spectral evaluation of the OH ion in biological apatites.

It appears reasonable to assume that the OH band intensity variations arise from differences in bonding imposed by the crystal fields on the OH ions in these apatites. The intensity of each OH band is dependent upon the square of the change in dipole moment which, in turn, depends upon the change in the electrical character of the atoms as they vibrate according to the coordinates which describe the vibration. It is apparent from the decreases in the OH band intensities that the dipole moment changes during the OH vibrations become progressively weaker in the Ca-, Sr-, Ba(OH)A sequence.

The intensities of OH bands of selected organic alcohols (R-OH) decrease as the electron-withdrawing power of the R group decreases.[44] The electronegativity of Ba (0.9) is less than those of Sr (1.0) and Ca (1.0), and the lower electron-withdrawing power at the center of the trigonal Ba plane may contribute to the lower OH band intensity. As previously discussed, the relative frequency shifts of the OH modes in the Ba-, Sr-, Ca(OH)A sequence as a function of assumed decreasing OH to PO_4 intermolecular distances are suggestive of a progressively stronger hydrogen-bond interaction. The progressively enhanced OH band intensities in this sequence are also consistent with a progressively stronger hydrogen bond interaction; however, there are essentially no increases in the band widths which are concomitant with stronger hydrogen bonding. The polarizing powers (e/r^2, where e is the ionic valence and r the ionic radius) of Ca, Sr, and Ba are 2.04, 1.59, and 1.11, respectively. A decrease in polarization of the OH ion decreases the tendency of the OH ion to form hydrogen bonds. The progressive decrease in cation polarizing power in the Ca-Sr-Ba sequence correlates with and may contribute to the possible OH- - -OPO_3 interaction and in turn to the decreases in OH band intensities.

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Registry No. $Ca_{10}(PO_4)_6O$, 12265-54-2; $Ba_{10}(PO_4)_6O$, 12397-85-2; $Sr_{10}(PO_4)_6O$, 12266-36-3; H_2O, 7732-18-5; $H_2{}^{18}O$, 14314-42-2; D_2O, 7789-20-0; Ca(OH)A, 1306-06-5; Ba(OH)A, 12356-34-2; Sr(OH)A, 12266-00-1; ^{44}Ca, 14255-03-9; ^{48}Ca, 13981-76-5; $Ca_5(OH)(PO_4)_3$, 12167-74-7; $Ba_5(OH)(PO_4)_3$, 12377-63-8; $Sr_5(OH)(PO_4)_3$, 12195-53-8.

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Octahedral Hexafluoro Complexes of the Tetravalent Actinides[1]

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Salts and solutions of the octahedral $UF_6{}^{2-}$, $NpF_6{}^{2-}$, and $PuF_6{}^{2-}$ ions were prepared. These represent a lower coordination number than previously known for tetravalent actinides in fluoro complexes. Absorption spectra of these hexafluoro complexes in the region of internal f-electron transitions are presented and are the weakest known for U(IV), Np(IV), and Pu(IV).

Introduction

Until relatively recently many scientists believed that six was a common coordination number, N, for trivalent and tetravalent actinides and lanthanides. The excellent work of Satten, *et al.*,[3-5] on the detailed interpretation of the internal f-electron transition spectra of salts of the octahedral $UCl_6{}^{2-}$ ion at low temperature showed that, as predicted by theory for an ion having O_h symmetry, the electronic transitions are missing and only relatively weak vibronic transitions are present. This and the finding that the overall molar absorptivities of the $UCl_6{}^{2-}$, $NpCl_6{}^{2-}$, and $PuCl_6{}^{2-}$ ions were markedly lower[6] than those then known for other U(IV), Np(IV), and Pu(IV) solutions along with slowly increasing X-ray evidence of the common existence of high coordination numbers for lanthanides and actinides raised suspicion that $N = 6$ might be uncommon for tetravalent and trivalent actinides and lanthanides. The preparation of hexabromo and hexaiodo complexes of the tetravalent actinides and the finding of low molar absorptivities for these complexes confirmed this and led to the conclusion that the tetravalent actinides normally prefer $N = 8$ or 9 with F^- or oxygen-containing ligands.[7] Later preparation of trivalent lanthanide[8] and actinide[9] hexahalide complexes and comparison of their absorption spectra to those of various other lanthanide and actinide species resulted in the conclusion that $N = 6$ is very rare indeed for the trivalent actinides and lanthanides.

In the last few years, the amount of X-ray structural analysis has increased rapidly, and it is now known that $N =$ 8, 9, 10, or 12 is much more common for trivalent and tetravalent actinides than is $N = 6$, and even with the smaller hexavalent actinides, $N > 6$ is common. In particular the fluorides have been much studied, and although $N = 6$ in the neutral hexavalent MF_6, several addition compounds with alkali and other fluorides are known[10] indicating a strong

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tendency toward $N > 6$ even for fluorides of the relatively small hexavalent actinides. In the pentavalent case, various salts of the UF_6^- ion can be prepared from aqueous HF,[11,12] but salts with $N > 6$ can also be prepared,[13,14] including $RbUF_6$ and its K^+ and NH_4^+ analogs which do not contain the hexafluoro complex and in which fluoride sharing occurs and $N = 8$.[15] Many complex fluoro salts of tetravalent actinides and lanthanides are known,[10,16,17] and considerable study has been devoted to the systematics of their structures.[17] Several of these salts have the composition M_2AnF_6, where M is an alkali metal or ammonia (or M_2 is a divalent metal ion) and An is an actinide (or Ce or Pr), and some have the composition $MAnF_5$. Although these salts have been casually called hexafluoro and pentafluoro complexes,[10,16] they are not, all of the M_2AnF_6 salts for which structures have been determined[17,18] having $N = 8$ or 9. A very recent review[17] of structural systematics in actinide fluoride complexes lists the known tetravalent actinide and lanthanide fluoride complex salts along with the coordination numbers of the An(IV) ions in all of the salts for which they are presently known. All the tetravalent actinide and lanthanide fluoride salts for which structures have been determined have coordination numbers in the range seven to ten, with eight and nine being most common. Also for U, Np, and Pu fluoro complexes of unknown structure such as aqueous fluoride solutions[19] and salts of unknown structure, the intensity of the colors or the nature of the absorption spectra in the cases measured indicates lack of O_h symmetry for the An^{4+} ions.

We report here the first preparation, both in solid salts and in solutions, of the octahedral hexafluoro complexes UF_6^{2-}, NpF_6^{2}, and PuF_6^{2-} having the weakest absorption spectra (for internal f-electron transitions) known for U(IV), Np(IV), and Pu(IV).

Experimental Section

Materials. Spectro grade acetonitrile and reagent grade acetone were dried and stored over anhydrous $CaSO_4$. Propane-1,2-diol carbonate, hereafter referred to as propylene carbonate (Jefferson Chemical Co.), was purified by distillation under reduced pressure (3 Torr) before use. Water content, as determined by Karl Fischer titration, was less than 15 ppm. The very deliquescent $(C_2H_5)_4NF$ (Eastman) was "dried" under vacuum but, as noted before,[12] is not anhydrous after such treatment. This compound was highly variable in quality; when necessary, it was recrystallized from hot absolute ethanol or by addition of excess acetone to a saturated ethanol solution. Propylene carbonate solutions of the material could also be partially decolorized by treatment with activated alumina and activated charcoal. The $[(C_2H_5)_4N]_2UCl_6$[12] and $[(C_2H_5)_4N]_2NpCl_6$[6] were prepared as before; UF_4 was from Mallinckrodt, and PuF_4 was prepared by fluorination of PuO_2 which in turn was made by calcination of plutonium oxalate that had been precipitated from HNO_3 solution.

Preparation of $[(C_2H_5)_4N]_2UF_6$. This compound is sensitive to both atmospheric moisture and oxygen. Although reasonably good preparations can be obtained on the bench top if air contact is minimized and filtering is by dry inert gas pressure, all preparations for which data are reported here were done in a dry bag through which a continuous slow flow of dry He passed. A mixture of 90% dry acetone–10% absolute ethanol was saturated with "dried" $(C_2H_5)_4NF$ by shaking with an excess of the solid for at least 2 hr (not done in the dry bag since the "dried" $(C_2H_5)_4NF$ is a hydrate anyway). Sixty milliliters of this solution in a 100-ml bottle was thoroughly sparged with dry He in the dry bag and 2 g of $[(C_2H_5)_4N]_2UCl_6$ was added. The bottle was capped and shaken vigorously until the solid dissolved. It was then alternately cooled in a Dry Ice bath and shaken vigorously until the product crystallized as fairly dense, fine crystals. Excessive cooling should be avoided since lighter and much coarser crystals of $(C_2H_5)_4NF$ and possibly $(C_2H_5)_4NCl$ can be obtained also. The solution was allowed to warm as much as possible without excessive redissolution of the product (to about −10 to 0°) and excess liquid was poured off, and the product was isolated by pressure filtering with dry He. The product was washed thoroughly with 1% absolute ethanol in dry acetone followed by dry acetone, both of these having been sparged with dry He. The compound was dried in a stream of dry He.

The slightly off-white salt was Cl^- free as determined turbidimetrically. Samples not prepared in inert atmosphere generally have a faint pinkish cast due to the presence of traces of UOF_5^{2-}.[12] The absorption spectrum of the salt has a peak at about 1950 nm of intensity corresponding to approximately three H_2O molecules per U atom. Vacuum drying produced a weight loss of 8.28% *vs.* 8.11% calculated for three H_2O molecules, removed the 1950-nm peak entirely, and produced absolutely no effect on the spectrum due to uranium indicating the absence of water in the U coordination sphere. No change in X-ray diffraction pattern could be detected on vacuum drying. This makes it somewhat uncertain as to whether the compound is a hydrate, but it appears likely that it does precipitate as a weak trihydrate. The compound was thereafter normally dried at 10^{-2} to 10^{-3} Torr.

Anal. Calcd for $[(C_2H_5)_4N]_2UF_6$: U, 38.9; F, 18.6; F/U = 6.00. Found: U, 37.4; F, 17.9; F/U = 6.00.

Although the dry compound can be handled briefly in laboratory air, it does react strongly, but slowly, with water vapor, gradually turning green even when stored over $Mg(ClO_4)_2$ desiccant. All handling of the salt was in the He-filled dry bag or in a drybox. The dry salt reacts slowly with atmospheric oxygen, gradually over weeks to months turning first the pink of UOF_5^{2-}[12] and finally the yellow of U(IV) when stored in a drybox at <4 ppm H_2O. The compound is stable indefinitely under vacuum. The X-ray diffraction pattern was essentially indistinguishable from that of $[(C_2H_5)_4N]_2UOF_5$.

Preparation of $[(C_2H_5)_4N]_2PuF_6$. PuF_4 was dissolved to saturation in 0.5 *M* $(C_2H_5)_4NF$ in propylene carbonate (requiring 2 to 3 days at 25° but much less time at higher temperature). To this solution, cooled to −20 to −30°, acetone, at the same temperature, was added slowly in increments until fine, dense crystals began to form. The solution was agitated to promote crystallization and a seven- to tenfold excess of acetone was normally used. Care was exercised not to over-cool the solution or to add acetone too rapidly since larger, less dense crystals of $(C_2H_5)_4NF$ can also be obtained. Yield was kept well below 100% to avoid contamination with excess $(C_2H_5)_4NF$. After allowing time for crystallization, the solution was warmed to near 25° and the product removed by centrifugation. The compound was washed twice with dry acetone and dried in a vacuum desiccator. The preparation was carried out in an inert atmosphere box having <1 ppm water and <50 ppm oxygen, but there is no reason to suspect that the compound is sensitive to oxygen.

The compound prepared in this manner was not a hydrate as determined by the virtual absence of absorption at 1930 nm.

Anal. Calcd for $[(C_2H_5)_4N]_2PuF_6$: Pu, 39.0; F, 18.6. Found: Pu, 38.2; F, 18.7.

Analyses. Uranium and fluoride analyses of $[(C_2H_5)_4N]_2UF_6$ were by the methods described in ref 12. Plutonium was determined in $[(C_2H_5)_4N]_2PuF_6$ by coulometry, and fluoride was determined by precipitation of PbClF (after first removing the plutonium as the insoluble hydroxide), redissolution, and analysis for chloride by the Volhard method.[20] From the chloride value, the fluoride content was calculated based on the stoichiometry of PbClF.

Spectrophotometric Measurements. Absorption spectra were obtained with Cary Model 14 recording spectrophotometers. Spectra of the solid salts were obtained in mulls in Kel-F brand chloro-fluoro carbon grease between glass or fused silica plates *vs.* a reference of $CaCO_3$ in Kel-F grease. Solution spectra were obtained in silica cells.

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The U(IV) solutions were prepared in a dry He atmosphere in solutions which had been sparged with dry He to remove dissolved oxygen. Dissolution of UF_4 or PuF_4 in $(C_2H_5)_4NF$-saturated propylene carbonate was slow at 25°, requiring 2–3 days to reach saturation (about 0.15 *M*), but was much more rapid at 60–80°. Reference solutions were identical with the samples except for the presence of the actinide compound of interest. Solutions of UF_6^{2-} were pale greenish brown; NpF_6^{2-} solutions were pale blue-green; and PuF_6^{2-} solutions were bright green.

Results and Discussion

Absorption spectra of solutions and solid salts of the UF_6^{2-}, NpF_6^{2-}, and PuF_6^{2-} ions are shown in Figures 1–3. In the case of U and Pu, the absorption spectra were the same whether acetonitrile or propylene carbonate was used. They were also the same whether the solutions were prepared by dissolving the $[(C_2H_5)_4N]_2AnF_6$ salts in the solvent with or without a large excess of $(C_2H_5)_4NF$, by dissolving the AnF_4 in solutions containing excess $(C_2H_5)_4NF$ (up to saturation), or by dissolving the $[(C_2H_5)_4N]_2AnCl_6$ in solutions containing excess $(C_2H_5)_4NF$ (the latter determined for U only). Propylene carbonate was more satisfactory, however, since the lower solubilities in acetonitrile required use of 10-cm cells. Also, simple solutions of the $[(C_2H_5)_4N]_2AnF_6$ salts in acetonitrile without excess $(C_2H_5)_4NF$ were unstable and gradually developed slight turbidity after several hours. The actinides are Chatt-Ahrland A-group elements forming much stronger fluoro than chloro complexes, thus allowing the use of the chloro complex (which was done in the Np case for convenience) to produce the AnF_6^{2-} ion in solution in the presence of an excess of fluoride. The fact that sufficient excess F^- was present in the Np solution in Figure 2 was established by comparison to the spectrum of a twofold dilution of this solution with $(C_2H_5)_4NF$-saturated propylene carbonate. No attempt was made to prepare solid $[(C_2H_5)_4N]_2NpF_6$.

The virtual identity of the spectra of the solid salts and the solutions in Figures 1 and 3 indicate beyond doubt that the same complex species are present in the salts and solutions. The absorption spectra are all very weak in comparison to all other known spectra of U, Np, and Pu(IV). The molar absorptivities of the ten strongest absorption peaks for U in Figure 1 average less than half those of UCl_6^{2-},[7] while those of the ten strongest for Np in Figure 2 are about a factor of 2.8 lower than the ten strongest for $NpCl_6^{2-}$,[6] and for Pu in Figure 3 the ten strongest peaks average a factor of 3 weaker than those of $PuCl_6^{2-}$.[7,21] The molar absorptivities of the fluoro complexes shown here are a factor of about 20 lower than those of the respective aquo ion spectra and other typical U(IV), Np(IV), and Pu(IV) absorption spectra, leaving no doubt that the metal ions are at a center of inversion in the present case. The effect on the intensities of internal f-electron transitions caused by the metal ion being at a center of inversion has been discussed in detail beginning with the work of Satten, *et al.*,[3-5] and has been recently reviewed[22] so will not be elaborated on here. Since the salts have a F/An ratio of 6 and dissolve readily in acetonitrile or propylene carbonate to give solutions having the same spectra as the solids, either with or without excess F^- present, the complexes must be the octahedral UF_6^{2-}, NpF_6^{2-}, and PuF_6^{2-}. Other possible species with a center of inversion such as eight-coordinate cubic are ruled out by the stoichiometry of the salt, since both the center of inversion and the ready solubility without change in spectrum are not compatible with fluoride sharing.

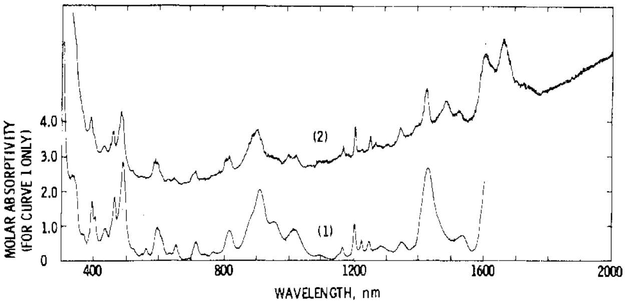

Figure 1. Absorption spectra of the hexafluoro complex of uranium(IV): (1) UF_4 dissolved in $(C_2H_5)_4NF$-saturated propylene carbonate, and (2) solid $[(C_2H_5)_4N]_2UF_6$ (arbitrary absorbance scale). The base line is not flat in (2) because of mismatch of light scatter between the sample and reference mulls.

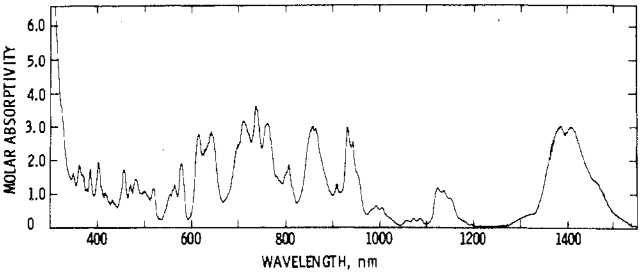

Figure 2. Absorption spectrum of the hexafluoro complex of neptunium(IV) prepared by dissolving $[(C_2H_5)_4N]_2NpCl_6$ in $(C_2H_5)_4NF$-saturated propylene carbonate.

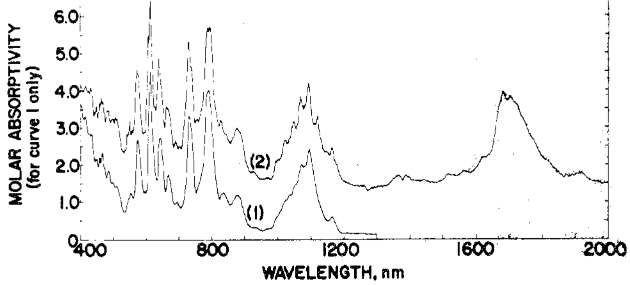

Figure 3. Absorption spectra of the hexafluoro complex of plutonium(IV): (1) $[(C_2H_5)_4N]_2PuF_6$ in propylene carbonate containing excess $(C_2H_5)_4NF$, and (2) solid $[(C_2H_5)_4N]_2PuF_6$ (arbitrary absorbance scale).

The lower intensity of the UF_6^{2-}, NpF_6^{2-}, and PuF_6^{2-} absorption spectra relative to the corresponding UCl_6^{2-}, $NpCl_6^{2-}$, and $PuCl_6^{2-}$ is in agreement with the trend observed with the heavier hexahalide complexes[7] and with the trend observed in the intensities of the UX_6^- transitions.[12] Although there is some resemblance between the absorption spectra of the AnF_6^{2-} and the corresponding $AnCl_6^{2-}$ with a shift of the transitions of the former to higher energy, the resemblance is much less than between the $AnCl_6^{2-}$ and $AnBr_6^{2-}$ or, in the case of U, between UBr_6^{2-} and UI_6^{2-}.[7] This is caused by two factors. First, the vibrational frequencies are larger in fluoro than in chloro complexes, causing the vibronic transitions to be spaced further from the positions of the pure electronic transitions and causing greater overlap of vibronic groups. Second, and most important, a larger shift in the energies of the electronic transitions is expected in going from chloro to fluoro than from chloro to bromo complexes because of the larger change in nephelauxetic effect, electronegativity, and ligand field strength be-

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tween Cl^- and F^- than between Cl^- and Br^-. The energy shifts are indeed large, but because they are, because not all transitions shift equally, and because of the wider vibronic groups, the mixing of groups and change of order of transitions is so severe that few transitions in the room temperature spectra of the $\mathrm{AnF_6}^{2-}$ can be unambiguously matched to corresponding transitions in the $\mathrm{AnCl_6}^{2-}$. Unfortunately we are not able at present, because of funding problems, to obtain low temperature spectra to unravel the details of the $\mathrm{AnF_6}^{2-}$ spectra.

Despite this, some of the transitions, particularly low energy ones, can be matched with certainty. Thus the transition centered at 5015 cm^{-1} in $\mathrm{UCl_6}^{2-}$ [23] (measured here for the $(\mathrm{C_2H_5})_4\mathrm{N}^+$ salt at 5016 cm^{-1}) is moved to 6109 cm^{-1} in $\mathrm{UF_6}^{2-}$, and the transitions at 6400 and 8240 cm^{-1} in $\mathrm{NpCl_6}^{2-}$ [22] are at 7150 and 8810 cm^{-1}, respectively, in $\mathrm{NpF_6}^{2-}$ whereas they are at 6200 and 8000 cm^{-1} in $\mathrm{NpBr_6}^{2-}$.[22] An attempt was made at actually measuring shifts in energy of transitions between the $\mathrm{AnF_6}^{2-}$ and $\mathrm{AnCl_6}^{2-}$ complexes, and from these, calculations of nephelauxetic effect were made. These calculations indicated that the change in nephelauxetic parameter might be as large as 20% which would indicate strong contribution to covalent bonding in the $\mathrm{AnCl_6}^{2-}$, $\mathrm{AnBr_6}^{2-}$, and $\mathrm{AnI_6}^{2-}$, but this is not certain and the results are not presented here because of the uncertainties in matching of transitions. Nevertheless, reasonably close comparison of the spectra of the $\mathrm{AnF_6}^{2-}$ to those of the $\mathrm{AnCl_6}^{2-}$, $\mathrm{AnBr_6}^{2-}$, and $\mathrm{AnI_6}^{2-}$ already published[7,22] indicates beyond doubt that even with constant symmetry, the absorption spectra of the tetravalent actinides can be quite sensitive to the metal ion environment. More detailed analysis of low temperature spectra would be highly desirable, but it should be remembered that because the molar absorptivities are quite low and the compounds are quite prone to hydrolysis (and in the case of $\mathrm{UF_6}^{2-}$ to oxidation), the presence of nonoctahedral impurities could be a serious experimental problem.

The lowest energy group for $[(\mathrm{C_2H_5})_4\mathrm{N}]_2\mathrm{UF_6}$ in Figure 1 centered at 6109 cm^{-1} consists of a pair of relatively strong peaks separated by 224 cm^{-1}. The very similar appearing corresponding group in $\mathrm{UCl_6}^{2-}$ [4,23] has been shown by Satten, *et al.*,[4] to be due to coupling of the odd fundamental vibrational mode of the octahedral complex ν_6 to both the ground and excited states of a forbidden and essentially missing electronic transition. The missing electronic transition is approximately at the center of the space between these two peaks and ν_6 is approximately equal to one-half the separation. Satten, *et al.*, reported one-half this separation as 83 cm^{-1} for $\mathrm{UCl_6}^{2-}$ while other data[24] indicate a value of 80 cm^{-1} for $[(\mathrm{C_2H_5})_4\mathrm{N}]_2\mathrm{UCl_6}$ at 70°K, and we also measure a value of 80 cm^{-1} for this compound at 25°. By analogy, we assign this separation in $\mathrm{UF_6}^{2-}$ as being $2 \times \nu_6$ and thus ν_6 is 112 cm^{-1} for $\mathrm{UF_6}^{2-}$. We measured one transition attributable to metal-halogen vibration in the infrared above 250 cm^{-1}, and we assign this transition at 405 cm^{-1} as the infrared active fundamental mode ν_3. The corresponding value for $\mathrm{UCl_6}^{2-}$ is 262 cm^{-1},[22] and little difference would be expected for $\mathrm{PuCl_6}^{2-}$, since the value reported for $\mathrm{ThCl_6}^{2-}$ is 259 cm^{-1} and that for $\mathrm{NpCl_6}^{2-}$ is 258 cm^{-1}.[22] The decreases in ν_3 and ν_6 in going from the $\mathrm{AnF_6}^{2-}$ to the $\mathrm{AnCl_6}^{2-}$ are somewhat larger than would be expected on the basis of change in halide mass alone and indicate, as expected, that stronger bonding occurs in the hexafluoro complexes than in the hexachloro complexes. The decreases in ν_3 of about 23% and of ν_6 of 13% for $\mathrm{UF_6}^{2-}$ relative to $\mathrm{UF_6}^-$ [12] are reasonable for such a change in metal ion charge.

The uv absorption spectrum of the $\mathrm{UF_6}^{2-}$ ion was obtained down to 195 nm, using the same 0.13 *M* solution for which the visible spectrum is shown in Figure 1 and a 0.0021-cm cell. As in the case of $\mathrm{UCl_6}^{2-}$,[7] five bands due to $5\mathrm{f}^2 \rightarrow 5\mathrm{f}^1 6\mathrm{d}$ transitions were observed. These are at (37,000), 39,800, (41,000), 43,100, and 44,400 cm^{-1} with the respective values of ϵ being (445), 2700, (1020), 950, and 815, where values in parentheses are for shoulders. The first strong $5\mathrm{f}^2 \rightarrow 5\mathrm{f}^1 6\mathrm{d}$ transition is shifted 8000 cm^{-1} from that in $\mathrm{UCl_6}^{2-}$,[7] and the other bands are shifted by similar amounts. This approximately 25% shift in energies of the $5\mathrm{f}^2 \rightarrow 5\mathrm{f}^1 6\mathrm{d}$ transitions compares with about 8% between $\mathrm{UCl_6}^{2-}$ and $\mathrm{UBr_6}^{2-}$ and about 15% between $\mathrm{UBr_6}^{2-}$ and $\mathrm{UI_6}^{2-}$,[7] again illustrating the greater change in nephelauxetic effect between F^- and Cl^- than between Cl^- and Br^- or Br^- and I^-. It has been noted that the energies of the $5\mathrm{f}^q \rightarrow 5\mathrm{f}^{q-1} 6\mathrm{d}$ transitions normally shift two to three times as much as the internal f-electron transitions with change in ligand.[22] This appears to be in reasonable agreement with the internal f-electron transition shifts that can be determined with certainty here. The shift of 8000 cm^{-1} between the $5\mathrm{f}^2 \rightarrow 5\mathrm{f}^1 6\mathrm{d}$ of $\mathrm{UF_6}^{2-}$ and $\mathrm{UCl_6}^{2-}$ is still much smaller though than the shift of 17,000 cm^{-1} between $\mathrm{UCl_6}^{2-}$ and the aquo ion where coordination number change also occurs.[22]

The $\mathrm{AnF_6}^{2-}$ appear to be the terminal An(IV) fluoro complexes in acetonitrile or propylene carbonate solutions, no change in the spectrum occurring even with a large excess of $(\mathrm{C_2H_5})_4\mathrm{NF}$ in the solutions. In aqueous solutions there is no evidence of appreciable conversion (small amounts could not be detected spectrophotometrically) of U(IV) to $\mathrm{UF_6}^{2-}$ at any alkali or ammonium fluoride concentration. The spectrum of U(IV) between 560 and 700 nm varies with $\mathrm{NH_4F}$ concentration in the range 3-12 *M*, but ϵ_{max} ranges from 15 to 41, increasing with increasing $\mathrm{NH_4F}$ concentration.[19] By contrast $\epsilon_{\mathrm{max}} = 0.85$ for $\mathrm{UF_6}^{2-}$ in this wavelength region. U(IV) does exist, though, in very viscous and low water content saturated aqueous solutions of $(\mathrm{C_2H_5})_4\mathrm{NF}$ essentially entirely as the $\mathrm{UF_6}^{2-}$ ion. Likewise the spectrum of Np(IV) in concentrated aqueous KF has ϵ_{max} values in the range 10 to 60[25] and thus shows no evidence of the $\mathrm{NpF_6}^{2-}$ ion. It has been noted that the spectrum of U(IV) in >10 *M* F^- solutions is very similar to that of $(\mathrm{NH_4})_4\mathrm{UF_8}$,[19] which has been shown to contain $\mathrm{UF_8}^{4-}$ ions as distorted tetragonal antiprisms.[26] In 7 *M* $\mathrm{NH_4F}$ solutions there is evidence of polymeric species.[19]

The reason for the lower maximum coordination number in fluoro complexes in the high dielectric constant, weakly complexing solvents used here compared to water is probably due to the absence of active protons for hydrogen bonding in these solvents. We propose that in water solution, all F^- ions whether in the An(IV) coordination sphere or not are hydrogen bonded to water. The net effect of such hydrogen bonding is to effectively share the F^- ions between the An ion and protons thereby weakening and lengthening the An–F bond and producing higher possible coordination numbers. In the nonprotonic solvents, such effect is not possible; the F^- ions interact very weakly with the solvent and very strongly with the An(IV) ions producing short An–F bonds

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and a maximum coordination number of six. Similarly in solid fluoro complex salts, the positive metal ions or hydrogen bonding NH_4^+ ion probably interact sufficiently strongly with the small nonpolarizable F^- ions in the crystals to pull them further away from the An(IV) ions allowing high coordination numbers. With very large, low charge density ions such as $(C_2H_5)_4N^+$ such an effect would be much weaker, and the lower coordination number AnF_6^{2-} ions are stable relative to higher coordination number arrangements.

Finally, it should be noted that extraction of hydrated UF_4 from water suspension into tridecyl- and tetradecylammonium fluoride in low dielectric solvents has been reported,[27] and it was claimed without any real evidence that the UF_6^{2-} ion was the species present in the water-saturated organic phase. That this claim is not correct is demonstrated by the fact that the reported absorption spectra of the solutions are not at all similar to that of UF_6^{2-} shown here and by the fact that the values reported for ϵ_{max} between 560 and 700 nm vary from 8 to 16 whereas that for UF_6^{2-} is 0.85.

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Registry No. $[(C_2H_5)_4N]_2UF_6$, 42294-80-4; $[(C_2H_5)_4N]_2PuF_6$, 42294-81-5; $[(C_2H_5)_4N]_2NpF_6$, 42294-82-6.

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Formation and Properties of Iron Titanium Hydride[1]

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The intermetallic compound FeTi reacts directly with hydrogen to form, in succession, hydrides of the approximate compositions FeTiH and $FeTiH_2$. The composition limits have been determined and are diagrammed. Both hydrides have dissociation pressures of over 1 atm at 0°, unlike the very stable TiH_2. The relative partial molar enthalpies of hydrogen have the rather low values of −3.36 kcal/g-atom of hydrogen in the lower hydride and −3.70 to −4.03 in the higher; the properties of the latter vary with the hydrogen content. Pronounced hysteresis effects are observed, the absorption isotherms of pressure *vs.* composition frequently being several atmospheres higher, at a given composition, than the desorption isotherms. The lower hydride, FeTiH, has tetragonal symmetry and a density of 5.88 g/cm³. The higher hydride has a cubic structure and a density of 5.47 g/cm³ ($FeTiH_{1.93}$). The hydriding behavior is quite sensitive to the composition of the solid phase. If Ti is in slight excess over the equiatomic proportion, the pressure–composition isotherms no longer exhibit the plateaus and inflections characteristic of the appearance of new phases.

Iron and titanium form two known stable intermetallic compounds, FeTi and Fe_2Ti.[2] It is also generally accepted that a third compound, $FeTi_2$, exists above 1000°, decomposing to FeTi and Ti below that temperature.[3] We have briefly noted previously[4] that one of these compounds, FeTi, will react directly with hydrogen to form an easily decomposed hydride which may be useful as a hydrogen storage medium. Our purpose here is to discuss the Fe-Ti-H system in some detail with particular emphasis on the reaction of FeTi with hydrogen and the formation and properties of two ternary hydrides, $FeTiH_{\sim 1}$ and $FeTiH_{\sim 2}$.

Experimental Section

The Fe–Ti alloys were prepared from zone-refined Fe and Ti in an arc furnace under an argon atmosphere, although it should be noted that no significant differences were observed when commercial grade Fe and Ti were substituted for the zone-refined starting material. Initially we had prepared the alloys in an induction furnace; however, it appeared that the resulting products were contaminated by the alumina crucible material, which had an inhibiting effect upon their reaction with hydrogen. Contamination of iron titanium alloys by alumina crucibles has been noted previously.[2] All the alloys were quite brittle and all samples were crushed to pass through a 10-mesh screen. It was not necessary to carry out the crushing step in an inert atmosphere. The samples, weighing ~10 g, were introduced into a high-pressure hydriding reactor, the construction of which has been previously discussed in detail.[5]

Our procedure for hydriding metals which form unstable hydrides, as in this instance, has also been described,[6] and only a brief synopsis will be given here. The reactor was loaded with the granular alloy samples, sealed, evacuated, and then heated to 400–450° while outgassing continuously. Upon reaching the cited temperature range, hydrogen was admitted to the reactor until the pressure was ~7 atm. There was usually a slight drop in hydrogen pressure at this point due to some solution of hydrogen in the metal phase. After ~30 min the reactor was evacuated and cooled to room temperature at which point H_2 was admitted to the reactor until the pressure was ~65 atm. Usually the metal–hydrogen reaction proceeded immediately with the evolution of heat. If no reaction took place over a 15-min period, the above procedure was repeated. It should be noted that if the alloy is in ingot form, rather than granular, the initiation of the reaction is somewhate more difficult and may require several such treatments. In order to obtain a highly active metal substrate, the sample was hydrided and dehydrided several times. Dehydriding was accomplished by outgassing and heating to ~200°.

The procedure for obtaining the pressure–composition isotherms presented here is essentially the same as that described previously.[5,6] Briefly, it consisted of equilibrating the metal hydride with hydrogen

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