THE COÖRDINATION CHEMISTRY OF THE ACTINIDES

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CONTENTS

I. INTRODUCTION

This review is a comprehensive survey of the coördination compounds formed by the actinide elements with organic ligands, both in the solid state and in solution.

There have been no previous reviews of the coördination chemistry of any of these elements, except for a short critical review on uranium (98). Two reviews on the general chemistry of thorium (277, 453) and Hyde's review on the radiochemistry of thorium (242) contain many references to coördination compounds. Croxton's comprehensive bibliography on uranium from 1789 to 1950 is an invaluable key to the literature (109). Katz and Seaborg's book (274) gives useful introductions to the compounds reviewed here, and especially to the solvent extraction of the actinides. The literature on the solvent extraction of the actinides is vast and no attempt is made here to review it completely; instead, summaries are given of what is now known of the complexes which are formed in these systems. More general reviews on solvent extraction are available (241, 247, 336, 373).

Compounds of simple carboxylic and sulfonic acids have been excluded, but acids containing other functional groups which could conceivably chelate are included. Only compounds whose stoichiometric compositions have been definitely established have been included. To keep the review within reasonable limits,

basic compounds have mostly been excluded. Within these limits an attempt has been made to give a complete coverage of the literature up to August, 1959.

The nomenclature of *Chemical Abstracts* for the ligands has been used throughout, except for a few common names for which the *Chemical Abstracts* names are given in parentheses at their first mention, and for some ligands in table 16 marked by asterisks.

For convenience of reference, all ligands containing both nitrogen and oxygen are classed as "nitrogen donors," although it is recognized that in some of these complexes only electron donation from oxygen may be involved. Likewise, in Section V all ligands containing sulfur (except sulfonic acids and their derivatives) are classed together, regardless of their possible structures.

Compounds discussed in the text are not normally included in the tables. In a few cases the formulas given in the tables are not those given by the original authors, but those which seemed more probable to the reviewer. Stoichiometric ratios are expressed as atoms of metal to molecules of ligand.
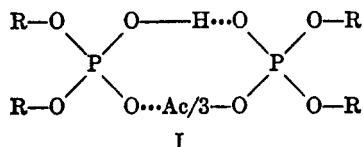
II. Actinium Complexes

Actinium is tervalent in all of its known compounds, closely resembling lanthanum, and it is to be expected that the coördination chemistry of actinium will resemble that of the lanthanides (359). The element has been available in the pure state only since 1950, and no coördination compounds have been isolated.

Actinium has been separated from neutron-irradiated radium by solvent extraction using organic solutions of HTTA[1] (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) (203); the extracting species is Ac(TTA)$_3$ (323).

In common with the lanthanides (476), actinium is extracted only to a small extent by tributyl phosphate, except in the presence of high concentrations of salting-out agents or mineral acids (409, 476).

The alkylphosphoric acids are much better extractants for the tervalent lanthanides and actinides than trialkyl phosphates (410). Dialkylphosphoric acids extract actinium in the form of Ac{H[(RO)$_2$PO]$_2$}$_3$, for which structure I has been suggested, by analogy with

$$\text{R—O} \diagdown \quad \diagup \text{O——H···O} \diagdown \quad \diagup \text{O—R}$$
$$\text{P} \qquad\qquad \text{P}$$
$$\text{R—O} \diagup \quad \diagdown \text{O···Ac/3—O} \diagup \quad \diagdown \text{O—R}$$

I

the presumed structures for the dimeric acids. The species extracted by monoalkylphosphoric acids may be polymeric.

[1] Abbreviations used in the tables and text for some of the compounds that form complexes are given below:
   HTTA = 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione.
   TBP = tributyl phosphate.
   EDTA = ethylenedinitrilotetraacetic acid.

III. Thorium Complexes

A. COMPLEXES WITH β-DIKETONES

The complex of thorium with acetylacetone (2,4-pentanedione), Th(C$_5$H$_7$O$_2$)$_4$, has been studied more than any other thorium complex. It was first described by Urbain in 1896 (531), and several variations on this method of preparation have since been given (26, 27, 79a, 256, 263, 332, 447, 574). Grdenić and Matković (195) have recently prepared the complex in two different monoclinic modifications; the α-form is isomorphous with cerium(IV) and uranium(IV) acetylacetonates, and the β-form with zirconium(IV) acetylacetonate. In the crystal of the α-form each thorium atom is surrounded by eight oxygen atoms at the corners of an Archimedean antiprism (194).

Thorium acetylacetonate is very soluble in most organic solvents except the aliphatic hydrocarbons. It is essentially monomeric in dilute chloroform, carbon disulfide, 1,2-dibromoethane, and benzene solutions (26, 531). The vapor pressure has been measured by the effusion method (572, 573), the quantity of effusate being determined by its rate of emission of α-particles. The vapor pressure is low (3.2 × 10^{-4} mm. at 100°C.), but sublimation has been used as a method of purification; the boiling point at atmospheric pressure is 260–270°C., but extensive decomposition occurs (371).

Other properties of the complex which have been studied are the diamagnetic susceptibility (240, 346), the dielectric polarization (101, 154), the refractive index (515), and the infrared (99, 372) and ultraviolet (290) absorption spectra. The complex exhibits an intense white fluorescence when exposed to ultraviolet light at low temperatures (99).

The complex is formed stepwise in aqueous solution, and stability constants for the species ThA^{3+}, ThA$_2^{2+}$, ThA$_3^+$, and ThA$_4$ (where A represents the radical C$_5$H$_7$O$_2^-$) have been measured by the potentiometric (254) and extraction (416, 456, 457, 458) methods.

Thorium acetylacetonate yields solid derivatives with ammonia and with aniline: [Th(C$_5$H$_7$O$_2$)$_4$]$_2$.NH$_3$ and [Th(C$_5$H$_7$O$_2$)$_4$]$_2$.C$_6$H$_5$NH$_2$ (26). The β-diketone complexes of many other metals yield compounds of this type, and their nature is obscure. If the nitrogen atoms were coördinated with metal atoms, the latter would have improbably high coördination numbers (unless some diketone radicals were unidentate), and it is more likely that the nitrogen atoms are held by hydrogen bonds to the diketone oxygen atoms.

The complex of thorium with dibenzoylmethane (1,3-diphenyl-1,3-propanedione) is also well known (164, 192, 467, 566, 567, 568). The crystallographic dimensions of the unit cell have been determined (542, 564); the complex is isomorphous with the corresponding compounds of cerium(IV) and uranium(IV). The complex is very stable to heat; the major thermal decom-

TABLE 1

Complexes of thorium with β-diketones

a. With compounds of the type RCOCH₂COR'		References
R	R'	
Ferrocenyl	Methyl	(565)
Phenyl	Methyl	(164, 467, 566, 567)
p-Methoxyphenyl	Methyl	(566, 567)
p-Methoxyphenyl	Phenyl	(566, 567)
m-Nitrophenyl	Phenyl	(566, 567)
p-Nitrophenyl	Phenyl	(566, 567)
3-Bromo-4-methoxyphenyl	Phenyl	(566, 567)
3-Nitro-4-methoxyphenyl	Phenyl	(566, 567)
Benzyl	Phenyl	(566, 567)
2-Furyl	Phenyl	(566, 567)

b. With cyclic β-diketones	
2-Benzoyl-1-indanone	(566, 567)
2-Acetyl-3,4-dihydro-1(2H)-naphthalenone	(566, 567)
2-Acetylcyclopentanone	(566, 567)
2-Acetylcyclohexanone	(566, 567)
3-Benzoylcamphor	(314, 566, 567)
3-Hydroxymethylenecamphor	(566, 567)

position product appears to be thorium benzoate (97). Other β-diketone complexes of thorium which have been isolated are listed in table 1.

The complex of thorium with HTTA has been studied by the solvent-extraction method (243, 335) and has been used for radiochemical separations (203, 347) and for measuring the stability constants of other thorium complexes (118, 541, 579); it has not been isolated. The thorium complexes of tropolone (131) and 2-hydroxy-1,4-naphthoquinone (581) have likewise been examined by the solvent extraction method.

1-(3,4-Dichlorophenyl)-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione has been recently introduced (241) as a reagent for the extraction of larger quantities of thorium into benzene than can be accomplished with the simpler β-diketones.

A number of aromatic polyhydroxy compounds containing the β-diketone grouping have been used as colorimetric reagents for the detection and determination of thorium. Those for which the stoichiometry of the thorium complexes in solution have been established are included in table 4.
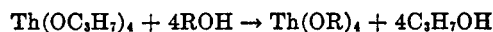
B. COMPLEXES WITH OTHER OXYGEN DONORS

Anhydrous thorium tetrachloride and tetrabromide react with oxygen donors to yield both addition and substitution products. Those which have been characterized are listed in table 3.

The alcoholates have been studied most (49). Primary and secondary alcohols yield addition compounds of the type ThCl₄.4ROH, in which the thorium atoms are presumably eight-coördinate, although some dissociation occurs. Tertiary amyl alcohol reacts in a more complex way to give alkyl chloride, olefin, and an indefinite thorium oxychloride.

Bradley and his colleagues have made a comprehensive study of the alkoxides of thorium, [Th(OR)₄]ₙ (44, 45, 48, 50). The tetraisopropoxide was prepared by the reaction between the isopropyl alcoholate of thorium tetrachloride and sodium isopropoxide:

$$ThCl_4.4C_3H_7OH + 4C_3H_7ONa \rightarrow$$
$$Th(OC_3H_7)_4 + 4NaCl + 4C_3H_7OH$$
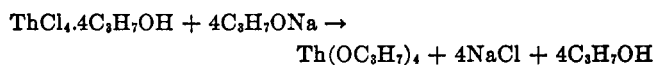
and the other alkoxides were prepared from this by alcohol interchange:

$$Th(OC_3H_7)_4 + 4ROH \rightarrow Th(OR)_4 + 4C_3H_7OH$$

These compounds are polymerized to various degrees by coördination of oxygen atoms of one molecule to the thorium atom of another. By varying the alkyl group the degree of polymerization can be changed. The tetramethoxide is a highly polymerized, insoluble, non-volatile white solid; but if sufficiently bulky alkyl groups are introduced, as in the compound Th[OC(C₂H₅)₃]₄, the polymerization can be completely suppressed and the compound is a volatile liquid. The molecular complexities of the alkoxides, measured ebullioscopically in benzene, are given in table 2. Bradley has discussed these results in terms of his general theory of alkoxide polymerization (41) and suggests that in the normal alkoxides the thorium atoms are predominantly eight-coördinate. A mixed chloride-phenoxide has been prepared (170), but its molecular complexity is not known.

TABLE 2

Molecular complexities of thorium alkoxides, [Th(OR)₄]ₙ

Primary		Secondary		Tertiary	
R	n	R	n	R	n
CH₃	Insoluble	(CH₃)₂CH	3.8	(CH₃)₃C	3.4
C₂H₅	Insoluble	CH₃(C₂H₅)CH	4.2	(CH₃)₂(C₂H₅)C	2.8
C₄H₉	6.44	(C₂H₅)₂CH	4.1	CH₃(C₂H₅)₂C	1.8
C₅H₁₁	6.20			(CH₃)₂(C₃H₇)C	2.6
(CH₃)₃CCH₂	4.01			(CH₃)₂[(CH₃)₂CH]C	2.3
				(C₂H₅)₃C	1.0
				CH₃(C₂H₅)(C₃H₇)C	1.7
				CH₃(C₂H₅)[(CH₃)₂CH]C	1.0

TABLE 3

Thorium complexes with oxygen donors

Ligand	Formula of Complex	References
Methyl alcohol	ThCl4.4CH4O	(49)
Acetaldehyde	ThCl4.2C2H4O (?)	(447)
Ethyl alcohol	ThCl4.2C2H6O	(49)
	ThCl4.4C2H6O	(49, 257, 447)
	ThBr4.4C2H6O	(571)
Acetone	ThCl4.2C3H6O	(257, 447)
Isopropyl alcohol	ThCl4.4C3H8O	(49)
Ethyl acetate	ThBr4.2C4H8O2	(571)
n-Butyl alcohol	ThCl4.3C4H10O	(49)
Pyrocatechol	(NH4)2Th(C6H4O2)3.5H2O	(446)
	(NH4)2Th(C6H4O2)3.7H2O	(449)
	K2Th3(C6H4O2)7.20H2O	(446)
	(C5H6N)2H2[Th(C6H4O2)4]	(552)
1,2-Diethoxyethane	Th(NO3)4.3C6H14O2.3H2O	(276)
(diethyl cellosolve)		
Salicylaldehyde	ThCl3(C7H5O2)	(257)
	ThCl2(C7H5O2)2	(257)
	ThCl4.2C7H6O2	(257)
Benzaldehyde	ThBr4.4C7H6O	(571)
	ThOBr2.2C7H6O.H2O	(571)
	ThBr2(C6H5COO)2.3C7H6O	(571)
Methyl salicylate	ThCl3(C8H7O3)3	(257, 447)
	ThCl2(C8H7O3)2	(257)
	ThCl(C8H7O3)3	(257)
	ThCl4.C8H8O3	(257)
Acetophenone	ThCl4.4C8H8O	(257)
	2ThBr4.7C8H8O	(571)
	2ThOBr2.C8H8O.2H2O	(571)
Cinnamaldehyde	ThCl4.4C9H8O	(445)
	ThCl4.2C9H8O	(447)
Propiophenone	2ThOBr2.C9H10O.4H2O	(571)
Ethyl benzoate	ThBr4.3C9H10O2	(571)
Hinokitiol	Th(C10H11O2)4	(243a)
3-Hydroxy-2-naphthoic acid	Th3(C11H6O3)6.C6H5N.5H2O	(423)
	Th3(C11H6O3)6	(423)
Benzophenone	ThCl4.4C13H10O	(257)

In common with most organic acids, tartaric, citric, and malic acids give basic salts with thorium (201).

Berzelius prepared a thorium tartrate by dissolving thorium hydroxide in tartaric acid (20), and subsequent workers have obtained basic precipitates by mixing aqueous solutions of thorium salts and tartrates (92, 201). The basic salts redissolve in an excess of sodium tartrate or tartaric acid solution (55, 56), and other basic salts may be obtained by evaporating these solutions (447).

Citric acid behaves similarly to tartaric acid (20, 90, 201). Bobtelsky and Graus have reëxamined the thorium–citrate system (33), using their method of "heterometric titration" (photometric titration of suspensions). When sodium citrate is added to thorium nitrate solution, a precipitate of the 1:1 complex is first formed, which redissolves on addition of more citrate to form a 2:3 complex. In aqueous ethanol the 1:1 complex is also precipitated, but it redissolves in an excess of citrate to form a 1:2 complex. Brown and Rieman (60) studied the thorium–citrate system by an ion-exchange method and deduced that the predominant complex formed between pH 2.1 and 3.5 is ThCit$_2^{2-}$, but these workers did not consider the possibility of complexes having nonintegral thorium/citrate ratios.

Thorium salicylate in the solid state is known only as a basic salt (121, 283, 584). Studies of the extraction of very dilute aqueous thorium solutions by solutions of salicylic acid in 4-methyl-2-pentanone and in chloroform (229) show the presence in the aqueous phase of a series of complexes with up to four molecules of salicylic acid to each thorium atom, and in the organic phase of the compound Th(HOC6H4COO)4.(HOC6H4COOH). The latter may be analogous to the 1:5 complex of thorium with 8-quinolol (*q.v.*). With *o*-methoxybenzoic acid a series of complexes is again formed in the aqueous phase, but in the organic phase only the simple complex Th(CH3OC6H4COO)4 obtains. Solvent extraction by a solution of salicylic acid in 2-furaldehyde has been proposed (95) for the separation of thorium from uranium, and the ready solubility of thorium salicylate in ethyl acetate provides a quantitative means of separating thorium from the rare earths (107). The extraction of thorium salicylate by isoamyl alcohol has also been studied (517).

Table 3 lists both addition compounds of thorium salts with oxygen donors, and thorium complexes with acidic oxygen donors. Complexes for which the stoichiometries in solution have been established are given in table 4.

C. SOLVENT EXTRACTION BY OXYGEN DONORS

The extraction of thorium salts by organic solvents (278) is qualitatively similar to that of the uranyl salts (see Section V,C,4), but it is less well understood. Extraction of thorium nitrate by ether was first reported in 1927 (244), although the solubility of the dry salt in ether had previously been used for analytical separations (39). Moissan and Martinsen (368) found that anhydrous thorium tetrachloride was almost insoluble in dry ether but dissolved easily in ether saturated

TABLE 4

Thorium complexes with oxygen donors in solution

Ligand	Ratio of Thorium to Ligand in Complex	References
3-Alizarinsulfonic acid	1:1	(125, 161, 471)
Aurintricarboxylic acid (Aluminon)	1:1	(382)
Carmine red	1:4	(143)
Carminic acid	1:4	(207)
Chlorotetracycline	1:1	(250, 469)
1,2-Dihydroxybenzene-3,5-disulfonic acid (Tiron)	2:3	(388)
2,5-Dihydroxy-1,4-benzoquinone	1:2	(166, 360)
2,5-Dihydroxy-3,6-diphenyl-1,4-benzoquinone	1:2	(166)
Morellin	1:4	(426)
Morin	1:2	(156, 157, 355)
Naphthazarin	1:2	(365)
Pyrocatechol violet	1:1, 2:1	(455)
Quercitin	1:2	(351)
Quinalizarin	1:1	(425)
Salicylaldehyde	1:1	(35)
Xanthone	1:4	(475)

with water; in this respect thorium tetrachloride resembles uranyl nitrate.

The solubilities (191) and heats of solution (153) of thorium nitrate in many oxygen-containing organic solvents have been determined.

In solvent extraction by alcohols, ketones, and ethers, each molecule of thorium nitrate is accompanied in the organic phase by about six molecules of water (280); the number of molecules of solvent attached is not known, nor the degree of dissociation of the nitrate groups. In marked contrast to uranyl nitrate, it will be seen from table 3 that only one solid addition compound of thorium nitrate with an oxygen donor has been reported; it is not clear whether this is due to the lower stability of the thorium complexes, or merely to the fact that these systems have received less attention.

Thorium nitrate is extracted by tributyl phosphate as $Th(NO_3)_4.2TBP$ (159, 222). This solvate is essentially anhydrous; Healy and McKay's value (216) of 0.06 for the water:thorium ratio at 25°C. is lower than that of Katzin and his coworkers (280) (0.3–0.4), but the latter value was obtained with tributyl phosphate of lower purity. Thorium is also extracted by tributyl phosphate from hydrochloric acid solutions (411, 412).

Dibutylphosphoric acid (284) and bis(2-ethylhexyl)-phosphoric acid (408) give solid thorium complexes with 1:4 stoichiometry. Bis(2-ethylhexyl)phosphoric acid also forms a 1:4 complex in solution (322); in contrast to the corresponding uranium(VI) system, addition of tributyl phosphate to this reagent reduces its extracting power for thorium (29).

A mixed thorium nitrate–bis(2-ethylhexyl)phosphate has been isolated, the infrared spectrum of which shows the nitrate groups to be coördinated (408).

Two long-chain monoalkylphosphoric acids have also been studied as extractants for thorium (322); they too give 1:4 complexes in solution.

D. COMPLEXES WITH NITROGEN DONORS

Organic bases can behave in three different ways towards thorium salts, as exemplified by the following reactions of pyridine:

(i) In aqueous media it precipitates thorium hydroxide (399, 400).

(ii) Pyridinium chloride forms a double salt with thorium tetrachloride, $(C_5H_6N)_2ThCl_6$ (72, 448).

(iii) Anhydrous thorium tetrachloride and tetrabromide yield addition compounds, formulated in table 5, in which pyridine is coördinated to the metal.

Thorium and many other metal salts are extracted from water by organic solutions of long-chain amines (58, 75, 96). It is probable that reactions of type (ii) (above) occur in these systems, and that the extracting species are alkylammonium salts of complex metal anions; these compounds fall outside the scope of this review.

TABLE 5

Thorium complexes with nitrogen donors

Ligand	Formula of Complex	References
Methylamine...............	$ThCl_4.4CH_5N$	(340)
Acetonitrile...............	$ThBr_4.4C_2H_3N$	(571)
2-Aminoethanol...........	$ThCl_3(C_2H_6NO)_2.6H_2O$	(53)
Ethylamine...............	$ThCl_4.4C_2H_7N$	(340)
	$ThBr_4.4C_2H_7N$	(341)
n-Propylamine............	$ThCl_4.4C_3H_9N$	(340)
2,2'-Iminodiethanol.......	$ThCl_3(C_4H_{10}NO_2).C_4H_{11}NO_2$	(53)
Pyridine................	$ThCl_4.C_5H_5N$	(340)
	$ThBr_4.C_5H_5N$	(341)
	$ThBr_4.3C_5H_5N$	(571)
Aniline..................	$ThCl_4.4C_6H_7N$	(340)
	$ThBr_4.4C_6H_7N$	(341, 571)
2,2',2''-Nitrilotriethanol.....	$ThCl_3(C_6H_{13}NO_3).4H_2O$	(53)
	$ThCl_3(C_6H_{14}NO_3).C_6H_{15}NO_3.4H_2O$	(53)
2,2'-(Ethylimino)diethanol..	$ThCl_3(C_6H_{14}NO_2).C_6H_{15}NO_2$	(53)
2-Mercaptobenzothiazole....	$Th(C_7H_4NS_2)_4$	(512, 556)
Toluidine................	$ThCl_4.3C_7H_9N$	(340)
Quinoline................	$ThCl_4.C_9H_7N$	(340)
Picrolonic acid...........	$Th(C_{10}H_7N_4O_5)_4.H_2O$	(217)
	$Th(C_{10}H_7N_4O_5)_4$	(128)
β-Naphthylamine..........	$ThCl_4.C_{10}H_9N$	(340)
Antipyrene...............	$2Th(NO_3)_4.5C_{11}H_{12}N_2O$	(294)
	$2Th(NO_3)_4.5C_{11}H_{12}N_2O.4H_2O$	(294)
	$Th(ClO_4)_4.6C_{11}H_{12}N_2O$	(560)
p-Phenylazophenol........	$ThCl_4.2C_{12}H_{10}N_2O$	(155)
N-Nitroso-N-[2-(p-tolylsulfonyl)phenoxy]hydroxylamine..................	$Th(C_{13}H_{11}N_2O_5S)_4$	(18)
5,6-Benzoquinaldic acid.....	$Th(C_{14}H_8NO_2)_4$	(325)
Cocaine..................	$ThCl_4.2C_{17}H_{21}NO_4$	(401)
Di-o-tolylthiovioluric acid...	$Th(C_{18}H_{14}N_3O_3S)_4$	(506)

Many of the addition compounds of thorium tetrahalides with bases included in table 5 contain four ligand molecules to each thorium atom; the thorium atoms here are probably eight-coördinate.

8-Quinolol is an important reagent for the gravimetric determination of thorium. Developments in the chemistry of the complex up to 1956 have been reviewed by Hollingshead (231), and Moeller, Schweitzer, and Starr (364) have reviewed its use in analysis.

As precipitated from solution the complex is orange-red and contains an additional molecule of 8-quinolol: $Th(C_9H_6NO)_4.C_9H_7NO$. The additional molecule is removed on heating above 80°C. (554), and the yellow product now has the formula $Th(C_9H_6NO)_4$. This reaction is reversible; the orange-red complex may be regenerated by warming the yellow complex with a solution of 8-quinolol (167). The only other 8-quinolol complexes which behave in this way are those of scandium (421, 422), uranium(VI), and plutonium(VI) (q.v.).

The nature of the binding of the additional molecule is obscure; it dissociates completely in organic solvents (361). Van Tassel and Wendlandt (532) claim from calorimetric data that the additional molecule is held only by weak forces in the crystal, but this conclusion is open to the objection discussed in connection with the uranyl complex.

The thorium chelates of several substituted 8-quinolols have also been studied. 5,7-Dichloro-8-quinolol, 5,7-dibromo-8-quinolol, and 5-chloro-7-iodo-8-quinolol

behave similarly to 8-quinolol in forming complexes with both 1:4 and 1:5 stoichiometry (362), but 5,7-di-iodo-8-quinolol gives only the 1:4 complex (555). Heating the 1:5 complexes of the first two ligands did not yield 1:4 complexes (554). Moeller and Ramaniah (362) found that the spectra of chloroform solutions of the 1:5 complexes resemble those of solutions of the 1:4 complexes to which an extra molecule of ligand has been added, and suggested that the fifth molecule of ligand is not coördinated in solution. Rao and Rao (430) came to the opposite conclusion from a study of the spectra of the 5,7-dibromo-8-quinolol complexes in dioxane, carbon tetrachloride, and acetone solutions. Dyrssen and his colleagues (136) have studied the solvent extraction of thorium by solutions of 5,7-dihalo-8-quinolols and find these reagents to be more powerful extracting agents than 8-quinolol. 2-Methyl-8-quinolol (8-hydroxyquinaldine) forms only the 1:4 complex with thorium (420), although the scandium and uranyl complexes crystallize with an "extra" molecule of this ligand.

The solution chemistry of the thorium–8-hydroxy-5-quinolinesulfonic acid system has been studied by pH titration at various metal:ligand ratios (441). With a 1:4 ratio the usual stepwise addition of four ligand molecules was observed; the precipitate which formed in some pH regions was presumed to be the 1:2 complex. 8-Hydroxy-7-iodo-5-quinolinesulfonic acid (ferron) has been suggested for the analytical precipitation of thorium (454), and the precipitate appears to be the 1:2 complex (128).

Thorin, o-(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid (II), also known as thoron, thoronol,
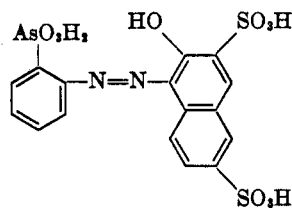
II
Thorin

naphtharson, and APANS, has been used extensively as a reagent for the colorimetric determination of thorium (521) since its introduction by Kuznetsov (300). It combines the benzenearsonic acid group, which will precipitate the Group IVB metals (553), with a typical mordant azo-dye structure. The thorium–thorin complex can be precipitated from acid solutions of 10^{-2} N; it contains one molecule of thorin to each atom of thorium, and about two molecules of water (70). Spectrophotometric studies in solution have shown the complex to contain two molecules of thorin to each atom of thorium (93, 402). Several formulations of the complexes are possible, but it is probable that the thorium atoms are directly bound to one or two oxygen

atoms of the arsonic acid groups and they may also be coördinated with the azo nitrogen atoms.

Some related complexes which have been suggested for the colorimetric determination of thorium and whose stoichiometries have been established are those with 4,5-dihydroxy-3-(p-sulfophenylazo)-2,7-naphthalenedisulfonic acid (SPADNS) (15), 4,5-dihydroxy-3,6-bis(4-sulfo-1-naphthylazo)-2,7-naphthalenedisulfonic acid (di-SNADNS) (114), and 1-nitroso-2-naphthol-3,6-disulfonic acid (nitroso R salt) (429).

Lambert and Grother (302) prepared complexes of thorium with a number of complex organic dyes containing nitrogen. The stoichiometries of five of these solid complexes were established, and it was found that the number of thorium atoms reacting with each dye molecule was equal to the number of sulfonic acid groups on that molecule. The complexes are evidently basic, and it is not possible on this evidence alone to decide whether other groups in the dye molecules chelate with the thorium atoms.

Cupferron (ammonium N-nitroso-N-phenylhydroxylamine) is an inferior precipitating agent for thorium (524), and the precipitate has not been characterized. Dyrssen and Dahlberg (134) have studied the extraction of thorium from dilute aqueous solutions into chloroform and 4-methyl-2-pentanone solutions of cupferron and have thus measured the stability constant of the neutral 1:4 complex (130). Elving and Olsen (141) have compared phenyl-, α-naphthyl-, and p-xenyl-N-nitrosohydroxylamines as analytical reagents for thorium.

N-Phenylbenzohydroxamic acid, $C_6H_5NOHCOC_6H_5$, which is structurally related to cupferron, has been used in chloroform solution for the solvent extraction of thorium and uranium(VI) (132). The thorium complexes formed by 1-nitroso-2-naphthol and 2-nitroso-1-naphthol in solution have very similar stability constants (135).

EDTA (ethylenedinitrilotetraacetic acid) forms with thorium a sparingly soluble crystalline hydrate, $Th(C_{10}H_{12}N_2O_8).2H_2O$ (54). The stability constant of this complex in aqueous solution is very high (10^{23}) (484), and for this reason the complex has found wide application in the volumetric determination of thorium (16, 483). The stoichiometries of the thorium complexes of EDTA and other aminopolycarboxylic acids in solution have been studied. With EDTA, both 1:1 and 1:2 complexes are formed (452, 543). For nitrilotriacetic acid and hexahydro-2,4,6-trioxo-5-pyrimidinyliminodiacetic acid (uramyldiacetic acid) the thorium complexes were shown to be anionic, and this was confirmed by the isolation of the respective ammonium salts:

$(NH_4)_2[Th(C_6H_7NO_6)_2].4H_2O$ and $(NH_4)_2[Th(C_6H_7N_3O_7)_2].4H_2O$
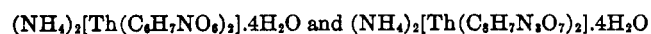
Thorium salts are hydrolyzed readily in aqueous solution, and this is true also of the complexes with EDTA

and related ligands. With EDTA in solutions of pH
<5.5 the ligand is probably sexidentate and, assuming
the thorium atom to have a coördination number of
eight, the remaining two coördination positions are
occupied by water molecules. At higher pH values
hydrogen ions are removed from the water molecules
and hydroxo complexes result. Martell and his cowork-
ers (38, 103) and Cabell (71) have studied the hydrolysis
of this and related complexes by potentiometric titra-
tion and have calculated stability constants for various
monomeric and polymeric hydrolysis products.

The complex of thorium with DTPA, (carboxy-
methylimino)bis(ethylenenitrilo)tetraacetic acid, whose
stability constant exceeds 10^{27}, is the most stable thor-
ium complex known; the ligand here is probably octo-
dentate (38).

In table 5 are listed both addition compounds of
thorium salts with nitrogen donors, and thorium com-
plexes with acidic nitrogen donors.

IV. PROTACTINIUM COMPLEXES

The meagre information available on the organic
coördination compounds of protactinium is derived en-
tirely from work on solvent extraction, and, with the
exception of the work of Bouissières and Vernois, re-
lates to the quinquevalent state. In no case has the
extracting species been definitely established. Katz and
Seaborg (274) have discussed all the relevant work up
to 1957.

Protactinium halides are extracted by ethers and
related solvents, probably as complex halide anions (78).

The extraction of protactinium from aqueous nitric
acid by tributyl phosphate is comparable with that of
thorium (210); neutral but hydrolyzed species are
thought to be involved.

Dialkylphosphoric and monoalkylphosphoric acids
are better extractants than trialkylphosphates for pro-
tactinium. Some quantitative work has been done on
the dependence of the extraction upon the alkylphos-
phoric acid concentration and the pH, but the results
are not concordant (210, 354, 493).

Bouissières and Vernois (40) found that protactin-
ium(IV) was not extracted from hydrochloric acid
solution by 4-methyl-2-pentanone nor by tributyl phos-
phate, but that it was extracted better than protactin-
ium(V) by benzene solutions of HTTA. It may be as-
sumed that protactinium(IV) is extracted as Pa(TTA)₄,
similarly to the β-diketone complexes of other quadri-
valent metals, but the formation of Pa(TTA)₅ would be
most unlikely; some partially hydrolyzed species is
probably involved, and this would explain the dimin-
ished extraction of protactinium(V) by these solutions.

Protactinium forms colored complexes with poly-
phenols and the spectra of some of these in solution
have been examined by Casey and Maddock (77).

TABLE 6

Uranium(IV) complexes with β-dicarbonyl compounds

a. With β-diketones, RCOCH₂COR'		References
R	R'	
Methyl	Methyl	(3, 27, 188, 482)
Ethyl	Methyl	(188, 482)
Ethyl	Ethyl	(188, 482)
n-Propyl	Methyl	(188)
n-Propyl	n-Propyl	(188)
Isopropyl	Methyl	(188, 482)
n-Butyl	Methyl	(188)
tert-Butyl	Methyl	(188, 482)
n-Pentyl	Methyl	(188)
n-Hexyl	Methyl	(188)
Ethoxymethyl	Methyl	(188)
Phenyl	Methyl	(3, 164, 188, 465, 482)
Phenyl	Phenyl	(3, 164, 192, 465)
Fluoromethyl	Methyl	(212)
Trifluoromethyl	Methyl	(188, 212, 478, 482)
Trifluoromethyl	Ethyl	(188)
Trifluoromethyl	n-Propyl	(188)
Trifluoromethyl	Isopropyl	(188)
Trifluoromethyl	n-Butyl	(188)
Trifluoromethyl	Isobutyl	(188)
Trifluoromethyl	tert-Butyl	(188, 478, 482)
Trifluoromethyl	n-Pentyl	(188)
Trifluoromethyl	Phenyl	(188)
Trifluoromethyl	Trifluoromethyl	(188, 212)
2-Furyl	Methyl	(188, 481, 482)
2-Furyl	Phenyl	(465)
3-Pyridyl	Phenyl	(465)
3-Methyl-5-isoxazolyl	Phenyl	(465)
b. With keto esters and keto aldehydes		
Ethyl acetoacetate		(264)
Methyl trifluoroacetylacetate		(188)
Ethyl trifluoroacetylacetate		(188, 264, 480, 482)
n-Butyl trifluoroacetylacetate		(188)
3-Ketobutanal		(482)
3-Keto-3-phenylpropanal		(482, 479)

V. URANIUM COMPLEXES

A. URANIUM(IV) COMPLEXES

1. Complexes with β-dicarbonyl compounds

The β-diketone complexes of uranium(IV) generally
resemble their thorium analogs, but in addition they
have the green color and paramagnetism typical of
uranium(IV) compounds and they are easily oxidized
in air.

Uranium(IV) acetylacetonate was first prepared by
Biltz and Clinch in 1904 (27). There were no subsequent
reports on any uranium(IV) diketone complexes until
the wartime work on volatile uranium compounds was
published, which included details of the preparation,
melting points, and volatilities of many of these com-
plexes. They are listed in table 6.

The acetylacetonate is isomorphous with the α-modi-
fication of the thorium complex (194, 195), and the
dibenzoylmethane complex is isomorphous with those
of cerium(IV) and thorium (542, 564). There are no
references to addition compounds of uranium(IV) acet-
ylacetonate with bases.

The magnetic susceptibility of uranium(IV) acetyl-acetonate has been measured over a wide range of temperature by Hutchison and Elliott (240). The results obeyed the Weiss–Curie law[2]

$$\chi = \frac{C}{T + \Delta}$$

above 195°K., and the magnetic moment of the uranium(IV) ion, after correction for the diamagnetism of the uranium(IV) and acetylacetonate ions, was calculated as $\mu = 3.21$ Bohr magnetons. Sacconi (465) measured the magnetic susceptibilities of some uranium(IV) complexes including that of benzoylacetone (1-phenyl-1,3-butanedione); as the measurements were made at only one temperature the Weiss constant, Δ, in the Weiss–Curie equation could not be obtained, and values for the magnetic moment of the uranium(IV) ion were calculated assuming the validity of the simple Curie law:

$$\chi = \frac{C}{T}$$

The magnetic moments, corrected for the diamagnetism of the complexing ions but not for the diamagnetism of the uranium(IV) ion, fell between $\mu = 2.7$ and $\mu = 2.8$. The apparent disagreement between these values and the value of $\mu = 3.21$ obtained by Hutchison and Elliott for the acetylacetonate is due to the absence of the Weiss constant from Sacconi's calculation. The experimental values for the magnetic susceptibilities are in good agreement; thus Sacconi obtained $\chi_m = 3275 \times 10^{-6}$ for the benzoylacetonate at 22.1°C., and Hutchison and Elliott obtained $\chi_m = 3264 \times 10^{-6}$ for the acetylacetonate at 20.7°C. The results of these magnetic measurements have been used for two different purposes: for establishing whether the ground state of the uranium(IV) ion contains $6d$ or $5f$ electrons, and for deducing the nature of the bonds present in the complexes. Owing to the large values of the Weiss constant for these substances and the uncertainty as to its interpretation, it is doubtful whether valid conclusions can be drawn on either of these questions. All that is known with certainty is that two unpaired electrons are present in the complexes as well as in the uranium(IV) ion.

The infrared spectrum of uranium(IV) acetylacetonate was recorded by Morgan (372), and Haszeldine and his coworkers (212) studied the ultraviolet absorption spectra of some fluorinated acetylacetone complexes. Rydberg (459, 462) has used the partition method to measure the stability constants for the species UA^{3+}, UA_2^{2+}, UA_3^{+}, and UA_4 which are present in aqueous solutions, and Betts and Leigh (24) have used this method to show that the species which ex-

---

[2] χ, magnetic susceptibility per gram; χ_m, magnetic susceptibility per mole; C, Curie constant; Δ, Weiss constant; T, degrees absolute.

tracts into benzene solutions of HTTA is the neutral 1:4 complex.

2. Complexes with other oxygen donors

Because uranium tetrachloride is one of the few inorganic salts both soluble in a wide variety of solvents and having well-defined absorption bands in the visible region, it was the subject of much early work in connection with theories of solvation (261, 262, 352). Spectra in a number of oxygen-containing organic solvents were recorded, and wide variations with solvent were found. These were recognized as being due to specific solvation effects, but no quantitative or structural significance could be given to the phenomena.

The recent application of ligand-field theory to the spectrum of the uranium(IV) ion (271) has now, in principle, made possible an interpretation of these spectra. Trzebiatowska and her colleagues (528) have reëxamined the spectrum of uranium tetrachloride in methanol and have also examined the spectra in tributyl phosphate and triisoamyl phosphate. In methanol the spectrum was generally similar to that in water, with small shifts in the maxima and splittings attributed to ligand-field effects. In tributyl phosphate the spectral changes were more pronounced; application of Job's method at several wavelengths showed that a 1:1 complex was formed with tributyl phosphate in methanol solution. Iwase and Isono (252a) have shown that in the solvent extraction of uranium tetrachloride by tributyl phosphate the extracted species is $UCl_4.3TBP$.

Zangen (578) has studied the extraction of uranium-(IV) by solutions of bis(2-butyloctyl)pyrophosphoric acid in kerosene; to explain the results three extracting species had to be postulated, viz:

$$U(R_2P_2O_7)_2; \; U(R_2P_2O_7)(H_2PO_4)_2; \; \text{and} \; U_2(R_2P_2O_7)(H_2PO_4)_6$$
$$R = C_{12}H_{25}.$$
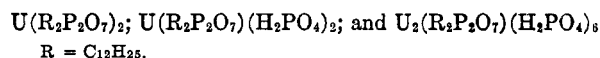
There is spectroscopic evidence for the formation of 1:1 complexes between uranium(IV) and glucose and methyl glucoside in aqueous solution (218).

Some miscellaneous uranium(IV) complexes with oxygen donors which have been isolated are listed in table 7.

3. Complexes with nitrogen donors

Miscellaneous compounds in this category which have been isolated are listed in table 8. Thermodynamic data are available for the compounds in this table prepared by Kalnins and Gibson, and infrared spectra for those prepared by Barr and Horton. Pyridine and quinoline yield addition compounds of the type formulated in the table and also the double salts (313)

$$[(C_5H_5N)^+]_2(UCl_6)^{2-} \text{ and } [(C_9H_8N)^+]_2(UCl_6)^{2-}$$
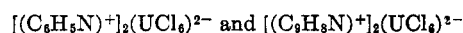
Uranium(IV) cupferrate, $U(C_6H_5N_2O_2)_4$, first prepared by Auger (11), has been used in analysis as a pre-

TABLE 7

Uranium(IV) complexes with oxygen donors

Ligand	Formula of Complex	References
Tartaric acid	$U(C_4H_4O_6)_2.2H_2O$	(312)
Pyrocatechol	$(NH_4)_4H_2[U_2(C_6H_4O_2)_7].6H_2O$	(444, 446)
	$K_4H_2[U_2(C_6H_4O_2)_7].3H_2O$	(444)
	$(CN_3H_6)_6[U_2(C_6H_4O_2)_7].14H_2O$	(444)
	$(NH_4)_2H_2[U(C_6H_4O_2)_4].16H_2O$	(350)
	$K_4[U(C_6H_4O_2)_4].12H_2O$	(350)
	$Na_4[U(C_6H_4O_2)_4].21H_2O$	(350)
	$(C_5H_5N)_2H_2[U(C_6H_4O_2)_4].6H_2O$	(350)
Citric acid	$U_3(C_6H_5O_7)_4.xH_2O$	(312)
Salicylic acid	$U(C_7H_4O_3)_2.4H_2O$	(550)
	$UCl_2(C_7H_5O_3)_2.2C_5H_5N$	(17)
Sulfosalicylic acid	$U(C_7H_4O_6S)_2$	(550)
1,5-Bis(p-methoxyphenyl)-3-pentadienone	$UCl_4(C_19H_{18}O_3)_2$	(424)
	$UCl_4(C_19H_{18}O_3)_2.2HCl$	(424)

cipitating agent (230) and for solvent extractions (171); a microphotograph of the crystals has been published (79).

Uranium(IV) resembles thorium in forming with EDTA a crystalline dihydrate, $U(C_{10}H_{12}N_2O_8).2H_2O$ (54).

Thorin (II; see page 120) has been used for the colorimetric determination of uranium(IV); the complex formed in solution has 1:2 stoichiometry, as has the thorium complex (162).

4. Complexes with phosphorus donors

Allison and Mann (7) prepared the following crystalline compounds from trialkylphosphines:

$UCl_4.2(C_2H_5)_3P$ $UBr_4.2(C_2H_5)_3P$

$UCl_4.2(C_3H_7)_3P$ $UBr_4.2(C_3H_7)_3P$

Attempts to prepare derivatives of uranium tetrachloride and tetrabromide with several trialkylarsines and chelating diarsines were unsuccessful.
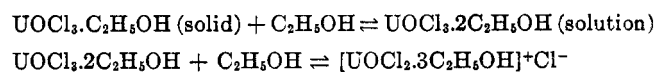
5. Complexes with sulfur donors

The solubility of uranium tetrachloride in dimethyl sulfide (108) indicates sulfur coördination to uranium(IV), but the system has not been studied in detail. Albers and Lange (4) suggested that dialkyldithiocarbamates of uranium(IV) were intermediates in their syntheses of the uranyl complexes.

#### B. URANIUM(III) AND URANIUM(V) COMPLEXES

Rulfs and Elving (451), in a study of the polarographic reduction of uranyl cupferrate, obtained evidence for the formation of a stable uranium(III) cupferrate in solution; and Grimaldi (197) has stated that uranium(III) is quantitatively precipitated by an ice-cold solution of cupferron. No other work has been published on organic coördination compounds of uranium(III).

Coördination compounds of uranium(V) have likewise been little explored. The peculiar compounds

$(C_5H_5NH)UOCl_5$ and $UOCl_3.C_2H_5OH$ possibly contain uranium(V) (46). The latter has an apparent molecular complexity in ethanol of 0.84, which suggests partial ionization; assuming the uranium atoms to be six-coördinate, the following equilibria have been postulated:

$$UOCl_3.C_2H_5OH \text{ (solid)} + C_2H_5OH \rightleftharpoons UOCl_3.2C_2H_5OH \text{ (solution)}$$

$$UOCl_3.2C_2H_5OH + C_2H_5OH \rightleftharpoons [UOCl_2.3C_2H_5OH]^+Cl^-$$

The pyridinium compound reacts with alcoholic ammonia to give uranium pentaethoxide, $U(OC_2H_5)_5$, and other pentaalkoxides may be obtained from this by alcohol interchange (42, 46). Other methods of preparation of the pentaalkoxides have been described (187, 267, 268, 520). The pentaethoxide, penta-1-propoxide, penta-1-butoxide, and penta-1-pentoxide are volatile liquids, dimeric in benzene solution; the pentamethoxide is a crystalline solid, trimeric in benzene solution (42). As with the thorium alkoxides, this polymerization is doubtless due to coördination between the metal and oxygen atoms of adjacent molecules. The dimeric pentaalkoxides may be formulated as in III:

III
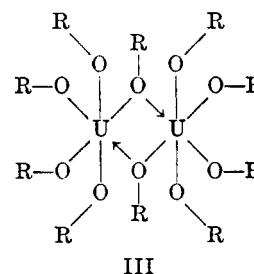
The trimeric pentamethoxide molecules may consist of cyclic trimers involving sixfold coördination, or it may be that a mixture of dimers and tetramers is present

TABLE 8

Uranium(IV) complexes with nitrogen donors

Ligand	Formula of Complex	References
Methylamine	$UCl_4.2CH_5N$	(272)
Ethylamine	$UCl_4.C_2H_7N$	(272)
	$UCl_4.2C_2H_7N$	(272)
n-Propylamine	$UCl_4.C_3H_9N$	(272)
	$UCl_4.4C_3H_9N$	(272)
Trimethylamine	$UCl_4.2C_3H_9N$	(477)
Pyridine	$UCl_4.2C_5H_5N$	(477)
	$2UCl_4.3C_5H_5N$	(17)
N-Nitroso-N-phenylhydroxyl-amine (cupferron)	$U(C_6H_5N_2O_2)_4$	(465)
Aniline	$UCl_4.2C_6H_7N$	(17)
Phenylglycine	$UCl_2(C_8H_8NO_2)_2.4H_2O$	(17)
Quinoline	$UCl_4.C_9H_7N$	(439)
N-Carboxymethylanthranilic acid	$U(C_9H_8NO_4)_4$	(116)
Quinaldic acid	$UCl_2(C_{10}H_6NO_2)_2.C_{10}H_7NO_2$	(17)
N-Nitroso-N-(1-naphthyl)-hydroxylamine (Neocupferron)	$U(C_{10}H_7N_2O_2)_4$	(465)
N,N'-Disalicylideneëthylene-diamine	$U(C_{16}H_{14}N_2O_2)_2$	(57, 123)

in solution, with coördination numbers for the uranium atoms of six and eight, respectively (42).

Some volatile uranium(V) compounds containing both alkoxy groups and β-keto ester groups have been prepared (264), $U(OR)_3(R'COCHCOOR'')_2$. The molecular weights of these compounds are not known but would make an interesting study, since if monomeric the compounds would contain seven-coördinate uranium. The volatile complexes formed by the fluorinated pentaalkoxide $U(OCH_2CF_3)_5$ with amines (264) pose a similar problem.

Other uranium alkoxides are conveniently mentioned here. Uranium tetraalkoxides, $U(OR)_4$ (3, 270), and some related compounds containing aluminum (3) have been prepared, but their complexities are not known. Uranium hexaethoxide is only slightly associated (266), but the hexamethoxide is predominantly dimeric (41). Uranyl alkoxides, $UO_2(OR)_2$, retain several molecules of their parent alcohols (43, 269).

C. URANYL COMPLEXES

1. Complexes with β-dicarbonyl compounds

Numerous uranyl complexes with β-diketones and related dicarbonyl compounds have been prepared; they are listed in table 9. Although they can be obtained with the stoichiometric composition

$$UO_2(RCOCH{=}COR')_2$$

they are more usually obtained either as hydrates or as organic solvates.

The acetylacetonate has been studied in most detail. As a monohydrate it was first prepared by Biltz and Clinch in 1904 (27), and subsequent workers prepared the anhydrous compound (1, 79a, 298, 482). The monohydrate has recently been prepared in three different crystallographic modifications (99), all of which yield the same anhydrous form on heating in vacuo. Two of these modifications have the yellow color typical of uranyl complexes with aliphatic ligands, but the other is red. The infrared and visible spectra of the crystals were studied, but no explanation for the difference in color could be found. Presumably the environment of the uranyl ions in the red form is unusual; the structures of the uranyl ions in the red and yellow forms cannot be very different, since the unsymmetrical stretching frequency of this ion in the red form (905 cm.$^{-1}$) is only a little different from that in the yellow forms (917, 925 cm.$^{-1}$). The anhydrous complex in benzene solution at 80°C. is dimeric, and it has been proposed that the dimers are held together by coördination of the diketone oxygen atoms to adjacent uranyl ions, as in formula IV. A similar process has been postulated to explain the polymerization of the uranium(V) and thorium alkoxides (q.v.). The nonvolatility of the complex (188, 482) is an indication that there are strong intermolecular forces in the crystal as well as in solution.

TABLE 9
Uranyl complexes with β-dicarbonyl compounds

a. With β-diketones, $RCOCH_2COR'$		Additional Molecules of Crystallization*	References
R	R'		
Ethyl	Methyl	—	(188, 482)
Ethyl	Ethyl	C_2H_5OH	(188)
n-Propyl	Methyl	—	(188)
n-Propyl	n-Propyl	—	(188)
Isopropyl	Methyl	—	(482)
tert-Butyl	Methyl	—	(482)
n-Pentyl	Methyl	—	(188)
n-Hexyl	Methyl	—	(188)
Trifluoromethyl	Methyl	C_2H_5OH,—	(188, 212, 478, 482)
Trifluoromethyl	tert-Butyl	—	(478, 482)
Phenyl	Methyl	$2.5H_2O$, C_2H_5OH, NH_3, C_5H_5N,—	(188, 198, 204, 251, 386, 466, 468, 482)
o-Methoxyphenyl	Methyl	C_2H_5OH,—	(188)
o-Methoxyphenyl	Phenyl	—	(251)
m-Methoxyphenyl	Phenyl	—	(251)
p-Methoxyphenyl	Phenyl	—	(251)
o-Nitrophenyl	Phenyl	—	(251)
m-Nitrophenyl	Phenyl	$1.5H_2O$	(251)
p-Nitrophenyl	Phenyl	$1.5H_2O$	(251)
m-Aminophenyl	Phenyl	—	(251)
p-Aminophenyl	Phenyl	—	(251)
2-Furyl	Methyl	C_2H_5OH,—	(188, 481, 482)
2-Furyl	Phenyl	$1.5H_2O$	(251, 468)
2-Pyridyl	Methyl	H_2O	(468)
2-Pyridyl	Phenyl	H_2O	(468)
3-Pyridyl	Methyl	H_2O	(468)
3-Pyridyl	Phenyl	—	(468)
4-Pyridyl	Phenyl	—	(251)
3-Methyl-5-isoxazolyl	Methyl	—	(468)
3-Methyl-5-isoxazolyl	Phenyl	—	(468)
b. With keto acids, keto esters, and keto aldehydes			
Ethyl trifluoroacetoacetate		H_2O	(188)
3-Ketobutanal		—	(482)
3-Ketohexanal		—	(188)
3-Keto-4,4'-dimethylpentanal		—	(482)
3-Keto-3-phenylpropanal (benzoylacet- aldehyde)		—	(479, 482)
Benzoylpyruvic acid		—	(306)
Methyl benzoylpyruvate		H_2O, CH_3OH	(306)
Ethyl benzoylpyruvate		H_2O	(306)

* A dash indicates that the complex analyzed was not solvated.

The dipole moment of uranyl acetylacetonate has been measured by Grinberg and Troitskaya (198), who obtained a value of 5.12 Debyes in benzene solution.

IV³
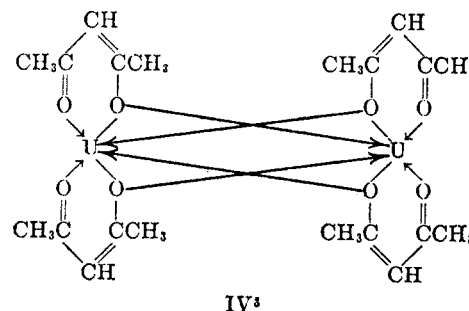
³ Uranyl oxygen atoms are not shown; they are out of the plane of the paper, above and below the uranium atoms.

This would suggest that the dimers are not held together as in IV but in some more unsymmetrical way; the result could also be explained by the presence of a trace of water or other coördinating solvent which might disrupt the dimers and give unsymmetrical solvates.

Uranyl acetylacetonate can be crystallized with ethyl alcohol, p-dioxane, acetophenone (99), acetylacetone (99, 458), ammonia (466), pyridine, and quinoline (204, 205, 466). Double salts of the type $R^+[UO_2(C_5H_7O_2)_3]^-$ have been prepared, with $R = NH_4$, CH_3NH_3, and $C_6H_5NH_3$ (204). This, together with the polymeric nature of the anhydrous complex, is a clear indication that the complex is coördinatively unsaturated, and therefore that the coördination number of the uranyl ion, at least in complexes of this type, exceeds four.

Sacconi and Giannoni (468b) have recorded and discussed the visible and ultraviolet absorption spectra of solutions of a number of uranyl complexes with aromatic β-diketones. The infrared spectra of several uranyl–diketone complexes, their hydrates, and their addition compounds with bases have also been studied (466), but the complexities of these spectra make it difficult to draw any definite conclusions from them.

The stability constants for the uranyl–acetylacetone complexes in aqueous solution have been measured by the pH titration (62, 253) and extraction (458) methods. The latter gave evidence for the formation of $UO_2(C_5H_7O_2)_2.C_5H_8O_2$ in the organic phase. Spectrophotometric and conductimetric studies in ethanol (528) showed the presence of a 1:1 complex, and its stability constant was measured.

Solvent extraction by organic solutions of HTTA is widely used for laboratory-scale separations of the actinides (373). The uranyl–HTTA system broadly resembles the uranyl–acetylacetone system. Benzene solutions containing an excess of HTTA extract the uranyl ion in the form of $UO_2(TTA)_2.HTTA$ (288, 397, 546), although the only crystalline complex which can be obtained is apparently $UO_2(TTA)_2.2H_2O$. This system has also been used for measuring the stability constants of various uranyl complexes with inorganic ligands (117). Extraction of uranyl nitrate by solutions of HTTA in organic solvents containing oxygen gives uranyl–TTA complexes and also complexes of uranyl nitrate with the solvent (219).

The uranyl complex of 6-isopropyltropolone likewise is extracted into chloroform with an additional molecule of the ligand (133).

The uranyl–dibenzoylmethane complex crystallizes with water (251, 466, 468), ethyl alcohol (188), ammonia, and pyridine (466, 468), and it has also been obtained with no additional ligands (468). The formation of this complex in dilute solution forms the basis of a sensitive colorimetric method for the determination of uranium (570).

2. Addition compounds of uranyl salts with oxygen donors

Bucholz (65), in 1805, dissolved uranyl nitrate in ethyl alcohol and obtained crystals by cooling the solution. Innumerable experiments of this type have been made since that date. The uranyl salts of inorganic acids are soluble in most organic solvents containing oxygen or nitrogen, and crystalline solvates have been isolated from many of the solutions. These solvates often contain water in addition to the organic solvent. Also, crystalline complexes of uranyl salts with other oxygen- or nitrogen-containing organic molecules may often be obtained by crystallizing the uranyl salts and organic components from a common solvent. Those addition compounds of uranyl salts with oxygen donors which have been isolated and characterized are listed in table 10.

TABLE 10
Complexes of uranyl salts with oxygen donors

Ligand	Formula of Complex	References
Ethers:		
Ethyl ether.......	$UO_2(NO_3)_2.2C_4H_{10}O$	(293, 424, 533, 540)
	$UO_2Cl_2.2C_4H_{10}O$	(424)
	$UO_2Br_2.2C_4H_{10}O$	(540)
	$UO_2(NO_3)_2.2C_4H_{10}O.2H_2O$	(2, 239, 282, 293, 533)
	$UO_2(NO_3)_2.4C_4H_{10}O.2H_2O$	(12, 533)
	$UO_2(NO_3)_2.C_4H_{10}O.3H_2O$	(239, 282, 338, 533, 540)
	$UO_2Cl_2.0.5C_4H_{10}O.H_2O$	(472)
	$UO_2(NO_3)_2.C_4H_{10}O.3NH_3$	(472)
	$UO_2(NO_3)_2.C_4H_{10}O.2NH_3$	(472)
	$UO_2Cl_2.C_4H_{10}O.3NH_3$	(437, 438)
	$UO_2Cl_2.C_4H_{10}O.2NH_3$	(437, 438)
	$UO_2Br_2.C_4H_{10}O.2NH_3$	(540)
	$UO_2I_2.C_4H_{10}O.2NH_3$	(540)
Bis(chloroethyl) ether..........	$UO_2(NO_3)_2.2C_4H_8Cl_2O$	(293)
Isopropyl ether....	$UO_2(NO_3)_2.2.5C_6H_{14}O.0.5H_2O$	(190)
n-Butyl ether......	$UO_2(NO_3)_2.2C_8H_{18}O$	(239, 293)
	$UO_2(NO_3)_2.2C_8H_{18}O.2H_2O$	(239)
1,2-Diethoxy-ethane (diethyl cellosolve).......	$UO_2(NO_3)_2.C_6H_{14}O_2.3H_2O$	(282)
	$UO_2(NO_3)_2.2C_6H_{14}O_2.2H_2O$	(282)
p-Dioxane........	$UO_2(NO_3)_2.2C_4H_8O_2$	(293)
Bis(2-butoxyethyl) ether (dibutyl carbitol, Butex)..	$UO_2(NO_3)_2.2C_{12}H_{26}O_3.2H_2O$	(239, 276)
	$UO_2(NO_3)_2.C_{12}H_{26}O_3.3H_2O$	(239)
9-Chloroxanthene..	$UO_2Cl_2.2C_{13}H_9OCl$	(165)
9-Bromoxanthene..	$UO_2Br_2.2C_{13}H_9OBr$	(165)
Alcohols:		
Ethyl alcohol......	$UO_2(NO_3)_2.2C_2H_5OH$	(424)
Isobutyl alcohol...	$UO_2(NO_3)_2.C_4H_9OH.2H_2O$	(282)
	$UO_2(NO_3)_2.3C_4H_9OH$	(282)
tert-Butyl alcohol..	$UO_2(NO_3)_2.3C_4H_9OH.3H_2O$	(282)
	$UO_2(NO_3)_2.4C_4H_9OH.2H_2O$	(282)
	$UO_2(NO_3)_2.3C_4H_9OH$	(282)
Ketones:		
Acetone..........	$UO_2(NO_3)_2.C_3H_6O.2H_2O$	(282)
	$UO_2(NO_3)_2.C_3H_6O.3H_2O$	(338)
	$UO_2SO_4.C_3H_6O.2H_2O$	(316)
2-Butanone.......	$UO_2(NO_3)_2.C_4H_8O.3H_2O$	(338)
4-Methyl-2-pentanone......	$UO_2(NO_3)_2.C_6H_{12}O.2H_2O$	(282)
	$UO_2(NO_3)_2.C_6H_{12}O$	(548)

TABLE 10—*Concluded*

Ligand	Formula of Complex	References
2,6-Dimethyl-pyran-4-one.....	$UO_2(NO_3)_2.2C_7H_8O_2$	(424)
	$UO_2SO_4.C_7H_8O_2$	(424)
	$UO_2Cl_2.2C_7H_8O_2$	(424)
	$UO_2Cl_2.2C_7H_8O_2.2HCl$	(424)
Acetophenone.....	$UO_2(NO_3)_2.2C_8H_8O$	(424)
	$UO_2Cl_2.2C_8H_8O$	(424)
2,3-Dimethyl-chromone.......	$UO_2Cl_2.2C_{11}H_{10}O_2$	(502)
Benzophenone.....	$UO_2(NO_3)_2.2C_{13}H_{10}O$	(424)
	$UO_2Cl_2.C_{13}H_{10}O$	(424)
Chalkone.........	$UO_2(NO_3)_2.2C_{15}H_{12}O$	(424)
	$UO_2(NO_3)_2.2C_{15}H_{12}O.CH_3COOH$	(424)
	$UO_2Cl_2.2C_{15}H_{12}O$	(424)
3,4-Methylene-dioxychalkone....	$UO_2Cl_2.C_{16}H_{12}O_3$	(424)
4-Methoxy-chalkone........	$UO_2(NO_3)_2.C_{16}H_{14}O_2$	(424)
	$UO_2Cl_2.C_{16}H_{14}O_2$	(424)
	$UO_2Cl_2.2C_{16}H_{14}O_2.2HCl$	(424)
	$UO_2Cl_2.2C_{16}H_{14}O_2.2CH_3COOH$	(424)
1,5-Diphenyl-3-pentadienone....	$UO_2Cl_2.C_{17}H_{14}O$	(424)
	$UO_2Cl_2.2C_{17}H_{14}O$	(119)
	$UO_2Cl_2.2C_{17}H_{14}O.2HCl$	(424)
	$UO_2Cl_2.2C_{17}H_{14}O.2CH_3COOH$	(424)
	$UO_2Br_2.2C_{17}H_{14}O.2CH_3COOH$	(424)
	$UO_2(NO_3)_2.2C_{17}H_{14}O.2CH_3COOH$	(424)
1-Phenyl-5-p-methoxyphenyl-3-pentadienone ...	$UO_2Cl_2.2C_{18}H_{16}O_2.2CH_3COOH$	(424)
2,5-Dibenzylidene-cyclopentanone..	$UO_2Cl_2.2C_{19}H_{16}O$	(424)
1,5-Bis(p-methoxyphenyl)-3-pentadienone....	$UO_2(NO_3)_2.2C_{19}H_{18}O_3$	(424)
	$UO_2Cl_2.C_{19}H_{18}O_3$	(424)
	$UO_2Cl_2.2C_{19}H_{18}O_3$	(119, 424)
	$UO_2Cl_2.2C_{19}H_{18}O_3.2HCl$	(424)
	$UO_2Br_2.2C_{19}H_{18}O_3$	(424)
	$UO_2(ClO_4)_2.C_{19}H_{18}O_3$	(424)
	$UO_2(C_2O_4).C_{19}H_{18}O_3$	(424)
	$UO_2(CH_3COO)_2.C_{19}H_{18}O_3.H_2O$	(424)
1,9-Diphenyl-1,3,6,8-nona-tetraen-5-one....	$UO_2Cl_2.2C_{21}H_{18}O$	(424)
2,5-Bis(p-methoxybenzylidene)-cyclopentanone..	$UO_2Cl_2.2C_{21}H_{20}O_3$	(424)
Acid chloride: Acetyl chloride....	$UO_2Cl_2.(CH_3CO)_2O$	(89)

There has been no structural work on any of these complexes; presumably they are of the same nature as the complexes present in the organic solutions discussed in Section V,C,4,(a).

3. Complexes with acidic oxygen donors

Uranyl tartrate has been known from the earliest days of uranium chemistry (442). Péligot (406, 407) gave details for the preparation of the mono- and tetra-hydrates, $UO_2(C_4H_4O_6).H_2O$ and $UO_2(C_4H_4O_6).4H_2O$; this work was repeated by Courtois (105), but Itzig (252) described the formation of a trihydrate. A considerable amount of work has been done on the optical properties of the uranyl salts of tartaric and other aliphatic hydroxy acids. Walden (544) found that the addition of potassium hydroxide and uranyl nitrate to solutions of tartaric acid, monomethyl tartrate, and malic, mandelic, and quinic acids caused a large increase in the optical rotatory powers of the solutions, whereas they had no effect on the rotations of chlorosuccinic, bromosuccinic, and 4-methylhexanoic acids. For malic and tartaric acids the rotations reached a maximum when the ratio of molecules of acid to potassium hydroxide to uranyl nitrate was 1:4:1–4. Clearly, both carboxyl and hydroxyl (or amino) groups must be present in the same molecule for the effect to be observed, which suggests a chelate structure for the complexes. Other workers have studied the effect, using a variety of bases and optically active acids (9, 84, 113, 199, 252, 296, 345); they are agreed that the addition of uranyl salts and bases enhances the rotation of the acids, but there is curiously little agreement among them as to the ratios of the three constituents which give the maximum enhancement. Kopatschek (295) found that the addition of sodium carbonate almost completely nullifies the effect; this is probably due to the formation of the very stable tricarbonatouranyl ion.

The Cotton effect, first observed in copper tartrate solutions, is exhibited also by uranyl tartrate solutions (61). This, too, is an indication of complex formation.

More recently, Neuman and his colleagues have used spectrophotometry, polarography, and pH titration to study solutions of the uranyl complexes of the aliphatic hydroxy acids. The visible absorption spectra of solutions of uranyl tartrate and its double salts with sodium and pyridine had previously been recorded (343, 344). For the uranyl–tartrate system in acid solutions, a mixture of complexes having uranyl:tartrate ratios of 1:1, 2:1, and 3:1 is present, the first predominating (145). In alkaline solutions, 1:1 and 3:2 complexes are formed (146). The shapes of the pH titration curves and the spectra suggest that the 1:1 complex in acid solution is dimeric and that both complexes formed in alkaline solution are trimeric (3:3 and 3:2). Feldman, Havill, and Neuman (146) suggest structures for these polymers which involve terdentate chelation, each uranyl ion being attached to two carboxyl groups and one hydroxyl group from the same acid molecule. The suggestion that chelates are formed is in accordance with Walden's results (544), but Dittrich (120), who measured the molecular weight of uranyl tartrate by its depression of the freezing point of water, found no evidence for association.

Courtois (105) described the hexa-, di-, and mono-hydrates of uranyl citrate, $(UO_2)_3(C_6H_5O_7)_2$, and Dittrich (120) had previously measured the electrical conductance of its solutions. Hakomori (206) detected the formation of a 1:1 complex in solutions of uranyl sulfate with sodium citrate, using a simple colorimetric method. Neuman and his colleagues, in studies analogous to those of the uranyl–tartrate system, have shown that in acid solution complexes with uranyl:citrate ratios of

both 1:1 and 2:1 are present, the former predominating and being dimeric (146, 147, 391). Heitner and Bobtelsky (220) have demonstrated the existence of 1:1 and 2:3 complexes in alkaline solution.

Other uranyl salts with hydroxy acids which have been isolated and characterized are the diethyl citrate (287), glycolate (105), lactate (105, 142), malate (9), and quinate (105).

The stoichiometries of the glycolate (2, 309), lactate (145, 146), and malate (145, 146, 206) complexes in solution have also been examined.

Ascorbic acid forms in solution a 1:1 uranyl complex (174, 196) which has been used for the colorimetric determination of uranium (443, 450, 508). The solid uranyl ascorbate complex, $UO_2(C_6H_7O_6)_2$ (386), and a basic ammonium uranyl ascorbate (173) have been isolated.

Uranyl salicylate, $UO_2(HOC_6H_4COO)_2$, has been crystallized in the anhydrous state (104, 106) and also as the nona- (384), penta- (550), tri- (8), and di- (104, 106) hydrates. Crystallographic data are available for the trihydrate (8) and the dihydrate (331). In aqueous solution the formation of a 1:2 uranyl salicylate complex has been demonstrated (129). Uranyl salicylate forms hydrated double salts or addition compounds with metals and organic bases, of four different types, whose stoichiometries (ignoring water of crystallization) may be summarized as follows:

(i) $B_2UO_2(OC_6H_4COO)_2$ (B = NH₄, Na, K) (73).

(ii) $BUO_2(HOC_6H_4COO)_3$ (B = NH₄, K, Ba/2, CH₃NH₃, (C₂H₅)₃NH, C₅H₅NH, o-CH₃C₆H₄NH₃, m-NO₂C₆H₄NH₃, 1,2,4-(CH₃)(NH₂)(NH₃)C₆H₃, CH₅N₃H) (205, 324, 517, 551, 582).

(iii) $BUO_2(HOC_6H_4COO)_2$ (B = C₆H₅NH₂, C₅H₁₁N) (205, 551).

(iv) $BUO_2(HOC_6H_4COO)X$ (B = C₅H₅N, X = NO₃; B = C₅H₅N, X = Cl; B = C₉H₇N, X = NO₃; B = C₄H₉NH₂, X = NO₃) (17, 324).

Complexes of types (i), (iii), and (iv) are red. The molecular weight of the first of the complexes of type (iv) in ethanol was measured by Barr and Horton (17) and found to correspond to half of the formula weight, indicating that two ions were produced. This probably rules out the formulation as a pyridinium salt, $[C_5H_5NH]^+[UO_2(C_7H_4O_3)NO_3.H_2O]^-$, since the nitrate group would probably ionize in ethanol giving a total of three ions, and it suggests that the pyridine and salicylate groups are both coördinated. Complexes of type (ii) are orange, and it is reasonable to assume that the three salicylate groups are equivalent. In compounds of type (iii) the bases may be coördinated to the uranyl ions. The uranyl complex of pyridine and 3-hydroxy-2-naphthoic acid, $(UO_2)_2(HOC_{10}H_6COO)_2(OC_{10}H_6COO).C_5H_5N.4H_2O$ (81), and the uranium(IV) complex of pyridine and salicylic acid included in table

TABLE 11

Uranyl complexes with acidic oxygen donors

Ligand	Formula of Complex	References
3-Oxoglutaric acid........	$UO_2(C_5H_4O_5)$	(386)
Pyrocatechol.............	$C_5H_6N.H[UO_2(C_6H_4O_2)_2]$	(149)
Pyrogallol...............	$C_5H_6N.H[UO_2(C_6H_4O_3)_2]$	(149)
Kojic acid...............	$UO_2(C_6H_5O_4)_2.0.5(?)H_2O$	(63)
Protocatechuic acid.......	$CH_6N_3.H(UO_2(C_7H_3O_4)_2].12H_2O$ (?)	(151)
Gallic acid..............	$K_2(UO_2)_3(C_7H_2O_5)_2$	(148)
	$KUO_2(C_7H_3O_5)$	(148)
	$K_2UO_2(C_7H_4O_5)_2$	(148)
Salicylaldehyde..........	$UO_2(C_7H_5O_2)_2$	(376)
Guaiacol................	$UO_2(C_7H_7O_2)_2$	(550)
2-Hydroxynaphthoquinone.	$UO_2(C_{10}H_6O_3)_2$	(328)
3-Hydroxy-2-methyl-1,4-naphthoquinone (phthiocol).............	$UO_2(C_{11}H_7O_3)_2$	(182)
o-Hydroxynaphthoic acid..	$KH[UO_2(C_{11}H_8O_3)_2]$	(151)
	$NaH[UO_2(C_{11}H_8O_3)_2].4H_2O$	(151)
	$CH_6N_3.H[UO_2(C_{11}H_8O_3)_2]$	(151)
	$BaH_2[UO_2(C_{11}H_8O_3)_2]_2$	(151)
3-Hydroxymethylenecamphor...............	$UO_2(C_{11}H_{15}O_2)_2.2H_2O$	(310)
1,4-Dihydroxyanthraquinone (quinizarin).....	$UO_2(C_{14}H_6O_4)$	(200)
1-Hydroxyanthraquinone ..	$UO_2(C_{14}H_7O_3)_2$	(183)
Myricitrin...............	$UO_2(NO_3)(C_{21}H_{19}O_{12})$	(577)
	$(UO_2)_3(NO_3)_2(C_{21}H_{18}O_{12})$	(577)

7 may be related to these. Methyl salicylate forms the red compound $C_5H_5N.UO_2(OC_6H_4COOCH_3)_2$ (205, 551).

Hök-Bernström (228) has studied the extraction of the uranyl ion by solutions of salicylic acid in 4-methyl-2-pentanone. The complexes $UO_2(HOC_6H_4COO)_2$ and $H[UO_2(HOC_6H_4COO)_3]$, or complexes stoichiometrically equivalent to them, were present in the organic phase, and $[UO_2(HOC_6H_4COO)]^+$ and $UO_2(OC_6H_4COO)$—or $UO_2(HOC_6H_4COO)(OH)$—in the aqueous phase. o-Methoxybenzoic acid behaved similarly, but did not form a 1:3 complex. The extraction of uranium(VI) by salicylic acid in isoamyl alcohol has also been studied as a function of the pH of the aqueous phase (517).

The 1:3 complex with salicylic acid in solution, and the solid complexes of type (ii) above which are formally salts of this, may be structurally analogous to the 1:3 uranyl complexes of acetylacetone, 8-quinolol, and cupferron, having the three salicylate groups symmetrically disposed about the uranyl axis.

Uranium(VI) forms 1:1 complexes in aqueous solution with 5-sulfosalicylic acid (158) and 3-chloromercuri-5-sulfosalicylic acid (507), and the double sodium uranyl sulfosalicylate, $Na_4UO_2(SO_3C_6H_3OCOO)_2.4H_2O$, has been isolated (329, 330). 2,5-Cresotic acid gives the uranyl complex $Na_2UO_2(CH_3C_6H_3OCOO)_2$ (440), analogous to the double salicylates of type (i) above, and 2,3-cresotic acid (525, 526) and 1-hydroxy-2-naphthoic acid (527) have been shown to form 1:1 complexes with the uranyl ion in aqueous solution.

Other uranyl complexes with acidic oxygen donors are listed in table 11. In addition to these, Müller (384) has prepared and analyzed many uranyl salts of substituted carboxylic acids and phenols. In table 12 are

TABLE 12

Uranyl complexes with acidic oxygen donors in solution

Ligand	UO₂: Ligand in Complex	References
3-Alizarinsulfonic acid.........	1:1	(538)
Aurintricarboxylic acid (Aluminon)................	1:1	(381)
Chlorotetracycline............	1:1	(250)
1,2-Dihydroxybenzene-3,5-disulfonic acid (Tiron).......	1:1	(344a, 470)
Dihydroxymaleic acid.........	1:1, 2:1	(225)
4,5-Dihydroxy-2,7-naphthalenedisulfonic acid (chromotropic acid)........	1:1	(258, 380, 470)
Kojic acid...................	1:1, 1:2	(63, 395)
Morellin....................	1:2	(427)
Myricitrin..................	1:1, 2:1, 3:1	(577)
2-Naphthol-3,6-disulfonic acid..	1:1	(431)
1-Nitroso-2-naphthol-3,6-disulfonic acid................	3:2	(431)
Reductone..................	1:1	(226, 227)
Resorcinol..................	1:2	(255)
Salicylaldehyde..............	1:1, 1:2	(34, 36)
Tropolone..................	1:2	(64, 131)

listed those uranyl complexes with acidic oxygen donors whose stoichiometries in solution have been established.

4. Solvent extraction by oxygen donors

The extraction of uranyl nitrate from aqueous solutions into ether, first described by Bucholz (65) but often erroneously (247, 274, 304) attributed to Péligot (405), has been exploited on a large scale for many years in the extraction of uranium from its ores, and more recently for the processing of reactor fuels. Many other solvents have now been developed for these and related purposes, and they are conveniently divided into two classes:

(a) Solvent extraction by ethers and other oxygen-containing organic solvents

Phase-rule diagrams for the three-component systems uranyl nitrate–organic solvent–water have been worked out by Katzin and Sullivan (282) and discussed by Katzin (279). The organic phases containing uranyl nitrate invariably also contain water, and the solid organic solvates of uranyl nitrate frequently do. The relations between the uranyl ions and the nitrate ions, water molecules, and organic solvent molecules will be discussed in turn.

Measurements of electrical conductance and viscosity show that uranyl nitrate solutions in water-saturated ether are substantially unionized (320). Solutions in alcohols and ketones are rather more ionized (528). The molecular weight of uranyl nitrate dihydrate in ether, measured ebullioscopically and extrapolated to infinite dilution, was found (67) to be 425 (the calculated value for $UO_2(NO_3)_2.2H_2O$ is 430), which confirms that the molecule is not ionized. The question as to whether the nitrate ions are covalently bound to the uranyl ions, or are associated with them in ion-pairs, is too subtle to be answered now.

Reports on the system anhydrous uranyl nitrate–ether are conflicting. The anhydrous salt is difficult to prepare and different workers may in fact have used different substances. Marketos (334) reported a violent reaction with ether. Gibson and Katz (185) also observed a violent reaction, but found the solubility to be low in very intensively dried ether (presumably it did not react with this either). Vdovenko, Koval'skaya, and Kovaleva (533) have measured the solubility of the anhydrous material over a range of temperature and have isolated the anhydrous etherate $UO_2(NO_3)_2$. $2C_4H_{10}O$.

In solutions in ethers, uranyl nitrate is normally accompanied by at least two molecules of water, and these form an essential part of the uranyl complex. This was clearly recognized as early as 1911 from thermochemical evidence (304) and has since found confirmation from phase-rule (281, 282), vapor pressure (175), ultraviolet spectroscopic (385), and infrared spectroscopic (464) studies. Ethereal solutions of uranyl nitrate in equilibrium with aqueous phases contain about four moles of water per mole of uranyl nitrate (175). Katzin (279) assumes the formation of a definite tetrahydrate, $[UO_2(NO_3)_2(H_2O)_4]$, but McKay (318) has criticized this physical picture. Solutions in higher ethers contain less water (535).

The organic solvent molecules function as electron donors. In general, the extracting powers of organic solvents for uranyl nitrate increase with increasing basicity and with decreasing steric hindrance near the oxygen atoms (513). Where there are several oxygen atoms in the molecule of the solvent, these act independently (190). The number of molecules of organic solvent which are associated with each uranyl ion in the solid complexes is variable, but frequently the total numbers of water and organic solvent molecules is either four or six (see table 10). In the organic phase this number can be obtained from calculations depending on the extent to which these solutions deviate from Raoult's law, and values between one and three are commonly obtained (317). The number which are attached to uranyl nitrate dihydrate in mixed solutions of 1,2-dichloroethane (assumed inert) and various coördinating solvents is one or two (144). The organic solvent molecules may be directly coördinated to the uranyl ions, or bound by hydrogen bonds to coördinated water molecules (175).

In the presence of nitric acid, and the nitrates of some organic cations, uranyl nitrate is extracted by these solvents in the form of the trinitratouranyl ion: $[UO_2(NO_3)_3]^-$ (273, 534). It is not known whether some water is also an essential part of this complex in organic solvents, but the addition of relatively large amounts of water does diminish the extent of complex formation (534).

Very little work has been done on the solvent extrac-

TABLE 13

Classes of organophosphorus compounds used for solvent extraction

Neutral Reagents	Acidic Reagents
Trialkyl phosphates, (RO)$_3$PO	Dialkylphosphoric acids, (RO)$_2$(OH)PO
Dialkyl alkylphosphonates, (RO)$_2$RPO	Monoalkylphosphoric acids, (RO)(OH)$_2$PO
Alkyl dialkylphosphinates, (RO)R$_2$PO	Dialkylphosphinic acids, R$_2$(OH)PO
Trialkylphosphine oxides, R$_3$PO	Monoalkylphosphonic acids, R(OH)$_2$PO

tion of uranyl salts other than the nitrate by solvents of this type, but uranyl thiocyanate is known to be extracted by ether (37).

(b) Solvent extraction by organophosphorus compounds

Many classes of organophosphorus compounds form particularly stable uranyl complexes. Tributyl phosphate was the first of these compounds to be recognized as a superior extracting agent for uranyl nitrate (547), and solvent extraction by this reagent has been intensively investigated both fundamentally and technically (29). The classes to which these reagents belong are summarized in table 13.

In general they are superior to the ethers as solvent extractants in that no salting-out agents are required. The neutral reagents extract molecules of uranyl nitrate and other salts, while the acidic reagents form highly extractable uranyl alkyl phosphates, phosphinates, and phosphonates.

Of the neutral reagents, tributyl phosphate has been studied in most detail; McKay and Healy (319) have briefly but critically reviewed this work up to 1958. Solvent extraction equilibria, and the limiting solubility of uranyl nitrate in tributyl phosphate, show that the complex contains two molecules of tributyl phosphate to one of uranyl nitrate. The complex in solution is not appreciably ionized at concentrations above about 0.5 molar (221); unlike the ether complexes, it does not contain water. Ferraro (152) has presented infrared evidence that the nitrate groups are coördinated to uranium in these complexes, but while this conclusion is doubtless true, the experimental method used is open to the objection that the complexes might have reacted with the material of the cell windows (176).

Several indirect lines of evidence show that the phosphoryl oxygen atom is coördinated to the uranyl nitrate molecule, but there is no evidence that the butoxy oxygen atoms are also involved. Assuming the uranyl ions to be in surroundings similar to those in rubidium uranyl nitrate (224), Kennedy (285) has suggested structure V for the uranyl nitrate–tributyl phosphate complex, and an analogous structure has recently been established for the crystalline triethyl phosphate complex by x-ray diffraction (315).

V
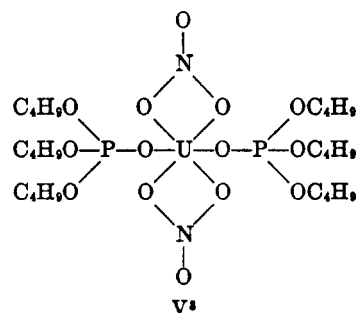
There is no tendency for the trinitratouranyl ion to be formed in tributyl phosphate, even in the presence of added nitric acid (216). The addition of amides to solutions of uranyl nitrate in tributyl phosphate produces spectral changes and an increase in the electrical conductance of the solutions, attributed to displacement of the coördinated nitrate groups by amide molecules (358).

Replacing the alkoxy groups in trialkyl phosphates progressively by alkyl groups causes an increase in the extracting powers of these reagents (214, 539), and a decrease in the stretching frequency of the phosphorus–oxygen bonds in the uncomplexed ligands (69). These phenomena both reflect the increasingly polar nature of the phosphorus–oxygen bond on going from phosphates through phosphonates and phosphinates, to phosphine oxides.

Replacing the alkoxy groups by phenoxy groups has the opposite effect, the negative inductive effect of the phenyl groups rendering the phosphoryl oxygen atom less basic. The extracting powers of these reagents fall as more phenyl groups are introduced, approaching those of the ethers, and at the same time the complexes formed in solution assume compositions similar to those of the ether complexes. This is illustrated by table 14, from the work of Healy, Kennedy, and Waind (215).

The uranyl nitrate complexes with neutral organophosphorus compounds have usually been studied in solution, but several solid anhydrous complexes have been described (69, 500, 501). Siddall (500) has obtained thermodynamic data for the formation of the uranyl

TABLE 14

Uranyl complexes with organophosphorus compounds in solution

| Extractant	Complex Formed in Organic Phase	Partition Coefficient*
Tributyl phosphate (TBP)	UO$_2$(NO$_3$)$_2$.2TBP	2230
Dibutyl phenyl phosphate (DBPP)	UO$_2$(NO$_3$)$_2$.2DBPP.0.5H$_2$O	170
Butyl diphenyl phosphate (DPBP)	UO$_2$(NO$_3$)$_2$.3DPBP.H$_2$O	11.3
Triphenyl phosphate (TPP)	UO$_2$(NO$_3$)$_2$.3TPP.3H$_2$O	—
Bis(2-butoxyethyl) ether (Butex)	UO$_2$(NO$_3$)$_2$.3Butex.4H$_2$O	1.54

* Thermodynamic partition coefficient for the extraction of uranyl nitrate from water into the undiluted organic solvent.

nitrate complexes of a number of trialkyl phosphates and dialkyl alkylphosphonates.

Most of the work on the extraction of uranium(VI) by neutral organophosphorus compounds has been done with the nitrate; uranyl chloride (30, 248, 303), uranyl sulfate (30, 223), and uranyl phosphate (30) are also extracted, but to a progressively diminishing extent in that order. The sulfate is extracted by tributyl phosphate only at high acidities (537), and the phosphate is extracted appreciably only by the trialkylphosphine oxides (30). Uranyl perchlorate extracts as $UO_2(ClO_4)_2 \cdot 2TBP \cdot 2H_2O$ (494, 496). It may be that the perchlorate ion, unlike the nitrate ion, cannot function as a bidentate group and the water molecules are necessary to maintain the sixfold coördination of the uranyl ion.

The acidic reagents listed in table 13 are still more powerful extractants than the neutral complexes.

Of the dialkylphosphoric acids, most work has been done on dibutylphosphoric acid (59, 137, 214) and bis(2-ethylhexyl)phosphoric acid (13). These acids are dimeric in most organic solutions (209). The species which is extracted from relatively dilute uranyl solutions is $UO_2[(RO)_2POO]_2[(RO)_2POOH]_2$, to which formula VI may be assigned. Solutions which are more concentrated in uranium give polymeric species containing

VI[3]
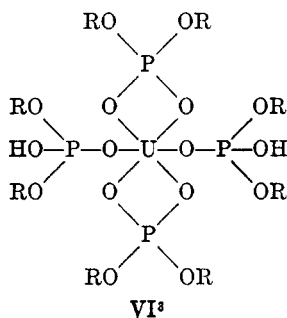
less than four molecules of acid to each uranium atom (formula VII) and from them a solid complex of 1:2 stoichiometry has been isolated (286, 408, 528). Solutions of uranyl nitrate in nitric acid of concentrations

VII[3]
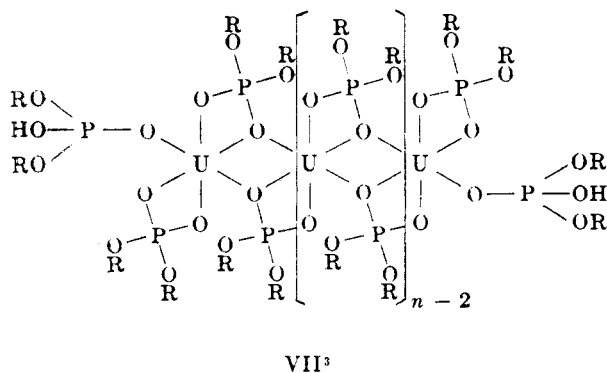
above 3 molar are extracted by dibutylphosphoric acid by a different mechanism (214), analogous to that

occurring in extractions with tributyl phosphate; species VIII is probably involved.

VIII[3]
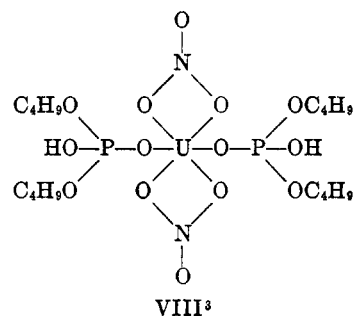
The monoalkylphosphoric acids are also used in the solvent extraction of uranium (28, 29), but less fundamental work has been published on these systems. A 1:1 uranyl complex with monobutylphosphoric acid has been isolated (528).

Mixtures of dialkylphosphoric acids with neutral organophosphorus compounds are more powerful extractants for uranium(VI) than either type of reagent alone (28, 29, 31). Phosphinic acids do not show this effect, and monoalkylphosphoric acids are less efficient extractants in the presence of neutral reagents. The order of efficiency of neutral reagents in enhancing the extracting powers of dialkylphosphoric acids is the same as the order of extracting powers of the neutral reagents alone: $(RO)_3PO < (RO)_2RPO < (RO)R_2PO < R_3PO$, a result which suggests that the neutral reagents function as electron donors. Kennedy (284) has suggested that species of type IX are extracted by the mixed reagents. These species are formed preferentially to those involving two added molecules of the free acids (VI), because the neutral reagents, unlike the acids, need not first be depolymerized.

IX[3]
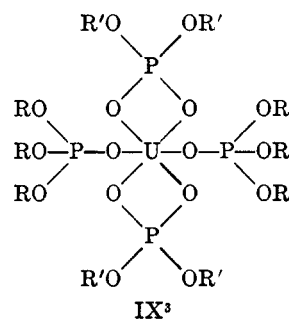
## 5. Addition compounds of uranyl salts with nitrogen donors

The patterns of behavior of uranyl salts toward organic bases resemble those of the thorium salts; the product may be uranyl hydroxide or a uranate of the base, a double salt of the base, or a complex with one or more molecules of base coördinated to the uranyl ion. Only compounds in the last category are considered here; those that have been isolated are listed in table 15.

No structural work has been done on any of these

TABLE 15

Complexes of uranyl salts with nitrogen donors

Ligand	Formula of Complex	References	Ligand	Formula of Complex	References
Acetonitrile............	UO2(NO3)2.2CH3CN	(293)	Quinoline.............	Na2UO2(CH3COO)4.2C9H7N	(246)
Nitrosomethane........	UO2(NO3)2.2CH3NO	(293)		K2UO2(CH3COO)4.2C9H7N	(246)
Urea..................	UO2(NO3)2.4CH4N2O	(181)		Na2UO2(C2O4)2.2C9H7N	(246)
Ethylenediamine.......	UO2(NO3)2.C2H8N2	(548)		K2UO2(C2O4)2.2C9H7N	(246)
2,5-Piperazinedione.....	UO2(NO3)2.C4H6N2O2	(10)	N-Methylacetanilide....	UO2(NO3)2.2C9H4NO	(434)
	UO2Cl2.C4H6N2O2.1.5H2O	(10)		UO2Cl2.2C9H11NO	(434)
2-(Dimethylamino)-ethanol..............	UO2(NO3)2.C4H11NO	(17)		UO2Br2.2C9H11NO	(434)
Pyridine..............	UO2(NO3)2.2C5H5N	(17, 239, 293, 432)	2-Methylquinoline......	UO2(NO3)2.C10H9N.H2O	(432)
			Phenacetin............	UO2(NO3)2.2C10H13NO2	(433)
	UO2(NO3)2.C5H5N.H2O	(17, 239, 432)		UO2Cl2.2C10H13NO2	(433)
	UO2Cl2.2C5H5N	(433)		UO2Cl2.3C10H13NO2	(433)
	UO2Cl2.C5H5N.H2O	(17)		UO2Cl2.2C10H13NO2.2H2O	(433)
Choline...............	UO2(NO3)2.C5H15NO2	(511)		UO2Cl2.2C10H13NO2.3H2O	(433)
Nitrobenzene..........	UO2(NO3)2.2C6H5NO2	(293)		UO2Cl2.2C10H13NO2.4H2O	(433)
Aniline...............	UO2Cl2.2C6H7N	(305)		UO2Br2.4C10H13NO2	(433)
	UO2SO4.2C6H7N.3H2O	(245)		UO2(C2O4).C10H13NO2.2H2O	(433)
	UO2(CH3COO)2.2C6H7N	(245)	N,N-Diethyl-p-nitrosoaniline........	UO2(NO3)2.C10H14N2O	(435)
	UO2(C2O4).2C6H7N.2H2O	(245)		UO2(NO3)2.2C10H14N2O	(435)
Hexamethylenetetra-mine...............	UO2(NO3)2.C6H12N4	(548)		UO2Cl2.2C10H14N2O	(435)
	UO2(CH3COO)2.C6H12N4	(311)		UO2Br2.2C10H14N2O	(435)
p-Toluidine...........	UO2Cl2.2C7H9N	(305)		UO2SO4.2C10H14N2O	(435)
o-Toluenediamine.......	UO2(NO3)2.2C7H10N2	(80)		UO2(CH3COO)2.C10H14N2O	(435)
	UO2(NO3)2.2C7H10N2.2H2O	(80)		UO2(C2O4).C10H14N2O	(435)
m-Toluenediamine......	UO2(NO3)2.3C7H10N2	(80)	N,N-Dibutylacetamide..	UO2(NO3)2.2C10H21NO	(144)
Acetanilide............	UO2(NO3)2.3C8H9NO	(434)	4-Nitrosoantipyrene.....	UO2(NO3)2.4C11H11N3O2	(436)
N,N-Dimethyl-p-nitrosoaniline............			Bromoantipyrene.......	UO2(NO3)2.2C11H11BrN2O	(436)
	UO2(NO3)2.C8H10N2O	(435)		UO2Cl2.2C11H11BrN2O	(436)
	UO2(NO3)2.2C8H10N2O	(435)		UO2Br2.2C11H11BrN2O	(436)
	UO2Cl2.2C8H10N2O	(435)	Antipyrene............	UO2(NO3)2.2C11H12N2O	(432, 369)
	UO2Br2.2C8H10N2O	(435)		UO2Cl2.2C11H12N2O	(432)
	UO2SO4.2C8H10N2O	(435)		UO2(ClO4)2.5C11H12N2O	(560)
	UO2(CH3COO)2.C8H10N2O (two forms)	(435)		UO2Br2.2C11H12N2O	(432)
				UO2SO4.2C11H12N2O.4H2O	(432)
	UO2(C2O4).C8H10N2O	(435)		UO2(CH3COO)2.2C11H12N2O	(433)
Quinoline.............	UO2(NO3)2.2C9H7N	(246)		UO2(C2O4).C11H12N2O.H2O	(433)
	UO2(NO3)2.C9H7N.H2O	(432)	Aminopyrine...........	UO2(NO3)2.2C13H17N3O (two forms)	(432, 433)
	UO2SO4.2C9H7N	(246)		UO2Cl2.C13H17N3O	(433)
	UO2(CH3COO)2.C9H7N	(246)		UO2Cl2.2C13H17N3O	(433)
	UO2(CH3COO)2.2C9H7N	(246)		UO2Cl2.C13H17N3O.H2O	(433)
	UO2(C2O4).2C9H7N	(246)		UO2Cl2.C13H17N3O.2H2O	(433)
	UO2(C4H4O6).2C9H7N	(246)		UO2Cl2.C13H17N3O.3H2O	(433)
			Cocaine...............	UO2(NO3)2.C17H21NO4	(401)

complexes. The infrared spectrum (17) of the uranyl nitrate–pyridine adduct, $UO_2(NO_3)_2.2C_5H_5N$, shows the nitrate groups to be coördinated to the uranyl ions; if these groups are bidentate as in the uranyl nitrate-triethyl phosphate adduct (315), then this complex could have the familiar ring of six ligand atoms around the uranyl axis, as in X:


X[3]
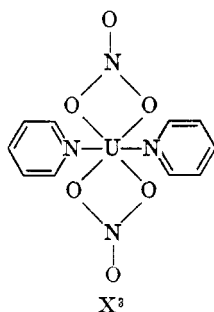
c. Complexes with acidic nitrogen donors

8-Quinolol has been used for the determination of uranium(VI) (the system with uranium(IV) has not been examined) by gravimetric, volumetric, and colorimetric methods. Work on this complex up to 1956 has been reviewed by Hollingshead (232). As precipitated from aqueous solution the complex is red and has the stoichiometric composition $UO_2(C_9H_6NO)_2.C_9H_7NO$. The "extra" molecule of 8-quinolol is lost on heating to about 230°C. and the green "normal" compound, $UO_2(C_9H_6NO)_2$, remains (367, 554). The red complex may be regenerated by warming the green complex with a solution of 8-quinolol (167).

The nature of the binding of the "extra" molecule of 8-quinolol in the red complex is an interesting question which has not been completely solved. Bullwinkel and Noble (66) have found that the red complex is an acid, and have prepared the salts $MUO_2(C_9H_6NO)_3$, where $M = Na$, $(C_2H_5)_4N$, and $(C_6H_5)_4As$. They formulate the acid as shown in formula XI (on page 132) and suggest that protons link the uranyl ions in chains. The symmetrical arrangement of the three bidentate ligands around the uranyl ion in XI is analogous to the

arrangement found in the double uranyl nitrates, acetates, and cupferrates and is a very plausible hypothesis. Bullwinkel and Noble further suggest that the "normal" green chelate is not made up of simple $UO_2(C_9H_6NO)_2$ molecules but is polymeric. Charles and his coworkers (85) have pointed out that a band at 14.1 μ in the absorption spectrum of 8-quinolol is absent in the spectra

XI[3]
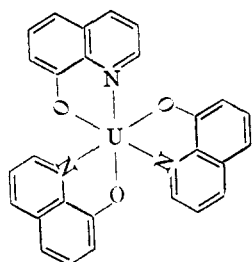
of the 8-quinolol–metal complexes, including the 1:3 uranyl complex, and this too suggests that the "extra" molecule of 8-quinolol is not loosely bound in the crystal.

The uranyl–8-quinolol system is thus closely analogous to the uranyl–acetylacetone system (see Section V,C,1); in the latter the complex with the "extra" molecule of ligand can also be formulated as an acid, $H[UO_2(C_5H_7O_2)_3]$, it forms salts, and the "normal" complex, $UO_2(C_5H_7O_2)_2$, is polymerized. The analogy holds also in solution; Dyrssen and Dahlberg (134) have found chloroform solutions of 8-quinolol to extract uranium(VI) as $[UO_2(C_9H_6NO)_3]^-$, which is analogous to the species extracted by organic solutions of several β-diketones.

Van Tassel and Wendlandt (532) have measured calorimetrically the difference in energy between the systems $[UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ (solid)] and $[UO_2(C_9H_6NO)_2$ (solid) $+ C_9H_7NO$ (solid)]. From the low value of 4.9 $\pm$ 0.2 kcal./mole which they find for this energy difference, Van Tassel and Wendlandt conclude that the "extra" molecule of 8-quinolol is held only by weak lattice forces. This interpretation ignores any energy of rearrangement of the "normal" complex when the "extra" molecule is removed, and the result could better be interpreted to mean that the energies of the bonds linking the "extra" molecules to the uranyl ions are comparable to those linking the units of the polymerized "normal" complex.

The uranyl complexes of substituted 8-quinolols generally resemble the corresponding thorium complexes. 5,7-Dichloro-8-quinolol, 5,7-dibromo-8-quinolol, 5,7-diiodo-8-quinolol, and 5-chloro-7-iodo-8-quinolol form complexes with both 1:3 and 1:2 stoichiometry (363, 555), but the latter cannot be obtained by heating the former (554). The extraction of uranium(VI) by chloroform solutions of these ligands has also been studied (136). 2-Methyl-8-quinolol forms a 1:3 complex (420)

which gives the 1:2 complex on heating (557). 8-Hydroxy-7-iodo-5-quinolinesulfonic acid (ferron) does not precipitate uranium(VI) (454) but forms a 1:2 complex with it in solution (353). 8-Hydroxy-5-quinolinesulfonic acid also forms a 1:2 uranyl complex in solution, but there is some evidence that this is polymerized (441).

The stability constants of a number of 1:2 uranyl complexes of substituted 8-quinolols and related ligands in aqueous dioxane have been measured (249); 1:3 complexes do not appear to be formed in these systems.

In the hope of preparing a terdentate chelating agent, Phillips and Duckwall (419) synthesized 7-(α-anilinobenzyl)-8-quinolol and prepared the thorium and uranyl derivatives; there was no evidence for terdentate chelation, but the uranyl compound contained the usual "extra" molecule of reagent and the thorium compound was probably impure.

In acid solutions cupferron will precipitate uranium(IV) but not uranium(VI); in neutral solutions uranyl salts give precipitates of the double uranyl cupferrates, $MUO_2(C_6H_5N_2O_2)_3$, where M = Na, K, Rb, Cs, NH_4 (171, 172, 233, 337). Ammonium uranyl cupferrate crystallizes in the cubic system (68, 233, 275), and preliminary x-ray data show that the three cupferrate groups are arranged symmetrically about the uranyl axis (233, 275). Polarographic reduction of the uranyl ion in acid solution in the presence of cupferron gave anomalous results, attributed to the formation of insoluble uranium(IV) cupferrate at the surface of the mercury (140).

The stability constants of the uranyl complexes of glycine (308), polyglycine peptides, histidine (307), and serine (309) have been measured, and much work has been done on the action of uranyl salts on enzymes and proteins (126).

Uranium(VI) forms rather weak complexes with aminopolycarboxylic acids. With EDTA the solid complex $UO_2(C_{10}H_{14}N_2O_8) \cdot H_2O$ has been isolated (51), and the existence of a 2:1 complex in aqueous solution has been demonstrated by pH titration (71), high-frequency titration (208), and ultraviolet spectroscopy (428). Nitrilotriacetic acid gives the solid complex $UO_2(C_6H_7NO_6) \cdot 5H_2O$ (52) and also a 1:1 complex in solution (71).

Uranyl complexes of many other acidic reagents containing nitrogen have been prepared and are listed in table 16. Those which have been studied in solution are given in table 17. Kiss and his collaborators (291, 292) and Bayer and Möllinger (19) have recorded and discussed the visible and ultraviolet absorption spectra of a number of other complexes in this category.

Although the synthesis of complicated chelating agents for uranium is clearly a popular research topic, the complexes themselves have received scant attention —indeed, little definite can be said of any of them. Many workers have assigned structural formulas to

TABLE 16

Uranyl complexes with acidic nitrogen donors

Ligand	Formula of Complex	References	Ligand	Formula of Complex	References
Aspartic acid...............	$UO_2(C_4H_6NO_4)_2.3H_2O$	(342)	N,N'-Bis(5-sulfosalicylidene)-ethylenediamine*..........	$UO_2(C_{16}H_{14}N_2O_8S_2).2H_2O$	(379)
Uric acid...................	$UO_2(C_5H_3N_4O_3)_2$	(384)	2-Salicylcinchoninic acid......	$UO_2(C_{17}H_9NO_5).4H_2O$	(550)
Anilinesulfonic acid	$UO_2(C_6H_6NO_3S)_2$	(342)	o-[(3-Methyl-2-quinolyl)-methyleneamino]phenol.....	$UO_2(CH_3COO)(C_{17}H_{13}N_2O)$	(487)
Quinolinic acid..............	$UO_2(C_7H_3NO_4).2H_2O$	(384)	N,N'-Disalicylidene-1,2-propanediamine*..........	$UO_2(C_{17}H_{16}N_2O_2)$	(417, 418)
Benzohydroxamic acid.......	$UO_2(C_7H_6NO_2)_2.H_2O$	(349)		$UO_2(C_{17}H_{16}N_2O_2).C_2H_5OH$	(417, 418)
Aminobenzoic acid...........	$UO_2(C_7H_6NO_2)_2.4H_2O$	(184)		$UO_2(C_{17}H_{16}N_2O_2).C_6H_5N$	(418)
Salicylohydroxamic acid......	$UO_2(C_7H_6NO_3)_2$	(25)	N,N'-Disalicylidene-1,3-propanediamine*..........	$UO_2(C_{17}H_{16}N_2O_2)$	(418)
o-Sulfonamidobenzoic acid....	$UO_2(C_7H_6NO_4S).3H_2O$	(383)	N,N'-Bis(α-methylsalicylidene)ethylenediamine*	$UO_2(C_{18}H_{18}N_2O_2)$	(418)
Isatin 2-oxime...............	$UO_2(C_8H_5N_2O_2)_2$	(234)		$UO_2(C_{18}H_{18}N_2O_2).C_2H_5OH$	(418)
Isatin 3-oxime...............	$UO_2(C_8H_5N_2O_2)_2$	(238)		$UO_2(C_{18}H_{18}N_2O_2).C_6H_5N$	(418)
N-Salicylideneglycine........	$UO_2(C_9H_7NO_3).2H_2O$	(376)	o-[(Phenylhydrazono)-2-pyridylmethylazo]benzoic acid.....................	$UO_2(C_{19}H_{13}N_5O_2).C_{19}H_{15}N_5O_2$	(488)
Salicylaldehyde semioxam-azone....................	$UO_2(C_9H_7N_3O_3).1.5H_2O$	(235)	α,α'-(2,5-Dinitrilopyridyl)di-o-cresol..................	$UO_2(C_{19}H_{14}N_3O_2)_2$	(473)
Adrenaline.................	$UO_2(C_9H_{12}NO_3)_2.H_2O$	(94)	α,α'-(2,6-Dinitrilopyridyl)di-o-cresol..................	$UO_2(C_{19}H_{14}N_3O_2)_2$	(473)
3,4-Dichloro-1,2-naphtho-quinone 1-monoxime.......	$UO_2(C_{10}H_4Cl_2NO_2)_2$	(474)	N,N'-Bis(5-sulfosalicylidene)-o-phenylenediamine*.......	$Na_2UO_2(C_{20}H_{12}N_2O_8S_2)$	(289)
3-Bromo-1,2-naphthoquinone 1-monoxime..............	$UO_2(C_{10}H_5BrNO_2)_2$	(474)	o-(Benzo[f]quinolin-3-yl-methyleneamino)phenol.....	$UO_2(CH_3COO)(C_{20}H_{13}N_2O)$	(489)
	$UO_2(C_{10}H_5BrNO_2)_2.3H_2O$	(474)	N,N'-Disalicylidene-o-phenyl-enediamine*..............	$UO_2(C_{20}H_{14}N_2O_2)$	(418)
	$UO_2(C_{10}H_5BrNO_2)_2.2C_2H_5OH$	(474)		$UO_2(C_{20}H_{14}N_2O_2).CH_3OH$	(418)
Quinaldic acid..............	$UO_2(C_{10}H_6NO_2)_2.2H_2O$	(17)		$UO_2(C_{20}H_{14}N_2O_2).C_2H_5OH$	(348)
N-Salicylidenealanine........	$UO_2(C_{10}H_9NO_3).2H_2O$	(376)		$UO_2(C_{20}H_{14}N_2O_2).C_6H_5N$	(418)
Salicylaldehyde 5-methyl-semioxamazone..........	$UO_2(C_{10}H_9N_3O_3).1.5H_2O$	(236)	o-[(6-Methyl-2-pyridyl)(phen-ylhydrazono)methylazo]-benzoic acid..............	$UO_2(C_{20}H_{18}N_5O_2).C_{20}H_{17}N_5O_2$	(491)
2-Hydroxy-1-nitroso-3-naphthoic acid............	$UO_2(C_{11}H_6NO_4)_2$	(115)	N,N'-Bis(α-methylsalicyli-dene)-o-phenylenediamine*..	$UO_2(C_{22}H_{18}N_2O_2)$	(418)
o-[N-(5-Bromo-2-pyridyl)]-formimidoylphenol........	$UO_2(C_{12}H_8BrN_2O)_2$	(473)	o-[(Phenylhydrazono)-8-quinolylmethylazo]benzoic acid.....................	$UO_2(C_{23}H_{15}N_5O_2)$	(492)
4-Bromo-2-N-2-pyridyl-formimidoylphenol........	$UO_2(C_{12}H_8BrN_2O)_2$	(473)	o-[(Phenylhydrazono)-2-quin-olylmethylazo]benzoic acid..	$UO_2(C_{23}H_{15}N_5O_2)$	(487)
4-Chloro-2-N-2-pyridyl-formimidoylphenol........	$UO_2(C_{12}H_8ClN_2O)_2$	(473)	o-[(6-Methyl-2-quinolyl)(phen-ylhydrazono)methylazo]-benzoic acid..............	$UO_2(C_{24}H_{17}N_5O_2).C_{24}H_{19}N_5O_2$	(492)
o-[N-(5-Chloro-2-pyridyl)]-formimidoylphenol........	$UO_2(C_{12}H_8ClN_2O)_2$	(473)	o-[(7-Methyl-2-quinolyl)(phen-ylhydrazono)methylazo]-benzoic acid..............	$UO_2(C_{24}H_{17}N_5O_2).C_{24}H_{19}N_5O_2$	(492)
o-[N-(5-Iodo-2-pyridyl)]-formimidoylphenol........	$UO_2(C_{12}H_8IN_2O)_2$	(473)	1,1'-(Ethylenebisnitrilometh-ylidene)di-2-naphthol.......	$UO_2(C_{24}H_{18}N_2O_2)$	(418)
o-N-(2-Pyridyl)formimidoyl-phenol...................	$UO_2(C_{12}H_9N_2O)_2$	(473)		$UO_2(C_{24}H_{18}N_2O_2).CH_3OH$	(418)
N-Salicylidenesulfanilic acid...	$Na_2UO_2(C_{13}H_9NO_4S)_2.2H_2O$	(376)	o-[Benzo[f]quinolin-3-yl(phen-ylhydrazono)methylazo]-benzoic acid..............	$UO_2(C_{27}H_{17}N_5O_2)$	(489)
N-(5-Sulfosalicylidene)aniline*.	$UO_2(C_{13}H_{10}NO_4S)_2.1.5H_2O$	(379)	1,1'-(o-Phenylenebisnitrilo-methylidene)di-2-naphthol..	$UO_2(C_{28}H_{18}N_2O_2)$	(418)
2-[(2-Hydroxy-1-naphthyl)-methyleneamino]aceto-hydroxamic acid..........	$UO_2(C_{13}H_{10}N_2O_3).1.5H_2O$	(377)		$UO_2(C_{28}H_{18}N_2O_2).CH_3OH$	(418)
2-Pyridylformimidoyl-p-cresol .	$UO_2(C_{13}H_{11}N_2O)_2$	(473)	N,N'-Disalicylidene-1,2-di-phenylethylenediamine*....	$UO_2(C_{28}H_{22}N_2O_2)$	(417, 418)
N^4-Salicylidenesulfanilamide...	$UO_2(C_{13}H_{11}N_2O_3S)_2$	(378)		$UO_2(C_{28}H_{22}N_2O_2).CH_3OH$	(418)
N-Nitroso-N-[2-(p-tolylsul-fonyl)phenoxy]hydroxyl-amine...................	$UO_2(C_{13}H_{11}N_2O_5S)_2$	(18)	2,2'-{(4-Methyl-2,6-pyridine-diyl)bis[(phenylhydrazono-methylene)azo]}dibenzoic acid.....................	$(UO_2)_2(C_{34}H_{23}N_9O_4)$	(491)
N^4-(5-Sulfosalicylidene)sulfa-nilamide.................	$UO_2(C_{13}H_{11}N_2O_6S_2)_2.H_2O$	(379)	1,1'-[(1,2-Diphenylethylene)-bis(nitrilomethylidyne)]di-2-naphthol...............	$UO_2(C_{36}H_{26}N_2O_2)$	(418)
Phenanthrenequinone monoxime................	$UO_2(C_{14}H_8NO_2)_2$	(202)			
	$UO_2(C_{14}H_8NO_2)_2.2C_2H_5OH$	(202)			
N-Salicylideneanthranilic acid .	$UO_2(C_{14}H_{10}NO_3)_2.H_2O$	(376)			
2-Phenylcinchoninic acid......	$UO_2(C_{16}H_{10}NO_2)_2$	(383)			
1-(p-Nitrophenylazo)-2-naph-thol..................	$UO_2(C_{16}H_{10}N_3O_3)_2.2C_{16}H_{11}N_3O_3$	(91)			
1,3-Diphenylvioluric acid.....	$UO_2(C_{16}H_{10}N_3O_4)_2$ (?)	(505)			
1-N-2-Pyridylformimidoyl-2-naphthol.................	$UO_2(C_{16}H_{11}N_2O)_2$	(473)			
o-(2-Quinolylmethylene-amino)phenol.............	$UO_2(CH_3COO)(C_{16}H_{11}N_2O)$	(485)			
o-(4-Quinolylmethylene-amino)phenol.............	$UO_2(C_{16}H_{11}N_2O)_2$	(487)			
2-[N-(o-Hydroxyphenyl)-formimidoyl]-3-methyl-quinoxaline...............	$UO_2(CH_3COO)(C_{16}H_{12}N_3O)$	(487)			
N,N'-Disalicylideneëthylene-diamine*................	$UO_2(C_{16}H_{14}N_2O_2)$	(418)			

* Name not conforming to *Chemical Abstracts* usage.

TABLE 17

Uranyl complexes with nitrogen donors in solution

Ligand	UO₂:Ligand in Complex	References
Benzohydroxamic acid.............	1:1, 1:2	(349)
Dimethylglyoxime.................	1:2	(8a)
Guanidine.......................	1:1	(180, 181)
3-(2-Arsonophenylazo)-4,5-dihydroxy-2,7-naphthalenedisulfonic acid (Arsenazo, Neothoron)............	1:1	(186, 498)
	2:3	(339)
1-Nitroso-2-naphthol-3,6-disulfonic acid............................	3:2	(431)
1-(2-Pyridylazo)-2-naphthol (PAN)...	1:2	(87, 186)
Salicylaldehyde semioxamazone......	1:2	(235)
Salicylamide.....................	1:1, 1:2	(83)
Salicylamidoxime.................	1:1	(14)
Urea............................	1:2 (in alcohol)	(180)
	1:4 (in water)	(181)
Nitrilotriacetic acid (NTA)........	1:1, 1:2	(71, 452)
Hexahydro-2,4,6-trioxo-5-pyrimidinylimino)diacetic acid (uramyldiacetic acid)...................	1:1, 1:2	(452)
Ethylenedinitrilotetraacetic acid (EDTA)......................	1:1	(452)
	1:1, 1:2, 2:1	(71)
1,2-Cyclohexenedinitrilotetraacetic acid (CDTA)..................	1:1	(452)
1,2-Cyclopentenedinitrilotetraacetic acid...........................	1:1	(452)
1,2-Cyclobutenedinitrilotetraacetic acid...........................	1:1	(452)

their products by analogy with the complexes of similar ligands with the transition metals, but this is an unreliable procedure when dealing with metals of unusual and possibly varying coördination numbers.

7. Complexes with sulfur donors

That sulfur is a weaker donor than oxygen toward uranium and thorium is shown by Wendlandt and Bryant's observation (558) that the solubilities of uranyl and thorium nitrates in tributyl thiophosphate are only about one-twentieth of those in tributyl phosphate, notwithstanding the similar dielectric constants of these media (ϵ^{25} = 6.82 and 8.05, respectively). Nevertheless, a number of solid complexes have been isolated which probably contain uranium(VI) coördinated to sulfur, and these are listed in table 18. The tendency of the alkylxanthic and dialkyldithiocarbamic acids to form double salts with three anions to each uranyl ion suggests that these ligands are bidentate and form the familiar ring of six atoms around the uranyl axis. Extraction by solutions of diethyldithiocarbamic acid has been used for the extraction of uranium from thorium and protactinium (389, 530).

Complexes formed in solution by uranyl nitrate with thiourea have the same stoichiometry as those formed with urea (180, 181).

The selenium compound included in table 18 and its sulfur analog are unlikely to contain selenium and sulfur coördinated with uranium; they are included there for ease of reference.

VI. NEPTUNIUM COMPLEXES

The coördination chemistry of neptunium generally resembles that of plutonium.

Neptunium(IV) is extracted by benzene solutions of HTTA as the neutral 1:4 complex (519); this complex has been isolated (301) but not analyzed. Neptunium(IV) and neptunium(VI) are extracted well by bis(2-butoxyethyl) ether from nitric acid solutions, but not neptunium(V) (22, 321). This is true also for tributyl phosphate (390), in which the extracted species have been shown to be $Np(NO_3)_4.2TBP$ and $NpO_2(NO_3)_2.2TBP$ (5). Neptunium(V) is, however, extracted by organic solutions of 1-nitroso-2-naphthol (16). Neptunium(IV) is extracted strongly by toluene solutions of monoöctylphosphoric acid under conditions where plutonium is in the relatively unextractable tervalent state; the identity of the extracting species has not been established (413). The stability constant of the 1:1 neptunium(IV) complex with EDTA has been measured by a polarographic method and found to have a value close to that of the thorium complex (259). Neptunium(V) also gives a 1:1 complex with this reagent in solution (177).

VII. PLUTONIUM COMPLEXES

A. COMPLEXES WITH OXYGEN DONORS

Plutonium acetylacetonate, $Pu(C_5H_7O_2)_4$, has been prepared as a volatile (112), brown, crystalline solid (122, 124). American workers (124, 515) reported that this was not isomorphous with thorium acetylacetonate, but comparison of their crystal data on the plutonium complex with the data of Grdenić and Matković (195) on the dimorphic thorium complex shows that the plu-

TABLE 18

Uranyl complexes with sulfur donors

Ligand	Formula of Complex	Reference
Thiolactic acid..............	UO₂(C₃H₅O₂S)₂	(297)
Thioglycolic acid.............	UO₂(C₄H₅O₄S₂)	(297)
Ethylxanthic acid...........	KUO₂(C₃H₅OS₂)₃	(580)
Isopropylxanthic acid........	KUO₂(C₄H₇OS₂)₃	(580)
Diethyldithiocarbamic acid....	K[UO₂(C₅H₁₀NS₂)₃].H₂O	(580)
Diethyldithiocarbamic acid (and homologs)............	[(C₂H₅)₂NH₂][UO₂(C₅H₁₀NS₂)₃]	(4)
	UO₂(C₅H₁₀NS₂)₂	(327)
	UO₂(C₅H₁₀NS₂)₂.4C₂H₅OH	(269)
Isopentylxanthic acid (and homologs).................	UO₂(C₆H₁₁OS₂)₂	(326)
Thianaphthenequinone 2-oxime...................	UO₂(C₈H₄NO₂S)₂.2H₂O	(237)
2,3-Dimethylthiochromone....	UO₂Cl₂.2C₁₁H₁₀OS	(503)
	UO₂Cl₂.2C₁₁H₁₀OS.2HCl	(504)
o-(2-Benzothiazolylmethyleneamino)phenol..........	UO₂(CH₃COO)(C₁₄H₉N₂OS)	(485)
o-(2-Benzoselenazolylmethyleneamino)phenol..........	UO₂(CH₃COO)(C₁₄H₉N₂OSe)	(486)
1,3-Diphenylthiovioluric acid	UO₂(C₁₆H₁₀N₃O₃S)₂	(184)
1,3-Ditolylthiovioluric acid...	UO₂(C₁₈H₁₄N₃O₃S)₂	(506)
o-[2-Benzothiazolyl(phenylhydrazono)methylazo]benzoic acid.................	UO₂(C₂₁H₁₃N₅O₂S).C₂₁H₁₅N₅O₂S	(490)

tonium complex is almost certainly isomorphous with the β-modification of the thorium complex (98a).

Rydberg (461) has used the solvent-extraction method to measure the stability constants of the plutonium–acetylacetone complexes which are formed stepwise in aqueous solution similarly to the acetylacetonates of thorium and uranium(IV).

Solvent extraction by organic solutions of HTTA has been used in radiochemical separations of plutonium (241), including the isolation of naturally occurring plutonium-239 (415). Cuninghame and Miles (110, 111) have given the most complete account of this system; the 4-valent state of plutonium is extracted much more strongly than the 3-, 5-, or 6-valent state.

The visible absorption spectrum of the plutonium(III) citrate complex closely resembles that of nitrate solutions of plutonium(III). The spectra are derived from transitions among the $5f$ electrons, and this resemblance shows that the $5f$ electrons are not involved in forming the citrate complex (178).

A neutral salicylate of plutonium(III), $Pu(C_7H_5O_3)_3$. $1.5H_2O$, and some basic salicylates of plutonium(IV) have been described (583).

Several alkoxides of plutonium(IV) have been isolated (47); no molecular-weight studies have been made, but the tetraisopropoxide is evidently coördinatively unsaturated, since it forms addition compounds with pyridine and with isopropyl alcohol. In this respect plutonium tetraisopropoxide resembles the isopropoxides of zirconium, hafnium, and cerium, but not thorium.

B. SOLVENT EXTRACTION BY OXYGEN DONORS

Plutonium(IV) nitrate is extracted by bis(2-butoxyethyl) ether, but the solution is unstable and deposits an insoluble hydrolysis product (529). Plutonyl nitrate is extracted by oxygen-containing solvents in a manner qualitatively similar to that of uranyl nitrate. Jensen (260) gives a table comparing the percentage extracted by various solvents. Bis(2-butoxyethyl) ether extracts plutonyl nitrate as the neutral molecule from solutions less than 0.07 N in nitric acid, but with higher concentrations of nitric acid, or on the addition of quaternary ammonium salts, the trinitratoplutonyl ion $[PuO_2(NO_3)_3]^-$ is extracted (213).

Plutonium(III), in common with the lanthanides, is extracted only weakly by tributyl phosphate, as the complex $Pu(NO_3)_3.3TBP$ (23, 497). Plutonium(IV) (23, 74, 160, 216) and plutonium(VI) (5, 23, 74) are extracted well by tributyl phosphate, as $Pu(NO_3)_4.2TBP$ and $PuO_2(NO_3)_2.2TBP$, respectively.

Monobutylphosphoric and dibutylphosphoric acids extract plutonium(IV) in the form of 1:1 complexes, and the stability constants for the formation of these complexes in aqueous solution have thus been measured (495). Plutonium(IV) monobutylphosphate has been

isolated as $Pu(C_4H_9PO_4)_2.xH_2O$ and its solubility in water measured over a wide range of conditions (370).

C. COMPLEXES WITH NITROGEN DONORS

8-Quinolol gives orthorhombic (515) $Pu(C_9H_6NO)_4$ (403) with plutonium(IV); with plutonium(VI) it gives $PuO_2(C_9H_6NO)_2.C_9H_7NO$, analogous to the 1:3 uranyl complex (211).

EDTA gives 1:1 complexes in aqueous solution with plutonium in the 3-, 4-, 5-, and 6-valent states (163, 176a, 179, 357, 374) and also 2:1 complexes with the first two of these (163). The plutonyl chelate has a greater stability constant than the corresponding uranyl chelate, but it undergoes self-reduction (163). Gel'man, Moskvin, and Artyukhin (176a, 179) have compared the stability constants of the 1:1 EDTA complexes of all four valency states of plutonium; they find that the constants decrease with decreasing ionic charge, i.e., $Pu^{4+} > Pu^{3+} > PuO_2^{2+} > PuO_2^+$. Plutonium(IV) solutions react with thorin to give a colored colloidal 1:1 complex which can be used for estimating plutonium (86). It is curious that there appears to be no reaction between plutonium(IV) and an isomer of thorin, o-(1-hydroxy-3,6-disulfo-2-naphthylazo)benzenearsonic


XII
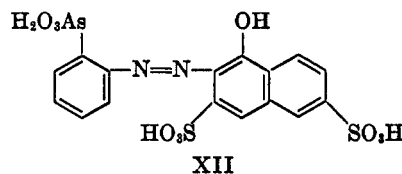
acid (XII), although the corresponding dihydroxy derivative of this isomer, o-(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)benzenearsonic acid (uranol) (XIII), does react to give a 1:1 complex (394).

XIII
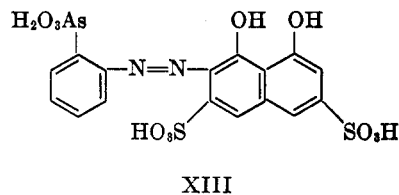
The implication is that in the latter case reaction occurs at the two hydroxy groups and that the phenylarsonic acid group does not react with plutonium(IV) unless some peculiar stereochemical requirement is satisfied.

In a search for organic reagents for the separation of plutonium(III) from plutonium(IV), Wolter (569) prepared and analyzed the plutonium(III) complex of 1-naphthohydroxamic acid, $Pu(C_{11}H_8NO_2)_3$, and the plutonium(IV) complex of the (presumably) quadridentate chelating agent bis[4(or 5)-$tert$-butyl-3,3'-ethylenebis(nitrilomethylidyne)]pyrocatechol (XIV), $Pu(C_{12}H_{30}N_2O_4)_2$.

XIV
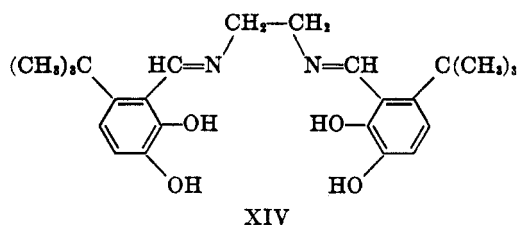
A number of other organic compounds of plutonium have been prepared but not analyzed (211, 403).

D. COMPLEXES WITH SULFUR DONORS

The solvent extraction of plutonium by ethyl sulfide (484a) and the formation of an extractable plutonium(VI) diethyldithiocarbamate (211) indicate sulfur coördination, but neither of these systems has been studied in detail.

VIII. COMPLEXES OF AMERICIUM AND HEAVIER ACTINIDES

Although no coördination compounds of these elements have been isolated, some information on their coördinating properties can be obtained from their ion-exchange and solvent-extraction behavior.

Tervalent actinides are commonly separated from one another by elution from cation-exchange columns, using as eluants citric (522, 523), lactic (523, 563), tartaric (189), and 2-hydroxy-2-methylpropionic (α-hydroxyisobutyric) (88, 509) acids. These separations depend more on differences in the complexing powers of the eluants toward the metals than on any specificity in the resins. The actinides are eluted in the order of their atomic numbers, the heavier ones being eluted first. This shows that the heavier ones form the stronger complexes with the eluants, as would be expected from their smaller ionic radii.

The stability constants of the EDTA complexes of the tervalent actinides from neptunium to californium show this same tendency, increasing gradually with increasing atomic number (169, 179, 375).

Glass (189) has compared several eluting agents for americium under the same column conditions; he finds lactic acid to be superior to hydracrylic acid, and α-alanine superior to β-alanine. This suggests that five-membered chelate rings involving the tervalent actinides are more stable than six-membered rings, and indeed all of the eluting agents mentioned above can form five-membered rings.

Solvent extraction of the tervalent actinides by tributyl phosphate shows the same general pattern as ion exchange; the partition coefficients increase with increasing atomic number (409). Americium has been shown to be extracted as $Am(NO_3)_3 \cdot 3TBP$ (409, 545), and the heavier actinides doubtless behave similarly.

Solvent extraction by solutions of HTTA is not so clear-cut; americium and curium are extracted to a lesser extent than the four following actinides, but there are no obvious regularities within the latter group (323).

In this group of elements, only americium and berkelium can exist in valency states higher than three in aqueous solution. Berkelium(IV) is extracted strongly by solutions of bis(2-ethylhexyl)phosphoric acid (414), and americium(VI) nitrate can be extracted into ether (274).

IX. DISCUSSION

For each valency state there are close resemblances between the various actinide elements, and they are conveniently discussed in valency groups.

Tervalent actinides closely resemble the lanthanides. This analogy, while invaluable in predicting the behavior of the elements in solution and in studies of the simpler compounds, is of little use in the present context, since we are almost equally ignorant of the structures of the tervalent lanthanide and actinide complexes. The lanthanide acetylacetonates, $M(C_5H_7O_2)_3$, are monomeric in benzene and carbon tetrachloride solutions (366); they are therefore six-coördinate and are presumed to be octahedral (359). But coördination numbers (towards oxygen) greater than six may be possible for the tervalent lanthanides and actinides, since Miller (356) has shown spectroscopically that the europium(III) ion in aqueous solution is probably surrounded by eight water molecules.

The quadrivalent actinides show a strong tendency to eightfold coördination. Many of the addition compounds of thorium tetrahalides with oxygen and nitrogen donors listed in tables 3 and 5 contain four molecules of the ligand to one of the thorium halide, and it is reasonable to assume eightfold coördination here.

The stereochemistry of eightfold coördination has been a matter for speculation for some years (392, 393). Marchi, Fernelius, and McReynolds worked out the numbers of possible geometrical and optical isomers for several configurations (333), and other workers have discussed the bond hybrids which might be involved (127, 138, 392, 393, 499).

The only eight-coördinate organic actinide complex whose structure is known is thorium acetylacetonate, where the eight oxygen atoms are arranged at the corners of an Archimedean antiprism. The isomorphous uranium(IV) compound presumably has this structure too; its magnetic moment shows two unpaired electrons to be present, which probably means that any bonding is of the "outer orbital" type. It would, however, be premature to discuss the bonding here in any detail, since the Archimedean antiprism arrangement would also be predicted from purely electrostatic considerations (396). This configuration is found in several inorganic compounds of thorium and uranium(IV) where the metal atoms are surrounded by eight oxygen atoms, and Kierkegaard (287) has pointed out that this con-

figuration is the preferred one for ions of this radius ratio. It is often suggested that the volatility of the metal acetylacetonates implies covalent binding (76, 518, 559), but a simpler explanation is that the intermolecular forces are small because the polar parts of the molecules are well shielded from the outside by the methyl groups.

Too little is known of the complexes of the quinquevalent actinides to permit of generalization.

The sexivalent actinide complexes, with the exception of the uranium(VI) alkoxides (see Section V,B), and the unusual compound (dipyridyl₃U)(SCN)₆ (7), are all derived from the dioxo ions MO_2^{2+}. These ions are linear and highly polar; it is thought that a positive charge of about four resides on the metal atoms, with single negative charges on the oxygen atoms (100, 139). The uranyl compounds whose crystal structures have been determined have a ring of four, five, or six atoms in the equatorial plane of the uranyl ion; the commonest number of atoms is six, and the ring may or may not be puckered (575). In sodium uranyl acetate, $NaUO_2(CH_3COO)_3$, the carboxyl groups are equivalent and bidentate, the six oxygen atoms forming a nearly planar ring (576). In the uranyl nitrate–triethyl phosphate complex there is also a ring of six oxygen atoms, in this case derived from two bidentate nitrato groups and two phosphoryl oxygen atoms (315). There have been no other complete structure determinations on uranyl complexes, but it is probable that in the double uranyl cupferrates, xanthates, and diethyldithiocarbamates, and in the β-diketone and 8-quinolol complexes containing "extra" ligand molecules, the three ligand molecules are equivalent and bidentate, as in sodium uranyl acetate. The types of bond which could hold the six ligand atoms in the equatorial plane of the uranyl ion have been examined by Coulson and Lester (102). They conclude that if covalent bonds are formed these must involve f orbitals, most probably the $6f$ orbitals, but that ionic binding may be more important than this. Furthermore, the distinction between ionic and covalent bonds for heavy atoms such as these may have little physical significance.

X. CONCLUSION

This subject is still in its infancy, despite the large number of compounds that have been prepared over the past one and a half centuries, because so little structural information is available. The classical methods of coördination chemistry developed by Werner for the transition metals have been of little use for the actinides. With the techniques of modern x-ray crystallography it is now practical to locate light atoms in crystals containing even the heaviest elements—Zachariasen and Plettinger's reëxamination of sodium uranyl acetate (576) is a prime example—and it is from this direction that the next advance must come.

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