Articles

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Photoluminescence Properties of the Copper(I) Chloride Clusters $Cu_4Cl_4L_4$ (L = Pyridine, Substituted Pyridine, or Saturated Amine)

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The spectroscopic properties, including emission spectra and lifetimes, absorption and diffuse-reflectance spectra, and excitation spectra, of a series of cuprous chloride clusters $Cu_4Cl_4L_4$ (L = pyridine, substituted pyridine, or saturated amine) are reported. The aromatic amine complexes $Cu_4Cl_4(py\text{-}x)_4$ each exhibit a single emission band in the solid state and in rigid glasses at 77 K (e.g., for L = py, λ_{max}^{em} = 519 nm and τ = 11.4 μs for the solid and λ_{max}^{em} = 577 nm and τ = 21.4 μs in glassy toluene). The emission λ_{max} is dependent on the pyridine substituent, following the order x = 4-phenyl > 3-diethylamide > H. In contrast, for L = morpholine or Et_3N, emission from the 77 K solids is not observed. These differences are interpreted in terms of possible assignments of the emitting state as a triplet metal-to-ligand charge transfer (^{3}MLCT) or triplet halide to pyridine charge transfer (^{3}XLCT) state rather than as a metal-localized excited state.

Introduction

There has been considerable recent interest in the photoluminescence properties of a wide variety of d^{10} metal complexes,[1] including those of Cu(I),[2,3] Ag(I),[3,4] Au(I),[3,5-8] Zn(II),[9-11] Cd(II),[10] Hg(II),[12] Ni(0),[13] Pd(0),[13-16] and Pt(0).[13-16] Among these are a number of polynuclear complexes for which one issue of interest is the extent of metal-metal interaction in the relevant excited states. Studies in this laboratory[17-20] have been concerned with photophysical properties of tetranuclear cuprous iodide clusters $Cu_4I_4L_4$, where L is an organic base such as pyridine or piperidine. Certain properties of these and related Cu(I) clusters have been described by others.[21-25] If L is an aromatic amine, the $Cu_4I_4L_4$ clusters often display multiple emissions in the visible range which show a thermochromism in both the solid and solution phases. For example, $Cu_4I_4(py)_4$ shows a very bright, long-lived, lower energy (LE) emission (λ_{max}^{em} = 690 nm in toluene solution) which has been variously attributed to a $d^9s^1 \rightarrow d^{10}$ metal-centered (MC) transition,[21-25] to a cluster-centered (CC) transition[17-20] or to a halide-to-metal charge-transfer (XMCT) transition.[20] A second, higher energy (HE) emission (λ_{max}^{em} = 480 nm in toluene solution), which is not observed if L is a saturated amine, has been attributed to a metal-to-ligand (e.g., pyridine) charge-transfer (MLCT) or halide-to-ligand L charge-transfer (XLCT)[20] transition. The possible XLCT and XMCT assignments for the HE and LE emissions, respectively, draw support from ab initio calculations in which the highest occupied molecular orbital (HOMO) of a model $Cu_4I_4(NH_3)_4$ cluster has been found to be largely iodide in character and the lowest unoccupied molecular orbital (LUMO) to be a delocalized metal cluster orbital (5s and 5p).[19,26]

As part of a continuing effort to elucidate the intriguing luminescence characteristics of the cuprous halide clusters, it appears particularly attractive to investigate the analogous chloride clusters. In this paper are reported the spectroscopic and luminescence properties of a series of monodentate nitrogen base copper(I) chloride clusters $Cu_4Cl_4L_4$ where L = pyridine (py), 4-phenylpyridine (Phpy), diethylnicotinamide (DEN), morpholine (mor), and triethylamine (Et_3N).

Experimental Section

Materials. Pyridine, morpholine, and triethylamine were dried over KOH (24 h) and then distilled under nitrogen. 4-Phenylpyridine was recrystallized from hot hexane. Diethylnicotinamide (Aldrich) was used

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as received. Dichloromethane and hexane were dried over CaH_2, and toluene was dried over Na metal under nitrogen. All these solvents were distilled under nitrogen just before use. Cuprous chloride (Aldrich) was purified by the literature method.[27]

Syntheses. The $Cu_4Cl_4L_4$ clusters (L = py, Phpy, DEN, Et_3N, mor) were synthesized by the published methods[28-30] except that the solid $Cu_4Cl_4(DEN)_4$ was isolated after sonicating a toluene solution of the product for about 0.5 h to induce precipitation. All solid materials obtained were washed with toluene and then with hexanes and were dried in a nitrogen or argon gas stream and stored in a glovebox under argon atmosphere (oxygen content in the glovebox was maintained below 5 ppm). All of the chloride clusters were markedly air sensitive. Elemental analyses (C/H/N) were obtained for the three pyridine type complexes described in the present investigation. In each case these were consistent with the $Cu_4Cl_4(py\text{-}x)_4$ formulation. Anal. Calcd for $Cu_4Cl_4(py)_4$ ($C_{20}H_{20}N_4Cl_4Cu_4$): C, 33.72; H, 2.83; N, 7.86. Found: C, 33.95; H, 2.87; N, 7.82. Calcd for $Cu_4Cl_4(Phpy)_4$ ($C_{44}H_{36}N_4Cl_4Cu_4$): C, 51.98; H, 3.57; N, 5.51. Found: C, 51.86; H, 3.70; N, 5.38. Calcd for $Cu_4Cl_4(DEN)_4$ ($C_{40}H_{56}N_8O_4Cl_4Cu_4$): C, 43.33; H, 5.09; N, 10.10. Found: C, 43.99; H, 5.24; N, 10.07. However, repeated analyses of the solid product isolated for the synthesis with L = morpholine gave values more consistent with the formula $Cu_4Cl_4(mor)_3$, suggesting that isolation of this material was accompanied by loss of one morpholine.

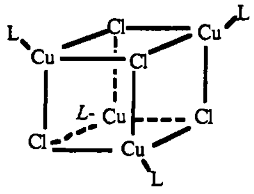
Measurements. The sample of $Cu_4Cl_4(Et_3N)_4$ used for X-ray powder diffraction analysis was mounted from the mother liquor in a 2 mm o.d. glass capillary (0.01-mm thickness, Charles Supper Co.) which was sealed with Apiezon vacuum grease (type N) or flame-sealed under argon. The solid samples for emission spectra and lifetime measurements were typically prepared in the glovebox with use of a 3 mm × 40 mm rectangular Suprasil clear fused-quartz cell with a 300-mm graded seal tube or 3 mm o.d. × 300 mm Pyrex tubing; the cells were capped with a Suba-Seal septum (Aldrich). The samples were immediately immersed in Dewar flasks containing liquid nitrogen, and the flasks were flame-sealed under argon. The solution samples were prepared by the cannula technique under nitrogen atmosphere using 5 mm o.d. × 300 mm Pyrex tubing or a 10 × 10 mm^2 Suprasil clear fused-quartz cell equipped with a 300-mm graded seal tube and capped with a Suba-Seal septum. Dewar flasks containing the solution samples were similarly flame-sealed as described above.

The UV-visible spectra were recorded on a HP 8452 diode array spectrophotometer. Diffuse-reflectance (DR) spectra were recorded on a Cary 14 UV-vis spectrophotometer equipped with an integrating sphere and On-Line Instrument Systems (OLIS) computer control systems in the laboratory of Professor G. Stucky at UCSB. Solid $MgCO_3$ was used as reference for the DR spectra. The emission and excitation spectra were recorded on a Spex Fluorolog2 spectrofluorimeter as described elsewhere.[20] The emission lifetimes were determined at 294 and 77 K by using a Quanta Ray DCR-1A Q-switched Nd:YAG laser system and techniques described previously.[20] The X-ray powder pattern of the $Cu_4Cl_4(Et_3N)_4$ cluster was recorded on a Scintag (Model XPH-105) diffractometer using Cu Kα radiation. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Results

General Information. The aromatic amine compounds $Cu_4Cl_4(py\text{-}x)_4$ (x = H, 4-Ph, 3-C(O)NEt$_2$) were isolated as yellow solids and proved to be extremely air sensitive. The $Cu_4Cl_4(Et_3N)_4$ cluster was kept under its mother liquor throughout the experiments due to the loss of the Et_3N ligand upon its isolation.[30] The X-ray powder diffraction pattern and intensity profiles for solid $Cu_4Cl_4(Et_3N)_4$ studied under its mother liquor matched well with those derived from the single-crystal cell parameters.[30]

Although crystal structures of a number of cuprous iodide clusters, $Cu_4I_4L_4$, have been well characterized,[31,32] structural information for similar chloride clusters, $Cu_4Cl_4L_4$, is rarer owing to the extreme air sensitivity of these compounds. White and co-workers have reported the crystal structures for the $Cu_4Cl_4L_4$ clusters where L = triethylamine (Et_3N)[30] and 2-(diphenylmethyl)pyridine[32] (dpmp). The phosphine clusters $Cu_4Cl_4(PR_3)_4$ have also been described.[33] In each case, these compounds adopt the "cubane" structure as in A. The tetrameric form of 1:1 adducts of copper(I) chloride with DEN, py, and other monodentate nitrogen bases has also been inferred by cryoscopic molecular weight measurement and stoichiometric analysis of the dioxygen products.[28,29] Similarly, cuprous iodide $Cu_4I_4L_4$ clusters retain their tetrameric composition in benzene solution.[20,25] Morse and co-workers[34] have shown by UV-vis spectral and vapor pressure osmometry studies that the dissociation of the tetrameric phosphine clusters $Cu_4Cl_4L_4$ (L = $MePh_2P$, Ph_3P) is negligible in benzene solution at 37 °C. (In contrast, the monomeric $CuClL_3$ complexes underwent ligand dissociation and self-assembly to give a mixture of species including tetrameric clusters.) Thus, the available information suggests that the 1:1 adducts of cuprous chloride with monodentate nitrogen ligands are present in aprotic solvents as the tetranuclear clusters.



A

Electronic Absorption Spectra. In CH_2Cl_2 solutions, the UV absorption spectra of the free pyridine ligands each display a $\pi\pi^*$ band with $\lambda_{max}{}^{ab}$ at ~256 nm, while those of the $Cu_4Cl_4(py\text{-}x)_4$ clusters each display a similar UV band plus a long and featureless tail extending toward the visible region. For py-x = py or DEN, the UV λ_{max} was red-shifted by 8–10 nm from that of the free ligand; for example, the spectrum of diethylnicotinamide gave a $\lambda_{max}{}^{ab}$ and 255 nm (ϵ = 3440 M^{-1} cm^{-1})[28,35] while that of the $Cu_4Cl_4(DEN)_4$ cluster gave a $\lambda_{max}{}^{ab}$ at 265 nm (ϵ = 14 000 M^{-1} cm^{-1}). A more dramatic red shift was observed for x = 4-phenyl; i.e., $Cu_4Cl_4(Phpy)_4$ in CH_2Cl_2 displayed a broad band with $\lambda_{max}{}^{ab}$ at 286 nm, 30 nm red-shifted from the $\pi\pi^*$ $\lambda_{max}{}^{ab}$ of free Phpy. Although there are similarities between the spectra of the chloride clusters $Cu_4Cl_4(py\text{-}x)_4$ and those of the iodide analogues,[20] one difference is that the UV $\lambda_{max}{}^{ab}$ values for the chloride clusters are shifted to lower energy compared to those of the corresponding free ligands while the analogous transitions of $Cu_4I_4(py\text{-}x)_4$ clusters are not. These band shifts follow the energy order py > DEN > Phpy, thus suggesting some MLCT character for the absorption bands of $Cu_4Cl_4(py\text{-}x)_4$.

Reflectance Spectra. The diffuse-reflectance (DR) spectra of solid $Cu_4Cl_4(py\text{-}x)_4$ clusters are summarized in Table I. The strongly emitting cluster $Cu_4Cl_4(py)_4$ displayed a $\lambda_{max}{}^{dr}$ at ~400 nm but exhibited an apparent negative reflectance at wavelengths below 300 nm, which prevented observation of the DR spectrum in that region. The DR spectrum of $Cu_4Cl_4(Phpy)_4$ exhibited a broad band centered at 384 nm which tails to ~500 nm. The room-temperature DR spectrum of the $Cu_4Cl_4(DEN)_4$ cluster, which does not emit at room temperature, clearly exhibited two broad peaks centered at 275 and 380 nm. The higher energy band corresponds approximately to the absorption band at 265 nm (in CH_2Cl_2 solution at room temperature). The lower energy DR band at 380 nm has no such analogue in the absorption spectrum but does in the excitation spectrum, which displays a $\lambda_{max}{}^{ex}$ at 400

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(35) (a) In ref 28 the peak at 285 nm reported for free ligand DEN could be due to impurity, since we and others do not observe it in the same medium and in MeOH.[35b] Likewise, the peak at 225 nm also reported for $Cu_4Cl_4(DEN)_4$ in CH_2Cl_2 would be an artifact due to solvent inner-filter effects (λ_{cutoff} < about 240 nm). (b) Ultra Violet Spectra. In *The Sadtler Standard Spectra*; Sadtler Research Laboratories: Philadelphia, PA, 1975–1978.

Table I. Spectroscopic Data for the $Cu_4Cl_4L_4$ Clusters in the Solid State

L	*T*, K	λ_{max}^{em}, nm[a]	$\Delta\nu_{1/2}$, 10^3 cm^{-1} [b]	τ, μs[c]	λ_{max}^{ex}, nm[d]	ΔE, 10^3 cm^{-1} [e]	λ_{max}^{dr}, nm[f]
py	298	527	~4.1	4.0 ± 0.2	425	4.55	400
	77	519	3.40	11.4 ± 0.2	403	5.55	
PhPy	298	620[g]	3.20	0.87 ± 0.01	357, 459	5.66	384[h]
	77	613[g]	2.60	3.8 ± 0.1[i]	360, 448	6.01	
DEN	77	530	3.40	28.2 ± 0.3	~357, 400	6.13	~275, 380
	77[j]	600	3.17	13.6 ± 0.3	438	6.16	

[a] Emission maxima (excitation wavelength at λ_{max}^{ex}). [b] Full width at half-height of the emission band. [c] Emission lifetime (monitored at λ_{max}^{em}). [d] Excitation maxima (monitored at λ_{max}^{em}). [e] Energy difference between the emission and lower energy excitation maxima. [f] Diffuse-reflectance maxima at 298 K vs $MgCO_3$. [g] Uncorrected. [h] Very broad (see text). [i] Double decay (in solid at 77 K, τ_1 = 3.33 μs and τ_2 = 4.13 μs and the corresponding prefactors A_1 = 3.8 and A_2 = 2.11). [j] In toluene.

Table II. Photophysical Data for the $Cu_4Cl_4L_4$ Clusters in Rigid Glasses (77 K)

L	solvent	λ_{max}^{em}, nm[a]	$\Delta\nu_{1/2}$, 10^3 cm^{-1} [b]	τ, μs[c]
py	toluene	577	3.40	21.4 ± 0.1
Phpy	CH_2Cl_2	596	3.10	4.6 ± 0.1[d]
	toluene	584	3.10	18.7 ± 0.1
DEN	CH_2Cl_2	560	3.30	9.0 ± 0.5
	toluene	600	3.17	13.6 ± 0.3

[a] Emission maxima (excitation wavelength at λ_{max}^{em}); uncorrected. [b] Full width at half-height of the emission band. [c] Emission lifetime (monitored at λ_{max}^{em}). [d] Double decay (in solid at 77 K, τ_1 = 3.33 μs and τ_2 = 4.13 μs and the corresponding prefactors A_1 = 3.8 and A_2 = 2.11). [e] Corrected.

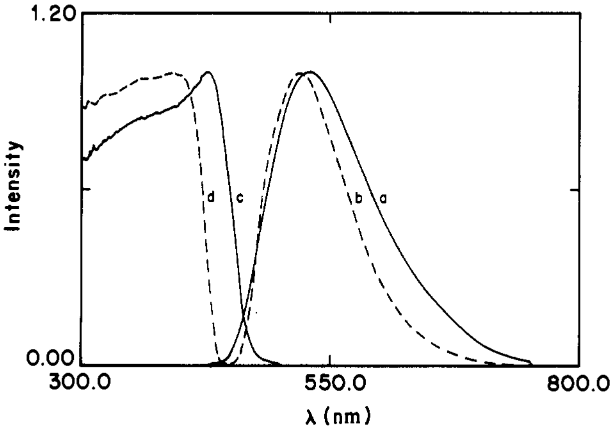

Figure 1. Corrected emission spectra at 298 K (a) and at 77 K (b) and excitation spectra at 298 K (c) and at 77 K (d) of solid $Cu_4Cl_4(py)_4$. Intensities were normalized for comparison.

nm for the solid at 77 K (see below). Similarly, the DR maxima of other $Cu_4Cl_4(py\text{-}x)_4$ clusters find parallels in the excitation spectra (see below).

Luminescence Spectra. At 77 K in the solid state, the $Cu_4Cl_4(py\text{-}x)_4$ clusters each exhibited an intense, unstructured, broad, and asymmetric emission band in the visible region (Figures 1–3, Tables I and II). At room temperature, weak emissions were observed only for solid $Cu_4Cl_4(py)_4$ (λ_{max}^{em} = 527 nm) and solid $Cu_4Cl_4(Phpy)_4$ (λ_{max}^{em} = 620 nm), in each case somewhat red-shifted relative to those of the 77 K solids (λ_{max}^{em} = 519 and 613 nm, respectively; e.g. Figure 1). The luminescence spectra of solid $Cu_4Cl_4(py)_4$ and of solid $Cu_4Cl_4(Phpy)_4$ proved independent of the excitation wavelength (within experimental uncertainty, ±2 nm) at 77 and at 298 K.

Emission was also observed for the $Cu_4Cl_4(py\text{-}x)_4$ clusters in 77 K glassy solutions of toluene or dichloromethane (e.g. Figure 3). In solution, the λ_{max}^{em} values for $Cu_4Cl_4(py)_4$ and $Cu_4Cl_4(DEN)_4$ clusters were red-shifted while that of $Cu_4Cl_4(Phpy)_4$ was blue-shifted relative to the respective solid-state spectrum (Table II). In addition, the solution-phase λ_{max}^{em} did display a modest dependence on the excitation wavelength; for example, λ_{max}^{em} for $Cu_4Cl_4(py)_4$ shifted from 577 to 590 nm as the λ_{ex} was increased from 350 to 420 nm (Figure 4), perhaps as the result of sol-

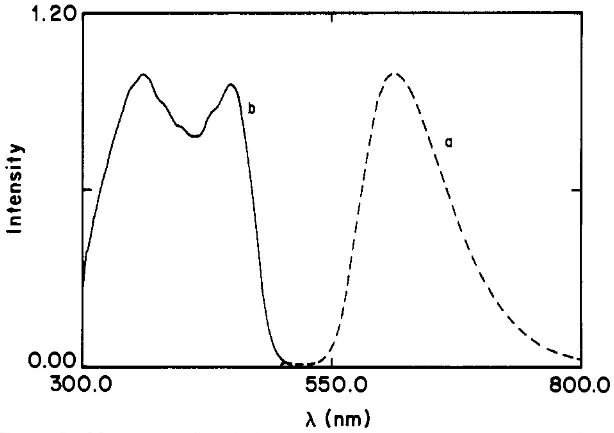

Figure 2. Uncorrected emission (a) and excitation (b) spectra of solid $Cu_4Cl_4(Phpy)_4$ at 77 K. Intensities were normalized for comparison.

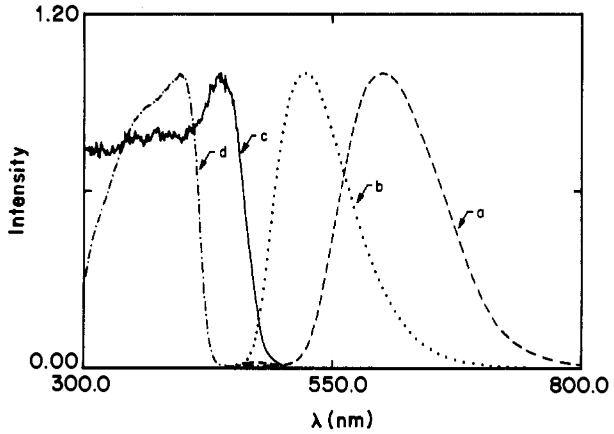

Figure 3. Emission spectra in toluene glass (a) and in solids (b) and excitation spectra in toluene glass (c) and in solids (d) of $Cu_4Cl_4(DEN)_4$ at 77 K. Intensities were normalized for comparison. Spectra in solids are uncorrected; those in toluene, corrected.

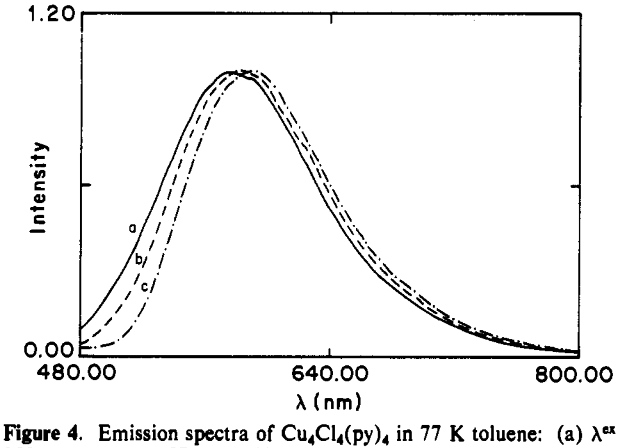

Figure 4. Emission spectra of $Cu_4Cl_4(py)_4$ in 77 K toluene: (a) λ^{ex} = 350 nm, λ_{max}^{em} = 577 nm; (b) λ^{ex} = 395 nm, λ_{max}^{em} = 583 nm; (c) λ^{ex} = 420 nm, λ_{max}^{em} = 590 nm.

vent–solute-induced microenvironmental heterogeneities.[2b]

For the two saturated amine clusters, no emission was observed for solid $Cu_4Cl_4(Et_3N)_4$ at 77 K. This cluster was not stable in the absence of excess Et_3N and decomposed when dissolved in toluene. Although an exceedingly weak emission centered at ~626 nm was seen at 77 K for the morpholine cluster when isolated as a solid, no emission was observed for $Cu_4Cl_4(mor)_4$ under its mother liquor. As described in the Experimental Section, it is likely that the isolated solid may not have the 4:4:4 stoichiometry.

Excitation Spectra. The excitation spectra of the $Cu_4Cl_4(py\text{-}x)_4$ solids were obtained during monitoring at the respective emission maxima. These data are summarized in Table I. The excitation spectrum of each cluster displayed one or more bands in the range 350–460 nm, although no corresponding absorption band or bands were observed for solution spectra in this region. For example, the excitation spectrum of solid $Cu_4Cl_4(py)_4$ at 77 K displayed a λ_{max}^{ex} at 403 nm with a shoulder at ~360 nm (Figure 1). The λ_{max}^{ex} shifted to 425 nm at ambient temperature. Two λ_{max}^{ex} bands were observed for solid $Cu_4Cl_4(Phpy)_4$: 360 and 448 nm (peak ratio 1:1) at 77 K, 357 and 459 nm (2:1) at 298 K (Figure 2). The excitation spectra of the solid $Cu_4Cl_4(py)_4$ and $Cu_4Cl_4(DEN)_4$ clusters also displayed less resolved shoulders at ~360 nm (Figures 1 and 3). The excitation spectra of $Cu_4Cl_4(DEN)_4$ dissolved in a toluene glass (77 K) displayed a λ_{max}^{ex} at 438 nm, somewhat longer wavelength than that of the solid (400 nm, Figure 3).

Luminescence Lifetimes. The emission lifetimes of the $Cu_4Cl_4(py\text{-}x)_4$ clusters are summarized in Tables I and II. At room temperature only solid $Cu_4Cl_4(py)_4$ and $Cu_4Cl_4(Phpy)_4$ displayed measurable lifetimes (4.0 μs and 849 ns, respectively). At 77 K, the $Cu_4Cl_4(py\text{-}x)_4$ clusters displayed lifetimes in the range 4–30 μs. Single-exponential decay was observed in each case except $Cu_4Cl_4(Phpy)_4$. For solid $Cu_4Cl_4(Phpy)_4$, luminescence decay at 77 K was best fit to a double exponential with $\tau_1 = 3.33$ μs (preexponential factor $A_1 = 3.8$) and $\tau_2 = 4.13$ μs ($A_2 = 2.1$); however, the 3.8-μs value listed in Table II is based on a best fit assuming a single-exponential decay.

Discussion

The following observations must be considered in assigning the luminescence spectra of the $Cu_4Cl_4L_4$ clusters. (1) Solids having L = py-x display strong, relatively long-lived emission at 77 K and weaker but observable emission bands at 298 K. Similar properties were observed for these materials dissolved in glassy toluene or CH_2Cl_2. (2) The energies of these bands are substituent sensitive and decrease in the order py ≥ DEN > Phpy. Analogous trends were observed for absorption, reflectance, and excitation spectral measurements. The excitation and emission maxima also proved temperature dependent, blue-shifting at lower *T*. (3) In contrast, if L was one of the saturated amines Et_3N or mor, no visible range emission was observed at 77 K from the solids under their respective mother liquors. (4) The excitation spectra for the $Cu_4Cl_4(py\text{-}x)_4$ clusters display maxima in the range 350–450 nm for which there are no corresponding features in the absorption spectra in solution. However, diffuse-reflectance spectra of the $Cu_4Cl_4(py\text{-}x)_4$ solids do indicate transitions in this region. For each py-x cluster, a substantial Stokes shift ($\sim 6 \times 10^3$ cm^{-1}) is observed between the lowest energy excitation maximum and the respective emission maximum, although these bands come close to overlapping.

Points 1–3 indicate that ligand $\pi_L{}^*$ orbitals must be involved in the excited states (ES's) leading to emission, since those $Cu_4Cl_4L_4$ clusters for which L is a saturated amine are nonemissive. Thus, the emitting ES is unlikely to be either a metal-centered or a Cu_4Cl_4-core-centered state, in contrast to an earlier assignment[36] of the luminescence from $Cu_4Cl_4(DEN)_4$ in solution as a metal-localized ($d^9s^1 \rightarrow d^{10}$) transition modified by metal–metal interactions. Triplet, ligand-centered, $^3\pi_L\pi_L{}^*$ ES's of the pyridine ligands are also excluded, since the phosphorescence spectra of the pyridinium ions Hpy-x$^+$ display λ_{max}^{em} values about 400 nm,[37] much higher energy than for the $Cu_4Cl_4(py\text{-}x)_4$ clusters. (However, spin-forbidden ligand $\pi_L\pi_L{}^*$ absorptions may be responsible for the short-wavelength-excitation maxima/shoulders for the $Cu_4Cl_4(py\text{-}x)_4$ complexes (Figures 1–3).) Other possible assignments for the emitting states would be triplet metal-to-ligand charge-transfer (MLCT) or halide-to-ligand charge-transfer (XLCT) ES's.

The characteristics of the $Cu_4Cl_4(py\text{-}x)_4$ emission bands parallel those described for the higher energy (HE) bands of the dual-emitting iodide analogues $Cu_4I_4(py\text{-}x)_4$. In both cases, the emissions are observed only for aromatic ligands, and the energies of these are sensitive to the pyridine substituent x. However, one important difference is that the emission bands for the chloride clusters occur at significantly lower energy than the HE bands of the respective iodide clusters, e.g., λ_{max}^{em} for $Cu_4Cl_4(py)_4$ (519 nm for the 77 K solid) is ~80 nm to the red of λ_{max}^{em} for the HE emission of $Cu_4I_4py_4$ (438 nm for the 77 K solid).[20] For the HE band of the $Cu_4I_4(py\text{-}x)_4$ clusters, there is some ambiguity regarding whether a ^{3}MLCT or ^{3}XLCT assignment is the best description,[20] since both types of transitions would be consistent with the necessity for π-unsaturated ligands L, substituent effects, etc. The suggestion of the ^{3}XLCT assignment has its origin in the preliminary ab initio calculations which concluded that for the hypothetical cluster $Cu_4I_4(NH_3)_4$ the highest occupied MO's are not metal centered but are >80% iodide p orbital in character.[19,26] The metal d-orbital contribution to the HOMO is small, and those occupied MO's which have substantial metal character are of much lower energy. Calculations also show the HOMO to be principally halide p orbital in character for the chloride analogue $Cu_4Cl_4(NH_3)_4$, but in this case there is a larger contribution from metal d orbital(s), given the better overlap of copper and chloride orbitals.[26] In this view, the calculations suggest that the emitting state or states of the $Cu_4Cl_4(py\text{-}x)_4$ clusters have more MLCT character than those responsible for the HE emission bands of the iodide analogues.

Examples of XLCT excited states are documented in a recent review,[38] which also draws the analogy between such metal complex ES's and the charge-transfer transitions seen in pyridinium halide ion pairs, $[RNC_5H_5{}^+],X^-$.[39] The $Cu_4X_4(py\text{-}x)_4$ clusters fit this analogy well; however, the observation (above) that λ_{max}^{em} for $Cu_4Cl_4(py\text{-}x)_4$ occurs at lower energy than the HE band for the respective iodide cluster would appear contradictory, given the reported halide ion optical electronegativities.[40] The key difference, however, is that the greater covalency of the Cu–I bonding in those clusters leads to decreased iodide anionicity,[41] hence to a greater lowering of all iodine orbital energies (relative to chloride analogues), including those of the essentially nonbonding HOMO.

In a related study from this laboratory,[20] it was argued that the lower energy (LE) emission band seen for the iodide cluster analogues $Cu_4I_4L_4$ when L is either an aromatic amine *or an aliphatic amine* (λ_{max}(LE) = 619 and 590 nm for L = py and piperidine, respectively, for solid $Cu_4I_4L_4$ at 77 K) is a cluster-centered (CC) transition largely I → Cu (or $I_4 \rightarrow Cu_4$) XMCT in character. Indeed, this very assignment prompted the present investigation of the chloride analogues; however, the present data argue against such an assignment for the emission from the $Cu_4Cl_4L_4$ clusters. This ambiguity suggests that the key feature determining the presence or absence of a cluster-centered (CC) emission band may have a different origin. In this context, Holt and co-workers[22] have noted that, for a series of $Cu_4I_4L_4$ clusters, only those with ground-state Cu–Cu distances less than the

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(36) (a) Henary, M.; Zink, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 7407–7411. (b) In ref 36a these authors reported for $Cu_4Cl_4(DEN)_4$ that λ_{em}^{max} = 15 100 cm^{-1} (662 nm) and τ = 7.3 μs in dichloromethane at 13 K with excitation at 406 nm.

(37) (a) Motten, A. G.; Kwiram, A. L. *J. Chem. Phys.* **1981**, *75*, 2608–2615. (b) Motten, A. G.; Kwiram, A. L. *Chem. Phys. Lett.* **1977**, *45*, 217–220.

(38) Vogler, A.; Kunkeley, H. *Comments Inorg. Chem.* **1990**, *9*, 201–220.

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(40) Ferraudi, G. J. *Elements of Inorganic Photochemistry*; John Wiley & Sons: New York, 1988; Chapter 5.

(41) Mulliken population analysis of the results of *ab initio* calculations[26] show that the residual charges on Cu and X are respectively +0.34 and −0.39 for $Cu_4I_4(NH_3)_4$ and +0.65 and −0.71 for $Cu_4Cl_4(NH_3)_4$.

summed Cu(I) van der Waals radii (2.8 Å) displayed the LE emission. Notably, Cu–Cu distances of those $Cu_4Cl_4L_4$ clusters for which crystal structures have been reported exceed 2.8 Å in each case;[42] e.g., the Cu–Cu distance for the nonemissive $Cu_4Cl_4(Et_3N)_4$ cluster is 3.07 Å.[30] This observation is consistent with the conclusion[20] that the LE emission band from the iodide $Cu_4I_4L_4$ clusters is a property of the Cu_4X_4 core and involves extensive interaction between the Cu(I) centers owing to the σ-bonding nature of the LUMO for those clusters with short metal–metal distances.

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Registry No. $Cu_4Cl_4(py)_4$, 104475-18-5; $Cu_4Cl_4(Phpy)_4$, 136144-92-8; $Cu_4Cl_4(DEN)_4$, 80105-82-4; $Cu_4Cl_4(mor)_4$, 136144-93-9; $Cu_4Cl_4(Et_3N)_4$, 97665-61-7.

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(42) Other examples of $Cu_4Cl_4L_4$ clusters which have been shown by X-ray crystallography to have the cubane type structure as in A with Cu–Cu distances in excess of 2.8 Å include those where L = 2-(diphenylmethyl)pyridine (2.901 Å),[32] 2-[bis(trimethylsilyl)methyl]pyridine (2.960 Å),[30] PPh_3 (3.306 Å),[33a] and PEt_3 (3.211 Å).[33b]

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Electronic Structure of Main-Group-Element-Centered Octahedral Gold Clusters

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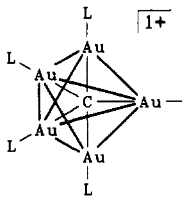
Molecular orbital calculations have been performed for the octahedral cluster ions $\{[(H_3P)Au]_6X_m\}^{m+}$ (X_1 = B, X_2 = C, X_3 = N) by using the first-principles self-consistent discrete-variational Xα method. The fragments Au_6^{2+} and $[(H_3P)Au]_6^{2+}$ have also been investigated, and the interpretation of their electronic structure forms the basis for an understanding of the main-group-element-centered clusters. Furthermore, a nearest-neighbor extended Hückel model is used to aid in elucidating the electronic structure of Au_6^{2+}. A major result, at variance with previous models for bonding in gold cluster compounds, is the prominent contribution of Au 5d orbitals, which is found to be as important as that of Au 6s orbitals. Their interplay, s–d hybridization, is symmetry-dependent and synergistic with both radial Au–ligand σ bonding and tangential Au–Au bonding. Relativistic effects strongly enhance this interaction mechanism and therefore are significant for the overall stability of the clusters. The central atom formally takes up four electrons that would otherwise reside in energetically unfavorable molecular orbitals, and it contributes to the stability of the cluster by forming radial bonds. Orbital and favorable electrostatic interactions decrease along the series X = B, C, N. However, for the boron-centered compound, repulsion between radially nonbonding Au d electron density and B 2p-derived density strongly reduces (or outweighs) the favorable interactions. The bonding interactions in the yet unsynthesized boron-centered cluster may be increased by employing more electronegative functional groups on the phosphine ligands although possibly at the expense of solvation and crystal packing problems. The flavor of the molecular orbital analysis, given here for octahedral gold clusters, notably the important role of Au 5d–6s hybridization, may be transferred to other gold cluster compounds, especially the closely related five-coordinated systems $\{[(R_3P)Au]_5Y_m\}^{m+}$ (Y_1 = C, Y_2 = N).

1. Introduction

The chemistry of gold has gained a new facet through the recent synthesis of the pentakis and hexakis auro methanium, ammonium, and phosphonium cations $\{[(C_6H_5)_3PAu]_5C\}^+$ (**1**), $\{[(C_6H_5)_3PAu]_5N\}^{2+}$ (**2**), $\{[(C_6H_5)_3PAu]_5P\}^{2+}$ (**3**), and $\{[(C_6H_5)_3PAu]_6C\}^{2+}$ (**5**).[1-4] Recent claims regarding the synthesis of $\{[(C_6H_5)_3PAu]_6N\}^{3+}$ (**6**) so far are unconfirmed.[5]



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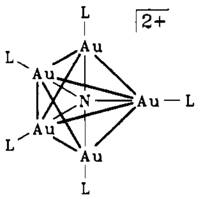

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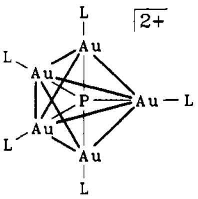

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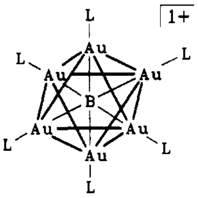

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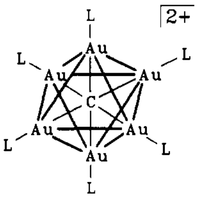

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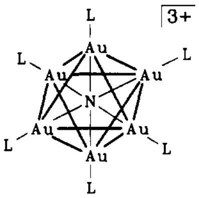

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The existence of these astonishing compounds provides interesting challenges to electronic structure theory. The cations exhibit a highly symmetrical structure (the gold atoms forming a regular trigonal bipyramid or octahedron) and thus invite theoretical analysis. The second- or third-row main-group element at the center is five- or six-coordinate and therefore violates the classical octet rule. Furthermore, the cluster ions feature quite short distances between the gold atoms indicative of bonds between the d^{10} monovalent coinage metal atoms. The term "aurophilicity"[1] has been coined to denote the phenomenon that polyaurated organogold compounds seem to have a strong propensity to bind more gold(I) units, $[LAu]^+$ (L = R_3P), to a central atom. Particularly striking examples are the compounds cited above, but other less symmetrical compounds have been synthesized.[6,7] Since gold is the heaviest coinage metal and it forms these unusual cations, it seemed likely that relativistic effects play a role in this type of bonding. A preliminary analysis of the electronic structure

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