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EXCIPLEX QUENCHING OF PHOTO-EXCITED COPPER COMPLEXES

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ABSTRACT

Exciplexes are less common in transition metal photochemistry than in organic photochemistry. However, Lewis bases and coordinating anions quench metal-to-ligand charge-transfer excited states of Cu(I) systems, and the quenching is ascribed to exciplex formation. A variety of structural arguments and steric effects lend strong support to the model. These results are related to the broader context of transition metal systems, and future areas of potential interest are briefly discussed.

INTRODUCTION

Cu(I) complexes containing heteroaromatic ligands tend to exhibit low-lying metal-to-ligand charge-transfer (MLCT) excited states. Complexes with chelating ligands such as 2,9-dimethyl-1,10-phenanthroline (dmp), e.g., $Cu(dmp)_2^+$, are relatively stable against dissociation of the heteroaromatic ligand (1) and are the focus of this review. In forming the MLCT excited state a radial redistribution of electron density occurs. Formally, a hole is created at the metal center, and an electron is promoted into a π^* orbital of the heteroaromatic ligand. As a result of the photo-induced charge separation, the reactivity of the copper complex is dramatically changed. Thus, the photo-excited complex is a powerful reductant because the electron in the ligand π^* orbital is relatively weakly bound and is readily released to oxidizing substrates (2-5). Analogous photochemistry has been observed for $Ru(NN)_3^{2+}$ and related systems, where NN denotes a bidentate heteroaromatic ligand (6-8). A further indication of the reducing ability of these kinds of excited states comes from studies involving semiconductor electrode surfaces. When thin films of the copper complexes are deposited at the surface of an n-type semiconductor, the photocurrent action spectrum closely follows the absorption spectrum of the complex (9-11). Detailed analysis shows that the sensitization occurs because the MLCT state can inject an electron into the conduction band of the electrode. Whether in solution or at a semiconductor surface, the quantum efficiency of electron transfer is limited by competing non-radiative decay processes which can be quite rapid.

By virtue of the hole which is created at the metal center, the excited state can also be expected to exhibit oxidizing character. Indeed, electron-transfer quenching by reducing agents is well known in the analogous Ru(II) systems (8). While we have not observed reductive quenching of the photoexcited copper systems, we have observed what can be considered a related process, namely exciplex quenching. Although exciplex interactions are well known in the photochemistry and photophysics of organic systems (12-16), they have rarely been observed in the domain of transition metal complexes. As we shall see, however, exciplex formation is undeniably an important process for the MLCT excited states of Cu(I) systems.

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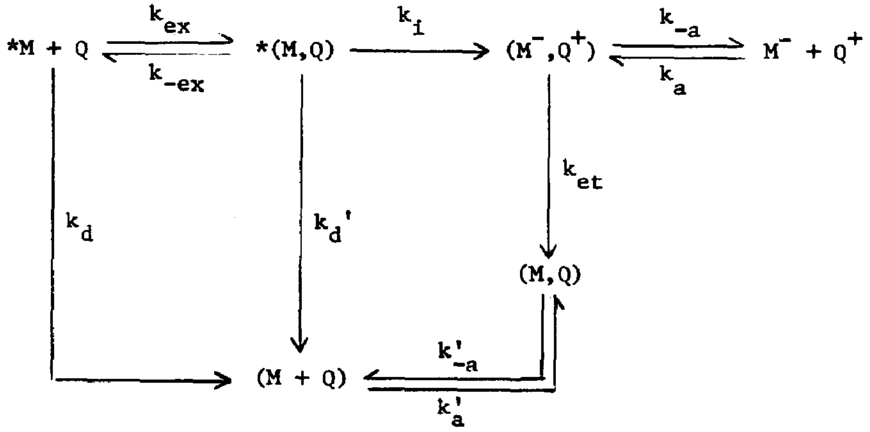
In the simplified Scheme presented below, the exciplex $*(M,Q)$ is a bound state formed between $^*M$, the excited state, and a quencher Q. If the quencher serves as an electron donor and the excited state acts as an electron deficient center, a valence bond description of the exciplex can, as a first approximation, be written:

$$\Psi = a\,\Psi(*MQ) + b\,\Psi(M^-Q^+). \qquad (1)$$

Here $\Psi(*MQ)$ denotes the (no-bond) resonance structure representing the excited state of M in combination with the ground state of Q, and $\Psi(M^-Q^+)$ denotes an ionic resonance structure. Studies of organic systems have shown that exciplex formation may be bypassed in polar media when net electron transfer occurs (16). In less polar media such systems tend to give essentially complete electron transfer (b >> a) within the exciplexes, but, in general, complete electron transfer is not required for the formation of an exciplex (17). In order to make the Scheme comprehensive, the exciplex is depicted as a precursor to (M^-,Q^+), the encounter complex formed between M^- and Q^+. However, in most of the studies described below, electron transfer is far from complete (a >>b).

SCHEME I



The rest of the discussion is organized as follows. First, we summarize a number of observations which led us to propose that donor/acceptor interactions significantly affect the dynamics of MLCT excited states of Cu(I) complexes (18). Then we describe experiments which confirmed the hypothesis, and we present a microphysical model which explains why exciplex quenching is so efficient in these systems. Finally, we will briefly relate this work to the broader discipline of transition metal photochemistry.

THE INFLUENCE OF LEWIS BASES ON EXCITED STATE DYNAMICS

$Cu(NN)_2{}^+$ Systems

Several years ago Wehry and Sundararajan reported that $^*Cu(dmp)_2{}^+$ gives no detectable luminescence in methanol solution at room temperature (19). Likewise, we have been unable to detect emission from $^*Cu(dmp)_2{}^+$ in acetone, acetonitrile or water, and for these media we estimate that the luminescence efficiency is less than one part in 10^5. The quenching is evidently solvent-induced because $^*Cu(dmp)_2{}^+$ is luminescent in the solid state (20). Whatever the nature of the quenching, it is not as effective in a low-temperature, rigid medium. Figure 1 reveals that $^*Cu(dmp)_2{}^+$ is emissive in a 4:1 ethanol/methanol solvent below about 100 K, the glass transition temperature (21).

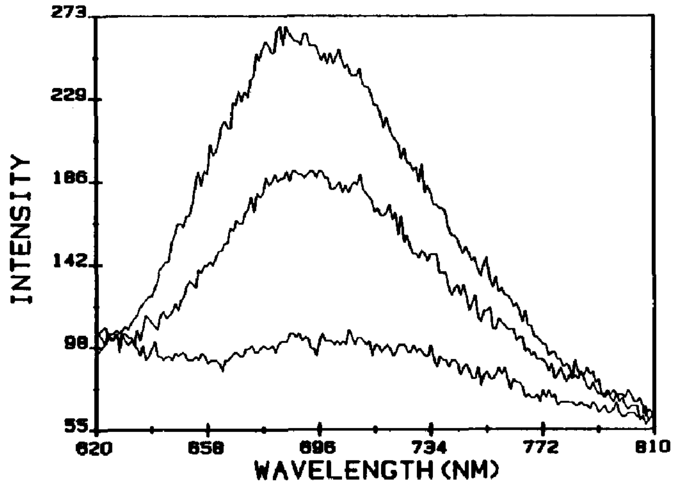


Figure 1. Emission from $^*Cu(dmp)_2{}^+$ in 4:1 ethanol/methanol. In order of decreasing (uncorrected) emission intensity, the sample temperature was 90 K, 100 K, and 110 K.

All of the above are coordinating solvents. In contrast, we have found that $^*Cu(dmp)_2{}^+$ is emissive in weakly basic solvents like chlorocarbons (18). Representative $Cu(NN)_2{}^+$ complexes exhibit submicrosecond lifetimes and luminescence efficiencies of the order of 10^{-4} in deoxygenated CH_2Cl_2 at room temperature (Table 1). Not surprisingly, introducing Lewis bases into the

TABLE 1
Luminescence Results in CH_2Cl_2 at 25°C.

Complex	Φ_{lum}	τ_{exp}, ns
$Cu(dmp)_2{}^+$	3×10^{-4}	90
$Cu(tmbp)_2{}^+$	7×10^{-5}	20
$Cu(dpp)_2{}^+$	1×10^{-3}	250

CH_2Cl_2 solutions has a profound effect on the emission. Figure 2 shows how the emission from $^*Cu(dmp)_2^+$ is quenched by the addition of acetone. Similar results--varying only in degree--are observed if methanol, acetonitrile or pyrazine is added. The quenching is primarily diffusional in nature, and Stern-Volmer analyses indicate the quenching rate constants are of the order of 10^7-10^9 $\underline{M}^{-1}$ s^{-1}.

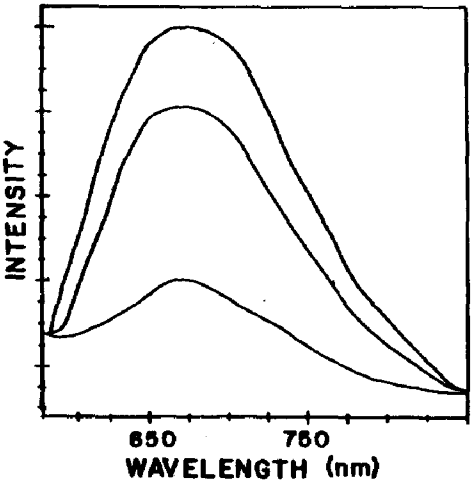


Figure 2. Quenching of $^*Cu(dmp)_2^+$ by acetone. In order of decreasing (uncorrected) emission intensity, the acetone concentration was 0, 0.54 and 2.72 mol dm^{-3}. The solvent was CH_2Cl_2, and the temperature was 20°C.

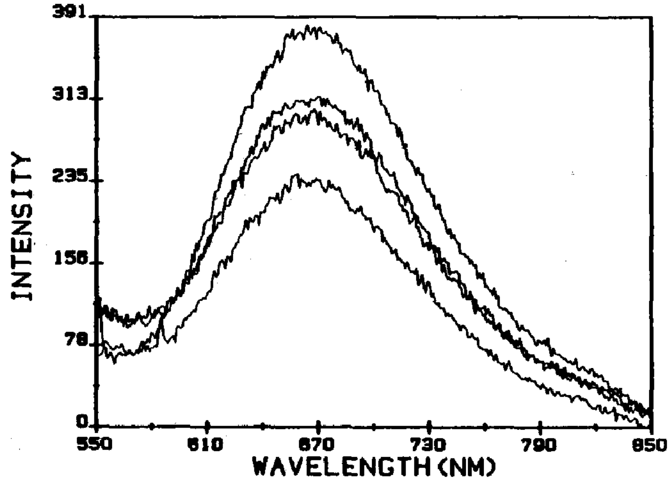


Figure 3. Emission from $^*Cu(dmp)_2^+$ as a function of counterion. In order of decreasing (uncorrected) emission intensity, the anion was $B(Ph)_4^-$, BF_4^-, ClO_4^- and NO_3^-. The solvent was CH_2Cl_2, the temperature was 25°C, and the absorbance was constant from sample to sample.

Coordinating anions also quench the emission. In Figure 3 the emission intensity from a $Cu(dmp)_2^+$ solution is depicted as a function of counterion (22). Within experimental error, the lifetime is the same for all solutions, indicating a static quenching mechanism is operative. If excess $[(\underline{n}\text{-}Bu)_4N]^+BPh_4^-$ is added to the NO_3^- solution, the emission intensity approaches that of the $[Cu(dmp)_2]^+BPh_4^-$ solution. We infer that coordinating anions quench the emission, but that unless relatively large anion concentrations are present, the quenching is restricted to those copper centers which are ion-paired in the ground state.

Mixed-Ligand Complexes

In the results described above the efficacy of quenching depended on the nucleophile used. With complexes of the type $Cu(PPh_3)_2(NN)^+$ we have observed that the efficiency of solvent-induced quenching is strongly dependent on the makeup of the copper complex as well. For the mixed-ligand complexes where NN is dmp or 1,10-phenanthroline (phen), the MLCT absorption maxima occur at almost identical wavelengths (23). Moreover, in the solid state the complexes emit at similar wavelengths and exhibit similar decay times over a range of temperatures (24). Thus, the intrinsic electronic properties of $Cu(PPh_3)_2(dmp)^+$ and $Cu(PPh_3)_2(phen)^+$ are practically indistinguishable. However, the photophysical properties of the complexes are very different in coordinating solvents (25). While the dmp complex exhibits relatively strong emission in methanol or acetonitrile at room temperature, almost no emission can be observed from the phen complex in either solvent. The implication is that the methyl substituents of the dmp group mitigate the solvent-induced quenching, presumably by steric means. This raises the question of what are the structural requirements for the quenching of the MLCT excited states by Lewis bases.

STRUCTURE CONSIDERATIONS

In the MLCT excited state the copper center is formally regarded as Cu(II); although, immediately after excitation, the coordination geometry must be that of the ground state Cu(I) system. As the nuclear framework responds to the electronic organization of the excited state, we would expect the geometry to evolve toward a structure more characteristic of Cu(II). Cu(I) is a d^{10} ion, well-suited for sp^3 hybridization, and commonly forms a pseudotetrahedral complexes. Cu(II), on the other hand, has a half-vacant d orbital and an extra unit of positive charge. As a result, Cu(II) tends to bind more ligands, and a coordination number of 5 or 6 is more typical.

In recent years a number of structural comparisons have been made between Cu(II) and Cu(I) complexes involving common ligands systems, and they illustrate distinct stereochemistries. In three different studies based upon sulfur ligands, Cu(I) favored an S_4 donor environment, while the Cu(II) form exhibited a coordination number of 5 or 6, either by taking up another available neutral donor or by binding to the counterion (26-28). In systems closely related to the present discussion, we have found that $Cu(tmbp)_2^+$ exhibits an N_4 donor set in the solid state whereas the Cu(II) analogue is five-coordinate even if the weak donor ClO_4^- is the only available ligand (29). (tmbp is 4,4',6,6'-tetramethyl-2,2'-bipyridine) Similar results have been observed with the dmp ligand (30).

Because PPh_3 readily reduces Cu(II), only the Cu(I) forms of the mixed ligand $Cu(PPh_3)_2(NN)^+$ systems have been characterized. In $Cu(PPh_3)_2(dmp)^+$ there is considerable crowding in the coordination shell about copper, and steric interactions between the methyl substituents of dmp and the aryl moieties of the PPh_3 groups demonstrably influence the structure and the reactivity. Compared with the phen analogue, the dmp complex exhibits longer metal-to-ligand bonds, and it is more prone to dissociate PPh_3 ligand(s) (25). Because of the crowding among ligands in $Cu(PPh_3)_2(dmp)^+$, the association of a fifth donor is expected to be more feasible in the case of the phen derivative. This would explain why the emission from the phen complex is quenched by donor solvents.

So far we have made the case that coordinating solvents and coordinating anions tend to quench the emission from MLCT excited states of Cu(I) complexes, provided there is room for expansion of the coordination sphere. And we have seen that Cu(II) tends to prefer a higher coordination number than Cu(I). These observations argue that Lewis bases quench the MLCT excited state, which formally involves a Cu(II) center, by way of an associative reaction. In the next section we show how a systematic investigation of steric effects lends further support for this hypothesis.

STERIC EFFECTS

Bulky substituents can severely perturb the ability of a Lewis base--or a Lewis acid--to undergo adduct formation. If the electronic structure, redox potential, etc. are unchanged by the introduction of the substituents, we can test the hypothesis that exciplex formation is involved in the deactivation process by comparing the quenching behavior of hindered and unhindered reagents. Pyridine derivatives are useful in this regard, except that they react with chlorocarbons, inducing the release of chloride ions (31). This effect is minimized by using 1,2-dichloroethane as the solvent and by employing freshly prepared solutions of the pyridines.

Pyridine is an excellent quencher of $^*Cu(dmp)_2^+$. A Stern-Volmer analysis of the quenching of emission intensity as a function of pyridine concentration yields a second-order rate constant of 1×10^9 $\underline{M}^{-1}$ s^{-1}. 2,6-dimethylpyridine exhibits a higher pK_a than pyridine (6.8 vs 5.2), consistent with the presence of the electron-donating methyl groups. However, 2,6-dimethylpyridine is a very poor ligand for metal ions because of steric repulsive interactions based on these same methyl substituents. Significantly, 2,6-dimethylpyridine does not quench $^*Cu(dmp)_2^+$, and we estimate that the quenching constant is much less than 10^6 $\underline{M}^{-1}$ s^{-1} (32). Introducing bulky groups onto the ligands about the copper center should also interfere with adduct formation. In line with this reasoning, even pyridine does not quench $^*Cu(dpp)_2^+$. Moreover, in a series of $Cu(PPh_3)_2(bpy)^+$ derivatives (bpy denotes 2,2'-bipyridine), we have found that the emission intensity is sharply increased when methylated bpy derivatives are used, but only when the methyl groups are adjacent to the donor nitrogens (33). The methyl substituents are required to be in those positions if they are to inhibit the expansion of the coordination number of the metal center. In view of the steric effects that have been described, the evidence for associative quenching of the MLCT excited states of Cu(I) complexes is compelling. What remains to be developed is an understanding of the microphysical basis of the quenching.

MICROPHYSICS OF EXCIPLEX FORMATION

Within the context of the Born-Oppenheimer approximation, we can analyze exciplex quenching in terms of the potential energy surfaces presented in Figure 4. The diagram is deceptively simple in appearance since the reaction coordinate specifies the concerted motion of various nuclei. On a trajectory from right to left along this coordinate, the separation between the copper complex and the quencher (Lewis base) decreases, and the structure of each component, especially the copper complex, reorganizes in response to the approach of the other. Implicitly, changes in solvation also occur. Consider first the case where the copper complex is in the excited state. When the quencher is close enough for the donor orbital of the quencher to overlap an unfilled orbital of the excited-state complex, the charge-transfer interaction described earlier lowers the total energy. This effect becomes more pronounced as the separation decreases and the overlap increases. At shorter distances other forces, e.g., core and/or interligand repulsions, take over, and the potential energy begins to rise steeply. In contrast, a purely dissociative surface is depicted for the case when the copper complex is in its ground electronic state, since the stable form of the Cu(I) system is 4-coordinate. In other words, the repulsive interactions are expected to dominate when the quencher approaches the copper(I) center.

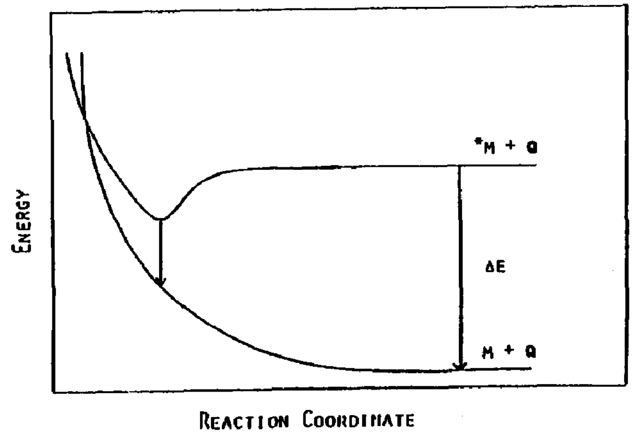


Figure 4. Potential energy surfaces illustrating exciplex formation. The emission energy of (uncomplexed) $^*Cu(dmp)_2^+$ is represented by ΔE. The minimum in the excited state surface corresponds to the exciplex.

With the aid of Figure 4 we can appreciate the fact that non-radiative decay is apt to be more facile in the exciplex. To see this, note that ΔE, the energy gap which must be spanned in order for the excited-state copper complex to decay to its ground state, is much narrower where the exciplex has formed. The reasons are two-fold: (1) the excited state is stabilized by virtue of the charge-transfer interaction; and (2) the ground state is destabilized by repulsive interactions. Accordingly, the Franck-Condon factors associated with level crossing to the ground state are likely to be more favorable in the exciplex. In other words, it is a consequence of the well-known energy gap law of photophysics. A similar explanation has recently been invoked by Mataga and co-workers in order to explain the short-lived nature of exciplexes formed from photoexcited porphyrins in combination with quinone acceptors (34,35).

The luminescence quenching studies are not necessarily indicative of the exciplex lifetime. In one limit the luminescence quenching would simply reflect the rate of exciplex formation. This is likely to be the case if there is a barrier to exciplex formation and the radiationless decay of the exciplex is rapid with respect to dissociation back to the excited state. In the simple picture, assumed in Figure 4, there is no barrier to exciplex formation, but various processes, such as a desolvation step or a structural reorganization step involving the copper complex, could introduce an activation requirement. Flash photolysis studies with picosecond time resolution have established that the upper limit for the exciplex lifetime for $Cu(dmp)_2^+$ in acetonitrile is 2 ns (36).

Before concluding this section, it is worth noting that the emission we observe from $^*Cu(dmp)_2^+$ in CH_2Cl_2 could actually be emission from a weakly bound exciplex wherein the solvent serves as the Lewis base. In accord with this possibility, Gray and co-workers have pointed out that alkylhalides can serve as donors toward coordinatively unsaturated metal centers (37). A solvent interaction of this type could be one reason why the lifetime of $*Cu(dmp)_2^+$ is shorter than the lifetime of the more hindered dpp system.

VISTA

By comparison with organic photochemistry, exciplex interactions have gone almost unrecognized in the field of transition metal photochemistry. In part this can be traced to differences in the ease with which potential quenchers can interact with the frontier orbitals of the excited states involved. In the case of organic systems the frontier orbitals are often π electron systems which are readily contacted by neighboring molecules. Comparatively weak interactions are expected in transition metal systems, especially when the metal center is coordinatively saturated. This is because the ligands present in the coordination sphere of the metal tend to shield the d orbitals and therefore reduce the possibility of orbital overlap involving near neighbors. Of course, complexes containing aromatic ligands may be susceptible to exciplex interactions typical of organic chromophores, but this requires that the ligand orbitals participate in the electronic reorganization involved in the formation of the excited state (38,39).

Another point is that it is often not necessary, nor perhaps even useful, to invoke this formalism in the study of outer-sphere electron transfer phenomena. However, as discussed above, in cases where only partial charge transfer occurs, the concept of an exciplex is clearly a pertinent one. For the MLCT states of the Cu(I) systems, the exciplex can be visualized in terms of the formation of a coordinate covalent bond from a Lewis base to copper. Such interactions are not limited to Cu(I) systems, but they will likely be restricted to complexes which can readily undergo an expansion of the coordination number. Analogous adducts appear to form upon the excitation of various 4-coordinate Ni(II) systems in donor media (40,41). Other examples may involve certain Cu(II) porphyrins (42). There is one report of exciplex formation involving a 6-coordinate Re(I) system (43). A somewhat different kind of exciplex formation has recently been proposed in a solid state system containing Cu(I) as a dopant (44).

Thus far, the emphasis has been on how exciplex interactions influence excited-state decay. Future work is expected to reveal what roles exciplexes play in shaping the reactivity of photoexcited transition metal systems. In this regard potentially fruitful areas of research include: (1) studies of ligand substitution reactions, in particular, those involving associative mechanisms, (2) studies of energy transfer reactions and (3) investigations of atom transfer reactions.

ACKNOWLEDGMENT

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