field splitting parameter Δ_{av} yields a value of 3.41 μm^{-1}. Using a value for the Jørgenson metal g value for Rh(III) of 2.7 μm^{-1} yields a minimum ligand f value of 1.5 for the ppy and bzq ligands. Due to the use of a minimum ^{3}LF energy and a probable overestimate of the contributions of bridging chlorides[41] to the average crystal field splitting parameter, this ligand f value represents a lower limit. However, it is clear from this estimate that ppy and bzq lie well above bpy and phen (f = 1.33) in the spectrochemical series.

This position indicates that the low-energy LF states which contribute to dual LF/MLCT emissions[42-45] of $IrCl_2(bpy)_2^+$ and $IrCl_2(phen)_2^+$ should make no contributions to the emissions of the Ir(III) dimers of the former ligands. Indeed, no evidence for LF emissions is found in these complexes. The observed MLCT emissions of the ppy and bzq dimers (490 and 510 nm, respectively) lie well below the MLCT components of the $IrCl_2(bpy)_2^+$ and $IrCl_2(phen)_2^+$ emissions (475 nm, both), as expected. This enhancement in the MLCT character of the lowest excited states of the dimers should decrease deactivation through LF excited states, which often takes the form of ligand labilization,[46-49] and improve the efficiency with which they participate in photoredox processes. A study of their electrochemical and photoredox properties is presently in progress.

The overall view of the spectroscopic effects of ppy and bzq as bidentate ligands with Rh(III) and Ir(III) which derives from the above considerations is a remarkable one. The relatively low energy MLCT emissions observed for their Ir(III) complexes indicate that they are good π-accepting ligands with sufficiently delocalized π^* orbitals to accomodate electron transfer from the Ir(III) metal center in the excited state. They are further sufficiently strong σ donors, largely through their Ir–C bonding, to enrich the electron density of Ir(III) sufficiently to render the metal somewhat more oxidizable than it is in comparable bpy and phen complexes. This synergistic combination of bonding effects is not sufficient to induce an MLCT emission in the Rh(III) dimers, but relatively intense absorption bands in these species in the region around 400 nm are assigned as MLCT transitions. Comparable bands are not seen in the absorption spectra of similar bpy and phen complexes of Rh(III), where they are probably buried at higher energies under the intense π–π^* ligand-centered absorptions. These spectroscopic results suggest that enhancement of the electron density at metal centers via metal–carbon σ bonding to π-conjugated ligands such as ppy and bzq may add new dimensions to the electrochemical and photochemical properties of the resultant complexes relative to those of fully N-coordinated bpy and phen complexes.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the Department of Energy, Project DE-AT03-78ER70277.

Registry No. $[Rh(ppy)_2Cl]_2$, 33915-80-9; $[Rh(bzq)_2Cl]_2$, 33915-76-3; $[Ir(ppy)_2Cl]_2$, 92220-65-0; $[Ir(bzq)_2Cl]_2$, 52352-02-0; $RhCl_3$, 10049-07-7; $IrCl_3$, 10025-83-9; benzo[*h*]quinoline, 230-27-3; 2-phenylpyridine, 1008-89-5.

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Picosecond Photolysis of Axial Ligands on Cobalt(II) and Cobalt(III) Porphyrins

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Abstract: Excited-state photoprocesses of cobalt(II) octaethylporphyrin (OEP), cobalt(II) tetraphenylporphyrin (TPP), $Co^{III}(OEP)(CN)$, and $Co^{II}(OEP)(CN)(\gamma\text{-picoline})$ in noncomplexing solvents and in the presence of coordinating species Me_2SO and piperidine have been studied. The transient absorption spectra suggest that the excited-state relaxation of cobalt(II) porphyrins proceeds via the tripdoublet, $^2T(\pi, \pi^*)$, and the $^2(\pi, d_{z^2})$ charge-transfer (CT) states and that rapid deactivation of the latter state competes favorably with axial ligand release, accounting for the low yield for photodissociation. When five-coordinate $Co^{III}(OEP)(CN)$ is excited, the transient spectra suggest that the initial (π, π^*) and (π, d) CT excited states decay to $^3(d_\pi, d_{z^2})$, followed by ligand loss to produce four-coordinate $[Co^{III}(OEP)]^+$. However, when six-coordinate $[Co^{III}(OEP)L_2]^+$ systems are excited, the transient spectra suggest that both five-coordinate $[Co^{III}(OEP)L]^+$ and four-coordinate $[Co^{III}(OEP)]^+$ are produced, both presumably from $^3(d_\pi, d_{z^2})$, which is not observed. In 1–4 M ligating solvents $[Co^{III}(OEP)L]^+$ rebinds a ligand in 250 ps to 1.4 ns, whereas $[Co^{III}(OEP)]^+$ is stable for ≥1 ns. This difference in stability is attributed to the five-coordinate species having a singlet ground state, while the four-coordinate species is a triplet ligand-field (d, d) state.

Binding and release of ligands from the iron porphyrin active site of hemoglobin and myoglobin are of considerable biological significance. While iron porphyrins are frequently used as synthetic model systems, cobalt(II) porphyrins are also known to bind O_2 and CO.[1-3] Cobalt(III) porphyrins exhibit catalase-like activity in the disproportionation of H_2O_2.[4]

A study of the photorelease of basic axial ligands from five-coordinate cobalt(II) deuteroporphyrin IX dimethyl ester

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Table I. Ground-State Absorption Spectra of Cobalt Porphyrins[a,b]

porphyrin	solvent	B(0,0)	Q(1,0)	Q(0,0)	main soln species
Co^{II}(OEP)	toluene	393 (11.1)	518 (0.45)	552 (1.0)	parent
Co^{II}(OEP)	CH_2Cl_2	391 (11.0)	516 (0.48)	551 (1.0)	parent
Co^{II}(OEP)	piperidine	396 (7)	518 (0.7)	545 (1.0)	M(P)(pip)
		410 (7)			$M(P)(pip)_2$
Co^{II}(TPP)	toluene	412 (17.6)	529 (1.0)		parent
Co^{II}(TPP)	CH_2Cl_2	408 (18)	525 (1.0)		parent
Co^{II}(TPP)	piperidine	422 (18)	532 (1.0)		$M(P)(pip)_2$
		412[c]			M(P)(pip)
Co^{III}(OEP)(CN)	CH_2Cl_2	421 (3.4)	515[c]	548 (1.0)	parent
		372 (2.0)			
Co^{III}(OEP)(CN)	pip/CH_2Cl_2 (1/9)	421 (15.1)	535 (1.7)	568 (1.0)	$[M(P)(pip)_2]^+$
		345 (3.2)			
Co^{III}(OEP)(CN)	Me_2SO/toluene (1/2)	419 (10.7)	535 (1.0)	565 (1.0)	$[M(P)(Me_2SO)_2]^+$
		345[c]			
Co^{III}(OEP)(CN)(γ-pic)	CH_2Cl_2	421 (14.8)	535 (1.7)	568 (1.0)	parent
		345 (3.2)			

[a] Abbreviations: TPP = *meso*-tetraphenylporphyrin; OEP = octaethylporphyrin. [b] Peak wavelengths in nm; relative peak heights in parentheses. [c] Shoulder.

(DPDME) has shown that the quantum yields for ligand ejection are low, in the range 0.01–0.1 for the ligands investigated.[5] On the other hand, the photorelease of CN^- from cobalt(III) horseradish peroxidase has a quantum yield >0.2.[6] The time resolution of these measurements did not permit the detection of excited states populated before the dissociated state was observed.

Here we present the results of picosecond transient absorption studies on several cobalt(II) (d^7) and cobalt(III) (d^6) porphyrins in which the metal is four-, five-, or six-coordinate prior to excitation. The present work builds upon previous results of cobalt(II) and cobalt(III) porphyrins in noncoordinating solvents, in which the low-lying electronic states that contribute to the excited-state deactivation have been identified:[7,8] $(\pi, \pi^*) \rightarrow (\pi, d_{z^2})$ for Co^{II} and $(\pi, \pi^*) \rightarrow (\pi, d_{z^2}) \rightarrow (d_\pi, d_z^2)$ for Co^{III}. Theoretical knowledge of the excited states along the relaxation pathways and of the ground-state multiplicities is used to explain the differences in the observed excited-state ligand release behavior for the various cobalt porphyrin complexes investigated.

Experimental Section

Details of the dual-beam picosecond laser apparatus used for the present studies have been described elsewhere.[9] A Quantel YG400 Nd:YAG laser produces 1064-nm pulses of ~35-ps duration at a repetition rate of 10 Hz. The 10-mJ fundamental pulse is divided into two pulses by a 50% beam splitter. One of these pulses is used to generate 532-nm (2 mJ) or 355-nm (300 μJ) excitation pulses in KD*P crystals. The second pulse travels down a variable-length (−300 ps to 12 ns) optical delay line and is focused into a cell containing $CCl_4/CHCl_3$ to produce a weak white-light monitoring flash.

Co^{II}(TPP) was obtained commercially (Midcentury, Posen, IL); Co^{II}(OEP), Co^{III}(OEP)(CN), and Co^{III}(OEP)(CN)(γ-picoline) were provided by Drs. D. Dolphin and P. D. Smith. Purity of the compounds was checked by TLC. All solvents used were spectral grade quality. Samples in 2-mm path-length cells were deoxygenated unless noted otherwise. Deoxygenation was achieved by bubbling the solutions with high-purity argon or by sealing samples after repeated freeze–pump–thaw cycles on a high-vacuum line. Some sample degradation after many (several thousand) 355-nm excitation flashes was noted only for the Co^{III}(OEP)(CN) complex in CH_2Cl_2/piperidine solvent mixtures.

Results

Cobalt(II) Porphyrins. Table I shows the changes in the ground-state spectra of Co^{II}(OEP) and Co^{II}(TPP) on going from deoxygenated toluene to deoxygenated piperidine solutions. The Soret band is split for Co^{II}(OEP), while it is red shifted without significant splitting in the case of Co^{II}(TPP). As discussed below, in neat piperidine Co^{II}(TPP) adds two axial ligands to make a six-coordinate Co^{II} complex, whereas Co^{II}(OEP) appears to exist mainly in the five-coordinate form with some contribution from the six-coordinate species. In very dilute (≤0.1 M) piperidine, both cobalt(II) porphyrins are predominately five-coordinate.

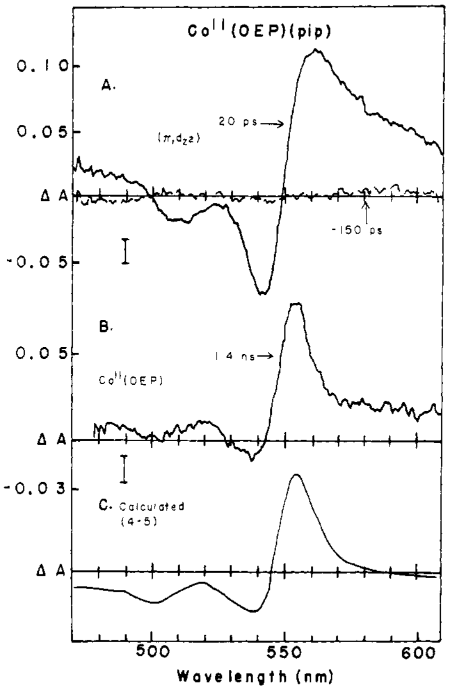

Figure 1. Transient absorption difference spectra (A and B) at two delay times following excitation of $\sim 2 \times 10^{-4}$ M Co^{II}(OEP)(pip) in 0.1 M piperidine in toluene with 35-ps flashes at 355 nm. Co^{II}(OEP)(pip) is the predominant species formed by dissolving Co^{II}(OEP) in this solvent mixture (see text). The difference spectrum shown in part C was constructed by substracting the ground-state spectrum of the five-coordinate Co^{II}(OEP)(pip), obtained by dissolving Co^{II}(OEP) in 0.1 M piperidine in toluene, from the ground-state spectrum of the four-coordinate Co^{II}(OEP) in toluene; both solutions had the same porphyrin concentration. The maximum error across the wavelength region shown is given at the left of each panel in Figures 1–4.

Figure 1 illustrates the transient behavior of five-coordinate Co^{II}(OEP) in dilute piperidine (0.1 M) in toluene induced by a 35-ps, 355-nm excitation flash. The absorption difference spectrum at 20 ps (Figure 1A) shows bleaching of the Q bands, with a relatively strong absorption increase tailing to the red to about 650 nm and slightly increasing in strength to the blue of the ground-state bands. These features are consistent with those expected for the formation of a $(a_{2u}(\pi), d_{z^2})$ charge-transfer (CT)

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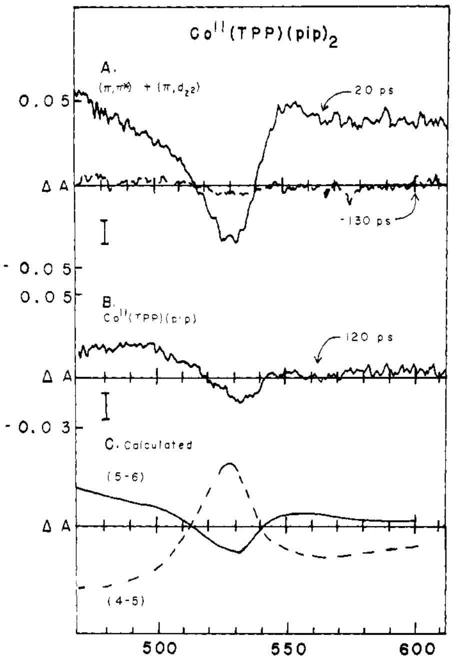

Figure 2. Transient absorption difference spectra (A and B) for ~2 × 10^{-4} M $Co^{II}(TPP)(pip)_2$ in neat (10 M) piperidine produced by excitation with 35-ps flashes at 355 nm. The six-coordinate complex was obtained by dissolving $Co^{II}(TPP)$ in this solvent (equilibrium constants in text). Panel C shows difference spectra for release of one axially bound piperidine from either the five-coordinate $Co^{II}(TPP)(pip)$ or the six-coordinate $Co^{II}(TPP)(pip)_2$, constructed from ground-state spectra of the authentic species. The latter were obtained by dissolving $Co^{II}(TPP)$ in toluene (four-coordinate), in 0.05 M piperidine in toluene (five-coordinate), or in neat piperidine (six-coordinate); the porphyrin concentration was the same in each case.

excited state, which should resemble the absorption changes due to the formation of the metallo-OEP π-cation radical with a $^2A_{2u}$ ground state.[7,10] Except for small shifts in the bleaching wavelengths due to the different state of coordination, the absorption changes are very similar to those observed previously at comparable delay times for the four-coordinate complex in toluene.[7] In that case, the difference spectrum was assigned to a ($a_{2u}(\pi)$, d_{z^2}) charge-transfer (CT) state, as discussed below in more detail. Also, a broad absorption across the 480–630-nm region broken by the Q-band bleachings was observed earlier in the 35-ps excitation flash that was assigned[11,12] to the $^2T(\pi, \pi^*)$ feeding the (π, d) CT.[7] The spectrum of Figure 1A for the five-coordinate complex did not change shape during the excitation flash. Therefore, we assign the spectrum mainly to the ($a_{2u}(\pi)$, d_{z^2}) CT excited state but cannot rule out some contribution from $^2T(\pi, \pi^*)$. These absorption changes give way with a decay time of <35 ps to a species responsible for the difference spectrum of Figure 1B. On the basis of the agreement between this difference spectrum and that calculated from the ground-state spectra of four- and five-coordinate $Co^{II}(OEP)$ (Figure 1C), we assign this longer lived transient as the four-coordinate species formed upon photodissociation of $Co^{II}(OEP)(pip)$. Piperidine (0.1 M) is observed to rebind to the Co^{II} with a time constant (pseudo-frst-order process) of ~9 ns to regenerate the five-coordinate ground-state complex, as measured by relaxation of the absorption increase at 555 nm. Excitation with 532-nm pulses produced similar absorption changes (not shown) except that the region between 510 and 550 nm could not be explored because of scattered pump light.

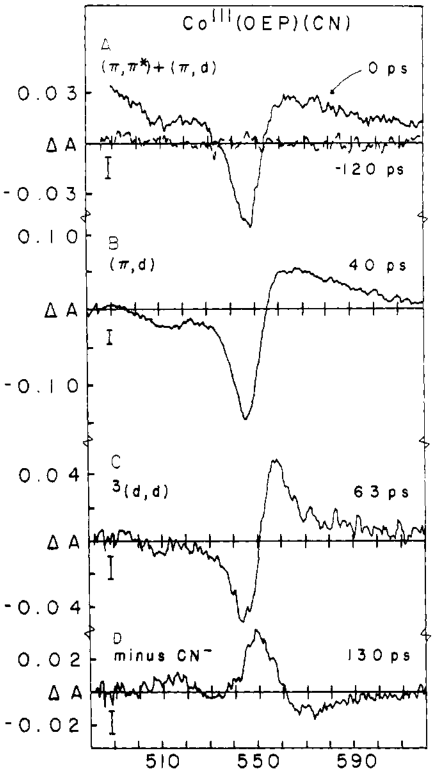

Figure 3. Transient absorption difference spectra for ~10^{-5} M $Co^{III}(OEP)(CN)$ in CH_2Cl_2 produced by excitation with 35-ps flashes at 355 nm. Reproduced from ref 7.

The absorption difference spectra obtained upon excitation of six-coordinate $Co^{II}(TPP)$ in neat piperidine with 355-nm flashes

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(10) (a) Most of the oscillator strength for absorption by these excited states should come from the porphyrin ring. Therefore, we expect (π, d) and (d, π*) ring ↔ metal CT states to have absorption difference spectra similar to those for the formation ring π-cation and π-anion radicals, respectively. Oxidation of cobalt(II) porphyrins first causes conversion to the cobalt(III) porphyrin followed by removal of an electron from either the ring highest filled $a_{1u}(\pi)$ orbital or the ring highest filled $a_{2u}(\pi)$ orbital (D_{4h} symmetry notation) to make the cobalt(III) porphyrin π-cation radical (see ref 10b–d and references therein). Therefore, we can only compare our Co^{II} transient spectra with spectra for formation of cobalt(III) porphyrin cation radicals or those of other transition-metal porphyrins. On the basis of the data in ref 10b,c, we expect the ($a_{2u}(\pi)$, d) CT state in the OEP complexes to exhibit spectra similar to those shown in Figures 1A and 3B: bleachings of the ground-state Q bands and absorption increase to the red tailing to past 650 nm, and small absorption changes between 450 and 500 nm. The transient spectra do not exhibit the distinct peak between 650 and 700 nm expected for the ($a_{1u}(\pi)$, d) cation radical on the basis of the data for $[Co^{III}(OEP)]^+Br^-$ in ref 10b,c. CT excited states of metallo-TPP complexes are expected to exhibit somewhat different behavior in the 500–650-nm region, based on the π-cation radical spectra. Systematic studies on these complexes in which the nature of the lowest CT state is varied by choice of macrocycle and counterion, where necessary, are planned in order to correlate the transient spectra with those expected from the π-radical data. Absorption changes expected for the (π, π*) excited states are noted in ref 11 and for (d, d) excited states in ref 7, 9, and 29. (b) Dolphin, D.; Muljiani, Z.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton, R. H. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 177–200. (c) Dolphin, D.; Felton, R. H. *Acc. Chem. Res.* **1974**, *7*, 26–32. (d) Felton, R. H. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, pp 53–125.

(11) On the basis of work in other metalloporphyrins in which the lowest excited state are (π, π*) in origin (see ref 12 and references therein for examples), we expect the (π, π*) excited states in the cobalt(II) and cobalt(III) porphyrins to exhibit the following features in the 450–650-nm region: OEP complexes should show broad featureless absorption in this region, broken by bleachings in the ground-state Q bands, while TPP complexes should show a strong new absorption between 450 and 500 nm, tailing through the Q-band bleachings to near 650 nm. The (π, π*) states of both macrocycles may show one or two weak new absorption peaks between 700 and 900 nm, not investigated in the current studies.

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are shown in Figure 2. Similar results were obtained by using 532-nm pump pulses in regions where comparisons could be made. There is evidence for only one transient during the excitation flash, and the absorption changes are similar to those found previously for Co^{II}(TPP) in toluene.[7,8] Most of the initial transient absorption obtained by using either 532- or 355-nm flashes decays with a time constant of <35 ps but appears to be shorter than the initial relaxation observed for Co^{II}(OEP). The decay time is probably <15 ps, as was found for Co^{II}(TPP) in toluene.[7,8] The broad absorption in this region (Figure 2A) is consistent with that expected for the (a$_{2u}$(π), d$_{z^2}$) CT excited state of metallo-TPP complex.[10] A (π, π*) excited state of the Co^{II}(TPP) complex also could contribute to the spectrum, although it does not appear to be totally responsible for it.[11] Small (but significant) absorption changes due to a longer lived species are obtained for Co^{II}(TPP) in neat piperidine by using either pump wavelength, as evidenced by the 120-ps spectrum in Figure 2B. The features of the spectrum are similar to those expected for the formation of a five-coordinate species via ligand release from the photoexcited six-coordinate complex (see solid spectrum in Figure 2C). The lifetime of this transient is 130 ± 20 ps in neat piperidine. Similar experiments on Co^{II}(TPP) were performed by using either 532- or 355-nm excitation flashes with toluene/piperidine mixtures in which the concentration ratio Co^{II}(TPP)(pip)$_2$/Co^{II}(TPP)(pip) is approximately 4/1 or 1/5. While difference spectra during the flash were similar to those found in neat piperidine (Figure 2A), no longer lived (> 35-ps relaxation) species were detected in these dilute piperidine solutions. An explanation for this lack of transient spectra with lower piperidine concentration is proposed in the Discussion section.

Cobalt(III) Porphyrins. The excited-state deactivation pathway of Co^{III}(OEP)(CN) in CH$_2$Cl$_2$ following excitation with 355-nm flashes has been worked out previously.[7] The time-resolved spectral behavior from our earlier study is reproduced in Figure 3, since these data form a framework for discussing the results in coordinating solvents. The chain of transient states (π, π*) → (π, d) → ^{3}(d, d) prior to the dissociated state has been identified.[7]

In the presence of coordinating solvents such as Me$_2$SO or piperidine, a six-coordinate ground-state species is formed. As shown in Table I, the absorption spectra of Co^{III}(OEP)(CN) in Me$_2$SO/toluene and piperidine/CH$_2$Cl$_2$ solutions are distinct from those observed in the noncoordinating solvent CH$_2$Cl$_2$ but are almost identical with that of an authentic six-coordinate species Co^{III}(OEP)(CN)(γ-pic) in CH$_2$Cl$_2$, thereby confirming a change in coordination number. Previous NMR studies of Co^{III}(TPP)(X$^-$) (X = I, Br, Cl, PF$_6$, ClO$_4$) indicate that while the counterion X$^-$ remains bound to the metal in noncoordinating solvents, it is replaced in coordinating solvents, L, to form the species [Co^{III}(TPP)(L)$_2$]$^+$X$^-$.[13] The same replacement is expected in the presence of Me$_2$SO and piperidine, particularly at the high concentrations used here. It appears that the visible absorption spectrum is determined primarily by the coordination number of the Co^{III} rather than by the ligand's identity.

The transient behavior produced by all of the six-coordinate Co^{III} complexes is, in general, similar. Results with Me$_2$SO (4 M) as the fifth and sixth ligands are shown in Figure 4. Similar results were obtained by using 532-nm excitation flashes at wavelengths where comparisons could be made. The spectrum of Figure 4A shows a strong absorption increase to the blue of 500 nm, a broad absorption tail extending past 600 nm, and bleaching of the ground-state Q bands of the six-coordinate species (Table I). The absorption increasing in strength between 520 and 480 nm and tailing past 600 nm indicates that a (π, π*) excited state probably contributes to the difference spectrum,[7,11,12] possibly with some (π, d$_{z^2}$) CT contribution, as in the five-coordinate case in CH$_2$Cl$_2$ (Figure 3A).[7] Unlike the five-coordinate case, the initial absorption changes do not evolve into spectra that can be assigned exclusively to (π, d) CT or (d, d) excited states as in Figure 3B,C. Instead, the absorption increases near 490 and 590 nm in Figure 4A decay essentially with the flash profile to a new transient having absorption peaks at 515 and 550 nm (Figure 4B). On the basis of comparisons with Table I and the difference spectrum of Figure 5, calculated from ground-state spectra of the authentic compounds, these new absorptions are assigned as the Q(1,0) and Q(0,0) bands of the five-coordinate species, [Co^{III}(OEP)(Me$_2$SO)]$^+$.

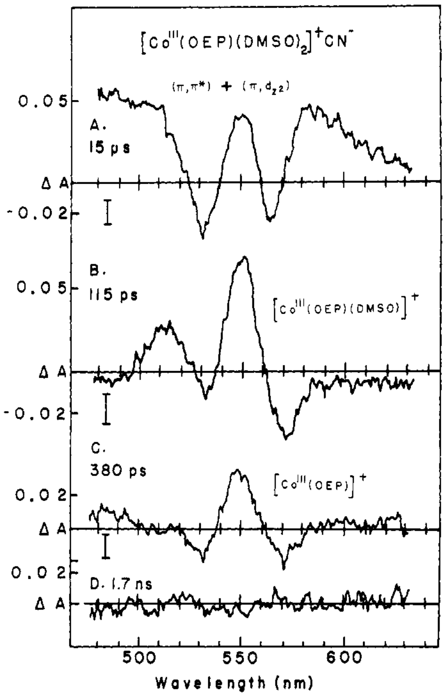

Figure 4. Transient absorption difference spectra following excitation of ~10^{-5} M Co^{III}(OEP)(CN) in 4 M Me$_2$SO in toluene with 35-ps flashes at 355 nm. The absorbing species is identified as [Co^{III}(OEP)(Me$_2$SO)$_2$]$^+$. Note that the four-coordinate species labeled in C probably is present in B as well. See text.

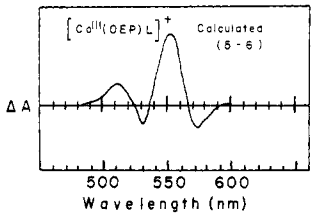

Figure 5. Calculated absorption difference spectrum constructed by subtracting the ground-state spectrum of the six-coordinate complex [Co^{III}(OEP)(pip)$_2$]$^+$CN$^-$ obtained by dissolving Co^{III}(OEP)(CN) in 1 M piperidine in CH$_2$Cl$_2$, from that of the five-coordinate Co^{III}(OEP)(CN) in neat CH$_2$Cl$_2$; the porphyrin concentration was the same for both spectra.

Figure 4C shows the difference spectrum observed at 380 ps. It differs from Figure 4B (115 ps) by the disappearance of the 515-nm transient absorption peak and the reduction in the intensity of the 550-nm peak. We attribute the Figure 4C (380 ps) spectrum to the four-coordinate species, [Co^{III}(OEP)]$^+$, on the basis of its resemblence to the transient spectrum so identified in Figure 3D. From the decay of the 515-nm absorption increase and the faster component of the decay at 550 nm, the five-coordinate species is found to relax to the six-coordinate species with a pseudo-first-order time constant of 250 ± 40 ps. The second-order rate constant for the addition of the sixth ligand is therefore calculated to be ~1 × 10^9 M^{-1} s^{-1}. Recovery of the longer lived absorption changes assigned to the four-coordinate species is complete by 1.7 ns (Figure 4D). (In the Discussion section we provide an explanation for the observation that the four-coordinate species is longer lived than the five-coordinate species.)

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(13) (a) Yamamoto, K.; Uzawa, J.; Chijimatsu, T. *Chem. Lett.* **1979**, 89–92. (b) Huet, J.; Gaudemer, A.; Boucly-Goester, C.; Boucly, P. *Inorg. Chem.* **1982**, *21*, 3413–3419. (c) Chapman, R. D.; Fleischer, E. B. *J. Am. Chem. Soc.* **1982**, *104*, 1575–1582.

Again, for $Co^{III}(OEP)(CN)(pip)$ in piperidine/CH_2Cl_2, (1:3) and (1:9), the absorbing species is $[Co^{III}(OEP)(pip)_2]^+$. The transient behavior during and shortly after the flash (not shown) is similar to that just described for Me_2SO as the axial ligands. However, the yield for the four-coordinate $[Co^{III}(OEP)]^+$ is considerably smaller than that in the solutions containing Me_2SO. After ejection, rebinding of piperidine to the five-coordinate complex also occurs with pseudo-first-order kinetics. The time constant for decay of the transient absorption at 515 or 550 nm due to the five-coordinate species in 2.5 M piperidine in CH_2Cl_2 is 830 ± 80 ps, while in 1 M piperidine the decay time is 1.4 ± 0.1 ns. On the basis of these values we estimate a rate constant of $\sim 6 \times 10^8$ M^{-1} s^{-1} for the conversion of $[Co^{III}(OEP)(pip)]^+ + pip \rightarrow [Co^{III}(OEP)(pip)_2]^+$. In these cases, recovery of the longer lived absorption changes due to the four-coordinate species requires ≥ 2 ns, slower than in 4 M Me_2SO.

The results for the authentic six-coordinate γ-picoline complex in CH_2Cl_2 (not shown) are consistent with the results reported above for the Me_2SO and piperidine complexes. The absorption changes for the dissociated species, observed after the excitation flash, appear to be due to a mixture of $Co^{III}(OEP)(CN)$ and $[Co^{III}(OEP)]^+$. For the γ-picoline complex in CH_2Cl_2, there is no excess of ligand present to occupy the vacant coordination sites, and the absorption changes assigned to the dissociated complexes showed negligible relaxation between ~60 ps and 6 ns, the longest delay employed.

Discussion

Co^{II}. Previous picosecond studies have examined the excited-state deactivation routes for $Co^{II}(OEP)$[7] and $Co^{II}(TPP)$[7,8] in the noncoordinating solvent toluene. The (π, π^*) excited states of these molecules are doublets and quartets, formed by interaction of the unpaired electron on the d^7 Co^{II} with the normal porphyrin singlets and triplets.[14] For both molecules, the relaxation of the excited species is rapid (<35 ps),[7,8] probably via the $^2A_{2u}(\pi, d_{z^2})$ CT state.[7] Such a low-lying CT state is prediced by iterative extended Hückel (IEH) theory and supported by near-IR absorption spectra.[14] Absorption changes observed early in the excitation flash were attributed to $^2T(\pi, \pi^*)$ preceding the CT state. These conclusions are consistent with the lack of emission from both molecules.[14] Note that all of the states proposed to lie along the deactivation pathway in the Co^{II} compounds, including the ground state, are doublets. Since no changes in multiplicity are required, this may account, at least in part, for the very short lifetimes observed. The low energy of the CT state probably also contributes to the rapid deactivation.

Similar rapid relaxations were found in the present study for both cobalt(II) porphyrins in neat piperidine or piperidine diluted with toluene, and we attribute the absorption changes observed during the excitation flash (Figures 1A and 2A) to the $(a_{2u}(\pi), d_{z^2})$ CT state, possibly with some contribution from the $^2T(\pi,\pi^*)$ state that feeds it.

While decay of the transient absorption and recovery of ground-state bleaching were found to be complete by 100 ps after zero-time for the four-coordinate $Co^{II}(OEP)$ or $Co^{II}(TPP)$ in neat toluene,[7,8] longer lived absorption changes are obtained following excitation in the presence of piperidine (Figures 1B and 2B). For the five-coordinate complex $Co^{II}(OEP)(pip)$ in 0.1 M piperidine, these absorption changes are fully developed by 100 ps. The difference spectrum shown at a 1.4-ns delay in Figure 1B compares extremely well with that shown in Figure 1C, which shows the absorption changes expected for the release of the axially bound piperidine. Assuming that the absorption changes in Figure 1B decay to $\Delta A = 0$ at times longer than could be obtained here (~12 ns), the time evolution of the absorption increase near 550 nm can be fit to an exponential with a 9-ns time constant.[15] The bimolecular rate consant of 1.1×10^9 M^{-1} s^{-1} calculated from this value and the 0.1 M piperidine concentration compares well with the value of 1×10^9 M^{-1} s^{-1} derived by Tetreau et al.[5] for the rebinding of piperidine to four-coordinate cobalt(II) deuteroporphyrin IX dimethyl ester (DPDME) in very dilute piperidine solutions. Thus, our assignment of the absorption changes in Figure 1B to the deligated species has spectral and kinetic support.

That $Co^{II}(OEP)(pip)$ is the predominant species excited (>90%) in 0.1 M piperidine can be determined from the equilibrium constant of 1862 M^{-1} for $Co^{II}(OEP) + pip \rightleftarrows Co^{II}(OEP)(pip)$, and a value of <1 M^{-1} for $Co^{II}(OEP)(pip) + pip \rightleftarrows Co^{II}(OEP)(pip)_2$ estimated from data on other cobalt(II) porphyrins.[2] In neat piperidine both $Co^{II}(OEP)(pip)$ and $Co^{II}(OEP)(pip)_2$ are present in the ground state, with the five-coordinate complex predominant.[2] Excitation of this mixture leads to absorption changes during the 355-nm flash that are similar to those reported above in the other solvents. However, no longer lived absorption changes are detected. One reason for this behavior, also observed for the $Co^{II}(TPP)$ complexes (Figure 2C), is that the difference spectra for release of one ligand from $Co^{II}(OEP)(pip)$ and from $Co^{II}(OEP)(pip)_2$ appear to be mirror images (about $\Delta A = 0$) at many wavelengths in the Q-band region. Thus, if ligand release occurs from both species following excitation of the mixture, there may be a partial cancellation of the absorption changes after the flash. Another possibility is rapid geminate recombination on a time scale of <35 ps. Although we cannot rule out this possibility, the shape of the difference spectrum during the flash and the differences between Figure 1A,B (and 1C) suggest that the initial absorption changes are mainly due to the (π, d) CT and possibly (π, π^*) excited states of the five-coordinate complex and not to the deligated species.

$Co^{II}(TPP)$ exists almost exclusively as the six-coordinate complex in neat piperidine. The single Soret band for $Co^{II}(TPP)$ in piperidine is suggestive of only one species, $Co^{II}(TPP)(pip)_2$, being present (Table I). This conclusion is consistent with the equilibrium constants reported for $Co^{II}(TPP)$ and the related $Co^{II}(p\text{-}OCH_3\text{–}TPP)$ in toluene/piperidine mixtures.[16,17] These arguments indicate that >95% of the $Co^{II}(TPP)$ in neat piperidine is in the six-coordinate form. Thus, on the basis of these considerations and the previous finding that the absorption changes for $Co^{II}(TPP)$ in toluene had completely decayed by ~50 ps,[7,8] it is reasonable to postulate that the weak absorption changes observed 120 ps after the flash in neat piperidine (Figure 2B) are due to release of bound piperidine. The agreement between the difference spectrum of Figure 2B and the calculated one of Figure 2C (solid curve) suggests that one axial ligand has been released following excitation of $Co^{II}(TPP)(pip)_2$. Furthermore, the time constant 130 ± 20 ps observed for recovery of these absorption changes in neat piperidine gives a calculated bimolecular rate constant of 7.6×10^8 M^{-1} s^{-1} for the rebinding. This value is close to that of 1×10^9 M^{-1} s^{-1} obtained above for $Co^{II}(OEP)$ and previously[5] for the rebinding of one ligand to the four-coordinate $Co^{II}(DPDME)$.

We view the rapid (<35 ps) initial relaxation (Figure 2A) as deactivation of the excited five-coordinate complex via the (π, d_{z^2}) CT excited state, as discussed above for this complex and for $Co^{II}(OEP)(pip)$. However, because of the similarities of these absorption changes and those ascribed to the deligated species in Figure 2B, we cannot rule out the possibility that ligand release and rapid geminate recombination contributes to the evolution of the difference spectra at early delay times for $Co^{II}(TPP)(pip)_2$.

Longer lived absorption changes after either a 355- or 532-nm excitation flash were not detected for $Co^{II}(TPP)$ in solutions containing piperidine diluted with toluene. In one case (1.0 M

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(14) Antipas, A.; Gouterman, M. *J. Am. Chem. Soc.* **1983**, *105*, 4896–4901.

(15) From our data, the program CONINFIN calculates that ΔA goes to zero at long delay times. Houser, J. J. *J. Chem. Educ.* **1982**, *59*, 776–777.

(16) (a) Equilibrium constants of 2430 and 4 M^{-1} have been reported for the four- to five- to six-coordinate complexes of $Co^{II}(pOCH_3\text{–}TPP)$ with piperidine in toluene (see ref 16b). A value of 4130 M^{-1} has been measured for the formation of the five-coordinate complex $Co^{II}(TPP)(pip)$ from the four-coordinate complex in toluene/piperidine mixtures (see ref 16c). (b) Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1150–1153, 1154–1158. (c) Walker, F. A.; Beroiz, B.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484–3489.

(17) An X-ray crystallographic study of $Co^{II}(TPP)(pip)_2$ has been carried out. Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84–89.

piperidine), the equilibrium constants reported above indicate that about 80% of the molecules are in the form of the six-coordinate complex, while in more dilute solution (0.05 M piperidine), the five-coordinate species is predominate (~85%). In both cases, the concentration of four-coordinate Co^{II}(TPP) is negligible. Comparison of the calculated difference spectra of Figure 2C indicates if the loss of one ligand from $Co^{II}(TPP)(pip)_2$ and the loss of one ligand from Co^{II}(TPP)(pip) were to occur following excitation of both species, then depending on the relative extents of these processes one might expect a partial or complete cancellation of the absorption changes. The TPP macrocycle makes the central metal more acidic than in OEP complexes and thus might be expected to bind the ligand more strongly.[2] The yield for release of one ligand from five-coordinate CO^{II}(OEP)L complexes may be somewhat larger, possibly because early excited states appear to be longer lived (but still <35 ps).

Our observations on cobalt(II) porphyrins are consistent with previous reports of low (~5%) yields for release of a nitrogenous base from five-coordinate Co^{II}(DPDME) complexes and from iron(II) porphyrins.[5,18,19] The spectra and kinetic results reported here and previously[7] for the Co^{II}(OEP) and Co^{II}(TPP) complexes suggest that such low yields appear to be caused by fast relaxation via the $^2(\pi, d_{z^2})$ CT to the doublet ground state competing with ligand release. (It is possible that in five-coordinate compounds both $^2(\pi, d_{z^2})$ and $^2(d_{z^2}, \pi^*)$ CT states are at low energy and contribute to radiationless decay.) This conclusion is also supported by the lack of emission from Co^{II}(TPP) in piperidine. Thus, on the basis of our data as a whole, we favor rapid radiationless decay of the initially excited complex over ligand ejection followed by very fast recombination as the reason for the low photodissociation yields in the Co^{II} complexes. However, we cannot rule out the possibility that the latter process contributes to some degree. Recent picosecond studies of ruthenium porphyrin π-cation radicals[20] and bisligated iron(II) porphyrins[21] have led to a similar conclusion. It should be noted that it has been suggested previously that low yields for photodissociation of porphyrin (P) complexes Fe^{II}(P)(CO), Fe^{III}(P)(NO), and Mn^{III}(P)(NO) in solution may be due to rapid relaxation via low-lying CT excited states.[6,19] Similar concepts[22a] have been discussed with regard to the low (≤5%) yields for release of O_2 or NO from hemoglobin and myoglobin observed in slower time scale flash photolysis studies,[23,24] although evidence has been provided that subnanosecond geminate recombination may play an important role in these biomolecules.[24,25]

In the present case, the (π, d) CT quenching state involves promotion of an electron from a filled ring orbital to the half-filled d_{z^2} orbital. Since increased electron density in the d_{z^2} orbital should weaken the metal–ligand bond,[22-26] such a CT state may be responsible for the ligand release that is observed.

Co^{III}. We have previously reported on the transient behavior of Co^{III}(OEP)(CN) in the noncoordinating solvent CH_2Cl_2.[7] Several states along the relaxation pathway were identified from time-resolved transient difference spectra (Figure 3). The transient absorption of Figure 3A, taken when the monitoring pulse and the excitation pulse overlap at the sample, shows a mixture of (π, π^*) and (π, d_{z^2}) CT states,[7] indicating a very rapid (<15 ps) quenching of the (π, π^*) state by the CT state. The spin multiplicity (singlet or triplet) of these two states cannot be determined on the basis of the spectral data. The CT state (Figure 3B) decays with a time constant of <35 ps to a low-lying (d_π, d_{z^2}) state, which is believed, by analogy to the nickel porphyrin case,[9,27] to be a triplet (Figure 3C). The (d, d) difference spectrum gives way with a time constant of 20–40 ps to a long-lived (>5-ns relaxation) transient species (Figure 3D). The final state has been ascribed to the formation of CN^--free $[Co^{III}(OEP)]^+$. This assignment is based mainly on absorption increases in the Q-band region observed upon replacement of CN^- with the $CF_3SO_3^-$ counterion which apparently is not bound as tightly to the metal.[28] This replacement mimics formation of the ligand-free species. Ligand ejection apparently occurs from the (d, d) excited state. A high yield (>20%) of CN^- ligand release has been reported from the cobalt(III) porphyrin moiety in cobalt(III) horseradish peroxidase, in a slower time scale experiment.[6] We suggested previously[7] that ligand release in the (d_π, d_{z^2}) state is reasonable, because promotion of an electron to the d_{z^2} orbital would weaken the metal–ligand bond.[22-26,29] Similar ligand ejection due to increased electrostatic repulsion toward σ-donating ligands in a (d, d) excited state also has been noted for nickel porphyrins[9,27a,b] and for some inorganic Co^{III} complexes.[30]

Excitation of a predominately six-coordinate $[Co^{III}(OEP)(L)_2]^+CN^-$ complex with either 355- or 532-nm flashes (for example, Figure 4) results in bleaching of the two visible ground-state bands near 535 and 570 nm (Table I), confirming that the six-coordinate species has been pumped. The transient absorption during the flash with any of the six-coordinate species is broad, increasing to shorter wavelengths (Figure 4A, and piperidine data not shown) and tailing to approximately 650 nm. On the basis of previous work and the discussion above, this absorption appears to be due mainly to a (π, π^*) excited state.[7,10-12] However, some contribution from the (π, d_{z^2}) CT state, as observed in the case of the five-coordinate Co^{III}(OEP)(CN) (Figure 3), is possible. The initial transient absorption measured near 500 and 590 nm decays in <35 ps, revealing absorption peaks near 510 and 550 nm (see Figure 4B and Table I). These new peaks are attributed mainly to the five-coordinate species, with the sixth ligand (Me_2SO, piperidine, or γ-picoline) having been ejected. This is most clearly seen by the agreement between these transient spectra (Figure 4B) and that calculated for the difference between the ground-state absorption of the authentic five- and six-coordinate compounds (Figure 5). There is no clear spectral evidence for a prior (d, d) state for any of these coordinate Co^{III} species as was observed following decay of the CT state for the five-coordinate Co^{III}(OEP)(CN) complex in CH_2Cl_2 (Figure 3B,C). At longer times a transient spectrum remains that we attribute to the ground-state four-coordinate species.

We believe that the most likely explanation for the spectral changes seen in Figure 4A–C is that the initially excited states,

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(24) Picosecond measurements in this field also have been reviewed by L. J. Noe. See ref 23a, pp 339–357.

(25) (a) Chernoff, D. A.; Hochstrasser, R. M.; Steele, A. W. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5606–5610. (b) Cornelius, P. A.; Hochstrasser, R. M.; Steele, A. W. *J. Mol. Biol.* **1983**, *163*, 119–128.

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(28) The CN^- was removed by addition of excess $Ag(CF_3SO_3)$ and precipitation of $Ag(CN)_2$ in CH_2Cl_2. Thus, replacement of the CN^- counterion with this species mimics the transient $[Co^{III}OEP)]^+ + CN^-$. In this case, the difference spectrum calculated from the ground-state spectrum with $CF_3SO_3^-$ counterion minus that with CN^- counterion shows two absorbance increases centered near 555 and 510 nm and two bleachings near 570 and 540 nm, consistent with the observed difference spectrum. For information on binding of other ligands to cobalt(III) porphyrins, see ref 13b.

(29) The CN^-–metal bond is almost exclusively of σ character for the case of Co^{III}. See: Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 2439–2444.

(30) Ford, P. C.; Wink, D.; Dibenedetto, J. *Prog. Inorg. Chem.* **1983**, *30*, 213–271.

shown in Figure 4A, decay into a $^3(d_\pi, d_{z^2})$ state. The latter in very short times (<10 ps) decays by two channels to produce both $[Co^{III}(OEP)(L)]^+$ and $[Co^{III}(OEP)]^+$, with the former in much greater yield. Thus, Figure 4B (115 ps) shows a difference spectrum due largely to the former species, while Figure 4C contains only the longer lived $[Co^{III}(OEP)]^+$. The longer life (~1 ns) of the four-coordinate species with respect to addition of ligands can be understood if its ground state is the high-spin $^3(d_\pi, d_{z^2})$, as expected for four-coordinate Co^{III}.[31] Thus, ligand addition becomes spin forbidden, as well as more difficult because of the increased electron density in the d_{z^2} orbital.

Decay of the absorption increase near 515 nm, due mainly to the five-coordinate species, and partial relaxation of the other features (Figure 4B,C) depend on the ligand and its concentration. As mentioned in the Results section, the calculated bimolecular rate constants for the process $[Co^{III}(OEP)(L)]^+ + L \rightarrow [Co^{III}(OEP)(L)_2]^+$ under the various conditions are all on the order of $10^9\ M^{-1}\ s^{-1}$, similar to that found for the rebinding of a ligand to the Co^{II} complexes here and previously.[5] Relaxation of the absorption changes attributed to the four-coordinate complex (see Figure 4C) also depends on the availability of ligands, but now to occupy two vacant coordination sites. In the case of 4 M Me_2SO in toluene, where there is an excess of ligands to reform a six-coordinate complex, the absorption changes have completely recovered by 1.7 ns (Figure 4D). The time required for this process is longer (≥2 ns) in the case of the two dilute (2.5 and 1.1 M) piperidine solutions investigated. In these three cases, this process involves reformation of the six-coordinate ground-state species $[Co^{III}(OEP)(L)_2]^+$. Absorption changes attributed to the mixed four- and five-coordinate species remain unchanged, however, out to 6 ns after excitation of $Co^{III}(OEP)(CN)(\gamma\text{-pic})$ in CH_2Cl_2 solution, where return of γ-pic and CN^- is both required.

The most likely candidate for the dissociative state in $[Co^{III}(OEP)L_2]$ is the (d_π, d_{z^2}) state. In the case of $Co^{III}(OEP)(CN)$ in CH_2Cl_2, the (π, d_{z^2}) CT state rapidly feeds the (d_π, d_{z^2}) state, which is lowest in energy[14] and which immediately precedes the transient absorption attributed to the CN^--free species (Figure 3).[7] The lack of observation of the (d, d) state prior to the deligated state with L = Me_2SO (Figure 4) or piperidine or γ-picoline can be explained by noting that the sixth ligand should be quite labile in this (d, d) state, hence preventing build-up of enough dissociative-state transient absorption to observe. In the case of $Co^{III}(OEP)(CN)$ in CH_2Cl_2, on the other hand, the formation of ionic species via ligand release is probably difficult enough to allow some buildup of the (d, d) transient, allowing its detection prior to ligand release (Figure 3C).

Alternative assignments for the photodissociative state seem less likely. One possibility is that binding of an axial ligand from the six-coordinate Co^{III} complex in the ground state makes the (π, d) CT lowest in energy. However, we have seen in the case of the Co^{II} complexes that the (π, d_{z^2}) CT state is strongly nonradiatively coupled to the ground state, yielding little ligand ejection. Or it could be that (d, d) and CT both have moved above $^3T(\pi, \pi^*)$ in $[Co^{III}(OEP)(L)_2]^+$. The finding that release of Me_2SO appears to have a comparable yield using excitation flashes at either 355 or 532 nm suggests that the photodissociative state does not occupy a high energy position between the Soret and visible bands. This implies that if the (π, π^*) states are lowest, then one of them is dissociative toward the ligands investigated here. Previous work, though, has revealed a lack of observable dissociation of axial ligands following excitation of closed shell metalloporphyrin complexes, such as those of Zn^{II} and Mg^{II}, where $^3T(\pi, \pi^*)$ is the lowest excited state.[32] These observations argue against (π, π^*) being the photodissociative state toward σ-bonded axial ligands. Thus, the picosecond results and this analysis suggest that the (d_π, d_{z^2}) state is lowest in energy in the six-coordinate Co^{III} complexes and gives rise to most, if not all, of the ligand release.

It should be pointed out that the suggestion here of (d_π, d_{z^2}) as the dissociative state is consistent with previous proposals that such a low-lying (d, d) state is the dissociative state in the release with high yield of CO from the iron porphyrin active site in carbonylhemoglobin and carbonylmyoglobin[6,22b-26] and of nitrogenous bases from nickel porphyrins.[9,29a,b]

Conclusions

The excited-state photoprocesses for $Co^{II}(OEP)$ and $Co^{II}(TPP)$ in both noncoordinating and coordinating solvents appear to be dominated by rapid (<35 ps) relaxation via the $^2A_{2u}(\pi, d_{z^2})$ charge-transfer state. Spectral and kinetic evidence for excited-state ligand ejection is observed with both 355- and 532-nm excitation flashes for $Co^{II}(OEP)(pip)$ and $Co^{II}(TPP)(pip)_2$. The (π, d_{z^2}) CT state is expected to be dissociative toward axial σ-bonding ligands such as piperidine. However, rapid nonradiative decay to the ground state apparently competes favorably with ligand ejection, giving low yields for ligand release. We see no firm evidence for dissociation followed by rapid recombination during the excitation flash, although a contribution from this process cannot be completely ruled out.

The transient behavior following excitation of $Co^{III}(OEP)(CN)$ in the noncoordinating solvent CH_2Cl_2 reveals the chain of excited states $(\pi, \pi^*) \rightarrow (\pi, d_{z^2}) \rightarrow (d_\pi, d_{z^2})$. Some decay of the (d, d) states appears to occur with loss of the CN^- ligand. The absorption difference spectra following excitation of $[Co^{III}(OEP)(L)_2]^+CN^-$ with L = Me_2SO, piperidine, or of $Co^{III}(OEP)(CN)(\gamma\text{-pic})$ clearly show ejection of the sixth ligand L. The lack of (d, d) transient absorption upon photolysis of these six-coordinate species is attributed to rapid release of the sixth ligand from this state, preventing buildup of enough (d, d) state to observe. From studies with L = Me_2SO of piperidine at several concentrations, we obtain recombination rate constants on the order of $10^9\ M^{-1}\ s^{-1}$. Decay of absorption changes due to the five-coordinate transient reveals a weak, longer lived difference spectrum that we attributed to the four-coordinate species. We postulate that the transient $^3(d_\pi, d_{z^2})$ state leads to loss of either one or two ligands and that the four-coordinate species lives longer than the five-coordinate since the expected multiplicities for the ground states of four-, five-, and six-coordinate species are triplet, singlet, and singlet.[31] We have discussed the relevance of our results and interpretations to photodissociation in hemoglobin, myoglobin, and other transition-metal porphyrin complexes.

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Registry No. $Co^{II}(OEP)$, 17632-19-8; $[Co^{III}(OEP)]^+$, 55845-54-0; $Co^{II}(TPP)$, 14172-90-8; $Co^{III}(OEP)(CN)$, 92186-32-8; $Co^{III}(OEP)(CN)(\gamma\text{-pic})$, 92186-33-9; $Co^{II}(OEP)(pip)$, 92186-37-3; $Co^{II}(TPP)(pip)_2$, 51321-48-3; $Co^{II}(TPP)(pip)$, 52633-66-6; $[Co^{III}(OEP)(Me_2SO)_2]^+CN^-$, 92186-35-1; $[Co^{III}(OEP)(Me_2SO)]^+$, 92186-36-2; Me_2SO, 67-68-5; piperidine, 110-89-4.

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