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Ab Initio Studies of the Copper(I) Tetramers $Cu_4X_4L_4$ (X = I, Br, Cl). Effects of Cluster Structure and of Halide on Photophysical Properties

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Ab initio calculations at the Hartree-Fock level are described for various compounds of the type $Cu_4X_4L_4$, in order to gain a better understanding of the rich luminescence behavior of these cuprous halide clusters. The calculations clearly demonstrate a relationship between the Cu–Cu distances (d_{Cu-Cu}) in these "cubane" type clusters and the energies and distortions (from the ground state) expected for the "cluster-centered" (CC) excited states, which arise primarily from a redistribution of charge within the Cu_4I_4 cluster core. Specifically, the lowest energy excited state in the pyridine complex $Cu_4I_4(py)_4$ (d_{Cu-Cu} = 2.69 Å) is such a CC state but the lowest excited state in the 2-(diphenylmethyl)pyridine complex $Cu_4I_4(dpmp)_4$ (d_{Cu-Cu} = ~2.90 Å) is a halide-to-ligand charge-transfer state. The calculations furthermore indicate that as one varies the halide from I to Br to Cl for the structurally analogous $Cu_4X_4(dpmp)_4$ series, the nature of the lowest excited state progressively changes and the extent of charge transfer to the ligand diminishes while intraligand and Cu d → s,p contributions increase. Altogether, the calculations indicate that the simplified excited-state models often employed for describing the photophysical properties of coordination compounds appear to be inadequate in these cases.

Introduction

Studies in this laboratory[1–5] and others[6–10] have demonstrated the remarkably rich luminescence behavior of the "cubane"-like tetranuclear cuprous halide clusters $Cu_4X_4L_4$ (where X = Cl, Br, I; L = a nitrogen or phosphine organic base) (Figure 1a). The most extensively probed member of this series is $Cu_4I_4(py)_4$ (**A**; py = pyridine), which displays two emissions with independent lifetimes, the apparent result of very weak coupling between the relevant excited states (ES's).[2,3] *Ab initio* calculations from this laboratory have provided a novel interpretation of these photophysical properties.[11] The calculations have now been extended to several analogs with a focus on the general question of how the molecular geometries influence the electronic structures of the $Cu_4X_4L_4$ clusters. Computations are also described for monomeric and dimeric fragments (CuXL and $Cu_2X_2L_2$) in order to evaluate changes in the electronic states as one builds up the tetranuclear clusters. Such investigations are extended to dimers of the general formula $Cu_2I_2L_4$ (Figure 1b), which also show interesting photophysical properties in the limited cases studied.[3]

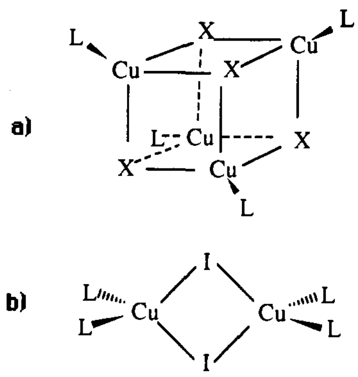

Figure 1. (a) Schematic structure of the cubane tetramers **A**–**D**. (b) Schematic structure of the dimers **E** and **F**.

Computational Details

Calculations were performed on VAX computers (Vaxstations 3100 and 3540) using the COLUMBUS set of programs,[12,13] which have been modified to include overlap population analysis.[11] The COLUMBUS programs, which have been described previously,[11–13] allow replacing atomic cores by effective potentials. Therefore the wave function need only describe the valence electrons. Even with this simplification, the present calculations were limited to the restricted Hartree-Fock level because of the complexity of the molecules and limitations of the computing facilities.

The bonding analysis was based on Mulliken's suggestion that overlap population be divided equally between the atoms involved.[14] The bond orders (total overlap populations) that result are positive for bonding interactions and negative in antibonding interactions. These bond orders

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(bo's), which are fractions of an electron, are valuable parameters for comparing bond strengths but are not normalized to integer values for bonds.

Geometrical parameters were not optimized in the calculations but were extracted from the X-ray structures of the appropriate compounds. Since ground-state (GS) structures were used for the calculations, the excited states (ES's) calculated are Franck–Condon states, the products of vertical excitation. The restricted open-shell Hartree–Fock method was used for open-shell wave functions; therefore each wave function is a pure spin state.

Calculations were carried out for the Cu_4X_4 "cubane" cores [T_d] (symbols in brackets are symmetries imposed) with geometric parameters drawn from those of the respective $Cu_4X_4(dpmp)_4$ clusters[15] (dpmp = 2-(diphenylmethyl)pyridine; X = I (**B**), Br (**C**), Cl (**D**)). These were followed by computations on the chloride clusters $Cu_4Cl_4(NH_3)_4$ [T_d] and $Cu_4Cl_4(py)_4$ [D_{2d}] with assumed geometries analogous to that of **D**. Dimers were examined with calculations on $Cu_2I_2(NH_3)_4$ [C_{2h}] and $Cu_2I_2(py)_4$ [D_{2h}] with assumed structures analogous to those of the tetramethylethylenediamine[16b] and pyridine dimers,[16a] respectively. Calculations were also carried out on a Cu_4I_4 [T_d] tetramer with geometrical parameters assumed to be those of crystalline CuI.[17] Earlier *ab initio* studies in this laboratory[11] were of $Cu_4I_4(NH_3)_4$ [T_d and D_{2d}] (as a model for $Cu_4I_4L_4$ clusters with saturated ligands), of $Cu_4I_4(py)_4$ [D_{2d}], and of the fragments $Cu_2I_2(py)_2$ [C_{2v}], CuIpy [C_s], Cu_4I_4 [T_d and D_{2d}], Cu_4 [T_d], I_4 [T_d], CuI, and pyridine with geometries modeled after that of $Cu_4I_4(py)_4$.[18]

The (core)-valence orbitals are as follows: Cu = (Ar) 3d, 4s, 4p; I = (Kr + 4d) 5s, 5p; Cl = (Ne) 3s, 3p; N = (He) 2s, 2p; C = (He) 2s, 2p; H = 1s. (The noble gas symbols in parentheses indicate the inner cores whose effects are evaluated as effective potentials.) The Cu 4p-orbital was represented as a single Gaussain function optimized for the dimer $Cu_2I_2(NH_3)_4$ as reported previously by Kyle *et al.*,[2c] and STO-3G functions were used for the H 1s-orbital. With these exceptions, the core potentials and the contracted Gaussian basis sets were those of Christiansen *et al.*,[19] the valence orbitals being represented as double-ζ by making independent the most diffuse Gaussian of each basis set.

Results and Discussion

In ambient toluene solution, the two independent emissions of **A** are evident as a weak, higher energy (HE) band with a $\lambda_{max}{}^{em}$ at 480 nm and lifetime τ of 450 ns and a more intense, lower energy (LE) emission with $\lambda_{max}{}^{em}$ = 690 nm and τ = 10.6 μs.[3] Similar emission properties are displayed by other $Cu_4I_4L_4$ clusters, but the HE band has been seen only for those clusters having π-unsaturated L's.[3,4] This fact and the results of the *ab initio* calculations led to the conclusion that the state responsible for the HE emission is largely halide-to-pyridine charge transfer (XLCT).[2c,3,11] In contrast, the LE band has been observed in the emission spectra of $Cu_4I_4L_4$ clusters having both aromatic and saturated amine L's, and the relevant ES has been termed "cluster centered" (CC), a mixture of iodide-to-copper charge transfer (XMCT) and metal-centered "d → s,p" (MC) in orbital parentage.[2c,3,11] The relatively poor coupling between the HE and LE excited states can be attributed to the large differences in the magnitudes and directions of the respective distortion coordinates of the CC and XLCT states relative to the GS.[3,11]

Table 1. Average Interatomic Distances in $Cu_nX_nL_m$ Compounds (Å)

compd	d_{Cu-Cu}	d_{Cu-X}	d_{Cu-N}	d_{X-X}
$Cu_4I_4(py)_4$ (**A**)[a]	2.69	2.70	2.04	4.51
$Cu_4I_4(dpmp)_4$ (**B**)[b]	2.92	2.69	2.07	4.39
$Cu_4Br_4(dpmp)_4$ (**C**)[b]	2.88	2.55	2.02	4.12
$Cu_4Cl_4(dpmp)_4$ (**D**)[b]	2.89	2.45	2.00	3.90
$Cu_2I_2(py)_4$ (**E**)[c]	2.70	2.64	2.06	4.54
$Cu_2I_2(Me_4en)_2$[d]	2.57	2.60	2.18	4.49

[a] Reference 18; py = pyridine. [b] Reference 15; dpmp = 2-(diphenylmethyl)pyridine. [c] Reference 16a. [d] Reference 16b; Me_4en = *N,N,N′,N′*-tetramethylethylenediamine; used as a model for **F**.

The CC state is formed upon excitation into an orbital whose principal component is the totally symmetric combination of the Cu s-orbitals. This MO, which constitutes the LUMO of the ground state in those compounds with saturated ligands, is Cu–Cu bonding and Cu–X antibonding. Populating this, therefore, would lead to structural distortions of the Cu_4X_4 core, consistent with the very large Stokes shifts observed for the CC emissions. Notable in this context is the report by Holt *et al.*[9] that CC emissions are found only for those clusters with Cu–Cu distances (d_{Cu-Cu}) less than twice the van der Waals radius of Cu(I) (i.e., less than 2.8 Å). Consistent with this suggestion, a CC emission band is seen[3,8] for $Cu_4I_4(py)_4$, with d_{Cu-Cu} = 2.69 Å, and $Cu_4I_4(pip)_4$ (pip = the saturated amine piperidine), with d_{Cu-Cu} = 2.65 Å, but not for $Cu_4Cl_4(Et_3N)_4$ (Et_3N = triethylamine), with d_{Cu-Cu} = 3.07 Å.[4]

$Cu_4I_4(dpmp)_4$. In this context, it is especially worthwhile to examine the photophysical properties of $Cu_4X_4L_4$ clusters for which changing X is not accompanied by major variations in molecular and crystal structures. This condition is met for the homologous series of 2-(diphenylmethyl)pyridine complexes $Cu_4X_4(dpmp)_4$. In these clusters, the Cu_4 tetrahedra are nearly identical with an average d_{Cu-Cu} ~2.90 Å[15] independent of X (Table 1). At 77 K, only one emission is seen for each complex, while at ambient *T*, these clusters display two thermally equilibrated emissions with identical lifetimes: The higher energy and much more intense emission was proposed to be XLCT by analogy with the HE emission of **A**.[5] Somewhat surprisingly (given this assignment), the emission maxima and excitation spectra of this band proved to be rather insensitive to the nature of X. This behavior was argued to result from two counterpoised trends, namely the respective relative ionicities resulting from the electronegativity order (Cl > Br > I) balanced against the trend in ionization energies (Cl > Br > I) for halogen atoms having the same charge.[5] The lower energy emission was not observable at 77 K but showed temperature-dependent relative intensity at higher *T*, and this band was attributed to emission from a CC state about 10^3 cm^{-1} above the XLCT state. The identical lifetimes of the XLCT and CC states from a particular $Cu_4X_4(dpmp)_4$ cluster imply facile communication between these two ES's and a significantly lower activation barrier for crossing between the ES surfaces than for **A**.

The previously published calculations concerning $Cu_4I_4(py)_4$ showed electronic characteristics of the Cu_4L_4 "cubane" core and of the CC ES's to be relatively insensitive to the nature of the ligand L as long as the Cu_4I_4 geometry was held constant.[11] For example, the HOMO was found to be ~80% I p-orbital in character and the lowest energy CC state to be about 55% XMCT and 45% MC (d → s,p) regardless of whether **A**, $Cu_4I_4(NH_3)_4$, or Cu_4I_4 was the calculated species.[11] Notably, these calculations were carried out for a Cu_4I_4 geometry assumed to be the same as that determined for the ground state of **A**. Therefore, consideration of the challenges posed by the photophysical properties of the isostructural $Cu_4X_4(dpmp)_4$ clusters began with calculations on the bare Cu_4X_4 cores with the geometries found for the respective dpmp compounds.

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Table 2. Calculated Bond Orders for Selected Tetrameric Species

cluster	state	Cu–Cu	Cu–X	Cu–N
$Cu_4I_4(py)_4$ (**A**)[a]	ground	0.01	0.10	0.02
	CC[b]	0.13	−0.04	0.03
	XLCT[c]	0.01	0.10	0.08
$Cu_4I_4(NH_3)_4$[a]	ground	0.00	0.12	0.01
	CC[b]	0.15	−0.03	0.01
Cu_4I_4 {py}[a,d]	ground	0.01	0.15	
	CC[b]	0.14	0.02	
Cu_4I_4 {dpmp}[e]	ground	0.01	0.15	
	CC[b]	0.07	0.07	
Cu_4Br_4 {dpmp}[e]	ground	0.00	0.14	
	CC[b]	0.06	0.08	
Cu_4Cl_4 {dpmp}[e]	ground	−0.01	0.12	
	CC[b]	0.05	0.07	
Cu_4I_4 {CuI}[f]	ground	0.00	0.11	
	CC[b]	0.03	0.07	
$Cu_4Cl_4(py)_4$[g]	ground	0.00	0.10	0.09
	ES	0.00	0.11	0.11

[a] From ref 11. [b] CC = cluster centered. [c] XLCT = halide-to-ligand charge transfer. [d] Cluster core of $Cu_4I_4(py)_4$. [e] Cluster cores of the $Cu_4X_4(dpmp)_4$ tetramers **B**–**D**. [f] Tetrameric fragment of crystalline CuI. [g] Geometry based on that of **D**.

Such a calculation for the Cu_4I_4 core *at the geometry of the dpmp tetramer* **B** (**B′**) gave results similar to those for the (smaller) Cu_4I_4 core of **A** (**A′**). The ground states for the respective geometries proved to be almost identical, with just a slightly larger charge separation for **B′** (0.232) than for **A′** (0.205). The Cu–I (covalent) bond order in the GS (0.15, as defined above) is virtually the same as that found for **A′** and is much less than that (0.28) calculated for the diatomic molecule Cu–I. However, the calculated CC excited states present substantial differences, the lowest ES of **B′** having substantially more XMCT character (80–90%) than that for **A′** (57–75%). Also the change in the Cu–Cu bond order upon excitation to that state is about half that calculated for **A′** (Table 2). The same trend is apparent for a cubic Cu_4I_4 fragment modeled after crystalline CuI,[17] where d_{Cu-Cu} is 4.28 Å and d_{Cu-I} is 2.62 Å. The lowest ES's are calculated to be entirely XMCT (>95%).

The relevant structural difference between Cu_4I_4 cores of **A** and **B** is d_{Cu-Cu}. The longer intermetallic distance in the dpmp compound means less Cu–Cu interaction, i.e., smaller d^{10}–d^{10} repulsion as well as smaller s–s attraction. These factors would affect differently the energies of one-electron excited states drawn from the XMCT and MC (Cu d → s,p) orbital parentages. In both cases, excitation would lead to increases in Cu s-orbital population, but only for a MC transition would a decrease in the d-orbital population be predicted. The energy of a MC state is thus expected to be higher for the weaker Cu–Cu interactions, consistent with the calculations which indicate that the contribution of MC character to the lowest ES (relative to XMCT contribution) decreases with increasing d_{Cu-Cu}.

In the above discussion, only changes in covalent interactions were considered. In a XMCT state, ionic interactions will also change with respect to the GS but are of secondary importance relative to covalency changes.[11,20] The covalent interactions are measured as overlap populations, which are functions of interatomic distance because both the MO coefficients and the sizes of overlap integrals change. While the net effect of the longer d_{Cu-Cu} in the dpmp tetramer relative to **A** appears negligible in the GS, that is not the case in the ES (Table 2). In the GS, the negative changes in the Cu s-orbital/Cu s-orbital overlap populations and positive changes in the Cu d-orbital/Cu d-orbital overlap populations counterbalance. On the other hand, the enhanced electron density in the Cu s-orbital in the CC state relative to the GS has less effect on the Cu–Cu and Cu–I bond orders for **B′** than it does for **A′**. The large bond order changes in the CC state of **A** have been interpreted as indicating that this state undergoes geometrical distortions relative to the GS.[11] The smaller bond order changes expected for the corresponding ES of **B** would suggest, therefore, less distortion.

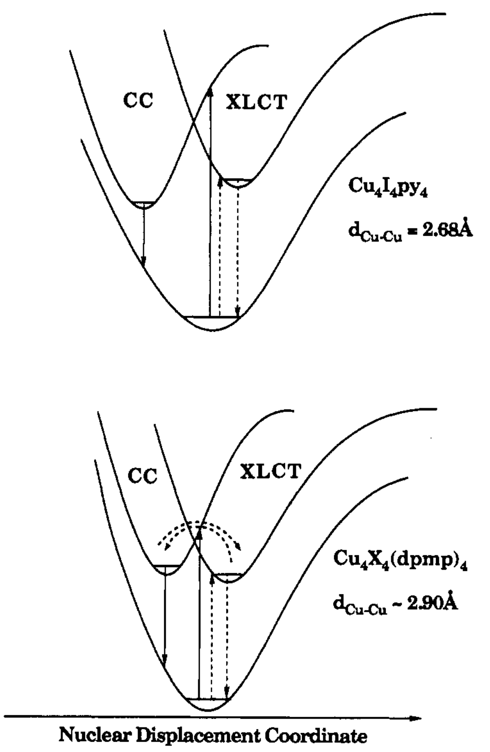

Figure 2. Hypothetical cross sections of the potential energy surfaces for the ground and lowest excited states of $Cu_4I_4L_4$ cubane compounds with Cu–Cu distances shorter than 2.8 Å (above) and longer than 2.8 Å (below).

The qualitative prediction of Holt[9] seems confirmed, and its justification can now be attempted (Figure 2). At longer d_{Cu-Cu}, the reduced Cu–Cu interaction leads to less distortion in the CC state relative to the ground state. The lesser distortion leads to greater communication with the XLCT state (when this is present). Cluster **B** is likely to be a borderline case, where the CC state is sufficiently separated from the XLCT state to be thermally populated from it and where the balance between the radiative and nonradiative deactivation rate constants leads to detectable emission from both ES's but with the same τ.[5] Apparently, the decreased Cu–Cu interactions for those cases where d_{Cu-Cu} is substantially longer than 2.8–2.9 Å leads to CC states which are not emissive.

$Cu_4X_4L_4$. Once the effect of the difference in the interatomic distances within the "cubane" core has been evaluated, it becomes possible to examine the luminescence results for tetramers composed of other halides. Such clusters generally have d_{Cu-Cu} values in excess of 2.8 Å and display only single-emission bands which are seen only when L is π-unsaturated. (An exception is $Cu_4Br_4(dpmp)_4$ (**C**), which displays a strong higher energy emission along with a weak, thermally promoted CC emission.) The emission in such complexes has been likened to the HE emission of **A** and assigned to a XLCT excited state.[4,5] In this context, the band energies might have been expected to be strongly dependent on the identity of the halide, but this is not the case for the isostructural $Cu_4X_4(dpmp)_4$ compounds. The emission energies are relatively insensitive to X but do follow the order I > Br > Cl,[5] which is counterintuitive, given the atomic and ionic orbital energy levels that would be estimated from ionization potentials of the respective halide ions X^- (Figure 3).[21] The excitation spectra are virtually halide independent.

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[20] By using the calculated atomic populations and the crystallographic interatomic distances, one can estimate the change in electrostatic repulsion among the Cu ions (q^2/d) upon excitation into the lowest singlet ES's to be ~8 and ~24 kJ/mol for the Cu_4I_4 tetramers at the geometries of **A** and **B**, respectively.

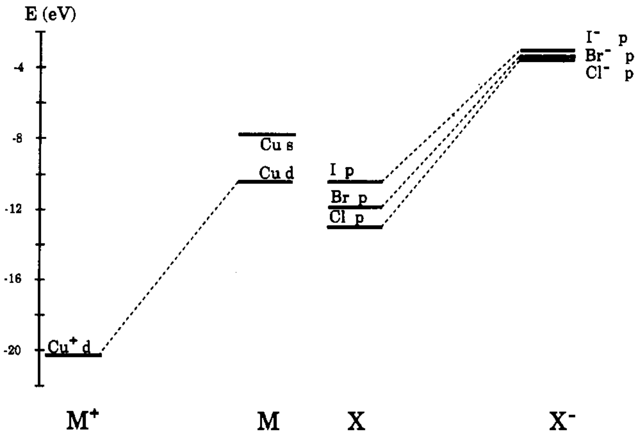

Figure 3. Energies of the valence orbitals of Cl, Br, I, and Cu, derived from gas-phase spectroscopy and thermodynamic data. For the neutral halogen atoms, the energies of the p-orbitals equal −IE(1) (IE(1) = first ionization energy), while those for the mononegative ions are the electron affinities (EA's). For a neutral Cu atom, the s-orbital energy equals −IE(1) and that of the d-orbitals is this value minus the spectroscopic d–s gap, while the d-orbital energy in Cu^+ is −IE(2). IE values and d–s gaps are from ref 21a; EA values are from ref 21b.

Table 3. Results of the SCF Calculations for Cu_4X_4 Cubanes[a] (Point Group T_d)

	state	transn	$-E$ (au)[b]	Cu[c]	d[d]	s[d]	p[d]	% XMCT[e]
Cu_4I_4	$^1A_1$		245.972	0.232	40.041	1.370	1.662	
	$^1T_2$	$t_2 \rightarrow a_1$	245.713	0.064	39.888	2.066	1.792	81.4
	$^3T_2$	$t_2 \rightarrow a_1$	245.721	0.059	39.893	2.252	1.618	82.3
	$^1T_1$	$t_1 \rightarrow a_1$	245.706	0.054	39.952	2.168	1.663	88.8
	$^3T_1$	$t_1 \rightarrow a_1$	245.709	0.053	39.953	2.212	1.623	89.0
Cu_4Br_4	$^1A_1$		253.770	0.335	40.054	1.221	1.384	
	$^1T_2$	$t_2 \rightarrow a_1$	253.501	0.192	39.785	2.063	1.384	68.0
	$^3T_2$	$t_2 \rightarrow a_1$	253.512	0.194	39.805	2.134	1.284	69.4
	$^1T_1$	$t_1 \rightarrow a_1$	253.490	0.183	39.871	2.107	1.290	76.9
	$^3T_1$	$t_1 \rightarrow a_1$	253.494	0.183	39.872	2.119	1.277	77.1
Cu_4Cl_4	$^1A_1$		260.100	0.440	40.030	1.046	1.166	
	$^1T_2$	$t_2 \rightarrow a_1$	259.822	0.323	39.591	1.952	1.165	51.5
	$^3T_2$	$t_2 \rightarrow a_1$	259.833	0.318	39.628	1.997	1.102	54.6
	$^1T_1$	$t_1 \rightarrow a_1$	259.809	0.322	39.585	2.002	1.124	51.3
	$^3T_1$	$t_1 \rightarrow a_1$	259.814	0.321	39.592	2.009	1.114	51.9

[a] Cluster cores of the $Cu_4X_4(dpmp)_4$ tetramers **B**–**D**. [b] Energy in hartrees, changed sign. [c] Charge on each atom, from Mulliken's population analysis. [d] Total Mulliken's population analysis. [e] The nature of the excited states is represented as percent contributions of "elementary" transitions to the total change in charge distribution. The values reported here for XMCT (halide-to-metal charge transfer) character are the percentage of the charge added to the Cu s and p orbitals that is subtracted from the iodines. The balance is in all of these cases d → s,p (metal-centered transition from Cu d- to Cu s- and p-orbitals).

One potential explanation for this surprising result is that the ES's involved remain XLCT in nature but with energies nearly equalized by the compensating effect of the different ionicities. Figure 3 illustrates the qualitative changes in the energies of several atomic orbitals as functions of ionicity. From this one can see that the p-orbitals of I and Cl, for example, could have similar energies if the iodo compound were significantly less ionic than the chloro analog. In other words, greater charge separation (i.e., ionicity) in the chloro cluster GS predicted by the relative electronegativity of Cl reduces the ionization energy of Cl.

As described above, calculations carried out on the "bare cores" Cu_4X_4 at the geometries of the iodo, bromo, and chloro clusters **B**–**D** show the expected ionicity increases across this series (charge separations of 0.232, 0.335, and 0.440, respectively; Table 3). In each case, the population analysis yields completely filled Cu d-orbitals; therefore, charge difference is concentrated in copper s and p levels (Cu_4 s,p populations of 3.032, 2.605, and 2.212, respectively). Lower electron density in the Cu s-orbitals, which provide the bonding component of the interaction between the metal atoms, leads to a downward trend in the ground-state Cu–Cu bond orders (0.005, 0.000, and −0.006, respectively), as expected.[22] The increased ionicity is also reflected in decreased covalency between Cu and X, as shown by the respective calculated Cu–X bond orders of 0.15, 0.14, and 0.12 (Table 2). Covalent X–X interactions are almost negligible (−0.02 to −0.01 bo's).

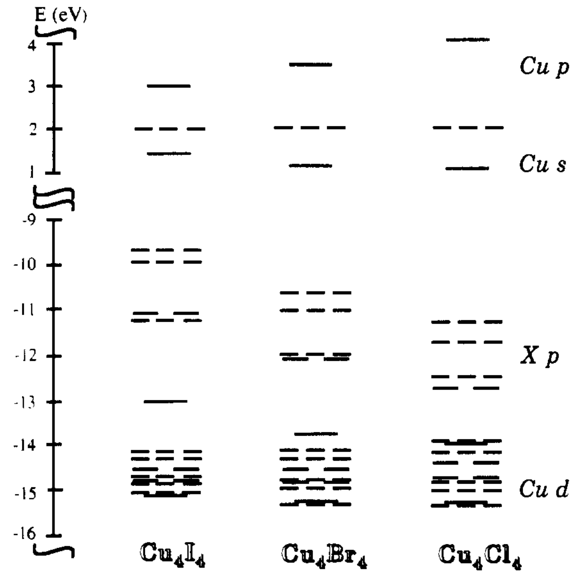

Figure 4. Molecular orbital diagrams of the ground states of the Cu_4X_4 cubane cores of **B**–**D**. The X p- and Cu d-orbitals are filled; the Cu p- and Cu s-orbitals are empty.

The MO diagrams obtained from these calculations are shown in Figure 4. As noted above, the GS of the Cu_4I_4 tetramer with the **B** geometry is closely analogous to that with the **A** geometry. The natures of the HOMO's are similar for the Cu_4X_4 cores with the appropriate **B**–**D** geometries; however, there is increasing Cu d-orbital character as one progresses from Cu_4I_4 to Cu_4Cl_4 (from 11% to 25%). In general, the filled orbitals display less Cu s-orbital character while the LUMO's display more over this series. The effect of the changing ionicities is evident in the energy differences between the (mostly halide p-orbital) HOMO's; $E_p(I) - E_p(Cl) = 1.53$ eV in these tetramers versus 2.55 eV for the neutral atoms.[21a]

The larger Cu d-orbital contribution to the HOMO for Cu_4Cl_4 relative to Cu_4I_4 is accompanied by a greater Cu d → s,p contribution to the CC state (45% vs 18%, respectively, in the lowest triplets) (Table 3). Furthermore, this suggests that the HE state thought to be responsible for the principal emission among the dpmp clusters would have more metal-to-ligand charge-transfer (MLCT) character for **C** and **D** than found in **B**. In the tetramers with the lighter halides, more charge would be extracted from the Cu d-orbitals, decreasing electron–electron repulsion in those orbitals and lowering the energy of this state.

Although different ionicities in the GS's and different electron correlation in the ES's could explain the nearly identical excitation spectra and very similar emission energies of the $Cu_4X_4(dpmp)_4$ clusters, another feature of Figure 4 must be addressed. The lower energies of the halide p-orbitals in the Cu_4Cl_4 and Cu_4Br_4 cluster cores (with respect to Cu_4I_4) lead to smaller gaps between these orbitals and the Cu d-orbitals. In the iodide tetramer **A**, the π levels of the aromatic ligands stand in splendid isolation

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(22) Soloveichik, G. L.; Eisenstein, O.; Poulton, J. T.; Streib, W. E.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3306–3312.

Table 4. Contributions to the Molecular Orbitals of $Cu_4Cl_4(py)_4$,[a] (Point Group D_{2d})

MO	*E* (eV)	Cu s,p[b,c]	Cu d[b,c]	Cl s[b,c]	Cl p[b,c]	py[b-d]	py p[b-d]
$17a_1$	4.40	30.8	0.5	12.6	4.2	51.8	16.8
$16b_2$	3.75	0.5	0.1	0.0	0.1	99.2	98.8
26e	3.74	0.8	0.1	0.0	0.0	99.1	96.4
$16a_1$	3.73	0.4	0.1	0.0	0.1	99.4	98.2
$10a_2$	3.25	1.6	0.1	0.0	0.1	99.8	99.5
25e	3.23	0.1	0.1	0.0	0.0	99.8	98.7
$10b_1$	3.20	3.5	0.1	0.0	0.1	99.6	93.2
LUMO							
HOMO							
$15b_2$	−8.50	1.5	18.1	0.0	8.0	72.5	61.0
24e	−8.59	1.5	18.9	0.0	7.3	72.3	60.9
$15a_1$	−8.84	3.5	10.1	0.0	0.0	86.4	72.2
$14b_2$	−9.34	1.9	32.1	0.0	61.4	4.5	4.0
23e	−9.41	2.3	30.5	0.0	60.6	6.7	5.8
22e	−9.83	2.8	30.0	0.0	64.0	3.3	3.0
$9a_2$	−9.84	2.7	29.2	0.0	65.2	2.9	2.7
$9b_1$	−10.02	0.0	0.8	0.0	0.1	99.1	99.1
$8a_2$	−10.02	0.0	2.3	0.0	0.6	97.1	97.1
21e	−10.03	0.0	0.6	0.0	1.0	98.3	98.3

[a] Reported are the lowest unoccupied and the highest occupied MO's. [b] For empty MO's, the numbers given are relative to the sum of the square of the relevant coefficients for the symmetry orbitals. Since the overlaps are completely neglected, these numbers have only a very qualitative value. [c] For filled orbitals, the numbers given are the percentage of the electrons in each MO attributed to that particular AO type by Mulliken's population analysis. [d] The column labeled "py" gives the values defined above summed over all the AO types of the atoms in the pyridine ligands. The column labeled "py p" gives the same values summed only over the p orbitals of all the atoms in the pyridines. Since the s orbitals do not contribute to π- and π^*-orbitals, orbitals with large and equal or nearly equal values in both these columns will have mainly pyridine π or π^* character.

between the Cu d- and I p-orbitals.[2c,11,23] A very different situation is found for a calculated $Cu_4Cl_4(py)_4$ with a geometry modeled after **D**. The three highest occupied MO's ($15b_2$, 24e, and $14a_1$; Table 4) are predominantly pyridine π-orbitals with some copper d-orbital character. The presence of such metal–ligand π interaction is also reflected by a calculated Cu–N bond order (0.09) in this case significantly larger than that found for **A** (0.02).

The HOMO–LUMO $b_2 \rightarrow b_1$ transition of this $Cu_4Cl_4(py)_4$ model was investigated by calculating the $^3A_2$ excited state resulting from that transition. As previously described for **A**,[11] the nature of the resulting ES provided does not excactly correspond to what one might be led to expect from a one-electron transition between the MO's. The calculated excited state shows significant XLCT and Cu d → s,p characters, each accounting for ~20% of the changes in the ES with respect to the GS. About half of such changes, however, can be attributed to intraligand contributions, including $\pi \rightarrow \pi^*$. The computed excitation-induced increase in Cu–N bo indicates that charge has been drawn from orbitals with Cu–N antibonding character. Almost no change is observed in the Cu–Cu, Cu–Cl, and Cl–Cl bond orders, while significant changes are found in the bonding within the ligands.

Thus, analysis of the GS MO's and certain ES's calculated for this $Cu_4Cl_4(py)_4$ model yields a picture significantly different from the HE excited state of **A**, which *ab initio* calculations concluded is largely XLCT in character. The present calculations are complex in their quantitative details, but they do provide valuable qualitative insight. For example, these results do show that, for an aromatic L, varying the halide leads to changes in the nature of both the GS and the lowest energy excited states. Thus, while the emission and excitation spectra of these $Cu_4X_4(dpmp)_4$ clusters appear quite similar,[5] these calculations indicate that the nature of the emitting excited state undergoes systematic changes in contributions from "simple" transitions, i.e., those between orbitals specific to certain locales (e.g., MLCT or $\pi \rightarrow \pi^*$) as one proceeds from X = I to X = Cl.

$(CuI)_nL_m$. Both the complete CI calculation including spin-orbit coupling of Ramirez Solís *et al.*[24] and our own more qualitative results identify the lowest state of molecular CuI, either at optimized geometry (2.42 Å) or at the distance found in **A** (2.70 Å), as Cu d → s,p in character, but with the first XMCT states very close in energy. The same is calculated for CuIL monomeric fragments with d_{Cu-I}, d_{Cu-N}, and angles the same as those in **A**, with only 10% of XMCT mixed into the lowest ES. When two CuIL units come together to form the hypothetical dimers $Cu_2I_2L_2$ (with geometries taken as a fragment of **A**), the lowest energy ES's are of mixed character similar to that described for tetrameric clusters. The Cu d → s,p component, however, still carries a heavier weight than it does in the tetramers, being between 50% and 70% of the lowest ES's of $Cu_2I_2(NH_3)_2$ and $Cu_2I_2(py)_2$. For the latter case, states of XLCT character appear separate from the CC state, as in the tetramer **A**. These results strongly suggest that the CC states owe their special natures to the interaction between two or more CuI units.

The luminescence properties of a few $Cu_2I_2L_4$ dimers have been investigated. For example, solid $Cu_2I_2(Et_4en)_2$ (**F**; Et_4en = *N,N,N′,N′*-tetraethylethylenediamine) displays emission (λ_{max} = 522 nm at ambient *T*, 544 nm at 77 K) with temperature dependence similar to that of the LE bands of solid $Cu_4I_4(py)_4$ and $Cu_4I_4(pip)_4$.[2,3,25] In contrast, emission from the $Cu_2I_2(py)_4$ dimer (**E**) is essentially temperature independent, presenting maxima of 502 nm at 295 K and 504 nm at 77 K,[1,3] behavior more typical of the HE emission of **A**.[26,27] Thus, although they occur at similar energies, the emissions from the Et_4en and pyridine dimers may have different orbital origins.

In order to investigate the latter hypothesis, calculations were carried out on the hypothetical dimer $Cu_2I_2(NH_3)_4$ with a geometry analogous to that of **F**. Also treated was $Cu_2I_2(py)_4$, although with the pyridine rings arranged in D_{2h} symmetry to facilitate computation. The HOMO's of $Cu_2I_2(NH_3)_4$ (Table 5) are about 73–93% I p-orbital character, the remainder being from Cu d- and s-orbitals, similar to the HOMO of $Cu_4I_4(NH_3)_4$.[11] Although this dimer, with calculated charges of +0.472 on Cu and −0.528 on I, appears significantly more ionic than either $Cu_4I_4(NH_3)_4$ (0.337 and −0.393, respectively) or the dimer fragment $Cu_2I_2(NH_3)_2$ (0.388 and −0.457), the calculated ES's of $Cu_2I_2(NH_3)_4$ are very similar to those other models, the lowest energy ES having slightly more Cu d → s,p (~50%) than XMCT (~35%) character, the balance being LMCT. The Cu–Cu distance used in this calculation (that for **F**[16b]) was 2.55 Å, even shorter than that for **A** (2.69 Å),[18] indicating strong cluster core interactions. The possibility of a CC state for such a dimer, and for **F**, is supported by the computation.

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(23) The combinations of the two higher energy π-orbitals of the pyridines have energies intermediate between the lowest I p-orbital and the highest Cu d-orbital of Cu_4I_4, as shown in Figure 4. The lone orbital present in that region is Cu–I bonding, with mainly I p-orbital character. The combinations of the two lower energy π^*-orbitals of the pyridines have energies below that of the LUMO of Cu_4I_4.

(24) Ramirez Solís, A.; Daudey, J. P.; Teichteil, C. *J. Chem. Phys.* **1990**, *93*, 7277–7283.

(25) Another emissive compound with neither the cubane core structure nor an aromatic ligand is the acetonitrile polymeric adduct $[CuI(CH_3CN)]_\infty$. It emits at room temperature with a 545-nm maximum and at 77 K with a 576-nm maximum, showing the same trend toward lower emission energies with decreasing temperature.[1]

(26) The HE emission has not been detected in solid **A** at room temperature, likely because it is too weak compared with the LE emission in the same conditions. However, the ambient-*T* emission of the polymer $[CuIpy]_\infty$[2] should be a good approximation for the HE emission of the solid tetramer, giving an emission maximum of 437 nm at ambient *T* vs 430 nm at 77 K.

(27) An adduct formed by cuprous iodide under pyridine, which is likely to have a higher pyridine-to-CuI ratio than the better characterized compounds, shows emission at 566 nm at 77 K.[12] Such emission, when considered together with the HE emission of **A** (430 nm at 77 K) and that of $Cu_2I_2(py)_4$ (504 nm at 77 K), suggests a trend toward longer wavelength emissions with increasing number of pyridine ligands per CuI unit.

Table 5. Contributions to the Molecular Orbitals of $Cu_2I_2(NH_3)_4$[a] (Point Group C_{2h})

MO	*E* (eV)	Cu sp[b,c]	Cu d[b,c]	I s[b,c]	I p[b,c]	L[b,c]
$13a_g$	7.43	52.4	1.4	10.6	25.4	10.2
$12b_u$	5.19	84.4	0.1	0.0	5.9	9.7
$12a_g$	4.61	55.2	0.2	12.1	6.6	25.9
LUMO						
HOMO						
$11b_u$	−7.19	3.5	19.3	0.0	72.5	4.7
$6a_u$	−7.31	6.4	14.5	0.2	78.7	0.2
$6b_g$	−7.68	0.0	6.8	0.0	93.1	0.1
$10b_u$	−7.70	0.7	9.2	0.0	85.4	4.7
$5b_g$	−8.25	8.4	1.2	0.0	90.2	0.2
$11a_g$	−8.42	11.5	22.6	0.3	55.6	10.0
$10a_g$	−9.52	1.0	72.5	0.0	0.0	26.4
$9b_u$	−10.43	1.6	92.7	0.0	0.1	5.6
$8b_u$	−10.58	6.8	57.6	0.0	11.5	24.2
$4b_g$	−11.04	0.0	98.2	0.0	1.5	0.4

[a] Reported are the lowest unoccupied and the highest occupied molecular orbitals. [b] For empty orbitals, the numbers given are relative to the sum of the square of the relevant coefficients for the symmetry orbitals in the molecular orbitals. Since the overlaps are completely neglected, these numbers have only a very qualitative value. [c] For filled orbitals, the numbers given are the percentage of the electrons in each MO that is attributed to that particular atomic orbital type by Mulliken's population analysis.

The Cu–Cu distance in $Cu_2I_2(py)_4$ is also short, 2.70 Å;[16a] therefore, a CC transition might be expected for the pyridine dimer as well. The calculated components of the HOMO's of **E** again are mainly of iodine p-orbital character, but there are some noteworthy differences between the MO's of **E** and of **A**.[11] As noted above, the pyridine π-orbitals of **A** are essentially undisturbed. On the other hand, the calculations for the $Cu_4Cl_4(py)_4$ model yielded extensive mixing of the symmetry orbitals deriving from the combination of medium-energy pyridine π-orbitals with Cu and Cl orbitals. In **E**, two of those four pyridine π-orbital combinations are essentially pure; the other two appear as a component in orbitals as much as 1 eV away. The calculated Cu–N bo, is smaller in **E** than in $Cu_4Cl_4(py)_4$ or **A** (−0.02 vs 0.09 and 0.02, respectively). As for $Cu_2I_2(NH_3)_4$, the calculation shows **E** to be more ionic than **A** (charges for Cu of 0.594 vs 0.360 and for I of −0.576 vs −0.406). Greater ionicity results in smaller percentages of Cu s- and p-orbital character in the filled MO's. This effect, in turn, produces smaller Cu–Cu bond orders (−0.01 for **E** and −0.02 for $Cu_2I_2(NH_3)_4$).

The excited states calculated for **E** (Table 6) conform to a model different from others found up to this point. They present ~50/50 mixing of metal-centered Cu d → s,p and charge transfer to the ligand characters. The reason could be the result of the coordinating two pyridines to the same Cu atom, which allows for greater interactions with each other and with the Cu_2I_2 core, perhaps leading to the novel mixing of charge transfer to the ligand and metal-centered characters. The presence of a single ES type of low energy is consistent with the observation of just one emission from **E** at any temperature, contrary to the behavior of **A**.

Table 6. Results of SCF Calculations for Excited States of $Cu_2I_2(py)_4$ (Point Group D_{2h})

state	transn	ΔE (10^3 cm^{-1})[a]	% MLCT[b]	% d → s,p[b]	% XLCT[b]
$^1B_{3u}$	$b_{3u} \rightarrow a_g$	45.1	6.3	53.5	40.2
$^3B_{3u}$	$b_{3u} \rightarrow a_g$	44.9	5.6	54.3	40.0
$^1B_{1u}$	$b_{1u} \rightarrow a_g$	48.1	10.9	40.0	49.1
$^3B_{1u}$	$b_{1u} \rightarrow a_g$	47.8	10.0	40.6	49.4
^3Ag	$a_g \rightarrow a_g$	49.5	10.5	53.7	35.7
^1A_u	$b_{1u} \rightarrow b_{1g}$	49.9	10.9	38.8	50.4
^3A_u	$b_{1u} \rightarrow b_{1g}$	49.9	10.8	38.8	50.4
^3A_g	$b_{1u} \rightarrow b_{1u}$	53.9	9.4	37.0	53.5
$^1B_{3u}$	$b_{1u} \rightarrow b_{2g}$	54.0	9.5	36.9	53.6
$^3B_{3u}$	$b_{1u} \rightarrow b_{2g}$	54.0	9.5	37.1	53.4
$^1B_{2u}$	$b_{1u} \rightarrow b_{3g}$	56.8	9.2	36.9	54.0
$^3B_{2u}$	$b_{1u} \rightarrow b_{3g}$	56.8	9.2	36.8	54.0

[a] Excited-state energy relative to the ground state assumed as zero. [b] The nature of the excited states is represented as percent contributions of "elementary" transitions to the total change in charge distribution. For example, the values reported for XLCT are the percentage of the charge added to the pyridine ligands that is subtracted from the iodines. MLCT = metal-to-ligand charge transfer; XLCT = halide-to-ligand charge transfer; d → s,p = metal-centered transition from Cu d- to Cu s- and p-orbitals.

Summary

Applications of *ab initio* methods to inorganic systems appear particularly apt to furnish new ideas on the electronic structure, photophysical properties, and structure-determining factors of such systems. No assumptions are made *a priori* on either the nature and strength of the interactions between the different atoms or their oxidation states. The results, therefore, can provide *a posteriori* a picture of inorganic compounds taken from a less biased perspective.

In the simplified models often employed to discuss the photophysical propeties of coordination compounds, each MO is assumed to be derived mainly from just one type of atomic orbital (or MO of a fragment, e.g., ligand π-orbitals). The interaction with other orbital types is treated as a perturbation and seen as changing the energy of the MO and giving it bonding or antibonding character but not changing its nature in a first approximation. In the polynuclear copper(I) compounds studied here and elsewhere,[11] the limits for validity of such a first approximation are breached. Our ground-state calculations clearly show that the MO's are heavily mixed in character. Furthermore, the excited-state calculations demonstrate that viewing the lowest energy states as being the simple result of HOMO–LUMO transitions fails to account for the considerable, accompanying electronic reorganization. Thus, although qualitative orbital parentage descriptions of excited states based on transitions between "localized" MO's often provide valuable insight into photochemical and photophysical properties of metal complexes, such descriptions are inadequate for the cuprous halide clusters discussed here and are likely to prove inadequate for other polynuclear systems.

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