April, 1984] © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **57**, 989—996 (1984) 989

Preparation and Circular Dichroism Spectra of Cobalt(III) Complexes Containing an Optically Active $NH_2CH_2CH(CH_3)X^-$-*N,X* (X=S or Se) Ligand

Kyoko Nakabayashi, Kaoru Doi, Masaaki Kojima, and Junnosuke Fujita*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

(Received September 24, 1983)

Several cobalt(III) complexes of the $[Co(apS\ or\ apSe)(N_4)]^{2+}$ type were prepared, where apS and apSe denote chiral 1-amino-2-propanethiolate-*N,S* and 1-amino-2-propaneselenolate-*N,Se* ligands, respectively, and N_4 is (en=ethylenediamine)$_2$, (*R*-chxn=(*R,R*)-1,2-cyclohexanediamine)$_2$, or tren=tris(2-aminoethyl)amine. Their circular dichroism (CD) spectra were compared with one another and with those of complexes containing such ligands as achiral 2-aminoethanethiolate-*N,S*, 2-aminoethaneselenolate-*N,Se*, or chiral 1-amino-2-propanolate-*N,O* (apO). The vicinal CD curves of *S*-apS obtained from CD spectra of the en and *R*-chxn complexes are similar and very large in magnitude in the d-d absorption band region. These curves are very similar to the CD spectrum of $[Co(S\text{-}apO)(NH_3)_4]^{2+}$. The vicinal CD curve of *S*-apSe shows a similar pattern, but the magnitude is smaller than those of the *S*-apS and *S*-apO ligands. The vicinal effect of the protonated *S*-apSH ligand is much smaller compared with that of its conjugate base (*S*-apS) ligand. The tren complexes of *S*-apS and *S*-apSe exhibit CD spectra fairly different from the vicinal CD curves of the respective ligands in the d-d absorption band region.

Nishide *et al.*[1] reported that cobalt(III) complexes containing a chiral aminoalkanolate-*N,O* chelate ligand such as *S*-apO (*S*-apOH=(*S*)-1-amino-2-propanol) exhibit exceptionally strong circular dichroism (CD) in the d-d absorption band region, which is attributed to the large vicinal effect of the alcoholate ligand. It is of interest to examine whether the corresponding thiolate-*N,S* and selenolate-*N,Se* chelate ligands give a similar effect. However, complexes with chiral aminoalkanethiolate-*N,S* or the corresponding selenolate-*N,Se* chelate ligands do not seem to be known except for $[Co(R\text{-}cys)(en)_2]^+$ and $[Co(S\text{-}pen)(en)_2]^+$ (en=ethylenediamine, *R*-cys=(*R*)-cysteinate(2-)-*N,S*, *S*-pen=(*S*)-penicillaminate(2-)-*N,S*).[2,3] The complexes with *R*-cys or *S*-pen will not be suitable for studying the vicinal effect, since the ligands have a carboxylato substituent and the chelate ring formed by *N,S* chelation will be conformationally unstable by forming hydrogen bonds between the carboxylato and other groups. In fact, the *R*-cys chelate ring in Λ-$[Co(R\text{-}cys)(en)_2]^+$ in crystals forms a δ conformer with the axially disposed carboxylato group.[3] It is known that the vicinal effect of a chiral ligand is particularly sensitive to the conformation in a complex.[4]

In the present study, we have prepared complexes of the $[Co(apS\ or\ apSe)(N_4)]^{2+}$ type, where apS and apSe denote 1-amino-2-propanethiolate-*N,S* and 1-amino-2-propaneselenolate-*N,Se* ligands, respectively, and N_4 is (en)$_2$, (*R*-chxn=(*R,R*)-1,2-cyclohexanediamine)$_2$, or tren=tris(2-aminoethyl)amine, and measured their CD spectra in order to see the vicinal effect of these chiral ligands. To our knowledge, the *S*- or *R*-apSe complexes prepared in this study are the first cobalt(III) complexes containing an optically active selenolate ligand.

Experimental

Ligands. The apSH ligand was prepared by the method of Owen[5] and resolved by the procedure of Piper *et al.*[6] to obtain $(+)_{589}$-apSH·HCl($[\alpha]_{589}=+34.2°$ (*c* 1.2, H_2O); lit, $[\alpha]_{589}=+35.3°$ (*c* 1.46, H_2O)[6]). The absolute configuration of the $(+)_{589}$-isomer has not been determined yet, but can be assigned to *S* configuration on the basis of the isomer distribution of $[Co(apS)(R\text{-}chxn)_2]^{2+}$ and related complexes, and CD spectra of these complexes (*vide infra*). Both *rac*- and $(+)_{589}$-apSH·HCl were oxidized with H_2O_2[7] to give the respective disulfide hydrochlorides $(NH_2CH_2CH(CH_3)S\text{-})_2\cdot 2HCl$ which were used to prepare cobalt(III)–apS complexes.

Racemic 2,2′-diselenodipropylamine dihydrochloride, $(NH_2CH_2CH(CH_3)Se\text{-})_2\cdot 2HCl$ was prepared by the method of Yokoyama *et al.*[8] and used to prepare cobalt(III)–apSe complexes without optical resolution.

Optically active *R*-chxn was obtained by resolving *rac*-chxn (Tokyo Kasei Kogyo Co., Ltd.) according to the method of Treptow,[9] and tren was obtained by separating from crude triethylenetetramine (Tokyo Kasei Co., Ltd.).[10]

$\Delta(\mathrm{lel}_3)$-*[Co(*R*-apS)(*R*-chxn)$_2$]SiF$_6\cdot$4H$_2$O*, $\Delta(\mathrm{oblel}_2)$-*[Co(*S*-apS)(*R*-chxn)$_2$]ZnCl$_4$*, $\Lambda(\mathrm{lelob}_2)$-*[Co(*S*-apS)(*R*-chxn)$_2$]ZnCl$_4\cdot$H$_2$O*. An aqueous solution (10 cm^3) containing *R*-chxn·2HCl (3.0 g, 16 mmol) and NaOH (1.28 g, 32 mmol) was deoxygenated by bubbling nitrogen for 15 min, and then was syringed into a deoxygenated, aqueous solution (10 cm^3) of $CoCl_2\cdot 6H_2O$ (1.90 g, 8 mmol) with stirring. The mixture became a pinkish orange suspension. To the mixture was added a deoxygenated aqueous solution (8 cm^3) containing *rac*-$(NH_2CH_2CH(CH_3)S\text{-})_2\cdot 2HCl$ (1.01 g, 4 mmol) and NaOH (0.32 g, 8 mmol). The mixture was stirred under an atmosphere of nitrogen for 3 h at room temperature. The resulting brown solution was filtered to remove a small amount of insoluble material, and the filtrate was passed through a column (ϕ2.7 cm × 5 cm) of SP-Sephadex C-25. The Sephadex charged with the product was placed on the top of a column (ϕ7 cm × 40 cm) of SP-Sephadex C-25, and the product was eluted with 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-}tartrate)_2]$, giving two main brown bands A and B. The first band A contains the Λ(*lelob*$_2$), and the second band B a mixture of the Δ(*lel*$_3$) and Δ(*oblel*$_2$) isomers. The structural assignment for the isomers was made on the basis of the elution order, formation ratio, and CD spectra of the isomers (*vide infra*). No indication of the presence of the Λ(*ob*$_3$) isomer was observed in the column chromatography. The eluate of band B was diluted 20 times with water, passed through an SP-Sephadex C-25 column (ϕ2.7 cm × 120 cm), and the complex adsorbed was eluted with 0.15 mol dm^{-3} $(NH_4)_2SO_4$. Bands B-I (Δ(*lel*$_3$)) and B-II (Δ(*oblel*$_2$)) were eluted separately in this order. Each eluate of bands A, B-I, and B-II was diluted with water and passed again through an SP-Sephadex C-25 column (ϕ1.5 cm × 2 cm). The column charged with A was washed thoroughly with 0.1 mol dm^{-3}

HCl (10 dm^3), and the complex was eluted with 0.8 mol dm^{-3} HCl. The eluate was evaporated to a small volume under reduced pressure. The concentrate was mixed with excess $ZnCl_2$ (0.2 g) in 3 mol dm^{-3} HCl (0.3 cm^3) to precipitate brown tetrachlorozincate of the complex. It was recrystallized from water–ethanol. Found: C, 29.47; H, 6.17; N, 11.52%. Calcd for $C_{15}H_{38}N_5Cl_4CoSZn$: C, 29.89; H, 6.35; N, 11.62%. The complex of B-I was eluted from the column with 0.4 mol dm^{-3} $(NH_4)_2SiF_6$. The eluate was allowed to stand overnight in a refrigerator to give purplish brown needles, which were collected and washed with cold water. Found: C, 30.26; H, 7.66; N, 11.89%. Calcd for $C_{15}H_{44}N_5CoF_6O_4SSi$: C, 30.45; H, 7.50; N, 11.84%. The complex of B-II was isolated as tetrachlorozincate by the same method as that for A. Found: C, 30.82; H, 6.31; N, 11.88%. Calcd for $C_{15}H_{36}N_5Cl_4CoSZn$: C, 30.81; H, 6.21; N, 11.98%. The total yield and the formation ratio, *Δ*(*lel*$_3$) (B-I): *Δ*(*oblel*$_2$) (B-II): *Λ*(*lelob*$_2$) (A) determined by reference to optical densities of the eluates were *ca.* 80% and 3.6:2.4:1, respectively. The main by-product was *Δ*-[Co(*R*-chxn)$_3$]$^{3+}$.

The same experiment was carried out using the optically active disulfide derived from (+)$_{589}$-apSH·HCl, instead of the racemic one. Two isomers, *Δ*(*oblel*$_2$) and *Λ*(*lelob*$_2$) were formed in the formation ratio of 2.3:1.

Λ- *and* Δ-*[Co(*S-*apS)(en)*$_2$*]SiF*$_6$*·0.5H*$_2$*O.* These complexes were prepared from $Co(ClO_4)_2\cdot 6H_2O$, en, and the optically active disulfide by a method similar to that for [Co(apS)(*R*-chxn)$_2$]$^{2+}$. After stirring for 3 h at room temperature, the product was chromatographed by use of an SP-Sephadex C-25 column and an eluent, 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$. Two brown bands of the *Λ*- and *Δ*-isomers were eluted separately, the former being eluted faster. Each eluate was diluted 20 times with water, and passed through a column of SP-Sephadex C-25. The column was washed with 0.02 mol dm^{-3} NH_4Cl (1 dm^3), and the complex was eluted with 0.4 mol dm^{-3} $(NH_4)_2SiF_6$. The eluate was left in a refrigerator to yield brown crystals. Found for the *Λ*-isomer: C, 19.76; H, 5.87; N, 16.66%. Found for the *Δ*-isomer: C, 19.94; H, 5.98; N, 16.83%. Calcd for $C_7H_{25}N_5CoF_6O_{0.5}SSi$: C, 20.00; H, 5.99; N, 16.66%. The total yield and the formation ratio, *Λ*-isomer: *Δ*-isomer based on optical densities of the eluates were *ca.* 90% and 1.9:1, respectively.

p-*[Co(*S-*apS)(tren)](ClO*$_4$*)*$_2$ *and* t-*[Co(*S-*apS)(tren)]ZnCl*$_4$*·0.5ZnCl*$_2$.[11] These complexes were prepared from $CoCl_2\cdot 6H_2O$ (8 mmol), tren (8 mmol), and the optically active disulfide (4 mmol), by a method similar to that for [Co(apS)(*R*-chxn)$_2$]$^{2+}$. After stirring for 2 d at room temperature, a small portion of the resulting solution was set aside to examine the formation ratio of the isomers, and to the rest was added 4 cm^3 of 60% $HClO_4$. Brown crystals were precipitated, collected, washed with ethanol, and recrystallized from 10^{-3} mol dm^{-3} HCl–60% $HClO_4$. Yield: 2.15 g. The complex was the *p*-isomer as confirmed by column chromatography (Dowex 50W×2, 2 mol dm^{-3} HCl). Found: C, 21.87; H, 5.37; N, 14.08%. Calcd for $C_9H_{26}N_5Cl_2CoO_8S$: C, 21.87; H, 5.30; N, 14.17%. The filtrate and washings were combined, diluted with water, and passed through a column (ϕ3 cm×35 cm) of Dowex 50W×2. By elution with 2 mol dm^{-3} HCl, two bands, T-I (dark brown, *t*-isomer) and T-II (brown, *p*-isomer) appeared separately. The eluate of fast-moving band T-I was collected and evaporated to a small volume under reduced pressure. On addition of $ZnCl_2$ (0.3 g) in 3 mol dm^{-3} HCl (0.4 cm^3) the concentrate gave pink precipitate, which was collected, washed with methanol and acetone, and air-dried. Yield: 0.18 g. Found: C, 18.91; H, 4.53; N, 18.91; Cl, 31.04%. Calcd for $C_9H_{26}Cl_5CoSZn_{1.5}$: C, 18.94; H, 4.60; N, 18.94; Cl, 31.06%. The eluate of band T-II was diluted with water, passed through an SP-Sephadex C-25 column, and the complex was eluted with 0.8 mol dm^{-3} $NaClO_4$. Upon evaporation of the eluate additional 1.3 g of the *p*-isomer perchlorate was obtained. The formation ratio of the *p*- to *t*-isomer contained in the reaction mixture was found to be 15:1 by column chromatography (Dowex 50W×2, 2 mol dm^{-3} HCl).

[Co(aeS)(en)$_2$*]Cl*$_2$*·H*$_2$*O and* Λ-*[Co(aeS)(en)*$_2$*](ClO*$_4$*)*$_2$ *(aeSH=2-aminoethanethiol).* The racemic complex was prepared by the method of Lane *et al.*[12] and resolved by column chromatography (SP-Sephadex C-25, 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$). From the first band the *Δ*-isomer was isolated as perchlorate. Found: C, 15.87; H, 4.82; N, 15.38%. Calcd for $C_6H_{22}N_5Cl_2CoO_8S$: C, 15.87; H, 4.88; N, 15.42%. The complex has been resolved by fractional crystallization of the diastereomer with $[Sb_2(d\text{-tartrate})_2]^{2-}$.[13]

Δ(lel$_3$)-*[Co(*R-*apSe)(*R-*chxn)*$_2$*](ClO*$_4$*)*$_2$*·2.5H*$_2$*O,* Δ(oblel$_2$)-*[Co(*S-*apSe)(*R-*chxn)*$_2$*](ClO*$_4$*)*$_2$*·2.5H*$_2$*O, and* Λ(lelob$_2$)-*[Co(*S-*apSe)(*R-*chxn)*$_2$*]*$^{2+}$. These complexes were prepared by a method similar to that for the corresponding apS complexes using $CoCl_2\cdot 6H_2O$ (1.19 g, 5 mmol), *R*-chxn·2HCl (1.88 g, 10 mmol), *rac*-$(NH_2CH_2CH(CH_3)Se\text{-})_2\cdot$ 2HCl (0.87 g, 2.5 mmol), and the equivalent amount of NaOH (1.0 g, 15 mol). The mixture was stirred for 3 h at room temperature. The resulting brown solution containing brown precipitate was mixed with water (1 dm^3) and the solution was poured on a column of SP-Sephadex C-25 (ϕ3 cm×150 cm). By elution with 0.2 mol dm^{-3} Na_2SO_4, the product adsorbed was separated into two brown bands, C and D. The first band C contains the *Δ*(*lel*$_3$) isomer, and the other D a mixture of the *Δ*(*oblel*$_2$) and *Λ*(*lelob*$_2$) isomers. No band indicative of the *Λ*(*ob*$_3$) isomer was observed. The eluate of band D was diluted 20 times with water, poured on a column (ϕ3 cm×70 cm)of SP-Sephadex C-25, and the complexes adsorbed were eluted with 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$. Two bands, D-I (*Λ*(*lelob*$_2$)) and D-II (*Δ*(*oblel*$_2$)) were eluted separately. Each eluate of bands C, D-I, and D-II was diluted with water, poured on a column (ϕ2 cm×2 cm) of SP-Sephadex C-25, and the complex was eluted with 0.8 mol dm^{-3} $NaClO_4$. The eluate was stored in a refrigerator overnight to yield crystals of the complex perchlorate, which were collected, washed with a small amount of cold water, and air-dried. Yields: *Δ*(*lel*$_3$)-isomer, 530 mg; *Δ*(*oblel*$_2$)-isomer, 65 mg; *Λ*(*lelob*$_2$)-isomer, 5 mg. The apSe complexes in solution are rather unstable, and decompose during the course of crystallization to decrease the yield extremely. Found for the *Δ*(*lel*$_3$)-isomer: C, 26.98; H, 5.89; N, 10.58%. Found for the *Δ*(*oblel*$_2$)-isomer: C, 27.19; H, 5.94; N, 10.58%. Calcd for $C_{15}H_{41}N_5Cl_2CoO_{10.5}Se$: C, 26.96; H, 6.18; N, 10.48%. The elemental analysis of the *Λ*(*lelob*$_2$)-isomer was not carried out because of a very low yield, and the complex was assumed to be anhydrous for determining the formation ratio of the isomers by spectrophotometric methods. The formation ratio, *Δ*(*lel*$_3$) (C): *Δ*(*oblel*$_2$) (D-II): *Λ*(*lelob*$_2$) (D-I), in the reaction mixture was 5.3:3.8:1.

Λ(R)- *and* Δ(S)-*[Co(apSe)(en)*$_2$*]ZnCl*$_4$*·H*$_2$*O and* Λ(S)- *and* Δ(R)-*[Co(apSe)(en)*$_2$*]SiF*$_6$*·H*$_2$*O.* The racemates of these diastereomers were prepared from $CoCl_2\cdot 6H_2O$ (0.4 g, 1.67 mmol), en (0.2 g, 3.34 mmol), and the diselenide (0.29 g, 0.84 mmol) by a method similar to that for [Co(apSe)(*R*-chxn)$_2$]$^{2+}$. The mixture was stirred for 3 h, and then chromatographed by use of an SE-Toyopearl[14] column (ϕ3 cm×20 cm). By elution with 0.1 mol dm^{-3} Na_2SO_4, two brown bands, E-I and E-II were eluted separately. Bands E-I and E-II contain racemates of the diastereomers, *Λ*(*R*) and *Δ*(*S*), and *Λ*(*S*) and *Δ*(*R*), respectively. Each eluate was diluted 20 times with water and passed through an SP-Sephadex C-25 column (ϕ2.7 cm×120 cm). By elution with 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$, the band was separated into two. The enantiomers being eluted faster were those of

$\Lambda(R)$ and $\Lambda(S)$ in E-I and E-II, respectively. The eluate of the $\Lambda(R)$ (or $\Delta(S)$) isomer was diluted 20 times with water and poured on an SP-Sephadex C-25 column (ϕ1.5 cm × 2 cm). The column was washed with 0.01 mol dm^{-3} HCl (8 dm^3), and the complex was eluted with 0.8 mol dm^{-3} HCl. The eluate was evaporated to a small volume under reduced pressure below 35 °C. To the concentrate was added $ZnCl_2$ (0.3 g) in 3 mol dm^{-3} HCl (0.4 cm^3). The solution was mixed with methanol and allowed to cool in a refrigerator overnight to yield brown powder, which was collected, washed with acetone, and air-dried. Found: C, 15.51; H, 4.50; N, 12.91%. Calcd for $C_7H_{26}N_5Cl_4CoSeZn$: C, 15.53; H, 4.84; N, 12.94%. The eluate of the $\Lambda(S)$ (or $\Delta(R)$) isomer was diluted 20 times with water and passed through an SP-Sephadex C-25 column (ϕ1.5 cm × 2 cm). The column was washed thoroughly with 0.01 mol dm^{-3} NH_4Cl (10 dm^3), and the complex was eluted with 0.4 mol dm^{-3} $(NH_4)_2SiF_6$. The eluate was allowed to cool in a refrigerator overnight to yield brown needles, which were collected, washed with cold water, and air-dried. Found: C, 17.75; H, 5.56; N, 14.94%. Calcd for $C_7H_{26}N_5CoF_6OSeSi$: C, 17.65; H, 5.50; N, 14.70%. The formation ratio, $\Lambda(R)+\Delta(S)$(E-I)$:\Lambda(S)+\Delta(R)$(E-II) determined by optical densities of the eluates was 1:4.

$(-)_{589}$-p-$[Co(S\text{-}apSe)(tren)](ClO_4)_2$ and t-$[Co(rac\text{-}apSe)(tren)](ClO_4)_2\cdot H_2O$. A mixture of racemic *p*- and *t*-[Co(apSe)(tren)]$^{2+}$ was prepared from $CoCl_2\cdot 6H_2O$ (4 mmol), tren (4 mmol), and the diselenide (2 mmol) by a method similar to that for [Co(apSe)(*R*-chxn)$_2$]$^{2+}$. The mixture was stirred for 4 d at room temperature, and then concd HCl was added to make the solution slightly acidic. The solution was chromatographed in a similar manner to that for [Co(apSe)(*R*-chxn)$_2$]$^{2+}$. By elution with 0.1 mol dm^{-3} Na_2SO_4 adjusted to pH 2 with HCl, two bands appeared; a fast-moving dark brown band (*p*-isomer) and a slow-moving dark green-brown one (*t*-isomer). The *p*-isomer was isolated as perchlorate by the same method as that for [Co(apSe)(*R*-chxn)$_2$]$^{2+}$. Yield: 700 mg. The *t*-isomer was isolated as tetrachlorozincate by the same method as that for Λ-[Co(*R*-apSe)(en)$_2$]$^{2+}$ and then converted into perchlorate by use of a QAE-Sephadex (ClO_4^- form) column. Yield: 100 mg. Found for the *t*-isomer: C, 19.35; H, 4.58; N, 12.61%. Calcd for $C_9H_{28}N_5Cl_2CoO_9Se$: C, 19.33; H, 5.04; N, 12.52%.

The *p*-isomer was resolved as follows; a mixture of the *p*-isomer perchlorate (0.27 g, 0.5 mmol) and potassium *d*-tartrate hemihydrate (0.117 g, 0.5 mmol) in 10 cm^3 of water was stirred for 30 min. The solution was evaporated to 1.5 cm^3 under reduced pressure below 35 °C and filtered to remove the potassium perchlorate precipitated. The filtrate was mixed with methanol (5 cm^3) and cooled (−10 °C) overnight. Brown granular crystals which formed were collected and recrystallized three times from water–methanol. Yield: 32 mg. No change in the $\Delta\varepsilon$ value was observed with further recrystallization. This diastereomer was converted into perchlorate by use of a QAE-Sephadex (ClO_4^- form) column. Found: C, 19.74; H, 4.72; N, 12.93%. Calcd for $C_9H_{26}N_5Cl_2CoO_8Se$: C, 19.97; H, 4.84; N, 12.93%. Attempts to resolve the *t*-isomer by column chromatography and by chemical methods were all unsuccessful.

Λ-$[Co(aeSe)(en)_2](ClO_4)_2$(aeSeH=2-Aminoethaneselenol). The racemic complex was prepared by the method of Stein *et al.*[15] and resolved by SP-Sephadex C-25 column chromatography using 0.1 mol dm^{-3} $Na_2[Sb_2(d\text{-tartrate})_2]$ as an eluent. The fast-moving Λ-isomer was isolated as perchlorate by the same method as that for [Co(apSe)(*R*-chxn)$_2$]$^{2+}$. Found: C, 14.23; H, 4.57; N, 13.92%. Calcd for $C_6H_{22}N_5Cl_2CoO_8Se$: C, 14.38; H, 4.43; N, 13.98%. The CD spectrum agreed well with that reported by Konno *et al.*[16] who resolved the complex by fractional crystallization of the diastereomer with $[Sb_2(d\text{-tartrate})_2]^{2-}$.

$[Co(S\text{-}apOH)(NH_3)_4]Br_3\cdot 2.5H_2O$. This complex was prepared by the method of Nishide *et al.*[1]

Measurements. Absorption and CD spectra were recorded on a Hitachi 323 spectrophotometer and a JASCO J-40 CS spectropolarimeter, respectively. Optical rotations at 589 nm were measured with a JASCO DIP-4 polarimeter.

Results and Discussion

Preparation and Structural Assignment of the Complexes. The present [Co(apS or apSe)(N$_4$)]$^{2+}$-type complexes were prepared by oxidizing Co^{II}-N$_4$ species with the disulfide or diselenide, $(NH_2CH_2CH(CH_3)X-)_2$ (X=S or Se) according to the method for analogous aminoalkanethiolato-*N,S*[12,17] or selenolato-*N,Se*[15] complexes of cobalt(III). Time required for the oxidation was nearly the same between the apS and apSe complexes, but different between the en and *R*-chxn, and the tren complexes. While the former complexes took a few hours to complete the oxidation, the latter complexes of apS and apSe 2 and 4 d, respectively. Such differences in reactivity seem to be related with reducing strength of Co^{II}-N$_4$ species toward the disulfide and diselenide. The apS complexes are stable in acidic solution, but slowly decompose in basic solution to give Co^{II} species. The apSe complexes are less stable than the corresponding apS complexes under the same conditions. The *p*-[Co(apSe)(tren)]$^{2+}$ complex in solution is the least stable among the complexes prepared in this study. Thus spectral measurements of the apSe complexes were carried out in 0.01 mol dm^{-3} $HClO_4$ solutions. The lower stability of the apSe complexes might be related to the fact that the complexes exhibit Se-to-Co^{III} charge transfer bands at lower energy (*ca.* 33000 cm^{-1}) than that of the corresponding bands of apS complexes (*ca.* 35000 cm^{-1}); coordinated selenolates are considered to be better reductants than coordinated thiolates.[15]

Except for the pink crystals of *t*-[Co(apS)(tren)]$ZnCl_4\cdot 0.5ZnCl_2$, all the complexes are brown in the solid state. The pink *t*-[Co(apS)(tren)]$ZnCl_4\cdot 0.5ZnCl_2$ complex indicates the ligation of the S atom to Zn^{2+} in crystals. Interaction between soft metal ions and thiolato cobalt(III) complexes have been investigated in some detail.[18] For example, a brown solution of [Co(aeS)(en)$_2$]$^{2+}$ in water turns red upon addition of Ag$^+$ or $HgCH_3^+$.[18] Since Zn^{2+} is a less soft acid than those ions, it interacts with the S atom of apS only in the solid state of *t*-[Co(apS)(tren)]$ZnCl_4\cdot 0.5ZnCl_2$. The interaction disappears when the complex is dissolved in water, a brown solution being obtained. The absorption spectrum is identical with that of the corresponding perchlorate which was prepared by use of an anion-exchange resin. Other tetrachlorozincates of the apS and apSe complexes prepared in this study form brown crystals and will involve no interaction between Zn^{2+} and the S or Se atom even in the solid state.

Both chelate rings of *S*(or *R*)-apS and *S*(or *R*)-apSe will be stabilized in the δ(or λ)-*gauche* conformation with the methyl group disposed equatorially, while the *R*-chxn chelate ring is forced to take the λ-*gauche* conformation. Thus there are four possible diastereomers of $[Co(apX)(R\text{-}chxn)_2]^{2+}$ (X=S, Se), which can be designated as $lel_3(\Delta(\lambda\lambda\lambda))$, $oblel_2(\Delta(\delta\lambda\lambda))$, $lelob_2(\Lambda(\delta\lambda\lambda))$, and $ob_3(\Lambda(\lambda\lambda\lambda))$. Each of the apS and apSe complexes formed three isomers in the preparation where the *rac*-dicalcogenide was used. The isomers were assigned on the basis of the elution order in column chromatography, the isomer distribution, and the CD spectra. In column chromatography, the lel_3 isomer will be eluted faster by elution with SO_4^{2-}, since its structure is most favorable in forming an ion pair with SO_4^{2-}.[19,20] By elution with $[Sb_2(d\text{-}tartrate)_2]^{2-}$, on the other hand, a Λ-isomer is usually eluted faster than a Δ-one.[21] For the isomer distribution, the Δ-isomer will be formed in a larger amount than the Λ-one, since the $lel_2(\Delta(\lambda\lambda))$ structure formed by two *R*-chxn ligands is less crowded than the $ob_2(\Lambda(\lambda\lambda))$ one.[22] For a relation between optical activity and absolute configuration of a complex, it is known that a complex with a positive main CD band in the first absorption band region takes Λ configuration (Figs. 1 and 2).[23] On the basis of these diagnoses, all the isomers of $[Co(apX)(R\text{-}chxn)_2]^{2+}$ (X=S, Se) were assigned as given in the experimental section.

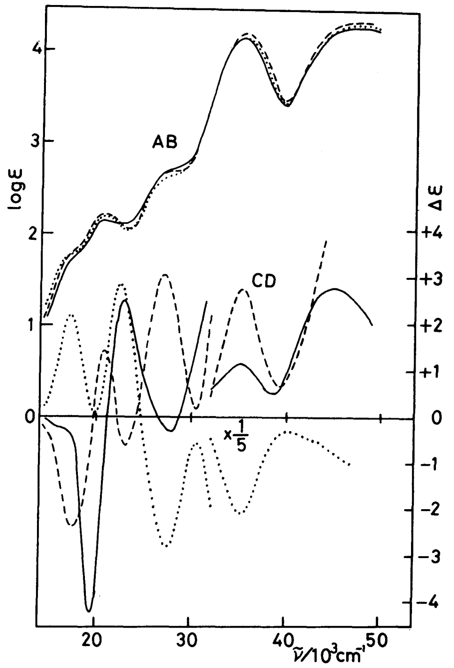

Fig. 1. Absorption and CD spectra of $\Delta(oblel_2)$-$[Co(S\text{-}apS)(R\text{-}chxn)_2]^{2+}$ (——), $\Delta(lel_3)$-$[Co(R\text{-}apS)(R\text{-}chxn)_2]^{2+}$ (-----), and $\Lambda(lelob_2)$-$[Co(S\text{-}apS)(R\text{-}chxn)_2]^{2+}$ (·····).

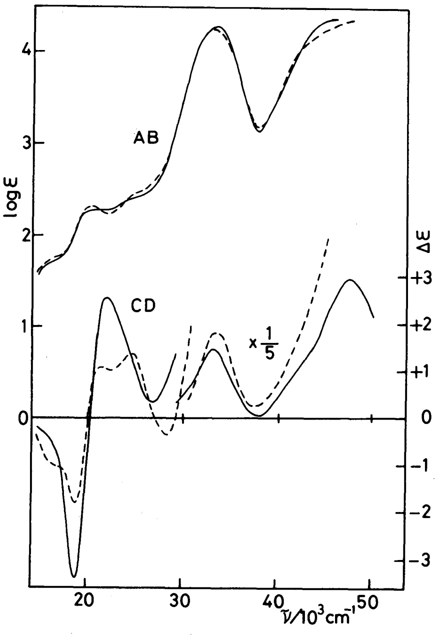

Fig. 2. Absorption and CD spectra of $\Delta(oblel_2)$-$[Co(S\text{-}apSe)(R\text{-}chxn)_2]^{2+}$ (—) and $\Delta(lel_3)$-$[Co(R\text{-}apSe)(R\text{-}chxn)_2]^{2+}$ (---).

In order to assign the absolute configuration of $(+)_{589}$-apSH·HCl, the same bis(*R*-chxn) complex was

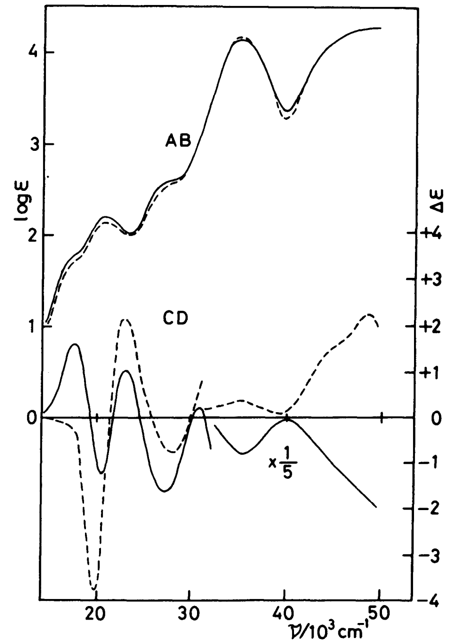

Fig. 3. Absorption and CD spectra of Λ-$[Co(S\text{-}apS)(en)_2]^{2+}$ (——) and Δ-$[Co(S\text{-}apS)(en)_2]^{2+}$ (----).

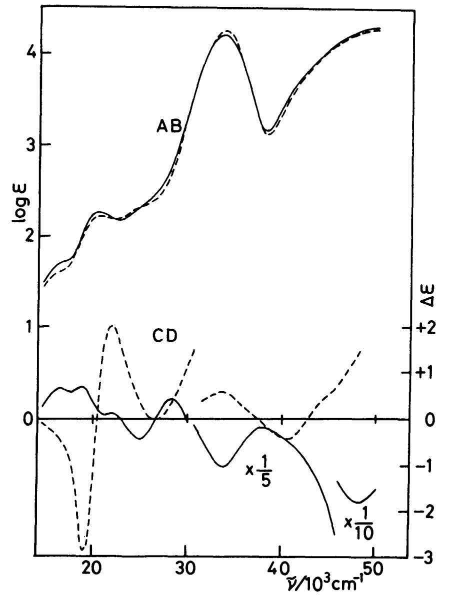

Fig. 4. Absorption and CD spectra of Λ-$[Co(S\text{-}apSe)(en)_2]^{2+}$ (——) and Δ-$[Co(S\text{-}apSe)(en)_2]^{2+}$ (----).

prepared by use of the optically active disulfide derived from (+)$_{589}$-apSH·HCl. Only two isomers, Δ(*oblel*$_2$) ($\delta\lambda\lambda$) and Λ(*lelob*$_2$)($\delta\lambda\lambda$) were formed. Thus the absolute configuration of (+)$_{589}$-apSH·HCl can be assigned to *S*, since the *S*-apS chelate ring will be stabilized in the *δ-gauche* conformation as stated previously.

In a similar manner, structures of diastereomeric pairs, Λ- and Δ-$[Co(S\text{-}apS)(en)_2]^{2+}$, and Λ- and Δ-$[Co(S\text{-}apSe)(en)_2]^{2+}$ were assigned. The absorption and CD spectra of these complexes are given in Figs. 3 and 4. The $[Co(apX)(tren)]^{2+}$(X=S, Se) complex forms two geometrical isomers, *p* and *t*.[11] The isomers were assigned by comparing the elution order in column chromatography, the formation ratio, and the absorption spectra with those of *p*- and *t*-$[Co(aeS)(tren)]^{2+}$ reported previously.[24] The optically active *p*- and *t*-$[Co(S\text{-}apS)(tren)]^{2+}$ isomers were prepared by use of the optically active disulfide. The optically active *p*-isomer of apSe was obtained by resolving the racemate with *d*-tartrate ions, but the resolution of the other *t*-isomer was not achieved. The absorption and CD spectra of the tren complexes are given in Figs. 5 and 6. The spectral data of all the complexes are listed in Table 1.

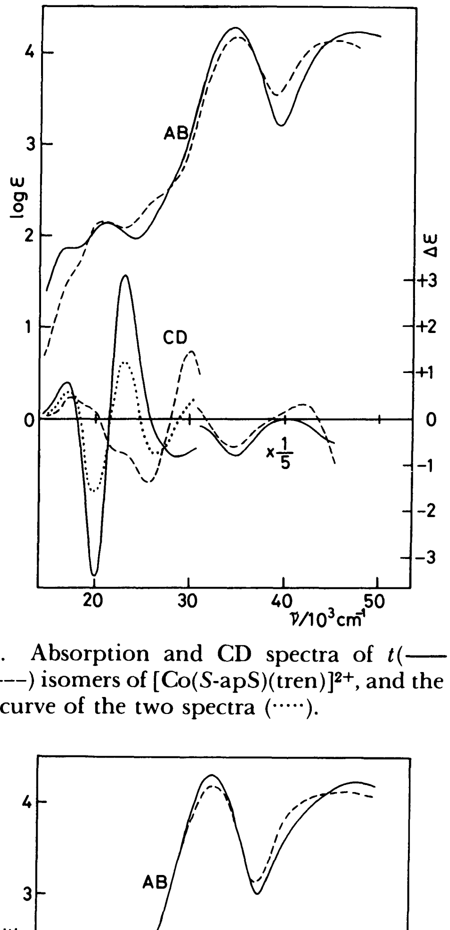

Fig. 5. Absorption and CD spectra of *t*(——) and *p*(----) isomers of $[Co(S\text{-}apS)(tren)]^{2+}$, and the mean CD curve of the two spectra (·····).

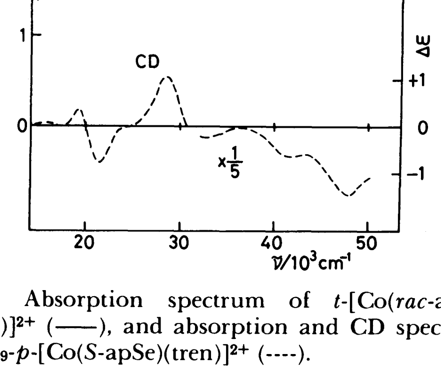

Fig. 6. Absorption spectrum of *t*-[Co(*rac*-apSe)(tren)]$^{2+}$ (——), and absorption and CD spectra of (−)$_{589}$-*p*-$[Co(S\text{-}apSe)(tren)]^{2+}$ (----).

Absorption and CD Spectra. All the apS and apSe complexes show absorption spectra similar to one another; the spectra exhibit the split first absorption band, shoulder in the second absorption band region, and the strong X-to-Co^{III} (X=S, Se) and N-to-Co^{III} charge transfer bands in the ultraviolet region. All the bands of apSe complexes shift to the low energy side compared with the corresponding bands of apS complexes. These spectral features are quite similar to those of $[Co(aeX)(en)_2]^{2+}$ (X=S, Se) reported previously.[12,13,15,25] Although spectral differences among the isomers are very small in the *R*-chxn and en complexes of apX (X=S, Se), the spectra of *p*- and *t*-$[Co(apX)(tren)]^{2+}$ (X=S, Se) isomers are fairly different from each other. Some tren complexes with a similar chelate ligand such as aeS[24] or an amino acidate ion[26–28] also show a fairly large difference between the *p*- and *t*-isomers. The *p*- and *t*-isomers are geometrical isomers in which the X atom (X=O, S, Se) occupies the position cis and trans, respectively, to the tertiary amine nitrogen which will exert a weaker ligand field than the primary amine nitrogens. Thus the splitting of the d-d transition components would differ between the geometrical isomers to cause different d-d absorption spectra.[29]

In Fig. 3 are shown CD spectra of Δ- and Λ-$[Co(S\text{-}apS)(en)_2]^{2+}$. The spectra in the d-d absorption band region are not enantiomeric, but rather similar in pattern. In general, the optical activity of a metal complex is understood as a superposition of the configurational (chiral arrangement of ligands around the metal ion) and the vicinal (chiral ligand) effects. When the optical activity of Δ- and Λ-$[Co(S\text{-}apS)(en)_2]^{2+}$ is this case, the spectra suggest that the vicinal effect of *S*-apS is stronger than the configurational effect in these isomers. Figures 7 and 8 show the configurational ($\Delta\varepsilon(\Lambda)=1/2\{\Delta\varepsilon[\Lambda(S)]-\Delta\varepsilon[\Delta(S)]\}$) and vicinal ($\Delta\varepsilon(S)=1/2\{\Delta\varepsilon[\Lambda(S)]+\Delta\varepsilon[\Delta(S)]\}$) effect curves, respectively, obtained from the observed CD spectra. The configurational CD curve for $\Delta\varepsilon(\Lambda)$ is very similar to the observed CD spectrum of Λ-$[Co(aeS)(en)_2]^{2+}$ indicating that the additivity in CD between the configurational and vicinal effects holds for $[Co(S\text{-}apS)(en)_2]^{2+}$. The vicinal CD curve of *S*-apS quite resembles that calculated from the observed CD spectra of $\Delta(\lambda\lambda\lambda)$-$[Co(R\text{-}apS)(R\text{-}chxn)_2]^{2+}$ and $\Delta(\delta\lambda\lambda)$-$[Co(S\text{-}apS)(R\text{-}chxn)_2]^{2+}$($1/2\{\Delta\varepsilon[\Delta(\delta\lambda\lambda)]$-$\Delta\varepsilon[\Delta(\lambda\lambda\lambda)]\}$). Thus it is clear that in the *S*-apS complexes, the vicinal effect is stronger than the configurational effect. The large vicinal effect of *S*-apS corresponds well to those of the structurally similar *S*-apO and related deprotonated aminoalkanolate ligands.[1] In Fig. 8 is given the CD

TABLE 1. ABSORPTION AND CD SPECTRAL DATA OF THE COMPLEXES

Complex	Absorption: $\tilde{\nu}/10^3\,cm^{-1}$ (log ε)	CD: $\tilde{\nu}/10^3\,cm^{-1}$ ($\Delta\varepsilon$)
Δ-[Co(R-apS)(R-chxn)$_2$]$^{2+\,a)}$	17.2(sh, 1.8), 20.5(2.23), 27.5(sh, 2.7) 35.0(4.17), 46.5(4.30)	17.6(−2.37), 20.7(+1.48), 23.2(−0.57) 27.2(+3.09), 35.2(+14.0)
Δ-[Co(R-apS)(R-chxn)$_2$]$^{2+\,a)}$	17.2(sh, 1.7), 20.6(2.16), 27.5(sh, 2.7), 35.1(4.11), 47.0(4.25)	19.6(−4.22), 22.8(+2.53), 27.8(−0.31), 35.1(+5.92), 45.0(+13.8)
Λ-[Co(R-apS)(R-chxn)$_2$]$^{2+\,a)}$	17.2(sh, 1.8), 20.5(2.19), 27.5(sh, 2.6), 35.0(4.13), 47.1(4.26)	17.1(+2.23), 22.3(+2.88), 27.5(−2.80), 35.1(−10.3)
Λ-[Co(R-apS)(en)$_2$]$^{2+\,a)}$	17.3(sh, 1.7), 20.6(2.17), 27.5(sh, 2.6), 35.3(4.13)	17.5(+1.62), 20.4(−1.21), 23.0(+1.03), 27.1(−1.61), 30.8(+0.23), 35.2(−3.97)
Δ-[Co(R-apS)(en)$_2$]$^{2+\,a)}$	17.3(sh, 1.7), 20.6(2.11), 27.7(sh, 2.5), 35.1(4.14)	19.7(−3.70), 23.0(+2.16), 28.0(−0.77), 35.1(+1.60)
p-[Co(R-apS)(tren)]$^{2+\,a)}$	17.2(sh, 1.5), 20.6(2.16), 25.3(sh, 2.3), 34.7(4.14), 45.0(4.11)	17.4(+0.46), 19.2(sh, +0.25), 22.2(sh, −0.7), 25.7(−1.41), 30.2(+1.44), 34.7 (−3.13), 42.1(+1.54)
t-[Co(R-apS)(tren)]$^{2+\,a)}$	16.9(1.85), 20.9(2.13), 34.3(4.23), 47.2(4.20)	16.9(+0.75), 20.0(−3.45), 23.1(+3.09), 28.9(−0.83), 35.1(−4.18)
Λ-[Co(aeS)(en)$_2$]$^{2+\,a)}$	17.0(sh, 1.7), 20.7(2.16), 27.8(sh, 2.5), 35.3(4.14)	17.2(+0.90), 19.2(+1.31), 21.9(−0.32), 26.3(−0.67), 35.3(−5.15), 48.5(−11.3)
Λ-[Co(S-apSH)(en)$_2$]$^{3+\,b)}$	20.5(2.14), 28.8(2.17), 37.4(3.85), 45.7(4.15)	19.7(+1.94), 22.7(−0.27), 26.5(+0.09), 29.9(+0.18), 40.9(−12.0), 47.6(−12.6)
Λ-[Co(S-apSH)(en)$_2$]$^{3+\,b)}$	20.4(2.15), 28.8(2.18), 37.5(3.89), 45.7(4.20)	20.2(−2.67), 25.8(−0.07), 28.3(+0.14), 36.0(−2.72), 41.7(+14.6), 46.5(+13.9)
Λ-[Co(aeSH)(en)$_2$]$^{3+\,b)}$	20.5(2.16), 29.0(2.37), 37.3(3.84), 46.0(4.15)	19.9(+2.17), 26.5(+0.11), 31.1(+0.20), 35.2(+2.68), 40.2(−5.36)
Δ-[Co(R-apSe)(R-chxn)$_2$]$^{2+\,c)}$	16.5(sh, 1.8), 20.1(2.30), 24.5(sh, 2.4), 33.1(4.22)	16.5(sh, −1.03), 18.7(−1.83), 21.5 (+1.11), 24.4(+1.43), 28.3(−0.33), 33.5(+9.33), 48.0(+30.3)
Δ-[Co(S-apSe)(R-chxn)$_2$]$^{2+\,c)}$	16.5(sh, 1.7), 20.5(2.26), 25.0(sh, 2.4), 33.2(4.24)	18.8(−3.34), 21.9(+2.64), 33.3(+7.56), 47.5(+15.2)
Λ-[Co(S-apSe)(en)$_2$]$^{2+\,c)}$	16.5(sh, 1.7), 20.2(2.26), 33.4(4.20),	16.5(+0.67), 19.0(+0.70), 22.0(+0.11), 24.9(−0.44), 28.0(+0.40), 33.8(−5.26), 48.0(−18.2)
Δ-[Co(S-apSe)(en)$_2$]$^{2+\,c)}$	16.5(sh, 1.6), 20.3(2.22), 33.4(4.22)	19.0(−2.84), 22.0(+2.01), 33.6(+3.12), 40.7(−2.03)
p-[Co(S-apSe)(tren)]$^{2+\,c)}$	16.0(sh, 1.6), 20.4(2.29), 32.8(4.17), 47.0(4.11)	15.5(+0.01), 19.2(+0.37), 21.4(−0.78), 28.5(+1.10), 32.8(−1.10), 41.5(−3.21), 48.0(−7.60)
t-[Co(rac-apSe)(tren)]$^{2+\,c)}$	16.0(sh, 1.8), 20.6(2.23), 32.6(4.29), 48.0(4.20)	
Λ-[Co(aeSe)(en)$_2$]$^{2+\,c)}$	16.5(sh, 1.7), 20.3(2.23), 24.8(sh, 2.3), 33.4(4.22)	16.7(sh, +0.70), 18.9(+1.27), 22.2(sh, −0.45), 24.5(−0.58), 27.9(+0.17), 33.6 (−4.63)

Solvent, a): water. b): concd H_2SO_4, c): 0.01 mol dm^{-3} $HClO_4$.

spectrum of [Co(S-apO)(NH_3)$_4$]$^{2+}$ for comparison. The spectrum is similar in both pattern and magnitude to the vicinal CD curve of *S*-apS, although the CD bands shift to the high energy side compared with the corresponding bands of *S*-apS. The result also supports the previous assignment that (+)$_{589}$-apSH·HCl has *S* configuration.

In order to observe the vicinal effect of *S*-apS in the [Co(S-apS)(N_4)]$^{2+}$-type complex, it is desirable to prepare [Co(S-apS)(NH_3)$_4$]$^{2+}$. However, attempts to prepare this complex have been unsuccessful, and instead we have prepared [Co(S-apS)(tren)]$^{2+}$, where no configurational chirality is involved. In Fig. 5 are shown the CD spectra of *p*- and *t*-[Co(S-apS)(tren)]$^{2+}$. In the d-d absorption band region, the isomers exhibit CD spectra quite different from each other. The CD pattern of the *t*-isomer resembles the calculated vicinal CD curve of *S*-apS (Fig. 8), but the magnitude is *ca.* 1.5 times as large. Similar differences in CD spectra between *p*- and *t*-isomers have been reported for some tren complexes.$^{1,32)}$ The tren complex is not suitable for observing the vicinal effect of *S*-apS in the [Co(S-apS)(N_4)]$^{2+}$-type complexes. It is interesting to note, however, that the mean curve of the CD spectra of *p*- and *t*-[Co(S-apS)(tren)]$^{2+}$ resembles more the calculated curve than the individual CD spectra (Fig. 5).

Nishide *et al.*$^{1)}$ reported that absorption and CD spectra of S-apO and related aminoalkanolato-*N,O* complexes of cobalt(III) change remarkably with changes in pH of solutions. Similar spectral changes were observed for the *S*-apS complexes. The changes are instantaneous and reversible, and attributed to an acid-base equilibrium of the thiol proton.$^{33)}$ Figure 9 shows the absorption and CD spectra of Δ- and Λ-[Co(S-apSH)(en)$_2$]$^{3+}$ in concd H_2SO_4, where the thiolate chelates will be completely protonated.$^{33)}$ Both isomers show much more simple absorption and CD patterns than those of their conjugate bases (Fig. 3). In the first absorption band region, the protonated Λ-isomer gives a large positive and a small negative CD

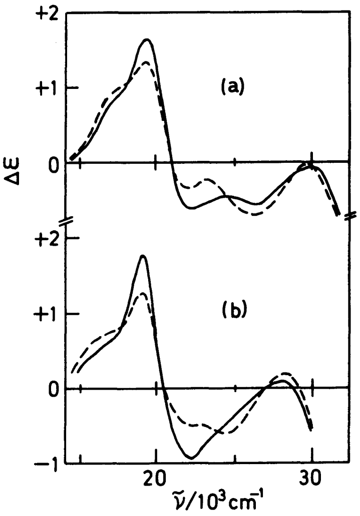

Fig. 7. (a): Configurational effect CD (Δε)Λ)) curve of $[\mathrm{Co}(S\text{-apS})(\mathrm{en})_2]^{2+}$ (——) and the observed CD spectrum of Λ-$[\mathrm{Co(aeS)(en)_2}]^{2+}$ (----). (b): Configurational effect CD (Δε)Λ)) curve of $[\mathrm{Co}(S\text{-apSe})(\mathrm{en})_2]^{2+}$ (——) and the observed CD spectrum of Λ-$[\mathrm{Co(aeSe)(en)_2}]^{2+}$ (----).

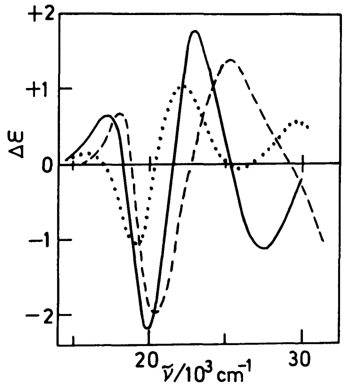

Fig. 8. Vicinal effect CD curves of S-apS (——) and S-apSe (·····) calculated from Δ- and Λ-$[\mathrm{Co}(S\text{-apX})(\mathrm{en})_2]^{2+}$ (X=S, Se), and the observed CD spectrum of $[\mathrm{Co}(S\text{-apO})(\mathrm{NH_3})_4]^{2+}$ (----).

band, and the other Δ-isomer only a large negative band. These CD patterns are very similar to those of the corresponding Λ(*lel*)- and Δ(*ob*)-isomers of a bis(en) complex containing a chiral diamine such as (*S*)-1,2-propanediamine.[34] The additivity between the configurational and vicinal effects also holds in the protonated complexes as shown in Fig. 10(a), where the configurational CD curve (Δε(Λ)) is compared with the CD spectrum of Λ-$[\mathrm{Co(aeSH)(en)_2}]^{3+}$ in concd $\mathrm{H_2SO_4}$. The calculated vicinal CD curve of *S*-apSH shows a single negative band in the first absorption band region, and the magnitude is much smaller than that of the vicinal CD curve of the conjugate base, *S*-apS (Figs. 8 and 10(b)). Very similar CD changes have been observed between the corresponding *S*-apO and *S*-apOH, and between related chiral aminoalkanolato and alcohol complexes. The results together with those described previously lead to the conclusion that aminoalkanethiolato-*N,S* cobalt(III) complexes exhibit optical activity very similar to that of the corresponding aminoalkanolato-*N,O* complexes in the d-d absorption band region.

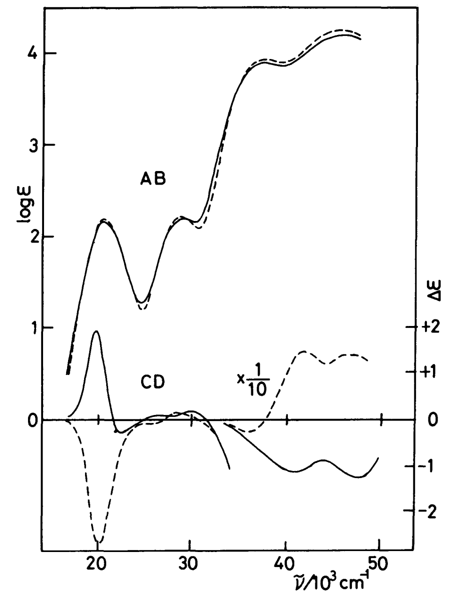

Fig. 9. Absorption and CD spectra of Λ(——) and Δ(----) isomers of $[\mathrm{Co}(S\text{-apSH})(\mathrm{en})_2]^{3+}$ in concd $\mathrm{H_2SO_4}$.

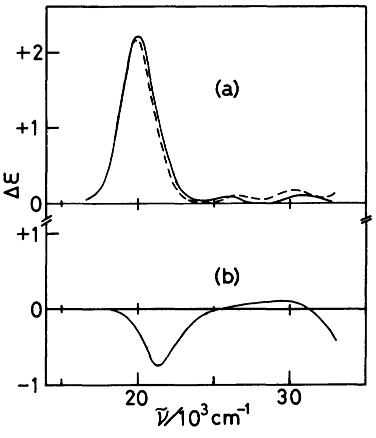

Fig. 10. (a): Configurational effect CD(Δε(Λ)) curve of $[\mathrm{Co}(S\text{-apSH})(\mathrm{en})_2]^{3+}$(——) and the observed CD spectrum of Λ-$[\mathrm{Co(aeSH)(en)_2}]^{3+}$ in concd $\mathrm{H_2SO_4}$ (-----). (b): Vicinal effect CD curve of *S*-apSH (——) calculated from Δ- and Λ-$[\mathrm{Co}(S\text{-apSH})(\mathrm{en})_2]^{3+}$.

On the other hand, optical activity of the apSe complexes seems to somewhat differ from that of the apS complexes in the d-d absorption band region. The CD spectra of Λ(*lel*)-$[\mathrm{Co}(S\text{-apSe})(\mathrm{en})_2]^{2+}$ and Δ(*lel*$_3$)-$[\mathrm{Co}(R\text{-apSe})(R\text{-chxn})_2]^{2+}$ are fairly different from those of the corresponding isomers of the apS complexes, although other isomers of these en and *R*-chxn complexes show CD patterns similar to those of the corresponding apS complexes (Figs. 1—4). In Figs. 7 and 8 are given the configurational (Δε(Λ)) and vicinal (Δε(*S*)) effect curves, respectively, obtained from the CD spectra of Λ- and Δ-$[\mathrm{Co}(S\text{-apSe})(\mathrm{en})_2]^{2+}$. The configurational effect resembles the CD spectrum of Λ-$[\mathrm{Co(aeSe)(en)_2}]^{2+}$, and the vicinal effect curve is also similar to that derived from the *R*-chxn complexes. Thus the additivity between the two effects also holds for the apSe complexes. While the configurational CD curve of $[Co(S\text{-apSe})(en)_2]^{2+}$ is quite similar to that of the corresponding *S*-apS complex, the vicinal CD curve of *S*-apSe is fairly small in magnitude as compared with those of *S*-apS and *S*-apO, although these curves show a similar pattern, giving (+), (−), and (+) bands from small to large wave numbers in the first absorption band region. Thus it can be concluded that the vicinal effect of the aminoalkaneselenolate-*N*, *Se* chelate ligands is smaller than those of the corresponding thiolate-*N,S* and alcoholate-*N,O* ligands.

We have shown that the protonated *S*-apSH complexes give absorption and CD spectra quite different from those of the deprotonated ones and similar to those of the corresponding (*S*)-1,2-propanediamine complexes. However, the protonated *S*-apSe complexes were not so stable as to allow the spectral measurements.

Figure 6 shows the CD spectrum of $(-)_{589}$-*p*-$[Co(apSe)(tren)]^{2+}$. The spectrum is quite different from the vicinal CD curve of *S*-apSe obtained from $[Co(S\text{-apSe})(en)_2]^{2+}$ as has been observed for the corresponding *S*-apS complexes. However, the fact that the CD magnitude is smaller than that of the corresponding *S*-apS complex agrees with the previous result that the vicinal effect of *S*-apSe is smaller than that of *S*-apS. The absolute configuration of apSe in the $(-)_{589}$-isomer may be assigned to *S*, since the CD pattern is rather similar to that of the corresponding *S*-apS complex. All attempts to resolve the *t*-isomer were unsuccessful.

The authors with to thank the Ministry of Education for Scientific Research Grant-in-Aid No. 58470032.

References

1) T. Nishide, K. Ogino, J. Fujita, and K. Saito, *Bull. Chem. Soc.* Jpn., **47**, 3057 (1974).

2) D. L. Herting, C. P. Sloan, A. W. Cabral, and J. H. Krueger, *Inorg. Chem.*, **17**, 1649 (1978).

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

4) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 3237 (1977); M. Kojima, M. Fujita, and J. Fujita, *ibid.*, **50**, 898 (1977).

5) T. C. Owen, *J. Chem. Soc., C*, **1967**, 1374.

6) J. R. Piper and T. P. Johnstone, *J. Org. Chem.*, **29**, 1657 (1964).

7) A. H. Nathan and M. T. Bogert, *J. Am. Chem. Soc.*, **63**, 2361 (1941).

8) A. Yokoyama, H. Sakurai, and T. Tanaka, *Chem. Pharm. Bull.*, **19**, 1089 (1971).

9) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

10) H. B. Jonassen and G. T. Strickland, *J. Am. Chem. Soc.*, **80**, 312 (1958).

11) The S (or Se) atoms in the *p*- and *t*-isomers are trans to the primary (*p*) and tertiary (*t*) tren amine nitrogens, respectively.

12) R. H. Lane, F. A. Sedor, M. J. Gilroy, P. F. Eisenhardt, J. P. Bennett, Jr., R. X. Ewall, and L. E. Bennett, *Inorg. Chem.*, **16**, 93 (1977).

13) K. Yamanari, J. Hidaka, and Y. Shimura, *Bull.Chem. Soc. Jpn.*, **50**, 2299 (1977).

14) M. Fujita, Y. Yoshikawa, and H. Yamatera, *Chem. Lett.*, **1982**, 437.

15) C. A. Stein, P. E. Ellis, Jr., R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **15**, 1618 (1976).

16) T. Konno, K. Okamoto, and J. Hidaka, *Chem. Lett.*, **1982**, 535.

17) D. L. Nosco and E. Deutsch, *Inorg. Synth.*, **21**, 19 (1982) and references cited therein.

18) M. J. Heeg, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **18**, 2036 (1979).

19) Y. Yoshikawa and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **6**, 523 (1970).

20) K. Sakakibara, Y. Yoshikawa, and H. Yamatera, *Bull. Chem. Soc. Jpn.*, **52**, 2725 (1979).

21) M. Kojima, H. Yamada, H. Ogino, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 2325 (1977).

22) S. E. Harnung, B. S. Sφrensen, I. Creaser, H. Maegaard, U. Pfenninger, and C. E. Schaffer, *Inorg. Chem.*, **15**, 2123 (1976).

23) See for example: C. J. Hawkins, "Absolute Configuration of Metal Complexes," John Wiley & Sons, New York (1971), p. 148.

24) W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*,**17**, 2165 (1978).

25) K. Hori, *Nippon Kagaku Zasshi*, **90**, 561 (1969).

26) E. Kimura, S. A. Yang, and J. P. Collman, *Inorg. Chem.*, **9**, 1183 (1970).

27) Y. Mitsui, J. Watanabe, Y. Harada, T. Sakkamaki, Y.Iitaka, Y. Kushi, and E. Kimura, *J. Chem. Soc., Dalton Trans.*, **1976**, 2095.

28) K. Akamatsu, T. Komorita, and Y. Shimura, *Bull.Chem. Soc. Jpn.*, **54**, 3000 (1981).

29) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).

30) B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965); C. T. Liu and B. E. Douglas, *ibid.*, **3**, 1356 (1964).

31) K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1965).

32) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 139 (1983).

33) I. K. Adzamli, D. L. Nosco, and E. Deutsch, *J. Inorg. Nucl. Chem.*, **42**, 1364 (1979).

34) A. J. McCaffery, S. F. Mason, B. J. Norman, and A. M. Sargeson, *J. Chem. Soc., A*, **1968**, 1304.