HALIDE COMPLEXES OF PENTAVALENT URANIUM*

JACK L. RYAN

Pacific Northwest Laboratories, Battelle Memorial Institute, Richland, Washington 99352

(Received 17 June 1970)

Abstract – New and simpler methods of preparing solutions and salts of the UF_6^- and UCl_6^- complexes are given. The preparation of the previously unknown hexahalide complexes UBr_6^- and Ul_6^- and oxohalide complexes UOF_5^{2-} , $UOCl_5^{2-}$, and $UOBr_5^{2-}$ is described. The chemical properties and stabilities of all of these complexes are discussed. The stability of uranium(V) toward disproportionation in several non-aqueous halide solutions is demonstrated. Absorption spectra of these uranium(V) hexahalide and oxohalide complexes in the regions of electron transfer transitions, internal 5*f* electron transitions, metal–oxygen vibrational frequencies, and metal–halogen vibrational frequencies are presented. These spectra are interpreted and related to the observed chemical properties of uranium(V) in these halide complexes.

INTRODUCTION

As RECENTLY emphasized by Selbin and Ortego in their review of the chemistry of uranium(V)[1], the literature on uranium(V) chemistry is quite meager when compared to the voluminous data on the other uranium valence states. Equimolar mixtures of known U(IV) and U(VI) compounds often have the same average stoichiometry as that proposed for U(V) compounds; and because results have often been reported only on the basis of stoichiometries, a considerable fraction of this meager U(V) literature must be viewed with skepticism. This lack of information on U(V) chemistry has been attributed to the ease of disproportionation of U(V) to U(IV) and U(VI)[1,2]. It should be remembered though that this is due to the high stability of the $UO_2^{2^+}$ entity; and as will be emphasized in this paper, in the absence of hydrolytic substances such as water, alcohols, etc. which produce the uranyl ion, U(V) is generally more stable than U(VI) and disproportionation does not occur readily.

Since U(V) has only one 5f electron which makes its absorption spectrum relatively simple, it is of considerable interest spectroscopically. It appears that a considerable amount of information concerning chemical bonding in actinide complexes could be obtained by the detailed study of various compounds having the $5f^1$ configuration. The U(V) halide complexes are of particular interest in this regard.

The UF_6^- ion was reported by Rampy[3] as the ammonium salt prepared by reduction of UF_6 with ammonia. The salt NOUF₆ was prepared by reduction of

*This paper is based on work performed under Contract No. AT(45-1)-1830 for the U.S. Atomic Energy Commission. Presented in part at the Symposium on Macroscopic Properties of the Actinides, 155th National Meeting of the American Chemical Society, San Francisco, April 1-5 (1968).

^{1.} J. Selbin and J. D. Ortego, Chem. Rev. 69, 657 (1969).

^{2.} J. Selbin, J. D. Ortego and G. Gritzner, Inorg. Chem. 7, 976 (1968).

^{3.} G. A. Rampy, GAT-T-697, 11-2-59, Goodyear Atomic Corp., available from U.S. Dept. of Commerce, Office of Tech. Services, Washington 25, D.C.

UF₆ with NO[4]. Na₃UF₈ was prepared by Ruedorff and Leutner[5]. Various salts of the UF₆⁻, UF₇²⁻ and UF₈³⁻ ions were prepared and studied by Penneman *et al.* using UF₅ (prepared from UF₄ plus UF₆) as starting material and carrying out reactions either at elevated temperature in bombs or in anhydrous or 48% aqueous HF[6–9]. More recently various workers have used similar methods to prepare and study other salts of these ions and this work is covered in the review by Selbin and Ortego[1]. Cs⁺, Me₄N⁺, Me₂NH₂⁺, and (C₆H₅)₄As⁺ salts of the UCl₆⁻ ion were prepared by Bagnall *et al.* by precipitation from thionyl chloride solutions of U(V) which were in turn obtained by prolonged refluxing of UO₃ in thionyl chloride[10]. The Rb⁺ and (C₃H₇)₄N⁺ salts have been prepared by a similar method[2]. The pyridinium salt of the UOCl₅²⁻ complex has been reported [11], but no evidence was given to show that the material contained U(V) instead of being an equamolar mixture of the well known UCl₆²⁻ and UO₂Cl₄²⁻ complexes and that report will be shown to be in error in this paper.

This paper discusses the preparation and properties of the remaining hexahalide complexes, UBr_6^- and UI_6^- . A new and faster method of preparing the UCl_6^- complex and several of its salts and some of the properties of the $UCl_6^$ complex are reported. A method for preparation of some of the salts of the $UF_6^$ complex which avoids the use of either fluorinating agents or UF_6 is discussed. The new oxohalide complexes UOF_5^{2-} , $UOCl_5^{2-}$, and $UOBr_5^{2-}$ are reported. Spectral data in the regions of the electron transfer transitions, internal 5*f* electron transitions, and in the far i.r. (metal-halogen vibration region) are reported for the various complexes. Much more detailed spectral study of the hexahalides is under way and will appear later [12].

EXPERIMENTAL

Materials. Spectro grade nitromethane and acetonitrile and reagent grade acetone were dried with anhydrous CaSO₄. 85% succinonitrile-15% acetonitrile solvent was prepared as before [13]. Propylene carbonate was obtained from Dr. J. M. Cleveland of Dow Chemical Company, Rocky Flats Division who purified and dried this Jefferson Chemical Company product.

Tetraethylammonium fluoride, chloride, and bromide were from Eastman. When used in the dry form, they were dried under vacuum at about 1 micron pressure. The fluoride forms extremely strong hydrates and prolonged pumping causes decomposition before the evolution of water is complete. For this reason the "dried" material was that which had been pumped on for not more than about two days and is still a hydrate. Tetraphenylarsonium chloride was obtained from City Chemical Corporation, New York. Tetraphenylarsonium bromide was prepared by adding HBr gas to a saturated aqueous solution of the chloride. The product was filtered, washed with aqueous HBr followed by a small amount of cold water, and dried by mild heating with a heat lamp. Anhydrous pyridine hydrochloride was prepared by adding HCl gas to a solution of spectro grade pyridine in petroleum ether, washing with petroleum ether, and drying in dry helium. All other common chemicals were reagent grade.

- 4. J. R. Geichman, E. A. Smith, S. S. Trond and P. R. Ogle, Inorg. Chem. 1, 661 (1962).
- 5. W. Ruedorff and H. Leutner, Ann. Chem. 632, 1 (1960).
- 6. R. A. Penneman, L. B. Asprey and G. Sturgeon, J. Am. chem. Soc. 84, 4608 (1962).
- 7. R. A. Penneman, G. D. Sturgeon and L. B. Asprey, Inorg. Chem. 3, 126 (1964).
- 8. L. B. Asprey and R. A. Penneman, Inorg. Chem. 3, 727 (1964).
- 9. G. D. Sturgeon, R. A. Penneman, F. H. Kruse and L. B. Asprey, Inorg. Chem. 4, 748 (1965).
- 10. K. W. Bagnall, D. Brown and J. G. H. du Preez, J. chem. Soc. 2603 (1964).
- 11. D. C. Bradley, B. N. Chakrovarti and A. K. Chatterjee, J. inorg. nucl. Chem. 3, 367 (1957).
- 12. J. R. Morrey and L. G. Morgan, Unpublished work.
- 13. J. L. Ryan and C. K. Jørgensen, J. phys. Chem. 70, 2845 (1966).

The source of uranium for all uranium compounds was reactor grade uranium metal. The metal (cleaned by 15M HNO₃ to remove oxide) was dissolved in HCl-acetone, and the solution was centrifuged to remove a very small amount of residue. $[(C_2H_5)_4N]_2UCl_6$ and $[(CH_3)_4N]_2UCl_6$ were prepared by adding $(C_2H_5)_4NCl$ and $(CH_3)_4NCl$ respectively in aqueous 12M HCl to such freshly prepared U(IV) solutions in acetone. The products were filtered, washed with 12M HCl and then acetone, and dried under a heat lamp. $[C_5H_5NH]_2UCl_6$ and $[(C_6H_5)_4As]_2UCl_6$ were prepared in a similar manner except that HCl saturated ethanol was used in place of aqueous 12M HCl. $[(C_2H_5)_4N]_2UBr_6$ was prepared as previously described[14]. $[(C_6H_5)_4As]_2UBr_6$ was prepared by dissolving uranium metal in conc. aqueous HBr at 25°, centrifuging thoroughly to remove insoluble residues, saturating with HBr gas, and adding $(C_5H_5)_4AsBr$ in HBr saturated ethanol. The compound was filtered, washed with HBr-ethanol followed by acetone, and dried by mild heating. All the U(IV) hexahalide salts were stored over Mg(ClO₄)₂ and $[(C_6H_5)_4As]_2UBr_6$ was also kept in the dark.

Technique. Much of the work with the U(V) solutions (such as the preparation of UCl_6^- and UBr_6^- in solution) could be carried out on the bench top if care was used to minimize the length of time of contact of the solutions with air. Also most of the solid compounds were hydrolyzed sufficiently slowly that they could be handled briefly in laboratory air. Nevertheless most of the work, including filtering, washing, drying, and handling of all solids for which analyses are reported and the preparation of solid samples for spectral measurements, etc. was done either in a gloved bag through which there was a constant flow of dry helium or in a dry box having an atmosphere of air of < 5 ppm water. All preparations were made in and all solutions handled in screw cap bottles which were opened only when necessary.

Preparation of U(V) compounds. $(C_2H_5)_4NUCl_6$ was prepared by heating a sealed chlorine saturated slurry of 0.3 to 0.6 g of $[(C_2H_5)_4N]_2UCl_6$ per ml of nitromethane to 80–90° for a few min. After cooling, the solution was re-saturated with chlorine and heated until all the U(IV) salt dissolved. Occasionally a third chlorine addition is required. The yield is improved by using a high ratio of the U(IV) salt to nitromethane, but it becomes increasingly difficult to dissolve and oxidize the U(IV) salt as the ratio is increased. The final solution was cooled to -30° , yielding deep yellow crystals which were isolated by pressure filtering with dry helium, washing with a small amount of nitromethane at its freezing point, and drying in a stream of helium.

Anal. Calcd. for (C₂H₅)₄NUCl₆: U, 41.0; Cl, 36.6. Found: U, 40.7; Cl, 35.9.

 $(C_6H_5)_4AsUCl_6[10]$ was prepared in the same manner as the tetraethylammonium salt. $[(C_6H_5)_4As]_2UCl_6$ shows a higher temperature coefficient of solubility than the tetraethylammonium salt. As a result the U(IV) salt is more readily dissolved and higher concentrations of the U(V) product can be obtained. If concentrated solutions were allowed to stand a few hr they often yielded large crystals. In some cases though, the solutions would not seed even when cooled, and the entire solution was frozen and remelted to induce crystallization. The compound was identified by its absorption spectrum.

 $(C_2H_5)_4NUBr_6$ was prepared by adding excess bromine to a dry nitromethane solution of $[(C_2H_5)_4N]_2UBr_6$ containing up to 50 per cent by volume of the salt in excess of its solubility. The oxidation proceeds rapidly at room temperature with the U(IV) salt dissolving and black crystals of the U(V) salt forming. The solution can be warmed briefly to speed dissolution of the U(IV) salt, but Br₂ attacks the hot solvent moderately rapidly. Occasionally light colored crystals are observed in the solution illuminated with a bright light. These disappear if more bromine is added. The solution was pressure filtered at 25° since cooling the solution results in crystallization of lighter colored impurities (probably ($C_2H_5)_4NBr_3$). The product was washed and dried in the same manner as the chloro salt.

Anal. Calcd. for (C₂H₅)₄NUBr₆: U, 28·1; Br, 56·5. Found: U, 28·2; Br, 55·8.

Black $(C_6H_5)_4$ AsUBr₆ was prepared in the same manner as the tetraethylammonium salt.

Anal. Calcd. for (C₆H₅)₄AsUBr₆: U, 21.6; Br, 43.6. Found; U, 21.7; Br, 44.3.

 $(C_6H_5)_4AsUF_6$ was prepared by adding solid $(C_6H_5)_4AsUCl_6$ to 48% aqueous HF. The yellow chloro complex salt is gradually converted to the slightly soluble, pale ice blue fluoro complex salt. The product was pressure filtered with dry helium, washed with 48% HF, and either dried directly in a stream of dry He or rinsed with a small amount of dry acetone before drying. The compound can also be obtained in as good or better quality by simply adding a nitromethane solution of $(C_6H_5)_4AsUCl_6$ plus chlorine to 48% HF without isolating the solid chloride salt.

14. J. L. Ryan and C. K. Jørgensen, Molec. Phys. 7, 17 (1963).

Anal. Calcd. for (C₆H₅)₄AsUF₆: U, 32·4; F, 15·5. Found: U, 31·9; F, 14·9.

Bright blue $[(C_2H_5)_4N]_2UOCl_5$ was prepared as follows. Undried but free-flowing (as purchased) $(C_2H_5)_4NCl$ was dissolved to approximately saturation in nitromethane. The solution was diluted ten-fold with undried acetone, and any precipitate forming immediately was discarded. The solution was cooled to -78° , and about 1-2 g of $(C_2H_5)_4NUCl_6$ was added per 50 ml of solution. The solution was agitated thoroughly while being allowed to gradually warm to about -10 to 0° so that most of the hydrolysis to $UOCl_5^{2-}$ occurred at low temperature. As soon as all yellow solids were gone and most of the yellow color was gone from the solution, the solution was warmed to about 15° and was pressure filtered with dry helium. The product was washed with dry acetone and dried in a stream of dry helium. When prepared in this manner, the product contained less than 1% U(IV) and (VI) as determined spectrophotometrically on the solid. The compound can also be prepared at room temperature, and the filtrate from the preparation of $(C_2H_5)_4NUCl_6$ can be used instead of solid $(C_2H_5)_4NUCl_6$, but the products obtained in this way generally contain a few per cent U(IV) and (VI).

Anal. Calcd. for [(C₂H₅)₄N]₂UOCl₅: U, 34·4; Cl, 25·6. Found: U, 34·0; Cl, 25·3.

Violet-blue $[(C_6H_5)_4A_5]_2UOCl_5$ was prepared in the same manner as the tetraethylammonium salt, except undried acetone saturated with undried $(C_6H_5)_4A_5Cl$ was used instead of an acetone-nitromethane mixture.

Anal. Calcd. for [(C₆H₅)₄As]₂UOCl₅: Cl, 14.8. Found: Cl, 14.6.

X-ray powder diffraction data was obtained for this compound with 31 lines measured. This data was indexed by Dr. A. S. Wilson using the computer program Index [15]. The best fit (monoclinic was not tried) was orthorhombic with the following lattice constants: $a_0 = 12 \cdot 16 \pm 0.02$ Å, $b_0 = 20 \cdot 51 \pm 0.02$ Å and $c_0 = 9.02 \pm 0.01$ Å. The average deviation between observed and calculated $\sin^2 \theta$ was 0.0004 and the maximum deviation was 0.0010. The calculated density, assuming two formula units per cell, is 1.77 g/ml and the density measured pycnometrically in isooctance was 1.73 g/ml.

Blue $(C_sH_sNH)_2UOCl_5 \cdot 2 \cdot 5 \cdot C_sH_sNHCl$ was prepared by adding about 10 ml of a concentrated solution of $C_sH_sNHUCl_6$ plus chlorine in nitromethane to a solution obtained by saturating 5 ml of undried nitromethane with C_sH_sNHCl and diluting to 75 ml with undried acetone. The solution was at -78° and was allowed to warm slowly with thorough agitation to about 10°. The compound was pressure filtered with dry helium, washed with dry acetone, and dried in helium. The compound is very deliquescent, converting rapidly to a pale green mixture of U(IV) and (VI) on contact with laboratory air.

Anal. Calcd. for (C5H5NH)2UOCl5.2.5 C5H5NHCl: U, 27.0; Cl, 30.2. Found: U, 26.6; Cl, 29.2.

Only one preparation of the pyridinium salt was made, and it cannot be said with certainty on the basis of only one preparation that the 2.5 moles of extra C_sH_sNHCl are present as a compound of crystallization, but it appears likely that this is the case.

Green $[(C_6H_5)_4As]_2UOBr_5$ was prepared by adding $(C_6H_5)_4AsUBr_6$ to an almost saturated (at 25°) solution of laboratory air dried $(C_6H_5)_4AsBr$ in undried acetone in a ratio of about 1 g per 30 ml. The solution was initially at -78° and was agitated thoroughly without appreciable warming until all black particles of the UBr_6^- salt were gone and the solution was no longer deep brown in color. The cold solution was pressure filtered with dry helium, and the product was washed with dry acetone (precooled to -78°) and dried in helium. The product appeared to be at least 95 per cent U(V) as determined spectrophotometrically on the solid assuming that the molar extinction coefficients of the oxobromo complex did not vary from those of the oxochloro complex by an extent greater than in the case of the U(IV) hexabromo and hexachloro complexes[14].

Anal. Calcd. for [(C₆H₅)₄As]₂UOBr₅: U, 16.8; Br, 28.2. Found: U, 16.7; Br, 28.5.

Green $[(C_2H_5)_4N]_2UOBr_5\cdot2\cdot5$ $(C_2H_5)_4NBr$ was prepared in the same manner as the tetraethylammonium salt of the oxychloro complex using $(C_2H_5)_4NUBr_6$ and undried $(C_2H_5)_4NBr$ as starting materials. Because of the low solubility of $(C_2H_5)_4NBr$ in the 10% nitromethane-90% acetone mixture, it was at first thought that the extra 2·5 moles of $(C_2H_3)_4NBr$ had simply coprecipitated with the product. Other preparations obtained at higher nitromethane to acetone ratios gave the same results though. Microscopic examination of the product indicated no inhomogeneity, and an X-ray powder pattern of the product did not indicate the presence of lines due to $(C_2H_5)_4NBr$. Thus it appears that the extra 2·5 moles of $(C_2H_5)_4NBr$ are actually in the compound.

15. J. B. Goebel and A. S. Wilson, J. Metals 19, 10 (1967).

Anal. Calcd. for $[(C_2H_5)_4N]_2UOBr_5 \cdot 2 \cdot 5 (C_2H_5)_4NBr$: U, 16.5; Br, 41.7, Br/U, 7.50. Found: U, 17.1; Br, 43.5, Br/U, 7.57.

Pink $[(C_2H_5)_4N]_2UOF_5 \cdot 2H_2O$ was prepared by the addition of about 2g $(C_2H_5)_4NUCl_6$ to 60 ml of saturated (at 25°) solution of "undried" (C_2H_5)₄NF in 90% acetone-10% absolute ethanol. The solution had been thoroughly sparged with dry helium to remove oxygen, and the addition was made at or slightly below 25°. The solution was vigorously agitated to break up any lumps of bluish or greenish material formed ($UOCl_{5}^{2-}$ or green mixed chlorofluoro complex intermediates) as rapidly as possible. The yield is poor at 25° but is markedly improved by cooling to $0-10^{\circ}$. Some care must be exercised in cooling the solution since excess $(C_2H_5)_4NF$ and $(C_2H_5)_4NCl$ can be crystallized out. The solution was pressure filtered with dry helium, and the product was washed thoroughly with dry, oxygen-free acetone in which excess $(C_2H_5)_4NF$ is only slightly soluble. Acetone was removed by a stream of dry helium. It may be that a somewhat better product could be obtained with partially dried instead of "as purchased" $(C_2H_5)_4NF$ but this was not tried. The product obtained in this manner contains a moderate amount of U(VI) and in most preparations U(IV) is spectrophotometrically detectable. It should be noted that the U(IV) species formed under these conditions[16] has very low molar extinction coefficients. Unlike the $UOCl_{5}^{2-}$ and $UOBr_{5}^{2-}$ salts, the compound is a hydrate as determined by the observation of bands due to water in the i.r. and near i.r. regions. The compound is converted to the anhydrous salt, by drying at about one micron pressure. The compound, if properly prepared, is free of chloride.

Anal. Calcd. for $[(C_2H_5)_4N]_2UOF_5 \cdot 2 H_2O: U, 36.9; F, 14.7;$ weight loss on drying, 5.58. Found: U, 36.0; F, 14.7, weight loss on drying, 5.36.

Bright pink $[(C_2H_5)_4N]_2UOF_5$ was prepared by vacuum drying the dihydrate.

Anal. Calcd. for [(C₂H₅)₄N]₂UOF₅: U, 39·1; F, 15·6. Found: U, 38·9; F, 15·6.

Analyses. All uranium analyses were by controlled potential coulometric titration [17]. In order to remove fluoride, fluoride containing samples were burned in air at 950° to convert to U_3O_8 which was then dissolved in nitric acid. Chloride and bromide were determined with an Aminco-Cotlove Automatic Chloride Titrator which uses coulometrically generated silver ions and an amperometric end point. Fluoride was determined by a micro method. Samples of fluoride complexes were dissolved in dry acetonitrile, and aliquots containing about 300 μ g of fluoride were taken immediately. (Precipitates begin to form slowly after a period of about 1 hr in acetonitrile solutions of $[(C_2H_5)_4N]_2UOF_5$ not containing excess fluoride.) These aliquots were added to U_3O_8 and the acetonitrile was allowed to evaporate. Pyrohydrolysis in a stream of moist air was carried out at 900°, and the HF was collected in a weak acetate buffer solution. The fluoride in this solution was determined by a fluoride specific ion electrode.

Spectral measurements. Absorption spectra in the u.v., visible and near i.r. regions were obtained with a Cary Model 14 recording spectrophotometer. Absorption spectra of the solid salts were obtained in mulls in Kel-F brand chloro-fluorocarbon grease between glass or fused silica plates vs. a reference of $CaCO_3$ in Kel-F grease. I.R. spectra were obtained with a Perkin-Elmer Model 521 using mineral oil mulls between sodium chloride plates. Far-i.r. spectra were obtained with a Beckman Model IR-11 using petrolatum mulls between polyethylene sheets. All mulls were prepared in a dry atmosphere.

CHEMICAL PROPERTIES OF COMPLEXES

Hexachloro and hexabromo complexes. Any complex, MX_y^{m-y} , which is stable with regard to decomposition to give free halogen and the metal in a lower oxidation state should be formed by the oxidation of a corresponding complex of the metal in a lower oxidation state, $MX_y^{m'-y}$, in solution[18]. The requirements of this method are as follows: the coordinating power of the solvent or impurities in the solvent must be sufficiently low that the desired complex, MX_y^{m-y} , is stable

- 16. J. L. Ryan, To be published.
- 17. G. L. Booman, W. B. Holbrook and J. E. Rein, Analyt. Chem. 29, 219 (1957).
- J. L. Ryan, In *Progress in Coordination Chemistry* (Proceedings of the 11th International Conference on Coordination Chemistry), (Edited by M. Cais) paper D16, p. 220. Elsevier, New York (1968).

with regard to dissociation. The starting complex, $MX_y^{m'-y}$, must also be either stable toward dissociation, or if it does react with the solvent or solvent impurities, the desired complex must be stable toward decomposition to free halogen and the product of such solvolysis. The solvent used must be relatively stable toward attack by the free halogen.

Salts of both the UCl_6^{2-} and UBr_6^{2-} ions are readily prepared and are stable convenient starting materials for preparation of the corresponding U(V) hexahalide complexes. The UCl_6^{2-} and UBr_6^{2-} complexes are both stable toward dissociation in a variety of weakly complexing, high dielectric organic solvents such as acetonitrile [14], nitromethane [19], and others. It would be expected that the corresponding U(V) complex would also be stable toward dissociation in these solvents. Nitromethane was chosen since it was more resistant to attack by free halogen than the nitriles.

When excess Br_2 is added to a solution of $[(C_2H_5)_4N]_2UBr_6$ in dry nitromethane, the solution very quickly becomes a much more intense red-brown color than a solution of Br_2 alone. The near i.r. absorption spectrum of such solutions is very similar to the known[10] spectrum of UCl_6^- as would be expected for the UBr_6^- ion and indicates complete oxidation to UBr_6^- . The chlorine oxidation of UCl_6^{2-} in nitromethane is slower, requiring about 2 hr for complete conversion to UCl_6^- at 25°. At higher temperatures the oxidation is faster and requires only a few min at 80°.

Both the UBr₆⁻ and UCl₆⁻ ions appear to be stable in dry nitromethane in the presence of excess of the respective elemental halogen. Bromine attacks nitromethane moderately rapidly producing HBr as one of the products. A similar but considerably slower reaction occurs with chlorine. The products of this reaction do not appear to react with the hexahalide ions or interfere with their absorption spectra. The result of this reaction is that the free halogen is eventually depleted and after a period of several hr to a few days the U(V) complexes gradually revert to U(IV). The hexabromo and to a much smaller extent the hexachloro ions appear to react weakly, probably with free halogen (in a manner analogous to the formation of Br₃⁻) or possibly with solvent impurities. Because of this, it was found that the molar extinction coefficients in the near i.r. varied slightly. Addition of a small amount of anhydrous HX which reacts with solvent impurities halide complexes[13,18] sharpens the absorption peaks and produces constant molar extinction coefficients.

Anhydrous HX also reacts strongly with water to form the hydronium ion, and addition of anhydrous HX will therefore decrease the sensitivity of solutions of UX_6^- to traces of moisture. In fact the dehydrating power of anhydrous hydrogen chloride and bromide are sufficient that UCl_6^- and UBr_6^- can be obtained from equamolar mixtures of U(IV) and (VI) in non-aqueous solvents such as nitromethane or acetonitrile. If an excess of HX is used, the following reaction proceeds well to the right: $UX_6^{2-} + UO_2X_4^{2-} + 10HX \rightleftharpoons 2UX_6^- + 2H_3O^+ + 4HX_2^$ where X^- is Cl^- or Br^- . This reaction emphasizes that in general it is only the high stability of the hexavalent uranyl ion that causes U(V) to be unstable relative to

19. J. L. Ryan, J. phys. Chem. 65, 1856 (1961).

U(IV) and (VI). If this stabilizing effect of the uranyl entity on U(VI) did not occur, the pentavalent state would be rather common for uranium and U(V) would undoubtedly be stable in aqueous solutions.

Solid salts of the UCl₆⁻ and UBr₆⁻ complexes can be prepared from nonaqueous solutions such as nitromethane providing that the solubility relationships are such that sufficient UX_6^- can be prepared in solution that the salts can be crystallized. Both the previously prepared [10] $(C_6H_5)_4$ AsUCl₆ and the previously unreported (C2H5)4NUCl6 were prepared in this manner. The previously reported [2] $(C_3H_7)_4NUCl_6$ has also been prepared in this manner[12]. This method of preparing UCl₆⁻ salts is much more convenient and rapid than previous methods [2,10] requiring only about 1-2 hr for the entire operation if the stable and conveniently stored U(IV) salts are on hand. Other salts of the UCl_6^- ion can no doubt be made by this method. The preparation of the triphenylphosphonium salt was attempted, but the cation was apparently destroyed by Cl₂ attack. Cs₂UCl₆ is not soluble in nitromethane but is soluble in the high dielectric solvent, 85%succinitrile-15% acetonitrile[13]. Unfortunately the nitriles were found to be attacked too rapidly by Cl_2 . Cs_2UCl_6 is also soluble in propylene carbonate[20]; and although $CsUCl_6$ was obtained in solution, it appeared to be considerably more soluble than the CsCl that is also produced by the reaction and was not isolated from the solution. One attempt was made to prepare the pyridinium salt in nitromethane. An extremely concentrated solution of C5H5NHUCl6 was obtained but either the solubility was not exceeded or the solution simply failed to seed. The tetramethylammonium salt could not be prepared from nitromethane because of insufficient solubility of the U(IV) salt.

 $(C_6H_5)_4$ AsUBr₆ and $(C_2H_5)_4$ NUBr₆ were prepared by Br₂ oxidation of the U(IV) salts as described in Experimental Section. An 0.6 M solution of CsUBr₆ was prepared in propylene carbonate containing I₂ to solubilize the CsBr formed, but the salt did not crystallize. The UBr₆⁻ salts appear to be somewhat more sensitive to moisture than the corresponding UCl₆⁻ salts. This is not unexpected considering the fact that the bromo complex is probably a considerably weaker complex than the chloro complex like the U(IV) case[14,21]. The tetraphenyl-arsonium salt is relatively low melting like the chloro salt[10] but appears to decompose fairly rapidly at the melting point, and the melting point was not determined. The tetraphenylarsonium salts of both UCl₆⁻ and UBr₆⁻ appear to be indefinitely stable (no U(IV) observed in the absorption spectra after $1\frac{1}{2}$ yr) if stored in dry air with minimal exposure to light. The tetraethylammonium salts appear to be much less stable and were always used within a few days of preparation.

Bagnall *et al.*[10] reported evidence for the ions UCl_7^{2-} and UCl_8^{3-} . The existence of such ions is certainly unexpected considering the lack of such higher complexes for U(IV) and the smaller ionic radius for U(V) than for U(IV). The evidence presented[10] for higher chloro complexes than UCl_6^- is based on the conductometric titration of a solution of $UCl_5 \cdot SOCl_2$ against pyridine in thionyl chloride and on the isolation of a salt of formula $[(CH_3)_4N]_3UCl_8$. Little, if any,

^{20.} Dr. J. M. Cleveland of the Dow Chemical Company, Rocky Flats Division brought the properties of this solvent to the author's attention.

^{21.} C. K. Jørgensen, Acta. chem. scand. 17, 251 (1963).

data exists in the literature to indicate the reactions involved in the use of pyridine in thionyl chloride as a titrant. Selenyl chloride has been reported to form a disolvate with pyridine[22], but an earlier report[23] indicates a monosolvate only. Careful examination of these reports together with the titration data available [23] raises some doubt as to whether such a titration is simply a titration with Cl⁻ ion. Presumably a similar situation would exist with thionyl chloride. The isolation of a salt with the stoichiometry $[(CH_3)_4N]_3UCl_8$ is no guarantee of the presence of the UCl₈³⁻ ion in the crystal or particularly in the solution from which it was obtained.

If dry $(C_2H_5)_4NCl$ is added to a nitromethane solution of a UCl_6^- salt, absolutely no change is observed in the absorption spectrum due to internal 5felectron transitions up to the point of saturation with $(C_2H_5)_4NCl$. Since $(C_2H_5)_4$ NCl is quite soluble in nitromethane and is essentially completely ionized, this amounts to a considerable range of chloride concentration. The absorption spectra of solutions of the UCl₆⁻ salts are identical in various solvents such as nitromethane, acetonitrile, acetone, propylene carbonate, etc. and are essentially the same as the spectra of the solid salts indicating no appreciable reaction with these solvents which might prevent formation of higher chloro complexes. It would certainly be expected that if the coordination number of the U(V) increased beyond six or that if the essentially octahedral symmetry of the UCl_6^- ion was destroyed, an appreciable spectral change would occur. This is known to be the case with the U(V) fluoride complexes [7]. Thus it can be concluded that higher chloro complexes than UCl₆⁻ do not form in nitromethane. Since this is not due to complexing of U(V) by the nitromethane, higher complexes would not be expected in other solvents either.

Hexaiodo complex. From the optical electronegativity of U(V) obtained from the spectral data for UCl_6^- and UBr_6^- as discussed later, it was predicted that the UI_6^- complex would be extremely unstable toward decomposition to U(IV) and iodine (I_3^{-}) . The preparation of bromide and iodide complexes of relatively strongly oxidizing metal ions by conversion of the chlorides with liquid HBr and HI respectively has recently been described [24,25]. It can be predicted as shown later in this paper that the UI_6^- ion will have molar extinction coefficients > 1000 throughout the entire visible region due to electron transfer transitions, and thus salts or moderately concentrated solutions of this ion will be intensely black in color. When anhydrous HI is condensed onto either $(C_2H_5)_4NUCl_6$ or $(C_6H_5)_4$ AsUCl₆ at -78° and allowed to melt in the manner used to prepare other unstable iodo complexes [24,25], the uranium salt is immediately converted to a material resembling carbon black. This black solid decomposes irreversibly to the red-brown color of I_3^- at about -30°, and a water leach of the product indicates U(IV) and insoluble I_3^- salts. If similar experiments are performed with salts (including the $(C_3H_7)_4N^+$, $(C_2H_5)_4N^+$, $(C_6H_5)_3PH^+$, and $(C_6H_5)_4As^+$) of $UO_2Cl_4^{2-}$, exactly the same results are obtained. Since black iodo complexes of U(IV) and

^{22.} I. Lindqvist and G. Nahringbauer, Acta crystallogr. 12, 638 (1959).

^{23.} G. B. L. Smith, Chem. Rev. 23, 165 (1938).

^{24.} J. L. Ryan, Inorg. Chem. 8, 2053 (1969).

^{25.} J. L. Ryan, Inorg. Chem. 8, 2058 (1969).

(VI) are not to be expected, both $UI_6^{2-}[14,26]$ and $UO_2I_4^{2-}[14,27]$ being red, it was concluded that the black unstable salts were salts of UI_6^- . These are thermally unstable at 25° decomposing to U(IV) and free iodine (I_3^-) . The tetraphenylarsonium salt appears to be the most stable (as also with UCI_6^- and UBr_6^-) of those prepared. If it is warmed very rapidly, some of the black color remains at 25° but disappears completely in less than a min at this temperature. The intensely colored UI_6^- complex can also be prepared in solution in nitromethane or acetonitrile by adding anhydrous HI to partially frozen solutions of the UCI_6^- salts, but it has an extremely short lifetime under these conditions.

The fact that UI_6^- , rather than $UO_2I_4^{2-}$, is obtained from the reaction of HI with $UO_2CI_4^{2-}$ is due principally to the dehydrating power of HI rather than its reducing power since $UO_2I_4^{2-}$ is a relatively stable complex toward reduction of the central metal compared to UI_6^- itself and several of the other iodide complexes which have been prepared in this manner [25]. When liquid HI is condensed onto one of the yellow $UO_2CI_4^{2-}$ salts, a bright red coloration, presumably due to $UO_2I_4^{2-}$, can sometimes be observed for an instant when the first HI contacts the solid. Apparently the $UO_2I_4^{2-}$ is deoxygenated and since UI_6 is totally unstable even at low temperature UI_6^- is formed.

Hexafluoro complex. The preparation of salts of the UF_6^- ion have either involved fluorination of U(IV) compounds, reduction of UF_6 , or use of UF_5 which is in turn prepared from UF_4 plus UF_6 as starting materials. Asprey and Penneman[8] have dissolved UF_5 in concentrated aqueous HF and have shown that U(V) is stable in such solutions. Since the actinides are Chatt-Ahrland A group acceptors, the fluoride complexes of U(V) can be expected to be much stronger than chloro complexes. Addition of a chloro complex of U(V) to a concentrated fluoride solution should then result in complete conversion to fluoro complexes. Thus it should be possible to use the easily prepared UCl₆⁻ complexes as starting materials for preparation of at least some UF_6^- salts.

 $(C_6H_5)_4AsUCl_6$ is converted to slightly soluble $(C_6H_5)_4AsUF_6$ by 48% aqueous HF. $(C_6H_5)_4AsUF_6$ is soluble in various inert high dielectric solvents such as acetonitrile. The absorption spectra of such solutions indicate that the UF_6^- ion is stable in the dry solvent, and molar extinction coefficients can be obtained from such solutions. The tetraethylammonium salt is apparently considerably more soluble in 48% HF, and rather large quantities of $(C_2H_5)_4NUCl_6$ can be added to 48% HF to produce blue U(V) solutions. The cesium salt of UF_6^- and presumably other salts can be precipitated from such solutions. This then is a convenient and rapid method of preparing at least some UF_6^- salts without requiring handling of reactive fluorine compounds such as UF_6 or F_2 itself.

Oxopentachloro complex. Bradley et al.[11] have reported the compounds $UOCl_3 \cdot C_2H_5OH$ and $(C_5H_5NH)_2UOCl_5$. These were prepared by adding $UCl_5 \cdot SOCl_2$ to ethanol. The $UOCl_3 \cdot C_2H_5OH$ was recovered by evaporation of the ethanol at 70°, and the $(C_6H_5NH)_2UOCl_5$ was precipitated by first saturating with hydrogen chloride and then adding pyridine. No evidence for these being U(V)

^{26.} K. W. Bagnall, D. Brown, P. J. Jones and J. G. H. du Preez, J. chem. Soc. 350 (1965).

^{27.} J. P. Day and L. M. Venanzi, J. chem. Soc. A, 1363 (1966).

compounds was presented except for the stoichiometry (which also matches that expected if disproportionation to U(IV) and (VI) had occurred) and the fact that the pyridinium salt was used to prepare what was assumed to be uranium pentaethoxide. It should be noted that if uranium pentaethoxide is stable it might also be possible to form it from an equimolar mixture of U(IV) and (VI) salts. The color of the $(C_5H_5NH)_2UOCl_5$ was reported to be pale green which is what would be expected for an equimolar mixture of UCl_6^{2-} and $UO_2Cl_4^{2-}$, the pyridinium salts of which are not appreciably soluble in ethanol containing hydrogen chloride. Ethanol is a water like solvent, and although it is not as strongly coordinating or hydrolytic as water itself, it is much more like water in these respects than solvents such as acetonitrile, nitromethane, acetone, etc. It would be surprising if U(V) chloride would be stable in pure ethanol particularly at 70°. When $(C_{2}H_{5})_{4}$ NUCl₆ is added to absolute ethanol immediate and complete disproportionation to U(IV) and (VI) occurs as determined spectrophotometrically. Saturation of this solution with anhydrous HCl does not cause reconversion to U(V). It should be noted however that if the $(C_2H_5)_4$ NUCl₆ is added after the ethanol has been saturated with HCl, it dissolves to produce a solution of UCl_6^{-} . Anhydrous HCl is known to markedly decrease the donor properties of ethanol [13,18]. It thus appears that the report [11] of these two U(V) oxochloride complexes is in error. Several reports of the preparation of UOCl₃ and UOBr₃ exist (see the review by Selbin and Ortego[1]). Although some or all of these reports may be correct, none (including the very crude spectral data of Kaufman and Rohmer [28]) offer adequate evidence that the products obtained are pure U(V)compounds.

If a very small amount of water is added to a nitromethane solution of UCl_6^- containing excess Cl⁻, the solution becomes blue in color (about like that of Pu(III)) and has an absorption spectrum like that shown in Fig. 1. This spectrum



Fig. 1. Absorption spectra of the uranium(V) oxochloro complex: (1) solid $[(C_2H_5)_4N]_2$ -UOCl₅ and (2) $[(C_2H_5)_4N]_2$ UOCl₅ in nitromethane containing excess anhydrous $(C_2H_5)_4NCl$ (below 1400 m μ only).

28. G. Kaufman and R. Rohmer, Bull. Soc. chim. Fr. 1969 (1961).

is very unlike the known solution spectra of the $UCl_6^{2-}[14]$ and $UO_2Cl_4^{2-}[29]$ ions which are the U(IV) and (VI) species which would be obtained under these conditions and is without question due to a U(V) species. Similar blue solutions are obtained by adding a UCl₆⁻⁻ salt to nitromethane solutions of "as purchased" but not vacuum dried $(C_2H_5)_4NCl$. If $(C_2H_5)_4NUCl_6$ is added to a concentrated solution of this undried $(C_2H_5)_4NCl$ in nitromethane, the blue product is not appreciably soluble and the UCl₆⁻ salt is slowly converted to blue solid. The absorption spectrum of this blue solid is almost identical to the solution spectrum. but the spectrum of material prepared in this manner shows the presence of a few percent of U(IV) and (VI) as the UCl_6^{2-} and $UO_2Cl_4^{2-}$ ions. This controlled hydrolysis of the UCl₆⁻ ion in the presence of excess Cl⁻ can be carried out in a variety of solvents. It was found, however, that if a very pure product essentially free of U(IV) and (VI) is desired it is best to carry out the reaction at low temperature, where the rate of disproportionation is apparently slowed more than the rate of hydrolysis, and under conditions where the salt is quite insoluble. The spectrum of the solid tetraethylammonium salt, $[(C_2H_5)_4N]_2UOCl_5$, prepared under such conditions and containing less than 1% U(IV) and (VI) is shown in Fig. 1.

The fact that the solution and solid spectra are essentially identical indicates that the same U(V) species are present. The solubility of the complex indicates that it is not a bridged polymer, and it is most probably simply the $UOCl_5^{2-}$ ion. The solid tetraethylammonium salt is remarkably stable to atmospheric moisture, remaining blue in color after months of complete exposure to laboratory air. It is not at all stable to liquid water, and the blue color disappears quickly in solvents in which the solid is soluble and which contain small amounts of water. The complex is not appreciably stable in dry nitromethane in the absence of excess chloride, the blue color disappearing in a few min. It is similarly unstable even in the presence of excess chloride if an appreciable amount of water is present. If the dry salt is dissolved in dry nitromethane containing dry $(C_2H_5)_4NCl$ disproportionation does not occur to an appreciable extent at least for several hr.

Solutions of $UOCl_5^{2-}$ are converted to UCl_6^- by even small amounts of anhydrous HCl. This instability to acid is a further argument against the reported[11] preparation of a pyridinium salt and even raises some possible question about the reported[30] salts of $NpOCl_5^{2-}$ about which more will be said later[31]. This result also indicates that the single oxygen of the $UOCl_5^{2-}$ complex is not held nearly as strongly relative to chlorides as are the two oxygens of U(VI).

The absorption spectrum of $[(C_6H_5)_4As]_2UOCl_5$ is essentially identical to that of the $(C_2H_5)_4N^+$ salt except for minor shifts in the peak positions. A shift of the rather broad band in the visible region from about 590 m μ in the tetraethylammonium salt to about 580 m μ in the tetraphenylarsonium salt causes the latter to have a violet cast. This salt is also not extremely sensitive to atmospheric moisture although it may be more so than the tetraethylammonium salt. The pyridinium salt of $UOCl_5^{2-}$ is also blue and has the same absorption spectrum as the tetraethylammonium salt confirming that the previous report[11] of this

^{29.} J. L. Ryan, Inorg. Chem. 2, 348 (1963).

^{30.} K. W. Bagnall and J. B. Laidler, J. chem. Soc. A, 516 (1966).

^{31.} J. L. Ryan, To be published.

compound was in error. The pyridinium salt of $UOCl_5^{2-}$ is unlike the tetrathylammonium or tetraphenylarsonium salts in that it is very sensitive to atmospheric moisture. This is not surprising since even $(C_6H_5NH)_2UCl_6$ is very deliquescent. Other salts of $UOCl_5^{2-}$ can undoubtedly be prepared by this method. The blue tetramethylammonium salt was precipitated by addition of undried chloroform and undried $(CH_3)_4NCl$ to a propylene carbonate solution of $(CH_3)_4NUCl_6$ plus chlorine but was not analyzed.

 $[(C_6H_5)_4As]_2UOCl_5$ was found to change reversibly from violet-blue to bluegrey up to about 150°. At higher temperatures irreversible disproportionation to U(IV) and (VI) occurred. UOCl₃ has been reported to be a brown solid which is stable and involatile in an evacuated ampoule up to 450°[32]. If this is correct, heating of the pyridinium salt of UOCl₅²⁻ under vacuum might be expected to produce UOCl₃ since pyridine hydrochloride is relatively volatile. A sample of $(C_5H_5NH)_2UOCl_5 \cdot 2 \cdot 5C_5H_5NHCl$ was evacuated to < 5 microns and was then heated until evolution of C_5H_5NHCl ceased (< 400°). The sample first turned green and the final residue was a brown powder. A small amount of yellow material (probably UCl₅) condensed just above the brown powder. The brown powder was not completely water soluble and probably contained some UO₂ or U₃O₈. The absorption spectrum of the brown powder above about 700 m μ (below which light scatter was severe) indicated U(IV). Thus is appears that UOCl₃, if such indeed exists, cannot be prepared in this manner.

Oxopentabromo complex. The green uranium(V) oxobromo complex, $UOBr_5^{2-}$, can be prepared by controlled hydrolysis of the UBr_6^- complex in the presence of excess Br^- in a manner analogous to the preparation of the oxochloro complex. The oxobromo complex is less stable in solution than the oxochloro complex. It disproportionates sufficiently rapidly that absorption spectra of freshly prepared solutions in dry nitromethane containing excess bromide contain large contributions due to U(IV) and (VI). Because of this, preparation of salts of the oxobromo complex must be carried out at low temperature under conditions of low compound solubility to avoid gross contamination with U(IV) and (VI) as the UBr_6^{2-} and $UO_2Br_4^{2-}$ ions. With these precautions products with not more than about 5% U(IV) plus U(VI) were obtained.

The tetraethylammonium salt of $UOBr_5^{2-}$ appears to contain 2.5 moles of extra tetraethylammonium bromide. The essential identity of the absorption spectra of the solid tetraphenylarsonium salt and tetraethylammonium salt and the fact that this spectrum is very similar to that of the $UOCl_5^{2-}$ complex as shown in Fig. 2 indicate that the extra 2.5 bromide ions are not in the uranium coordination sphere. The green color of the $UOBr_5^{2-}$ complex in contrast to the blue $UOCl_5^{2-}$ is due to strong electron transfer absorption below about 460 m μ in the bromo complex. Both salts are relatively stable to atmospheric moisture and can be handled for brief periods in laboratory air but do not show the stability to atmospheric moisture over prolonged periods exhibited by $[(C_2H_5)_4N]_2UOCl_5$.

Oxopentafluoro complex. The pink UOF_5^{2-} complex is obtained by the hydrolysis of the UF_6^- complex in the presence of excess fluoride in a variety of solvents including nitromethane, acetonitrile, and even ethanol or water if these

^{32.} I. A. Glukhov, S. S. Eliseev and E. E. Vozdaeva, Russ. J. inorg. Chem. (English transl.) 13, 483 (1968).



Fig. 2. Absorption spectra of uranium(V) oxohalide complexes: (1) solid $[(C_2H_5)_4N]_2$ -UOF₅, (2) solid $[(C_2H_5)_4N]_2$ UOCl₅, and (3) solid $[(C_2H_5)_4N]_2$ UOBr₅·2·5(C₂H₅)₄NBr.

are saturated with the extremely soluble $(C_2H_5)_4NF$. The tetraethylammonium salt can be prepared from several of these solvents using $(C_2H_5)_4NUCl_6$ as starting material since $(C_2H_5)_4NUF_6$ was not prepared. As with the preparation of $(C_6H_5)_4AsUF_6$ from the corresponding chloro complex, complete replacement of chlorides by fluorides can be expected. The use of mixed ethanol-acetone instead of other solvents for preparation of the salt is based on the high solubilities of $(C_2H_5)_4NCl$ and $(C_2H_5)_4NF$ relative to the solubility of the product. Also color producing reactions were observed between nitromethane and $(C_2H_5)_4NF$ or its impurities.

The UOF_5^{2-} complex appears to be much more stable toward disporportionation than either $UOCl_5^{2-}$ or $UOBr_5^{2-}$. This is demonstrated by the fact that a pink solid (presumably containing UOF_6^{2-}) is obtained if $(C_6H_5)_4AsUF_6$ is treated with saturated aqueous $(C_2H_5)_4NF$ and by the fact that UOF_5^{2-} peaks (along with those of U(IV)) were observed in the spectrum of a solution of $(C_2H_5)_4NUCl_6$ in saturated aqueous $(C_2H_5)_4NF$. The complex does disproportionate rather readily in the absence of excess fluoride if hydrolytic substances are present, and in fact the tetraethylammonium salt cannot be washed with even a few per cent ethanol in acetone containing no excess fluoride. The salt is also unstable to prolonged exposure to atmospheric moisture. It does appear though that, in F⁻ saturated, non-hydrolytic solvents which are very low in water that U(V) is the stable valence state. Thus in dry acetonitrile saturated with vacuum "dried" $(C_2H_5)_4NF$ (which is however not anhydrous) the following reaction proceeds well to the right under the influence of u.v. light:

$$UCl_6^{2-} + UO_2Cl_4^{2-} + 10F^- \rightleftharpoons 2UOF_5^{2-} + 10Cl^-.$$

The complex does appear, unlike the oxochloro and oxobromo complexes, to be relatively unstable toward oxidation by oxygen. Even dry $[(C_2H_5)_4N]_2UOF_5$ appears to be attacked slowly by dry (4 ppm H₂O) air. The most stable solutions of the UOF_5^{2-} complex were obtained by adding $(C_2H_5)_4AsUF_6$ to oxygen free acetonitrile saturated with vacuum "dried" $(C_2H_5)_4NF$ which still contains enough water to produce the UOF_5^{2-} ion. The absorption spectrum of such a solution is shown in Fig. 3. The UOF_5^{2-} complex appears to be the only appreciably stable U(V) oxofluoro complex which is formed in solution. This is demonstrated by the invariance of the absorption spectrum with varying fluoride concentration from no excess F⁻ to saturated $(C_2H_5)_4NF$ solutions and with varying water concentrations which cause rapid disproportionation. When vacuum "dried" (but still hydrated) tetraethylammonium fluoride is added incrementally



Fig. 3. Absorption spectra of the uranium(V) oxofluoro complex: (1) solid $[(C_2H_5)_4N]_2$ -UOF₅·2H₂O, (2) solid $[(C_2H_5)_4N]_2$ UOF₅, and (3) UOF₅²⁻ in acetonitrile prepared by dissolving $(C_6H_5)_4$ AsUF₆ in a concentrated solution of vacuum "dried" but not anhydrous $(C_2H_5)_4NF$ (below 1650 mµ only).

to a solution of $(C_6H_5)_4AsUF_6$ in dry acetonitrile, the absorption spectrum changes gradually from that of the UF_6^- ion to that of the UOF_5^{2-} ion without the appearance of higher fluoro complexes such as UF_7^{2-} . Addition of 48% aqueous HF to solutions of the UOF_5^{2-} ion causes conversion to UF_6^- .

The tetraethylammonium salt of UOF₅²⁻ precipitates as a dihydrate which is converted to the anhydrous material by vacuum drying. The absorption spectra of the hydrated and the anhydrous salt and the UOF_{5}^{2-} ion in solution are compared in Fig. 3. Although the salt as prepared here contains a moderate amount of U(IV) and (VI), its absorption spectrum contains only slight contribution due to these impurities since the molar extinction coefficients of the U(IV) and (VI) species involved [16] are lower than those for UOF_5^{2-} . Spectra (1) and (2) and spectrum (1) in Fig. 2 contain a very small contribution due to U(IV) in these samples. Thus, the small peaks in the 1100–1300 and 1600–1800 m μ regions are at least partially due to U(IV). The fine structure in the 400-500 m μ region in spectrum (1), Fig. 3 is due to U(VI). The relatively small difference in the spectra of the hydrated and anhydrous salts indicate that the two moles of water are not in the uranium coordination sphere. It appears more likely that the two moles of water are hydrogen bonded to the fluoride atoms of the UOF_{5}^{2-} ion producing minor distortion of the complex and small changes in the absorption spectrum as in the case of hydrogen bonding of stronger hydrogen bond donors to actinide chloro and bromo complexes [29,33]. This hypothesis is in agreement with the observation in the i.r. region that the U-O frequencies decrease from 872 and 780 cm^{-1} to 852 and 760 cm^{-1} upon drying the salt. This would indicate a stronger metal-oxygen bond in the hydrated material as would be expected if the metal fluorine bonds were weaker in the hydrate. It would appear from the very close similarity of the absorption spectra of the anhydrous salt and the UOF_5^{2-} ion in the solution that the ion in solution is not hydrated. $[(C_2H_5)_4N]_2UOF_5$ is isostructural with $[(C_2H_5)_4N]_2UF_6$. Since the absorption spectrum of the latter compound indicates that it contains the octahedral UF_6^{2-} ion[16] the U(V) salt apparently contains the simple UOF_5^{2-} ion.

ELECTRONIC AND VIBRONIC SPECTRA OF HEXAHALIDE COMPLEXES

The absorption spectrum of the UF_6^- ion in solid CsUF₆ has been discussed by Reisfeld and Crosby[34], and the solution spectrum of the UCl_6^- ion has been discussed by Selbin *et al.*[2]. It is possible by comparison of the absorption spectra of the various hexahalides in both solids and solutions to gain information not presented in this earlier work and to help confirm or reject some of the earlier interpretations. Since much more detailed analysis of the spectra of all the hexahalide complexes (including both liquid nitrogen and liquid helium temperature absorption spectra) is currently in progress[12], only conclusions from the room temperature visible, near i.r., and far i.r. spectra are discussed here.

The absorption spectra (due to internal 5*f* transitions) of the solid tetraphenylarsonium salts are shown in Fig. 4 and the positions and the intensities of the absorption bands for the UX_6^- ions in solution are listed in Table 1. It is quite

^{33.} J. L. Ryan, Inorg. Chem. 3, 211 (1964).

^{34.} M. J. Reisfeld and G. A. Crosby, Inorg. Chem. 4, 65 (1965).



Fig. 4. Absorption spectra of uranium(V) hexahalide complexes: (1) solid (C_6H_5)₄AsUF₆, (2) solid (C_6H_5)₄AsUCl₆, and (3) solid (C_6H_5)₄AsUBr₆. The relatively weak peak at 1130 m μ and the somewhat more intense narrow group between 1660 and 1700 m μ in all spectra are due to the (C_6H_5)₄As⁺ ion.

evident from the virtual identity of the absorption spectrum of $(C_6H_5)_4AsUF_6$ in Fig. 4 and that of $CsUF_6[34]$ that $(C_6H_5)_4AsUF_6$ contains the UF_6^- ion as is known to be the case for the cesium salt[9,34,35]. (This is not the case for $RbUF_6$ which has a different absorption spectrum[9] and does not contain the UF_6^- ion[36].) It is also apparent from the close similarity of the spectra in Fig. 4 that all three of the hexahalide salts contain the MX_6^- ions. The molar extinction coefficients of the hexahalide complexes (Table 1) are of a reasonable order of magnitude for octahedral complexes (compare to the intensities for the UOF_5^{2-}

35. A. Rosenzweig and D. T. Cromer, Acta crystallogr. 23, 865 (1967).

36. J. H. Burns, H. A. Levy and O. L. Keller, Jr., Acta crystallogr. 24B, 1675 (1968).

UF	6-	UCL	6	UBr ₆ -			
σ	E	σ	E	σ	E		
(16,000)	(0.14)	(11,760)	(1.3)	(10,810)	(3.0)		
16,130	0.39	11,570]	4.8	10 500	8.6		
15,630	0.77	11,440}∓	4.7	10,390			
14,120	0.53	10,560	3.7	9850	6.4		
13,070	0.51	9940	3.7	9420	5.8		
7905	0.84	7112	0.7	7045	0.7		
7553	1.6	6923	4.4	6909	7.0		
7513	1.7	6891	11.0	6878	22.0		
7386	5.0	6807	13.8	6826	15.8		
7246	1.0	6715	8.5	6769	23.0		
†		6686	1.8	(6744)	(7 · 0)		
6849	~ 0.08	6491	0.1	6609	0.2		

Table 1. Intensities of transitions of UX_6^- complexes in solution*

 σ is the wave number in cm⁻¹ and ϵ is the molar extinction coefficient. The UF₆⁻ ion is in acetonitrile and the others are in nitromethane. Shoulders in parenthesis.

*This band was not measured because of solvent interference.

‡These two bands were incompletely resolved.

and $UOCl_5^{2-}$ ions in Figs. 1 and 3) and increase with increase in halide mass as also observed for U(IV) hexahalides[14]. Although appreciable shifts in positions of the transitions occur with change of halide, quantitative estimates of the nephelauxetic effect are difficult because of the limited number of transitions available. The nephelauxetic effect does appear to be at least as large as that observed in the uranium(IV) hexahalide complexes[14] though.

As previously pointed out [2,34], octahedral hexahalide complexes of U(V)might be expected to show only four peaks $(\Gamma_7 \to \Gamma_8, \Gamma_7 \to \Gamma_{7'}, \Gamma_7 \to \Gamma_{8'}$ and $\Gamma_7 \rightarrow \Gamma_6$) if only pure electronic transitions were considered. As shown by Satten et al. in the case of the UCl_6^{2-} complex [37,38], the much more detailed absorption spectra actually observed results from vibronic coupling arising from simultaneous change of electronic and vibrational states. Actually in O_h symmetry the pure electronic lines are forbidden as electric dipole transitions and only the vibronic transitions are usually observed[37-39]. The absorption spectrum of $CsUF_6$ has been interpreted on this basis by Reisfeld and Crosby assuming that all the pure electronic transitions were either very weak or entirely missing. Actually the UF_6^- ion in $CsUF_6$ is known to be distorted slightly from octahedral symmetry [9, 34, 35], and it has been noted that only relatively minor distortion of the octahedron can produce significant increases in the intensity of the pure electronic transitions in the case of other 4f and 5f group hexahalide complexes [13, 33, 38, 40]. Thus it cannot be expected that the pure electronic transitions for the UX_6^- will necessarily be completely missing or extremely weak.

It is apparent from Fig. 4 that the UX_6^- spectra all show three similar groups of

^{37.} R. A. Satten, D. J. Young and D. M. Gruen, J. chem. Phys. 33, 1140 (1960).

^{38.} S. A. Pollack and R. A. Satten, J. chem. Phys. 36, 804 (1962).

^{39.} R. A. Satten, J. chem. Phys. 29, 658 (1958).

^{40.} J. R. Morrey, Inorg. Chem. 2, 163 (1963).

peaks with the fourth group (in the region above $1600 \text{ m}\mu$ in the case of UF_6^-) presumably being above the wavelength range shown for UCl_6^- and UBr_6^- . This fourth group or at least part of it has been observed at about $2600 \text{ m}\mu$ for UCl_6^- [2]. The three band groups observable in all three UX_6^- consist (starting at the high energy end) of a relatively narrow doublet, a broad doublet, and a group of somewhat more intense very sharp peaks.

 $\Gamma_7 \rightarrow \Gamma_{7'}$. The lowest energy group present for all three complexes in Fig. 4 is shown on an expanded scale in Fig. 5. This group consists in all three hexahalides of a series of transitions which appear to be equally spaced on each side of a relatively strong narrow central peak. This central peak is interpreted here to be the pure electronic transition with vibronic transitions equally spaced at higher and lower energies. This interpretation agrees with the interpretation of this region for the UCl₆⁻ solution spectrum by Selbin *et al.*[3]. It is not in agreement with the interpretation of the spectrum of UF₆⁻ in CsUF₆ by Reisfeld and Crosby [34] who assigned the pure electronic transition to the very weak, lowest energy member of this group for UF₆⁻. It should be noted, however, that the pure electronic transition was assigned in both cases[2, 34] as the $\Gamma_7 \rightarrow \Gamma_{7'}$ transition, and there is no reason on the part of this writer to consider this assignment incorrect.

The frequencies of the transitions in the $\Gamma_7 \rightarrow \Gamma_{7'}$ group, their separation from the proposed pure electronic transition, the frequencies observed in the far i.r., and their proposed assignment are given in Table 2. The assignment of the fundamental modes of the UX_6^- complex, ν_3 and ν_4 , is based on their direct measurement in the i.r., ν_3 being the strongest i.r. transition observed and ν_4 the second



Fig. 5. Absorption spectra of uranium(V) hexahalide complexes in the 1200–1560 m μ region: (1) solid (C₂H₅)₄NUBr₆, (2) solid (C₂H₅)₄NUCl₆, and (3) solid (C₆H₅)₄AsUF₆.

		V ibrational	mode	involved		ν_3		$ u_4 $	ν_6			pure	electronic		$ \nu_6 $	ν_4	ν_3
Table 2. Transitions in the 6500–8500 cm ⁻¹ region for UX_6^- salts*	Br ₆	¢	I.K.	frequencies		214		87	68,62‡						68,62‡	87	214
	(C ₂ H ₅₎₄ NUI	Separation	trom center	peak		215		84	58		22	0	26		64	87	219
	1			υ		7038		6907	6881		6845	6823	6797		6759	6736	6604
	Cle	4	I.K.	frequencies		310		122		65,56‡				65.56‡		122	310
	(C ₂ H ₅₎₄ NU	Separation	from center	peak		308		119	94	(58)	25	0	27	(23)	97	125	309
				ь		7109		6920	6895	(6860)	6826	1089	6774	(6729)	6704	6676	6492
	JF ₆	-	I.K.	frequencies		525		173								173	525
	(C ₆ H ₅₎₄ Ast	Separation	from center	peak	(619)	524	339	166	129			0			(611)	162	526
				σ	(8032)†	7937	7752†	7579	7542			7413			(7294)	7251	6887

, • , 0000 \$ f e Halide complexes of pentavalent uranium

171

* σ is the wave number of the transition in cm⁻¹: shoulders are in parenthesis. †These are very weak but real transitions. ‡These are observed as incompletely resolved doublets in the i.r.

strongest. Some other transitions were observed in the i.r. for $(C_6H_5)_4AsUF_6$, but these were known to be due to transitions within the $(C_6H_5)_4As^+$ ion, and they are not listed in Table 2. The assignment of ν_6 (i.r. inactive) is based on the fact that the odd vibrational modes of the MX_6^- complex are expected [2] to couple most strongly with the electronic transitions and the fact that the transitions in question are the strongest of all in the vibronic spectrum of the UCl₆- and UBr_6^- salts and are relatively strong in the UF_6^- salt. The values for the odd fundamental modes of the UX_6^- complexes in the salts shown in Table 2 are then: UF_6^- , $\nu_3 = 525 \text{ cm}^{-1}$, $\nu_4 = 170 \text{ cm}^{-1}$, $\nu_6 = \sim 129 \text{ cm}^{-1}$; UCl_6^- , $\nu_3 = 309 \,\mathrm{cm^{-1}}, \ \nu_4 = 122 \,\mathrm{cm^{-1}}, \ \nu_6 = 95 \,\mathrm{cm^{-1}}; \ \mathrm{UBr_6^-}, \ \nu_3 = 215 \,\mathrm{cm^{-1}}, \ \nu_4 = 87 \,\mathrm{cm^{-1}}, \ \nu_6 = 100 \,\mathrm{cm^{-1}}, \ \nu_6 = 1$ 61 cm⁻¹. The change of these frequencies with change in halide mass is very reasonable in comparison with what would be expected. The fact that a broad doublet is observed in the i.r. spectrum of $(C_2H_5)_4$ NUBr₆ at a frequency roughly equal to that of v_6 (i.r. inactive) is probably fortuitous since a similar doublet is observed at nearly the same frequency for $(C_2H_5)_4$ NUCl₆. Although this i.r. frequency might be due to transitions within the $(C_2H_5)_4N^+$ ion, it seems more likely that it is due to cation-anion vibrational frequencies (lattice vibrations). Support for this comes from comparison of the i.r. spectra of the $(CH_3)_4N^+$, $(C_2H_5)_4N^+$, and Cs^+ salts of the UCl_6^{2-} and UBr_6^{2-} ions[41]. In the UCl_6^- salt this frequency is observed in the vibronic spectrum (Fig. 5) as relatively weak shoulders coupled to the electronic transition at a position separated from ν_6 . In $(C_2H_5)_4$ NUBr₆ it probably just happens to coincide with the i.r. inactive v_6 and is probably hidden by ν_6 in the vibronic spectrum. The weak transitions about 25 cm^{-1} above and below the pure electronic transitions in $(C_2H_5)_4NUCl_6$ and $(C_2H_5)_4$ NUBr₆ are also probably due to coupling to lattice vibrations. Actually curve resolution techniques and low temperature spectra indicate many more transitions than shown in Table 2, and these probably result from various causes including possible breaking of the degeneracy of the fundamental modes. These will be discussed later [12].

The values obtained here for the *odd* fundamental modes for $(C_2H_5)_4NUCl_6$ agree well with those obtained by Selbin *et al.*[2] for UCl_6^- in solution. The correctness of this interpretation is supported by the complete disappearance of the peaks on the low energy side of the pure electronic transition for $(C_6H_5)_4$ -As UCl_6 at liquid helium temperatures [12].

 $\Gamma_7 \rightarrow \Gamma_{8'}$. The next higher energy group of peaks for the UX_6^- consist of a pair of relatively broad transitions at 14,180 and 12,250 cm⁻¹ for $(C_6H_5)_4AsUF_6$, 10,430 and 9950 cm⁻¹ for $(C_2H_5)_4NUCl_6$ and 9805 and 9435 cm⁻¹ for $(C_2H_5)_4$ -NUBr₆. The lower energy band was assigned by Reisfeld and Crosby[34] in the case of CsUF₆ as the $\Gamma_7 \rightarrow \Gamma_{8'}$ transition vibronically coupled to ν_3 , and the higher energy band was assigned as the $\Gamma_7 \rightarrow \Gamma_6$ transition vibronically coupled to the odd mode, ν_4 . This assignment was undoubtedly influenced by the fact that they did not observe a narrow, somewhat more intense group of bands at higher energy. This was in turn probably due to the fact that their CsUF₆ contained some U(IV), and they apparently attributed all the absorption in this region to this impurity. Examination of spectra of samples which contained U(IV) and com-

W. E. Keder and J. L. Ryan, Paper presented to the 22nd Northwest Regional Meeting of the American Chemical Society. Richland, Washington, (June 16-17, 1967).

parison to the spectrum shown in Fig. 4 shows that the spectrum of $(C_6H_5)_4$ AsUF₆ in Fig. 4 does not contain any contribution from U(IV) and that the narrow group centered at about 15,900 is real for UF₆⁻. This narrow group is of course present also in UCl₆⁻ where U(IV) interference is not present.

The broad pair referred to at the first of the preceeding paragraph was assigned by Selbin *et al.*[2] in the case of the UCl₆⁻ solution spectrum to a split (Kramer's doublet) $\Gamma_7 \rightarrow \Gamma_{8'}$ transition (having unresolved vibronic levels). Their support for this was the roughly equal intensity of the two bands which would not be expected if they were vibronic levels above and below an unobserved center electronic level. Further support for this assignment comes from the fact that in going from UF_6^- to UBr_6^- the separation between these bands, although of an order of magnitude which would not exclude vibronic origin, changes by a much greater ratio between the UF_6^- and UCl_6^- ions than between the UCl_6^- and UBr_6^- ions whereas the reverse would be expected for vibronic origin.

 $\Gamma_7 \rightarrow \Gamma_6$. The remaining group of bands observed for all the UX₆⁻ ions (Fig. 4) is a relatively narrow group centered at about $15,900 \text{ cm}^{-1}$ for $(C_6H_5)_4$ AsUF₆, 11,470 cm⁻¹ for $(C_2H_5)_4NUCl_6$, and 10,560 cm⁻¹ for $(C_2H_5)_4NUBr_6$. In $(C_2H_5)_4$ -NUCl₆ this group consists of a pair of sharp peaks at 11,560 and 11,376 cm⁻¹ with shoulders at about 11,770 and 11,155 cm⁻¹. The center pair of peaks are interpreted here as due to coupling of the ν_6 mode to a missing (within the limits of resolution of the 25° spectrum) electronic transition. The shoulders are then due to coupling of the v_3 mode to this missing electronic peak. Thus the measured separation between the two peaks is 184 cm^{-1} (2 × ν_6) and between the two shoulders is 615 cm⁻¹ ($2 \times \nu_3$) with the missing pure electronic transition at the common center, 11,470 cm⁻¹. The lower intensity of the transitions on the low energy side further supports this argument as does the fact that the center peak is present after melting and freezing $(C_6H_5)_4$ AsUCl₆ which causes physical distortion (see also Ref. [40]). Low temperature results [12] also confirm this interpretation. Selbin et al.[2] observed a single peak in the UCl_6^- solution spectrum (assigned as the $\Gamma_7 \rightarrow \Gamma_6$ electronic transition) with a shoulder on the high energy side which they tentatively assigned as due to vibronic coupling with the totally symmetric mode, ν_1 . Actually, the solution spectra measured here (Table 1) show this peak partially resolved; and, within the limits of resolution, the solution spectrum agrees with the present interpretation.

As seen in Fig. 4 the UBr_6^- spectrum in this region is very similar to that of UCl_6^- . For $(C_2H_5)_4NUBr_6$ a pair of peaks are observed at 10,493 and 10,620 cm⁻¹ separated by 127 cm⁻¹ (2 × ν_6) with shoulders at 10,765 and 10,335 cm⁻¹ separated by 430 cm⁻¹ (2 × ν_3). The missing pure electronic transition would then be at the common center, 10,555 cm⁻¹. The UF₆⁻ spectrum in this region appears to be somewhat more complex. Actually more than four transitions are observed (mostly as poorly resolved shoulders) and the low energy member of the most prominent pair is the most intense which indicates that the pair are probably not the two vibronic transitions expected from coupling with ν_6 . The separation also is too large for this. It appears that the pure electronic transition may be present in this case. The UF₆⁻ octahedron is known to be distorted in CsUF₆ but the situation is unknown for UCl₆⁻ and UBr₆⁻. It should be noted that the molar extinction coefficients (Table 1) of UF₆⁻ are much lower than for UCl₆⁻ and UBr₆⁻

and this causes an experimental problem resulting in poorer resolution in spectra of solid UF₆⁻ salts. Also the overlap with the broad transitions at lower energy is worse for UF₆⁻ than for UCl₆⁻ and UBr₆⁻. Because of this, it appears that complete interpretation of this region will have to await higher resolution low temperature spectra[12]. Nevertheless the general similarity in appearance of this region and the fact that its total width is approximately $2 \times \nu_3$ indicates that it results from the same electronic transition as the corresponding UCl₆⁻ and UBr₆⁻ peaks (assigned by Selbin *et al.* as $\Gamma_7 \rightarrow \Gamma_6$ in the case of UCl₆⁻).

The lack of an observable pure electronic transition in UCl₆⁻ and UBr₆⁻ for the region assigned [2] as due to the $\Gamma_7 \rightarrow \Gamma_6$ transition and the marked presence of the pure electronic transition in the group assigned [2,34] as due to the $\Gamma_7 \rightarrow \Gamma_{7'}$ transition raises an interesting question. Is the presence of the pure electronic transition for $\Gamma_7 \rightarrow \Gamma_{7'}$ due to distortion (known to be present to a small extent in CsUF₆) or is it due to magnetic dipole contribution? It should be noted that the pure electronic $\Gamma_7 \rightarrow \Gamma_{7'}$ transition is present to about the same extent in all the UX_6^- . It appears from Table 1 to be somewhat less intense in UF₆⁻ than in UCl₆⁻ and UBr₆⁻, but its greater width (Fig. 5) indicates that the oscillator strengths vary much less than the values of ϵ . It also appears to have about the same intensity (relative to the vibronic peaks) in all salts or in solutions of a given UX_6^- . Thus if it is due to distortion, it appears that the distortion is inherent in all UX_6^- complexes and is related to the nature of the bonding (orbitals involved) and not to steric effects such as the size of the halogen or size or nature of the cation associated with the UX_6^- anion.

The apparent absence of the pure electronic $\Gamma_7 \rightarrow \Gamma_6$ transition and its presence in $(C_6H_5)_4$ AsUCl₆ which has been melted and then frozen would tend to indicate that there is not appreciable distortion in the UCl₆⁻ and UBr₆⁻ complexes. (It should be noted that melting and quick freezing of $(C_6H_5)_4$ AsUCl₆ also appreciably intensifies the $\Gamma_7 \rightarrow \Gamma_{7'}$ electronic transition.) Eisenstein and Pryce [42] have stated that the $\Gamma_7 \rightarrow \Gamma_6$ transition is not expected as a magnetic dipole transition. They have also stated that magnetic dipole transitions should be possible to $\Gamma_{7'}$, Γ_8 and $\Gamma_{8'}$ levels and that of these the magnetic dipole contribution to the $\Gamma_7 \rightarrow \Gamma_{7'}$ transition should be strongest by a factor of ten. If this is the case and the assignments are correct, it would appear that the relatively strong, narrow electronic transition (assigned as the pure electronic in Table 2) in the 6800 to 7500 cm⁻¹ region for the UX_6^- is due to magnetic dipole contribution to the $\Gamma_7 \rightarrow \Gamma_{7'}$ transition. It is hoped that work now in progress[12] will answer this question.

ELECTRONIC AND I.R. SPECTRA OF OXOHALIDE COMPLEXES

The absorption spectra of the uranium(V) oxohalide complexes are shown in Figs. 1-3. No absorption peaks were observed in the 2000 to 2500 m μ region for any of these complexes. It appears that all of these complexes show four groups of transitions as in the hexahalide complexes. It might be tempting to treat the oxohalide complexes as slightly distorted octahedral species and to assign these four transitions to the same four transitions in order of energy as assigned in the case of the MX_6^- . It should be noted though that this would assign the lowest 42. J. C. Eisenstein and M. H. L. Pryce, *Proc. R. Soc. Lond.*, 255A, 181 (1960).

energy and the third lowest energy transitions to Γ_8 levels which are expected to be split into pairs of Kramer's doublets by distortion from octahedral symmetry. It has been noted [1] that the separation between the pair assigned as the split $\Gamma_7 \rightarrow$ $\Gamma_{8'}$ for various U(V) complexes appears to increase as distortion from octahedral symmetry increases. The third lowest energy transition in the oxohalide complexes is certainly not as wide as would be expected (based on the behavior of the MX_6^- and other U(V) species) if it contained both components of a split $\Gamma_7 \rightarrow \Gamma_{8'}$ transition. A more reasonable explanation might be to assign the two center groups (which overlap in UOF_5^{2-}) to the split $\Gamma_7 \rightarrow \Gamma_{8'}$ since the spread between these increases markedly in going from UOF₅²⁻ to UOBr₅²⁻, and the distortion from octahedral symmetry would also increase in this direction. Since the energy shifts between the hexahalide and oxohalide complexes are quite large, the possibility that the energy levels are no longer in the same order cannot be excluded. Because of this and the lack of similarity of detail of the spectra to those of the UX_6^- and other U(V) spectra and uncertainty as to the symmetry of the UO X_5^{2-} , no attempt will be made to assign these transitions on the basis of the present data. Comparison of the data of Figs. 1 and 3 with the data of Table 1 indicates that about a five-fold increase in intensity occurs in going from the UX_6^- to the corresponding UOX_5^{2-} . This and the apparent lack of vibronic structure in the UOX_5^{2-} spectra are consistent with the absence of a center of symmetry in the UOX_{5}^{2-} .

Several addition compounds of general formula UCl_5L are known. All of the spectra of these which have been published[2,10,43-45] (and the spectrum of $(C_2H_5)_4NUCl_6$ in ethanol which is somewhat less than saturated with anhydrous HCl) resemble the spectrum of UCl_6^- much more closely than the $UOCl_5^{2^-}$ spectrum does. This no doubt indicates that the U-O bond is much stronger in the $UOCl_5^{2^-}$ complex than is the U-L bond in the UCl_5L complexes and that the field around the U(V) ion is much more distorted in the $UOCl_5^{2^-}$ than in the UCl_5L . This conclusion is also supported by the electron transfer spectra as discussed in the next section.

The far i.r. spectrum of $[(C_2H_5)_4N]_2UOCl_5$ shows bands at about 120 and 253 cm⁻¹, the latter being the more intense and having weak but narrow and distinct side bands at 296 and 197 cm⁻¹. $[(C_2H_5)_4N]_2UOBr_5 \cdot 2 \cdot 5 (C_2H_5)_4NBr$ has similar bands at 80 and 190 cm⁻¹ with the latter more intense band having a weak, narrow sideband at 250 cm⁻¹. The decrease in these metal halogen frequencies (particularly the most intense band) vs. the values for the UCl₆⁻ and UBr₆⁻ complexes is due to the expected weaker metal-halogen bonds in the oxohalide complex having strong metal-oxygen bonds. The tetraethylammonium salts of the UOX₅²⁻ each show two frequencies apparently due to uranium-oxygen vibrations. These are: UOF₅²⁻, 760 and 853 cm⁻¹; UOCl₅²⁻, 813 and 913 cm⁻¹; UOBr₅²⁻, 817 and 919 cm⁻¹. The lower values for UOF₅²⁻ are no doubt due to the effect of a much stronger uranium-fluorine bond than uranium-chlorine or -bromine bond (A group behavior). This then results in a weaker metal-oxygen bond in the UOF₅²⁻ complex.

^{43.} K. W. Bagnall, D. Brown and J. G. H. du Preez, J. chem. Soc. 5217 (1965).

^{44.} D. G. Karraker, Inorg. Chem. 3, 1618 (1964).

^{45.} R. E. Panzer and J. F. Suttle, J. inorg. nucl. Chem. 20, 229 (1961).

J. L. RYAN

ELECTRON TRANSFER SPECTRA

The electron transfer spectra of UCl_6^- and UBr_6^- are shown in Fig. 6. The lowest energy electron transfer bands of UCl_6^- and UBr_6^- are at 25,300 and 17,400 cm⁻¹ respectively. The optical electronegativity of U(V) can be calculated from the equation:

$$\sigma_{\rm obs} = [x_{\rm opt}(X) - x_{\rm uncor}(M)] 30 \,\rm kK \tag{1}$$

where σ_{obs} is the wave number in kK (= 1000 cm⁻¹) of the first electron transfer band, $x_{opt}(X)$ is the optical electronegativity of the ligand, and $x_{uncor}(M)$ is the optical electronegativity of the central metal ion in a definite oxidation state uncorrected for spin-pairing energy and other forms of relativistic effects [46,47]. Values of $x_{uncor}(M)$ of 2·16 and 2·22 are obtained from the data for UCl₆⁻ and UBr₆⁻. This value of 2·2 for U(V) compares to a value of 1·8 for U(1V)[14,47] and 2·3 for U(VI)[47]. Comparison of these values with the value of about 1·8 for U(VI) in uranyl halide complexes [14,47] indicates again that it is the pronounced stabilization of U(VI) in the uranyl entity that causes U(V) compounds to disproportionate so readily.

From the above, it can be calculated that the first electron transfer band for the unstable UI_6^- complex would be at about 7400 cm⁻¹ (1350 m μ). Considering the typical width of the electron transfer bands it is apparent that the internal 5*f* electron transition spectrum of UI_6^- could not be obtained even if the experimental problem of measuring the spectrum without ever warming the compound



Fig. 6. Electron transfer spectra of uranium(V) hexahalide complexes: (1) 8.7×10^{-3} M UBr₆⁻ in nitromethane and (2) 9.8×10^{-3} M UCl₆⁻ in nitromethane. Path length is 0.0108 cm.

^{46.} C. K. Jørgensen, *Molec. Phys.* 5, 271 (1962).
47. C. K. Jørgensen, *Progress in Inorganic Chem.* Vol. 12. In press.

above its decomposition temperature were solved. The first electron transfer band for UF_6^- would be expected at about 50,000 cm⁻¹, and thus the bands observed in the ultraviolet by Reisfeld and Crosby[34] are no doubt due to $5f \rightarrow 6d$ transitions.

The electron transfer transitions are moved considerably toward higher energy in the UOX₅²⁻ complexes vs. the UX₆⁻ complexes. U.V. spectra of solutions of appropriate concentrations (using 0.1 cm-cells) of $[(C_2H_5)_4N]_2UOCl_5$ in dry acetonitrile containing excess dry $(C_2H_5)_4NCl$ always consisted of a group of peaks having halfwidths of about 700 cm⁻¹. These peaks are apparently due to $5f \rightarrow 6d$ transitions. Their positions matched rather closely those for UCl₆²⁻ but their relative intensities did not. Whether these were due to $UOCl_5^{2-}$ or to UCl_6^{2-} impurity was not certain; but in several attempts, no bands attributable to UOCl₅²⁻ electron transfer transitions could be obtained. Absorption spectra of solid $[(C_2H_5)_4N]_2UOBr_5 \cdot 2 \cdot 5 (C_2H_5)_4NBr$ and $[(C_6H_5)_4As]_2UOBr_5$ were obtained and it appears that the first electron transfer transition is a broad shoulder at about $375 \text{ m}\mu$ (26,700 cm⁻¹). This corresponds to a shift of 9300 cm^{-1} to higher energy from the value for UBr₆⁻. A similar value is obtained for the shift in the absorption cutoffs shown for $UOBr_5^{2-}$ and UBr_6^{-} in Figs. 2 and 4 respectively. This value corresponds to 0.3 electronegativity units and results from the pronounced anisotropic [47,48] nature of the UOX_5^{2-} complexes. Thus the very strong metaloxygen bond results in accompanying abnormally weak metal-halogen bonds as also manifested in the i.r. spectra discussed earlier. This effect is not as pronounced as the effect of the two oxygen atoms on U(VI) where the measured x_{uncor} (M) changes by 0.5 electronegativity units [14,47] in going from UCl₆ to $UO_2Br_4^{2-}$. This of course agrees with the chemical behavior, $UOCl_5^{2-}$ being readily deoxygenated by HCl in nitromethane whereas $UO_2Cl_4^{2-}$ is not. The change of 0.3 electronegativity units in going from UBr₆⁻ to UOBr₅²⁻ results in $x_{\text{uncor}}(M)$ for U(V) in UOBr₅²⁻ of 1.9. Comparison of this value to the value of 1.8 for both U(IV) in the UX_6^{2-} environment and U(VI) in the $UO_2X_4^{2-}$ environment shows why the $UOBr_5^{2-}$ ion is quite unstable toward disproportionation.

Although the electron transfer spectra of UCl_5 addition compounds have not generally been measured, their colors[1] indicate that their electron transfer transitions are shifted much less from those of UCl_6^- than are those of $UOCl_5^{2-}$. This indicates much stronger uranium-chlorine bonds in the UCl_5L than in $UOCl_5^{2-}$ and thus stronger uranium-oxygen than uranium-ligand bonds. This is in agreement with the observations on their internal *f* electron spectra, and it emphasizes again the high affinity of the higher valence actinide ions for the oxide ligand.

Acknowledgements – The author wishes to express his appreciation to Mr. L. G. Morgan for helpful discussions of the absorption spectra and for his permission to cite unpublished work. The author also thanks Dr. W. E. Keder who measured many of the i.r. spectra and Mr. C. E. Plucinski for analytical assistance.

48. C. K. Jørgensen, In Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964, p. 11. Publishing House of the Hungarian Academy of Sciences, Budapest (1965).