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The Formation and Stereochemistry of $[\mathrm{Co^{III}}_3(\text{L-cys-}N,S)_n(\mathrm{aet})_{6-n}]^{3-n}$ Type *S*-Bridged Complexes (n=0—6, L-cys=L-cysteinate, and aet=2-aminoethanethiolate)

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Synopsis. Three kinds of *S*-bridged trinuclear complexes, $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_3}(\text{L-cys-}N,S)_6]^{3-}$, $\Delta_{\mathrm{LLL}}\Delta$- and $\Delta_{\mathrm{LLL}}\Lambda$-$[\mathrm{Co_3}(\text{L-cys-}N,S)_3(\mathrm{aet})_3]^0$, and $[\mathrm{Co_3(aet)_6}]^{3+}$,[1] were formed by the reaction of a mixture of Δ_{LLL}-*fac*-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ (L-cys=L-cysteinate) and *fac*-$[\mathrm{Co(aet)_3}]$ (aet=2-aminoethanethiolate) with $[\mathrm{CoCl(NH_3)_5}]^{2+}$. The reaction with an excess amount of $\mathrm{Co^{2+}}$ led to the formation of seven kinds of *S*-bridged complexes, $[\mathrm{Co_3}(\text{L-cys-}N,S)_n(\mathrm{aet})_{6-n}]^{3-n}$ (n=0—6).

Several *S*-bridged trinuclear metal complexes with L-cysteinate (L-cys) or 2-aminoethanethiolate (aet) have been investigated because of their stereochemical and spectrochemical interest.[2–12] Recently, it was found that the formation of $[\mathrm{M^{III}}\{\mathrm{Co^{III}}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (M=Co, Fe) by the reaction of Δ_{LLL}-*fac*-$[\mathrm{Co^{III}}(\text{L-cys-}N,S)_3]^{3-}$ with an excess amount of Co(II) or Fe(II) was accompanied by the inversion of the starting Δ_{LLL} complex and that only the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomer was formed.[9–11] On the other hand, the reaction with Co(III) or Fe(III) proceeded with a retention of the Δ_{LLL} configuration, and the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ isomer was selectively formed.[9–11] However the mechanism of this inversion is still unknown. In order to elucidate the stereoselectivity and the mechanism of the inversion for the *S*-bridged trinuclear complexes with L-cysteinate, an attempt was made to investigate the mixed-type trinuclear complexes containing L-cysteinate and 2-aminoethanethiolate. In this paper, we report the reactions of a mixture of Δ_{LLL}-*fac*-$[\mathrm{Co^{III}}(\text{L-cys-}N,S)_3]^{3-}$ and *fac*-$[\mathrm{Co^{III}(aet)_3}]$ with Co(III) and with Co(II). The reaction products were characterized on the basis of the absorption and CD spectra and their column chromatographic behavior in comparison with that of $[\mathrm{Co_3}(\text{L-cys-}N,S)_6]^{3-}$ and $[\mathrm{Co_3(aet)_6}]^{3+}$.

Experimental

1a) Reaction with Co(III). To a solution of $[\mathrm{CoCl(NH_3)_5}]\mathrm{Cl_2}$ (0.18 g, 0.72 mmol) in 15 $\mathrm{cm^3}$ of water was added *fac*-$[\mathrm{Co(aet)_3}]$[3] (0.20 g, 0.70 mmol), followed by the dropwise addition of a solution containing Δ_{LLL}-*fac*-$\mathrm{K_3}[\mathrm{Co}(\text{L-cys-}N,S)_3]9\mathrm{H_2O}\cdot0.5\mathrm{KCl}$[11] (0.51 g, 0.70 mmol) in 5 $\mathrm{cm^3}$ of water. The mixture was stirred at room temperature for 30 min and then filtered to remove any insoluble materials. The dark brown filtrate was poured onto a cation-exchange column (SP-Sephadex C-25 $\mathrm{Na^+}$ form, 3.5 cm×90 cm). The negative-charged band (green) containing $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_3}(\text{L-cys-}N,S)_6]^{3-}$ [10,11,13] was eluted quickly with water, and then the neutral band was eluted slowly with water and finally separated into two bands, F-1 (brown) and F-2 (green), in this order. The formation ratio of the two isomers was about 1 : 1. Each eluate was concentrated to dryness with a rotary evaporator. The crude F-2 isomer was recrystallized from water and the F-1 isomer from water by adding a large amount of ethanol. Found for F-1: C, 22.83; H, 5.24; N, 9.86%. Calcd for $[\mathrm{Co_3}(\text{L-cys-N,S})_3(\mathrm{aet})_3]\cdot4\mathrm{H_2O}\cdot0.5\mathrm{C_2H_5OH}$=$\mathrm{C_{16}H_{44}N_6O_{10.5}S_6Co_3}$: C, 22.41; H, 5.17; N, 9.80%. Found for F-2: C, 20.01; H, 5.52; N, 9.31%. Calcd for $[\mathrm{Co_3}(\text{L-cys-}N,S)_3(\mathrm{aet})_3]\cdot8\mathrm{H_2O}$=$\mathrm{C_{15}H_{49}N_6O_{14}S_6Co_3}$: C, 19.87; H, 5.45; N, 9.27%. ^{13}C NMR for F-1: δ 19.50 ($\mathrm{CH_3}$ of ethanol), 34.89 ($\mathrm{CH_2S}$ of aet), 38.36 ($\mathrm{CH_2S}$ of L-cys), 49.79 ($\mathrm{CH_2NH_2}$ of aet), 60.13 ($\mathrm{CH_2}$ of ethanol), 66.36 (CH of L-cys), 177.96 (COO of L-cys). The ^{13}C NMR spectrum of the F-2 isomer could not be measured because of its low solubility in water. The remaining band, adsorbed on the top of the column, contained only $[\mathrm{Co_3(aet)_6}]^{3+}$, which was eluted with a 0.2 mol $\mathrm{dm^{-3}}$ aqueous NaCl solution and separated into two bands, meso ($\Delta\Lambda$, brown) and racemic ($\Delta\Delta$ and $\Lambda\Lambda$, green) isomers[4,13,14] in this order.

1b) Reaction with Co(II). To a solution of $\mathrm{CoCl_2\cdot6H_2O}$ (1.0 g, 4.2 mmol) in 15 $\mathrm{cm^3}$ of water was added *fac*-$[\mathrm{Co(aet)_3}]$[3] (0.2 g, 0.70 mmol), followed by the dropwise addition of a solution containing Δ_{LLL}-*fac*-$\mathrm{K_3}[\mathrm{Co}(\text{L-cys-}N,S)_3]\cdot9\mathrm{H_2O}\cdot0.5\mathrm{KCl}$[11] (0.51 g, 0.70 mmol) in 5 $\mathrm{cm^3}$ of water. The mixture was stirred at room temperature for 30 min and then filtered to remove any insoluble materials. The dark brown filtrate was poured onto a cation-exchange column (SP-Sephadex C-25, $\mathrm{Na^+}$ form, 3.5 cm×90 cm). The negative-charged NC band was quickly eluted with water, and then the neutral A band was slowly eluted with water and finally separated into four bands, A-1 (brown), A-2 (green), A-3 (brown), and A-4 (green), in this order. After the neutral A band had been eluted with water, the positive-charged band adsorbed on the top of the column was eluted with a 0.2 mol $\mathrm{dm^{-3}}$ aqueous NaCl solution. The first-eluted B band was separated into four bands; B-1 (brown), B-2 (green), B-3 (brown), and B-4 (green), the secondly eluted C band into three bands; C-a (pink), C-1 (brown), and C-2 (green), and the last-eluted D band containing $[\mathrm{Co_3(aet)_6}]^{3+}$ into two bands; meso (D-1, brown) and racemic (D-2, green) isomers.[4,13,14] The NC eluate was poured onto an anion-exchange column (QAE-Sephadex A-25, $\mathrm{Cl^-}$ form, 3.5 cm×90 cm). No band was eluted with water. After the column had been swept with water, the negative-charged band adsorbed on the top of the column was eluted with a 0.2 mol $\mathrm{dm^{-3}}$ aqueous NaCl solution. The first-eluted B′ band was separated into three bands; B′-1 (green), B′-2 (brown), and B′-3 (green), and the secondly eluted C′ band into two bands; C′-1 (brown) and C′-2 (green). Finally, the green D′ band containing $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_3}(\text{L-cys-}N,S)_6]^{3-}$ [10,11,13] was eluted. The pink C-a band was found to be an unreacted $\mathrm{Co^{2+}}$ species from its absorption spectrum. In this reaction, the complex could not be isolated from each eluate because of its quite small amount. Accordingly, the concentration of each eluate was estimated on the basis of the extinction coefficients of $[\mathrm{Co_3(aet)_6}]^{3+}$ [14] and $[\mathrm{Co_3}(\text{L-cys-}N,S)_6]^{3-}$.[11]

2) Measurements. The electronic absorption specta were recorded with JASCO UVIDEC-1 and UVIDEC-610 spectrometers, and the CD spectra with a JASCO J-20 spectropolarimeter. The ^{13}C NMR spectrum was recorded with a JEOL JNM-FX-90Q NMR spectrometer in a $\mathrm{D_2O}$ solvent at the probe temperature. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as the internal reference.

Results and Discusston

Three configurations, $\Delta\Delta$, $\Lambda\Lambda$, and $\Delta\Lambda$, with respect to the absolute configuration of the two terminal *fac*-[Co(bidentate-*N,S*)$_3$] moieties are possible for each of the *S*-bridged trinuclear complexes, [Co$_3$(L-cys-*N,S*)$_n$(aet)$_{6-n}$]$^{3-n}$ (n=0—6) (Fig. 1). In addition, another type of isomers arising from the arrangement of the L-cys-*N,S* and aet ligands are possible for each of the [Co$_3$(L-cys-*N,S*)$_n$(aet)$_{6-n}$]$^{3-n}$ (n=0—6) complexes (Table 1). The reaction of a mixture containing Δ_{LLL}-*fac*-[Co(L-cys-*N,S*)$_3$]$^{3-}$ and *fac*-[Co(aet)$_3$] with [CoCl(NH$_3$)$_5$]$^{2+}$ produced the F-1 (brown) and F-2 (green) neutral isomers besides $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$ and [Co$_3$(aet)$_6$]$^{3+}$. Figure 2 illustrates the absorption and CD spectra of the F-1 and F-2 isomers. The absorption spectra of the F-1 and F-2 isomers coincide well with those of [Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$ [10–12] and [Co$_3$(aet)$_6$]$^{3+}$. [4,14] The CD spectra of the F-1 and F-2 isomers are in good agreement with those of $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$ [12] and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$ [10,11] respectively. These facts suggest that the green isomer is $\Delta_{\mathrm{LLL}}\Delta$-[Co$_3$(L-cys-*N,S*)$_3(aet)_3$], while the brown isomer is the $\Delta_{\mathrm{LLL}}\Lambda$ one. Thus, for the reaction with [CoCl(NH$_3$)$_5$]$^{2+}$ the starting Δ_{LLL}-*fac*-[Co(L-cys-*N,S*)$_3$]$^{3-}$ and/or *fac*-[Co(aet)$_3$] complexes bridge to the Co(III) ion through the facial thiolato donor atoms, forming three types of trinuclear complexes; $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$, $\Delta_{\mathrm{LLL}}\Delta$- and $\Delta_{\mathrm{LLL}}\Lambda$-[Co$_3$(L-cys-*N,S*)$_3(aet)_3$]^0, and [Co$_3(aet)_6$]$^{3+}$. This formation mechanism is consistent with the fact that the reaction of Δ_{LLL}-*fac*-[Co(L-cys-*N,S*)$_3$]$^{3-}$ with [CoCl(NH$_3$)$_5$]$^{2+}$ produced only $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$, retaining the absolute configuration of the starting Δ_{LLL} complex.[10,11] The overall absorption spectra of the $\Delta_{\mathrm{LLL}}\Delta$ (green) and $\Delta_{\mathrm{LLL}}\Lambda$ (brown) isomers are similar to each other, but a notable difference is observed in the lowest energy region; the $\Delta_{\mathrm{LLL}}\Delta$ (green) isomer has an absorption peak at 18.18×10^3 cm^{-1} , while the corresponding absorption component for the $\Delta_{\mathrm{LLL}}\Lambda$ (brown) isomer appears as a shoulder at 18.9×10^3 cm^{-1} (Fig. 2). A similar difference in the absorption spectra between the $\Delta\Delta$ or $\Lambda\Lambda$ isomer (green) and the $\Delta\Lambda$ isomer (brown) was also observed for [Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$ [10–12] and [Co$_3$(aet)$_6$]$^{3+}$.[4,14]

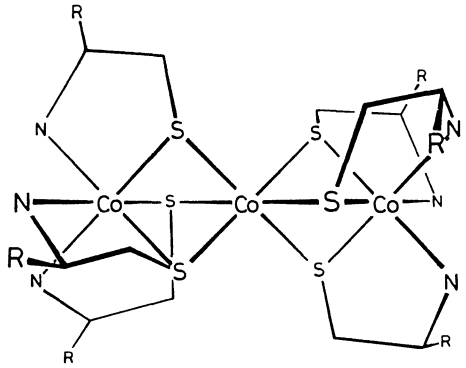

Fig. 1. Structure of [Co$_3$(L-cys-*N,S*)$_n$(aet)$_{6-n}$]$^{3-n}$ having the $\Delta\Lambda$ configuration. (R=H for aet, R=COO$^-$ for L-cys)

In contrast with the reaction with [CoCl(NH$_3$)$_5$]$^{2+}$, the reaction with an excess amount of Co^{2+} gave a number of trinuclear complexes, of which absorption and CD spectral behavior agrees well with that of [Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$ and [Co$_3$(aet)$_6$]$^{3+}$. The last-eluted D band of a cation-exchange column and the last-eluted D′ band of an anion-exchange column contained [Co$_3$(aet)$_6$]$^{3+}$ and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$

Table 1. Possible Isomers and Formation Ratio of Isomers for [Co$_3$(L-cys-*N,S*)$_n$(aet)$_{6-n}$]$^{3-n}$(n=0—6)

Complexes	Possible Isomers	Eluates	Assignments	Formation Ratio (%)	$\Delta:\Lambda$
[Co$_3$(aet)$_6$]$^{3+}$	$\Delta\Delta$, $\Lambda\Lambda$	D-1(brown)	$\Delta\Lambda$	2.6	50 : 50
	$\Delta\Lambda$	D-2(green)	$\Delta\Delta$+$\Lambda\Lambda$ (1 : 1)	2.7	
[Co$_3$(L-cys-*N,S*)(aet)$_5$]$^{2+}$	$\Delta_{\mathrm{L}}\Delta$, $\Lambda_{\mathrm{L}}\Lambda$	C-1(brown)	$\Delta\Lambda$	7.6	38 : 62
	$\Delta_{\mathrm{L}}\Lambda$, $\Delta\Lambda_{\mathrm{L}}$	C-2(green)	$\Delta\Delta$+$\Lambda\Lambda$ (1 : 3)	7.3	
[Co$_3$(L-cys-*N,S*)$_2$(aet)$_4$]$^+$	$\Delta_{\mathrm{LL}}\Delta$, $\Delta_{\mathrm{L}}\Delta_{\mathrm{L}}$	B-1(brown)	$\Delta\Lambda$	2.4	29 : 71
	$\Lambda_{\mathrm{LL}}\Lambda$, $\Lambda_{\mathrm{L}}\Lambda_{\mathrm{L}}$	B-2(green)	$\Delta\Delta$	1.7	
	$\Delta_{\mathrm{LL}}\Lambda$, $\Delta_{\mathrm{L}}\Lambda_{\mathrm{L}}$	B-3(brown)	$\Delta\Lambda$	7.6	
	$\Delta\Lambda_{\mathrm{LL}}$	B-4(green)	$\Lambda\Lambda$	11.2	
[Co$_3$(L-cys-*N,S*)$_3$(aet)$_3$]	$\Lambda_{\mathrm{LLL}}\Delta$, $\Delta_{\mathrm{LL}}\Delta_{\mathrm{L}}$	A-1(brown)	$\Delta\Lambda$	2.1	20 : 80
	$\Lambda_{\mathrm{LLL}}\Lambda$, $\Lambda_{\mathrm{LL}}\Lambda_{\mathrm{L}}$	A-2(green)	$\Lambda\Lambda$	7.3	
	$\Delta_{\mathrm{LLL}}\Lambda$, $\Delta_{\mathrm{LL}}\Lambda_{\mathrm{L}}$	A-3(brown)	$\Delta\Lambda$	7.1	
	$\Delta_{\mathrm{L}}\Lambda_{\mathrm{LL}}$, $\Delta\Lambda_{\mathrm{LLL}}$	A-4(green)	$\Lambda\Lambda$	6.0	
[Co$_3$(L-cys-*N,S*)$_4$(aet)$_2$]$^-$	$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{L}}$, $\Delta_{\mathrm{LL}}\Delta_{\mathrm{LL}}$	B′-1(green)	$\Lambda\Lambda$	2.1	14 : 86
	$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{L}}$, $\Lambda_{\mathrm{LL}}\Lambda_{\mathrm{LL}}$	B′-2(brown)	$\Delta\Lambda$	4.5	
	$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{L}}$, $\Delta_{\mathrm{LL}}\Lambda_{\mathrm{LL}}$ $\Delta_{\mathrm{L}}\Lambda_{\mathrm{LLL}}$	B′-3(green)	$\Lambda\Lambda$	9.1	
[Co$_3$(L-cys-*N,S*)$_5$(aet)]$^{2-}$	$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LL}}$, $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LL}}$	C′-1(brown)	$\Delta\Lambda$	0.8	5 : 95
	$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LL}}$, $\Delta_{\mathrm{LL}}\Lambda_{\mathrm{LLL}}$	C′-2(green)	$\Lambda\Lambda$	6.6	
[Co$_3$(L-cys-*N,S*)$_6$]$^{3-}$	$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$, $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$	D′(green)	$\Lambda\Lambda$	11.4	0 : 100

The number of the subscript L for Δ or Λ denotes the number of the L-cys-*N,S* ligand in the terminal moiety.

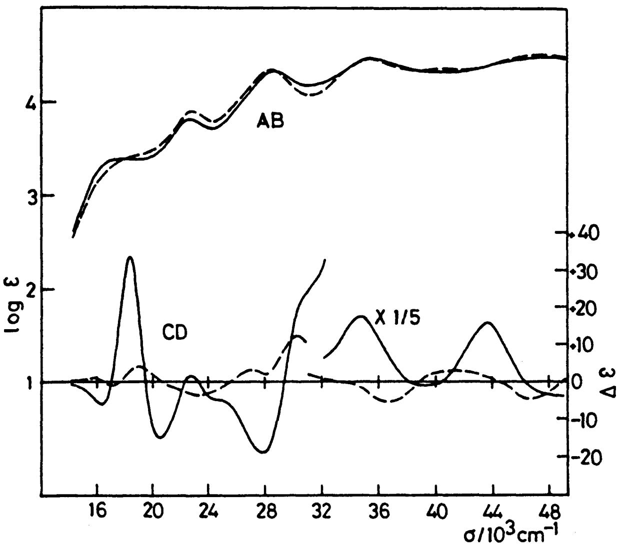

Fig. 2. Absorption and CD spectra of the ΔLLLΔ (——) and ΔLLLΛ (----) isomers of [Co$_3$(L-cys-*N*,*S*)$_3$(aet)$_3$].

respectively. Taking these absorption and CD spectral and column chromatographic behavior into consideration, it is probable that the C, B, A, B′, and C′ adsorbed bands contained the *S*-bridged trinuclear complexes, [Co$_3$(L-cys-*N*,*S*)(aet)$_5$]$^{2+}$, [Co$_3$(L-cys-*N*,*S*)$_2$(aet)$_4$]$^{+}$, [Co$_3$(L-cys-*N*,*S*)$_3$(aet)$_3$]^{0}, [Co$_3$(L-cys-*N*,*S*)$_4$(aet)$_2$]$^{-}$, and [Co$_3$(L-cys-*N*,*S*)$_5$(aet)]$^{2-}$ respectively. The formation of all seven kinds of complexes, [Co$_3$(L-cys-*N*,*S*)$_n$(aet)$_{6-n}$)]$^{3-n}$ (n=0—6), indicates that the L-cys-*N*,*S* and aet ligands dissociate from the starting ΔLLL-*fac*-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ and *fac*-[Co(aet)$_3$] complexes through the reaction with Co^{2+}, followed by the rearrangement of these ligands to form a trinuclear structure. The green isomers showing an absorption peak at ca. 18X10^3 cm^{-1} are assignable to take the ΔΔ or ΛΛ configuration, while the brown isomers showing a shoulder at ca. 19X10^3 cm^{-1} take the ΔΛ configuration (vide supra). Moreover, the CD spectra of the isomers are classified into the three CD patterns of ΔLLLΔLLL-, ΔLLLΛLLL-, and ΛLLLΛLLL-[Co$_3$(L-cys-*N*,*S*)$_6$]$^{3-}$.[10—12] Accordingly, the absolute configuration (ΔΔ, ΔΛ, or ΛΛ) for each trinuclear isomer can be assigned on the basis of the absorption and CD spectra as given in Table 1, although it is difficult to determine the arrangement of the L-cys-*N*,*S* and aet ligands. The formation ratios of the isomers obtained by the reaction with an excess amount of Co^{2+} are summarized in Table 1. The ratio of the Δ and Λ terminals in each trinuclear complex (Δ:Λ) was evaluated from the values of the formation ratio of the ΔΔ, ΔΛ, and ΛΛ configurations (Table 1). No ΔΔ isomer was formed for [Co$_3$(L-cys-*N*,*S*)$_6$]$^{3-}$, [Co$_3$(L-cys-*N*,*S*)$_5$(aet)]$^{2-}$, [Co$_3$(L-cys-*N*,*S*)$_4$(aet)$_2$]$^{-}$, and [Co$_3$(L-cys-*N*,*S*)$_3$(aet)$_3$], which contain the [Co(L-cys-*N*,*S*)$_3$]$^{3-}$ and/or [Co(L-cys-*N*,*S*)$_2$(aet)]$^{-}$ terminals. Of these complexes, [Co$_3$(L-cys-*N*,*S*)$_6$]$^{3-}$ gave only the ΛLLLΛLLL isomer (D′), as in the case of the reaction of ΔLLL-*fac*-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with an excess amount of Co^{2+}[10,11] and the two isomers of [Co$_3$(L-cys-*N*,*S*)$_5$(aet)]$^{2-}$, ΛLLLΔLL (C′-1) and ΛLLLΛLL (C′-2), were formed in a ratio of about 1:8. This behavior indicates that the [Co(L-cys-*N*,*S*)$_3$]$^{3-}$ and [Co(L-cys-*N*,*S*)$_2$(aet)]$^{-}$ terminals prefer strongly the Λ configuration to the Δ one. The Λ configurational preference is observed even for the [Co(L-cys-*N*,*S*)(aet)$_2$]$^{+}$ terminal; the C-2 eluate containing ΔLΔ- and ΛLΛ-[Co$_3$(L-cys-*N*,*S*)(aet)$_5$]$^{2+}$ showed the same CD spectral pattern as did ΛLLLΛLLL-[Co$_3$(L-cys-*N*,*S*)$_6$]$^{3-}$,[10,11] suggesting that the ΛLΛ isomer is dominant in the C-2 eluate.[15] Thus, the L-cys-*N*,*S* ligand exerts a significant influence on the Λ configurational selectivity for the trinuclear structure, and the influence for each trinuclear complex can be estimated from the ratios of Δ:Λ. That is, the values of the Λ terminal increase almost in proportion to the number of the L-cys-*N*,*S* ligand in the trinuclear complex (Table 1). This result is in contrast with the fact that mononuclear complexes with the L-cys-*N*,*S* ligand prefer the Δ configuration.[16—18]

References

1) In this paper, the chemical formulas of [Co$_3$(L-cys-*N*,*S*)$_6$]$^{3-}$ and [Co$_3$(aet)$_6$]$^{3+}$ are used instead of [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ and [Co{Co(aet)$_3$}$_2$]$^{3+}$ (Refs. 10—12,14).

2) D. C. Jicha and D. H. Busch, *Inorg. Chem.*, **1**, 872, 878 (1962).

3) D. H. Busch and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962).

4) G. R. Brubaker and B. E. Douglas, *Inorg. Chem.*, **6**, 1562 (1967).

5) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **9**, 1878 (1970).

6) R. E. DeSimone, T. Ontko, L. Wardman, and E. L. Blinn, *Inorg. Chem.*, **14**, 1313 (1975).

7) E. L. Blinn, P. Bulter, K. M. Chapman, and S. Harris, *Inorg. Chim. Acta*, **24**, 139 (1977).

8) P. R. Bulter and E. L. Blinn, *Inorg. Chem.*, **17**, 2037 (1978).

9) M. J. Heeg, E. L. Blinn, and E. Deutsch, *Inorg. Chem.*, **24**, 1118 (1985).

10) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, *Chem. Lett.*, **1985**, 1017.

11) K. Okamoto, S. Aizawa, T. Konno, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **59**, 3859 (1986).

12) S. Aizawa, K. Okamoto, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 1601 (1988).

13) The eluate showed absorption and CD spectra identical with those of the complex characterized in previous papers (Refs. 4, 10, 11, 14).

14) S. Miyanowaki, T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 2987 (1988).

15) The formation ratio, ΔLΔ:ΛLΛ, roughly calculated from the CD intensity was about 1:3.

16) R. D. Gillard and R. Maskill, *Chem. Commun.*, **1968**, 160.

17) M. Kita, K. Yamanari, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **55**, 2873 (1982).

18) H. C. Freeman, C. J. Moore, W. G. Jackson, and A. M. Sargeson, *Inorg. Chem.*, **17**, 3513 (1978).