May, 1984] © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 1227—1234 (1984) 1227

# Synthesis and Stereoselectivity of Cobalt(III) Complexes of Quadridentate Ligands Possessing SNNS Array of Donor Atoms

Kazuaki YAMANARI,* Norimatsu TAKESHITA, and Yoichi SHIMURA
*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560*

(Received November 17, 1983)

Several thiolato complexes of $[Co(SNNS)(diamine)]^+$ type were prepared (diamine stands for en=1,2-ethanediamine, *R*-pn=(*R*)-1,2-propanediamine, and *RR*-chxn=(*R,R*)-1,2-cyclohexanediamine) and characterized from their visible–UV absorption, circular dichroism, and $^{13}C$ NMR spectra, where SNNS denotes two kinds of open-chain quadridentate ligands, $H_2$endet=3,6-dimethyl-3,6-diazaoctane-1,8-dithiol and *R*-$H_2$pndet=(*R*)-3,4,6-trimethyl-3,6-diazaoctane-1,8-dithiol. Both the SNNS ligands gave the two geometrical isomers, *cis-α*(dark green) and *cis-β*(dark violet), whereas 3,7-dimethyl-3,7-diazanonane-1,9-dithiolate(2−) ligand gave no stable monomeric complex. Interestingly, stereoselective complex formation was found in *Δ-cis-α*-$[Co(R\text{-pndet})(en\ or\ RR\text{-chxn})]^+$, $\Delta(S^NR^N)$-*cis-β*-$[Co(endet)(R\text{-pn}\ or\ RR\text{-chxn})]^+$, and $\Delta(S^NR^N)$-*cis-β*-$[Co(R\text{-pndet})(en\ or\ RR\text{-chxn})]^+$, the *Δ-cis-α* configuration of the former complex being the novel one having the equatorially-oriented terminal chelate rings on the tertiary nitrogen atoms.

In a previous communication, we reported the stereochemistry of cobalt(III) complexes with a quadridentate ligand having SNNS donor set. Two geometrical isomers of the $[Co(N)_4(thiolato)_2]^+$ type complex were first separated by column chromatography.[1] The earlier attempt to prepare this type of complexes using bidentate ligand was unsuccessful in spite of the chromatographic analysis.[2] These circumstances show that the quadridentate ligand possessing SNNS donor set is promising for the stereochemical investigation of cobalt(III) complexes.

In this paper, three kinds of open-chain SNNS quadridentate ligands 3,6-dimethyl-3,6-diazaoctane-1,8-dithiol($H_2$endet), 3,7-dimethyl-3,7-diazanonane-1,9-dithiol($H_2$tndet), and (*R*)-3,4,6-trimethyl-3,6-diazaoctane-1,8-dithiol(*R*-$H_2$pndet) were used to prepare several cobalt(III) complexes $[Co(SNNS)(diamine)]^+$ (diamine=en, *R*-pn, and *RR*-chxn), $[Co(SNNS)(CN)_2]^-$, and [Co(SNNS)(aet)].[3] The complexes were separated, optically resolved by the chromatographic techniques, and characterized from their visible-UV absorption, circular dichroism(CD), and $^{13}C$ NMR spectra. For the complex $[Co(SNNS)(diamine)]^+$, the two geometrical isomers, *cis-α* and *cis-β*, are possible as shown in Fig. 1. This type of geometrical isomers were found for the endet and *R*-pndet ligands, whereas no stable mononuclear complex was detected for the tndet ligand. Furthermore, the optically active *R*-pndet ligand showed complete stereoselectivity in *cis-α* and *cis-β*-$[Co(R\text{-pndet})(en\ or\ RR\text{-chxn})]^+$.

## Experimental

*Preparation of Ligand.* *3,6-Dimethyl-3,6-diazaoctane-1,8-dithiol($H_2$endet), $[HSCH_2CH_2N(CH_3)CH_2-]_2$:* The ligand was prepared from thiirane[4] and *N,N′*-dimethyl-1,2-ethanediamine as described by Karlin and Lippard.[5] $^{13}C$ NMR (benzene): $\delta$=22.99 ($CH_2\underline{C}H_2SH$), 42.66 ($N\underline{C}H_3$), 55.72 ($N\underline{C}H_2CH_2SH$), and 61.13 ($N\underline{C}H_2CH_2N$). Found: C,48.25; H,9.53; N,13.05%. Calcd for $H_2$endet·1/6 $C_6H_6$=$C_9H_{21}N_2S_2$: C, 48.53; H,9.56; N,12.65%. A solution of $H_2$endet (1 mmol) in methanol (5 $cm^3$) was added to a warm solution of $Ni(CH_3CO_2)_2\cdot 4H_2O$ (1 mmol) in methanol (10 $cm^3$). The brown solid, which separated immediately, was filtered, washed with ethanol, and vacuum dried. Found: C, 36.24; H, 6.85; N, 10.56%. Calcd for [Ni(endet)]=$C_8H_{18}N_2S_2Ni$: C, 36.25; H, 6.85; N ,10.57%.

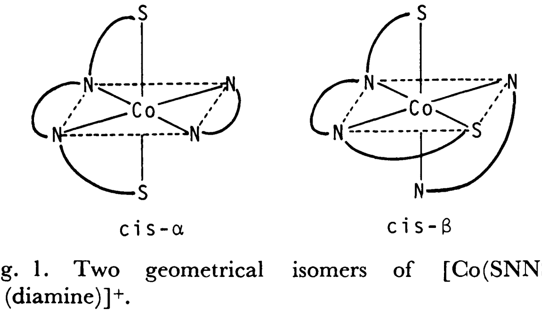


Fig. 1. Two geometrical isomers of [Co(SNNS)-(diamine)]$^+$.

*3,7-Dimethyl-3,7-diazanonane-1,9-dithiol($H_2$tndet), $[HSCH_2CH_2N(CH_3)CH_2-]_2CH_2$:* This ligand was obtained in the same manner as that of $H_2$endet, where *N,N′*-dimethyl-1,3-propanediamine[6] is substituted for *N,N′*-dimethyl-1,2-ethanediamine. $^{13}C$ NMR (benzene): $\delta$=23.10 ($CH_2\underline{C}H_2SH$), 25.70 ($NCH_2\underline{C}H_2CH_2N$), 42.34 ($N\underline{C}H_3$), 55.67 ($N\underline{C}H_2CH_2SH$), and 60.87 ($N\underline{C}H_2CH_2CH_2N$). Found: C,51.01; H, 9.85; N,12.09%. Calcd for $H_2$tndet·1/6 $C_6H_6$=$C_{10}H_{23}N_2S_2$: C, 51.02; H, 9.85; N, 11.90%. A solution of $H_2$tndet (1 mmol) in methanol (5 $cm^3$) was added to a warm solution of $Ni(CH_3CO_2)_2\cdot 4H_2O$ (1 mmol) in methanol (10 $cm^3$). To this mixture was added 0.3 g of $NaClO_4$ dissolved in 2 $cm^3$ of methanol. The resulting solution was concentrated by a rotary evaporator to give dark brown crystals, which were collected by filtration and washed with ethanol. Found: C, 26.52; H, 5.06; N, 6.91%. Calcd for $[Ni\{Ni(tndet)\}_2](ClO_4)_2$=$C_{18}H_{40}N_4S_4O_8Cl_2Ni_3$: C, 26.50; H, 4.94; N, 6.87%.

*(R)-3,4,6-Trimethyl-3,6-diazaoctane-1,8-dithiol(R-$H_2$pndet), $HSCH_2CH_2N(CH_3)CH(CH_3)CH_2N(CH_3)CH_2CH_2SH$:* The ligand was prepared from thiirane and (*R*)-*N,N′*-dimethyl-1,2-propanediamine[7] according to the same method. The purity was relatively low compared with those of $H_2$endet and $H_2$tndet and therefore checked by the nickel(II) complex formation. The dark brown Ni(II) trimer was obtained in a similar way by the method of the above tndet complex. Found: C, 28.22; H, 5.51; N, 6.92%. Calcd for $[Ni\{Ni(R\text{-pndet})\}_2]Br_2\cdot CH_3OH$=$C_{19}H_{44}N_4S_4Br_2ONi_3$: C, 28.22; H, 5.48; N, 6.93%.

*Preparation and Separation of the Cobalt(III) Complexes.* *cis-α- and cis-β-[Co(endet)(diamine)]$ClO_4$ (diamine=en, R-pn, and RR-chxn):* To a solution of 3.15 g of $[Co(en)_3]Cl_3\cdot 3H_2O$ in 20 $cm^3$ of water was added a mixture of 1.74 g of $H_2$endet and 0.6 g of NaOH in 20 $cm^3$ of water. The mixed solution was stirred for 2 h at room temperature. After filtration of the gummy precipitate, the resulting dark green filtrate was poured onto a column of SP-Sephadex C-25 ($Na^+$ form 4×50 cm), washed with water, and eluted with 0.1 mol dm$^{-3}$ NaClO$_4$. Two partly overlapping bands, dark green and dark violet, were eluted in this order. The total yield of the desired products was *ca.* 30% and the amount of the former isomer was somewhat higher than that of the latter one. As described later, the dark green and the dark violet isomers were assigned to *cis-α-* and *cis-β-*[Co(endet)(en)]$^+$, respectively. Each eluate was concentrated in a vacuum evaporator to give crystals of the desired perchlorate salt. Found for the dark green isomer (*cis-α*): C, 28.33; H, 6.20; N, 13.12%. Found for the dark violet isomer (*cis-β*): C, 28.17; H, 6.22; N, 13.17%. Calcd for [Co(endet)(en)]ClO$_4$=$C_{10}H_{26}N_4S_2O_4CoCl$: C, 28.27; H, 6.17; N, 13.19%. The perchlorate salt was converted into the corresponding chloride salt using a column of QAE-Sephadex A-25 (Cl$^-$ form). The highly soluble chloride salt was used for $^{13}$C NMR measurements.

The complexes containing *R*-pn or *RR*-chxn ligand were prepared and separated in the same manner as described above except for the use of *Δ*-[Co(*R*-pn)$_3$]$^{3+}$ or *Δ*-[Co(*RR*-chxn)$_3$]$^{3+}$, respectively, as a starting material. The two geometrical isomers, dark green and dark violet, were obtained in each case. Found for the dark green *R*-pn isomer: C, 29.59; H,6.34; N, 12.41%. Calcd for *cis-α-*[Co(endet)(*R*-pn)]ClO$_4$·0.5H$_2$O=$C_{11}H_{29}N_4S_2O_{4.5}CoCl$: C, 29.50; H, 6.53; N, 12.51%. Found for the dark violet *R*-pn isomer: C, 30.35; H, 6.51; N, 12.80%. Calcd for *cis-β-*[Co(endet)(*R*-pn)]ClO$_4$=$C_{11}H_{28}N_4S_2O_4CoCl$: C, 30.10; H, 6.43; N, 12.77%. Found for the dark green *RR*-chxn isomer(*cis-α*): C, 35.10; H, 6.75; N, 11.70%. Found for the dark violet *RR*-chxn isomer(*cis-β*): C, 35.14; H, 6.74; N, 11.60%. Calcd for [Co(endet)(*RR*-chxn)]ClO$_4$=$C_{14}H_{32}N_4S_2O_4CoCl$: C, 35.11; H, 6.73; N, 11.70%.

*Diastereomer Separation of* cis-α- *and* cis-β-*[Co(endet)(diamine)]$^+$(diamine=*R-*pn and* RR-*chxn)*: The general procedure in chromatography was as follows: Small amount of each isomer was dissolved in water, adsorbed onto a column of cation exchanger (Dowex 50W×2, Na$^+$ form; 3×15 cm) and eluted with 0.3 mol dm$^{-3}$ Na$_2$SO$_4$. The eluate was collected into 5 cm$^3$ portions and the CD spectra of the fractions were measured. Two diastereomers were confirmed in each of *cis-α-*[Co(endet)(*R*-pn)]$^+$ and *cis-α-*[Co(endet)(*RR*-chxn)]$^+$, though the elution order is reversed, namely the last eluted isomer $(-)^{\mathrm{CD}}_{570}$-*cis-α-*[Co(endet)(*R*-pn)]$^+$ corresponding to the first eluted one $(-)^{\mathrm{CD}}_{570}$-*cis-α-*[Co(endet)(*RR*-chxn)]$^+$. On the other hand, both *cis-β-*[Co(endet)(*R*-pn)]$^+$ and *cis-β-*[Co(endet)(*RR*-chxn)]$^+$ gave the only one diastereomer, which showed the two negative CD bands in the first d-d absorption band region. In the cases of *cis-α* complexes, the oxidation products, probably sulfenato complexes, partly overlapped on the front of the first eluted band, which was collected and rechromatographed in the same manner. The diastereomer separation using SP-Sephadex C-25(Na$^+$ form) gave almost the same results even when the optically active reagents such as *RR*-$C_4H_4O_6^{2-}$ and [Sb$_2$(*RR*-$C_4H_2O_6$)$_2$]$^{2-}$ were used as an elution agent. These chromatographic results were supported by the $^{13}$C NMR data as shown later.

cis-α *and* cis-β-*Na[Co(endet)(CN)$_2$]*: To a suspension of Na[CoBr$_2$(CN)$_2$(NH$_3$)$_2$](2.19 g) in 50 cm$^3$ of water, which was prepared by treating *cis(CN)-cis(SO$_3$)-trans(NH$_3$)*-[Co(CN)$_2$(SO$_3$)$_2$(NH$_3$)$_2$]$^{3-}$ [8] with a HBr solution, was added a solution of H$_2$endet (1.39 g) and NaOH (0.53 g) in 15 cm$^3$ of water and the mixture was stirred for 3 h. After filtration of the precipitate, the filtrate was poured onto a column of QAE-Sephadex A-25 (Cl$^-$ form, 3×50 cm), washed with water, and eluted with 0.08 mol dm$^{-3}$ NaCl. The two bands, red purple and light brown, were eluted in this order. Each band was concentrated, reloaded onto a column of Sephadex G-15 to remove the NaCl, and eluted with water. The eluate was evaporated to dryness because of high solubility in water or ethanol. Found for the red purple isomer: C, 26.90; H, 4.99; N, 12.50%. Calcd for *cis-α-*Na[Co(endet)(CN)$_2$]·2H$_2$O·1.2NaCl=$C_{10}H_{22}N_4S_2O_2CoNa_{2.2}Cl_{1.2}$: C, 26.90; H, 4.97; N, 12.55%. Found for the light brown isomer: C, 32.33; H, 5.84; N, 14.72%. Calcd for *cis-β-*Na[Co(endet)(CN)$_2$]·2H$_2$O=$C_{10}H_{22}N_4S_2O_2CoNa$: C, 31.91; N, 5.89; N, 14.89%.

fac(S)-*[Co(endet)(aet)]*: To a solution of [Co(NH$_3$)$_6$]Cl$_3$ (0.53 g) in 10 cm$^3$ of water was added a solution of H$_2$endet (0.46 g) and Haet (0.15 g) in 10 cm$^3$ of water and the mixture was stirred 2 h at room temperature. After filtration of the precipitate, the filtrate was poured onto a column of Sephadex A-25 (Cl$^-$ form), and eluted with water. The dark green band was collected and evaporated to dryness below 20 °C. Found: C, 34.88; H, 7.06; N, 12.24%. Calcd for *fac(S)*-[Co(endet)(aet)]=$C_{10}H_{24}N_3S_3Co$: C, 35.18; H, 7.08; N, 12.31%.

*Complexes Containing tndet Ligand*: The same preparative method as that of [Co(endet)(en)]$^+$ was applied to this system. The solution of [Co(en)$_3$]Cl$_3$ became temporarily dark green by the addition of tndet ligand but then changed to dark brown to give a large amount of a gummy precipitate. The column chromatograph of the filtrate gave no desirable monomeric species in this system. The change of diamine from en to *R*-pn or *RR*-chxn led to similar results.

cis-α- *and* cis-β-*[Co(*R*-pndet)(diamine)]$^+$(diamine=en and* RR-*chxn)*: The complexes were prepared in the same manner as that of [Co(endet)(diamine)]$^+$ where *R*-H$_2$pndet was substituted for H$_2$endet. The column chromatography using Dowex 50W×2 (Na$^+$ form, 3×15 cm; 0.4 mol dm$^{-3}$ NaCl) gave the two geometrical isomers, green and violet in this order, for both [Co(*R*-pndet)(en)]$^+$ and [Co(*R*-pndet)(*RR*-chxn)]$^+$. The earlier eluted green band was rechromatographed to remove the partly overlapping oxidation products. Each band was fractionated into 5 cm$^3$ portions and their CD spectra were checked. Interestingly, each band was composed of a single species, that is, complete stereoselectivity was observed in *cis-α*(green)- and *cis-β*(violet)-[Co(*R*-pndet)(diamine)]$^+$ (diamine=en and *RR*-chxn). No solid complex was isolated because of their low yield. The concentration value for the CD intensity determination was calculated from the measured absorbance using the absorption coefficient of *cis-α-* or *cis-β-*[Co(endet)(*R*-pn)]$^+$.

cis-α- *and* cis-β-*[Co(endese)(en)]$^+$ and* cis-α- *and* cis-β-*[Co(endesi)(en)]$^+$ (endese=3,6-dimethyl-3,6-diazaoctane-1,8-disulfenic acid, [HOSCH$_2$CH$_2$N(CH$_3$)CH$_2$–]$_2$ and endesi=3,6-dimethyl-3,6-diazaoctane-1,8-disulfinic acid, [HO$_2$SCH$_2$CH$_2$N(CH$_3$)CH$_2$–]$_2$)*: A stoichiometric amount of 0.6% aqueous H$_2$O$_2$ (1.76×10$^{-2}$ mmol) was added to a solution of *cis-α-* or *cis-β-*[Co(endet)(en)]ClO$_4$(0.88×10$^{-2}$ mmol) in 5 cm$^3$ of water, leading to an orange-red solution instantly. The oxidation was followed by the absorption spectral measurements. The absorption spectra of *cis-α-* and *cis-β-*[Co(endese)(en)]$^+$ in Table 1 were measured when the absorption intensity became maximum in the region of 380—420 nm, which is the characteristic region to the coordinated sulfenato group. The formation of the corresponding sulfinato complex was negligible because the oxidation from the coordinated sulfenato to the sulfinato group proceeds approximately 10$^3$ times slower than that from the coordinated thiolate to the sulfenate.[9]

The corresponding sulfinato complex *cis-α-* or *cis-β-*[Co(endesi)(en)]$^+$ was prepared in the same manner using a large excess of 30% H$_2$O$_2$ and kept to standing for 1 or 2 d to complete the reaction. In the case of *cis-α-*[Co(endesi)(en)]$^+$ the desired solid complex was obtained. Found: C, 23.73; H, 5.40; N, 10.98%. Calcd for *cis-α-*[Co(endesi)(en)]ClO$_4$·H$_2$O=$C_{10}H_{28}N_4S_2O_9CoCl$: C, 23.70; H, 5.57; N, 11.05%. The data of *cis-β-*[Co(endesi)(en)]$^+$ in Table 1 were calculated by assuming that the absorption coefficient at 31250 cm$^{-1}$ is the same as that of the *cis-α* isomer at 28380 cm$^{-1}$.

*Measurement.* The visible and ultraviolet absorption spectra were measured on a Hitachi 330 spectrophotometer and CD spectra with a JASCO MOE-1 spectropolarimeter in aqueous solutions. The $^{13}$C NMR spectra were recorded with a JEOL FX-90Q NMR spectrometer.

## Results and Discussion

*Characterization of Geometrical Isomers.* The *cis-α* and *cis-β* isomers (Fig. 1) of the [Co(endet)(en)]$^+$ complex have $C_2$ and $C_1$ symmetries, respectively, and are assignable on the basis of $^{13}$C NMR spectra. The dark green isomer showed five signals (26.30, 45.21, 52.53, 62.25, and 72.71 ppm) and therefore is assigned to the *cis-α* geometry. The dark violet isomer showed ten signals (17.74, 26.60, 29.20, 42.37, 46.76, 47.11, 58.24, 63.88, 64.34, and 70.89 ppm), which is consistent with the *cis-β* geometry. The absorption spectra of

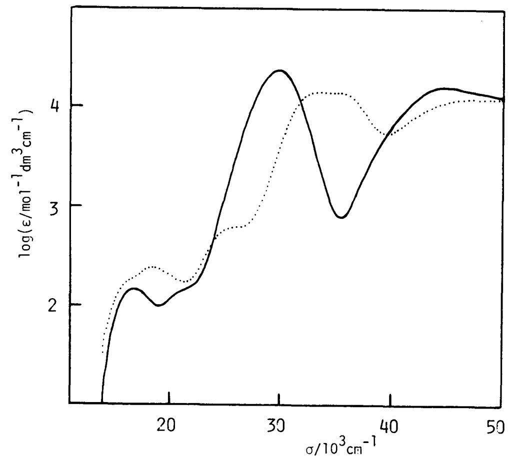


Fig. 2. Absorption spectra of [Co(endet)(en)]ClO$_4$: *cis-α* (——) and *cis-β* (----).

Table 1. Absorption data of [Co(SNNS)X$_2$]$^{n+}$

| SNNS | $X_2$ | Assignment | Wave number (Intensity) σ$_{max}$/10$^3$ cm$^{-1}$(log(ε/mol$^{-1}$ dm$^3$ cm$^{-1}$)) | | |
|---|---|---|---|---|---|
| | | | 1st band | 2nd band | CT band |
| endet | en | *cis-α* | 16.95 (2.18) | | 29.69 (4.35) |
| | | | 21.3 (2.18) a) | | 44.54 (4.18) |
| | | *cis-β* | 16.4 (2.24) | 25.9 (2.75) a) | 33.50 (4.15) |
| | | | 18.57 (2.37) | | 35.21 (4.14) |
| | | | | | 47.2 (4.07) a) |
| | *R*-pn | *cis-α* | 16.93 (2.16) | | 29.76 (4.33) |
| | | | 21.1 (2.07) a) | | 44.50 (4.18) |
| | | *cis-β* | 16.3 (2.25) a) | 25.7 (2.87) a) | 33.40 (4.14) |
| | | | 18.65 (2.41) | | 35.09 (4.13) |
| | | | | | 46.73 (4.09) |
| | *RR*-chxn | *cis-α* | 16.84 (2.23) | | 29.66 (4.31) |
| | | | 21.1 (2.21) a) | | 43.76 (4.20) |
| | | *cis-β* | 16.1 (2.19) a) | 25.5 (2.53) a) | 33.67 (4.14) |
| | | | 18.52 (2.37) | | 34.97 (4.14) |
| | | | | | 45.56 (4.13) |
| | 2CN | *cis-α* | 18.94 (2.64) | | 32.45 (4.36) |
| | | | 25.3 (2.55) a) | | 45.8 (4.15) a) |
| | | | | | 49.19 (4.21) |
| | | *cis-β* | 17.0 (1.96) a) | 27.23 (3.30) | 34.57 (4.10) |
| | | | 21.5 (2.83) a) | | 38.3 (4.00) a) |
| | aet | *fac(S)* | 16.20 (2.60) | 21.6 (2.78) a) | 34.60 (4.26) |
| | | | | 28 (3.50) c) | 36.7 (4.20) a) |
| | | | | | 46.8 (4.00) a) |
| endese b) | en | *cis-α* | 19 (2.85) a) | | 23.50 (4.30) |
| | | | | | 35.59 (3.45) |
| | | | | | 44.54 (4.25) |
| | | *cis-β* | 19.62 (3.06) | | 25.81 (3.93) |
| | | | | | 34.51 (3.81) |
| | | | | | 46.30 (4.01) |
| endesi b) | en | *cis-α* | 20 (2.3) a) | | 28.38 (4.06) |
| | | | | | 42.23 (4.11) |
| | | *cis-β* | 20.6 (2.8) a) | | 31.25 (4.06) |
| | | | | | 33.3 (4.04) |
| | | | | | 44.39 (4.13) |

a) Shoulder. b) See Experimental section. c) This band may be due to the oxidized impurities.

$[Co(N)_4(S)_2]$ type complexes are shown in Fig. 2 and Table 1. The first d-d absorption band of each isomer is composed of two components. Since the interval between the components is larger for the dark green isomer than for the dark violet, the former isomer can be assigned to the *cis-α* structure of *trans(S)* chromophore and the latter to the *cis-β* of *cis(S)*. The complexes showed an intense band in 29000—34000 $cm^{-1}$ region, which is assigned to the $Co(\sigma^*)\leftarrow S(\sigma)$ ligand-to-metal charge transfer (LMCT) transition.10) The LMCT band of the *cis-α* isomer appears at 29690 $cm^{-1}$ but that of the *cis-β* at 33500 $cm^{-1}$ with its splitting component at 35210 $cm^{-1}$. Such a difference has been observed between geometrical isomers having two sulfide (thioether)11) or sulfito12) donor atoms: In general the charge transer (CT) band of *trans(S)* isomer locates at lower energy than that of *cis(S)* one. Thus the relative positions of CT bands confirm the above structural assignments. This criterion is also valid for the other complexes $[Co(endet)(R\text{-}pn)]^+$, $[Co(endet)(RR\text{-}chxn)]^+$, $[Co(R\text{-}pndet)(en)]^+$, and $[Co(R\text{-}pndet)(RR\text{-}chxn)]^+$: the first eluted green isomer has the *cis-α* geometry and the second eluted violet one the *cis-β* geometry.

The absorption spectra of other thiolato complexes $[Co(endet)(CN)_2]^-$ and [Co(endet)(aet)] are shown in Fig. 3. In $[Co(endet)(CN)_2]^-$ three geometrical isomers, *cis-α*, *cis-β*, and *trans(CN)*, are possible. The red purple isomer exhibited the single LMCT band at 32450 $cm^{-1}$ and therefore is assigned to the *cis-α* geometry. If the initial *cis(CN)*-configuration of the starting material $Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]$ is retained after the reaction, the light brown isomer should have the *cis-β* geometry in agreement with the presence of two LMCT components at 34570 and 38300 $cm^{-1}$. The green isomer of [Co(endet)(aet)] showed the very similar absorption spectrum to *fac(S)*-$[Co(aet)_3]$ and *fac(S)*-$[Co(\text{L-cysteinato})_3]^{3-}$.10) Thus this isomer can be assigned to the *fac(S)* geometry with *cis-β* configuration of the quadridentate ligand. The *mer(S)* configuration is very novel for a $[Co(N)_3(\text{thiolato})_3]$ type complex and there has been no example except *mer(S)*-$[Co(2\text{-pyridinethiolato})_3]$.13)

Figure 4 presents the absorption spectra of $[Co(endese)(en)]^+$ and $[Co(endesi)(en)]^+$. The usual oxidation reactions with $H_2O_2$ do not involve Co-S cleavage9,10,14) and the initial geometrical structures should be retained. In fact, both the *cis-α* sulfenato and *cis-α* sulfinato complexes showed the intense CT band at lower energy side than the corresponding *cis-β* complexes, respectively (Table 1).

*Synthesis and Stereochemistry of the Complexes of Sulfur-containing Quadridentate Ligand.* Several cobalt(III) complexes with quadridentate ligands possessing NSSN array of donor atoms, $NH_2(CH_2)_xS(CH_2)_yS(CH_2)_zNH_2$, have been studied so far.15) The results showed that only the *cis-α* isomer is formed in the case of $x=y=z=2$ and only the *cis-β* and *trans* isomers in the case of $x=z=2$ and $y=3$ for the mononuclear $[Co(NSSN)X_2]$ complexes. The skeleton of present thiolato ligands $HS(CH_2)_xN(CH_3)(CH_2)_yN(CH_3)(CH_2)_zSH$ is similar to the above one except for the position of sulfur atoms. However, the present SNNS ligands gave both *cis-α* and *cis-β* isomers in the case of $x=y=z=2$ (endet and *R*-pndet) and no mononuclear species in the case of $x=z=2$ and $y=3$ (tndet). Such striking difference can be attributable to the high bridging ability of thiolato groups and the special property of the tndet ligand described below.

Nickel(II) acetate reacted with $H_2$endet in methanol solution to give the brown complex [Ni(endet)]. However, the tndet ligand did not give the mononuclear complex but the trimeric one $[Ni\{Ni(tndet)\}_2](ClO_4)_2$. A similar Ni(II) trimer has been reported on the occasion of the detritylation of 1,9-bis(tritylthio)-3,7-diazanonane),16) the trimer being probably in equilibrium with the monomer in methanol. This was confirmed from the synthesis of some mixed-metal trimer by allowing the Ni(II) trimer to react with $Pd^{2+}$ or $Cd^{2+}$.17) The synthesis of $[Co(tndet)(diamine)]^+$ was unsuccessful and some kind of polynuclear complex, whose composition was poorly characterized, was formed in the present case. Recently, Lippard and his co-workers prepared the iron complexes of $H_2$endet and $H_2$tndet ligands. Zubieta and his co-workers also reported the molybdenum complexes of the same ligands. In

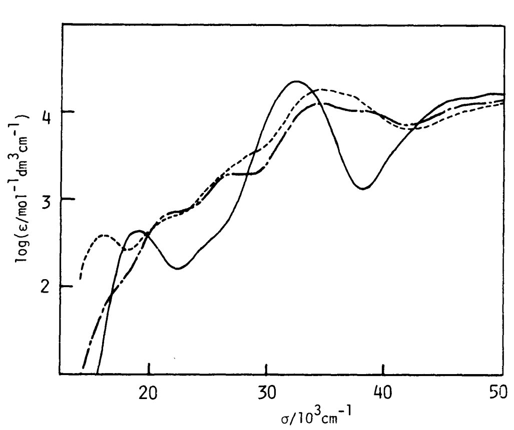


Fig. 3. Absorption spectra of *cis*-α-$[Co(endet)(CN)_2]^-$ (——), *cis*-β-$[Co(endet)(CN)_2]^-$ (————), and *fac(S)*-[Co(endet)(aet)] (----).

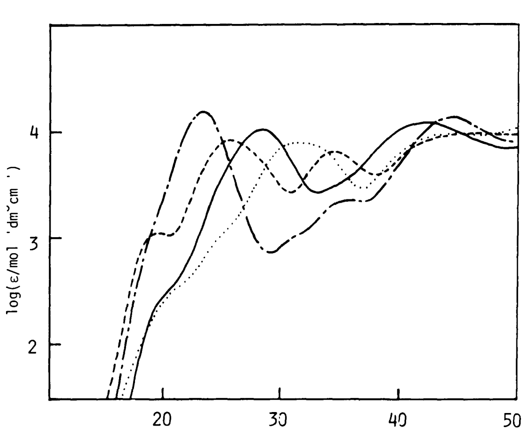


Fig. 4. Absorption spectra of *cis*-α-$[Co(endese)(en)]^+$ (————), *cis*-β-$[Co(endese)(en)]^+$ (----), *cis*-α-$[Co(endesi)(en)]^+$ (——), and *cis*-β-$[Co(endesi)(en)]^+$ (······).

these investigations, some unusual structures were found for the complexes containing tndet ligand: The pseudo tetrahedral complex $[\mathrm{Fe(Htndet)(NO)_2}]$ has a 12-membered chelate ring in which the two nitrogen atoms of the quadridentate ligand are not coordinated to the iron atom.18) A similar feature of the structure was found in $[\mathrm{Mo_2O_4(Htndet)_2}]$.19) In these cases the tndet ligand is protonated to produce a six-membered ring └N-C-C-C-N-H┘ with a chair conformation, which is responsible for the poor complex formation in the present tndet ligand.

The synthetic efforts was also made for $[\mathrm{Co(endet)X_2}]$, where $\mathrm{X_2}$ denotes $2(\mathrm{NH_3})$, $2(\mathrm{NO_2^-})$, $\mathrm{C_2O_4^{2-}}$, $\mathrm{CH_3COCHCOCH_3^-}$, $\mathrm{CO_3^{2-}}$, $2(\mathrm{CN^-})$, and aet$^-$, all preparations except the latter two ligands producing no mononuclear cobalt(III) complex. This fact means that the stable complex is formed only when the remaining two coordination sites are occupied by such tightly bound ligands as $2(\mathrm{CN^-})$ and aet$^-$.

*Stereoselective Formation of Diastereomers.* Figure 5 shows the $^{13}$C NMR spectra of *cis-α*- and *cis-β*-[Co(endet)(*RR*-chxn)]$^+$. The *cis-α* isomer exhibited twelve signals (24.73 (strong), 25.60, 27.06, 33.46, 34.54, 52.25, 52.69, 59.35, 61.52 (strong), 63.58, 72.19, and 73.38 ppm in $\mathrm{D_2O}$), which imply the *cis-α* isomer having $\mathrm{C_2}$ symmetry is a diastereomeric mixture of $\Delta(R^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$ and $\Lambda(S^{\mathrm{N}}S^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$. On the other hand, the *cis-β* isomer showed fourteen signals (23.79, 24.22, 25.85, 28.72, 32.24, 34.30, 45.13, 50.55, 56.84, 61.66, 62.14, 62.96, 65.83, and 69.13 ppm in DMSO-$d_6$), which indicate the stereoselective formation of single $\mathrm{C_1}$ *cis-β* diastereomer. These results are completely in accord with those of the chromatographic separation: Two diastereomers were confirmed for *cis-α*-[Co(endet)(*R*-pn)]$^+$ and *cis-α*-[Co(endet)(*RR*-chxn)]$^+$, whereas the single diastereomer was found for *cis-β*-[Co(endet)(*R*-pn)]$^+$ and *cis-β*-[Co(endet)(*RR*-chxn)]$^+$.

The CD spectra of *cis-α* diastereomers are shown in Figs. 6 and 7. The earlier eluted *R*-pn isomer *cis-α*-$(+)^{\mathrm{CD}}_{600}$-[Co(endet)(*R*-pn)]$^+$ corresponds to the later eluted *RR*-chxn one *cis-α*-$(+)^{\mathrm{CD}}_{600}$-[Co(endet)(*RR*-chxn)]$^+$ (Fig. 6). Both the *cis-α*-$(+)^{\mathrm{CD}}_{600}$ isomers showed a positive dominant CD band in the first absorption band region and therefore are assigned to the $\Lambda(S^{\mathrm{N}}S^{\mathrm{N}})$ absolute

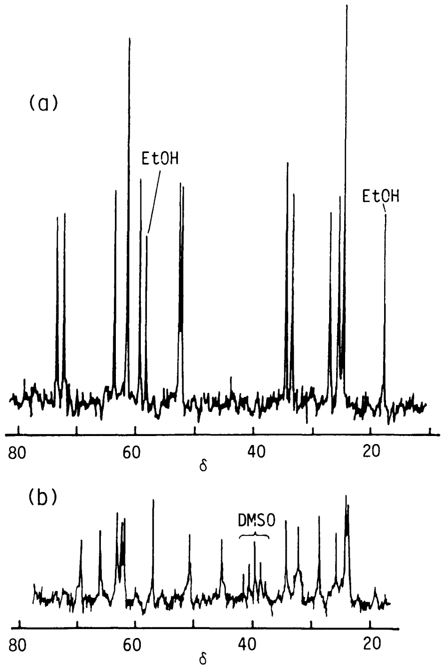


Fig. 5. $^{13}$C NMR spectra of [Co(endet)(*RR*-chxn)]$^+$: (a) *cis-α* in $\mathrm{D_2O}$; ethanol($\delta$ 58.27 vs $\mathrm{Me_4Si}$) was used as the internal standard. (b) *cis-β* in DMSO-$d_6$; DMSO ($\delta$ 39.5 vs $\mathrm{Me_4Si}$) was used as the internal standard.

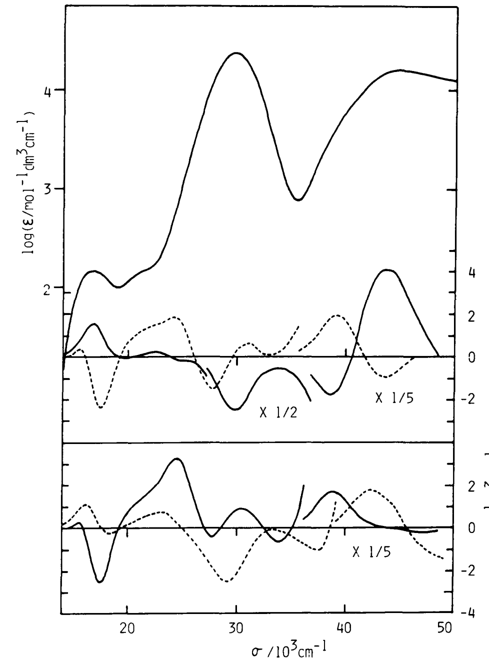


Fig. 6. Absorption and CD spectra of *cis-α*-[Co(endet)(*R*-pn)]$^+$ (upper): 1st eluted $(+)^{\mathrm{CD}}_{600}$-isomer (——) and 2nd eluted $(-)^{\mathrm{CD}}_{570}$-isomer (----). CD spectra of *cis-α*-[Co(endet)(*RR*-chxn)]$^+$(lower): 1st eluted $(-)^{\mathrm{CD}}_{570}$-isomer (——) and 2nd eluted $(+)^{\mathrm{CD}}_{600}$-isomer (----).

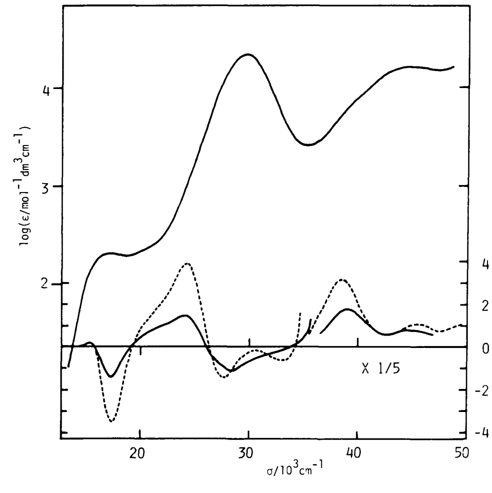


Fig. 7. Absorption and CD spectra of *cis-α*-[Co(*R*-pndet)(diamine)]$^+$: diamine=en (——) and *RR*-chxn (----).

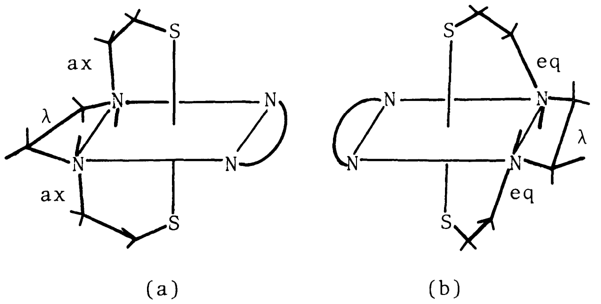
TABLE 2. CD DATA OF [Co(SNNS)(diamine)]$^+$

| SNNS | diamine | Assignment | Wave number (Intensity) | |
|---|---|---|---|---|
| | | | $\sigma_{ext}/10^3$ cm$^{-1}$($\Delta\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) | |
| [*cis*-α complexes] | | | | |
| endet | *R*-pn | $\Lambda(S^NS^N)$ | 16.84(+1.54) | 29.87(−4.95) |
| | | | 19.5 (−0.035) | 38.76(−8.84) |
| | | | 22.57(+0.240) | 43.73(+20.4) |
| | | $\Delta(R^NR^N)$ | 15.55(+0.350) | 27.78(−1.48) |
| | | | 17.57(−2.39) | 31.2 (+0.678) |
| | | | 21.5 (+1.50)$^{a)}$ | 39.2 (+9.77) |
| | | | 24.27(+1.85) | 43.67(−4.72) |
| | *RR*-chxn | $\Delta(R^NR^N)$ | 15.5 (+0.272) | 27.28(−0.389) |
| | | | 17.45(−2.42) | 30.40(+0.864) |
| | | | 21.5 (+1.3)$^{a)}$ | 33.86(−0.631) |
| | | | 24.53(+3.15) | 38.93(+8.16) |
| | | | | 47.2 (−1.1) |
| | | $\Lambda(S^NS^N)$ | 16.25(+1.04) | 29.41(−2.38) |
| | | | 18.4 (−0.25) | 37.74(−0.987) |
| | | | 22.94(+0.694) | 42.37(+8.51) |
| *R*-pndet | en | $\Delta\lambda(R^NR^CR^N)$ | 15.3 (+0.164) | 28.3 (−1.12) |
| | | | 17.18(−1.43) | 31.5 (−0.4)$^{a)}$ |
| | | | 21.5 (+0.9)$^{a)}$ | 39.20(+8.84) |
| | | | 24.00(+1.46) | 44.80(+3.81) |
| | *RR*-chxn | $\Delta\lambda(R^NR^CR^N)$ | 15.22(+0.144) | 27.62(−1.46) |
| | | | 17.33(−3.52) | 33.11(−0.692) |
| | | | 21.2 (+1.6)$^{a)}$ | 38.54(+15.8) |
| | | | 24.21(+3.92) | 45.25(+5.04) |
| [*cis*-β complexes] | | | | |
| endet | *R*-pn | $\Delta(S^NR^N)$ | 16.47(−1.50) | 32.31(+28.2) |
| | | | 20.75(−1.65) | 36.04(−33.3) |
| | | | 24.48(+2.60) | 43.29(+10.5) |
| | *RR*-chxn | $\Delta(S^NR^N)$ | 16.31(−1.64) | 32.27(+29.3) |
| | | | 20.62(−1.85) | 35.84(−31.8) |
| | | | 24.39(+3.26) | 43.10(+8.82) |
| *R*-pndet | en | $\Delta\lambda(S^NR^CR^N)$ | 16.35(−1.32) | 32.21(+26.6) |
| | | | 20.62(−1.87) | 35.91(−34.0) |
| | | | 24.69(+2.72) | 42.94(+8.41) |
| | *RR*-chxn | $\Delta\lambda(S^NR^CR^N)$ | 16.31(−1.82) | 32.27(+33.5) |
| | | | 20.64(−2.43) | 35.91(−36.6) |
| | | | 24.39(+3.62) | 42.55(+7.70) |

a) Shoulder.

configuration concerning the skew pair of chelate rings and the tertiary nitrogen atoms. The remaining diastereomers *cis*-α-(−)$^{CD}_{570}$-[Co(endet)(*R*-pn)]$^+$ and *cis*-α-(−)$^{CD}_{570}$-[Co(endet)(*RR*-chxn)]$^+$ exhibited a negative main CD band in the same region, which are assigned to the $\Delta(R^NR^N)$ absolute configuration.

Each single diastereomer was found in *cis*-α-[Co(*R*-pndet)(en)]$^+$ and *cis*-α-[Co(*R*-pndet)(*RR*-chxn)]$^+$. When the methyl group on the medial chelate ring of quadridentate ligand takes an equatorial position, the medial chelate ring is fixed to the most stable λ conformation. Therefore, two diastereomers, $\Delta\lambda$($R^NR^CR^N$) and $\Lambda\lambda$($S^NR^CS^N$), are possible for *cis*-α-[Co(*R*-pndet)(diamine)]$^+$ in Fig. 8. Each the obtained diastereomer showed three CD bands, (+), (−), and (+), from the lower energy side in the first absorption



(a) (b)

Fig. 8. Two diastereomers of *cis*-α-[Co(*R*-pndet)(diamine)]$^+$: (a) $\Lambda\lambda(S^NR^CS^N)$ and (b) $\Delta\lambda(R^NR^CR^N)$.

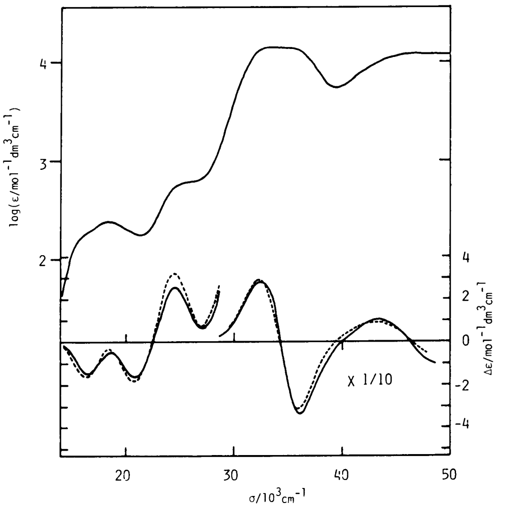


Fig. 9. Absorption and CD spectra of *cis*-β-[Co(endet)-(diamine)]$^+$: diamine=*R*-pn (——) and *RR*-chxn (----).

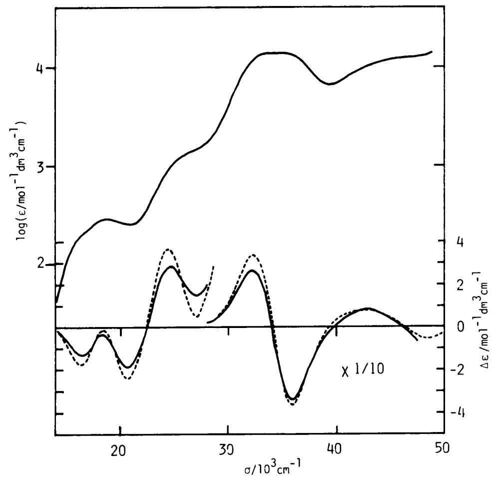


Fig. 10. Absorption and CD spectra of *cis*-β-[Co(*R*-pndet)(diamine)]$^+$: diamine=en (——) and *RR*-chxn (----).

band region (Fig. 7). Since the negative CD band becomes dominant, the complexes can be assigned to the $\Delta\lambda(R^{N}R^{C}R^{N})$ absolute configuration which has the equatorially oriented terminal chelate rings on the tertiary nitrogen atoms. It has long been generally thought that the configuration $\Lambda\lambda(S^{N}R^{C}S^{N})$ is more preferable in *cis*-α geometry because the configuration $\Delta\lambda(R^{N}R^{C}R^{N})$ suffers the greatest ring strain in the backbone and two adjacent chelate rings. However, the latter $\Delta\lambda(R^{N}R^{C}R^{N})$ or the related $\Delta\lambda(R^{N}R^{C}R^{C}R^{N})$ configuration has been recently reported in several chromium(III) and cobalt(III) complexes containing the quadridentate ligands such as (*S*)-*N,N'*-bis(2-pyridylmethyl)-1,2-propanediamine, (1*S*,2*S*)-*N,N'*-bis(2-pyridylmethyl)-1,2-cyclohexanediamine(abbrev. *SS*-picchxn),[20] and (1*R*,2*R*)-*N,N'*-dimethyl-1,2-cyclohexanediamine-*N,N'*-diacetate (*N,N'*-Me$_2$-*RR*-chxnda).[21] The configurations of Δ-*cis*-α-[CrCl$_2$(*RR*-picchxn)]ClO$_4$[22] and Δ-*cis*-α-[Co(*N,N'*-Me$_2$-*RR*-chxnda)(en)]ClO$_4$[23] have been explicitly determined by the X-ray structure analysis. The CD spectral patterns of *cis*-α-[Co(*R*-pndet)(en)]$^+$ and *cis*-α-[Co(*R*-pndet)(*R*-chxn)]$^+$ are very similar to that of Δ-*cis*-α-[Co(*N,N'*-Me$_2$-*RR*-chxnda)-(en)]$^+$, especially in the first absorption band region.[20] This fact supports that the present *cis*-α complexes have the rare $\Delta\lambda(R^{N}R^{C}R^{N})$ configuration.

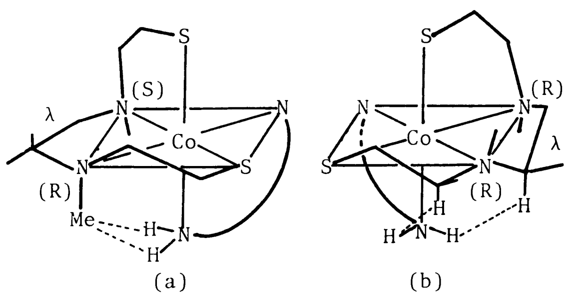


Fig. 11. Possible diastereomers of *cis*-β-[Co(*R*-pndet)-(diamine)]$^+$: (a) $\Delta\lambda(S^{N}R^{C}R^{N})$ and (b) $\Lambda\lambda(R^{N}R^{C}R^{N})$.

The CD spectra of the *cis*-β complexes, [Co(endet)-(*R*-pn)]$^+$, [Co(endet)(*RR*-chxn)]$^+$, [Co(*R*-(pndet)(en)]$^+$, and [Co(*R*-pndet)(*RR*-chxn)]$^+$ are shown in Figs. 9 and 10. They are very resemble to one another all over the regions measured. The results indicate that each the *cis*-β diastereomer is formed stereoselectively in agreement with the $^{13}$C NMR results and has the same absolute configuration. The Δ configuration is assigned to these complexes on the basis of the net negative CD sign in the first absorption band region.

In *cis*-β-[Co(*R*-pndet)(diamine)]$^+$, only two diastereomers, $\Delta\lambda(S^{N}R^{C}R^{N})$ and $\Lambda\lambda(R^{N}R^{C}R^{N})$, are possible owing to the λ conformation of the medial chelate ring as in Fig. 11. In the $\Lambda\lambda(R^{N}R^{C}R^{N})$ structure(b), there is a steric repulsion between the two amine protons of bidentate diamine and the two methylene protons adjacent to the tertiary amine of the quadridentate. On the other hand, the steric crowding between the methyl group on the *R*-N atom and the amine protons of bidentate diamine in the $\Delta\lambda(S^{N}R^{C}R^{N})$ structure(a) can be eliminated partly by the conformational change of the terminal chelate ring. Therefore the actual diastereomer is limited to the $\Delta\lambda(S^{N}R^{C}R^{N})$ configuration. In conclusion, all the four *cis*-β complexes obtained stereoselectively can be assigned to $\Delta(S^{N}R^{N})$ configuration on the basis of the analogous CD patterns.

## References

1) K. Yamanari, N. Takeshita, T. Komorita, and Y. Shimura, *Chem. Lett.*, **1981**, 861.

2) C. Stein, S. Bouma, J. Carlson, C. Cornelius, J. Maeda, C.Weshler, E. Deutsch, and K. O. Hodgson, *Inorg. Chem.*, **15**, 1183 (1976).

3) Abbreviations used for ligands are as follows: en=1,2-ethanediamine, $NH_2CH_2CH_2NH_2$; *R*-pn=(*R*)-1,2-propanediamine, $NH_2CH(CH_3)CH_2NH_2$; *RR-chxn*=(*R,R*)-1,2-cyclohexanediamine, $\overline{\mathrm{CH_2CH_2CH(NH_2)CH(NH_2)CH_2CH_2}}$; and Haet=2-aminoethanethiol, $NH_2CH_2CH_2SH$.

4) S. Searles, E. F. Lutz, H. R. Hays, and H. E. Mortensen, *Org. Synth.*, **42**, 59 (1962).

5) K. D. Karlin and S. J. Lippard, *J. Am. Chem. Soc.*, **98**, 6951 (1976).

6) W. O. Kermack and T. W. Wight, *J. Chem. Soc.*, **1935**, 1421.

7) J. A. Tiethof and D. W. Cooke, *Inorg. Nucl. Chem. Lett.*, **8**, 1013 (1972).

8) A. V. Babaeva and I. B. Baranovskii, *Zh. Neorg. Khim.*, **7**, 783 (1962); *Chem. Abstr.*, **57**, 402g.

9) D. L. Herting, G. P. Sloan, A. W. Carbral, and J. H. Kruger, *Inorg. Chem.*, **17**, 1649 (1978).

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

11) J. Hidaka, S. Yamada, and Y. Shimura, *Chem. Lett.*, **1974**, 1487; K. Yamanari, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **50**, 2451, 2643 (1977).

12) K. Akamatsu, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **50**, 533 (1977).

13) M. Kita, K. Yamanari, and Y. Shimura, *Chem. Lett.*, **1983**, 141.

14) I. K. Adzamli, K. Libson, J. D. Lydon, R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **18**, 303 (1979).

15) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563, 1572 (1969); B. Bosnich, W. R. Kneen, and A. T. Phillip, *ibid.*, **8**, 2567 (1969), *J. Chem. Soc., A*, **1970**, 264; J. H. Worrell, T. E. MacDermott, and D. H. Busch, *J. Am. Chem. Soc.*, **92**, 3317 (1970); R. W. Hay, P. M. Gidney, and G. A. Lawrence, *J. Chem. Soc., Dalton Trans.*, **1975**, 779.

16) R. W. Hay, A. L. Galyer, G. A. Lawrence, *J. Chem. Soc., Dalton Trans.*, **1976**, 939.

17) M. G. B. Drew, D. A. Rice, and K. M. Richards, *J. Chem. Soc., Dalton Trans.*, **1980**, 2075.

18) L. M. Baltusis, K. D. Karlin, H. N. Rabinowitz, J. C. Dowan, and S. J. Lippard, *Inorg. Chem.*, **19**, 2627 (1980).

19) P. L. Dahlstrom, J. R. Hyde, P. A. Vella, and J. Zubieta, *Inorg. Chem.*, **21**, 927 (1982).

20) Y. Yamamoto and Y. Shimura, *Bull. Chem. Soc. Jpn.* **53**, 395 (1980), **54**, 2924, 3351 (1981).

21) S. Yoshikawa, M. Asami, M. Inoue, and S. Yano, presented at the 29th Symposium on the Coordination Chemistry in Japan, Hamamatsu, 1979, Abstract, No. 1B09.

22) Y. Yamamoto, Y. Hata, and Y. Shimura, *Chem. Lett.*, **1981**, 1559.

23) T. Murata, M. Asami, M. Yashiro, S. Yano, M. Kosaka, and S. Yoshikawa, presented at the 33rd Symposium on the Coordination Chemistry in Japan, Osaka, 1983, Abstract, No. 1A16.