Investigation of the Lowest Electronic States of Osmium(II) Tetratolylporphyrins: Photophysics of Metalloporphyrin (d,π^*) Charge Transfer States

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Abstract: The nature of the lowest excited states of a series of osmium(II) porphyrins has been investigated using static and time-resolved emission spectroscopy and ultrafast transient absorption measurements. It is found that a metal-to-ring $^3(d,\pi^*)$ charge transfer excited state is the lowest excited state of the $\mathrm{Os^{II}P(CO)(L)}$ and $\mathrm{Os^{II}P(L)_2}$ complexes, where the porphyrin macrocycle (P) is either tetratolyl- or octaethylporphyrin and the axial ligand L is a σ-donor such as pyridine. Previous studies on OsTTP(CO)(py) had led to the assignment of the lowest excited state as the $^3(\pi,\pi^*)$ state of the porphyrin ring. The results on the $\mathrm{Os^{II}}$ porphyrins can be contrasted with those found previously for the analogous $\mathrm{Ru^{II}}$ porphyrins, in which the lowest excited state was found to switch from $^3(\pi,\pi^*)$ in the RuP(CO)(L) complexes to $^3(d,\pi^*)$ in the $\mathrm{RuP(L)_2}$ compounds. The studies further establish the electronic origin of the red-region features in the absorption spectra of metalloporphyrin $^3(\pi,\pi^*)$ and $^3(d,\pi^*)$ excited states. The combined results demonstrate the critical role played by π-accepting and σ-donating axial ligands in controlling the nature of the lowest excited states, the electronic properties, and excited state dynamics of the biologically-relevant d^6 metalloporphyrins.

Introduction

The elucidation of the relationships among molecular composition and structure, electronic properties, and ground- and excited-state reactivity is a prime motivation for studies of the chemistry and spectroscopy of tetrapyrrole complexes *in vivo* and *in vitro*. The number and type of the axial ligands coordinated to the central metal ion are often important factors in these relationships. This is particularly true for transition metal porphyrins having a d^6 electronic configuration, for which the filled d_π (d_{xz},d_{yz}) orbitals have energies comparable to the top HOMOs of the porphyrin ring.[1-3] In these complexes *axial* back bonding between the metal d_π orbitals and the empty π^* orbitals of a π-accepting ligand can compete with *equatorial* back bonding between the d_π orbitals and the empty $e_g(\pi^*)$ LUMOs of the porphyrin macrocycle.[1-3] This competition can have profound effects on the electronic structure, vibrational properties, and photophysical behavior of the complexes.[1-13] These properties are further modified by the presence and nature of a second axial ligand that is *trans* to the π-accepting ligand.

There has been considerable interest in exploring such relationships in simple iron porphyrins as models for the chemistry of the biologically significant hemeprotein complexes.[1,2,14a] However, it is not possible to explore in depth the consequences of axial ligation on the photophysics of the iron porphyrins since the fate of these photoexcited molecules is ultrafast (typically <1 ps) nonradiative deactivation via a manifold of low energy ligand field and metal ↔ ring charge transfer (CT) excited states.[2,15] The (d,d) and most of the CT excited states are moved to much higher energy and are thus relatively unimportant in the excited-state dynamics of the analogous $\mathrm{Ru^{II}}$ and $\mathrm{Os^{II}}$ compounds.[3] This is due to the larger crystal-field splittings and the raised energies of the metal d-orbitals with respect to the porphyrin frontier MO's in the second- and third-row d^6 porphyrin complexes. The ruthenium and osmium porphyrins thus provide excellent systems for probing in detail the contribution of σ-donating and π-accepting axial ligands to the nature, lifetimes, emission and other properties of the lowest electronic excited states.

The axial ligation of π-accepting moieties such as CO has a substantial effect on the ordering of the electronic states and the

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excited-state spectral and dynamical properties of the Ru^{II} porphyrins.[3,10,12] The lowest electronic state of the Ru^{II}P(CO)(L) complexes is the phosphorescent $^3(\pi,\pi^*)$ state of the porphyrin ring [P = octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP) and L is a σ-donating ligand such as pyridine or piperidine)]. This state deactivates on the microsecond time scale.[3,12] By contrast, the lowest electronic state of the Ru^{II}P(L)$_2$ complexes is a nonemissive $^3(d,\pi^*)$ metal → ring CT state that decays on the nanosecond time scale.

The photophysical behavior of osmium(II) porphyrins appears to differ from that of their Ru(II) analogues in several significant ways.[3,11] The lowest excited state of OsOEP(CO)(py) has been identified as a $^3(d,\pi^*)$ CT excited state having an unusually broad emission near 800 nm and a lifetime of 16 ns.[3a] This behavior is in marked contrast to that noted above for RuOEP(CO)(py) and is suggestive of significant differences in the electronic manifolds of the second- and third-row d^6 metalloporphyrins. On the other hand, the relatively sharp emission near 650 nm reported for the corresponding TTP complex, OsTTP(CO)(py), has been assigned to the $^3(\pi,\pi^*)$ state of the macrocycle[13] (TTP is tetra-*p*-tolylporphyrin, the complexes of which have essentially identical electronic properties as the corresponding TPP complexes). The lowest excited state and emission properties of OsTTP(CO)(py) thus appear to be similar to those of RuTPP(CO)(py), although the 9-ns excited-state lifetime reported for the Os(II) complex is significantly shorter than the 34-μs lifetime of the Ru(II) analogue. The modulation of the nature and properties of the lowest excited states in the Ru^{II} and Os^{II} porphyrins by the axial ligands and perhaps the macrocycle is quite striking and has prompted us to initiate further investigations of these systems.

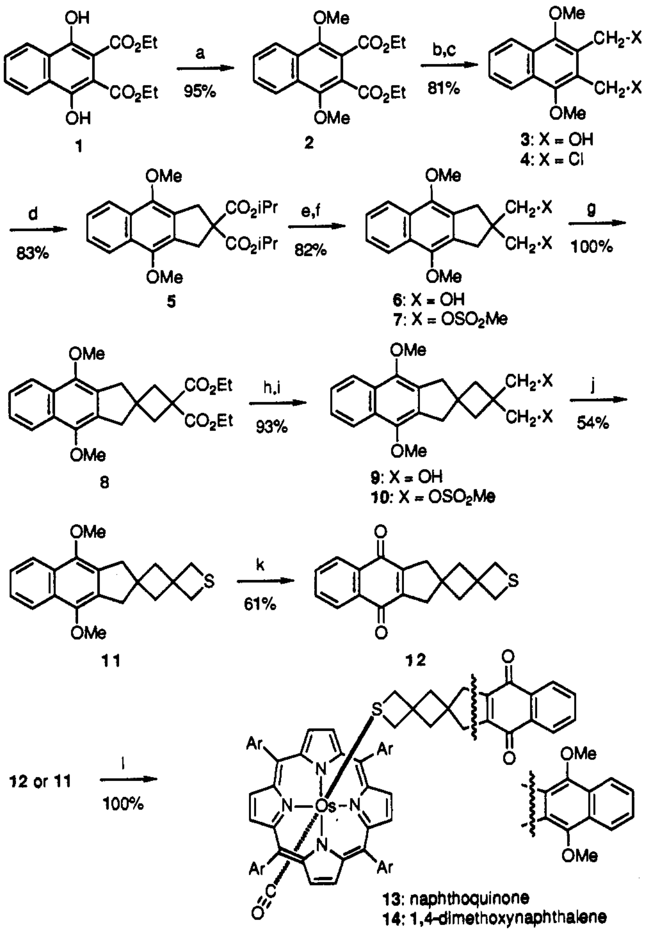
The observation of a relatively high energy $^3(\pi,\pi^*)$ excited state of OsTTP(CO)(py),[13] coupled with the excellent binding properties of Os^{II}P(CO) complexes with respect to an axial ligand *trans* to the carbonyl ligand,[1] also prompted us to investigate these complexes as platforms for potential novel electron donor–acceptor systems. In particular, we have synthesized a complex in which the axial ligand L in Os^{II}TTP(CO)(L) is a thio-terminated spirocyclobutane bridge to a naphthoquinone electron acceptor as a means to investigate electron transfer from an excited triplet state (of the osmium(II) porphyrin) to a quinone linked to the porphyrin via the metal ion. We wish to compare the results with those we recently obtained on a complementary system in which photodriven electron transfer occurs from the lowest excited singlet state (of a zinc(II) porphyrin) to naphthoquinone linked via a similar bridge to the periphery of the porphyrin macrocycle.[16] The issue of whether the metal–ligand bonds should be included as contributions to the distance-dependence of electron transfer pathways in metalloproteins is a topic of current research interest.[14b] Our work on this new donor/acceptor system as well as that on the photophysics of a series of osmium(II) porphyrins is the subject of this article.

Experimental Section

General. Solvents were dried using standard procedures. Air- and moisture-sensitive reactions were run under an argon atmosphere. Organic solutions were dried over anhydrous magnesium sulfate. ^{1}H NMR chemical shifts are given in parts per million downfield from tetramethylsilane in deuteriochloroform solution. Coupling constants *J* are in hertz. IR spectra were recorded on neat films; data are reported in reciprocal centimeters.

Synthesis (See Scheme 1). Dimethoxynaphthalene–Thietane 11 and Naphthoquinone–Thietane 12. These compounds were prepared as ligands for coordination to OsTPP(CO)(EtOH) according to Scheme 1. Experimental details and spectroscopic characterization will be presented elsewhere.[17,18]

Scheme 1 Synthesis of Axially Ligated Os(TTP)–Quinone[a]



[a] Reagents: (a) MeI, K$_2$CO$_3$, acetone, 60 °C; (b) LiAlH$_4$, THF, 0 °C; (c) SOCl$_2$, ZnCl$_2$; (d) CH$_2$(CO$_2$iPr)$_2$, LiH. THF, DMF, 55 °C; (e) LiAlH$_4$, THF, –20 °C: (f) MeSO$_2$Cl, pyridine; (g) CH$_2$(CO$_2$Et)$_2$, NaH, THF, xylenes, reflux; (h) DIBAL, THF. 50 °C; (i) MeSO$_2$Cl, pyridine; (j) Na$_2$S·9H$_2$O, DMF, aqueous EtOH, 75 °C; (k) BBr$_3$, CH$_2$Cl$_2$, 0 °C; (l) OsTTP(CO)(EtOH), CH$_2$Cl$_2$.

OsTTP(CO)(naphthoquinone–thietane) (13). A solution of 3 mg (0.01 mmol) of naphthoquinone–thietane **12** in 0.5 mL of dichloromethane was added to a stirred purple solution of 12 mg (0.01 mmol) of OsTTP(CO)(EtOH) in 1 mL of dichloromethane. The solution was thrice filtered through a fine frit and allowed to crystallize overnight by pentane diffusion to give 15 mg of purple crystals (quantitative yield): ^{1}H NMR (at –45 °C) –2.24 (d, *J* = 10, 2 H, thietane CH_2), –0.43 (d, *J* = 10, 2 H, thietane CH_2), 0.56 (s, 2 H, cyclobutane CH_2), 0.83 (s. 2H. cyclobutane CH_2), 1.23 (s, 4 H. benzylic CH_2), 1.74 (s, 6 H, OCH_3), 2.70 (s. 12 H, tolyl CH_3), 7.52–7.57 (m. 10 H. tolyl *ortho* CH_2 and partially obscured naphthoquinone CH), 7.92–7.97 (m, 8 H, tolyl *meta* CH_2), 8.10 (d, *J* = 7, 2 H, naphthoquinone CH), 8.57 (s, 8 H, vinyls); IR 2918, 1924, (CO), 1664 (C=O), 1010.

OsTTP(CO)(dimethoxynaphthalene–thietane) (14). By using the procedure described for **13**, 3 mg (0.01 mmol) of dimethoxynaphthalene–thietane **11** was converted to 15 mg (quantitative yield) of **14** as purple crystals: ^{1}H NMR (at –45 °C) –2.22 (d, *J* = 10, 2 H, thietane CH_2), –0.38 (d, *J* = 10, 2 H, thietane CH_2), 0.50 (s, 2 H, cyclobutane CH_2), 0.79 (s, 2 H, cyclobutane CH_2), 2.23–2.30 (m, 4 H, benzylic CH_2), 2.68 (s, 12 H, tolyl CH_3), 3.68 (s, 6 H, OCH_3), 7.52–7.57 (m , 10 H, tolyl *ortho* CH_2 and partially obscured naphthyl CH), 7.92–7.97 (m, 8 H, tolyl *meta* CH), 8.10 (d, *J* = 7, 2 H, naphthyl CH), 8.55 (s. 8 H, vinyl CH).

Complexation of Simple Ligands to OsTTP(CO). The following four complexes were prepared in a fashion analogous to that described for **13**, except as specified.

OsTTP(CO)(DMSO): ^{1}H NMR –0.32 (br s, 6 H, bound DMSO Me's), 2.71 (s, 12 H, tolyl Me's), 7.49 (overlapping d, 4 H, *J* = 7, *o*-tolyl), 7.54 (overlapping d, 4 H, *J* = 7, *o*-tolyl), 7.95 (d, *J* = 8, 4 H, *m*-tolyl), 8.12 (d, *J* = 8, 4 H, *m*-tolyl), 8.56 (s, 8 H, vinyls); IR 2950, 1899 (CO), 991.

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OsTTP(CO)(adamantylamine). The complex was prepared according to the general procedure except that 4 mL of toluene was added and the resulting solution was heated at 80 °C for 1 h: ^1H NMR –6.03 (s, 2 H, NH_2-Os), –2.41 (s, 6 H, $(-CH_2)_3C-NH_2-$), 0.10 and 0.67 (two d, J = 12.5, 6 H, three $-CH_2-$'s), 0.78 (s, 3 H, $(CHCH_2)_3C-NH_2$), 2.66 (s, 12 H, tolyl CH_3). 7.46 (overlapping d. 4 H. J = 7. *o*-tolyl). 7.50 (overlapping d, 4 H, J = 7, *o*-tolyl), 7. 87 (d, J = 8, 4 H, *m*-tolyl), 8.07 (d, J = 8, 4 H, *m*-tolyl), 8.50 (s, 8 H, vinyls); IR 2950, 1917 (CO), 1010.

OsTTP(CO)(1,2-dimethylimidazole): ^1H NMR –1.56 (s, 3 H, 2-Im-Me), 0.65 (s, 1 H. 4-Im-*H*), 2.03 (s, 3 H, Im-1-Me), 2.84 (s. 12 H, tolyl CH_3), 4.59 (s, 1 H, 5-Im-H), 7.42 (overlapping d, 4 H, J = 6. *o*-tolyl), 7.48 (overlapping d, 4 H, J = 6, *o*-tolyl), 7.87 (d, J = 6, 4 H, *m*-tolyl), 8.05 (d, J = 6, 4 H, *m*-tolyl), 8.44 (s, 8 H, vinyl CH); IR 2950, 1909 (CO), 1010.

OsTTP(CO)(pyridine): ^1H NMR 1.58 (d, J = 6, 2 H, 2-Pyr-H), 2.65 (s, 12 H, tolyl CH_3), 5.21 (t. J = 7, 3-pyr-H), 6.10 (t, J = 7, 4-pyr-H), 7.43 (overlapping d, 4 H, J = 7, *o*-tolyl), 7.49 (overlapping d, 4 H, J = 7, *o*-tolyl), 7.85 (d, J = 8, 4 H, *m*-tolyl), 8.05 (d, J = 8, 4 H, *m*-tolyl), 8.48 (s, 8 H, vinyl CH); IR 2921, 1920 (CO), 1452.

General Considerations for OsTTP(CO)(L) Complexes. Os^{II}TTP(CO)(L) complexes with L = pyridine (py), dimethylimidazole (DIM), adamantylamine (ADM), dimethyl sulfoxide (DMSO), S–naphthoquinone (S–NQ, **11**), and S–dimethoxynaphthalene (S–DMN, **12**) exhibit essentially the same ground electronic state absorption spectra which, except for some small features between 580 and 630 nm, are identical to the literature spectrum of OsTTP(CO)(py)[13] (see below). The spectrum of the latter complex is shown in Figure 1A.

The OsTTP(CO)(L) complexes were rigorously purified in order to remove highly emissive trace impurities. These impurities when present even in trace amounts were found to mask and/or distort the emission characteristics of the OsTTP(CO)(L) complexes due to their significantly higher emission quantum yields. As described further in the Results section, one impurity is the metal free (i.e. free base) porphyrin. Removal of H_2TTP to the level that its prominent fluorescence was suppressed required repeated chromatography using activated basic alumina (Activity I) with toluene + 1% pyridine as the eluent.

The other impurity encountered in the study of the OsTTP(CO)(L) complexes appears to be an oxidation product having (i) a ground-state absorption spectrum with a strong Soret band at 390 nm, a shoulder near 450 nm, and Q bands at 580 and 625 nm, (ii) a sharp phosphorescence at 770 nm, and (iii) a phosphorescence lifetime of several microseconds at 295 K. A species with a similar absorption spectrum has been found previously upon illumination of OsTPP(CO)(py) in benzene in the presence of small amounts of molecular oxygen and was identified as the Os^{VI} species $OsTPP(O)_2$.[19] The absorption and emission spectra of the impurity are also similar in their overall characteristics to the analogous $OsOEP(O)_2$ species, the lowest excited state of which has been assigned as $^3(d,\pi^*)$.[3a]

The formation of the impurity in our systems is clearly associated with the presence of oxygen and appears to be facilitated by light. On the basis of this information, we tentatively assign the species as $OsTTP(O)_2$. Although this emissive impurity was found to form in a variety of solvents (such as CH_2Cl_2, toluene, or 3-methylpentane), its formation appears to be suppressed if the solvent contains a small amount of a potential ligand such as pyridine. We take this observation to mean that instead of formation of the dioxo adduct, minor photooxidation in the presence of pyridine results in the formation of trace $OsTPP(py)_2$ (the latter is removed along with free base during column chromatography).[1,3–6] As described in the Results section, the bispyridine complex is also either nonemissive or emits at a much longer wavelength than the OsTTP(CO)(py), and thus even if present would not distort the emission spectrum of the carbonyl complex. For these reasons, care was taken in the optical measurements to flow or routinely change the sample to avoid the buildup of photochemical products.

Os^{II}OEP(CO)(MeOH) was purchased from Porphyrin Products (Logan, Utah). Os^{II}OEP(CO)(py) was prepared by dissolving the carbonyl–methanol complex in neat pyridine. Following evaporation of the pyridine, the resultant carbonyl–pyridine complex was dissolved in the solvent of interest (e.g. CH_2Cl_2, toluene, 3-methylpentane). Very small amounts of H_2OEP were removed by chromatography on basic alumina. We found that the OsOEP(CO)(L) complexes were much less susceptable than the OsTTP(CO)(L) compounds to the formation of the apparent oxidation product.

$Os^{II}TTP(py)_2$ and $Os^{II}OEP(py)_2$ were prepared by photolysis of the corresponding Os^{II}P(CO)(py) complexes in degassed pyridine, as has been described previously.[1,4–6,12b] The photolyses were followed by monitoring the disappearance of the Q bands of the carbonyl–pyridine complex (see Figure 1) and the formation of the single strong Q band of the bispyridine adduct in the 490–510-nm region.

Spectroscopy. Spectral grade solvents were used for all spectroscopic studies. Samples used for emission studies were degassed by either repeated freeze–pump–thaw cycles on a high-vacuum line or bubbling with argon. Ground electronic state absorption spectra were acquired on Perkin-Elmer Lambda 3B or Model 330 spectrometers. Emission measurements employed a Spex Fluorolog II spectrofluorometer equipped with a Hamamatsu R928 photomultiplier tube. Emission spectra were typically acquired using a detection bandpass of 2 nm and were corrected for the detection spectral sensitivity. Excitation spectra of the emission were measured for all compounds investigated in order to verify that the emission originated from the compound of interest.

Emission lifetimes were acquired on samples excited with an ~500-μJ 30-ps 532-nm excitation flash. The emission was collected at 90° from the excitation direction, passed through long-wavelength pass filters and a monochromator, and detected with a Hamamatsu R1913 photomultiplier. The output of the PMT was amplified using a single stage of a Stanford Research SR445 amplifier and then directed to a Tektronix 7912AD transient digitizer. The overall response of the system was ~2 ns (as determined by monitoring the overall rise and settling time of the system to a scattered 532-nm 30-ps laser pulse).

Most of the transient absorption measurements were carried out on a spectrometer utilizing ~1-mJ 30-ps 532-nm excitation flashes and a weak broad band (400–1000 nm) probe pulse of comparable duration.[20] Pump probe delays of up to 12 ns were obtained using an optical delay line. The extended wavelength spectra shown in Figures 3–6 were derived from the data acquired in overlapping 150-nm-wavelength intervals. Each spectrum reflects the average of data acquired using approximately 300 laser flashes and has a standard deviation in ΔA of ±0.005. Faster transient absorption studies utilized a spectrometer having a 100-μJ 150-fs excitation flash at 582 nm and a similarly temporally short but broad band probe flash; delay times up to 4 ns were obtainable on this apparatus.[21]

Results

Ground-State Optical Absorption Spectra. The ground electronic absorption spectra of OsTTP(CO)(py) in Figure 1A is essentially the same as the spectra reported previously for this molecule and for the analogous TPP complex.[1,4,6,13] The spectrum of OsTTP(CO)(py) is also representative of the spectra of the other OsTTP(CO)(L) complexes investigated here [L = ADM, DIM, DMSO, S–NQ (**11**), S–DMN (**12**)]. The spectrum of OsTPP(CO)(py) consists of a strong Soret, or B(0,0), band at 404 nm, a weaker Q(1,0) band at 509 nm, and a weak shoulder near 560 that can be assigned as the Q(0,0) band. The Q bands correspond to transitions from the ground state S_0 to the first excited singlet state S_1 while the B band reflects excitation to S_2. There also appears to be a rather broad weak tail extending from the Q(1,0)/Q(0,0) region to past 600 nm. Such absorption could plausibly reflect transitions to $^1(d,\pi^*)$ CT excited states on the basis of MO calculations on the osmium(II) porphyrins.[3] Additionally, the spectra were frequently found to contain very weak features riding on this tailing absorption, as has been noted previously for OsTTP(CO)(py) and OsTTP(CO)(MeOH). As discussed below, such features observed between 580 and 650 nm appear to be due in large measure to trace impurities such as H_2TTP.

The spectrum of Os^{II}OEP(CO)(py) in Figure 1B is identical with those reported previously.[1,3] As is typical for metalloporphyrins, the Soret transition is slightly to the blue from that in the corresponding TTP or TPP complexes and the Q(0,0) transition has gained significant intensity. These differences between the octaalkyl and tetraaryl macrocycles reflect the effect of the macrocycle substituents on the energies of the ring $a_{1u}(\pi)$

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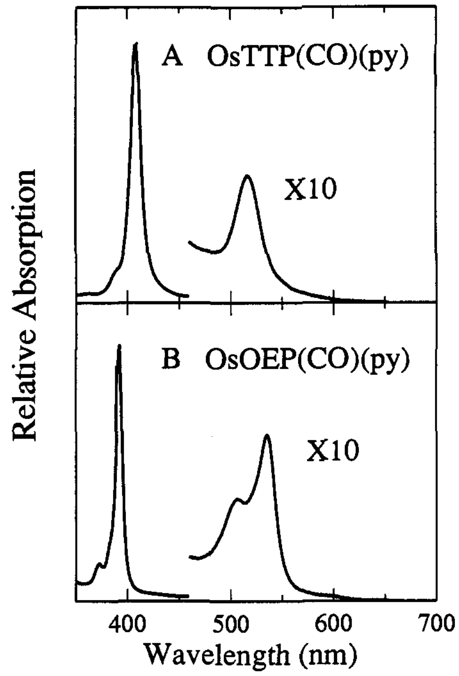

Figure 1. Ground-state absorption spectra at 295 K of OsTTP(CO)(py) (A) and OsOEP(CO)(py) (B) both in toluene + 1% pyridine. Q bands of both complexes have been multiplied by the indicated factor for clarity.

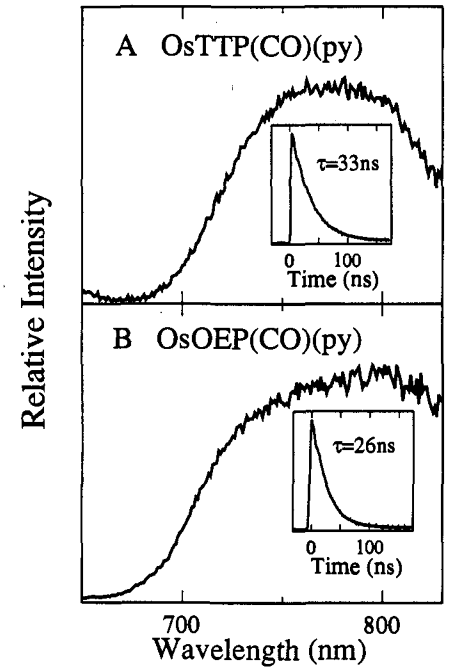

Figure 2. Steady-state emission spectra of OsTTP(CO)(py) (A) and OsOEP(CO)(py) (B) at 295 K acquired by exciting into the Q bands of each complex. Spectra are corrected for the detection spectral sensitivity. Insets show time evolution of emission intensity following excitation of complexes with a 30-ps flash.

Table 1. $^3(d,\pi^*)$ Lifetimes for Osmium Porphyrins[a]

compd	lifetime (ns)	compd	lifetime (ns)
OsTTP(CO)(py)	33 ± 2	OsTTP(CO)(S–NQ)	38 ± 2
OsTTP(CO)(ADM)	30 ± 2		50 ± 15[b]
OsTTP(CO)(DMIM)	18 ± 2	OsTTP(CO)(S–DMN)	39 ± 3
OsTTP(CO)(DMSO)	29 ± 2	OsOEP(CO)(py)	26 ± 2
		$OsTTP(py)_2$	1.4 ± 0.4[c]
			1.0 ± 0.2[d]

[a] Phosphorescence decay time measured between 750 and 800 nm in ~10-nm intervals for samples at 295 K in degassed toluene unless noted otherwise. [b] Transient absorption decay in 3-methylpentane. [c] Transient absorption decay in toluene. [d] Transient absorption decay in pyridine.

and $a_{2u}(\pi)$ HOMOs and on the mixing of the nearly degenerate configurations arising from promotion of an electron from $a_{1u}(\pi)$ or $a_{2u}(\pi)$ to $e_g(\pi^*)$.[2]

Emission Spectra. Room temperature emission spectra for OsTTP(CO)(py) and OsOEP(CO)(py) in degassed solutions are shown in Figure 2, spectra A and B, respectively. Excitation spectra verify that the emission arises from the desired compounds. The emission for both complexes is unusually broad (fwhm ~ 2500 cm^{-1}). There is also a substantial energy gap (~5000 cm^{-1}) between the center of the emission band and the Q(0,0) $S_0 \rightarrow S_1$ absorption band. The large absorption/emission shift suggests that the emission can be characterized as phosphorescence from the lowest triplet excited states of the carbonyl–pyridine complexes.

The emission spectrum we find for OsOEP(CO)(py) is similar to that reported previously for this compound at 77 K.[3a] However, the spectrum we observe for OsTTP(CO)(py) in Figure 2A, and for the other OsTTP(CO)(L) complexes (not shown), is much different from the emission spectrum assigned previously to this compound.[13] In the earlier investigation, a strong emission band was found near 650 nm and a weaker band was seen near 710 nm. These features were assigned as phosphorescence from the $^3(\pi,\pi^*)$ excited state of OsTTP(CO)(py). We have found similar 650- and 710-nm emissions in samples of the OsTTP(CO)(L) complexes prior to repeated column chromatography. Excitation spectra of the 650- and 710-nm emissions in samples that were not rigorously purified revealed a four-banded visible region absorption spectrum characteristic of a metal-free porphyrin. A similar conclusion is drawn regarding the small 650-nm feature that remains in the spectrum of Figure 2A. The excitation bands observed near 580 and 650 nm likely correspond to the weak features reported previously at these wavelengths in the absorption spectra of OsTTP(CO)(py) and OsTTP(CO)(MeOH).[13] We believe that these weak absorptions represent, at least in part, the $Q_x(1,0)$ and $Q_x(0,0)$ bands of H_2TTP. Similarly, we believe that the 650- and 710-nm emission bands observed previously correspond to the Q(0,0) and Q(0,1) fluorescence bands of H_2TTP on the basis of the excitation spectra and the similarity to the fluorescence emission of H_2TPP. Additionally, the reported lifetime of 9 ns for the decay of the 650-/710-nm emission from OsTTP(CO)(py) samples[13] is also consistent with what one would expect for H_2TTP fluorescence based on the literature data for H_2TPP.[2,22] Our experience is that even at H_2TTP levels where it is virtually not observable in the absorption spectrum, the long-wavelength tail of the free base fluorescence can overwhelm the true phosphorescence from OsTTP(CO)(py) shown in Figure 2A. An additonal complication that we encountered is an apparent oxidation product having a strong and relatively sharp phosphorescence at 770 nm that also can distort and/or mask the phosphorescence from the OsTTP(CO)(L) complexes if precautions were not taken to avoid its formation (see Experimental Section).

Emission Lifetimes. Room temperature phosphorescence decays for the OsTTP(CO)(L) complexes exhibit first-order kinetic behavior in all cases and generally give lifetimes in the range of 30–40 ns (Table 1). Representative kinetic data and an exponential fit are shown for OsTTP(CO)(py) in the inset to Figure 2A. The initial amplitudes of the kinetic traces were measured as a function of wavelength from ~700 to 830 nm for several of the complexes and were found to track the steady-state phosphorescence spectra exemplified by spectrum for OsTTP(CO)(py) in Figure 2A.

However, it should be noted that detection in the vicinity of the small feature near 650 nm in the emission spectrum led to a much shorter time constant (~12 ns). This shorter-wavelength emission and its associated short lifetime are especially easy to observe in samples that are not as rigorously purified as the sample used for Figure 2A. A time constant of ~12 ns is the same within our experimental error as the known fluorescence lifetime of H_2TPP,[22] thus reinforcing our assignment of the 650-nm emission to H_2TTP.

The phosphorescence decay curve for OsOEP(CO)(py) and an exponential fit to the data are shown in the inset to Figure 2B. The decay time constant of 26 ns is only slightly shorter than the value of 33 ns for OsTTP(CO)(py) (Table 1). Our lifetime for OsOEP(CO)(py) is slightly longer than the value of 16 ns reported previously for this compound.[11b]

Transient Absorption Spectra. Time-resolved absorption spectra extending from 580 to 920 nm for OsTTP(CO)(py) at 127 ps and 12 ns after excitation with a 30-ps flash are shown in Figure 3A. The spectra at the two delay times have the same spectral profile, although by 12 ns the spectrum has decayed somewhat. The extent of this decay is consistent with the 33-ns time constant observed for the phosphorescence lifetime of this complex. Hence, we assign transient absorption shown in Figure 3A and the phosphorescence shown in Figure 2A to the same triplet excited state. The three-banded transient absorption spectrum between 580 and 920 nm shown in Figure 3A is found to develop during the 30-ps excitation flash. Assuming that the lowest singlet and triplet excited states do not have identical red-region transient spectra (as is normally the case for porphyrins[25]), then we can conclude that intersystem crossing from the singlet to triplet manifold must occur on a shorter time scale (*vide infra*).

The transient absorption spectrum observed following excitation of OsTTP(CO)(py) with a 30-ps flash is essentially the same at 295 and 160 K (Figure 4A). Similar spectra are observed for the other OsTTP(CO)(L) complexes, as is evidenced by the representative data shown in Figure 5. There also appears to be essentially no solvent dependence of the transient absorption spectra. This is exemplified by the data for the carbonyl–pyridine complex in Figures 3A, 4A, and 5A.

We examined in somewhat more detail the transient absorption decay of quinone complex OsTTP(CO)(S–NQ) (**13**) since this molecule is of particular interest with respect to possible photoinitiated electron transfer. The spectrum shows a modest decay between 73 ps and 5.7 ns without changing shape (Figure 5E). As the asymptote of the decay has not been reached by 12 ns, we assume that the spectrum decays to $\Delta A = 0$, which corresponds to complete deactivation to the ground electronic state. The data spanning the wavelength region shown in Figure 5E when analyzed globally in this manner give a time constant of 50 ± 15 ns. The triplet lifetime determined by this method agrees reasonably well with the value of 38 ± 2 ns determined via emission decay (Table 1). The agreement is good considering that the transient absorption data span less than one lifetime of the decay.

The transient absorption behavior of OsOEP(CO)(py) is similar to that for OsTTP(CO)(py). The transient absorption spectrum of OsOEP(CO)(py) shown in Figure 3B grows with the 30-ps excitation flash and maintains the same shape over the 12-ns limit of the picosecond spectrometer. The extent of the decay during this time is consistent with the 26-ns lifetime determined via phosphorescence decay. The spectrum is essentially the same at 295 and 78 K (Figure 4B). Additionally, our transient absorption spectrum of OsOEP(CO)(py) agrees well, in the region of overlap from 600 to 790 nm, with the spectrum obtained previously for this complex.[11a] However, in the previous study, a small change in the spectrum was noted during the first 50 ps after a 7-ps pulse, from which a lifetime of 40 ± 5 ps was estimated for the S_1 excited state. We searched for such a short-lived component following excitation of OsOEP(CO)(py) with a 150-fs flash at 582 nm. Although the absorption changes were small due to the weak absorption of this complex at the excitation wavelength, our results indicate that the spectrum observed at 127 ps in Figure 3B develops in <1 ps with no clear indication of an earlier transient state. Since the lowest singlet and triplet excited states of porphyrins generally have different red-region spectra,[25] our results suggest that intersystem crossing occurs on the subpicosecond time scale.

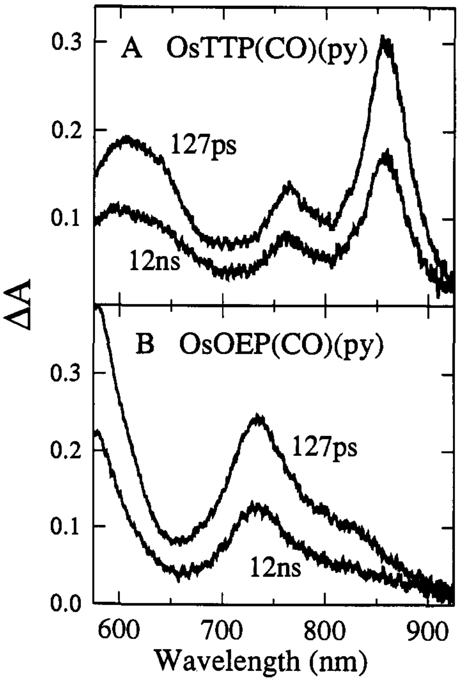

Figure 3. Transient absorption spectra at 295 K of OsTTP(CO)(py) (A) and OsOEP(CO)(py) (B) in toluene + 1% pyridine acquired at the indicated delay times following excitation.

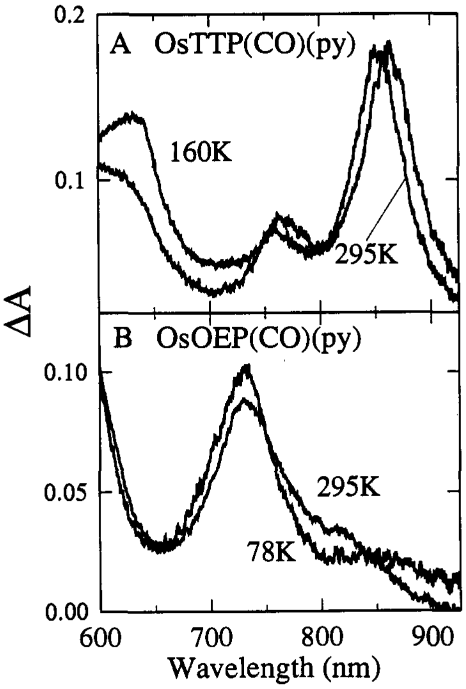

Figure 4. Transient absorption spectra of OsTTP(CO)(py) in EPA + 1% pyridine (A) and OsOEP(CO)(py) in 3-methylpentane (B) obtained at the indicated temperatures. All spectra were acquired at 127 ps following excitation.

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(23) The 12-ns S_1 lifetime of H_2OEP is calculated from the fluorescence quantum yield of ~0.1 and natural radiative lifetime of ~120 ns.[2]

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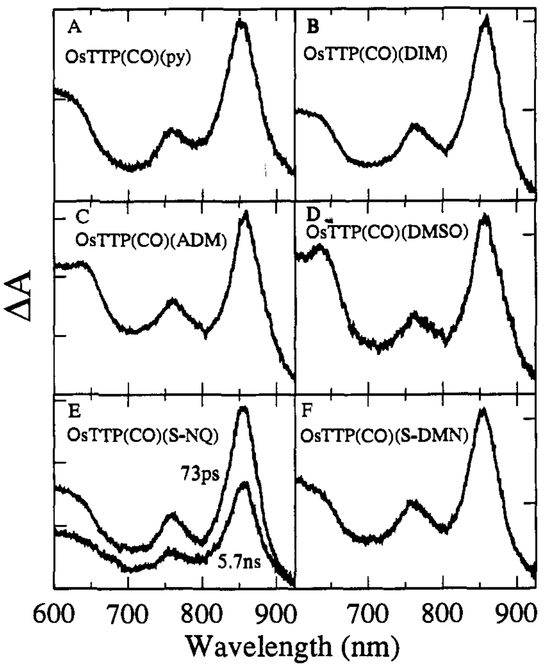

Figure 5. Transient absorption spectra at 295 K of six OsTTP(CO)(L) complexes investigated in this work. Solvents used were EPA + 1% pyridine (A), 3-methylpentane (B, C, D, F), and hexane (F). All spectra were acquired at 73 ps following excitation except (E) as noted.

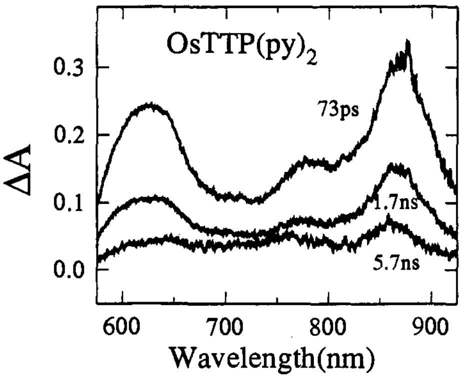

Figure 6. Transient absorption spectra at 295 K of OsTTP$(py)_2$ in toluene obtained at the indicated delay times following excitation.

Finally, we examined the photophysical behavior of OsTTP$(py)_2$ (Figure 6). The transient absorption spectrum for this complex is essentially the same as the spectra of the carbonyl–pyridine and other OsTTP(CO)(L) compounds. The spectrum of OsTTP$(py)_2$ is similar in toluene (Figure 6) and pyridine (not shown), and does not change shape in either solvent between 30 ps and 12 ns. However, the bispyridine complex shows a much faster deactivation than the carbonyl complexes. Single-exponential fits to data acquired at delay times between 30 ps and 12 ns and spanning the wavelength region shown in Figure 6 give an excited-state lifetime of 1.4 ± 0.4 ns in toluene and 1.0 ± 0.2 ns in pyridine (Table 1).

Discussion

Assignment of the Lowest Triplet Excited State of the OsP(CO)(L) Complexes. The lowest triplet excited state of OsOEP(CO)(py) has been assigned as a (d,π^*) CT state on the basis of the unusually broad emission spectrum (see Figure 2B) and the results of interactive extended Hückel calculations.[3a] Differences in the transient absorption spectrum of this complex and the spectra of osmium(II) porphyrins believed to have a $^3(\pi,\pi^*)$ lowest excited state have given support to this interpretation.[11] We have observed similar phosphorescence and transient absorption spectra as those observed previously for OsOEP(CO)(py) and concur with the previous assignment.

In contrast, the lowest excited state of OsTTP(CO)(py) has been assigned as the $^3(\pi,\pi^*)$ state of the porphyrin ring.[13] This suggests a macrocycle-induced switch in the nature of the lowest excited state compared to OsOEP(CO)(py). The assignment was based on the observed emission properties, including a strong band at 650 nm and a weaker band at 710 nm having widths typical of porphyrin (π,π^*) emissions. However, as discussed in the Results section, we assign these two emission bands instead as the Q(0,0) and Q(0,1) fluorescence bands of trace H_2TTP impurity. The true emission of OsTTP(CO)(py), verified by excitation spectra, is a very broad phosphorescence that is very similar to that of OsOEP(CO)(py) (Figure 2). Again, the phosphorescence spectra of both complexes are substantially broader than is typical for metalloporphyrin (π,π^*) emissions. Hence, the phosphorescence of OsTTP(CO)(py), like that of OsOEP(CO)(py), is most consistent with the lowest excited state being $^3(d,\pi^*)$.

The assignment of $^3(d,\pi^*)$ as the lowest excited state of the OsP(CO)(L) complexes is strongly supported by the transient absorption spectra. In fact, we believe that the transient absorption data make this assignment essentially unambiguous for the OsTTP(CO)(L) and OsTTP$(py)_2$ complexes. The three-banded transient absorption spectra for OsTTP(CO)(py) and the other OsTTP(CO)(L) complexes in Figures 3A, 4A, and 5 are very similar to the ground-state absorption spectrum of the π-anion radical of ZnTPP.[24] One expects similarities between the absorption spectrum of a porphyrin anion and a porphyrin (d,π^*) metal → ring CT state,[12b,25] in as much as an electron has been added in both states to an $e_g(\pi^*)$ LUMO of the porphyrin ring, and the electronic spectra of metalloporphyrins are dominated by transitions involving the porphyrin macrocycle. Of course, in the CT excited state an electron is removed from a metal orbital (a d_π orbital in the osmium(II) porphyrins), and this change in metal configuration may result in some differences in the spectra of the anions and the (d,π^*) CT state. Nonetheless, the metal perturbation appears to be small, at least for the metallo-TPP complexes, based on the very close agreement between the three-banded red-region spectra of the ground state of the ZnTPP anion and the $^3(d,\pi^*)$ excited state of the OsTTP(CO)(L) complexes studied here and of the RuTPP$(L)_2$ complexes studied previously.[12a,b] The $^3(d,\pi^*)$ excited state of RuTPP$(py)_2$ is also short-lived ($\tau \sim 15$ ns), and exhibits only weakly- or non-emissive properties similar to those we attribute here to the $^3(d,\pi^*)$ excited state of the OsTPP(CO)(L) complexes.

On the other hand, the lowest excited state of the RuTPP(CO)(L) complexes has been assigned as the $^3(\pi,\pi^*)$ state.[3a,10,12] These photoexcited compounds are highly phosphorescent, deactivate on the microsecond time scale, and possess a two-banded absorption spectrum between 600 and 900 nm. In particular, the spectra of the $^3(\pi,\pi^*)$ states of RuTPP(CO)(py)[10,12] and a variety of metallo-TPP complexes[25,26] are consistently found to contain a strong absorption band in the vicinity of 850 nm and a weaker band near 750 nm that have an intensity ratio comparable to that of the bands at similar positions in the $^3(d,\pi^*)$ spectra of the RuTTP$(L)_2$ complexes. However, the $^3(\pi,\pi^*)$ spectra lack the prominent third band with a maximum in the 600–650-nm region found in the spectra of the $^3(d,\pi^*)$ states (and the anions). Hence, on the basis of these comparisons, we conclude that the three-banded red-region transient absorption spectra observed for the OsTTP(CO)(L) complexes in Figures 3A, 4A, and 5 and for OsTTP$(py)_2$ in Figure 6 are inconsistent with the lowest excited state of these molecules being a $^3(\pi,\pi^*)$ excited state and are fully consistent with an assignment of the lowest excited state as a $^3(d,\pi^*)$ metal → ring CT excited state.

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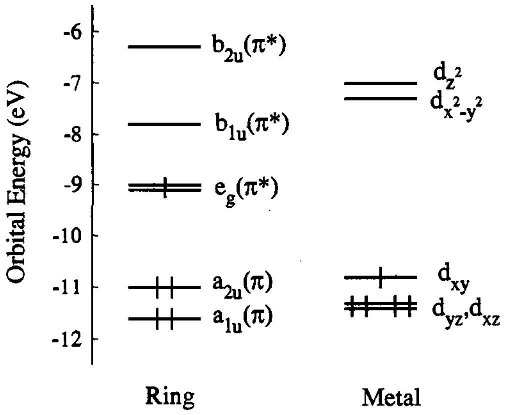

Figure 7. Schematic representation of molecular orbitals in OsTTP(CO)L complexes showing the electronic configuration of the metal-to-ring charge transfer state. Approximate orbital energies are from refs 2, 3a, and 27. Note that the ordering of the a_{1u} and a_{2u} orbitals and possibly also the b_{2u} and b_{1u} orbitals will change depending on whether the macrocycle is OEP or TTP/TPP.

The finding that the $^3(\pi,\pi^*)$, $^3(d,\pi^*)$, and anion spectra share common near-IR transitions can be traced to the electronic configurations of the states. Specifically, compared to the electronic ground state of neutral porphyrins, all three states have an electron added to the $e_g(\pi^*)$ LUMO of the macrocycle. Thus, within a simple one-electron picture all three states might be expected to possess a dipole-allowed transition involving promotion of the $e_g(\pi^*)$ electron to the next empty LUMO, either the $b_{1u}(\pi^*)$ or $b_{2u}(\pi^*)$ orbital (Figure 7).[2,27] In fact, the long-wavelength transition of the ZnTPP and ZnEtio anions (at 830 and 870 nm, respectively) is thought to derive from promotion of an electron from the e_g to b_{1u} orbitals.[24,28d] The comparable band in the ZnTPP $^3(\pi,\pi^*)$ spectrum also is thought to involve the $e_g \rightarrow b_{1u}/b_{2u}$ promotion.[29] This analysis can be taken one step further, as has been discussed recently concerning the $^3(\pi,\pi^*)$ spectra.[25] Specifically, we believe that a consistent interpretation of the red-region spectra of the OsTTP(CO)(L) and OsTTP(py)$_2$ complexes under investigation, and of the $^3(\pi,\pi^*)$, $^3(d,\pi^*)$, and anion spectra in general, is obtained if the prominant long-wavelength transition is associated largely with the $e_g \rightarrow b_{1u}$ electron promotion in the metallo-TPP complexes and with $e_g \rightarrow b_{2u}$ in metallo-OEP complexes.

The reasoning underlying this point of view is as follows. The $b_{1u}(\pi^*)$ and $b_{2u}(\pi^*)$ porphyrin LUMOs have nodal properties that are similar to the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ HOMOs.[2,27] In particular, the a_{2u} and b_{2u} orbitals place electron density at the central nitrogens to which the metal is coordinated and at the meso carbons to which the aryl rings of TPP (or TTP) complexes are bonded; the a_{1u} and b_{1u} orbitals have nodes at the nitrogens and place considerable electron density at the β-pyrrole carbons to which the alkyl groups of OEP (or Etio) complexes are bonded. The substituent effects place the a_{1u} orbital higher in energy than a_{2u} for metallo-OEP complexes and visa versa for the metallo-TPP complexes, as has been established from the ground-state electronic spectra and ESR investigations of the cations.[2,30,31] The red-region $^3(\pi,\pi^*)$, $^3(d,\pi^*)$, and anion spectra are most easily explained if a similar change in ordering occurs for the b_{1u} and b_{2u} orbitals. Namely, due to the differences in electron density placed at the central nitrogen atoms, we expect the transition involving the $e_g \rightarrow b_{2u}$ electron promotion to be much more sensitive to the nature of the central metal ion and the axial ligands than a transition involving $e_g \rightarrow b_{1u}$, as has been discussed recently for $^3(\pi,\pi^*)$ spectra.[25]

A consistent explanation of the spectra is thus obtained if for the metallotetraaryl complexes the b_{1u} orbital is lower in energy than b_{2u}, associating the $e_g \rightarrow b_{1u}$ electron promotion with the prominant lowest energy transition in the $^3(\pi,\pi^*)$, $^3(d,\pi^*)$, and anion spectra. This assignment explains the finding that this band is generally found in the relatively narrow region between 830 and 870 nm in a variety of metallo-TPP systems: (i) in the spectra of the $^3(\pi,\pi^*)$ excited state of a large number of metallo-TPP complexes, including the RuTTP(CO)(L) systems, that differ in the central metal ion and axial ligands,[10,12,25,26] (ii) in the spectra of the $^3(d,\pi^*)$ excited state of RuTPP(py)$_2$, R uTPP(pip)$_2$, and RuOEP(P-n-Bu$_3$)$_2$,[12a,b] and the OsTPP(CO)(L) and OsTTP(py)$_2$ complexes studied here, and (iii) in the spectra of the ZnTPP anion.[24] The weaker band consistently observed ~1400 cm^{-1} to higher energy than the ~850-nm band in the $^3(\pi,\pi^*)$, $^3(d,\pi^*)$, and anion spectra of metallo-TPP complexes may reflect the first vibrational overtone (see Figures 4A, 5A, 6, and 7).[25] (The additional band observed between 600 and 650 nm in the $^3(d,\pi^*)$ and anion spectra, but not in this region in the $^3(\pi,\pi^*)$ spectra, may arise from mixing of several higher energy configurations, as has been discussed for the anions.[24])

On the other hand, the prominant long-wavelength feature exhibits a considerable variation in position (650–850 nm) for the $^3(\pi,\pi^*)$, $^3(d,\pi^*)$, and anion spectra of metallo-OEP complexes,[11,12,24,25,28,32] which would seem to be consistent with the assignment of the transition as substantially involving the $e_g \rightarrow b_{2u}$ electron promotion. For example, the prominant red-region band in the $^3(\pi,\pi^*)$ spectrum is found at 800 nm for RuOEP(CO)(py),[12a,b] 755 nm for Zn^{II}OEP,[25] and 715 nm for Sn^{IV}OEPCl$_2$.[25] A moderately intense band in the red-region $^3(d,\pi^*)$ spectrum of several RuP(L)$_2$ complexes is found to vary between 630 and 830 nm.[12a,b] The moderately strong transition in the spectrum of the ZnEtio anion occurs near 850 nm, whereas the longest wavelength feature in the spectrum of the ZnOEP anion appears to occur near 620 nm.[24,28,32] On the basis of these comparisons, it is clear that, unlike those of the metallotetraarylporphyrins, the number and positions of features in the red region of the transient absorption spectra of the metallo-OEP complexes cannot be utilized with certainty to distinguish the $^3(\pi,\pi^*)$ and $^3(d,\pi^*)$ excited states. Nonetheless, the transient absorption spectra of OsOEP(CO)(py) in Figures 3B and 4B are consistent with the assignment, given here and previously,[3,11] of the lowest excited state of this complex as a $^3(d,\pi^*)$ excited state. This assignment is based on (i) the broad and featureless phosphorescence spectrum of OsOEP(CO)(py) and (ii) comparison with the similarly broad phosphorescence spectrum of OsTTP(CO)(py), a complex that we have further identified as having a $^3(d,\pi^*)$ CT state based on its more straightforward transient absorption data.

The origin of the weak feature that appears to be present ~1600 cm^{-1} to longer wavelength than the prominant 730-nm feature in the $^3(d,\pi^*)$ transient spectrum of OsOEP(CO)(py) is less certain. One possibility is that the weak long-wavelength feature represents the (0,0) transition and that the 730-nm band represents the (0,1) band. This situation would correspond to a shift in intensity ratios of the two features in the excited-state spectrum of the OsOEP(CO)(py) compared to the analogous TTP complexes just described.[33] Another possibility is that the weak feature reflects an electronic transition from the $^3(\pi,\pi^*)$ state that may be slightly higher in energy than, and thermally accessible from, the $^3(d,\pi^*)$ state. The observation that this weak feature may decrease in intensity relative to the strong feature near 730 nm

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when the temperature is reduced provides some support for this possibility (Figure 4B). However, the relatively weak effect of temperature on the spectra of both OsOEP(CO)(py) and OsTTP(CO)(py) in Figure 4 indicates that a temperature-dependent contribution of $^3(\pi,\pi^*)$ is not substantial and that the $^3(d,\pi^*)$ state is largely if not solely responsible for the transient absorption data during and after the 30-ps flash.

Comparison of the Lowest Excited States in the Ruthenium(II) and Osmium(II) Porphyrins. Several interesting issues are raised by our assignment of the $^3(d,\pi^*)$ metal → ring CT state as the lowest excited state of OsTTP(CO)(py) and by the same assignment here and previously[3,11] for OsOEP(CO)(py). First, we conclude that there is not a macrocycle-induced switch in the lowest excited state in the OsP(CO)(L) complexes when the porphyrin macrocycle is changed from TPP (or TTP) to OEP. Second, the finding of $^3(d,\pi^*)$ as the lowest excited state of the OsP(CO)(py) and the other OsP(CO)(L) complexes investigated stands in marked contrast to the results on the corresponding $Ru^{II}P(CO)(py)$ complexes and a number of other $Ru^{II}P(CO)(L)$ systems in which the lowest excited state has been identified instead as the ring $^3(\pi,\pi^*)$ state.[3,10,12] Interestingly, $^3(d,\pi^*)$ has been identified as the lowest excited state of both the $Os^{II}P(L)_2$ and $Ru^{II}P(L)_2$ complexes, and for TPP, TTP, and OEP macrocycles and a number of σ-donating ligands such as pyridine (see above and refs 3, 11, and 12).

The nature of the lowest excited states and the optical properties of the complexes can be understood by examining the effects of π-backbonding.[1-3,9,11,12] In particular, one must consider the competing effects of *equatorial* π-backbonding between the filled d_π orbitals of the Os^{II} or Ru^{II} ion and the empty $e_g(\pi^*)$ LUMOs of the porphyrin ring and of *axial* π-backbonding between the d_π orbitals and the empty π^* orbitals of a π-accepting axial ligand such as CO. MO calculations indicate that the d_π orbitals of the ruthenium(II) and osmium(II) porphyrins are energetically comparable to or somewhat higher than the $a_{1u}(\pi)$ and $a_{2u}(\pi)$ HOMOS of the ring; the $e_g(\pi^*)$ orbitals are at higher energy and, in the carbonyl complexes, the $CO(\pi^*)$ orbitals are at higher energy still.[3]

Equatorial metal → ring π-backbonding and the associated increase in the ring HOMO-LUMO energy gap is thought to give rise to the blue shift in the ground-state absorption bands of the $Ru^{II}P(CO)(py)$ and $RuP(py)_2$ complexes relative to typical closed-shell complexes such as zinc porphyrins.[3] The somewhat smaller blue shift of the $S_0 \rightarrow S_1$ Q bands of the $Ru^{II}P(CO)(py)$ compared to $Ru^{II}P(py)_2$ seems to reflect a diminished equatorial π-backbonding due to the lowering of the energy of the d_π orbitals as a result of $d_\pi \rightarrow CO(\pi^*)$ axial π-backbonding. A similar perspective on the importance of π-backbonding on the vibrational properties of such complexes has been derived from resonance Raman investigations.[9]

The reduced energy of the metal d_π orbitals in the carbonyl complexes together with the increased ring HOMO → LUMO gap are further manifested in the switch in the nature of the lowest excited state from the ring $^3(\pi,\pi^*)$ state of the RuP(CO)(py) compounds to the $^3(d,\pi^*)$ metal → ring CT excited state in the $RuP(py)_2$ complexes. It is evident, however, that in the RuP(CO)(L) complexes the $^3(d,\pi^*)$ state lies only slightly (<50 meV) above, and is thermally accessible from, the $^3(\pi,\pi^*)$ state, facilitating deactivation of the latter and giving rise to strong temperature dependence of the excited-state deactivation rate.[12c]

The increased energy of the $5d_\pi$ orbitals in the osmium(II) porphyrins compared to the $4d_\pi$ orbitals in the ruthenium(II) porphyrins has important consequences for the optical properties and electronic states. In the Os^{II} complexes, the reduced energy gap and increased mixing between the metal d_π and ring $e_g(\pi^*)$ LUMOs raises the energy of the $e_g(\pi^*)$ LUMOs, increasing the energy spacing with the $a_{1u}(\pi)/a_{2u}(\pi)$ HOMOs and thus the energies of the ring (π,π^*) excited states. This is manifest in a small additional blue shift in the ground-state absorption bands compared to the corresponding ruthenium(II) porphyrins. A similar increase in the energy of the ring $^3(\pi,\pi^*)$ state is expected, and this is supported by the phosphorescence spectra of several osmium(II) porphyrins thought to have $^3(\pi,\pi^*)$ as the lowest state.[3] An increase in the energy of the $^3(\pi,\pi^*)$ state is likely responsible in part for the observation that the $^3(d,\pi^*)$ state is the lowest excited state of both the OsP(CO)(py) and $OsP(L)_2$ complexes. However, we expect that the predominant source of this ordering of excited states is derived from the higher energy of the $5d_\pi$ orbitals of osmium(II) porphyrins compared to the $4d_\pi$ orbitals of Ru^{II} and thus a smaller gap from $e_g(\pi^*)$. Hence, unlike the case of the $Ru^{II}P(CO)(L)$ complexes, in which $^3(d,\pi^*)$ lies slightly above $^3(\pi,\pi^*)$, axial π-backbonding of the $5d_\pi$ and $CO(\pi^*)$ orbitals in the $Os^{II}P(CO)(L)$ complexes does not lower the energy of $5d_\pi$ orbitals sufficiently to raise the energy of the metal → ring $^3(d,\pi^*)$ state above the ring $^3(\pi,\pi^*)$ state.

Excited-State Deactivation Rates. The increased mixing of the metal d_π and ring $e_g(\pi^*)$ LUMOs in the osmium(II) porphyrins compared to the ruthenium(II) porphyrins results in increased spin–orbit coupling.[3] This should enhance intersystem crossing from the singlet to triplet manifolds. As intersystem crossing from $^1Q(\pi,\pi^*)$ to the $^3(\pi,\pi^*)$ state in $Ru^{II}TTP(CO)(L)$ appears to occur in <350 fs,[25] we expect the singlet lifetimes in the corresponding Os complexes to occur on an equally short time scale. This expectation is further indicated by the ~1-ps $^1Q(\pi,\pi^*)$ lifetime for the third-row platinum(II) porphyrins,[2,11b] which reflects predominantly intersystem crossing to $^3(\pi,\pi^*)$. A subpicosecond rate of intersystem crossing from $^1(\pi,\pi^*)$ to $^3(\pi,\pi^*)$ followed by internal conversion to $^3(d,\pi^*)$ thus seems reasonable and is supported by our subpicosecond resolution transient absorption results on OsOEP(CO)(py), in which we find no evidence for a transient state prior to $^3(d,\pi^*)$. We do not understand the discrepancy with the earlier results indicating a 40-ps $^1(\pi,\pi^*)$ lifetime for this compound,[11a] a lifetime which again seems unusually long based on the results on the Ru^{II} and Pt^{II} complexes.

Although the OsP(CO)(py) and $OsP(py)_2$ complexes have the $^3(d,\pi^*)$ CT state as the lowest electronic excited state, the ~1 ns decay time observed for $OsTTP(py)_2$ and $OsOEP(py)_2$ is significantly shorter than the 15–35 ns lifetime observed for OsTTP(CO)(py) and OsOEP(CO)(py) (Table 1 and ref 11). Phosphorescence has not been observed for either bispyridine complex (this work and ref 3). One possibility for the lack of observed emission from the bispyridine complexes is that it occurs at a wavelength longer than the phosphorescence from the

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(33) This assignment would imply (i) that the excited states of the OEP and TPP complexes would differ in geometry compared to the respective ground states, leading to different Franck–Condon factors for the vibronic transitions and/or (ii) that the features between 700 and 900 nm in the $^3(\pi,\pi^*)$ and $^3(d,\pi^*)$ spectra (see Figure 4) arise from mixing between the configurations derived from the $e_g \rightarrow b_{1u}$ and $e_g \rightarrow b_{2u}$ electron promotions, by analogy to interaction between the $(a_{1u}.e_g)$ and $(a_{2u}.e_g)$ configurations that give rise to the Q and Soret bands in the ground-state spectrum according to the four-orbital model.[29] Configuration interaction would lead to a weak electronic transition in the red, with the intensity of the (0.0) band and thus its ratio with the (1,0) band ~1300–1700 cm^{-1} to higher energy, being controlled by the degeneracy of the parent configurations. A difficulty with direct analogy to the four-orbital model for the ground-state absorption spectrum is the insensitivity of the red-region spectrum of the TPP complexes to the axial ligands and the great sensitivity of the spectrum to axial ligation in the OEP complexes. The results could be explained within the framework of a MO/CI picture if the b_{1u} orbital is substantially lower than b_{2u} and predominates in giving rise to the strong "(0,0)" ~850-nm transition and the weaker "(1,0)" transition near 750 nm in the TPP complexes, as described in the text. However, if the b_{2u} drops very close to b_{1u} in the OEP complexes then significant CI would weaken the (0,0) transition in certain complexes (depending on the metal ion and the axial ligands). This energetic shift would give rise to a variability in the peak positions and intensity ratios of the (0.0) and (1,0) bands in the red-region spectra of the OEP $^3(d,\pi^*)$, $^3(\pi,\pi^*)$, and anion spectra. Such a change in intensity ratio would be analogous to the situation for the Q bands in the ground-state absorption spectra of metallo-TPP complexes.[2]

(34) Callis, J. B.; Gouterman, M.; Jones, Y. M.; Henderson. B. M. *J. Mol. Spectrosc.* **1971**, *39*, 410–420.

carbonyl–pyridine complexes and thus is beyond the detection limit of the instrumentation employed (i.e. past 900 nm; Figure 3A). One does expect the $^3(d,\pi^*)$ state to lie lower in energy for the bispyridine complexes relative to the carbonyl–pyridine complexes; in the latter, $d_\pi \rightarrow CO(\pi^*)$ π-backbonding will lower the d_π orbitals and raise the energy of the $d_\pi \rightarrow e_g(\pi^*)$ CT state relative to the bispyridine complexes, which lack a π-accepting ligand.

Perhaps the predominant effect of the lower energy of the $^3(d,\pi^*)$ state in the bispyridine complexes compared to the carbonyl–pyridine complexes is to increase the rate of nonradiative decay through an improved Franck–Condon (vibrational overlap) factor. The rate of radiationless decay has been found to depend exponentially on energy gap, and for the $^3(\pi,\pi^*)$ states of a number of aromatic molecules the empirical decay law has the form $\delta \ln k/\delta \Delta E \sim 10^{-3}$ cm.[35] Hence, an increase by a factor of ~20 in the decay rate of the $^3(d,\pi^*)$ state of the $Os^{II}P(L)_2$ complexes compared to the $Os^{II}P(CO)(L)$ complexes (Table 1) can be explained by a modest (~0.4 eV) decrease in the energy gap from the ground electronic state. Such a shift is not unreasonable on the basis of the MO calculations.[3] A similar mechanism is thought to contribute to the significantly faster (nanoseconds vs microseconds) deactivation rate to the ground electronic state of the $^3(d,\pi^*)$ state (the lowest excited state) of the $Ru^{II}P(L)_2$ complexes compared to the $^3(d,\pi^*)$ state of the $Ru^{II}P(CO)(L)$ complexes, which is at higher energy than (and thermally accessible from) the $^3(\pi,\pi^*)$ state.[12c]

In analogy to the Ru^{II} complexes, there may also be an electronic contribution to the increased rate of decay of the $^3(d,\pi^*)$ state of the $Os^{II}P(L)_2$ complexes compared to the $Os^{II}P(CO)(L)$ complexes. In particular, there will be reduced spin–orbit coupling in the carbonyl complexes: axial $d_\pi \rightarrow CO(\pi^*)$ backbonding will lower the energy of the d_π orbitals and thus decrease the mixing (equatorial π-backbonding) of the metal d_π orbitals and the ring $e_g(\pi^*)$ orbitals.[3] This electronic contribution will supplement the energy-gap reduction effect on the Franck–Condon factor in yielding a faster rate of radiationless deactivation in the $^3(d,\pi^*)$ CT excited state of the osmium(II) and ruthenium(II) porphyrin bispyridine and related complexes compared to the carbonyl-containing complexes.

Finally, we note that the excited-state decay time of the quinone-containing complex OsTPP(CO)(S–NQ) is essentially the same as that for OsTPP(CO)(S–DMN) and the other OsTTP(CO)(L) compounds. This result together with the lack of a signature of ionic products in the transient absorption data indicates that electron transfer does not occur to any appreciable extent in this system. This finding can be traced to an insufficient driving force intramolecular photoinitiated electron transfer of OsTTP(CO)(S–NQ) dissolved in necessarily nonligating (i.e. low dielectric) solvents. We now know from the results of our study that the lowest excited state of the OsTTP(CO)(L) and OsTPP(CO)(L) complexes is not the ring $^3(\pi,\pi^*)$ state having an energy of ~1.9 eV as proposed from previous work, but is instead of $^3(d,\pi^*)$ metal → ring CT excited state lying ~1.6 eV above the ground state.

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[35] Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.