M hydrobromic acid. The eluate on evaporation yields crystals of *s-fac*-[Co(dien)$_2$]Br$_3$.

Acknowledgments. We are grateful for the use of facilities at the Research School of Chemistry, Australian National University, Canberra, to complete some of the experimental work (F. R. K.). We thank Dr. D. W. Watts (University of Western Australia) for valuable discussions and for advice on the ion association constants measurements and Dr. G. Gainsford (Australian National University) for assistance in preparing the figures. dien was kindly provided by Union Carbide (Australia) Ltd.

Registry No. *s-fac*-[Co(dien)$_2$]$^{3+}$, 38318-04-6; *u-fac*-[Co(dien)$_2$]$^{3+}$, 38318-05-7; *mer*-[Co(dien)$_2$]$^{3+}$, 38318-06-8; ClO_4^-, 14797-73-0; NO_3^-, 14797-55-8; CH_3COO^-, 71-50-1; Br^-, 24959-67-9; Cl^-, 16887-00-6; SO_4^{2-}, 14808-79-8; SeO_3^{2-}, 14124-67-5; HPO_4^{2-}, 14066-19-4; PO_4^{3-}, 14265-44-2.

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Polarographic Study of Metal Complexes. XII.[1] Pentacyanocobaltate(III) Complexes

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Received January 7, 1974 AIC40008W

The pentacyanocobaltate(III) complexes of the $[Co(CN)_5X]$ type are reduced in one or two steps to the $[Co^{I}(CN)_5]^{4-}$ ion leaving the sixth ligand, X^{m-}, at the dropping mercury electrode (dme), where the ligand X denotes the ion I^-, Br^-, Cl^-, SCN^-, NO_2^-, N_3^-, $S_2O_3^{2-}$, or SO_3^{2-}. The evidence from which we drew this conclusion was provided with the anodic wave responsible for the ligand X liberated from the Co(I) complex. The $[Co^{I}(CN)_5H]^{3-}$ formula has been widely accepted as a final reduction product. In this work, however, the stoichiometric relation between $[Co^{I}(CN)_5]^{4-}$ and H^+ ion was determined to be always 2:1, suggesting a dimeric configuration of the pentacyanocobaltate(I) ion in neutral and acidic solutions. The $[Co^{I}(CN)_5\text{-}H\text{-}Co^{I}(CN)_5]^{7-}$ ion is neither reducible nor oxidizable electrochemically at the dme. Two conclusions were drawn about the anodic oxidation of $[Co^{I}(CN)_5]^{4-}$. One of them is that the electron transfer from 3d orbitals of cobalt to mercury atoms can proceed only through the $[(CN)_5Co^{I}\text{-}Hg]$ intermediate. The other is that the peculiar feature of $[Co^{I}(CN)_5]^{4-}$ of extracting a proton from water molecules can be attributed solely to the trans influence of the fifth cyanide.

Introduction

The question of the composition and structure of the pentacyanocobaltate(I) ion formed by the reduction of pentacyanocobaltate(II) and -cobaltate(III) complexes still remains in a controversial state in spite of a number of works done on this subject.[2] Moreover, there are conflicting views about the oxidation state of the pentacyanocobaltates formed from $[Co^{II}(CN)_5]^{3-}$ and hydrogen gas, by the disproportionation of $[Co^{II}(CN)_5]^{3-}$ in aqueous solution or by the chemical reduction of $[Co^{II}(CN)_5]^{3-}$ with $NaBH_4$, Na-Hg amalgam, etc.[3-5] The $[Co^{I}(CN)_5H]^{3-}$ formula has been widely accepted as a final reduction product since Griffith and Wilkinson[6] 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^+ ion can proceed in water.

The cathodic reduction of pentacyanocobaltate(III) complexes has briefly been reported previously.[7,8] Hence, the present paper chiefly deals with the composition and structure of the pentacyanocobaltate(I) ion formed by the cathodic reduction at the dropping mercury electrode (dme).

Experimental Section

The preparation of pentacyanocobaltate(III) complexes was carried out according to the scheme of reactions

$$\textit{trans-}[Co(CN)(SO_3)(NH_3)_4]\cdot 2H_2O \rightarrow$$

$$\textit{trans-}[Co(CN)(OH_2)(NH_3)_4]Cl_2{}^{9} \xrightarrow[\text{or KX}]{\text{NaX}}$$

$$\textit{trans-}[Co(CN)X(NH_3)_4]^{q+} \xrightarrow{4KCN} K_n[Co(CN)_5X]$$

where the ligand X represents the ion I^-, N_3^-, NO_2^-, $S_2O_3^{2-}$, or SCN^-. The novel intermediate complexes of the trans-$[Co(CN)X(NH_3)_4]$ type[10] were prepared by treating the monocyanoaquotetraamminecobalt(III) chloride[9] with sodium or potassium salt of the ligand in excess at 80–95° for 1 hr. The absorption spectra in visible and uv regions of the $[Co(CN)X(NH_3)_4]$ complexes showed that the first spin-allowed d–d band shifts toward the direction of a shorter wavelength in the following order of the ligand X: N_3^-, CO_3^{2-}, $NH_2C_2H_5$, py, NH_2CH_3, NCS^-, NH_3, NO^-, SO_3^{2-}, CN^-, PPh_3.

The order of this spectrochemical series suggests the complexes to have a trans configuration rather than a cis one, since it is in agreement with that of the tetraamminecobalt(III) complexes with a trans configuration. That is, no isomerization occurs during the substitution reaction. The monocyanotetraamminecobalt(III) complexes were recrystallized from hot water containing 6% acetic acid except for the complexes with $X = S_2O_3^{2-}$ and CO_3^{2-}. The former complex is quite insoluble both in water and in organic solvents. The results of elementary analyses only for the novel intermediate complexes are available (see paragraph at end of paper regarding supplementary material).

The finally desired pentacyanocobalt(III) complexes were prepared by treating these monocyanotetraamminecobalt(III) complexes with the calculated amount of KCN at optimum temperatures. For the pentacyano complex with $X = I^-$, the reaction proceeded gently still at 0°, while that for $X = N_3^-$ or SCN^- proceeded at 50–60°. For X =

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(10) The novel monocyano complexes of this type other than these have also been prepared and identified by elementary analyses: $X = PPh_3$ (triphenylphosphine), NO^-, py (pyridine), $NH_2C_2H_5$, NH_2CH_3, or CO_3^{2-}.

Table I. Absorption Data of Pentacyanocobaltate(III) Complexes

Complex	A band, spin forbidden	I band, spin allowed	II band, spin allowed	III or special band, charge transfer		
$K_3[Co(CN)_6]$	25.67 (1.86)[a,b]	32.46 (2.32)	38.91 (2.12)			
$K_3[Co(CN)_5Cl]$	19.86 (0.04)	25.64 (2.32)		32.10 (2.09)[d]	38.00 (2.42)[e]	44.31 (4.21)
$K_3[Co(CN)_5Br]$	19.46 (0.96)	25.22 (2.21)		35.00 (2.98)[d]		41.46 (4.25)
$K_3[Co(CN)_5I]$	20.22 (1.98)	24.16 (2.32)		30.66 (3.44)	38.46 (4.26)	
$K_3[Co(CN)_5N_3]\cdot 2H_2O$	*c*	26.31 (2.83)		32.51 (3.87)		
$K_3[Co(CN)_5(NO_2)]$	*c*	28.32 (2.49)[d]		31.77 (3.36)		43.33 (4.20)
$K_3[Co(CN)_5SCN]$	*c*	26.62 (2.22)[e]		37.91 (4.22)		
$K_4[Co(CN)_5S_2O_3]$	*c*	27.32 (2.30)[e]		37.41 (4.20)		
$K_4[Co(CN)_5SO_3]\cdot 3H_2O$		29.86 (2.55)		37.80 (4.17)		

[a] The absorption maxima are given in frequencies of $10^3 \times cm^{-1}$. [b] Numerals in parenthese refer to the absorption intensities expressed in log ϵ. [c] The A band is very weak and is buried beneath the I band. [d] Shoulder band. [e] Broad band.

$S_2O_3^{2-}$, SO_3^{2-}, or NO_2^-, the temperature was kept at 80–90° during the reaction. For example, the azidopentacyanocobalt(III) complex was prepared as in

$$[Co(CN)N_3(NH_3)_4]N_3\cdot H_2O + 4KCN \rightarrow K_3[Co(CN)_5N_3]\cdot 2H_2O + 5NH_3 + KN_3$$

That is, the cyanoazidotetraamminecobalt(III) azide (10 g), KCN (11 g), and 7 g of active charcoal powder were mixed with 90 ml of water. The mixture was heated at 50° for 30 min under mechanical stirring. The reaction proceeded gently, evolving ammonia. To the orange-red filtrate were added, drop by drop, methanol and ethanol successively in order to avoid the separation of an oily layer. The aimed-at complex precipitated from the solution and was filtered and washed with methanol and ethanol. The crude product was dissolved in the minimum amount of cold water and precipitated again by adding methanol and ethanol.

The preparation of the other pentacyano complexes was quite similar to this procedure except for the temperature. The substitution reaction of the monocyanotetraamminecobalt(III) complex with cyanide ions, in general, proceeded more mildly and at lower temperatures than that of the corresponding pentaamminecobalt(III) complex. Such a mild reaction of replacing four ammonia ligands with cyanides is essential for avoiding the contamination of $K_3[Co(CN)_6]$. The presence of active charcoal seems likely to promote the detachment of ammonia ligands at lower temperatures.

Bromo- and chloropentacyano complexes were prepared by the method of Fujita.[11] It seems wise to describe it here, since it is published in Japanese.

Preparation of $K_3[Co(CN)_5Cl]$. The chloropentaamminecobalt(III) chloride (15.0 g), KCN (34.5 g), and 2 g of active charcoal were mixed with 70 ml of water under ice cooling. The reaction proceeded gently at 0°, evolving ammonia. After 30 min, the mixture was filtered. To the orange-yellow filtrate were added methanol and ethanol successively. The desired complex separated from the solution. The method of purification was the same as described above.

Preparation of $K_3[Co(CN)_5Br]$. The bromopentaamminecobalt(III) bromide (38.4 g), KCN (34.5 g), and 4 g of charcoal were mixed with 100 ml of water at 25°. The subsequent procedures were the same as mentioned above. The finally obtained complex was identified by elementary analyses. The results of analyses are supplied as microfilm supplements. The absorption data in visible and uv regions are collected in Table I. Figure 1 shows some examples of absorption spectra of pentacyanocobaltate(III) complexes in water.

Apparatus. Experimental setup and the method of measurements were the same as employed previously.[12,13] The amperometric titrations were performed with the conventional polarographic cell in a stream of pure nitrogen after degassing dissolved oxygen. The rate of the flow of mercury, *m*, and the drop time, *t*, were as follows: $m = 1.60$ mg sec^{-1}, $t = 4.4$ sec in a 0.5 *M* Na_2SO_4 solution on an open circuit with the height, 90.0 cm, of the mercury head.

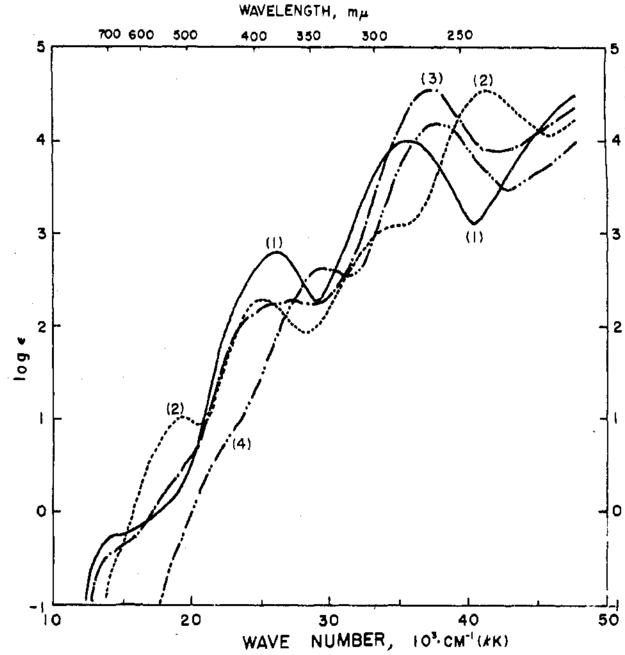

Figure 1. Absorption spectra in visible and ultraviolet regions: (1) ——, $K_3[Co(CN)_5N_3]\cdot 2H_2O$; (2) - - - -, $K_3[Co(CN)_5Br]$; (3) · — · —, $K_4[Co(CN)_5S_2O_3]$; (4) — · · —, $K_4[Co(CN)_5SO_3]\cdot 3H_2O$; measured in H_2O.

Results and Discussion

The electrode processes of pentacyanocobaltate(III) complexes are classified into two groups: one group of chloro-, bromo-, iodo-, thiocyanato- and aquopentacyanocobalt(III) complexes gives rise to well-defined two one-electron reduction waves of Co(III) → Co(II) → Co(I), while the other group of nitro-, azido-, thiosulfato-, and sulfitopentacyanocobalt(III) complexes gives the two-electron reduction wave of one step in 0.5 *M* Na_2SO_4 aqueous solutions at the dme. All the limiting currents are strictly diffusion controlled and are proportional to the complex concentration over the wide range between 5×10^{-4} and 5×10^{-2} *M*.

The $[Co^{III}(CN)_6]^{3-}$ ion, on the other hand, gives no cathodic reduction wave at the dme in aqueous solutions.

In order to solve the problem whether or not the sixth ligand, X, is released at Co(I) state, the anodic wave of pentacyanocobaltates was recorded with a Kalousek commutator.[14] Figure 2 exemplifies one of the typical Kalousek polarograms for the pentacyanocobaltate(I) ion which at the fixed constant potential (−1.60 V *vs.* sce) was cathodically formed from the thiosulfatopentacyanocobaltate(III) ion at the dme. The pentacyanocobaltate(I) ion, however, is never oxidized anodically in such aqueous solutions, since the primary reduction product, $[Co^I(CN)_5]^{4-}$, turns immediately into the anodically inactive species by extracting a proton from water

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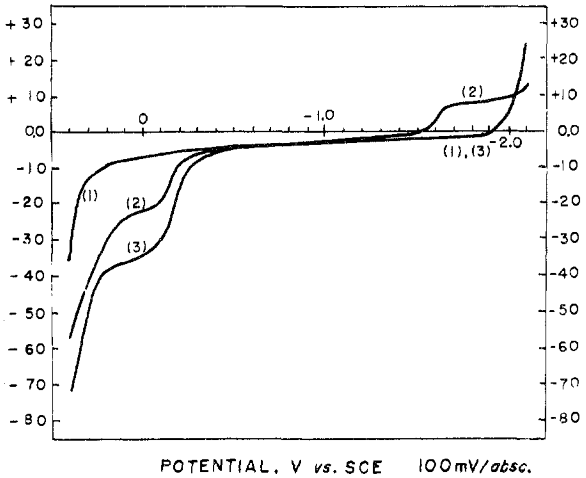

Figure 2. Commutated polarograms of $K_4[Co(CN)_5S_2O_3]$ (10^{-2} *M*) recorded with a Kalousek commutator circuit in 0.5 *M* Na_2SO_4 aqueous solution (25°): (1) for 0.5 *M* Na_2SO_4 alone; (2) for 0.5 *M* Na_2SO_4 containing 10^{-2} *M* $K_4[Co(CN)_5S_2O_3]$; (3) for 0.5 *M* Na_2SO_4 containing 10^{-2} *M* $Na_2S_2O_3 \cdot 5H_2O$. Constant auxiliary potential -1.60 V (*vs.* sce); $f = 13.5$ Hz, from $+0.4$ to -2.1 V (*vs.* sce); $m = 1.60$ mg sec^{-1}; $t = 4.4$ sec.

molecules. That is, the protonated pentacyanocobalt(I) ion gives no anodic wave due to the oxidation of cobalt(I) itself. Therefore, we cannot help thinking that the anodic wave observed in Figure 2 is due to the oxidation of the free ligand, X^{m-}, liberated from the pentacyanocobaltate(I) ion. In fact, the anodic half-wave potential of the Kalousek polarogram quite agrees with that of the corresponding single ion, X^{m-}, for every pentacyano complex, suggesting that the sixth ligand, X, is rapidly released from the Co(I) complex at the dme. It has already been established that the reaction between $[Co^I(CN)_5]^{4-}$ and H^+ ion proceeds rapidly not only in acidic solutions but still in neutral aqueous solutions to give the anodically inactive $[Co^I(CN)_5H]^{3-}$ ion.[15] Hence, at the constant potential of -1.75 V (*vs.* sce), the pentacyanocobaltate(I) ion is continuously formed and reacts with H^+ on the dme, as in

$$[Co^{III}(CN)_5S_2O_3]^{4-} \xrightarrow{2e} [Co^I(CN)_5S_2O_3]^{6-} \rightarrow [Co^I(CN)_5]^{4-} + S_2O_3^{2-} \xrightarrow{H^+} [Co^I(CN)_5H]^{3-}$$

Moreover, the cathodic reductions of Co(III) → Co(I) and of $2H^+ \rightarrow H_2$ can take place simultaneously on the dme at the constant potential of -1.75 V (*vs.* sce). This finding suggested to us the idea of employing the limiting diffusion currents of both polarographic waves to follow the chemical reaction between $[Co^I(CN)_5]^{4-}$ and H^+ ion by means of amperometric titrations. That is, the amperometric titration is based on this protonation reaction that converts polarographically active H^+ ions into polarographically inactive species of $[Co^I(CN)_5H]^{3-}$, since the protonated pentacyanocobalt(I) complex is neither reduced nor oxidized electrochemically at the dme. Chemically, however, the protonated pentacyanocobalt(I) complex is immediately oxidized into the pentacyanocobalt(III) ion in solution, *e.g.*, by a trace of dissolved oxygen. Thus, we must pay attention that the anodically inactive Co(I) complex is still chemically active and oxidizable. That is, the chemical oxidation and the anodic oxidation should clearly be distinguished from each other. As mentioned later, the distinction would probably be attributed to the difference in the mechanisms of the electron-transfer reaction. The mechanism of an outer-sphere type may operate for the former oxidation, whereas that of an inner-sphere type, for the latter.

The amperometric titrations of the parent Co(III) complexes $K_n[Co^{III}(CN)_5X]$ were carried out with 0.2 *N* HCl under a stream of pure nitrogen at the fixed constant potential of -1.75 V (*vs.* sce), at which the faradaic current reaches a limiting plateau, indicating the incessant formation of the $[Co^I(CN)_5]^{4-}$ ion on the dme. The concentration of the $[Co^I(CN)_5]^{4-}$ ion formed is strictly proportional to the concentration of the parent $K_n[Co(CN)_5X]$ complex used. The neutral aqueous solution to be titrated was prepared by dissolving the crystals of the pentacyanocobaltate(III) complex at 10^{-2} *M* in a 0.5 *M* Na_2SO_4 solution which had been deaerated by passing nitrogen through it prior to the titration. The 35-ml solution containing 10^{-2} *M* pentacyanocobalt(III) complex was titrated through a buret with 0.2 *N* HCl. At the beginning of titration, the faradaic current ($Co^{III} \rightarrow Co^I$) remains constant while the H^+ ions of the titrant (0.2 *N* HCl) added are being consumed by the $[Co^I(CN)_5]^{4-}$ ion to be titrated. The polarographically active H^+ ions are immediately captured and inactivated by the $[Co^I(CN)_5]^{4-}$ ion formed continuously on the dme at -1.75 V (*vs.* sce). The indicator is the titrant (H^+) that is added to the solution; its cathodic current ($2H^+ \rightarrow H_2$) starts only after the 10^{-2} *M* $[Co^I(CN)_5]^{4-}$ ion to be titrated has reacted quantitatively with H^+ ions. The equivalence point of titration is indicated by the beginning of an increase in the cathodic limiting current for the reduction of $2H^+ \rightarrow H_2$. That is, the new current, corresponding to the reduction of excess hydrogen ions, starts to increase only after all the $[Co^I(CN)_5]^{4-}$ ions have been protonated with the titrant (H^+). Figure 3 illustrates the amperometric titration curve of the $[Co^I(CN)_5]^{4-}$ ion formed at -1.75 V (*vs.* sce) by the reduction of the $K_4[Co(CN)_5S_2O_3]$ complex with 0.2 *N* HCl. The current values obtained for the limiting diffusion current were corrected for dilution according to the formula

$$(i_l)_{\text{cor}} = i_l \frac{v + x}{v} \qquad (1)$$

Here, the initial volume v of the complex solution was 35 ml for every case. The corrected current values, $(i_l)_{\text{cor}}$, were plotted against the volume x (ml) of the titrant (0.2 *N* HCl) added. Since the equivalence point is obtained with very good accuracy as the point of intersection of the linear extrapolations of the two branches of the titration curve, it was sufficient to take two current readings before and two after the equivalence point and to connect each pair of current values by straight lines.

A blank test was carried out, in advance, individually for every background solution such as 0.5 *M* Na_2SO_4 solution with 0.01 *M* $Na_2S_2O_3 \cdot 5H_2O$, 0.01 *M* NaBr, 0.01 *M* $NaNO_2$, 0.01 *M* NaN_3, and so on, after assuming that the sixth ligand, X^{m-}, was completely released from the 10^{-2} *M* complex at the dme. A straight line without a break was obtained for every background solution containing 10^{-2} *M* free ligand, X^{m-}; the ($2H^+ \rightarrow H_2$) current increased linearly as a function of the titrant concentration after being corrected for dilution, indicating that no reaction of capturing H^+ ions occurs between the free ligand X^{m-} and H^+ ions. That is, the protonation reaction to the free ligand X^{m-} is practically negligible compared with that of the $[Co^I(CN)_5]^{4-}$ ion. Thus, the free ligand ion X^{m-} liberated from the Co(I) complex was confirmed not to exert any influence on the amperometric titration curve for every case at -1.75 V (*vs.* sce).

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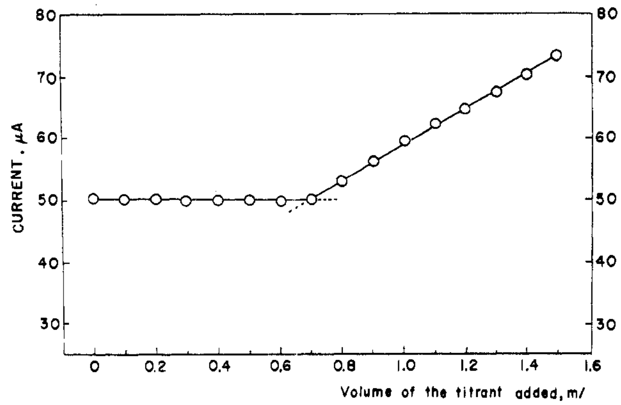

Figure 3. The amperometric titration curve of $K_4[Co(CN)_5S_2O_3]$ (10^{-2} *M*) with 0.2 *N* HCl ($f = 1.173$) at the constant potential of −1.75 V (*vs.* sce) in 0.5 *M* Na_2SO_4 supporting electrolyte (25°). The complex solution to be titrated: 35 ml.

The stoichiometric ratio of $[Co^I(CN)_5]^{4-}$ to H^+ can be written as

$$B_{[Co(CN)_5]^{4-}/H^+} = \frac{A_{comp}}{A_{HCl}} \tag{2}$$

where A_{comp} and A_{HCl} are the molar concentrations of the complex and the titrant, respectively. Since 35 ml of the parent Co(III) complex solution (10^{-2} *M*) and *x* ml of the titrant (0.2 *M* HCl) were used, A_{comp} and A_{HCl} were estimated as

$$A_{comp} = 10^{-2} \times \frac{35}{1000} = 3.5 \times 10^{-4}\ M$$

$$A_{HCl} = C_{HCl} \times \frac{x}{1000} = 0.2 \times 1.173 \times \frac{x}{1000}\ M$$

where C_{HCl} is the formal concentration (0.2 *M*) of the titrant consumed at the equivalence point. The ratio of the formal concentration (0.2 *M*) to the absolute one for the titrant (HCl) is a factor *f* which, when multiplied by the formal concentration C_{HCl} of the titrant, yields the absolute concentration of HCl. Namely, the factor *f* must be such a coefficient as to give the true absolute concentration of the titrant (HCl) when it is multiplied by the formal concentration (0.2 *M*) of the titrant. Here, the factor *f* of 0.2 *M* HCl was determined experimentally to be 1.173. Table II summarizes the results of amperometric titrations with 0.2 *M* HCl of the pentacyanocobaltate(I) ion formed cathodically from several kinds of pentacyanocobaltate(III) complexes. Thus, the molar ratio of the $[Co^I(CN)_5]^{4-}$ ion to H^+ was approximately 2:1, irrespective of the kind of the sixth ligand, X. Hence, this result would also become additional direct evidence for the detachment of the sixth ligand, X, upon the cathodic reduction of pentacyanocobaltate(III) complexes. This result, combined with the evidence[6] for the existence of a direct linkage between the cobalt and H^+, suggests that the pentacyanocobaltate(I) complex takes a dimeric configuration through a cobalt-hydrogen linkage.

The totally irreversible electrode process for pentacyanocobaltate(III) complexes might accordingly be represented as

$$[Co^{III}(CN)_5X]^{n-} \xrightarrow{e} [Co^{II}(CN)_5X]^{(2+1)-} \xrightarrow{e} [Co^{I}(CN)_5X]^{(n+2)-} \rightarrow$$

$$[Co^I(CN)_5]^{4-} + X^{m-} \xrightarrow{H^+} [Co^I(CN)_5\text{-H-}Co^I(CN)_5]^{7-}$$

where $X = Cl^-, Br^-, I^-, SCN^-, OH_2, N_3^-, NO_2^-, SO_3^{2-}$, or $S_2O_3^{2-}$.

Table II. Results of Amperometric Titrations (25°)[a]

Complex	Vol of HCl added at equiv pt, ml	$10^4 \times$ mol cm^{-3} of HCl consumed at equiv pt	$[Co^I(CN)_5]^{4-}$: H^+ molar ratio at equiv pt
$K_4[Co(CN)_5S_2O_3]$	0.69	1.62	2.16
$K_4[Co(CN)_5SO_3]\cdot 3H_2O$	0.70	1.64	2.13
$K_3[Co(CN)_5N_3]\cdot 2H_2O$	0.71	1.67	2.11
$K_3[Co(CN)_5Cl]$	0.68	1.60	2.19
$K_3[Co(CN)_5Br]$	0.67	1.57	2.22
$K_3[Co(CN)_5I]$	0.67	1.57	2.22
$K_3[Co(CN)_5NO_2]$	0.73	1.71	2.04
$K_3[Co(CN)_5SCN]$	0.72	1.69	2.07

[a] The concentration of the complex solution (35 ml) 10^{-2} *M*; titrant 0.2 *N* HCl ($f = 1.173$); background solution 0.5 *M* Na_2SO_4.

Thus, it is not out of the way to presume that the self-protonation reaction to the sixth position results finally in dimerization of $[Co^I(CN)_5]^{4-}$ ions. Of particular interest is the fact that such a *μ*-hydrido binuclear pentacyanocobaltate(I) ion can be yielded spontaneously by a subsequent chemical reaction of rapid protonation, indicating that the $[Co^I(CN)_5]^{4-}$ ion with the vacant sixth position is a very strong base which extracts a proton from water molecules. In addition, the anodically inactive properties of the $[Co^I(CN)_5\text{-H-}Co^I(CN)_5]^{7-}$ ion are explained fully in terms of the *μ*-hydrido-bis[pentacyanocobaltate(I)] configuration. That is, if we focus our attention only around the cobalt, the *μ*-hydrido binuclear structure simulates that of the $[Co^{III}(CN)_6]^{3-}$ ion which is cathodically inactive, with respect to the steric geometry wherein a mercury atom (the dropping mercury electrode as an electron donor or acceptor) cannot approach directly the cobalt from the sixth position even after taking into consideration the small size of a proton. Here, to account for the cathodically inactive behavior of the $[Co^{III}(CN)_6]^{3-}$ ion, the assumption is made that the vacant 3d orbitals of cobalt(III) are tightly shielded with $Co{=}C{=}N^-$ bonds against the attack of mercury atoms (dme) as an electron donor. Likewise, the 3d orbitals of cobalt(I) in the dimeric structure of $[\{Co^I(CN)_5\}_2H]^{7-}$ are electrochemically shielded with $Co{=}C{=}N^-$ or Co–H–Co bonds against the attack of a mercury atom as an electron acceptor, so that the mercury atom cannot approach the cobalt sterically, the situation being quite similar to the case where the magnetic shielding causes the chemical shift in nuclear magnetic resonance spectra.

This speculation on the electron-transfer mechanism of the inner-sphere type is reinforced by the fact that the aquated *cis*- and *trans*-tetracyanocobaltate(I) ions are anodically active, while *cis*- and *trans*-$[Co^I(CN)_4(SO_3)_2]^{7-}$ ions are anodically inactive in the presence of excess SO_3^{2-}, suggesting that the steric geometry of forming the Co-Hg bond is favorable for *cis*- and *trans*-$[Co^I(CN)_4]^{3-}$ ions, but not for the latter of the six-coordinate Co(I) complexes, since no coordination site remains available for forming the Co-Hg bond in the latter. Namely, the anodic waves responsible for oxidation of *cis*- and *trans*-$[Co^I(CN)_4(OH_2)_2]^{3-}$ ions were provided with Kalousek polarograms of *cis*- and *trans*-$[Co^{III}(CN)_4(SO_3)_2]^{5-}$ ions in 0.5 *M* Na_2SO_4 containing no free ligands of SO_3^{2-} at the fixed constant potential where the aquated Co(I) species were cathodically formed on the dme, whereas no anodic waves were observed for a pair of *cis*- and *trans*-disulfitotetracyanocobaltates in a 0.5 *M* Na_2SO_3 solution. Consequently, the correlation between the anodic behavior of tetracyanocobaltate(I) ions and their structure[16] is quite consistent with that for the pentacyanocobaltate(I) ions in their interpretation that the formation of the Co-Hg bond is essential for the electron transfer from the Co(I) to a mercury atom.

Furthermore, the amperometric titrations with 0.2 *N* HCl were carried out for the *cis*- and *trans*-$[Co^{I}(CN)_4(OH_2)_2]^{3-}$ ions which had been cathodically formed on the dme from *cis*-$Na_2K_3[Co^{III}(CN)_4(SO_3)_2]\cdot{}^5/_2H_2O$, *trans*-$Na_5[Co(CN)_4(SO_3)_2]\cdot 3H_2O$, and $Na[Co(CN)_4en]\cdot 3.5H_2O$ in 0.5 *M* Na_2SO_4 at the constant potential. The results, however, indicated that no reaction between $[Co^{I}(CN)_4]^{3-}$ and H^+ occurs under the same experimental conditions as for the case of pentacyano complexes. That is, the peculiar feature of the $[Co^{I}(CN)_5]^{4-}$ ion of extracting a proton from water molecules is concluded to be ascribed solely to the existence of the fifth cyanide in the coordination sphere. The counterbond weakening effect of the fifth cyanide from its trans effect[17] would induce kinetically not only the complete detachment of the sixth ligand, X, at the Co(I) site, but also a rapid self-protonation and dimerization of the resulting Co(I) complex, *i.e.*, the anodic inactivation of $[Co^{I}(CN)_5]^{4-}$. The trans influence, *i.e.*, the extent to which the fifth cyanide weakens the bond trans to itself, may be interpreted as becoming greater as the oxidation state of cobalt decreases. The strongly basic and anodically active character of $[Co^{I}(CN)_5]^{4-}$ can be thus attributed to the extreme case of the trans influence of the fifth cyanide to the bare sixth position. This suggests that only the vacant sixth coordination site is correlated closely to the electron-transfer mechanism of $[Co^{I}(CN)_5]^{4-}$.

Further additional evidence for the inner-sphere type mechanism of the electron-transfer reaction is provided with the completely reversible process of the $[Co^{I}(CN)_5]^{4-}$-$[Co^{II}(CN)_5]^{3-}$ couple under the deprotonating conditions where the hydrido bridge is broken.[15] Under the deprotonating conditions, *i.e.*, in a strongly alkaline solution, the anodic waves responsible for the oxidation of X^{m-} and $[Co^{I}(CN)_5]^{4-}$ can be detectable with the Kalousek commutator.[14] We have confirmed that all pentacyanocobaltate(III) complexes give rise to the identical reversible anodic-cathodic wave for the redox reaction of the $[Co^{I}(CN)_5]^{4-}$-$[Co^{II}(CN)_5]^{3-}$ couple, irrespective of the kind of the sixth ligand, X, on the dme in a 10 *N* NaOH solution. In agreement with the observation of Hanzlik and Vlcek,[15] we have also recognized that the anodic inactivation of $[Co^{I}(CN)_5]^{4-}$ appears more pronounced with decreasing concentration of OH^-, the wave height of the anodic curve becoming abruptly smaller below 4 *N* NaOH. Figure 4 shows one example of the Kalousek polarogram of $K_4[Co(CN)_5S_2O_3]$ at 10^{-2} *M* in a 10 *N* NaOH solution. As is evident from the curve in the figure, the cathodic and anodic half-wave potentials (−0.92 V *vs.* Hg pool) are observed to coincide, suggesting that the Co(I)-Co(II) system is strictly reversible. The Co(II)-Co(III) system, however, could not be observed distinctively for all pentacyanocobaltate(III) complexes in alkaline solutions.

This behavior in alkaline solutions suggests that the electron transfer from 3d orbitals of cobalt to a mercury atom takes place only through the Co-Hg linkage under the conditions where the sixth coordination site is vacant.

The cathodic half-wave potentials and their electrode processes for pentacyanocobaltates are summarized in Table III.

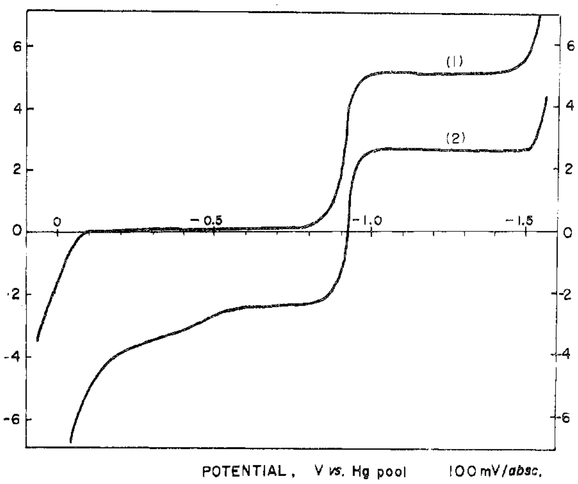

Figure 4. The cathodic-anodic curve of $K_4[Co(CN)_5S_2O_3]$ (10^{-2} *M*) recorded with a Kalousek commutator circuit in 10 *N* NaOH solution: (1) conventional polarographic curve; (2) commutated curve, constant auxiliary potential = −1.70 V (*vs.* Hg pool anode), *f* = 13.5 Hz, from +0.1 to −1.6 V (*vs.* Hg pool anode).

Table III. Cathodic Half-Wave Potentials for Pentacyanocobaltate(III) Complexes (25°)[a]

Complex	1st step	2nd step	Change of oxidn state
$K_4[Co(CN)_5S_2O_3]$	−1.38		Co(III) → Co(I)
$K_4[Co(CN)_5SO_3]\cdot 3H_2O$	−1.56		Co(III) → Co(I)
$K_3[Co(CN)_5N_3]\cdot 2H_2O$	−1.31		Co(III) → Co(I)
$K_3[Co(CN)_5NO_2]$	−1.44		Co(III) → Co(I)
$K_3[Co(CN)_5Cl]$	−1.01	−1.34	Co(III) → Co(II) → Co(I)
$K_3[Co(CN)_5Br]$	−0.85	−1.26	Co(III) → Co(II) → Co(I)
$K_3[Co(CN)_5I]$	−0.80	−1.30	Co(III) → Co(II) → Co(I)
$K_3[Co(CN)_5SCN]$	−0.85	−1.27	Co(III) → Co(II) → Co(I)
$K_3[Co^{II}(CN)_5]$	−1.28[b]		Co(II) → Co(I)

[a] Voltage unit V *vs.* sce (25°); background solution 0.5 *M* Na_2SO_4. [b] In the presence of an excess of 1 *M* KCN.

From these results obtained thus far, it appears reasonable to conclude that the electron-transfer mechanism of the inner-sphere type may operate only through the $[(CN)_5Co^{I}\text{-}Hg]$ intermediate activated complex for the anodic oxidation of $[Co^{I}(CN)_5]^{4-}$. Quite in analogy with this, the inner-sphere type mechanism through the $[(CN)_4Co^{I}\text{-}Hg]$ intermediate may be valid for the anodic oxidation of aquated *cis*- and *trans*-tetracyanocobaltate(I) ions which were formed cathodically from *cis*- and *trans*-$[Co^{III}(CN)_4(SO_3)_2]^{5-}$ ions in the absence of SO_3^{2-}.

Acknowledgment. The author wishes to thank Mr. Yukio Ishiuchi (postgraduate student) for the assistance in the measurements.

Registry No. $K_3[Co(CN)_6]$, 13963-58-1; $K_3[Co(CN)_5Cl]$, 14705-98-7; $K_3[Co(CN)_5Br]$, 14650-10-3; $K_3[Co(CN)_5I]$, 14650-11-4; $K_3[Co(CN)_5N_3]$, 14705-99-8; $K_3[Co(CN)_5NO_2]$, 14854-72-9; $K_3[Co(CN)_5SCN]$, 20596-50-3; $K_4[Co(CN)_5S_2O_3]$, 51838-66-5; $K_4[Co(CN)_5SO_3]$, 51838-65-4.

Supplementary Material Available. Observed and calculated results of elementary analyses will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2180.

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