Isolation and Circular Dichroism of the Isomers of Dicyanobis[(*R*,*R*)-1,2-cyclohexanediamine] and bis[(*S*)-propylenediamine]cobalt(III) Complexes

Kazuo Kashiwabara (née Konya), Toshimasa Yamanaka, and Kazuo Saito
Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980
Naoto Komatsu, Nobuhiro Hamada, Hiroaki Nishikawa, and Muraji Shibata
Department of Chemistry, Faculty of Science, Kanazawa University, Marunouchi, Kanazawa 920

(Received July 31, 1975)

Three isomers of *trans*- and *cis*-$[Co(CN)_2\{(R,R)\text{-1,2-cyclohexanediamine}\}_2]^+$ and five isomers of the corresponding (*S*)-propylenediamine complexes have been isolated by chromatography with Dowex 50W-X8 and SP-Sephadex columns, their geometrical structures being assigned on the basis of the ligand field absorption and PMR spectra. Isomers of *cis*-$[Co(CN)_2\{(S)\text{-propylenediamine}\}_2]Cl$, which have different placement of methyl groups of (*S*)-propylenediamine, gave different methyl PMR resonances with different chemical shifts. The absolute configuration of the isomers was determined from the circular dichroism in the first spin-allowed d-d and the charge transfer band region. The configurational and the vicinal effect have been discussed.

Although several methods have been developed for the preparation of mixed cyano-diamine and cyano-ammine cobalt(III) complexes,[1–7] only a few studies[8,9] have been reported on the optically active complexes. The cyanide ion is the ligand which gives the strongest ligand field and a π-back donating character. It is interesting to compare the circular dichroism (CD) of the cyano-diamine complexes with those which have been extensively studied so far.[10] McCaffery *et al.*[8] showed that CD spectra of *cis*-$[CoL_2(en)_2]^{n+}$ have different patterns from the corresponding tris(diamine) complexes whenever the ligand L is well separated from neutral nitrogen donors in the spectrochemical series. When $L=CN^-$, two peaks with the same sign were observed in the region of the octahedral T_{1g} absorption.

The purpose of this study is to investigate the CD behavior more extensively for a variety of mixed cyano complexes of cobalt(III). We report preparation and characterization of the isomers of $[Co(CN)_2(R,R\text{-chxn})_2]^+$ and $[Co(CN)_2(S\text{-pn})_2]^+$ (chxn=1,2-cyclohexanediamine, pn=propylenediamine). Their visible and ultraviolet absorption, CD and PMR spectra are discussed for assigning the geometrical and optical isomers.

Experimental

Preparation and Separation of the Isomers of Dicyanobis[(R,R)-*1,2-cyclohexanediamine*]*cobalt(III) Complexes.* One gram of potassium cyanide was dissolved in 150 ml of dimethyl sulfoxide (DMSO) at 60 °C. To this solution was added 2 g of *trans*-$[CoCl_2(R,R\text{-chxn})_2]Cl\cdot 1/2H_2O$ in portions with stirring. The color of the solution turned from green to orange instantly. The solution was allowed to stand at 60 °C for 30 min., cooled to room temperature and poured into a column (120×4 cm) of an SP-Sephadex C-25 ion exchanger. The column was washed with water in order to remove DMSO. When the adsorbed band was eluted with a 0.05 M aqueous solution of sodium perchlorate at a rate 2 ml/min, one orange yellow and then two light yellow bands were eluted. The first orange yellow eluate was evaporated to dryness at 40 °C in a rotary evaporator under reduced pressure. Thirty ml of acetone was added to dissolve sodium perchlorate, leaving orange yellow residues which were then dissolved in a minimum amount of hot water and filtered. The filtrate was kept in a refrigerator overnight to obtain orange yellow crystals, C-1. Yield about 400 mg. Found: C, 37.53; H, 6.40; N, 18.89%. Calcd for $[Co(CN)_2\text{-}(R,R\text{-chxn})_2]ClO_4\cdot 1/2H_2O$: C, 37.56; H, 6.53; N, 18.77%.

The second and the third light yellow eluates were evaporated at 40 °C in rotary evaporators to dryness. Five ml portions of ethanol were added to extract the light yellow precipitates and the ethanol solutions were evaporated to dryness. The residues were dissolved in minimum amounts of hot water and the solutions were cooled in a refrigerator. Light yellow needlelike crystals were obtained from the two lots, C-2 and C-3. The yield was about 100 mg for both C-2 and C-3. These products were much more soluble than C-1. Found for C-2: C, 37.08; H, 6.60; N, 19.00%. Found for C-3: C, 37.41; H, 6.56; N, 18.79%. Calcd for $[Co(CN)_2(R,R\text{-chxn})_2]ClO_4\cdot 1/2H_2O$: C, 37.56; H, 6.53; N, 18.77%.

Preparation and Separation of the Isomers of Dicyanobis[(S)-*propylenediamine*]*cobalt(III) Complexes. Method 1):* To a cold solution (*ca.* 0 °C) of 10 g of $[Co(S\text{-pn})_3]Cl_3$[11] in 800 ml of water was added dropwise 2.5 g of potassium cyanide in 10 ml of cold water with stirring. Activated charcoal (2 g) was added and the solution was allowed to stand at room temperature for several days. The orange yellow solution was filtered and the filtrate was added at a rate 0.3 ml/min to a column (4×40 cm) of the ion exchanger (Dowex 50W-X8, 100—200 mesh) in the sodium form. After the column was washed with water the adsorbed band was eluted with a 0.2 M aqueous sodium chloride solution at a 0.15 ml/min rate. This procedure separated the adsorbed band into four bands. The first orange yellow band gave only one kind of crystal (P-1), which was assigned to *trans*-$[Co(CN)_2(S\text{-pn}_2)]Cl$ from the visible absorption spectrum (*vide infra*). The fourth band which remained at the top of the column consisted mainly of $[Co(S\text{-pn})_3]^{3+}$. During the progress of elution with the same eluent, both the second and the third band were separated into three bands. The six portions of eluates were individually concentrated under reduced pressure at 40 °C and treated with ethanol to precipitate sodium chloride, which was filtered off. Addition of ethanol, evaporation and filtration were repeated several times to remove sodium chloride as far as possible. Diethyl ether was added to the ethanol solutions to precipitate crude products, which were recrystallized by dissolving them in minimum amounts of water at 40 °C and keeping the solutions in a refrigerator. The six portions of light yellow crystals were named P-2, P-3, P-4, P-5, P-6 and P-7 in the order of elution and assigned to geometrical isomers of *cis*-$[Co(CN)_2(S\text{-pn})_2]Cl$ on the basis of the visible absorption spectra. P-2, P-3, P-4 and P-6 were in good crystalline state and gave satisfactory results on elemental analysis. The yields of P-5 and P-7 were os poor that only spectral measurements were made and satisfactory elemental analysis was not carried out. Found for P-1: C, 29,77; H, 7.54; N, 26.66%. Calcd for $[Co(CN)_2(S\text{-pn})_2]Cl\cdot 3/2H_2O$: C, 29.96; H, 7.23; N, 26.21%. Found for P-2: C, 30.46; H, 7.32; N, 26.40%. Calcd for $[Co(CN)_2(S\text{-pn})_2]Cl\cdot H_2O$: C, 30.73; H, 7.09; N, 26.88%. Found for P-3: C, 31.57; H, 7.51; N, 27.27%. Calcd for $[Co(CN)_2(S\text{-pn})_2]Cl\cdot 1/2H_2O$: C, 31.75; H, 6.99; N, 27.77%. Found for P-4: C, 32.24; H, 7.43; N, 28.07%. Calcd for $[Co(CN)_2(S\text{-pn})_2]Cl$: C, 32.61; H, 6.84; N, 28.51%. Found for P-6: C, 30.06; H, 7.17: N, 26.46%. Calcd for $[Co(CN)_2(S\text{-pn})_2]Cl\cdot 3/2H_2O$: C, 29.96; H, 7.23; N, 26.21%.

Method 2) The same method as for the corresponding (*R*,*R*)-1,2-cyclohexanediamine complexes was applied, using *trans*-$[CoCl_2(R\text{-pn})_2]Cl$ in DMSO. One orange band and two light yellow bands were separated in an SP-Sephadex column. The orange one was assigned to the *trans* isomer of $[Co(CN)_2(R\text{-pn})_2]^+$, and the light yellow ones were to the *cis* isomers, on the basis of the visible absorption spectra. However, the two light yellow bands could not be separated further even on elution at a very small elution rate. The elemental analysis for these three isomers gave satisfactory results.

Measurement. The electronic absorption spectra were obtained with a Hitachi EPU-2A spectrophotometer and a Hitachi 323 recording spectrophotometer. The CD spectra were recorded on a JASCO Model ORD/UV-5 and J-20 spectropolarimeter. The PMR spectra were measured with a JEOL Model JNM MH 60 II spectrometer in deuterium oxide using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal reference. Infrared spectra were measured as KBr disk with a DS 301 infrared spectrometer of Japan Spectroscopic Company.

Results and Discussion

Preparation, Separation and Characterization of the Isomers. The preparation of mixed cyano cobalt(III) complexes has been known to be difficult because of the strong tendency of cyanide ions to coordinate to a central cobalt(III) ion. In recent years, however, some preparative studies on the mixed complexes have been developed by several groups.[1-7] In the present work, two methods have been adopted to prepare the optically active dicyanobis(diamine)cobalt(III) complexes. One is the reaction of *trans*-$[CoCl_2(\text{diamine})_2]^+$ with KCN in DMSO.[5] The other is based on the reaction of $[Co(\text{diamine})_3]^{3+}$ with KCN in an aqueous solution in the presence of activated charcoal.[4] The former method is effective for preparing the *trans* dicyano isomers, the formation ratio *trans*/*cis* being about 2. In the latter method, the yields of the *trans* isomer were very poor as compared with those of the corresponding *cis* isomers. The yields for each isomer are very similar to those of the corresponding ethylenediamine complexes. The geometrical structure, *trans* or *cis*, was determined on the basis of the visible absorption spectra which are almost identical with those of the corresponding ethylenediamine complexes respectively; *i.e.* the *trans* isomer is well characterized by the splitting of its first absorption band, but the *cis* isomers show no splitting in the same region.

The bidentate ligand, propylenediamine, is unsymmetrical due to the placement of a methyl group on the chelate ring so that five geometrical isomers are possible for the $[Co(CN)_2(S\text{-pn})_2]^+$ complex as shown in Fig. 1. When the configuration (Δ and Λ) around the cobalt ion is considered, six isomers are possible for the *cis* dicyano complexes. The isomers would be expected to be nearly energetically equivalent because of the nearly symmetrical nature of pn. Several workers have studied such a geometrical isomerism. Most of them could observe no distinct differences in the chemical and spectroscopic properties.

For the tris(*R*-pn)cobalt(III) complexes, MacDermott[12] and Kojima *et al.*[13] separated the geometrical isomers (*facial* and *meridional*), although they could not observe any distinguishable differences in the visible and ultraviolet absorption, CD and PMR spectra. Sudmeier *et al.*[14] observed nonequivalent methyl resonances only in the 251 MHz PMR spectrum of *N*-deuterated Δ-$[Co(R\text{-pn})_3]^{3+}$ with Co-59 decoupling. Recently, the Co-59 NMR was successfully applied to this system.[15-17] For the bis(*R*-pn) complexes, MacDermott[18] tried to separate the isomers of $[Co(NO_2)_2(R\text{-pn})_2]^+$ and isolated three isomers. However, assignment of the structure only distinguished the *trans*(dinitro) and *cis*(dinitro) isomer. For the mono(*R*-pn) complexes, Lewis and Alexander[19] isolated the two isomers of $\Delta(C_3)$-*cisβ*-$[Co(R\text{-pn})(2,3,2\text{-tet})]^{3+}$ (2,3,2-tet : 3,7-diaza-1,9-nonanediamine), which differ only in the placement of the methyl group of the *R*-pn. They could not observe, however, distinct differences in the visible absorption, CD and PMR spectra. On the other hand, Halloran and Legg[20] isolated the four isomers of *uns-cis*-$[Co(R\text{-pn})(\text{edda})]^+$(edda : ethylenediamine-*N*,*N'*-diacetate) and observed a shift by 0.13 ppm for the methyl resonances between *cis*, *cis* (N–O) and *cis*,*trans*(N–O) isomers, which differ only in the placement of the methyl group of the *R*-pn.

In a previous paper,[21] some isomers of bis(L-hydrogenaspartato)(*R*-pn) and (L-aspartato)bis(*R*-pn)cobalt(III) complexes were isolated and characterized on the basis of the visible absorption, CD and PMR spectra. In the present work, we could separate all the isomers of *cis*-$[Co(CN)_2(S\text{-pn})_2]^+$ using a Dowex 50W-X8 ion exchange resin. This is useful for the separation of low charge complexes in contrast to an SP-Sephadex ion exchanger which is very good for high charge complexes.

Only one band was observed on the chromatographic separation of *trans*-$[Co(CN)_2(S\text{-pn})_2]^+$. The PMR spectrum of the isomer exhibits a doublet (J=6 Hz) due to the CH_3 group of the coordinated *S*-pn at 1.23 ppm. Since the chemical environments of the methyl protons of the coordinated two *S*-pn are equivalent in the *trans* isomer, it is impossible to determine whether the obtained isomer is *trans-cis* or *trans-trans* isomer, or a mixture of the two (Fig. 1). However, the *trans-trans* isomer seems to be most predominant as in the corresponding dichloro complexes.[22]

For the *cis* dicyano complexes, P-2, P-3 and P-4 are assigned to Δ configuration around the cobalt ion and P-5, P-6 and P-7 to Λ on the basis of the CD spectra. Crystals P-5 and P-7 gave identical visible and ultraviolet absorption spectrum with those of P-2, P-3, P-4 and P-6, and the *cis* structure is verified although satisfactory elemental analysis was not obtained. The

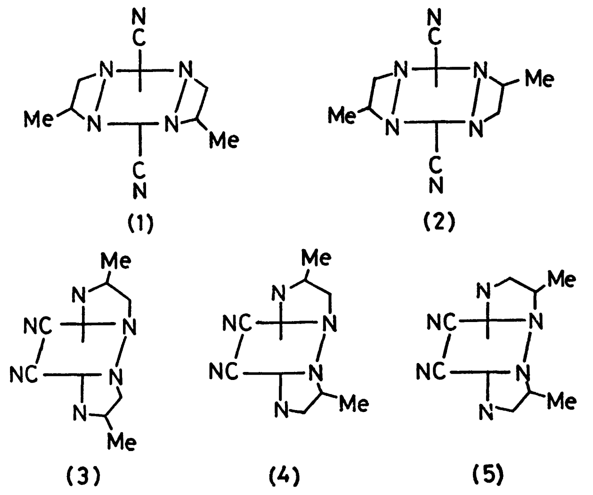

Fig. 1. Geometrical isomers of [Co(CN)$_2$(*S*-pn)$_2$]$^+$. (1) *trans-cis*, (2) *trans-trans*, (3) *cis-trans*, (4) *cis*(C$_1$), (5) *cis-cis*.

cis-trans and *cis-cis* isomers (Fig. 1) have a C$_2$ symmetry axis and the *cis*(C$_1$) isomer has only a C$_1$ symmetry axis. The PMR spectra of P-2 and P-4 exhibit a doublet (J=6 Hz) due to the methyl groups of *S*-pn at 1.19 ppm and 1.34 ppm, respectively. P-3 showed two doublets at 1.19 ppm and 1.34 ppm and was assigned to the *cis*(C$_1$) isomer (Fig. 1). P-2 and P-4 isomers exhibit a significant difference in the methyl resonance. The absorption of P-4 isomer is shifted downfield relative to that of P-2. Assuming that the major environmental factor contributing to this shift is the relative position of the methyl group in the complex, such a difference in the chemical shift might arise from the intramolecular nonbonding interactions and the influence of ligating atoms, specifically the arrangement of ligating atoms in the other coordination sites. In a series of mixed en-pn and tris(pn) complexes of cobalt(III), the chemical shift hardly differs at all. The great chemical shift difference between P-2 and P-4 isomers seems to be due to the arrangement of cyanide ions. The chemical shift of the methyl group in [Co(pn)$_3$]$^{3+}$ is at about 1.37 ppm,[14] while in [Co(CN)$_4$(*R*-pn)]$^-$ it is at about 1.25 ppm.[23] The methyl groups in the *cis-trans* isomer in Fig. 1 are nearer the cyanide ions than those in the *cis-cis* isomer. Thus we tentatively assigned P-2 isomer to *cis-trans* and P-4 to *cis-cis*. P-5, P-6 and P-7 showed a similar PMR behavior to P-2, P-3 and P-4, respectively. Hence we tentatively assigned P-5 to *cis-trans*, P-6 to *cis*(C$_1$) and P-7 to *cis-cis*.

The infrared absorption of these isomers was measured in the 4000—400 cm^{-1} region. Coordinated cyanide ions in each isomer showed a strong stretching ν(C≡N) band at *ca.* 2200 cm^{-1} which exhibited no splitting.

Circular Dichroism and Absolute Configuration. The observed absorption and CD spectral data for [Co(CN)$_2$(*R,R*-chxn)$_2$]$^+$ and [Co(CN)$_2$(*S*-pn)$_2$]$^+$ are summarized in Table 1.

Figure 2 shows the visible and ultraviolet absorption and CD spectra of *trans*-[Co(CN)$_2$L$_2$]$^+$ (L=*R,R*-chxn or *R*-pn) in water and of *trans*-[CoCl$_2$(*R,R*-chxn)$_2$]$^+$ in methanol. The first absorption band, $^1T_{1g}\leftarrow{}^1A_{1g}$, of cobalt(III) complexes in an octahedral field splits into $^1A_{2g}+{}^1E_g\leftarrow{}^1A_{1g}$ in a tetragonal field. Yamatera[24] showed that the $^1A_{2g}$ band for *trans*-CoN$_4$X$_2$$^+$ should have roughly the same energy as the $^1T_{1g}$ band of CoN$_6$$^{3+}$. Furthermore, for axial ligand, X, which is lower than N in the spectrochemical series, ^1E_g should be lower in energy than $^1A_{2g}$. The first two peaks in the CD spectra of *trans*-dihalobis(diamine)cobalt(III) complexes are generally assigned to the ^1E_g and $^1A_{2g}$ levels in the order of increasing energy.[25,26] For the *trans*-[Co(CN)$_2$(*R,R*-chxn)$_2$]$^+$ complexes, the axial ligands, CN$^-$, lie higher in the spectrochemical series than the basal cyclohexanediamine, so that the crystal field

Table 1. Absorption and CD spectral data for the dicyano complexes ($\tilde{\nu}$ in 10^3 cm^{-1})

Complex	I Band		II Band	
	$\tilde{\nu}_{\max}$ (log ε)	$\tilde{\nu}^{\mathrm{CD}}_{\mathrm{ext}}$ ($\Delta\varepsilon_{\mathrm{ext}}$)	$\tilde{\nu}_{\max}$ (log $\varepsilon_{\max}$)	$\tilde{\nu}^{\mathrm{CD}}_{\mathrm{ext}}$ ($\Delta\varepsilon_{\mathrm{ext}}$)
[Co(CN)$_2$(*R,R*-chxn)$_2$]ClO$_4$				
C-1 (*trans*)	22 (sh)	20.85 (−0.28)	32.00 (1.84)	30.60 (−0.36)
	24.40 (1.83)	24.50 (+2.28)		
C-2 (*cis-Λ*)	24.80 (1.97)	25.50 (+2.24)	32.26 (2.00)	32.40 (−0.20)
C-3 (*cis-Δ*)	24.90 (2.00)	21.60 (−0.38)	32.30 (1.99)	32.60 (+0.06)
		24.30 (+1.06)		
		28.60 (−0.14)		
[Co(CN)$_2$(*S*-pn)$_2$]Cl				
P-1 (*trans*)	22 (sh)	21.00 (+0.25)	32.10 (1.80)	31.35 (+0.14)
	24.51 (1.80)	24.66 (−1.07)		
P-2 (*cis-trans-Δ*)	24.60 (1.98)	25.80 (−1.39)	32.27 (1.96)	32.68 (+0.18)
P-3 (*cis*(C$_1$)-*Δ*)	24.83 (1.91)	25.64 (−1.10)	32.20 (1.90)	32.77 (+0.15)
P-4 (*cis-cis-Δ*)	25.10 (1.92)	26.00 (−0.98)	32.27 (1.93)	33.00 (+0.19)
P-6 (*cis*(C$_1$)-*Λ*)	25.21 (1.94)	22.00 (+0.42)	32.22 (1.96)	33.30 (−0.02)
		25.00 (−0.58)		35.33 (+0.01)
		30.00 (+0.12)		

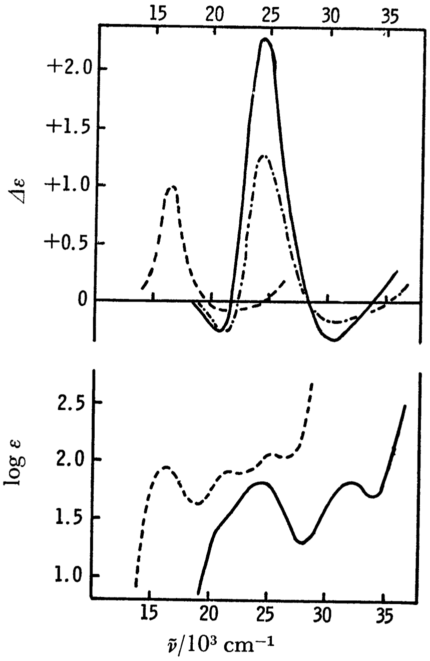

Fig. 2. Absorption and CD spectra of *trans*-$[Co(CN)_2(R,R\text{-chxn})_2]^+$ in H_2O (——), *trans*-$[Co(CN)_2(S\text{-pn})_2]^+$ in H_2O (—·—·—) and *trans*-$[CoCl_2(R,R\text{-chxn})_2]^+$ in methanol (— — —).

model expects the ^1E_g band to be at a higher energy than the $^1A_{2g}$ band. In the visible absorption spectra in Fig. 2, two components are observed in the first absorption band region. On the other hand, for the CD spectra two components, a small negative and a strong positive band, are observed in the first absorption band region, which we assign to $^1A_{2g}$ and ^1E_g component, respectively, in the order of increasing energy. The sign of the Cotton effect for each component is consistent for the dihalo and dicyano complexes, and related to the conformation of the chelate rings. The intensity of the Cotton effect for the dicyano complexes is much stronger than expected, as compared with the corresponding dihalo complexes. It seems that the conformation of the chelates is almost the same as for the dihalo and the dicyano complexes. A more complete molecular orbital treatment would be necessary to interpret the spectroscopic properties. However, quite recently similar differences in CD intensity were observed for *trans*-*R*,*R*-$[CoX_2(3,2,3\text{-tet})]^+$, *trans*-*S*,*S*-$[CoX_2(S,R,R,S\text{-}sk\text{-}3,2,3\text{-tet})]^+$ and *trans*-*S*,*S*-$[CoX_2(R,R\text{-}R,R\text{-}sk\text{-}3,2,3\text{-tet})]^+$ ($X=Cl^-$, CN^-).[27]

Figure 3 shows the CD spectra for the complexes obtained from the second (C-2) and the third (C-3) fraction of *cis*-$[Co(CN)_2(R,R\text{-chxn})_2]^+$ in H_2O. The CD spectrum of C-2 shows a very strong positive band in the first absorption band region which suggests a Λ configuration on the basis of an empirical rule.[10] C-3 shows two small negative bands and a strong positive band in the first absorption band region, which are rather complicated for the assignment of the absolute configuration. In the ultraviolet region, however, these two isomers gave very contrasting CD spectra; the CD spectrum of C-2 is similar to that of *cis*-Λ-$[Co(CN)_2(en)_2]Cl\cdot H_2O$, the absolute configuration of which was determined by X-ray analysis.[28] Ogino *et al.*[29] suggested that in tris(diamine)cobalt(III) ions the configurational and the vicinal effect are also additive for the CD in the charge transfer region. This empirical rule would be useful for assigning the absolute configuration of dicyanobis(diamine) complexes. We have thus assigned the C-2 isomer to be Λ form.

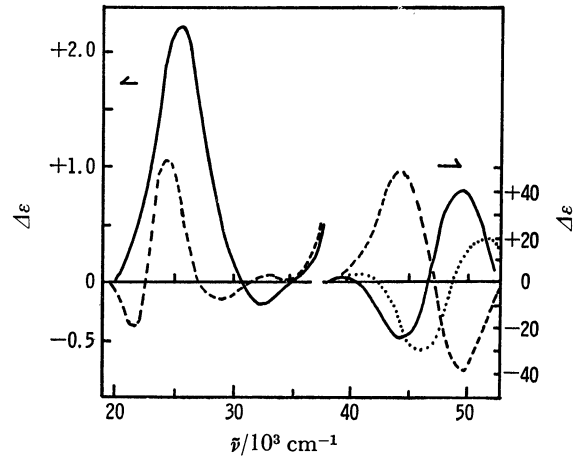

Fig. 3. CD spectra of *cis*-$[Co(CN)_2(R,R\text{-chxn})_2]^+$ in H_2O. C-2 (——), C-3 (— — —) and *cis*-Λ-$[Co(CN)_2(en)_2]Cl\cdot H_2O$ (……).

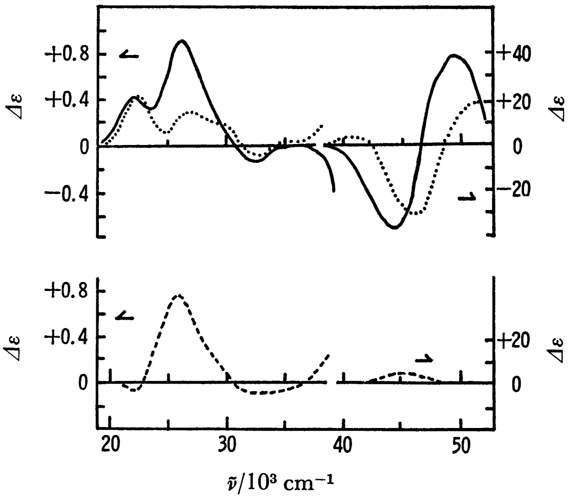

Fig. 4. Calculated configurational and vicinal CD curves of *cis*-$[Co(CN)_2(R,R\text{-chxn})_2]^+$. (C-2 − C-3)/2 (——), (C-2 + C-3)/4 (— — —) and *cis*-Λ-$[Co(CN)_2(en)_2]^+$ (……).

The configurational and vicinal curves of *cis*-$[Co(CN)_2(R,R\text{-chxn})_2]^+$ are shown in Fig. 4. They were derived from the observed curves by use of the following relations.

$$\Delta\varepsilon(L) = 1/4\cdot[\Delta\varepsilon(\Lambda_{2L})+\Delta\varepsilon(\Delta_{2L})]$$

$$\Delta\varepsilon(\Delta) = 1/2\cdot[\Delta\varepsilon(\Delta_{2L})-\Delta\varepsilon(\Lambda_{2L})]$$

$$\Delta\varepsilon(\Lambda) = 1/2\cdot[\Delta\varepsilon(\Lambda_{2L})-\Delta\varepsilon(\Delta_{2L})]$$

where $\Delta\varepsilon(\Delta_{2L})$ and $\Delta\varepsilon(\Lambda_{2L})$ are the observed CD for the Δ and the Λ diastereoisomer, respectively, of *cis*-$[Co(CN)_2(R,R\text{-chxn})_2]^+$ complex and $\Delta\varepsilon(\Delta)$ and $\Delta\varepsilon(\Lambda)$ are the configurational CD, and $\Delta\varepsilon(L)$ is the vicinal CD for (*R*,*R*)-1,2-cyclohexanediamine ligand. The pattern of configurational CD curves agrees with the observed CD of the corresponding ethylenediamine complex, except that the intensity of the peak at 2.62 $\times 10^4$ cm^{-1} (assigned to B_1 transition in C_{2v} symmetry by McCaffery *et al.*[8]) is strong in the cyclohexanediamine complex. The pattern of derived vicinal CD curves is similar to the observed CD spectrum of *trans*-$[Co(CN)_2(R,R\text{-chxn})_2]^+$.

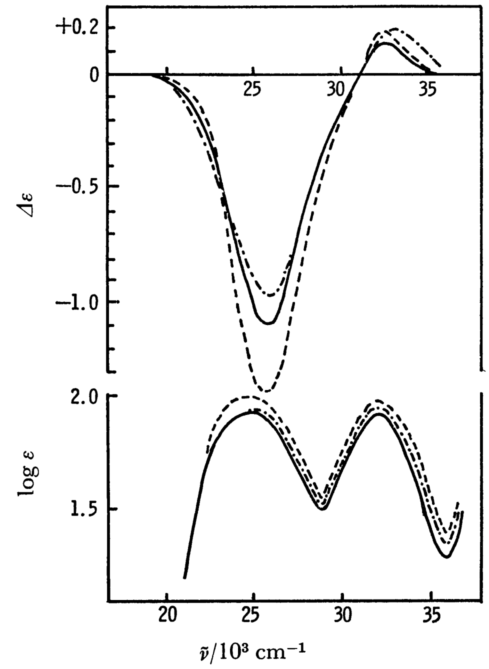

Fig. 5. Absorption and CD spectra of *cis*-$[Co(CN)_2(S\text{-pn})_2]^+$ in H_2O. P-2 (— — —), P-3 (——) and P-4 (—·—·—).

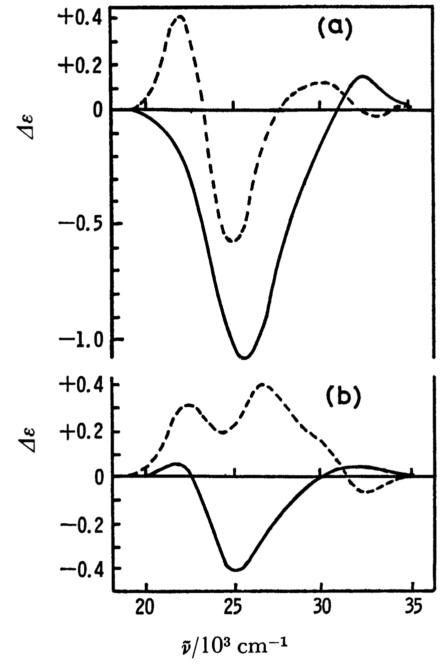

Fig. 6. (a) CD spectra of *cis*-$[Co(CN)_2(S\text{-pn})_2]^+$ in H_2O. P-3 (——) and P-6 (— — —). (b) Calculated configurational and vicinal CD curves of *cis*-$[Co(CN)_2(S\text{-pn})_2]^+$. (P-6−P-3)/2 (— — —) and (P-6+P-3)/4 (——).

Figure 5 shows the visible absorption and CD spectra of P-2, P-3 and P-4 isomer of $[Co(CN)_2(S\text{-pn})_2]^+$. The absorption and CD behavior are similar to those of the corresponding cyclohexanediamine complexes. The absorption maximum for each complex is slightly shifted, the intensity differing slightly from each other. However, the pattern is typical of *cis*-dicyanobis(diamine) complexes. The CD spectra of P-2, P-3 and P-4 are in contrast to that of *cis*-Λ-$[Co(CN)_2(R,R\text{-chxn})_2]^+$ in Fig. 3. When configurational and vicinal contribution are taken into consideration, these complexes are assigned to isomers of *cis*-Δ-$[Co(CN)_2(S\text{-pn})_2]^+$. Although the CD strength of these isomers in the first absorption band region differs somewhat from each other, geometrical isomers due to the placement of the methyl groups of propylenediamine give no difference in CD behavior.

Figure 6 shows the CD spectra of P-3 and P-6 isomer of $[Co(CN)_2(S\text{-pn})_2]^+$, the geometrical structure of which seems to be *cis*(C_1) (Fig. 1). The calculated configurational and vicinal curves are almost the same as those calculated for the cyclohexanediamine complexes. On the basis of these CD data, P-2, P-3 and P-4 are assigned to Δ-configuration and P-5, P-6 and P-7 to Λ-configuration.

References

1) P. R. Ray and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951).

2) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).

3) M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).

4) K. Konya, H. Nishikawa, and M. Shibata, *ibid.*, **7**, 1165 (1968).

5) M. Muto, T. Baba, and H. Yoneda, This Bulletin, **41**, 2918 (1968).

6) K. Kuroda, *Nippon Kagaku Zasshi*, **89**, 720 (1968).

7) N. Maki and S. Sakuraba, This Bulletin, **42**, 1908 (1969).

8) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, **1965**, 132; *J. Chem. Soc.*, **1965**, 5094.

9) K. Ohkawa, J. Hidaka, and Y. Shimura, This Bulletin, **40**, 2830 (1967).

10) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Interscience, New York, 1971, Ch. 5.

11) F. P. Dwyer, F. L. Garvan, and A. Schulman, *J. Amer. Chem. Soc.*, **75**, 1526 (1959).

12) T. E. MacDermott, *Inorg. Chim. Acta*, **2**, 81 (1968).

13) a) M. Kojima, Y. Yoshikawa, and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **9**, 689 (1973). b) M. Kojima and K. Yamasaki, This Bulletin, **48**, 1093 (1975).

14) J. L. Sudmeier, G. L. Blackmer, C. H. Bradley, and F. A. L. Anet, *J. Amer. Chem. Soc.*, **94**, 757 (1972).

15) A. Johnson and G. W. Everett, Jr., *Inorg. Chem.*, **12**, 2801 (1973).

16) K. L. Craighead, *J. Amer. Chem. Soc.*, **95**, 4434 (1973).

17) Y. Koike, F. Yajima, A. Yamasaki, and S. Fujiwara, *Chem. Lett.*, **1974**, 177.

18) T. E. MacDermott, *Inorg. Chim. Acta*, **3**, 246 (1969).

19) R. H. Lewis and M. D. Alexander, *ibid.*, **5**, 86 (1971).

20) L. J. Halloran and J. I. Legg, *Inorg. Chem.*, **13**, 2193 (1974).

21) Y. Kojima and M. Shibata, *ibid.* **10**, 2382 (1971).

22) C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

23) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, This Bulletin, **42**, 3184 (1969).

24) H. Yamatera, *ibid.*, **31**, 95 (1958).

25) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

26) R. S. Treptow, *ibid.*, **5**, 1593 (1966).

27) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 828, 847, 861 (1975).

28) K. Matsumoto, S. Ooi, and H. Kuroya, *ibid.*, **44**, 2721 (1971).

29) K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).