

# The Polarography of the Tricyano Cobalt(III) Complexes

Nobufumi MAKI and Kuwako OHKAWA\*

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

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Previously, several dicyano complexes of the  $[\text{Co}(\text{CN})_2\text{N}_4]$  type have been found to undergo the step-by-step reduction of  $\text{Co(III)} \rightarrow \text{Co(II)} \rightarrow \text{Co(I)} \rightarrow \text{Co(0)}$  in DMSO (dimethyl sulfoxide) at the dropping mercury electrode (DME), where  $\text{N}_4$  represents four nitrogen donors, which may come from two ligands, en, dip, and phen, or from four ammonia ligands.<sup>1)</sup> However, it is not yet clear how the tricyano cobalt(III) complexes behave in DMSO. The present communication is concerned with the behavior of the *fac*- and *mer*-tricyano-diethylenetriaminecobalt(III) complexes<sup>2)</sup> in DMSO.

These complexes were prepared by treating the  $[\text{Co}(\text{S}_2\text{O}_3)_3\text{dien}]^{3-}$  ion with KCN. That is, an aqueous solution (20 ml) containing 8 g of KCN was stirred, drop by drop, into a mixture of  $[\text{CoCl}_3\text{dien}]$  (10 g) and  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (29.6 g) dissolved in water (70 ml). The reaction below  $5^\circ\text{C}$  yielded the *mer*-complex, while that at  $70\text{--}80^\circ\text{C}$  produced the corresponding *fac*-complex. The former was purified by concentrating the solution of the complex *in vacuo* at room temperatures, and the latter, by crystallizing it from hot water ( $80^\circ\text{C}$ ). The purity was ascertained by elementary analyses and by studying the absorption spectra.

One would expect that the tricyano cobalt(I) complex would be present upon reduction in DMSO. Indeed, we did find that the *fac*- and *mer*- $[\text{Co}^{\text{III}}(\text{CN})_3\text{dien}]$  complexes give rise to two well-defined waves at DME in DMSO (100%) containing 0.1 M tetraethylammonium perchlorate; the steps, each corresponding to a gain of one electron, represent the reduction of  $\text{Co(III)} \rightarrow \text{Co(II)}$  and that of  $\text{Co(II)} \rightarrow \text{Co(I)}$ , while no further reduction to the metal takes place over the potential range between 0 and  $-2.7\text{ V}$  (*vs.* SCE). A linear-dependence of the current upon the concentration of the complex was confirmed over the range between  $5 \cdot 10^{-4}$  and  $10^{-2}\text{ M}$  for the *fac*-isomer, and over the range between  $5 \cdot 10^{-4}$  and  $3.5 \cdot 10^{-3}\text{ M}$  for the *mer*-isomer, since the solubility of the latter in DMSO is much smaller than the former. The current of each step was proportional to the square root of the mercury pressure on DME; the values of  $i_d/\sqrt{h_{\text{corr}}}$  were constant, irrespective of the mercury pressure, suggesting a diffusion-controlled feature.

Figure 1 illustrates the current-potential curves of the tricyano and dicyano complexes measured under the same experimental conditions. Thus, the wave-height is roughly proportional to the number of electrons participating in the electrode processes, the half-wave

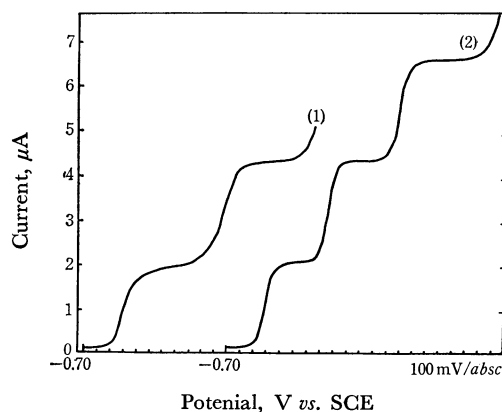


Fig. 1. Current-potential curves obtained at  $10^{-3}\text{ M}$  in DMSO containing  $0.5\text{ M }[(\text{C}_2\text{H}_5)_4\text{N}]\text{ClO}_4$  ( $25^\circ\text{C}$ ): (1) *mer*- $[\text{Co}(\text{CN})_3\text{dien}]$ ; (2) *trans*- $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$ .

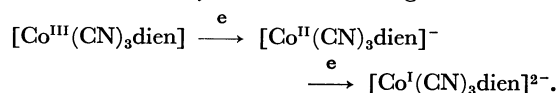
TABLE 1. HALF-WAVE POTENTIALS OF MIXED CYANO COBALT(III) COMPLEXES IN DMSO CONTAINING  $0.1\text{ M }[(\text{C}_2\text{H}_5)_4\text{N}]\text{ClO}_4$  ( $25^\circ\text{C}$ )

Compound	1st Wave $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{II}}$	2nd Wave $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{I}}$	3rd Wave $\text{Co}^{\text{I}} \rightarrow \text{Co}^0$
<i>fac</i> - $[\text{Co}(\text{CN})_3\text{dien}] \cdot \text{H}_2\text{O}$	-1.37	-1.83	no reduction
<i>mer</i> - $[\text{Co}(\text{CN})_3\text{dien}] \cdot 3\text{H}_2\text{O}$	-1.09	-1.74	no reduction
<i>cis</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$	-0.95	-1.48	-1.99
<i>trans</i> - $[\text{Co}(\text{CN})_2\text{en}_2]\text{NO}_3$	-0.97	-1.52	-1.99
<i>cis</i> - $\text{Na}[\text{Co}(\text{CN})_4\text{en}] \cdot 7/2\text{H}_2\text{O}$	-1.59	-1.78	no reduction

V *vs.* SCE

potentials of which are summarized in Table 1. Here, it is of interest to note that a great difference was found to exist in the half-wave potentials of both waves between the *fac*- and *mer*-isomers. The values for the first and the second steps of the *fac*-isomer lie at potentials more negative than those for the *mer*-isomer by 280 and 90 mV respectively, indicating that the *fac*-cobalt(III) and cobalt(II) species are more stable towards the electrochemical reduction than are the *mer* ones. Such a large difference in reduction potentials has never yet been reported for steric isomers. Inversely, this result can be invoked to emphasize the larger stability of the resulting tricyano cobalt(I) complex with a *mer* form. The three cyanides located on coplanar coordination sites (*mer* form) may contribute much more to the stability of the univalent cobalt than those on a non-planar configuration do, as can be inferred from a comparison of *cis*- and *trans*-complexes with cyanides.<sup>3)</sup>

The net processes of the electrode reaction can be fully interpreted in terms of the "inert-inert"-type reduction without any structural changes as follows:



3) N. Maki and K. Yamamoto, This Bulletin, **43**, 2450 (1970).

\* Present address: Department of Chemistry, Faculty of Engineering, Tokushima University, Tokushima.

1) N. Maki, This Bulletin, **42**, 3617 (1969).

2) The *mer*- $[\text{Co}(\text{CN})_3\text{dien}]$  complex was reported by Konya *et al.*, while the *fac*-isomer was first prepared by Yoneda; H. Nishikawa and M. Shibata, *Inorg. Chem.*, **7**, 1165 (1968); H. Yoneda, Proc. 14th Symposium on Coord. Chem. Japan, (1963), p. 33.