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A Picosecond Kinetic Study of the Excited-State Properties of Some Osmium Octaethylporphyrins

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Abstract: Four osmium porphyrin complexes, Os(OEP)LL′ [(OEP) = octaethylporphyrin], have been investigated by picosecond laser flash photolysis using a double-beam, mode-locked Nd:glass system delivering 6-ps (fwhm) pulses at 527 nm with 1–2 mJ/pulse. Time-resolved excited-state spectra were recorded from the time of photolysis to 5 ns after photolysis. For the four compounds studied $[Os(OEP)[P(OMe)_3]_2$, Os(OEP)CO(py), Os(OEP)NO(OMe), and $Os(OEP)O_2$ [(Me = methyl, py = pyridine, and O_2 = dioxo)], the initial excited state, S_1, decayed in ≤ 8, ~50, ~36, and ~13 ps, respectively. The yields of the later excited state, T_1, were ~0.8, unmeasurable, ~0.6, and ~1.0, respectively. The T_1 states lived for times 6.2, 16, 5.5, and 6 ns, respectively. A third relaxation time of ~15 ps was found for Os(OEP)NO(OMe). The lowest energy excited states for the first two complexes were previously identified as (d,π^*) and for the second two as (π,π^*) and a red shift of the excited-state absorption of the former with respect to the latter is observed. For the two molecules with lowest energy (π,π^*) states, S_1 and T_1 are identified as $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$, i.e., singlet and triplet states. For the two molecules with lowest energy (d,π^*) states, spin should not be a good quantum number, and S_1 is identified as a limited set of (d,π^*) states produced after subpicosecond relaxation of the initial photoexcited $^1(\pi,\pi^*)$ state.

Introduction

This paper reports the results of investigations of the excited-state properties of a series of osmium(II) octaethylporphyrins, also known as osmochromes because of their relationship to the hemochromes.[2] While these molecules are interesting in themselves, there are at least three other reasons for studying them. First, they are closely related to the biologically important iron(II) porphyrins found in hemoglobin, cytochrome P450, and other redox catalysts.[2] Second, they have unique electrochemical properties that may make them useful for future photochemical studies of elementary electron-transfer processes.[3] Third, while the hemochromes, $Fe(porphyrin)L_2$, are all rather labile in solution such that reliable spectral and other physical data on these species can only be obtained in the presence of excess ligand L, the osmochromes are kinetically inert and hence are useful model compounds for the Fe(II) porphyrins.[2]

The $(nd)^6$ compounds of Fe(II), Ru(II), and Os(II) are capable of π-backbonding with both the porphyrin ring and the axial ligands.[4–6] However, the ligand-field splitting in Fe(II) is not large enough to shift the ligand-field (d,d) states above the (π,π^*) states of the porphyrin ring, thus complicating greatly the low-energy excited states in Fe(II) porphyrins. The increased sizes of the d orbitals of Ru(II) and Os(II) allow stronger interactions with the surrounding ligands and produce larger ligand-field splittings. The larger d-orbital size also suggests that π-backbonding effects will be larger and therefore amenable to study. Because the energies of the d_{xy}, d_{xz}, and d_{yz} orbitals are more nearly the same for Fe(II) and Os(II) than for Fe(II) and Ru(II), the Os(II) porphyrins are slightly better models of Fe(II) porphyrins.[7,8]

Recent work[3,9] on doubly linked diporphyrin compounds has demonstrated that excited singlet (S_1) states can yield electron-transfer (ET) products in <6 ps. An important parameter in studying the photochemistry of these elementary ET processes is the redox span of the potential ET products. The half-wave reduction potential for Os(III) porphyrin/Os(II) porphyrin couples can be varied from +0.92 to −0.56V vs. SCE simply by changing the nature of the axial ligands.[2] Thus Os(II) porphyrins can function as versatile electron donors. Inasmuch as the $S_1 \rightarrow$ ET reactions of diporphyrins studied thus far are extremely fast (τ < 6 ps), the excited-state lifetimes of the porphyrin subunits are not critical in most cases.

Osmium Porphyrin Electronic States

The spectroscopy of metal-free porphyrins can be understood in terms of the two highest occupied orbitals (HOMO's) $a_{1u}(\pi)$ and $a_{2u}(\pi)$, and the two lowest unoccupied orbitals (LUMO's), $e_g(\pi^*)$. With strong σ-donor ligands such as trimethylamine, NMe_3, and trimethyl phosphite, $P(OMe)_3$, the filled Os(II) orbitals d_{xy}, d_{xz}, d_{yz} lie above the porphyrin HOMO's.[8] In addition, the d_{xz}, d_{yz} (or d_π) orbitals of the metal can back-bond with the empty $e_g(\pi^*)$ porphyrin orbitals.[8] (The z axis is taken to be the direction of the axial ligands, perpendicular to the plane of the porphyrin ring.) The equatorial back-bonding interaction between the d_π and the $e_g(\pi^*)$ orbitals raises the energy of $e_g(\pi^*)$ relative to that of a metal-free porphyrin. If the σ-donor ligands are replaced with π-acceptor ligands, the d_π electrons shift from equatorial to axial back-bonding. The ligands pyridine (py), carbon monoxide (CO), and nitrosonium (NO^+) are increasingly good π acceptors. Along this series of ligands in Os porphyrin complexes there is increased axial and decreased equatorial back-bonding, and both the filled d_π and the empty $e_g(\pi^*)$ orbitals shift to lower energy. Experimentally the $^1(\pi,\pi^*)$ level bathochromically shifts, the lowest excited state changes from (d,π^*) to (π,π^*) and the first oxidation potential becomes more positive, changing from metal oxidation to ring oxidation.[7,8]

Two of the compounds studied in this work have (d,π^*) lowest energy excited states. They are the octaethylporphinatobis(trimethyl phosphite)osmium(II), $Os(OEP)[P(OMe)_3]_2$, and the carbonyl(octaethylporphinato)(pyridine)osmium(II), Os(OEP)-CO(py). The other two compounds have (π,π^*) lowest energy excited states. They are the methoxonitrosonium(octaethyl-

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Table I. Properties of Os(OEP)LL′

L	L′	α (nm)[a]	Os(III)/Os(II) $E_{1/2}$ (V)[b]	δ (ppm)[c]	ref
NMe_3	NMe_3	500	−0.56	7.74	2
$P(OMe)_3$	$P(OMe)_3$	522	−0.08	9.10	2, 11
CO	pyridine	537	+0.49	9.64	2, 11
NO^+	OMe	567	+0.92[d]	10.45	12
O	O	594		10.75	2, 7

[a] Wavelength of the lowest energy $\pi \rightarrow \pi^*$ absorption band. [b] Half-wave reduction potential vs. SCE. [c] Chemical shifts of the porphyrin methine protons. [d] Probably ring oxidation.

porphinato)osmium(II), Os(OEP)NO(OMe), and the dioxo(octaethylporphinato)osmium(VI), $Os(OEP)O_2$. The absorption spectra of these latter two compounds are of the *hyper* type.[6-8] That is, they show extra allowed absorption bands not due to transitions between porphyrin ring orbitals. In these compounds the π^* orbitals of the axial ligands (l_π^*) are low enough in energy for transitions $^1(\pi,l_\pi^*)$ to appear in the visible–near-UV absorption spectrum. Indeed, the lowest energy $^3(\pi,\pi^*)$ excited state of $Os(OEP)O_2$ is probably mixed with a higher energy $^3(\pi,l_\pi^*)$ state.[8]

It is worth noting that there is little difference between Os(II) compounds with strong axial back-bonding due to strong π-acceptor ligands and Os(VI) compounds with strong π-donor ligands.[8] In a sense, Os(VI) in $Os(OEP)O_2$ can be effectively thought of as Os(II) because the empty metal d_π orbitals are mixed with the filled p_x, p_y orbitals of the trans oxygen ligands.

Table I shows quantitatively how changing from equatorial to axial back-bonding affected experimental parameters. In particular, Table I shows the bathochromic shift of the long-wavelength absorption of the Os(II) porphyrins as ligands become better π acceptors. Switching the d_π electron density to the axial ligands also raises the half-wave reduction potential of $Os^{III}OEP(L)L'/Os^{II}OEP(L)L'$ as shown in Table I. The electron-rich d_π orbitals of $Os^{III}OEP(NMe_3)_2$ are difficult to reduce to Os(II), while the d_π levels of Os(OEP)NO(OMe) are so low in energy that the oxidized form is probably a porphyrin π-cation radical rather than Os(III).[2] Withdrawing electron density from the metal into the axial π system also deshields the methine protons. The NMR chemical shifts increase as the axial back-bonding increases. It is also noteworthy that the NMR chemical shift for Os^{II}(OEP)NO(OMe) is nearly identical with that for $Os^{VI}(OEP)O_2$. This is good evidence for the oxidation-state ambiguity that occurs in these compounds.

The objectives of this picosecond study were (a) to detect, if possible, the relaxation of the singlet excited states and to see how this is affected by the nature of the lowest energy excited states, which were expected to be (d,π^*) in some cases and (π,π^*) in others; and (b) to see if the spectra of the excited states of these molecules is dependent on whether the states are (d,π^*) or (π,π^*).

Experimental Methods

The compounds studied were synthesized according to published procedures.[11-14] The trimethyl phosphite complex, $Os(OEP)[P(OMe)_3]_2$, was found to react photochemically in chlorinated solvents. This reaction has been described more fully elsewhere.[15] The picosecond absorbance measurements were made on a double-beam, mode-locked Nd:glass laser system[16,17] employing a SIT-vidicon detector. The change-in-absorbance data (ΔA) shown at a designated time after excitation at 527 nm with a 6-ps (fwhm) laser pulse are the average of 20 pairs of laser shots. One laser shot of a pair recorded the double-beam ratios at 250 wavelengths when the sample was not excited. The other shot repeated the measurements when the sample was excited. The $\log_{10}$ of the ratio of these double beam ratios yielded the reported ΔA values. The standard deviation of the mean ΔA value is the calculated error of the measurement. For $|\Delta A|$ values less than 0.4, the error in ΔA is 0.010 to 0.015; for $|\Delta A|$ values greater than or equal to 0.4, the error in ΔA is 0.015 to 0.020. However, at the extreme ends of the spectra where the measuring light is very low, the error in ΔA can be as high as 0.02 to 0.03.

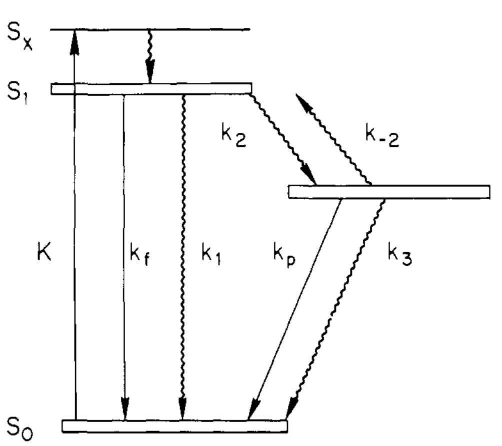

Figure 1. Decay scheme for low-lying excited states of osmium(II) porphyrins (reproduced from ref 6).

A 0.25-m double monochromator (DMC) in the subtractive dispersion mode was placed after the sample but before the final spectrograph to reject stray light. It was equipped with two 150-grooves/mm gratings and a 10-mm intermediate slit which passed about 300 nm of spectral information. However, the sharp drop in transmitted light at the edges of the band-pass region truncated the ΔA values to zero at these edges. Also, the white light used to probe the ΔA's decreased drastically below 420 nm. Therefore, the truncation in ΔA's found in this region was similar to that produced at the edges of the DMC's band-pass.

The white probe light was generated by focusing 1054-nm laser light into a 5-cm cell containing D_2O. The duration of the weak probe pulse was 8 ps (fwhm). The 6-ps excitation pulse at 527 nm contained 1–2 mJ of energy. A Laser Precision energy meter coupled to a sample-and-hold circuit and a PDP 11/03-controlled A-to-D converter ensured that data from pulses outside this energy interval were rejected. After passing through the DMC, the white probe light was dispersed by a 150-grooves/mm grating in a second 0.25-m monochromator. The 0.2-mm-wide entrance slit yielded a spectral resolution of 4.8 nm.

The triple monochromator arrangement, however, does not eliminate scattered 527-nm photolysis light in the 500–550-nm region. This is a particular problem for measuring the extent of ground-state recovery for $Os(OEP)[P(OMe)_3]_2$ and Os(OEP)CO(py) because their low energy $\pi \rightarrow \pi^*$ absorption bands are in this region. Also, the lack of probe light below 420 nm means that the recovery of their Soret bands cannot be measured. Thus the bleaching of the ground state absorbance for these compounds in the 490-nm region is used to estimate the amount of $S_1 \rightsquigarrow S_0$ internal conversion. The estimates of T_1 yield in this paper are based on the assumption that the difference in molar absorptivity between the S_1 and S_0 states is about equal to that between the T_1 and S_0 states. It is reasonable that this be true at the peak of the ground-state absorption bands. But it is less likely to be true for the above two compounds at $\lambda \sim 490$ nm, which is not a peak. In contrast, the low energy $\pi \rightarrow \pi^*$ absorption bands of Os(OEP)NO(OMe) and $Os(OEP)O_2$ are red shifted sufficiently that their ground-state recoveries can be measured easily. A second problem is caused by an occasional, intense Raman band in the probe light's 700-nm region. The ratioing of two probe pulses for each laser shot minimizes errors; however, some ΔA measurements appear distorted at ~700 nm. Notes in the appropriate figure captions point out the likely occurrences of such artifacts.

All samples were degassed by repeated freeze–pump–thaw cycles and kept in flame-sealed cells. The concentrations were in the $1-5 \times 10^{-4}$ M range and the optical path length of the cells was 2 mm.

Phosphorescence decay was detected for all porphyrin complexes except $Os(OEP)[P(OMe)_3]_2$ by redirecting the pump pulse into a black box containing the 2-mm sample cell and a Varian VPM-152 photomultiplier tube coupled to a Toktronix 7844 oscilloscope. Front surface excitation was used and scattered 527-nm laser light was absorbed by appropriate cutoff filters. With this setup, emission lifetimes as short as 2 ns could be measured.

Results

The general picture for radiationless decay in the (π,π^*) states of porphyrins, as in other aromatic molecules, is shown in Figure

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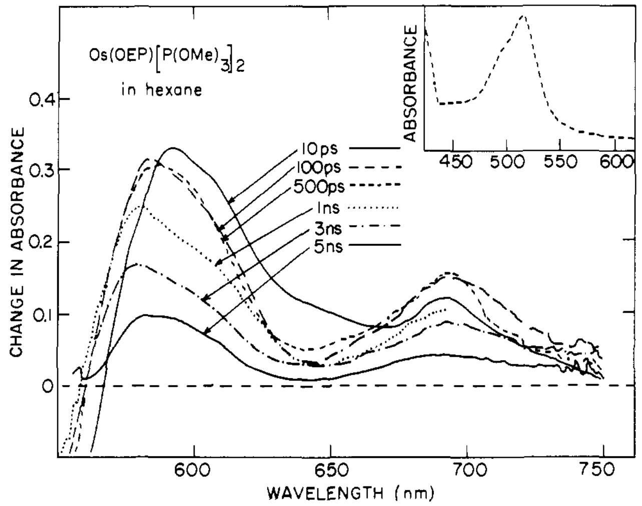

Figure 2. Change-in-absorbance spectra for Os(OEP)[P(OMe)$_3$]$_2$, 2.2 × 10^{-4} M, in hexane at the indicated times after excitation. The inset shows the ground-state absorbance profile. See the text for an error discussion. Data taken 1 ns after excitation for λ >690 nm have been omitted because of an artifact due to a Raman band in the white probe light (see text and Figure 11).

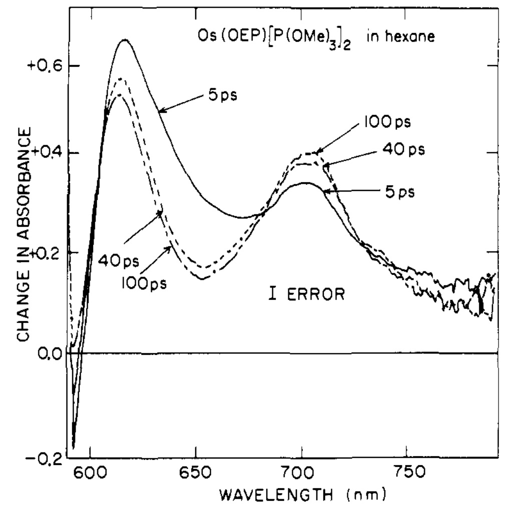

Figure 3. Change-in-absorbance spectra for Os(OEP)[P(OMe)$_3$]$_2$, 5.5 × 10^{-4} M, in hexane.

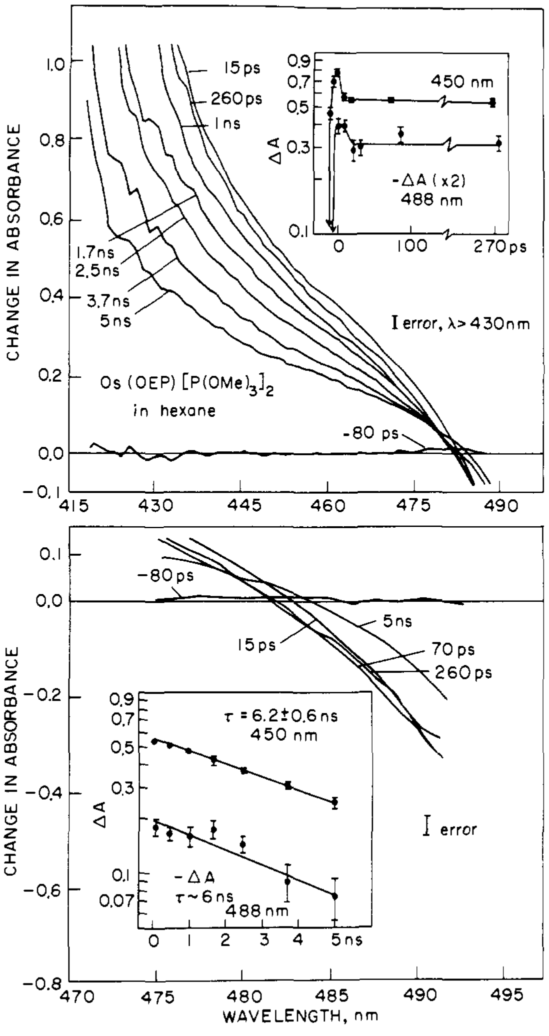

Figure 4. Change-in-absorbance spectra for Os(OEP)[P(OMe)$_3$]$_2$, 2.7 × 10^{-4} M, in hexane on the blue side of the 527-nm excitation pulse.

1.[6] Excitation from the ground state (S_0) to any singlet state (S_x) "quickly" ($\lesssim 1$ ps) relaxes to the lowest excited singlet (S_1), which can undergo intersystem crossing to the lowest triplet excited state (T_1, rate k_2) in competition with radiationless decay (k_1) and fluorescence decay (k_f) back to S_0. In turn, T_1 can decay via nonradiative transitions to S_0 (k_3), can phosphoresce (k_p), and can back intersystem cross to S_1 (k_{-2}). The porphyrin complexes reported here do not fluoresce; hence k_f is insignificant, and the decay of S_1 is set by $\tau(S_1) = (k_1 + k_2)^{-1}$. The phosphorescence quantum yields, Φ_p, for the complexes with lowest excited states $^3(\pi,\pi^*)$ were reported as 3 × 10^{-3} (77 K) for Os(OEP)NO(OMe) and 5 × 10^{-3} (300 K) for Os(OEP)O$_2$.[7] Since the triplet yield, $\Phi(T_1) = k_2/(k_1 + k_2)$, should be substantially higher than these values in a complex containing the heavy atom Os, the low observed values for Φ_p imply that $k_p << k_3$. Additionally, k_{-2} is probably negligible because the energy gap $E(S_1) - E(T_1)$ is much greater than k_BT, the Boltzmann energy.[7] The result is that we expect to observe two transient decays: one corresponds to S_1 decaying to S_0 and T_1 with $\tau(S_1) = (k_1 + k_2)^{-1}$; the second corresponds to T_1 returning to the ground state with $\tau(T_1) = k_3^{-1}$.

In the case of the Os(OEP)[P(OMe)$_3$]$_2$, no phosphorescence was observed; in the case of Os(OEP)CO(py), a weak phosphorescence of unusual character was observed with $\Phi_p = 6 \times 10^{-4}$ at 77 K.[7,8] As a result both systems are believed to have lowest energy excited states of (d,π^*) character.[7,8] In the Appendix we discuss spin–orbit coupling in such states, and it is shown that spin is not expected to be a good quantum number. Surprisingly, our transient absorbance studies for these two compounds give kinetics qualitatively similar to the studies on the compounds where the lowest energy excited states are expected to be (π,π^*), for which spin is a fairly good quantum number. As a result, for all systems we shall refer to the initial excited state as S_1 and the later excited state as T_1. In the case of two molecules with lowest energy (π,π^*) states, S_1 and T_1 can be identified with $S = 0$ and $S = 1$ excited states. In the Discussion and Appendix we consider the nature of the S_1 and T_1 states in the two molecules with lowest energy (d,π^*) states.

Os^{II}(OEP)[P(OMe)$_3$]$_2$. The transient absorbance data obtained after exciting Os(OEP)[P(OMe)$_3$]$_2$ are shown in Figures 2–4. A detailed kinetic analysis at several wavelengths (Figures 4 and 5, for example) shows transients with two relaxation lifetimes: ≤8 ps and 6.2 ± 0.6 ns. To be certain that the ≤8 ps growth of absorbance at 700 nm (Figure 2) was real, a more concentrated sample was excited. The resulting spectra are illustrated in Figure 3, which clearly shows the short-time (≤8 ps) absorbance change. The long-time (6 ns) absorbance change is quite apparent throughout the spectra in Figures 2 and 4. (See Figures 4 and 5 for kinetic plots.) Thus we initially observe an excited state, S_1, which subsequently decays to a excited state, T_1 according to a kinetic scheme:

$$S_1 \rightsquigarrow T_1 + S_0 \ (\sim 20\%),\ \leq 8 \text{ ps} \qquad \text{(Ai)}$$

$$T_1 \rightsquigarrow S_0,\ \sim 6 \text{ ns} \qquad \text{(Aii)}$$

The estimate of singlet yield is based on the return of absorbance at λ 490 nm during the first 20 ps. In later sections we discuss

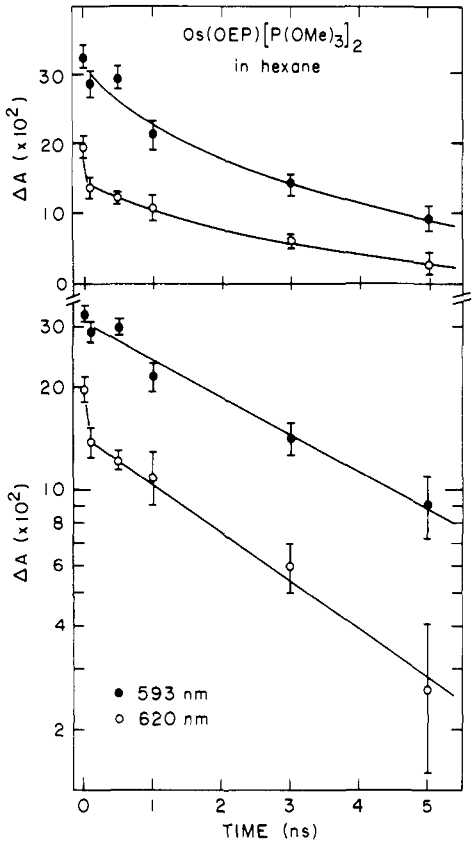

Figure 5. Change-in-absorbance plots as a function of time for Os(OEP)[P(OMe)$_3$]$_2$, at 593 and 620 nm for data taken from Figure 2. The absorbance increases at both wavelengths decay with the same lifetime, 5 ± 1 ns. In addition, a faster decay is indicated in the data at 620 nm. The data in Figure 4 show the lifetime of this decay process to be ≤8 ps.

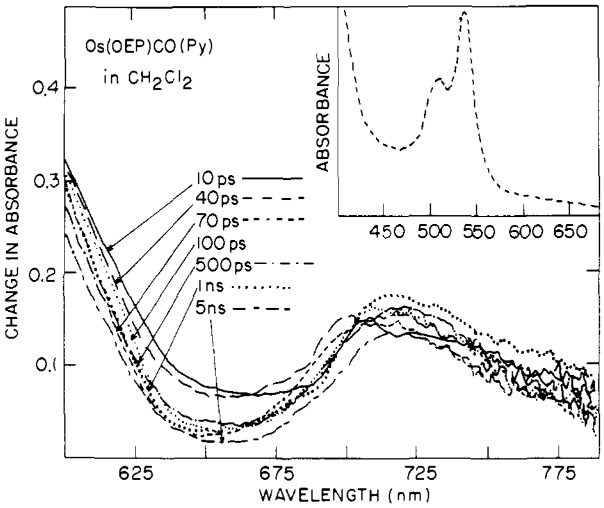

Figure 6. Change-in-absorbance spectra for Os(OEP)CO(py), 1.8 × 10^{-4} M, in methylene chloride. The inset shows the ground-state absorbance profile.

the nature of the S$_1$ and T$_1$ states.

Os^{II}(OEP)CO(py). The picosecond transient spectra are given in Figures 6 to 8. A band at 725 nm grows in with a relaxation time of 50 ± 10 ps. Interference from the scattered pump light made it impossible to estimate the ground-state recovery during this period. Another region where a 40 ± 5 ps decay of absorbance is observed is 625 to 650 nm. These data are consistent with a decay scheme:

$$S_1 \rightsquigarrow T_1 + S_0\ (?\%),\ \sim 50\ \text{ps} \qquad \text{(Bi)}$$

$$T_1 \rightsquigarrow S_0,\ \sim 16\ \text{ns} \qquad \text{(Bii)}$$

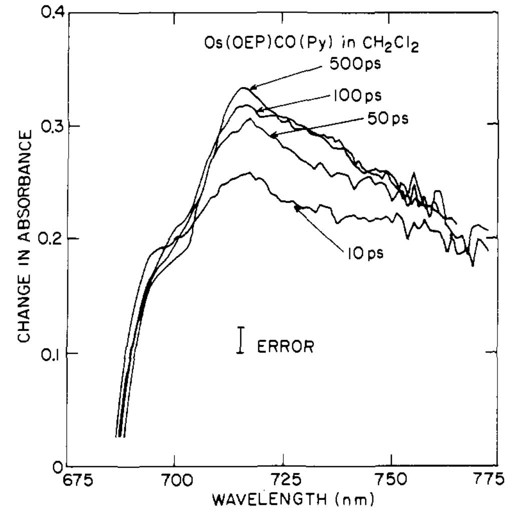

Figure 7. Change-in-absorbance spectra for Os(OEP)CO(py), 3.6 × 10^{-4} M, in methylene chloride.

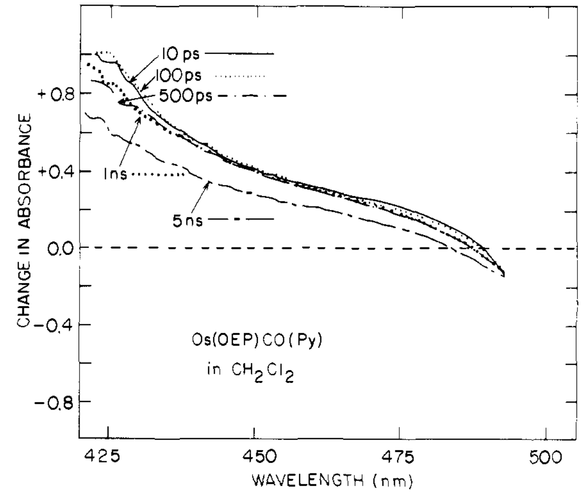

Figure 8. Change-in-absorbance spectra for Os(OEP)CO(py), 1.8 × 10^{-4} M, in methylene chloride on the blue side of the 527-nm excitation pulse.

The T$_1$ state shows very little decay during the first 5 ns of its lifetime. The T$_1$ lifetime calculated from the transient absorbance data is 10 ± 3 ns. Laser excitation enabled the phosphorescence to be detected directly (see Experimental Methods). Figure 9 illustrates the emission decay curves and the analysis; the phosphorescence decay time of this compound is 16 ± 1 ns.

Os^{II}(OEP)NO(OMe). The extent of axial back-bonding is further increased for Os(OEP)NO(OMe) by push–pull electron transmission paths. The methoxide ligand is a σ donor and the nitrosonium ion is a strong π acceptor. The change-in-absorbance data in Figure 10 show that the ground-state absorbance is restored with a time of 36 ± 7 ps at 575 nm. In addition, the absorbance feature at 600 nm appears to blue shift in 15 ± 5 ps. Based on the recovery of the ground-state absorption at 575 nm, the triplet yield is 60%. The lowest energy excited state, which is $^3(\pi,\pi^*)$, shows a broad featureless absorption from 600 to 650 nm (Figure 10). The lifetime of $^3(\pi,\pi^*)$ is 4 ± 2 ns from transient absorbance data. A more accurate lifetime is obtained from direct measurement of the phosphorescence decay, 5.5 ± 0.5 ns. The decay scheme for Os(OEP)NO(OMe) can then be described as:

$$^1(\pi,\pi^*) \rightsquigarrow {}^1(\pi,\pi^*)',\ \sim 15\ \text{ps} \qquad \text{(Ci)}$$

$$^1(\pi,\pi^*)' \rightsquigarrow {}^3(\pi,\pi^*) + S_0\ (\sim 40\%),\ \sim 36\ \text{ps} \qquad \text{(Cii)}$$

$$^3(\pi,\pi^*) \rightsquigarrow S_0,\ \sim 5\ \text{ns} \qquad \text{(Ciii)}$$

The type of change involved in step Ci is not clear at present.

Os^{VI}(OEP)O$_2$. The compound with the strongest axial back-bonding in this series of complexes is Os(OEP)O$_2$. Although it

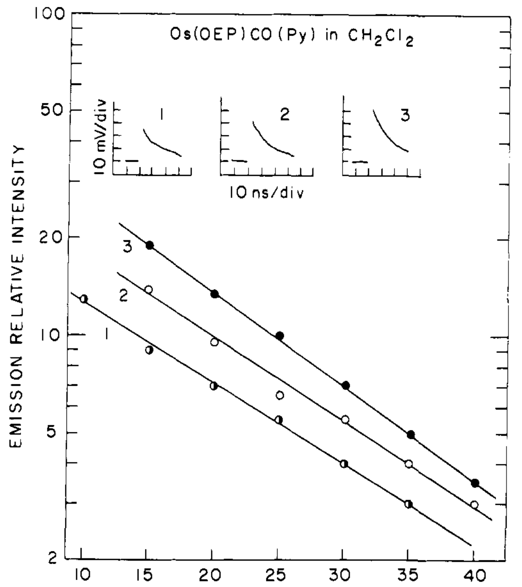

Figure 9. Phosphorescence decay curves for Os(OEP)CO(py) in degassed CH_2Cl_2 solutions. Three runs are shown. The phosphorescence lifetime is 16 ± 1 ns.

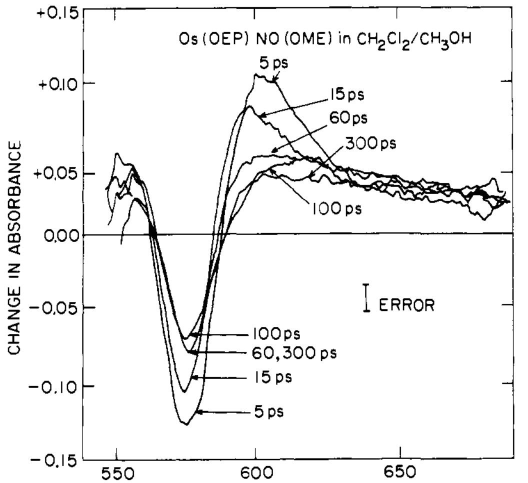

Figure 10. Change-in-absorbance spectra for Os(OEP)NO(OMe), 2.0 × 10^{-4} M, in methylene chloride/methanol (1:1).

is formally Os(VI), there is little difference between this molecule with its strong π-donor ligands and an Os(II) with strong π-acceptor ligands. The picosecond change-in-absorbance data are illustrated in Figure 11. Kinetic plots are given in Figure 12. Both the excited-state absorbance increase at ~650 nm and the ground-state bleach at 600-nm decay with times of 7.5 ± 2 ns. A direct measurement of the phosphorescence decay of 6 ± 1 ns agrees well with this value. The excited-state absorbance at ~650 nm shows an additional 13 ± 3 ps transient (Figure 12). Since the ground-state bleaching does not vary in the very short time-frame, the quantum yield of T_1 formation must be close to 100%. Thus the decay scheme for $Os(OEP)O_2$ can be described as:

$$^1(\pi,\pi^*) \rightsquigarrow {}^3(\pi,\pi^*),\ \sim 13\ \text{ps} \qquad \text{(Di)}$$

$$^3(\pi,\pi^*) \rightsquigarrow S_0,\ \sim 6\ \text{ns} \qquad \text{(Dii)}$$

Discussion

Excited-State Spectra. Comparison of the various transient absorbance spectra in Figures 2–4, 6–8, and 10 and 11 shows that the main excited-state absorbance along the series $Os(OEP)[P(OMe)_3]_2$, Os(OEP)CO(py), Os(OEP)NO(OMe), and $Os(OEP)O_2$ occurs at ~690, ~715, ~600, and ~675 nm, respectively. The main absorption bands in the excited state are expected to be due to the four-orbital transitions $a_{1u}(\pi)$, $a_{2u}(\pi) \rightarrow e_g(\pi^*)$. In the ground state these red shift along the series (Table I), and it might be expected that the excited-state spectra would similarly red shift, *if the excited states of the four molecules were of the same nature.* We find, however, that there is a red shift from $Os(OEP)[P(OMe)_3]_2$ to Os(OEP)CO(py) and also from Os(OEP)NO(OMe) to $Os(OEP)O_2$ but that the excited-state

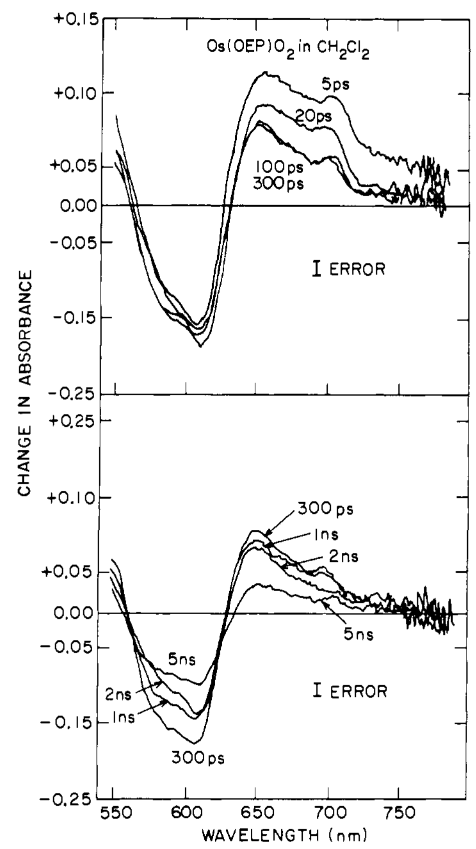

Figure 11. Change-in-absorbance spectra for $Os(OEP)O_2$, 2.3 × 10^{-4} M, in methylene chloride. The absorbance increase peaks in the 700-nm region may be artifacts due to a Raman band in the white probe light (see text).

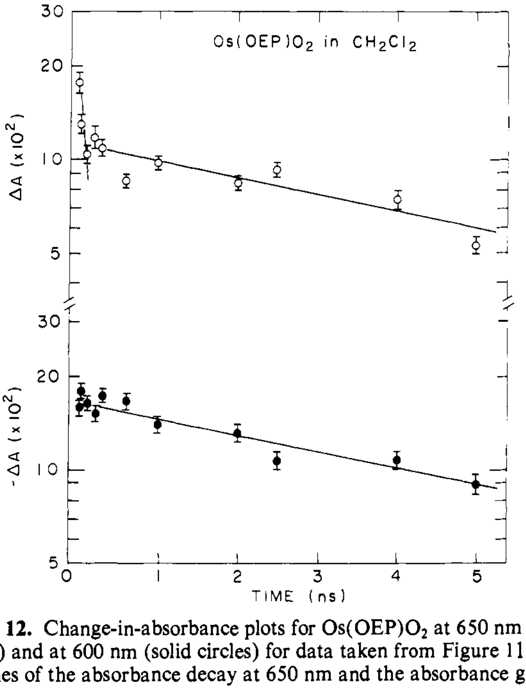

Figure 12. Change-in-absorbance plots for $Os(OEP)O_2$ at 650 nm (open circles) and at 600 nm (solid circles) for data taken from Figure 11. The lifetimes of the absorbance decay at 650 nm and the absorbance growth at 600 nm are the same, 7.5 ± 2 ns. In addition, the data at 650 nm show a decay process with a lifetime of 13 ± 3 ps.

Table II. Summary of Lifetimes and Quantum Yields for the Decay of S_1 and T_1 States of Os(OEP)LL′[a,b]

L	L′	solvent	$\tau(S_1)$ (ps)	$\tau(T_1)$ (ns)	$\Phi(T_1)$[c]
$P(OMe)_3$	$P(OMe)_3$	hexane	≤8	6.2 ± 0.6	0.8
CO	pyridine	CH_2Cl_2	50 ± 10	16 ± 1	*d*
NO^+	OMe	CH_2Cl_2/ CH_3OH	36 ± 7	5.5 ± 0.5	0.6
O	O	CH_2Cl_2	13 ± 3	6 ± 1	1.0

[a] Degassed solutions at 22 °C. [b] A third transient is shown by Os(OEP)NO(OMe) at ~15 ps. See text for discussion. [c] Estimated from the extent of ground-state recovery after the decay of S_1. The error is ±0.1. See text for discussion. [d] Scattered excitation light precluded an estimate of $\Phi(T_1)$.

absorbances of the former two are to the red of those of the latter two. Earlier work predicts that the lowest energy excited states of the former two are (d,π^*) in nature while those of the latter two are (π,π^*). It is quite reasonable to expect that $\pi \rightarrow \pi^*$ transitions will have different energy in (d,π^*) excited states than in (π,π^*) excited states. Also, transitions of a different nature are possible in the two types of excited states. Thus we believe that the excited-state absorbances among the four molecules provide support for the previous prediction concerning the nature of the lowest energy excited states of the four Os(OEP)LL′ complexes reported here.

Kinetics. The decay processes observed in the four Os(OEP)LL′ complexes are summarized in Table II. All show initial excited states S_1 that decay in the time range ≤8 to 50 ps. Naively one would be inclined to identify S_1 as a singlet state and T_1 as a triplet. While this is proper for Os(OEP)NO(OMe) and Os(OEP)O_2, whose lowest energy excited states are (π,π^*) in nature, it is not proper for Os(OEP)$[P(OMe)_3]_2$ and Os(OEP)CO(py), if their lowest energy excited states are (d,π^*). As shown in the Appendix, spin is not a good quantum number for (d,π^*) excited states. Hence, it is not clear what the nature of the S_1 state should be for these two compounds. Indeed, we expect for these molecules behavior like that observed for osmium(II) (5-chlorophenanthrolene)$_3^{2+}$, which has a (d,π^*) excited-state lifetime of 66 ± 2 ns with no evidence for an S_1 excited state with a lifetime above 6 ps.[18] However, there is a clear difference between the excitation process in $Os^{II}(5\text{-Cl-phen})_3^{2+}$ and the Os(OEP)LL′ complexes studied here. For in our case the initial excited state is $^1(\pi,\pi^*)$, whereas in the phenanthrolene case it is (d,π^*).

We can envision two possible explanations for the S_1 states observed in Os(OEP)$[P(OMe)_3]_2$ and Os(OEP)CO(py): (1) The chain of reasoning by which we deduce that the lowest excited states of these two molecules are (d,π^*) and of the other two are (π,π^*) may be faulty and all may be (π,π^*). (2) The lowest excited states of these two molecules may be (d,π^*), but the states S_1 and T_1 observed in the data are not related to spin $S = 0$ and $S = 1$. The initially formed excited state is expected to be $^1(\pi,\pi^*)$, and the state S_1 represents its relaxation products produced within ~1 ps. These could be some subset of the (d,π^*) excited states discussed in the Appendix. The transition $S_1(d,\pi^*) \rightsquigarrow T_1(d,\pi^*)$ then represents sublevel relaxation among the (d,π^*) manifold of states.

We believe that the second explanation is more likely; i.e., the initially formed $^1(\pi,\pi^*)$ state quickly relaxes to a subset of the (d,π^*) states. Because spin is not a good quantum number, it is not clear at present what this subset is. (See Appendix.) Further experiments can clarify the nature of the S_1 and T_1 states in Os(OEP)LL′ complexes. Transient absorbance studies at low temperature and longer times should show whether the expected differences between (d,π^*) and (π,π^*) excited states appear. In particular, because of the failure of spin as a quantum number, the (d,π^*) states should be shorter lived. Studies of the temperature dependence of the phosphorescence emission might also clarify the nature of the long-lived metastable state.

Two other osmium porphyrins might be interesting for future study, as their lowest triplet states are of the $^3(\pi,l_\pi^*)$ type.[8] Os(OEP)$(NO)_2$ and Os(OEP)NO(ClO_4) have their long-wavelength ground-state absorptions between those of Os(OEP)NO(OMe) and Os(OEP)O_2, yet no emission can be detected from either of them. Also of interest would be the transient decay of Os(OEP)$(py)_2$, where weak charge-transfer absorption bands are observed in the near-infrared absorption spectrum.

Comparison with Other Metalloporphyrins. Picosecond studies on metalloporphyrins have already appeared. As expected, the closed-shell metal complexes Sn(OEP)Cl_2[19] and Zn(PPDME)[20] [PPDME = protoporphyrin IX dimethyl ester] show slow relaxation of the $^1(\pi,\pi^*)$ state, 500 and 2600 ps, respectively. Cu^{II}(PPDME)[21] and Ag^{II}(PPDME)[21,22] have doublet ground states. Both reach the lowest doublet excited state, the tridoublet $^2T_1(\pi,\pi^*)$, during the flash time. The subsequent decay is:[21,22]

$$^2T_1(\pi,\pi^*) \rightsquigarrow {}^4T_1(\pi,\pi^*) + {}^2S_0,\ 450\ \text{ps (Cu)},\ \sim 12\ \text{ps (Ag)} \qquad \text{(Ei)}$$

followed by a longer quartet relaxation to $^2S_0$. Picosecond studies have also been reported on Fe(II),[23,24] Fe(III),[24,25] Ni(II),[20,22] Pd(II),[20] Pt(II),[20] and Co(II)[25] porphyrins. Iron(II) cytochrome is isovalent to the Os(II) porphyrins reported here. Iron(II) cytochrome shows only one decay, presumably,[24]

$$^1(\pi,\pi^*) \rightsquigarrow S_0,\ \sim 1\ \text{ps} \qquad \text{(Fi)}$$

The very short lifetime of the Fe(II) porphyrin is attributed to low-energy $^1(d,d)$ levels between $S_1(\pi,\pi^*)$ and the ground state.[24] Ni^{II}(PPDME) shows a 10-ps transient as well as a 260-ps decay. Dzhagarov et al.[22] propose the decay scheme for Ni porphyrins as:

$$^1(d,d) \rightsquigarrow {}^3(d,d),\ \sim 10\ \text{ps} \qquad \text{(Gi)}$$

$$^3(d,d) \rightsquigarrow S_0,\ \sim 260\ \text{ps} \qquad \text{(Gii)}$$

However, Rentzepis et al.[20] prefer:

$$^1(\pi,\pi^*) \rightsquigarrow {}^1(d,d),\ \sim 10\ \text{ps} \qquad \text{(Hi)}$$

$$^1(d,d) \rightsquigarrow S_0,\ \sim 260 \qquad \text{(Hii)}$$

Schemes Gi and Gii would be more consistent with the general interpretation of porphyrin decays; i.e., there is fast relaxation (<6 ps) to the lowest excited state having the same multiplicity as the ground state. Pd^{II}(PPDME) shows the decay path:[20]

$$^1(\pi,\pi^*) \rightsquigarrow {}^3(\pi,\pi^*),\ \sim 19\ \text{ps} \qquad \text{(Ii)}$$

$$^3(\pi,\pi^*) \rightsquigarrow S_0,\ \text{slow} \qquad \text{(Iii)}$$

However, Pt^{II}(PPDME) shows direct production of $^3(\pi,\pi^*)$ in <1.7 ps.[20] The absence of an observable S_1 state in Pt(PPDME) is in contrast to our ready observation of S_1 in Os(OEP)NO(OMe).

In summary then, Fe(II),[24] Fe(III),[24,25] Co(II),[25] Pt(II),[20] and Os^{II}(OEP)$[P(OMe)_3]_2$ show first excited states that decay during the flash. The Pt(II) complex decays into a $^3(\pi,\pi^*)$ state, while the Os(II) complex decays into a (d,π^*) state, and the other three return to the ground state. Ni(II),[20,22] Ag(II)[21,22] Pd(II),[20] and the three remaining Os(II)/Os(VI) complexes show first excited states that decay in the time range 10 to 50 ps. These first excited states are identified quite differently, including $^1(\pi,\pi^*)$ [Pd, Os], $^2T_1(\pi,\pi^*)$ [Ag], $^1(d,d)$ [Ni], $S_1(d,\pi^*)$ [Os]. Subsequent longer lived metastable states are shown in all these complexes. Of the

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open d shell metals studied so far, only Cu(II) shows a first excited state with a relaxation time substantially longer than 50 ps (eq Ei).

The findings of picosecond spectroscopy throw light on a contentious issue in the relaxation processes of excited states of metalloporphyrins. Gurinovich et al.[26] have estimated the yield for $S_1 \rightsquigarrow S_0$ to be between 0 and 0.18 for several metalloporphyrins. Calorimetric studies from one of our laboratories[27] found values from 0.22 to 0.43 for similar metals. The early picosecond studies of Magde et al.[19] reported a value of 0.19 for the process $S_1 \rightsquigarrow S_0$ in $Sn(OEP)Cl_2$. In the studies reported here, Os(OEP)NO(OMe) unambiguously shows a quantum yield of $S_1 \rightsquigarrow S_0$ of ~40%. For Ag(II)[21,22] the yield of ${}^2T_1(\pi,\pi^*) \rightsquigarrow {}^2S_0$ seems much larger than the yield ${}^2T_1(\pi,\pi^*) \rightsquigarrow {}^4T_1(\pi,\pi^*)$. *It is therefore not true that large rates for intersystem crossing necessarily dominate the rate for internal conversion from the first excited state to the ground state.*

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Appendix. Spin-Orbit Coupling in (d,π^*) States

We consider here the spin–orbit coupling between ${}^1(d,\pi^*)$ and ${}^3(d,\pi^*)$ states. There are 16 states that arise from the transition $e_g(d_\pi) \rightarrow e_g(\pi^*)$. In LS coupling these states are: ${}^1A_{1g}$; ${}^3A_{1g}$ ($\mathcal{A}_{2g},\mathcal{E}_g$); ${}^1A_{2g}$; ${}^3A_{2g}$ ($\mathcal{A}_{1g},\mathcal{E}_g$); ${}^1B_{1g}$; ${}^3B_{1g}$ ($\mathcal{B}_{2g},\mathcal{E}_g$); ${}^1B_{2g}$; ${}^3B_{2g}$ ($\mathcal{B}_{1g},\mathcal{E}_g$). The script letters refer to space-spin symmetry. In addition there are eight more charge-transfer transitions $b_{2g}(d_{xy}) \rightarrow e_g(\pi^*)$, which the iterative extended-Hückel calculations put at lower energy.[7] The (d_{xy},π^*) states are ${}^1E_g$ and ${}^3E_g$ ($\mathcal{E}_g$, $\mathcal{A}_{1g}$, $\mathcal{A}_{2g}$, $\mathcal{B}_{1g}$, $\mathcal{B}_{2g}$). All states of the same space-spin symmetry can mix. We have examined these mixing elements and find that ${}^1A_{1g}$ is coupled with ${}^3A_{2g}$ ($\mathcal{A}_{1g}$) by the one-center spin–orbit integral of the Os d_π orbital. This should have value ~2500 cm^{-1}.[28] Similarly there is coupling of ${}^1A_{2g}$ with ${}^3A_{1g}$ ($\mathcal{A}_{2g}$), of ${}^1B_{1g}$ with ${}^3B_{2g}$ ($\mathcal{B}_{1g}$), and of ${}^1B_{2g}$ with ${}^3B_{1g}$ ($\mathcal{B}_{2g}$). Since the electrostatic and exchange splitting among these states should be about the size of the spin-orbit integral or smaller, it becomes clear that the designation of singlet and triplet is no longer valid for these states.

The problem of singlet–triplet coupling in (d,π^*) states has been studied by Crosby and co-workers,[29] and a detailed theory was presented for the (d,π^*) charge-transfer states of tris(2,2′-bipyridine)ruthenium(II) and related molecules.[30] They first consider the spin–orbit coupled states of the d^5 metal center, which are then coupled to the unpaired π^* electron of the ring. We can qualitatively approach the (d,π^*) states of Os(OEP)LL′ compounds in the same way. The $e_g(d_\pi)$ orbitals split into two pairs in the manner of the *j* splitting of $p_{3/2}$ and $p_{1/2}$ orbitals in atoms. If we treat the magnitude of angular momentum, $|j_z|$ about the *z* (perpendicular to the porphyrin plane) axis as a good quantum number, these levels will be $d_{3/2} \equiv [d_{+1}, \bar{d}_{-1}]$ at higher energy and $d_{1/2} \equiv [\bar{d}_{+1}, d_{-1}]$ at lower energy. [The notation d_{+1}, $\bar{d}_{+1}$ refers to α or β spin of the d_π orbitalwith $l_z = \pm 1$. The subscripts $^1/_2$ and $^3/_2$ are $|j_z|$ values.] In addition the orbitals [d_{xy}, $\bar{d}_{xy}$] will spin–orbit couple to the $d_{3/2}$ levels. We then expect three pairs of spin–orbital levels: $d^u_{3/2}$, $d^l_{3/2}$, and $d_{1/2}$, where the first two pairs are mixtures of $[d_{+1}, \bar{d}_{-1}]$ and $[d_{xy}, \bar{d}_{xy}]$, the third pair is $[\bar{d}_{+1}, d_{-1}]$, and u,l are for upper and lower energy. Thus $d^u_{3/2}$ is the highest energy spin–orbital of the Os^{III} core.

The transition $d^u_{3/2} \rightarrow e_g(\pi^*)$ gives rise to eight states of space-spin symmetry $\mathcal{A}_{1g} + \mathcal{A}_{2g} + \mathcal{B}_{1g} + \mathcal{B}_{2g} + 2\mathcal{E}_g$. These states cannot be characterized as either singlets or triplets. Presumably the S_1 states observed in Os(OEP)[P(OMe)$_3$]$_2$ and Os(OEP)-CO(py) represent some subset of these eight states preferentially populated on relaxation from ${}^1(\pi,\pi^*)$.

We might note that for the eight states ($d_{1/2},\pi^*$) there are four states with $S_z = 0$ of symmetry $\mathcal{A}_{1g} + \mathcal{A}_{2g} + \mathcal{B}_{1g} + \mathcal{B}_{2g}$ and four states with $S_z = \pm 1$ of symmetry $2\mathcal{E}_g$. In this case the $S_z = 0$ states are relatively unmixed with the states $S_z = \pm 1$, so S_z is a relatively good quantum number. However, the eight states ($d_{1/2},\pi^*$) would be expected to be at higher energy than the states ($d^u_{3/2}$, π^*) and hence not the ones produced by radiationless decay from the initial ${}^1(\pi,\pi^*)$ photoexcited state.

Registry No. Os(OEP)[P(OMe)$_3$]$_2$, 52649-92-0; Os(OEP)CO(py), 51286-85-2; Os(OEP)NO(OMe), 59296-74-1; Os(OEP)O$_2$, 51349-77-0.

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