Studies of Mixed Cyano Cobalt(III) Complexes.
I. The Cyano-Diamine Series

By Kuwako OHKAWA, Junnosuke FUJITA and Yoichi SHIMURA

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Notwithstanding the strong tendency of cyanide to be coordinated to cobalt(III), a smaller number of mixed cyano cobalt(III) complexes have been known than of mixed ammine complexes. In particular, we know of extremely few cobalt(III) complexes which contain organic amines with cyanide.[1]

In the present paper, the preparation and the properties of mixed cyano complexes of a new type, $M[Co^{III}(CN)_4an]$ (an=en and tn),* which contains only one organic diamine molecule as a chelate ring, will be reported and discussed in comparison with those of the related bis(diamine) complexes, $[Co^{III}(CN)_2an_2]X$ (an=en, pn and tn).*

Experimental

Preparation. — *Potassium Tetracyanoethylenediaminecobalt(III) Monohydrate:* $K[Co(CN)_4en]\cdot H_2O$.— Into a 200 ml. aqueous solution of 10 g. of *t*-$[CoCl_2(NH_3)_2en]Cl\cdot 1/2\,H_2O$,[2] 15 g. of potassium thiosulfate dissolved in 200 ml. of water was stirred. The greenish brown solution obtained was then warmed on a water bath until it gave a brownish red solution. Then 10 g. of potassium cyanide dissolved in 100 ml. of water was stirred drop by drop into this solution. An orange yellow solution evolving ammonia gas was obtained. After this had been warmed on a water bath for a while, it was filtered. The filtrate was concentrated to a volume of about 200 ml. on a water bath; then 18.2 g. of barium chloride dihydrate dissolved in 100 ml. of hot water was added to remove the thiosulfate ions as a precipitate of barium thiosulfate. This precipitate was filtered, and the filtrate was evaporated further to a volume of about 50 ml. and then cooled in ice. The crude orange crystals thus formed were filtered, washed with methanol, and dried in air.

The product of this was dissolved in a minimum amount of water, and about one-fourth the volume of methanol was added. After the mixture had cooled at 0°C for half an hour, the precipitate was removed by filtration. Methanol was added to the filtrate, and the mixture was cooled in ice. The pure

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

* en=ethylenediamine $NH_2CH_2CH_2NH_2$
tn=trimethylenediamine $NH_2CH_2CH_2CH_2NH_2$
pn=propylenediamine $NH_2CH_2CH(CH_3)NH_2$

[2] J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

product obtained by repeating the procedure three times was orange-colored crystalline plates which were effloresced on exposure to the air. The crystals freshly dried were analyzed for water of crystallization. The analyses for the other components were performed by using samples dehydrated in vacuo at 80°C.

Found: C, 26.96; H, 3.28; N, 31.10. Calcd. for $C_6H_8N_6KCo=K[Co(CN)_4en]$: C, 27.48; H, 3.18; N, 32.05%.

Found: H_2O, 6.42. Calcd. for $K[Co(CN)_4en]\cdot H_2O$: H_2O, 6.42%.

Sodium Tetracyanoethylenediaminecobalt(III) 3.5 Hydrate: $Na[Co(CN)_4en]\cdot 3.5H_2O$.— This was obtained by almost the same method as the potassium salt described above, using sodium thiosulfate and sodium cyanide.

The recrystallized orange crystals were soluble in methanol; therefore, ethanol was used for precipitation from the aqueous solution after the impurities had been removed by adding methanol.

Found: C, 28.07; H, 3.47; N, 33.29. Calcd. for $C_6H_8N_6NaCo=Na[Co(CN)_4en]$: C, 29.28; H, 3.28; N, 34.15%.

Found: H_2O, 20.39. Calcd. for $Na[Co(CN)_4en]\cdot 3.5H_2O$: H_2O, 20.39%.

Dicyanobis(propylenediamine)cobalt(III) Thiosulfate Monohydrate; $[Co(CN)_2pn_2]_2S_2O_3\cdot H_2O$.—This complex was prepared by almost the same method as that given by Rây and Sarma[1] for the preparation of $[Co(CN)_2en_2]_2S_2O_8\cdot H_2O$.

Into 150 ml. of an aqueous solution of 12.6 g. of *t*-$[CoCl_2pn_2]ClO_4$,[3] 16.6 g. of $Na_2S_2O_3\cdot 5H_2O$ dissolved in 150 ml. of water was stirred. After the green color of the solution had turned to brownish-violet, a 1 : 2 mixture of methanol and ethanol was added. When the mixture had cooled about 9 g. of bright brownish-violet crystals were formed. These were filtered, washed with methanol, and dried in air. These crystals (perhaps $Na[Co(S_2O_3)_2pn_2]$) were then dissolved in 150 ml. of water, and into the solution 13.2 g. of potassium cyanide dissolved in 150 ml. of water was stirred. The brownish yellow solution obtained was evaporated on a water bath until yellow crystals appeared. These crystals were filtered and recrystallized from hot water or from the aqueous solution by adding methanol.

Found: C, 30.19; H, 6.56; N, 26.21. Calcd. for $C_{16}H_{40}N_{12}O_3S_2Co_2=[Co(CN)_2pn_2]_2S_2O_3$: C, 30.47; H, 6.39; N, 26.66%.

Found: H_2O, 3.41. Calcd. for $[Co(CN)_2pn_2]_2S_2O_3\cdot H_2O$: H_2O, 3.39%.

Dicyanobis(trimethylenediamine)cobalt(III) Thiosulfate: $[Co(CN)_2tn_2]_2S_2O_3$.—To 100 ml. of an aqueous solution of 3.2 g. of *t*-$[CoCl_2tn_2]Cl$,[4] 5 g. of $Na_2S_2O_3\cdot 5H_2O$ dissolved in 50 ml. of water was added with continuous stirring, and then after ten minutes 50 ml. of an aqueous solution of 1 g. of potassium cyanide was added. The solution was concentrated on a water bath until crude dark yellow crystals began to appear. The crystals recrystallized from hot water were yellow and anhydrous.

Found: C, 30.15; H, 6.41; N, 26.99. Calcd. for $C_{16}H_{40}N_{12}O_3S_2Co_2=[Co(CN)_2tn_2]_2S_2O_3$: C, 30.47; H, 6.39; N, 26.66%.

Trinitroamminetrimethylenediaminecobalt(III): $[Co(NO_2)_3(NH_3)tn]$.—A mixture containing 10 g. of *m*-$[Co(NO_2)_3(NH_3)_3]$ and 30 ml. of a 10% aqueous solution of trimethylenediamine was heated gently on a free flame. After the evolution of ammonia gas had ended, the unreacted materials were separated by filtration. The filtrate was concentrated on a water bath until brownish-red needle crystals were formed. The crude crystals were then recrystallized from hot water containing a few drops of acetic acid.

Found: C, 12.73; H, 4.70; N, 30.83. Calcd. for $C_3H_{13}N_6O_6Co=[Co(NO_2)_3(NH_3)tn]$: C, 12.51; H, 4.55; N, 29.17%.

Dichloroaquoamminetrimethylenediaminecobalt(III) Chloride Monohydrate: $[CoCl_2(OH_2)(NH_3)tn]Cl\cdot H_2O$. Finely powdered $[Co(NO_2)_3(NH_3)tn]$ was dissolved in concentrated hydrochloric acid by warming it on a water bath. After the evolution of gas had ceased, a dark green solution was obtained; this was then cooled in ice. The dark green crystals thus obtained were filtered, washed with alcohol, and dried in air.

Found: C, 12.61; H, 6.19; N, 13.98. Calcd. for $C_3H_{15}N_3OCl_3Co\cdot H_2O=[CoCl_2(OH_2)(NH_3)tn]Cl\cdot H_2O$: C, 12.32; H, 5.86; N, 14.37%.

Barium Tetracyanotrimethylenediaminecobalt(III) Tetrahydrate: $Ba[Co(CN)_4tn]_2\cdot 4H_2O$.—To 200 ml. of an aqueous solution of 10 g. of $[CoCl_2(OH_2)(NH_3)tn]Cl\cdot H_2O$, 18.1 g. of $Na_2S_2O_3\cdot 5H_2O$ dissolved in 100 ml. of water was added, and then 7.2 g. of sodium cyanide in 150 ml. of water was stirred in drop by drop. The brownish yellow solution thus obtained was evaporated on a water bath to a volume of about 100 ml., and then 15 g. of $BaCl_2\cdot 2H_2O$ dissolved in 150 ml. of water was added and the mixture was cooled. After the filtration of barium thiosulfate, the mother liquor was concentrated further until crystals began to appear. These orange yellow crystals were then filtered and recrystallized from hot water.

In this preparation, an excess of barium chloride was used in order to convert potassium salt into the less soluble barium salt. The potassium salt which was prepared by the same method as the ethylenediamine complex was much contaminated by the barium salt.

Found: C, 24.43; H, 4.26; N, 24.91; H_2O, 10.32. Calcd. for $C_{14}H_{20}N_{12}BaCo_2\cdot 4H_2O=Ba[Co(CN)_4tn]_2\cdot 4H_2O$: C, 24.60; H, 4.13; N, 24.59; H_2O, 10.54%.

Absorption Measurements.—A Beckman DU and a Shimadzu QR-50 spectrophotometer were used to obtain visible and ultraviolet absorption spectra in the range from 30 to $150\times 10^{13}\,sec^{-1}$. All the complexes obeyed Beer's law in aqueous solutions in the $1-10^{-5}$ mol./l. range at room temperature. A Hitachi EPI-2G infrared spectrophotometer equipped with a potassium bromide foreprism and a grating double monochrometer was used to obtain infrared spectra in both the Nujol mull and the KBr disk methods.

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[3] A. Werner and A. Fröhlich, *Ber.*, **40**, 2228 (1907).

[4] A. Werner and G. Lindenberg, *Ann.*, **386**, 271 (1912).

Results and Discussion

The Method of Preparation.—In general, it has been recognized that the cobalt(III) complexes which coordinate one ethylenediamine molecule besides four unidentate ligands are rather difficult to prepare. The sulfitocomplex ion, $[Co(SO_3)_2(NH_3)_2en]^-$,2) which is prepared5) from $[Co(SO_3)_2(NH_3)_4]^-$ and ethylenediamine, is known as a starting material for the preparation of the complexes of this type.6) The trans isomer of $[CoCl_2(NH_3)_2en]Cl$2) which was used for the present preparation of tetracyanoethylenediaminecobalt(III) complex was prepared by warming this sulfito complex with hydrochloric acid, but the yield was rather low. The direct reaction of $[CoCl_2(NH_3)_2en]^+$ with cyanide gave no desired complex unless the chloro complex was transformed to the thiosulfato complex $[Co(S_2O_3)_2(NH_3)_2en]^-$. In the present work, the latter complex was not separated. Rây and Sarma1) have prepared the dicyano complex $[Co(CN)_2en_2]^+$ from the bis(thiosulfato)complex $[Co(S_2O_3)_2en_2]^-$,7) while Chan et al.8) have reported that no mixed cyano complex was produced by the direct reaction of $[CoCl_2en_2]^+$ with cyanide in an aqueous solution.

An attempt to isolate a pure tetracyanopropylenediamine complex failed because of

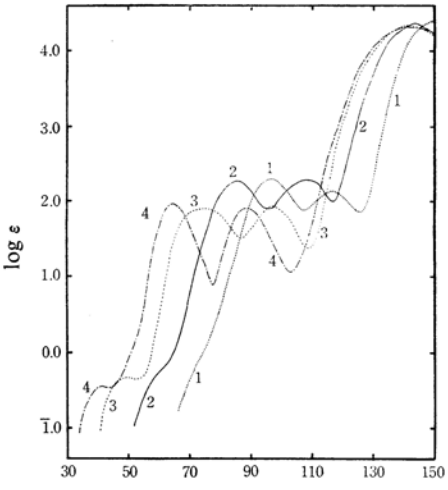

Fig. 1. Absorption curves of $[Co(CN)_{6-2x}(en)_x]^{2x-3}$ series.
1 : $[Co(CN)_6]^{3-}$
2 : $[Co(CN)_4en]^-$
3 : *cis*-$[Co(CN)_2en_2]^+$
4 : $[Co\ en_3]^{3+}$

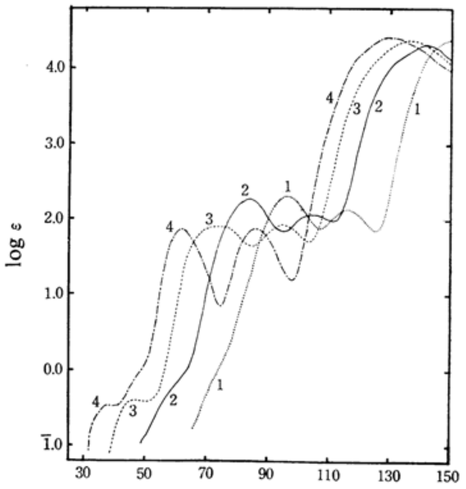

Fig. 2. Absorption curves of $[Co(CN)_{6-2x}(tn)_x]^{2x-3}$ series.
1 : $[Co(CN)_6]^{3-}$
2 : $[Co(CN)_4tn]^-$
3 : *cis*-$[Co(CN)_2tn_2]^+$ (thiosulfate)
4 : $[Co\ tn_3]^{3+}$

TABLE I. ABSORPTION DATA OF $[Co^{III}(CN)_{6-2x}(an)_x]^{2x-3}$ SERIES ν_{max} 10^{13} sec^{-1}(log ε)

Complex	Spin-forbidden band		Spin-allowed band		Allowed band
	A	B	I	II	
$K_3[Co(CN)_6]$	ca. 75($\bar{1}$.9)	—	96.8(2.29)	116.8(2.12)	150 (4.28)
$K[Co(CN)en]\cdot H_2O$	ca. 61($\bar{1}$.8)	—	85.3(2.26)	108.4(2.28)	143.4(4.34)
$Ba_{1/2}[Co(CN)_4tn]\cdot 2H_2H$	ca. 61($\bar{1}$.8)	—	83.7(2.26)	105.1(2.06)	141.9(4.32)
cis-$[Co(CN)_2en_2]Cl$	49.7 ($\bar{1}$.67)	—	74.2(1.91)	97.1(1.93)	142.1(4.32)
cis-$[Co(CN)_2pn_2]_{1/2}(S_2O_3)_{1/2}\cdot 1/2H_2O$	50.6 ($\bar{1}$.73)	—	74.5(1.90)	97.4(1.94)	140.8(4.38)
cis-$[Co(CN)_2tn_2]_{1/2}(S_2O_3)_{1/2}$	47.2 ($\bar{1}$.60)	—	73.6(1.89)	95.6(1.97)	137.0(4.38)
$[Co\ en_3](ClO_4)_3$	41.5 ($\bar{1}$.52)	ca. 52($\bar{1}$.8)	63.9(1.94)	88.4(1.90)	141.8(4.32)
$[Co\ pn_3]Cl_3$	41.6 ($\bar{1}$.65)	ca. 52(0.0)	64.5(1.92)	88.8(1.88)	140.7(4.34)
$[Co\ tn_3](ClO_4)_3$	38.0 ($\bar{1}$.54)	ca. 50(0.0)	61.7(1.87)	86.0(1.88)	130.6(4.41)

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

6) Y. Shimura, This Bulletin, **31**, 311 (1958).

7) P. R. Rây and S. N. Maulik, *J. Indian Chem. Soc.*, **10**, 655 (1933).

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

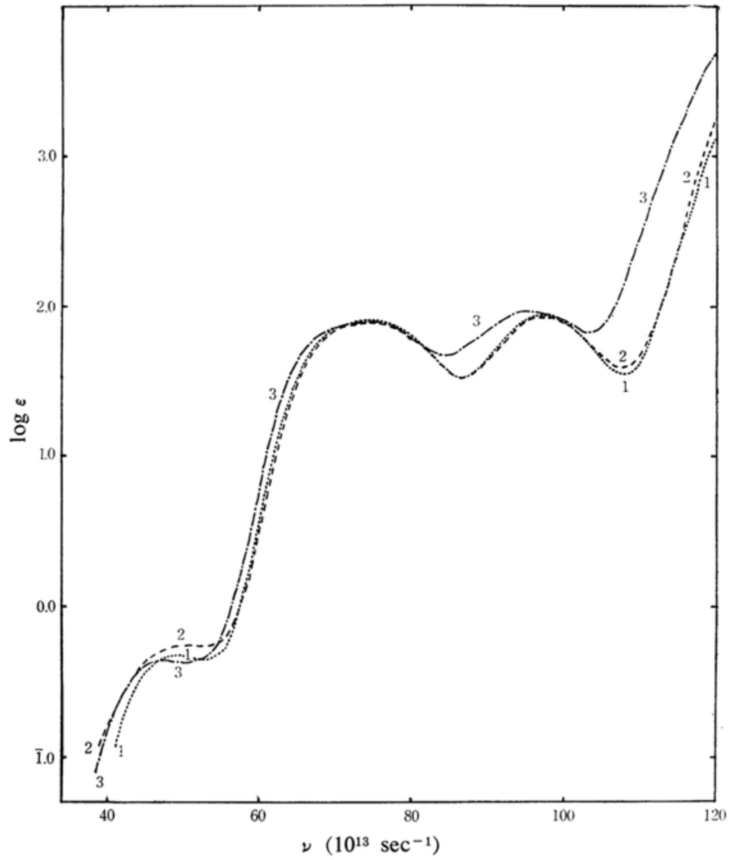

Fig. 3. Absorption curves of *cis*-$[Co(CN)_2an_2]^+$ complexes (thiosulfate).
1: $[Co(CN)_2en_2]^+$ 2: $[Co(CN)_2pn_2]^+$ 3: $[Co(CN)_2tn_2]^+$

the extreme solubility of the complex.

For the preparation of the tetracyanotrimethylenediamine complex, a dark green complex, $[CoCl_2(OH_2)(NH_3)tn]^+$, was employed instead of $[CoCl_2(NH_3)_2tn]^+$, since the purification of the latter was hard.

The method for the preparation of dicyanobis(trimethylenediamine) and dicyanobis(propylenediamine) complexes was a modification of the method of Rây and Sarma described above for the corresponding ethylenediamine complex.

Visible and Ultraviolet Absorption Spectra.—Table I lists the numerical data of the absorption maxima of the complexes measured. In the table, the first four absorption bands are assigned to ligand field bands. The last strong band could be attributed to a characteristic absorption caused by the ligands, cyanides and diamines.

In a previous paper,[9] we have discussed the experimental relationships between the ligand field bands of cobalt(III) complexes, which also fit the complexes measured in the present work.

Figure 1 shows that the absorption frequencies of the first and second spin-allowed bands of the cyano-ethylenediamine series shift to shorter wavelengths in proportion to the number of ligand cyanides, as has been observed in the oxalato-ammine series.[10] The same relation is seen in the cyano-trimethylenediamine series. The absorption intensities of these cyano complexes, on the other hand, exhibit no such regular relation. The A bands of the weak spin-forbidden absorptions are observed on the longer wavelength side of the first spin-allowed bands. All the B bands of cyano complexes are hidden by the feet of the strong first bands.

Theoretically, two geometrical isomers, cis and trans, exist in the dicyanobis(ethylenediamine)cobalt(III) ion, but so far only one species has been obtained. Chan et al.[8] determined through the optical resolution that

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[9] J. Fujita and Y. Shimura, This Bulletin, **36**, 1281 (1963).

[10] Y. Shimura and R. Tsuchida, ibid., **28**, 572 (1955).

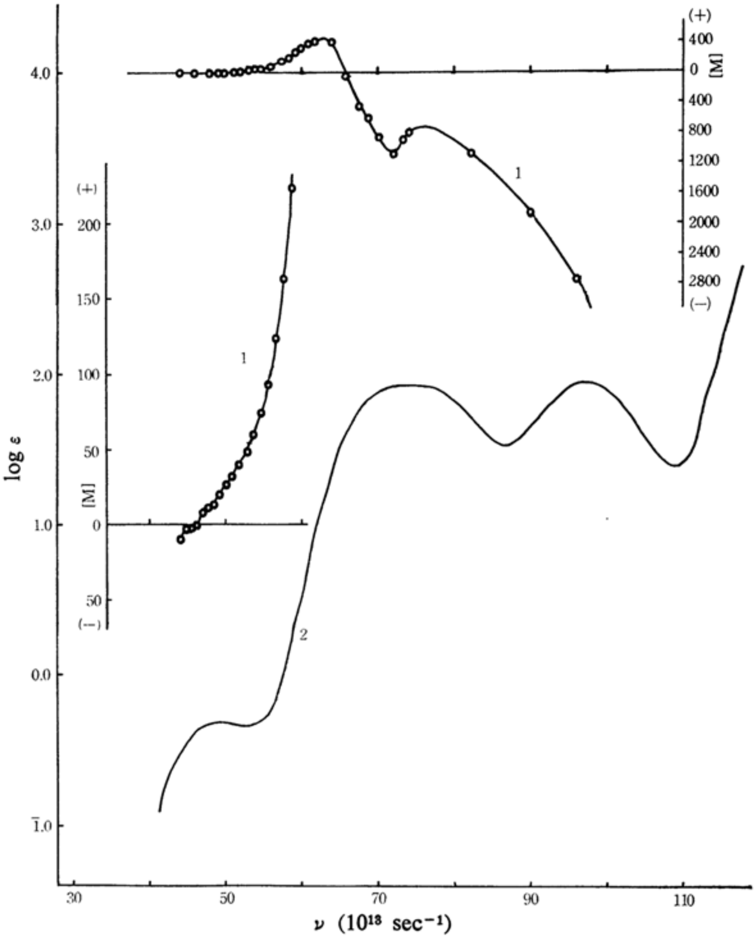

Fig. 4. Rotatory dispersion and absorption curves of $(+)_{546}$-*cis*-$[Co(CN)_2en_2]^+$.
1 Rotatory dispersion curves 2 Absorption curve

this complex takes the cis configuration. The absorption spectra of the dicyanobis(propylenediamine) and dicyanobis(trimethylenediamine) complexes closely resemble the ethylenediamine complex with the cis configuration. It may be concluded, therefore, that all three of the dicyano complexes prepared in this work correspond to the cis isomers.

The Rotatory Dispersion of $[Co(CN)_2en_2]^+$. —As has been described above, Chan et al.(8) have resolved the dicyanobis(ethylenediamine) cobalt(III) complex into its optically-active forms through its α-bromocamphor-π-sulfonate. In the present study, we have determined the rotatory dispersion of the $(+)_{546}$-isomer (Fig. 4). It exhibits a positive Cotton effect in the region of the first spin-allowed absorption band. The amplitude of this partial dispersion is as large as those of the same type of cobalt(III) complexes, such as $[CoCl_2en_2]^+$,(11) and $[Co(NO_2)_2en_2]^+$.(12)

It is interesting to note that no remarkable Cotton effect is shown in the region of the A spin-forbidden band of the complex. This might be because the Cotton effects are too weak to be measured, or because this small partial dispersion is hidden by the foot of the dispersion of the first spin-allowed absorption band. Mason(13) reported a very weak circular dichroism band ($\varepsilon_l - \varepsilon_r = +0.008$) in the region of the A spin-forbidden band of the $(+)_D$-$[Co\ en_3]^{3+}$ ion. Kling and Woldbye(14) have found several weak Cotton effects in the spin-forbidden bands of the tris(ethylenediamine) chromium (III) and related complexes.

Infrared Spectra.—Figure 5 shows the infrared absorption spectra of the C≡N stretching region for the cyano-diamine complexes. The

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11) J. Hidaka, S. Yamada and R. Tsuchida, ibid., **31**, 921 (1958).

12) J. Hidaka, Y. Shimura and R. Tsuchida, ibid., **33**, 847 (1960).

13) S. F. Mason, *Quart. Rev.*, **17**, 20 (1963).

14) O. Kling and F. Woldbye, *Acta Chem. Scand.*, **15**, 704 (1961).

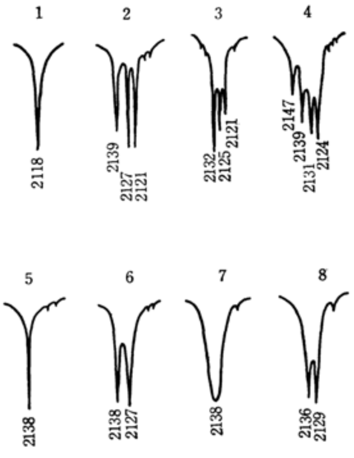

Fig. 5. Infrared absorption spectra in the region of $\nu(C\equiv N)$.
1 : $K_3[Co(CN)_6]$
2 : $K[Co(CN)_4en]$
3 : $Na[Co(CN)_4en]\cdot 3.5H_2O$
4 : $Ba[Co(CN)_4tn]_2\cdot 4H_2O$
5 : racemic *cis*-$[Co(CN)_2en_2]Cl$
6 : optically active *cis*-$[Co(CN)_2en_2]Cl\cdot H_2O$
7 : *cis*-$[Co(CN)_2pn_2]_2S_2O_3\cdot H_2O$
8 : *cis*-$[Co(CN)_2tn_2]_2S_2O_3$

complex ion $[Co(CN)_6]^{3-}$ which has an O_h symmetry exhibits only one triply-degenerate $C\equiv N$ stretching band,[15] while the mixed-diamine complex shows a group of $C\equiv N$ stretching bands split by the lowering of the symmetry. The complex ion $[Co(CN)_4en]^-$ exhibits three $C\equiv N$ stretching bands, although the theoretical number of this stretching band is four. The complex ion $[Co(CN)_4tn]^-$ distinctly shows four peaks. The optically-active dicyanobis(ethylenediamine) and racemic dicyanobis(trimethylenediamine) complexes, whose approximate symmetries are C_{2v}, exhibit two peaks, while the racemic dicyanobis(ethylenediamine) and dicyanobis(propylenediamine) complexes show no splitting. It is curious that there is a marked difference in the $C\equiv N$ stretching band between the resolved and the racemic bis(ethylenediamine) complexes.

It is interesting to note that the magnitude of the splitting of the $C\equiv N$ stretching bands in these cyanodiamine complexes is 1/10 those of the $C=O$ stretching bands in several carbonyl complexes.[16] This suggests that the character of the bonding between the cyanide and the cobalt(III) ion in the former complexes would be considerably weak compared with that between the carbon monoxide and the metal atom in the latter ones.

Summary

Several new mixed cyano-diamine complexes, $M[Co(CN)_4en]\cdot xH_2O$ ($M=K, x=1$; $M=Na, x=3.5$), $Ba[Co(CN)_4tn]_2\cdot 4H_2O$, $[Co(CN)_2pn_2]_2S_2O_3\cdot H_2O$ and $[Co(CN)_2tn_2]_2S_2O_3$, have been prepared, and their infrared, visible and ultraviolet absorption spectra have been determined. From these spectral results, it has been concluded that the two dicyano complexes are cis isomers.

No remarkable Cotton effect has been observed in the region of the spin-forbidden band of the *cis*-$[Co(CN)_2en_2]^+$.

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Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

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[15] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 101 (1962).

[16] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).