

rhombohedral cases, the h, c description requires only  $1/3N$  symbols. Thus the nine-layer rhombohedral case may be described simply as chh; the twelve-layer rhombohedral case as cchh. In this way one can see the basic simplicity of these patterns, even though  $N$  is large, and the correspondingly simple patterns of the corner and face sharing octahedra which they produce. As a consequence of these simple stacking sequence patterns, face sharing of octahedra containing cations can be avoided altogether through simple patterns

of octahedral site vacancies. Alternatively, simple patterns of cation substitution can put different kinds of central cations in the octahedra sharing faces and/or corners.

Both the nine-layer and the twelve-layer models proposed have primitive rhombohedral lattices. The reflection absences noted for  $Ba_4Re_2B^{II}O_{12}$  compounds very nearly correspond to the rhombohedral lattice requirement, and the atomic positions used for a trial structure are in space group  $166, R\bar{3}m$ .

CONTRIBUTION FROM THE HANFORD LABORATORIES,  
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## Hydrogen Bonding to Chloro and Bromo Complexes of Uranium(IV)<sup>1</sup>

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Received July 26, 1963

Spectrophotometric studies of nonaqueous solutions of U(IV) in the presence and absence of hydrogen bond donors are used to demonstrate the ability of the  $UCl_6^{-2}$  and  $UBr_6^{-2}$  complexes to form hydrogen bonds with primary, secondary, and tertiary alkylammonium ions and with hydronium ion. This hydrogen bonding partially distorts the octahedral field around the  $U^{+4}$  ion in the  $UCl_6^{-2}$  and  $UBr_6^{-2}$  complexes and thereby allows the normally forbidden electric dipole induced internal  $5f$  electronic transitions to occur. The occurrence of such transitions in the hexachlorouranate(IV) complex in anion-exchange resins indicates distortion of the complex, most probably due to hydrogen bonding.

Hydrogen bonding of hydronium ion and primary, secondary, and tertiary alkylammonium ions to the complexes  $MO_2Cl_4^{-2}$  where M is U(VI), Np(VI), or Pu(VI) has been demonstrated.<sup>2</sup> These complexes contain oxygen as well as chloride as ligands and it was not determined whether this hydrogen bonding was through the chloride or the oxygen of the complex. Thus it was not possible to predict whether such hydrogen bonding might be expected with simple chloro complexes. Because of this the  $UCl_6^{-2}$  system was examined for evidence of hydrogen bonding.

The hexachlorouranate(IV) complex has been shown to be the species absorbed by anion-exchange resins<sup>3</sup> and extracted into tertiary alkylammonium extractants.<sup>4</sup> Both of the systems are ones in which hydrogen bonding occurs in the case of the  $MO_2Cl_4^{-2}$  complexes.<sup>2</sup> Careful examination of the absorption spectra of U(IV) chloride in anion-exchange resins<sup>3</sup> and in tertiary ammonium extracts<sup>4</sup> showed that there are distinct differences between these spectra and the spectra of  $[(C_2H_5)_4N]_2UCl_6$  in nitromethane in which no hydrogen-bond donor is present. The visible and near-infrared absorption spectrum of  $UCl_6^{-2}$  has been extensively interpreted by Satten and co-workers.<sup>5,6</sup> The  $UBr_6^{-2}$  complex has been prepared and its absorption spectrum interpreted.<sup>7-9</sup>

In this work the existence of hydrogen bonding of the  $UCl_6^{-2}$  complex to a variety of hydrogen-bond donors will be shown and the effect of this hydrogen bonding on the absorption spectrum will be discussed. Hydrogen bonding to the complex  $UBr_6^{-2}$  will also be demonstrated.

### Experimental

**Materials Used.**—Alkylammonium chlorides were prepared and purified as before.<sup>2</sup>  $[(C_2H_5)_4N]_2UCl_6$  and  $[(C_2H_5)_4N]_2UBr_6$  were also prepared by the methods used previously.<sup>3,9</sup> Secondary and tertiary alkylammonium perchlorates were prepared by partial neutralization of the free amines (obtained from Eastman) with concentrated perchloric acid. Water and excess amine were removed by vacuum drying at 60°. No further purification of these slightly colored salts was carried out. (Note: No evaluation of the stability of these alkylammonium perchlorates was made and they were prepared and handled only in small quantities.) Triethylammonium iodide was prepared by neutralization of the free amine with concentrated HI. It was recrystallized from acetone until it was colorless. The preparation of the anhydrous  $UCl_4$  used is discussed elsewhere.<sup>10</sup> Solutions of U(IV) chloride in organic solvents containing HCl were prepared by dissolving uranium metal directly in the HCl-containing solvent.  $[(C_6H_5)_3PH]_2UCl_6$  was prepared by a slight modification of the previous method.<sup>7,8</sup> An acetone solution of triphenylphosphine saturated with HCl was added to a solution prepared by dissolving uranium metal directly in HCl-acetone. The resultant crystals were washed with acetone and vacuum dried at room temperature. Nitromethane and acetonitrile were Eastman Spectro Grade and acetone was C.P. grade.

**Spectrophotometric Measurements.**—Spectrophotometric measurements were made with a Cary Model 14 recording spec-

(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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(3) J. L. Ryan, *J. Phys. Chem.*, **65**, 1856 (1961).

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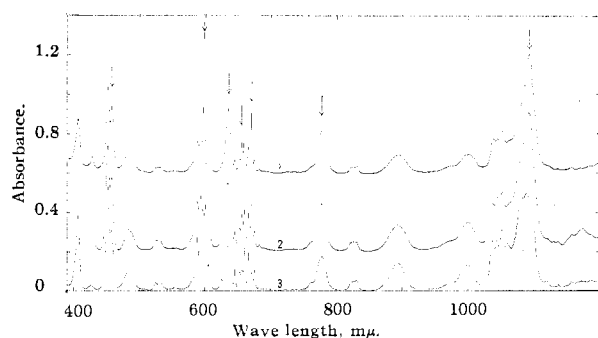


Fig. 1.—Absorption spectra of various hexachlorouranate(IV) systems: (1)  $2.7 \times 10^{-2} M$   $UCl_6$  in acetone saturated with  $C_6H_{17}NH_3Cl$  (absorbance scale displaced 0.6); (2)  $4.3 \times 10^{-2} M$   $[(C_2H_5)_4N]_2UCl_6$  in  $1 M$   $(C_2H_5)_2NH_2ClO_4$  solution in nitromethane (absorbance scale displaced 0.2); and (3)  $4.3 \times 10^{-2} M$   $[(C_2H_5)_4N]_2UCl_6$  in nitromethane; 2.00-cm. cells.

trophotometer. Absorption spectra of solutions were obtained in 1.00-, 2.00-, or 10.0-cm. silica cells. The absorption spectrum of  $[(C_2H_5)_4N]_2UCl_6$  in acetone was obtained only in a 10-cm. cell, using a zero to 0.1 absorbance range slidewire for the spectrophotometer because of the very low solubility of this compound in acetone. Resin spectra and spectra of solid salts were obtained as described previously.<sup>2,3</sup> Spectra shown in the figures are reproduced photographically from the instrument recordings.

### Discussion

**Hexachlorouranate(IV).**—The visible and near-infrared absorption spectra of the  $UCl_6^{-2}$  and  $UBr_6^{-2}$  complexes are due to internal  $5f$  transitions. In actinide complexes such as these in which the  $U^{+4}$  ion is at a center of symmetry, the pure electronic transitions are missing, except as exceedingly weak magnetic dipole transitions, because of parity considerations.<sup>5,6,11</sup> The visible and near-infrared spectrum of  $UCl_6^{-2}$  in solid crystals of  $Cs_2UCl_6$ ,  $[(CH_3)_4N]_2UCl_6$ , and  $[(C_2H_5)_4N]_2UCl_6$  has been shown to consist almost entirely of vibronic transitions (simultaneous change in  $5f$  electronic state and vibrational state).<sup>5,6</sup> The visible near-infrared spectrum of  $UBr_6^{-2}$  is essentially the same as that of  $UCl_6^{-2}$  except for an energy shift ascribed to a larger nephelauxetic effect in the hexabromide than in the hexachloride.<sup>9</sup>

Pollack and Satten<sup>6</sup> have shown that incorporation of impurities into the crystal structure of the  $UCl_6^{-2}$  salts produces distortion and asymmetry in the  $UCl_6^{-2}$  ion and allows the electronic transitions to be observed. Morrey<sup>10</sup> has shown that if  $Cs_2UCl_6$  is melted and rapidly quenched the resulting strain introduces sufficient asymmetry to allow the electronic transitions to occur to some degree. These transitions disappear after the sample has remained at room temperature for several days.

Hydrogen bonding to the chloride atoms of the  $UCl_6^{-2}$  complex can be expected to distort the octahedral symmetry. Under these conditions with the  $U^{+4}$  no longer at a site of symmetry the electronic transitions should appear. Figure 1 compares the absorption spectra of  $[(C_2H_5)_4N]_2UCl_6$  in nitromethane in which no hydrogen bond donor is present with the spectra of two

systems in which hydrogen-bond donors are present. It is apparent that the presence of hydrogen-bond donors produces distinct changes in the  $UCl_6^{-2}$  spectrum. These changes consist of marked development of narrow absorption bands or over-all increases in intensity of less well resolved absorption bands in positions where some of the pure electronic transitions are expected from the data of Satten and co-workers.<sup>5,6</sup> The positions where increased intensity occurs in the presence of hydrogen bond donors are marked by arrows in Fig. 1.

In Fig. 2 the absorption spectrum (from 560 to 700  $m\mu$ ) of  $[(C_2H_5)_4N]_2UCl_6$  in acetonitrile, in which no hydrogen-bond donor is present, is compared with the absorption spectrum of  $U(IV)$  chloride in acetonitrile containing 0.3  $M$   $H_2O$  and saturated with  $HCl$ . Essentially the only difference in the two spectra of Fig. 2 is an increase in intensity at four wave lengths (marked by arrows) in the solution containing hydronium ion. These four wave lengths are at almost exactly the positions of the electronic transitions in this region for the crystalline salts of  $UCl_6^{-2}$ . The absorption peaks at 657 and 672  $m\mu$  were both found to be exactly at the center of the two sets of vibronic peaks situated on either side of them. In the case of the peak at 635  $m\mu$  the various transitions are not sufficiently resolved to interpret although an over-all intensity increase occurs. In all three of these cases there is sufficient overlap of the vibronic transitions associated with the three different electronic transitions to make more complete interpretation difficult.

The group centered at about 598  $m\mu$  is much clearer since this group apparently does not overlap others. In the petrolatum mull spectrum of solid  $Cs_2UCl_6$  at room temperature this region is resolved by the Cary Model 14 into three sets of vibronic transitions located symmetrically around the missing electronic transition at  $597.7 \pm 0.2 m\mu$ . These transitions occur at about 40, 112, and 263  $cm^{-1}$  above and below the center position, with those at 40  $cm^{-1}$  appearing only as shoulders. This agrees within experimental accuracy with the much more precise measurements of Satten and co-workers.<sup>5,6</sup> The spectra of quaternary ammonium or cesium salts of  $UCl_6^{-2}$  in inert nonaqueous solvents (see Fig. 2) are essentially the same (including relative peak intensities) as that of solid  $Cs_2UCl_6$  in this region except that the vibronic transitions located 40  $cm^{-1}$  from the electronic transition are not resolved, the energy separations are changed slightly, and there is a shoulder at or very near the center position. This shoulder appears to be due to a weak appearance of the electronic transition due to slight distortion of the  $UCl_6^{-2}$  complex, either because of ion pair formation with the cation or because of weak interaction of the complex with the solvent. The strength of this weak electronic transition varies with solvent and is least for acetonitrile, somewhat greater for nitromethane, and greater yet for acetone where it actually occurs as a weak peak. (A similar effect shows up in the group at about 2000  $m\mu$ .) If a strong hydrogen-bond donor is

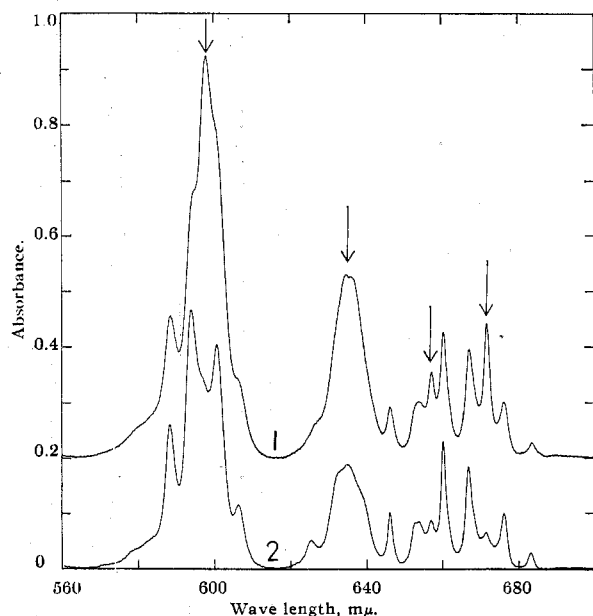


Fig. 2.—The effect of hydrogen bonding on the absorption spectrum of  $\text{UCl}_6^{-2}$ . (1)  $3.9 \times 10^{-2} M \text{U(IV)} + 0.3 M \text{H}_2\text{O}$  in HCl-saturated acetonitrile (absorbance scale displaced 0.2) and (2)  $3.9 \times 10^{-2} M [(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UCl}_6$  in acetonitrile; 2.00-cm. cells.

present the intensity of the center peak at about  $598 \text{ m}\mu$  increases very markedly (Fig. 2). In various solvents and with various hydrogen-bonding agents the positions of the peaks change slightly, but the peak which develops in the presence of the hydrogen-bond donor is always at the center of its associated vibronic peaks. It appears then that the  $\text{UCl}_6^{-2}$  ion acts as a hydrogen-bond acceptor and that the resultant hydrogen bond distorts the octahedral field around the  $\text{U}^{+4}$  ion sufficiently to allow the normally forbidden electronic transitions to appear as electric dipole radiation.

Various attempts to prepare secondary or tertiary alkylammonium salts of  $\text{UCl}_6^{-2}$  were unsuccessful. Addition of excess tertiary, secondary, or primary alkylammonium chlorides to  $\text{UCl}_4$  in various nonaqueous solvents (acetone, nitromethane, or acetonitrile) indicated that in all cases the  $\text{UCl}_6^{-2}$  ion undergoes hydrogen-bond formation (see Fig. 1). Later addition of excess  $\text{R}_4\text{NCl}$  to these solutions destroys the hydrogen bonding and converts the absorption spectrum back to the non-hydrogen-bonded type. This is due to the fact that  $\text{Cl}^-$  is a better hydrogen-bond acceptor than is the  $\text{UCl}_6^{-2}$  complex. Addition of moist HCl (but not of  $\text{H}_2\text{O}$  alone) or secondary or tertiary ammonium perchlorates or iodides to  $(\text{R}_4\text{N})_2\text{UCl}_6$  salts in nonaqueous solvents produces the hydrogen-bonded spectrum to varying degrees with the iodide being the least effective. Perchlorate<sup>12,13</sup> and iodide are both relatively weak hydrogen-bond acceptors. (Iodide is much weaker than chloride as a complexing agent for U(IV) and does not enter the coordination sphere under these conditions.<sup>9</sup>) Very weak hydrogen bonding of the triphenylphosphonium ion to  $\text{UCl}_6^{-2}$  apparently occurs as

(12) J. Bufalini and K. H. Stern, *J. Am. Chem. Soc.*, **83**, 4362 (1961).

(13) W. E. Keder, A. S. Wilson, and L. L. Burger "Amine Systems in Solvent Extraction," presented at the Symposium on Aqueous Reprocessing Chemistry for Irradiated Fuels, Brussels, Belgium, April 23-26, 1963.

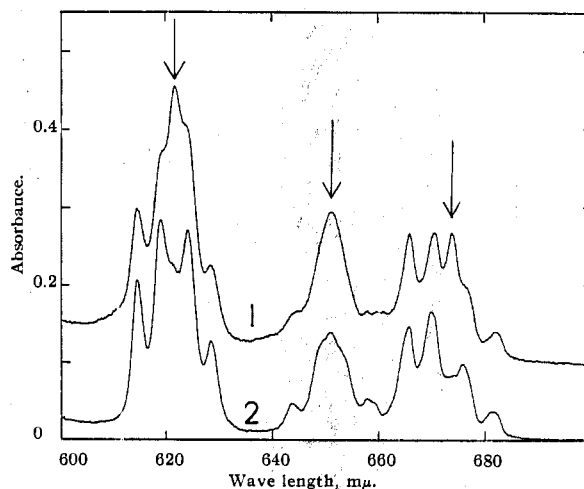


Fig. 3.—The effect of hydrogen bonding on the absorption spectrum of  $\text{UBr}_6^{-2}$ . (1)  $1.7 \times 10^{-2} M [(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UBr}_6$  in  $1 M (\text{C}_2\text{H}_5)_2\text{NH}_2\text{ClO}_4$  in nitromethane (absorbance scale displaced 0.1) and (2)  $1.7 \times 10^{-2} M [(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UBr}_6$  in nitromethane; 2.00-cm. cells.

evidenced by a small increase in the strength of the electronic peaks in solutions of  $[(\text{C}_6\text{H}_5)_3\text{PH}]_2\text{UCl}_6$  vs. solutions of  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{UCl}_6$ . In general the same reactions occur in hydrogen bonding to  $\text{UCl}_6^{-2}$  as were observed in the case of  $\text{UO}_2\text{Cl}_4^{-2}$ .<sup>2</sup> In all cases the hydrogen bonding has qualitatively the same effect on the  $\text{UCl}_6^{-2}$  absorption spectrum (namely, increase in intensity of the same electronic transitions) as shown in the representative spectra of Fig. 1 and 2. Since the intensity of the electronic transitions in the spectra of  $\text{UCl}_6^{-2}$  will depend on both the degree of distortion of the  $\text{UCl}_6^{-2}$  complex (strength and number of hydrogen bonds to each  $\text{UCl}_6^{-2}$  anion) and the percentage of  $\text{UCl}_6^{-2}$  anions in solution which are hydrogen bonded, it does not appear feasible to use the intensity of the electronic transitions as more than a qualitative estimate of hydrogen-bond strength.

Re-examination of the absorption spectra of anion-exchange resin loaded with U(IV) from aqueous solutions<sup>3</sup> and the spectra of tertiary amine extracts of U(IV) indicates that they are hydrogen-bonded systems. In the case of the amine extraction, hydrogen bonding is undoubtedly between the Cl ligand and the tertiary ammonium ion. With the ion-exchange resin, hydrogen bonding is no doubt to the hydronium ion. Whether this hydrogen bonding is simply to hydronium ion or is to hydronium ion already bonded to excess chloride in the resin cannot be said with certainty. In the latter case the effective charge on the hexachloro complex would still be  $-2$  and each complex would occupy two resin sites. In the case of the  $\text{UO}_2\text{Cl}_4^{-2}$  complex this was not the case.<sup>2</sup>

Cobalt(II) chloride loads onto the anion-exchange resin to much higher loadings from slightly acidic  $\text{LiCl}^{14}$  or from aqueous HCl and mixed aqueous HCl-alcohol solutions<sup>15</sup> than expected for divalent  $\text{CoCl}_4^{-2}$ . The

(14) J. L. Ryan, unpublished results.

(15) G. Jansen, Jr., Sc. D. Thesis, Massachusetts Institute of Technology, 1959.

absorption spectrum of cobalt(II) chloride absorbed into anion-exchange resins from aqueous HCl is somewhat different from that of  $[(C_2H_5)_4N]_2CoCl_4$  in acetonitrile containing excess  $R_4NCl$ , but is almost identical with that of  $CoCl_2$  in an acetonitrile solution 0.3 *M* in  $H_2O$  and saturated with HCl gas or  $CoCl_2$  in acetonitrile containing excess  $(C_2H_5)_2NH_2Cl$ .<sup>14</sup> There is independent evidence that  $CoCl_4^{-2}$  is a rather strong hydrogen-bond acceptor.<sup>13</sup> It appears that hydrogen bonding to chloro complexes is a rather general phenomenon and also that hydrogen bonding of hydronium ion to chloro complexes in anion-exchange resins is perhaps quite common. Under these conditions the formal charge on the complex anion may not necessarily reflect the number of sites occupied by the complex.

Attempts to load the nonhydrogen-bonded  $UCl_6^{-2}$  onto anion-exchange resin were unsuccessful. Loadings from nonaqueous solutions of  $UCl_4$  not containing excess HCl did not produce the hexachloro complex spectrum and those performed in the presence of HCl always gave the hydrogen-bonded hexachloro spectrum.

**Hexabromouranate(IV).**—The absorption spectra (from 600 to 700  $m\mu$ ) of  $[(C_2H_5)_4N]_2UBr_6$  in nitromethane in the presence and absence of a large excess of  $(C_2H_5)_2NH_2ClO_4$  are compared in Fig. 3. At three wave lengths (marked by arrows) there is a marked increase in intensity when the hydrogen bond donor is present. In the region 640–700  $m\mu$  the transitions are either insufficiently resolved or are too badly overlapping to allow easy interpretation. The group centered at about 621  $m\mu$  corresponds to the group centered at about 598  $m\mu$  in the  $UCl_6^{-2}$  spectrum. In the case of the  $UBr_6^{-2}$  complex, the electronic transition is present as a shoulder at 621  $m\mu$  in a nitromethane solution of  $[(C_2H_5)_4N]_2UBr_6$ . This shoulder is weaker in acetonitrile (as in the case of  $UCl_6^{-2}$ ). Addition of a large excess of  $(C_2H_5)_2NH_2ClO_4$  produces hydrogen bonding, allowing the electronic transition to become much stronger relative to the vibronic transitions situ-

ated about 65 and 175  $cm^{-1}$  to each side of it. If excess  $(C_2H_5)_4NBr$  is then added to the solution containing the  $(C_2H_5)_2NH_2ClO_4$  the hydrogen bonding to  $UBr_6^{-2}$  is destroyed because of the successful competition of free  $Br^-$  ions with  $Br$  ligands for the available hydrogen bonds. Hydrogen bonding was also observed when  $(C_2H_5)_3NHClO_4$  was used instead of  $(C_2H_5)_2NH_2ClO_4$ . Although no quantitative measurements were made, it appears that  $UBr_6^{-2}$  is a weaker hydrogen-bond acceptor than  $UCl_6^{-2}$ , as would be expected from the electronegativities of the two halogens.

### Conclusions

Hydrogen bonding between alkylammonium and hydronium cations as donors and the complex anions  $MO_2Cl_4^{-2}$  (where *M* is a hexavalent actinide)<sup>2</sup> and  $UCl_6^{-2}$  and  $UBr_6^{-2}$  has been demonstrated. Some evidence exists for similar hydrogen bonding to  $CoCl_4^{-2}$ . It seems likely that such hydrogen bonding to chloro complex anions may be a common phenomenon. In the systems in which hydrogen bonding to complex anions was demonstrated, the complexes present in anion-exchange resins were the hydrogen-bonded types. Because of this, hydrogen bonding should be considered a factor in the absorption of metal complexes by anion-exchange resins and their extraction by alkylamines.

High invasion of acid into anion-exchange resins occurs from metal salt solutions.<sup>16,17</sup> It seems reasonable that a major factor causing this high acid invasion might be the formation of hydrogen bonds between the hydronium ions of this acid and the counterions (chloride, nitrate, etc.) in the resin matrix.

**Acknowledgment.**—The author expresses his appreciation to Dr. J. R. Morrey for helpful discussions regarding the interpretation of the absorption spectra and for supplying the anhydrous  $UCl_4$ .

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