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Luminescent mixed ligand copper(I) clusters $(CuI)_n(L)_m$ (L = pyridine, piperidine): thermodynamic control of molecular and supramolecular species[☆]

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Contents

Abstract

The photophysical properties of neutral adducts of CuI and the N-bound ligands pyridine (py) and piperidine (pip) of the type $Cu_nX_nL_m$ were studied as a function of the concentrations of the ligand L. For L = py, variation in the UV–Vis absorption and luminescence spectroscopic properties as a function of ligand concentration is rationalized as the result of

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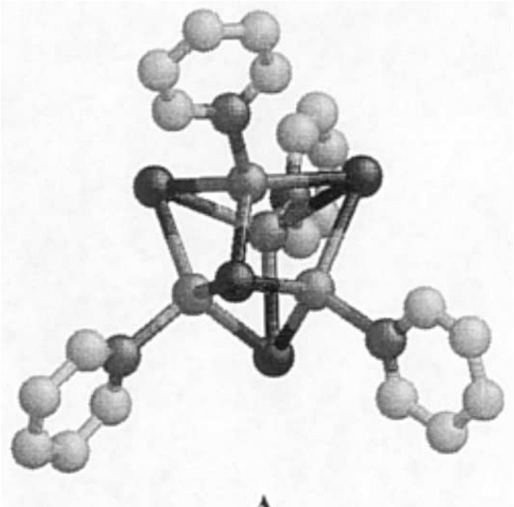
labile equilibria involving several species, most prominently the dinuclear complex $Cu_2I_2(py)_2$ and the 'cubane' cluster $Cu_4I_4py_4$. The ease of ligand exchange in solution was exploited for the self-assembly of mixed-ligand tetrameric compounds $Cu_4I_4(py)_n(pip)_m$ (where $n + m = 4$), which were identified through their photophysical properties. Factors determining these emission properties are discussed.

Keywords: Photophysical properties; N-bound ligands; Copper(I); Luminescence; Clusters

1. Introduction

Polynuclear adducts of cuprous halide salts and organic bases of general formula $Cu_nX_nL_m$ ($X = Cl$, Br or I; $L =$ N- or P-bound ligand) have been known since the beginning of the 20th century [1]. Copper(I) with a d^{10} electronic configuration lies at the border between transition and main group elements, and the polynuclear complexes are at an intersection between coordination compounds and supramolecular systems. Such adducts display an unusual wealth of stoichiometries and geometries [2–8], dependent on synthetic conditions. For example, CuI(pyridine) is obtained as a 'cubane' (closed) tetramer $Cu_4I_4(py)_4$ (**A**) from toluene or water through both homogeneous and heterogeneous synthetic routes, but as a 'step' polymer $(CuI(py))_n$ when isolated from acetonitrile [8d]. The diversity of structural types and stoichiometries can be attributed to the relative flatness of the ground-state potential energy surfaces of these d^{10} complexes. Kinetic barriers between different structures in solutions are low, so the species present are largely determined by thermodynamic control.



A

Numerous copper(I) complexes are luminactive, even at ambient temperature [8–13]. Hardt and coworkers [9] drew early attention to their remarkable luminescence properties with observations that compounds with aromatic nitrogen heterocycle ligands display emission spectra that are strikingly sensitive to temperature, a phenomenon they termed 'luminescence thermochromism'. The most extensive studies have been of cubane-type $[CuXL]_4$ clusters, especially the prototypical **A**, the properties of which will be summarized briefly. At 77 K, the luminescence from **A**, whether in a well characterized crystalline solid or in frozen toluene solution, appears blue to the eye, but at ambient temperature the emission from the solid appears yellow and that from toluene solution appears red. This behavior has been attributed to emissions from two excited states of similar energies but dissimilar orbital parentages that are poorly coupled owing to the different coordinates taken by molecular distortions relative to the ground state [8g]. The 77 K emission is dominated by a higher energy band that has been attributed (on the basis of ab initio calculations, ligand substituent effects, etc.) to a halide (I^-) to ligand (pyridine) charge transfer (XLCT) state. Although strong at low temperature, this emission is extremely weak at room temperature, where a lower energy emission dominates. Calculations and other considerations led to the conclusion that the latter band originates from an excited state (ES) of mixed halide-to-metal charge transfer (XMCT) and copper-centered $d \rightarrow s,p$ character [8f]. The term 'cluster centered' (CC) was coined to emphasize that the transition is localized on the Cu_4I_4 cluster and is essentially independent of ligand L [8d]. $Cu_4I_4(pip)_4$ (**B**), the analogous cluster of the saturated amine piperidine ($pip = C_5H_{10}NH$), displays a luminescence band similar to the CC band of **A**, but does not display an XLCT emission owing to the absence of ligand π^* orbitals. Thus, luminescence thermochromism is the norm for $Cu_4I_4L_4$ clusters when L is π-unsaturated, but is not seen when L is saturated.

Another factor contributing to the luminescence thermochromism of **A** is the dramatic red shift in the energy of the CC band in going from solid or frozen solution samples to fluid solutions [8d]: (an intermediate value of λ_{max}^{em} was seen in poly(methyl methacrylate) [10a], indicating steep rigidochromism. The ab initio calculations and the emission band Stokes shifts for **A** (up to $16\,300\ cm^{-1}$ for the CC band in 296 K toluene solution; $7600\ cm^{-1}$ for the XLCT band under the same conditions) also indicate that CC excited states are quite distorted relative to both the GS and XLCT excited states [8f,i]. Such distortion was suggested as the cause of the lack of communication between XLCT and CC states, and the reason for the rigidochromism of the LE band, as well as for the large reorganization energies found for electron transfer reactions of the CC* excited state of **A**.

This paper will discuss the facile interconversion between adducts formed by CuI with N-bound bases, which is revealed by their UV–Vis absorption and emission. Simple mass-action manipulation, i.e. changing the ratio of components, allows access to compounds of various stoichiometry, homo- as well as hetero-leptic, whose photophysical properties are discussed in light of those of **A** and **B**.

2. Experimental

2.1. Materials

Cuprous iodide (Alfa Products) was purified as reported [14]. Dichloromethane (Aldrich) was distilled from calcium hydride under N_2. Toluene and benzene were dried and distilled from sodium metal or from CaH_2 under N_2. Piperidine (Aldrich) was kept over KOH pellets, under Ar. Pyridine (Aldrich) was used directly from the bottle. Deuterium oxide (D_2O) was from Aldrich; 99% deuteration. Gases were obtained from Linde. Suba Seals (Aldrich) were used to cap the reaction and storage vessels and the cells and tubes used for UV–Vis spectroscopy. Microbore Teflon tubing from Cole–Palmer or double-point cannulae from Fisher were used to connect different vessels through the capping seals, allowing transfer of gases, liquids, and solids in suspension. Commercial and Suprasil quartz tubing were purchased from Aereus–Amersil or Wilmad.

2.2. Preparations

The pyridine tetramer $Cu_4I_4(py)_4$ (**A**) was prepared according to published procedures [8d]. Cuprous iodide was dissolved in a concentrated (3.5 M) KI aqueous solution, and the solution was stirred while a stoichiometric amount of the ligand was added. The resulting white precipitate was filtered out and washed with H_2O, EtOH and hexanes, and dried by blowing N_2 over it overnight. The compound obtained was a purer white when the synthesis was performed with Schlenk and cannula techniques under Ar atmosphere. The X-ray powder pattern was consistent with that derived from the single-crystal literature data [2a].

The piperidine tetramer $Cu_4I_4(pip)_4$ (**B**) was obtained as described above for **A**, and a modification of this synthesis was also used to prepare the N-deuterated analog, $Cu_4I_4(C_5H_{10}ND)_4$. Oven-dried, pulverized KI was dissolved in degassed D_2O (10 ml) to give a 3.5 M solution. Finely powdered CuI (100 mg, 5.25×10^{-4} mol) was added to a 5 ml volume of this solution, nearly all dissolving. Piperidine (60 μl, 6.1×10^{-4} mol) was dissolved in the remainder of the KI–D_2O solution and allowed to react for a few minutes, before being combined with the stirred CuI solution. A white solid immediately started precipitating. This was collected by filtration, washed with D_2O, and dried overnight by Ar flow. IR spectroscopy showed peaks at 3240 cm^{-1} for the N–H stretch of coordinated piperidine, and at 2400 cm^{-1} expected for the corresponding N–D stretch in a 1/3 ratio, indicating ca. 75% deuteration in the product.

The dimer $Cu_2I_2(py)_4$ (**C**) was prepared as reported [8d]. Enough pyridine was added to dissolve entirely a sample of CuI, then an excess of hexanes was added to the resulting yellow solution, making it colorless and separating a pale yellow–green powder. When kept under its mother liquor, the solid did not appear to be air sensitive over a number of days in this condition. The product's identity was confirmed by its emission properties [8d] and by the correspondence of its X-ray powder pattern with that calculated from the published geometry obtained through single-crystal X-ray spectroscopy [2c]. When separated from the supernatant, **C** was a mustard yellow color and rapidly lost pyridine, turning eventually into the white tetramer **A**.

The pyridine/piperidine mixed-ligand tetrameric clusters were formed in situ in the solutions used for spectroscopic measurements. An excess of CuI (4 to 5 mg) was weighed in a 10 ml volumetric flask, which was connected on one side with another flask containing dry CH_2Cl_2 or toluene, and on the other with the appropriate cell for the desired spectroscopic measures. All vessels were dried in an oven at 80°C and cooled under Ar to minimize contamination by H_2O. The system was degassed by entraining with Ar for ca. 30 min., then the solvent was transferred into the CuI-containing volumetric flask and appropriate amounts of the ligands were added using 10 μl syringes. The total concentration of ligands was 2×10^{-3} M for the emission measurements and 8×10^{-4} M for the absorption spectra; therefore, the concentrations of tetrameric clusters had upper limits of 5×10^{-4} M and 2×10^{-4} M, respectively. The volumetric flask was sonicated for 1 h, always under Ar overpressure, to insure the establishment of thermodynamic equilibrium before transferring the solution into the cell. Five different types of solution were prepared using the following stoichiometric py/pip ratios and volumes: 4/0 (1.6 μl/0 μl), 3/1 (1.2 μl/0.5 μl), 2/2 (0.8 μl/1.0 μl), 1/3 (0.4 μl/1.5 μl), 0/4 (0 μl/2.0 μl).

2.3. Instrumentation and procedures

Sample cells used for emission and absorption spectroscopy and lifetime were made of Suprasil quartz. Freeze–pump–thaw (f–p–t) cycles were performed on solutions in 1 cm O.D. tubes with a Rotaflow stopcock or in a 1 cm square fluorescence cell provided with a 10 ml side flask and a Rotaflow stopcock. Electronic absorption spectra were recorded with a Cary 118 spectrophotometer with digital modification by On-Line Instrument Systems (OLIS), or with a Hewlett-Packard 8452A diode array spectrophotometer. Infrared spectra were measured with a BioRad FTS-60 FT-IR spectrometer, at 2 cm^{-1} resolution. Solid samples were diluted with oven-dried KBr before being pressed into pellets. Low-resolution powder diffraction data were collected by a Scintag Pad-X automated X-ray diffractometer, using Cu–K_α radiation, $\lambda = 1.54$ nm. The driving software was NSRDX5, running on a Vaxstation 2000 computer. The samples were usually rapidly spread in a shallow depression etched in a steel block, held inside an O-ring-sealed dome with a thin polyethylene ceiling. The resulting intensity profiles were compared with those derived from single-crystal cell parameters from the literature, calculated by using the program LAZY-PULVERIX.

Emission and excitation spectra were recorded utilizing a Spex Fluorolog 2 spectro-fluorimeter equipped with a Hamamatsu R928A water-cooled PMT configured for photon counting and interfaced with a computer running Spex DM3000f software. Emission spectra were corrected for PMT response. Both emission and excitation spectra were corrected for lamp intensity variation by the ratio method with a Rhodamine-6G reference. A cut-off filter was usually placed in front of the emission monochromator to block scattered excitation light. Slits were always such that the relevant bandwidth (emission or excitation) was no more than 2 nm. The emissions were usually monitored at 90° from the excitation beam, but for some solid samples, especially when in the 3 mm flat cell, a better signal was obtained in a front face configuration. Emission lifetimes measurements were averages of 64 transients using the third harmonic (355 nm) of a Continuum NY 61-20 seeded, Q-switched Nd/YAG laser operating at 20 Hz as the excitation source and detection techniques described previously [15]. The usual experimental error on the lifetime measurements could be estimated as ± 5%.

3. Results and discussion

3.1. Solid CuI with excess pyridine

The emission spectrum of a sample of pulverized CuI under pyridine changed as the excess ligand was depleted by room temperature evaporation. Qualitatively, the 77 K luminescence evolved from yellow for the wet solid, to green when all liquid had evaporated, to blue over a longer time. The color of the solid turned from bright yellow to green then to white. The final product was identified as **A** through its emission characteristics and X-ray powder diffraction pattern [2a]. Even this product lost pyridine under continued vacuum pumping action for a few hours to leave CuI, identified from its X-ray powder diffraction pattern.

The 77 K emission spectrum of the initial bright yellow adduct displayed a single emission band with λ_{max}^{em} at 566 nm, which decayed exponentially with $\tau = 11$ μs. The excitation spectrum gave a λ_{max}^{ex} at 426 nm with a 360 nm shoulder. The emission of the CuI-saturated frozen pyridine was slightly red-shifted, with λ_{max}^{em} at 582 nm and $\tau = 15$ μs (Fig. 1). These properties are sufficiently close to those of a

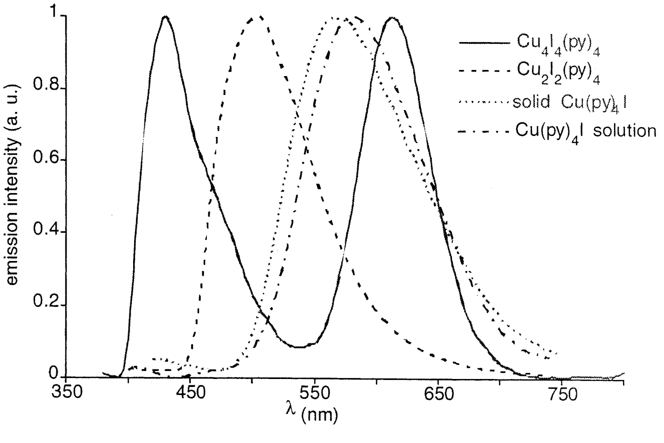


Fig. 1. Emission spectra at 77 K of CuI–pyridine adducts: solid **A**, $\lambda_{exc} = 345$ nm; solid **C**, $\lambda_{exc} = 380$ nm; solid CuI(py)$_4$I, $\lambda_{exc} = 390$ nm; Cu(py)$_4$I in pyridine, $\lambda_{exc} = 380$ nm. All spectra are normalized to a unity maximum intensity.

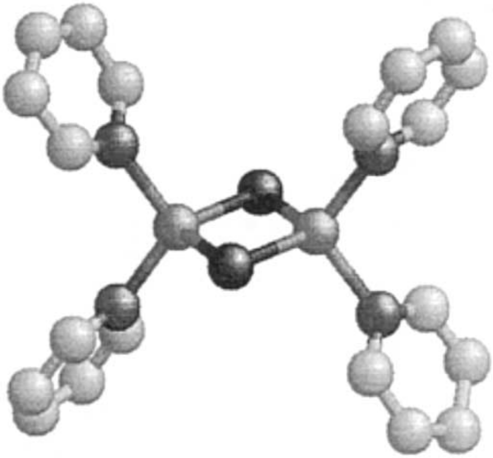
well characterized sample of solid $[Cu(py)_4]PF_6$ ($\lambda_{max}^{em} = 555$ nm, $\tau = 14.1$ μs at 77 K) and of a frozen pyridine solution of this same material ($\lambda_{max}^{em} = 578$ nm, $\tau = 15.2$ μs at 77 K) [8k] that it appears that the luminactive species under these conditions is largely the mononuclear cation $Cu(py)_4^+$, formed as the result of reaction with the large stoichiometric excess of pyridine (Eq. (1)).

$$CuI + \text{excess pyridine} \rightarrow [Cu(py)_4]I \qquad (1)$$

The intermediate green solid was identified through emission spectroscopy and X-ray powder diffraction as the dimer $Cu_2I_2(py)_4$ (**C**) [2c], which was also prepared by an independent route [8d]. The solid-state emission spectrum of this material presented a λ_{max}^{em} of 502 nm at 296 K (504 nm at 77 K) (Fig. 1). This band became narrower and the excitation maximum shifted from 398 to 391 nm at lower temperature. The emission lifetime τ at ambient temperature was measured to be 1.6 μs, and at 77 K to be 55 μs. The diffuse reflectance spectrum was similar to the excitation spectrum, with a λ_{max} at 402 nm and a low-energy tail extending to 500 nm.

3.2. Solutions of $Cu_4I_4(py)_4$ (*A*) and $Cu_4I_4(pip)_4$ (***B***)

The tetranuclear clusters **A** and **B** are soluble in moderately polarizable solvents, such as benzene and acetone, but not in protonic liquids (H_2O, EtOH) or in hexanes. When excess solid **A** was dissolved in toluene, the solution and the residual solid displayed the characteristic photophysical properties of this material [8d] and demonstrated no evidence of decomposition.



The ambient-temperature emission spectrum is dominated by the strong CC* emission band centered at 690 nm in deaerated toluene (582 nm for the solid) which displayed an exponential decay with a lifetime of 10.6 μs (11.1 μs for the solid). Addition of excess pyridine to the toluene solution modestly enhanced the apparent solubility of **A**, although it is not clear whether this was due to mass-action effects on chemical equilibria in the solution (or at the solid's surface) or simply some type of specific solvation effect. Notably, there was no effect on the position and lifetime of the CC* emission band at added pyridine concentrations up to at least 100 mM (for a 1 mM solution of **A**), indicating no significant formation at room temperature of species of lower nuclearity and higher L-to-CuI ratios such as **C** or $Cu(py)_4I$ under these conditions. On the other hand, when **A** was dissolved in CH_2Cl_2, there was a residual precipitate identified as CuI through its red emission ($\lambda_{max}^{em} = 685$ nm) [9c] and powder diffraction pattern. Although the ambient-temperature photophysical properties of the solutions were well behaved ($\lambda_{max}^{em} = 690$ nm, $\tau = 6.8$ μs), better homogeneity was readily achieved by addition of small concentrations of excess pyridine with no other effects being observed up to at least 100 mM.

Qualitatively, it was noted that solutions of both **A** and **B** were more stable if the tetramers had been formed in situ by adding CuI to dilute solutions of the ligands. This suggests that decomposition may be catalyzed by impurities formed in the older samples.

The piperidine tetramer **B** was less soluble than **A** and the resulting solutions were less stable, even though there was little apparent difference in the rate and extent of CuI dissolution in CH_2Cl_2 solutions to which pyridine or piperidine had been added. The electronic spectra were indistinguishable from those of solutions prepared directly from the tetramers **A** and **B**. The absorption spectra of solutions prepared by adding pyridine or piperidine (8×10^{-4} M), respectively, and equilibrating with saturated CuI each displayed a broad band of similar intensity ($\varepsilon \approx 2.6 \times 10^4$ M^{-1} cm^{-1}), centered at 287 nm for **A** and 285 nm for B (Fig. 2). Given that this band is independent of the aromaticity of the ligand L, it appears that it is characteristic of the core Cu_4I_4 cluster, perhaps the HOMO (mostly iodide

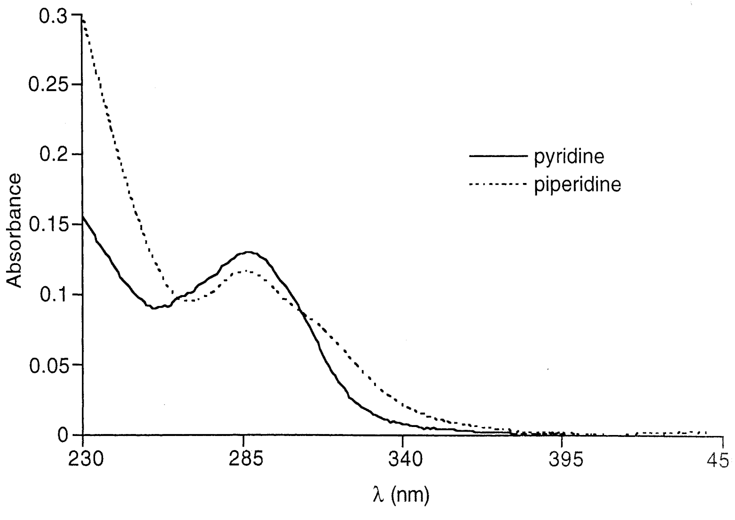


Fig. 2. Absorption spectra of CuI + 8×10^{-4} M pyridine or piperidine in CH_2Cl_2, 3 mm path length, after subtraction of ligand and solvent absorptions.

in character) to LUMO (mostly metal) cluster-centered transition suggested by ab initio calculations [8f].

As previously reported [8d], the 294 K luminescence spectrum of **B** dissolved in deaerated toluene solution shows a single CC* emission band centered at 680 nm (λ_{max}^{em} 584 nm for the solid at 294 K). The decay of this emission required a fit to a biexponential function, corresponding to lifetimes of 110 and 340 ns ($\tau_{solid} = 13.6$ µs at 294 K). The ratio of the two components of this fit depended on the concentration of **B**, the shorter lifetime becoming more dominant as the concentration increased, although the position and width of the emission band were unchanged within experimental error. Addition of excess piperidine also decreased the contribution of the slower component. For example, a 1 mM toluene solution of **B** with 5×10^{-2} M piperidine showed only a monoexponential decay, with $\tau = 110$ ns. Addition of excess ligand also increased the intensity of the room temperature emission of **B**, up to a maximum, without changing its energy as long as the excitation wavelength was shorter than about 360 nm. These observations suggest that **B** is labile toward piperidine dissociation.

$$Cu_4I_4(pip)_4 = Cu_4I_4(pip)_3 + pip \tag{2}$$

Notably, though, the CC* emission band of **B** in CH_2Cl_2 solution was only slightly blue-shifted (to 680 nm) relative to that in toluene, and the emission decay was strictly monoexponential, with $\tau = 95$ ns at 294 K, regardless of concentration and the presence or absence of excess ligand. The emission quantum yields of **A** and **B** in CH_2Cl_2 were measured by integration of the emission spectra, with $Ru(bpy)_3^{2+}$ in air-saturated H_2O ($\Phi_{em} = 0.028$) [16] used as a standard in the simplified formula for optically dilute cases [17].

$$\Phi_x = \Phi_s\left(\frac{A_s}{A_x}\right)\left(\frac{n_x^2}{n_s^2}\right)\left(\frac{D_x}{D_s}\right) \tag{3}$$

where x is the unknown, s denotes standard, A is the absorbance at the excitation wavelength (330 nm for all samples), D the integrated emission and n the refractive index of the solution to the luminescence. The dilute (10^{-4} M) solutions were prepared as above and subjected to four f–p–t cycles before the measurement. The lifetimes at 680 nm were used as a test of the extent of deaeration achieved, yielding satisfying values. From these data, the ambient-temperature emission quantum yields at 680 nm were determined as 0.09 for the pyridine tetramer and 6×10^{-4} for the piperidine one, consistent with values determined previously for toluene solution [8d].

For a single emitting state, the quantum yield Φ is related to the emission lifetime τ according to $\Phi = k_r\tau$, where k_r is the rate constant for radiative decay. In this context, the calculated values for k_r (1.3×10^4 s^{-1} and 0.6×10^4 s^{-1}) for **A** and **B**, respectively) are quite similar for the two clusters in ambient-temperature CH_2Cl_2. Thus, the dramatic differences in luminescence lifetimes must be attributed to differences in the nonradiative deactivation mechanisms.

One possible explanation for the differences in the nonradiative rates of **A** and **B** would be coupling of the CC* state to the high-energy piperidine N–H vibrational modes not present with the pyridine ligands of **A**. For example, the role of such vibrations in nonradiative deactivation of metal complexes has been demonstrated by noting the longer lifetimes found for the luminactive excited states of rhodium-(III) ammine complexes when the coordinated ammonias were perdeuterated [18]. This possibility was tested by probing the photophysics of an analog of **B** for which the N–H protons had been $>75\%$ exchanged with D_2O. Surprisingly, the photophysical behavior of this N-deuterated piperidine tetramer **B′** did not differ significantly from that of **B**. The ambient-temperature CC* emission maxima were found at ca. 680 nm in toluene or dichloromethane solution and at 584 nm for the solid, and the lifetimes determined for **B′** appeared identical to those of **B**: 95 ns in CH_2Cl_2 solution, 110 ns in toluene and 14 μs for the solid.

Notably, the mechanism through which the CC* excited state of **B** deactivates more rapidly than **A** is active only in fluid solution. One possibility is that bending vibrations involving the σ backbone of the piperidine, rather than the N–H bond, couples the CC* state to the ground state, but it seems likely that this should carry over to the solid state. Another possibility is that the greater basicity of piperidine allows a stronger interaction with the cluster core. In this context, one might note that the CC* lifetime of the cluster $Cu_4I_4(morph)_4$ (morph = the saturated ligand tetrahydro-1,4-oxazine) in ambient-temperature toluene (540 ns) [10a] is intermediate between those of **A** (10.6 μs) and **B** (110 ns), whereas the basicity of morpholine is similarly intermediate between those of piperidine and pyridine ($pK_a = 8.3$ versus 11.1 and 5.3, respectively) [19].

3.3. Mixed-ligand $Cu_4I_4(py)_n(pip)_{(4-n)}$ clusters

Fig. 3 presents the emission spectra generated for a series of solutions prepared as described in Section 2 by the reaction of solid CuI and various mixtures of the two ligands in CH_2Cl_2. The behavior of analogous solutions prepared in toluene was similar. In all the solutions, the CC* emission dominates the spectra and there is a systematic change in properties in going from **B** (py/pip ratio 0/4) to **A** (4/0). The emission maximum moves systematically from 676 nm for the 0/4 solution to 690 nm for the 4/0 solution, and the excitation maximum goes from 320 to 312 nm with intermediate values for the mixed-ligand solutions. More dramatically, the CC* emission intensities are widely different, becoming gradually fainter with increasing proportion of piperidine, which is a reflection of the much shorter lifetimes under these circumstances.

The CC* emission decays monitored at 680 nm in CH_2Cl_2 (355 nm excitation) were found to be monoexponential when a single type of ligand was present, but when the solution contained both ligands a nonexponential behavior was observed. The emission lifetimes of these solutions could be analyzed using bi- or tri-exponential functions and appear to derive from the simultaneous emission of several species whose lifetimes are rather regularly spaced. As shown above, the formation of species of lower nuclearity and higher L-to-CuI ratios requires a very large excess of ligand. Thus, for the present solutions, the emitting species are dominated by the $Cu_4I_4L_4$ stoichiometry, and the multiexponential behavior can be explained by

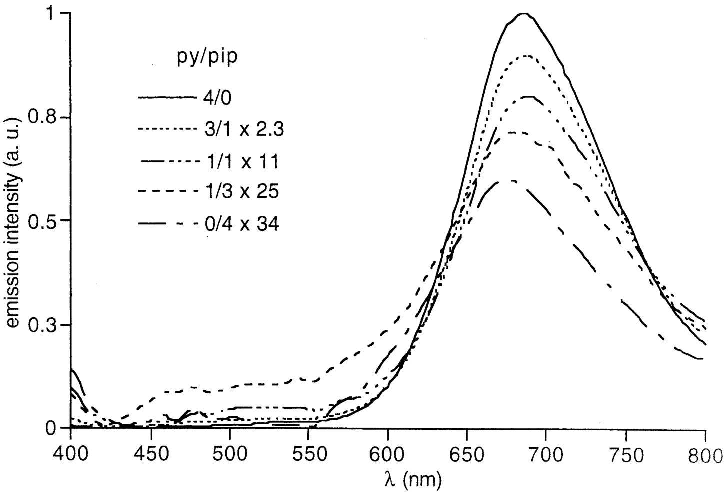


Fig. 3. Room-temperature emission spectra of solutions of CuI in CH_2Cl_2 with a total pyridine plus piperidine concentration of 2×10^{-3} M, in different proportions ($\lambda_{exc} = 330$ nm). Their intensities have been scaled by using the factors shown.

Table 1
Photophysical properties of mixed ligand complexes

	τ (μs)	
	CH_2Cl_2	$C_6H_5CH_3$
$Cu_4I_4py_4$	6.8 ± 0.3	10.6 ± 0.3
$Cu_4I_4py_3pip$	3.3 ± 0.4	3.4 ± 0.8
$Cu_4I_4py_2pip_2$	1.20 ± 0.25	1.0 ± 0.5
$Cu_4I_4pypip_3$	0.40 ± 0.08	0.34 ± 0.08
$Cu_4I_4(pip)_4$	0.095 ± 0.006	0.11, 0.34

formation of a roughly statistical mixture of the homoleptic and heteroleptic tetramers $Cu_4I_4(py)_4$, $Cu_4I_4(py)_3(pip)$, $Cu_4I_4(py)_2(pip)_2$, $Cu_4I_4(py)(pip)_3$, and $Cu_4I_4(pip)_4$. The fits of multiple data sets collected for the different ligand ratios gave self-consistent estimates for the CC* emission lifetimes of various heteroleptic species with pre-exponential factors consistent with a statistical, mass-action-driven distribution of those species. From these values, summarized in Table 1, it is clear that the emission lifetimes of the $Cu_4I_4(py)_{4-x}(pip)_x$ species are attenuated sharply with increasing piperidine substitution, reflecting the apparent role of a piperidine-mediated deactivation mechanism.

In contrast, the decays monitored for the weak XLCT emission at 500 nm were monoexponential in all cases ($\tau \approx 150$ ns). The intensity of this band decreased with decreasing pyridine concentration, and no emission from the 0/4 solution was detected at this wavelength, but the XLCT emission lifetime was nearly invariant with the pip/py ratio. Analysis of the 680 nm emission supports a nearly statistical distribution of homo- and hetero-leptic species, so most of the pyridine in a 1/3 solution is expected to be in the tetramers with just one or two py (about 42% of the bound pyridine for each) and **A** would represent but 0.4% of the total cluster concentration). Thus, it appears that the XLCT emission originates from pyridine-containing heteroleptic clusters as well, suggesting that the XLCT state is relatively independent of the number of pyridine ligands bound to the cubane core. This conclusion is consistent with calculations on **A** indicating that pyridine ligands bound to different Cu centers interact only very weakly with each other and with the core.

The distribution of the mixed-ligand solutions appears to be roughly statistical, suggesting the stability of the pyridine and piperidine adducts with the Cu_4I_4 core to be similar. Such a result is not unexpected for a d^{10} compound. The bonding interaction of the nitrogen lone pair with the empty s and p orbitals of Cu is only slightly stronger than the repulsive overlap with its filled d orbitals, as previous calculations made plain [8f]. The mixed-ligand CuI compounds reported here are not unique; other tetrameric adducts have previously been isolated by Holt and coworkers [4a], one of the ligands always being CH_3CN, and by Bowmaker and coworkers [3h].

In summary, the solution behavior of CuI plus pyridine or piperidine indicates a system in which many easily interconverted species are in equilibria whose positions depends on various factors. CuI reacts with N-donor ligands, such as pyridine or piperidine, to form a large number of monomeric and multimeric adducts that are in thermodynamically controlled equilibrium at ambient temperature and ambient pressure. A striking example is the heterogeneous reaction between pyridine and CuI, which leads to a series of adducts with decreasing py-to-CuI ratio as the ligand evaporates. In solution, the various species are separated by extremely low kinetic barriers, and variations in solvent, temperature, pressure or concentration of the components can radically affect their proportions. In ambient-temperature solutions with 1:1 ratios of CuI and the amine ligands pyridine or piperidine, the luminactive $Cu_4I_4L_4$ clusters are clearly favored, but when large excesses of a ligand such as pyridine are present, species with a higher ligand content such as $Cu_2I_2(py)_4$ and $Cu(py)_4^+$ may readily form.

Fast exchange of solution and coordinated pyridine had previously been indicated by NMR studies of **A** in benzene and toluene solutions [8d], implying that these are labile equilibria. For solutions of the $Cu_4I_4L_4$ clusters, **A** in dichloromethane and **B** in toluene, both appear to dissociate some of the ligand. Addition of excess piperidine to toluene solutions of **B** results in increased emission intensity and changes the emission decay from a double to a single exponential, the slower component decreasing in importance as the piperidine concentration increases. The longer lifetime component with a $\tau \approx 340$ ns is quite similar to that calculated for the $Cu_4I_4(py)(pip)_3$ mixed-ligand cluster. When mixtures of the ligands are present, self-assembly of mixed-ligand tetrameric adducts $Cu_4I_4(py)_n(pip)_m$ (where $n + m = 4$) appear to be roughly statistical and the spectroscopic properties of the heteroleptic compounds are intermediate between those of their homoleptic analogs. For instance, the ambient-temperature lifetimes of the CC* emissions decrease markedly with the increasing number of piperidine ligands, reflecting the effect of the pip ligand on the nonradiative deactivation rate of the CC* excited state.

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