CHEMISTRY LETTERS, pp. 1949 - 1952, 1984.

ELECTRODE REACTIONS OF THIOCYANATOPENTACYANOCOBALTATE(III) COMPLEX

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It has been difficult to judge decisively whether the $[Co^{II}(CN)_5]^{3-}/[Co^{I}(CN)_5]^{4-}$ system is nernstian or not, since the $[Co^{I}(CN)_5]^{4-}$ ion extracts a proton from water to dimerize itself into an electroinactive dimeric species, $[\{Co^{I}(CN)_5\}_2H]^{7-}$. The present study affirmed that a completely reversible electrode reaction of the Co(II)/Co(I) couple proceeds in 100% dimethyl sulfoxide. The standard electrode potential of the $[Co^{II}(CN)_5]^{3-}/[Co^{I}(CN)_5]^{4-}$ couple was - 1.272 V vs. NHE at (25 ± 0.1) °C ($\Delta G° = + 122.7$ kJ mol^{-1}).

Pentacyanocobaltates(III), $[Co^{III}(CN)_5X]^{3-}$ ($X = I^-$, Br^-, Cl^-, and SCN^-), are reduced at the dropping mercury electrode (DME) to the $[Co^{II}(CN)_5]^{3-}$ species and then to $[Co^{I}(CN)_5]^{4-}$. The latter undergoes in aqueous solutions a protonation-dimerization to form an electroinactive dimeric species, $[(CN)_5Co^{I}\text{-}H\text{-}Co^{I}(CN)_5]^{7-}$.[1,2] According to Hanzlík and Vlček,[3] the $[Co^{II}(CN)_5]^{3-}/[Co^{I}(CN)_5]^{4-}$ couple in aqueous 12 mol dm^{-3} KOH solution was reversible. Re-examination, however, revealed that this system was in fact quasi-reversible.

The purpose of this study is to confirm the nernstian nature of the $[Co^{II}(CN)_5]^{3-}/[Co^{I}(CN)_5]^{4-}$ couple in an aprotic nonaqueous medium. The present study deals with the reduction of $[Co^{II}(CN)_5]^{3-}$ in 100% dimethyl sulfoxide (DMSO) containing 0.1 mol dm^{-3} $[Bu_4N][PF_6]$, and it was found that $[Co^{II}(CN)_5]^{3-}/[Co^{I}(CN)_5]^{4-}$ couple was reversible in this system. The DMSO solvent was purified by refluxing it with Al_2O_3, and then with CaH_2, at 70 °C for 72 h, respectively, and by distillation twice in vacuo. The apparatus for cyclic voltammetry was set up by combination of Hokuto-Denko Galvanostat/Potentiostat Model HA 101, Hokuto-Denko Function Generator Model HB-107A, and an X•Y Recorder Model WX-4422 HIR of Graphtech Inc., Tokyo. The $[Co^{II}$-

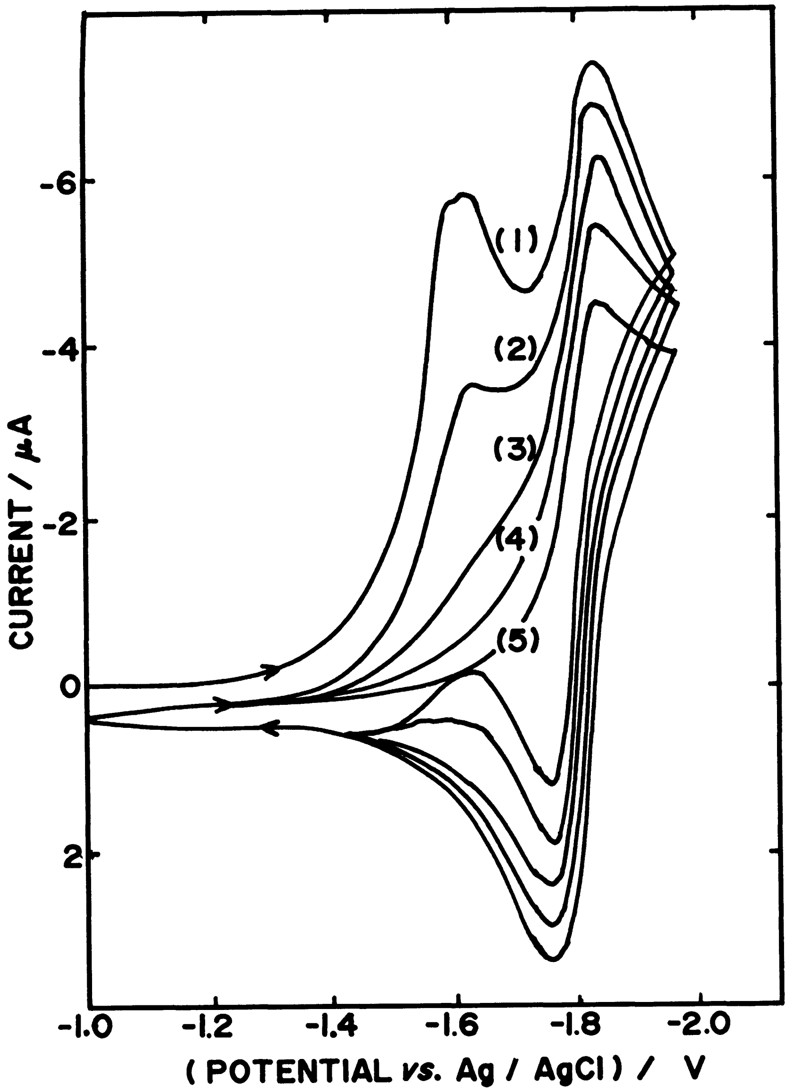

Fig. 1. Multiple triangular sweep cyclic voltammograms of 5 mmol dm^{-3} Li$_3$[Co(CN)$_5$SCN] in DMSO containing 0.1 mol dm^{-3} [Bu$_4$N][PF$_6$] (25 °C). Switching potentials, - 1.97 and 0.0 V vs. Ag/AgCl (in DMSO saturated with KCl).

(CN)$_5$]$^{3-}$ ion was produced in situ by the reduction of Li$_3$[Co(CN)$_5$SCN], because K$_6$[Co$_2^{II}$(CN)$_{10}$] is sensitive towards exposure to air and the other pentacyanocobaltates capable of supplying [Co^{II}(CN)$_5$]$^{3-}$ ions were insoluble in DMSO. The lithium salt was preferred to the potassium salt in view of the more negative reduction potential of lithium ion. To the authors' knowledge Li$_3$[Co(CN)$_5$SCN] is the only choice as the parent complex for the study of $[Co^{II}(CN)_5]^{3-}$/ $[Co^{I}(CN)_5]^{4-}$ couple in DMSO.[4)]

The $Li_3[Co(CN)_5SCN]$ complex in DMSO gave rise to the two-step wave, being similar to that in aqueous media.[5)] The only difference was the fact that the totally irreversible wave of the 2nd step ($Co^{II} \rightarrow Co^{I}$) in aqueous media turned into a completely reversible wave in DMSO. The wave of the 1st step ($Co^{III} \rightarrow Co^{II}$) behaved in a totally irreversible manner. Upon the reduction, the degradation of the coordination number from six to five always occurred even in the presence of excess SCN^- ions. Evidence is provided by the fact that no influence of excess SCN^- ions on the shape of the wave was observed at all. Moreover, there was no anodic wave of the $Co^{II} \rightarrow Co^{III}$ oxidation for the equilibrium mixture of the Co(II) and Co(III) complexes which had been prepared by the constant potential electrolysis under a nitrogen atmosphere in $[Bu_4N][PF_6]$ DMSO solutions both in the presence of 1 mol dm^{-3} LiSCN and its absence, suggesting a complete detachment of the 6th ligand, SCN^-, from the Co(II) coordination sphere. On the other hand, the wave-shape of the 2nd polarographic step in DMSO coincided with that of the theoretical curve for a nernstian system of the one-electron reduction; the plot of E vs. log $[(i_l - i)/i]$ was a straight line with a slope of 59.1 mV at 25 °C. The overall electrode reactions were as follows:

for the 1st step,

$$[Co^{III}(CN)_5SCN]^{3-} + e \rightarrow [Co^{II}(CN)_5SCN]^{4-} \quad (1)$$

$$[Co^{II}(CN)_5SCN]^{4-} \rightarrow [Co^{II}(CN)_5]^{3-} + SCN^- \quad (2)$$

for the 2nd step,

$$[Co^{II}(CN)_5]^{3-} + e \rightarrow [Co^{I}(CN)_5]^{4-} \quad (3)$$

Thus, the electrode reaction of the 1st step was totally irreversible, whereas that of the 2nd step was reversible, implying that the $[Co^{II}(CN)_5]^{3-}$ species remains structurally intact throughout the 2nd step (3).

Figure 1 shows multiple cyclic voltammograms for $Li_3[Co(CN)_5SCN]$ at hanging mercury drop electrode. For repeated cycling the 1st cathodic peak current, $i^c_{p,1}$ ($Co^{III} \rightarrow Co^{II}$), decreased and decayed to zero, while there was no corresponding anodic peak current ($Co^{II} \rightarrow Co^{III}$). Contrarily the 2nd cathodic peak current, $i^c_{p,2}$ ($Co^{II} \rightarrow Co^{I}$), decreased with repeating cyclic scans, while

Table 1. Dependences of Peak Currents and Potentials on the Scan Rate of a Triangular Sweep Cyclic Voltammetry for 5 mmol dm^{-3} $Li_3[Co(CN)_5SCN]$ (25 °C)

	Scan rate / mV s^{-1}						
	50	100	150	200	250	300	350
$E^c_{p,1}$ /V	- 1.651	- 1.624	- 1.625	- 1.627	- 1.650	- 1.662	- 1.680
$E^c_{p,2}$ /V	- 1.840	- 1.841	- 1.842	- 1.842	- 1.843	- 1.844	- 1.848
E^a_p /V	- 1.781	- 1.782	- 1.783	- 1.782	- 1.781	- 1.781	- 1.782
ΔE_p /mV	59	59	59	60	62	63	66
$i^c_{p,1}$ /μA	- 3.50	- 5.48	- 5.68	- 7.69	- 7.74	- 8.36	- 9.98
$i^c_{p,2}$ /μA	- 3.20	- 5.29	- 6.94	- 7.44	- 7.52	- 8.08	- 9.32
i^a_p /μA	+ 3.20	+ 5.29	+ 6.85	+ 7.31	+ 7.55	+ 8.15	+ 8.99
$i^a_p/i^c_{p,2}$	- 1.00	- 1.00	- 0.99	- 0.98	- 1.00	- 1.00	- 0.97

V vs. Ag/AgCl(DMSO); potentials were corrected for iR drop; R = 1262 ohm (internal resistance between HMDE and reference electrode). 0 V vs. Ag/AgCl(DMSO) = + 0.30 V vs. SCE(aq) = + 0.54 V vs. NHE (25 °C).$^{6)}$ Supporting electrolyte: 0.1 mol dm^{-3} $[Bu_4N][PF_6]$ DMSO(100%) soln.

the corresponding anodic peak current, i^a_p ($Co^I \rightarrow Co^{II}$), increased until a steady-state pattern was attained. The separation between the cathodic and anodic peak potentials, ΔE_p = 59 mV, indicated a nernstian nature of the 2nd step. Table 1 summarizes the dependence of the two cathodic and the anodic peak currents and potentials on the scan rate of a sweep (r). The $i^c_{p,2}$ and i^a_p values are proportional to $r^{1/2}$ and the ratio of $i^a_p/i^c_{p,2}$ is unity, irrespective of r. The standard electrode potential of the $[Co^{II}(CN)_5]^{3-}/[Co^I(CN)_5]^{4-}$ couple was - 1.272 V vs. NHE at (25 ± 0.1) °C ($\Delta G°$ = + 122.7 kJ mol^{-1}).

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(Received September 11, 1984)