# A Method of Preparing Dicyano Cobalt(III) Complexes with a *Trans*-Configuration

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Recently, Konya *et al.*1) reported the preparation of cyano-ammine and amine cobalt(III) complexes in a water solution, while Yoneda *et al.*2) independently described the synthesis of the dicyanobis(ethylenediamine)cobalt(III) complex in dimethyl sulfoxide (DMSO).

In the present communication, the step-by-step substitution method *via* the monocyanomonochloro complex of the [Co(CN)ClN$_4$]-type has been attempted in DMSO and found to be suitable for replacing a chloro-ligand with a CN$^-$ ion without disrupting the complex. This method has been used in the preparation of *trans*-[Co(CN$_2$)-(NH$_3$)$_4$]NO$_3$·H$_2$O and *trans*-[Co(CN)$_2$en(NH$_3$)$_2$]Cl·H$_2$O (a new compound). The direct substitution in DMSO *via* the dichloro complex was not adequate for obtaining dicyano-ammine complexes, since the substitution was always accompanied by a disproportionation.

**Preparation of *trans*-[Co(CN)$_2$(NH$_3$)$_4$]NO$_3$·H$_2$O.** The dimethyl sulfoxide (500 m*l*) in which 3.00 g of KCN had been completely dissolved at 60°C was transferred into a three-necked flask equipped with a reflux condenser and a mechanical stirrer. To this solution were added 11.7 g of *trans*-[Co(CN)Cl(NH$_3$)$_4$]NO$_3$.3) The suspension was heated on a water bath at 70—85°C for three hours. After the solution had been allowed to stand overnight, orange-yellow crystals separated from the solution, they were then filtered and washed with acetone. The crude complex was recrystallized from hot water. 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$_3$·H$_2$O: Co, 22.74; C, 9.27; N, 37.84; H, 5.45%.

**Preparation of *trans*-[Co(CN)$_2$en(NH$_3$)$_2$]Cl·H$_2$O.** The complex was prepared according to the following reaction steps: *trans*-[Co(CN)(SO$_3$)-(NH$_3$)$_4$]·2H$_2$O4) $\xrightarrow{\text{en}}$ *cis*-[Co(CN)(SO$_3$)en-(NH$_3$)$_2$] $\xrightarrow{\text{HCl}}$ *cis*-[Co(CN)Clen(NH$_3$)$_2$]Cl $\xrightarrow[\text{in DMSO}]{\text{KCN}}$ *trans*-[Co(CN)$_2$-en(NH$_3$)$_2$]Cl·H$_2$O. (1) The water solution (100 m*l*) containing 30 g of *trans*-[Co(CN)(SO$_3$)(NH$_3$)$_4$]·2H$_2$O4) was treated with ethylenediamine (8.6 g) at 80°C for two hours. The starting complex was once dissolved completely in a solution, evolving ammonia; then again deeper-colored brown crystals deposited from the solution. This reaction mixture was further heated for four hours, filtered, and washed with hot water, ethanol, and ether. The product of *cis*-[Co(CN)(SO$_3$)en(NH$_3$)$_2$] (12 g) was used for the next reaction without further purification, since it is insoluble in water. (2) Thirty grams of *cis*-[Co(CN)(SO$_3$) en(NH$_3$)$_2$] were treated with 300 m*l* of concentrated HCl at 80—85°C for five hours. Red crystals of *cis*[Co(CN)Clen(NH$_3$)$_2$]Cl were obtained by adding 200 m*l* of ethanol to the solution under ice cooling. (3) Analogously to the case of the dicyanotetra-ammine complex, 6 g of *cis*-[Co(CN)Clen(NH$_3$)$_2$]Cl were continuously stirred in small portions into 300 m*l* of dimethyl sulfoxide containing 2.3 g of KCN, and then the mixture was heated at 80°C for an hour. The yellow solution soon became muddy as the reaction proceeded, it was filtered and washed with acetone. The crude product 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)$_2$en(NH$_3$)$_2$]Cl·H$_2$O: Co, 22.79; C, 18.58; N, 32.49; H, 6.24%.

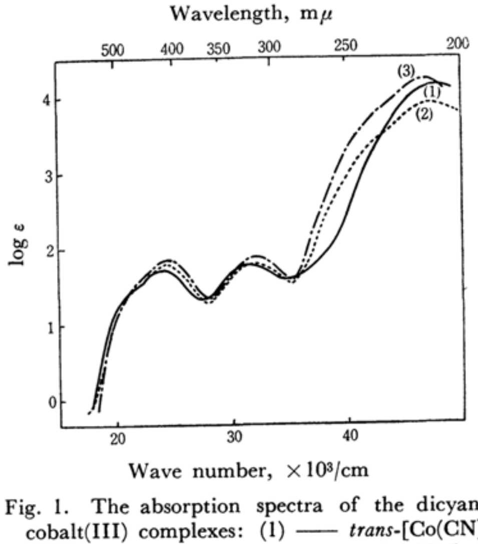

Fig. 1. The absorption spectra of the dicyano-cobalt(III) complexes: (1) —— *trans*-[Co(CN)$_2$-(NH$_3$)$_4$]NO$_3$·H$_2$O; (2) ...... *trans*-[Co(CN)$_2$en-(NH$_3$)$_2$]Cl·H$_2$O; (3) — - — *trans*-[Co(CN)$_2$en$_2$]-NO$_3$.

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