Inorganica Chimica Acta, 18 (1976) 77–112

ICA Review

Actinide Complexes with the Most Common Organic Ligands Forming Five- and Six-Membered Chelating Rings.

U. CASELLATO, M. VIDALI* and P. A. VIGATO
Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Via Vigonovese, 52, 35100 Padova, Italy
**Istituto di Chimica Generale, Università di Padova, Italy*

Received July 14, 1975

Contents

1. Introduction

A number of good reviews on various aspects of the coordination chemistry of the actinides have been published. Except the comprehensive article of Comyns in 1960,[55] which covered all the prepared complexes of the 5*f* elements known at that time, the reviews regard particular aspects of the chemistry of the actinides. Remarkable attention has been directed toward aqueous solution behaviour[53,108,112,128], liquid–liquid ion exchange[105,106,129,133,144], halides of the actinides and related complexes,[32,33,111] and the structural aspects of the actinide complexes[46]; in addition organometallic compounds[89,100,110] and the electronic spectral studies have been discussed and reviewed[150]. Recently a good monograph on the actinide elements has been published,[6] however there is a lack of information on the physico-chemical data and their correlation, where possible, with structural investigations on chelate complexes.

A critical discussion of these properties for all the known actinide chelate complexes is far too large a matter for a review. The aim of this article is to present a critical and comparative discussion of the behaviour of the actinides in their various oxidation states with the most usual organic chelating ligands: tropolone, 8-hydroxyquinoline, β-diketones, Schiff bases and azo derivatives. Particular attention has been directed toward the preparative methods, the geometry of coordination of the adducts on varying the bite and the coordination power of the chelating ligands, their infrared, n.m.r., electronic spectra and, where available, the first results using photoelectron spectroscopy. The use of these chelating agents in the analytical determination and separation of the actinides has been also considered.

Abbreviations

Hacac = acetylacetone
H(HFAA) = hexafluoroacetylacetone
HBA = benzoylacetone
HPHD = 1-phenylhexane-1,3-dione
HBTA = benzoyltrifluoroacetone
HTTA = thenoyltrifluoroacetone
HTHD = dipivaloylmethane

HFOD = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-octane-4,6-dione
HDBM = dibenzoylmethane
HFTA = 2-furoyltrifluoroacetone
HNTA = 2-naphthoyltrifluoroacetone
HTFA = trifluoroacetylacetone
Htrop = 2-hydroxycyclohepta-2,4,6-trien-1-one
HOx = 8-hydroxyquinoline
HBSB = bidentate Schiff base
HTRSB = tridentate Schiff base
HTSB = tetradentate Schiff base
HPSB = pentadentate Schiff base
HsalenNRR′ = N,N-RR′-ethylenesalicylaldimine
H_2salen = N,N′-ethylenebis(salicylaldimine)
H_2salophen = N,N′-*o*-phenylenebis(salicylaldimine)
H_2glioxamph = glioxalbis(2-hydroxyanyl)
H_2salstien = N,N′-stilbenebis(salicylaldimine)
HsaldienN$(CH_3)_2$ = N,N-dimethyl-N′-salicylidene-1,5-diamino-3-aza pentane
H_2saldien = N,N′-bis(salicylidene)-1,5-diamino-3-aza pentane
H_2saldpt = N,N′-bis(salicylidien)-1,7-diamino-4-aza heptane
dmf = dimethylformamide
dmso = dimethylsulphoxide

2. The Actinide Ions

The first and most remarkable peculiarity of the actinide elements is the great variety of known oxidation states, while for the lanthanides the 3+ oxidation number is the most commonly found (Table I).

The variety in the oxidation states pertains especially to the first half of the actinide group where we have a situation in which the *5f*, *6d*, *7s* and *7p* orbitals (especially from uranium to americium) can be involved in bonding. This situation is indicated by the fact that the actinides are much more prone to complex formation than are the lanthanides where the bonding is more ionic since less energy is required to convert *5f* electrons to *6d* electrons than to convert *4f* electrons to *5d* electrons for the lanthanides.[158]

The difference from the lanthanide chemistry is usually attributed to the contribution of covalent bonds involving *5f* electrons.

For the ground state of actinium and thorium it is reasonable to believe that *5f* orbitals are empty, therefore the *6d* orbitals seem to be preferred in bonding; from protoactinium to neptunium the energy difference between the *6d* and *5f* is not larger and beyond neptunium the further electrons seem to prefer the *5f* orbitals (Figure 1).

The half filled configuration f^7 is therefore reached with curium and the completely filled shell f^{14} with lawrentium. Especially the first electrons entering the *5f* shell are not well shielded as the *4f* electrons of the lanthanides and so they can be used in bonding.

Even in the case where the *5f* shell is preferred, the actinides can exist in high oxidation states, as shown for neptunium, plutonium and americium. As the *5f* shell is filled the participation of *5f* electrons in bonding becomes more difficult, resulting in a much marked stabilisation of the trivalent oxidation state for the heavier actinides.

The actinide complexes generally possess a large number of electronic transitions in the near ultraviolet, visible and infrared region. These spectra have been used for studies about structure and bonding of actinide complexes. There are three different types of electronic transitions. Transitions may occur between two *f* levels of different angular momentum and the absorptions, not much disturbed by the environment, are quite narrow; they lie as not very intense bands in the ultraviolet, visible and near infrared region and generally only the transitions involving no change of the spin multiplicity are observed. On the contrary the *5f*→*6d* transitions are more disturbed by the influence of the environment, this causing a broadening of bands, which can be observed as very intense in the ultraviolet region.

Finally the electronic transitions occurring between the *5f* orbitals and the orbitals of the coordinated ligands are strongly affected by the nature of the ligands. Generally they are quite intense and the bright colors of many actinide complexes are ascribed to charge transfer bands.

It was suggested that spectral changes may occur in the low energy region both when ligands are changed within a given stereochemistry and when the coordination number from 6 to 8 would have a considerable effect on the spectra.

The most studied complexes have the electronic configuration $5f^1$ (protoactinium(IV)) and $5f^2$ (uranium(IV)). As shown by Figure 2, the 8-coordinated complexes give completely different spectra from those of 6-coordinated complexes. The differences, however, between dodecahedral and square antiprismatic stereochemistry are not very appreciable and therefore a correct identification of these two stereochemistries from spectral data alone is precluded.[35] (Figure 2).

It has been reported, from the analysis of the absorption spectra of some uranyl complexes at 77°K, that the intensities and the position of the electronic transitions are principally determined by the geometry

TABLE I. Oxidation States of the Actinides and Lanthanides.[a]

	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
2							○			○	○	○	○	○	
3	▲	○	○	○	○	○	▲	▲	▲	▲	▲	▲	▲	▲	▲
4		▲	○	○	○	▲	○	○	○						
5			▲	○	▲	○	○								
6,				▲	○	○	○								
7					○	○									
	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
2				○		○	○						○	○	
3	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
4		○	○						○						

[a] ▲ = The most stable oxidation state. ○ = Other known oxidation states.

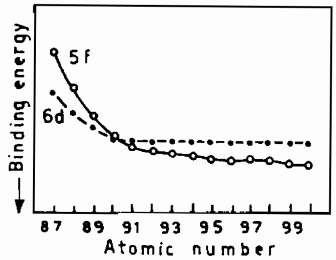


Fig. 1. Qualitative representation of electron binding energies in the heaviest elements (J. J. Katz and G. T. Seaboeg, "The Chemistry of the Actinide Elements", Methuen, London (1957) p. 465).

of the equatorial coordination of the uranyl(VI) ion, the chemical nature of the ligands influencing only the vibrational structure of the spectra.[86] However, even if such a correlation is theoretically possible, other observations at 4.2 °K do not confirm unequivocally this interpretation.[65]

3. Molecular Polyhedra of Complexes of the Actinide Ions

The coordination polyhedra of the actinide ions have been extensively investigated and sufficiently well characterized in the solid state especially by X-ray investigations, while ambiguities remain in solution, where a more complicated system takes place.[136] These ions generally present very high coordination numbers. The coordination number of less than six is discouraged by size of metals, with the exception of complexes with particular ligands such as $N(SiMe_3)_2^-$,[31] NEt_2^- [109,184] which stabilize low coordination numbers.

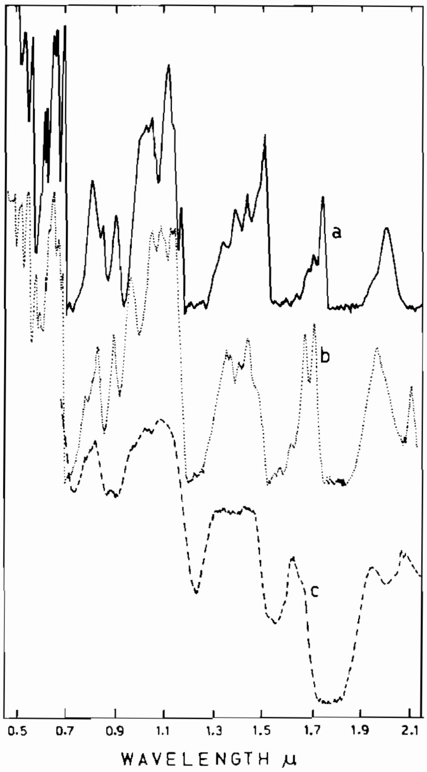
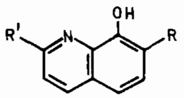
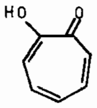
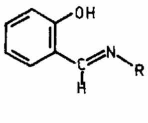
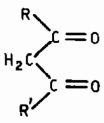


Fig. 2. The electronic spectra of: a) α-U(acac)$_4$ at 77 °K, b) β-U(acac)$_4$ at 77 °K, c) U(DBM)$_4$ at 300 °K.

The hexacoordination is usually found for actinides in their highest oxidation state, which corresponds to a minimum ionic radius; hepta, octa and nona-coordinations are more common. Obviously the type of polyhedron obtainable is influenced by the nature of the ligand and the configuration

TABLE II. Geometric Features of Ligands and the Related Complexes Obtained.

Ligand	Donor Atoms	Bite, Å	Ligand Configuration	Oxidation States of Actinides	Types of Complexes reported[a]
	O‿N	2.6	Planar R,R′ = H, aryl or alkyl group	3 4 5 6	$M(Ox)_3$ [unknown]. $M(Ox)_4$ [8]; $M(Ox)_4L$ [9]; $M(Ox)_4HOx$ [9]. $MO_2(Ox)\cdot xH_2O$ [unknown]; $MO_2(Ox)(HOx)_2\cdot 2H_2O$ [unknown]. $MO_2(Ox)_2$ [7]; $MO_2(Ox)_2HOx$ [7]; $MO_2(Ox)_2L$ [7]; $MO_2(Ox)_3^-$ [8].
	O‿O	2.6	Planar	4 5 6	$M(trop)_4$ [8]; $M(trop)_4L$ [9]; $M(trop)_4Htrop$ [9]; $M(trop)_5^-$ [10]. $M(trop)_4X$ [9]. $MO_2(trop)_2$ [7]; $MO_2(trop)_2L$ [7]; $MO_2(trop)_2Htrop$ [7].
	O‿N N‿N	2.9 2.9	Planar R = aryl, alkyl, $-CH_2-CH_2-N(CH_3)_2$, N-aryl or -alkyl salicylaldimine	4 6	$M(TSB)_4$ [8 proposed]; $M(TSB)L_2Cl_2$ [8 proposed]. $MO_2(BSB)_2L$ [7]; $MO_2(TRSB)_2$ [7]; $MO_2(TSB)L$ [7]; $MO_2(PSB)$ [7].
	O‿O	2.7	Planar R,R′ = aryl or alkyl group	3 4 5 6	$M(\beta\text{-dike})_3$ [7]; Cs $M(\beta\text{-dike})_4$ [8]. $M(\beta\text{-dike})_4$ [8]; $M(\beta\text{-dike})_4L$ [9]. $M(OEt)_{5-x}(\beta\text{-dike})_x$ [unknown]. $MO_2(\beta\text{-dike})_2L$ [7]; $MO_2(\beta\text{-dike})_2(\beta\text{-Hdike})$ [7]; $MO_2(\beta\text{-dike})_2$ [7].

[a] The coordination number found or proposed is reported in parenthesis [ ]. Abbreviations: (PSB) = pentadentate Schiff base; (TSB) = tetradentate Schiff base; (TRSB) = tridentate Schiff base; (BSB) = bidentate Schiff base; L = neutral monodentate ligand.

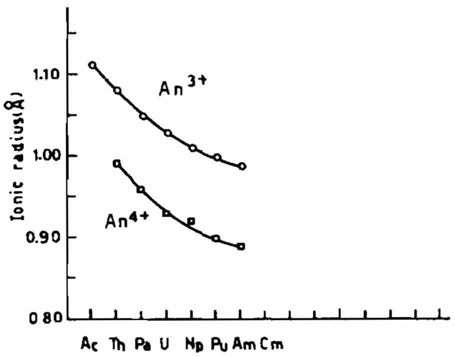


Fig. 3. The ionic radius of actinides in the 3+ and 4+ oxidation state against their atomic number.

geometries theoretically attainable with monodentate ligands provide the most illuminating basis for the stereochemical discussion of experimentally preparable complexes. However we consider in the present review only the polyhedra generated by bidentate or polydentate ligands with oxygen or nitrogen donor atoms, because they have received the greatest attention and have been studied in more details.

These ligands may be distinguished by their rigidity, coplanarity, distance of the donor atoms (bite); the more compact the ligand and the smaller the bite, the more effective the ligand in generating high coordination structures. Very compact ligands are the peroxo group (bite 1.5 Å) and nitrato group (2.1 Å).[123]

The difference of the bite and the type of complexes formed for the examined ligands is given in Table II.

For the tropolonato and oxinato adducts of actinides(IV), a ten-coordination has been reported, while for β-diketonato and salicylaldiminato an eight-coordination; only for thorium(IV) have nine-coordinated complexes of the type $Th(acac)_4L$ been reported.[24,165] Uranyl(VI) ion reaches in the tropolonato and oxinato complexes also the eight-coordination, while with β-diketonato and salicylaldiminato adducts it reaches the maximum value of seven. In the oxinato and tropolonato ligands the more compact planar conformation and the minor intraligand repulsion factor allow a higher coordination number.

The metal ion size and charge offer two other parameters to be considered in the type of the obtainable complexes.

In Figure 3 we report the ionic radius of actinides in various oxidation states against their atomic number.

The contraction of ionic radius with increasing atomic number is connected to the maximum obtainable coordination number; with tropolonato and 8-hydroxyquinolato ligands it is possible to prepare thorium(IV) and uranium(IV) ten-coordinated complexes and only eight-coordinated complexes of neptunium(IV) and plutonium(IV).

A. Seven-coordination

The theoretically possible polyhedra consistent with this coordination number are reported in Fig. 4.

It has been pointed out that the energy differences between the different shapes are small compared with the intermolecular forces generated by ordering.[136]

For the actinidyl(VI) ions one polyhedron only must be taken into account, and it is given by the pentagonal bipyramid – which only allows the *trans* O–M–O group to be linear. Most complexes exhibit a mononuclear pentagonal bipyramidal geometry but polynuclear configurations have been found also; in this case the ligand oxygens bridge two metals. Typical examples are given by $UO_2(acac)_2$,

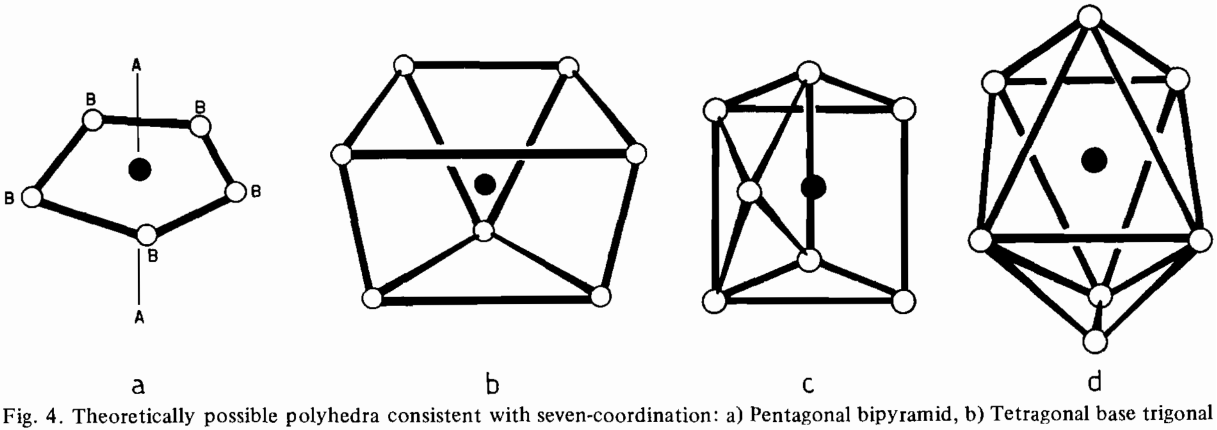


Fig. 4. Theoretically possible polyhedra consistent with seven-coordination: a) Pentagonal bipyramid, b) Tetragonal base trigonal base, c) Capped trigonal prism, d) Capped octahedron.

$UO_2(trop)_2$ and very probably by $PuO_2(trop)_2$; also the complex UO_2(salen) is stabilized by analogous types of bridges.

For the actinides in other oxidation states, the linear arrangement typical of MO_2^{2+} group is not present and even if a variety of seven-coordinated complexes would be found, the size and charge of metal ions discourage such a geometry; a higher coordination number is probably reached in the complexes for which a seven-coordinated structure would be formally proposed.

Neutral chelate complexes of the type Am(diketone)$_3$ are reported to be seven-coordinated; Am(THD)$_3$ is dimeric with each metal ion surrounded by seven oxygen atoms. Its coordination polyhedron is given by a capped trigonal prism[70] (Figure 5).

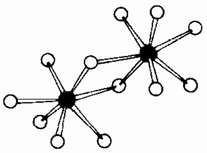


Fig. 5. The dimeric configuration of Am(THD)$_3$.

B. Eight-coordination

The possible configurations of octa-coordination, which is very common in the actinide complexes examined, are given in Fig. 6.

The cube, for its simplicity, may be assumed to be the basic polyhedron for eight-coordination. However this type of coordination has never been obtained for the actinide complexes with the ligands here examined; such a polyhedron is present in complexes of the type $(NEt_4)_4[U(NCS)_8]$, $(NEt_4)_4[U(NCSe)_8]$ or $(NEt_4)_4[Pa(NCS)_8]$ and $(NEt_4)_4[Pa(NCSe)_8]$; cubic coordination may exist for uranium in Na_2UF_8.

The hexagonal bipyramid is characteristic of actinidyl(VI) complexes, where the apical positions are occupied by oxygen atoms.

In the square antiprism all eight sites are equivalent; the dodecahedron is composed of two interpenetrating bisphenoids, such that the eight sites are divided into symmetrically equivalent sets of four, A and B respectively (Fig. 6).

Two parameters must be considered in the antiprism; they are called *s* and *l* and the shape of the antiprism is determined by the ratio *l*:*s* or alternatively by the angle ϑ made by the vector from the central atom to one of the ligands with the axis. On the contrary three parameters are required to specify the shape of the dodecahedron: ϑ_A and ϑ_B, which are the angles between the $\bar{4}$ axis with

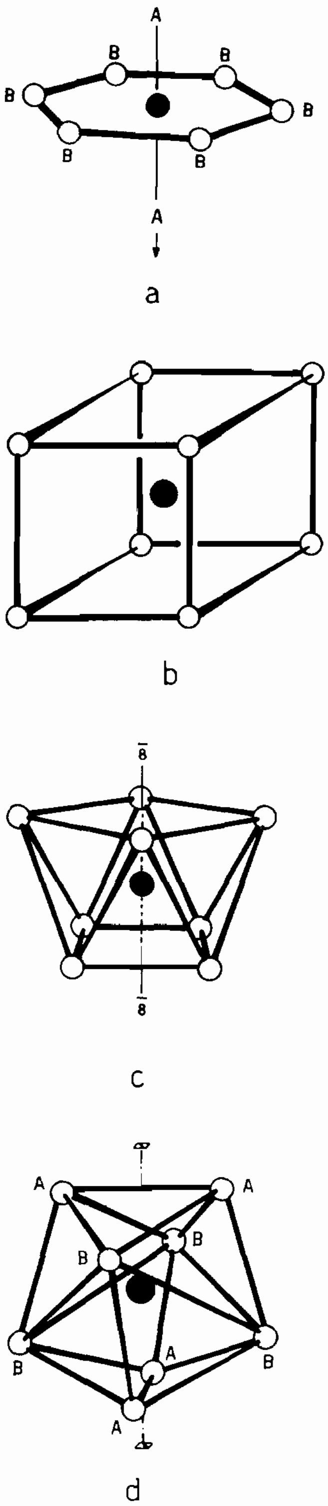


Fig. 6. Theoretically possible polyhedra consistent with eight-coordination: a) Hexagonal bipyramid, b) Cube, c) Square antiprism, d) Dodecahedron with triangular faces.

M–A and M–B vector, and the ratio of the bond lengths r_A/r_B. There are nine possible stereoisomers for M(symmetrical bidentate ligand)$_4$: three for the square antiprism and six for the dodecahedron.

For neutral tetrakis complexes the D_2 or D_{2d} isomers are preferred, these configurations minimising the ring strain in the ligands.

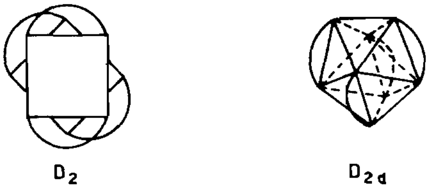


Fig. 7. The two most usual isomers preferred by neutral tetrakis complexes.

The D_2 symmetry has been found in the α and β form of thorium and uranium tetrakis(acetylacetonato) while the D_{2d} is present in U(DBM)$_4$.

The structure in the solid state, however, is not always maintained in solution and n.m.r. studies on diketone derivatives of uranium(IV) have shown a symmetry in solution less than D_2 or D_{2d}. In solution a more flexible framework, in which a rapid intramolecular distorsion from one of the stereochemical configurations to another can occur, must be considered and in Fig. 8 it is shown how slight distortions can convert a cubic isomer into a square antiprism or into a dodecahedron.

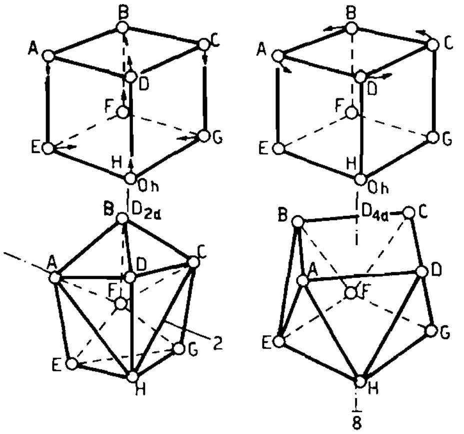


Fig. 8. The two most important ways of distorting the cube to produce a square antiprism or a dodecahedron.

The hexagonal bipyramid has two sets of non equivalent ligand sites A and B and its shape is specified by the ratio of bond lengths r_A/r_B. This polyhedron is not energetically favoured and has been found only when a O–M–O linear group is present. Such configuration has been proposed for $UO_2(Ox)_3^-$ even if no structural data are available.

C. Nine- and Ten-coordination

The types of polyhedra compatible with the nine-coordination are reported in Fig. 9.

The D_{3h} tricapped trigonal prism is the most usual and stable polyhedron and has been found in many transition metal complexes; generally it is defined by hybridisation of one *s*, three *p* and five *d* orbitals and it is significant therefore that the only known examples of the less favourable capped square antiprism are confined to lanthanide and actinide complexes.

For complexes of the type [M(bidentate ligand)$_4$ (monodentate ligand)] with a capped square antiprism configuration, seven isomers are possible. Th(trop)$_4$(dmf) and Th(Ox)$_4$(dmso) are two examples of this polyhedron.

In the Th(trop)$_4$(dmf) the monodentate ligand occupies a vertex adjacent to the cap (C_s symmetry)

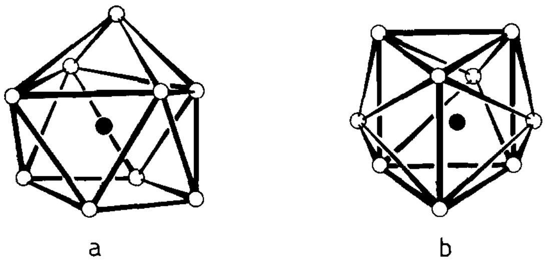


Fig. 9. Theoretically possible polyhedra consistent with nine-coordination: a) Capped square antiprism, b) Symmetrically tricapped trigonal prism.

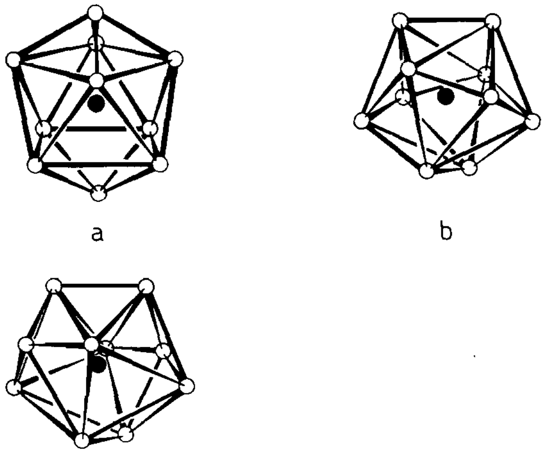


Fig. 10. Theoretically possible polyhedra consistent with ten-coordination: a) Bicapped square antiprism, b) Bicapped dodecahedron, c) C_{2v} polyhedron based on dodecahedron.

while in the complex $Th(Ox)_4(dmso)$ the monodentate occupies the cap above one of the square faces of the antiprism (C_{4v} symmetry). No examples of C_1 symmetry are available at the moment.

For ten-coordination three polyhedra must be considered as shown in Fig. 10.

No structural data are available with the ligands here investigated at the moment and a ten-coordination has been proposed only for complexes of the type $[M(trop)_5]^-$ (M = U, Th, Pa) and $[Th(Ox)_5]^-$.

4. Tropolonato Complexes

A. Tropolonato Complexes with Actinides(VI)

Tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) can be regarded as the enolic form of a cyclic α-diketone; its ability to form very stable solid complexes with the uranyl ion in the ratio 2:1 and 3:1 has been pointed out[68] and complexes of the type $UO_2(trop)_2$ and $UO_2(trop)_2Htrop$ have been reported[147] (Table III).

The yellow-orange compound $UO_2(trop)_2Htrop$ was easily prepared by reacting uranyl salts and tropolone (molar ratio 1:4) in methanol and drying the precipitate at 80 °C. Thermogravimetric analysis of the compound indicates that the neutral molecule of tropolone is lost at 155 °C and that $UO_2(trop)_2$ is obtained. $UO_2(trop)_2Htrop$ is reported as a seven-coordinated compound in the solid state, while in dimethylsulphoxide it is unstable and liberates a molecule of tropolone, very probably with the formation of the adduct $UO_2(trop)_2(dmso)$.

More difficult is a correct discussion of the $UO_2(trop)_2$ complex obtained by Plymale and Smith from the reaction in methanol between stoichiometric amounts of uranyl salts and tropolone,[147] because more recently some different conclusions have been reported.[64a] The complex, according to these latter results, must be formulated as $UO_2(trop)_2(MeOH)$. Such a complex remains unchanged on heating at 80 °C, the methanol being evolved in the temperature range 142–172 °C. The resulting $UO_2(trop)_2$ is stable and non-hygroscopic and when treated with benzene (0.02% H_2O) yields a second form of $UO_2(trop)_2$ which contains variable amounts of H_2O. These two $UO_2(trop)_2$ complexes are insoluble in inert organic solvents and on the basis of their physico-chemical properties they have been reported to be not monomers in the solid state. Taking into account that the most probable coordination number for the uranyl ion in the equatorial plane is five, two possible structures have been proposed (Figure 11). The structure a in Fig. 11 is reported as more stable and assigned to the complex $UO_2(trop)_2$ on the basis of its stability in water and the easy transformation of $UO_2(trop)_2xH_2O$ into $UO_2(trop)_2$ on dehydrating.

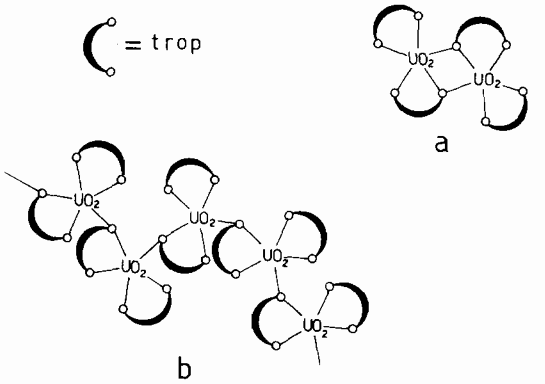


Fig. 11. The two polymeric configurations proposed for the two forms of $UO_2(trop)_2$.

TABLE III. Some IR Data (cm^{-1}) of Actinide(VI) Tropolonato Complexes.

Complex	ν_3(O–M–O)	Some Characteristic Absorptions of Coordinated Neutral Ligand	Reference
$UO_2(trop)_2$	912	–	64a
$UO_2(trop)_2 \cdot xH_2O$	915	3600–3000 ν(OH)	64a
$UO_2(trop)_2EtOH$	906	–	64a
$UO_2(trop)_2py$	904	–	64a
$UO_2(trop)_2dmso$	896	1018 ν(S=O)	64a
$UO_2(trop)_2pyN–O$	898	1212 ν(N–O)	64a
$UO_2(trop)_2H_2O$	906	3350, 3200 ν(O–H); 1663 δ(OH_2)	64a
$UO_2(trop)_2CyO$*	914	1696 ν(C=O of CyO)	64a
$UO_2(trop)_2PhNH_2$	899	3500–3200 ν(NH); 1616 δ(NH_2)	64a
$UO_2(trop)_2Ph_3PO$	899	–	64a
$UO_2(trop)_2Htrop$	929	–	147, 148
$PuO_2(trop)_2$	921	–	148
$PuO_2(trop)_2Htrop$	922	–	148

*CyO = cyclohexanone.

The polymeric form b could represent the configuration of $UO_2(trop)_2xH_2O$, the presence of water stabilizing this structure by hydrogen bonding between some of the chelate oxygen atoms.

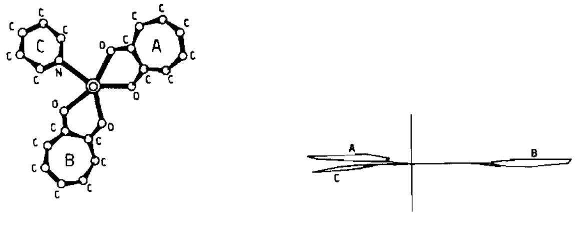
The three complexes $UO_2(trop)_2(MeOH)$, $UO_2(trop)_2$ and $UO_2(trop)_2xH_2O$ react with neutral monodentate ligands (L), containing an oxygen or a nitrogen donor, in anhydrous benzene to give $UO_2(trop)_2L$ adducts. For $UO_2(trop)_2py$ and $UO_2(trop)_2(EtOH)$, a complete X-ray investigation has been carried out.[26,52] The former complex crystallized with monoclinic symmetry in the space group I2/a with eight molecules in a unit cell. The stereochemistry of the complex is shown in Fig. 12.

Four tropolonato oxygens and the nitrogen of the pyridine are coordinated in the plane perpendicular to the linear uranyl group, so that the coordination geometry around the uranium atom is pentagonal bipyramidal. Fig. 12b shows that the ligand molecules are individually approximately planar and slightly twisted out of the coordination plane.[26]

In the case of $UO_2(trop)_2(EtOH)$, the coordination plane perpendicular to the uranyl group consists of the four oxygen atoms of the two tropolonato and the oxygen atom of the ethanol molecule, forming a slightly irregular pentagon (Fig. 13).

The hydrogen atom of the ethanol forms a weak hydrogen bond with the oxygen atom of tropolone of a neighbouring molecule. This explains the absence of the stretching frequency νOH in the range 3600–3100 cm^{-1} in the i.r. spectrum of this complex as in the $UO_2(trop)_2(MeOH)$ which is, probably, in an analogous configuration. For $UO_2(trop)_2L$ (L = monodentate ligand) adducts, an index of coordinating ability of the ligands toward the $UO_2(trop)_2$ substrate has been reported;[64b] the sequence of relative stability by u.v. data is given by: $ROH < py < dmso < pyN \rightarrow O < Ph_3PO < Ph_3AsO$.

The preparation of $PuO_2(trop)_2Htrop$ has been also reported;[148] it may be easily obtained by reaction between plutonyl(VI) nitrate and tropolone in a molar ratio 1:4. The visible spectrum in dimethylformamide or dimethylsulphoxide confirms the hexavalent oxidation state of the plutonium. This complex exhibits an infrared spectrum and an X-ray powder pattern very similar to $UO_2(trop)_2Htrop$; this suggests a seven-coordination for the plutonium(VI) ion with two bidentate and one monodentate tropolone ligands in the solid state. More difficult is a correct formulation of the complex reported as $PuO_2(trop)_2$, obtained by reaction of the stoichiometric amount of plutonyl(VI) nitrate and tropolone (1:2); as the complex has been recrystallized from dimethylsulphoxide, probably its composition is $PuO_2(trop)_2(dmso)$.



a b

Fig. 12. Projection of $UO_2(trop)_2Py$ on the mean equatorial plane (a) and down a direction perpendicular to the uranyl group (b).

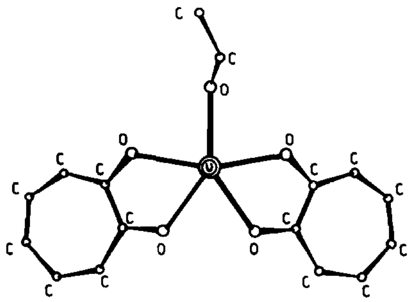


Fig. 13. The molecular configuration of $UO_2(trop)_2EtOH$.

B. Tropolonato Complexes of Actinides(IV)

The tetrakis chelate of thorium(IV) $Th(trop)_4$, prepared by mixing thorium tetrachloride and tropolone in molar ratio 1:4 in a chloroform solution, is isomorphous to $Ce(trop)_4$ and sublimes without significant degradation.[135] In the gaseous state it seems reasonable that an eight-coordination is reached and physico-chemical data are strongly indicative of a complex in which all four ligands are equivalent in solution and in the solid state. The analogous uranium tetrakistropolonato may be easily prepared by the reaction of an aqueous solution of UCl_4 with tropolone. Tetrakisisopropyltropolonates of thorium(IV) and uranium(IV) have also been prepared in a similar way.[162]

The tetrakistropolonato derivatives of thorium readily form adducts with nucleophilic or basic molecules, including water, to form nine-coordinate thorium complexes; thus the electron-acceptor activity of thorium is evidenced by the formation with dimethylsulphoxide of the $Th(trop)_4(dmso)$ complex.[134]

$Pu(trop)_4$ has been prepared by mixing plutonium(IV) nitrate and tropolone in methanol and $Np(trop)_4$ may be prepared from tropolone dissolved in CH_2Cl_2, CH_3CN or alcohol and $NpCl_4$.[34,148]

Protoactinium(IV) tetrachloride reacts with four molecular equivalents of lithium tropolonate to give the blue–green solid $Pa(trop)_4$, very unstable in atmosphere.

TABLE IV. IR Data (cm^{-1}) for Actinide(IV) Complexes with Tropolone.

Compound	ν(C=O)	ν(C=C)	Other Characteristic Bands	Colour
$Th(trop)_4$	1592	1512		White
$Pa(trop)_4$	1591	1513		Blue–green
$U(trop)_4$	1592	1512		Reddish-brown
$Np(trop)_4$	1591	1512		Brown
$Pu(trop)_4$	1590	1513		Red–brown
$Th(trop)_4dmf$	1585	1507	1650 ν(C=O dmf)	Pale yellow
$Pa(trop)_4dmf$	1590	1512	1652 ν(C=O dmf)	Blue–green
$U(trop)_4dmf$	1588	1510	1653 ν(C=O dmf)	Brown
$U(trop)_4dmso$	1592	1513	1040 ν(S=O dmso)	Brown
$LiTh(trop)_5$	1595	1518		Pale yellow
$LiPa(trop)_5$	1593	1517		Blue–green
$LiU(trop)_5$	1592	1517		Brown

The tetrakistroplonato adducts of the Th, U, Pa react with lithium tropolonate to yield $Li[M(trop)_5]$, the most convenient preparation employing oxygen free dimethylsulphoxide as solvent, while neither $Np(trop)_4$ nor $Pu(trop)_4$ react with lithium tropolonate. This has been explained as a consequence of the actinide contraction, neptunium(IV) (ionic radius 0.92 Å) and plutonium(IV) (ionic radius 0.90 Å) being too small to surround five molecules of tropolone. It is thus obvious that $Pu(trop)_4$ and $Np(trop)_4$ can be recrystallized unchanged from dimethylformamide, while $Th(trop)_4$ and $Pa(trop)_4$ form isostructural 1:1 adducts of the type $M(trop)_4dmf$. The structural conformation analysis of $Th(trop)_4dmf$ has been carried out and the polyhedron of coordination observed in this complex is a monocapped square antiprism (Figure 14, Table IV).

The species $Li[M(trop)_5]$ (M = Th, U, Pa) are reported as examples of ten-coordination; they are highly associated in a saturated chloroform solution. Electronic spectra of $U(trop)_4$ and $Li[U(trop)_5]$ in dmso or dmf are substantially identical, indicating that reactions of the type:

$$U(trop)_4 + n\ dmso \rightarrow U(trop)_4 \cdot n\ dmso$$

$$Li[U(trop)_5] + n\ dmso \rightarrow U(trop)_4 \cdot n\ dmso + Li^+ + trop^-$$

take place. However, when the spectra of $U(trop)_4$ and $Li[U(trop)_5]$ are carried out in nujol mull, where no reaction is expected, the spectra of the two adducts are very different at room temperature and at 77 °K.[162]

C. Tropolonato Complexes with Actinides in Other Oxidation States

Substantially only the protoactinium(V) complexes of the type $Pa(trop)_4X$ (X = Cl, Br) have been obtained by reaction of PaX_5 or of $PaOX_3$ with an excess of the ligand in dichloromethane. The preparation of $Pa(trop)_5$ from $Pa(trop)_4X$ and Litrop failed because the protoactinium(V) ionic radius (0.90 Å) appears to be too small to form a pentakis-complex and only $Pa(trop)_4OEt$ may be obtained. This last adduct reacts with $HClO_4$ to form $Pa(trop)_4ClO_4$.

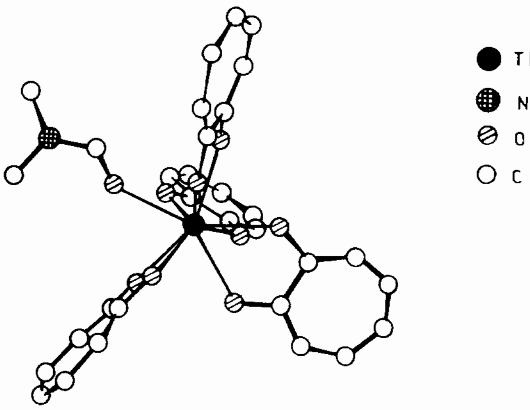


Fig. 14. The molecular structure of $Th(trop)_4dmf$.

All the protoactinium(V) tropolonato adducts are air stable. Dark-red crystals may be obtained when $Pa(trop)_4Cl$ is dissolved in hot dmso and precipitated with isopentane or CH_2Cl_2. This adduct has been formulated as Pa(trop)Cl·dmso and the νSO, which lies at 1045 cm^{-1}, indicates a very weak lattice interaction.

The infrared spectra of all the actinide tropolonato complexes show a very sharp band at around 505 cm^{-1}, not present in the spectrum of sodium tropolonate. This band has been tentatively associated with the M–O (tropolonate) vibrations.

5. β-Diketone Complexes

A. β-Diketone Complexes with Actinides(VI)

Numerous uranyl complexes with β-diketones and related dicarbonyl compounds have been reported.

TABLE V. IR Data (cm^{-1}) for Pa(V) Complexes with Tropolone.

Compound	ν(C=O)	ν(C=C)	ν(S=O)	$\nu(ClO_4)$	Color
$Pa(trop)_4Cl$	1592	1523			Yellow
$Pa(trop)_4Br$	1590	1520			–
$Pa(trop)_4ClO_4$	1592	1522		1120 1100	Yellow
$Pa(trop)_4OEt$	1593	1518			Yellow
$Pa(trop)_4Cl \cdot dmso$	1591.	1520	1045		Reddish-yellow

Although they can be obtained with the stoichiometric composition $UO_2(\beta\text{-dike})_2$.[25,87,152,157] they are more usually obtained as $UO_2(\beta\text{-dike})_2L$ (L = monodentate ligand).[56,188] The monohydrate $UO_2(acac)_2 \cdot H_2O$ has been prepared by slow addition of an aqueous solution of NaOH to a warm aqueous solution containing equivalent quantities of uranyl nitrate and acetylacetone. Three different crystalline forms of this complex were found, two of which yellow monoclinic and orthorhombic and one red orthorhombic. These three crystalline forms only differ for the cell dimension and the spatial group. The red form is unstable and changes into the yellow forms in air or in dichloroethane.

The structure of the yellow monoclinic complex $UO_2(acac)_2 \cdot H_2O$ has been reported.[78,79] The polyhedron of coordination is a bipyramid with seven oxygen atoms localized at the corners. The pentagonal basis of the bipyramid is formed by the four oxygens belonging to the chelate rings and the oxygen of water molecule (Figure 15).

No structural data are available for the red form of the monohydrate complex. The electronic and i.r. spectra for the three monohydrate complexes do not account for the difference in the colour of the compounds, being almost identical. The photoelectron spectrum of $UO_2(acac)_2 \cdot H_2O$ has been recorded at 190 °C.[57] At this temperature the molecule of water is still present in the target chamber, consequently the band at 2.74 eV could be due to oxygen lone pairs of the water. The bands at 8.42 eV and 9.66 eV must be assigned to the b_{1g}, b_{2u} and b_{3u}, b_{1u} levels of the ligands respectively. The following bands at 10 and 11 eV can be suspected to derive from nonbonding electrons and probably connected with molecular orbitals mainly localized on the oxygens of the uranyl group.

$UO_2(acac)_2 \cdot H_2O$ is readily dehydrated at 100 °C under vacuum to give the anhydrous $UO_2(acac)_2$. The anhydrous compound cannot be represented by a tetracoordination in the equatorial plane. Ebullioscopic measurements in benzene solution show that the compound is dimeric. It has been proposed that the dimer may be held together by coordination of acetylacetone oxygen atoms of the adjacent uranyl compound as in Fig. 16.

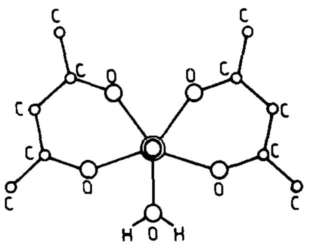


Fig. 15. The molecular configuration of $UO_2(acac)_2H_2O$.

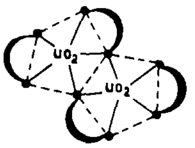


Fig. 16. The proposed configuration of $UO_2(acac)_2$.

$UO_2(acac)_2$ readily forms adducts with neutral ligands containing nitrogen or oxygen as donor atoms.[25,90] This, together with the dimeric nature of the anhydrous complex, is a clear indication that $UO_2(acac)_2$ is coordinatively unsaturated.

The infrared spectra of these adducts[137,151] show a very strong band attributed to the antisymmetric ν_3(O–U–O) in the range 910–900 cm^{-1}; a second band of low intensity, attributed to the symmetric vibration of the uranyl group, is sometimes present in the range 830–828 cm^{-1}.

The U–O stretching of the uranium–oxygen bond of acetylacetonato is found in the range 550–400 cm^{-1}.[137] A series of complexes of the type $UO_2(acac)_2L$ were studied by thermogravimetric methods and by differential thermal analysis.[188] In all these complexes, the monodentate ligand is evolved by a one-step process; the monodentate ligands, containing an oxygen donor atom, begin to come off in the 83°–107°C temperature range, followed by the decomposition of the anhydrous complex in the range 190–227 °C. For complexes with monodentate ligands containing a nitrogen donor atom the decomposition temperatures were much higher.

The adduct obtained in the presence of ammonia for pH control has been investigated. It was previously formulated as $UO_2(acac)_2NH_3$[152] and $(NH_4)[UO_2(acac)_3]$.[90] Elemental analysis and the low molar conductivity (0.5 ohm^{-1}) exclude these formulations, the compound being correctly formulated as the β-ketoamine adduct in Fig. 17.[91,92]

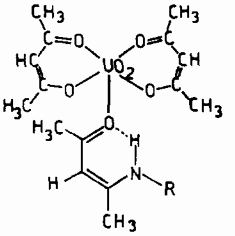


Fig. 17. The configuration of $UO_2(acac)_2(acacNHR)$.

By direct reaction between uranyl acetylacetonate and ammonia, the same β-ketoamine adduct is obtained. This formulation is in agreement with the i.r. and ^1H nmr spectra[92] (Tables VI and VII).

Replacement of ammonia by a wide variety of primary or secondary aliphatic amines yields similar β-ketoamine adducts, while tertiary amines yield the normal product $UO_2(acac)_2NR_3$.[92] Uranyl dibenzoylmethane yields only the normal adduct $UO_2(DBM)_2NHR$.[92]

A large series of uranyl β-ketoenolates have been prepared and their properties discussed on the basis of infrared and electronic spectra.[137,151,152,153,157]

The complexes of the type $UO_2(\beta\text{-dike})_2H_2O$ are soluble only in organic solvents containing oxygen or nitrogen atoms capable of electron donation; they are sparingly soluble or insoluble in CCl_4 or CS_2. This behaviour leads to the assumption that the interaction occurs by direct coordination of the solvent molecules to the central atom as for $UO_2(acac)_2H_2O$. In $UO_2(\beta\text{-dike})_2xH_2O$, where x varies from 1 to 2.8, the water is strongly bound and is eliminated only with difficulty. The electronic spectra of all the uranyl β-diketone complexes have the same shape, scarcely affected by the nature of the solvent. Three bands are present in the regions 240–280, 303–340 and 376–403 nm respectively. The first two correspond to those of the complexing agent, even if they are shifted to lower and higher wavelengths. The shift of the original bands of the free ligand in the spectra of the complexes can be ascribed to polarization suffered by the ligands as a consequence of the coordination around the uranium central atom. The third band, absent in the spectra of β-diketones, is due to the uranyl group.[19,149,153]

The uranyl β-diketones are particularly suited to an i.r. investigation because of the reliability with which the more significant vibrations may be assigned and the versatility with which they form base adducts. So the influence in the i.r. spectra has been investigated varying the chelate ring substituents (R_1, R_2, R_3 in Fig. 18), varying the adducted base B, and varying the substituent R in an adducted pyridine molecule.[93]

Since the ligand orbitals of the β-diketone group are theoretically, energetically and occupationally suitable for participation in both (U→L) donor and (L→U) acceptor π-interaction with the uranyl ion, electron withdrawing substituents will decrease the donor ability of the carbonyl group. This is evidentiated by the high ν(C–O) values in uranyl trifluoroacetylacetonates and it is a general feature of all transition and non-transition metal β-ketoenolates comprising electron withdrawing substituents.[97] At the same time, U–O bonding will be facilitated by such substituents, leading to a positive contribution to ν(U–O). Conversely, electron releasing substituents will increase the σ-bonding and facilitate O→U σ-bonding, both effects providing a positive contribution to ν(U–O). This is evidentiated by the monotonic increase in the ν(U–O) values with electron releasing ability of the substituents.

Electron releasing pyridine substituents will increase the donor ability of the heterocyclic nitrogen atom and the resulting increased ligand field strength will shift ν(U–O) to lower frequencies. Accordingly ν_3(O–U–O) exhibits a marked decrease for strongly electron releasing substituents; however this shift is not significantly sensitive to the range of substituents with positive σ.

Electron releasing β-ketoenolato substituents lead to a decrease in both ν(O–U–O) and ν(C–O). ν(C–O) exhibits similar substituent sensitivity within each series of complexes; ν(U–O) is especially sensitive to the substituent in the anhydrous complexes. It has been suggested that in the adducts the electronic effects of the substituents influence not only the electron density in the chelate ring and O–U–O bonds but also within the adducted molecule. This was substantiated by the nmr spectra of the complexes $UO_2(\beta\text{-dike})_2py$. The nmr spectra show that β-ketoenolato substituents, which lead to deshielding of the pyridine proton in the 4-position, shield the proton in the 2-position and *vice versa*, while the 3-position is unaffected. It is also observed that the decrease in the ν_3(O–U–O) induced by electron releasing pyridine substituents is accompanied by an increase in both ν(U–O) and ν(C–O).

TABLE VI. IR Data (cm^{-1}) for Some Uranyl β-Ketoenolate Complexes with β-Ketoamines and Amines.[92]

Complex	$\nu_{as}NH$	ν_sNH	ν(C–O) (ketoam)	ν(C–O) (β-dike)	ν_3(O–U–O)
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)NH_2$	3372	3214	1585	1575	912
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)NHCH_3$			1612	1578	912
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)NHC_2H_5$			1605	1578	898
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)N(CH_3)_2$				1525	906
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)N(C_2H_5)_2$				1597	905
$UO_2(acac)_2 \cdot N(CH_3)_3$				1568	900
$UO_2(acac)_2 \cdot N(C_2H_5)_3$				1575	903
$UO_2(DBM)_2 \cdot NH_3$	3335	3260		1542	904
$UO_2(DBM)_2 \cdot NH_2CH_3$	3341	3281		1538	902
$UO_2(DBM)_2 \cdot NH_2C_2H_5$	3340	3280		1532	906

TABLE VII. ^{1}H Nmr Data (δ) for some Uranyl β-Diketoenolate Complexes with β-Ketoamines and Ammonia.[92]

Complex	N–H···O	>CH ring	>CH adduct	NH_3
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)NH_2$	10.80	5.80	5.31	
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)NHCH_3$	11.62	5.77	5.35	
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)NHC_2H_5$	11.52	5.77	5.31	
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)N(CH_3)_2$		5.77	5.42	
$UO_2(acac)_2 \cdot O{=}C(CH_3)CH{=}C(CH_3)N(C_2H_5)_2$		5.77	5.45	
$UO_2(acac)_2 \cdot N(CH_3)_3$		5.81		
$UO_2(acac)_2 \cdot N(C_2H_5)_3$		5.82		
$UO_2(DBM)_2 \cdot NH_3$		7.20		3.70

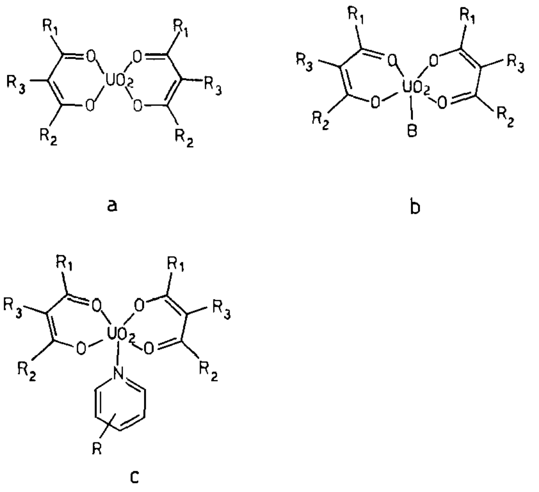


Fig. 18. Uranyl β-diketone adducts obtained varying R in β-diketone (a), the base B (b) and R in pyridine ring (c).

This implies that the transfer of negative charge to uranium which leads to increased electrostatic repulsion in the O–U–O bond and hence lowers ν_3(O–U–O), is partly relieved by U–O π-bonding.

Complexes of the type $UO_2(\beta\text{-dike})_2(4ZpyN{\rightarrow}O)$ have been investigated by i.r. and nmr spectroscopic techniques. The U–O stretching frequency in these complexes does not vary with the nature of the substituents of the amine N-oxide and thus the frequency is comparable to that of aquo complexes. No trend between the "substituent parameter" (σ) of the 4ZpyN→O and the chemical shift data of the proton nearest to the nitrogen atom has been observed in this type of complexes.[168] The middle proton of the β-diketones gives a single band and the chemical shift is a function of β-diketones only (Table VIII). In an attempt to find out whether sulphoxides, which have many similarities with phosphine oxides, act as synergists in the system UO_2/Hdiketones/sulphoxides, the complexes $UO_2(\beta\text{-dike})_2$(sulphoxide) have been studied.[169,170] The shift in the S–O stretching frequencies (47–100 cm^{-1}) indicates that the sulphoxides form a rather strong bond with the uranium; this shift is quite similar to the shift in the P–O stretching frequencies of the analogous complexes with tributylphosphate (TBP).[73] The chemical shift of the middle proton of the β-diketone in these complexes is insensitive to the donor ligands and is observed as a sharp band (Table IX).

Benzoylpicolinoylmethane (Hpicmet) and benzoylnicotinoylmethane (Hnicmet) form uranyl compounds of the type $UO_2(picmet)_2$ and $UO_2(nicmet)_2$. The nature of these complexes is polymeric, of the type shown in Fig. 19; this polymeric configuration well explains their insolubility and high thermal stability.[152]

These complexes with concentrated HNO_3 give $UO_2(Hpicmet)_2(NO_3)_2$ and $UO_2(Hnicmet)_2(NO_3)_2$,

TABLE VIII. ^1H Nmr Spectra (δ) of the Middle CH Proton of the β-Diketones for the Complexes $UO_2(\beta\text{-dike})_2$-4-Z-pyN–O.[168]

Z/ β-dike	H	CH_3	OCH_3	Cl	NO_2
TTA	6.95	7.03	7.03	7.04	7.05
BTA	7.13	7.18	7.15	7.19	7.23
BA	6.68	6.67	6.66	6.68	6.75
DBM	7.47	–	7.45	–	7.58
TAA	6.38	6.37	6.38	6.40	6.41
HFAA	6.78	6.82	6.79	6.82	6.87

where the nitrate groups are covalently bound to uranium; the same complexes may be also obtained by treating aqueous solutions of uranyl nitrate with alcoholic solutions of the β-diketones.

There are numerous reports on the preparation and characterization of uranyl–thenoyltrifluoroacetone complexes. These complexes have been synthesized in order to study the extraction of the uranyl(VI) ion from acid solution into nonaqueous media. The nature and the composition of uranyl–TTA complex in aqueous–alcoholic medium were investigated by spectrophotometric and potentiometric methods.[2] The ratio UO_2/TTA in the complex, in dilute solutions, is 2:3 in agreement with the bridged structure proposed in Fig. 20. There is no evidence of the existence in solution of a 1:2 complex.

The solid complex isolated from an aqueous–alcoholic solution has the composition $UO_2(TTA)_2\cdot 2H_2O$. The electronic spectra of $UO_2(TTA)_2\cdot 2H_2O$ and of the 2:3 complex formed directly in solution (50% alcohol) are identical, with maxima at 337 and 380 nm. This may indicate that $UO_2(TTA)_2\cdot 2H_2O$ exists as a 2:3 complex in this solution.

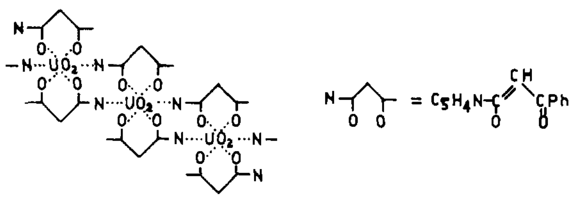


Fig. 19. The polymeric structure of $UO_2(\text{picmet})_2$.

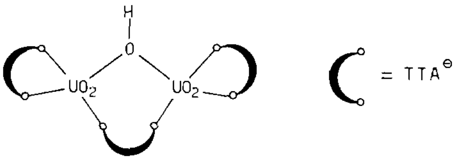


Fig. 20. The bridged structure proposed for $(UO_2)_2(TTA)_3OH$.

Two different yellow monoclinic forms crystallize from ethanol and methanol, their composition being $UO_2(TTA)_2\cdot EtOH$ and $UO_2(TTA)_2\cdot 3MeOH$ respectively, while the orange orthorhombic $UO_2(TTA)_2\cdot H_2O$ crystallizes from benzene or carbon tetrachloride.[17]

The yellow forms change color to orange on exposure to air at room temperature; X-ray analysis

TABLE IX. Characteristic IR (cm^{-1}) and ^1H Nmr (δ) Bands for Uranyl(VI) Complexes of the Type $UO_2(\beta\text{-dike})_2(\text{sulphoxide})$.[169,170]

Complex[a]	ν(C–O)	ν_3(O–U–O)	ν(S=O)	Chemical Shift γCH
$UO_2(acac)_2 2H_2O$	1570	910	–	5.83
$UO_2(acac)_2$dpso	1565	903	988	5.77
$UO_2(acac)_2$dbso	1570	909	980	5.85
$UO_2(acac)_2$dhso	–	–	–	5.76
$UO_2(TTA)_2 2H_2O$	1615, 1605	900	–	6.84
$UO_2(TTA)_2$dpso	1620, 1590	910	980	6.85
$UO_2(TTA)_2$dbso	1620, 1590	918	975	6.81
$UO_2(TTA)_2$dhso	1613, 1604	909	954	6.76
$UO_2(TTA)_2$diso	1613, 1601	914	962	6.78
$UO_2(DBM)_2 2H_2O$	1590	894	–	7.25
$UO_2(DBM)_2$dpso	1590	895	983	7.17
$UO_2(DBM)_2$dbso	1590	897	960	7.23
$UO_2(DBM)_2$dhso	1592	898	971	7.20
$UO_2(DBM)_2$diso	1592	900	963	7.21
$UO_2(BTA)_2$dhso	1613, 1598	911	946	6.97
$UO_2(BTA)_2$diso	1612, 1598	917	968	6.97
$UO_2(BA)_2$dhso	1592	898	957	6.50
$UO_2(BA)_2$diso	1592	899	977	6.48

[a] dpso = diphenylsulphoxide; dbso = dibenzylsulphoxide; dhso = dihexylsulphoxide; diso = diisopentylsulphoxide.

of this compound shows that it is identical with $UO_2(TTA)_2\cdot H_2O$; the orange orthorhombic complex changes to the yellow monoclinic one when exposed to atmosphere saturated with alcohol vapours.

The i.r. spectra of the monoclinic and orthorhombic complexes are different in the carbonyl stretching region: the yellow adducts show two bands, whereas the red a single band. Another interesting feature is the shift of the O–U–O asymmetric stretching (ν_3) from 940 cm^{-1} in $UO_2(TTA)_2\cdot EtOH$ to 891 cm^{-1} in the orthorhombic $UO_2(TTA)_2\cdot H_2O$. Similarly, the symmetric stretching (ν_1) shifts from 790 cm^{-1} $UO_2(TTA)_2\cdot 3MeOH$ and 800 cm^{-1} in $UO_2(TTA)_2\cdot EtOH$ to 828 cm^{-1} in $UO_2(TTA)_2\cdot H_2O$.

These shifts to higher and lower frequencies of ν_3 and ν_1 in the monoclinic forms can be ascribed to the presence of the molecules of bulky alcohol which could constrain the O–U–O group. Substitution of the alcohol by water relieves the strain and the shifts are reversed.

The coordinated water in $UO_2(TTA)_2\cdot H_2O$ can be substituted by monodentate ligands to give complexes of the type $UO_2(TTA)_2L$. There are conflicting reports[73,170] on the configuration of the complex $UO_2(TTA)_2(TBP)$; because two carbonyl peaks at about 1600 cm^{-1} are present in the i.r. spectrum, it was supposed that one TTA is monodentate, the peak at the higher frequency (1622 cm^{-1}) being ascribed to the free ketonic carbonyl function.

The splitting of the carbonyl band is not a proof of the presence of a monodentate diketone group since a similar splitting has been observed in some $M(TTA)_2$ compounds.[122] The position of this band in a β-diketone depends on the electronegativity of the substituents bound to the C=O group.

The CF_3 group, increasing the force constant of the carbonyl bond, shifts the C=O stretching of the fluorinated chelates to higher frequency,

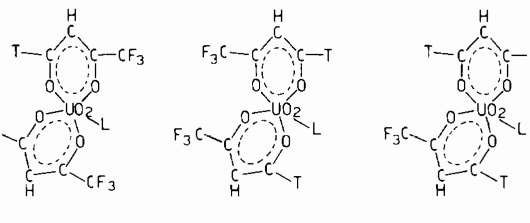
The ^1H n.m.r. spectrum of $UO_2(TTA)(TBP)$ shows only a single sharp line for the methynic middle proton of TTA. If a structure involving monodentate diketone is invoked for the complex, this proton should have two magnetically different environments; the i.r. and ^1H n.m.r. data indicate that both the β-diketones in this complex are bidentate.

The n.m.r. data show that for a given $UO_2(TTA)_2L$ complex the three different configurations in Fig. 21 are possible.

The *trans* and only one *cis* configurations have been found but there is no way of choosing the *cis* isomers only by n.m.r. data.

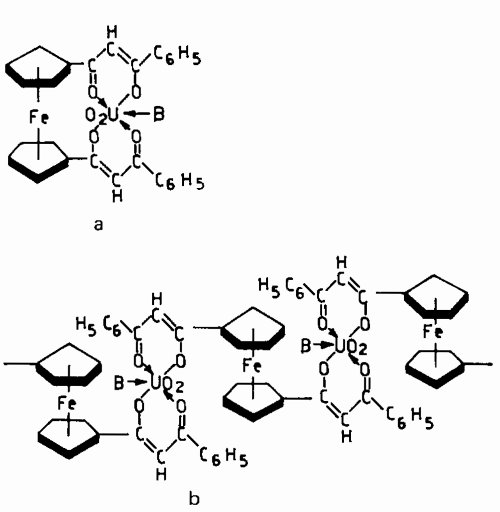
Ternary complexes of the uranyl(VI) ion with TTA and 1,10-phenanthroline (phen) or bipyridine (bipy) of composition $UO_2(TTA)_2\cdot phen$ and $UO_2(TTA)_2\cdot bipy$ have been prepared; no data except elemental analyses are available.[119]

A series of complexes derived from the reaction of uranyl(VI) nitrate with 1(phenylpropane-1,3-dione)ferrocene and 1,1′-bis(phenylpropane-1,3-dione)ferrocene have been prepared and characterized.[182] Two configurations for 1,1′-bis(phenylpropane-1,3-dione)ferrocene complexes are possible (Fig. 22).



cis (T T) cis (F_3F_3) trans

Fig. 21. The three possible configurations of $UO_2(TTA)_2L$.

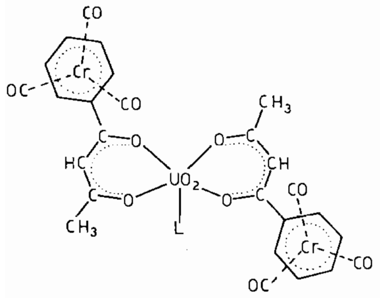


B = neutral monodentate ligand

Fig. 22. Monomeric and polymeric configurations possible for the uranyl complexes with 1,1′-bis(phenylpropane-1,3-dione)ferrocene.

Molecular weight data seem to exclude a monomeric configuration, and suggest a polymeric one. The coordination of uranyl ion to the β-diketone fragment of ferrocene does not influence the band centered at 510 nm due to the forbidden *d–d* transition on the iron atom. This suggests that direct interactions between iron and uranium atoms do not exist. Uranyl complexes with tricarbonylchromium benzoylacetone have been prepared;[44] the configuration of the complexes is reported in Fig. 23.

The two i.r. bands in the range 2200±1800 cm^{-1}, characteristic of the C–O carbonyl stretching, were not significantly affected by the coordination to uranyl of the β-diketone moiety; this suggests that



L = neutral monodentate ligand

Fig. 23. The configuration of $UO_2(Cr(CO)_3C_6H_5COCHCO\text{-}CH_3)_2L$.

also in the ligand the β-diketone is essentially in the enolic form.

Complexes derived from benzoylacetanilides[172] and pyridylacetoacetamide[98] have been characterized. Analytical and physico-chemical data indicate that the complexes have the general formula $UO_2(AA)_2L$ (AA = chelating ligand) essentially similar to those derived from β-diketones.

B. β-Diketone Complexes with Actinides(V).

This class of compounds is one of the largest groups of known uranium(V) compounds; however it is also poorly characterized since little more than elemental analysis and some physical properties are known.[161]

The complexes are all alkoxycompounds and may be prepared by treating uranium pentaethoxide with β-diketones or β-diketoesters in different molar ratio in benzene.[22,23]

The derivatives have the general formula $U(OEt_{5-x})L_x$ (L = β-diketone or β-ketoesters and x = 1,2,3). The failure to prepare tetra and pentasubstituted derivatives by refluxing the $U(OEt)_5$ with fivefold excess of ligand for several hours could be ascribed either to steric hindrance or to a saturated coordination state of the metal in the trisubstituted derivative. The β-diketone compounds will exchange their ethoxy groups with *t*-butoxy group when refluxed with *t*-butyl alcohol.

A single protactinium compound, the bright yellow $Pa(acac)_2Cl_3$, has been reported. This complex is prepared by treating $PaCl_5$ with an excess of acetylacetone in dichloromethane solution. Only the chelate adduct of neptunium(V) with HTTA and tributylphosphate has been reported; it has the composition $HNpO_2(TTA)_2TBP$.[107]

C. β-Diketone Complexes with Actinides(IV).

The complexes of the actinides(IV) with β-diketones of the type $M(\beta\text{-dike})_4$ have been widely studied in order to perform gas-chromatographic separation of actinides from fission products. β-diketones have been also used as solvent extraction reagents for the actinide elements. These complexes are easy to prepare, the most usual method being addition of the ligand to an aqueous solution of the actinide, with adjustment of the pH with alkali until the complex is precipitated (Table X). Thenoyltrifluoroacetone derivatives only may be obtained, without any adjustment of the pH, when the stoichiometric amount of HTTA is added to an alcoholic solution of the actinide salts.[19]

The 1:4 chelates of Np(IV) and Pu(IV) with β-diketones are always formed in their extraction with β-diketones. A different stoichiometry of these two actinide–TTA complexes can be observed on extraction from nitric solutions if the organic phase contains another complexing agent such as tributylphosphate or tributylphosphine oxide (L). In this case $M(TTA)_3(NO_3)\cdot L$ or $M(TTA)_2(NO_3)_2\cdot 2L$ can be identified in addition to the chelate $M(TTA)_4$.[104]

All the actinides(IV) tetrakis(β-diketonato) complexes are eight-coordinate and a square antiprismatic or dodecahedral structure has been found in the solid state.

The thorium and uranium tetrakis(acetylacetonates) are dimorphic and the crystals of the two forms (α and β) are of monoclinic symmetry, but of different space group.[83,84,176]

The tetrakis(acetylacetonato) complexes of cerium and uranium(IV) (β-form) correspond to the D_2 symmetry and are isomorphous.[185,175] For the neptunium and plutonium α and β modifications have been found; $Np(acac)_4$ is formed, in non

TABLE X. Tetrakis(β-diketone) Complexes of Actinides(IV) Known.

Hacac	H(HFAA)	HBA	HPHD	HBTA	HDBM	HTTA	HTHD	HFOD
$Th(acac)_4$		$Th(BA)_4$	$Th(PHD)_4$		$Th(DBM)_4$	$Th(TTA)_4$	$Th(THD)_4$	$Th(FOD)_4$
$U(acac)_4$	$U(HFAA)_4$	$U(BA)_4$	$U(PHD)_4$	$U(BTA)_4$	$U(DBM)_4$	$U(TTA)_4$	$U(THD)_4$	$U(FOD)_4$
$Np(acac)_4$						$Np(TTA)_4$[a]		$Np(FOD)_4$
$Pu(acac)_4$		$Pu(BA)_4$				$Pu(TTA)_4$		

[a] Identification uncertain.

aromatic polar solvents such as diethylether or acetone, usually below room temperature. The most stable form at room temperature seems to be the β-modification while the β-form of $Th(acac)_4$ transforms to the α-form at room temperature. β-$Np(acac)_4$ has been isolated by extracting it from aqueous solutions (pH = 4.5–5.0) into benzene or other aromatic solvents and evaporating the resulting solution,[4,176] an X-ray structural investigation has been reported.

The observed stability of the acetonylacetonato complexes at room temperature decreases in the order: β-$Zr(acac)_4 \geqslant \beta$-$Ce(acac)_4$, β-$U(acac)_4$, β-$Np(acac)_4 > \beta$-$Th(acac)_4$ and α-$Th(acac)_4 \geqslant \alpha$-$Ce(acac)_4$, α-$U(acac)_4$, α-$Np(acac)_4$, α-$Zr(acac)_4$.

An increase in the M–O bond distance seems to stabilize the α-form in comparison with the β-form. The molecular structure of β-$M(acac)_4$ (M = U, Th, Np) is reported in Fig. 24.

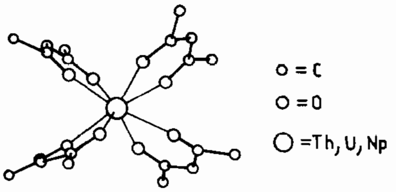


Fig. 24. The molecular structure of β-$M(acac)_4$ (M = U, Th, Np).

The square antiprismatic or triangular dodecahedral structure is lost when the actinide β-diketonates are dissolved and there are some ^1H n.m.r. data which indicate a less symmetrical structure in solution.[164]

Mixing two different chelates such as $U(EtCOCHCOEt)_4$ and $U(Bu^tCOCHCOBu^t)_4$, separate signals are obtained for all the molecular species including the mixed chelate.

The protons of the groups –COCHCO– for unmixed complexes lie all within 1 ppm, but for mixed chelates the shifts are spread out over more than 9 ppm. This observation has been explained by assuming two or more nonequivalent sites for chelating ring in all of these unmixed as well as mixed molecules.

In the unmixed complexes the signals from different sites are not observed separately because they reflect the average shifts for the sites. Because the internal geometry of the chelate ring is essentially independent of the alkyl substituent, only second-order effects are available to change the shifts of the two different sites from molecule and so the observed shift for unmixed chelates vary little. In the mixed chelates every ligand occupies one site preferentially.

On this basis, the ground state polyhedron for these complexes cannot be in solution D_2 square antiprism of D_{2d} dodecahedron. In both of these polyhedra all four coordination sites are equivalent and there cannot be two or more nonequivalent sites. It was found that the molecular structure of M(dibenzoylmethane)$_4$ for uranium and thorium (isomorphous) is a triangular faced dodecahedron;[192] by contrast in $CDCl_3$ solution the ^1H n.m.r. spectra indicate that the structure is an undistorted square antiprism.[191]

The infrared spectra for a series of uranium and thorium tetrakis(β-diketonates) have been carried out also in comparison with the very similar Zr^{IV}, Hf^{IV} and Ce^{IV} analogues. The vibrational frequencies in the range 1750–500 cm^{-1} vary only slightly with changing mass of the metal.[18,72,194] Intense bands are found in the 1700–1500 cm^{-1} region, corresponding to C=O + C=C stretching vibrations. The multiplicity of the peaks may be due to combination bands or to the splitting of the C=O + C=C stretching as a result of the lowered symmetry induced by asymmetrical ligands.

In the far i.r. region two bands assigned to the metal–oxygen stretching modes are present. The $M(acac)_4$ spectra show one strong band in the 220–250 cm^{-1} region and one in the 397–400 cm^{-1}. The former band is relatively broad and metal sensitive, having a tendency to shift toward lower frequency with an increase in the mass of the metal and can be assigned to the nearly pure M–O stretching mode; the latter is assigned to a predominant M–O stretching mode.

The totally symmmetric M–O stretching mode appears in $M(acac)_4$ in the 448–463 cm^{-1} range as weak to medium intensity band (or a shoulder) in the infrared spectra and as a strong polarized line in the infrared spectra.

The methods to obtain the tetrakis-adducts cannot be used to prepare mixed β-diketonato complexes containing unsubstituted halogen atoms bound to the central metal ion. The better method to prepare pure uranium(IV) compounds in a good yield is the reaction of thallium(I) acetylacetonato with uranium tetrahalide in anhydrous organic medium. The thallous complex used in the appropriate molar ratio allows one to substitute progressively the halogen atoms.[66]

In this way complexes having the formula $U(acac)_2Cl_2L_2$ (L = neutral monodentate ligand) have been prepared; the simple compound $U(acac)_2Cl_2$ has not been obtained in the organic media used, the two empty coordination positions on the uranium atom being filled by the coordination of the solvent used. The higher U–O antisymmetric stretching has been found as only one band around 400 cm^{-1}. The second one has not been assigned owing to the simultaneous presence in the 270–200 cm^{-1} region of absorptions due to vibrational modes of the ligands and of the U–Cl and U–L bonds.[66]

The melting points of the uranium(IV) complexes decrease as the length of the chain in R for the ligand CH_3COCH_2COR increases; a similar behaviour has been found for CF_3COCH_2COR derivatives.[82]

Nearly all of the actinide(IV) compounds sublime readily under vacuum and this property provides a convenient way of purifying them. The fractional sublimation of these chelates has been studied for the separation of the actinides from the lanthanides.

The substitution of fluorine for hydrogen($-CF_3$ for $-CH_3$) and replacement of normal alkyl groups with branched alkyl groups in the β-diketones increases the volatility. However, the most volatile of these chelates, $U(CF_3COCHCOCF_3)_4$, is too unstable for any practical use.

Using acetylacetone it is possible to separate scandium(III), thorium(IV) and uranium(IV) from the lanthanides owing to the great difference in thermal stability. The scandium(III), thorium(IV) and uranium(IV) chelates are volatile whereas the lanthanides are thermally unstable and non volatile.[20]

The possibility of similar separation of the actinides from each other has been also investigated. Using HTHD and HFOD, air stable tetrakis-chelates have been obtained.[171]

The volatility of the M(FOD)$_4$ chelates is approximately equal to that of Er(FOD)$_3$; despite a molecular weight of about 1400, compared to 1052 for Er(FOD)$_3$, the shielding of the M^{4+} ion by the FOD ligands more than compensates for their larger molecular weight.

Although volatilization does not appear to be a practical method for separating U(FOD)$_4$, Np(FOD)$_4$ and Pu(FOD)$_4$, it may be useful for separating these actinides from light lanthanides and trivalent actinides.

Magnetic measurements were carried out on β-diketone–uranium(IV) complexes from room temperature to that of liquid nitrogen or liquid helium.[195] The relationships between the reciprocal molar magnetic susceptibility and temperature for U(acac)$_4$, U(BAC)$_4$, U(TFA)$_4$, U(DBM)$_4$ and U(TTA)$_4$ are reported in Fig. 25.

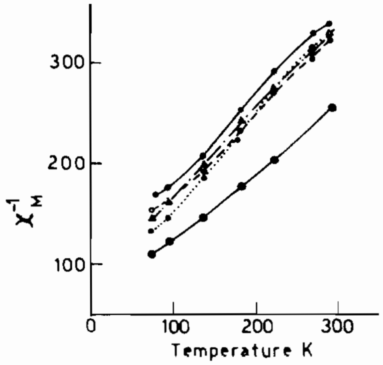


Fig. 25. Reciprocal susceptibility against temperature of complexes: U(DBM)$_4$ (–●—●–), U(acac)$_4$ (●···●···●), U(TFA)$_4$ (– · – △ – · –), U(BA)$_4$ (– ○ – – ○ –), U(TTA)$_4$) (–○—○–).

These complexes were found to follow the Curie–Weiss law over the temperature range investigated except for the lowest part, where a slight positive deviation from the straight line is observed.

The complex U(acac)$_4$ with square antiprismatic structure shows a relatively lower magnetic moment (2.92 B.M.) than that of U(DBM)$_4$ (3.43 B.M.) with dodecahedral structure.

Recently the photoelectron spectra of tetrakis (acetylacetonato) complexes of thorium(IV) and uranium(IV) have been reported.[57] The spectra of Th(acac)$_4$ and U(acac)$_4$ are very similar, apart from a band centered at 6.77 eV in the spectrum of the uranium complex. This band, weak and broad, absent in the thorium complex spectrum, was attributed to 5*f* electron ionizations. Such band in the fluorinated U(TFA)$_4$ is shifted to 7.83 eV owing to the higher electronegativity of the fluorine atoms. The other bands in the range 8–12 eV were assigned to the chromophore. The spectra beginning at 12 eV are too much diffuse arising from the overlap of ionization bands of electrons localized in the C–C and C–H region.

D. β-Diketone Complexes with Actinides(III)

Very few compounds of actinides(III) with β-diketones have been isolated on a preparative scale. Complexes of the type M(dike)$_3$ are unknown for U(III) and Np(III), all of which are too readily oxidized to the quadrivalent state to sustain preparative work-up. These problems do not arise with Am(III); neutral chelate complexes of the type Am(β-dike)$_3$ are easily prepared when ammonia is added to an aqueous solution of $AmCl_3$ and diketone.[62] When an excess of the cesium salt of the β-diketone is added to $AmCl_3$ the complex Cs[Am(β-dike)$_4$] is obtained.[40]

The crystal and molecular structures of some of these complexes have been reported. Am(THD)$_3$ is monoclinic with space group $P2_1/n$.[70] The most striking feature is the occurrence of $Am_2(THD)_6$ dimer; as a consequence each americium atom is surrounded by seven oxygen atoms. The coordination polyhedron is described by an octahedron with local distortion in the proximity of the extra ligand; a distorted capped trigonal prism is the most likely for

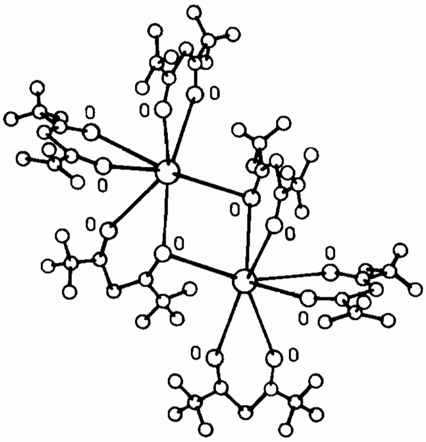


Fig. 26. The molecular structure of $[Am(THD)_3]_2$.

this complex and the coordination geometry is illustrated in Fig. 26.

The molecular character of the $Am_2(THD)_6$ crystal accounts for its volatility and ability to sublime without decomposition; it sublimes at 124°–135 °C at 10^{-5} torr and melts at 216–218 °C. $Cs[Am(HFA)_4]$ is of orthorhombic symmetry and the americium(III) ion is 8-coordinate; the resulting geometry is a dodecahedron of approximately D_2 symmetry. The crystals isomorphous with $Cs[Eu(HFA)_4]$ are composed of chains of $[Am(HFA)_4]^-$ and Cs^+ ions;[40] between the chains there are only F···F contacts, which suggests a reason for the volatility.

The preparation of $Cs[Cm(HFA)_4]H_2O$, which is isostructural with the corresponding neodimium compound, has been reported.[40,62] It is obtained by reaction of CsHFA with the stoichiometric amount of $CmCl_3$ in ethanol. Although similar complexes of the higher actinides have not been isolated, it has been found that Ac(III), Am(III), Cm(III) and Cf(III) are extracted by substituted 1,3-diketones in the form of 1:3 chelates. These complexes are reported in Table XI.[118]

The extraction of the Cf chelates occurs at pH values lower than Am and Cm which are extracted practically at the same pH, while the Ac chelates are extracted at higher pH (see Fig. 27).

Surprisingly the compounds of Ac(III) with HFTA and HTTA, extracted from aqueous solution, have the composition $Ac(OH)(FTA)_2$ and $Ac(OH)(TTA)_2$ respectively; this behaviour contrasts with the assumption that an increase of the radius decreases the hydrolysis.

In the extraction of Am(III) with $HTTA/CHCl_3$ in the presence of various adducting agents (A), it turns out that the formation of adduct chelates $Am(TTA)_3xA$ (x = 1,2) improves the transfer of the metal ion into the organic phase. The most stable adduct chelates are formed by tributylphosphate while the most unstable are found with 1-nitrobutane.[116,138,159]

TABLE XI. Known Actinide(III) β-Diketone Complexes, $[M(\beta\text{-dike})_3]$.

HFTA	HTTA	HBTA	HNTA
		$Ac(BTA)_3$	$Ac(NTA)_3$
	$Am(TTA)_3$	$Am(BTA)_3$	$Am(NTA)_3$
	$Cm(TTA)_3$	$Cm(BTA)_3$	$Cm(NTA)_3$
$Cf(FTA)_3$	$Cf(TTA)_3$	$Cf(BTA)_3$	$Cf(NTA)_3$

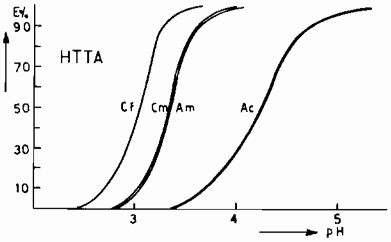


Fig. 27. Percentage extraction of some trivalent actinides with 0.5 *M* HTTA/xylene.

6. 8-Hydroxyquinoline and Its Derivative Complexes

A. 8-Hydroxyquinoline and Its Derivative Complexes with Actinides(VI)

The coordination power of 8-hydroxyquinoline is very well known only for uranyl(VI) ion; attempts to prepare the analogous neptunyl(VI) and plutonyl(VI) adducts failed because the ligand reduces both hexavalent elements to lower oxidation states.[113]

The reaction between uranyl(VI) salts and 8-acetoxyquinoline leads to the formation of two different adducts. One precipitates at pH 6.8 as orange $(UO_2(Ox)_2)_2HOx$ and the other at pH 5.0 as dark-red $UO_2(Ox)_2HOx$.[29] It has also been reported that at pH 6.8 the composition of the orange compound is initially $UO_2(Ox)_2HOx$, which would have a less thermal stability than the dark-red adduct. It has been supposed that the formation of $(UO_2(Ox)_2)_2HOx$ is due to a partial loss of the neutral ligand on drying at 110 °C for 2 hr.[116] When 8-hydroxyquinoline is used, only the compound $UO_2(Ox)_2HOx$ is obtained.[80,103,131,132]

The thermogravimetric behaviour of the two complexes generated by hydrolysis of 8-acetoxyquinoline from aqueous solution is reported in Fig. 28 along with that of $UO_2(Ox)_2HOx$ produced by 8-hydroxyquinoline.[28]

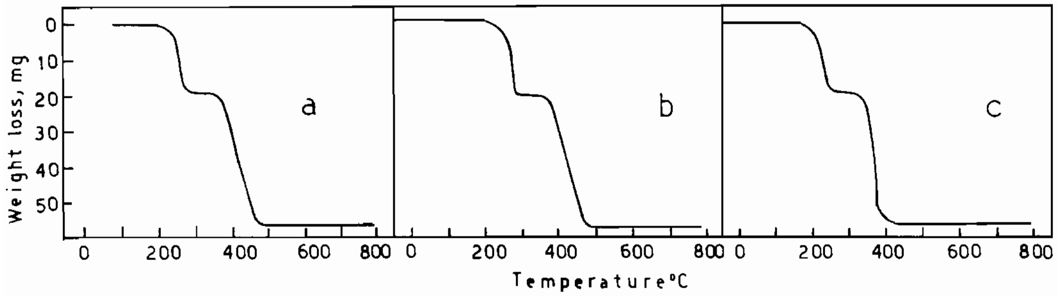


Fig. 28. The thermogravimetric behaviour of: a) $UO_2(Ox)_2HOx$, b) $[UO_2(Ox)_2]_2HOx$ (both generated by hydrolysis of 8-acetoxyquinoline), c) $UO_2(Ox)_2HOx$ (produced by 8-hydroxyquinoline).

The two $UO_2(Ox)_2HOx$ complexes, prepared in the two different ways, were found to behave in a quite similar manner; they are thermally stable up to about 200 °C (Fig. 28) and lose HOx at 200–300 °C, the remaining organic material is released between 375 °C and 475 °C to form U_3O_8.

The thermogravimetric curve of $(UO_2(Ox)_2)_2HOx$, Fig. 28 c, is quite similar to that in Fig. 28a and 28b.

The product obtained by elimination of the HOx molecule is always the olive-green complex $UO_2(Ox)_2$. Heating $UO_2(Ox)_2HOx$ for 48 hr at 210 °C to obtain $UO_2(Ox)_2$ has been found to lead to partial decomposition of the bis complex. The best conditions to prepare the bis complex $UO_2(Ox)_2$ are given by heating the dark-red compound *in vacuo* for 4 hr at 210–215 °C. Heating periods up to 37 hr have little effect on the composition of $UO_2(Ox)_2$.[58]

The differential thermal analysis of the complex $UO_2(Ox)_2HOx$ gives endothermic peaks with maxima at 150 °C, 300 °C and 450 °C. Since no gaseous product is evolved, the peak at 150 °C is due to some rearrangement reaction. The peak at 300 °C corresponds to the loss of the third molecule of 8-hydroxyquinoline and the peak at 450 °C is due to the loss of the remaining chelating agent and to the general decomposition of the complex.[104]

From the i.r. spectra of $UO_2(Ox)_2HOx$ and $(UO_2(Ox)_2)_2HOx$, it is impossible to assess the differences in their molecular structure. The peak of the antisymmetric ν_3(O–U–O) lies at 891 cm^{-1} in the dark-red complex and at 888 cm^{-1} in the orange one. In the spectrum of UO_2Ox_2 the peaks at 1056 and 1068 cm^{-1}, occurring in the spectra of the dark-red and orange compounds, disappear and the ν_3-(O–U–O) shifts from about 890 cm^{-1} to 920 cm^{-1}.[125] The spectral differences indicate only that a drastic change occurs in the configuration of the olive-green $UO_2(Ox)_2$ from the similar $UO_2(Ox)_2HOx$ and $(UO_2(Ox)_2)_2HOx$.

The complex $UO_2(Ox)_2HOx \cdot CHCl_3$, obtained by crystallization from chloroform, has been well investigated through X-ray structural determinations.[91,95] The chloroform molecule is present as solvent of crystallization; therefore it is not surprising that the diffraction patterns of the red crystals are different from that of the red powder; the difference arises from the molecule of solvent present in the crystals, the molecular geometry of the two complexes being the same[75] (Fig. 29):

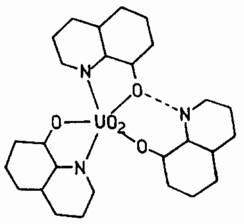


Fig. 29. The molecular configuration of $UO_2(Ox)_2HOx$.

The three molecules of 8-hydroxyquinoline are in the plane perpendicular to the O–U–O group, giving an arrangement which is completely coplanar with the uranium atom. The neutral HOx molecule is monodentate toward uranium but is bonded via a hydrogen bond to a neighbouring molecule by a link from its nitrogen to a phenolic oxygen. so the conclusion already reported that $UO_2(Ox)_2HOx$ was an acid which could be written as $H[UO_2Ox_3]$ is certainly wrong.[38] It is also wrong that the neutral molecule is an uncoordinate crystal lattice component. The infrared spectrum of $UO_2(Ox)_2HOx$ exhibits two bands centered at about 2650 cm^{-1} and 2050 cm^{-1} [60] (Fig. 30).

These bands are not present in $UO_2(Ox)_2$ but appear in the hydrochloride salt of 8-hydroxyquinoline. The shift of the stretching frequency $^{+}$N–H which should lie at 3200 cm^{-1}, has been attributed to strong hydrogen bonding of the type $^{+}$N–H···Cl.[50,69,124,139]

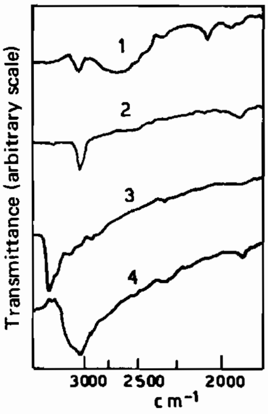


Fig. 30. The i.r. spectra of: 1) $UO_2(Ox)_2HOx$, 2) $UO_2(Ox)_2$, 3) $UO_2(Ox)_2NH_3$, 4) HOx.

The presence of the 2600 and 2050 cm^{-1} bands in $UO_2(Ox)_2HOx$ well agrees with the hydrogen bond $^+N–H\cdots O$. Certainly, intermolecular hydrogen bonding as suggested by Bullwinkel and Noble[38] cannot occur. A survey of many compounds, in which $^+N–H\cdots O$ bonding occurs, shows that the most probable N–O distance is 2.8–2.9 Å.[146]

In $UO_2(Ox)_2HOx$ the N–O distance is 2.71 Å which suggests a strong hydrogen bond.[95]

No X-ray structural data, using single crystal, are available for the orange $(UO_2(Ox)_2)_2HOx$. It shows no powder lines, but only two haloes, corresponding to spacing of about 4.2 Å and 8.5 Å.

The compound is amorphous and appears to be a polymer with chains or layers in which the uranium atoms are separated by about 4.2 or 8.5 Å.[126]

It has been suggested that the basic polymeric unit is composed of the 1:3 and 1:2 compounds held together by a bond between the nitrogen atom of the monodentate 8-hydroxyquinoline and the uranium atom of the 1:2 compound.

The basic polymeric units should be bonded by proton bridge between the uranyl oxygens of the 1:2 compound in adjacent units. Since in the infrared spectrum of this complex the $^+N–H\cdots O$ band system is present, the proton must be located on the nitrogen atom and so another form of configuration must be proposed for the polymeric $(UO_2(Ox)_2)_2\cdot HOx$.[61]

No structural information is available for $UO_2(Ox)_2$, however a tetracoordination in the equatorial plane must be excluded and a higher coordination number should be reached via phenolic oxygen bridges with a subsequent dimeric or polymeric configuration. In dry hot dichloroethane the bis-compound may be recrystallized unchanged; in dichloroethane saturated with water, in 95% ethanol, methanol, acetone, and chloroform it shows the disprotonation to $UO_2(Ox)_2HOx$ and other U(VI) species, always contaminated by adducts of the type $UO_2(Ox)_2S$ (S = solvent). In polar solvents such as dimethylsulphoxide it forms the complex $UO_2(Ox)_2$(dmso).

It is to be noted that in solution both the red $UO_2(Ox)_2HOx$ and orange $(UO_2(Ox)_2)_2HOx$ at high pH are converted to the ionic $M[UO_2(Ox)_3]$ (M = Na^+, NR_4^+, Ph_4As^+). A ^1H n.m.r. spectrum of this ionic complex indicates that all three ligands are equivalently bound which implies that the uranyl group has an equatorial coordination number six,[16] the three ligands being twisted out of the plane normal to the linear uranyl group. An attempt to determine the structure was not successful.[5]

Substituted 8-hydroxyquinoline ligands have been used to study the uranyl complexes for analytical purposes. Generally they are thermally less stable than the equivalent 8-hydroxyquinoline adducts. So the 2-methyl-8-hydroxyquinoline uranyl complex begins to lose the 2Me-molecule of 55 °C and the chelate $UO_2(2MeOx)_2$ has a stability range much smaller than that of the 8-hydroxyquinoline chelate.[187]

These conclusions are in accordance with the differential thermal analyses. $UO_2(2Me\text{-}Ox)_2\cdot 2Me\text{-}HOx$ gives two fairly large endothermic peaks with maxima at 250° and 300 °C, the first endothermic peak starts at 55 °C.[104]

Some remarkable differences have been found in uranyl complexes with 5,7-dihalo-8-hydroxyquinoline. The primary composition $UO_2(5{,}7X\text{-}Ox)_2\cdot 5{,}7X\text{-}HOx$ (X = Cl, Br) assigned to the complexes obtained by precipitation from an aqueous acetone solution,[130] has been subsequently corrected to $UO_2(5{,}7X\text{-}Ox)_2\cdot OC(CH_3)_2$; the correct composition is difficult to assign because of the insolubility of the reagents and of the presence of water in the complexes.

In the i.r. spectra the C=O stretching frequency confirms the presence of acetone in all the reported complexes. In the spectra of the dichloro complexes only one band at 1690 cm^{-1} is present, while a doublet centered at 1675 cm^{-1} is present in the dibromo species. The coordination of the acetone rather than a third molecule of dihalo ligand has been explained as a result of the steric hindrance of the substituent in the 7-position; the bands due to $^+N–H\cdots O$ are not present. Similar conclusions arise from other 7- or 2,7-substituted 8-hydroxyquinoline complexes, for which a 1:3 adduct has not been obtained due to intraligand repulsion as shown in Fig. 31.

Their thermal conversion to $UO_2(5{,}7X\text{-}Ox)_2$ is possible but the presence of the relatively large atoms

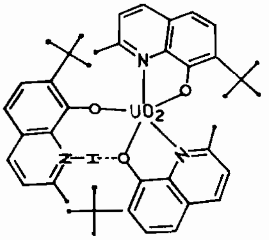


Fig. 31. Configuration of the 1:3 uranyl-2,7-substituted 8-hydroxyquinoline adducts showing the intraligand repulsions.

prohibits association and coordinative saturation is reached through a water molecule.[185]

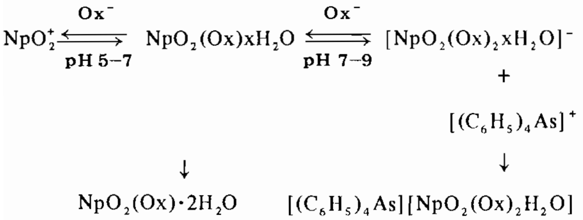
A different behaviour is given by 7Ph-HOx for which the adduct 1:3 has been prepared because in the ligand the phenyl group is twisted out of the plane of the quinoline ring.

Bulky substituents in the 2-position as n-butyl, phenyl and the like, also prevent the formation of the 1:3 adduct.[57]

B. 8-hydroxyquinoline and Its Derivative Complexes with Actinides(V)

The complex formation of the pentavalent neptunium with 8-hydroxyquinoline is particularly interesting since no correspondence in the chemical behaviour can be observed in the other actinides. The addition of the 8-hydroxyquinoline to a solution of pentavalent neptunium at pH 5–7 precipitates slowly the yellow-green $NpO_2(Ox)\cdot 2H_2O$ as granular powder.[113]

The two water molecules can be replaced by dimethylsulphoxide to give $NpO_2(Ox)\cdot 2dmso$. At higher pH $NpO_2(Ox)\cdot 2H_2O$ dissolves and a yellow solution containing $[Np(Ox)_2]^-$ is obtained; this anion, precipitated as $[(C_6H_5)_4As][NpO_2(Ox)_2\cdot H_2O]$ with tetraphenylarsonium chloride, can be extracted into chloroform. The following reaction scheme has been proposed for the system NpO_2^+/8-hydroxyquinoline:[113]



$$\begin{array}{ccc} NpO_2^+ \underset{pH\ 5-7}{\overset{Ox^-}{\rightleftharpoons}} & NpO_2(Ox)xH_2O \underset{pH\ 7-9}{\overset{Ox^-}{\rightleftharpoons}} & [NpO_2(Ox)_2xH_2O]^- \\ & & + \\ & & [(C_6H_5)_4As]^+ \\ & \downarrow & \downarrow \\ & NpO_2(Ox)\cdot 2H_2O & [(C_6H_5)_4As][NpO_2(Ox)_2H_2O] \end{array}$$

The various oxinato complexes of Np(V) have different absorption spectra so that the formation of these compounds can be followed easily.

The green-brown chelate $PuO_2(Ox)(HOx)_2\cdot 2H_2O$ has been prepared as a flocky solid at pH 5–7.[113]

It has been reported that the hexavalent plutonium forms the complex $PuO_2(Ox)_2HOx$, analogous to $UO_2(Ox)_2HOx$,[99] but it may be noted that the hexavalent transuranium elements undergo reduction reaction with 8-hydroxyquinoline at the pH necessary for the precipitation of the oxinato adduct and so the previously proposed $PuO_2(Ox)_2HOx$ is not correctly formulated. All the neptunium and plutonium oxinato complexes maintain the H_2O molecule even after heating at 120 °C (Table XII).

Very different is the chemical behaviour of Pa(V), where a more complicated system takes place as a consequence of the hydrolysis of the ion. It has been proposed that a complex compound with 8-hydroxyquinoline is formed, the average composition being $H_2[Pa(OH)_{4.5}(Ox)_{2.5}]$.[117]

With 5,7-dibromo-8-hydroxyquinoline, the hydrolysis of Pa(V) is greater and it is supposed that the complex $H_2[Pa(OH)_6\cdot(5,7\text{-}Br\text{-}Ox)]$ is formed.

C. 8-Hydroxyquinoline and Its Derivative Complexes with Actinides(IV)

8-hydroxyquinoline was recommended for the determination of thorium until 1929.[103] The complex may be prepared by using 8-hydroxyquinoline, or 8-acetoxyquinoline and its first formulation was $Th(Ox)_4HOx$.[30,80,102] More recently it has been suggested that the thorium–8-hydroxyquinoline ratio is not strictly 1:5, but that the composition is very difficult to reproduce from one preparation to another; the average ratio of bound 8-hydroxyquinoline to thorium was found to be 1:4.9. The deficiency of 8-hydroxyquinoline may be due to partial hydrolysis of thorium or to the presence of coordinated water.[58b,174]

The complex $Th(Ox)_4HOx$ gives three endothermic peaks with maxima at 150 °C, 310 °C and 410 °C. The peak at 150 °C, due to the change of the complex to the 1:4 chelate, contains a small endothermic shoulder at 140 °C. It has been reported that $Th(Ox)_4HOx$ decomposes thermally according to a two-step reaction:[177]

$$2Th(Ox)_4HOx \longrightarrow (Th(Ox)_4)_2\cdot HOx + HOx$$

$$(Th(Ox)_4)_2HOx \longrightarrow 2Th(Ox)_4 + HOx$$

This could explain the occurrence of the two peaks and also the gas evolution peaks found in the neighbourhood of 150 °C. The two peaks at 310 °C and 410 °C are attributed to the loss of the remaining ligand molecules and to the subsequent pyrolysis of the chelate.[104,130,173,178,190]

TABLE XII. Actinide(V) Complexes with 8-Hydroxyquinoline and Its Substituted Derivatives Obtained by Precipitation from Aqueous or Aqueous Dioxane Solutions

Metal Ion	Ligand	Complex	Color	pH	Experimental Conditions
Np(V)	HOx	$NpO_2(Ox) \cdot 2H_2O$	Yellow	5	Water
Pu(V)	HOx	$PuO_2(Ox)(HOx)_2 \cdot 2H_2O$	Greenish-brown	5–7	Water
Np(V)	HOx	$(C_6H_5)_4AsNpO_2(Ox)_2H_2O$	Yellow-green	7–9	Water; addition of $(C_6H_5)_4AsCl$
Np(V)	2Me-HOx	NpO_2(2Me-Ox)(2Me-HOx)$\cdot H_2O$	Yellow	8.5	Water
Pu(V)	2Me-HOx	PuO_2(2Me-Ox)(2Me-HOx)$\cdot H_2O$	Green	8	Water
Pu(V)	5,7Cl-HOx	PuO_2(5,7Cl-Ox)(5,7-HOx)$_2 \cdot H_2O$	Green	5	30% Dioxane–70% water
Pu(V)	$5SO_3$-HOx	Pu($5SO_3$-Ox)($5SO_3$-HOx)$_2 \cdot 2H_2O$	Green	5–6	50% Dioxane–50% water

It has been reported that the neutral molecule is coordinated to the thorium ion through the phenolate oxygen only and that the acidic proton is located on the nitrogen atom.[59]

In the i.r. spectrum of $Th(Ox)_4HOx$ the two bands, characteristic of $^+N–H \cdots O$ bond centered at about 2625 cm^{-1} and at about 2100 cm^{-1}, are present. They are very similar to those observed in the spectrum of $UO_2(Ox)_2HOx$ and, as expected, they are not present in the spectrum of $Th(Ox)_4$.

The coordination number of thorium should be nine in $Th(Ox)_4HOx$. It appears to exist only in the solid state and in its ^1H n.m.r. spectrum in d_5-dmso the peaks are broadened as a consequence of ligand exchange.

The ^1H n.m.r. spectrum of $Th(Ox)_4$ shows only one set of ligand resonances indicating that all four ligands are magnetically equivalent.[17]

On dissolving $Th(Ox)_4HOx$ in warm dichloroethane, the tetrakis-compound immediately precipitates; with a large excess of HOx a red solution has been obtained and it has been suggested that the ion pair $[H_2Ox]^+[Th(Ox)_5]^-$, in which all ligands of the anion are bidentate, may be present.[1]

In dmso the pentakis-compound yields $Th(Ox)_4 \cdot$ 2dmso; its i.r. spectrum shows a strong band at 1030 cm^{-1} assigned to ν(SO) of uncoordinated dmso and a weaker band at 970 cm^{-1} consistent with the presence of dmso coordinated through its oxygen atom.[7] The molecular structure of this adduct is shown in Fig. 32.[166]

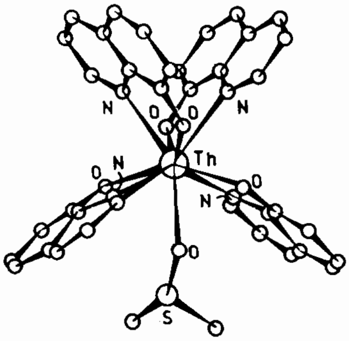


Fig. 32. The molecular structure of $Th(Ox)_4$dmso.

The 8-hydroxyquinoline rings are arranged in a square antiprismatic configuration about the metal ion; only one dmso is coordinated. The oxine ligands are essentially planar and the Th–N distances are longer than Th–O. The results of this structure investigation suggest that the postulated nine-coordination in $Th(Ox)_4HOx$ is feasible.

The formation of the pentakis-complexes is not sensitive to substitution in the 7-position of the 8-hydroxyquinoline ring with the exception of bulky groups, such as *t*-butyl, which yields the tetrakis-compound.

On the other hand, substituents in the 2-position may prevent the formation of the pentakis-complex. Fig. 33 shows the best conditions for a complete precipitation of Th(2Me-Ox)$_4$.

With a 125% excess of 2Me-HOx the precipitation is not quantitative; with a 150% excess of reagent the precipitation of the chelate is at least 99% complete at pH 5.5–5.6 and with a 200% excess this degree of completeness is attained at pH 5.4–5.5.[187] Th(2Me-Ox)$_4$ is stable up to 185 °C where it begins to decompose slowly, and for a good determination of thorium it can be preferred to 8-hydroxyquinoline chelate because this latter begins to decompose at about 80 °C.[189]

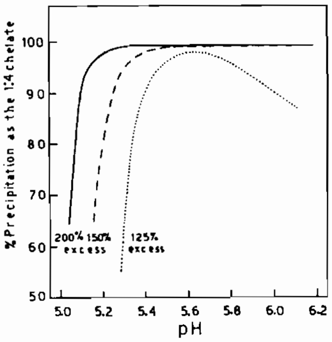


Fig. 33. Percentage precipitation of Th(2Me-Ox)$_4$ against pH.

TABLE XIII. Known Actinide(IV) Complexes with 8-Hydroxyquinoline and Its Derivatives.

HOx	2Me-HOx	5X-HOx	5,7X-HOx	7X-HOx
$Th(Ox)_4 \cdot HOx$;[a] $Th(Ox)_4$	$Th(2Me\text{-}Ox)_4$	$Th(5X\text{-}Ox)_4 \cdot 5X\text{-}HOx$	$Th(5,7X\text{-}Ox)_4$	$Th(7X\text{-}Ox)_4 \cdot X\text{-}HOx$
$U(Ox)_4 \cdot HOx$; $U(Ox)_4$[b]			$U(5,7X\text{-}Ox)_4$	
$Np(Ox)_4$	$Np(2Me\text{-}Ox)_4$	$Np(5X\text{-}Ox)_4$	$Np(5,7X\text{-}Ox)_4$	
$Pu(Ox)_4$		$Pu(5X\text{-}Ox)_4$	$Pu(5,7X\text{-}Ox)_4$	

[a] The composition of the adduct is very difficult to reproduce and the average U/oxine ratio is 1/4.8. [b] The existence of $U(Ox)_4$ is not certain. The spectra of the pentakis-complexes show two bands at 2625 cm^{-1} and 2100 cm^{-1} due to the $^{+}N{-}H \cdots O$ bond system.

Since the chemistry of the uranium(IV) compounds is similar to that of thorium(IV), one may predict complexes of the type $U(Ox)_4 \cdot HOx$. Such complexes have been found using 8-hydroxyquinoline, 5,7-dichloro- and 5,7-dibromo-8-hydroxyquinoline. They appear to be stable to oxidation since, after two weeks, there is not apparent decomposition. They are soluble in chloroform but only slightly in acetone and ethyl alcohol. $U(Ox)_4HOx$ shows different TGA curves than the thorium analogue.[186]

The uranium(IV) complex begins to lose weight at about 130 °C, giving a break in the curve at 235 °C approximated to $U(Ox)_4$ but a horizontal weight level is not obtained. Also in the cases of the 5,7-dichloro- and 5,7-dibromo-oxinato complexes there is no evidence for the formation of the 1:4 adduct.

In the D.T.A. curves of $U(Ox)_4HOx$ there is little evidence that the neutral molecule of 8-hydroxyquinoline is lost by sublimation. However the exothermic peak at 225 °C may be caused by a rearrangement reaction of the 1:4 adduct which may mask the endothermic sublimation reaction. The pentakis-uranium(IV) and thorium(IV) complexes with oxine very probably possess identical structures and even if the exact structure is still unknown a ten-coordination for $U(Ox)_4HOx$ should be excluded (Table XIII).

Plutonium(IV) and neptunium(IV) form with 8-hydroxyquinoline and its substituted derivatives complexes of the type $M(Ox)_4$. These complexes are very probably eight-coordinated; compounds with more than four ligands per metal atom were not obtained. All these complexes are soluble in polar organic solvents and the u.v. spectra in $CHCl_3$ are similar. Neptunium(IV) is extracted into a chloroform solution as $Np(Ox)_4$ or $Np(5,7Cl\text{-}Ox)_4$ while a very anomalous complex which is ascribed to the formation and extraction of basic species is obtained for plutonium(IV).[114]

D. 8-Hydroxyquinoline and Its Derivative Complexes with Actinides(III)

Complexes of the type $M(Ox)_3$ are known only for plutonium(III) and transplutonic elements; for uranium(III) and neptunium(III) the oxidation to the quadrivalent state occurs too readily to allow the preparation of the oxinato adducts. The yellow-green $Pu(Ox)_3$ can be prepared by mixing a solution of plutonium(III) salts and 8-hydroxyquinoline, in presence of sulphite or dithionite as reductants at pH 7.2, under a nitrogen atmosphere. The u.v. spectrum is characteristic of a plutonium(III) adduct and indicates that an amount of plutonium(IV) less than 4% is present.[112]

This compound is very readily oxidised in air giving the brown $Pu(Ox)_4$. Different is the behaviour of the transplutonium elements, for which the oxidation state 3+ is stable and consequently the tris-complexes are easily obtained. $Am(Ox)_3$ and the analogous complexes with the substituted 8-hydroxyquinoline are prepared from aqueous or aqueous dioxane solution at the appropriate pH value (Table XIV).

$Am(Ox)_3$ is very sparingly soluble in organic media while $Am(halooxine)_3$ complexes are more soluble. The americium(III) oxinato complex is extracted with chloroform as $Am(Ox)_2OH$.[115]

The tendency to hydrolysis has been found also for actinium(III), curium(III) and californium(III) 8-hydroxyquinolinato adducts which are extracted as $Ac(Ox)_2OH$, $Cm(Ox)_2OH$ and $Cf(Ox)(OH)_2$.[74,117] This different hydrolytic behaviour is a consequence of the different ionic radius of these actinides. Am(III) and Cm(III), on the basis of their very similar ionic radii, are expected to form complexes of identical composition, while Cf(III), for its smaller ionic radius, hydrolyses more strongly and is extracted as $Cf(Ox)(OH)_2$. The 5,7-chlorooxinato complexes of all these trivalent actinides are extracted as $M(5,7Cl\text{-}Ox)_3$.

In Fig. 34 the percentage of extraction of oxinato complexes against pH shows that the trivalent actinides are extracted at pH 4–7 and that Cf(III), Am(III), and Cm(III) are extracted practically at the same pH value.

TABLE XIV. Actinide(III) Complexes with 8-Hydroxyquinoline and Its Substituted Derivatives Obtained by Precipitation from Aqueous or Aqueous Dioxane Solutions.[115]

Metal Ion	Ligand	Composition of the Complex	Color	pH of Precipitation	Experimental Conditions
Pu(III)	HOx	$Pu(Ox)_3$	Yellow–green	7.2	Aqueous Solution
Am(III)	HOx	$Am(Ox)_3$	Yellow–green	5.5–6.5	Aqueous Solution
Am(III)	2Me-HOx	$Am(2Me\text{-}Ox)_3$	Bright green	5.1–5.9	30% Dioxane
Am(III)	2,7Cl-HOx	$Am(2,7Cl\text{-}Ox)_3$	Green	5.7–6.0	65% Dioxane

TABLE XV. IR Data (cm^{-1}) for Uranyl Complexes with Tridentate Schiff Bases.

Complex	ν(NH)	ν(C=N)	ν_3(O–U–O)	Color
$UO_2(salenNHC_6H_5)_2$	3237	1625	871	Pink Crystals
$UO_2(salenNHC_2H_5)_2$	3234	1628	895	Orange–red Powder
$UO_2(salenN(CH_3)_2)_2$	–	1624	885	Orange–red Powder
$UO_2(HsalenNHC_6H_5)_2(NO_3)_2$	3414	1654	914	Yellow Powder
$UO_2(HsalenNHC_2H_5)_2(NO_3)_2$	3260	1634	908	Yellow Powder

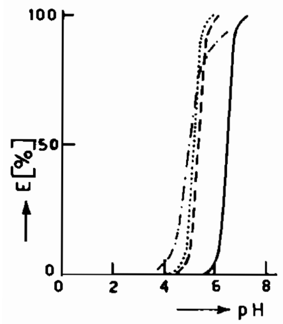


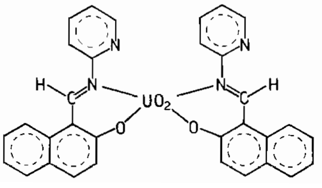
Fig. 34. The percentage of extraction of oxinato complexes of Cf(III) (········), Am(III) (-------), Cm(III) (– · – · –), Ac(III) (———) against pH.

7. Schiff Base Complexes

A. Schiff Base Complexes with Actinides(VI)

The Schiff bases derived from salicylaldehyde have been widely studied and a large series of uranyl complexes have been characterized.

Bidentate Schiff base complexes of uranyl(VI) ion have been prepared and studied.[154,193] Some of them are of the type $UO_2(HBSB)_2(NO_3)_2$ where the neutral ligands are coordinated to the metal ion. The i.r. spectra show that both the nitrate groups are coordinated to the central ion as monodentate ligands and therefore the uranyl(VI) ion is eight-coordinate. A similar configuration has been proposed for the analogues $UO_2(HBSB)_2X_2$ ($X = Cl^-, CH_3COO^-$).[180] A complex of the type:



has also been reported. The proposed equatorial coordination number four is unusual in the uranyl (VI) Schiff bases chemistry;[88] more probably this compound contains a solvent molecule or is not monomeric.

The reaction between the tridentate Schiff bases HsalenNRR′ (derived from salicylaldehyde and N-substituted ethylenediamine) and various uranyl(VI) salts have been studied.[179] With $UO_2(NO_3)_2 \cdot 6H_2O$ under mild conditions such ligands give complexes of the type $UO_2(HsalenNRR')_2(NO_3)_2$ where the nitrato groups are reported to be coordinated as unidentate ligands. Because the Schiff bases act as bidentate ligands forming six-membered chelate rings $\overset{\frown}{N\,O}$, the resulting geometry of these adducts is an irregular hexagonal bipyramid. On reacting thallous(I) derivatives of HsalenNRR′ with $UO_2Cl_2 \cdot 3H_2O$, the complexes $UO_2(salenNRR')_2$ were obtained. The complexes crystallize from ethanol and the X-ray structure analysis of $UO_2(salenN(CH_3)_2)_2$ shows a pentagonal bipyramidal environment[10,51] (Table XV, Fig. 35).

Two oxygen and three nitrogen atoms form the base of the bipyramid and the uranyl oxygens occupy the apical positions; therefore two modes of ligand coordination in the same molecule occur in accordance with the ^1H n.m.r. spectra, where two peaks for CH_3 groups have been observed. A projection of the molecule down a direction perpendicular to the uranyl group is also given in Fig. 35b.

It may be seen that the complex exhibits an overall "stepped" geometry with the CH_2–CH_2 carbon atoms out of the equatorial plane by 0.24 and 0.53 Å. For the complexes $UO_2(salenNHR)_2$ a similar coordination has been proposed, even if a single stretching band for N–H was found. Probably the free NH group, not involved in the coordination

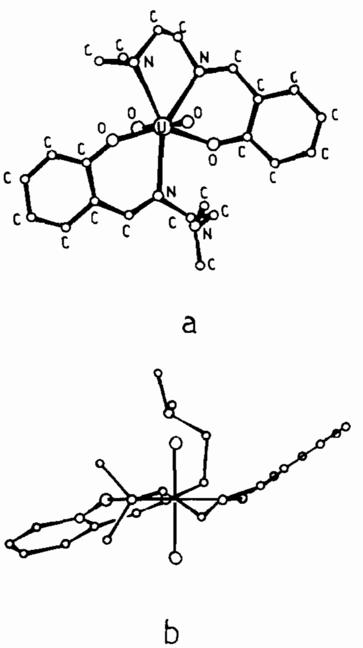


Fig. 35. Projection of $UO_2(salenN(CH_3)_2)_2$ on the mean equatorial plane (a) and down a direction perpendicular to the uranyl group (b).

to the central metal ion, forms a hydrogen bond with a phenolic oxygen of a Schiff base ligand with a subsequent shift to lower frequency of the N–H stretching.

An interesting group of the quadridentate Schiff base uranyl(VI) complexes is represented by the N,N′-bis-salicylidenaldinime adducts. They may be formulated as $UO_2(TSB)(L)$ (L = neutral monodentate ligand[47,48,145] (Table XVI). The presence of ethanol or methanol in the coordination sphere in the case of the complexes $UO_2(TSB)ROH$ is not fully evident in the i.r. spectra, but may be confirmed by ^1H n.m.r. spectral and X-ray diffraction studies. Such complexes undergo substitution reaction of the coordinated ethanol with various neutral monodentate ligands. Interchange reactions of the type:

$$UO_2(TSB)L + L' \rightarrow UO_2(TSB)L' + L$$

indicate the following stability sequence depending on the nature of the neutral monodentate ligand: $Ph_3PO > dmso > py \geqslant aniline > EtOH$.

In order to elucidate the mode of bonding of these quadridentate Schiff bases, the X-ray structure determinations of the complexes UO_2(salophen)-EtOH and UO_2(salen)MeOH were carried out.[11,12,13]

In UO_2(salen)MeOH, the chelating ligands are bent away in opposite direction with respect to the equatorial plane. The N–C–C–N group is in a near *gauche* conformation and its torsion angle is 51.8°. This conformation and the maintenance of the trigonal nature of the nitrogen cause the salicylaldehyde groups to adopt a stepped geometry. In UO_2(salophen)EtOH, a *cis* configuration for the N–C–C–N group is dictated by the stereochemistry of the ligand and so a boat conformation in the complex is required (Fig. 36).

As for the neutral alcohol molecule, a hydrogen bond (which explains the absence in the infrared spectrum of the stretching OH in the range 3600–3100 cm^{-1}), takes place between the oxygen of the alcohol and the phenolic oxygen of a Schiff base. A very interesting complex is given by the aquoglioxal-bis-(2-hydroxyanil)dioxouranium(VI), which may be obtained as blue–violet crystals by reaction between uranyl(VI) salts and the stoichiometric amount of 2,2′-bisbenzoxazoline in absolute ethanol. The ^1H n.m.r. spectra show that a molecule of water is present in this complex. The stereochemistry of this adduct is shown in Fig. 37.[8] The blue–violet color of the $UO_2(glioxamph)\cdot H_2O$ complex is probably due

TABLE XVI. I.R. Data (cm^{-1}) for Uranyl Complexes with Quadridentate Schiff Bases.

Complex	ν(C=N)	ν_3(O–U–O)	Other Characteristic Bands	Color
UO_2(salophen)(EtOH)	1602, 1598	910	–	Red Crystals
UO_2(salen)(EtOH)	1638, 1627	912	–	Red–yellow Crystals
UO_2(sal-1,3-propen)(EtOH)	1640, 1620	912	–	Red–yellow Crystals
UO_2(salophen)(py)	1605, 1598	895	–	Red Powder
UO_2(salen)(py)	1630, 1620	888	–	Red Powder
UO_2(sal-1,3-propen)(py)	1640, 1625	897	–	Red Powder
UO_2(salophen)($PhNH_2$)	1620	893	3320–3270 $\nu(NH_2)$	Yellow Powder
UO_2(salophen)(dmso)	1605	892	992 ν(S=O)	Bright Yellow Powder
UO_2(salen)(dmso)	1622	879	991 ν(S=O)	Orange Powder
UO_2(sal-1,3-propen)(dmso)	1622	882	995 ν(S=O)	Orange Crystals
UO_2(salophen)(Ph_3PO)	1604	895	1143 ν(P–O)	Yellow Powder
UO_2(salen)(Ph_3PO)	1620	883	1150 ν(P–O)	Yellow Powder
UO_2(sal-1,3-propen)(Ph_3PO)	1622, 1615	885	1160 ν(P–O)	Yellow Powder

to the mesomery conferred by planarity of the coordinated ligand.

In all the $UO_2(TSB)L$ complexes the configuration is given by a pentagonal bipyramid around the central ion. The U–N distances are always remarkably longer than suggested by the difference in covalent radii.[142,196] In complexes with 3*d* ions of known structure there are two types of bonding to the metal. In the complexes of Cu(II) and Co(II) the metal–nitrogen and metal–oxygen distances are roughly equivalent while with titanium(IV) and iron(III) the metal–oxygen bonds are much shorter than metal–nitrogen bonds.[14,15,37,96,156] This behaviour has been explained by Pearson's Hard–Soft Acid–Base concept.[143] Nitrogen would be expected to be less strongly bound to a hard acid as UO_2^{2+} because the oxygen has a relatively higher base strength toward such an acid.

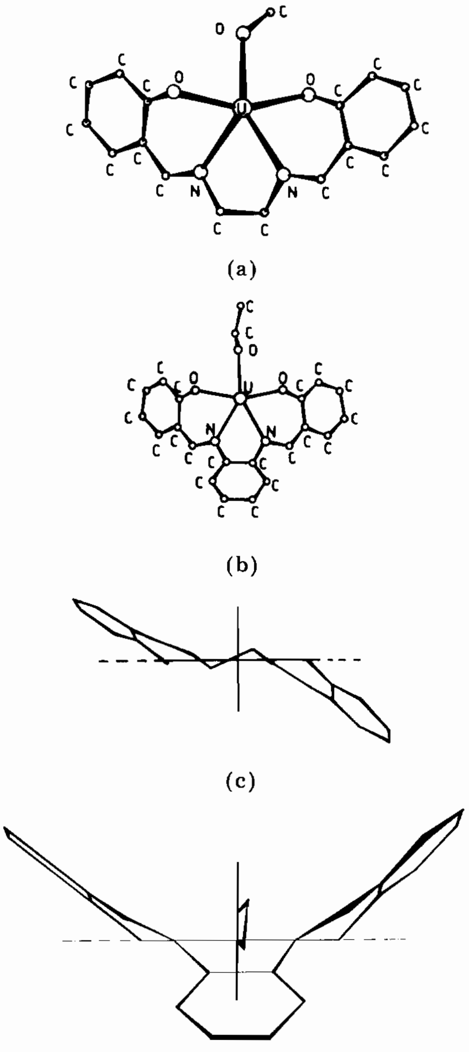


Fig. 36. Projection of UO_2(salen)MeOH and UO_2(salophen)-EtOH on the mean equatorial plane (a, b) and down a direction perpendicular to the uranyl group (c, d).

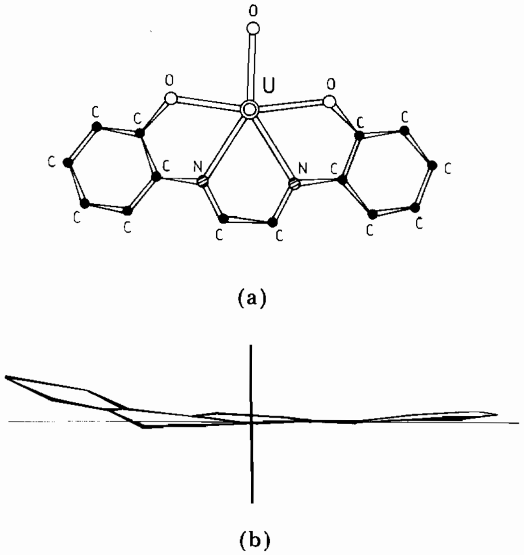


Fig. 37. Projection of UO_2(glioxamph)·H_2O on the mean equatorial plane (a) and down a direction perpendicular to the uranyl group (b).

The kinetic data on the reaction between UO_2^{2+} and the organic ligand 2,2′-bisbenzoxazoline (H_2B) were attributed to the reaction:

$$UO_2(S)_n^{2+} + H_2B \longrightarrow UO_2(B)(S) + 2H^+$$

(S indicates ethanol or water molecules).

A reaction scheme alternative to the bimolecular reaction reported above and also in agreement with the available experimental data could be the slow isomerization of the molecule H_2B to the tautomeric Schiff base form as shown in Fig. 38, followed by fast coordination to uranyl ion. However some evidence that the rate is not independent of $[UO_2^{2+}]$ indicates that the hypothesis of a direct bimolecular reaction is to be preferred. A rate law of the type: rate = $k[UO_2(S)_n][H_2B]$ was suggested. The positive value of the entropy of activation ($\Delta S^{\neq}$ = 12.1 e.u.) indicates that during the formation of the transition state there is a synchronous release of a number of solvent molecules and/or protonated solvent molecules.

Studies on uranyl complexes with optically active quadridentate Schiff bases have been carried out to obtain information on the conformation of the chelate rings and also on the distortion of the complex molecule as a whole.[141]

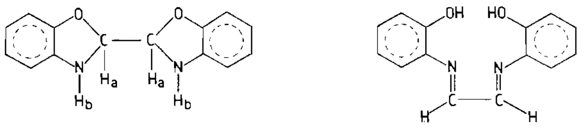


Fig. 38. Tautomeric isomers of 2,2′-bisbenzoxazoline.

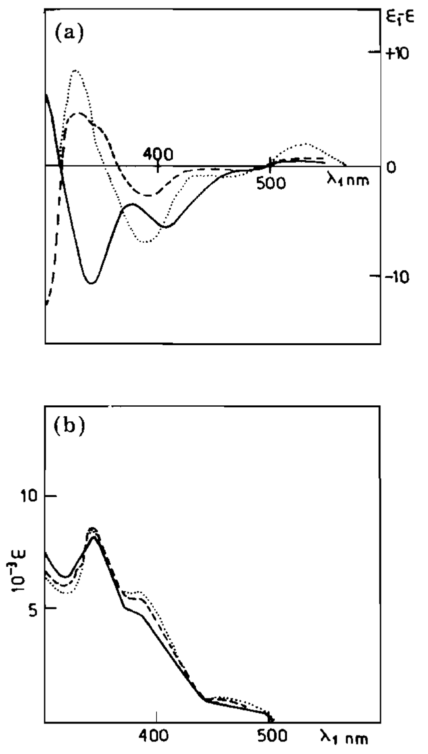


Fig. 39. The C.D. (a) and U.V. (b) spectra of the complex UO_2(sal(−)stien (stien = stilbendiamine) in $CHCl_3$ (——), CH_3OH (- - - - -), dmf (·······).

The overall coordination number is again seven. Circular dichroism spectra of the complex with salstien, carried out in different solvents, show that significant changes of the curves are found only in $CHCl_3$ solution where the five-coordination in the equatorial plane is removed by dissociation of the neutral additional ligand. It must be pointed out that no significant change can be detected in the u.v. spectra, this suggesting that the C.D. spectra are a more useful test for detecting changes in the coordination number (Fig. 39).

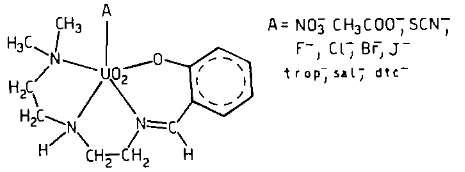


Fig. 40. The proposed configuration of UO_2(saldienN-$(CH_3)_2$)A.

Using the quadridentate Schiff base HsaldienN-$(CH_3)_2$, complexes of the type UO_2(saldienN-$(CH_3)_2$)A (A = Cl, Br, I, NO_3 *etc.*) were obtained.[180] They are non-electrolytes in CH_2Cl_2 solution, indicating that the bond between uranium and the anion is essentially covalent in nature; the ^1H n.m.r. spectra indicate that the Schiff base acts as quadridentate ligand, so the most probable configuration in the equatorial plane is given in Fig. 40 (Table XVII). This is confirmed by X-ray diffraction studies.[9] For the analogous uranyl(VI) complexes containing the tridentate Schiff base salenN$(CH_3)_2^-$, the configuration in Fig. 41 was proposed.

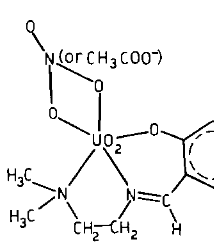


Fig. 41. The proposed configuration of UO_2(salenN$(CH_3)_2$)A.

For the acetato complexes it is easy to distinguish between mono and bidentate character in its mode of coordination toward a central metal; for the nitrato complexes the splitting of the doubly degenerate ν_3 into ν_4 and ν_1 is not a good guide to distinguishing between the two coordination modes. More information about this linking mode arises from the far i.r. spectra where the stretching U–O(NO_3) is known to lie. Two strong i.r. bands are assigned to the uranium–nitrate oxygen stretching for UO_2(salenN-$(CH_3)_2$)NO_3 at 201 and 252 cm^{-1} and one band at 261 cm^{-1} for UO_2(saldienN$(CH_3)_2$)NO_3. A similar behaviour has been found for other uranyl nitrato adducts.[183]

The u.v. spectra of these UO_2(saldienN$(CH_3)_2$)A complexes are very similar, as expected for electronic transitions mainly localized on the Schiff base moiety bonded to uranyl group, and show three rather detectable band maxima in the charge-transfer region above 340–350 nm. It may be argued that the apical oxygens→*f* transition of the uranyl moiety, centered at about 390–450 nm, has been covered by strong absorption corresponding to the charge-transfer from equatorial ligands to the uranium atom. Probably a charge-transfer $\pi \rightarrow f$ from the Schiff base orbitals to the *f* orbitals of the uranium takes place.

TABLE XVII. Comparison of the Infrared Data (cm^{-1}) of Mixed Uranyl Complexes with Quadridentate and Tridentate Schiff Bases.

Compound[a]	ν(NH)	ν(C=N)	ν_3(O–U–O)	ν_2(O–U–O)	Other Characteristic Bands	Color
$UO_2L_a(NO_3)$	3186	1617	907	255	1484 ν_4, 1278 $\nu_1(NO_3)$; 261 $\nu(U{-}ONO_2)$	Orange–red Crystals
$UO_2L_b(NO_3)$	–	1614	892	268	1476 ν_4, 1298 $\nu_1(NO_3)$; 252,201 $\nu(U{-}ONO_2)$	Yellow Powder
$UO_2L_a(CH_3COO)$	3191	1619	899	256	1639 ν_{as}, 1356 ν_s(–COO); 275 $\nu(U{-}OCOCH_3)$	Orange–yellow Crystals
$UO_2L_b(CH_3COO)$	–	1613	902	254	1538 ν_{as}, 1415 ν_s(–COO); 270 $\nu(U{-}OCOCH_3)$	Yellow Powder
UO_2L_a(trop)	Not resolved	1622	882	–	1610 ν(C=O trop)	Orange Powder
UO_2L_b(trop)	–	1624	896	–	1592 ν(C=O trop)	Orange–red Crystals
UO_2L_a(sal)	3223	1622	885	–	1658 ν(C=O sal)	Orange Powder
UO_2L_a(dtc)	3232	1620	886	–		Orange Powder
UO_2L_a(F)	3183	1625	889	258	412(br) ν(U–F)	Yellow Powder
UO_2L_a(Cl)	3180	1617	907	254	228 ν(U–Cl)	Yellow Powder
UO_2L_a(Br)	3167	1617	908	249	142 ν(U–Br)	Orange–yellow Powder
UO_2L_a(I)	3112	1624	892	258		Orange–red Powder
UO_2L_a(NCS)	3204	1615	906	252	2012 ν(C≡N); 797 ν(C=S)	Orange–red Powder

[a] L_a = saldienN$(CH_3)_2$; L_b = salenN$(CH_3)_2$.

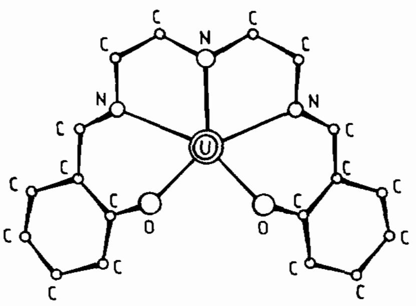


Fig. 42. The molecular configuration of UO_2saldien.

The potentially pentadentate H_2saldien is particularly suitable for the preparation of a series of seven-coordinate complexes with large cations such as UO_2^{2+}. The complex may be obtained as solvate from various solvents such as CH_3CN, EtOH, C_6H_6, C_5H_5N; however, all these adducts undergo an easy conversion to UO_2(saldien).[47]

The X-ray molecular structure of UO_2(saldien) shows that it has the expected seven-coordinate geometry[3] (Fig. 42).

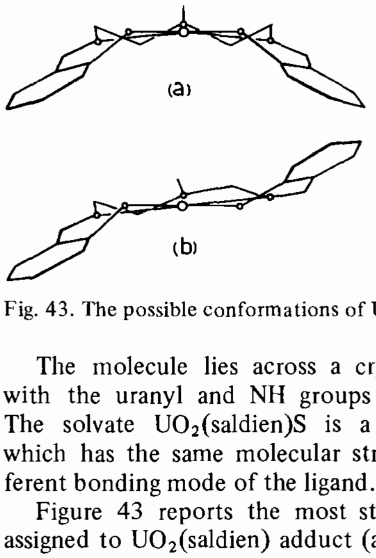


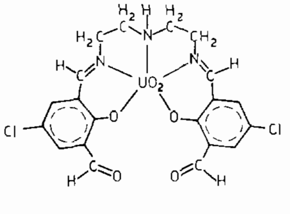
Fig. 43. The possible conformations of UO_2saldien.

The molecule lies across a crystal mirror plane with the uranyl and NH groups within the plane. The solvate UO_2(saldien)S is a metastable form, which has the same molecular structure with a different bonding mode of the ligand.

Figure 43 reports the most stable conformation assigned to UO_2(saldien) adduct (a) whilst conformation (b), apparently less stable, is assumed to occur in the solvate adduct. Their interconversion does not require inversion of the configuration of the middle secondary amine nitrogen atom.

A series of uranyl(VI) complexes related to UO_2-(saldien), with 5-Cl, 5-Br, 3-OMe, 3,5-Cl and 5,6-benzo substituents on the salicylic moiety, has been reported; they were prepared as solvates and characterized by their X-ray diffraction patterns and i.r. spectra. By contrast, the longer ligand system N,N′-bissalicylidene-1,7-diamino-4-aza-heptane and N,N′-bissalicylidene-1,7-diamino-4-aza-methylheptane are much more reluctant to form seven-coordinate uranium(VI) compounds. These ligands, with trimethylenediamine chelate rings, appear to be too large for ideal coordination to uranyl(VI) ion.

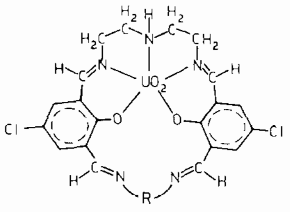
The synthesis and the characterization of a complex obtained by reaction of diethylenetriamine with 2,6-diformyl-4-chlorophenol in the presence of uranyl(VI) ion has been recently reported.[45] This complex is quite similar to UO_2(saldien) as shown in Fig. 44.



Complex $[UO_2A]$

Fig. 44. The proposed configuration of the complex obtained by reaction of uranyl nitrate, diethylenetriamine and 2,6-diformyl-4-chlorophenol.

In this complex the two uncoordinated formyl groups are sufficiently close to each other to allow an intramolecular cyclisation by treatment with diamines (Fig. 45).



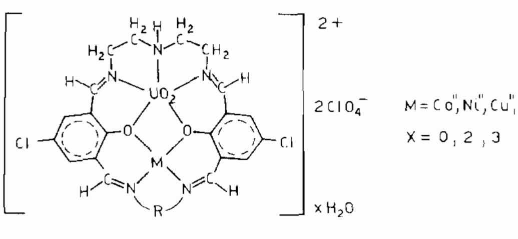
R	Complex
$-CH_2-CH_2-$	$[UO_2B_a]$
$-CH_2-CH_2-CH_2-$	$[UO_2B_b]$
$-CH_2-CH(CH_3)-$	$[UO_2B_c]$
$-CH_2-CH_2-NH-CH_2-CH_2$	$[UO_2B_d]$

Complexes $[UO_2B]$

Fig. 45. The proposed configuration of the cyclic complexes obtained from $[UO_2A]$ (Fig. 44) and diamines.

These complexes do not show the i.r. bands due to the C=O groups while the absorptions of the coordinated and uncoordinated C=N azomethyne groups are not resolved. No appreciable shift of the antisymmetric stretching ν_3 and bending ν_2 of the O–U–O group was observed after cyclisation. These cyclic complexes may act as ligands towards transition metal ions and some compounds have been reported (Fig. 46).

Marked differences upon coordination of the second metal ion are noted in the i.r. spectra, principally in the bands associated with the ν(C=N, νC–O and ν_3(O–U–O) modes. The νC=N is shifted to higher frequencies while the νC–O to lower. The simultaneous shift in the binuclear complexes to higher and lower frequencies for νC=N and νC–O modes respectively, is due to the coordination of the second metal which localizes the C=N double bond and seems to reduce the amount of partial double character of the phenolic C–O link.



Complexes $[UO_2BM](ClO_4)_2$

Fig. 46. The configuration of the binuclear complexes obtained from $[UO_2B]$ (Fig. 45) and cobalt(II), nickel(II) and copper(II) perchlorate.

The only significant change of the modes of uranyl (VI) group is the shift to higher frequencies of the antisymmetric stretching ν_3(O–U–O) on going from mononuclear to binuclear complexes. This shift could be explained by a decreased tendency to transfer charge from the phenolic oxygens to the uranium upon coordination of the second ion (Table XVIII).

The electronic spectra of the binuclear complexes do not allow an unambiguous identification of the stereochemistry about the 3*d* transition metal ion. The magnetic moments well agree with a distortion of the N_2O_2 chromophore from planar towards tetrahedral arrangement.

B. Schiff Base Complexes with Actinides(IV)

Few chelate compounds of uranium(IV) with Schiff bases have been characterized and the interest in preparing such complexes lies in the production of stable high-coordinated adducts for studies of the f^2 electronic system. The first known example of this type is NN′-ethylenebis(salicylideneiminato)uranium (IV), U(salen)$_2$.[36,160] The complex was prepared by reaction of the uranium(IV) tetrasalicylaldehydato with an excess of dry ethylenediamine under a nitrogen atmosphere. More recently the same complex was prepared by reacting UCl_4·2dme (dme = dimethoxyethane) with a thallous derivative of H_2salen in tetrahydrofuran (THF). The complex is generally soluble in common organic solvents and stable toward either decomposition or air oxidation both in the solid state and in solution. The complex is assumed to contain a single uranium(IV) atom complexed by two quadridentate molecules, this implying an eight-coordination geometry. Attempts to prepare U(salen)$_2$ under mild conditions failed. UCl_4 reacts with H_2salen in THF at room temperature to give a yellow–orange 1:1 product, formulated as UCl_4H_2salen·2THF,[42] which by treatment with

TABLE XVIII. IR Data (cm^{-1}) for Cyclic Uranyl Complexes Containing a Second Metal Ion.

Compound[a]	ν(NH)	ν(C=N)	ν(C–O)	ν_3(O–U–O)	Color
UO_2A	3252	1630	1320	892	Orange–red Powder
UO_2B_a	3247	1633	1308	896	Orange Powder
$UO_2B_aNi(ClO_4)_2 \cdot 2H_2O$	3235	1674, 1638	1291	926	Yellow Powder
$UO_2B_aCu(ClO_4)_2$	3222	1667, 1634	1282	922	Green Powder
$UO_2B_aCo(ClO_4)_2$	3251	1667, 1636	1289	921	Yellow Powder
UO_2B_b	3200	1628	1310	885	Orange–red Powder
$UO_2B_bNi(ClO_4)_2 \cdot 3H_2O$	3239	1655, 1645	1298	925	Yellow Powder
$UO_2B_bCu(ClO_4)_2 \cdot EtOH$	Not Resolved	1655, 1623	1290	924	Green Powder
$UO_2B_bCo(ClO_4)_2 \cdot 2H_2O$	3260	1650, 1635	1298	925	Yellow Powder
UO_2B_c	3174	1630	1307	897	Orange–red Powder
$UO_2B_cNi(ClO_4)_2 \cdot 3H_2O$	3230	1667, 1632	1287	920	Yellow Powder
$UO_2B_cCu(ClO_4)_2 \cdot 2EtOH$	3228	1667, 1629	1289	927	Green Powder
$UO_2B_cCo(ClO_4)_2 \cdot 2H_2O$	3240 broad	1650, 1639	1285	924	Yellow Powder
UO_2B_d	3230 broad	1632	1314	897	Orange–red Powder
$UO_2B_dNi(ClO_4)_2$	3294, 3197	1662, 1629	1292	920	Yellow Powder

[a] For the meaning of the labelling A, B_a, B_b, B_c, B_d see Fig. 49, 50, 51.

pyridine in $CHCl_3$ followed by heating *in vacuo* at 150 °C for two days yields the green $UsalenCl_2$. The nonelectrolytic nature of the complex should account for a structure in which the coordination number six is present, but a higher coordination number is probably reached by oxygen bridges. The complex, recrystallized from THF, yields the green $U(salen)_2Cl_2 \cdot (THF)_2$. The same complex may be obtained by treating the thallous derivative of H_2salen in THF with a stoichiometric amount of $UCl_4 \cdot 2$dme in THF followed by precipitation with n-hexane. The complex is not stable to air and on exposure to moisture it decomposes rapidly. The coordination of THF groups is confirmed by two bands at 1030 and 870 cm^{-1} in the i.r. spectrum, attributed to the asymmetric and symmetric C–O stretching respectively. As previously supposed for $U(salen)_2$, $U(salen)_2Cl_2 \cdot (THF)_2$ is monomeric and the uranium atom is octacoordinated with the chloro groups on opposite sides of the salen ligand. A ligand redistribution reaction in THF between $U(salen)_2$ and UCl_4 has been studied; equimolecular quantities of UCL_4 and $U(salen)_2$ react with dipyridine according to the following stoichiometry:[43]

$$UCl_4 + U(salen)_2 + 2\ dipy \longrightarrow 2\ U(salen)Cl_2dipy$$

The final product, $U(salen)Cl_2dipy$, is probably preceded by the formation of the 1:1 $U(salen)_2UCl_4$ species. Also the conjugate bases of acetylacetone, dipivaloylmethane and N-methylsalicylideneimine (mesal) react with equimolar quantities of $U(salen)_2$ and UCl_4 yielding the mixed complexes U(salen)-$(acac)_2$, $U(salen)(THD)_2$ and $U(salen)(mesal)_2$. These reactions were carried out in THF in the presence of anhydrous ammonia. The complexes resulting from the reactions were separated quite easily after elimination of ammonium chloride. These reactions proceed in two separate steps: the first one is the reaction of $U(salen)_2$ with UCl_4 over a time sufficient to reach the equilibria:

$$U(salen)_2 + UCl_4 \rightleftharpoons U(salen)_2 \cdot UCl_4$$

$$U(salen)_2 \cdot UCl_4 \rightleftharpoons 2\ U(salen)Cl_2$$

in such a way that $U(salen)Cl_2$ is the predominant species.

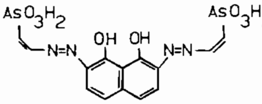
The formation of the 1:1 adduct $U(salen)_2 \cdot UCl_4$ seems to be a necessary requirement for the redistribution reaction to take place. It has been shown that $U(salen)_2$ and $U(acac)_4$ do not react appreciably under comparable conditions. The mixed uranium (IV) complexes were also obtained by reacting preformed $U(salen)Cl_2$ with HTHD in the presence of ammonia. Proof of the existence of mixed complexes of uranium(IV) was obtained by mass spectrometry of $U(salen)(acac)_2$ and $U(salen)(THD)_2$ which appear to be the most volatile compounds among those prepared. The mixed complexes $U(salen)(chelate)_2$ are monomeric as shown by cryoscopic molecular weight determinations. For these complexes a monomeric structure has been proposed in which the uranium atom attains its usual eight-coordination and salen donor atoms may have a substantially planar arrangement. $Th(salen)_2$ and $Th(salen)Cl_2 \cdot (THF)_2$ have been prepared using the same method as the uranium(IV) analogues; they are yellow, the former stable in air, the latter unstable.

Their infrared spectra are very similar to the analogous uranium(IV) complexes. The peaks assigned to the stretching frequencies ν(C=N) fall for $Th(salen)_2$ at 1632 and 1622 cm^{-1}, for $Th(salen)Cl_2 \cdot (THF)_2$ at 1625 cm^{-1}; they lie at 1632 and 1623 cm^{-1} for $U(salen)_2$ and 1628 cm^{-1} for $U(salen)Cl_2 \cdot (THF)_2$. In the far infrared region, the absorption due to the vibrational modes of Th–Cl and U–Cl in the mixed complexes should contribute to the broad band at about 260–240 cm^{-1}.

8. Azo Complexes

A. Arsenazo Derivatives

The functional groups responsible for the formation of complexes between the ligands arsenazo and actinides are:



Thorium(IV), uranium(IV) and uranyl(VI) ion form covalent bonds with the groups AsO_3H_2 and OH. A special role is played by the M–N coordinate link. In addition to the considerable increase in stability resulting from the formation of two six-membered, almost aromatic chelate rings, complex formation leads to the transfer of some positive charge to the chromophoric centre of the molecule (the azo group), resulting in a marked deepening of the colour.

1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid (apans) was first reported to form in solution a thorium(IV) complex in which the ratio Th:apans is 2:3.[41,54,120,121] Spectrophotometric analyses indicate on the contrary that in the complex the correct ratio Th:apans is 1:2.[140] It was found that the analogous uranium(IV) complex also contains two molecules of apans per metal ion.[77]

2,2′-1,8-dihydroxy-3,6-disulpho-2,7-naphthylene-bis(azo)dibenzene arsonic acid (arsenazo III) is an extremely sensitive colorimetric reagent for thorium and uranium. With uranyl(VI) ion it forms only a complex with 1:1 composition; this is confirmed by measurements in solution and also by the non-dependence of the electronic spectrum on the UO_2^{2+}:arsenazo III ratio; the spectrum remains unchanged from 1:1 to 10^5:1. A possible structure of this complex is given in Fig. 47.

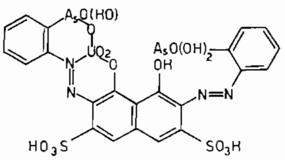


Fig. 47. A possible configuration of the uranyl complex with arsenazo III.

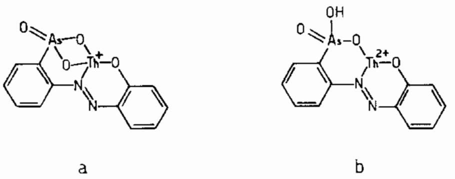


Fig. 48. The suggested coordination around Th(IV) in Th(arsenazo III) (a) and $Th(arsenazo\ III)_2$ (b).

The molar absorptivity increases with the acidity of the solution independently of the type of acid used and of the metal/ligand ratio. In acid solution (11.6 *M* HNO_3) another complex is present, which differs only in the molar absorptivity at 656 nm (8.8×10^3 for this species *vs.* 5.3×10^3 for UO_2-arsenazo).[27] With thorium(IV) and uranium(IV), arsenazo III forms the complexes M(arsenazo III) and $M(arsenazo\ III)_2$. A greater ligand:metal ratio in the complexes is prevented by hindrance; the ligand: metal ratio in the complex is always 1:2 when a large excess (10–20 fold) of the ligand is used.

It has been suggested that in Th(arsenazo III) the ligand is coordinated as shown in Figure 48a) while in $Th(arsenazo\ III)_2$ it is bound as in Figure 48b).[155]

Recently the behaviour of the Th–arsenazo III system in acid solution has been reported.[27] In Fig. 49 the molar absorptivity, at 662 nm, against acidity of the solution for $C_{arsenazo\ III} \gg C_{metal}$ and for $C_{metal} \gg C_{arsenazo\ III}$ are reported.

It may be noted that the previously reported species M_2L_2, ML_3 and ML_4 (L = arsenazo III) are not present.[39]

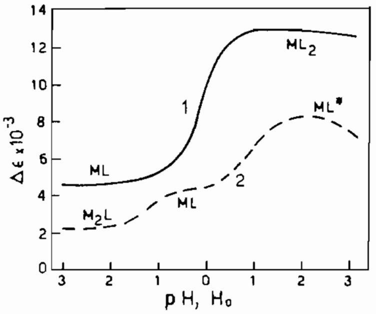
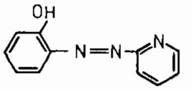


Fig. 49. The molar absorptivity at 662 nm against acidity for the systems: a) $Conc._{arsenazo\ III} \gg Conc._{metal}$; 2) $Conc._{metal} \gg Conc._{arsenazo\ III}$.

B. Pyridylazo Derivatives

The functional groups responsible for the formation of complexes between pyridylazo ligands and actinide ions are:



Such ligands were used principally as analytical reagents for the determination of traces of uranium.[21]

1-(2-pyridylazo)-2-naphthol (HPAN) has been described to form in alkaline aqueous solution (pH = 8) containing complexing agents such as EDTA, the uranyl–PAN complex in the molar ratio 2:1.[49,163] The addition of complexing agents is very effective in eliminating interference from other ions. No spectrophotometric evidence is available for the formation of complexes containing a molar ratio different from 2:1. Below pH 4 no complex formation between uranium and HPAN was observed.[101] These ligands may coordinate to the central metal ion with the pyridine nitrogen, the azo nitrogen farthest from the heterocyclic one and the *o*-hydroxyl group. In the most probable configuration of the resulting complexes the two ligands must act one as bidentate and the other as tridentate in accordance with uranyl tridentate Schiff base derivatives.[10,51,179] A more complicated behaviour has been found for the system uranyl–4-(2-pyridylazo)-resorcinol (H_2PAR). Potentiometric titrations have shown that complexes containing a ligand:metal ratio greater than 2:1 were not formed,[81] while in alkaline medium (pH > 8.5) a complex 1:2 is formed.[76] A study on the complexation of uranyl(VI) ion with H_2PAR in aqueous solution at pH < 8.5 with an excess of ligand demonstrated that two different uranyl 1:1 chelates were formed, one at pH < 4 and the other at pH > 6.[167] At pH < 4 it was found that the complex $[UO_2(HPAR)]^+$ was formed according to the following equilibria:

$$UO_2^{2+} + H_3PAR^+ \rightleftharpoons [UO_2(HPAR)]^+ + 2H^+$$

$$UO_2^{2+} + H_2PAR \rightleftharpoons [UO_2(HPAR)]^+ + H^+$$

In the second formation region at pH > 6 the complex $[UO_2(HPAR)]^+$ undergoes a reaction according to the following equilibrium:

$$[UO_2(HPAR)]^+ \rightleftharpoons UO_2(PAR) + H^+$$

Continuous variation plots indicated the existence of a 1:1 complex over the pH range 3.1–8. Solid compounds, not well characterized, may be precipitated at pH = 1.85 as deep red crystals and at pH 3.35 as dark red–brown crystals when ammonia (0.5 *M*) is added dropwise to a perchlorate solution (1*M*) of uranyl(VI) salts and H_2PAR.

C. Thiazolylazo Derivatives

Little information is available about the interaction of the actinide ions with thiazolylazo dyes. Because of their similarity with pyridylazo ligands, they are used as possible analytical and complex forming reagents; however the corresponding complexes have not been isolated in the solid state. The equilibria involved, the composition and the stability of the chelates obtained by the reaction of uranyl(VI) salts and 1-(2-thiazolylazo)-2-hydroxy-4-dimethylaminobenzene, 2-(2-thiazolylazo)-1-hydroxy-5-diethylaminobenzene, 4-(2-thiazolylazo)-resorcinol (TAR), 2-(2-thiazolylazo)-4-methoxyphenol (TAMR) and 2-(2-thiazolylazo)-5-methoxyphenol (TAMH) have been studied. The ligand:uranyl ratio of the complexes obtained in solution is always 1:1. A green–violet crystalline product was obtained by treating a perchlorate solution (1*M*) of uranyl nitrate and TAR with ammonia (1*M*). The precipitate formulated as $UO_2TAR \cdot 2H_2O$ strongly absorbs H_2O; no physico-chemical measurements on this complex were carried out. The complexes derived from TAMR and TAMH can be easily extracted into amyl alcohol or isobutylmethylketone. The spectrophotometric results show that the chelates $UO_2TAMH(NO_3) \cdot S$ and $UO_2TAMR(NO_3) \cdot S$ (S = solvent) are the species extracted into the organic phase.

9. Conclusions

The present review is, to the best of our knowledge, the most complete source of information dealing with preparative methods and physico-chemical data on actinide complexes in their various oxidation states with the most usual coordinating organic ligands. Considerable additional work would be required on the transplutonium elements to better define their coordinating properties, especially in the solid state.

It is hoped that research workers and teachers will find this compilation useful.

10. References

1 J. Abraham and A. Corsini, *Analyt. Chem., 42,* 1528 (1970).
2 K. M. Abubacker and N. S. Krishna-Prasad, *J. Inorg. Nucl. Chem., 16,* 296 (1961).
3 M. N. Aktar, E. D. McKenzie, R. E. Paine and A. J. Smith, *Inorg. Nucl. Chem. Letters, 5,* 673 (1969).
4 B. Allard, *Acta Chem. Scand., 26,* 3492 (1972).
5 V. Amirthalingham, *Acta Cryst., 13,* 61 (1960).
6 K. W. Bagnall, "The Actinide Elements", Elsevier, 1972.
7 K. W. Bagnall, D. Brown, D. H. Hotal and F. Lux, *J. Chem. Soc. (A),* 465 (1968).
8 G. Bandoli, L. Cattalini, D. A. Clemente, M. Vidali, and P. A. Vigato, *Chem. Comm.,* 344 (1972).
9 G. Bandoli and D. A. Clemente, private communication.
10 G. Bandoli, D. A. Clemente, F. Benetollo, M. Vidali, P. A. Vigato, and U. Casellato, *Inorg. Nucl. Chem. Letters, 9,* 433 (1973).

11 G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali and P. A. Vigato, *Inorg. Nucl. Chem. Letters, 8,* 961 (1972).
12 G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali and P. A. Vigato, *Chem. Comm.,* 1330 (1971).
13 G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali and P. A. Vigato, *J. Chem. Soc. Dalton,* 2331 (1973).
14 E. N. Baker, D. Hall and T. N. Waters, *J. Chem. Soc. (A),* 400 (1970).
15 E. N. Baker, D. Hall and T. N. Waters, *J. Chem. Soc. (A),* 406 (1970).
16 B. Baker and D. T. Sawyer, *Inorg. Chem., 8,* 1160 (1969).
17 Y. Baskin and J. R. Ferraro, *J. Inorg. Nucl. Chem., 30,* 241 (1968).
18 Y. Baskin and N. S. Krishna-Prasad, *J. Inorg. Nucl. Chem., 25,* 1011 (1963).
19 G. Basu and R. L. Belford, *J. Inorg. Nucl. Chem., 28,* 252 (1966).
20 E. W. Berg and J. J. C. Acosta, *Anal. Chim. Acta, 40,* 101 (1968).
21 W. Berger and H. Elvers, *Z. Anal. Chem., 171,* 185 (1959).
22 A. M. Bhandari and R. N. Kapoor, *Can. J. Chem., 44,* 1468 (1966).
23 A. M. Bhandari and R. N. Kapoor, *Aust. J. Chem., 20,* 233 (1967).
24 W. Bilz, *Annalen, 331,* 334 (1904).
25 W. Bilz and J. A. Clinch, *Z. Anorg. Chem., 40,* 218 (1904).
26 G. Bombieri, S. Degetto, G. P. Marangoni, R. Graziani and E. Forsellini, *Inorg. Nucl. Chem. Letters, 9,* 233 (1973).
27 J. Boràk, Z. Slovàk and J. Fischer, *Talanta, 17,* 215 (1970).
28 J. Bordner and L. Gordon, *Talanta, 9,* 1003 (1962).
29 J. Bordner, E. D. Salesin and L. Gordon, *Talanta, 8,* 579 (1961).
30 M. Borrel and R. Paris, *Anal. Chim. Acta, 4,* 267 (1950).
31 D. C. Bradley, J. S. Ghotra and F. A. Hart, *Inorg. Nucl. Chem. Letters, 10,* 209 (1974).
32 D. Brown, "Inorganic Chemistry", Series One, Vol. 7, Lanthanides and Actinides, K. W. Bagnall Editor, Butterworth, London (1972), p. 87.
33 D. Brown, *Advanced Inorg. Chem. Radiochem., 12,* 1 (1969).
34 D. Brown and C. E. F. Richard, *J. Chem. Soc. (A),* 3373 (1970).
35 D. Brown, B. Whittaker and N. Edelstein, private communication.
36 D. Brown and F. J. Wolter, *Chem. Abstr., 51,* 5590 (1957).
37 S. Bruckner, M. Calligaris, C. Nardin and L. Randaccio, *Acta Crystl., B25,* 1671 (1969).
38 E. P. Bullwinkel and P. Nobel, *J. Am. Chem. Soc., 80,* 2955 (1958).
39 B. Budèsinsky, *Collection Czech. Chem. Comm., 28,* 2909 (1963).
40 J. H. Burns and M. D. Danford, *Inorg. Chem., 8,* 1780 (1969).
41 C. H. Byrd and C. V. Banks, *U.S. Atomic Energy Comm. Document ISC 456,* June 1953.
42 F. Calderazzo, M. Pasquali and N. Corsi, *Chem. Comm.,* 784 (1973).
43 F. Calderazzo, M. Pasquali and T. Salvatori, *J. Chem. Soc. Dalton,* 1102 (1974).
44 U. Casellato, M. Vidali and P. A. Vigato, *J. Inorg. Nucl. Chem.,* in press.
45 U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Nucl. Chem. Letters, 10,* 437 (1974).
46 L. Cattalini, U. Croatto, S. Degetto and E. Tondello, *Inorg. Chim. Acta Rev., 5,* 19 (1971).
47 L. Cattalini, S. Degetto, M. Vidali and P. A. Vigato, *Inorg. Chim. Acta, 6,* 173 (1972).
48 L. Cattalini, P. A. Vigato, M. Vidali, S. Degetto and U. Casellato, *Inorg. Nucl. Chem., 37,* 1721 (1975).
49 K. L. Cheng, *Anal. Chem., 30,* 1027 (1958).
50 B. Chenon and C. Sandorfy, *Can. J. Chem., 36,* 1181 (1958).
51 D. A. Clemente, G. Bandoli, F. Benetollo, M. Vidali, P. A. Vigato and U. Casellato, *J. Inorg. Nucl. Chem., 36,* 1999 (1974).
52 D. A. Clemente, G. Bandoli, M. Vidali, P. A. Vigato, R. Portanova and L. Magon, *J. Cryst. Mol. Struct., 3,* 221 (1973).
53 J. M. Cleveland, *Coord. Chem. Rev., 5,* 101 (1970).
54 J. Clinch, *Anal. Chim. Acta, 14,* 162 (1956).
55 A. E. Comyns, *Chem. Rev., 60,* 115 (1960).
56 A. E. Comyns, B. M. Gatehouse and R. E. Wait, *J. Chem. Soc.,* 4655 (1958).
57 G. Condorelli, I. Fragalà, A. Cassol and E. Tondello, private communication.
58 a) A. Corsini and J. Abraham, *Talanta, 15,* 562 (1968).
b) A. Corsini and J. Abraham, *Talanta, 17,* 439 (1970).
59 A. Corsini and J. Abraham, *Chem. Comm.,* 856 (1968).
60 A. Corsini, J. Abraham and M. Thompson, *Chem. Comm..* 1101 (1967).
61 a) A. Corsini, J. Abraham and M. Thompson, *Talanta, 18,* 481 (1971).
b) A. Corsini and J. Abraham, *Can. J. Chem., 48,* 2360 (1970).
62 M. D. Danford, J. H. Burns, C. E. Higgins, J. R. Stokely and W. H. Baldwin, *Inorg. Chem., 9,* 1953 (1970).
63 V. W. Day and J. L. Hoard, *J. Am. Chem. Soc., 92,* 3626 (1970).
64 S. Degetto, G. Marangoni, G. Bombieri, R. Graziani, E. Forsellini and L. Baracco, *J. Chem. Soc.,* in press.
65 L. Di. Sipio and E. Tondello, private communication.
66 L. Doretti, P. Zanella, S. Faleschini and G. Faraglia, *J. Inorg. Nucl. Chem., 35,* 3171 (1973).
67 L. Doretti, P. Zanella, G. Faraglia and S. Faleschini, *J. Organometall. Chem., 43,* 339 (1972).
68 Y. Dutt and R. P. Singh, *J. Indian Chem. Soc., 42,* 767 (1965).
69 R. F. Evans and W. Kynaston, *J. Chem. Soc.,* 1005 (1962).
70 C. S. Erasmus and J. C. A. Boeyens, *Acta Cryst., B25,* 1843 (1970).
71 S. Faleschini, L. Doretti, P. Zanella, F. Madalosso, P. A. Vigato and M. Vidali, unpublished results.
72 R. C. Fay and T. J. Pinnavaia, *Inorg. Chem., 7,* 508 (1968).
73 J. R. Ferraro and T. V. Healy, *J. Inorg. Nucl. Chem., 24,* 1463 (1962).
74 D. Feinander and C. Keller, *Inorg. Nucl. Chem. Letters, 5,* 625 (1969).
75 J. E. Fleming and H. Lynton, *Can. J. Chem., 45,* 1637 (1967).
76 T. M. Florence and Y. Farrar, *Analyt, Chem., 35,* 1613 (1963).
77 J. K. Foreman, C. J. Riley and J. D. Smith, *Analyst, 82,* 89 (1957).
78 E. Frasson, G. Bombieri and C. Panattoni, *Nature, 202,* 1325 (1964).
79 E. Frasson, G. Bombieri and C. Panattoni, *Coord. Chem. Rev., 1,* 145 (1966).
80 F. Frere, *J. Am. Chem. Soc., 55,* 4362 (1933).

81 W. J. Geary, G. Nickless and F. H. Pollard, *Anal. Chim. Acta, 26,* 575 (1962).
82 H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. E. Nobis, J. R. Thirtle, H. L. Yale and F. A. Yoeman, *J. Am. Chem. Soc., 78,* 2790 (1956).
83 D. Grdenic and B. Matkovic, *Acta Cryst., 12,* 817 (1959).
84 D. Grdenic and B. Matkovic, *Nature, 182,* 465 (1958).
85 D. Grdenic and B. Matkovic, *Acta Cryst., 16,* 456 (1963).
86 C. Görller-Warland and S. De Jaegere, *Spectrochim. Acta, 28A,* 257 (1971).
87 A. A. Grinberg and A. D. Thoitskaia, *Chem. Abst., 52,* 2477i (1958).
88 S. I. Gusev, V. I. Kumov, E. V. Sokolova and A. S. Pesis, *Russ. J. Inorg. Chem.* (English edition), *6,* 958 (1961).
89 H. Gysling and M. Tsutsui, *Advances in Organometal. Chem., 9,* 361 (1970).
90 K. Hager, *Z. Anorg. Allgem. Chem., 162,* 85 (1927).
91 J. M. Haigh and D. A. Thornton, *Inorg. Nucl. Chem. Letters, 6,* 231 (1970).
92 J. M. Haigh and D. A. Thornton, *J. Inorg. Nucl. Chem., 33,* 1787 (1971).
93 J. M. Haigh and D. A. Thornton, *J. Mol. Structure, 8,* 351 (1971).
94 D. Hall, A. D. Rae and T. N. Waters, *Proc. Chem. Soc.,* 21 (1964).
95 D. Hall, A. D. Rae and T. N. Waters, *Acta Cryst., 22,* 258 (1967).
96 D. Hall and T. N. Waters, *J. Chem. Soc. (A),* 2644 (1960).
97 R. D. Hancock and D. A. Thornton, *J. Mol. Structure, 4,* 377 (1969).
98 H. J. Harries, *J. Inorg. Nucl. Chem., 29,* 2484 (1967).
99 B. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rowley, *J. Chem. Soc.,* 1010 (1947).
100 R. G. Hayes and J. L. Thomas, *Organometal. Chem. Rev. A, 7,* 1 (1971).
101 M. H. Hayes and J. S. Wright, *Talanta, 11,* 607 (1964).
102 F. Hecht and Ehrmann, *Z. Analyt. Chem., 100,* 98 (1935).
103 F. Hecht and W. Reich-Rohrwig, *Monasth. Chem., 53–54,* 596 (1929).
104 G. R. Horton and W. W. Wendlant, *J. Inorg. Nucl. Chem., 25,* 241 and 247 (1963).
105 E. K. Hulet and D. D. Bodé, "Inorganic Chemistry", Series One, Vol. 7, Lanthanides and Actinides, K. W. Bagnall Editor, Butterworth, London (1972), p. 1.
106 H. M. N. Irving, *Quart. Rev., 5,* 200 (1951).
107 H. M. N. Irving and D. M. Edgington, *J. Inorg. Nucl. Chem., 20,* 321 (1961).
108 A. D. Jones and G. R. Choppin, *Actinides Rev., 1,* 311 (1969).
109 R. G. Jones, G. Karmas, G. A. Martin, and H. Gilman, *J. Am. Chem. Soc., 78,* 4285 (1956).
110 B. Kanellakopulos and K. W. Bagnall, "Inorganic Chemistry", Series One, Vol. 7, Lanthanides and Actinides, K. W. Bagnall Ed., Butterworth, London (1972), p. 299.
111 J. J. Katz and J. Sheft, *Advanced Inorg. Chem. Radiochem., 2,* 195 (1960).
112 C. Keller, "The Chemistry of the Transuranium Elements", Verlag Chemie GmbH, Weinheim Bergstr., Germany (1971).
113 C. Keller and S. H. Eberle, *Radiochim. Acta, 8,* 65 (1967).
114 C. Keller and S. H. Eberle, *Radiochim. Acta, 4,* 141 (1965).
115 C. Keller, S. H. Eberle and K. Mosdzelewki, *Radiochim. Acta, 5,* 185 (1966).
116 C. Keller, D. Feinauer and H. Schweizer, *Radiochim. Acta, 26,* 185 (1971).
117 C. Keller and K. Mosdzelewki, *Radiochim. Acta, 7,* 185 (1967).
118 C. Keller and H. Schreck, *J. Inorg. Nucl. Chem., 31,* 1121 (1969).
119 L. I. Kononenko and L. M. Burtnenko, *Russian J. Inorg. Chem.* (English ed.), *13,* 101 (1968).
120 V. I. Kuznetsov, *Compt. Rend. Acad. Sci. U.S.S.R., 31,* 898 (1941).
121 V. I. Kuznetsov, *J. Gen. Chem. U.S.S.R., 14,* 914 (1944).
122 N. C. Li, S. M. Wang and W. R. Walker, *J. Inorg. Nucl. Chem., 27,* 2263 (1965).
123 S. J. Lippard, *Progress in Inorganic Chemistry,* A. Cotton Editor, Vol. 8, p. 109 (1967).
124 R. C. Lord and R. E. Nerrifield, *J. Chem. Phys., 21,* 166 (1953).
125 R. J. Magee and L. Gordon, *Talanta, 12,* 445 (1965).
126 R. J. Magee and I. Woodward, *Talanta, 13,* 709 (1966).
127 E. D. McKenzie, R. E. Paine and S. J. Selvey, *Inorg. Chim. Acta, 10,* 41 (1974).
128 A. E. Martell and L. G. Sillen, "Stability Constants", Spec. Publ. no. 17 and Spec. Pub. no. 25, Suppl. no. 1, Chem. Soc. London, 1964, 1971.
129 F. S. Martin and R. J. W. Holt, *Quart. Rev., 13,* 327 (1959).
130 T. Moeller and M. V. Ramaniah, *J. Am. Chem. Soc., 76,* 2022 (1954).
131 T. Moeller and M. V. Ramaniah, *J. Am. Chem. Soc., 76,* 5251 (1954).
132 T. Moeller and D. H. Wilkins, *Inorg. Synth., 4,* p. 110, McGraw-Hill, New York, 1953.
133 G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", Wiley, New York, 1957.
134 E. L. Muetterties, *J. Am. Chem. Soc., 88,* 305 (1966).
135 E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc., 87,* 4706 (1965).
136 E. L. Muetterties and C. M. Wright, *Quart. Rev., 21,* 109 (1967).
137 K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc., 83,* 4533 (1961).
138 L. Newman and P. Klotz, *J. Inorg. Nucl. Chem., 29,* 1481 (1967).
139 R. H. Nuttal, D. W. Sharp and T. C. Waddington, *J. Chem. Soc.,* 4965 (1960).
140 A. R. Palmer, *Anal. Chim. Acta, 19,* 458 (1958).
141 A. Pasini, M. Gullotti and E. Cesarotti, *J. Inorg. Nucl. Chem., 34,* 3821 (1972).
142 L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, 1960, p. 518.
143 R. G. Pearson, *J. Am. Chem. Soc., 85,* 3533 (1963).
144 D. F. Peppard, *Advanced Inorg. Chem. Radiochem., 9,*1 (1966).
145 P. Pfeiffer, Th. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *J. Für Prakt. Chemie, 149,* 217 (1937).
146 G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", Freeman, S. Francisco, 1960, p. 28.
147 D. L. Plymale and W. H. Smith, *J. Inorg. Nucl. Chem., 30,* 2267 (1968).
148 D. L. Plymale and W. H. Smith, *J. Inorg. Nucl. Chem., 31,* 233 (1969).

149 E. Rabinowitch and R. L. Belford, "Spectroscopy and Photochemistry of Uranyl Compounds", Pergamon, Oxford (1964).

150 J. L. Ryan, "Inorganic Chemistry", Series One, Vol. 7, Lanthanides and Actinides, K. W. Bagnall Editor, Butterworth, London (1972), p. 323.

151 L. Sacconi, G. Garoti and P. Paoletti, *J. Chem. Soc.*, 4257 (1958).

152 L. Sacconi and G. Giannoni, *J. Chem. Soc.*, 2368 (1954).

153 L. Sacconi and G. Giannoni, *J. Chem. Soc.*, 2751 (1954).

154 I. A. Savick, A. K. Pikaev, V. G. Lebedev, E. U. Kuz'michaeva and V. I. Spitsyn, *Russ. J. Inorg. Chem.* (English Ed.), *7,* 254 (1962).

155 S. B. Savvin and M. P. Volynec, *Zhur. Neorgen. Khim.*, *8,* 2470 (1963).

156 W. P. Schaefer and R. E. Marsh, *Acta Cryst., B25,* 1675 (1969).

157 H. I. Schlesinger, H. C. Brown, J. J. Katz, S. Archer and R. A. Lad, *J. Am. Chem. Soc.*, *75,* 2446 (1953).

158 G. Seaborg, *Ann. Rev. Nucl. Sci., 18,* 53 (1968).

159 T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem., 29,* 1475 (1967).

160 J. Selbin and J. D. Ortego, *J. Inorg. Nucl. Chem., 29,* 1449 (1967).

161 J. Selbin and J. D. Ortego, *Chem. Rev., 69,* 657 (1969).

162 J. Selbin and J. D. Ortego, *J. Inorg. Nucl. Chem., 30,* 313 (1968).

163 S. Shibata, *Anal. Chim. Acta, 22,* 479 (1960).

164 T. H. Siddal and W. E. Stewart, *Chem. Comm.*, 922 (1969).

165 R. F. Sieck, J. J. Richard, K. Iversen and C. V. Banks, *Analyt. Chem., 43,* 913 (1971).

166 N. Singer, B. F. Studd and A. G. Swallow, *Chem. Comm.*, 342 (1970).

167 L. Sommer, V. M. Ivanov and H. Novotna, *Talanta, 14,* 329 (1967).

168 M. S. Subramanian and V. K. Manchanda, *J. Inorg. Nucl. Chem., 33,* 3001 (1971).

169 M. S. Subramanian, S. A. Pai and V. K. Manchanda, *Aust. J. Chem., 26,* 85 (1973).

170 M. S. Subramanian and A. Viswanatha, *J. Inorg. Nucl. Chem., 31,* 2575 (1969).

171 H. A. Swain and D. G. Karraker, *Inorg. Chem., 9,* 1766 (1970).

172 A. Syamal, *Inorg. Nucl. Chem. Letters, 4,* 543 (1968).

173 J. E. Tacchet and D. T. Sawyer, *Inorg. Chem., 3,* 692 (1964).

174 K. Takiyama, E. D. Salesin and L. Gordon, *Talanta, 5,* 231 (1960).

175 H. Titze, *Acta Chem. Scand., 24,* 405 (1970).

176 H. Titze and B. Allard, *Acta Chem. Scand., 24,* 715 (1970).

177 J. H. Van Tassel and W. W. Wendlandt, *J. Am. Chem. Soc., 81,* 813 (1959).

178 J. H. Van Tassel, W. W. Wendlandt and E. Sturm, *J. Am. Chem. Soc., 83,* 810 (1961).

179 M. Vidali, P. A. Vigato, G. Bandoli, D. A. Clemente and U. Casellato, *Inorg. Chim. Acta, 6,* 671 (1972).

180 M. Vidali, P. A. Vigato and U. Casellato, *J. Inorg. Nucl. Chem., 37,* 955 (1975).

181 M. Vidali, P. A. Vigato, U. Casellato, E. Tondello and O. Traverso, *J. Inorg. Nucl. Chem., 37,* 1715 (1975).

182 P. A. Vigato, U. Casellato, D. A. Clemente, G. Bandoli and M. Vidali, *J. Inorg. Nucl. Chem., 35,* 4131 (1973).

183 P. A. Vigato, M. Vidali and U. Casellato, *Gazz. Chim. Ital., 104,* 1283 (1974).

184 G. W. Watt and K. F. Gadd, *Inorg. Nucl. Chem. Letters, 9,* 203 (1973).

185 W. W. Wendlandt, *Anal. Chim. Acta, 15,* 533 (1956).

186 W. W. Wendlandt, *Analyt. Chem., 28,* 499 (1956).

187 W. W. Wendlandt, *Anal. Chim. Acta, 17,* 274 (1957).

188 W. W. Wendlandt, J. L. Bear and G. R. Horton, *J. Phys. Chem., 64,* 1289 (1960).

189 W. W. Wendlandt and G. R. Horton, *J. Inorg. Nucl. Chem., 19,* 272 (1961).

190 W. W. Wendlandt and G. R. Horton, *Analyt. Chem., 34,* 1098 (1962).

191 C. Wiedenheft, *Inorg. Chem., 8,* 1174 (1969).

192 V. Wolf and W. Barmighauser, *Acta Cryst., 13,* 778 (1960).

193 S. Yamada and A. Takeuchi, *Bull. Chem. Soc. Japan, 42,* 2549 (1969).

194 T. Yoshimura, C. Miyake and S. Imoto, *Bull. Chem. Soc. Japan, 46,* 2096 (1973).

195 T. Yoshimura, C. Miyake and S. Imoto, *Bull. Chem. Soc. Japan, 47,* 515 (1974).

196 W. H. Zachariasen, "Crystal Chemistry of the 5*f* Elements: The Actinide Elements", Ed. G. T. Seaborg and J. J. Katz, McGraw-Hill, New York, 1955, p. 623.