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

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SUMMARY

Hydrogen uranyl phosphate (HUP), $HUO_2PO_4{\cdot}4H_2O$, 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 (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), α-$Zr(HPO_4)_2{\cdot}H_2O$ (refs. 2,3), $SnCl_2{\cdot}2H_2O$ (ref. 4), and $K_4Fe(CN)_6{\cdot}3H_2O$ (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, $HUO_2PO_4{\cdot}4H_2O$ (HUP). Readily prepared from $UO_2(NO_3)_2{\cdot}6H_2O$ and H_3PO_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).

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Structurally, HUP is a lamellar solid, consisting of alternating $(UO_2PO_4)_n^{n-}$ and protonated hydration sheets, Fig. 1. The former are waffle-like, with each U atom coordinated to four equatorial O atoms from four different PO_4^{3-} groups and to two axial O atoms that form the 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.

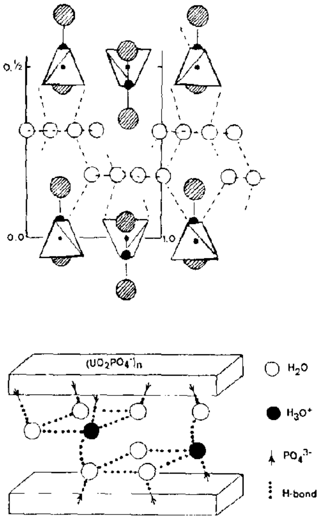

Fig. 1. Projection of the HUP structure along [100] (top). The water molecules of the network about z = 3/4 have been omitted for clarity. The large shaded circles designate the uranyl oxygen atoms, medium open circles the water molecules, medium solid circles uranium, and small solid circles phosphorus. Oxygen atoms of 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 = 6.995Å and c = 17.491 Å (ref. 9).

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

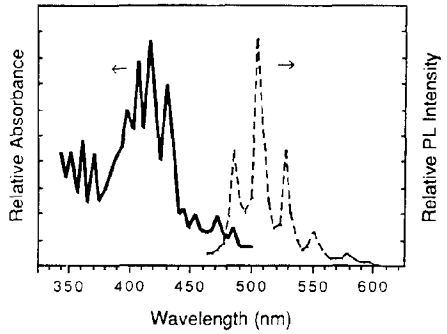

Fig. 2. Relative absorbance and photoluminescence of HUP.

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 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 $\emptyset_r$ of nearly unity) and long lifetime (lifetime τ, 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.

$$HUO_2PO_4 + 1/n\,M^{n+} \longrightarrow M_{1/n}UO_2PO_4 + H^+ \qquad (1)$$

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* ~6.9 Å, indicating unaltered $(UO_2PO_4)_n^{n-}$ 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 ~1000 cm^{-1}, arising from phosphate stretching modes (ref. 47).

TABLE 1

FULLY-SUBSTITUTED URANYL PHOSPHATE DERIVATIVES[a]

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); $[Co(NH_3)_4CO_3]$(38); NH_4(6,7,18,19,28,41,42); n-$CH_3(CH_2)_3NH_3$(7,38); n-$CH_3(CH_2)_7NH_3$(7,35); C_5H_5NH(7,43); N_2H_5(43)

Divalent, $M_{1/2}UP$

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_2(44,59,62); NpO_2(44)

Trivalent, $M_{1/3}UP$

M = La(32,33); Ce(32); Pr(32); Nd(32); Eu(32,34); Gd(32); Tb(32); Dy(32); Yb(32); $[Co(NH_3)_6]$(38); $[Cr(urea)_6]$(39)

PARTIALLY-SUBSTITUTED URANYL PHOSPHATE DERIVATIVES[a]

$[Cu(2,9\text{-dimethyl-}4,7\text{-diphenyl-}1,10\text{-phenanthroline})_2]_{0.2}[n\text{-}C_4H_9NH_3]_{0.8}UP$ (36)
$[Cu(2,9\text{-dimethyl-}1,10\text{-phenanthroline})_2]_{0.2}[n\text{-}C_4H_9NH_3]_{0.8}UP$ (36)
$H_{0.95}\{[Ru(NH_3)_5]_2(\mu\text{-pyrazine})\}_{0.01}UP$ (37)
$H_{0.7}[Cr(NH_3)_6]_{0.1}UP$ (39,40)
$H_{0.1}[Cr(NH_3)_5(H_2O)]_{0.3}UP$ (39)
$H_{0.25}[Cr(ethylenediamine)_3]_{0.25}UP$ (39)
$H(piperidine)_{0.62}UP$ (43)
$H(pyrazine)_{0.32}UP$ (43)
$H(dimethylaminomethylferrocene)_{0.8}UP$ (43)

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[a] 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[a,b]	Interlamellar Spacing, Å	$Ø_r$[c]	$\tau(\mu s)$[d]
HUP	8.69	0.70	450
NH_4UP	9.01	0.60	450
$n\text{-}CH_3(CH_2)_3NH_3UP$	14.39	0.0014	2
$n\text{-}CH_3(CH_2)_7NH_3UP$	18.76	nonemissive	
$Ca_{1/2}UP$	10.34	0.36	320
AgUP	8.45	nonemissive	
$H_{0.7}[Cr(NH_3)_6]_{0.1}UP$	9.10	0.007 (UO_2^{2+}) 0.002 (Cr(III))	
$[Cr(urea)_6]_{1/3}UP$	13.0	nonemissive	
$Nd_{1/3}UP$	11.04	nonemissive	

[a] Data are taken from refs. 7,32,39, and 40.

[b] Waters of hydration are omitted for simplicity.

[c] Radiative quantum yield

[d] Lifetime

For several HUP derivatives, specifically those possessing closed-shell cations (e.g., Ca^{2+} and NH_4^+), efficient, long-lived PL characteristic of the UO_2^{2+} moiety is seen at 295 K: like HUP, $Ø_r$ values for these solids approach unity and τ values approach 0.5 ms. At the other extreme, solids prepared from ions like Nd^{3+} and Ag^+, 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^{3+} (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 UO_2^{2+} species, greatly facilitating energy transfer studies.

Complete exchange of aquated Eu^{3+} ions occurs with protons from HUP to yield $Eu_{1/3}UO_2PO_4{\cdot}4.6H_2O$ (EuUP). This is a general reaction that has been observed with lanthanide ions, leading to the compounds, $Ln_{1/3}UO_2PO_4{\cdot}xH_2O$ (LnUP; Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Yb; x = 3.7-4.6) (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 Eu^{3+} *f-f* absorption bands (ref. 34). Exclusive excitation of the UO_2^{2+} chromophore gives a PL spectrum that is a combination of UO_2^{2+} (~500-550 nm) and Eu^{3+} (~580-710 nm) emission, Fig. 3. Additional evidence for host-to-guest energy transfer comes from the excitation spectrum and lifetime data. The excitation spectrum of Eu^{3+}, monitored at 690 nm, exhibits the vibronic structure of 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 Eu^{3+} PL intensity. The rise time of ~6 μs matches the lifetime of UO_2^{2+} PL, consistent with excitation of the lanthanide ion by the uranyl ion; the Eu^{3+} PL decay time of ~120 μs is consistent with coordination of the interlamellar Eu^{3+} ions by at least six waters of hydration (ref. 48).

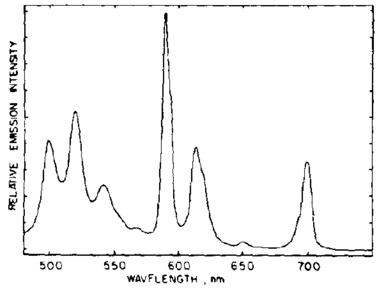

Fig. 3. Uncorrected PL spectrum of EuUP at 295 K. The front-surface PL was obtained for the solid by exciting at 436 nm. Reprinted from ref. 34 with permission.

Energy transfer efficiency is close to unity in EuUP with a rate constant of ~2×10^5 s^{-1}. High-resolution PL measurements taken at 12 K indicated that at least two 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, $H_{0.7}[Cr(NH_3)_6]_{0.1}UO_2PO_4 \cdot 6H_2O$ (HCrUP), $H_{0.1}[Cr(NH_3)_5(H_2O)]_{0.3}UO_2PO_4 \cdot 4H_2O$, and $[Cr(urea)_6]_{1/3}UO_2PO_4$. 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 $Cr(NH_3)_6{}^{3+}$ 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 $Cr(NH_3)_6{}^{3+}$ and $UO_2{}^{2+}$ absorption bands and matches the spectrum obtained for a physical mixture of appropriate salts. The emission spectrum displays both $UO_2{}^{2+}$ (~500-620 nm) and $Cr(NH_3)_6{}^{3+}$ (~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 $\emptyset_r$ values for $UO_2{}^{2+}$ and Cr(III) PL of ~ 7×10^{-3} and 2×10^{-3}, respectively. It is interesting to note that $\emptyset_r$ for $Cr(NH_3)_6{}^{3+}$ in

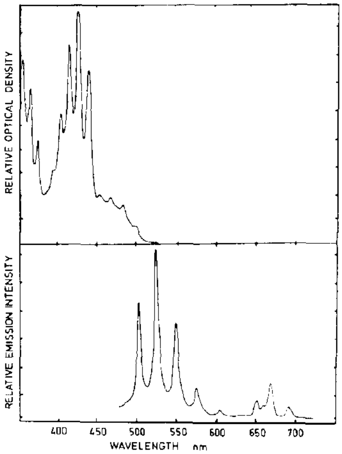

Fig. 4. Absorption (top panel) and uncorrected PL (bottom panel) spectra of HCrUP at 295 K. The front-surface PL spectrum was obtained for the pure solid by exciting at 435 nm. Adapted from ref. 40.

aerated aqueous solution at 295 K is considerably smaller, 5.5 x 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 NH_4^+ and NH_3 appear in the solid's IR spectrum. These spectral changes are consistent with the replacement of NH_3 by H_2O in the Cr(III) coordination sphere. Ion-exchange chromatography shows the principal product to be $Cr(NH_3)(H_2O)_5^{3+}$ with a smaller quantity of $Cr(NH_3)_2(H_2O)_4^{3+}$ present; the same products were obtained from photolysis of the $Cr(NH_3)_6^{3+}$ perchlorate salt in aqueous solution (refs 50,51). A lower-limit quantum yield for the appearance of NH_4^+ and NH_3 ($\emptyset_a$) in HCrUP at 405 nm, where light is absorbed almost exclusively by the uranyl ion, is ~0.1 at 295 K. Host-to-guest energy transfer is thus shown to provide an efficient route to interlamellar reactivity.

INTERLAMELLAR ACID-BASE/PRECIPITATION CHEMISTRY

An important structural aspect of HUP is that the sheets of protonated H_2O 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 $AgUO_2PO_4{\cdot}3H_2O$ (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:

$$AgUO_2PO_4\,_{(s)} + HCN\,_{(g)} \Longleftrightarrow HUO_2PO_4\,_{(s)} + AgCN\,_{(s)} \qquad (2)$$

This equation is idealized in that the lamellar compounds are really $H_{1-x}Ag_xUO_2PO_4$ solid solutions. The reaction products were identified by X-ray powder diffraction, from which it was inferred that 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

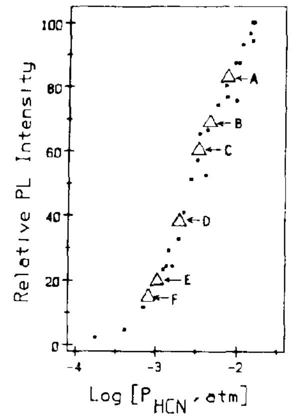

Fig. 5. PL intensity at 525 nm of a sample of silica-dispersed AgUP as a function of the partial pressure of HCN gas. Data, represented by the squares, were obtained in random order and are plotted relative to the maximum PL value observed at high P_{HCN}. Points labeled A-F are "doped" samples of $H_{1-x}Ag_xUO_2PO_4$ used for calibration. Reprinted from ref. 52 with permission.

for eq. 2 was found to be ~1.5 x 10^6 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 ~10^6 to 10^8 atm^{-1} and 0.3, respectively (refs. 53,54).

$$Ag^+(aq) + HCN_{(g)} \rightleftharpoons H^+(aq) + AgCN_{(s)} \qquad (3)$$

$$AgUO_2PO_{4\,(s)} + H^+(aq) \rightleftharpoons HUO_2PO_{4\,(s)} + Ag^+(aq) \qquad (4)$$

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),

$\{[Ru(NH_3)_5]_2(\mu\text{-pyrazine})\}^{5+}$, and $[Cu(dmp)_2]^+$ (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 $H_{0.95}(C\text{-}T)_{0.01}UO_2PO_4$, H(C-T)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 UO_2^{2+} PL efficiency to $\varnothing_r$~0.004. Decay curves were found to be nonexponential, with 1/e decay times on the order of 25-100 µs. 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 H(C-T)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 $Cu(dmp)_2^+$. Partial ion exchange occurs between $Cu(dmp)_2^+$ and the *n*-butylammonium (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, $[Cu(dmp)_2]_x[BA]_{1-x}UO_2PO_4\cdot 2H_2O$ (CudmpUP) with x ~0.2 (ref. 36).

$$x[Cu(dmp)]_2^+ + BAUP \rightarrow [Cu(dmp)_2]_x[BA]_{1-x}UO_2PO_4\cdot 2H_2O + xBA^+ \qquad (5)$$

Samples of CudmpUP are orange-red, characteristic of $Cu(dmp)_2^+$. 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 Cu(I) complex, Fig. 6 (ref. 57).

The emission spectrum of CudmpUP is dominated by bands at 690 and 730 nm that are characteristic of the $Cu(dmp)_2^+$ complex and unchanged by intercalation; PL from the solid is inefficient and short-lived, with $\varnothing_r \sim 6 \times 10^{-4}$ and $\tau \sim 140$ ns. Most noteworthy regarding the CudmpUP emission spectrum is that the uranyl PL is completely quenched. Since $Cu(dmp)_2^+$ possesses both a low-lying excited state and the ability to be oxidized by excited 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 $Cu(dmp)_2^{2+}$ 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 Br_2 reduction remain in the lattice to maintain charge neutrality.

Subsequent exposure of the bromine-treated CudmpUP solid to N_2H_4 vapor reduces the Cu(II) back to Cu(I), as evidenced by the return of the characteristic $Cu(dmp)_2^+$ 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, $[Cu(bcp)_2]^+$ (bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), partially intercalates into BAUP to form $[Cu(bcp)_2]_{0.2}[BA]_{0.8}UO_2PO_4{\cdot}2H_2O$ and displays structural and optical properties that are similar to those of CudmpUP (ref. 36).

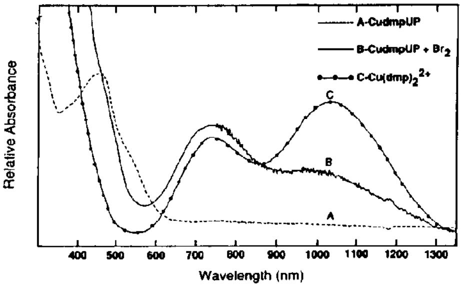

Fig. 6. Visible absorption spectra of CudmpUP before oxidation (A) and after oxidation by Br_2 (B). Spectrum C is that of $Cu(dmp)_2^{2+}$, obtained in water after dissolution of the nitrate salt. Reprinted from ref. 36 with permission.

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 $HUO_2AsO_4{\cdot}4H_2O$ (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 UO_2^{2+} ions, eq. 6, or by thermal decomposition, a "self-intercalation" reaction, eq. 7, wherein the intercalating UO_2^{2+} ions originate from the host lattice (ref. 59).

$$2HUO_2PO_4 + UO_2^{2+} \rightleftharpoons (UO_2)_3(PO_4)_2 + 2H^+ \qquad (6)$$

$$3HUO_2PO_4 \rightleftharpoons (UO_2)_3(PO_4)_2 + H_3PO_4 \qquad (7)$$

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 (τ ~5-10 μs), 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, $HNpO_2PO_4$ (HNpP) (ref. 44): HNpP can be converted to $(NpO_2)_3(PO_4)_2{\cdot}5H_2O$ (NpP) by the same two reaction routes described above for the conversion of HUP to UP. Furthermore, "cross-intercalation" reactions (UO_2^{2+} into HNpP; 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 NpO_2^{2+} and 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 UO_2^{2+} and NpO_2^{2+} hydrolyze extensively to yield strongly acidic solutions.

A fascinating reactivity comparison was provided by repeated unsuccessful attempts to intercalate NpO_2^+ into HUP and HNpP, a sharp contrast with the ease in which 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 NpO_2^+ vs. 1.71 Å in 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 $HUO_2(PO_4)_{1-x}(AsO_4)_x$ (HUPAs) (ref. 46). These expectations have been realized by using mixtures of H_3AsO_4 and H_3PO_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-

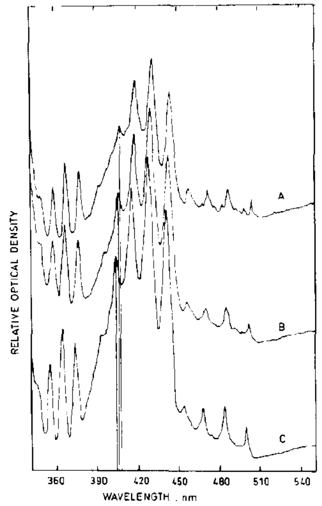

Fig. 7. Visible absorption spectra (295 K) of $HUO_2(PO_4)_{1-x}(AsO_4)_x$ samples: x=1.00 (HUAs), 0.48, and 0.00 (HUP), curves A, B, and C, respectively. Vertical lines are included to highlight spectral shifts. Reprinted from ref. 46 with permission.

to-arsenate ratio increases. Electronic spectra of these samples display a gradual red shift of ~100 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 $(UO_2)_3(PO_4)_{2-2x}(AsO_4)_{2x}$ solids ($0 \leq x \leq 1$) through intercalative ion-exchange reactions with 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.

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