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preferential orientation with increasing pressure even when finely ground. After release of pressure and grinding, the effect of anisotropy has vanished.

As seen, Fe(phen)$_2$(N$_3$)$_2$ is not completely converted from high- to low-spin form with increase of pressure. It is necessary to know that the thermodynamic criterion for increase of conversion with pressure is that the volume of the system as a whole decreases with increasing conversion at constant pressure and temperature.[10] This may be realized by bond shortening or closer packing of the molecules due to changes in their electronic structure.

Single-crystal results of a related compound Fe(dip)$_2$(NCS)$_2$ reveal that the Fe–N(dip) bond length increases from about 2.17 Å in the $^5T_2$ ground state (293 K) to about 2.03 Å in the $^1A_1$ ground state (100 K). The difference of 0.14 Å clearly reflects the change in radius of the iron(II) ion in going from the high-spin $t_2{}^4e^2$ to the low-spin $t_2{}^6$ configuration. The Fe–N(NCS) bond length shortens to about 0.08 Å.[11] In agreement with IR results,[12] there is no increasing of the N–C bond length of the NCS$^-$ ligand on passing from the $^5T_2$ state to the $^1A_1$ state. In the absence of other structural data, one assumes a similar FeN bond shortening in the other studied Fe(phen)$_2$(X)$_2$ compounds. However, from the chemistry of coordinated azides it is quite apparent that the larger the π-donor interaction between the p orbitals on N (bound to the metal M) and the d(π) orbitals on the metal M, the larger the difference between the two N–N distances. Another structural parameter of interest is the M–N$_\alpha$–N$_\beta$ bond angle, which varies between 117 and 132°,[13,14] in the expected range for the angle of a trigonally hybridized N$_\alpha$ atom. With increase of pressure the back-donation of the metal d(π) electrons to the ligand π orbitals increases and may cause a strengthening of the structural effects above. Thus it may appear for Fe(phen)$_2$(N$_3$)$_2$ that steric factors and/or crystal packing may influence the sharpness of the spin transition. In this connection it is interesting to know that the quadrupole splitting ΔE_Q(LS) in Fe(phen)$_2$(N$_3$) is about 2 times greater than observed in Fe(phen)$_2$(NCS)$_2$ and Fe(phen)$_2$(NCSe)$_2$ (Table I).

On the other hand, spectroscopic investigations on azido complexes place the azide ligand at the beginning of the spectrochemical series.[15] These ligands, which may act as π donors, have rather low f values, which are proportional to the ligand field parameter Δ and the covalent bonding. From the literature[15] we get the following sequence for the ratio of the different ligand field parameters: $\Delta(\mathrm{Cl^-}):\Delta(\mathrm{N_3^-}):\Delta(N\mathrm{CS^-}):\Delta(\mathrm{CN^-}) = 0.78:0.83:1.02:1.7$. From this, one expects that with decreasing f values the transformation is increasingly hindered, leaving a certain amount of high-spin residual. This trend seems to be observed by Fisher and Drickamer.[8] However, a related study on Fe(phen)$_2$(X)$_2$ with X = Cl, Br is currently under way in our laboratories.

In this connection, it is noteworthy that Fe(phen)$_2$(CN)$_2$·H$_2$O, which exhibits a very high degree of back-bonding to the empty cyanide ligand π^* levels, exists in the low-spin state at 0.001 kbar. Obviously, the dominant effect is the increase in the ligand field with pressure due to the increased back-bonding. The increase in the ligand field overcomes the spin-pairing energy and thus brings about the high-spin to low-spin transition.

Theoretical considerations on the problem of spin transitions as a function of pressure are in progress.

Acknowledgment. The author is grateful to F. Schmock and H. G. Hauck for the preparation of the compounds. Sincere thanks are also expressed to H. Wasinski for this experimental assistance. Financial support from the Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. Fe(phen)$_2$(NCS)$_2$, 14692-67-2; Fe(phen)$_2$(NCSe)$_2$, 15744-97-5; Fe(phen)$_2$(N$_3$)$_2$, 14873-48-4.

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Excited-State Properties of Lamellar Solids Derived from Hydrogen Uranyl Phosphate

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Received March 22, 1983

The excited-state properties of the layered compound hydrogen uranyl phosphate (HUP), HUO$_2$PO$_4$·4H$_2$O, and of solids derived therefrom have been examined; the derivatives, prepared by intercalative ion-exchange reactions, have compositions based on stoichiometric proton substitution by NH$_4{}^+$, pyridinium, *n*-butylammonium, *n*-octylammonium, K$^+$, and Ag$^+$, 0.5 equiv of Ca^{2+} and Zn^{2+}, and 0.4 equiv of Cu^{2+}. These compounds have all been characterized by elemental analysis, IR spectroscopy, and X-ray powder diffraction; the last confirms the retention of the lamellar structure upon cationic substitution and reveals that the interlamellar spacing can vary considerably with the choice of cation. All of the samples exhibit electronic absorption spectra characteristic of the UO$_2{}^{2+}$ chromophore. Except for the *n*-octylammonium, Ag$^+$ and Cu^{2+} salts, the samples all exhibit yellow-green emission characteristic of the UO$_2{}^{2+}$ moiety when excited with blue or near-UV light at 295 K. Emission decay curves are exponential for all of the luminescent solids and yield lifetimes, τ, ranging from ~1 to 450 μs. HUP and its K$^+$, NH$_4{}^+$, pyridinium, and Ca^{2+} derivatives are all highly emissive with measured radiative quantum efficiencies, ϕ_r, approaching unity at 295 K. Values of τ and ϕ_r have been used to calculate radiative (k_r) and nonradiative (k_{nr}) rate constants for excited-state decay. Values of k_r are nearly constant at ~(1–2) × 10^3 s^{-1} for the samples, whereas k_{nr} values span several orders of magnitude. Possible quenching mechanisms for the weakly emissive and nonemissive solids are described and compared with previously reported solution data.

The excited-state properties of inorganic solids are receiving considerable attention as a means of characterizing electronic structure and physical processes occurring within the solid. Useful applications of luminescence, traditionally the basis for such studies, have included the design of phosphors[1] and light-emitting diodes,[2] as well as the characterization of semiconductor electrodes[3] and colloids.[4] Although numerous

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inorganic solids have been examined, relatively few systems have been amenable to a systematic study of excited-state properties based on stoichiometric chemical substitution. A compound that attracted our interest in this regard is hydrogen uranyl phosphate (HUP), $HUO_2PO_4 \cdot 4H_2O$. Besides exhibiting intense luminescence characteristic of the uranyl (UO_2^{2+}) moiety,[5] this layered solid undergoes intercalative ion-exchange reactions with mono- and divalent cations to produce a large family of structurally related solids with the formula $M^{n+}{}_{1/n}UO_2PO_4 \cdot xH_2O$ (n = 1, 2).[6]

In this paper we report on the excited-state properties of HUP and some of its derivatives formed by partial or complete substitution of the proton by alkali, alkaline-earth, transition-metal, ammonium, alkylammonium, and pyridinium ions. We show that HUP and several of its derivatives are highly emissive at 295 K while other substituents appear to completely quench the luminescence. For the emissive solids, unimolecular rate constants, extracted from lifetime and quantum yield measurements, are used to establish correlations between the composition of the solids and their excited-state deactivation routes. These results are compared with those reported for other uranyl species, and quenching mechanisms are discussed. Besides providing insight into the electronic structure and excited-state processes of these solids, the studies described herein also illustrate the use of luminescence as a probe of intercalation, a reaction which is being extensively studied with use of a wide variety of lamellar host solids.[7]

Experimental Section

Materials and Synthesis. All chemicals were analytical reagent grade. Metal salts were recrystallized from triply distilled water; other reagents were used as received. Starting materials included $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2(CH_3CO_2)_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, and $CaCl_2 \cdot 2H_2O$ from Baker, $Zn(NO_3)_2 \cdot 6H_2O$, NH_4NO_3, and NH_4Cl from Fisher, H_3PO_4, $ZnCl_2$, KNO_3, KCl, and $AgNO_3$ from Mallinckrodt, $NaCH_3CO_2$ from Drake Brothers, $(2,2'\text{-bpy})_3RuCl_2 \cdot 6H_2O$ from G. F. Smith, and *n*-butylamine, *n*-octylamine, pyridine, D_2O, and D_3PO_4 from Aldrich. The alkylamines were isolated and recrystallized as HCl salts prior to reaction with HUP. Pyridine was protonated with HCl (pH ~4) prior to reaction with HUP. All manipulations were carried out in air except those involving the deuterated species, which were handled in a N_2-filled glovebag. HUP was prepared as described previously from H_3PO_4 and $UO_2(NO_3)_2 \cdot 6H_2O$.[6] This compound was substituted with various mono- and divalent cations by modification of a literature procedure.[6] In a typical synthesis, a slurry was prepared that consisted of ~250 mg of HUP suspended in 25 mL of a 2 M solution of the cation to be introduced. Chloride or nitrate served as the counterion and did not affect the physical properties of the product; no evidence for nitrate incorporation in the solid was found by IR spectroscopy. The slurry was magnetically stirred at room temperature for 2 days; over this period, initially neutral solutions would reach the final pH of 1–2. After the reaction was complete, the slurry was filtered and the solid washed with 100 mL of distilled water until the washings were free of dissolved ions. The solid was then air-dried in a fume hood for 24 h, at which point it was stored in a tightly stoppered vial. Desiccants were avoided since dehydration can drastically affect the physical properties of the solid. In the case of the Cu derivative, only a partially exchanged product (~25% of the expected quantity by atomic absorption, vide infra) was obtained by this route. A more highly substituted product resulted by slurrying a partially exchanged solid in 4 M copper nitrate at 75 °C for 2 days. This route yielded a material whose Cu content was 84% (by atomic absorption spectrometry) of that expected for a fully substituted product. Attempts to prepare DUP by the reaction of uranyl nitrate with D_3PO_4 in D_2O yielded only a partially substituted product by IR analysis.

X-ray Diffraction Powder Patterns. X-ray data were obtained with a Philips Electronic Instruments X-ray source and a Debye-Scherrer camera. Exposure times were 4 h to Ni-filtered Cu Kα radiation. The patterns were measured to ±0.05 mm with a Norelco film recorder and indexed in tetragonal symmetry, with use of *c* lattice values derived from 00*l* data; *a* lattice values were approximately equal to 6.99 Å, the value reported for single-crystal HUP.[8]

Elemental Analyses. Microanalyses were obtained for HUP and several of its derivatives from Galbraith Laboratories, Knoxville, TN. Anal. Calcd for $UH_9O_{10}P(HUO_2PO_4 \cdot 4H_2O)$: H, 2.07; N, 0.00. Found: H, 1.93; N, 0.006. Calcd for $UC_5H_6NO_6P$ ($NC_5H_6UO_2PO_4$): C, 13.49; H, 1.36; N, 3.15. Found: C, 13.19; H, 1.35; N, 3.07. Calcd for $UC_4H_{18}NO_9P$ ($n\text{-}C_4H_9NH_3UO_2PO_4 \cdot 3H_2O$): C, 9.74; H, 3.65; N, 2.84. Found: C, 9.21; H, 3.22; N, 2.72. Calcd for $UC_8H_{26}NO_9P$ ($n\text{-}C_8H_{17}NH_3UO_2PO_4 \cdot 3H_2O$): C, 17.50; H, 4.73; N, 2.55. Found: C, 17.09; H, 4.62; N, 2.75. Calcd for $UH_{10}NO_9P$ ($NH_4UO_2PO_4 \cdot 3H_2O$): H, 2.30; N, 3.20. Found: H, 2.28; N, 3.20. For metal derivatives, the weight percent of the metal was determined by a Vollhard titration in the case of Ag and by atomic absorption spectrometry for Ca, Zn, K, and Cu with use of techniques and instrumentation previously described.[9] The samples were prepared for analysis by dissolution in 1 M HCl. Anal. Calcd for $UCa_{0.5}H_8O_{10}P$ ($Ca_{0.5}UO_2PO_4 \cdot 4H_2O$): Ca, 4.38. Found: Ca, 4.25. Calcd for $UZn_{0.5}H_8O_{10}P$ ($Zn_{0.5}UO_2PO_4 \cdot 4H_2O$): Zn, 6.98. Found: Zn, 7.0. Calcd for UKH_6O_9P ($KUO_2PO_4 \cdot 3H_2O$): K, 8.53. Found: K, 8.6. Calcd for $UAgH_6O_9P$ ($AgUO_2PO_4 \cdot 3H_2O$): Ag, 20.46. Found: Ag, 20.2. Calcd for $UCu_{0.5}H_8O_{10}P$ ($Cu_{0.5}UO_2PO_4 \cdot 4H_2O$): Cu, 6.78. Found: Cu, 5.7. The last analysis corresponds to $H_{0.16}Cu_{0.42}UO_2PO_4 \cdot 4H_2O$, i.e., partial substitution.

Spectra. IR spectra were taken on a Beckman Model IR 4250 instrument. Spectra were run on dilute KBr pellets and Nujol or Fluorolube mulls containing the solids. Only for the Cu derivative, which appeared to react with KBr (a black coloration developed), was there any significant difference in IR spectra obtained by the two techniques. Electronic absorption spectra were obtained on a Cary 17-D UV–vis–near-IR spectrophotometer by spreading a Nujol mull of the solid on filter paper; Nujol on filter paper served as a reference. Uncorrected emission spectra were acquired with an Aminco-Bowman spectrophotofluorometer and red-sensitive PMT described previously.[10] Samples were placed in a cuvette facing the detection optics and irradiated "head on" with a Xe lamp or Coherent Radiation CR-12 Ar ion laser, whose outputs were deflected off of a mirror in the sample compartment and onto the sample. When ultraviolet excitation was used, a Melles Griot 03-FCG-055 filter was placed in front of the PMT to eliminate the overtone from the exciting light. Excitation spectra were also obtained with the "head-on" geometry; the spectrometer's Xe lamp was used for excitation, and emission was monitored at 520 nm.

Emissive Quantum Yields. Values of ϕ_r were obtained with use of a technique reported for solid samples which is based on differences in intensity of the light reflected from the sample and from a highly reflective MgO powder.[11] Interference filters were used in conjunction with the emission spectrometer's monochromator to select wavelengths. "Head-on" excitation was employed, and measurements were corrected for detector sensitivity, as previously described.[12] The salt $[Et_4N]_2[MnBr_4]$, prepared as described in the literature, served as a standard and gave ϕ_r values of 0.60–0.65, in good agreement with the reported range of 0.50–0.68.[11]

Lifetimes. Values of τ were acquired by exciting samples with the 450-nm output of an NRG DL 0.03 dye laser (~7 ns fwhm) pumped by an NRG 0.7-5-200 pulsed N_2 laser (0.7-MW peak power); Coumarin 450 dye was employed. The samples were irradiated "head-on" in the Aminco-Bowman spectrometer, as described above, but the PMT

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Table I. Physical Properties of HUP and Derivatives[a]

compd[b]	interlamellar spacing, Å[c]		τ, μs[e]		ϕ_r[f]	$10^{-3}k_r$, s^{-1} [g]	$10^{-3}k_{nr}$, s^{-1} [h]
	this work	lit.[d]	295 K	77 K			
$HUP{\cdot}4H_2O$	8.69	8.69	320	400	0.70	2.2	0.9
$HUP{\cdot}4H_2O$[i]			430				
$NH_4UP{\cdot}3H_2O$	9.01	9.05	450	600	0.60	1.3	0.9
pyHUP	9.28	. . .	250	310	0.32	1.3	2.7
$n\text{-}BuNH_3UP{\cdot}3H_2O$	14.39	14.20	1.8	350	0.0014	0.8	560
$n\text{-}OctNH_3UP{\cdot}3H_2O$	18.76	18.60	. . .	150	. . .	. . .	. . .
$KUP{\cdot}3H_2O$	8.90	8.89	450	450	0.65	1.4	0.8
$AgUP{\cdot}3H_2O$	8.45	. . .	. . .	. . .	. . .	. . .	. . .
$Ca_{0.5}UP{\cdot}4H_2O$	10.34	10.35	320	350	0.36	1.1	2.0
$Zn_{0.5}UP{\cdot}4H_2O$	8.60	. . .	140	140	0.18	1.3	6.1
$Cu_{0.42}H_{0.16}UP{\cdot}4H_2O$[j]	8.71	8.71	. . .	. . .	. . .	. . .	. . .

[a] Crystallographic and emissive properties of HUP and related samples (295 K) prepared by intercalative ion-exchange reactions as described in the text. Vacant entries in the portion of the table representing emissive properties correspond to samples for which we were unable to detect luminescence. [b] Samples investigated; as described in the text, the indicated waters of hydration are approximate. [c] Interlamellar spacings obtained from 00*l* lines of X-ray diffraction powder patterns; spacings obtained from several 00*l* lines from each sample were internally consistent. All samples could be indexed to tetragonal unit cells with *a* within ±0.05 of 6.99 Å. [d] Literature values for interlamellar spacings for previously characterized solids. All are taken from ref 6 except for the $n\text{-}BuNH_3^+$ and $n\text{-}OctNH_3^+$ derivatives, which were obtained from ref 16. In cases where X-ray data were sufficiently precise, the crystallographic *c* spacing was found to be twice the interlamellar spacing.[8,17] This is probably the case for our samples as well. [e] Measured lifetime, obtained for emissive samples with 450-nm excitation as described in the Experimental Section. [f] Radiative quantum efficiency (295 K), obtained for emissive samples with 460-nm excitation as described in the Experimental Section. [g] Unimolecular rate constant for radiative decay, calculated by using eq 3 in the text. [h] Unimolecular rate constant for nonradiative decay, calculated by using eq 4 in the text. [i] Data for a slurry of HUP in its mother liquor, the filtrate from its synthesis; emission from the mother liquor was negligible at 295 K. We believe that the measured lifetime for the slurry is a more reliable value and that the discrepancy from the value of τ for the solid indicates degradation of the solid under our experimental conditions (see Results and Discussion and Experimental Section). For the ϕ_r measurement of the solid, degradation did not appear to be a problem owing to the much lower excitation intensity employed. [j] Cu content is approximate and was determined by atomic absorption spectrometry.

was a RCA 1P-28 model whose base was wired to permit the output to be fed directly into a Tektronix Model 466 storage oscilloscope. For strongly emissive samples the output at 30 pulses/s could be photographed directly from the oscilloscope to give the intensity–time plot; for weakly emissive samples, decay curves were obtained by operating the oscilloscope in the storage mode, which averaged ~150 pulses with the laser operating at 20 or 30 pulses/s. Typical peak incident intensities were ~0.2 kW/cm^2, although no difference in decay characteristics was observed for HUP at 77 K when the intensity was reduced by a factor of 100 with use of neutral density filters. Higher intensities tended to degrade samples, particularly HUP. Decay curves obtained on slurries of all of the emissive solids in distilled water were identical with those obtained with the dry solids, except for HUP, which appeared to degrade under those conditions. The longest lifetimes observed for HUP were obtained from slurries of HUP in its mother liquor (the filtrate from its synthesis); emission from the mother liquor was negligible at room temperature. Lifetimes at 77 K were obtained with a quartz Dewar assembly that mated to the emission spectrometer's sample chamber. Dry, powdered samples were irradiated in 1 mm o.d. glass tubes. For all samples, plots of log (intensity) vs. time were linear over at least 2 lifetimes. Values of τ and ϕ_r were determined on at least two different samples of each compound. The solids $UO_2(NO_3)_2{\cdot}6H_2O$[13] and $NaUO_2(CH_3CO_2)_3$[14] and a degassed aqueous solution of Ru(2,2′-bpy)$_3$Cl$_2$[15] served as lifetime standards. Lifetimes measured for these compounds with use of the setup described above were in good agreement with literature values.

Results and Discussion

In sections below we describe structural and excited-state properties of HUP and several of its derivatives. Characterization is based on X-ray, IR, electronic absorption, and emissive data. Correlations of these properties with the composition of the solid are discussed with reference to other uranyl systems.

1. X-ray Data. HUP is a well-studied compound which undergoes intercalative ion-exchange reactions with numerous mono- and divalent cations, as represented by eq 1 and 2; many

$$HUO_2PO_4 + M^+ \rightarrow MUO_2PO_4 + H^+ \qquad (1)$$

$$M = Li, Na, K, NH_4, n\text{-}C_4H_9NH_3, n\text{-}C_8H_{17}NH_3, Ag$$

$$HUO_2PO_4 + 0.5M^{2+} \rightarrow M_{0.5}UO_2PO_4 + H^+ \qquad (2)$$

$$M = Mg, Ca, Zn, Ba, Cu$$

of these compounds are naturally occurring minerals of the torbernite family.[6,16] These solids, along with arsenate analogues, have been characterized by X-ray diffraction powder patterns and in several cases, including HUP, by single-crystal X-ray diffraction.[6,8,17,18] They are hydrates with a lamellar structure consisting of alternating sheets of $(UO_2PO_4)_n^{n-}$ and water molecules. The former are wafflelike in structure, each U atom being coordinated to four equatorial O atoms from four PO_4^{3-} groups in addition to the two apical O atoms that constitute the UO_2^{2+} moiety. The water molecules form squares linked through H bonding; cations are believed to either substitute for H_2O at a corner of the square or to occupy the center of the square, leading to formulations of the sheets as $M^{n+}{\cdot}3H_2O$ and $M^{n+}{\cdot}4H_2O$.[17,18] Although three and four waters of hydration represent the fully hydrated composition of many of these compounds, there is evidence for several of the solids that the hydrate phase is nonstoichiometric.[19] Hydration stoichiometries reported by various workers show a wide range, so the exact hydration stoichiometry may vary considerably with experimental conditions.[6]

We have prepared samples of HUP and its K$^+$, Ag$^+$, NH_4^+, $n\text{-}C_4H_9NH_3^+$ ($n\text{-}BuNH_3^+$), $n\text{-}C_8H_{17}NH_3^+$ ($n\text{-}OctNH_3^+$), $C_5H_5NH^+$ (pyH$^+$), Ca^{2+}, Cu^{2+}, and Zn^{2+} salts using the in-

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tercalative ion-exchange reactions given by eq 1 and 2. X-ray diffraction powder patterns were obtained for all of the compounds and were indexed to tetragonal unit cells. The interlamellar spacings (distance from the middle of one plane to the middle of the adjacent plane), determined from 00*l* data, are reported in Table I; while values for the interlamellar spacings vary over a wide range, values for the *a* lattice parameter are all within ±0.05 Å of the 6.99 Å found for single-crystal HUP.[8] Except for the pyridinium, Zn, and Ag derivatives, powder patterns of all of the solids in this study have been published and are in good agreement with our data.[6,16] For $HUP \cdot 4H_2O$, the data appear to correspond to what has been referred to as the phase I polymorph ($P4/ncc$), although our interlamellar spacing is half the crystallographic *c* value reported.[20] Our inability to see the full crystal lattice in this and several other samples could reflect the insensitivity of our experimental setup; reflections with odd values of *l*, from which the *c* lattice constant is derived, are expected to be very weak for systems derived from the HUP framework.

Table I shows that most substituents for HUP increase the interlamellar spacing. The largest perturbations are observed with the alkylammonium salts and, as reported previously,[16] indicate that the alkyl chains are oriented substantially in the *c* direction so as to push the layers apart. The much smaller separation with the pyridinium salt suggests that this substituent has little extension in the *c* direction. Modest effects observed with the other substituents may reflect a finer balance between the size of the cation and the perturbation of the H-bonding network that is believed to extend between layers via the O atoms of the PO_4^{3-} groups.[8] Hydrogen bonding could be strongly affected by the changes in hydration stoichiometry that accompany some of the ion-exchange reactions.

With regard to hydration, we should mention that our samples have been prepared and handled under conditions that should correspond to maximum hydration. Table I gives literature hydration values that are approximate for reasons discussed above. We obtained similar values for several of our samples by elemental analysis. IR data (vide infra) also provided a qualitative measure of the extent of hydration.

2. IR Spectra. The IR spectra of HUP and several derivatives, obtained with use of KBr pellets, are presented in Figure 1. Curve A, the HUP spectrum, accords well with previously reported data.[21,22] Dominating this spectrum is an absorption band centered at ~1000 cm^{-1}, which was previously assigned to phosphate stretching modes.[22] The strong sharp band at ~930 cm^{-1} and a much weaker band at ~830 cm^{-1} have been assigned as UO_2^{2+} asymmetric and symmetric stretching modes, respectively.[22] Bands due to water occur at ~3400 and 1620 cm^{-1}, and an asymmetric mode of H_3O^+ is believed to be the origin of the broad band at ~1750 cm^{-1}.[21] As was reported previously,[22] exchange of HUP with metal ions causes little substantive change in the spectrum, although we do see a small decrease in the 1750-cm^{-1} band (loss of H_3O^+) and an increase at 1620 cm^{-1}. Similar changes are observed with the n-$BuNH_3^+$ and n-$OctNH_3^+$ salts, curves B and C, respectively. Additionally, other bands characteristic of the organic species are observed, including several in the 1400–1600-cm^{-1} region which are similar to bands reported for the protonated amines.[23] Bands due to water are still present as well, confirming that the solid is hydrated.

In contrast to all of the other species we examined, the pyridinium salt of HUP appeared from both elemental analysis and its IR spectrum, curve D of Figure 1, to lack water in its structure; the very weak absorption at ~3500 cm^{-1} compared to the phosphate band at ~1000 cm^{-1} is particularly telling. Pyridine, like the alkylamines, introduces new bands into the IR spectrum when it substitutes into HUP. The bands from ~1450 to 1650 cm^{-1} are ring-stretching vibrations and exhibit a pattern very similar to that reported for the pyridinium ion and very different from those reported for free pyridine or metal-bound pyridine.[23,24] These results support the conclusion drawn from the X-ray data (vide supra) that the pyridine rings are roughly perpendicular to the *c* axis; this orientation would permit them to displace water molecules without disturbing the lamellar structure.

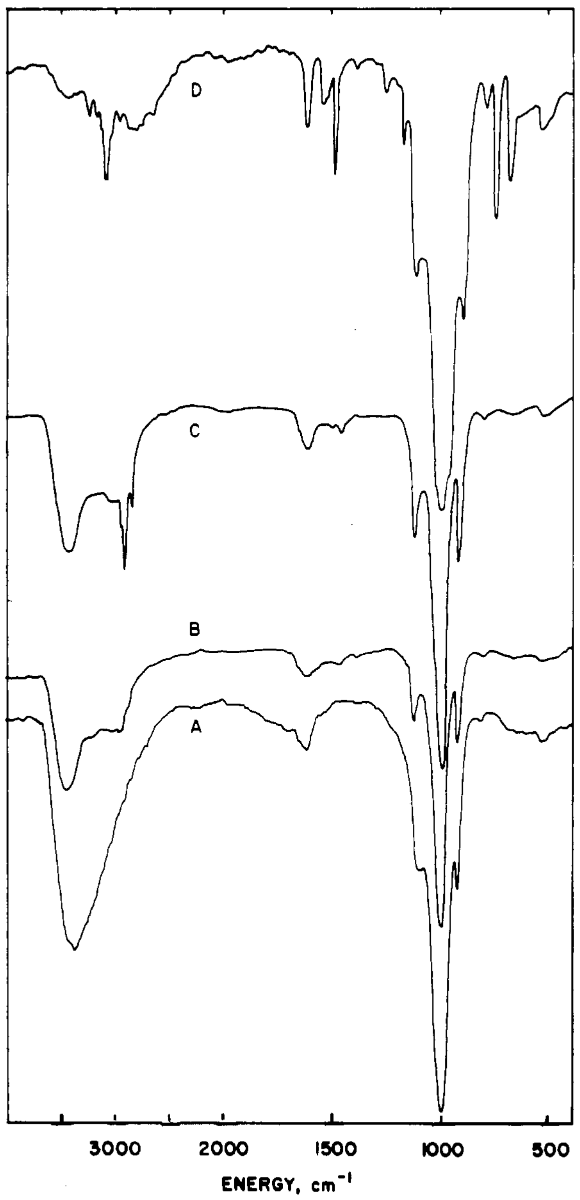

Figure 1. Infrared spectra of (A) HUP, (B) n-$BuNH_3UP$, (C) n-$OctNH_3UP$, and (D) pyHUP. All spectra were obtained at 295 K with use of KBr pellets.

Besides the compounds of Table I, which all yielded the broad, structureless phosphate band at 1000 cm^{-1} characteristic of the uranyl phosphate sheets, we also examined a sample of HUP exposed to the desiccant $CaCl_2$. As reported previously,[22] dehydration causes drastic changes in this spectral region, suggestive of a puckering of the $(UO_2PO_4)_n^{n-}$ sheets;

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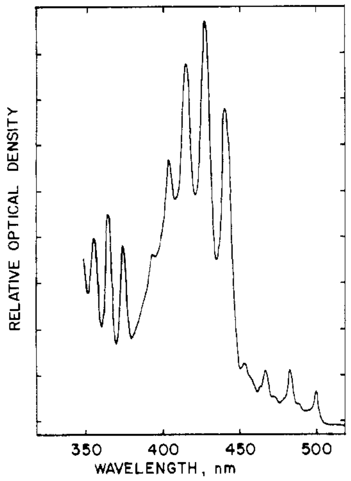

Figure 2. Absorption spectrum of HUP (295 K), obtained as a Nujol mull on filter paper.

a powder pattern of this sample is very much different from that of a hydrated sample. The 1000-cm^{-1} band is thus a fairly sensitive probe of the integrity of the structure. We also examined the intensity ratio of the UO_2^{2+} symmetric and asymmetric stretching bands for all of the Table I compounds; the weak intensity of the symmetric stretching band is consistent with a slight distortion from a centrosymmetric structure. Although overlap with the phosphate bands precluded a quantitative analysis, the intensity ratios appeared roughly similar for all of these compounds, suggesting a similar UO_2^{2+} geometry in all of the samples.

3. Electronic Spectra. With the exception of the Cu derivative, which is blue-green, all of the solids prepared are yellow to yellow-green. This color derives from the spectrum of the UO_2^{2+} moiety, which has a characteristic vibronic structure.[25] As illustrated in Figure 2 for HUP, the spectrum consists of several band envelopes with each envelope containing a progression of sharp peaks. All of our samples, including the Cu derivative, exhibit similar spectra in the 350–500-nm region.

The spectra of solid HUP and its Ca and Cu derivatives have previously been examined in detail at 77 K along with many other UO_2^{2+}-containing compounds.[26a] These studies revealed that several overlapping electronic transitions were present in the 350–500-nm region and that the spectral features were governed by the symmetry of the equatorial ligands. For the near-D_{4h} site symmetry present about U in HUP and its derivatives, three bands were predicted and observed. The spectral pattern and O–O band positions at 19 885 cm^{-1} ($^1A_g \rightarrow {}^1E_g(f)$), 22 635 cm^{-1} ($^1A_g \rightarrow {}^1B_{2g}(f)$), and 26 760 cm^{-1} ($^1A_g \rightarrow {}^1B_{1g}(f)$) reported for the Cu derivative[26] accord well with our data for HUP and its derivatives. Although overlap of the bands complicates a complete analysis, localization of the transitions on the UO_2^{2+} moiety is indicated by the spacings in the vibronic progressions. These average ~700 cm^{-1} and are consistent with an excited-state symmetric stretching mode progression of UO_2^{2+}.[27]

One other noteworthy feature concerns the Cu derivative. Figure 3 shows that the blue-green color arises from a low-energy absorption band with λ_{max} at ~660 nm. There is a second absorption band which is found at ~810 nm. These two bands are similar to those observed in a single-crystal absorption spectrum of the related complex $Cu_{0.5}UO_2AsO_4$.[28] The bands can reasonably be assigned to d–d transitions on the basis of similar bands of other Cu(II) complexes[29] and their low extinction coefficients, ϵ; low values of ϵ are inferred from comparisons with the uranyl bands, whose absorptivities for monomeric solution species are $\lesssim$20 M^{-1} cm^{-1}.[5] Low-energy bands are neither expected nor observed for the other substituents employed, since they are all closed-shell ions.

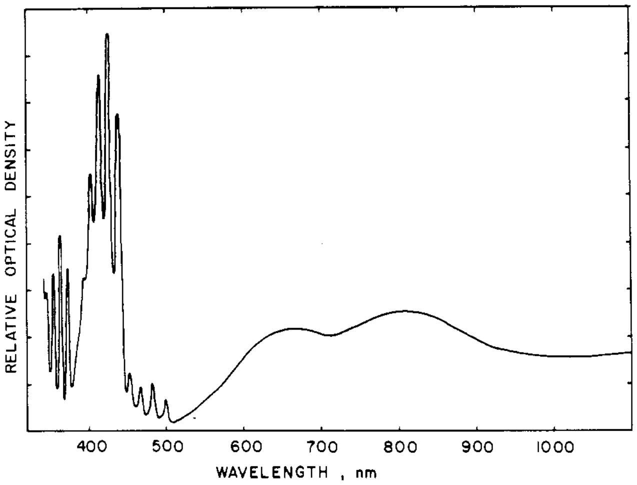

Figure 3. Absorption spectrum of $Cu_{0.42}H_{0.16}UP$ (295 K), obtained as a Nujol mull on filter paper. We are uncertain as to the origin of the absorption beyond ~1000 nm.

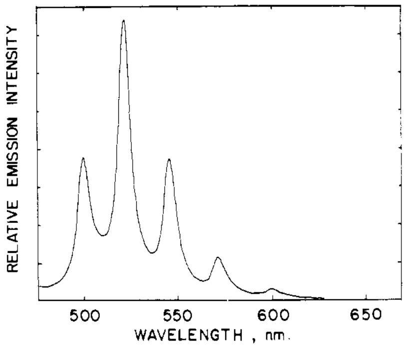

Figure 4. Uncorrected emission spectrum (295 K) of HUP. The powdered sample was excited with 457.9-nm excitation from an Ar ion laser.

4. Emissive Properties. a. Spectral Distribution. We found that HUP and several of its derivatives (NH_4^+ pyH$^+$, *n*-$BuNH_3^+$, K^+, Ca^{2+} and Zn^{2+}) emit at room temperature with blue and near-UV excitation. The yellow-green luminescence observed is characteristic of uranyl salts,[25] and the variation in emissive intensity among compositions may account for the modest color differences encountered (vide supra), the more emissive samples appearing more yellow-green when viewed under fluorescent room lights. Figure 4 presents an uncorrected 295 K emission spectrum of HUP obtained with 457.9-nm Ar ion laser excitation. The spectrum is insensitive to composition for the solids examined under the low-resolution (bandwidth ~5 nm) conditions employed. Figure 4 shows that the spectrum consists of a vibronic progression spanning ~500–630 nm with average spacings between the bands of ~840 cm^{-1}. This energy roughly corresponds to the ground-state uranyl symmetric stretching mode, again suggestive of a transition largely localized on the uranyl moiety. The difference in vibronic spacings found in absorption and emission spectra indicates distortion in the emissive excited

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state relative to the ground-state structure.

We found the emission spectra of HUP, NH_4UP, and $Ca_{0.5}UP$ to be independent of excitation wavelength over the range 350–500 nm. Moreover, we found that excitation spectra of these solids mimic their absorption spectra, indicating that the emissive excited states of these materials are efficiently populated from their upper excited states.

b. Excited-State Kinetics. We obtained lifetimes, τ, and radiative quantum efficiencies, ϕ_r, for all of the emissive solids. The lifetimes were acquired with use of 450-nm excitation from a N_2-pumped dye laser. All of the samples exhibited a simple first-order decay over several lifetimes. Typical values of τ, summarized in Table I, were ~140–450 μs except for the n-$BuNH_3^+$ derivative with a value of ~2 μs. Lifetimes of ~10^2–10^3 μs have been reported for other highly emissive uranyl salts.[30] Previously reported τ values for HUP and related compounds (HUP, 440 μs; KUP, 280 μs; $Ca_{0.5}UP$, 200 μs)[31] either are in good agreement with our values or are somewhat lower; discrepancies may reflect sensitivity to experimental conditions.

Estimates of ϕ_r, defined as photons emitted per photons absorbed, were obtained with use of a technique based on a comparison of light reflected from the samples and from a nonabsorbing standard, MgO powder, in the same geometry.[11] This difference represents photons absorbed by the sample and is divided into the number of photons emitted; intensities are obtained from areas under the appropriate bands, as described in the Experimental Section.

Table I reveals that except for the n-$BuNH_3^+$ derivative with $\phi_r \approx 10^{-3}$, all of the emissive samples have extraordinarily high ϕ_r values approaching unity with 460-nm excitation. Since the error in the technique employed has been estimated as being ±25%,[11] it is difficult to say just how close to unity ϕ_r is for these solids, but they are clearly highly emissive both by eye and by comparison with other efficient emitters such as $[NEt_4]_2[MnBr_4]$.[11] The ϕ_r value for HUP of 0.70 is in reasonable accord with a value of 0.85 previously reported.[31b] A large ϕ_r value is also supported by thermal effects, which can be used to establish an upper limit on ϕ_r: In contrast to many solids for which ϕ_r increases dramatically with declining temperatures,[32] we visually observed only modest increases in emission intensity at 77 K for the most highly emissive samples. We made a more quantitative investigation of the effect by looking for lifetime enhancement at 77 K. Table I reveals that little difference in τ is observed in passing from 295 to 77 K for the highly emissive samples. On the other hand, both the n-$BuNH_3^+$ and n-$OctNH_3^+$ salts exhibited enormous increases in both emission intensity and τ, perhaps related to changes in excited-state chemical reactivity (vide infra). We should note, however, that comparisons at the two temperatures may also reflect structural changes.

The simple unimolecular decay of HUP and its emissive derivatives permits the calculation of their first-order radiative and nonradiative rate constants k_r and k_{nr} by eq 3 and 4. In

$$k_r = \frac{\phi_r}{\tau} \tag{3}$$

$$k_{nr} = \frac{1}{\tau} - k_r \tag{4}$$

terms of these rate constants, $\tau = (k_r + k_{nr})^{-1}$ and $\phi_r = k_r(k_r + k_{nr})^{-1}$.[33] Table I summarizes the calculated k_r and k_{nr} values for the solids examined. We must point out that uncertainties in these values arise not only from experimental uncertainties but also, in some cases, from material properties as well. Several samples of HUP gave slightly lower ϕ_r and τ values. We attribute this to slight variations in the degree of hydration of the samples. HUP emission appears to be particularly sensitive to hydration, being rapidly quenched by exposure to desiccants or to excessive heating; in the latter case, changes in emissive properties were observed when high excitation intensities were employed.

A key result which emerges from Table I is that, for the samples examined, k_r is relatively invariant to composition, being ~(0.8–2.2) × 10^3 s^{-1}. Changes in τ and ϕ_r primarily reflect changes in k_{nr}. Studies with other uranyl salts have established correlations between k_r and the uranyl coordination symmetry, higher symmetries corresponding to smaller rate constants; average k_r values of ~2900, 560, and 440 s^{-1} have been measured for symmetries of D_{2h}, D_{3h}, and D_{4h}, for example.[30] Although our k_r values for the HUP-derived solids appear somewhat high in light of their near-D_{4h} microsymmetry (vide supra), this difference, if significant, may reflect the more asymmetric packing environments of the HUP-derived solids.

c. Quenching Mechanisms. An important feature of the HUP family of solids is that their chemical diversity permits an examination of the factors that influence nonradiative excited-state deactivation. We note, for example, that quenching does not correlate well with the interlamellar spacing: the pyH^+ and Ca^{2+} derivatives emit brightly, but the Ag^+ and n-$OctNH_3^+$ derivatives do not emit at all. There is also no correlation with the oxidation state of the substituent: K^+ and Ca^{2+} luminesce; Ag^+ and Cu^{2+} do not. We also attempted to investigate the role of vibrational modes on nonradiative deactivation by substituting D_2O for H_2O, which has a marked effect on some systems.[34] Although we were unable to prepare a sample with more than 50% incorporation of D_2O (based on IR spectra), the luminescence intensities of partially substituted samples appeared essentially the same as that of HUP.

The variation in luminescent properties with composition shown in Table I is intriguing and reminiscent of solution studies involving the uranyl ion. An important difference, of course, is the steric constraint imposed by the crystal lattice, which can strongly influence emission by, e.g., governing the ability of the uranyl moiety to engage in ground-state and/or excited-state complex (exciplex) formation. The simplest prospective quenchers to treat, in solution studies as well as in this study, are closed-shell ions. Ions such as K^+, Ca^{2+}, and Zn^{2+} have no low-lying excited states with which to quench emission by energy transfer (eq 5), nor are they readily oxidizable so as to permit quenching by electron transfer to the excited uranyl ion, UO_2^{2+*} (eq 6).

$$UO_2^{2+*} + Q \rightarrow Q^* + UO_2^{2+} \tag{5}$$

$$UO_2^{2+*} + Q \rightarrow Q^+ + UO_2^+ \tag{6}$$

As expected, little difference relative to HUP emission is observed with these ions. In solution studies, only minor quenching of uranyl emission by Na^+, Ca^{2+}, and Zn^{2+} was reported and, as with other systems, was thought to involve exciplex formation.[35] A point we should mention in connection with the solid-state data is the potential role of impurities. Although we have no evidence for their presence, trace impurities from the reagents can

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conceivably enter the lattice and influence the solid's emissive properties.

The other transition metals employed, Cu^{2+} and Ag^+, proved to be efficient quenchers, as they were in solution.[35] In principle, both could quench by electron transfer (eq 6), since the excited uranyl ion should be an extremely strong oxidizing agent ($E°$ for $UO_2^{2+*}/UO_2^+ \simeq 2.60$ V vs. NHE;[35] $E°$ for $Ag^{2+}/Ag^+ \simeq 1.98$ V vs. NHE;[36] $E°$ for Cu^{3+}/Cu^{2+} has been estimated as $\gtrsim 1.8$ V vs. NHE[36]). While this seems like a plausible mechanism for Ag^+, we feel that energy transfer (eq 5) is more likely for Cu^{2+}, since it does possess low-lying excited states (Figure 3). If electron transfer does occur, the back-reaction to generate UO_2^{2+} is energetically very favorable ($E°$ for $UO_2^{2+}/UO_2^+ = 0.06$ V vs. NHE[35]) and would be expected to regenerate the original species. We, in fact, saw no change in sample appearance over hour-long irradiation periods.

The other derivatives examined, NH_4^+, pyH^+, n-$BuNH_3^+$, and n-$OctNH_3^+$, ranged from highly emissive to nonemissive. Both the NH_4^+ and pyH^+ derivatives exhibited little quenching relative to HUP, presumably for the reasons invoked for the closed-shell ions. On the other hand, at room temperature, n-$BuNH_3UP$ exhibited emission that was weaker by ~2 orders of magnitude and emission from n-$OctNH_3UP$ could not be detected. Mechanistically, since neither amine has a low-lying excited state, we suspect that quenching proceeds by a photoredox reaction, perhaps analogous to that reported for alcohols in solution (eq 7).[25,37] Such reactions are mechanistically complex. We are presently preparing related amine derivatives of HUP and conducting long- and short-term photolysis experiments to elucidate the quenching mechanism. It is worth noting that at 77 K both the n-$BuNH_3^+$ and n-$OctNH_3^+$ derivatives emit brightly with long lifetimes (Table I). One possible explanation for this low-temperature behavior may be the cessation of a photoreaction such as that described above, perhaps owing to the introduction of steric constraints.

$$UO_2^{2+} + RCH_2OH \rightarrow UO_2^+ + R\dot{C}HOH + H^+ \quad (7)$$

Conclusion

We have shown in this paper that HUP and several of its derivatives prepared by intercalative ion-exchange reactions lend themselves to a systematic examination of excited-state properties. The luminescence exhibited by many of these layered compounds is characteristic of the UO_2^{2+} moiety and serves as a probe of excited-state deactivation processes. Layered compounds in general are receiving considerable attention with regard to intercalation chemistry, yet relatively few studies have examined changes in optical properties accompanying intercalation.[38] The correlations established in this paper suggest that, for suitable hosts, changes in chemical composition accompanying such reactions can be profitably examined by changes in electronic absorption and emission properties. Studies in progress in our laboratories will apply these spectroscopic probes to a broader range of HUP derivatives and reactions.

Acknowledgment. This work was generously supported by the National Science Foundation (Grant CHE-7911218). A.B.E. acknowledges support as an Alfred P. Sloan Fellow (1981–1983). We thank Prof. L. F. Dahl for helpful discussions.

Registry No. HUP, 18433-48-2; NH_4UP, 12161-21-6; pyHUP, 62392-62-5; n-$BuNH_3UP$, 87481-58-1; n-$OctNH_3UP$, 87481-59-2; KUP, 12026-79-8; AgUP, 12244-18-7; $Ca_{0.5}UP$, 68197-84-2; $Zn_{0.5}UP$, 73370-48-6; $Cu_{0.5}UP$, 87462-90-6.

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Spectra and Structure of Organophosphorus Compounds. 22.[†] Microwave, Infrared, and Raman Spectra, Structure, Vibrational Assignment, and Normal-Coordinate Analysis of Methylphosphonothioic Difluoride

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Received October 22, 1982

The microwave spectrum of methylphosphonothioic difluoride, CH_3PSF_2, has been investigated from 18.5 to 39.0 GHz. Both a- and b-type transitions were observed, and R-branch assignments have been made for the ground vibrational state. The rotational constants in the ground vibrational state were found to be $A = 4366.24 \pm 0.03$, $B = 2596.38 \pm 0.01$, and $C = 2496.86 \pm 0.01$ MHz. From a diagnostic least-squares adjustment to fit the rotational constants, the following heavy-atom bond distances were obtained by assuming reasonable structural parameters for the methyl group and skeletal angles: $r(P—C) = 1.809 \pm 0.004$ Å, $r(P—F) = 1.547 \pm 0.003$ Å, and $r(P{=}S) = 1.878 \pm 0.003$ Å. The infrared (3500–40 cm^{-1}) and Raman (3500–10 cm^{-1}) spectra have been recorded for both the gaseous and solid phases of CH_3PSF_2. Additionally, the Raman spectrum of the liquid was recorded and qualitative depolarization values were obtained. All of the normal modes have been assigned on the basis of infrared band contours, depolarization values, and group frequencies. A normal-coordinate calculation has been carried out by utilizing a modified valence force field to calculate the frequencies and the potential energy distribution. All of these results are compared to similar quantities in some corresponding molecules.

Introduction

Although we have recently carried out a number of spectroscopic studies of compounds containing the difluorophosphine (PF_2) moiety, notably HPF_2,[1] CH_3POF_2,[2,3] PF_2CN,[4] CH_3PF_2,[5] $CH_3CH_2PF_2$,[6] and $(CH_3)_2CHPF_2$,[7] very few compounds with the phosphorus lone pair coordinated with a sulfur

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[†] For paper 21 in this series, see: J. R. Durig, A. E. Stanley, and Y. S. Li, *J. Mol. Struct.*, **78**, 247 (1982).

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