CHEMISTRY LETTERS, pp. 217-220, 1977. Published by the Chemical Society of Japan

REACTION OF PENTACYANOCOBALTATE(II) WITH THALIUM(I) CHLORIDE

Yoshiharu HISAMATSU and Masaakira IGUCHI
Department of Chemistry, Faculty of Science, Science University of Tokyo
Kagurazaka, Shinjuku-ku, Tokyo 162

Hydrogen uptake of a solution containing pentacyanocobaltate(II) ions was found to be inhibited by Tl(I) ions. It was confirmed by a rapid-scan spectroscopic method that pentacyanocobaltate(II) ions react with Tl(I) ions in an aqueous solution to give the dimeric complex, $[(CN)_5CoTlCo(CN)_5]^{5-}$. The dimeric complex containing Co-Tl-Co linkage was successfully isolated as a solid state.

Hydrogen uptake of a solution containing pentacyanocobaltate(II) ions, $[Co(CN)_5]^{3-}$, prepared in a hydrogen atomosphere, is accelerated in the presence of metal cations of such metals as alkali and alkali earth, etc.[1)] Univalent cations, such as K^+, Na^+ and Li^+, greatly accelerate the H_2 uptake, but thalium ions inhibit it. Crouch et al.[2)] suggested that Tl(I) ions react with $[Co(CN)_5]^{3-}$ in an aqueous solution to give the dimeric complex, $[(CN)_5CoTlCo(CN)_5]^{5-}$. We confirmed the fact that the dimeric complex was formed by the reaction of $[Co(CN)_5]^{3-}$ with Tl(I) ions. The dimeric complex is considered to inhibit the H_2 uptake.

Further, study has been made of the isolation of the dimeric complex. It was found that low temperature and certain large counterions give suitable conditions for the stability and isolation of the dimeric complex. A relatively stable solid complex containing Co-Tl-Co linkage was successfully isolated.

Formation of the dimeric complex, $[(CN)_5CoTlCo(CN)_5]^{5-}$.

The complex was formed by simultaneously mixing a deaerated solution of $CoCl_2$, KCN (molar ratio $[Co^{2+}] : [CN^-] = 1 : 5$) and TlCl. The spectrum of the complex was measured by a stopped- flow method with a rapid-scan spectrophotometer, Hitachi Manufacturing Co., model RSP-2. Figure 1 shows how the spectrum changes with time before it stabilizes. Pentacyanocobaltate(II) ions are rapidly formed by the reac-

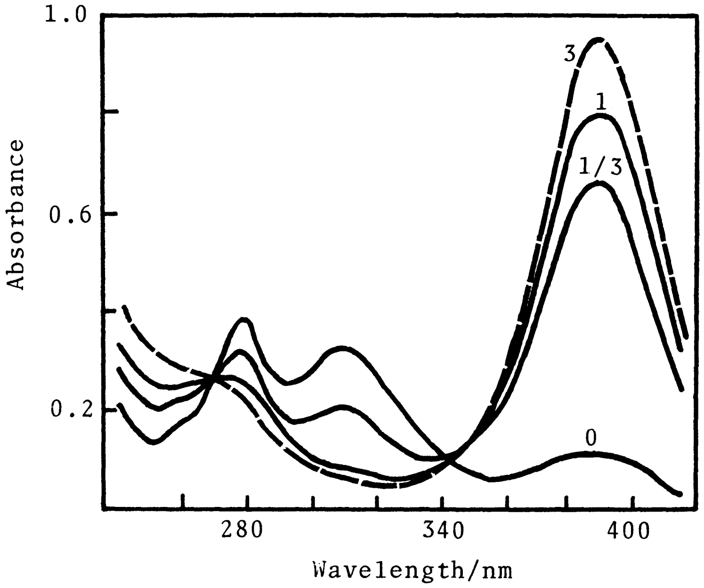

Figure 1.
Time dependence of the spectrum of a solution containing $CoCl_2$, KCN and TlCl. The number on each curve is the time in seconds after mixing the above three reagents.
Initial concentration:
[Co] = 1.0 x 10^{-4} M
Molar ratio:
[CN]/[Co] = 5, [Tl]/[Co] = 0.5

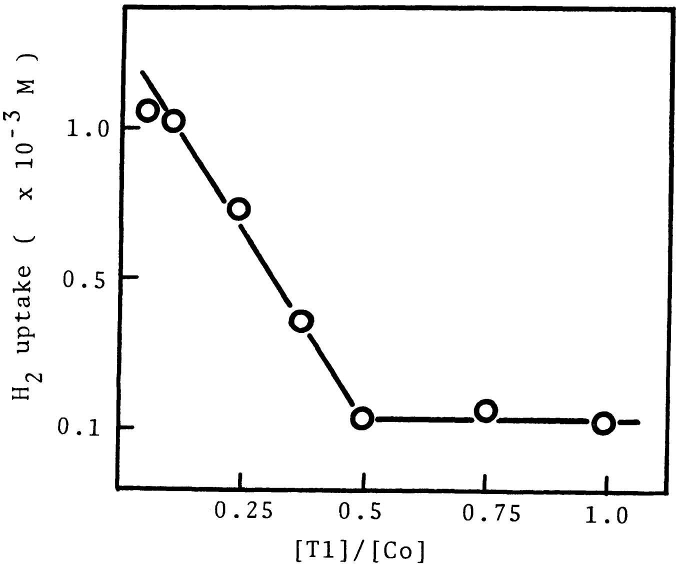

Figure 2.
Effect of the molar ratio, [Tl]/[Co] , on the H_2 uptake by a cyanocobaltate (II) solution at 25°C.
Initial concentration:
[Co] = 5 x 10^{-3} M
Molar ratio:
[CN]/[Co] = 5

tion of Co(II) ions with CN^- ions and then react with Tl(I) ions to form the dimeric complex characterized by an intense charge transfer band at 389 nm, ε_{molar}= ca. 2 x 10^4 $cm^{-1}M^{-1}$. The isosbestic points are observed approximately at 270 nm and 350 nm.

The high value of the molar extinction coefficient at 389 nm supports that metal-metal bonded configuration exists. The position and intensity of the absorption band are very much similar to those of the dimeric complex suggested by Crouch et al.[2) and to those of the two dimeric complexes with tin(II) chloride[3) and mercury(II)[4) reported by Lim and Vlček et al. When the concentration is lower than 10^{-3}M, the slow decrease with time in the absorbance at 389 nm shows the decomposition of the dimeric complex. Further, the reaction of pentacyanocobaltate(II) ions with Tl(I) ions in more concentrated solutions with various molar ratios was followed by measuring the H_2 uptake with a Warburg manometer. As is shown in Figure 2, the H_2 uptake reaches the lowest value at a ratio of Tl(I) ions to $[Co(CN)_5]^{3-}$ of 0.5 and remains constant. This indicates a consumption of 1 mole of Tl(I) ions for 2 moles of $[Co(CN)_5]^{3-}$. These results suggest that the over-all reactions are represented by

$$Co^{2+} + 5CN^- \longrightarrow [Co(CN)_5]^{3-} \qquad (1)$$

$$2[Co(CN)_5]^{3-} + Tl^+ \longrightarrow [(CN)_5CoTlCo(CN)_5]^{5-} \qquad (2)$$

Isolation of the dimeric complex, $[(CN)_5CoTlCo(CN)_5]^{5-}$.

An aqueous solution of TlCl was added to a deaerated aqueous solution of $CoCl_2$ and KCN (molar ratio $[Co^{2+}]$: $[CN^-]$ = 1 : 5) in a reaction vessel cooled with ice-water in nitrogen atomosphere, until the molar ratio $[Tl^+]$: $[Co^{2+}]$ in the mixture exceeded 1 : 2. A deaerated aqueous solution of CsCl and then methanol were added to the resulting solution immediately after the change in color of the solution from the original green to dark brown. The orange crystals which precipitated was filtered and washed with an ice-cooled and deaerated water-methanol mixture (1 : 1), and then with methanol under nitrogen and was dried in vacuo.

Analyses of metallic elements, K, Cs, Co and Tl, of the solid were made with an atomic absorption spectrophotometer and a flame spectrophotometer. The results are shown in table 1. The approximate molar ratio of Co to C to N to Tl was 2.2 : 9.2 : 9.2 : 1.0 . The infrared spectra (KBr discs) of the solid in the C-N streching region showed a strong band at 2103 cm^{-1} and two shoulders at 2122 cm^{-1} and 2135 cm^{-1}. Accordingly, two $Co(CN)_5$ groups are probably connected each other by one thalium atom. This is supported by the fact that the absorption spectrum of the aqueous solution of the solid shows a strong band at 389 nm, the same wave length as that of the complex studied in solutions. From the analytical results, the formula of the solid is calculated to be $K_{1.5}Cs_{3.2}[Co_{2.2}(CN)_{9.2}Tl]\cdot 2.9H_2O$.

This suggests that the general formula of the solid is $K_xCs_y[Co_2(CN)_{10}Tl]\cdot 3H_2O$, in which the relation x + y = 5 holds from the conditions of electrical neutrality.

Table 1. Analytical results

Element	K	Cs	Co	Tl	C	N	H
Found(%)	5.20	39.27	11.89	19.10	10.23	11.89	0.53

The solid is stable in air for several months and decomposes above ca. 100°C.

References and Notes

1) M. Iguchi, Nippon Kagaku Zasshi, 63, 634 (1942).
G. A. Mills, S. Weller, and A. Wheeler, J. Phy. Chem., 63, 403 (1959).
N. K. King and M. E. Winfield, J. Am. Chem. Soc., 80, 2060 (1958), 83, 3366 (1961).
B. De Vries, J. Catalysis, 1, 489 (1962).
O. Piringer and A. Farcas, Z. Phys. Chem. N. F., 46, 190 (1965).
J. M. Pratt and R. J. P. Williams, J. Chem. Soc. (A), 1967, 1291.
2) E. C. C. Crouch and J. M. Pratt, Chem. Commun., 1969, 1243.
3) A. A. Vlček and F. Basolo, Inorg. Chem., 5, 156 (1966).
4) H. S. Lim and F. C. Anson, ibid., 10, 103 (1971).
5) This solid is extremely soluble in water, but difficult to recrystallise because of its decomposition and air-oxidation in an aqueous solution.

(Received December 8, 1976)