CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE, KANAZAWA UNIVERSITY, KANAZAWA, JAPAN

# Preparation and Properties of Cobalt(III) Complexes of the Cyanoammine and Cyanodiamine Series

BY KAZUO KONYA, HIROAKI NISHIKAWA, AND MURAJI SHIBATA

*Received November 3, 1967*

The four new complexes of the mixed cyanoammine and -diamine series *cis*- and *trans*-$Co(CN)_2(NH_3)_4^+$, *trans*-$Co(CN)_2(en)_2^+$, and *mer*-$Co(CN)_3$dien were prepared and characterized by visible and ultraviolet absorption spectra as well as infrared spectra. In addition, the known complexes, *mer*-$Co(CN)_3(NH_3)_3$, *cis*-$Co(CN)_2(en)_2^+$, and $Co\ CN(NH_3)_5^{2+}$ have also been prepared. All of these complexes were synthesized by the reaction of potassium cyanide with $Co(NH_3)_6^{3+}$, $Co(en)_3^{3+}$, or $Co(dien)_2^{3+}$ in the presence of activated charcoal at low temperature (0–5°).

## Introduction

Several studies have been made on mixed cyanodiamine (or -ammine) complexes of cobalt(III).[1-5] In these studies, it was recognized that the direct synthesis of these complexes from their components and also the indirect synthesis by the reaction between the luteo or praseo type of complex and cyanide in aqueous solution were usually unsuccessful. A few complexes, however, have been prepared by the use of a particular method. The dicyano[1] and tetracyano[5] complexes *cis*-$Co(CN)_2(en)_2^+$ and $Co(CN)_4(en)^-$ were synthesized from the sulfur-coordinated complexes $Co(S_2O_3)_2(en)_2^-$ and $Co(S_2O_3)_2(NH_3)_2(en)^-$, respectively. The monocyano and tricyano complexes $CoCN(NH_3)_5^{2+}$ and *mer*-$Co(CN)_3(NH_3)_3$ were synthesized with a solution of potassium tricarbonatocobaltate(III),[3] and the former was also obtained by the use of the cyanosulfito complex $CoCNSO_3(NH_3)_4$.[4] Recently, the dicyano complex *cis*-$Co(CN)_2(en)_2^+$ was also obtained from the reaction of *trans*-$CoCl_2(en)_2^+$ and a cyanide in dimethyl sulfoxide.[6]

In the present work, we have found that the reaction of a luteo type of complex with cyanide in a cold aqueous solution gives mixed cyano complexes in the presence of activated charcoal. This paper deals with this new reaction for the preparation of the complexes belonging to the cyanoammine or cyanodiamine series.

## Experimental Section

**Preparation.** (1) ***cis*-Dicyanotetraamminecobalt(III) Chloride Monohydrate, *trans*-Dicyanotetraamminecobalt(III) Chloride, and *mer*-Tricyanotriamminecobalt(III): *cis*-$[Co(CN)_2(NH_3)_4]Cl\cdot H_2O$, *trans*-$[Co(CN)_2(NH_3)_4]Cl$, and *mer*-$Co(CN)_3(NH_3)_3$.**—To a cold solution (*ca.* 0°) of 17 g (0.05 mol) of $[Co(NH_3)_6](O_2CCH_3)_3$ in 200 ml of water, 10 g (0.15 mol) of potassium cyanide in 50 ml of cold water was added dropwise with stirring. Two grams of activated charcoal was added to the above solution, and the mixture was kept in a refrigerator for 1 week without stirring (or 3–4 days with stirring). After that, the reaction mixture was filtered, and the filtrate was diluted to 600 ml with water. About 150 ml of this solution was poured into a column (30 × 300 mm) of a cation-exchange resin (Dowex 50W-X8, 200–400 mesh) in the lithium form. The column was washed with a suitable amount of water, whereby the tricyano complex species $Co(CN)_3(NH_3)_3$ was swept away in the effluent. This effluent, therefore, was stored for the recovery of the complex. The elution was started with a 0.2 *M* LiCl solution at the rate of 0.2 ml/min. During this process a colored band at the top of the column separated into three bands. The first eluted band, an orange one, was confirmed to be the *trans*-$Co(CN)_2(NH_3)_4^+$ isomer by spectroscopic measurements. The second band, a yellow one, was the *cis* isomer. The third band which remained at the top of the column was a mixture of the monocyano $CoCN(NH_3)_5^{2+}$ and the unreacted $Co(NH_3)_6^{3+}$ species. The former was eluted by a 2 *M* LiCl solution, and the latter, by a 6 *M* LiCl solution.

The above-mentioned column method was applied to every 150 ml of the filtrate. All of the eluted solutions for each of the first and second bands were collected and concentrated under reduced pressure at room temperature. The *trans* and *cis* isomers were obtained when the concentrates were cooled in a refrigerator; yields, 350 mg for the *trans* and 2.5 g for the *cis* isomer.

*Anal.* Calcd for $C_2H_{12}N_6ClCo$ = *trans*-$[Co(CN)_2(NH_3)_4]Cl$: C, 11.20; H, 5.64; N, 39.17. Found: C, 11.27; H, 5.79; N, 39.07.

*Anal.* Calcd for $C_2H_{12}N_6ClCo\cdot H_2O$ = *cis*-$[Co(CN)_2(NH_3)_4]Cl\cdot H_2O$: C, 10.33; H, 6.08; N, 36.14. Found: C, 10.56; H, 5.92; N, 35.85.

On the other hand, the effluent obtained at the washing stage was poured into a column (30 × 300 mm) of an anion exchanger (Amberlite IRA 410) in the chloride form. A suitable amount of water was passed through the column in order to recover the complex in the effluent. The effluent was treated by the procedures described above for the recovery of dicyano complexes. Recrystallization was repeated several times from water; yield, about 2 g.

*Anal.* Calcd for $C_3H_9N_6Co$ = *mer*-$Co(CN)_3(NH_3)_3$: C, 19.16; H, 4.82; N, 44.68. Found: C, 19.08; H, 4.78; N, 44.54.

(2) ***trans*-Dicyanobis(ethylenediamine)cobalt(III) Chloride and *cis*-Dicyanobis(ethylenediamine)cobalt(III) Chloride: *trans*-$[Co(CN)_2(en)_2]Cl$ and *cis*-$[Co(CN)_2(en)_2]Cl$.**—To a cold solution (*ca.* 0°) of 17 g (0.05 mol) of $[Co(en)_3]Cl_3$ in 200 ml of water, 10 g (0.15 mol) of potassium cyanide in 50 ml of cold water was added dropwise with stirring. Activated charcoal (2 g) was then added, and the whole was kept in a refrigerator for 1 week (or for 3–4 days with stirring). The resulting solution was then treated as described in the case of the dicyanotetraammine complexes. The *trans* isomer was obtained when the concentrate from the first eluted solution was cooled in a refrigerator, while the *cis* isomer was precipitated by the addition of ethanol to the concentrate from the second solution. Total yields were 0.4 and 3 g for the *trans* and the *cis* isomer, respectively.

*Anal.* Calcd for $C_4H_{16}N_4ClCo$ = $[Co(CN)_2(en)_2]Cl$: C,

---

[1] P. Ray and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951).
[2] N. R. S. Gupta, *Z. Anorg. Allgem. Chem.*, **326**, 108 (1963).
[3] M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).
[4] H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964).
[5] K. Ohkawa, J. Fujita, and Y. Shimura, *Bull. Chem. Soc. Japan*, **38**, 66 (1965).
[6] H. Yoneda, T. Baba, and M. Muto, *ibid.*, **40**, 1736 (1967).

27.03; H, 6.05; N, 31.48. Found (for *trans*): C, 27.10; H, 6.21; N, 31.23. Found (for *cis*): C, 27.26; H, 5.76; N, 31.98.

(3) *mer*-Tricyanodiethylenetriaminecobalt(III): *mer*-**Co(CN)$_3$dien.**—To a cold solution of 17 g (0.05 mol) of [Co(dien)$_2$]Cl$_3$[7] in 200 ml of water, 13 g (0.2 mol) of potassium cyanide in 50 ml of cold water was added dropwise with stirring. Activated charcoal (2 g) was then added, and the mixture was kept in a refrigerator for 3–4 days with stirring. Thereafter, the reaction mixture was treated with the procedure employed in the case of *mer*-Co(CN)$_3$(NH$_3$)$_3$; yield, 1.5 g.

*Anal.* Calcd for $C_7H_{13}N_6Co$ = Co(CN)$_3$dien: C, 35.01; H, 5.46; N, 35.00. Found: C, 35.32; H, 5.30; N, 35.31.

(4) **Others.**—The *trans* and *cis* isomers of the $Co(CN)_2(NH_3)_4^+$ complex were also synthesized as perchlorates by the use of 0.2 *M* NaClO$_4$ instead of 0.2 *M* LiCl in the experiment of preparation 1. The *trans* isomer was regarded as hemihydrate, and the *cis* isomer, as anhydride.

It was found that a little decrease in the amount of potassium cyanide and the existence of a free ammonia in the reaction system of preparation 1 gave the monocyano species, $CoCN(NH_3)_5^{2+}$, dominantly. A 6% aqueous ammonia solution (250 ml) and 6.5 g (0.1 mol) of KCN were used instead of the cold water (200 ml) and 10 g of KCN in preparation 1. Elution was carried out with a 0.5 *M* NaCl solution for the removal of the by-products, and then continued with a 2 *M* NaClO$_4$ solution for the object. The analytical results of the isolated compound showed small discrepancies, but the electronic and infrared spectra showed results identical with those reported previously;[4] yield, 3.5 g.

*Anal.* Calcd for $CH_{15}N_6Cl_2O_8Co$ = [Co(CN)(NH$_3$)$_5$](ClO$_4$)$_2$: C, 3.26; H, 4.10; N, 22.78. Found: C, 3.93; H, 4.02; N, 23.14.

The reaction of cyanide with (+)D-[Co(en)$_3$]Cl$_3$ was also carried out in the same way as described in preparation 2.

**Measurements.**—The absorption spectra of the complexes in aqueous solution, in the visible and ultraviolet region, were obtained with a Hitachi EPU-2A spectrophotometer. Infrared spectra were determined as KBr disks or Nujol mulls using a Japan Spectroscopic Co. DS 301 infrared spectrometer (4000–650 cm$^{-1}$) and a Hitachi EPI-L spectrophotometer (700–250 cm$^{-1}$).

## Results and Discussion

**The Method of Preparation.**—The number of known complexes belonging to the cyanoammine series was few because of the lack of a suitable preparative method. Nagarajaiah, *et al.*,[8] examined the interaction of each of the ammine complexes such as $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$, and $CoCl(NH_3)_5^{2+}$ with excess of cyanide in aqueous solution at room temperature, and they deduced the formation of pentacyano complex species in these three cases. The attempt by Block[9] to prepare some of the cyanoammine complexes by the action of cyanide on the $Co(NH_3)_6^{3+}$ complex did not prove successful, but led to the formation of the insoluble [Co(NH$_3$)$_6$][Co(CN)$_6$] complex. Chan and Tobe[10] have reported that no mixed cyano complex was prepared by the reaction between the complex $CoCl_2(en)_2^+$ and cyanide in aqueous solution.

In this study we have prepared several complexes belonging to the cyanoammine and cyanodiamine series. Of those complexes, four—*cis*- and *trans*-$Co(CN)_2(NH_3)_4^+$, *trans*-$Co(CN)_2(en)_2^+$, and *mer*-Co(CN)$_3$dien—are new compounds. Recently, we learned that Yoneda, *et al.*,[11] have also synthesized the complex *trans*-$Co(CN)_2(en)_2^+$ in a nonaqueous solution. The important point in our method is the use of activated charcoal at low temperature (0–5°). Another feature of this method is that the reaction gives some of the possible mixed complexes at the same time and that ion-exchange chromatography was used for the separation of these complexes. The reaction of cyanide with optically active tris(ethylenediamine)cobalt(III) chloride did not give any optically active cyanoethylenediamine complexes, but produced all of the possible geometrical isomers. (Evidence for the existence of the $Co(CN)_4(en)^-$ species has been confirmed by the measurement of the absorption spectrum, but the isolation of the complex is under way.) The yield of the *trans* isomer of the Co(C)$_2$(N)$_4$-type complex was much less than that of the corresponding *cis* isomer. This fact may be the reason that the *trans* isomer has been missed in spite of earlier efforts to obtain it.[5,10]

**Visible and Ultraviolet Absorption Spectra.**—The absorption curves of the cyanoammine and the cyanodiamine complexes are shown in Figures 1 and 2, respectively. The spectra of *mer*-Co(CN)$_3$(NH$_3$)$_3$, $CoCN(NH_3)_5^{2+}$, and *cis*-$Co(CN)_2(en)_2^+$ showed results identical with those reported previously.[3-5] Since the spectrum of the complex Co(CN)$_3$dien is similar to that of the known *mer*-Co(CN)$_3$(NH$_3$)$_3$ complex, the same configuration (*mer*) is assumed for the diethylenetriamine complex (Figures 1 and 3).

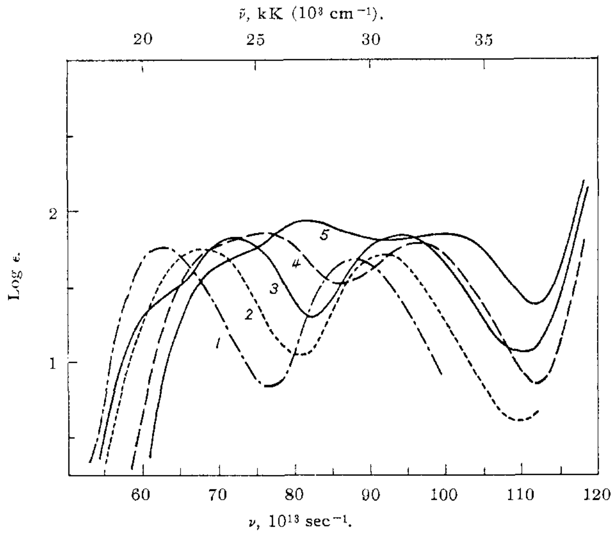

Figure 1.—Absorption spectra of the $Co(CN)_x(NH_3)_{6-x}$ series ($x$ = 0, 1, 2, 3): (1) $Co(NH_3)_6^{3+}$, —-—-—; (2) $Co(CN)(NH_3)_5^{2+}$, ---------; (3) *trans*-$Co(CN)_2(NH_3)_4^+$, ———; (4) *cis*-$Co(CN)_2(NH_3)_4^+$, — — —; (5) *mer*-Co(CN)$_3$(NH$_3$)$_3$, ———.

The absorption spectra of *cis*- and *trans*-$Co(CN)_2(NH_3)_4^+$ are analogous to those of the corresponding ethylenediamine complexes (Figure 3).

Recently, Kuroda and Gentile[12] reported the *cis*-diisocyanoethylenediamine complex, and they stated that the first absorption band of the complex resembled that of the *cis*-diisocyanotriethylenetetramine com-

---

[7] F. G. Mann, *J. Chem. Soc.*, 466 (1934).

[8] H. S. Nagarajaiah, A. G. Sharpe, and D. B. Wakefield, *Proc. Chem. Soc.*, 385 (1959).

[9] B. P. Block, *J. Inorg. Nucl. Chem.*, **14**, 294 (1960).

[10] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 966 (1963).

[11] H. Yoneda, private communication.

[12] K. Kuroda and P. S. Gentile, presented at the 10th International Conference on Coordination Chemistry, Nikko, Japan, Sept 1967.

TABLE I

ABSORPTION DATA FOR THE $Co(CN)_x(NH_3)_{6-x}$ AND THE $Co(CN)_{2x}(en)_{3-x}$ SERIES ($x = 0, 1, 2, 3$)

| Complex | Band I ($\nu_{max}$,[e] log $\epsilon_{max}$) | Band II | Ref |
|---|---|---|---|
| $[Co(NH_3)_6]Cl_3$ | 62.9 (1.76) | 88.3 (1.68) | |
| $[Co(CN)(NH_3)_5](ClO_4)_2$ | 68.1 (1.74) | 91.8 (1.71) | *a*, *b*, *c* |
| *cis*-$[Co(CN)_2(NH_3)_4]Cl \cdot H_2O$ | 75.9 (1.84) | 96.0 (1.77) | *a* |
| *trans*-$[Co(CN)_2(NH_3)_4]Cl$ | *Ca.* 63( sh[f]), 71.8 (1.82) | 94.3 (1.83) | *a* |
| *mer*-$Co(CN)_3(NH_3)_3$ | *Ca.* 73 (sh), *ca.* 82 (*ca.* 1.9) | 100.4 (1.84) | *a*, *b* |
| *mer*-$Co(CN)_3$dien | *Ca.* 72 (sh), *ca.* 81 (*ca.* 2.0) | 101.9 (1.96) | *a* |
| $[Co(en)_3]Cl_3 \cdot 3H_2O$ | 63.9 (1.94) | 88.4 (1.90) | |
| *cis*-$[Co(CN)_2(en)_2]Cl$ | 74.2 (1.91) | 97.1 (1.93) | *a*, *d* |
| *trans*-$[Co(CN)_2(en)_2]Cl$ | *Ca.* 64 (sh), 73.2 (1.78) | 96.2 (1.79) | *a* |
| $K[Co(CN)_4en] \cdot H_2O$ | 85.3 (2.26) | 108.4 (2.28) | *d* |
| $K_3[Co(CN)_6] \cdot 3H_2O$ | 96.8 (2.29) | 116.8 (2.12) | |

[a] Present work. [b] See ref 3. [c] See ref 4. [d] See ref 5. [e] Units: $10^{13}$ sec$^{-1}$. [f] Shoulder.

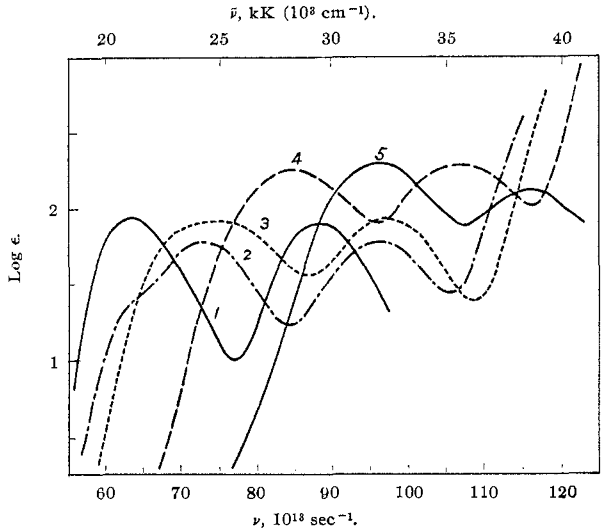

Figure 2.—Absorption spectra of the $Co(CN)_{2x}(en)_{3-x}$ series ($x = 0, 1, 2, 3$): (1) $Co(en)_3^{3+}$, ———; (2) *trans*-$Co(CN)_2(en)_2^+$, — – — – —; (3) *cis*-$Co(CN)_2(en)_2^+$, --------; (4) $Co(CN)_4(en)^-$, ———; (5) $Co(CN)_6^{3-}$, ———.

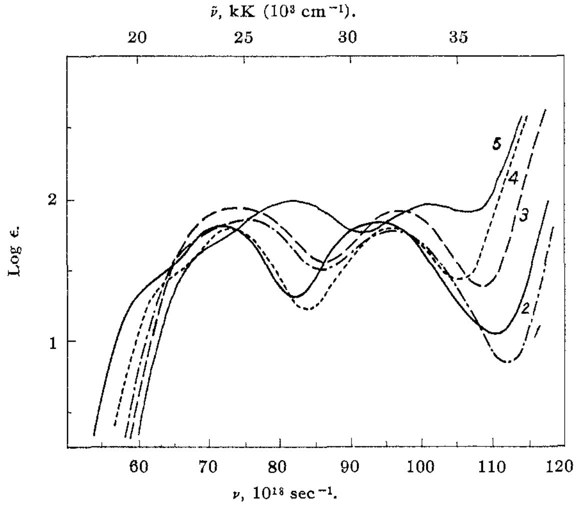

Figure 3.—Absorption spectra of the *cis*- and *trans*-$Co(C)_2(N)_4$ complexes and *mer*-$Co(CN)_3$dien: (1) *cis*-$Co(CN)_2(NH_3)_4^+$, —·—·—; (2) *trans*-$Co(CN)_2(NH_3)_4^+$, ———; (3) *cis*-$Co(CN)_2(en)_2^+$, – – – –; (4) *trans*-$Co(CN)_2(en)_2^+$, --------; (5) *mer*-$Co(CN)_3$dien, ———.

plex[13] and was at the position of that of the $Co(N)_6$-type complex. However, the spectrum of their isocyanobis(ethylenediamine) complex is very similar to that of our *trans*-$Co(CN)_2(en)_2^+$ complex. In the latter, one might regard the shoulder, which is shown at about 64 × $10^{13}$ sec$^{-1}$ (*ca.* 21,400 cm$^{-1}$) (Figure 3) as one of two components in the first band. The other component lies at about 73 × $10^{13}$ sec$^{-1}$ (24,400 cm$^{-1}$). Such a large splitting has never been observed in any complexes of the $Co(N)_6$ type. Moreover, the position of the second absorption band of the complex (Table I, 96.2 × $10^{13}$ sec$^{-1}$) is close to that (97.1 × $10^{13}$ sec$^{-1}$) of the corresponding *cis* complex, which belongs to the $Co(C)_2(N)_4$-type. The same relation is found in the corresponding *trans*-$Co(CN)_2(NH_3)_4^+$ complex. Therefore, it is not reasonable to assume the existence of N-coordinated cyanide ligands in the present tetraammine and bis(ethylenediamine) complexes. Judging from these facts and the infrared spectra, it seems reasonable to assume that the complexes obtained in this work take a *trans*-cyano configuration.

According to our discussion, a strong possibility is considered that two isomers, assigned as *cis*-diisocyanotriethylenetetraminecobalt(III) complexes by Kuroda and Gentile,[13] have *trans*-dicyano configurations. Even if the existence of two geometrical isomers of the *trans*-dicyanotriethylenetetramine complex is true, one might understand it according to the recent discussion of Buckingham, *et al.*[14] In this configuration, two nitrogen atoms of imino groups are asymmetric. Therefore, it is possible to consider two geometrical isomers, racemic and *meso* forms, corresponding to tartaric acid which has two asymmetric atoms.

The predicted positions of the absorption bands of the mixed cyanoammine and -diamine complexes are listed in Table II. The values of the first bands were calculated according to the results of the crystal-field treatment of Yamatera's method.[15] On the other hand, the values of the second bands were calculated on the basis of "the rule of average environment";[16,17]

---

(13) K. Kuroda and P. S. Gentile, *Inorg. Nucl. Chem. Letters*, **3**, 151 (1967).

(14) D. A. Buckingham, P. A. Marzilli, and M. A. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967).

(15) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

(16) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press Ltd., London 1962, p 109.

(17) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **40**, 1868 (1967).

TABLE II

THE PREDICTED BAND POSITIONS FOR THE FIRST AND THE SECOND ABSORPTION BANDS

| Complex | Band I[a] | Band II |
|---|---|---|
| $[Co(NH_3)_6]Cl_3$ | 62.9 | 88.3 |
| $[Co(CN)(NH_3)_5](ClO_4)_2$ | 62.9 (b), 71.4 (a) | 93.0 |
| *cis*-$[Co(CN)_2(NH_3)_4]Cl \cdot H_2O$ | 71.4 (a), 79.8 (b) | 97.8 |
| *trans*-$[Co(CN)_2(NH_3)_4]Cl$ | 62.9 (b), 79.8 (a) | 97.8 |
| *mer*-$Co(CN)_3(NH_3)_3$ | 71.4, 79.8, 88.3 | 102.5 |
| $[Co(en)_3]Cl_3 \cdot 3H_2O$ | 63.9 | 88.4 |
| *cis*-$[Co(CN)_2(en)_2]Cl$ | 72.1 (a), 80.3 (b) | 97.9 |
| *trans*-$[Co(CN)_2(en)_2]Cl$ | 63.9 (b), 80.3 (a) | 97.9 |
| $K[Co(CN)_4(en)] \cdot H_2O$ | 80.3 (b), 88.6 (a) | 107.3 |
| $K_3[Co(CN)_6] \cdot 3H_2O$ | 96.8 | 116.8 |

[a] When an absorption band is split into two components, the degenerate one (truly or accidentally) is labeled a and another nondegenerate one b.

the wave numbers of the band of an octahedral complex $MA_nB_{6-n}$ are situated at

$$\sigma(MA_nB_{6-n}) = (n/6)\sigma(MA_6) + [(6 - n)/6]\sigma(MB_6)$$

where $\sigma(MA_6)$ and $\sigma(MB_6)$ represent the wave numbers of the nonmixed complexes $MA_6$ and $MB_6$, respectively. The maximum of the first band for the *cis*-$Co(CN)_2(NH_3)_4^+$ complex lies at a slightly higher frequency than that for the *cis*-$Co(CN)_2(en)_2^+$ complex (Table I). This fact is understood by considering that the ratio of the intensities of two components in the former complex is different from the ratio in the latter.

From a comparison of Table II with Table I and Figures 1 and 2, one might point out the following facts. (1) In the first bands of the *trans*-$Co(C)_2(N)_4$ type, the positions of the components at lower frequency (at about 63 × $10^{13}$ $sec^{-1}$) are nearly the predicted ones, but the other components at higher frequency (at about 72–73 × $10^{13}$ $sec^{-1}$) deviate from the predicted ones (at about 80 × $10^{13}$ $sec^{-1}$). Deviations from the predicted values to such an extent were also observed in the other cyano complexes,[18] *e.g.*, $Co(CN)_5OH_2^{2-}$. (2) The splittings of the first absorption bands for the *cis*-$Co(C)_2(N)_4$ type and the *mer*-$Co(C)_3(N)_3$ type of complexes are nearly the predicted values. (3) The absorption intensities of these cyano complexes exhibit no such regularity as is seen in the oxalatoammine series.[19] (4) The positions of the second bands are nearly equal to the predicted ones.

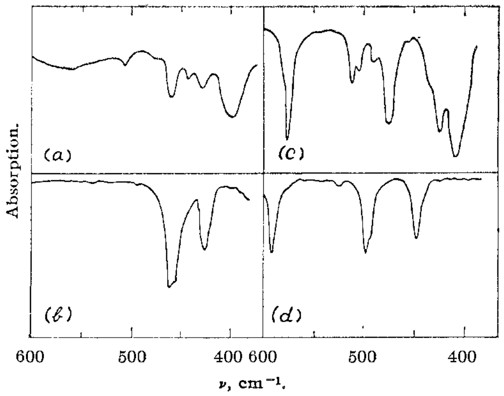

Figure 4.—Far-infrared spectra of the *cis*- and *trans*-$Co(C)_2(N)_4$ type of complex in the region 600–400 $cm^{-1}$: (a) *cis*-$[Co(CN)_2(NH_3)_4]Cl \cdot H_2O$; (b) *trans*-$[Co(CN)_2(NH_3)_4]Cl$; (c) *cis*-$[Co(CN)_2(en)_2]Cl$; (d) *trans*-$[Co(CN)_2(en)_2]Cl$.

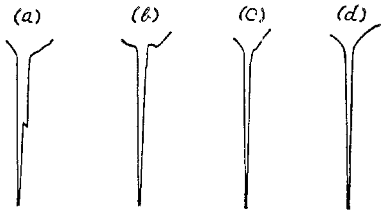

Figure 5.—Infrared absorption spectra of the *cis*- and *trans*-$Co(C)_2(N)_4$ type of complexes in the region of $\nu(C\equiv N)$: (a) *cis*-$[Co(CN)_2(NH_3)_4]Cl \cdot H_2O$; (b) *trans*-$[Co(CN)_2(NH_3)_4]Cl$; (c) *cis*-$[Co(CN)_2(en)_2Cl$; (d) *trans*-$[Co(CN)_2(en)_2]Cl$.

**Infrared Absorption Spectra.**—Several methods[20-23] have been applied to the distinction between the *cis* and *trans* isomers of bis(ethylenediamine) complexes of cobalt(III). Baldwin[22] has suggested that the most consistent variation between the spectra of *cis* and *trans* isomers is found in the $CH_2$ rocking region (900–870 $cm^{-1}$); the *cis* isomer shows two peaks, and the corresponding *trans* isomer shows only one peak. The complex *cis*-$[Co(CN)_2(en)_2]Cl$ has two distinct bands at 892 and 881 $cm^{-1}$, and the corresponding *trans* isomer obtained in this work has only a peak at 893 $cm^{-1}$. More definite support was obtained from the far-infrared spectra. Figure 4 shows the spectra of the *cis* and *trans* isomers of the dicyano complexes. Hughes and McWhinnie[23] have showed that a correlation may be made between the configuration of the ethylenediamine complex and the complexity of its spectrum in the region of 610–500 $cm^{-1}$; the *trans* isomers of the bis(ethylenediamine) complexes give no more than three strong bands in this region, but the *cis* isomers invariably give at least four (sometimes occurring as shoulders). In Figure 4, the patterns of the *cis* isomers of the $Co(C)_2(N)_4$ type of complexes are more complicated than those of the *trans* isomers by the lowering of the symmetry; the peaks for *trans*-$[Co(CN)_2(NH_3)_4]Cl$ whose symmetry is $D_{4h}$ with a center of symmetry are less than the half of those for the corresponding *cis* isomer which has a $C_{2v}$ symmetry.

Ohkawa, *et al.*,[5] have reported that racemic *cis*-$Co(CN)_2(en)_2^+$ shows no splitting, but the optically active complex exhibits two C≡N stretching bands at the region of 2130 $cm^{-1}$. In the present four complexes of the $Co(C)_2(N)_4$ type, the *cis*-$Co(CN)_2(NH_3)_4^+$ complex exhibits splitting only in the C≡N stretching band (Figure 5).

---

(18) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).
(19) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **28**, 572 (1955).
(20) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 1521 (1960).
(21) M. M. Chamberlain and J. C. Bailar, *ibid.*, **81**, 6412 (1959).
(22) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).
(23) M. N. Hughes and W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **28**, 1659 (1966).