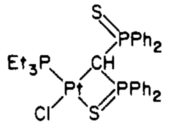
during the formation of the complex.

Discussion

The dynamic process in $[PtCl(PEt_3)\{C(PPh_2S)_3\}]$ (I) is closely related to that which we have described previously for $[PtCl(PEt_3)\{CH(PPh_2S)_2\}]$ (III).[7] In the latter molecule the phosphorus sulfide ligand is bound via a strong Pt–C bond, which provides a fixed pivot for the exchange of the coordinated and noncoordinated sulfur atoms of the ligand. This exchange is rapid on the NMR time scale at 25 °C, but the isomer of III in which the coordinated sulfur is trans to chlorine rather than trans to phosphorus is static at this temperature. The difference between these two isomers must reflect a labilization of the P=S group in III by the trans effect of the triethylphosphine ligand.[7] This phenomenon is even more dramatically illustrated by the present example since very similar Pt–S bonds must serve both for the fixed pivot and for the labile point of exchange. The difference between the two roles is produced merely by the different trans effects of the chloride and triethylphosphine ligands, which occupy the coordination positions trans to P(2) and P(3), respectively, in structure I. Even at 145 °C the Pt–S bond trans to chloride remains inert; P(2) does not participate in the exchange process, and its NMR signal remains sharp. With respect to this type of phenomenon it is usual to differentiate between the kinetic "trans effect", which may be caused by either ground-state or transition-state phenomena, and the "trans influence", which is a ground-state bond weakening as measured by parameters such as bond lengths or NMR coupling constants.[23,26] In the present case a difference in Pt–S bond strength is shown both in the bond lengths, 2.282 (3) Å trans to Cl and 2.351 (4) Å trans to P, and in the two-bond Pt–P coupling constants, 128 and 48 Hz, respectively. It is therefore probable that a ground-state bond weakening is responsible for the kinetic effect. Moreover, the dynamic behavior of $[Pt(PEt_3)_2\{C(PPh_2S)_3\}][BF_4]$ (II) confirms that the bond weakening is indeed a result of the trans influence since the introduction of the second triethylphosphine involves both coordinated P=S groups in the exchange process and also lowers the activation energy. Examples where the kinetic trans effect, NMR coupling constants, and bond lengths can be correlated in such a simple and direct way within a single molecule are very rare.



III

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Registry No. I, 101859-87-4; II, 101915-81-5; $[PtCl_4(PEt_3)_2]$, 15692-96-3; $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$, 19394-82-2.

Supplementary Material Available: Complete ORTEP plot (Figure 4S), anisotropic temperature factors for the heavy atoms (Table S2), selected intermolecular distances (Table S3), complete bond lengths (Table S4), and complete bond angles (Table S5) (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (16 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

Contribution from the Chemical Technology Division,
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Raman Spectroscopic Studies of UO_2^{2+} Association with Hydrolytic Species of Group IV (4)[†] Metals

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Raman spectra have been obtained of UO_2^{2+} in hydrolyzed Zr(IV) and Hf(IV) solutions and of UO_2^{2+} adsorbed by solid hydrous ZrO_2, HfO_2, and ThO_2. The symmetric stretching vibration (ν_1) of UO_2^{2+} was shifted from 872 to 835 cm^{-1} in the hydrolyzed metal solutions, indicating that UO_2^{2+} was complexed by the Zr(IV) and Hf(IV) hydrolytic species. Heating or aging of the solutions caused a substantial reduction in the amount of complexed UO_2^{2+}. The ν_1 band was observed at ~820 cm^{-1} in all of the hydrous oxide spectra. Although the spectra of the solid hydrous oxides indicated that UO_2^{2+} was similarly bound to all three, the behavior of UO_2^{2+} in hydrolyzed Zr(IV) and Hf(IV) solutions was significantly different from that reported for previous studies of UO_2^{2+} in hydrolyzed Th(IV) solutions. The observed differences are discussed and are related to the structures of the hydrolytic species. The changes in color and spectra reported for UO_2^{2+} in heated hydrolyzed Th(IV) solutions may be due to the formation of a distinct thorium(IV) uranate compound.

Introduction

Hydrolysis dominates the aqueous chemistry of the quadrivalent metals. Complexation, ion exchange, and solubility properties of the metals are profoundly affected by the presence of mono- and polynuclear hydrolysis products. The distribution of hydrolytic species is a complicated function of metal concentration, solution acidity, and concentration and identity of additional ions. In many cases, the chemistry is further complicated by the slow aggregation of hydrolysis products into polymeric hydroxides, which eventually precipitate from solution. A particularly troublesome example is the polymerization and precipitation of Pu(IV) in fuel reprocessing streams. While most published studies of hydrolysis[1] treat the behavior of a single metal ion in noncomplexing media, practical systems tend to be less ideal and often contain appreciable concentrations of several metal ions. In such systems, interactions between hydrolytic species may significantly alter the chemical behavior of the species of interest.

Previous investigations[2] in our laboratory showed that Pu(IV) polymerization and precipitation are inhibited by the presence of uranyl ion, UO_2^{2+}. Raman spectroscopic studies[3] revealed that

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[†] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(1) A compilation and critical review of data through 1974 are given in: Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976: (a) pp 156–159; (b) pp 176–182; (c) pp 158–168.

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addition of uranyl to hydrolyzing Th(IV) solutions results in the formation of a hydroxyl-bridged UO_2^{2+}/Th(IV) complex which, upon mild heating, is converted to a uranate-like species. The present study is an extension of that work to the hydrolysis of Zr(IV)/UO_2^{2+} solutions. Solutions containing 0–0.50 M Zr(IV) and 0–0.20 M UO_2^{2+} in the pH range 0–4 were examined. Solutions of Hf(IV) were also examined, as were uranyl-loaded, solid hydrous oxides. Chloride, rather than nitrate, solutions were studied because the structure of the hydrolytic species in Zr(IV) and Hf(IV) chloride solutions have been determined[4,5] and because the chloride ion has no vibrational spectrum. The term "solution" is used somewhat loosely throughout this report; the extensively hydrolyzed samples are more properly referred to as well-dispersed sols.

Experimental Section

Chemicals. The following chemicals were reagent grade or better and were used without further purification: $ZrOCl_2 \cdot 8H_2O$ (Alfa Products, Puratronic); $UO_2Cl_2 \cdot 3H_2O$ (Alfa Products); hydrous zirconia, "$Zr(OH)_4$" (A. D. Mackay Chemicals); certified 1 N NaOH, 1 N HCl, and pH 1 and 4 buffers (Fisher Scientific). Hafnium oxychloride, $HfOCl_2 \cdot 8H_2O$, was prepared by multiple recrystallization of an aqueous solution prepared from $HfCl_4$ (A. D. Mackay, reactor grade). Crystalline $Th(NO_3)_4 \cdot 5H_2O$ was obtained locally.

Hydrolyzed Solutions. Weighed amounts of the metal salts were dissolved in 0.50 M uranyl chloride solution and were diluted with water and NaOH solution to the desired volume and pH. The gelatinous precipitates that invariably formed during base addition dissolved within a few minutes. Samples stored for several months in sealed tubes appeared to be free of precipitates. A glass electrode calibrated with pH 1 and 4 buffers was used to measure solution pH. Measurements were made 30 min after the final addition of base or water and were repeated when spectra were recorded, ~24 h later. Solutions containing Zr(IV) typically exhibited a pH decrease of 0.1–0.2 units over this interval. Thermally aged samples were prepared by heating the solutions in an 85 °C oil bath for 1–5 days. These solutions were cooled to room temperature before pH measurements were made or spectra were recorded.

In the concentrated solutions studied, maintenance of constant ionic strength would have required extremely high concentrations of supporting electrolyte and would have severely limited the solubility of the hydrolyzed Zr(IV). Thus, there were no attempts to maintain constant ionic strength in the samples. Even if constant ionic strength were assumed, the samples containing Zr(IV) or Hf(IV) were so far from equilibrium[1a] that no meaningful constants could be derived from the data.

Hydrous Oxides. Excess NaOH was added to solutions of the metal salts; the resulting suspensions were stirred for 48 h and filtered. The solids recovered were resuspended in water and stirred for an additional 24 h. The gelatinous materials recovered by filtration were dried for 1–2 h at 60 °C. The hard, glassy solids were broken up by stirring in water for 4 h, filtered, air-dried, and ground to powders. The Raman spectrum of the solid hydrous ZrO_2 thus prepared was identical with that of the commercially obtained material.

Uranyl-loaded hydrous oxides were prepared by adding 350 mg of the hydrous oxide to 10.0 mL of uranyl chloride solution (0.05 M and 0.01 M solutions were used). After 2 h of stirring at room temperature, the solids were covered by filtration, throughly washed with water, and air-dried.

Raman Spectra. A Ramanor HG-2S spectrometer (Jobin Yvon-Instruments SA) equipped with a Nicolet 1170 signal averager was used to record spectra over the region 100–1740 cm^{-1}. The system and its configuration for 90° scattering have been described in detail elsewhere.[6] The 5145-Å line from an argon ion laser was used for excitation, except when sample fluorescence was prohibitive. Excitation with the 6471-Å line from a krypton ion laser produced satisfactory spectra of fluorescent samples.

Base line subtraction and peak integration were performed on an IBM 9000 computer. The intensity of the water bending vibration at 1640 cm^{-1} was used for approximate normalization of the data. Further quantitative interpretation of the band intensities was unjustified.

Results

Spectra of Freshly Prepared Solutions. In concentrated acidic chloride and perchlorate solutions, the predominant Zr(IV) species is a cyclic tetramer,[1a,4,5] $Zr_4(OH)_8(H_2O)_{16}^{8+}$, which is also the cation found in crystalline $ZrOCl_2 \cdot 8H_2O$.[7,8] More hydrolyzed solutions contain polymeric tetramer aggregates.[5,9,10] The structure proposed[5] for the Zr–O network in these aggregates is essentially identical with that in a single layer of tetragonal ZrO_2.[11] The ultimate product of Zr(IV) hydrolysis is amorphous hydrous zirconia; crystalline modifications have been prepared[12] by refluxing hydrolyzed solutions of $ZrOCl_2 \cdot 8H_2O$.

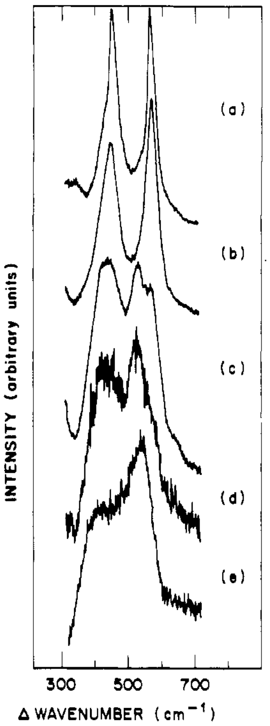

Figure 1. Raman spectra of Zr(IV) at various stages of hydrolysis: (a) crystalline $ZrOCl_2 \cdot 8H_2O$; (b) 0.50 M Zr(IV) in 1 M HCl; (c) 0.50 M Zr(IV), pH ~0.4; (d) 0.50 M Zr(IV), pH ~0.7; (e) amorphous hydrous zirconia, "$Zr(OH)_4$". The higher frequency band is polarized. Exponential- quadratic base lines have been subtracted from all spectra except spectrum a. Excitation was at 5145 Å.

Raman spectra (300–700 cm^{-1}) of Zr(IV) at various stages of hydrolysis are shown in Figure 1. Spectra of crystalline $ZrOCl_2 \cdot 8H_2O$ and amorphous hydrous zirconia are included for comparison. Spectra of oriented single crystals[13] of $ZrOCl_2 \cdot 8H_2O$ revealed that as many as six bands, predominantly Zr–O(H) stretches, contribute to the spectrum shown in Figure 1a. The progressive shift to lower wavenumber is due to simultaneous replacement of coordinated water molecules by hydroxyl and aggregation of the tetramers into polymeric sheets. The complexity of the spectra does not allow us to distinguish between the two processes. Burkov[14] has reported spectra similar to those shown in parts b and c of our Figure 1 and has assigned bands in this region to various Zr–O vibrations, but his interpretation neglects the polymerization that occurs with further hydrolysis. His discussion does not include Mak's[7] revision of the tetramer geometry[8] from D_{4h} to D_{2d}.

Raman spectra of hydrolyzed uranyl nitrate solutions have been described.[15,16] In the present study, hydrolyzed uranyl chloride solutions yielded similar spectra with the symmetric stretching bands (ν_1) of the hydrated uranyl ion and its dinuclear and tri-

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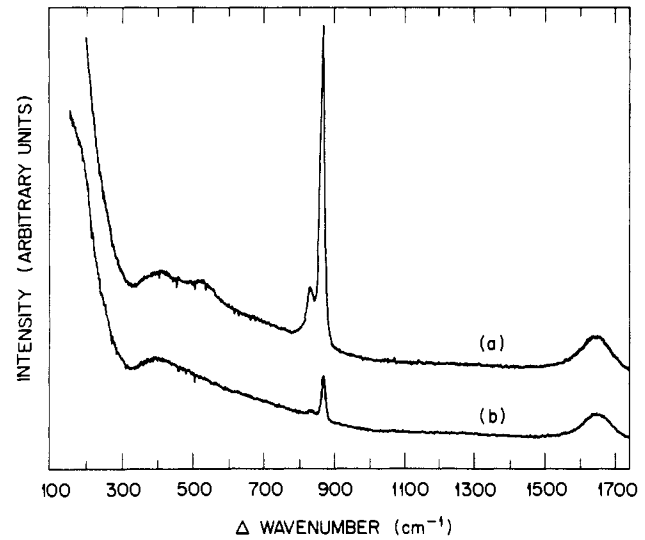

Figure 2. Raman spectra of a hydrolyzed Zr(IV)/UO_2^{2+} solution (0.50 M Zr(IV), 0.20 M UO_2^{2+}, pH 2.25): (a) exciting light polarized ⊥ to the plane formed by the incident and scattered radiation; (b) exciting light polarized ∥ to the plane. Excitation was at 5145 Å.

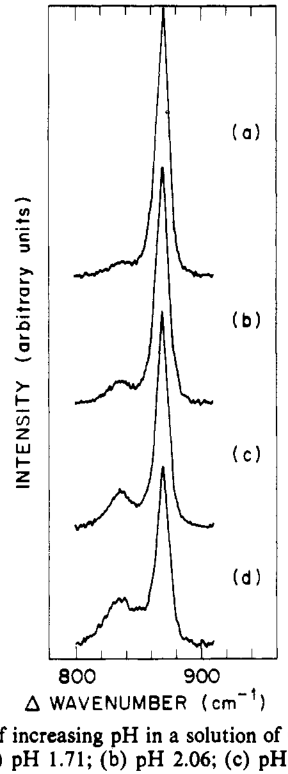

Figure 3. Effects of increasing pH in a solution of 0.25 M Zr(IV) and 0.10 m UO_2^{2+}: (a) pH 1.71; (b) pH 2.06; (c) pH 2.53; (d) pH 2.98. Both bands are polarized. Excitation was at 5145 Å.

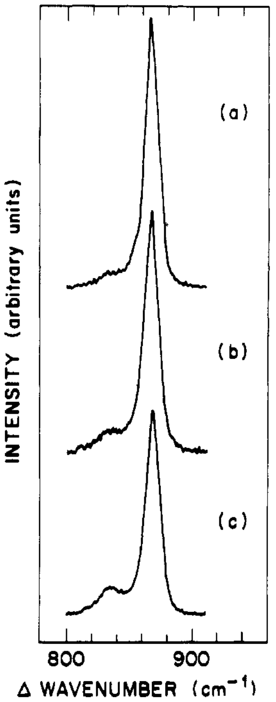

Figure 4. Effects of varying Zr(IV) concentration in a solution containing 0.20 M UO_2^{2+}: (a) 0.10 M Zr(IV), pH 2.35; (b) 0.25 M Zr(IV), pH 2.25; (c) 0.50 M Zr(IV), pH 2.25. Excitation was at 5145 Å.

nuclear hydrolysis products at 872, 853, and 840 cm^{-1}, respectively. Additional bands due to uranyl and ligand vibrations were expected in the spectra of the polynuclear species, but such bands were observed only in the spectra of solutions supersaturated with uranyl hydroxide and were much weaker in intensity than ν_1.

Acidic solutions containing Zr(IV) and uranyl yielded spectra resembling those of the separate components. As solution pH was increased, however, a new polarized band appeared at 835 cm^{-1}. Representative spectra are shown in Figure 2. The increased intensity at 835 cm^{-1} was accompanied by a decrease in intensity of the 872 cm^{-1} band assigned to "free" hydrated uranyl, or "monomer". In addition, the intensity of the 835-cm^{-1} band increased as Zr(IV) concentration was increased. These effects are illustrated in the spectra of Figures 3 and 4. Assignment of the band at 835 cm^{-1} to a pure uranyl hydrolysis product was ruled out by its frequency and by the acidity of the solutions. At the concentrations employed, independent uranyl hydrolysis was insignificant below pH 2.8.[1b,17] The 853-cm^{-1} band characteristic of uranyl "dimer", $(UO_2)_2(OH)_2^{2+}$, was observed only in the spectrum of the most basic solution (Figure 3d). We therefore assigned the 835-cm^{-1} band to ν_1 of UO_2^{2+} complexed by the Zr(IV) hydrolytic species. The 835-cm^{-1} band was also observed in the spectra of hydrolyzed Hf(IV)/UO_2^{2+} solutions. In the hydrolyzed Th(IV) solutions described previously,[3] a band at 851 cm^{-1} was assigned to ν_1 of UO_2^{2+} complexed by Th(IV) hydrolytic species.

The low-wavenumber spectra of solutions containing the complexed uranyl were similar to the spectrum shown in Figure 1d, although shifted slightly to lower wavenumber. The shift, we believe, was due to greater Zr(IV) aggregation in those solutions. No bands attributable to U–O(H) stretching vibrations were observed. As was mentioned above, however, these bands are generally not observed in the spectra of hydrolyzed uranyl solutions and are not intense, even in the spectrum of crystalline $(UO_2)_2(OH)_2Cl_2(H_2O)_4$.[18]

Effects of Aging. A substantial decrease in pH (0.8–1.5 pH units), in keeping with Clearfield's[12] results, was recorded for heated solutions. Solutions prepared with pH ≥3 precipitated when heated. The 835-cm^{-1} band was greatly diminished or altogether absent from the spectra of heated solutions; the intensity of the 872-cm^{-1} band was increased accordingly. The low-wavenumber spectra of heated solutions appeared unchanged. Similar results were obtained from unheated solutions that were maintained for several months at room temperature.

These results are profoundly different from those of the Th(IV) studies.[3] Although hydrolyzed Th(IV)/UO_2^{2+} solutions exhibited a similar pH decrease when heated, they also underwent a dramatic color change from yellow to orange. The intensity of the band assigned to complexed uranyl was greatly diminished in the Raman spectra of these solutions, but the band assigned to free uranyl showed only a slight increase. A new, broad polarized band was observed at 665 cm^{-1} and was ascribed to the symmetric U–O stretch of a uranate-like species.

Adsorption by Hydrous Oxides. Complexation of uranyl by polynuclear hydrolytic species is clearly related to adsorption by

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Table I. Comparison of ν_1 Frequencies for UO_2^{2+} Adsorbed by Solid Hydrous Oxides and Complexed by Hydrolytic Species in Solution

hydrous oxide (MO_2)	UO_2^{2+} adsorbed from 0.01 M soln, pH 3.38		UO_2^{2+} adsorbed from 0.05 M soln, pH 4.01		UO_2^{2+} complexed by hydrolytic M(IV) species, pH 1.5–4
	final pH	ν_1, cm^{-1}	final pH	ν_1, cm^{-1}	ν_1, cm^{-1}
ZrO_2	2.91	820	3.69	821	835
HfO_2	3.53	821	3.92	822	835
ThO_2	3.83	820	4.04	822	851[a]

[a] From ref 3.

solid hydrous oxides. The cation-exchange properties of the hydrous oxides[19] are due to the acidic character of the metal hydroxyl groups. Uranyl adsorption by hydrous oxides has been studied extensively;[19-24] double oxygen bridges bind uranium atoms to metal atoms at the hydrous oxide surface. It has been shown[24] that uranyl adsorbed from basic carbonate solutions is free of carbonate ligands; it is not known whether the species adsorbed from these solutions contain additional hydroxo ligands.

Hydrous oxides and uranyl-loaded hydrous oxides of Zr(IV), Hf(IV), and Th(IV) were prepared as described above; their Raman spectra are shown in Figure 5. Other than ν_1, no bands attributable to uranyl were observed in the spectra of the solids. Results are summarized in Table I; ν_1 frequencies observed for complexation by hydrolytic species are included for comparison. Given the compositions of the solutions employed in the sorption experiments, it is extremely unlikely that the adsorbed uranyl species were polynuclear or contained additional hydroxyl ligands. The observed ν_1 frequencies are appropriate for uranyl coordinated by two bridging oxygens, and the differences in the observed frequencies are insignificant. Maya[24] has reported ν_1 at 814–816 cm^{-1} for uranyl adsorbed by hydrous ZrO_2; the differences from our values may be systematic or may be due to adsorbed hydroxo species. We note, however, that his hydrous ZrO_2, prepared from nitrate solutions, yields a different spectrum than our hydrous ZrO_2, which was prepared from chloride solutions.

Discussion

It has long been established that the uranyl bond lengths[25] and stretching frequencies[26,27] are affected by the number and type of additional ligands bound to the uranium atom. Increasing the uranium coordination[25] or introducing a stronger (vis-à-vis the spectrochemical series) ligand[27] causes a weakening of the short collinear bonds that define the uranyl group, and a resultant decrease in the U–O bond stretching force constant, F_{UO}. The observed symmetric and antisymmetric stretching frequencies (ν_1 and ν_3) are primarily functions of F_{UO} but are also affected by interactions of the U–O bonds with each other and with the ligand coordinates. Jones[26] has discussed this in detail and has determined that the errors in F_{UO} caused by neglecting the interaction terms are small. It is not our intention to calculate force constants based on a single vibrational frequency but to emphasize that measurement of only ν_3 or, in our case, ν_1 does provide considerable information about the uranyl coordination environment.

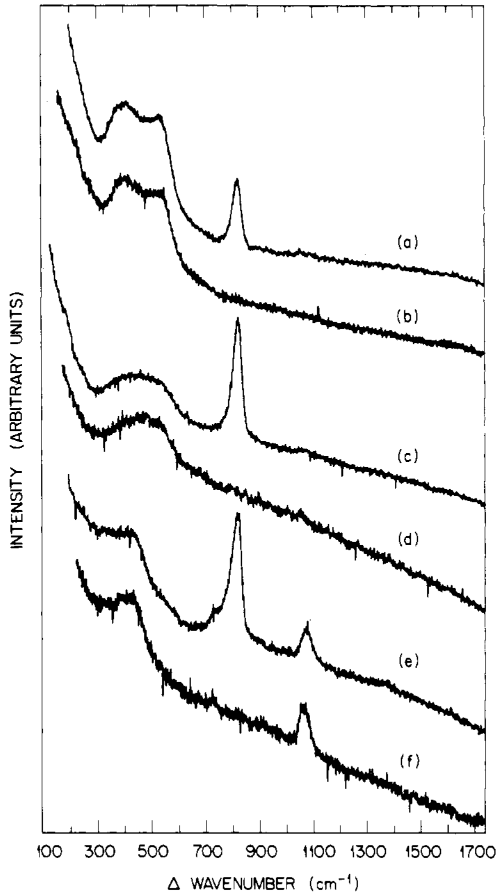

Figure 5. Raman spectra of hydrous oxides and UO_2^{2+} loaded hydrous oxides: (a) loaded ZrO_2; (b) ZrO_2; (c) loaded HfO_2; (d) HfO_2; (e) loaded ThO_2; (f) ThO_2. Excitation was at 6471 Å.

In the case of uranyl adsorbed from solution by hydrous oxides, we assume that the uranium atoms are bound to the surface by double oxygen bridges.[19] We expect that the effects of these ligands on ν_1 will be similar irrespective of which metal is at the opposite end of the oxo bridge. The spectra indicate that this is indeed the case. The solution spectra, however, indicate that the $Zr(IV)/UO_2^{2+}$ and $Hf(IV)/UO_2^{2+}$ interactions observed in this study are distinctly different from the $Th(IV)/UO_2^{2+}$ interaction reported previously.[3] We propose the following explanation, noting that identical results were obtained for Hf(IV) and Zr(IV).

The 835-cm^{-1} frequency observed for UO_2^{2+} associated with Zr(IV) is 15 cm^{-1} lower than that observed for the doubly hydroxyl-bridged uranyl dimer. This decreased frequency suggests that either more than two bridging hydroxyl groups are involved or that the link is through "stronger" ligands. In the system under study, the only stronger ligands available are oxygen bridges or extremely acidic bridging hydroxyls. Essentially all Zr(IV) in solution is present as the cyclic tetramer at pH ≤ 0.[1a] In the pH region where uranyl attachment is observed, the tetramers are extensively aggregated (i.e., polymeric), and the polymer structure[5] is closely related to that of the solid hydrous oxide.[12,28] If we accept Aberg's picture of the polymer structure, a planar network of tetramers linked through double hydroxyl and oxygen bridges, it is apparent that uranyl attachment must occur at the edges of

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the polymer sheet. It is also apparent that a single Zr(IV) species may not form more than two bridging bonds in the uranyl equatorial plane without appreciable distortion of the Zr(IV) coordination polyhedron. Nonequatorial coordination of uranyl is unknown[29] and shall not be considered. Attachment of two or more Zr(IV) species to uranyl could provide the extensive coordination suggested by the ν_1 frequency; if such were the case, however, we should observe a progression of shifted ν_1 bands as the number of attached Zr(IV) species increases. Only one band, its frequency constant, is observed; thus we reject the explanation of extensive uranyl coordination. We conclude, instead, that the uranyl group is attached to the edge of the Zr(IV) polymer by a pair of oxygen (or extremely acidic hydroxyl) bridges in a manner analogous to adsorption. Heating the hydrolyzed Zr(IV) solutions promotes condensation and crystallization[12] of the Zr(IV) species, decreasing the solution pH and reducing the number of sites available to uranyl. Either of these effects would produce the observed dissociation of the Zr(IV)/UO_2^{2+} complex.

In contrast to the hydrolyzed Zr(IV)/UO_2^{2+} solutions, hydrolyzed Th(IV)/UO_2^{2+} solutions show ν_1 of complexed uranyl at 851 cm^{-1}, essentially the same frequency observed for the dinuclear uranyl hydrolytic species. Baes and Mesmer noted that Th(IV) is the largest of the tetravalent cations and the most resistant to hydrolysis. In the pH region where uranyl complexation is observed, the predominant Th(IV) species[1c,30] are monomers, dimers, and tetramers, rather than large polymeric aggregates. We suggest that discrete hydroxyl-bridged Th(IV)/UO_2^{2+} clusters, true mixed hydrolytic species, are formed in these solutions.

The color change and the spectral changes observed in the earlier study[3] of heated Th/UO_2^{2+} solutions can only be due to a profound change in the uranium environment. The pH decreases recorded for the heated solutions indicate that condensation similar to that observed in Zr(IV) solutions has occurred, but the uranium is clearly incorporated, rather than excluded from the resulting structure. As was earlier proposed, the 665-cm^{-1} symmetric stretching vibration observed in the Raman spectra of heated Th(IV)/UO_2^{2+} solutions could be due to a considerable lengthening[26] of the short collinear U–O bonds characteristic of the uranyl group. Other structural possibilities include (a) a configuration in which the uranyl oxygen atoms are shared with other atoms, as in $U_3O_8(OH)_2$,[31] or (b) one in which the uranyl group is not present in the final structure and the 665-cm^{-1} band is due to the symmetric stretching of strongly coordinated equatorial ligands. All three structures have been observed in uranates formed by hydrothermal synthesis.[31,32] We note that the only strong band in the Raman spectrum of $U_3O_8(OH)_2$ is a symmetric U–O stretch at 690 cm^{-1}.[33]

Boekschoten and Kema[34] have reported the formation of two distinct oxide compounds of Th(IV) and U(VI) in heated slurries, formed by NaOH precipitation of uranyl and thorium nitrate solutions. The compound formed at 220–260 °C was formulated as $ThUO_5$, and its powder pattern indicated a hexagonal lattice. A poorly crystallized second compound, designated only as the low-temperature Th(IV)/U(VI) compound, was formed at 85 °C. The authors claim that the low-temperature compound contains no water and no sodium. No further studies of these compounds appear to have been performed. We are attempting to isolate crystals of the low-temperature compound, which if it indeed exists, is most likely responsible for the unusual colors and spectra of the heated hydrolyzed Th(IV)/UO_2^{2+} solutions.

Conclusion

We have examined the hydrolysis of mixed Zr(IV)/UO_2^{2+} and Hf(IV)/UO_2^{2+} solutions and have determined that the interaction between uranyl and the hydrolytic species is analogous to ion-exchange adsorption at the surface of a hydrous oxide. No unusual reactions have been observed. We suggest that the hydrolyzed Th(IV)/UO_2^{2+} solutions studied previously contained, initially, discrete polynuclear mixed-metal clusters and, ultimately, an unknown thorium uranate. The substantial differences in the behavior of the Th(IV)/UO_2^{2+} and Zr(IV)/UO_2^{2+} systems may be explained but could not have been predicted from the available data on hydrolysis of the individual species.

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Registry No. $Zr(OH)_4$, 14475-63-9; $Hf(OH)_4$, 12027-05-3; $Th(OH)_4$, 13825-36-0; UO_2Cl_2, 7791-26-6.

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