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Evidence from Picosecond Transient Absorption and Kinetic Studies of Charge-Transfer States in Copper(II) Porphyrins

Dongho Kim,[†] Dewey Holten,*[†] and Martin Gouterman[‡]

Contribution from the Departments of Chemistry, Washington University,
St. Louis, Missouri 63130, and University of Washington, Seattle, Washington 98195.
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Abstract: Excited-state dynamics of copper(II) tetraphenylporphyrin [Cu(TPP)] and copper(II) etioporphyrin [Cu(Etio)] depends dramatically on the coordinating properties of the solvent system. Relaxation of transient absorption and recovery of ground-state bleaching following excitation with 35-ps flashes at 355 nm range from >10 ns in the noncoordinating solvent, toluene, to ~100 ps in the coordinating solvent, piperidine. Lifetimes of intermediate duration are observed in toluene/piperidine mixtures; for Cu(TPP) the time constants are 650 ps and 2.1 ns in 1 and 0.3 M piperidine, respectively. Analogous results are found for Cu(Etio) and in pyridine. Despite such variation in kinetic behavior, transient difference spectra observed for both Cu porphyrins are essentially independent of solvent. These results are interpreted as follows. Excitation of the four-coordinate (uncomplexed) Cu^{II} porphyrins in toluene results in rapid (<35 ps) population of the excited tripdoublet (^{2}T) state, followed by intersystem crossing to the quartet (^{4}T) in <500 ps and establishment of the $^2T \rightleftarrows {}^4T$ equilibrium. The previously observed quenching of emission above 77 K in noncoordinating solvents has been attributed to relaxation of the $^2T \rightleftarrows {}^4T$ manifold to the $^2S_0$ ground state via thermal excitation to a CT state lying at higher energy. Our data show very fast quenching (10 to 150 ps) when a basic axial ligand is coordinated to the metal, which we attribute to a lower energy gap between the CT state and the $^2T \rightleftarrows {}^4T$ manifold. In solutions of basic ligands where the coordination in the ground state is incomplete, quenching occurs during collision with the ligand at a rate of ~10^9 M^{-1} s^{-1}, followed by rapid deactivation through the CT state of the five-coordinate complex. The nature of the quenching CT state is discussed, and it is proposed that it is a $^2[a_{2u}(\pi), d_{x^2-y^2}]$ state because calculations show that this state drops in energy with expansion of the core and motion of the Cu atom out of plane.

Introduction

Copper(II) porphyrins are interesting complexes from both a theoretical$^{1-6}$ and experimental$^{6-19}$ point of view. Cu^{II} has a d^9 electronic configuration. The unpaired electron in the $d_{x^2-y^2}$ orbital couples with the normal porphyrin (π,π^*) excited states to form the singdoublet, $^2Q(\pi,\pi^*)$, the tripdoublet, $^2T(\pi,\pi^*)$, and the quartet, $^4T(\pi,\pi^*)$. These complexes do not exhibit the typical fluorescence of closed-shell metalloporphyrins, but rather moderately strong phosphorescence from the tripdoublet–quartet manifold.$^{7-11}$ The luminescence spectrum, lifetime, and yield are highly temperature dependent.$^{8-10}$ The quartet is lower in energy than the tripdoublet by 200–700 cm^{-1} depending on the porphyrin macrocycle, and the two states apparently differ in both radiative and nonradiative rates to the ground doublet state.^{9,11}

Variations in the absorption and emission properties of Cu^{II}, Ag^{II}, Ag^{III}, and Au^{III} porphyrins have been rationalized on the basis of iterative extended Hückel (IEH) calculations and redox potentials.^{6} The Cu^{II} and Au^{III} complexes emit, while Ag^{II} and Ag^{III} complexes do not. The calculations indicate that the metal $d_{x^2-y^2}$ orbital rises in energy along the series Cu < Ag < Au; this orbital lies in energy between the porphyrin ring highest filled orbitals $a_{1u}(\pi)$ and $a_{2u}(\pi)$ and lowest empty $e_g(\pi^*)$ in the Cu and Ag complexes, while it is above the $e_g(\pi^*)$ for Au porphyrins. The $d_{x^2-y^2}$ orbital is half-filled in complexes of these metals having valence II. Thus, several charge-transfer (CT) transitions are possible:$^{1,3-6}$ first, (π,d) transitions from ring $a_{1u}(\pi)$ or $a_{2u}(\pi)$ to metal $d_{x^2-y^2}$; second, (d, π^*) transitions from metal $d_{x^2-y^2}$ to ring $e_g(\pi^*)$. CT transitions from the filled d orbitals to $e_g(\pi^*)$ are predicted to be at higher energy, as are (d,d) transitions, such as $(d_{z^2}, d_{x^2-y^2})$.

The lack of emission from the Ag porphyrins was attributed to one of the CT states lying below the normally emissive $^2T(\pi,\pi^*)$ and $^4T(\pi,\pi^*)$: (d,π^*) in the case of Ag^{II} and (π,d) in the case of Ag^{III}.^{6} The fact that emission was observed from Au^{III} porphyrins was taken to be consistent with the (π,d) state being higher in energy than in the Ag^{III} complexes and above the lowest (π,π^*) states.

The Cu^{II} porphyrins are particularly interesting, because a number of observations suggest that a CT state lies close in energy above the ^{2}T and ^{4}T in noncomplexing solvents (four-coordinate Cu). (i)Emission from Cu^{II}(Meso)^{20} is strongly quenched above 77 K, although this is not found for other metalloporphyrins, such as Zn, Pd, or Pt.^{21} This suggests that a nonluminescent CT state is thermally accessible. (ii) The Cu^{II}(TPP)^{20} emission is anomalously broad, and at 77 K decays with nonexponential, multiphasic kinetics.^{8,9} It has been proposed that the broadness of the emission could be due to a perturbation by a close-lying CT state. (iii)

[†] Washington University.
[‡] University of Washington.

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(20) Abbreviations used for porphyrin macrocyles: TPP = tetraphenylporphyrin, Etio = etioporphyrin, MPDME = mesoporphyrin IX dimethyl ester, PPDME = protoporphyrin IX dimethyl ester, OEP = octaethylporphyrin.

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The $Cu^{II}(TPP)$ absorption shows a continuously rising absorption tail with shoulders near 715 and 675 nm (the ^2T emission maximum is near 750 nm at 77 K). The (π,d) or (d,π^*) CT states may underlie this broad absorption.[6,8,9] (iv) The luminescence of $Cu^{II}(TPP)$ is quenched in pyridine.[6] Since this ligand is a σ donor, it has been suggested that the increased electron density on the metal would raise the energy of the half-filled $d_{x^2-y^2}$ orbital. This might lower the energy of the (d,π^*) state to below the (π,π^*) state and quench emission.[6] (v) Analysis of Zeeman measurements suggest that the polarization of some of the emission peaks for Cu^{II} porphyrins can be explained only if there is a second-order spin–orbit coupling involving the emitting (π,π^*) states and a CT state $^2B_{2u}$ $[d_{x^2-y^2} \rightarrow b_{2u}(\pi^*)]$.[11] This implies that the CT state may not lie too far above the (π,π^*) in noncomplexing solvents.

In order to explore the role of CT states in the photophysical behavior of Cu^{II} porphyrins, we have investigated the transient difference spectra and kinetics of $Cu^{II}(TPP)$ and $Cu^{II}(Etio)$ with picosecond transient absorption and kinetic spectroscopy. We find that the excited-state relaxation of these molecules in the noncomplexing solvent toluene is similar to that observed in a previous study of $Cu^{II}(PPDME)$;[16a,20] there is some evidence that <15% of the initial transient absorption decays with a time constant of <500 ps while the major component requires >10 ns to relax. Recently it has been reported that $Cu^{II}(PPDME)$ in pyridine has its excited-state lifetime reduced to 45 ps,[16b] and that the lifetime of Cu^{II} cytochrome *c* is pH dependent.[16c] In this paper we report the transient spectra of $Cu^{II}(Etio)$ and $Cu^{II}(TPP)$ in pyridine and piperidine as well as in solutions where these are mixed with toluene. Our work corroborates the reported quenching[16b] and provides a more detailed model for the quenching mechanism. In neat (10 M) piperidine, photoexcited $Cu^{II}(Etio)$ and $Cu^{II}(TPP)$ are found to decay completely with a time constant of about 100 ps. Mainly five-coordinate species are pumped in this case. The time constant for the decay decreases as the ligand concentration is reduced, in which case mainly uncomplexed molecules are excited. The latter data suggest that a basic axial ligand is picked up by an excited four-coordinate species at a nearly diffusion-controlled rate ($\sim 10^9$ M^{-1} s^{-1}). Subsequent deactivation and loss of the ligand appears to be rapid (≤40 ps). A mechanism for quenching by a $^2[a_{2u}(\pi),d_{x^2-y^2}]$ CT state is suggested.

Experimental Section

The dual-beam picosecond transient absorption spectrometer has been described in detail elsewhere.[22] It is based on a passively mode-locked Nd:YAG laser system that delivers single, 35-ps, 1064-nm, 10-mJ pulses at a 10-Hz repetition rate. Excitation flashes at 532 or 355 nm were obtained by harmonic generation in KD*P crystals. Excitation flashes were generally reduced to ~300 μJ. In some cases, unattenuated 532-nm excitation flashes containing 2 mJ were employed. "White-light" (450–900 nm) probe pulses of ~35 ps duration were generated from the fundamental in $CHCl_3/CCl_4$. All data were taken at room temperature. Samples were normally flowed to avoid decomposition and reexcitation of unrelaxed sample in the excited volume by successive laser shots. Concentrations were adjusted for an absorption maximum of 0.3–0.5 in the Q-band region. Cu(TPP) was purchased from MidCentury Chemicals and purified by repetitive column chromatography (Fisher A-540 Alumina). Cu(Etio) was from a sample used earlier;[9] prior to our current use it was checked by thin layer chromatography, which showed it remained pure. Spectral grade solvents were employed.

Results

Ground-State Absorption and Complex Formation. Ground-state absorption data for Cu(Etio) and Cu(TPP) in the three neat solvents are listed in Table I. Binding of axial ligands (complexation) results in the red shift of the absorption spectra. This is more pronounced in the Soret bands than in the visible region. Previous work has shown that Cu(MPDME)[20] forms a monopiperidinate complex, with no evidence for addition of a second axial ligand to make the six-coordinate species.[13] On the basis of the measured equilibrium constant of 0.21 M^{-1}, it can be calculated that in neat piperidine (10.1 M) about 70% of the Cu(MPDME) contain five-coordinate Cu^{II}. On the basis of work on other metalloporphyrins,[14] Cu(Etio) might be expected to have an equilibrium constant similar to that for Cu(MPDME), while that for Cu(TPP) should be somewhat larger. The ground-state spectra substantiate this view. An equilibrium constant of 0.05 M^{-1} at ~30 °C has been reported for the formation of the monopyridinate complex of Cu(TPP).[15] Pyridine is less nucleophilic than piperidine and should make complexes less readily. On the basis of this discussion, we have included in the last column of Table I estimates for the percentage of Cu(Etio) and Cu(TPP) that are complexed in neat pyridine and piperidine.

Table I. Summary of Ground-State Absorption Data[a]

compound	solvent	B(0,0)	Q(1,0)	Q(0,0)	% complexed[b]
Cu(Etio)	toluene	397 (21)	525 (1.0)	562 (1.8)	0
	pyridine	397 (19)	525 (1.0)	562 (1.7)	<20
	piperidine	411 (9), 397 (12)	532 (1.0)	566 (1.3)	50–70
Cu(TPP)	toluene	416 (23)	538 (1.0)	575 (0.1)	0
	pyridine	420 (19)	545 (1.0)	590 (0.2)	35–55
	piperidine	427 (16)	550 (1.0)	590 (0.3)	>90

[a] Peak wavelengths are in nanometers. Numbers in parentheses are peak heights relative to the Q(1,0) band. [b] Estimates based on data in ref 13 and 14 and ground-state absorption data in this table.

Thus, for Cu(Etio) in pyridine <20% of the molecules have an axial ligand bound to the metal, while >90% of the Cu(TPP) in piperidine appear to be complexed. More will be said about the relative percentage of complexed vs. uncomplexed molecules excited with the 355-nm flashes along with the picosecond data.

Excited-State Relaxation in Toluene. Excited-state difference spectra for Cu(Etio) and Cu(TPP) in toluene at several time delays with respect to the 35-ps, 355-nm excitation flash are shown in Figures 1A and 2A, respectively. Data at the negative delay times give a measure of the baseline and indicate that no transient species remain in the excited volume between laser shots. The transient absorption at positive delays (after the pump flash) for Cu(Etio) is broad and relatively featureless across the 490- to 630-nm region, gradually increasing in strength to shorter wavelengths. Bleaching in the strong ground-state Q(0,0) band near 560 nm and in the weaker Q(1,0) band at 525 nm is apparent (see Table I). The transient absorption decreases by <10% between the short and long delays and the difference spectrum remains virtually unchanged. A similar set of measurements for Cu(TPP) is shown in Figure 2A. In this case, the transient absorption increases dramatically in amplitude below 530 nm and exhibits a weaker tail extending past 620 nm. Bleaching in the Q(1,0) band at 540 nm is apparent (see Table I); the ground-state Q(0,0) band is weaker than the Q(1,0) in most metallo-TPP compounds.[1] The transient absorption relaxes by 10–15% between 40 ps and 2.4 ns.

The time evolution of the bleaching at 562 nm for Cu(Etio) in toluene is shown in Figure 3 (triangles). Similar data for the absorption increase at 495 nm for Cu(TPP) are shown in Figure 4. In each case, the transient absorption and bleaching grow with the instrument-limited response and exhibit similar kinetic behavior. There may be an initial fast step to the decay for Cu(Etio) in toluene (Figure 3), but the small amplitude of the component makes it difficult to determine the time constant accurately. There also appears to be a small, initial component for Cu(TPP). In both cases the time constant is <500 ps. The major, longer lived transient absorption and bleaching for both Cu^{II} porphyrins require >10 ns to relax. These kinetic results are in general similar to those observed previously[16] for Cu(PPDME) in benzene following excitation with 530-nm flashes, but in that case the amplitude of the initial component was larger than observed here and decayed with a 450 ± 50 ps time constant. The lifetime also appeared to depend on the pump-flash intensity.[16] Excitation of Cu(Etio) in toluene with stronger (2 mJ) 532-nm flashes yielded spectral and kinetic behavior similar to that shown in Figures 1A and 2A, where weaker 355-nm pump pulses were used. Kinetic data are summarized in Table II.

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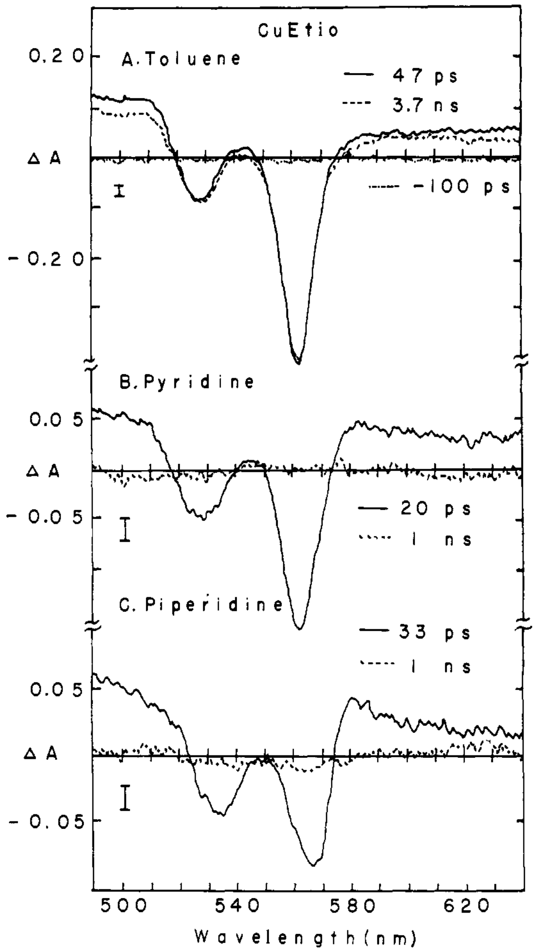

Figure 1. Transient absorption spectra in the Q-band region for Cu(Etio) in toluene (A), pyridine (B), and piperidine (C) at short and long time delays following excitation with 355-nm flashes. Each spectrum is the average of approximately 500 spectra. The maximum standard deviation in ΔA was 0.01 over the wavelength region shown, as indicated on the left of each panel.

Table II. Kinetic Summary[a]

compound	solvent	[L][b]	τ	$k(\times 10^{-8})$[c]
Cu(Etio)	toluene		>10 ns[d]	
	pyridine	12.4	100 ± 20 ps	8 ± 2
	piperidine	10.1	150 ± 20 ps	(7)
	tol/pip = 9/1	1.0	1.1 ± 0.2 ns	9 ± 2
Cu(TPP)	toluene		>10 ns[d]	
	pyridine	12.4	⩽40 ps	(⩾20)
	piperidine	10.1	115 ± 20 ps	(8)
	tol/pip = 9/1	1.0	650 ± 70 ps	15 ± 2
	tol/pip = 9.7/0.3	0.30	2.1 ± 0.3 ns	16 ± 2

[a] Samples excited with 35-ps, 355-nm excitation flashes. [b] Concentration of basic ligand in M. [c] Second-order rate constant $k^{-1} = \tau[L]$ in $M^{-1}\ s^{-1}$: values in this column have been multiplied by 10^{-8}. Values in parentheses mean that ⩾30% of the molecules excited are complexed in these cases (see text). [d] There is evidence for a shorter lived transient comprising ⩽15% of the overall transient absorption and decay (see text).

Transient Absorption and Kinetics in Pyridine. Transient difference spectra as a function of delay time for Cu(Etio) in pyridine are shown in Figure 1B. Bleaching maxima are at the same wavelengths as in toluene (Figure 1A) and correspond to the ground-state absorption maxima in pyridine and in toluene (Table I). This suggests that mainly the uncomplexed, four-coordinate species have been pumped with the 355-nm flashes. This is consistent with the fact that probably only a few percent of the molecules are five-coordinate in this case. The transient spectrum over the 490- to 630-nm region at the 20-ps delay (during the flash) in Figure 1B is similar to that observed in toluene and extends featureless to past 750 nm (data to 630 nm are shown). However, in marked contrast to the behavior in toluene the transient difference spectrum relaxes completely with a time constant of 100 ± 20 ps (Table II) without changing shape.

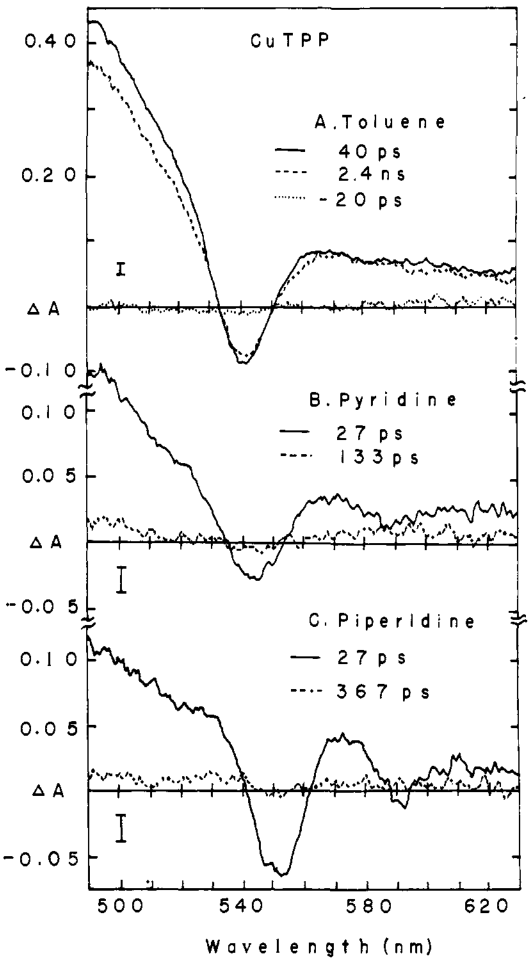

Figure 2. Transient absorption spectra in the Q-band region for Cu(TPP) in toluene (A), pyridine (B), and piperidine (C) at short and long time delays following excitation with 355-nm flashes. Each spectrum is the average of approximately 500 spectra. The maximum standard deviation in ΔA was 0.01 over the wavelength region shown, as indicated on the left of each panel.

The transient absorption for Cu(TPP) in pyridine (Figure 2B) also is similar to the spectrum observed in toluene (Figure 2A). The wavelength of the Q(1,0)-band bleaching maximum in pyridine near 530 nm is slightly to the red of that in toluene. There is also a hint of a dip at 585 nm on the broad positive absorption that could reflect bleaching in the Q(0,0) band due to excitation of some five-coordinate species (Figure 2B and Table I). However, the magnitudes of these spectral features and small differences from the spectra in toluene suggest that ≤30% of the Cu(TPP) excited have an axial pyridine attached. On the other hand, as in the case of Cu(Etio), decay of the transient absorption and bleaching for Cu(TPP) in pyridine is much more rapid than observed in toluene. The time profile for decay of the absorption changes (not shown) is only slightly longer than the 35-ps pulse profile, placing an upper limit of ≤40 ps on the relaxation (Table II). However, the time constant most probably is 10–40 ps.

Transient Absorption and Kinetics in Piperidine. Transient difference spectra for Cu(Etio) and Cu(TPP) in neat piperidine are shown in Figures 1C and 2C, respectively. In both cases the transient absorption is very similar to that observed in pyridine and toluene. However, the ground-state bleaching maxima in piperidine are red shifted from the positions observed in the other two solvents, indicating that mainly (>70%) complexed species have been pumped (compare with Table I). The transient absorptions and bleachings for Cu(Etio) and Cu(TPP) grow with the instrument-limited response and decay with time constants

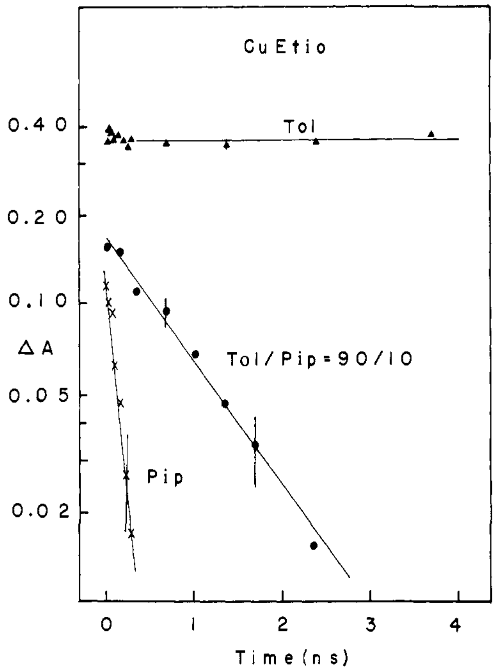

Figure 3. Kinetics for decay of bleaching in the Q(0,0) band for Cu(Etio) in toluene (Δ), piperidine (×), and toluene/piperidine = 90/10 (●). Note the ordinate is a log scale.

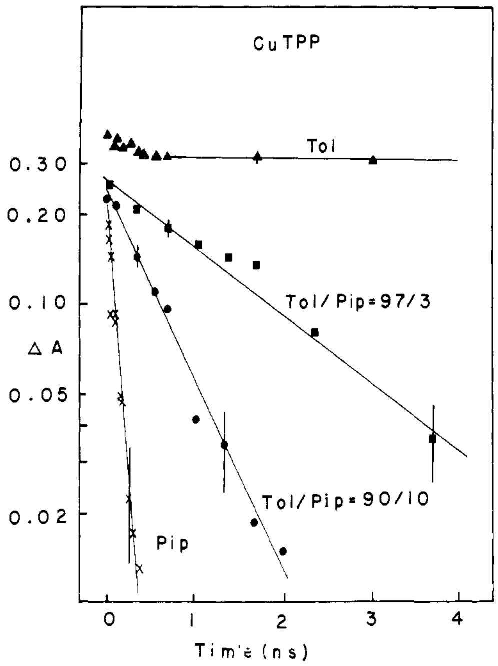

Figure 4. Kinetics for decay of transient absorption at 495 nm for Cu(TPP) in toluene (Δ), piperidine (×), toluene/piperidine = 90/10 (●) and toluene/piperidine = 97/3 (■). Note the ordinate is a log scale.

of 150 ± 20 and 115 ± 20 ps, respectively (crosses in Figures 3 and 4). The difference spectra do not change shape during the lifetimes of the transients. Thus, the decay times in neat piperidine also are much faster than those observed in toluene (Table II).

The lifetimes of the transient states increase as the concentration of piperidine is reduced. On the basis of the equilibrium constant of 0.21 M^{-1} for binding of piperidine by Cu(MPDME),[13] we estimate that about 20% of the Cu(Etio) is complexed in 1 M piperidine (toluene/piperidine = 9/1). Transient absorption (not shown) in this solvent mixture is the same as reported above for the other solvents (Figure 1), and the ground-state bleaching maxima are at essentially the same wavelength as in pyridine and toluene. The latter behavior indicates that ≤10% of the Cu(Etio) excited by the 355-nm flashes in 1 M piperidine are in the form of a ground-state monopiperidinate complex. The decay of the transient absorption and bleaching is fit well by (pseudo-) first-order kinetics as shown in Figure 3 (circles) with a time constant of 1.1 ± 0.2 ns (Table II).

Similar behavior was found for Cu(TPP) in dilute piperidine solutions. Again, transient absorptions were similar to those found in the other solvents, strongly increasing in strength to the blue of 540 nm (Figure 2). Based on the ground-state spectra and bleaching maxima in the transient difference spectra (not shown), we estimate that for Cu(TPP) 15–25% of the molecules excited in 1 M piperidine were complexed; in 0.3 M piperidine (toluene/piperidine = 97/3) <10% of the species pumped were complexed. In other words, the transient behavior in these dilute piperidine solutions is dominated by processes following excitation of uncomplexed, four-coordinate Cu^{II} species. The decays are fit well by (pseudo-) first-order kinetics with time constants of 650 ± 70 ps and 2.1 ± 0.3 ns for Cu(TPP) in 1 and 0.3 M piperidine, respectively (Figure 4 and Table II).

Discussion

Cu(Etio) and Cu(TPP) in Toluene. Kobayashi et al.[16] reported decay kinetics following excitation of Cu(PPDME) with 7-ps, 530-nm flashes. The results were interpreted as follows:

$$^2Q \rightarrow {}^2T \quad (<10\ \text{ps}) \qquad \text{(i)}$$
$$^2T \rightarrow {}^4T \quad (\sim 450\ \text{ps}) \qquad \text{(ii)}$$
$$^2T + {}^4T \rightarrow {}^2S_0 \quad (>1\ \text{ns}) \qquad \text{(iii)}$$

The first step is conversion of initially excited singdoublet to the tripdoublet and was too fast to be observed. The second step represents establishment of the tripdoublet–quartet equilibrium. The 450-ps kinetics were found for decay of the absorption increase at 480 nm and the recovery of the bleaching at 570 nm. The amplitude of this component appeared to comprise 20–30% of the overall decay. The lifetime of this step was found to depend on the strength of the excitation flash, which was varied in energy from 1 to 5 mJ; the 450-ps value is for the lower pump energy. The reason for the flash-strength dependence was not understood. The final process is relaxation of the tripdoublet–quartet manifold to the ground doublet state, which Kobayashi et al.[16] found to take >1 ns. The long time constant is consistent with the luminescence lifetime of 100 μs at 77 K.[8]

We also have found that the major component (>85%) of the transient absorption and ground-state bleaching has a long (>10 ns) relaxation time for both Cu(Etio) and Cu(TPP). There is some evidence for an earlier step with a lifetime <500 ps (Figures 3 and 4), apparently faster for Cu(Etio) than for Cu(TPP). However, unlike the work of Kobayashi et al.,[16] we were unable to determine accurately the lifetime of the short time decay because of its small amplitude. Indeed we found little difference in the transient absorption spectra between short and long times throughout the spectral range studied. That ^2T and ^4T might have similar absorption spectra was suggested from early picosecond studies on Cu(OEP) and Cu(TPP) by Magde et al.,[19] who used photographic rather than the vidicon-based detection used here. These authors argued that this similarity in spectra might be the case because the two states differ only in how the unpaired metal electron couples with the ring π-system. However, ^2T and ^4T might have a different absorption in some spectral region—in particular at 480 nm, where the kinetics for the $^2T \rightarrow {}^4T$ relaxation was determined.[16a] We should note that assignment of the transient spectra observed in Figures 1A and 1B to ^2T and/or ^4T is consistent with work on other metalloporphyrins,[19] where (π,π^*) excited-state absorption spectra generally have strong absorption to the blue of 500 nm with a weaker tail extending to longer wavelengths. It also appears that in many cases transient spectra for TPP derivatives have Soret region maxima red shifted from those with octaalkyl substitution, such as Etio. This may account for the differences between Figures 1A and 2A.

We now turn to the focal point of the current investigation, the transient behavior of Cu^{II} porphyrins in basic solvents.

Excited-State Dynamics in Coordinating Solvents. Two main situations in basic solvents must be distinguished. First are cases where a significant fraction (>70%) of the molecules excited by the 355-nm flashes are complexed in the ground state, i.e., have a basic axial ligand coordinated to the metal. Cu(TPP) and Cu(Etio) in neat piperidine are good examples (Table I and Figures 1C and 2C). Second are cases where a low percentage (≤30%) of the molecules pumped are ligated in the ground state. Based on the ground-state bleachings in the transient difference spectra, it appears that to first approximation all the other systems studied fall into this category. This provides a convenient framework for discussing the results in coordinating solvents.

As pointed out in the Introduction, earlier work on Cu porphyrins in which quenching of luminescence was observed with rise in temperature and in pyridine led to the hypothesis that there is a rapidly quenching CT state at somewhat higher energy than $^2T \rightleftarrows {}^4T$ in noncoordinating solvents, which shifts to lower energies in coordinating solvents.[6,8] This hypothesis readily explains the results reported here. In particular, time constants for decay of Cu(TPP) and Cu(Etio) in neat piperidine are 150 and 115 ps, respectively, with no evidence for more than one component (Figure 3 and 4 and Table II). The transient absorptions in piperidine (Figures 1C and 2C) are very similar to those in toluene (Figures 1A and 2A), even though the kinetics are dramatically different. This observation suggests that the ligated ^2T and ^4T have similar absorption spectra as the corresponding states of the uncomplexed species. The interpretation also requires that the relaxation of the CT to the ground state is very fast (<35 ps) and that the observed 115- and 150-ps lifetimes reflect mainly decay of the tripdoublet–quartet mainfold to the CT.

We believe that the time constant for relaxation of the $^2T \rightleftarrows {}^4T$ state to the ground state depends principally on two factors: (i) the degree of complexation in the ground state and (ii) the energy gap between the $^2T \rightleftarrows {}^4T$ states, which lie at ~1.7 eV, and the quenching state. Very fast relaxation (<35 ps) from the CT state is reasonable, as shown by work on a number of transition-metal porphyrins, including those of Co^{II} and Co^{III}.[24] Studies of Co^{II} porphyrins are particularly relevant, since Co^{II} has one unpaired electron, as does Cu^{II}. These studies also indicate that CT states, such as (π,d), have transient spectra different from porphyrin (π,π^*) states.[24] Thus, the alternative interpretation for Cu^{II} that the transient absorption in piperidine is due to a low-lying CT state, with the 115- and 150-ps lifetimes being due to relaxation of the CT, appears to be less likely than that proposed above.

Let us apply this analysis first to the Cu(TPP) data in toluene/piperidine mixtures. The time constant for decay of photoexcited Cu(TPP) was found to depend on the piperidine concentration as shown in Figure 4. The transient difference spectra (not shown) were similar to those observed in toluene. These results suggest that the kinetic behavior reflects diffusion of excited ($^2T \rightleftarrows {}^4T$) Cu(TPP) to encounter a piperidine, which complexes to the metal. Again, we propose that the rapid deactivation proceeds via a CT state of the resulting five-coordinate complex. From the observed lifetimes (τ = 650 ps and 2.1 ns) and known concentrations ([L] = 1.0 and 0.3 M), we calculate second-order rate constants ($k^{-1} = \tau[L]$) of 1.5×10^9 and 1.6×10^9 M^{-1} s^{-1}. Theses values are listed in the last column of Table II. The good agreement between the rate constants obtained via this procedure for Cu(TPP) in the two piperidine concentrations indicates that only one axial ligand is picked up in the excited state. This tends to support, but does not prove, the view that excitation of a five-coordinate ground-state complex, such as is the case in neat piperidine discussed above, does not result in the binding of a second axial ligand in the excited state to form a six-coordinate complex. The observation of similar kinetics for decay of the excited-state absorption and recovery of ground-state bleaching following excitation of uncomplexed species indicates that ejection of the ligand acquired in the excited state occurs rapidly compared to, but during or following, deactivation through the CT.

A similar analysis applies to the Cu(Etio) data in toluene/piperidine mixtures. From the observed lifetime of 1.1 ns (Figure 3 and Table II) in 1 M piperidine, we calculate a second-order rate constant of 9×10^8 M^{-1} s^{-1}. The somewhat slower rates observed for Cu(Etio) compared to Cu(TPP) in dilute piperidine can be explained by assuming that the equilibrium constant for complex formation in the $^2T \rightleftarrows {}^4T$ excited states of Cu(Etio) is lower than for Cu(TPP), as it is in the ground state (Table I). That the bimolecular rate constants for both molecules are smaller than the calculated[23] diffusion-limited value of 5×10^9 M^{-1} s^{-1} in neat piperidine (7×10^9 M^{-1} s^{-1} in pyridine) suggests that there is an activation energy, implying that the CT is above the $^2T \rightleftarrows {}^4T$ even in the monopiperidinate complexes.

While we can explain the small difference in rate constants between Cu(TPP) and Cu(Etio) in dilute piperidine by appealing to a difference in equilibrium constants, another factor comes into play when these compounds are in pyridine. For both Cu porphyrins, the relaxation is faster in neat pyridine than in neat piperidine, even though there is less complex formation in the ground state and, thus, fewer complexed species are pumped (Tables I and II). We explain this by assuming that the energy gap between the $^2T \rightleftarrows {}^4T$ states and the CT quenching state is lower in the pyridine complexes than in piperidine complexes. We attribute the difference in observed decay times for Cu(TPP) and Cu(Etio) in neat pyridine of ≤40 and 100 ps, respectively, mainly to the fact that the degree of complexation is much higher in the ground state for Cu(TPP) than it is for Cu(Etio), but still only 35–55% (Table I). Thus, if the Cu(TPP)(py) are not pumped exclusively, but some Cu(TPP) are also excited, then the ≤40-ps lifetime is actually made up of a very fast decay of the complexed species and a somewhat slower decay of the uncomplexed species. The maximum bimolecular quenching time calculated from the diffusion-limited rate constant is ~10 ps. Thus, even upon excitation of four-coordinate complexes, the observed rapid decay implies little or no activation energy between $^2T \rightleftarrows {}^4T$ and the quenching CT in the five-coordinate complex, Cu^{II}(TPP)(py).

For Cu(Etio) in neat pyridine, where little complex formation occurs in the ground state and few Cu(Etio)(py) are pumped, we see only a single decay of 100 ps, representing predominantly the bimolecular process. That the lifetime is longer than the calculated diffusion-limited value indicates that there may be a small activation energy in this case.

It is useful to relate our views to the quenching of emission observed in Cu cytochrome *c*. At room temperature Reynolds et al.[16c] report that Cu cytochrome *c* at pH 2.5 and pH 13.0 shows relaxations of >1 ns, while at pH 8.0 the lifetime is 10 ps. These data are consistent with our results if pH 2.5 and 13.0 represent four coordination while pH 8.0 represents five. The short quenching time of the latter is then comparable to the ≤40-ps time we find for Cu(TPP) in pyridine, which is 35–55% complexed in the ground state. Although Cu cytochrome *c* phosphoresces at low temperature,[25] the observed lifetime is substantially shorter than that of Cu porphyrin in nonligating solvents, implying a nonzero activation energy between the $^2T \rightleftarrows {}^4T$ states and the quenching CT state.

[We might note that our studies require that Cu cytochrome *c* be four-coordinate at pH 2.5 and 13.0 and five-coordinate at pH 8.0. In their discussion, Reynolds et al.[16c] followed Findley et al.[26] and took the coordination numbers as five and six for the two cases. That Cu cytochrome *c* at pH 2.5 and 13.0 is four-coordinate and at 8.0 is five-coordinate is consistent with the studies on Cu myoglobin by Alston and Storm,[27] who established coordination number by ESR and CD data, and with a recently completed resonance Raman study by Shelnutt et al.[28]]

What Is the Nature of the CT State? Our results indicate that, with a basic axial ligand attached to the metal, the lifetime of

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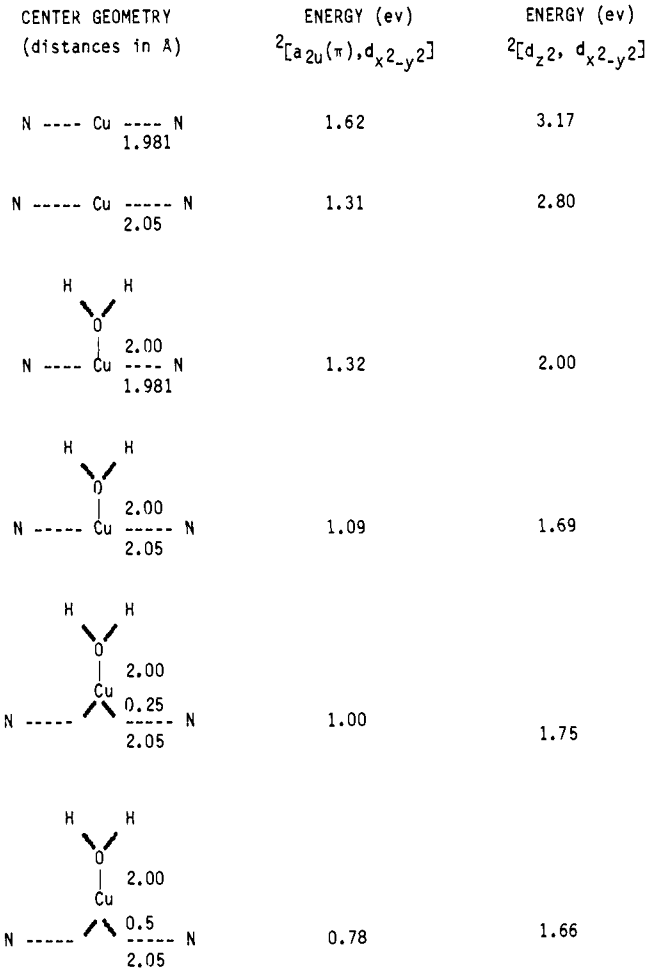

Figure 5. Diagram to show change in energy of $^2[a_{2u}(\pi),d_{x^2-y^2}]$ and $^2[d_{z^2},d_{x^2-y^2}]$ with core expansion, addition of a water ligand, and movement of the Cu out of plane.

the CT state responsible for quenching of $^2T \rightleftarrows {}^4T$ appears to be too short relative to other components to permit observation of its transient spectrum. Thus, the present measurements do not provide spectral characterization of whether the (d,π^*) or (π,d) is lowest in the five-coordinate complex; to first approximation the two CT states should exhibit transient absorption similar to the metalloporphyrin π anion radical, and π cation radical, respectively.[24]

Previous work does not provide a conclusive answer to this question either, since controversy remains as to which of the two CT states is lower in noncoordinating solvents (with both CT above the $^2T \rightleftarrows {}^4T$). The key is the position in energy of the Cu half-filled $d_{x^2-y^2}$ orbital with respect to the porphyrin ring highest filled $a_{1u}(\pi)$ and $a_{2u}(\pi)$ vs. the lowest empty $e_g(\pi^*)$. The higher in energy above the $a_{1u}(\pi)$, $a_{2u}(\pi)$ the $d_{x^2-y^2}$ lies, then the lower in energy the (d,π^*) becomes relative to the (π,d). PEEL calculations by the Swedish group[3,4] predict the (d,π^*) to be lowest, while Xα calculations by Case and Karplus[5] put the (π,d) lowest. Antipas et al.[6] argued on the basis of IEH calculations and redox potentials that the (d,π^*) probably should be lower in the four-coordinate case. (All the calculations place the $d_{x^2-y^2}$ below the $e_g(\pi^*)$ in Cu porphyrins.) Some experimental results favor the (π,d); photoelectron spectroscopy shows that the extra electron goes on to the Cu rather than the ring when the Cu porphyrin or phthalocyanine is reduced.[12] Zeeman measurements favor the (d,π^*) on the basis of symmetry arguments to explain polarization of the emission observed at low temperatures.[11]

Recently Shelnutt and Gouterman carried out iterative extended Hückel calculations on Cu^{II} porphyrins with and without H_2O as an axial ligand, allowing for expansion of the core size that Raman-frequency shifts establish as occurring when Cu^{II} porphyrins are ligated.[28] In these calculations the $^2[a_{2u}(\pi),d_{x^2-y^2}]$ CT state is shown to undergo the energy changes shown in Figure 5 as the geometry changes. These calculations then suggest a mechanism for the rapid quenching on ligation. The $^2[a_{2u}(\pi),d_{x^2-y^2}]$ state may be at energies comparable to or even higher than $^2T \rightleftarrows {}^4T$. However, once the CT state is formed, the energy rapidly drops through a combined nuclear motion involving opening of the ring and motion of the metal out of plane. This mechanism is similar to one developed by Waleh and Loew[29] for the photodissociation of carbonylheme, in which case the (d_π,d_{z^2}) state drops in energy with dissociation of the CO.

Another candidate for a quenching state is $^2[d_{z^2},d_{x^2-y^2}]$. The calculated energy for this state is also given in Figure 5, as taken from the same calculations.[28] Since this state is calculated to be at substantially higher energy than the CT state, particularly in the four-coordinate species where a thermally activated quenching is observed, we prefer the CT state as the cause of quenching.

Conclusions

We have examined the quenching of the excited states of two copper porphyrins in ligating and nonligating solvents. Ligation dramatically increases the quenching rate. A consistent qualitative interpretation can be given for the data by considering two variables: (i) the degree of complexation in the ground state and (ii) the energy gap (activation energy) between the $^2T \rightleftarrows {}^4T$ manifold and the quenching CT state. The degree of ground-state complexation follows the order: Cu cyt-*c* (pH 8) > Cu(TPP)pip > Cu(Etio)pip > Cu(TPP)py > Cu(Etio)py. The activation energy would follow the order: Cu(P)(4-coordinate) > Cu(P)pip > Cu(P)py > Cu cyt-*c*, where P stands for either TPP or Etio, which we cannot yet clearly distinguish based on the present data.

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Registry No. [Cu(TPP)], 14172-91-9; [Cu(Etio)], 27177-54-4.

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