X-ray Photoelectron Spectroscopic Studies on Monomeric and Dimeric Iron Porphyrins

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Abstract: The Fe $2p_{3/2}$ and N 1s X-ray PES binding energies for the dimeric iron porphyrin complexes μ-nitrido-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron] and μ-oxo-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron] are reported. In addition, X-ray PES binding energies for the monomeric $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron cation with selected anions (ClO_4^-, Br^-, Cl^-, and N_3^-) are found to be correlated with the half-wave potentials for reduction in the noncoordinating solvent dichloromethane. Comparisons are made between the previously reported infrared, Mössbauer, X-ray crystallographic, magnetic susceptibility, and electrochemical results and the X-ray PES data in an attempt to unambiguously assign the electron environment of the μ-nitrido complex. In contrast to the μ-oxo dimer and the monomers, the electronic configuration about each five-coordinate Fe atom in the μ-nitrido dimer has been shown to be low spin.

Introduction

Recently, the synthesis,[2] molecular stereochemistry,[3] and electrochemistry[7] of $(TPPFe)_2N$[4,5] have been reported. This compound is the first μ-nitrido complex bridging two first-row transition metals to be synthesized and, as such, studies of its physical and chemical properties are of some interest.

Magnetic susceptibility measurements[2] of $(TPPFe)_2N$ indicate a magnetic moment of $\mu_{eff} = 2.04\ \mu_B$ per dimeric unit which is virtually independent of temperature, and which has been interpreted as arising from one unpaired electron per dimer. The Mössbauer spectrum at 300 K is sharp and indicates that on the time scale of the experiment (10^{-7} s) the two Fe atoms are equivalent. Thus, based on the N(−III) charge assignments of bridging nitrogen atoms for second- and third-row transition-metal complexes,[6] and the Mössbauer data, both Fe atoms in the dimer were considered as possessing a formal Fe(III ½) oxidation state.[3] The alternative formalism of an Fe(III)/Fe(IV) dimer with rapid electronic exchange is also plausible. However, these are both formalisms and the actual oxidation state of the Fe atom is unknown. Likewise, the spin state of the Fe center is open to question. In contrast to the well-characterized $(TPPFe)_2O$, the electronic ground state of the μ-nitrido dimer has not been unambiguously assigned.

Mössbauer data have been interpreted[2] as being closer to a low-spin Fe(III) than to a high-spin Fe(III), although neither of these assignments fits the data very well. Crystallographic data[3] show that the Fe atom of $(TPPFe)_2N$ is displaced from the plane of the four porphinato nitrogen atoms by 0.32 Å. This displacement is substantially shorter than for most high-spin complexes of iron(III) porphyrins[5] and, based on this, a low-spin ground state has been suggested.[3] Electrochemical results for $(TPPFe)_2N$ add nothing to support any argument for a particular spin assignment or metal oxidation state, but do reveal a remarkable stabilization of the iron atoms' oxidation state(s). Comparison of reduction potentials between $(TPPFe)_2N$ and the isoelectronic $[(TPPFe)_2O]^-$ in CH_2Cl_2 shows a 690-mV stabilization of the former complex.

In earlier ESCA studies of porphyrins,[8-15] X-ray PES has been utilized successfully for elucidating rapid chemical exchange. Most notable has been the location of the inner hydrogen atoms of the free-base porphyrin. X-ray studies[16] have indicated two N–H bonds diagonally situated, while ^{13}C[17] and ^1H NMR[18] gave evidence for a rapid N–H tautomerism in solution. This problem was finally resolved by X-ray PES data that clearly showed two nonequivalent nitrogen types in the free-base porphyrin. It was hoped that, in the present study, a resolution of the Fe oxidation state(s) in $(TPPFe)_2N$ could be obtained from X-ray PES. Since the time scale of this technique is 10^8 faster than the Mössbauer time scale (10^{-15} vs. 10^{-7} s), it was hoped that we might be able to resolve two separate Fe peaks, one for Fe(III) and a second, at higher binding energy, for Fe(IV). It was also hoped that we would be able to resolve the binding energy of the bridging nitrogen from that of the eight pyrrole nitrogens.

Experimental Section

Materials. $(TPPFe)_2O$ and TPPFeCl were used as received from Strem Chemical Co. $(TPPFe)_2N$ was the generous gift of Professor Irwin Cohen. TPPFeBr, $TPPFeClO_4$, and $TPPFeN_3$ were prepared by acid hydrolysis of $(TPPFe)_2O$ according to literature methods.[19,26] OEPFeCl and $OEPFeClO_4$ were synthesized by the methods of Dolphin et al.[20] The supporting electrolyte, TBAP, was purchased from Eastman Chemicals and dried in vacuo prior to use. CH_2Cl_2 was obtained from Fisher Scientific and was distilled from P_2O_5 prior to making the electrochemical measurements.

Electrochemistry. The polarographic equipment has been described in a previous publication.[21] All solutions were made to 0.10 M TBAP in CH_2Cl_2 and 1.5 mM in porphyrin. Potentials are reported in volts vs. the saturated calomel electrode.

X-ray Photoelectron Spectroscopy. The X-ray PES spectra were recorded on a Hewlett-Packard 5950A spectrometer at a probe temperature of 300 K, using monochromatized Al Kα X-ray radiation. The temperature was also lowered to 283 K for analysis of the dimeric compounds, but no appreciable effect of temperature was observed. The spectrometer system and our preparation of samples for use with it have been previously described.[12,13] Charging of insulating compounds was minimized by preparing sample films thin enough that photoelectrons from the gold substrate were readily detectable.[13,22] This procedure has been applied successfully elsewhere.[13,23] Since it is difficult to establish a valid external reference-energy level for insulators,[22] we have chosen the hydrocarbon C 1s peak as a convenient internal reference for all binding energies reported here, and have assigned it the value of 284.5 eV. Any differences in binding energy of 1s electrons due to contaminant hydrocarbons are likely to be very small.[22] With the use of the flood gun of the X-ray PES spectrometer we observed that all photopeaks from a given insulating sample were shifted by the same amount (within the error of measurement) when the induced positive surface charge on an insulating porphyrin was reduced by very low kinetic energy electrons. Quoted binding energies are reproducible to a precision of ±0.1 eV for N 1s and Cl $2p_{3/2}$ electrons. Because of band broadening the uncertainty in the measurement of Fe $2p_{3/2}$ electron energies ranged from ±0.2 to ±0.5 eV, depending on the compound.

Results

The binding energies of N 1s, Fe $2p_{3/2}$, and, where appropriate, Cl $2p_{3/2}$ electrons of the selected iron porphyrin com-

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Table I. Binding Energies and Half-Wave Potentials for a Series of Monomeric Iron(III) and Iron(II) Porphyrins

porphyrin	counterion, X^-	$E_{1/2}$, V[a]	Fe $2p_{3/2}$[b]	binding energies,[c] eV N 1s	 Cl 2p
$[TPPFe^{III}]^+$	N_3^-	−0.42	710.5 (4.0)	398.5	
	Cl^-	−0.30	711.2 (4.4)	398.5	198.4
	Br^-	−0.23	711.8 (5.0)	398.7	
	ClO_4^-	+0.21	712.3 (5.0)	398.6	207.7
$[OEPFe^{III}]^+$	Cl^-	−0.50	710.9 (4.0)	398.4	198.1
	ClO_4	+0.11	711.9 (5.0)	398.4	207.5
$[NCH_3TPPFe^{II}]Cl$[d]			709.3 (3.0	398.2	(198.0)

[a] Electrode reaction TPPFeX + e ⇆ TPPFe; measured in CH_2Cl_2 containing 0.1 M TBAP, potential referenced to SCE. [b] Bandwidth in electronvolts given in parentheses. [c] Binding energies referenced to C 1s = 284.5 eV. [d] Reference 13.

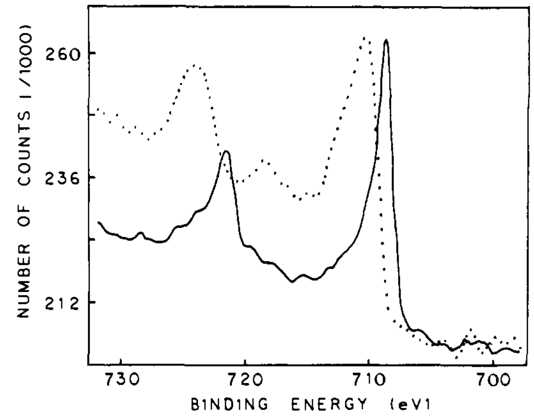

Figure 1. X-ray photoelectron spectrum of [—] $(TPPFe)_2N$ and [···] $(TPPFe)_2O$.

Table II. Binding Energies for Dimeric Iron Porphyrins

porphyrin	metal oxidation state	binding energy,[b] eV Fe $2p_{3/2}$[a]	 N 1s
$(TPPFe)_2N$	see text	708.5 (1.6)	398.3
$(TPPFe)_2O$	3	710.5 (3.1)	398.3

[a] Bandwidth in electronvolts given in parentheses. [b] Binding energies referenced to C 1s = 284.5 eV.

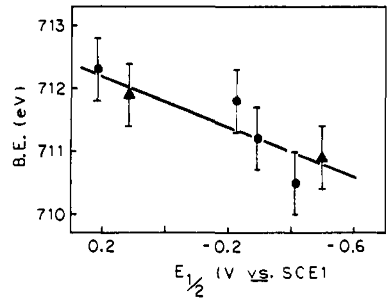

Figure 2. Plot of Fe $2p_{3/2}$ binding energy vs. half-wave potential for reduction of TPPFeX and OEPFeX in CH_2Cl_2, 0.1 M TBAP. For compound identification, see Table I.

plexes were measured and are listed in Tables I and II, along with the full width at half-height for Fe $2p_{3/2}$ bands. X-ray photoelectron spectra typical of the Fe 2p binding energy region (700–730 eV) are depicted in Figure 1. The peak of lower binding energy (BE) is assigned to the Fe $2p_{3/2}$ spin component while that at higher BE is assigned to Fe $2p_{1/2}$. None of the monomeric complexes yielded Fe 2p spectra in which the $^3/_2$ component could be resolved with confidence into its several constituent peaks, even though there are excellent grounds for affirming their existence (vide infra).

Included in Table I are the polarographic half-wave potentials for the electroreduction of each monomeric complex, which were measured at a Pt button in CH_2Cl_2. In this nonbonding solvent, the complex exists in the associated form TPPFeX (where X = the counterion ClO_4^-, Br^-, Cl^-, or N_3^-) rather than as the dissociated $TPPFe^+$ species. This has been confirmed by conductivity measurements[24] and NMR[25] for $TPPFeClO_4$.

The Fe $2p_{3/2}$ binding energies for all monomeric TPPFeX complexes were found to be linearly related to their respective polarographic half-wave potentials for reduction of Fe(III). This is illustrated in Figure 2. Included in this plot are the complexes OEPFeCl and $OEPFeClO_4$. The least-squares best fit of the data yields $\Delta BE/\Delta E_{1/2}$ of 2.1.

Discussion

Monomeric Species. Binding energies of Fe $2p_{3/2}$ observed in this study for monomeric Fe(III) complexes ranged from 710.5 eV for $TPPFeN_3$ to 712.3 eV for $TPPFeClO_4$. This latter complex has been characterized as possessing an intermediate spin state ($S = {^3/_2}$)[25,26] while the remaining five-coordinate complexes are high spin ($S = {^5/_2}$). As seen in Table I, all complexes gave extremely broad metal peaks (4–5 eV width at half-height), generally characteristic of paramagnetic transition-metal ions. Carlson[27] has discussed at length the considerable problem of band broadening in paramagnetic transition-metal complexes, considering both multiplet splitting and shakeup and shake-off processes. For the present series of complexes, the multiplet splitting will be chiefly determined by two factors: the extent of decoupling in the 3d orbital due to strong field ligand bonding and the extent to which the 3d electrons are delocalized in the complex. The d^5 case is the simplest for multiplet splitting since only two final states can occur following photoionization from a p orbital, neglecting configuration interaction.[27] Thus calculations have been made[28] which have included multiplet, splitting, spin-orbit coupling, and crystal-field effects on the 2p spectrum of Mn(II) in MnF_2 (Figure 5.27 of ref 27). This calculated 2p spectrum reproduces the essential details of the experimental spectra observed for the TPPFeX complexes and for $(TPPFe)_2O$ (Figure 1), all of which are very similar in appearance with the notable exception of $TPPFeClO_4$, which has $S = {^3/_2}$.

As expected, the increase in binding energy of Fe core electrons in the monomers was inversely related to the ability of the counterion to donate electron density to the Fe center. $TPPFeClO_4$ had the highest Fe $2p_{3/2}$ BE observed in this series, which is consistent with the previous assignment of the ClO_4^- counterion as a weak-field ligand.[26,29] Likewise TPPFeX, where X is the strong-field ligand Br^-, Cl^-, or N_3^-, had proportionately lower Fe $2p_{3/2}$ BE as more electron density was donated by the ligand to the metal.

If the binding energy shifts are related to a change in charge density about the Fe(III) center, it is reasonable to assume that the same variations in electron density should also be reflected in polarographic half-wave potentials for reduction. This was observed as shown in Table I. Here, as the counterion increased in field strength, a substantial shift to more negative potentials was observed. This cathodic shift reflects the ability of the counterion to stabilize the positively charged Fe(III) center. To demonstrate that both experimental methods are affected by and are a measure of the same underlying forces, a plot of Fe $2p_{3/2}$ BE vs. $E_{1/2}$ for the $Fe^{III/II}$ couple was constructed (Figure 2). The linear correlation observed substantiates the claim.

In an earlier X-ray PES study of Ag(II) and Ag(III) porphyrins,[9] a 0.7-eV difference was observed between the N 1s binding energies for TPPAg and OEPAg. The increase in positive charge on nitrogen for the TPPAg complex was due to the electron-withdrawing nature of the four porphyrin phenyl substituents compared to the eight electron-donating ethyl groups. In other studies, in which a series of first-row transition-metal complexes of the form TPPM(II)[12] or OEPM(II)[8] was investigated, little change in the BE of N 1s was observed over the series. In the present study, the complexes OEPFeCl and $OEPFeClO_4$ were included for comparison on this point.

It is readily apparent from the N 1s and Fe $2p_{3/2}$ binding energies listed in Table I that for Fe(III), at least, little of the Fe(III)-center charge stabilization by the counterion is detected at the pyrrole-nitrogen core. Thus, for a closely related series of monomeric species, it appears that no difference is discernible between electron density supplied equatorially (from the porphyrin structure) or axially (from the metal counterion).

Dimeric Species. Binding energies for $(TPPFe)_2O$ and $(TPPFe)_2N$ are shown in Table II. As seen from Figure 1, the former complex resembles the other high-spin complexes of TPPFeX and OEPFeX in that the peaks are broad (4 eV at half-height) and satellite structure is abundant, indicating a highly paramagnetic species. Binding energies are consistent with the other complexes in the series (Table I). It is important to note that the general appearance of the $(TPPFe)_2O$ spectrum (Figure 1) is almost identical with that of TPPFeCl, although the peaks are a bit narrower. As noted above, the form of this 2p spectrum is very well reproduced by the calculations of Gupta and Sen[28] for MnF_2 (see Figure 5.27 of ref 27).

For the $(TPPFe)_2N$ molecule only a single narrow peak is observed for Fe $2p_{3/2}$. This clearly indicates the presence of one type of Fe atom on the X-ray PES time scale (10^{-15} s) and seems to rule out the possibility of exchange between two nonequivalent Fe atoms in the dimer. The peak width at half-height is 1.6 eV, totally unlike the broad peaks for $(TPPFe)_2O$. In fact, the general appearance of the 2p region agrees with results for the diamagnetic d^{10} complex $(NCH_3)TPPZnCl$,[13] and strongly implies low-spin Fe in the dimer. This could either be one low-spin and one high-spin Fe with an electron hopping rapidly between them, which now appears unlikely in view of the X-ray PES time scale, or alternatively could indicate that there are two low-spin iron atoms in the dimer.

Extreme care must be taken in comparing BEs between monomeric and dimeric complexes. However, it is interesting to note that the BE of 708.5 eV for $(TPPFe)_2N$ is almost 4 eV below that for $TPPFeClO_4$. Furthermore, this BE is below that for Fe(II) in $(NCH_3)TPPFeCl$ and is close to those for other Fe(II) complexes such as $TPPFe(py)_2$ and $K_4Fe(CN)_6{\cdot}3H_2O$.[8] This substantial increase in electron density is consistent with the IR data[2] for $(TPPFe)_2N$, which shows the strong electron-donating ability of the nitride presumably due to the low electronegativity and high negative charge of an N^{3-} bridge. The IR data also indicated that the nitride bridge of $(TPPFe)_2N$ does not carry as great a negative charge as in other M_2N systems.[6] This would be shown in X-ray PES by more electron density (lower BE) at the central metal atom and less at the nitrido nitrogen (higher BE). This is observed in the case of the central metal. The nitrogen 1s spectrum for $(TPPFe)_2N$ is of course dominated by the peak at 398.3 eV from the eight pyrrole nitrogens, but a small shoulder at 397.5 eV presents itself as a likely candidate for the nitrido contribution. This is in accord with the result of 396.6 eV for the simple nitride CrN,[30] considering the above argument from IR data.

Based on the X-ray PES results calling for equivalent Fe centers, the following formalisms might be proposed:

$$TPPFe^{III\ 1/2}–N^{3-}–Fe^{III\ 1/2}TPP \qquad (I)$$

$$TPPFe^{III}–N^{2-}–Fe^{III}TPP \qquad (II)$$

$$TPPFe^{II}–N^{0}–Fe^{II}TPP \qquad (III)$$

Formalism I is that proposed by Summerville and Cohen.[2] Its assignment is difficult to rationalize with the X-ray PES results, since the BE of the Fe $2p_{3/2}$ for Fe(III ½) is expected to be greater than that of Fe(III). Yet a BE of 708.5 eV is observed for $(TPPFe)_2N$, comparable to $(NCH_3)TPPFeCl$ (709.3 eV). With formalism II, one would expect nitrogen hyperfine structure in the ESR spectrum. This is not seen. Formalism III contradicts the Mössbauer data. The isomer shift of iron in $(TPPFe)_2N$ is 0.099 mm/s at 300 K and is thus comparable to shifts for other Fe(III) low-spin complexes.

The electrochemistry of the two dimeric systems is also unenlightening here. Comparison of the reduction potentials of the isoelectronic species $[(TPPFe)_2O]^+$ and $(TPPFe)_2N$ shows that the nitrido-bridged dimer is reduced at potentials 690 mV more cathodic than the μ-oxo dimer.[7] The magnitude and direction of the potential shift could be explained by either formalism II or III. Thus, from the available data we cannot unambiguously assign any one formalism and are forced to conclude that there exists substantial delocalization of one unpaired electron over both Fe atoms and the bridging N atom. This accords with Carlson's analysis of the factors influencing peak broadening in X-ray PES.[31] What is clearly suggested from the X-ray PES data, in contrast to the Mössbauer and crystallographic data, is that the environment about the Fe center is low spin. This marks the second case[32] of a five-coordinate iron prophyrin designated as such.

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References and Notes

(1) (a) University of Houston; (b) Purdue University.
(2) D. A. Summerville and I. A. Cohen, *J. Am. Chem. Soc.*, **98**, 1747 (1976).
(3) W. R. Scheidt, D. A. Summerville, and I. A. Cohen, *J. Am. Chem. Soc.*, **98**, 6623 (1976).
(4) Abbreviations used: μ-nitrido-bis[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron], $(TPPFe)_2N$; μ-oxo-bis[$\alpha,\beta, \gamma,\delta$-tetraphenylporphinatoiron], $(TPPFe)_2O$; $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron cation, $TPPFe^+$; octaethylporphinatoiron cation, $OEPFe^+$; tetrabutylammonium perchlorate, TBAP; dichloromethane, CH_2Cl_2; *N*-methyl[$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron] chloride, $NCH_3TPPFeCl$.
(5) W. R. Scheidt, *Acc. Chem. Res.*, **10**, 339 (1977).
(6) W. P. Griffith, *Coord. Chem. Rev.*, **8**, 369 (1972).
(7) K. M. Kadish, J. S. Cheng, I. A. Cohen, and D. A. Summerville in "Electrochemical Studies of Biological Systems", D. T. Sawyer, Ed., ACS Symposium Series, No. 38, American Chemical Society, Washington, D.C., 1977, Chapter 5.
(8) M. V. Zeller and R. G. Hayes, *J. Am. Chem. Soc.*, **95**, 3855 (1973).
(9) D. H. Karweik, N. Winograd, D. G. Davis, and K. M. Kadish, *J. Am. Chem. Soc.*, **96**, 591 (1974).
(10) Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799 (1974).
(11) H. Falk, O. Hofer, and H. Lehner, *Monatsh. Chem.*, **105**, 366 (1974).
(12) D. H. Karweik and N. Winograd, *Inorg. Chem.*, **15**, 2336 (1976).

(13) D. K. Lavallee, J. G. Brace, and N. Winograd, *Inorg. Chem.*, **18**, 1776 (1979).
(14) J. P. Macquet, M. M. Millard, and T. Theophanides, *J. Am. Chem. Soc.*, **100**, 4741 (1978).
(15) S. Kitagawa, I. Morishima, T. Yonezawa, and N. Sato, *Inorg. Chem.*, **18**, 1345 (1979).
(16) J. L. Hoard, *Science*, **174**, 1295 (1971).
(17) J. J. Katz and T. R. Janson, *Ann. N.Y. Acad. Sci.*, **206**, 579 (1973).
(18) C. B. Storm and Y. Teklu, *J. Am. Chem. Soc.*, **94**, 1745 (1972).
(19) A. D. Adler, F. R. Longo, and V. Varadi, *Inorg. Synth.*, **16**, 213–220 (1976).
(20) D. H. Dolphin, J. R. Sams, and T. B. Tsin, *Inorg. Chem.*, **16**, 711 (1977).
(21) K. M. Kadish, L. A. Bottomley, and J. S. Cheng, *J. Am. Chem. Soc.*, **100**, 2731 (1978).
(22) C. D. Wagner, "Energy Calibration of Electron Spectrometers", in press, and references cited therein.
(23) G. M. Bancroft, I. Adams, H. Lampe, and T. K. Shaw, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 191 (1976).
(24) K. M. Kadish, L. A. Bottomley, and D. Schaeper, submitted for publication.
(25) H. Goff, private communication.
(26) C. A. Reed, T. Mashiko, S. P. Bentley, M. E. Kastner, W. R. Scheidt, K. Spartalion, and G. Lang, *J. Am. Chem. Soc.*, **101**, 2948 (1979).
(27) T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, 1975.
(28) R. P. Gupta and S. K. Sen, *Phys. Rev. B*, **10**, 71 (1974).
(29) M. M. Maltempo, *Q. Rev. Biophys.*, **9**, 181 (1976).
(30) D. N. Henrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).
(31) Reference 27, p 235.
(32) TPPFeNO as reported by W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.*, **97**, 17 (1975).

On the Mechanism of Autoxidation of Iron(II) Porphyrins. Detection of a Peroxo-Bridged Iron(III) Porphyrin Dimer and the Mechanism of Its Thermal Decomposition to the Oxo-Bridged Iron(III) Porphyrin Dimer

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Abstract: Addition of dioxygen to toluene solutions of Fe^{II}P (P = a porphyrin dianion) at −80 °C leads to the formation of a new intermediate **1** which has been detected by visible and ^{1}H NMR spectroscopy. **1** reacts quantitatively with Fe^{II}P according to the equation $\mathbf{1} + 2\mathrm{Fe^{II}P} \rightarrow 2\mathrm{PFeOFeP}$. A peroxo-bridged, dimeric structure, PFe^{III}–O–O–Fe^{III}P, is proposed for **1** on the basis of its composition, its antiferromagnetism (as determined by the temperature dependence of the ^{1}H NMR contact shifts and the magnetic susceptibility, 2.1 μ_B at 181 K, 2.7 μ_B at 224 K) and the detection of a mixed ligand species involving two differently substituted porphyrins. Upon warming **1** decomposes quantitatively by the reaction $2\,\mathbf{1} \rightarrow 2\mathrm{PFeOFeP} + \mathrm{O_2}$ with no other species detected during the reaction. The dioxygen produced has been detected by mass spectroscopy and by its reaction with Fe^{II}P. The kinetics of this reaction have been determined over the temperature range −22 to −40 °C. The reaction is first order in **1** with $\Delta H^{\ddagger} = 14.5 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -15 \pm 1$ eu. Isotopic labeling of the dioxygen used to form **1** reveals that the isotopic composition of the O$_2$ released due to decomposition of **1** is identical with that used in its formation. However, when two labeled species PFeO$_2$FeP and P′FeO$_2$FeP′ are decomposed, the porphyrin ligands do scramble: PFeOFeP, P′FeOFeP′, and PFeOFeP′ all are formed. Based on these observations, a mechanism for the decomposition of **1** to PFeOFeP is proposed.

Introduction

The interaction of dioxygen with Fe^{II} compounds, particularly Fe^{II} porphyrins, has received considerable attention because of its relevance to the physiological problems of dioxygen transport, storage, and utilization. Autoxidation of simple Fe^{II} porphyrins, as well as other iron complexes, produces μ-oxo Fe^{III} dimers via the stoichiometry[1]

$$4\mathrm{Fe^{II}} + \mathrm{O_2} \rightarrow 2\mathrm{Fe^{III}\text{–}O\text{–}Fe^{III}} \qquad (1)$$

Several studies have indicated that the reaction 1 exhibits kinetic behavior which is first order in dioxygen and second order in Fe^{II} complex.[2-4] Consequently, a bridged FeOOFe species, variously described as Fe^{II}-O$_2$-Fe^{II} (dioxygen bridge)[3,5] or Fe^{III}-O$_2$-Fe^{III} (peroxo bridge),[3] has been postulated to form during the initial stages of autoxidation. However, very little is known about the structure, properties, and chemical reactivity of these postulated FeOOFe complexes. Prior to the work described here, the only cases of observation of adducts of the stoichiometry Fe$_2$O$_2$ were in the crustacean respiratory pigment hemerythrin[6] and the oxygenation of a synthetic iron macrocyclic complex.[7] However, for other metals ample precedent exists for the formation of MOOM units. The formation of Co^{III}-O-O-Co^{III} units by oxygenation of Co^{II} complexes is particularly well documented.[8] Although FeOOFe units have long remained undetected, their probable existence has exerted an influence on the synthetic chemistry involved in constructing models for the reversible dioxygen binding sites of the hemoglobins and myoglobins. In several cases, particularly in the various strapped and picket-fence porphyrins, steric bulk has been built into the iron-binding macrocycles so that the close approach is effectively prohibited.[7,10]

Because of the difficulty in detecting the FeOOFe unit, the mechanism of its conversion into the final product, the μ-oxo Fe^{III} dimer, has not been investigated. Nevertheless, some speculation on this problem has been offered. The cleavage of the O-O bond in the FeOOFe unit to form two ferryl ions, Fe^{IV}-O, has been frequently postulated.[2,3,4,10] Attack of Fe^{II} on the oxygen atoms of the FeOOFe unit via the equation

$$\mathrm{FeOOFe} + \mathrm{Fe^{II}} \rightarrow \mathrm{FeO} + \mathrm{FeOFe} \qquad (2)$$

has been proposed, but the steric congestion required to bring three metal complexes into contact with the O$_2$ unit has also been noted as a severe drawback to such a process.[11] In con-

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