

1.3 V, the signal disappears, suggesting that a porphyrin dication is generated. However, after $[(\text{OEP})\text{Nb}]_2\text{O}_3$ is electrolyzed at 1.3 V for 45 min, a new free-radical signal is observed at $g = 2.004$ with a width of 9 G. This is the signal of a monomeric Nb(V) porphyrin cation radical and demonstrates that decomposition of the dimer occurs even after the second oxidation by bulk electrolysis. This decomposition is not observed on the cyclic voltammetric time scale.

In conclusion, we have shown that the porphyrin niobium dimer $[(\text{P})\text{Nb}]_2\text{O}_3$ can be reduced and oxidized in three one-electron-transfer steps. On the cyclic voltammetric time scale, the first reduction and the first two oxidations appear to be reversible. However, on longer time scales these electrode reductions are followed by chemical reactions whose ultimate product is a mo-

nomeric niobium porphyrin. Following reduction on long time scales, $(\text{P})\text{Nb}(\text{O})$ or one of its reduced forms is the primary species in solution. The exact nature of the monomeric species following oxidation is not known at this time, but these products are presently being investigated. In later studies¹⁶ we will present the detailed electrochemistry of several monomeric niobium(V) porphyrin species that are synthesized by literature techniques. The results from these studies will further develop the electrochemistry of the Nb porphyrin systems.

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Polarized X-ray Absorption Near-Edge Structure of Highly Oxidized Chromium Porphyrins

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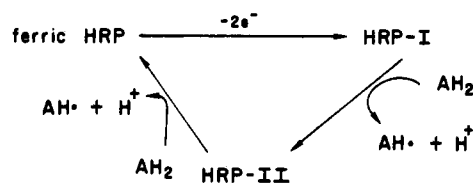
Polarized X-ray absorption near-edge spectra have been measured for $\text{Cr}^{\text{IV}}(\text{TTP})\text{O}$ and $\text{Cr}^{\text{V}}(\text{TTP})\text{N}$ (TTP is the dianion of 5,10,15,20-tetra-*p*-tolylporphyrin). These spectra, which are very similar for the two molecules, show an intense preedge absorption feature polarized perpendicular to the porphyrin plane. The absorption edges are relatively featureless when the polarization is parallel to the porphyrin plane. On the basis of multiple-scattered-wave $X\alpha$ calculations, the intense preedge feature is interpreted as a bound \rightarrow bound transition with significant metal character in the excited state. This transition, which has been observed in many metal-oxo species, was not observed in the putative ferryl ($\text{Fe}=\text{O}$) intermediates of horseradish peroxidase. The reasons for this absence in $\text{Fe}=\text{O}$ species and its relationship to the reactivity of metal-oxo porphyrin complexes are discussed in light of the present results.

Introduction

When a core electron is excited with a sufficiently energetic photon, transitions to higher lying bound states and into the continuum are possible. For first-row transition metals, X-ray photons of energies from 4 to 9.6 keV have the appropriate energy to excite a 1s electron. The resulting X-ray absorption spectra are characterized by an abrupt increase in absorbance (the K absorption edge) at the excitation threshold. The absorption is frequently highly structured, both in the edge region and for 500–1000 eV above the edge. For the extended X-ray absorption fine structure (EXAFS) region (beginning about 50 eV above the edge), single scattering treatments give an adequate description of most of the structure.¹ In contrast, theoretical interpretation of edge spectra has proven difficult since in this region the long wavelength of the excited photoelectron permits extensive multiple-scattering interactions. Despite the theoretical difficulties, there is great interest in X-ray edge spectra since they can be quite sensitive to the detailed electronic structure and molecular geometry around the absorbing atom.

Recently, studies of polarization effects in single crystals have been used to simplify the interpretation of X-ray absorption edges.² Such measurements are possible as a result of the highly polarized

Scheme I



nature (typically 95–99%) of synchrotron radiation.³ For K absorption edges, the initial state is the totally symmetric 1s orbital; hence, the polarization properties of the edge structure are a direct reflection of the symmetry properties of the final state. This symmetry information provides additional information against which calculated edge spectra can be compared. In recent work, the combination of polarized measurements and multiple-scattered-wave $X\alpha$ calculations has proven to be a useful tool for interpreting the X-ray absorption edge structure of Mo^4 and Cu^5 complexes. We report here the results of applying these experimental and theoretical approaches to the X-ray absorption edge spectra of two highly oxidized metalloporphyrin complexes.

Metalloporphyrins are found at the active site of many metalloproteins. For the heme monooxygenase and peroxidase enzymes, a highly oxidized iron porphyrin is thought to be present at the active site. A particularly well-studied enzyme of this type is the peroxidase isolated from horseradish roots. The catalytic

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cycle (Scheme I) of horseradish peroxidase (HRP) involves initial oxidation to the formally Fe(V) compound I (HRP-I). On reaction with substrate, HRP-I is reduced to the formally Fe(IV) compound II (HRP-II), which in turn reacts with substrate to regenerate resting HRP. Both HRP-I and HRP-II are thought to contain an Fe(IV) ferryl porphyrin, (por)Fe=O, with the extra oxidation equivalent in HRP-I residing in a porphyrin π -cation.

Ferryl porphyrins have limited stability. However, analogous metal-oxo complexes of the earlier transition metals (Ti, V, Cr) are quite stable and have been studied extensively. A characteristic feature of the X-ray absorption edge spectra of metal-oxo complexes is the presence of a very intense preedge transition.⁶ Recently, X-ray absorption spectra have been measured for HRP-I, HRP-II, and closely related model compounds.^{7,8} The EXAFS data for these species showed the expected short (~ 1.6 Å) Fe=O bond. Surprisingly, the absorption edges lacked the characteristic intense metal-oxo preedge transition.

In order to elucidate the general features of (por)M=O absorption edge structure, we have measured polarized X-ray absorption edge spectra for (TTP)Cr^{IV}=O (1) (TTP = dianion of 5,10,15,20-tetra-*p*-tolylporphyrin). In contrast with the ferryl species, chromyl porphyrins are sufficiently stable to be crystallized. For comparison, we have also examined the polarized absorption edge spectra of (TTP)Cr^V≡N (2). The polarized X-ray absorption edge structures for these and related hypothetical complexes, and for a ferryl porphyrin, were calculated by using a multiple-scattered-wave X α approach.

Experimental Section

X-ray Absorption Measurements. X-ray absorption data were measured as fluorescence excitation spectra by using an array of 17 NaI(Tl) detectors. Data were collected at the Stanford Synchrotron Radiation Laboratory under dedicated conditions (3.0 GeV, ~ 50 mA) on the focused beam line II-2. A v-slit was used to decrease the horizontal acceptance of the mirror to 1 mrad in order to improve the energy resolution. Energy monochromatization was achieved by using a Si(220) double crystal monochromator. The absorption spectrum of a Cr foil was measured simultaneously with acquisition of the Cr(por) data, and relative energies were calibrated with respect to the first inflection point of the Cr metal absorption edge, defined to be 5988.8 eV. The fluorescence data for each detector channel were examined visually for the presence of Bragg diffraction peaks. After the Bragg peaks were removed by using a linear interpolation, a weighted average⁹ of the different channels was calculated for each scan. The data shown represent the average of three to four scans of ca. 15 min. each. The total irradiation time, including EXAFS measurements (to be reported elsewhere), was ca. 12 h for each crystal. Comparison of diffraction intensities before and after the absorption measurements showed no evidence of radiation-induced crystal decomposition.

Crystal Orientation and Alignment. Crystals of the chromium porphyrins were prepared as previously described.^{10,11} Crystals of 1 and 2 are isomorphous, with space group $P2_1/c$ and 4 molecules per unit cell. The structure is such that the two distinct Cr=O (or Cr≡N) directions differ by 3°. Individual crystals were mounted in a sealed capillary to prevent evaporation of mother liquor. The crystals selected for study had dimensions $0.9 \times 0.3 \times 0.2$ mm for 1 and $1.2 \times 0.4 \times 0.4$ mm for 2. Crystal orientations were determined using a Nicolet P₂ automated diffractometer, and the crystals were oriented and aligned in the X-ray beam as previously described.⁵ The three orientations that were examined for each crystal are defined in Figure 1.

Theoretical Calculations. Theoretical calculations were performed in a multiple-scattered-wave X α (MSW X α) formalism,¹² using the "extended-continuum" method.^{5,13} In this approach, final states with

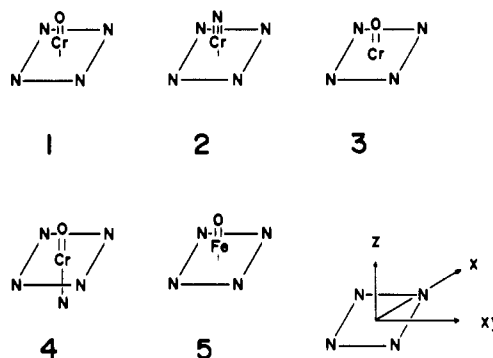


Figure 1. Molecules studied. The porphyrin moiety is abbreviated as a parallelogram containing four nitrogens. The axial imidazole is shown as a single N. Molecules 1 and 2 exist and were studied experimentally; all 5 species were studied theoretically. The three experimental orientations of the polarization vector relative to the porphyrin are shown by the arrows labeled *x*, *xy*, and *z*.

energies greater than V_{II} (the interstitial potential) are treated with continuum-like boundary conditions. An outer sphere is not used, and the interstitial region is extended to infinity. This method is useful not only for energies greater than zero (true continuum region) but also for $V_{II} < E < 0$. This latter region corresponds to bound final states in self-consistent calculations. Extended-continuum and self-consistent calculations have been shown to give similar results and have the advantage of using the same molecular potential for both continuum and bound-state regions. In all calculations, the angular basis function were truncated at $l = 5$ for all atomic centers and extended to $l = 10$ for the outer region. Lifetime and instrumental broadening effects were accounted for by convolving the calculated spectra with a Lorentzian function of 2 eV width.

Spectra were calculated by using several different muffin tin radii. Variations in muffin tin radii gave significant changes in the relative amplitudes of different transitions, but no change in the calculated energies. Thus, while relative energies are meaningful, the agreement between calculated and experimental amplitudes may be regarded as somewhat fortuitous. In the past, a 15% overlap of muffin tin radii has been found to give good agreement between theoretical and calculated spectra.^{4,12} This overlap was used for all of the spectra shown here. Using the same overlap for all calculations, it is possible to make at least qualitative comparisons between calculated amplitudes.

Polarized edge spectra were calculated for the known, five-coordinate, complexes 1 and 2 and for several related hypothetical complexes (see Figure 1). The latter included a five-coordinate complex with the Cr in the plane (3), a six-coordinate analogue of chromyl tetra-*p*-tolylporphyrin (4), and a five-coordinate ferryl analogue (5). In all cases, the complexes studied were idealized to C_{4v} symmetry. The porphyrin ring was approximated by four equatorial nitrogens and the axial imidazole in 4 by a single nitrogen, thus giving six- or seven-atom clusters. Bond lengths and angles were taken from the known structures of 1 and 2 with the exception of the axial Cr-N bond in 4, which was taken as 2.0 Å. Spectra were calculated for $\hat{e} \parallel z$ and $\hat{e} \parallel x$ (see Figure 1). The idealized C_{4v} symmetry requires that the calculated *x* and *xy* orientations be identical.

The hypothetical ferryl model (5) is not identical in structure with postulated ferryl porphyrins in HRP, since the latter are thought to have axial imidazole ligation. Structure 5 is similar, however, to that of $[(CH_3OH)Fe(TTP)O]^+$, a compound that was found experimentally to have an X-ray absorption edge structure very similar to that of HRP-I and HRP-II.⁷ The advantage of 5 is that the *only* difference between its structure and the structure of 1 is the identity of the metal atom. Since 1 offers the only experimentally accessible polarized (por)M=O edge structure, the use of 5 rather than a biologically more realistic six-coordinate ferryl porphyrin permits direct determination of the effect of the change in metal. In any event, experimental spectra⁷ suggest that axial ligation has little effect on the edge spectra of ferryl porphyrins.

Results

The polarized X-ray absorption edge spectra of 1 and 2 in the *x* and *z* orientations are shown in Figure 2. The most striking feature of these spectra is the intense preedge absorption feature at ~ 5990 eV. This feature is nearly completely *z* polarized. The

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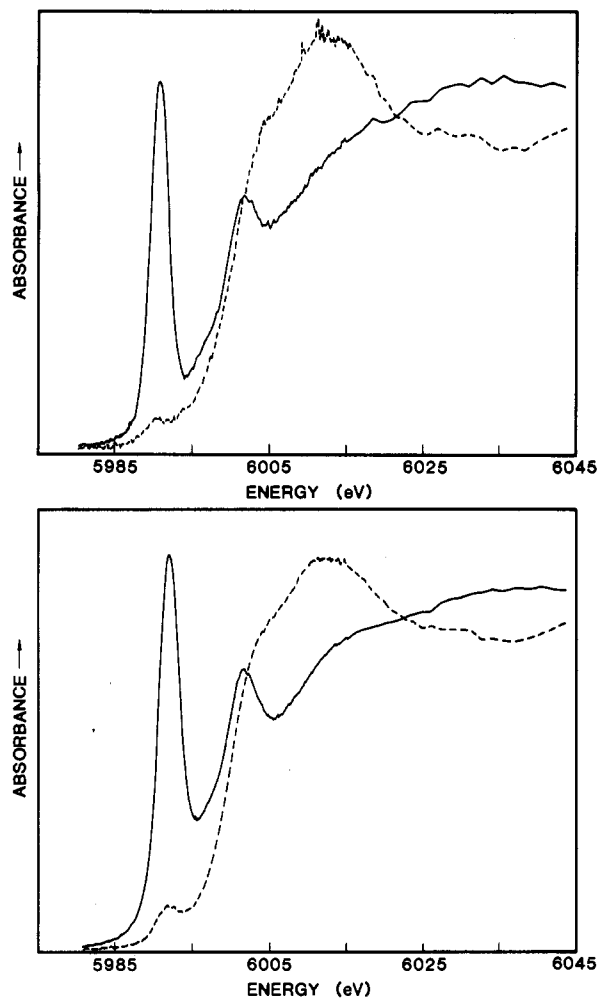


Figure 2. Polarized X-ray absorption edge spectra for chromium porphyrins: upper, $\text{Cr}^{\text{IV}}=\text{O}(\text{TTP})$; lower, $\text{Cr}^{\text{V}}\equiv\text{N}(\text{TTP})$. Solid curve is $\hat{\epsilon}\parallel z$; dashed curve is $\hat{\epsilon}\parallel x$ (see Figure 1 for definitions). Note the ~ 1 eV shift in the energy of the white line between $\text{Cr}(\text{IV})$ and $\text{Cr}(\text{V})$. All spectra have been normalized to give an edge jump of 1.0.

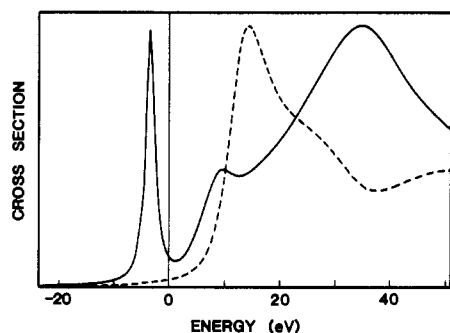


Figure 3. Calculated X-ray absorption edge spectra for chromium porphyrins. Calculated spectra for 1, corresponding to experimental spectra shown in the upper portion of Figure 2. The continuum threshold is shown by the vertical line.

small intensity of this transition observed for the x orientation can be accounted for by the imperfect alignment of symmetry related molecules in the unit cell and by the incomplete polarization of the X-ray beam. The energy of this transition varies by 1 eV between 1 (5991 eV) and 2 (5992 eV).

The spectrum from the xy orientation (not shown) is nearly identical with that of the x orientation, except in the vicinity of 6005 eV. At this energy, the xy spectra have 3–5% greater amplitude than is observed for the x orientation. The difference between x and xy arises from the less than 4-fold symmetry of the porphyrin. For both 1 and 2, the porphyrin is strongly buckled (saddle-shaped).^{10,11}

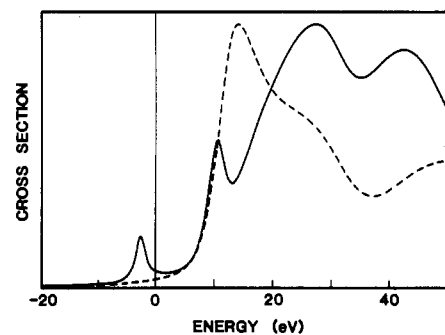


Figure 4. Calculated X-ray absorption edge spectra for a hypothetical six-coordinate chromium porphyrin (4). Solid curve is $\hat{\epsilon}\parallel z$; dashed curve is $\hat{\epsilon}\parallel x$ (see Figure 1 for definitions). Note the appearance of a new transition in the z direction.

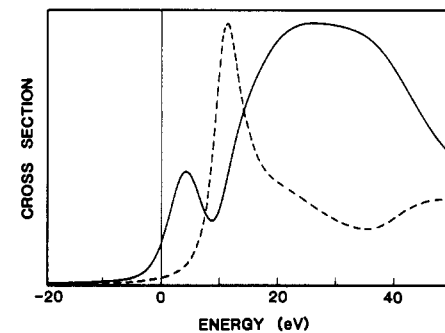


Figure 5. Calculated X-ray absorption edge spectra for a five-coordinate ferryl porphyrin (5). Scale and plotting format are same as in Figures 2–4. Note the absence of preedge spike in the z orientation. Calculations do not include quadrupole transitions or vibronic coupling; hence, the weak $1s \rightarrow 3d$ transition, observed for most Fe complexes, is absent.

The calculated edge spectra for 1 are plotted in Figure 3, with plot limits that correspond approximately to those of Figure 2. In qualitative terms, the calculated spectra are strikingly similar to the experimental spectra, although (vide supra) this agreement is sensitive to the size of the muffin tin radii. The final state for this transition is composed of approximately 57% Cr- d and 13% O- p orbitals. The calculated spectra for 2 (not shown) are extremely similar to those for 1, with the preedge spike occurring approximately 1 eV closer to the continuum threshold.

In order to test the sensitivity of the calculations to the details of the geometry, we calculated spectra for the hypothetical molecules 3 and 4. In the context of our simplified model, the displacement of the Cr from the plane has no effect on the calculated spectra. Inclusion of an axial nitrogen has no effect on the $\hat{\epsilon}\parallel x$ spectrum (Figure 4). However, the axial nitrogen does affect the $\hat{\epsilon}\parallel z$ spectra, which shows a decreased amplitude for the preedge transition and the appearance of a new, broad resonance ~ 30 eV above the preedge spike. This new feature occurs at the same energy as a shoulder on the high-energy side of the principal maximum in the x -polarized spectrum.

The calculated spectra for the hypothetical five-coordinate ferryl complex 5 are shown in Figure 5. The most striking feature of these spectra is the absence of the intense preedge transition in the z -polarized spectrum. Except for this change, the calculated spectrum for 5 is very similar to that for the isostructural complex 1.

Discussion

Intense preedge transitions are common in first-row transition-metal $\text{M}=\text{O}$ complexes. In the case of CrO_4^{2-} , MSW $X\alpha$ calculations indicate that this feature is due to a transition to a bound state of primarily metal 3d character.^{12,14} In addition,

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polarized measurements of the $V=O^{15}$ and the $O=U=O^{16}$ units indicate that the metal-oxo preedge peak is strongly polarized in the direction of the $M=O$ bond. On the basis of these results, it was suggested that the bound state responsible for the preedge transition is an antibonding molecular orbital containing metal d_{z^2} and oxygen p_z .¹⁵ Our results, consistent with these previous measurements, show that the preedge feature in **1** and **2** is strongly z -polarized. The apparent presence of a small preedge feature in the x - and xy -polarized spectra can be accounted for by the crystal structure, which gives a slight misalignment of the two different $M=O$ directions, and by the incomplete polarization of the beam.

The preedge feature in **1** and **2** is ca. 100 times more intense than the dipole-forbidden $1s \rightarrow 3d$ transition in centrosymmetric complexes. This intensity is only consistent with a dipole-allowed, p -symmetry final state. The preedge transition has a well-defined energy, with fwhm of 2.8 eV for **1** and 3.5 eV for **2**. This width is comparable to the lifetime and monochromator broadening, and is consistent with a bound final state. In contrast, nonbound continuum features are generally much broader (fwhm ~ 10 – 20 eV).⁵

In general, the energy of a metal-localized bound \rightarrow bound transition is expected to be reasonably insensitive to the details of the molecular geometry, while continuum shape-resonance features are expected to have a strong geometric dependence. Our calculations show that the preedge feature is relatively insensitive to molecular geometry, showing only a decrease in amplitude between the five- and six-coordinate models. This is consistent with bound final-state character for this transition. In contrast, all of the higher energy features, and in particular the new z -polarized feature in the six-coordinate calculation, show behavior expected for continuum resonances.

The energy of continuum resonance features is approximately proportional to $1/R^2$, where R is the absorber-scatterer distance.¹⁷ The only difference between the calculated spectra for **1** and **4** is the presence of a new z -polarized peak in **4**. This new peak occurs at the same energy as a shoulder observed in the calculated x -polarized spectra (at ~ 25 eV). Both features are reasonably assigned as continuum resonances involving the axial and the pyrrole nitrogens, respectively. The same Cr–N distance (2.00 Å) was used for both bonds, hence the continuum resonances are expected to occur at the same energy. The only difference between the x - and the xy -polarized experimental spectra (not shown) is the amplitude at ~ 6005 eV. Given the Cr–N(pyrrole) continuum resonance assignment at 6015 eV, a feature at 6005 eV would correspond to an atom at 3–4 Å. This is completely reasonable, since it is only for the more distant carbon atoms that the deviations of the porphyrin from C_{4v} symmetry become significant.

The preedge transition for **2** is shifted by 1 eV to higher energy relative to that for **1**. Direct comparison of **1** and **2** is difficult, due to the change in axial ligation (O for **1**, N for **2**). However, the observed edge shift is consistent with the increase in formal oxidation state from Cr(IV) (**1**) to Cr(V) (**2**). In contrast, there is no discernible shift in the energies of the higher energy features between Cr(IV) and Cr(V). This may be due in part to the breadth of the higher energy features, which makes precise determination of their energies difficult. In addition however, this differing sensitivity to oxidation state is expected theoretically since the Cr oxidation state should have little effect on the relative energies of either the $1s$ initial state or the continuum final states while the oxidation state will have a large effect on the energy of the $3d$ state.

In a molecular orbital picture, the final state in the preedge transition can be viewed as an A_1 symmetry antibonding combination of metal $3d_{z^2}$ and $4p_z$ and ligand $2s$ and $2p_z$ orbitals.^{15,18} The normally forbidden $1s \rightarrow 3d$ transition is made allowed by

admixture of odd-parity metal p and ligand orbitals. The intensity of this transition will depend on the extent of this mixing, and hence will be a sensitive function of the strength of the metal-oxygen bond. The decrease in the calculated preedge intensity for **3** thus reflects a weakening of the $M=O$ bond due to the presence of a second axial ligand.

A different mechanism must be invoked to understand the absence of a preedge transition in the ferryl spectra (Figure 5), since an axial ligand was not used in these calculations. There are two additional electrons in the Fe porphyrin, which occupy metal-oxygen antibonding orbitals (E symmetry).^{19–21} Although this will not directly affect the z -polarized preedge transition, it will cause a weakening of the $M=O$ bond. The calculations show that this weakening is sufficient to decrease the preedge transition strength below the limits of detection. The experimental observation of relatively weak preedge transitions for HRP-I and HRP-II is thus seen to reflect a weakening of the Fe=O relative to the Cr=O bond. Consistent with this, the Fe=O bond in HRP-I is ~ 0.06 Å longer than the Cr=O bond in **1**.^{7,22} This approach emphasizes the potential of X-ray absorption edge spectroscopy for studying the electronic structure of transition-metal complexes.

It is interesting to compare this interpretation with known porphyrin chemistry. Büchler has noted that the relative reactivities are $TiO(por) \sim VO(por) \ll CrO(por) < MnO(por) < FeO(por)$; this was attributed to the increased number of d electrons causing an increased repulsion of the p electron pairs at the terminal oxo group, thus destabilizing and activating the oxygen atom.²³ This interpretation is consistent with our model, since the observed decrease in preedge transition strength for $(por)Fe=O$ relative to $(por)Cr=O$ ⁷ indicates a weaker Fe=O bond, and hence a more active oxygen atom. It is also consistent with the fact that analogous $(por)M=O$ species do not exist for later transition metals, since adding still more electrons would be so destabilizing as to prevent formation of $M=O$ altogether.

Conclusions

Polarized X-ray absorption edge measurements of chromium oxene and nitrene porphyrins have revealed the presence of an intense preedge transition polarized in the direction of the Cr=O or Cr=N bond. Excellent agreement is found between the experimental spectra and spectra calculated by using extended-continuum and MSW $X\alpha$ methods. The intense preedge transition is found to have predominantly metal d character, with small amounts of metal p and oxygen (or nitrogen) s and p character. The final state for this transition can be identified, in a molecular orbital picture, with a metal + ligand σ antibonding orbital. This identification can be used to correlate the preedge intensity with the reactivity patterns of first-row metal-oxo porphyrins. The observation of only weak preedge transitions for high-valent iron porphyrins⁷ is seen to be consistent with, rather than in conflict with, their assignment as ferryl porphyrins.

Although the preedge intensity is quite sensitive to the molecular bonding, the energy of this feature appears to be insensitive to the molecular environment, as expected for a bound \rightarrow bound transition. In contrast, the broad transitions at ~ 6015 eV seem to behave like continuum resonances, with energies that are insensitive to oxidation state but increase (in the calculations) for shorter metal-ligand bonds. For "normal" (e.g. non-oxo) porphyrins, these continuum resonances will dominate the isotropic absorption spectra. This interpretation would suggest, therefore, that the energy of "normal" metalloporphyrin edges will depend primarily on the average metal-ligand bond length and only slightly on the metal oxidation state. This precise effect has been observed for iron porphyrins, where the edge energies were found

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to vary significantly with spin-state changes but only slightly with oxidation-state changes.²⁴

Perhaps the most striking aspect of this work is the degree to which the experimental spectra are reproduced by using a simple six-atom model and non-self-consistent calculations. Previous studies^{25,26} have suggested that 30-50 atom clusters are required to obtain reasonable agreement with experiment. The outer-shell atoms may well contribute to the detailed structure of metalloporphyrin edges;²⁶ however, the recent work demonstrates that it is possible to reproduce the major features of the experimental

spectra by using only first-shell atoms. The relative ease of our calculations suggests that it may be feasible to use the MSW $X\alpha$ extended continuum method to study low-symmetry complexes.

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Proton NMR Investigation of the Electron-Exchange Reaction between Hexaammineruthenium(II) and Hexaammineruthenium(III) Ions

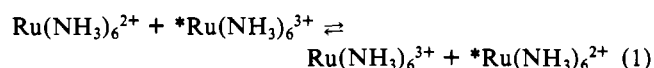
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The rate of the electron-self-exchange reaction between $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+}$ has been measured by proton NMR line broadening. The system is complicated by the aquation of $[\text{Ru}(\text{NH}_3)_6]^{2+}$, which results in reduction of the small amount of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ present. To reduce this difficulty, measurements were performed at 4 °C. Rate constants are $(6.6 \pm 1.0) \times 10^3$ and $(9.9 \pm 0.2) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for solutions of 0.125 and 0.250 M $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$, respectively. These rate constants are in order-of-magnitude agreement with those previously reported. The reaction appears to be catalyzed by chloride ion. A rate constant for the uncatalyzed reaction at 4 °C and an ionic strength $\sim 0.5 \text{ M}$ is estimated to be $3.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$. The activation enthalpy is about 5 kcal mol⁻¹.

Introduction

The electron-exchange reaction (1) between the hexaammine complexes of ruthenium(II) and ruthenium(III) is of central importance to the study of electron-transfer reactions of metal complexes. Both complexes are relatively substitution-inert, so



that the mechanism of the reaction is outer sphere. With low-spin (t_{2g})⁶ and (t_{2g})⁵ 4d electron configurations there are no electronic spin state changes; a single t_{2g} electron is transferred between a singlet and a doublet state. There is little inner coordination sphere reorganization required, for the ruthenium-nitrogen bond lengths differ by only 4 pm between these low-spin states.¹ Consequently, the rate of the reaction is determined largely by outer-sphere, solvation, effects. The importance of the reaction lies in this fact, that it is a probe of the outer-sphere reorganization energy, uncomplicated by other effects.

The rate of the reaction is relatively slow, due at least in part to the small size and consequent strong solvation of the complex ions. The rate was first measured by Meyer and Taube,² using an elegant technique that exploited the oxidation state difference in the near-infrared spectrum of the first overtone of the N-H stretching vibration. This provided an isotopic label for the different oxidation states when one state was deuterated. The experiments were difficult, and the rates could not be determined precisely. Furthermore, some unexplained nonreproducibility was encountered. Nevertheless, their rate constant of $(8 \pm 1) \times 10^2$

$\text{M}^{-1} \text{ s}^{-1}$ at 25 °C with $\mu = 0.013$ in trifluoroacetic acid has been used successfully in the calculation of other rate constants by the Marcus cross-reaction relationship. Alternatively, a value of $4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at $\mu = 0.16$ in acetate buffer has been used, although this value is based on a less precise, indirect measurement of electron-transfer-catalyzed hydrogen-deuterium exchange, also subject to unexplained catalysis. (The value of $4.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ sometimes quoted³⁻⁵ for $\mu = 0.1$ should in fact be $(4 \pm 3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ obtained from these results.)

The direct measurement of the self-exchange rate gave an unexpectedly high activation energy of $10.3 \pm 1.0 \text{ kcal mol}^{-1}$. More recently, Brown and Sutin⁵ measured the rate of the cross-reaction between $[\text{Ru}(\text{en})_3]^{3+}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+}$. With the assumption that the self-exchange rate constants are the same for the hexaammine and the tris(ethylenediamine) complexes, they extracted a self-exchange rate constant of $3.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C and $\mu = 0.1$ in $\text{CF}_3\text{SO}_3\text{H}$ solution. The activation enthalpy of the self-exchange reaction was calculated with the use of some additional thermodynamic data to be a more reasonable 4.5 kcal mol⁻¹.

In view of the uncertainties inherent in the original work and the assumptions now known to be incorrect required in the cross-reaction study, we have made another attempt at a direct measurement of the rate of the self-exchange reaction.

Experimental Section

Materials. Except for the weighing of solids and the purification of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, all procedures were carried out under an atmosphere of

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