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Studies of Mixed Cyano Cobalt(III) Complexes. II.[1] The Geometrical Isomers of $[CoX(CN)en_2]^+$

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Two new mixed cyano complexes, *cis*-$[CoCl(CN)en_2]Cl$ (red) and *cis*-$[CoBr(CN)en_2]Br$ (deep rose), have been synthesized and resolved into their optical isomers. The splitting patterns of the ligand field absorption bands of the cis and the trans isomers of the halogenocyanobis(ethylenediamine)cobalt(III) ion have been discussed in relation to the geometrical configurations of the complexes and to the σ- and π-antibonding contribution of the cyanide or the halide ligands to the metal d-orbitals. These studies have been made successfully using the circular dichroism data of the optically active *cis*-$[CoX(CN)en_2]X$ (X=Cl, Br).

Recently several papers[1-4] have appeared dealing with the mixed cyano-ammine or the mixed cyano-diamine complexes of cobalt(III). A rather normal character of cyanide as a ligand for cobalt(III) has been well established, although the ligand has an exceptionally high position in the spectrochemical series. From a spectrochemical point of view, the mixed cyano cobalt(III) complexes which contain the halogeno ligands or both the halogeno and the ammine ligands are very interesting, since the position of a halogeno ligand in the spectrochemical series is well separated from the position of an ammine ligand in the direction opposite to that of the cyanide ligand. Chan and Tobe[5,6] prepared some such complexes, namely, the trans forms of $[CoX(CN)en_2]X$ (X=Cl, Br); however, the corresponding cis forms are yet unknown.

In the present paper, the syntheses of the missing cis forms of $[CoX(CN)en_2]X$ (X=Cl, Br) and their resolution into their optical isomers will be described. Besides proving the cis structure, the optical resolution will give a convenient tool for the assignment of the d-d absorption bands; the splitting patterns of the so-called first and second absorption bands are reflected profoundly in the circular dichroism spectra. The geometrical structures of the related mixed cyano cobalt(III) complexes will also be discussed.

Experimental

Materials.—*The Dark Yellow Form of* $Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot 6H_2O$.—To a solution of 15 g. of sodium cyanide in 200 ml. of water, 36 g. of $NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$[7] was added. The desired complex precipitated gradually, and ammonia was evolved simultaneously. After about three hours, the resulting mixture was cooled in an ice bath and filtered. Another crop of the crude complex was obtained from the filtrate by cooling it in an ice bath and by adding alcohol. The yield was 37 g. This yellow complex was recrystallized from water below 35—40°C.

Found: C, 6.64; H, 1.61; N, 15.50. Calcd. for $C_2H_6N_4O_6S_2Na_3Co = Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]$: C, 6.42; H, 1.62; N, 14.98%.

Found: H_2O, 22.28. Calcd. for $Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot 6H_2O$: 22.41%.

The Orange-yellow form of $Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot 5H_2O$.—To a solution of 10 g. of sodium cyanide in 150 ml. of water, 24 g. of $NH_4[Co(SO_3)_2(NH_3)_4]\cdot 3H_2O$[7] was added. The mixture was then warmed on a water bath and evaporated gently. When orange crystals began to appear, the reaction mixture was cooled in an ice bath. The complex was filtered and recrystallized from hot water by the addition of ethanol. Yield: 9 g.

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1) Part I of this series: K. Ohkawa, J. Fujita and Y. Shimura, This Bulletin, **38**, 66 (1965).

2) N. R. S. Gupta, *Z. anorg. Chem.*, **325**, 108 (1963).

3) H. Siebert, ibid., **327**, 63 (1964).

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

5) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, **1963**, 966.

6) S. C. Chan, ibid., **1964**, 2716.

7) A. Werner and H. Grüger, *Z. anorg. Chem.*, **16**, 398 (1898).

Found: C, 6.82; H, 1.87; N, 14.45. Calcd. for $C_2H_6N_4O_6S_2Na_3Co = Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]$: C, 6.42; H, 1.62; N, 14.98%.

Found: H_2O, 19.08. Calcd. for $Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot5H_2O$: 19.40%.

The Dark Yellow Form of $K_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot H_2O$.—This was prepared by the same method as was the dark yellow form of $Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot6H_2O$. To a solution of 20 g. of potassium cyanide in 100 ml. of water, 28 g. of $NH_4[Co(SO_3)_2(NH_3)_4]\cdot3H_2O$7) was added. To complete the reaction the mixture was then stirred. After the solution had been cooled in an ice bath for one hour, the dark yellow complex which had deposited was filtered and washed with water-methanol (1 : 1) and methanol. Another crop of the complex was obtained from the filtrate by the addition of methanol. The crude complex was recrystallized from water by the addition of methanol. Yield: 25 g.

Found: C, 5.89; H, 1.75; N, 13.66. Calcd. for $C_2H_6N_4O_6S_2K_3Co = K_3[Co(CN)_2(SO_3)_2(NH_3)_2]$: C, 5.69; H, 1.43; N, 13.26%.

Found: H_2O, 4.14. Calcd. for $K_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot H_2O$: 4.09%.

cis-$[Co(CN)(SO_3)en_2]$.—Thirty grams of the orange-yellow or the dark-yellow form of $M_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot xH_2O$ (M=Na or K) was covered with 300 ml. of a 10% aqueous solution of ethylenediamine. When the mixture was heated on a water bath, it changed to a brown solution. After several minutes, a glittering complex began to crystallize. The mixture was kept on a water bath about three hours and then filtered. The crude complex was washed with a little of hot water about three times, with water, and finally with ethanol. Yield: 5.8 g.

The crystals which were recrystallized from hot water were pale brownish yellow and anhydrous.

Found: C, 20.22; H, 6.07; N, 23.47. Calcd. for $C_5H_{16}N_5O_3SCo = [Co(CN)(SO_3)en_2]$: C, 21.07; H, 5.65; N, 24.57%.

cis-$[CoCl(CN)en_2]Cl\cdot H_2O$.—In 135ml. of concentrated hydrochloric acid, 13 g. of *cis*-$[Co(CN)(SO_3)en_2]$ was suspended; this solution was then warmed on a water bath for about three hours. The color of the solution changed from yellow to red. After the solution had been evaporated to half of the original volume, it was filtered and 70 ml. of ethanol was added to the filtrate. The solution was then cooled in an ice bath; a red complex deposited gradually. The product was recrystallized from warm water by the addition of alcohol and washed with a water-ethanol mixture (1 : 2) and then with ethanol several times. Yield: 3.8 g.

Found: C, 21.71; H, 6.00; N, 24.97. Calcd. for $C_5H_{16}N_5Cl_2Co = [CoCl(CN)en_2]Cl$: C, 21.75; H, 5.84; N, 25.37%.

Found: H_2O, 6.56; Cl, 24.60. Calcd. for $[CoCl(CN)en_2]Cl\cdot H_2O$: H_2O, 6.12; Cl, 24.12%.

cis-$[CoBr(CN)en_2]Br\cdot H_2O$. — This complex was prepared by the same method as was the chloro complex, using 9.5 g. of *cis*-$[Co(CN)(SO_3)en_2]$ and 100 ml. of concentrated hydrobromic acid. Yield: 3 g.

Found: C, 16.46; H, 4.71; N, 19.00; Br, 43.63. Calcd. for $C_5H_{16}N_5Br_2Co = [CoBr(CN)en_2]Br$; C, 16.48; H, 4.42; N, 19.21; Br, 43.90%.

Found: H_2O, 4.73. Calcd. for $[CoBr(CN)en_2]Br\cdot H_2O$: 4.60%.

The Optical Resolution of cis-$[CoCl(CN)en]_2]^+$.—Racemic *cis*-$[CoCl(CN)en_2]Cl\cdot H_2O$ (9.06 g.) was dissolved in 90 ml. of water at about 35°C by rigorous shaking. To this solution, a solution of 5.31 g. of ammonium (+)-*d*-bromocamphor-π-sulfonate ($NH_4\cdot$*d*-BCS) in 50 ml. of water was added at room temperature. After a few minutes, the diastereomer $(+)_{589}$-$[CoCl(CN)en_2]$(*d*-BCS) began to separate as rosy crystals. To complete the reaction, the mixture was stirred, allowed to stand for about ten minutes, and then filtered. The diastereomer was washed with a little ice water five times and then with ethanol, and dried in air. The yield was 6.6 g. The recrystallization was made from a little water by the addition of alcohol. The diastereomer is optically stable in water.

Found: C, 32.66; H, 5.54; N, 12.98. Calcd. for $C_{15}H_{30}N_5O_4SClBrCo = [CoCl(CN)en_2](C_{10}H_{14}O_4SBr)$: C, 32.74; H, 5.50; N, 12.73%.

For a 0.05% solution of the diastereomer in a 2 dm. tube:

$\alpha_{589} = (+)\ 0.14°$, $\alpha_{546} = (+)\ 0.11°$.

The recrystallized diastereomer (2.26 g.) and potassium iodide (7 g.) were ground in a mortar with a few drops of water. Ten milliliters of water was then added the mixture, and the resultant mixture was triturated for about half an hour. The complex thus deposited was separated by suction, and washed with a little ice water three times and then with alcohol. The complex was then recrystallized from warm water by the addition of alcohol in an ice bath.

Found: C, 16.57; H, 4.50; N, 19.32. Calcd. for $C_5H_{16}N_5ClICo = [CoCl(CN)en_2]I$: C, 16.34; H, 4.39; N, 19.06%.

For a 1/150 F solution of the complex in a 1/2 dm. tube:

$\alpha_{589} = (+)\ 0.02°$, $\alpha_{546} = (-)\ 0.10°$.

The Optical Resolution of cis-$[CoBr(CN)en_2]^+$—This complex was resolved by the same method as was the chloro complex. Racemic *cis*-$[CoBr(CN)en_2]Br\cdot H_2O$ (4.43 g.) was dissolved in 50 ml. of water at about 45°C by rigorous shaking. To this solution, a solution of 3.66 g. of ammonium (+)-*d*-bromocamphor-π-sulfonate in 20 ml. of water was added. After a few minutes, the precipitated diastereomer $(+)_{589}$-$[CoBr(CN)en_2]$(*d*-BCS) was filtered, washed with a little ice water several times and then with ethanol, and dried in air. The yield was 2.9 g. The diastereomer is optically unstable in water.

For a 0.05% solution of the diastereomer in a 2 dm. tube:

$\alpha_{589} = (+)0.12°$, $\alpha_{546} = (-)0.10°$

The diastereomer (3.0 g.) was ground in a mortar with 6 ml. of concentrated hydrobromic acid; the complex thus deposited was filtered and washed with ethanol. The complwx recrystallized was anhydrous.

Found: C, 16.60; H, 4.52; N, 19.40. Calcd. for $C_5H_{16}N_5Br_2Co = [CoBr(CN)en_2]Br$: C, 16.48; H, 4.42; N, 19.21%.

For a 1/150 F solution of the complex;
in a 1/2 dm. tube, $\alpha_{589} = (+)\ 0.06°$;
in a 1/5 dm. tube, $\alpha_{546} = (-)\ 0.12°$.

trans-$[CoCl(CN)(NH_3)_4]Cl$.—The orange-colored complex3) of $[Co(CN)(SO_3)(NH_3)_4]$ (10 g.) was suspended in 100 ml. of concentrated hydrochloric acid and warmed gently on a water bath. The color of the mixture became orange yellow, and sulfur dioxide gas was evolved. After about half an hour, the supernatant liquid was decanted off; another 100 ml. of concentrated hydrochloric acid was added to the residue. The resulting mixture was warmed on a water bath for an hour, cooled to room temperature, and then allowed to stand overnight. The complex was separated from the liquid and washed several times by decantation using concentrated hydrochloric acid. This was washed with alcohol and dried in air. Yield: 9 g. This orange-yellow complex is rapidly aquated in water. No recystallization was made.

Found: C, 5.07; H, 5.59; N, 28.68; Cl, 31.58. Calcd. for $CH_{12}N_5Cl_2Co = [CoCl(CN)(NH_3)_4]Cl$: C, 5.36; H, 5.40; N, 31.26; Cl, 31.68%.

trans-[$CoBr(CN)(NH_3)_4$*]*Br.—This complex was prepared by the same method as was the chloro complex, using 10 g. of $[Co(CN)(SO_3)(NH_3)_4]$³⁾ and 100 ml. of concentrated hydrobromic acid. Yield: 10 g.

Found: C, 3.53; H, 3.93; N, 20.26; Br, 52.78. Calcd. for $CH_{12}N_5Br_2Co = [CoBr(CN)(NH_3)_4]Br$: C, 3.84; H, 3.86; N, 22.40; Br, 51.10%.

The trans forms of $[CoX(CN)en_2]X$ (X=Cl, Br) were prepared by the method of Chan.⁵,⁶⁾

Measurements. — The absorption spectra were measured by a Beckman DU Spectrophotometer. The solvent employed for *cis*-$[CoX(CN)en_2]X$ (X=Cl, Br) was water, and for *trans*-$[CoX(CN)en_2]X$, 70% perchloric acid. The circular dichroism spectra were recorded on a Spectropolarimeter, ORD/UV-5, of the Japan Spectroscopic Co. A Rudolph photoelectric spectropolarimeter, Model 200S-80, was used to check the optical rotation. All the measurements were made at room temperature.

Results and Discussion

The Geometrical Configurations of the Complexes.—Chan and Tobe⁵⁾ derived *trans*-$[CoCl(CN)en_2]Cl$ from the orange-colored form of $[Co(CN)(SO_3)en_2]$. In the present study of the synthesis of the corresponding cis isomer, a new isomer of $[Co(CN)(SO_3)en_2]$ was used as the parent compound; it was pale brownish-yellow in color and was derived from the brown form of $[Co(SO_3)_2(NH_3)_4]^-$ through an intermediate complex $[Co(CN)_2(SO_3)_2(NH_3)_2]^{3-}$. Two isomers of $M_3[Co(CN)_2(SO_3)_2(NH_3)_2]$, dark-yellow and orange-yellow, were obtained from the reaction between $[Co(SO_3)_2(NH_3)_4]^-$ and alkali cyanide. Babaeva and Baranovskii⁸⁾ had already obtained the yellow potassium salt as dihydrate and had assigned the cis(CN)-cis(SO_3)-trans(NH_3) structure to the complex. The structure of the new orange-yellow complex is unknown, At any rate, both the isomers produced the same yellow form of $[C(CN)(SO_3)en_2]$. This yellow-$[Co(CN)(SO_3)en_2]$ is less soluble in water than its orange-colored isomer, which has been prepared by Chan and Tobe. The cis configuration of the red-$[CoCl(CN)en_2]Cl$, which was derived from the yellow-$[Co(CN)(SO_3)en_2]$, was established by its optical resolution; accordingly, it is certain that the yellow-$[Co(CN)(SO_3)en_2]$ is the cis isomer, and the orange-$[Co(CN)(SO_3)en_2]$, the trans isomer (see Fig. 1).

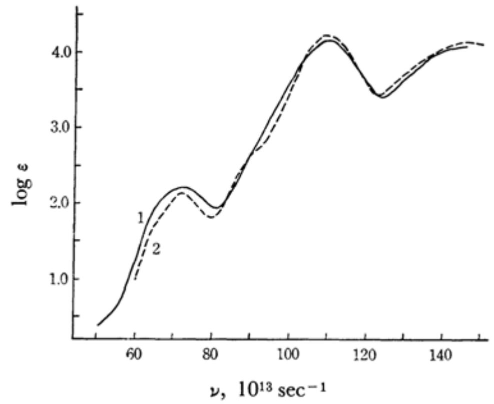

Fig. 1. Absorption spectra of $[Co(CN)(SO_3)en_2]$.
1—— absorption curve of *cis*-$[Co(CN)(SO_3)en_2]$ in 4% NH_3 aq.
2---- absorption curve of *trans*-$[Co(CN)(SO_3)en_2]$ in aqueous solution.

The corresponding tetrammin complex, $[Co(CN)(SO_3)(NH_3)_4]$, which is known only in one form (an orange colored form³⁾), may be the trans isomer. The diffuse reflectance spectra of $[CoX(CN)(NH_3)_4]X$ (X=Cl, Br) support the theory that all these tetrammine complexes are trans isomers (see Table I).

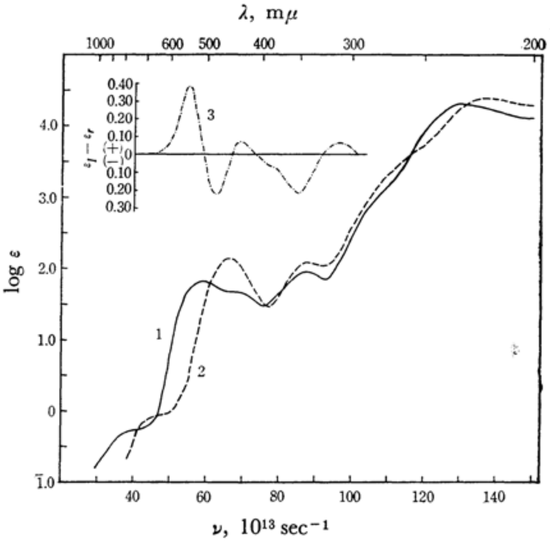

Fig. 2. Absorption and circular dichroism spectra of $[CoCl(CN)en_2]^+$.
1—— absorption curve of *cis*-$[CoCl(CN)en_2]Cl\cdot H_2O$ in aqueous solution.
2---- absorption curve of *trans*-$[CoCl(CN)en_2]Cl\cdot H_2O$ in 70% $HClO_4$.
3-·-· CD curve of $(-)_{546}$-*cis*-$[CoCl(CN)en_2]I$ in aqueous solution.

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

TABLE I. ABSORPTION DATA OF *cis*- AND *trans*-$[CoX(CN)N_4]X$ ν, $10^{13}sec^{-1}$, (log ε)

Complex	A Band	I Band	II Band	Charge transfer band $p_\pi(X)\rightarrow d_{z^2}$	Charge transfer band $p_\sigma(X)\rightarrow d_{z^2}$
cis-$[CoCl(CN)en_2]Cl$	ca. 40 ($\bar{1}$.74)	59.2 (1.82) ca. 69 sh	87.6 (1.95)	ca. 111 sh	130 (4.29)
trans-$[CoCl(CN)en_2]Cl$*	ca. 48 ($\bar{1}$.94)	66.2 (2.14)	88.6 (2.08)	ca. 106 sh	136 (4.37)
trans-$[CoCl(CN)(NH_3)_4]Cl$**	42	65.6	91.5	—	—
cis-$[CoBr(CN)en_2]Br$	37.6 (0.72)	58.5 (1.98) ca. 68 sh	—	ca. 97 sh	119 (4.29)
trans-$[CoBr(CN)en_2]Br$*	ca. 45 (0.74)	64.9 (2.11)	—	ca. 102 sh	124.5(4.44)
trans-$[CoBr(CN)(NH_3)_4]Br$**	42	64.5	—	—	—

* Measured in 70% $HClO_4$. ** Data of diffuse reflectance spectra.

TABLE II. CD DATA OF $(-)_{546}$-*cis*-$[CoX(CN)en_2]^+$ (X=Cl, Br)

Complex	Absorption band region	ν_{max} ($10^{13}sec^{-1}$)	$(\varepsilon_l-\varepsilon_r)_{max}$
$[CoCl(CN)en_2]I$	I	55.2 62.2 69.6	+0.38 −0.22 +0.07
	II	ca. 79.2 85.0 96.2	ca. −0.08 +0.02 +0.08
$[CoBr(CN)en_2]Br$	I	53.6 60.7 68.0	+0.38 −0.25 +0.10

TABLE III. PREDICTED SHIFTS OF THE FIRST AND SECOND BANDS DUE TO THE REPLACEMENT OF LIGANDS*

Electronic transition	$[CoN_6]$		*trans*-$[CoX_2N_4]$ X($\pm z$)		*cis*-$[CoX_2N_4]$ X($+x$, $+y$)		*trans*-$[CoXYN_4]$ X($+z$), Y($-z$)		*cis*-$[CoXYN_4]$ X($+x$), Y($+y$)		$[CoX_6]$	
$d_{xy}\rightarrow d_{x^2-y^2}$	0	T_{1g}	0	A_{2g}	$\frac{1}{2}\delta_\sigma(X)+\frac{1}{2}\delta_\pi(X)$	B_1	0	A_2	$\frac{1}{4}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)+\frac{1}{4}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$	A′	$\delta_\sigma(X)+\delta_\pi(X)$	T_{1g}
$d_{yz}\rightarrow d_{y^2-z^2}$	0		$\frac{1}{2}\delta_\sigma(X)+\frac{1}{2}\delta_\pi(X)$	E_g	$\frac{1}{4}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)$	A_2 & B_2	$\frac{1}{4}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)+\frac{1}{4}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$	E	$\frac{1}{4}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$	A″	$\delta_\sigma(X)+\delta_\pi(X)$	
$d_{zx}\rightarrow d_{z^2-x^2}$	0		$\frac{1}{2}\delta_\sigma(X)+\frac{1}{2}\delta_\pi(X)$		$\frac{1}{4}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)$		$\frac{1}{4}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)+\frac{1}{4}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$		$\frac{1}{4}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)$	A″	$\delta_\sigma(X)+\delta_\pi(X)$	
$d_{xy}\rightarrow d_{z^2}$	0	T_{2g}	$\frac{2}{3}\delta_\sigma(X)$	B_{2g}	$\frac{1}{6}\delta_\sigma(X)+\frac{1}{2}\delta_\pi(X($	A_1	$\frac{1}{3}\delta_\sigma(X)+\frac{1}{3}\delta_\sigma(Y)$	B_2	$\frac{1}{12}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)+\frac{1}{12}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$	A′	$\delta_\sigma(X)+\delta_\pi(X)$	T_{2g}
$d_{yz}\rightarrow d_{x^2}$	0		$\frac{1}{6}\delta_\sigma(X)+\frac{1}{2}\delta_\pi(X)$	E_g	$\frac{5}{12}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)$	A_2 & B_2	$\frac{1}{12}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)+\frac{1}{12}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$	E	$\frac{1}{3}\delta_\sigma(X)+\frac{1}{12}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$	A″	$\delta_\sigma(X)+\delta_\pi(X)$	
$d_{zx}\rightarrow d_{y^2}$	0		$\frac{1}{6}\delta_\sigma(X)+\frac{1}{2}\delta_\pi(X)$		$\frac{5}{12}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)$		$\frac{1}{12}\delta_\sigma(X)+\frac{1}{4}\delta_\pi(X)+\frac{1}{12}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(Y)$		$\frac{1}{12}\delta_\sigma(X)+\frac{1}{3}\delta_\sigma(Y)+\frac{1}{4}\delta_\pi(X)$	A″	$\delta_\sigma(X)+\delta_\pi(X)$	

* The parameters δ_σ and δ_π are defined as Yamatera's.

Table IV. The absorption and CD data (calculated and observed) of *cis*- and *trans*-$[CoXYen_2]^+$

ν, $10^{13}sec^{-1}$

X·Y	Band region	*trans*		*cis*			Parameters**
		Absorption max.	Calcd. value	Absorption max.	Circular dichroism max.	Calcd. value	
Cl(CN)	I band	66.2	$63.9(A_2)$ $64.0(E)$	59.2 69 sh	55.2 62.2 69.6	$55.8(A'')$ $64.0(A')$ $72.1(A'')$	$\delta(CN)=32.9$ $\delta(Cl)=-32.2$
	II band	88.6	$85.0(B_2)$ $90.4(E)$	87.6	79.2* 85.0* 96.2*	$79.2(A'')$ $85.0(A')$ $96.2(A'')$	$\delta_\sigma(CN)=36.5$ $\delta_\sigma(Cl)=-30.5$ $\delta_\pi(CN)=-8.4$ $\delta_\pi(Cl)=-7.4$
Br(CN)	I band	64.9	$62.5(E)$ $63.9(A_2)$	58.5 68 sh	53.6 60.7 68.0	$54.2(A'')$ $62.5(A')$ $72.1(A'')$	$\delta(CN)=32.9$ $\delta(Br)=-38.6$
2(CN)	I band			74.4	68b) 81b)	$72.2(A_2, B_2)$ $80.4(B_1)$	$\delta(CN)=32.9$
	II band			97.3	90b) 99b)	$90.3(B_1)$ $101.5(A_2, B_2)$	$\delta_\sigma(CN)=36.5$ $\delta_\pi(CN)=-8.4$
2Cl	I band	48.8*,a) 64.9*,a)	$48.8(E_g)$ $64.9(A_{2g})$	55.9	49.4c) 52.9c)	$47.8(B_1)$ $55.8(A_2, B_2)$	$\delta(Cl)=-32.2$

* From these values the parameters were estimated.

** The zero line of the parameter δ is settled to the band positions of $[Co\,en_3]^{3+}$: 63.9($\times 10^{13}sec^{-1}$) for the first band and 88.4($\times 10^{13}sec^{-1}$) for the second band.

a) Y. Shimura and R. Tsuchida, This Bulletin, **28**, 572 (1955).

b) A. J. McCaffery, S. F. Mason and B. J. Norman, *Chem. Commun.*, **1965**, 133.

c) J.-P. Mathieu, *Bull. soc. chim. France*, [5] **3**, 476 (1936).

The Ligand Field Absorption Bands.—The absorption curves of *cis*- and *trans*-$[CoCl\cdot(CN)en_2]^+$ are shown in Fig. 2 with the circular dichroism (CD) curve of $(-)_{546}$-*cis*-$[CoCl(CN)\cdot en_2]^+$. The absorption data of this and related complexes are summarized in Table I. The main difference between the absorption curves of the two geometrical isomers occurs in the first band region. That is, the first band of the trans isomer does not show any split, while that of the cis isomer seems to split into two components. This behavior is considerably different from that of the first bands of *cis*- and *trans*-$[CoCl_2en_2]^+$.9) Basolo et al. have already pointed out a similar fact about the absorption bands of *cis*- and *trans*-$[CoCl(NO_2)en_2]^+$.10)

The absorption behavior in the first bands of *cis*- and *trans*-$[CoCl(CN)en_2]^+$ can reasonably be elucidated on the basis of Yamatera's theoretical treatment.11) The expected patterns of the split and shift of the first and second bands can be seen in Table III, in which those of two geometrical isomers of the $[CoXYN_4]$ type are newly constructed. The *trans*-$[CoCl(CN)en_2]^+$ ion belongs to the approximate symmetry of C_{4v}, and the cis isomer, to the C_s symmetry. It may be expected that the first band of the trans isomer splits into two components, A′ and E, and the cis siomer, into three components, A′ and 2A′′. Now, the expected components of the first bands of the two geometrical isomers can be calculated by using some parameters, δ, which can be estimated from the observed values of the first bands of $[Co\,en_3]^{3+}$, $[Co(CN)_6]^{3-}$ and *trans*-$[CoCl_2en_2]^+$. The calculation are based on the following definitions:

$$\delta(X) = \delta_\sigma(X) + \delta_\pi(X)$$
$$\delta(Y) = \delta_\sigma(Y) + \delta_\pi(Y)$$

The results are shown in Table IV, along with the observed data. When the observed bands are considered in connection with the calculated values, it may be understood that the two expected components for the trans isomer are located so close to each other that the observed band does not split. The three expected components of the cis isomer correspond with the three CD bands of $(-)_{546}$-*cis*-$[CoCl(CN)en_2]^+$ in their first band region, as is shown in Table IV.

Thus, it can easily be explained that the superposition of the expected absorption components which correspond to the three CD bands gives the two-maxima in the absorption curve measured. The parameter values, $\delta(Cl)=-32.2$ and $\delta(CN)=32.9$, which were used here are also fit for the first band region (the absorption and CD bands12,13)) of *cis*-$[CoCl_2en_2]^+$ or *cis*-$[Co(CN)_2en_2]^+$.

As may be seen in Fig. 3 and Tables I, II and IV, the splitting patterns of the first band of the *cis*- and *trans*-$[CoBr(CN)en_2]^+$ closely resemble

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9) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **271**, 101 (1952).

10) F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

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

12) J.-P. Mathieu, *Bull. soc. chim. France*, [5] **3**, 476 (1936).

13) A. J. McCaffery, S. F. Mason and B. J. Norman, *Chem. Commun.*, **1965**, 133.

those of the corresponding isomers of $[CoCl(CN) \cdot en_2]^+$, and the expected components of the cis isomer also match the observed CD bands of $(-)_{546}$-*cis*-$[CoBr(CN)en_2]^+$.

In general, no distinct splitting has been observed in the second absorption band of the cobalt(III) complexes. The second band of *cis*-$[CoCl(CN) \cdot en_2]^+$ is no exception, as may be seen in Fig. 2. According to the theoretical consideration, however, the second band of *trans*-$[CoCl(CN)en_2]^+$ may be expected to split into two components (B_2 and E), and that of the cis isomer, into three components (A′ and 2A″). In fact, the CD curve of $(-)_{546}$-*cis*-$[CoCl(CN)en_2]^+$ shows three CD bands in its second band region, that is, a negative band (at about 79.2×10^{13}sec^{-1}), another negative band (85.0×10^{13}sec^{-1}) and a positive band, (96.2×10^{13} sec^{-1}) listing from the longer to the shorter wavelengths.

In the same way as in the first band region, the parameters, δ_σ and δ_π, in the second band of *cis*-$[CoCl(CN)en_2]^+$ can be estimated by using the observed values; the following parameter values can thus be reasonably obtained:

$$\delta_\sigma(CN)=36.5 \qquad \delta_\pi(CN)=-8.4$$

$$\delta_\sigma(Cl)=-30.5 \qquad \delta_\pi(Cl)=-7.4.$$

The two expected components in the second band of the trans isomer are also derived from these four parameters (Table IV). Recently, the CD curve of $(+)_{546}$-*cis*-$[Co(CN)_2en_2]^+$ has been reported by McCaffery et al.[13] in the 515—260 mμ region. The observed CD bands agree well with the values calculated from the present parameter values (Table IV). The CD spectrum of $(-)_{546}$-*cis*-$[CoBr(CN)en_2]^+$ in the second band region is overlapped by the charge transfer absorption band due to the coordinated bromo ligand, and so the evaluation of the parameter values, δ_σ(Br) and δ_π(Br), was impracticable.

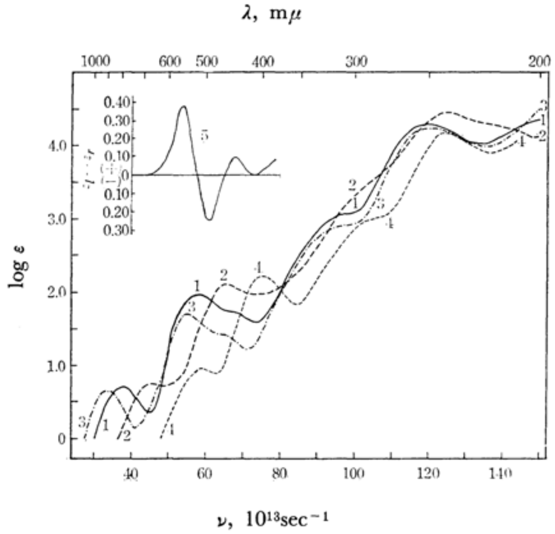

Fig. 3. Absorption and circular dichroism spectra of $[CoBr(CN)en_2]^+$ and the related complexes.

1—— absorption curve of *cis*-$[CoBr(CN)en_2]Br \cdot H_2O$ in aqueous solution.

2—— absorption curve of *trans*-$[CoBr)CN)en_2]$-$Br \cdot H_2O$ in 70% $HClO_4$.

3-·-·· absorption curve of *trans*-$[CoBr(NH_3)en_2]$-$Br_2 \cdot H_2O$ in aqueous solution.

4---- absorption curve of $K_3[CoBr(CN)_5]$ in aqueous solution.

5—— CD curve of $(-)_{546}$-*cis*-$[CoBr(CN)en_2]Br$ in aqueous solution.

The Charge Transfer Absorption Bands.— The present halogenocomplexes show two intense charge-transfer absorption bands due to the coordinated halogeno ligand X. The maxima of the shorter wavelength band, which was assigned to a $p_\sigma(X)$—d_{z^2} transfer,[14] are summarized in Table V, along with those of the related monohalogeno complexes.

From Figs. 2 and 3 and Table V, it may be seen that the bands of *cis*-$[CoX(CN)en_2]^+$ are located at longer wavelengths than those of the trans isomer. The band position of a cis isomer is about the same as that of the corresponding halogeno-pentammine complex; these are in the range from 130 to 133 ($\times10^{13}$sec^{-1}) for the chloro-complexes and from 117 to 120 ($\times10^{13}$sec^{-1}) for the bromo-complexes. On the other hand, the band position of *trans*-$[CoX(CN)en_2]^+$ is about the same as that of the corresponding halogeno-pentacyano complexes. These facts suggest that the position of a charge transfer band depends on which kind of ligand occupies the trans position on the halogeno ligand, and that it does not depend on the kind of ligand in cis positions.

TABLE V. THE CHARGE TRANSFER BAND MAXIMA ($p_\sigma(X) \rightarrow d_{z^2}$) OF MONOHALOGENO COMPLEX IONS

ν, 10^{13}sec^{-1}

Complex ion	X=Cl	X=Br	Ref.
cis-$[CoX(CN)en_2]^+$	130	119	
$[CoX(NH_3)_5]^{2+}$	132.2	118.4	a
cis-$[CoX(NH_3)en_2]^{2+}$	131	117	b
trans-$[CoX(NH_3)en_2]^{2+}$	133	120	b
trans-$[CoX(CN)en_2]^+$	136	125	
$[CoX(CN)_5]^{3-}$	135	124.5	c

a) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **266**, 49 (1951).

b) T. Yasui and Y. Shimura, This Bulletin, **36**, 1286 (1963).

c) J. Fujita, Private communication.

As far as the charge-transfer band is concerned. these complexes may be approximated as being a linear complex [X-Co-A], where A is NH_3, 1/2en or CN^-.

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[14] H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).