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Anion-Induced Quenching of $^*Cu(dmp)_2^+$

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As the counterion is varied, the emission quantum yield of $^*Cu(dmp)_2^+$ (dmp is 2,9-dimethyl-1,10-phenanthroline) varies by as much as 30% in fluid CH_2Cl_2 while the lifetime is unchanged. These results are explained in terms of a static quenching mechanism that occurs within ion pairs present in solution. Anions do not quench the emission of the corresponding complex of 2,9-diphenyl-1,10-phenanthroline, and BPh_4^- does not quench the emission of $^*Cu(dmp)_2^+$, even though significant ion pairing occurs. On the basis of these observations and related studies involving Lewis bases, the quenching is associated with inner-sphere coordination of the anion to copper in the excited state.

Introduction

Charge separation is a key process in a variety of currently interesting energy conversion schemes.[1,2] Thus, photoelectrochemical cells may be devised such that oxidative events take place at a photoanode while a reductive half-reaction takes place at the cathode somewhere else in the cell. Probably the simplest imaginable charge separation process occurs at the molecular level in the formation of a charge-transfer excited state. In the $Cu(NN)_2^+$ systems of interest here, where NN denotes a derivative of 1,10-phenanthroline, absorption of visible light populates a metal-to-ligand charge-transfer (CT) excited state in which the metal center is formally oxidized to Cu(II) and a ligand is reduced to the radical-anion form.[3,4]

One of the intriguing aspects of CT excited states is the possibility of probing distinct reaction centers (charge centers) by judicious choice of reagents. In previous studies we have shown that a variety of oxidizing agents can quench the CT excited state by an electron-transfer mechanism,[5-7] presumably via contact with the π^* orbitals of the (reduced) ligand. More recently, we have shown that various Lewis bases quench the excited states by an associative reaction involving the (oxidized) copper center.[8] Here we show that a variety of coordinating anions are able to quench the CT states of $Cu(NN)_2^+$ systems by the associative mechanism and that in dilute solution the quenching efficiencies depend on ion-pairing equilibria. As a consequence, the emission yields in fluid solution are sensitive to the nature of the counterion as well as the solvent.

Experimental Section

Materials. The dmp ligand (2,9-dimethyl-1,10-phenanthroline) was purchased from G.F. Smith Chemical Co., while dpp (2,9-diphenyl-1,10-phenanthroline) was synthesized by a literature method.[9] Compounds containing $Cu(dmp)_2^+$ and $Cu(dpp)_2^+$ with different anions were prepared by variations on a previously reported procedure.[10] All compounds gave satisfactory analyses. Methylene chloride (distilled-in-glass grade) was purchased from Burdick & Jackson and used without further purification. The $[Ru(2,2'\text{-bipyridine})_3]Cl_2$ standard was purchased from G. F. Smith Chemical Co. as were $[(n\text{-Bu})_4N]ClO_4$ and $[(n\text{-Bu})_4N]BF_4$. Sodium tetraphenylborate was purchased from Aldrich, and the $(n\text{-Bu})_4N^+$ salt was obtained by a literature method.[11]

Table I. Emission Data and Ion-Pairing Efficiencies for $Cu(dmp)_2^+$ Systems

anion	$10^4\Phi$	τ, ns	% Q[a]	% IP[b]
BPh_4^-	3.2	92		34
BF_4^-	2.6	90	18	45
ClO_4^-	2.5	94	23	46
NO_3^-	2.2	92	30	36

[a] Quenching efficiency where BPh_4^- is assumed to be a nonquencher. [b] Ion-pairing efficiency at 50 μM.

Table II. Conductance Results[a] and Ion-Pairing Parameters for $Cu(dmp)_2^+$ Systems

anion	Λ_0, Ω^{-1} cm^2 mol^{-1}	$10^{-4}K_A$,[b] M^{-1}	r,[c] Å
BPh_4^-	94	2.0	5.8
BF_4^-	127	4.1	5.3
ClO_4^-	118	4.3	5.3
NO_3^-	158	2.4	5.7

[a] Concentration range 0.025–0.625 mM. [b] For method of calculations see Experimental Section. [c] Calculated from the K_A values and eq 2.

Instrumentation. Absorbance measurements were made on either a McPherson EU-700-D or a Cary 17D spectrophotometer. Steady-state fluorescence measurements were performed on a Perkin-Elmer MPF 44B fluorometer interfaced to an Apple IIE microcomputer. Lifetime measurements were performed on a system previously described.[7] Conductance measurements were made with a McKee-Pedersen Instruments 1010 Wheatstone bridge, a Knight KG-635 DC oscilloscope, and a Washburn conductivity cell that had a cell constant of 0.21 cm^{-1}.

Methods and Calculations. Emission quantum yields were determined by the method of Parker and Rees.[12] All measurements were made on samples that had been deoxygenated by repeated freeze-pump-thaw cycles, and a value of 0.042 was used for the emission quantum yield of the ruthenium bipyridine standard at 25 °C in water.[13]

The constant for the ion-pairing equilibrium is defined in eq 1, where $Cu(dmp)_2|X^-$ denotes the ion pair. Since submillimolar concentrations

$$Cu(dmp)_2^+ + X^- \xrightleftharpoons{K_A} Cu(dmp)_2^+|X^- \qquad (1)$$

of ions were present, we assumed that the ionic conductance satisfied the limiting equation proposed by Onsager.[14] The equilibrium constant K_A and the limiting conductance were estimated by the method of Fuoss and Kraus,[15,16] wherein the mean ionic activity coefficient is calculated from Debye-Huckel theory.

Results

In methylene chloride solution at room temperature the intensity of the emission spectrum of $Cu(dmp)_2^+$ has been found to vary with the counterion while the emission intensity from $Cu(dpp)_2^+$ is constant for the same series. Figure 1 shows how the emission of the dmp complex depends on the anion. Each sample had the same absorbance at the excitation wavelength and each spectrum was run at the same instrumental sensitivity. Emission yields are

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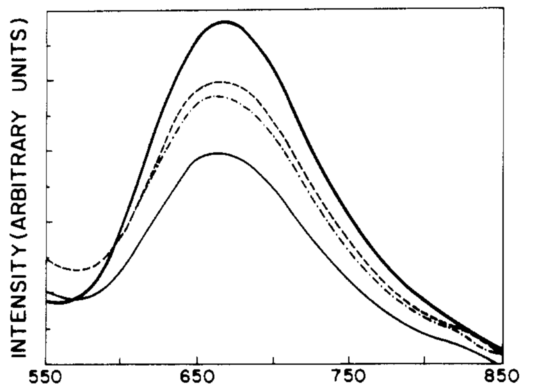

Figure 1. Uncorrected emission spectra of 50 μM $[Cu(dmp)_2]X$ in CH_2Cl_2 at 20 °C: $X^- = BPh_4^-$ (—, thick trace); $X^- = BF_4^-$ (- - -); $X^- = ClO_4^-$ (–·–); $X^- = NO_3^-$ (—, thin trace).

compiled in Table I. As can be seen from Figure 1 or Table I, the emission was most intense when the anion was BPh_4^-. The anion dependence of the emission was also evident from studies of solutions containing added electrolyte. For example, as increasing amounts of $[N(n\text{-}Bu)_4]BPh_4$ were added to a solution containing $[Cu(dmp)_2]BF_4$, the emission intensity increased toward that of a solution of $[Cu(dmp)_2]BPh_4$. On the other hand, the addition of $[N(n\text{-}Bu)_4]NO_3$ to a solution containing $[Cu(dmp)_2]BPh_4$ led to partial quenching of emission. Finally, the addition of any of the anions except BPh_4^- to a solution of $[Cu(dmp)_2]BPh_4$ led to quenching of the emission intensity and, when enough electrolyte was added, the emission lifetime as well.

Although the luminescence yield of solutions containing $Cu(dmp)_2^+$ varied with the anion, the emission lifetime was constant within experimental error (Table I). This indicates that, at least for low anion concentrations, the quenching occurs by a static, i.e., a nondiffusional, mechanism.[17] Since ion-pairing was considered likely, we carried out conductance measurements in order to characterize the equilibria. The conductivity data are summarized in Table II. On the basis of the estimated K_A values, 30–50% of the $Cu(dmp)_2^+$ in solution is ion-paired at the concentration levels used in the luminescence studies (Table I). For a given anion the percentage of ion pairs present sets an *upper limit* on the fraction of excited states that are subject to static quenching.

Discussion

Ion-Pairing Equilibria. The magnitudes of the experimentally determined K_A values in Table II accord with values that have been reported in the literature for comparable systems.[18] The center-to-center distance r between the cation and the anion can be estimated from the K_A value via the Bjerrum–Fuoss equation:[19]

$$K_A = \frac{4\pi N r^3}{3000} \exp\left(\frac{e^2}{4\pi\epsilon k T r}\right) \qquad (2)$$

where N is Avogadro's number, e is the charge on the electron, ϵ is the permittivity of the medium, k is Boltzmann's constant, and T is the temperature. The distances calculated with this expression are listed in Table II. A nominal hard-sphere radius of 6.7 Å can be estimated for $Cu(dmp)_2^+$ from crystal structure data,[20] and radii for the various anions have previously been tabulated.[21] For contact pairs involving NO_3^-, ClO_4^-, and BF_4^- the summed hard-sphere radii range from 8.6 to 8.9 Å—all distances appreciably larger than the estimates based on eq 2. For the case of BPh_4^- the sum of the radii is 11.5 Å. The deviations between the distances calculated by the two methods may be explained by deficiencies in the Fuoss–Bjerrum equation and/or penetration of the anions into pockets between the dmp ligands of the cation. In the case of BPh_4^- interpenetration might be expected in order to permit stacking between aromatic moieties. Stacking interactions are believed to be important in the solid-state packing of the copper complexes themselves, even though the ions involved have the same charge.[22]

The Ion Pair as a Precursor to Quenching. As noted above, quenching occurs when $Cu(dmp)_2^+$ and X^- coexist in a precusor complex at the moment of excitation, as diffusional quenching is inefficient when the total anion concentration is only 50×10^{-6} M. Even with a diffusion-controlled second-order rate constant, $k_d \simeq 10^{10}$ M^{-1} s^{-1}, the maximum possible value for the pseudo-first-order quenching constant would be 5×10^5 s^{-1}. Since the intrinsic decay rate of the excited state is around 10^7 s^{-1}, a dynamic process could account for at best about a 5% quenching of the emission yield. It follows that the observed quenching is almost entirely due to the static mechanism.

Of all the anions studied, BPh_4^- is clearly the weakest quencher, in keeping with the fact that it is a weak Lewis base; vide infra. If we assume that this ion is effectively a nonquencher, quenching efficiencies can be calculated from the other anions (Table I). Under this assumption, the fraction of copper complexes that suffers emission quenching is always less than the fraction that is ion-paired. This trend might be explained by the presence of solvent-separated as well as contact ion pairs in solution if quenching occurs only within contact pairs. The alternative explanation is that the quenching process is inherently inefficient. In this view the existence of the ion pair is a necessary but not sufficient condition for quenching.[23] The latter hypothesis finds some support in recent studies of a related quenching phenomenon involving a series of Lewis bases where we have found that the entropy of activation for quenching is of the order of −100 J deg^{-1} mol^{-1}.[24]

Intimate Mechanism. Anion-induced luminescence quenching has previously been observed in organic[25] and inorganic systems.[26,27] In particular, Balzani and co-workers have shown that heteropolymetalate ions can engage in static quenching of Ru(II) systems by an electron-transfer mechanism.[26] However, electron-transfer quenching seems totally implausible for ions like BF_4^- and ClO_4^-, which have been used in this work. Meyer and co-workers have identified a second mechanism of anion-induced quenching of inorganic excited states.[27] They proposed that formation of the outer-sphere complex (ion pair) preferentially stabilized the excited state in comparison with the ground state, facilitating radiationless decay in accord with the energy gap law. This mechanism can also be rejected for the present systems because the $Cu(dpp)_2^+$ system undoubtedly forms ion pairs, and its emission is not quenched.

By analogy with previous work on $Cu(NN)_2^+$ systems,[8] it seems likely that the anions quench the excited state via a pathway involving *inner-sphere* complex formation. In line with this idea, X-ray structural studies have shown that $Cu(NN)_2^{2+}$ systems tend to bind even weakly basic anions such as ClO_4^- in order to become five-coordinate.[28,29] Since the metal center is formally Cu(II) in the excited state, an associative reaction with the anion is quite feasible. The absence of quenching in the case of $Cu(dpp)_2^+$ is

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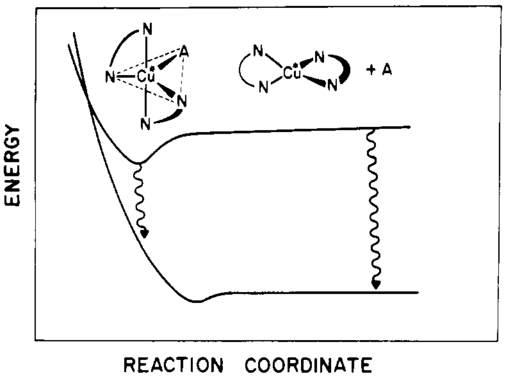

Figure 2. Schematic reaction coordinate for the approach of the anionic quencher A toward $Cu(dmp)_2^+$. (Charges are omitted for clarity.) The lower curve represents the ground state, where a shallow minimum occurs due to outer-sphere complex formation. The upper curve represents the CT excited state, in which the anion moves in close enough to form an inner-sphere complex. The wiggly arrows indicate the relative energies associated with the nonradiative decay process at two locations along the reaction coordinate.

explained because the bulky phenyl substituents interfere with formation of the five-coordinate adduct.[30]

The reaction coordinate diagram in Figure 2 indicates why association of a fifth donor can result in quenching of the excited state. From left to right, the reaction coordinate is constructed such that the center-to-center distance between the copper and the anion increases. Also implicit in the coordinate is the internal reorganization that occurs in the individual ions as they begin to interact with each other, as well as changes in solvation. The lower curve in Figure 2 depicts the energy of reaction between the anion and $Cu(dmp)_2^+$ in the ground state. The upper curve depicts the same reaction, except the copper complex is assumed to be in its CT excited state. Since the ground-state complex is an 18-electron system, only a weak outer-sphere interaction is expected at a relatively long copper-to-anion separation. On the other hand, the metal center is electron-deficient in the CT excited state, and any anion that can act as a Lewis base is liable to form an inner-sphere complex with copper. In accord with the ground-state structures of corresponding Cu(II) systems, the adduct is expected to have a trigonal-bipyramidal structure with the anion coordinated in an equatorial position. A deeper potential "well" is therefore associated with the excited-state system. This, plus the possibility that the corresponding interaction may be repulsive in the ground state, implies that the energy gap between the ground and excited states will be significantly narrowed as a consequence of binding the anion. In turn, the radiationless decay rate should be enhanced and excited states quenching should be observed.

Conclusions

The CT excited state of $Cu(dmp)_2^+$ is subject to static quenching by coordinating anions in fluid CH_2Cl_2. The anion-induced quenching can be explained in terms of excited state complex formation; however, the inner-sphere adducts are short-lived and have not been directly observed. Whether the associated species may be classified as bona fide intermediates along the quenching pathway or whether they are better classified as some type of transition-state species has yet to be established.

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S–S Photohomolysis at Dimolybdenum(V) RSS^- and S_2^{2-} Bridges

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Dimolybdenum(V) complexes of the general form $[Mo_2(NC_6H_4CH_3)_2(S_2P(OC_2H_5)_2)_2S(O_2CCH_3)(SSR)]$ (R = alkyl or aryl), which contain the SMo_2SSR fragment with RSS^- bridging by its β-sulfur, and those of the form $[Mo_2(NAr)_2(S_2P(OC_2H_5)_2)_2S(O_2CR')]_2S_2$ (Ar = $p\text{-}C_6H_4CH_3$, C_6H_5; R′ = CH_3, $n\text{-}C_7H_{15}$), which contain the SMo_2SSMo_2S unit with an interdimer S_2^{2-} bridge, photolyze under fluorescent lighting to give products characteristic of S–S homolysis. Dimer radicals representable by $[SMo_2S]^\bullet$ were indicated but not directly observed. For R = aryl, SMo_2SSR quickly photolyzes and subsequently equilibrates with SMo_2SSMo_2S and RSSR; for R = alkyl, the photolysis is extremely slow. A mixture of SMo_2SSMo_2S compounds differing in their imido group and/or their carboxylate group also photoequilibrate to give scrambled disulfide products. Reactions of SMo_2SSMo_2S with $C_6H_5CH_2SH$, $(C_6H_5)_3P$, or $(C_2H_5O)_3P$ were also photolytic.

Introduction

Sulfide–disulfide–polysulfide ligand chemistry has drawn much attention of late for transition-metal chemistry in general and for molybdenum chemistry in particular.[1-3] Recent molybdenum studies amply demonstrate the chalcogen interconversions, frequently accompanied by formal metal redox processes involving Mo(VI), Mo(V), and Mo(IV).[4-10] Major interest in sulfido-molybdenum areas draws from interest in biomolybdenum enzymes[11-13] and industrial hydrodesulfurization,[14-16] both of which are believed to involve Mo–S sites.

Disulfide complexes of the general forms $[Mo_2(NTo)_2(S_2P(OEt)_2)_2S(O_2CMe)(SSR)]$ (**1**) and $[Mo_2(NAr)_2(S_2P(OEt)_2)_2S\text{-}$

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