

Stereoelectronic Aspects of Inter-Metal Nitrogen Atom Transfer Reactions between Nitridomanganese(V) and Chromium(III) Porphyrins

Lawrence A. Bottomley* and Frank L. Neely

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received August 1, 1996[⊗]

Reactions of nitridomanganese(V) porphyrins with chromium(III) porphyrins resulted in the irreversible formation of nitridochromium(V) porphyrins and manganese(III) porphyrins. The progress of these reactions has been followed spectrophotometrically, electrochemically, and spectroscopically by EPR. Kinetic analysis of the spectrophotometric data obtained during these reactions for a variety of substituted porphyrins showed the reactions to be first order in each of the reactants. Rate constants were dependent upon the electronic and steric effects of the porphyrin substituent, upon the identity of the anion bound to the chromium(III) reactant, and upon the solvent dielectric constant. We propose that the mechanism of these nitrogen atom transfer reactions involves the nucleophilic attack of the nitridomanganese porphyrin donor on the cationic chromium(III) porphyrin acceptor facilitating a net, two-electron redox process mediated by a heterobimetallic μ -nitrido intermediate. This report represents the first systematic study of the stereochemical effects involved in the complete, inter-metal nitrogen atom transfer between two metalloporphyrins.

Introduction

Atom transfer reactions involve the transfer of a single atom and at least one electron from a donor to an acceptor molecule.¹ Metalloporphyrins participate in complete or incomplete atom transfer reactions as both donors and acceptors.² Inter-metal oxygen atom transfer reactions are typically incomplete for this class of compounds. For example, homo- and heterobimetallic μ -oxo complexes are readily prepared by reaction of an oxochromium(IV) porphyrin oxygen atom donor with metal-(II) macrocyclic oxygen atom acceptor complexes.³ In contrast, inter-metal nitrogen atom transfer reactions are generally complete processes. Takahashi discovered the first complete inter-metal nitrogen atom transfer reaction between nitridomanganese(V) and chromium(II) porphyrins involving a three-electron exchange.⁴ Woo has observed a similar reaction between nitridomanganese(V) and manganese(II) porphyrins.⁵

In a preliminary communication,⁶ we demonstrated that reaction of $\text{NMn}^{\text{V}}(\text{OEP})$ with $\text{ClCr}^{\text{III}}(\text{TPP})$ in benzene proceeded rapidly, irreversibly, and quantitatively to the manganese(III) and chromium(V) products, *i.e.* $\text{NMn}(\text{OEP}) + \text{ClCr}(\text{TPP}) \rightarrow \text{ClMn}(\text{OEP}) + \text{NCr}(\text{TPP})$.⁷ This was the first example of complete inter-metal nitrogen atom transfer between two metalloporphyrins which involved a net, two-electron exchange. We proved that the reaction rate was first order in each of the reactants and that the reaction rate can be significantly diminished either by the placement of steric groups on the porphyrin periphery or by addition of nitrogenous bases capable of axial ligation with the chromium(III) reactant. It has since been

demonstrated that a two-electron nitrogen atom exchange is not limited to the transfer of the nitride from manganese(V) to chromium(III) porphyrins. Woo has observed nitrogen atom transfer from manganese(V) to manganese(III) porphyrins.⁸ We have extended our studies to include the nitrogen atom transfer from chromium(V) to chromium(III) porphyrins⁹ and have generalized the manganese(V) to chromium(III) reaction to other macrocyclic complexes.¹⁰

In this report, we present the first systematic study of the stereochemical effects involved in the complete, inter-metal nitrogen atom transfer between two metalloporphyrins. We have found that the nitrogen atom transfer rate is dependent upon the electronic and steric effects of the porphyrin substituent, upon the identity of the anion bound to the chromium(III) reactant, and upon the solvent dielectric constant and donor strength. A mechanism for this novel atom transfer reaction is proposed.

Experimental Section

Materials. All manganese and chromium porphyrins used in this study were prepared by the method of Adler.¹¹ The free-base form of Baldwin's capped porphyrin, $\text{H}_2(\text{C}_2\text{Cap})$, was synthesized and purified by the method of Almog.¹² Metal ion insertion into this porphyrin was accomplished as previously described by Ellis.¹³ Nitridomanganese and nitridochromium porphyrins utilized in this study were prepared according to the procedure of Buchler¹⁴ from the corresponding hydroxomanganese(III) or hydroxochromium(III) porphyrins. Product purity was verified by UV-vis, NMR, and mass spectral measurements.

[⊗] Abstract published in *Advance ACS Abstracts*, October 1, 1997.

(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401–1449.
 (2) Woo, L. K. *Chem. Rev.* **1993**, *93*, 1125–1136.
 (3) (a) Elliott, R. L.; Nichols, P. J.; West, B. O. *Aust. J. Chem.* **1986**, *39*, 975. (b) Liston, D. J.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1568–1576.
 (4) Takahashi, T. Ph.D. Dissertation, University of Michigan, 1985.
 (5) Woo, K. L.; Goll, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3755–3756.
 (6) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1989**, *111*, 5955–5957.
 (7) Abbreviations used: monovalent anion = X^- ; 1,2-dichloroethane = DCE; porphyrin dianion = POR; *meso*-tetraphenylporphyrinato dianion = TPP; substituted *meso*-tetraphenylporphyrinato dianion = T-R-PP; octaethylporphyrinato dianion = OEP.

(8) Woo, K. L.; Czaplá, D. J.; Goll, J. G. *Inorg. Chem.* **1990**, *20*, 3915–3916.
 (9) (a) Neely, F. L. Ph.D. Dissertation, Georgia Institute of Technology, 1989. (b) Neely, F. L.; Bottomley, L. A. *Inorg. Chem.* **1997**, *36*, 5432–5434.
 (10) Neely, F. L.; Bottomley, L. A. *Inorg. Chim. Acta* **1992**, *192*, 147–149.
 (11) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.
 (12) Almog, J.; Baldwin, J. E.; Crossley, M. J.; DeBernardis, J. F.; Dyer, R. L.; Huff, J. R.; Peters, M. K. *Tetrahedron* **1988**, *37*, 3587.
 (13) Ellis, P. E.; Linard, J. E.; Szymanski, T.; Jones, R. D.; Budge, J. R.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1889–1896.
 (14) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Raap, A.; Gersonde, K. *Inorg. Chem.* **1983**, *22*, 879–884.

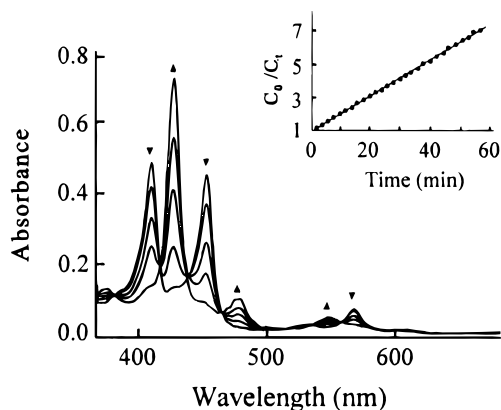


Figure 1. Electronic spectra acquired as a function of time after mixing equal volumes of 62 μM solutions of NMn(OEP) and ClCr(T-4-Me-PP) dissolved in benzene. The inset figure depicts an analysis of the absorbance data for ClCr(T-4-Me-PP) as a function of time verifying that the reaction is first order in this reactant and second order overall. The ordinate has been normalized to the initial concentration of reactant for purposes of display. Identical traces were obtained for the decrease in concentration of NMn(OEP) and the increase in concentration of the products NCr(T-4-Me-PP) and ClMn(OEP).

All reagents were obtained from Aldrich Chemical Co. and purified in the manner previously described.¹⁵

Instrumentation and Methods. Visible spectral measurements were obtained with a diode array rapid-scanning spectrometer system composed of a Tracor Northern Model 6050 spectrometer containing a crossed Czerny–Turner spectrograph in conjunction with a Tracor Northern Model 1710 multichannel analyzer. Spectra were acquired by irradiation of the sample with polychromatic light from a xenon arc lamp and the subsequent spatial dispersion of the transmitted radiation onto a 512 diode array detector by a grating with a 300 groove/mm rule and a blaze of 500 nm. Wavelength calibration was achieved with either a holmium oxide or an NIST standard filter. All measurements reported herein represent the ensemble average of at least 56 spectral acquisitions. For display purposes, a five-point Savitsky–Golay smoothing algorithm was applied to each spectrum depicted. EPR experiments were performed on a Varian E3 spectrometer. All experiments were carried out at ambient temperature ($23 \pm 1^\circ\text{C}$).

For kinetic studies, equimolar solutions approximately 60 μM in XCr(POR) or NMn(POR) were prepared in distilled benzene and their electronic spectra were obtained. Equal volumes of each solution were mixed, and the solutions were rapidly injected into a cuvette with an optical path length of 0.71 mm. Electronic spectra were acquired over time with the rapid-scanning spectrometer system. The concentrations of reactants and products were calculated by solving four simultaneous equations at the absorbance maximum for the Soret band of each reactant and product in solution. Analysis of the concentration data as a function of time indicated that the data were best-fit by a second-order rate law. The rate constants given in each of the tables is the mean value from at least three separate experiments plus or minus the standard deviation from replicated determinations.

Results

The reaction of NMn(OEP) with ClCr(TPP) resulted in the rapid, quantitative, and irreversible production of ClMn(OEP) and NCr(TPP). Electronic absorption spectra acquired during the course of this reaction are depicted in Figure 1. Well-defined isosbestic points are observed at 410, 435, and 464 nm. The final spectrum is that of a mixture of NCr(TPP) and ClMn(OEP) in the exact concentration ratios as that of the reactants. Spectrophotometric analysis of mixtures of solutions containing NCr(TPP) and ClMn(OEP) in concentration ratios up to 10:1 showed no evidence of any significant back-reaction even after maintaining these solutions at 40 $^\circ\text{C}$ for 72 h.

(15) Bottomley, L. A.; Deakin, M. R.; Gorce, J.-N. *Inorg. Chem.* **1984**, 23, 3563.

Table 1. Effect of Solvent Dielectric Constant on the Rate Constant for the Reaction between NMn(OEP) and ClCr(TPP)

solvent	dielectric const	rate const ($\text{M}^{-1} \text{s}^{-1}$)	solvent	dielectric const	rate const ($\text{M}^{-1} \text{s}^{-1}$)
C_6H_6	2.27	48 ± 6	CH_2Cl_2	9.08	350 ± 20
CHCl_3	4.79	66 ± 5	$\text{CH}_2\text{ClCH}_2\text{Cl}$	10.35	1170 ± 140
$\text{C}_6\text{H}_5\text{Cl}$	5.70	200 ± 17			

The kinetics of the manganese(V) to chromium(III) nitrogen atom transfer reaction were determined from the changes in the electronic spectrum of the reaction mixture as a function of time. Data analysis was performed at the absorption maxima of each of the products and reactants. A typical analysis of the data is depicted in the inset of Figure 1. This reaction is first order in each of the reactants; at 23 $^\circ\text{C}$, a second-order rate constant of $48 \pm 6 \text{ M}^{-1} \text{ s}^{-1}$ was obtained.

In an effort to identify long-lived intermediates, this reaction was monitored with EPR spectrometry and electrochemistry. Upon reaction of an equimolar aliquot of NMn(OEP) with ClCr(TPP) in benzene under strictly anaerobic conditions, an EPR signal centered at $g = 1.985$ increased in intensity with time. No signals were observed for either reactants or the Mn product at ambient temperatures. The spectrum is identical to that previously reported for NCr(TTP) and NCr(OEP). The intense 11-line pattern and the symmetrical hyperfine structure^{14,16} are consistent with the four pyrrole N atoms and the axial nitrido group being magnetically equivalent. The isotropic signal at $g_0 = 1.985$ is invariant with changes in the porphyrin structure. Similarly, when the reaction was carried out in an electrochemical cell, the cyclic voltammetric fingerprints¹⁷ of the reactants were replaced by those of the products. No new or transient redox processes were observed within the accessible solvent/supporting electrolyte potential range of 0.1 M TBAP in DCE.

Solvent Effects. Solvent donor strength and dielectric constant have a marked influence on the rate of the reactions under study. Table 1 lists the rate constants measured for the nitrogen atom transfer between NMn(OEP) and ClCr(TPP) as a function of solvent. Over the limited solvent series listed in this table, the log of the rate constant increased linearly with dielectric constant. However, in pyridine, no nitrogen atom transfer between NMn(OEP) and ClCr(TPP) was observed. In benzene solution containing the reactants and pyridine in a 1:1:2 molar ratio, the observed rate constant was one-eighth that observed in the absence of pyridine. As the relative concentration of pyridine was increased, the rate of the reaction decreased. No reaction was observed at relative pyridine concentrations greater than 10. Solvents with dielectric constants higher than those listed in Table 1 possess appreciable solvent donor strength (e.g. benzonitrile, dimethyl sulfoxide, pyridine, etc.). With these solvents, greatly diminished reaction rates were observed, suggesting that the donor ability of the solvent plays a more important role in inhibiting the reaction than the solvent dielectric in facilitating the formation of a key reaction intermediate (vide infra).

The rate constants were invariant with changes in solution ionic strength. The ionic strength of benzene was systematically varied by addition of $n\text{-Bu}_4\text{NClO}_4$ to the reagent solutions. The observed rate constants determined at a salt concentration of

(16) Groves, J. T.; Takahashi, T.; Butler, W. M. *Inorg. Chem.* **1983**, 22, 884–887.

(17) (a) Bottomley, L. A.; Neely, F. L.; Gorce, J.-N. *Inorg. Chem.* **1988**, 27, 1300–1303. (b) Bottomley, L. A.; Kadish, K. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1212–1214. (c) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1983**, 22, 342–349. (d) Kadish, K. M.; Kelly, S. L. *Inorg. Chem.* **1979**, 18, 2968. (e) Kelly, S. L.; Kadish, K. M. *Inorg. Chem.* **1982**, 21, 3631. (f) Bottomley, L. A.; Neely, F. L. *Inorg. Chem.* **1990**, 29, 1860–1865.

Table 2. Influence of the Chromium(III) Counterion on the Rate of the Reaction of XCr(TPP) with NMn(OEP) Determined in Benzene

reactant	Soret		reactant	Soret	
	band (nm)	rate const (M ⁻¹ s ⁻¹)		band (nm)	rate const (M ⁻¹ s ⁻¹)
(ClO ₄)Cr(TPP)	457	>2000	ClCr(TPP)	451	48 ± 6
(TFA)Cr(TPP)	455	650 ± 30	(N ₃)Cr(TPP)	448	40 ± 2
(SCN)Cr(TPP)	453	340 ± 20	FCr(TPP)	437	5 ± 0.2

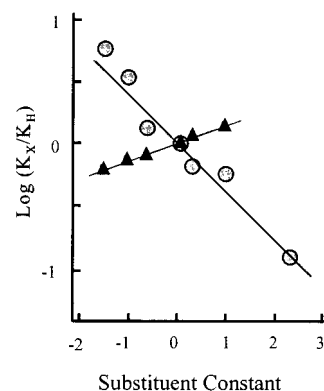
Table 3. Dependence of Rate Constants (M⁻¹ s⁻¹) on the Identity of the Nitrogen Atom Donor and Acceptor Phenyl Ring Substituents

nitrogen atom donor	nitrogen atom acceptor	solvent	
		C ₆ H ₆	CH ₂ ClCH ₂ Cl
NMn(OEP)	ClCr(T-4-PhCH ₂ O-PP)	33 ± 2	676 ± 20
	ClCr(T-4-MeO-PP)	36 ± 5	826 ± 58
	ClCr(T-4-Me-PP)	41 ± 3	947 ± 104
	ClCr(TPP)	48 ± 6	1170 ± 140
	ClCr(T-4-F-PP)	60 ± 3	1280 ± 160
	ClCr(T-4-Cl-PP)		1700 ± 200
	ClCr(T-4-F ₃ C-PP)	110 ± 3	
NMn(T-4-PhCH ₂ O-PP)	ClCr(OEP)		86 ± 10
NMn(T-4-MeO-PP)			50 ± 4
NMn(T-4-Me-PP)			20 ± 4
NMn(TPP)			15 ± 0.3
NMn(T-4-F-PP)			10 ± 0.3
NMn(T-4-Cl-PP)			9.0 ± 0.2
NMn(T-4-F ₃ C-PP)			1.8 ± 0.2

10⁻⁵ M were identical to those at 10⁻³ M. However, the observed rate constants were markedly dependent upon the concentration of chloride (in the form of *n*-Bu₄NCl) added to solution. The observed rate decreased with increasing concentration of *n*-Bu₄NCl. In fact, no appreciable reactivity was observed over a 24 h period when the [*n*-Bu₄NCl]/[ClCr(TPP)] ratio exceeded 5. Previous work has shown that ClCr(POR) has little affinity for an anionic ligand.^{17c,18}

Counterion Effects. The influence of the Cr^{III}(POR) counterion on the rate of nitrogen atom transfer was determined by reaction of NMn(OEP) with XCr(TPP) where X = F⁻, Cl⁻, TFA⁻, N₃⁻, SCN⁻, and ClO₄⁻. The rate constants obtained are listed in Table 2. The rate constants varied over 2 orders of magnitude, illustrating the dramatic influence of counterion identity on the reaction. Anions with coordinating abilities less than that of TFA⁻ (e.g., ClO₄⁻) reacted too quickly to obtain reliable rate data with our method. The rate constants were found to be exponentially related both to the wavelength of the Soret band maximum for XCr(TPP) and to Jorgensen's *f* parameter, an empirically based measure of ligand field strength for anions.¹⁹ Such relationships demonstrated that the rate constants were inversely related to the ligand field strength of the chromium(III) counterion.

Substituent Effects. The influence of the steric and inductive effects of porphyrin ring substituents on the rate of the nitrogen atom transfer reaction was determined for both the donor and the acceptor metalloporphyrins. The inductive effect of phenyl ring substituents on the chlorochromium(III) porphyrin acceptor was determined by monitoring the kinetics of the reaction of selected para-substituted chromium tetraphenylporphyrins with NMn(OEP). Table 3 contains a listing of the rate constants obtained in benzene and in DCE. Note that the span in *k*_{obsd} ranges from 33 to 110 M⁻¹ s⁻¹ in benzene and from 676 to 1700 M⁻¹ s⁻¹ in DCE. In both solvents, electron-withdrawing substituents facilitate the reaction. A Hammett-Taft linear free

**Figure 2.** Linear free energy relationships for the reaction of NMn(OEP) with a series of chlorochromium(III) para-substituted tetraphenylporphyrin nitrogen atom acceptors (triangles) and the reaction of nitridomanganese(V) para-substituted tetraphenylporphyrin nitrogen atom donors with ClCr(OEP) (circles) in DCE.

energy relationship was constructed (Figure 2), and a ρ value of 0.17 was obtained for the rate data acquired in each solvent using σ_p as a measure of the electron-donating or -withdrawing effect of the phenyl ring substituent. This ρ value attests to a significant inductive effect, especially when one considers the distance of the substituent on the para position of the phenyl ring to the nitrido reaction site.

The inductive effect of phenyl ring substituents on the NMn(POR) donor was determined by monitoring the kinetics of the reaction of selected para-substituted nitridomanganese tetraphenylporphyrins with ClCr(OEP). The rate constants for this series are also listed in Table 3. Note that the span in rate constants determined in DCE ranges from 1.8 to 86 M⁻¹ s⁻¹, significantly lower than when the donor and acceptor porphyrins were reversed (vide supra). This decrease in rate reflects the increased basicity of OEP relative to that of the substituted tetraphenylporphyrins and is consistent with the trend observed with the substituted tetraphenylporphyrin nitrogen atom acceptor study. A Hammett-Taft linear free energy relationship (Figure 2) gave a ρ value of -0.40. The sign of ρ indicates that the reaction rate increases with increasing nucleophilicity of the nitridomanganese reaction center. The magnitude indicates that the donor porphyrin is twice as sensitive to the effect of induction by phenyl ring substituents as the acceptor porphyrin.

Steric effects on the nitrogen atom transfer reaction were probed using ortho-substituted tetraphenylporphyrins. Tetraphenylporphyrins possessing one ortho substituent on each of the phenyl rings displayed reduced rates of reactivity when such substitution was on either the nitride donor or the acceptor complex. For example, the rate of the reaction of NMn(OEP) with ClCr(T-2-MeO-PP) was about 30% of the observed rate of the reaction between NMn(OEP) and ClCr(T-4-MeO-PP). Similarly, a comparable diminution in rate was observed for the reaction between NMn(T-2-MeO-PP) and ClCr(OEP) compared with the reaction between NMn(T-4-MeO-PP) and ClCr(OEP). Ortho-substituted metallotetraphenylporphyrins possess six interconvertible atropisomers. The diminished rates observed for the ortho-substituted metallotetraphenylporphyrins imply markedly different rates for each atropisomer. Tetraphenylporphyrins possessing two ortho substituents on each of the phenyl rings of either the nitride donor or the acceptor were unreactive. Specifically, no reaction was observed between NMn(OEP) and the two potential nitrogen atom acceptors ClCr-[T-2,6-(MeO)₂-PP] and ClCr-[T-2,4,6-(MeO)₃-PP] or between NCr(OEP) and ClMn-[T-2,6-(MeO)₂-PP] or ClMn-[T-2,4,6-(MeO)₃-PP]. From this finding, we infer that the all-syn atropisomer is unreactive. A comparable decrease in rate was

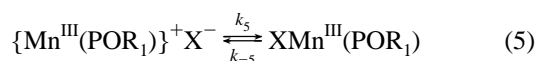
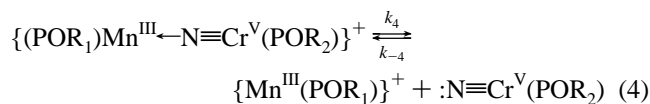
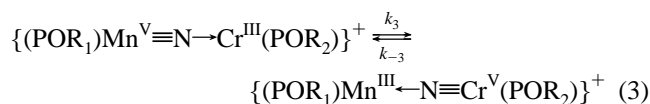
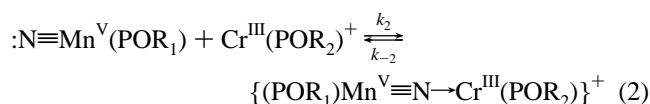
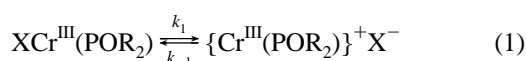
(18) (a) Summerville, D. A.; Jones, R. D.; Hoffman, B. M.; Basolo, F. J. *Am. Chem. Soc.* **1977**, *99*, 8195. (b) Basolo, F.; Jones, R. D.; Summerville, D. A. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 771.

(19) Jorgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon Press: Elmsford, N.Y., 1962.

previously observed in the conversion of nitridomanganese porphyrins into (acylimido)manganese porphyrin complexes.^{20,21} Reaction of NMn(C₂Cap) with ClCr(OEP) proceeded at a rate comparable to that of NMn(TPP) whereas reaction of NMn(OEP) and ClCr(C₂Cap) proceeded at a rate approximately 25 times slower than that of NMn(TPP).

Discussion

In our preliminary communication,⁶ we suggested that the initial step in the nitrogen atom transfer sequence involved back-side nucleophilic attack on the five-coordinate chromium(III) center. This suggestion is at odds with the observed dependence of reaction rate on $[n\text{-Bu}_4\text{NCl}]/[\text{ClCr(TPP)}]$ and reaction of NMn(OEP) with ClCr(C₂Cap); *vide infra*. We now propose the following mechanism for the inter-metal nitrogen atom transfer reaction between NMn(POR) and XCr(POR):



The initial step is the ionization of the chromium(III) complex via loss of the anion. Kelly and Kadish²² have published conductivity data which infer that the extent of ionization of chromium(III) porphyrins differs markedly with anion ligand field strength. Their evidence indicates that ~40% of (ClO₄)Cr(TPP) is ion-paired in CH₂Cl₂ or DCE compared to only 2% for ClCr(TPP). This fact and the marked dependence of the rate of reaction between NMn(OEP) and ClCr(TPP) in the presence of added chloride suggest that the dissociated, four-coordinate $\{\text{Cr}(\text{POR})\}^+$ is the nitrogen atom acceptor. The dependence of the reaction rate on both solvent dielectric constant (Table 1) and anion ligand field strength (Table 2) provides additional support of this hypothesis. Ionization of the coordinately and covalently bound anion should be favored in solvents of higher dielectric strength, since this property measures the inherent ability of the solvent to separate charges. Similarly, weakly coordinating anions should make better leaving groups and promote the formation of the cationic

nitrogen atom acceptor. Alternatively, the reaction may be inhibited by the formation of the six-coordinate, anionic chromium(III) complex $\{(\text{Cl})_2\text{Cr}(\text{POR})\}^+$. However, there is no literature precedent for such a complex and our efforts to provide spectroscopic or electrochemical evidence for its existence (at $1 \leq [\text{Cl}^-]/[\text{ClCr(TPP)}] \leq 100$) have been in vain.

We propose that the second step involves nucleophilic attack by the nitrido lone pair on the cationic chromium(III) porphyrin, forming a positively charged heterobinuclear μ -nitrido intermediate. We have yet to obtain spectroscopic or electrochemical evidence of its existence and thus conclude that this intermediate is present in very low concentration. Support for this proposed step arises from the results of several experiments. First, when the reaction of NMn(OEP) with ClCr(TPP) was carried out in benzene/pyridine solution, the rate constants were inversely proportional to $[\text{pyridine}]$. It has been previously shown that pyridine readily binds to the chromium(III) center but does not bind to the vacant axial position of NMn(POR).¹⁸ Thus, as the pyridine concentration is increased, the equilibrium between the five-coordinate ClCr(POR) and four-coordinate $\{\text{Cr}(\text{POR})\}^+$ complexes is shifted to either of the six-coordinate Cl(py)Cr(POR) or $\{(\text{py})_2\text{Cr}(\text{POR})\}^+ \text{Cl}^-$ complexes. The formation of either six-coordinate complex renders the chromium center inaccessible to the nitrido lone pair. Second, the nonreactivity of the porphyrins possessing substituents at the 2,6-positions of the phenyl rings infers the formation of a binuclear intermediate, since such substitution has been shown to inhibit formation of μ -oxo-bridged²³ and μ -nitrido-bridged²⁴ iron porphyrin dimers. Third, the linear free energy trends demonstrate that the reaction rate is significantly enhanced by increasing the nucleophilic character of the donor and the electrophilic character of the acceptor, which is consistent with the notion of nucleophilic attack. Fourth, we have recently communicated the synthesis and spectral characterization of an analogous cationic heterobimetallic μ -nitrido complex, $\{(\text{POR})\text{Re}=\text{N} \rightarrow \text{Cr}(\text{POR})\}^+$, formed by reaction of NRe(POR) with ClCr(POR).²⁵

The cationic heterobinuclear μ -nitrido dimer then undergoes an intramolecular, bridging nitrogen atom mediated, two-electron transfer as shown in eq 3. The product of this electron transfer reaction dissociates to form NCr(POR) and $\{\text{Mn}(\text{POR})\}^+$. Kelly and Kadish^{17e} have concluded from conductivity measurements that the extent of ionization of XMn(POR) is significantly less than that of XCr(POR). We suggest that the affinity of the manganese(III) center for anionic axial ligands provides a plausible driving force for the dissociation of the heterobinuclear μ -nitrido complex.

Woo and co-workers have proposed a similar mechanism involving the reversible nitrogen atom transfer between manganese(V) and manganese(III) porphyrins.²⁶ Since chromium(V) and chromium(III) porphyrins also undergo reversible nitrogen atom transfer, a common mechanism seems likely.⁹ All steps in our proposed mechanism have been written as equilibria even though we have not observed the reverse process with the nitrogen atom donor-acceptor pairs reported herein. We have concluded that eq 2 is rate determining on the basis of the lack of observed reversibility, our inability to detect binuclear intermediates, and the known facility of inner-sphere electron transfer reactions.²⁷ Application of the steady-state

(20) Bottomley, L. A.; Luck, J. F.; Neely, F. L.; Quick, J. S. In *Redox Chemistry and Interfacial Behavior of Biological Molecules*; Dryhurst, G., Niki, K., Eds.; Plenum: New York, 1988; pp 77–86.

(21) Bottomley, L. A.; Neely, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 6748–6752.

(22) Kelly, S. L.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 679.

(23) Morgan, B.; Dolphin, D. In *Structure and Bonding*; Buchler, J. W., Ed.; Springer-Verlag: Berlin, 1987, Vol. 64, pp 115–204.

(24) Wagner, W. D.; Nakamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 4044–4045.

(25) Tong, C.; Bottomley, L. A. *Inorg. Chem.* **1996**, *35*, 5108–5109.

(26) Woo, L. K.; Goll, J. G.; Czapl, D. J.; Hays, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 8478.

(27) Haim, A. *Prog. Inorg. Chem.* **1983**, *30*, 273.

approximation yields the following kinetic expression:

$$k_f = \frac{k_1 k_2}{k_{-1}[X^-] + k_2[\text{NCr(POR)}]} \approx \frac{k_1 k_2}{k_{-1}[X^-]} \quad (6)$$

We submit that the absence of the back-reaction between NCr(POR) and XMn(POR) may reflect the differential stability of NCr(POR) compared to NMn(POR), *i.e.* $K_{\text{eq}}(\text{reacn 4}) > K_{\text{eq}}(\text{reacn 2})$, as well as the extent of ionization of XCr(POR) compared to XMn(POR), *i.e.* $K_{\text{eq}}(\text{reacn 5}) > 1/K_{\text{eq}}(\text{reacn 1})$. The dramatic dependence of reaction rate on counterion ligand

field strength and solvent dielectric constant supports this claim. Present efforts are directed toward generalizing the scope of this reaction with other metallomacrocyclic nitrogen atom donor-acceptor pairs.

Acknowledgment. We thank Profs. L. Keith Woo, John Groves, and Laren Tolbert for helpful suggestions. Support of this research by a grant from the DHHS National Institute of Heart and Lung (No. HL-33734) is gratefully acknowledged.
IC960919C