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Stereoselective Formation and Characterization of *S*-Bridged Dinuclear Λ- and Δ-$[\mathrm{Co}\{\mathrm{Co}(\text{didentate-}N,S)_3\}(\text{D-pen-}N,O,S)]$-Type Complexes (didentate=2-Aminoethanethiolate, L-Cysteinate, and D-Penicillaminate (D-pen))

Toshiaki Yonemura,* Sayuri Nakahira, Tomoharu Ama, Hiroshi Kawaguchi, Takaji Yasui, Ken-ichi Okamoto,† and Jinsai Hidaka††

Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780

†Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

††Department of Industrial Chemistry, Faculty of Engineering, Kinki University in Kyushu,
Iizuka, Fukuoka 820

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Novel *S*-bridged dinuclear cobalt(III) complexes having different absolute configurations in $[\mathrm{Co}(\text{didentate-}N,S)_3]$ moieties, Λ- and Δ-$[\mathrm{Co}\{\mathrm{Co}(\text{didentate-}N,S)_3\}(\text{D-pen-}N,O,S)]^{+\text{ or }2-}$ (didentate=2-aminoethanethiolate (aet), L-cysteinate (L-cys), and D-penicillaminate (D-pen)), were prepared stereospecifically. The dinuclearizing reaction of Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ with $[\mathrm{CoCl(NH_3)_5}]^{2+}$ and D-penicillaminate proceeded with configurational retention in the $[\mathrm{Co}(\text{L-cys-}N,S)_3]$ moiety, while the reaction using the Co(II) ion instead of $[\mathrm{CoCl(NH_3)_5}]^{2+}$ was accompanied by a configurational inversion in the $[\mathrm{Co}(\text{L-cys-}N,S)_3]$ moiety. The occurrence of the configurational inversion was related to the intramolecular N–H···O hydrogen bonds between two ligands in the formation process of the dinuclear complexes. The newly prepared dinuclear complexes were characterized on the basis of their electronic absorption, CD, ^{13}C NMR, and IR spectral data. Electrochemical measurements of $[\mathrm{Co}\{\mathrm{Co}(\text{didentate-}N,S)_3\}(\text{D-pen-}N,O,S)]^{+\text{ or }2-}$ gave two redox waves at ca. −0.61 V and −0.85 to −1.04 V (vs. Ag/AgCl). The former wave corresponds to the Co(III)/Co(II) redox of the $[\mathrm{Co}(S)_3(\text{D-pen-}N,O,S)]$ moiety, and the latter one to that of the $[\mathrm{Co}(\text{didentate-}N,S)_3]$ moiety.

The thiolato sulfur atom in 2-aminoethanethiolate, L-cysteinate, or D-penicillaminate bridges two transition metal ions to form the di- and trinuclear complexes of μ-thiolato structures.1—13) The di- and trinuclear cobalt(III) complexes with those ligands have been extensively investigated concerning spectrochemical and stereochemical interest.3,8—13) It has been pointed out that $[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ and $[\mathrm{Co}(\text{D-pen-}N,S)_3]^{3-}$ are selectively formed in the Δ_{LLL}-*fac*(*S*) and Λ_{DDD}-*fac*(*S*) forms, respectively, because both the L-cys and D-pen chelate rings prefer the *lel* (parallel for C$_3$ axis) conformation with the equatorial carboxylate groups in the mononuclear complexes.13,14) In previous papers concerning the trinuclear complexes, it has been reported that the reaction of Δ_{LLL}-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$ with the Co(III) complex led to the formation of only $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$-$[\mathrm{Co_3}(\text{L-cys-}N,S)_6]^{3-}$, though the reaction with Co(II) ion led to the formation of $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$- and $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$-$[\mathrm{Co_3}(\text{L-cys-}N,S)_6]^{3-}$ accompanying a configurational inversion of the starting tris(L-cysteinato) complex.9—11) However, this configurational inversion was not completely stereoselective at room temperature; $\Delta\Delta:\Delta\Lambda:\Lambda\Lambda=5:23:72$.11) This configurational inversion may be attributed to the formation of the intramolecular hydrogen bonds and labilization of the Δ_{LLL}-*fac*(*S*)-$[\mathrm{Co}(\text{L-cys-}N,S)_3]$ moiety by an interaction with the Co(II) ion.10) Recently, a novel dinuclear complex, $[\mathrm{Co}\{\mathrm{Co}(\text{D-pen-}N,S)_3\}(\text{D-pen-}N,O,S)]^{2-}$, in which D-pen ligands coordinate to Co(III) ions as didentate and tridentate ligands, was reported, however, it was not clear whether this dinuclear complex was formed stereoselectively.13)

The present report deals with preparations of the dinuclear complexes, $[\mathrm{Co}\{\mathrm{Co}(\text{didentate-}N,S)_3\}(\text{D-pen-}N,O,S)]^{+\text{ or }2-}$ (didentate=aet, L-cys, and D-pen) and $[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}(\text{dien})]$ (dien=diethylenetriamine) (Fig. 1). In addition, we show that Λ_{LLL}- or Δ_{LLL}-$[\mathrm{Co}\{\mathrm{Co}(\text{L-cys-}N,S)_3\}(\text{D-pen-}N,O,S\text{ or dien})]^{2-\text{ or }0}$ is formed stereoselectively by the reaction among the Δ_{LLL}-$[\mathrm{Co}(\text{L-cys-}N,S)_3]^{3-}$, Co(II) ion or Co(III) complex, and the tridentate ligand (D-pen or dien). The electronic absorption, CD, and ^{13}C NMR spectral be-

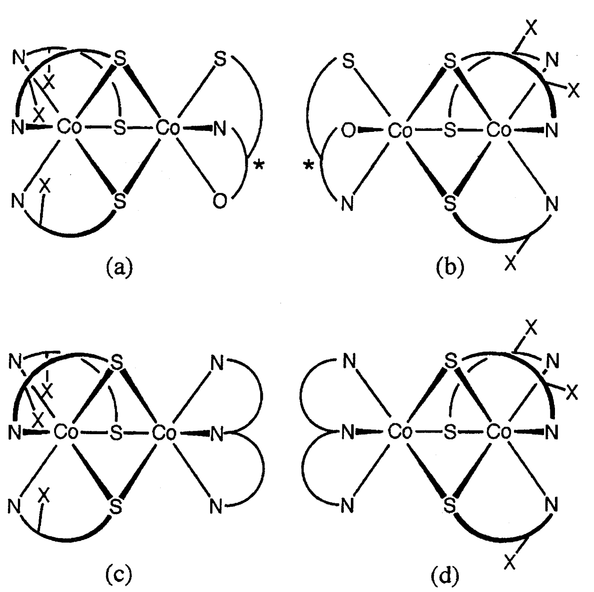

Fig. 1. Structures of (a) Λ- and (b) Δ-[Co{Co(didentate-N,S)$_3$}(D-pen-N,O,S)]$^{+\text{ or }2-}$ and (c) Λ- and (d) Δ-[Co{Co(didentate-N,S)$_3$}(dien)]$^{0\text{ or }3+}$ (didentate-N,S: aet (X=H), L-cys and D-pen (X=COO$^-$)).

haviors and cyclic voltammograms or half-wave potentials of the [Co{Co(didentate-N,S)$_3$}(D-pen-N,O,S or dien)]-type complexes, newly prepared, are discussed in relation to their geometrical and absolute configurations.

Experimental

Preparation of Complexes. 1) $(-)^{\rm CD}_{546}$- (A) and $(+)^{\rm CD}_{546}$-[Co{Co(aet-N,S)$_3$}(D-pen-N,O,S)]$^+$ (B). A solution containing 2.28 g (20.1 mmol) of 2-aminoethanethiol hydrochloride in 5 cm^3 of water was added to a solution containing 3.20 g (13.4 mmol) of $CoCl_2\cdot6H_2O$ in 10 cm^3 of water, followed by the addition of a solution containing 1.00 g (6.7 mmol) of D-penicillamine in 8 cm^3 of water and ca. 3 cm^3 of 2 mol dm^{-3} KOH aqueous solution. The pH of the mixed solution was adjusted to 7 with a 2 mol dm^{-3} KOH solution. Lead dioxide (0.5 g) was added to the solution with stirring. While keeping the pH constant at 7, the solution was stirred at 30 °C for 30 min. The reaction solution was cooled to room temperature and filtered to remove any insoluble materials. The filtrate was diluted with water and poured onto an SP-Sephadex C-25 column (K$^+$ form, 9 cm×20 cm). After sweeping the column with water, the adsorbed band was separated into three bands, dark brown (A-1), dark green (A-2), and dark green (A-3), in this elution order, by development with a 0.2 mol dm^{-3} KCl aqueous solution. It was confirmed on the basis of the absorption spectral data that the A-2 and A-3 bands contained trinuclear complexes, [Co$_3$(aet-N,S)$_{6-n}$(D-pen-N,S)$_n$]$^{3-n}$ (n=1, 2), similar to [Co$_3$(aet- or D-pen-N,S)$_6$]$^{3+\text{ or }3-}$.[3,13)] The A-1 band containing the desired complexes was transferred into another SP-Sephadex C-25 column (K$^+$ form, 4.7 cm×90 cm) and circulated three times with the same eluent. The band was separated into two bands of brown (**A**) and greenish brown (**B**) colors. The eluates from these two bands exhibited enantiomeric CD spectra with (−) and (+) signs at 546 nm, respectively.

The early eluate was concentrated to a small volume with a rotary evaporator at below 25 °C, and a large amount of methanol was added to the concentrated solution to eliminate KCl. After this procedure was repeated several times, the concentrated solution was passed through a Sephadex G-10 column (3.6 cm×80 cm) by eluting with water in order to completely remove KCl. After the eluate was again concentrated to a small volume, a large amount of methanol was added. The solution was allowed to stand at room temperature for one week in order to deposit brown crystals (complex **A**). The crystals were collected by filtration, washed with acetone, and then dried on calcium chloride under reduced pressure.

The late eluate was treated with the same procedure as that used for the early eluate. The chloride salt was converted to the nitrate salt by using a short QAE-Sephadex A-25 column (NO$_3^-$ form, 2.2 cm×40 cm). A small amount of methanol, and then a large amount of acetone, were added to the concentrated eluate. The resulting greenish brown complex **B** was collected by filtration, washed with acetone, and then dried on calcium chloride under reduced pressure. Found for the early eluted $(-)^{\rm CD}_{546}$ isomer (**A**): C, 24.21; H, 5.50; N, 9.58%. Calcd for $C_{11}H_{27}N_4O_2S_4ClCo_2\cdot H_2O\cdot0.25C_3H_6O$: C, 24.35; H, 5.65; N, 9.67%. Found for the late eluted $(+)^{\rm CD}_{546}$ isomer (**B**): C, 22.78; H, 5.09; N, 11.53%. Calcd for $C_{11}H_{27}N_5O_5S_4Co_2\cdot H_2O\cdot0.1C_3H_6O$: C, 22.72; H, 5.33; N, 11.72%.

2) $(-)^{\rm CD}_{550}$-[Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (C). A solution containing 1.64 g (13.4 mmol) of L-cysteine and 2.00 g (13.4 mmol) of D-penicillamine in 15 cm^3 of water and small amount of 2 mol dm^{-3} KOH aqueous solution was added to a solution containing 3.20 g (13.4 mmol) of $CoCl_2\cdot6H_2O$ in 10 cm^3 of water. The pH of the mixed solution was adjusted to 7 with a 2 mol dm^{-3} KOH solution. Lead dioxide (0.5 g) was added into the solution with stirring. While keeping the pH constant at 7, the solution was stirred at 30 °C for 30 min. The reaction solution was cooled to room temperature and filtered in order to remove any insoluble materials. The filtrate was diluted with water and poured onto a QAE-Sephadex A-25 column (Cl$^-$ form, 9 cm×20 cm). After sweeping the column with water, the adsorbed band was separated into three bands of brown (C-1), dark brown (C-2), and dark green (C-3) colors in this elution order by development with a 0.2 mol dm^{-3} KCl aqueous solution. It was confirmed on the basis of the absorption spectral data that the C-2 and C-3 bands contained trinuclear complexes, [Co$_3$(L-cys-N,S)$_{6-n}$(D-pen-N,S)$_n$]$^{3-}$ (n=0—6).[11,13)] The C-1 band containing the desired complex was transferred into another QAE-Sephadex A-25 column (Cl$^-$ form, 4.7 cm×90 cm) and circulated five or six times with the same eluent. The band separated into two bands of reddish brown and brown colors. The absorption and CD spectra indicated that the reddish brown band contained [Co{Co(L-cys-N,S)$_n$(D-pen-N,S)$_{3-n}$}(D-pen-N,O,S)]$^{2-}$ (n=1,2)[15)] and that the brown band contained only the $(-)^{\rm CD}_{550}$ isomer (complex **C**). The eluate from the brown band was concentrated to a small volume with a rotary evaporator below 25 °C, and a large amount of methanol was added to the concentrated solution to eliminate KCl. This procedure was repeated several times. A complete elimination of KCl was carried out using a Sephadex G-10 column. The complex was converted from the potassium salt to the cesium one by treating it with a short SP-Sephadex C-25 column (Cs^+ form, 2.2 cm×40 cm). A small amount of methanol and acetone was added to the concentrated eluate to deposit a brown precipitate (complex **C**). The precipitate was filtered, washed with acetone, and then dried on calcium chloride under reduced pressure. Found: C, 17.72; H, 3.43; N, 5.54%. Calcd for $C_{14}H_{24}N_4O_8S_4Cs_2Co_2 \cdot 4.5H_2O \cdot 0.2C_3H_6O$: C, 17.88; H, 3.51; N, 5.71%.

3) $(+)^{CD}_{550}$-[Co{Co(L-cys-*N,S*)$_3$}(D-pen-*N,O,S*)]$^{2-}$ (D). A solution containing 2.18 g (3.36 mmol) of Δ_{LLL}-*fac*(*S*)-K_3[Co(L-cys-*N,S*)$_3$]$\cdot 6.5H_2O$[16] in 30 cm^3 of water and 0.50 g (3.36 mmol) of D-penicillamine were added to a suspension containing 0.84 g (3.36 mmol) of $[CoCl(NH_3)_5]Cl_2$[17] in 100 cm^3 of water. The mixed solution was adjusted to pH 7 with a 2 mol dm^{-3} KOH solution, and stirred at 30 °C for 30 min keeping pH 7. The reaction solution was cooled to room temperature and filtered in order to remove any insoluble materials. The filtrate was diluted with water and poured onto a QAE-Sephadex A-25 column (Cl^- form, 9 cm×20 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.2 mol dm^{-3} KCl aqueous solution. The separated two bands, dark brown (D-1) and dark green (D-2), were eluted out in this order. From the absorption spectral data it was confirmed that the D-2 eluate contained the same trinuclear complexes as C-2, [Co$_3$(L-cys-*N,S*)$_{6-n}$(D-pen-*N,S*)$_n$]$^{3-}$ (n=0—6). Although the D-1 band, containing the desired complex, was recyclically developed on another QAE-Sephadex A-25 column (Cl^- form, 4.7 cm×90 cm), no other bands were separated. The D-1 band was eluted from the column. The brown precipitate (**D**) was obtained by the same procedure as that described in 2). Found: C, 17.70; H, 3.34; N, 5.58%. Calcd for $C_{14}H_{24}N_4O_8S_4Cs_2Co_2 \cdot 4.5H_2O \cdot 0.2C_3H_6O$: C, 17.88; H, 3.51; N, 5.71%.

4) $(-)^{CD}_{565}$-[Co{Co(D-pen-*N,S*)$_3$}(D-pen-*N,O,S*)]$^{2-}$ (E). This complex was prepared by the method described in the literature.[13] Moreover, when a similar reaction was carried out using $[CoCl(NH_3)_5]Cl_2$[17] instead of the Co(II) ion, only the $(-)^{CD}_{565}$ isomer (**E**) was selectively formed.

5) $(-)^{CD}_{550}$-[Co{Co(L-cys-*N,S*)$_3$}(dien)] (F). A solution containing 4.36 g (6.72 mmol) of Δ_{LLL}-*fac*(*S*)-K_3[Co(L-cys-*N,S*)$_3$]$\cdot 6.5H_2O$[16] and 0.68 g (6.72 mmol) of diethylenetriamine in 30 cm^3 of water was added to a solution containing 1.60 g (6.72 mmol) of $CoCl_2 \cdot 6H_2O$ in 20 cm^3 of water. The pH of the mixed solution was adjusted to 7 with a 2 mol dm^{-3} KOH solution. Lead dioxide (0.5 g) was added into the solution with stirring. While keeping the pH constant at 7, the solution was stirred at 30 °C for 30 min, whereupon the color of the solution turned from deep green to greenish brown. The solution was cooled to room temperature and filtered in order to remove any insoluble materials. The filtrate was passed through the columns (6.5 cm×5 cm) of QAE-Sephadex A-25 (Cl^- form) and SP-Sephadex C-25 (K^+ form). The greenish-brown band containing uncharged complex was eluted with water. The eluate was concentrated to a small volume with a rotary evaporator below 25 °C, and a large amount of methanol was added to the concentrated solution to deposit KCl. After this procedure was repeated several times, the concentrated solution was passed through a Sephadex G-10 column (3.6 cm×80 cm) by elution with water in order to completely remove KCl. The eluate was concentrated to a small volume, and a small amount of ethanol and acetone was added to the concentrated solution. The greenish brown complex **F** deposited was collected by filtration, washed with acetone, and then dried on calcium chloride under reduced pressure. Found: C, 23.12; H, 5.77; N, 12.35%. Calcd for $C_{13}H_{28}N_6O_6S_3Co_2 \cdot 5.5H_2O$: C, 23.00; H, 5.80; N, 12.40%.

6) $(+)^{CD}_{550}$-[Co{Co(L-cys-*N,S*)$_3$}(dien)] (G). This complex was prepared by the method described in the literature.[12]

Measurements. The electronic absorption spectra were recorded on a JASCO UVIDEC-670 or UVIDEC-610C spectrophotometer and the CD spectra on a JASCO J-22 or J-600 spectropolarimeter. All of the measurements were carried out in aqueous solutions at room temperature. The infrared spectra were recorded with a JASCO FT/IR-5300 infrared spectrophotometer using the Nujol method. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-AM-500 NMR spectrometer at the probe temperature in D_2O. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as an internal reference. The cyclic voltammograms were recorded with a Yanaco P-900 apparatus using a glassy-carbon working electrode (Yanaco, GC-P2). An aqueous Ag/AgCl/NaCl (3 mol dm^{-3}) electrode (Bioanalytical Systems, Inc., RE-1B) and platinum wire were used as reference and auxiliary electrodes, respectively. Electrochemical experiments were conducted at 22±1 °C in a 0.1 mol dm^{-3} aqueous solution of $NaNO_3$ as the supporting electrolyte and 1.0 mmol dm^{-3} complex concentrations. Rotating disk electrode voltammetry (RDE) measurements were carried out with a glassy-carbon rotating-disk working electrode (2000 rev min^{-1}) attached to a Yanaco P-10-RE Mark II head. The other experimental conditions were the same as those for the CV measurements.

Results and Discussion

Structural Assignments and Properties. All of the obtained complexes are easily soluble in water at 25 °C. The absorption spectra of **A** and **B** show the d–d transition bands in the region 16—24×10^3 cm^{-1} and the intense bands due to the sulfur-to-metal charge transfer (SMCT) transition at ca. 37×10^3 cm^{-1} (Fig. 2 and Table 1).[9—13,18—20] Such spectral behaviors are quite similar to that of the dinuclear D-pen-*N,O,S* complex, [Co{Co(D-pen-*N,S*)$_3$}(D-pen-*N,O,S*)]$^{2-}$ (**E**).[13] The ^{13}C NMR spectral patterns of **A** and **B** resemble each other; their spectra give eleven resonance peaks due to two methyl, quaternary, methine, and carboxylate carbon atoms of a D-pen ligand and six methylene ones of three unequivalent aet ligands in **A** and **B**, respectively (Fig. 3). These results indicate that **A** and **B** are diastereomeric isomers (Λ and Δ) of the dinuclear complex, [Co{Co(aet-*N,S*)$_3$}(D-pen-*N,O,S*)]$^+$, having a C_1 symmetry (Fig. 1). For two possible diastereomers, the CD spectral behavior of **A** is similar to that of **E**, which has the Λ configuration. The CD spectrum of **B** is almost enantiomeric to those of **A** and **E** (Figs. 2 and

Table 1. Absorption and CD Spectral Data of Dinuclear Complexes

Complex ion	Absorption maxima $\sigma/10^3$ cm^{-1}	(log ε/mol^{-1} dm^3 cm^{-1})	CD extrema $\sigma/10^3$ cm^{-1}	($\Delta\varepsilon$/mol^{-1} dm^3 cm^{-1})
Λ-[Co{Co(aet-*N*,*S*)$_3$} (D-pen-*N*,*O*,*S*)]$^+$ (**A**)	17.1	(2.8sh)	18.32	(−15.74)
	20.3	(3.3sh)	21.41	(+5.87)
	22.52	(3.46)	23.47	(+7.69)
	28.3	(4.0sh)	27.93	(+23.43)
	31.75	(4.20)	34.0	(−23.4sh)
			36.90	(−28.22)
			43.86	(−33.02)
Δ-[Co{Co(aet-*N*,*S*)$_3$} (D-pen-*N*,*O*,*S*)]$^+$ (**B**)	16.3	(2.8sh)	15.60	(−6.22)
	18.5	(3.0sh)	18.32	(+13.62)
	22.47	(3.55)	22.42	(−5.32)
	28.6	(4.0sh)	25.32	(−6.29)
	31.65	(4.16)	28.01	(−9.92)
	39.06	(4.28)	31.5	(+6.1sh)
			34.97	(+17.13)
			38.17	(+19.75)
			44.25	(+13.92)
Λ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$} (D-pen-*N*,*O*,*S*)]$^{2-}$ (**C**)	16.7	(2.8sh)	18.11	(−13.55)
	20.0	(3.3sh)	21.05	(+7.10)
	22.42	(3.51)	23.42	(+7.43)
	28.3	(4.0sh)	27.70	(+24.07)
	31.65	(4.17)	36.76	(−29.85)
	38.17	(4.24)	43.10	(−27.31)
Δ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$} (D-pen-*N*,*O*,*S*)]$^{2-}$ (**D**)	15.6	(2.7sh)	15.60	(−6.91)
	17.6	(2.9sh)	18.41	(+17.95)
	22.32	(3.54)	22.22	(−9.29)
	28.7	(4.0sh)	27.88	(−11.22)
	37.09	(4.31)	34.97	(+24.25)
	46.30	(4.36)	44.05	(+23.22)
Λ_{DDD}-[Co{Co(D-pen-*N*,*S*)$_3$} (D-pen-*N*,*O*,*S*)]$^{2-}$ (**E**)[a]	16.8	(3.1sh)	17.70	(−12.59)
	19.0	(3.4sh)	21.98	(+11.62)
	27.6	(4.0sh)	26.55	(+26.76)
	35.71	(4.23)	33.15	(−28.42)
	44.45	(4.39)	35.7	(−21.2sh)
			38.76	(+4.38)
			42.74	(−28.79)
Λ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$} (dien)] (**F**)	18.21	(2.84)	18.02	(−2.83)
	22.94	(3.35)	20.62	(+5.08)
	28.9	(3.6sh)	22.99	(−0.37)
	31.65	(4.04)	24.10	(−0.28)
	39.37	(4.38)	28.4	(+5.9sh)
			31.25	(+13.97)
			35.0	(−6.3sh)
			38.46	(−27.56)
			45.46	(−7.45)
Δ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$} (dien)] (**G**)[b]	18.48	(2.83)	18.66	(+4.33)
	23.17	(3.34)	20.79	(−8.74)
	32.0	(4.1sh)	22.73	(−1.24)
	37.59	(4.45)	25.0	(−1.4sh)
	46.40	(4.37)	27.9	(−7.4sh)
			31.23	(−32.76)
			36.76	(+38.57)
			45.25	(+47.99)

sh denotes a shoulder. a) Ref. 13. b) Ref. 12.

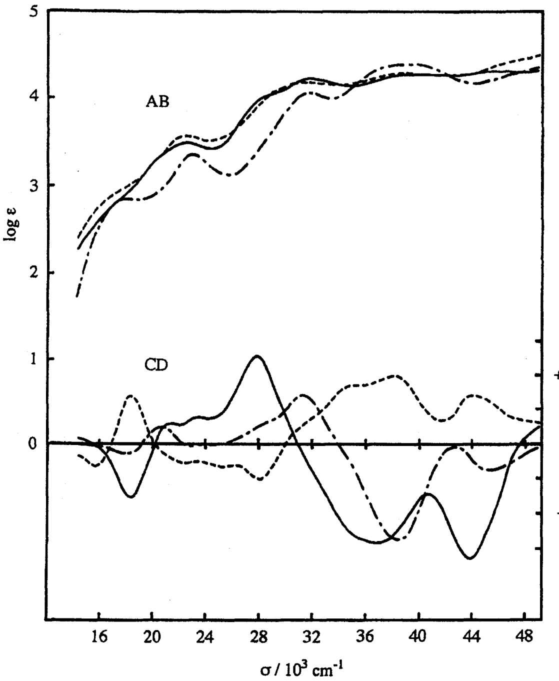

Fig. 2. Absorption and CD spectra of the complexes: Λ-[Co{Co(aet-N,S)$_3$}(D-pen-N,O,S)]$^+$ (**A**) (—), Δ-[Co{Co(aet-N,S)$_3$}(D-pen-N,O,S)]$^+$ (**B**) (---), and Λ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(dien)] (**F**) (–•–).

4). Accordingly, **A** and **B** are assignable to Λ- and Δ-[Co{Co(aet-N,S)$_3$}(D-pen-N,O,S)]$^+$, respectively.

Both complexes **C** and **D** exhibited quite similar absorption spectral behaviors to those of complexes **A**, **B**, and **E** (Fig. 4 and Table 1). In the ^{13}C NMR spectrum of **C**, four resonance peaks due to the carboxylate carbon atoms of the L-cys and D-pen ligands were observed in the 185—177 ppm region (Fig. 3). One of the COO$^-$ resonance peaks of complex **C** is located at δ=185.01, while three peaks are located at δ=178.54, 178.42, and 177.92. Since the resonance peak due to the

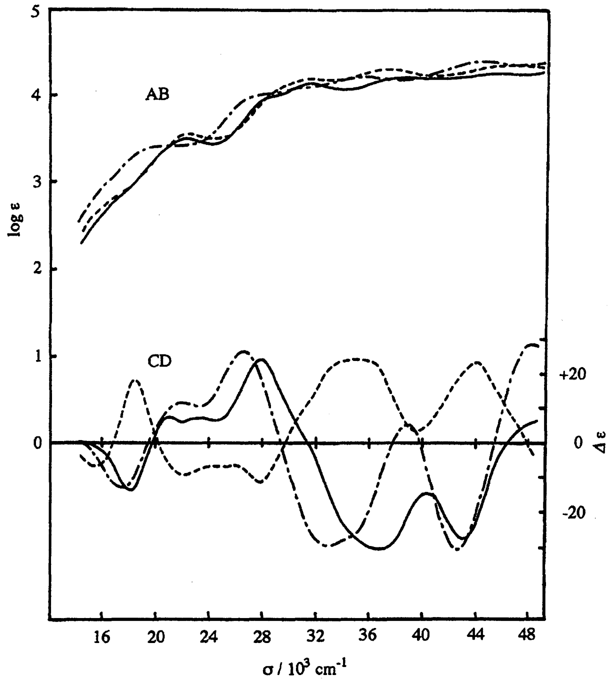

Fig. 4. Absorption and CD spectra of the dinuclear complexes: Λ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**C**) (—), Δ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**D**) (---), and Λ_{DDD}-[Co{Co(D-pen-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**E**) (–•–).

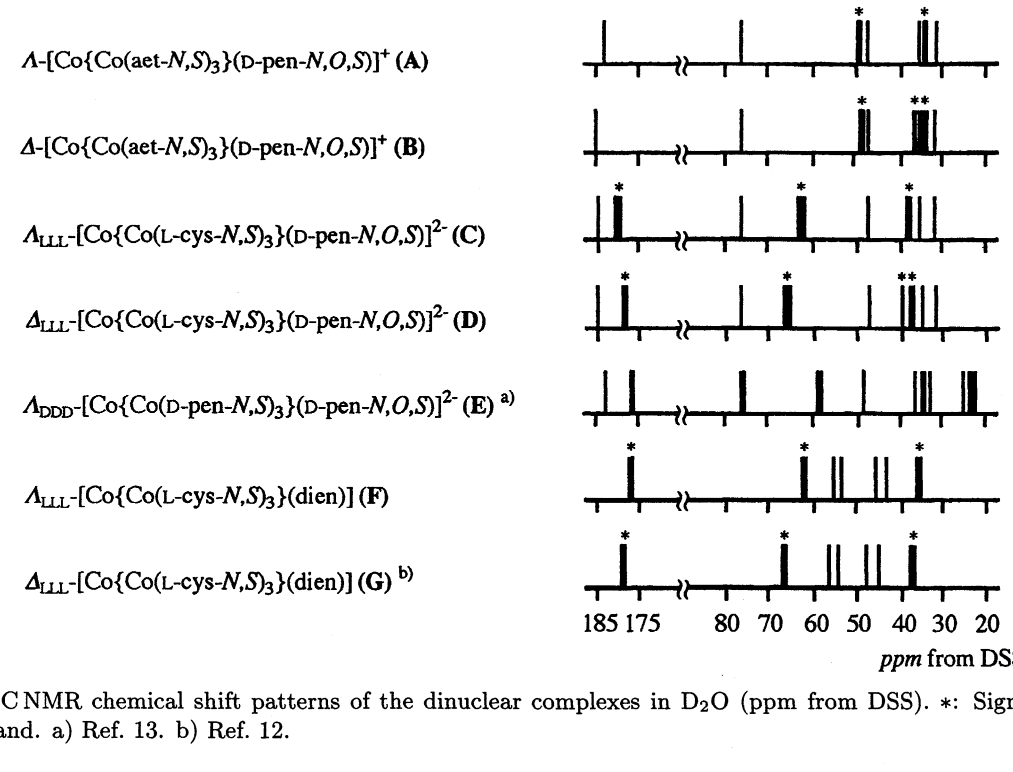

Fig. 3. ^{13}C NMR chemical shift patterns of the dinuclear complexes in D$_2$O (ppm from DSS). $*$: Signals of aet or L-cys ligand. a) Ref. 13. b) Ref. 12.

coordinated carboxylate carbon appear in a lower magnetic field than those of the uncoordinated ones,[13] it is reasonable to consider that three carboxylate groups in the complex **C** are uncoordinated, and that only one carboxylate group coordinates to the Co(III) ion. One resonance peak due to the quaternary carbon atom is located relatively upfield (δ=48.28) compared with those of the corresponding carbon atoms in the complexes **E** and [Co{Co(D-pen-*N*,*S*)$_3$}(dien)], and two resonance peaks due to the methyl carbon atoms in the D-pen ligand are located at δ=35.54 and 33.77.[13] It can be interpreted from these results that although three sulfur atoms in the L-cys ligands function to bridge two Co(III) ions, the sulfur atom in the D-pen ligand does not. The resonance peaks of the corresponding carbons between complexes **C** and **D** were observed almost in the same field as each other. These facts suggest that **C** and **D** are diastereomeric isomers (Λ_{LLL} and Δ_{LLL}) of [Co{Co(L-cys-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$ having C_1 symmetry (Fig. 1). The CD spectral behavior of **C** is similar to those of **A** and **E**, whereas the CD spectrum of **D** is almost enantiomeric to those of **A**, **C**, and **E**. Accordingly, **C** and **D** are assignable to Λ_{LLL}- and Δ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$, respectively.

Complex **F** exhibits a quite similar absorption spectral behavior to that of complex **G**, Δ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$}(dien)] (Fig. 2 and Table 1).[12] The CD spectrum of **F** is almost enantiomeric to that of **G**. In the ^{13}C NMR spectrum of **F**, three resonance peaks of the carboxylate carbon atoms of the L-cys ligands appear at ca. 176 ppm (Fig. 3), suggesting that the three carboxylate groups are free from coordination.[13] These results indicate that **F** is assignable to Λ_{LLL}-[Co{Co(L-cys-*N*,*S*)$_3$}(dien)].

The absorption and CD bands in the region of 16—40×10^3 cm^{-1} of the D-pen-*N*,*O*,*S* complexes (**A**—**E**) shift to the lower energy side than those of the dien complexes (**F**, **G**), as shown in Figs. 2 and 4 and Table 1. In the d–d absorption band region, the CD bands of [Co{Co(didentate-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$ (**A**—**E**) are more intense than those of [Co{Co(L-cys-*N*,*S*)$_3$}(dien)] (**F**, **G**). These spectral behaviors in **A**—**E** may be related to the steric interaction around the methyl groups in the tridentate D-pen-*N*,*O*,*S* ligand. In the SMCT band region (32—40×10^3 cm^{-1}), the CD bands of the D-pen-*N*,*O*,*S* complexes (**A**—**E**) are relatively broad due to an overlapping of the two SMCT components compared with those of the dien ones (**F**, **G**) (Figs. 2 and 4). These spectral behaviors reflect the difference between the $CoNOS_4$ and CoN_3S_3 chromophores of the D-pen-*N*,*O*,*S* complexes and the two CoN_3S_3 ones of the dien complexes.

Formation of Intramolecular Hydrogen Bonds. In Λ- and Δ-[Co{Co(aet-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^+$ (Λ(**A**) and Δ(**B**)), ^{13}C NMR resonance peaks due to the methylene carbon atoms neighboring amino nitrogen atoms appear with almost the same chemical shift (Fig. 3). However, in the L-cys dinuclear complexes, the methine carbon atoms of the Λ_{LLL} isomers (**C**, **F**) exhibit resonance peaks in the region of δ=67—61, shifting about 3.5—4.5 ppm upfield compared with the methine carbon atoms in the Δ_{LLL} isomers (**D**, **G**). This shift difference is related to the formation of intramolecular hydrogen bonds between the amino proton on the L-cys ligands and the carboxylate oxygen atom on the other L-cys ligands in the Λ_{LLL} isomer. That is, although the carboxylate groups which take the *lel* conformation by the axial orientation in the Λ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$] moiety can form hydrogen bonds with the amine protons, the equatorial carboxylate groups in the Δ_{LLL} one cannot.[10] The formation of the intramolecular hydrogen bond is also revealed by the IR spectral data of the several samples which have protonated oxygen or not (Fig. 5). Complexes **C** and **F** involving the intramolecular hydrogen bond (COO···H–N–H) exhibited sharp peaks which can be assigned to the coordinated carboxylato C=O stretching of the tridentate D-pen ligand at 1543 and 1551 cm^{-1}, respectively, and those assigned to the uncoordinated carboxylate C=O stretching of the L-cys ligand at 1615 and 1620 cm^{-1}. A tendency similar to this has also been observed for other complexes.[21] However, **D**, **E**, and **G**, which have free COO$^-$ groups and coordinated NH$_2$ and carboxylato groups, exhibited broad peaks in the 1530—1680 cm^{-1} region (Fig. 5). Such broad bands are observed in mononuclear complexes, [Co(D-pen-*N*,*S*)$_3$]$^{3-}$, [Co(L-cys-*N*,*S*)$_3$]$^{3-}$, and [Co(D-pen-*N*,*O*,*S*)$_2$]$^-$, which do not involve an intramolecular hydrogen bond.[22] These ^{13}C NMR and IR spectral behaviors provide useful information for structural assignments of complexes involving an intramolecular hydrogen bond.

Formation of Isomers. In the preparation of [Co{Co(aet-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^+$, the reaction of a mixture of [Co(aet-*N*,*S*)$_3$] and the D-pen ligand with Co(II) produced both the Λ(**A**) and Δ(**B**) isomers. The formation ratio of Λ and Δ was 1 : 1. In preparing of [Co{Co(L-cys-*N*,*S*)$_3$}(D-pen-*N*,*O*,*S*)]$^{2-}$, the reaction of a mixture of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ and D-pen with the Co(III) complex at 30 °C proceeded with the retention of the Δ_{LLL}-*fac*(*S*) configuration to give only the Δ_{LLL} dinuclear complex (**D**). On the other hand, when a mixture of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ and the D-pen ligand reacted with Co(II), a configurational inversion from Δ_{LLL} to Λ_{LLL} in the *fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$] moiety occurred, and only the Λ_{LLL} dinuclear complex (**C**) was produced stereospecifically. In the reaction of a mixture of Δ_{LLL}-*fac*(*S*)-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ and dien with Co(II), furthermore, a similar stereospecific inversion was observed; only the Λ_{LLL} dinuclear complex (**F**) was produced. Such a phenomenon has also been found in the preparation of the trinuclear complex, [Co$_3$(L-cys-*N*,*S*)$_6$]$^{3-}$,[9—11] though the configurational inversion was not complete; the formation ratio of the three isomers ($\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$, $\Delta_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$,

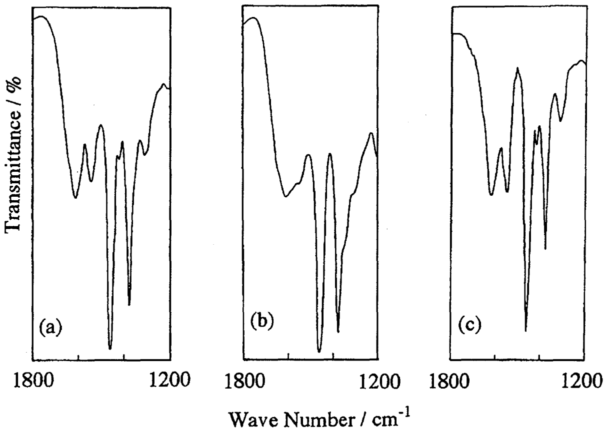

Fig. 5. IR spectra of the dinuclear complexes in Nujol: (a) Λ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**C**), (b) Δ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**D**), and (c) Λ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(dien)] (**F**).

and $\Lambda_{\mathrm{LLL}}\Lambda_{\mathrm{LLL}}$) was about 5 : 23 : 72.[11] These configurational inversions observed for the di- and trinuclear complexes suggest that the Λ_{LLL} configuration involving the intramolecular hydrogen bonds between the carboxylato oxygens and amine protons is more stable than the Δ_{LLL} configuration. Further, the molecular model constructions suggest that the steric repulsion around the S atoms on the L-cys ligands in the Δ_{LLL} dinuclear complexes (**D**, **G**) is larger than that in the $\Delta_{\mathrm{LLL}}\Delta_{\mathrm{LLL}}$ trinuclear complex. These take advantage of the stereospecific formation of the Λ_{LLL} isomers (**C**, **F**) in the L-cys dinuclear complexes. The stereospecificity was very remarkable in the D-pen dinuclear complex (**E**); the D-pen dinuclear complex was formed only in the Λ_{DDD} form by the reaction of Λ_{DDD}-*fac*(S)-[Co(D-pen-N,S)$_3$]$^{3-}$ with either Co(II) ion or the Co(III) complex. The formation of the Δ_{DDD} isomer is prevented by a steric repulsion among the lone paired electrons of S atoms and the methyl groups of the D-pen-N,S or D-pen-N,O,S ligands. It has been previously pointed out that although the Co(II) ion brings about a configurational inversion in the formation of the trinuclear complex,[10] it is not obvious whether only the Co(II) ion accelerates this complete inversion in the formation of the dinuclear complex.

Further, it is worth noting that the [Co{Co(L-cys- or D-pen-N,S)$_3$}(L-cys-N,O,S)]$^{2-}$ complex containing L-cys-N,O,S as a tridentate ligand could not be obtained in the present work.

Redox Properties. The electrochemical experiments were performed by cyclic voltammetry (CV) and rotating disk electrode voltammetry (RDE) equipped with a glassy carbon electrode in a 0.1 mol dm^{-3} NaNO$_3$ aqueous solution. The cyclic voltammogram of **A**, which was initiated at −0.4 V with a negative potential scan, yielded two reduction waves ($E_{\mathrm{pc}}(1)$ and $E_{\mathrm{pc}}(2)$) coupled with one oxidation wave ($E_{\mathrm{pa}}(1)$) (Fig. 6). No other redox couple was observed in the potential region of +0.8 to −1.2 V (vs. Ag/Ag$^+$). The peak current is proportional to the square root of the scan rate, and the ratio of the anodic peak current to the cathodic one is nearly unity for each of the complexes. At a scan rate of 100 mV s^{-1}, the observed first peak separation ($\Delta E_{\mathrm{p}}=|E_{\mathrm{pc}}-E_{\mathrm{pa}}|$) is 100—160 mV for a series of [Co{Co(didentate-N,S)$_3$}(D-pen-N,O,S or dien)]-type complexes (Table 2). These results indicate that the first redox reactions (1), which occurred at $E^{\circ\prime}((E_{\mathrm{pc}}+E_{\mathrm{pa}})/2)=-0.61$ (**A**)—−0.49 (**G**) V, are electrochemically quasi-reversible. Quasi-reversible one electron reduction waves were observed for these complexes; the values of $E^{\circ\prime}$ by CV coincided with $E_{1/2}$ by RDE within the experimental error. On the other hand, the second redox reactions (2), which occurred at $E_{1/2}=-0.85$ (**A**)—−1.04 (**G**) V, were irreversible in CV, and no anodic peak currents were observed. Therefore, these $E_{1/2}$ values are those obtained by RDE. In the first redox process (1), the $E^{\circ\prime}$ value for each [Co{Co(didentate-N,S)$_3$}(D-pen-N,O,S)] (**A**—**D**) indicates almost the same potential ($E^{\circ\prime}\approx-0.61$ V). Taking two kinds of moieties, [Co(didentate-N,S)$_3$] and [Co(S)$_3$(D-pen-N,O,S)], into consideration, each of the definite formal potentials (ca. −0.61 V) corresponds to the redox potential of the Co(III)/Co(II) couple for the [Co(S)$_3$(D-pen-N,O,S)] moiety. However, only the $E^{\circ\prime}$ value for complex **E** shifts slightly to the positive side ($E^{\circ\prime}=-0.57$ V). A similar positive shift was also observed for the corresponding dien complexes, **F** and **G**. It is noted that although the $E_{1/2}$ values of the dien complexes are somewhat negative compared with those of the D-pen-N,O,S complexes, their redox systems are quite similar to each other. Consequently, the

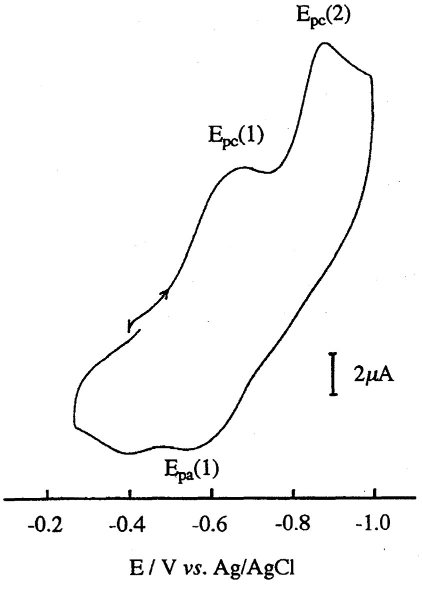

Fig. 6. Cyclic voltammogram of 1.0 mmol dm^{-3} Λ-[Co{Co(aet-N,S)$_3$}(D-pen-N,O,S)]$^+$ (**A**) in 0.1 mol dm^{-3} aqueous solution of NaNO$_3$. The scan rate is 100 mV s^{-1}.

Table 2. Electrochemical Data Obtained by Means of CV and RDE Measurements[a)]

Complex	Redox process	E_{pc}	E_{pa}	$E^{\mathrm{o}\prime}$ [b)] or $E_{1/2}$ [c)]	ΔE_{p} [d)]
Λ-[Co{Co(aet-N,S)$_3$}(D-pen-N,O,S)]$^+$ (**A**)	(1)	−0.67	−0.55	−0.61	0.12
	(2)	−0.89	—	−0.85	—
Δ-[Co{Co(aet-N,S)$_3$}(D-pen-N,O,S)]$^+$ (**B**)	(1)	−0.68	−0.55	−0.62	0.13
	(2)	−0.89	—	−0.85	—
Λ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**C**)	(1)	−0.68	−0.52	−0.60	0.16
	(2)	—	—	−1.00	—
Δ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**D**)	(1)	−0.66	−0.52	−0.59	0.14
	(2)	—	—	−1.02	—
Λ_{DDD}-[Co{Co(D-pen-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (**E**)	(1)	−0.68	−0.45	−0.57	0.23
	(2)	—	—	−0.96	—
Λ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(dien)] (**F**)	(1)	−0.59	−0.49	−0.54	0.10
	(2)	—	—	−1.02	—
Δ_{LLL}-[Co{Co(L-cys-N,S)$_3$}(dien)] (**G**)	(1)	−0.54	−0.44	−0.49	0.10
	(2)	—	—	−1.04	—

a) In V vs. Ag/AgCl (3 mol dm^{-3} NaCl) from cyclic voltammetry (CV) or rotating disk electrode voltammetry (RDE); 22±1 °C in water (0.1 mol dm^{-3} NaNO$_3$) with scan rate 100 mV s^{-1}. b) $E^{\mathrm{o}\prime}=(E_{\mathrm{pa}}+E_{\mathrm{pc}})/2$ from CV. c) $E_{1/2}$ values from RDE. d) $\Delta E_{\mathrm{p}}=|E_{\mathrm{pc}}-E_{\mathrm{pa}}|$.

second redox process (2) ($E_{1/2}=-0.85$ to -1.04 V) is attributable to the redox reaction of the Co(III)/Co(II) couple for the [Co(didentate-N,S)$_3$] moiety. From these results, the redox reactions are represented by the following scheme;

$$[\mathrm{Co^{III}\{Co^{III}(didentate}\text{-}N,S)_3\}(\text{D-pen-}N,O,S)]^{+\ \mathrm{or}\ 2-}+\mathrm{e}^-$$
$$\rightleftharpoons [\mathrm{Co^{II}\{Co^{III}(didentate}\text{-}N,S)_3\}(\text{D-pen-}N,O,S)]^{0\ \mathrm{or}\ 3-} +\mathrm{e}^- \qquad (1)$$
$$\rightleftharpoons [\mathrm{Co^{II}\{Co^{II}(didentate}\text{-}N,S)_3\}(\text{D-pen-}N,O,S)]^{-\ \mathrm{or}\ 4-} \qquad (2)$$

The reduction potential difference resulting from the difference in the configurations of the complexes is very slight; the $E^{\mathrm{o}\prime}$ values for Δ_{LLL} isomers are more negative by only 0—20 mV, compared to those for the corresponding Λ_{LLL} isomers (Table 2). The difference is more profound for the change of the tridentate ligand from D-pen-N,O,S to dien-N,N,N; [Co{Co(L-cys-N,S)$_3$}(dien)] (−0.54 V (**F**) or −0.49 V (**G**)) is reduced more easily by ca. 90 mV than [Co{Co(L-cys-N,S)$_3$}(D-pen-N,O,S)]$^{2-}$ (−0.60 V (**C**) or −0.59 (**D**)).

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