Bright Phosphorescence of a Trinuclear Copper(I) Complex: Luminescence Thermochromism, Solvatochromism, and "Concentration Luminochromism"

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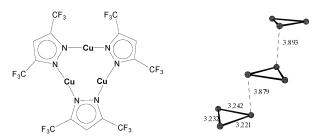Received June 17, 2003; E-mail: omary@unt.edu; dias@uta.edu

Trinuclear d[10] complexes have garnered considerable interest in recent years in large part because of their fascinating luminescence properties.[1−5] Some of these compounds show very interesting behavior in the presence of various reagents (solvents, heavy metals, and Lewis acids). For example, Balch reported that a trinuclear Au(I) complex exhibits "solvoluminescence", a spontaneous orange emission upon contact with solvent following irradiation with long-wavelength UV light.[2a] Related complexes were found to form charge-transfer complexes with nitro-9-fluorenones,[2b] and some form hourglass figures on standing in air.[2c] Burini and Fackler reported the formation of acid−base supramolecular stacks with visible luminescence on interaction of nucleophilic Au(I) trinuclear complexes with several types of electrophiles, including naked heavy metal ions[3a] and neutral inorganic[3b] and organic[3c] Lewis acids and electron acceptors. Gabbaï and co-workers have reported that a trinuclear Hg(II) complex forms 1:1 adducts with aromatic hydrocarbons, which become brightly phosphorescent at room temperature due to a mercury heavy atom effect.[4] Meanwhile, photophysical studies for trinuclear complexes of Cu(I) and Ag(I) did not receive as much attention as their other d[10] counterparts.[1,5]

We have undertaken a systematic study of trinuclear, dinuclear, and mononuclear complexes of Cu(I) and Ag(I) with fluorinated pyrazolate ligands such as $[3,5-(CF_3)_2Pz]^-$ and have found that these complexes exhibit bright, tunable luminescence. These classes of complexes are targeted as potential candidates for emitting materials in molecular light-emitting devices (LEDs) because fluorination increases their volatility, thus facilitating thin-film fabrication, and because the presence of a closed-shell transition metal should enhance the phosphorescence.[4,6] Fluorinated ligands also endow other beneficial properties such as improved thermal and oxidative stability, and reduced concentration quenching of luminescence to metal adducts.[6−8] Such ligands also enable the isolation of exceedingly rare molecules such as $[HB(3,5-(CF_3)_2Pz)_3]MCO$ (where M = Ag, Au).[9]

In this paper, we describe the photophysical properties of the trinuclear copper(I) complex $\{[3,5-(CF_3)_2Pz]Cu\}_3$, henceforth referred to as **Cu$_3$**, which exhibits multicolor bright phosphorescent emissions that are sensitive to temperature, solvent, and concentration. The synthesis and structure of the **Cu$_3$** complex were reported earlier.[10] The structure (Chart 1) shows weak intramolecular (3.221−3.242 Å) and essentially no intermolecular Cu⋯Cu interactions (3.879; 3.893 Å).[11]

Photoluminescence emission and excitation spectra for crystals of **Cu$_3$** are shown in Figure 1.[12] The compound exhibits a bright orange emission in the solid state at room temperature. Interestingly, the emission color of **Cu$_3$** becomes red upon cooling to intermediate temperatures between room temperature and 77 K, but becomes

Chart 1. Molecular Structure and Packing Diagram of **Cu$_3$**[10]

orange again at 77 K. The orange emission at 77 K is due to the combination of two bands, a major red peak at ∼665 nm and a yellow shoulder at ∼590 nm. The yellow shoulder disappears at higher temperatures, leaving only the red emission, but band broadening at room temperature leads to orange emission. The lifetime of the major peak was 52.6 ± 0.8 μs at room temperature and 64.4 ± 1.0 μs at 77 K. The shoulder that appears at 77 K has a lifetime of 104 ± 2 μs.

Solutions of **Cu$_3$** exhibit luminescence that is greatly enhanced at cryogenic temperatures. We have discovered that the **Cu$_3$** luminescence can be easily fine- and coarse-tuned to multiple bright visible colors by each of the following factors: solvent, concentration, temperature, and excitation wavelength. Figure 2 shows selected examples of some spectra and photographs illustrating these dramatic changes in rigid frozen solutions.

The interesting luminescence behavior of crystals and rigid solutions of **Cu$_3$** implies a rather sophisticated photophysical behavior that we can only speculate upon at this stage. The facts that the bright orange-red emission of the **Cu$_3$** crystals has a structureless profile even at cryogenic temperature and that microsecond lifetimes were obtained are consistent with an assignment to a copper-based phosphorescence. The emission is likely related to Cu−Cu interactions because the $^3D_3$ lowest triplet sublevel of a free Cu(I) ion has an energy of 21 930 cm^{-1} (i.e., in the blue region).[13] At first glance, one is tempted to assign the **Cu$_3$** emission to intramolecular and not intermolecular Cu−Cu interactions on the basis of the crystal structural data above. However, further insights are gained by the frozen solutions data in Figure 2, which show structureless emissions whose energies (and colors) are solvent-dependent and exhibit red shifts upon increasing the concentration in some solvents to approach the solid-state behavior. These results suggest that the emission may be related to intermolecular interactions between **Cu$_3$** units. The crystal structure (Chart 1) shows that trimer units are connected by Cu−Cu interactions to form infinite zigzag chains. While the intermolecular Cu−Cu distances are too long for ground-state bonding interactions, it is not unreasonable to propose that they will contract in the excited state and cause the low-energy visible emissions, as suggested for

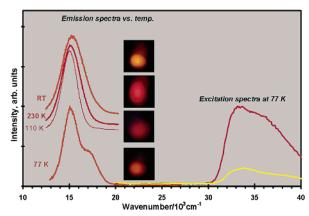† The University of Texas at Arlington.
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Figure 1. Photoluminescence spectra of **Cu₃**. All emission spectra were scanned with $\lambda_{ex} = 300$ nm, while the two excitation spectra monitored the emission at 550 nm (bottom) and 650 nm (top).
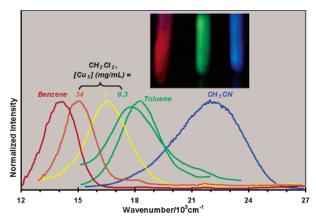

Figure 2. Representative emission spectra of rigid frozen solutions (77 K) of **Cu₃** versus solvent and concentration. Lifetimes at λ_{max} (left-to-right, respectively) are 80 ± 3, 62 ± 1, 52 ± 2, 98 ± 2, 84 ± 1, and 21 ± 1 μs. The photograph shows selected CH_2Cl_2, toluene, and CH_3CN frozen solutions in supracell quartz tubes exposed to UV light immediately after removal from a liquid nitrogen bath. The temperature increase on removing the sample from the bath changes the emission color of the CH_2Cl_2 solution from orange to red.

other Cu(I) and d¹⁰ systems.[14] The huge Stokes' shifts ($>18\,000$ cm⁻¹ !) suggest largely distorted excited states, consistent with this assignment. To understand the origin of the yellow shoulder observed at 77 K, we note that the excitation profile is similar for this shoulder and the major red peak, while the two bands have significantly different lifetimes. Thus, the excitation route is the same for the two bands, but they decay independently. The two bands are tentatively assigned to different sublevels of the emitting "triplet" excited state that is split by spin−orbit coupling. Crosby suggested that such sublevels behave independently and decay differently in metal complexes even if only one emission band is observed.[15]

The remarkable luminescence behavior of **Cu₃** and the sensitivity of the emission to various factors warrant further comments. The data are reminiscent of several novel optical phenomena that have been reported individually for other metal complexes. These phenomena are observed collectively for **Cu₃** together with another new phenomenon. The temperature dependence of the luminescence color seen for both solids and solutions of **Cu₃** illustrates "luminescence thermochromism", a phenomenon reported most notably for tetranuclear Cu(I) clusters.[5] The solvatochromism of the **Cu₃** luminescence is related to a few fascinating recent observations for several classes of d¹⁰ and d⁸ complexes.[16] The changes in luminescence energies in different solvents are related to both the

extent of excited-state association of **Cu₃** and the different electronic structure of various *[**Cu₃**·solvent] complexes. What is unusual about the results here is not only the selectivity even for similar solvents (e.g., toluene vs benzene) and the versatility of solvents in which **Cu₃** shows luminescence solvatochromism, but also the qualitative changes in the visible emission colors and spectra when the **Cu₃** concentration is varied in the same solvent. The most striking changes were seen in dichloromethane, in which the luminescence was tuned to essentially all visible colors between blue and red by varying the **Cu₃** concentration. This "concentration luminochromism", in which multiple visible colors are emitted by controlling the luminophore concentration, is an unprecedented optical phenomenon, to our knowledge.

Besides the scientific significance of these results, the observation of bright phosphorescence for crystals and sublimed thin films at room temperature is prompting us to pursue using **Cu₃** and related fluorinated complexes as emitting materials for molecular LEDs. Work is underway to control the photo- and electroluminescence properties of these complexes and to investigate the coinage metal family group trends.

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