Synthesis and Stereochemistry of (Diamine)(2,9-dimethyl-4,7-diazadecane-2,9-dithiolato)cobalt(III) Complexes and Their Derivatives

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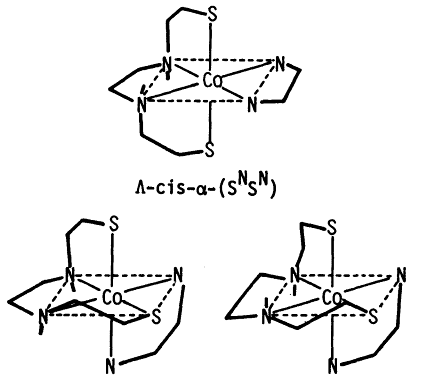
(Received April 24, 1984)

Several (diamine)(2,9-dimethyl-4,7-diazadecane-2,9-dithiolato)cobalt(III) complexes, [Co(SNNS)(diamine)]$^+$ (diamine=1,2-ethanediamine and (*R,R*)-1,2-cyclohexanediamine), were prepared and characterized by the visible-UV absorption, circular dichroism(CD), and ^{13}C NMR spectra. The above SNNS quadridentate ligand gave only the *cis-β* geometrical isomer, which was chromatographically separated into two diastereomers owing to the configurations of chiral nitrogen atoms. All the thiolato and the corresponding sulfinato complexes exhibited two CD bands of opposite signs in the Co(σ^*)←S(σ) ligand-to-metal charge transfer band region. The sign pattern was found to be in connection with the absolute configurations of these complexes.

For the complex [Co(SNNS)(diamine)]$^+$ where SNNS denotes a quadridentate ligand having SNNS donor set, three geometrical isomers, *cis-α*-(R^NR^N/S^NS^N), *cis-β*-(R^NR^N/S^NS^N), and *cis-β*-(R^NS^N/S^NR^N), are possible as shown in Fig. 1. One of such quadridentate ligands 3,6-dimethyl-3,6-diazaoctane-1,8-dithiol (H$_2$endet) gave *cis-α* and *cis-β*-(R^NS^N/S^NR^N) isomers together and the other (*R*)-3,4,6-trimethyl-3,6-diazaoctane-1,8-dithiol(*R*-H$_2$pndet) gave *Δ-cis-α*-(R^NR^N) and *Δ-cis-β*-(S^NR^N) isomers only.[1] However, the complexes containing these ligands were generally prepared in low yield and unstable in aqueous solutions owing to the air-oxidation. This may be mainly due to the high reactivity of the thiolato group bonded to the primary carbon.



Λ-cis-α-(S^NS^N)

Δ-cis-β-(S^NR^N) Δ-cis-β-(S^NS^N)

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

In this paper, a new SNNS quadridentate ligand 2,9-dimethyl-4,7-diazadecane-2,9-dithiol (H$_2$dddt), where the thiols are attached to the tertiary carbon, was used to prepare several cobalt(III) complexes [Co(SNNS)-(diamine)]$^+$ (diamine=en, *R*-pn, *RR*-chxn, tn, *NN'*-Me$_2$en, meso-bn, and phen)[2] and their oxidation derivatives. The geometrical and optical isomers were chromatographically separated and characterized by the visible-UV absorption, circular dichroism(CD), and ^{13}C NMR spectra. In this system, only two kinds of *cis-β* isomers, *cis-β*-(R^NR^N/S^NS^N) and *cis-β*-(R^NS^N/S^NR^N), were found. The absolute configurations of the optical isomers were discussed in relation to the CD signs in the first d-d and the Co(σ^*)←S(σ) ligand-to-metal charge transfer (LMCT) band regions.

Experimental

Preparation of 2,9-Dimethyl-4,7-diazadecane-2,9-dithiol (H$_2$dddt), [HSC(CH$_3$)$_2$CH$_2$NHCH$_2$–]$_2$: This ligand was prepared according to the reference.[3] ^{13}C NMR (benzene): δ 31.03 (–C($\underline{C}$H$_3$)$_2$SH), 45.82 (–$\underline{C}$(CH$_3$)$_2$SH), 50.04 (–NH$\underline{C}$H$_2$C-(CH$_3$)$_2$SH), and 63.80 (–NH$\underline{C}$H$_2$$\underline{C}H_2$NH–). Found: C, 51.84; H, 10.21; N, 11.65%. Calcd for H$_2$dddt·0.07 C$_6$H$_6$=C$_{10.42}$-H$_{24.42}$N$_2$S$_2$: C, 51.74; H, 10.08; N, 11.56%.

Preparation of cis-β-*[Co(dddt)(diamine)]ClO$_4$ (Diamine=en,* R-*pn,* RR-*chxn, tn,* NN'-*Me$_2$en, meso-bn, and phen):* To a solution of 0.5 g of [Co(NH$_3$)$_6$]Cl$_3$ in 30 cm^3 of water was added a mixture of 0.46 g of H$_2$dddt and 0.24 g of en in 10 cm^3 of water and then a small amount of activated charcoal. The mixed solution was stirred at 70 °C for 1 h. After removing the precipitate the filtrate was poured onto a column of SP-Sephadex C-25 (Na$^+$ form) and eluted with water and then 0.1 mol dm^{-3} NaClO$_4$ to give a dark violet band, which was assigned to *cis-β* isomer by the absorption spectrum. The eluate was concentrated on a rotary evaporator and cooled to give the perchlorate salt. The presence of *cis-α* isomer was undetectable in spite of the repeated experiments. Found for en complex: C, 32.09; H, 6.65; N, 12.30%. Calcd for *cis-β*-[Co(dddt)(en)]ClO$_4$=C$_{12}$H$_{30}$N$_4$S$_2$O$_4$ClCo: C, 31.82; H, 6.68; N, 12.37%.

The other complexes of *R*-pn, *RR*-chxn, tn, *NN'*-Me$_2$en, and meso-bn were prepared according to the same method as that of *cis-β*-[Co(dddt)(en)]ClO$_4$ except for the use of an appropriate diamine instead of en. Found for *R*-pn complex: C, 33.61; H, 6.91; N, 12.01%. Calcd for *cis-β*-[Co(dddt)(*R*-pn)]ClO$_4$=C$_{13}$H$_{32}$N$_4$S$_2$O$_4$ClCo: C, 33.44; H, 6.91: N, 12.00%. Found for *RR*-chxn complex: C, 38.01; H, 7.18; N, 11.03%. Calcd for *cis-β*-[Co(dddt)(*RR*-chxn)]ClO$_4$=C$_{16}$H$_{36}$N$_4$S$_2$O$_4$-ClCo: C, 37.91; H, 7.16; N, 11.05%. Found for tn complex: C, 33.65; H, 6.92; N, 12.06%. Calcd for *cis-β*-[Co(dddt)(tn)]ClO$_4$=C$_{13}$H$_{32}$N$_4$S$_2$C$_4$ClCo: C, 33.44; H, 6.91; N, 12.00%. Found for meso-bn complex: C, 35.04; H, 7.09; N, 11.68%. Calcd for *cis-β*-[Co(dddt)(meso-bn)]ClO$_4$=C$_{14}$H$_{34}$N$_4$S$_2$O$_4$ClCo: C, 34.96; H, 7.13; N, 11.65%. Found for *NN'*-Me$_2$en complex: C, 35.00; H, 7.16; N, 11.56%. Calcd for *cis-β*-[Co(dddt)(*NN'*-Me$_2$en)]ClO$_4$=C$_{14}$H$_{34}$N$_4$S$_2$O$_4$ClCo: C, 34.96; H, 7.13; N, 11.65%.

The complex *cis-β*-[Co(dddt)(phen)]ClO$_4$ was prepared as follows: to a solution of 0.5 g of [Co(CO$_3$)(phen)$_2$]Cl in 15 cm^3 of water was added a mixture of 0.23 g of H$_2$dddt and 0.2 g of (C$_2$H$_5$)$_3$N in 5 cm^3 of water. The mixed solution was stirred at 40 °C for 1 h and filtered. The filtrate was poured onto a column of SP-Sephadex C-25(Na$^+$ form) and eluted with 0.1 mol dm^{-3} NaClO$_4$. The brown band was evaporated on a rotary evaporator and cooled to give the desired perchlorate. Found: C, 45.47; H, 5.25; N, 9.64%. Calcd for *cis-β*-[Co-(dddt)(phen)]ClO$_4$·0.5H$_2$O=C$_{22}$H$_{31}$N$_4$S$_2$O$_{4.5}$ClCo: C, 45.40; H, 5.37; N, 9.63%.

Diastereomer Separation of cis-β-*[Co(dddt)(diamine)]*$^+$ *(Diamine=en and* RR-*chxn)*: An aqueous solution of *cis*-*β*-[Co(dddt)(en)]ClO$_4$ was poured onto a column of Dowex 50W×2 (Na$^+$ from, ϕ4×5 cm) and eluted with 0.2 mol dm^{-3} Na$_2$SO$_4$. Two bands, dark violet (**A1**) and brown (**A2**), were eluted in this order. Each eluate was concentrated by a vacuum evaporator. After repeated removal of Na$_2$SO$_4$ deposited, a small amount of NaCl was added to the filtrate to yield the desired crystals. The formation ratio **A1**/**A2** was *ca.* 8, which was almost identical to that determined by the column chromatography of the reaction solution. Found for **A1** isomer: C, 36.74; H, 7.78; N, 14.13%. Calcd for *cis*-*β*-[Co(dddt)(en)]Cl: 0.25H$_2$O=C$_{12}$H$_{30.5}$N$_4$S$_2$O$_{0.25}$ClCo: C, 36.64; H, 7.81; N, 14.24%. Found for **A2** isomer: C, 36.41; H, 7.70; N, 14.03%. Calcd for *cis*-*β*-[Co(dddt)(en)]Cl·0.5H$_2$O=C$_{12}$H$_{31}$N$_4$S$_2$O$_{0.5}$ClCo: C, 36.22; H, 7.85; N, 14.08%.

The column separation using SP-Sephadex C-25 (Na$^+$ form, ϕ4×60 cm) was ineffective. The use of NaClO$_4$ or NaCl as an eluent was troublesome because in the former case the desired perchlorate salt crystallized in the column and in the latter case evaporation of the eluate caused coprecipitation of the complex chloride and NaCl. Acidic eluent has been usually used to prevent the racemization *via* proton exchange at secondary nitrogen centers. However, it is well known that the thiolato cobalt(III) complexes give the protonated species in an acid media.[4] In this system, the protonated species caused the band broadening and the significant decrease of the elution rate. Therefore, the column chromatography was achieved under neutral conditions.

In *cis*-*β*-[Co(dddt)(*RR*-chxn)]$^+$, the Dowex chromatography of the reaction mixture gave two bands, dark violet (**B1**) and brown (**B2**), in this order. The absorption and CD spectral measurements confirmed that the former band contains two species (**B1-I** and **B1-II**) and the latter single one. No solid complex **B1-I** or **B1-II** was isolated because the less soluble pseudo racemate composed of **B1-I** and **B1-II** tended to deposit. The CD spectra of **B1-I** and **B1-II** were measured with the fractionated solutions, whose concentrations were calculated from the measured absorbance using the absorption coefficient of **B1** complex. The formation ratio **B1**/**B2** was 2.8. Found for **B1** complex: C, 37.84; H, 7.17; N, 11.06%. Found for **B2** complex: C, 37.86; H, 7.13; N, 10.97%. Calcd for *cis*-*β*-[Co(dddt)(*RR*-chxn)]ClO$_4$=C$_{16}$H$_{36}$N$_4$S$_2$O$_4$ClCo: C, 37.90; H, 7.16; N, 11.05%.

Preparation and Diastereomer Separation of cis-β-*[Co(dddsi)(diamine)]*$^+$ *(H$_2$dddsi=2,9-dimethyl-4,7-diazadecane-2,9-disulfinic Acid, [HO$_2$SC(CH$_3$)$_2$CH$_2$NHCH$_2$-]$_2$ and Diamine=en and* R,R-*chxn)*: In general, sulfinato complexes can be prepared *via* H$_2$O$_2$ oxidation of the corresponding thiolato complexes. To the reaction mixture of *cis*-*β*-[Co(dddt)(en)]$^+$ was added an excess H$_2$O$_2$ and the resulting solution was kept standing for 3 d. The resulting yellow solution was poured onto a column of SP-Sephadex C-25 (Na$^+$ form, ϕ4×60 cm) and eluted with 0.1 mol dm^{-3} Na$_2$SO$_4$ to give two yellow bands (**C1** and **C2** in this order). The formation ratio **C1**/**C2** was about 8. Both isomers showed twelve ^{13}C NMR signals and therefore have the *cis*-*β* geometry. The oxidation of the pure isomer **A1**-*cis*-*β*-[Co(dddt)(en)]$^+$ yielded only **C1** sulfinato complex. These facts indicate that no isomerization occurs during the oxidation reaction. The solid complexes were isolated by the same way as described above. Found for **C1** isomer: C, 27.04; H, 6.02; N, 10.57%. Found for **C2** isomer: C, 26.85; H, 6.03; N, 10.40%. Calcd for *cis*-*β*-[Co(dddsi)(en)]ClO$_4$·H$_2$O=C$_{12}$H$_{32}$N$_4$S$_2$O$_9$ClCo: C, 26.94; H, 6.03; N, 10.47%.

The oxidized solution of **B1**-*cis*-*β*-[Co(dddt)(*RR*-chxn)]$^+$ was separated by a column of Dowex 50W×2 (Na$^+$ form, ϕ4×8 cm; 0.15 mol dm^{-3} Na$_2$SO$_4$). The earlier eluted fractions (**D1-I**) showed a positive CD band in the spin-allowed first d-d absorption band region and the latter fractions (**D1-II**) a negative and a positive band from the lower energy in the same region. Found for **D1-I** isomer: C, 32.01; H, 6.59; N, 9.21%. Calcd for *cis*-*β*-[Co(dddsi)(*R*,*R*-chxn)]ClO$_4$·1.5H$_2$O=C$_{16}$H$_{39}$N$_4$S$_2$O$_{9.5}$ClCo: C, 32.14; H, 6.57; N, 9.37%. The concentration of **D1-II** was calculated from the measured absorbance by assuming that the absorption coefficient of **D1-II** is the same as that of **D1-I**. The complex **D2**-*cis*-*β*-[Co(dddsi)(*R*,*R*-chxn)]ClO$_4$ was obtained by the oxidation reaction of the corresponding **B2** complex. Found: C, 32.74; H, 6.24; N, 9.56%. Calcd for *cis*-*β*-[Co(dddsi)(*RR*-chxn)]ClO$_4$·H$_2$O=C$_{16}$H$_{38}$N$_4$S$_2$O$_9$ClCo: C, 32.63; H, 6.50; N, 9.51%.

Measurement. The visible and ultraviolet absorption spectra were measured on a Hitachi 330 spectrophotometer and CD spectra with a JASCO MOE-1 spectropolarimeter in

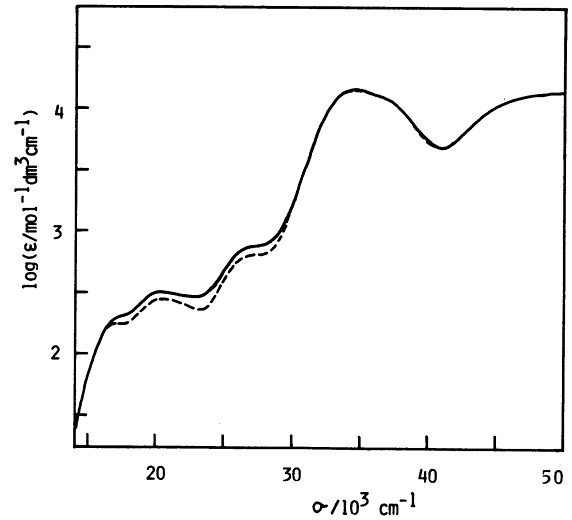


Fig. 2. Absorption spectra of *cis*-*β*-[Co(dddt)(en)]$^+$: **A1** isomer (——) and **A2** isomer (----).

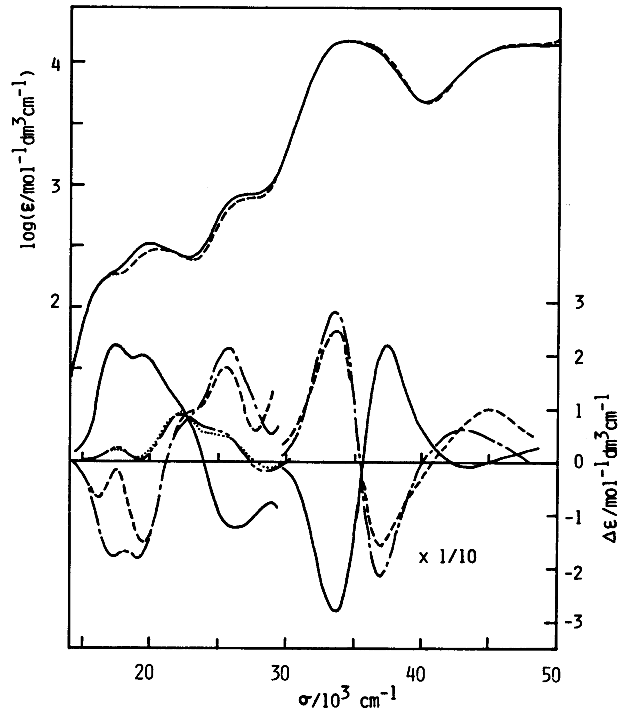


Fig. 3. Absorption and CD spectra of *cis*-*β*-[Co(dddt)(*RR*-chxn)]$^+$: **B1-I** isomer (——), **B1-II** isomer (— — —), **B1** isomer (—·—·—), the calculated curve by the equation $(\Delta\varepsilon_{B1\text{-}I}+\Delta\varepsilon_{B1\text{-}II})/2$ (········), and **B2** isomer (----).

TABLE 1. ABSORPTION DATA OF *cis*-β-[Co(SNNS)(DIAMINE)]$^+$

SNNS	Diamine	Isomer	Assignment	σ_{max}(log ε)	
				d-d band[a]	CT band[a]
dddt	en	**A1**	(R^NR^N/S^NS^N)	17.2(2.30)[c]	34.42(4.198)
				20.35(2.525)	37.0(4.11)[c]
				27.0(2.90)[c]	47.0(4.15)[c]
		A2	(R^NS^N/S^NR^N)	17.2(2.27)[c]	34.36(4.184)
				20.51(2.470)	37.0(4.10)[c]
				27.0(2.83)[c]	47.0(4.15)[c]
	RR-chxn	**B1**	Λ-$(R^NR^N)(R^CR^C)$	17.2(2.26)[c]	34.42(4.184)
			Δ-$(S^NS^N)(R^CR^C)$	20.20(2.515)	37.0(4.06)[c]
				27.0(2.92)[c]	47.4(4.16)
		B2	Δ-$(S^NR^N)(R^CR^C)$	17.2(2.26)[c]	34.36(4.184)
				20.40(2.464)	37.0(4.09)[c]
				27.0(2.88)[c]	47.4(4.17)
	R-pn[b]			17.1(2.29)[c]	34.41(4.214)
				20.35(2.494)	36.9(4.12)[c]
				27.32(2.861)	47.0(4.16)[c]
	tn[b]			16.8(2.31)[c]	34.08(4.148)
				20.02(2.516)	37.0(4.05)[c]
				26.7(2.91)[c]	46.99(4.111)
	NN'-Me$_2$en[b]			16.26(2.24)[c]	33.66(4.158)
				20.02(2.517)	36.2(4.07)[c]
				26.0(2.87)[c]	45.37(4.115)
	phen[b]			16.61(2.195)	33.44(4.28)[c]
				20.7(2.71)[c]	36.79(4.525)
				27.7(3.50)[c]	39.5(4.28)[c]
					43.96(4.583)
dddsi	en	**C1**	(R^NR^N/S^NS^N)	22.91(2.765)	30.92(4.278)
					34.0(4.15)[c]
					44.94(4.031)
		C2	(R^NS^N/S^NR^N)	22.94(2.747)	30.96(4.260)
					34.0(4.13)[c]
					45.05(4.028)
	RR-chxn	**D1-I**	Λ-$(R^NR^N)(R^CR^C)$	22.73(2.795)	30.63(4.243)
					33.3(4.15)[c]
					44.15(4.028)
		D2	Δ-$(S^NR^N)(R^CR^C)$	22.30(2.770)	30.49(4.246)
					33.5(4.12)[c]
					43.86(4.043)

a) Wave numbers and ε values are given in 10^3 cm^{-1} and cm^{-1} mol^{-1} dm^3, respectively. b) No chromatographic separation for these complexes was attempted. c) Shoulder.

aqueous solutions. The ^{13}C NMR spectra were recorded with a JEOL FX-90Q NMR spectrometer.

Results and Discussion

Characterization of Geometrical Isomers. The absorption spectra and data of [Co(N)$_4$(thiolato)$_2$] type complexes are shown in Figs. 2 and 3 and Table 1. Both isomers **A1**- and **A2**-[Co(dddt)(en)]$^+$ showed very similar absorption spectra. The intense band in 30000—40000 cm^{-1} region, which is assigned to the Co(σ^*)←S(σ) LMCT transition,[5] is composed of two components at 34400 and *ca.* 37000 cm^{-1} for each isomer. Such a spectral pattern is characteristic of *cis(S)* geometry.[1] Therefore, both isomers can be assigned to the *cis*-β geometry. This assignment was confirmed by the ^{13}C NMR spectra (Table 2): each isomer showed twelve or eleven signals, which is consistent with the *cis*-β geometry of C_1 symmetry. The thiolato complexes containing the other diamines were also assigned to *cis*-β isomer on the basis of the absorption spectra.

The yield of the first eluted isomer is considerably higher than that of the second one in either *cis*-β-[Co(dddt)(en)]$^+$ or *cis*-β-[Co(dddt)(*RR*-chxn)]$^+$. For the complexes containing triethylenetetramine (trien) as a quadridentate ligand, the strain minimization cal-

TABLE 2. ^{13}C NMR DATA (ppm FROM Me$_4$Si)[a]

Complex	Chemical shift
A1-[Co(dddt)(en)]$^+$	31.35, 32.94, 36.41, 36.63, 43.29, 46.38, 48.06, 50.28, 52.66, 53.42, 66.69, 68.10
A2-[Co(dddt)(en)]$^+$	31.87, 33.36,[b] 37.20, 44.06, 46.44, 47.50, 49.45, 52.75, 56.08, 66.70, 70.33
C1-[Co(dddsi)(en)]$^+$	20.49, 22.33, 25.90, 26.39, 44.43, 44.81, 51.74, 52.99, 58.57, 60.03, 76.12, 78.94
C2-[Co(dddsi)(en)]$^+$	20.49, 22.33, 25.90, 26.39, 44.16, 44.59, 51.74, 53.04, 58.57, 60.03, 76.07, 78.94

a) All complexes were converted into the soluble sulfate salts for measurement. b) The intensity is *ca.* twice those of others.

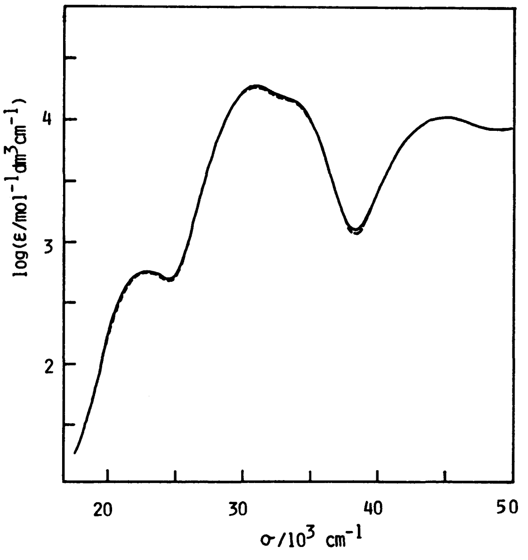


Fig. 4. Absorption spectra of *cis*-β-[Co(dddsi)(en)]$^+$: **C1** isomer (——) and **C2** isomer (----).

culations were carried out by several groups.6) These calculations indicated that *cis*-β-(R^NR^N/S^NS^N) isomer is more stable than *cis*-β-(R^NS^N/S^NR^N) one. This was experimentally confirmed by the higher yield of *cis*-β-(R^NR^N/S^NS^N) isomer in [CoX_2(trien)]$^{n+}$(X_2=$NH_2CH_2CO_2^-$,6b) $2NH_3$,6c) $2NCS^-$,7) and $2CN^-$8)). Therefore, it is reasonable to consider that **A1** isomer has the *cis*-β-(R^NR^N/S^NS^N) structure and **A2** isomer the *cis*-β-(R^NS^N/S^NR^N) one. Similarly **B1** isomer was assigned to a pair of the diastereomers of *Λ*-*cis*-β-(R^NR^N)(R^CR^C) and *Δ*-*cis*-β-(S^NS^N)(R^CR^C), but **B2** isomer was found to be stereoselectively composed of *Δ*-*cis*-β-(S^NR^N)(R^CR^C) as described later. Another empirical criterion of the geometry assignment may be derived from ^{13}C NMR spectra. The chemical shift of *cis*-β-(R^NR^N/S^NS^N) isomer always locates at the higher magnetic field than that of the corresponding *cis*-β-(R^NS^N/S^NR^N) one in all [CoX_2(trien)]$^{n+}$ complexes so far isolated (X_2=$2NH_3$,6c) $2NCS^-$,7) $2CN^-$,8) and en9)). In the present system, **A1** isomer exhibited the ^{13}C NMR resonances at somewhat higher magnetic field than **A2** one, which leads to the assignment that **A1** and **A2** isomers are *cis*-β-(R^NR^N/S^NS^N) and *cis*-β-(R^NS^N/S^NR^N), respectively. Thus, the same assignment was derived from the formation ratio and the relative position of ^{13}C NMR chemical shift.

The absorption spectra of sulfinato complexes are shown in Figs. 4 and 5 and Table 1. All sulfinato complexes showed the intense LMCT band of two components at 27000—37000 cm^{-1}, which is characteristic for the S-bonded sulfinato complex.10) Both isomers **C1**- and **C2**-[Co(dddsi)(en)]$^+$ could be assigned to the *cis*-β geometry based on the ^{13}C NMR spectra (Table 2) and the absorption spectral resemblance to *cis*-β-[Co(endesi)(diamine)]$^+$.1) The formation ratio **C1**/**C2** in the sulfinato complex was almost identical to the ratio **A1**/**A2** in the starting thiolato complex and the oxidation of *cis*-β-(R^NR^N/S^NS^N)-[Co(dddt)(en)]$^+$ (**A1** isomer) gave only **C1** isomer. Therefore, **C1** isomer is assignable to *cis*-β-(R^NR^N/S^NS^N) and **C2** one to *cis*-β-(R^NS^N/S^NR^N). From a similar argument, **D1** isomer was attributed to a pair of diastereomers of *Δ*-*cis*-β-(S^NS^N)(R^CR^C) and *Λ*-*cis*-β-(R^NR^N)(R^CR^C), and **D2** isomer to *Δ*-*cis*-β-(S^NR^N)(R^CR^C).

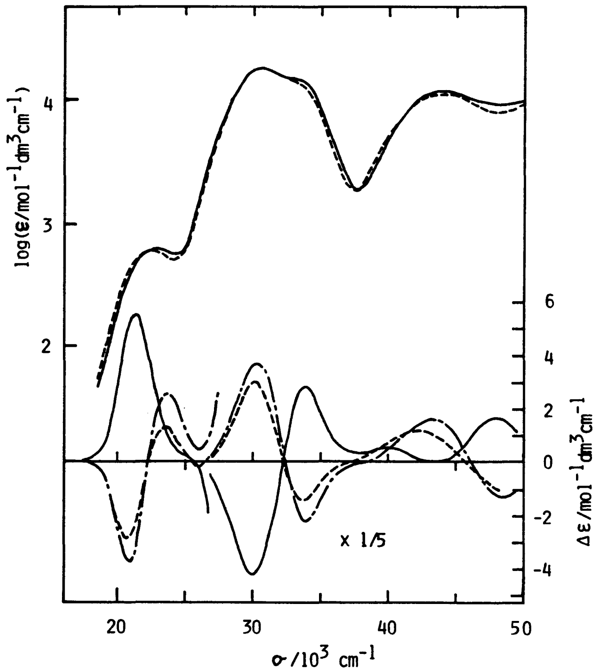


Fig. 5. Absorption and CD spectra of *cis*-β-[Co(dddsi)(RR-chxn)]$^+$: **D1-I** isomer (——), **D1-II** isomer (— — —), and **D2** isomer (----).

Synthesis and Property of Cobalt(III) Complexes with SNNS Ligand. Several cobalt(III) complexes of [Co(SNNS)(diamine)]$^+$ type could be prepared using the dddt quadridentate ligand $^-SC(CH_3)_2CH_2NHCH_2CH_2NHCH_2C(CH_3)_2S^-$. This ligand did not react directly with the tris(diamine)cobalt(III) complexes such as [Co(en)$_3$]$^{3+}$ and [Co(RR-chxn)$_3$]$^{3+}$, though the endet (R=H) and R-pndet (R=CH_3) ligands having general skeleton $^-SCH_2CH_2N(CH_3)CH_2CHRN(CH_3)CH_2CH_2S^-$ reacted immediately with these complexes.1) In the latter ligands, it was found that the mononuclear complex formation is possible only when the remaining two coordination sites are occupied by such tightly bound ligands as diamine, $2CN^-$, and $NH_2CH_2CH_2S^-$. However, in the present dddt ligand, the formation of [Co(dddt)ox]$^-$ (ox=$^-O_2CCO_2^-$) was confirmed by the absorption spectrum. The thiolato complexes with endet or R-pndet were liable to oxidation by air in aqueous solutions but the dddt complexes were not. The complete oxidation of the thiolato complex to the sulfinato one with an excess of H_2O_2 necessitated *ca.* 3 d at room temperature in the dddt complex. Such long time was not needed for the endet complexes.1) These facts indicate that the dddt ligand has not so higher reactivity as the endet or R-pndet. This is attributable to the structure of dddt where the thiolate are bonded to the tertiary carbon. A similar situation is encountered between cysteinate(cyst) $NH_2CH(CO_2^-)CH_2S^-$ and penicillaminate(pen) $NH_2CH(CO_2^-)C(CH_3)_2S^-$: The former ligand and its analog $NH_2CH_2CH_2S^-$, where the thiolate is bonded to the primary carbon, tend to form polymeric complexes with μ-thiolato structure because of residual reactivity after coordination.11) Bis(terdentato)cobalt(III) complex has been reported only for the penicillaminate.[12]

The endet and *R*-pndet ligands gave both *cis*-α and *cis*-β isomers[1] but the dddt only *cis*-β one. In general, cobalt(III) complexes containing two or three thiolato groups prefer the *cis(S)* geometry as found in *trans(N)*- and *trans(O)*-$[Co(\text{D-pen})_2]^-$,[12b] *fac(S)*-$[Co(NH_2CH_2CH_2S)_3]$,[5] and *fac(S)*-$[Co(\text{L-cyst})_3]^{3-}$,[5] because of the strong structural trans effect of the thiolato sulfur atom.[13] The fact that only *cis*-β isomers with the *cis(S)* geometry were found in the dddt ligand agrees well with the above general tendency of the thiolato complexes. The endet and *R*-pndet ligands have the methyl group on the nitrogen atoms. The steric repulsion between the two methyl groups may be weakened in the *cis*-α structure rather than in the *cis*-β one, which is responsible for the formation of *cis*-α isomer in the endet and *R*-pndet complexes. A similar substituent effect has been observed for the edda complexes $[Co(\text{edda})X_2]^+$ (edda=ethylenediamine-*N,N′*-diacetate and X_2=en or $2NH_3$):[14] A trace of *cis*-β isomer was found for the edda complexes but no *cis*-β isomers for the *N,N′*-dimethyl- and *N,N′*-diethyl-edda complexes.

A linear flexible edda-type ONNO ligand apparently resembles the present SNNS ligand. In the edda complexes, *cis*-α isomer is dominantly formed[14] and the formation of *cis*-β isomer depends mainly on the properties of the bidentate ligands[15] and the reaction temperature.[16] No couple of *cis*-β isomers, *cis*-β-(R^NR^N/S^NS^N) and *cis*-β-(R^NS^N/S^NR^N), has been known so far,[17] though the possible existence of two *cis*-β isomers in $[Co(\text{edda})(H_2O)_2]^+$ and $[Co(\text{edda})CO_3]^-$ was suggested by a ^1H NMR study.[15c] The X-ray structural study showed that *cis*-β-$[Co(\text{edda})(H_2O)_2]ClO_4$ is the racemate consisting of Λ-*cis*-β-(R^NS^N) and Δ-*cis*-β-(S^NR^N)[15c] and Δ-*cis*-β-[Co(edda)(*R*-pn)]Cl takes the (S^NR^N) configuration[18] in the crystalline state. Thus, it has been concluded that the (S^NR^N) configuration represents the thermodynamically stable isomer in solution as well as in the solid state.[18] Such conclusion is in good agreement with that for the endet and *R*-pndet complexes where *cis*-α and only *cis*-β-(R^NS^N/S^NR^N) isomers were found. However, two *cis*-β isomers have been found for the present dddt complexes, the *cis*-β-(R^NR^N/S^NS^N) configuration being predominant. The stereochemistry of the dddt complexes resembles that of the trien complexes rather than the edda complexes.

Absolute Configurations of Thiolato and Sulfinato Complexes. The CD spectra are shown in Figs. 3 and 5. **B1-I** isomer showed three positive CD components in the first d-d absorption band region and therefore is assigned to the Λ-*cis*-β-$(R^NR^N)(R^CR^C)$ configuration.[1] Since **B1-II** isomer showed main two negative CD components in the same region, it can be assigned to the Δ-*cis*-β-$(S^NS^N)(R^CR^C)$ configuration. The CD spectrum of less soluble **B1** isomer is the same as that calculated from equimolecular amount of **B1-I** and **B1-II**, which means that **B1** isomer is a pseudoracemate composed of **B1-I** and **B1-II**. Only one diastereomer **B2** was found for the later eluted band. On the basis of the two negative CD bands in the first d-d absorption band region, the Δ-*cis*-β-$(S^NR^N)(R^CR^C)$ configuration is assigned to it. It is noteworthy that such complete stereoselectivity was found in other sys-

Table 3. CD data of *cis*-β-[Co(SNNS)(*RR*-chxn)]$^+$

SNNS	Isomer	Assignment	$\sigma_{ext}(\Delta\varepsilon)$ a)	
			d-d band region	CT region
dddt	**B1-I**	Λ-$(R^NR^N)(R^CR^C)$	17.39(+2.19)	33.67(−28.2)
			19.34(+1.99)	37.38(+22.0)
			22.4(+1.0) b)	43.10(−1.03)
			26.25(−1.24)	
	B1-II	Δ-$(S^NS^N)(R^CR^C)$	17.24(−1.78)	33.56(+28.2)
			19.16(−1.82)	36.90(−21.4)
			22.4(+0.7) b)	43.1(+6.15)
			25.64(+2.13)	
	B1(**B1-I**+**B1-II**)		17.39(+0.27)	
			22.35(+0.90)	
			25.0(+0.59) b)	
			28.5(−0.18)	
	B2	Δ-$(S^NR^N)(R^CR^C)$	16.13(−0.67)	33.44(+24.8)
			19.49(−1.53)	36.92(−15.8)
			22.5(+0.88) b)	45.2(+9.8)
			25.38(+1.78)	
dddsi	**D1-I**	Λ-$(R^NR^N)(R^CR^C)$	21.32(+5.61)	29.99(−22.1)
				33.84(+14.9)
				40.0(+2.89)
				48.0(+8.66)
	D1-II	Δ-$(S^NS^N)(R^CR^C)$	20.88(−3.95)	30.30(+19.4)
			23.61(+2.68)	33.96(−11.6)
				43.2(+8.46)
				48.5(+6.72)
	D2	Δ-$(S^NR^N)(R^CR^C)$	20.75(−2.90)	30.13(+15.1)
			23.53(+1.23)	33.67(−7.12)
			25.9(−0.18)	42.19(+5.97)

a) Wave numbers and $\Delta\varepsilon$ values are given in $10^3 cm^{-1}$ and $cm^{-1} mol^{-1} dm^3$, respectively. b) Shoulder.

TABLE 4. THE RELATIONSHIP BETWEEN CD SIGN PATTERNS AND ABSOLUTE CONFIGURATIONS IN THE THIOLATO AND SULFINATO COMPLEXES WITH TWO OR MORE SULFUR DONOR ATOMS

Complex[a]	Structure	$\sigma_{\mathrm{ext}}(\Delta\varepsilon)$[b]		Ref.
		First d-d band region[c]	LMCT region	
Thiolato complexes				
$[\mathrm{Co(endet)}(R\text{-pn})]^+$	Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}})$	16.47(−1.50) 20.75(−1.65)	32.31(+28.2) 36.04(−33.3)	1)
$[\mathrm{Co(endet)}(RR\text{-chxn})]^+$	Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	16.31(−1.64) 20.62(−1.85)	32.27(+29.3) 35.84(−31.8)	1)
$[\mathrm{Co}(R\text{-pndet})(\mathrm{en})]^+$	Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{C}}R^{\mathrm{N}})$	16.35(−1.32) 20.62(−1.87)	32.21(+26.6) 35.91(−34.0)	1)
$[\mathrm{Co}(R\text{-pndet})(RR\text{-chxn})]^+$	Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{C}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	16.31(−1.82) 20.64(−2.43)	32.27(+33.5) 35.91(−36.6)	1)
$[\mathrm{Co(dddt)}(RR\text{-chxn})]^+$	Λ-*cis*-β-$(R^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	17.39(+2.19) 19.34(+1.99)	33.67(−28.2) 37.38(+22.0)	e)
	Δ-*cis*-β-$(S^{\mathrm{N}}S^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	17.24(−1.78) 19.16(−1.82)	33.56(+28.2) 36.90(−21.4)	e)
	Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	16.13(−0.67) 19.49(−1.53)	33.44(+24.8) 36.92(−15.8)	e)
$[\mathrm{Co}(\textsc{d}\text{-pen})_2]^-$	*trans(O)*[d]	17.03(+6.96)	34.13(−10.2) 38.03(+12.5)	12b)
	trans(N)[d]	19.73(−8.68)	33.73(+36.9) 37.93(−19.5)	12b)
$[\mathrm{Co(dpt)_2}]^+$	*cis(S)*[d]	16.89(+0.79)	33.90(−5.98) 38.68(+10.9)	21)
Sulfinato complexes				
$[\mathrm{Co(dddsi)}(RR\text{-chxn})]^+$	Λ-*cis*-β-$(R^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	21.32(+5.61)	29.99(−22.1) 33.84(+14.9)	e)
	Δ-*cis*-β-$(S^{\mathrm{N}}S^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	20.88(−3.95)	30.30(+19.4) 33.96(−11.6)	e)
	Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$	20.75(−2.90)	30.13(+15.1) 33.67(−7.12)	e)
$[\mathrm{Co(dti)_3}]^{3-}$	Δ	23.8(−3.92)	27.4(+11.2) 35.0(−5.99)	22)
$[\mathrm{Co(aesi)_3}]$	Λ-*fac(S)*	22.7(+2.04)	31.7(−10.9) 36.4(+7.86)	5)
$[\mathrm{Co}(\textsc{l}\text{-cysi})(\mathrm{aesi})_2]^-$	Δ-*fac(S)*	22.7(−2.87)	31.7(+15.5) 35.7(−13.3)	5)
$[\mathrm{Co}(\textsc{l}\text{-cysi})_3]^{3-}$	Δ-*fac(S)*	22.7(−3.16)	31.8(+18.0) 35.7(−17.2)	5)
$[\mathrm{Co}(\textsc{l}\text{-cymi})_3]$	Δ-*fac(S)*	22.5(−2.91)	31.7(+15.1) 35.6(−14.8)	5)
$[\mathrm{Co(SO_3)_2(en)_2}]^-$	Δ-*cis(S)*	21.05(−1.83)	34.25(+25.7) 38.02(−28.7)	19)

a) Ligand abbreviations: Hdpt=$NH_2CH_2CH(SH)CH_2NH_2$, H_2dti=$HO_2SCH_2CH_2SO_2H$, Haesi=$NH_2CH_2CH_2SO_2H$, L-H_2cysi=$NH_2CH(CO_2H)CH_2SO_2H$, and L-Hcymi=$NH_2CH(COOCH_3)CH_2SO_2H$. b) Wave numbers and $\Delta\varepsilon$ values are given in $10^3\,\mathrm{cm^{-1}}$ and $\mathrm{cm^{-1}\,mol^{-1}\,dm^3}$, respectively. c) Only dominant bands are shown. d) The definition of absolute configuration based on the skew pairs of chelate rings is ineffective for these complexes. e) This work.

tem of Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{N}})$-$[\mathrm{Co(endet)}(R\text{-pn or }RR\text{-chxn})]^+$ and Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{N}})$-$[\mathrm{Co}(R\text{-pndet})(\text{en or }RR\text{-chxn})]^+$.1) The corresponding Λ-*cis*-β-$(R^{\mathrm{N}}S^{\mathrm{N}})$ structure has been considered to be less stable in these complexes because of a steric repulsion between the two amine protons on bidentate diamine and the two methylene protons adjacent to the tertiary amine of the quadridentate. The same discussion is effective for the present complex *cis*-β-$[\mathrm{Co(dddt)}(RR\text{-chxn})]^+$. The configurations of the sulfinato complexes were determined by the CD sign in the first absorption band region, being in agreement with those based on the oxidation reaction of the corresponding thiolato complexes: **D1-I** and **D1-II** isomers are Λ-*cis*-β-$(R^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$ and Δ-*cis*-β-$(S^{\mathrm{N}}S^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$, respectively, and **D2** isomer Δ-*cis*-β-$(S^{\mathrm{N}}R^{\mathrm{N}})(R^{\mathrm{C}}R^{\mathrm{C}})$.

A clear relationship between absolute configuration and CD sign could be found in the LMCT band region. All the present complexes showed two intense CD bands of opposite signs at 30000—40000 $\mathrm{cm^{-1}}$ for the thiolato complexes and at 27000—37000 $\mathrm{cm^{-1}}$ for the sulfinato complexes. The sign pattern in this region always relates to that in the first d-d band region, that is, (+)(−)CT from the lower energy corresponds to (−)d-d, and (−)(+)CT to (+)d-d. Therefore, the complexes with (+)(−) and (−)(+) patterns from the lower energy in the LMCT band region can be assigned to the Δ and Λ configurations, respectively.

Table 4 collects the thiolato and sulfinato complexes with two or more sulfur donor atoms. All complexes have the *cis(S)* geometry and showed two intense CD bands of opposite signs as well as characteristic LMCT absorption band with two components. It is very interesting that the above empirical relationship about absolute configuration is applicable to all thiolato and sulfinato complexes with two or more sulfur donor atoms no matter what the ligands may be. This is exemplified in the system containing monodentate ligand $[Co(SO_3)_2(en)_2]^-$.[19] The thiolato and sulfinato complexes in Table 4 have only CD contribution owing to the skew pairs of chelate rings and their LMCT transitions overlap neither with two d-d transitions nor with the other LMCT transitions such as Co-$(\sigma^*)\leftarrow$N(σ), the situations being responsible for the above result. The empirical relationship does not hold for the *trans(S)* complexes such as *cis*-α-[Co-(endet)(diamine)]$^+$,[20] *cis*-α-[Co(*R*-pndet)(diamine)]$^+$,[1] and *trans(S)*-$[Co(mp)_2(en)]^+$ (mp=2-pyridinethiolate), because they show the single LMCT band at relatively lower energy. In the complexes containing sulfenato and/or thioether groups, there is also no simple relationship because another CD contribution owing to the chiral sulfur donor atoms adds to that owing to the skew pairs of chelate rings.

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2) Abbreviations used for ligands are as follows: en=1,2-ethanediamine, *R*-pn=(*R*)-1,2-propanediamine, *RR*-chxn=(*R*,*R*)-1,2-cyclohexanediamine, tn=1,3-propanediamine, *N*,*N*′-Me$_2$en=*N*,*N*′-dimethyl-1,2-ethanediamine, meso-bn=(2*R*, 3*S*)-2,3-butanediamine, and phen=1,10-phenanthroline.

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