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Contribution from the Department of Chemistry and Quantum Institute, University of California,
Santa Barbara, California 93106, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Pressure Effects on Copper(I) Complex Excited-State Dynamics. Evidence Supporting an Associative Nonradiative Deactivation Mechanism

Daniel R. Crane,[1] John DiBenedetto,*[1] Cynthia E. A. Palmer,[2] David R. McMillin,*[2]
and Peter C. Ford*[1]

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The effects of hydrostatic pressure on the metal to ligand charge-transfer (MLCT) excited-state emission lifetimes for the copper(I) complexes $Cu(dmp)_2^+$ and $Cu(dpp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline, dpp = 2,9-diphenyl-1,10-phenanthroline) have been determined in CH_2Cl_2 solution. In the absence of added quenchers, volumes of activation ΔV_n^* for the nonradiative decay pathway have been determined to be −3.4 and −1.6 cm^3/mol, respectively. For the previously reported quenching of $[Cu(dmp)_2^+]^*$ by the cosolvents CH_3CN and CH_3OH, ΔV_q^* values of −6.2 and −5.4 cm^3/mol were measured. These data are consistent with the proposal that an associative mechanism plays a role in the nonradiative deactivation of the MLCT excited state of the less sterically crowded $(dmp)_2$ complex.

Introduction

Investigations of the effects of hydrostatic pressure (*P*) on metal complex excited-state (ES) dynamics have provided valuable insight into the mechanisms of relevant ES mechanisms.[3-5] One major advantage is that *P* can be varied continuously over large ranges, thus providing a systematic perturbation of the medium. The present study focuses on the ES dynamics of the copper(I) complexes $Cu(dmp)_2^+$ (A) and $Cu(dpp)_2^+$ (B) (dmp = 2,9-dimethyl-1,10-phenanthroline, dpp = 2,9-diphenyl-1,10-phenanthroline), each of which displays ambient-temperature luminescence from lowest energy, triplet metal to ligand charge-transfer (MLCT) states in fluid CH_2Cl_2 solutions.[6,7] Subsequent studies have revealed that the MLCT emission from $Cu(dmp)_2^+$ solution but not that from $Cu(dpp)_2^+$ solution is quenched by the presence of various Lewis bases including the donor solvents CH_3CN and CH_3OH.[8,9] The mechanism proposed for this process involves an association between the MLCT ES of the former ion and one of these donors to form a nonemissive five-coordinate ES intermediate that decays more rapidly than the original MLCT state. The present investigation was initiated on the anticipation that such a pathway should display a significant dependence on the hydrostatic pressure.

Experimental Section

Materials. The complex salts $[Cu(dmp)_2]BPh_4$ and $[Cu(dpp)_2]BPh_4$ were prepared according to published procedures.[6,7,9] The solvent CH_2Cl_2 (Fisher ACS grade) was washed with concentrated H_2SO_4, dried over $CaCl_2$, and then distilled from $LiAlH_4$ or passed through a column of activated alumina. Acetonitrile (Burdick and Jackson High Purity grade) and methanol (Fisher ACS Spectroanalyzed grade) were used without further purification.

Sample Preparation for High-Pressure Luminescence Experiments. Methylene chloride solutions of the copper(I) salts were prepared at 20–50 μM concentrations for experiments in the absence of quenchers and at 40–90 μM for experiments in the presence of the added quencher acetonitrile or methanol. The solutions were degassed by bubbling with dinitrogen in a glovebox filled with N_2. Exact solution concentrations were determined after preparation and degassing by measuring the absorption spectrum on a Cary 118 spectrophotometer (A, ϵ_{454nm} = 7950 M^{-1} cm^{-}1; B, ϵ_{440nm} = 3230 M^{-1} cm^{-1}). Degassed acetonitrile or methanol was then added quantitatively via syringe in the glovebox. The resulting solution (about 1 mL) was loaded into a small glass capsule (25 mm in length, 8 mm in diameter) that was subsequently capped with a Teflon piston with two Viton O-rings. (The capsule/piston combination was designed to transmit the applied pressure without exchanging solution with the surrounding medium.) The capsule was placed into a modified Nova-Swiss four-window, 400-MPa (4-kbar) high-pressure spectroscopic cell. The high-pressure cell was then filled with degassed pressure-transmitting fluid (pure CH_2Cl_2 or CH_2Cl_2 with the appropriate concentration of quencher) and sealed.

Apparatus for Lifetime Measurements under Pressure. The high-pressure cell loaded as described was attached to an Enerpac hand pump and gauge, which were used to generate and measure the applied pressures.[3] The apparatus used for lifetime measurements was based on a Quanta Ray DCR-1A Nd/YAG pulse laser with harmonic generator operating at 532 nm as the excitation source. The emission was monitored at right angles at 670 nm with an RCA 8892 or EMI 9816A PMT through a Spex single or double monochromator. The signal from the PMT was processed by a Tektronix 7912 AD transient digitizer and a Tektronix 4052 microcomputer.[3]

Experimental Procedures for Lifetime Measurements. All experiments were carried out at room temperature (23 ± 1 °C). For a particular pressure run, three to six luminescence lifetime measurements were performed at each pressure. A period of approximately 10 min was allowed for equilibration subsequent to changing pressure in the cell. Lifetime measurements were generally made over the following approximate pressure sequence in order to check for any hysteresis (there was none in the reported data): (1) ambient pressure, (2) 100 MPa, (3) 200 MPa, (4) 300 MPa, (5) 200 MPa, (6) 250 MPa, (7) 100 MPa, (8) 150 MPa, (9) 100 MPa, (10) 50 MPa, (11) ambient pressure.

Results and Discussion

The copper(I) complexes $Cu(dmp)_2^+$ (A) and $Cu(dpp)_2^+$ (B) in ambient-temperature dichloromethane solutions display emission spectra that have been assigned as luminescence from d–π* MLCT states, the lowest ES being largely triplet in character.[6,7,9,10] While there is some evidence, based on temperature-dependent luminescence spectra,[6b] supporting contribution to the emission from a higher energy singlet MLCT state, the independence of the measured emission lifetime (τ) over the same temperature regime indicates that τ is determined by decay processes from the triplet. Steric effects on ES lifetimes are significant, with B having a substantially longer emission lifetime than A. Furthermore, the 2,9-dimethylphenanthroline complex A has been shown to be subject to a second-order quenching by Lewis bases, while B, with the more sterically demanding 2,9-diphenylphenanthroline ligand,

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(1) University of California.

(2) Purdue University.

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Table I. Photophysical Data for the Complexes $Cu(dmp)_2^+$ and $Cu(dpp)_2^+$ in CH_2Cl_2 Solution[a]

	$Cu(dmp)_2^+$	$Cu(dpp)_2^+$
	No Added Quencher	
τ(0.1 MPa)[b]	90	258
τ(150 MPa)	70	231
τ(300 MPa)	58	211
$\Delta V_n^\ddagger$[c]	−3.4 ± 0.2 (4)	−1.6 ± 0.2 (5)
	0.30 M CH_3CN	
τ(0.1 MPa)	63	260
τ(91 MPa)	50	246
τ(264 MPa)	39	227
$\Delta V_n^\ddagger$(app)	−4.3 ± 0.2 (2)	−1.2 ± 0.2 (2)
	0.30 M CH_3OH	
τ(0.1 MPa)	66	NA
τ(105 MPa)	52	
τ(264 MPa)	42	
$\Delta V_n^\ddagger$(app)	−4.0 ± 0.2 (2)	

[a] BPh_4^-; $T = 23 \pm 1$ °C. [b] τ values in ns. [c] $\Delta V_n^\ddagger$ values in cm^3/mol; number of independent pressures is in parentheses.

is not similarly quenched.[8,9] It has been proposed that the quenching mechanism involves association of the Lewis base Q with the formally d^9 "Cu(II)" metal center of the MLCT state to form a short-lived, pentacoordinate excited-state complex that decays rapidly by an independent nonradiative pathway (Scheme I).[8] Notably, any MLCT transition should enhance a metal center's reactivity toward nucleophiles;[11] however, this tendency should be accentuated for Cu(I), given that Cu(II) generally has a higher coordination number. An associative character of a contributing pathway to the nonradiative decay of Cu(I) MLCT states would also be consistent with $^3A^*$ having a shorter lifetime (90 ns) than $^3B^*$ (260 ns) in CH_2Cl_2, the nonemissive character of the parent complex $Cu(phen)_2^+$,[10] and the observation of MLCT emission from several other Cu(I) complexes constructed with ligands designed to minimize interactions of the metal center with the solvent.[12]

Scheme I

$$[Cu(dmp)_2^+]^* + Q \overset{K_q}{\rightleftharpoons} [Cu(dmp)_2Q^+]^*$$

$$[Cu(dmp)_2^+]^* \xrightarrow{k_r} Cu(dmp)_2^+ + h\nu$$

$$[Cu(dmp)_2^+]^* \xrightarrow{k_n} Cu(dmp)_2^+$$

$$[Cu(dmp)_2Q^+]^* \xrightarrow{k_n'} Cu(dmp)_2Q^+ \xrightarrow{\text{fast}} Cu(dmp)_2^+ + Q$$

The application of pressure to CH_2Cl_2 solutions of either A or B led to systematic decreases in the emission lifetimes. Table I summarizes some lifetime data at ambient pressure and at 300 MPa, while Figure 1 displays graphically this effect for each as plots of ln (τ°/τ) vs P (where τ° is the lifetime for P = 0.1 MPa). From these data, it is clear that the emission lifetimes for $^3A^*$ are significantly the more pressure sensitive.

For emission from a single ES or collection of thermally equilibrated ES's, the measured luminescence lifetime τ is the inverse of the total decay rate constant k_d:

$$\tau = k_d^{-1} \tag{1}$$

where k_d is the sum of the radiative (k_r), reaction (k_p), and nonradiative (k_n) rate constants for ES deactivation. For the present case, the emission quantum yields at ambient temperature are small ($\leq 10^{-3}$),[10] and unimolecular photoreactions are not observed; hence, the dominant deactivation pathway is nonradiative, and the pressure sensitivity of τ reflects that of the various nonradiative deactivation pathways.

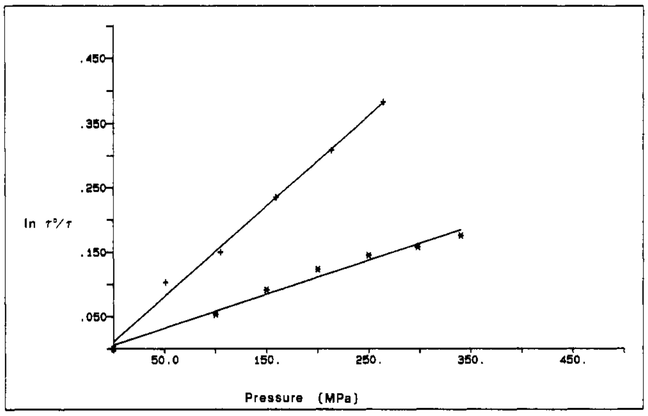

Figure 1. Pressure dependences of the MLCT lifetimes of Cu(I) complexes in CH_2Cl_2 solution (23 ± 1 °C). Pluses (+) represent $Cu(dmp)_2^+$; stars (*) represent $Cu(dpp)_2^+$.

The volume of activation $\Delta V_i^\ddagger$ for a dynamic process characterized by the rate constant k_i is defined by the relationship[5]

$$\Delta V_i^\ddagger = -RT\left(\frac{d(\ln k_i)}{dP}\right)_T \tag{2}$$

Thus the $\Delta V_n^\ddagger$'s for the nonradiative decay of $^3A^*$ and $^3B^*$ in CH_2Cl_2 in the absence of added quenchers are proportional to the slopes of the plots in Figure 1 (i.e., $\Delta V_n^\ddagger = -RT \times$ slope). From such slopes were calculated the average $\Delta V_n^\ddagger$ values −3.4 ± 0.2 and −1.6 ± 0.2 cm^3/mol for A and B, respectively (Table I).

Consistent with earlier reports,[8,9] the addition of 0.3 M acetonitrile or methanol shortened the observed emission lifetime of $^3A^*$ by 25–30%, while the addition of 0.3 N CH_3CN had no effect on that of $^3B^*$ (Table I). In pure acetonitrile, the luminescence lifetime for $^3B^*$ was considerably shorter (90 ns) than in pure dichloromethane (260 ns), while that for $^3A^*$ has been shown to be too short to measure with the present apparatus (2 ns).[9]

The "quenching constant" k_q (see below) for the effect of the added cosolvents in CH_2Cl_2 can be calculated from the equation

$$k_q = \frac{\tau^{-1} - (\tau^\circ)^{-1}}{[Q]} \tag{3}$$

where τ is the lifetime at a certain pressure P, τ° is the lifetime in the absence of quencher at the same pressure, and [Q] is the concentration of the quencher. From these limited data, the calculated k_q's are 1.6×10^7 and 1.4×10^7 M^{-1} s^{-1}, for quenching of $^3A^*$ by CH_3CN and CH_3OH, respectively, at ambient pressure. These values are within experimental uncertainties of those reported before.[9] No value for k_q can be calculated for $^3B^*$, since quenching was not observed for 0.3 M CH_3CN in CH_2Cl_2 solution and since the effect of using CH_3CN as the pure solvent includes global effects separate from any bimolecular quenching mechanism.

Simple plots of ln (τ°/τ) vs P for the above CH_2Cl_2 solutions of A and of B give $\Delta V^\ddagger$(apparent) values. These are respectively −4.3 ± 0.2 and −4.0 ± 0.2 cm^3/mol for the luminescence decay of $^3A^*$ in 0.3 M CH_3CN and in 0.3 M CH_3OH, both more negative than in neat CH_2Cl_2. In contrast, for $^3B^*$ the $\Delta V^\ddagger$(apparent)'s are −1.2 ± 0.2 cm^3/mol in 0.3 M CH_3CN in CH_2Cl_2 solution and −1.4 ± 0.2 cm^3/mol in neat CH_3CN, both values marginally more positive than in neat CH_2Cl_2.

The $\Delta V^\ddagger$(apparent) values determined above include contributions from several terms (i.e., $k_d = k_n + k_q[Q]$). The quenching constants k_q can be separately calculated at each pressure at which τ was determined according to eq 3, and the $\Delta V_q^\ddagger$ values can be determined from plots of ln (k_q°/k_q) vs P, e.g., Figure 2. There is much greater scatter in these plots than in Figure 1 as well as the suggestion of some curvature; however, it is clear that the k_q's

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Table II. $\Delta V_i^{\ddagger}$ Values for $Cu(dmp)_2^+$ and $Cu(dpp)_2^{+\,a}$

soln	$\Delta V_d^{\ddagger\,b}$	$\Delta V_n^{\ddagger\,c}$	$\Delta V_q^{\ddagger\,d}$
$Cu(dmp)_2^+$ in CH_2Cl_2	−3.4 ± 0.2	−3.4	
$Cu(dmp)_2^+$ in 0.3 M CH_3CN/CH_2Cl_2	−4.0 ± 0.2	−3.4	−6.2 ± 0.5
$Cu(dmp)_2^+$ in 0.3 M CH_3OH/CH_2Cl_2	−4.0 ± 0.2	−3.4	−5.4 ± 0.5
$Cu(dpp)_2^+$ in CH_2Cl_2	−1.6 ± 0.2	−1.6	
$Cu(dpp)_2^+$ in 0.3 M CH_3CN/CH_2Cl_2	−1.4 ± 0.2	−1.6	
$Cu(dpp)_2^+$ in CH_3CN	−1.2 ± 0.2	−1.2	

[a] Determined at 23 ± 1 °C; BPh_4^- salts in each case; $\Delta V^{\ddagger}$ values in cm^3/mol. [b] Determined from the slopes of $\ln(\tau^\circ/\tau)$ vs P plots. [c] The $\Delta V^{\ddagger}$ value in neat solvent. [d] Calculated from slopes of $\ln(k_q^\circ/k_q)$ vs P plots; k_q calculated according to eq 3.

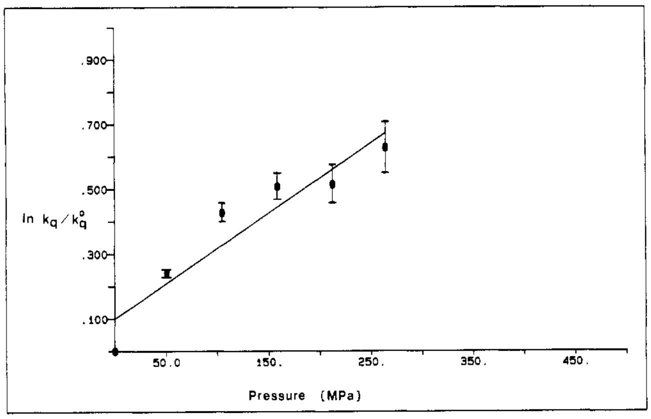

Figure 2. Pressure effects on the rate constant k_q for the quenching of the MLCT state of $Cu(dmp)_2^+$ by methanol (0.30 M) in dichloromethane solution (23 ± 1 °C).

for $^3A^*$ are considerably more pressure sensitive than are the k_d's. The $\Delta V_q^{\ddagger}$ values determined from the slopes were −6.2 ± 0.5 cm^3/mol for 0.3 M CH_3CN and −5.4 ± 0.4 cm^3/mol for 0.3 M CH_3OH.

The $\Delta V^{\ddagger}$ values summarized in Table II illustrate the contrasting responses to pressure of the excited-state decay rates for $Cu(dmp)_2^+$ and $Cu(dpp)_2^+$. Even in neat CH_2Cl_2, the $\Delta V_n^{\ddagger}$'s are substantially more negative for $^3A^*$ than for $^3B^*$. The small negative value of $\Delta V_n^{\ddagger}$ for $^3B^*$ is within the range of those seen in this laboratory for other metal complex excited states decaying nonradiatively via a unimolecular weak coupling mechanism.[5,13] The more negative $\Delta V_n^{\ddagger}$ for $^3A^*$ is outside this range and suggests participation of an associative pathway as a component of the nonradiative deactivation for the less sterically demanding $Cu(dmp)_2^+$ ion, i.e., that the k_n pathway in this case may involve formation of a solvent complex with the ES prior to nonradiative decay. However, since there is no indication that $^3B^*$ undergoes a similar mechanism for deactivation, it is unlikely that $^3A^*$ decays solely via an associative pathway.

The differences between the ES properties of A and B are further accentuated when the activation volumes for the k_q's are considered. For $^3A^*$, the $\Delta V^{\ddagger}$'s for k_q are substantially more negative than those for k_d in neat dichloromethane. In contrast, $\Delta V_d^{\ddagger}$ values for $^3B^*$ in neat CH_2Cl_2, in 0.3 M CH_3CN in CH_2Cl_2, and in neat CH_3CN are identical within experimental uncertainty. Although the partial molar volumes of neither the excited state $^3A^*$ nor the putative excited-state complex $[Cu(dmp)_2Q]^*$ are known, one may safely assume that the latter will be smaller than the sum of the $\bar{V}$'s for $^3A^*$ plus Q. Thus an associative pathway as illustrated in Scheme I, where $k_q = K_q k_n'$, should display a negative $\Delta V^{\ddagger}$. The magnitude of the negative $\Delta V_n^{\ddagger}$ for $^3A^*$ in CH_2Cl_2 plus the even more negative values of $\Delta V_q^{\ddagger}$ confirm the associative nature of major contributions to the nonradiative deactivation mechanism from the MLCT excited state of $Cu(dmp)_2^+$ as suggested in Scheme I. Correspondingly, the medium-insensitive, small negative values of $\Delta V_n^{\ddagger}$ for $^3B^*$ confirm the role of the sterically bulky 2,9-diphenylphenanthroline ligand in blocking access of various bases to metal coordination sites of the MLCT excited state.[14]

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(14) A reviewer has suggested that the dynamic quenching mechanism involves a selective outer-sphere solvation of the more polar quencher molecules with the MLCT excited state of $Cu(dmp)_2^+$, which would also be enhanced by higher pressures. While this possibility is difficult to exclude, it seems unlikely that such interactions would be specific to the dmp complex and that the phenyls of dpp would prevent such a mechanism, unless the interaction involved the metal center. Furthermore, it should be noted that neither the ground-state absorption spectra nor the shapes and positions of the MLCT emission bands of $Cu(dpp)_2^+$ and $Cu(dmp)_2^+$ in CH_2Cl_2 solution are affected by addition of 0.3 M CH_3CN.