May, 1988] Bull. Chem. Soc. Jpn., 61, 1601—1606 (1988)

S-Bridged Polynuclear Complexes. II. Formation and Some Properties of [M{Co(L-cys-*N*,*S*)$_3$}$_2$]-Type Complexes (M=Fe(III), Co(III), and Ni(II); L-cys=L-cysteinate)

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(Received August 29, 1987)

Three trinuclear complexes with Δ_{LLL}- and/or Λ_{LLL}-*fac(S)*-[Co(L-cys-*N*,*S*)$_3$] terminals, $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-, and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Ni{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{4-}$, were newly prepared. These complexes were characterized from their electronic absorption, CD, and ^{13}C NMR spectra. Each reaction of Δ_{LLL}-*fac(S)*-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with Fe(II) and Co(II) was accompanied by the inversion of the absolute configuration of the one or both terminals to give the $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomers, while the reaction with Fe(III), Co(III), or Ni(II) proceeded with the retention of the terminal to give the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ isomer. The voltammetric study revealed that the formal potential of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (−0.16 V) is more anodic than that of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (−0.43 V). These redox potentials are discussed in relation to the formation ratios of the isomers for the trinuclear complexes.

A few transition metal complexes with thiolate type ligands, such as 2-aminoethanethiolate (aet) and L-cysteinate (L-cys), have some unique properties in an aqueous solution. For example, the sulfur donor atoms of the ligands bridge two metal ions to give trinuclear complexes with μ-thiolato structure.[1–10] We previously reported that $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ was formed selectively by the reaction of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with an excess amount of Co(II).[9,10] The inversion of the absolute configuration of the terminals seems to be related to the redox property of the central metal. From this point of view, the present authors have attempted to introduce a transition metal such as iron and nickel as the central metal of the trinuclear complex. In the present work, the formations of the trinuclear complexes, $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-, and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Ni{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{4-}$, were confirmed by the reaction of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with Fe(III), Fe(II), Co(II), and Ni(II) respectively. These complexes are characterized on the basis of their electronic absorption, CD, and ^{13}C NMR spectral behavior. The configurational inversions, which were observed for each reaction of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with Fe(II) and Co(II), are discussed in relation to the redox properties of these trinuclear complexes.

Experimental

Preparation of Complexes. 1) Δ_{LLL}-*fac*(*S*)-K$_3$[Co(L-cys-*N*,*S*)$_3$]·9H$_2$O·0.5KCl: This complex was prepared by the method described in the literature.[11]

2) $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$-$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-K$_3$[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]·9H$_2$O·0.25KCl: To a solution containing 0.6 g (2.2 mmol) of FeCl$_3$·6H$_2$O in 40 cm^3 of water was added a solution containing 2.8 g (3.8 mmol) of Δ_{LLL}-*fac*(*S*)-K$_3$[Co(L-cys-*N*,*S*)$_3$]·9H$_2$O·0.5KCl in 50 cm^3 of water, whereupon the color of the solution immediately turned from deep green to reddish brown. The solution was then stirred at room temperature for 15 min. To this was added a large amount of ethanol in an ice bath. the resultant complex was recrystallized twice from water by adding ethanol in an ice bath. It was found, from the QAE-Sephadex A-25 column chromatographic technique and from absorption and CD spectral measurements, that the complex contained only $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$-$\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$. Found: C, 18.19; H, 4.08; N, 7.14%. Calcd for $\mathrm{C_{18}H_{48}N_6O_{21}S_6Cl_{0.25}K_{3.25}FeCo_2}$: C, 18.22; H, 4.08; N, 7.08%.

3) $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-H$_3$[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]·5H$_2$O·3HCl: To a solution containing 0.19 g (0.68 mmol) of FeSO$_4$·7H$_2$O in 10 cm^3 of water was added a solution containing 1.0 g (1.36 mmol) of Δ_{LLL}-*fac*(*S*)-K$_3$[Co(L-cys-*N*,*S*)$_3$]·9H$_2$O·0.5KCl in 30 cm^3 of water. The mixture was stirred at room temperature for 15 min and then poured onto a column of QAE-Sephadex A-25 (Cl$^-$ form, 3.5 cm×90 cm). After the column had been swept with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} aqueous solution of NaCl. A large amount of the brownish red band (B-1) and small amounts of the brownish green (B-2) and brown (B-3) ones were eluted in this order. The B-2 eluate showed absorption and CD spectra identical with those of $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{360}$-$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$,[9,10] while the B-1 and B-3 eluates contained $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ and a by-product respectively. The B-1 eluate was concentrated to ca. 50 cm^3 with a rotary evaporator below 25 °C. This solution was adjusted to pH 2—3 by adding a 1 mol dm^{-3} hydrochloric acid in an ice bath. The resultant complex was collected by filtration and washed with ethanol and ether. Found: C, 19.76; H, 4.13; N, 7.59%. Calcd for $\mathrm{C_{18}H_{46}N_6O_{17}S_6Cl_3FeCo_2}$: C, 19.82; H, 4.25; N, 7.70%.

4) $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$-$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-H$_3$[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]·5H$_2$O·3HCl·0.5NaCl: This complex was prepared and chromatographed by a procedure similar to that used in **3**) under dilute conditions (FeSO$_4$·7H$_2$O 0.095 g (0.34 mmol)), water 160 cm^3; the starting Δ_{LLL}-*fac*(*S*) complex 0.50 g (0.68 mmol), water 160 cm^3). The four bands, reddish brown (C-1), brownish red (C-2), brownish green (C-3), and brown (C-4), were eluted in this order. The C-2 and C-3 eluates showed absorption and CD spectra identical with $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$-$\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ and $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{360}$-$\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-

$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ [9,10] respectively. The C-1 and C-4 eluates contained $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$-ΔLLLΛLLL-$[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ and a by-product respectively. The formation ratio of ΔLLLΛLLL- and ΛLLLΛLLL-$[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ was about 37:63. After moving only the C-1 eluate into another column of QAE-Sephadex A-25 (Cl^- form, 3.5 cm×25 cm), the adsorbed band was eluted with a saturated aqueous solution of NaCl. The eluate was immediately adjusted to pH 2—3 by adding a 1 mol dm^{-3} hydrochloric acid in an ice bath. The resultant complex was collected by filtration and washed with ethanol and ether. Found: C, 19.09; H, 3.91; N, 7.61%. Calcd for $\mathrm{C_{18}H_{46}N_6O_{17}Na_{0.5}S_6Cl_{3.5}FeCo_2}$: C, 19.30; H, 4.14; N, 7.50%.

5) $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$-ΔLLLΛLLL-$\mathrm{K_3}[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]\cdot 8.5\mathrm{H_2O}$: This complex was prepared and chromatographed by a procedure similar to that used in **3**), but using $\mathrm{CoCl_2\cdot 6H_2O}$ instead of $\mathrm{FeSO_4\cdot 7H_2O}$ ($\mathrm{CoCl_2\cdot 6H_2O}$ 0.082 g (0.34 mmol), water 40 cm^3; the starting ΔLLL-*fac*(*S*)-complex 0.50 g (0.68 mmol), water 40 cm^3). After the eluate had been circulated in the same column twice, three bands, brown (A-1), brownish green (A-2), and a small amount of brownish green (A-3), were eluted in this order. The A-2 and A-3 eluates showed absorption and CD spectra identical with those of $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$-ΛLLLΛLLL- and $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{360}$-ΔLLLΔLLL-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ respectively,[9,10] while the A-1 eluate contained $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$-ΔLLLΛLLL-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$. The formation ratio of the three isomers, A-1, A-2, and A-3, was about 23:72:5. The A-1 eluate was concentrated to a small volume with a rotary evaporator below 25 °C. The deposited NaCl was then filtered off, and the filtrate was passed through columns of Sephadex G-10 (3.5 cm×90 cm) and then SP-Sephadex C-25 (K^+ form, 3.5 cm×25 cm) by elution with water. The eluate was then concentrated to a small volume again. To this was added a large amount of ethanol in an ice bath. The resultant complex was collected by filtration and washed with ethanol and ether. Found: C, 18.57; H, 4.14; N, 7.22%. Calcd for $\mathrm{C_{18}H_{47}N_6O_{20.5}S_6K_3Co_3}$: C, 18.60; H, 4.08; N, 7.22%.

When the above reaction was carried out under a nitrogen atmosphere and the reaction solution was oxidized by exposure to air, the ΛLLLΛLLL isomer was formed selectively.

6) $(+)^{\mathrm{CD}}_{600}$-ΔLLLΔLLL-$\mathrm{H_4}[\mathrm{Ni}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]\cdot 3\mathrm{H_2O}\cdot 2\mathrm{HCl}$: To a solution containing 0.087 g (0.37 mmol) of $\mathrm{NiCl_2\cdot 6H_2O}$ in 5 cm^3 of water was added a solution containing 0.50 g (0.68 mmol) of ΔLLL-*fac*(*S*)-$\mathrm{K_3}[\mathrm{Co}(\text{L-cys-}N,S)_3]\cdot 9\mathrm{H_2O}\cdot 0.5\mathrm{KCl}$ in 20 cm^3 of water, whereupon the color of the solution immediately turned from deep green to brownish green. The solution was stirred at room temperature for 10 min and then filtered. The filtrate was adjusted to pH 2—3 by adding a 1 mol dm^{-3} hydrochloric acid in an ice bath. The resultant complex was collected by filtration and washed with ethanol and ether. It was found, from the QAE-Sephadex A-25 column chromatographic technique and the absorption and CD spectral measurements, that the complex contained only $(+)^{\mathrm{CD}}_{600}$-ΔLLLΔLLL-$[\mathrm{Ni}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{4-}$. Found: C, 21.06; H, 4.14; N, 8.24%. Calcd for $\mathrm{C_{18}H_{42}N_6O_{15}S_6Cl_2Co_2Ni}$: C, 21.15; H, 4.14; N, 8.22%.

Formation Ratio of Isomers. a) It was found, under the same reaction conditions as those described in **5**), that the formation ratio of the three isomers of $[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ depends on the concentration of Co(II). That is, when 0.162 g (0.68 mmol) and 0.324 g (1.36 mmol) of $\mathrm{CoCl_2\cdot 6H_2O}$ were used instead of 0.081 g (0.34 mmol) in **5**), the formation ratios of ΔLLLΔLLL-, ΔLLLΛLLL-, and ΛLLLΛLLL-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ were about 0:9:91 and 0:6:94 respectively.

The formation ratio for the isomers of $[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ was confirmed by using 0.095 g (0.34 mmol) of $\mathrm{FeSO_4\cdot 7H_2O}$ instead of $\mathrm{CoCl_2\cdot 6H_2O}$ as in **5**); the ratio of ΔLLLΔLLL-, ΔLLLΛLLL-, and ΛLLLΛLLL-$[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ was 0:5:95.

b) In an acidic solution (40 cm^3) adjusted to ca. pH 1 by the addition of a 1 mol dm^{-3} hydrochloric acid was suspended 0.50 g (0.68 mmol) of ΔLLL-*fac*(*S*)-$\mathrm{K_3}[\mathrm{Co}(\text{L-cys-}N,S)_3]\cdot 9\mathrm{H_2O}\cdot 0.5\mathrm{KCl}$. To this was then added an acidic solution (ca. pH 1) containing an excess amount of $\mathrm{CoCl_2\cdot 6H_2O}$ (0.324 g, 1.36 mmol) in 40 cm^3 of water. While the mixture was stirred for 15 min, the starting complex was gradually dissolved and the color of the solution turned to deep greenish brown. The solution was chromatographed in the same manner as in **5**). The formation ratio of ΔLLLΔLLL-, ΔLLLΛLLL-, and ΛLLLΛLLL-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ was 62:38:0.

Measurements. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and JASCO UVIDEC-610C spectrophotometers, and the CD spectra with a JASCO J-20 spectropolarimeter. The ^{13}C NMR spectra were recorded with a JEOL JNM-FX-100 or FX-90Q NMR spectrometer at the probe temperature in $\mathrm{D_2O}$ solvent. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference. The pH of the aqueous solution was measured with a Hitachi-Horiba pH meter, model F7-SS, equipped with a glass and saturated calomel electrodes. The cyclic voltammograms were recorded with a Hokuto Denko potentiogalvanostat, model HA-201, to which a linear potential scanner, model HB-103, was attached. A hanging Hg drop microelectrode or a Pt working electrode, a Pt wire counter electrode with a sufficiently large surface area, and a 3.33 mol dm^{-3} KCl calomel reference electrode were used for the potentiostatic measurements in a 0.01 mol dm^{-3} sodium nitrate solution at room temperature (25±1 °C). The electrode potential data were corrected to those for the standard hydrogen electrode (SHE).

Results and Discussion

Structural Assignment. Three isomers, ΔLLLΔLLL, ΔLLLΛLLL, and ΛLLLΛLLL, are expected for $[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]$-type complexes (M=Fe(III) and Ni(II)), considering the absolute configuration of the two terminal moieties, *fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]$ (Fig. 1), as in the case of $[\mathrm{Co}\{\mathrm{Co(aet)_3}\}_2]^{3+}$ and $[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$.[3,9,10] The absorption and CD spectra of the isomers are shown in Figs. 2—4, and their data are summarized in Table 1. Of the two isomers, $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$ and $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$, which were obtained by the reaction of ΔLLL-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ with a stoichiometric amount of Co(II), the $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$ isomer exhibits absorption and CD spectra identical with those of the isomer determined to be ΛLLLΛLLL-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ by X-ray structure analysis[10] (Fig. 2). The $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$ isomer exhibits an absorp-

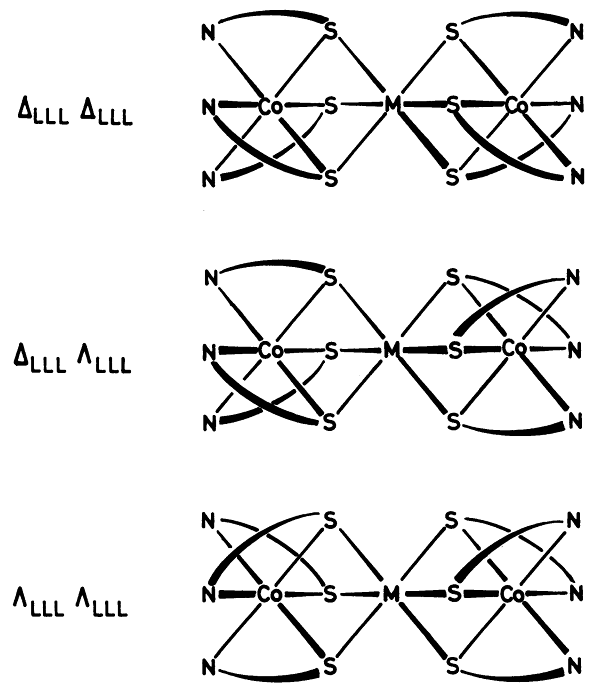

Fig. 1. Three isomers expected for [M{Co(L-cys-*N*,*S*)$_3$}$_2$]-type complexes.

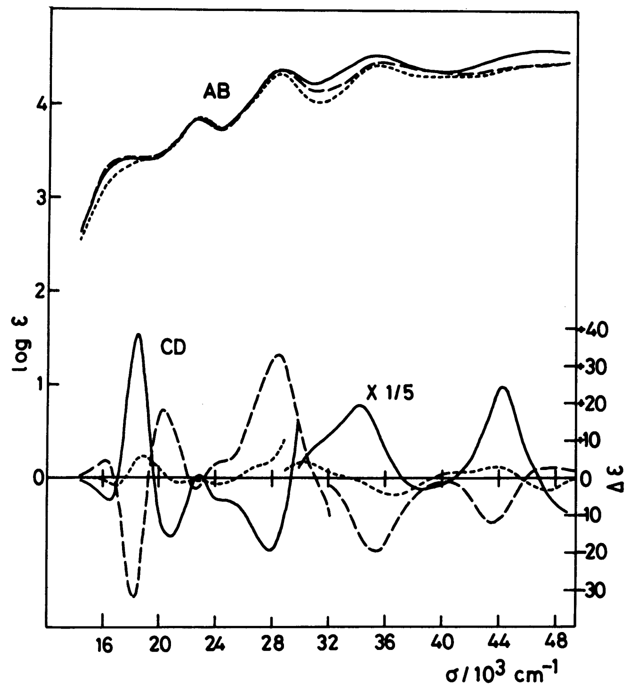

Fig. 2. Absorption and CD spectra of [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$; $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{360}$- (——), $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$- (-----), and $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$- (·····).

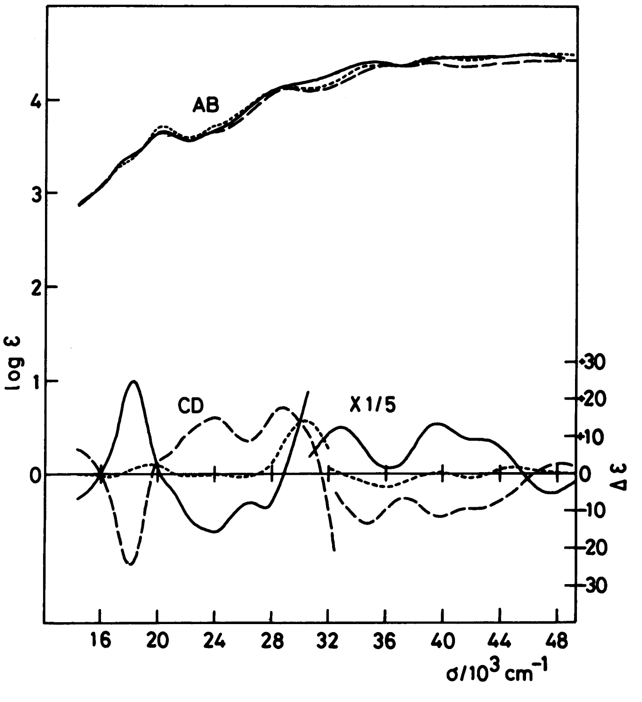

Fig. 3. Absorption and CD spectra of [Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$; $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$- (——), $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$- (-----), and $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$- (·····).

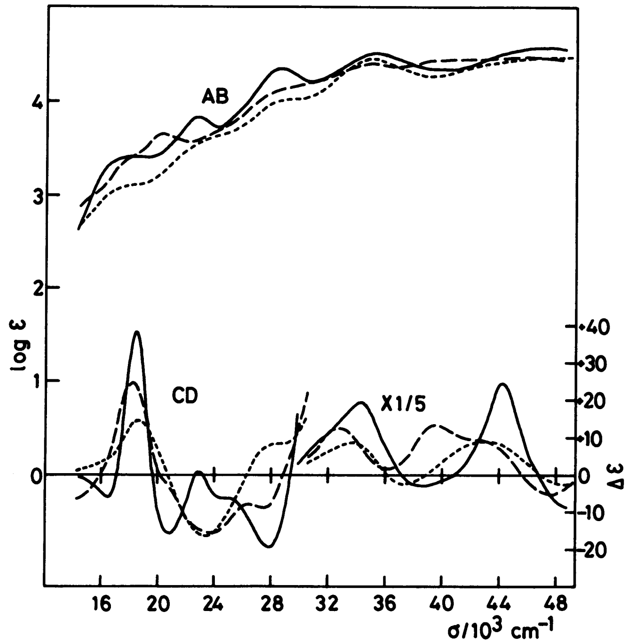

Fig. 4. Absorption and CD spectra of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ isomers; $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{360}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (——), $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (-----), and $(+)^{\mathrm{CD}}_{600}$-[Ni{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{4-}$ (·····).

tion spectrum quite similar to that of $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, but it exhibits quite a different CD spectrum from $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$- and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ [9,10] (Fig. 2). Furthermore, the ^{13}C NMR spectrum of the $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$ isomer exhibits six resonance lines (38.2, 38.8, 63.3, 66.4, 178.0, and 179.0 ppm) due to the methylene, methine, and carboxylato carbon atoms, whereas each of the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ isomers exhibits three resonance lines (D_3 symmetry).[9,10] According to the model construction, the symmetry of the $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomer is lower than or equal to C_3, therefore, this isomer can be expected to exhibit six or more resonance lines. These facts

Table 1. Absorption and CD Data of [M{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{n-}$ (M=Fe(III), Co(III), and Ni(II))

	Absorption maxima $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\log \varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$)	CD extrema $\sigma/10^3\,\mathrm{cm}^{-1}$ ($\Delta\varepsilon/\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$)
$(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$	17.54 (3.35sh)	18.18 (+24.8)
	20.24 (3.64)	23.81 (−15.7)
	28.57 (4.12sh)	27.32 (−9.0)
	35.34 (4.39)	32.79 (+61.9)
	40.00 (4.42sh)	39.37 (+66.0)
	46.73 (4.47)	42.7 (+46.0sh)
		47.62 (−26.3)
$(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$	17.24 (3.29sh)	16.44 (−0.8)
	20.20 (3.70)	19.68 (+2.4)
	29.07 (4.11)	22.83 (−0.4)
	35.46 (4.35sh)	25.77 (−0.8)
	39.68 (4.44)	30.40 (+14.0)
		35.71 (−16.7)
		39.68 (+1.3)
		41.66 (−5.0)
		44.64 (+7.75)
$(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$	17.24 (3.33sh)	18.02 (−24.5)
	20.12 (3.66)	23.81 (+14.9)
	29.07 (4.11)	28.74 (+17.6)
	36.23 (4.36)	34.72 (−65.9)
	39.06 (4.38)	39.68 (−57.6)
		43.1 (−45.0sh)
		48.31 (+13.2)
$(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$	18.02 (3.36sh)	16.77 (−2.1)
	22.83 (3.85)	18.79 (+5.5)
	28.41 (4.31)	21.55 (−1.3)
	35.46 (4.39)	24.21 (−1.7)
	48.08 (4.43)	26.9 (+3.2sh)
		30.30 (+19.4)
		36.76 (−22.3)
		40.3 (+5.74sh)
		43.85 (+13.2)
		47.39 (−16.2)
$(+)^{\mathrm{CD}}_{600}$-[Ni{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{4-}$	17.54 (3.08sh)	18.59 (+14.4)
	23.26 (3.58sh)	23.36 (−16.2)
	28.57 (4.05sh)	28.41 (+8.3)
	34.97 (4.43)	33.67 (+42.1)
		37.45 (−13.2)
		43.10 (+43.4)

sh denotes a shoulder.

suggest that the $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{360}$ isomer is $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$.

The three isomers which were obtained by the reaction of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with Fe(III) or Fe(II) exhibit absorption spectral behavior quite similar to one another (Fig. 3 and Table 1), as in the case of [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$. The two isomers, $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$ and $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$, exhibit intense CD bands which are almost enantiomeric over the whole region, while the remaining one, $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$, exhibits weak CD bands (Fig. 3). The CD spectral pattern of the $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$ isomer approximately coincides with that of $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$,[9,10] except for the ambiguity around 20—27×10^3 cm^{-1} (Fig. 3). On the other hand, the $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$ isomer exhibits a CD spectral pattern similar to that of $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ [9,10] (Fig. 3). These facts suggest that the $(+)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$ isomer is $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ and that the $(-)^{\mathrm{CD}}_{600}\cdot(-)^{\mathrm{CD}}_{530}$ isomer is the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ one. Accordingly, the remaining $(-)^{\mathrm{CD}}_{600}\cdot(+)^{\mathrm{CD}}_{530}$ siomer can be assigned to $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-[Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$.

The reaction of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ with Ni(II) formed only the $(+)^{\mathrm{CD}}_{600}$ isomer, exhibiting intense absorption bands over the whole region similar to those of [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ and [Fe{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (Fig. 4). Furthermore, the CD spectral behavior of the $(+)^{\mathrm{CD}}_{600}$ isomer agrees with that of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (Fig. 4). Accordingly, the $(+)^{\mathrm{CD}}_{600}$ isomer is tentatively assigned to $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Ni}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{4-}$.

CD Spectra. In the energy region higher than ca. $32\times10^3\,\mathrm{cm}^{-1}$, the CD spectral patterns of the three $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{n-}$ complexes (M=Fe(III), Co(III), and Ni(II)) are similar to that of the mononuclear complex, Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$, as in the case of their absorption spectral patterns (Figs. 4 and 5). The absorption bands at ca. $34\times10^3\,\mathrm{cm}^{-1}$ are probably related to the sulfur-to-metal charge transfer bands[12–14] in the terminals, and the CD bands in the corresponding region are commonly positive. Though the overall CD spectral patterns resemble one another in the region of $14-32\times10^3\,\mathrm{cm}^{-1}$, some absorption and CD spectral deviations are observed in the region of $20-30\times10^3\,\mathrm{cm}^{-1}$. The deviations in this region are probably due to the characteristic chromophore, $\mathrm{FeS_6}$, $\mathrm{CoS_6}$, or $\mathrm{NiS_6}$, at the center of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{n-}$ (M=Fe(III), Co(III), or Ni(II)), besides the common chromophore, $\mathrm{CoS_3N_3}$, in the terminals.

The similarity in the CD spectral patterns of the present trinuclear complexes led us to attempt a CD curve analysis on the assumption that the CD contributions of the chiralities in the trinuclear complexes are additive, as in the case of the mononuclear cobalt(III) complexes.[15–17] The trinuclear complexes in this work formally have the following three CD contributions; (1) the configurational chirality (Δ or Λ) arising from the skew pair of the chelate rings in the terminals, (2) the chirality due to the asymmetric carbon atoms in the L-cys ligands, and (3) the chirality (*R* or *S*) due to the asymmetric sulfur donor atoms bridging the two metal ions. Of the three types of chiralities, the three asymmetric sulfur donor atoms in the Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]$ terminal are regulated to the *R* configuration for the Fe(III) trinuclear complex and to the *S* configuration for the Co(III) one, while those in the Λ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]$ terminal are regulated to the *S* configuration for the Fe(III) complex and to the *R* configuration for the Co(III) one. Accordingly, the CD contributions due to the asymmetric sulfur donor atoms of both terminals in $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ trinuclear complex cancell each other out, as in the case of the configurational chiralities, Δ and Λ. Taking this assumption into consideration, the observed CD curves of $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (M=Fe(III) and Co(III)) seem to exhibit only a vicinal CD contribution due to the asymmetric carbon atoms in the L-cys ligands. In fact, the calculated vicinal CD curves, $1/2\{\Delta\varepsilon(\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}})+\Delta\varepsilon(\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}})\}$, for the Fe(III) and Co(III) trinuclear complexes are, over the whole region, quite similar to the observed curves of $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ and $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ respectively, as is shown in Fig. 6. These results indicate that the observed CD curves of the $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ complexes are composed mainly of the contribution due to the asymmetric carbon atoms of the L-cys ligands, and probably suggest that the additivity on the CD curve is substantiated for the present trinuclear complexes.

Inversion and Redox Reaction. The reaction of Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ with Co(III),[9,10] Fe(III), or Ni(II) proceeded with a retention of the Δ_{LLL}-*fac*(*S*) configuration to give $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{n-}$. By contrast, the reaction with Co(II) or Fe(II) was accompanied by the inversion to the Λ_{LLL} of the Δ_{LLL}-

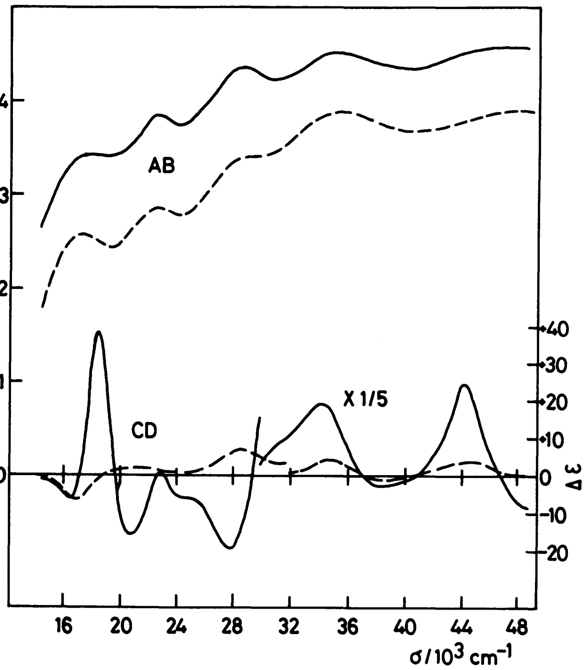

Fig. 5. Absorption and CD spectra of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (——) and Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ (-----).

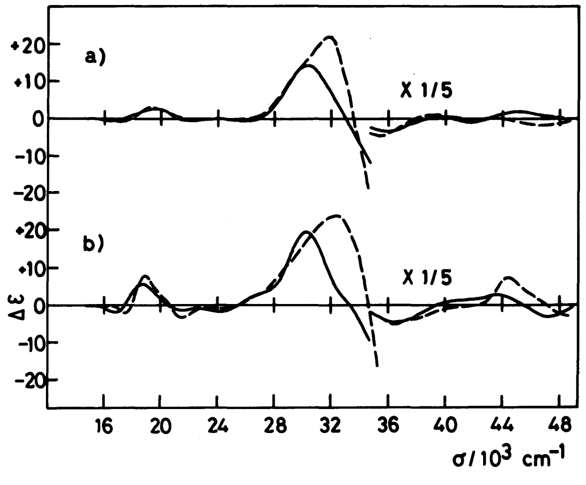

Fig. 6. The observed CD curves of $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (——) and the calculated CD curves for $1/2\{\Delta\varepsilon(\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}})+\Delta\varepsilon(\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}})\}$ (-----); a) M=Fe and b) M=Co.

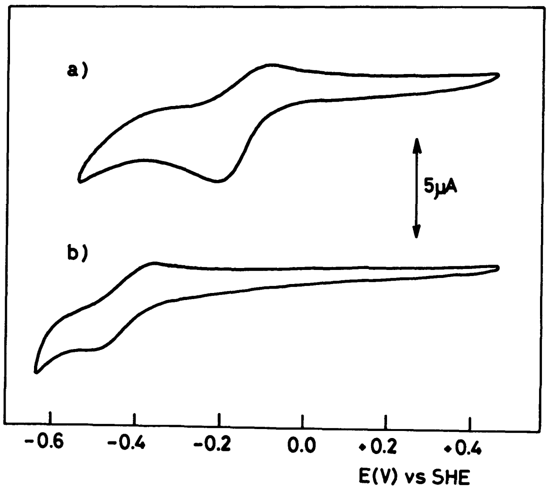

Fig. 7. Cyclic voltammograms of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$: scan rate, 10 mV s^{-1}; 0.01 mol dm^{-3} $\mathrm{NaNO_3}$ soln.; Hg electrode; 25 °C; a) M=Fe, $E°=-0.16$ V, $\Delta E_p=100$ mV and b) M=Co, $E°=-0.43$ V, $\Delta E_p=90$ mV.

fac(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]$ terminals. The inversion ratio runs parallel to the concentration of Co(II) or Fe(II) in the reaction, and under a nitrogen atmosphere these reactions are completely accompanied by the inversion to give only $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$. It is obvious that Fe(II) and Co(II) promote the inversion of the Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]$ terminals, consequently, the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomer forms easily.

The reaction of Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ with Fe(II) was accompanied by a more remarkable inversion to Λ_{LLL} than that with Co(II). In order to elucidate the difference in inversion for the reactions with Fe(II) and Co(II), the redox potentials of $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{M}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (M=Fe(III) and Co(III)) were measured in a 0.01 mol dm^{-3} sodium nitrate solution at the hanging Hg drop microelectrode. All the potentials were referred to the SHE, and the symbols denote the following: E_{pa} is the anodic peak potential, E_{pc} is the cathodic peak potential, and ΔE_{p} is $(E_{\mathrm{pa}}-E_{\mathrm{pc}})$. The formal potential, $E°_{298}$, is taken as the average of E_{pa} and E_{pc}. $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ and $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ display a quasi-reversible ($\Delta E_{\mathrm{p}}=90$—100 mV) cyclic response in different potential ranges, and no other redox process is observed in the potential range of −0.6—+0.9 V (Fig. 7). These results are interpreted in terms of the following one-electron redox reaction.

$$[\mathrm{M^{III}}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-} + e^- \rightleftharpoons [\mathrm{M^{II}}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{4-} \quad (\mathrm{M} = \mathrm{Co\ or\ Fe})$$

The formal potential of $[\mathrm{Fe}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (−0.16 V) is more anodic than that of $[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}_2]^{3-}$ (−0.43 V). This relationship corresponds to that of the formal potentials for the $\mathrm{Co^{III}N_6}$- and $\mathrm{Fe^{III}N_6}$-type complexes with the cyclic amine ligands.[18,19] These facts indicate that the central metal M is presumably redox active and that the redox potential of the Fe(II) center is more anodic than that of the Co(II) center. Taking these electrochemical properties into consideration, it is suggested that, in the formation process of the trinuclear complex by the reaction with the bivalent metal ion, the Fe(II) bridged with sulfur donor atoms of Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$, namely, $\mathrm{Fe^{II}(S_3CoN_3)}$, has a lower oxidation tendency than the Co(II) one, $\mathrm{Co^{II}(S_3CoN_3)}$. This suggestion is consistent with the fact that the formation of the $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$ isomer is promoted more remarkably by the reaction of Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]$ with Fe(II) than by that with Co(II), because the Δ_{LLL}-*fac*(*S*) terminals in the reaction with Fe(II) are labilized more than those in the reaction with Co(II).

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