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## Anion Exchange and Non-Aqueous Studies of the Anionic Chloro Complexes of the Hexavalent Actinides<sup>1</sup>

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Spectrophotometric studies of anion-exchange resins, of solid crystalline salts, and of non-aqueous solutions were used to identify the hexavalent actinide chloride species absorbed by anion-exchange resins and those extracted by liquid alkylammonium extractants. The actinide(VI) tetrachloro complexes were found to undergo hydrogen bond formation with hydronium ion, hydrogen chloride, and tertiary, secondary, and primary alkylammonium ions. The species absorbed by anion exchange resins appear to be  $[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{MO}_2\text{Cl}_4)_2]^{-3}$  from aqueous solutions and  $\text{MO}_2\text{Cl}_4^{-2}$  from alcohol solutions. The species present in the organic phase in solvent extraction by tertiary alkylamines are the tetrachloro complexes hydrogen bonded to the alkylammonium ions. In extraction by liquid quaternary alkylammonium extractants, the species in the organic phase are the simple  $\text{MO}_2\text{Cl}_4^{-2}$  ions. The only effect of this hydrogen bonding on the visible and near-visible absorption spectra of the actinide(VI) tetrachloro complexes is to change the relative peak intensities of the symmetrical metal-oxygen vibrational spectra.

The absorption of U(VI),<sup>2,3</sup> Np(VI),<sup>4</sup> and Pu(VI)<sup>4</sup> by anion-exchange resins from concentrated hydrochloric acid solutions has been demonstrated by Kraus and co-workers. The anion-exchange absorption of U(VI) chloride from mixed alcohol-water solutions of hydrochloric acid has been investigated by Korkisch and co-workers,<sup>5,6</sup> who proposed that the  $\text{UO}_2\text{Cl}_4^{-2}$  ion is the species absorbed. The extraction of U(VI) from hydrochloric acid by tertiary amines has been demonstrated by Coleman, *et al.*,<sup>7</sup> and has been studied more extensively by Bizot and Trémillon.<sup>8</sup> The extraction of U(VI), Np(VI), and Pu(VI) from hydrochloric acid by tri-*n*-octylamine has been studied by Keder.<sup>9</sup> Bizot and Trémillon<sup>8</sup> concluded that the uranyl(VI) chloride species extracted into tertiary amines is  $\text{UO}_2\text{Cl}_4^{-2}$  based on amine capacity measurements. Wilson<sup>10</sup> also has found that the amine to uranium ratio in the organic phase approaches two at high aqueous uranium concentrations. Keder<sup>9</sup> found that the distribution ratios of hexavalent actinides into tri-*n*-octylamine from hydrochloric acid show a second order dependence on amine concentration which also is indicative of extraction of a doubly charged anion.

Although both resin and amine loading experiments and amine dependence experiments usually give useful information regarding the complex species present in the organic phase, both have been found to give erroneous results at times. Resin loading experiments are limited in their applicability by poor kinetics of metal

complex absorption at high metal loadings<sup>11</sup> and by resin invasion complications.<sup>12</sup> These become particularly important in dealing with non-aqueous solutions or concentrated aqueous salt solutions. Amine loading experiments likewise are complicated by second organic phase formation and insolubility of the amine metal complex salt in the organic diluents. Thus the maximum loading of Pu(IV) nitrate into tri-*n*-octylamine corresponds to an amine to plutonium ratio ranging from 4 to about 2.3, depending on the diluent,<sup>10</sup> whereas it has been shown that  $\text{Pu}(\text{NO}_3)_6^{-2}$  is the complex present in the organic phase.<sup>13</sup> Variable dependences of extraction coefficient on amine concentration as a function of diluent have been pointed out by Keder.<sup>9</sup>

Rubidium, cesium, tetraethylammonium, and tetramethylammonium compounds of the general formula  $\text{M}_2\text{UO}_2\text{Cl}_4$  have long been known<sup>14</sup> and their structure<sup>15</sup> indicates that they are salts of the  $\text{UO}_2\text{Cl}_4^{-2}$  ion. The absorption spectra of these salts either in the solid state or in non-aqueous solutions were, surprisingly, quite different from the spectra of uranyl(VI) chloride loaded anion exchange resins or tri-*n*-octylamine extracts of U(VI) from hydrochloric acid, indicating that the simple  $\text{UO}_2\text{Cl}_4^{-2}$  ion is not the species present in the organic phase. The purpose of this work is to elucidate the nature of the hexavalent actinide chloride species present in anion exchange resins and tertiary amine extracts, and to explain the apparent discrepancy between amine dependence and loading data and the spectral observations.

### Experimental

**Actinide(VI) Chloride Solutions.**—Uranyl(VI) chloride solutions were prepared by dissolving  $\text{UO}_3$  (obtained from ignition of

(1) This paper is based on work performed under Contract No. AT(45-1)-1350 for the U. S. Atomic Energy Commission.

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(10) A. S. Wilson, Hanford Laboratories, private communication.

(11) J. L. Ryan and E. J. Wheelwright, Atomic Energy Commission Research and Development Report HW-55893 (Hanford Laboratories), January 2, 1959.

(12) K. A. Kraus and F. Nelson in "The Structure of Electrolytic Solutions," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 362-363.

(13) W. E. Keder, J. L. Ryan, and A. S. Wilson, *J. Inorg. Nucl. Chem.*, **20**, 131 (1961).

(14) E. Rimbach, *Ber. deut. chem. Ges.*, **37**, 461 (1904).

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uranyl nitrate) in concentrated hydrochloric acid. The solutions were taken to dryness and redissolved in concentrated hydrochloric acid twice to ensure the complete absence of nitrate.

Pure plutonium(IV) chloride prepared from anion exchange purified plutonium nitrate<sup>11</sup> as described previously<sup>16</sup> was evaporated to about 600 g. of plutonium per liter. This was then oxidized to Pu(VI) by treatment with electrolytically produced ozone.<sup>17</sup> In one case the plutonium solution was heated with a heat lamp during the oxidation. This appeared to increase the rate of plutonium oxidation considerably, but the oxidation of HCl by ozone was increased to such an extent that periodic addition of concentrated hydrochloric acid was necessary to prevent hydrolysis of the remaining Pu(IV). The solutions were used immediately following ozone treatment and the valence state was checked spectrophotometrically immediately prior to use. The Pu(VI) solutions in either dilute or concentrated hydrochloric acid appeared to be relatively stable for several days. Neptunyl(VI) chloride solutions were prepared in the same manner as the plutonium solutions using pure neptunium(IV) chloride prepared as previously described.<sup>16</sup> The oxidation of the neptunium with ozone was much more rapid than the oxidation of plutonium. Although the Np(VI) solutions in dilute hydrochloric acid were stable for a period of a few days, Np(VI) in 12 M HCl was reduced to Np(IV) so rapidly that the absorption spectrum of pure Np(VI) in 12 M HCl could not be obtained.

**Alkylammonium Chlorides.**—Tetramethylammonium chloride was obtained from Eastman. Tetraethylammonium chloride was prepared as described previously<sup>18</sup> from Eastman tetraethylammonium bromide. Tetra-*n*-propylammonium chloride was prepared by neutralization of tetra-*n*-propylammonium hydroxide obtained either from Eastman or by anion exchange conversion of Eastman tetra-*n*-propylammonium iodide. Tetra-*n*-butylammonium chloride was prepared by anion exchange conversion of tetra-*n*-butylammonium iodide in mixed acetone-water solution.

Trimethylamine hydrochloride was obtained from K and K Laboratories, Inc. A water solution of the initially slightly colored material was evaporated until crystallization began, a large excess of acetone was added, and the crystals so obtained were filtered and washed with acetone. This process was repeated until a saturated aqueous solution of the compound was colorless. Triethylamine, tripropylamine, and diethylamine hydrochlorides were prepared by neutralization of the free amines obtained from K and K Laboratories or Eastman. The initially reddish brown salts were purified in the same manner as the trimethylamine hydrochloride. *n*-Octylamine hydrochloride was prepared by neutralizing Eastman *n*-octylamine in acetone solution with HCl gas. The compound was crystallized from the acetone at  $-78^\circ$ , recrystallized from acetone twice, and dried.

**Preparation of Cesium and Quaternary Ammonium Uranyl(VI) Chloride Salts.**—The salt  $\text{Cs}_2\text{UO}_2\text{Cl}_4$  was prepared by addition of cesium chloride to uranyl(VI) chloride in 12 M HCl. The compound was recrystallized from hot hydrochloric acid through which HCl was being passed. No analysis of this previously reported<sup>14,18</sup> salt was performed.

The salt  $[(\text{CH}_3)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  was prepared by mixing solutions of uranyl(VI) chloride and tetramethylammonium chloride in 8–12 M HCl. This previously reported<sup>14,18,19</sup> salt was not analyzed.

The salt  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  was prepared either by precipitation from hydrochloric acid or from acetone solution. It then was recrystallized from hot hydrochloric acid either with or without addition of HCl gas during cooling and was dried either over a solid  $\text{Mg}(\text{ClO}_4)_2\text{—NaOH}$  mixture or by washing with acetone and drying under a heat lamp. Although the compound

was reported previously,<sup>14,15</sup> analyses were performed. The infrared spectrum of this compound shows it to be anhydrous as reported by Rimbach<sup>14</sup> and Staritzky, *et al.*,<sup>15</sup> and not hydrated as reported by Dieke and Duncan.<sup>18</sup> The salt was much less soluble in lithium chloride solutions than in hydrochloric acid.

*Anal.* Calcd. for  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UO}_2\text{Cl}_4$ : U, 35.4; Cl, 21.1; N, 4.17. Found: U, 35.3; Cl, 21.0; N, 4.14.

The compound  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  precipitates upon mixing solutions of tetra-*n*-propylammonium chloride and uranyl(VI) chloride in  $<6.8 M$  aqueous hydrochloric acid, dilute to saturated aqueous lithium chloride, and mixtures of *ca.* 80 volume % ethanol or acetone and concentrated hydrochloric acid. The absorption spectra of these preparations showed them to be the same irrespective of the solvent used. From aqueous hydrochloric acid solutions  $>7.5 M$  a different compound is obtained which has a distinctive absorption spectrum and will be discussed separately. The absorption spectrum of solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  is virtually identical with those of the solid cesium, tetramethylammonium, and tetraethylammonium salts. The absorption spectra of all of these in nitromethane solution are identical. The pure salt was prepared by recrystallization from hot 6 M HCl and was dried over a solid  $\text{Mg}(\text{ClO}_4)_2\text{—NaOH}$  mixture. It was anhydrous as determined from the infrared spectrum.

*Anal.* Calcd. for  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$ : U, 30.3; Cl, 18.1; C, 36.7; N, 3.57. Found: U, 30.0; Cl, 18.1; C, 36.4; N, 3.50.

A second tetra-*n*-propylammonium uranyl(VI) chloride (compound II) was precipitated from 12 M HCl which is distinctly different from  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  (compound I). Compound II is obtained as thin, generally square plates by crystallization from  $>7.8 M$  aqueous hydrochloric acid, whereas I is obtained as fine granular crystals at 6.8 M HCl or less. The dividing point between the acid ranges in which I and II precipitate may vary somewhat depending on conditions (such as  $(\text{C}_3\text{H}_7)_4\text{NCl}$  to uranyl ratio, temperature, seeding, etc.); however, no conditions were found whereby anything other than pure I was obtained at 6 M HCl and pure II at 12 M HCl. The X-ray diffraction patterns of I and II are distinctly different. The visible and near-visible absorption spectra of solid crystals of I and II are also different, a characteristic which was useful in determining the conditions under which the two compounds could be obtained. These spectra were obtained from petrolatum mulls of crystals which had been vacuum filtered but not otherwise dried.

It was readily determined from spectrophotometric evidence that II decomposed upon drying. Pure I was not obtained from this decomposition, and the spectrum of the product of decomposition was variable depending upon the drying conditions. The residue left upon drying of II was found to contain a Cl/U ratio of less than four. If the residue was dissolved in nitromethane the spectrum appeared to be due to a mixture, but addition of chloride as quaternary ammonium salt produced the  $\text{UO}_2\text{Cl}_4^{-2}$  spectrum. Addition of water instead of chloride to the nitromethane solution had no effect, but addition of HCl gas plus a small amount of water converted the spectrum to that of the original undried salt. Addition of chloride either in the presence or absence of water to a nitromethane solution of  $\text{UO}_2\text{Cl}_2\cdot\text{H}_2\text{O}$  also produced the  $\text{UO}_2\text{Cl}_4^{-2}$  spectrum without producing the spectrum of II as an intermediate. Addition of HCl plus water to a nitromethane solution of  $\text{UO}_2\text{Cl}_2\cdot\text{H}_2\text{O}$  did produce the spectrum of II. This and the fact that II precipitates only from hydrochloric acid more concentrated than that required to obtain  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  made it appear very improbable that the Cl/U ratio of II was less than four. It therefore was concluded that II was not simply a salt of a hydrated chloro complex containing less than four chlorides per uranium but that it contained the hydronium ion.

The ratio of nitrogen to uranium in II was determined from analysis of solutions of the 12 M HCl-washed (but not dried) crystals in water. Twelve analyses of five separate preparations (including samples precipitated directly and samples recrystallized from warm hydrochloric acid through which HCl gas was being passed) were performed. No single analysis deviated from the average by more than the experimental error.

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(18) G. H. Dieke and A. B. F. Duncan, "Spectroscopic Properties of Uranium Compounds," McGraw-Hill Book Co. Inc., New York, N. Y., 1949, p. 137.

Since II was presumed to contain the hydronium ion, attempts were made to dry it in the HCl atmosphere. These attempts were only partially successful. It was found that in an HCl atmosphere even weak drying agents such as calcium chloride decomposed the compound; this decomposition was relatively slow, however. A sample of the compound was recrystallized by slow cooling from warm hydrochloric acid through which HCl gas was passed. This resulted in relatively large crystals of the compound having a low surface to volume ratio. These were filtered, washed with 12 *M* HCl, and dried as a shallow layer over concentrated sulfuric acid in an HCl atmosphere. After 65 hr. the crystals were free flowing and appeared to be dry, but spectrophotometric examination showed no decomposition. A sample was rapidly weighed, dissolved in water, and analyzed for uranium and chloride. (The compound dried in this manner or even dried until decomposition has definitely started evolves both HCl and water upon heating.) A sample was heated to what appeared to be constant weight with a heat lamp and the weight loss and uranium and chloride were determined on the residue.

If II, either dry or wet with concentrated hydrochloric acid, is washed with acetone or ethanol, it is converted immediately to pure I. This apparently is due to the fact that both II and I are somewhat soluble in these solvents and II dissolves rapidly and reprecipitates I. If II is shaken rapidly with a very large excess of diethyl ether (which was chosen because of its low dielectric constant and in which II appears to be insoluble), the aqueous concentrated hydrochloric acid is removed with less than 20% conversion of II to I. Less rapid washing with ether causes greater conversion to I, apparently due to the solubility of II in the aqueous HCl-ether mixture of the solid-liquid interface. Samples of II dried with ether and showing only about 15% conversion to I were dissolved in water and the Cl/U ratio determined.

*Anal.* Calcd. for  $[(C_2H_5)_4N]_3[H_3O(H_2O)_x(UO_2Cl_4)_2]$ : N/U, 1.50; Cl/U, 4.00; U (assuming  $x = 2$ ), 33.11, Cl (assuming  $x = 2$ ), 19.73; U (assuming  $x = 3$ ), 32.70; Cl (assuming  $x = 3$ ), 19.48. Found: N/U, 1.51 (undried samples); Cl/U, 4.01 (dried in HCl atmosphere over  $H_2SO_4$ ); Cl/U, 4.04 (ether-dried); U, 33.00 (dried in HCl atmosphere over  $H_2SO_4$ ); Cl, 19.7 (dried in HCl atmosphere over  $H_2SO_4$ ).

The above analyses verify the composition of II as shown except for the amount of water,  $x$ , present in the hydronium ion in the compound. This can be obtained from the weight loss on heating the compound if the composition of the residue after heating is known. Part of the residue can be considered to be I and the rest either  $UO_2Cl_2 \cdot H_2O$  or  $UO_2OHCl$ . Whether  $UO_2Cl_2 \cdot H_2O$  or  $UO_2OHCl$  is formed as part of the residue can be determined by the Cl to U ratio in the residue. (A sample of uranyl chloride heated under the same conditions as the sample of II was found to be principally  $UO_2Cl_2 \cdot H_2O$  with a small amount of  $UO_2OHCl$ .)

*Anal.* Calcd. for  $2[(C_2H_7)_4N]_3[H_3O(H_2O)_x(UO_2Cl_4)_2] \Delta 3[(C_2H_7)_4N]_2UO_2Cl_4 + UO_2Cl_2 \cdot H_2O + 2HCl + 7H_2O$ : wt. loss, 6.84; U in residue, 35.1; Cl in residue 18.3; Cl/U in residue, 3.50. Found (sample dried in HCl over  $H_2SO_4$ ): wt. loss, 6.87; U in residue, 35.0; Cl, in residue, 18.1; Cl/U in residue, 3.50. This value of three water molecules associated with the oxonium ion agrees with that found in solution by Tuck and Diamond<sup>19</sup> and others.<sup>20</sup>

The preparation of other quaternary ammonium uranyl(VI) chloride salts containing the hydronium ion was attempted. Neither tetraethylammonium nor tetra-*n*-butylammonium yielded such a compound from 12 *M* HCl. From hydrochloric acid saturated with HCl at 0° a tetraethylammonium salt precipitated which had the visual appearance of II and not of  $[(C_2H_5)_4N]_2UO_2Cl_4$ . The visual absorption spectrum of crystals allowed to warm to room temperature was found to be similar to the spec-

trum of samples of II which had undergone partial decomposition. The spectrum also was found to be changing rapidly with time. Thus it appears that the tetraethylammonium salt of  $[H_3O(H_2O)_x(UO_2Cl_4)_2]^{-3}$  does form but that it is much less stable than the tetra-*n*-propylammonium salt.

Tetra-*n*-butylammonium uranyl(VI) chloride was prepared by mixing tetra-*n*-butylammonium chloride and uranyl(VI) chloride in 12 *M* HCl. This compound, unlike the cesium, tetramethylammonium, and tetrapropylammonium salts which formed relatively dense crystalline salts, formed soft waxy crystals which were difficult to wash free of the mother liquor. This undoubtedly is due to the increased length of the alkyl chains. As a result the compound was never prepared in satisfactorily pure form and was not analyzed. The very close similarity of the absorption spectrum of the solid crystals and that of a nitromethane solution of the compound to those of other  $UO_2Cl_4^{-2}$  salts indicated that the compound was  $[(C_4H_9)_4N]_2UO_2Cl_4$ . Other salts prepared in a similar manner from 12 *M* HCl, which were not analyzed for the same reason, were the trimethylphenylammonium and hexadecyltrimethylammonium salts. These also appeared from examination of their absorption spectra to be  $UO_2Cl_4^{-2}$  salts.

**Preparation of Secondary and Tertiary Alkylammonium Uranyl(VI) Chloride Salts.**— $[(CH_3)_3NH]_2UO_2Cl_4$  was prepared by adding  $(CH_3)_3NHCl$  in 12 *M* HCl to uranyl(VI) chloride in 12 *M* HCl. The compound was recrystallized by dissolving it in hot concentrated hydrochloric acid and cooling the solution with HCl passing through. It was dried over  $Mg(ClO_4)_2$ . The dry crystals did not contain water as determined by infrared analysis, although a slight wave length shift between the visible absorption spectra of the wet and dried solid might indicate that the compound precipitated as a hydrate. The spectrum of the dry crystals and that of damp crystals precipitated from ethanol are identical.

*Anal.* Calcd. for  $[(CH_3)_3NH]_2UO_2Cl_4$ : U, 44.7; Cl, 26.7; N, 5.27. Found: U, 43.7; Cl, 26.2; N, 5.27.

$[(C_2H_5)_3NH]_2UO_2Cl_4$  was prepared, recrystallized, and dried in the same manner as the trimethylammonium salt. The absorption spectra of the wet and dry crystals were identical and the infrared spectrum indicated the absence of water.

*Anal.* Calcd. for  $[(C_2H_5)_3NH]_2UO_2Cl_4$ : U, 38.6; Cl, 23.0; N, 4.54. Found: U, 38.6; Cl, 22.4; N, 4.63.

$[(C_2H_7)_3NH]_2UO_2Cl_4$  was prepared in the same manner as the trimethylammonium and triethylammonium salts. The absorption spectra of the wet and dry crystals were identical.

*Anal.* Calcd. for  $[(C_2H_7)_3NH]_2UO_2Cl_4$ : U, 34.0; Cl, 20.2. Found: U, 34.6; Cl, 19.4.

$[(C_2H_5)_2NH]_2UO_2Cl_4$  was prepared by addition of  $(C_2H_5)_2NH_2Cl$  to uranyl(VI) chloride, each in 12 *M* HCl. The compound was recrystallized from warm concentrated hydrochloric acid and was dried over  $Mg(ClO_4)_2$ . No weight loss or difference in analysis was observed if the compound was heated strongly with a heat lamp despite the fact that the treatment caused a change in absorption spectrum and X-ray diffraction pattern of the solid. The compound was anhydrous as determined by infrared spectrum.

*Anal.* Calcd. for  $[(C_2H_5)_2NH]_2UO_2Cl_4$ : U, 42.5; Cl, 25.3; N, 5.00. Found: U, 42.2; Cl, 25.3; N, 5.01.

**Preparation of Alkylammonium Neptunyl(VI) and Plutonyl(VI) Chloride Salts.**— $[(C_2H_5)_4N]_2NpO_2Cl_4$  was prepared by addition of  $(C_2H_5)_4NCl$  in 12 *M* HCl to a concentrated solution of Np(VI) in about 3 *M* HCl. The compound was washed with 12 *M* HCl, followed immediately by an acetone rinse, since Np(VI) was found to be reduced rapidly by concentrated hydrochloric acid. The compound was dried over  $Mg(ClO_4)_2$ .

*Anal.* Calcd. for  $[(C_2H_5)_4N]_2NpO_2Cl_4$ : Np, 35.3; Cl, 21.1. Found: Np, 34.7; Cl, 20.5.

$[(C_2H_5)_4N]_2PuO_2Cl_4$  was prepared in the same manner as the Np analog. Although this compound has been reported previously and is well characterized,<sup>19</sup> it was analyzed.

*Anal.* Calcd. for  $[(C_2H_5)_4N]_2PuO_2Cl_4$ : Pu, 35.5; Cl, 21.1. Found: Pu, 34.6; Cl, 21.4.

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The compound  $[(C_2H_5)_4N]_2PuO_2Cl_4$  was prepared by precipitation from about 6 *M* HCl. The compound was not analyzed but the absorption spectrum of a nitromethane solution of the dry salt was identical with that of the tetraethylammonium salt. One attempt was made to prepare  $[(C_2H_5)_4N]_3[H_3O(H_2O)_5(PuO_2Cl_4)_2]$ , but when HCl was added to the concentrated Pu(VI) solution warming occurred and the Pu(VI) was rapidly reduced to Pu(IV). Because of the difficulty of preparing concentrated Pu(VI) chloride solutions, the attempt was not repeated.

$[(C_2H_5)_3NH]_2PuO_2Cl_4$  was precipitated from about 8 *M* HCl, washed with acetone, and dried over  $Mg(ClO_4)_2$ .

*Anal.* Calcd. for  $[(C_2H_5)_3NH]_2PuO_2Cl_4$ : Pu, 38.7; Cl, 22.9. Found: Pu, 38.7; Cl, 22.8.

**Resin Capacity Measurements.**—Dowex 1, X-4 (50 to 100 mesh) (capacity 4.30 mequiv./g. dry chloride form) was used in uranium capacity determinations. The resin was equilibrated with the 10 *M* HCl uranyl(VI) chloride solutions with continuous shaking for 1 week at 25°. The resin was removed from the solution by vacuum filtration on sintered glass and was eluted with 0.1 *M* HNO<sub>3</sub>. Uranium was determined in both the residual aqueous phase and in the eluate from the resin. A correction for solution adhering to the resin beads was made by eluting glass beads similarly contacted. This correction was very small and was only applicable to the two highest uranium concentrations.

**Analyses.**—All uranium analyses were by controlled potential coulometric titration.<sup>21</sup> Neptunium and plutonium were determined on aqueous solutions by controlled potential coulometric titration<sup>22,23</sup> and on non-aqueous solutions by  $\alpha$ -counting. Chloride was determined by the Volhard method; nitrogen by the Kjeldahl method. Carbon analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Water in nitromethane was determined by titration with Karl Fischer reagent.

**Non-aqueous Solvents.**—The nitromethane was Eastman spectro grade and was dried with Drierite (anhydrous CaSO<sub>4</sub>). The acetone was C.P. grade, the acetonitrile was Eastman practical grade, and the acetic anhydride was reagent grade.

**Spectrophotometric Measurements.**—Spectrophotometric measurements were made with a Cary Model 14 recording spectrophotometer with cell compartment thermostated at 25° unless otherwise stated. All absorption spectra of solutions were obtained with 1.00-cm. silica cells except that of  $C_2H_5UO_2Cl_4$  in nitromethane, for which a 10-cm. cell was used because of the low solubility of the compound. Absorption spectra of crystalline compounds were obtained from mulls of the compounds in petrolatum using calcium carbonate in petrolatum as blank. Spectra of mulls were obtained either by use of 1.00-cm. silica cells with 0.90-cm. silica inserts or by use of silica or glass plates held apart by spacers of the appropriate thickness (about 0.1 cm.). Spectra of compounds which could be melted without decomposition (notably  $[(C_2H_5)_2NH_2]_2(UO_2Cl_4)$ ) also were obtained on solid films of the compounds between silica plates. Absorption spectra of resins containing U(VI) were obtained using 0.5-cm. silica cells with resin treated similarly, except for the presence of uranium, as the blank. Absorption spectra of resins containing Np(VI) and Pu(VI) were obtained in the same manner but with 1.00-cm. cells.

Slit widths were variable within the following limits: solution spectra, 0.01–0.1 mm.; Dowex 1, X-1 and Dowex 1, X-4 (50 to 100 mesh) spectra, 0.5-cm. cells, 0.04–0.4 mm.; 1.00-cm. cells, 0.2–0.7 mm.; and mull spectra, 0.07–0.3 mm. The spectra reported are reproduced photographs of the recorded curves.

## Results

**Resin Studies.**—Figure 1 shows the absorption

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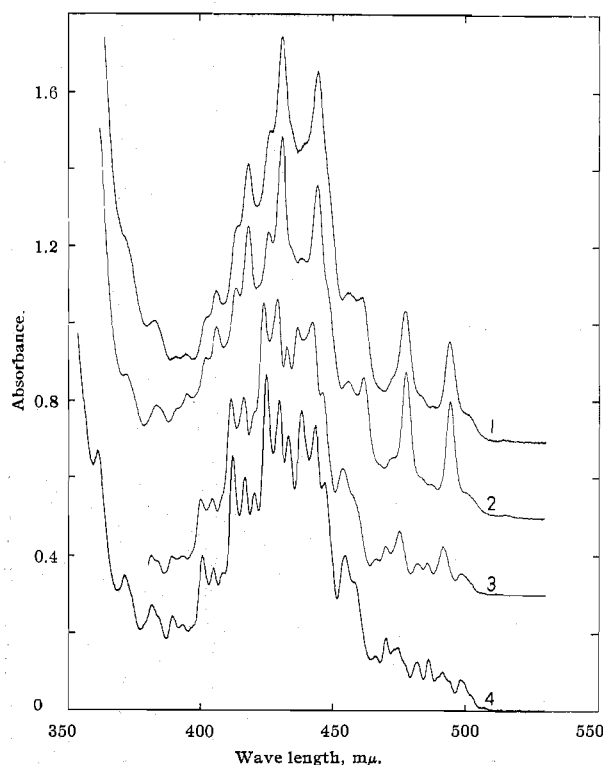


Fig. 1.—Comparison of the absorption spectra of U(VI) chloride on anion-exchange resin and in tertiary amine extractant with the absorption spectra of the  $UO_2Cl_4^{-2}$  ion: (1) U(VI) loaded on Dowex 1, X-4 (50 to 100 mesh) anion-exchange resin from 9 *M* HCl (absorbance scale displaced 0.7), (2) U(VI) extracted into 10 volume % tri-*n*-octylamine in xylene from 4 *M* HCl (absorbance scale displaced 0.5), (3) 0.060 *M*  $[(C_2H_7)_4N]_2UO_2Cl_4$  in nitromethane (absorbance scale displaced 0.3), and (4) solid  $[(C_2H_7)_4N]_2UO_2Cl_4$ .

spectrum of U(VI) loaded on Dowex 1, X-4 anion-exchange resin from 9 *M* HCl, the absorption spectrum of U(VI) extracted into tri-*n*-octylamine in xylene from 4 *M* HCl, and the absorption spectra of  $[(C_2H_7)_4N]_2UO_2Cl_4$  as the solid salt and in nitromethane solution. The absorption spectrum of the resin appears to be independent of resin cross-linkage, hydrochloric acid concentration, and degree of resin loading. The absorption spectrum of  $[(C_2H_7)_4N]_2UO_2Cl_4$  in nitromethane is somewhat different from that of the crystalline solid. That this difference is not due to partial dissociation of the tetrachloro complex in nitromethane is demonstrated by the fact that no change occurs upon addition of a large excess of  $(C_2H_7)_4NCl$  or  $(C_2H_5)_4NCl$  to the solution. This difference between the spectrum of  $UO_2Cl_4^{-2}$  in the solid salt and in non-aqueous solutions is of about the same order of magnitude as that observed in previous work with other actinide complex anions.<sup>16,24,25</sup> The absorption spectra of the cesium salt and of all the quaternary ammonium salts of  $UO_2Cl_4^{-2}$  in nitromethane are identical. The absorption spectra of the soluble quaternary ammonium salts in acetonitrile, acetone, or acetic anhydride are almost the same as the spectra of these salts in nitromethane. In the solid salts the absorption spectrum varies some-

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(25) J. L. Ryan, *ibid.*, **65**, 1099 (1961).

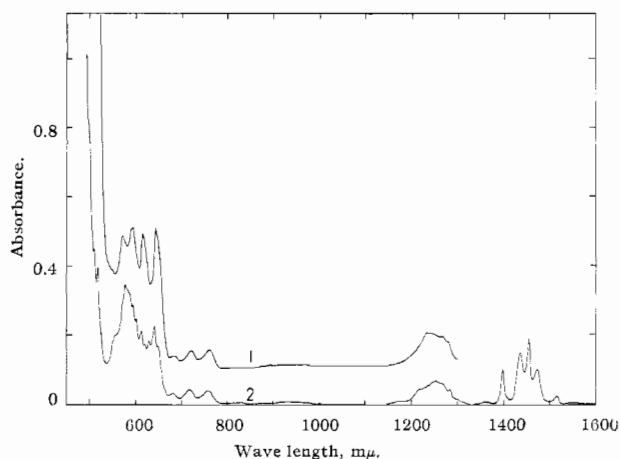


Fig. 2.—Comparison of the absorption spectrum of Np(VI) chloride in tertiary amine extractant with that of the  $\text{NpO}_2\text{Cl}_4^{-2}$  ion: (1) 0.035 *M* Np(VI) extracted into 10 volume % triaurylamine in xylene from 4 *M* HCl (absorbance scale displaced 0.1) and (2) 0.030 *M*  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpO}_2\text{Cl}_4$  in nitromethane.

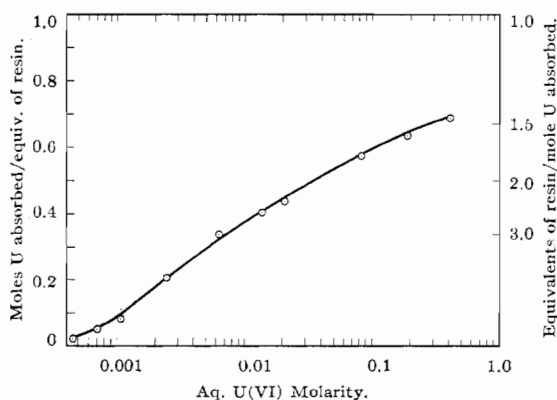


Fig. 3.—Absorption of U(VI) from 10 *M* HCl by Dowex 1, X-4.

what with the cation but this variation is usually less than the difference between the solid salt and solution spectra of Fig. 1. The absorption spectrum of the solid cesium salt is essentially identical with that of the tetra-*n*-propylammonium salt of Fig. 1.

The absorption spectra of U(VI) in the resin and in the tertiary amine extractant are almost identical. It is apparent from Fig. 1, though, that the simple  $\text{UO}_2\text{Cl}_4^{-2}$  ion is not the species present in the anion-exchange resin and in the amine extractant. In the case of Np(VI) also the spectrum of the  $\text{NpO}_2\text{Cl}_4^{-2}$  ion is quite different from the spectrum of Np(VI) chloride in the amine extractant (Fig. 2). It was found that in the presence of resin Np(VI) is rapidly reduced even in lithium chloride solutions of low acidity. This reduction also occurs rapidly in concentrated hydrochloric acid in the absence of resin. Because of this the resin spectrum could not be obtained without a considerable amount of Np(IV) or Np(V) present. When correction was made for this, the spectrum of the Np(VI) loaded resin was essentially identical to that of the amine solution of Fig. 2.

Rimbach<sup>14</sup> has reported the salts  $\text{K}_2\text{UO}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{UO}_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ . Keder<sup>9</sup> has found that the spectrum of the solid potassium salt, although some-

what different from that of  $\text{Cs}_2\text{UO}_2\text{Cl}_4$ , is quite different from that of the amine and resin spectra shown in Fig. 1. Also, addition of sufficient water to saturate nitromethane solutions containing the  $\text{UO}_2\text{Cl}_4^{-2}$  ion has very little effect on the spectrum. If excess chloride is present in the nitromethane the effect is even less. If large amounts of water are added to an acetone solution of  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UO}_2\text{Cl}_4$ , the spectrum changes, apparently due to dissociation of the tetrachloro complex, but the spectral changes produced do not correspond to those required to produce the resin spectrum. This indicates that the resin species is not simply a hydrated tetrachloro ion.

The results of a resin loading experiment carried out in 10 *M* HCl are shown in Fig. 3. The resin loading exceeds the expected resin capacity for a divalent ion at an aqueous uranium concentration of only 0.035 *M*. It seems improbable that uranium invasion is sufficient to account for this at such a low aqueous uranium concentration, and this result is taken to indicate that the charge per uranium atom of the complex in the resin phase is probably less negative than  $-2$ . (The absorption spectrum of resin loaded to this degree was obtained from a mull of ground resin in petrolatum. Although the resolution obtainable with this type of sample was not nearly as good as obtained with unground resin in 0.5-cm. cells, the spectrum appeared to be the same as that obtained in 0.5-cm. cells with resin of lower loading.) Since no break occurs in the curve of Fig. 3 below aqueous uranium concentrations where uranium invasion probably becomes significant, no conclusion can be made regarding the charge of the complex other than that it is probably less negative than  $-2$ .

In order to determine whether a lower chloro complex such as a trichloro complex was responsible for the resin spectrum two non-aqueous studies were carried out. One of these consisted of the incremental addition of  $(\text{C}_2\text{H}_5)_4\text{NCl}$  to a solution of uranyl(VI) chloride in nitromethane or acetone. The spectrum of the  $\text{UO}_2\text{Cl}_4^{-2}$  ion eventually was obtained with no evidence of a spectrum corresponding to that of the resin as an intermediate. The presence or absence of water (in excess of that associated with the uranyl(VI) chloride dried over anhydrous  $\text{CaSO}_4$ ) had no effect on the results. The reverse experiment was carried out in which increments of  $\text{AgClO}_4$  were added to  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  in either dry or damp nitromethane. The same results were obtained, indicating that a chloro complex with a chlorine to uranium ratio of less than four probably is not responsible for the resin spectrum.

Since the exchange sites of the anion-exchange resins used in this study are quaternary ammonium cations, it seemed reasonable to expect that under proper conditions one of the soluble quaternary ammonium cations would precipitate a salt of the same complex anion as that absorbed by the anion-exchange resins. A series of quaternary ammonium cations was studied, and it was found that the uranyl(VI) chloride salt precipitated by tetra-*n*-propylammonium chloride from concentrated hydrochloric has an absorption spectrum in the

solid phase which is identical with that of the U(VI) loaded anion exchange resin (Fig. 4). The conditions of preparation and identification of this compound are discussed in the Experimental section. As discussed there, the dry compound decomposes with evolution of HCl and water. If the dry compound (dried either over  $\text{H}_2\text{SO}_4$  in HCl gas or by ether washing) is dissolved in nitromethane (or acetone or acetonitrile) dissociation occurs and the spectrum indicates a mixture. If HCl gas and a trace of water are added to the system or if the undried crystals (moist with concentrated aqueous HCl) are dissolved in these solvents, the spectra are essentially identical with that of the solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$ . Thus the pure compound is unstable both in the solid phase and in non-aqueous solution except in the presence of excess hydrated hydrochloric acid. As mentioned in the Experimental section, addition of  $\text{R}_4\text{NCl}$  to a nitromethane solution of the residue left after the thermal decomposition of  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  produces the  $\text{UO}_2\text{Cl}_4^{-2}$  ion spectrum. Addition of HCl gas plus a small amount of water produces the spectrum of the original salt. Addition of water alone to a nitromethane solution of this residue has no effect and addition of HCl gas alone in the absence of water does not produce the spectrum of the original undecomposed salt.

If  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  slightly damp with 12 M HCl is dissolved in nitromethane and  $(\text{C}_2\text{H}_5)_4\text{NCl}$  is added, the absorption spectrum is converted from that of the resin and the solid salt (shown in Fig. 4) to that of the simple  $\text{UO}_2\text{Cl}_4^{-2}$  ion. The reverse reaction also occurs. If HCl gas is added to a nitromethane (or acetone or acetonitrile) solution of an  $(\text{R}_4\text{N})_2\text{UO}_2\text{Cl}_4$  salt containing some water, the spectrum is converted to that of the resin and solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  (see Fig. 5). Addition of wet HCl to  $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  in these solvents produced the same effect. Thus addition of HCl gas and water to nitromethane solutions of  $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  or  $(\text{R}_4\text{N})_2\text{UO}_2\text{Cl}_4$  produces an absorption spectrum identical with the anion exchange resin and solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$ , and addition of chloride as  $\text{R}_4\text{NCl}$  produces the  $\text{UO}_2\text{Cl}_4^{-2}$  ion spectrum. The difference in the two absorption spectra of Fig. 5 and the difference between the spectra of solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  and solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  is due to the presence or absence of acid and is not due to a difference in the amount of chloride in the complex. Apparently this difference in absorption spectra is due to hydrogen bonding of the hydronium ion to the tetrachlorouranyl(VI) complex.

Bufalini and Stern<sup>26</sup> have shown that chloride ion is a strong hydrogen bond acceptor. The fact that addition of quaternary ammonium chloride to nitromethane solutions containing the hydrogen bonded tetrachloro complex converts the spectrum to that of the simple  $\text{UO}_2\text{Cl}_4^{-2}$  ion can be interpreted on the basis of a competition between the tetrachlorouranyl(VI) complex

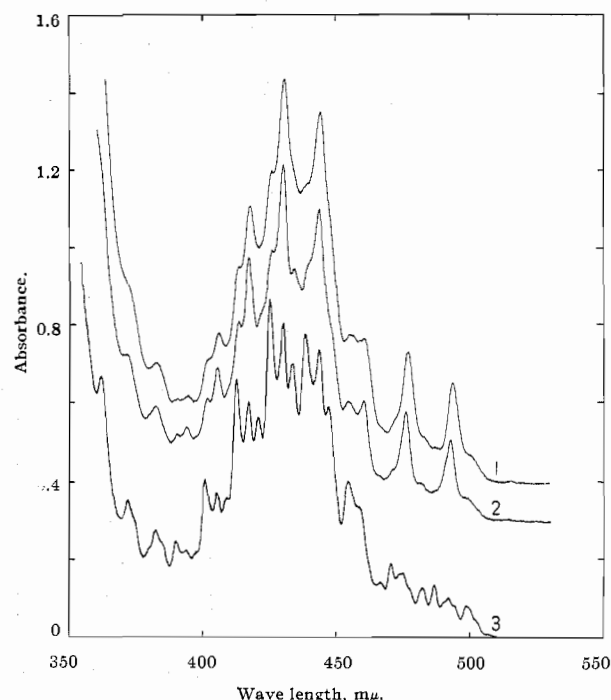


Fig. 4.—Comparison of the absorption spectrum of U(VI) chloride on anion-exchange resin with the absorption spectra of two solid tetra-*n*-propylammonium uranyl(VI) chloride salts: (1) U(VI) loaded on Dowex 1, X-4 (50 to 100 mesh) anion exchange resin from 9 M HCl (absorbance scale displaced 0.4), (2) solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  (absorbance scale displaced 0.3), and (3) solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$ .

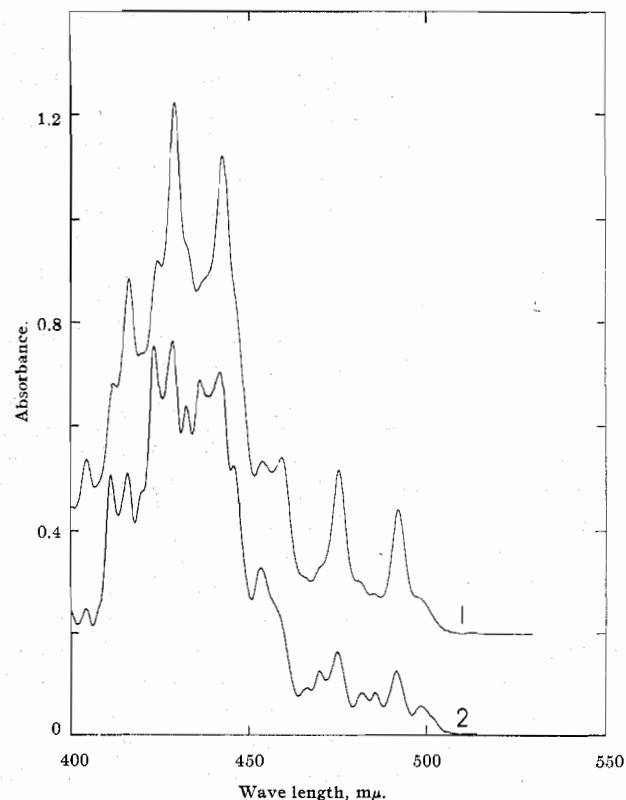


Fig. 5.—Effect of addition of HCl and water to nitromethane solutions containing  $\text{UO}_2\text{Cl}_4^{-2}$  ion: (1) 0.060 M  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  in HCl saturated nitromethane containing 0.3 M  $\text{H}_2\text{O}$  (absorbance scale displaced 0.2) and (2) 0.060 M  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  in dry nitromethane.



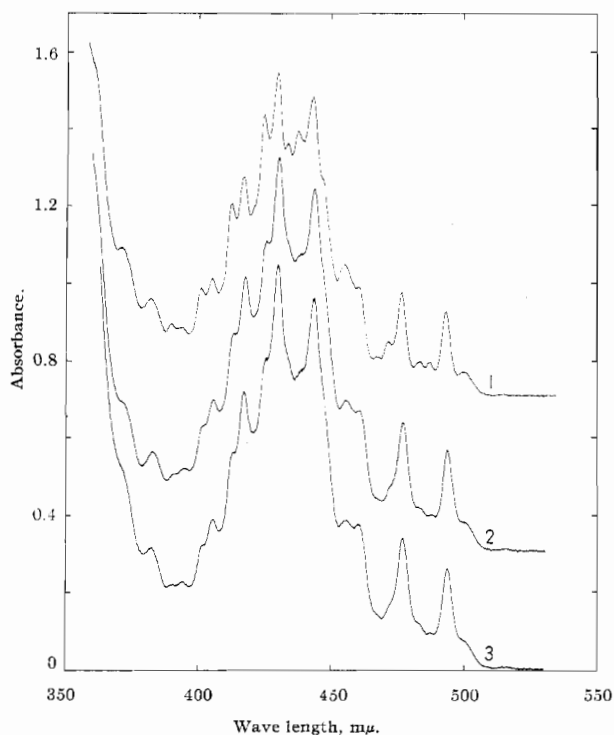


Fig. 6.—Absorption spectra of U(VI) loaded on Dowex 1, X-4 (50 to 100 mesh) anion exchange resin from various media: (1) loaded from 0.6 *M* HCl–2.1 *M* H<sub>2</sub>O in ethanol (absorbance scale displaced 0.7), (2) loaded from 0.1 *M* HCl–10 *M* LiCl (absorbance scale displaced 0.3), and (3) loaded from 9 *M* HCl.

and the chloride ion as hydrogen bond acceptors for the hydrated hydrogen ion acting as the hydrogen bond donor. Addition of excess chloride to the non-aqueous solutions of the hydrogen-bonded tetrachlorouranyl(VI) complex results in hydrogen bonding to the chloride and releases the  $\text{UO}_2\text{Cl}_4^{-2}$  ion. Addition of wet hydrogen chloride to solutions of  $\text{UO}_2\text{Cl}_4^{-2}$  causes the hydrogen bonding of the hydronium ion to the tetrachloro complex.

In Fig. 5 the effect of addition of HCl to a wet nitromethane solution of  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  is shown. Addition of HCl gas (to saturation) to a nitromethane solution of this salt in the absence of water ( $1.2 \times 10^{-3}$  *M* H<sub>2</sub>O *vs.* 0.1 *M*  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$ ) produces almost but not exactly the same absorption spectrum as curve 1 of Fig. 5. The difference between the spectrum obtained in this way and curve 2 of Fig. 5 indicates possibly a small amount of  $\text{UO}_2\text{Cl}_4^{-2}$  remaining. Addition of dry HCl to a nitromethane solution of  $\text{UO}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  or to a nitromethane solution of the residue left after heating  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  (containing a Cl to U ratio of 3.5) does not produce absorption spectra like that attributed to the hydrogen-bonded tetrachlorouranyl(VI) complex, but addition of both HCl and water does produce this spectrum. The conclusion from this is that once formed the tetrachloro complex is capable of undergoing hydrogen bond formation with acidic hydrogen which is not present as hydronium ion. In this case the hydrogen bond donor is probably molecular HCl. The effect on the absorption spectrum of the tetra-

chloro complex is apparently the same as that in hydrogen bonding to hydronium ion.

In the salt  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  it is presumed that the hydrogen bonding is to the triply hydrated oxonium ion,  $\text{H}_3\text{O}(\text{H}_2\text{O})_3^+$ . The very close similarity of the absorption spectrum of the U(VI) chloride loaded anion exchange resin to that of  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  (Fig. 4) indicates that the uranyl(VI) chloride species in the anion-exchange resin is also the tetrachloro complex hydrogen bonded to hydronium ion. Although it cannot be said with certainty that the hydration of the hydronium ion or the ratio of hydronium ion to uranyl is the same in the resin as that in the solid tetra-*n*-propylammonium salt, it seems probable that the species in the resin phase in contact with aqueous solution is actually  $[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]^{-8}$ . This would also be quite consistent with the capacity data of Fig. 3.

Since the species present in the resin phase when uranyl(VI) chloride is absorbed from concentrated hydrochloric acid contains the hydronium ion, absorption of other species should be favored by low acidity. No detectable difference in the resin spectrum was observed over the range of hydrochloric acid concentration from which appreciable resin absorption occurs (3–12 *M* HCl). The absorption spectrum of resin loaded from slightly acid lithium chloride appears upon casual examination to be the same as that loaded from hydrochloric acid. The absorption spectrum of U(VI) loaded on Dowex 1, X-4 from 10 *M* LiCl–0.1 *M* HCl is compared to that loaded from 9 *M* HCl in Fig. 6. Careful comparison of these two spectra indicates some difference which may correspond to a few per cent of the simple non-hydrogen bonded  $\text{UO}_2\text{Cl}_4^{-2}$ . Resin loaded from 10 *M* LiCl–0.01 *M* HCl gives almost the same spectrum. Resin loaded from lithium chloride at lower acidity showed the presence of what appeared to be hydrolyzed species. Anion-exchange resins have been shown to absorb hydrochloric acid strongly from concentrated lithium chloride solutions to produce a resin phase which is much higher in acid than the solution phase.<sup>27</sup> Thus it should perhaps not be surprising that the complex containing the hydronium ion is still the principal species present in the resin loaded from low acid lithium chloride solutions.

Korkisch and co-workers<sup>5,6</sup> have studied the absorption of U(VI) from mixed alcohol–hydrochloric acid solutions. By eliminating both water and HCl the probability of absorbing a non-hydrogen bonded chloro complex should be greatest. Resin was loaded with uranyl(VI) chloride from hydrochloric acid and washed extensively with absolute ethanol saturated with LiCl. This caused gradual conversion of the resin spectrum to that of the  $\text{UO}_2\text{Cl}_4^{-2}$  ion. Resins loaded from alcohol solutions of hydrochloric acid containing a high percentage of alcohol also contain principally the simple  $\text{UO}_2\text{Cl}_4^{-2}$  complex. The absorption spectrum of U(VI) loaded on Dowex 1, X-4 from 95 volume % ethanol–

(27) F. Nelson and K. A. Kraus, *J. Am. Chem. Soc.*, **80**, 4154 (1958).

0.6 M HCl-2.1 M H<sub>2</sub>O is shown in Fig. 6. The absorption spectrum of this resin is not the same as that loaded from aqueous hydrochloric acid or lithium chloride solutions and is at least principally due to UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup>. This spectrum is somewhat different from that of UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> in nitromethane. This difference is most prominent in the higher ratio of the absorbance of the 476 and 493 m $\mu$  peaks to the absorbance of the 455 m $\mu$  peak than in the case of the UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> in nitromethane. This ratio does not change when the HCl and water content are further lowered or when the resin is washed with LiCl-saturated ethanol. In fact anion-exchange resin loaded from a solution of [(C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>N]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> in pure methanol has exactly the same absorption spectrum as that shown in Fig. 6 for the ethanol-hydrochloric acid mixture. In this case there is no possibility of a hydronium ion containing complex being present in the resin. Thus this small difference is not due to the presence of some tetrachlorouranyl(VI) complex bonded to the hydrated hydronium ion but is due instead to the difference in solvent medium. The ratio of the absorbance of the peak located at about 475 m $\mu$  (change in peak position up to about 3 m $\mu$  is observed with change in solvents) to that of the peak located at about 455 m $\mu$  was found to change with solvent for (R<sub>4</sub>N)<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> salts. This ratio is 0.49 for acetonitrile, 0.52 for nitromethane, 0.62 for acetic anhydride, 0.65 for acetone, and 0.72 for xylene. The value of this ratio is 0.78 for the resin loaded from alcohol solution. It appears that the molar extinction coefficients of the two UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> peaks located at about 475 and 492 m $\mu$  are quite sensitive to environment. From this and the otherwise close similarity of the spectrum of the resin loaded from alcohol, and UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> in non-aqueous solvents, it was concluded that the species present in the resin phase in equilibrium with dilute hydrochloric acid in alcohol is the simple UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> ion with very little if any of the hydronium ion containing complex. It is of course possible that some hydrogen bonding to alcohol is responsible for the difference between the spectrum of the resin loaded from alcohol and the spectrum of UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> ion in non-aqueous solvents.

**Amine Extraction Studies.**—The extraction of [H<sub>3</sub>O(H<sub>2</sub>O)<sub>3</sub>(UO<sub>2</sub>Cl<sub>4</sub>)<sub>2</sub>]<sup>-3</sup> or similar hydronium ion containing species from hydrochloric acid by tertiary amine extractants does not agree with the amine loading data<sup>8,10</sup> or more importantly with the amine dependence data.<sup>9</sup> Both of these methods indicate reaction of two molecules of amine per uranium atom. Since both of these methods are in excellent agreement, a logical explanation for the apparent discrepancy was required. Primary, secondary, and tertiary ammonium ions are known to behave as hydrogen bond donors in their halide salts<sup>28-31</sup> and the activity of nitrate ion in solutions of alkylammonium nitrate salts in non-aqueous solutions has been interpreted on the basis of

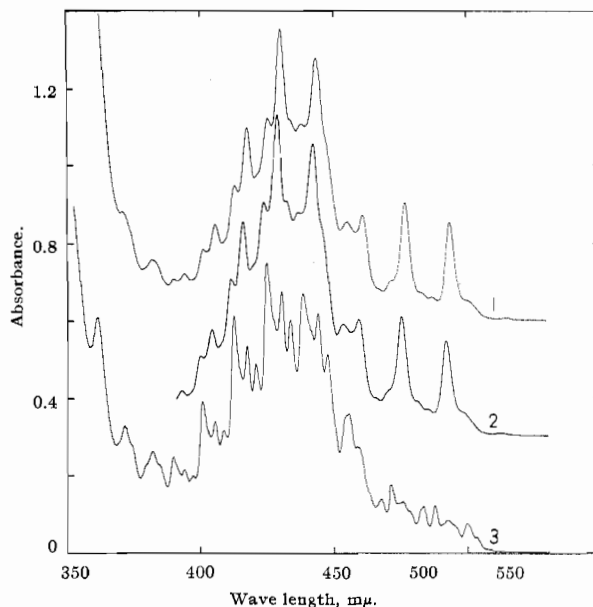


Fig. 7.—Comparison of the absorption spectrum of U(VI) in a tertiary amine extractant with the absorption spectra of [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> as a solid salt and in nitromethane solution: (1) U(VI) extracted into 10 volume % tri-*n*-octylamine in xylene from 4 M HCl (absorbance scale displaced 0.6), (2) 0.050 M [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> in nitromethane (absorbance scale displaced 0.3), and (3) solid [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub>.

hydrogen bonding.<sup>32</sup> Infrared studies have shown that in the alkylamine hydrochlorides strong hydrogen bonds of the type N—H---X occur.<sup>29-31</sup> The bond strengths were found to be greatest with tertiary amines and with chloride as the halide.<sup>31</sup> These hydrogen bonds to chloride were observed in both the solid salts and in the salt dissolved in the conjugate amine<sup>30</sup> or in chloroform.<sup>29</sup> If hydrogen bonding of the alkylammonium ion to the UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> ion also occurs, it would be reasonable to expect that it would produce almost the same effect on the spectrum of the U(VI) tetrachloro complex as that caused by hydrogen bonding to the hydronium ion.

Figure 7 shows the spectra of [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> as the solid salt and as a solution in nitromethane and the spectrum of U(VI) extracted into tri-*n*-octylamine in xylene from 4 M HCl. The absorption spectrum of this salt in nitromethane, acetonitrile, or acetone is almost identical with that of the tri-*n*-octylamine extract and is quite different from the spectrum of the cesium or quaternary ammonium salts of UO<sub>2</sub>Cl<sub>4</sub><sup>-2</sup> in the non-aqueous solvents. (The spectrum in acetone is slightly different from those in nitromethane or acetonitrile, apparently due to slight dissociation. This can be prevented by addition of a slight excess of R<sub>3</sub>NHCl.) The absorption spectra of [(CH<sub>3</sub>)<sub>3</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub>, [(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub>, and [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub> in nitromethane are identical with that of [(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH]<sub>2</sub>UO<sub>2</sub>Cl<sub>4</sub>. Thus the tetrachlorouranyl(VI) complex undergoes hydrogen bond formation with secondary or tertiary alkylammonium ions in non-aqueous solutions, and this produces almost the same

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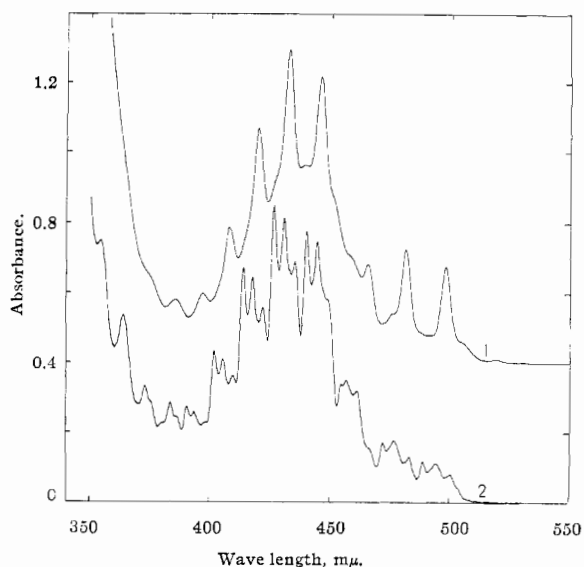


Fig. 8.—Absorption spectra of solid  $[(C_2H_5)_2NH_2]_2UO_2Cl_4$ : (1) high temperature form supercooled to  $25^\circ$  (absorbance scale displaced 0.4) and (2) stable room temperature form.

effect on the absorption spectrum of the tetrachloro complex as that produced by hydrogen bonding to the hydronium ion. Close examination of the spectra reveal slight differences in the spectrum of the tetrachlorouranyl(VI) complex hydrogen bonded to hydronium ion and that of the complex hydrogen-bonded to alkylammonium ions. The most marked of these is the fact that in all cases of hydronium ion bonding the absorbance of the peak at about  $475\text{ m}\mu$  is slightly less than that of the pair of peaks at about  $455$  and  $460\text{ m}\mu$ , whereas in the case of the alkylammonium ion bonding the reverse is true.

The absorption spectrum of solid  $[(C_2H_5)_3NH]_2UO_2Cl_4$  (Fig. 7) is almost identical with that of  $[(C_3H_7)_4N]_2UO_2Cl_4$ , indicating the absence of this hydrogen bonding in the solid phase. The spectrum of  $[(CH_3)_3NH]_2UO_2Cl_4$  is somewhat different but is still more like that of the solid quaternary ammonium salts than like that of its nitromethane solution. Although this difference might be due to some hydrogen bonding in the solid state, it probably is due instead to distortion of the complex by the crystal lattice. The solid tri-*n*-propylammonium salt has an absorption spectrum very much like that of some of the quaternary ammonium salts.

The compound  $[(C_2H_5)_2NH_2]_2UO_2Cl_4$  has two solid phase modifications having distinctive X-ray diffraction patterns. The high temperature phase is obtained rapidly above about  $100^\circ$ , but at  $25^\circ$  this reverts only very slowly (usually in 1 to 10 days) to the low temperature form. The absorption spectra of the two phases are shown in Fig. 8. It is apparent that the spectrum of the low temperature form is that of the simple  $UO_2Cl_4^{-2}$  ion. The absorption spectrum of the high temperature form (at  $25^\circ$ ) appears to be a somewhat distorted spectrum of the hydrogen-bonded complex. At  $100^\circ$  (which is near the transition temperature), however, the absorption spectrum of this salt is much

more similar to that of the tertiary and secondary alkylammonium salts in nitromethane. It appears then that in the high temperature form of this salt hydrogen bonding similar to that appearing in the non-aqueous solvents is present. This compound melts at  $220$ – $230^\circ$ . All of the quaternary and tertiary ammonium salts of  $UO_2Cl_4^{-2}$  which were prepared decompose without melting. This low melting point relative to the other salts is further evidence of hydrogen bonding, which would decrease the ionic character of the compound.

If  $R_4NCl$  is added to a nitromethane (or acetone or acetonitrile) solution of the  $(R_3NH)_2UO_2Cl_4$  or  $(R_2NH_2)_2UO_2Cl_4$  salts the spectrum is converted from that of the hydrogen-bonded complex to that of the simple  $UO_2Cl_4^{-2}$  complex. This apparently is due to the replacement of the tetrachlorouranyl(VI) complex by chloride as the hydrogen bond acceptor and is analogous to the release of the  $UO_2Cl_4^{-2}$  ion from the hydronium ion bonded tetrachloro complex which was discussed previously. If  $R_3NHCl$  is added instead, the same conversion to the spectrum of  $UO_2Cl_4^{-2}$  occurs, but much larger amounts are required (complete conversion occurs only at very high concentration of  $R_3NHCl$ ) than in the case of  $R_4NCl$ . This apparently occurs because chloride is capable of acting as acceptor for more than one hydrogen bond<sup>28,30</sup> and at high concentrations the chloride of the hydrogen-bonded tertiary alkylamine hydrochloride is still an effective competitor with the  $UO_2Cl_4^{-2}$  ion as a hydrogen bond acceptor. If  $R_2NH_2Cl$  is added instead, the spectrum remains that of the hydrogen-bonded uranyl tetrachloro complex. In this case the chloride already is satisfied by two hydrogen bonds and apparently does not compete with the tetrachlorouranyl(VI) complex.

If U(VI) is extracted into tri-*n*-octylamine in xylene from lithium chloride at low acidity and the uranium to tri-*n*-octylammonium ion ratio is kept low, the organic phase contains a mixture of the free and the hydrogen-bonded tetrachlorouranyl species. If the ratio of uranium to tri-*n*-octylammonium ion is high only the hydrogen-bonded species is observed. In extraction from hydrochloric acid, only the hydrogen-bonded tetrachlorouranyl(VI) complex is observed. This effect probably is due to the fact that the excess hydrochloric acid which is known to extract into tertiary amine extractants interacts with any excess tri-*n*-octylamine hydrochloride and prevents it from competing with the tetrachlorouranyl(VI) complex for hydrogen bonds.

Attempts to prepare a primary alkylammonium uranyl(VI) chloride salt were unsuccessful. Primary amine hydrochlorides up to butyl were found to be insoluble in nitromethane, acetone, or acetonitrile, but *n*-octylamine hydrochloride is soluble in acetone. An acetone solution of uranyl chloride saturated with *n*-octylamine hydrochloride has the same spectrum as  $(R_3NH)_2UO_2Cl_4$  and  $(R_2NH)_2UO_2Cl_4$  salts, indicating that the primary alkylammonium ion also hydrogen bonds to the tetrachlorouranyl(VI) complex. The

extraction of U(VI) chloride from hydrochloric acid by a long chain quaternary ammonium extractant was examined. The spectrum of U(VI) extracted from 4 or 12 M HCl into 10 volume % Aliquat 336 (commercially available methyl trioctylammonium chloride) in nitrobenzene is that of the simple  $\text{UO}_2\text{Cl}_4^{-2}$  ion. Thus the long chain quaternary ammonium extractants apparently do not behave like the quaternary ammonium anion exchange resin and do not extract the complex containing the hydronium ion.

Figure 9 shows the absorption spectra of  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{PuO}_2\text{Cl}_4$  in nitromethane,  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{PuO}_2\text{Cl}_4$  in nitromethane, Pu(VI) extracted into trilaurylamine in xylene from 4 M HCl, and Pu(VI) loaded on Dowex 1, X-4 from 10 M LiCl-0.1 M HCl. The same problem of instability of valence state that was encountered with Np(VI) was encountered with Pu(VI) but to a much lesser degree. Because of this an attempt to prepare a salt analogous to  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  was unsuccessful due to reduction to Pu(IV). It is apparent from Fig. 9 that in the case of plutonium(VI) also, the tetrachloro complex undergoes hydrogen bond formation with the hydrated hydronium ion in the case of absorption by anion-exchange resin and with the tertiary ammonium ion in the case of extraction by tertiary amines.

### Discussion

The tendency of the actinide(VI) tetrachloro complexes to form hydrogen-bonded species and the absorption of complexes containing hydronium ion by anion-exchange resins in this case raises the question of whether this system is unique or if complexes of other metals, particularly chloro complexes, behave similarly. If the hydrogen bonding to the actinide(VI) tetrachloro complexes is to the chloride, it seems probable that such hydrogen bonding also would occur with other chloro complexes. Such hydrogen bonding, if it does occur with other chloro complexes, would be a significant factor which should not be neglected in explaining the alkylamine extraction and anion exchange behavior of metal chloro complexes.

Since the hydrogen bonding to the actinide(VI) tetrachloro complexes was observed spectrophotometrically, an analysis of the effect of hydrogen bonding on the spectra of these tetrachloro complexes might hopefully shed some light on the nature of the bonding. The fine structure of the visible absorption spectra of the hexavalent actinides generally is attributed to the symmetrical vibrations in the metal-oxygen bonds of the  $\text{MO}_2$  entity.<sup>33</sup> Hydrogen bonding in the actinide(VI) tetrachloro complexes produces distinct changes in the metal-oxygen vibrational spectra relative to the spectra of the simple  $\text{MO}_2\text{Cl}_4^{-2}$  ions. Careful examination of the visible absorption spectrum of solid  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  (see Fig. 4) shows that this spectrum consists of at least six series of vibrational peaks. The

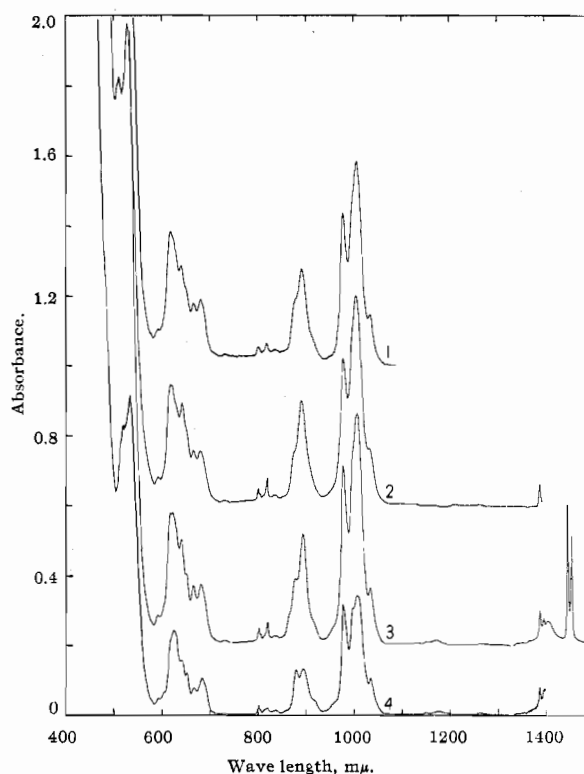


Fig. 9.—Absorption spectra of Pu(VI) chlorides: (1) Pu(VI) loaded on Dowex 1, X-4 (50 to 100 mesh) from 0.1 M HCl-10 M LiCl (absorbance scale displaced 1.0), (2) 0.039 M Pu(VI) extracted into 10 volume % trilaurylamine in xylene from 4 M HCl (absorbance scale displaced 0.6), (3) 0.047 M  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{PuO}_2\text{Cl}_4$  in nitromethane (absorbance scale displaced 0.2), and (4) 0.030 M  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{PuO}_2\text{Cl}_4$  in nitromethane.

separation of these peaks within a given series is  $712 \pm 5 \text{ cm}^{-1}$ . In  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  six series of peaks also are observed (Fig. 4). These appear to be at almost the same wave lengths as those of  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  and the separation within a series is  $715 \pm 3 \text{ cm}^{-1}$ . The difference between the absorption spectra of the  $\text{UO}_2\text{Cl}_4^{-2}$  ion and the hydrogen bonded tetrachlorouranyl(VI) complex is principally a marked increase in intensity of two of these series of vibrational peaks. This also is confirmed in Fig. 5, where the spectra of equal concentrations of the tetrachloro complex and the hydrogen-bonded tetrachloro complex are shown. The difference between these two spectra corresponds to a marked increase in two series of vibrational peaks with very little difference in intensity of the other series. The asymmetric U-O stretching frequency of uranyl(VI) salts is observed in the infrared at 850 to 1000  $\text{cm}^{-1}$ .<sup>34</sup> For  $[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{UO}_2\text{Cl}_4$  this is at 923  $\text{cm}^{-1}$  and for  $[(\text{C}_3\text{H}_7)_4\text{N}]_3[\text{H}_3\text{O}(\text{H}_2\text{O})_3(\text{UO}_2\text{Cl}_4)_2]$  the peak is considerably broadened so that assignment of the exact position is difficult but is between 908 and 930  $\text{cm}^{-1}$ . In  $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{UO}_2\text{Cl}_4$  there appears to be a decrease of about 30  $\text{cm}^{-1}$  in the symmetrical vibration frequency of one series of peaks in the visible range in going from the stable low temperature form to the metastable high tempera-

(33) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 220-223.

(34) L. H. Jones, *Spectrochim. Acta*, **10**, 395 (1958).

ture hydrogen-bonded form at 25°. There is a corresponding decrease of 38 cm.<sup>-1</sup> and a considerable broadening of the asymmetric vibrational peak under these conditions. If the visible absorption spectrum of the high temperature hydrogen-bonded form is obtained at 100°, which is above or at least near the transition temperature, this difference in the symmetrical vibrational frequency is not observed.

It does not appear possible to conclude from this analysis whether the observed hydrogen bonding to the actinide(VI) tetrachloro complex is to the oxygen of the

MO<sub>2</sub> entity or to chloride. The fact that no corresponding spectral evidence for hydrogen bonding was observed in studies of alkylammonium salts of the UO<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub><sup>-</sup> complex<sup>13,25,32</sup> tends to make the chloride suspect as the hydrogen bond acceptor but cannot be considered proof of this. It is difficult to say whether hydrogen bonding, if it does occur, would have a significant effect on the absorption spectra of chloro complexes of the type MCl<sub>x</sub><sup>-x+m</sup>, in which the spectra are due to electronic transitions and the M-O vibrational effects are absent.

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## Partial Ionic Character of Metal-Chlorine Bonds<sup>1</sup>

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Several simple "ionic" models for the bonding in metallic chlorides are tested. These include the hard sphere ion model, the polarizable sphere, and a localized molecular orbital model with partial covalent bonding. van der Waals' repulsions are included. All integrals are evaluated from experimental data. In the MO model the coulomb integrals are considered as functions of  $x$ , the fractional "ionic character" of each bond. Binding energies can be calculated about equally well by either the covalent bonding or polarization approach. It seems feasible to develop a semi-empirical MO method in inorganic chemistry for both absolute (binding) energies and relative (spectroscopic) energies. The best value of  $x$  was found for each system and the resulting ionicities of 50–90% appear reasonable. Other criteria for  $x$  such as the equalization of electronegativities and the principle of electroneutrality are criticized.

Inorganic chemistry is in great need of a theory of binding which enables heats of reaction, activation energies, and similar quantities to be estimated. Recent advances such as crystal field, or ligand field, theory have emphasized differences in energy between ground and excited states only. Also the electron distribution pattern in inorganic systems is of great interest. No experimental or theoretical method is known which gives a reasonably exact answer to the electron distribution problem in any cases but the simplest.

It is very common to adopt a conceptual approach in which the various bonds of a molecule or complex ion are ascribed different degrees of "ionic" and "covalent" character.<sup>2</sup> It is well known that such terms as "per cent ionic character" have no precise meaning except in terms of a model. Nevertheless the concept is useful and interesting.

In this paper we will consider the bonding in a number of metallic chlorides. One chief interest is to try to evaluate the ionicity of such compounds. Bonding energies also have been calculated to compare

with experimental results. The ionic character is calculated by means of a localized, two-center molecular orbital method, *e.g.*

$$\psi_{MO} = \phi_a + \lambda\phi_c \quad (1)$$

where  $\phi_a$  is an atomic orbital of a valence electron on the chlorine atom,  $\phi_c$  is an atomic orbital on the metal atom, and  $\lambda$  is a mixing coefficient. If  $x$  is defined as the fractional charge (negative) on the chlorine atom, and if overlap is neglected, then it follows that

$$x = \frac{1 - \lambda^2}{1 + \lambda^2} \quad (2)$$

100 $x$  is also the per cent ionic character of the bond.

Since many of these metal chlorides are certainly very ionic, the hard sphere ion model and the polarized ion model also have been tested. Many such calculations already have been made, especially for the alkali chlorides.<sup>3</sup>

For the sake of completeness and to ensure the use of consistent experimental data, the calculations were repeated even for cases already in the literature. Good agreement was generally found with the earlier calculations. It should be noted that all results refer to

(1) Presented in part at the Seventh International Conference on Coordination Chemistry, Stockholm, June, 1962.

(2) Recent work which may be referred to includes (a) J. K. Wilmschurst, *J. Chem. Educ.*, **39**, 132 (1962); (b) H. Shull, *J. Am. Chem. Soc.*, **82**, 1287 (1960); (c) L. E. Orgel, "An Introduction to Transition-Metal Chemistry," Methuen, London, 1960, Chapter 8; (d) J. Hinze, M. A. Whitehead, and H. H. Jaffé, *J. Am. Chem. Soc.*, **85**, 148 (1963); (e) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, Chapter 3.

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