm. In the CD spectrum, the optically resolved isomer showed little CD over the whole region after 24 h. These spectral changes indicate that, in a dilute aqueous solution, the cleavage of Ni–S bonds occurs to afford the mononuclear *cis*(*S*)-$[Co(aet)_2(en)]^+$ species, followed by the racemization at the Co^{III} chiral center. Consistent with this, the H_2O_2 oxidation of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ in water produced a mononuclear sulfinato Co^{III} complex, C_2-*cis*(*S*)-[Co(NH$_2$CH$_2$CH$_2$SO$_2$-*N*,*S*)$_2$(en)]$^+$.[17b]



Scheme 4.

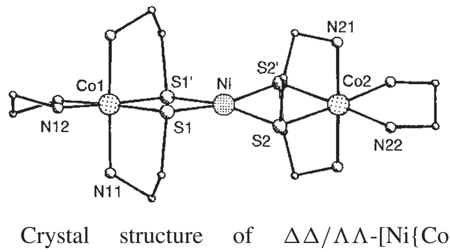


Fig. 14. Crystal structure of ΔΔ/ΛΛ-$[Ni\{Co(aet)_2(en)\}_2]^{4+}$. Hydrogen atoms are omitted for clarity.

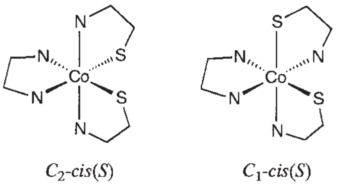


Chart 2.

The relative unstability of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ in water suggested that other S-bridged polynuclear complexes composed of *cis*(*S*)-$[Co(aet)_2(en)]^+$ units are prepared by the use of this $Co^{III}Ni^{II}Co^{III}$ trinuclear complex as a starting material, instead of the mononuclear *cis*(*S*)-$[Co(aet)_2(en)]^+$ complex that is hard to isolate.[23] Thus, the reactions of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with Pd^{II} were examined, expecting that the central Ni^{II} ion in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ would be replaced by Pd^{II} to form an analogous S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex. As expected, $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ was isolated in a good yield by the reaction of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with 1 molar equiv of $[PdCl_4]^{2-}$ in water under moderate conditions (Scheme 4).[17d] On the other hand, the replacement of the central Pd^{II} ion in $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ by Ni^{II} did not occur, even when $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ was treated with excess Ni^{2+}. Furthermore, in water $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ exhibited little absorption and CD spectral changes with time at least for a few hours, which is in contrast to the case for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$. Accordingly, it is assumed that the Pd–S bonds in $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ are considerably stronger than the Ni–S bonds in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$. Only the *racemic* form of ΔΔ-C_2C_2 and ΛΛ-C_2C_2 with a D_2 symmetrical structure was formed for $[Pd\{Co(aet)_2(en)\}_2]^{4+}$, as in the case for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$. When $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ was reacted with 2 molar equiv of $[PdCl_4]^{2-}$, an S-bridged $Co^{III}Pd^{II}$ dinuclear complex with one C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit, $[PdCl_2\{Co(aet)_2(en)\}]^+$, was produced.[17d] This complex was also obtained by treating $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ with 1 molar equiv of $[PdCl_4]^{2-}$ (Scheme 4), which indicates that the S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear structure is readily converted to the S-bridged $Co^{III}Pd^{II}$ dinuclear structure by reacting with an additional Pd^{II} ion. Interestingly, it was found that the $Co^{III}Pd^{II}$ dinuclear structure is easily reverted back to the $Co^{III}Pd^{II}Co^{III}$ trinuclear structure; treatment of $[PdCl_2\{Co(aet)_2(en)\}]^+$ with 0.5 molar equiv of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ at room temperature led to the isolation of $[Pd\{Co(aet)_2(en)\}_2]^{4+}$. From these results, it was shown that $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ acts as a source of the *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit available for the construction of S-bridged polynuclear structures and that the Cl^- ions in $[PdCl_2\{Co(aet)_2(en)\}]^+$ can be replaced by two S atoms of the *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit.

Similar 1:1 and 1:2 reactions of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with $[PtCl_4]^{2-}$ in water produced S-bridged $Co^{III}Pt^{II}Co^{III}$ trinuclear and $Co^{III}Pt^{II}$ dinuclear complexes composed of C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units, $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ and $[PtCl_2\{Co(aet)_2(en)\}]^+$, respectively (Scheme 4).[17g] It is noteworthy that $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ gave both the *meso* ($\Delta\Lambda$) and *racemic* ($\Delta\Delta/\Lambda\Lambda$) forms, which were separated and optically resolved by cation-exchange column chromatography. This result is inconsistent with the selective formation of the *racemic* form for $[Pd\{Co(aet)_2(en)\}_2]^{4+}$. The MM2 calculations for the *meso* and *racemic* forms of $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ indicated that the *meso* form would be of higher energy than the *racemic* form by ca. 55 kJ mol^{-1}.[17g] Thus, it is reasonable to assume that for $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ the thermodynamically unstable *meso* form created at the first stage converts to the *racemic* form because of the kinetic lability of the Pd–S bonds, while the robustness of the Pt–S bonds prevents the *meso* form from converting to the *racemic* form for $[Pt\{Co(aet)_2(en)\}_2]^{4+}$. No significant absorption or CD spectral changes with time were noticed for the $\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$ isomers of $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ at least for one day, which implies that the intermolecular or intramolecular exchange of the two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units, as well as their racemization, does not occur for the $Co^{III}Pt^{II}Co^{III}$ trinuclear complex.

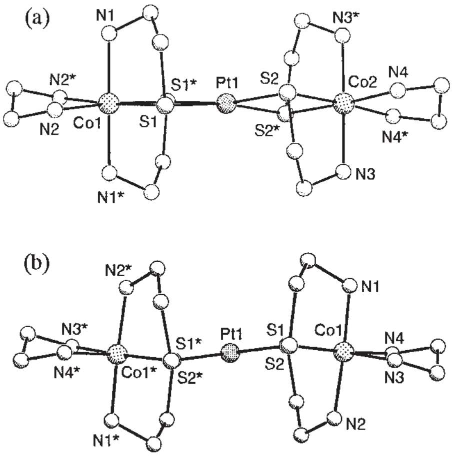


Fig. 15. Crystal structures of $\Delta\Delta/\Lambda\Lambda$-$[Pt\{Co(aet)_2(en)\}_2]^{4+}$ (a) and $\Delta\Lambda$-$[Pt\{Co(aet)_2(en)\}_2]^{4+}$ (b). Hydrogen atoms are omitted for clarity.

The linear-type S-bridged trinuclear structures for both the *meso* ($\Delta\Lambda$) and *racemic* ($\Delta\Delta/\Lambda\Lambda$) forms of $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ were established by X-ray structural analyses (Fig. 15).[17g] The crystal of $\Delta\Delta/\Lambda\Lambda$-$[Pt\{Co(aet)_2(en)\}_2]Cl_4$ is isomorphous with $\Delta\Delta/\Lambda\Lambda$-$[Ni\{Co(aet)_2(en)\}_2]Cl_4$ and $\Delta\Delta/\Lambda\Lambda$-$[Pd\{Co(aet)_2(en)\}_2]Cl_4$. Thus, the direct comparison of the structural parameters for $M = Ni^{II}, Pd^{II}, Pt^{II}$ coordinated by the didentate-*S,S* metalloligand, C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$, can be made (Table 3). The M–S bond distances in $\Delta\Delta/\Lambda\Lambda$-$[Pt\{Co(aet)_2(en)\}_2]^{4+}$, $\Delta\Delta/\Lambda\Lambda$-$[Pd\{Co(aet)_2(en)\}_2]^{4+}$, and $\Delta\Delta/\Lambda\Lambda$-$[Ni\{Co(aet)_2(en)\}_2]^{4+}$ average 2.314(2) Å, 2.310(1) Å, and 2.204(1) Å, respectively. This is in parallel with the covalent radii for Pd^{II} and Pt^{II}, which are evaluated to be essentially equal and larger than that for Ni^{II}.[25] The dihedral angles between two MS_2 trigonal planes decrease in the order $M = Ni^{II}$ (16.2°) > Pd^{II} (14.0°) > Pt^{II} (13.1°), indicative of the preference of square-planar geometry over tetrahedral geometry on going from Ni^{II} to Pd^{II} and from Pd^{II} to Pt^{II}. On the other hand, the bond distances and angles concerning the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units for the three $Co^{III}MCo^{III}$ complexes are quite similar to each other. However, the Co–S bond distances for $\Delta\Delta/\Lambda\Lambda$-$[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (average 2.238(1) Å) are somewhat shorter than those for $\Delta\Delta/\Lambda\Lambda$-$[Pd\{Co(aet)_2(en)\}_2]^{4+}$ (average 2.246(1) Å) and $\Delta\Delta/\Lambda\Lambda$-$[Pt\{Co(aet)_2(en)\}_2]^{4+}$ (average 2.248(2) Å), presumably due to the weaker Ni–S bonds. As shown in Fig. 15b, the central Pt^{II} ion in the *meso* form of $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ is situated in a perfect square-planar environment, which differs from the distorted square-planar geometry found in the *racemic* form, although the Pt–S bond distances in the *meso* form (average 2.318(5) Å) are essentially the same as those in the *racemic* form. Furthermore, while the Pt^{II} ion lies almost on the plane made by each CoS_2 trigonal plane in the *racemic* form, two pairs of adjacent CoS_2 and PtS_4 planes are not co-planar in the *meso* form, yielding a flat chair-like conformation for which the folding angle between each CoS_2 plane and the PtS_4 plane along the common S–S line is 166.0°. Molecular model examinations revealed that in the *meso* form there exists a cross-plane interaction between the aet chelate rings of the two C_2-*cis*(*S*)-

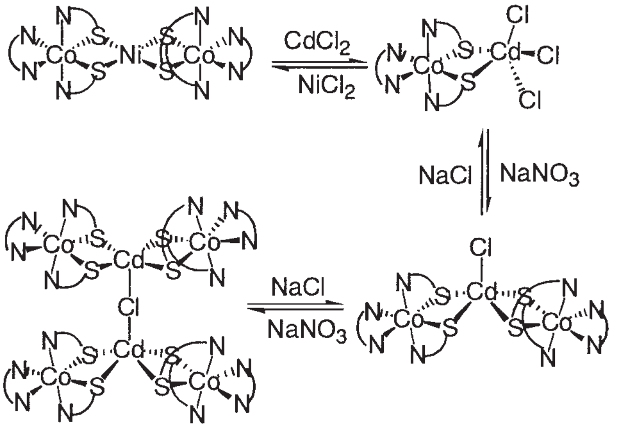
Table 3. Selected Bond Distances (Å) and Angles (deg) (Averaged) for $\Delta\Delta/\Lambda\Lambda$-$[M\{Co(aet)_2(en)\}_2]^{4+}$ ($M = Ni^{II}, Pd^{II}, Pt^{II}$)

	$[Ni\{Co(aet)_2(en)\}_2]^{4+}$	$[Pd\{Co(aet)_2(en)\}_2]^{4+}$	$[Pt\{Co(aet)_2(en)\}_2]^{4+}$
M–S	2.204(1)	2.310(1)	2.314(2)
Co–S	2.238(1)	2.246(1)	2.248(2)
Co–N	1.987(3)	1.986(4)	1.994(6)
S–M–S (bite)	86.83(5)	84.85(6)	84.14(9)
S–Co–S	85.19(5)	87.85(7)	87.25(1)

$[Co(aet)_2(en)]^+$ units, which is effectively decreased by the bending of the two pairs of adjacent planes along the common S–S line.

Analogous S-bridged trinuclear complexes composed of *cis*(*S*)-$[Co(aet)_2(R\text{-}pn)]^+$ units (*R*-pn = (*R*)-1,2-propanediamine), $[M\{Co(aet)_2(R\text{-}pn)\}_2]^{4+}$ ($M = Ni^{II}, Pd^{II}, Pt^{II}$), have also been prepared by methods similar to those used for $[M\{Co(aet)_2(en)\}_2]^{4+}$.[27]

2.2 Aggregation of *cis*(*S*)-$[Co(aet)_2(en)]^+$ by Cd^{II}. While the expected $Co^{III}MCo^{III}$ trinuclear complexes, $[M\{Co(aet)_2(en)\}_2]^{4+}$ ($M = Pd^{II}, Pt^{II}$), were obtained by the 1:1 reactions of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with $[MCl_4]^{2-}$ in water, a similar reaction with $CdCl_2$ under the same conditions did not give a $Co^{III}Cd^{II}Co^{III}$ trinuclear complex, $[Cd\{Co(aet)_2(en)\}_2]^{4+}$. Instead, it was found that an S-bridged $Co^{III}Cd^{II}$ dinuclear complex, $[CdCl_3\{Co(aet)_2(en)\}]$, in which a $[Cd^{II}Cl_3]^-$ moiety is bound by one C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit through two sulfur-bridges, is produced by the reaction of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with excess $CdCl_2$ (Scheme 5).[17c,e] This neutral $Co^{III}Cd^{II}$ complex is soluble in water, showing a molar conductivity of 333 $\Omega^{-1}\,cm^2\,mol^{-1}$. This suggests that $[CdCl_3\{Co(aet)_2(en)\}]$ is converted to a cationic species in water, eliminating at least one Cl^- ion from the coordination sphere of the Cd^{II} center. When $[CdCl_3\{Co(aet)_2(en)\}]$ was treated with an appropriate amount of $NaNO_3$ in water, an S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear complex, $[CdCl\{Co(aet)_2(en)\}_2](NO_3)_3$, in which two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units are linked by a $[Cd^{II}Cl]^+$ moiety, was produced.[17e] This $Co^{III}Cd^{II}Co^{III}$ trinuclear complex was found to be further converted into a $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear complex, $[Cd_2Cl\{Co(aet)_2(en)\}_4](NO_3)_7$, by treatment with $NaNO_3$ in water.[17e] Notably, when $[Cd_2Cl\{Co(aet)_2(en)\}_4](NO_3)_7$ was treated with an appropriate amount of NaCl in water, $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$ was reproduced. Moreover, this trinuclear complex was reconverted into $[CdCl_3\{Co(aet)_2(en)\}]$ by treatment with NaCl in water. These results clearly indicate that the S-bridged $Co^{III}Cd^{II}$ dinuclear, $Co^{III}Cd^{II}Co^{III}$ trinuclear, and $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear structures composed of the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units are interconvertible to one another by controlling the concentrations of Cl^- ion versus NO_3^- ion in solution (Scheme 5). In addition, it was found that $[CdCl_3\{Co(aet)_2(en)\}]$ can be reverted back to $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ by treatment with excess Ni^{2+} in water.[17e] Since the reaction of $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ with excess Ni^{2+} did not produce $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, it is considered that the Cd–S bonds in $[CdCl_3\{Co(aet)_2(en)\}]$ are weaker than the Pd–S bonds in $[Pd\{Co(aet)_2(en)\}_2]^{4+}$. This is compatible with the Cd–S bond distances observed in $[CdCl_3\{Co(aet)_2(en)\}]$ (average 2.663(2) Å), which are much longer than those in $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ (average 2.310(1) Å). In these $Co^{III}Cd^{II}$ dinuclear, $Co^{III}Cd^{II}Co^{III}$ trinuclear, and $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear structures, each Cd^{II} ion uniformly adopts a five-coordinate geometry, having at least one Cl^- ion in the coordination sphere. Attempts to remove the bridging Cl^- ion from the hexanuclear $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ by treatment with a large amount of $NaNO_3$ in water were unsuccessful. Accordingly, it is reasonable to assume that the Cd^{II} ion bound by the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units inherently prefers the five-coordinate geometry.



Scheme 5.

The structures of a series of the $Co^{III}Cd^{II}$ dinuclear, $Co^{III}Cd^{II}Co^{III}$ trinuclear, and the $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear complexes, $[CdCl_3\{Co(aet)_2(en)\}]$, $[CdCl\{Co(aet)_2(en)\}_2](NO_3)_3$, $[Cd_2Cl\{Co(aet)_2(en)\}_4](NO_3)_7$, were established by X-ray structural analyses.[17e] As shown in Fig. 16a, the Cd^{II} ion in the dinuclear $[CdCl_3\{Co(aet)_2(en)\}]$ is coordinated by two thiolato S atoms from one C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit and three Cl atoms. The bond angles subtended at the Cd^{II}

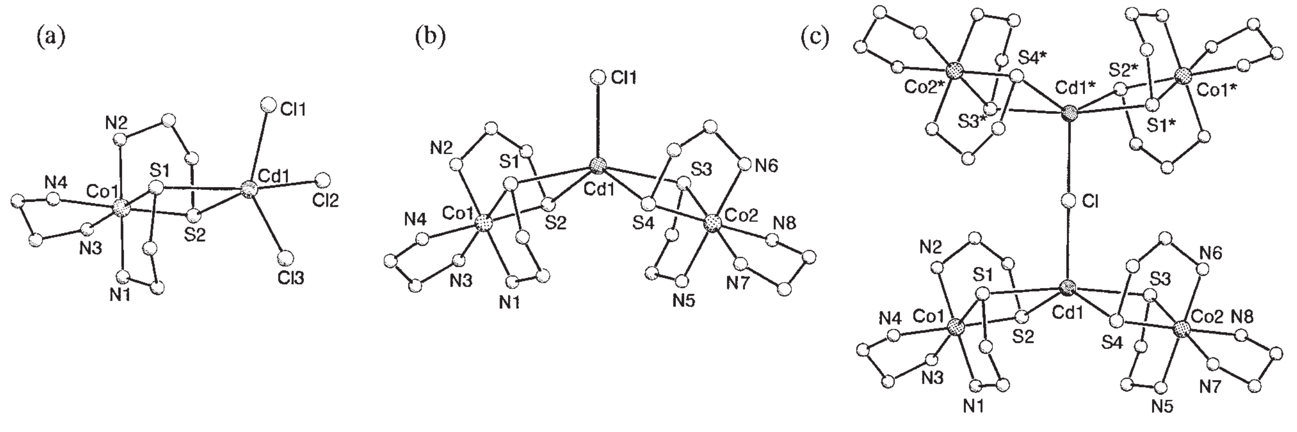


Fig. 16. Crystal structures of Δ/Λ-$[CdCl_3\{Co(aet)_2(en)\}]$ (a), $\Delta\Delta/\Lambda\Lambda$-$[CdCl\{Co(aet)_2(en)\}_2]^{3+}$ (b), and $\Delta\Delta\Delta\Delta/\Lambda\Lambda\Lambda\Lambda$-$[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ (c). Hydrogen atoms are omitted for clarity.

ion require a distorted trigonal-bipyramidal coordination geometry with the S1 and Cl2 atoms at the axial positions. In the $Co^{III}Cd^{II}Co^{III}$ trinuclear complex, the Cd^{II} ion is coordinated by four S atoms from two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units, besides one Cl atom (Fig. 16b). The crystal of $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$ consists of the ΔΔ and ΛΛ isomers, which combine to form the *racemic* compound. In the hexanuclear complex, each of the two Cd^{II} ions is coordinated by four S atoms from two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units to form an S-bridged $Co^{III}Cd^{II}Co^{III}$ trinuclear moiety. The two trinuclear moieties are connected with each other by a Cd–Cl–Cd linkage, which completes an unique $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear structure in $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ (Fig. 16c). As a result, each Cd^{II} ion in $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ is situated in a five-coordinate geometry with four S and one Cl donor atoms, like the Cd^{II} ion in the trinuclear $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$. In $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$, either the Δ or Λ configurational C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ unit is selectively incorporated, giving only the ΔΔΔΔ and ΛΛΛΛ isomers with an approximate D_2 symmetry.

The coordination geometry about the Cd^{II} ions in $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$ and $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ can be described as an intermediate between the trigonal bipyramid and square pyramid. For the coordination geometry of five-coordinate complexes, Addison et al. has introduced an angular structural index parameter, $\tau = (\beta - \alpha)/60$, where α and β represent the two largest angles ($\beta > \alpha$); the τ value is zero for an ideal square pyramid ($\alpha = \beta = 180°$), while the value becomes unity for an ideal trigonal bipyramid ($\alpha = 120°$, $\beta = 180°$).[28] For $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$ and $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ the τ values become 0.46 and 0.54, respectively, which suggests a distorted square-pyramidal geometry for $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$ and a distorted trigonal-bipyramidal geometry for $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ (Table 4). However, it is noticed that the three bond angles for $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$ (117.20(6)°, 131.53(6)°, 111.20(6)°), which correspond to the basal angles for the trigonal-bipyramidal geometry, are closer to the ideal trigonal angle of 120° than those for $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ (110.2(1)°, 139.13(8)°, 110.6(1)°). This conflict would result from the index parameter τ, which is based only on the two largest angles defined by four of five donor atoms that correspond to the basal angles for the square-pyramid. Thus, this index parameter was modified so as to take into account the remaining one donor atom and the basal angles for the trigonal-bipyramid as given in Eq. 1.

$$\begin{aligned}\chi &= \{(\beta - \alpha) + (\gamma + \delta - \alpha)\}/180 \\ &= (\beta + \gamma + \delta - 2\alpha)/180\end{aligned} \tag{1}$$

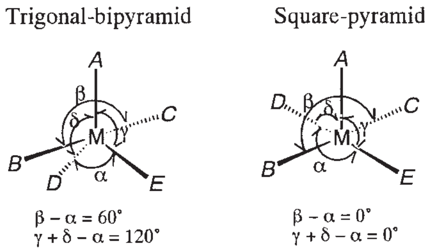


Chart 3.

In Eq. 1, α and β represent the two largest angles defined by four of five donor atoms, *B*, *C*, *D*, and *E* ($\beta = B$–M–C, $\alpha = D$–M–E, $\beta > \alpha$), and γ and δ represent the angles concerning the remaining donor atom *A* ($\gamma = A$–M–D, $\delta = A$–M–E) (Chart 3). That is, β and α correspond to the basal angles for the square-pyramid, while γ, δ and α correspond to the basal angles for the trigonal-bipyramid. For an ideal square-pyramidal geometry, this index parameter χ is equal to zero ($\alpha = \beta = 180°$, $\gamma = \delta = 90°$; $\beta - \alpha = 0$, $\gamma + \delta - \alpha = 0$), while it becomes unity for an ideal trigonal-bipyramidal geometry ($\alpha = \gamma = \delta = 120°$, $\beta = 180°$; $\beta - \alpha = 60°$, $\gamma + \delta - \alpha = 120°$). The χ values for $[CdCl_3\{Co(aet)_2(en)\}]$, $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$, and $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$ become 0.75, 0.69, and 0.63, respectively (Table 4), which defines that all the Cd^{II} atoms in the present S-bridged polynuclear complexes have a distorted trigonal-bipyramidal geometry, rather than a square-pyramidal geometry. Moreover, it is seen from the χ values that the distortion from the trigonal bipyramid to square pyramid increases in the order of the $Co^{III}Cd^{II}$ dinuclear $[CdCl_3\{Co(aet)_2(en)\}]$, the $Co^{III}Cd^{II}Co^{III}$ trinuclear $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$, and the $(Co^{III}Cd^{II}Co^{III})_2$ hexanuclear $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$.

The corresponding $Co^{III}Cd^{II}Co^{III}$ trinuclear complexes with a coordinated Br^- or I^- ion, $[CdX\{Co(aet)_2(en)\}_2]^{3+}$ (X = Br, I), have also been prepared and structurally characterized, but the formation of the hexanuclear $[Cd_2X\{Co(aet)_2(en)\}_4]^{7+}$ has not been recognized.[17f]

2.3 Aggregation of *cis*(*S*)-$[Co(aet)_2(en)]^+$ by Hg^{II}. In order to clarify the effect of linking metal ion on the chiral selective aggregation of *cis*(*S*)-$[Co(aet)_2(en)]^+$ units, the reactions of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with Hg^{II} were also investigated. The 1:2 reaction of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with $HgBr_2$ in water gave an S-bridged $Co^{III}Hg^{II}$ dinuclear complex, $[HgBr_2\{Co(aet)_2(en)\}]^+$.[17i] X-ray analysis indicated that, in this $Co^{III}Hg^{II}$ structure, the Hg^{II} ion has a distorted tetrahedral geometry (S–Hg–S = 79.5(1)°, Br–Hg–Br = 106.03(8)°), coordinated by two S atoms from one C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ units (average Hg–S = 2.585(5) Å) and two Br^- ions (average Hg–Br = 2.585(3) Å), leading to the cationic dinuclear species (Fig. 17a). This result is distinct from the five-coordinated geometry of Cd^{II} in the related $Co^{III}Cd^{II}$ dinuclear complex, $[CdCl_3\{Co(aet)_2(en)\}]$.

Table 4. Bond Angles (deg) Concerning the Angular Structural Parameter χ for $[CdCl_3\{Co(aet)_2(en)\}]$, $[CdCl\{Co(aet)_2(en)\}_2]^{3+}$, and $[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$

	$[CdCl_3\{Co(aet)_2(en)\}]$	$[CdCl\{Co(aet)_2(en)\}_2]^{3+}$	$[Cd_2Cl\{Co(aet)_2(en)\}_4]^{7+}$
β	161.65(6)	158.89(5)	171.34(7)
α	129.06(6)	131.53(6)	139.13(8)
γ	116.08(6)	117.20(6)	110.6(1)
δ	114.67(7)	111.20(6)	110.6(1)

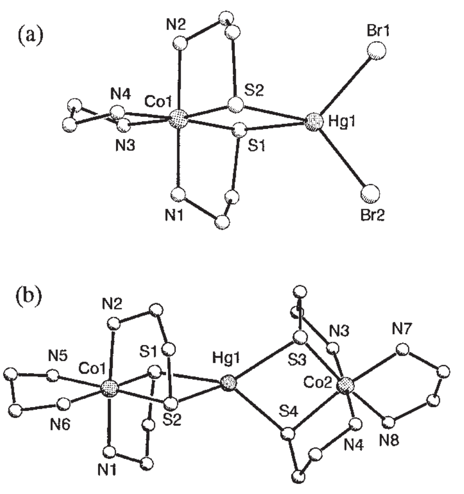
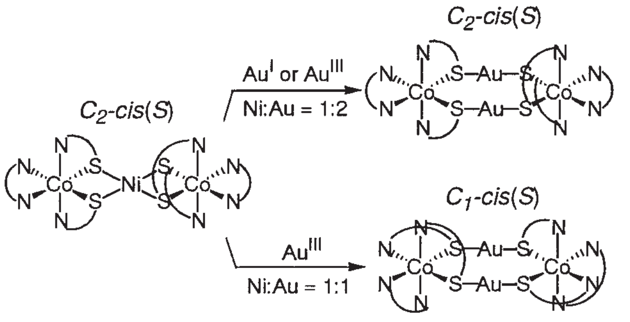


Fig. 17. Crystal structures of Δ/Λ-[HgBr$_2${Co(aet)$_2$(en)}]$^+$ (a) and $\Delta\Lambda$-[Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ (b). Hydrogen atoms are omitted for clarity.

When [HgBr$_2${Co(aet)$_2$(en)}]$^+$ was treated with 0.5 mol equiv of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ in water, an S-bridged Co^{III}Hg^{II}Co^{III} trinuclear complex, [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$, was produced.[17i] This Co^{III}Hg^{II}Co^{III} trinuclear complex was also prepared by the 1:1 reaction of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ with Hg(ClO$_4$)$_2$ in water. X-ray analysis revealed that in [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ the central Hg^{II} ion is coordinated by four thiolato S atoms from two terminal C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units to adopt a distorted tetrahedral geometry (S1–Hg–S2 = 80.8(1)°, S3–Hg–S4 = 81.7(1)°), as shown in Fig. 17b. The Hg–S bond distances (2.521(4)–2.591(4) Å) are within the range normally observed for tetrahedral Hg^{II}S$_4$ spheres. It should be noted that in this Co^{III}Hg^{II}Co^{III} trinuclear structure the two C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units have the $\Delta\Delta$ and $\Lambda\Lambda$ configurations to give the *meso* form. This is in contrast to the fact that [M{Co(aet)$_2$(en)}$_2$]$^{4+}$ (M = Ni^{II}, Pd^{II}) and [CdCl{Co(aet)$_2$(en)}$_2$]$^{3+}$ produced only the *racemic* ($\Delta\Delta/\Lambda\Lambda$) form. Molecular model examinations reveal that there exists a steric repulsion between the SCH$_2$ methylene groups of the two C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units when [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ adopts the *racemic* form. Thus, the chirality of the S-bridged trinuclear complexes composed of C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units was found to be controlled by the choice of the linking metal ion.

2.4 Aggregation of *cis*(*S*)-[Co(aet)$_2$(en)]$^+$ by Au^I. Treatment of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ with 2 molar equiv of [Au^{I}Cl{S(CH$_2$CH$_2$OH)$_2$}] in water (60 °C) produced an S-bridged Co$^{III}{}_2$Au$^I{}_2$ tetranuclear complex, C_2C_2-[Au$_2{}^I${Co(aet)$_2$(en)}$_2$]$^{4+}$, in a high yield (Scheme 6).[17h] X-ray analysis indicated that in this tetranuclear structure the same configurational C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units are linked by two linear Au^I atoms through four sulfur-bridges (average Au–S = 2.301(3) Å, S–Au–S = 176.9(1)°) to afford a *racemic* ($\Delta\Delta/\Lambda\Lambda$) compound (Fig. 18a). The intramolecular Au–Au distance in C_2C_2-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ is 2.9640(9) Å, indicative of the presence of a bonding interaction between two Au^I ions.[26] It was noticed that in the crystal the two complex-cations are connected through a weak Au···Au interaction (3.229(1) Å), which forms a dimer of the Co$^{III}{}_2$Au$^I{}_2$ tetranuclear structure.



Scheme 6.

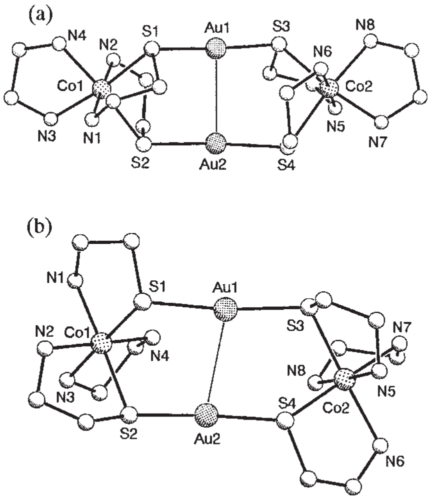
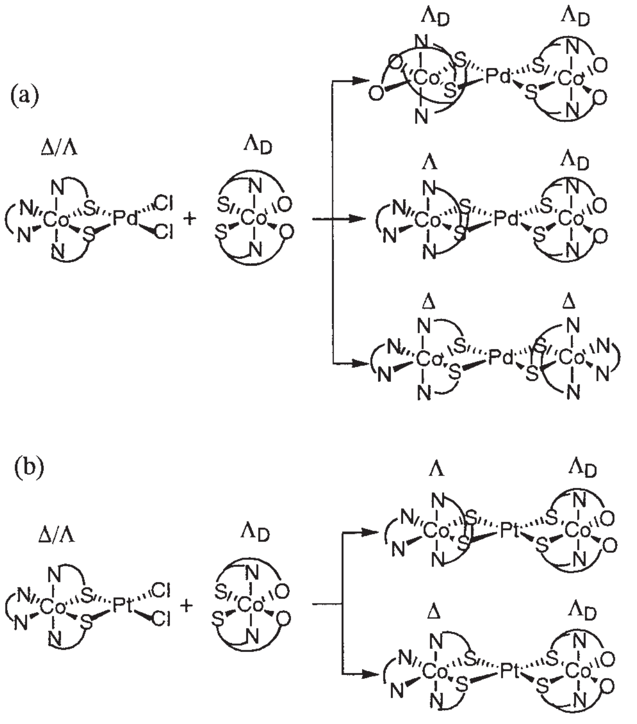


Fig. 18. Crystal structures of $\Delta\Delta/\Lambda\Lambda$-$C_2C_2$-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ (a) and $\Delta\Delta/\Lambda\Lambda$-$C_1C_1$-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ (b). Hydrogen atoms are omitted for clarity.

A similar reaction of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ with 2 molar equiv of [Au^{III}Cl$_4$]$^-$ in water also produced the same Co$^{III}{}_2$Au$^I{}_2$ tetranuclear structure in C_2C_2-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$.[17h] Since this complex was obtained in a low yield, it is assumed that *cis*(*S*)-[Co(aet)$_2$(en)]$^+$ acts not only as a metalloligand, but also as a reducing agent for Au^{III}. When [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ was treated with 1 molar equiv of [Au^{III}Cl$_4$]$^-$ under the same conditions, however, another S-bridged Co$^{III}{}_2$Au$^I{}_2$ tetranuclear complex with the same formula, C_1C_1-[Au$^I{}_2${Co(aet)$_2$(en)}$_2$]$^{4+}$, was isolated (Scheme 6).[17h] The absorption spectrum of C_1C_1-[Au$^I{}_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ is significantly different from that of C_2C_2-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ over the whole region. Moreover, in the ^{13}C NMR spectrum, C_1C_1-[Au$^I{}_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ exhibits six main signals, which is in contrast to the fact that only three signals are observed in the ^{13}C NMR spectrum of C_2C_2-[Au$_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ having a D_2 symmetry. From these results, together with the elution behavior in the SP-Sephadex C-25 column, C_1C_1-[Au$^I{}_2${Co(aet)$_2$(en)}$_2$]$^{4+}$ was assigned to have an S-bridged Co$^{III}{}_2$Au$^I{}_2$ tetranuclear structure consisting of unprecedented C_1-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units (Chart 2). This S-bridged Co$^{III}{}_2$Au$^I{}_2$ structure was confirmed by X-ray analysis (Fig. 18b), although a detailed structural discussion was precluded because of poor crystal quality and positional



Scheme 7.

disorders. Thus, it was shown that the 1:1 reaction of $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ with $[Au^{III}Cl_4]^-$ is accompanied by the geometrical isomerization of C_2-*cis*(*S*) to C_1-*cis*(*S*) to produce C_1C_1-$[Au^I{}_2\{Co(aet)_2(en)\}_2]^{4+}$, while the corresponding 1:2 reaction proceeds with retention of the C_2-*cis*(*S*) geometry to give C_2C_2-$[Au^I{}_2\{Co(aet)_2(en)\}_2]^{4+}$. The detailed mechanism of these reactions is not clear at present, but it is likely that some redox intermediate is closely related to the stabilization of the C_1-*cis*(*S*) geometry for the 1:1 reaction.

2.5 Reactions with *trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$. As described in Section 2.1, only the *racemic* form (ΔΔ/ΛΛ) was formed for $[Pd\{Co(aet)_2(en)\}_2]^{4+}$ by the reaction of $[PdCl_2\{Co(aet)_2(en)\}]^+$ with $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, which serves as a source of the *cis*(*S*)-$[Co(aet)_2(en)]^+$ unit. From this result, it was expected that either Δ- or Λ-$[PdCl_2\{Co(aet)_2(en)\}]^+$ is selectively incorporated in the S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear structure by the reaction with some cobalt(III) complex acting as a didentate-*S*,*S* metalloligand. Thus, the *racemic* Δ/Λ-$[PdCl_2\{Co(aet)_2(en)\}]^+$ was reacted with 1 molar equiv of Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$ having two thiolato groups in a *cis* position,[4g] which is an appropriate candidate for this purpose (Scheme 7a). As expected, this reaction gave the $\Lambda\Lambda_D$ isomer of the S-bridged $Co^{III}Pd^{II}Co^{III}$ trinuclear complex consisting of one Λ-C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ and one Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$ units, $[Pd\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$.[18a] This result clearly indicates that Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$ functions as a chiral didentate-*S*,*S* metalloligand that replaces the two Cl atoms in $[PdCl_2\{Co(aet)_2(en)\}]^+$. As shown in Fig. 19a, this S-bridged trinuclear structure corresponds well with that of ΔΔ/ΛΛ-$[Pd\{Co(aet)_2(en)\}_2]^{4+}$. However, the central PdS_4 sphere is not so distorted from a square-planar to a tetrahedral geometry, the dihedral angle between the PdS1S2 and PdS3S4 planes being only 8.4°. This may be ascribed to the absence of any significant steric interaction between Λ-C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ and Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$. One may assume that Δ-$[PdCl_2\{Co(aet)_2(en)\}]^+$ and excess Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$, which are not involved in the formation of $\Lambda\Lambda_D$-$[Pd\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$, remain in solution. However, the existence of Δ-$[PdCl_2\{Co(aet)_2(en)\}]^+$ and Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$ was little noticed in the reaction solution. Instead, it was found that $\Lambda_D\Lambda_D$-$[Pd\{Co(\text{D-pen-}N,O,S)_2\}_2]^0$ and ΔΔ-$[Pd\{Co(aet)_2(en)\}_2]^{4+}$, besides $\Lambda\Lambda_D$-$[Pd\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$, are formed in a ratio of ca. $\Lambda_D\Lambda_D:\Lambda\Lambda_D:\Delta\Delta = 1:2:1$ (Scheme 7a).[18a] This result implies that metathesis occurred between Δ-$[PdCl_2\{Co(aet)_2(en)\}]^+$ and Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$, because of the cleavage of Pd–S bonds.

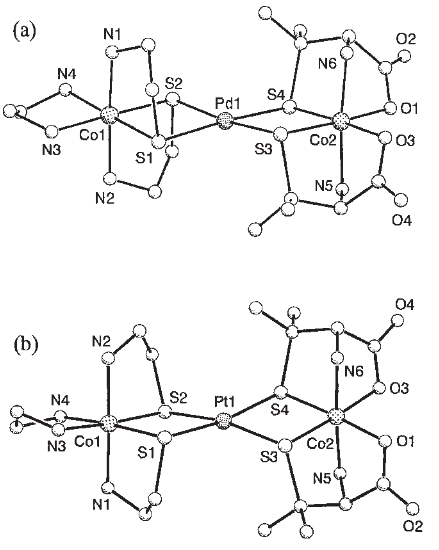
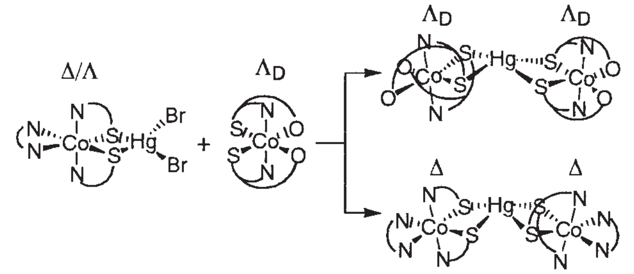


Fig. 19. Crystal structures of $\Lambda\Lambda_D$-$[Pd\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$ (a) and $\Delta\Lambda_D$-$[Pt\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$ (b). Hydrogen atoms are omitted for clarity.

When the *racemic* $Co^{III}Pt^{II}$ dinuclear complex, Δ/Λ-$[PtCl_2\{Co(aet)_2(en)\}]^+$, was reacted with Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$ in a 1:1 ratio in water, the sterically unfavorable $\Delta\Lambda_D$ isomer of $[Pt\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$, together with its $\Lambda\Lambda_D$ isomer, was produced ($\Lambda\Lambda_D:\Delta\Lambda_D = 8:5$) (Scheme 7b).[17g] On the other hand, only slight formation of $[Pt\{Co(aet)_2(en)\}_2]^{4+}$ and $\Lambda_D\Lambda_D$-$[Pd\{Co(\text{D-pen-}N,O,S)_2\}_2]^0$ was noticed. This result is quite in contrast to the case for the reaction of Δ/Λ-$[PdCl_2\{Co(aet)_2(en)\}]^+$ with Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$, which can be ascribed to the much stronger Pt–S bonds in $[PtCl_2\{Co(aet)_2(en)\}]^+$. The structure of the $\Delta\Lambda_D$ isomer of $[Pt\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$, in which Δ-$C_2$-*cis*(*S*)-$[Co(aet)_2(en)]^+$ and Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$ units are spanned by a Pt^{II} ion, was determined by X-ray analysis (Fig. 19b). The bond distances and angles concerning the C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ and the Λ_D-*trans*(*N*)-$[Co(\text{D-pen-}N,O,S)_2]^-$ units in this complex are quite similar to those found in $\Lambda\Lambda_D$-$[Pd\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$. However, the geometry about the central Pt^{II} ion in $\Delta\Lambda_D$-$[Pt\{Co(aet)_2(en)\}\{Co(\text{D-pen-}N,O,S)_2\}]^{2+}$ is significantly distorted from square-planar to tet-

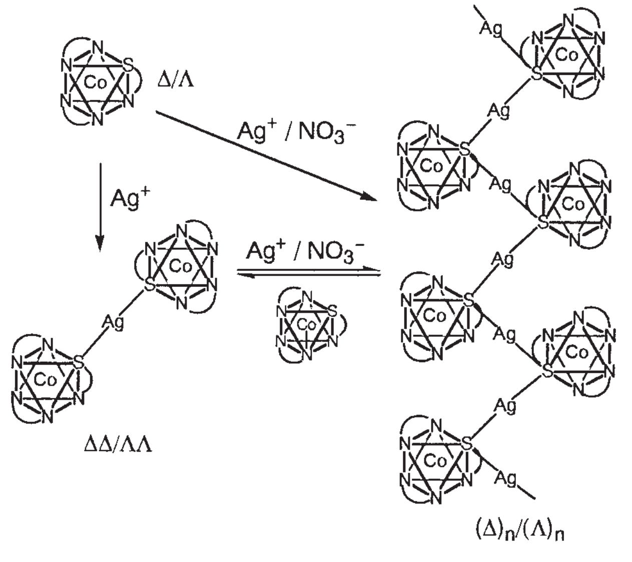


Scheme 8.

rahedral geometry, compared with the geometry about the Pd^{II} ion in $\Lambda\Lambda_D$-[Pd{Co(aet)$_2$(en)}{Co(D-pen-*N*,*O*,*S*)$_2$}]$^{2+}$; the dihedral angle between the two PtS_2 planes for $\Delta\Lambda_D$-[Pt{Co(aet)$_2$(en)}{Co(D-pen-*N*,*O*,*S*)$_2$}]$^{2+}$ is 16.3°. Molecular model studies pointed out that this distortion minimizes the cross-plane interaction between the methyl groups of the D-pen ligands and the methylene groups of the aet ligands which exists in the $\Delta\Lambda_D$ configurational S-bridged trinuclear structure.

A similar 1:1 reaction of Δ/Λ-[HgBr$_2${Co(aet)$_2$(en)}]$^+$ with Λ_D-*trans*(*N*)-[Co(D-pen-*N*,*O*,*S*)$_2$]$^-$ (60 °C for 1 h) was also carried out, expecting the formation of [Hg{Co(aet)$_2$(en)}{Co(D-pen-*N*,*O*,*S*)$_2$}]$^{2+}$, in which a Hg^{II} ion is bound by C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ and *trans*(*N*)-[Co(D-pen-*N*,*O*,*S*)$_2$]$^-$ units.[17i] However, SP-Sephadex C-25 column chromatography of the reaction solution indicated that very little of the desired divalent species was formed. Instead, the formation of [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ and $\Lambda_D\Lambda_D$-[Hg{Co(D-pen-*N*,*O*,*S*)$_2$}$_2$]^0 was recognized (Scheme 8). While the *meso* ($\Delta\Lambda$) form of [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ was selectively produced by the reaction of [HgBr$_2${Co(aet)$_2$(en)}]$^+$ with [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$, [Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ thus obtained was CD active. Furthermore, the optically pure $\Delta\Delta$ isomer was obtained by elongation of the reaction time to ca. 1.5 h. These results imply that the *racemic* C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ unit converted at least in part to the Δ form during the reaction, representing a quite rare example of chiral amplification for polynuclear systems. The mechanism of this reaction may be explained by the equilibrium between Δ- and Λ-[Co(aet)$_2$(en)]$^+$ units and the predominant formation of the quasi-*meso* form ($\Lambda_D\Delta$) of [Hg{Co(D-pen-*N*,*O*,*S*)$_2$}{Co(aet)$_2$(en)}]$^{2+}$, which is subject to disproportionation to $\Lambda_D\Lambda_D$-[Hg{Co(D-pen-*N*,*O*,*S*)$_2$}$_2$]^0 and $\Delta\Delta$-[Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$.[17i] The crystal structure of $\Delta\Delta$-[Hg{Co(aet)$_2$(en)}$_2$]Cl$_4$ composed of the two Δ-C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units was established by X-ray analysis.[17i] In this $Co^{III}Hg^{II}Co^{III}$ trinuclear structure, the central Hg^{II} ion is situated in an environment markedly distorted from a tetrahedral geometry, having two short (2.488(5) Å) and two long (2.772(6) Å) Hg–S bonds. In addition, one of Cl^- anions contacts with the Hg^{II} ion with a distance of 3.007(7) Å. Thus, the coordination geometry of the Hg^{II} atom in this complex may be regarded as a distorted trigonal-bipyramid, like the geometry of the Cd^{II} atom in $\Delta\Delta/\Lambda\Lambda$-[CdCl{Co(aet)$_2$(en)}$_2$]$^{3+}$. It is noted that the trinuclear structure in $\Delta\Delta$-[Hg{Co(aet)$_2$(en)}$_2$]$^{4+}$ deviates significantly from linearity (Co–Hg–Co = 144.9(1)°), which effectively decreases the steric repulsion between the two Δ configurational C_2-*cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units.

The reactions of Λ_D-*trans*(*N*)-[Co(D-pen-*N*,*O*,*S*)$_2$]$^-$ with transition metal ions (M = Pd^{II}, Pt^{II}, Cd^{II}, Hg^{II}, Ag^{I}, Au^{I}) have also been carried out. While the reactions with M = Pd^{II}, Pt^{II}, Cd^{II}, Hg^{II} afforded S-bridged trinuclear complexes, [M{Co(D-pen-*N*,*O*,*S*)$_2$}$_2$] (M = Pd^{II}, Pt^{II}, Hg^{II})[18g,i,19a] and [Cd(H$_2$O){Co(D-pen-*N*,*O*,*S*)$_2$}$_2$],[18b] an unique cyclic hexanuclear structure in [M$_3${Co(D-pen-*N*,*O*,*S*)$_2$}$_3$] was constructed by the reactions with M = Ag^{I}, Au^{I}.[18c] Furthermore, the geometrical isomerization of [Co(D-pen-*N*,*O*,*S*)$_2$]$^-$ from *trans*(*N*) to *trans*(*O*) was recognized in the course of the formation of [M$_3${Co(D-pen-*N*,*O*,*S*)$_2$}$_3$].



Scheme 9.

3. Mono(thiolato)-Type System

3.1 Reactions of [Co(aet)(en)$_2$]$^{2+}$ with Ag^I. The 2:1 reaction of [Co(aet)(en)$_2$]X$_2$ (X = NO$_3$, ClO$_4$)[24c,e] with AgX in water gave an S-bridged $Co^{III}Ag^{I}Co^{III}$ trinuclear complex, [Ag{Co(aet)(en)$_2$}$_2$]X$_5$ (Scheme 9).[14b,d] X-ray analysis for its ClO_4^- salt showed that in the $Co^{III}Ag^{I}Co^{III}$ trinuclear structure the central Ag^I ion is coordinated by two thiolato S atoms from two terminal octahedral [Co(aet)(en)$_2$]$^+$ units.[14d] The S–Ag–S angle (164.50(8)°) deviates from 180°, which is ascribed to weak interactions between Ag^I ion and ClO_4^- anions (Ag···O = 2.88–3.01 Å). The Co–S (2.259(2) Å) and Ag–S (2.400(1) Å) bond distances in [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$ are similar to those observed for the related $Co^{III}Ag^{I}Co^{III}$ trinuclear structure in [Ag{Co(tga)(en)$_2$}$_2$]$^{3+}$.[14c] A crystal of [Ag{Co(aet)(en)$_2$}$_2$](ClO$_4$)$_5$ consists of the $\Delta\Delta$ and $\Lambda\Lambda$ isomers, which combine to form a *racemic* compound. The two bridging S atoms adopt the *S* configuration for the $\Delta\Delta$ isomer and the *R* configuration for the $\Lambda\Lambda$ isomer. The same stereochemical behavior has been found in [Ag{Co(tga)(en)$_2$}$_2$]$^{3+}$.

As illustrated in Fig. 20, the absorption spectrum of [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$ in water resembles that of 2 mol of [Co(aet)(en)$_2$]$^{2+}$, giving the first d–d band at ca. 20×10^3 cm^{-1} and the sulfur-to-cobalt CT band at ca. 35×10^3 cm^{-1}. However, [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$ shows no distinct shoulder at the lower energy side of the first d–d band, such as is characteristically observed for [Co(aet)(en)$_2$]$^{2+}$.[24d] This suggests that the [Co(aet)(en)$_2$]$^{2+}$ units in [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$ are still linked by a Ag^I ion to form an S-bridged structure in wa-

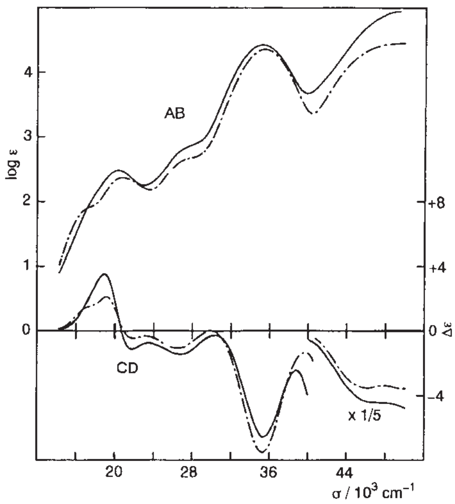


Fig. 20. Electronic absorption and CD spectra of ΛΛ-$[Ag\{Co(aet)(en)_2\}_2]^{5+}$ (—) and Λ-$[Co(aet)(en)_2]^{+}$ (×2) (-••-) in H_2O.

ter.[6] The absorption spectrum in the solid state (nujol paste) is essentially the same as that in water, which supports this suggestion. The CD spectrum of ΛΛ-$[Ag\{Co(aet)(en)_2\}_2]^{5+}$ is similar to that of 2 mol of Λ-$[Co(aet)(en)_2]^{2+}$ over the whole region (Fig. 20). As described in Section 1.2, the chirality due to asymmetric sulfur atom coordinated to Co^{III} center contributes significantly to the CD spectrum, especially in the sulfur-to-cobalt CT band region. If the trinuclear structure of $[Ag\{Co(aet)(en)_2\}_2]^{5+}$ found in the crystal is retained in solution, the CD spectral feature of ΛΛ-$[Ag\{Co(aet)(en)_2\}_2]^{5+}$, which possesses an additional chirality due to two *R* configurational S atoms, would be different from that of 2 mol of Λ-$[Co(aet)(en)_2]^{2+}$. Accordingly, it is reasonable to assume that the chiral configuration of the bridging S atoms in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$ is not fixed in solution, presumably because of the intramolecular and/or intermolecular exchange of the two $[Co(aet)(en)_2]^{2+}$ units.

When $[Ag\{Co(aet)(en)_2\}_2](NO_3)_5$ was treated with 1 molar equiv of $AgNO_3$ in water, another S-bridged $Co^{III}Ag^{I}$ complex, $[Ag\{Co(aet)(en)_2\}](NO_3)_3$, which consists of $[Co(aet)(en)_2]^{2+}$ and Ag^{I} in a 1:1 ratio, was produced (Scheme 9).[14d,g] This complex was also obtained directly from the 1:1 reaction of $[Co(aet)(en)_2](NO_3)_2$ with $AgNO_3$ in water. X-ray analysis demonstrated that $[Ag\{Co(aet)(en)_2\}](NO_3)_3$ is not a discrete S-bridged $Co^{III}Ag^{I}$ dinuclear complex, but a one-dimensional $(Co^{III}Ag^{I})_n$ polymeric complex. As shown in Fig. 21, the thiolato S atom of each $[Co(aet)(en)_2]^{2+}$ unit is bound to two Ag^{I} ions, and each Ag^{I} ion is coordinated by two S atoms from two different $[Co(aet)(en)_2]^{2+}$ units (S–Ag–S = 173.14(6)°). As a result, the $[Co(aet)(en)_2]^{2+}$ octahedrons are alternately linked by Ag^{I} ions to form a one-dimensional zigzag chain. In $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$, the Ag–S bonds (average 2.539(2) Å) are ca. 0.14 Å longer than those in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$. This may be ascribed mainly to the relatively strong bonding interaction of each Ag^{I} ion with three NO_3^- anions (Ag···O = 2.657(6) Å, 2.725(7) Å, and 2.924(7) Å), which could diminish the electrophilicity of Ag^{I} ion toward the thiolato group in $[Co(aet)(en)_2]^{2+}$. In $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$, the $[Co(aet)(en)_2]^{2+}$ units have the same absolute configuration to form a chiral $(Co^{III}Ag^{I})_n$ chain. Furthermore, $[Ag\{Co(aet)(en)_2\}]_n(NO_3)_{3n}$ was subject to spontaneous resolution, indicating that the same configurational $(Co^{III}Ag^{I})_n$ chains are aggregated in one crystal.

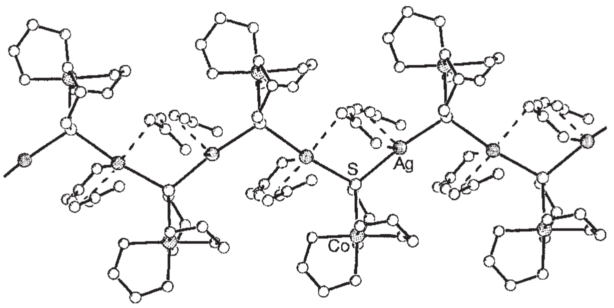
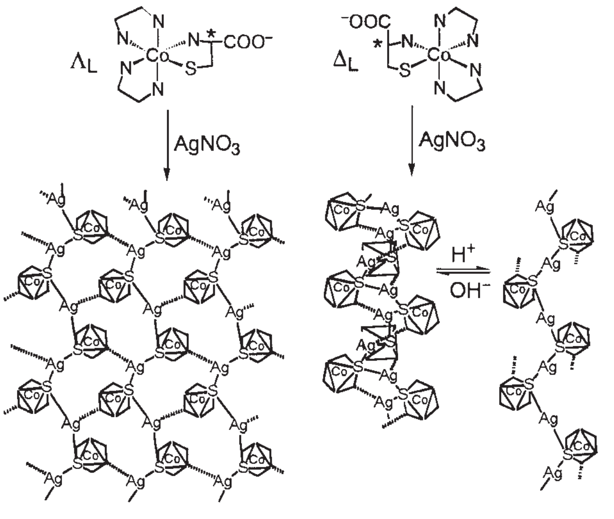


Fig. 21. Crystal structure of spontaneously resolved $(\Lambda)_n$-$[Ag\{Co(aet)(en)_2\}]_n(NO_3)_{3n}$. Nitrate anions, which do not contact with Ag^{I}, besides hydrogen atoms, are omitted for clarity.

In contrast to the 1:1 reaction of $[Co(aet)(en)_2]^{2+}$ with $AgNO_3$ in water, the corresponding 1:1 reaction with $AgClO_4$ or $AgBF_4$, followed by the addition of $NaClO_4$ or $NaBF_4$, did not produce the S-bridged $(Co^{III}Ag^{I})_n$ chain complex, $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$, but gave only the S-bridged trinuclear complex, $[Ag\{Co(aet)(en)_2\}_2]^{5+}$. It is considered that neither ClO_4^- nor BF_4^- anion contacts with Ag^{I} ion as closely as does NO_3^- anion, because of their non-planar geometry and lower nucleophilic character. Thus, the chain structure in $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$ seems to be stabilized by the close contact of NO_3^- anions with Ag^{I} ion, which weakens the electrophilicity of Ag^{I} ion so as to permit the thiolato group in $[Co(aet)(en)_2]^{2+}$ to bind to two Ag^{I} ions. Although $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$ is no other than the aggregate of the mononuclear $[Co(aet)(en)_2]^{2+}$, the chain structure in $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$ can be regarded as resulting from the aggregation of the $Co^{III}Ag^{I}Co^{III}$ trinuclear structure in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$ (Scheme 9). Since this aggregation is achieved by the linkage of additional Ag^{I} ion with each μ_2-thiolato group in $[Ag\{Co(aet)(en)_2\}_2]^{5+}$, a variety of aggregates based on S-bridged polynuclear complexes could be constructed if the nucleophilicity of μ_2-thiolato group is increased and/or the electrophilicity of linking metal ion is decreased to form μ_3-thiolato bridging structure. Remarkably, it was found that the S-bridged structure in $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$ was found to discriminate the chiral configurations (Δ and Λ) of $[Co(aet)(en)_2]^{2+}$ to exclusively give a pair of enantiomeric chains, $(\Delta\text{-}Co^{III}Ag^{I})_n$ and $(\Lambda\text{-}Co^{III}Ag^{I})_n$. Furthermore, the enantiomeric chains for $[Ag\{Co(aet)(en)_2\}]_n^{3n+}$ were found to separate spontaneously from one another as homochiral crystals. It should be noted that none of the mononuclear Δ/Λ-$[Co(aet)(en)_2](NO_3)_2$ and the trinuclear ΔΔ/ΛΛ-$[Ag\{Co(aet)(en)_2\}_2](NO_3)_5$ are spontaneously resolved.[14d,24e] Accordingly, it is considered that the high organization of the $[Co(aet)(en)_2]^{2+}$ octahedrons in a one-dimensional S-bridged array leads to spontaneous resolution, which would provide an important insight into the design and construction of polynuclear systems that are subject to spontaneous resolution.[29]

The corresponding Se-bridged polymeric complex with a



Scheme 10.

one-dimensional zigzag chain structure, $[Ag\{Co(aes)(en)_2\}]_n(NO_3)_{3n}$ (aes = 2-aminoethaneselenolate), has been prepared by the 1:1 reaction of $[Co(aes)(en)_2](NO_3)_2$ with $AgNO_3$ in water, and it was found that $[Ag\{Co(aes)(en)_2\}]_n(NO_3)_{3n}$ is also subject to spontaneous resolution.[14g]

3.2 Reactions of $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ with Ag^I (Co:Ag = 1:1). Since the reaction of $[Co(aet)(en)_2]^{2+}$ with $AgNO_3$ in a 1:1 ratio gave the S-bridged $(Co^{III}Ag^I)_n$ polymeric complex having a one-dimensional zigzag chain structure, it was expected that similar $(Co^{III}Ag^I)_n$ chain structures would be formed by using the Λ_L or Δ_L diastereomer of $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$,[24f] instead of $[Co(aet)(en)_2]^{2+}$. Indeed, the 1:1 reaction of Λ_L-$[Co(L\text{-}cys\text{-}N,S)(en)_2](ClO_4)$ with $AgNO_3$ in water, followed by the addition of $NaNO_3$, gave an S-bridged $Co^{III}Ag^I$ polymeric complex with the 1:1 stoichiometry of $[Co(L\text{-}cys)(en)_2](NO_3)\cdot AgNO_3$ (Scheme 10).[14e] X-ray analysis revealed that the thiolato S atom of each octahedral Λ_L-$[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ unit is bound to two Ag^I ions to form a one-dimensional zigzag $(Co^{III}Ag^I)_n$ chain structure in $(\Lambda_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]_n{}^{2n+}$ (average Co–S = 2.263(3) Å, Ag–S = 2.506(3) Å). While this chain structure resembles that found in $[Ag\{Co(aet)(en)_2\}]_n{}^{3n+}$, the S–Ag–S angle (149.62(7)°) in $(\Lambda_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]_n{}^{2n+}$ is significantly deviated from 180°, compared with that (173.14(6)°) in $[Ag\{Co(aet)(en)_2\}]_n{}^{3n+}$. A detailed inspection of the extended structure indicated that the COO^- group of each Λ_L-$[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ unit, which adopts an equatorial orientation, chelates to Ag^I ion of the adjacent zigzag chain (Ag–O2 = 2.490(8) Å, Ag–O1 = 2.598(1) Å). Thus, in $(\Lambda_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]_n{}^{2n+}$, the $(Co^{III}Ag^I)_n$ chains are connected with one another through Ag–O bonds, which completes a two-dimensional sheet-like structure made up by the cyclic $Co^{III}{}_3Ag^I{}_3$ network unit, as shown in Fig. 22a.

A similar 1:1 reaction of the Δ_L diastereomer of $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ with $AgNO_3$ also produced the 1:1 adduct of $(\Delta_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]_n(NO_3)_{2n}$, the structure of which was established by X-ray analysis.[14e] Interestingly, the complex cation was found to be a one-dimensional helix coordination polymer consisting of the asymmetric Δ_L-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]^{2+}$ units (Fig. 22b). The thiolato S atom of each octahedral Δ_L-$[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ unit is bound to two Ag^I ions to form an infinite $(Co^{III}Ag^I)_n$ chain (average Co–S = 2.251(2) Å, Ag–S = 2.552(2) Å), as in the case of $(\Lambda_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]_n{}^{2n+}$. However, each Ag^I ion is weakly coordinated by the COO^- group of the Δ_L-$[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ unit attached to the same chain (Ag–O2 = 2.539(6) Å), besides the two S atoms from two different Δ_L-$[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ units, so that the chain forms a left-handed helix structure around the crystallographic 3_2 screw axis. In contrast to the case of $(\Lambda_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]_n{}^{2n+}$, the COO^- group of the Δ_L-$[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ unit in this helix structure adopts an axial orientation, which is responsible for the remarkable difference in the aggregation of the octahedral $[Co(L\text{-}cys\text{-}N,S)(en)_2]^+$ units assisted by Ag^I ions.

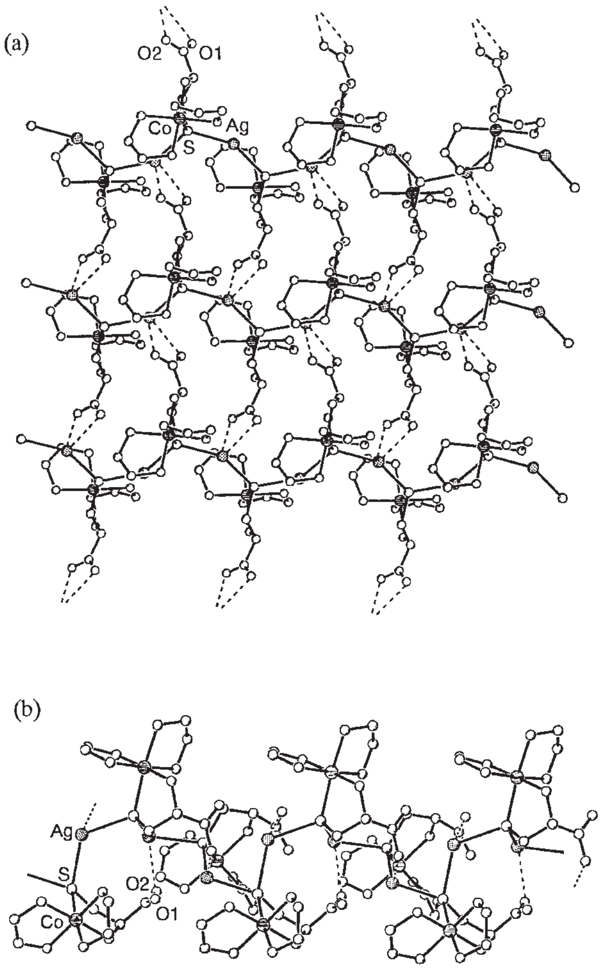


Fig. 22. Crystal structures of $(\Lambda_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]^{2n+}$ (a) and $(\Delta_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]^{2n+}$ (b). Hydrogen atoms are omitted for clarity.

The addition of HNO_3 to an aqueous solution of $(\Delta_L)_n$-$[Ag\{Co(L\text{-}cys\text{-}N,S)(en)_2\}]_n(NO_3)_{2n}$ afforded another polymeric complex, $(\Delta_L)_n$-$[Ag\{Co(L\text{-}Hcys\text{-}N,S)(en)_2\}]_n(NO_3)_{3n}$, which is assumed to have a one-dimensional zigzag chain structure such as found in $[Ag\{Co(aet)(en)_2\}]_n(NO_3)_{3n}$, rather than a helix structure, based on the IR and the solid state absorption and CD spectra.[14e] This complex was also prepared directly by the 1:1 reaction of Δ_L-$[Co(L\text{-}Hcys\text{-}N,S)(en)_2]^{2+}$ with $AgNO_3$ in water, followed by the addition of HNO_3. Interestingly, when an aqueous solution of $(\Delta_L)_n$-[Ag{Co(L-Hcys-*N*,*S*)(en)$_2$}]$_n$(NO$_3$)$_{3n}$ was neutralized with NaOH, the helix structure in $(\Delta_L)_n$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}]$_n$(NO$_3$)$_{2n}$ was re-constructed. This result obviously indicates that the 1D zigzag $(\Delta_L\text{-Co}^{III}\text{Ag}^{I})_n$ structure is reverted back to the helix structure by changing the pH of the solution (Scheme 10). Here it should be noted that the polymeric structures in $(\Lambda_L)_n$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}]$_n{}^{2n+}$ and $(\Delta_L)_n$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}]$_n{}^{2n+}$ are comparable with the two-dimensional β-sheet and the one-dimensional α-helix structures for protein, respectively. While the β-sheet and α-helix structures are driven and sustained by the inter- or intrastrand hydrogen bonds between NH and CO groups originated from the flexible polypeptide chain, the bonding interaction between free COO$^-$ groups and bridging Ag^I ions is of great importance in the formation of the two-dimensional sheet-like and one-dimensional helix structures in $(\Lambda_L)_n$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}]$_n{}^{2n+}$ and $(\Delta_L)_n$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}]$_n{}^{2n+}$.

3.3 Reactions of [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ with Ag^I (Co:Ag = 2:1). As described above, the construction of highly organized chiral molecular architectures can be achieved by the introduction of simple L-cys ligand with a free COO$^-$ group in an octahedral complex-unit and that their overall topologies are controlled by its diastereomerism. Thus, several other reactions of Λ_L- or Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ with Ag$^+$ were also investigated by changing the reaction stoichiometry and counter anions, in order to find the key factors to control supramolecular structures composed of simple mono(thiolato)-type octahedrons.

The 2:1 reaction of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$](ClO$_4$) with AgClO$_4$ in water gave the 2:1 adduct of $\Lambda_L\Lambda_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3$.[14e] X-ray analysis showed that the central Ag^I ion is coordinated by two thiolato S atoms from two octahedral Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units, forming an S-bridged Co^{III}Ag^{I}Co^{III} trinuclear structure (Co–S = 2.263(1) Å, Ag–S = 2.393(1) Å, S–Ag–S = 172.39(6)°). The overall structure in $\Lambda_L\Lambda_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ is very similar to that found in [Ag{Co(aet)(en)$_2$}$_2$]$^{5+}$, except for the presence of free COO$^-$ groups. The corresponding 2:1 adduct of $\Delta_L\Delta_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3$ was prepared by using Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ and NaOH (1:1), instead of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$](ClO$_4$).[14f] X-ray analysis confirmed that this complex also has an S-bridged Co^{III}Ag^{I}Co^{III} trinuclear structure, in which two Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are linked by a Ag^I ion through sulfur-bridges (average Co–S = 2.257(5) Å, Ag–S = 2.383(5) Å, S–Ag–S = 165.4(2)°). However, it was recognized that $\Lambda_L\Lambda_L$- and $\Delta_L\Delta_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](ClO$_4$)$_3$ form hydrogen bonding networks that are not identical. That is, in the $\Lambda_L\Lambda_L$ complex each trinuclear Co^{III}Ag^{I}Co^{III} cation is connected to four adjacent trinuclear cations through four single COO$^-$···H$_2$N hydrogen bonds (average O···N = 2.865 Å), while each trinuclear Co^{III}Ag^{I}Co^{III} cation is connected to three adjacent trinuclear cations through two single and one double COO$^-$···H$_2$N hydrogen bonds (average O···N = 2.942 Å) in the $\Delta_L\Delta_L$ complex (Fig. 23).

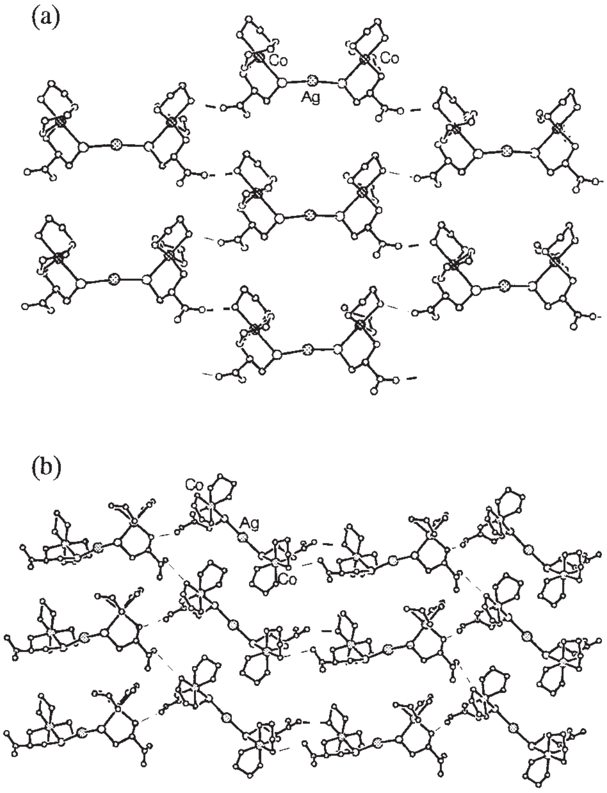


Fig. 23. Crystal structures of $\Lambda_L\Lambda_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ (a) and $\Delta_L\Delta_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$]$^{3+}$ (b), showing hydrogen bonding networks. Hydrogen atoms are omitted for clarity.

A similar 2:1 reaction of Λ_L-[Co(L-cys-*N*,*S*)(en)$_2$](ClO$_4$) with AgNO$_3$ in water, followed by the addition of NaNO$_3$, also produced the Co^{III}Ag^{I}Co^{III} trinuclear complex, $\Lambda_L\Lambda_L$-[Ag{Co(L-cys-*N*,*S*)(en)$_2$}$_2$](NO$_3$)$_3$. However, when an aqueous solution of a 1:1 mixture of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ and NaOH was treated with AgNO$_3$ in a Co:Ag = 2:1 ratio, an unexpected product containing Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ and Ag^I in a 3:1 ratio was isolated.[14f] This complex was also obtained in a higher yield on treating a 1:1 mixture of Δ_L-[Co(L-Hcys-*N*,*S*)(en)$_2$](ClO$_4$)$_2$ and NaOH with AgNO$_3$ in a Co:Ag = 3:1 ratio. X-ray analysis of this 3:1 adduct revealed that the Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ unit is bound to a Na^I ion through a carboxylate O atom (Na–O = 2.376(6) Å), besides being bound to an Ag^I ion through a thiolato S atom (Ag–S = 2.519(2) Å). This result clearly indicates that [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ can act not only as a simple monodentate-*S* metalloligand, but also as a didentate-*O*,*S* metalloligand. In the extended structure, each Ag^I ion is coordinated by three S atoms from three Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units in a trigonal-planar geometry, while each Na^I ion is coordinated by six O atoms from three Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units and three water molecules in a trigonal-prismatic environment. As a result, the Δ_L-[Co(L-cys-*N*,*S*)(en)$_2$]$^+$ units are linked alternatively by Ag^I and Na^I ions to construct a two-dimensional honeycomb layer structure, in which three Ag^I and three Na^I ions form a hexagon, as shown in Fig. 24. Here, it should be noted that one NO$_3{}^-$ ion is situated at the center of each hexagon. Since the formation of $(\Delta_L)_3$-[AgNa{Co(L-cys-*N*,*S*)(en)$_2$}$_3$]$^{5+}$ was not recognized for the corresponding reaction with AgClO$_4$, the presence of NO$_3{}^-$ ion, the size of which is best fitted for the cavity of the hexagon, would stabilize the Co$^{III}{}_3$Ag^{I}Na^I honeycomb structure.

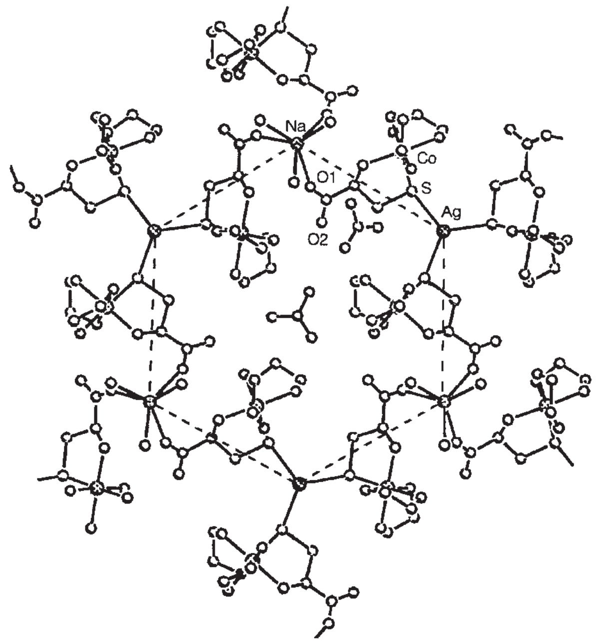


Fig. 24. Crystal structure of $(\Delta_{\mathrm{L}})_{3n}$-[AgNa{Co(L-cys-*N*,*S*)(en)$_2$}$_3$]$^{5n+}$, showing a 2D honeycomb structure. Only the nitrate anion located at the center of each hexagon is presented and hydrogen atoms are omitted for clarity.

4. Concluding Remarks

It was shown that a large variety of S-bridged metallo-aggregates having several chiral centers can be constructed from the octahedral cobalt(III), rhodium(III), iridium(III), and chromium(III) complexes with 2-aminoethanethiolate (aet) or L-cysteinate (L-cys), which function as effective S-donating metalloligands.

The tris(thiolato)-type *fac*(*S*)-[M(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ (M = Co$^{\mathrm{III}}$, Rh$^{\mathrm{III}}$, Ir$^{\mathrm{III}}$, Cr$^{\mathrm{III}}$) complexes readily reacted with various transition metal ions to form diverse S-bridged metallo-aggregates, the structures of which are highly dependent on the coordination geometry of the reacting metal ions. It was found that the donating ability of thiolato groups in *fac*(*S*)-[M(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ can be tuned by the change of a metal ion, which allows one to control the spectroscopic and electrochemical properties of the S-bridged metallo-aggregates as well as their dynamic behavior. In this tris(thiolato)-type system, several striking chemical phenomena, such as geometrical isomerization from *fac*(*S*) to *mer*(*S*), chelate transfer of aet in *fac*(*S*)-[M(aet)$_3$], and spontaneous reduction of reacting metal ions, were recognized through the aggregation of the *fac*(*S*)-[M(aet or L-cys-*N*,*S*)$_3$]$^{0\text{ or }3-}$ octahedrons. Furthermore, it was found that the aggregation of the tris(thiolato)-type octahedrons induces some fascinating chiral behavior, such as chiral discrimination, chiral amplification, chiral inversion, and spontaneous resolution.

While the isolation of the bis(thiolato)-type mononuclear complex, *cis*(*S*)-[Co(aet)$_2$(en)]$^+$, is extremely difficult, the metal replacement reactions for [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$, which is easily prepared from [CoCl$_2$(en)$_2$]$^+$ and [Ni(aet)$_2$], opened the way to create S-bridged metallo-aggregates based on the *cis*(*S*)-[Co(aet)$_2$(en)]$^+$ octahedrons. That is, treatment of [Ni{Co(aet)$_2$(en)}$_2$]$^{4+}$ with transition metal ions produced a variety of S-bridged polynuclear complexes consisting of the *cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units. It was found that the geometrical and chiral configurations of the *cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units incorporated in the S-bridged metallo-aggregates can be controlled by the choice of reacting metal ions. Furthermore, the use of *trans*(*N*)-[Co(D-pen-*N*,*O*,*S*)$_2$]$^-$ as a chiral didentate-*S*,*S* metalloligand led to the chiral selective incorporation of the *cis*(*S*)-[Co(aet)$_2$(en)]$^+$ units in the S-bridged trinuclear structures.

One-dimensional and two-dimensional S-bridged polymeric structures, besides a discrete trinuclear structure, were constructed by the aggregation of the mono(thiolato)-type [Co(aet or L-cys-*N*,*S*)(en)$_2$]$^{2+\text{ or }+}$ assisted by Ag$^{\mathrm{I}}$ ions. It was found that the choice of counter anions, as well as the reaction stoichiometries, is the important factor for the thiolato group in [Co(aet or L-cys-*N*,*S*)(en)$_2$]$^{2+\text{ or }+}$ to take a μ_3-bridging mode, which is responsible for the formation of the dimensional structures. Furthermore, the free carboxylate group in [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ was found to have an ability to bind with metal ions, leading to the creation of fascinating one-dimensional and two-dimensional metallo-aggregates. It is worth to note that their dimensional structures are controlled by the diastereomerism of [Co(L-cys-*N*,*S*)(en)$_2$]$^+$ and the pH of reaction solutions.

Finally, the results presented in this review point out that a large variety of attractive chiral metallo-aggregates consisting of transition metal ions with different electronic and oxidation states and coordination geometries can be constructed by the controlled design of metalloligands with several donor sites and by the proper choice of reacting metal ions and reaction conditions, even when only a simple and achiral organic ligand is employed in the systems.

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References

1 a) E. Deutsch, M. J. Root, and D. L. Nosco, *Adv. Inorg. Bioinorg. Mech.*, **1**, 269 (1982). b) P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, **76**, 121 (1987). c) B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, **30**, 769 (1991). d) D. W. Stephan and T. T. Nadasdi, *Coord. Chem. Rev.*, **147**, 147 (1996). e) M. Murata, M. Kojima, A. Hioki, M. Miyagawa, M. Hirotsu, K. Nakajima, M. Kita, S. Kashino, and Y. Yoshikawa, *Coord. Chem. Rev.*, **174**, 109 (1998). f) A. C. Marr, D. J. E. Spencer, and M. Schröder, *Chem. Rev.*, **219**, 1055 (2001).

2 a) B. A. Lange, K. Libson, E. Deutsch, and R. C. Elder, *Inorg. Chem.*, **15**, 2985 (1976). b) D. L. Herting, C. P. Sloan, A. W. Cabral, and J. H. Krueger, *Inorg. Chem.*, **17**, 1649 (1978). c) I. K. Adzamli, K. Libson, J. D. Lydon, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **18**, 303 (1979). d) H. Macke, V. H. Houlding, and A. W. Adamson, *J. Am. Chem. Soc.*, **102**, 6888 (1980). e) M. Kita, K. Yamanari, K. Kitahama, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **54**, 2995 (1981). f) M. Kita, K. Yamanari, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **55**, 2873 (1982). g) K. Okamoto, H. Umehara,

and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **60**, 2875 (1987). h) W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **27**, 1068 (1988). i) T. Konno, H. Umehara, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **62**, 3015 (1989). j) T. Konno, H. Umehara, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **67**, 416 (1994). k) K. Okamoto, K. Arashi, J. Hidaka, and T. Konno, *Bull. Chem. Soc. Jpn.*, **67**, 2736 (1994). l) C. Galves, D. G. Ho, A. Azod, and M. Selke, *J. Am. Chem. Soc.*, **123**, 3381 (2001).

3 a) P. J. Farmer, T. Solouki, D. K. Mills, T. Soma, D. H. Russell, J. H. Reibenspies, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, **114**, 4601 (1992). b) P. J. Farmer, T. Solouki, D. K. Mills, T. Soma, D. H. Russell, and M. Y. Darensbourg, *Inorg. Chem.*, **32**, 4171 (1993). c) R. M. Buomono, I. Font, M. J. Maguire, J. H. Reibenspies, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, **117**, 963 (1995). d) C. A. Grapperhaus, M. Y. Darensbourg, L. W. Summer, and D. H. Russell, *J. Am. Chem. Soc.*, **118**, 1791 (1996). e) C. A. Grapperhaus, M. J. Maguire, T. Tuntulani, and M. Y. Darensbourg, *Inorg. Chem.*, **36**, 1860 (1997).

4 a) R. C. Elder, G. J. Kennard, M. D. Payne, and E. Deutsch, *Inorg. Chem.*, **17**, 1296 (1978). b) W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **17**, 2165 (1978). c) K. Yamanari and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **53**, 3605 (1980). d) V. H. Houlding, H. Macke, and A. W. Adamson, *Inorg. Chem.*, **20**, 4279 (1981). e) L. Roecker, M. E. Dickman, D. L. Nosco, R. J. Doedens, and E. Deutsch, *Inorg. Chem.*, **22**, 2022 (1983). f) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 2958 (1983). g) K. Okamoto, K. Wakayama, H. Einaga, S. Yamada, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **56**, 165 (1983). h) T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **57**, 3104 (1984). i) T. Konno, K. Okamoto, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **58**, 1119 (1985). j) K. Okamoto, N. Fushimi, T. Konno, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **64**, 2635 (1991).

5 a) S. G. Murray and F. R. Hartley, *Chem. Rev.*, **81**, 365 (1981). b) M. Y. Darensbourg, I. Font, D. K. Mills, M. P. Pala, and J. H. Reibenspies, *Inorg. Chem.*, **31**, 4965 (1992). c) P. J. Farmer, J. H. Reibenspies, P. A. Lindahl, and M. Y. Darensbourg, *J. Am. Chem. Soc.*, **115**, 4665 (1993). d) T. Tuntulani, G. Musie, J. H. Reibenspies, and M. Y. Darensbourg, *Inorg. Chem.*, **34**, 6279 (1995). e) D. C. Goodman, R. M. Buonomo, P. J. Farmer, J. H. Reibenspies, and M. Y. Darensbourg, *Inorg. Chem.*, **35**, 4029 (1996). f) G. Musie, J. H. Reibenspies, and M. Y. Darensbourg, *Inorg. Chem.*, **37**, 302 (1998). g) J. J. Smee, M. L. Miller, C. A. Grapperhaus, J. H. Reibenspies, and M. Y. Darensbourg, *Inorg. Chem.*, **40**, 3601 (2001).

6 M. Hirotsu, A. Kobayashi, T. Yoshimura, and T. Konno, *J. Chem. Soc., Dalton Trans.*, **2002**, 878.

7 a) D. L. Nosco, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **19**, 2545 (1980). b) J. D. Lydon, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **21**, 3186 (1982). c) T. Konno, Y. Miyashita, and K. Okamoto, *Chem. Lett.*, **1997**, 85. d) Y. Miyashita, N. Sakagami, Y. Yamada, T. Konno, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **71**, 2153 (1998). e) T. Konno, K. Haneishi, M. Hirotsu, T. Yamaguchi, T. Ito, and T. Yoshimura, *J. Am. Chem. Soc.*, **125**, 9244 (2003).

8 a) D. H. Busch and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962). b) G. R. Brubaker and B. E. Douglas, *Inorg. Chem.*, **6**, 1562 (1967). c) R. E. Desimone, T. Ontko, L. Wardman, and E. L. Blinn, *Inorg. Chem.*, **6**, 1313 (1975). d) E. L. Blinn, P. Butler, K. M. Chapman, and S. Harris, *Inorg. Chim. Acta*, **24**, 139 (1977). e) G. R. Brubaker, M. G. Henk, and D. W. Johnson, *Inorg. Chim. Acta*, **100**, 201 (1985). f) D. W. Johnson and T. R. Brewer, *Inorg. Chim. Acta*, **154**, 221 (1988).

9 a) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, *Chem. Lett.*, **1985**, 1017. b) K. Okamoto, S. Aizawa, T. Konno, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **59**, 3859 (1986). c) S. Aizawa, K. Okamoto, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 1601 (1988). d) T. Konno, S. Aizawa, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **62**, 585 (1989). e) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **63**, 792 (1990). f) T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **63**, 3027 (1990). g) T. Konno, K. Nakamura, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **66**, 2582 (1993). h) T. Konno and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **68**, 610 (1995).

10 a) Y. Miyashita, N. Sakagami, Y. Yamada, T. Konno, J. Hidaka, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **71**, 661 (1998). b) Y. Miyashita, Ph. D. Thesis, University of Tsukuba, Tsukuba, Japan, 1999. c) K. Tokuda, Ph. D. Thesis, Gunma University, Gunma, Japan, 2000. d) Y. Miyashita, Y. Yamada, K. Fujisawa, T. Konno, K. Kanamori, and K. Okamoto, *J. Chem. Soc., Dalton Trans.*, **2000**, 981. e) Y. Miyashita, N. Mahboob, S. Tsuboi, Y. Yamada, K. Fujisawa, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **74**, 1295 (2001). f) Y. Miyashita, M. Hamajima, Y. Yamada, K. Fujisawa, and K. Okamoto, *J. Chem. Soc., Dalton Trans.*, **2001**, 2089. g) N. Mahboob, Y. Miyashita, Y. Yamada, K. Fujisawa, and K. Okamoto, *Polyhedron*, **21**, 1809 (2002).

11 a) T. Konno, K. Okamoto, and J. Hidaka, *Chem. Lett.*, **1990**, 1043. b) T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **30**, 2255 (1991). c) T. Konno, T. Nagashio, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **31**, 1160 (1992). d) T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **33**, 538 (1994). e) T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **67**, 101 (1994). f) K. Okamoto, T. Konno, and J. Hidaka, *J. Chem. Soc., Dalton Trans.*, **1994**, 533. g) T. Konno, K. Okamoto, and J. Hidaka, presented at the 42nd Symposium on Coordination Chemistry of Japan, Nara, 1992, Abstr., 362. h) T. Konno, Y. Kageyama, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **67**, 1957 (1994). i) Y. Kageyama, T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chim. Acta*, **239**, 19 (1995).

12 a) K. Okamoto, T. Konno, Y. Kageyama, and J. Hidaka, *Chem. Lett.*, **1992**, 1105. b) K. Okamoto, Y. Kageyama, and T. Konno, *Bull. Chem. Soc. Jpn.*, **68**, 2573 (1995). c) T. Konno and K. Okamoto, presented at the 30th International Conference on Coordination Chemistry, Kyoto, 1994, Abstr., 196. d) T. Konno and K. Okamoto, *Inorg. Chem.*, **36**, 1403 (1997). e) T. Konno, K. Tokuda, T. Suzuki, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **71**, 1049 (1998). f) M. Hirotsu, Y. Nozaki, T. Yoshimura, W. Mori, and T. Konno, *Mol. Cryst. Liq. Cryst.*, **379**, 461 (2002). g) T. Konno, K. Tokuda, T. Abe, and M. Hirotsu, *Mol. Cryst. Liq. Cryst.*, **342**, 45 (2000).

13 a) T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **31**, 3875 (1992). b) T. Konno, C. Sasaki, and K. Okamoto, *Chem. Lett.*, **1996**, 977. c) K. Okamoto, C. Sasaki, Y. Yamada, and T. Konno, *Bull. Chem. Soc. Jpn.*, **72**, 1685 (1999). d) T. Konno, Y. Chikamoto, K. Okamoto, T. Yamaguchi, T. Ito, and M. Hirotsu, *Angew. Chem., Int. Ed.*, **39**, 4098 (2000).

14 a) R. H. Lane, N. S. Pantaleo, J. K. Farr, W. M. Coney, and M. G. Newton, *J. Am. Chem. Soc.*, **100**, 1610 (1978). b) M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **18**, 2036 (1979). c) M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **19**, 554 (1980). d) T. Konno, K. Tokuda, K. Okamoto, and M. Hirotsu, *Chem. Lett.*, **2000**, 1258. e) T. Konno, T. Yoshimura, K. Aoki, K. Okamoto, and M. Hirotsu, *Angew. Chem., Int. Ed.*, **40**, 1765 (2001). f) T. Konno, T. Kawamoto, R. Kuwabara, T. Yoshimura, and M. Hirotsu, *Chem. Lett.*, **2002**, 304. g) T. Konno, T. Yoshimura, G. Masuyama, and

M. Hirotsu, *Bull. Chem. Soc. Jpn.*, **75**, 2185 (2002).

15 a) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872 (1962). b) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 878 (1962). c) D.-X. Kang, M. Poor, and E. L. Blinn, *Inorg. Chim. Acta*, **168**, 209 (1990). d) H.-W. Xu, Z.-N. Chen, S. Ishizaka, N. Kitamura, and J.-G. Wu, *Chem. Commun.*, **2002**, 1934.

16 a) T. Konno, K. Yonenobu, J. Hidaka, and K. Okamoto, *Inorg. Chem.*, **33**, 861 (1994). b) T. Konno and K. Okamoto, *Chem. Lett.*, **1995**, 675. c) T. Konno, Y. Yoshinari, and K. Okamoto, *Chem. Lett.*, **1995**, 989. d) T. Konno, Y. Gotoh, and K. Okamoto, *Inorg. Chem.*, **36**, 4992 (1997). e) K. Okamoto, Y. Yoshinari, Y. Yamada, N. Sakagami, and T. Konno, *Bull. Chem. Soc. Jpn.*, **71**, 1363 (1998).

17 a) T. Konno, K. Okamoto, and J. Hidaka, *Inorg. Chem.*, **31**, 160 (1992). b) T. Konno, J. Hidaka, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **68**, 1353 (1995). c) T. Konno and K. Okamoto, *Chem. Lett.*, **1996**, 975. d) T. Konno, T. Machida, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **71**, 175 (1998). e) T. Konno, K. Tokuda, J. Sakurai, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **73**, 2767 (2000). f) T. Konno and K. Okamoto, presented at the 46th Symposium on Coordination Chemistry of Japan, Higashi-Osaka, 1996, Abstr., 301. g) H. Honda, T. Yoshimura, M. Hirotsu, T. Kawamoto, and T. Konno, *Inorg. Chem.*, **41**, 2229 (2002). h) T. Konno, M. Hattori, T. Yoshimura, and M. Hirotsu, *Chem. Lett.*, **2002**, 230. i) T. Konno, M. Honda, Y. Chikamoto, T. Kawamoto, T. Yoshimura, and M. Hirotsu, *Chem. Lett.*, **2002**, 472. j) Y. Chikamoto, T. Yoshimura, H. Honda, M. Hirotsu, T. Kawamoto, and T. Konno, *Mol. Cryst. Liq. Cryst.*, **379**, 455 (2002).

18 a) T. Konno, N. Matsuno, K. Okamoto, and M. Hirotsu, *Chem. Lett.*, **1999**, 1243. b) Y. Yamada, M. Tsuboi, A. Hirano, Y. Miyashita, K. Fujisawa, and K. Okamoto, *Inorg. Chim. Acta*, **332**, 108 (2002). c) T. Konno, M. Hattori, T. Yoshimura, and M. Hirotsu, *Chem. Lett.*, **2000**, 852.

19 a) K. Okamoto, T. Yonemura, T. Konno, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **65**, 794 (1992). b) K. Okamoto, M. Matsumoto, Y. Miyashita, N. Sakagami, J. Hidaka, and T. Konno, *Inorg. Chim. Acta*, **260**, 17 (1997). c) T. Konno, K. Tokuda, and K. Okamoto, *Chem. Commun.*, **1998**, 1697. d) K. Tokuda, K. Okamoto, and T. Konno, *Inorg. Chem.*, **39**, 333 (2000). e) T. Konno, Y. Shimazaki, T. Yamaguchi, T. Ito, and M. Hirotsu, *Angew. Chem., Int. Ed.*, **41**, 4711 (2002). f) M. Hirotsu, R. Endo, T. Yoshimura, and T. Konno, *Bull. Chem. Soc. Jpn.*, **76**, 1215 (2003).

20 a) T. Tuntulani, J. H. Reibenspies, P. J. Farmer, and M. Y. Darensbourg, *Inorg. Chem.*, **31**, 3497 (1992). b) G. J. Colpas, R. O. Day, and M. J. Maroney, *Inorg. Chem.*, **31**, 5053 (1992). c) G. Musie, P. J. Farmer, T. Tuntulani, J. H. Reibenspies, and M. Y. Darensbourg, *Inorg. Chem.*, **35**, 2176 (1996). d) C.-H. Lai, J. H. Reibenspies, and M. Y. Darensbourg, *Angew. Chem., Int. Ed. Engl.*, **35**, 2390 (1996).

21 a) T. Beissel, F. Birkelbach, E. Bill, T. Glaser, F. Kesting, C. Krebs, T. Weyhermuller, K. Wieghardt, C. Butzlaff, and A. X. Trautwein, *J. Am. Chem. Soc.*, **118**, 12376 (1996). b) T. Glaser, F. Kesting, T. Beissel, E. Bill, T. Weyhermuller, W. M-Klaucke, and K. Wieghardt, *Inorg. Chem.*, **38**, 722 (1999). c) T. Glaser, E. Bill, T. Weyhermuller, W. M-Klaucke, and K. Wieghardt, *Inorg. Chem.*, **38**, 2632 (1999). d) C. Krebs, T. Glaser, E. Bill, T. Weyhermuller, W. M-Klaucke, and K. Wieghardt, *Angew. Chem., Int. Ed.*, **38**, 359 (1999). e) B. Albela, E. Bill, O. Brosch, T. Weyhermuller, and K. Wieghardt, *Eur. J. Inorg. Chem.*, **2000**, 139.

22 a) M. J. Heeg, E. L. Blinn, and E. Deutsch, *Inorg. Chem.*, **24**, 1118 (1985). b) T. Konno, K. Okamoto, and J. Hidaka, *Acta Crystallogr.*, **C49**, 222 (1993).

23 a) C. Stein, S. Bouma, J. Carlson, C. Cornelius, J. Maeda, C. Weschler, E. Deutsch, and K. O. Hodgson, *Inorg. Chem.*, **15**, 1183 (1976). b) T. Yonemura, Z.-P. Bai, K. Okamoto, T. Ama, H. Kawaguchi, T. Yasui, and J. Hidaka, *J. Chem. Soc., Dalton Trans.*, **1999**, 2151.

24 a) M. Kita, K. Yamanari, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **56**, 3272 (1983). b) M. P. Schubert, *J. Am. Chem. Soc.*, **55**, 3336 (1933). c) D. L. Nosco and E. Deutsch, *Inorg. Synth.*, **21**, 19 (1982). d) V. H. Houlding, H. Macke, and A. W. Adamson, *Inorg. Chem.*, **20**, 4279 (1981). e) T. Konno, T. Yoshimura, and M. Hirotsu, *Acta Crystallogr.*, **C57**, 538 (2001). f) H. C. Freeman, C. J. Moore, W. G. Jackson, and A. M. Sargeson, *Inorg. Chem.*, **17**, 3513 (1978).

25 a) A. F. Wells, "Structural Inorganic Chemistry," 5th ed, Clarendon Press, Oxford (1984). b) B. E. Douglas, D. H. McDaniel, and J. J. Alexander, "Concepts and Models of Inorganic Chemistry," John & Sons Ltd., New York (1994).

26 P. Pyykkö, *Chem. Rev.*, **97**, 597 (1997).

27 a) Y. Yamada, Y. Maeda, Y. Miyashita, K. Fujisawa, T. Konno, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **73**, 1219 (2000). b) Y. Yamada, Y. Maeda, T. Konno, K. Fujisawa, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **73**, 1831 (2000). c) Y. Yamada, Y. Miyashita, K. Fujisawa, and K. Okamoto, *Bull. Chem. Soc. Jpn.*, **75**, 1151 (2002).

28 A. W. Addison, T. N. Rao, J. Reedijk, J. R. Rijn, and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.

29 a) J. Jacques, A. Collet, and S. H. Wilen, "Enantiomers, Racemates and Resolutions," John & Sons Ltd., New York (1981). b) S. Nagasato, I. Katsuki, Y. Motoda, Y. Sunatsuki, N. Matsumoto, and M. Kojima, *Inorg. Chem.*, **40**, 2534 (2001). c) I. Katsuki, Y. Motoda, Y. Sunatsuki, M. Matsumoto, T. Nakashima, and M. Kojima, *J. Am. Chem. Soc.*, **124**, 629 (2002).

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