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# Photochemical and Photophysical Properties of Tetranuclear and Hexanuclear Clusters of Metals with $d^{10}$ and $s^2$ Electronic Configurations

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## Introduction

Although transition metal complex photochemistry and photophysics have occupied the interest of numerous investigators for several decades, relatively little attention has been paid to metal ions with the  $nd^{10}$  and  $nd^{10}(n+1)s^2$  (i.e., " $s^2$ ") configurations. In combination with various anionic and neutral ligands, these metal ions form a wide variety of cluster compounds, some of which have been known to be luminescent when irradiated with ultraviolet light. Prominent examples of this family are cuprous iodide clusters such as  $Cu_4I_4(py)_4$  (1, py = pyridine, Figure 1),<sup>1</sup> which some years ago were reported<sup>2</sup> to show "luminescence thermochromism"; that is, they display bright emissions with colors markedly dependent on the temperature. Here we present an overview of recent studies carried out both independently and jointly in the authors' laboratories focusing upon the remarkably rich, but relatively unexplored, photochemical and photophysical properties of various tetra- and hexanuclear  $d^{10}$  and  $s^2$  metal ion clusters in solution.

Clusters of the  $d^{10}$  and  $s^2$  metals display a variety of geometries. Examples are "cubane" structures such as  $Tl_4(OCH_3)_4$ ,<sup>3</sup> an  $M_4$  tetrahedron with face-bridging methoxides, and 1 with face-bridging iodides plus pyridines at the apices.<sup>4</sup> Edge bridging of an  $M_4$  tetrahedron gives an "adamantane"  $M_4Y_6$  skeleton which can also bind ligands at the apices<sup>5,6</sup> to give species such as  $Zn_4(SPh)_{10}^{4-}$ . Other structures include  $M_4$  squares as in  $Au_4Cl_4(\text{piperidine})_4$ ,<sup>7,8</sup>  $M_4$  rectangles as in  $Hg_4Cl_4(2\text{-pyridylphenyl})_4$ <sup>9</sup> and a "stair step" isomer of  $Ag_4I_4(PPh_3)_4$ .<sup>10</sup> Hexanuclear complexes with  $M_6$  octahedra may have face-bridging ligands as in the  $s^2$  cluster  $Sn_6O_4(OCH_3)_{11-13}$  or have bidentate ligands

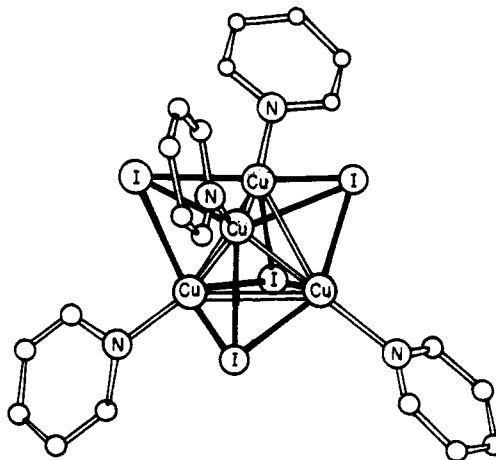


Figure 1. The structure of the  $Cu_4I_4(py)_4$  cluster (1), redrawn using the ChemX molecular modeling program from the Cambridge data base (ref 1).

which both bridge edges and cap apices as in  $Cu_6L_6$  (L is a mono- or dithiocarbamate).<sup>14-17</sup>

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Peter C. Ford earned his Ph.D. with K. B. Wiberg at Yale in 1966 and then spent a year as an NSF postdoctoral fellow at Stanford with Henry Taube. In 1967 he joined the faculty of the University of California, Santa Barbara, where he has held the rank of professor since 1977. Awards include an Alexander von Humboldt Senior Scientist Award at the University of Regensburg in 1992. Research interests include the mechanisms of homogeneous catalysis and photocatalysis and the photochemistry and photophysics of coordination and organometallic compounds of the transition elements.

Arnd Vogler earned his Ph.D. with E. O. Fischer at The Technical University Munich in 1965. After postdoctoral studies at the Moscow State University and at the University of Southern California with Arthur Adamson, he joined the Institut für Anorganische Chemie, Universität Regensburg, in 1970, where he now holds the rank of professor. His research is concerned with the photochemical and photophysical properties of metal complexes including transition and main group metal complexes, organometallics, and bioinorganic compounds.

It is not obvious why clusters such as 1 hang together and show photooptical properties distinct from those of mononuclear fragments. The bonding may be largely electrostatic, the  $M_nX_x$  cores largely determined by the most efficient packing of cations and anions. The filled subshells of the  $d^{10}$  or  $s^2$  ions should (to a first approximation) contribute little to covalent metal-metal bonding, although extended Hückel MO calculations argue for small covalency contributions from mixing with empty higher energy orbitals.<sup>18</sup> Ab initio calculations at the restricted Hartree-Fock-self-consistent field level (using relativistically corrected core potentials) also conclude that weak Cu-Cu bonding in 1 will result from the balance of such contributions.<sup>19</sup> A feature which makes these systems particularly interesting is the prediction that excited states (ES) for which there is a substantially increased electronic population in metal  $ns$  or  $np$  orbitals should have enhanced metal-metal bonding. The result would be excited states significantly distorted from the ground states in a manner that should have marked effects on the photophysical and photochemical properties of these materials. As will be seen below, the luminescence and reaction properties of the  $d^{10}$  and  $s^2$  clusters are strongly influenced by such excited-state distortions.

### Spectra of $d^{10}$ and $s^2$ Complexes

The absorption spectra of various mononuclear  $d^{10}$  group Ib complexes display bands assigned to metal-centered, metal to ligand charge transfer (MLCT), charge transfer to solvent (CTTS), ligand to metal charge transfer (LMCT), intraligand (IL), and ligand to ligand charge transfer (LLCT) transitions, depending on natures of the metal and ligands.<sup>20-25</sup> In contrast to complexes with  $d^n$  ( $0 < n < 10$ ) configurations, the  $d^{10}$  and  $s^2$  complexes cannot display ligand field ( $d-d$ ) bands; instead the metal-centered bands are limited to interconfigurational  $nd \rightarrow (n+1)s$  or  $nd \rightarrow (n+1)p$  electronic transitions. These are often mixed in character, examples being absorptions of Cu(I) halides attributed to mixed  $d-s$ /LMCT character<sup>22</sup> and of  $CuCl_n^{(n-1)-}$  solutions suggested to be of mixed  $d-s$ /CTTS nature.<sup>23</sup>

The  $d$  orbitals of the group IIb metals are much more stable; thus,  $d-s$  and MLCT transitions may not appear above 200 nm.<sup>26</sup> The UV absorptions of Hg(II) compounds are of the LMCT type,<sup>27</sup> but for Zn(II) complexes even LMCT absorptions may not show up above 200 nm. With certain ligands low energy intraligand

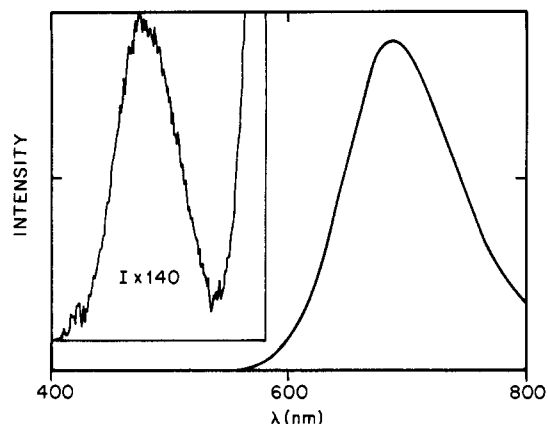


Figure 2. Emission and absorption spectra of the copper(I) cluster  $Cu_4I_4(py)_4$  (1) in ambient temperature toluene solution. Reprinted with permission from ref 40. Copyright 1991 American Chemical Society.

and LLCT bands have been observed.<sup>28-31</sup> For main group metal complexes, metal-centered, LMCT, IL, and LLCT absorptions have been identified.<sup>32</sup> The  $s^2$  complexes are characterized by low-energy metal-centered  $s-p$  transitions.<sup>33-35</sup> Emissions generally exhibit large shifts from absorption maxima attributed to strong distortions between the ground- and excited-state geometries. For example, the "seesaw"-shaped  $SbCl_4^-$  and  $BiCl_4^-$  ions may distort to tetrahedra in their  $s-p$  excited states.<sup>33</sup>

### Spectroscopic Properties of $d^{10}$ Metal Clusters

**Tetranuclear Copper(I) Clusters.** Earlier luminescence studies of the "cubane" Cu(I) clusters  $Cu_4X_4L_4$  were largely of solids.<sup>1,36,37</sup> Recent investigations have demonstrated strong analogies between the photophysical properties of well-characterized solids and the same materials in solutions.<sup>38-44</sup> The rich luminescence properties of the  $Cu_4X_4L_4$  clusters are illustrated by the emission spectrum of 1 in toluene solution (Figure 2). At ambient temperature two emissions can be detected, an intense lower energy (LE) band at  $\lambda_{max}^{em} = 690$  nm and a much weaker, higher energy (HE) band at 490 nm.<sup>40</sup> The poor coupling between the two relevant excited states is indicated by the different

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Table I. Photophysical Properties of Representative  $\text{Cu}_4\text{I}_4\text{L}_4$  Clusters in Toluene Solution (Except Where Noted)<sup>a,b</sup>

L	HE				LE			
	T (K)	$\lambda_{\text{max}}$	$\lambda_{\text{max}}^{\text{ex}}$	$\tau$	$\lambda_{\text{max}}$	$\lambda_{\text{max}}^{\text{ex}}$	$\tau$	$\tau$
pyridine	294	480	325, 352	0.45	690	325	10.6	
	77	436	350	32.9	583	317	26.5	
solid (1)	77	438	365	23.2	619	330	25.5	
4- <i>tert</i> -butylpyridine	294	468		0.35	696		10.3	
	77	434		38.7	595		43.5	
solid state	77	437	362	29.2	650	327	38.8	
4-benzylpyridine	294	473		0.56	692		11.0	
4-phenylpyridine	294	520		0.12	694		9.4	
3-chloropyridine	294	537 <sup>c</sup>		0.35	675		12.7	
piperidine	294				680		0.11	
morpholine	294				671		0.51	
	77				630		19.8	
P( <i>n</i> -Bu) <sub>3</sub>	294				654		2.23	

<sup>a</sup>  $\lambda$  in nanometers;  $\tau$  in microseconds. <sup>b</sup> Data from ref 40.

emission lifetimes ( $\tau$ ), 10.6 and 0.45  $\mu\text{s}$ , respectively. Upon lowering  $T$ , the LE band shifts first to the red, then sharply to the blue at the solution glass transition. Simultaneously, the HE band, hardly discernible in the room temperature spectrum, becomes much more prominent. The combined effects are responsible for the "luminescence thermochromism". Notably, solid 1 is white, dilute solutions of 1 are colorless, and the absorption spectrum shows no significant absorbance above 400 nm. UV absorptions increase toward shorter wavelength with strong bands below 300 nm due to the presence of iodide and pyridine. Diffuse reflectance spectra display weak transitions in the 300–400-nm region. Similarly, the excitation spectra also demonstrate the presence of absorptions in this region.

A key experiment in Regensburg<sup>45</sup> showed that the bright LE emission band of 1 is mimicked by the luminescence spectrum of the saturated amine analog  $\text{Cu}_4\text{I}_4(\text{morpholine})_4$  (2) ( $\lambda_{\text{max}} = 671$  nm in toluene). Thus, this emission cannot be the result of a charge-transfer excited state involving  $\pi$ -unsaturated ligand orbitals; instead an assignment as a  $\text{Cu}_4$  cluster  $d \leftarrow s$  transition was proposed.<sup>45</sup> Subsequent studies at Santa Barbara demonstrated that the two bands seen for the emission spectra of 1 are also present for other  $\text{Cu}_4\text{I}_4(\text{py-x})_4$  ( $\text{py-x}$  = substituted pyridine), while only the more intense LE emission was seen for 2 and other saturated amine clusters  $\text{Cu}_4\text{I}_4\text{L}_4$ .<sup>38,40</sup> The LE band position proved to be independent of the pyridine substituents, but the HE band was red-shifted by electron-withdrawing substituents. Thus, the latter meets the criteria of a charge-transfer transition where the acceptor orbital in the excitation is a ligand  $\pi^*$  orbital. This was initially suggested to be emission from a MLCT ( $d \rightarrow \pi^*$ ) excited state.<sup>38</sup>

The proposals that the states responsible for the LE and HE emissions from 1 are of  $d-s$  and  $d-\pi^*$  origin, respectively, were subsequently challenged by our preliminary *ab initio* calculations, which clearly showed that the highest occupied molecular orbitals in both 1 and  $\text{Cu}_4\text{I}_4(\text{NH}_3)_4$  (a model for 2) are composed largely of iodide  $p$  orbitals.<sup>41</sup> Thus, excited-state assignments must account for major components of iodide to metal charge transfer (XMCT) and iodide to ligand charge transfer (XLCT) character for the LE and HE emissions, respectively.<sup>40</sup> The results of more thorough calculations which also take electronic reorganization

into account indicate that the emissive state is of mixed  $d-s/\text{XLCT}$  character delocalized over the  $\text{Cu}_4\text{I}_4$  core with roughly equal contributions from each component.<sup>19</sup> For simplicity we have referred to this excited state as "cluster centered" (CC). The emission lifetimes (Table I) are consistent with a triplet assignment for both emissive states.

The excitation spectrum of 1 displays different maxima depending on whether the LE or HE emission maximum is the monitoring wavelength.<sup>40</sup> Interestingly, the  $\lambda_{\text{max}}^{\text{ex}}$  for the so-called HE band occurs at lower energy than does that for the LE emission (Table I); thus the Stokes shift<sup>46</sup> for the latter ( $1.64 \mu\text{m}^{-1}$ ) is much greater than that for the former ( $0.77 \mu\text{m}^{-1}$ ). As noted above, the independent lifetimes further indicate the relatively uncoupled behavior of the two emission bands for 1 and related complexes (Table I). In solution, the LE emission is the longer lived for various  $\text{Cu}_4\text{I}_4(\text{py-x})_4$ , although lifetime differences are much less at temperatures below the solution glass transition. Of course, the claim of two uncoupled emissions from the same compound leads one to suspect instead the presence of two luminescence active molecular components in such solutions. Nonetheless, the close analogies between the photophysical properties of the  $\text{Cu}_4\text{I}_4\text{L}_4$  clusters in solution and those of crystallographically well-characterized solids argues strongly for the integrity of these molecular properties.

The very large Stokes shift for the LE emission band of the  $\text{Cu}_4\text{I}_4(\text{py-x})_4$  complexes and the corresponding band of other  $\text{Cu}_4\text{I}_4\text{L}_4$  is consistent with the mixed  $d-s/\text{XMCT}$  assignment for this excited state. Population of  $4s$  orbitals delocalized over the  $\text{Cu}_4$  core should lead to enhanced Cu–Cu bonding and, according to the calculations,<sup>19</sup> to less Cu–I bonding. Hence, this excited state should be significantly distorted from the ground state. An analogy can be drawn to the square planar  $d^8$  complexes in face to face arrangements, examples being the dinuclear species<sup>47</sup>  $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$  and  $\text{Pt}(\text{CN})_4^{2-}$  oligomers.<sup>48</sup> Excitation of the  $\sigma_{\text{MM}}^* \rightarrow \sigma_{\text{MM}}^b$

(46) "Stokes shift" is defined as the energy difference between the absorption and emission maxima of the same electronic transition and multiplicity. However, the emitting excited state often cannot always be identified in absorption, so in the present case we will use the often employed operational definition of the Stokes shift as the energy difference between the excitation and emission maxima.

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transitions of such species leads to markedly enhanced metal-metal bonding in the excited state. Much less distortion would be expected for the XLCT excited state of a  $\text{Cu}_4\text{I}_4(\text{py-x})_4$  cluster, a conclusion which is consistent with the smaller Stokes shifts seen for the HE emissions. Furthermore, the coordinates along which a XLCT state would be distorted are different from those for a d-s/XMCT ES. Thus, we propose that it is *these differences in the magnitude and direction of the respective distortion coordinates which lead to the poor coupling between the two excited states.*

For analogous chloride clusters,  $\text{Cu}_4\text{Cl}_4\text{L}_4$ , emissions have been observed only when L is an unsaturated nitrogen heterocycle having empty low-energy  $\pi^*$  orbitals.<sup>42</sup> Accordingly, the emission would appear to originate from an XLCT or MLCT excited state, the XLCT assignment being favored by the results of ab initio calculations which continue to show the HOMO as being predominantly composed of halide orbitals. The absence of a d-s/XMCT emission similar to the LE emission seen for the iodide clusters 1 and 2 would be consistent with the observation by Holt<sup>37</sup> that such emissions are found only for clusters with Cu-Cu distances ( $d_{\text{Cu-Cu}}$ ) less than twice the van der Waals radius of Cu(I) (1.4 Å). For 1 and 2, these distances are less than 2.7 Å; in contrast,  $d_{\text{Cu-Cu}}$  values exceeding 3.0 Å are typical for analogous chloride clusters. The empirical requirement of a short  $d_{\text{Cu-Cu}}$  can be attributed to the nature of the acceptor orbitals in the cluster-centered state. The intermetallic interactions of these s orbitals are Cu-Cu bonding; thus the excited-state potential energy surface must be strongly dependent on  $d_{\text{Cu-Cu}}$ .<sup>43</sup>

In this context, a particularly interesting  $\text{Cu}_4\text{X}_4\text{L}_4$  (X = Cl, Br, and I) series is one based on the 2-(diphenylmethyl)pyridine (dpmp) ligand. The structures of the isomorphous solids have been determined, and the average  $d_{\text{Cu-Cu}}$  values are nearly the same ( $\sim 2.90$  Å) for all three clusters.<sup>49</sup> Thus, one can compare the properties of homologous halide clusters without having to compensate for major variation of the molecular or crystal structures. At 77 K, the three solids (and glasses of solutions of these in toluene) each show a single XLCT band as the dominant feature in the luminescence spectra, and these follow the energy order  $\text{I} > \text{Br} > \text{Cl}$ .<sup>43</sup> This order seems counterintuitive to the XLCT assignment, given the normal generalization that ionization energies of halide anions increase across the series  $\text{I}^- \rightarrow \text{Cl}^-$ . However, ab initio calculations show that the halide ionicity in the ground-state clusters increases over the same series in a manner which compensates for the effects of ionization energy on the (largely halide p orbital) cluster HOMOs. Notably, when the temperature is raised, the spectra of iodo and bromo solids begin to display a second feature, a long-wavelength shoulder we attribute to a cluster-centered emission (Figure 3).<sup>43</sup> The intensity of this band increases with  $T$ , but the lifetime remains the same as that of the much stronger XLCT emission. Thus, in contrast to 1, the d-s/XMCT and XLCT states for the dpmp clusters are in thermal equilibrium, and the former are slightly higher in energy ( $\sim 10^3 \text{ cm}^{-1}$  for  $\text{Cu}_4\text{Br}_4(\text{dpmp})_4$ ).<sup>43</sup>

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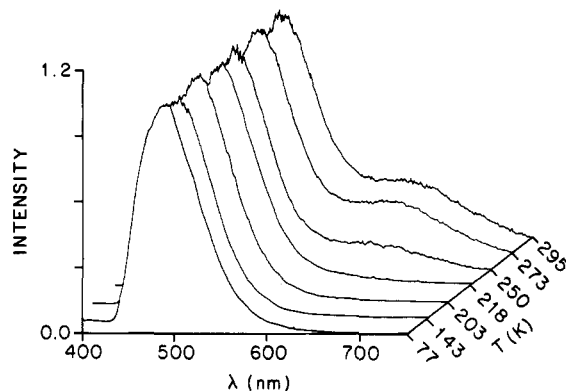


Figure 3. Temperature dependence of the emission spectrum of solid  $\text{Cu}_4\text{Br}_4(\text{dpmp})_4$  (380-nm excitation).

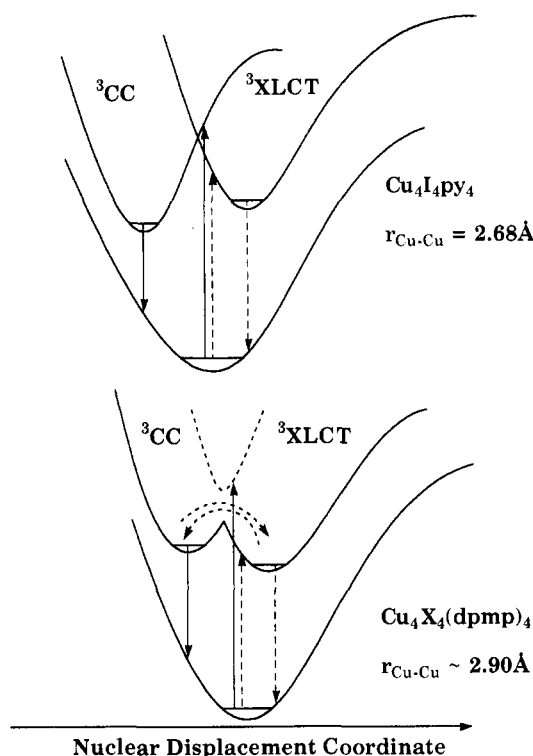


Figure 4. Proposed model for potential energy surfaces for the XLCT and CC (d-s/XMCT) excited states in  $\text{Cu}_4$  clusters: Top:  $\text{Cu}_4\text{I}_4(\text{py})_4$ . Bottom:  $\text{Cu}_4\text{I}_4(\text{dpmp})_4$ .

Figure 4 proposes a qualitative model for the emitting excited states of the clusters  $\text{Cu}_4\text{I}_4(\text{py})_4$  and  $\text{Cu}_4\text{X}_4(\text{dpmp})_4$ .<sup>43</sup> The poor coupling between the XLCT and the cluster-centered d-s/XMCT excited states of 1 is attributed to a high curve-crossing barrier, so that once the molecule is prepared in either state, internal conversion would be slow relative to other photophysical processes. For the dpmp clusters, the CC state is somewhat above the XLCT state, and the barrier height must be small since the two states are coupled at all  $T$ . These differences apparently lie in the copper-copper distances of the  $\text{Cu}_4$  cores. In the cluster-centered d-s/XMCT excited state, electron density has been transferred into the  $\sigma_{\text{MM}}^b$  orbitals; thus, the energy and shape of this state's potential surface depend strongly on the extent of Cu-Cu interaction. By contrast, the XLCT emissions are little affected by  $d_{\text{Cu-Cu}}$ . The packing of large iodide and smaller Cu(I) spheres in 1 and 2 gives relatively small  $\text{Cu}_4$  tetrahedra with greater overlap between relevant metal orbitals. Packing with

Table II. Emission Spectra of Tetrameric and Hexameric d<sup>10</sup> Cluster Complexes in Solution or Glasses

complex <sup>a</sup>	solvent	T (K)	emissive excited state	$\lambda_{\max}$ (nm)	$\tau$ ( $\mu$ s)	Stokes shift (cm <sup>-1</sup> )	ref
Cu <sub>6</sub> (mtc) <sub>6</sub>	toluene	rt <sup>b</sup>	d-s/LMCT	725	1 × 10 <sup>-6</sup>	9460	51
Ag <sub>4</sub> (P(OCH <sub>3</sub> ) <sub>3</sub> ) <sub>4</sub> Cl <sub>4</sub>	toluene	77	d-s	483		5610	56
Ag <sub>4</sub> (PPh <sub>3</sub> ) <sub>4</sub> Cl <sub>4</sub>	toluene	77	d-s	480		12 500	56
Ag <sub>6</sub> (mtc) <sub>6</sub>	toluene	77	d-s/LMCT	607	1.3 × 10 <sup>-4</sup>	11 300	51
Ag <sub>6</sub> (dte) <sub>6</sub>	toluene	77	d-s/LMCT	550	2.1 × 10 <sup>-5</sup>	5020	51
Au <sub>4</sub> (dta) <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> OH	77	d-s	743		9800	58
Au <sub>4</sub> (pip) <sub>4</sub> Cl <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> OH	77	d-s	700		18 500	58
Hg <sub>4</sub> (pyph) <sub>4</sub> Cl <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> OH	77	LMCT/(d-s)	500		13 300	61
Hg <sub>4</sub> (SPh) <sub>6</sub> (PPh <sub>3</sub> ) <sub>4</sub> <sup>2+</sup>	toluene	77	LMCT/(d-s)	690		10 510	61
Zn <sub>4</sub> O(acetate) <sub>6</sub>	CH <sub>2</sub> Cl <sub>2</sub>	rt	LMCT	372	1 × 10 <sup>-8</sup>	19 415	64
Zn <sub>4</sub> (SPh) <sub>10</sub> <sup>2-</sup>	CH <sub>3</sub> CN	rt	LMCT	360	3.5 × 10 <sup>-11</sup>	9260	69a
Cd <sub>4</sub> (SPh) <sub>10</sub> <sup>2-</sup>	CH <sub>3</sub> CN	rt	LMCT		3.9 × 10 <sup>-10</sup>	16 360	69a

<sup>a</sup> Abbreviations: mtc = di-*n*-propylmonothiocarbamate, dtc = di-*n*-propyldithiocarbamate, dta = dithioacetate, pip = piperidine, pyph = 2-pyridylphenyl. <sup>b</sup> Room temperature.

the chlorides tends to give larger Cu<sub>4</sub> tetrahedra with less Cu-Cu interaction, a result which may explain the failure to observe the cluster-centered emission for Cu<sub>4</sub>-Cl<sub>4</sub>(py)<sub>4</sub> or Cu<sub>4</sub>Cl<sub>4</sub>(Et<sub>3</sub>N)<sub>4</sub>. For the dpmp clusters, the packing in the Cu<sub>4</sub>X<sub>4</sub> core appears to be influenced by the steric bulk of the 2-(diphenylmethyl)pyridine ligand, and the *d*<sub>Cu-Cu</sub> for all three are held at ~2.9 Å. For these complexes, the Cu-Cu interactions are apparently strong enough to give a CC excited state energy above but close to that of the XLCT state from which the emission is principally observed.

**Other Polynuclear Copper(I) Complexes.** The structure of the hexanuclear complex Cu<sub>6</sub>(mtc)<sub>6</sub> (mtc<sup>-</sup> = di-*n*-propylmonothiocarbamate) features an octahedron of Cu(I). Under ambient conditions, this species shows an intense luminescence with  $\lambda_{\max}^{\text{em}} = 725$  nm and  $\tau = 1$   $\mu$ s in toluene (Table II).<sup>50</sup> The Stokes shift between the excitation and the emission maxima under these conditions was 0.97  $\mu\text{m}^{-1}$ . In analogy to the tetrahedral complexes, we have attributed this emission to the presence of a lowest energy triplet d-s/LMCT.<sup>50</sup>

Although the emphasis here is on tetra- and hexanuclear clusters, it should be noted that other polynuclear Cu(I) complexes display luminescence associated with metal-metal interactions. For example, trinuclear Cu(I) arylthiolates have recently been reported to show tribo- and photoluminescence in the solid state.<sup>51</sup> Also, Cu<sup>+</sup> ions doped into  $\beta$ -alumina are reported show excimer luminescence originating from dimers formed upon d-s excitation<sup>52</sup> in analogy to certain mononuclear Pt(II) complexes which give dinuclear excimers in solution.<sup>53</sup> Cluster emission may also be involved in the 500–600-nm luminescence observed for the protein metallothionein when this protein was loaded by the d<sup>10</sup> ions Cu<sup>+</sup>, Ag<sup>+</sup>, and Au<sup>+</sup>.<sup>54</sup>

**Silver(I) and Gold(I) Clusters.** Some emission data for silver(I) clusters are summarized in Table II. For Ag<sub>4</sub>Cl<sub>4</sub>L<sub>4</sub> (L = P(OCH<sub>3</sub>)<sub>3</sub> or P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>) (Table II), the emitting state was first proposed to be a triplet d-s excited state characterized by enhanced metal-metal bonding in the tetrahedral Ag<sub>4</sub><sup>1+</sup> core.<sup>55</sup> However, given

the oxidizing nature of Ag<sup>+</sup>, a mixed d-s/LMCT may be a more appropriate label. The compound Ag<sub>4</sub>I<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub> has two isomers, one a "cubane" for which each Ag<sup>+</sup> ion has three equivalent Ag<sup>+</sup> neighbors, the other a distorted "chair" with a smaller average number of nearest Ag<sup>+</sup> neighbors. Both emit, but the former emits at longer wavelength, an observation attributed to greater delocalization of d and s orbitals within the cubane structure.<sup>56</sup>

The hexanuclear Ag(I) dithiocarbamate complexes Ag<sub>6</sub>(mtc)<sub>6</sub> and Ag<sub>6</sub>(dte)<sub>6</sub> (dte<sup>-</sup> = di-*n*-propyldithiocarbamate) also display low-temperature emissions analogous to that described above for Cu<sub>6</sub>(mtc)<sub>6</sub> (Table II). Again these were proposed to occur from cluster-centered d-s/LMCT states.<sup>50</sup>

Tetrameric Au(I) complexes (Au<sub>4</sub> squares instead of tetrahedra) are also emissive (Table II).<sup>57</sup> In analogy to the Cu<sub>4</sub> and Ag<sub>4</sub> clusters, the emission is assumed to originate from a cluster-centered d-s state. For gold, LMCT contributions may not be as important, given that the mononuclear Au(I) complexes AuCl<sub>2</sub><sup>-</sup> and AuBr<sub>2</sub><sup>-</sup> show d-s absorptions well below the LMCT bands.<sup>24</sup> Several binuclear Au(I) complexes have also been shown to be luminescent under ambient conditions.<sup>58</sup>

**Clusters of the Group IIb Metals.** For the d<sup>10</sup> M(II) ions of the group IIb metals, the d orbitals are much more stable than those of the Ib metals.<sup>61</sup> This is reflected by the observation that the low-energy transitions of simple Zn<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup> complexes are generally of the LMCT type,<sup>24,26,31</sup> and only for Hg<sup>2+</sup> may there be significant d-s/LMCT mixing.<sup>60,61</sup> Accordingly, there should be little metal-metal bonding in the ground states of the clusters. However, the (*n*+1)s orbitals populated in an LMCT state are  $\sigma_{\text{MM}}^{\text{b}}$ , and electronic excitation should lead to contraction of the cluster core. In this context, it is notable that the emissions from group IIb clusters show Stokes shifts comparable to those seen for the group Ib clusters.

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For example, the tetranuclear Hg(II) compounds  $\text{Hg}_4\text{-Cl}_4(2\text{-pyridylphenyl})_4$  and  $\text{Hg}_4(\text{SPh})_6(\text{PPh}_3)_4^{2+}$  in 77 K toluene glasses are emissive with respective  $\lambda_{\text{max}}^{\text{em}}$  values of 500 and 690 nm. In contrast the mononuclear compound  $\text{Hg}(\text{SPh})_2$  displays no luminescence, and  $[\text{Hg}(\text{PPh}_3)_2](\text{ClO}_4)_2$  shows only a weak ligand-centered emission. For  $\text{Hg}_4(\text{SPh})_6(\text{PPh}_3)_4^{2+}$  the lowest energy absorption band appears at 325 nm, and this was concluded to be a mixed metal-centered 5d–6s and LMCT transition. The emission was also proposed to occur from a d–s/LMCT state, and the large Stokes shift ( $1.6 \mu\text{m}^{-1}$ ) again suggests strong excited-state distortion relative to the ground state.

The tetranuclear Zn(II) cluster  $\text{Zn}_4\text{O}(\text{acetate})_6$  offers a somewhat different structure, a  $\text{Zn}_4$  tetrahedron with an oxide in the center. This was chosen for study as a possible molecular model for the semiconductor  $\text{ZnO}$ ,<sup>62</sup> since in both cases the Zn(II) is surrounded tetrahedrally by oxides at similar distances.<sup>63</sup> The luminescence spectrum of  $\text{Zn}_4\text{O}(\text{acetate})_6$  in methylene chloride displays an intense UV emission band (390 nm) under ambient conditions (Table II).<sup>63</sup> This was assigned as fluorescence from a cluster LMCT state, but the nature of the emission from the  $\text{Zn}_4\text{O}$  moiety may be more complex.<sup>64,65</sup> A decrease of the particle size of  $\text{ZnO}$  is associated with well-defined changes of the optical properties. In bulk  $\text{ZnO}$ , the valence band is composed of the filled oxide p orbitals, and the conduction band is composed of the empty Zn(II) 4s orbitals. The LMCT band gap absorption occurs at relatively low energy ( $27\,400 \text{ cm}^{-1}$ ), while the band gap emission is almost in resonance with the absorption since the excitation is delocalized and not associated with structural changes.<sup>62</sup> For smaller particles, the quantum-size effect<sup>66,67</sup> leads to band gap increases, and the absorption as well as the emission is blue-shifted with regard to the bulk. Since the number of atoms in the quantum-size particles remains large, a Stokes shift is not observed. However, on a molecular scale, the number of interacting atoms is small, the LMCT absorption is further blue-shifted ( $\lambda_{\text{max}}^{\text{abs}} = 216 \text{ nm}$ ), and the emission occurs with a sizable Stokes shift since the molecular cluster undergoes an excited-state distortion.

The polynuclear complexes  $\text{Zn}_4(\text{SPh})_{10}^{2-}$ ,  $\text{Cd}_4(\text{SPh})_{10}^{2-}$ , and  $\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}^{4-}$  may similarly be taken as molecular models for the optical properties of the solid materials  $\text{ZnS}$  and  $\text{CdS}$ . Emissions from the cluster compounds are weak, lifetimes are very short<sup>68</sup> (Table II), and efficient photodecomposition competes with radiative deactivation. The emission is assumed to originate from a LMCT state of the cluster. Intraligand luminescence appears at shorter wavelength. In this context it is of interest that well-defined  $[\text{CdS}]_4$  particles can be

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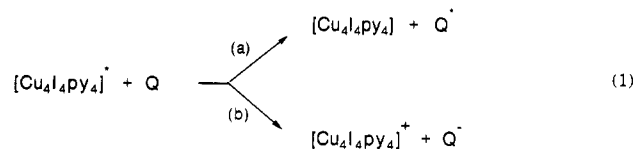
incorporated into the cavities of zeolites.<sup>69</sup> These are not emissive when isolated but are luminescent if they are interconnected at higher loading densities.

The emission from  $d^{10}$  clusters is not restricted to group Ib and IIb metals. Dimeric and trimeric Pd(0) and Pt(0) complexes have been also shown to be emissive.<sup>70</sup> The luminescent excited states are apparently of the d–p type. Emissive Pd(0) and Pt(0) clusters of higher nuclearity have not yet been reported.

### Photochemical Properties of $d^{10}$ Metal Clusters

Photochemical studies of  $d^{10}$  metal clusters are as yet quite limited. The structures and configurations of the Cu(I) clusters are thermodynamically controlled, and the ground states are thermally labile. Thus, photoreactions such as ligand labilization or cluster fragmentation would be rapidly reversible and observable only by flash photolysis. On the other hand, the long luminescence lifetimes for clusters such as  $\text{Cu}_4\text{I}_4(\text{py})_4$  should allow observation of bimolecular processes and suggest the possibility of utilizing the excited states to undergo energy transfer or to sensitize charge separation processes via electron transfer. In this context, the energy ( $E^\circ$ ) of the long-lived cluster-centered excited state of 1 ( $1^*$ ) was estimated<sup>40</sup> to be  $1.74 \mu\text{m}^{-1}$ , and the oxidation potential of  $1^*$  (defined as  $-E_{1/2}(1^+/1^*)$ ) was estimated from  $E^\circ$  and ground-state electrochemical properties to be  $\sim 1.86 \text{ V}$ .<sup>71</sup>

Recent studies have now demonstrated quenching of  $1^*$  by a series of uncharged tris( $\beta$ -dionato)chromium(III) complexes  $\text{CrL}_3$ .<sup>71</sup> These quenchers display a remarkable range of reduction potentials ( $E_{1/2} = 2.51$  to  $-0.87 \text{ V}$  vs ferrocenium/ferrocene in  $\text{CH}_2\text{Cl}_2$ ) but have excited-state energies ( $1.22$ – $1.28 \mu\text{m}^{-1}$  independent of the ligand substituents) below the estimated  $E^\circ$  of the LE state.<sup>72</sup> Thus each  $\text{CrL}_3$  can quench  $1^*$  by energy transfer, and indeed, all the  $\text{CrL}_3$  do so with rate constants  $k_2 > \sim 4.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . Those with the least negative  $E_{1/2}(\text{Q}/\text{Q}^-)$  values may also quench  $1^*$  by competitive electron transfer (eq 1), and  $k_2$  values approaching diffusion limits in these cases suggest contributions from such a pathway.<sup>71</sup> Electron-transfer



quenching was also seen for a series of organic quenchers which have  $\pi\pi^*$  state energies too high for energy transfer to be viable ( $>1.74 \mu\text{m}^{-1}$ ), and  $E_{1/2}(\text{Q}/\text{Q}^-)$  values in the range of  $-1.37$  to  $-0.94 \text{ V}$  vs ferrocene.<sup>71</sup> Substantially negative  $\Delta G_{\text{el}}^\circ$  (free energy change of the ES electron-transfer process) values are required for

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electron-transfer quenching of  $1^*$  to be competitive with radiative and nonradiative deactivation. This suggests that electron transfer from the d-s/XMCT excited state is unusually slow, perhaps because the enhanced Cu-Cu bonding in  $1^*$  lends a large inner sphere contribution to the total reorganization energy accompanying the electron transfer. In addition, electron transfer between  $1^*$  and Q leads to charge separation ( $1^+$  plus  $Q^-$ ) and adds a substantial outer sphere solvent reorganization energy as well. These properties are receiving more detailed attention in our laboratories.

### Spectroscopic Properties of $s^2$ Metal Clusters

The interactions between  $s^2$  ions in clusters should be similar to those for  $d^{10}$  ions. In the ground state the coupling of the metal centers should be weak and dependent on second-order mixing with unfilled higher energy orbitals. Consequently, the absorption spectra of clusters are analogous to those for mononuclear components. This is exemplified by the spectrum of  $Tl_4(OCH_3)_4$ , which shows an s-p absorption ( $\lambda_{max} = 227$  nm) close to that for  $Tl^+$  in methanol.<sup>73</sup> However, the empty p orbitals of the  $s^2$  clusters are metal-metal bonding in character while the HOMO is composed of the filled, antibonding, s orbitals; thus the s-p excited state of an  $s^2$  cluster should be significantly distorted from the ground state. In this context, it is notable that emission of the  $Tl_4(OCH_3)_4$  tetramer occurs at much longer wavelength ( $\lambda_{max}^{em} = 640$  nm) than that of the solvated  $Tl^+$  ion. Again, this large shift is attributed to excitation-induced distortions, presumably a contraction along the metal-metal bonds of the  $Tl(I)_4$  tetrahedron.

The compound  $Sn_6O_4(OCH_3)_4$  is another polynuclear  $s^2$  complex whose luminescence ( $\lambda_{max}^{em} = 565$  nm) was attributed to a cluster emission.<sup>74</sup> Again, the absorption spectrum seems to consist of the s-p band ( $\lambda_{max}^{abs} = 325$  nm) of the isolated mononuclear  $SnO_2(OCH_3)_2^{2-}$  components. HOMO to LUMO excitation should again

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lead to enhanced intermetallic bonding, and the  $Sn(II)_6$  octahedron should undergo a contraction. This is apparently reflected in the considerable red shift of the emission bands.<sup>74</sup>

### Summary

A number of the  $d^{10}$  and  $s^2$  metal clusters are brightly luminescent, some with strongly medium dependent and temperature dependent spectral profiles. Such emissions are often from excited states assigned as having a mixed d-s/XMCT character, the key feature being enhanced electronic population in metal-metal bonding orbitals in these states as evidenced by the large Stokes shifts between excitation and emission maxima. The observation of such emission bands is strongly favored by relatively short metal-metal distances in the clusters. This behavior parallels that of the  $d^8$ - $d^8$  dimers held by bridging ligands in cofacial configurations for which excitation leads to substantially increased bonding between metal centers.<sup>47</sup> With  $\pi$ -unsaturated ligands L, emissions from XLCT excited states are often observed, and the luminescence thermochromism of such complexes is the result of different temperature and medium rigidity responses of these two types of excited states. The poor coupling between d-s/XMCT and XLCT states in clusters such as  $Cu_4I_4(py)_4$  can be attributed to high barrier heights for curve crossing owing to different distortion trajectories once the molecule is prepared in one of the respective excited states. Ongoing studies in these laboratories continue to survey different luminative  $d^{10}$  and  $s^2$  cluster systems and to apply an arsenal of synthetic, theoretical, photophysical, and photochemical tools to extend our quantitative understanding of the relevant excited states.

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## Additions and Corrections

Vol. 25, 1992

### Michael J.S. Dewar\* and Caoxian Jie: Mechanisms of Pericyclic Reactions: The Role of Quantitative Theory in the Study of Reaction Mechanisms.

Page 537. As pointed out by Professor Borden, we wrongly attributed to him the ab initio HF/3-21G calculations of secondary deuterium kinetic isotope effects in the first two complete paragraphs on page 542. As the senior author, M.J.S.D. accepts full responsibility for this error and apologizes unreservedly.