both in the equation itself and in $Q(b)$

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{|z_1z_2|e^2}{kDT}\right)^3 Q(b) \qquad (10)$$

where

$$b = |z_1z_2|e^2/aDkT \qquad (11)$$

As the temperature rises, the dielectric constant decreases; over the temperature range 5–55° the product varies only about 6%. Although the theoretical values employed in ref. 3 were computed from the uncorrected Onsager–Wilson theory, and it would be impossible to carry out the correction made in this paper because of lack of data for $K(0)$ at temperatures other than 25°, the combination of factors just mentioned makes it improbable that the term $\Delta\lambda/\lambda_0$ would change appreciably over the temperature range investigated, even though the actual conductance of the solutions varies considerably.

We may conclude from the consistency of the experimental data of ref. 3 that the value of $K(0)$ changes probably less than 10% from the values employed at 25°. This is within the precision with which the equilibrium constant may be determined from a single set of conductance data.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS COMPANY]

Some New Uranium Complexes[1]

BY JOHN T. BARR AND CHARLES A. HORTON

RECEIVED DECEMBER 22, 1951

A study has been made of the action of organic bases, acidic complexing agents and amino acids upon organic solutions of uranium compounds. The type of product which was obtained was a function of both the oxidation state of the uranium and of the type of complexing agent. Organic bases precipitated uranium ammines. Acidic complexing agents did not form identifiable products, although spectrophotometric evidence indicated that enolized 1,3-diketones complexed to some extent. The addition of an external base to solutions of a uranium compound and an acidic complexing agent precipitated mixed complexes containing both organic and inorganic groups. Complexing agents which themselves contained an amino group reacted readily with uranyl salts to form inner complexes, and with uranium(IV) salts to form mixed complexes. The infrared absorption spectra of 9 of the complexes and ammines are presented, and a mechanism is proposed to account for the formation of the complexes.

It has been found in this work that many of the same complexing agents which are known to coördinate uranium in aqueous media also react with uranium compounds in non-aqueous solution. However, many of the products which are formed in non-aqueous solution differ greatly from those formed in aqueous media.

A typical method of preparation of inner complexes consists of the cautious addition of an alkali to a solution of a bidentate complexing agent and a uranium salt in water, thus obtaining a precipitate of the complex.[2] When, in this work, the same method was extended to non-aqueous systems, with the substitution of an amine for the alkali, and *n*-butyl acetate, or a similar oxygenated solvent for the water, a product was obtained which did not resemble an inner complex in nature. These new complexes were more soluble in water than in organic solvents. Many did not melt below 350° and a number were ionic in character, consisting of a complex cation and an inorganic anion.

The exact nature of the product was a function of the oxidation state of the uranium, and of the type of complexing agent. Organic bases alone precipitated uranyl and uranium(IV) salts as ammines. Complexing agents which contained only acidic functional groups (*i.e.*, salicylic acid) did not form precipitates with either type uranium salts, although spectrophotometric evidence indicated partial reaction in some cases. Presumably, the product was an organic-soluble inner complex. The addition of an organic base to solutions of uranium compounds and acidic bidentate complexing agents in an organic solvent gave, with uranyl compounds, an electrolyte in which one of the inorganic anions had been replaced by a bidentate organic anion in the coördination sphere of the uranyl ion. One molecule of the organic base and one molecule of water completed the normal coördination number of 4 for the uranyl ion. The second inorganic anion was ionic. Two inorganic anions were displaced by bidentate groups from the uranium(IV) salts, and two molecules of the base were combined in the complex. The remaining two inorganic anions are thought to have been included in the coördination sphere of the uranium, in order to satisfy the normal coördination number of 8 for the uranium(IV) ion. However, the inorganic anions were very readily hydrolyzed by aqueous solutions.

Complexing agents which themselves contained a basic group (N-phenylglycine, quinaldinic acid) gave immediate precipitates with uranium solutions. Uranyl compounds precipitated as aquated inner complexes. Uranium(IV) compounds gave products similar to those described in the previous paragraph except that the two basic coördinating groups were replaced by a third molecule of the amino acid.

Uranium(V) and (VI) chlorides were precipitated from carbon tetrachloride solution by bases and amino acids, to give products which were stable to storage under the solvent for short periods, and which underwent immediate hydrolysis upon ex-

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[1] This paper is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company at Oak Ridge, Tennessee.

[2] H. Gilman and R. G. Jones, Report AECD-2613, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. Declassified September 30, 1949.

posure to moist air. Deliberate hydrolysis of the uranium(VI) chloride–pyridine product gave a mixture which contained principally dipyridineuranyl chloride. Complexing agents which did not contain basic functional groups were oxidized immediately upon addition to solutions of these higher-valence chlorides, and the compounds formed with amines and amino acids decomposed upon standing for several hours.

Experimental

Reagents and Apparatus.—The uranyl nitrate hexahydrate was the Mallinckrodt analytical reagent product. The dihydrate was prepared for the hexahydrate by vacuum desiccation over sulfur acid.[3] Uranyl chloride trihydrate was prepared by dissolving Mallinckrodt uranium trioxide in concentrated hydrochloric acid, and recrystallizing the product. Uranium(IV) and -(V) chlorides were obtained from the Y-12 Plant, Carbide and Carbon Chemicals Company. Uranium(VI) chloride was prepared by vacuum sublimation of the pentavalent chloride.[4] Anhydrous uranyl fluoride was supplied by the Inorganic and Physical Section of this Laboratory.

Solutions of anhydrous uranyl chloride were prepared by suspending a known amount of anhydrous uranyl fluoride in some oxygenated solvent, such as *n*-butyl acetate or dioxane, and treating the mixture with anhydrous hydrogen chloride until solution was effected. The excess acid was removed by partial distillation of the solvent, and the solution was made up to volume. Qualitative tests on solutions so prepared showed the absence of fluoride ions.

The complexing agents and solvents used were the commercially-available, reagent grade materials, except for the N-phenylglycine. This was obtained by treatment of an aqueous solution of the technical grade Eastman potassium salt with activated charcoal, recrystallization of the salt from water, and precipitation of the free acid from solution by the addition of hydrochloric acid.

Carbon and hydrogen microanalyses were obtained by the conventional combustion method. The residue from this combustion was weighed as urano-uranic oxide (U_3O_8) for the uranium analyses.[5] Nitrogen was determined by the Kjeldahl method, chlorine by the Volhard method, and water by titration with Karl Fischer reagent. Molecular weights were determined in a Menzies–Wright apparatus, using absolute ethanol as the solvent.

Absorption spectra in the visible region were obtained on a Beckman model B spectrophotometer, using a 1.000-cm. Corex cell, and the blue-sensitive photocell. Infrared absorption spectra of 9 of the ammines and complexes were determined in the 2–15 μ region, using a Perkin–Elmer double-beam recording instrument equipped with sodium chloride cells and prism.[6] The solid samples were prepared by mulling in mineral oil. The spectra of uranium(IV) chloride, uranyl fluoride, uranyl nitrate hexahydrate, lactic acid, quinaldinic acid and dimethylethanolamine presented in Fig. 2 were also obtained for purposes of comparison. The remaining spectra necessary for interpretation were taken from the data of Randall and co-workers.[7] The breaks in several of the spectra are due to loss of sensitivity of the instrument in regions of high absorption, which resulted in overcompensation for the absorption of the mineral oil.

Preparative Procedure.—The method used for the preparation of complexes requiring the addition of an external base was to mix a warm, filtered solution of the uranium compound in butyl acetate and a solution containing a twofold excess of the complexing agent. Slightly more than the theoretical amount of base was then added dropwise with thorough stirring. The resulting solution was allowed to stand for a short time and was filtered. Precipitation was usually instantaneous and quantitative.

The ammines were prepared by the similar addition of an organic base to the uranium salt solution. The same method was used to prepare complexes from amino acids and uranium salts. Amino alcohols reacted similarly to other amines, with the exception that the presence of the second coördinating group within the molecule allowed the replacement of the molecule of water which was present in the normal uranyl monoammines.

In most cases, the complexes could not be purified by conventional recrystallization methods, either because of very low solubility, or because of a tendency toward oxidation or hydrolysis. After filtration of the initial precipitates, these compounds were subjected to several successive digestions with ethyl ether, methyl or ethyl alcohol, and, usually, acetone, and were then dried by extended evacuation at room temperature. This limited purification did not give products whose analyses corresponded as closely to the theoretical as might have been desired, nevertheless, the agreement was sufficient to determine the molecular ratio of the constituents.

Dipyridineuranyl Nitrate.—The theoretical amount of pyridine was added to a solution of uranyl nitrate hexahydrate to effect complete precipitation of the aquopyridineuranyl nitrate. The precipitate was removed by filtration, washed with ether, recrystallized from an ethanol–ether or dioxane–ether mixture, and vacuum dried. The product was dissolved in pyridine, and was reprecipitated by cooling after the addition of an equal volume of ether. After washing with ether and drying, the bright yellow crystals smelled of pyridine, and slowly lost weight upon standing in a vacuum desiccator. This compound was soluble in the lower alcohols, ketones and amines, slightly soluble in ethyl acetate, and insoluble in benzene, ether, chloroform and water.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot H_2O \cdot C_5H_5N$: C, 12.22; H, 1.44; U, 48.47. Found: C, 12.20; H, 1.47; U, 48.40. Calcd. for $UO_2(NO_3)_2 \cdot 2C_5H_5N$: C, 21.74; H, 1.93; U, 43.11. Found: C, 21.20; H, 1.75; U, 44.00.

Several uranium ammines have been described in part by Rascanu[8] and Spacu.[9] However, none of the explosive characteristics described by Rascanu for the nitrates were found, nor was it found necessary to dehydrate the solutions by distilling a portion of the solvent. The aquopyridineuranyl compound was formed first in all cases from hydrated uranyl compounds, regardless of the amount of hydration.

Dimethylethanolamineuranyl Nitrate.—The addition of 3 ml. of dimethylethanolamine to 10 g. of uranyl nitrate hexahydrate in 50 ml. of butyl acetate gave an immediate precipitate. Digestion of the solid with ether and with methanol gave 7.5 g. of a red-orange microcrystalline solid, which was slightly soluble in methyl and ethyl alcohol and pyridine, and insoluble in esters and other solvents. Water decomposed the product.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot (CH_3)_2NCH_2CH_2OH$: C, 9.94; H, 2.29; U, 49.27. Found: C, 10.17; H, 2.55; U, 49.75.

Tripyridinediuranium(IV) Chloride.—The addition of 1.8 ml. of pyridine to a solution of 5.0 g. of uranium(IV) chloride in 50 ml. of butyl acetate caused complete precipitation of the uranium ammine. The solution was filtered, and the solid was digested twice with 50-ml. portions of ether, once with 25 ml. of ethanol, and again with 50 ml. of ether. The dried solid weighed 7.0 g., and melted at 235°. The light-green, finely crystalline material was insoluble in ether, benzene, chloroform, very slightly soluble in ethanol and pyridine, and soluble in dimethylformamide, from which it was reprecipitated as an oil by the addition of ether. The compound was hydrolyzed by water to give a basic solution and a black precipitate.

Anal. Calcd. for $2UCl_4 \cdot 3C_5H_5N$: C, 18.06; H, 1.52; U, 47.75. Found: C, 18.08; H, 1.89; U, 48.40.

This unusual compound provided a sensitive test for the presence of uranium(IV) compounds in organic solutions. The precipitate formed immediately even at concentrations below 0.001 *M* in all solvents tried except dimethylform-

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[3] Gmelins' Handbook of Inorganic Chemistry, System 55, 8th ed., 1936.

[4] C. C. Sterett and V. P. Calkins, Report MDDC-1473, U. S. Atomic Energy Commission, Oak Ridge, Tennessee. Declassified November 11, 1947.

[5] These analyses were determined by Miss Frances Ball.

[6] These spectra were obtained by Miss Patricia Woltz.

[7] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structure," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[8] R. Rascanu, *Ann. sci. univ. Jassy*, **16**, 32, 459 (1930).

[9] P. Spacu, *Z. anorg. allgem. Chem.*, **230**, 181 (1936).

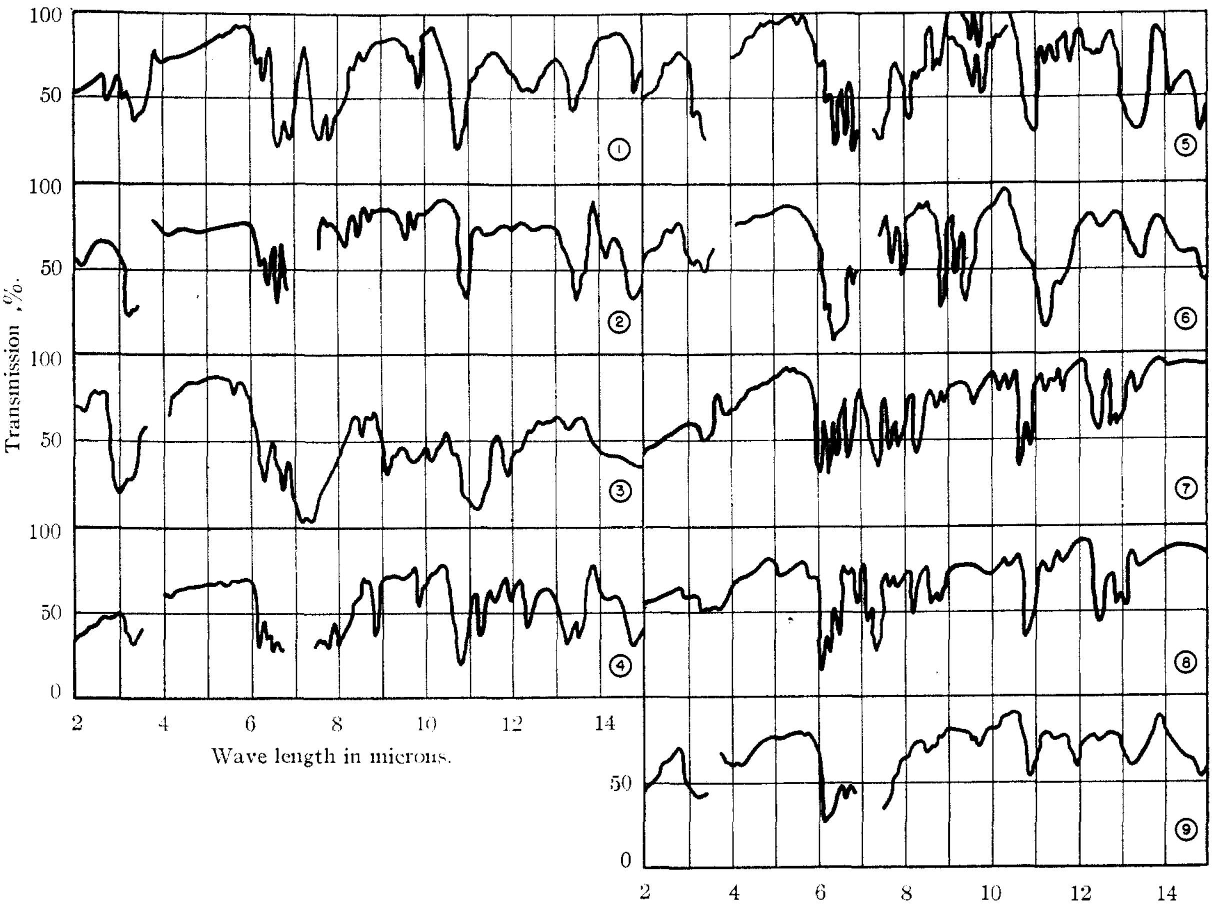

Fig. 1.—Infrared absorption spectra: 1, dipyridineuranyl nitrate; 2, tripyridinediuranium(IV) chloride; 3, dimethylethanolamineuranyl nitrate; 4, salicylatoaquopyridineuranyl nitrate; 5, dichlorodisalicylatodipyridineuranium (IV); 6, lactatoaquopyridineuranyl nitrate; 7, diquinaldinatodiaquouranyl; 8, dichlorodiquinaldinatoquinaldineuranium(IV); 9, bis-(N-phenylglycinato)-tetraaquouranium(IV) chloride.

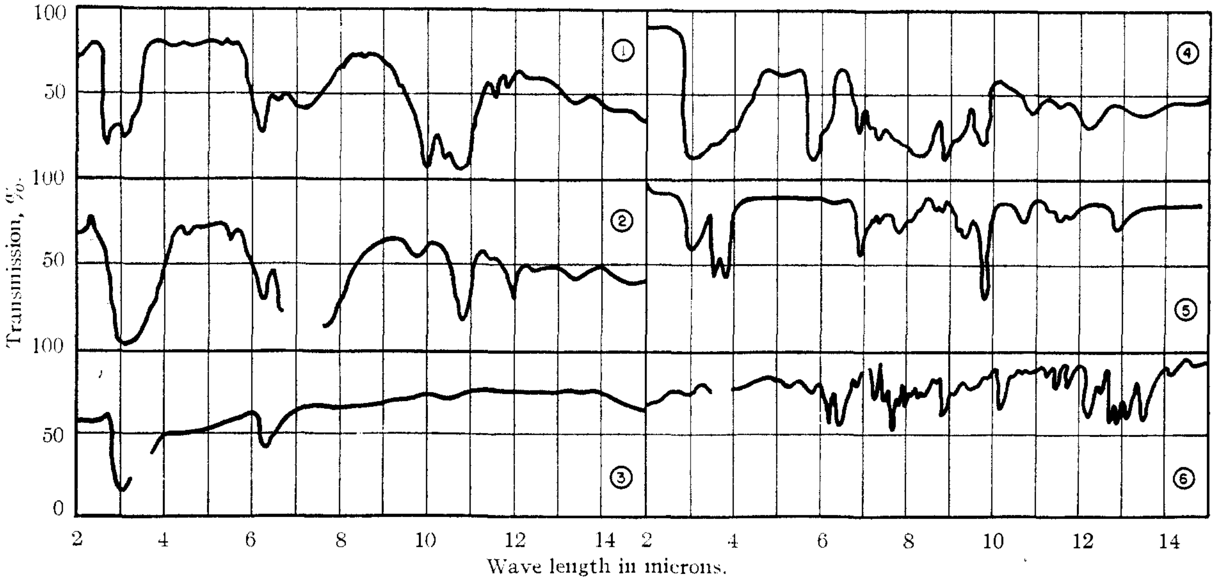

Fig. 2.—Infrared absorption spectra: 1, uranyl fluoride; 2, uranyl nitrate hexahydrate; 3, uranium(IV) chloride; 4, lactic acid; 5, dimethylethanolamine; 6, quinaldinic acid.

amide. It did form in alcohols, ethers, esters and alkyl phosphates.

Dianilineuranium(IV) Chloride.—The reaction of uranium(IV) chloride with aniline under conditions similar to those used for pyridine gave a dark green crystalline compound which decomposed at 210°.

Anal. Calcd. for $UCl_4 \cdot 2C_6H_5NH_2$: C, 25.46; H, 2.49; N, 4.95. Found: C, 25.83; H, 2.72; N, 5.24.

Salicylatoaquopyridineuranyl Nitrate.—Four milliliters of pyridine was added dropwise and with good stirring to a solution of 10 g. of uranyl nitrate hexahydrate and 10 g. of salicylic acid in 100 ml. of warm butyl acetate. All the uranium precipitated after standing at room temperature for a short time, leaving a nearly colorless supernate. The yield was 11.0 g. of the dark red complex. Recrystallization from ethanol gave monoclinic crystals with a density of 1.967, which sintered at 100° and darkened at 150°, but which did not melt below 350°. The product was soluble in water, pyridine, acetone and ethanol, and was insoluble in benzene, hexane, chloroform and ethyl ether.

Anal. Calcd. for $[H_2O \cdot C_5H_5N \cdot UO_2(C_7H_5O_3)]^+NO_3^-$: C, 25.44; H, 2.13; U, 42.03. Found: C, 25.50; H, 1.73; U, 42.34.

Karl Fischer titration showed the presence of one molecule of water. The molecular weight in boiling ethanol was 287, one-half the formula weight of 566. The slightly acidic water solution of the complex was stable to storage, and toward slightly alkaline reagents, but the color was destroyed by strong acids and bases. The solution was a conductor of electricity, and tests for nitrate ion were obtained. No change was noted upon the addition of a solution of 8-hydroxyquinoline. If uncomplexed uranyl ion had been present the uranyl hydroxyquinolinate should have precipitated. These factors led to the assignment of a complex cation structure to the compound.

Salicylatoaquo-*n*-butylamineuranyl Nitrate.—Substitution of *n*-butylamine for pyridine in the above procedure gave a quantitative yield of this red-orange compound, which had similar solubilities, and which did not melt below 350°.

Anal. Calcd. for $[H_2O \cdot C_4H_9NH_2 \cdot UO_2(C_7H_5O_3)]^+NO_3^-$: C, 23.60; H, 3.24. Found: C, 23.21; H, 3.04.

Analogous compounds were prepared using as the external base ammonia (bright orange powder, non-fusible) and quinoline (brick-red crystals, melting point above 300°). These compounds were similar to the pyridine compound in their solubilities, but were not characterized further. This type of compound will form in the same classes of solvents as will the aquopyridineuranyl nitrate, that is, in ethers, esters, the higher alcohols and ketones, and the brilliant red color of the pyridine compound makes this reaction a fairly sensitive color test for the presence of uranyl compounds in organic solutions. The limit of detection with the unaided eye is in the range of 0.0005 *M* solutions. The color will not develop in dimethylformamide or tributyl phosphate.

Salicylatoaquopyridineuranyl Chloride.—The substitution of uranyl chloride trihydrate for uranyl nitrate hexahydrate gave as the product a mixture of aquopyridineuranyl chloride and salicylatoaquopyridineuranyl chloride. Fractional crystallization from methanol served to separate the more soluble yellow ammine from the red-brown complex. Neither compound melted below 350°. The complex sintered and darkened at 100–150°.

Anal. Calcd. for $UO_2Cl_2 \cdot H_2O \cdot C_5H_5N$: C, 13.62; H, 1.59; U, 53.98. Found: C, 14.20; H, 1.76; U, 54.47. Calcd. for $[H_2O \cdot C_5H_5N \cdot UO_2(C_7H_5O_3)]^+Cl^-$: C, 26.70; H, 2.22; U, 44.11. Found: C, 26.21; H, 2.73; U, 45.13.

Dichlorodisalicylatodipyridineuranium(IV).—The addition of 5 ml. (an excess) of pyridine to a solution of 10.0 g. of uranium(IV) chloride and 20.0 g. of salicylic acid in 125 ml. of butyl acetate gave a greenish-white precipitate weighing 22.0 g., after digestion with ether and drying, with a melting point of 165°. This weight corresponded to a composition of approximately two molecules each of pyridine and salicylic acid and two chloride ions for each uranium atom. Analysis of the crude material confirmed this ratio.

Anal. Calcd. for $2C_5H_5N \cdot UCl_2(C_7H_5O_3)_2$: C, 32.40; H, 2.75; U, 32.11. Found: C, 33.41; H, 3.02; U, 34.56.

This compound was stable when free of solvent, but it was oxidized rapidly in contact with acetone or ethanol, and hydrolyzed immediately in aqueous solutions, with the formation of uranium(IV) oxide. Conditions for recrystallization could not be found which did not yield predominately uranyl products. For example, recrystallization from pyridine gave dipyridineuranyl chloride in good yield. This was a yellow solid which decomposed at 115°.

Anal. Calcd. for $UO_2Cl_2 \cdot 2C_5H_5N$: C, 24.05; H, 2.20. Found: C, 23.85; H, 2.18.

The molecular weight in boiling ethanol corresponded to one-third the formula weight.

Diquinaldinatodiaquouranyl.—The addition of 3 g. of quinaldinic acid in 50 ml. of hot butyl acetate to a solution of 2 g. of uranyl nitrate hexahydrate in 50 ml. of butyl acetate gave an immediate precipitate. Digestion of the solid with ether, followed by recrystallization from ethanol, gave about 2 g. of the light yellow product, a true inner complex. This compound melted at 245°, and was soluble in ethanol, acetone and methyl ethyl ketone, and was insoluble in ethyl ether, dioxane and benzene. It was slightly soluble in water, but was decomposed by strong acids and bases.

Anal. Calcd. for $UO_2(C_{10}H_6O_2N)_2 \cdot 2H_2O$: C, 36.80; H, 2.78; U, 36.48. Found: C, 36.00; H, 2.43; U, 35.81.

Dichlorodiquinaldinatoquinaldineuranium(IV).—The reaction of 5 g. of quinaldinic acid with 2 g. of uranium(IV) chloride in 125 ml. of butyl acetate gave a curdy, cream-colored precipitate. Digestion with two portions of ether and recrystallization from ethanol gave 2.5 g. of light yellow-green solid which sintered at 160° and decomposed at 225°. The compound was slightly soluble in methanol, ethanol, and acetone and insoluble in other organic solvents. It reacted with water to give a brown precipitate and an acidic solution. Addition of sulfuric acid to this solution and distillation into silver nitrate solution gave a precipitate of silver chloride.

Anal. Calcd. for $UCl_2(C_{10}H_6O_2N)_2 \cdot C_{10}H_7O_2N$: C, 43.75; H, 1.96; U, 28.91. Found: C, 43.08; H, 2.12; U, 29.86.

Bis-(N-phenylglycinato)-tetraaquouranium(IV) Chloride.—A solution of 15 g. of N-phenylglycine in 75 ml. of butyl acetate was added slowly to a solution of 10.0 g. of uranium(IV) chloride in 150 ml. of butyl acetate. The resulting oil was stirred under ether until it solidified, and the solid was digested several times with ether. There remained after drying 23.0 g. of the light green, amorphous dichlorobis-(N-phenylglycinato)-N-phenylglycineuranium-(IV). This crude complex could not be purified further because of its susceptibility toward oxidation.

Five grams of this solid was dissolved by warming with 25 ml. of water containing 1 ml. of 6 *N* hydrochloric acid, and 10 ml. of saturated sodium chloride solution was added. The solid was removed by filtration after thorough chilling, washed with ethanol and ether, and recrystallized from a water–dioxane mixture. The dried solid was light green in color, and weighed 2.0 g. It was insoluble in all solvents tested except water and methanol. Water was lost at 115, and decomposition occurred above 220°.

Anal. Calcd. for $[4H_2O \cdot U(C_8H_8O_2N)_2]^{++}2Cl^-$: C, 28.20; H, 2.29; Cl, 10.41; H_2O, 10.56. Found: C, 27.72; H, 3.12; Cl, 10.49; H_2O, 9.6.

Reaction of Uranium(VI) Chloride with Pyridine.—The addition of 0.5 ml. of pyridine to a solution of 0.5 g. of uranium(VI) chloride in 50 ml. of carbon tetrachloride gave a dark brown precipitate and a colorless supernate. The precipitate was hydrolyzed by washing with 2 ml. of 50% aqueous ethanol, and the resulting light yellow solid was recrystallized twice from a pyridine–ether mixture to yield 0.1 g. of dipyridineuranyl chloride, m.p. 112–115°, with decomposition.

Infrared Spectra.—The infrared spectra of the ammines and complexes are presented in Fig. 1. Interpretations were made with the help of the spectra-structure correlation given by Randall and co-workers,[7] Barnes,[10] Colthup,[11] and Kline and Turkevich.[12] It is important to note that these assignments and interpretations are based on more or less empirical relationships, and thus the conclusions presented are merely the speculations of the authors. Nevertheless, it is interesting to observe some of the correlations and trends existing between complexes containing similar groups.

It was found that in each of the complexes in which pyridine was a component some of the bands normally present in pyridine were no longer present in the complex. This was also true for the other coördination groups studied, although the effect was less pronounced.

In the six complexes which contained pyridine the following bands vanished in all cases: 2.76, 5.02, 5.46, 5.93 (probably C=N stretching), and 10.09 (C=C ring stretch-

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(10) R. B. Barnes, R. C. Gore, U. Liddel and Van Z. Williams, "Infrared Spectroscopy, Industrial Applications and Bibliography," Reinhold Publishing Corp., New York, N. Y., 1944.

(11) N. B. Colthup, *J. Optical Soc. Amer.*, **40**, 397 (1950).

(12) C. H. Kline, Jr., and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944).

ing), μ. The 6.33 and 9.36 μ bands disappeared in all except lactatoaquopyridineuranyl nitrate; the 6.94 μ band in all but dipyridinouranyl nitrate.

A new band at 11.2 μ appeared in the salicylato- and lactatouranyl and the salicylatouranium(IV) complexes. Similar new bands were noted at 11.65 μ for the quinaldinic acid derivative, and at 11.97 μ for the phenylglycine derivative of uranium(IV) chloride. A shift of this sort is expected with the attachment of heavier groups on the postulated U–O–C(O)R linkages involved in these complexes. In addition, a band at 13.0–13.2 μ appeared in all pyridine complexes except the dipyridineuranyl nitrate and tripyridinediuranium(IV) chloride. This might again be due to a U–O–C(O)R linkage, which is absent in the latter two compounds.

In both the uranium(IV) and uranyl salicylatopyridine complexes the unassigned salicylic acid band at 3.90 μ disappeared. In the uranyl derivative the 6.02 μ carbonyl group stretching vibration and the 8.66 μ band also vanished. In the comparable lactic acid derivative the 5.02 and 7.30 μ bands were absent. The missing 5 μ band is probably a carboxylic acid type carbonyl vibration. In both salicylatopyridine complexes new bands were observed at 11.2, 11.5 and 13.2 μ; in the lactatopyridine complex at 13.1 μ.

In both the uranium(IV) and uranyl derivative of quinaldinic acid the ligand bands normally at 5.24, 6.65, 7.63, 10.15 and 11.5 μ vanished in the complexes. In both complexes new bands appeared at about 6.0, 6.8, 6.9, 8.6 and 8.8 μ.

In dimethylethanolamineuranyl nitrate, many bands of dimethylethanolamine attributed to the tertiary nitrogen disappeared. One band, which appeared in this complex at 7.08 μ, is probably due to the quaternization of the nitrogen.

Discussion

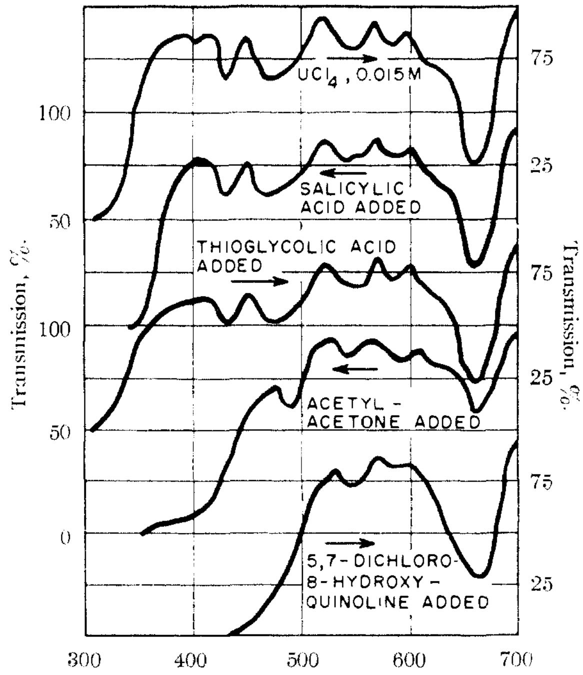

Fig. 3.—Spectrophotometric evidence for the reaction of complexing agents with uranium(IV) chloride in *n*-butyl acetate solution.

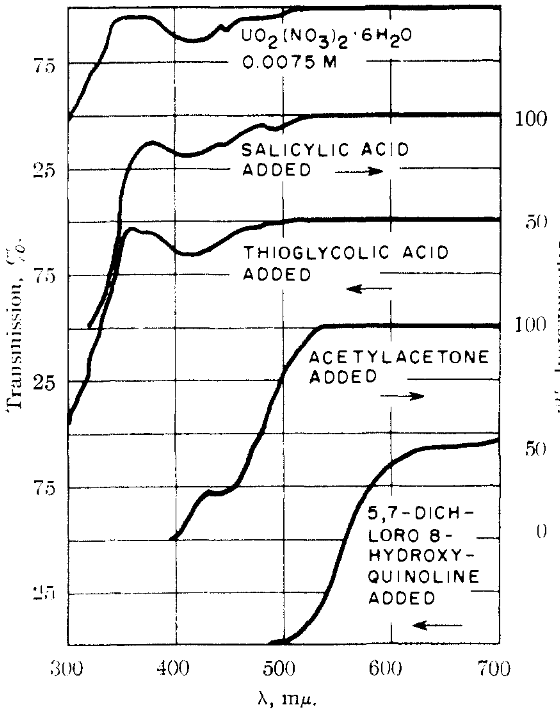

Fig. 4.—Spectrophotometric evidence for the reaction of complexing agents with uranyl nitrate hexahydrate in *n*-butyl acetate solution.

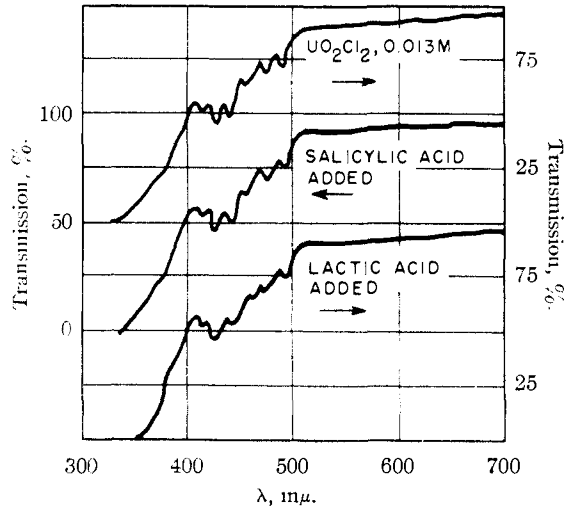

Fig. 5.—Spectrophotometric evidence for the reaction of complexing agents with uranyl chloride in *n*-butyl acetate solution.

One possible explanation for the formation of such widely different products in different solvents may be found in a comparison of the degree of ionization of uranium salts in aqueous and non-aqueous solvents. In aqueous solutions uranyl and uranium(IV) compounds exist primarily as the completely ionized anion and a highly hydrated cation, while in *n*-butyl acetate the salts exist as solvated molecular species.[13] In aqueous solution the cation would be susceptible to successive stepwise attack by complexing agents to form a totally coördinated complex. On the other hand, in non-ionizing solvents the separation of anion and cation apparently proceeds only after the attack by an external base upon the molecule. The preferred attachment of the additional basic group weakens the attraction of the uranium atom for the electrons of the partly-covalent, partly-ionic shared pair of the inorganic anion. In the presence of an acidic function which

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[13] L. I. Katzin, D. M. Simon and J. R. Ferraro, THIS JOURNAL, 74, 1191 (1952).

could form a more covalent bond with the uranium than could the original anion (*e.g.*, a carboxylic acid), stepwise attack on the cation could then proceed. The process would, however, be interrupted at the point where the total number of coördinating groups surrounding the uranium atom becomes equal to the maximum coördination number of the uranium atom. At this point the bonds between the uranium atom and any remaining inorganic anions would become strongly ionic in nature, and the resulting new type complex, being insoluble in the organic solvent, would be removed from the sphere of reaction. This point apparently is reached after the substitution of one bidentate organic acid type complexer in uranyl salts, and after the substitution of the second molecule of such a complexer in uranium(IV) salts.

Some confirmation of the part which the base plays in this reaction may be found in the fact that complexing agents which contained only acidic functional groups, such as salicylic acid, had little effect on uranium compounds in organic solution, and required the addition of an external base for reaction. This base was found combined in the product. On the other hand, a complexing agent which itself contained a basic group, such as quinaldinic acid, reacted readily with organic solutions of uranium salts to give complex compounds.

This relationship may be seen in Figs. 3–5. These figures contain the spectra of solutions of uranium compounds in butyl acetate to which various complexing agents were added. The carboxylic acids cause relatively slight changes in the spectra. Acetylacetone produced a decided bathochromic shift in the spectra. Several of the hydroxyanthraquinones and flavones, which have structures similar to that of enolized acetylacetone, showed similar results. None of these complexing agents, however, gave precipitates with uranium compounds; thus the products must have been inner complexes. The extensive alteration of the spectra produced by 2,4-dichloro-8-hydroxyquinoline is typical of the results obtained with amino acids, and is indicative of actual chemical combination of the complexing agent with the uranium compound. Solutions more concentrated than those used to obtain the spectra gave precipitates with oxine derivatives and amino acids.

The lack of reaction of hydrated uranyl compounds was not due to the protective action of the water of hydration, as is demonstrated by a comparison of Figs. 4 and 5, which show that anhydrous uranyl chloride underwent no more reaction than did uranyl nitrate hexahydrate. Distillation of a portion of the solvent to remove the water of hydrated compounds also did not cause further reaction between purely acidic complexing agents and uranyl salts.

The changes observed in the infrared spectra of the uranium complexes as compared to the spectra of their components help to confirm the hypothesis that the organic ligands are bound to the uranium, rather than being present as purely ionic components of the complexes. Pyridine appears to be bound by linkage between the tertiary nitrogen atom and the uranium. Only the attachment of a very heavy atom would account for such a profound change in the spectrum of pyridine. The bidentate acids are bound through both the carboxylic group and the second function.

The correlations and trends noted between complexes containing similar functions confirm the chemical evidence that these complexes are members of the same family of compounds, and form a new type of uranium compounds. The reaction of organic bases and complexing agents with uranium compounds in aqueous solution, or the recrystallization of uranium inner complexes from a solvent such as pyridine has been reported to give compounds which contain both organic base and complexing groups.[2] Such compounds were solvated inner complexes, however, and were not ionic in character. This is believed to be the first time that a complex electrolyte of mixed coördination has been demonstrated for a uranium compound, although there are several compounds reported in the literature which should be re-examined in the light of present knowledge.[14]

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