# A Preparation Method of Dicyano-Cobalt(III) Complexes using Silver Cyanide

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The $CN^-$ ion is located at the end position of the spectrochemical series and has the strongest coordinating ability of cobalt(III) complexes of the Werner-type, while $Cl^-$ ion is located above this. Such a difference in bonding character between them is the reason why direct substitution1) is difficult. For example, the $[Co(CN)_2en_2]^+$ ion can be obtained only *via* the $[Co(S_2O_3)_2en_2]^-$ ion.2)

In the present report, however, the substitution of Cl-ligands has been found possible even in water solution under the condition that $CN^-$ ions are present in a very dilute concentration. For this purpose, we have adopted silver cyanide, the solubility of which in water is $2.2 \cdot 10^{-5}$ g/100 g water (20°C), and succeeded in obtaining directly dicyano-cobalt(III) complexes including new compounds, *cis*-$[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$ and *cis*-$[Co(CN)_2phen_2]NO_3 \cdot 6H_2O$.3)

**Preparation of cis-$[Co(CN)_2en_2]NO_3$.** To a suspension of *trans*-$[CoCl_2en_2]NO_3$(20 g) in 200 m*l* of water were added 20 g of AgCN powder. The paste-like mixture was further diluted with 500 m*l* of water after half an hour and heated on a water bath (90°C) for three hours. The solution was filtered, and the yellow filtrate obtained was concentrated on a water bath by evaporation and allowed to stand. On cooling, yellow crystals separated from solution. The crude product was recrystallized once from hot water. Found: Co, 19.77; C, 24.09; N, 33.59; H, 5.83%. Calcd for $[Co(CN)_2en_2]NO_3$: Co, 20.10; C, 24.58; N, 33.44; H, 5.50%.

The perchlorate was similarly prepared by using *trans*-$[CoCl_2en_2]ClO_4$ as the starting complex instead of the nitrate. Found: Co, 17.91; C, 21.63; N, 25.17; H, 4.90%. Calcd for $[Co(CN)_2en_2]ClO_4$: Co, 17.82; C, 21.80; N, 25.42; H, 4.88%.

**Preparation of cis-$[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$.** Dicyanobis(2,2′-dipyridyl)cobalt(III) complex was prepared by the following method: Fifteen grams of *trans*-$[CoCl_2dip_2]NO_3$4) were mixed with AgCN (10g) and a few milliliters of water. The paste-like mixture was allowed to stand for a while and further diluted with 500 m*l* of water. The mixture was heated on a water bath (70—80°C) for an hour and filtered. The residue was repeatedly extracted with hot water. The extracted solution and filtrate were added together and concentrated by evaporation. On cooling, lustrous needle-shaped yellow crystals deposited from solution, which were then filtered and washed with cold water, ethanol and ether. The product was recrystallized once from hot water. Found: Co, 11.98; C, 54.19; N, 19.95; H, 3.41%. Calcd for $[Co(CN)_2dip_2]NO_3$: Co, 12.14; C, 54.45; N, 20.20; H, 3.32%.

**Preparation of cis-$[Co(CN)_2phen_2]NO_3 \cdot 6H_2O$.** Twenty grams of *trans*-$[CoCl_2phen_2]NO_3$5) were treated with 15 g of AgCN in 500 m*l* of water at 60—70°C for an hour. Silky yellow crystals deposited from the filtrate. Found: Co, 10.87; C, 58.31; N, 18.11; H, 3.38%. Calcd for $[Co(CN)_2 \cdot phen_2]NO_3$: Co, 11.05; C, 58.55; N, 18.38; H, 3.02%. The NMR spectra in 99.75% $D_2O$ indicated that the complexes were cis-isomers, as shown in Fig. 1.

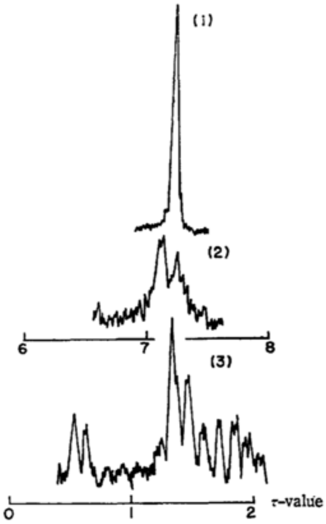

Fig. 1. The NMR spectra of dicyano-cobalt(III) complexes obtained in 99.75% $D_2O$; (1) *trans*-$[Co(CN)_2en_2]NO_3$, (2) *cis*-$[Co(CN)_2en_2]NO_3$, (3) *cis*-$[Co(CN)_2dip_2]NO_3 \cdot 7H_2O$.

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