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New Methods of Preparing the Mixed Cyano Cobalt(III) Complexes[*1]

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The following new cyano cobalt(III) complexes have been prepared by treating the corresponding chloro complexes with silver cyanide: *cis*-$[Co(CN)_2dip_2]NO_3\cdot 7H_2O$, *cis*-$[Co(CN)_2dip_2]_2SO_4\cdot 12H_2O$, *cis*-$[Co(CN)_2en(NH_3)_2]NO_3$, $[Co(CN)_3en(NH_3)]\cdot H_2O$, and *trans*-$[Co(CN)dg_2(NH_3)]\cdot \frac{1}{2}H_2O$. This method has also been used in the preparation of the following compounds: *cis*-$[Co(CN)(NO_2)en_2]NO_3\cdot H_2O$,[*2] *cis*-$[Co(CN)(SO_3)en_2]$, *trans*-$[Co(CN)(SO_3)en_2]$, *cis*-$[Co(CN)(OH_2)en_2]SO_4\cdot 2H_2O$,[*2] *cis*-$[Co(CN)_2en_2]NO_3$,[*2] *cis*-$[Co(CN)_2pn_2]NO_3$,[*2] *cis*-$[Co(CN)_2phen_2]NO_3\cdot 6H_2O$,[*2] and *cis*-$[Co(CN)_2phen_2]Cl\cdot 4H_2O$. Another new method has been attempted in dimethyl sulfoxide or an acetonitrile-water solution by the step-by-step substitution of a chloro ligand with a CN^- ion *via* the monocyanomonochloro complex of the $[Co(CN)Cl\ N_4]$-type; we thus succeeded in obtaining these dicyano-ammine complexes, *trans*-$[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$, *trans*-$[Co(CN)_2en(NH_3)_2]Cl\cdot H_2O$, and *cis*-$[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$. The methods of preparing the following new complexes are also described: *trans*-$Na[Co(CN)_2dg_2]\cdot 2H_2O$, *trans*-$K[Co(CN)_2dg_2]\cdot \frac{3}{2}H_2O$, *trans*-$(NH_4)_2[Co(CN)dg_2(SO_3)]\cdot 4H_2O$, and *trans*-$H[Co(CN)dg_2Cl]\cdot 4H_2O$. The absorption spectra in the visible, ultraviolet, and infrared regions have been measured.

The direct substitution of diacido-cobalt(III) complexes, $[CoX_2N_4]$, with CN^- ions has heretofore been considered to be difficult. For example, the $[Co(CN)_2en_2]^+$ ion could be obtained only *via* the $[Co(S_2O_3)_2en_2]^-$ ion.1) When the dichloro complex is treated with potassium cyanide, a disproportionation occurs to produce such precipitates as $[Co\ en_3][Co(CN)_5OH]$. One of the reasons for this is certainly the hydrolysis of potassium cyanide in solution, and another, the difference in bonding character between Co–Cl and Co=C=N$^-$. The method of Rây and Sarma1) is based on the similarity in coordinate bond character between Co–S_2O_3 and Co=C=N$^-$ in the sphere of the bis(ethylenediamine)cobalt(III) complex. Their method, however, is invalid for the preparation of dicyano-bis(2,2′-dipyridyl) and dicyanobis(1,10-phenanthroline)cobalt(III) complexes.

Recently, Yoneda *et al.*2) have succeeded in obtaining the *trans*-$[Co(CN)_2en_2]Cl$ complex in dimethyl sulfoxide. In such a non-aqueous solution, the substitution occurs only gently and is not accompanied by the disruption of the complex, since the dissociation and hydrolysis of potassium cyanide are depressed to some extent.

Regarding the cobalt(III) complexes of the cyano-ammine series, Konya *et al.*3) have reported the preparation of *cis*- and *trans*-$[Co(CN)_2(NH_3)_4]Cl$. Independently of their work, other methods of preparing the nitrates of these isomers have been attempted and will be described in the present

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[*1] Presented at the 18th Symposium on Coordination Chemistry, Kyoto, October 18, 1968.

[*2] The complex cation is known, but has not yet been reported as a compound.

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

2) H. Yoneda, T. Baba and M. Muto, This Bulletin, **40**, 1736 (1967); M. Muto, T. Baba and H. Yoneda, *ibid.*, **41**, 2918 (1968).

3) K. Konya, H. Nishikawa and M. Shibata, *Inorg. Chem.*, **7**, 1165 (1968).

report. On the other hand, Shibata *et al.*[4] reported the syntheses of $[Co(CN)(NH_3)_5]Cl_2$ and $[Co(CN)_3(NH_3)_3]$, while Siebert[5] independently described the preparation of the former, $[Co(CN)(NH_3)_5]X_2$ (X=Cl, Br, NO_3, ClO_4 or ½SO_4). By the successive substitution method of the tricarbonatocobaltate(III) complex developed by Shibata *et al.*[4] an odd number of CN^- ligands is introduced into the coordination sphere of the ammine cobalt(III) complex in the presence of active charcoal. Recently, Kuroda[6] reported a similar method of preparing the dicyano complex, *cis*-$[Co(CN)_2en_2]ClO_4$, *via* the carbonato complex, $[Co(CO_3)en_2]ClO_4$. Several years ago, Cambi and Daglia[7] reported the isolation of $K_2[Co(CN)_5(NH_3)]$. The complexes of *cis*- and *trans*-$M[Co(CN)_4(NH_3)_2]$, however, are now still missing members in this series.

Several other papers dealing with the mixed cyano cobalt complexes are listed as Ref. 8—10.

In the present work, the direct substitution of chloro ligands has been found to be possible in water provided that the cyanide ions are present in a very dilute concentration. For this purpose, we have adopted the silver cyanide, the solubility of which in water is $2.2 \cdot 10^{-5}$ g/100 g water at 20°C, and have succeeded in obtaining directly the mixed ligand complexes of cyano-cobalt(III), as listed in the synopsis.

On the other hand, the syntheses of ammine complexes with a *trans*-configuration have been carried out in dimethyl sulfoxide with potassium cyanide. The following complexes were obtained: *trans*-$[Co(CN)_2(NH_3)_4]NO_3 \cdot H_2O$ and *trans*-$[Co(CN)_2en(NH_3)_2]Cl \cdot H_2O$.

The present paper will deal with the preparation methods and the absorption spectra of these cyano cobalt(III) complexes.

Experimental

Preparation of *cis*-$[Co(CN)_2en_2]NO_3$ (anhydrous). Twenty grams of *trans*-$[CoCl_2en_2]NO_3$ were suspended in 700 m*l* of distilled water, mixed with 20 g of AgCN, and heated on a water bath (90°C) for three hours. The color of the solution changed from green to yellow. The solution was then filtered, concentrated by evaporation, and allowed to stand. On cooling, yellow crystals separated from the solution; they were recrystallized once from hot water. Found: Co, 19.98; C, 24.49; N, 33.49; H, 5.63%. Calcd for $[Co(CN)_2en_2]NO_3$: Co, 20.10; C, 24.58; N, 33.44; H, 5.50%.

The dicyanobis(propylenediamine)cobalt(III) nitrate was analogously prepared by treating *trans*-$[CoCl_2pn_2]NO_3$ (20 g) with AgCN (20 g) in 500 m*l* of water below 60°C for half an hour. The orange-yellow filtrate was concentrated *in vacuo* below 50°C with a rotatory evaporator. Finally the complex was precipitated from the concentrated solution with the addition of ethanol. Found: Co, 18.22; C, 30.04; N, 30.21; H, 6.26%. Calcd for $[Co(CN)_2pn_2]NO_3$: Co, 18.35; C, 29.91; N, 30.52; H, 6.28%.

The perchlorate, *cis*-$[Co(CN)_2en_2]ClO_4$, was analogously prepared: 20 g of *trans*-$[CoCl_2en_2]ClO_4$ were treated with 20 g of AgCN in 600 m*l* of water at 90°C for three hours. The complex has no crystallization water. Found: Co, 17.90; C, 21.78; N, 25.34; H, 4.90%. Calcd for $[Co(CN)_2en_2]ClO_4$: Co, 17.83; C, 21.80; N, 25.42; H, 4.88%.

Preparation of *cis*-$[Co(CN)_2(NH_3)_4]NO_3 \cdot H_2O$. Forty grams of *trans*-$[Co(CN)Cl(NH_3)_4]NO_3$[11] were mixed with 29 g of AgCN in 400 m*l* of acetonitrile containing 5% of water at room temperature and then heated on a water bath (50—60°C) for three hours. The temperature of the solution was kept below 60°C during the reaction. No smell of ammonia was recognized. The suspension was then filtered, and the residue was repeatedly washed with water. The orange-yellow water solution was concentrated *in vacuo* below 50°C with a rotatory evaporator. Orange-yellow crystals separated from the solution when it was allowed to stand overnight. The crude complex was recrystallized from hot water containing a trace of acetic acid. Found: Co, 22.65; C, 9.11; N, 37.69; H, 5.70%. Calcd for $[Co(CN)_2(NH_3)_4]NO_3 \cdot H_2O$: Co, 22.74; C, 9.27; N, 37.84; H, 5.45%.

Preparation of [*cis*-$Co(CN)_2en(NH_3)_2]NO_3$. This complex was quite analogously prepared. That is, 60 g of *trans*-$[CoCl_2en(NH_3)_2]NO_3$[12] were treated with 80 g of AgCN in 500 m*l* of acetonitrile containing 5% of water at 80°C for three hours. Found: Co, 21.97; C, 18.04; N, 36.88; H, 5.31%. Calcd for $[Co(CN)_2en(NH_3)_2]NO_3$: Co, 22.06; C, 17.99; N, 36.70; H, 5.28%.

Preparation of *cis*-$[Co(CN)_3en(NH_3)] \cdot H_2O$. Sixty grams of *trans*-$[CoCl_2en(NH_3)_2]Cl \cdot H_2O$[12] were treated with 100 g of AgCN in 500 m*l* of acetonitrile containing 10% of water at 90°C for ten hours. Large yellow crystals were obtained. Found: Co, 25.41; C, 25.92; N, 36.15; H, 5.66%. Calcd for $[Co(CN)_3en(NH_3)] \cdot H_2O$: Co, 25.39; C, 25.87; N, 36.21; H, 5.65%.

Preparation of *cis*-$[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$.[13] Fifteen grams of *trans*-$[CoCl_2dip_2]NO_3$[14],[*3] were treated with 10 g of AgCN in 500 m*l* of water on a water bath

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[4] M. Shibata, M. Mori and E. Kyuno, *ibid.*, **3**, 1573 (1964).

[5] H. Siebert, *Z. anorg. u. allgem. Chem.*, **327**, 63 (1964).

[6] K. Kuroda, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 720 (1968).

[7] L. Cambi and E. Daglia, *Gazz. chim. ital.*, **88**, 691 (1964).

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

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

[10] G. Favini and E. Paglia, *J. Inorg. Nucl. Chem.*, **8**, 155 (1958).

[11] K. Ohkawa, J. Hidaka and Y. Shimura, This Bulletin, **39**, 1715 (1966).

[12] N. Maki and K. Okawa, *J. Electroanal. Chem.*, **8**, 262 (1964).

[13] N. Maki, This Bulletin, **42**, No. 9 (1969) in the press: N. Maki, T. Hamazaki and S. Sakuraba, *ibid.*, **41**, 1735 (1968).

[14] F. M. Jaeger and J. A. van Dijk, *Z. anorg. u. allgem. Chem.*, **227**, 273 (1936).

[*3] dip=2,2′-dipyridyl; $C_{10}H_8N_2$.

(80°C) for three hours. Lustrous, needle-shaped yellow crystals were obtained from the filtrate. The crude complex was recrystallized from hot water. Found: Co, 9.51; C, 43.15; N, 15.97; H, 5.03%. Calcd for $[Co(CN)_2dip_2]NO_3\cdot 7H_2O$: Co, 9.64; C, 43.22; N, 16.04; H, 4.95%.

The solubility of the complex in water was 1.0904 g/100 g water (25°C). The corresponding sulfate was obtained by using *trans*-$[CoCl_2dip_2]_2SO_4$ (anhydrous) instead of *trans*-$[CoCl_2dip_2]NO_3$ as the starting complex. Found: Co, 10.12; C, 45.54; N, 14.45; H, 5.01%. Calcd for $[Co(CN)_2dip_2]_2SO_4\cdot 12H_2O$: Co, 10.17; C, 45.60; N, 14.50; H, 4.88%.

Preparation of *cis*-$[Co(CN)_2phen_2]NO_3\cdot 6H_2O$.[13),*4] Twenty grams of *trans*-$[CoCl_2phen_2]NO_3$[15)] were treated with 15 g of AgCN in 500 m*l* of water at 70—80°C for three hours. The suspension was then filtered and concentrated by evaporation. When the solution was allowed to stand, silky yellow crystals deposited on the wall of the beaker. Found: Co, 9.11; C, 48.39; N, 15.17; H, 4.67%. Calcd for $[Co(CN)_2phen_2]NO_3\cdot 6H_2O$: Co, 9.19; C, 48.68; N, 15.29; H, 4.40%.

The solubility of the complex in water was 0.6736 g/100 g water; in absolute methanol, 0.1952 g/100 g methanol; and in absolute ethanol, 0.0111 g/100 g ethanol at 25°C.

The chloride of the complex was obtained by treating the nitrate with a solution of potassium chloride, for the chloride of the complex is less soluble in water than the nitrate. Found: Co, 10.08; C, 54.07; N, 14.66; H, 4.52%. Calcd for $[Co(CN)_2phen_2]Cl\cdot 4H_2O$: Co, 10.18; C, 53.95; N, 14.52; H, 4.18%.

Preparation of *cis*-$[Co(CN)(NO_2)en_2]NO_3\cdot H_2O$. The orange-red crystals of *cis*-$[CoCl(NO_2)en_2]NO_3$[16)] (60 g) were treated with 30 g of AgCN in 500 m*l* of water at 80—90°C for an hour. The color of the solution changed from red to yellow. The solution was then filtered, concentrated by evaporation, and allowed to stand. Bright yellow crystals deposited. The yield was 84% of theory. Found: Co, 17.69; C, 18.03; N, 29.65; H, 5.67%. Calcd for $[Co(CN)(NO_2)en_2]NO_3\cdot H_2O$:[17)] Co, 17.80; C, 18.13; N, 29.61; H, 5.48%.

Preparation of *trans*-$[Co(CN)(SO_3)en_2]$. Twenty grams of *trans*-$[CoCl(SO_3)en_2]\cdot H_2O$[18)] were treated with 10 g of AgCN in 500 m*l* of water at 90°C for three hours. Brownish-yellow crystals were thus obtained. Found: Co, 20.53; C, 20.89; N, 24.77; H, 5.78%. Calcd for $[Co(CN)(SO_3)en_2]$: Co, 20.66; C, 21.06; N, 24.56; H, 5.66%.

Preparation of *cis*-$[Co(CN)(SO_3)en_2]$ (anhydrous). The complex was prepared by the following two methods: (1) To a solution in which *trans*-$[Co(CN)(SO_3)(NH_3)_4]\cdot 2H_2O$[6)] (30 g) had been completely dissolved there were added 135 m*l* of 10% ethylenediamine under continuous stirring; the solution was then heated and evaporated on a water bath for three hours. The reaction took place, evolving ammonia. The yield was 54% of theory. Found: Co, 20.37; C, 21.22; N, 24.56; H, 5.71%. Calcd for $[Co(CN)(SO_3)en_2]$: Co, 20.66; C, 21.06; N, 24.56; H, 5.66%.

(2) Analogously, 20 g of *cis*-$[CoCl(SO_3)en_2]\cdot 3H_2O$ were treated with 10 g of AgCN in 500 m*l* of water at 90°C for three hours. The *cis*-$[Co(CN)(SO_3)en_2]$ complex (anhydrous) was obtained from the filtrate. Found: Co, 20.68; C, 20.97; N, 24.83; H, 5.91%. Calcd for $[Co(CN)(SO_3)en_2]$: Co, 20.66; C, 21.06; N, 24.56; H, 5.66%.

Preparation of *trans*-$[Co(CN)dg_2(NH_3)]\cdot {}^1/_2H_2O$.[*5] The complex was prepared by the following three methods:

(1) Thirty-four grams of *trans*-$[CoCldg_2(NH_3)]\cdot H_2O$[19)] were treated with 20 g of AgCN in 500 m*l* of water at 90°C for three hours. Bright brownish-yellow crystals were obtained from the filtrate. The crude product was recrystallized from hot water containing acetic acid. Found: Co, 17.33; C, 32.00; N, 24.51; H, 5.38%. Calcd for $[Co(CN)dg_2(NH_3)]\cdot \frac{1}{2}H_2O$: Co, 17.27; C, 31.68; N, 24.63; H, 5.32%.

(2) To 15.0 g of *trans*-$[Co(CN)(OH_2)(NH_3)_4]Cl_2$[6)] in 150 m*l* of water there were added 14.4 g of dimethylglyoxime. The mixture was heated on a water bath for three hours. The reaction proceeded, evolving ammonia, according to the following scheme:[20)]

$$[Co(CN)(OH_2)(NH_3)_4]^{2+} + 2dgH \rightarrow [Co(CN)dg_2(NH_3)] + 3NH_3.$$

Every half hour during the reaction, 5—7 g of ammonium acetate were added to the solution. A total of 20 g of ammonium acetate was used. Lustrous orange-yellow crystals separated from solution when it was allowed to stand. The product was filtered and washed with 80% ethanol to eliminate traces of unreacted dimethylglyoxime. The yield was more than 82% of theory. Found: Co, 17.21; C, 31.44; N, 24.89; H, 5.45%. Calcd for $[Co(CN)dg_2(NH_3)]\cdot \frac{1}{2}H_2O$: Co, 17.27; C, 31.68; N, 24.63; H, 5.32%.

(3) A solution of 400 m*l* containing 27 g of potassium cyanide was mixed with a solution of 100 g of $[Codg_2(NH_3)_2]Cl\cdot 5H_2O$[21)] dissolved in 400 m*l* of water and heated on a water bath for an hour at 90°C. The insoluble orange-yellow crystals which were deposited from the solution were filtered and washed with cold water several times and then with ethanol. The crude complex was recrystallized from hot water containing acetic acid. Found: Co, 17.22; C, 31.43; N, 24.78; H, 5.40%. Calcd for $[Co(CN)dg_2(NH_3)]\cdot \frac{1}{2}H_2O$: Co, 17.27; C, 31.68; N, 24.63; H, 5.32%.

Preparation of *trans*-$K[Co(CN)_2dg_2]\cdot {}^3/_2H_2O$.[22)] The complex was prepared by the following two methods:

(1) A solution (200 m*l*) containing 13.7 g of potassium cyanide was mixed with a solution of 50 g of

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[*4] phen=1,10-phenanthroline; $C_{12}H_8N_2$.

15) P. Pfeiffer and Br. Werdelmann, *Z. anorg. u. allgem. Chem.*, **236**, 31 (1950).

16) A. Werner and L. Gerb, *Ber.*, **34**, 1740 (1901).

17) Independent of this work, the preparation of the nitrite of the complex, *cis*-$[Co(CN)(NO_2)en_2]NO_2$, has been reported; *cf.*, Ref. 8.

18) A. Werner and M. Pokrowska, *Liebig. Ann.*, **386**, 81 (1912).

[*5] dg_2=a pair of dimethylglyoximes: $2CH_3\cdot C(NO)\cdot C(NOH)\cdot CH_3$.

19) L. Tschugaeff, *Ber.*, **39**, 2694 (1906); *ibid.*, **40**, 3499 (1907).

20) N. Maki, T. Itoh and S. Sakuraba, This Bulletin, **41**, 529 (1968).

21) L. Tschugaeff, *Z. anorg. u. allgem. Chem.*, **46**, 160 (1905).

22) N. Maki, This Bulletin, **38**, 2013 (1965).

$[Codg_2(NH_3)_2]Cl\cdot 5H_2O$21) dissolved in 300 ml of water under stirring and then heated on a water bath until the reaction mixture had been evaporated to one-third of its former volume. From the smell of ammonia evolved, it could be discerned that the following reaction was in progress:

$$[Codg_2(NH_3)_2]Cl\cdot 5H_2O+2KCN\rightarrow K[Co(CN)_2dg_2]\cdot \tfrac{3}{2}H_2O+2NH_3+2KCl.$$

During the course of the reaction, insoluble orange-yellow crystals deposited. These crystals were ascertained to be the *trans*-$[Co(CN)dg_2(NH_3)]\cdot\frac{1}{2}H_2O$19) complex by the elementary analyses and by the study of the absorption spectra in the IR, UV, and visible regions.23) These crystals of the cyano-ammine complex were filtered off during the reaction, and the filtrate was further concentrated by evaporation. On cooling, large needle-shaped yellow crystals were obtained. Found: Co, 14.41; C, 29.63; N, 20.55; H, 4.32; K, 9.50%. Calcd for $K[Co(CN)_2dg_2]\cdot\frac{3}{2}H_2O$: Co, 14.47; C, 29.49; N, 20.63; H, 4.21; K, 9.60%.

Sodium salt of the complex was obtained by using sodium cyanide instead of potassium cyanide. Found: Co, 14.63; C, 29.97; N, 20.14; H, 4.49%. Calcd for $Na[Co(CN)_2dg_2]\cdot 2H_2O$: Co, 14.73; C, 30.01; N, 20.00; H, 4.53%.

(2) Seventy-eight grams of *trans*-$[Co(CN)dg_2(NH_3)]\cdot\frac{1}{2}H_2O$19) were suspended in 800 ml of water containing 16 g of potassium cyanide. To the suspension there were stirred 25 g of active charcoal. Then the suspension was warmed on a water bath for ten hours at 40—50°C. The substitution occurred gently and slowly, evolving ammonia, below 50°C. The charcoal was filtered off, and the filtrate was concentrated by evaporation at 60—70°C until needle-shaped yellow crystals were deposited. Found: Co, 14.39; C, 29.61; N, 20.40; H, 4.10%. Calcd for $K[Co(CN)_2dg_2]\cdot\frac{3}{2}H_2O$: Co, 14.47; C, 29.49; N, 20.63; H, 4.21%. The aiming dicyano complex was very soluble in water, while the starting of the monocyanoammine complex was insoluble. Therefore, the isolation was easy and complete.

Preparation of *trans*-$(NH_4)_2[Co(CN)dg_2(SO_3)]\cdot 4H_2O$. To a solution (1.2 l) containing 40 g of *trans*-$[Co(CN)(SO_3)(NH_3)_4]\cdot 2H_2O$6) there were added 50 g of dimethylglyoxime (dgH). The mixture was then boiled at 100°C for three hours. The reaction took place, evolving ammonia. No deposition of metallic cobalt was observed. After cooling, the solution was filtered to eliminate the unreacted dimethylglyoxime, and then the filtrate was further concentrated by evaporation on a water bath at 80°C. When it was allowed to stand, orange-yellow crystals separated from the solution; they were filtered and washed with ethanol and ether. The crude product was recrystallized from hot water. Found: Co, 11.50; C, 21.33; N, 19.07; H, 6.32%. Calcd for $(NH_4)_2[Co(CN)dg_2(SO_3)]\cdot 4H_2O$: Co, 11.71; C, 21.47; N, 19.48; H, 6.01%.

Preparation of *trans*-$H[Co(CN)dg_2Cl]\cdot 4H_2O$. Thirty grams of *trans*-$(NH_4)_2[Co(CN)dg_2(SO_3)]\cdot 4H_2O$ were dissolved in 500 ml of water. To this solution there were added 300 ml of concentrated HCl. The temperature of the solution was maintained at 50—60°C for ten hours under continuous stirring. The reaction proceeded, evolving sulfur dioxide. The yellow precipitates were separated from the solution when the reaction was over. The mixture was filtered and washed several times with ethanol and ether. The crude complex was purified by treating it again with 200 ml of concentrated HCl at 60°C. Above 90°C, it could be seen that the CN-ligands were partly replaced with Cl^- ions to produce the $H[CoCl_2dg_2]$ complex. The residue was filtered and washed with concentrated HCl, ethanol and ether. Found: Co, 13.69; C, 25.69; N, 16.73; H, 5.50%. Calcd for $H[Co(CN)dg_2Cl]\cdot 4H_2O$: Co, 13.91; C, 25.51; N, 16.53; H, 5.47%.

Preparation of *cis*-$[Co(CN)(OH_2)en_2]SO_4\cdot 2H_2O$. Into 150 g of the *trans*-$[Co(CN)(SO_3)en_2]$ obtained previously there were stirred, drop by drop, 150 ml of concentrated H_2SO_4 in ice. The reaction occurred immediately, evolving SO_2 and yielding a viscous liquid of $[Co(CN)(SO_4)en_2]$, which tends to aquate in water. The aimed-at aquo complex was precipitated from the solution with the addition of methanol. The yield was 38%. Found: Co, 16.48; C, 17.01; N, 19.83; H, 6.40%. Calcd for $[Co(CN)(OH_2)en_2]SO_4\cdot 2H_2O$: Co, 16.59; C, 16.90; N, 19.71; H, 6.24%.

Preparation of *trans*-$[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$. Dried crystals of potassium cyanide were ground into fine powder in a porcelain mortar, and 3.00 g of them were dissolved in 500 ml of dimethyl sulfoxide at 60°C. Then the solution was transferred into a three-necked flask equipped with a reflux condenser and a mechanical stirrer. To this solution there were added 11.66 g of *trans*-$[Co(CN)Cl(NH_3)_4]NO_3$.11) The suspension was heated on a water bath at 70—85°C for three hours. When the solution was then allowed to stand overnight, orange-yellow crystals were deposited from the solution; they were filtered and washed with acetone several times. The crude complex was recrystallized from hot water below 50°C. The yield was 53.4% of theory. Found: Co, 22.51; C, 9.08; N, 37.72; H, 5.60%. Calcd for $[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$: Co, 22.74; C, 9.27; N, 37.84; H, 5.45%.

Preparation of *trans*-$[Co(CN)_2en(NH_3)_2]Cl\cdot H_2O$. This complex was prepared according to the following reaction steps:

$$\begin{aligned}&trans\text{-}[Co(CN)(SO_3)(NH_3)_4]\cdot 2H_2O\xrightarrow{\text{en}}\\ &\qquad cis\text{-}[Co(CN)(SO_3)en(NH_3)_2]\xrightarrow{\text{HCl}}\\ &\qquad cis\text{-}[Co(CN)Clen(NH_3)_2]Cl\xrightarrow[\text{in DMSO}]{\text{KCN}}\\ &\qquad trans\text{-}[Co(CN)_2en(NH_3)_2]Cl\cdot H_2O.\end{aligned}$$

(1) Thirty grams of *trans*-$[Co(CN)(SO_3)(NH_3)_4]\cdot 2H_2O$5) were dissolved in 100 ml of a water solution containing 8.6 g of ethylenediamine, and then the mixture was heated on a water bath (80°C) for two hours. The complex was once dissolved completely in solution, and then again deeper-colored yellow or brown crystals separated from the solution as a result of the reaction. The reaction mixture was further heated on a water bath for three or four hours, filtered while in a hot state, and washed several times with hot water, ethanol, and ether. The *cis*-$[Co(CN)(SO_3)en(NH_3)_2]$ complex (12 g) was thus obtained; it was used for the next reaction without further purification, since it was insoluble in water.

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23) Previously, it was speculated that these crystals were the $[Co(dgH)_3]\cdot 2.5H_2O$ complex, but this speculation should be corrected; *cf.*, Ref. 22.

(2) Thirty grams of *cis*-$[Co(CN)(SO_3)en(NH_3)_2]$ (anhydrous) were dissolved in 300 m*l* of concentrated HCl and heated on a water bath at 80—85°C for five hours. The color of the solution changed from orange-yellow to red. At last, the solution became a half of its former volume. The solution was once filtered. To the filtrate there were added, drop by drop, 200 m*l* of absolute ethanol under ice cooling. Then, fine red crystals were separated from the solution. The *cis*-$[Co(CN)Cl\,en(NH_3)_2]Cl$ complex is pure enough to be used for the next procedure without further recrystallizations.

(3) Dried powder of potassium cyanide (2.30 g) was completely dissolved in 300 m*l* of dimethyl sulfoxide at 70—80°C in a flask which equipped with a reflux condenser and a mechanical stirrer. Then, 6.0 g of *cis*-$[Co(CN)Cl\,en(NH_3)_2]Cl$ were added in small portions to the solution and the mixture was heated at 80°C for an hour. The yellow solution soon became muddy as the reaction proceeded. The reaction mixture was allowed to stand overnight, filtered and washed with acetone several times. The crude complex was recrystallized from hot water below 60°C. Found: Co, 22.63; C, 18.50; N, 32.61; H, 6.39%. Calcd for $[Co(CN)_2en(NH_3)_2]Cl\cdot H_2O$: Co, 22.79; C, 18.58; N, 32.49; H, 6.24%.

Preparation of *trans*-$[Co(CN)_2en_2]NO_3$. This complex was prepared by the method of Muto *et al.*[2] That is, 4.68 g of *trans*-$[CoCl_2en_2]NO_3$ were treated with 3.00 g of KCN in 500 m*l* of dimethyl sulfoxide for three hours at 70°C. The crude complex was recrystallized from hot water below 60°C. Found: Co, 20.22; C, 24.39; N, 33.43; H, 5.69%. Calcd for $[Co(CN)_2en_2]NO_3$: Co, 20.10; C, 24.58; N, 33.44; H, 5.73%.

Measurements. The absorption spectra in the visible and ultraviolet regions were determined with a Beckmann DU spectrophotometer. The IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer, model 337, with a KBr-pellet. The proton spectra were recorded on a Hitachi-Perkin-Elmer high resolution NMR spectrometer, model R-20. As a solvent for the NMR measurements we used 99.75% D_2O at 35°C.

Results and Discussion

The Method of Syntheses. The CN^- ion is located at the end position of the spectrochemical series and has the strongest coordinating ability among the cobalt(III) complexes of the Werner type. Hence, the attack on the acido-cobalt(III) complexes by the cyanide ions causes the ligands with lesser coordination ability to be expelled totally or partly from the coordination sphere and results in an overall rearrangement of the ligands; *i. e.*, a disproportionation occurs, since the ligands in general tend to surround a cobalt with bonds of the same nature or similar covalent character as far as possible.

The results of the preparations, however, suggest that the substitution of chloro ligands is possible even in a water solution by the use of silver cyanide. When the cyanide ions are present in a very dilute concentration, the substitution can take place only without any accompanying disproportionation, because the silver ion leaves the reaction system as a precipitate of AgCl and the equilibrium of silver cyanide moves in the direction of dissociation to supply Ag^+ or CN^- ions.

For the preparation of dicyano-ammine complexes, the attempts to let the dichloro-ammine complexes cited below react with AgCN have failed due to the disruption of the complex used: *cis*-$[CoCl_2(NH_3)_4]NO_3$, *trans*-$[CoCl_2(NH_3)_4]NO_3$, and *trans*-$[CoCl_2tn_2]NO_3$.[*6]

TABLE 1. THE ABSORPTION MAXIMA OF THE MIXED CYANO COBALT(III) COMPLEXES

Compound	I-band	II-band	C.T.-band
cis-$[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$	25.23(1.86)	31.28(2.03)	47.26(4.31)
trans-$[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$	*ca.* 22(1.81) 24.02(1.95)	31.60(2.05)	47.80(4.14)
cis-$[Co(CN)_2en(NH_3)_2]NO_3$	24.63(1.91)	32.46(1.96)	47.31(4.41)
trans-$[Co(CN)_2en(NH_3)_2]Cl\cdot H_2O$	*ca.* 22.4(1.55) 24.40(1.77)	32.10(1.78)	47.60(3.89)
cis-$[Co(CN)_2en_2]NO_3$	24.73(1.91)	32.37(1.93)	47.37(4.32)
trans-$[Co(CN)_2en_2]NO_3$	*ca.* 22(1.38) 24.33(1.90)	32.38(1.93)	47.62(4.44)
trans-$Na[Co(CN)_2dg_2]\cdot 2H_2O$	*ca.* 26(2.3)	*ca.* 30.7(3.24)	*ca.* 36.7(3.90) 41.40(4.45)
cis-$[Co(CN)(SO_3)en_2]$	24.39(2.13)	——*	36.76(4.20)
trans-$[Co(CN)(SO_3)en_2]$	22.99(1.97)	*ca.* 30(2.4)	36.23(4.19)
cis-$[Co(CN)(OH_2)en_2]SO_4\cdot 2H_2O$	22.37(2.11)	*ca.* 30(2.4)	36.23(4.22)
cis-$[Co(CN)(NO_2)en_2]NO_3\cdot H_2O$	23.42(2.12)	31.45(3.36)	42.02(4.22)
trans-$[Co(CN)dg_2(NH_3)]\cdot \frac{1}{2}H_2O$	——*	——*	——* 42.30(4.52)
trans-$[Co(CN)(SO_3)(NH_3)_4]\cdot 2H_2O$	23.50(2.16)	30.70(1.73)	42.41(3.41)
cis-$[Co(CN)(OH_2)(NH_3)_4]Cl_2$	21.91(1.90)	30.00(1.81)	42.20(3.48)
$[Co(CN)(NH_3)_5](ClO_4)_2\cdot \frac{1}{2}H_2O$	22.72(1.77)	30.71(1.73)	42.40(3.40)
$[Co(CN)_3en(NH_3)]\cdot H_2O$	25.51(1.90)	32.36(1.92)	48.31(4.45)
$[Co(CN)_3dien]$	26.45(2.45)	33.33(2.39)	48.54(4.11)

Unit: wave number, 10^3/cm; absorbance (log ε); dien=diethylenetriamine; * shoulder band

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[*6] tn=trimethylenediamine; $NH_2CH_2CH_2CH_2NH_2$.

In addition to these complexes, the substitution of the following complexes with KCN in a dimethyl sulfoxide has been attempted, but all attempts have failed, and for the same reason: *trans*-$[CoCl_2pn_2]NO_3$,[*7] *trans*-$[CoCl_2dip_2]NO_3$, *trans*-$[CoCl_2phen_2]NO_3$, and *trans*-$[CoCl_2(NH_3)_4]NO_3$.

Accordingly, for obtaining dicyano-ammine complexes the step-by-step substitution method *via* the monocyano-monochloro complex of the $[Co(CN)ClN_4]$-type has been adopted and found to be suitable for replacing a chloro ligand with a CN^- ion without disrupting the complex, as has been described previously.

In connection with this, the method using silver cyanide always gave rise to the *cis*-isomer rather than the *trans*-isomer, even if a *trans*-isomer was used as the starting complex, except in the case of the preparation of *trans*-$[Co(CN)(SO_3)en_2]$, in which the method using silver cyanide carried out in a water solution gave a *trans*-isomer. On the other hand, the method using KCN in dimethyl sulfoxide always gave a *trans*-isomer.

The dimethylglyoximato-cobaltate(III) complex, $H[CoCl_2dg_2]$, did not react with AgCN because the aquation of the complex was too rapid to allow the replacement of the Cl-ligands with CN^- ions within the sphere of coordination. The disruption of the complex used is ascribed to the formation of diaquocobalt(III) cyanide, $[Co(OH_2)_2dg_2]CN$. Thus, the substitution with CN^- ions has to take place within the sphere of coordination.

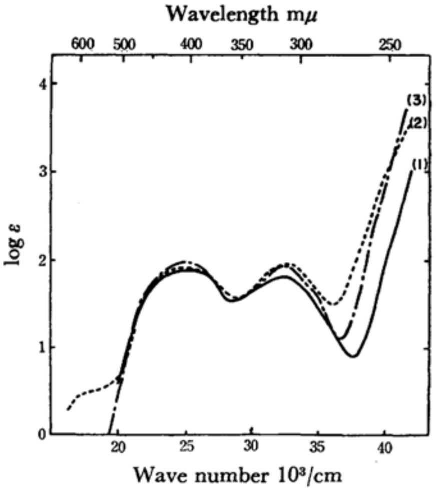

Fig. 2. The absorption spectra of the cyano cobalt(III) complexes with a *cis*-configuration: (1) —— *cis*-$[Co(CN)_2(NH_3)_4]NO_3 \cdot H_2O$; (2) ------ *cis*-$[Co(CN)_2en(NH_3)_2]NO_3$; (3) —-—-— *cis*-$[Co(CN)_2en_2]NO_3$.

Absorption Spectra in the Visible and Ultraviolet Regions. Table 1 shows the numerical data of the absorption maxima of the cobalt(III) complexes measured.

In the table, the first two absorption bands are assigned to ligand-field bands. The third, or last, strong band can be attributed to a charge-transfer caused by the ligands, such as CN and SO_3.

Figures 1 and 2 show that the first spin-allowed band of dicyano cobalt(III) complexes of the

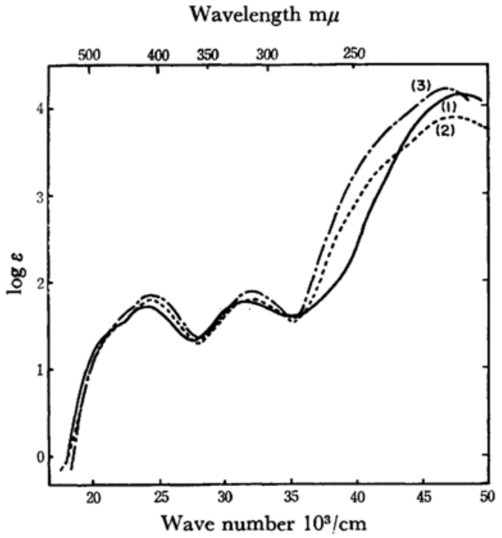

Fig. 1. The absorption spectra of the cyano cobalt(III) complexes with a *trans*-configuration: (1) —— *trans*-$[Co(CN)_2(NH_3)_4]NO_3 \cdot H_2O$; (2) ------ *trans*-$[Co(CN)_2en(NH_3)_2]Cl \cdot H_2O$; (3) —-—-— *trans*-$[Co(CN)_2en_2]NO_3$.

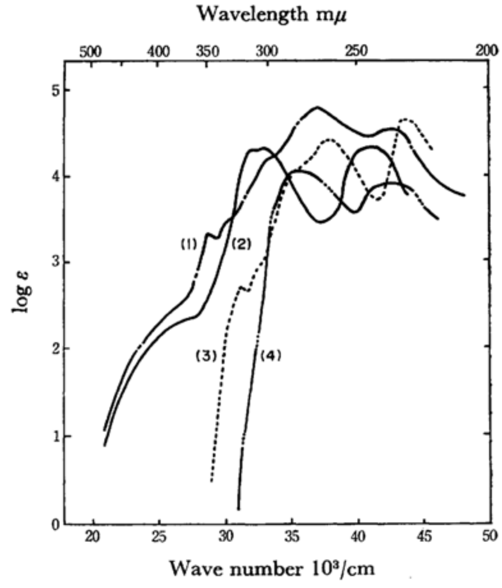

Fig. 3. The absorption spectra of the dicyano cobalt(III) complexes with 2,2′-dipyridyl and 1,10-phenanthroline, and of their ligands only: (1) —-—-— *cis*-$[Co(CN_2)phen_2]NO_3 \cdot 6H_2O$; (2) —— *cis*-$[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$; (3) ------ 1,10-phenanthroline; (4) —-—-—- 2,2′-dipyridyl in ethanol.

[*7] pn = propylenediamine; $NH_2CH(CH_3)CH_2NH_2$.

ethylenediamine-ammine series for *cis*- and *trans*-isomers shifts towards a shorter wavelength according to the order of the spectrochemical series, except in the case of the *cis*-$[Co(CN)_2(NH_3)_4]^+$ ion.[3]

In agreement with the spectra obtained by Konya *et al.*[3] and Muto *et al.*,[2] all the first bands of *trans*-isomers split into two components, while those of *cis*-ones do not show any splitting.

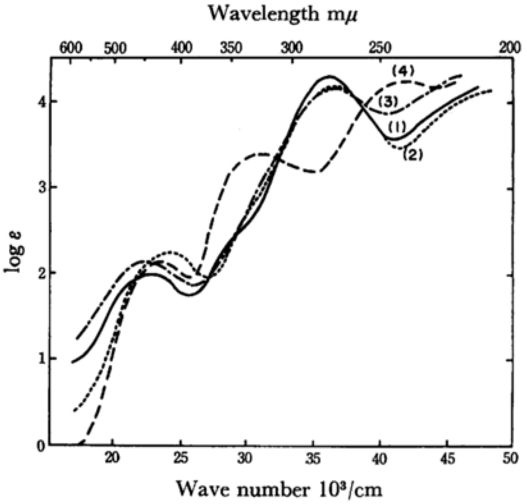

Fig. 4. The absorption spectra of the monocyano cobalt(III) complexes: (1) —— *trans*-$[Co(CN)(SO_3)en_2]$; (2) ------ *cis*-$[Co(CN)(SO_3)en_2]$; (3) –·–·– *cis*-$[Co(CN)(OH_2)en_2]SO_4\cdot 2H_2O$; (4) – – – – *cis*-$[Co(CN)(NO_2)en)_2]NO_3\cdot H_2O$.

TABLE 2. FREQUENCIES (cm^{-1}) OF THE C≡N STRETCHING VIBRATION FOR THE MIXED CYANO COBALT(III) COMPLEXES IN SOLID STATE

Compound	Frequency (cm^{-1})	
cis-$[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$	2190 s	2140 s
trans-$[Co(CN)_2(NH_3)_4]NO_3\cdot H_2O$	2130 s	
cis-$[Co(CN)_2en(NH_3)_2]NO_3$	2150 s	2130 s
trans-$[Co(CN)_2en(NH_3)_2]Cl\cdot H_2O$	2145 s	2080 w
cis-$[Co(CN)_2en_2]NO_3$	2150 s	2130 s
trans-$[Co(CN)_2en_2]NO_3$	2150 s	
cis-$[Co(CN)_2dip_2]NO_3\cdot 7H_2O$	2150 s	2130 s
cis-$[Co(CN)_2phen_2]NO_3\cdot 6H_2O$	2140 s	2130 s
trans-$Na[Co(CN)_2dg_2]\cdot 2H_2O$	2150 s	2130 s
trans-$K[Co(CN)_2dg_2]\cdot \frac{3}{2}H_2O$	2140 s	
trans-$(NH_4)_2[Co(CN)dg_2(SO_3)]\cdot 4H_2O$	2170 s	2140 m
trans-$[Co(CN)dg_2(NH_3)]\cdot \frac{1}{2}H_2O$	2140 s	
cis-$[Co(CN)(NO_2)en_2]NO_3\cdot H_2O$	2145 s	
cis-$[Co(CN)(NO_2)en_2]ClO_4$	2175 w	2128 m
cis-$[Co(CN)(SO_3)en_2]$	2173 m	2152 m
trans-$[Co(CN)(SO_3)en_2]$	2150 s	
$[Co(CN)(NH_3)_5](ClO_4)_2\cdot \frac{1}{2}H_2O$	2140 s	
cis-$[Co(CN)(OH_2)(NH_3)_4]Cl_2$	2170 w	2140 s
cis-$[Co(CN)_3en(NH_3)]\cdot H_2O$	2140 s	
$[Co(CN)_3dien]$	2140 s	2090 m
trans-$[Co(CN)dg_2(OH_2)]$	2176 s	

s=strong; m=medium; w=weak

Figure 3 shows the spectra of *cis*-dicyano-bis(2,2′-dipyridyl) and -bis(1,10-phenanthroline)cobalt(III) complexes, and of their ligands, respectively. The absorption spectrum of the latter complex agreed above all with that reported by Favini and Paglia[10] as a whole, but it did not necessarily coincide in detail, especially with regard to the presence of a small peak at around 27—29 kK.

Figure 4 shows the absorption spectra of the monocyano-cobalt(III) complexes prepared by the method using silver cyanide in water. The spectra quite agreed with those obtained by Ohkawa *et al.*[8] and by Chan and Tobe.[9]

Infrared Absorption Spectra. Table 2 lists the frequencies of the C≡N stretching vibrations measured for the mixed cyano cobalt(III) complexes.

Generally, a complex with a *trans*-configuration exhibits only one C≡N stretching band, while some of the complexes with a *cis*-configuration show two or more of their C≡N stretching bands split by the lowering of the symmetry, although there are some exceptions.

The differentiation between *cis*- and *trans*-isomers for bis(ethylenediamine)cobalt(III) complexes has been made in the infrared spectra of the CH_2-rocking vibrations in the region of 870—900 cm^{-1}. According to Baldwin,[24] the complexes with a *cis*-configuration show two bands, while those with a *trans*-structure exhibit one. Table 3 shows the frequencies of the CH_2-rocking vibrations in the regions measured.

Hughes and McWhinnie[25] suggested there is a correlation between the structure of the steric isomers and the complexity of that part of the

TABLE 3. FREQUENCIES (cm^{-1}) OF ABSORPTION BANDS IN THE REGIONS OF 870—900 cm^{-1} OF THE COMPLEXES OF $[Coen_2XY]$-TYPE

Compound	Frequency (cm^{-1})	
cis-$[Co(CN)_2en_2]NO_3$	893 m	887 sh
trans-$[Co(CN)_2en_2]NO_3$	896 s	
cis-$[Co(CN)_2en_2]Cl$	889 s	878 s
trans-$[Co(CN)_2en_2]Cl$	889 s	
cis-$[Co(CN)(SO_3)en_2]$	894 m	886 m
trans-$[Co(CN)(SO_3)en_2]$	892 m	
cis-$[Co(CN)Cl\ en_2]Cl\cdot H_2O$	889 s	877 s
cis-$[Co(CN)Br\ en_2]NO_3\cdot H_2O$	894 m	884 sh
cis-$[Co(CN)(NO_2)en_2]NO_3\cdot H_2O$	890 m	874 sh
trans-$[Co(SO_3)Cl\ en_2]$	883 m	

s=strong; m=medium; sh=shoulder band.

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24) M. E. Baldwin, *J. Chem. Soc.*, **1960**, 4369.

25) M. N. Hughes and W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **28**, 1659 (1966).

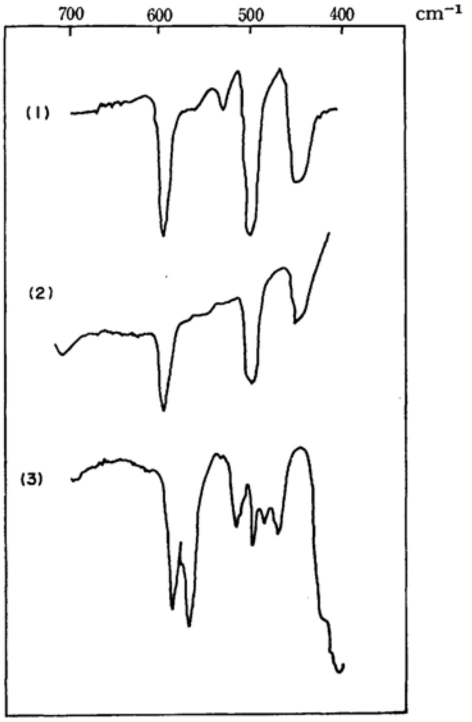

Fig. 5. Far-infrared spectra of dicyano cobalt(III) complexes in the region 400—700 cm^{-1}: (1) *trans*-[Co(CN)$_2$en(NH$_3$)$_2$]Cl·H$_2$O; (2) *trans*-[Co(CN)$_2$en$_2$]NO$_3$; (3) *cis*-[Co(CN)$_2$en$_2$]NO$_3$.

spectrum, in which most bands are assigned to some "metal-ligand" stretching vibrations, *i. e.*, in the far-infrared region of 620—450 cm^{-1}. According to them, no *trans*-complex of the bis(ethylenediamine)-type has more than three strong bands between 604 and 510 cm^{-1}, while all the *cis*-complexes have more than three strong bands between 608 and 503 cm^{-1}.

Figure 5 shows the IR pattern of *trans*-[Co(CN)$_2$-en(NH$_3$)$_2$]Cl·H$_2$O (a new complex) in comparison with those of the *cis*- and *trans*-dicyanobis(ethylenediamine)cobalt(III) complexes.

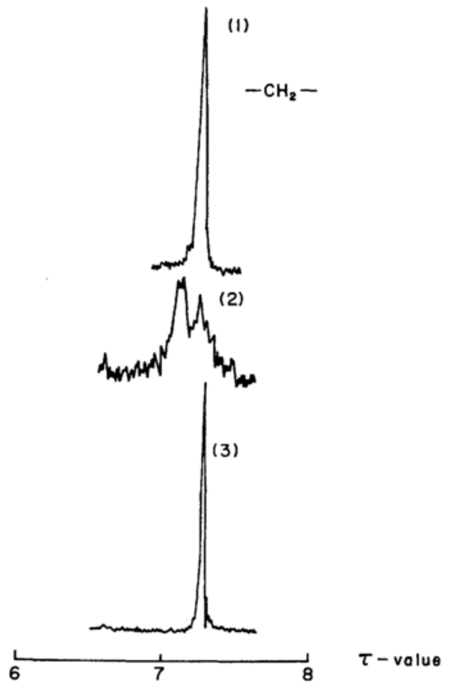

Fig. 6. The NMR spectra of dicyano cobalt(III) complexes obtained in 99.75% D$_2$O: (1) *trans*-[Co(CN)$_2$en$_2$]NO$_3$; (2) *cis*-[Co(CN)$_2$en$_2$]NO$_3$; (3) *trans*-[Co(CN)$_2$en(NH$_3$)$_2$]Cl·H$_2$O.

Nuclear Magnetic Resonance Spectra. Figure 6 indicates the proton spectra of some dicyano complexes obtained in D$_2$O. The complex with a *trans*-configuration exhibits only one band, while those of *cis*-isomers show two or more bands. This result might be used for the differentiation of the *cis*- and *trans*-pair of ethylenediamine complexes.

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