SHORT COMMUNICATIONS

Preparation of the Dicyano-bisethylenediamine Cobalt(III) Complex by the Use of a Non-aqueous Solvent

Hayami YONEDA, Tetsuo BABA*[1] and Masayuki MUTO
Chemistry Department, Wakayama University, Masagocho, Wakayama

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Two peculiarities may be noticed about the preparation of $[\mathrm{Co(CN)_2}\mathit{en}_2]^+$. One is the fact that only the cis-form is known. The other is the way of its preparation. Usually, diacido-bisethylenediamine complexes, $[\mathrm{CoX_2}\mathit{en}_2]^+$ can be prepared from *trans*-$[\mathrm{CoCl_2}\mathit{en}_2]^+$ by the substitution of X for Cl. However, the cyano mixed complex can not be prepared directly from *trans*-$[\mathrm{CoCl_2}\mathit{en}_2]^+$, but is obtained only *via trans*-$[\mathrm{Co(S_2O_3)_2}\mathit{en}_2]^-$. When the dichloro complex is treated with potassium cyanide in an aqueous solution, disproportionation occurs to produce $[\mathrm{Co}\mathit{en}_3]^{3+}$ and $[\mathrm{Co(CN)_6}]^{3-}$. This fact indicates that the incoming cyano groups expel the other kinds of ligands from the coordination sphere. On the other hand, it is generally known that cobalt(III) ammine complexes are quite labile in an alkaline solution. In the preparation of the cyano mixed complex the reaction mixture is fairly alkaline due to the hydrolysis of the added potassium cyanide. This alkalinity of the solution might make the complex labile and lead it to disproportionation.

In our previous report[1] on the decomposition of cobalt(III) ammines, the proton dissociation mechanism was proposed. In that mechanism, it was assumed that, in the decomposition process, the proton dissociation from the coordinated $\mathrm{NH_3}$ takes place first, and that then the $\mathrm{NH_2}^-$ thus produced left the coordination sphere. A similar proton dissociation may be considered in the present case. Therefore, it was felt necessary to work under conditions where the proton dissociation can not occur. To fulfill these conditions, we tried to use dimethylsulfoxide as a solvent and succeeded in obtaining the cyano diamine mixed complex directly from the dichloro complex. The details of the preparation will be described below.

Six grams of NaCN were dissolved in 70 m*l* of dimethylsulfoxide on a boiling-water bath. With this amount of solvent, however, some of the cyanide remained undissolved. Paying no attention to such undissolved cyanide, 10 g of the acid-free *trnas*-$[\mathrm{CoCl_2}\mathit{en}_2]\mathrm{NO_3}$ were added in small portions under constant stirring and heating. The green color of the solution gradually changed into the characteristic yellow color of the *cis*-$[\mathrm{Co(CN)_2}\mathit{en}_2]^+$ complex. The reaction mixture was then placed on a boiling-water bath for one hour in order to complete the reaction. After one hour's heating and stirring, the green complex disappeared. At the end of the reaction, the solution became reddish orange, and a large amount of an orange powder was deposited. After the reaction mixture had been cooled to room temperature, the precipitate was filtered, washed with ethanol, and dried. The crude product was orange. Yield, 7 g. When this crude product was recrystallized from hot water, yellow crystals were obtained. Yield, 4 g.

The absorption spectrum of the product coincided completely with that of *cis*-$[\mathrm{Co(CN)_2}\mathit{en}_2]\mathrm{Cl}$.[2] Found: C, 27.01; H, 5.32; N, 31.64%. Calcd for $[\mathrm{Co(CN)_2}\mathit{en}_2]\mathrm{Cl}$: C, 27.03; H, 5.29; N, 31.53%. The color of the crude product varied from orange to orange yellow. Whether or not it contains the trans-form of the complex is now being investigated. The details of the results will be reported later.

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*[1] On leave from Minoshima High School, Minoshima, Wakayama.

[1] H. Yoneda, This Bulletin, **31**, 74 (1958).

[2] K. Ohkawa, J. Fujita and Y. Shimura, This Bulletin, **38**, 66 (1965).