

## EXCITED-STATE PROPERTIES OF LAMELLAR SOLIDS DERIVED FROM METAL COMPLEXES AND HYDROGEN URANYL PHOSPHATE

LYNN R. HUNSBERGER and ARTHUR B. ELLIS\*

Chemistry Department, University of Wisconsin-Madison, Madison, WI  
53706 (USA)

### SUMMARY

Hydrogen uranyl phosphate (HUP),  $\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ , is a layered solid that undergoes intercalative ion-exchange reactions with guest cationic species spanning the periodic table. The host lattice exhibits highly efficient green photoluminescence (PL) characteristic of the uranyl ( $\text{UO}_2^{2+}$ ) moiety. Structural and optical perturbations of the host and guest generally accompany intercalation reactions. Guest metal complexes have afforded an opportunity to study host-to-guest energy transfer, interlamellar acid-base/precipitation chemistry, interlamellar redox chemistry, and host lattice substitution chemistry. These reactions are summarized in this article.

### INTRODUCTION

Layered inorganic compounds have played an important role in the area of solid-state chemistry (refs. 1,2). Some well-known examples include transition metal dichalcogenides (ref. 1),  $\alpha\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  (refs. 2,3),  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (ref. 4), and  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  (ref. 5). By serving as hosts for a broad range of guest species, these solids have had a substantial impact on such diverse fields as catalysis, battery technology, and superconductivity.

One compound that has received considerable attention in the literature is hydrogen uranyl phosphate tetrahydrate,  $\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$  (HUP). Readily prepared from  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  (ref. 6), HUP exhibits high proton conductivity (refs. 2,8–25), which has led to its use in miniature fuel cells and electrochromic displays (ref. 26), and serves as a parent compound to a range of solids with interesting structural and spectroscopic properties (refs. 6,7,27–43).

---

\*Author to whom correspondence should be addressed.

Structurally, HUP is a lamellar solid, consisting of alternating  $(\text{UO}_2\text{PO}_4)_n^{n-}$  and protonated hydration sheets, Fig. 1. The former are waffle-like, with each U atom coordinated to four equatorial O atoms from four different  $\text{PO}_4^{3-}$  groups and to two axial O atoms that form the  $\text{UO}_2^{2+}$  moiety. The water molecules, roughly one-fourth of which are protonated, form squares linked through hydrogen bonding. These structural features are illustrated in Fig. 1.

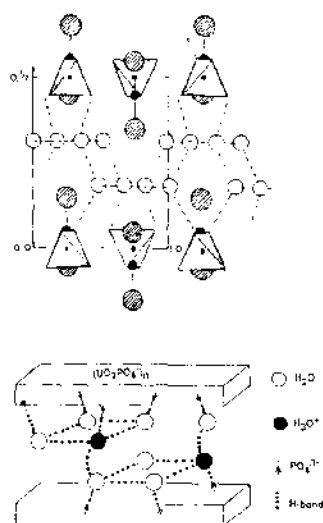


Fig. 1. Projection of the HUP structure along [100] (top). The water molecules of the network about  $z = 3/4$  have been omitted for clarity. The large shaded circles designate the uranyl oxygen atoms, medium open circles the water molecules, medium solid circles uranium, and small solid circles phosphorus. Oxygen atoms of  $\text{PO}_4^{3-}$  are at the vertices of the tetrahedra. Adapted from ref. 9. Shown at the bottom is a schematic representation of the water layers in HUP. Adapted from ref. 18.

Single-crystal and polycrystalline studies of HUP have shown slight structural variations with both synthetic method and temperature; several phases have been reported in the literature (refs. 13,45). At room temperature, however, HUP adopts a tetragonal structure (P4/ncc) with cell parameters of  $a = 6.995\text{\AA}$  and  $c = 17.491\text{\AA}$  (ref. 9).

HUP exhibits rich electronic absorption and emission spectra, Fig. 2.

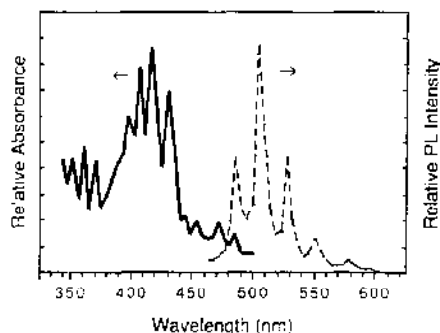
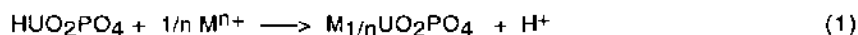


Fig. 2. Relative absorbance and photoluminescence of HUP.

The yellow solid emits intense yellow-green photoluminescence (PL) with UV or near-UV excitation. Spectral features indicate that the electronic transitions are dominated by the  $\text{UO}_2^{2+}$  moiety: vibronic structure characteristic of the uranyl ion is evident in both absorption and emission spectra (ref. 7). The visible absorption bands of HUP are relatively weak, providing a large optical window for spectroscopic investigation of host-guest interactions. Samples of HUP are also excellent hosts for exploring excited-state chemistry, owing to the high radiative efficiency (quantum yield  $\Phi_r$  of nearly unity) and long lifetime (lifetime  $\tau$ , based on exponential decay, of nearly 0.5 ms) of the excited solid (ref. 7).

HUP undergoes intercalative ion-exchange reactions with numerous cations, as represented generically by eq. 1; waters of hydration are omitted for simplicity.



Representative cations that have been introduced are listed in Table 1.

Structural data indicate that the Table 1 derivatives retain the lamellar structure of HUP. Most derivatives adopt a tetragonal structure with a  $\sim 6.9$  Å, indicating unaltered  $(\text{UO}_2\text{PO}_4)_n^{n-}$  sheets. As might be expected, the  $c$  values tend to increase with guest intercalant size. The interlamellar  $d$ -spacings, (i.e., the distance between adjacent uranyl phosphate layers, equal to  $c/2$  (ref. 9)) for several compounds, as determined from x-ray powder diffraction data, are listed in Table 2. Additional evidence that the layered structure is intact is the presence of a strong IR band at  $\sim 1000$   $\text{cm}^{-1}$ , arising from phosphate stretching modes (ref. 47).

TABLE 1

FULLY-SUBSTITUTED URANYL PHOSPHATE DERIVATIVES<sup>a</sup>Monovalent, MUP

M = Li(6,18,27,28); Na(6,18,19,27,28); K(6,7,18,19,27,28); Rb(27);  
Cs(27); Ag(7,18,19,52); Tl(19); [Co(NH<sub>3</sub>)<sub>4</sub>CO<sub>3</sub>](38);  
NH<sub>4</sub>(6,7,18,19,28,41,42); *n*-CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>(7,38);  
*n*-CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>NH<sub>3</sub>(7,35); C<sub>5</sub>H<sub>5</sub>NH(7,43); N<sub>2</sub>H<sub>5</sub>(43)

Divalent, M<sub>1</sub>/2UP

M = Mg(6); Ca(6,7); Sr(6); Ba(6); Mn(29,30); Fe(31); Co(29,30);  
Ni(29,30); Cu(29,30); Zn(7,29,30); Cd(29,30); UO<sub>2</sub>(44,59,62);  
NpO<sub>2</sub>(44)

Trivalent, M<sub>1</sub>/3UP

M = La(32,33); Ce(32); Pr(32); Nd(32); Eu(32,34); Gd(32); Tb(32);  
Dy(32); Yb(32); [Co(NH<sub>3</sub>)<sub>6</sub>](38); [Cr(urea)<sub>6</sub>](39)

PARTIALLY-SUBSTITUTED URANYL PHOSPHATE DERIVATIVES<sup>a</sup>

[Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)<sub>2</sub>]<sub>0.2</sub>

[*n*-C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>]<sub>0.8</sub>UP (36)

[Cu(2,9-dimethyl-1,10-phenanthroline)<sub>2</sub>]<sub>0.2</sub>[*n*-C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>]<sub>0.8</sub>UP (36)

H<sub>0.95</sub>[Ru(NH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>(μ-pyrazine)<sub>0.01</sub>UP (37)

H<sub>0.7</sub>[Cr(NH<sub>3</sub>)<sub>6</sub>]<sub>0.1</sub>UP (39,40)

H<sub>0.1</sub>[Cr(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sub>0.3</sub>UP (39)

H<sub>0.25</sub>[Cr(ethylenediamine)<sub>3</sub>]<sub>0.25</sub>UP (39)

H(piperidine)<sub>0.62</sub>UP (43)

H(pyrazine)<sub>0.32</sub>UP (43)

H(dimethylaminomethylferrocene)<sub>0.8</sub>UP (43)

<sup>a</sup> Waters of hydration omitted for simplicity. References are given parenthetically.

Spectroscopically, the chromophores associated with intercalated guest cations are generally observable in the electronic spectrum of the intercalated solids (refs. 29,33,36-40,44). Whether PL characteristic of the guest is seen depends on guest excited-state properties and on host-guest interactions. Two extremes in PL properties are indicated in Table 2.

TABLE 2

Compound <sup>a,b</sup>	Interlamellar Spacing, Å	$\phi_r^c$	$\tau(\mu s)^d$
HUP	8.69	0.70	450
NH <sub>4</sub> UP	9.01	0.60	450
<i>n</i> -CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>3</sub> UP	14.39	0.0014	2
<i>n</i> -CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> NH <sub>3</sub> UP	18.76	nonemissive	
Ca <sub>1/2</sub> UP	10.34	0.36	320
AgUP	8.45	nonemissive	
H <sub>0.7</sub> [Cr(NH <sub>3</sub> ) <sub>6</sub> ]0.1UP	9.10	0.007 (UO <sub>2</sub> <sup>2+</sup> ) 0.002 (Cr(III))	
[Cr(urea) <sub>6</sub> ]1/3UP	13.0	nonemissive	
Nd <sub>1/3</sub> UP	11.04	nonemissive	

<sup>a</sup> Data are taken from refs. 7,32,39, and 40.

<sup>b</sup> Waters of hydration are omitted for simplicity.

<sup>c</sup> Radiative quantum yield

<sup>d</sup> Lifetime

For several HUP derivatives, specifically those possessing closed-shell cations (e.g., Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>), efficient, long-lived PL characteristic of the UO<sub>2</sub><sup>2+</sup> moiety is seen at 295 K: like HUP,  $\phi_r$  values for these solids approach unity and  $\tau$  values approach 0.5 ms. At the other extreme, solids prepared from ions like Nd<sup>3+</sup> and Ag<sup>+</sup>, which have low-lying excited states or are oxidizable, render the solids nonemissive through energy- and electron-transfer processes. Other solids derived from HUP exhibit host and/or guest PL, as will be described below.

The unique structural and spectroscopic properties of HUP and its derivatives have led us to investigate the ground- and excited-state reaction chemistry of many of these solids. Among the reaction paths identified have been excited-state, host-to-guest energy transfer, interlamellar acid-base/precipitation chemistry, interlamellar redox chemistry, and host lattice substitution chemistry. The results of these studies, summarized below, reveal natural links between metal coordination chemistry and solid-state reactivity.

#### HOST-TO-GUEST ENERGY TRANSFER

Intercalative ion-exchange reactions of HUP with Eu<sup>3+</sup> (refs. 32,34) and Cr(III) Werner complexes (refs. 39,40) have led to solids that undergo

efficient host-to-guest, energy-transfer processes. These solids were chosen because the guest ions are selectively excitable and exhibit PL distinguishable from that of the host  $\text{UO}_2^{2+}$  species, greatly facilitating energy transfer studies.

Complete exchange of aquated  $\text{Eu}^{3+}$  ions occurs with protons from HUP to yield  $\text{Eu}_{1/3}\text{UO}_2\text{PO}_4 \cdot 4.6\text{H}_2\text{O}$  (EuUP). This is a general reaction that has been observed with lanthanide ions, leading to the compounds,  $\text{Ln}_{1/3}\text{UO}_2\text{PO}_4 \cdot x\text{H}_2\text{O}$  (LnUP; Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Yb;  $x = 3.7\text{--}4.6$ ) (refs. 32-34). The structural and optical properties of these solids are sensitive to the degree of hydration. For fully-hydrated samples, the interlamellar spacing decreased smoothly with the size of the intercalant (ref. 32). With the exception of the Ce, Pr, and Nd derivatives, which emit weakly, all others emit brightly at 295 K.

The electronic spectrum of EuUP is similar to that of HUP, owing to the extremely weak nature of the  $\text{Eu}^{3+}$   $f\text{--}f$  absorption bands (ref. 34). Exclusive excitation of the  $\text{UO}_2^{2+}$  chromophore gives a PL spectrum that is a combination of  $\text{UO}_2^{2+}$  ( $\sim 500\text{--}550$  nm) and  $\text{Eu}^{3+}$  ( $\sim 580\text{--}710$  nm) emission, Fig. 3. Additional evidence for host-to-guest energy transfer comes from the excitation spectrum and lifetime data. The excitation spectrum of  $\text{Eu}^{3+}$ , monitored at 690 nm, exhibits the vibronic structure of  $\text{UO}_2^{2+}$ , paralleling the structure found in the absorption spectrum of EuUP. Pulsed excitation into the uranyl absorption band causes a rise and fall in  $\text{Eu}^{3+}$  PL intensity. The rise time of  $\sim 6$   $\mu\text{s}$  matches the lifetime of  $\text{UO}_2^{2+}$  PL, consistent with excitation of the lanthanide ion by the uranyl ion; the  $\text{Eu}^{3+}$  PL decay time of  $\sim 120$   $\mu\text{s}$  is consistent with coordination of the interlamellar  $\text{Eu}^{3+}$  ions by at least six waters of hydration (ref. 48).

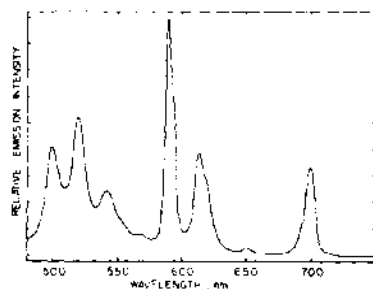


Fig. 3. Uncorrected PL spectrum of EuUP at 295 K. The front-surface PL was obtained for the solid by exciting at 436 nm. Reprinted from ref. 34 with permission.

Energy transfer efficiency is close to unity in EuUP with a rate constant of  $\sim 2 \times 10^5 \text{ s}^{-1}$ . High-resolution PL measurements taken at 12 K indicated that at least two  $\text{Eu}^{3+}$  lattice sites are present at that temperature.

Several Cr(III) Werner complexes have been shown to undergo partial or complete intercalative ion-exchange reactions with HUP, producing the compounds,  $\text{H}_{0.7}[\text{Cr}(\text{NH}_3)_6]_{0.1}\text{UO}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (HCrUP),  $\text{H}_{0.1}[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})]_{0.3}\text{UO}_2\text{PO}_4 \cdot 4\text{H}_2\text{O}$ , and  $[\text{Cr}(\text{urea})_6]_{1/3}\text{UO}_2\text{PO}_4$ . No emission is observed at 295 K for the last two solids, although both show PL characteristic of the Cr(III) species at 77 K (ref. 39). The  $\text{Cr}(\text{NH}_3)_6^{3+}$  derivative (HCrUP), on the other hand, displays weak PL at 295 K. Furthermore, like EuUP, HCrUP exhibits efficient host-to-guest energy transfer (ref. 40).

The absorption spectrum of HCrUP, Fig. 4, arises from the unperturbed superpositioning of  $\text{Cr}(\text{NH}_3)_6^{3+}$  and  $\text{UO}_2^{2+}$  absorption bands and matches the spectrum obtained for a physical mixture of appropriate salts. The emission spectrum displays both  $\text{UO}_2^{2+}$  ( $\sim 500$ -620 nm) and  $\text{Cr}(\text{NH}_3)_6^{3+}$  ( $\sim 640$ -700nm) PL, Fig. 4. Evidence for energy transfer comes from excitation spectra: spectral features characteristic of the uranyl ion are found while monitoring Cr(III) emission. Energy transfer occurs at nearly unit efficiency with  $\phi_T$  values for  $\text{UO}_2^{2+}$  and Cr(III) PL of  $\sim 7 \times 10^{-3}$  and  $2 \times 10^{-3}$ , respectively. It is interesting to note that  $\phi_T$  for  $\text{Cr}(\text{NH}_3)_6^{3+}$  in

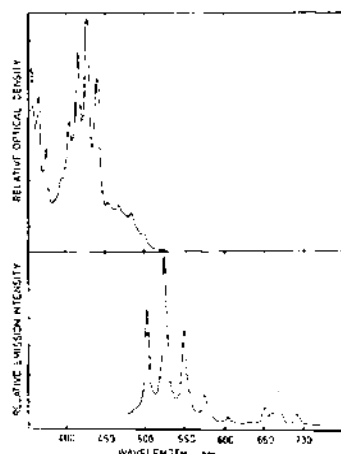


Fig. 4. Absorption (top panel) and uncorrected PL (bottom panel) spectra of HCrUP at 295 K. The front-surface PL spectrum was obtained for the pure solid by exciting at 435 nm. Adapted from ref. 40.

aerated aqueous solution at 295 K is considerably smaller,  $5.5 \times 10^{-6}$  (ref. 49).

Photolysis of HCrUP leads to aquation of the metal complex, providing additional evidence for energy transfer. Upon prolonged photolysis of the yellow HCrUP, the solid turns successively orange, red, and green, corresponding to a gradual redshift in the lowest energy Cr(III) absorption bands; simultaneously, bands attributable to  $\text{NH}_4^+$  and  $\text{NH}_3$  appear in the solid's IR spectrum. These spectral changes are consistent with the replacement of  $\text{NH}_3$  by  $\text{H}_2\text{O}$  in the Cr(III) coordination sphere. Ion-exchange chromatography shows the principal product to be  $\text{Cr}(\text{NH}_3)(\text{H}_2\text{O})_5^{3+}$  with a smaller quantity of  $\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{3+}$  present; the same products were obtained from photolysis of the  $\text{Cr}(\text{NH}_3)_6^{3+}$  perchlorate salt in aqueous solution (refs 50,51). A lower-limit quantum yield for the appearance of  $\text{NH}_4^+$  and  $\text{NH}_3$  ( $\phi_a$ ) in HCrUP at 405 nm, where light is absorbed almost exclusively by the uranyl ion, is  $\sim 0.1$  at 295 K. Host-to-guest energy transfer is thus shown to provide an efficient route to interlamellar reactivity.

#### INTERLAMELLAR ACID-BASE/PRECIIPITATION CHEMISTRY

An important structural aspect of HUP is that the sheets of protonated  $\text{H}_2\text{O}$  molecules can be regarded as two-dimensional aqueous acidic solutions. This observation prompted us to examine whether standard aqueous acid-base/precipitation chemistry could occur in the layered matrix.

We have found that hydrated  $\text{AgUO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}$  (AgUP) reacts with wet, gaseous HCN to yield HUP and AgCN (ref. 52), representing an interlamellar analog of the Liebig titration (ref. 53). Hydrolysis of AgCN in the reaction medium establishes a chemical equilibrium:



This equation is idealized in that the lamellar compounds are really  $\text{H}_{1-x}\text{Ag}_x\text{UO}_2\text{PO}_4$  solid solutions. The reaction products were identified by X-ray powder diffraction, from which it was inferred that  $\text{Ag}^+$  ions have been coaxed out of the interlamellar region, leading to a AgCN precipitate on the surface of the HUP crystallites. Because HUP emits and AgUP does not, the PL intensity varies with HCN partial pressure, serving as the basis for a titration, Fig. 5.

By using Ag-doped HUP samples as standards, the equilibrium constant



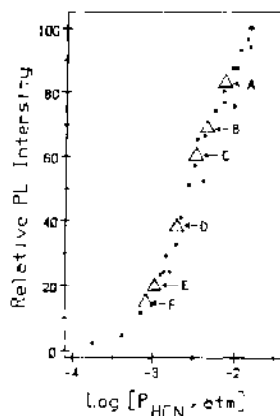
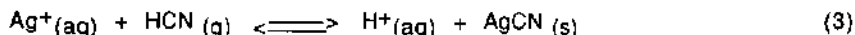


Fig. 5. PL intensity at 525 nm of a sample of silica-dispersed AgUP as a function of the partial pressure of HCN gas. Data, represented by the squares, were obtained in random order and are plotted relative to the maximum PL value observed at high  $P_{\text{HCN}}$ . Points labeled A-F are "doped" samples of  $\text{H}_{1-x}\text{Ag}_x\text{UO}_2\text{PO}_4$  used for calibration. Reprinted from ref. 52 with permission.

for eq. 2 was found to be  $\sim 1.5 \times 10^6 \text{ atm}^{-1}$ . This value is in good agreement with the product of solution and ion-exchange equilibrium constants: eq. 2 can be written as the sums of eqs. 3 and 4, which have equilibrium constants of  $\sim 10^6$  to  $10^8 \text{ atm}^{-1}$  and 0.3, respectively (refs. 53,54).



It is also noteworthy that AgUP is acting as a chemical sensor for HCN, albeit a relatively insensitive one.

#### INTERLAMELLAR REDOX CHEMISTRY

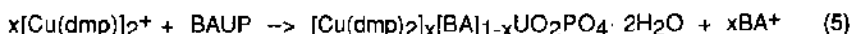
As was shown in the AgUP/HCN system, gases can react with interlamellar hydrated metal guest ions, mimicking chemistry found in aqueous solution. Redox chemistry of metal complexes represents another major reaction class that can in principle be studied in the interlamellar milieu. We have employed both the Creutz-Taube complex (C-T),

$\{[\text{Ru}(\text{NH}_3)_5]_2(\mu\text{-pyrazine})\}^{5+}$ , and  $[\text{Cu}(\text{dmp})_2]^+$  ( $\text{dmp}$  = 2,9-dimethyl-1,10-phenanthroline) to explore interlamellar redox processes.

The C-T complex undergoes a partial (~ 5%) intercalative ion-exchange reaction with HUP to form the purple compound  $\text{H}_{0.95}(\text{C-T})_{0.01}\text{UO}_2\text{PO}_4$ ,  $\text{H}(\text{C-T})\text{UP}$  (ref. 37). The electronic spectrum is obtained by superimposing bands of the uranyl ion and the C-T complex; band maxima for the C-T complex occur at 565 and 1620 nm, the latter being the celebrated intervalence transition (ref. 56). Intercalation greatly reduces the  $\text{UO}_2^{2+}$  PL efficiency to  $\phi_f \sim 0.004$ . Decay curves were found to be nonexponential, with 1/e decay times on the order of 25-100  $\mu\text{s}$ . A multiplicity of lattice sites with different quenching efficiencies could cause the nonexponential behavior. The C-T complex could be quenching uranyl PL by energy or electron transfer.

Passing bromine gas over the  $\text{H}(\text{C-T})\text{UP}$  solid causes the C-T absorption bands to disappear. The compound changes color from purple to yellow, consistent with oxidation of the C-T complex to form trivalent Ru centers. It is noteworthy that partial regeneration of the purple color occurs over several days, presumably indicating formation of a divalent Ru species in the lattice.

Another complex that undergoes interlamellar redox chemistry is  $\text{Cu}(\text{dmp})_2^+$ . Partial ion exchange occurs between  $\text{Cu}(\text{dmp})_2^+$  and the *n*-butylammonium ( $\text{BA}^+$ ) derivative of HUP (this solid is often used as an intercalative ion-exchange precursor, since its large interlamellar spacing of ~14 Å facilitates exchange with bulky cations (ref. 38)), giving a solid,  $[\text{Cu}(\text{dmp})_2]_x[\text{BA}]_{1-x}\text{UO}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{Cu}(\text{dmp})\text{UP}$ ) with  $x \sim 0.2$  (ref. 36).



Samples of  $\text{Cu}(\text{dmp})\text{UP}$  are orange-red, characteristic of  $\text{Cu}(\text{dmp})_2^+$ . The color arises from a broad, intense absorption band at ~460 nm, which has been assigned to a metal-to-ligand charge transfer (MLCT) transition of the  $\text{Cu}(\text{I})$  complex, Fig. 6 (ref. 57).

The emission spectrum of  $\text{Cu}(\text{dmp})\text{UP}$  is dominated by bands at 690 and 730 nm that are characteristic of the  $\text{Cu}(\text{dmp})_2^+$  complex and unchanged by intercalation; PL from the solid is inefficient and short-lived, with  $\phi_f \sim 6 \times 10^{-4}$  and  $\tau \sim 140$  ns. Most noteworthy regarding the  $\text{Cu}(\text{dmp})\text{UP}$  emission spectrum is that the uranyl PL is completely quenched. Since  $\text{Cu}(\text{dmp})_2^+$  possesses both a low-lying excited state and the ability to be oxidized by excited  $\text{UO}_2^{2+}$ , quenching could conceivably occur by excited-state energy- and/or electron-transfer processes.

Using bromine vapor as an oxidant, it is possible to convert the Cu(I) complex in CudmpUP to its Cu(II)-intercalated counterpart. Loss of the MLCT band of Cu(I) and the introduction of new absorption bands attributable to  $d-d$  transitions of  $\text{Cu}(\text{dmp})_2^{2+}$  species are evident in Fig. 6; EPR data also support the formation of the Cu(II) species. The oxidized CudmpUP displays no PL in the visible region. Since the Cu(II) complex possesses low-lying excited states, quenching is believed to occur by an energy-transfer process. 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  $\text{Br}_2$  reduction remain in the lattice to maintain charge neutrality.

Subsequent exposure of the bromine-treated CudmpUP solid to  $\text{N}_2\text{H}_4$  vapor reduces the Cu(II) back to Cu(I), as evidenced by the return of the characteristic  $\text{Cu}(\text{dmp})_2^+$  MLCT absorption and PL bands. Alternatively, partial reduction could be achieved by photolysis of the bromine-treated CudmpUP solid with 468-nm light. This partial reduction also occurs in solution and a mechanism for it has been proposed (ref. 58).

Another, bulkier Cu(I) complex containing bidentate N-donor ligands,  $[\text{Cu}(\text{bcp})_2]^+$  ( $\text{bcp}$  = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), partially intercalates into BAUP to form  $[\text{Cu}(\text{bcp})_2]_{0.2}[\text{BA}]_{0.8}\text{UO}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  and displays structural and optical properties that are similar to those of CudmpUP (ref. 36).

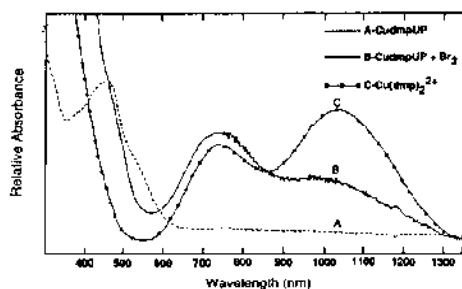
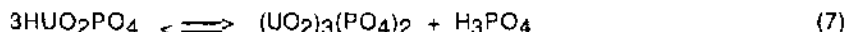
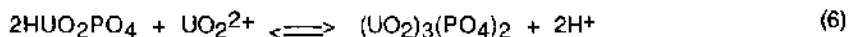


Fig. 6. Visible absorption spectra of CudmpUP before oxidation (A) and after oxidation by  $\text{Br}_2$  (B). Spectrum C is that of  $\text{Cu}(\text{dmp})_2^{2+}$ , obtained in water after dissolution of the nitrate salt. Reprinted from ref. 36 with permission.

### HOST LATTICE SUBSTITUTION CHEMISTRY

Besides using transition metal complexes as intercalants, we were intrigued by the notion that the actinyl ion of the host lattice might be intercalated. These studies, along with the preparation of solid solutions of HUP and its isostructural analog  $\text{H}\text{UO}_2\text{AsO}_4 \cdot 4\text{H}_2\text{O}$  (HUAs), identified a means for chemically modifying the host lattice, in effect tuning the coordination chemistry of the actinyl ions present therein.

We have found that HUP can be converted to a lamellar octahydrate of uranyl phosphate, UP, by two independent routes: intercalation with  $\text{UO}_2^{2+}$  ions, eq. 6, or by thermal decomposition, a "self-intercalation" reaction, eq. 7, wherein the intercalating  $\text{UO}_2^{2+}$  ions originate from the host lattice (ref. 59).



These reactions are reversible, the UP formed by either route slowly reverting to HUP at room temperature over several days. Since HUP is highly emissive and UP only weakly so ( $\tau \sim 5\text{-}10 \mu\text{s}$ ), the rate for eq. 7 can be determined; the rate of intercalation, eq. 6, can be determined from changes in X-ray powder diffraction data. Arrhenius plots have been obtained for the two reactions (ref. 59).

Similar chemistry obtains for the hydrated, isostructural neptunyl analog of HUP,  $\text{HNpO}_2\text{PO}_4$  (HNpP) (ref. 44): HNpP can be converted to  $(\text{NpO}_2)_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$  (NpP) by the same two reaction routes described above for the conversion of HUP to UP. Furthermore, "cross-intercalation" reactions ( $\text{UO}_2^{2+}$  into HNpP;  $\text{NpO}_2^{2+}$  into HUP) proceed under stoichiometric conditions to yield hydrated lamellar solids. The absorption spectra of these nonemissive solids is a composite of  $\text{NpO}_2^{2+}$  and  $\text{UO}_2^{2+}$  electronic transitions. Conducting the "cross-intercalation" reactions with high concentrations of intercalating ion leads to substantial substitution of actinyl ions in the host lattice sheets. This lability of host lattice uranyl and neptunyl ions may result from solution acidity, since HUP and HNpP are acid soluble and solutions of  $\text{UO}_2^{2+}$  and  $\text{NpO}_2^{2+}$  hydrolyze extensively to yield strongly acidic solutions.

A fascinating reactivity comparison was provided by repeated unsuccessful attempts to intercalate  $\text{NpO}_2^{2+}$  into HUP and HNpP, a sharp contrast with the ease in which  $\text{NpO}_2^{2+}$  intercalated into these hosts. This remarkable selectivity is consistent with the fact that binding constants

for the dication are invariably much higher than for the monocation (ref. 60). This effect, in turn, likely reflects the difference in charge-to-size ratios of the ions (Np-O bond length of 1.85 Å in  $\text{NpO}_2^+$  vs. 1.71 Å in  $\text{NpO}_2^{2+}$  (ref. 61)).

Substituting the phosphate ion in HUP with its isostructural arsenate analog provides another technique for tuning the optical and structural properties of the host lattice. Like HUP, HUAs at 295 K adopts a tetragonal structure with cell parameters of  $a = 7.16$  Å and  $c = 17.61$  Å (ref. 46). The structural similarities between HUAs and HUP suggested that the two solids might form solid solutions of composition  $\text{HUO}_2(\text{PO}_4)_{1-x}(\text{AsO}_4)_x$  (HUPAs) (ref. 46). These expectations have been realized by using mixtures of  $\text{H}_3\text{AsO}_4$  and  $\text{H}_3\text{PO}_4$  in the synthesis of the solids: the stoichiometries used in solution are preserved in the isolated solids.

Structural and spectroscopic evidence support the synthesis of solid solutions. X-ray powder diffraction data reveal that the  $a$  and  $c$  lattice parameters vary linearly with composition, in accord with Vegard's Law. Infrared spectra of HUPAs samples exhibit a band arising from the uranyl asymmetric stretching mode that gradually red-shifts as the phosphate-

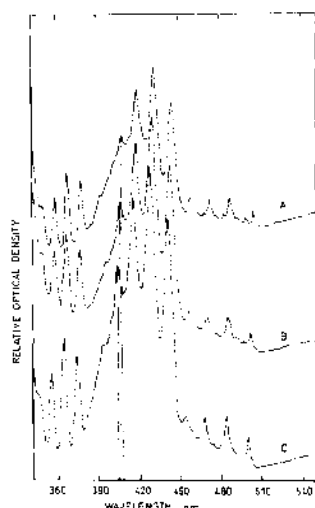


Fig. 7. Visible absorption spectra (295 K) of  $\text{HUO}_2(\text{PO}_4)_{1-x}(\text{AsO}_4)_x$  samples:  $x=1.00$  (HUAs), 0.48, and 0.00 (HUP), curves A, B, and C, respectively. Vertical lines are included to highlight spectral shifts. Reprinted from ref. 46 with permission.

to-arsenate ratio increases. Electronic spectra of these samples display a gradual red shift of  $\sim 100 \text{ cm}^{-1}$  in uranyl absorption bands in passing from HUP through HUPAs solid solutions to HUAs, Fig. 7. This same trend is observed in the HUPAs PL spectra. Quantum yields and lifetimes of HUPAs solids also show slight variations with composition, with the largest values obtained for the end-member solids, HUP and HUAs.

Like HUP and HUAs, the HUPAs solid solutions are readily converted to lamellar  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 2x(\text{AsO}_4)_2$  solids ( $0 \leq x \leq 1$ ) through intercalative ion-exchange reactions with  $\text{UO}_2^{2+}$  or by the self-intercalation reactions described above for HUP and HNpP (ref. 62).

## CONCLUSION

The studies summarized herein demonstrate the versatility of HUP as a lamellar host lattice. Intercalative ion-exchange reactions using HUP lead to derivatives that can be used to explore reaction chemistry of considerable breadth: host-to-guest energy transfer, interlamellar acid-base/precipitation chemistry, interlamellar redox chemistry, and host lattice substitution chemistry are some of the reactions paths that have been characterized through structural and optical probes afforded by HUP.

## REFERENCES

- 1 M.S. Whittingham and A.J. Jacobson, "Intercalation Chemistry"; Academic Press: New York (1982).
- 2 A. Clearfield, Chem. Rev., 88 (1988) 125.
- 3 J.M. Troup and A. Clearfield, Inorg. Chem., 16 (1977) 3311.
- 4 E.R. Mognaschi, A. Chierico and G. Parravicini, J. Chem. Soc. Faraday I, 74 (1978) 2333.
- 5 T. Matsuo, Y. Kume, H. Suga and S. Seki, J. Phys. Chem. Solids, 37 (1976) 499.
- 6 F. Weigel and G. Hoffmann, J. Less-Common Met., 44 (1976) 99.
- 7 M.M. Olken, R.N. Biagioni and A.B. Ellis, Inorg. Chem., 22 (1983) 4128.
- 8 M.G. Shilton and A.T. Howe, Mat. Res. Bull., 12 (1977) 701.
- 9 B. Morosin, Acta Cryst., B34 (1978) 3732.
- 10 P.E. Childs, A.T. Howe and M.G. Shilton, J. Power Sources, 3 (1978) 105.
- 11 A.T. Howe and M.G. Shilton, J. Solid State Chem., 28 (1979) 345.
- 12 M.G. Shilton and A.T. Howe, J.C.S. Chem. Comm., (1979) 194.
- 13 P.E. Childs, T.K. Halstead, A.T. Howe and M.G. Shilton, Mat. Res. Bull., 13 (1978) 609.
- 14 A.T. Howe and M.G. Shilton, J. Solid State Chem., 34 (1980) 149.

- 15 C. Poinsignon, A. Fitch and B.E.F. Fender, *Solid State Ionics*, 9&10 (1983) 1049.
- 16 Y.T. Tsai, W.P. Halperin and D.H. Whitmore, *J. Solid State Chem.*, 50 (1983) 263.
- 17 E. Skou, I.G. Krogh Anderson, K.E. Simonsen and E. Krogh Anderson, *Solid State Ionics*, 9&10 (1983) 1041.
- 18 M. Pham-Thi and Ph. Colomban, *Solid State Ionics*, 17 (1985) 295.
- 19 M. Pham-Thi, Ph. Colomban and A. Novak, *J. Phys. Chem. Solids*, 46 (1985) 493.
- 20 *Ibid.*, 565.
- 21 S.B. Lyon and D.J. Fray, *Solid State Ionics*, 15 (1985) 21.
- 22 B.K. Sen and S. Sen, *Solid State Ionics*, 18&19 (1986) 1025.
- 23 P. Barboux, R. Morineau and J. Livage, *Solid State Ionics*, 27 (1988) 221.
- 24 J.C. Badot, N. Baffier, A. Fourier-Lamer and Ph. Colomban, *Solid State Ionics*, 28-30 (1988) 1617.
- 25 K. Metcalfe and T.K. Halstead, *Solid State Ionics*, 26 (1988) 209.
- 26 A.T. Howe, S.H. Sheffield, P.E. Childs and M.G. Shilton, *Thin Solid Films*, 67 (1980) 365.
- 27 N. Pavković, M. Marković and B. Kojić-Prodić, *Croatica Chemica Acta*, 55 (1982) 405.
- 28 C.M. Johnson, M.G. Shilton and A.T. Howe, *J. Solid State Chem.*, 37 (1981) 37.
- 29 R. Pozas-Tormo, S. Bruque Gamez, M. Martinez-Lara and L. Moreno-Real, *Can. J. Chem.*, 66 (1988) 2849.
- 30 R. Pozas-Tormo, L. Moreno-Real, M. Martínez-Lara and S. Bruque-Gamez, *Can. J. Chem.*, 64 (1986) 30.
- 31 E. De Grave and R. Vochten, *Solid State Comm.*, 65 (1988) 315.
- 32 G.L. Rosenthal and A.B. Ellis, *J. Less-Common Met.*, 139 (1988) 299.
- 33 R. Pozas-Tormo, L. Moreno-Real, M. Martinez-Lara and S. Bruque-Gamez, *Inorg. Chem.*, 26 (1987) 1442.
- 34 M.M. Olken, C.M. Verschoor and A.B. Ellis, *Inorg. Chem.*, 25 (1986) 80.
- 35 Ph. Colomban and M. Pham Thi, *Rev. Chim. Mineral.*, 22 (1985) 143.
- 36 A.T. Jacob and A.B. Ellis, *Inorg. Chem.*, in press.
- 37 C.M. Verschoor and A.B. Ellis, *Solid State Ionics*, 22 (1986) 65.
- 38 R. Pozas-Tormo, L. Moreno-Real, M. Martínez-Lara and E. Rodríguez-Castellón, *Can. J. Chem.*, 64 (1986) 35.
- 39 M.M. Olken, C.M. Verschoor and A.B. Ellis, *J. Lumin.*, 31&32 (1984) 552.
- 40 M.M. Olken and A.B. Ellis, *J. Am. Chem. Soc.*, 106 (1984) 7468.
- 41 G.J. Kearly, A.N. Fitch and B.E.F. Fender, *J. Mol. Struct.*, 160 (1987) 91.
- 42 M. Marković, N. Pavković and N.D. Pavković, *J. Res. Natl. Bur. Stand.*, 93 (1988) 557.
- 43 L. Moreno Real, R. Pozas Tormo, M. Martinez Lara and S. Bruque, *Mat. Res. Bull.*, 22 (1987) 19.

- 44 P.K. Dorhout, R.J. Kissane, L.R. Avens, K.D. Abney, P.G. Eller and A.B. Ellis, *Inorg. Chem.*, in press.
- 45 M.G. Shilton and A.T. Howe, *J. Solid State Chem.*, 34 (1980) 137.
- 46 P.K. Dorhout, G.L. Rosenthal and A.B. Ellis, *Inorg. Chem.*, 27 (1988) 1159.
- 47 V. Pekarek and V. Vesely, *J. Inorg. Nucl. Chem.*, 27 (1965) 1151.
- 48 W.DeW. Horrocks, Jr. and D.R. Sudnick, *J. Am. Chem. Soc.*, 101 (1979) 334.
- 49 A.D. Kirk and G.B. Porter, *J. Phys. Chem.*, 84 (1980) 887.
- 50 M.R. Edelson and R.A. Plane, *Inorg. Chem.*, 3 (1964) 231.
- 51 A.D. Kirk, L.A. Frederick and C.F.C. Wong, *ibid.*, 18 (1979) 448.
- 52 G.H. Dieckmann and A.B. Ellis, *Inorg. Chem.*, 26 (1987) 4147.
- 53 See, for example: J.N. Butler, *Ionic Equilibrium, A Mathematical Approach*; Addison-Wesley: Reading, MA (1964) 280.
- 54 F.D. Rossini, "Selected Values of Chemical Thermodynamic Properties"; Circular 500; U.S. Government Printing Office: Washington, DC (1952) 222,229,594.
- 55 *CRC Handbook of Chemistry and Physics*, 65th ed.; R.C. Weast, ed.; CRC Press: Boca Raton, FL (1984) D-51.
- 56 C. Creutz and H. Taube, *J. Am. Chem. Soc.*, 95 (1973) 1086.
- 57 C.C. Phifer and D.R. McMillin, *Inorg. Chem.*, 25 (1986) 1329.
- 58 S. Sundararajan and E.L. Wehry, *J. Phys Chem.*, 76 (1972) 1528.
- 59 G.L. Rosenthal and A.B. Ellis, *J. Am. Chem. Soc.*, 109 (1987) 3157.
- 60 J.J. Katz, G.T. Seaborg and L.R. Morss, "The Chemistry of the Actinide Elements", 2nd ed., Vol. 1, Chapman and Hall, NY, 1986, p.483.
- 61 J.H. Burns and C. Musikas, *Inorg. Chem.*, 16 (1977) 1619.
- 62 P.K. Dorhout, G.L. Rosenthal and A.B. Ellis, *Solid State Ionics*, 32&33 (1989) 50.