Heterobimetallic *μ*-Nitrido Complexes Formed by Incomplete Nitrogen Atom Transfer Reactions between Nitridorhenium(V) and Chlorochromium(III) Porphyrins

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Atom transfer reactions involve transfer of an atom and one or more electrons from a donor molecule to an acceptor molecule. Such transfers can be complete or incomplete processes.[1,2] Metalloporphyrins participate in atom transfer reactions as both donors and acceptors. Complete intermetal oxygen atom transfer is uncommon; incomplete transfers produce dinuclear, *μ*-oxo complexes.[3] Nitrogen atom transfers between metalloporphyrin complexes are typically complete intermetal transfer processes. For example, complete nitrogen atom transfer reactions between the NMn^{V}(POR) donor and the Cr^{II}(POR), XCr^{III}(POR) Mn^{II}(POR), or XMn^{III}(POR) acceptors as well as between the NCr^{V}(POR) donor and the XCr^{III}(POR) acceptor have been reported.[4−8] Neely,[6] Bottomley,[7] and Woo[8] have independently proposed that these reactions proceed by a common mechanism. Nucleophilic attack of the NM(POR) donor on either the cationic metal(III) or a neutral metal(II) porphyrin acceptor is followed by a net three or two electron redox process mediated by the bridging nitrogen atom. Various efforts to provide spectroscopic or electrochemical evidence for the putative dinuclear intermediate have been unsuccessful. The only precedents in the porphyrin literature are the (*μ*-nitrido)-iron porphyrin complex[9] and (*μ*-nitrido)vanadium dibenzotetramethyltetraaza[14]annulene complex.[10] In this report, we present the synthesis and spectroscopic characterization of the first heterobimetallic nitrogen-bridged metalloporphyrin complexes.

Recently, Buchler reported the synthesis and structural characterization of NRe(POR).[11] We have evaluated the nitrogen transfer reactivity of these compounds with ClCr^{III}(TPP) under the identical conditions previously used for NMn(POR). Figure 1 shows the spectral changes observed[12] during the course of the reaction of an equimolar mixture of NRe(OEP) with ClCr(TPP) in DCE. The intensity of the Soret bands at 410 nm for NRe(OEP) and at 449 nm for ClCr(TPP) diminished as the intensity of a new Soret band at 400 nm increased. Isosbestic points were observed at 401, 419, and 429 nm and indicate the absence of any long-lived intermediates. Noticeably absent is a Soret band at 424 nm which is characteristic of NCr(TPP),[13] the expected product of complete nitrogen atom transfer. The ratio of reactants was systematically varied. Spectra acquired following reaction completion were dependent upon the ratio of reactants indicating an equilibrium reaction. For example, a Soret peak at 410 nm was present in the final spectrum only in reactions where NRe(OEP) was in excess. Also, the intensity of the Soret peak at 449 nm decreased with increasing NRe(OEP):ClCr(TPP) ratios but remained constant at ratios greater than 2. Analysis of the spectral data revealed that the reaction stoichiometry was one-to-one and that the product spectrum is comprised of a Soret band at 400 nm (log $\epsilon = 5.17 \pm 0.02$), a shoulder at 449 nm (log $\epsilon = 4.94 \pm 0.04$), and a single visible band at 581 nm (log $\epsilon = 2.60 \pm 0.08$). The equilibrium constant was calculated to be $3.8\ (\pm 0.2) \times 10^5\ \mathrm{M}^{-1}$ at 23 ± 1 °C. Similar results were observed for the reactions between NRe(OEP) and ClCr(TTP) or ClCr(OEP).

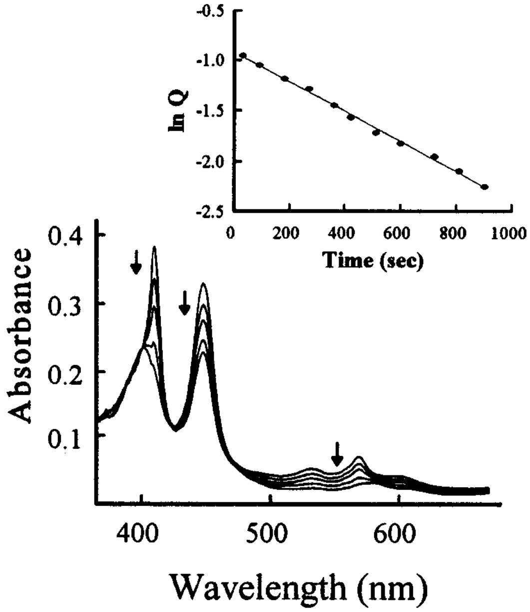

Figure 1. Electronic spectra acquired as a function of time for the reaction between NRe(OEP) and ClCr(TPP). The initial concentrations of both reactants were 44 *μ*M. The inset depicts the kinetic analysis plot demonstrating that the reaction is second order overall.[25]

The reaction of NRe(OEP) with ClCr(TPP) was also monitored with ^{1}H NMR spectroscopy. The spectrum of NRe(OEP) in CDCl$_3$ was comprised of the following resonances: $\delta = 10.5$ ppm (s, 4H), 4.2 ppm (q, $J = 7.6$ Hz, 16H) and 2.0 ppm (t, $J = 7.6$ Hz, 24H). The spectrum obtained for the paramagnetic reactant ClCr(TPP) was comprised of a broadened singlet at 9.7 ppm (8 pyrrole protons) and a broadened multiplet between

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(4) Abbreviations: POR = porphrinato dianion; TTP = 5,10,15,20-tetra-*p*-tolyporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; OEP = 2,3,7,8,13,17,18-octaethylporphyrinato dianion; DCE = dichloroethane; FAB = fast atom bombardment.

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7.5−8.2 ppm (20 phenyl protons). The spectrum of the product was comprised of the following resonances: 7.5−8.2 ppm (broad m, 20H), 6.5 ppm (broad s, 4H), 4.4 ppm (broad s, 16H), and 1.9 ppm (broad s, 24H). There was also a resonance at 9.7 ppm too broad to obtain accurate integration. Comparison of the product and reactants spectra revealed that shifts in the ethyl group proton resonances are small whereas the shift in the meso-protons on OEP ring were substantial (4 ppm). Spectra acquired following reaction of NRe(OEP) with ClCr(OEP) and with ClCr(TTP) possessed comparable spectral features.

The vibrational spectra of NRe(OEP) and ClCr(TPP) and their reaction products were obtained in the range of 600−4000 cm^{-1} by diffuse reflectance IR spectroscopy. The IR spectrum of NRe(OEP) is characterized by a strong absorption at 1090 cm^{-1} which has been assigned to the $\mathrm{Re{\equiv}N}$ stretching vibration.[11] The spectrum of the product contained fingerprint vibrations for both OEP and TPP and the intensity of the strong $\mathrm{Re{\equiv}N}$ stretching vibration is significantly diminished. In addition, a new moderate intensity peak emerged at 1123 cm^{-1}. The product of the reaction between NRe(TPP) and ClCr(TPP) produced a new, moderately intense peak at 1103 cm^{-1}.

Product identity was proven by FAB mass spectrometry. The FAB spectrum of the product of the equimolar reaction of NRe(OEP) with ClCr(TPP) exhibited a cluster of peaks centered at a *m*/*z* ratio of 1397.2. This *m*/*z* ratio is in agreement with that expected for the heterobimetallic *μ*-nitrido-bridged porphyrin product, {(OEP)ReNCr(TPP)}$^+$. A fragment ion at *m*/*z* 733.3 (corresponding to {NRe(OEP)}$^+$) was always observed whereas the fragment ion for {NCr(TPP)}$^+$ was absent. The intensity of the fragment ion at *m*/*z* of 664 (corresponding to {Cr(TPP)}$^+$) was consistently ≤30% of the intensity of the {NRe(OEP)}$^+$ unless an excess of ClCr(TPP) was used in the reaction. These findings infer dissimilar bond order between Re−N and Cr−N in the dinuclear complex. Similarly, the FAB spectrum taken on the products of the reaction of NRe(OEP) with ClCr(TTP) and ClCr(OEP) gave clusters centered at 1453.4 and 1317.6, the value expected for {(OEP)ReNCr(TTP)}$^+$ and {(OEP)ReNCr(OEP)}$^+$, respectively. Although other heterobimetallic *μ*-nitrido complexes have been reported,[16,17,21−23] this is the first account of porphyrin containing complexes.

We have tentatively assigned the new absorption bands at 1123 cm^{-1} for [(OEP)ReNCr(TPP)]$^+$ and the band at 1103 cm^{-1} for [(TPP)ReNCr(TPP)]$^+$ as the $\mathrm{Re{\equiv}N{\rightarrow}Cr}$ asymmetric stretching vibration. We note that the asymmetric stretching vibration in (TPP)FeNFe(TPP) is at 910 cm^{-1}.[18,19] However, asymmetric vibration frequencies for the heterobimetallic *μ*-nitrido bridge $\mathrm{Re{\equiv}N{\rightarrow}Cr}$ are generally higher than that of the homobinuclear *μ*-nitrido-bridged complexes.[9,10,18−20] Our assignment is consistent with those of Hewkin[16] and Chatt[17] for *μ*-nitrido complexes with ligands other than porphyrins. Differing frequencies for the asymmetrical stretching vibration reflect significant differences in bonding linkages between the heterobimetallic $\mathrm{Re{\equiv}N{\rightarrow}Cr}$ and the homobimetallic $\mathrm{Fe{=}N{=}Fe}$ complexes. The former involves dative coordination of a terminal nitride ligand to a coordinatively unsaturated chromium center, while the latter contains covalent bonding between the N and Fe atoms. This hypothesis is supported by the observation that addition of small quantities of methanol or pyridine to DCE solutions of the heterobimetallic $\mathrm{Re{\equiv}N{\rightarrow}Cr}$ complex instantaneously produced the NRe(OEP) reactant and the methanol or pyridine adducts of ClCr(TPP).

Kinetic analysis of the reaction between NRe(OEP) and ClCr(TPP) was performed by analyzing absorbance changes of the Soret bands as a function of time and concentration using the method developed by King[24] (see inset of Figure 1). The analysis[25] revealed that the reaction was first order in each reactant and second order overall. A second-order forward reaction rate constant, k_1, was determined to be 43 ± 6 M^{-1} s^{-1} at 23 ± 1 °C. The observed rate of the reaction was inversely proportional to the concentration of added Cl$^-$.

We propose that the formation of the heterobimetallic *μ*-nitrido complex proceeds via the following sequence:

$$\mathrm{XCr(POR)} \rightleftharpoons \mathrm{[Cr(POR)]^+ + X^-} \qquad (1)$$

$$\mathrm{NRe(POR) + [Cr(POR)]^+ \rightleftharpoons [(POR)Re{\equiv}N{\rightarrow}Cr(POR)]^+} \qquad (2)$$

This mechanism assumes a common reaction pathway for NRe(POR), NCr(POR), and NMn(POR). We note that the expected product for complete nitrogen atom transfer, *i.e.* ClRe$^{\mathrm{III}}$(POR), is presently unknown. Thus, formation of the *μ*-nitrido complex reflects either the presence of a barrier to intramolecular electron transfer or the thermodynamic stability of the dinuclear species relative to the monomeric Re(III) species. Current efforts are directed toward obtaining diffraction quality crystals of this novel heterobimetallic complex as well as evaluating the nitrogen atom transfer reactivity of NMo(POR) and NW(POR).

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[14] Vibrational spectra were obtained on the products of a 1:2 and 1:3 NRe(OEP):ClCr(TPP) reaction in DCE following evaporation of the solvent.

[15] Identical FAB mass spectra were obtained on reaction products before or after evaporation of the DCE solvent (thioglycerol matrix).

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[25] For the reaction NRe(OEP) + ClCR(TPP) ⇌ [(OEP)ReNCr(TPP)]-Cl, the d[ClCr(TPP)]/dt is equal to k_1[ClCr(TPP)[NRe(OEP)] − k_2[(OEP)ReNCr(TPP)Cl]. Thus, from King's method, the integrated rate law for a second order equilibrium reaction is

$$\ln\left(\frac{[\mathrm{ClCr(TPP)}]_t - [\mathrm{ClCr(TPP)}]_\mathrm{e}}{[\mathrm{ClCr(TPP)}]_t + [\mathrm{NRe(OEP)}]_\mathrm{e} + (1/K_\mathrm{f})}\right) = \ln Q$$

$$\ln Q = -k_1([\mathrm{ClCr(TPP)}_\mathrm{e} + [\mathrm{NRe(OEP)}]_\mathrm{e} + (1/K_\mathrm{f}))t + \text{constant}$$

where $[\mathrm{ClCr(TPP)}]_t$ and $[\mathrm{NRe(OEP)}]_t$ are concentrations of species ClCr(TPP) and NRe(OEP) at time t; $[\mathrm{ClCr(TPP)}]_\mathrm{e}$ and $[\mathrm{NRe(OEP)}]_\mathrm{e}$ are concentrations of the ClCr(TPP) and NRe(OEP) when the reaction equilibrium was established.