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Kinetic and Equilibrium Study of the Reaction of (*meso*-Tetrakis(*p*-sulfonatophenyl)porphinato)diaquorhodate(III) with Chloride, Bromide, Iodide, and Thiocyanate Ions in Aqueous Solution

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The reaction of Cl^-, Br^-, I^-, and NCS^- with (*meso*-tetrakis(*p*-sulfonatophenyl)porphinato)diaquorhodate(III) ($RhTPPS(H_2O)_2{}^{3-}$) has been studied at 15, 25, and 35 °C in 0.10 M H^+ with $\mu = 1.00$ M ($NaClO_4$). The values of the acidity constants K_{a_1} and K_{a_2} at 25 °C are $(9.7 \pm 0.1) \times 10^{-8}$ and $(1.6 \pm 0.2) \times 10^{-10}$ M, respectively. The values of the first stability constants are 0.74 ± 0.11, 1.82 ± 0.10, 41.2 ± 1.8, and $(1.22 \pm 0.04) \times 10^4$ M^{-1} for Cl^-, Br^-, I^-, and NCS^-, respectively. The value of the second stability constant for NSC^- is 3.68 ± 0.42 M, and the values for the remaining ions are <0.03. The kinetics of the addition of the first anion to $RhTPPS(H_2O)_2{}^{3-}$ are first order in anion concentration up to 0.90 M. The values of the second-order rate constants at 25 °C are $(2.64 \pm 0.11) \times 10^{-3}$, $(5.71 \pm 0.14) \times 10^{-3}$, $(2.01 \pm 0.03) \times 10^{-2}$, and $(2.73 \pm 0.06) \times 10^{-2}$ M^{-1} s^{-1}, for Cl^-, Br^-, I^-, and NCS^-, respectively. The values of ΔH^* and ΔS^* for the reaction with Cl^-, Br^-, I^-, and NCS^- are respectively 13.4 ± 0.6 kcal/mol and -25.4 ± 1.9 cal/(deg mol), 13.8 ± 0.3 kcal/mol and -22.6 ± 1.1 cal/(deg mol), 12.8 ± 0.8 kcal/mol and -23.4 ± 2.5 cal(deg mol), and 16.5 ± 0.2 kcal/mol and -10.3 ± 0.6 cal/(deg mol). There has been about a 10^6 increase in the rate constant for substitution compared to that of $Rh(H_2O)_6{}^{3+}$ and a 500-fold increase compared to that of $Rh(NH_3)_5H_2O^{3+}$. The tentative conclusion is made that associative activation is occurring in these reactions.

Introduction

The axial ligand substitution reactions of cobalt(III) and chromium(III) porphyrins have been reported to be faster than normal.[2-11] The porphyrin ligand labilizes the axial positions. In order to see how general this labilization effect is, it was decided to prepare and to study the reactions of sodium (*meso*-tetrakis(*p*-sulfonatophenyl)porphinato)diaquorhodate(III), $RhTPPS(H_2O)_2{}^{3-}$. While this investigation was underway, a report on the reactions of $RhTPPS(H_2O)_2{}^{3-}$ with NSC^- and CN^- was published.[12] However, there were substantial differences between the results obtained in this laboratory and those reported. This paper reports the results of the investigation of the reactions of $RhTPPS(H_2O)_2{}^{3-}$ with NCS^-, I^-, Cl^-, and Br^- in 0.10 M $HClO_4$.

Experimental Section

The materials and spectrophotometric techniques used have been described previously.[9] The $Na_3RhTPPS(H_2O)_2$ was synthesized by refluxing 100 mg of $RhCl_3(H_2O)_3$ in 10 mL of dimethylformamide until the solution became yellow (about 20 min). This solution was added to 150 mL of CH_3OH containing 60 mg of Na_4TPPS_4 (Man-Win Coordination Chemicals, Washington, D.C.) and the solution was refluxed for 30 min. A 50-mL sample of H_2O was added, and the solution was evaporated to 20 mL on a water bath. This solution was chromatographed on a water-washed alumina column using 0.02 M NaOH as the eluent. This removed the excess Rh(III).

Scheme I

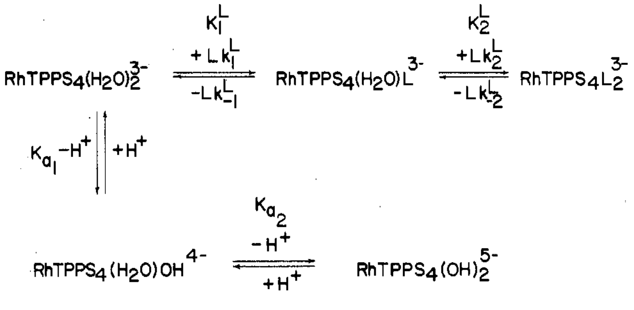

Table I. Values of K_{a_1} and K_{a_2} at $\mu = 1.00$ M ($NaClO_4$) for $RhTPPS(H_2O)_2{}^{3-}$

T, °C	K_{a_1}	pK_{a_1}	K_{a_2}	pK_{a_2}
15	$(2.64 \pm 0.05) \times 10^{-8}$	7.58	$(9.15 \pm 0.04) \times 10^{-9}$	8.04
25	$(9.67 \pm 0.12) \times 10^{-8}$	7.01	$(1.59 \pm 0.24) \times 10^{-10}$	9.80
35	$(1.17 \pm 0.04) \times 10^{-7}$	6.93	$(2.52 \pm 0.26) \times 10^{-10}$	9.60

The $RhTPPS(H_2O)_2{}^{3-}$ than was passed through a Sephadex G-10 column in order to remove extraneous ions. The $Na_3RhTPPS(H_2O)_2$ was isolated by evaporating to dryness the solution from the Sephadex column. Anal. Calcd for $Na_3[Rh(C_{44}H_{24}N_4S_4O_{12})(H_2O)_2]\cdot 22H_2O$: Rh, 6.72; C, 34.5; H, 3.00; N, 3.66; S, 8.36. Found: Rh, 6.71; C, 35.3; H, 2.77; N, 4.15; S, 8.48.

Results

Acid Dissociation Constants. Figure 1 depicts the absorbance change at 430 nm, $\mu = 1.00$ M ($NaClO_4$), and 35 °C as a function of pH. Because the absorbance change occurs over a pH range of 4, it is clear that this is not a single deprotonation but a multiple deprotonation. Taking into account the mass balance, Beer's law, and the definitions of K_{a_1} and K_{a_2} (Scheme I), we can derive eq 1. In eq 1, A is the absorbance at a particular $[H^+]$ ($[H^+] = 10^{-pH}$), A_a is the absorbance of the solution at a pH <5 ($RhTPPS(H_2O)_2{}^{3-}$), A_b is the absorbance of a solution at a pH >12 ($RhTPPS(OH)_2{}^{5-}$), and A_{ab} is the absorbance of the solution containing only $RhTPPS(OH)H_2O^{4-}$. The wavelength was 430 nm. The

$$A = \frac{A_a[H^+]^2 + A_{ab}K_{a_1}K_{a_2}[H^+] + A_bK_{a_1}K_{a_2}}{[H^+]^2 + K_{a_1}[H^+] + K_{a_1}K_{a_2}} \qquad (1)$$

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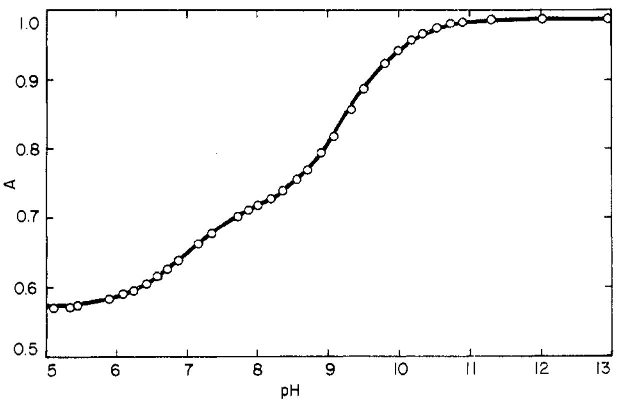

Figure 1. The plot of A vs. pH at 35 °C, λ = 430 nm, and μ = 1.00 M ($NaClO_4$) for $ThTPPS(H_2O)_2^{3-}$. The solid line is the computer fit of the data of eq 1.

Table II. Values of K_1^L and K_2^L at 25 °C, μ = 1.00 M ($NaClO_2$), and $[H^+]$ = 0.100 M

L	K_1^L, M^{-1}	K_2^L, M^{-1}
NCS^-	(1.22 ± 0.04) × 10^4	3.68 ± 0.42
I^-	(4.12 ± 0.18) × 10^1	<0.03
Br^-	1.82 ± 0.10	<0.03
Cl^-	0.74 ± 0.11	<0.03

Table III. Molar Absorptivities of the Compounds Studied in μ = 1.00 M ($NaClO_4$)

compd	λ_{max},[a] nm	ϵ_{max}, 10^5 M^{-1} cm^{-1}
$RhTPPS(H_2O)_2^{3-}$ [b]	417	2.15
$RhTPPS(OH)H_2O^{4-}$	417.5	1.78[c]
$RhTPPS(OH)_2^{5-}$ [d]	418	1.66
$RhTPPS(Cl)(H_2O)^{4-}$ [b]	418	1.91[c]
$RhTPPS(Br)H_2O^{4-}$ [b]	418.5	1.79[c]
$RhTPPS(I)H_2O^{4-}$ [b]	420	1.52
$RhTPPS(NCS)H_2O^{4-}$ [b]	420	1.74
$RhTPPS(NCS)_2^{5-}$ [b]	422	1.68[c]

[a] Soret band. [b] 0.10 M $HClO_4$. [c] Calculated by using the appropriate equilibrium constant; see ref 9. [d] 0.1 M NaOH and μ = 1.00 M ($NaClO_4$).

data were fit to eq 1 by using a nonlinear least-squares program.[13] The values of A_a and A_b were fixed at the experimentally determined values and A_{ab}, K_{a_1}, and K_{a_2} were determined. The derived values of K_{a_1} and K_{a_2} are reported in Table I. The uncertainties, as well as all others in this paper, are 1 standard deviation of the parameter.

Stability Quotient. The values of the stability constants K_1^L and K_2^L (Scheme I) were determined in 0.100 M $HClO_4$, at μ = 1.00 M ($NaClO_4$) and at 25.0 °C.

From Beer's law, the mass balance, and the definitions of K_1^L and K_2^L, eq 2 can be derived. In eq 2, A_r is the absorbance

$$A = \frac{A_r + A_p K_i^L[L]}{1 + K_i^L[L]} \tag{2}$$

of the solution of the reactant, A_p is the absorbance of the solution of the product, K_i^L is the respective stability constant, and A is the absorbance of the solution at the particular L concentration. The A vs. [L] data were fit to eq 2 by using the nonlinear least-squares program with A_r held constant at the experimentally determined value. Figure 2 is a typical curve with the solid line being the computer-calculated line.

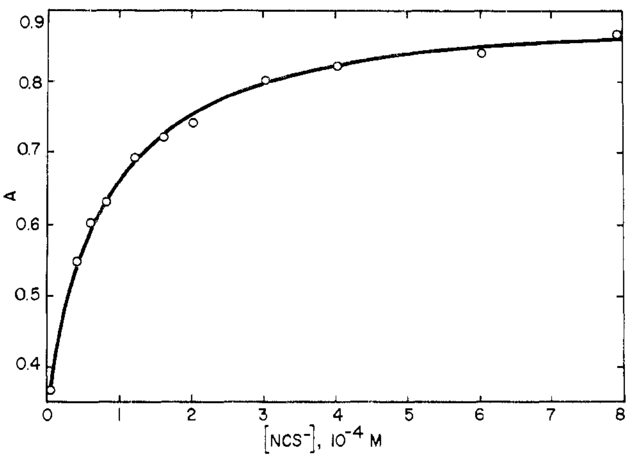

Figure 2. The plot of A vs. $[NCS^-]$ at 25 °C, λ = 430 nm, $[H^+]$ = 0.10 M, and μ = 1.00 M ($NaClO_4$) for $RhTPPS(H_2O)_2^{3-}$. The solid line is the computer fit of the data to eq 2.

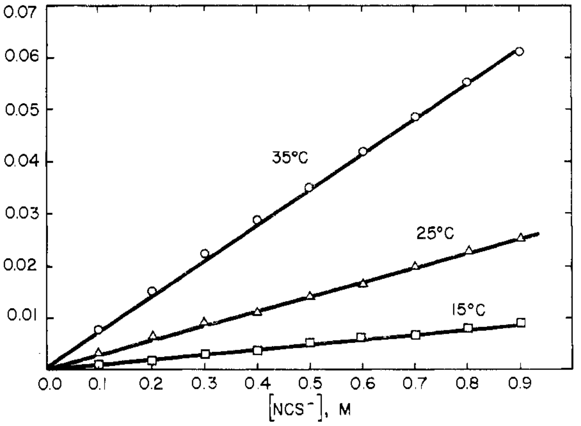

Figure 3. The plot of k_{obsd}^{NCS} vs. $[NCS^-]$ at the various temperatures, λ = 430 nm, $[H^+]$ = 0.10 M, and μ = 1.00 M ($NaClO_4$) for $RhTPPS(H_2O)_2^{3-}$. The solid line is the computer fit of the data to eq 4 with k_{-1}^L fixed at zero.

Table IV. The Kinetic Data for the Reaction $RhTPPS(H_2O)_2^{3-} + L \rightleftharpoons RhTPPS(L)H_2O^{3-} + H_2O$ $[H^+]$ = 0.100 M and μ = 1.00 M ($NaClO_4$)

L	[L] range, M	T, °C	k_1^L, 10^{-3} M^{-1} s^{-1}	k_{-1}^L, 10^{-3} M^{-1} s^{-1}
Cl^-	0.2-0.9	15	1.10 ± 0.05	0.58 ± 0.02
	0.1-0.9	25	2.64 ± 0.11	2.33 ± 0.05
	0.2-0.9	35	5.38 ± 0.25	3.62 ± 0.12
Br^-	0.2-0.9	15	2.55 ± 0.09	1.28 ± 0.04
	0.05-0.9	25	5.71 ± 0.14	2.60 ± 0.05
	0.10-0.9	35	13.0 ± 0.3	4.48 ± 0.10
I^-	0.02-0.9	15	8.50 ± 0.20	0.27 ± 0.08
	0.05-0.9	25	20.1 ± 0.3	0.72 ± 0.05
	0.05-0.9	35	38.7 ± 0.6	1.50 ± 0.11
NCS^-	0.1-0.9	15	9.83 ± 0.36	
	0.1-0.9	25	27.3 ± 0.6	
	0.1-0.9	35	68.5 ± 0.8	

The results are presented in Table II. In Table III are reported the wavelengths of the Soret band and the molar absorptivities of the compounds of interest.

Kinetics. The anation of $RhTPPS(H_2O)_2^{3-}$ by NCS^-, I^-, Br^-, and Cl^- was studied at various temperatures in 0.100 M $[H^+]$ and μ = 1.00 M ($NaClO_4$). The reactions are $[H^+]$ independent at $[H^+]$ >10^{-4}. The rate law is

$$\frac{-d[RhTPPS(H_2O)_2^{3-}]}{dt} = (k_1^L[L] + k_{-1}^L)[RhTPPS(H_2O)_2^{3-}] \tag{3}$$

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(13) R. H. Moore, Report LA 2367, Los Alamos Scientific Laboratory, March 4, 1960, and addend, January 14, 1963. Modified by N. Robers (East Texas State University) for an IBM 360/50.

Table V. Activation Parameters for the Reactions $RhTPPS(H_2O)_2^{3-} + L^- \rightarrow RhTPPS(L)H_2O^{4-} + H_2O$

L	ΔH^*, kcal/mol	ΔS^*, cal/(deg mol)
Cl^-	13.4 ± 0.6	−25.4 ± 1.9
Br^-	13.8 ± 0.3	−22.6 ± 1.1
I^-	12.8 ± 0.8	−23.4 ± 2.5
NCS^-	16.5 ± 0.2	−10.3 ± 0.6

The kinetic studies were performed under pseudo-first-order conditions with

$$k_{obsd}{}^{L} = k_1{}^{L}[L] + k_{-1}{}^{L} \qquad (4)$$

where $k_{obsd}{}^{L}$ is the pseudo-first-order rate constant. Figure 3 is a representative plot of k_{obsd} vs. $[NCS^-]$. Table IV contains a summary of the kinetic data derived by a least-squares fit of the data of eq 4. Because of the extrapolation to obtain $k_{-1}{}^{L}$, not much reliance can be placed on those data, especially for the reactions with I^-. The activation parameters were calculated by a nonlinear least-squares fit of the data to the Eyring–Polanyi equation and are reported in Table V.

Discussion

Acid Dissociation Constants. Krishnamurthy reported only one inflection in the pH vs. A plot between pH 6 and 9 at 415 and 418 nm.[12] The derived pK_a was 7.60 ± 0.05. However as can be seen from Figure 1, there are clearly two inflection points between pH 6 and 10. The pK_a of 7.0 is somewhat close to the value of 7.6 reported by Krishnamurthy.[12] Krishnamurthy might have not observed any change in absorbance at 415 and 418 nm that would have corresponded to the conversion of $RhTPPS(OH)_2^{5-}$, since the spectral differences between $RhTPPS(OH)H_2O^{4-}$ and $RhTPPS(OH_2)^{5-}$ are very small at these wavelengths. The results reported here were derived from the titration at 430 nm.

There are not a great number of Rh(III) complexes with which to compare the pK_a's of $RhTPPS(H_2O)_2^{3-}$. Perhaps the most interesting ones are in the series $RhCl_n(H_2O)_{6-n}{}^{3-n}$ (n = 0–3). The pK_a's of $Rh(H_2O)_6^{3+}$, $RhCl(H_2O)_5^{2+}$, *cis*-$RhCl_2(H_2O)_4^+$, *trans*-$RhCl_2(H_2O)_4^+$, *fac*-$RhCl_3(H_2O)_3$, and *mer*-$RhCl_3(H_2O)_3$ are 3.4, 4.9, 5.7, 6.0, 7.3, and 7.0, respectively.[14] The increase in pK_a for each additional Cl^- added is about 1.1. Since the pK_a of $RhTPPS(H_2O)_2^{3-}$ is 7.0, it appears that the $TPPS^{6-}$ exerts an effect that is about equivalent to three Cl^- ligands on the Rh(III) with respect to a loss of an aquo ligand proton. The pK_a of the *trans*-$Rh(NH_2C_2H_4NH_2)_2(H_2O)_2^{3+}$ is 4.4.[15] Clearly, the four nitrogens of the $TPPS^{6-}$ ligand are placing more electron density on Rh(III) than the primary amino groups of $NH_2C_2H_4NH_2$. The second pK_a of *trans*-$Rh(NH_2C_2H_4NH_2)_2(H_2O)_2^{3+}$ is 7.6, whereas the second pK_a of $RhTPPS(H_2O)_2^{3-}$ is 9.8. Apparently the OH^- ligand is affecting each Rh(III) compound in about the same way in terms of the acidity of the remaining aquo ligand since the change in pK_a is about 3 in each case.

Stability Constants. The trend in the values of the stability constants clearly indicates that Rh(III) is behaving as a soft acid toward NCS^-, I^-, Br^-, and Cl^-. The behavior of all of the chromium(III) and cobalt(III) porphyrin complexes studied so far indicates that they are soft acids.[2-11] This is not surprising in view of the delocalized electron density in the prophyrin ligand that is apparently available to the metal ion. The mode of bonding of the NCS^- is unknown. One would anticipate that the ligand would be sulfur bonded, because of the apparent softness of the Rh(III).

The large difference between $K_1{}^{NCS}$ and $K_1{}^{I}$ has been observed also for $CoTPPS(H_2O)_2^{3-}$ and $CoTMyP(H_2O)_2^{5+}$.[9,10] Also the values of $K_1{}^{Py}$ are much larger than $K_1{}^{NCS}$ for $CoTMpyP(H_2O)_2^{5+}$ and $CoTCPP(H_2O)_2^{3-}$.[7,8] These observations imply that π bonding is important in the metal–ligand bonding.

Kinetics. Since the reaction of NCS^-, I^-, Br^-, and Cl^- with $RhTPPS(H_2O)_2^{3-}$ shows no deviation from second-order kinetics up to 0.90 M, there is no kinetic evidence for an intermediate. Also, there is no other evidence for an intermediate in the reactions. Hence, the occurrence of an A or D type mechanism for the reactions can be dismissed. This leaves, by default, that the reactions are occurring by an I stoichiometric mechanism.[16] The mode of activation for the reactions is not so certain.

The activation parameters do not imply dissociative activation. In the anation reactions of cobalt(III) porphyrins, the values of ΔS^* range from +7 to +20 cal/(deg mol) and the values of ΔH^* range from 18 to 21 cal/(deg mol).[9,10] Other anation reactions of Co(III) complexes that have been concluded to occur by dissociative activation show positive values for ΔS^*.[9]

In the series of complexes $RhCl_n(H_2O)_{6-n}{}^{3-n}$ (n = 0–5) the anation by Cl^- has been investigated.[14] Dissociative activation is concluded to be occurring in all cases. In general the ΔS^* values are positive, and the ΔH^* values are in the range of 20–30 kcal/mol. Similar observations and conclusions were made for the reactions of Br^- with $Rh(H_2O)_6^{3+}$ and of Cl^- with $Rh(H_2NC_2H_4NH_2)_2(H_2O)_2^{3+}$.[15,18,19] With these values to compare to the values of the activation parameters for the anation reactions of $RhTPPS(H_2O)_2^{3-}$ (Table V), the tentative conclusion is made that associative activation is occurring in these reactions.

It has been observed that when porphines are complexed to Co(III) and Cr(III), the metal becomes more labile to axial substitution. The extent of labilization is dependent upon the other metal complex to which it is being compared. This is especially true for Rh(III). In $RhCl_n(H_2O)_{6-n}{}^{3-n}$ (n = 0–5) there is a wide range in the rate constants for anation by Cl^-.[14] However this wide range is due to a very large trans effect exerted by the Cl^- ligand. In those cases in which no trans labilization is possible, the rate constant at 25 °C is on the order of $10^{-9}\ M^{-1}\ s^{-1}$. For example, for *trans*-$RhCl_4(H_2O)_2^-$ the rate constant at 25 °C is $2.8 \times 10^{-9}\ M^{-1}\ s^{-1}$.[13] Hence there is about a 10^6 increase in labilization for Cl^- ion and a 10^7 increase for NSC^-. The rate constant for the addition of Cl^- to *trans*-$Rh(NH_2C_2H_4NH_2)_2(H_2O)_2^{3+}$ is 3×10^{-8} at 25 °C.[14] This is about a 10^5 increase in labilization for Cl^-. At 35 °C the Cl^- anation rate constant for $Rh(NH_3)_5H_2O^{3+}$ is about $9.5 \times 10^{-6}\ M^{-1}\ s^{-1}$.[18] On the assumption of a halving of the rate constant for 25 °C, this would give an increase in labilization of only 500 for the $RhTPPS(H_2O)_2^{3-}$. Clearly, there is a great dependence of the reactivity of Rh(III) upon the nonreactivity ligands. However, TPPS has labilized Rh(III). The labilization due to porphine for Co(III) is about 10^9 and for Cr(III) it is about 10^2 to 10^3.[11] This dependency of reactivity upon inert ligands is very prevalent in Cr(III) reactions, also.

It has been suggested that the labilizing ability of the porphyrin results from the mixing of the d orbitals of the metal and the π-ligand orbitals.[4] This results in the loss of the formal d^3 or d^6 character of the Cr(III) and Co(III). Krishnamurthy has suggested that Rh(III) is not labilized as much as Co(III) because of the higher energy of the d orbitals which prevent effective mixing with the ligand orbitals.[12] However, in view of the observation that Cr(III) is not labilized as much as

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

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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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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 $2.3 \times 10^4\ M^{-1}\ s^{-1}$ 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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