smooth repartition of the intensity among the various vibrational modes, with visible as well as Soret excitation; (iii) dispersion of the depolarization ratios. For example, the depolarization ratio of the 1535-cm^{-1} mode of complex **1** varies from 0.4 at 454.5 nm to 0.6 at 514.5 nm and 0.75 at 530.8 nm whereas the depolarization ratio of the 1552-cm^{-1} mode of Fe(TPP)Cl is 0.12 at 454.5 and 514.5 nm, in agreement with the expected value of 0.125 for a polarized mode in D_{4h} symmetry. The comparison is not so striking in the case of complex **2**, as there is already some dispersion for the vibrations of Ni(TPP) itself, this molecule having the S_4 symmetry.[11]

Discussion

Complex **1** possesses only one plane of symmetry, thus belonging to the C_s point group, and complex **2** has no element of symmetry. This drastic departure from fourfold symmetry does not show up on the absorption spectra: no splitting of the $\alpha\beta$ bands is observed in the Ni series (**2**, $\lambda_{max}(\alpha\beta)$ 615 (sh) and 548 nm, in C_6H_6; NiTPP, λ_{max} 525 nm), while the hyper character of the spectra of the Fe^{III} complexes already precludes such an observation. The symmetry lowering is expected to alter the Raman spectra in the following ways: the number of vibrational modes should increase, as the out-of-plane modes of E_g symmetry become RR active, and the depolarization ratios should become dependent on the excitation frequencies, as the symmetric and antisymmetric invariants are mixed in low-symmetry groups. Actually these features are observed in the spectra of complexes **1** and **2** and thus are a mere consequence of the lowering of symmetry.

Dispersion of the depolarization ratios renders more difficult the assignment of the spectrum of the Fe insertion complex in terms of marker bands, A, B, C, and D.[3] Let us recall that the occurrence of B (dp) and the frequency of band D (p) are dependent on the presence of a pentacoordinated species[3] whereas the frequencies of band A (p) and C (ap) are sensitive to both the spin and oxidation states of the iron according to ref 12 or mostly to the spin according to ref 3. Bands A and C may still be clearly identified with use of the following criteria: intensity enhancement with blue excitation for band A and depolarization ratio higher than 0.75 for band C.

Linear relationships have been proposed linking band C frequency to the core radius of metalloporphyrins.[3,13] They cannot be used for such distorted structures as the ones considered here. A more complete equation has been derived in which ν_c frequency is linked to both the core radius and the tilt of the pyrroles.[14] It does not seem relevant here, inasmuch as each pyrrole unit is tilted differently over the mean 4 N plane.[5,9] From a qualitative point of view one may notice that the ν_c frequency of complex **1** is among the lowest measured for this band. In agreement with this finding, though a core radius cannot be strictly defined, a rather large mean value of 2.10 Å is obtained from the $C_t\cdots N_1(N_2,N_3)$ and $C_t\cdots N_4$ distances, calculated by triangulation from the X-ray data.[5] For complex **2** a higher value is measured for ν_c and a lower "core radius" (2.07 Å) is calculated from X-ray data.[15]

Previous RR studies of Fe(TPP) derivatives[3,12] have emphasized the role of spin in the determination of the Raman frequencies, so that one may question our choice of Fe(TPP)(Cl) as a reference compound. The RR data available for intermediate-spin derivatives[16-18] show that they are closer to those of low-spin than those of high-spin complexes. Accordingly the choice as a reference of a low-spin hexacoordinated Fe^{III} complex such as Fe(TPP)(Im)$_2$Cl or of a low-spin pentacoordinated Fe^{II} complex such as Fe(TPP)(CS) would have been relevant too. With use of RR data of these reference compounds[3,12] the lowering of the high-frequency doublet would be even more important.

The C_β–C_β and C_α–C_m stretches are predominant in the high-frequency modes.[19] Though the C_β–C_β and C_α–C_m bond lengths of complexes **1** and **2** are not different from those of regular D_{4h} metalloporphyrins, the tilt of one pyrrole unit (N_4) brings the corresponding C_β–C_β bond out of the mean 4 N plane (for example, in complex **2**, dihedral angles between the 4 N plane and pyrroles N_1–N_4 are respectively 13.3, 5.9, 3.6, and 46.4°).[15] Thus, the π conjugation within the macrocycle is decreased; as a consequence, the corresponding vibrational frequencies are decreased.

In summation, occurrence of new vibrational modes below 1000 cm^{-1}, dispersion of the depolarization ratios, and frequency lowering of the two highest porphyrinic vibrational modes are characteristic features of the RR spectra of ligand-inserted metalloporphyrins. Studies are under way to show that those features are to be expected whenever one of the pyrroles is severely tilted.

Registry No. **1**, 79311-02-7; **2**, 55822-49-6.

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Texas A&M University, College Station, Texas 77843

Oxidation of 2,6-Di-*tert*-butylphenol by Molecular Oxygen. Catalysis by Tetrakis(bipyridyl)(μ-peroxo)(μ-hydroxo)dicobalt(III)

Stephen A. Bedell[1] and Arthur E. Martell*

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The active sites in metalloenzymes contain coordinated metal ions in a molecular environment that is favorable for the formation of dioxygen complexes that may be involved as intermediates in biological oxidations.[2] For example, cytochrome P-450 enzymes contain iron porphyrin complexes similar to those functioning as oxygen carriers in the transport and storage proteins hemoglobin and myoglobin.[3] Recent studies of the active sites of tyrosinase, responsible for the hydroxylation of tyrosine, suggest an active center able to bind dioxygen to copper in a binuclear fashion.[4] A binuclear copper(I) model has also been suggested as the active site of the arthropod oxygen-transport protein hemocyanin.[5]

Models for such oxidation catalysts generally involve the "end-on", σ-type complexes, because of their similarity to dioxygen-binding complexes in biological systems. The cobalt–Schiff's base–dioxygen complex systems have been the

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[1] Abstracted in part from a dissertation to be submitted by Stephen A. Bedell to the Faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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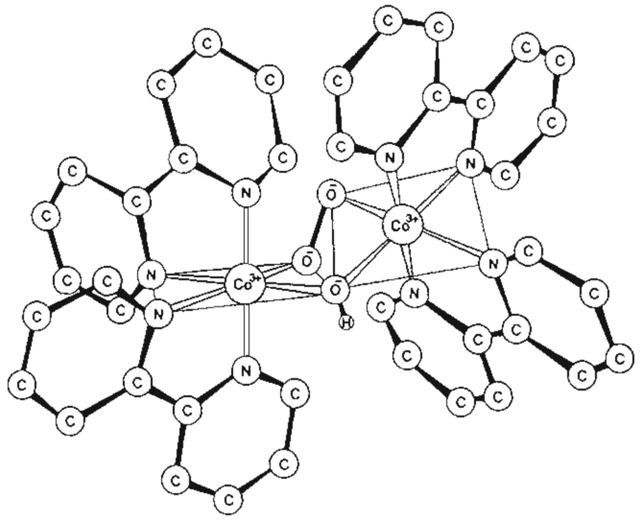
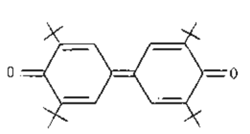
most widely investigated.[6,7] To a lesser degree, porphyrin complexes of iron and cobalt have been studied as catalysts for various oxidations.[8,9] Although some copper complexes have proven to be extremely efficient oxidation catalysts[10-12] and presumably involve dioxygen complex intermediates, the nature of the dioxygen adduct has not been determined.

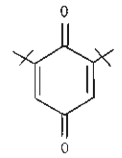
We now report the catalytic oxidation of 2,5-di-*tert*-butylphenol by molecular oxygen in the presence of bis(bipyridyl)cobalt(II) through the formation of the dioxygen complex tetrakis(bipyridyl)(μ-peroxo)(μ-hydroxo)dicobalt(III) (**1**).



1 TETRAKIS(DIPYRIDYL)-μ-PEROXO-μ-HYDROXODICOBALT(III) (SCHEMATIC)



2 3,5,3',5'-TETRA-t-BUTYLDIPHENOQUINONE (DPQ)



3 2,6-DI-t-BUTYLBENZOQUINONE (BQ)

Experimental

In a typical experiment, the bis(bipyridyl)cobalt(II) complex is formed in a 95 wt % methanol–water mixture and 0.5 equiv of potassium hydroxide is added under oxygen at 1 atm. The reaction vessel is water jacketed and maintained at 35.00 ± 0.05 °C. Inlet and outlet tubes ensure a steady supply of oxygen, which is passed first through an Ascarite absorption tube and then through a 95% methanol scrubber. A separate experiment showed, by visible absorption spectra, that the bis(bipyridyl)cobalt(II) complex at the concentrations employed was completely oxygenated within 30 min after addition of the potassium hydroxide. After sufficient time was allowed for complete oxygenation of the cobaltous complex, an aliquot of the substrate, 2,6-di-*tert*-butylphenol, was added. During the reaction, samples were withdrawn through a septum with a microliter syringe and injected into a Hewlett-Packard 5830A gas chromatograph, fitted with a 6-ft × 8-in. 80–100 WAW column with 10% UCW-982. As an internal standard, 1,2,4,5-tetramethylbenzene was added to the reaction vessel. Reactions were followed by the disappearance of the chromatographic peak for 2,6-di-*tert*-butylphenol.

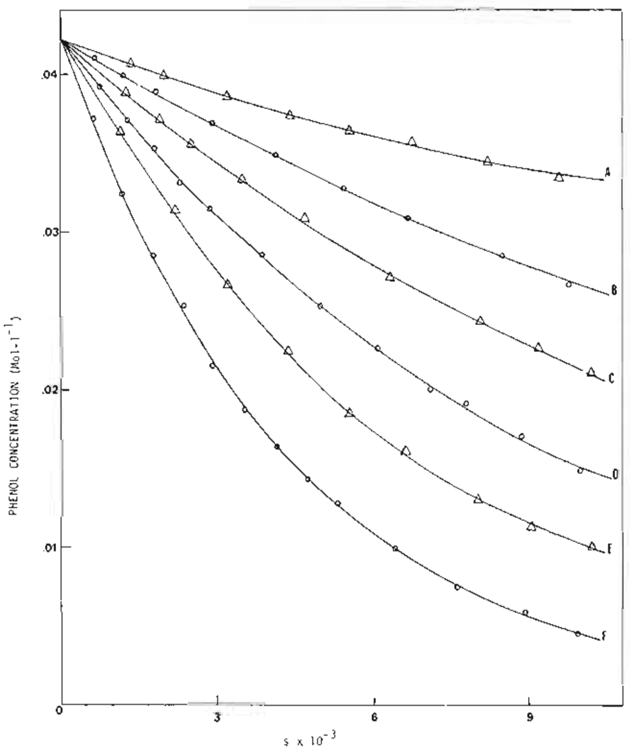


Figure 1. Plot of 2,6-di-*tert*-dibutylphenol concentrations vs. time. Initial phenol concentration = 0.0423 M. $[Co_2(bpy)_4O_2(OH)]^{3+}$ concentrations: A, 0.0053 M; B, 0.0106 M; C, 0.0159 M; D, 0.0212 M; E, 0.0317 M; F, 0.0423 M.

During the course of the reaction, a precipitate formed which was identified by elemental analysis, NMR, and its mass spectrum as 3,3',5,5'-tetra-*tert*-butyldiphenoquinone (DPQ, **2**). Also produced and identified by gas chromatography–mass spectrometry was the oxygen-insertion product 2,6-di-*tert*-butylbenzoquinone (BQ, **3**). Product analysis by 90- and 200-MHz NMR was carried out on chloroform solutions prepared by evaporation of the reaction mixture and dissolving the residue in chloroform, followed by extraction of the cobalt complex with water.

Results and Discussion

Figure 1 shows a plot of substrate concentration vs. time for various cobalt complex concentrations. A plot of ln [substrate] vs. time produced straight lines with slope = k_{obsd}. A plot of ln k_{obsd} vs. ln [catalyst] produced a straight line with a slope equal to 1.00 ± 0.06, indicating first-order dependence on the dioxygen complex concentration. The y intercept corresponds to the logarithm of the second-order rate constant, $k = (4.6 \pm 0.4) \times 10^{-3}\ M^{-1}\ s^{-1}$. Similar variation of di-*tert*-butylphenol concentration shows first-order rate dependence and results in a calculated rate constant in good agreement with that above.

The rate law can then be written as

$$\frac{-d[\text{phenol}]}{dt} = k[Co(bpy)_2O_2(OH)Co(bpy)_2{}^{3+}][\text{phenol}]$$

The formation of the binuclear, dibridged oxygen complex in aqueous solution has been studied in detail.[13] Although the present work was done in 95% methanol, electronic absorption spectra similar to that of the aqueous system indicate that the formation of the binuclear dioxygen complex also occurs in this medium. Further evidence is the intense brown color produced upon addition of the potassium hydroxide to the completely formed cobaltous complex, indicative of the pH-

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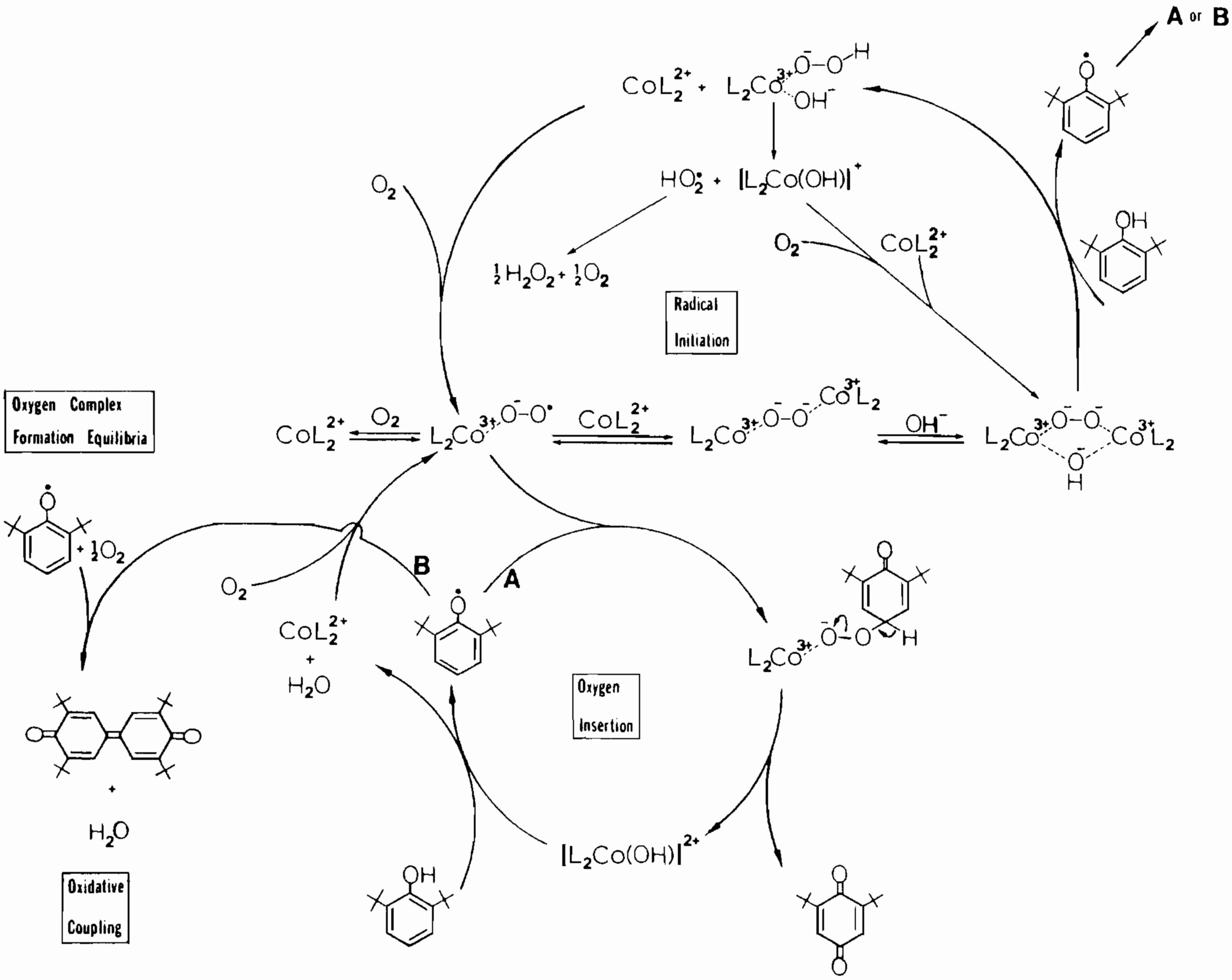

Figure 2. Proposed scheme for oxidation of 2,6-di-*tert*-butylphenol by molecular oxygen, with tetrakis(bipyridyl)(μ-peroxo)(μ-hydroxo)dicobalt(III) as a catalyst.

dependent olation reaction of the monobridged dioxygen complex.

The possibility that the oxidation of the phenol takes place via the well known base-catalyzed oxidation reaction[14,15] was ruled out by running the reaction in the absence of the metal complex at the same pH. No reaction occurred under these conditions within the time span of the catalytic kinetic runs described above.

The tendency toward irreversible oxidation of the oxygen complex to an inert cobalt(III) complex incapable of maintaining its ability to complex dioxygen was considered. In a separate experiment, the dioxygen complex was formed under conditions employed in catalytic studies at a concentration of 0.0423 M. Electronic absorption spectra indicated a constant dibridged oxygen complex concentration throughout the lifetime of the catalytic runs.

Figure 2 shows a proposed mechanism for the reaction. Although Drago[7] suggested hydrogen abstraction by the mononuclear cobalt–oxygen complex of salen [bis(salicylaldehyde ethylenediimine)], it is reasonable to expect that the peroxo-bridged species could also abstract hydrogen from the phenol. However, the mononuclear species is in equilibrium with the dinuclear oxygen complex, and is indicated as the reactive intermediate in Figure 2. The role of a metal–substrate–peroxide complex shown in step A is supported by the work of Nishinaga,[16] who was able to isolate (peroxy-*p*-quinolato)cobalt(III) complexes in the oxygenation of 4-alkyl-2,6-di-*tert*-butylphenols with Co(II) Schiff base complexes as catalysts. After formation of this intermediate, bond scission and protonation produce the benzoquinone and the hydroxocobalt(III) chelate, which serves as the active hydrogen abstractor in the catalytic cycle.

The 2,6-di-*tert*-butylphenoxy radical is required for the formation of DPQ, and observation of the latter as a reaction product may be taken as an indication of the phenoxy radical as an intermediate (reaction sequence B). The phenoxy radical may also interact with the activated dioxygen to produce the partial oxygen-insertion product, BQ, through sequence A. Sequence A is favored over sequence B at high dioxygen complex concentrations. The amount BQ produced ranged from about 8 to 27% (the remainder was DPQ) as the ratio of phenol to dioxygen complex was decreased from 8.0 to 0.4.

Studies of the oxidation of this phenol and other substrates with poly(amine)cobalt(II) complexes as catalysts are continuing in this laboratory. The wide range of stabilities and metal–dioxygen coordinate bond strengths available with cobalt(II)–poly(amine) complexes[17,18] may provide interesting

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

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Registry No. **1**, 83897-67-0; **2**, 2455-14-3; **3**, 719-22-2; oxygen, 7782-44-7; 2,6-di-*tert*-butylphenol, 128-39-2; bis(bipyridyl)cobalt(II), 15878-94-1.

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.[6–10] 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 $(FeTPP)_2O$ (**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 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.

Table I

no.	compd[a]	temp, K	isomer shift,[b] mm/s	quadrupole splitting, mm/s	ref
1	$(FeTPP)_2O$	131	0.40 (1)	0.62 (1)	this work
2	$[(FeTMP)_2O]ClO_4$	77	0.39	0.57	8
3	$[(FeTMP)_2O](ClO_4)_2$	77	0.38	0.51	8
4	$(FeTPP)_2N$	131	0.18 (1)	1.08 (1)	this work
5	$[(FeTPP)_2N]ClO_4$	131	0.03 (1)	2.00 (1)	this work
6	$(FeTPP)_2C$	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.

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 $(FeTPP)_2N$ (**4**) to the monocation[15,16] $(FeTPP)_2N^+$ (**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 at the iron. The μ-carbido dimer[17] $(FeTPP)_2C$ (**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

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

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0020-1669/83/1322-0367$01.50/0