Co(III), both of which have d orbitals of similar energy, the situation appears to be more complex than simple d orbital energy differences.

Acknowledgment. This research was supported by the Robert A. Welch Foundation, Houston, Texas. J.G.L wishes to express his gratitude to the Robert A. Welch Foundation and the South African C.S.I.R. for the financial support as well as to the University of the Orange Free State, Bloemfontein, South Africa, for granting the leave.

Registry No. $RhTPPS(H_2O)_2^{3-}$, 66035-54-9; NCS^-, 302-04-5; I^-, 20461-54-5; Cl^-, 16887-00-6; Br^-, 24959-67-9; $RhTPPS(OH)H_2O^{4-}$, 73002-74-1; $RhTPPS(OH)_2^{5-}$, 73002-75-2; $RhTPPS(Cl)H_2O^{4-}$, 73002-76-3; $RhTPPS(Br)H_2O^{4-}$, 73002-77-4; $RhTPPS(I)H_2O^{4-}$, 73002-78-5; $RhTPPS(NCS)H_2O^{4-}$, 73002-79-6; $RhTPPS(NCS)_2^{5-}$, 73017-48-8; $Na_3RhTPPS(H_2O)_2$, 73017-49-9.

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Kinetics and Mechanism of the Reductions of (4,4′-Bipyridine)pentacyanoferrate(III) and (Pyridine)pentacyanoferrate(III) by (Ethylenediaminetetraacetato)cobaltate(II)[1]

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Received November 13, 1979

The title reactions proceed in two stages. The first stage corresponds to an inner-sphere oxidation reduction reaction that yields binuclear complexes containing Co(III) and Fe(II) linked by cyanide bridges. The binuclear complexes $(EDTA)CoNCFe(CN)_4L^{4-}$ (L = pyridine or 4,4′-bipyridine) exhibit the characteristic iron(II) to N-heterocycle charge-transfer bands at slightly shorter wavelengths (362 and 432 nm) than the parent mononuclear complexes (365 and 437 nm). Rate constants for the formation and dissociation to reactants of $(EDTA)CoNCFe(CN)_4L^{4-}$ (L = 4,4′-bipyridine) have been measured at 25 °C, pH 8.0, and ionic strength 0.10 M. The values are 2.3×10^4 M^{-1} s^{-1} and 16 s^{-1}, respectively. The binuclear complexes are metastable intermediates and disappear via a rate law of the form $a[CoEDTA^{2-}]/(1 + b[CoEDTA^{2-}])$ to produce quantitatively $CoEDTA^-$ and $Fe(CN)_5L^{3-}$. For pyridine at 25 °C, pH ~8, and ionic strength 0.10 M, a = 4.0 M^{-1} s^{-1} and $b = 4.5 \times 10^2$ M^{-1}. For 4,4′-bipyridine under the same conditions, a = 6.9 M^{-1} s^{-1} and $b = 1.4 \times 10^3$ M^{-1}. It is suggested that the binuclear complexes represent a "dead-end" toward the formation of mononuclear products and that these are formed via an alternate outer-sphere pathway for reaction between $CoEDTA^{2-}$ and $Fe(CN)_5L^{2-}$.

The reaction between hexacyanoferrate(III) and (ethylenediaminetetraacetate)cobaltate(II) results, initially, in the formation of a cyano-bridged binuclear complex[2-5] and, finally, in the production of $Fe(CN)_6^{4-}$ and $CoEDTA^{2-}$. The first mechanism[2] proposed to explain the observations involved the classic[6] three-step inner-sphere sequence, namely, formation of precursor complex, intramolecular electron transfer, and dissociation of successor complex. However, in recent work[4,5] it has been suggested that the binuclear complex formed in the inner-sphere reaction between $Fe(CN)_6^{3-}$ and $CoEDTA^{2-}$ represents a dead-end and that $Fe(CN)_6^{4-}$ and $CoEDTA^-$ are formed via a parallel outer-sphere pathway. In order to obtain additional information related to this reaction, we have carried out a kinetic study of the reduction of (4,4′-bipyridine)pentacyanoferrate(III) (hereafter abbreviated as $Fe(CN)_5bpy^{2-}$) by $CoEDTA^{2-}$. The propensity of $CoEDTA^{2-}$ to undergo inner-sphere reactions[2-5,7] and the ability of 4,4′-bipyridine to act as a bridging ligand[8,9] led us to anticipate the possible formation of a Fe^{II}–Co^{III} binuclear complex with the metal ions bridged by 4,4′-bipyridine. Unfortunately, this expectation was not borne out and only a cyano-bridged binuclear complex is formed. In comparison, and recognizing that only a cyano-bridged binuclear complex can be formed, we also carried out a kinetic study of the reaction between (pyridine)pentacyanoferrate(III), $Fe(CN)_5py^{2-}$, and $CoEDTA^{2-}$.

Experimental Section

Preparation of Complexes. For 4,4′-bipyridinium (4,4′-bipyridine)pentacyanoferrate(III) trihydrate, $bpyH_2[Fe(CN)_5bpy]\cdot 3H_2O$, 0.35 g of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was added to a solution of 4,4′-bipyridine in 55 mL of water. After 40 min in the dark, the resulting solution was filtered, and the filtrate was treated with 0.5–0.6 mL of concentrated hydrobomic acid, whereby the solution turned from brown to dark purple. Bromine vapor was allowed to dissolve in the solution until a sharp color change from purple to yellow occurred, at which time a yellow-green precipitate formed. The resulting mixture was allowed to cool to 0 °C, and then the precipitate was collected and washed with ethanol and ether. The product was recrystallized from hot water (0.32 g in 70 mL at 60 °C). The solid obtained was washed with ethanol and ether and then dried under vacuum. Anal. Calcd for $FeC_{25}H_{24}N_9O_3$: Fe, 10.07; C, 54.17; N, 22.74; H, 4.36. Found: Fe, 10.09, 10.20, 10.27; C, 54.65, 54.86; N, 22.76, 22.99; H, 4.36, 4.29. An acid–base titration of the compound with a standard sodium hydroxide solution to a phenol red end point showed the presence of 2.09 protons/mol of compound.

Lithium (pyridine)pentacyanoferrate(III) was prepared in solution by an ion-exchange method. A 0.16-g sample of $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was added to a solution of 2 mL of pyridine in 20 mL of water at 0 °C. After 40 min in the dark, 15 mL of 0.100 M $Ce(NH_4)_2(NO_3)_6$ in 2.06 N H_2SO_4 was added dropwise, and then water was added to bring the total volume to 100 mL. The resulting solution was added to a column of Bio-Rex 9 in the sulfate form. The column was rinsed thoroughly with water, and then the complex $Fe(CN)_5py^{2-}$ was eluted off with 25 mL of 1.42 M $LiClO_4$ followed by 75 mL of water. The resulting stock solution was stored in low actinic glassware at ~2 °C.

Potassium (ethylenediaminetetraacetato)cobaltate(III) was the sample used in previous work.[4] Sodium (ethylenediaminetetraacetato)cobaltate(II) was prepared in solution by the addition of a 10% excess of Na_2H_2EDTA to the appropriate amount of $Co(ClO_4)_2$.

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0020-1669/80/1319-1616$01.00/0

Table I. Absorption Spectra of $Fe^{II}(CN)_5L^{n-}$ Binuclear and Mononuclear Complexes in Aqueous Solution

complex	λ_{max}, nm	$10^{-3}\epsilon$, $M^{-1}\ cm^{-1}$
$(EDTA)Co^{III}NCFe^{II}(CN)_4bpy^{4-}$	432	7.1
$(EDTA)Co^{III}NCFe^{II}(CN)_4py^{4-}$	362	5.3
$Fe^{II}(CN)_5bpy^{3-}$	437	5.8
$Fe^{II}(CN)_5py^{3-}$	365	3.7
$(NH_3)_5Co^{III}bpyFe^{II}(CN)_5$	505	6[a]
$(NH_3)_5Rh^{III}bpyFe^{II}(CN)_5$	515	[b]

[a] From ref 8. [b] From KBr pellet.[15]

Materials. 4,4′-bipyridine was recrystallized twice from hot water. Lithium perchlorate was recrystallized once from hot water. Argon was purified by passing it through a column of BTS catalyst. The water used in all the experiments was house-distilled water passed through a Barnstead ion-exchange demineralizer and distilled in a modified (all-glass) Corning Model AG-1b apparatus. Bio-Rex 9 was purified by rinsing it successively with 1 M NaOH, water, 0.5 M H_2SO_4, and water. All other chemicals were reagent grade and used as received.

Analyses. The cobalt(II) perchlorate stock solution used in the preparation of $CoEDTA^{2-}$ solutions was standardized spectrophotometrically.[10] Iron was analyzed by a standard method.[11] $LiClO_4$ solutions were standardized by an ion-exchange procedure. The concentration of the stock solution of $Fe(CN)_5py^{2-}$ was measured spectrophotometrically as the corresponding iron(II) complex after reduction with ascorbic acid. The molar absorbance used was 3.7 × 10^3.[12] C, H, and N analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Instruments. Spectrophotometric measurements were carried out with a Cary 17 or 118 spectrophotometer. Stopped-flow measurements were done on a Durrum Model D-110 instrument interfaced to an IBM 1800 computer. pH measurements were carried out with an Orion Model 801 instrument.

Kinetics Measurements. For slow reactions, appropriate aliquots of the solutions of $CoEDTA^{2-}$ and of the iron(III) complex were added to a solution containing the desired amounts of buffer, lithium perchlorate, and nitrogen heterocycle. The resulting solution was added to a spectrophotometric cell which was placed in the thermostated cell compartment of the spectrophotometer, and a recording of absorbance vs. time (30–40 points during 3 half-lives) was obtained. The wavelengths of observation were 370 and 440 nm for pyridine and 4,4′-bipyridine, respectively. First-order rate constants were obtained from a linear least-squares fit of $\ln (A_t - A_\infty)$ vs. t. For fast reactions, solutions of $CoEDTA^{2-}$ at the final desired pH and ionic strength were mixed in the stopped-flow apparatus with solutions of $Fe(CN)_5bpy^{2-}$ at the same pH and ionic strength, and the increase in absorbance at 440 nm was followed. All kinetic measurements were carried out at 25 °C, pH 7.8, and ionic strength 0.10 M.

Spectra of Intermediates. The spectra of the binuclear intermediates formed in the reactions were obtained with solutions prepared in the same manner as for the kinetic measurements, except that the solutions were mixed at 0 °C and the cell compartment of the spectrophotometer was kept at 10 °C. The spectra were scanned several times in order to calculate the spectrum at time zero, but no changes were observed during the first 5 min.

Results

In agreement with previous work[2,3] with other iron(III) cyanide complexes, we found that mixing $Fe(CN)_5L^{2-}$ (L = bpy or py) with an excess of $CoEDTA^{2-}$ results in the rapid formation of binuclear complexes containing Fe(II) and Co(III), and this stage is followed by the slow disappearances of the binuclear complexes and quantitative formation of $CoEDTA^-$ and $Fe^{II}(CN)_5L^{3-}$. The spectra of solutions containing the binuclear complexes were measured at 10 °C to slow down the process by which they disappear. High $CoEDTA^{2-}$ concentrations were used in order to shift the equilibrium represented by eq 1 as far to the left as possible.

$$Fe(CN)_5L^{2-} + CoEDTA^{2-} \rightleftharpoons (NC)_4LFe^{II}CNCo^{III}EDTA^{4-} \quad (1)$$

Table II. Rate Constants for the Disappearance of $(EDTA)Co^{III}NCFe^{II}(CN)_4bpy^{4-}$ [a]

$10^4[CoEDTA^{2-}]_0$, M	$10^5[Fe(CN)_5bpy^{2-}]_0$, M	10^3k_{obsd},[b] s^{-1}
5.35	1.89	1.90 ± 0.17
7.68	4.93	2.61 ± 0.06
9.60	5.31	3.15 ± 0.07
19.2	5.13	3.50 ± 0.19
19.2	5.41	3.50 ± 0.20
24.0	5.44	3.86 ± 0.10

[a] At 25 °C, pH 7.8 ± 0.1, ionic strength 0.10 M ($LiClO_4$), and [bpy] = (3.9–4.0) × 10^{-4} M. [b] Each entry is the average of four or more independent measurements.

Table III. Rate Constants for the Disappearance of $(EDTA)Co^{III}NCFe^{II}(CN)_4py^{4-}$ [a]

$10^4[CoEDTA^{2-}]_0$, M	$10^5[Fe(CN)_5py^{2-}]_0$, M	10^3k_{obsd},[b] s^{-1}
4.08	3.17	1.31 ± 0.01[c]
6.12	4.76	1.81 ± 0.01[d]
8.16	6.35	2.43 ± 0.04
10.2	6.35	2.82 ± 0.04
16.3	6.35	3.85 ± 0.12
20.4	6.35	4.25 ± 0.07
24.5	6.35	4.56 ± 0.16

[a] At 25 °C, pH 7.9 ± 0.1, ionic strength 0.10 M ($LiClO_4$), and [py] = 7.84 × 10^{-4} M. [b] Each entry is the average of four or more independent measurements. [c] [py] = 3.92 × 10^{-4} M. [d] [py] = 5.88 × 10^{-4} M.

However, the reactions were somewhat less than quantitative, and therefore the concentrations of the binuclear complexes were calculated from the equilibrium constants for eq 1 (measured as described below). The spectra of the binuclear complexes were calculated from the observed spectra, the known contribution of the excess $CoEDTA^{2-}$ (obtained from blank measurements), and the calculated contribution of the unreacted $Fe(CN)_5L^{2-}$. The wavelengths for the absorption maxima and corresponding molar absorbances of the binuclear complexes are listed in Table I. Included in Table I are the values for the parent mononuclear complexes and of selected 4,4′-bipyridine-bridged binuclear complexes. It will be seen that the binuclear complexes produced in the $CoEDTA^{2-}$–$Fe(CN)_5L^{2-}$ (L = py, bpy) reactions exhibit the iron(II) to heterocyclic ligand charge-transfer bands at wavelengths shorter than those of the parent mononuclear iron(II) complexes.

Preliminary measurements of the rate of disappearance of the binuclear complex formed in the $Fe(CN)_5bpy^{2-}$–$CoEDTA^{2-}$ reaction indicated the presence of inflection points in the absorbance vs. time curves after about 1 half-life. Removal of oxygen did not have any effect, but addition of excess 4,4′-bipyridine to prevent the aquation of the $Fe(CN)_5bpy^{3-}$ produced in the reaction eliminated the inflection point. Therefore, all measurements were carried in the presence of enough excess nitrogen heterocycle to prevent aquation of the iron(II) mononuclear product. The $\ln (A_t - A_\infty)$ vs. t plots showed slight deviations from linearity during the first few minutes of the reaction. The possible source of these small deviations will be discussed below. Rate constants for the reactions of $Fe(CN)_5bpy^{2-}$ and $Fe(CN)_5py^{2-}$ are listed in Tables II and III, respectively. The dependence of k_{obsd} upon $CoEDTA^{2-}$ concentration is given by eq 2. Values of a and

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$$k_{\text{obsd}} = a[\text{CoEDTA}^{2-}]/(1 + b[\text{CoEDTA}^{2-}]) \qquad (2)$$

b for each compound were obtained from a nonlinear least-squares fit of k_{obsd} to [CoEDTA^{2-}]. For bpy and py values of a and b are 6.9 M^{-1} s^{-1} and 1.4 × 10^3 M^{-1} and 4.0 M^{-1} s^{-1} and 4.5 × 10^2 M^{-1}, respectively. For comparison, values of a and b for $Fe(CN)_6^{3-}$ and $Fe(CN)_5P(C_6H_5)_3^{2-}$ at 30 °C, pH 6.0, and ionic strength 0.26 M are 2.6 M^{-1} s^{-1} and 2.7 × 10^2 M^{-1} and 3.1 M^{-1} s^{-1} and 1.5 × 10^3 M^{-1}, respectively.[13]

In order to estimate the reduction potential of the $Fe(CN)_5bpy^{2-/3-}$ couple, the equilibrium constant for reaction 3 was determined by a spectrophotometric method. The

$$\text{Fe(CN)}_5\text{bpy}^{2-} + \text{Fe(CN)}_6^{4-} \rightleftharpoons \text{Fe(CN)}_5\text{bpy}^{3-} + \text{Fe(CN)}_6^{3-} \qquad (3)$$

measurements (4) were carried out at 25 °C, pH 8.0 (tris buffer), and ionic strength 0.10 M ($LiClO_4$) with [$Fe(CN)_5bpy^{2-}$] = 6.65 × 10^{-5} M and [$Fe(CN)_6^{4-}$] = 2.03, 4.06, 6.09, and 7.10 × 10^{-4} M. The equilibrium constant for eq 3 was calculated from the expression $K = x^2/(a_0 - x)(b_0 - x)$ where a_0 and b_0 are the initial concentrations of $Fe(CN)_5bpy^{2-}$ and $Fe(CN)_6^{4-}$, respectively, and x is the equilibrium concentration of $Fe(CN)_5bpy^{3-}$ or $Fe(CN)_6^{3-}$ calculated from $(A/(l - \epsilon_1 a_0 - \epsilon_2 b_0))/(\epsilon_3 + \epsilon_4 - \epsilon_1 - \epsilon_2)$. A is the absorbance of the equilibrated solution at 440 nm, l is the cell path length, $\epsilon_1 = 1.2 \times 10^3$, $\epsilon_2 = 2$, $\epsilon_3 = 5.3 \times 10^3$, and $\epsilon_4 = 6.5 \times 10^2$ M^{-1} cm^{-1} are the molar absorbances at 440 nm of $Fe(CN)_5bpy^{2-}$, $Fe(CN)_6^{4-}$, $Fe(CN)_5bpy^{3-}$, and $Fe(CN)_6^{3-}$, respectively. From the measured value $K = 4.0 \pm 0.2$ and using 0.42 V[14] for the reduction potential of $Fe(CN)_6^{3-}$, we calculate a reduction potential of 0.46 V for $Fe(CN)_5bpy^{2-}$.

The rate of formation of $(EDTA)Co^{III}NCFe^{II}(CN)_4bpy^{4-}$ was measured by the stopped-flow technique at 25 °C, pH 8.0, and ionic strength 0.10 M. Three independent sets of measurements were carried out with [CoEDTA^{2-}] = 2.60 × 10^{-4} M and [$Fe(CN)_5bpy^{2-}$] = 2.56 × 10^{-5} M. Plots of ln $(A_\infty - A_t)$ vs. t were somewhat curved because A_∞ values were not steady (disappearance of the binuclear complex). From initial slopes, the average value of k_{obsd} was 22 ± 1 s^{-1}.

Discussion

The reductions of $Fe(CN)_5L^{2-}$ by CoEDTA^{2-} when L = bpy or py display the same stoichiometric and kinetic characteristics as those studied previously with L = CN^- and $P(C_6H_5)_3$.[2,3,5,13] The rapid, large increase in absorbance attending the CoEDTA^{2-}–$Fe(CN)_5L^{2-}$ reaction followed by a slower, smaller increase noted in the present work is ascribed to the formation of a Co(III)–Fe(II) binuclear complex and its subsequent disappearance.[15] The assignment of an Fe(II) oxidation state is on a firm basis since the binuclear complexes exhibit the metal to ligand charge-transfer bands characteristic[12] of pentacyanoferrate(II) complexes of nitrogen heterocycles. The wavelength for maximum absorbance recorded immediately upon mixing the reactants is shifted to slightly lower wavelengths relative to the wavelength of maximum absorbance reported for the corresponding mononuclear complexes (Table I). This shift in wavelength is consistent with the binding of a Co(III) center to the N of a CN^- bound to Fe(II). Thus, it has been shown that protonation of a CN^- in pentacyanoferrate(II) complexes of nitrogen heterocycles results in a shift of the MLCT band to higher energies,[12] perhaps because the proton, as well as the Co(III) center, removes electron density from the iron(II). It must be emphasized that for bpy (as well as py), the shift in the absorbance maximum of the mononuclear $Fe(CN)_5^{3-}$ complex upon binding the Co(III) complex is toward *shorter* wavelengths, a result incompatible with attachment of the Co(III) center to the remote N of bpy: for such attachment, a considerable shift (70–80 nm) toward *longer* wavelengths[8,16] would have obtained.

Table IV. Equilibrium and Rate Constants for Eq 4, 5, and 6[a]

L	k_1/k_{-1}[b]	k_3/k_{-3}[c]	k_2[d]	k_{-2} or k_{-3}[e]	k_3
bpy	1.4 × 10^3	3.3 × 10	5.0 × 10^{-3}	2.1 × 10^{-1}	6.9
py	4.5 × 10^2	4.9 × 10	8.8 × 10^{-3}	8.2 × 10^{-2}	4.0
CN^- [f]	8.3 × 10^2	7.1	5.4 × 10^{-3}	6.4 × 10^{-1}	4.5
$P(C_6H_5)_3$ [g]	1.5 × 10^3	9 × 10^2	2.1 × 10^{-3}	3.0 × 10^{-2}	3.1

[a] At 25 °C, ionic strength 0.10 M, and pH 8.0. [b] From parameter b in eq 2. [c] From reduction potentials of CoEDTA$^{-/2-}$ (0.37 V), $Fe(CN)_5py^{2-/3-}$ (0.47 V), $Fe(CN)_5bpy^{2-/3-}$ (0.46 V), $Fe(CN)_6^{3-/4-}$ (0.42 V), and $Fe(CN)_5P(C_6H_5)_3^{2-/3-}$ (0.54 V). [d] From a/b in eq 2. [e] From k_3/k_{-3} and k_3. [f] From parameter a in eq 2. At pH 5.0 and ionic strength 0.59 M.[4] [g] At pH 5.0, ionic strength 0.26 M, and 30 °C.[13]

Some additional evidence for a cyanide-bridged structure in the bpy complex comes from a comparison of the rates of formation and dissociation of the binuclear complex $(EDTA)Co^{III}NCFe^{II}(CN)_4L^{4-}$ for L = bpy with the rates of formation and dissociation of the binuclear complexes for L = CN^- and $P(C_6H_5)_3$ where the cyanide-bridged structure is obligatory.[13] As shown, the formation of the binuclear complex according to eq 4 is less than quantitative, at the CoEDTA^{2-}

$$\text{CoEDTA}^{2-} + \text{Fe(CN)}_5\text{L}^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{EDTA})\text{Co}^{\text{III}}\text{NCFe}^{\text{II}}(\text{CN})_4\text{L} \qquad (4)$$

concentration used, and therefore the stopped-flow measurements yield values of $k_{\text{obsd}} = k_1[\text{CoEDTA}^{2-}] + k_{-1}$. Using the measured value of k_{obsd} = 22 s^{-1} and k_1/k_{-1} = 1.4 × 10^3 M^{-1} (see below), we calculate k_1 = 2.3 × 10^4 M^{-1} s^{-1} and k_{-1} = 16 s^{-1} (25 °C, ionic strength 0.10 M). These values compare favorably with the values[13] (30 °C and ionic strength 0.26 M) k_1 = 3.8 × 10^4 M^{-1} s^{-1} and k_{-1} = 189 s^{-1} for L = CN^- and k_1 = 2.0 × 10^4 M^{-1} s^{-1} and k_{-1} = 13.4 s^{-1} for L = $P(C_6H_5)_3$. Therefore, we infer that for bpy, as must be the case for CN^- and $P(C_6H_5)_3$, a CN^--bridged binuclear complex is formed.

On the basis of cyanide-bridged structures, there are two possible geometric isomers for the binuclear complexes of formula $(EDTA)Co^{III}NCFe^{II}(CN)_4L^{4-}$, namely, the structures with the bridging cyanide cis or trans with respect to the ligand L. Presumably, both isomers are formed, since the ln $(A_\infty - A_t)$ vs. t plots displayed small deviations (differences between experimental absorbance and absorbance calculated from the linear least-squares fit of ln $(A_t - A_\infty)$ vs. t) from linearity during the first half-life, a result compatible with the presence of two species disappearing at different rates. In this context, it is noteworthy that no such deviations were reported[5,14] for L = $P(C_6H_5)_3$, where the steric effect of the phosphine ligand prevents binding of the Co(III) to the cyanide groups cis to $P(C_6H_5)_3$.

The cyanide-bridged, binuclear complexes are metastable intermediates and decompose to yield the mononuclear products CoEDTA$^-$ and $Fe(CN)_5L^{3-}$. Two different mechanism have been proposed to account for the decomposition reactions.[2-5] Reaction 5 represents the dissociation of the binuclear complex via Co–N bond fission, whereas in reaction 6 the mononuclear products are the result of an alternate, outer-

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(15) At first glance, the slow increases in absorbance associated with the disappearance of the binuclear complexes appear to be incompatible with their higher molar absorbances as compared to those of the mononuclear products. However, at the CoEDTA^{2-} concentrations used in the kinetic measurements, the *equilibrium* concentrations of the binuclear complexes are such that their *apparent* molar absorbances are less than those of the mononuclear products.

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$$(\mathrm{EDTA})\mathrm{Co^{III}NCFe^{II}(CN)_4L^{4-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{CoEDTA^-} + \mathrm{Fe(CN)_5L^{3-}} \quad (5)$$

$$\mathrm{CoEDTA^{2-}} + \mathrm{Fe(CN)_5L^{2-}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{CoEDTA^-} + \mathrm{Fe(CN)_5L^{3-}} \quad (6)$$

sphere pathway for the Co(II)–Fe(III) reaction. For the mechanism represented by eq 4 and 5, the value of k_{obsd} (eq 2) is given by $k_2K_1[\mathrm{CoEDTA^{2-}}]/(1 + K_1[\mathrm{CoEDTA^{2-}}])$. For the mechanism represented by eq 4 and 6, $k_{\mathrm{obsd}} = k_3[\mathrm{CoEDTA^{2-}}]/(1 + K_1[\mathrm{CoEDTA^{2-}}])$. Regardless of mechanism, the empirical parameter b in eq 2 is equal to K_1, the equilibrium constant for eq 4. The values of K_1 measured in the present work for bpy and py are listed in Table IV, together with those measured previously for $\mathrm{P(C_6H_5)_3}$ and $\mathrm{CN^-}$. The values fall in the narrow range 4.5×10^2–1.5×10^3 and, surprisingly, display no discernible trend with the oxidation potential of the Fe(III) complex. Depending on whether eq 5 or 6 is operative, the physical significance of the empirical parameter a is either k_2K_1 or k_3. Values of k_2 and k_3 are listed in Table IV. Values of k_{-2} or k_{-3}, estimated from the equilibrium constant K_3 for eq 6 (calculated from the appropriate reduction potentials), and the values of k_3 and K_1k_2 are also listed in Table IV. A choice between the two mechanistic interpretations was made previously[4] by comparing the value of k_{-2}, the rate constant for the replacement of one carboxylate of $\mathrm{EDTA^{4-}}$ by the N end of a CN in $\mathrm{Fe(CN)_5L^{3-}}$, with other values for substitution reactions at a Co(III)–EDTA center. It will be seen that the values of k_{-2} fall in the range 0.03–0.64 $\mathrm{M^{-1}\ s^{-1}}$, whereas rate constants for substitution of Co(III)–EDTA are in the 2×10^{-3}–$3 \times 10^{-6}\ \mathrm{s^{-1}}$ range.[17-19] The values of k_{-1} appear to be too high for substitution at a Co(III)–EDTA center, and, therefore, we favor the mechanism represented by eq 4 and 6. A similar argument can be applied to the rate constant k_2. These constants fall in the range $(2.1$–$8.8) \times 10^{-3}\ \mathrm{s^{-1}}$ and measure the loss of the $\mathrm{NCFe(CN)_4L^{3-}}$ moiety from the coordination sphere of pentadentate Co(III)–EDTA complex. The similar loss of $\mathrm{Cl^-}$ from $\mathrm{Co(EDTA)Cl^{2-}}$ proceeds with a rate constant of $2.8 \times 10^{-6}\ \mathrm{s^{-1}}$. Again this comparison suggests that the values of k_2, calculated on the assumption of eq 5 being operative, are unreasonably high for a substitution process at a Co(III) center. Therefore, eq 6 represents a more attractive alternative.

Additional, indirect support for the outer-sphere interpretation implied in eq 6 comes from calculations of the rate constants for the reactions of $\mathrm{Fe(CN)_5py^{2-}}$ or $\mathrm{Fe(CN)_5bpy^{2-}}$ with $\mathrm{CoEDTA^{2-}}$ using the Marcus cross relation corrected for electrostatic effects.[20] From the values of the self-exchange rate constants, 4.0×10^5 and $3.5 \times 10^{-7}\ \mathrm{M^{-1}\ s^{-1}}$ for $\mathrm{Fe(CN)_5L^{2-/3-}}$ and $\mathrm{CoEDTA^{-/2-}}$,[21-23] respectively, $E°$ values of 0.47, 0.46, and 0.37 V for $\mathrm{Fe(CN)_5py^{2-/3-}}$, $\mathrm{Fe(CN)_5bpy^{2-/3-}}$, and $\mathrm{CoEDTA^{-/2-}}$,[24] respectively, and radii of 5.0, 5.8, and 4.0 $\times 10^{-8}$ cm for $\mathrm{Fe(CN)_5py^{2-/3-}}$, $\mathrm{Fe(CN)_5bpy^{2-/3-}}$, and $\mathrm{CoEDTA^{-/2-}}$, respectively,[25,26] we calculate rate constants of 3.8 and 3.2 $\mathrm{M^{-1}\ s^{-1}}$ for the $\mathrm{Fe(CN)_5py^{2-}}$–$\mathrm{CoEDTA^{2-}}$ and $\mathrm{Fe(CN)_5bpy^{2-}}$–$\mathrm{CoEDTA^{2-}}$ reactions, respectively. The excellent agreement between these calculated values and the values 4.0 and 6.9 $\mathrm{M^{-1}\ s^{-1}}$ (Table IV) obtained by using experimental measurements and the interpretation embodied in eq 4 and 6 provides strong reinforcement of the outer-sphere interpretation.

Registry No. $\mathrm{Fe(CN)_5bpy^{2-}}$, 73295-95-1; $\mathrm{Fe(CN)_5py^{2-}}$, 61332-63-6; $\mathrm{CoEDTA^{2-}}$, 14931-83-0; $\mathrm{bpyH_2[Fe(CN)_5bpy]}$, 73295-97-3; $\mathrm{Li_2Fe(CN)_5py}$, 73295-98-4; $\mathrm{(EDTA)Co^{III}NCFe^{II}(CN)_4bpy^{4-}}$, 73308-28-8; $\mathrm{(EDTA)Co^{III}NCFe^{II}(CN)_4py^{4-}}$, 73295-99-5; $\mathrm{Fe^{II}(CN)_5bpy^{3-}}$, 37475-72-2; $\mathrm{Fe^{II}(CN)_5py^{3-}}$, 37475-75-5; $\mathrm{Na_3[Fe(CN)_5NH_3]}$, 14099-05-9.

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(26) The radius of $\mathrm{CoEDTA^{2-}}$ is taken to be equal to that of $\mathrm{FeEDTA^{2-}}$.

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Acid–Base Properties of (α,ω-Alkanediamine)pentaamminecobalt(III) Complexes in Aqueous Solution

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Received October 23, 1979

The pK_{a} values of $[\mathrm{Co(NH_3)_5\{NH_2(CH_2)_nNH_3\}}]^{4+}$ (n = 2–8 and 10) have been determined at 25 °C and I = 0.1 M (NaCl). The p$K_{\mathrm{a_1}}$ and p$K_{\mathrm{a_2}}$ values of both $[\mathrm{Co(NH_3)_4\{NH_2(CH_2)_4NH_3\}_2}]^{5+}$ and *cis*-$[\mathrm{Co(en)_2\{NH_2(CH_2)_4NH_3\}_2}]^{5+}$ have also been determined under the same experimental conditions. The absorption spectrum of $[\mathrm{Co(NH_3)_5\{NH_2(CH_2)_nNH_2\}}]^{3+}$ was found to be more intense than that of $[\mathrm{Co(NH_3)_5\{NH_2(CH_2)_nNH_3\}}]^{4+}$, especially, in the ultraviolet region. The spectral difference between these two species becomes more significant as the methylenic chain length becomes shorter. The increased ultraviolet absorbance in $[\mathrm{Co(NH_3)_5\{NH_2(CH_2)_nNH_2\}}]^{3+}$ was ascribed to the appearance of a charge-transfer band, whose origin was identified as the intramolecular hydrogen bonding between the free amino group and an N–H proton of the coordinated ammines or amino group.

Introduction

Metal complexes containing (2-aminoethyl)ammonium ion ($\mathrm{Hen^+}$) are known for cobalt(III),[1-8] platinum(II),[9,10] iron(II),[11] and ruthenium(II) and -(III).[12] Numerous chromium(III) complexes containing $\mathrm{Hen^+}$ have also been known.[13]

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