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Temperature Dependence of Luminescence from $Cu(NN)_2^+$ Systems in Fluid Solution. Evidence for the Participation of Two Excited States

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The photophysical properties of a series of homochelated complexes of the type $Cu(NN)_2^+$ are reported where (NN) denotes a heteroaromatic ligand. For the (NN) ligands 2,9-dimethyl-1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, and 4,4′,6,6′-tetramethyl-2,2′-bipyridine, the emission quantum yields are 2.1×10^{-4}, 2.5×10^{-4}, and 0.5×10^{-4}, respectively, in CH_2Cl_2 solution at 25 °C. Under these conditions the lifetimes are 90, 80, and 18 ns, respectively, for the same series of compounds. In each case the emission intensity is found to decrease as the solution temperature is lowered. This is interpreted in terms of two emitting states where the population of the upper level, which has a more favorable radiative rate constant, requires thermal energy. Detailed temperature studies of the 2,9-dimethyl-1,10-phenanthroline complex have been carried out, and the results have been analyzed by assuming that the two excited states are thermally equilibrated. We conclude that the lowest energy emitting state exhibits a radiative rate constant of ca. 10^3 s^{-1}, typical of a triplet state. The other state lies some 1800 cm^{-1} to higher energy and exhibits a radiative rate constant of ca. 10^7 s^{-1}. This state is ascribed singlet multiplicity. Tentatively, both states are assumed to derive from the lowest energy charge-transfer configuration of the complex.

Introduction

Previously, we have reported observing photoinduced electron-transfer reactions on exciting the low-lying metal-to-ligand charge-transfer excited state(s) of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) in aqueous solutions containing various Co(III) substrates.[1-3] We have also reported that the same complex, which is denoted $Cu(dmp)_2^+$, exhibits charge-transfer emission in CH_2Cl_2 solution at room temperature and that the emission is dynamically quenched by a series of nitroaromatic molecules as well as tris(acetylacetonato)cobalt(III).[4] Because of the profound solvent effects that have been observed for this system,[3,4] it is difficult to relate these results directly, but both types of experimental observations can be understood in terms of a reactive charge-transfer excited state that is strongly reducing.[5]

The chemical and physical properties of such charge-transfer states have been of considerable interest recently. One reason is that they may prove useful in energy conversion processes.[6-8] From a more fundamental point of view, they can be used as novel reagents in studies of electron-transfer reactions, particularly those involving large driving forces.[9,10] In the particular case of copper(I) the development of luminescence spectroscopy holds promise because of the dearth of convenient spectroscopic handles available. The method may be especially important in studies of copper-containing proteins where several interesting luminophores have recently been described.[11-13]

For these various reasons we have continued our studies of $Cu(dmp)_2^+$ and related systems. For some time now we have been investigating the unusual temperature dependence of emission from $Cu(dmp)_2^+$, which we have observed in solution.[14,15] Here we report the results of these studies that can be understood in terms of a model based on two excited states separated by ca. 1800 cm^{-1}. Analogous behavior is shown by $Cu(bcp)_2^+$ and $Cu(tmbp)_2^+$, where bcp denotes 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline and tmbp denotes 4,4′,6,6′-tetramethyl-2,2′-bipyridine. The latter forms, to the best of our knowledge, the first bis(bipyridyl) complex of copper(I) that has been found to be emissive in fluid solution.

Table I. Spectral and Temporal Data at 25 ± 1 °C in CH_2Cl_2 Solvent[a]

complex	$\lambda_{max}{}^{abs}$, nm	ϵ, M^{-1} cm^{-1}	$\lambda_{max}{}^{em}$,[b] nm	$10^4\phi$	τ, ns
$Cu(dmp)_2^+$	454	7 950	670	2.1	90
$Cu(bcp)_2^+$	478	13 200	685	2.5	80
$Cu(tmbp)_2^+$	454	7 180	680	0.5	18

[a] All emission measurements are taken from deoxygenated solutions. [b] Emission maxima are uncorrected.

Experimental Section

Materials. $[Cu(dmp)_2]BF_4$, $[Cu(bcp)_2]PF_6$, and $[Cu(tmbp)_2]NO_3$ were prepared by a method previously described.[1] The ligands dmp and bcp were obtained from Aldrich and used without further purification. The tmbp was synthesized by the method described by Linnell[16] and recrystallized from hexane. Burdick and Jackson distilled-in-glass methanol and methylene chloride were used as solvents for all solution studies.

Apparatus. Absorption measurements were carried out on either a McPherson EU-700-D series spectrophotometer or a Cary 17D spectrophotometer. The emission spectra were obtained with a Perkin-Elmer MPF-44B fluorescence spectrophotometer. The lifetime measurements and time-resolved spectra were obtained by using a nitrogen-pumped dye laser with an instrumental pulse width of 8 ns, which has been described previously.[17] A Princeton Applied Research

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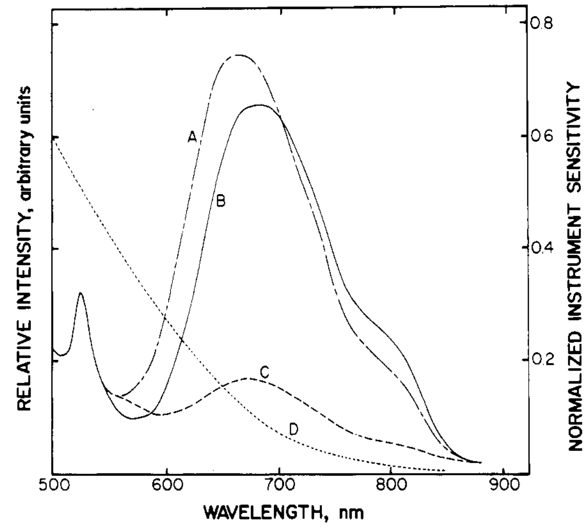

Figure 1. Uncorrected emission spectra of (A) Cu(dmp)$_2^+$, (B) Cu(bcp)$_2^+$, and (C) Cu(tmbp)$_2^+$ obtained in CH$_2$Cl$_2$ at 25 ± 1 °C. The detector response curve of the fluorimeter is also presented (D). The weak peak at ca. 525 nm is solvent Raman.

Model 162 boxcar averager with a Model 164 gated integrator was used in the laser experiments where time-resolved spectra were obtained with a McKee-Pedersen Model MP-1018B monochromator. Temperature control was achieved with a Lauda K-2/RD circulating water bath or with an Oxford Instruments DN-704 cryostat.

Methods. The emission spectra of thoroughly deoxygenated solutions of the complexes in CH$_2$Cl$_2$ were obtained by excitation at the respective λ_{max}^{abs} (see Table I). Deoxygenation of all samples was accomplished by repetitive freeze/pump/thaw cycles. All samples were equilibrated in the cell holder for 30 min at each temperature. Emission decay curves were monitored with use of a 5-ns gate and the lifetimes calculated from the slopes of standard log plots. Dyes (Exciton) were chosen to exhibit a lasing maximum that overlapped the absorption spectrum; Coumarin 460 was used for Cu(dmp)$_2^+$ and Cu(tmbp)$_2^+$ while Coumarin 480 was used Cu(bcp)$_2^+$. A 640-nm cutoff filter was employed between the cell holder and detector to minimize scatter. The quantum yields of emission were measured by the method of Parker and Rees[18] using Ru(bpy)$_3^{2+}$ as a standard at room temperature (ϕ 0.042[19]) and 77 K (ϕ 0.38[20]). At intermediate temperatures the quantum yields were obtained relative to the room-temperature yield of Cu(dmp)$_2^+$, neglecting any temperature dependence of the refractive index. We corrected the emission intensities for changes in $A(T)$, the absorbance as a function of temperature, using the expression

$$I_{cor} = I_{obsd}/(1 - 10^{-A(T)})$$

where I denotes emission intensity.

Results

Room-Temperature Measurements. Spectral data and lifetimes are presented in Table I; uncorrected emission spectra are presented in Figure 1. In each case the solutions give excitation maxima that agree with the respective absorption maxima within experimental error. The relative emission quantum yields vary by a factor of ca. 5 through the series, the absolute emission intensity being weak in each case.

The lifetimes have been secured from standard log plots and are considered to be accurate to ±10%. The previously reported lifetime of 54 ns for Cu(dmp)$_2^+$ is much too low, possibly because of the presence of quenching impurities in those experiments.[4] A solution of Cu(bcp)$_2^+$ was taken to be representative and excited at eight different wavelengths over the range 465–500 nm. Within experimental error the lifetime was independent of the exciting wavelength.

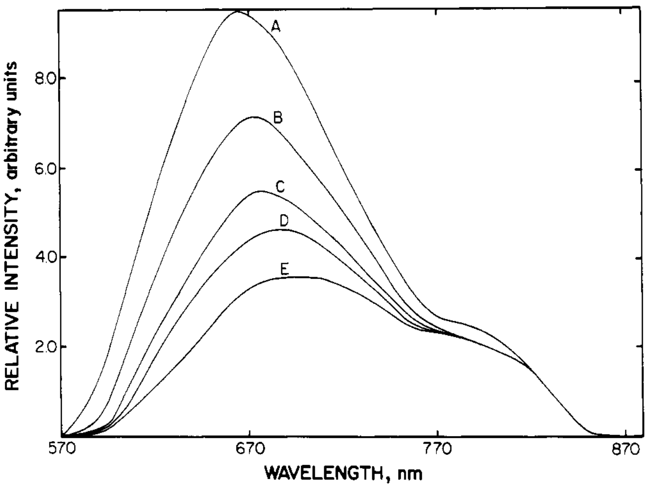

Figure 2. Uncorrected emission spectra of Cu(dmp)$_2^+$ in CH$_2$Cl$_2$ as a function of temperature: A, 24.1 °C; B, 11.5 °C; C, 0.7 °C; D, −15.4 °C; E, −28.4 °C.

Table II. Temperature-Dependent Properties of Cu(dmp)$_2^+$ [a]

T, °C	τ,[b] ns	$10^4\phi$	T, °C	τ,[b] ns	$10^4\phi$
24.1	90	2.09	−4.7	93	1.57
21.3	87	1.93	−15.4	104	1.43
11.5	91	1.73	−28.4	102	1.32
0.7	96	1.60	−196[c]	1900	14.3

[a] Solvent is CH$_2$Cl$_2$ except as noted. [b] Major component. [c] Solvent is a 4:1 v/v ethanol-methanol glass.

Variable-Temperature Measurements. For all three complexes the emission intensity *decreases* as the temperature of the solution is lowered. Emission spectra of Cu(dmp)$_2^+$ are presented as a function of temperature in Figure 2. There are also slight red shifts in the positions of the emission maxima as the temperature is lowered; e.g., the emission maximum shifts from 670 to 703 nm over the temperature change from +24 to −35 °C in Figure 2. Although solubility imposes a lower limit on the temperatures available, it is evident from Figure 2 that the fall-off in emission intensity is less pronounced at very low temperatures where relatively temperature-independent emission is observed. Similar behavior is observed for Cu(bcp)$_2^+$ and probably Cu(tmbp)$_2^+$ as well, although the signal from the latter is so weak that we are less certain of this point. The temperature dependence cannot be explained by changes in absorbance because the solution absorbance *increases* with decreasing temperature in each case. Some sharpening of the charge-transfer absorption envelope and solvent contraction (α = 0.001 37 mL °C^{-1} for CH$_2$Cl$_2$[21]) explain the absorbance changes.

To gain insight into the excited-state processes involved, Cu(dmp)$_2^+$ has been selected as a representative case, and the lifetime and emission quantum yield have been studied as a function of temperature (Table II). Despite the scatter in the results, it is clear that the lifetime variation is not large, there being a change of only ca. 10% over a range of 50 °C. There is, however, another component that is resolved in the decay curve at lower temperatures; the additional, more rapidly decaying transient is clearly apparent around −30 °C. (Compare Figure 3A with Figure 3B.) It should be noted that laser scatter and solvent Raman have been eliminated with a long-wave-pass filter. Time-resolved emission spectra are very similar if measured at the instrumental maximum or after an 80-ns delay apart from the Raman band that appears at short times, but there is a slight blue shift in the emission obtained with "zero" time delay. The relevant spectra for the

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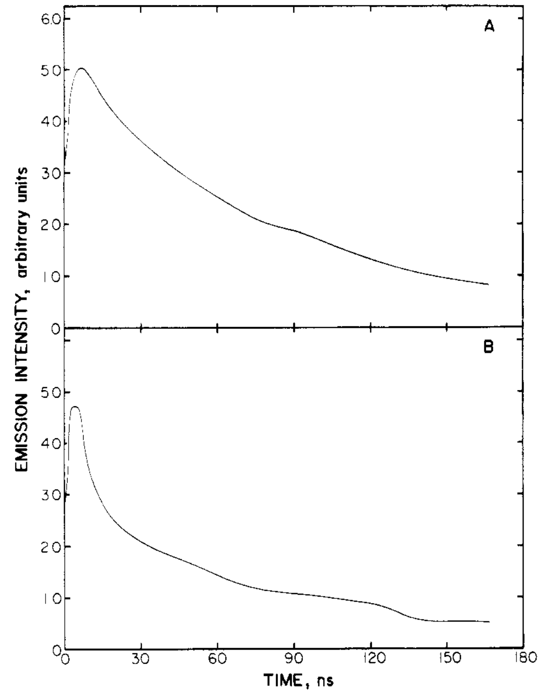


Figure 3. Emission decays for Cu(dmp)$_2^+$ in CH$_2$Cl$_2$ at 24 °C (A) and −30 °C (B). Note the rapid component in part B that has vanished after ≲10 ns.

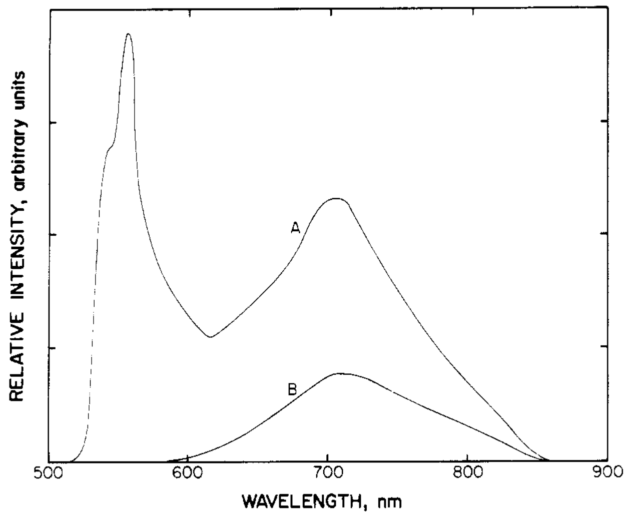


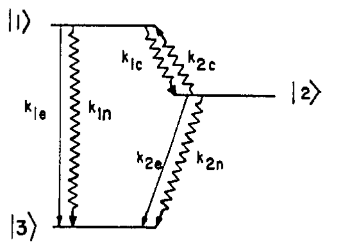
Figure 4. Time-resolved emission spectra of Cu(bcp)$_2^+$ in CH$_2$Cl$_2$ at −30 °C. The spectra were resolved by using the McKee–Pedersen monochromator. The wavelength of excitation was 478 nm. Spectrum A is taken at the time of the instrumental maximum; spectrum B is taken after an 80-ns delay.

case of Cu(bcp)$_2^+$ are presented in Figure 4.

Discussion

Orbital Parentage. As previously concluded for the case of Cu(dmp)$_2^+$,[4] the emission from each complex is most reasonably assigned to a metal-to-ligand charge-transfer state having d$^9\pi^{*1}$ orbital parentage. (The absorption spectra are rather complex in the CT region, and detailed state assignments are not yet available.) In support of these assignments we note that the lowest lying absorption bands occur in the visible region and, characteristically for charge-transfer (CT) transitions, are not found in solutions containing only Cu(I) or the ligands. In view of the low quantum yields for emission and the emission lifetimes, the respective decay schemes must involve states for which the radiative process is in some sense "forbidden". The most obvious possibility is that triplet CT excited states are involved.

Scheme I



That the quantum efficiency of emission from Cu(tmbp)$_2^+$ is significantly lower than that of either Cu(dmp)$_2^+$ or Cu(bcp)$_2^+$ is interesting in view of the fact that a similar trend is observed for the tris(bipyridine) and tris(phenanthroline) complexes of ruthenium(II).[22] Larger excited-state distortions might be expected in the case of the more flexible bipyridine ligand; however, the Stokes shifts are similar to those of the phenanthroline analogues. Of course, structural differences may occur in the ground state as well. Differential solvation effects have been suggested to be important in determining the relative emission efficiencies of the ruthenium systems,[23] but the Cu(I) systems may be more complicated, especially considering the dramatic substituent effects that have been observed.[17,24]

Multiple-Level Scheme. The temperature dependence of the emission argues for the participation of at least two excited states. If a single excited state were involved, one would expect the efficiency of the emissive process to increase as the temperature is lowered. (This follows because for a given excited state the radiative rate constant is usually temperature independent whereas a variety of nonradiative decay processes may be thermally activated.[25]) The simplest explanation of the temperature results invokes two low-lying excited states such that the population of the upper level requires thermal energy. In general, the two different electronic states could be associated with the same molecule, or alternatively, two stoichiometrically distinct species could be involved. It seems safe to assume that the former is the case since all three molecules exhibit similar behavior and since analogous results have been observed from Cu(I) systems in the solid state[26,27] where there are presumably fewer possibilities for changes in speciation etc.

A diagrammatic presentation of the energy levels involved is given in Scheme I where the two excited states and the ground state are labeled |1⟩, |2⟩, and |3⟩, respectively, in order of decreasing energy. The important rate constants connecting the levels are also indicated in Scheme I; radiative paths are indicated with straight arrows and nonradiative paths with wiggly arrows. Vibrational relaxation is assumed to be rapid compared to electronic relaxation. The steady-state emission properties of a three-level system of this type depend upon the relative values of the various rate constants as well as the relative energies of the levels;[28-32] two limiting cases will be considered.

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Kinetic Limit. This case has been considered in detail by Parker.[33] The basic assumption is that $|1\rangle$ achieves a steady-state concentration that is negligibly affected by the k_{2c} process. *Delayed* emission then occurs from $|1\rangle$ with an efficiency given by eq 2, where ϕ_{1c} denotes the efficiency by

$$\phi_{\text{delayed}} = \frac{k_{1c}}{k_{1c} + k_{1n} + k_{1e}} \frac{k_{2c}}{k_{2c} + k_{2n} + k_{2e}} \frac{k_{1e}}{k_{1c} + k_{1n} + k_{1e}} \quad (1)$$

$$\phi_{\text{delayed}} = \phi_{1c}\phi_{2c}\phi_{1e} \quad (2)$$

which $|1\rangle$ converts to $|2\rangle$, ϕ_{2c} represents the efficiency of back-conversion, and ϕ_{1e} is the efficiency of prompt emission from $|1\rangle$. As long as vibrational relaxation is rapid compared to that of the k_{1c} process, this model requires that most of the photons emitted from state $|1\rangle$ appear within the lifetime of state $|1\rangle$, i.e. as prompt emission (see eq 2). As will become evident below, the spectra depicted in Figure 2 are dominated by emission from state $|1\rangle$, and these data contradict the requirement that $\phi_{\text{delayed}} < \phi_{1e}$. In order to obtain a more workable model, we must assume that the k_{2c} process is important in determining the steady-state concentration of $|1\rangle$.

Equilibrium Limit. In the limit that $k_{1c} >> W_1$ and $k_{2c} >> W_2$, where $W_1 = k_{1e} + k_{1n}$ and $W_2 = k_{2e} + k_{2n}$, the steady-state populations of $|1\rangle$ and $|2\rangle$ are determined by Boltzmann statistics, and the ratio of the populations of levels $|1\rangle$ and $|2\rangle$ are described by an equilibrium constant $K = k_{2c}/k_{1c}$ (see the Appendix). The respective emission quantum yields ϕ_{1e} and ϕ_{2e} are then described by eq 3 and 4.[30,31] In our laser studies

$$\phi_{1e} = \frac{k_{1e}K}{W_1K + W_2} \quad (3)$$

$$\phi_{2e} = \frac{k_{2e}}{W_1K + W_2} \quad (4)$$

a single exponential decay is observed once the laser pulse is extinguished. If states $|1\rangle$ and $|2\rangle$ remain thermally equilibrated during the decay process, this lifetime is expressed by eq 5.[31] However, more stringent conditions are required for

$$\tau = \frac{1 + K}{W_1K + W_2} \quad (5)$$

k_{1c} and k_{2c} if the levels are to remain equilibrated during the decay. Strictly speaking, W_1 must equal W_2 and the k_{1c} and k_{2c} processes must be rapid compared to the decay process. On the other hand, if k_{1c}, $k_{2c} >> W_1$, W_2, the levels can, to a good approximation, be regarded as equilibrated.[34]

According to this model, the relative proportion of emission stemming from $|1\rangle$ should decrease with decreasing temperature. Evidence of this is found in the corrected emission spectra (Figure 5). Subtracting a low-temperature spectrum from a high-temperature spectrum reveals that an emission that maximizes around 700 nm is lost as the temperature decreases. At the same time the intensity due to a component maximizing around 800 nm remains relatively constant.

The fact that two components with different emission spectra are observed may also figure in the explanation of the weak transient observed during the laser flash, although the latter effect is not the focus of this study. First note that the appearance of a transient is not inconsistent with the equilibrium model. If state $|1\rangle$ is selectively populated initially, a transient emission—which would be quite weak if both k_{1c} and k_{2c} are large—is expected prior to the equilibration of the levels.[35,36] In this event, at short times the emission from state $|1\rangle$ would be enhanced compared to emission from state $|2\rangle$, and this could explain the apparent shift of the emission maximum toward shorter wavelengths in the "time-zero" spectrum of Figure 4. Alternatively, the transient might be attributable to another excited state of the complex or another species in solution, e.g. the complex in some other state of solvation or ion pairing. The proper characterization of this part of the emission will require much more effort.

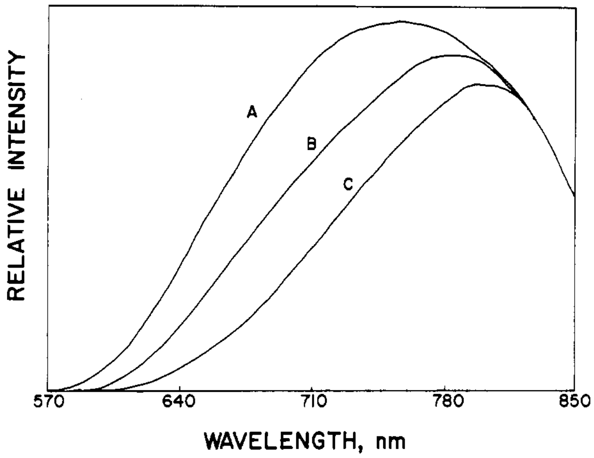

Figure 5. Corrected emission spectra of $Cu(dmp)_2^+$ in CH_2Cl_2 as a function of temperature: A, 21.3 °C; B, 0.7 °C; C, −35.0 °C.

Since the data are more readily rationalized in the equilibrium limit, we have used this model to carry out a more detailed analysis. To do this, we rewrite K as in eq 6, where

$$K = \frac{g_1}{g_2} \exp(-\Delta E/RT) \quad (6)$$

ΔE is the energy difference between states $|1\rangle$ and $|2\rangle$ and g_1 and g_2 denote their respective degeneracies. The number of parameters to be estimated is reduced by combining eq 3–5 to give eq 7, where ϕ is the total measured emission yield.

$$\frac{\phi}{\tau} = \frac{\phi_{1e} + \phi_{2e}}{\tau} = \frac{k_{1e}K + k_{2e}}{1 + K} \quad (7)$$

Making the assumptions (1) that k_{1e} and k_{2e} are temperature independent, (2) that $g_1 = 1$ and $g_2 = 3$, ignoring any orbital degeneracies (vide infra), and (3) that ΔE can be taken from the peak-to-peak energy difference of the two components resolved from the corrected spectra, least-squares analysis of the ϕ/τ data yields

$$k_{1e} \approx 2 \times 10^7 \text{ s}^{-1} \qquad k_{2e} \approx 1 \times 10^3 \text{ s}^{-1}$$

$$\Delta E \approx 1800 \text{ cm}^{-1}$$

These estimates are subject to considerable errors. Aside from the scatter in the data and the severe corrections required for the emission spectra, k_{2c} may not be large enough to ensure equilibration in view of the energy gap involved. On the basis of the weak intensity of the preequilibrium transient, k_{1c} is estimated to be 10^{11}–10^{12} s^{-1} at room temperature. For the ΔE value quoted this would require that k_{2c} be 10^7–10^8 s^{-1}. Since $W_2 \approx 1/\tau \approx 10^7$ s^{-1}, k_{2c} may only be of the order of W_2. If k_{2c} is too low, the actual steady-state concentration of $|1\rangle$ would be less than that calculated by using eq 6, causing us to underestimate k_{1e}. In this sense the calculated k_{1e} value might be considered as a lower limit. Realistically, k_{1e} and k_{2e} should be regarded as order-of-magnitude estimates; ΔE is probably good to ca. 20%. As a partial check of the results, note that ϕ/τ can be taken as an estimate of k_{2e} at very low

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temperatures so long as $k_{1c} >> W_1$. Using the data from the glass, we obtain $k_{2e} = 7.5 \times 10^2\ s^{-1}$, in reasonable agreement with the least-squares results.

Level Assignments. Both $|1\rangle$ and $|2\rangle$ can confidently be attributed to CT states,[4] but several possibilities remain for specific assignments. For example, from the viewpoint of one-electron orbital energies different excited states arise depending on which of the (split) metal 3d orbitals is the origin of the promoted electron; i.e., some states can be envisaged as having both CT and d–d excitation. In fact, depending on the d-orbital occupation the geometry may vary,[37] and this, among other things, may affect the respective transition moments. Alternatively, different ligand π^* orbitals can serve as the terminus for the transferred electron.[38] Still another possibility is that the levels can differ in spin multiplicity.[26]

Given the fact that intersystem crossing is usually rapid in metal complexes,[29] state $|2\rangle$, the lowest energy excited state, is expected to be a triplet state. In accord with this assignment, the estimated k_{2e} value falls into the "normal" range for triplet states (1–$10^4\ s^{-1}$).[39] Although we have no a priori way of assigning a multiplicity to state $|1\rangle$, the k_{1e} value we obtain seems too large for a triplet state. (Note that the order of magnitude obtained for k_{1e} does not depend on our assumed value of $g_1/g_2 = {}^1/_3$.) Even in the case of osmium(II) complexes where the spin–orbit coupling interaction should be much larger, the radiative rate constant from analogous triplet CT states is only ca. $10^5\ s^{-1}$.[40] On the other hand, the calculated k_{1e} value falls in the range expected for singlet states (10^6–$10^9\ s^{-1}$),[39] in support of assumption 2 above. In the absence of any theoretical results to the contrary, we presume that states $|1\rangle$ and $|2\rangle$ can be associated with the lowest energy CT configuration of the complex.[41]

A final point worth noting is that the calculated ΔE is in fair agreement with spectroscopically obtained singlet–triplet splittings that have been reported for related ruthenium(II) and iron(II) complexes exhibiting low-lying metal-to-ligand CT excited states.[42] It should be emphasized that such comparisons can only be made in a qualitative sense because the d–π^* orbital overlap patterns are likely to be very different for these systems. As a consequence the exchange integrals, and hence the ΔE values,[43] will differ as well.

Conclusions. The temperature dependence of the solution emission from complexes of the type $Cu(NN)_2^+$ can be understood in terms of two thermally equilibrated excited states separated by ca. 1800 cm^{-1}. The lower of the two is assigned as a triplet state associated with the lowest energy $d^9\pi^{*1}$ configuration. The other state has a substantially greater radiative rate constant and is tentatively assigned to the associated singlet charge-transfer state. A similar scheme has been found to adequately describe emission from $Cu(PPh_3)_2(NN)^+$ systems in the solid state.[26,27] Thus, a multiple-level scheme of this type may be of general importance in determining the photophysical properties of copper(I) complexes involving heteroaromatic ligands.

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Appendix

The steady state is defined by eq 8 and 9, where I_a is the

$$\eta_1 I_a = W_1[1] + k_{1c}[1] - k_{2c}[2] \quad (8)$$

$$\eta_2 I_a = W_2[2] + k_{2c}[2] - k_{1c}[1] \quad (9)$$

absorption rate and $\eta_1 I_a$ and $\eta_2 I_a$ are the respective pump rates of states $|1\rangle$ and $|2\rangle$, the concentrations of which are expressed as [1] and [2]. Combining these equations and defining $\beta = \eta_2/\eta_1$ yield eq 10. When $k_{2c} >> W_2$ and $k_{1c} >> W_1$, the

$$K = \frac{[1]}{[2]} = \frac{W_2 + (\beta + 1)k_{2c}}{\beta W_1 + (\beta + 1)k_{1c}} \quad (10)$$

expression for K reduces to k_{2c}/k_{1c} as stated in the text. Equations 3 and 4 in the text assume $\eta_1 = 1$ and $\eta_2 = 0$.

Registry No. $Cu(dmp)_2^+$, 21710-12-3; $Cu(bcp)_2^+$, 47895-81-8; $Cu(tmbp)_2^+$, 47718-57-0.

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Nitrogen-15 and Boron-11 Nuclear Magnetic Resonance Studies of Trimethylamine Adducts of the Mixed Trihalides of Boron

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^{15}N and ^{11}B NMR spectra have been measured for the trimethylamine adducts of the mixed trihalides of boron. $J(^{11}B–^{15}N)$, though covering a narrow range, correlates well with $\delta(^1H)$, $\delta(^{13}C)$, $J(^1H–^{11}B)$, and $J(^{11}B–^{19}F)$ and less so with $\Delta\delta(^{11}B)$ (the complexation shift) parameters, which have been related to the B–N electron density or bond strength. $\delta(^{15}N)$ and $\delta(^{11}B)$ do not show such a correlation but rather correlate with each other, showing primary dependence on halogen-induced effects, those species containing fluorine falling on a separate curve from the other halogens. Pairwise additivity is observed for $\delta(^{11}B)$, $\delta(^{15}N)$, and $J(^{11}B–^{15}N)$, with pairwise parameters showing correlations with the sum of electronegativities or van der Waals radii.

Introduction

The use of nuclear magnetic resonance to study the trimethylamine–boron trihalide adduct system began with our ^1H study[1] nearly 20 years ago, shortly thereafter further extended by the work of Heitsch[2] and ourselves.[3] With our preparation of trimethylamine adducts of the mixed trihalides

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