chains, and the average number of d electrons per metal is $^2/_3$. In contrast, our electron-counting scheme based upon **4** leads to one d electron per metal ion. In agreement with this counting, the d_{z^2} band of MTe_4 is found to be $^1/_2$ filled in the present calculations. Our study suggests that the three CDW's originate from a Fermi surface consisting of four sets of two nearly flat pieces such as shown in Figure 5. Note from Figure 3 that the energy dispersion of the d_{z^2} band is quite significant along the interchain direction (e.g., Z → A and R → A). It is this kind of substantial interchain interaction that leads to the Fermi surface of Figure 5.

Concluding Remarks

MSe_4 chains of $(MSe_4)_nI$ compounds have each metal ion located at the center of an antiprism made up of two *rectangular* Se_4 units (**2**), where each Se_4 unit can be regarded as consisting of two Se_2^{2-} dimers. However, MTe_4 chains of binary compounds MTe_4 have each metal ion located at the center of an antiprism made up of two *square* Te_4 units (**3**). Unlike the case of MSe_4 chains in $(MSe_4)_nI$,[2a] the shortest interchain Te–Te distance in MTe_4 is *shorter* than the side of a square Te_4 unit within a MTe_4 chain. Consequently, the crystal structure of MTe_4 can be better represented as in **4**, which leads to the view that in MTe_4 each metal ion M^{4+} (d^1) is surrounded by eight Te_2^{2-} dimers. The band structure of MTe_4 shows the presence of a $^1/_2$-filled d_{z^2} band that gives rise to the Fermi surface with two nearly flat pieces (Figure 5). From such a Fermi surface, one can derive three CDW nesting vectors, which are in reasonable agreement with experiment. Our study shows that multidimensional character is much stronger in MTe_4 than in $(MSe_4)_nI$.

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Photophysical Studies of Uranyl Complexes. 4. X-ray Photoelectron and Luminescence Studies of Hydrolyzed Uranyl Salts

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The solid-state hydrolysis products of uranyl ion, UO_2^{2+}, have been studied with use of X-ray photoelectron and luminescence spectroscopy. The products, consisting of uranium oxides and various forms of uranyl hydroxide, gave "averaged" uranium 4f photoelectron binding energies of 381.5–381.8 eV and oxygen 1s binding energies of 530.8–531.9 eV. Evidence for carbon dioxide chemisorption from the atmosphere was observed by monitoring the carbon 1s line for samples that had been exposed to the atmosphere for extended periods of time. The luminescence spectra of all sets of hydrolysis products were essentially identical, consisting of two well-defined, broad peaks at 10 K. The luminescence lifetimes of each pair of bands were found to be identical within experimental error. A lifetime of 100–115 μs was observed for most samples, yielding a ground-state vibrational energy of 700–730 cm^{-1}. For other products, the emission lifetimes were significantly smaller, giving ground-state vibrational energies of less than 700 cm^{-1} and implying that counterion interactions were operable in several of the hydrolysis product mixtures.

Introduction

The solid-state hydrolysis products of uranium have been the subject of several studies. The compounds, formed by the hydrolysis of uranyl salts by bases such as sodium and ammonium hydroxide, exhibit variable chemical compositions that are heavily dependent on the method of preparation. Parameters that have been shown to affect these compositions include aging of the precipitates under carefully controlled conditions approaching equilibrium,[1] temperature,[2] or pressure[3] experienced by several forms of the solid hydrolysis precipitates, and the hydroxide/uranium ratio used.[1] As a result, not only are different chemical compositions formulated for these compounds (among them, $Na_2O·8UO_3$,[4] $Na_2U_7O_{22}$ (uranates),[1] $U_3O_8(OH)_2$,[5] and $3UO_3·NH_3·5H_2O$[6]), but also mixtures of various pure compounds almost always result in these precipitates. The chemistry of many of the compounds in these hydrolysis product mixtures has been discussed extensively in a review,[7] however, and several have been structurally documented as being true uranyl hydroxides; uranium oxides have also been shown to be present in the mixture of hydrolysis products.[5]

The present study is one that further attempts to obtain a clear and more complete picture of the chemistry of this mixture of compounds that comprise the hydrolysis products of the uranyl ion. By the use of both X-ray photoelectron and luminescence spectroscopy, along with other characterizational techniques such as energy dispersive X-ray and infrared spectroscopy, mass spectrometry, and scanning electron microscopy, a more complete physical chemistry and analytical picture of the aqueous hydrolysis products can be obtained.

Experimental Section

Because of the rather large number of compounds and compound mixtures produced by varying the preparative procedure, two standard sets of products were prepared and used for all measurements for the present study. First, two different concentrations of the uranyl ion solution being hydrolyzed were used in order to determine if there was any initial uranyl ion solution concentration dependence on the

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final product. Second, variable counterions such as chloride, nitrate, and acetate were used in preparing the uranyl solutions at the two different concentrations so as to check for an anion dependency. The same hydrolysis precipitate for a given synthetic route was used to perform all analyses and spectroscopic studies in order that data for a particular preparation were comparable to those data for other different synthetic routes.

All hydrolysis products were produced by the slow, dropwise addition of a 1.0 M aqueous solution of sodium or ammonium hydroxide to a vigorously stirred solution of either a 0.1 or 1.0 M solution of uranyl chloride, nitrate, or acetate. The addition of base was continued until all precipitation had ceased. The samples were then filtered on a Buchner funnel, washed with cold, distilled, deionized water in order to remove any unreacted base or uranyl salt, and allowed to air dry on the filter bed. Elemental analyses were performed by the microanalytical laboratory of the chemistry department at the University of California, Berkeley, CA. The analytical data for the series of commpounds used in the present studies were as follows:

Anal. Found for sample A (hydrolysis of 0.1 M $UO_2(NO_3)_2\cdot 6H_2O$ with 1.0 M NaOH): U, 71.1; Na, 3.14; C, 0.03; H, 0.97. % U/% Na = 22.64. Found for sample B (hydrolysis of 0.1 M $UO_2Cl_2\cdot 3H_2O$ with 1.0 M NaOH): U, 73.1; Na, 3.66; C, 0.04; H, 0.91. % U/% Na = 19.97. Found for sample C (hydrolysis of 0.1 M $UO_2(CH_3COO)_2\cdot 2H_2O$ with 1.0 M NaOH): U, 70.6; Na, 4.38; C, 0.03; H, 0.97. % U/% Na = 16.11. Found for sample D (hydrolysis of 1.0 M $UO_2(NO_3)_2\cdot 6H_2O$ with 1.0 M NaOH): U, 72.2% Na, 4.32; C, 0.05; H, 0.98. % U/% Na = 16.71. Found for sample E (hydrolysis of 1.0 M $UO_2Cl_2\cdot 3H_2O$ with 1.0 M NaOH): U, 71.4; Na, 3.48; C, 0.04; H, 0.97. % U/% Na = 20.52. Found for sample F (hydrolysis of 1.0 M $UO_2(CH_3COO)_2\cdot 2H_2O$ with 1.0 M NaOH): U, 72.3; Na, 3.56; C, 0.03; H, 0.92. % U/% Na = 20.31. Found for sample G (hydrolysis of 0.1 M $UO_2(NO_3)_2\cdot 6H_2O$ with 1.0 M NH_4OH): U, 72.9; C, 0.05; N, 1.38; H, 1.33. % U/% N = 52.83. Found for sample H (hydrolysis of 0.1 M $UO_2Cl_2\cdot 3H_2O$ with 1.0 M NH_4OH): U, 71.2; C, 0.04; N, 1.35; H, 1.36. % U/% N = 52.74. Found for sample I (hydrolysis of 0.1 M $UO_2(CH_3COO)_2\cdot 2H_2O$ with 1.0 M NH_4OH): U, 71.7; C, 0.06; N, 1.35; H, 1.37. % U/% N = 53.11.

Infared spectra were obtained as both Nujol mulls and KBr pellets on a Perkin-Elmer Model 283 infrared spectrometer. Scanning electron microscopy data were taken with an AMR Model 1000 scanning electron microscopy equipped with an energy dispersive X-ray spectrometer. Variable-temperature mass spectra of the solids were obtained by a heated inlet on an AEI Model MS 12 mass spectrometer utilizing an electron beam energy of 70 eV. A McPherson Model 36 spectrometer using Mg Kα radiation (1253.6 eV) was used to collect X-ray photoelectron spectra. The photoelectron peaks were fitted with use of a nonlinear least-squares fitting program incorporating both Gaussian and Lorentzian curves (CURVY, developed by Prof. W. L. Jolly and A. Bakke, Department of Chemistry, University of California, Berkeley, CA), and all binding energies were charge referenced to the contaminant (adventitious) carbon 1s line with use of a value of C 1s equal to 284.6 eV. Finely powdered samples were dusted on Scotch-brand tape and checked visually for decomposition after each set of spectra was obtained, but none was detected. The stability of the samples to radiation was further corroborated by the spectra being time independent within the time frame for collecting data. X-ray powder diffraction data were taken with a Debye–Scherrer powder camera (114.6 mm) using Cu Kα radiation.

All luminescence spectra were obtained on a high-resolution spectrometer. The samples were excited by the 325-nm output (10-mW power) of a He–Cd laser (Liconix), with all the plasma lines being filtered out by a UV-transmitting filter. The emission was collected at 90° to the exciting beam and analyzed by a 1-m grating monochromator (Spex Model 1704). All data were obtained at 5 Å resolution, and further increases in resolving power of the system did not yield further improvement in the emission features. The luminescence was finally detected by a cooled (−20 °C) photomultiplier tube (EMI Model 9558, S-20 response); the output current was converted to voltage on the Spex digital photometer and displayed on a strip-chart recorder.

None of the uranyl hydrolysis products exhibited luminescence at room temperature, but cooling the samples to 77 K did lead to the observation of measurable emission in the green region of the spectrum. Further cooling of the samples to 10 K in a closed-cycle refrigator system (Lake Shore Cryotronics Model LTS-21) provided the maximum luminescence quantum yields. The samples were found to be quite photosensitive; accordingly, each determination of any spectroscopic property was repeated a minimum of three times on a fresh sample. The photodecomposition proved to be most efficient in the high vacuum of the refrigerator system, and a comparison of the photodecomposed material with known uranium oxides indicated that the photoreaction was probably a dehydration of the hydrolysis product.

Measurements of the emission lifetimes of the uranyl hydrolysis products were obtained by exciting the samples with a pulsed UV source, converting the photomultiplier current to voltage via a 200-kΩ load resistor, and then photographing the decay curve off a storage oscilloscope. The source of UV pulses was a nitrogen laser (200-kW output in 300 ps at 337 nm), and the decay curves were processed to yield the luminescence decay time with standard least-squares analysis. The lifetime of each peak in the emission spectrum was obtained separately and found to be identical within experimental error for a given compound. In no case was it found that the decay curves contained anything other than a simple exponential decay.

Results and Discussion

As expected, the complexes that resulted from the hydrolysis of the parent uranyl salts were of variable composition with respect to uranium oxide, uranyl hydroxides, cations such as sodium and ammonium, and water. Elemental analyses showed the precipitates to contain variable amounts of sodium or ammonium cations, while the thermolysis of the solids (monitored by mass spectrometry) also showed a variable water content for each of the samples. The elemental analyses were consistent with varying amounts of products of the type $UO_2(OH)_2\cdot xH_2O$ and $UO_3\cdot xH_2O$ for the base-effected hydrolysis products, with small amounts of sodium and ammonium ions being occluded in the lattice. X-ray photoelectron, infrared, and luminescence data (discussed below) also supported formulas of these types. When the initial precipitates were examined by energy dispersive X-ray spectroscopy and elementally mapped, some segregation of the sodium ion in the bulk was observed; accordingly, all samples were ground with an agate mortar and pestle before spectroscopic measurements were made in order to assure a homogeneous bulk sample.

The analytical data for the NH_4OH-effected hydrolysis products were consistent with the previously reported complex of stoichiometry[8] $3UO_3\cdot NH_3\cdot 5H_2O$;[6] again, however, this principal product was also found to be a mixture of forms of $UO_2(OH)_2$ and UO_3 contaminated with the ammonium cation, and the amount of water again varied from sample to sample.

All attempts to prepare one synthtically pure sample of uranyl hydroxide product that was contaminant free were unsuccessful. All NaOH-hydrolysis compounds contained approximately 3–5% sodium, regardless of the rate at which NaOH was added to the solution of the parent salt, the concentration of the parent salt, or the anionic counterion. The sodium and ammonium cations could only be faintly detected in the X-ray photoelectron spectra. The only exception to this was the hydrolysis of $UO_2Cl_2\cdot 3H_2O$, in which the final hydrolysis product also always contained traces (1% or less) of the chloride ion. An examination of infrared spectra, wet chemical analyses, and other analytical and spectroscopic data failed to show any acetate or nitrate species after hydrolysis. X-ray photoelectron spectra gave no evidence for these anions on the surface, the only exception being the carbonate discussed below. The most consistently reproducible analytical

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results were obtained for the NH_4OH-effected compound; the hydrogen and nitrogen analyses, for example, were virtually identical for all three samples studied here. Also, the X-ray photoelectron and luminescence spectral data discussed below would be consistent with minor amounts of other hydrolysis products being present as contaminants. Previous reports[5] have noted that small changes in the structures of some of the hydrolysis products studied here can occur without being detected in the X-ray diffraction patterns. These changes would result in minor products that could not be easily detected.

Attempts were also made to synthesize a single, pure sample of $UO_3 \cdot 2H_2O$ by using the technique of utilizing $La(OH)_3$ as the hydrolyzing base.[5] While indeed a fairly high-purity compound could be obtained, there was always a certain amount of lanthanum present in the sample (in agreement with the results of the previous investigators[5], which could be detected by X-ray photoelectron spectroscopy. Accordingly, these samples were not used, since any oxygen 1s or other photoelectron line might reflect oxygen species associated with the lanthanum rather than only those related to the uranium.

In agreement with the results reported by previous investigators,[5] the initial precipitates consisted of the β and γ forms of $UO_2(OH)_2$[9–11] and $UO_3 \cdot 2H_2O$.[5,8] Infrared and X-ray powder diffraction data were in excellent agreement with those previously reported for the compounds. Additionally, grinding the sample in a mortar and pestle also produced α-$UO_2(OH)_2$, a modification transformation documented by the same workers.[5] It was also assumed that lowering the temperature to the cryogenic temperatures used in the luminescence studies, coupled with the mechanical grinding effects, changed β- and γ-$UO_2(OH)_2$ to α-$UO_2(OH)_2$, an effect also observed before.[5] Also, dehydration of $UO_3 \cdot 2H_2O$ to form γ-UO_3[5] apparently occurred under the vacuum conditions of both the luminescence and the X-ray photoelectron experiments, since the X-ray photoelectron spectra reported below for several of the samples were virtually identical with those reported previously for that compound. There is no way of knowing if this dehydration was complete or if it involved both waters of hydration and any hydroxyl groups in the compound. In light of the ground-state vibrational energy values and excited-state emission lifetimes discussed below in the luminescence results, it also seemed that there was decomposition (presumably through dehydration, also) of the uranyl hydroxide species to a uranium oxide such as uranate. The interconversion between forms of the uranyl hydroxides and uranium oxides has been discussed in detail.[12] In all other measurements taken on ground samples at room temperatures, the data were thus assumed to be a mirror of all three forms of uranyl hydroxide as well as these uranium oxides (or uranates[8]).

As a result of the lack of exact reproducibility in preparation of the samples, a set of samples was prepared in which three parameters were varied: initial concentration of the uranyl ion solution, the counterion used with the uranyl ion, and the base used to hydrolyze the uranyl ion. These samples were then used for the present study in which all spectroscopic studies were conducted on the *same* preparative batch of that sample. Unlike many previous studies involving this class of compounds, data taken with use of one technique could then be directly compared to the data collected with use of another technique.

Table I. Binding Energies[a–c] of Uranyl Salts and Their Hydrolysis Products

sample	O 1s[c]	U $4f_{7/2}$[c]	U $4f_{5/2}$[d]
$UO_2Cl_2 \cdot 3H_2O$	531.9 (2.3)	382.3 (2.4)	393.0 (2.4)
$UO_2(NO_3)_2 \cdot 6H_2O$	532.1 (2.8)	382.1 (3.9)	392.8 (3.9)
$UO_2(CH_3COO)_2 \cdot 2H_2O$	531.9 (2.4)	382.5 (3.2)	393.3 (3.3)
A	530.8 (2.8)	381.5 (2.9)	392.3 (2.6)
B	530.8 (2.6)	381.5 (2.9)	392.4 (2.5)
C	531.1 (3.0)	381.8 (2.7)	392.6 (2.7)
D	531.1 (3.0)	381.8 (2.6)	392.5 (2.5)
E	531.0 (2.9)	381.8 (2.8)	392.4 (2.6)
F	530.9 (3.1)	381.6 (2.5)	392.4 (2.4)
G	530.8 (2.9)	381.7 (2.6)	392.2 (2.6)
H	531.2 (3.0)	381.8 (2.7)	392.0 (2.6)
I	531.9 (3.0)	381.8 (2.7)	392.4 (2.6)

[a] In eV. [b] Calibrated against the adventitious carbon line taken as C 1s = 284.6 eV. [c] Reproducibility ±0.2 eV for three samples. [d] Numbers in parentheses represent the full width at half-maximum (fwhm) of the photoelectron line, in eV.

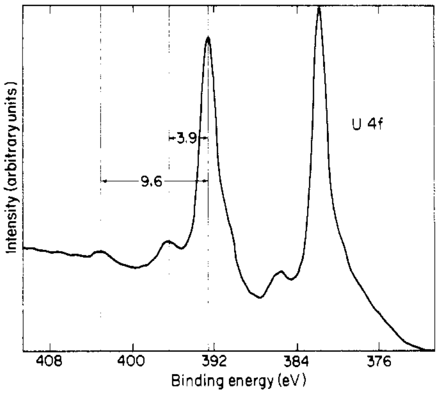

Figure 1. The uranium $4f_{5/2}$ and $4f_{7/2}$ photoelectron lines and associated satellite structure of sample E (hydrolysis of 1.0 M $UO_2Cl_2 \cdot 3H_2O$ with NaOH).

X-ray Photoelectron Spectroscopy. Values of the binding energies for the series of hydrated uranium oxides and uranyl hydroxides are given in Table I, along with the binding energies of the parent uranyl salts. The oxygen 1s and uranium 4f spin–orbit doublet (as shown in Figure 1) are reported, along with the line widths (fwhm). Particular attention was given to the satellite structure associated with the 4f levels of several of the samples and their location relative to the main peaks. These principal peak–satellite patterns have been compared to previously reported data concerning uranium photoelectron lines of uranium oxides.

Uranium 4f Lines. The maximum $4f_{7/2}$ binding energies for the hydrolysis products exhibited a narrow range of values of 381.5–381.8 eV. These values agreed quite well with the ones reported by Teterin et al.[13] (382.0 eV) and Allen et al.[14] (381.7 eV) for uranium(VI) oxide species such as γ-UO_3.[15] In light of the rather marked effect on binding energies of the uranium 4f level that a variation in the water content of uranium–oxygen systems will exhibit,[16] the large variation of hydration for this oxide,[17] and the presence of the uranyl hydroxides, this small range of only 0.3 eV was somewhat surprising. The

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half-widths of these lines ranged from 2.5 to 2.9 eV, considerably less (except in the case of $UO_2Cl_2{\cdot}3H_2O$) than the line widths of the parent, nonhydrolyzed salts. Surface charging from the hydrolysis products was somewhat minimal, ranging from ~1.5 eV for the NaOH-effected products (relative to the adventitious carbon 1s line at 284.6 eV) to less than 1 eV for the NH_4OH-effected ones. The line width for the uranium $4f_{7/2,5/2}$ peaks could thus be considered due to a composite peak formed by the electronic states of the uranium hydroxide and oxide species.

Another characteristic of the uranium 4f spectrum that was helfpul in establishing the electronic character of the central uranium species was that of the satellite structure found on the high-binding-energy side of the principal photoelectron lines. Pireaux and co-workers[18] and other investigators[13] have shown that these satellites (due to charge transfer from the ligand oxygen–uranium bonding band, of dominant oxygen 2p character, to the empty uranium 5f level[19,20] can be used to "fingerprint" the oxidation and chemical species state of uranium present in a number of oxides and other compounds.[21] In the present set of hydrolysis products, this area of the spectra of the uranium $4f_{7/2}$ and $4f_{5/2}$ regions consists of either poorly defined or weak peaks for most of the samples which could not be fitted by the least-squares program (nonconvergence). Two samples, however, B and E, exhibited pronounced doublets in this area. The spectrum of B contained peaks at 3.8 and 9.9 eV, while the spectrum of E contained peaks at 3.9 and 9.6 eV (Figure 1). The satellite features shown in Figure 1 would be in very good agreement[13] with a hydrated γ-uranium(VI) oxide if the assumption were made that variation of the chemical environment or coordination sphere of the dioxouranium(VI) metal ion center or hydration could shift the satellite positions. These satellites have been shown to vary widely as a function of the various oxides of uranium,[13] and the positions of the satellites in the spectra of B and E are virtually identical with those reported for γ-UO_3.[13] Thus, the satellite data were in excellent agreement with the oxygen 1s data below. The effect on these satellites of varying the amounts of contaminants such as sodium or ammonium ions in a systematic fashion is unknown. Unfortunately, there was no way to systematically study this effect in the present series of products, since the amount of sodium or ammonium ion remained essentially constant for this type of precipitate and could not be changed as a function of the preparative technique. Indeed, it is highly probable that interaction effects involving trace species such as the ammonium cation were responsible for the lack of these satellites in the NH_4OH-effected hydrolysis as well as the variations in the line widths and binding energies of the uranium 4f lines. These effects were apparently operable in the luminescence processes discussed below.

Oxygen 1s Lines. The oxygen 1s binding energies for the hydrolysis products, shown in Table I, ranged from 530.8 to 531.9 eV for the averaged photoelectron lines. Their line width was approximately 3.0 eV, somewhat broader than those of either the parent $UO_2Cl_2{\cdot}3H_2O$ or $UO_2(CH_3COO)_2{\cdot}2H_2O$ salts.[22] In the case of the oxygen lines for the NaOH-effected hydrolysis products, this line could be deconvoluted into two separate lines (Table II). The first line, at a binding energy of ~531.5 eV, was consistent with an hydroxyl group and could be readily assigned to the hydrated forms of the $UO_2(OH)_2$ species which contain true hydroxide species.[9-11] A photoelectron line with this binding energy, however, could also be assigned to species such as hydrated UO_3 and was in excellent agreement with the value of 531.1 eV previously reported for this hydrate[13] as well as oxide layers resulting from the chemisorption of oxygen onto uranium metal.[23] Thus, this particular line appeared to be a component of the oxygen 1s spectrum of both the several forms of uranyl hydroxide and uranium(VI) oxide. This oxygen line at ~531.5 eV was the predominant line in each of the doublets (Table II), indicating its importance to the overall photoelectron line.

Table II. Binding Energies[a-c] of the Deconvoluted Oxygen 1s Photoelectron Lines of NaOH-Promoted Uranyl Hydrolysis Products

sample	O 1s (I)[d]	O 1s (II)[e]	width[f]	area ratio (I:II)
A	*g*	*g*	*g*	*g*
B	530.4	531.1	2.3	1:2.2
C	530.1	531.5	2.1	1:1.7
D	530.2	531.4	2.3	1:2
E	530.2	531.5	2.3	1:1.4
F	530.2	531.3	2.7	1:1.7

[a] In eV. [b] Calibrated against the adventitious carbon line taken as C 1s = 284.6 eV. [c] Reproducibility ±0.2 eV for three samples. [d] Lattice "oxide" value; see text. [e] Lattice "hydroxide" value; see text. [f] Full width at half maximum, fwhm, in eV. [g] Could not be fitted as two peaks.

The second line in the oxygen 1s doublet, with a binding energy of 530.1–530.4 eV, could also be attributed to a lattice oxide species such as γ-UO_3[24] and other lattice oxides such as contained in uranates,[8] this binding energy value having also been reported for a number of uranium oxides such as U_4O_9. These oxide spectra also exhibited a higher binding energy component at ~531 eV. Doublet oxygen spectra such as these observed for the uranium hydrolysis products have been reported for other metal–oxygen systems in which both lattice oxide and hydroxide species are known to exist, i.e., CoOOH[25] and γ-FeOOH.[26] This doublet has also been reported for mixed-metal oxides that have hydroxide functional groups chemisorbed on the surface.[27] One should note that the ratio of the two lines in the oxygen doublet was not constant, reflecting the variation of the composition of the hydrolysis products with respect to the uranium oxides, hydroxides, and possible decomposition products.

One other factor that almost undoubtedly affected the line shapes, areas, and binding energies of the oxygen 1s spectra of the uranium hydrolysis products was the extensive variation of the water content of the samples. Previous researchers[14] have indicated that varying the water content of uranium oxides has a dramatic effect on the oxygen 1s lines. The dehydration of γ-UO_3, known in a wide variety of hydrated forms,[15] was difficult to effect in that study, with a concomitant deoxygenation of the sample also occurring. The resulting oxygen binding energy of that oxide was more than 1 eV lower than those of the other uranium oxides in the series. A certain contribution from bulk capillary water, which is removed by some distance from the immediate hydrolysis product surface,

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(22) The oxygen 1s binding energies for these hydrated parent uranyl salts are actually an average of the binding energies of the oxygen in different bonding environments within the molecule. In these two salts, the oxygen is present in the uranyl, acetate or nitrate, and water components; consequently, the core 1s photoelectron lines should reflect these bonding differences and thus form a composite, or "average", binding energy for each compound.

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to the oxygen binding energy was also possible; this has been reported for the hydrolysis products of iron(III) in which peak broadening was observed.[28]

One other point concerning the interpretation of the oxygen 1s photoelectron spectra should be noted. The average binding energy in Table I for a given hydrolysis product varied from 530.8 to 531.9 eV. This range of values encompassed the set of binding energies that are usually observed in the 531.0–531.6-eV range[29] and assigned to the carbonate functional group. The actual O 1s binding energy for a typical uranyl carbonate such as $K_4UO_2(CO_3)_3$ is 530.6 eV,[30] which also coincides with the "oxide" component of the doublets tabulated in Table II. Because of the basicity of the uranium hydrolysis products studied here, chemisorption of carbon dioxide from the atmosphere by the samples and subsequent complexation as a uranyl carbonate cannot be precluded. Other researchers[31] have observed the absorption of CO_2 by other basic actinide complex surfaces such as plutonium(IV) polymers formed by the NaOH-effected hydrolysis of plutonium(IV) salts in aqueous solutions; this in effect forms Pu(IV) carbonate complexes as surface layers.

Indeed, there was tentative evidence in this study to support such a phenomenon with the present series of hydrolysis products. First, the elemental analyses always indicated a certain amount of bulk carbon to be present in the samples, the carbon content increasing slightly upon standing in the open air for several weeks. Second, small infrared bands or inflections at 890 and 1350 cm^{-1} that appeared in the spectra of the Pu(IV) polymers also appeared in the infrared spectra of the uranyl hydroxide samples studied here. A reaction of this type should not be unexpected for the basic uranium hydrolysis products studied here, especially in light of their similarity to the Pu(IV) polymers. Also, many metal hydroxides such as $Pb(OH)_2$ also exhibit carbonate layers in their X-ray photoelectron spectra.[32]

When studying the oxygen 1s spectra of compounds such as the present ones in this study and attributing photoelectron lines to different chemical environments, one should thus take several precautions to prevent incorrectly assigning a carbonate species as a surface oxide or hydroxide. First, in the case of a dioxouranium(VI) species, one should look at the shake-up satellites of the uranium 4f photoelectron lines as discussed above. In the case of the $UO_2(CO_3)_3^{4-}$ complex, the satellites are at 3.8 and 10.6 eV to the high-binding-energy side of the main $4f_{5/2,7/2}$ peaks, these are considerably different from those observed from γ-UO_3 and other uranium oxides.[13,14] A rigorous attempt should be made to ensure that these satellite lines cannot be attributed to any other uranium carbonate species as well. Second, and more importantly, the carbon 1s region of the spectrum should be checked for the presence of a peak attributable to a carbonate layer. This peak will typically exhibit a binding energy ~3 eV higher than that of adventitious carbon.[29] In the present research, all samples were observed to be free of this line before data were collected.

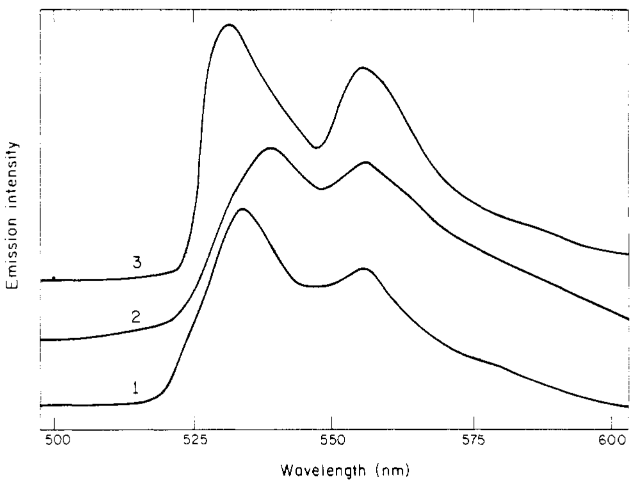

Figure 2. Luminescence spectra obtained for the uranyl ion hydrolysis products prepared from uranyl nitrate hexahydrate, $UO_2(NO_3)_2{\cdot}6H_2O$: (1) sample A (hydrolysis of 0.1 M $UO_2(NO_3)_2{\cdot}6H_2O$ by NaOH); (2) sample D (hydrolysis of 1.0 M $UO_2(NO_3)_2{\cdot}6H_2O$ by NaOH); (3) sample G (hydrolysis of 0.1 M $UO_2(NO_3)_2{\cdot}6H_2O$ by NH_4OH).

Table III. Uranyl Hydrolysis Product Luminescence Data

sample[a, b]	wave-length max, Å	wave-length energy, cm^{-1}	emission lifetime, μs	ground-state energy separation, cm^{-1}
A (NO_3^-, 0.1 M)	5334	18 749	102 ± 2	734
	5551	18 015		
B (Cl^-, 0.1 M)	5373	18 611	115 ± 3	646
	5566	17 965		
C (CH_3COO^-, 0.1 M)	5409	18 488	102 ± 2	705
	5623	17 783		
D (NO_3^-, 1.0 M)	5379	18 592	78 ± 2	561
	5546	18 031		
E (Cl^-, 1.0 M)	5327	18 772	99 ± 4	557
	5490	18 215		
F (CH_3COO^-, 1.0 M)	5411	18 480	87 ± 1	604
	5594	17 876		
G (NO_3^-, 0.1 M)	5331	18 758	103 ± 3	722
	5545	18 036		
H (Cl^-, 0.1 M)	5351	18 688	74 ± 3	516
	5503	18 172		
I (CH_3COO^-, 0.1 M)	5399	18 522	100 ± 3	700
	5611	17 822		

[a] The uranyl counterion and the concentration $[UO_2^{2+}]$ of the hydrolyzed solution are in parentheses. [b] Samples A–F were hydrolyzed with 1.0 M NaOH, while G–I were hydrolyzed with 1.0 M NH_4OH.

Luminescence Spectroscopy. The luminescence associated with the uranyl hydrolysis products was fundamentally different from that obtained in similar studies on the parent uranyl ion salts. Whereas the luminescence spectrum of uranyl nitrate hexahydrate at cryogenic temperatures consisted of a series of well-defined sharp emission bands,[33] the analogous spectra of the hydrolysis products obtained from uranyl nitrate were fairly broad in character and did not contain any vibration fine structure and the wavelengths of the emission were considerably red shifted relative to the spectrum of the uranyl salts. Representative spectra of three hydrolysis products obtained from uranyl nitrate may be seen in Figure 2. The inability to resolve the vibronic structure indicated a disordered solid;[34] this was not surprising in view of the dehydration that possibly occurred under the vacuum conditions of the experiment.

Furthermore, while the luminescence spectra of uranyl nitrate,[33] chloride,[35] and acetate[36] were all dissimilar, the spectra of the three hydrolysis products obtained from each of these sources were essentially identical. In each case, the

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line shape observed was that shown in Figure 2. Each spectrum contained two well-defined peaks, which actually were quite broad in comparison to those of the luminescence spectra of most uranyl salts at these cryogenic temperatures (10 K). The spectra did exhibit qualitative differences in that the wavelength maxima of the peaks varied somewhat with the identity of the counterion present in the original uranyl salt used to prepare the hydrolysis product and with the nature of the base used to hydrolyze the uranyl ion. The wavelength positions of the observed luminescence maxima and the energies of these have been collected in Table III.

A fundamental question that must be answered concerned whether both peaks observed in the emission spectrum of a given hydrolysis product actually originated from the same uranium species or whether they reflected the presence of different uranyl species. This question could be resolved by measurement of the emission lifetime associated with each band. The luminescence lifetime was observed at each of the maxima listed in Table III, and it was found that in every case the lifetimes of both peaks were absolutely identical within experimental error. The lifetimes may also be found in Table III. This observation provided very strong evidence to indicate that the two luminescence peaks observed in the spectrum of each hydrolysis product were due to emission from a single emitting uranium species and did not reflect the presence of multiple emitting species in the hydrolysis products. This emission must be presumed to come from γ-UO_3, the α-$UO_2(OH)_2$[10] resulting from the low temperature, or some other type of octahedral uranate decomposition product (see below).

Given that the two peaks listed in Table III for each uranyl species originate from the luminescence of a single uranyl species, one is then able to interpret the energy spacing between the peaks as reflecting a ground-state vibrational energy associated with one of the species. In simple uranyl salts, this progression is based on the totally symmetrical uranyl ion stretching mode, and energy values for this mode have been tabulated by these workers for a variety of uranyl salts.[33] For the simple salts, an average value of 860 cm^{-1} was obtained. The energy differences obtained from the spectra of the hydrolysis products are shown in Table III, and it may be immediately seen that all ground-state vibrational energies were significantly smaller than those obtained for the uranyl salts.

With both uranyl nitrate and acetate, three emission band systems were found; they exhibited origins at approximately 486, 507, and 530 nm.[33,36] A comparison of these values to those shown in Table III for the hydrolysis products reflected the degree of red shifting that the luminescence had undergone. The lifetime values were also significantly shorter than those obtained with the simple parent uranyl ion salts; a lifetime of 660 μs for UO_2^{2+} in uranyl nitrate hexahydrate was observed, for instance. The luminescence data thus provided very strong evidence for the existence of a new uranium species in the hydrolysis products that was quite different in nature from the parent uranyl species. The luminescence data thus strongly agreed with the marked change in the luminescence spectrum of $UO_2(NO_3)_2 \cdot 6H_2O$ when two water molecules were replaced with hydroxy groups.[33,37]

The lifetime and ground-state vibrational energy data (Table III) permitted a classification of the hydrolysis products. In several instances, a lifetime of 100–115 μs was obtained, and a ground-state vibrational energy of 700–730 cm^{-1} for these compounds was calculated from the emission data. These ground-state vibrational energy values and excited-state emission lifetimes were precisely in the range expected for uranium(VI) in an approximately octahedral coordination geometry[38] that has been previously reported. They are also virtually identical with those reported for a series of lithium tungsten uranates.[39] A definitive assignment of the species responsible for the emission was not possible, since potential products formed from decomposition by dehydration could not be documented as forming; also, virtually no emission data exist for many of them. Unfortunately, a complete and comprehensive understanding of hydrolysis complexes such as studied here may never be possible due to the number of experimental (and synthetic) parameters involved and the inherent complexity of the uranium(VI) oxide–water systems.

For other products, the emission lifetime was measured as being significantly smaller, and the ground-state vibrational energies of these hydrolysis products were also found to be much reduced below 700 cm^{-1}. This behavior was most pronounced for the uranyl hydroxide products obtained from NaOH addition to 1.0 M uranyl ion solutions. These data implied that significant counterion effects existed in both the formation of several of the hydrolysis products and the resulting luminescence and X-ray photoelectron spectra discussed above; nothing, however, can be said about the exact nature of these effects.

In addition to dehydration effects that change the basic chemistry and concomitant X-ray photoelectron and luminescence spectra, aging will also exhibit marked effects on the samples. As discussed above, chemisorption of carbon dioxide, with subsequent reaction to form mixed uranium(VI) oxide–hydroxide–carbonate complexes, occurs on prolonged standing in air. Exposure to light and heat also potentially results in dehydration as well as decarboxylation of the bulk lattice. Other processes may also be operable in these precipitates, processes such as olation[40] and oxolation that have been shown to change the chemical composition of other metal hydroxides such as chromium(III) on aging. No detailed studies of these effects were conducted in this investigation, primarily because this would have necessitated introducing even more experiental parameters into an already extremely complex system.

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Registry No. $UO_2(NO_3)_2$, 10102-06-4; UO_2Cl_2, 7791-26-6; $UO_2(CH_3COO)_2$, 541-09-3; $UO_2(OH)_2$, 13470-18-3; UO_3, 1344-58-7; U_4O_9, 12037-15-9.

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