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

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 unsual 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.[6-10] 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 π system. For example, oxidation of the μ-oxo dimer (FeTPP)$_2$O (**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 π system, resulting in a π-radical-cation dimer.[7] We wish to report the Mössbauer-effect spectra of several oxidized iron 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 π 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 (σ) and the quadrupole splitting (ΔE_q) for the neutral and oxidized μ-oxo dimers[8,14] indicates that the oxidation has been from the porphyrin π system and that the electron density at the iron has not changed in all three compounds. Infrared data have also indicated[7] the existence of π cation radicals in the oxidized μ-oxo dimers **2** and **3**. In dramatic contrast, the oxidation of (FeTPP)$_2$N (**4**) to the monocation[15,16] (FeTPP)$_2$N$^+$ (**5**) pro-

Table I

| no.	compd[a]	temp, K	isomer shift,[b] mm/s	quadrupole splitting, mm/s	ref
1	(FeTPP)$_2$O	131	0.40 (1)	0.62 (1)	this work
2	[(FeTMP)$_2$O]ClO$_4$	77	0.39	0.57	8
3	[(FeTMP)$_2$O](ClO$_4$)$_2$	77	0.38	0.51	8
4	(FeTPP)$_2$N	131	0.18 (1)	1.08 (1)	this work
5	[(FeTPP)$_2$N]ClO$_4$	131	0.03 (1)	2.00 (1)	this work
6	(FeTPP)$_2$C	131	0.10 (1)	1.88 (1)	this work
7	FeTPP(CCl$_2$)	131	0.10 (1)	2.28 (1)	this work
8	Fe(TPP)Cl	4.2	0.41	0.46	10
9	[Fe(TPP)Cl]SbCl$_6$	77	0.40	0.55	8
10	Fe(O)(TPP)(1-MeIm)	77	0.11	1.25	9
11	Japanese radish peroxidase compound I	77	0.10	1.33	11
12	Japanese radish peroxidase compound II	77	0.11	1.44	11
13	horseradish peroxidase compound I	77	0.00	1.20	12
14	horseradish peroxidase compound II	77	0.03	1.36	12

[a] All spectra recorded in this work were run on solid samples.
[b] All isomer shifts are reported with respect to Fe metal.

duces 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 at the iron. The μ-carbido dimer[17] (FeTPP)$_2$C (**6**) is isoelectronic with the μ-nitrido monocation, **5**, and the μ-oxo dication, **3**, but its Mössbauer parameters are similar to only those of **5**. This shows that the electronic structures of the μ-carbido dimer and the μ-nitrido dimer cation are similar to one another but distinct from that of the μ-oxo dication. The related carbene complex **7**, like the μ-carbido complex, has a Mössbauer isomer shift that is quite small, indicative of lowered electron density at the iron relative to Fe(II) or Fe(III) complexes. It should be noted that oxidation states are of course only a useful formalism and are not observables. Mössbauer parameters yield only information about

(1) Abbreviations: TPP, tetraphenylporphyrinato(2–); TMP, tetrakis(*p*-methoxyphenyl)porphyrinato(2–); 1-MeIm, 1-methylimidazole; EPR, electron paramagnetic resonance.

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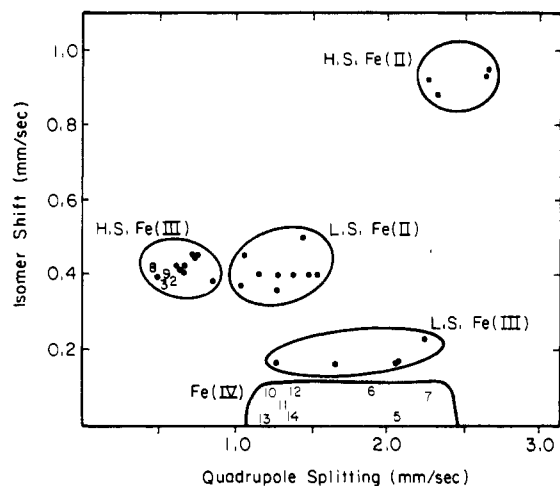
Figure 1. Plot of Mössbauer parameters for tetraarylporphyrins. Numbered points are taken from Table I. Unnumbered data are given in ref 11. All isomer shifts are relative to iron metal.

the nature of the electron density at the iron nucleus, so care must be used to avoid oversimplification of the descriptions of electronic structure. Qualitative comparisons, however, between related complexes can be made.

In addition, we have examined the infrared spectra of **4–7** as Nujol mulls. There are no major bands in the 1290–1270-cm^{-1} region. A strong absorption in this region has been associated with π-radical-cation character in a variety of tetraarylporphyrin complexes.[7] The absence of this band supports the proposal that the oxidation of μ-nitrido and the μ-carbido dimers is metal rather than porphyrin based. Furthermore, the electron paramagnetic resonance spectrum of the μ-nitrido dimer, **4**, argues against a π-radical-cation formulation. The small nitrogen hyperfine splitting in the EPR spectrum[18,19] of **4** argues that the unpaired electron density interacts with the bridging nitrogen atom mostly through spin polarization. Thus, the combination of Mössbauer, infrared, and EPR spectra argues that the μ-nitrido dimer, **4**, is best represented formally as Fe(3.5+)/Fe(3.5+), in accord with theoretical calculations.[20]

The nature of the electronic structure of the μ-carbido dimer, **6**, may be represented in its extremes as two iron(II) porphyrins bridged by a carbenic carbon atom, as a dimer of iron(III) porphyrin π radical cations, or as a dimer of iron(IV) porphyrins. The Mössbauer parameters of **6**, however, clearly eliminate the first two descriptions as being major contributors to the overall electron density. From Table I, the isomer shift and the quadrupole splitting of the μ-carbido dimer are typical of those associated in other systems with oxidation of the iron. In addition, the lack of the infrared marker band for porphyrin π radical cations and the chemical stability of this dimer to oxygen and water are consistent with this description. The dichlorocarbene complex, **7**, has a rather small isomer shift, indicative of reduced electron density at the iron nucleus compared to common Fe(II) or Fe(III) complexes.

We have presented in Figure 1 a useful plot of isomer shift vs. quadrupole splitting for a representative number of (porphyrinato)iron complexes in various electronic configurations. It is clear from this figure that there are discrete and well-separated regions associated with each of these configurations, as has been noted before for ferrous and ferric porphyrin complexes.[11] This figure should be taken as only a general guide.

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 π 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)]SbCl$_6$ 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 π 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 (tetraarylporphyrin)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 metal-based orbitals to those of the porphyrin. For the dichlorocarbene complex, the Mössbauer parameters are similar to those of the μ-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[2]) to S (from a cysteine thiolate in cytochrome P-450[4]). 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.

School of Chemical Sciences   **Daniel R. English**
University of Illinois at   **David N. Hendrickson***
    Urbana-Champaign   **Kenneth S. Suslick***
Urbana, Illinois 61801

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Tunable Exchange Interaction in μ-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 polymetallic 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 polymetallic 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

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