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# THE PHOTOLUMINESCENCE PROPERTIES OF THE COPPER(I) CLUSTERS $Cu_4I_4A_4$ (A = AROMATIC AMINE) IN SOLUTION

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## SUMMARY

Solutions of the copper(I) tetranuclear clusters $Cu_4I_4A_4$ (A = pyridine or substituted pyridine) in room temperature toluene display two luminescence bands in the visible region of the spectrum. The higher energy emission has been assigned as a transition from a metal-to-pyridine charge transfer state on the basis of pyridine substituent effects, while the much more intense lower energy emission has been assigned as a cluster-centered transition owing to its presence even when A is a saturated amine. The two emissions display relatively long, but different, lifetimes and appear to originate from states which are essentially uncoupled. Calculations using effective relativistic core potential methods suggest that the cluster-centered emission is from an excited state which can be visualized as the result of electronic promotion from a HOMO which is largely iodide in character to a LUMO which is largely copper (4s and 4p) in character.

## INTRODUCTION

The photophysical properties of mononuclear and polynuclear complexes of copper(I) are extremely rich. For example, metal to ligand charge transfer (MLCT) emission has been observed from ambient temperature solutions of certain mononuclear Cu(I) complexes of sterically bulky ligands (refs. 1,2). One such case is $Cu(dpp)_2^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) for which the MLCT luminescence lifetime is 258 ns in 25 $^{o}$C dichloromethane (ref. 2). A large number of polynuclear copper(I) complexes have also been demonstrated to be luminescent in the solid state (refs. 3,4), and the photoproperties of these materials have been the subject of investigation of the possible correlations to structural considerations. Much less attention has been addressed to the solution phase photophysical properties of the polynuclear

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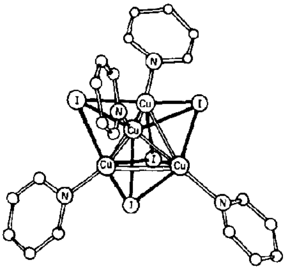
copper(I) systems, although Kunkely and Vogler have described the photoemission spectra in ambient temperature of the tetranuclear complexes $Cu_4I_4py_4$ (py = pyridine) and $Cu_4I_4mor_4$ (mor = morpholine) in room temperature benzene (ref. 5). In these cases, similar broad visible range emission bands were noted for both the cluster of the aromatic amine pyridine and that of the saturated amine morpholine. Thus, it was concluded that a MLCT assignment was inappropriate and that these emissions should be assigned to s -> d transitions (ref. 5).

The structure of the $Cu_4I_4py_4$ cluster has been determined by x-ray crystallography (ref. 6) to be a tetrahedral array of copper(I) centers enclosed in another tetrahedron of iodides. The pyridines appear at the vertices of the $Cu_4$ tetrahedron. Figure 1 is a representation of this structure.

Figure 1: The Structure of $Cu_4I_4py_4$ (ref. 6).



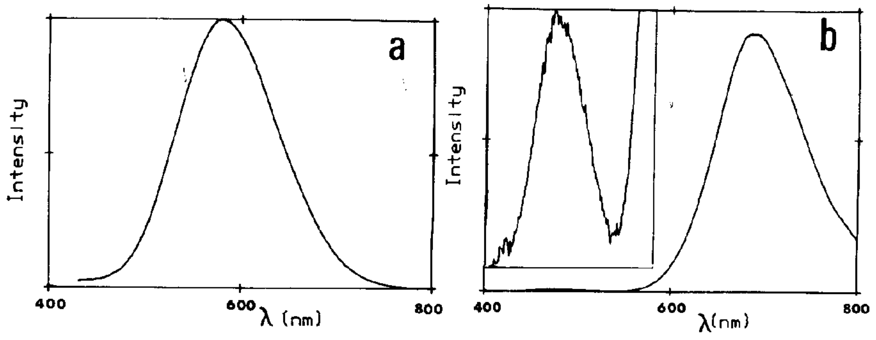
Given that copper(I) has a $3d^{10}$ electronic configuration, little metal-metal bonding between Cu(I) centers in polynuclear complexes would be expected to result from the ground state interactions of the d-orbitals. (However, configuration interaction with the 4s and 4p orbitals may lead to modest metal-metal bonding interactions (ref. 7).) In contrast, an excited state (e.s.) formed by promotion of an electron from an antibonding metal d-orbital of a polynuclear Cu(I) compound, such as proposed (ref. 5) for the emissive e.s. of $Cu_4I_4A_4$, may be expected to display enhanced metal-metal bonding. Such behavior has been argued for a variety of dinuclear metal complexes e.g., the $d^8$-$d^8$ dimer $Pt_2(u\text{-}P_2O_5H_2)_4{}^{4-}$ (refs. 8-10) and the $d^{10}$-$d^{10}$ dimer $Pd_2$(bisdiphenylphosphinomethane$)_3$ (refs. 11,12), which have no formal, ground state bonding between the metal centers. These display unusually long-lived emissions from triplet excited states assigned as arising from $\sigma^{*}_{mm}$ -> $\sigma^{b}_{mm}$ orbital parentages. Transient resonance Raman spectral studies support the view that the metal-metal bonding is enhanced in the excited state (ref 13). The potential analogy between the excited state properties of such dinuclear systems and those of the tetranuclear Cu(I) clusters stimulated the present reinvestigation of the solution phase luminescence properties and theoretical study of the latter systems.

## RESULTS AND DISCUSSION

### 1. Emission Spectral Properties

The luminescence spectra recorded at ambient temperature for the $Cu_4I_4py_4$ cluster as solid crystals and as a solution in toluene are illustrated in Figures 2a and 2b.

Figure 2: Emission spectra at 294 K of $Cu_4I_4py_4$ a) in the solid, b) in toluene solution (inset is expanded scale showing the MLCT emission in solution). Excitation wavelength was 350 nm in each case



Notably, in each case, a strong, broad emission band is observed, but, in agreement with previous workers (ref. 5, 14), the position of the band is markedly affected by the medium. The solid state spectrum maximum occurs at 580 nm, the solution phase maximum at 690 nm. The luminescence decays of these emissions proved to be exponential with the lifetimes 11.1 and 10.6 µs for the solid and solution phase systems, respectively, at 294 K. Although medium dependent, the position of this emission band proved essentially independent of substituents on the pyridines (Table 1), a fact which prompted our initial assignment (ref. 15) of the longlived, emissive e. s. as a triplet metal cluster centered (MCC) excited state (see below).

TABLE 1
Maxima and Lifetimes for the MLCT and MCC Emission Bands of $Cu_4I_4A_4$ in Toluene Solution[a]

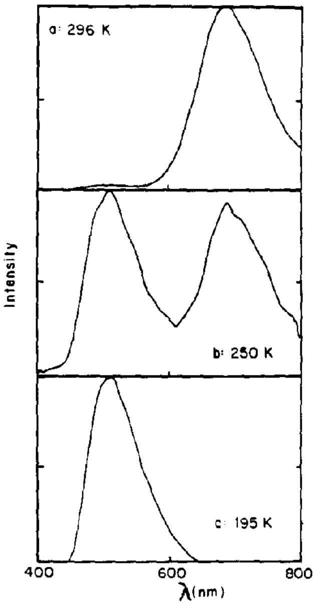
| A | $\lambda_{MLCT}$ | $\tau$ | $\lambda_{MCC}$ | $\tau$ |
|---|---|---|---|---|
| 4-t-butylpyridine | 468 nm | 0.40 μs | 696 nm | 11.1 μs |
| 4-benzylpyridine | 473 | 0.56 | 692 | 11.6 |
| pyridine | 480 | 0.45 | 690 | 10.7 |
| 4-phenylpyridine | 520 | 0.13 | 694 | 10.2 |
| 3-chloropyridine | 537 | 0.35 | 675 | 12.6 |
| piperidine | b | | 680 | 0.11 |
| morpholine | b | | 671 | 0.51 |

a. In $N_2$ deaerated solution at 294 K.
b. No emission observed in 294 K solution or at lower temperatures.

A close examination of the solution phase spectrum shows a second band at 480 nm (see inset in Figure 2b) also displaying exponential decay but with a shorter lifetime of 450 ns. A similar pattern of emission bands has been noted for a series of other $Cu_4I_4A_4$ complexes when A is a substituted pyridine (Table 1). At lower temperatures the relative intensities of these two bands change dramatically so that at 77 K the higher energy emission is clearly the dominant peak in the luminescence spectrum. This pattern is illustrated in Figure 3 for the 4-phenylpyridine derivative. The sensitivity of the higher energy band to the nature of the ligand substituents, plus the fact that analogous bands are not seen in the spectra of those complexes where A is a saturated amine, led to the assignment of this to radiative decay from a copper to pyridine MLCT excited state (ref. 15).

The solution phase emission behaviors of these complexes display some truly remarkable properties (refs. 14 and 16).

Figure 3 (below, left side): Luminescence spectra of $Cu_4I_4$(4-phenylpyridine)$_4$ in deaerated toluene solution at a) 296 k, b) 250 K and c) 195 K. Excitation at 350 nm in each case; Intensities normalized to the tallest peak in each spectrum.



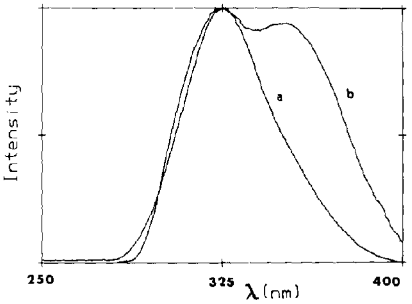
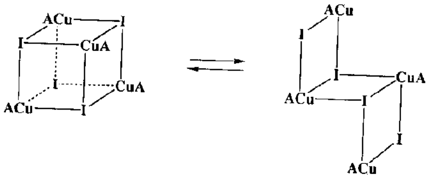


Figure 4 (right side): Excitation spectra of the MCC and MLCT emission bands of $Cu_4I_4py_4$ in 294 K toluene solution: a) MCC at 690 nm; b) MLCT at 476 nm

A key one is that the lifetimes of the MLCT and MCC bands are both relatively long and remain different from each other even in ambient temperature fluid solutions. A second is that the two emitting states are sufficiently uncoupled that the higher energy MLCT state can be quenched by Lewis bases (presumably via formation of exciplexes as described previously for the MLCT state of certain mononuclear Cu(I) complexes (refs. 2,17)) without affecting the lifetime of the stronger, lower energy MCC emission. A third is the remarkable temperature dependence of the relative intensities of the two bands which is illustrated for toluene solutions of the 4-phenylpyridine cluster in Figure 3. A fourth is that the excitation spectra of the two emission bands differ significantly even in ambient temperature solution (Figure 4). All of the above observations are clear indications that the excited states responsible for these two emissions are essentially uncoupled, i.e., that internal conversion processes between the higher energy MLCT state and the MCC state are significantly slower than are other pathways leading to the deactivation of the former.

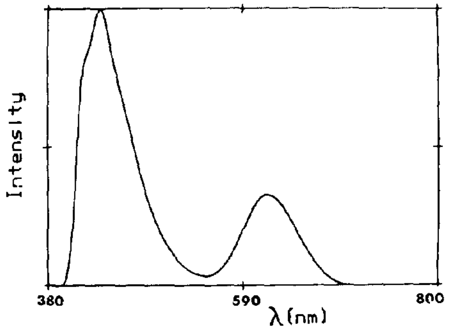
Given that the observation of two independent emissions from nonequilibrated excited states of a single transition metal complex is very rare under such ambient temperature fluid solution conditions, one is tempted to attribute the two emissions to the presence of two different chemical species in the solution. This explanation would be especially attractive given that Cu(I) complexes are extremely labile and that polymeric forms of the same $(CuIpy)_n$ stoichiometry are known and display exclusively MLCT type emissions. Therefore, one might argue that the two emissions are from two isomeric forms of the Cu(I) tetramer in labile equilibrium, e.g., closed and open forms such as

(Eq. 1)



the closed form being responsible for the MCC emission, the open form being responsible for the MLCT emission. The principal argument against this proposal is drawn from the photophysical behavior of the clusters in crystalline solids in which the structures have been shown to be the tetrahedral. At room temperature only MCC emission was observed in the solid samples (Figure 2a); however, as the temperature is lowered, the higher energy MLCT emission band ($\lambda_{max}$ 438 nm) becomes prominent (Figure 5) in a manner analogous to that of the toluene solutions under similar conditions. Furthermore, even in the crystalline solid the two emissions are uncoupled as evidenced by the dependence of their relative intensities on the excitation wavelength. Thus, we conclude that both the MLCT and MCC emissions are photophysical properties of tetranuclear cluster $Cu_4I_4A_4$ when A is an aromatic amine; however, we are extending our investigations of these systems to test this conclusion more critically.

Figure 5: Emission spectrum of crystalline $Cu_4I_4py_4$ in the solid state at 77 K. Excitation at 350 nm.



2. Theoretical Studies

A set of ab initio calculations was carried out in order to gain greater insight into the structures and the spectroscopy, especially the MCC transitions, of the tetrahedral $Cu_4I_4A_4$ molecules and of other species of the $(CuI)_nA_m$ stoichiometry. The development of relativistic effective core potentials (ref. 18) which enable the wavefunction to be restricted to valence electrons, allows accurate calculations even on such large systems. The ARGOS set of programs (ref. 19) written by R. M. Pitzer was used. Hartree-Fock calculations provided the molecular orbitals, orbital energies and total energies of the complexes.

Basis functions were taken from ref. 18. It seemed likely that the 4p-orbitals would be important on copper, so three possibilities were considered. For a dimer $Cu_2I_2(NH_3)_4$, a single gaussian set of p-functions was placed on each Cu, and its exponent was optimized (to 0.0979). The total Cu p-population is 0.302 electrons on each Cu and use of the p-functions lowered the total energy of the dimer by 0.0768 hartrees, hence, the Cu p-orbitals do make significant contributions to the wave function. Comparison was made to two other Cu p-functions: the STO-3G and the Los Alamos contracted (2p) functions (refs. 20,21) which are standard bases in GAUSSIAN88. Calculations on tetrahedral

$Cu_4I_4(NH_3)_4$ showed that the optimized single gaussian gave a lower energy than either of the comparisons, so it was used in all subsequent computations.

More flexible "double-zeta" basis sets were made by allowing the most diffuse function of each of the contracted gaussians (except the Cu 4p and H 1s functions) to be a separate basis function. STO-3G functions were used on hydrogens.

In order to keep the problem a tractable size, the calculations were for the most part carried out for A = $NH_3$; this of course excluded the MLCT states from consideration. Calculations were carried out for the following species: a) CuI(py) and CuI($NH_3$) monomers, b) the dimers $Cu_2I_2(NH_3)_2$ and $Cu_2I_2(NH_3)_4$, c) an "open" trinuclear cluster $Cu_3I_3(NH_3)_3$ (a model for the "stairstep" polymer, (CuI(py))n, from which structure (ref. 22) the bond lengths and angles were taken) and d) the tetrahedral cluster $Cu_4I_4(NH_3)_4$. For calculations on the mono-, di- and tetranuclear structures, the Cu-Cu, Cu-I, Cu-N bond lengths and relevant bond angles were taken from the x-ray structure of $Cu_4I_4py_4$ (ref. 6). Ammonia was assumed to be tetrahedral with the same N-H bondlengths as free $NH_3$.

Calculations on the hypothetical monomeric species CuIA were carried out to examine possible differences in the interactions between the metal and the amine ligands $NH_3$ or pyridine. Results of the computations in terms of the net charges on each atom or fragment are summarized in Table 2. Notably the net ligand charges on py and $NH_3$ are quite close, +0.118 and +0.097, respectively. The calculations suggest that $\pi$-interactions between the Cu and the N of pyridine are at most minor. Sigma overlap populations, although much larger and bonding, are modest, and the Cu 4s - N 2p overlap dominates the Cu-N sigma interaction. In addition the HOMO-LUMO gap is nearly the same in both monomers. Also, for each monomer the HOMO is almost completely (97%) composed of the iodine p-orbitals for each molecule, and the LUMO is primarily Cu 4s with minor contributions from Cu 4p and N 2s. Thus, these results suggest that use of $NH_3$ instead of pyridine in the calculations does not greatly alter the electronic structure of the $(CuI)_nA_m$ complexes. A similar conclusion might also be drawn from examining key features of the crystal structures of $Cu_4I_4py_4$ and $Cu_4I_4mor_4$ (ref. 6). The Cu-Cu, Cu-N and Cu-I bond lengths are nearly identical for the two structures despite the possibility for $\pi$-bonding interactions between the Cu(I) center and the pi-unsaturated pyridine.

Table 2: Results of <u>ab initio</u> Hartree Fock calculations on copper(I) iodide amine complexes $(CuI)_nA_m$ using relativististic effective core potentials

| Parameter Calculated | $CuI(NH_3)$ | CuI(py) | $Cu_4I_4(NH_3)_4$ |
|---|---|---|---|
| Atomic Charges | | | |
| Cu | +0.474 | +0.459 | +0.337 |
| I | -0.571 | -0.577 | -0.393 |
| A | +0.097 | +0.118 | +0.056 |
| HOMO | | | |
| Energy[a] | -0.2870 | -0.2780 | -0.3079 |
| %Cu | 2.5 | 2.2 | 17.4 |
| %I (all p) | 97.2 | 97.1 | 80.6 |
| LUMO | | | |
| Energy[a] | +0.0412 | +0.0493 | +0.1308 |
| %Cu | b | b | 92 |
| %I | b | b | 8 |

a) Energies in hartrees. b) not calculated

The Hartree-Fock computations on the tetrahedral $Cu_4I_4(NH_3)_4$ reveal an important feature of the highest energy occupied molecular orbitals including the HOMO itself. For each of these, the predominant contributors to the molecular orbitals are the iodine p-orbitals. Indeed, the HOMO is 80.6% iodine and only 17.4% copper in composition. The calculations on the two dimers and the trimer each give very similar compositions of the HOMO. Thus, according to these calculations for each of the $(CuI)A_m$ species examined, the HOMO is principally an iodine nonbonding orbital, although it has a slightly Cu-Cu antibonding character. In contrast, the LUMO for the tetranuclear cluster was computed to be 92% copper and but 8% iodide in composition. From overlap population calculation, the LUMO was concluded to be Cu-Cu bonding in character owing to mixing of the Cu 4s orbitals but also antibonding with respect to the Cu-I interactions. Thus, the previous suggestions that the lowest excited state of such clusters was the result of 3d -> 4s excitation or of delocalized orbitals of the $Cu_4$ core (refs. 5 and 15) appear overly simplistic. According to these computational results, this e. s. is apparently the result of excitation between orbitals delocalized over the $Cu_4I_4$ core best represented as a ligand (i.e., $I_4$) to metal (i.e., $Cu_4$) charge transfer transition.

In the context of the above calculations, it is notable that the chloride cluster $Cu_4Cl_4(py)_4$ displays only a single emission band in either the solid or in solution. The luminescence spectrum of the solid salt showed a band maximum of 531 nm at 294 K and of 522 nm at 77 K. In 294 K toluene solution, the observed band maximum was 510 nm for a very weak emission. While the shift to higher energy would be qualitatively consistent with the above ligand-to-metal charge transfer assignment of the cluster centered transition, an alternative assignment would be that the emission observed for $Cu_4Cl_4py_4$ is from a MLCT state. The latter would be consistent with the absence of observable emission from the piperidine complex $Cu_4Cl_4(pip)_4$ (solid state) and with the red shifts for emissions from $Cu_4Cl_4$(4-phenylpyridine) (602 nm in 294 K toluene, ref. 23) and $Cu_4Cl_4$(N,N-diethylnicotinamide)$_4$ (662 nm in 13 K $CH_2Cl_2$, ref. 24).

In summary, it is clear that the $Cu_4I_4A_4$ solutions display complex photophysical behavior indicating emission from several poorly coupled excited states. Owing to the high lability of Cu(I), it is difficult to exclude the possibility that this behavior results from the presence of multiple species. However, the analogous properties of these materials in the solid state argues for this behavior being characteristic of the intact tetrahedral clusters. Results from ab initio calculations indicate that the intense lower energy emission bands are from iodide to metal charge transfer excited states; however, these preliminary conclusions are being tested by experimental and computational refinement (ref. 25).

## EXPERIMENTAL PROCEDURES

### 1. Synthesis of Compounds

The $Cu_4I_4A_4$ clusters were prepared by published procedures (refs. 26,27) and recrystallized from benzene. The analogous chloride clusters $Cu_4Cl_4A_4$ were prepared as described (ref. 27) under $N_2$ and stored under argon.

2. Luminescence Procedures

All spectra and lifetimes were obtained using deaerated solutions prepared using vacuum line techniques. Spectra were obtained using a SPEX Fluorolog 2 model III emission spectrometer interfaced with a SPEX Datamate II data station. Lifetimes were measured on a YAG laser system described previously (ref. 28), while time resolved spectra were obtained using an apparatus which employs nitrogen laser for excitation and a PAR 4400 boxcar system for data recording and manipulation (ref. 29).

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