

solution, succinic acid being the sole organic product. Therefore, inner-sphere electron transfer through the unprotonated forms of complexes **4**, **5**, and **6** would conform to the present picture for this type of mechanism. It is noted that acetylenedicarboxylic acid has been shown to be a less effective electron-mediating structural unit as compared to fumaric acid when the strong reductant $[\text{Cr}(\text{OH})_2]^{2+}$ is used.¹⁴ It seems plausible that for the weaker reductant TiOH^{2+} the outer-sphere reduction of the unprotonated form of **6** is energetically as favorable as or more favorable than the inner-sphere path.

The presence of two α -carbonyl groups suitable for the formation of a chelated precursor complex with the reductant is thought to be responsible for the very high rates of electron transfer in the Cr^{2+} reductions of oxalatotetraamminecobalt(III)³⁰ and oxalatopentaamminecobalt(III).³¹ This was bolstered by the observation of a decrease in the rate of inner-sphere Cr^{2+} reduction by 3–4 orders of magnitude when binuclear μ -oxalato complexes which contain only one remote carbonyl oxygen are the oxidants. Finally, if no carbonyl oxygen is available at all as in the tetranuclear μ_4 -oxalato complex **7**, an outer-sphere mechanism has been observed.¹⁰ A very similar pattern emerges from this study when TiOH^{2+} is the reductant. Thus the unprotonated $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$ is reduced by TiOH^{2+} at a very high rate⁶ (Table III), whereas complex **7** is reduced very slowly via an outer-sphere mechanism. Although the inner-sphere TiOH^{2+} reduction of $[(\text{NH}_3)_4\text{CoC}_2\text{O}_4]^+$ is surprisingly slow bearing in mind the Cr^{2+} results, a rate enhancement by a factor of 15 is still observed as compared to the reduction of the unprotonated μ -oxalato complex **4**.

The importance of chelation in inner-sphere electron transfer^{6,27} is also demonstrated by the observation that the binuclear μ -salicylato complex **3** is reduced by Cr^{2+} , V^{2+} , and TiOH^{2+} very slowly via outer-sphere mechanisms, indicating that either the phenolic OH group alone is not suitable for precursor complex formation or electron transfer through the ligand is energetically not favorable (it should be noted that both oxygen atoms of the carboxylate are coordinated to Co(III) and are not available for the reducing aquo ions). In contrast, reduction of the mononuclear salicylatopentaamminecobalt(III) complex by Cr^{2+} ²¹ and TiOH^{2+} (or $[\text{Ti}(\text{OH})_2]^{3+}$)⁷ shows marked enhancement of rates of reduction respectively due to attack of the reductant at the

adjacent carbonyl oxygen and chelation at the phenolic hydroxy group.

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Registry No. **1**, 52362-69-3; **2**, 61168-69-2; **3**, 52362-75-1; **4**, 65665-32-9; **5**, 58769-41-8; **6**, 61168-66-9; **7**, 41655-88-3; **8**, 52827-96-0; **9**, 61168-68-1; $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$, 21560-02-1; $\text{Ti}(\text{OH})_2^{3+}$, 17524-20-8.

Supplementary Material Available: Table I showing kinetic data for the reductions of complexes **1–9** and $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]^+$ by $\text{Ti}(\text{III})$ (2 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) M. Orhanovic and J. E. Early, *Inorg. Chem.*, **14**, 1478 (1975).
- (2) J. P. Birk, *Inorg. Chem.*, **14**, 1724 (1975).
- (3) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976).
- (4) A. Bakac and M. Orhanovic, *Inorg. Chim. Acta*, **21**, 173 (1977).
- (5) A. Adegite and F. Ojo, *Inorg. Chem.*, **16**, 477 (1977).
- (6) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975).
- (7) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **15**, 1934 (1976).
- (8) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).
- (9) K. Wieghardt and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 651 (1974).
- (10) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 736 (1973).
- (11) K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, 2548 (1973).
- (12) K. Wieghardt, *Z. Anorg. Allg. Chem.*, **391**, 142 (1972).
- (13) H. Siebert and G. Tremmel, *Z. Anorg. Allg. Chem.*, **390**, 292 (1972).
- (14) M. Hery and K. Wieghardt, *J. Chem. Soc., Dalton Trans.*, 1536 (1976).
- (15) R. H. Pierson and E. St. Clair Gantz, *Anal. Chem.*, **26**, 1809 (1954).
- (16) Like Martin and Gould,⁶ we found significant oxidation of $\text{Ti}(\text{III})$ by the rubber serum caps.
- (17) F. R. Duke and P. R. Quinney, *J. Am. Chem. Soc.*, **76**, 3800 (1954).
- (18) P. Chaudhuri and H. Diebler, *J. Chem. Soc., Dalton Trans.*, 596 (1977).
- (19) H. Krentzien and F. Brito, *Chem. Abstr.*, **73**, 78, 656 (1970).
- (20) R. L. Pecsok and A. N. Fletcher, *Inorg. Chem.*, **1**, 155 (1962).
- (21) A. H. Martin, A. Liang, and E. S. Gould, *Inorg. Chem.*, **15**, 1925 (1976).
- (22) I. Baldea, K. Wieghardt, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 78 (1977).
- (23) M. Hery and K. Wieghardt, *Inorg. Chem.*, **16**, 1287 (1977).
- (24) M. R. Hyde, K. L. Scott, K. Wieghardt, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 153 (1976).
- (25) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973).
- (26) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1969).
- (27) A. Haim, *Acc. Chem. Res.*, **8**, 264 (1975).
- (28) R. D. Foust and P. C. Ford, *J. Inorg. Nucl. Chem.*, **36**, 930 (1974).
- (29) M. Hery and K. Wieghardt, unpublished results.
- (30) C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 500 (1970).
- (31) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).
- (32) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).
- (33) R. Davies, M. Green, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1171 (1972).

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Oxidation-Reduction Reactions between Cobalt(II) and -(III) Chelate and Iron(III) and -(II) Cyanide Complexes. Outer- vs. Inner-Sphere Mechanisms¹

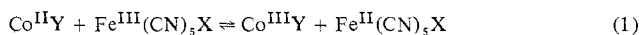
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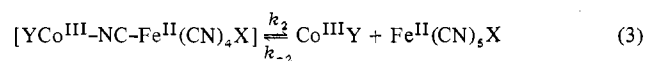
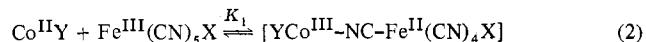
Both the forward and reverse reactions for the systems $\text{Co}^{\text{II}}(\text{chelate}) + \text{Fe}^{\text{III}}(\text{CN})_5\text{X} \rightleftharpoons \text{Co}^{\text{III}}(\text{chelate}) + \text{Fe}^{\text{II}}(\text{CN})_5\text{X}$ have been studied at ionic strength 0.26 M, at pH 6.00, and at several temperatures. The chelates were ethylenediaminetetraacetate ion (EDTA), 1,2-propylenediaminetetraacetate ion (PDTA), and *trans*-1,2-cyclohexanediaminetetraacetate ion (CyDTA). The X was either CN^- or triphenylphosphine (Ph_3P). Rate data for the forward reactions follow the same pattern as in earlier studies: a rapid formation of a binuclear cyano-bridged complex and a slow formation of mononuclear products. The reverse reactions were studied more extensively. Runs were done in the presence and absence of ascorbic acid (added to drive the reactions to completion). Equilibrium constants for the overall reaction were calculated from data obtained in the absence of ascorbic acid. These values were in good agreement with constants obtained from kinetic data. Trends in rates and activation parameters and comparisons with similar systems lead to the conclusion that the reactions occur by an outer-sphere mechanism. This is the same conclusion Haim reached based on limited studies at 25 °C.

The electron-transfer reaction between cobalt(II)-chelate complexes of the type $\text{Co}^{\text{II}}\text{Y}$ (where Y = EDTA, PDTA, CyDTA, etc.) and iron(III)-cyanide oxidants, $\text{Fe}^{\text{III}}(\text{CN})_5\text{X}$

(where X = CN^- , $\text{P}(\text{C}_6\text{H}_5)_3$, etc.) has the overall stoichiometry

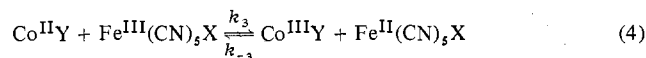


In the initial studies reported²⁻⁵ for this reaction the presence of a deeply colored intermediate was taken as evidence of an inner-sphere electron-transfer process and the reaction was treated according to the scheme



In this scheme the intermediate observed is the binuclear successor complex between cobalt(III) and iron(II) centers. The mononuclear products are formed via the dissociation of this binuclear complex. For purposes of discussion this mechanism is termed "inner sphere".

An alternate mechanism has been proposed by Haim and co-workers⁶ which attributes the formation of mononuclear products to a direct outer-sphere electron-transfer path between iron(III) and cobalt(II) reactants. The proposed scheme involves the formation of the same cobalt(III)-iron(II) species observed above (i.e., eq 2) with eq 4 representing the pathway



for product formation. For purposes of discussion this mechanism is termed "outer sphere".

Both the "inner-sphere" and "outer-sphere" mechanisms outlined above lead to the same rate law, viz.

$$\text{rate} = \frac{a[\text{Co}^{\text{II}}\text{Y}][\text{Fe}^{\text{III}}(\text{CN})_5\text{X}]}{1 + b[\text{Co}^{\text{II}}\text{Y}]} \quad (5)$$

when $[\text{Co}^{\text{II}}\text{Y}] \gg [\text{Fe}^{\text{III}}(\text{CN})_5\text{X}]$. Plots of the inverse of the observed first-order rate constant k_{obsd}^{-1} vs. $[\text{Co}^{\text{II}}\text{Y}]^{-1}$ are linear with $a = k_2K_1$ and $b = K_1$ for the inner-sphere scheme and $a = k_3$ and $b = K_1$ for the outer-sphere scheme. Thus, the rate data obtained can be treated to yield inner- or outer-sphere constants and the choice of mechanism must be made on indirect (nonkinetic) evidence.

Haim and co-workers obtained this indirect evidence from the study of the reverse reaction (i.e., the reduction of $\text{Co}^{\text{III}}\text{EDTA}$ by $\text{Fe}(\text{CN})_6^{4-}$). Their study led them to conclude that the cobalt(III)-iron(II) species was a "dead end" to the production of products. In a study using four different pentacyanoiron(III) oxidants, Ewall and Huchital⁷ proposed that both paths were operative with the choice of inner sphere or outer sphere dependent on the value of K_1 (eq 2).

In an effort to find other avenues of evidence we have further investigated both the forward and reverse reactions of eq 1 under both sets of ionic strength and pH conditions reported for these systems in the literature. We have determined the values of k_2 (dissociation, inner-sphere path), k_3 (outer-sphere path), and k_{-3} (reverse reaction) and their associated activation parameters. The results at ionic strengths 0.66 and 0.26 M are comparable and lead to the same conclusion—that both the forward and reverse reactions occur by an outer-sphere mechanism. The results of the studies at ionic strength 0.26 M are reported here.

Experimental Section

Materials. $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$, NaOH, and ascorbic acid were Fisher reagent grade chemicals. $\text{Na}_3\text{Fe}(\text{CN})_6$ was purchased from Pfaltz and Bauer, PDTA as the acid from LaMont Laboratories and CyDTA as the acid from J. T. Baker. All of the above were used without further purification. NaClO_4 was initially prepared by reaction of Na_2CO_3 with HClO_4 and purified by recrystallization. Later work employed G. F. Smith hydrated reagent NaClO_4 . Results of experiments using both preparations agreed within experimental error. $\text{Na}_3\text{Fe}(\text{CN})_6 \cdot \text{P}(\text{C}_6\text{H}_5)_3 \cdot 2\text{H}_2\text{O}$ was prepared and analyzed as described by Nast and Krieger.⁸ The hexadentate chelated cobalt(III) complexes (CoY^- , Y = EDTA, ethylenediaminetetraacetate; PDTA, 1,2-propylenediaminetetraacetate; CyDTA, *trans*-1,2-cyclohexanedi-

Table I. Derived Parameters for the Slow Reaction for $\text{Co}^{\text{II}}(\text{chelate})$ and $\text{Fe}(\text{CN})_6^{3-}$

$\text{Co}^{\text{II}}\text{CyDTA}^a$			
$T, ^\circ\text{C}$	K_1, M^{-1}	$10^3k_2, ^b \text{s}^{-1}$	$10k_3, ^c \text{M}^{-1} \text{s}^{-1}$
10.02 ± 0.04	76.9 ± 2.4	4.27 ± 0.13	3.46 ± 0.05
14.97 ± 0.02	56.4 ± 3.3	7.81 ± 0.45	4.41 ± 0.08
19.99 ± 0.02	35.2 ± 3.0	14.5 ± 1.0	5.09 ± 0.02
25.00 ± 0.02	26.2 ± 1.7	22.0 ± 1.4	5.77 ± 0.03
$\text{Co}^{\text{II}}\text{PDTA}^a$			
$T, ^\circ\text{C}$	$10^{-2}K_1, \text{M}^{-1}$	$10^3k_2, ^d \text{s}^{-1}$	$k_3, ^e \text{M}^{-1} \text{s}^{-1}$
19.98 ± 0.02	6.02 ± 0.21	2.36 ± 0.04	1.42 ± 0.04
25.00 ± 0.02	3.55 ± 0.30	4.79 ± 0.17	1.70 ± 0.14
30.03 ± 0.02	2.70 ± 0.06	8.88 ± 0.08	2.40 ± 0.04
35.00 ± 0.02	2.32 ± 0.14	13.9 ± 0.40	3.22 ± 0.10

^a Ionic strength 0.26 M; pH 6.00. ^b $\Delta H_2^\ddagger = 17.9 \pm 0.6 \text{ kcal mol}^{-1}$, $\Delta S_2^\ddagger = -5.94 \pm 0.40 \text{ cal mol}^{-1} \text{ deg}^{-1}$. ^c $\Delta H_3^\ddagger = 5.25 \pm 0.40 \text{ kcal mol}^{-1}$, $\Delta S_3^\ddagger = -40.7 \pm 1.4 \text{ cal mol}^{-1} \text{ deg}^{-1}$. ^d $\Delta H_2^\ddagger = 20.6 \pm 0.8 \text{ kcal mol}^{-1}$, $\Delta S_2^\ddagger = +0.27 \pm 1.5 \text{ cal mol}^{-1} \text{ deg}^{-1}$. ^e $\Delta H_3^\ddagger = 9.4 \pm 0.8 \text{ kcal mol}^{-1}$, $\Delta S_3^\ddagger = -25.7 \pm 2.5 \text{ cal mol}^{-1} \text{ deg}^{-1}$.

aminetetraacetate) were prepared according to literature procedures.⁹⁻¹¹ Visible spectra showed absorption maxima and molar absorptivities in agreement with literature values.^{6,12,13}

Solution Preparation. Stock solutions of all chemicals were prepared by weight except for cobalt(II) nitrate solutions which were standardized by titration with standard EDTA using xylenol orange indicator.¹⁴ Cobalt(II)-chelate solutions were prepared in situ for each run using a 10% excess of the appropriate chelate. Hexacyanoferrate(II) solutions were analyzed spectrophotometrically after oxidation to the iron(III) complex with peroxydisulfate using a molar absorbance of $1023 \text{ M}^{-1} \text{ cm}^{-1}$ at 420 nm for $\text{Fe}(\text{CN})_6^{3-}$. Concentrations of cobalt(III) chelates and iron(III) complexes were checked spectrophotometrically. Sample solutions were prepared so that kinetic runs were at $I = 0.26 \text{ M}$ and pH 6.00. The pH was set using the multidentate chelate, NaOH, and NaClO_4 and checked before and after each run using a Fisher Accumet Model 520 pH meter.

Kinetic Measurements. All runs were carried out under pseudo-first-order conditions. For the forward reactions the cobalt(II) chelates were in excess, whereas for the reverse reactions the iron(II) complex was in excess. Kinetic measurements and spectra were obtained using a Cary 15 spectrophotometer. The wavelengths of observation for kinetic runs were at the maxima for the most absorbing species (420 nm for the forward reactions and 536–540 nm for the reverse reactions).

Results

Forward Reaction. When $\text{Co}^{\text{II}}\text{EDTA}$ or related complexes are mixed with ferricyanide ion or substituted pentacyanoferrate(III) complexes, there is a rapid color change representing the formation of the cobalt(III)-iron(II) species (written as $[\text{YCo}^{\text{III}}\text{-NC-Fe}^{\text{II}}(\text{CN})_4\text{X}]$). This is followed by a slower reaction to form the final cobalt(III) and iron(II) products. Kinetic measurements were made on this process. Reactions were carried out at pH 6.00 and $I = 0.26 \text{ M}$ under conditions where the cobalt(II)-chelate complex was in large excess. The absorbance data at 420 nm obeyed a first-order kinetic scheme ($\log(A_t - A_\infty)$ plotted against time). The first-order rate constants obtained from these plots were then treated according to eq 5 as outlined above. The results are reported in Table I for Y = CyDTA and PDTA. The results for Y = EDTA and X = CN^- or triphenylphosphine were, within experimental error, identical with literature values.⁷ A linear regression plot of the temperature variation of K_1 yields the values $\Delta H_1^\circ = -12.4 \pm 0.6 \text{ kcal mol}^{-1}$ for Y = CyDTA and $\Delta H_1^\circ = -11.2 \pm 1.0 \text{ kcal mol}^{-1}$ for Y = PDTA. Linear-regressed Eyring plots for k_2 and k_3 yielded activation parameters for each path. These are shown in Table I.

Reverse Reaction. Kinetic studies on the reverse reaction, the oxidation of $\text{Fe}^{\text{II}}(\text{CN})_5\text{X}$ by $\text{Co}^{\text{III}}\text{Y}$, have been reported⁶ for only one system and at only one temperature. We have

Table II. Rate Constants for the Reduction of $\text{Co}^{\text{III}}\text{Y}$ by $\text{Fe}^{\text{II}}(\text{CN})_6\text{X}^a$

$T, ^\circ\text{C}$	$10^2 k_{-3}, \text{M}^{-1} \text{s}^{-1}$			
	Y = EDTA, X = CN^-	Y = PDTA, X = CN^-	Y = CyDTA, X = CN^-	Y = EDTA, X = Ph_3P
15.0 ^c	11.3 ± 0.1			1.41 ± 0.03
20.0	19.7 ± 0.4	8.82 ± 0.24	1.59 ± 0.02	
25.0	29.7 ± 0.3	13.9 ± 0.2	2.59 ± 0.03	3.08 ± 0.03
30.0	46.4 ± 0.4	21.6 ± 0.1	4.05 ± 0.06	5.22 ± 0.14
35.0	70.4 ± 0.7	32.8 ± 0.1	6.70 ± 0.08	8.38 ± 0.07
	$\Delta H_{-3}^\ddagger = 15.4 \pm 0.3$ $\Delta S_{-3}^\ddagger = -9.3 \pm 0.2$	$\Delta H_{-3}^\ddagger = 15.0 \pm 0.2$ $\Delta S_{-3}^\ddagger = -12.0 \pm 0.2$	$\Delta H_{-3}^\ddagger = 16.3 \pm 0.2$ $\Delta S_{-3}^\ddagger = -11.2 \pm 0.2$	$\Delta H_{-3}^\ddagger = 16.8 \pm 0.2$ $\Delta S_{-3}^\ddagger = -8.8 \pm 0.2$

^a pH 6.0; ionic strength 0.26 M. [Ascorbic acid] = 6.70×10^{-3} M; $[\text{Co}^{\text{III}}\text{Y}] = (2.20\text{--}2.35) \times 10^{-4}$ M. ^b Temperature variation between runs was ± 0.1 °C (different Y's); ± 0.04 °C otherwise. ^c For Y = EDTA, X = Ph_3P , the temperature was 17.0 °C. ^d kcal mol⁻¹. ^e cal mol⁻¹ deg⁻¹.

Table III. Comparison of Rate Constants for the Reduction of $\text{Co}^{\text{III}}\text{Y}$ by $\text{Fe}(\text{CN})_6^{4-}$ ^a

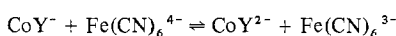
Complex	$10^2 k_{-3}, \text{M}^{-1} \text{s}^{-1}$	
	With ascorbic acid ^b	Without ascorbic acid ^c
CoEDTA ⁻	29.7 ± 0.3	29 ± 3
CoPDTA ⁻	13.9 ± 0.2	14 ± 2
CoCyDTA ⁻	2.59 ± 0.03	2.6 ± 0.4

^a Temperature 25.0 °C; pH 6.00; ionic strength 0.26 M. ^b Obtained from slopes of k_{obsd} vs. $[\text{Fe}^{\text{II}}]$ (see text) plots. ^c Obtained from initial slopes of absorbance vs. time data. Each entry is the average of at least 4 runs.

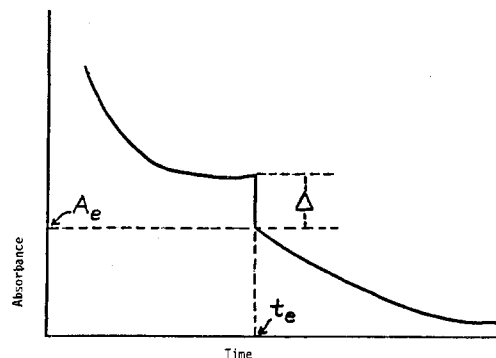
extended these studies to all the systems where the forward reaction has been investigated. As the reductions of $\text{Co}^{\text{III}}\text{EDTA}$ and other similar chelate complexes by $\text{Fe}(\text{CN})_6^{4-}$ are thermodynamically unfavorable, ascorbic acid was added to the solutions. Under these conditions the $\text{Fe}^{\text{II}}(\text{CN})_6\text{X}$ products were rapidly reduced, maintaining pseudo-first-order conditions for all reactions independent of initial $\text{Fe}(\text{II})$ concentration. Tests in the absence of $\text{Fe}(\text{II})$ confirmed that $\text{Co}^{\text{III}}\text{Y}$ complexes were not reduced by ascorbic acid at pH 6 to any appreciable extent compared to $\text{Fe}(\text{II})$ reduction. Pseudo-first-order rate constants k_{obsd} for the loss of $\text{Co}^{\text{III}}\text{Y}$ were obtained from slopes of $\log(A_t - A_\infty)$ vs. time plots, all of which were linear for at least 4 half-lives. For each system k_{obsd} was plotted vs. the concentration of $\text{Fe}(\text{II})$ reductant. Each plot was linear with a zero intercept and thus the second-order rate constants k_{-3} were obtained from the slopes of these lines. The results for the four systems studied are reported in Table II. Least-squares analyses of the temperature variations of these constants resulted in the activation parameters listed in Table II. Temperature control was ± 0.04 °C for replicate runs.

Although the direct reductions are unfavorable on the whole under the reaction conditions used, there is a substantial absorbance change (up to 40–50% of total $\text{Co}^{\text{III}}\text{Y}$ loss) even when the reaction is run in the absence of ascorbic acid. Analysis of the data, however, is complicated by the formation of the intermediate (via eq 2). Thus, initial-rate studies were used to determine the second-order rate constants. The resultant k_{-3} values are reported in Table III for the $\text{Co}^{\text{III}}\text{Y}/\text{Fe}(\text{CN})_6^{3-}$ systems along with comparison values obtained in the presence of ascorbic acid.

Equilibrium Constants. The reverse reaction in the absence of ascorbic acid occurs to a reasonable extent under the experimental conditions employed. Using this information and the fact that ascorbic acid rapidly reduces $\text{Fe}(\text{CN})_6^{3-}$ allows us a facile method to determine the equilibrium constants for the reaction



and designated K_c . Reactions were conducted at pH 6.00 and ionic strength 0.26 M. The reactants $(\text{Fe}(\text{CN})_6^{4-})$ in excess

**Figure 1.** Schematic absorbance–time plot for the reduction of CoY^- by $\text{Fe}(\text{CN})_6^{4-}$ in the absence of and after the addition of ascorbic acid.

over $\text{Co}^{\text{III}}\text{Y}$) were mixed in the absence of ascorbic acid and the absorbance change followed at the spectral maximum of the cobalt(III) species. When the absorbance leveled off, ascorbic acid was added and the reaction was followed to completion. A typical absorbance vs. time curve is shown in Figure 1, which can be explained as follows.

Initially there are two complexes in solution, CoY^- and $\text{Fe}(\text{CN})_6^{4-}$. At the wavelength chosen, only CoY^- absorbs, and the absorbance change reflects the disappearance of this complex. As the reaction proceeds, the concentrations of CoY^{2-} and $\text{Fe}(\text{CN})_6^{3-}$ products, and hence the cobalt(III)–iron(II) species (I_1), become appreciable. Five species are now present in solution with both I_1 and CoY^- contributing to the observed absorbance. After the system reaches equilibrium (t_e), ascorbic acid is added. This causes the destruction of $\text{Fe}(\text{CN})_6^{3-}$ and I_1 , leaving CoY^- as the only absorbing species. Once again the absorbance change reflects the disappearance of CoY^- . Now, however, the CoY^- reacts until it is completely consumed.

The difference between the initial absorbance, A_0 , and the absorbance at equilibrium, A_e , is proportional to the concentration of CoY^- reacted. From this and the reaction stoichiometry, values of K_c can be obtained. The equation used was

$$K_c = \frac{a^2}{A_e([\text{Fe}^{\text{II}}]_i \epsilon - a)} \quad (6)$$

where $a = (A_0 - A_e)$, $[\text{Fe}^{\text{II}}]_i$ is the initial $\text{Fe}(\text{CN})_6^{4-}$ concentration, and ϵ is the extinction coefficient of the CoY^- complex. Values of K_c and associated thermodynamic parameters are listed in Table IV.

The validity of this approach to the determination of K_c is shown through the quantity Δ (see Figure 1). The value of Δ is directly related to the concentration of I_1 , this being the only absorbing species which is destroyed upon addition of ascorbic acid. Thus, the equilibrium constant K_1 can be calculated. Values at 25 °C are 300 for Y = EDTA, 23 for

Table IV. Equilibrium Constants for the Reduction of CoY⁻ by Fe(CN)₆⁴⁻ at Ionic Strength 0.26 M^a

T, °C	10 ² K _e , M ⁻¹		
	Co(EDTA) ⁻	Co(PDТА) ⁻	Co(CyDTA) ⁻
20.13	7.40	5.40	3.44
25.10	10.3	6.53	4.34
30.04	13.1	9.20	5.95
35.18	16.8	10.9	7.95
	ΔH ^o ^b = 9.8 ± 0.4 ΔS ^o ^c = 27.9 ± 1.2	ΔH ^o = 9.5 ± 0.7 ΔS ^o = 26.5 ± 2.3	ΔH ^o = 10.4 ± 0.4 ΔS ^o = 28.9 ± 1.2

^a [CoY⁻]₀ = 2 × 10⁻⁴ M, [Fe(CN)₆⁴⁻]₀ = (5–10.5) × 10⁻³ M.
^b kcal mol⁻¹. ^c cal mol⁻¹ deg⁻¹.

Table V. Kinetic and Thermodynamic Results for Forward and Reverse Reactions of CoY²⁻ with Fe(CN)₆³⁻ ^a

X = CN ⁻	10 ³ k ₂ = 9.56	k ₃ = 2.61	10 ² k ₋₃ = 29.7
Y = EDTA	ΔH [‡] ^b = 22.3 ΔS [‡] ^c = +7.1	ΔH [‡] = 9.5 ΔS [‡] = -24.8	ΔH [‡] = 15.4 ΔS [‡] = -9.3
X = CN ⁻	10 ³ k ₂ = 4.79	k ₃ = 1.70	10 ² k ₋₃ = 13.9
Y = PDТА	ΔH [‡] = 20.6 ΔS [‡] = +0.27	ΔH [‡] = 9.4 ΔS [‡] = -25.7	ΔH [‡] = 15.0 ΔS [‡] = -12.0
X = CN ⁻	10 ³ k ₂ = 22.1	k ₃ = 0.577	10 ³ k ₋₃ = 2.59
Y = CyDTA	ΔH [‡] = 17.9 ΔS [‡] = -5.9	ΔH [‡] = 5.3 ΔS [‡] = -40.7	ΔH [‡] = 16.3 ΔS [‡] = -11.2
X = Ph ₃ P	10 ³ k ₂ = 1.09	k ₃ = 2.19	10 ² k ₋₃ = 3.08
Y = EDTA	ΔH [‡] = 23.0 ΔS [‡] = +6.4	ΔH [‡] = 12.3 ΔS [‡] = -15.8	ΔH [‡] = 16.8 ΔS [‡] = -8.8

^a pH 6.00; I 0.26 M; T = 25 °C. ^b kcal mol⁻¹. ^c cal mol⁻¹ deg⁻¹.

Y = CYDTA, and 320 for Y = PDТА. All values are in good agreement with those reported previously.⁷

Discussion

Two distinctly different mechanisms, inner sphere (reactions 2 and 3) and outer sphere (reactions 2 and 4), have been postulated to account for the stoichiometric significance of reaction 1. The results of the forward reaction treated by both mechanisms and of the reverse reaction are presented in Table V. The original inner-sphere interpretation reflected the fact that all systems exhibited a common complex rate law and that a cyano-bridged binuclear intermediate was identified in each case. The equilibrium-constant and rate-constant trends for the formation of this intermediate (K₁) and its subsequent first-order dissociation (k₂) were satisfactorily explained in terms of steric interactions which are present in the PDТА and CyDTA systems but absent in the EDTA system^{4,5} or in terms of charge and size effects upon replacement of a cyano group by another ligand. Examination of K₁ and k₂ values listed in Table V tends to support this argument. Alternatively, however, the results are also in accord with the outer-sphere mechanism proposed by Haim and co-workers.⁶ The decrease in k₃ going from EDTA to CyDTA is small (a factor of less than 5) and can be attributed to small steric constraints.

Several approaches might be considered to distinguish between these two mechanisms. One such approach is to study the reverse reactions. By invoking the principle of microscopic reversibility, the reaction between CoY⁻ and Fe(CN)₆⁴⁻ should proceed by either an inner-sphere or outer-sphere process. For the outer-sphere case the observed rate constant is simply k₋₃. For the inner-sphere case the rate law is expected to be in the form of eq 5 with a = k₋₁K₋₂ and b = K₋₂. Using the values for K_e obtained in this study along with the known values of K₁, K₋₂ can be calculated to be 28 M⁻¹, 23 M⁻¹, and 2.0 M⁻¹, respectively, for the EDTA, PDТА, and CyDTA systems (I = 0.26 M). The magnitude of K₋₂ for the first two systems is sufficient to instill hyperbolic behavior in their respective plots of the pseudo-first-order constants vs. the concentration of the excess reagent.¹⁵ Such behavior is not observed because

Table VI. Activation Parameters Calculated for Inner- and Outer-Sphere Processes: Dependence on Ionic Strength^a

I, M	ΔH ₂ [‡] , kcal mol ⁻¹		ΔS ₂ [‡] , cal mol ⁻¹ deg ⁻¹		ΔH ₃ [‡] , kcal mol ⁻¹		ΔS ₃ [‡] , cal mol ⁻¹ deg ⁻¹		Ref
	Y = EDTA		Y = CyDTA		Y = PDТА		Y = PDТА		
0.26	22.3	+7.1	7	9.5	-24.8	<i>b</i>			<i>b</i>
0.66	25.4	+16.1	4	8.7	-26.5	<i>b</i>			<i>b</i>
0.26	17.9	-5.9	<i>b</i>	5.3	-40.7	<i>b</i>			<i>b</i>
0.66	23.0	+10.9	4	5.5	-40.6	<i>b</i>			<i>b</i>
0.26	20.6	+0.27	<i>b</i>	9.4	-25.7	<i>b</i>			<i>b</i>
0.66	26.5	+14.5	5	7.7	-31.3	<i>b</i>			<i>b</i>

^a Fe(CN)₆³⁻ as oxidant. ^b This work.

the equilibrium described by K₋₂ is slow compared to the proposed dissociation of the intermediate (k₋₁). A steady-state treatment on the cobalt(III)-iron(II) species yields the rate law

$$\text{rate} = k_{-2}[\text{Fe}(\text{CN})_6^{4-}][\text{CoY}^-] - \frac{k_1 k_2}{k_{-1}}[\text{Fe}(\text{CN})_6^{3-}][\text{CoY}^{2-}] \quad (7)$$

The second term in eq 7 is negligible or zero since any Fe(CN)₆³⁻ which might form is rapidly reduced back to Fe(CN)₆⁴⁻ by ascorbic acid.¹⁶ Thus, the absence of curvature cannot be used as a criterion for mechanism.

In the absence of this type of direct evidence the mechanism must be deduced, as in other electron-transfer reactions,¹⁷ from indirect evidence. Such evidence was presented by Haim and co-workers in their study.⁶ If the reduction of CoY⁻ by Fe(CN)₆⁴⁻ proceeds by an inner-sphere mechanism, the observed second-order rate constant reflects the substitution of Fe(CN)₆⁴⁻ into the first coordination sphere of CoY⁻ to produce the cyano-bridged binuclear species. However, substitution rates (ring-opening processes) of CoEDTA⁻ complexes^{6,18} fall in the range 10⁻³–10⁻⁶ s⁻¹ and should be even slower for CoPDТА⁻ and CoCyDTA⁻ complexes.¹⁹ These rates are much less than the redox rates (0.026–0.30 M⁻¹ s⁻¹).²⁰

Hence, the outer-sphere mechanism is more realistic for the reverse reaction, and, when microscopic reversibility considerations are used, the forward reaction also proceeds by an outer-sphere mechanism.

Comparisons of the activation parameters for the forward reaction among themselves and with other similar processes support the above conclusions. The activation parameters for the k₂ process (see Table V) are not in line with those for dissociation of similar CoYX²⁻ (X = OH⁻, Cl⁻, Br⁻) complexes. It has been demonstrated that these reactions proceed by an S_N1 mechanism²¹ and exhibit entropies of activation which vary by only a few entropy units as a function of ionic strength. Our results as shown in Table VI indicate a marked dependence on ionic strength for the k₂ (inner-sphere) path but not for the k₃ (outer-sphere) path.

Additional support for the outer-sphere mechanism is found in the application of the Marcus relationship²²

$$k_{12} = (k_{11} k_{22} K_{12})^{1/2} \quad (8)$$

where k₁₁ and k₂₂ are self-exchange rates and K₁₂ is the equilibrium constant for the reaction. Using self-exchange rate constants of 2 × 10⁻⁷ and 1 × 10⁺⁵ M⁻¹ s⁻¹^{23,24} for CoEDTA^{-1/2} and Fe(CN)₆^{-3/4}, respectively, and the value of K₁₂ from the present work, k₁₂ is calculated to be 0.5 M⁻¹ s⁻¹, which is in reasonable agreement with the value of k₃ = 2.61 obtained here.²⁵

For the reverse reaction (the reduction of CoY⁻ by Fe(CN)₆⁴⁻) the rate constants decrease in the order EDTA >

PDTA > CyDTA. This order is not unexpected since Co-CyDTA⁻ is known¹² to be a weaker oxidizing agent than CoEDTA⁻. The equilibrium constants for these reactions are in agreement with the rate data. The decrease in k_{-3} values can be attributed partly to the greater size of the CyDTA chelate, resulting in a greater tunneling distance and thus a lower probability for barrier penetration.²⁶ The rate constant for the reduction of CoEDTA⁻ by Fe(CN)₅PPh₃³⁻ is explained by a decrease in electrostatic interaction and a weaker driving force (lower ΔE°) for the reaction.

Registry No. Co^{II}CyDTA, 65802-32-6; Co^{II}PDTA, 52021-76-8; Co^{II}EDTA, 11063-56-2; Fe(CN)₆³⁻, 13408-62-3; Fe(CN)₅(Ph₃P)²⁻, 22548-72-7.

References and Notes

- Presented in part before the Division of Inorganic Chemistry, 2nd Joint conference of the Chemical Institute of Canada and the American Chemical Society, Montreal, P. Q., Canada, May 1977.
- A. W. Adamson and E. Gonick, *Inorg. Chem.*, **2**, 129 (1963).
- D. H. Huchital and R. G. Wilkins, *Inorg. Chem.*, **6**, 1022 (1967).
- D. H. Huchital and R. J. Hodges, *Inorg. Chem.*, **12**, 998 (1973).
- D. H. Huchital and F. C. Maepa, *J. Coord. Chem.*, **2**, 277 (1973).
- L. Rosenheim, D. Speiser, and A. Haim, *Inorg. Chem.*, **13**, 1571 (1974).
- R. X. Ewall and D. H. Huchital, *Inorg. Chem.*, **14**, 494 (1975).
- R. Nast and K. W. Krieger, *Z. Anorg. Allg. Chem.*, **341**, 189 (1965).
- F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).
- F. P. Dwyer and L. G. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).
- F. P. Dwyer and L. G. Garvan, *J. Am. Chem. Soc.*, **83**, 2610 (1961).
- B. Grossman, Ph.D. Thesis, State University of New York at Buffalo, 1969, pp 109-110.
- W. H. Woodruff, B. A. Burke, and D. W. Margerum, *Inorg. Chem.*, **13**, 2573 (1974).
- A. I. Vogel "A Textbook of Quantitative Inorganic Analysis", 3rd ed, Wiley, New York, N.Y., 1961, p 443.
- B. A. Watts, J. V. Turner, and D. A. Watts, *Aust. J. Chem.*, **29**, 551 (1976).
- The second-order rate constant for this reaction has been reported as greater than $10^6 \text{ M}^{-1} \text{ s}^{-1}$ by U. S. Mehrotra, M. C. Agrawal, and S. P. Mushran, *J. Phys. Chem.*, **73**, 1996 (1969).
- See for example J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965); J. P. Candlin and J. Halpern, *ibid.*, **4**, 1086 (1965).
- R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).
- H. Ogino, M. Takahashi, and N. Tanaka, *Bull. Chem. Soc. Jpn*, **47**, 1426 (1974).
- The 10^{-3} s^{-1} is for the OH⁻-assisted ring opening. Under the present experimental conditions a value of 10^{-6} s^{-1} is more applicable. Comparison of this value with the redox constants indicates that the ring-opening process is 15-100 times slower.
- M. H. Evans, B. Grossman, and R. G. Wilkins, *Inorg. Chim. Acta*, **14**, 59 (1975).
- See for example R. G. Linck, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, 303 (1972).
- Y. A. Im and D. H. Busch, *J. Am. Chem. Soc.*, **83**, 3357 (1961).
- M. Shporer, G. Ron, A. Lowenstein, and G. Navon, *Inorg. Chem.*, **4**, 361 (1965).
- Such agreements with Marcus-theory predictions have been taken as reasonable evidence of outer-sphere processes. However, some contributions by an inner-sphere path cannot be ruled out.
- This same argument has been used to explain the relative rates at which Cr²⁺ reacts with Co(NH₃)₆³⁺ and Co(en)₃³⁺: A. M. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29**, 42 (1960).

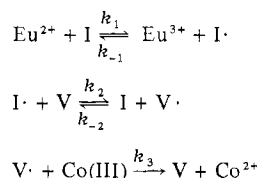
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Electron Transfer. 32. Synergism in Redox Catalysis, Leading to Four-Membered in Vitro Electron-Transport Chains¹

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Several pairs of redox catalysis have been found to exhibit catalytic effectiveness, for the Eu²⁺ reduction of Co(en)₃³⁺, considerably more marked than the sum of the individual catalyses. One catalyst in each pair has a donor site which may function as a lead-in group and appears to react with Eu²⁺ via an inner-sphere process; the other member may participate only in outer-sphere electron transfer. The proposed catalytic sequence, illustrated for the combination of isonicotinamide (I) and methylviologen (V), leads to a rate law (eq 4 in the text) corresponding to that observed. Specific rates for some



of the steps comprising each of the catalytic sequences have been obtained from studies on single-catalyst systems, whereas the ratio k_2/k_{-2} is determined by the standard potentials of the catalysts. For most sets of conditions here examined, the specific rate of the overall reaction approaches $k_1 k_2 k_3 / k_{-1} k_{-2}$. The observed specific rate for the reaction, as catalyzed by the isonicotinamide-methylviologen couple, is found to be in reasonable agreement with that obtained by combination of the known specific rates for the individual steps, both in 1 M HClO₄ and in acetate buffer. Ratios of reactant to catalyst in the latter medium can be adjusted to estimate a value of k_2 which, in conjunction with the E_0 values for the catalysts in this medium, allows assignment of a specific rate to each step in the sequence. Radicals derived from both catalysts react rapidly and completely with Co(en)₃³⁺. The enhanced effectiveness of the two catalysts in tandem arises because the radical from the outer-sphere member (e.g., V[•]) which attains the greater steady-state concentration, is generated by the action of Eu²⁺ at a lower specific rate than the radical from the inner-sphere member (e.g., I[•]).

In an earlier report² we pointed out the formal analogy between in vivo electron-transport chains and electron-transfer reactions catalyzed by external organic species in solution. The latter processes, however, may at best be considered highly abbreviated models of the bio systems, for they feature, aside from the metal ion centers which furnish the driving force for

the net reaction, only a single catalytic intermediary.

The present communication deals with several systems in which the in vitro electron-transfer chain has been expanded to four members by inclusion of two catalysts exhibiting a combined action greatly exceeding the sum of their individual effects. The "outer-members" of the chains, Co(en)₃³⁺ and