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Circular Dichroism Spectra of Cobalt(III) Complexes Containing One or Two Azido, Isothiocyanato, and Nitro Ligands. II.[1] *trans*-Type Bis[(1*R*,2*R*)-1,2-cyclohexanediamine] Complexes

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The *trans* dianiono type complexes of cobalt(III) containing (1*R*,2*R*)-1,2-cyclohexanediamine, *trans*-[Co(X)$_2$(*R*,*R*-chxn)$_2$]$^+$, and -[Co(X)(X')(*R*,*R*-chxn)$_2$]$^+$ (X and X'=N_3^-, NCS^-, or NO_2^-) were prepared and their circular dichroism (CD) spectra measured in the visible and ultraviolet regions. The CD and absorption behaviors in the so-called specific absorption band region are compared with those of *cis*-type bis(ethylenediamine) complexes and discussed in relation to the origin of the specific band. In addition, three isomers of the [Co(NCS)(NH$_3$)(*R*,*R*-chxn)$_2$]$^{2+}$ complex are assigned on the basis of their CD spectra.

In a previous paper,[1] circular dichroism (CD) spectra of bis(ethylenediamine) complexes of cobalt(III) with a *cis* configuration were discussed, especially with emphasis on the so-called specific absorption band in the near ultraviolet region. The specific absorption band is moderately intense, and specific for certain aniono ligands, such as azido, isothiocyanato, nitro, and sulfito ligands. The origin of these bands has been attributed to charge-transfer transitions between the aniono ligand and the central metal, or to intraligand transitions. A previous study[1] suggests an interaction between two aniono ligands in the *cis* positions through the central cobalt(III) ion. This kind of electronic interaction between two NCS^-, NO_2^-, or Cl^- ligands have frequently been proposed for complexes which have two aniono ligands in the *trans* positions.[2-6] Thus, the specific band of a *trans* dianiono complex is more bathochromic than that of the corresponding *cis* isomer,[4,5] with some exceptions.[6]

The present paper deals with *trans* dianiono type complexes, including mixed complexes, of cobalt(III) containing (1*R*,2*R*)-1,2-cyclohexanediamine (abbreviated as *R*,*R*-chxn) for the purpose of studying their CD spectra in the region of the specific absorption bands of azido, isothiocyanato, and nitro ligands.

Experimental

*Preparation and Optical Resolution. (1) (1*R*,2*R*)-1,2-Cyclohexanediamine*: The ligand was optically resolved by the method of Asperger and Liu.[7] The less soluble diastereomer, (*R*,*R*-chxnH$_2$) (*d*-tart), showed a constant optical rotation $[\alpha]_{589}=+12.1°$ (*d*-tart denotes the $(+)_{589}$-tartrate(2−) ion). Found: C, 45.18; H, 7.60; N, 10.55%. Calcd for $C_{10}H_{20}N_2O_6$: C, 45.45; H, 7.63; N, 10.60%. For preparative purposes, a stock solution of *R*,*R*-chxn was conveniently prepared by the addition of a calculated amount of $Ba(OH)_2\cdot 8H_2O$ to a hot suspension of the less soluble diatereomer. After cooling overnight in a refrigerator, the precipitated $BaSO_4$ was removed.

(2) trans-[CoCl$_2$(R,R-chxn)$_2$]Cl·H$_2$O: This complex was prepared following exactly the method of Treptow.[8] Found: C, 35.79; H, 7.41; N, 13.60%. Calcd for $[CoCl_2(C_6H_{11}N_2)_2]Cl\cdot H_2O$: C, 35.01; H, 7.35; N, 13.61%.

(3) trans-[Co(N$_3$)$_2$(R,R-chxn)$_2$]Cl·0.5H$_2$O: The dichloro complex, *trans*-[CoCl$_2$(*R*,*R*-chxn)$_2$]Cl·H$_2$O (0.4 g), was dissolved in 20 cm^3 of methanol at 30 °C, and 25 mg of LiN_3 was added with stirring. The azide of the dichloro complex, *trans*-[CoCl$_2$(*R*,*R*-chxn)$_2$]N$_3$·*n*H$_2$O, quickly separated out. The suspension in methanol was vigorously stirred at 30 °C until the azide salt dissolved (about 5 min). Then another 25 mg of LiN_3 was added to the solution and the resulting suspension was further stirred for 15 min. To the resulting blue-violet solution of the azidochloro complex was added 50 mg of LiN_3, and the mixture was heated to 50 °C and stirred for 40 min. This was then cooled in ice to stop the reaction, and concentrated to about 10 cm^3 with a vacuum evaporator. After cooling in a refrigerator overnight, the dark blue-violet crystals that separated out were filtered, washed with ether and air-dried. 110 mg. Recrystallization was performed from methanol by the addition of ether. Found: C, 34.86; H, 6.93; N, 32.78%. Calcd for $[Co(N_3)_2(C_6H_{14}N_2)_2]Cl\cdot 0.5H_2O$: C, 34.66; H, 7.03; N, 33.33%.

(4) trans-[Co(NCS)$_2$(R,R-chxn)$_2$]Cl·H$_2$O: To a solution of 0.4 g of the dichloro complex in 20 cm^3 of methanol was added 340 mg of $LiSCN\cdot H_2O$, and the mixture was stirred for 30 min at 65 °C. Then, crystals began to separate out. After further stirring for 15 min, the mixture was ice-cooled for half an hour. The resulting reddish-orange crystals were filtered, washed with ice-cold methanol and ether, and air-dried. 180 mg. Recrystallization was carried out from hot methanol (60 °C, 8 cm^3). Found: C, 36.64; H, 6.66; N, 18.72%. Calcd for $[Co(NCS)_2(C_6H_{14}N_2)_2]Cl\cdot H_2O$: C, 36.80; H, 6.62; N, 18.39%.

(5) trans-[Co(NO$_2$)$_2$(R,R-chxn)$_2$]Cl·2.5H$_2$O: To a solution of the dichloro complex (0.4 g) in 20 cm^3 of methanol was added 140 mg of $LiNO_2\cdot H_2O$. The mixed solution was stirred at 60 °C for 2 h, and the separated crystals were filtered off. The filtrate was evaporated to 7 cm^3 and stored in a refrigerator overnight. The resulting crystals were filtered off. The yellow-orange lustrous crystals obtained (both the first and second crops) were the *cis*-isomer. The filtrate was evaporated to dryness. The residual solid was suspended in 4 cm^3 of ethanol and filtered. 99 mg. The product was recrystallized from ethanol by the addition of ether, and the resulting fine yellow-orange crystals were filtered, washed with ether, and air-dried. Found: C, 31.75; H, 7.32; N, 18.35%. Calcd for $[Co(NO_2)_2(C_6H_{14}N_2)_2]Cl\cdot 2.5H_2O$: C, 31.35; H, 7.23; N, 18.28%.

(6) trans-[CoCl(NCS)(R,R-chxn)$_2$]Cl·3H$_2$O: To a solution of the dichloro complex (0.4 g) in 20 cm^3 of methanol at 30 °C was added 85 mg of $LiSCN\cdot H_2O$. When the mixed solution was stirred for 10 min, the color of the solution changed from green to dark violet. The solution was evaporated to 5 cm^3

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and stored in a refrigerator overnight. After the removal of the reddish-violet precipitate of the *cis*-chloroisothiocyanato complex, the filtrate was again stored overnight in a refrigerator. The resulting blue-violet precipitate of the desired complex was filtered with suction and washed with ether. 35 mg. The second crop of the blue-violet precipitate was obtained when the filtrate was stored in a refrigerator for further 3 days. 32 mg. The two crops of the crude *trans* complex were combined and reprecipitated from methanol (2 cm^3) by adding ether (8 cm^3). The reprecipitated product was filtered and washed with ether and air-dried. Found: C, 34.51; H, 7.29; N, 14.87%. Calcd for $[CoCl(NCS)(C_6H_{14}N_2)_2]Cl\cdot 3H_2O$: C, 33.19; H, 7.29; N, 14.89%.

(7) trans-$[CoCl(NO_2)(\mathrm{R,R}\text{-}chxn)_2]Cl\cdot 1.5H_2O$: The reaction was carried out at 30 °C by adding 70 mg of $LiNO_2\cdot H_2O$ to a solution containing 0.4 g of the dichloro complex in 20 cm^3 of methanol. After stirring for 10 min, the reacted solution of dark orange color was cooled in ice for 2 h. The resulting crystals (the *cis*-chloronitro complex) were removed by filtration, 10 cm^3 of ether was added to the filtrate, and then the mixture was stored in a refrigerator overnight. The second crop of *cis* complex crystals separated out was filtered off, and the filtrate was further cooled for 3 days in a refrigerator. The third crop of crystals yielded in a small quantity, and this was filtered off. The fourth crop, which was obtained upon evaporating the filtrate to about 4 cm^3, was a mixture of *cis* and *trans* complexes. To the filtrate from the fourth crop was added 2 cm^3 of ether, and after a period the *trans* complex separated out. After storage in a refrigerator for 2 h, the crystals were filtered, washed with a little cold methanol and ether, and air-dried. 75 mg. Reddish-orange fine crystals were obtained by recrystallization from methanol (3 cm^3) upon the addition of ether (4 cm^3). Found: C, 33.87; H, 7.31; N, 15.97%. Calcd for $[CoCl(NO_2)(C_6H_{14}N_2)_2]Cl\cdot 1.5H_2O$: C, 33.42; H, 7.25; N, 16.24%.

(8) trans-$[Co(NCS)(NO_2)(\mathrm{R,R}\text{-}chxn)_2]Cl\cdot 1.5H_2O$: To a solution of 0.4 g of the dichloro complex in 20 cm^3 of methanol was added 70 mg of $LiNO_2\cdot H_2O$. After the mixture had been stirred for 10 min at 30 °C, 80 mg of $LiSCN\cdot H_2O$ was added to it and the reaction temperature was raised to 60 °C. *After stirring for 70 min, the reacted solution was evaporated* to dryness. The resulting solid was dissolved in water and the solution was adsorbed on a column (20 × 220 mm) containing a cation-exchange resin (Dowex 50W × 8, K^+ form). The eluting agent, a 0.1 M KCl solution, was made to flow at a rate of 2 cm^3/min. While 6.8—11.5 dm^3 of the eluting agent flowing, the yellow-to-orange colored eluate (4.7 dm^3) was collected in 20-cm^3 portions in a fraction collector. The middle (56—180 th) fractions were confirmed to contain the desired *trans*-isothiocyanatonitro complex by checking the absorption spectra. These were combined and evaporated at 30 °C. After the separated KCl crystals had been removed by filtration several times, the eluate was evaporated to dryness. The complex was extracted from the residual solid using 20 cm^3 of methanol, and the undissolved KCl crystals were filtered off. In order to remove the remaining KCl, careful fractional precipitation was carried out by the addition of ether to the methanol extract. The desired complex obtained as a later fraction was filtered, washed with ether, and air-dried. Found: C, 34.45; H, 6.84; N, 18.66%. Calcd for $[Co(NCS)(NO_2)(C_6H_{14}N_2)_2]Cl\cdot 1.5H_2O$: C, 34.40; H, 6.88; N, 18.52%.

(9) trans-$[Co(N_3)(NCS)(\mathrm{R,R}\text{-}chxn)_2]^+$: As in the course of preparing the diazido complex (3), four 25-mg portions of LiN_3 were added over a 30-min period to a stirred solution containing 0.8 g of the dichloro complex in 40 cm^3 of methanol at 30 °C. To the blue-violet reaction mixture (the *cis*- and *trans*-azidochloro complexes) was added 165 mg of $LiSCN\cdot H_2O$, and the solution was heated to 60 °C and stirred for 15 min. The color of the solution turned to red-violet. After the reaction had been stopped by ice-cooling, an equal volume of ether was added to the solution and the resulting mixture was evaporated to dryness with a vacuum evaporator. The solid was dissolved in water and subjected to chromatography on a column containing a cation-exchanger CM-Sephadex C-25 using a 0.1 M NaCl solution as the eluting agent. The earlier eluate contained the desired *trans*-azidoisothiocyanato complex. The isomerization to *cis* occurred even at 25 °C and the *trans* complex could not be isolated in crystal.

(10) trans-$[Co(N_3)(NO_2)(\mathrm{R,R}\text{-}chxn)_2]^+$: To a solution of 0.8 g of the dichloro complex in 40 cm^3 of methanol at 30°C was added 140 mg of $LiNO_2\cdot H_2O$ with stirring. This stirring was continued for 10 min. Upon the addition of 100 mg of LiN_3, the azide salt of the dichloro complex separated out. The suspension was heated to 60 °C and stirred for 20 min. The resulting solution was evaporated to dryness, and the solid obtained was dissolved in water and subjected to chromatography on a column (27 × 980 mm) containing CM-Sephadex C-25 with a 0.1 M NaCl solution at a rate of 0.23 cm^3/min. When 1.5 dm^3 of the eluting agent was passed over the column, the *trans* species reached the bottom of the column. At this time, the eluate began to be collected in 10-cm^3 portions and the 28—38 th fractions were confirmed to contain the desired *trans*-azidonitro complex (the *trans*-dinitro and -diazido complexes were contained in the 1—15 th and 44—50 th fractions, respectively). The isomerization to *cis* occurred rapidly, and isolation of the complex was unsuccessful.

(11) Three Isomers of the $[Co(NCS)(NH_3)(\mathrm{R,R}\text{-}chxn)_2]^{2+}$ *Complex*: To a solution containing 0.8 g of the dichloro complex in 40 cm^3 of methanol at 30 °C was added 170 mg of $LiSCN\cdot H_2O$, and the mixed solution was stirred for 10 min. After adding an equal volume of ether, the reaction mixture was evaporated to dryness with a vacuum evaporator. The resulting violet solid was placed in a 250-cm^3 pressure cylinder, which was placed in a dry ice-methanol bath, and ammonia was condensed over the solid. After about 15 cm^3 of ammonia had been condensed, the container was tightly capped and allowed to stand at room temperature (21°C) for about 15 min. The color of the ammonia solution changed to reddish-orange. Then, the cap was removed and the ammonia was evaporated. After the resulting orange product had been dried over P_2O_5 *in vacuo*, it was dissolved in an appropriate amount of water and subjected to chromatography on a cation-exchanger column (CM-Sephadex C-25, 25 × 850 mm) with a 0.15 M NaCl solution. While 12.4—19.6 dm^3 of the eluting agent was made to flow through the column in one month, the three desired isomers were eluted out in well separated bands. Each of the three eluates was evaporated to dryness on a vacuum evaporator at 30 °C, and the resulting solid was extracted with a minimum amount of methanol and undissolved NaCl was removed by filtration. After evaporating each of the methanol solutions to dryness at 10 °C, the resulting solid (contaminated with a small amount of NaCl) was dissolved in 3 to 4 cm^3 of water.

1) To the aqueous solution obtained from the first eluted band (FI) was added 0.3 g of NaI with stirring The iodide salt precipitated was filtered, washed with a small amount of ethanol and ether, and air-dried. 100 mg. The iodide dissolved in 15 cm^3 of water, and changed to a chloride solution by employing a cation-exchange resin (Cl^- form). The chloride solution was evaporated to dryness by the freeze-drying method, and the resulting chloride salt was dissolved in 2 cm^3 of water and the solution was evaporated gently to dryness in a vacuum desiccator over P_2O_5. Reddish-orange crystals. 55

mg (F1). Found: C, 32.39; H, 7.62; N, 17.36%. Calcd for $[Co(NCS)(NH_3)(C_6H_{14}N_2)_2]Cl\cdot 2.5H_2O$: C, 32.34; H, 7.52; N, 17.40%.

2) To the aqueous solutions obtained from the second and third eluted bands (F2 and F3) were added 0.5 and 1.5 g of $LiClO_4\cdot 3H_2O$ with stirring, respectively. The perchlorate salts precipitated were filtered, washed with an ethanol–ether mixture and then ether, and air-dried. 144 mg (F2) and 200 mg (F3). The perchlorate salts were dissolved in an appropriate amount of water, and the solutions were changed to chloride solutions using an ion-exchange method. The chloride solutions were evaporated to dryness by freeze-drying, the resulting powders were dissolved in 3 and 4 cm^3 of water, respectively, and then to the solutions were added 1.0 and 0.75 g of $LiClO_4\cdot 3H_2O$ with stirring. After storage in a refrigerator for 2 days, the perchlorate salts were filtered, washed sufficiently with an ethanol–ether mixture to eliminate the contaminant $LiClO_4\cdot 3H_2O$, then with ether, and air-dried. Reddish-orange crystals. 50 mg (F2) and 73 mg (F3). Found for F2: C, 29.51; H, 5.70; N, 15.70%. Found for F3: C, 29.62; H, 5.89; N, 15.74%. Calcd for $[Co(NCS)(NH_3)(C_6H_{14}N_2)_2](ClO_4)_2$: C, 29.46; H, 5.89; N, 15.85%.

(12) Bis(ethylenediamine) Complexes: The *trans* complexes were prepared according to methods described in the literature, except for the two new complexes, for which the methods will be described below. *Cis* and *trans* isomers of chloronitrobis(ethylenediamine)cobalt(III) chloride were prepared by the method of Werner.[9,10]

trans-*[Co(N₃)(NCS)(en)₂]ClO₄*: To a solution of 12.0 g of *cis*-$[CoCl(NCS)(en)_2]ClO_4$[10] in 75 cm^3 of water (60 °C) was added 2.5 g of NaN_3. The resulting solution was stirred at 60 °C for about 2 h. After diluting with an appropriate amount of water, the solution was subjected to chromatography on a column (26×800 mm, Dowex 50W×8, H$^+$ form) using a 0.2 M $LiClO_4$ solution as the eluting agent. The elution was continued at a rate of 1.5—2.0 cm^3/min until the first series of bands (containing *trans* complexes) were eluted out. The eluates were fractionated and the intermediate fractions, with the first d-d absorption band at about 528 nm, were combined and evaporated to dryness on a vacuum evaporator below 35 °C. In order to remove the eluting agent, $LiClO_4\cdot 3H_2O$, the solid obtained was suspended in ethanol, filtered, washed sufficiently with ethanol. This was recrystallized from water (55 °C), filtered, washed with water, ethanol, and then ether, and air-dried. Found: C, 15.46; H, 4.21; N, 29.63%. Calcd for $[Co(N_3)(NCS)(C_2H_8N_2)_2]ClO_4$: C, 15.86; H, 4.26; N, 29.59%.

trans-*[Co(N₃)(NO₂)(en)₂]ClO₄*: To a solution containing 4.0 g of *trans*-$[CoCl(NO_2)(en)_2]Cl\cdot H_2O$[9] in 40 cm^3 of water (60 °C) was added 1.0 g of NaN_3. Then the azide salt of chloronitro complex precipitated out. The resulting suspension was stirred at 60 °C for 90 min. After diluting with water, the solution was subjected to chromatography on a column (Dowex 50 W×8, H$^+$ form) with a 0.1 M LiCl solution. When the elution was continued for 8 days using a 0.1 M LiCl solution of about 25 dm^3, the first series of bands containing *trans* complexes were eluted out. The earlier fractions, which showed the first d-d absorption band at about 481 nm, were combined and evaporated to 20 cm^3 below 35 °C. To the concentrated eluate was added a solution of 2.0 g of $LiClO_4\cdot 3H_2O$ in 4 cm^3 of water. After a period, the perchlorate salt of the desired complex crystallized out. After standing for 1 h, the crystals were filtered (0.8 g), recrystallized from warm water (55 °C), filtered, washed with water, ethanol, and then ether, and air-dried. Lustrous red-orange flakes. 0.5 g. Found: C, 12.92; H, 4.42; N, 30.27%. Calcd for $[Co(N_3)(NO_2)(C_2H_8N_2)_2]ClO_4$: C, 13.11; H, 4.40; N, 30.57%.

Measurements. The absorption spectra were measured using Shimadzu UV-200 and Beckman DU spectrophotometers. The CD spectra were recorded with Jasco ORD/UV-5, J-10, and J-20 spectropolarimeters. The optical rotation was checked using Yanagimoto Model 185 and Jasco ORD/UV-5 spectropolarimeters. The measurements were made at room temperature in aqueous or methanol solutions ranging in concentration from 0.005 to 0.0001 M. The cell lengths were 1, 0.2, and 0.1 cm.

Results and Discussion

Characterization of trans *Dianiono Complexes.* Eight cobalt(III) complexes of *trans*-dianionobis[(1*R*,2*R*)-1,2-cyclohexanediamine] type were derived from *trans*-$[CoCl_2(R,R\text{-chxn})_2]Cl\cdot H_2O$ upon treatment with LiN_3, LiSCN, or $LiNO_2$ in methanol. Only one of these, the *trans*-dinitro complex, is a known complex, which was recently prepared by Brennan and Douglas for the first time.[11] *trans*-to-*cis* isomerization was observed in the isolation procedure of some *trans* complexes containing azido ligand from the eluates, and the azidoisothiocyanato and azidonitro complexes could not be isolated as crystals. The *trans* structures of all the complexes were determined by comparing the visible and ultraviolet absorption bands with those of *cis* and *trans* isomers of the corresponding ethylenediamine complex (Table 1).

Configuration of Three Isomers of the Ammineisothiocyanato Complex. Three isomers are possible for the $[Co(NCS)(NH_3)(R,R\text{-chxn})_2]^{2+}$ ion: one is the *trans* isomer and the other two are the diastereomeric *cis* isomers. All the isomers of the $[Co(NCS)(N)_5]$ type show very similar absorption spectra, and they are indistinguishable on the basis of their absorption spectra. The configurations of the three isomers are assigned, therefore, on the basis of their CD spectra. The *cis* isomers have two kinds of chiralities: one is the "configurational" chirality ($\varDelta$ or $\varLambda$) due to the two chxn chelate rings and the other the "vicinal" chirality due to the asymmetric carbon atom of the *R*,*R*-diamine (including "conformational" chirality). It has been established that the CD contributions of the two kinds of chiralities are separable and additive in several cobalt(III) complexes containing five-membered chelate rings.[12—15] Thus, for the CD of the diastereomeric *cis* ammineisothiocyanato isomers, $\varDelta RR$ and $\varLambda RR$, the following equations can be written, where R represents the *R*,*R*-chxn ligand,

$$\Delta\varepsilon(\varLambda RR) = \Delta\varepsilon(\varLambda) + 2\Delta\varepsilon(R) \tag{1}$$

and

$$\Delta\varepsilon(\varDelta RR) = \Delta\varepsilon(\varDelta) + 2\Delta\varepsilon(R). \tag{2}$$

Because $\Delta\varepsilon(\varLambda)$ should be equal to $-\Delta\varepsilon(\varDelta)$, one obtains

$$\Delta\varepsilon(\varLambda) = \frac{1}{2}[\Delta\varepsilon(\varLambda RR) - \Delta\varepsilon(\varDelta RR)] \tag{3}$$

and

$$\Delta\varepsilon(R) = \frac{1}{4}[\Delta\varepsilon(\varLambda RR) + \Delta\varepsilon(\varDelta RR)]. \tag{4}$$

Therefore, if a pair of *cis* isomers can be selected from the three isomers, the configurational CD contribu-

Table 1. Absorption peak positions (in 10^3 cm^{-1}) and intensities (log ε in parenthesis) of the $[Co(X)(X')(diamine)_2]^+$ complexes

(X)(X′)	Diamine	Config.	First d-d band	"Specific" or charge transfer bands	
$(N_3)_2$	*R*,*R*-chxn	*trans*	17.7(2.52)	29.8(4.08)	46.5(4.38)
	en	*trans*	17.8(25.4)	30.0(4.13)	46.0(4.28)
	en	*cis*[1]	19.3(2.52)	33.1(4.06)	46.5(4.30)
$(NCS)_2$	*R*,*R*-chxn	*trans*	19.6(2.43)	32.5(3.54)	47 (4.4)
	en	*trans*	19.7(2.44)	31.6(3.49)	
	en	*cis*[1]	20.4(2.54)	32.5(3.46)	
$(NO_2)_2$	*R*,*R*-chxn	*trans*	23.1(2.28)	29.3(3.53)	40.2(4.38)
	en	*trans*	23.4(2.28)	29.5(3.56)	40.3(4.31)
	en	*cis*[1]	22.8(2.23)	31.1(3.56)	41.7(4.32)
$(N_3)(NCS)$	*R*,*R*-chxn	*trans*	18.9	32.6	46.6
	en	*trans*	18.9(2.49)	32.3(3.94)	47 (4.4)
	en	*cis*[1]	19.6(2.51)	32.4(3.91)	47 (4.3)
$(N_3)(NO_2)$	*R*,*R*-chxn	*trans*	20.7	29	33.4
	en	*trans*	20.8(2.60)	29 (3.7)	33.8(4.00)
	en	*cis*[1]	20.4(2.65)	33.1(3.92)	
$(NCS)(NO_2)$	*R*,*R*-chxn	*trans*	21.6(2.38)	32 (3.3)	41 (4.3)
	en	*trans*	21.8(2.38)	34 (3.4)	42 (4.2)
	en	*cis*[1]	21.2(2.48)	31.0(3.52)	41 (4.1)
Cl(NCS)	*R*,*R*-chxn	*trans*	18.1(2.12)	31 (3.3)	37 (3.6)
	en	*trans*	17.9(2.16)	30.9(3.30)	37 (3.4)
	en	*cis*[1]	19.9(2.24)	32 (3.2)	
$Cl(NO_2)$	*R*,*R*-chxn	*trans*	21.5(1.98)	29.9(3.03)	42 (4.3)
	en	*trans*	21.6(1.98)	29.4(3.21)	40.1(4.26)
	en	*cis*	20.1(1.94)	29.9(3.20)	41.6(4.21)

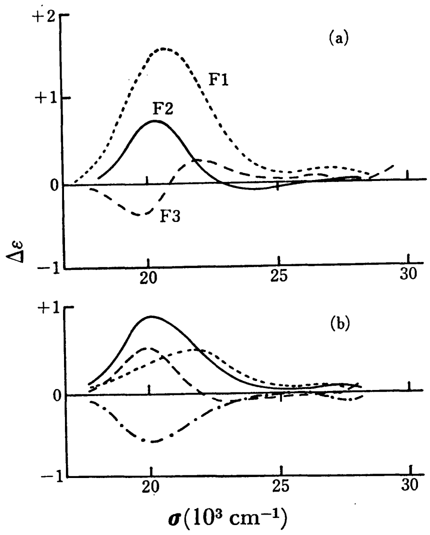

Fig. 1. CD spectra of three isomers of $[Co(NCS)(NH_3)(R,R\text{-}chxn)_2]^{2+}$ (a), and calculated curves of $(1/2)[\Delta\varepsilon(F1)-\Delta\varepsilon(F3)]$ (——), $(1/2)[\Delta\varepsilon(F2)-\Delta\varepsilon(F3)]$ (------), and $(1/2)[\Delta\varepsilon(F1)-\Delta\varepsilon(F2)]$ (······) (b). The CD curve ($\Delta\varepsilon \times 2$) of $\Delta(-)_{589}$-$[Co(NCS)(NH_3)(en)_2]^{2+}$ is also shown in (b) (-·-·-).

tion can be calculated from their observed CD spectra. The configurational CD curve thus calculated is considered to be similar in shape to the observed CD curve of the corresponding en complex. Fig. 1(a) shows the CD curves in the d-d absorption band region for the three isomers which are designated as F1, F2, and F3 in the order of elution, and Fig. 1(b) shows the calculated curves for $(1/2)[\Delta\varepsilon(F1)-\Delta\varepsilon(F3)]$, $(1/2)[\Delta\varepsilon(F2)-\Delta\varepsilon(F3)]$, and $(1/2)[\Delta\varepsilon(F1)-\Delta\varepsilon(F2)]$ together with the observed CD curve of $\Delta(-)_{589}$-$[Co(NCS)(NH_3)(en)_2]^{2+}$. The calculated $(1/2)[\Delta\varepsilon(F1)-\Delta\varepsilon(F3)]$ curve is similar in shape to (but reverse in sign to and about twice as intense as) the observed curve of Δ-$[Co(NCS)(NH_3)(en)_2]^{2+}$. It is therefore concluded that F1 and F3 form the *cis* pair and F2 is the *trans* isomer and that F1 is the Λ(*ob*) isomer and F3 the Δ(*lel*) isomer (this is consistent with the fact that the formation ratio of F1 to F3 is 1: 1.19). Furthermore, if the configurational contribution of the chxn complex is of the same magnitude as that of the en complex, it can be deduced that the optical purity of the $(-)_{589}$-$[Co(NCS)(NH_3)(en)_2]^{2+}$ complex derived from the resolved $[CoCl(NCS)(en)_2]^+$ complex was a little lower than 50% and that its true CD intensity may be about twice the reported value.[1]

CD and Absorption Spectra. It is acceptable, from the first d-d absorption band positions, that the ligand strength of chxn is almost the same as that of en. Two or three CD bands are observed in the first d-d absorption band region (Table 2). Although the *trans*-$[Co(X)_2(R,R\text{-}chxn)_2]^+$ complexes are of D_2 symmetry, if they are considered to be of the *trans*-$[Co(X)_2(N)_4]^+$ type, they are approximately of D_{4h} symmetry. Accordingly, the first spin-allowed d-d transition, ${}^1A_{1g}\rightarrow{}^1T_{1g}$, in O_h is split into the ${}^1A_{1g}\rightarrow{}^1E_g$ and ${}^1A_{1g}\rightarrow{}^1A_{2g}$ transitions. Then, the CD bands observed at about 21000 cm^{-1} are considered to correspond to the nondegenerate com-

TABLE 2. CD DATA OF THE *trans*-$[Co(X)(Y)(R,R\text{-chxn})_2]^{n+}$ COMPLEXES IN THE FIRST d-d BAND REGION

(Wave numbers are given in 10^3 cm^{-1})

(X)(Y)	$\sigma_{ext}(\Delta\varepsilon)$ in H_2O	$\sigma_{ext}(\Delta\varepsilon)$ in CH_3OH	Fig. No.
$(N_3)_2$	17 (+0.19)	16.1(+0.56)	Fig. 2
	18 (+0.18)	18 (+0.20)	
	21.3(−0.24)	21.2(−0.12)	
$(NCS)_2$	19.7(+0.76)	19.2(+0.76)	Fig. 3
	22.9(−0.28)	22.8(−0.20)	
$(N_3)(NCS)$	19.1(+0.40)[a]		Fig. 6
	22.0(−0.21)[a]		
Cl(NCS)		17.5(+0.75)	
		21.3(−0.14)	
$(NCS)(NH_3)$	20.3(+0.75)		Fig. 5
	23.7(−0.06)		
$(NO_2)_2$	21.8(−1.01)	21.9(−1.04)	Fig. 4
	24.6(+0.52)	24.9(+0.24)	
$(N_3)(NO_2)$	18.4(−0.28)[a]		Fig. 7
	20.9(+0.25)[a]		
	23.3(−0.02)[a]		
$(NCS)(NO_2)$	19.8(−0.17)	19.8(−0.12)	Fig. 8
	22.4(+0.37)	22.2(+0.31)	
$Cl(NO_2)$		18.7(−0.06)	
		20.8(+0.23)	

a) These Δε values are estimated by assuming that the molar extinction ccefficients of the first d-d absorption band are the same as those of the corresponding en complexes.

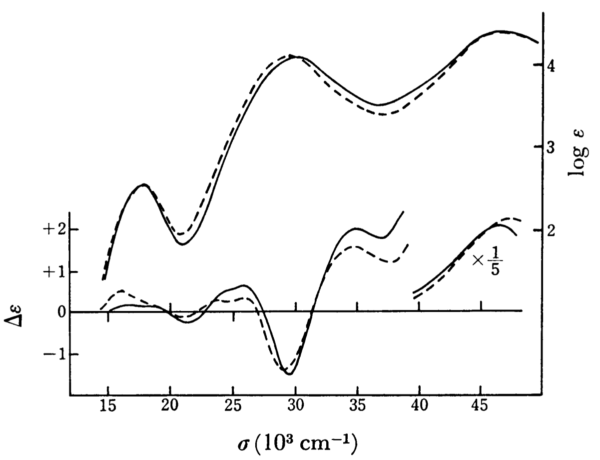

Fig. 2. Absorption and CD spectra of *trans*-$[Co(N_3)_2(R,R\text{-chxn})_2]Cl\cdot0.5H_2O$ in water (——) and in methanol (------).

ponent, $^1A_{1g}\rightarrow{}^1A_{2g}$, and those observed at the lower ($X=N_3^-$ and NCS^-) or higher ($X=NO_2^-$) energy positions to the degenerate component, $^1A_{1g}\rightarrow{}^1E_g$. In the diazido complex, however, two CD bands corresponding to the $^1A_{1g}\rightarrow{}^1E_g$ component are observed at about 16000 and 18000 cm^{-1} (Fig. 2). This band splitting can be reasonably interpreted by symmetry lowering to D_2. It is remarkable that the CD band assigned to the $^1A_{1g}\rightarrow{}^1A_{2g}$ transition in the diazido complex, which is observed at 21300 cm^{-1} in an aqueous solution, is located just in the trough of the absorption curve. This appears to suggest that, in this complex, the absorption band intensity of this nondegenerate component is very weak and the observed absorption peak corresponds to the degenerate component.

In the diazido complex, two strong CD bands of opposite signs are observed in the specific band region, exactly corresponding to the main absorption peak and the shoulder on its higher energy side (Fig. 2 and Table 3). The two positive CD bands at 24000—26000 cm^{-1} are then thought to belong to the second d-d band which is completely hidden. Also in the diisothiocyanato complex, two CD bands of opposite signs are observed in the specific band region (Fig. 3 and Table 3). In this case, the lower energy band of negative sign is much weaker than the higher energy one of positive sign. The negative band is considered to be partly

TABLE 3. CD DATA OF THE *trans*-$[Co(X)(Y)(R,R\text{-chxn})_2]^{n+}$ COMPLEXES IN THE ULTRAVIOLET REGION (wave numbers are given in 10^3 cm^{-1})

(X)(Y)	Solvent	$\sigma_{ext}(\Delta\varepsilon)$ Second d-d band region		$\sigma_{ext}(\Delta\varepsilon)$ "Specific" band region		$\sigma_{ext}(\Delta\varepsilon)$ Intense band region	
$(N_3)_2$	H_2O	25 (+0.5)	25.9(+0.63)	29.7(−1.5)	35.0(+2.0)	46.7(+10.6)	
	CH_3OH	24.0(+0.3)	26.1(+0.36)	29.3(−1.45)	35.0(+1.6)	47.3(+11.6)	
$(NCS)_2$	H_2O			28 (−0.1)	34 (+1.2)	44.0(+11.0)	
	CH_3OH			27 (−0.1)	34 (+1.0)	45.0(+11.6)	
$(N_3)(NCS)$[a]	H_2O	25 (+0.2)	28 (+0.2)	30.8(−0.2)	35 (+1.3)	45 (+11.4)	
Cl(NCS)	CH_3OH	26.0(+0.1)		31.0(+0.43)	34.8(−0.8)	40.7(+10.2)	
$(NCS)(NH_3)$	H_2O	29.0(+0.05)		31.0(−0.04)	36 (+1)	44.7(+12.5)	
$(NO_2)_2$	H_2O	29.3(+0.12)		32 (−0.7)	34.3(−1.1)	41.3(+8.0)	
	CH_3OH			31.8(−0.6)	37 (+1.7)	41.3(+6.2)	45.7(−2.4)
$(N_3)(NO_2)$[a]	H_2O	26.4(+0.2)		30.3(+0.1)	33.1(−0.5)	43.3(+9.3)	
$(NCS)(NO_2)$	H_2O	28.1(+0.18)		33.2(−0.6)		42.5(+10.3)	
	CH_3OH	28.0(+0.05)		30.3(−0.2)	32.8(−0.3)	43.0(+8.9)	
$Cl(NO_2)$	CH_3OH	27.2(+0.28)		34.1(−1.5)		41.0(+8.0)	

a) The Δε values are estimated by assuming that the molar extinction coefficients of the fisrt d-d absorption band are the same as those of the corresponding en complexes.

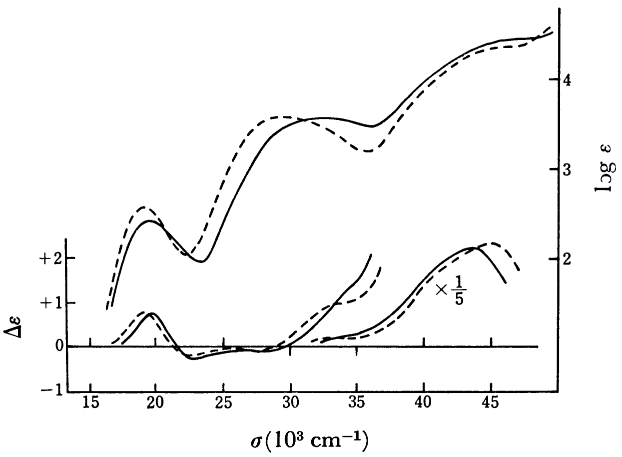

Fig. 3. Absorption and CD spectra of *trans*-[Co(NCS)$_2$-(*R*,*R*-chxn)$_2$]Cl·H$_2$O in water (——) and in methanol (------).

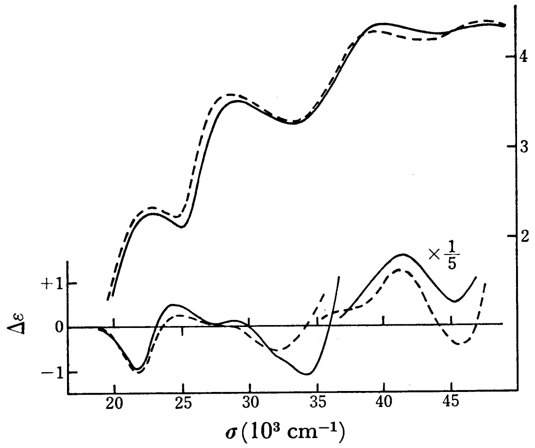

Fig. 4. Absorption and CD spectra of *trans*-[Co(NO$_2$)$_2$-(*R*,*R*-chxn)$_2$]Cl·2.5H$_2$O in water (——) and in methanol (------).

cancelled by the CD bands for the second d-d transition, which probably have a positive net sign like the analogous *trans*-[Co(X)$_2$(*R*,*R*-chxn)$_2$]$^+$ complexes (X=F$^-$, Cl$^-$, Br$^-$,[8] and N$_3^-$).

In the two pseudohalogeno complexes, a positive CD band is observed in an energy region higher than the specific absorption band.

If the specific absorption bands of the present pseudohalogeno complexes are assigned to the $p\pi$(ligand)→d_{z^2} charge-transfer transitions, the relatively weaker absorption intensity of the higher energy component can be explained by the electric-dipole forbidden character of the $p\pi_g$(ligand)→d_{z^2}(e_g→a_{1g} in D_{4h}) transition and the relatively stronger CD intensity of the component can be interpreted by its magnetic-dipole allowed character. Furthermore, the red shift of the specific absorption band of the *trans*-dianiono type complexes (in comparison with the *cis*-dianiono complexes) can be attributed to the relatively stronger absorption intensity of the lower energy electric-dipole allowed component, the $p\pi_u$→d_{z^2}(e_u→a_{1g} in D_{4h}) transition. A similar interpretation has been made for the CD spectra of the charge-transfer band region of the halogeno complexes, *trans*-[Co(X)$_2$(*R*,*R*-chxn)$_2$]$^+$ (X=Cl$^-$ and Br$^-$), although the signs of these two CD bands are the reverse of the present complexes.[8]

The assignment of the specific bands of the present pseudohalogeno complexes to the $p\pi$→d_{z^2} charge-transfer transitions is consistent with the previous CD study of the *cis*-type bis(ethylenediamine) complexes. The same assignment has also been made in absorption spectral studies of [Co(X)(NH$_3$)$_5$] and [Co(X)(CN)$_5$] complexes[16,17] and a redox study of [Co(NCS)-(NH$_3$)$_5$]$^{3+}$.[18]

For the corresponding nitro complex (Fig. 4 and Table 2) in aqueous solution, two CD bands of opposite signs are observed under the "nitro-specific band" and the lower energy positive band is weaker than the higher energy negative band. However, the signs of these are reverse to the pseudohalogeno complexes. On the other hand, it has been reported that the analogous (−)$_{589}$-*trans*,*trans*-[Co(NO$_2$)$_2$(*N*-Me-en)$_2$]$^+$ complex shows the same CD pattern in this region as that of the present pseudohalogeno complexes.[19]

Concerning the solvent effect on the absorption and CD spectra of the three dianiono complexes, it was found that the specific absorption bands apper at higher energies in water than in methanol; the shift is very wide especially for the isothiocyanato complex (2600 cm^{-1} interval). The shift is in the same direction as that reported for the charge-transfer band in some halogeno complexes.[20]

In a previous paper[1] on the *cis*-type bis(ethylenediamine) complexes, it was found that the dipseudohalogeno complexes show two CD bands in the specific band region, while the amminepseudohalogeno complexes show a single CD band. In Fig. 5, the calculated CD curve of the configurational effect for the *cis*-[Co-(NCS)(NH$_3$)(*R*,*R*-chxn)$_2$]$^{2+}$ complexes and the observed CD curve for the *trans* complex are shown together with their absorption spectra. The configurational CD

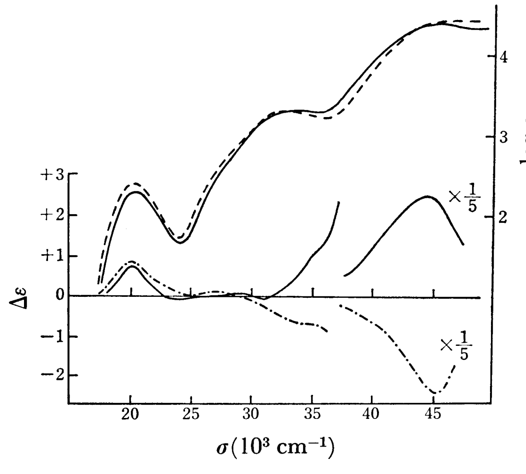

Fig. 5. Absorption and CD spectra of *trans*-[Co(NCS)-(NH$_3$)(*R*,*R*-chxn)$_2$](ClO$_4$)$_2$ (——) and calculated Λ configurational curve of *cis*-[Co(NCS)(NH$_3$)(*R*,*R*-chxn)$_2$]$^{2+}$ (-·-·-). Absorption spectrum of Δ-[Co-(NCS)(NH$_3$)(*R*,*R*-chxn)$_2$](ClO$_4$)$_2$ is shown in broken line.

curve has the same pattern as the observed CD curve[1] of Δ-$[Co(NCS)(NH_3)(en)_2]^{2+}$ over all the regions, and has a single CD band corresponding to the absorption peak of the specific band. The CD band can be assigned to the degenerate charge-transfer transition, $p\pi$(ligand) $\rightarrow d_{z^2}(e \rightarrow a_1$ in $C_{4v})$. However, in the case of the *trans*-$[Co(NCS)(NH_3)(R,R\text{-chxn})_2]^{2+}$ complex which has the same approximate symmetry, C_{4v}, as the *cis* complex, the positive CD band in shoulder and another very weak negative CD band on the lower energy side appear to correspond to the specific absorption band, because the positive shoulder is located rather far from the absorption peak.

The absorption curves in the specific band region of the *trans* mixed complexes $[Co(X)(X')(\text{diamine})_2]^+$ (X and X'$=N_3^-$, NCS^-, and NO_2^-) are very different from the intermediate of the "parent" complexes $[Co(X)_2(\text{diamine})_2]^+$ and $[Co(X')_2(\text{diamine})_2]^+$ (see Figs. 6—8). This absorption behavior suggests that the specific bands are not due to the intraligand transitions and that there is some strong interaction, for example, a $p\pi$-$d\pi$ interaction, between the ligands in the *trans* positions through the central cobalt(III) ion. The CD data of the *trans*-$[Co(X)(X')(R,R\text{-chxn})_2]^+$ (X, X'$=$ N_3^-, NCS^-, NO_2^-, and Cl^-) complexes are presented in Tables 2 and 3 and Figs. 6—8. The azidoisothiocyanato complex shows two CD bands under the specific absorption band (Fig. 6): one is the weaker negative CD band of lower energy and the other the stronger positive one of higher energy. The CD behavior is the same as that of the "parent" complexes, *trans*-$[Co(N_3)_2(R,R\text{-chxn})_2]^+$ and -$[Co(NCS)_2(R,R\text{-chxn})_2]^+$. Accordingly, the two CD bands at about 25000 and 28000 cm^{-1} are considered to belong to the second d-d band. The azidonitro complex (Fig. 7) exhibits a very strange absorption spectrum which is remarkably different from the intermediate of the "parent" complexes, and a negative CD band is located under the intense absorption band at 33400 cm^{-1} and two positive CD bands are observed under the shoulder at about 29000 cm^{-1}. It is more probable to consider that the lowest energy CD band corresponds to the second d-d absorption band, which is hidden. Then, the weak positive and strong negative CD bands at 30300 and 33100 cm^{-1} are assigned to the specific absorption band. A single strong positive CD band is observed under another intense absorption band in the higher energy region. In summary, the CD behavior of the mixed complexes in the specific absorption band region is complicated as in the case of the *cis*-type bis(ethylenediamine) complexes, but it seems a common behavior that two CD bands are observed under the specific band, and the higher energy one of which is the stronger.

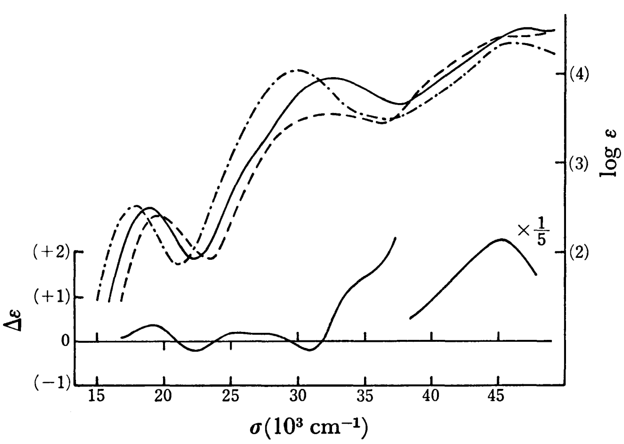

Fig. 6. Absorption and CD spectra of *trans*-$[Co(N_3)(NCS)(R,R\text{-chxn})_2]^+$ eluate (——). (The intensities are estimated by assuming that the molar extinction coefficient of the first d-d band is the same as the corresponding en complex.) Absorption spectra of *trans*-$[Co(N_3)_2(R,R\text{-chxn})_2]Cl\cdot 0.5H_2O$ (–·–·–) and -$[Co(NCS)_2(R,R\text{-chxn})_2]Cl\cdot H_2O$ (------) are shown for comparison.

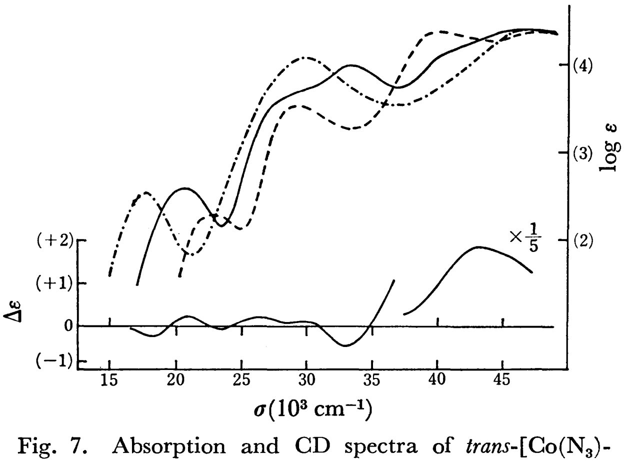

Fig. 7. Absorption and CD spectra of *trans*-$[Co(N_3)(NO_2)(R,R\text{-chxn})_2]^+$ eluate (——). (The intensities are estimated by assuming that the molar extinction coefficient of the first d-d band is the same as the corresponding en complex.) Absorption spectra of *trans*-$[Co(N_3)_2(R,R\text{-chxn})_2]Cl\cdot 0.5H_2O$ (–·–·–) and -$[Co(NO_2)_2(R,R\text{-chxn})_2]Cl\cdot 2.5H_2O$ (------) are shown for comparison.

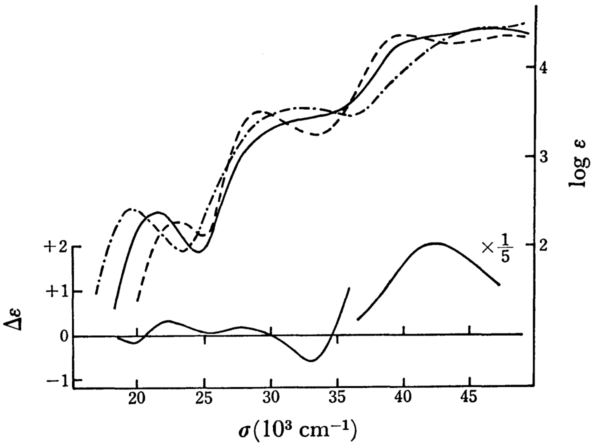

Fig. 8. Absorption and CD spectra of *trans*-$[Co(NCS)(NO_2)(R,R\text{-chxn})_2]Cl\cdot 1.5H_2O$ (——). Absorption spectra of *trans*-$[Co(NCS)_2(R,R\text{-chxn})_2]Cl\cdot H_2O$ (–·–·–) and -$[Co(NO_2)_2(R,R\text{-chxn})_2]Cl\cdot 2.5H_2O$ (------) are shown for comparison.

Finally, the four complexes containing only N_3^- or NCS^-, that is, $(N_3)(N_3)$, (NCS)(NCS), (N_3)(NCS), and (NCS)(NH_3) complexes, exhibit the (−, +) CD pattern under the specific absorption band. The five complexes containing Cl^- or NO_2^-, namely, $(NO_2)(NO_2)$, $(NCS)(NO_2)$, $(N_3)(NO_2)$, Cl(NCS), and $Cl(NO_2)$ complexes, appear to exhibit the reverse CD pattern, (+, −), under the specific band. Furthermore, the higher energy CD component of the specific band is stronger than the lower energy CD component for all nine complexes. Lastly, it was observed that all the complexes exhibit one strong CD band in the region of 41000—48000 cm^{-1} and that the sign is always positive (Table 3).

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