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Direct Measurement of Electron Self-Exchange Rates of Cobalt Porphyrins. 1. Outer-Sphere Exchange[1]

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Abstract: Because of recent interest shown in electron-transfer behavior of metalloproteins and metalloporphyrins, the development of new methods for measuring the self-exchange rates of cobalt porphyrins is described. Outer-sphere exchange rates were measured by reacting (5,10,15,20-tetraphenylporphinato)cobalt(III), $Co^{III}TPP$, with the methyl-labeled (5,10,15,20-tetra-*p*-tolylporphinato)cobalt(II), $Co^{II}TTP$, in the presence of pyridine-d_5 in deuteriochloroform and monitoring the appearance of $Co^{III}TPP$ through the *p*-methyl peak of its ^1H NMR spectrum as a function of time, which is possible due to the downfield isotropic shifts of $Co^{II}TTP$'s ^1H NMR spectrum. This reaction is taken to be a valid approximation of the actual $Co^{III}TPP$–$Co^{II}TPP$ exchange. Equilibrium constants of coordination of pyridine to $Co^{II}TTP$ and $Co^{III}TPP(Cl)$ are reported, from which it is calculated that the predominant $Co^{III}TPP$ species present under conditions used here is the bis(pyridine) complex, $Co^{III}TPP(py)_2{}^+Cl^-$. Its rate of exchange is dependent on the state of coordination of pyridine to $Co^{II}TTP$. Rate constants at 27.7 °C in $CDCl_3$ as follows were determined: $[Co^{III}TPP(py)_2{}^+Cl^- + Co^{II}TTP]$, $k_{11} = 0.0191\ M^{-1}\ s^{-1}$; $[Co^{III}TPP(py)_2{}^+Cl^- + Co^{II}TTP\ (py)]$, $0.129\ M^{-1}\ s^{-1}$; $[Co^{III}TPP(py)_2{}^+Cl^- + Co^{II}TTP(py)_2]$, $9.69\ M^{-1}\ s^{-1}$. Observed activation parameters at 0.070 M total pyridine-d_5 are $\Delta H^{\ddagger} = 8.4 \pm 1.9$ kcal/mol and $\Delta S^{\ddagger} = -34 \pm 6$ eu.

Interest in metalloporphyrins' biological roles has been reviewed in several volumes.[3] One of the most important of these roles is that of the cytochromes as a major link in the mitochondrial respiratory electron-transport chain. It is partly because of the biological importance of such electron-transfer metalloproteins that the physical chemistry of these processes has recently received great interest.[4,5] Some of the synthetic porphyrins have recently found successful application as such model compounds, due to their physical and chemical similarity to those contained in the metalloproteins.[6] In particular, the electron-transfer behavior of these metalloporphyrins has recently received great attention.[6-12]

In virtually all of the prior studies of the metalloporphyrins' electron-transfer chemistry there was a common underlying experimental principle. This chemistry, as well as that of the metalloproteins themselves, has been interpreted in terms of the well-understood principles of electron transfer in simpler inorganic systems, of which Marcus' theory has found the most successful applicability.[4]

It is on the basis of the Marcus theory equations that all outer-sphere electron-transfer reactions of metalloporphyrins have heretofore been studied. The experimental method has involved measuring cross-reaction rates between oxidized metallorporphyrins and small inorganic reducing agents. Such calculations of outer-sphere self-exchange rates have been made for only five metalloporphyrin redox couples so far, as listed in Table I.

Table I. Outer-Sphere Electron Exchange Rates of Metalloporphyrins

porphyrin system[a]	reductant	k_{11}, $M^{-1}\ s^{-1}$	ref
$FeTMPyP(H_2O)^{5+/4+}$	$Ru(NH_3)_6{}^{2+}$	$>1 \times 10^9$	12
$FeTMPyP(H_2O)(OH)^{4+/3+}$	$Ru(NH_3)_6{}^{2+}$	1.2×10^6	12
$FeTPPS(H_2O)^{3-/4-}$ [b]	$V(H_2O)_6{}^{2+}$	$\sim 1 \times 10^3$	6
$CoTMPyP(H_2O)_2{}^{5+/4+}$	$Ru(NH_3)_6{}^{2+}$	20	11
$CoTPPS(H_2O)_2{}^{3-/4-}$	$Fe(EDTA)^{2-}$	6.1×10^{-2}	*c*

[a] TMPyP = tetrakis[4-(*N*-methylpyridyl)]porphine; TPPS = porphinetetrakis(4-benzenesulfonate). [b] pH 2 ($HClO_4$). [c] Taniguchi, V. T.; Fleischer, E. B. unpublished results.

Table II. Equilibrium Constants of Coordination of Pyridine-d_5 to $Co^{III}TPP(Cl)$ in $CDCl_3$

T,[a] K	$\langle \log K_3 \rangle$[b]	$\langle \log K_4 \rangle$[b]
277.2	6.10	4.76
290.0	5.47	4.12
300.9	4.98	3.62
315.4	4.38	3.01
328.7	3.87	2.49
$\sigma_{\log K}$	0.11	0.09
ΔH, kcal/mol	-18.1 ± 1.2	-18.4 ± 0.9
ΔS, eu	-37.2 ± 3.9	-44.7 ± 3.0

[a] ±0.9 K. [b] Expectation values from van't Hoff plots. Refer to eq 3 for definitions.

The self-exchange rates listed here are, however, only estimates, since measurements were not direct but rather were predictions based on cross reactions and assumed validity of the Marcus equations. Predictions of cross-reaction rates between some species of known self-exchange rates have, in fact, been shown by Chou, Creutz, and Sutin[13] to deviate from the actual, measured cross-reaction rates. So although the Marcus theory has in general shown validity as a theoretical treatment of these reactions, there have been occasional large discrepancies. Therefore, knowledge of the actual self-exchange rates of these and other metalloporphyrin redox couples, experimentally verifiable by direct measurement, would be quite valuable as a confirmation of the validity of the Marcus theory in these models of biological systems.

General Method. The direct measurement of outer-sphere electron self-exchange rates here involves the reaction of two metalloporphyrins of a redox couple, one of which has been labeled by substitution with a methyl group. The specific metalloporphyrins involved are the cobalt(III) complex of tetraphenylporphine, abbreviated $Co^{III}TPP$, and the cobalt(II) complex of

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(1) A preliminary communication of this work has appeared recently: *J. Chem. Soc., Chem. Commun.* **1981**, 332.

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the methyl-labeled tetra-*p*-tolylporphine, $Co^{II}TPP$. The general reaction observed, therefore, is

$$Co^{II}TTP + Co^{III}TPP = Co^{II}TPP + Co^{III}TTP \qquad (1)$$

(omitting additional ligands present).

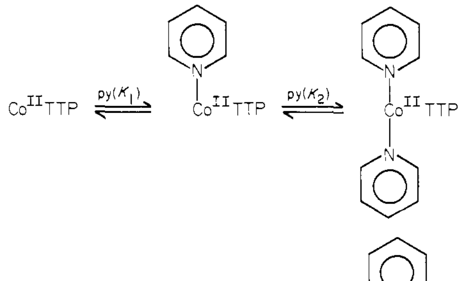
The exact method of measuring the electron-exchange rate involves monitoring the reaction above by ^1H NMR spectrometry. The reason for the feasibility of this method is that the ^1H NMR spectrum of paramagnetic (d^7) $Co^{II}TTP$ is quite distinct from that of the six-coordinate diamagnetic (d^6) $Co^{III}TTP(L)_2$. The line broadening and downfield isotropic shifts in the ^1H NMR spectrum of $Co^{II}TTP$ have been described previously by La Mar and Walker;[14] spectra of the diamagnetic $Co^{III}TPP$ complexes have been reported by Yamamoto.[15]

The cobalt(III) complex of TPP requires an anion as a charge balance. This is added in the synthesis of the complex and remains coordinated in a noncoordinating solvent (e.g., chloroform). This anionic ligand (for example, chloride) is often capable of acting as a *bridging ligand* between the cobalt(II) and cobalt(III) porphyrins. (This special case of anion-bridged inner-sphere exchange is described in a separate report.[16]) It is necessary, therefore, to *add* a ligand which displaces this anionic ligand but is not itself capable of acting as a bridging ligand, in order to ensure observation of the *outer-sphere exchange*. The ligand chosen for the comprehensive outer-sphere exchange studies here is pyridine-d_5.

Under these conditions, the methyl resonance of $Co^{III}TTP$ occurs at δ 2.63 from Me_4Si[17] while that of $Co^{II}TTP$ is at ~ 3.5–4.1 ppm, depending on the presence of ligands in solution.[18] Thus, simple mixing of solutions of these two porphyrins initiates reaction 1 above, and the rate of appearance of $Co^{III}TTP$ is measured by the formation of the Co^{III} *p*-methyl resonance and the diminution of the Co^{II} *p*-methyl resonance.

The rate of this reaction, eq 1, is taken to be a valid approximation of the actual self-exchange of either (TPP or TTP) couple because this substitution by H or CH_3 at the *p*-phenyl position has very little effect on the chemistry of the cobalt centers undergoing electron transfer. Redox potentials of the two couples are also very close, as will be shown later.

Since the exchange reactions are run in the presence of a coordinating ligand (viz., pyridine-d_5) in order to ensure observation of the outer-sphere reaction, the equilibria obtained are shown in eq 2 and 3. Thus there are actually several species capable of undergoing electron transfer in these solutions. Therefore, it also seems reasonable that the exchange reaction proceeds at a rate dependent on the concentrations of these various species. Results of previous studies of similar equilibria suggest that $Co^{III}TPP$ has a much greater tendency to form the pyridine complexes than does $Co^{II}TTP$ (i.e., $K_3K_4 >> K_1K_2$).[19,20] Reactions 4–8 would therefore be expected to be simultaneously occurring



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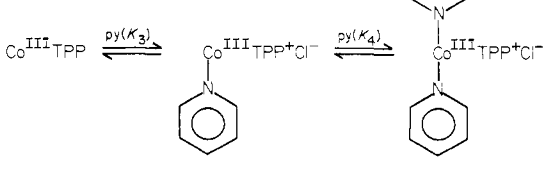

(3)

$$Co^{II} + py \underset{}{\overset{fast}{\rightleftharpoons}} Co^{II}(py)$$

$$K_1 = \frac{[Co^{II}(py)]}{[Co^{II}][py]} \qquad (4)$$

$$Co^{II}(py) + py \overset{fast}{\rightleftharpoons} Co^{II}(py)_2$$

$$K_1K_2 = \frac{[Co^{II}(py)_2]}{[Co^{II}][py]^2} \qquad (5)$$

$$*Co^{II} + Co^{III}(py)_2 \rightleftharpoons Co^{II} + *Co^{III}(py)_2 \quad k_0 \qquad (6)$$

$$*Co^{II}(py) + Co^{III}(py)_2 \rightleftharpoons Co^{II}(py) + *Co^{III}(py)_2 \quad k_1 \qquad (7)$$

$$*Co^{II}(py)_2 + Co^{III}(py)_2 \rightleftharpoons Co^{II}(py)_2 + *Co^{III}(py)_2 \quad k_2 \qquad (8)$$

during the course of this exchange reaction. In all these reactions, the presence of the porphyrin ligand is assumed, but omitted for abbreviation, and the asterisk indicates labeling of the porphyrin ligand by substitution with methyl.

On the basis of these equations, the observed rate of exchange is expected to have contributions from the exchange with each of the Co(II) species. So by rearrangement of the equilibrium constant equations

$$V_{exch} = (k_{11})_{obsd}[Co^{II}]_{total}[Co^{III}]_{total} \qquad (9)$$

$$V_{exch} = k_0[Co^{II}][Co^{III}]_t + k_1[Co^{II}(py)][Co^{III}]_t + k_2[Co^{II}(py)_2][Co^{III}]_t \qquad (10)$$

$$V_{exch} = k_0[Co^{II}][Co^{III}]_t + k_1K_1[Co^{II}][py][Co^{III}]_t + k_2K_1K_2[Co^{II}][py]^2[Co^{III}]_t \qquad (11)$$

$$V_{exch} = \left(\frac{k_0 + k_1K_1[py] + k_2K_1K_2[py]^2}{1 + K_1[py] + K_1K_2[py]^2}\right)[Co^{II}]_t[Co^{III}]_t \qquad (12)$$

V_{exch}, therefore, has a definite pyridine concentration dependence which involves the equilibrium constants of coordination to the cobalt porphyrins.

Experimental Section

Syntheses. The free bases TPP and TTP were synthesized by the procedure of Adler et al.[21] under the optimum conditions determined by Bhatti et al.[22] and purified to reduce chlorin content with 2,3-dichloro-5,6-dicyanobenzoquinone by the procedures reported by Barnett, Hudson, and Smith.[23]

The cobalt(II) complexes of the porphyrins were made by literature methods[24] and recrystallized from chloroform-methanol. Visible spectra for the two ($Co^{II}TPP$ and $Co^{II}TTP$) in benzene were essentially the same and matched that reported in the literature for $Co^{II}TPP$.[25] NMR spectra

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[16] Part 2: see following article in this issue.

[17] In this paper, positive δ values signify shifts downfield from the reference.

[18] NMR spectra of these compounds, similar to those reported in the literature, are reproduced in Figures S1–S3 of the supplementary material.

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also showed them to be the pure Co(II) complexes.[14]

Co^{III}TPP(Cl) was synthesized by the HCl-catalyzed air oxidation of Co^{II}TPP described by Sakurai et al.,[26] and the visible spectrum in methanol matched that of literature reports.[27]

Instrumentation. Visible spectra for compound characterizations and ligand coordination studies were taken with a Beckman ACTA-III UV-visible spectrophotometer at an ambient temperature of 25.5 ± 0.2 °C.

Proton NMR spectra for monitoring reactions were taken on a Bruker WH-90 Fourier transform spectrometer at 90 MHz. Variable temperature is controlled with Bruker's B-ST 100/700 unit; low temperature is achieved with liquid nitrogen-cooled dry nitrogen flowing over the sample tube. The variable-temperature control was calibrated with methanol according to the method described by van Geet.[28]

Ligand Coordination Studies. The most convenient technique for studying the equilibria between Co^{II}TTP and pyridine is visible spectrophotometry. The spectrum of Co^{II}TPP shows a shift of the visible peak from ~529 nm in chloroform to ~533 nm in pyridine.[29] Therefore, changes in absorbance were monitored in solutions of constant [Co^{II}TTP] but varying [pyridine] in chloroform (Mallinckrodt ChromAR, which uses 2-methyl-2-butene rather than ethanol as preservative). Equilibrium constants were determined at the *x* axis intercept of the transformed equations

$$\log\left(\frac{A_0 - A}{A - A_n}\right) = \log\,[\mathrm{py}] + \log K_n \qquad (13)$$

where *A* is the observed absorbance of each solution and A_n is the absorbance of the species containing *n* coordinated pyridine molecules.

Co^{III}TPP-Pyridine. Theoretically, the coordination of pyridine to Co^{III}TPP could also be studied spectrophotometrically since the visible spectrum of Co^{III}TPP in pyridine[29] differs from that of Co^{III}TPP(Cl) in chloroform.[30] However, based on the measurement for the reaction

$$\mathrm{Co^{III}TPP^+} + 2\mathrm{py} \overset{\beta_2}{\rightleftharpoons} \mathrm{Co^{III}TPP(py)_2{}^+}$$

that $\beta_2 \simeq 10^{15.6}$ for the electrochemically generated Co^{III}TPP$^+$,[19] and on some preliminary kinetics experiments at very low [pyridine], it appeared that a plot of absorbance vs. log [py] would show inflections (from which K's are determined) only at low [py] and that the sigmoidal curves would overlap, complicating calculations by the standard method.

There is another physical property of Co^{III}TPP which is sensitive to its state of coordination, however. Yamamoto[15] showed that the ^{1}H NMR chemical shifts of the β-pyrrole protons in mono- and bis(pyridine) complexes of Co^{III}TPP were slightly different. So in deuteriochloroform, complexes of 4-methylpyridine, L, showed $\delta_{\mathrm{mono(L)}}$ 8.99 while $\delta_{\mathrm{bis(L)}}$ 9.08. The appearance of these two β-pyrrole peaks was also observed here in solutions of low [py]. Thus, in solutions of known [py], the relative sizes of the upfield peak—due to Co^{III}TPP(py) and, presumably, a very small amount of Co^{III}TPP(Cl)—and the downfield peak—due to Co^{III}TPP(py)$_2$—should give information about the equilibrium constants of coordination.

In dilute solutions in chloroform, the displaced chloride ion is presumably not solvated but probably exists as an ion pair with the Co^{III}TPP(py)$_n$ species. The equations applicable to these equilibria (eq 3) are (again omitting "TPP" for abbreviation)

$$K_3 = \frac{[\mathrm{Co^{III}(py)^+Cl^-}]}{[\mathrm{Co^{III}(Cl)}][\mathrm{py}]} \qquad (14)$$

$$K_4 = \frac{[\mathrm{Co^{III}(py)_2{}^+Cl^-}]}{[\mathrm{Co^{III}(py)^+Cl^-}][\mathrm{py}]} \qquad (15)$$

$$C_3 \equiv [\mathrm{Co^{III}(Cl)}] + [\mathrm{Co^{III}(py)^+Cl^-}] + [\mathrm{Co^{III}(py)_2{}^+Cl^-}] \qquad (16)$$

$$P_0 \equiv [\mathrm{py}]_0 = [\mathrm{py}] + [\mathrm{Co^{III}(py)^+Cl^-}] + 2[\mathrm{Co^{III}(py)_2{}^+Cl^-}] \qquad (17)$$

Rearrangement of eq 14 and 15 gives

$$\frac{[\mathrm{Co^{III}(py)^+Cl^-}] + [\mathrm{Co^{III}(Cl)}]}{[\mathrm{Co^{III}(py)_2{}^+Cl^-}]} = \frac{1 + K_3[\mathrm{py}]}{K_3K_4[\mathrm{py}]^2} \equiv R \qquad (18)$$

The experimental method here consists of measuring this ratio, *R*, from the NMR spectra in several solutions of known total [Co^{III}TPP] and [py-d_5]. Reasonable first approximations of K_3 and K_4 are made, from which is calculated [py] (by combination of the equilibrium constant and mass-balance equations), then the ratio R_{calcd}, *expected* with these K's. The estimates of K_3 and K_4 are adjusted by trial and error to minimize the sum of squares of differences between the logarithms of the observed and calculated ratios, R_{obsd} and R_{calcd}.

The temperature dependence of R_{obsd} was studied in the range of 277–329 K. The total concentration [Co^{III}TPP]$_0$ was also corrected for temperature since the density of the solvent is temperature dependent. The relative change in density of CDCl$_3$ was assumed to be approximately the same as that of CHCl$_3$[31] and concentration corrections were made on this basis. Specific values of R_{obsd} and [Co^{III}TPP]$_0$ are listed in Table S1 of the supplementary material.

Kinetics. The first solution prepared contained the Co^{II}TTP to be reacted, dissolved in 400 μL of solvent (Aldrich 99%D pyridine-d_5 in deuteriochloroform[32]) in a 5-mm NMR tube. A stock Co^{III}TPP solution was also made by dissolving Co^{III}TPP(Cl) in the same solvent to give an approximately equimolar solution.

Next, an initial NMR spectrum of the Co^{II}TTP was taken. Then, at a recorded time, an equal volume of Co^{III}TPP solution (400 μL) was added to the same NMR tube, it was quickly returned to the probe, and several consecutive spectra were taken and stored on disk. By this procedure, transformation of the data at a later time produced a series of spectra of the cobalt porphyrin mixture which showed a Co^{III}TTP methyl resonance peak continually increasing in size. Eventually, the two methyl peaks showed a constant ratio, and a static spectrum was obtained, when equilibrium was reached in the reaction.

Rate Constant Calculation. Within this series of consecutive spectra, the *extent of exchange reaction*, ξ, at the midpoint of each spectral acquisition was calculated by comparison of the ratio of the integrals of the two methyl peaks in each spectrum, R_t, to this ratio at the end of the observable exchange, R_∞. Then, by application of the McKay equation for exchange kinetics[33]

$$V_{\mathrm{exch}} = -\frac{1}{t}\ln(1-\xi) = k_{\mathrm{exch}}\left(\frac{[\mathrm{Co^{II}}][\mathrm{Co^{III}}]}{[\mathrm{Co^{II}}] + [\mathrm{Co^{III}}]}\right) = k_{11}[\mathrm{Co^{II}}][\mathrm{Co^{III}}] \qquad (19)$$

the first-order exchange rate constant (with which the system approaches equilibrium), k_{exch}, can be calculated. The concentrations involved are those of all species undergoing exchange: i.e., total Co(II) and Co(III) concentrations. This is related to the second-order rate constant, k_{11}, by the sum of concentrations of the species involved.

$$k_{11}\ (\mathrm{M^{-1}\ s^{-1}}) = \frac{k_{\mathrm{exch}}(\mathrm{s^{-1}})}{[\mathrm{Co^{II}}] + [\mathrm{Co^{III}}](\mathrm{M})} \qquad (20)$$

Thus, a reliable approximation of the metalloporphyrin self-exchange rate is directly measured.

Temperature Dependence Studies. The experimental technique described above for the measurement of kinetics at room temperature is applicable to the study of reactions at other temperatures. Temperature settings used were the same as those for the measurements of K_3 and K_4, the range being 277–329 K. The temperature dependence was studied at three different pyridine-d_5 concentrations from 0.07 M to 0.35 M.

Solutions in these runs were equilibrated in water baths at the temperature to be studied before mixing them to initiate the reaction. The initial spectrum of Co^{II}TTP was also taken at this temperature. The basic technique for obtaining rate constants was otherwise as described above.

Results

Ligand Coordination Studies. Absorbance changes for the first coordination of pyridine to Co^{II}TTP in chloroform are shown in Figure S4 of the supplemental material. The equilibrium constant was calculated analytically as described in the Experimental Section, and the plot of the transformed equation is shown in Figure 1. The *x* axis intercept and its uncertainty, as indicated by the deviation from linearity of the data, can be calculated by

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(31) Brunel, R. F.; Van Bibber, K. *International Critical Tables* **1928**, *3*, 27–35.

(32) Deuteriochloroform used in all experiments was Merck 99.5%D, redistilled initially and purged with dry nitrogen gas before use.

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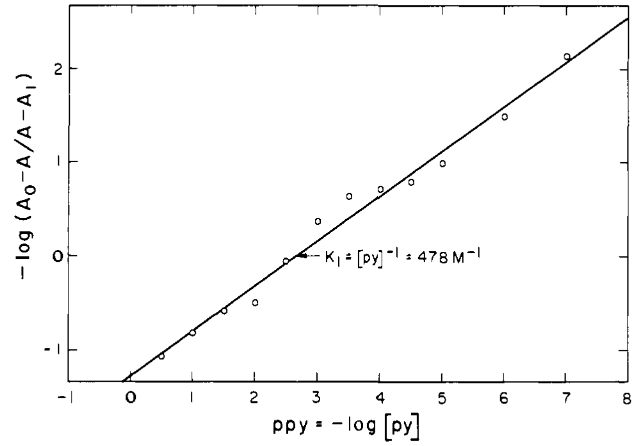

Figure 1. Analytical derivation of K_1 from plot of eq 13 for data of first coordination of pyridine to $Co^{II}TTP$.

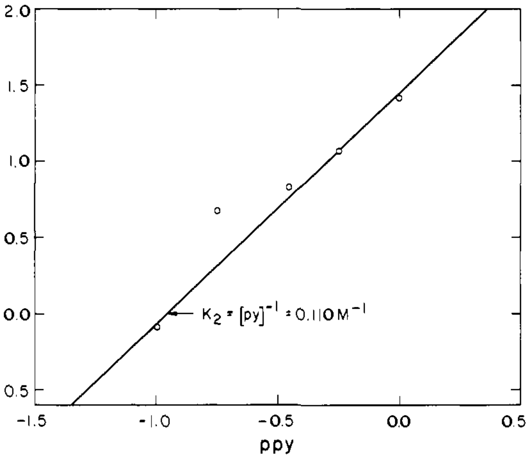

Figure 2. Plot of eq 13 for data of second coordination of pyridine to $Co^{II}TTP$ (K_2) in chloroform. The point at ppy = -0.750 was rejected from calculations as excessively deviant.

standard statistical methods.[34] The result from the spectrophotometric measurement at 25.5 °C is

$$\log K_1 = 2.680 \pm 0.061$$

$$K_1 = 478 \pm 67\ M^{-1}$$

This compares favorably with previous values for $Co^{II}TPP$ in toluene (450 ± 50),[20] $Co^{II}TTP$ in toluene (552 ± 23),[35] and $Co^{II}T(p\text{-}OCH_3)PP$ in toluene (485 ± 29).[36]

The plot of eq 13 for data from the second coordination of pyridine is shown in Figure 2. Similarly, this equilibrium constant was calculated as

$$\log K_2 = -0.957 \pm 0.170$$

$$K_2 = 0.110 \pm 0.043\ M^{-1}$$

The relatively large uncertainty is due to the narrow [py] range in which this equilibrium is accessible to monitor, but the result compares favorably with the only similar result found for such a system. By extrapolation of low-temperature measurements, Walker[37] estimated that $K_2 \approx 0.132$ at room temperature for coordination of 3,4-lutidine to $Co^{II}T(p\text{-}OCH_3)PP$.

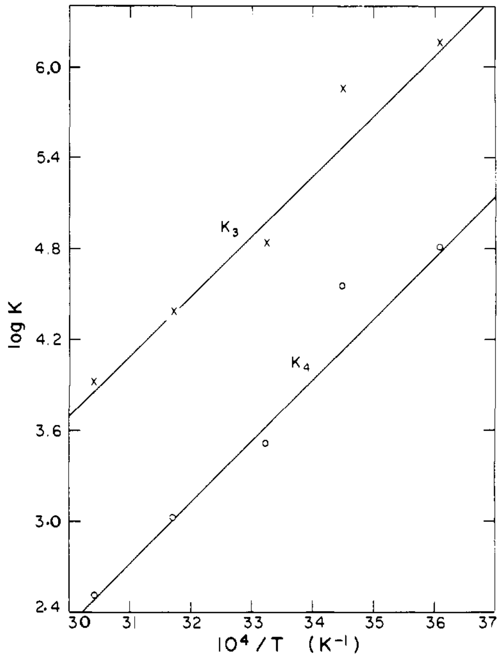

Figure 3. van't Hoff plots of the equilibrium constants of coordination of pyridine-d_5 to $Co^{III}TPP(Cl)$ in $CDCl_3$. K_3 and K_4 are as defined in eq 3. Rejection from calculations of the points at $10^4/T = 34.5\ K^{-1}$ was justified by their large systematic deviation.

Since the pyridine concentration dependence studies of the outer-sphere exchange rates were run at temperatures other than 25.5 °C, the changes in equilibrium constants could be calculated from the enthalpies of coordination, ΔH_1 and ΔH_2. Since the equilibrium constants for $Co^{II}TTP$–pyridine were found to be equal within experimental error to those of $Co^{II}T(p\text{-}OCH_3)PP$ with pyridine (K_1) and 3,4-dimethylpyridine (K_2), the enthalpies of these reactions were also assumed to be very close for $Co^{II}TTP$ and $Co^{II}T(p\text{-}OCH_3)PP$. These were measured by Walker[36,37] as

$$\Delta H_1 = -8.5\ \text{kcal/mol}$$

$$\Delta H_2 = -1.8\ \text{kcal/mol}$$

Also, these values and those for $Co^{II}TPP$–pyridine reported by Ginzburg et al.[38] were equal within experimental error. The equilibrium constants are therefore estimated as

$$K_1(27.7\ °C) = 430\ M^{-1}$$

$$K_2(27.7\ °C) = 0.108\ M^{-1}$$

Constants for the $Co^{III}TPP$–pyridine equilibria were determined by the method described in the Experimental Section. The van't Hoff plots showing the results of the temperature dependence study are shown in Figure 3.

Observed Rate Constants. Values of $(k_{11})_{obsd}$ were obtained from the McKay equation plots as described in the Experimental Section. The slope of the regression line gives k_{exch} and is calculated by least-squares analysis. Since the extent of reaction at time zero *must be* zero, the regression equations are modified so that the y axis intercept is constrained to be zero. The slope is then derived simply[34] as

$$k_{exch} = \frac{\sum t \ln (1 - \xi)}{\sum t^2} \qquad (21)$$

Also, the linear correlation coefficient, calculated as the geometric mean of the slope obtained from regression of ln $(1 - \xi)$ about t and the slope from regression of t about ln $(1 - \xi)$, is

$$r = \frac{\sum t \ln (1 - \xi)}{(\sum t^2 \sum [\ln (1 - \xi)]^2)^{1/2}} \qquad (22)$$

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[34] Bevington, P. R. "Data Reduction and Error Analysis for the Physical Sciences"; McGraw-Hill: New York, 1969; Chapter 6.

[35] Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484–3489.

[36] Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1150–1153.

[37] Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1154–1159.

[38] Ginzburg, S. F.; Brivina, L. P.; Ponomarev, G. V.; Khrapov, V. V. *Koord. Khim.* **1977**, *3*, 1779–1785.

Table III. Pyridine Concentration Dependence of $(k_{11})_{\mathrm{obsd}}$

$[\mathrm{py}]_0$, M	$[\mathrm{Co^{II}}]_{\mathrm{total}}$, μM	$[\mathrm{Co^{III}}]_{\mathrm{total}}$, μM	$10^3 k_{\mathrm{exch}}$, $\mathrm{s^{-1}}$	r^a	$(k_{11})_{\mathrm{obsd}}$,^{b} $\mathrm{M^{-1}\,s^{-1}}$
0.030	5391	5772	1.41	0.997	0.126 (6)
0.070	6521	7316	2.14	0.994	0.155 (15)
0.10	6325	7425	3.44	0.999	0.25 (2)
0.20	6065	7259	3.68	0.996	0.277 (28)
0.20	6650	7350	4.27	0.997	0.305 (31)
0.20	6732	7352	4.44	0.991	0.315 (32)
0.35	5931	7162	5.89	0.995	0.45 (2)
0.50	6356	7085	7.95	0.994	0.58 (6)
0.50	5057	5831	6.43	0.997	0.59 (6)
0.50	6768	7826	9.05	1^c	0.62 (6)
1.00	5093	5891	11.31	0.998	1.03 (10)
1.00	5858	7419	13.92	1^c	1.05 (5)
2.00	6158	7459	30	1^c	2.2 (4)
11.6	5371	6561	>36		>3

[a] Linear correlation coefficient of McKay equation plot. [b] Estimated uncertainty, $\sigma_{k_{11}}$, in last digit(s) of k_{11} are in parentheses. [c] Only two usable data points.

Examples of relevant intermediate quantities derived from the exchange reaction at 0.030 M pyridine-d_5 in $\mathrm{CDCl_3}$ are listed in Table S2, and the McKay equation plot derived therefrom is shown in Figure S5, both in the supplementary material. The intermediate results from the pyridine concentration dependence study are listed in Table III.

Resolution of Rate Constants. In order to calculate the contributions to the observed rate from the various exchanges involving different ligated species (eq 6–8), we must correlate all the various equilibria involved to calculate the concentration of each species involved. These include the following relations and definitions: K_1 through K_4, as defined by eq 2 and 3.

$$C_2 \equiv [\mathrm{Co^{II}}] + [\mathrm{Co^{II}(py)}] + [\mathrm{Co^{II}(py)_2}] \tag{23}$$

$$C_3 \equiv [\mathrm{Co^{III}(Cl)}] + [\mathrm{Co^{III}(py)^+Cl^-}] + [\mathrm{Co^{III}(py)_2{}^+Cl^-}] \tag{24}$$

$$P_0 \equiv [\mathrm{py}] + [\mathrm{Co^{II}(py)}] + 2[\mathrm{Co^{II}(py)_2}] + [\mathrm{Co^{III}(py)^+Cl^-}] + 2[\mathrm{Co^{III}(py)_2{}^+Cl^-}] \tag{25}$$

Again, the porphyrin ligand is implied in the notation above and includes total TPP and TTP concentrations. Combination of these equilibrium constant and mass-balance equations gives the following function of $[\mathrm{py}]_{\mathrm{free}}$, wherein $\beta_n \equiv K_1K_2...K_n$.

$$\beta_4[\mathrm{py}]^5 + \{\beta_4(2C_2 + 2C_3 - P_0) + K_1K_3(K_2 + K_4)\}[\mathrm{py}]^4 + \{\beta_3(2C_2 + C_3 - P_0) + K_1K_3K_4(C_2 + C_3 - P_0) + K_1K_2 + K_1K_3 + K_3K_4\}[\mathrm{py}]^3 + \{K_1K_2(2C_2 - P_0) + K_1K_3(C_2 + C_3 - P_0) + K_3K_4(2C_3 - P_0) + K_1 + K_3\}[\mathrm{py}]^2 + \{K_1(C_2 - P_0) + K_3(C_3 - P_0) + 1\}[\mathrm{py}] - P_0 = 0 \tag{26}$$

Solution of this fifth-order equation in [py] using the measured values of K_1 to K_4 and the concentrations of reagents particular to each experiment yields the value of $[\mathrm{py}]_{\mathrm{free}}$. With this, the cobalt porphyrin concentrations can be calculated. Performance of this procedure for each of the systems of this study gives the concentrations of each species as listed in Table IV. Equation 10 is now amenable to statistical calculations. Since $[\mathrm{Co^{III}}]_t$ is assumed to be constant, the following linear equation is used for resolution of the rate constants.

$$(k_{11})_{\mathrm{obsd}}[\mathrm{Co^{II}}]_t = k_0[\mathrm{Co^{II}}] + k_1[\mathrm{Co^{II}(py)}] + k_2[\mathrm{Co^{II}(py)_2}] \tag{27}$$

Knowledge of the individual porphyrin concentrations allows easy resolution of the rate constants, $k_0 - k_2$, by multiple linear regression analysis. The usual normal equations necessary for multiple regression[39] apply here, except that the regression line

Table IV. Pyridine Concentration Dependence of Cobalt Porphyrin Concentrations

$[\mathrm{py}]_0$, M	$[\mathrm{Co^{II}}]$, μM	$[\mathrm{Co^{II}(py)}]$, μM	$[\mathrm{Co^{II}(py)_2}]$, μM	$[\mathrm{Co^{III}(py)^+}]$, μM	$[\mathrm{Co^{III}(py)_2{}^+}]$, μM	$(k_{11})_{\mathrm{obsd}}$, $\mathrm{M^{-1}\,s^{-1}}$
0.030	770	4614	6.94	97.3	5675	0.126 (6)
0.070	293	6195	32.9	35.4	7281	0.155 (15)
0.10	179	6094	52.0	22.4	7403	0.25 (2)
0.20	76.1	5875	114	9.64	7249	0.277 (28)
0.20	83.9	6442	124	9.81	7340	0.305 (31)
0.20	84.9	6521	126	9.81	7342	0.315 (32)
0.35	40.1	5688	203	5.18	7157	0.45 (2)
0.50	29.2	6016	311	3.53	7081	0.58 (6)
0.50	23.0	4784	250	2.88	5828	0.59 (6)
0.50	31.2	6407	330	3.91	7822	0.62 (6)
1.00	10.9	4594	488	1.43	5890	1.03 (10)
1.00	12.6	5286	559	1.81	7417	1.05 (5)
2.00	6.0	5069	1083	0.90	7458	2.2 (4)
11.6	0.43	2290	3081	0.13	6561	>3

Table V. Temperature Dependence of $(k_{11})_{\mathrm{obsd}}$

$[\mathrm{py}]_0$, M	T,^{a} K	$[\mathrm{Co^{II}}]_{\mathrm{total}}$, μM	$[\mathrm{Co^{III}}]_{\mathrm{total}}$, μM	$10^3 k_{\mathrm{exch}}$, $\mathrm{s^{-1}}$	r^b	$(k_{11})_{\mathrm{obsd}}$,^{c} $\mathrm{M^{-1}\,s^{-1}}$
0.070	277.2	6757	6469	1.03	0.999	0.078 (10)
	290.0	6852	6976	0.824	0.994	0.060 (6)
	300.9	6521	7316	2.14	0.996	0.155 (15)
	315.4	6719	7383	4.23	0.996	0.30 (3)
	328.7	6806	7838	11.42	1.000	0.78 (8)
0.20	277.2	6332	7961	2.36	0.995	0.165 (10)
	290.0	6683	6920	3.26	0.997	0.24 (2)
	300.9	6650	7350	4.27	0.997	0.305 (31)
	315.4	5189	8831	5.88	1.000	0.42 (2)
	328.7	5606	7009	7.82	0.998	0.62 (6)
0.35	277.2	6639	7332	2.52	0.999	0.18 (3)
	290.0	6593	7613	3.83	0.998	0.27 (3)
	300.9	5931	7162	5.89	0.995	0.45 (2)
	315.4	6428	7209	9.37	0.997	0.69 (6)
	328.7	4825	8853	14.67	0.996	1.07 (11)

[a] ±0.9 K. [b] Linear correlation coefficient of McKay equation plot. [c] Estimated uncertainty, $\sigma_{k_{11}}$, in last digit(s) of k_{11} are in parentheses.

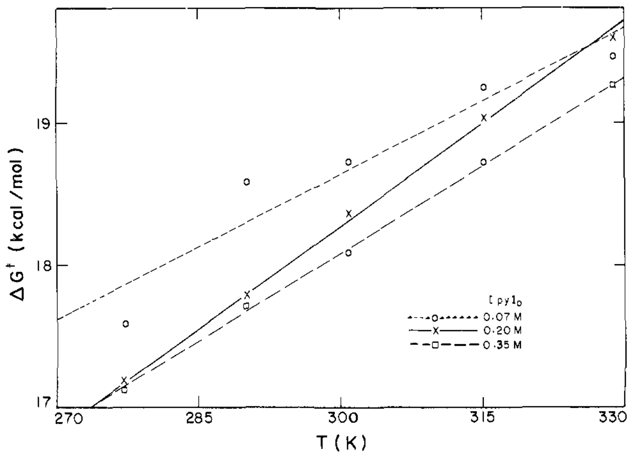

Figure 4. Temperature dependence of free energies of activation for outer-sphere exchanges.

must be constrained to pass through the origin, since at zero cobalt(II) concentration, there must be no observable exchange. Also, the dependent variable, $(k_{11})_{obsd}[Co^{II}]_t$, has unequal uncertainties at each point, so all variables in the normal equations are weighted by the variance of the dependent variable. Analysis of the rate data (Table IV) by this method yields the following values for the rate constants.

$$Co^{III}(py)_2{}^+Cl^- + Co^{II} \qquad k_0 = 0.0191\ M^{-1}\ s^{-1}$$

$$Co^{III}(py)_2{}^+Cl^- + Co^{II}(py) \qquad k_1 = 0.129 M^{-1}\ s^{-1}$$

$$Co^{III}(py)_2{}^+Cl^- + Co^{II}(py)_2 \qquad k_2 = 9.69\ M^{-1}\ s^{-1}$$

The multiple correlation coefficient is $R = 0.9981$.

Temperature Dependence and Activation Parameters. Table V lists intermediate results of the temperature dependence study, including $(k_{11})_{obsd}$ under the conditions of each run.

Calculations of activation parameters are usually made on the basis of Eyring's transition-state theory.[4,40] The equation derived therefrom, used for determining the parameters, is

$$k = \frac{k_B T}{h}\exp(-\Delta G^\ddagger/RT) = \frac{k_B T}{h}\exp\left(-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \qquad (28)$$

where k_B is Boltzmann's constant and h is Planck's constant. Rate constants as measured (Table V) were all converted to their corresponding free energies of activation by rearrangement of eq 33.

$$\Delta G^\ddagger = RT[\ln(k_B/h) + \ln(T/k)] \qquad (29)$$

Uncertainties in $\Delta G^\ddagger$ were derived following a usual propagation of errors analysis.[41]

$$R^{-2}\sigma_{\Delta G^\ddagger}{}^2 = \left[1 + \ln\left(\frac{k_B}{h}\right) + \ln\left(\frac{T}{k}\right)\right]^2 \sigma_T{}^2 + T^2\left(\frac{\sigma_k}{k}\right)^2 \qquad (30)$$

Enthalpy and entropy of activation were calculated simply from

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \qquad (31)$$

The quantities derived from this analysis at each $[py]_0$ are listed in Table VI, and eq 31 is plotted in Figure 4.[42] Free energies of activation at 298 K were estimated by interpolation and their corresponding estimates of error calculated by appropriate statistics.[43] In the figure, it is seen that the trends in $\Delta G^\ddagger$ at 0.20 and 0.35 M $[py]_0$ showed very good linearity. The series of data at $[py]_0 = 0.07$ M were not as well behaved, however. There is no definite cause for any of these data to be spurious and none is sufficiently deviant from the line of regression to justify rejection by standard statistical methods.[44] So the data are retained, but yield higher uncertainties than the other runs.

Table VI. Activation Parameters of Outer-Sphere Exchanges

	$\Delta G^\ddagger$ ($\sigma_{\Delta G^\ddagger}$), cal/mol		
T,[a] K	$[py]_0 = 0.070$ M	$[py]_0 = 0.20$ M	$[py]_0 = 0.35$ M
277.2	17 590.3 (92.0)	17 177.6 (55.8)	17 129.7 (102.1)
290.0	18 583.1 (73.9)	17 784.1 (65.3)	17 716.2 (77.8)
300.9	18 730.9 (74.8)	18 336.1 (59.4)	18 093.7 (51.0)
315.4	19 249.3 (76.6)	19 038.5 (52.9)	18 727.4 (69.4)
328.7	19 468.4 (79.5)	19 618.4 (76.5)	19 261.9 (79.4)
$\Delta H^\ddagger$, kcal/mol	8.3 ± 1.9	3.9 ± 0.5	5.8 ± 0.6
$\Delta S^\ddagger$, cal·K^{-1}·mol^{-1}	−34 ± 6	−48 ± 2	−41 ± 2
$\Delta G_{298}{}^\ddagger$, kcal/mol	18.57 ± 0.12	18.18 ± 0.01	18.00 ± 0.01

[a] ±0.9 K.

Table VII. Observed Free Energy Changes of Outer-Sphere Exchange Reactions

$[py]_0$, M	R_∞	K_{eq}	ΔG_{obsd}, cal/mol
11.6	1.53_4	1.55	−262
2.00	1.88	2.34	−508
0.35	2.18	3.12	−680
0.20	2.06	3.41	−733
0.20	2.07	3.61	−767
0.070	2.03_1	3.28	−710
0.030	1.71_3	2.62	−575

Scheme I

$$\begin{array}{rl} Co^{III}TPP^+ + e^- = Co^{II}TPP & E_{1/2} = +0.58\ V \\ Co^{II}TPP = Co^{III}TPP^+ + e^- & -E_{1/2} = -0.57\ V \\ \hline Co^{II}TTP + Co^{III}TPP^+ = Co^{II}TPP + Co^{III}TTP^+ & \Delta E \simeq 0.01\ V \end{array} \left.\right\} \text{vs. SCE}$$

Reduction Potential Differences. As mentioned previously, the TPP and TTP complexes were chosen as reactants for the outer-sphere exchange reactions because previously studied thermodynamic and kinetic properties of their cobalt complexes suggested that the presence of the p-methyl substituent has little effect on the chemistry of the cobalt center. Among the evidence suggesting this were the potentials of the cobalt(III)–cobalt(II) redox couples of the two complexes. These potentials were measured electrochemically by Tezuka et al.[45] by cyclic voltammetry in dimethylformamide solution. The difference in their potentials appeared to be ~0.01 V, as suggested by Scheme I. But this difference is approximately the experimental uncertainty of the measurements. It can be seen that the sum of these two half-reactions yields a cell reaction which is essentially that being run here to study the electron exchange. Since the equilibrium constant of the reaction is an exponential function of the cell potential, ΔE, it seemed that a fairly precise measure of this difference in half-cell potentials could be obtained.

Values of the equilibrium constant, K_{eq}, could be calculated for the several kinetic runs in which R_∞ could be measured with reasonably high certainty. An important consideration in obtaining thermodynamic parameters from these data is that there are several reactions occurring simultaneously in these systems. Thus, the observed equilibrium constant is dependent on the overall free energy change, ΔG_{obsd}, arising from each of the separate reactions.

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(39) Reference 34, Chapter 9.

(40) Moore, W. J. "Physical Chemistry", 4th ed.; Prentice-Hall: Englewood Cliffs, NJ, 1972; p 385.

(41) Reference 34, p 60.

(42) Resolution of individual rate constants at each temperature (as was done with the data at 300.9 K) was precluded by the small number of data (three). So *statistically significant* rate constants could not be calculated by multiple linear regression; in some cases, for example, these came out as negative values.

(43) Crow, E. L.; Davis, F. A.; Maxfield, M. W. "Statistics Manual"; Dover: New York, 1960; p 162.

(44) Proschan, F. *Am. J. Phys.* **1953**, *21*, 520–525.

(45) Tezuka, M.; Ohkatsu, Y.; Osa, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1435–1436.

Table **VIII.** Literature Reports of Cobalt(III)-Cobalt(II) Self-Exchange Rates

system	μ, M	k(25 °C), M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	ref
$Co(NH_3)_6^{3+/2+}$		$\lesssim 10^{-11}$			*a,b*
$Co(en)_3^{3+/2+}$	0.98	3.4×10^{-5}	13.5	−32	*c-e*
trans-$Co([14]dieneN_4)(H_2O)_2^{3+/2+}$	1.0 ($HClO_4$)	4.5×10^{-5}			53
$Co([14]dieneN_4\text{-one})(H_2O)_2^{3+/2+}$	1.0 ($HClO_4$)	4.4×10^{-3}			53
$Co^{III/II}$(cyt *c*)		5.1×10^{-3}	10.6	−33	*f*
$Co([14]tetraeneN_4)(H_2O)_2^{3+/2+}$	1.0 ($HClO_4$)	5.0×10^{-2}			53
$CoTPPS^{3-/4-}$	0.1 ($NaClO_4$)	6.1×10^{-2}			*g*
$Co^{III}TPP(py)_2/Co^{II}TPP(py)$	0.07 M py-d_5/$CDCl_3$	1.3×10^{-1}	8.3	−34	this work
$Co(diaminosar)^{3+/2+}$	0.2 ($LiClO_4$)	5×10^{-1}			*e*
$Co(H_2O)_5Cl^{2+}/Co(H_2O)_6^{2+}$	3.0 ($NaClO_4$)	1.0			*h*
$Co(sar)^{3+/2+}$	0.2 (NaCl)	2			*e*
$Co(H_2O)_6^{3+/2+}$	1.0 ($NaClO_4$)	2.7	11.8	−17	*i*
$Co^{III/II}TPP(py)_2$	py-d_5/$CDCl_3$	9.7			this work
$Co(bpy)_3^{3+/2+}$	0.1 (KNO_3)	17.5			*j,k*
$CoTMPyP(H_2O)_2^{5+/4+}$	0.5 ($NaNO_3$)	20			11
$Co(phen)_3^{3+/2+}$	0.1 (KNO_3)	44			*j, l, m*

[a] Stranks, D. R. *Discuss. Faraday Soc.* 1960, *29*, 73-79. [b] Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* 1964, *86*, 1686-1691. [c] Lewis, W. B.; Coryell, C. D.; Irvine, J. W. *J. Chem. Soc.* 1949, 5386-5392. [d] Dwyer, F. P.; Sargeson, A. M. *J. Phys. Chem.* 1961, *65*, 1892-1894. [e] Sargeson, A. M. *Chem. Br.* 1979, *15*, 23-27. [f] Chien, J. C. W. *J. Phys. Chem.* 1978, *82*, 2158-2171. [g] Taniguchi, V. T.; Fleischer, E. B., unpublished results. [h] Conocchioli, T. J.; Nancollas, G. H.; Sutin, N. *Inorg. Chem.* 1966, *5*, 1-5. [i] Habib, H. S.; Hunt, J. P. *J. Am. Chem. Soc.* 1966, *88*, 1668-1671. [j] Neumann, H. M., personal communication quoted by Farina, R.; Wilkins, R. G. *Inorg. Chem.* 1968, *7*, 514-518. [k] Cummins, D.; Gray, H. B. *J. Am. Chem. Soc.* 1977, *99*, 5158-5167. [l] Haim, A.; Sutin, N. *Inorg. Chem.* 1976, *15*, 476-478. [m] Wherland, S.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* 1976, *73*, 2950-2954.

Thus, ΔG_{obsd} appears as a mole fraction weighted average of each exchange, as

$$\Delta G_{obsd} = \Delta G_0{}^{\circ}X_0 + \Delta G_1{}^{\circ}X_1 + \Delta G_2{}^{\circ}X_2 \qquad (32)$$

where X_n is the mole fraction of each species $Co^{II}(py)_n$ (implied porphyrin) and ΔG_n, the associated free energy change of each exchange reaction. Therefore, the contributions of each exchange are most easily calculated by multiple linear regression with eq 32. The observed free energy changes are listed in Table VII.

Analysis of the data with eq 32 using X_n calculated from concentrations shown previously (Table IV) gives the following values for ΔG_n and for ΔE.

n	ΔG_n, cal/mol	ΔE, mV
0	375	−16.3
1	−750	+32.5
2	184	−8.0

The multiple correlation coefficient $R > 0.998$, showing good correlation to the model described.

It is seen that there is indeed only a small difference in the potentials of the CoTPP and CoTTP redox couples. For the two bis(pyridine) complexes, which most closely approximate true self-exchange, this difference is only 8 mV; for reaction of species of different ligation, it is somewhat larger, as might be expected.

Conclusions

Immediately suggested by the kinetics results of the outer-sphere exchanges should be a comparison of the rates and activation parameters to these quantities for other, previously studied, similar reactions. Table VIII is a summary of some cobalt(III)–cobalt(II) self-exchange rates that have been reported in the literature.

It has been suggested by Sutin[46] that for metalloporphyrin electron transfers proceeding via the porphyrin π system, their rates may be expected to be similar to those for the corresponding phenanthroline complexes because of the similarity of the extensively conjugated ligands (if the spin states of the metal are the same in both complexes). Weight has been lent to this hypothesis by the similar exchange rates of $CoTMPyP(H_2O)_2^{5+/4+}$ and $Co(phen)_3^{3+/2+}$ as well as the similar rates of $FeTMPyP(imidazole)_2^{5+/4+}$ ($k_{11} \geq 10^7$ M^{-1} s^{-1}) and $Fe(phen)_3^{3+/2+}$ ($k_{11} \geq 10^8$ M^{-1} s^{-1}).[12] Considering the obvious differences in the systems (e.g., metalloporphyrin charges and solvent), the value of k_{11} for the $Co^{III/II}TPP(py)_2$ couple is also quite close to that of the aforementioned cobalt couples, suggesting that electron transfer still occurs through the porphyrin's π-electron cloud.

Aside from arguments such as this, very little work has been done toward the deduction of the exact mechanism by which outer-sphere electron exchanges such as these occur. The various axial and peripheral electron-transfer processes through porphyrins have been discussed by Castro,[47] who draws the conclusion that the exact path of transfer in peripheral processes is very difficult to ascertain but suggests that some reactions may proceed with a porphyrin π-ion radical as a possible intermediate in the course of formation of the metalloporphyrins' stable oxidation states, though this phenomenon is not suggested as likely in this particular system. Accordingly, conclusions about mechanism can be drawn from the results reported here on the basis of hypotheses such as Sutin's but are not definitive with respect to microscopic detail.

Electron transfers are assumed by Marcus' theory to exhibit the free-energy relationships[4]

$$\Delta G_{12}{}^* = {}^1\!/_2(\Delta G_{11}{}^* + \Delta G_{22}{}^*) + \Delta G_{12}{}^0(1 + \alpha) \qquad (33)$$

where

$$\alpha = {}^1\!/_4\Delta G_{12}{}^*(\Delta G_{11}{}^* + \Delta G_{22}{}^*)^{-1} \qquad (34)$$

and

$$\Delta G^* = \Delta G^{\ddagger} + RT \ln (hZ/kT) \qquad (35)$$

On the basis of the expected contribution to the free energy of activation made by the free energy of reaction, the lower rates of exchange observed with $Co^{II}TTP$ and $Co^{II}TTP(py)$ seem reasonable, since there is intuitively a larger barrier for the reaction when it has departed from a true self-exchange (by removal of the pyridine ligands so that rearrangement of these ligands is required to form the products).

Various explanations have been offered for the slowness of cobalt(III)–cobalt(II) exchanges relative to other metal electron exchanges. The example commonly cited is the very slow $Co(NH_3)_6^{3+/2+}$ exchange, which was early attributed to the change in spin multiplicity.[48] Most early cobalt(II) complexes studied were high spin ($t_{2g}{}^5e_g{}^2$) and the required unfavorable transformation to low spin preceding electron transfer to cobalt(III) ($t_{2g}{}^6$) was assumed to cause the slow rate of exchange. On the basis of exchanges involving low-spin Co(II) complexes, Broccardo,[49] Endicott and co-workers,[50,51] and Durham[52] concluded that other

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(46) Sutin, N. *Chem. Br.* **1972**, *8*, 148–151.

(47) Castro, C. E. in reference 3b; Vol. 5, Chapter 1.

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factors contributed to this phenomenon since these exchanges were also relatively slow. In the reactions involving the low-spin Co(II) complexes, the relatively larger inner-sphere reorganizational barrier (due to Jahn–Teller distortion) seemed to be a significant factor. So considerable distortions are necessary in the cobalt macrocycles in both oxidation states (according to the Franck–Condon principle) before electron transfer occurs. Quantum mechanical calculations by Jortner and co-workers[53] have shown that both these factors (spin change and Franck-Condon barrier) are important in the $Co(NH_3)_6^{3+/2+}$ exchange. The inner-sphere reorganization of the precursor complex (formed from initial interaction of the separated reactants) to attain the activated complex conformation is most likely the rate-determining step in the $Co^{III/II}TPP(py)_2$ outer-sphere transfer.

Comparison of the activation parameters for the outer-sphere exchanges indicates that those for $Co^{III/II}TPP(py)_n$ [at 0.07 M py-d_5, at which $Co^{II}TPP(py)$ is near its maximum concentration] are fairly well in line with other Co(III)–Co(II) exchanges. Activation entropies for electron exchange reactions generally fall in the range of −40 to −20 eu.

In past Marcus theory treatments of self-exchanges, reductants used in cross-reactions [e.g., $Ru(NH_3)_6^{2+}$ or $Fe(EDTA)^{2-}$] were used in aqueous solution. Such reagents have solubilities in some organic solvents so low as to be impractical for reactions with hydrophobic systems such as those involving TPP ligands. The feasibility of self-exchange studies in nonpolar solvents, as shown by the techniques described here, indicates another distinction of these methods from traditional treatments.

Naturally, however, the extension of the methods described herein to aqueous systems certainly appears feasible also. The studies of CoTPP in organic solvents under various conditions (particularly variable [py] to attain various states of ligation, but also temperature dependencies etc.) show the potential for versatility of these methods. The upper limit of rate of exchange reliably measured by the reaction between "labeled" and "unlabeled" complexes requires $k_{exch} \lesssim 0.03$ s^{-1}, which is determined by the practical rate of acquisition of spectra. The method would be particularly appropriate for corroboration of the exchange rate constants for the cobalt–porphyrin systems previously studied by Marcus theory treatments: $CoTMPyP^{5+/4+}$ [$k_{11} = 20$ M^{-1} s^{-1} by reaction with $Ru(NH_3)_6^{2+}$] and $CoTPPS^{3-/4-}$ [$k_{11} \simeq 6.1 \times 10^{-2}$ M^{-1} s^{-1} by reaction with $Fe(EDTA)^{2-}$]. For the former system, total porphyrin concentrations of ($[Co^{II}]_t + [Co^{III}]_t) \lesssim 10^{-3}$ M would be necessary to achieve an observably low rate, but these should be easily monitored with high-field NMR instruments.

The CoTMPyP system is ideally suited to such a study, in fact, since the labeled reactant can easily be made by *deuteriomethylation* with CD_3I in the course of the usual synthesis of $Co^{III}TMPyP$.[54] Labeling by deuteration offers an even closer approximation of true self-exchange. The CoTPPS system can be studied similarly to CoTPP by labeling the *p*-benzenesulfonate substituents with methyl at one *m*-phenyl position to make Co^{III}(*m*-TTPS).

With this demonstration of its feasibility, the method described herein seems to be generally applicable for the study of any sufficiently slow reactions involving species (especially macrocyclic ligands) for which substitution of hydrogen by methyl causes sufficiently little change in the chemistry of interest.

Registry No. $Co^{III}TPP(Cl)$, 60166-10-1; $Co^{II}TTP$, 19414-65-4; $Co^{III}TPP(py)_2{}^+Cl^-$, 78694-29-8; $Co^{II}TTP(py)$, 60470-23-7; $Co^{II}TTP(py)_2$, 78694-27-6; $Co^{III}TTP(N_3)$, 80642-19-9; $Fe(EDTA)^{2-}$, 15651-72-6.

Supplementary Material Available: Figures of ^1H NMR spectra, absorbance changes during the K_1 determination, and the McKay equation plot for $[py]_0 = 0.03$ M and a table of R_{obsd} values used in calculating K_3 and K_4 and of intermediate results for the $[py]_0 = 0.03$ M run (7 pages). Ordering information is given on any current masthead page.

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Direct Measurement of Electron Self-Exchange Rates of Cobalt Porphyrins. 2. Inner-Sphere Exchange

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Abstract: Inner-sphere electron exchanges between cobalt(III) and cobalt(II) complexes of 5,10,15,20-tetra-*p*-tolylporphine, TTP, were studied. The $Co^{III}TTP$ compounds retain a coordinated anion in the absence of added ligand, and the exchanges of the Co(TTP) complexes are fast enough to cause extensive broadening of the ^1H NMR spectra. The effect of various bridging ligands was studied, and most rates were determined at the temperatures of coalescence of the *p*-methyl peaks in several solutions of varying concentrations, yielding rate constants and activation parameters for exchange. For the chloride-bridged exchange in $CDCl_3$, these are $k_{11}(298\ K) = 2.71 \times 10^4$ M^{-1} s^{-1}, $\Delta H^* = 10.3 \pm 1.5$ kcal/mol, $\Delta S^* = -3.6 \pm 4.7$ cal·K^{-1}·mol^{-1}. The order of bridging efficiencies found is $I^- > N_3^- \approx SCN^- > Br^- > Cl^-$. A solvent dependence study of the chloride-bridged exchange showed relative rates in benzene-d_6, $CDCl_3$, and tetrahydrofuran-d_8 in the ratios of 18:1:0.31. The results indicate a catalysis by 4–6 orders of magnitude through mediation of the anion compared to the corresponding outer-sphere exchange rates.

As an extension of the studies of the outer-sphere electron exchange of cobalt porphyrins,[3] the inner-sphere exchange behavior was also studied and is described here. The inner-sphere mechanism involves a ligand bridging the reactants in the transfer. Both electron-transfer mechanisms have been discussed in detail elsewhere.[4,5]

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