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## Flash Photolysis and Quenching Studies of Copper(I) Systems in the Presence of Lewis Bases: Inorganic Exciplexes?

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Picosecond flash photolysis studies of  $\text{Cu}(\text{dmp})_2^+$  and  $\text{Cu}(\text{bcp})_2^+$  have been carried out, where dmp denotes 2,9-dimethyl-1,10-phenanthroline and bcp is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. In each case the excited-state absorption spectrum resembles that of the radical anion of 1,10-phenanthroline, consistent with the charge-transfer nature of the excited state. With this technique we have for the first time been able to measure the excited-state lifetime ( $2 \pm 0.3$  ns at 20 °C) of  $\text{Cu}(\text{dmp})_2^+$  in acetonitrile. The quenching kinetics of photoexcited  $\text{Cu}(\text{dmp})_2^+$  by acetonitrile, acetone, and *p*-dioxane in  $\text{CH}_2\text{Cl}_2$  solution have been determined from studies of the luminescence lifetime, and the results are interpreted in terms of a mechanism in which deactivation follows the formation of a complex denoted as  $^*\text{Cu}\cdots\text{Q}$ . The fact that  $\Delta H^\ddagger$  is negative for all three quenchers suggests that  $^*\text{Cu}\cdots\text{Q}$  may represent an exciplex in which the quencher (Lewis base) serves as a fifth donor for the copper center. Exciplex emission has not been detected; however, the kinetic data indicate that the steady-state concentration of  $^*\text{Cu}\cdots\text{Q}$  is quite small. Whether the five-coordinate adduct represents a kinetic intermediate, a successor complex, or even the transition state of the reaction cannot be determined rigorously from our data, but bond formation has been shown to be an essential part of the quenching process. Finally, we consider reasons why exciplexes are not commonly observed for the excited states of transition-metal complexes.

### Introduction

Complexes of copper(I) with heteroatomic ligands such as 2,9-dimethyl-1,10-phenanthroline (dmp) exhibit low-lying metal-to-ligand charge-transfer excited states.<sup>1,2</sup> Although the complexes themselves are generally stable in light, McMillin and co-workers have shown that photoinduced electron transfer from  $\text{Cu}(\text{dmp})_2^+$  to various cobalt(III) complexes can be observed in solution and that the charge-transfer (CT) excited state of  $\text{Cu}(\text{dmp})_2^+$  survives long enough to undergo bimolecular reactions.<sup>3</sup> Wehry and Sundararajan originally reported  $\text{Cu}(\text{dmp})_2^+$  to be nonemissive in methanol solution at room temperature;<sup>4</sup> however, subsequent work has shown that the complex is luminescent when dissolved in weak donor solvents such as methylene chloride.<sup>5</sup>

The luminescence efficiency is very dependent upon the medium because a novel type of emission quenching occurs in the presence of Lewis bases such as acetonitrile or methanol.<sup>5-9</sup> Systematic investigations of steric effects suggest that the quenching occurs by an associative process, in which the coordination number of the copper center is increased from four to five.<sup>6,9</sup> The fact that related copper(II) systems<sup>10-12</sup> have been found to be penta-coordinate is also consistent with the proposed quenching reaction since the metal center is formally divalent in the CT excited state. Accordingly, the quenching has been attributed to excited-state complex, i.e., exciplex, formation.<sup>9</sup> In order to gain more insight into this process, we have carried out picosecond excited-state absorption measurements and we have studied the temperature dependence of the quenching by various Lewis bases. Finally, we consider the reasons why exciplexes, species that are very commonly observed with organic systems, have rarely been detected in the photochemistry of transition-metal complexes.

### Experimental Section

**Materials.** The copper complex was prepared as before from  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  or  $\text{Cu}(\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$  in 1:1 (v/v) water/methanol.<sup>13</sup>  $[\text{Cu}(\text{dmp})_2]\text{B}(\text{Ph})_4$  was obtained via a metathetical procedure by the addition of sodium tetraphenylborate (Baker) and was recrystallized from 3:1 acetone/methanol. Anal. Calcd: C, 78.24; H, 5.51. Found: C, 78.31; H, 5.76.  $[\text{Cu}(\text{bcp})_2]\text{BF}_4$ , where bcp denotes 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, was prepared similarly.

High-purity distilled-in-glass grade methylene chloride was obtained from Burdick and Jackson and used without further purification. Acetonitrile was obtained from Baker, dried twice over activated molecular sieves, and distilled from fresh sieves. Spectral grade acetone was obtained from Fisher and purified according to the method of Werner.<sup>14</sup> High-purity distilled-in-glass grade dioxane was purchased from Burdick and Jackson and purified by a literature procedure.<sup>15</sup>

**Methods.** For the luminescence studies, samples were deoxygenated by repeated freeze/pump/thaw cycles and lifetimes were obtained by

fitting the emission decay to eq 1, where  $I(t)$  is the emission intensity at

$$I(t) = A \exp(-t/\tau) + B \quad (1)$$

time  $t$ ,  $\tau$  is the lifetime,  $A$  is the luminescence intensity at  $t = 0$  and  $B$  is a base-line parameter. A least-squares algorithm was used in which  $\tau$  was refined by an iterative technique while  $A$  and  $B$  were optimized by linear regression for each value of  $\tau$ . The data set generally included  $4^{1/2}$  lifetimes, and the precision in the determination of  $\tau$  is estimated to be 5%. For each quencher, the second-order quenching constant  $k_q$  was estimated from a least-squares fit of the data to eq 2,<sup>16</sup> where  $\tau_0$  is

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[\text{Q}] \quad (2)$$

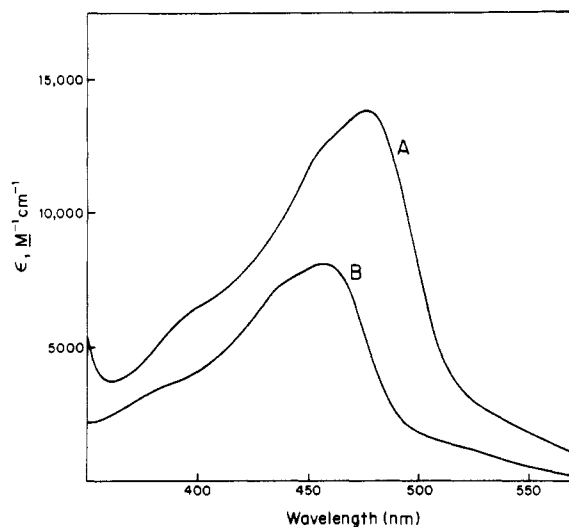
the lifetime in the absence of quencher and  $[\text{Q}]$  is the molar concentration of quencher. Although  $\tau_0$  could be measured directly, it was treated as an adjustable parameter (vide infra). The effect of temperature on sample volume was very small, and no adjustments of the quencher concentrations were required.

Lifetimes from excited-state absorption data were obtained by least-squares analysis. For the transient absorption measurements, fresh sample was continuously supplied to the laser beam region with a flow system. Because such a short time scale was investigated, it was not necessary to deoxygenate the samples.

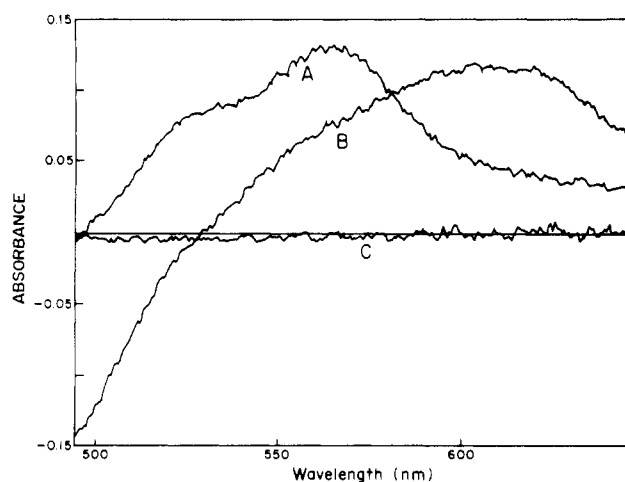
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**Figure 1.** Absorption spectra of  $\text{Cu}(\text{bcp})_2^+$  (A) and  $\text{Cu}(\text{dmp})_2^+$  (B) in  $\text{CH}_2\text{Cl}_2$  at 20 °C.

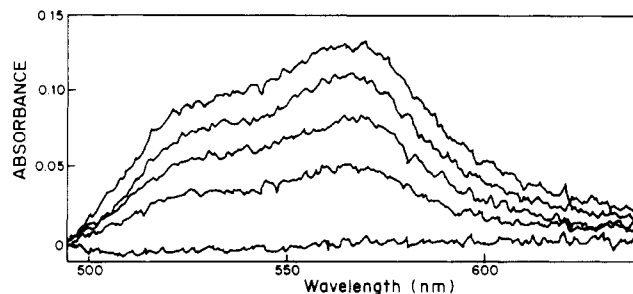


**Figure 2.** Time-resolved absorbance-difference spectra measured 47 ps after excitation with a 30-ps, 355-nm excitation flash in  $\text{CH}_2\text{Cl}_2$  at 20 °C: (A)  $^*\text{Cu}(\text{dmp})_2^+$  vs.  $\text{Cu}(\text{dmp})_2^+$ ; (B)  $^*\text{Cu}(\text{bcp})_2^+$  vs.  $\text{Cu}(\text{bcp})_2^+$ . Trace C is a base-line spectrum, acquired for  $\text{Cu}(\text{dmp})_2^+$  at -100 ps, where the "white-light" probe pulse arrives at the sample before the excitation pulse.

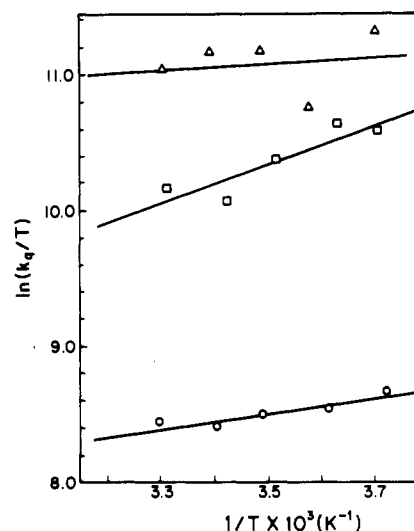
**Equipment.** The equipment for the luminescence lifetimes<sup>17</sup> and the transient absorption measurements<sup>18</sup> has been described previously. Samples for luminescence measurements were thermostated with a Lauda K-2/RD circulating bath while the transient absorption measurements were carried out at ambient temperature ( $\approx 20$  °C). Ground-state absorption spectra were run on a Cary 17D or 14 spectrophotometer.

## Results

**Absorption Measurements.** Figure 1 depicts the ground state absorption spectra of  $\text{Cu}(\text{bcp})_2^+$  (A) and  $\text{Cu}(\text{dmp})_2^+$  (B) in  $\text{CH}_2\text{Cl}_2$  solution. Time-resolved absorbance-difference spectra for both complexes are shown in Figure 2. These spectra reveal the difference in absorbance between a sample excited with a 30-ps, 355-nm flash and unexcited sample. For these spectra the delay between the excitation and "white-light" probe pulses was 47 ps, but there was no measurable decline in the amplitude of the absorbance changes to delays of greater than 5 ns, consistent with the luminescence lifetime of 55 ns in aerated  $\text{CH}_2\text{Cl}_2$  for  $\text{Cu}(\text{dmp})_2^+$ . Excited-state absorption maxima are at approximately 570 and 610 nm, respectively, for  $^*\text{Cu}(\text{dmp})_2^+$  (Figure 2A) and  $^*\text{Cu}(\text{bcp})_2^+$  (Figure 2B), where the asterisk indicates



**Figure 3.** Time-resolved absorbance-difference spectra of  $^*\text{Cu}(\text{dmp})_2^+$  in  $\text{CH}_3\text{CN}$  at 20 °C. In order of decreasing amplitude, the spectra were recorded at delays of 47 ps, 347 ps, 1.01 ns, 1.68 ns, and 8.35 ns following the excitation pulse.



**Figure 4.** Eyring plots of lifetime quenching data. The quenchers were acetonitrile ( $\Delta$ ), acetone ( $\square$ ), and dioxane ( $\circ$ ). The solvent was  $\text{CH}_2\text{Cl}_2$ .

electronically excited forms. In the case of  $\text{Cu}(\text{bcp})_2^+$ , ground-state bleaching is evident in the absorbance-difference spectrum below about 520 nm. The time-resolved absorption spectrum of  $\text{Cu}(\text{dmp})_2^+$  is essentially the same in  $\text{CH}_2\text{Cl}_2$  (Figure 2A) and  $\text{CH}_3\text{CN}$  (Figure 3). However, in the latter solvent the absorbance-difference spectrum decays with a lifetime of  $2.0 \pm 0.3$  ns (Figure 3).

**Luminescence Quenching.** Second-order quenching constants,  $k_q$ , were estimated from the Stern-Volmer plots of lifetime data (eq 2) because relatively high concentrations of quencher were used. In the absence of specific interactions, the association constant between  $\text{Cu}(\text{dmp})_2^+$  and the quencher can be estimated to be about  $0.2 \text{ M}^{-1}$ .<sup>17,19</sup> Hence, when the quencher concentration is 0.5 M, about 10% of the copper complex should be associated. Consequently, static as well as dynamic, or diffusional, quenching is possible. If so, the analysis is more straightforward when lifetime data rather than emission intensity data are used.<sup>20</sup> There also appeared to be fewer complications with the background, i.e., blank emission, in the lifetime experiment. The high levels of quencher employed may also have affected solvation of the complex because the experimental  $\tau_0^{-1}$  value consistently fell slightly above the least-squares plot of eq 2. For example, with acetone at 2 °C the measured  $\tau_0 = 96 \pm 3$  ns whereas the Stern-Volmer analysis yielded  $\tau_0 = 111 \pm 5$  ns. Even though the effect was small, the experimental  $\tau_0$  values were omitted from the data treatment.

The second-order quenching constants are plotted as a function of temperature in Figure 4. Although both singlet and triplet CT states contribute to the luminescence from  $\text{Cu}(\text{dmp})_2^+$ ,<sup>21</sup> to

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Table I. Quenching of  $^*Cu(dmp)_2^+$  by Lewis Bases in  $CH_2Cl_2^a$ 

quencher	$k_q(25^\circ C)$ , $M^{-1} s^{-1}$	$\Delta H^\ddagger$ , $kJ mol^{-1}$	$\Delta S^\ddagger$ , $J mol^{-1} K^{-1}$
	$1.4 \times 10^6$	-5	-145
	$7.5 \times 10^6$	-12	-150
$CH_3CN$	$1.9 \times 10^7$	-2	-110

<sup>a</sup> Estimated errors in  $\Delta H^\ddagger$  are  $\pm 2$   $kJ mol^{-1}$  and in  $\Delta S^\ddagger$  are  $\pm 20$   $J mol^{-1} K^{-1}$ .

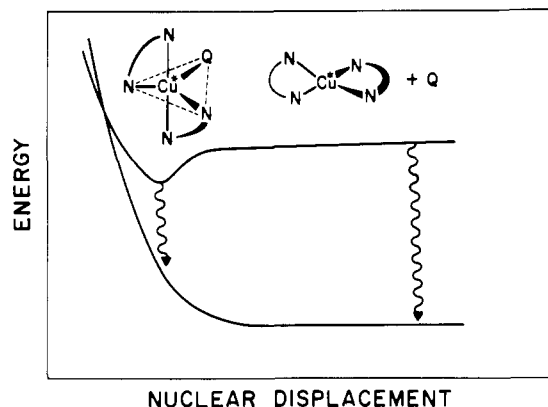


Figure 5. Schematic energy surfaces for exciplex quenching. From right to left the interaction distance between the quencher Q and the copper complex decreases. The lower curve pertains to the ground state while the upper curve represents the excited state. The arrows illustrate that the energy gap is smaller in the exciplex configuration.

a good approximation the quenching constant reflects the intrinsic rate constant for quenching of the triplet CT state.<sup>17</sup> Activation parameters derived from the plots in Figure 4 are compiled in Table I.

### Discussion

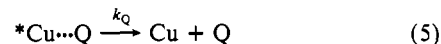
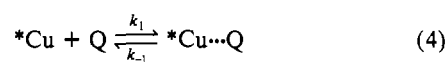
**Potential Energy Considerations.** To fix ideas, a brief overview of exciplex quenching is given. The relevant energy surfaces are indicated in Figure 5. Movement from right to left across the abscissa represents in a single coordinate the nuclear motion involved when the quencher approaches the copper center. Any attendant structural reorganization within the copper complex or the quencher (base) is also implicit in this coordinate. The lower curve in Figure 5 is drawn as strictly repulsive because the  $d^{10}$  Cu(I) center, an 18-electron system, is assumed to be coordinatively saturated in its ground electronic state. However, in the CT excited state the metal is formally  $d^9$  Cu(II), a 17-electron system that is prone to the addition of a fifth ligand. Accordingly, the upper surface in Figure 5 contains a relative minimum that represents the five-coordinate exciplex.

Formation of an exciplex may facilitate net radiationless decay back to the ground-state surface via several different mechanisms. First, the energy gap separating the two surfaces is significantly decreased in the exciplex configuration. Thus, an increase in the nonradiative decay rate might be anticipated on the basis of the energy gap law.<sup>22</sup> Second, if the two surfaces approach each other very closely, mixing of the two zero-order states may occur, facilitating crossing from the excited-state to the ground-state surface.<sup>23</sup> A further possibility is that coordination of a fifth ligand could induce a reordering of the excited-state manifold such that an intrinsically short-lived excited state drops below the emissive CT state and mediates decay.<sup>24</sup> In any event deactivation

is only one step in the overall quenching process; the rates of the other steps involved also influence the mechanistic interpretation, as discussed further below.

**Transient Absorption Spectra.** Some of the relevant rate data can be gleaned from transient absorption measurements. In previous work the excited-state absorption spectra of analogous CT excited states have resembled the spectra of the corresponding ligand radical anions,<sup>25-27</sup> and the data in Figures 1 and 2 are consistent with this trend. In dimethyl ether the radical anion of 1,10-phenanthroline is reported to exhibit an absorption maximum around 550 nm,<sup>28,29</sup> which is plausibly related to the band observed at 570 nm in Figure 1. No change in shape or peak position of the spectrum was observed as a function of time. However, the four-coordinate CT excited state and the proposed exciplex contain the same radical anion; hence, it would be difficult to distinguish the two forms from absorption measurements. If the sharp decrease in the lifetime of the excited-state absorption in acetonitrile is attributed to exciplex quenching, it follows from the data in Figure 3 that the lifetime of the proposed exciplex cannot exceed 2 ns. According to the kinetic scheme discussed below, the exciplex lifetime could be even shorter if the formation constant is small.

**Kinetic Scheme.** Some type of inefficiency occurs in the quenching process because the  $k_q$  values in Table I fall well below the diffusion limit. A minimal kinetic scheme capable of rationalizing these results is presented in eq 3-5. In this scheme



$^*Cu$  denotes the CT excited state, which has a lifetime of  $\tau_0 = k_0^{-1}$  in the absence of quenching.  $Cu$  denotes the ground-state chromophore, and  $^*Cu \cdots Q$  denotes a complex formed between  $^*Cu$  and  $Q$ . All deexcitation processes are assumed to be irreversible.

An approximate rate expression can be developed for this scheme if the concentration of  $^*Cu \cdots Q$  remains small such that it can be treated as a steady-state intermediate. Under these conditions the second-order quenching rate constant  $k_q$  has the form

$$k_q = \frac{k_1}{1 + k_{-1}/k_Q} \quad (6)$$

Since  $^*Cu \cdots Q$  achieves its maximum concentration, relative to  $^*Cu$ , when the two species are in equilibrium, a sufficient condition for eq 6 is that  $K[Q] \ll 1$  where  $K = k_1/k_{-1}$ . Inefficiency arises within this scheme if the  $k_{-1}$  step competes with the  $k_Q$  step, but the kinetics are most transparent when  $k_Q \ll k_{-1}$  in which case eq 6 reduces to

$$k_q = \frac{k_1}{k_{-1}} k_Q = K k_Q \quad (7)$$

where  $K$  is the formation constant defined above.<sup>30</sup> Further insight into the detailed nature of the quenching process can be obtained from an analysis of the temperature dependence of the quenching rates.

**Analysis of Activation Parameters.** The striking fact about the parameters in Table I is that the activation enthalpies are all

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(30) The pitfalls associated with proposing complexes that have not been directly observed are appreciated; however, in this case the kinetic evidence is compelling.

**Table II.** Data for Associative Reaction of Cu(II) Complexes

complex	base	$K$ , $M^{-1}$	$k_1$ , $M^{-1} s^{-1}$	$k_{-1}$ , $s^{-1}$	$\Delta H_1^*$ , $kJ mol^{-1}$	$\Delta S_1^*$ , $J K^{-1} mol^{-1}$	medium	ref
Cu(DnBDC) <sub>2</sub> <sup>a</sup>	py	0.4	$0.8 \times 10^9$	$2 \times 10^9$	0	-84	toluene (25 °C)	<i>b</i>
	piperidine	3.9	$1.4 \times 10^9$	$0.4 \times 10^9$	0	-71	toluene (25 °C)	<i>b</i>
Cu(DDC) <sub>2</sub> <sup>c</sup> [Cu(tren)(OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> <sup>e</sup>	py	0.4	$2.2 \times 10^8$	$5.8 \times 10^8$	-12.9	-126	benzene (27 °C)	<i>d</i>
	py	1.7	$1.5 \times 10^5$	$0.9 \times 10^3$	+25.1	-61	H <sub>2</sub> O, (20 °C)	<i>f</i>

<sup>a</sup>DnBDC is di-*n*-butyldithiocarbamate. <sup>b</sup>Corden, B. J.; Rieger, P. H. *Inorg. Chem.* **1971**, *10*, 263–272. <sup>c</sup>DDC is diethyldithiocarbamate. <sup>d</sup>Farmer, J. B.; Herring, F. G.; Tapping, R. L. *Can. J. Chem.* **1972**, *50*, 2079–2087. <sup>e</sup>Tren is tris(β-aminoethyl)amine. <sup>f</sup>Reference 34.

negative. The activation entropies are also very negative, and this explains why the quenching rate *increases* as the temperature *decreases*. At first glance this seems counterintuitive because even a diffusion-controlled reaction is expected to slow down as the temperature decreases because of the increase in solvent viscosity. However, according to eq 7, the experimentally determined activation enthalpies are given as

$$\Delta H^* = \Delta H_1 + \Delta H_Q^* \quad (8)$$

where  $\Delta H_1$  denotes the enthalpy associated with the formation of \*Cu...Q and  $\Delta H_Q^*$  is the enthalpy of activation associated with the  $k_Q$  step. Consequently, when the binding energy of \*Cu...Q is very strong, the  $\Delta H_1$  term in eq 8 may dominate and render  $\Delta H^*$ , the overall activation enthalpy, negative. Since tight binding is compatible with exciplex formation, an exothermic  $\Delta H^*$  has often been taken to be a signature of exciplex quenching.<sup>31–33</sup> While our results are consistent with exciplex formation, they also suggest that the adduct would be difficult to detect spectroscopically. To see this, note that the transient absorption data indicate that  $k_Q$  is *at least*  $5 \times 10^8 s^{-1}$  in acetonitrile. Since  $k_q = 1.8 \times 10^7 M^{-1} s^{-1}$  for the same quencher in CH<sub>2</sub>Cl<sub>2</sub>, it follows that  $K$  is no greater than about  $0.04 M^{-1}$  (consistent with the previously stated requirement of the steady-state approximation).

In an alternative explanation \*Cu...Q might be construed as an outer-sphere encounter complex. If so, the binding energy of the encounter complex cannot explain the activation enthalpies as the  $\Delta H^*$  values do not follow the trend of outer-sphere binding energies predicted by simple electrostatic arguments. Of all the quenchers, acetonitrile has the largest dipole moment, yet it gives the least negative  $\Delta H^*$ . In addition, dioxane was specifically chosen as a Lewis base with a minimal dipole moment, and it gives an intermediate value of  $\Delta H^*$ . Therefore, if \*Cu...Q is simply an encounter complex, the  $\Delta H_Q^*$  term in eq 8 must be negative. Literature comparisons, based on the previously cited analogy between the CT excited-state and ground-state copper(II), suggest that a negative activation enthalpy is possible. Pertinent kinetic and thermodynamic data for *associative* reactions of copper(II) systems are compiled in Table II. In nearly all cases  $\Delta S_1^*$  is negative, while large in magnitude, and  $\Delta H_1^*$  is negative or zero. The one exception occurs with Cu(tren)(OH<sub>2</sub>)<sub>2</sub><sup>2+</sup> where the substitution reaction exhibits a positive  $\Delta H_1^*$ ; however, this example is unique in that a water molecule must be displaced by the incoming ligand.<sup>34</sup> In the quenching reaction, a negative  $\Delta H_Q^*$  can occur for the same reason that  $\Delta H_1$  is negative when there is an exciplex: a new chemical bond is formed during the attack of the nucleophile. In line with this reasoning, the Gutmann donor numbers predict the nucleophilicity increases in the order ace-

tonitrile < *p*-dioxane < acetone,<sup>35</sup> and this is also the trend of increasing exothermicity within the measured  $\Delta H^*$  values (Table I). The two mechanistic alternatives considered above are really limiting cases of a continuum of possibilities. The role of the five-coordinate form may vary from system to system; it could represent a chemical intermediate, the transition state, or a successor complex along the reaction coordinate.

### Conclusions

Flash photolysis studies of Cu(dmp)<sub>2</sub><sup>+</sup> and Cu(bcp)<sub>2</sub><sup>+</sup> have been carried out. Consistent with the proposed charge-transfer character, the excited-state absorption spectra resemble those of the respective ligand radical anions. The method yields a room-temperature lifetime of  $2.0 \pm 0.3$  ns for the CT excited state of Cu(dmp)<sub>2</sub><sup>+</sup> in acetonitrile, and this represents the first direct measure of the lifetime in a donor solvent. In addition, the quenching kinetics of photoexcited Cu(dmp)<sub>2</sub><sup>+</sup> by a series of Lewis bases have been measured in Cu(dmp)<sub>2</sub><sup>+</sup> over a range of temperatures. A kinetic scheme involving an intermediate denoted as \*Cu...Q has been used to rationalize the results. Unfortunately, the rates are such that \*Cu...Q does not accumulate, and it has not been observed directly. The activation parameters reveal that bond making is important to the quenching process, and this is most easily interpreted in terms of exciplex formation. On the other hand, relaxation to the ground state rapidly follows attack of the fifth ligand, and it is not clear that the lifetime is long enough for the species to develop a well-defined geometry and a characteristic solvent environment.

Although exciplexes are often implicated in bimolecular reactions involving the excited states of organic molecules,<sup>36,37</sup> there have been few claims of exciplex formation in the inorganic literature.<sup>38</sup> In many of the examples from the organic literature exciplex formation involves considerable charge transfer between the excited state and the quencher, and the complex is most easily studied in nonpolar media. In polar media exciplexes are usually unstable with respect to dissociation of the ions.<sup>36,37</sup> Most often, the photochemistry of transition-metal complexes is investigated in polar media, and this may be one reason why exciplex formation is seldom observed.<sup>38</sup> In our systems there is minimal charge transfer between the excited state and the quencher as a result of what, at least formally, involves the development of a coordinate covalent bond. Here the excited state surface itself is not dissociative; instead, rapid crossing to a dissociative ground-state surface occurs. The picture which emerges is that while the excited states of coordination compounds experience forces which favor the formation of exciplexes, these species are subject to extremely rapid radiationless decay processes.

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