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 $k_{11}(298\ K) = 2.71 \times 10^4\ M^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 10.3 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = -3.6 \pm 4.7\ cal{\cdot}K^{-1}{\cdot}mol^{-1}$. 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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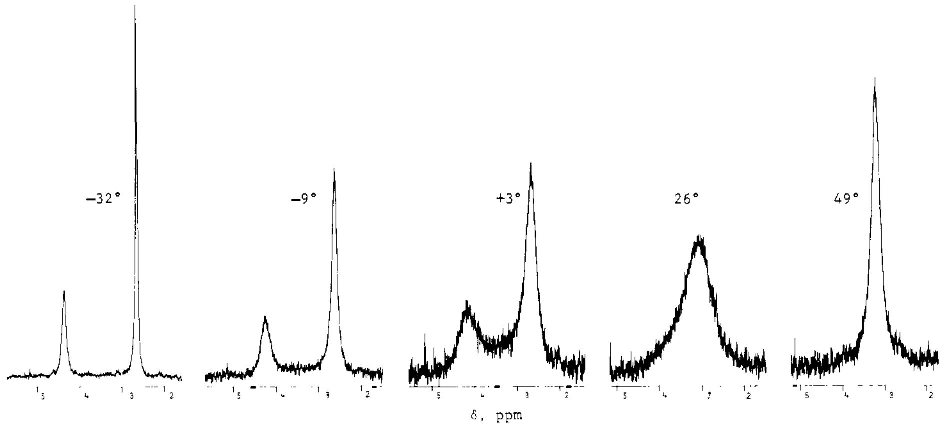

Figure 1. Temperature dependence of the *p*-methyl line shapes in 90-MHz ^{1}H NMR spectra of a mixture of Co^{II}TTP + Co^{III}TTP(Cl) in CDCl$_3$.

The specific porphyrins involved in the exchange reactions here are the cobalt(II) and cobalt(III) complexes of 5,10,15,20-tetra-*p*-tolylporphine, TTP. In the absence of an added coordinating ligand, Co^{III}TTP can retain a coordinated anionic ligand as a charge balance. This anionic ligand (for example, a halide) is often capable of acting as a bridging ligand between the cobalt(II) and cobalt(III) porphyrins, facilitating the inner-sphere exchange.

Although quite a few studies of heteronuclear inner-sphere transfer reactions have been made (and reviewed elsewhere),[6] less work has been done on inner-sphere electron *self-exchange* reactions of metal complexes. A pertinent early example was the study of the chloride-bridged inner-sphere exchange between Co^{II}TPP–Co^{III}TPP(Cl) in benzene,[7] which will be discussed later.

For relatively fast exchanges ($k_{11} \gtrsim 10^3$ M^{-1} s^{-1}), nuclear magnetic resonance methods have been developed for measuring rates. Both inner- and outer-sphere exchanges can be studied by such methods, examples of which include the exchange between Cu(I)–Cu(II) from the ^{63}Cu NMR spectrum,[8] V(IV)–V(V) by ^{51}V NMR,[9] MnO_4^{2-}–MnO_4^- by ^{55}Mn NMR,[10] and $Fe(CN)_6^{4-}$–$Fe(CN)_6^{3-}$ by ^{14}N NMR;[11] also, the chloride-bridged inner-sphere exchange between the Co(II)–Co(III) complexes of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (abbreviated [14]tetraeneN$_4$) was measured by line broadening of the methyl ^{1}H NMR resonance.[12]

In order to obtain a qualitative idea of the inner-sphere transfer behavior, we initially ran the reaction by the method used for the outer-sphere exchanges as described in part 1;[3] i.e., the Co(III) complex of tetraphenylporphine, Co^{III}TPP, was reacted with cobalt(II) tetra-*p*-tolylporphine and the appearance of the Co^{III}TTP *p*-methyl ^{1}H NMR resonance was watched for, being distinct from that of Co^{II}TTP owing to the latter's downfield isotropic shift due to paramagnetism.[13] It was immediately seen that this reaction was much too fast (at room temperature) to monitor its progress. The ^{1}H NMR spectrum showed that exchange was, in fact, fast enough to coalesce the two (Co^{II} and Co^{III}) *p*-methyl signals into one peak. It seemed reasonable that this rate could be adjusted by temperature change, so the qualitative temperature dependence of the NMR spectrum was studied. Spectra of this mixture were taken at 90 MHz over a temperature range of 81 K, and the dependence of the *p*-methyl line shape is shown in Figure 1, which dramatically indicates the temperature-dependent exchange behavior. At −32 °C, the exchange is slow on the NMR time scale; as the temperature is raised, the signals are noticeably broadened by the faster exchange until around room temperature (at these concentrations), when they are indistinguishable on the NMR time scale and have coalesced into one peak; above this coalescence temperature, this peak sharpens again.

At the point at which two peaks of equal population in an NMR spectrum have just coalesced, according to theory,[14,15] the first-order rate constant, k_{exch}, is simply proportional to the separation that the peaks *would have in the absence of exchange*, $\Delta\nu_0$, which in turn is just equal to the line width at half-height of the coalesced peak, $\omega_{1/2}^{coal}$. Thus

$$k_{exch} = 2^{1/2}\pi\omega_{1/2}^{coal} \tag{1}$$

Also, the second-order exchange rate constant, with which the two species react, is related to k_{exch} by the sum of concentrations of exchanging species.

$$k_{11}\ (\text{M}^{-1}\ \text{s}^{-1}) = \frac{k_{exch}\ (\text{s}^{-1})}{[\text{Co}^{II}] + [\text{Co}^{III}]\ (\text{M})} \tag{2}$$

In the past, k_{exch} has been determined by this method—i.e., determining the coalescence temperature, T_c, as closely as possible then using eq 1.[14] Since the coalescence point of the system studied here seems accessible, this appeared to be a convenient method for measuring these rates.

It is also immediately apparent that solutions of different total porphyrin concentrations will require different temperatures to achieve exchange fast enough to coalesce their signals. Since the rate constant can be calculated at each of these temperatures, the activation parameters can be determined from the spectra of several samples. As long as the coalescence point is accessible, this method has an advantage over the method of plotting $\omega_{1/2}$ vs. [reactant] in that the activation parameters can be simultaneously determined from the study of just a few samples. By the latter method, several samples are needed to obtain a rate at any single temperature.

In the experiments performed here, the cobalt complexes are both of tetra-*p*-tolylporphine, a system which gives a direct measurement of the actual self-exchange of the Co$^{III/II}$TTP couple.

Also reported here is a study of the effect of various bridging ligands on the inner-sphere exchange rate, which gives further mechanistic information.[16] In order to do this, several other

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complexes, including halides and pseudohalides, of Co^{III}TTP were synthesized for the exchange reactions. Finally, a qualitative solvent dependence of this exchange was studied by running the chloride-bridged reaction in benzene-d_6 and tetrahydrofuran-d_8 in addition to the deuteriochloroform used for most of the reactions.

Experimental Section

Syntheses. Co^{II}TTP. The Co(II) complex of tetra-*p*-tolylporphine was made from the free base[17] by standard literature methods[18] as described in part 1 of this report.[3]

Co^{III}TTP(Cl). A synthesis similar to that described in the literature for the tetraphenylporphine complex[19] was used to make Co^{III}TTP(Cl). After synthesis, crystals of Co^{III}TTP(Cl) were obtained by slow evaporation of solvent from the product dissolved in dichloromethane–heptane.

Co^{III}TTP(Br). This synthesis was identical with that for Co^{III}TTP(Cl) except that *hydrobromic* acid was used.

Co^{III}TTP(I). The synthesis of the iodide complex was more difficult. An initial attempt using hydriodic acid and the procedure above showed excessive oxidation of the HI to free iodine, with very little oxidation of the Co^{II}TTP.

The procedure with HI was next modified, by which a successful variation was developed. Co^{II}TTP (0.25 g) was suspended in 250 mL of methanol and then four 3.00-mL aliquots of hydriodic acid were added periodically every 24 h. At the end of this time the solution was filtered, but most of the Co^{II}TTP had still not dissolved. The methanol filtrate was concentrated by slow evaporation to the air, which also allowed absorption of water and eventually caused precipitation of the Co^{III}TTP product, which was filtered and vacuum dried. Recrystallization from dichloromethane–heptane or iodomethane–heptane gave ~10 mg of crystalline Co^{III}TTP(I). This yield is quite low (<5%), but a pure product is produced; this seems to be the most satisfactory synthesis therefore.

Co^{III}TTP(N$_3$). The same basic method of acid catalysis of air oxidation was used to make the azide complex. An ether solution of hydrazoic acid was made by a literature method,[20] producing (at half scale) a final volume of ~200 mL, which was 1–2 M in HN$_3$.

Next, 0.20 g of Co^{II}TTP was suspended in 200 mL of methanol, then 50.0 mL of the HN$_3$/Et$_2$O solution was added. This mixture was stirred in a glass-stoppered flask for 5 days, then filtered, and showed almost complete dissolution of the porphyrin. The filtrate was concentrated on a rotary evaporator to ~50 mL of methanol solvent. Then ~100 mL of H$_2$O was added, and the suspension was coagulated by digesting it on a steam bath. The solid was filtered, vacuum-dried, Soxhlet-extracted with HN$_3$/Et$_2$O, and then recrystallized from dichloromethane-heptane. The visible spectrum in CHCl$_3$–CH$_3$OH closely matched that of Co^{III}TPP(Cl):[21] $\lambda_{max} \approx 427$ nm.

Co^{III}TTP(SCN). Again, air oxidation was effected in the presence of free acid. Thiocyanic acid is an unstable gas, so fresh solutions should be used. Potassium thiocyanate (10.0 g) was dissolved in 200 mL of methanol with stirring and warming. Then a *slight deficiency* of 70% aqueous perchloric acid (8.8 mL) was slowly added with stirring. This caused immediate precipitation of KClO$_4$. After addition of all the HClO$_4$, the solution (now HSCN in CH$_3$OH) was distilled at atmospheric pressure (~65 °C) until ~30 mL was left in the pot. This should not be distilled to dryness. The HSCN–CH$_3$OH distillate is colorless. A few drops added to concentrated aqueous ferric perchlorate turned the solution deep red, so the presence of HSCN was confirmed.

Methanol was added to the distillate to make 250 mL; then 0.20 g of Co^{II}TTP was suspended in it. After being stirred 2 days in a glass-stoppered Erlenmeyer flask, the solution was filtered (and showed no residual Co^{II}TTP) and then was concentrated on a rotary evaporator to ~50 mL. Water (~150 mL) was added to precipitate the Co^{III}TTP(SCN), which was filtered and vacuum dried. The visible spectrum in CHCl$_3$-CH$_3$OH looked typically like Co^{III}TTP.

Elemental Analyses. All compounds described above were analyzed by Galbraith Laboratories (Knoxville, TN). Results of these analyses, including theoretical and observed percentages, are summarized in Table I.[22]

Table I. Elemental Analyses of Cobalt Porphyrin Samples

sample		% C	% H	% N	% (X)
Co^{II}TTP	calcd	79.22	4.99	7.70	8.10 (Co)
	found	78.50	5.25	7.59	8.04
Co^{III}TTP(Cl)	calcd	75.54	4.75		4.65 (Cl)
	found	74.46	5.13		6.22
Co^{III}TTP(Br)	calcd	71.38	4.49		9.89 (Br)
	found	71.54	4.77		10.83
Co^{III}TTP(I)	calcd				14.85 (I)
	found (1)				15.40
	found (2)				15.44
Co^{III}TTP(SCN)	calcd	74.89	4.62	8.91	4.08 (S)
	found	74.93	5.00	8.91	3.75
Co^{III}TTP(N$_3$)	calcd	74.89	4.71	12.74	
	found	73.42	4.96	12.34	

Table II. Summary of ^{1}H NMR Chemical Shifts (δ^b) of Cobalt Tetratolylporphines^a

	proton			
compd	β-pyrrole	*o*-phenyl	*m*-phenyl	*p*-methyl
Co^{II}TTP	15.97	13.07	9.72	4.13
Co^{III}TTP(Cl)	8.62	8.10	7.52	2.64
Co^{III}TTP(Br)	8.80	8.12	7.54	2.66
Co^{III}TTP(I)	8.95	8.07	7.58	2.69
Co^{III}TTP(SCN)	8.82	8.05	7.52	2.65
Co^{III}TTP(N$_3$)	9.20	8.28	7.61	2.71

^{a} Solvent: CDCl$_3$. Spectra taken at 250.13 MHz. ^{b} Downfield from tetramethylsilane.

Aside from the observation of residual solvent, the analyses showed that the porphyrins were essentially of the composition expected. In particular, the thiocyanate and azide complexes were definitely not bis(ligand) complexes, and the iodide complex was not in the form of triiodide.

^{1}H NMR Spectra. The spectrum of each of the compounds synthesized above was checked in order to further ensure purity with respect to oxidation state and organic impurities. The resonances due to porphyrin (β-pyrrole, *o*- and *m*-phenyl, and *p*-methyl) are the only significant peaks present in every case. In some spectra, a small amount of impurity appears as two peaks around δ 1; this is assumed to be *n*-heptane retained during recrystallization.

Also, the spectra of the Co(III) porphyrins show signals atypically broad for Co(III) compounds.[23] A similar observation has been made by Yamamoto et al.[24] for Co^{III}TPP(Cl) in tetrachloroethane-d_2. This broadening was attributed to the presence of the Co^{III}TPP$^{2+\cdot}$ π-cation radical. The same qualitative behavior was exhibited by each of the Co^{III}TTP complexes here, but the broadening was evident to different extents depending on the coordinated anion. In every Co^{III}TTP complex, however, the chemical shift of the *p*-methyl peak was about 2.7 ppm and still distinct from that of Co^{II}TTP.

Chemical shift data for all of the cobalt porphyrins are summarized in Table II.

Instrumentation. Routine visible spectra for characterization of compounds were taken with a Beckman ACTA-111 UV–visible spectropho-

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(22) Several of the compounds—in particular the halide complexes which were recrystallized from dichloromethane–heptane—show consistently high hydrogen and halogen analyses. It seems that this recrystallization step allows (at least temporary) retention of the solvents in the crystals formed. Co^{III}TPP(Cl)(py) has been shown by X-ray crystallography to crystallize with benzene solvent retained. (Sakurai, T.; Yamamoto, K.; Seino, N.; Katsuta, M. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2514–2517.) This phenomenon is particularly apparent in the analysis of the chloride complex, Co^{III}TTP(Cl)—which was freshly prepared and recrystallized before the analysis—but also in the bromide, iodide, and azide complexes. The assumption of 2.2% CH$_2$Cl$_2$ and 3.8% C$_7$H$_{16}$ in the chloride sample gives the following analyses: Calcd: C, 74.45; H, 5.13; Cl, 6.22. Found: C, 74.46; H, 5.13; Cl, 6.22. The remaining compounds were not recrystallized this way. The heptane does in fact appear as a slight impurity in the ^{1}H NMR spectra of some of these samples but in relatively small amounts which would not affect the exchange reactions. Additionally, the solvent was slowly lost during handling afterward.

(23) Figures of the NMR spectra of the Co^{III}TTP complexes are reproduced in the supplementary material.

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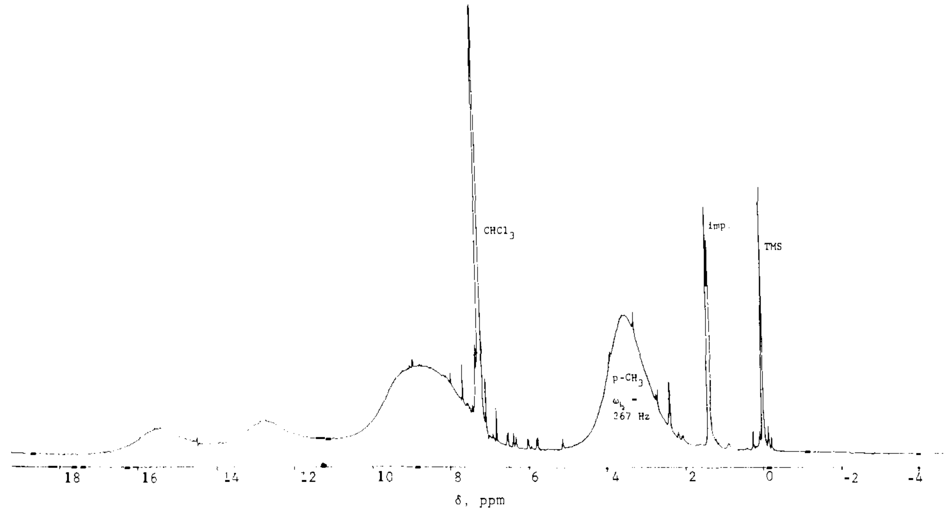

Figure 2. 250-MHz ^{1}H NMR spectrum of the mixture Co^{II}TTP + Co^{III}TTP(Cl) undergoing electron exchange in CDCl$_3$ at the *p*-methyl peaks' coalescence point (T_c = 319 K; [Co^{II}TTP] = [Co^{III}TTP(Cl)] = 6.48 mM).

tometer. The spectrophotometric titration of Co^{III}TPP(Cl) with tetrahydrofuran in chloroform was run at ambient temperature (25 °C) on a Varian Cary 219 UV–visible spectrophotometer.

Proton NMR spectra for the initial qualitative temperature dependence study of the chloride-bridged inner-sphere exchange were run at 90 MHz on the Bruker WH-90 spectrometer described in part 1.[3] Spectra for the characterizations of Co^{III}TTP complexes and for the quantitative rate constant determinations by band-shape analysis were taken with a Bruker WM-250 Cryospec Fourier transform spectrometer operating at 250.13 MHz. The variable-temperature control was calibrated with both methanol (low temperature) and ethylene glycol (high temperature) according to the methods described by van Geet[25] and showed an accuracy of ±1 K throughout the temperature range used in these studies. The sample temperature was therefore assumed to be equal to the control setting within this estimated error range.

Kinetics. Experiments run with CDCl$_3$ as solvent were set up by preparing stock solutions of each porphyrin reactant. These were made by dissolving in deuteriochloroform (Merck 99.5%D redistilled periodically and purged with dry nitrogen gas before use) in separate 1.00-mL volumetric flasks ~10 mg of each solid porphyrin, weighed as accurately as possible to be equimolar. The first solution to be monitored was made by mixing 200 μL of each stock solution in a 5-mm NMR tube, adjusting either volume slightly in order to further ensure equimolar final concentrations and a sample volume ≥400 μL. A series of solutions was made by diluting various total volumes of porphyrin solution with pure CDCl$_3$ to give solutions of equal volume but varying total porphyrin concentrations (always equimolar in Co^{II}TTP and Co^{III}TTP).

The first sample (of highest concentration) was next checked by its ^{1}H NMR spectrum. The temperature was adjusted appropriately in order to bring the observed spectrum to the coalescence point of the *p*-methyl peaks. The line width of the coalesced *p*-methyl peak was measured directly from the spectrum obtained at the coalescence temperature, T_c. A sample of one such spectrum is shown in Figure 2. This procedure was performed for each of the sample solutions.[26] Further, since some spectra were taken at temperatures significantly deviant from room temperature (at which the solutions were prepared), corrections were made for changes in concentration due to expansion or contraction of the solvent with temperature changes. The *relative* change in density of CDCl$_3$ was assumed to be approximately the same as that of CHCl$_3$,[27] and concentration corrections were made on this basis.

With benzene-d_6 as solvent, the stock porphyrin solution preparation was modified because of the lower solubility of the porphyrins in benzene. This solvent was also used only for the chloride-bridged exchange. Stock solution was made by dissolving 4.06 mg of Co^{II}TTP (5.58 μmol) and 4.35 mg of Co^{III}TTP(Cl) (5.70 μmol) together in C$_6$D$_6$ (Merck 99.5%D) in a 4.00-mL volumetric flask. This solution was diluted as necessary with C$_6$D$_6$ to give desired final porphyrin concentrations. The density change with temperature of C$_6$D$_6$ was also accounted for similarly to CDCl$_3$.[27] Spectra of these solutions were analyzed as described above for those in CDCl$_3$.

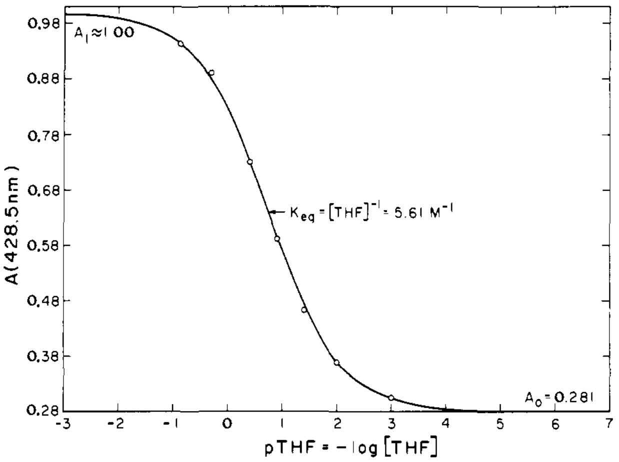

Figure 3. Spectrophotometric titration of Co^{III}TPP(Cl) with tetrahydrofuran in chloroform solvent.

Kinetics in Tetrahydrofuran-d_8. Although some other polar solvents such as methanol form bis(ligand) complexes with Co^{III}TPP, the claim has been made by Yamamoto[28] on the basis of ^{1}H NMR chemical shift data that Co^{III}TPP(Cl) in THF-d_8 exists as Co^{III}TPP(Cl)(THF-d_8) with chloride remaining coordinated. Since this coordination is a requirement for the exchange to proceed by an inner-sphere mechanism, further corroboration of the state of ligation in this system was desired.

The equilibrium constant between Co^{III}TPP(Cl) and tetrahydrofuran was studied spectrophotometrically with a titration set up similarly to that for the Co^{II}TTP–pyridine equilibrium study.[3] Changes in absorbance were monitored in solutions of constant [Co^{III}TPP] but varying [THF] in chloroform.

As will be seen from the results, the presence of only one coordinated THF is verified. The exchange reaction in THF-d_8 was initially set up as for that in benzene-d_6; but it was found that the exchange was not fast enough even at the highest concentration and at 67 °C, near the boiling point of THF, to bring about coalescence of the *p*-methyl peaks. The rate determination method used therefore was that of measuring the dependence of the line width of the Co^{II}TTP *p*-CH$_3$ resonance as a function of [Co^{III}TTP(Cl)(THF-d_8)].

Results

Kinetics in CDCl$_3$ and C$_6$D$_6$. Observed rate constants, $k_{\rm exch}$ and k_{11}, related by eq 2, were determined as described in the Experimental Section. Experimental data from the systems used for these rate measurements are listed in Table S1 of the supplementary material.

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[25] (a) van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227–2229. (b) *Ibid.* **1970**, *42*, 679–680.

[26] Typically, there were five samples for each run. In some samples of some runs, T_c was either not accessible in CDCl$_3$ or the results calculated from an apparently satisfactory spectrum were obviously spurious. In other cases, data from more than one run were combined for analysis.

[27] Brunel, R. F.; Van Bibber, K. *Int. Crit. Tabl.* **1928**, *3*, 27–35.

[28] Yamamoto, K. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)* **1976**, *70*, 71–78.

Table III. Dependence of the $Co^{II}TTP$ *p*-Methyl Line Width on $[Co^{III}TTP(Cl)(THF\text{-}d_8)]$ in THF-d_8 solvent[a]

sample no.	$[Co^{III}]$,[b] mM	$\omega_{1/2}$,[c] Hz
1	11.40	54.5
2	7.60	43
3	6.51	40
4	5.70	39

[a] $T = (300 \pm 1)$ K. [b] $[Co^{II}TTP] = 11.25$ mM. [c] ±1 Hz.

$Co^{III}TPP(Cl)$–THF Equilibrium. Results of the spectrophotometric titration of $Co^{III}TPP(Cl)$ with tetrahydrofuran in chloroform are shown in the plot (Figure 3) of absorbance vs. pTHF (= −log [THF]). This shows only one inflection in one smooth curve up to 60 vol % THF, suggesting that there is indeed only one THF-d_8 molecule coordinated to $Co^{III}TPP(Cl)$ even in pure THF-d_8. The equilibrium constant of coordination can be determined from the x axis intercept of the transformed equation

$$\log\left(\frac{A - A_0}{A_1 - A}\right) = \log\,[\mathrm{THF}] + \log K_{eq} \qquad (3)$$

Calculation of this intercept and error analysis of the data can be performed by standard statistical methods,[29] with the results

$$\log K_{eq} = 0.7493 \pm 0.0067$$

$$K_{eq} = 5.61 \pm 0.09$$

Kinetics in Tetrahydrofuran-d_8. Determination of the exchange rate constant in THF-d_8 was determined from the line-broadening trend of the $Co^{II}TTP$ *p*-CH_3 peak with varying $[Co^{III}TTP]$. Table III shows the variation of the linewidth at half-height, $\omega_{1/2}$, at 300 K. The rate constant can be calculated simply from linear regression of $\pi\omega_{1/2}$ vs. $[Co^{III}]$, yielding the slope

$$k_{11} = (8.84 \pm 0.56) \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$$

with a correlation coefficient $r = 0.996$. This rate constant is considerably lower than those found in $CDCl_3$ and C_6D_6 and explains why coalescence could not be reached.

Activation Parameters. In order to extract activation parameters, we converted each rate constant, k_{11} (Table S1), to its corresponding free energy of activation by eq 4. Uncertainties

$$\Delta G^* = RT\,[\ln\,(k_B/h) + \ln\,(T/k)] \qquad (4)$$

in rate constants calculated by NMR methods such as band-shape analysis are typically on the order of 10%.[30] This estimate appears valid in these systems also, as evidenced by the deviations in $\omega_{1/2}$ ($=\Delta\nu_0$) among the samples within each run, listed in Table S1, which would theoretically be approximately constant but which show a mean standard deviation of 9% among all the runs in the table. Thus the assumption $\sigma_k/k \approx 0.10$ was made. Estimated errors in ΔG^* were then calculated following a usual propagation of errors analysis[31]

$$R^{-2}\sigma_{\Delta G^*}^2 = \left[1 + \ln\left(\frac{k_B}{h}\right) + \ln\left(\frac{T}{k}\right)\right]^2 \sigma_T^2 + T^2\left(\frac{\sigma_k}{k}\right)^2 \qquad (5)$$

where k_B is Boltzmann's constant and h is Planck's constant. Enthalpy and entropy of activation were calculated from linear regression of

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (6)$$

Intermediate results of these calculations (ΔG^*, $\sigma_{\Delta G^*}$) are listed in Table IV. Finally, Table V lists the calculated activation parameters, 90% confidence intervals of log k_{11}(298 K)—calculated from the confidence limits $\Delta G_{298}^* \pm t_{0.05,n-2}\,\sigma_{\Delta G_{298}^*}$, where t is the upper percentage point of Student's t distribution for sample size n—and the corresponding k_{11}(298 K).

Table IV. Intermediate Results of Inner-Sphere Exchange Rate Measurements

bridging ligand	T_c (σ_T), K	$10^{-4}k_{11}$, $\mathrm{M^{-1}\ s^{-1}}$	$\Delta G^{\ddagger}$ ($\sigma_{\Delta G^{\ddagger}}$), cal/mol
Cl^- (run 1)	319 (1)	9.17	11473.0 (73.9)
	323 (1)	12.08	11448.0 (74.3)
	339 (2)	26.36	11522.0 (98.6)
Cl^- (run 2)	321 (1)	8.24	11617.1 (74.3)
	324 (1)	11.04	11543.4 (74.6)
	328 (1)	16.91	11416.0 (74.8)
	337 (2)	25.78	11464.9 (98.3)
	358 (4)	52.51	11716.3 (156.0)
Cl^- (C_6D_6)	297 (1)	45.01	9700.6 (68.4)
	301 (1)	59.93	9668.0 (68.9)
	308 (1)	80.85	9723.7 (69.8)
	318 (1)	117.6	9822.8 (71.2)
Br^-	270 (1)	9.85	9582.8 (65.4)
	273 (1)	13.39	9528.7 (65.6)
	278 (1)	18.38	9538.3 (66.1)
	288 (1)	27.11	9679.2 (67.4)
	299 (1)	36.90	9888.0 (69.0)
	305 (1)	46.96	9952.3 (69.8)
	309 (1)	50.40	10047.5 (70.4)
	311 (1)	66.00	9949.8 (70.5)
	333 (2)	127.9	10261.1 (93.2)
I^-	205 (3)	~14	7020.4 (116.1)
	212 (3)	20.93	7104.9 (114.5)
	213 (2)	~20	7159.6 (82.8)
	217 (2)	27.08	7171.4 (82.3)
	220 (2)	33.33	7185.8 (81.9)
SCN^-	253 (1)	11.14	8884.9 (62.5)
	256 (1)	13.63	8893.6 (62.7)
	263 (1)	15.06	9098.8 (63.8)
	274 (1)	18.01	9404.2 (65.4)
	289 (1)	35.26	9563.9 (67.3)
	297 (1)	50.05	9638.0 (68.3)
	302 (1)	78.86	9537.4 (68.8)
	310 (1)	132.1	9488.4 (69.7)
	335 (2)	251.1	9877.6 (91.6)
N_3^-	234 (1)	10.90	8191.5 (59.4)
	239 (1)	14.63	8236.8 (59.9)
	244 (1)	22.23	8216.3 (60.2)
	258 (1)	38.55	8434.1 (61.9)

Conclusions

Comparisons of halide-mediated inner-sphere electron transfers and of outer-sphere transfers involving cobalt complexes of various macrocycles were reported by Endicott and coworkers,[12,32] Results were similar to those found for the porphyrin systems studied here. The self-exchange rate between Co(III)–Co(II) complexes of [14]tetraeneN_4 was $1.0 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ (25 °C, 0.1 M CF_3SO_3H) for the chloride-bridged inner-sphere exchange compared to $5 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$ (25 °C, 1.0 M $HClO_4$) for the outer-sphere Co([14]tetraeneN_4)$(H_2O)^{3+/2+}$ exchange.[33] Thus, electron exchange of $Co^{III/II}$([14]tetraeneN_4) was catalyzed by a factor of 2×10^5 by the mediation of a chloride ion. For $Co^{III/II}TTP$, catalysis was by factors of 10^4–10^6: i.e., $2.7 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ for the chloride-bridged inner-sphere exchange compared to rates of 0.019–9.7 $\mathrm{M^{-1}\ s^{-1}}$ for the outer-sphere exchanges of the pyridine complexes, depending on the degree of ligation of pyridine to the porphyrins.[3] This enhancement of rates is attributed to a much smaller inner-sphere reorganizational energy required to change conformations of reactants to those of the activated complex and also

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(31) Reference 29, p 60.

(32) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Bala-kirshnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431–1440.

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Table V. Summary of Inner-Sphere Electron-Exchange Results

bridging ligand	solvent	$10^{-3}k_{11}$(298 K), $M^{-1}\ s^{-1}$	log k_{11}(298 K) (90% Cl)	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal·K^{-1}·mol^{-1}
I^-	$CDCl_3$	8170	6.91 ± 0.35	4.9 ± 1.9	−10.5 ± 8.8
Br^-	$CDCl_3$	373	5.57 ± 0.03	6.2 ± 0.4	−12.1 ± 1.3
Cl^-	$CDCl_3$	27.1	4.43 ± 0.23	10.3 ± 1.5	−3.6 ± 4.7
	C_6D_6	497	5.70 ± 0.05	7.7 ± 1.3	−6.5 ± 4.4
	THF-d_8	8.84	3.95 ± 0.03		
SCN^-	$CDCl_3$	649	5.81 ± 0.07	5.9 ± 0.3	−12.2 ± 0.9
N_3^-	$CDCl_3$	2130	6.33 ± 0.30	5.8 ± 0.8	−10.1 ± 3.4

to a smaller (second coordination sphere) solvent reorganizational energy.

There is in fact a definite solvent dependence of the inner-sphere exchanges. The chloride-bridged exchange is a factor of 18 faster in C_6D_6 than in $CDCl_3$, which in turn is over 3 times faster than in THF-d_8. This is also a reasonable trend, considering the relative degrees of solvent reorganization necessary in each of these systems. La Mar and Walker[13] have shown that there is negligible ordering of toluene-d_8 around Co^{II}TTP at room temperature. Polarizable, oxygen-containing molecules (especially H_2O, but including THF) are known to have considerably greater order about such complexes, however. A correspondingly greater energy of reorganization of this solvent would be expected and is evidenced in the observed exchange rates. $CDCl_3$ seems intermediate between the polar THF-d_8 and nonpolar benzene-d_6.

The effect of the bridging ligand is also obvious. The observed bridging efficiency shows the "normal" order[16] of $I^- > Br^- > Cl^-$, with an average 1.24 ± 0.10 orders of magnitude between the rates. The behavior of the thiocyanate and azide complexes is also interesting. The fact that the two rates are of comparable magnitude suggests that Co^{III}TTP(SCN) in its stable state is sulfur bound.[16]

The faster rates of inner-sphere compared to outer-sphere transfers are especially reflected in the entropies of activation, ΔS^{*}, which are noticeably lower in magnitude; in comparison, activation entropies of outer-sphere self-exchanges generally fall in the range of −40 to −20 cal·K^{-1}·mol^{-1}. This is consistent with the lesser degree of reorganization of the inner and outer (solvent) coordination spheres, as hypothesized above, and from an improvement in the electronic transmission factor.

Several inner-sphere electron-transfer reactions involving metalloporphyrins have been investigated,[34-37] which were all reductions with chromium(II). Since Marcus' theory[38] has as a requirement the occurrence of electron transfer by an outer-sphere mechanism, self-exchange rates of metalloporphyrins were not readily calculable by this theory and were therefore not reported. The actual inner-sphere *self-exchange* reaction of a synthetic metalloporphyrin reported was that mentioned previously: the Co^{III}TPP(Cl)–Co^{II}TPP exchange in benzene was monitored by ^{60}Co labeling.[7] The exchange *rate*, however, was too fast to measure accurately by this technique. At 7 °C, complete exchange was observed in <10 s, suggesting $k_{11} > 2.5 \times 10^3\ M^{-1}\ s^{-1}$. Since the actual rate calculated from results reported here is $k_{11} \approx 2.2 \times 10^5\ M^{-1}\ s^{-1}$ ($\tau_{exch} \simeq 0.12$ s) in C_6D_6, this observation is consistent.

The measurement of such relatively fast electron exchange rates by band-shape analysis is a generally applicable method. For the rates to be calculated from line widths at coalescence points, the coalescence temperature obviously must be accessible. Even at points distant from coalescence, rates are extractable by general band-shape analysis.[39]

The results of this study have shown further evidence for the phenomenon of catalysis by halide and pseudohalide mediation of electron-exchange reactions. Also, the first accurate measurements of such rates for metalloporphyrins have been reported, the methods for which should be generally applicable to similar studies of other systems of interest. In paricular, the methods should be applicable to the study of any sufficiently fast exchange reaction including possible fast outer-sphere exchanges, such as those of iron or manganese porphyrins.

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Registry No. Co^{II}TTP, 19414-65-4; Co^{III}TTP(Cl), 80642-16-6; Co^{III}TTP(Br), 34829-90-8; Co^{III}TTP(I), 80642-17-7; Co^{III}TTP(SCN), 80642-18-8; Co^{III}TTP(N_3), 80642-19-9.

Supplementary Material Available: Figures of the ^{1}H NMR spectra of the Co^{III}TTP complexes and a table of experimental parameters from the systems (7 pages). Ordering information is given on any current masthead page.

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