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Photoluminescence studies of iodobis-(tricyclohexylphosphine)copper(I) and iodobis- (tricyclohexylphosphine)copper(I) benzene solvate

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Abstract Two newly prepared complexes were found to exhibit strong solid state emission behavior. The complexes are iodobis-(tricyclohexylphosphine)copper(I) and iodobis-(tricyclohexylphosphine)copper(I) benzene solvate. To understand the emission behavior of these complexes, density functional theory (DFT) calculations were employed. These calculations allowed the identification of major atomic contributions to HOMO, LUMO and LUMO + *n* orbitals. The excitation mechanism was found to be a combination of ligand to metal charge transfer (LMCT) and metal to ligand charge transfer (MLCT), with the dominance of the former. The emission lifetimes were also investigated and the decays of the complexes were found to be a bi-exponential in both methanol and cyclohexane.

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1. Introduction

The coordination chemistry of Cu(I) is both interesting and important due to its extensive structural and stoichiometric variation. Additionally, Cu(I) chemistry has catalytic applications and is involved in certain biochemical reactions. The presence of copper in copper-containing proteins establishes

the need for modeling of its coordination sites (Rudmann et al., 2002).

Copper(I) complexes with phosphine based ligands have received considerable attention in the past few years since these complexes can be used as sensitizers for conducting materials, which is an important goal in material sciences (Tsubomura et al., 2005).

Specially designed copper(I) complexes have long lifetimes for the excited MLCT state (Kovalevsky et al., 2004). Some copper halide compounds are used as imaging systems for electronic applications (Chesnut et al., 1999).

For photophysical properties, many papers (Horvath, 1994; McMillin and McNett, 1998; Kutal, 1990; Blasse, 1999; Tasboyama et al., 2007; McCormick et al., 2006; Jia et al., 2005; Bowmaker et al., 2002) have dealt with mononuclear copper(I) complexes. Horvath (1994) has made some extensive studies on the photophysical properties of some copper(I) complexes

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and suggested that photoinduced redox process in some systems may be medium-dependent and involve the formation and decay of hydride intermediates. Kutal (1990) has reported a wide diversity of metal-ligand combinations of d^{10} metal complexes based on the spectroscopic and photochemical properties.

Simon et al. (1996), Ford et al. (1999), Vitale and Ford (2001), De Angelis et al. (2006) and Cariati et al. (2005) have reported an extensive review on the emission behavior of polynuclear copper(I) complexes. Yam and co-workers (Yam et al., 1994, 1996a,b,c, 1997, 1998; Yam, 1997) have studied the photoluminescence properties of a class of multinuclear alkynyl-copper(I) complexes, which display several acetylide bonding modes and a diversity of polynuclear copper(I) structures.

Blaskie and McMillin (1980) have reported the complete quenching of the metal to ligand charge transfer emission exhibited by $\text{Cu}(\text{dmp})_2^+$ (where $\text{dmp} = 2,9\text{-dimethyl-}1,10\text{-phenanthroline}$) in a weakly basic solvent such as chloroform by acetonitrile, methanol and water. The excited state and redox properties of cuprous phenanthroline and bipyridine derivatives have received much attention recently due to their broad absorption bands in the visible region with high extinction coefficients (Horvath, 1994; Kutal, 1990; Kalyanasundaram, 1992; Ferraudi and Muralidharan, 1981).

In this paper, it is observed that $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2$ {iodobis-(tricyclohexylphosphine)copper(I)} and $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2\cdot\text{C}_6\text{H}_6$ {iodobis-(tricyclohexylphosphine)copper(I) benzene solvate} exhibit strong emission behavior, are reported. To probe the nature of transitions leading to emission, density functional calculations were employed. The fluorescence decay studies of these complexes in methanol and cyclohexane are also presented.

2. Experimental

2.1. Preparations

The two complexes were synthesized on the basis of a stoichiometry of 1:1:2 ($\text{Cu(I)}:\text{I}:\text{Ligand}$) and consequently characterized by X-ray crystallography (Seddigi, xxxx). For fluorescence emission and lifetimes measurements, samples were prepared by dissolving the complexes in methanol and cyclohexane. The concentration of each complex was kept at 10^{-5} M in all samples. All the measurements were performed at 25 °C.

2.2. Solid state emission

The emission spectra of the prepared complexes were recorded using spectrofluorometer (Shimadzu, Model RF 5301 PC). A special set-up was developed. The test sample was spread uniformly on a double-sided tape attached to a 0.5 in. $\times$ 1.5 in. piece of non-emitting black cardboard.

The excitation wavelength was scanned to get the maximum emission. The maximum emission was obtained at an excitation wavelength of 230 nm. A xenon lamp was applied as a broad light source for the excitation of the samples in this spectrofluorometer. Emission spectra of the complex were recorded in 300–700 nm region at room temperature.

2.3. Ab initio calculations

The calculations were carried out using PC-based Gaussian 98W software package (Frisch et al., 1998). The chosen basis

set was LANL1DZ, representing core orbitals (non-valent) for heavy atoms (I, Cu and P) in the form of primitive Gaussian type orbitals. The Z-matrix for $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2$ was constructed. Owing to the size of the molecules under investigation, the calculations were performed with the alkyl and aryl phosphine ligands replaced by a PH_3 group.

2.4. Absorption and fluorescence spectra

Absorption spectra were taken for the complexes dissolved in methanol and cyclohexane. A lamda-5 (Perkin–Elmer) UV/VIS spectrophotometer was employed. With regard to fluorescence spectra, SPF-500 spectrofluorometer, equipped with a xenon arc lamp, was used. All fluorescence spectra were corrected for lamp intensity and photo-multiplier sensitivity.

2.5. Fluorescence lifetimes

A mode-locked Nd:YAG laser in combination with a cavity-dumped synchronously-pumped dye laser was used as an excitation source to study the fluorescence decays of the complexes in methanol and cyclohexane. The excitation wavelength was set at 300 nm. Excited-state lifetimes were measured by using a time-correlated single-photon counting spectrometer described elsewhere (Than Htun et al., 1995).

3. Results and discussion

3.1. Solid state emission

The coordination around the copper atom in both complexes is nearly trigonal planar. The detailed structural aspects of the prepared complexes will be reported elsewhere. Both complexes emit radiation around a wavelength of 380 nm, when excited at 230 nm. The solid state emission of $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2\cdot\text{C}_6\text{H}_6$ is shown in Fig. 1.

Usually, Cu(I) has no emission since it has no $d-d$ transition (d^{10} system), but to understand the emission behavior of the CuI phosphine complexes, *ab initio* method was used. In particular, to obtain a description of frontier molecular orbitals for the complexes, density functional theory (DFT) calculations were employed. The major contributing atomic orbitals

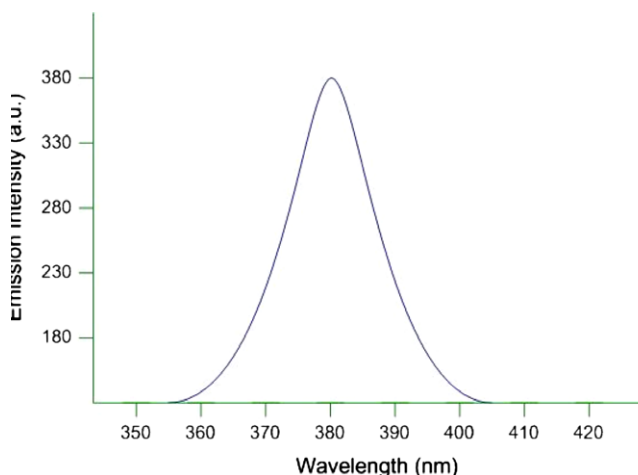


Figure 1 Emission spectrum of $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2\cdot\text{C}_6\text{H}_6$.

to HOMO and LUMO molecular orbitals of motifs observed for the complexes are shown in Table 1.

In HOMO (Table 1), there is a good contribution from both metal and ligands. Definitely, there is more contribution from ligand orbitals. In LUMO, there is good contribution from both metal and ligand, with more contribution coming from metal orbitals. Both LMCT and MLCT excitation mechanisms are operating, but there is more contribution from the former. Both of these competing mechanisms explain the strong emission behavior of the prepared complexes.

3.2. Emission lifetime studies

The studied complexes demonstrate broad absorption bands with absorption maximum at about 250 nm in both methanol and cyclohexane. However, the absorption spectra are resolved into two bands in methanol showing a shoulder at about 270 nm. Since iodide and tricyclohexylphosphine ligands have no acceptor orbital of low energy required for metal to ligand charge transfer transitions, the absorption spectra of the copper (I) complexes may be characterized by charge transfer to solvent (Horvath, 1994; Adamson and Fleischauer, 1975).

In methanol, $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$ complex display an observable emission band at about 400 nm in addition to an intense emission band at about 330 nm. Although, $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2$ has an emission at 330 nm, the emission band at 400 nm is not readily notable in methanol. The fluorescence spectrum of $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$ in methanol is shown in Fig. 2. In cyclohexane, the two complexes have shown a broad emission band at about 330 nm but the emission at 400 nm is also not notable.

The fluorescence decays of the complexes in both solvents were measured at 330 nm and 400 nm respectively, by exciting at 300 nm. As reported in Tables 2 and 3, the fluorescence decays at both emission wavelengths can be fit into a bi-exponential with two components. Fig. 3 shows the fluorescence decays of $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$ at 330 nm and 400 nm in methanol.

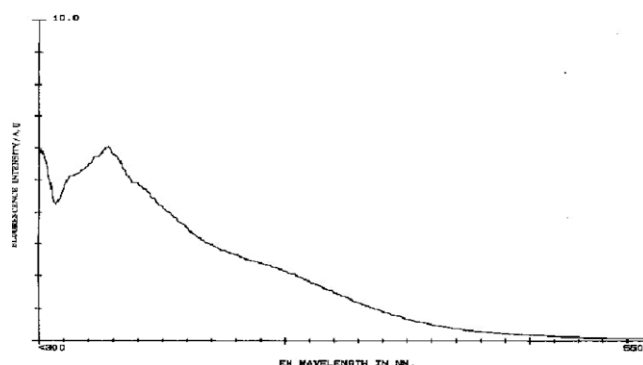


Figure 2 Fluorescence spectrum of $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$ in methanol.

In both solvents, the decay profiles of all complexes have generally shown a faster decay of the short-lived component at the longer wavelength (400 nm) in contrast with the long-lived component.

Copper in the ground-state is formally a Cu (I) ($3d^{10}$) in all complexes. Immediately after being excited, it is quite likely that the copper becomes Cu (II) ($3d^9$), yet the complexes still retain the same geometry of the ground-state copper (I) complexes. Thus, the intense emission band at 330 nm may be attributed to a charge transfer to solvent excited-state emission and subsequently the short-lived component may well be the time component from that excited-state.

With simple ligands, the coordination of Cu(I) is almost invariably tetrahedral. But for Cu(II), a common coordination is five or six. Kinetically, copper(I) complexes in solution are quite labile to ligand substitution (Roundhill, 1994). Therefore, it is possible that Cu (II) being in the excited-state becomes coordinatively unsaturated and the excited-state may then be perturbed by interaction with the surrounding solvent molecules.

Table 1 Major contributing atomic orbitals to HOMO and LUMO molecular orbitals of the emitting CuI complexes.

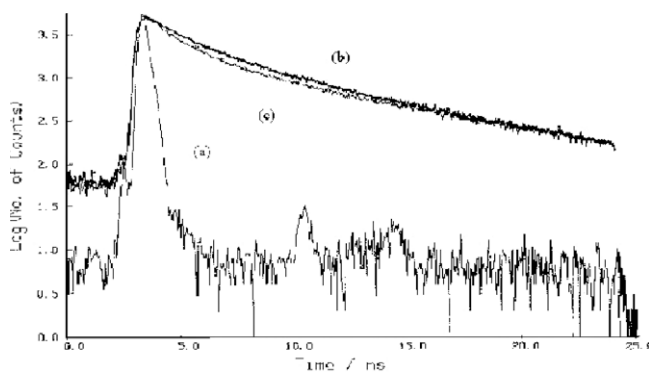
Atom	HOMO	LUMO and LUMO + n		
	HOMO 21	LUMO 22	LUMO 23	LUMO 24
Cu	−0.33480 7D-1	0.92892 3S	0.27941 5P _x	−0.16556 5P _z
	−0.10182 8D-1	−0.67348 6P _y	0.29725 6P _x 1.04433 6P _y −0.71090 6P _z	0.98113 6P _z
I	0.48403 3P _z	0.27941 4P _y	−0.22084 4P _x	−0.22153 4P _z
	0.48090 4P _z			
P1	−0.11357 2S	−0.22512 1S	0.53588 P _x	−0.18168 1S
	0.10537 4P _z	−0.88761 2S	0.11648 4P _y	−0.72298 2S −0.11691 3P _z 0.16904 4P _y −0.28633 4P _z
P2	0.11357 2S	−0.22512 1S	0.53588 4P _x	0.18168 1S
	0.10537 4P _z	−0.88761 2S	0.11648 4P _y	0.72298 2S −0.11691 3P _z −0.16904 4P _y −0.28633 4P _z

Table 2 Fluorescence lifetimes of copper(I) complexes in methanol.^a

Complexes	Fluorescence band at $\lambda_{em} = 330$ nm				Fluorescence band at $\lambda_{em} = 400$ nm			
	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A'_1	τ'_1 (ns)	A'_2	τ'_2 (ns)
$\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2$	0.956	1.88	1.13	5.56	1.29	1.45	0.606	7.21
$\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$	0.937	2.27	0.875	6.23	1.17	1.59	0.687	7.24

^a $\lambda_{exc} = 300$ nm.**Table 3** Fluorescence lifetimes of copper(I) complexes in cyclohexane.^a

Complexes	Fluorescence band at $\lambda_{em} = 330$ nm				Fluorescence band at $\lambda_{em} = 400$ nm			
	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A'_1	τ'_1 (ns)	A'_2	τ'_2 (ns)
$\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2$	1.52	2.48	0.826	6.17	1.80	1.68	0.480	7.68
$\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$	1.40	2.23	0.957	5.62	1.87	1.64	0.462	7.07

^a $\lambda_{exc} = 300$ nm.**Figure 3** Fluorescence decays of $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$ in methanol. (a) Pump pulse (b) 330 nm and (c) 400 nm.

However, the interaction with benzene cannot be excluded in the case of $\text{CuI}(\text{P}(\text{C}_6\text{H}_{11})_3)_2 \cdot \text{C}_6\text{H}_6$. This interaction seems to lower the energy of the system causing the fluorescence emission to be shifted at 400 nm. Hence, the long-lived component may offer the possibility of the formation of metal-centered exciplex between a coordinatively unsaturated metal complex and surrounding molecules in the excited-state. Further, the surrounding molecules may act as a ligand quenching the fluorescence emission of the charge transfer to solvent excited-state and causing the lifetime of short-lived component shorten at longer wavelength.

Time-resolved emission measurements have indicated that the excitation with 300 nm UV pulses initiates the formation of at least two different species emitting in the range of 300–500 nm. On the basis of the experimental data, it is therefore concluded that the observed bi-exponential behavior may be due to the overlap between the two fluorescence emission bands.

4. Conclusions

Both of iodobis-(tricyclohexylphosphine)copper(I) and iodobis-(tricyclohexylphosphine)copper(I) benzene solvate show strong emission. Interpretation of the emission spectra obtained for the solid state species of known structure was realized with the aid of DFT calculations. These calculations allowed the identification of major atomic contributions to

HOMO, LUMO and LUMO + n orbitals. The excitation mechanism were found to be a combination of LMCT and MLCT, with the dominance of the former.

The decays of the complexes were found to be a bi-exponential in both methanol and cyclohexane. Recent experimental data provides qualitative information about the formation of exciplex in both solvents between a coordinatively unsaturated metal complex and surrounding molecules. Further work on these complexes such as temperature effect, ligand substitution, solvent effect is needed to shed more light on the photochemical behavior of these complexes in the excited-state.

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