

Reduction of Ethylenediaminetetraacetatocobaltate(III) Complexes by Hexacyanoferrate(II)<sup>1</sup>

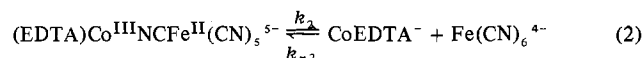
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Kinetic studies of the reduction of some ethylenediaminetetraacetatocobaltate(III) complexes by hexacyanoferrate(II) have been carried out at 25° and ionic strength 0.59 *M* in the presence of ascorbic acid (added to drive the reactions to completion). Second-order rate constants for CoEDTA<sup>-</sup>, Co(EDTA)Cl<sup>2-</sup>, and Co(EDTA)OH<sub>2</sub><sup>2-</sup> are 0.21 ± 0.02, 7.0 ± 0.2, and 3.4 ± 0.2 *M*<sup>-1</sup> sec<sup>-1</sup>, respectively. The oxidation of CoEDTA<sup>2-</sup> by Fe(CN)<sub>6</sub><sup>3-</sup> has been reexamined at pH 10, and it is found that the primary mononuclear cobalt(III) product is the hexadentate species CoEDTA<sup>-</sup>. The mechanism of these oxidation reduction reactions is assigned on the basis of indirect criteria. It is concluded that although the binuclear, cyano-bridged complex (EDTA)Co<sup>III</sup>NCFe<sup>II</sup>(CN)<sub>5</sub><sup>5-</sup> (previously identified by Adamson and Gonick) is the predominant primary product formed by the interaction between CoEDTA<sup>2-</sup> and Fe(CN)<sub>6</sub><sup>3-</sup>, the binuclear complex is not the immediate precursor of the mononuclear products CoEDTA<sup>-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup>. These are formed by an alternate, outer-sphere electron-transfer pathway. An outer-sphere mechanism is also indicated for the Fe(CN)<sub>6</sub><sup>4-</sup> reductions of Co(EDTA)OH<sub>2</sub><sup>2-</sup> and Co(EDTA)Cl<sup>2-</sup>.

The first product detected in the oxidation of ethylenediaminetetraacetatocobaltate(II) by hexacyanoferrate(III) is a metastable binuclear complex containing cobalt(III) and iron(II).<sup>2-4</sup> Eventually, the binuclear complex disappears and the mononuclear species CoEDTA<sup>-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> are produced. The mechanism proposed<sup>2-4</sup> to account for these observations involves the inner-sphere electron-transfer reaction between CoEDTA<sup>2-</sup> and Fe(CN)<sub>6</sub><sup>3-</sup>, followed by the dissociation of the binuclear complex formed in the first reaction.



Although the hexadentate species CoEDTA<sup>-</sup> is shown as the product of the dissociation of the binuclear complex, the nature of the primary cobalt(III) mononuclear species could not be established.<sup>2-4</sup> Under the conditions of the experiments,<sup>2-4</sup> the rate of ring closure of Co(EDTA)OH<sub>2</sub><sup>2-</sup> is fast<sup>5</sup> compared to the rate of production of mononuclear complexes and therefore the authors noted<sup>2-4</sup> that either Co(EDTA)OH<sub>2</sub><sup>2-</sup> or CoEDTA<sup>-</sup> could be formed in reaction 2 but that only the hexadentate species would be detectable.

The values of *k*<sub>1</sub>/*k*<sub>-1</sub> and of *k*<sub>2</sub> have been measured<sup>2-4</sup> and the latest reported values are 831 *M*<sup>-1</sup> and 5.40 × 10<sup>-3</sup> sec<sup>-1</sup>, respectively, at 25°, pH 5.00, and ionic strength 0.66 *M*. The equilibrium constant *K* for the overall reaction, estimated<sup>2</sup> from the appropriate oxidation potentials, is ~100. Since *K* = (*k*<sub>1</sub>/*k*<sub>-1</sub>)(*k*<sub>2</sub>/*k*<sub>-2</sub>), it is possible to calculate *k*<sub>-2</sub> and the value obtained is ~0.04 *M*<sup>-1</sup> sec<sup>-1</sup>. In view of the very slow rate of ring opening of CoEDTA<sup>-</sup>,<sup>5-7</sup> such a high value for *k*<sub>-2</sub> seemed implausible to us. We therefore made a direct measurement of the rate of reduction of CoEDTA<sup>-</sup> by Fe(CN)<sub>6</sub><sup>4-</sup>. For purposes of comparison, we also studied the Fe(CN)<sub>6</sub><sup>4-</sup> reductions of Co(EDTA)Cl<sup>2-</sup> and Co(EDTA)OH<sub>2</sub><sup>2-</sup>.

Finally, since the earlier measurements<sup>2-4</sup> of the CoEDTA<sup>2-</sup>-Fe(CN)<sub>6</sub><sup>3-</sup> reaction were restricted to a pH of 5.0 and since these are conditions under which the rate of ring closure of Co(EDTA)OH<sub>2</sub><sup>2-</sup> is at maximum, we carried out some measurements at pH 10. Under these conditions, the dominant pentadentate species is Co(EDTA)OH<sub>2</sub><sup>2-</sup> and its rate of ring closure is sufficiently slow compared to the redox reaction that the question of the identity of the primary mononuclear cobalt(III) species can be resolved directly.

## Experimental Section

**Materials.** Potassium ethylenediaminetetraacetatocobaltate(III) dihydrate was prepared and recrystallized three times according to literature procedures.<sup>8</sup> Dehydration of the salt was accomplished by heating at 105° to constant weight. Monopotassium chloroethylenediaminetetraacetatocobaltate(III) was prepared and purified according to literature procedures.<sup>9</sup> Disodium hydroxoethylenediaminetetraacetatocobaltate(III) was prepared as described in the literature.<sup>5</sup> The purity of the materials was ascertained by cobalt analyses<sup>10</sup> and by comparison of the visible spectra measured in this work with literature values.<sup>11,12</sup> Our values of wavelength for maximum absorbance and molar absorptivity at the maxima are as follows: CoEDTA<sup>-</sup>, 534 nm and 318 *M*<sup>-1</sup> cm<sup>-1</sup>; Co(HEDTA)Cl<sup>-</sup>, 584 nm and 230 *M*<sup>-1</sup> cm<sup>-1</sup>. Disodium hydroxoethylenediaminetetraacetatocobaltate(III) is very hygroscopic, and therefore solutions of this salt were standardized spectrophotometrically after decomposition to CoEDTA<sup>-</sup> (a quantitative reaction<sup>5</sup>) in a pH 5.0 acetate buffer. Sodium hexacyanoferrate(II) was recrystallized from water and analyzed by titration with cerium(IV) standard solutions<sup>13</sup> and spectrophotometrically after peroxydisulfate oxidation to hexacyanoferrate(III).<sup>14</sup> Potassium hexacyanoferrate(III) was recrystallized from water and analyzed spectrophotometrically.<sup>14</sup> Sodium perchlorate was made by reaction of sodium carbonate with perchloric acid and purified by two recrystallizations. Stock solutions of NaClO<sub>4</sub> were analyzed gravimetrically using tetraphenylarsonium chloride as the precipitating agent.<sup>15</sup> Distilled water was passed through a Barnstead ion-exchange demineralizer and then was distilled in a Corning Model AG-1b apparatus. All other chemicals were reagent grade. Buffer solutions were prepared with NaCH<sub>3</sub>CO<sub>2</sub>-CH<sub>3</sub>CO<sub>2</sub>H for pH ~5, tris(hydroxymethyl)aminomethane-HClO<sub>4</sub> for pH ~8, and NaHCO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> for pH ~10.

(8) F. P. Dwyer, E. C. Gyarfás, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

(9) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **80**, 4480 (1958).

(10) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

(11) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **29**, 311 (1956).

(12) A. Pidcock and W. C. E. Higginson, *J. Chem. Soc.*, 2798 (1963).

(13) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience, New York, N. Y., p 135.

(14) The molar absorptivity of Fe(CN)<sub>6</sub><sup>3-</sup> at 420 nm is 1023 *M*<sup>-1</sup> cm<sup>-1</sup>.

(15) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1533 (1968).

(1) (a) This work was supported in part by National Science Foundation Grant GP-9669. (b) Abstracted in part from the B.S. theses of L. R. and D. S., State University of New York at Stony Brook, 1973 and 1972, respectively.

(2) A. W. Adamson and E. Gonick, *Inorg. Chem.*, **2**, 129 (1963).

(3) D. Huchital and R. G. Wilkins, *Inorg. Chem.*, **6**, 1022 (1967).

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(5) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958).

(6) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1998 (1960).

(7) S. P. Tanner and W. C. E. Higginson, *J. Chem. Soc. A*, 59 (1966).

**Kinetic Measurements.** The desired amounts of buffer, sodium perchlorate, ascorbic acid, and sodium hexacyanoferrate(II) were mixed, and a stream of nitrogen was bubbled through the solution for 15–20 min. The appropriate volume of a solution of the desired cobalt(III) complex was added, and the absorbance of the resulting solution was measured as a function of time with a Cary 14 recording spectrophotometer. The wavelengths used were 534, 582, and 567 nm for  $\text{CoEDTA}^-$ ,  $\text{Co(EDTA)Cl}^{2-}$ , and  $\text{Co(EDTA)OH}_2^-$ , respectively. All the measurements of the rates of reduction of the cobalt(III) complexes were carried out at 25° and ionic strength 0.59 *M* in the presence of  $5.6 \times 10^{-3}$  *M* ascorbic acid. The pH of each solution was measured at the end of a run using an Orion 801 or a Corning 12 pH meter.

## Results

The reductions of the ethylenediaminetetraacetatocobaltate(III) complexes are thermodynamically unfavorable.<sup>2</sup> Therefore, in order to simplify the kinetic studies of these reductions, ascorbic acid, which is known to reduce hexacyanoferrate(III) quite rapidly,<sup>16</sup> was added to the solutions. In this manner, equilibria such as those represented by eq 1 and 2 were shifted to the left. Moreover, since the hexacyanoferrate(II) concentration is constant<sup>17</sup> during the measurements, pseudo-first-order conditions are strictly maintained even in runs where the initial ratio  $[\text{Fe(II)}]/[\text{Co(III)}]$  is smaller than 1.

Summaries of the results of the kinetic measurements for the hexacyanoferrate(II) reductions of  $\text{CoEDTA}^-$  and  $\text{Co(EDTA)Cl}^{2-}$  are presented in Tables I and II, respectively. Measurements in the absence of Fe(II) were carried out to ascertain the extent of direct reduction of the cobalt(III) complexes by ascorbic acid. For  $\text{CoEDTA}^-$ , direct reduction by ascorbic acid was negligible at pH 4.5 but became detectable at pH 7.5. However, even at this pH, the maximum contribution of ascorbic acid reduction to the disappearance of  $\text{CoEDTA}^-$  was 10%. For  $\text{Co(EDTA)Cl}^{2-}$ , ascorbic acid reduction at pH 7.5 was prohibitively fast compared to reduction by  $\text{Fe(CN)}_6^{4-}$ , and therefore measurements were restricted to pH ~4.5. Under these conditions, the maximum contribution of ascorbic acid reduction to the disappearance of  $\text{CoEDTA}^-$  was 15%. The pseudo-first-order rate constants  $k_{\text{obsd}}$  for the disappearance of  $\text{CoEDTA}^-$  and  $\text{Co(EDTA)Cl}^{2-}$  were obtained from the slopes of the linear  $\log(A_t - A_\infty)$  vs. *t* plots, and the values obtained are listed in columns 3 and 2 of Tables I and II. Second-order rate constants for the  $\text{CoEDTA}^-$ - $\text{Fe(CN)}_6^{4-}$  and  $\text{Co(EDTA)Cl}^{2-}$ - $\text{Fe(CN)}_6^{4-}$  reactions are listed in columns 4 and 3 of Tables I and II, respectively. These constants were calculated from the expression  $k_{\text{obsd}}/[\text{Fe(II)}]$ , after correcting  $k_{\text{obsd}}$  for the ascorbic acid reduction, where necessary. A rate law of the form  $k[\text{Co(III)}]\cdot[\text{Fe(II)}]$  accounts reasonably well for the observations, with *k* being independent of pH from 4.5 to 7.9 in the case of  $\text{CoEDTA}^-$ .<sup>18</sup>

(16) N. Winograd, H. N. Blount, and T. Kuwana, *J. Phys. Chem.*, **73**, 3456 (1969).

(17) The steady-state concentration of  $\text{Fe(CN)}_6^{3-}$  can be easily calculated from the scheme  $\text{Co(III)} + \text{Fe(CN)}_6^{4-} \rightarrow \text{Co(II)} + \text{Fe(CN)}_6^{3-}$  followed by  $2\text{Fe(CN)}_6^{3-} + \text{C}_6\text{H}_8\text{O}_4 \rightarrow 2\text{Fe(CN)}_6^{4-} + 2\text{H}^+ + \text{C}_6\text{H}_6\text{O}_4$ . Under the most favorable conditions for the formation of large steady-state amounts of  $\text{Fe(CN)}_6^{3-}$ , less than 0.1% of the  $\text{Fe(CN)}_6^{4-}$  is oxidized.

(18) The first and fourth measurements listed in Table I were performed in an effort to learn if the radicals generated in the  $\text{Fe(CN)}_6^{3-}$ -ascorbic acid reaction are capable of reducing  $\text{CoEDTA}^-$ . These runs were carried as described in the Experimental Section except that  $\text{Fe(CN)}_6^{4-}$  was omitted and  $\text{Fe(CN)}_6^{3-}$  was added last. In this manner  $\text{Fe(CN)}_6^{4-}$  was produced *in situ* by the reaction of  $\text{Fe(CN)}_6^{3-}$  with ascorbic acid, and any reaction of  $\text{Co(III)}$  with the radicals generated could be detected by comparing the observed (extrapolated) absorbance at time 0 with that calculated from the concentration of  $[\text{Co(III)}]$  and its molar absorbance. Excellent agreement between extrapolated and calculated values of  $A_0$  was obtained, and we conclude that, under our experimental conditions,  $\text{Co(III)}$  disappears by reaction with  $\text{Fe(CN)}_6^{4-}$  and not with radicals derived from the one-electron oxidation of ascorbic acid.

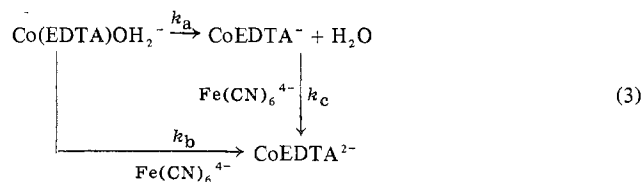
Table I. Kinetics of the  $\text{CoEDTA}^-$ - $\text{Fe(CN)}_6^{4-}$  Reaction<sup>a</sup>

$10^3 [\text{Fe(CN)}_6^{4-}]$ , <i>M</i>	pH	$10^3 k_{\text{obsd}}$ , <sup>b</sup> sec <sup>-1</sup>	<i>k</i> , <sup>c</sup> <i>M</i> <sup>-1</sup> sec <sup>-1</sup>
1.00 <sup>e</sup>	7.8	0.02 <sup>d</sup>	
	4.5	0.25	0.25
2.98	7.5	0.63	0.20
3.00	4.8	0.67	0.22
5.00 <sup>e</sup>	4.8	1.28	0.26
5.01	4.8	1.22	0.24
5.02	7.4	0.88	0.17
5.06	7.4	1.08	0.21
5.06	4.6	1.03	0.20
5.07	4.8	0.92	0.18
5.22	7.9	1.03	0.19
5.23	7.8	1.05	0.20
5.23	7.3	1.05	0.20
6.96	7.5	1.49	0.21
8.93	7.5	1.96	0.22

Av 0.21 ± 0.02

<sup>a</sup> At 25°, ionic strength 0.59 *M*, [ascorbic acid] =  $5.6 \times 10^{-3}$  *M*, and  $[\text{Co(III)}] = (1.78-1.87) \times 10^{-4}$  *M*. <sup>b</sup> From slopes of  $\log(A_t - A_\infty)$  vs. *t* plots. <sup>c</sup> For pH  $4.6 \pm 0.2$ ,  $k = k_{\text{obsd}}/[\text{Fe(CN)}_6^{4-}]$ ; for pH  $7.6 \pm 0.3$ ,  $k = (k_{\text{obsd}} - 2 \times 10^{-5})/[\text{Fe(CN)}_6^{4-}]$ . <sup>d</sup> Blank measurement. No  $[\text{Fe(II)}]$  added. <sup>e</sup> Produced *in situ* by the ascorbic acid- $\text{Fe(CN)}_6^{3-}$  reaction.

In the earlier work<sup>2,3</sup> on the  $\text{CoEDTA}^{2-}$ - $\text{Fe(CN)}_6^{3-}$  reaction at pH 5, the intermediacy of the species  $\text{Co(EDTA)OH}_2^-$  could neither be proved nor ruled out. Therefore, it was of interest to study the reduction of this species by  $\text{Fe(CN)}_6^{4-}$ . At pH 5 and convenient concentrations of  $\text{Fe(CN)}_6^{4-}$ , ring closure in  $\text{Co(EDTA)OH}_2^-$  is competitive with reduction, and therefore the following procedure was adopted to determine the rate constant for the  $\text{Co(EDTA)OH}_2^-$ - $\text{Fe(CN)}_6^{4-}$  reaction. Assuming the kinetic scheme represented by eq 3,



it can be shown<sup>19</sup> that, provided the wavelength of observation corresponds to an isosbestic point between  $\text{Co(EDTA)OH}_2^-$  and  $\text{CoEDTA}^-$  and the concentration of  $\text{Fe(CN)}_6^{4-}$  remains constant during the run, eq 4 is applicable. The

$$A_t - A_\infty = (A_0 - A_\infty) \left[ \frac{(k_c - k_b)[\text{Fe(II)}]}{(k_c - k_b)[\text{Fe(II)}] - k_a} e^{-(k_a + k_b[\text{Fe(II)}])t} - \frac{k_a}{(k_c - k_b)[\text{Fe(II)}] - k_a} e^{-k_c[\text{Fe(II)}]t} \right] \quad (4)$$

rate constants  $k_a$ ,  $k_b$ , and  $k_c$  are defined in eq 3;  $A_0$ ,  $A_t$ , and  $A_\infty$  are the absorbances per unit path length at time 0, at *t*, and at the completion of the reaction, respectively. The wavelength of observation was 567 nm, an isosbestic point for  $\text{Co(EDTA)OH}_2^-$  and  $\text{CoEDTA}^-$  with molar absorbance  $257 \text{ M}^{-1} \text{ cm}^{-1}$ . The observed absorbances were fitted to eq 4 with a nonlinear least-squares program<sup>20</sup> using  $A_t - A_\infty$  as the dependent variable, *t* as the independent variable, and the two preexponential terms and the two exponents as adjustable parameters. Since the concentration of  $\text{Fe(CN)}_6^{4-}$  is constant during the runs because of the presence of excess ascorbic acid, the two exponential parameters are pseudo-first-order rate constants. Excellent fits were ob-

(19) P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).

(20) Report LA 2367 and Addenda, Los Alamos Scientific Laboratory, Los Alamos, N. M., Mar 4, 1960, and Jan 14, 1963, respectively.

Table II. Kinetics of the Co(EDTA)Cl<sup>2-</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> Reaction<sup>a</sup>

$10^4 [\text{Fe}(\text{CN})_6^{4-}], M$	$10^3 k_{\text{obsd}},^b \text{ sec}^{-1}$	$k,^c M^{-1} \text{ sec}^{-1}$	$10^4 [\text{Fe}(\text{CN})_6^{4-}], M$	$10^3 k_{\text{obsd}},^b \text{ sec}^{-1}$	$k,^c M^{-1} \text{ sec}^{-1}$
	0.12		5.03	3.61	6.9
1.01	0.79	6.6	6.99	5.00	7.0
3.02	2.25	7.1	8.90	6.30	6.9
3.26	2.53	7.4			Av 7.0 ± 0.2

<sup>a</sup> At 25°, ionic strength 0.59 M, pH 4.5 ± 0.2, [ascorbic acid] = 5.6 × 10<sup>-3</sup> M, and [Co(III)] = 3.59 × 10<sup>-4</sup> M. <sup>b</sup> From slopes of log (A<sub>t</sub> - A<sub>∞</sub>) vs. t plots. <sup>c</sup> k = (k<sub>obsd</sub> - 1.2 × 10<sup>-4</sup>)/[Fe(CN)<sub>6</sub><sup>4-</sup>].

tained, and the values of k<sub>obsd</sub> = (k<sub>a</sub> + k<sub>b</sub>[Fe(II)]) and k'<sub>obsd</sub> = k<sub>c</sub>[Fe(II)] are listed in columns 2 and 3 of Table III, respectively. In order to calculate k<sub>b</sub>, the second-order rate constant for the Co(EDTA)OH<sub>2</sub><sup>-</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> reaction, it is necessary to have values of k<sub>a</sub>, the rate constant for ring closure in Co(EDTA)OH<sub>2</sub><sup>-</sup>.<sup>21</sup> These values are available, but under somewhat different experimental conditions than those used in the present work.<sup>5</sup> Therefore, the rate of ring closure in Co(EDTA)OH<sub>2</sub><sup>-</sup> was measured at 25° and ionic strength 0.59 M, by following the absorbance change at 340 nm. With [Co(III)] = (2.67-3.31) × 10<sup>-4</sup> M and pH 4.7-4.9, values of 10<sup>3</sup>k<sub>a</sub> were 2.17, 2.17, 2.17, 2.17, 2.28, and 2.28 sec<sup>-1</sup>, yielding an average for k<sub>a</sub> of (2.21 ± 0.05) × 10<sup>-3</sup> sec<sup>-1</sup>. The values of k<sub>b</sub>, calculated from the expression (k<sub>obsd</sub> - k<sub>a</sub>)/[Fe(II)], are listed in column 4 of Table III. The agreement between k<sub>b</sub> values from different runs is considered satisfactory for a relatively complicated scheme such as the one presented in eq 3. It is also possible to calculate the second-order rate constant for the CoEDTA<sup>-</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> reaction from the values of k'<sub>obsd</sub> (k = k'<sub>obsd</sub>/[Fe(II)]). The average value obtained is 0.24 ± 0.02 M<sup>-1</sup> sec<sup>-1</sup> compared to 0.21 ± 0.02 M<sup>-1</sup> sec<sup>-1</sup> measured directly. The agreement between the two sets of measurements is considered entirely satisfactory and provides strong support for the reaction scheme given in eq 3.

Since previous measurements of the CoEDTA<sup>2-</sup>-Fe(CN)<sub>6</sub><sup>3-</sup> reaction were restricted to pH 5, we carried out a (limited) number of kinetic and stoichiometric measurements at a pH near 10 where the rate of ring closure of pentadentate cobalt(III) is very slow.<sup>5</sup> The measurements were carried out as described previously<sup>2-4</sup> (25°, ionic strength 0.66 M, and [Fe(III)] = 1.00 × 10<sup>-4</sup> M). With [CoEDTA<sup>2-</sup>] = 2.00 × 10<sup>-3</sup> M, pH 9.8, the observed pseudo-first-order rate constants were 3.54 and 3.61 × 10<sup>-3</sup> sec<sup>-1</sup>; with [CoEDTA<sup>2-</sup>] = 4.00 × 10<sup>-3</sup>, pH 9.7, the rate constants were 4.46 and 4.49 × 10<sup>-3</sup> sec<sup>-1</sup>. Using the previous interpretation<sup>2-4</sup> of the CoEDTA<sup>2-</sup>-Fe(CN)<sub>6</sub><sup>3-</sup> reaction (eq 1 and 2), the measured rate constants yield values at pH 9.75 ± 0.05 of k<sub>1</sub>/k<sub>-1</sub> = 7.4 × 10<sup>2</sup> M<sup>-1</sup> and k<sub>2</sub> = 6.0 × 10<sup>-3</sup> sec<sup>-1</sup>. These are in good agreement with previous reported values<sup>2,4</sup> at pH 5.00: k<sub>1</sub>/k<sub>-1</sub> = 6.7 × 10<sup>2</sup> and 8.3 × 10<sup>2</sup> M<sup>-1</sup>; k<sub>2</sub> = 5.4 × 10<sup>-3</sup> and 6.1 × 10<sup>-3</sup> sec<sup>-1</sup>. At the completion of the kinetic runs, the solutions were examined spectrophotometrically and the Co(III) species formed was found to have maxima at 535 and 377 nm with molar absorbance 322 and 230 M<sup>-1</sup> cm<sup>-1</sup>, in excellent agreement with values calculated for quantitative formation of CoEDTA<sup>-</sup>. Since at pH 9.75 the half-life for ring closure in Co(EDTA)OH<sub>2</sub><sup>-</sup> is ~4 hr whereas the Fe(III)-Co(II) reactions are complete in ca. 30 min, we conclude that CoEDTA<sup>-</sup> is the primary cobalt(III) mononuclear product of the oxidation of CoEDTA<sup>2-</sup> by Fe(CN)<sub>6</sub><sup>3-</sup>.

(21) An additional quantity necessary is the rate of reduction of Co(EDTA)OH<sub>2</sub><sup>-</sup> by ascorbic acid. This contribution was found to be negligible by running a blank with all the components except Fe(CN)<sub>6</sub><sup>4-</sup>. The ratio of rate of reduction by ascorbic acid at 5.6 × 10<sup>-3</sup> M to rate of ring closure was less than 0.01.

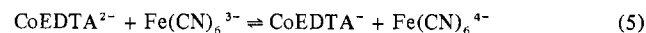
Table III. Kinetics of the Co(EDTA)OH<sub>2</sub><sup>-</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> Reaction<sup>a</sup>

$10^3 [\text{Fe}(\text{CN})_6^{4-}], M$	$10^2 k_{\text{obsd}},^b \text{ sec}^{-1}$	$10^3 k'_{\text{obsd}},^b \text{ sec}^{-1}$	$k_b,^c M^{-1} \text{ sec}^{-1}$
1.00	0.57	0.25	3.5
2.98	1.20	0.71	3.3
3.00	1.25	0.72	3.4
5.04	1.83	1.07	3.2
5.09	2.03	1.22	3.6
7.03	2.80	1.73	3.7
7.05	2.35	1.43	3.0
9.01	3.03	2.22	3.1
9.03	3.25	2.18	3.4
9.04	3.37	2.33	3.5
			Av 3.4 ± 0.2

<sup>a</sup> At 25°, ionic strength 0.59 M, [ascorbic acid] = 5.6 × 10<sup>-3</sup> M, pH 4.8 ± 0.1, and [Co(III)] = (2.54-3.30) × 10<sup>-4</sup> M. <sup>b</sup> From non-linear squares fitting of measured absorbances to eq 4. <sup>c</sup> k<sub>b</sub> = (k<sub>obsd</sub> - 2.21 × 10<sup>-3</sup>)/[Fe(CN)<sub>6</sub><sup>4-</sup>].

## Discussion

The identification of the hexadentate species CoEDTA<sup>-</sup> as the primary mononuclear product of the CoEDTA<sup>2-</sup>-Fe(CN)<sub>6</sub><sup>3-</sup> reaction at pH 10, coupled with the pH independence of the Fe(CN)<sub>6</sub><sup>3-</sup> oxidation of CoEDTA<sup>2-</sup> and the Fe(CN)<sub>6</sub><sup>4-</sup> reduction of CoEDTA<sup>-</sup> in the pH range from 5 to 10, shows that the overall equilibrium between mononuclear species is properly described by eq 5.<sup>22</sup> When the present



measurements of the CoEDTA<sup>-</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> reaction are combined with the earlier measurements and interpretation (eq 1 and 2 with k<sub>1</sub>/k<sub>-1</sub> = 831 M<sup>-1</sup> and k<sub>2</sub> = 5.40 × 10<sup>-3</sup> sec<sup>-1</sup>),<sup>2-4</sup> the equilibrium constant for eq 5 is (k<sub>1</sub>/k<sub>-1</sub>)(k<sub>2</sub>/k<sub>-2</sub>) = 831 × 5.4 × 10<sup>-3</sup>/0.21 = 21. The agreement between this value and the value of 100 estimated<sup>2</sup> from the appropriate oxidation potentials is satisfactory. The consistency between kinetic and equilibrium data cannot, however, be taken as a confirmation of the mechanism given in eq 1 and 2. Another mechanism, consistent with all the available data, accounts for the formation of the mononuclear products on the basis of a direct outer-sphere electron-transfer path between cobalt(II) and iron(III) rather than *via* dissociation of the binuclear complex. In the alternate mechanism<sup>23</sup> (eq 1 and 5, with eq 5 now having mechanistic significance with forward and reverse rate constants k<sub>3</sub> and k<sub>-3</sub>, respectively), CoEDTA<sup>2-</sup> and Fe(CN)<sub>6</sub><sup>3-</sup> react predominantly by an inner-

(22) At this point, eq 5 has only stoichiometric significance. As the discussion progresses, eq 5 will be assigned mechanistic significance.

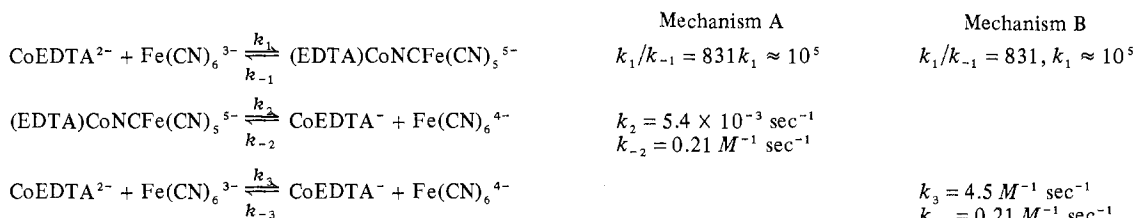
(23) Similar mechanistic patterns have been previously recognized in a study of the Ru(NH<sub>3</sub>)<sub>5</sub>Cl<sup>2+</sup>-Cr<sup>2+</sup> reaction: W. G. Movius and R. G. Linck, *J. Amer. Chem. Soc.*, 92, 2677 (1970). Ru(III) and Cr(II) react predominantly by an inner-sphere mechanism to produce the binuclear successor complex (NH<sub>3</sub>)<sub>5</sub>RuClCr(H<sub>2</sub>O)<sub>5</sub><sup>4+</sup>. The mononuclear products Ru(NH<sub>3</sub>)<sub>5</sub>OH<sub>2</sub><sup>2+</sup> and Cr(H<sub>2</sub>O)<sub>5</sub>Cl<sup>2+</sup> are formed by dissociation of the binuclear complex or *via* an alternate minor inner-sphere mechanism. The form of the rate law indicates equilibrium formation of a complex between the reactants, but it does not specify whether the complex is the immediate predecessor of the products or whether these are formed by an alternate interaction between the reactants which does not involve the complex.

Table IV. Rate Constants for Substitution and Redox Reactions of Co<sup>III</sup>-EDTA Complexes

Reaction	$k_f^a$	$k_r^b$	Ref
CoEDTA <sup>-</sup> + H <sub>3</sub> O <sup>+</sup> ⇌ Co(EDTA)OH <sub>2</sub>	2.97 × 10 <sup>-4</sup>	2.33 × 10 <sup>-4</sup>	c
CoEDTA <sup>-</sup> + H <sub>2</sub> O ⇌ Co(EDTA)OH <sub>2</sub> <sup>-</sup>	2.26 × 10 <sup>-6</sup>	2.21 × 10 <sup>-3</sup>	d
CoEDTA <sup>-</sup> + OH <sup>-</sup> ⇌ Co(EDTA)OH <sub>2</sub> <sup>2-</sup>	3.5 × 10 <sup>-2</sup>	4.33 × 10 <sup>-5</sup>	e
Co(EDTA)Cl <sup>2-</sup> ⇌ CoEDTA <sup>-</sup> + Cl <sup>-</sup>	2.8 × 10 <sup>-6</sup>		f
CoEDTA <sup>-</sup> + Fe(CN) <sub>6</sub> <sup>4-</sup> ⇌ ?	0.21		g
Co(EDTA)OH <sub>2</sub> <sup>-</sup> + Fe(CN) <sub>6</sub> <sup>4-</sup> ⇌ ?	3.4		g
Co(EDTA)Cl <sup>2-</sup> + Fe(CN) <sub>6</sub> <sup>4-</sup> ⇌ ?	7.0		g

<sup>a</sup> Rate constant for forward reaction at 25°. <sup>b</sup> Rate constant for backward reaction at 25°. <sup>c</sup> Reference 6. <sup>d</sup>  $k_r$  measured in present work;  $k_f$  calculated from  $K = k_f/k_r$  where  $K$  is  $1.02 \times 10^{-3}$ . <sup>e</sup>  $k_r$  from reference 5;  $k_f$  calculated from  $K = k_f/k_r$  where  $K = 8.16 \times 10^2 M^{-1}$ . <sup>f</sup> Extrapolated to 25° from higher temperature data in ref 6. <sup>g</sup> This work.

## Scheme I



sphere mechanism to produce the binuclear complex identified by Adamson and Gonick as (EDTA)CoNCFe(CN)<sub>5</sub><sup>5-</sup>. This pathway, although  $\sim 2 \times 10^4$  more efficient than the outer-sphere path in bringing about the redox process between Fe(III) and Co(II), is a "dead end" as far as production of mononuclear Fe(II) and Co(III) products is concerned. The two interpretations are summarized in Scheme I, together with the assigned rate constants.

Although the available data are insufficient to differentiate between the two mechanisms, we favor mechanism B on the basis of the following indirect arguments. According to mechanism A, the reduction of CoEDTA<sup>-</sup> by Fe(CN)<sub>6</sub><sup>4-</sup> proceeds by an inner-sphere reaction whereby the nitrogen end of one CN<sup>-</sup> in Fe(CN)<sub>6</sub><sup>4-</sup> first penetrates the coordination sphere of cobalt(III) to produce the cyano-bridged iron(II)-cobalt(III) binuclear complex, a process which would proceed with a rate constant of  $0.21 M^{-1} \text{ sec}^{-1}$ . Direct displacement of a carboxylate group by the N end of bound cyanide is unlikely in view of the dissociative character of cobalt(III) substitution reactions, and the intermediacy of an aquopentadentatecobalt(III) complex is precluded by the known rate ( $k = 2.26 \times 10^{-6} \text{ sec}^{-1}$  at 25°) of formation of Co(EDTA)OH<sub>2</sub><sup>-</sup> from CoEDTA<sup>-</sup>. Therefore, we conclude that the reduction of CoEDTA<sup>-</sup> by Fe(CN)<sub>6</sub><sup>4-</sup> proceeds by an outer-sphere mechanism, and, using microscopic reversibility considerations, the oxidation of CoEDTA<sup>2-</sup> by Fe(CN)<sub>6</sub><sup>3-</sup> which results in the formation of CoEDTA<sup>-</sup> and Fe(CN)<sub>6</sub><sup>4-</sup> also proceeds by an outer-sphere mechanism; e.g., mechanism B obtains.

Arguments based on the slow rates of substitution of Co<sup>III</sup>-EDTA complexes as compared to the rates of reduction by Fe(CN)<sub>6</sub><sup>4-</sup> indicate that the Fe(CN)<sub>6</sub><sup>4-</sup> reductions of Co(EDTA)OH<sub>2</sub><sup>-</sup> and Co(EDTA)Cl<sup>2-</sup> also proceed by an outer-sphere mechanism. The pertinent information is summarized in Table IV. Except for the reaction of CoEDTA<sup>-</sup> with OH<sup>-</sup> (which results in decomposition of the complex<sup>6</sup>), substitution rates of Co<sup>III</sup>-EDTA complexes fall in the range  $10^{-3}$ – $10^{-6} \text{ sec}^{-1}$ , whereas the redox rates are in the range  $0.21$ – $7.0 M^{-1} \text{ sec}^{-1}$ , and therefore the classic criterion invoked to assign an outer-sphere mechanism is applicable in the present systems. The arguments based on rate comparisons are particularly compelling in the cases of Co(EDTA)OH<sub>2</sub><sup>-</sup> and Co(EDTA)Cl<sup>2-</sup>. The displacements of H<sub>2</sub>O or Cl<sup>-</sup> by the

dangling carboxylate ligand proceed with rate constants of  $2.21 \times 10^{-3}$  and  $1.2 \times 10^{-6} \text{ sec}^{-1}$ , respectively, whereas the corresponding rate constants for reduction by Fe(CN)<sub>6</sub><sup>4-</sup> are  $3.4$  and  $7.0 M^{-1} \text{ sec}^{-1}$ , respectively. Therefore, unless Fe(CN)<sub>6</sub><sup>4-</sup> exerts a specific (and mysterious) labilizing effect on approaching the cobalt(III) complexes, substitution on cobalt(III) is precluded, and the redox reactions proceed by an outer-sphere mechanism.

Additional, indirect support for the outer-sphere interpretation of the Fe(CN)<sub>6</sub><sup>3-</sup>-CoEDTA<sup>2-</sup> reaction that produces the mononuclear species comes from a calculation<sup>3</sup> of the rate constant for this reaction using Marcus' equation  $k_{12} = (k_{11} \cdot k_{22} K_{12})^{1/2}$ . With  $k_{11} = 2 \times 10^{-7} M^{-1} \text{ sec}^{-1}$ ,  $k_{22} = 10^5 M^{-1} \text{ sec}^{-1}$ , and  $K_{12} = 10^2$ , Huchital and Wilkins<sup>3</sup> obtained  $k_{12} \approx 1 M^{-1} \text{ sec}^{-1}$  for the predicted outer-sphere rate constant of the Fe(CN)<sub>6</sub><sup>3-</sup>-CoEDTA<sup>2-</sup> reaction and noted that this value was several orders of magnitude smaller than their measured rate constant for the inner-sphere pathway. The agreement of the predicted value with the value  $4.5 M^{-1} \text{ sec}^{-1}$  obtained from the measured parameters and the interpretation based on mechanism B is excellent and reinforces the present interpretation. The faster reaction rate of CoEDTAOH<sub>2</sub><sup>-</sup> as compared to CoEDTA<sup>-</sup> can also be rationalized on the basis of Marcus' equation. Since CoEDTAOH<sub>2</sub><sup>-</sup> is less stable than CoEDTA<sup>-</sup> by a factor of  $10^3$ , provided that the exchange rates for the hexadentate and pentadentate species are the same, we would expect the reduction of CoEDTAOH<sub>2</sub><sup>-</sup> to be faster than that of CoEDTA<sup>-</sup> by a factor of  $(10^3)^{1/2} \approx 31$ , in excellent agreement with the observed factor of 16.

All in all, it appears that the outer-sphere mechanism for the Fe(CN)<sub>6</sub><sup>4-</sup> reductions of Co(EDTA)OH<sub>2</sub><sup>-</sup> and Co(EDTA)Cl<sup>2-</sup> and parallel inner- and outer-sphere reactions for the Fe(CN)<sub>6</sub><sup>3-</sup>-CoEDTA<sup>2-</sup> reaction are pretty firmly established. The occurrence of parallel inner- and outer-sphere pathways has been, by now, widely recognized. However, the present interpretation of the CoEDTA<sup>2-</sup>-Fe(CN)<sub>6</sub><sup>3-</sup> reaction differs from previous proposed mechanisms in that dissociation of the successor binuclear complex is ruled out. One might ask, therefore, how general is the interpretation of binuclear successor complex formation as a "dead end" and the need of an alternate pathway to mononuclear products. In the case of binuclear complex detection and bridging ligand transfer, such an interpretation can be discarded quite con-

vincingly.<sup>23</sup> However, when bridging ligand transfer does not obtain, then the alternate outer-sphere pathway is at least plausible.<sup>24</sup>

(24) There is one requirement that must be fulfilled for the alternate interpretation (mechanism B) to be physically meaningful. The product of the equilibrium constant for binuclear complex formation

Registry No. CoEDTA<sup>-</sup>, 15136-66-0; Co(EDTA)Cl<sup>2-</sup>, 23467-31-4; Co(EDTA)OH<sub>2</sub><sup>-</sup>, 24340-68-9; Fe(CN)<sub>6</sub><sup>4-</sup>, 13408-63-4; CoEDTA<sup>2-</sup>, 14931-83-0; Fe(CN)<sub>6</sub><sup>3-</sup>, 13408-62-3.

and the parameter commonly interpreted as the dissociation of the binuclear complex must be  $<10^{10} M^{-1} \text{sec}^{-1}$ , the upper limit for a diffusion-controlled reaction.

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## Saturated Macrocyclic ( $N_4$ ) Complexes of Cobalt(III) Containing Cobalt-Alkyl Bonds. Preparation and Properties<sup>1</sup>

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A photochemical approach to the preparation of  $\text{Co}^{\text{III}}(\text{N}_4)\text{YR}$  complexes has been devised where ( $\text{N}_4$ ) is some saturated or partly saturated quadridentate macrocyclic nitrogen donor ligand, R is an alkide or alkenide ligand, and Y is some ligand such as  $\text{H}_2\text{O}$ ,  $\text{NCS}^-$ , etc. The photoredox decompositions of  $\text{Co}(\text{NH}_3)_5\text{O}_2\text{CR}^{2+}$  complexes in acidic aqueous solutions were used for sources of R radicals; when photolyses were performed in the presence of  $\text{Co}^{\text{II}}(\text{N}_4)$  complexes, the radical-cobalt(II) reactions were found to be rapid and reasonably efficient. Complexes have been prepared with ( $\text{N}_4$ ) = a cyclic tetramine or a cyclic diimine-diamine, and  $\text{R} = \text{CH}_3$  or  $\text{C}_2\text{H}_5$ . Side reactions and other problems of the preparative method are mentioned. The product  $\text{Co}^{\text{III}}(\text{N}_4)\text{YR}$  complexes are very stable coordination complexes. Some apparently five-coordinate  $\text{Co}(\text{N}_4)\text{CH}_3^{2+}$  complexes have been prepared and partially characterized. Although  $\text{CH}_3^-$  seems to be a good ligand with relatively high crystal field strength in the complexes with saturated equatorial ( $\text{N}_4$ ) ligands, the absorption spectra of  $\text{Co}^{\text{III}}(\text{N}_4)(\text{OH})_2\text{CH}_3$  complexes with relatively unsaturated ( $\text{N}_4$ ) ligand systems exhibit features which are not well understood.

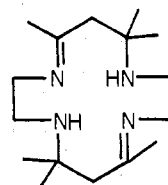
### Introduction

Since the discovery<sup>2</sup> that the stable, natural product, coenzyme B<sub>12</sub>, is a cobalt(III) complex containing a  $\sigma$ -bonded alkyl ligand, there has been considerable interest in the preparation and study of analogous synthetic complexes.<sup>3</sup> One point of interest in these studies has been the elucidation of the conditions which result in "stabilization" of cobalt(III)-alkyl moieties. Prior to the present study all the known complexes containing stable cobalt(III)-alkyl bonds contained highly unsaturated ligands (e.g., corrin, bis(dimethylglyoxime), cyanide, etc.) cis to the organic ligand. The relative ease of preparation of such unsaturated cobalt-alkyl complexes compared to the numerous failures to prepare cobalt-alkyl complexes containing only saturated ligands, led to a belief that unsaturation of the equatorial ligand systems (with perhaps a concomitant enhancement of metal-ligand bond strength), was a necessary prerequisite to the formation of stable cobalt(III)-alkyl complexes.<sup>3,4</sup> In this report we describe the preparation and characteriza-

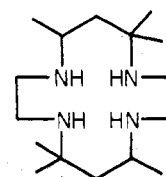
tion of the first cobalt(III)-alkyl complexes with saturated equatorial ligand systems.

### Experimental Section

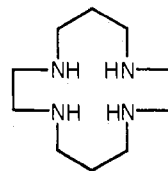
The acetato-, phenylacetato-, and acrylatopentaamminecobalt(III) complexes were prepared as perchlorate salts by standard procedures.<sup>5</sup> The  $\text{Co}^{\text{II}}(\text{N}_4)^{6,7}$  complexes with  $\text{N}_4 = \text{Me}_6[14]\text{dieneN}_4$ ,<sup>8</sup>  $\text{Me}_6[14]\text{-aneN}_4$ ,<sup>6</sup> and  $\text{Me}_4[14]\text{tetraeneN}_4$ <sup>9,10</sup> were prepared as described previously and isolated as the  $(\text{CoCl}_4)^{2-}$  salts.



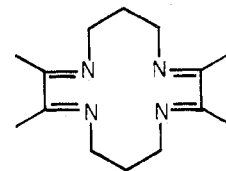
$\text{Me}_6[14]\text{dieneN}_4$



$\text{Me}_6[14]\text{aneN}_4$



$[14]\text{aneN}_4$



$\text{Me}_4[14]\text{tetraeneN}_4$

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(6) Abbreviations for macrocyclic ligands are based on suggestions by Busch and coworkers.<sup>7</sup> In this study we use  $\text{Me}_6[14]\text{-tetraeneN}_4 = 2,3,9,10\text{-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene}$ ,  $\text{Me}_6[14]\text{dieneN}_4 = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene}$ ,  $\text{Me}_6[14]\text{aneN}_4 = C\text{-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$ , and  $[14]\text{aneN}_4 = 1,4,8,11\text{-tetraazacyclotetradecane}$ .

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