between magnetic and dielectric properties. To pursue the investigation of the two distinct conductivity regimes observed in this type of conductor, we have initiated measurements of the microwave properties of alloy samples of the form $Cu_xNi_{1-x}(L)I$, where L = pc and tatbp.[25] In these materials a fraction of the copper ions is replaced by nickel ions that do not possess a local moment, which allows us to follow the effects of the concentration of local moments on both conductivity and dielectric losses.[26]

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**Supplementary Material Available:** Crystallographic details (Table SI) and anisotropic thermal parameters (Table SII) (3 pages); $10|F_c|$ vs $10|F_o|$ (Table SIII) (5 pages). Ordering information is given on any current masthead page.

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# Structural, Optical, and Redox Properties of Lamellar Solids Derived from Copper(I) Complexes and *n*-Butylammonium Uranyl Phosphate and Arsenate

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A family of hydrated, layered solids has been prepared from intercalative ion-exchange reactions of *n*-butylammonium uranyl phosphate (BAUP) or arsenate (BAUAs), $(n\text{-}C_4H_9NH_3)UO_2EO_4\cdot 3H_2O$ (E = P, As), with $Cu(LL)_2^+$ complexes (LL is dmp = 2,9-dimethyl-1,10-phenanthroline or bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline). The products obtained were analyzed as having compositions $[Cu(LL)_2]_x[BA]_{1-x}UO_2EO_4\cdot 2H_2O$ with $x \sim 0.2$. X-ray powder diffraction data reveal that the compounds are single phases that can be indexed on the basis of a tetragonal unit cell. The solids exhibit absorption and photoluminescence (PL) properties characteristic of the $Cu(LL)_2^+$ species; the Cu(I) complexes completely quench the uranyl PL. Once intercalated, the Cu(I) complexes can be oxidized by using $Br_2$ vapor and rereduced either by photochemical means or by $N_2H_4$ vapor, as shown by changes in electronic and EPR spectra.

## Introduction

Layered phosphates and arsenates are proving to be versatile host lattices for intercalative ion-exchange reactions.[1] We and others have shown that a variety of transition-metal complexes can be intercalated into such hosts as $\alpha\text{-}Zr(HPO_4)_2$ (ZrP), $HUO_2PO_4\cdot 4H_2O$ (HUP), $HUO_2AsO_4\cdot 4H_2O$ (HUAs), $(n\text{-}C_4H_9NH_3)UO_2PO_4\cdot 3H_2O$ (BAUP), and $(n\text{-}C_4H_9NH_3)UO_2AsO_4\cdot 3H_2O$ (BAUAs).[2-9] The intercalants have participated in a variety of reactions, including excited-state energy transfer,[2] ligand photosubstitution,[4] and acid–base/precipitation chemistry.[5]

An appealing set of candidate intercalants are Cu(I) complexes with bidentate ligands, $Cu(LL)_2^+$. In particular, the room-temperature photoluminescence (PL) and redox activity of the complexes $Cu(dmp)_2^+$ and $Cu(bcp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline; bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) have permitted extensive characterization of ground- and excited-state reactivity.[10-16] We sought to determine how these properties would be influenced by incorporation of the complexes into suitable lamellar host solids.

We report in this paper that single-phase, hydrated, lamellar solids of approximate composition $[Cu(LL)_2]_x[BA]_{1-x}UO_2EO_4\cdot 2H_2O$ (E = P, As; BA = *n*-butylammonium; $x \sim 0.2$) can be prepared by intercalative ion-exchange reactions of the Cu(I) complexes with BAUP and BAUAs. Optical measurements reveal that while the photophysical properties of the Cu(I) complexes remain largely intact upon intercalation, strong host–guest interactions occur: the Cu(I) complexes quench the host $UO_2^{2+}$ PL. We also demonstrate that the Cu(I) complexes undergo reversible redox chemistry that parallels their solution reactivity.

## Experimental Section

**Materials.** Reagent grade $CuSO_4\cdot 5H_2O$ was supplied by Matheson Coleman and Bell; 2,9-dimethyl-1,10-phenanthroline ("neocuproine"; 98%), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ("bathocuproine"; 99%), L-ascorbic acid (99%), and hydrazine monohydrate (98%) were supplied by Aldrich; reagent grade bromine was supplied by J. T. Baker; analytical grade $UO_2(NO_3)_2\cdot 6H_2O$ and $H_3PO_4$ (85%) were supplied by Mallinckrodt; and $As_2O_5$ (99.9%) was supplied by Cerac. All materials were used as received. A 1.0 M solution of $H_3AsO_4$ was prepared by dissolving 11.5 g of $As_2O_5$ into 100 mL of boiling, triply distilled water. HUAs and HUP were prepared from uranyl nitrate and arsenic and phosphoric acid, respectively, as previously described.[3,17] BAUAs and BAUP were prepared from reactions of *n*-butylamine with HUAs and HUP, respectively, as described previously.[18]

For the intercalants prepared below, Cu analyses were conducted by ICP emission spectroscopy using a Leeman Laboratories ICP 2.5 inductively coupled plasma emission spectrophotometer. Compounds were dissolved in a minimum amount of concentrated $HCl/HNO_3$, followed by dilution with deionized water. Standardized solutions for the ICP analyses were prepared by dissolving copper wire (Malin Co.) in a min-

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imum quantity of $HNO_3$, followed by dilution with deionized water. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) for determining hydration values employed a Netsch Geratebau STA 409 thermal analysis system. Typically, 50-mg samples were heated in air in alumina crucibles from 25 to 500 °C at 2.5 °C/min.

**$[Cu(dmp)_2]NO_3{\cdot}2H_2O$ and $[Cu(bcp)_2]NO_3{\cdot}2H_2O$.** These complexes were prepared by using a slightly modified literature preparation.[19] In a typical synthesis, $CuSO_4{\cdot}5H_2O$ was dissolved in an acetate-buffered solution containing equal parts by volume of methanol, ethanol, and water. To this solution 2.2 equiv of ligand and excess $NaNO_3$ were added. After addition of L-ascorbic acid to effect reduction, the solution was concentrated, yielding orange-red crystals. Products were recrystallized from an ethanol/water solution. Anal. Calcd for $[Cu(dmp)_2]NO_3{\cdot}2H_2O$, $C_{28}H_{28}N_5O_5Cu$: Cu, 10.99. Found: Cu, 10.86. $\epsilon_{454}$ in $CH_2Cl_2$ = 8200 $M^{-1}$ $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 8.52 (4 H, d, $J_{HH}$ = 4 Hz), 8.05 (4 H, s), 7.78 (4 H, d, $J_{HH}$ = 4 Hz), 2.44 (12 H, s). Anal. Calcd for $[Cu(bcp)_2]NO_3{\cdot}2H_2O$, $C_{52}H_{44}N_5O_5Cu$: Cu, 7.20. Found: Cu, 7.58. $\epsilon_{477}$ in $CH_2Cl_2$ = 13 700 $M^{-1}$ $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 8.06 (4 H, s), 7.77 (4 H, s), 7.64 (20 H, m), 2.58 (12 H, s).

**$[Cu(dmp)_2][NO_3]_2{\cdot}2H_2O$.** This compound was prepared as described in the literature.[20] Anal. Calcd for $C_{28}H_{28}N_6O_8Cu$: Cu, 9.93. Found: Cu, 10.47.

**$[Cu(LL)_2]_x[BA]_{1-x}UO_2EO_4{\cdot}2H_2O$ (LL = dmp, bcp; E = P, As; $x \sim 0.2$).** In a representative reaction, the Cu(I) complex was dissolved in a 1:1 ethanol/water mixture to make 125 mL of a ~20 mM solution and slurried in a 1.5:1 mol ratio with BAUP or BAUAs at 45 °C for 3 days. The solution was filtered and washed with ethanol/water until the washings were colorless (usually 200 mL). The orange-red solid obtained was air-dried overnight and placed in a tightly sealed vial.

The Cu(I) loading level in the isolated compounds was determined by ICP and spectrophotometric analyses, the latter by dissolving the lattice in an acidified alcohol solution. Because of the low solubility of the copper complexes, a mixture of ethanol/water/HCl was required (1:1 ethanol/water mixture; pH of water/HCl before addition of ethanol = 2.6, as measured with a Corning Model 7 pH meter). The absorptivities of Cu(I) complexes in this medium were determined by preparing a series of physical mixtures of the Cu(I) complex and BAUP or BAUAs: for $Cu(dmp)_2^+$, $\epsilon_{454}$ = 7740 $M^{-1}$ $cm^{-1}$ with BAUP and 7260 $M^{-1}$ $cm^{-1}$ with BAUAs; for $Cu(bcp)_2^+$, $\epsilon_{477}$ = 12 300 $M^{-1}$ $cm^{-1}$ for either BAUP or BAUAs. The absorbances of these solutions were noted to decrease with time so that measurements were made as soon as dissolution was complete. The ICP analysis was performed as described above.

From thermogravimetric data, Cu analyses (ICP and spectrophotometric) and elemental analyses (E&R Microanalytical Lab, Inc.) the approximate compositions of the solids of this study are as follows. Anal. Calcd for $[Cu(dmp)_2]_{0.22}[BA]_{0.78}UO_2PO_4{\cdot}2H_2O$: C, 19.75; H, 3.33; N, 4.12; Cu, 2.48; U, 42.17; P, 5.49. Found: C, 23.21; H, 3.35; N, 4.30; Cu, 2.47; U, 39.50; P, 5.26. Calcd for $[Cu(dmp)_2]_{0.17}[BA]_{0.83}UO_2AsO_4{\cdot}2H_2O$: C, 16.50; H, 3.09; N, 3.59; Cu, 1.84; U, 40.47; As, 12.74. Found: C, 17.63; H, 2.89; N, 3.90; Cu, 1.90; U, 39.08; As, 12.71. Calcd for $[Cu(bcp)_2]_{0.21}[BA]_{0.79}UO_2PO_4{\cdot}2H_2O$: C, 27.09; H, 3.53; N, 3.66; Cu, 2.14; U, 38.12; P, 4.96. Found: C, 28.26; H, 3.36; N, 3.93; Cu, 2.03; U, 36.85; P, 4.56. Calcd for $[Cu(bcp)_2]_{0.18}[BA]_{0.82}UO_2AsO_4{\cdot}2H_2O$: C, 23.47; H, 3.28; N, 3.33; Cu, 1.77; U, 36.79; As, 11.58. Found: C, 24.50; H, 3.10; N, 3.45; Cu, 1.56; U, 35.97; As, 12.07. Solids were also analyzed for the presence of ethanol by heating them to ~65 °C at $10^{-5}$ Torr and capturing the volatile components in an NMR tube. The $^1H$ NMR spectrum (Bruker WP200SY) revealed that no ethanol was present.

**Structure.** Powder X-ray diffraction data were collected on a Nicolet I2 rotating-stage powder diffractometer using Cu K$\alpha$ radiation; an internal Si standard was employed. The patterns and cell constants were indexed and refined by using least-squares analysis. Diffraction patterns were indexed on the basis of tetragonal unit cells. Values of $1/d^2$ and *hkl* assignments based on a least-squares analysis are available as supplementary material. Infrared spectra were obtained on a Mattson Polaris NU-10000 FT-IR spectrophotometer using KBr pellets.

**Optical Measurements.** Electronic spectra were recorded on a Varian Cary 17-D UV-vis-near-IR spectrophotometer, using silicone grease mulls, as previously reported.[3] PL spectra with 458-nm excitation were obtained by using a Photon Technologies Inc. Model 01-150 high-intensity illumination system, which includes a Model 01-150X1 150-W Xe lamp, an elliptical mirror, and a Model 01-001 0.25-m monochromator. The PL signal was directed through a McPherson Model 270 0.35-m monochromator and detected with a Hamamatsu R943-02 GaAs PMT. The PL intensity was obtained by using a LeCroy Model 4604 photon counter, and data were collected by using an Apple IIe microprocessor. Lifetimes were determined as described previously, using 450-nm excitation and a Hamamatsu R446 PMT for 690-nm detection of Cu(I) PL. Plots of log (intensity) vs time were linear over at least 2 lifetimes. Quantum yields were determined as previously described.[3]

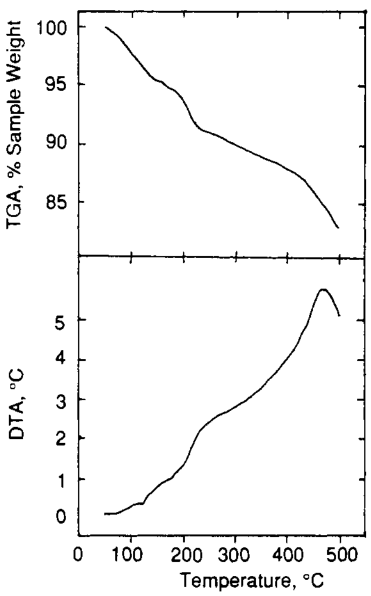

Figure 1. TGA and DTA data for CudmpUP.

**Redox Chemistry.** Bromine vapor was used to effect oxidation of the Cu(I)-intercalated solids. In a typical reaction, 25–50 mg of $[Cu(dmp)_2]_{0.22}[BA]_{0.78}UO_2PO_4{\cdot}2H_2O$ were placed in a 450-mL closed vessel containing ~5 mL of $Br_2$. The sample was fully oxidized within a few minutes, as determined by visible spectroscopy. Chemical reduction of the oxidized sample with $N_2H_4$ vapor was accomplished in a similar manner and was completed after ~45 min, as determined by visible and EPR spectroscopies. EPR spectra were obtained from solid samples by using a Varian E-15 spectrometer. An internal cell-within-a-cell DPPH standard was used to calibrate the signal. Photochemical reduction of the oxidized sample was carried out by using the 468-nm line of a Coherent Innova $Kr^+$ laser (~350 $mW/cm^2$); reduction was usually detected after ~30 min.

## Results and Discussion

A family of powdered samples, $[Cu(LL)_2]_x[BA]_{1-x}UO_2EO_4{\cdot}2H_2O$ (LL is dmp = 2,9-dimethyl-1,10-phenanthroline or bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; BA = ($n$-$C_4H_9NH_3$); E = P, As; $x \sim 0.2$), have been prepared and characterized. In the sections below, we describe the synthesis and composition, and structural, optical, and redox properties of these materials.

**Synthesis and Composition.** The $[Cu(LL)_2]_x[BA]_{1-x}UO_2EO_4{\cdot}2H_2O$ solids can be prepared by the intercalative ion-exchange reaction

$$x[Cu(LL)_2]^+ + BAUP \xrightarrow[45°C]{EtOH/H_2O} [Cu(LL)_2]_x[BA]_{1-x}UP + x[n\text{-}C_4H_9NH_3]^+ \quad (1)$$

wherein the Cu(I) complex exchanges with some of the $n$-butylammonium cations within the uranyl phosphate (BAUP) or arsenate (BAUAs) hosts. The use of an ethanol/water mixture at elevated temperatures improves the solubility of the Cu(I) precursor and leads to a single-phase product. Occasionally, solids with $x$ as large as ~0.4 have been isolated, but $x$ ~0.2 is typical. Efforts to intercalate the complexes under analogous conditions by using HUP or HUAs as precursors were unsuccessful, presumably due to the large size of the guest ion.

In many respects the physicochemical properties of the four solids of this study (dmp or bcp ligands bonded to Cu(I) with phosphate or arsenate host lattices) are sufficiently similar that data collected for $[Cu(dmp)_2]_{0.22}[BA]_{0.78}UO_2PO_4{\cdot}2H_2O$ (CudmpUP) can be regarded as illustrative.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were performed to assess hydration. Shown in

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**Table I.** Lattice Parameters[a]

| compd | $a$, Å | $^1/_2c$,[b] Å |
|---|---|---|
| $[Cu(dmp)_2]_{0.22}[BA]_{0.78}UP{\cdot}2H_2O$ | 6.974 (5) | 16.99 (7) |
| fully hydrated[c,d] | ... | ... |
| $[Cu(dmp)_2]_{0.17}[BA]_{0.83}UAs{\cdot}2H_2O$ | 7.179 (2) | 16.83 (3) |
| fully hydrated[c] | 7.31 (2) | 19.54 (6) |
| $[Cu(bcp)_2]_{0.21}[BA]_{0.79}UP{\cdot}2H_2O$ | 7.009 (3) | 19.99 (3) |
| fully hydrated[c] | 6.976 (3) | 22.87 (2) |
| $[Cu(bcp)_2]_{0.18}[BA]_{0.82}UAs{\cdot}2H_2O$ | 7.207 (3) | 19.51 (4) |
| fully hydrated[c] | 7.259 (8) | 23.48 (7) |
| BAUP | 6.987 (5) | 14.61 (1) |
| BAUAs | 7.183 (9) | 15.48 (2) |

[a] All samples were single phases that could be indexed to tetragonal unit cells. Errors in table entries are estimated standard deviations based on least-squares refinement. [b] The $c/2$ lattice parameter represents the interlamellar spacing, viz., the interplanar spacing between adjacent uranyl phosphate layers.[28] [c] A fully hydrated sample is obtained by adding triply distilled water directly onto the sample. [d] The fully hydrated CudmpUP yielded two phases.

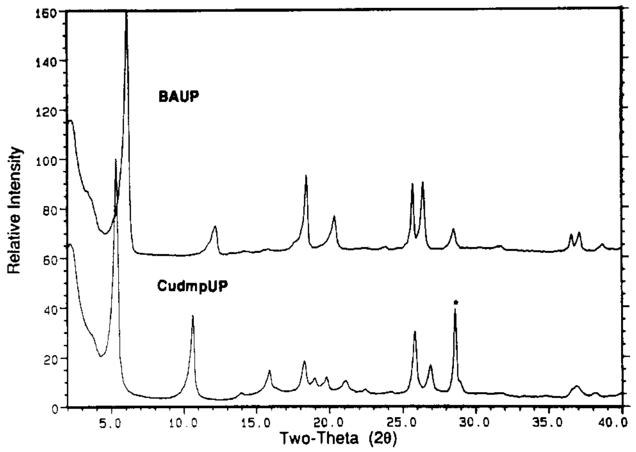

**Figure 2.** X-ray powder diffraction patterns for CudmpUP and the starting material, BAUP. The internal silicon standard is denoted by an asterisk.

Figure 1 are typical TGA and DTA traces for CudmpUP, which reveal that the air-dried solid is approximately a dihydrate. The drop in the TGA at temperatures greater than ~250 °C is likely due to decomposition of the Cu(I) complex, the nitrate salt of which decomposes at ~260 °C.[21] Decomposition would mask loss of additional water, so the hydrate values given should be treated as lower limits. Given our synthetic conditions, we were concerned that ethanol might have been incorporated into the solids,[22] but the volatile products collected upon heating the compounds in vacuo showed no evidence of the alcohol by $^1H$ NMR spectroscopy.

**Structure.** All of the isolated solids were single phases, based on powder X-ray diffraction data that are summarized in Table I. The X-ray data indicate the Cu(I)-intercalated materials to be lamellar solids whose powder patterns, like those of the BAUP[3,23] and BAUAs precursors, can be indexed in tetragonal symmetry. Shown in Figure 2 are X-ray powder diffraction patterns of CudmpUP and the starting material, BAUP.

The Table I data indicate that the $a$ lattice parameter is insensitive to the presence of the Cu(I) complex and reflects the choice of phosphate or arsenate host lattice. However, after intercalation of the Cu(I) complex, there is generally a ~1-5-Å increase in the interlamellar spacing, $c/2$. The choice of ligand appears to influence the interlamellar spacing, with the more sterically demanding bcp causing greater lattice expansion than dmp. It is noteworthy that the addition of triply distilled water to these air-dried powders causes an additional ~3-4-Å increase in the interlamellar spacing, as shown in Table I, and reduces sample crystallinity. Allowing the compounds to dry in air restores the original powder pattern within a few minutes. No attempt was made to quantify the amount of additional water taken up by the lattice.

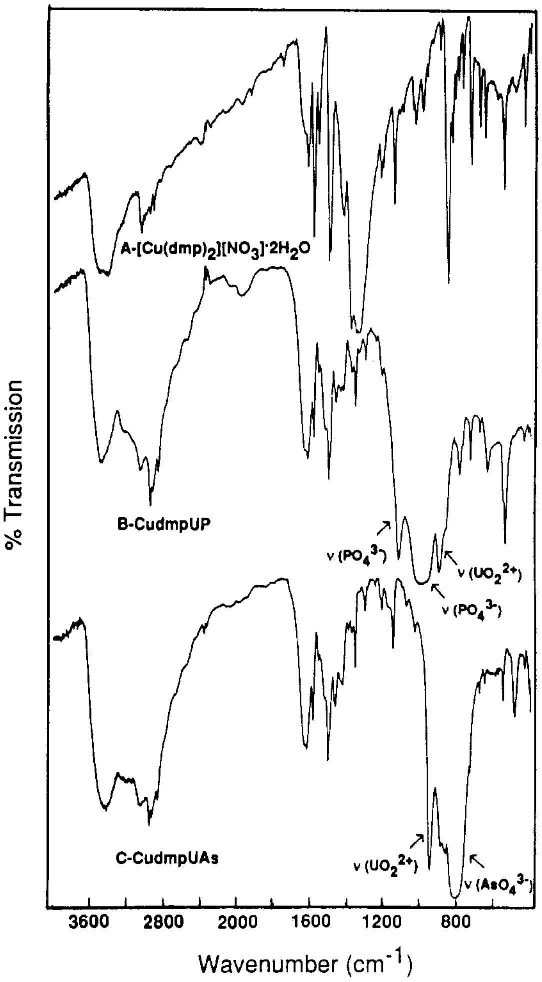

**Figure 3.** Infrared spectra of $[Cu(dmp)_2][NO_3]{\cdot}2H_2O$ (A), CudmpUP (B), and CudmpUAs (C). Spectra were obtained from KBr pellets at room temperature.

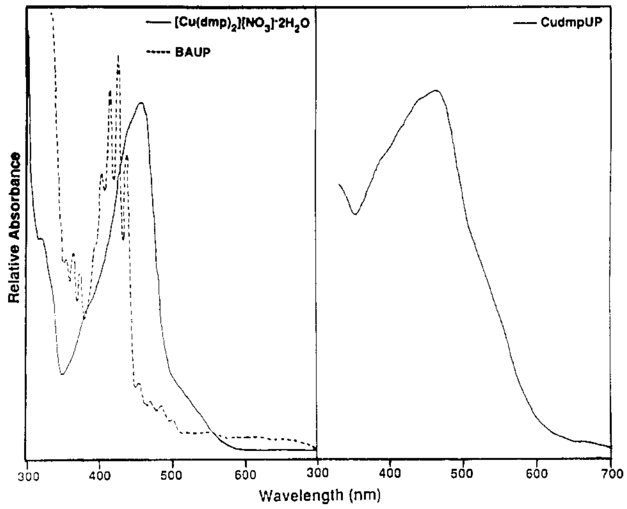

**Figure 4.** Visible absorption spectra (295 K): left panel, $Cu(dmp)_2^+$ in $CH_2Cl_2$ (—) and BAUP (---); right panel, CudmpUP (—). The solid samples were prepared as silicone grease mulls on filter paper.

Retention of the original lamellar structure in the intercalated compounds was further confirmed by the phosphate infrared stretching frequencies. The peaks located at ~1120 and ~1000

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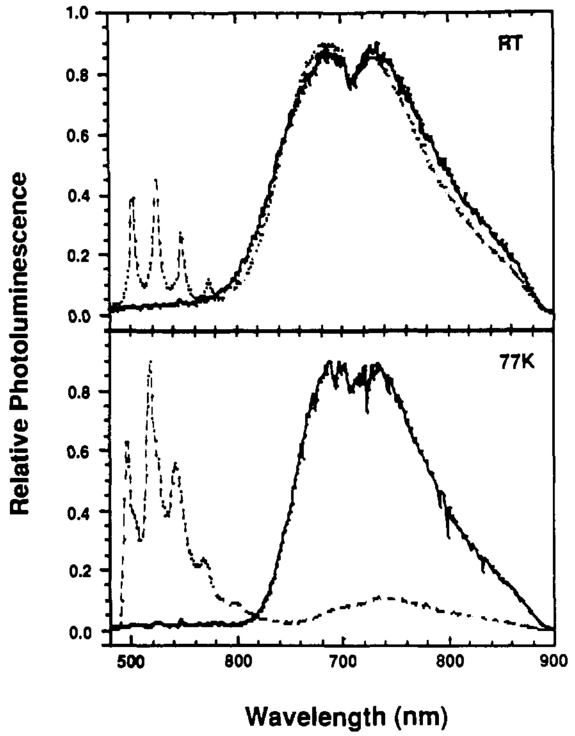

**Figure 5.** Uncorrected PL spectra for CudmpUP (—) and a concentration-matched physical mixture of BAUP and $[Cu(dmp)_2][NO_3]\cdot 2H_2O$ (- - -). Spectra in the upper panel were obtained at room temperature, and those in the lower panel, at 77 K. Spectra were normalized to a common maximum intensity. The samples were excited at 458 nm. Sharp dips in the 77 K spectra were caused by bubbles in the liquid nitrogen.

$cm^{-1}$ have been assigned to the phosphate stretching modes in HUP,[24,25] while the peak at ~810 $cm^{-1}$ has been assigned to the arsenate stretching mode in HUAs.[26,27] These stretching frequencies are retained in the intercalated solids, as illustrated in Figure 3 for CudmpUP and CudmpUAs. Figure 3 also shows that the IR spectra of the intercalated solids appear to be the sum of the uranyl phosphate (arsenate) bands and the characteristic $[Cu(dmp)_2][NO_3]\cdot 2H_2O$ bands.

**Optical Properties.** The $Cu(dmp)_2^+$- and $Cu(bcp)_2^+$-intercalated compounds are orange-red and red, respectively. Figure 4 shows that the color for the $Cu(dmp)_2^+$-intercalated compounds derives from an intense band with $\lambda_{max} \sim 460$ nm that is present in the absorption spectrum of $[Cu(dmp)_2][NO_3]\cdot 2H_2O$ and is assigned as a metal-to-ligand charge transfer (MLCT) transition.[29,30] It is noteworthy that the red edge of the CudmpUP spectrum in Figure 4 is enhanced relative to the solution spectrum, an effect that might be attributed to a flattening distortion in the Cu(I) guest molecule[31,32] and/or to the presence of multiple guest occupation sites in the lattice.[2] The absence in Figure 4 of the structured absorption due to $UO_2^{2+}$ that is present in the accompanying BAUP spectrum is a consequence of the roughly 1000-fold greater absorptivity of the Cu(I) complex.

Table II. Emissive Properties[a]

| compd | $\tau$,[b] ns | $10^4\phi_r$[c] | $10^{-3}k_r$,[d] $s^{-1}$ | $10^{-6}k_{nr}$,[e] $s^{-1}$ |
|---|---|---|---|---|
| $[Cu(dmp)_2]_{0.22}[BA]_{0.78}UP\cdot 2H_2O$ | 140 | 5.6 | 4.0 | 7.1 |
| $[Cu(dmp)_2]_{0.17}[BA]_{0.83}UAs\cdot 2H_2O$ | 92 | 5.5 | 6.0 | 11 |
| $[Cu(bcp)_2]_{0.21}[BA]_{0.79}UP\cdot 2H_2O$ | 220 | 6.1 | 2.8 | 4.5 |
| $[Cu(bcp)_2]_{0.18}[BA]_{0.82}UAs\cdot 2H_2O$ | 150 | 5.9 | 3.9 | 6.7 |
| $[Cu(dmp)_2][NO_3]\cdot 2H_2O$[f] | 320 | 16 | 5.0 | 3.1 |
| $[Cu(bcp)_2][NO_3]\cdot 2H_2O$[f] | 380 | 34 | 8.9 | 2.6 |
| $Cu(dmp)_2^+$[g] | 90 | 2.1 | 2.3 | 11 |
| $Cu(bcp)_2^+$[g] | 80 | 2.5 | 3.1 | 12 |

[a] Emissive data were obtained at 295 K. [b] Lifetimes were obtained with 450-nm excitation, as described in the Experimental Section. [c] The radiative quantum efficiencies were obtained with 450-nm excitation, as described in the Experimental Section. Errors in the radiative quantum efficiencies have been estimated to be ±25%.[33] [d] Unimolecular radiative rate constants were calculated by using eq 2 in the text. [e] Unimolecular nonradiative rate constants were calculated by using eq 3 in the text. [f] Emissive properties were obtained from solid samples. [g] The $[Cu(dmp)_2]BF_4$ and $[Cu(bcp)_2]PF_6$ salts were dissolved in $CH_2Cl_2$ at 25 °C. Data were taken from ref 12.

All of the Cu(I)-loaded solids showed room-temperature PL characteristic of the Cu(I) complex.[12] Figure 5 compares the uncorrected PL of CudmpUP with a concentration-matched (1:4 mole ratio) physical mixture of $[Cu(dmp)_2][NO_3]\cdot 2H_2O$ and BAUP, at 295 and 77 K. The characteristic Cu(I) PL band maxima at 690 and 730 nm are evident at both temperatures and are unshifted by intercalation; identical band positions are found for the $Cu(bcp)_2^+$ complex before and after intercalation. This Cu(I) PL has been investigated in detail by McMillin et al. and described as two excited states of MLCT origin in thermal equilibrium.[12] The other solids display similar features, indicating that intercalation does not drastically alter the excited-state manifold of the Cu(I) complex.

Additional support for this notion comes from photophysical measurements of the Cu(I)-intercalated compounds. Table II presents lifetimes $\tau$ and radiative quantum yields $\phi_r$ of the intercalated solids, and solid-state and solution data for the copper(I) nitrate salts. Corresponding unimolecular rate constants for radiative and nonradiative decay were calculated using eq 2 and 3 and are also given in Table II. In general, the Cu(I) PL is

$$k_r = \phi_r/\tau \qquad (2)$$

$$k_{nr} = 1/\tau - k_r \qquad (3)$$

inefficient and short-lived. The values shown in Table II for the Cu(I)-intercalated solids are intermediate between the solid-state and solution values,[12] as might be expected. Although we have not carried out photophysical measurements as a function of loading level, it is worth mentioning that we may be in a regime where self-quenching processes contribute to our data.[34]

A more substantive effect resulting from intercalation is the complete quenching of host $UO_2^{2+}$ PL between 500 and 600 nm, as revealed by the physical mixture/intercalated-solid comparison of Figure 5. Because BAUP is only weakly emissive at 295 K, this effect is much more pronounced at 77 K, where BAUP rivals HUP in emissive efficiency.[3] While some contribution to quenching may arise from the trivial mechanism (absorption of $UO_2^{2+}$ PL by the Cu(I) complex), the comparisons of Figure 5 argue that the Cu(I) complex quenches the $UO_2^{2+}$ PL by excited-state energy and/or electron transfer: in the former case, the Cu(I) complexes possess low-lying MLCT excited states;[19] in the latter case they are oxidizable by excited $UO_2^{2+}$.[13,16] All

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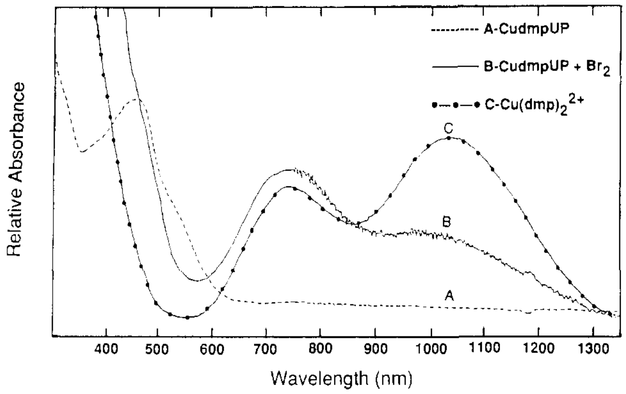

**Figure 6.** Visible absorption spectra of CudmpUP before oxidation (A; ---) and after oxidation by $Br_2$ (B; —). Spectrum C (•—•) is that of $Cu(dmp)_2^{2+}$, obtained in water after dissolution of the nitrate salt. Spectra A and B were prepared as silicone grease mulls on filter paper.

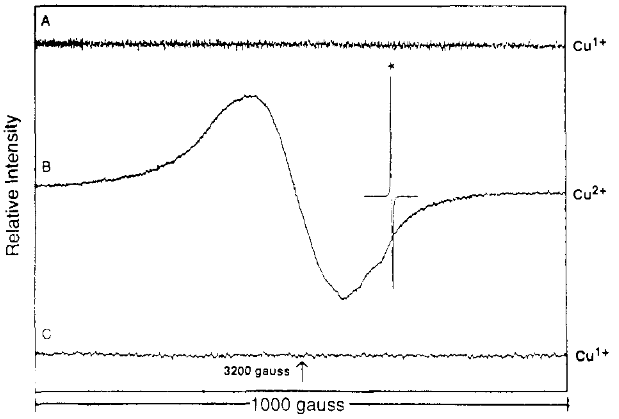

**Figure 7.** EPR spectra of solid CudmpUP (A) and of CudmpUP after oxidation with $Br_2$ (B) and after reduction with $N_2H_4$ (C). Spectra were obtained at room temperature. The DPPH calibration peak is denoted with an asterisk.

of the other Cu(I)-intercalated guests caused similar quenching of $UO_2^{2+}$ PL at 295 and 77 K.

**Oxidation.** It is well established that $Cu(dmp)_2^+$ can be oxidized to $Cu(dmp)_2^{2+}$.[11,19] We wanted to ascertain whether similar chemistry obtains in the layered host. Oxidation using $Br_2$ vapor was successful: the compounds rapidly changed from orange-red to green. A comparison of the electronic spectrum of the oxidized compound with an aqueous solution of $Cu(dmp)_2^{2+}$ is shown in Figure 6. After exposure to $Br_2$, the characteristic Cu(I) MLCT band is no longer present in the visible spectrum of the oxidized species, but the characteristic weak d–d transitions of the $Cu^{2+}$ $d^9$ system can be seen in the near-IR region. That the oxidized layered solid's spectrum does not exactly match that of $Cu(dmp)_2^{2+}$ likely reflects different cation environments. Further evidence that the $Cu(dmp)_2^+$ has been oxidized is shown by the EPR trace of Figure 7. The $Cu(dmp)_2^+$ compound is converted from an EPR-silent $d^{10}$ system to an EPR-active $d^9$ system; little change in the EPR spectrum was observed on cooling to 77 K.

The newly oxidized $Cu(dmp)_2^{2+}$ compound displays no PL in the visible region. It resembles hydrated cupric ion in its efficient quenching of uranyl emission in solution[35] and in the HUP[3] host lattice. Quenching likely occurs by energy transfer, since the complex has low-lying excited states.

The insensitivity of the IR phosphate stretching region to the oxidation reaction provides evidence that the gross integrity of the CudmpUP lamellar structure is preserved. However, considerable loss of crystallinity was evident from X-ray powder diffraction patterns of the oxidized solids, which were sufficiently poor that indexing was not possible.

Mechanistically, we presume for steric reasons that the oxidized Cu complex is not very mobile and remains within the lattice during oxidation. This would require that products resulting from $Br_2$ reduction remain in the lattice to maintain charge neutrality.

Exposing the newly-oxidized, Cu(II)-intercalated compound to $N_2H_4$ vapor caused reduction of the complex back to Cu(I), as judged by loss of the EPR signal and the return of the characteristic $Cu(dmp)_2^+$ MLCT absorption band (slightly shifted to $\lambda_{max} \sim 440$ nm) and PL properties. Moreover, the IR spectrum revealed no loss of the lamellar structure. The Cu(II)-intercalated solid could alternatively be photochemically reduced with exposure to 468-nm light. The mechanism that has been proposed for the photoreduction involves the homolytic cleavage of a copper-(II)–water bond in an acidic medium, yielding $H^+$, $OH^•$, and Cu(I).[36] Complete photoreduction of Cu(II) to Cu(I) was not achieved in solution, nor were we able to accomplish this in the layered solid.[36] No attempt was made to isolate the products of the photoreduction.

Interestingly, efforts to intercalate Cu(II) directly into BAUP or BAUAs by using $[Cu(dmp)_2][NO_3]_2$ were unsuccessful. The resulting materials were either contaminated with $[Cu(dmp)_2]^+$ or consisted of multiple phases. Attempts to intercalate first dmp and then $Cu^{2+}$ were unsuccessful: A single-phase, dmp-intercalated solid was prepared, but intercalation with $Cu^{2+}$ yielded only $Cu_{0.5}UP$ as shown by X-ray powder diffraction patterns.[37] Further investigations into this area are being undertaken in our laboratories.

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**Supplementary Material Available:** Tables of X-ray powder diffraction data (9 pages). Ordering information is given on any current masthead page.

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