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UV-Vis Absorption and CD Spectroelectrochemical Studies on S-Bridged Polycobalt(III) Complexes with 2-Aminoethanethiolate or L-Cysteinate

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The UV-vis spectroelectrochemical properties of S-bridged tricobalt(III) complexes $[Co^{III}\{Co^{III}(aet\ or\ L\text{-}cys)_3\}_2]^{3+\ or\ 3-}$ and dicobalt(III) complexes $[Co^{III}\{Co^{III}(aet\ or\ L\text{-}cys)_3\}(dien)]^{3+\ or\ 0}$ (aet = 2-aminoethanethiolate, L-cys = L-cysteinate, dien = diethylenetriamine) were investigated using a thin-layer quartz cell with a platinum mesh working electrode. The absorption spectroelectrochemical measurements for the tricobalt(III) complexes indicated that a two-electron reduction proceeds through pseudo two-steps, $Co^{III}Co^{III}Co^{III} \rightarrow Co^{III}Co^{II}Co^{III} \rightarrow Co^{III}Co^{II}Co^{II}$ for the aet complex, while through pseudo one-step for the L-cys complex. The CD spectroelectrochemical measurements demonstrated that the optically active isomer ($\Delta\Delta$ form) of the aet tricobalt(III) complex loses chirality during the one-electron reduction, whereas the $\Delta_{LLL}\Delta_{LLL}$ isomer of the L-cys tricobalt(III) complex is reduced with an inversion of configuration, to form the $\Lambda_{LLL}\Lambda_{LLL}$ isomer. The $\Lambda_{LLL}\Lambda_{LLL}$ isomer is reduced with a retention of configuration. The aet and L-cys dicobalt(III) complexes were converted to the corresponding tricobalt(III) complexes by electrochemical reduction, accompanied by the release of the Co(II) ion and dien ligand. It was also elucidated that this conversion occurred with a retention of configuration.

Mononuclear complexes with aminothiolate ligands, such as 2-aminoethanethiolate (aet) and L-cysteinate (L-cys), have been used as building blocks to construct a variety of S-bridged polynuclear complexes. In particular, it has been established that the octahedral complexes *fac*(*S*)-$[M(aet\ or\ L\text{-}cys)_3]^{0\ or\ 3-}$ ($M = Co^{III}, Rh^{III}, Ir^{III}, Cr^{III}$) react with other metal ions, M′, which prefer to take an octahedral coordination geometry, to form the linear-type trinuclear complexes $[M'\{M(aet\ or\ L\text{-}cys)_3\}_2]^{n+\ or\ n-}$ ($M' = Fe^{III}, Co^{III}, Ni^{II}$, etc.).[1-19] Among them, the typical linear-type S-bridged trinuclear complexes containing Co(III) ion in the center, $[Co^{III}\{M(aet\ or\ L\text{-}cys)_3\}_2]^{3+\ or\ 3-}$ ($M = Co^{III}, Rh^{III}, Ir^{III}$), are stable in water and are well characterized spectrochemically.[10-15] They can be obtained by the reactions of *fac*(*S*)-$[M(aet\ or\ L\text{-}cys)_3]^{0\ or\ 3-}$ with Co(II) ion or $[Co^{III}Cl(NH_3)_5]^{2+}$. The Co(II) complexes $[Co^{II}\{M(aet\ or\ L\text{-}cys)_3\}_2]^{2+\ or\ 4-}$ can also be isolated as intermediates in the reactions with Co(II) ion in the case of $M = Rh^{III}$ and Ir^{III}, although they are easily oxidized by air to the corresponding Co(III) complexes.[14,15] However, mixed valence cobalt complexes $[Co^{II}\{Co^{III}(aet\ or\ L\text{-}cys)_3\}_2]^{2+\ or\ 4-}$ cannot be studied due to their electrochemical instability.[11,14]

The trinuclear complexes also contain stereochemical interests. Namely, both *meso* ($\Delta\Lambda$) and *rac* ($\Delta\Delta/\Lambda\Lambda$) isomers of the trinuclear complexes with aet are obtained when the starting mononuclear complexes *fac*(*S*)-$[M(aet)_3]$ are racemates consisting of equal amounts of Δ and Λ isomers. On the other hand, *fac*(*S*)-$[M(L\text{-}cys)_3]^{3-}$ has only the Δ_{LLL} absolute configuration because of the preferred *lel* conformation of the L-cysteinate chelate rings with the equatorial carboxylato groups.[20,21] When Δ_{LLL}-*fac*(*S*)-$[M(L\text{-}cys)_3]^{3-}$ ($M = Co^{III}, Rh^{III}, Ir^{III}$) reacts with $[Co^{III}Cl(NH_3)_5]^{2+}$, $\Delta_{LLL}\Delta_{LLL}$-$[Co^{III}\{M(L\text{-}cys)_3\}_2]^{3-}$ are obtained stereoselectively, where the starting *fac*(*S*)-$[M(L\text{-}cys)_3]^{3-}$ units retain the Δ_{LLL} absolute configuration in two terminals of the trinuclear structures.[10,14,15] In contrast, the reaction of Δ_{LLL}-*fac*(*S*)-$[Co^{III}(L\text{-}cys)_3]^{3-}$ with Co(II) ion proceeds with the inversion of the starting Δ_{LLL} configuration to give the $\Lambda_{LLL}\Lambda_{LLL}$ isomer stereoselectively.[10] In the case of Δ_{LLL}-*fac*(*S*)-$[Rh^{III}(L\text{-}cys)_3]^{3-}$, the reaction with Co(II) ion at room temperature proceeds with the retention of the Δ_{LLL} configuration to give only the $\Delta_{LLL}\Delta_{LLL}$ isomer, although the absolute configurational inversions of the terminal *fac*(*S*)-$[Rh^{III}(L\text{-}cys)_3]^{3-}$ moieties occur at high temperature to produce the $\Lambda_{LLL}\Lambda_{LLL}$ and $\Delta_{LLL}\Lambda_{LLL}$ isomers.[14] Moreover, the reaction of Δ_{LLL}-*fac*(*S*)-$[Ir^{III}(L\text{-}cys)_3]^{3-}$ with Co(II) ion forms only the $\Delta_{LLL}\Delta_{LLL}$ isomer without inversion even at high temperature.[15] Considering these facts, the electrochemistry of the tricobalt(III) complexes seems to be especially important. In addition, the stereoselective formation of dicobalt(III) complexes with diethylenetriamine (dien), Δ_{LLL}- and Λ_{LLL}-$[Co^{III}\{Co^{III}(L\text{-}cys)_3\}(dien)]$, were also established.[22,23] Accordingly, it is expected that the important information about the configurational conversion can be given by monitoring the UV-vis spectra of the redox species of these polycobalt(III) complexes.

In this work, the UV-vis spectroelectrochemical properties of the tricobalt(III) complexes $[Co^{III}\{Co^{III}(aet\ or\ L\text{-}cys)_3\}_2]^{3+\ or\ 3-}$ and the dicobalt(III) complexes $[Co^{III}\{Co^{III}(aet\ or\ L\text{-}cys)_3\}(dien)]^{3+\ or\ 0}$ were investigated (Scheme 1), using a thin-layer quartz cell with a platinum mesh working

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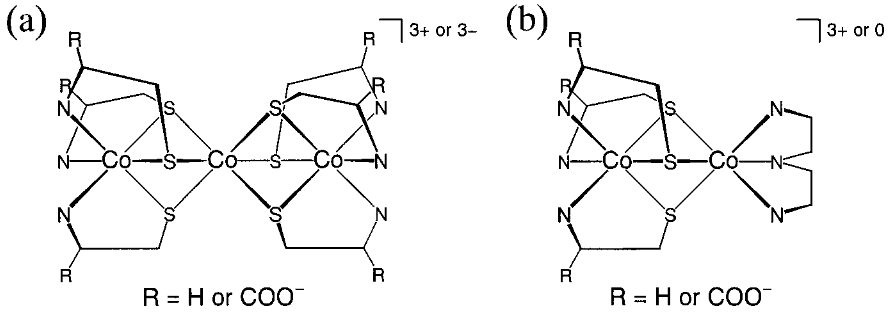


Scheme 1. Structures of (a) tricobalt(Ⅲ) complexes $\Delta\Delta$- or $\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{aet or L-cys})_3\}_2]^{3+\text{ or }3-}$ and (b) dicobalt(Ⅲ) complexes Δ- or $\Delta_{\rm LLL}$-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{aet or L-cys})_3\}(\text{dien})]^{3+\text{ or }0}$; where R = H for aet and R = COO$^-$ for L-cys.

Table 1. UV-Vis Absorption and CD Spectral and Cyclic Voltammetric Data for Present Polycobalt(Ⅲ) Complexes

Complex	Absorption maxima[a)] λ/nm	CD extrema[b)] λ/nm	Redox potentials[c)] $E_{\rm pc}$ ($E_{\rm pa'}$)/V
$\Delta\Lambda$-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\mathrm{aet})_3\}_2]^{3+}$ [d)]	552$^{\rm sh}$, 436, 350, 276		−0.70 (−0.63), −0.89
$\Delta\Delta$-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\mathrm{aet})_3\}_2]^{3+}$ [d)]	545, 440, 347, 276	605$^-$, 537$^+$, 481$^-$, 432$^-$, 349$^-$, 314$^+$, 275$^+$, 236$^-$, 221$^+$	−0.70 (−0.64), −0.89
$\Delta_{\rm LLL}\Delta_{\rm LLL}$-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{L-cys})_3\}_2]^{3-}$ [e)]	565, 442, 350, 285, 211	610$^-$, 542$^+$, 485$^-$, 439$^+$, 415$^-$, 359$^-$, 292$^+$, 260$^-$, 227$^+$	−0.63 (−0.52)
$\Lambda_{\rm LLL}\Lambda_{\rm LLL}$-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{L-cys})_3\}_2]^{3-}$ [e)]	562, 444, 350, 281, 220$^{\rm sh}$	616$^+$, 543$^-$, 489$^+$, 435$^-$, 344$^+$, 277$^-$, 223$^-$	−0.68 (−0.58)
Δ-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\mathrm{aet})_3\}(\mathrm{dien})]^{3+}$ [f)]	549$^{\rm sh}$, 431, 314, 253	550$^+$, 484$^-$, 437$^+$, 318$^-$, 257$^+$, 236$^-$, 218$^+$	−0.50[g)]
$\Delta_{\rm LLL}$-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{L-cys})_3\}(\mathrm{dien})]$[f)]	541, 432, 313$^{\rm sh}$, 266, 216	536$^+$, 481$^-$, 440$^-$, 320$^-$, 272$^+$, 221$^+$	−0.44

a) sh denotes a shoulder. b) + and − denote positive and negative extrema. c) vs Ag/AgCl, scan speed = 0.10 V s^{-1} d) Ref. 12. e) Ref. 10. f) Ref. 22. g) Very weak reduction waves are also observed at −0.70 and −0.90 V as shoulders.

electrode for the spectroelectrochemical techniques, which enabled the recording of spectral changes during the electrochemical redox reactions.[19] Since these complexes can have a chiral center arising from the absolute configuration of the terminal *fac*(*S*)-$[\mathrm{Co^{III}}(\text{aet or L-cys})_3]^{0\text{ or }3-}$ units, not only the absorption but also the CD spectroelectrochemical measurements were carried out for the optical isomers to examine the stereochemistry of the redox reactions of these complexes more carefully.

Experimental

Preparation of Complexes. The mononuclear complexes *fac*(*S*)-$[\mathrm{Co^{III}}(\mathrm{aet})_3]$[1] and $\Delta_{\rm LLL}$-*fac*(*S*)-$\mathrm{K_3}[\mathrm{Co^{III}}(\text{L-cys-}N,S)_3]$[24] were prepared by the methods found in the literature. The tricobalt(Ⅲ) complex $[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\mathrm{aet})_3\}_2]\mathrm{Br_3}$ was prepared,[1,12] and three isomers ($\Delta\Lambda$, $\Delta\Delta$, and $\Lambda\Lambda$) were chromatographically separated according to the procedures described in the literature.[12] $\mathrm{K_3}[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{L-cys-}N,S)_3\}_2]$ was prepared by the procedure in the literature,[10] where each of the $\Delta_{\rm LLL}\Delta_{\rm LLL}$ and $\Lambda_{\rm LLL}\Lambda_{\rm LLL}$ isomers were obtained selectively by the reaction of $\Delta_{\rm LLL}$-*fac*(*S*)-$\mathrm{K_3}[\mathrm{Co^{III}}(\text{L-cys-}N,S)_3]$ with $[\mathrm{Co^{III}Cl(NH_3)_5}]\mathrm{Cl_2}$ or $\mathrm{Co^{II}Cl_2{\cdot}6H_2O}$, respectively. The dicobalt(Ⅲ) complex $[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\mathrm{aet})_3\}(\mathrm{dien})]\mathrm{Cl_3}$ was prepared and resolved into the Δ and Λ isomers by the procedures in the literature.[22] The $\Delta_{\rm LLL}$ isomer of $[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{L-cys})_3\}(\mathrm{dien})]$ was selectively prepared.[22]

Measurements. Electrochemical measurements were performed by a CV-50W apparatus, Bioanalytical Systems, Inc. (BAS), using a glassy-carbon working electrode. Spectroelectrochemical measurements were performed by a CV-1B apparatus (BAS) using a thin-layer quartz cell (light-path length = 0.2 mm) with a platinum mesh working electrode. UV-vis absorption and CD spectra were recorded with a JASCO CT-10TP multichannel spectrophotometer and a JASCO J-600 spectropolarimeter, respectively. In both electrochemical and spectroelectrochemical measurements, an aqueous Ag/AgCl/NaCl (3 mol dm^{-3}) and a platinum wire were used as reference and auxiliary electrodes, respectively. All the measurements were carried out at room temperature in an aqueous solution, which was bubbled with $\mathrm{N_2}$ gas and contained 0.1 mol dm^{-3} $\mathrm{NaNO_3}$ as a supporting electrolyte. In the electrochemical measurements, ca. 10 mg of each complex was dissolved in 10 cm^3 of the aqueous solution. In the spectroelectrochemical measurements, absorbances of absorption maxima were adjusted to ca. 1.

Results and Discussion

The UV-vis absorption and CD spectral data for $[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{aet or L-cys})_3\}_2]^{3+\text{ or }3-}$ and $[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{aet or L-cys})_3\}(\mathrm{dien})]^{3+\text{ or }0}$ were reported in previous papers.[10,12,22] The cyclic voltammetric data were also reported for some of the polycobalt(Ⅲ) complexes, but under different conditions.[11,14,15,23] Before the spectroelectrochemical measurements, we carried out cyclic voltammetry experiments under identical conditions for all complexes. These data are summarized in Table 1. Considering the difference of the refer-

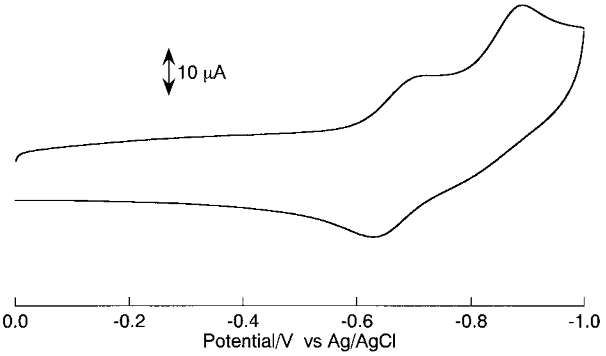


Fig. 1. Cyclic voltammogram of ΔΛ-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}_2]^{3+}$; scan rate 0.10 V $\mathrm{s^{-1}}$.

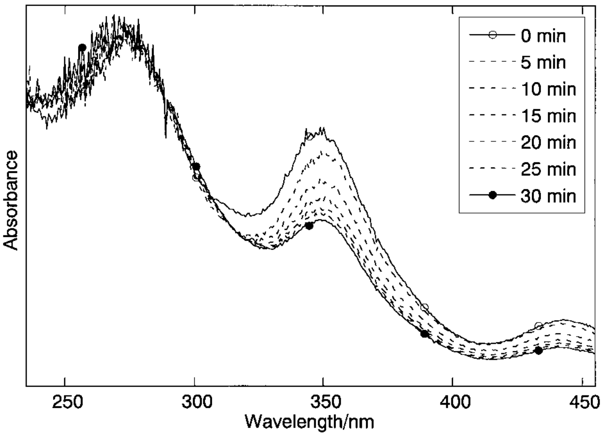


Fig. 2. Absorption spectral changes of ΔΛ-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}_2]^{3+}$ during reduction at −0.7 V.

ence electrodes, the present electrochemical data are approximately in agreement with the reported data.[11,14,15,23] The cyclic voltammogram of a representative complex, ΔΛ-$[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\mathrm{aet})_3\}_2]^{3+}$, is given in Fig. 1.

Tricobalt(III) Complexes with aet Ligands. The $\mathrm{Co_t^{III}Co_c^{III}Co_t^{III}}$ complexes with aet ligands, $[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}_2]^{3+}$, show two redox waves in the negative potential region (Table 1 and Fig. 1). For the tricobalt(III) complexes, $\mathrm{Co_c}$ and $\mathrm{Co_t}$ denote the central and terminal cobalt ions, respectively. As in the previous paper,[15] the first one-electron reduction wave at $E^{\circ\prime}$ = ca. −0.7 V has been assigned to the reduction of the central Co(III) ion, $\mathrm{Co_c(III)/Co_c(II)}$, and the second one-electron reduction wave at E_{pc} = ca. −0.9 V has been assigned to the reduction of one of two terminal Co(III) ions, $\mathrm{Co_t(III)/Co_t(II)}$. Since the *meso* and *rac* isomers show similar UV-vis absorption spectra and cyclic voltammograms, the easily obtained *meso* isomer was used for experiments. The absorption spectral changes of ΔΛ-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}_2]^{3+}$ during reduction at −0.7 V (the first one-electron reduction potential E_{pc}) are shown in Fig. 2. The intensity of the bands at 348 and 436 nm decreased gradually, whereas the band at 273 nm remained unchanged. This indicates that the first one-electron reduction forms the $[\mathrm{Co_c^{II}}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}_2]^{2+}$ species as expected, taking into consideration that the bands at 348 and 436 nm are due to the $\mathrm{Co_c^{III}S_6}$ chromophore and the band at 273 nm is due to the $\mathrm{Co_t^{III}N_3S_3}$ chromophores. In the case of reduction at −1.0 V, the band at 273 nm due to the $\mathrm{Co_t^{III}N_3S_3}$ chromophores also decreased in intensity. This indicates that the two-electron reduction forms the $[\mathrm{Co_c^{II}}\{\mathrm{Co_t^{II}}(\mathrm{aet})_3\}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}]^{+}$ species. To analyze this reduction behavior at −1.0 V, $\ln[(A_\infty - A_t)/\ (A_\infty - A_0)]$ values at 273 and 348 nm vs time (min) are plotted, where A_∞, A_t, and A_0 denote the absorbance of the solution at equilibrium ($t = \infty$), time t, and initial ($t = 0$). As shown in Fig. 3, the values of $\ln[(A_\infty - A_t)/(A_\infty - A_0)]$ change with time along two straight lines in both bands, where the slopes of the two lines switch at ca. 6 min. Moreover, the intensity of the band at 273 nm, which is due to the $\mathrm{Co_t^{III}N_3S_3}$ chromophores, is almost constant for the initial 6 min. These facts imply that the two-electron reduction at −1.0 V proceeds by pseudo two-steps and the second reduction starts after the first reduction step has almost finished, that is, $\mathrm{Co_t^{III}Co_c^{III}Co_t^{III}} \rightarrow \mathrm{Co_t^{III}Co_c^{II}Co_t^{III}} \rightarrow \mathrm{Co_t^{III}Co_c^{II}Co_t^{II}}$.

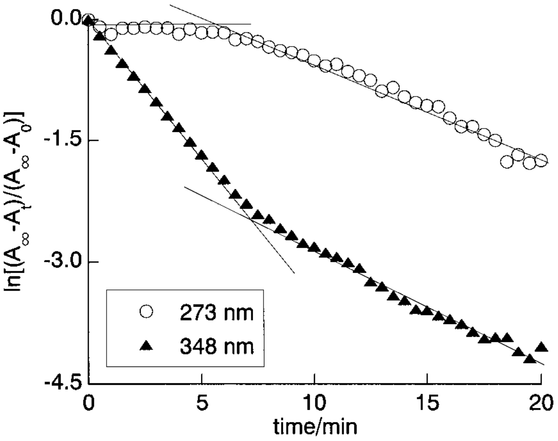


Fig. 3. Changes with time of absorbances for ΔΛ-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}_2]^{3+}$ during reduction at −1.0 V.

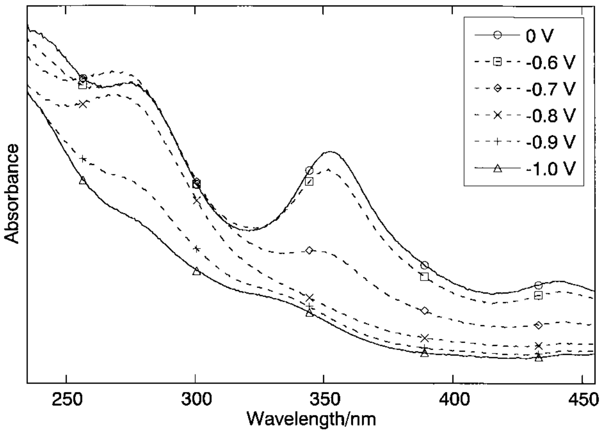
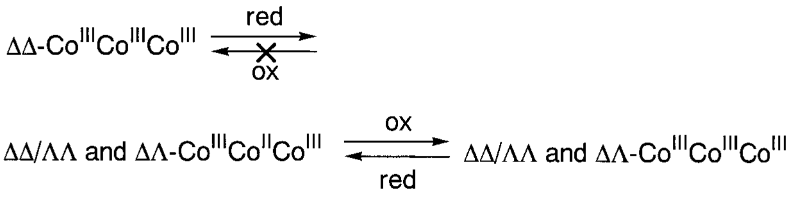


Fig. 4. Absorption spectral changes of ΔΛ-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{aet})_3\}_2]^{3+}$ during reduction at various potentials.

The absorption spectral changes due to reduction at various potentials are shown in Fig. 4. In these measurements, the complex was reduced at −0.6 V for 5 min in the beginning, and subsequently the potential was moved gradually in the negative direction from −0.6 to −1.0 V in a 5 min interval. No new bands were observed in this potential region. There was little change in the $\mathrm{Co_t^{III}N_3S_3}$ chromophore band at 273 nm at



Scheme 2. Redox reactions for aet tricobalt(Ⅲ) complexes.

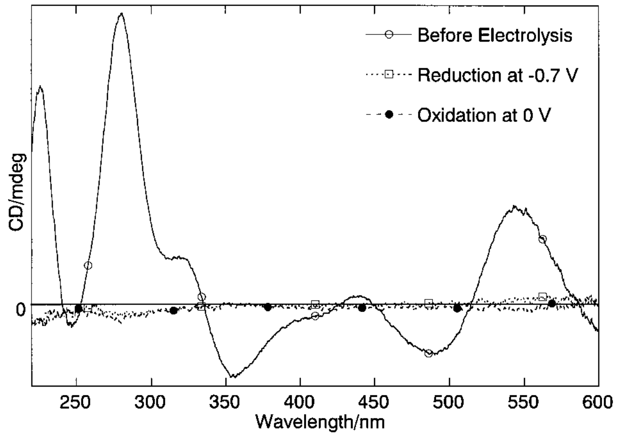


Fig. 5. CD spectral changes of $\Delta\Delta$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$ during reduction at −0.7 V.

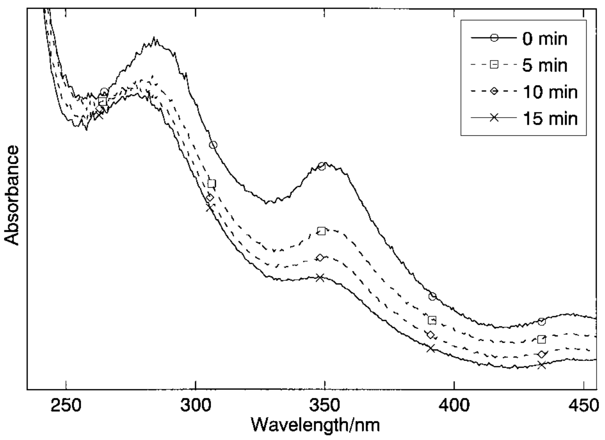


Fig. 6. Absorption spectral changes of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$ during reduction at −0.7 V.

−0.6, −0.7, and −0.8 V, but reduction at −0.9 and −1.0 V weakened this intensity, indicating further reduction. This result indicates that only the $\mathrm{Co_c}$(Ⅲ) ion is reduced at potentials less negative than −0.8 V, and the second reduction to form the $\mathrm{Co_t}^{\mathrm{III}}\mathrm{Co_c}^{\mathrm{II}}\mathrm{Co_t}^{\mathrm{II}}$ species proceeds at potentials more negative than −0.9 V. The reversibility of the absorption spectra was confirmed by the oxidation at 0 V after the reduction for 30 min. However, it is difficult to judge whether the isomerization reactions take place during reduction and following oxidation using only the absorption spectroelectrochemical technique because of the spectral similarity between *meso* and *rac* isomers.

In order to obtain valuable information about stereochemistry, the CD spectroelectrochemical measurements using the optically active isomer were also carried out under the same conditions as the above absorption spectroelectrochemical ones. The CD spectra of the original $\Delta\Delta$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$, the electrogenerated species at −0.7 V, and the subsequently oxidized species at 0 V, are shown in Fig. 5. The one-electron reduction of $\Delta\Delta$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$ led to optical inactivity, indicating the formation of equal amounts of Δ- and Λ-*fac*(*S*)-$[\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3]$ units. Additionally, the reversibility of the CD spectra by the following oxidation at 0 V was not observed, although the absorption spectral pattern and intensity recovered after oxidation (vide supra). These results indicate that some of the Δ-*fac*(*S*)-$[\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3]$ units in the terminals were inverted during the reduction of the central $\mathrm{Co_c}$(Ⅲ) ion, namely, an isomerization of the ΔΔ form to the ΛΛ and/or ΔΛ form occurs due to the weak bonding of the $\mathrm{Co_c}$(Ⅱ) ion with the sulfur atoms. The reaction of a mixture of *fac*(*S*)-$[\mathrm{Co}^{\mathrm{III}}(\mathrm{aet})_3]$ and Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}^{\mathrm{III}}(\text{L-cys-}N,S)_3]^{3-}$ with Co(Ⅱ) ion forms all seven kinds of the possible isomers for the complexes $[\mathrm{Co}^{\mathrm{III}}_3(\text{L-cys})_n(\mathrm{aet})_{6-n}]^{(3-n)+}$ (n = 0–6),[13] suggesting an easy ligand exchange between two terminal units. Further, calculated structural energies for $[\mathrm{M'}\{\mathrm{M}(\mathrm{aet})_3\}_2]^{n+}$ indicate little difference between isomers.[18] Accordingly, it should be considered that the present solution of $[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$, which is electrochemically reduced and then oxidized, contains both *meso* and *rac* isomers (Scheme 2).

Tricobalt(Ⅲ) Complexes with L-cys Ligands. The cyclic voltammograms of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$- and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$ display only one redox wave with a relatively large peak separation at $E^{\circ\prime}$ = ca. −0.6 V, which is tentatively assigned to be due to $\mathrm{Co_c}$(Ⅲ)/$\mathrm{Co_c}$(Ⅱ),[11] although the corresponding aet complex shows two redox waves in the negative potential region (Table 1). The absorption spectral changes of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$ during reduction at −0.7 V are shown in Fig. 6. It was expected that the one-electron reduction of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$ produces an absorption spectral change similar to that of $[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$, for which only the central $\mathrm{Co_c}$(Ⅲ) is initially reduced. However, the peak intensities at 350 and 442 nm due to the $\mathrm{Co_c}^{\mathrm{III}}\mathrm{S_6}$ chromophore, and also at 285 nm due to the $\mathrm{Co_t}^{\mathrm{III}}\mathrm{N_3S_3}$ chromophores were weakened by reduction even at −0.7 V. Interestingly, the intensity of these bands was weakened at a similar rate (Fig. 7). The weakening of the peak intensity might be due to the equilibrium between $\mathrm{Co_t}^{\mathrm{III}}\mathrm{Co_c}^{\mathrm{II}}\mathrm{Co_t}^{\mathrm{III}}$ and $\mathrm{Co_t}^{\mathrm{III}}\mathrm{Co_c}^{\mathrm{III}}\mathrm{Co_t}^{\mathrm{II}}$ species. On the other hand, the absorption spectra for the reduced species of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$ at −1.0 V is similar to that for the two-electron reduced species of $[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$. Therefore, the second reduction of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$ may proceed at −1.0 V, even though further redox waves were not observed in the electrochemical measurements. Moreover, the absorption spectra of the parent

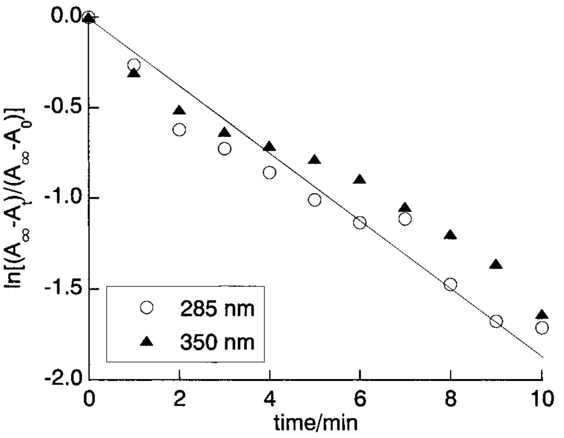


Fig. 7. Changes with time of absorbances for $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ during reduction at −0.7 V.

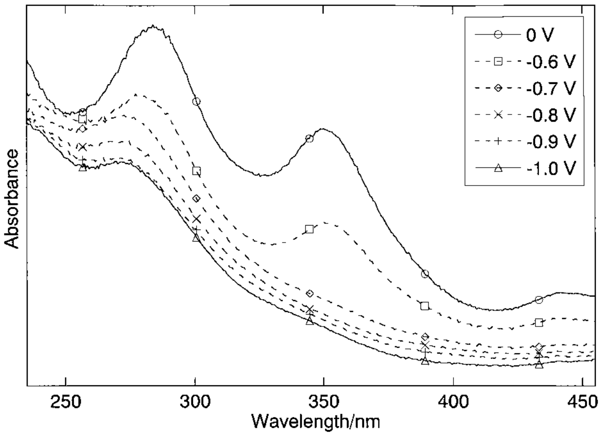


Fig. 8. Absorption spectral changes of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ during reduction at various potentials.

$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ and the reduced species at various potentials are shown in Fig. 8. This absorption spectral behavior is different from that of the corresponding aet complex (Fig. 4). These results imply some substituent effects by $\mathrm{COO^-}$ groups on the L-cys ligands. In addition, the measurements using $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ showed similar results to those using the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ isomer. The absorption spectral pattern and intensity were recovered when they were oxidized at 0 V, although there is a possibility that these complexes are isomerized during reduction and following oxidation.

The CD spectroelectrochemical measurements for both $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomers of $[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ were carried out. As shown in Fig. 9, the CD spectrum of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ was dramatically changed during the one-electron reduction at −0.7 V. It is noted that the CD spectrum at −0.7 V is similar to that of $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ at −0.7 V. Further, the CD spectrum of the subsequently oxidized species at 0 V is in agreement with that of the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomer. On the other hand, in the case of $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$, the CD spectrum was recovered completely by the oxidation at 0 V after reduction at −0.7 V. These results indicate that reduction of the central $\mathrm{Co_c}$(III) ion of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ leads to the complete inversion of the Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3]$ units to the Λ_{LLL} configuration, and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ is reduced without the inversion of the configurations (Scheme 3). The main reason for the inversion of the Δ_{LLL} terminal units, which is observed during the reduction of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$, is the intramolecular hydrogen bonds between the amino protons on the L-cys ligands and the carboxylato oxygen atom on the other L-cys ligands in the Λ_{LLL} terminal units.[10] Namely, the Δ_{LLL} units are inverted to the Λ_{LLL} configuration during reduction, taking advantage of the structural stability of the Λ_{LLL} absolute configuration. In addition, the lability of the $\mathrm{Co_c}$(II) species is favorable to the inversion. This fact that the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ configuration is preferred in the tricobalt(III) structure, although the Δ_{LLL} isomer is more stable than the Λ_{LLL} isomer in the mononuclear complexes, has been spectroelectrochemically proven by the present work.

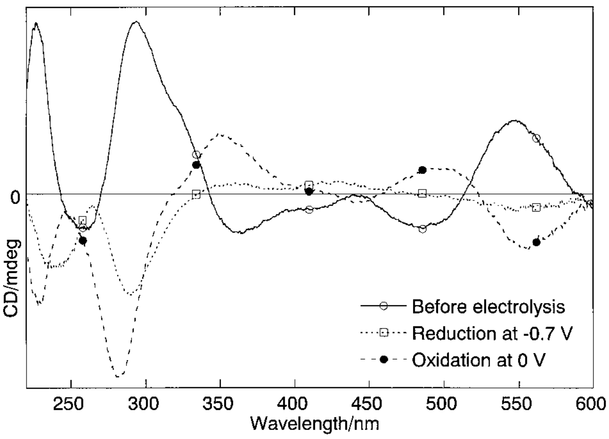
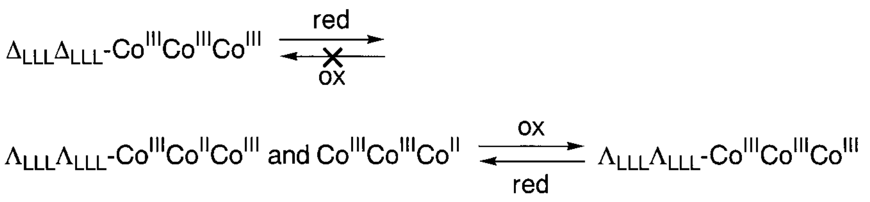


Fig. 9. CD spectral changes of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c^{III}}\{\mathrm{Co_t^{III}}(\mathrm{L\text{-}cys})_3\}_2]^{3-}$ during reduction at −0.7 V.

Dicobalt(III) Complexes with aet or L-cys Ligands. The cyclic voltammograms of the dicobalt(III) complexes $[\mathrm{Co^{III}}\{\mathrm{Co^{III}}(\text{aet or L-cys})_3\}(\mathrm{dien})]^{3+\ \mathrm{or}\ 0}$ showed almost irreversible reduction waves at E_{pc} = ca. −0.5 V (Table 1). Since these complexes are composed of two $\mathrm{Co^{III}N_3S_3}$ chromophores, it is difficult to assign the reduction waves. In order



Scheme 3. Redox reactions for L-cys tricobalt(III) complexes.

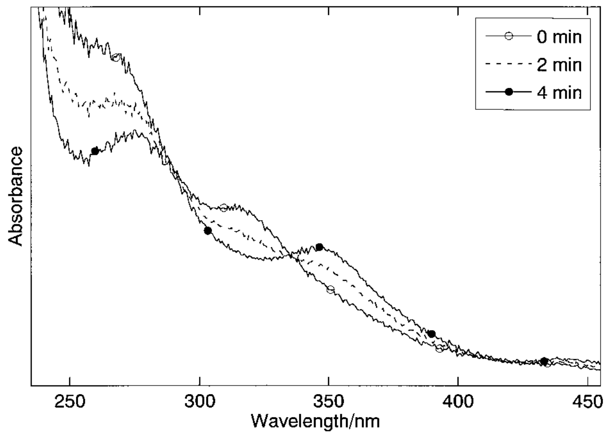


Fig. 10. Absorption spectral changes of Δ-[Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{3+}$ during reduction at -0.6 V.

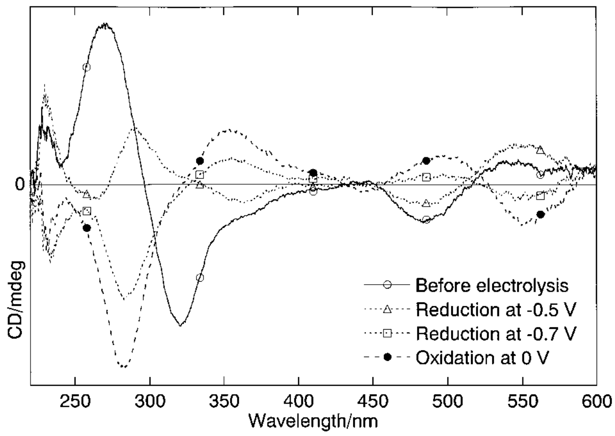


Fig. 12. CD spectral changes of Δ_{LLL}-[Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(L-cys)$_3$}(dien)] during reduction at -0.5 and -0.7 V.

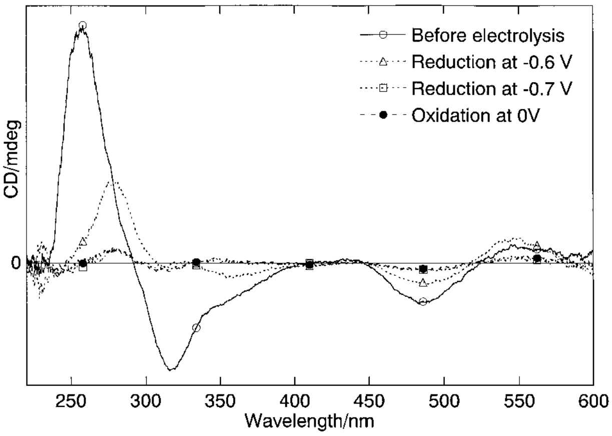
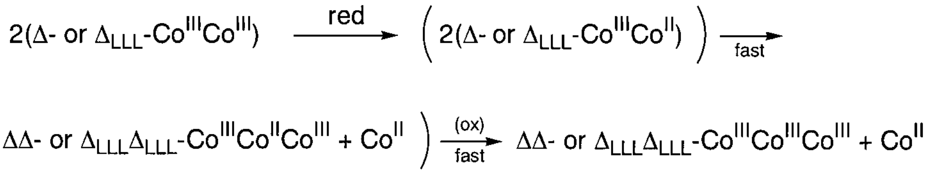


Fig. 11. CD spectral changes of Δ-[Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{3+}$ during reduction at -0.6 and -0.7 V.

to elucidate the reduction process, the spectroelectrochemical experiments were carried out for the dicobalt(Ⅲ) complexes by the same method as that used for the tricobalt(Ⅲ) complexes. The absorption spectral changes of Δ-[Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{3+}$ during reduction at -0.6 V are shown in Fig. 10. The peaks at 265 and 315 nm, which are characteristic of the dicobalt(Ⅲ) complex, shifted to 275 and 346 nm gradually, with an isosbestic point at 336 nm. This spectral pattern is similar to that of [Co$_{\mathrm{c}}^{\mathrm{III}}${Co$_{\mathrm{t}}^{\mathrm{III}}(aet)_3$}$_2$]$^{3+}$. Further, the spectral patterns at potentials more negative than -0.7 V are similar to those of the electrogenerated species of [Co$_{\mathrm{c}}^{\mathrm{III}}${Co$_{\mathrm{t}}^{\mathrm{III}}(aet)_3$}$_2$]$^{3+}$ shown in Figs. 2–4. Additionally, the absorption spectrum of the electrogenerated species became similar to that of [Co$_{\mathrm{c}}^{\mathrm{III}}${Co$_{\mathrm{t}}^{\mathrm{III}}(aet)_3$}$_2$]$^{3+}$ when it was oxidized at 0 V. Considering these results, and the fair stability of [Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{3+}$ in aqueous solution, it is reasonable to assume that reduction of the dicobalt(Ⅲ) complex forms the tricobalt(Ⅲ) structure, accompanied by the release of the Co(Ⅱ) ion and dien ligand. Absorbances of the spectra support the formation of 1 mol of the tricobalt(Ⅲ) complex from 2 mol of the dicobalt(Ⅲ) complex. Since absorptions due to the Co(Ⅱ) ion and dien ligand are weak, they can be neglected. As shown in Fig. 11, the positive CD extremum at 257 nm for Δ-[Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{3+}$ is shifted to 279 nm during reduction at -0.6 V. This spectrum is also similar to that of $\Delta\Delta$-[Co$_{\mathrm{c}}^{\mathrm{III}}${Co$_{\mathrm{t}}^{\mathrm{III}}(aet)_3$}$_2$]$^{3+}$, shown in Fig. 5. This indicates that the dicobalt(Ⅲ) complex is converted to the tricobalt(Ⅲ) complex with the absolute configuration of the Δ-*fac*(*S*)-[Co$^{\mathrm{III}}$(aet)$_3$] unit retained. Proposed reduction paths, including absolute configurations for the aet complexes, are shown in Scheme 4. Namely, Δ-[Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{3+}$ is reduced at -0.6 V and the electrogenerated species Δ-[Co$^{\mathrm{II}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{2+}$ is formed. This species is unstable and immediately rearranges to $\Delta\Delta$-[Co$_{\mathrm{c}}^{\mathrm{II}}${Co$_{\mathrm{t}}^{\mathrm{III}}(aet)_3$}$_2$]$^{2+}$. Since the trinuclear complex with the Co$_{\mathrm{c}}$(Ⅱ) ion is electrochemically unstable at -0.6 V, $\Delta\Delta$-[Co$_{\mathrm{c}}^{\mathrm{III}}${Co$_{\mathrm{t}}^{\mathrm{III}}(aet)_3$}$_2$]$^{3+}$ forms by spontaneous oxidation. It should be considered that the rearrangement and oxidation process is faster than the inversion of the absolute configuration by the labile Co(Ⅱ) ion. However, these CD signals almost vanish during reduction at -0.7 V (Fig. 11). This is in agreement with the result of the spectroelectrochemical measurements for the tricobalt(Ⅲ) complex. The Λ isomer of [Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(aet)$_3$}(dien)]$^{3+}$ showed the same absorption spectral changes and enantiomeric CD spectral changes as those of the Δ isomer, as expected.

The absorption spectroelectrochemical experiment for Δ_{LLL}-[Co$^{\mathrm{III}}${Co$^{\mathrm{III}}$(L-cys)$_3$}(dien)] showed peak shifts from 264 and 317 nm to 282 and 353 nm with an isosbestic point at 341 nm during reduction at -0.5 V. This indicates that the



Scheme 4. Reduction reactions for aet and L-cys dicobalt(Ⅲ) complexes.

conversion to the corresponding tricobalt(III) complex, $[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$, was observed, similar to the case of the aet complexes. The CD spectra of the original Δ_{LLL}-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Co}^{\mathrm{III}}(\text{L-cys})_3\}(\mathrm{dien})]$ and the electrogenerated species are shown in Fig. 12. The CD spectrum at −0.5 V is similar to that of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$, indicating the conversion occurs with retention of the Δ_{LLL} configuration. However, the CD spectrum at −0.7 V shows the inversion to the Λ_{LLL} configuration, as observed for the L-cys tricobalt(III) complex. Moreover, the oxidized species at 0 V seems to be $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$. Accordingly, it is considered that the electrochemical reduction of the dicobalt(III) complex with L-cys ligands also forms the tricobalt(III) structure (Scheme 4), and that the configurational conversion occurs after the dicobalt(III) structure is changed to the tricobalt(III) structure. Any intermediate Co(II) species such as Δ- or Δ_{LLL}-$[\mathrm{Co}^{\mathrm{II}}\{\mathrm{Co}^{\mathrm{III}}(\text{aet or L-cys})_3\}(\mathrm{dien})]^{2+\text{ or }-}$ was not observed, even by the spectroelectrochemical measurements. Although the corresponding measurements using Λ_{LLL}-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Co}^{\mathrm{III}}(\text{L-cys})_3\}(\mathrm{dien})]$ were not performed in the present work, it is easily predicted that the electrochemical reduction and following oxidation of Λ_{LLL}-$[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Co}^{\mathrm{III}}(\text{L-cys})_3\}(\mathrm{dien})]$ will produce $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{L-cys})_3\}_2]^{3-}$. It has been noted that the S-bridged tricobalt(III) complexes $[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\text{aet or L-cys})_3\}_2]^{3+\text{ or }3-}$ are very stable and therefore often the end product in many reactions. Namely, the reactions of *fac*(*S*)-$[\mathrm{Co}^{\mathrm{III}}(\mathrm{aet})_3]$ with potentially reducing metal ions such as Fe^{2+} or VO^{2+} and potentially oxidizing metal ions such as Cr^{3+}, $\mathrm{UO_2}^{4+}$, and Ce^{4+},[5] and the $\mathrm{NO_3}$ oxidation of *fac*(*S*)-$[\mathrm{Co}^{\mathrm{III}}(\mathrm{aet})_3]$[7] resulted in the isolation of $[\mathrm{Co_c}^{\mathrm{III}}\{\mathrm{Co_t}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{3+}$. In addition, the electrochemical reduction of the tetracobalt(III) complex, $[\{\mathrm{Co}^{\mathrm{III}}{}_2(\mathrm{aet})_2\}\{\mathrm{Co}^{\mathrm{III}}(\mathrm{aet})_3\}_2]^{4+}$,[25] also formed the tricobalt(III) complex.[26] It can now be said that the tricobalt(III) complexes are also formed by the rearrangement of the dicobalt(III) complexes $[\mathrm{Co}^{\mathrm{III}}\{\mathrm{Co}^{\mathrm{III}}(\text{aet or L-cys})_3\}(\mathrm{dien})]^{3+\text{ or }0}$.

Conclusion

In this work, the UV-vis absorption and CD spectroelectrochemical properties of S-bridged polycobalt(III) complexes were investigated. It is elucidated that the electrochemical reduction results in the formation of more stable structures and configurations, accompanied by the dissociation and recoordination of the ligands. It is worth spectroelectrochemically observing the Co(II) species in these redox reactions. The CD spectroelectrochemical techniques, which have been seldom reported, are especially useful for the exploration of stereochemistry of optically active compounds in future work.

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26 Unpublished result.