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Kinetics of Substitution Reactions of α,β,γ,δ-Tetra(*p*-sulfonatophenyl)porphinatodiaquocobaltate(III)

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Some equilibrium and kinetic studies have been made of α,β,γ,δ-tetra(*p*-sulfonatophenyl)porphinatodiaquocobaltate(III) [$CoTPPS_4(H_2O)_2^{3-}$]. The pK_{a_1} of $CoTPPS_4(H_2O)_2^{3-}$ was found to be 5.72. The stability constants of $CoTPPS_4(NCS)H_2O^{4-}$, $CoTPPS_4(I)H_2O^{4-}$, and $CoTPPS_4(NCS)_2^{5-}$ were determined spectrophotometrically to be 2640 ± 308, 11.4 ± 1.1, and 2.78 ± 0.84 M^{-1}, respectively, at 25 °C. The pseudo-first-order rate constant for the formation of $CoTPPS_4(NCS)H_2O^{4-}$ had the form $k_{obsd} = k^{NCS}[NCS^-]$. The value of k^{NCS} at 25 °C was 324 ± 20 $M^{-1}\ s^{-1}$. The activation parameters were $\Delta H^* = 18.4 \pm 1.1$ kcal/mol and $\Delta S^* = 14.4 \pm 3.7$ cal/(deg mol). The pseudo-first-order rate constant for the formation of $CoTPPS_4(I)H_2O^{4-}$ had the form $k_{obsd} = k^I[I^-] + k^I{}_r$. A pseudo-first-order approach to equilibrium was implied. The value of k^I at 25 °C was 118 ± 10 $M^{-1}\ s^{-1}$. The activation parameters were $\Delta H^* = 20.8 \pm 1.1$ kcal/mol and $\Delta S^* = 20.7 \pm 3.6$ cal/(deg mol). From the form of the rate law and the relative values of $K_1{}^{NCS}/K_1{}^I$ and k^{NCS}/k^I, an I_d mechanism was suggested. The increased rate of the anation reactions of $CoTPPS_4(H_2O)_2^{3-}$ over those of α,β,γ,δ-tetra(4-*N*-methylpyridyl)porphinediaquocobalt(III) [$CoTMpyP(H_2O)_2^{5+}$] was ascribed to the increased availability of electron density for the cobalt in $CoTPPS_4(H_2O)_2^{3-}$ over that in $CoTMpyP(H_2O)_2^{5+}$.

Introduction

The substitution reactions of cobalt(III) porphines have been the subjects of several recent papers.[1-6] It is clear that the porphine exhibits a cis-labilizing effect upon the cobalt(III). The increased amount of electron density placed upon the cobalt(III) by the porphine makes the cobalt(III) less positive, more like cobalt(II), and stabilizes a five-coordinate reactive intermediate during the course of the substitution reactions.[1,2] If this reasoning is correct, then porphines with electron-donating groups at the α, β, γ, and δ positions should enhance the cis-labilizing effect compared to porphines with electron-withdrawing groups at the α, β, γ, and δ positions. To test this hypothesis, the substitution reactions of α,β,γ,δ-tetra(*p*-sulfonatophenyl)porphinatodiaquocobaltate(III) [$CoTPPS_4(H_2O)_2^{3-}$] were studied and compared to the substitution reactions of α,β,γ,δ-tetra(4-*N*-methylpyridyl)porphinediaquocobalt(III) [$CoTMpyP(H_2O)_2^{3-}$].

Experimental Section

Materials. In general the chemicals used have been previously described.[3] The silica gel D-O8 was obtained from Coast Engineering Laboratory, the aluminum(III) oxide was purchased from Alupharm Chemicals Corp., and the Sephadex G-10 was obtained from Fine Chemical, Inc. The sodium α,β,γ,δ-tetra(*p*-sulfonatophenyl)porphine, Na_3TPPS_4, was either synthesized in this laboratory or purchased from Strem Chemicals, Inc.

The $TPPS_4$ was synthesized from α,β,γ,δ-tetraphenylporphine (TPP). The TPP was synthesized using the procedure developed by Adler.[7] The method previously devised by Fleischer and co-workers for the sulfonation of the free TPP was used for this work.[8] The $Na_3CoTPPS_4(H_2O)_2$ was synthesized by insertion of cobalt into the $TPPS_4$.

The pure ammonium salt of $TPPS_4$ synthesized as above was dissolved in a methanolic solution of sodium methoxide to form Na_3TPPS_4, which was precipitated by adding a 3-volume excess of acetone. The resulting compound was filtered and added to a refluxing solution of *N,N*-dimethylformamide (DMF), followed by the addition of a 10-fold excess of $CoSO_4 \cdot 7H_2O$. The solution was heated at 140 °C for about 15 min while a flow of air bubbled through the solution to oxidize the Co(II) to Co(III). The solution was cooled and passed through a basic alumina column to remove the excess Co(III). The $CoTPPS_4(H_2O)_2^{3-}$ was eluted with dilute NaOH. The material was concentrated on a steam bath and then passed through a Sephadex G-10 column to separate the light molecular weight impurities. The eluent was collected, dried on a steam bath, and then further dried in an oven at 100 °C for 2 h.[9] The analyses of C, H, and N were performed by Galbraith Laboratories, Inc., and the Co analysis was performed in this laboratory using a Perkin-Elmer 303 atomic absorption instrument. Anal. Calcd for $Na_3CoTPPS_4(H_2O)_2$, $Na_3CoC_{44}H_{28}N_4S_4O_{14}$: C, 48.38; H, 2.56; N, 5.13; S, 11.72; Co, 5.39. Found: C, 44.31; H, 3.23; N, 4.92; S, 10.54; Co, 5.23. The above procedure was repeated except that the Na_4TPPS was purchased from Strem Chemicals, Inc. Anal. Calcd for $Na_3CoTPPS_4(H_2O)_2$, $Na_3CoC_{44}H_{28}N_4S_4O_{14}$: C, 48.38; H, 2.56; N, 5.13; S, 11.72; Co, 5.39. Found: C, 45.15; H, 3.02; N, 4.85; S, 11.96; Co, 5.31.

Table I. Molar Absorptivities of Some Cobalt(III) Porphines

Compd	λ_{max},[a] nm	ε, 10^5 $M^{-1}\ cm^{-1}$
$CoTPPS_4(H_2O)_2^{3-}$ [b]	424	2.24
$CoTPPS_4(OH)H_2O^{4-}$ [c]	426	2.00
$CoTPPS_4(NCS)H_2O^{4-}$ [b,d]	428	1.38
$CoTPPS_4(NCS)_2^{5-}$ [b,e]	442	1.29
$CoTPPS_4(I)H_2^{4-}$ [b,f]	413	0.78

[a] Soret band. [b] 0.10 M $HClO_4$, $\mu = 1.00$ M ($NaClO_4$), and 25 °C. [c] pH 6.57 and 7.16, $\mu = 1.00$ M ($NaClO_4$), and 25 °C. [d] ε calculated using $K_1{}^{NCS} = 2637\ M^{-1}$. [e] ε calculated using $K_2{}^{NCS} = 2.78\ M^{-1}$. [f] $[I^{-1}] = 0.90$ M and ε calculated using $K_1{}^I = 11.35\ M^{-1}$.

Anion-exchange chromatography of the $(NH_4)_3TPPS_4$, Na_3TPPS_4, and both preparations of the $Na_3CoTPPS_4(H_2O)_2$ using Bio-Rad Cellex-D in the nitrate form showed only one colored band upon elution. This second preparation was used for spectrophotometric measurements and kinetic studies.

Spectrophotometric Measurements. The visible spectrum, acidity constants, and stability constants were determined as reported.[3]

Kinetics. The kinetics of the anation reactions were studied as previously reported with the exception that the pseudo-first-order rate constants were derived from plots of log ($A - A_\infty$) vs. *t*, where *A* is the absorbance at time *t* and A_∞ is the absorbance after 10 half-lives.[3]

Results and Discussion

Spectra. Table I contains the positions of the Soret bands and the values of the molar absorptivities, ε, for the compounds studied. The values for $CoTPPS_4(NCS)H_2O^{4-}$, $CoTPPS_4(NCS)_2^{5-}$, and $CoTPPS_4(I)H_2O^{4-}$ were calculated since the values of the stepwise stability constants were such that a solution containing only one species could not be prepared.[3] The spectra are similar to those reported for the $CoTMpyP(H_2O)_2^{5+}$.[3]

The ε values at 424 nm of $CoTPPS_4(H_2O)_2^{3-}$ were determined at 21 different concentrations of $CoTPPS_4(H_2O)_2^{3-}$ between 3.75×10^{-5} and 2.25×10^{-7} M. The average value of ε in 0.100 M $HClO_4$ and with $\mu = 1.00$ M ($NaClO_4$) was $(2.28 \pm 0.07) \times 10^{-5}\ M^{-1}\ cm^{-1}$. This and all other uncertainties in this paper are standard deviations. The deviations appeared to be random. Over the concentration ranges studied and at 0.100 M [H^+], only one specie exists.

Acid Dissociation Constant. From a plot of A_{424} vs. pH at 25 °C and $\mu = 1.00$ M ($NaClO_4$) (Figure 1), apparently a single deprotonation is occurring at about pH 5. Then, $[H^+] = K_{a_1}(A - A_b)/(A_a - A)$ where *A* is the absorbance of a

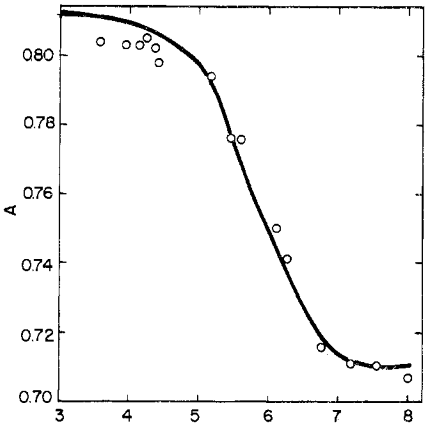

Figure 1. A_{424} vs. pH for the determination of K_{a_1}. The solid line is the least-squares fit of the data to the equation $[H^+] = 1.90 \times 10^{-6}(A - 0.711)/(0.811 - A)$.

$CoTPPS_4(H_2O)_2^{3-}$ solution at a hydrogen ion concentration $[H^+]$ (determined by the equation pH = $-\log [H^+]$), A_b is the absorbance of a solution of $CoTPPS_4(OH)(H_2O)^{4-}$, A_a is the absorbance of a solution of the conjugate acid, and K_{a_1} is defined by eq 1. The value of K_{a_1}, derived from a nonlinear

$$CoTPPS_4(H_2O)_2^{3-} \overset{K_{a_1}}{\rightleftharpoons} CoP(OH)H_2O^{4-} + H^+ \qquad (1)$$

least-squares fit of the data, was determined to be $(1.90 \pm 0.50) \times 10^{-6}$ M.[3] The value of K_{a_1} for $CoTMpyP(H_2O)_2^{5+}$ was $(3.45 \pm 0.63) \times 10^{-6}$ M.[3] Although this change in K_{a_1} is consistent with more electron density on the aquo oxygen in $CoTPPS_4(H_2O)_2^{3-}$ than in $CoTMpyP(H_2O)_2^{5+}$, and hence in turn on the cobalt, the values are too similar to attach much significance to them.

The values of the acid dissociation constants are reported to be about 2.5×10^{-5} M^2 for $H_4TPPS_4^{2-}$ and about 7.4×10^{-3} M^2 for H_4TMpyP^{6+}.[10,11] This 300-fold change in K_a is clearly in the direction that would be expected based upon

$$H_4(\text{porphine})^{(2+n)+} \overset{K_a}{\rightleftharpoons} H_2(\text{porphine})^{n+} + 2H^+$$

simple charge considerations. Also, this is the expected change if the electron density available for proton binding is decreased in $TMpyP^{4+}$. The suggested decrease could occur because of the electron-withdrawing effect of the positively charged *N*-methylpyridyl groups. Adler and Meot-Ner studied the substituent effect of a series of $\alpha,\beta,\gamma,\delta$-tetra(substituted phenyl)porphines where the substituents were *p*-CN, *o*-CH_3, *p*-Cl, *o*-OC_2H_5, *p*-H, *p*-CH_3, *p*-*i*-C_3H_7, *p*-OCH_3, *p*-CH_3CONH_2, and *p*-OH.[12] The value of K_a ranged from 2.4×10^{-1} to 6.9×10^{-4} M^2. As expected, K_a decreases in going from the electron-withdrawing *p*-CN to the electron-donating *p*-OH.

For some $\alpha,\beta,\gamma,\delta$-tetra(para-substituted phenyl)porphines of In^{3+}, TiO^{2+}, and Ru^{2+} the rotation of the phenyl group about the plane of the four pyrrole groups occurs very rapidly on the NMR time scale at about 60 °C in 1,1,2,2-tetrachloroethane solutions.[13] This would allow a means by which both σ- and π-electronic effects in the phenyl group could be transmitted to the central part of the porphine. Also, there was no rotation when there were ortho substituents on the meso phenyl groups.[13] However, turning again to the data of Adler and Meot-Ner, the phenyl substituent effects are transferred into the porphine macrocycle even when the substituent is in the ortho position.

Table II. Kinetic and Activation Parameters for the Anation Reactions of $CoTPPS_4(H_2O)_2^{3-}$ with NCS^- and I^-

Ligand	Concn range studied, M	Temp, °C	k^X, M^{-1} s^{-1}
NCS^-	0.10–0.80	15	84.8 ± 9.6
	0.10–0.80	20	146 ± 13
	0.005–0.15	25	324 ± 20
	0.005–0.15	35	923 ± 65
	0.005–0.15	45	1847 ± 255
$\Delta H^* = 18.4 \pm 1.1$ kcal/mol; $\Delta S^* = 14.4 \pm 3.7$ cal/(deg mol)			
I^-	0.10–0.90	5	6.59 ± 1.20
	0.10–0.50	15	39.4 ± 3.2
	0.04–0.50	25	118 ± 10
	0.04–0.50	35	291 ± 37
	0.01–0.50	45	1000 ± 150
$\Delta H^* = 20.8 \pm 1.1$ kcal/mol; $\Delta S^* = 20.7 \pm 3.6$ cal/(deg mol)			

Stability Constants. The stability constants at 25 °C, $[H^+] = 0.100$ M, and $\mu = 1.00$ M ($NaClO_4$) for reaction 2 were determined. The value of *i* is 1 or 2 and the stability constant

$$CoTPPS_4(X)_{i-1}(H_2O)_{3-i}^{(2+i)-} + X^- \overset{K_i^X}{\rightleftharpoons} CoTPPS_4(X)_i(H_2O)_{2-i}^{(3+i)-} + H_2O \qquad (2)$$

is given by eq 3. The $K^X{}_i$ were determined as previously

$$K_i{}^X = \frac{[CoP(X)_i(H_2O)_{2-i}{}^{(3+i)-}]}{[CoP(X)_{i-1}(H_2O)_{3-i}{}^{(2+i)-}][X^-]} \qquad (3)$$

reported[3] and $K_1{}^{NCS}$, $K_2{}^{NCS}$, and $K_1{}^{I}$ were 2640 ± 380, 2.78 ± 0.84, and 11.4 ± 1.1 M^{-1}, respectively. The comparable values for $CoTMpyP(H_2O)_2^{5+}$ were 6400 ± 1550, 13.7 ± 1.1, and 34.0 ± 5.6 M^{-1}, respectively. This is a decrease in the stability constants by a factor of about 2.5–5.

If only the total charge on the cobalt(III) porphine is considered, the observed change is in the expected direction. This is also the expected direction if the cobalt(III) in $CoTPPS_4(H_2O)_2^{3-}$ has more electron density than cobalt(III) in $CoTMpyP(H_2O)_2^{5+}$. That is to say, from an equilibrium standpoint the cobalt in $CoTPPS_4(H_2O)_2^{3-}$ is more like Co(II) than it is in $CoTMpyP(H_2O)^{5+}$. Walker and her co-workers have noted this same trend in stability constants for a series of meta- and para-substituted *meso*-phenylporphines of Ni(II), V(IV) and VO^{2+}.[14]

Kinetics. Equation 4 represents the reaction studied at $[H^+]$

$$CoTPPS_4(H_2O)_2^{3-} + NCS^- \rightarrow CoTPPS_4(NCS)H_2O^{4-} + H_2O \qquad (4)$$

= 0.100 M and $\mu = 1.00$ M ($NaClO_4$). The addition of the second NCS^- is kinetically unobservable and must be very fast in comparison to the addition of the first NCS^-. This was noted also in the reaction of $CoTMpyP(H_2O)_2^{5+}$ with NCS^- and the reasoning for this conclusion has been presented.[3,5]

The observed pseudo-first-order rate law was

$$\frac{-d[CoTPPS_4(H_2O)_2^{3-}]}{dt} = k^{NCS}{}_{obsd}[CoTPPS_4(H_2O)_2^{3-}]$$

Plots of $k^{NCS}{}_{obsd}$ vs. $[NCS^-]$ at 15 °C (Figure 2) and at other temperatures have zero intercepts. This implied that $k^{NCS}{}_{obsd} = k^{NCS}[NCS^-]$ (Table II). The activation parameters were obtained from a fit of k^{NCS} to the Erying–Polanyi equation.[15]

It has been reported that the rate law for the reaction of $CoTPPS_4(H_2O)_2^{3-}$ with NCS^- at pH 5 has the form[1]

$$\frac{-d[CoTPPS_4(H_2O)_2^{3-}]}{dt} = k^{NCS}{}_{obsd}[CoTPPS_4(H_2O)_2^{3-}]$$

with

$$k^{NCS}{}_{obsd} = k_1[NCS^-]/(k_2/k_3 + [NCS^-]) \qquad (5)$$

The $k^{NCS}{}_{obsd}$ data could be fit to eq 5 using a nonlinear least-squares program. However, the standard deviations associated with k_1 and k_2/k_3 were higher than those associated with k^{NCS}. Also, the values of k_1 did not increase mono-

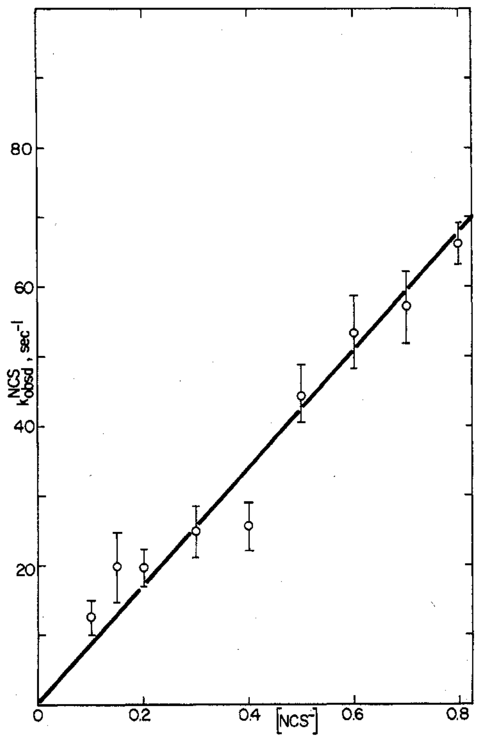

Figure 2. k_{obsd} vs. [NCS$^-$] at 15 °C. The line is the computer-calculated least-squares fit of the data.

tonically with temperature, implying that, in fact, the data at 0.10 M H^+ do not justify eq 5. It should be noted explicitly that this is a comparison of the rate law at two different pH values. At pH 5, 16% of the $CoTPPS_4(H_2O)_2^{3-}$ is in the monohydroxy form.

In the reaction of $CoTPPS_4(H_2O)_2^{3-}$ with I^- at $[H^+] = 0.100$ M and $\mu = 1.00$ M ($NaClO_4$), the observed rate law was

$$\frac{-d[CoTPPS_4(H_2O)_2^{3-}]}{dt} = k^I[I^-][CoTPPS_4(H_2O)_2^{3-}] - k^I_r[CoTPPS_4(I)(H_2O)^{4-}]$$

This rate law is indicative of an incomplete reaction (eq 6).[15]

$$CoTPPS_4(H_2O)_2^{3-} + I^- \underset{k^I_r}{\overset{k^I}{\rightleftarrows}} CoTPPS_4(I)H_2O^{4-} + H_2O \qquad (6)$$

The second I^- ligand did not add under the conditions of this investigation. Plots of k^I_{obsd} vs. [I^-] were similar to Figure 2 except that the intercepts were nonzero. Under pseudo-first-order conditions, interpretation of the rate law gives $k^I_{obsd} = k^I[I^-] + k^I_r$, consistent with what is observed (Table II). The value of (k^I/k^I_r) at 25 °C is 10.4 ± 1.3 M^{-1} whereas the value of $K_1{}^I$ determined by equilibrium measurements was 11.4 ± 1.1 M^{-1}. This good agreement gives additional support for eq 6. There was no observable reaction of $CoTPPS_4(H_2O)_2^{3-}$ with Br^- or Cl^-.

Since the observed rate law was second order and there was no evidence of any intermediate, the reaction proceeded by an interchange (I) mechanism.[16] The ratio of the stability constants $(K_1{}^{NCS}/K_1{}^I)$ is 233 and the ratio of the rate constants (k^{NCS}/k^I) is 22. The relative invariance of the rate constants toward the entering ligand implies that the reactions are dissociatively activated and that an I_d mechanism is operative.[16]

In the reactions of $CoTMpyP(H_2O)_2^{5+}$ with NCS^- and I^- the values of ΔH^* and ΔS^* are 19 ± 2 and 20 ± 1 kcal/mol and 7 ± 7 and 10 ± 2 cal/(deg mol), respectively.[3] The increased reactivity of $CoTPPS_4(H_2O)_2^-$ is due to an increase in ΔS^* of 7–10 cal/(deg mol), as compared to $CoTMpyP(H_2O)^{5+}$. This ΔS^* effect has been noted previously.

Thiocyanate ion adds about 500 times faster to $\alpha,\beta,\gamma,\delta$-tetra(*p*-phenylcarboxylate)porphinatodiaquocobaltate(III), $Co(TCPP)(H_2O)_2^{3-}$, than to $CoTMpyP(H_2O)_2^{5+}$.[2] For $CoTPPS_4(H_2O)_2^{3-}$, there is about 100 times increase when compared to $CoTMpyP(H_2O)_2^{5+}$. Clearly the electron-withdrawing 4-*N*-methylpyridyl group retards the reaction compared to the negatively charged groups. It has been established that the para substituent of the $\alpha,\beta,\gamma,\delta$-phenyl groups alters the ground-state properties of the pyrrole macrocycle (vida ante).[12,14] The ΔG^* for insertion of Cu(II) into a variety of para-substituted $\alpha,\beta,\gamma,\delta$-tetraphenylporphines increases as the para substituent becomes more electron withdrawing.[17] We conclude that there is more *available* electron density that could interact with the cobalt(III) ion in $CoTPPS_4(H_2O)_2^{3-}$ and $CoTCPP(H_2O)_2^{3-}$ than in $CoTMpyP(H_2O)_2^{5+}$ and that this increased electron density increases the lability of the cobalt(III).

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Registry No. $CoTPPS_4(H_2O)_2^{3-}$, 58881-09-7; $CoTPPS_4(OH)H_2O^{4-}$, 59366-37-9; $CoTPPS_4(NCS)H_2O^{4-}$, 59301-88-1; $CoTPPS_4(NCS)_2^{5-}$, 59301-89-2; $CoTPPS_4(I)H_2O^{4-}$, 59301-90-5; NCS^-, 302-04-5; I^-, 20461-54-5.

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