variations of oxidation and oxygenation rates, and possibly variations in the mechanisms of catalysis involving dioxygen complexes as intermediates.

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Communications

Mössbauer Spectra of Oxidized Iron Porphyrins

Sir:

Highly oxidized porphyrin complexes\(^1\) are demonstrated intermediates in a number of heme proteins, including catalase,\(^2\) peroxidase,\(^3\) and cytochrome P-450,\(^4\) as well as in photosynthetic reaction centers.\(^5\) Because of the unusual electronic properties and the novel reactivities that these intermediates show, there is current interest in the preparation of synthetic analogues of (porphyrinato)iron complexes oxidized beyond the Fe(III) state.\(^6\) The nature of such oxidized species is a matter of some controversy, since oxidation can occur either from the metal-based orbitals or from the porphyrin \(\pi\) system. For example, oxidation of the \(\mu\)-oxido dimer (FeTPP)_2O (1) to the dication was originally formulated as a metal-based oxidation.\(^6\) Recent investigations, however, have provided a strong case for oxidation of the porphyrin \(\pi\) system, resulting in a \(\pi\)-radical-cation dimer.\(^7\) We wish to report the Mössbauer spectra of a series of oxidized porphyrin complexes, including a series of single-atom-bridged dimers and a related dichlorocarbene complex. We find that changing the bridging atom from oxygen to nitrogen or carbon shifts the site of oxidation from the porphyrin \(\pi\) system to the metal.

The Mössbauer parameters for a series of porphyrin complexes are given in Table I. All compounds exhibit a single quadrupole-split doublet in the absence of an applied magnetic field. The constancy of the isomer shift (\(\sigma\)) and the quadrupole splitting (\(\Delta E_Q\)) for the neutral and oxidized \(\mu\)-oxido dimers\(^8\) indicates that the oxidation has been from the porphyrin \(\pi\) system and that the electron density at the iron has not changed in all three compounds. Infrared data have also indicated\(^9\) the existence of \(\pi\) cation radicals in the oxidized \(\mu\)-oxido dimers 2 and 3. In dramatic contrast, the oxidation of (FeTPP)_2N (4) to the monocation\(^10,11\) (FeTPP)_2N^+ (5) produces significant changes in the Mössbauer parameters. The diminished isomer shift demonstrates reduced \(s\)-electron density at the iron in 5, and the increase in the quadrupole splitting is consistent with a major change in the electronic environment of the iron. The \(\mu\)-carbido dimer\(^12\) (FeTPP)_2C (6) is isoelectronic with the \(\mu\)-nitrido monocation, 5, and the \(\mu\)-oxido dication, 3, but its Mössbauer parameters are similar to only those of 5. This shows that the electronic structures of the \(\mu\)-carbido dimer and the \(\mu\)-nitrido dimer cation are similar to one another but distinct from that of the \(\mu\)-oxido dication. The related carbene complex 7, like the \(\mu\)-carbido complex, has a Mössbauer isomer shift that is quite small, indicative of lower electron density at the iron relative to Fe(II) or Fe(III) complexes. It should be noted that oxidation states of iron of course only a useful formalism and are not observations. Mössbauer parameters yield only information about

\section*{Table I}

<table>
<thead>
<tr>
<th>compda</th>
<th>temp, K</th>
<th>isomer shift, b</th>
<th>quadrupole splitting, mm/s</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>(FeTPP)_2O</td>
<td>131</td>
<td>0.40 (1)</td>
</tr>
<tr>
<td>2</td>
<td>[(FeTPP)_2O]ClO_4</td>
<td>77</td>
<td>0.39</td>
</tr>
<tr>
<td>3</td>
<td>[(FeTPP)_2O]ClO_4</td>
<td>77</td>
<td>0.38</td>
</tr>
<tr>
<td>4</td>
<td>(FeTPP)_2N</td>
<td>131</td>
<td>0.18 (1)</td>
</tr>
<tr>
<td>5</td>
<td>[(FeTPP)_2N]ClO_4</td>
<td>131</td>
<td>0.03 (1)</td>
</tr>
<tr>
<td>6</td>
<td>(FeTPP)_2C</td>
<td>131</td>
<td>0.10 (1)</td>
</tr>
<tr>
<td>7</td>
<td>FeTPP[Cl(C_2)]</td>
<td>131</td>
<td>0.11 (1)</td>
</tr>
<tr>
<td>8</td>
<td>FeTPPCl</td>
<td>4.2</td>
<td>0.41</td>
</tr>
<tr>
<td>9</td>
<td>[FeTPP]Cl</td>
<td>131</td>
<td>0.40</td>
</tr>
<tr>
<td>10</td>
<td>Fe(O)(TPP)(1-MeIm)</td>
<td>77</td>
<td>0.11</td>
</tr>
<tr>
<td>11</td>
<td>Japanese radish peroxidase compound I</td>
<td>77</td>
<td>0.10</td>
</tr>
<tr>
<td>12</td>
<td>Japanese radish peroxidase compound II</td>
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<td>0.11</td>
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<td>13</td>
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<td>0.00</td>
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<tr>
<td>14</td>
<td>horseradish peroxidase compound II</td>
<td>77</td>
<td>0.03</td>
</tr>
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</table>

\subsection*{Notes}

\begin{enumerate}
\item Abbreviations: TPP, tetraphenylporphyrinato(2-); TMP, tetraakis(\(p\)-methoxyphenyl)porphyrinato(2-); 1-MeIm, 1-methylimidazole; EPR, electron paramagnetic resonance.
\item Felton, R. H.; Owen, G. S.; Dolphin, D.; Fajer, J. J. Am. Chem. Soc. 1971, 93, 6332.
\item Moss, T. H.; Ehrenberg, A.; Bearden, A. J. Biochemistry 1969, 8, 4159.
\item (13) This compound was obtained in solution in a previous study.\(^14\) A solid sample was prepared by adding 0.5 equiv of I to dissolved in dry CH_2Cl_2 and 1 equiv of AgClO_4 dissolved in dry acetonitrile to 1 equiv of (FeTPP)_2N dissolved in dry CH_2Cl_2 under nitrogen by using standard Schlenk-ware techniques. After being stirred at room temperature for 2 h, the solution was opened to air, filtered, and reduced in volume, and hexanes were added. The resulting red-purple powder was collected and recrystallized from toluene/hexanes. Anal. Calc. for C_88H_68N_9O_4Fe_2: C, 72.86; H, 3.89; N, 8.69; Cl, 2.44; Fe, 7.70. Found: C, 73.21; H, 4.14; N, 8.92; Cl, 2.66; Fe, 7.52.
\end{enumerate}
Thus, as the ligated atom becomes more electronegative, the site of oxidation in these complexes shifts from being metal based to residing in the porphyrin \( \pi \) system, as one might have expected on an intuitive basis. In keeping with this trend, comparison of the Mössbauer parameters of FeTPP(Cl) with those of its monomeric cation in [FeTPP(Cl)]SbC\(_6\) indicates that oxidation has occurred from porphyrin-based orbitals rather than from those of iron.\(^9\) This is in keeping with the high electronegativity of Cl, which would not be expected to stabilize a charge removal from the iron rather than from the porphyrin \( \pi \) system.

In summary, the nature of highly oxidized iron porphyrin complexes is extremely sensitive to the nature of axial coordination. In the series of single-atom-bridged dimers of (tetraarlylporphyrin)iron complexes, as the bridge atom changes from carbon or nitrogen to oxygen, the Mössbauer spectra clearly show a change in the site of oxidation from the metal-based orbitals to those of the porphyrin. For the dichlorocarbene complex, the Mössbauer parameters are similar to those of the \( \mu \)-carbido dimer, indicating similar electron densities at the iron. In the heme proteins which support high-oxidation-state intermediates, the axial ligation varies from N (from a histidine imidazole in peroxidase\(^3\)) to O (from a tyrosine phenolate in catalase\(^4\)) to S (from a cysteine thiolate in cytochrome P-450\(^5\)). In light of the vastly differing modes of reactivity that these enzymes show, the importance of a detailed understanding of the electronic structure of highly oxidized porphyrins is clear.

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Registry No. 1, 12582-61-5; 2, 80766-28-5; 3, 79633-64-0; 4, 59114-43-1; 5, 83967-78-6; 6, 75249-87-5; 7, 65979-89-7; 8, 16456-81-8; 9, 78023-40-2; 10, 82512-02-5; peroxidase, 9003-99-0.

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Tunable Exchange Interaction in \( \mu \)-Oxalato Copper(II) Dinuclear Complexes

Sir:

Several structural–magnetic correlations have been proposed in the last few years, which have led to a better understanding of the mechanism of the interaction between magnetic centers in polynuclear complexes.\(^1\)-\(^4\) Generally, a dependence of the exchange parameter \( J \) on a structural parameter such as a bond length or a bond angle has been demonstrated. Such an approach, whatever its importance may be, does not allow the construction of a molecular engineering of the polynuclear systems. Indeed, it does not seem that the value of this structural parameter can be controlled during the synthesis process. On the other hand, our group is engaged in the design...