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Studies of Mixed Cyano Cobalt(III) Complexes. III.[1] Some Cis Isomers of Monocyanobisethylenediamine Series

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Five new cis isomers of the $[Co(X)(CN)en_2]^{n+}$ complexes, namely, those of $X=NH_3$, OH_2, OH^-, I^- and NO_2^-, have been prepared and resolved into their optically active isomers. A new trans isomer of $X=NO_2^-$ has also been prepared. The splitting of the d→d absorption bands of the geometrical isomers of the $[Co(X)(CN)en_2]^{n+}$ complexes have been discussed in reference to their visible and ultraviolet absorption spectra, rotatory dispersion and circular dichroism spectra.

Previously only three examples of the complex of *cis*-$[Co(X)(CN)en_2]^{n+}$ type, where X represents a unidentate ligand, have been known, namely those of $X=Cl^-$, Br^- and SO_3^{2-}, for which the second paper of this series has given the detailed descriptions.[1] A series of the corresponding trans complexes was reported by Chan and Tobe,[2,3] who prepared the trans isomers of $X=Cl^-$, Br^-, SO_3^{2-}, OH_2 and OH^-. Now, most of mixed cyano cobalt(III) complexes are known in only one form of the two geometrical isomers which are possible for them; thus some dicyanobis(diamine) complex, $[Co(CN)_2(diamine)_2]^+$, are known in their cis forms only,[2,4] and a tricyanotriammine complex is known in only its mer (meridional) form.[5] It will be worthwhile, therefore, to examine whether it will be possible to prepare some more pairs of the cis and trans isomers of the $[Co(X)(CN)en_2]^{n+}$ type complexes; the present paper concerns to the results of this attempt. As a result of this study, several new complexes have been prepared and examined in their visible and ultraviolet absorption spectra, and furthermore the CD (circular dichroism) spectra have been measured and discussed for the cis isomers which have been resolved into their optically active isomers.

Experimental

1) *cis* - Cyanoaquobisethylenediaminecobalt - (III) Bromide. Twelve grams of *cis*-$[Co(Br)(CN)en_2]Br\cdot H_2O$[1] and 8 g of silver oxide were ground in a mortar with 18 m*l* of water. After the silver bromide precipitated had been removed by filtration, 18 m*l* of concentrated hydrobromic acid was added to the orange red filtrate, and then 35 m*l* of ethanol was added. The desired complex crystallized out when the solution was cooled in an ice bath. The red orange crystals were gathered by filtration, washed with methanol and acetone, and then dried in air. Yield: 3.2 g. This was recrystallized as follows; the crude complex was dissolved in a small volume of water and a few drops of concentrated hydrobromic acid was added to it. The resulted solution was filtered, and to the filtrate an appropriate amount of ethanol or acetone was added and then the mixture was cooled in an ice bath. The crystals were washed with methanol and acetone, and dried in air.

Found: C, 15.80; H, 4.77; N, 18.40%. Calcd for $C_5H_{18}N_5OBr_2Co=[Co(CN)(OH_2)en_2]Br_2$: C, 15.68; H, 4.74; N, 18.29%.

Optical Resolution. The racemic complex (3.1 g) was dissolved in 40 m*l* of water, and a solution of 2.6 g of ammonium (+)-bromocamphor-π-sulfonate (NH_4·d-BCS) in 30 m*l* of water was added to it with stirring. After a few minutes, a pale orange diastereomer began to deposit. It was collected by filtration, washed several times with a little ice water and then with acetone. and dried in air. Yield: 1.9 g.

Found: C, 36.34; H, 5.54; N, 8.26%. Calcd for $C_{25}H_{46}N_5O_9S_2Br_2Co=[Co(CN)(OH_2)en_2]$ (d-BCS)$_2$: C, 35.60; H, 5.50; N, 8.30%.

The diastereomer was dissolved in 20% hydrobromic acid and to this solution was added a large volume of ethanol, and the mixture was cooled in an ice bath for crystallization of the optically active complex salt. It was a dihydrated salt. The water of hydration was removed by drying it in a vacuum at 77—81°C for about 42 hr. $[M]^{15}_{546}=(+)668°$, $[M]^{15}_{589}=(+)440°$, in 0.1 N sulfuric acid.

Found: C, 15.79; H, 4.56; N, 18.76%. Calcd for $[Co(CN)(OH_2)en_2]Br_2$: C, 15.68; H, 4.74; N, 18.29%.

By extensive dehydration of the (+)-*cis*-$[Co(CN)(OH_2)en_2]Br_2\cdot 2H_2O$ salt, the coordinated water molecule was expelled and an optically active salt, $(+)_{559}$-*cis*-$[Co(Br)(CN)en_2]Br$, was obtained. The dehydration continued for about a month or so, in a vacuum desiccator over concentrated sulfuric acid. The optical purity of the product was rather high, judging from the CD value of $(\varepsilon_l-\varepsilon_d)_{560}=0.30$ as compared with the

1) Part II of this series: K. Ohkawa, J. Hidaka and Y. Shimura, This Bulletin, **39**, 1715 (1966).
2) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, **1963**, 966.
3) S. C. Chan, *ibid.*, **1964**, 2716.
4) K. Ohkawa, J. Fujita and Y. Shimura, This Bulletin, **38**, 66 (1965).
5) M. Shibata, M. Mori and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).

value reported for the pure complex,[1] $(\varepsilon_l-\varepsilon_d)_{560}=0.40$.

2) *cis*-Hydroxocyanobisethylenediaminecobalt-(III) Ion. This was not separated as solid salts. The absorption and CD spectra and RD (rotatory dispersion) of this ion were measured for the solution of the corresponding cyanoaquo complex ion in 0.1 N NaOH.

3) *cis*-Iodocyanobisethylenediaminecobalt(III) Iodide. The orange red solution obtained from 12 g of *cis*-$[Co(Br)(CN)en_2]Br\cdot H_2O$ and 8 g of silver oxide as in 1) was acidified by concentrated hydroiodic acid (about 4.5 m*l*) and diluted by adding 16 m*l* of water. The solution was cooled in an ice bath overnight, and filtered. To the filtrate 7 more milliliters of concentrated hydroiodic acid was added. When it was gently warmed on a water bath at about 65°C, the color of solution became black purple. After about four hours, it was filtered while warming. The black purple crystals were washed with ice water and with methanol. Yield: 3.7 g. This was recrystallized from warm water by adding a small amount of sodium iodide.

Found: C, 13.25; H, 3.59; N, 15.24%. Calcd for $C_5H_{16}N_5I_2Co=[Co(I)(CN)en_2]I$: C, 13.09; H, 3.51; N, 15.26%.

4) *cis*-Iodocyanobisethylenediaminecobalt(III) Perchlorate. The iodide was saturated in water at about 30°C, and a large amount of sodium perchlorate was dissolved to it. This was cooled to room temperature. The desired perchlorate deposited with a little contamination, the starting iodide. This was purified by repeating the above procedure. Recrystallization was made from water.

Found: C, 13.94; H, 3.79; N, 16.22%. Calcd for $C_5H_{16}N_5O_4ClICo=[Co(I)(CN)en_2]ClO_4$: C, 13.92; H, 3.74; N, 16.23%.

Optical Resolution. Two grams of racemic *cis*-$[Co(I)(CN)en_2]I$ and 0.69 g of silver acetate were ground with 10 m*l* of water. Silver iodide precipitated was filtered off and a few drops of concentrated sulfuric acid added to the filtrate. When the mixture was cooled in an ice bath, the complex sulfate precipitated, which was collected by filtration. The preparations in this scale were repeated four times. The products of the four preparations were combined and recrystallized from warm water by adding a few drops of concentrated sulfuric acid. The needle crystals obtained were filtered and washed with methanol. To 135 m*l* of aqueous solution of the sulfate (3.8 g), 1.31 g of ammonium (+)-bromocamphor-π-sulfonate in 30 m*l* of water was added with stirring. After half an hour, the diastereomer deposited was filtered and washed with ice water several times and then with acetone. Yield: 1.32 g.

Found: C, 28.11; H, 5.00; N, 10.81%. Calcd for $C_{15}H_{30}N_5O_4SBrICo=[Co(I)(CN)en_2](d\text{-}BCS)$: C, 28.05; H, 4.71; N, 10.90%.

The diastereomer was ground with a saturated aqueous solution of sodium perchlorate, and the complex settled was filtered and washed with water-ethanol mixture (1 : 1) and with ethanol. $[M]^{15}_{546}=(-)1200°$, $[M]^{15}_{589}=(-)488°$.

Found: C, 13.92; H, 3.73; N, 15.91%. Calcd for $[Co(I)(CN)en_2]ClO_4$: C, 13.92; H, 3.74; N, 16.23%.

5) *cis*-Cyanoamminebisethylenediaminecobalt-(III) Bromide. A powdered sample of *cis*-$[Co(Br)(CN)en_2]Br$ (7.0 g) was suspended in 250 m*l* of liquid ammonia in a high-pressure reaction vessel immersed in a dry ice - acetone bath. After several hours, excess ammonia was expelled by raising the temperature to the room temperature; the color of mixture changed from rose to orange yellow. About 150 m*l* of ethanol was added to the residue and the orange yellow solid was separated by filtration. The product was washed with ethanol and acetone and dried in air. Yield: 6.5 g. This was recrystallized from water by adding acetone and by cooling in an ice bath.

Found: C, 15.94; H, 5.25; N, 21.81%. Calcd for $C_5H_{19}N_6Br_2Co=[Co(CN)(NH_3)en_2]Br_2$: C, 15.72; H, 5.01; N, 22.00%.

Optical Resolution. To a solution of 2.6 g racemic *cis*-$[Co(CN)(NH_3)en_2]Br_2$ in 30 m*l* of water, 2.2 g of ammonium (+)-bromocamphor-π-sulfonate in 20 m*l* of water was added with stirring. After twenty minutes, the diastereomer deposited was filtered off and then dried in air. Yield: 1.9 g. The optically active bromide, $(-)_{546}$-*cis*-$[Co(CN)(NH_3)en_2]Br_2$, was derived from the diastereomer by dissolving it in 20% hydrobromic acid and by adding methanol and acetone to it.

$$[M]^{15}_{546}=(-)160°,\ [M]^{15}_{589}\simeq 0\,.$$

Found: C, 15.39; H, 5.14; N, 21.28; H_2O, 2.69%. Calcd for $C_5H_{19}N_6Br_2Co\cdot\frac{1}{2}H_2O=[Co(CN)(NH_3)en_2]Br_2\cdot\frac{1}{2}H_2O$: C, 15.40; H, 5.17; N, 21.56; H_2O, 2.30%.

The corresponding $(+)_{546}$-enantiomer was derived from $(+)_{589}$-*cis*-$[Co(Br)(CN)en_2]Br$ by the same procedure for the racemic complex. But the optical purity of this product was about 30%; $(\varepsilon_l-\varepsilon_d)=0.12$ at 456 mμ.

6) *cis*-Cyanonitrobisethylenediaminecobalt(III) Bromide. Potassium nitrite (2.5 g) was added to a solution of 10 g of *cis*-$[Co(Br)(CN)en_2]Br\cdot H_2O$ in 40 m*l* of water and the mixture was warmed on a water bath; then the color of the solution became orange yellow. After a few hours, crystals began to appear, which were dissolved again by adding water to the mixture. A little lithium bromide was added to the solution. The resultant solution was concentrated by evaporation and then cooled in a refrigerator, while dark yellow crystals were deposited. They were separated from the mother liquor and washed with ice water and methanol. Yield: 1.8 g. This was recrystallized from warm water by adding a small portion of lithium bromide and by cooling in an ice bath.

Found: C, 17.88; H, 5.35; N, 24.08%. Calcd for $C_5H_{18}N_6O_3BrCo=[Co(CN)(NO_2)en_2]Br\cdot H_2O$: C, 17.21; H, 5.20; N, 24.07%.

Optical Resolution. Firstly, the bromide was converted to nitrite by treating it with equi-molar volume of an aqueous solution of silver nitrite. The needle crystals were obtained by usual recrystallization procedure.

Found: C, 20.31; H, 5.39; N, 32.27%. Calcd for $C_5H_{16}N_7O_4Co=[Co(CN)(NO_2)en_2]NO_2$: C, 20.21; H, 5.43; N, 32.99%.

Ammonium (+)-bromocamphor-π-sulfonate (1.3 g) in 20 m*l* of water was added to a solution of 2.4 g of racemic *cis*-$[Co(CN)(NO_2)en_2]NO_2$ in 50 m*l* of warm water and whole of them was cooled in a refrigerator. The diastereomer deposited was filtered off and washed with small amount of ice water and then with methanol. Yield: 0.6 g. The diastereomer was ground with lithium bromide and then with about 10 m*l* of water. About 10 m*l* of methanol was added to this mixture; then the optically active bromide crystallized out gradually.

Found: C, 18.38; H, 5.03; N, 25.65%. Calcd for $C_5H_{16}N_6O_2BrCo$=[Co(CN)(NO_2)en$_2$]Br: C, 18.14; H, 4.87; N, 25.38%.

7) *trans*-Cyanonitrobisethylenediaminecobalt-(III) Perchlorate. This complex was prepared by the method same as that of the corresponding cis complex, using 5 g of *trans*-[Co(Br)(CN)en$_2$]Br·H_2O,[3] 1.1 g of sodium nitrite and a small portion of sodium perchlorate. Yield: 2 g. The crude complex was recrystallized from water. The pure complex was light yellow.

Found: C, 17.15; H, 4.55; N, 23.70%. Calcd for $C_5H_{16}N_6O_6ClCo$=[Co(CN)(NO_2)en$_2$]ClO_4: C, 17.13; H, 4.60; N, 23.96%.

Measurements. The absorption spectra were measured by a Beckman DU Spectrophotometer. The CD spectra were recorded with a Roussel-Jouan dichrographe or with a Spectropolarimeter ORD/UV-5 of the Japan Spectroscopic Co. The RD curves were obtained with a Yanagimoto Recording Spectropolarimeter Model-185. All the measurements were made at room temperature.

Results and Discussion

The data of spin-allowed d→d absorption bands observed for the cis and the trans isomers are presented in Table 1. The first absorption bands of the cis isomers more or less split into two (or three) components, while those of the trans isomers do not show such split. As has been discussed in the former paper,[1] this behavior is a characteristic one of the $[Co(X)(Y)(A)_4]^{n+}$ type complexes, where the unidentate ligands X and Y

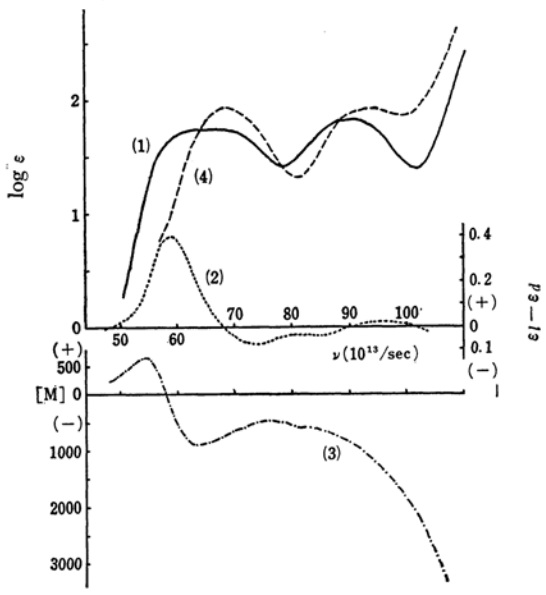

Fig. 1. Absorption (1) and CD spectra (2), and RD (3) of *cis*-[Co(CN)(OH_2)en$_2$]Br_2 and absorption spectrum (4) of the trans isomer, in 0.1 N H_2SO_4.

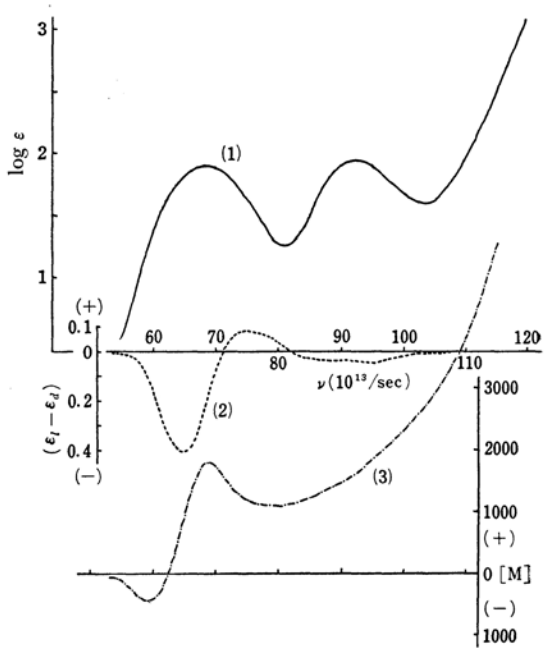

Fig. 2. Absorption (1) and CD spectra (2), and RD (3) of *cis*-[Co(CN)(NH_3)en$_2$]Br_2 in water.

take their positions on the spectrochemical series, above and behind the ligand A, respectively.

As may be seen in Fig. 1, only the longer wavelength components of the first absorption band of the *cis*-(CN)(OH_2) isomer are strongly optical-active, while other components of the d→d absorption bands are less active. Similar behavior has been observed for the *cis*-(CN)(NH_3) and the *cis*-(CN)(NO_2) isomers also (Figs. 2 and 3). On the contrary, for the *cis*-(OH)(CN), *cis*-(Cl)(CN), *cis*-(Br)(CN) and *cis*-(I)(CN) isomers, the second component of the first absorption band also showed rather strong CD (Figs. 4 and 5). According to well-known Yamatera's treatment,[6] frequencies of the three components of the first absorption band of the *cis*-$[Co(X)(CN)en_2]^{n+}$ complex can be expressed by (i) $\frac{3}{4}\delta$(en)+$\frac{1}{4}\delta$(X), (ii) $\frac{1}{2}\delta$(en) +$\frac{1}{4}\delta$(X)+$\frac{1}{4}\delta$(CN) and (iii) $\frac{3}{4}\delta$(en)+$\frac{1}{4}\delta$(CN) respectively, where δ(en), δ(X) and δ(CN) are parameters concerning to the ligand en, X and CN^- respectively. From the observed positions of the longer wavelength components, (i) the parameter δ(X) can be evaluated as follows, taking a zero line at the ligand NH_3 tentatively; NO_2^-: +4.4, NH_3: 0, OH_2: −23.6, OH^-: −30.8, Cl^-: −38.4, Br^-: −44.0, I^-: −56.8 ($\times 10^{13}$ sec^{-1}). These values, however, are true only qualitatively, because of uncertainties of the CD peak positions. Serious cancellations may be occured between the first and the second components, which have reversed CD signs to each other.

6) H. Yamatera, This Bulletin, **31**, 95 (1958).

TABLE 1. SINGLET-SINGLET LIGAND FIELD ABSORPTION BANDS OF THE GEOMETRICAL ISOMERS OF $[Co(X)(CN)en_2]^{n+}$ COMPLEXES

X	cis isomer		trans isomer	
	I-band	II-band	I-band	II-band
CN^-	74.2 (1.91)	97.1 (1.93)	—	—
SO_3^{2-}	72.0 (2.21)	—	72.2 (2.13) *ca.* 64 sh	—
NO_2^-	68.7 (2.07)	—	71.9 (2.03)	—
NH_3	68.8 (1.89)	92.6 (1.93)	—	—
OH_2	67.6 (1.74) *ca.* 62 (1.73)	90.8 (1.83)	68.6 (1.92)	93.0 (1.91)
OH^-	65.6 (1.90) *ca.* 56 sh	86.1 (2.02)	66.9 (1.90)	91.4 (1.84)
Cl^-	*ca.* 69 sh 59.2 (1.82)	87.6 (1.95)	66.2 (2.14)	—
Br^-	*ca.* 68 sh 58.5 (1.98)	—	64.9 (2.11)	—
I^-	56.5 (2.19)	—	—	—

The frequencies of maximum positions are presented by the unit of $10^{13}\,sec^{-1}$ and the maximum intensities, $\log \varepsilon_{max}$, in parentheses.

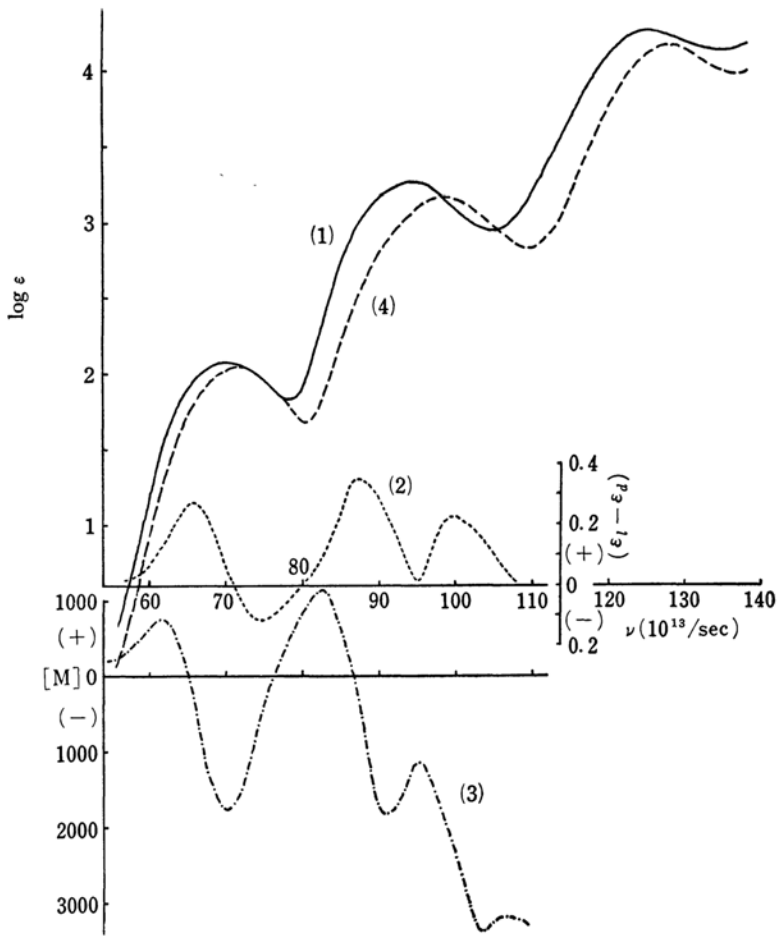

Fig. 3. Absorption (1) and CD spectra (2) and]RD (3) of *cis*-$[Co(CN)(NO_2)en_2]Br$ and absorption spectrum (4) of the trans isomer, in water.

Table 2. CD data and absolute configurations of the optically active cis isomers

Complex	Solubility of d-BCS salt	Absolute configuration	CD bands in I-band region: ν_{ext} by $10^{13}\,sec^{-1}$ and $(\varepsilon_l-\varepsilon_d)_{ext}$ in parentheses		
$(+)_{589}$-$[Co(CN)_2en_2]Cl$[a]	less soluble	Δ	68.0 (+0.30)	81.8 (+0.17)	
$(+)_{546}$-$[Co(CN)(NO_2)en_2]Br$	less soluble	Δ	65.9 (+0.28)	75.0 (−0.14)	
$(-)_{546}$-$[Co(CN)(NH_3)en_2]Br_2$	less soluble	Λ	64.8 (−0.42)	*ca.* 76 (+0.08)	
$(+)_{546}$-$[Co(CN)(OH_2)en_2]Br_2$	less soluble	Δ	58.9 (+0.40)	73.2 (−0.08)	
$(+)_{546}$-$[Co(OH)(CN)en_2]^+$	—	Δ	57.1 (+0.51)	69.0 (−0.57)	
$(-)_{546}$-$[Co(Cl)(CN)en_2]I$	less soluble	Δ	55.2 (+0.38)	62.2 (−0.22)	69.6 (+0.07)
$(-)_{546}$-$[Co(Br)(CN)en_2]Br$	less soluble	Δ	53.8 (+0.40)	60.7 (−0.30)	67.9 (+0.11)
$(-)_{546}$-$[Co(I)(CN)en_2]ClO_4$	less soluble	Δ	50.6 (+0.23)	57.8 (−0.33)	

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

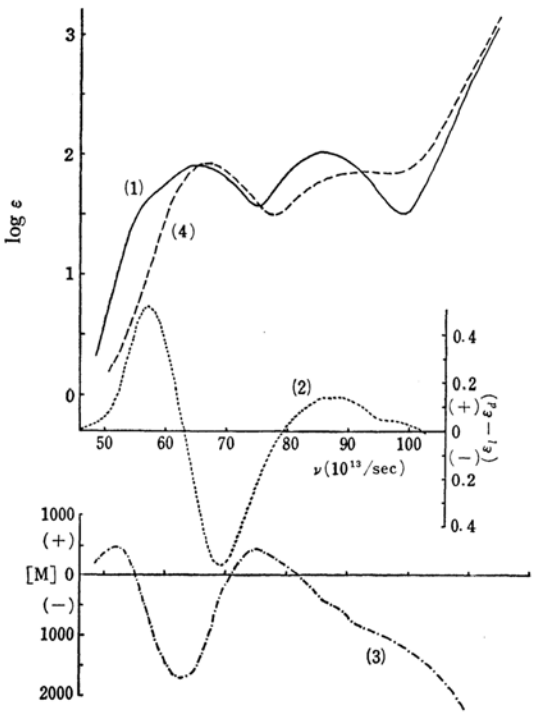

Fig. 4. Absorption (1) and CD spectra (2), and RD (3) of *cis*-$[Co(OH)(CN)en_2]Br$ and absorption spectrum (4) of the trans isomer, in 0.1 N NaOH.

Recently, absolute configuration of the dicyano complex, $(+)_{589}$-$[Co(CN)_2en_2]^+$ has been determined as $\Delta(C_2)$ by X-ray techniques.[7] From the comparison of the CD signs of the first components of the first absorption bands presented in Table 2, the same absolute configuration Δ may be assigned to the complex enantiomers which form less soluble diastereomer with (+)-bromocamphor-π-sulfonate. Only one exception was found for solubility criterion. This is *cis*-$(CN)(NH_3)$ isomers; the $(-)_{546}$-enantiomer forms the less soluble diastereomer with (+)-bromocamphor-π-sulfonate but have (−) sign of the first CD component and therefore may be assigned to the Λ configuration. These assignments of absolute configurations are consistent with the conclusion from interconversion processes among these isomers (see Experimental part).

The *cis*-iodocyano complex has a very strong spin-forbidden band at 37.7 ($\times 10^{13}\,sec^{-1}$), whose intensity reaches $\log \varepsilon_{max}=1.54$. No CD band was detected, however, in the region of this spin-forbidden band. The same is true for the spin-forbidden band of the *cis*-(Br)(CN) isomer; $\nu_{max}=37.6$ ($\times 10^{13}\,sec^{-1}$), $\log\varepsilon_{max}=0.72$.

Table 3 summarizes the data of the charge-transfer absorption bands of the cis and the trans isomers. Clearly the bands of the cis isomer are located at longer wavelength than those of the corresponding trans isomer, except for the case of the $[Co(CN)(SO_3)en_2]$ complex. As was discussed in the former paper,[1] this effect may be attributed to a hypsochromic influence of the cyanide ligand, which is coordinated at the trans position to the ligand X in the trans isomer. In the cis isomer, ethylenediamine is coordinated at the trans position

Table 3. Charge-transfer absorption bands of the geometrical isomers of $[Co(X)(CN)en_2]^{n+}$ complexes

The frequencies of maximum positions are presented by the unit of $10^{13}\,sec^{-1}$ and the maximum intensities, $\log \varepsilon_{max}$, in parentheses

X	*n*	cis isomer	trans isomer
Cl^-	1	*ca.* 111 sh 130 (4.29)	*ca.* 116 sh 136 (4.37)
Br^-	1	*ca.* 97 sh 119 (4.29)	*ca.* 102 sh 124.5 (4.44)
I^-	1	81.8 (3.40) 106.9 (4.20)	— —
NO_2^-	1	94.7 (3.25) 125.6 (4.27)	98.7 (3.17) 128.0 (4.17)
SO_3^{2-}	0	109.9 (4.16)	109.5 (4.24)

7) H. Kuroya, private communication.

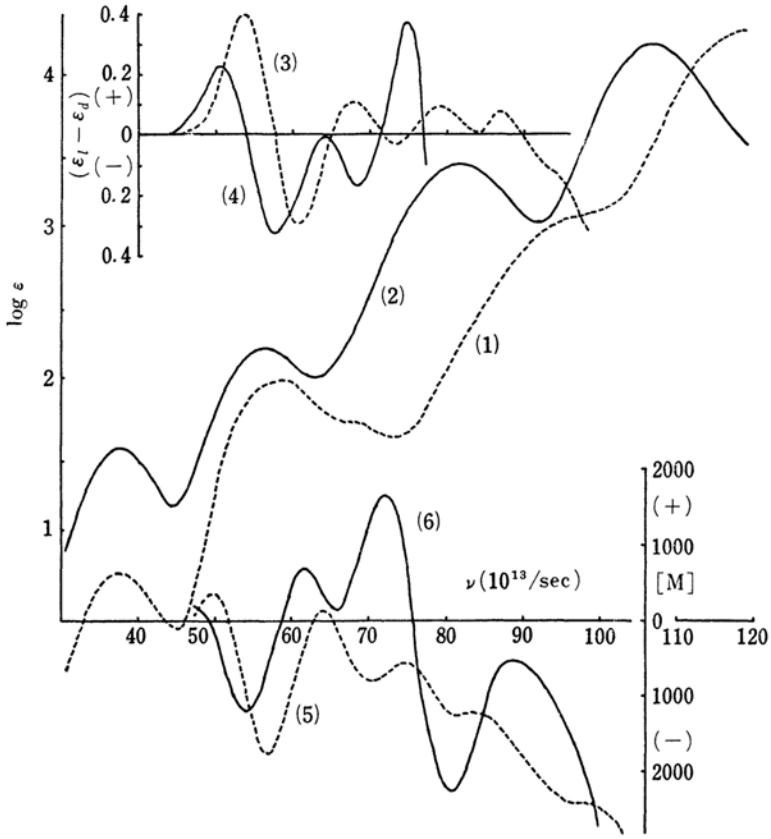

Fig. 5. Absorption (1, 2) and CD spectra (3, 4), and RD (5, 6) of *cis*-[Co(X)(CN)en_2]Y in water.
1, 3 and 5: X=Y=Br^-, 2, 4 and 6: X=I^-, Y=$\frac{1}{2}SO_4^{2-}$

to the ligand X, and the position of the charge-transfer band is about the same as that of the corresponding pentammine or monoamminebisethylenediamine complex (see Table 5 of paper II[1]) of this series). Exceptionally, two isomers of the [Co(CN)$(SO_3)en_2$] complex showed almost identical charge-transfer bands.[1]) The reason for this has remained unknown.