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Notes

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Substituent Effects and the Photoluminescence of $Cu(PPh_3)_2(NN)^+$ Systems

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Complexes of low-valent metal ions involving heteroaromatic ligands like 1,10-phenanthroline or 2,2′-bipyridine may exhibit low-lying metal-to-ligand charge-transfer (MLCT) excited states which are significantly redox active.[1,2] In the case of ruthenium(II) the introduction of ring substituents has sometimes been found to signficantly alter the excited-state properties.[2-6] Recently we reported that the emission quantum yields are dramatically different for the MLCT excited states of $Cu(PPh_3)_2(1,10\text{-phen})^+$ and $Cu(PPh_3)_2(2,9\text{-}Me_2\text{-}1,10\text{-phen})^+$.[7] To explore further the nature of substituent effects on copper(I) systems, we have examined a series of complexes of the type $Cu(PPh_3)_2(NN)^+$, where (NN) denotes one of the 2,2′-bipyridine derivatives from Chart I, and the results are reported herein.

Experimental Section

Preparation of Samples. $[Cu(PPh_3)_x]BF_4$ was prepared from excess triphenylphosphine and $Cu(BF_4)_2 \cdot xH_2O$ in ethanol. The mixed-ligand complexes were prepared by adding a solution of (NN) to $[Cu(PPh_3)_x]BF_4$ in absolute ethanol. The bpy and 4,4′-dmbp were purchased from G. F. Smith. The mbp and trmbp ligands were prepared by Kauffmann's method.[8] The tmbp ligand was prepared by the method of Linnell.[9] Complexes were purified by repeated recrystallization from absolute ethanol until the emission spectra did not change with further recrystallization. Methanol (Burdick & Jackson Laboratories—distilled in glass) was used without further purification. Solutions of the complexes in methanol were degassed prior to use by repeated freeze-pump-thaw cycles and stored under a nitrogen atmosphere.

Apparatus and Techniques. All emission experiments were performed with a Perkin-Elmer MPF-44B fluorimeter. The signals were recorded on a Hewlett-Packard Model 7015B X-Y recorder. All absorption data were obtained with a Cary 17D spectrometer. Relative quantum yields were obtained by application of the formula[10]

$$Q_x = Q_r(D_x/D_r)$$

where r and x denote the reference standard ($Cu(PPh_3)_2(bpy)^+$) and the complex under study, respectively, D is the area under the emission spectrum, and all solutions had the same absorbance at 350 nm, the irradiating wavelength. Corrected spectra were used to make the comparisons.

Chart I

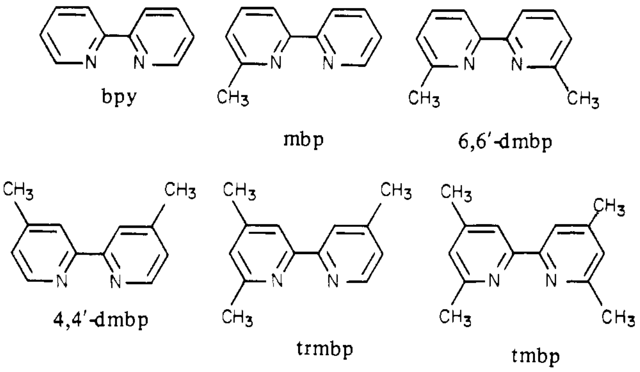

Table I. Spectral Characteristics of $[Cu(PPh_3)_2(NN)]BF_4$ in Absolute Methanol at 295 K

(NN)	$\lambda_{max}{}^{abs}$, nm	ϵ, L mol^{-1} cm^{-1}	$\lambda_{max}{}^{em}$, nm	ϕ_{rel}
bpy	355	2820	650	1
mbp	348	2870	610	1.6
6,6′-dmbp	340	2850	565	8.4
4,4′-dmbp	347	3200	640	1.2
trmbp	345	3160	635	1.2
tmbp	335	2850	553	11.1

Results and Discussion

The results of the absorption and emission studies are compiled in Table I, where, for ease of discussion, the compounds are grouped into two sets. The first set consists of bpy and derivatives with methyl groups in the 6- and/or 6′-positions; the second set is comprised of an analogous series based on 4,4′-dmbp.

The most significant trend in the absorption data of each group is the progressive hypsochromic shift in the MLCT absorption maximum as methyl groups are introduced. Day and Sanders have analyzed in detail the effects of methyl substituents on the MLCT transitions of bis(1,10-phenanthroline)copper(I) complexes in terms of inductive and hyperconjugative perturbations of the ligand π orbitals as well as ligand-dependent shifts in the metal 3d orbital energies.[11] For the mixed-ligand complexes described here, steric effects may also be significant. Thus unfavorable ligand/ligand contacts have been observed in the structure of $Cu(PPh_3)_2(2,9\text{-}Me_2\text{-}1,10\text{-phen})^+$, which tends to undergo phosphine dissociation in the ground state.[12] Likewise, the complexes of interest here having "front-side" methyls have had to be studied in the presence of excess phosphine to suppress dissociation. With so many variables a quantitative analysis is precluded, but it can be noted that the half-wave potentials of aromatic systems generally shift cathodically as methyl substituents are introduced.[13] Since, to a first approximation, the charge-transfer transition can be viewed as an oxidation of the metal center with a concomitant reduction of the (NN) ligand, the observed

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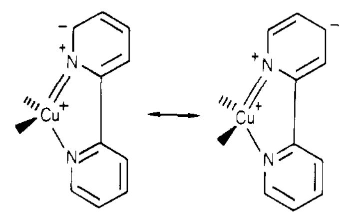
0020-1669/83/1322-0691$01.50/0

Scheme I



shifts in absorption band maxima are in accord with predictions based on the ligand acceptor properties.

With progressive methylation there is also a smooth hypsochromic shift in the emission maxima; however, the changes in the relative emission quantum yields are highly cooperative (Table I). Although progressive methylation leads to more efficient radiative decay within each group, a dramatic increase in efficiency occurs when the *second* methyl group is introduced into a "front-side" position. Ways in which the methyl groups can affect important decay processes are considered below.

Energy-Gap Effect. All else the same, the rate of nonradiative decay from an electronically excited state to the ground state is expected to decrease as the energy gap between the states increases. This principle has recently been invoked to explain trends in the emission of the MLCT states of a series of osmium(II) complexes.[14] The fact that the emission efficiency we observe increases with higher emission energy is in accord with this principle; however, this effect per se does not explain the sharp increases in emission efficiency that occur when both the 6- and 6′-positions carry methyl groups.

Perturbation of Acceptor Modes. On account of their lower frequency, C–C vibrations are less favorable than C–H vibrations as acceptor modes in electronic-to-vibrational energy conversion processes,[2,15] and this could in principle result in diminished nonradiative decay rates in the methylated derivaties. But there are at least three reasons for doubting the significance of this effect. (i) With the assumption that the electron in the π^* orbital of the excited state is delocalized over the entire ligand framework, the large differences between complexes with two "front-side" methyls as opposed to those with "front-side" methyl group are not anticipated. (ii) Corresponding substituent effects are not observed in the solid state.[16] (iii) Deuteration of the ring positions has little effect on the decay kinetics of the MLCT excited states of analogous ruthenium(II)[17] and osmium(II) systems.[14].

Solvent Interactions. Since the mixed-ligand complexes exhibit much lower emission yields in solution compared with those in the solid state,[16] coupling to solvent is apparently the key factor determining nonradiative decay rates. Accordingly, the most likely role of the methyl groups is in somehow influencing the interactions between solvent molecules and the excited state(s) of the complex. While the list of possibilities is perhaps not exhausted, two interaction mechanisms suggested by previous ground-state studies can be discussed.

Specific solvation effects might be expected at the 4- and 6-positions of the bipyridine moiety, where an accumulation of charge density is anticipated in the excited state; see, for example, the two resonance structures depicted in Scheme I. The introduction of methyl substituents at these positions could conceivably alter the solvation of the bipyridine ligand.[18] What seems unlikely is that such an effect could give rise to the strong distinction between "front-side" and "back-side" positions as demanded by the emission data.

On the other hand, an obviously distinctive characteristic of the "front-side" methyls is their proximity to the metal center, suggesting that the methyl groups in the 6- and 6′-positions might uniquely affect solvation of the metal center in the excited state. In studies of related $Cu(NN)_2^+$ systems, where Lewis bases have been found to quench the charge-transfer emission, we have pointed out that an expansion of the coordination number of copper might be expected in an MLCT excited state.[19,20] In the mixed-ligand complexes as well, association of a fifth ligand would open new channels for nonradiationless decay. Thus the effect of the "front-side" methyls could be to suppress the association of solvent by means of imposing a steric barrier.

Perturbation of Radiative Decay Rates. A reviewer has pointed out that the methyl groups may affect the radiative decay rates. However, insofar as the molar absorptivities reflect the relative probabilities of radiative decay,[21] no such effect is indicated.

Conclusions

Marked substituent effects are observed upon the photophysical properties of complexes of the type $Cu(PPh_3)_2(NN)^+$, especially with respect to substitution at the 6- and 6′-positions of the bpy moiety. They appear to be due to changes in the coupling of the excited states to the solvent. It is possible that the most significant role of the "front-side" methyls is in inhibiting quenching processes associated with expansion of the coordination number of the metal.[22]

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Registry No. $[Cu(PPh_3)_2(bpy)]BF_4$, 80320-16-7; $[Cu(PPh_3)_2(mbp)]BF_4$, 84130-44-9; $[Cu(PPh_3)_2(6,6'\text{-}dmbp)]BF_4$, 84142-99-4; $[Cu(PPh_3)_2(4,4'\text{-}dmbp)]BF_4$, 84143-00-0; $[Cu(PPh_3)_2(trmbp)]BF_4$, 84130-46-1; $[Cu(PPh_3)_2(tmbp)]BF_4$, 84130-48-3.

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(22) That other effects are also important is shown by the fact that emission is readily detected from $Cu(tmbp)_2^+$ in CH_2Cl_2 solution but not from $Cu(6,6'\text{-}dmbp)_2^+$ under the same conditions: Del Paggio, A. A.; McMillin, D. R., unpublished results.

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Preparation and Use of $W(CO)_3(NCR)_3$ (R = Et, Pr) as Improved Starting Materials for Syntheses of Tricarbonyl(η^6-cycloheptatriene)tungsten and Other Substituted Carbonyl Complexes[1]

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The most prominent ligand feature of organonitriles in transition-metal complexes is the facility by which they can be replaced by other ligands.[2a] A very convenient and com-

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