On the Composition of the Pentacyanocobaltate(I) Complex

Nobufumi Maki and Yukio Ishiuchi

Department of Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu

(Received February 16, 1971)

The question of the composition and structure of the pentacyanocobaltate(I) ion formed by the reduction of pentacyano-cobaltate(II) and -cobaltate(III) complexes still remains in a controversial state in spite of a number of works done on this problem.[1] Nowadays, however, the $[Co^{I}(CN)_5H]^{3-}$ formula has been widely accepted and used as the most possible structure since Griffith and Wilkinson[2] proposed it on the basis of the proton NMR spectrum. In addition, it has already been established that the reaction between $[Co^{I}(CN)_5]^{4-}$ and H^+ can proceed in water.[3]

In the present study, the stoichiometric relation between $[Co^{I}(CN)_5]^{4-}$ and H^+ was determined to be always 2:1, suggesting a dimeric configuration of the pentacyanocobaltate(I) complex in solution. That is, the findings that both the polarographic reductions of Co(III)→Co(I) and of $2\ H^+ \rightarrow H_2$ can take place simultaneously at -1.75 V (*vs.* SCE) at the dropping mercury electrode (DME)[4] suggested to us the idea of employing the diffusion currents of both waves to follow the reaction between $[Co^{I}(CN)_5]^{4-}$ and H^+ by means of amperometric titrations.

The titrations of the parent complexes, $K_m[Co(X)(CN)_5]$, were carried out with 0.2 N HCl under a stream of nitrogen at the constant potential (-1.75 V) at which the current had reached a limiting plateau, indicating the formation of the $[Co^{I}(CN)_5]^{4-}$ ion at the DME, where the ligand, X, denotes the ion, $S_2O_3^{2-}$, SO_3^{2-}, N_3^-, NO_2^-, SCN^-, I^-, Br^-, or Cl^-, or the molecule, OH_2. The neutral solution to be titrated was prepared by dissolving the crystals of the complex at 10^{-2} M in a 0.5 M Na_2SO_4 solution which had been deaerated by nitrogen. As one example, Figure 1 illustrates the titration of the $[Co^{I}(CN)_5]^{4-}$ ion formed by the reduction of the $K_4[Co(S_2O_3)(CN)_5]$ complex with 0.2 N HCl. At the beginning of titration, the current remains constant while the H^+ ions are being consumed by the $[Co^{I}(CN)_5]^{4-}$ to be titrated. The end-point is indicated by the beginning of an increase in the reduction wave of H^+ ions; the new current corresponds to the reduction of excess hydrogen ions. The following reaction schemes are considered to be the most plausible:

$$\begin{tikzcd}
2[Co^{III}(S_2O_3)(CN)_5]^{4-} \arrow[r, "2e"] & 2[Co^{I}(S_2O_3)(CN)_5]^{6-} \arrow[d] \\
 & 2[Co^{I}(CN)_5]^{4-} + 2S_2O_3^{2-} \arrow[d] \\
 & [Co^{I}(CN)_5\text{-}H\text{-}Co^{I}(CN)_5]^{7-}.
\end{tikzcd}$$

A blank test was carried out, in advance, individually for 0.5 M Na_2SO_4, 0.01 M $Na_2S_2O_3$[5], 0.01 M NaBr[5], and so on, but a straight line without a break was obtained for each solution; the $(2H^+ \rightarrow H_2)$ current increased linearly at -1.75 V when 0.2 N HCl (0—1.5 m*l*) was added, indicating that no reaction of capturing H^+ ions takes place between them.

The sixth ligand, such as $S_2O_3^{2-}$, was confirmed by using a Kalousek commutator[6] to be released from the $[Co^{I}(X)(CN)_5]^{n-}$ ion at the DME.

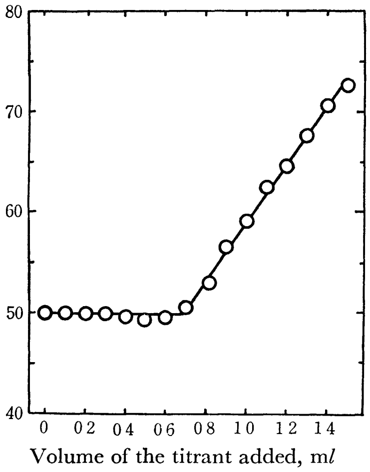

Fig. 1. Amperometric titration curve of the $[Co(S_2O_3)(CN)_5]^{4-}$ ion (35 m*l*) with 0.2N HCl (f=1.173) at -1.75V (*vs.* SCE). The concn. of the complex: 10^{-2}M in 0.5M Na_2SO_4 (25°C).

Table 1. Results of amperometric titrations

Compound	Volume of HCl added at equiv. point m*l*	Mole of HCl consumed at equiv. point	Ratio of $[Co^{I}(CN_5)]^{4-}$/ H^+ at equiv. point
$K_4[Co(S_2O_3)(CN)_5]$	0.69	1.62×10^{-4}	2.16
$K_4[Co(SO_3)(CN)_5]\cdot 3H_2O$	0.70	1.64×10^{-4}	2.13
$K_3[Co(N_3)(CN)_5]\cdot 2H_2O$	0.71	1.67×10^{-4}	2.11
$K_3[CoBr(CN)_5]$	0.67	1.57×10^{-4}	2.22

Table 1 summarizes some of the results. Thus, the molar ratio of the $[Co^{I}(CN)_5]^{4-}$ ion to H^+ was approximately 2:1, irrespective of the kind of the ligand, X.

This result, combined with the evidence [2] of the existence of a direct linkage between the metal and H^+, suggests that the pentacyanocobaltate(I) complex takes a dimeric structure through a cobalt-hydrogen linkage, such as has been mentioned above.

---

1) *E.g.*, J. Kwiatek, "Catalysis Review," Vol. 1, ed. by H. Heinemann, Marcel Dekker, New York, N. Y. (1968), pp. 38—152.

2) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, **1959**, 2757.

3) J. Hanzlík and A. A. Vlček, *Chem. Commun.*, **1969**, 47.

4) N. Maki, J. Fujita, and R. Tsuchida, *Nature*, **183**, 458 (1959).

5) The ionic strength was adjusted to a unit by adding Na_2SO_4.

6) M. Kalousek, *Collect. Czech. Chem. Commun.*, **13**, 105 (1948).