

finement of the structure. The initial assignment of disorder for one Cp ring started at 70%–30% but refined toward 50%–50%, where it was fixed for the remainder of the refinement. Except for the hydrogens on the disordered Cp ring, hydrogens were included in the structure factor calculations as for **1a**.

Inspection of the residuals showed that the data was affected by secondary extinction, and an extinction parameter<sup>21</sup> was refined in subsequent cycles of least squares. Inspection of the penultimate difference Fourier map showed a ring of electron density around the periphery of the disordered Cp ring. Half-occupancy hydrogen atom positions were then calculated and included in the structure factor calculations.

The final residuals for 356 variables refined against the 3537 data for which  $F^2 > 3\sigma(F^2)$  were  $R = 2.23\%$ ,  $wR = 3.11\%$ , and  $GOF = 2.071$  (the corresponding values for the model without the half-occupancy hydrogens were  $R = 2.55\%$ ,  $wR = 4.07\%$ ,  $GOF = 2.704$ ). The  $R$  value for all 4067 data was 2.96%.

The  $p$  factor for the weighting scheme was set to 0.02 during the last cycles of least-squares refinement. The largest peaks in the final difference Fourier map had electron densities of 0.20–0.36 e/Å<sup>3</sup> and were located near the disordered Cp ring. The positional and equivalent thermal parameters of nonhydrogen atoms are given in Table IV; anisotropic thermal parameters, positions of the hydrogen atoms, and the

values of  $F_o$  and  $F_c$  are available as supplementary material.

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**Registry No. 1**, 78305-62-1; **Na<sup>+</sup>1a**, 85454-65-5; **PPN<sup>+</sup>1a-CH<sub>3</sub>CN**, 92284-05-4; **2**, 92269-84-6; **3**, 92269-85-7; **4**, 92269-86-8; **5**, 92269-87-9; **6**, 92269-88-0; **Cp<sub>2</sub>CoMn(NO)<sub>2</sub>CO**, 92269-91-5; **Cp<sub>2</sub>CoMn(NO)<sub>2</sub>PPh<sub>3</sub>**, 92269-92-6; **[CpMn(CO)(NO)(PMe<sub>3</sub>)]BF<sub>4</sub>**, 92269-90-4; **[CpRe(CO)(NO)(PMe<sub>3</sub>)]BF<sub>4</sub>**, 89727-22-0; **(CpCoNO)<sub>2</sub>**, 51862-20-5; **[CpMn(CO)<sub>2</sub>NO]BF<sub>4</sub>**, 31960-39-1; **[CpRe(CO)(NO)NCCCH<sub>3</sub>]BF<sub>4</sub>**, 92269-93-7; **CpCr(NO)<sub>2</sub>Cl**, 12071-51-1; **CpMo(NO)<sub>2</sub>Cl**, 12305-00-9; **CpW(NO)<sub>2</sub>Cl**, 53419-14-0; **[CpRe(CO)<sub>2</sub>(NO)]BF<sub>4</sub>**, 31960-40-4; **(MeCpCoNO)<sub>2</sub>**, 85454-64-4; **ClSnMe<sub>3</sub>**, 1066-45-1; **ClSnPh<sub>3</sub>**, 639-58-7; **Cl<sub>2</sub>SnPh<sub>2</sub>**, 1135-99-5.

**Supplementary Material Available:** A listing of observed and calculated structure factors for complexes **PPN<sup>+</sup>1a** and **6** (57 pages). Ordering information is given on any current masthead page.

## Efficient Host-to-Guest Excited-State Energy Transfer in a Lamellar Solid: Photoluminescence and Photoaquation of Hexaamminechromium(III)-Substituted Hydrogen Uranyl Phosphate

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**Abstract:** A layered solid of approximate composition  $H_{0.7}[Cr(NH_3)_6]_{0.1}UO_2PO_4 \cdot 6H_2O$  has been prepared by precipitation from an aqueous  $H_3PO_4$  solution containing  $UO_2^{2+}$  and  $Cr(NH_3)_6^{3+}$  ions. An X-ray powder pattern of the solid shows a single phase which indexes in tetragonal symmetry with an interlamellar spacing of  $\sim 9.10$  Å. Absorption and photoluminescence (PL) spectra of the compound are a superposition of  $UO_2^{2+}$  and  $Cr(NH_3)_6^{3+}$  bands. Excitation spectra and radiative quantum yields indicate that the excited host  $UO_2^{2+}$  chromophore transfers energy to the Cr(III) complex with nearly unit efficiency. Prolonged visible photolysis of the solid at 295 K yields  $Cr(NH_3)(H_2O)_5^{3+}$  and  $Cr(NH_3)_2(H_2O)_4^{3+}$  as the principal products. Lower limit quantum yields for the initial appearance of interlamellar  $NH_4^+$  and  $NH_3$ , measured by IR spectroscopy, are  $\sim 0.1$  with excitation of either the  $UO_2^{2+}$  or  $Cr(NH_3)_6^{3+}$  chromophore, demonstrating that ligand photosubstitution in a lamellar solid can be very efficient.

Intercalation chemistry<sup>1</sup> and solid-state photoprocesses<sup>2</sup> have been the subjects of intense investigation. Despite the substantial interest in these two areas, relatively few studies have explored their common ground, the excited-state properties of lamellar solids. We recently reported on the emissive properties of the layered compound hydrogen uranyl phosphate (HUP),  $HUO_2P \cdot O_4 \cdot 4H_2O$ , and of solids derived therefrom by cationic substitution.<sup>3</sup> The substantial quenching of uranyl emission observed with  $Ag^+$ ,  $Cu^{2+}$ , and  $n-C_4H_9NH_3^+$  prompted us to prepare HUP derivatives

wherein host-guest, excited-state interactions might be more directly probed.

We report in this paper on the excited-state properties of  $Cr(NH_3)_6^{3+}$ -substituted HUP. Specifically, we demonstrate that this solid exhibits photoluminescence (PL) and photoreactivity characteristic of the Cr(III) complex upon excitation of either the guest Cr(III) or host  $UO_2^{2+}$  chromophore. Besides providing evidence for energy transfer, this system demonstrates that efficient ligand photosubstitution can obtain in a layered solid and, more generally, illustrates the ability of lamellar solids to serve as novel media for studying excited-state processes.

### Results and Discussion

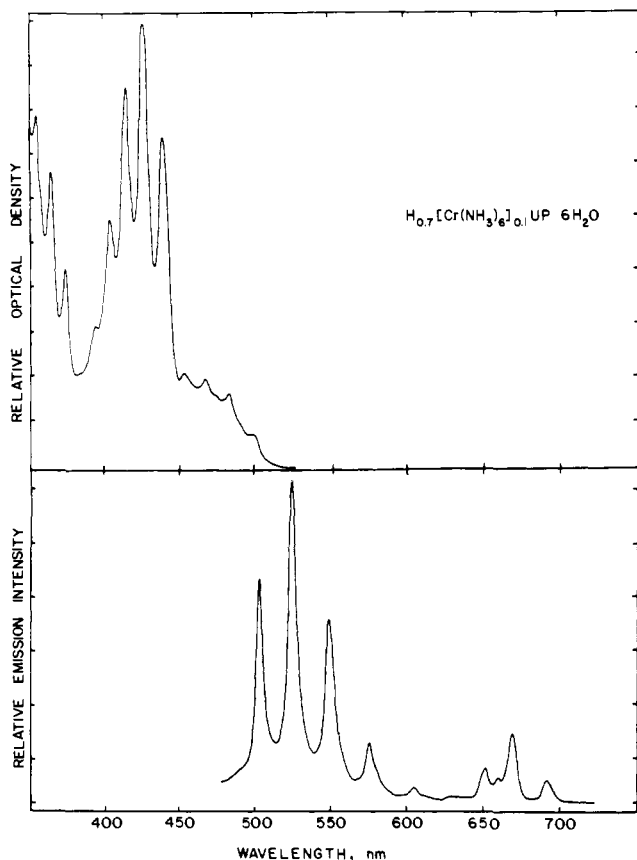
The introduction of a wide variety of mono- and divalent cations into the lamellar HUP lattice by intercalative ion-exchange reactions<sup>3,4</sup> suggested to us that the host lattice might also be amenable to the incorporation of trivalent cations. With its well-characterized solution PL and photoreactivity,  $Cr(NH_3)_6^{3+}$

(1) For a recent overview, see: "Intercalation Chemistry"; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982.

(2) For reviews involving solid-state photochemistry of transition-metal complexes relevant to this study, see, for example: (a) Simmons, E. L.; Wendlandt, W. W. *Coor. Chem. Rev.* **1971**, *7*, 11–27. (b) Fleischauer, P. D. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 9. For reviews involving solid-state energy transfer, see, for example: (a) Reisfeld, R. *Struct. Bonding (Berlin)* **1976**, *30*, 65–97. (b) Reisfeld, R.; Jørgenson, C. K. *Ibid.* **1982**, *49*, 1–36.

(3) Olken, M. M.; Biagioni, R. N.; Ellis, A. B. *Inorg. Chem.* **1983**, *22*, 4128–34.

(4) Weigel, F.; Hoffmann, G. *J. Less-Common Met.* **1976**, *44*, 99–123.



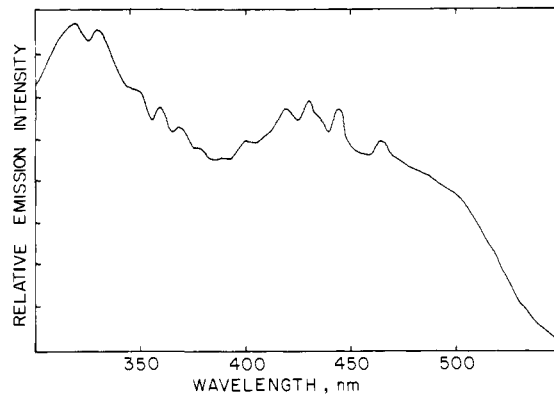
**Figure 1.** Absorption (top panel) and uncorrected PL (bottom panel) spectra of HCrUP at 295 K. The absorption spectrum was obtained by spreading a silicone grease mull of the solid on filter paper; silicone grease on filter paper served as a reference. The front-surface PL spectrum was obtained for the pure solid by exciting at 435 nm.

was a logical candidate for lattice substitution.<sup>5-9</sup> Powdered samples of  $\text{Cr}(\text{NH}_3)_6^{3+}$ -substituted HUP are readily synthesized and characterized under ambient conditions. In sections below, we describe the synthesis and structure of this solid, its PL properties, and its photochemistry.

**Synthesis and Structure.** Solids of general formula  $\text{H}_x[\text{Cr}(\text{NH}_3)_6]_{1/3(1-x)}\text{UO}_2\text{PO}_4 \cdot y\text{H}_2\text{O}$  can be isolated as precipitates from aqueous solution. The solid investigated in this study was prepared by combining equal volumes of 1 M  $\text{H}_3\text{PO}_4$  solution with a 1 M  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution which was saturated with  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$ . The ensuing precipitation reaction produced a yellow compound which, by elemental and spectrophotometric analysis, has an approximate composition of  $\text{H}_{0.7}[\text{Cr}(\text{NH}_3)_6]_{0.1} \cdot \text{UO}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , abbreviated hereafter as HCrUP.

An X-ray diffraction powder pattern of the yellow material can be indexed in tetragonal symmetry and indicates the presence of a single phase. The  $a$  lattice value of 6.99 Å is roughly equal to that of single-crystal HUP; however, the interlamellar spacing is  $\sim 9.10$  Å and indicates swelling relative to the HUP lattice (8.69-Å spacing<sup>3,4</sup>). Although the swelling is consistent with and expected for introduction of  $\text{Cr}(\text{NH}_3)_6^{3+}$  into the interlamellar region of the solid, the actual sites that the Cr(III) complex occupies relative to the wafflelike  $(\text{UO}_2\text{PO}_4)_n^{2-}$  sheets and to the interlamellar  $\text{H}_2\text{O}$  molecules are not presently known.

With regard to electronic structure, the absorption spectrum of HCrUP, shown in the top panel of Figure 1, appears to be a superposition of the structured HUP spectrum<sup>3</sup> and that of Cr-



**Figure 2.** Corrected excitation spectrum of HCrUP powder at 295 K, monitoring  $\text{Cr}(\text{NH}_3)_6^{3+}$  emission at 660 nm.

$(\text{NH}_3)_6^{3+}$ . The latter is dominated by two broad bands with  $\lambda_{\text{max}}$  values of  $\sim 460$  ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ ) and 350 nm ( ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ );<sup>5</sup> in fact, a physical mixture of HUP and  $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$  ( $\sim 10:1$  mole ratio) yields a virtually identical spectrum. To a good approximation, then, the host and guest chromophores do not appear to perturb one another in HCrUP.

**PL Properties.** Samples of HCrUP visually exhibit weak green emission when excited by blue or near-UV light. As shown in the bottom panel of Figure 1, the PL spectrum consists of two structured band envelopes: the envelope from  $\sim 500$  to 620 nm is characteristic of  $\text{UO}_2^{2+}$ <sup>3,10</sup> and that from  $\sim 640$  to 700 nm is characteristic of  $\text{Cr}(\text{NH}_3)_6^{3+}$  ( ${}^2\text{E}_g \rightarrow {}^4\text{A}_{2g}$ ).<sup>8,9</sup> The emissive properties of HCrUP provide strong evidence for efficient host-to-guest energy transfer in the solid, a phenomenon reflected in excitation spectra, radiative quantum yields, and temporal measurements.

An excitation spectrum in which the Cr(III) PL is monitored at 660 nm is shown in Figure 2. Qualitatively, it appears to mimic the HCrUP absorption spectrum in that vibronic structure characteristic of the  $\text{UO}_2^{2+}$  ion is superimposed on bands attributable to the Cr(III) complex. The presence of features characteristic of the host  $\text{UO}_2^{2+}$  chromophore while monitoring PL from the guest Cr(III) species is indicative of energy transfer; in the absence of this process, only Cr(III) bands should be observed in the excitation spectrum. We also examined the excitation spectrum for  $\text{UO}_2^{2+}$  PL (emission observed at 520 nm). The spectrum differs from Figure 2 in its low-energy onset which occurs at  $\sim 500$  nm; this blue-shift indicates that guest-to-host energy transfer is inefficient. The HCrUP  $\text{UO}_2^{2+}$  excitation spectrum, in fact, strongly resembles that of HUP.

Radiative quantum yields,  $\phi_r$ , indicate that host-to-guest energy transfer is extremely efficient. For Cr(III) PL, a  $\phi_r$  value of  $\sim 2 \times 10^{-3}$  is measured with 505-, 436-, and 405-nm excitation where the Cr(III) complex absorbs  $\sim 100$ , 20, and 10% of the absorbed light, respectively. This invariance of  $\phi_r$  as excitation is partitioned in different ways between the two chromophores suggests that energy transfer approaches unit efficiency. The  $\text{UO}_2^{2+}$ -based PL supports this conclusion:  $\phi_r$  is  $\sim 7 \times 10^{-3}$  with 405-nm excitation in HCrUP, reflecting substantial quenching compared to  $\phi_r \approx 0.7$  in HUP.<sup>3</sup> We also examined the PL spectrum of HCrUP at 77 K. Although a modest difference in the structure of the Cr(III) bands is seen (presumably reflecting the disappearance of "hot" bands), the integrated intensities of the  $\text{UO}_2^{2+}$ - and Cr(III)-based PL bands are essentially unchanged for 295 K. One other feature worth noting with regard to  $\phi_r$  for Cr(III) PL is that the value of  $\sim 2 \times 10^{-3}$  for HCrUP is substantially larger than the value of  $5.5 \times 10^{-6}$  reported for  $\text{Cr}(\text{NH}_3)_6^{3+}$  ions in aerated aqueous solution at 295 K.<sup>8</sup>

Acquisition of reliable temporal data proved difficult owing to weak PL intensities and the photoreactivity of the solid (vide infra). These problems notwithstanding, uranyl ion PL resulting from pulsed 337-nm excitation did provide additional evidence for

(5) Ramasami, T.; Endicott, J. F.; Brubaker, G. R. *J. Phys. Chem.* **1983**, *87*, 5057-9.

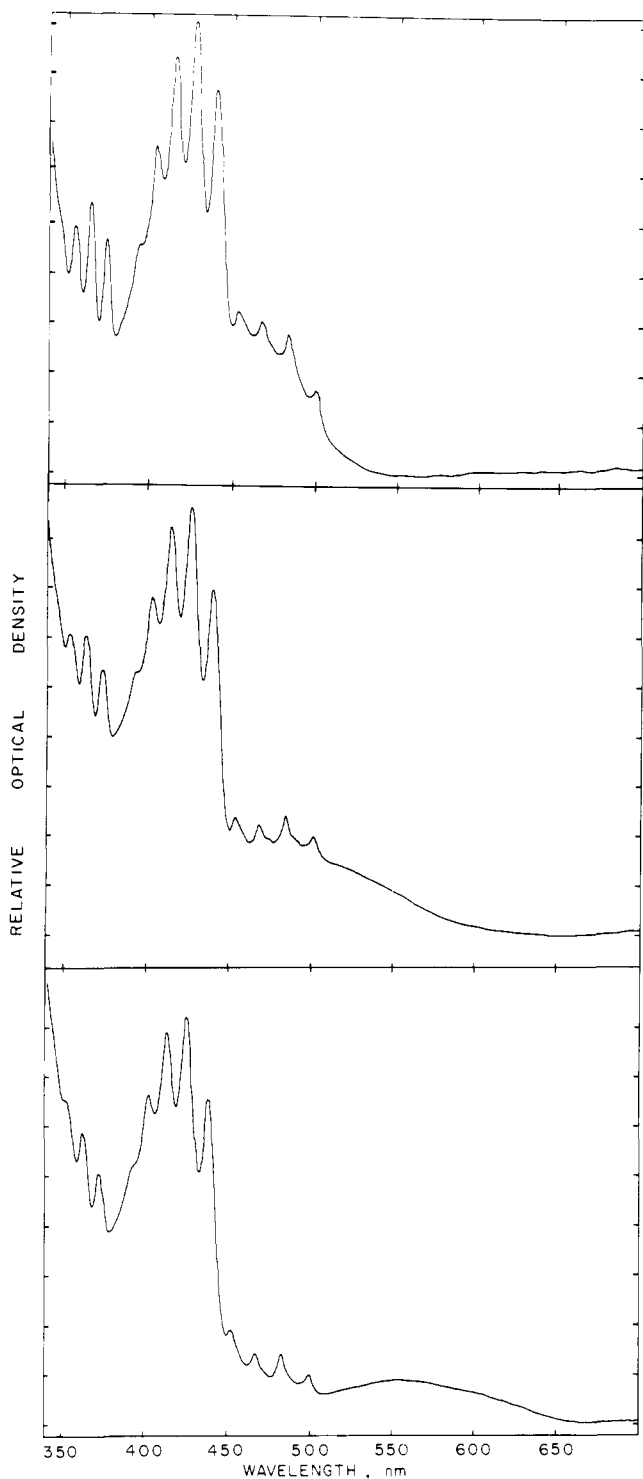
(6) Edelson, M. R.; Plane, R. A. *Inorg. Chem.* **1964**, *3*, 231-3.

(7) Kirk, A. D.; Frederick, L. A.; Wong, C. F. C. *Ibid.* **1979**, *18*, 448-50.

(8) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887-91.

(9) Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 53-61.

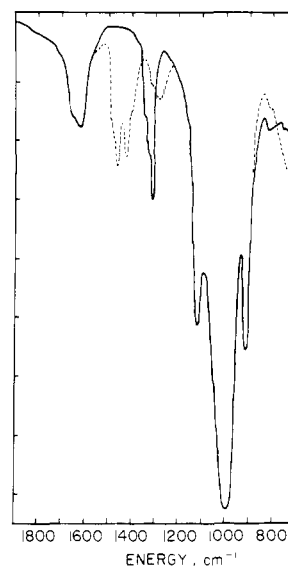
(10) Burrows, H. D.; Kemp, T. *J. Chem. Soc. Rev.* **1974**, *3*, 139-65.



**Figure 3.** Absorption spectral changes corresponding to photolysis of a silicone grease mull of HCrUP on filter paper. The top panel is the spectrum of the yellow powder before photolysis; the middle panel corresponds to a color change to red induced by 457.9-nm Ar<sup>+</sup> laser photolysis; and the bottom panel corresponds to a color change to green after long-term photolysis of the red sample with 514.5-nm Ar<sup>+</sup> laser excitation.

quenching by the guest complex. In particular, the measured decay time of  $\sim 25 \mu\text{s}$  is considerably less than the 450- $\mu\text{s}$  value determined for HUP<sup>3</sup> and parallels the trend in  $\phi_r$  found with the two solids.

**Photochemistry.** The well-studied solution photoaquation of  $\text{Cr}(\text{NH}_3)_6^{3+}$  prompted us to examine HCrUP for photoreactivity.<sup>6,7</sup> Upon prolonged visible photolysis, samples of HCrUP turn successively orange, red, and green. Accompanying these color changes is a progressive red-shift of the lowest energy Cr(III)



**Figure 4.** Infrared spectral changes (transmission) corresponding to prolonged photolysis of a KBr pellet of HCrUP with 496.5-nm Ar<sup>+</sup> laser excitation. The solid and dashed curves are the spectra before and after photolysis, respectively.

absorption bands, as pictured in Figure 3. The direction of the shift upon photoaquation is as anticipated based upon the spectrochemical series.<sup>11</sup> Loss of coordinated  $\text{NH}_3$  is also evidenced by IR spectral changes. When a KBr pellet of HCrUP is photolyzed, a monotonic increase in absorbance is observed from  $\sim 1350$  to  $1500 \text{ cm}^{-1}$ , as shown in Figure 4; the spectral pattern that develops resembles that of  $\text{NH}_4\text{UP}\cdot 3\text{H}_2\text{O}$ ,<sup>3</sup> indicating formation of  $\text{NH}_4^+$  and  $\text{NH}_3$  in the interlamellar region. Decomposition of the green solid with 2 M  $\text{HNO}_3$ , followed by ion-exchange chromatography,<sup>12</sup> reveals that the principal product in prolonged photolyses is  $\text{Cr}(\text{NH}_3)(\text{H}_2\text{O})_5^{3+}$  with a smaller quantity of  $\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{3+}$ , analogous to results obtained for  $\text{Cr}(\text{NH}_3)_6^{3+}$  solutions when  $\text{ClO}_4^-$  is the counterion;<sup>6</sup> in dark control experiments with HCrUP,  $\text{Cr}(\text{NH}_3)_6^{3+}$  was nearly quantitatively recovered. The temperature of photolyzed samples was kept below  $35^\circ\text{C}$ , since thermal decomposition occurs above  $\sim 50^\circ\text{C}$ .

Short-term photolyses of HCrUP ( $\lesssim 30\%$  conversion) provide additional evidence for energy transfer and demonstrate that photoaquation can be reasonably efficient in a layered solid. Lower limit quantum yields (uncorrected for substantial scattering from the KBr pellet) for the appearance of interlamellar  $\text{NH}_4^+$  and  $\text{NH}_3$ ,  $\phi_a$ , are  $\sim 0.03$ ,  $0.06$ , and  $0.10$  at 514.5, 457.9, and 405 nm, respectively. Given the insensitivity of the solution photoaquation quantum yields to excitation wavelength,<sup>6,7</sup> we suspect that these  $\phi_a$  values are all roughly equivalent with the apparent trend reflecting the decrease in optical density (enhanced scattering) with increasing wavelength. The key feature regarding energy transfer is the substantial  $\phi_a$  value at 405 nm where light is absorbed almost exclusively by the  $\text{UO}_2^{2+}$  chromophore.

Aside from illustrating energy transfer, the magnitude of  $\phi_a$  is interesting in its own right. Although the measured values of  $0.03$ – $0.10$  are considerably less than the reported solution values of  $\sim 0.3$ – $0.5$  for the conversion of  $\text{Cr}(\text{NH}_3)_6^{3+}$  to  $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ ,<sup>6,7</sup> they are substantial and indicate that photoaquation in a lamellar solid can be reasonably efficient. Interestingly, the photoreaction is far less efficient at 77 K: prolonged 457.9-nm excitation yields no change in the PL spectrum (no Cr(III) PL is observed after prolonged 295 K photolyses) nor in the color of HCrUP samples. Since HCrUP PL properties are relatively insensitive to temperature (vide supra), the difference in reactivity appears to derive primarily from steric rather than electronic factors. One possible explanation is that molecular mobility is

(11) Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw-Hill: New York, 1962; p 91.

(12) Mønsted, L.; Mønsted, O. *Acta Chem. Scand.* 1973, 27, 2121–30.

sufficiently reduced at 77 K as to preclude net reactivity.

Perhaps the most significant feature of the HCrUP system is that it underscores the notion that solids may provide a variety of novel media for probing the steric and electronic factors governing molecular photoreactivity. Well-studied solution reactions such as photoaquation and photoredox chemistry are particularly useful probes of environmental effects on reactivity. In this vein, we note that zeolites have served as hosts for the efficient photoaquation of  $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ ,<sup>13</sup> for electron-transfer reactions involving excited  $\text{Ru}(\text{bpy})_3^{2+}$ ,<sup>14</sup> and for the photoassisted catalytic oxidation of isopropyl alcohol ( $\text{UO}_2^{2+}$ -exchanged zeolite).<sup>15</sup> These systems along with HCrUP are clearly representative of excited-state chemistry of enormous scope.

### Experimental Section

**Materials and Synthesis.** All chemicals were analytical reagent grade and were used as received. Starting materials included  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Baker) and anhydrous  $\text{CrCl}_3$  (Aldrich).  $\text{HUP}$ ,<sup>3</sup>  $\text{NH}_4\text{UP} \cdot 3\text{H}_2\text{O}$ ,<sup>3</sup> and  $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$ <sup>9</sup> were prepared as previously described. Synthesis of HCrUP was performed under dim red light. In a typical procedure, 10 mL of a 1 M  $\text{UO}_2(\text{NO}_3)_2$  solution was saturated with  $\text{Cr}(\text{NH}_3)_6(\text{NO}_3)_3$  (~0.3 g). Subsequently, 10 mL of 1 M  $\text{H}_3\text{PO}_4$  was added to this solution and, after being mixed, the solution was allowed to stand at room temperature. After a few minutes, a yellow precipitate forms and is filtered within ~30 min. The solid is washed with triply distilled  $\text{H}_2\text{O}$  until the filtrate is colorless with pH ~7 and then air-dried for ~24 h. The dried powder was stored in the dark in tightly stoppered vials. A microanalysis for HCrUP was obtained from Galbraith Laboratories, Knoxville, TN. Anal. Calcd for  $\text{UCr}_{0.1}\text{H}_{14.5}\text{N}_{0.6}\text{O}_{12}\text{P}$  ( $\text{H}_{0.7}[\text{Cr}(\text{NH}_3)_6]_{0.1}\text{UO}_2\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ): H, 2.99; N, 1.72; P, 6.33. Found: H, 3.00; N, 1.88; P, 6.54. Spectrophotometric analyses of known quantities of HCrUP dissolved in 2 M  $\text{HNO}_3$  were consistent with this stoichiometry; an absorptivity of  $40 \text{ M}^{-1} \text{ cm}^{-1}$  for  $\text{Cr}(\text{NH}_3)_6^{3+}$  at  $460 \text{ nm}$ <sup>67</sup> was used in the analysis. An X-ray diffraction powder pattern of the solid, obtained as described previously,<sup>3</sup> was indexed in tetragonal symmetry with a *c* lattice value derived from 001 data of ~9.10 Å; the *a* lattice value was 6.99 Å, the value reported for single-crystal HUP.<sup>16</sup>

**Spectra.** IR spectra were taken on a Beckman Model IR 4250 instrument using KBr pellets. Electronic absorption spectra were obtained on a Cary 17-D UV-vis-near-IR spectrophotometer by spreading a silicone grease (Dow-Corning high-vacuum grease) mull of the solid on filter paper; silicone grease on filter paper served as a reference. Uncorrected PL spectra were acquired with an Aminco-Bowman spectrofluorimeter and red-sensitive PMT using "head-on" excitation with the instrument's Xe lamp, as described previously.<sup>3</sup> A Dewar assembly used for 77 K PL spectra has also been described.<sup>3</sup> The excitation spectrum of HCrUP was obtained with the same instrumentation and sample geometry used for PL spectra and is corrected for the output of the Xe lamp used for excitation; spectra were recorded from 300 to 600 nm, monitoring either the Cr(III) PL at 660 nm or the  $\text{UO}_2^{2+}$  PL at 520 nm.

(13) Camara, M. J.; Lunsford, J. H. *Inorg. Chem.* **1983**, *22*, 2498-501.

(14) (a) Faulkner, L. R.; Suib, S. L.; Renschler, C. L.; Green, J. M.; Bross, P. R. In "Chemistry in Energy Production"; Wymer, R. G., Keller, O. L., Eds.; NTIS: Springfield, VA, 1982; Conference 801226, pp 99-114. (b) DeWilde, W.; Peeters, G.; Lunsford, J. H. *J. Phys. Chem.* **1980**, *84*, 2306-10. (c) Quayle, W. H.; Lunsford, J. H. *Inorg. Chem.* **1982**, *21*, 97-103.

(15) Suib, S. L.; Kostapapas, A.; Psaras, D. *J. Am. Chem. Soc.* **1984**, *106*, 1614-20.

(16) Morosin, B. *Phys. Lett. A* **1978**, *65A*, 53-4.

**Emissive Quantum Yields and Lifetimes.** Values of  $\phi_r$  for both the Cr(III) and  $\text{UO}_2^{2+}$  PL of HCrUP were obtained with the Aminco-Bowman instrument using techniques described previously.<sup>3</sup> A lifetime for the  $\text{UO}_2^{2+}$  PL was acquired by using a pulsed  $\text{N}_2$  laser (337-nm excitation) setup.<sup>3</sup> Attempts to obtain the PL intensity-time profile of the Cr(III) emission with a red-sensitive Hamamatsu R928 PMT were unsuccessful owing to its weak intensity and the photoreactivity of the solid; both 337- and 450-nm excitation ( $\text{N}_2$ -pulsed dye laser) were employed in these experiments.

**Photolyses.** Optical sources were a 60-W light bulb, an Oriel 200-W high-pressure Hg lamp, filtered to isolate 405-nm light (10-nm fwhm interference filter), and the 514.5- and 457.9-nm lines of a Coherent Radiation CR-12 Ar<sup>+</sup> laser. Light intensities were measured with a Tektronix J16 radiometer equipped with a J6502 probe head. Exhaustive photolyses for photoproduct identification were conducted on ~500-mg samples of HCrUP using the 60-W light bulb for excitation; samples were ground at ~12-h intervals. Over 4 days of photolysis the yellow powder turned orange, red, and, finally, green. The green solid was dissolved in 2 M  $\text{HNO}_3$  and subjected to ion-exchange chromatography using a Dowex 50X8-400 cation-exchange resin.<sup>12</sup> A solution of 0.5 M HCl, used to elute  $\text{UO}_2^{2+}$ , was followed by 2 M  $\text{H}_2\text{SO}_4$  to elute the various Cr(III) complexes present in the photolysate. Elution with 0.1 M  $\text{LaCl}_3$ , which would isolate polynuclear Cr(III) species, if present,<sup>17</sup> yielded no such compounds. Dark control experiments led to virtually quantitative recovery of  $\text{Cr}(\text{NH}_3)_6^{3+}$ . Electronic spectral changes accompanying prolonged photolysis of HCrUP were obtained with a silicone grease mull of the powder on filter paper; spectra were recorded after several photolysis periods. To obtain lower limit quantum yields for the appearance of interlamellar  $\text{NH}_4^+$  and  $\text{NH}_3$ ,  $\phi_a$ , experiments were conducted with ~100-mg KBr pellets containing ~4% HCrUP by weight. Samples were irradiated in the die used for their preparation using 405-, 457.9, or 514.5-nm light masked to just fill the ~0.5-cm<sup>2</sup> surface area; incident power was ~1-10 mW and sample optical densities were 0.7-1.5. The progress of the reaction was monitored at ~2-20 min intervals in the 1350-1500 cm<sup>-1</sup> region of the IR corresponding to  $\text{NH}_4^+$  absorption. The growth in integrated absorption in this region (spectra obtained in absorption mode) was related to the absolute quantity of  $\text{NH}_4^+$  produced by comparison with the  $\text{NH}_4^+$  IR absorption intensity in a  $\text{NH}_4\text{UP} \cdot 3\text{H}_2\text{O}$  sample dispersed in a KBr pellet. Because the die was mounted on a rigid plate, it could reproducibly be positioned in front of the photolysis source and in the IR spectrometer. To obtain a lower limit for  $\phi_a$ , the quantity of  $\text{NH}_4^+$  produced was divided by the intensity incident on the sample minus the intensity transmitted through the sample ( $\leq 10\%$  depending upon excitation wavelength). Values of  $\phi_a$  are lower limits because no correction was made for the appreciable light scattering observed; qualitatively, scattering increased as the optical density of the sample decreased. Extraction of  $\phi_a$  values was based on five or six irradiation periods with  $\leq 30\%$  total conversion of  $\text{Cr}(\text{NH}_3)_6^{3+}$  to  $\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ . Good linearity in the data was found including extrapolation to zero conversion at zero time. Values of  $\phi_a$  are the average of three sets of data for freshly prepared samples; reproducibility was  $\pm 20\%$ . Low-temperature irradiation of HCrUP powder was carried out at 77 K in a suprasil tube (2-mm inner diameter) using 457.9-nm excitation.

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(17) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197-3200.