Inorg. Chem. **1991**, *30*, 559-561 **559**

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Steric Influences on the Photoluminescence from Copper(I) Phenanthrolines in Rigid Media

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Received May 7, 1990

Data for a series of copper(I) phenanthrolines in an alcohol glass at 90 K have revealed that substituents in the 2,9-positions of the ligand have a pronounced influence on the energy, intensity, and lifetime of the photoluminescence. All of the complexes exhibit intense metal-to-ligand charge-transfer absorption bands of similar energy in the visible region. However, the absorption maxima and, to an even greater extent, the emission maxima shift to higher energy as bulkier substituents are introduced. At the same time, the emission quantum yields and lifetimes increase. The results can be understood in terms of contrasting geometric preferences of the ground and excited states involved. Whereas the d^{10} ground state tends toward idealized D_{2d} symmetry, the d^9 excited state favors a D_2 symmetry. Bulkier ligands inhibit geometric relaxation within the excited state and give rise to higher energy excited states. Consequently, nonradiative decay is less efficient in these systems, and the quantum yields and excited-state lifetimes are enhanced.

Introduction

Since the discovery that $[Cu(dmp)_2]^+$ (where dmp denotes 2,9-dimethyl-1,10-phenanthroline) is photoluminescent at room temperature in methylene chloride,[1] a great deal of effort has been invested in the exploration of the photochemistry and photophysics of this and related systems.[2-10] In particular, studies have shown that substituents in the 2,9-positions of the phenanthroline ligand dramatically influence the energy[11] and intensity[12] of the metal-to-ligand charge-transfer (CT) absorption, as well as emission[11,13] from the excited state. In solution, the emission intensity and lifetime increase with increasing steric bulk of the substituents in the 2,9-positions. One reason is that in fluid solution the excited complex is prone to formation of a five-coordinate adduct (exciplex) with even the weakest of Lewis bases, since the excited state is coordinatively unsaturated.[2,3,14-17] Bulky groups in the 2,9-positions of the phenanthroline sterically hinder expansion of the coordination number, and therefore inhibit exciplex quenching. The present study, involving the ligands depicted in Figure 1, reveals that even in a rigid glass at 90 K, where exciplex quenching is quite improbable, the steric demands of the substituents still have a profound effect on the emission. The results can be understood in terms of a geometric relaxation that occurs after formation of the excited state.

Experimental Section

Materials. High-purity distilled-in-glass methanol and anhydrous ethanol were purchased from Burdick & Jackson and Mid West Solvent Co., respectively. Laser dyes were obtained from Exciton. The mmp and dmp ligands were purchased from G. F. Smith and Aldrich, respectively, and were used without further purification, while the dbp ligand was synthesized by a previous literature method.[18] Ligand L1 (Figure 1) was synthesized as before.[19] Ligand L2, or 2,9-bis((2-methylanilino)-methyl)-1,10-phenanthroline, was prepared as follows: (i) reaction of *o*-toluidine with 1,10-phenanthroline-2,9-dicarboxyaldehyde,[20] catalyzed by *p*-toluenesulfonic acid in refluxing benzene, gave the corresponding diimine (91%, FAB mass spectrum *m/z* 415, $[M + H]^+$); (ii) reduction with excess $NaBH_4$ in EtOH/THF afforded ligand L2 (92%, *m/z* 419, $[M + H]^+$).

The compounds $[Cu(mmp)_2]BPh_4$, $[Cu(dmp)_2]BF_4$, and $[Cu(dbp)_2]BF_4$ were prepared by variations of a reported procedure.[21] The purity of the $[Cu(mmp)_2]BPh_4$ and $[Cu(dmp)_2]BF_4$ compounds was spectroscopically confirmed. The compound $[Cu(dbp)_2]BF_4$ gave a satisfactory microanalysis (Anal. Calc: C, 65.34; H, 6.59; N, 7.62. Found: C, 65.56; H, 6.57; N, 7.72). Copper(I) complexes of the tweezer ligands L1 and L2 were obtained by reacting the ligand with $[Cu(CF_3SO_3)]_2 \cdot C_6H_6$[22] in a 4:1 ratio under an inert atmosphere. The complexation reaction was carried out in methylene chloride for the L1 ligand and in acetonitrile for the L2 ligand. After purification by chromatography (CH_3CN eluent), the solids $[Cu(L1)_2]CF_3SO_3$ (78%, *m/z* 1444, $[M]^+$) and $[Cu(L2)_2]CF_3SO_3$ (86%, *m/z* 899, $[M]^+$) were isolated as orange-red powders.

Equipment. Mass spectra were determined from compounds in a *p*-nitrobenzyl alcohol matrix with a ZAB-HFVG Analytical instrument. All absorption and emission measurements at 90.0 ± 0.1 K were made in an Oxford Instruments Model DN 1704 cryostat. Absorption data were measured on a Cary 17D UV-vis spectrophotometer. Corrected emission spectra were obtained with an SLM-Aminco SPF 500C spectrofluorometer. Lifetimes were determined by use of a nitrogen-pumped dye laser and boxcar averaging detection system described previously.[5]

Methods. Samples were dissolved in 4:1 (v/v) EtOH/MeOH to yield an optical density of 0.3 at 454 nm. The solutions were then deoxygenated by repeated freeze-pump-thaw cycles, and the atmosphere was replaced by $N_2(g)$. The $[Cu(L1)_2]CF_3SO_3$ sample was prepared in an inert atmosphere and handled under minimal light exposure to minimize oxidation or other side reactions of the $Cr(CO)_3$(arene) moiety. At least 1 h was allowed for the sample and the cryostat to equilibrate.

In the lifetime experiments, samples were excited at 450 nm with the aid of either coumarin 440 or coumarin 460 as the laser dye, and the

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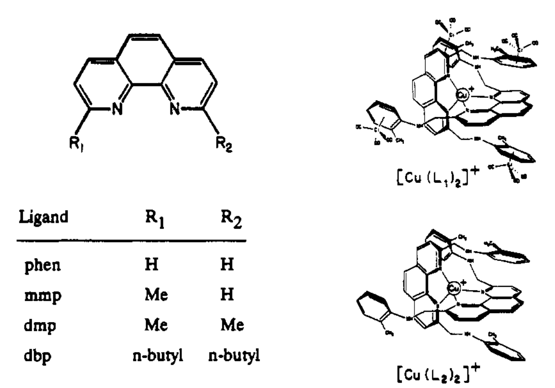

Ligand	R_1	R_2
phen	H	H
mmp	Me	H
dmp	Me	Me
dbp	n-butyl	n-butyl

Figure 1. Left: simple derivatives of 1,10-phenanthrolines. Right: top, $[Cu(L1)_2]^+$; bottom, $[Cu(L2)_2]^+$.

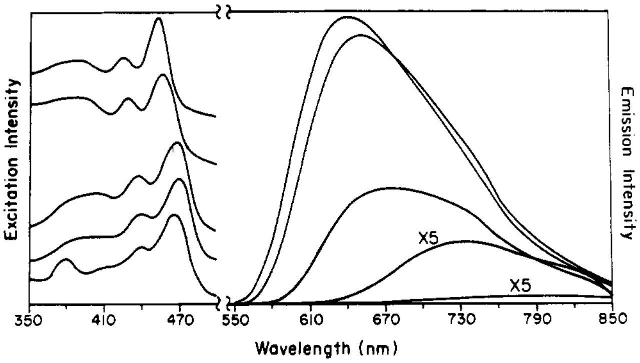

Figure 2. Left: corrected excitation spectra for $[Cu(L1)_2]^+$, $[Cu(L2)_2]^+$, $[Cu(dbp)_2]^+$, $[Cu(dmp)_2]^+$, and $[Cu(mmp)_2]^+$, from top to bottom. Right: corrected emission spectra for the same series. All spectra were recorded in a 4:1 (v/v) ethanol/methanol glass at 90 K.

Table I. Emission Data at 90 K in 4:1 (v/v) Ethanol/Methanol

complex	λ_{max},[a] nm	ϕ[b,c]	τ,[c] μs	k_r[b]
$[Cu(L1)_2]^+$	640	1.00	5.1	1.0
$[Cu(L2)_2]^+$	650	0.82	3.8	1.1
$[Cu(dbp)_2]^+$	665	0.40	1.8	1.1
$[Cu(dmp)_2]^+$	730	0.062 (±20%)	0.57	0.6
$[Cu(mmp)_2]^+$	790	0.0074 (±40%)		

[a] From corrected spectra. [b] Relative to $[Cu(L1)_2]^+$. [c] Estimated errors in ϕ and τ are ±10% and ±5%, respectively, except as noted.

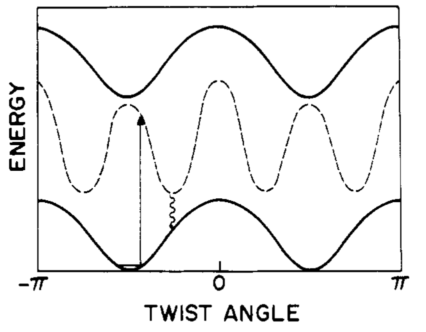

Figure 3. Configuration coordinate diagram appropriate for excited-state D_2 flattening. Idealized D_{2d} symmetry occurs at twist angles of $\pm\pi/2$ radians. The lower solid curve represents the ground-state potential surface. The dashed curve is for an excited state subject to a D_2 distortion, and the upper solid curve is for a CT state that does not distort. Singlet excited states are omitted for clarity but are expected to parallel the triplet excited states. The solid arrow represents an absorption, and the curved arrow represents a nonradiative decay process.

lifetimes (τ) were estimated by using an iterative search procedure.[3] In the steady-state emission experiments, samples were excited at 454 nm (10-nm band-pass) while the emission monochromator was scanned from 550 to 850 nm with a 5-nm band-pass. The excitation spectra were obtained by monitoring the instrumental emission maximum (10-nm band-pass) and exciting from 350 to 500 nm with a 5-nm band-pass. In all of the steady-state emission experiments, a 520-nm long-pass filter was used to minimize the background. Quantum yields (ϕ) were calculated, relative to $[Cu(L1)_2]^+$, from eq 1, where I_S is the area of the

$$\phi = \frac{I_S(1 - 10^{-R})}{I_R(1 - 10^{-S})} \tag{1}$$

corrected emission spectrum of the sample and I_R is that of the reference. R and S are the absorbances at the exciting wavelength of the reference and sample, respectively. The relative radiative rate constant, k_r, was calculated from eq 2.

$$\phi = \tau k_r \tag{2}$$

Results and Discussion

All of the complexes exhibit visible absorption bands of similar energy that can be attributed to a metal-to-ligand charge-transfer absorption. In the case of the L1 system, however, the CT absorption appears as a shoulder on a much stronger band associated with the $Cr(CO)_3$(arene) moieties. As can be seen from the corrected excitation spectra presented in Figure 2, energy absorbed by the $Cr(CO)_3$(arene) is not funneled into the emitting CT state. With the exception of the mmp complex, the excitation maximum shifts to longer wavelength as the steric bulk of the substituent decreases. Even larger bathochromic shifts can be seen in the corrected emission maxima at 90 K, as shown in Figure 2. Therefore, the energy difference between the CT absorption maximum and the emission maximum decreases as larger substituents are introduced onto the phenanthroline ligand. Spectral data along with lifetimes, relative quantum yields, and relative radiative rate constants are compiled in Table I.

The variation of emission energies and lifetimes within Table I is attributed to geometric relaxation, which occurs in the excited state. In the ground state the metal ion has a d^{10} configuration, and each complex is considered to have an idealized D_{2d} geometry.[11] In contrast, the lowest energy triplet excited state formally contains a d^9 metal center and is therefore unstable with respect to a Jahn–Teller distortion toward a more flattened, D_2 geometry;[23,24] see the configurational coordinate diagram in Figure 3. When there is a change from D_{2d} symmetry to D_2 symmetry in the excited state, the energies of the ground and excited states merge closer together (as indicated by the dashed excited-state potential energy surface in Figure 3), and nonradiative decay becomes more facile. At the same time, the excited-state lifetime and the emission quantum yield decrease. The larger the distortion is, the larger the effect. On the other hand, complexes containing bulky substituents exhibit a longer lifetime, higher quantum yield, and higher energy emission because the flattening distortion is sterically inhibited.

The change in the equilibrium geometry between the ground and the excited states can also give rise to a red shift in the absorption spectrum. The effect is illustrated in Figure 3, where, for convenience, a spin-forbidden transition from the ground state to the triplet CT is shown. Transitions into the wells of the D_2 excited-state surface can only be accessed if flattened conformations occur in the ground electronic state because electronic excitation occurs as a vertical transition. Significant D_2 deformations can occur within the ground electronic state as a result of zero-point vibrational motion if D_2 flattening corresponds to a low-energy vibration. This may well be the case, since crystallographic studies have revealed that the dihedral angle between phenanthroline ligands is quite variable in these systems and is apparently largely determined by lattice forces.[25-27] Alternatively, the ground state may also be subject to a small D_2 distortion that varies with the substituent.[6] A similar electronic spectrum would

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be expected from either type of ground state.[28] In contrast to the ground state, the excited state is severely flattened; hence, there is a large difference between the absorption and emission energies.

The absorption maximum of the $[Cu(mmp)_2]^+$ system is somewhat anomalous because it occurs at a higher energy than that of $[Cu(dmp)_2]^+$. However, the mmp ligand differs from the others in that it carries only one alkyl substituent, and the energies of the π^* orbitals of phenanthroline are known to vary with the degree of substitution.[29]

Thus, the evidence is convincing that geometric relaxation of the excited state is a very important factor influencing the lifetimes of the charge-transfer states of $[Cu(dmp)_2]^+$ and related systems. Previous results on mixed-ligand complexes of copper(I) can be explained in the same way.[30] In addition, essentially the same model has been used to account for fluorescence lifetimes and quantum yields for a series of stilbene derivatives.[31,32]

We should also point out that the solvent medium has an influence upon the geometric relaxation within the excited state. This effect can be demonstrated by a comparison of the data for the $[Cu(L1)_2]^+$ and $[Cu(L2)_2]^+$ systems. Locally at the metal center, the interligand steric interactions are expected to be similar for the two complexes. Nevertheless, the emission maximum occurs at higher energy for the $[Cu(L1)_2]^+$ system because flattening of the complex involves movement of the phenanthrolines against the solvent cage as well as against each other. In essence, substituents that protrude into the solvent medium experience a drag, which hinders the excited-state rearrangement. In accord with this reasoning $[Cu(dmp)_2]^+$ and $[Cu(dbp)_2]^+$ emit at almost the same wavelengths in fluid CH_2Cl_2 solution at room temperature, while they exhibit quite different emission maxima in a rigid matrix at 90 K.

Finally, it is interesting to note that, despite the high emission intensities and long lifetimes exhibited by $[Cu(L1)_2]^+$ and $[Cu(L2)_2]^+$ in a rigid glass, the same complexes give almost no detectable emission in fluid solution. The quenching can probably be attributed to another type of structural reorganization that can occur in fluid solution, namely internal exciplex formation between the copper center and one of the aniline nitrogens. As noted above, interactions with Lewis bases are very effective at quenching CT states in these copper systems.[14-17] If longer lifetimes in fluid solutions are to be obtained, bulky substituents must be designed or chosen so as to avoid internal exciplex quenching.

Acknowledgment. We thank Dr. Dan Lee of Purdue University for the synthesis of the 2,9-di-*n*-butyl-1,10-phenanthroline ligand. This research was supported by NSF Grant CHE-8719538.

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Vibrational Spectra of Niobium(V) Fluoro and Oxo Fluoro Complexes Formed in Alkali-Metal Fluoride Melts

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Received November 21, 1989

Raman spectra of the molten system $LiF-NaF-KF-K_2NbF_7$ at 650 °C indicate the presence of NbF_7^{2-} ions with vibrational frequences at 626 (p), 371 (dp) and 290 cm^{-1} (dp). With the addition of small amounts of oxide, vibrational frequences due to a $NbOF_n^{(n-3)-}$ species are observed at 921 (p), 583 (p) and 307 cm^{-1} (dp) for oxide to niobium(V) mole ratios up to approximately 2. The most probable value of n is 5. Infrared spectra of solidified melts support the existence of a niobium-oxygen double bond in this complex. The vibrational spectrum is in accord with the band pattern of monomeric $NbOF_5^{2-}$ with a C_{4v} symmetry. Further additions of oxide lead to formation of $NbO_2F_n^{(n-1)-}$ complexes. Bands in the Raman spectrum of the melt at 878 and 815 cm^{-1} and in the infrared spectrum of the solidified melt at 879 and 809 cm^{-1} are ascribed to stretching vibrations of the NbO_2 entity. The Raman spectrum and the infrared spectra are consistent with the presence of $NbO_2F_4^{3-}$ ions of C_{2v} symmetry. Melts saturated with oxide show vibrational frequencies that are likely to be due to $[NbO_3F_n]^{(1+n)-}$-containing species which, furthermore, seem to polymerize.

Introduction

Only very few Raman spectroscopic investigations have been performed on fluoride melts. This is probably due to the experimental difficulties in handling such extremely corrosive systems at elevated temperatures. Most of the previous publications have been concerned with the species formation in the industrial important cryolite melts.[1-3] As far as we know, only one investigation concerning fluoride melts containing refractory metal fluorides (ZrF_4) has been reported in the literature.[4]

This is rather surprising since it is well-known[5-7] that refractory metals such as niobium and tantalum can be plated from metal fluorides dissolved in alkali-metal fluoride melts and in this way give very corrosion-resistant surface layers.

Solid K_2NbF_7 has been shown to contain discrete NbF_7^{2-} ions with a C_{2v} symmetry.[8] The Raman spectrum[9] of this salt has bands at 388, 630, and 782 cm^{-1}. Contrary to this, solid $CsNbF_6$, which contains octahedral NbF_6^-, shows Raman bands[9] at 280, 562, and 683 cm^{-1}. Infrared spectra[10] of solid K_2NbF_7 and spectra[10] of Nb(V) in molten KF-LiF showed bands characteristic of the NbF_7^{2-} ion.

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