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POLAROGRAPHY OF CIS- AND TRANS-TETRACYANO-COBALTATE(III) COMPLEXES

Nobufumi MAKI
Department of Chemistry, Faculty of Engineering
Shizuoka University, Hamamatsu

The cis-$[Co^{III}(CN)_4(SO_3)_2]^{5-}$ ion in which four cyanides take a non-planar configuration was found to be reduced in two steps from Co(III) to Co(0) via the Co(I) complex, whereas the trans-$[Co^{III}(CN)_4(SO_3)_2]^{5-}$ ion in which four cyanides take a coplanar structure is reduced to the Co(I) complex and not to Co(0) state at the dropping mercury electrode in aqueous solutions. This cis- vs. trans-distinction with regard to the stability of cobalt(I) complexes may be extended to other kinds of tetracyano complexes, such as cis-$Na[Co(CN)_4en]\cdot 3.5\ H_2O$, trans-$K[Co(CN)_4(NH_3)_2]\cdot H_2O$, and trans-$K[Co(CN)_4(OH_2)_2]\cdot(3/4)H_2O$. The trans-tetracyano-diaqua complex was speculated to be present in a form of polymerized complexes in solution on the basis of the difference in anodic behavior between the resulting Co(I) complex and the aquated Co(I) species formed from the tetracyanodisulfito complexes.

The difference in polarographic behavior of steric isomers has so far been investigated by several authors.[1,2,3] However, since the effect of structural difference on the electrochemical reaction appears too little to be detected by means of conventional polarography, a mere shift of cathodic half-wave potential($E_{1/2}$) has been found for cis- and trans-isomers of the $[Co\ N_4X_2]$ type involving negatively charged ligand, X, such as NO_2^-, where N_4 comes from two ethylenediamine ligands or from four ammonia ligands, while any shift was not observed for a pair of isomers with neutral ligands.[1]

Contrary to this result, a great difference would be expected for a pair of isomers with ligands of strong π-bonding character. The present communication deals with the first finding of the difference in electrode pathways themselves between cis- and trans-tetracyanodisulfitocobaltate(III) ions in aqueous solutions.

The current-potential curve of cis-$Na_2K_3[Co^{III}(CN)_4(SO_3)_2]\cdot(5/2)H_2O$[4]

was found to be composed of two waves of which the first and the second step represented reduction from Co(III) to Co(I) and to Co(0) state, respectively, whereas that of trans-$Na_5[Co^{III}(CN)_4(SO_3)_2]\cdot 3H_2O$[5] consisted of one wave which, corresponding to an acceptance of two electrons, represented reduction from Co(III) to Co(I) and no further reduction to Co(0) state at the dropping mercury electrode(DME). Here, aqueous solutions of 0.5 M Na_2SO_3 and 0.5 M Na_2SO_4 were used as supporting electrolytes on recording the polarograms of the complexes of 10^{-3} to 10^{-2} M at the DME. No fundamental difference in cathodic behavior was found between in the presence and in the absence of free ligands, SO_3^{2-}, in excess, while the difference was found in anodic oxidations. All the cathodic limiting currents were diffusion-controlled below 40°C and strictly linearly related to the complex concentration in the range of 10^{-3} to 10^{-2} M in 0.5 M Na_2SO_3 and in 0.5 M Na_2SO_4. The diffusion coefficient calculated from the Ilkovič equation for the trans-isomer was 4.65×10^{-6} cm^2/s at 25°C in 0.5 M Na_2SO_3, while that of the cis-isomer was 4.42×10^{-6} cm^2/s at 25°C under the same conditions. Each limiting current increases linearly with temperature over the temperature range of 5°C to 40°C. Above 40°C, however, it shows a kinetically-controlled feature, probably due to the thermal disruption in part of the resulting cobalt(I) complex during reduction. The temperature coefficients of the first and the second steps of the cis-isomer were 1.60%/°C and 1.72%/°C at 25°C in 0.5 M Na_2SO_3 solution, respectively, while the coefficient for the trans-isomer was 1.73%/°C at 25°C in the same solution. Normal shape of instantaneous current-time curves was always observed during the life of a single drop at every potential where the current reached the limiting plateau, suggesting no specific adsorption of the depolarizer on the DME during reduction. The instantaneous current increased with time to the powers of 0.18 - 0.21 for cis- and trans-isomers of 5×10^{-3} M both in 0.5 M Na_2SO_3 and in 0.5 M Na_2SO_4 solutions.

These results suggest that the net electrode processes are as follows:

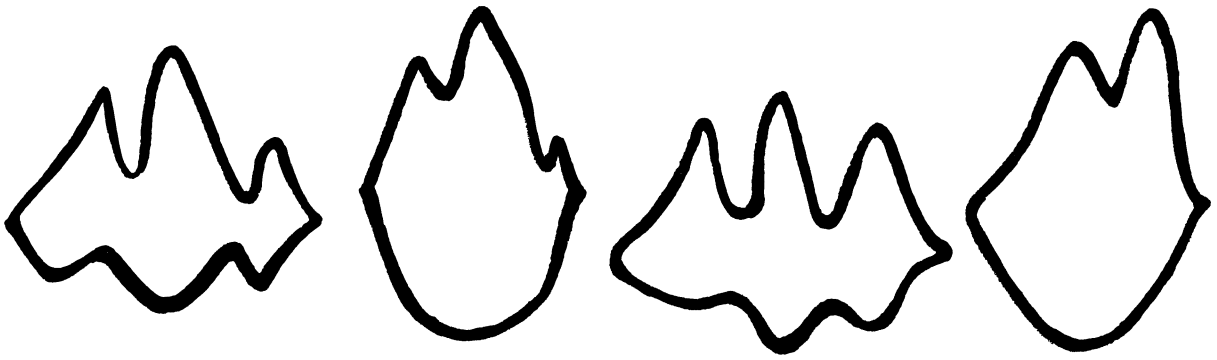
$$cis\text{-}[Co^{III}(CN)_4(SO_3)_2]^{5-} \xrightarrow{2e} cis\text{-}[Co^{I}(CN)_4(SO_3)_2]^{7-} \xrightarrow{e} cis\text{-}[Co^{0}(CN)_4(SO_3)_2]^{8-}$$

$$\xrightarrow[\text{rapidly}]{} [Co^{0}(CN)_4]^{4-} + 2\ SO_3^{2-} \xrightarrow[\text{partially}]{} Co(\text{metal});$$

$$trans\text{-}[Co^{III}(CN)_4(SO_3)_2]^{5-} \xrightarrow{2e} trans\text{-}[Co^{I}(CN)_4(SO_3)_2]^{7-}.$$

Thus, the tetracyano cobalt(I) complex in which four cyanides take a planar structure is no longer reduced to Co(0) state at the DME, whereas the cobalt(I)

complex in which four cyanides take positions of a non-planar configuration is further reduced to Co(0) state. This cis- and trans-distinction with regard to the stability of Co(I) complexes can be fully interpreted on the basis of the fact that the cobalt(I) complex (d^8) with ligands of π-bonding nature possesses a tendency of taking a coplanar structure rather than a tetrahedral one, analogously to that of Ni(II) complexes (d^8). Besides the formation of the Co(I) complex, evidence for the existence of the zero-valent cobalt complex,[6-8] $[Co^0(CN)_4]^{4-}$, for cis-isomer is provided by the fact that there are two anodic indentations responsible for oxidations from Co(0) to Co(I) and to Co(III) on the oscillopolarogram of the Heyrovský-Forejt type in 0.5 M Na_2SO_4 solution, because the metallic cobalt which has once released the ligands usually gives only one indentation, corresponding to the dissolution of cobalt to aquacobalt(II) ion, on the anodic branch and is never oxidized electrochemically to Co(III) state without ligands. For the trans-isomer, two anodic indentations were also present in 0.5 M Na_2SO_4, but these indentations represent oxidations from Co(I) to Co(III) through Co(II) state, as has been previously reported.[9] In contrast to this anodic behavior, no anodic indentation was observed in the solution with an excess of sulfite ions for both cis- and trans-isomers, suggesting that cis- and trans-tetracyanodisulfitocobaltate(I) complexes are not oxidized electrochemically. Reversely, the two anodic indentations in noncomplexing media indicate that the aquated species of disulfito cobalt(I) complexes are oxidizable at the DME. This result of anodic behavior is obviously inconsistent with that obtained previously for the trans-$K[Co^{III}(CN)_4(OH_2)_2]\cdot(3/4)H_2O$ complex whose degraded diaquacobalt(I) complex is never oxidized electrochemically at the DME in 0.5 M Na_2SO_4 solution.[9] Therefore, the diaquacobalt(I) complex degraded from trans-$K[Co^{III}(CN)_4(OH_2)_2]\cdot(3/4)H_2O$ is not the same as the aquated cobalt(I) complex formed from trans-$Na_5[Co^{III}(CN)_4(SO_3)_2]\cdot 3H_2O$ in 0.5 M Na_2SO_4 solution. To explain such a difference in anodic behavior it appears to be necessary to assume that the trans-tetracyanodiaquacobaltate(I) ion degraded from trans-$K[Co(CN)_4(OH_2)_2]\cdot(3/4)H_2O$ may be present in a form of polymerized complexes involving several hydroxo-bridging ligands in aqueous solutions. This speculation is reinforced by the possibility that the parent complex, trans-$K[Co(CN)_4(OH_2)_2]\cdot(3/4)H_2O$, might be a sort of polynuclear complexes on the basis of spectroscopic data; the logarithmic absorption intensity, log ε, of the second spin-allowed band is approximately



(1) (2) (3) (4)

Fig. 1 Oscillopolarograms of dE/dt - E(potential) curves: (1) cis-$Na_2K_3[Co(CN)_4(SO_3)_2]\cdot(5/2)H_2O$ in 0.5 M Na_2SO_4; (2) cis-$Na_2K_3[Co(CN)_4(SO_3)_2]\cdot(5/2)H_2O$ in 0.5 M Na_2SO_3; (3) trans-$Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ in 0.5 M Na_2SO_4; (4) trans-$Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ in 0.5 M Na_2SO_3.

3.8, the value of which is extraordinarily greater than expected as being a mononuclear cobalt(III) complex of the [Co C_4 O_2] type. Moreover, the second shoulder band is located at the place of considerably shorter wavelength than expected and seems to be similar in its broad shape to that of most binuclear cobalt(III) complexes. These spectroscopic data, combined with the nonintegral number of crystallization water, $(3/4)H_2O$, and more negative values of $E_{1/2}$, incline us to conceive the trans-$K[Co(CN)_4(OH_2)_2]\cdot(3/4)H_2O$ complex to be present in a form of polymer not only in Co(I) state but also in the Co(III) complex.

Figure 1 exemplifies the dE/dt - E(potential) curves for cis-$Na_2K_3[Co(CN)_4(SO_3)_2]\cdot(5/2)H_2O$ and trans-$Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$ of 10^{-2} M in solutions with or without sulfite ions in excess. The applied span voltage was 0 V to - 2.0 V (vs. Hg pool). These results of anodic behavior with a current-controlled oscillopolarograph were in agreement with those obtained by using a Kalousek commutator[10] at fixed potentials where the cobalt(I) complexes were formed at the DME. That is, the Kalousek polarograms of both isomers in 0.5 M Na_2SO_4 showed quasi-reversible anodic waves of one or two steps, exactly corresponding to the two electron oxidation from Co(I) to Co(III), at the fixed potential of - 1.70 V (vs. SCE), while no anodic wave was found for both isomers in 0.5 M Na_2SO_3 at the same constant potential.

The half-wave potentials and their electrode processes are summarized in Table 1. From the table it will not be out of the way to conclude that the

Table 1. HALF-WAVE POTENTIALS OF WAVES FOR TETRACYANOCOBALTATE(III) COMPLEXES(25°C)

COMPOUND	1st step(change of valence)	2nd step(change of valence)	SUPPORTING ELECTROLYTE
cis-$Na_2K_3[Co(CN)_4(SO_3)_2]\cdot(5/2)H_2O$[*1]	- 1.32[*6] (3 → 1)	- 1.58[*6] (1 → 0)	0.5 M Na_2SO_4
	- 1.38 (3 → 1)	- 1.75 (1 → 0)	0.5 M Na_2SO_3
trans-$Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$[*1] ca	- 1.21 (3 → 1)	no reduction	0.5 M Na_2SO_4
	- 1.22 (3 → 1)	no reduction	0.5 M Na_2SO_3
trans-$K[Co(CN)_4(OH_2)_2]\cdot(3/4)H_2O$[*1]	- 1.03 (3 → 2)	- 1.41 (2 → 1)	0.5 M Na_2SO_4
trans-$K[Co(CN)_4(NH_3)_2]\cdot H_2O$[*1]	- 0.78 (3 → 2)	- 1.05 (2 → 1)	0.5 M Na_2SO_4
	- 0.98 (3 → 2)	- 1.37 (2 → 1)	NH_4Cl + NH_3 buffer (pH = 11.0)
cis-$Na[Co(CN)_4en]\cdot 3.5\ H_2O$	- 1.17 (3 → 0)		0.5 M Na_2SO_4
	- 1.36_4 (3 → 1)	- 1.51 (1 → 0)	0.5 M Na_2SO_4 + 2 M en
	- 1.59 (3 → 2)	- 1.78 (2 → 1)	DMSO containing 0.1 M $[(C_2H_5)_4N]ClO_4$
trans-$Na[Co(CN)_4(P{\equiv}\phi_3)_2]\cdot 3H_2O$[*2,3]	- 0.98 (3 → 1)		" " " "
trans-$Na[Co(CN)_4(As{\equiv}\phi_3)_2]\cdot 3H_2O$[*2,4]	- 0.58 (3 → 2)	- 1.06 (2 → 1)	" " " "
$K_4[Co(CN)_4\text{-en-}Co(CN)_4]\cdot H_2O$	- 0.32 (2 → 3)[*5]	- 1.23 (2 → 1)	0.5 M Na_2SO_4 + 1.5 M en + 0.00084% Triton X 100

*1 Insoluble in DMSO(dimethyl sulfoxide); *2 insoluble in water; *3 $P{\equiv}\phi_3$, triphenylphosphine; *4 $As{\equiv}\phi_3$, triphenylarsine; *5 anodic wave; *6 in units of volt vs. SCE (25°C).

cis-tetracyanocobaltate(I) complexes are all further reduced to Co(0) state, i.e., polarographically active, whereas the trans-tetracyanocobaltate(I) complexes are never reduced, i.e., polarographically inactive as far as the polarography in aqueous solutions is concerned. On the other hand, the cis-$[Co^{III}(CN)_4en]^-$ ion in DMSO is reduced to Co(I) state in a stepwise fashion with a complete retention of the original structure and further reduction to Co(0) state does not occur in spite of the cis-configuration, while in noncomplexing aqueous media the cis-$[Co^{III}(CN)_4en]^-$ ion undergoes direct reduction to Co(0) state and the intermediate Co(I) complex cannot be detected on the d. c. polarogram. The Co(I) complex in aqueous media can be detectable only in the presence of ethylenediamine in large excess, although it dimerizes into a form of binuclear complexes.[9,11,12]

The discrepancy between them is attributed solely to the difference in the labilities of Co(II) and Co(I) complexes in aqueous and in nonaqueous media. Thus, the lability used in polarographic sense may change from solvent to solvent, whereas the lability defined by Taube[13] is independent of the kind of solvents so far as the solvent does not participate in substitution reactions. Moreover, the lability used here should be taken into account under the conditions where the potential is applied. In this respect, the lability in polarographic sense is essentially different from the Taube lability referring to the rate at which the complex moves toward its thermodynamically stable form in any solvent. More concretely, the former is concerned with the rate of the solvolysis which replaces the ligands bound to the metal with solvent molecules under the conditions where the potential is applied, while the latter with the rate of ligand exchange reactions with the same kinds of free ligands present in solution. In this sense, further reduction from Co(I) to Co(0) state or oxidation from Co(I) to Co(III) state is closely related to the lability of the Co(I) complex in water toward solvolysis(i.e., aquation). Further discussion concerning the "lability" will be presented in due course.

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