Metalloporphyrin Photochemistry with Matrix Isolation

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Abstract: The photochemistry of a number of metalloporphyrin oxoanion complexes has been examined by matrix isolation techniques, using both frozen solvent glasses and polymer films. After an extensive search for a noncoordinating, unreactive, glasing solvent, a 3:1 mixture of 2,2-dimethylbutane and tert-butylbenzene was found to work well at temperatures below 70 K. Alternatively, the photochemistry of metalloporphyrin was monitored in polymer films by the evaporation on a sapphire window of metalloporphyrin solutions in toluene containing either poly (methyl methacrylate) or poly (α-methylstyrene). The polymer films have the added advantage of a greatly increased temperature range, providing diffusional isolation even at room temperature. The photoreduction of the metal by homolytic $\alpha$-bond cleavage and loss of the axial ligand appears to be a general mechanism for all metalloporphyrin complexes examined. The formation of metal-oxo species from photolysis of metalloporphyrin oxoanion complexes in solution derives from secondary, thermal reactions.

The use of frozen inert gas matrices, frozen solvent glasses, and polymer films has been well-established22 for spectroscopic studies of metalloporphyrins,23 especially the (relatively) volatile four-coordinate metal(II) complexes.24-26 Matrix isolation, however, has only rarely been used for photochemical studies of metalloporphyrins. The unexpected formation of Fe(porph)O(O) from laser photolysis of the co-condensation products of Fe(porph) and O$_2$ at 15 K is a notable exception.32a Glasses of 2-methyltetrahydrofuran have been used for the photolyses of Mn(porph)(N$_3$)$_2$ and Cr(porph)(N$_3$)$_2$ at 77 K, but reactions with this non-innocent matrix were observed.21

To explore the mechanism of photochemical oxygen atom transfer, we have examined the photochemistry of several porphyrin complexes by matrix isolation techniques. We find that both frozen solvent glasses and polymer films, if properly chosen, can be used effectively over a wide temperature range for a variety of metalloporphyrin complexes. Our results suggest that the photoreduction of porphyrin metal centers by homolytic metal-ligand $\alpha$-bond cleavage is a general reaction and oxygen atom transfer and other reactions observed with solution photochemistry actually result from secondary thermal reactions.

Experimental Section

Materials. Solvents used were of reagent grade and distilled from sodium or from sodium—benzophenone prior to use. Low molecular weight (\approx 81 kD) poly(methyl methacrylate) (PMMA) or poly (α-methylstyrene) (PMS) were obtained from Aldrich Chemical Company and used as received. Inorganic salts were purchased from Aldrich and used without further purification. H$_2$TPP, Mn(TPP)(Cl), [Mn(TPP)]O$_2$, Fe(TPP)(Cl)$_2$, and [Fe(TPP)]O were prepared by published methods.32b The oxoanion complexes have been fully characterized in the literature.

literature and are synthesized either by metathesis of the chloride complexes with the appropriate silver or sodium salt or by cleavage of [M-(TPP)2]Cl with the appropriate acid. Mn(TPP)(ClO4), Mn(TPP)(NO3), Mn(TPP)(NCS), Mn(TPP)(ClO4), Mn(TPP)(SO3)2, and Fe(TPP)(ClO4) were prepared by the former method, and Mn(TPP)(SO3)H and Fe(TPP)(NO3) were prepared by the latter method.

**Instrumentation.** Matrix-isolated UV-visible spectra were recorded on an IBM double monochromator spectrophotometer (Model 9430); other routine spectra were taken with a Hewlett-Packard 8452A diode array spectrophotometer. For low-temperature matrix-isolation studies, a Janis Research Co. closed cycle refrigeration system (Model C5W21-OL-5), cooled by a Leybold-Heraeus Cryogenator (RW-3), was used. Temperature control was maintained by a Scientific Instruments digital temperature controller (Model 9600). The controller uses a silicon diode sensor with a ±0.5 K accuracy in the 1.5–35 K range.

The chemical reactions. All photochemical reaction solutions were prepared in a Vacuum Atmospheres inert atmosphere box (<2 ppm O2). In a typical experiment with a solvent glass, a saturated solution of the metalloporphyrin complex in a 3:1 (v/v) mixture of 2,2-dimethylbutane and tert-butylbenzene was placed under inert atmosphere in a sample holder or charge transfer bands. These overlap and mix so extensively that they were examined as a whole; a 390-420-nm band-pass filter suffices to isolate these bands. UV-visible spectra of both starting complexes and final products were compared to authentic samples.

**Photoaction Studies.** The determination of which bands in the absorption spectrum of a given molecule are responsible for the photoaction was accomplished by the use of commercially available narrow-pass and long-pass filters. The Soret (B) band (420-480 nm) and the Q (Q) bands (>500 nm) could each be isolated by selection of the appropriate narrow-band-pass filter. In the case of manganese porphyrins, to the blue of the Soret band, are the N, L, M and porphyrin to metal-oxo species (eqs 2 and 3). The possibility that all oxoanion complexes may actually undergo initial a-bond cleavage as in MnIV(TPP)(O)4 was inferred from the nature of the observed photo-oxidation mechanisms. In the first class, both nitrate and nitrite oxygen atom transfer from the oxoanion to the metal and photoreduction of the metal. In the second class, nitrate and nitrite complexes underwent 1-bond cleavage to form MnIV(TPP)(O)4 (eq 1, TPP = 5,10,15,20-tetraphenylporphyrinate(2-)). In the case of perchlorate and periodate complexes, the formation of [Mn(TPP)(O)]+- MnIV(TPP)(O)4 from MnIII(TPP)(O)4, as shown in eq 3. The possibility that all oxoanion complexes may actually undergo initial a-bond cleavage as in eq 3, followed in some cases by a rapid thermal reaction to form metal-oxygen species (eqs 4 and 5), was also recognized. Solution photochemical studies could not differentiate between these two mechanisms.

![Figure 1. Photolytic conversion of [Mn(TPP)]3(SO4)2 to MnIII(TPP) under matrix-isolation conditions in a poly(α-methylstyrene) film at 298 K. Very similar spectra were also observed at 10 K. Arrows indicate the change in absorbance during irradiation.](image)

\[
\text{Mn(TPP) (O)}_{3} \xrightarrow{hv} \text{MnIV(TPP)(O)} + \text{XO}^{*} \quad (1)
\]

\[
\text{Mn(TPP)(O)}_{2} \xrightarrow{hv} \text{[Mn(TPP)(O)]}^{+} + \text{XO}^{*} \quad (2)
\]

\[
\text{Mn(TPP)(O)}_{2} \xrightarrow{hv} \text{MnIV(TPP)(O)} + \text{XO}^{*} \quad (3)
\]

\[
\text{MnIV(TPP)(O)} + \text{XO}^{*} \rightarrow \text{MnIV(TPP)(O) + XO}^{*} \quad (4)
\]

\[
\text{MnIII(TPP) + XO}^{*} \rightarrow \text{[Mn(TPP)(O)]}^{+} + \text{XO}^{*} \quad (5)
\]
Table 1. Photochemical Products and Quantum Yields in Solution and Frozen Matrix

<table>
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<th>complex</th>
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<th>matrix product</th>
<th>10^6%</th>
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<td>Mn(TPP)(NO₃)</td>
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<td>Mn(TPP)(NO₂)</td>
<td>3.2</td>
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</tr>
<tr>
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<td>7.1</td>
<td>Mn(TPP)²⁺</td>
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<tr>
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<tr>
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<td>photostable†</td>
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<td>Fe(TPP)</td>
</tr>
</tbody>
</table>

*Samples irradiated with a 300-W Xe arc lamp using narrow pass filters. UV-vis spectra were compared to authentic samples. Results were the same in solution at 10 K, in polymer matrix at 10 K, and in polymer matrix at 298 K. Quantum yields were determined with use of the 366-nm line of a low-pressure Hg arc; results were the same to within experimental error (±10%) at both 30 and 298 K. Matrix-isolated Mn(TPP)(OH) and [Fe(TPP)]²⁺ species were also photoreduced; quantum yields were not determined but were qualitatively similar to the other complexes. †Reference 6, Reference 7.

Figure 2. Photolytic conversion of Fe(TPP)(ClO₄) to Fe(TPP) under matrix isolation conditions in a poly(o-methylstyrene) film at 10 K. Very similar spectra were also observed at 298 K. Arrows indicate the change in absorbance during irradiation.

show the near-UV band associated with halide-to-metal charge-transfer transition. The absence of accessible charge-transfer transitions in consistent with the lack of photochemical reactivity. Thus, the photoreduction of the metal center appears to be a general mechanism. There are no other reactions in these complexes observed in these systems. The porphyrins do not decompose and they do not fluoresce. The low quantum yields for photoreduction reflect very high efficiency of nonradiative decay processes for metalloporphyrins. This is to be expected since this photochemistry arises only from high-lying (rather than the lowest energy) excited states. The subsequent thermal chemistry is probably determined by several factors, including the relative stabilities of the leaving groups and the remnant porphyrin species, as well as relative solution energies of products.

The one apparent exception to this photoreduction route is Mn(TPP)(ClO₄). Both in solution and in matrices, the direct formation of Mn(TPP)(Cl) is observed. In solution photolysis, this can be explained by the extreme reactivity of Mn(TPP)(Cl)²⁺, after all four oxygen equivalents are incorporated into substrate, the remaining chloride forms Mn(TPP)(Cl). Under matrix-isolation conditions, however, the secondary thermal reactions should not have occurred, especially at 10 K. We suggest that here too the initial photoreaction is a-bond cleavage and photoreduction to form Mn(TPP) and ClO₄⁻. ClO₄⁻ species, however, are known to undergo efficient photochemical reactions, resulting finally in Cl⁻ that even in the matrix could give the observed Mn(TPP)(Cl). Given the relatively low quantum yields of metalloporphyrin photoreduction, the secondary photochemical reactions of ClO₄⁻ predominate the observed products.

Conclusions

We have shown that both solvent glasses and polymer films are viable alternatives for matrix-isolation studies of nonvolatile metalloporphyrin complexes. The photoreduction of the metal by homolytic a-bond cleavage and loss of the axial ligand appears to be a general mechanism for all metalloporphyrin complexes examined. This is consistent with the nature of the excited states involved. Irradiation of the lowest energy π to π* transitions does not produce photochemical reactions in these complexes. Metalloporphyrin photochemistry is unusual in this way: the observed photochemical processes do not come from the lowest available excited state.

Spin Frustration: A Hexanuclear Ferric Complex with a S = 5 Ground State Ions

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Abstract: The preparation and characterization of a hexanuclear FeIII complex possessing an unusual S = 5 ground state are described. Reaction of 1,1-bis(N-methylimidazol-2-yl)-1-hydroxymethane (1) with [Fe2(OAce)3]X (2), where L = pyridine or H2O and X = ClO4- or NO3-, in CH3CN followed by recrystallization in CH2Cl2 affords crystals of [Fe6(OH)(O-Ac)12]Cl8. Complex 3 and [Fe2(OH)(O-Ac)3]Br crystallize in the triclinic space group P1 with a = 12.167 Å, b = 12.921 Å, c = 15.394 Å, α = 114.41°, β = 119.76°, γ = 119.37°. V = 2087.4 (6) Å3, and Z = 1 at -100 °C. The structure was refined with 4179 observed reflections (F > 6.0σ) to give R = 0.0465 and Rw = 0.0591. The molecule resides at a center of inversion, making only three of the iron ions unique. Two of the iron ions have O2- coordinated spheres, while the third has an O2- environment due to binding by one of the imidazole nitrogen atoms; the second imidazole ring of complex I remains uncoordinated. Complex 3 consists of two μ-oxo FeIII triangular complexes bridged together at two vertices by two μ2-OH and four μ2-O2CCH3 ions. 57Fe Mössbauer data can be fit to two quadrupole-split doublets in a 2:1 area ratio with δ = 0.383 (3) and 0.406 (6) mm/s and ΔEQ = 0.729 (5) and 1.056 (11) mm/s, respectively, at 300 K. The parameters are consistent with high-spin FeIII. Magnetic susceptibility data at 10.00 K in the temperature range 6-350 K reveal an increase in effective moment with decreasing temperature from 9.21 μB at 346 K to a maximum of 10.90 μB at 20.00 K. Variable-field magnetization data measured to 1.57 K at 40.00 kG saturate at a reduced magnetization M/μNpB of 9.2. Fitting of the magnetization data by full-matrix diagonalization and including axial zero-field interactions establish the ground state as having S = 5 with g = 1.94 and D = 0.22 cm⁻¹. The origin of this ground state is described in terms of spin frustration within the hexanuclear core, and the results are compared to those found for a similar hexanuclear complex for which a S = 0 ground state was found.

Introduction

Polynuclear oxo- or hydroxo-bridged transition-metal centers have been found in a variety of iron1 and manganese2 metalloproteins. Hemerythrin3 methane monoxygenase4 and ribonucleotide reductase5 have diiron active sites with μ-oxo and μ-carboxylato bridges. In the course of making model complexes for these oxo-diiron protein sites, several interesting polynuclear ferric complexes with Feα, Feβ, Feγ, Feδ, and Feε compositions have been reported.6 The largest nuclearity discrete oxo-hydroxo ferric heteronuclear complex is heminuclear: [Fe4Mo6O4(OH)10(O2CPh)20] (M = MnIII, CoII).7 The pursuit of model complexes for the active sites of catalases and the water oxidation center of photosystem II has also yielded polynuclear manganese complexes with compositions of Mn11II,MnIII3, Mn11II,MnIII4, Mn11II,MnIII5, Mn11II,MnIII6, Mn11II,MnIII7, Mn11II,MnIII8, and Mn11II,MnIII9. The most

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