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Permalink
https://escholarship.org/uc/item/87h8j0d5

Journal
Inorganic Chemistry, 32(6)

ISSN
0020-1669

Authors
Ryu, Chong Kul
Vitale, Marcello
Ford, Peter C

Publication Date
1993-03-01

DOI
10.1021/ic00058a020

Peer reviewed
Photoluminescence Properties of the Structurally Analogous Tetranuclear Copper(1) Clusters Cu₄X₄(dpmp)₄ (X = I, Br, Cl; dpmp = 2-(Diphenylmethyl)pyridine)

Chong Kul Ryu, Marcello Vitale, and Peter C. Ford

Department of Chemistry, University of California, Santa Barbara, California 93106

Received July 22, 1992

 Reported are the photophysical properties of the copper(I) halide clusters Cu₄X₄(dpmp)₄ with the bulky organic base 2-(diphenylmethyl)pyridine (X = I, Br, Cl) which have been shown by previous crystal structure determinations to have "cubane"-like Cu₄X₄ cores with very similar Cu–Cu distances (2.87–3.01 Å). As solids at 77 K, these compounds each exhibit a strong, relatively long-lived emission band [λₘₐₓ/em = 467, 487, and 505 nm; τ = 18.1, 10.0, and 10.0 ns (for X = I, Br, and Cl, respectively)], which is attributed to radiative decay from a halide to ligand charge transfer (XLCT) excited state. At higher temperatures, a weak shoulder appeared in the emission spectra of Cu₄I₄(dpmp)₄ and Cu₄Br₄(dpmp)₄ solids (at ~570 and ~626 nm, respectively), and the relative intensities of these shoulders could be fit to the function A exp(–ΔE/RT), with ΔE ~ 990 ± 370 cm⁻¹ for the appearance of these shoulders. The excited state (ES) lifetimes observed for these shoulders were identical to those observed for the still dominant higher energy bands. In analogy to earlier results with the copper(I) iodide cluster Cu₄I₄(py), this longer wavelength band was attributed to emission from a Cu₄I₄ core centered ES of mixed halide-to-copper charge transfer (XMCT) and metal centered "d-to-s" (MC) orbital parentage. The nature of such transitions in Cu₄X₄L₄ clusters is discussed with respect to the Cu–Cu distances in the ground state structures.

Figure 1. "Cubane"-type structure of the Cu₄X₄L₄ clusters where L is a nitrogen or phosphorus organic base and X is a halide. For I, II, and III, L = 2-(CH₃P)₂py (dpmp) and X = I, Br, and Cl, respectively.

between these ES can be attributed to the much greater distortion of the CC state.

Of particular interest is the role of metal-metal interactions in the relevant excited states of these and related di0 metal ion clusters, especially the CC state, since the filled, highest energy d-orbitals are formally antibonding while the empty s-orbitals are bonding with respect to the copper–copper interactions within the cluster core. Since both the XMCT and MC components of the emission spectra are the result of local emission interactions, both MC and XMCT contribute to the observed emissions.


with modified Schlenk techniques. All samples were checked via X-ray powder diffraction analyses of solids and the X-ray powder diffraction

Experimental Section

Materials. Acetonitrile (AN) and methanol were distilled over CaH2 under N2 atmosphere. Toluene was dried and distilled over Na metal under N2. Cuprous halides (CuI, CuBr and CuCl) were purified by the literature methods. 2-(Diethylaminoethyl)piperidine and X = Cl, Br or I. The crystal structures of these compounds have been determined and shown to be isomorphous and isostructural in the tetragonal space group I41/acd. For each of these clusters the Cu4 tetrahedra are nearly identical and are nearly identical and

display an average dCu-Cu ~ 2.90 Å. Described here are the photochemical properties of these complexes.

Physical Measurements. High resolution powder diffraction data were collected for each sample by a Scintag PAD X automated X-ray diffractometer by using Cu Ka radiation. The Cu4(dpmp)2, Cu4Br(dpmp)2, Cu4Cl(dpmp)2 clusters were prepared as described previously. All syntheses and manipulation of the solutions were performed under argon atmosphere with modified Schlenk techniques. All samples were checked via X-ray powder diffraction analyses of solids and the X-ray powder diffraction pattern, and intensity profiles were shown to match well with those derived from the single crystal cell parameters.

Emission Spectra. The luminescence properties of the respective Cu4(dpmp)2 solids at room temperature. Each of these DR spectra exhibits two broad bands, one centered at 260–270 nm and the other at ~370 nm (Figure 2), although the brighter emitters (I and II) displayed some interference for the higher energy band due to apparent "negative reflectance" in the short wavelength region. In order to reduce this, the samples were diluted with MgCO3 to 1% by weight. The higher energy band obviously corresponds to the ligand centered electronic absorption and/or excitation spectra, see below) these absorptions have ε values of 278 and 67 M-1 cm-1, 227 and 72 M-1 cm-1 and 120 and 37 M-1 cm-1 for I1, II and III, respectively. Notably, absorptions in this region gave linear Beer's law plots over the concentration range 10-3 to 10-1 M for all three compounds in AN solutions, indicating that the clusters remain intact at these concentrations. Absorptions at λ > 300 nm are not seen in the spectra of KI, dpmp or [Cu(AN)4]BF4 individually in AN solution at comparable concentrations. Notably, the observation by Holt that CC emissions are found only for this compound.

Emission Spectra. The respective Cu4(dpmp)2 solids in AN solution at room temperature. The λmax of II and III at 260 and 270 (sh) nm are the same as the π−π* maxima of the free ligand dpmp in the same medium with molar extinction coefficients (ε) ~4-fold higher, consistent with the presence of four dpmp ligands in each cluster. The spectrum of the iodide analog, I, in AN solution displays an intense band at λmax = 248 nm (ε = 5.90 × 10-4 M-1 cm-1) and a shoulder at 270 nm (3.4 × 10-4 M-1 cm-1). The former band is close to that observed for KI in AN solution with ε ~4-fold higher, as expected. The only absorption spectra features unique to the clusters are longer wavelength shoulders which tail to 400 nm. For the wavelengths 340 and 370 nm (chosen because of their correspondence to features in the diffuse reflectance and/or excitation spectra, see below) these absorptions have ε values of 278 and 67 M-1 cm-1, 227 and 72 M-1 cm-1 and 120 and 37 M-1 cm-1 for I, II and III, respectively. Notably, absorptions in this region gave linear Beer's law plots over the concentration range 10-3 to 10-1 M for all three compounds in AN solutions, indicating that the clusters remain intact at these concentrations. Absorptions at λ > 300 nm are not seen in the spectra of KI, dpmp or [Cu(AN)4]BF4 individually in AN solution at comparable concentrations.
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Figure 2. Diffuse reflectance spectra of solid Cu(X)(dpmp)$_4$ vs MgCO$_3$ at 298 K.

Table II. Photophysical Properties of Cu(X)(dpmp)$_4$ as Solids

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\lambda_{\text{em}}$ (nm)$^a$</th>
<th>$\Delta\nu/2$ (10$^3$ cm$^{-1}$)$^b$</th>
<th>$\lambda_{\text{ex}}$ (nm)$^c$</th>
<th>$\Delta\nu$ (10$^3$ cm$^{-1}$)$^d$</th>
<th>$\tau$ (µs)$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>446 (sh) / 467</td>
<td>3.4</td>
<td>333 (sh), 360, 372 (sh)</td>
<td>6.4</td>
<td>18.1</td>
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<tr>
<td>298</td>
<td>440, 462 (sh)</td>
<td>370 (br)</td>
<td>4.3</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>570</td>
<td>370 (sh)</td>
<td>9.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>487</td>
<td>3.3</td>
<td>327 (sh), 357, 374 (sh)</td>
<td>7.5</td>
<td>10.0</td>
</tr>
<tr>
<td>298</td>
<td>480, ~626 (sh)</td>
<td>360 (br)</td>
<td>6.9</td>
<td>0.54</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.8</td>
</tr>
<tr>
<td>77</td>
<td>505</td>
<td>3.0</td>
<td>330 (sh), 366, 383 (sh)</td>
<td>7.5</td>
<td>10.0</td>
</tr>
<tr>
<td>298</td>
<td>500</td>
<td>360 (br)</td>
<td>7.8</td>
<td>2.7</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Emission maxima. $^b$ Full width at half-maximum. $^c$ Excitation maxima. $^d$ $\Delta\nu = \nu_{\text{max}} - \nu_{\text{em}}$. $^e$ Measured lifetime. / sh = shoulder; br = broad.

was observed in the emission spectrum of I ($\sim$ 570 nm) and that of II ($\sim$ 626 nm).

The emission spectrum ($\lambda_{\text{em}} = 380$ nm) of solid CuBr(dpmp)$_4$ displayed the dependence on temperature (77-295 K) indicated in Figure 5 with spectral intensities at $\sim$ 480 nm normalized to 1. At 77 K, only one emission band ($\lambda_{\text{em}} = 487$ nm) was apparent, but a second emission band at $\sim$ 626 nm became evident at 203 K and continued to grow in relative intensity with increasing T. The ratio R of the integrated areas of the two bands were determined from a Gaussian analysis of the band shapes, and a numerical fit of $R = A \exp(-\Delta\nu/RT)$ gave a value of 990 ± 370 cm$^{-1}$ for $\Delta\nu$ for the appearance of the red emission. A similar result was obtained with 320 nm excitation.

Figure 4. Excitation and emission spectra of solid CuBr(dpmp)$_4$ at 298 K.

Figure 5. Temperature dependence of emission spectra of solid CuBr(dpmp)$_4$ with 380 nm excitation.

Frozen AN solutions (77 K) of I, II and III at various concentrations (10$^{-3}$-10$^{-5}$ M) exhibited broad emission bands with similar band shapes and widths ($\Delta\nu/2 \sim 3400$ cm$^{-1}$) (Figure 6) and with $\lambda_{\text{em}}$ at 500, 512 and 530 nm, respectively (Table III), red-shifted about 25-30 nm from those seen for the respective solids at 77 K. The shapes and positions of these bands proved to be independent of sample concentration over a 10$^{-3}$-10$^{-5}$ M range. The emission spectra in 77 K toluene glassy solutions were very similar and displayed bands at 501, 496 and 530 nm, respectively. Emission was not detected from AN or toluene solutions of any of the CuX(dpmp)$_4$ clusters at ambient temperature.
The excitation spectra of all three CuX₄(dpmp)₄ clusters as solids or in frozen AN solutions proved to be independent of λₘₐₓ from 320 to 380 nm.

**Excitation Spectra.** The excitation spectra of the respective CuX₄(dpmp)₄ solids were obtained by monitoring at the respective emission maxima. These data are summarized in Table II.

At room temperature, the excitation spectra of solid I, II and III each displayed a broad band centered at ∼365 nm (Figure 4). The spectra were differentiated only by small edge effects in the energy order I > II > III but were independent of whether the emission was monitored at λₘₐₓ or at the longer wavelength tail. Thus, in each case, these emissions apparently originate from a common excited state or several equilibrated components displayed lifetimes comparable to those at the higher concentration. The possible intervention of impurities as the origin of the emission tail can be ruled out. There was some overlap between the respective excitation and emission spectra. At 77 K, the excitation spectra of solid I, II and III displayed relatively narrow but similar maxima at λₘₐₓ ∼ 365 nm (shoulders at ∼330 and ∼375 nm) along with a edge effect similar to that observed at room temperature (Figure 4). However, there was less overlap between excitation and emission spectrum of each CuX₄(dpmp)₄ than seen at room temperature (Figures 3 and 4).

In frozen AN solution, the excitation spectra of the respective CuX₄(dpmp)₄ clusters were measured both at concentrations ≤10⁻⁴ M and ∼10⁻³ M while monitoring the respective λₘₐₓ. At the lower concentration, each compound displayed an excitation band at λₘₐₓ ∼ 340 nm (Table III) which was narrower and displayed less edge effect than for the solid at 77 K. However, at the higher concentration, homogeneous solutions of each CuX₄(dpmp)₄ displayed a λₘₐₓ at ∼350 nm plus a shoulder at ∼380 nm, features closer to those observed for the solid state. The excitation spectra of I, II and III in glassy toluene solutions are very similar to those in frozen AN solutions.

**Luminescence Lifetimes.** In each case studied, the emission decays observed for each three clusters as solids proved to be single exponentials with lifetimes independent of the monitoring wavelength (Table II). The same was true for 77 K frozen acetonitrile solutions prepared with concentration of ∼10⁻³ M (Table III). For solutions prepared with [CuX₄(dpmp)₄] ≤ 10⁻⁴ M, the luminescence decays tended to be nonexponential, but analysis according to an assumed double exponential showed the longer components displayed lifetimes comparable to those at the higher concentrations; e.g., τ₁ = 1.56 μs (preexponential weighting factor A₁ ∼ 1) and τ₂ = 3.6 μs (A₂ ∼ 1) for [I] = 1.26 × 10⁻⁴ M.

**Discussion.** The three compounds of interest here (I, II and III) have been shown to have "cubane"-type Cu₄X₄ tetrahedra, isomorphous and isostuctural to the Cu₄X₄ tetrahedra so that the Cu and halide atoms are aligned at alternate corners of the distorted "cubane" while the ligands bound to each Cu form another, much larger, tetrahedron (Figure 1). The average Cu–Cu distances in the Cu₄ tetrahedra are very close, the respective values being 2.89 ± 0.01, 2.88 ± 0.01 and 2.92 ± 0.08 Å for the chloride, bromide and iodide clusters. The principal structural differences result from the increasing sizes of the halides leading to larger X₄ tetrahedra and to some extension of the Cu–N bond lengths (1.995, 2.024 and 2.065 Å, respectively) owing to steric crowding between the bulky organic ligand and the halides. In all other respects the clusters are structurally very analogous.

The following observations must be considered in assigning the excited states responsible for the emissions observed for the CuX₄(dpmp)₄ complexes: (1) For each the optical spectrum in acetonitrile solution shows absorbances at wavelengths longer than those bands which can be assigned to the π–π* absorptions of the aromatic ligand or to the halide. These absorbances follow linear Beer’s law behavior over the concentration range 10⁻⁴ to 6 × 10⁻³ M thus indicate that the species responsible, presumably the CuX₄(dpmp)₄ clusters, remain intact in solution. (2) In the same wavelength region (∼370 nm) the diffuse reflectance spectra of the solids display bands which match well with the λₘₐₓ observed in the excitation spectra of these materials as well as of AN solutions of the same. (3) At 77 K, the emission spectrum of each CuX₄(dpmp)₄ (either as a solid or in frozen AN solution) displays a visible region band, the energy order following the sequence I > II > III. These bands are slightly red-shifted in frozen solution relative to the solids. At 298 K, the emission bands for solid CuX₄(dpmp)₄ are slightly blue-shifted relative to the 77 K spectra while no emission was observed from the solutions. (4) There is a substantial Stokes shift (6400–7800 cm⁻¹) for the solids at 77 K between the respective excitation and emission maxima. (5) Luminescence lifetimes are relatively long (>40 μs at 77 K, >0.5 μs at 298 K) implying that the transitions involved are forbidden, most likely spin-forbidden emissions from triplet ES. (6) As solids, the CuX₄(dpmp)₄ clusters show a low energy shoulder in the emission spectrum at higher temperature which has a lifetime identical to that of the principal emission band.

A survey of possible excited states relevant to the emission spectra of these dpmp clusters would have to include ligand centered π–π* state(s), CuX₄(dpmp)₄ cluster centered state(s) (the result of either XMCT or d–s transitions or a mixture of the two), MLCT states and/or halide to ligand charge transfer (XLCT) states. Of these, the π–π* ES is unlikely to be the emitting state given that phosphorescence spectra of pyridinium salts display λₘₐₓ values (∼400 nm) at much higher energy than seen for CuX₄(dpmp)₄. As noted in the Introduction, a variety of arguments led to the conclusion that the intense LE band in the emission spectrum of CuX₄(dpmp)₄ is from a CC excited state of mixed XMCT/d–s character while the HE band (much less intense at room temperature) is of XLCT character. These were based in part on ab initio calculations which concluded that, for A as well as for the hypothetical cluster CuX₄(NH₄)₄, the highest occupied molecular orbitals in the ground state are not metal centered but are largely iodide p-orbitals (>80%) in character. Occupied MO's which have substantial metal character were at much lower energy. Examples of XLCT ES's are well documented in a recent
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the energy of the LE band found for the other CuL4(py-R)4 clusters much lower than seen for CuL4(dpmp)4, the Stokes shift is much larger (>10 000 cm⁻¹) and the band significantly narrower (∼2000 cm⁻¹) under comparable conditions. These observations support the conclusion that the single bands observed in the 77 K emission spectra of I, II and III, like the HE band of A and the single emission seen for CuL4(py)4, involve ligand π-orbitals, i.e., are either MLCT or XLCT. Therefore, in analogy to the assignments of the HE emission from A and the emission from CuL4(py)4, the ES responsible for these emission bands in the dpmp cluster are assigned as being 3XLCT in character.

How can one justify this assignment in the context of the emission energy order I > II > III which seems counterintuitive given the optical electronegativity order I < Br < Cl? The explanation can be drawn from the ionicity of the CuX4 cores.3 The ionicity of cuprous halides increases in sequence CuI < CuBr < CuCl, and the increasing ionicity of the clusters CuX4L4 < CuBrX4L4 < CuClX4L4 is suggested also by ab initio calculations.9 Greater anionicity leads to higher energy halide orbitals as also does the effect of the higher covalency in the CuX4 cores of the heavier halides.22 These opposing effects on the HOMO energies tend to balance each other and to cancel the expected impact of differing electronegativities.23

It is notable that, regardless of the precise assignment of the emission bands seen in the 77 K emission spectrum for the cuprous iodide cluster I, this band is clearly analogous to the HE band seen in the emission spectrum of A rather than the much more predominant lower energy band given a CC assignment for the latter species. This would appear to be consistent with the proposal7 that this type of emission requires a GS structure with Cu–Cu distances less than 2.8 Å. Notably, the dCu–Cu for I, II and III (∼2.90 Å) all lie somewhat outside this proposed limit. However, although no LE emission was seen in the 77 K spectra of these structurally very similar complexes, all three display emissions at longer wavelengths characteristic of CC emissions when the spectra were recorded at temperatures above 200 K (Figure 5). Since the extent of this LE emission is temperature dependent with the apparent activation energies ∼1000 cm⁻¹, and the lifetimes at both wavelengths are identical, the logical explanation is that the two states responsible for these two emission bands are in thermal equilibrium and that the ES leading to the lower energy emission is actually at a higher energy on the excited state manifold than is the ES leading to the major emission band. The seeming incongruity of this switch can easily be attributed to the CC state being much more distorted than is the XLCT ES relative to the GS.

Figure 7 proposes a qualitative model for the emitting excited states of the clusters CuL4(py)4 and CuL4(dpmp)4. For A the CC state leads not only to the lower energy emission band, but because it gives the longer lived and most intense emission at room temperature it has also been argued to be the lower energy ES. In contrast, the CC ES in the dpmp clusters such as I and II has been shown by temperature effects to be about 1000 cm⁻¹ higher in energy than the XLCT ES which is responsible for the principal emission band at all T and is the only emission seen at low T. The poor coupling in the pyridine complex between these two ES is attributed to high barrier height at the curve crossing, so that once the molecule is prepared in either state, the internal

(23) From +1.5 to −1.5 V vs Ag/AgCl, only one cyclic wave was observed with positive potential for I and III, E1/2 = 0.58 and 0.57 V (peak separations ∆Ep = 87 and 90 mV), respectively. The cyclic voltammogram of I was complicated by iodide oxidation especially with the Pt-disk working electrode. The first positive scan with a clean Pt-disk electrode showed an irreversible anodic peak at Ep = 0.44 V followed by one oxidation wave at Ep = 0.69 V (ΔEp = 100 mV). Similar results were observed with a Au-disk working electrode. Under the same electrochemical conditions, the CV for free KI showed similar results with peaks at Ep = 0.22 V (ΔEp = 155 mV) and 0.68 V (ΔEp = 84 mV). This result suggests that the E1/2 of I may be higher than that of II and III.
conversion rate is slow relative to other photophysical processes. A much lower barrier height is proposed for the dpmp complexes so that the two states are in thermal equilibrium thus have the same lifetimes under conditions where both emissions are evident.

In what manner can one rationalize these differences? It is clear that the Cu–Cu internuclear distances in the GS have major influence on the emission properties in the context that the CC emissions are certainly less likely to be observed for those complexes having the longer d_{Cu–Cu}. For example, no emission has been seen for CuCl(Et$_2$N)$_4$ (d$_{Cu–Cu}$ = 3.07 Å), strong CC emission is seen for A and B (d$_{Cu–Cu}$ = 2.65 and 2.68 Å, respectively), and a weak temperature dependent CC emission is seen for solid I and II (d$_{Cu–Cu}$ ~ 2.90 Å). In contrast, it would appear (on a limited basis set for comparison) that XLCT emissions are dependent on the nature of the ligand L but are not affected by the Cu–Cu internuclear distances.

Interaction between the filled d-orbitals is Cu–Cu repulsive, while interaction between the Cu s-orbitals is Cu–Cu bonding. In the CC ES, electron density has moved from copper d- to copper s-orbitals, thus the energy of this ES and the shape of its potential surface depends strongly on the extent of Cu–Cu interaction. The shorter d$_{Cu–Cu}$ values would hence lead to greater overlap between relevant orbitals and larger metal–metal interaction. The packing of the large iodide spheres with the smaller Cu(I) spheres in the Cu$_4$I$_4$L$_4$ clusters A and B with relatively small ligands L forces the copper atoms into a Cu$_4$ tetrahedron with short d$_{Cu–Cu}$ values to give greater orbital overlap and a lowest energy, highly distorted CC ES. In contrast, the packing with the smaller chlorides in the chloride clusters C and Cu–Cl$_4$(py)$_4$, gives a larger Cu$_4$ tetrahedron, and as a result no CC emission is seen for either of these clusters. The three dpmp clusters may differ from these other examples in the context that the packing in the Cu$_4$X$_4$ core appears to be dominated by the steric bulk of the 2-(diphenylmethy1)pyridine ligand which (fortuitously) holds the d$_{Cu–Cu}$ for all three at ~2.9 Å, a value at which the Cu–Cu interactions are apparently strong enough to give a moderately distorted CC ES whose energy is above but near that of the lowest energy XLCT state from which the emission is principally observed.

Conclusions

The photophysical properties of the copper(I) halide clusters Cu$_4$X$_4$(dpmp)$_4$, have been interpreted to derive from the presence of two ES of different origins but close energies. The higher energy, more intense emission is thought to originate from the lowest lying ES, which is assigned as XLCT by analogy with the HE emission of Cu$_4$I$_4$(py)$_4$. A weak temperature dependent emission band is attributed, on the other hand, to a CC ES of slightly higher energy than the XLCT. The activation barrier for the communication between the two excited states is lower in these compounds than it is in Cu$_4$I$_4$(py)$_4$. The relative insensitivity of the emission and excitation energy to the nature of the halide is tentatively explained as the result of the ionicity trend having an effect equal and opposite to the electronegativity trend.

Listing of Abbreviations. The following abbreviations were used in the text: A = Cu$_4$I$_4$(py)$_4$; AN = CH$_3$CN; B = Cu$_4$I$_4$(pip)$_4$; C = Cu$_4$Cl$_4$(Et$_2$N)$_4$; CC = cluster centered; dpmp = 2-(diphenylmethyl)pyridine; DR = diffuse reflectance; ES = excited state(s); Et$_3$N = triethylamine; GS = ground state; HE = higher energy; HOMO = highest occupied molecular orbital; I = Cu$_4$I$_4$(dpmp)$_4$; II = Cu$_4$Br$_4$(dpmp)$_4$; III = Cu$_4$Cl$_4$(dpmp)$_4$; L = ligand; LE = lower energy; MC = metal centered; MLCT = metal-to-ligand charge transfer; pip = piperidine; py = pyridine; X = halide; XLCT = halide-to-ligand charge transfer; XMCT = halide-to-metal charge transfer.

Acknowledgment. This research was supported by the U.S. National Science Foundation (Grants CHE-8722561 and CHE-9024845). We thank Professors G. Stucky and W. Kaska for allowing access to the diffuse reflectance spectrometer and electrochemical instruments, respectively. We also thank Dr. N. L. Keder for aid in X-ray powder diffraction studies.