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Photostudies of $[Cu(bpy)(PPh_3)_2]^+$, $[Cu(phen)(PPh_3)_2]^+$, and $[Cu(dmp)(PPh_3)_2]^+$ in Solution and in Rigid, Low-Temperature Glasses. Simultaneous Multiple Emissions from Intraligand and Charge-Transfer States[1]

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Abstract: Spectral studies of a series of complexes of the type $[Cu(biL)(PPh_3)_2]^+$ have been carried out where biL denotes 2,2′-bipyridine, 1,10-phenanthroline, and 2,9-dimethyl-1,10-phenanthroline which will be abbreviated as bpy, phen, and dmp, respectively. The dmp complex, unlike the others, emits fairly efficiently in fluid solution and has been studied in detail. All three complexes exhibit metal-to-ligand charge transfer (d–π^*) transitions in solution around 360 nm, but solutions of the dmp complex give an extra visible absorption band which is attributable to a second copper complex formed according to the equilibrium: $[Cu(dmp)(PPh_3)_2]^+ = [Cu(dmp)]^+ + 2PPh_3$. This dissociation of PPh_3 is readily suppressed by the addition of excess PPh_3, and under these conditions, the $E_{1/2}$ of the complex is estimated to be $\gtrsim$0.7 V vs. SCE. Under the same conditions, the complex has an emission lifetime of 330 ns and an emission quantum yield of 1.4×10^{-3}. PPh_3 is not a quencher, but both electron-transfer and energy-transfer quenching have been observed. The reduction potential of the excited complex is estimated to be ca. −0.9 V vs. SCE. In rigid glasses at low temperature all three complexes exhibit broad, structureless emissions with lifetimes in the microsecond domain which can be assigned to ^{3}d–π^* states. Additional components with lifetimes in the millisecond domain have been observed for the phen and dmp complexes. The latter have characteristic vibronic structures which enable us to assign them as $^3\pi$–π^* emissions involving the coordinated heterocyclic ligands. The occurrence of multiple emissions from these systems is rationalized in terms of current models from the literature. Finally, weak sub-nanosecond components have been time resolved from the total emission spectra of the phen and bpy complexes, and possible origins for these components are discussed.

Excited states of transition-metal complexes are receiving increasing attention because they may be viewed as new reagents, often differing dramatically in reactivity from their ground-state precursors.[2] A further impetus for the investigation of these systems stems from the possibility that they may find application in solar energy conversion schemes.[3] From a more fundamental point of view, transition-metal complexes are of interest because of the diversity in the types of excited states which are found. Indeed, a metal complex is in some sense a molecule of molecules which exhibits excited states of varying orbital parentage including metal-centered (MC), ligand-centered (IL), and charge-transfer (CT) states, as well as states with mixed orbital parentage.[4-6] Since the lowest energy excited state is often the longest lived, its character is important in determining what kind of reactivity is observed. For example, CT states are prone to undergo redox reactions, while MC states are likely to undergo ligand-substitution reactions. Some latitude is possible because in many systems the nature of the lowest energy excited state can be affected by chemical modification of ligands[7-9] or by judicious choice of solvent.[10]

On the other hand, the photophysical and photochemical properties of some metal complexes are more complex and reflect two or more participating excited states which may be distinguished by spin multiplicity,[11] by orbital parentage,[12] by the ligands involved,[13] or by more subtle effects.[14] In such systems the rates of interconversion among levels dictate the response to light.[15,16] However, the factors which determine how rapidly excited states equilibrate are not fully understood, and although some patterns are beginning to emerge, further studies are clearly needed. Of interest in this regard are systems where unusally slow interconversions can be identified, e.g., by emission spectroscopy.

Our group has begun investigating the emission properties of copper(I) complexes involving heteroaromatic ligands.[11e,12d,17,18] The d^{10} configuration of the metal center and the π^* orbitals of the ligand centers combine to produce low-lying metal-to-ligand CT and IL states which are reflected in the emissions from these systems. Here we report photoproperties of complexes of the type

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$[Cu(biL)(PPh_3)_2]^+$ where biL represents 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, and 2,2′-bipyridine, denoted as phen, dmp, and bpy, respectively.[19] All three complexes exhibit emission from a $^3d-\pi^*$ CT state in the glass, and the phen and dmp systems give distinct emissions from nearby $^3\pi-\pi^*$ IL states as well. Interestingly, in alcohol solution at room temperature CT emission is only detected from the dmp complex.

Experimental Section

Preparative Methods. The methods for preparing the phen[12d] and bpy[18] derivatives have already been described, so only the procedure for the dmp complex is reported here. One equivalent of $Cu(BF_4)_2 \cdot nH_2O$ (Research Organic/Inorganic Chemical Corp.) and 6 equiv of triphenylphosphine (recrystallized from ethanol) were refluxed in ethanol (EtOH) until the color changed from blue to white. The solid obtained had a percent copper which was too low for $[Cu(PPh_3)_4]BF_4$ and presumably contained coprecipitated PPh_3. A weighed amount of this material was suspended in ether with stirring and 1 equiv (based on copper) of dmp (Aldrich) was slowly added and the color changed from white to yellow. After being stirred for several hours, the reaction mixture was cooled and yellow crystals of $[Cu(dmp)(PPh_3)_2]BF_4$ were collected by suction filtration, washed with ether, and recrystallized from methanol (MeOH) containing a slight excess of PPh_3. (Anal. Calcd: C, 68.00; H, 4.79; N, 3.17. Found: C, 67.91; H, 4.71; N, 3.39.) The complex could be obtained with other anions by similar routes. Solutions of the dmp complex were quite stable in air, but solutions of the bpy and phen complexes slowly change color unless kept under nitrogen. The chromium complexes used in the quenching studies were prepared by literature methods.[20]

Electrochemical Studies. Conductivity measurements were made with use of a McKee-Pedersen Instruments 1010 Wheatstone Bridge and a Knight KG-635 DC oscilloscope. All solutions were thermostated at 25 °C and a standard aqueous KCl solution was used to determine the conductivity cell constant.

All cyclic voltammograms were determined in a conventional three-compartment cell, using a Bioanalytical Systems Model CV-1B cyclic voltammetry unit and a Hewlett-Packard 7015 B X-Y recorder. The supporting electrolyte was 0.05 M $[n\text{-}Bu_4N]PF_6$ in MeOH, and a AgCl/Ag electrode was used as the reference electrode. For convenience, all potentials quoted have been corrected to an SCE reference by adding −0.03 V to the experimental AgCl/Ag potentials. A carbon-paste or a pyrolytic graphite electrode served as the working electrode. All solutions were deoxygenated with nitrogen or argon and a scan rate of 100 or 50 mV/s was usually employed.

Luminescence Studies. The compounds used as quenchers were purified by recrystallization, and the observed melting points agreed with the literature values. Electronic absorption spectra were measured with use of either a McPherson EU-700-D or a Cary 17D spectrophotometer. Emission spectra were obtained with a Perkin-Elmer MPF-44B fluorimeter. Burdick-Jackson distilled-in-glass MeOH and Gold Shield EtOH were used in the luminescence experiments and all samples were thoroughly deoxygenated by successive freeze–pump–thaw cycles. The emission spectra used in the quenching studies were obtained by exciting at 395 nm (410 nm in the case of anthracene) and changes in the emission intensity of $[Cu(dmp)(PPh_3)_2]^+$ were observed at 530 nm. While the absorbance of the quenchers at 530 nm was negligible, small corrections for their absorbance at the exciting wavelength were made according to the method of Demas and Adamson.[21]

The spectra of the millisecond components of emission (77 K) were resolved by using a phosphoroscope and the lifetimes were obtained by using a variation of the method of Lewis and Kasha.[22] The instrumentation used to resolve the shorter-lived emission both temporally and spectrally has been described elsewhere.[23] Lifetimes were calculated from the slopes of standard log plots. The low-temperature measurements were obtained by immersing the samples in liquid nitrogen or by using either an Air Products cryostat or an Oxford Instruments DN-704 liquid nitrogen cryostat. The quantum yield for solution luminescence was determined by the method of Parker,[24] using aqueous $[Ru(bpy)_3]^{2+}$ as a standard ($\phi_{lum} = 0.042 \pm 0.003$[25]) and correcting for differences in the refractive indices. The emission spectra were corrected by the method of Lippert.[26]

Table I. Conductance Measurements for $[Cu(dmp)(PPh_3)_2]^+$

anion	concn, M	Λ_M, ohm^{-1} cm^{-1} M^{-1}
ClO_4^-	4.4×10^{-4}	86
ClO_4^-	1.1×10^{-4}	105
BF_4^-	1.0×10^{-3}	84
BF_4^-	2.5×10^{-4}	113

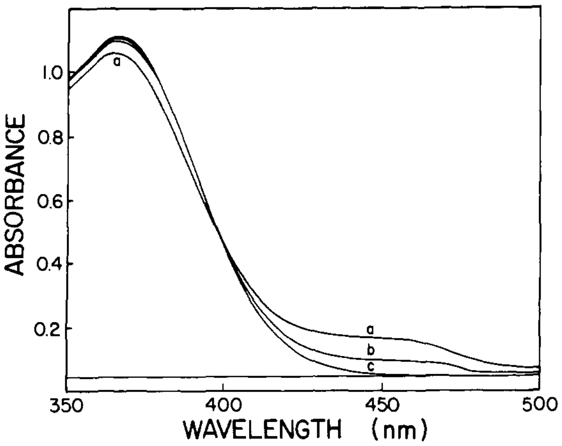

Figure 1. Visible absorption spectrum of 0.4 mM $[Cu(dmp)(PPh_3)_2]^+$ in MeOH containing: (a) no added PPh_3; (b) 0.4 mM PPh_3; (c) 4.0 mM PPh_3.

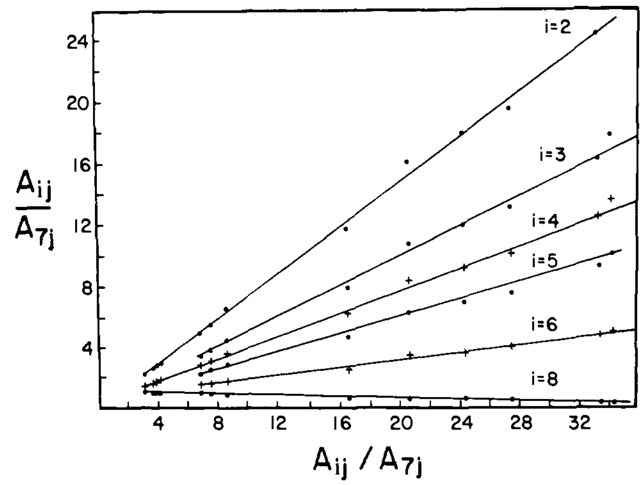

Figure 2. Plots for the graphical matrix rank method test for two absorbing species without explicit consideration of stoichiometry. A_{ij} is the absorbance of the jth solution at the ith wavelength.

Results

Solution Properties of $[Cu(dmp)(PPh_3)_2]^+$. The complex has been isolated as the perchlorate, tetrafluoroborate, hexafluorophosphate, and tetraphenylborate salts, and the molar conductance values of the ClO_4^- and BF_4^- salts in MeOH are presented in Table I. The absorption spectrum of a MeOH solution containing $[Cu(dmp)(PPh_3)_2]^+$ is presented in Figure 1. When excess PPh_3 is added to the solution, the shoulder at 450 nm decreases while the absorption increases at the 365 nm maximum. If the copper concentration is 0.4 mM, the shoulder is almost completely suppressed by a tenfold excess of PPh_3. A series of solutions with a constant total copper ion concentration, but with varying amounts of added PPh_3, shows an isosbestic point at 400 nm. (See

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(19) Preliminary results on the phen and bpy systems have been reported in ref 12d and ref 18, respectively.

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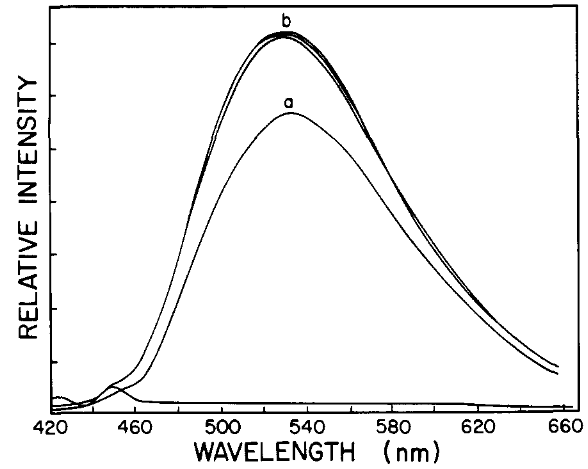

Figure 3. Room-temperature emission spectrum (uncorrected) of 0.4 mM $[Cu(dmp)(PPh_3)_2]^+$ excited at 395 nm in MeOH containing: (a) no added PPh_3; (b) increasing amounts of added PPh_3 (10-, 30-, and 50-fold excesses).

Table II. Lifetime of Photoexcited $[Cu(dmp)(PPh_3)_2]^+$ as a Function of Temperature

T, K	τ, μs	T	τ, ns
150	45.9	250	978 ns
175	18.8	290	330 ns
200	6.51		

Figure 1.) Over the range of 0.02 mM to 0.6 mM the absorbance at the isosbestic wavelength is directly proportional to the copper concentration (ϵ 1040 M^{-1}/cm^{-1}). The graphical matrix rank method of Coleman, Varga, and Mastin was applied to the $[Cu(dmp)(PPh_3)_2]^+$ system in an attempt to determine the number of absorbing species present in solution.[27] Plotting absorbance ratios at various combinations of three wavelengths for a variety of different solutions gives the series of straight lines shown in Figure 2. In contrast to these results, spectra of solutions containing $[Cu(bpy)(PPh_3)_2]^+$ with 1–4 equiv of excess PPh_3 are essentially superimposable on each other, and the same is true in the case of the phen system.

At room temperature in MeOH $[Cu(dmp)(PPh_3)_2]^+$ exhibits an (uncorrected) emission spectrum which maximizes at 530 nm. Initially, the addition of PPh_3 results in an increase in the emission intensity, but as more PPh_3 is added the intensity reaches a limiting value and is no longer dependent on the phosphine concentration (Figure 3). In the presence of excess PPh_3 the quantum yield of the luminescence is 1.4×10^{-3}. The emission lifetime in MeOH as a function of temperature is given in Table II.

The results of a series of quenching studies are presented in Table III along with the reduction potentials of the quenchers employed. The quenching rate constants have been calculated from eq 2:

$$P^0/P = 1 + K_{sv}[Q] \qquad (1)$$

$$K_{sv} = k_q\tau \qquad (2)$$

where P^0 = emission intensity in the absence of quencher, P = emission intensity when the quencher concentration is [Q], K_{sv} = Stern–Volmer constant, k_q = bimolecular quenching rate constant, and τ = lifetime of the excited state species in the absence of quencher. The K_{sv} values have been obtained from least-squares analyses of the data, using eq 1.

Low-Temperature Emissions from the $[Cu(biL)(PPh_3)_2]^+$ Systems. The spectrum of the dmp complex dissolved in a frozen MeOH/EtOH glass (1:4 v/v) at 77 K is presented in Figure 4 and reveals a weak maximum at 455 nm, a shoulder at 490 nm, and a stronger maximum at 523 nm. The phen complex has an emission with a weak maximum at 460 nm and a more intense maximum at 575 nm. Both the spectra of the dmp complex and the phen complex could be time resolved into two principal com-

Table III. Results of Quenching Studies of Photoexcited $[Cu(dmp)(PPh_3)_2]^+$

quencher	K_{SV}, M^{-1}	k_q, M^{-1} s^{-1}	$E_{1/2}$, V, vs. SCE
m-dinitrobenzene	1.87×10^3	5.7×10^9	-0.90^a
nitrobenzene	7.26×10^2	2.2×10^9	-1.15^a
p-nitroanisole	4.38×10^2	1.3×10^9	-1.3^b
anthracene	1.40×10^3	4.2×10^9	$-1.96,^c +1.14^d$
$Cr(tfbzac)_3{}^f$	1.74×10^3	5.0×10^9	-0.8^e
$Cr(tfac)_3{}^g$	4.41×10^2	1.3×10^9	-1.0^e
$Cr(acac)_3{}^h$	1.58×10^2	4.8×10^8	-1.7^e

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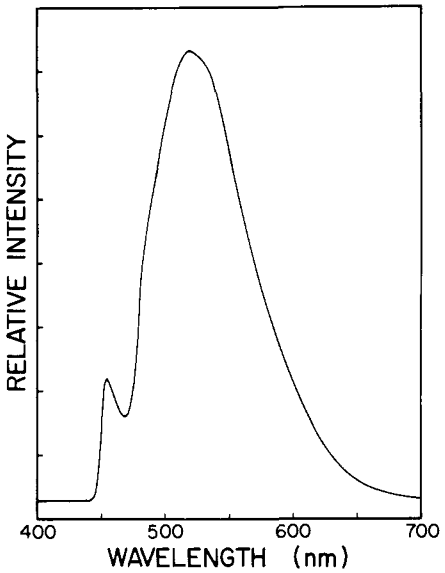

Figure 4. Total emission spectrum (uncorrected) of $[Cu(dmp)(PPh_3)_2]^+$ at 77 K in 4:1 (v/v) EtOH/MeOH glass excited at 365 nm.

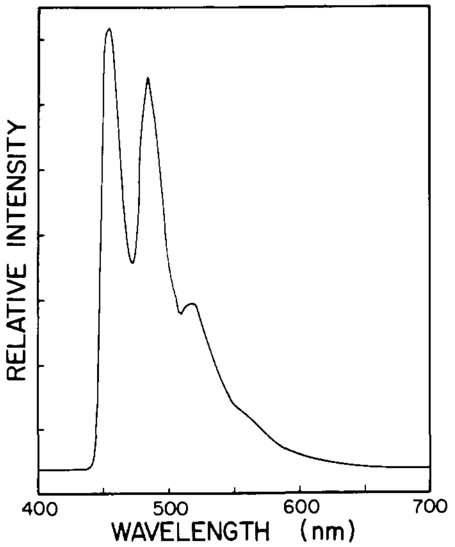

Figure 5. Emission spectrum (uncorrected) of the 9.5 ms component from photoexcited $[Cu(dmp)(PPh_3)_2]^+$ viewed through a phosphoroscope at 77 K in a 4:1 (v/v) EtOH/MeOH glass. λ_{ex} = 365 nm.

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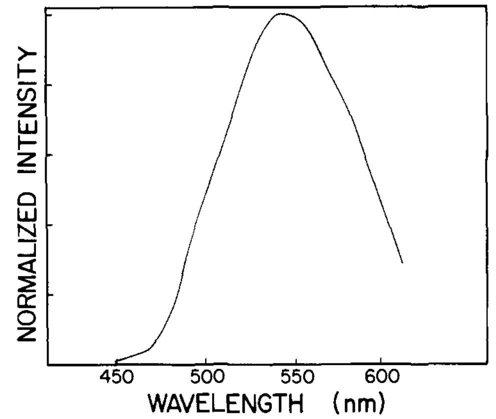

Figure 6. Time resolved emission spectrum (corrected) of the 225 μs component of $[Cu(dmp)(PPh_3)_2]^+$ at 90 K in a 4:1 (v/v) EtOH/MeOH glass. λ_{ex} = 365 nm.

ponents, the spectra of which are presented in Figures 5 and 6 for the dmp complex. The 9.5 ms (77 K) component (Figure 5) has been resolved with a phosphoroscope, and the 225 μs (90 K) component (Figure 6) has been resolved with the laser apparatus. Analogous components could also be resolved for the phen complex with lifetimes of 8.5 ms and 115 μs, respectively. In contrast the spectrum of the bpy complex exhibits a single maximum at 605 nm which predominantly reflects a component with a lifetime of 4 μs. The bpy samples appeared to give some signal through the phosphoroscope ($\tau \gtrsim 1$ ms), but the signal was so weak that further analysis was not attempted. In addition very weak, very short-lived components could also be detected from the bpy and phen samples, having $\tau \lesssim 1$ ns. A similar component may also have been present in the spectrum of $[Cu(dmp)(PPh_3)_2]^+$, but could not be unambiguously distinguished from the solvent blank. Time-resolved spectra of the two components which have been observed for $[Cu(bpy)(PPh_3)_2]^+$ in the glass at 90 K are presented in Figure 7.

The total emission spectra of all three complexes are quite sensitive to temperature in the MeOH/EtOH solvent. On warming the bpy and phen samples from 77 K the emissions that have been described steadily weaken and can hardly be detected on our fluorimeter above ca. 100 K. In the case of the dmp complex, only the structured component of the emission vanishes, however (Figure 8).

Discussion

Electrochemical Studies of $[Cu(dmp)(PPh_3)_2]^+$. The molar conductance values obtained in MeOH fall in the range expected for a 1:1 electrolyte[28a] and, as expected, increase when the sample is diluted.[28b] Thus the anions are dissociated in solution, suggesting the Cu(I) complex is four-coordinate. The cyclic voltammogram of a solution of $[Cu(dmp)(PPh_3)_2]^+$ containing excess phosphine exhibited anodic waves at 1.2 and ~0.7 V vs. SCE. The former is attributable to PPh_3, but the latter involves the copper complex. Since no cathodic wave was observed, the $E_{1/2}$ value of the complex has not been established, but it is presumably ≥0.7 V.[29]

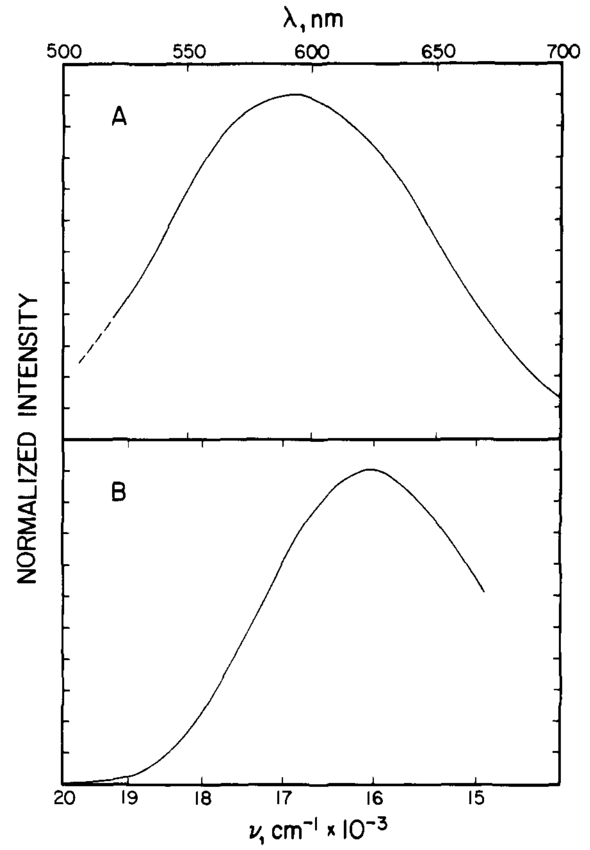

Figure 7. (A) The sub-nanosecond component of $[Cu(bpy)(PPh_3)_2]^+$ taken with a 5 ns gate at approximately the time of the instrumental maximum. (B) The 4 μs component of $[Cu(bpy)(PPh_3)_2]^+$ taken with a 50 ns gate approximately 90 ns after the time of the instrumental maximum. Both spectra have been taken at 90 K.

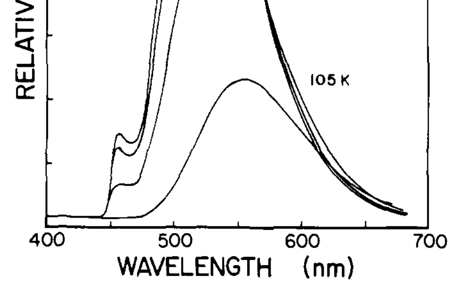

Figure 8. Total emission spectrum (uncorrected) of $[Cu(dmp)(PPh_3)_2]^+$ excited at 365 nm in 4:1 (v/v) EtOH/MeOH as a function of temperature.

Absorption Studies in Fluid Solution. All three complexes exhibit absorption maxima in the near UV which can be attributed to metal-to-ligand charge-transfer transitions. The λ_{max} values are 356, 365, and 365 nm, respectively, for the bpy, phen, and dmp complexes. No other absorption maxima occur to lower energy for the phen and bpy samples, but another maximum is observed at about 450 nm for solutions of $[Cu(dmp)(PPh_3)_2]^+$ in MeOH as shown in Figure 1. The sensitivity of the absorption spectrum of the dmp complex to the addition of PPh_3 suggests that an equilibrium is set up involving free PPh_3 and various copper-containing species. Three straightforward equilibria can be envisaged for the dissociation of PPh_3:

$$2[Cu(dmp)(PPh_3)_2]^+ = [Cu(dmp)_2]^+ + [Cu(PPh_3)_3]^+ + PPh_3 \quad (3)$$

$$[Cu(dmp)(PPh_3)_2]^+ = [Cu(dmp)(PPh_3)]^+ + PPh_3 \quad (4)$$

$$[Cu(dmp)(PPh_3)_2]^+ = [Cu(dmp)]^+ + 2PPh_3 \quad (5)$$

Although not explicitly indicated in these equations, it is assumed

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(28) (a) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. (b) Cooke, D. W. *Inorg. Chem.* **1966**, *5*, 1141.

(29) Chemical events attending the electrode process, e.g., dissociation of phosphine or ligand induced reduction of Cu(II), could result in a cathodic shift of the response.

that Cu(I) remains four-coordinate in all cases by coordinating solvent and/or anion.

The spectra require that upon dissociation of PPh_3 a copper-containing species be formed which has an absorption maximum at ~450 nm. The $[Cu(dmp)_2]^+$ ion is well known to absorb in this region, and the literature claims that $[Cu(dmp)]^+$ does as well, although few details are available.[30] Because of the presence of a phosphine ligand, the MLCT band of $[Cu(dmp)(PPh_3)]^+$ would be expected to occur at a significantly shorter wavelength;[18,31] hence, either eq 3 or eq 5 is expected to give rise to the species in question. Further analysis reveals that eq 3 does not occur to any significant extent. First of all, the absorbance at the isosbestic wavelength is directly proportional to the total copper concentration. This implies that *all* of the Cu(I)-containing species absorb at 400 nm, and independent measurements show that Cu(I)/phosphine complexes do not. Second, if eq 3 described the equilibrium in solution, the molar absorptivity of $[Cu(dmp)_2]^+$ should be twice that of $[Cu(dmp)(PPh_3)_2]^+$ at the isosbestic wavelength. However, ϵ_{400} is 4565 M^{-1} cm^{-1} for $[Cu(dmp)_2]^+$ and ϵ_{400} is only 1040 M^{-1} cm^{-1} for $[Cu(dmp)(PPh_3)_2]^+$. Assuming the formation of $[Cu(dmp)]^+$ explains the absorption at 450 nm, the question arises whether the phosphine dissociation is a cooperative process, i.e., whether or not $[Cu(dmp)(PPh_3)]^+$ is present in solution along with $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(dmp)]^+$. Since the graphs of the absorbance ratios in Figure 2 are all linear and an isosbestic point is observed, only two absorbing species are indicated; therefore, we conclude that the equilibrium process described by eq 4 is negligible. This follows unless the absorption spectrum of $[Cu(dmp)(PPh_3)]^+$ is fortuitously identical with that of $[Cu(dmp)(PPh_3)_2]^+$.

In concluding this section, one additional point is worth emphasizing: Regardless of the details of the equilibrium involved, the addition of excess PPh_3 has been shown to force the equilibrium until essentially all of the Cu(I) is present as $[Cu(dmp)(PPh_3)_2]^+$. Hence the discussion of the emission experiments pertaining to this complex is not dependent on equilibria operating in the *ground state*.[32]

Emission Studies of $[Cu(dmp)(PPh_3)_2]^+$ in Fluid Solution. The increase in solution luminescence which is observed upon the addition of small amounts of PPh_3 is attributed to a shift in concentration of $[Cu(dmp)(PPh_3)_2]^+$, which is presumed to be the emitting species. Although dissociative equilibria may also operate in the excited state, the fact that the emission maximum does not shift with added phosphine tends to disfavor this possibility. (It can also be noted that analogous emission is seen in a rigid glass, vide infra, where photodissociative phenomena are less likely to occur.) The fact that the emission intensity becomes constant when excess PPh_3 is added shows that PPh_3 is *not* an effective quencher for this system, a fact which simplifies analysis considerably.

The broad structureless emission spectrum of $[Cu(dmp)(PPh_3)_2]^+$ is similar to the emission spectra of related systems which have been assigned CT parentage.[12d,18] If it is assumed that a single emitting state occurs and that it is populated with unit efficiency, the radiative lifetime of the emission is estimated to be $\tau_{rad} \approx \tau/\phi \approx 240$ μs. Although this treatment may be simplistic, the magnitude of the calculated τ_{rad} suggests that the radiative process is slow, presumably implicating a triplet level in the decay scheme. (A reviewer suggested that the 545 nm emission might be attributable to an exciplex of PPh_3 with the complex, but this seems unlikely for two reasons. One is that the emission intensity changes very little when the concentration of free PPh_3 is varied over a wide range, and the other is that analogous emission is observed in a rigid glass, vide infra.)

The reducing character of the CT excited state is demonstrated by the data in Table III. The nitrobenzene derivatives are generally thought to quench by oxidative electron transfer to give the corresponding radical anions.[33] Quenching by *m*-dinitrobenzene is found to be essentially diffusion controlled, and a steady decrease in quenching rate is observed on going to nitrobenzene and to *p*-nitroanisole. In view of the fall-off in quenching rate,[33] the reduction potential of the excited state is estimated to be −0.9 V vs. SCE. Accordingly, the shift in potential in going from ground to excited state $[Cu(dmp)(PPh_3)_2]^+$ is $\gtrsim 1.6$ V. This shift is seen to be reasonable in view of the energetics involved. Because the lowest singlet and triplet CT states are thought to be close-lying,[11e,12d,14] the zero–zero energy of the emitting CT state can be roughly gauged by half the sum of the energies of the absorption and emission maxima or 2.9 V in the case of $[Cu(dmp)(PPh_3)_2]^+$. Consequently, the potential of the excited state could be even more than 1.6 V cathodic of the ground state potential. Anthracene and the chromium compounds are also effective quenchers (see Table III), although with these systems an energy transfer quenching mechanism is also possible, and in fact probable in the case of anthracene.

Emission Studies of the $[Cu(biL)(PPh_3)_2]^+$ Systems in a Rigid Environment. All three complexes exhibit a broad, structureless component with a lifetime in the microsecond range. The lifetimes *and* the emission intensities decrease in the order dmp > phen > bpy, suggesting that nonradiative decay processes increase in efficiency along the same sequence and are significantly more effective in the bpy complex. Analogously broad emission spectra have been observed from CT states of $[Cu(dmp)_2]^+$ [17] and, as noted above, from $[Cu(dmp)(PPh_3)_2]^+$ in solution. Based on these comparisons and the relatively long lifetimes which are observed, the microsecond components are plausibly assigned to triplet charge-transfer states, denoted $^3d-\pi^*$ states.

The other component which has been clearly resolved from the total emission spectrum of the dmp complex has a lifetime of 9.5 ms and exhibits well-defined vibronic structure (Figure 5). A similar component with a lifetime of 8.5 ms is resolved from the phen complex. In both cases the millisecond components exhibit vibronic structures similar to—but not identical to—the $^3\pi-\pi$ phosphorescence spectra of the free phenanthroline ligands. In addition, the lifetimes of the $^3\pi-\pi^*$ states of the *free* ligands are also considerably longer under these conditions, being 2 s in the case of dmp and 1.4 s in the case of phen. Such differences are commonly observed in the phosphorescence spectra of phenanthroline moieties coordinated to metal centers;[12d,14] accordingly, the millisecond components can be assigned to $^3\pi-\pi^*$ states of the *coordinated* ligands. In principle, the millisecond and the microsecond components could originate from two different excited states of the same $[Cu(biL)(PPh_3)_2]^+$ unit or from two stoichiometrically distinct molecules in solution. Although it is perhaps impossible to eliminate the latter possibility completely, several lines of argument support assigning *both* components to the same complex. For convenience only the $[Cu(dmp)(PPh_3)_2]^+$ system will be discussed in detail, but most of the arguments apply to the $[Cu(phen)(PPh_3)_2]^+$ system as well. To begin with, we can examine the ways by which a second molecule could appear in solution.

The trivial case of an adventitious impurity is discussed first. A solvent impurity is unlikely because the solvent emission is spectrally different from those in Figure 5 and 6, and the solvent emission requires UV excitation. Moreover, the complex gives a similar total emission spectrum in a $CHCl_3/CH_2Cl_2$ (1:1 v/v) glass. It is also very unlikely that an impurity has been introduced with the copper complex because the same total emission spectrum has been obtained from independent samples involving different anions prepared by three different investigators over a 2-year time span.

A more subtle possibility is that a second species could arise if the compound is subject to chemical decomposition in solution. In this regard we must consider the possbility of photodecomposition. Although photoinduced ligand substitution can lead to

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[30] Sundararajan, S.; Wehry, E. L. *J. Phys. Chem.* **1972**, *76*, 1528.

[31] This expectation is borne out by preliminary studies of the absorption spectrum of $[Cu(dmp)(PPh_3)Br]$. Buckner, M. T.; McMillin, D. R., unpublished results.

[32] A reviewer has pointed out that the equilibria could be different in the excited state; this possibility will be dealt with later.

[33] Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

problems with inert complexes, e.g., d^6 systems,[34] because a buildup of ligand-substituted product can develop, it is much less likely to be a concern for a labile system like copper due to the readiness with which copper complexes undergo ligand exchange. Photoredox decomposition is also possible, but no loss of Cu(I) was detected under illumination over relevant time periods. A second emitting species could also arise via a thermal process, and the obvious concern is the PPh$_3$ dissociation described above. However, the same total emission spectrum is obtained for near-UV excitation of glassy samples irrespective of whether PPh$_3$ is added or not. It should also be noted that the extent of PPh$_3$ dissociation is small at room temperature and *decreases* as the temperature is lowered. Moreover, in order for this equilibrium to explain the two components, the species involved would fortuitously have to display quite disparate emission quantum yields. Finally, *both* components of the emission exhibit an excitation spectrum having the same MLCT maximum in the vicinity of 370 nm.

Taking a different tack, we can ask what species *could* be responsible for the emissions detected. As discussed above, the 9.5 ms component may unambiguously be attributed to $^3\pi$–π^* emission of *coordinated* dmp. Besides [Cu(dmp)(PPh$_3$)$_2$]$^+$, the obvious complexes of dmp which could form are [Cu(dmp)$_2$]$^+$, [Cu(dmp)]$^+$, and [Cu(dmp)(PPh$_3$)X]$^{n+}$ where X might be anion (n = 0) or solvent (n = 1). Now the emission spectrum of [Cu(dmp)$_2$]$^+$ has been thoroughly studied[17,18] and it does not exhibit either of the components in question. Although [Cu(dmp)]$^+$ has not been isolated, since its absorption spectrum appears to have bands which are similar in energy to those of [Cu(dmp)$_2$]$^+$, any emission spectrum it may have should be similar as well; hence it can be excluded. The fact that the total emission spectrum is independent of added PPh$_3$ tends to eliminate the possibility of [Cu(dmp)(PPh$_3$)X]$^{n+}$ emission. In addition, if a species of the type [Cu(dmp)(PPh$_3$)X]$^{n+}$ were involved, it would have to have the same absorption and excitation spectrum as [Cu(dmp)(PPh$_3$)$_2$]$^+$ in the near-UV region, and this seems improbable.

On the basis of this analysis, we feel the millisecond and microsecond components in the low-temperature emission spectra of [Cu(dmp)(PPh$_3$)$_2$]$^+$ or [Cu(phen)(PPh$_3$)$_2$]$^+$ can be attributed to different triplet states of the same parent complex, even though molecules rarely exhibit simultaneous emissions from different states with the same multiplicity. At least three models have been proposed to rationalize the systems that do, and our systems can readily be understood in these terms.[12b,35]

The most straightforward case arises when there is microenvironmental heterogeneity.[36] This effect can occur when there are significant solute–solvent interactions, when the solvent reorientation/relaxation time is long compared to the excited state lifetime(s), and when the solvation varies from solute to solute so that a distribution of emission energies and lifetimes arises for a particular type of excitation. Another possibility arises if the molecule of interest can exhibit different structures in the ground and excited states, e.g., different tautomers, or conformers. A third possibility occurs with molecules that have a single ground-state structure, but which involve excited states with quite dissimilar equilibrium geometries, e.g., because of differences in orbital parentage. By all three models, structurally distinct excited species (possibly involving the molecule and solvent) may arise and interconversion between species may not be facile in a rigid matrix; hence, separate emissions may be observed. Since solvent rigidity plays a pivotal role in all three of the models and since [Cu(dmp)(PPh$_3$)$_2$]$^+$ emits in fluid solution as well as in a glass, the temperature dependence of its emission spectrum is of interest. As can be seen from Figure 8, the $^3\pi$–π^* component effectively vanishes above ~100 K which is approximately the glass transition temperature of the solvent.[37] The loss of the $^3\pi$–π^* component may occur because interconversion with the ^{3}d–π^* state becomes more efficient or because other radiationless processes become more efficient. Either way, the observation of multiple emissions is facilitated by a rigid solvent matrix, consistent with the above models. We can therefore seek to determine which model is most likely to pertain to our system. Because the $^3\pi$–π^* and ^{3}d–π^* components are observed in both CHCl$_3$/CH$_2$Cl$_2$ and MeOH/EtOH glasses, and because the components observed clearly have *different* orbital parentages, something other than microenvironmental heterogeneity is presumably involved.[38] Moreover, since our spectral studies on [Cu(dmp)PPh$_3$)$_2$]$^+$ in solution have failed to indicate more than one ground-state species, we have no data in support of the second model. On the other hand, the last model discussed seems very plausible. To see this, consider the electronic configurations involved. The ^{3}d–π^* state formally involves a d^9 metal center, and being subject to the pseudo-Jahn-Teller effect, would be expected to distort considerably from the ground state insofar as the configuration about the metal is concerned. (Of course, some geometry changes may be expected at the ligands as well, particularly at dmp which is formally anionic in the excited state.) On the other hand, the perturbed $^3\pi$–π^* state formally involves Cu(I), and little change in geometry about the metal would be expected. Therefore, the ^{3}d–π^* and $^3\pi$–π^* states would in fact be expected to undergo different types of distortion, and radiationless transitions between them could be slow in a low-temperature glass.

Table IV. Well-Characterized Emissions from [Cu(biL)(PPh$_3$)$_2$]$^+$ Species in Glasses

complex	λ_{max}, nm	τ	assignment
[Cu(dmp)(PPh$_3$)$_2$]$^+$	450, 485, 519^a	9.5 ms (77 K)	$^3\pi$–π^*
	545	225 μs (90 K)	^{3}d–π^*
[Cu(phen)(PPh$_3$)$_2$]$^+$	461, 495, 526	8.5 ms (77 K)	$^3\pi$–π^*
	608	115 μs (90 K)	^{3}d–π^*
[Cu(bpy)(PPh$_3$)$_2$]$^+$	620^a	4 μs (90 K)	^{3}d–π^*

^{a} Uncorrected.

Accepting the notion that differences in the excited-state geometries result in the multiple emissions, then one must wonder why multiple emissions occur so rarely, since in principle every excited state of a molecule exhibits a unique geometry. Although understanding the rates of radiationless transitions is a formidable task, we may gain some insight from empirical comparisons. For increasingly many systems exhibiting multiple emissions, the energy gap separating the emitting levels seems to be an important consideration. Watts and Missimer discuss Rh(III) and Ir(III) systems and point out that multiple emissions have so far been observed only in cases where Δ, the energy gap between the emitting levels, is less than about 1100 cm^{-1}. When Δ is around 1600 cm^{-1}, for example, multiple emissions are not observed.[12b] Similarly, Wrighton and co-workers[8] report that in complexes of the type *fac*-[SRe(CO)$_3$(phen)]$^+$, multiple emissions are observed when Δ is in the neighborhood of 1000 cm^{-1}, although these authors do not seem to be dealing with the zero–zero energies of the excited states involved. Thus the energy gaps for the Cu(I) are of interest.

For convenience the wavelengths of the low-temperature $^3\pi$–π^* and ^{3}d–π^* spectra are collected in Table IV. The zero–zero energy of the $^3\pi$–π emission of the phen complex can be estimated from the highest energy vibronic component.[39] A crude estimate of the zero–zero energy of the ^{3}d–π^* state can be obtained from the average of the energies of the absorption maximum and the ^{3}d–π^* emission maximum. The calculations suggest that the $^3\pi$–π^* state is about 50 cm^{-1} below the ^{3}d–π^* state. Taking into

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(37) Angell, C. A.; Sare, J. M.; Sare, E. F. *J. Phys. Chem.* **1978**, *82*, 2622.

(38) Even if the multiple emissions occur because two electronically and structurally distinct excited states are involved, however, the local environment can still play an important role by favoring the relaxation of a given molecule toward one structure or the other.[12b]

(39) Herstroeter, W. G.; Lamola, A. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 4537.

account the splitting between the ^{1}d–π^* and ^{3}d–π^* states, however, a somewhat larger gap and the opposite ordering are predicted. (A plausible singlet–triplet splitting is 1000 cm^{-1}, vide infra.) A similar calculation shows that the ^{3}d–π^* and $^3\pi$–π^* states have comparable energies in the dmp complex. Although these results are very approximate, they are consistent with the idea that the simultaneous emissions tend to arise from excited states with similar energies.

The remaining components that can be discussed are the extremely short-lived components ($\tau \lesssim 1$ ns) which have been resolved for the bpy and phen samples. As can be seen in Figure 7, in the case of the bpy complex this component gives a broad, structureless spectrum which is somewhat blue-shifted from the ^{3}d–π^* component. Similar behavior is observed for the phen complex.[12d] Due to their weak intensities, we do not have excitation spectra for these components, and therefore we cannot be as confident in assigning them to the respective $[Cu(biL)(PPh_3)_2]^+$ species or even in assigning them an orbital parentage. However, the most plausible assignments would be to CT states. The sub-nanosecond components occur at too low energies to be IL emissions from PPh$_3$,[40] and are probably too short lived to be MC emissions.[18] (We should note, however, that arguments based solely on lifetime date are somewhat tenuous.) In view of the relative energies and lifetimes of these components compared with those of the corresponding ^{3}d–π^* components, it is tempting to assign the sub-nanosecond components as ^{1}d–π^* emissions, but the results are too sketchy to do so at this time. It is curious in this regard that the sub-nanosecond components give spectra which are slightly broader than those of the ^{3}d–π^* components. Clearly the proper characterization of the sub-nanosecond components will require much further effort.

Conclusions

These studies illustrate the intriguing photochemical and photophysical properties exhibited by Cu(I) systems. In a general way the solution measurements involving $[Cu(dmp)(PPh_3)_2]^+$ demonstrate the need to define species in labile complexes of this type. The fact that PPh$_3$ dissociation appears only to be significant in the case of the dmp complex may be due to ligand/ligand repulsive effects associated with the methyl substituents in the 2 and 9 positions of dmp. Naively, one might have anticipated that the three, structurally analogous $[Cu(biL)(PPh_3)_2]^+$ complexes would behave very similarly, but our results show that the situation is much more subtle. The photoproperties are very sensitive to the nature of the biL ligand. Perhaps most striking is the fact that only the dmp complex gives rise to appreciable CT luminescence in solution at room temperature. An interesting challenge is to determine what interplay of steric, electronic, vibronic, etc., considerations is involved in determining the properties of photoexcited Cu(I) systems.

A final point worth noting is the possible connection between the Cu(I) systems that exhibit multiple emissions in a rigid glass and outer-sphere electron-transfer phenomena. The $[Cu(dmp)(PPh_3)_2]^+$ and $[Cu(phen)(PPh_3)_2]^+$ systems appear to exhibit ^{3}d–π^* and $^3\pi$–π^* emissions from geometrically distinct excited states, i.e., from separate minima in a configuration space. And the relatively slow interconversion between the states involved seems to depend on these states having similar energies. Formally, converting from the ^{3}d–π^* state to the $^3\pi$–π^* state can be viewed as a ligand-to-metal electron-transfer process, and conversely, converting from the $^3\pi$–π^* state to the ^{3}d–π^* state can be viewed as a metal-to-ligand electron-transfer process. Electron-transfer processes are known to be inhibited by the need for significant structural rearrangements in going from reactant to product states and, so long as the gap does not become too large, to occur more rapidly as the energy gap separating the reactant and product states increases.[41]

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Communications to the Editor

Circular Dichroism of (C_3)-Cyclotriveratrylene-d_9: An Example of Exciton Optical Activity due to Isotopic Substitution

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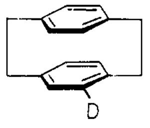
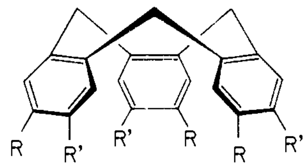
Recently, intense interest has been devoted to the study of the chiroptical properties of compounds owing their chirality to the presence of deuterium. In particular, the carbonyl chromophore has been extensively investigated.[1] In contrast, the only available example of an aromatic derivative showing relevant circular dichroism (CD) properties is (*S*)-(−)-4-deuterio[2.2]paracyclophane (1).[2]



S(−)·1



	R	R'
P(−)·2	OCH$_3$	OH
M(−)·3	OCH$_3$	OCD$_3$
P(−)·4	OC$_2$H$_5$	OCH$_3$
M(−)·5	OC$_2$H$_5$	O*i*C$_3$H$_7$
M(−)·6	OCH$_3$	O*i*C$_3$H$_7$

In a previous paper,[3] we reported the CD spectra of some (C_3) chiral derivatives of cyclotriveratrylene (CTV) and their interpretation in terms of exciton coupling between the transition

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