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ACTINIDE COMPLEXES WITH CARBOXYLIC ACIDS

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CONTENTS

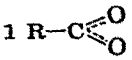
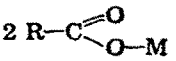
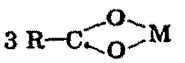
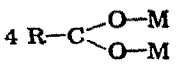
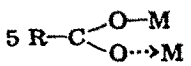
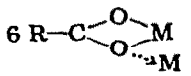
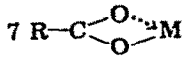
A. INTRODUCTION

Most of the chemical elements are known to form stable carboxylate derivatives [1] and because carboxylic acids are potentially bidentate ligands with a very short O···O distance (bite), the large actinide cations very easily form complexes of them with high coordination. The best known compounds are

the formates, acetates and oxalates, where the remainder of the molecule is sufficiently small to allow easy packing in the crystal lattice. Using monocarboxylic acids as the basis for a discussion of the carboxylate complexes, they can be divided into seven groups according to the type of M—O_2CR interaction (Table 1). The antisymmetrical types clearly cannot be uniquely characterized, but could exist in a continuous range between the unidentate type and the symmetrical chelating or bridging type. The ionic nature of the formate group in sodium formate is readily shown by X-ray analysis; the equivalence of the two C—O bonds [2] contrasts markedly with the situation in lithium acetate dihydrate [4]. In this compound the acetate ion functions as unidentate ligand; the bond length of C—O in the CO—M unit is 1.33 Å while that of the free carbonyl portion is 1.22 Å. Although no satisfactory crystal-structure determinations have been made for simple sodium acetate it seems from the identity of the solution and solid state spectra of sodium acetate that

TABLE 1

Carboxylate coordination types

Type	Coordination	Examples
1 	Uncoordinated	$Na(HCOO)$ [2]; $Na(CH_3COO)$ [222,223]
2 	Monomeric	$Li(CH_3COO) \cdot 2\,H_2O$ [4]; $Co(CH_3COO)_2 \cdot 4\,H_2O$ [3]; $(Ph_4As)_2[U(pdc)_3] \cdot 3\,H_2O$[a] [191]; $(Ph_4As)_2[UO_2(pdc)_2] \cdot 6\,H_2O$[a] [187]; $Na[UO_2(oda)_2] \cdot n\,H_2O$[a] [195]
3 	Bidentate, chelating symmetrical	$Na[UO_2(CH_3COO)_3]$ [10]; $Zn(CH_3COO)_2 \cdot 2\,H_2O$ [9]
4 	Bidentate, bridging symmetrical	$[UO_2(CH_3COO)_2(Ph_3PO)]_2$ [67]; $[UO_2(CH_3COO)_2(Ph_3AsO)]_2$ [67]; $[Cu(CH_3COO)_2\,H_2O]_2$ [7]; $[Cr(CH_3COO)_2 \cdot H_2O]_2$ [8]
5 	Bidentate, bridging unsymmetrical	$[UO_2(oda)]_n$[a] [192]; $[UO_2(pdc) \cdot H_2O]_n$[a] [186]; $Cu(HCOO)_2 \cdot 4\,H_2O$ [5]; $Cu(HCOO)_2$ [6]
6 	Bidentate, chelating symmetrical and bridging unsymmetrical	$[UO_2NO_3$(salicylic acid) (dimethylaminopyridine)$]_n$ [224]; $U(CH_3COO)_4$ [86]
7 	Bidentate, chelating unsymmetrical	$Sn(CH_3COO)_4$ [14]

[a] H_2oda = oxydiacetic acid; H_2pdc = pyridine-2,6-dicarboxylic acid.

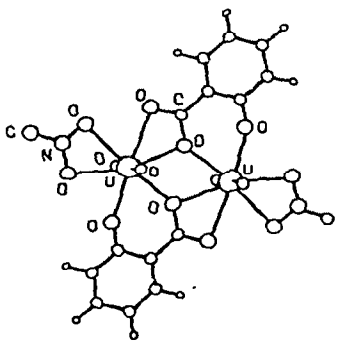
there is little cation—anion interaction. In $Li(CH_3COO) \cdot 2\ H_2O$, the hydrogen bonding must clearly influence the spectroscopic properties [11]. The main effect of coordination of the acetate ion will clearly be on the COO antisymmetric and symmetric stretching frequencies. In comparison with sodium acetate, the spectra of unidentate acetate groups show a large increase in the antisymmetric stretching COO and a similar decrease in the symmetric stretching COO, these frequencies corresponding approximately to C=O and C—O respectively.

With increasing size of metal, a weak interaction with the second oxygen atom becomes possible and the compound moves from type 2 to type 4 (Table 1); the major difference between type 2 and type 4 is that the antisymmetric COO is generally higher (100 cm^{-1}) in the first coordination type than in the second one; in both cases there is a drastic change in the intensity in the two stretching modes associated with the carboxylic groups in comparison with ionic carboxylates. The antisymmetric stretching becomes more intense than the symmetric one. If coordination occurs symmetrically as in types 4 or 6 both the COO stretching bonds may be changed by the same amount. The $\Delta\nu$ between antisymmetric and symmetric stretching has been proposed for differentiating between chelating and bridging forms of carboxylate ligands. This hypothesis is founded on the premise that in chelating acetates the O—C—O angle will be smaller than in bridging acetates.

An increase in this angle should decrease the symmetric and increase the antisymmetric COO and hence increase the $\Delta\nu$; in both cases the intensities of the two bands are comparable. The use of IR spectroscopy alone to differentiate between the two types of coordination seldom yields meaningful results [1,121].

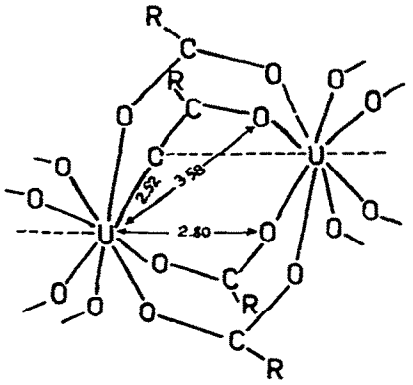
M—O frequencies have also been used to obtain correlations between the spectra and structure of the carboxylate complexes. The difference found in molecules containing differently coordinated acetates were such as to make structural deductions of unknown carboxylate complexes hazardous [12—14].

The coordination type 6 has been observed in the complex $[UO_2(NO_3)$ (salicylic acid)dimethylaminopyridine$]_2$ (1). To a certain extent a similar



(1)

coordination mode also takes place in $U(CH_3COO)_4$ (2) where some carboxy-



(2)

lic groups behave both as bidentate and bridging groups.

The tendency of the tetravalent actinide ions in aqueous solution is to form neutral salts with strong acids and basic salts with weak acids, but in non aqueous solvents neutral salts of weak acid can be obtained. The coordination number of the tetravalent actinide ions in the carboxylates generally ranges for 8 to 10. The thorium compounds are the best characterized, but there is sufficient information to indicate that uranium(IV) behaves like thorium, the main difference arising from the much stronger tendency of the uranium(IV) to hydrolyse and to be oxidized by oxygen. Neptunium(IV) and plutonium(IV) behave in a similar fashion to uranium(IV) with less (neptunium) or no (plutonium) tendency to oxidize.

The pentavalent actinide ions differ considerably in the composition and properties of their carboxylates. The carboxylates of protoactinium(V) contain the polynuclear grouping O—Pa—O—Pa— whereas the pentavalent transuranium ions form dioxocations MO_2^+ which are present in aqueous solution and in all salts prepared from aqueous solutions. PaO^{3+} forms strong complexes and is easily hydrolysed whereas NpO_2^+, PuO_2^+ and AmO_2^+ have a low tendency toward complex formation and hydrolysis.

The hexavalent state is known for uranium, neptunium, plutonium and americium. In the crystalline compounds examined the group $(O—M—O)^{2+}$ is always present as a structural unit and is linear. In these actinyl compounds further coordination occurs on or near the equatorial plane giving rise to a pentagonal or hexagonal bipyramidal polyhedron. Hydrolysis of the hexavalent actinide ions occurs at low pH ($\simeq 3$) and basic carboxylates are formed easily; these have a strong tendency to polymerize.

Generally there is an appreciable similarity in the behaviour of the actinide ions in the same valence state while there is a large difference in the information available for the individual actinides, decreasing in the order U >> Th > Pu > Np > Am > Cm > others. Solid carboxylates are known for thorium(IV), protoactinium(IV) and (V), uranium(IV) and (VI), neptunium(IV) and (V), plutonium-(III), (IV), (V) and (VI), americium(III) and (VI) and curium(III). The α-radiation from any of the actinides will affect the stability of solid compounds, an

example being the experimental observation that it is possible to prepare compounds of curium(IV) with ^{244}Cm (half-life 18 years) but not with ^{242}Cm (half-life 162 days) the difference in chemical behaviour being due to the much higher specific α-activity of ^{242}Cm which leads to faster radiation decomposition than is the case with the longer-lived ^{244}Cm; similarly plutonium hexafluoride is decomposed by the α-radiation of the plutonium more rapidly than its neptunium analogue, simply because neptunium has a much longer half-life and is therefore less intensely radioactive. Thus it is necessary to specify the isotope used in order to know the stability of the complex prepared and the decomposition process under the action of its own α-radiation.

The only isotope of actinium with a half-life long enough to permit a macroscopic amount to be studied is ^{277}Ac ($t_{1/2}$ = 22 years) which decays by β^- emission. The most stable isotope of thorium, ^{232}Th, is an α-emitter with a half-life of 1.4×10^{10} years, making it handleable without undue precautions. There is only a single isotope of protoactinium with a half-life over a month, ^{231}Pa, for which $t_{1/2} = 3.28 \times 10^4$ years. Uranium is the heaviest element to occur in nature in recoverable amounts, the isotopes, all α-emitters occurring in the following proportions: ^{238}U = 99.28% with a half-life of 4.5×10^9 years, ^{235}U = 0.71% with a half-life of 7.00×10^8 years and ^{234}U = 0.005% with a half-life of 2.35×10^5 years. There is only one isotope of neptunium which is easily prepared and sufficiently stable to be obtainable in massive quantities: this is ^{237}Np with a half-life of 2.14×10^6 years. It is formed by neutron irradiation of uranium. There are several plutonium isotopes with half-lives enough to permit the handling of massive amounts of them. ^{239}Pu is the most readily available, being produced in reactors by the irradiation of uranium.

There are two isotopes of americium with sufficiently long half-lives to make handling of massive quantities practicable, both being α-emitters; ^{241}Am with a half life of 458 years and ^{243}Am, 7400 years. Although the half-life of ^{241}Am is shorter, fewer steps are required for its formation and it is more readily available.

There are two isotopes of curium which are available in gram quantities. These are both α-emitters with short half-lives; ^{242}Cm, 162 days and ^{244}Cm, 18 years.

Many studies on the photochemical reactions of uranyl(VI) ion with carboxylic acids have been carried out and comprehensive reviews have been published [246,247,262]. Interesting observations of the photochemistry of uranyl—carboxylic acid systems include:

a) Even though uranium(IV) is the reduced form of uranium normally reported as a product of photolysis, this does not necessarily imply that it is a primary photochemical species because uranium(V) can disproportionate as follows: 2 U(V) → U(IV) + U(VI). Thus, the primary photoreaction can be an electron transfer from the acid substrate to UO_2^{2+}.

b) The experimental data obtained are insufficient to provide precise mechanistic information. For example, a complex of a uranyl—carboxylic acid substrate has been assumed to be a photosensitive cluster

$UO_2^{2+} + S(Substrate) \rightarrow UO_2S^{2+}$

and was assumed to undergo an intramolecular photoredox reaction

$UO_2S^{2+} \xrightarrow{h\nu} UO_2S^{2+*}$

$UO_2S^{2+*} \rightarrow U(IV) + Products$

However, the linear relation between the reciprocal quantum yield of uranium-(IV) formation and the reciprocal concentration of the substrate, which is inferred from the above assumed mechanism, does not support the above assumption. In fact, the linearity can be inferred both from the mechanism that considers a complex formation and from the alternative mechanism, which takes into consideration an intermolecular (collisional) mechanism.

According to some ESR results [256], both "sensitized" and normal modes (i.e. Ligand to Metal Charge Transfer (LMCT) and kinetic encounter) can operate on the same molecule. In the sensitization mechanism, however, the uranium(V) is reoxidized to uranium(VI) by a free radical instead of undergoing dismutation

$RCOO_2 \cdot + U(V) + H^+ \rightarrow RH + CO_2 + U(VI)$

The mechanism of the photochemistry of uranyl ion—carboxylic acid systems has been mainly centered around the kinetic encounter and complex formation theories. Evidently, the essential difference between the two mechanisms lies in the nature of the excited states responsible for the observed photoreactions.

Trivalent actinides have only a small tendency to hydrolyse and therefore neutral salts of strong and weak acids can be prepared from aqueous solution without difficulty. The carboxylates of the trivalent actinides are generally very similar to those of the trivalent lanthanides; compounds of neptunium-(III) and plutonium(III) are relatively easily oxidized especially in solution, while americium(III) does not react with oxygen at all.

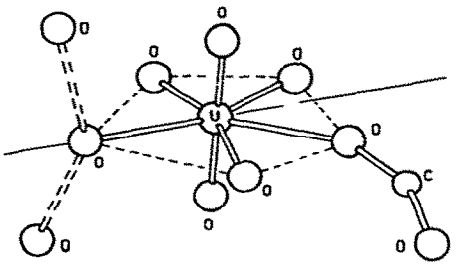
A number of good reviews [111,231,245,252] and monographs [127,173, 248] deal with various aspects of the chemistry of the actinides and recently a very interesting article concerning the preparation of solid carboxylate compounds of actinides has been published [226]. In this report some data on complex formation equilibria of these salts in aqueous solution are also provided.

Although numerous carboxylate compounds have been characterized, only recently have a few structures been determined. In addition in more recent years carboxylate complexes with neutral ligands have been prepared and characterized and, recently, a review of lanthanide and actinide carboxylate chemistry has been published [272]. The aim of the present article is to give a review of the work done in this field with particular regard to the more recent publications and to cover the lack of information on the physicochemical properties of these complexes and their correlation, where possible, with structural investigations.

B. ACTINIDE(VI) FORMATES

$UO_2(HCOO)_2H_2O$ was prepared by the reaction of formic acid on UO_3 or on a solution of uranyl(VI) nitrate and hydrogen peroxide [46,47]. More recently it has been prepared by adding crystals of $UO_2(NO)_3 \cdot 6\ H_2O$ to a large excess of pure formic acid at room temperature. The monohydrate has been also prepared [39] by adding dilute ammonia to uranyl(VI) nitrate to precipitate ammonium diuranate and dissolving this latter in excess dilute formic acid.

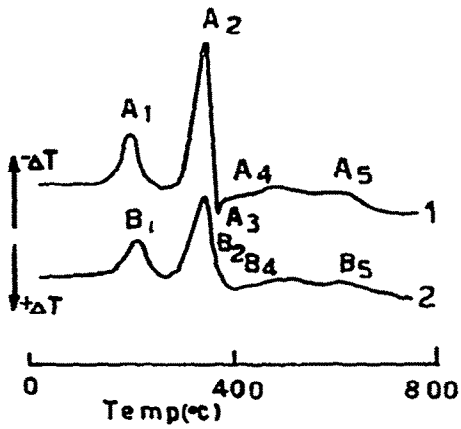
Infrared spectroscopic studies show that all the formate groups in $UO_2(HCOO)_2H_2O$ are equivalent; $\nu_{asym}COO$ lies at 1560 cm^{-1} and $\nu_{sym}COO$ at 1360 cm^{-1} while ν_3O—U—O is at 930 cm^{-1} and ν_1 at 864 cm^{-1}. Very recently the crystal and molecular structure of uranyl(VI) diformate monohydrate has been established by X-ray diffraction [263]. This compound crystallizes in the orthorhombic space group $Fdd2$, with a = 5.994(1), b = 19.331(3), c = 11.550(2) Å, z = 8. The uranium atom is surrounded by seven oxygen atoms forming a pentagonal bipyramid (3). The equatorial plane, slightly



(3)

distorted, contains one oxygen from the water molecule and four oxygen atoms from the formato groups. The different polyhedra are linked together first by the formato groups forming infinite formate—uranium—formate chains and secondly by the hydrogen bonds involving the water molecule. The anhydrous $UO_2(HCOO)_2$ was prepared by dehydrating the monohydrate at 170°C for 5 h under vacuum. Thermogravimetric analysis shows that the decomposition pattern of the uranyl(VI) formate monohydrate in air is the same as in an inert atmosphere. At 340°C the residue is not only UO_3 but also the basic formate UO(OH)(HCOO) is present which then decomposes to UO_3 in the temperature range 370—480°C. The differential thermal analysis of $UO_2(HCOO)_2H_2O$ in air and in argon confirms the stages observed in the thermograms; the two curves are practically identical (Fig. 1).

The loss of one water molecule is shown by the endothermic peaks A_1 or B_1, the decarboxylation of the anhydrous formate is shown by the endothermic peaks A_2 or B_2 and the formation of U_3O_8 from UO_3 gives the endothermic peaks A_5 and B_5. The exothermic peak A_3, absent in the curve under inert conditions, may be accounted for by the oxidation of CO to CO_2. The exothermic peaks A_4 and B_4 may be due to the decomposition of UO(OH)(HCOO), but the exothermic nature of the reaction suggests that a recrystallization, perhaps of amorphous UO_3 to the α form, is a more likely explanation of the peak. The



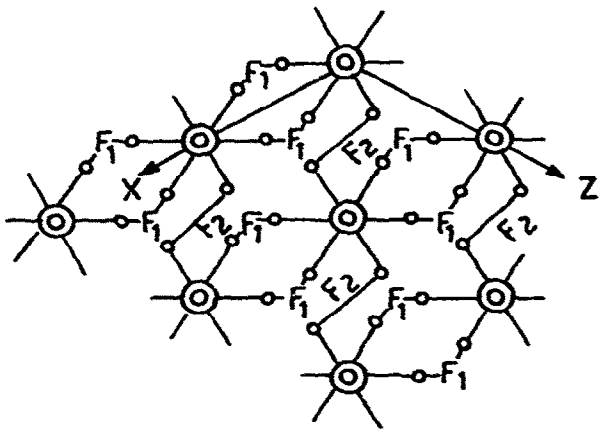


Fig. 1. DTA curves of $UO_2(HCOO)_2 \cdot H_2O$ in air (1) and in argon (2).

Fig. 2. The two linkage modes (F_1 and F_2) of the formate groups in $Na[UO_2(HCOO)_3] \cdot H_2O$.

decarboxylation reaction can be

$$3\ UO_2(HCOO)_2 \rightarrow 2\ HCOOH + 4\ CO + H_2O + 3\ \alpha\text{-}UO_3$$

The presence of CO_2 in the gases produced can be achieved by the dehydrogenation of formic acid (according to the reaction $HCOOH \rightarrow H_2 + CO_2$) and by the reaction $UO_2(HCOO)_2 \rightarrow UO(OH)(HCOO) + CO_2$ producing the intermediate basic formate.

When $UO_2(HCOO)_2 \cdot H_2O$ is treated with water vapour, at 30—70°C, it loses formic acid yielding $UO_2(OH)(HCOO) \cdot H_2O$. This hydroxyformate when refluxed in water, gives an orange residue formulated as $UO_2(OH)_2$ [41]. The position of $\nu_{asym}COO$ or $\nu_{sym}COO$ in the IR spectra of $UO_2(HCOO)_2 \cdot H_2O$ and $UO_2(OH)(HCOO) \cdot H_2O$ [41,48] suggests the presence of formato groups bridging two uranium atoms [229]; a different coordination environment has been supposed for anhydrous $UO_2(HCOO)_2$ since its IR spectrum is very different in the carboxylic frequency region. Powder crystallographic data show that $UO_2(HCOO)_2 \cdot H_2O$ is orthorhombic with space group *Fddd* and cell constants $a = 5.84$ Å, $b = 11.55$ Å, $c = 19.50$ Å [29] while $UO_2(OH)(HCOO) \cdot H_2O$ has an orthorhombic cell with $a = 10.55$, $b = 13.52$, $c = 16.02$ Å [49].

A red basic formate $Tl[UO_2(OH)_2(HCOO)]$ has been obtained [48] when equal volumes of equimolar cold aqueous solutions of thallous formate and uranyl formate were mixed. This red formate, stirred in the absence of light for 4 h at 70—80°C, turns yellow and gives rise to a different compound, formulated as $UO_2(OH)(HCOO) \cdot H_2O$ with thermogravimetric behaviour similar to that observed for uranyl formate monohydrate.

Luminescence spectra of anhydrous or monohydrate uranyl formate have been recorded at room temperature and at 77 K [50]. The frequency of the exciting radiation changes neither the relative intensity nor the wavelength of the bands of luminescence thus indicating that all the transitions originate

from the same excited state. The observed bands have been interpreted as transitions from the first electronically excited state to different vibrational levels on the ground state. The resonance band corresponding to the transition from the first excited state ($v' = 0$) to the ground state ($v = 0$) has been found at 20,568 cm^{-1} for uranyl formate monohydrate and at 20,206 cm^{-1} for anhydrous uranyl formate in agreement with previously reported results [51]. The reduction of 362 cm^{-1} for the anhydrous compound is probably due to the change of the crystalline system as a consequence of dehydration. In the luminescence spectrum of anhydrous uranyl formate the ν_{asym} O—U—O does not appear and this indicates that the crystal field around the uranyl ion is completely symmetric.

Recently the uranyl formate, $Na[UO_2(HCOO)_3] \cdot H_2O$, has been prepared and investigated by X-ray diffraction and IR techniques [52]. The compound can be prepared by adding sodium formate to uranyl formate monohydrate in formic acid at 80°C. Slow cooling of the formic acid solution yields yellow crystals of $Na[UO_2(HCOO)_3] \cdot H_2O$. It crystallizes in the monoclinic system, the unit cell parameters being: $a = 6.741$, $b = 24.43$, $c = 6.332$ Å; $\beta = 117.63°$. The structural data together with IR spectra show two types of formate ions (F_1 and F_2) to be present in the complex and the molecule of water is not coordinated to the uranium atom. It was supposed that the coordination number of the uranyl ion is six with an idealized structure of the type shown in Fig. 2. The uranyl ions lie in the xz plane and form infinite chains parallel to the x axis with the bidentate F_1 type formate ions. The U—U distance along one of these chains is 6.75 Å. These chains are linked with each other by F_2 type formate ions. The oxygen atoms of the uranyl ion are located on the side of the xz plane at a distance of 1.74 Å from the uranium atom. Such a plane forms an infinite anion of formula $[UO_2(HCOO)_3]_n^-$. The cations Na^+ and the water molecules are located between these planes. The main photoreaction of the UO_2^{2+}—formic acid system is the direct oxidation of formate to CO_2, with the concomitant reduction of uranium(VI) to uranium(IV) [55,253—255]. Spectral data [247] show that, in solutions containing uranyl ion and formic acid, a complex (probably $[UO_2(HCOO)]^+$) is formed which absorbs much more than the free uranyl ion. This fact, coupled with the observation that the rate of the photoreaction increases with increasing formic acid concentration until saturation value, indicates that the primary photochemical act is an electron transfer within the complex

$$[UO_2(HCOO^-)]^+ \xrightarrow{h\nu} UO_2^+ + HCOO$$

This primary photoreaction is followed by dismutation of UO_2^+ and interaction of two ·COOH radicals, yielding HCOOH and CO_2. Support for the formation of the ·COOH radicals was given by ESR measurements carried out on frozen solutions [256]. The available data, however, cannot exclude that the photoreaction occurs by kinetic encounters between photoexcited UO_2^{2+} ions and acid molecules.

$(NH_4)_2[UO_2(HCOO)_4]$ has been precipitated from an ammonium formate—

uranyl formate solution that had been prepared by ion exchange metathesis [264]. The compound is light sensitive and rapidly darkens when allowed to stand in the light, probably as a consequence of photochemical formation of compounds of uranium in lower oxidation states. It begins to decompose on heating at about 80°C and forms U_3O_8 quantitatively when heated above 350°C in air or in vacuo.

C. ACTINIDE(IV) FORMATES

The preparations of $Th(HCOO)_4 \cdot 2\ H_2O$ [22—24] and $Th(HCOO)_4 \cdot 3\ H_2O$ [22,24,25] were described some years ago; more recently the preparation of these compounds has been repeated under different experimental conditions in order to obtain complexes with different metal to water ratios [26]. Only the complex $Th(HCOO)_4 \cdot 3\ H_2O$ has been obtained by reacting $Th(OH)_4$ with formic acid at different concentrations (between 20 and 84%) and at different reaction temperatures [26—28]. It is insoluble in organic solvents and loses the three water molecules when washed with acetone or heated at 100—120°C to give the anhydrous $Th(HCOO)_4$. $Th(HCOO)_4 \cdot 2/3\ H_2O$ has been prepared by the addition of crystals of thorium nitrate to an excess of formic acid [29].

Thermogravimetric analysis of $Th(HCOO)_4 \cdot 3\ H_2O$ in nitrogen [27], indicates that the compound loses water molecules between 92 and 171°C with the formation of anhydrous $Th(HCOO)_4$. The thermograms have shown the formation of $Th(HCOO)_4 \cdot 2/3\ H_2O$.

Structural data on $Th(HCOO)_4 \cdot 3\ H_2O$ and $Th(HCOO)_4$ have been reported [30]. The former has a monoclinic cell with $a = 6.77$, $b = 8.81$, $c = 9.61$ Å, $\beta = 109.11°$; the possible space group being $P2_1(C_2 2)$ or $P2_1/m(C_{2h}^2)$ with $z = 2$. These data differ substantially from those reported by other authors [31], particularly as far as the cell parameters are concerned. Such differences may be due to the use of Mo radiation which can cause some imprecision. Each thorium atom is surrounded by eight oxygen atoms of eight bridging formate groups, forming a distorted Archimedic antiprism, and by two oxygen atoms of two water molecules located on the square faces. Thorium thus reaches a coordination number of 10 and the complex can be formulated as $[Th(HCOO)_4 \cdot 2\ H_2O]H_2O$.

$Th(HCOO)_4$ was reported to crystallize in the orthorombic system [30] with cell parameters $a = 6.78$, $b = 7.32$, $c = 16.92$ Å; $z = 4$. More recently, using the Debye-Scherrer method, structural data [32] concerning anhydrous $Th(HCOO)_4$ prepared from thorium(IV) chloride and dry formic acid at 60—70°C [33] have shown the compound has a tetragonal body centered cell ($a = 7.973$, $c = 6.588$ Å, $z = 2$, space group $S_4 2$); this product is a modification of that obtained by dehydration of $Th(HCOO)_4 \cdot 3\ H_2O$ [30].

The basic formate $Th(OH)(HCOO)_3$ was prepared [27] when an inert gas, saturated with water vapour, was passed over $Th(HCOO)_4$. The basic formate was collected as solid residue after the heterogeneous reaction

$$H_2O_{gas} + Th(HCOO)_{4\ solid} \rightarrow Th(OH)(HCOO)_{3\ solid} + HCOOH_{gas}$$

had taken place.

It has been reported that polynuclear formato complexes of thorium are formed by the reaction of thorium formate and inorganic salts [28] and in Table 2 a series of known formato compounds is reported; they are classified in order of increasing number of ligand groups in the inner sphere. All the formato compounds are crystalline solids; the lower members are quite stable in air but the higher $Cs_3[Th(HCOO)_7]$ and $Cs_4[Th(HCOO)_8]$ are strongly hygroscopic and readily decompose upon storage. The stability of these compounds is also influenced by the cation; thus the caesium, rubidium and potassium derivatives can be easily prepared, while the preparation of lithium and sodium ones fails. Molar conductance data for hexa-, hepta- and octa-formato-complexes give values corresponding to three, four and five ion electrolytes, whereas for the lower members of the series in Table 2, higher molar conductances than expected have been found. These anomalous values have been explained by the replacement of formato-groups by water molecules; this process must be reversible since the compounds can be recrystallized from water. The stability of aqueous solutions of the formato compounds increases on ascending the genetic series.

The IR spectra, in the 3600—400 cm^{-1} region, of the complexes $M[Th(HCOO)_5]$ ($M^+ = K^+$, Rb^+, Cs^+), $Cs_2[Th(HCOO)_6]$, $Ba[Th(HCOO)_6] \cdot 2\ H_2O$, $Ba[Th(HCOO)_6]$ and $M_4[Th(HCOO)_8]$ ($M^+ = Na^+$ and Rb^+) have been reported [35]. In all the complexes the formato groups are coordinated to thorium(IV),

TABLE 2

Formato-complexes of thorium (IV)

Compounds[a]	Ref.
$Th(HCOO)_4 \cdot 2\ H_2O$	23
$Th(HCOO)_4 \cdot 3\ H_2O$	25
$K[Th(HCOO)_5]$	34
$PyH[Th(HCOO)_5]$	34
$Cs[Th(HCOO)_5]$	26
$Ba[Th(HCOO)_6] \cdot 2\ H_2O$	34
$Ba[Th(HCOO)_6]$	26
$Cs_2[Th(HCOO)_6]$	26
$(NH_4)_2[Th(HCOO)_6]$	34
$Sr[Th(HCOO)_6] \cdot 2\ H_2O$	34
$Cs_3[Th(HCOO)_7]$	26
$Cs_4[Th(HCOO)_8]$	26
$[Th_3(OH)_5(HCOO)_6] \cdot x \cdot n\ H_2O$ where $x \cdot n\ H_2O = ClO_4 \cdot 12\ H_2O$; $NO_3 \cdot 10\ H_2O$; $HCOO \cdot 2\ H_2O$; $SCN \cdot 7\ H_2O$; $ClO_3 \cdot 16\ H_2O$	28
$Na[Th_3O(OH)_4(HCOO)_6(ClO_4)] \cdot 9\ H_2O$	28
$Na[Th_3O(OH)_4(HCOO)_6(ClO_3)] \cdot 13\ H_2O$	28

[a] Since the nature of the water molecules in formato-compounds is not yet definitely established, water molecules are arbitrarily shown outside the bracket in all the formulae.

but no conclusion has been reached on the coordination behaviour of the formato groups. In a previous study [36] it was suggested that in the tetra- and hexa-formato compounds of thorium, bridging formato-groups are present, but that in $Cs_4[Th(HCOO)_8]$ and $Cs_3[Th(HCOO)_7]$ there may be unidentate formato groups connected to thorium. The IR spectra of these last two complexes show bands at 1120—1135 and 615 cm^{-1}, absent in the IR spectra of those in which only bridging formato groups are known to exist. These bands are also absent in the spectra of $Na_4[Th(HCOO)_8]$ and $Rb_4[Th(HCOO)_8]$; in these two complexes there is no absorption in the 1700 cm^{-1} range which can be observed for unidentate formato groups. The spectra of $Ba[Th(HCOO)_6]$ and $Ba[Th(HCOO)_6] \cdot 2\ H_2O$ are identical in the range of the formato group vibrations. The water present in the second compound is very probably water of crystallization.

Only one complex containing a monodentate oxygen donor ligand, $Th(HCOO)_4 \cdot DMSO$, has been reported [37]. This complex can be obtained by reaction of $Th(HCOO)_4 \cdot 3\ H_2O$ with dimethyl sulphoxide (DMSO). The lowering of the ν_{S-O} in its spectrum in comparison with the free ligand, indicates that the DMSO is coordinated to thorium through the oxygen atom. $U(HCOO)_4$ precipitates as dark green crystals when UCl_4 is refluxed with dry formic acid [38]; a purer grey-green anhydrous compound can be obtained when uranium(IV) tetraacetylacetonate is refluxed for 10 min with dry formic acid [39]. The thermogravimetric data of this compound show that in air the residue at the first stage (220°C) consists entirely of $UO_2(HCOO)_2$, whereas in argon only one decomposition step to UO_2 is observed, without the formation of the intermediate uranyl formate (Table 3). The DTA results confirm this behaviour. In curve 1 of Fig. 3, for the reaction in air, the exothermic peak A_1 corresponds to the formation of uranyl formate and is followed by other peaks due to the decarboxylation of uranyl formate itself. In argon (curve 2 of Fig. 3) the single endothermic peak B_1 confirms that uranium(IV) formate decomposes to uranium dioxide in one step. The analy-

TABLE 3

Thermogravimetric behaviour of $U(HCOO)_4$ [39]

Temperature range (°C)[a]	Supposed compound formed
In air	
120—220	$UO_2(HCOO)_2$ [b,c]
240—330	α-UO_3 [c] + some basic uranium(IV) formate
330—450	UO_3
580—700	U_3O_8 [c]
In argon	
230—380	$UO_{2.13}$

[a] Heating rate = 6° min^{-1}. [b] Confirmed by chemical analysis. [c] Confirmed by X-ray analysis.

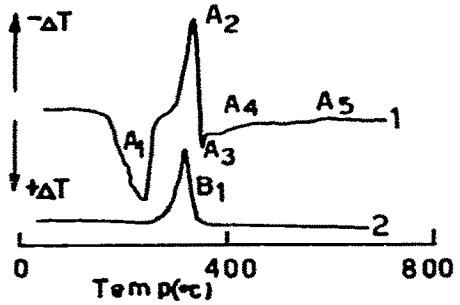


Fig. 3. DTA curves of $U(HCOO)_4$ in air (1) and in argon (2).

sis of the products of thermal decomposition in vacuo suggests that for $U(HCOO)_4$ a decarboxylation occurs of the type

$$2\ U(HCOO)_4 \rightarrow 3\ HCOOH + 4\ CO + H_2 + CO_2 + 2\ UO_2$$

The reaction, under inert conditions, follows a linear law with an activation energy of 28.5 ± 1 kcal mol^{-1}.

$U(HCOO)_4$ exists in three allotropic species [230]. The α-modification and γ-modification are enantiotropic with each other and the reversible transmutation $\alpha \rightleftharpoons \gamma$ is endothermic in the sense of the formation of the γ species. The β-modification is metastable and transmutes irreversibly and endothermically into the γ species. $U(HCOO)_4$ has been also prepared [40] by electrochemical reduction of uranyl(VI) formate in formic acid solution and adding ethanol to this solution in an inert atmosphere. The light green precipitate obtained, $UO(HCOO)_2$, when refluxed in pure formic acid for several hours gives α-$U(HCOO)_4$ isomorphous with the anhydrous uranium(IV) formate prepared by the methods discussed above. β-$U(HCOO)_4$ has been obtained by treating the oxoformate $UO(HCOO)_2$ with formic acid in an HCl stream under reflux. α-$U(HCOO)_4$ is not sensitive to oxygen in a dry atmosphere; water vapour, without oxygen, causes an initial loss of formic acid, giving rise to a solid residue of unknown composition; the most probable species seems to be $UO(HCOO)_2 \cdot 2\ H_2O$ or $U(OH)_2(HCOO)_2 \cdot H_2O$. The second step leads to the formation of $UO(OH)(HCOO) \cdot H_2O$ and the third hydrolysis step gives $UO_2 \cdot H_2O$ as the final residue. These results can be described by the following reaction scheme [41]

$$\alpha\text{-}U(HCOO)_4(s) + 3\ H_2O(g) \rightarrow \left\{\begin{matrix} U(OH)_2(HCOO)_2 \cdot H_2O \\ \text{or} \\ UO(HCOO)_2 \cdot 2\ H_2O \end{matrix}\right\}_{(S)} + 2\ HCOOH(g)$$

$$UO(HCOO)_2 \cdot 2\ H_2O(s) \rightarrow UO(OH)(HCOO) \cdot H_2O(s) + HCOOH(g)$$

and

$$\left\{\begin{matrix} U(OH)_2(HCOO)_2 \cdot H_2O(s) \\ UO(OH)(HCOO) \cdot H_2O(s) \end{matrix}\right\} \rightarrow UO_2 \cdot H_2O(s) + HCOOH(g)$$

Magnetic susceptibility studies in the temperature range 82—300 K for the compound $U(HCOO)_4$, obtained by shaking $U(HCOO)_3$ and formic acid in air for about 1—3 h, have been reported [17]. The effective magnetic moment found for this complex at room temperature is 2.98 B.M. Subsequent magnetochemical studies [42] of the perfectly anhydrous $U(HCOO)_4$, $Pa(HCOO)_4$ and $Np(HCOO)_4$, obtained by the reaction of the corresponding tetrachlorides with thoroughly dried formic acid [33] have been carried out. The effective magnetic moment of $U(HCOO)_4$ was found to be 3.27 B.M. at room temperature and a distorted symmetry from the cubic previously proposed [17] has been assumed. All three complexes obey the Curie—Weiss law ($\chi = C/T - \vartheta$) in the 80—300 K temperature range with extrapolated Weiss constants of $\vartheta = -3$ K for $Pa(HCOO)_4$, -90 K for $U(HCOO)_4$ and -86 K for $Np(HCOO)_4$. The magnetic moments at room temperature of $Pa(HCOO)_4$ and $Np(HCOO)_4$ have been found to be 1.23 and 3.25 B.M. respectively.

The diffuse reflectance spectra of these eight-coordinated $An(HCOO)_4$ ($An = Pa^{IV}$, U^{IV}, Np^{IV}) have been measured in the range 5,500—45,500 cm^{-1} at room temperature [43]. The tetraformates of protoactinium(IV), uranium(IV) and neptunium(IV) represent the electronic configuration $5f^1$, $5f^2$, and $5f^3$ respectively, perturbed by a crystal field of a slightly distorted eight-field cubic symmetry. The spectra in the range of the internal $5f^q \rightarrow 5f^q$ transition show a complexity due to repulsion interaction, spin-orbit coupling and crystal-field influence as found in the spectra of other actinide ions. $5f^q$ spectra of the corresponding chlorides and formates are quite similar, shifted toward higher wavenumbers in the latter case. Since the metal ion symmetry is different in each complex, D_{2d} in $AnCl_4$ [44] and $S_4(C_2)$ in $An(HCOO)_4$ [45], the similarity in the spectra suggests that it is the eight neighbour ligand atoms which predominantly determine the crystalline field around the actinide ion and that the tetragonal distortion of the cubic ligand framework has only a small effect on the $5f^q$ energy levels. The energy variation of the $5f^q \rightarrow 5f^{q-1}6d^1$ transition as a function of q is more pronounced in the predominantly ionic tetraformates than in the more covalent tetrachlorides. The crystal structure of $An(HCOO)_4$ ($An = Th^{IV}, Pa^{IV}$, U^{IV}, Np^{IV}) has been studied by X-ray diffraction data obtained by the Debye-Scherrer method [32]. Protoactinium and neptunium formates are isotypic with a tetragonal body centered cell, as already reported for the thorium analogue. The powder pattern of the uranium formate could be indexed with a monoclinic unit cell. The unit cell constants of these compounds are given in Table 4. The most probable space group for $Np(HCOO)_4$ is $I\bar{4}$; neptunium is surrounded by eight oxygen atoms which belong to four formate groups. The IR spectra of $U(HCOO)_4$ and $Np(HCOO)_4$ are very similar [33], indicating the coordination around the two ions is very comparable. The site symmetry of the uranium atom is lowered to 2 compared to $\bar{4}$ in $Np(HCOO)_4$ indicating some different bonding of the oxygen atoms. The close relationship of the compounds is also expressed by molar volume (Table 4) which decreases with increasing actinide contraction in the series Th, Pa, U, Np.

TABLE 4

Lattice constants and molar volume of $M(HCOO)_4$ (M = Th, Pa, U, Np) [32]

Compound	Unit cell constants (Å)	Complexes/unit cell	V_{mole} (cm^3)
$Th(HCOO)_4$	$a = 7.973$, $c = 6.588$	2	126.1
$Pa(HCOO)_4$	$a = 7.915$, $c = 6.517$	2	123.0
$U(HCOO)_4$	$a = 11.31$, $b = 6.576$, $c = 11.89$, $\beta = 114.5°$	4	121.2
$Np(HCOO)_4$	$a = 7.819$, $c = 6.446$	2	118.7

D. ACTINIDE(III) FORMATES

$U(HCOO)_3$ has been obtained as a fine crystalline dark olive-green precipitate by reducing a solution of UCl_4, in anhydrous formic acid, with zinc amalgam [17]. Uranium(III) formate is insoluble both in formic acid and in other organic solvents; it dissolves slowly in water with oxidation to uranium(IV). The IR spectra show bands characteristic of H_2O and OH but the analytical results indicate a low percentage (less than 1%) of them. The effective magnetic moment for $U(HCOO)_3$ (3.56 B.M.) differs from $Nd(HCOO)_3$ by only 0.08 B.M. and is close to the theoretical value calculated for three f electrons assuming Russell-Saunders coupling. Since both these compounds are isoelectronic and isomorphous [20] and therefore have the same field symmetry C_{5v}^3, this is evidence that the electronic structure of U^{3+} is (Rn) $5f^3$.

The blue $Pu(HCOO)_3$ was prepared by addition to formic acid [18] of $Pu(OH)_3$, obtained by dissolving plutonium metal in 12 N HCl and adjusting the blue plutonium(III) solution to pH 8 with 8 N NaOH. X-ray powder diffraction patterns show $Pu(HCOO)_3$ is isomorphous with several lanthanide [19,20] and uranium(III) formates [17]. It has been suggested from IR spectra in the 350—250 cm^{-1} region that there is a great degree of ionic character in the metal—anion bond for plutonium(III) formate as compared to the lanthanide-(III) formates. The thermal decomposition of $Pu(HCOO)_3$ in air proceeds directly to plutonium dioxide; no stable intermediates have been indicated in the thermogram. $Pu(HCOO)_3$ has also been prepared [21] by submerging plutonium metal in a CCl_4/CH_3OH mixture; an exothermic reaction occurs and a blue-green solution is obtained. To this solution formic acid (90%) is added and a blue precipitate of $Pu(HCOO)_3$ is immediately obtained in a 30% yield. Thermogravimetric and IR spectra completely agree with the product obtained with the method reported above [18].

Americium(III) formate has been prepared by treating americium(III) hydroxide with an excess of concentrated formic acid at 50°C. From the solution, on evaporation of formic acid, pink $Am(HCOO)_3$ can be obtained [15]. X-ray powder data show $Am(HCOO)_3$ to have a hexagonal cell with constants: $a = 10.55$ and $c = 4.07$ Å. More recently the thermal decomposition of $Am(HCOO)_3 \cdot 0.2\ H_2O$ has been studied by using mass spectrometric identifica-

TABLE 5

Known actinide(III) formate complexes

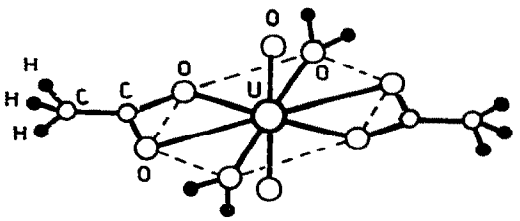
Compound	Experimental conditions	Colour	Ref.
$Am(HCOO)_3$	$Am(OH)_3$ in an excess of HCOOH and by evaporation of the resulting solution	Pink	15
$U(HCOO)_3$	Reduction of UCl_4 with zinc amalgam in anhydrous HCOOH	Dark olive-green	17
$Pu(HCOO)_3$	$Pu(OH)_3$ in HCOOH or Pu in CCl_4/CH_3OH mixture added to HCOOH	Blue	18, 21

tion of gaseous decomposition products and X-ray identification of solid residues [16]. The decomposition of this compound proceeds to $Am_2O_2CO_3$ which yields Am_2O_3 on further heating; as an intermediate AmO(HCOO) seems to be formed.

The experimental conditions for the preparation of these actinide(III) formates are summarized in Table 5.

E. ACTINIDE(VI) ACETATES

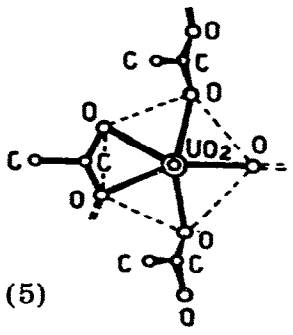
Uranyl acetate $UO_2(CH_3COO)_2$ and its hydrated forms are referred to as the simple acetates; "double" uranyl acetates are characterized by the formulae $M'UO_2(CH_3COO)_3 \cdot x\,H_2O$ and $M''(UO_2)_2(CH_3COO)_6$; the "triple" salts are usually characterized by the formula $M'M''(UO_2)_3(CH_3COO)_9 \cdot x\,H_2O$. Yellow crystals, with a greenish tinge due to fluorescence, of diaquo uranyl diacetate can be obtained by warming uranyl nitrate hexahydrate or UO_3 with acetic acid [53—56]. The crystal symmetry of the complex is orthorhombic, the space group being $Pba2_1$ [57] and not $Pbn2_1$ as previously reported [58]. A



(4)

structure of type (4) has been proposed; the IR spectrum shows a single strong and broad band at about 1500 cm^{-1} due to the vibrations ν_{asym} COO, ν_{sym} COO and CH_3 deformation. The presence of such a single band seems to indicate a very important coupling between these different vibrational modes [57]; which can be explained by the four vibrations simultaneously entering into resonance. The ν_{asym} O—U—O lies at 970 cm^{-1} and ν_{sym} O—U—O at 867 cm^{-1}.

The crystal and molecular structure of uranyl(VI) acetate dihydrate has been recently reported [265]. It is of interest because it leads to different conclusions to those reported on the basis of IR spectra [57]. The crystals are orthorhombic, space group *Pnam*, with $a = 9.622$, $b = 14.833$ and $c = 6.808$ Å. The uranium atom is in a distorted pentagonal bipyramidal environment. The equatorial plane contains an oxygen from one water molecule, two oxygens from a chelating acetate group and two oxygens from two different bidentate bridging acetate groups; thus one half of the acetates act exclusively in a chelating capacity and the other half exclusively in a bidentate bridging capacity. The bidentate bridging acetate groups join the bipyramids to form linear chains parallel to the *c* axis. The other water molecule is external to the primary coordination shell of the uranium and is hydrogen bonded to the water molecule of one bipyramid and to two chelating acetate oxygen atoms of two bipyramids in an adjacent chain. The coordination polyhedron about the uranium is (5) and the environment of the non-bonded water molecule is (6)



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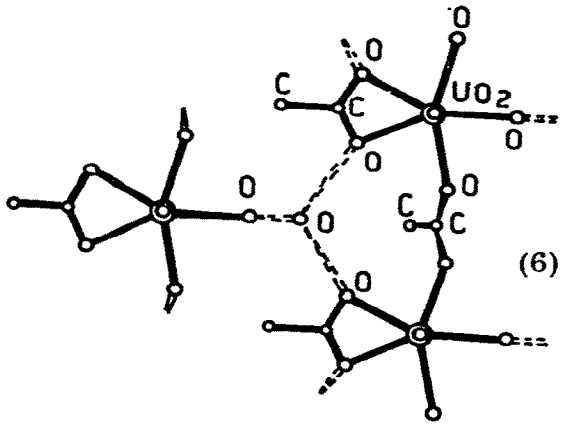


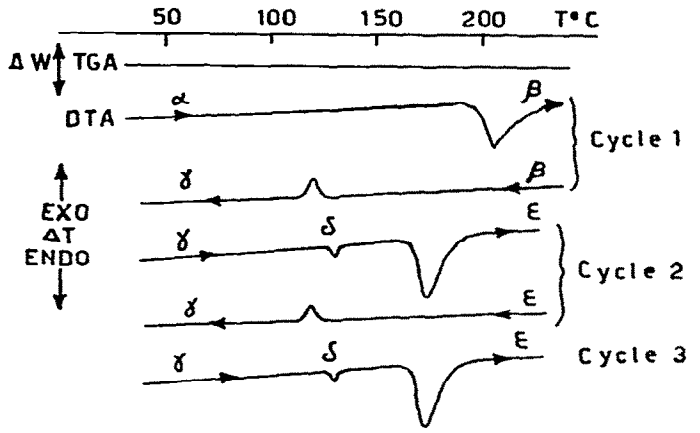
(6)

The thermal decomposition of $[UO_2(CH_3COO)_2H_2O] \cdot H_2O$ has been studied [57,59—61]. It was first found that the complex was stable up to 100°C; the water molecules were then released up to 159°C. The anhydrous salt was stable until 247°C, then rapidly decomposed at 380°C [59]. Other reports do not agree with such results because it has been found the water is lost between 65 and 120°C. No monohydrate was found and the anhydrous salt was reported to be stable up to 200°C when slow decomposition occurred; the decomposition is complete at 297°C. More recently the thermal decomposition of $[UO_2(CH_3COO)_2H_2O] \cdot H_2O$ has been completely studied in nitrogen and in air [61]. The compound loses the water molecules between 96 and 140°C; the anhydrous salt is stable up to 245°C, at which temperature it starts to decompose very slowly; decomposition is complete at 345°C. Differential thermal analysis in air gives an endothermic peak between 95 and 140°C when $[UO_2(CH_3COO)_2H_2O] \cdot H_2O$ loses water molecules and another small endothermic peak followed by a large exothermic one at 320°C which tails off by 344°C. It has been suggested that the initial small endothermic peak is

due to the formation of UO_2 taking place at a faster rate than subsequent strongly exothermic oxiding reactions. In nitrogen the dehydration takes place between 94 and 145°C and the decomposition takes place slowly between 260 and 370°C; differential thermal analysis in nitrogen shows an endothermic peak between 95 and 140°C due to the loss of the water and an endothermic peak beginning at 295°C; there is no subsequent exothermic peak as in air. These results suggest that the initial stage in the decomposition could be the fission of the U—acetate bond. The large exothermic peak in the air DTA due in part to the reaction
$3\ UO_2 + O_2 \rightarrow U_3O_8$ is preceded by a small endothermic peak which could be due to the break of the U—O(acetate) bond. The DTA curve in nitrogen agrees with this hypothesis as only the endothermic peak is present. X-ray powder diffraction analysis of the decomposition product shows that in air uranyl acetate dihydrate decomposes into U_3O_8 whereas in nitrogen the main product is a non-stochiometric UO_{2+x} with a small amount of U_3O_8.

Anhydrous uranyl acetate can be easily prepared by reaction of acetic anhydride on uranyl nitrate hexahydrate [62,63] or by freeze-drying aqueous solutions of uranyl acetate and KBr [65]. The IR spectrum of the latter compound has been recorded; the type of spectra obtained depends on the $[UO_2(CH_3COO)_2H_2O] \cdot H_2O$/KBr ratio. In the spectrum of the sample with small molar ratio, a peak at 1713 cm^{-1}, assigned to the C=O stretching mode of the uncoordinated acetate groups, is present; this peak disappears when the molar ratio increases. Moreover the ν_3 O—U—O appears as a strong double peak at 929 and 930 cm^{-1} for the small molar ratio sample but as a single strong peak at 942 cm^{-1} for that of high molar ratio. The presence of the bands characteristic of the ionic carboxylic groups at 1713 cm^{-1} may be due to some substitution of the carboxylic group by bromine ions.

Five distinct allotropic species of anhydrous uranyl acetate have been detected by differential enthalpic analysis [66]. The differential thermal analysis of the anhydrous $UO_2(CH_3COO)_2$ has been carried out in the 30—250° temperature range; it was found that no weight loss occurred in this range. On heating the salt, an endothermic peak at 209°C was found and on returning to room temperature an exothermic peak at 120°C is noted. If the product undergoes subsequent cycles of heating and cooling the following DTA curves (7) can be seen. These different thermic effects, without change in weight, have been interpreted as allotropic transformations. The different species have been designated with the symbols $\alpha, \beta, \gamma, \delta, \epsilon$ in the function of the period of the cycle where they were observed. Measurements of the ΔS were carried out only for the transformation $\alpha \rightarrow \beta$ (0.8 kcal mol^{-1}) and $\delta \rightarrow \epsilon$ (1.2 kcal mol^{-1}). The values are small, as expected for allotropic transformations. IR spectra of these allotropic species have been reported and there are some morphological differences on going from low to high temperature. These differences are due to a change in the inner structure without change in the coordination of the uranium atom. The main modes are reported in Table 6. IR spectra in the 1000—800 cm^{-1} region show multiple bands for O—U—O



(7)

modes and differences have been noted in the ν_{sym} O—U—O mode. This band is very weak for the α and γ species, double and weak for the δ and ϵ and medium for the β species. The presence in the IR spectrum of the β species of a medium ν_{sym} O—U—O band may be due to some asymmetry of the coordination around the central atom.

By treating $[UO_2(CH_3COO)_2(H_2O)]H_2O$ with neutral monodentate ligands, monomeric and dimeric complexes can be obtained on varying the solvent and the reaction conditions [67—70] (Table 7). The monomeric complexes of the type $[UO_2(CH_3COO)_2(L)_2]$ (L = monodentate ligand) can be described as hexacoordinated species in the equatorial plane of the uranyl group as found for $[UO_2(NO_3)_2(Ph_3AsO)_2]$ [71]. The experimental values of molecular weight measurements are below the theoretical ones, indicating that molecules of the neutral monodentate ligand are partially lost in solution. The IR spectra of these complexes show two bands at about 1550 and 1470 cm^{-1}, attributed respectively to the antisymmetric and the symmetric stretching vibrations of COO (Table 8). By comparison of the X-ray powder photographs of $[UO_2$-

TABLE 6

IR frequencies (cm^{-1}) of the five allotropic species of anhydrous uranyl acetate [66]

Compound	$\nu_{asym\,COO}$	$\nu_{sym\,COO}$	δ_{OCO}	$\rho_{w\,OCO}$	$\nu_{asym\,OUO}$	$\nu_{sym\,OUO}$
$\alpha UO_2(CH_3COO)_2$	1545	1395	682	643	965, 958 949	855
$\beta UO_2(CH_3COO)_2$	1545 1530	1395	680	642	955, 949	854, 846
$\gamma UO_2(CH_3COO)_2$	1545	1395	680	644	959, 950	857
$\delta UO_2(CH_3COO)_2$	1545	1395	679	640	961, 956 950	855, 853
$\epsilon UO_2(CH_3COO)_2$	1545 1530	1395	680	643	957, 948	855, 840

TABLE 7

Reaction conditions for the preparation of monomeric and dimeric uranyl(VI) acetate complexes with neutral monodentate ligands

Ligand	Solvent	Molar ratio (UO_2 : L)	Product	M.P. (°C)	Ref.
Ph_3PO	Acetone	1 : 1	Dimeric		67
Ph_3PO	CH_3NO_2	1 : 2.5	Monomeric		67
Ph_3AsO	Methanol	1 : 1	Dimeric	245	67
Ph_3AsO	Acetone	1 : 2	Monomeric	260	67
Me_3NO	Ethanol	1 : 6	Dimeric	170	68
HMPA[a]	Acetone	1 : 2	Dimeric	227	69
$(C_6H_5)_2SO$	Acetone	1 : 1	Monomeric	116	70

[a] HMPA = $((CH_3)_2N)_3PO$.

$(CH_3COO)_2(Ph_3PO)_2]$ and $[UO_2(CH_3COO)_2(Ph_3AsO)_2]$ the compounds were found to be isomorphous. Using a 1 : 1 UO_2^{2+} : L (L = Ph_3PO or Ph_3AsO) molar ratio, the dimeric species $[UO_2(CH_3COO)_2L]_2$ can be isolated. The structure of $[UO_2(CH_3COO)_2(Ph_3PO)]_2$ has been determined [67]. It consists of discrete molecules with two $[UO_2(CH_3COO)_2(Ph_3PO)]$ related by a center of symmetry and bridged by acetate groups so that the resulting coordination number of the uranium is seven. The pentagonal base of the bipyramid is defined by two oxygen atoms of a chelate acetate group, two oxygens of the bridging acetate groups and the oxygen of the ligand as shown in Fig. 4. The chelate acetate groups appear to be regular. The bridging acetates are tilted at

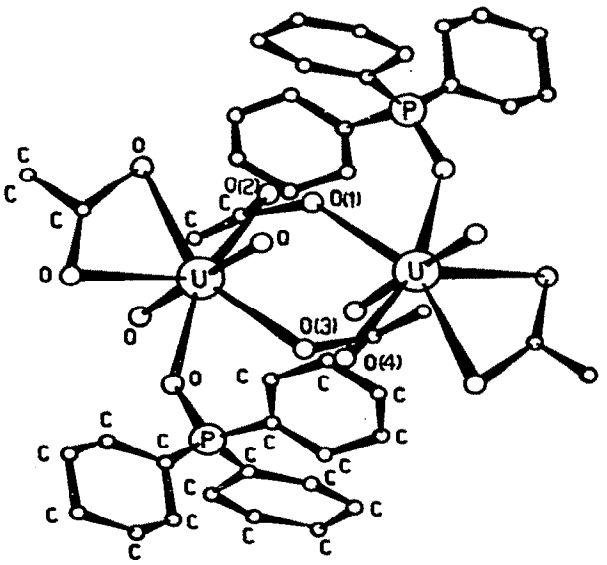


Fig. 4. Molecular structure of the dimeric complex $[UO_2(CH_3COO)_2(Ph_3PO)]_n$.

TABLE 8

Crystallographic data for mononuclear and dinuclear uranyl(VI) acetate complexes

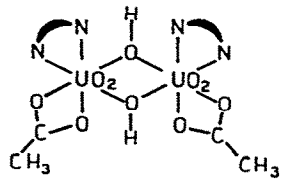
Compound	$UO_2(CH_3COO)_2(Ph_3PO)_2$	$UO_2(CH_3COO)_2(H_2O)$	$UO_2(CH_3COO)_2(Ph_3AsO)_2$	$[UO_2(CH_3COO)_2(Ph_3PO)]_2$	$[UO_2(CH_3COO)_2 \cdot (Ph_3AsO)]_2$
Unit cell	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	*Pnam*	$P2_1/c$	$P1$ or $P\bar{1}$	$P\bar{1}$
a	9.88	9.622	9.86	8.34	8.31
b	19.13	14.833	19.16	11.02	11.05
c	10.87	6.808	10.88	13.68	13.66
z	2	4	2	1	1
α				101.50°	101.50°
β	116.30°		116.32°	91.12°	91.10°
γ				109.12°	109.12°
Ref.	275	265	273	67	273

67° with respect to the bridging plane defined by the O(1), O(2), O(3) and O(4) atoms in Fig. 4. IR data for this binuclear complex in the range 1600—1300 cm^{-1}, show four bands at 1533, 1524, 1456 and 1425 cm^{-1} for the ν_{asym} and the ν_{sym} stretching vibrations of the COO groups in agreement with the two types of chelating modes of the acetate groups [219].

The presence of the dimeric compounds has also been recognized in solution by molecular weight determinations; the experimental values are slightly below theoretical values indicating that molecules of ligand are lost in solution.

With the ligands CH_3CN and hexamethylphosphoramide, only binuclear species have been obtained, containing one molecule of ligand per atom of uranium. The complexes are not electrolytes in methanol and nitromethane. An acetate-bridged structure has likewise been proposed for these complexes $[UO_2(CH_3COO)_2(Ph_3PO)]_2$ [67] even though physicochemical data supporting this structure have not been published.

The complexes $[UO_2(OH)(CH_3COO)(L)]$ can be isolated as light crystalline precipitates from aqueous solutions of uranyl acetate, by addition of 1,10-phenanthroline or 2,2'-bipyridyl (L). They are soluble in alcoholic media [72] and $[UO_2(OH)(CH_3COO)(phen)]$ has a molar conductance in methanol of $75\Omega^{-1}$ cm^2. Thermogravimetric studies on this complex show 0.5 moles of water are lost at fairly high temperature (190—195°C); this has been explained by assuming the complex has a dimeric structure of the type (8) which on



(8)

heating at 190°C changes to an oxocomplex with the loss of one molecule of water.

Many years ago it was reported [73] that UO_2^{2+} forms the double salt $M'[UO_2(CH_3COO)_3]nH_2O$ where $M' = Li^+, Na^+, K^+, NH_4^+, Rb^+, Cs^+, Ag^+, C_6H_5NH_3^+$, by the reaction of aqueous solutions of $[UO_2(CH_3COO)_2(H_2O)_2]$ with alkali acetate. On the basis of measurements of ionic diffusion rate, their molecular weights have been calculated and it was found that in each case the uranyl group is combined with three acetate groups to form the anion $[UO_2(CH_3COO)_3]^-$. This anionic nature of the complex has also been confirmed by measurements of molar conductance [73] which have shown that $M'[UO_2(CH_3COO)_3]$ dissociates into two ions in aqueous solution. This is possible only if anionic complexes are formed. Physicochemical investigations have shown that the acetate ions act as bidentate towards the uranyl group. X-ray diffraction studies [10] have confirmed that every acetato group in $[UO_2(CH_3COO)_3]^-$ is joined through two oxygen atoms to the central uranium atom of the uranyl group. The configuration about the uranium atom is shown in Fig. 5.

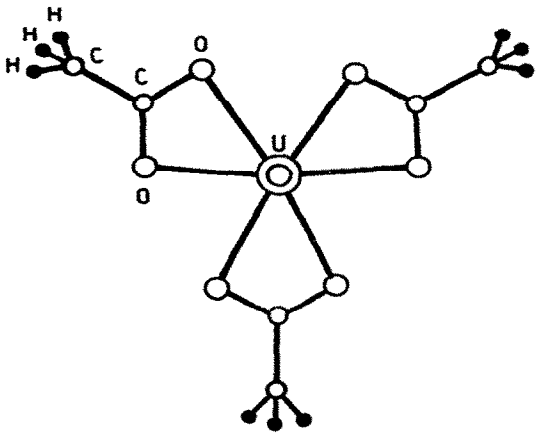


Fig. 5. Molecular configuration around the UO_2^{2+} group in the complex $Na[UO_2(CH_3COO)_3]$.

The complex has a cubic symmetry with space group $P2_13$ and a = 10.688 Å. The U—O bond distances in the uranyl group are 1.71 ± 0.04 Å, whereas the U—O distances in the equatorial plane are 2.49 ± 0.02 Å. The O—C—O coordination angles are 121° and the C—O distances are 1.26 ±.0.05 Å and 1.28 ± 0.04 Å (equal within the limits of experimental error). The deviation in the hexagon of coordinated oxygen from complete planarity with the uranium atom is very small (±0.04 Å) and the authors pointed out, by comparing their results with others from the literature, that wherever sterically possible, the equatorial bonds lie in a plane normal to the uranyl(VI) axis. Sodium is bonded to a six acetate oxygen with Na—O distance of 2.37 Å.

Actinyl(VI) triacetate complexes of the type $Na[MO_2(CH_3COO)_3]$ (M = Np^{VI} green, Pu^{VI} pink, Am^{VI} lemon yellow) have been prepared by the same method as the analogous uranyl(VI) complex [74,75]. The IR spectra of all these complexes are almost identical except for the shift in the O—M—O frequencies (Table 9). The forces within the carboxyl group of the acetate are altered considerably on going from sodium acetate to the $Na[MO_2(CH_3COO)_3]$

TABLE 9

IR frequencies of CH_3COONa and of the complexes of the type $Na[MO_2(CH_3COO)_3]$ (M = U, Np, Pu, Am) [75]

Complex	$\nu_{asym\,COO}$	$\nu_{sym\,COO}$	δ_{COO}	$\nu_{3\,OMO}$	$\nu_{1\,OMO}$	$\nu_1 + \nu_3$
CH_3COONa	1578	1408	645			
$Na[UO_2(CH_3COO)_3]$	1537	1472	678	934	856	1781
$Na[NpO_2(CH_3COO)_3]$	1536	1472	677	934	844	1770
$Na[PuO_2(CH_3COO)_3]$	1540	1470	677	930	818	1739
$Na[AmO_2(CH_3COO)_3]$	1541	1467	675	914	749	

complexes. However in the four triacetate complexes there are small differences in the observed frequencies; thus the bond strengths within the acetate groups are not appreciably different on going from the uranium(VI) to the americium(VI) complex. The ν_1 O—M—O symmetric stretching frequencies are very weak in their IR spectrum and have been confirmed by the combination frequencies $\nu_1 + \nu_3$ observed for U, Np and Pu compounds. From these data the M—O force constant of the O—M—O group decreases in the order $U^{VI} > Np^{VI} > Pu^{VI} > Am^{VI}$; even though the M—O distance becomes smaller in the same order. These data are in contrast with the previous studies [74] where the force constants were found to decrease in the order $Np^{VI} > U^{VI} > Pu^{VI} > Am^{VI}$; however these later force constants were calculated only from the ν_3 O—M—O asymmetric stretching frequency. When these results were corrected with the interaction constants, an inversion of neptunium and uranium occurred in the order.

The neptunyl(VI), plutonyl(VI) and americyl(VI) triacetate complexes [76,77] are isostructural with the uranyl one as confirmed by their cell constants and refraction index (Table 10). The magnetic susceptibility of $Na[PuO_2(CH_3COO)_3]$ has been measured over the temperature range 90—300 K [78]. Because the sample decomposes owing to the instability of Pu(VI), several measurements have been done proving that the drop in susceptibility is small over the temperature range examined. From the mean of the results, the susceptibility is $3305 \cdot 10^{-6}$ at 300 K; this value is the same as the spin only value of $3333 \cdot 10^{-6}$ theoretically predicted. A similar agreement exists at 200 K and 90 K; moreover $Na[PuO_2(CH_3COO)_3]$ obeys the Curie law in the experimental temperature range, the Weiss constant being zero.

$[MO_2(CH_3COO)_3]^-$ complexes absorb on anion exchangers and are efficiently extracted by tertiary amines or long-chain quaternary ammonium salts dissolved in an organic diluent [76]. In these solutions the tetraacetate anions $[MO_2(CH_3COO)_4]^{2-}$ ($M = U^{VI}$, Np^{VI}, Pu^{VI}) have been identified. It may be tentatively supposed that a coordination around the central metal occurs as in $[UO_2(NO_3)_4]^{2-}$ where two nitrates act as bidentate and two as unidentate ligands [232]. Complexes of the type $LnUO_2(CH_3COO)_5 \cdot n\ H_2O$ ($Ln = La^{III}$, Nd^{III}) have been prepared [79—81] by mixing acetic acid solutions of the appropriate lanthanide oxide and $[UO_2(CH_3COO)_2H_2O] \cdot H_2O$ and allowing them to stand in air to crystallize. These mixed complexes are coloured (Nd =

TABLE 10

Cell constants for cubic $Na[MO_2(CH_3COO)_3]$ and refractive index at 25°C [75]

Compound	a (Å)	Refractive index
$Na[UO_2(CH_3COO)_3]$	10.694	1.5015
$Na[NpO_2(CH_3COO)_3]$	10.679	1.5105
$Na[PuO_2(CH_3COO)_3]$	10.670	1.518
$Na[AmO_2(CH_3COO)_3]$	10.653	1.528

yellowish-pink, La = yellow-green) soluble in water and can be recrystallized from weakly acidic solution or methanol. The molar conductance in methanol shows the compounds are non-electrolytes while in aqueous solution they dissociate. Cryoscopic determinations of their molecular weight in dimethyl sulphoxide agree with the behaviour drawn from the molar conductance in methanol and suggest that the complexes are dinuclear non-electrolyte compounds. It has been reported that both the uranyl(VI) and lanthanide ions enter into the inner sphere linked by a bridging acetate group, but no further evidence for this speculation has been given. Both compounds give virtually the same thermogravimetric curves with endothermic peak effects at 130—200°C accompanied by weight loss and an exothermic effect at 400—480°C due to the combustion of the substance.

A general inspection of the data concerning the photochemistry of the UO_2^{2+}—acetic acid system indicates that two photochemical reactions may occur depending upon reaction conditions [246,247,257], i.e. the sensitized decarboxylation

$$CH_3COOH \xrightarrow[UO_2^{2+}]{h\nu} CH_4 + CO_2$$

and the photooxidation—reduction

$$UO_2^{2+} + 2\,H^+ + 2\,CH_3COOH \xrightarrow{h\nu} C_2H_6 + 2\,CO_2 + 2\,H_2O + U^{4+}$$

Since the proportion of C_2H_6 increases with increasing $CH_3COOH + CH_3COO^-$: U^{4+} ratio, a possible working hypothesis [247] is that the decarboxylation occurs when light is absorbed by free uranyl ions (which then react by encounters with CH_3COOH molecules) and that photooxidation of the organic substrate involves excited uranyl acetate complex. In order to further test the course of the above mentioned photoreaction, ESR investigations were made [256]. The ESR results, i.e. the production of $\cdot CH_3$ and $\cdot CH_2COOH$ radicals, suggest the occurrence of both oxidative decarboxylation and a process of a hydrogen-atom abstraction from C—H bonds. In this context it is interesting to note that this situation is similar to that found with a solution of ceric ammonium nitrate in acetic acid, which decomposes solely through a LMCT process.

F. ACTINIDE(V) ACETATES

$NpO_2(CH_3COO) \cdot 2\,H_2O$ has been prepared by treating freshly prepared NpO_2OH with glacial acetic acid [226]. The preparation of plutonium(V) acetate using the same procedure failed due to disproportionation of plutonium(IV) and plutonium(VI) acetate [225]. $NpO_2(CH_3COO) \cdot 2\,H_2O$ is readily soluble in water but insoluble in alcohol; it loses the two water molecules in two steps at about 90°C and 160°C. The final decomposition occurs at 280—310°C leading to the dioxide NpO_2.

Recently the barium neptunyl(V) triacetate dihydrate $Ba[NpO_2(CH_3COO)_3] \cdot 2\ H_2O$ has been prepared and its crystal structure determined by X-ray diffraction methods [150]. The body-centered tetragonal unit cell, with dimensions $a = 19.167(5)$ and $c = 9.476(3)$ Å, contains eight formula units of $Ba[NpO_2(CH_3COO)_3] \cdot 2\ H_2O$. The spece group is $I42d$. The neptunium (V) atoms are found to be involved in triatomic NpO_2^+ ions. These are linear within experimental error (178.5(9)°) and the Np—O distance is 1.85(2) Å. Six oxygen atoms belonging to three acetate ions fill the equatorial region of the neptunyl ion, giving the neptunium atom a hexagonal-bipyramidal coordination overall. The six equatorial oxygen atoms lie very nearly in the plane; the linear NpO_2^+ portion is perpendicular to this plane within experimental error. While the point symmetry at the neptunium atom in the crystal is actually C_2, the entire $[NpO_2(CH_3COO)_3]^{2-}$ bipyramid has nearly D_{3h} symmetry. These hexagonal bipyramids are cross-linked by sharing their acetate oxygen atoms with Ba^{2+}.

The Ba^{2+} ion is coordinated by eight oxygen atoms, one each from six different acetate ions and two from water molecules. This polyhedron has a two-fold axis and is best described as intermediate between a dodecahedron and a square antiprism.

It has been shown from IR studies [269—271] of the stretching frequencies of NpO_2^{2+} and NpO_2^+ ions that the Np—O bonds are weaker in the latter. The effect of changing Np(VI) to Np(V) keeping the equatorial plane fixed can be achieved by comparing the $Ba[NpO_2(CH_3COO)_3]\ 2\ H_2O$ structure with that of $Na[NpO_2(CH_3COO)_3]$ which has the same ligand and a very similar configuration. The axial oxygen atoms of the NpO_2^{2+} and NpO_2^+ ions are bonded only to the neptunium atoms and the equatorial regions are occupied by a planar array of acetate ions. Each acetate ion is shared with two other cations: Na^+ in the first instance and Ba^{2+} in the second. These cations are also linked to four other oxygen atoms from different acetate ions and the larger Ba^{2+} ion has two additional H_2O molecules in its coordination polyhedron. The Np—O bond lengths are 1.85(2) and 1.71(4) Å in NpO_2^+ and NpO_2^{2+}, respectively; this clearly shows the weakening of the bond.

G. ACTINIDE(IV) ACETATES

The earliest information on acetato compounds of thorium(IV) dates from 1829 [22] when $Th(CH_3COO)_4$ was prepared from thorium hydroxide or thorium carbonate in concentrated acetic acid; the chemical analysis was not given. The method used suggests that a basic thorium acetate was probably formed. Almost 40 years later [23] the preparation of $Th(CH_3COO)_4$ from $Th(OH)_4$ or $ThCl_4$ by treatment with acetic acid was described. Anhydrous $Th(CH_3COO)_4$ has also been prepared by adopting special conditions (e.g. the use of acetic anhydride, organic solvents held over dehydrating agents etc.) [88—92]. It forms anisotropic prismatic crystals and an X-ray diffraction investigation has been carried out [93] (Fig. 6). It is isomorphous to

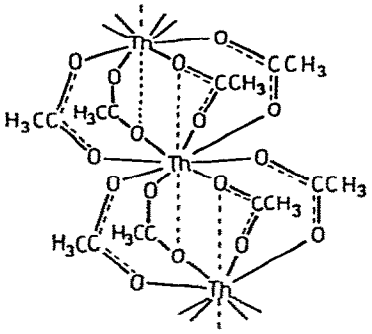
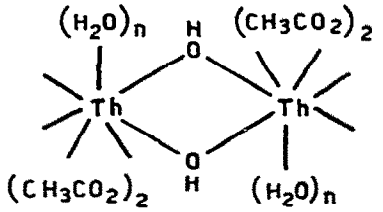


Fig. 6. Molecular configuration of $Th(CH_3COO)_4$.

$U(CH_3COO)_4$ and in this compound the coordination number around the central metal ion is increased to ten with two acetato groups acting as tridentate ligands. The IR spectrum in the COO stretching region indicates a marked deformation of the carboxylic groups as a result of their coordination to the metal atom. Several absorption bands are observed in the range 1300—1600 cm^{-1} at the following frequencies: 1568(s), 1545(s), 1518(vs), 1452(vs), 1410(s), 1380(s) and 1350(s) cm^{-1}. By analogy with $U(CH_3COO)_4$, in the $Th(CH_3COO)_4$ IR spectrum $\nu_{asym}COO$ could lie at 1568 and 1545 cm^{-1} and $\nu_{sym}COO$ at 1410 and 1380 cm^{-1}.

Thermogravimetric results show that $Th(CH_3COO)_4$ does not decompose when heated up to 250°C. Decomposition takes place above 300°C accompanied by an endothermic effect, which merges with a marked exothermic effect and a sharp loss in mass. Thorium dioxide is formed above 370°C with formation of acetone and carbon dioxide.

$Th(OH)_m(CH_3COO)_{4-m} \cdot n\ H_2O$ are readily formed in aqueous solution when an alkali metal and ammonium acetate are added to thorium acetate [94]. The composition of some hydroxide acetates indicates that they are at least dimeric. As a result of the marked tendency of thorium to form bonds with the hydroxo groups, all of these hydroxide acetates are apparently polymerized to a greater or lesser extent by hydroxo bridges. Two possible geometries have been proposed for $Th(OH)_2(CH_3COO)_2$ one with hydroxo and acetate bridges (10), the other with hydroxo bridges only (9).



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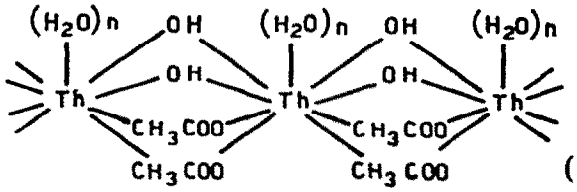


(10)

The compound contains some water so the coordination number of thorium may be greater than eight.

An analogous structure may be assumed for other hydroxo acetato complexes of thorium with a gradual replacement of the acetato groups by hydroxo groups; water molecules complete the coordination around the thorium atom. On heating, these compounds show a slow dehydration, initially by losing coordinated water and then as a result of the decomposition of hydroxo groups. A vigorous decomposition of the organic moiety of the compounds accompanied by a marked exothermic effect and the formation of ThO_2 occurs in the range 250—370°C.

By reaction of $Th(OH)_4$ in an acetic acid solution of guanidinium acetate the complex $(CN_3H_6)[Th(CH_3COO)_6]n\ H_2O$ has been prepared [95]. This compound has been also prepared on heating an acetic acid solution of $Th(OH)_4$ and guanidinium acetate in molar ratio 1 : 12 at 50—60°C [96]. The anhydrous $(CN_3H_6)_2Th(CH_3COO)_6$ was prepared from $Th(CH_3COO)_4$ and guanidinium acetate in a 1 : 2 molar ratio; the compound is sparingly soluble in water and insoluble in the common organic solvents. Its IR spectrum, like that of thorium tetraacetate, does not show the characteristic $\nu_{C=O}$ of the COOH group at about 1700 cm^{-1}. The presence of several bands in the range of the stretching vibrations of the C=O and C—O groups indicate that the carboxylic group undergoes deformation as a result of the coordination of the acetato groups to thorium. Absorption bands are present at the following frequencies (cm^{-1}): 1582(s), 1560(vs), 1470(vs), 1420(s). A strong absorption is observed in the range of the COO bending vibrations at the following frequencies (cm^{-1}): 618 (med), 665(s), 675(vs), 697(med) indicating deformation of the O—C—O angle. X-ray diffraction studies indicate that the compound has the space group $Pa3$ with a = 13.5 Å and z = 4. Thermogravimetric data show it is stable to above 200°C, and melts at about 175°C. In the range 200—280°C it decomposes with 82% loss in mass and complete combustion takes place at 470—500°C: the residue is pure ThO_2.

$U(CH_3COO)_4$ has been successfully prepared by photochemical reduction of alcoholic solutions of uranyl(VI) acetate in the presence of acetic anhydride [82]. Not all the methods employing aqueous solution were successful because of hydrolysis of uranium(IV) in this solution. It has been found that if a solution of uranyl acetate dihydrate in acetic acid with a small amount of water (or UO_2Cl_2 in anhydrous glacial acetic acid) is refluxed or warmed with Zn amalgam or Zn, uranyl(VI) is reduced to uranium(IV) and $ZnU(CH_3COO)_6$ can be obtained; this compound, by addition of a stoichiometric amount of HCl in acetic acid solution, can be converted into $U(CH_3COO)_4$ [83,84].

$U(CH_3COO)_4$ is oxidized to uranyl(VI) acetate in moist air; thermogravimetric analyses show that $U(CH_3COO)_4$ undergoes thermal decomposition through the formation of the corresponding uranyl acetate as intermediate product which then decomposes very rapidly to give UO_3 or a mixture of UO_3 and U_3O_8.

When iron or magnesium is used as reducing agent the compounds $MgU(CH_3COO)_6$ or $FeU(CH_3COO)_6$ have been obtained [85]. The new acetates are classified as double acetates rather than complex salts containing [U-

$(CH_3COO)_6]^{2-}$ ion, although the latter possibility is not excluded. They are well defined crystalline compounds but are not isomorphous.

$ZnU(CH_3COO)_6$ has also been prepared by reaction of $U(CH_3COO)_4$ with an excess of $Zn(CH_3COO)_2$ in acetic acid; $ZnU(CH_3COO)_6$ gives a nearly identical X-ray powder photograph to that of $U(CH_3COO)_4$ indicating that the zinc acetate retains the parent structure of uranium(IV) acetate; no lines belonging to $Zn(CH_3COO)_2$ are observed.

Magnetic moments for $U(CH_3COO)_4$, $MgU(CH_3COO)_6$ and $U(CH_3COO)_4 x$ $Zn(CH_3COO)_2$ are almost equal, suggesting an identical environment for the U(IV) ion. The magnetic moment of $FeU(CH_3COO)_6$ corresponds to the high spin state of the iron(II) but with a slightly lowered value (Table 11).

An X-ray investigation of U(IV) tetracetate has been made on single crystals obtained from glacial acetic acid; the crystals were mainly fine fibers along the monoclinic c axis [86] with space group $C2/c$, $z = 4$, $a = 17.80$, $b = 8.35$ and $c = 8.33$ Å. The structure consists of infinite columns parallel to the c axis direction in which each acetate ion belongs to two uranium ions. Acetate ion bridges are situated obliquely to the c axis direction. The coordination around the uranium atom is ten, with a bicapped square antiprism geometry; such a coordination is realized by two acetate ions with both their oxygen atoms near the uranium (2.52 and 2.80 Å) and six acetate ions with only one oxygen atom near to the same uranium ion (at 2.52 Å) (Fig. 7).

By boiling 1 : 2 aqueous solutions of acetic acid and $U(CH_3COO)_4$ an insoluble grey-green precipitate formulated as $U(OH)(CH_3COO)_3$ is obtained [87]; the compound is most probably polymeric with hydroxo bridges. Upon heating at 190°C in vacuo 1 mole of acetic acid per formula weight is lost and the hydroxyl bond in the IR spectrum disappears, leading to a polymeric compound of the type $UO(CH_3COO)_2$ with O—U—O—U linkages. There is no evidence in the IR spectrum of a strong multiply bonded UO^{2+} entity in the structure.

Complexes of $Th(CH_3COO)_4$ and $U(CH_3COO)_4$, with oxygen donor ligands have not been established; recently the effect of thorium(IV) and uranium(IV)

TABLE 11

The most important IR frequencies and magnetic data of uranium(IV) acetates and double acetates

Compound	$\nu_{asym\,COO}$ (cm^{-1})	$\nu_{sym\,COO}$ (cm^{-1})	μ_{eff} (B.M.)	Ref.
$U(CH_3COO)_4$	1560, 1515	1402, 1345	2.69	85, 87
$U(OH)(CH_3COO)_3$	1545, 1515	1410, 1345		87
$(UO(CH_3COO)_2)_n$	1550	1410, 1340		87
$U(CH_3COO)_4 \cdot x\ Zn(CH_3COO)_2$	1560, 1510	1410	2.63	85
$MgU(CH_3COO)_6$	1600, 1530	1380	2.66	85
$FeU(CH_3COO)_6$	1580, 1520	1400	7.42	85

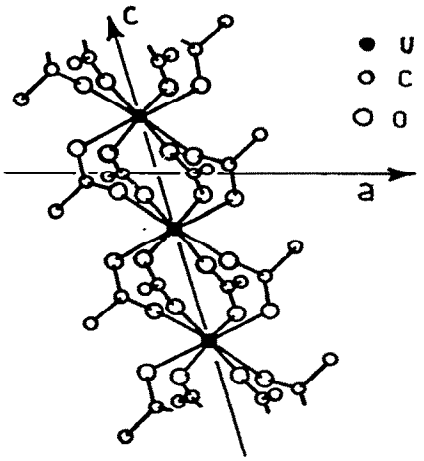


Fig. 7. The polymer chain in $U(CH_3COO)_4$.

acetates with the neutral monodentate ligands dimethylformamide, dimethylsulphoxide, triphenylphosphine oxide or hexamethylphosphoramide has been studied [97]. It has been found that the polymer had broken up in the presence of these ligands but, on cooling, only the original polymer acetate could be obtained, which is an indication of the high crystal energy of the polymeric acetate structure.

Thorium(IV) and uranium(IV) halogenoacetates have been prepared [97] by heating the tetraacetates with the haloacetic acid, either alone or in a hydrocarbon such as benzene or toluene and this procedure gives $M(CF_3COO)_4$, $M(CCl_3COO)_4$, $M(CHCl_2COO)_4$ and $M(CH_2ClCOO)_4$ (M = Th, U). In the IR spectra of the thorium(IV) and uranium(IV) haloacetates (Table 12) the asymmetric COO stretching increases markedly with the electron withdrawing capacity of the halogenated methyl group, with no marked mass effect and

TABLE 12

IR data for thorium(IV) and uranium(IV) halogenoacetates [97]

Compound	$\nu_{asym\,COO}$ (cm^{-1})	$\nu_{sym\,COO}$ (cm^{-1})	δ_{COO} (cm^{-1})
$Th(CH_2ClCOO)_4$	1580, 1540	1430, 1395	715, 700
$U(CH_2ClCOO)_4$	1566, 1540	1426, 1396	718, 698
$Th(CHCl_2COO)_4$	1590, 1570	1425	738, 715
$U(CHCl_2COO)_4$	1590	1416	730, 708
$Th(CCl_3COO)_4$	1618	1425, 1400	740, 692
$U(CCl_3COO)_4$	1610	1425, 1397	735, 688
$Th(CF_3COO)_4$	1634	1492	727
$U(CF_3COO)_4$	1625	1488	727

the COO stretching frequency decreases as the mass of the substituted methyl group increases but is not noticeably affected by the electron withdrawing ability of this group as reported for IR spectra of the sodium salts of these acids [98].

The preparation of the complexes of these compounds with the amide ligands N,N-dimethylacetamide (dma), N,N-diphenylacetamide (dpa) and $(CH_3)_3CCON(CH_3)_2$ (dmpa) is easy. A suspension of the haloacetate is treated with the ligand, and the carboxylate immediately dissolves; addition of 2-methylbutane precipitates the complex [97].

Trifluoro- and trichloroacetates yield with dma the tris complexes $M(RCOO)_4 \cdot 3$ dma in the case of both trichloroacetates and Th(IV) trifluoroacetate but with U(IV) trifluoroacetate the product isolated is $[U(CF_3COO)_3dma]_2O$. All the tris dma complexes are unstable decomposing easily to $[M(RCOO)_3dma]_2O$ even under nitrogen and in a refrigerator. Complexes of this structure have been obtained for thorium(IV) and uranium(IV) trifluoro, trichloro and dichloroacetoacetates with the more bulky ligand dmpa (Table 13). The IR spectra suggest carboxylate groups in the amide complexes of the monochloroacetates and uranium dichloroacetates may be bridging or bidentate for the antisymmetric COO stretch appears at 1660—1592 cm^{-1} whereas in the spectra of thorium dichloroacetate complexes there are both high frequencies, dma 1708 cm^{-1}, dpa 1718 cm^{-1}, dmpa 1690 cm^{-1} and low frequency, which suggests that both uni- and bidentate (or bridging) carboxylate groups are present. The same applies to all the complexes of the

TABLE 13

Known actinide(IV) halogenoacetate complexes with amide ligands[a] [97]

Substrate	dma	dmpa	dpa
$X = CF_3COO$			
ThX_4	ThX_4dma $[ThX_3dma]_2O$	$[ThX_3dmpa]_2O$	
UX_4	$[UX_3dma]_2O$	$[UX_3dmpa]_2O$	
$X = CCl_3COO$			
ThX_4	$ThX_4 \cdot 3$ dma $[ThX_3dma]_2O$	$[ThX_3dmpa]_2O$	
UX_4	$UX_4 \cdot 3$ dma $[UX_3dma]_2O$	$[UX_3dmpa]_2O$	
$X = CHCl_2COO$			
ThX_4	ThX_4dma	$[ThX_3dmpa]_2O$	$[ThX_3dpa]_2O$
UX_4	$[UX_3dma]_2O$	$[UX_3dmpa]_2O$	$[UX_3dpa]_2O$
$X = CH_2ClCOO$			
ThX_4	ThX_4dma		ThX_4dpa
UX_4	$UX_4 \cdot 0.5$ dma		

[a] dma = N,N-dimethylacetamide, dmpa = $(CH_3)_3CCON(CH_3)_2$, dpa = N,N-diphenylacetamide.

trichloro and trifluoroacetates (Table 14). Certainly the range 1692—1720 cm^{-1} appears to be the normal range for the $\nu_{asym}COO$ frequency of unidentate carboxylate groups in *d* transition metal trifluoroacetates, whereas compounds in which bridging or bidentate carboxylate groups are present exhibit this mode at 1660—1592 cm^{-1} and in ionic species the observed frequency is in the range 1667—1678 cm^{-1}. Although $\Delta\nu(\nu_{asym} - \nu_{sym})COO$ is probably not a reliable guide to the bonding mode, it is however significant that in

TABLE 14

IR spectra of actinide(IV) halogenoacetate complexes with amide ligands[a] [97]

Compound	ν_{asym} OCO (cm^{-1})	ν_{sym} OCO (cm^{-1})	δ_{OCO} (cm^{-1})
X = $ClCH_2COO$			
ThX_4 · dma	1590	1435	719, 700
	1555	1420	675
UX_4 · 0.5 dma	1576	1425	700, 662
	1556		
X = Cl_2CHCOO			
ThX_4 · dma	1708	1440	726, 709
	1620	1430	700
$ThX_3(dpa)_2O$	1718, 1640	1420	703, 676
	1615		650
$ThX_3(dmpa)_2O$	1690, 1660	1425	715, 705
	1620	1410	
$UX_3(dma)_2O$	1680	1430	740, 721
	1648	1410	708
$UX_3(dpa)_2O$	1678	1435	725, 715
	1650	1410	701
$UX_3(dmpa)_2O$	1673	1445	750, 720
	1647	1416	710
X = Cl_3COO			
ThX_4 · 3 dma	1706	1410	770, 751
	1630	1315	
$ThX_3(dmpa)_2O$	1690, 1645	1380	715, 705
	1628	1330	
UX_4 · 3 dma	1716, 1702	1425, 1410	760, 728
	1635	1315	680
$UX_3(dmpa)_2O$	1690, 1675	1450	720, 685
	1650, 1630	1415	
X = F_3CCOO			
ThX_4 · 3 dma	1745	1430	757, 725
	1715	1415	
$ThX_3(dmpa)_2O$	1740, 1718	1470	757, 732
	1680, 1646	1425	
$UX_3(dma)_2O$	1740, 1720	1460	755, 725
	1690, 1670	1430	700
$UX_3(dmpa)_2O$	1695	1450	725, 695
	1640	1416	675

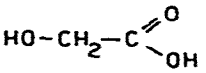
[a] Abbreviations dma, dpa and dmpa are as in Table 13.

these complexes in which the presence of bidentate or bridging carboxylate group is suspected, the difference is between 137 and 193 cm^{-1}; this is very different for complexes in which unidentate carboxylate groups are thought to be present, for here $\Delta\nu$ is between 245—315 cm^{-1}; these two sets of values must be of some significance.

The visible and near IR spectra of the uranium(IV) halogenoacetates and their complexes with monodentate ligands were recorded by reflectance and in solution; the spectra are characteristic of uranium(IV) in an environment having high coordination number (>8). They are of no assistance in determining the symmetry of the environment of the uranium atom.

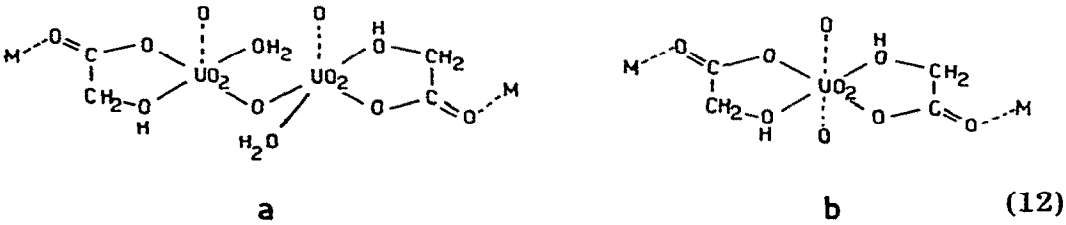
H. ACTINIDE(VI) GLYCOLATES

Glycolic acid (11) is the simplest polyfunctional ligand which can coordi-



(11)

nate to a metal atom through the hydroxylic and one of the carboxylic atoms, so forming a five membered chelate ring. Structural data on various rare earth glycolates [238—240] confirm such a configuration of the ligand around the central metal ion and the IR spectra of a series of transition metal glycolates have been interpreted on the basis of this mode of coordination [241]. The reaction of an aqueous solution of uranyl(VI) nitrate hexahydrate with equimolar amounts or with an excess of the ligand yields the yellow $[(UO_2)_2(OHCH_2COO)_2(O)(H_2O)_2]_n$ [242]. The yellow complex $[UO_2(OHCH_2COO)_2]_n$ has been obtained only by reacting uranium trioxide with a large excess of glycolic acid in water and it is soluble in water. For these two complexes the configurations (12)a and (12)b respectively have been proposed [242]. In both



a b (12)

cases the IR data suggest the glycolate anion acts as bidentate ligand towards each uranium atom, through the hydroxylic and one carboxylic oxygen atom. The oxygen atoms which are not engaged in the formation of the initial monomeric units can fill the coordination sphere of adjacent uranium atoms giving rise to polymeric structure [184,186,187,191,193—195,238—240]. The polymeric nature of $[UO_2(OHCH_2COO)_2]_n$ is confirmed by IR data; the ν_{asym} COO lies at 1565 cm^{-1} lower than that found in the sodium glycolate (1600 cm^{-1}).

The separation $\nu_{asym} - \nu_{sym} = 162$ cm^{-1} and the difference in their relative intensity agree with a coordination of the carboxylic group of the type b; the uranyl group being surrounded equitorially by six oxygen atoms. The solubility of the complex in water and the presence of a shoulder at 1600 cm^{-1}, probably due to the ν_{asym} COO of terminal free C=O, seem to suggest a low value of n. A polymeric configuration has also been assumed for $[(UO_2)_2(OHCH_2COO)(O)(H_2O)_2]_n$ owing to its insolubility and to the presence of the ν_{asym} COO at 1584 and 1540 cm^{-1}; the equatorial pentacoordination around the uranyl group is filled by a water molecule and by an oxygen bridge.

It is known from IR [243], potentiometric [276], and calorimetric data [250] that in aqueous solution, as well as $[UO_2(OHCH_2COO)]^+$ and $[UO_2(OHCH_2COO)_2]$, the species $[UO_2(OHCH_2COO)_3]^-$ is supposed to exist. In this last compound the three ligands could act mainly as simple monocarboxylates, so forming four membered chelate rings and giving rise to a structure similar to $[UO_2(CH_3COO)_3]^-$ [10]. Attempts to obtain the $M'[UO_2(OHCH_2COO)_3]$ complex in the solid state, under a variety of conditions, failed. In every case complexes of the type $M'[(UO_2)_2(OHCH_2COO)_2(O)(H_2O)]$ (M' = Na, Cs) have been obtained; they could be polymeric since ν_{asym} COO is at 1560 cm^{-1} and the IR spectrum is very similar to that of $[(UO_2)_2(OHCH_2COO)_2(O)(H_2O)_2]$. When these uranyl complexes are dissolved in fused pyridine N-oxide or in dimethylsulphoxide, complexes of the type $[(UO_2)_2(OHCH_2COO)_2(O)(L)_2]$ (L = pyNO or DMSO) have been obtained; ν_{asym} COO lies at 1555 cm^{-1} suggesting the carboxyl bridge is maintained.

Attempts to identify other ways of coordination of the glycolate ligand in the solid state, on the basis of the OH in plane bending and C—OH stretching absorption shifts [243], have been unsuccessful. No drastic shifts (ca. 25 cm^{-1}) for the C—OH stretching and little change of the relative intensity have been observed for these complexes and for sodium and barium glycolate salts. No shift has been found from the glycolate acid to the transition metal glycolate complexes [241]. The OH in plane bending absorption, which falls at about 1480 cm^{-1} [241], has been found only in the anhydrous complex with a metal : ligand ratio of 1 : 2 but is absent in uranyl complexes with 1 : 1 metal : ligand ratio, containing water, oxygen or a hydroxyl group in the molecule. This can be due to the sensitivity of this absorption band to hydrogen bonding due to coupling effects.

I. ACTINIDE(IV) GLYCOLATES

The physicochemical and preparative studies of the reaction of $Th(NO_3)_4 \cdot 5\ H_2O$ with sodium glycolate in aqueous solution and glycolic acid in acetone using potentiometric, photocolorimetric and electrical conductivity methods have been reported [244]. The method of continuously changing concentration was used to determine whether the components of the system form compounds with different composition depending on the component molar ratio. At molar reacting component ratio from 1 : 1 to 1 : 8 (thorium to

ligand) no precipitate forms immediately when thorium nitrate and sodium glycolate are mixed; fine transparent colourless crystals separated from 1 : 4.5, 1 : 5, 1 : 6 and 1 : 8 solutions after several days. The compound has been formulated as $Th(OHCH_2COO)_4 \cdot 2\ H_2O$ and is insoluble in acetone, ethanol, dioxan, chloroform and slightly soluble in methanol. The differential thermal analysis shows an endothermic peak at 165°C, probably corresponding to the loss of the water molecules and two exothermic effects at 319 and 395°C, corresponding to the stepwise decomposition of the substance.

When an acetone solution of $Th(NO_3)_4 \cdot 5\ H_2O$ is treated with an excess of glycolic acid, thorium triglycolate containing partly nitrated glycolate groups ($ONO_2CH_2COO^-$) is formed. This reaction is apparently similar to the reaction with acetic acid in the same medium [94], i.e. $Th(OH)(OHCH_2COO)_3 \cdot H_2O$ is formed. The nitric acid liberated in the reaction reacts with the hydroxyl group of the glycolate with the partial formation of $ONO_2CH_2COO^-$ groups and this explains the presence of nitrogen in the thorium glycolate molecule.

Until now the main photoreaction of the uranyl(VI) ion in the presence of carboxylic ligands has been the direct oxidative decarboxylation of the organic ligands with the concomitant reduction of uranium(VI) to uranium-(IV) [246,247]. Such studies have been mainly confined to the identification and quantum yield determinations of photodecomposed organic materials, while only very recently has attention been paid to the possibility of obtaining stable uranium(IV) compounds in this manner [236,242].

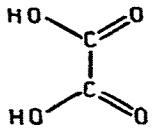
$U(OHCH_2COO)_4 \cdot 2\ H_2O$ has been obtained as dark green crystals by irradiation of an aqueous solution of uranyl nitrate (1.5×10^{-2} M) and a tenfold excess of glycolic acid for 10 h.

When the glycolate ligand is added to aqueous solutions of uranyl nitrate, there is a modification in the shape and intensity of the electronic spectrum of the UO_2^{2+} ion due to the formation of the complex [248—250]. The spectrum in the 400—500 nm region is more intense and shows much less vibrational structure than most other known uranyl(VI) complexes [247]. Such a change may well result from a charge-transfer from the ligand to the metal ion (LMCT). Furthermore the characteristic emission spectrum of the UO_2^{2+} is very sensitive to the presence of glycolate ligand; luminescence disappearing according to the Stern-Volmer's law in the pH range 1—2. In this range the quenching constant obtained by monitoring the emission intensity is identical to that obtained with laser flash determination of emission lifetime of the UO_2^{2+} at variable glycolate concentrations. From emission quenching studies a general trend emerged whereby at pH > 2 it would seem that the UO_2^{2+} is found in a non-fluorescent glycolate complex. After laser determination of the UO_2^{2+} lifetime (τ) in the absence of the carboxylate ligand, the quenching constant K_q was determined from the slope of the plot K_q versus τ. The K_q value for glycolic acid is $5 \cdot 10^8$ dm^3 mol^{-1} s^{-1} and the lifetime of $(UO_2^{2+})^*$ in water at 20°C is $\tau = 1.3\ \mu$s. The photolysis of uranyl glycolate complex in aqueous solution with light absorbed by the LMCT band using a high pressure Hg lamp (interference filter $\lambda = 436$ nm) leads to oxidative decarboxylation of the

ligand and to the formation of a tetravalent uranium glycolate complex [242]. $U(OHCH_2COO)_4 \cdot 2\ H_2O$ and $Th(OHCH_2COO)_4 \cdot 2\ H_2O$, showing an identical IR spectrum, most probably have the same structural configuration. Their IR spectra show a broad band at 1575 or 1570 cm^{-1} ($\nu_{asym}COO$) and a sharp less intense one at 1391 ($\nu_{sym}COO$). The IR results are in agreement with a structure in which the polyfunctional ligand coordinates to a uranium or a thorium atom both through the hydroxyl group and one of the oxygen atoms of the carboxylic group so forming a five membered chelate ring. In the electronic spectra of the uranium complex in water with 1 M glycolic acid or KBr pellets at 293 K, at least fourteen bands occur; the features of this spectrum are similar to those found for some other eight coordinate complexes of uranium(IV). As it is probable that the structure of this complex is not far from square antiprismatic, the assignment of these bands to *f—f* transitions within the f^2 uranium(IV) entity, is reasonable [242].

J. ACTINIDE(VI) OXALATES

Oxalic acid (13) is particularly interesting in having the possibility of bind-



(13)

ing a metal forming four or five membered chelate rings (99,139,140); in addition it can act as quadridentate ligand [140,266].

Uranyl(VI) oxalate trihydrate, $UO_2(C_2O_4) \cdot 3\ H_2O$, can be prepared by addition of a hot saturated solution of oxalic acid to a concentrated solution of uranyl(VI) nitrate at 80°C [130]. The crystals, separated on standing, are monoclinic with $a = 5.623(5)$, $b = 17.065(2)$, $c = 9.451(3)$ Å and $\beta = 98.74(1)°$; the space group is $P2_1/c$ with $z = 4$. The most noticeable feature of this structure is the tetradentate nature of the oxalate groups (Figs. 8, 9). Each oxalate group acts as a bridge between two uranyl ions using all the four oxygen atoms for coordination. There are two oxalate groups associated with the uranyl ion, each using two oxygen atoms for coordination. One of the three water molecules is also coordinated to the uranyl group, thereby making the uranium atom seven coordinate; the other two water molecules are not involved in coordination to the uranium atom. There is hydrogen bonding between the free water molecules and the water molecule coordinated to the uranium atoms; in addition, two oxygen atoms of each oxalate group also appear to be hydrogen bonded to the free water molecules [131].

The discrepancies in the nature of the oxide produced when $UO_2(C_2O_4) \cdot 3\ H_2O$ is decomposed in air may be accounted for by the varieties of ambient atmospheres which make contact with the residue [117,132—135]. In the presence of air the formation of UO_2 is followed by conversion to U_3O_8 if the diffusion of oxygen into the product is prevented; if the oxygen is allowed to

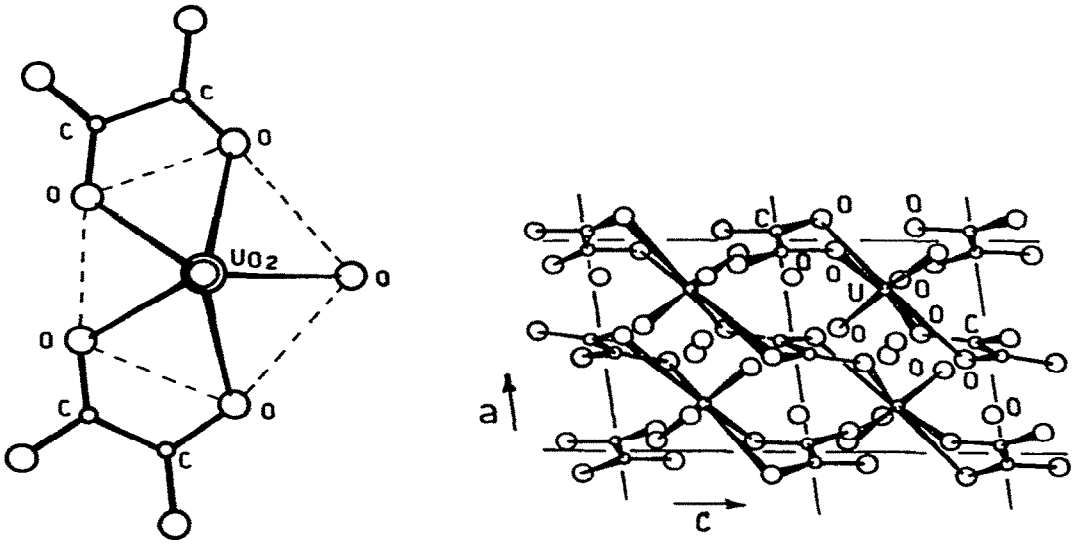


Fig. 8. Schematic drawing of the molecular structure of $UO_2C_2O_4 \cdot 3\ H_2O$.

Fig. 9. (010) projection of the unit cell of $UO_2C_2O_4 \cdot 3\ H_2O$.

react with UO_2, amorphous UO_3 is formed and then U_3O_8.

Little information on the complex formation of oxalate ions with neptunium(VI) is available in the literature [136]. With low concentration of neptunium(VI) in solutions containing excess oxalic acid, there is evidently stepwise formation of complexes with one and two oxalate groups in the coordination sphere of NpO_2^{2+}

$$NpO_2^{2+} + C_2O_4^{2-} \rightarrow NpO_2C_2O_4$$

$$NpO_2C_2O_4 + C_2O_4^{2-} \rightarrow NpO_2(C_2O_4)_2^{2-}$$

Spectrophotometric experiments carried out to obtain proof of the formation of the oxalate complexes of neptunium(VI) with a ratio of ligand : metal greater than 2 did not give positive results. $NpO_2C_2O_4 \cdot 3\ H_2O$ has been prepared as a greyish-green crystalline powder by adding oxalic acid at room temperature to a nitric acid solution of Np(IV), containing $KBrO_3$. On prolonged storage even in the cold, it gradually decomposes as a result of intramolecular reduction of the neptunium(VI). This is indicated by the fact that when old precipitates are dissolved in dilute nitric acid, neptunium(IV) oxalate is present in the undissolved residue.

$PuO_2C_2O_4 \cdot 3\ H_2O$ has been separated as a red precipitate by the addition of crystalline oxalic acid to a 1.5—2 N nitric acid solution of plutonium(IV) [137]. At 180°C the plutonium(VI) oxalate decomposes explosively. The compound is only slightly soluble in water and dilute mineral acids, but

soluble in dilute aqueous solutions of ammonium oxalate or carbonate. One mole of ammonium oxalate in solution can dissolve one mole of plutonium-(VI) oxalate to produce a cherry-red solution, suggesting the formation of the complex $(NH_4)_2[PuO_2(C_2O_4)_2]$; this compound has not been isolated in the solid state and its existence remains to be demonstrated.

The structure determinations of three ammonium uranyl oxalates in which the uranyl : oxalate ratio varies from 1 : 3 to 1 : 1.5 have been reported [99,138—140]. In all cases crystals have been prepared by evaporation at 80°C or over so that anhydrous species were formed and the complex ions were certain to involve only uranyl and oxalate. Ammonium uranyl trioxalate $(NH_4)_4[UO_2(C_2O_4)_3]$ can only be prepared above 60°C and although it has been previously stated that an equimolecular mixture of the two oxalates is necessary [141], really much more oxalate is necessary. The crystals are monoclinic, space group $C2/c$ (a = 10.031(9), b = 11.519(10), c = 14.213(10) Å; β = 101.46(6)°; z = 4). Two of the oxalate groups are coordinated to give five membered chelate rings, the third to give a four membered ring. The geometry around the uranium atom is approximately hexagonal bipyramidal. Crystals of ammonium uranyl dioxalate $(NH_4)_2[UO_2(C_2O_4)_2]$ and ammonium diuranyl trioxalate $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$ were formed together by evaporation of water containing uranyl oxalate and ammonium oxalate. Crystals of the diuranyl oxalate and needle-shaped crystals of the uranyl dioxalate have been separated under the microscope. $(NH_4)_2[UO_2(C_2O_4)_2]$ is triclinic; space group $P\bar{1}$; a = 12.91(2), b = 7.20(1), c = 6.31(1) Å; α = 110.56, β = 107.85, γ = 84.25°; z = 2. The compound contains NH_4^+ and the uranyl group five coordinated by oxalate ions, giving approximately pentagonal bipyramidal geometry around the uranium atom. One oxalate group is bidentate and the other is bidentate to one uranium atom and unidentate to another. This produces infinite chains $[UO_2(C_2O_4)_2]_n^{2n-}$ parallel to the c axis.

The crystals of ammonium diuranyl trioxalate $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$ are monoclinic with space group $P2_1/n$ (a = 9.46(2), b = 13.61(2), c = 6.12(1) Å; β = 92.7(1)°; z = 2). The crystal contains NH_4^+ ions and uranyl groups again five coordinated by oxalate ions giving approximately pentagonal bipyramidal geometry about the uranium atom. One oxalate group is placed on a centre of symmetry and is quadridentate, coordinated to two uranium atoms. The other is bidentate to one uranium atom and unidentate to another. This produces infinite double chains $[C_2O_4(UO_2)C_2O_4UO_2(C_2O_4)]_n^{2n-}$ parallel to the c axis.

The most important difference between the three complexes is the change in coordination of the UO_2^{2+} group from five to six (Fig. 10). Five individual oxygen atoms can be placed around UO_2^{2+} with a U—O distance of ca. 2.35—2.40 Å and with a non bonded O···O distance of ca. 2.70—2.80 Å. It has been suggested that to place six individual oxygen atoms in a regular hexagon would require O···O equal to 2.4 Å; examples are O—O (1.50), NO_3 (2.10) and CH_3COO^- (2.20) which form uranyl(VI) complexes hexacoordinated in the equatorial plane [10,142,143,145]. O···O in a free oxalate group is ca. 2.7 Å [146] and so only five coordinated UO_2^{2+} would be expected as it occurs

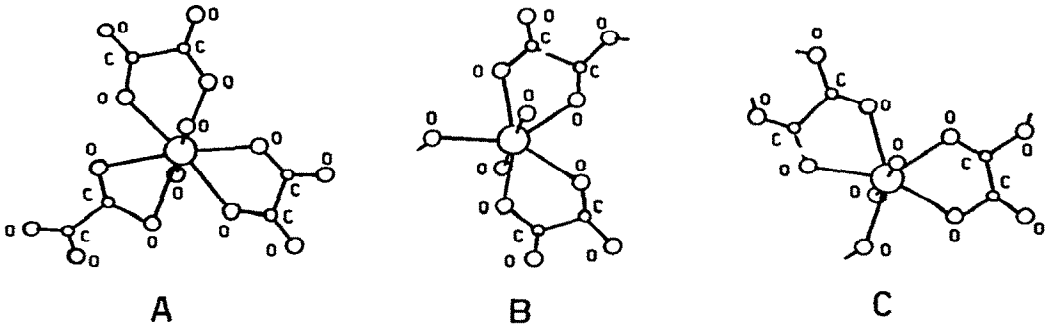
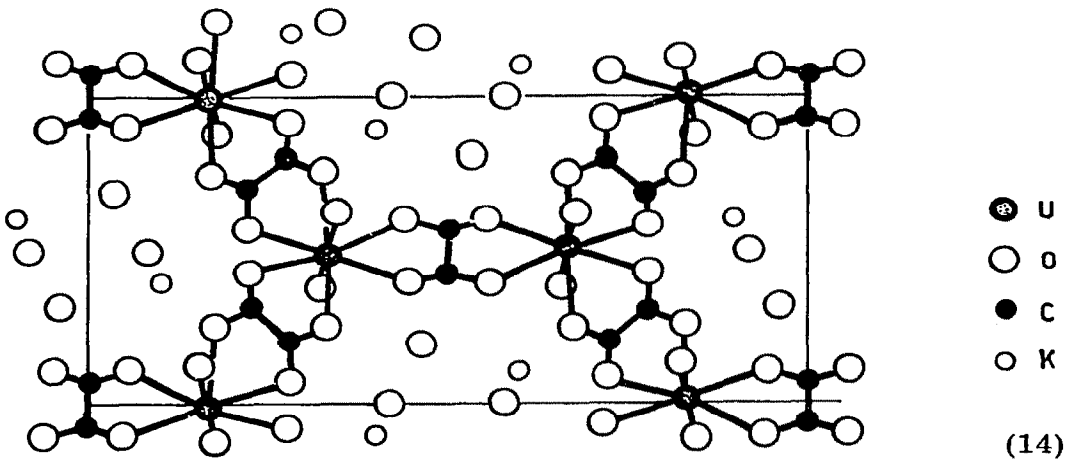


Fig. 10. Schematic drawing of the molecular structure of the anions of the three uranyl(VI) oxalate complexes: $[UO_2(C_2O_4)_3]^{4-}$ (A); $[UO_2(C_2O_4)_2]_n^{2n-}$ (B); $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$ (C).

for the 2 : 3 and 1 : 2 complexes. The driving force for the formation of the 1 : 3 complex was supposed to be the high concentration of oxalate ion solution; in this 1 : 3 complex one of the oxalate groups is bidentate from adjacent oxygen atoms with a bite of 2.21 Å and a very long U—O distance (2.57 Å). The bite of oxalate acting as bidentate in the 1,3-positions forming a four membered chelate ring is considerably shorter than the bite of the oxalate which forms a five membered chelate ring. On the basis of these structure determinations it has been concluded that three oxalates forming five membered chelate rings cannot be coordinated to the UO_2^{2+} in its equatorial plane owing to the too large O···O bite. This supposition is not correct because a subsequent X-ray determination on the complex $K_2(UO_2)_2(C_2O_4)_3 \cdot 3\,H_2O$ [266] has demonstrated that it is possible to have a uranyl(VI) ion associated with three oxalate groups.

The complex $K_2[(UO_2)_2(C_2O_4)_3] \cdot 3\,H_2O$ [266] prepared as chunky crystals by dissolving uranyl oxalate and potassium oxalate in water at 80°C has shown a different structure than the anhydrous $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$ [140]. It is monoclinic, space group $P2_1/n$ with $a = 8.85(1)$, $b = 19.67(1)$, $c = 5.37(1)$ Å; $\beta = 91.5(2)°$; $Z = 2$. The (001) projection of the unit cell is (14). The uranyl



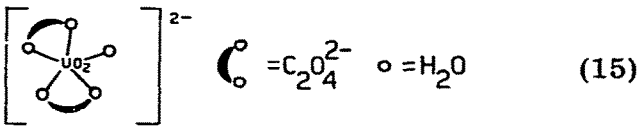
(14)

ions are linear with O—U—O = 179(2)°. The average U—O distance of the uranyl ions is longer than that in uranyl oxalate [131] and is reflected by the decrease of about 30 cm^{-1} for the ν_3 O—U—O. Six oxygen atoms at an average U—O distance of 2.45(4) Å form a puckered hexagon around the uranyl ion, the oxygen atoms deviating between 0.2 to 0.6 from a plane through uranium which is almost perpendicular to the O—U—O axis. Each uranyl(VI) ion is thus associated with three oxalate groups forming polymeric anions $[(UO_2)_2(C_2O_4)_3]_n^{2n-}$ that extend throughout the crystal. The K^+ ions fit into the polyhedra formed by oxygen atoms of the oxalate groups and water molecules. These are eight oxygen atoms within a sphere of radius of 3.2 Å about the K^+ ion. All the oxalate groups are planar and tetradentate bridging two uranyl(VI) ions.

Compounds described by the general formula $M'_2[UO_2(C_2O_4)_2(H_2O)_2]$ have been extensively studied; they are very stable in solution and may be formed according to the reaction [147—149]

$$UO_2(C_2O_4) + C_2O_4^{2-} \overset{H_2O}{\rightleftharpoons} [UO_2(C_2O_4)_2(H_2O)_2]^{2-}$$

A structure of type (15) has been proposed for these complexes after con-



(15)

sidering the interaction between $[UO_2(C_2O_4)_2(H_2O)]^{2-}$ and nitrate ions in a non aqueous medium. This reaction results in the incorporation of only one nitrate group in the inner sphere of the complex, the nitrate group acting as a unidentate ligand. The coordination geometry is also confirmed by the formation of complexes with the composition $[UO_2X(C_2O_4)_2]^{3-}$ (X = Cl, Br, SCN, F, OH) [151—153]. It is quite probable that both the original $[UO_2(C_2O_4)_2(H_2O)]^{2-}$ and the mixed compounds derived from it are five coordinate. The thermal decomposition of the hydrate complexes leads to the formation of anhydrous complexes stable over a relatively wide temperature range; most of them are rehydrated when treated with water. [154].

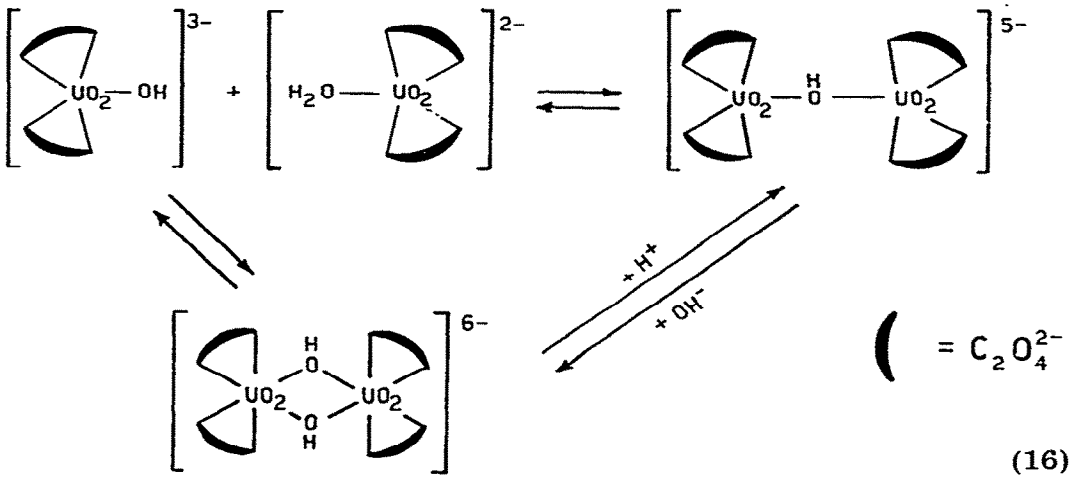
More recently the preparation and the physicochemical properties of $Tl_2[UO_2(C_2O_4)_2(H_2O)] \cdot H_2O$ have been reported [155]. This is prepared by mixing equimolecular portions of saturated solutions of thallium(I) oxalate and uranyl oxalate at 60°C. That two water molecules are lost at 115°C is confirmed by elemental analysis and by the presence of an OH stretching frequency at 3590 cm^{-1} for the initial compound and its absence in the heated product. The decomposition of the anhydrous oxalate gives Tl_2UO_4, which is isostructural with Rb_2UO_4 and Cs_2UO_4 [156]. The IR bands at 750, 675 and 663 cm^{-1} indicate U—O distances comparable to those in alkali metal uranates [157].

Complexes with the composition $M'_3[UO_2(OH)(C_2O_4)_2] \cdot n\ H_2O$ and

$M'_5[(UO_2)_2(OH)(C_2O_4)_4] \cdot n\ H_2O$ have been prepared and some of their properties discussed [158,159]. It has been shown that the first type of complexes, obtained by the reaction

$$[UO_2(C_2O_4)(H_2O)_2]^{2-} + OH^- \rightarrow [UO_2(OH)(C_2O_4)_2]^{3-}$$

may suffer a subsequent reaction according to the scheme (16)

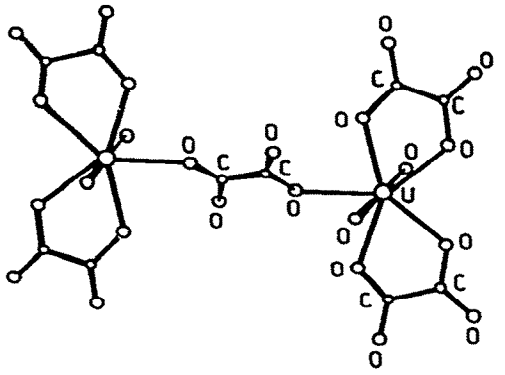


(16)

It has been shown that the action of urea on dioxobis(oxalate)diaquouranates(VI) gives complexes of the type $M'_2[UO_2(C_2O_4)_2(urea)] \cdot x\ H_2O$; the compounds crystallize when hot solutions of the aquo complexes to which urea has been added, are cooled [160]. The replacement of the aquo group by urea depends markedly on the concentration and also on the outer-sphere çation in the original dioxobis(oxalate)-diaquouranate(VI). The reaction is reversible and proceeds to completion only when the solution contains a definite excess of urea. Only one urea molecule coordinates to the central metal ion; thermogravimetric studies of these dioxobis-oxalato(urea)uranates-(VI) show the urea molecule decomposes in the temperature range 160—200°C, higher than the temperature of the decomposition of the free urea. The replacement of the aquo group in these complexes by urea has no significant influence on the thermal stability of the oxalate groups coordinated to the uranyl ion.

Recently the crystal and molecular structure of potassium uranyl(VI) oxalate $K_6[(UO_2)_2(C_2O_4)_5] \cdot 10\ H_2O$ has been established by X-ray diffraction [267]. Yellow crystals of this compound may be obtained by cooling an aqueous solution of potassium oxalate and uranyl(VI) acetate in a $C_2O_4^{2-}/UO_2^{2+} = 6$ ratio. The compound crystallizes in space group $P\bar{1}$ with $a = 10.103$, $b = 10.944$, $c = 10.021$ Å; $\alpha = 121.4°$; $\beta = 104.7°$; and $\gamma = 63.8°$. Previous studies on $M'_6[(UO_2)_2(C_2O_4)_5] \cdot n\ H_2O$ [204] suggested the presence of a dinuclear anion $[(UO_2)_2(C_2O_4)_5(H_2O)_2]^{6-}$ with one oxalate group bridging two uranyl(VI) ions in a hexagonal bipyramidal environment. Later [268] it was suggested

that the anion $[(UO_2)_2(C_2O_4)_5]^{6-}$ is formed, the water molecule being of crystallization. The structure confirms such a conclusion and shows each uranyl(VI) ion is equatorially surrounded by five oxygen atoms in a pentagonal bipyramid environment (17). Two equivalent uranium atoms are bonded



(17)

by a bridging oxalate group symmetrically coordinated by one oxygen atom to each uranium atom. Two bidentate oxalate groups and one oxygen atom of the bridging oxalate group lie in the equatorial plane of each uranyl(VI) ion. The mean U—O equatorial distance is 2.38 Å while the U—O distance of the uranyl(VI) group is 1.82Å . In the bridging oxalate group the C—C distance is rather large (1.66 Å). None of the water molecules takes part in uranium coordination. Thermogravimetric data on this compound shows eight water molecules are lost in the temperature range 60—110°C, the other two water molecules being lost between 110 and 220°C. For this reason the presence of water in the coordination sphere of UO_2^{2+} was suggested. The structure determination shows that two water molecules are bound more strongly to K^+ ions, have a weaker thermic factor of agitation and hence are lost on heating, at higher temperature.

An aqueous solution of ammonium uranyl(VI) oxalate treated with an excess of H_2O_2 gives a deeply coloured solution in the pH range 4.8—5, the colour changing from yellow to orange with increasing pH. From this solution, after standing for 48 h, $(NH_4)_2[UO_2(O_2)(C_2O_4)(H_2O)] \cdot 2\ H_2O$ has been isolated [161,162]. The complex is monoclinic with a = 28.20, b = 20.15, c = 10.70 Å and β = 99.36°; the TGA shows a continuous weight loss up to 185°C corresponding to the loss of H_2O and peroxy oxygens [163].

Two other types of uranyl oxalate complexes with urea have been reported: $UO_2(C_2O_4)$(urea) and $UO_2(C_2O_4) \cdot 3$(urea) [164]. These compounds decompose without melting and the temperature at which decomposition starts decreases with the number of urea molecules present: 310°C for $UO_2(C_2O_4)$-(urea) and 150°C for $UO_2(C_2O_4) \cdot 3$(urea). With acetamide only the complex $UO_2(C_2O_4)(CH_3CONH_2)$ has been reported; it has been suggested that the acido group in $UO_2(C_2O_4)$(urea) and in $UO_2(C_2O_4)(CH_3CONH_2)$ is coordinated by more than one uranium atom. A similar coordination environment is

probably found in the complex $UO_2(C_2O_4)(Bu_3PO)$ obtained by the reaction between $(NH_4)_2[UO_2(C_2O_4)_2(H_2O)] \cdot 2\ H_2O$ or $[UO_2C_2O_4(H_2O)] \cdot 2\ H_2O$ and tributylphosphine oxide [165].

It has been found that on adding aqueous solutions of oxalic acid to aqueous solutions of uranyl(VI) nitrate containing dimethylformamide, a yellow-green compound corresponding to $UO_2C_2O_4 \cdot 3$ dmf has been obtained [166]. Uranyl(VI) oxalate complexes with hydrazine $UO_2C_2O_4(N_2H_4) \cdot 0.75\ H_2O$ and $UO_2(C_2O_4) \cdot 2\ N_2H_4 \cdot H_2O$ have been prepared [167]. The endothermic effects at 140 and 130°C have been ascribed to the evolution of water and the exothermic effects at 200, 270 and 210°C to the dissociation of hydrazine or to its oxidation by atmospheric oxygen, while the effects at 335 and 355°C are due to the oxidation of oxalate ions. In the decomposition of both complexes the initial salt $UO_2(C_2O_4)$ is obtained [168]. The photochemistry of uranium(VI) oxalate complexes is almost entirely that of uranyl ion catalyzed decomposition of oxalate ion. The results obtained could be explained on the basis of the following processes:

a) uranyl-sensitized decomposition of oxalic acid, which may be represented by the concurrent reactions

$$H_2C_2O_4 \xrightarrow[UO_2^{2+}]{h\nu} H_2O + CO_2 + CO \qquad (1)$$

$$H_2C_2O_4 \xrightarrow[UO_2^{2+}]{h\nu} HCOOH + CO_2 \qquad (2)$$

b) photochemical oxidation of oxalic acid by uranyl ions (especially in the absence of oxygen)

$$H_2C_2O_4 + UO_2^{2+} \xrightarrow{h\nu} U^{4+} + 2\ CO_2 + 2\ H^+ \qquad (3)$$

The system has been accurately calibrated for use in chemical actinometry in the blue and near-ultraviolet and representative quantum yields have been reported [247]. The quantum yields used in the actinometric application are those based on the amount of oxalate decomposition and a recent redetermination of these has been made with results in good agreement with the earlier ones [258]. Other work gives the fractional contributions of reactions [255], assuming these to be correct and based on CO and CO_2 analyses [259]. The complete series of reactions occurring is not yet fully understood. The proportions of products depend on pH and the primary process may be the photoactivation of $[UO_2(HC_2O_4)]^+$, $UO_2C_2O_4$ and UO_2^{2+} to respective excited states which then undergo hydrolytic and redox reactions. Evidence concerning the kinds of complexes present has been provided by combined photochemical, spectroscopic and pH variation studies of uranyl oxalate solutions [260]. In this work the species $[UO_2H_2C_2O_4]^{2+}$, $UO_2C_2O_4$ and $[UO_2(C_2O_4)_2]^{2-}$ were identified and their first dissociation constants at 25°C were evaluated as $2.7 \cdot 10^{-3}$, $1.5 \cdot 10^{-6}$ and $1.8 \cdot 10^{-5}$ respectively.

It is of interest that recent flash-photolysis experiments give results which show no marked difference from those obtained in the low-intensity photochemical work and provide confirmation of the existence of relatively long-lived intermediates [261]. As far as the direct photochemical oxidation (eqn. 3) is concerned, a scheme has been proposed [260] in which an LMCT mechanism produces CO_2 and uranium(IV) by single electron transfer steps.

K. ACTINIDE(V) OXALATES

The behaviour of protoactinium(V) toward oxalic acid is different from that of neptunium(V) and plutonium(V). Freshly precipitated $Pa_2O_5 \cdot x\ H_2O$ dissolves in 0.1 M oxalic acid solution and white $PaO(OH)(C_2O_4) \cdot 2\ H_2O$ precipitates on acidification of this solution with HCl [227]. Addition of aqueous ammonia results in the formation of higher oxalato complexes such as $[PaO(C_2O_4)_2]^-$. At pH > 5 $Pa(OH)(C_2O_4) \cdot 6\ H_2O$ has been isolated. $PaO(OH)(C_2O_4) \cdot 2\ H_2O$ loses H_2O at 120—130°C and at 335°C the decomposition to the pentoxide starts. IR data indicate the presence of a polynuclear grouping O—Pa—O—Pa in this compound.

Pale green $NpO_2HC_2O_4 \cdot 2\ H_2O$ has been prepared by adding a solution of neptunium(V) in dilute hydrochloric acid to oxalic acid in t-butylalcohol [169]; its electronic spectrum in water is characteristic of neptunium(V) and shows a shift of the chief absorption peak from 10,173 to 10,204 cm^{-1} attributed to the complexing of NpO_2^+ ion by oxalate [170]. The compound has a magnetic moment of 3.17 B.M. Compounds of general composition $MNpO_2(C_2O_4) \cdot n\ H_2O$, where $M = Na^+$, K^+, NH_4^+ or Cs^+, are obtained by adding the nitrate of the corresponding cations to a neutral solution of neptunium(V) containing oxalate ions [171]; it is necessary to take sufficient $C_2O_4^{2-}$ to give a stoichiometric ratio to NpO_2^+ equal to 1 : 1. These compounds are not hygroscopic, are stable for long periods and are insoluble in organic solvents; the absorption spectra of solutions of the compounds which had been kept in a desiccator for three months shows only absorption bands due to neptunium(V).

Neptunium(V) and plutonium(V) are very soluble in water in the presence of oxalic acid or alkali metal oxalate [226]. Depending on the oxalate ion concentration, the solutions contain the complexes $MO_2(C_2O_4)^-$ or $MO_2(C_2O_4)^{3-}$ the stability of which have been determined [64]. When treated with $Co(NH_3)_6Cl_3$ the anion $Np(C_2O_4)_2^{3-}$ forms greenish-yellow crystals of $Co(NH_3)_6[NpO_2(C_2O_4)_2] \cdot 2\ H_2O$. The complex is stable with time, not hygroscopic and is almost insoluble in water, alcohol, acetone and diethylether.

Rose-coloured $NH_4PuO_2(C_2O_4) \cdot 6\ H_2O$ has been prepared by the addition of ammonium oxalate to a solution of plutonium(V) in HNO_3, followed by the addition of alcohol, the latter being necessary because of the high solubility of the compound in water. Repeated washing of the precipitate with alcohol and ether produces a product containing less water of hydration [172].

L. ACTINIDE(IV) OXALATES

Thorium(IV) oxalate hexahydrate $Th(C_2O_4)_2 \cdot 6\ H_2O$ can be precipitated when oxalic acid is added to a solution of thorium(IV) in dilute nitric acid at room temperature [120]; it is also obtained when the stoichiometric quantity of oxalic acid is added to an ethanolic solution of hydrated thorium nitrate. With an excess of oxalic acid the compound $H_2Th_2(C_2O_4)_5 \cdot 9\ H_2O$ is obtained [120]. $Th(C_2O_4)_2 \cdot 6\ H_2O$ can be obtained as a more crystalline product by the method of homogeneous precipitation with methyl oxalate [109]. An endothermic peak centered at 145°C, found in the DTA curve of this compound has been assigned to the transition

$$Th(C_2O_4)_2 \cdot 6\ H_2O \rightarrow Th(C_2O_4)_2 \cdot 2\ H_2O + 4\ H_2O$$

while the endothermic peak at 270°C has been assigned to the reaction

$$Th(C_2O_4)_2 \cdot 2\ H_2O \rightarrow Th(C_2O_4)_2 + 2\ H_2O$$

and the endothermic peaks at 385°C and 560°C to the decomposition of the anhydrous $Th(C_2O_4)_2$ to ThO_2 [115,116]; the dehydration of $Th(C_2O_4)_2 \cdot 2\ H_2O$ at 100°C, previously reported, is very probably incorrect [117]. The thermal decomposition of $Th(C_2O_4) \cdot 6\ H_2O$ in air has recently been reinvestigated [251]. In this study two endothermic effects at about 70—130°C and 230—250°C corresponding to the removal of water and an exothermic peak at about 370—450°C due to the decomposition of the oxalate groups are found. These effects correspond to three stages in the loss in mass on the thermogravimetric curve: four water molecules are removed in the range 70—130°C, a further water molecule is removed at 230—260°C and in the range 300—500°C the decomposition of the compound with the formation of thorium dioxide occurs. There is no distinct boundary between the loss of the last water molecule and the decomposition of the oxalate groups so that it is difficult to obtain the anhydrous thorium oxalate by thermal decomposition; the formation of the completely anhydrous compound is accompanied by partial decomposition of the oxalate groups. The removal of the first four water molecules has almost no influence on the stretching frequencies of the oxalato groups so that it may be assumed that in the hexahydrate, four water molecules are less firmly bound than the other two. The latter are present in the dihydrate in molecular and not dissociated form. The subsequent removal of the fifth water molecule leads to considerable changes in the spectrum. These changes have been explained by assuming that the last water molecule is present not as molecular water, but in dissociated form, the hydroxide group apparently being bound to the thorium atom and the proton being present in the form of hydrogen oxalate group $HC_2O_4^-$. Thus thorium oxalate monohydrate would correspond to $Th(OH)(C_2O_4)(HC_2O_4)$. When anhydrous thorium oxalate is heated in air it is converted into the carbonate as indicated by the IR spectrum of the product obtained after heating the hexahydrate at about 400°C. On subsequent heating the thorium carbonate formed decomposes to

ThO_2. Thus, according to this recent work, the thermal decomposition of $Th(C_2O_4)_2 \cdot 6\ H_2O$ in air can be represented by the following scheme

$$Th(C_2O_4)_2 \cdot 6\ H_2O \xrightarrow{70-130^\circ C} Th(C_2O_4)_2 \cdot 2\ H_2O \xrightarrow{230-250^\circ C} Th(C_2O_4)(HC_2O_4)(OH) \xrightarrow{300^\circ C} Th(C_2O_4)_2 \rightarrow \text{thorium carbonate or oxide carbonate} \xrightarrow{600^\circ C} ThO_2$$

$U(C_2O_4)_2 \cdot 6\ H_2O$ has been prepared by the reaction of uranium(IV) chloride, sulphate or hydroxide with a saturated solution of oxalic acid or by the reduction of uranyl(VI) acetate dihydrate with sodium dithionite in acid solution followed by treatment with oxalic acid [108]. This compound begins to evolve water of hydration at 65°C, giving a break in the curve at 115°C, which corresponds to $U(C_2O_4)_2 \cdot 2\ H_2O$. Above 115°C further weight loss takes place until 155°C and the composition approaches $U(C_2O_4)_2 \cdot H_2O$. Anhydrous $U(C_2O_4)_2$ is not formed; the monohydrate decomposes directly to the metal oxide like some rare earth oxalate hydrates [109,110]. In the DTA curve, the peak at about 125°C has been attributed to the transition

$$U(C_2O_4)_2 \cdot 6\ H_2O \rightarrow U(C_2O_4)_2 \cdot 2\ H_2O + 4\ H_2O$$

while the 185°C peak has been assigned to the transition

$$U(C_2O_4)_2 \cdot 2\ H_2O \rightarrow U(C_2O_4)_2 \cdot H_2O + H_2O$$

The 290°C peak is due to the simultaneous evolution of the remaining water and to the total disruption of the metal oxalate to metal oxide or mixture of metal oxides.

Neptunium(IV) oxalate hexahydrate has been precipitated through the addition of a saturated solution of oxalic acid to a nitric solution of neptunium(IV) in hot (50°C) 1 M nitric acid [112]; neptunium(IV) oxalate dihydrate has been prepared by heating the hexahydrate at 160°C for 10 min. DTA, effluent gas analysis and thermogravimetric measurements suggest the following decomposition scheme

$$Np(C_2O_4)_2 \cdot 6\ H_2O \rightarrow Np(C_2O_4)_2 \cdot 2\ H_2O + 4\ H_2O$$

$$Np(C_2O_4)_2 \cdot 2\ H_2O \rightarrow Np(C_2O_4)_2 + 2\ H_2O$$

$$Np(C_2O_4)_2 \rightarrow NpO_2 + 2\ CO_2 + 2\ CO$$

The initial weight loss begins at 45°C in dry argon atmosphere and is characterized by a large endothermic peak (45—130°C). The intermediate, resulting from the loss of four moles of H_2O, is $Np(C_2O_4)_2 \cdot 2\ H_2O$ which undergoes further decomposition at 230°C yielding NpO_2. The effect of an oxidizing atmosphere does not show discernable differences in the decomposition of the hexahydrate, while the decomposition of the dihydrate shows a marked acceleration in the oxidizing atmosphere. DTA data show a noticeable transition from two well defined endothermic peaks found in argon to a badly defined endothermic one, beginning at 230°C which merges at 300°C with a

large well defined exotherm (300—430°C). The effluent gas analysis of H_2O, CO and CO_2 shows a much greater degree of overlapping in the oxidizing atmosphere. The appearance of this large exothermic peak can probably be explained by the oxidation of CO to CO_2, after it is formed by the decomposition reaction. X-ray diffraction patterns and IR spectra of material heated for various periods in the temperature range 230—300°C, where the existence of $Np(C_2O_4)_2$ is supported by DTA and effluent gas analysis, show a gradual transition from the dihydrate to an amorphous material which ultimately ends up as the dioxide. In the decomposition of the neptunium(IV) oxalate intermediate carbonate formation does not take place.

Yellow-green plutonium(IV) oxalate hexahydrate may be precipitated by the addition of oxalic acid to an acidic solution of plutonium(IV) and may be dried by washing with alcohol and holding under vacuum [104,118,122]. Another hydrate compound, $Pu(C_2O_4)_2 \cdot 2\ H_2O$, has been precipitated by the addition of 10% excess oxalic acid solution to a solution of plutonium in 7 N HNO_3 at 50° or 75°C [123]. The dihydrate has been also prepared by repeated washing of the hexahydrate with alcohol or acetone and storing in a vacuum desiccator. If the freshly precipitated hexahydrate is contacted intimately with acetone, a bright pink acetone complex, $Pu(C_2O_4)_2 \cdot 2\ H_2O \cdot x\ (CH_3)_2CO$, is formed and slowly decomposes to the dihydrate. Thermogravimetric investigations have also provided indications of other hydrates, as the tetrahydrate and the monohydrate. In an inert atmosphere $Pu(C_2O_4)_2 \cdot 4\ H_2O$ decomposes to the monohydrate at 80°C and this is slowly dehydrated to produce the anhydrous oxalate at 80 to 150°C. The latter is decomposed at 160 to 250°C to form trivalent plutonium oxalate $Pu_2(C_2O_4)_3$ which is completely converted to PuO_2 at 500°C. Slow heating in air results in the formation of plutonium(IV) oxalate only [124,125].

Tetraoxalate complexes of the type $M'_4[M(C_2O_4)_4] \cdot x\ H_2O$ ($M' = K^+$, Na^+ and NH_4^+) are known for thorium(IV), uranium(IV), neptunium(IV) and plutonium(IV) [120,126—128,228]. They are prepared by dissolving the hydrate oxalates $M(C_2O_4)_2 \cdot 6\ H_2O$ in a solution of alkali metal or ammonium oxalate and crystallize when the solution is allowed to evaporate slowly in air or when ethanol is added. The crystal and molecular structure of $K_4[Th(C_2O_4)_4] \cdot 4\ H_2O$ has been reported. The crystals are triclinic (a = 9.562, b = 13.087, c = 10.387 Å; α = 115.75°, β = 80.90°, γ = 112.66°; space group $P\bar{1}$). Each thorium is surrounded by ten oxygens at the vertices of a slightly irregular square antiprism (Fig. 11). As the oxalate groups span position 1—2, 3—6, 4—7, 5—9 and 8—10 of the polyhedron, a chiral structure results, but equal numbers of right and left-handed polyhedra occur in the crystal. The oxalates at 1—2 and 8—10 are quadridentate (lying across centres of symmetry at 0, 0, 0 and 1/2, 1/2, 0) and so bridging adjacent polyhedra and producing chains together to 110. The water molecules link the chains together by hydrogen-bonding in the [100], [111] and [110] directions.

IR, magnetic and thermal analysis data of a series of uranium(IV) tetraoxalates have been reported [126,129]. Their IR spectra are very simple and

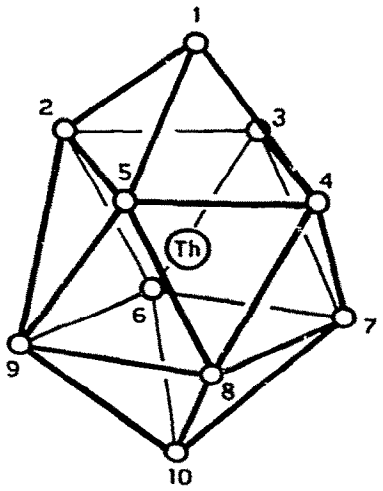


Fig. 11. Bicapped square antiprismatic coordination of thorium in the complex $K_4[Th(C_2O_4)_4] \cdot 4\ H_2O$.

on the basis of the reported data the appearance of two bands attributable to the antisymmetric COO in the 1700—1600 cm^{-1} region may agree with a quadridentate character of some oxalate groups as found for $K_4[Th(C_2O_4)_4] \cdot 4\ H_2O$; the other oxalate groups act as bidentate toward one uranium(IV) atom, forming a five membered chelate ring with the central metal ion (Table 15). The μ_{eff} at room temperature of the compounds are in the range 2.50—3.20 B.M.; they increase with increasing temperature in the range 100—300 K. (Table 16). Many of the products of thermal decomposition have been identified by X-ray diffraction data.

TABLE 15

IR spectra and magnetic data for tetraoxalato uranium(IV) complexes.

Compound	ν_{O-H} (cm^{-1})	$\nu_{asym\,OCO}$ (cm^{-1})	$\nu_{sym\,OCO}$ (cm^{-1})	μ_{eff} (T°) (B.M.)	Ref.
$Na_2C_2O_4 \cdot H_2O$	3420	1640	1330		126
$U(C_2O_4)_2 \cdot 6\ H_2O$	3400	1640	1310		126
$(NH_4)_4U(C_2O_4)_4 \cdot 6\ H_2O$	3380	1660, 1620	1310, 1275	2.53 (297)	126
$K_4U(C_2O_4)_4 \cdot 5\ H_2O$	3370	1660, 1620	1310, 1270	2.94 (298)	126
$Ca_2U(C_2O_4)_4 \cdot 4\ H_2O$	3450 br	1660	1300	2.99 (299)	129
$Sr_2U(C_2O_4)_4 \cdot 4\ H_2O$	3420 br	1650	1290	3.10 (299)	129
$Ba_2U(C_2O_4)_4 \cdot 8\ H_2O$	3420	1640	1290	2.73 (299)	129
$Cd_2U(C_2O_4)_4 \cdot 6\ H_2O$	3420 br	1660, 1640	1310	3.21 (299)	129
$Pb_2U(C_2O_4)_4 \cdot 6\ H_2O$	3420 br	1660, 1640	1295	3.19 (299)	129

TABLE 16

Thermal behaviour of uranium(IV) tetraoxalates

Compound	Products of thermal decomposition (temp. °C)	Ref.
$(NH_4)_4U(C_2O_4)_4 \cdot 6\ H_2O$	$(NH_4)_4U(C_2O_4)_4 \cdot 3\ H_2O$ (120); U_3O_8 (1000)	126
$K_4U(C_2O_4)_4 \cdot 5\ H_2O$	$K_4U(C_2O_4)_4$ (130); $2\ K_2CO_3 + U_3O_8$ (400);	
	$K_2CO_3 + K_2UO_4$ (700)	126
$Cs_4U(C_2O_4)_4 \cdot 3\ H_2O$	$Cs_4U(C_2O_4)_4$ (130); $Cs_2CO_3 + Cs_2UO_4$ (300);	
	U_3O_8 (1400)	126
$Ca_2U(C_2O_4)_4 \cdot 4\ H_4O$	$Ca_2U(C_2O_4)_4$ (230); $2\ CaCO_3 + U_3O_8$ (460);	
	$CaUO_4 + Ca_3UO_6$ (800)	129
$Sr_2U(C_2O_4)_4 \cdot 4\ H_2O$	$Sr_2U(C_2O_4)_4$ (240); $2\ SrCO_3 + U_3O_8$ (380);	
	$SrUO_4 + Sr_3UO_6$ (900)	129
$Ba_2U(C_2O_4)_4 \cdot 8\ H_2O$	$Ba_2U(C_2O_4)_4$ (210); $BaUO_4 + Ba_3UO_6$ (900)	129
$Cd_2U(C_2O_4)_4 \cdot 6\ H_2O$	$Cd_2U(C_2O_4)_4$ (190); $CdUO_4 + CdO$ (650)	129
$Pb_2U(C_2O_4)_4 \cdot 6\ H_2O$	$Pb_2U(C_2O_4)_4$ (200); $PbUO_4 + PbO$ (520)	129

M. ACTINIDE (III) OXALATES

The actinium compound was prepared as large, dense white crystals, by homogeneous precipitation from a solution of actinium(III) in formic acid (2.7—6.8 mg of $^{227}Ac\ ml^{-1}$) at 90—95°C, the oxalate ion being provided by hydrolysis of dimethyloxalate [100]. The degree of hydration is uncertain. A thermogravimetric study has shown that the decomposition of a product of constant weight occurs at or below 600°C and that no further change in weight occurs up to a temperature of 1340°C. It was also concluded that the product of ignition of actinium(III) oxalate at 1340°C is not the oxide Ac_2O_3, previously reported to form at 900°C in air [101] but a basic carbonate of the type $(AcO)_2CO_3$. Hydrated plutonium(III) oxalate may be precipitated from a dilute HNO_3 solution of trivalent plutonium by the addition of oxalic acid or sodium oxalate [102]. Since the hydrate is isomorphous with $La_2(C_2O_4)_3 \cdot 10\ H_2O$ and has similar unit cell dimensions (a = 11.596, b = 9.599, c = 10.171 Å, β = 118.94°) [103] it is almost certainly a decahydrate also. There is disagreement on the temperature required for dehydration of the plutonium(III) oxalate. In one investigation it was found that in air at 180°C or in vacuum at 230°C the hydrated oxalate forms the dihydrate $Pu_2(C_2O_4)_3 \cdot 2\ H_2O$ which then decomposes to the anhydrous oxalate at 200°C in air and 350°C in vacuo [104]. In another investigation it was found that the anhydrous compound could be prepared by heating the hydrate in air at 225°C or in hydrogen below 300°C; decomposition of the oxalate to PuO_2 was reported to be appreciable at 300°C and almost complete at 400°C [119]. In a third investigation it was found that the decahydrate decomposes through a number of steps, the path depending on the atmosphere in which the compound is heated [105]. The reactivity of oxide prepared by oxalate decomposition is greater than that made from other compounds, which suggests the oxalate is the pre-

ferred source of PuO_2 to be used for the preparation of other plutonium compounds.

Pink monoclinic $Am_2(C_2O_4)_3 \cdot 10\ H_2O$ (a = 11.19, b = 9.63, c = 10.24 Å; β = 114.4°) precipitates when an excess of oxalic acid is added to a solution of Am^{III}. It is isotypic with $La_2(C_2O_4)_3 \cdot 10\ H_2O$ which at the same time confirms the decahydrate. Americium(III) oxalate is sparingly soluble, the solubility minimum in $HNO_3/H_2C_2O_4$ of 0.4 mg Am l^{-1} occurring at 0.10 M HNO_3 and 0.07 M $H_2C_2O_4$ (23°C) [113]. On thermal decomposition it passes through a series of intermediate hydrates containing 7, 4, 3, 2, 1 and 1/2 molecules of water, to give the anhydrous salt; above 300°C it decomposes into AmO_2 [114].

Curium(III) forms the white decahydrate $Cm_2(C_2O_4)_3 \cdot 10\ H_2O$ [106]; approximately the same temperature increment is required to remove each of the seven water molecules and the ninth and tenth but a greater temperature increment is needed to remove the eighth molecule of water, so $Cm_2(C_2O_4)_3 \cdot 10\ H_2O$ and $Cm_2(C_2O_4)_3 \cdot 3\ H_2O$ have the greatest temperature range of stability in vacuo. The loss of water is complete at 280°C and the decomposition of oxalate itself takes place with completion of dehydration. Initially the anhydrous oxalate decomposes into a 1 : 1 oxalate carbonato compound and CO, the latter decomposing to the extent of 60%. At 360°C this 1 : 1 complex decomposes to $Cm_2(CO_3)_3$ with the liberation of CO and CO_2 in the ratio 1 : 2. The carbonate begins to decompose at 420°C; a postulated scheme for the decomposition of $Cm_2(C_2O_4)_3 \cdot 10\ H_2O$ between 20 and 800°C is reported in Table 17. In the higher temperature range, a change in the valence state of the curium introduces features similar to those found in the decomposition of praseodymium and terbium carbonate [107].

TABLE 17

Proposed scheme for decomposition of curium(III) oxalate 10-hydrate [106]

T_D(°C)[a]	Compound	Products
60	$Cm_2(C_2O_4)_3 \cdot 10\ H_2O$	$Cm_2(C_2O_4)_3$
300	$Cm_2(C_2O_4)_3$	$Cm_2(CO_3)_{1.5}(C_2O_4)_{1.5} + 1.5\ CO$
360	$Cm_2(CO_3)_{1.5}(C_2O_4)_{1.5}$	$Cm_2(CO_3)_3 + 0.5\ CO + CO_2$
420	$Cm_2(CO_3)_3$	$Cm_2O(CO_3)_2 + CO_2$
510	$Cm_2O(CO_3)_2$	$Cm_2O_2CO_3 + CO_2$
550	$Cm_2O_2CO_3$	$Cm_2O_{3+x} + x\ CO + 1 - x\ CO_2$
~550	Partial oxidation	
590	$Cm_2O_{3+x} + x\ CO_2$	$Cm_2O_{3+x} + CO$
~750	$2\ Cm_2O_{3+x} + C$	$2\ Cm_2O_{3+x'} + x - x'\ CO_2$

[a] T_D Decomposition temperature (heating rate = 100°C h^{-1}; dynamic vacuum $< 10^{-6}$ mm Hg).

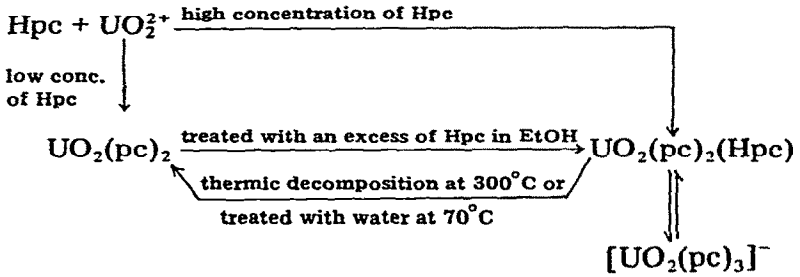
N. ACTINIDE(VI) PYRIDINE-2-CARBOXYLATES

It is well known that the uranyl(VI) ion forms with some chelating ligands, such as acetylacetone or 8-hydroxyquinoline, complexes containing a metal ligand ratio 1 : 2 and 1 : 3 [173]. Similarly the ligand pyridine-2-carboxylic acid (Hpc) forms the complexes $UO_2(pc)_2$ and $UO_2(pc)_2(Hpc)$. Both complexes have been prepared in aqueous solution; the first complex can be obtained by using a higher metal to ligand concentration and a higher pH (i.e. 0.005 M uranium, 0.01 M Hpc and pH 3.5), the second one by using a lower pH and a higher ligand concentration (0.02 M uranium, 0.1 M Hpc and pH 1.7). Both complexes have very low solubility in water, alcohol, diethylether and benzene. Thermogravimetric analysis shows the 1 : 3 complex is stable up to 250°C; above this temperature it loses one molecule of Hpc and the 1 : 2 chelate is formed. $UO_2(pc)_2$, obtained thermally or prepared in aqueous solution, decomposes to U_3O_8 [174]. In aqueous solution the 1 : 3 compound gives rise to the dissociation

$$UO_2(pc)_2(Hpc) \rightarrow H^+ + [UO_2(pc)_3]^-$$

The complexes $Na[UO_2(pc)_3]$ and $(Ph_4As)[UO_2(pc)_3] \cdot 3\,H_2O$ can be obtained from an aqueous solution of the 1 : 3 complex by addition of cations such as Na^+ or Ph_4As^+.

$UO_2(pc)_2(Hpc)$ is stable as a suspension in water only if an excess of α-picolinic acid is present; it is completely converted into $UO_2(pc)_2$ when treated with water at 70°C; obviously the 1 : 2 chelate changes into 1 : 3 when it is treated with an excess of ligand. The scheme of the chemical behaviour of the uranium(VI)/Hpc system is



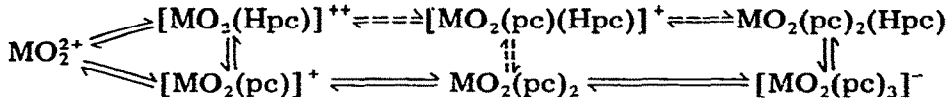
Under vacuum the transformation

$$UO_2(pc)_2(Hpc) \rightarrow UO_2(pc)_2 + Hpc$$

occurs at 150°C.

The analogous complexes of neptunium(VI), plutonium(VI) and americium-(VI) have been reported [175] by using experimental conditions very similar to those employed for the uranyl(VI) ones. Thermogravimetric data show that the 1 : 2 chelate cannot be formed from the 1 : 3 complex by heating and that the temperature of the onset of thermal decomposition becomes lower

passing from uranium(VI) to americium(VI). The chemical behaviour of the MO_2^{2+}/Hpc system can be written as



Only the species $[MO_2(pc)(Hpc)]^+$ was postulated as an intermediate while the other species have been all characterized. The first stage in the complexation reactions is the formation of the adduct $[MO_2(Hpc)]^{2+}$; it forms at very low pH. The last stage is the formation of the 1 : 3 anion obtained at high pH and pyridine 2-carboxylic acid concentration. Mixed complexes of the type $UO_2(pc)_2HL$ (HL = 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline or 9-hydroxyacridine) have been synthesized [174]. They are thermally less stable than $UO_2(pc)_2(Hpc)$.

IR and ^1H NMR data [175] indicate that the 1 : 3 complexes contain two ligand anions bonded via one oxygen of the carboxylic group and the nitrogen of the pyridine ring to the metal and one further ligand bonded via only the carboxylic group; the dissociable hydrogen is attached to the nitrogen of this molecule. The coordination in these complexes is similar to $[UO_2(oxine)_2$-(Hoxine)] [233—235].

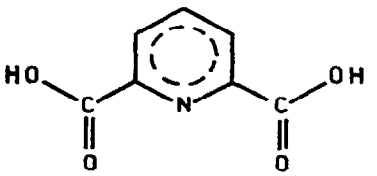
The pyridine 3-carboxylate (H-3pc) complexes are of the type $[MO_2$-$(3pc)_2H_2O] \cdot H_2O$ (M = U(VI), Np(VI), Pu(VI) and Am(VI)) with a coordination around the central metal ion as in $[UO_2(CH_3COO)_2H_2O] \cdot H_2O$ [265]. This is because the pyridine 3-carboxylate is not capable of forming five membered chelate rings. 1 : 3 complexes have not been prepared [175].

O. ACTINIDE(V) PYRIDINE-2-CARBOXYLATES

The green $NpO_2(pc) \cdot 2\ H_2O$ has been prepared by precipitation from aqueous solution; it is sparingly soluble in water, alcohol and acetone, but dissolves readily in aqueous solution containing excess ligand at ca. pH 4 to form a complex anion of the type $[NpO_2(pc)_2 \cdot x\ H_2O]^-$. The water molecules of $NpO_2(pc)_2 \cdot 2\ H_2O$ can be replaced by other neutral monodentate ligands such as dmso to give $[NpO_2(pc)(dmso)_2]$ in which the two dmso molecules are most probably coordinated to the central metal ion. $NpO_2(pc) \cdot 2\ H_2O$ loses the water molecules when heated at 125°C and is decomposed at 370°C; its IR spectrum shows ν_{asym} COO at 1586, 1568 and ν_{sym} COO at 1414 cm^{-1} [226].

P. ACTINIDE(VI) PYRIDINE- AND PYRIDINE-N-OXIDE-2,6-DICARBOXYLATES

Pyridine-2,6-dicarboxylic acid (H_2pdc) (18) is a polyfunctional ligand cap-



(18)

able of forming monomeric or polymeric species by coordination with metal ions [176—183]. By reacting uranyl(VI) salts with H_2pdc in aqueous solution the polymeric species pentacoordinated $[UO_2(pdc)(H_2O)]_n$ [184,185] and the hexacoordinated $[UO_2(pdc)_2]^{2-}$ [187] have been isolated. The first complex can be prepared as a white-yellow flocculent precipitate when an equimolecular amount of $UO_2Cl_2 \cdot 3\ H_2O$ is added to a saturated solution of H_2pdc in ethyl acetate. The second compound with formulation $(Ph_4As)_2[UO_2(pdc)_2] \cdot 6\ H_2O$ has been obtained as greenish-yellow crystals by mixing aqueous solutions, previously heated at 80°C, of $UO_2(NO_3)_2 \cdot 6\ H_2O$, H_2pdc and Ph_4AsCl in the molar ratio 1 : 6 : 6. Uranium(VI) is quantitatively precipitated from aqueous solution in the pH range 2.1—6.9 with H_2pdc in the presence of Ph_4AsCl [185]. $[UO_2(pdc)(H_2O)]_n$ crystallizes in the hexagonal space group $P6_1$ ($z = 6$, $a = b = 14.685(2)$, $c = 9.313$ Å) [186]. The repeating unit consists of a linear uranyl(VI) group equatorially surrounded by five ligand atoms: two carboxylate oxygens and the nitrogen of one pdc ion, a bridging oxygen atom of an adjacent pdc unit and one water molecule. The carboxylate bridging between adjacent uranyl groups leads to a polymeric structure in the form of a helix oriented parallel to the 6_1 axis. The five equatorial atoms coordinated to the uranyl group are not exactly coplanar. The structure is characterized by a pattern of helices all with the same sense with a Van der Waals diameter of about 21 Å. Each helix is surrounded by six other helices with an axis to axis distance of $a = 14.68$ Å; the polymeric chains are partially interpenetrating. The helices are linked together by hydrogen bonding between coordinated water and free C=O groups (Figs. 12, 13). The crystals of (Ph_4As)-$[UO_2(pdc)_2] \cdot 6\ H_2O$ are triclinic (space group $P\bar{1}$ with $a = 15.12(1)$, $b = 11.21$-(1), $c = 9.35(1)$ Å; $\alpha = 101.22(2)°$, $\beta = 100.27(2)°$, $\gamma = 100.53(2)°$, $z = 1$); the uranium atom is eight coordinate, the O—U—O group being equatorially surrounded by an irregular hexagon of four oxygen atoms and two nitrogen atoms from two tridentate dicarboxylate groups. The complex anion is roughly planar and can be considered to have approximately D_{2h} symmetry [187]. The arsenic atom of the cations is approximately tetrahedrally surrounded by benzene rings. The projection of the structure of this complex

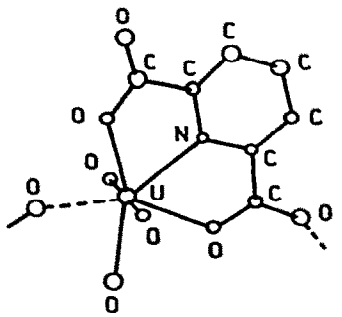


Fig. 12. Molecular model of the repeating unit $UO_2(pdc)(H_2O)$.

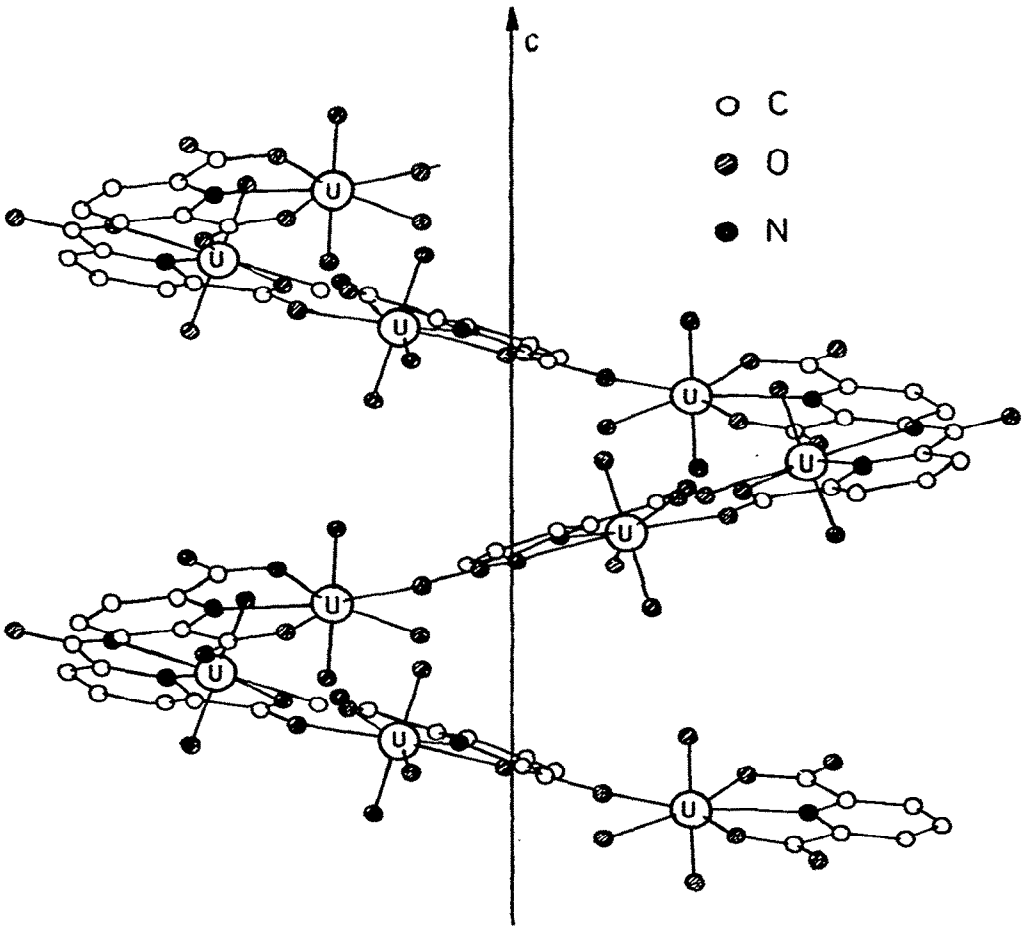
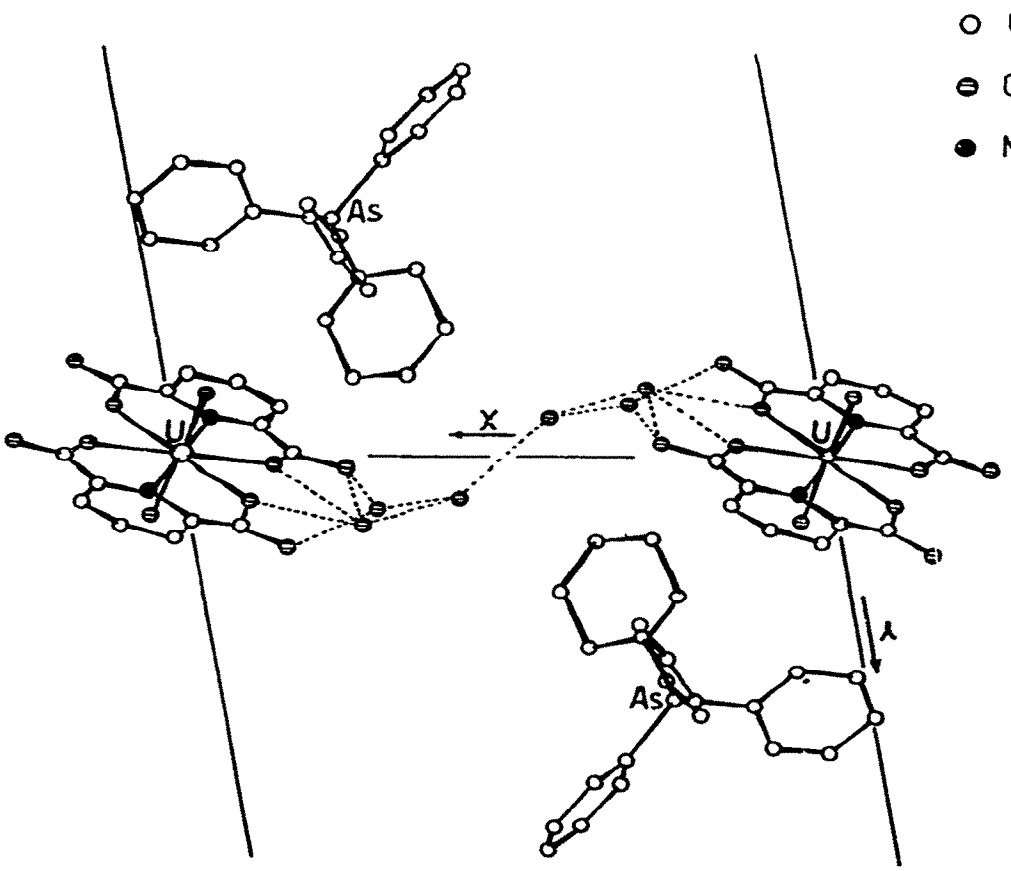


Fig. 13. Projection of the structure of $[UO_2(pdc)(H_2O]_n$ along the [001] direction.

along [001] is (19). The six water molecules are not directly bonded to uranium and their loss involves a three step process with evolution of one, three and two molecules in the 20—25°, 35—60° and 70—120°C temperature ranges. The anhydrous product slowly absorbs six water molecules when exposed to moist air. No change is observed in the IR spectra taken at the various stages apart from the gradual disappearence of the broad OH stretch in the 3600—3300 cm^{-1} range. The presence of one band for the antisymmetric COO stretching frequency at 1615 cm^{-1} indicates, in agreement with X-ray data, that there is only one type of carboxylic group and all the carboxylic oxygen atoms are engaged in coordinate bonds. The IR spectrum of $(Ph_4As)_2[UO_2(pdc)_2] \cdot 6\ H_2O$ displays two absorption bands in the carboxylic stretching region at 1680, 1640 cm^{-1} and 1380 cm^{-1}. The separation between the antisymmetric and symmetric stretching bands of the carboxylic groups is much

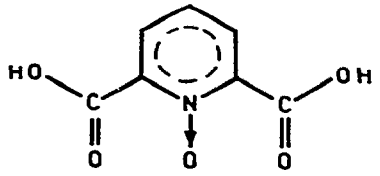


(19)

higher than in the free anion and the higher frequency bands are more intense.

A series of uranyl(VI) dipicolinate adducts with neutral ligands has been reported [184,189]. The dipicolinate anion acts in all these complexes as a tridentate ligand toward each uranium atom. The complex $[UO_2(pdc)(eu)]_n$ (eu = ethylurethane), on the basis of IR evidence, was reported to be polymeric [184,189] while the others (Table 18) are presumed to be monomeric on the basis of the absence of the lower antisymmetric COO stretching mode associated with a bridging or chelating function in the polymeric compound [188]. Thermoanalytical data on these complexes show that the stage corresponding to the loss of the neutral ligand is well separated from that corresponding to the decarboxylation.

With the aim of preparing polymeric uranyl(VI) complexes, the ligand pyridine-2,6-dicarboxylic acid N-oxide (H_2pdcNO) (20) has been considered [190];



(20)

TABLE 18

Some characteristic IR absorptions of dipicolinate complexes

Compound [a]	ν_{asym} O—U—O (cm^{-1})	ν_{asym} O—C—O (cm^{-1})	Some characteristic bands of the coordinated neutral ligands (cm^{-1})	Ref.
$[UO_2(pdc) \cdot H_2O]_n$	940s	1615s	(3550—3250) br (ν_{OH})	188
$[UO_2(pdc)(pyNO)_2]$	898s	1675s	1219s (ν_{NO})	
$[UO_2(pdc)(eu)]_n$	932	1650, 1580	1670 ($\nu_{C=O}$)	189
$[UO_2(pdc)(urea)_2]$	906	1682	1640 ($\nu_{C=O}$)	
$[UO_2(pdc)(alam)_2]$	920	1673	1640 (ν_{NH})	
$[UO_2(pdc)(dmso)_2]$	909	1676	990 ($\nu_{S=O}$)	
$[UO_2(Hpdc)_2 \cdot 2\ H_2O]$	940	1665		188
$(Ph_4As)_2[UO_2(pdc)_2] \cdot 6\ H_2O$	912	1680, 1640		187
$[UO_2(pdc)(4\ Me—pyN—O)_2]$	900	1668	1221 ($\nu_{N—O}$)	188

[a] eu = ethylurethane; alam = allylamine; pyNO = pyridine-N-oxide; dmso = dimethylsulphoxide.

this ligand differs from H_2pdc only in the oxygen atom bonded to the nitrogen. By reacting $UO_2(NO_3)_2 \cdot 6\ H_2O$ with H_2pdcNO in aqueous solution at room temperature, yellow-green crystals, corresponding to the formula UO_2(pdcNO) $\cdot$ 3 H_2O have been obtained. Its IR spectrum shows ν_3O—U—O at 925 cm^{-1}, a sharp band at 1590 cm^{-1}, a broad band at 1640 cm^{-1} due to antisymmetric COO vibration and bands at 3460, 3540 and 3580 cm^{-1} due to the stretching of H_2O. The crystals are monoclinic with space group $P2_1/n$, a = 16.506(18), b = 10.618(3), c = 6.697(2) Å; β = 90.36(2)°; z = 4 [190]. The structure consists of dimeric moleculs with two UO_2(pdcNO) $\cdot$ 3 H_2O

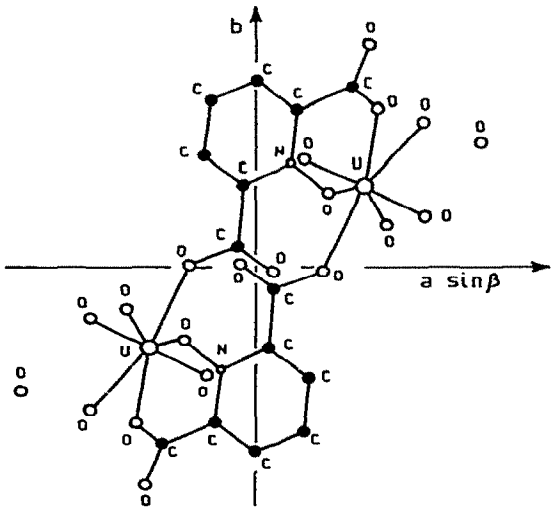


Fig. 14. Molecular structure of $[UO_2(pdcNO)(H_2O)_2]_2 \cdot 2\ H_2O$.

units related by a centre of symmetry and bridged by a carboxylic oxygen atom of the ligand. The coordination polyhedron is a pentagonal bipyramid; the pentagonal base is defined by two oxygen atoms, one from a monodentate carboxylic group, the second from the pyridine oxide, a third oxygen atom from the other bridging monodentate carboxylic group and by two water molecules. The third water molecule is away from the coordination sphere (Fig. 14).

Q. ACTINIDE(IV) PYRIDINE-2,6-DICARBOXYLATE

The crystal structure and the physicochemical properties of the uranium-(IV) complex $(Ph_4As)_2[U(pdc)_3] \cdot 3\ H_2O$ have been reported [191]. The compound can be obtained by addition of UCl_4 to an excess of H_2pdc and Ph_4AsCl in aqueous solution and the crystals which form overnight remain unchanged for many months in contact with a normal atmospheric environment. The complex crystallizes in the monoclinic system as small pale green prisms (space group $P2_1/c$; $a = 18.12(2)$, $b = 14.69(2)$, $c = 27.53(3)$ Å, $\beta = 113.50(5)^\circ$; $z = 4$). The uranium atom is nonacoordinate being linked by three dipicolinato ions acting as terdentate ligands. The coordination polyhedron has the approximate D_{3h} symmetry and can be described as a distorted tricapped trigonal prism with the three nitrogen atoms located outside the midpoints of the rectangular faces of the prism. The planes of the ligands are approximately orthogonal to one another and the three nitrogen atoms and the uranium atom are coplanar (Fig. 15). The IR spectrum of this complex is very similar to $(Ph_4As)_2[UO_2(pdc)_2] \cdot 6\ H_2O$; in particular the COO stretching bands are of comparable intensity and lie at the same frequencies for both uranium(IV) and uranium(VI) species.

R. ACTINIDE(VI) AND ACTINIDE(IV) OXYDIACETATES

Oxydiacetic acid (H_2oda) (21) has two carboxyl groups and an ether oxygen atom in the α-position of both of them. This ligand can coordinate to a

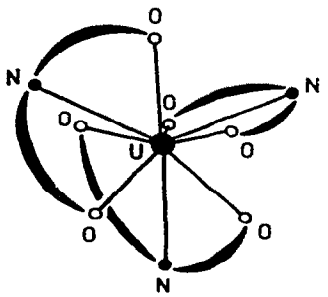
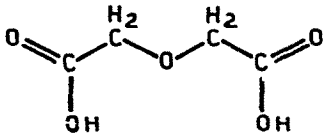


Fig. 15. The coordination polyhedron of the complex $(Ph_4As)_2[U(pdc)_3] \cdot 3\ H_2O$.



(21)

central metal ion through the ether oxygen and the oxygen atoms of the carboxylate groups, also with the possibility of formation of polymeric species.

From the reaction of $UO_2(NO_3)_2 \cdot 6\ H_2O$ and H_2oda or its disodium salt in the molar ratio 1 : 1, two $[UO_2(oda)]_n$ ($n = \infty$), depending on the concentrations of the reactants, have been prepared [192]. They have the same stoichiometry but different IR spectra. A polymeric structure was suggested on the basis of their composition, insolubility and absence of coordinated solvent molecule; such a structure was subsequently confirmed by X-ray analysis [193,194] of the complex obtained from dilute solution. The ligand molecule is shared between three uranium atoms and shows nearly C_{2v} symmetry. Two carboxylate oxygens and the ether oxygen of the same ligand are located at the corners of an irregular equatorial pentagon forming two five membered rings with the uranium atom; the two other carboxylate oxygens of the ligand are linked to the two contiguous uranium atoms. The other two corners of the pentagon are occupied by the carboxylate oxygens of the two different ligands. The linear uranyl group is perpendicular to the equatorial plane. The entire structure can be described in terms of a three dimensional network of cross-linked uranium ligand chains with screw symmetry (Fig. 16).

From uranyl(VI) nitrate and Na_2oda in the molar ratio 1 : 2, both in water and in methanol, the complex $Na[UO_2(oda)_2] \cdot 2\ H_2O$ can be obtained. The complex is monoclinic with space group $P2_1/c$ and cell parameters: a = 19.64(2), b = 13.22(1), c = 7.14(1) Å, β = 97.16(6)°, z = 4 [195]. The anionic ligands act as a tridentate and a coordination number of eight for uranium is realized by an irregular hexagon of six oxygen atoms bonded in the base plane which is normal to the linear uranyl group (Fig. 17). The complex $UO_2(oda)(pyNO)_2$

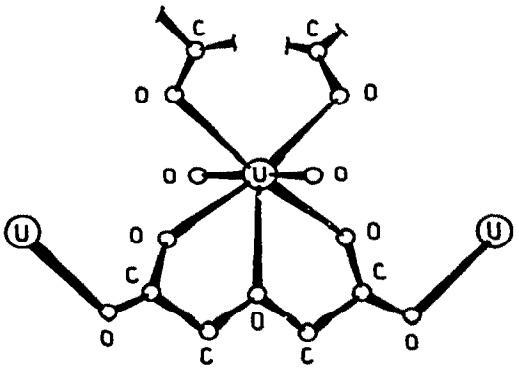


Fig. 16. Molecular structure of $[UO_2(oda)]_n$.

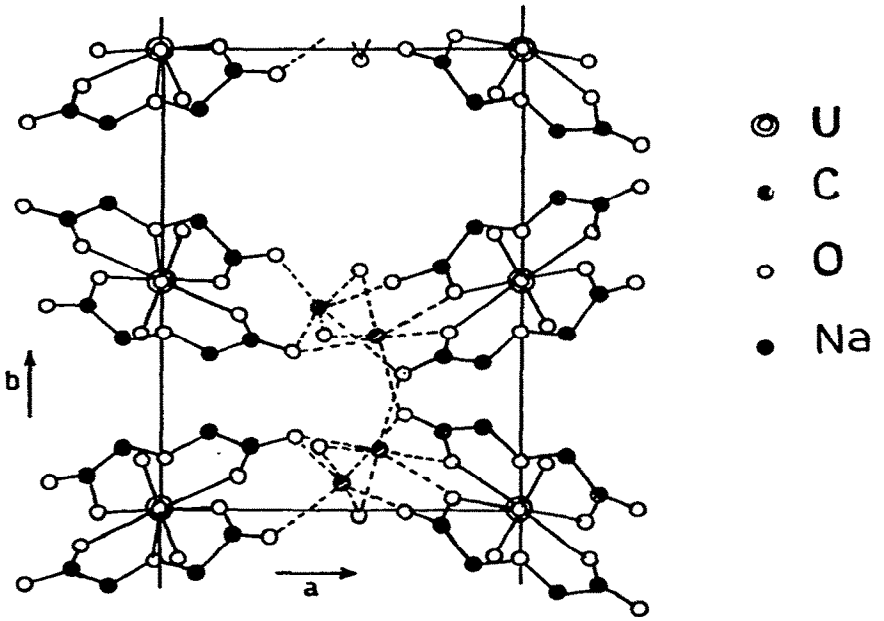


Fig. 17. Molecular structure of $Na[UO_2(oda)_2] \cdot 2\ H_2O$.

has been obtained from $[UO_2(oda)]_n$ in a concentrated methanolic solution of pyridine N-oxide [192]. An intermediate complex, $UO_2(oda)(pyNO)$, containing only one molecule of pyridine N—O, with a polymeric structure has also been prepared; it reacts with another molecule of pyridine N-oxide to give the complex $UO_2(oda)(pyNO)_2$.

The reaction of $Th(NO_3)_4 \cdot 4\ H_2O$ with H_2oda in the molar ratio 1 : 2 or in excess of the ligand in aqueous or methanolic solution leads to the formation of the complex $[Th(oda)_2]_n$ [196]. The complex has a polymeric structure which is destroyed by a large excess of pyridine N-oxide in methanol to give $[Th(oda)_2(pyNO)_3] \cdot 3\ H_2O$. In $[Th(oda)_2]_n$ two carboxylate oxygens and one ether oxygen of the oxydiacetate anion are involved in two five membered chelate rings with a thorium atom; the remaining two carboxylate oxygens coordinate two other thorium atoms. Moreover the features of the IR spectra (Table 19) suggest that all the carboxylate groups are equivalent and no evidence for free CO groups is afforded. Thus a ten coordination number around each thorium atom has been suggested (Fig. 18).

$Na[Th(oda)_3] \cdot n\ H_2O$ (n = 2, 3) has been prepared by adding Na_2oda to a suspension of $[Th(oda)_2]_n$ in methanol in a molar ratio of 1 : 1. A complex with the same metal ligand ratio (1 : 3) but containing two molecules of $NaNO_3$ is obtained by reaction of $Th(NO_3)_4 \cdot 4\ H_2O$ with an excess of Na_2oda in methanol.

The structures of thorium(IV) and uranyl(VI) oxydiacetate complexes have been discussed on the basis of IR methods and normal coordinate analysis [218]. The antisymmetric and the symmetric stretching frequencies of the

TABLE 19

IR frequencies of the oxydiacetate ion and uranyl (VI) and thorium (IV) complexes

Compound	$\nu_{asym\,COO}$ (cm^{-1})	$\nu_{sym\,COO}$ (cm^{-1})	$\nu_{asym\,COC}$ [a] (cm^{-1})	$\nu_{sym\,COC}$ [a] (cm^{-1})	$\nu_{3\,OUO}$ (cm^{-1})	Ref.
$Na_2(oda) \cdot H_2O$	1620 vs	1420 s	1143 s	1063 m		192
$Na_2(oda)$	1600 vs	1418 s	1138 s	1053 m		192
$[UO_2(oda)]_\infty$ [b]	1613 w, 1565 vs	1440 ms	1109 ms	1034 ms	930 s, 944 s	192
$[UO_2(oda)]_\infty$ [b]	1570 vs	1430 m	1113 ms	1046 ms	940 s	192
$Na_2[UO_2(oda)_2] \cdot n\,H_2O$	1670 vs, 1615 vs	1420 s	1119 m	1031 m	917 s	192
$[UO_2(oda)(pyNO)_2]$	1660 vs	1390 ms	1092 m	1037 m	895 s	192
$[UO_2(oda)(pyNO)]_\infty$	1700 s, 1560 vs	[c]	1096 m	1036 m	913 s	192
$[Th(oda)_2]_n$	1585 vs	1426 s	1040 s	1118 s		196, 218
$[Th(oda)_2(pyNO)_3] \cdot 3\,H_2O$	1640 vs	1404 s	1042 m	1098 m		196, 218
$Na_2[Th(oda)_3] \cdot 2\,NaNO_3$	1653 vs	1409 s	1042 m	1113 m		196, 218
$Na_2[Th(oda)_3] \cdot n\,H_2O$	1645 vs	1406 s	1042 m	1107 m		196, 218

[a] Recent calculations [218] have shown there is an inversion in the assignment of the $\nu_{sym\,COC}$ and $\nu_{asym\,COC}$ the former being higher than the latter. [b] The two complexes differ only in their IR spectra. [c] Not assigned because of overlapping with pyridine N-oxide bands.

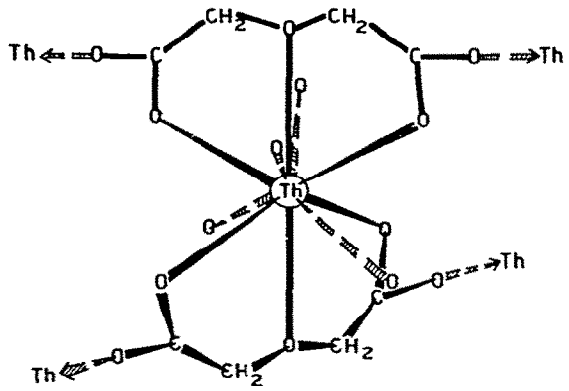


Fig. 18. Proposed configuration for $Th(oda)_2$.

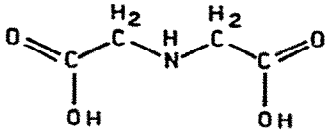
—C—O—C— ether group is shifted towards lower frequencies in the complexes in comparison with the disodium salt. These two bands are about equally intense whereas in the ligand the band at higher frequency is the more intense; these differences support coordination of the ether oxygen to the central metal ion [192,196—199,218]. The separation between the two COO stretching frequencies helps clarify the coordination modes of the ligand. This separation (182 cm^{-1} in the disodium salt of the ligand) decreases in the polymeric complexes (125 cm^{-1} and 159 cm^{-1} in the uranyl(VI) and in the thorium(IV) complexes respectively) and increases in all the monomeric ones. The structure of $[UO_2(oda)(pyNO)]_n$ can be derived from that of $[UO_2(oda)]_n$ by introducing a molecule of pyridine N-oxide which fills a coordination site on the uranium atom. Half of the carboxylate oxygen atoms, which form the polymeric structure, are free and the corresponding C=O bonds, having become nearly pure double bonds, give rise to the 1700 cm^{-1} band. The other half are coordinated and relative C=O linkages are responsible for the broad band at 1560 cm^{-1}. The anionic complexes $Na[Th(oda)_3] \cdot 2\ NaNO_3$ and $Na[Th(oda)_3] \cdot n\ H_2O$ show identical spectra, except for two bands assigned to the ionic nitrate group in the second one. This finding suggests that the anionic $[Th(oda)_3]^{2-}$ entity is the same for both complexes; each thorium atom should coordinate six carboxylic oxygens and three ether oxygens so that the anionic entity is arranged as for $[Yb(oda)_3]^{3-}$ [200]. A comparison between the polymeric $[UO_2(oda)]_n$ and $[Th(oda)_2]_n$ shows that the Th—O frequencies are lower than the corresponding U—O ones, suggesting that once the bonds are formed the strength of the metal—oxygen bond is weaker in the thorium complex. The higher separation between antisymmetric and symmetric stretching frequencies of the carboxylate groups for the thorium complex supports this suggestion (Table 19).

On irradiation of an aqueous solution of $UO_2(NO_3)_2 \cdot 6\ H_2O$ containing a large excess of H_2oda using a high pressure Hg lamp (interference filter $\lambda = 436$ nm) a colour change from yellow to green was observed and the UV spectrum

clearly indicated the presense of uranium(IV) species. From this solution by addition of acetone the complex $U(oda)_2 \cdot 2\ H_2O$ was obtained, while by addition of NaOH and EtOH the complex $Na_2[U(oda)_3] \cdot 2\ H_2oda \cdot H_2O$ was recovered. Their IR spectra are identical to those monitored for $[Th(oda)_2]_n$ and $Na_2[Th(oda)_3] \cdot n\ H_2O$ respectively [196], suggesting the same mode of coordination. The IR spectrum of $Na_2[U(oda)_3] \cdot 2\ H_2oda \cdot H_2O$, showing a doublet at 1726, 1640 cm^{-1}, due to the ν_{asym} COO, clearly indicates the presence of H_2oda as a molecule of crystallization [236,242].

S. ACTINIDE(VI) AMINOPOLYCARBOXYLATES

The iminodiacetic acid (H_2ida) (22) forms the compound $UO_2(Hida)_2$ with



(22)

uranyl(VI) ion [201,202] when stoichiometric amounts of uranyl(VI) nitrate hexahydrate and H_2ida are mixed in water solution and the pH adjusted with sodium hydroxide pellets to ca. 3—3.5; from this solution prismatic yellow crystals precipitate. It must be noted that the same 1 : 2 (metal : ligand) product has been isolated if solutions in a 1 : 1 ratio are mixed. The complex is insoluble in most common organic solvents and water; its thermogram is essentially the same with either air or nitrogen as the atmosphere. The DTA thermogram shows endothermic peaks at 149°, 278.5° and 315°C in nitrogen; the TGA curve shows the compound is stable up to 197°C. The peak at 149°C, not corresponding to any weight loss in the TGA curve, may be the result of crystalline transformations. The absence of any absorption beyond 1660 cm^{-1} indicates there are no unionized carboxyl groups in the compound, thus suggesting that the protons may be attached to the nitrogens rather than to the carboxylate oxygens. The strong absorption peaks ranging from 1550 to 1610 cm^{-1} indicate the carboxylate groups are coordinating in more than one manner; the coordination of the amino group is inhibited by the protonation. The antisymmetric ν_3 O—U—O stretching lies at 916 cm^{-1}. The crystal structure confirms the uranyl ion is coordinated with four carboxylate groups in the equatorial plane which forms a hexagonal bipyramid. Each ligand is chelated through a bidentate carboxylic moiety to one uranyl unit and coordinated through the other monodentate carboxylic moiety to another uranyl unit. As suggested by IR data [201], the carboxylic groups are both ionized and the proton is linked to a nitrogen atom. The resulting structure consists of polymeric chains running parallel to $0\bar{1}0$. The nitrogen proton is involved in linear hydrogen bonding with the oxygen of an adjacent chain. In this way the chains are linked to each other through a network of hydrogen bonds (Fig. 19).

By reaction of $UO_2(NO_3)_2 \cdot 6\ H_2O$ and Na_2ida in a molar ratio 1 : 1, the

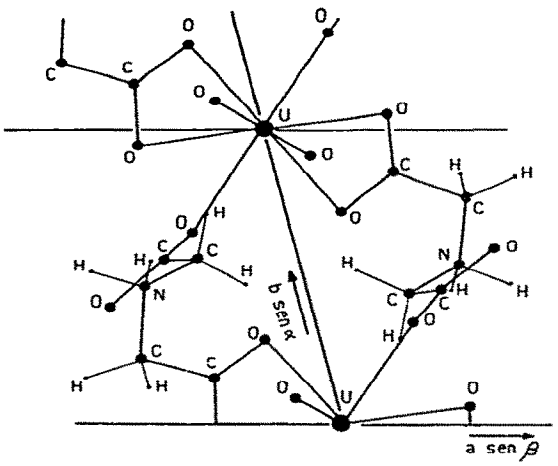
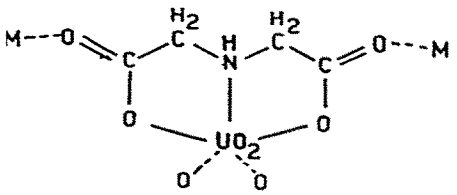


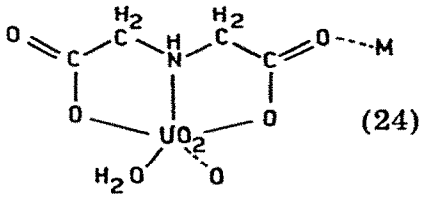
Fig. 19. Molecular structure of $UO_2(Hida)_2$.

three complexes $[UO_2(ida)]_n$, $[UO_2(ida)(H_2O)]_n$, and $[UO_2(ida)(H_2O)_2]$ have been obtained; the first compound was obtained in water, the second in a water/methanol mixture and the third in methanol; in these complexes the ligand coordinates to the central metal ion forming two condensed five membered chelate rings with the consequent formation of the U—N bond. Their IR spectra agree with these configurations [237] (23—25) respectively.



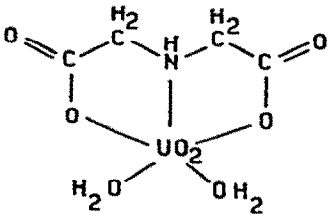
(23)

$[UO_2(ida)]_n$



(24)

$[UO_2(ida)(H_2O)]_n$



(25)

$UO_2(ida)(H_2O)_2$

The ν_{N-H} for the three compounds lie at 3260, 3240 and 3220 cm^{-1} and the ν_{asym} COO at 1545, 1557 and 1565 cm^{-1} respectively. $[UO_2(ida)]_n$, when treated with fused pyridine N-oxide, leads to the complex $UO_2(ida)(pyNO)_2$ while $[UO_2(ida)(H_2O)]_n$, with a methanolic solution of pyridine N-oxide,

preserves the polymeric nature giving the complex $[UO_2(ida)(pyNO)]_n$.

Research on uranyl(VI) chelates of analytically important aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (H_4edta) and its analogues have been restricted principally to solution studies [206,220,221]. The uranyl(VI) complexes with nitrilotriacetic acid (H_3nta) and H_4edta in a 1 : 1 molar ratio were first prepared in 1942 [207,208]. More recently the 1 : 2 uranyl(VI)—edta chelate has also been prepared [203]. A comparison of the thermal properties and IR spectra of uranyl(VI) chelates of H_3nta with a metal : ligand ratio of 1 : 1 and 2 : 3, of edta with ratio 1 : 1 and 2 : 1, of H_4cdta (H_4cdta = *trans*-cyclohexanediaminetetraacetic acid) with ratios of 1 : 1 and 2 : 1 has been reported [201]. For the 1 : 2 metal to ligand complexes UO_2(Hnta) · 2 H_2O, $UO_2(H_2edta)$ · 2 H_2O, $UO_2(H_2cdta)$ · 3 H_2O, all the carboxylic groups are ionized; the protons are very probably bonded to the nitrogens rather than to the carboxylate oxygens and the coordination of the amino group is inhibited by the protons. For the more complex compound $(UO_2)_2$(edta) · 2 H_2O the shift to lower frequencies of the asymmetric stretchings may be the result of either a reduction of the inductive effect associated with removal of the formal charge on amino nitrogen and enhancement of carboxylate coordination or the change in type of coordination from mono to bidentate. For the complex $(UO_2)_3(nta)_2$ · 10 H_2O at least three molecules of water must be coordinated strongly to the cation in view of the fact that decarboxylation begins even when three molecules of water are still present in the compound. It was concluded that the uranyl(VI) group is coordinated with three carboxylates in UO_2(Hnta) · 2 H_2O, two carboxylates and one water molecule in $(UO_2)_3(nta)_2$ · 10 H_2O, either all four or at least two carboxylate groups in $UO_2(H_2edta)$ · 2 H_2O and $UO_2(H_2cdta)$ · 3 H_2O and only two carboxylate groups in $(UO_2)_2$(cdta) · 6 H_2O.

T. ACTINIDE(V) AMINOPOLYCARBOXYLATES

Addition of ethylenediaminetetraacetic acid to a neutral solution of neptunium(V) leads to the formation of an amorphous grey precipitate of (NpO_2)-(H_2edta) · 5 H_2O [171]. When the pH is brought to 7—8, the precipitate dissolves completely; a compound of composition $(Co(NH_3)_6)[NpO_2(edta)]$ · 3 H_2O with reddish-yellow colour is then precipitated from this solution by slowly adding a 0.05 M $Co(NH_3)_6Cl_3$ solution.

U. ACTINIDE(IV) AMINOPOLYCARBOXYLATES

The thorium(IV) and uranium(IV) complexes M(edta) · 2 H_2O have been prepared by adding $Th(NO_3)_4$ · 4 H_2O or $U(SO_4)_2$ · x H_2O respectively to a boiling aqueous solution of H_4edta. White crystals of the thorium(IV) compound and green ones of the uranium(IV) analogue separate when the resulting solution is concentrated. The anhydrous complexes are obtained by heating the dihydrates at 214° and 135°C respectively [209]. Potentiometric titra-

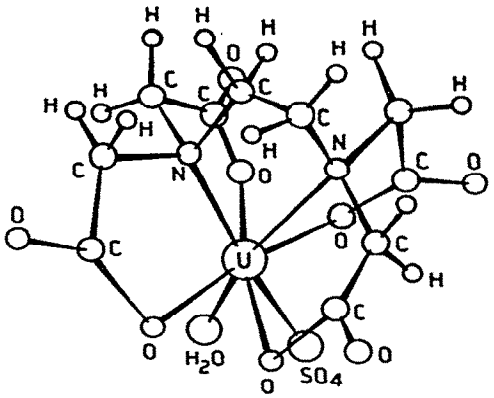
tions of thorium(IV) ion with H_4edta have shown that the hydrolysis of the 1 : 1 chelate occurs above pH 6 with the probable formation of a dimeric species $[Th_2(OH)_2L_2]^{2-}$ [210]. The ^1H NMR spectra of the 1 : 1 Th(IV) : edta complex exhibit one sharp acetate peak and one sharp ethylenic peak. On the basis of these data no conclusions can be made regarding the structure of the dimeric unit [211]. The ^1H NMR data gave no evidence of the formation of 2 : 3 or 1 : 2 Th(IV) : edta complexes when the appropriate ratios of metal to ligand are used.

The complexes of uranium(IV) with H_4edta have been the subject of a number of investigations and complexes with metal to ligand ratios of 1 : 1, 1 : 2, 2 : 1 and 2 : 3 have been reported [205,212—214]. U(edta) · 2 H_2O has been found stable between pH 0.0 and 3.5; at higher pH values the complex apparently loses a proton to form $[U(edta)(H_2O)(OH)]^-$ which undergoes the reaction

$$2\,[U(edta)(H_2O)(OH)]^- \rightleftharpoons [U(edta(OH)]_2^{2-}$$

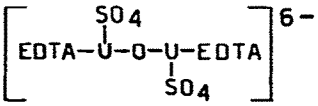
to form a dimeric hydroxyl bridged species. A dodecahedron or quasi dodecahedron with trigonal faces has been suggested for the structure of U(edta) · 2 H_2O [215,216]; however a cubic symmetry or a slightly perturbed cubic one has been proposed as more reasonable because of the low magnetic moment of the complex [217]. It was also established that the limited solubility of U(edta)$(H_2O)_2$ in water (6.55 mM at 25°C) can be increased by dissolving the complex in solutions containing ionic complexing agents such as oxalate, carbonate, sulphate, citrate, tartrate or fluoride ions; these anions replace one or both of the coordinate waters of the complex. The enhanced solubility of uranium(IV)—edta complex in water containing Na_2SO_4 indicates that the SO_4^{2-} ions replace one or both of the coordinated water molecules when the complex dissolves.

The acid—base titration of the uranium—edta complex in 1 M Na_2SO_4 indicates that each uranium(IV) ion has one coordinated water molecule. Thus the data imply that the remaining two coordination sites on the eight-coordinated uranium(IV) ion in the U(IV)—edta complex are occupied by one water molecule and one SO_4^{2-} ion and that the complex exists in aqueous Na_2SO_4 solutions from pH 1.00 to 3.00 as $[U(edta)(H_2O)(SO_4)]^{2-}$. The value for the magnetic moment of this complex in solution at pH 2.0 (3.01 B.M.) and the pseudocontact shift calculations agree with a cubic solution structure for the complex. Because the ^1H NMR spectra of the complex from pH 1.0 to 3.0 indicate a highly symmetrical structure in solution, a rapid exchange must occur between the coordinated water molecules and SO_4^{2-} ions. A structure consistent with all the data is (26). The U(IV)—edta complex that begins to form in 1.0 M Na_2SO_4 solution above pH 3.0, has a magnetic moment at pH 6.5 (2.51 B.M.) indicative of spin-pairing through the formation of an oxo-bridged dimeric species. The appearence of ten ill-defined proton ^1H NMR peaks at low temperatures can be explained by a decrease in the exchange rate for water mole-



(26)

cules with coordinated SO_4^{2-} ions to give a stable solution structure of the form (27).

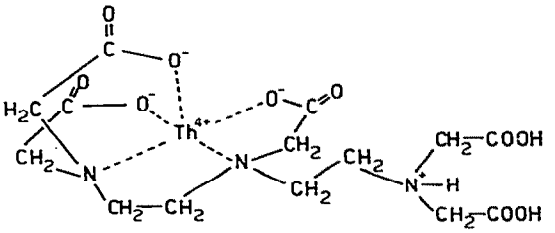


(27)

A thorium(IV) complex having the formula [Th(Hdtpa)(H_2O)] (H_5dtpa = diethylenetriaminepentaacetic acid) can be prepared as a white crystalline solid by adding an aqueous solution of H_5dtpa to an aqueous solution of Th-$(NO_3)_4 \cdot 4\ H_2O$. The IR spectrum of this complex shows a single peak at 1600 cm^{-1}; this peak has been attributed to the carboxylic groups coordinated to the thorium(IV) ion. From the IR spectrum, however, the presence of uncoordinated COO^- groups cannot be excluded since they absorb in the same region as coordinated carboxylic groups. Nevertheless, it may be reasoned that the proton in the complex is associated with the most basic group. Since the COO^- group is absent it is concluded that all of the carboxylic groups are coordinated and that dtpa is octadentate in the acid complex [144]. As the pH increases to 8—9 it has been supposed that a hydroxo group replaces one of the carboxylic groups.

In the second complex the ligand should act as heptadentate. The first complex contains seven fused five membered chelate rings, which account for its remarkably high hydrolytic stability [210].

More recently the aqueous IR and ^1H NMR spectra of the 1 : 1 complexes of Th(IV)—H_5dtpa have been studied as a function of the ratio a (a = moles of bases added/moles of metal ion) [211]. The structure of the 1 : 1 Th(IV)—dtpa complex at a = 0 (pH 0.90) has been proposed to be (28) with the imino-



(28)

diacetic group completely protonated because the IR data indicate an absorption at 1730 cm^{-1} signifying a protonated carboxylic group. Addition of an equimolecular amount of copper(II) to the Th(IV)—dtpa at $a = 0$ only produces a slight interaction of Cu(II) with this protonated iminodiacetic group at this pH (0.90). IR spectra of the 1 : 1 Cu(II)—Th(IV)—dtpa solution indicate the peak at 1730 cm^{-1} is approximately the same as in the 1 : 1 Th(IV)—dtpa complex, thus confirming the contribution of copper(II) coordination must be small.

As base (NaOD) is added very slowly to the complex in going from $a = 0$ to $a = 4$ (pD = 1.56), both IR and ^1H NMR spectra indicate that no free acetic groups remains in this region. In going from $a = 4$ (pD = 1.46) to $a = 5$ (pD = 5.3) only a slight change in the ^1H NMR spectra is noted and virtually no change occurs in the IR spectra. Thus it seems all five carboxylate groups and all three nitrogens of the dtpa must be coordinated to the thorium(IV) ion. The monohydroxo thorium chelate is formed when the potentiometric titration proceeds from $a = 5$ to $a = 6$ [210]. IR data for the dtpa complex at $a = 6$ (pD = 10.24) show only one strong band at 1610 cm^{-1}, suggesting that all carboxyl groups are coordinated. It was concluded that a nine coordinated monohydroxo chelate is formed at $a = 6$; so the previous report that the hydroxo complex has a free carboxyl group replaced by an OH group, is very probably wrong.

Thorium(IV) complexes, having the formula $ThO(ida) \cdot 2H_2O$ and $Th(ida)_2 \cdot 2\ H_2O$ have been prepared [237] from hydrate thorium(IV) nitrate and Na_2ida, and from $Th(OH)_4$ and H_2ida in aqueous solution respectively. Their IR spectra are very similar to those found for analogous complexes of uranium(IV), prepared by photochemical methods under the same experimental conditions reported for glycolate and oxydiacetate complexes, suggesting a similar coordination around the central metal ion with the coordination of the amino group to the thorium atom.

V. ACTINIDE(III) AMINOPOLYCARBOXYLATES

The faint violet Am(III)—ethylenediaminetetraacetate $Am(Hedta) \cdot x\ H_2O$ forms when $Am(OH)_3$ is treated with an aqueous solution containing a stoichiometric amount of the acid. No other solid actinide(III) aminocarboxylates have been prepared but investigations in solution have shown the tendency of the cations to fill the inner coordination sphere with eight or nine donor atoms. Iminodiacetic acid forms 1 : 3 complexes, nitrilotriacetic acid forms 1 : 2 and diethylenetriaminepentaacetic acid forms only 1 : 1 complexes [226].

W. CONCLUSIONS

Much of the work described relates to two of the earlier actinide elements, thorium and uranium. It is readily apparent from the content of this review

that much remains to be done in the transuranium and more particularly in the transplutonium region of the actinides. In particular, recent investigations, carried out on thorium(IV) and uranium(IV) and (VI) compounds with polydentate acids such as oxydiacetate, iminodiacetate, pyridine-2,6-dicarboxylate etc., will have to be extended to the transuranium elements.

It has been proved that different complexes have been obtained on changing the experimental conditions only slightly, so although a lot of work has been done in the preparative field, much attention must be paid to rationalizing the results and a systematic study of the compounds obtained in order to prevent incomplete data leading to erroneous conclusions. Attention ought also to be paid to the interaction of carboxylate compounds of actinides with neutral mono and polydentate ligands. Recently the structures of several carboxylate compounds have been determined, covering an area of little previous investigation. Such studies provide a better rationalization of the geometries of the complexes with their IR data. The complete X-ray determination of some compounds, such as $[UO_2(CH_3COO)_2(H_2O)] \cdot H_2O$, has allowed the correction of the previous coordination geometry proposed on the basis of IR data. In addition the X-ray determination of $K_2[(UO_2)_2(C_2O_4)_3] \cdot 4\ H_2O$ has allowed us to verify the possibility, considered not very probable in recent years, to have three chelating ligands with a bite of about 2.6—2.7 Å in the equatorial plane of UO_2^{2+}.

The strong tendency to give polynuclear structures for the carboxylate compounds of actinides, makes physicochemical studies (^1H NMR, IR, Raman etc.) very difficult but undoubtedly these investigations will have to be much developed in the future.

The use of the photochemistry in the synthesis of new actinide complexes has been recently employed in the preparation of a series of uranium(IV) compounds by photolysis of uranyl(VI) complexes; much attention should be payed to this approach in the future.

Finally a requirement for a complete correlation between the properties of the carboxylate complexes in the solid state and in solution provides an impetus for study in this area.

REFERENCES

1 C. Oldham, Progr. Inorg. Chem., 10 (1968) 223.
R.E. Tapscott, R.L. Belford and I.C. Paul, Coordin. Chem. Rev., 4 (1969) 323.
G.H. Nancollas, Coordin. Chem. Rev., 5 (1970) 379.
2 W.H. Zachariasen, J. Am. Chem. Soc., 62 (1940) 1011.
3 J.N. van Niekerk and F.R. Schoening, Acta Crystallogr., 6 (1953) 609.
4 V. Amirthalingam and V.M. Padmanabhan, Acta Crystallogr., 11 (1958) 896.
5 R. Kiriyama, H. Ibamoto and R. Matsuo, Acta Crystallogr., 7 (1954) 482.
6 G.A. Barclay and C.H.L. Kennard, J. Chem. Soc., (1961) 3289.
7 J.N. van Niekerk and F.R.L. Schoening, Acta Crystallogr., 6 (1953) 227.
8 J.N. van Niekerk, F.R.L. Schoening and J.F. de Wet, Acta Crystallogr., 6 (1953) 501.
9 J.N. van Niekerk, F.R.L. Schoening and J.H. Talbot, Acta Crystallogr., 6 (1953) 720.
10 W.H. Zachariasen and H.A. Plettinger, Acta Crystallogr., 12 (1959) 526.

11 J.L. Galigné, M. Mouvet and F. Falgueirettes, Acta Crystallogr., Sect. B, 26 (1970) 368.
12 Y. Kuroda and M. Kubo, Spectrochim. Acta, Part A, 23 (1967) 2779.
13 U. Lorenzelli and F. Gesmundo, Atti Accad. Naz. Lincei, Cl. Sci. Fis. Mat. Natur., Rend., 36 (1964) 485.
14 N.W. Alcock, V.M. Tracy and T.C. Waddington, J. Chem. Soc. Dalton, (1976) 2243.
15 F. Weigel and N. Ter. Meer, Inorg. Nucl. Chem. Lett., 3 (1967) 403.
16 F. Weigel and N. Ter. Meer, Z. Naturforsch. B, 25 (1971) 504.
17 B. Jezowska-Trzebiatowska and J. Drozdzynski, J. Inorg. Nucl. Chem., 31 (1969) 727.
18 L.R. Crisler, J. Inorg. Nucl. Chem., 34 (1972) 3263.
19 A. Pabst, J. Chem. Phys., 11 (1943) 145.
20 I. Mayer, M. Steinberg, F. Feigenblatt and A. Glasner, J. Phys. Chem., 66 (1962) 1737.
21 L.R. Crisler, J. Inorg. Nucl. Chem., 35 (1973) 4309.
22 J.J. Berzelius, Pogg. Ann., 16 (1829) 385.
23 J.J. Chydenius, Pogg. Ann., 119 (1863) 43.
24 Gmellins Handbuch der anorganischen Chemie. 8. Auflage. Syst.-Nr. 44. Thorium und Isotope, Verlag Chemie, Weinheim, 1955, pp. 3, 302.
25 P.T. Cleve, Bih. Svenska Akad. Handl., 2 N. 6 (1874) 15 (quoted in ref. 24).
26 V.A. Golovnya and O.M. Ivanova, Russ. J. Inorg. Chem., 8 (1963) 1290.
27 B. Claudel and B. Mentzen, Bull. Soc. Chim. Fr. (1966) 1547.
28 H. Reihlen and M. Debus, Z. Anorg. Allg. Chem., 178 (1929) 157.
29 B. Sahoo, S. Panda and D. Patnaik, J. Indian Chem. Soc., 37 (1960) 594.
30 M. Chevreton, B. Claudel and B. Mentzen, J. Chem. Phys., 65 (1968) 890.
31 E'.G. Arutyunyan, A.S. Antsyshkina and E'.Ya. Balta, J. Struct. Chem. (USSR), 7 (1966) 448.
32 J. Hauck, Inorg. Nucl. Chem. Lett., 12 (1976) 617.
33 E.W. Bohres, Rep. Jul-1080-NC (1974).
34 R. Weinland and A. Stark, Ber. Dtsch. Chem. Ges., 59 (1926) 471.
35 K.I. Petrov, A.K. Molodkin, O.D. Saralidze and O.M. Ivanova, Russ. J. Inorg. Chem., 13 (1968) 895.
36 O.N. Evstaf'eva, O.M. Ivanova, A.K. Molodkin, G.A. Dvoryantseva and M.I. Struchkova, Dokl. Akad. Nauk SSSR, 172—174 (1967) 118.
37 A.K. Molodkin, O.M. Ivanova, Z.V. Belyakova and L.E. Kolesnikova, Russ. J. Inorg. Chem., 15 (1970) 1692.
38 A. Rosenheim and M. Kelmy, Z. Anorg. Allg. Chem., 206 (1932) 31.
39 G.D. Buttress and M.A. Hughes, J. Chem. Soc. A, (1968) 1272.
40 R. Bressat, B. Claudel and A. Navarro, Bull. Soc. Chim. Fr., 12 (1968) 4807.
41 A. Navarro, Ann. Chim. (Paris), 6 (1971) 349.
42 H.J. Schenk, E.W. Bohres and K. Schwochau, Inorg. Nucl. Chem. Lett., 11 (1975) 201.
43 H.J. Schenk, E.W. Bohres and K. Schwochau, J. Inorg. Nucl. Chem., 37 (1975) 2491.
44 D. Brown, T.L. Hall and P.T. Moseley, J. Chem. Soc. Dalton Trans., (1973) 686.
45 E.W. Bohres, J. Hauck, K. Schwochau and O. Greis, to be published.
46 G. Courtois, Bull. Soc. Chim. Fr., 4 (1913) 449.
47 A. Muller, Z. Anorg. Allg. Chem., 93 (1915) 267.
48 S. Sampath and G. Aravamudan, J. Inorg. Nucl. Chem., 35 (1973) 1377.
49 B. Claudel, B. Mentzen, A. Navarro and J.P. Puaux, C.R. Acad. Sci., Ser. C, 275 (1972) 1417.
50 B. Claudel and H. Sautereau, Spectrochim. Acta, Part A, 29 (1973) 1687.
51 C. Gorller-Walrand and S. De Jaegere, J. Chim. Phys. Phys.-Chim. Biol., 69 (1972) 726.
52 B. Claudel, B. Mentzen, A. Navarro and H. Sautereau, J. Inorg. Nucl. Chem., 38 (1976) 759.
53 C. Dittrich, Z. Phys. Chem., 29 (1899) 449.
54 J. Wertcheim, J. Prakt. Chem., 29 (1843) 209.
55 G. Courtois, C.R. Acad. Sci., Ser. C, 158 (1914) 1511.
56 A. Muller, Z. Anorg. Allg. Chem., 109 (1920) 235.
57 B. Mentzen and G. Giorgio, J. Inorg. Nucl. Chem., 32 (1970) 1509.

58 V. Amirthalingam, D.V. Chandran and V.M. Padmanabhan, Acta Crystallogr., 12 (1959) 821.
59 C. Duval, Anal. Chim. Acta, 20 (1959) 263.
60 I. Kobayashi, Rikagaku Kenkyusho Hokoku, 36 (1960) 710.
61 P.S. Clough, D. Dollimore and P. Grundy, J. Inorg. Nucl. Chem., 31 (1969) 361.
62 L. Vannino, Chem. Ztg., 35 (1911) 1005.
63 E. Spath, Monatsh. Chem., 33 (1912) 235.
64 A.D. Gel'man, A.I. Moskin, L.M. Zaittsen and M.P. Mefodeve, The Complex Compounds of Transuranium Elements, Consultants Bureau, New York, 1962.
65 G.L. Caldow, A.B. Van Cleave and R.L. Eager, Can. J. Chem., 38 (1960) 772.
66 G. Giorgio, B. Mentzen, M. Breysse and B. Claudel, J. Inorg. Nucl. Chem., 32 (1970) 1517.
67 C. Panattoni, R. Graziani, G. Bandoli, B. Zarli and G. Bombieri, Inorg. Chem., 8 (1969) 320.
68 B. Zarli, L. Volponi, L. Sindellari and G. De Paoli, J. Inorg. Nucl. Chem., 35 (1973) 231.
69 B. Zarli, G. Dall'Olio and L. Sindellari, J. Inorg. Nucl. Chem., 38 (1976) 491.
70 V.V. Savant and C.C. Patel, J. Inorg. Nucl. Chem., 31 (1969) 2319.
71 C. Panattoni, R. Graziani, U. Croatto, B. Zarli and G. Bombieri, Inorg. Chim. Acta, 2 (1968) 43.
72 P. Markov and T.V. Sargeeva, Russ. J. Inorg. Chem., 6 (1961) 1049.
73 H. Brintzinger and F. Jahn, Z. Anorg. Allg. Chem., 231 (1937) 342.
74 L.H. Jones and R.A. Penneman, J. Chem. Phys., 21 (1953) 542.
75 L.H. Jones, J. Chem. Phys., 23 (1955) 2105.
76 J.L. Rian and W.E. Keder, Advan. Chem. Seri., 71 (1967) 335.
77 L.B. Asprey, S.E. Stephanou and R.A. Penneman, J. Am. Chem. Soc., 73 (1951) 5715.
78 J.K. Dawson, J. Chem. Soc., (1952) 2705.
79 Z.M. Alikhanova and G.V. Ellevert, Russ. J. Inorg. Chem., 16 (1971) 63.
80 N.V. Zubova, V.M. Makarov, V.D. Nikol'skii, P.M. Petrov, E.G. Teterin and N.T. Chebotarev, Russ. J. Inorg. Chem., 13 (1968) 442.
81 N.V. Zubova, V.M. Makarov, V.D. Nikol'skii, P.M. Petrov, E.G. Teterin and N.T. Chebotarev, Russ. J. Inorg. Chem., 13 (1968) 493.
82 K.K. Tripathy, B. Sahoo and D. Patnaik, J. Indian Chem. Soc., 36 (1959) 739.
83 R.C. Paul, J.S. Ghotra and M.S. Bains, J. Inorg. Nucl. Chem., 27 (1965) 265.
84 R.C. Paul, M.S. Saran, J.S. Ghotra and M.S. Bains, Indian J. Chem., 7 (1969) 381.
85 D. Grdenic and B. Korpar-Colig, J. Inorg. Nucl. Chem., 30 (1968) 1751.
86 I. Jelenic, D. Grdenic and A. Bezjak, Acta Crystallogr., 17 (1964) 758.
87 J. Selbin and M. Schober, J. Inorg. Nucl. Chem., 28 (1966) 817.
88 G. Iantsch and W. Urbach, Helv. Chim. Acta, 2 (1919) 490.
89 S. Panda and D. Patnark, J. Indian Chem. Soc., 33 (1956) 877.
90 R.N. Kapoor, K.C. Pande and M.C. Metrotra, J. Indian Chem. Soc., 35 (1918) 157.
91 K.N. Kovalenko, D.V. Kazachenko and O.N. Samsonova, Russ. J. Inorg. Chem., 8 (1963) 1163.
92 R.C. Paul, M.S. Saran and M.S. Bains, Indian J. Chem., 7 (1969) 384.
93 A.A. Eliseev, A.K. Molodkin and O.M. Ivanova, Russ. J. Inorg. Chem., 12 (1967) 1507.
94 K.N. Kovalenko, D.V. Kazachenko and O.N. Samsonova, Russ. J. Inorg. Chem., 8 (1963) 407.
95 G. Canneri, Gazz. Chim. Ital., 55 (1925) 33.
96 A.K. Molodkin, O.M. Ivanova and G.A. Skotnikova, Russ. J. Inorg. Chem., 12 (1967) 57.
97 K.W. Bagnall and O.V. Lopez, J. Chem. Soc. Dalton, (1976) 1109.
98 E. Spinner, J. Chem. Soc., (1964) 4217.
99 N.W. Alcock, J. Chem. Soc. Dalton, (1973) 1610.
100 D. Butterfield and R. Woollatt, J. Inorg. Nucl. Chem., 30 (1968) 801.
101 M.L. Salutsky and H.W. Kirby, Anal. Chem., 28 (1956) 1780.

102 I.L. Jenkins, F.H. Moore and M.L. Waterman, Chem. Ind. (London), (1963) 35.
103 D.M. Chackraburtty, Acta Crystallogr., 16 (1963) 834.
104 J.K. Dawson and R.M. Elliott, Report AERE C/R-1207 (1953).
105 G.S. Rao, M.S. Subramanian and G.A. Welch, J. Inorg. Nucl. Chem., 25 (1963) 1293.
106 V. Scherer and M. Fochler, J. Inorg. Nucl. Chem., 30 (1968) 1433.
107 R.L.N. Sastry, S.R. Yoganarasimhan, P.N. Mehrota and C.N.R. Rao, J. Inorg. Nucl. Chem., 28 (1966) 1165.
108 L.E. Marchi, in L.F. Audrieth Ed., Inorganic Synthesis, Vol. 3, McGraw-Hill, New York, 1950, p. 166.
109 W.W. Wendlandt, Anal. Chem., 30 (1958) 58.
110 W.W. Wendlandt, Anal. Chem., 31 (1959) 408.
111 J.M. Clevelend, Coord. Chem. Rev., 5 (1970) 101.
112 J.W. Lindsay, H.N. Robinson, H.L. Bramlet and A.J. Johnson, J. Inorg. Nucl. Chem., 32 (1970) 1559.
113 A.G. Burney and J.A. Porter, Inorg. Nucl. Chem. Lett., 3 (1967) 79.
114 T.L. Markin, J. Inorg. Nucl. Chem., 7 (1958) 290.
115 W.W. Wendlandt, T.D. George and G.R. Horton, J. Inorg. Nucl. Chem., 17 (1961) 273.
116 R.W.M.D'Eye and P.G. Sellman, J. Inorg. Nucl. Chem., 1 (1955) 143.
117 V.M. Padmanabham, S.C. Saraiya and A.K. Sundaram, J. Inorg. Nucl. Chem., 12 (1960) 356.
118 G.R. Waterbury, R.M. Douglass and C.F. Metz, Anal. Chem., 33 (1961) 1018.
119 E.S. Maxwell, in G.T. Seaborg and J.J. Katz Eds., The Actinide Elements, National Nuclear Energy Series, Vol. IV-14A, McGraw-Hill, New York, 1954, p. 420.
120 A.K. Molodkin, T.A. Balakaeva and A.N. Kuchumova, Russ. J. Inorg. Chem., 13 (1968) 1095.
121 K. Nakamoto and P.J. McCarthy, Spectroscopy and Structure of Metal Chelate Compounds, J. Wiley, New York, 1968, p. 268.
122 E. Staritzky and A.L. Truitt, in G.T. Seaborg and J.J. Katz Ed., The Actinide Elements, National Nuclear Energy Series, Vol. IV-14A, McGraw-Hill, New York, 1954, p. 797.
123 A.I. Moskvin and A.D. Gel'man, Russ. J. Inorg. Chem., 3 (1958) 188.
124 I.L. Jenkins and M.J. Waterman, J. Inorg. Nucl. Chem., 26 (1964) 131.
125 A. Glasner, J. Inorg. Nucl. Chem., 26 (1964) 1475.
126 S.K. Awasthi, K.L. Chawal and D.M. Chackraburtty, J. Inorg. Nucl. Chem., 35 (1973) 3805.
127 C. Keller, The Chemistry of the Transuranium Elements, Verlag Chemie, GmbH, (1971), p. 280.
128 A.D. Gel'man and L.P. Sokhina, Russ. J. Inorg. Chem., 3 (1958) 49.
129 S.K. Awasthi, K.L. Chawla and D.M. Chackraburtty, J. Inorg. Nucl. Chem., 36 (1974) 2521.
130 A. Colani, Bull. Soc. Chim. Fr., 37 (1925) 856.
131 N.C. Jayadevan and D.M. Chackraburtty, Acta Crystallogr., Sect. B, 28 (1972) 3178.
132 A. Boullè, R. Jary and M. Dominè-Bergès, C.R. Acad. Sci., Ser. C, 230 (1950) 300.
133 I. Kobayashi, Rep. Inst. Chem. Res., Kyoto Univ., 36 (1960) 710.
134 R. Bressat, B. Claudel and Y. Trambouze, Bull. Soc. Chim. Fr., (1963) 464.
135 G.D. Buttress and M.A. Huges, J. Chem. Soc. A, (1968) 1985.
136 M.P. Mefod'eva, N.N. Krot, T.V. Smirnova and A.D. Gel'man, Sov. Radiochem., 11 (1969) 187.
137 A.D. Gel'man and L.E. Drabkina, Russ. J. Inorg. Chem., 3 (1958) 57.
138 N.W. Alcock, Chem. Commun., (1968) 1327.
139 N.W. Alcock, J. Chem. Soc. Dalton, (1973) 1614.
140 N.W. Alcock, J. Chem. Soc. Dalton, (1973) 1616.
141 M.G. Wyruboff, Bull. Soc. Chim. Fr. Minerol., 32 (1909) 340.
142 N.W. Alcock, J. Chem. Soc., A, (1968) 1588.

143 G.A. Barclay, T.M. Sabine and J.C. Taylor, Acta Crystallogr., 19 (1965) 205.
144 R.E. Sievers and J.C. Bailar Jr., Inorg. Chem., 1 (1961) 174.
145 N.K. Dalley, M.H. Mueller and S.H. Simonsen, Inorg. Chem., 10 (1971) 323.
146 B. Beagley and R.W. Small, Acta Crystallogr., 17 (1964) 783.
147 Complex Compounds of Uranium, I.I. Charnyaev Ed., translated from Russian, published by the Israel Program for Scientific Translations, Jerusalem, 1966.
148 R.N. Shchelokov, V.I. Belomestnykh and Yu.N. Mikailov, Russ. J. Inorg. Chem., 14 (1969) 829.
149 R.N. Shchelokov and V.I. Belomestnykh, Russ. J. Inorg. Chem., 14 (1969) 1491.
150 J.H. Burns and C. Musikas, Inorg. Chem., 16 (1977) 1619.
151 I.I. Chernyaev and R.N. Shchelokov, Russ. J. Inorg. Chem., 6 (1961) 284.
152 I.I. Chernyaev and R.N. Shchelokov, Russ. J. Inorg. Chem., 8 (1963) 795.
153 I.I. Chernyaev and R.N. Shchelokov, Russ. J. Inorg. Chem., 8 (1963) 1035.
154 I.I. Chernyaev, V.A. Golovnya and R.N. Shchelokov, Russ. J. Inorg. Chem., 2 (1957) 1763.
155 N.C. Jayadevan, R.M.A. Dias and D.M. Chackraburtty, J. Inorg. Nucl. Chem., 35 (1973) 1037.
156 L.M. Kovba, E.A. Ippolitova, Yu.P. Simanov and V.I. Spitsyn, Dokl. Akad. Nauk SSSR, 120 (1958) 1042.
157 H.R. Hoekstra and R.H. Marshall, Advan. Chem. Seri., 71 (1967) 211.
158 R.N. Shchelokov and V.I. Belomestnykh, Russ. J. Inorg. Chem., 15 (1970) 70.
159 R.N. Shchelokov and V.I. Belomestnykh, Russ. J. Inorg. Chem., 15 (1970) 74.
160 R.N. Shchelekov and V.I. Belomestnykh, Russ. J. Inorg. Chem., 12 (1967) 843.
161 Y. Baskin and N.S. Krishna Prasad, J. Inorg. Nucl. Chem., 26 (1964) 1385.
162 N.S. Krishna Prasad, J. Inorg. Nucl. Chem., 21 (1961) 379.
163 G.V. Jere and C.C. Parel, J. Inorg. Nucl. Chem., 20 (1961) 343.
164 V.P. Markov and I.V. Tsapkina, Russ. J. Inorg. Chem., 7 (1962) 1057.
165 S.M. Sinitsyna and N.M. Sinitsyn, Dokl. Chem., 166—168 (1966) 467.
166 A.S. Solovkin and E.M. Indikov, Russ. J. Inorg. Chem., 13 (1968) 1051.
167 G.N. Volchkov, E.I. Krylov, V.A. Sharov and A.A. Khakhalov, Russ. J. Inorg. Chem., 15 (1970) 21.
168 P.G. Hagan and J.M. Cleveland, J. Inorg. Nucl. Chem., 28 (1966) 2905.
169 G. Gibson, D.M. Gruen and J.J. Katz, J. Am. Chem. Soc., 74 (1952) 2103.
170 R. Sjoblom and J.C. Hindman, J. Am. Chem. Soc., 73 (1951) 1744.
171 A.D. Gel'man, V.I. Blokhin, T.N. Bukhtiyarova and N.N. Krot, Russ. J. Inorg. Chem., 15 (1970) 975.
172 A.D. Gel'man and V.P. Zaitseva, Dokl. Chem., 157—159 (1964) 805.
173 U. Casellato, M. Vidali and P.A. Vigato, Inorg. Chim. Acta, 18 (1976) 77.
174 S.H. Eberle and W. Robel, Inorg. Nucl. Chem. Lett., 4 (1968) 113.
175 S.H. Eberle and W. Robel, Inorg. Nucl. Chem. Lett., 6 (1970) 359.
176 G. den Boef and F. Poppa, Talanta, 15 (1968) 1058.
177 D.V. Naik and C. Curran, Inorg. Chem., 10 (1971) 1017.
178 G. Starhs and R.E. Dickerson, Acta Crystallogr. Sect., B, 24 (1968) 571.
179 B.H. Bersted, R.L. Belford and I.C. Paul, Inorg. Chem., 7 (1968) 1557.
180 M.G.B. Drew, R.W. Watthews and R.A. Walton, J. Chem. Soc. A, (1970) 1405.
181 G. Gaw, W.R. Robinson and R.A. Walton, Inorg. Nucl. Chem. Lett., 7 (1971) 695.
182 K.J. Palmer, R.Y. Wong and J.C. Lewis, Acta Crystallogr., Sect B, 28 (1972) 223.
183 J. Albertsson, Acta Chem. Scand., 26 (1972) 1023.
184 S. Degetto, G. Marangoni, L. Baracco, S. Gurrieri and G. Siracusa, J. Inorg. Nucl. Chem., 37 (1975) 1185.
185 G. Marangoni, S. Degetto and U. Croatto, Talanta, 20 (1973) 1217.
186 A. Immirzi, G. Bombieri, S. Degetto and G. Marangoni, Acta Crystallogr., Sect. B, 31 (1975) 1023.

187 G. Marangoni, S. Degetto, R. Graziani, G. Bombieri and E. Forsellini, J. Inorg. Nucl. Chem., 36 (1974) 1787.
188 L. Cattalini, L. Baracco, S. Degetto and G. Marangoni, Atti Acad. Peloritana, Pericolanti, Cl. Sci. Fis., Mat. Nat., 51 (1971) 267.
189 L. Cattalini, L. Baracco, S. Degetto, G. Marangoni, L. Maresca and L. Sindellari, Gazz. Chim. Ital., 104 (1974) 915.
190 G. Bombieri, S. Degetto, E. Forsellini, A. Immirzi and G. Marangoni, Proceedings of the Yugoslav Centre of Crystallography, Suppl. to Vol. 11, (1976) 17, A49.
191 L. Baracco, G. Bombieri, S. Degetto, E. Forsellini, R. Graziani and G. Marangoni, Inorg. Nucl. Chem. Lett., 10 (1974) 1045.
192 G. Bor, L. Magon, L. Maresca and G. Natile, J. Chem. Soc. Dalton, (1973) 1308.
193 G. Bombieri, E. Forsellini, R. Graziani, G. Tomat and L. Magon, Inorg. Nucl. Chem. Lett., 8 (1972) 1003.
194 G. Bombieri, U. Croatto, R. Graziani, E. Forsellini and L. Magon, Acta Crystallogr., Sect. B, 30 (1974) 407.
195 G. Bombieri, R. Graziani and E. Forsellini, Inorg. Nucl. Chem. Lett., 9 (1973) 551.
196 G. Sbrignadello, G. Tomat, G. Battiston, G. De Paoli and L. Magon, Inorg. Chim. Acta, 18 (1976) 195.
197 G. Pregaglia, G. Mazzanti and D. Morero, Ann. Chim. (Rome), 49 (1959) 1784.
198 M.J. Taylor, J. Chem. Soc. A, (1967) 1462.
199 H. Wieser and P.J. Krueger, Spectrochim. Acta, Part A, 26 (1970) 1349.
200 J. Albertsson, Acta Chem. Scand., 22 (1968) 1563.
201 M. Krishnamurthy and K.B. Morris, Inorg. Chem., 8 (1969) 2620.
202 G. Bombieri, E. Forsellini, G. Tomat, L. Magon and R. Graziani, Acta Crystallogr., Sect. B, 30 (1974) 2659.
203 T.R. Bhat and M. Krishnamurthy, J. Inorg. Nucl. Chem., 26 (1964) 587.
204 R.N. Shchelokov and V.I. Belomestnykh, Russ. J. Inorg. Chem., 12 (1967) 45..
205 N.N. Krot, N.P. Ermolaev and A.D. Gel'man, Russ. J. Inorg. Chem., 7 (1962) 1062.
206 J.J.R. Frausto da Silva and M. Lourdes Sadler Simoes, J. Inorg. Nucl. Chem., 32 (1970) 1313.
207 H. Brintzinger and G. Hesse, Z. Anorg. Allg. Chem., 249 (1942) 113.
208 H. Brintzinger and G. Hesse, Z. Anorg. Allg. Chem., 249 (1942) 299.
209 H. Brintzinger, H. Thiele and U. Muller, Z. Anorg. Allg. Chem., 251 (1943) 285.
210 R.F. Boguchi and A. Martell, J. Am. Chem. Soc., 80 (1958) 4170.
211 A.R. Fried and A.E. Martell, J. Am. Chem. Soc., 93 (1971) 4695.
212 T.D. Smith, J. Inorg. Nucl. Chem., 11 (1959) 314.
213 P.N. Palei and Hsü Li-yiian, Russ. J. Inorg. Chem., 6 (1961) 1337.
214 N.P. Ermolaev and N.N. Krot, Russ. J. Inorg. Chem., 8 (1963) 1282.
215 J.L. Hoard and J.V. Silverton, Inorg. Chem., 2 (1963) 235.
216 D.L. Ehman and D.T. Sawyer, Inorg. Chem., 9 (1970) 204.
217 B. Jezowka-Trzebiatowska, J. Chim. Phys. Phys.-Chim. Biol., 60 (1963) 843.
218 G. Sbrignadello, G. Tomat and G. Battiston, VIII convegno Nazionale di Chimica Inorganica, Jesolo, 1975, A23.
G. Battiston and G. Sbrignadello, Inorg. Chim. Acta, 26 (1978) 145.
219 L. Maresca and G. Bor, private communication.
220 K.S. Rajan and A.E. Martell, J. Inorg. Nucl. Chem., 26 (1964) 789.
221 J.J.R. Frausto da Silva and M. Lourdes Sadler Simoes, Talanta, 15 (1968) 609.
222 K. Ito and H.J. Bernstein, Can. J. Chem., 34 (1956) 170.
223 K. Nakamura, J. Chem. Soc. Jpn., 79 (1958) 1411, 1420.
224 L.R. Nassimbeni, A.L. Rodgers and J.M. Haigh, Inorg. Chim. Acta, 20 (1976) 149.
225 M. Aley Jr., Q.C. Johnson, H.D. Cowan and J.F. Lemons, J. Inorg. Nucl. Chem., 25 (1967) 2327.
226 S.H. Eberle, Comprehensive Inorganic Chemistry, Vol. 5, Pergamon Press, 1973, p. 431.
227 R. Muxart, R. Guillanmont and G. Boussieres, Actinides Rev., 1 (1969) 223.

228 L.P. Sokhina and A.D. Gel'man, Russ. J. Inorg. Chem., 5 (1960) 487.
229 M. Bideau, R. Bressat, B. Mentzen and A. Navarro, C.R. Acad. Sci., Ser. C, 271 (1970) 225.
230 R. Bressat, B. Claudel and A. Navarro, C.R. Acad. Sci., Ser. C, 266 (1968) 1260.
231 L. Cattalini, U. Croatto, S. Degatto and E. Tondello, Inorg. Chim. Acta, Rev., 5 (1971) 19.
232 I.I. Kapshukov, Yu. F. Volkov, E.P. Moskvichev, I.A. Lebedev and G.N. Yakovlev, J. Struct. Chem., 12 (1971) 77.
233 D. Hall, A.D. Rae and T.N. Waters, Acta Crystallogr., 22 (1967) 258.
234 J.M. Haigh and D.A. Thornton, Inorg. Nucl. Chem. Lett., 6 (1970) 231.
235 J.E. Fleming and H. Lynton, Can. J. Chem., 45 (1967) 1637.
236 G. Sbrignadello, G. Battiston, G. Tomat and O. Traverso, Inorg. Chim. Acta, 24 (1977) L43
237 G. Battiston, G. Sbrignadello and G. Tomat, private communication.
238 I. Grenthe, Acta Chem. Scand., 25 (1971) 3347.
239 I. Grenthe, Acta Chem. Scand., 25 (1971) 3721.
240 I. Grenthe, Acta Chem. Scand., 26 (1972) 1479.
241 K. Nakamoto, P. McCarty and B. Miniatas, Spectrochim. Acta, 21 (1965) 379.
242 G. Sbrignadello, G. Tomat, G. Battistion, P.A. Vigato and O. Traverso, J. Inorg. Nucl. Chem., in press.
243 R. Larsson, Acta Chem. Scand., 19 (1965) 783.
244 D.V. Kazachenko and K.N. Kovalenko, Russ. J. Inorg. Chem., 11 (1966) 871.
245 D. Brown, in K.W. Bagnall Ed., Inorganic Chemistry, Series I, Vol. 7, Lanthanides and Actinides, Butterworths, London, 1972, p. 87.
246 E. Rabinowitch and R.L. Belford, Spectroscopic and Photochemistry of Uranyl Compounds, Pergamon Press, Oxford, 1964.
247 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, London, 1970.
248 K.W. Bagnall, The Actinide Elements, Elsevier, Amsterdam, 1972.
249 A. Cassol, P. Di Bernardo, R. Portanova and L. Magon, Inorg. Chim. Acta, 7 (1973) 353.
250 P. Di Bernardo, A. Bismondo, R. Portanova, O. Traverso and L. Magon, Inorg. Chim. Acta, 18 (1976) 47.
251 Yu.Ya. Kharitonov, A.K. Molodkin and T.A. Balakaeva, Russ. J. Inorg. Chem., 14 (1969) 174.
252 A.D. Jones and G.R. Choppin, Actinides Rev., 1 (1969) 311.
253 E. Baur, C. Oullet and E. Wackerlin, Z. Wiss. Photogr., Photophys. Photochem., 30 (1931) 88.
254 B. Sahoo and D. Patuaik, J. Indian Chem. Soc., 36 (1959) 483.
255 G.E. Heckler, A.E. Taylor, C. Jensen, D. Percival, R. Jensen and P. Fung, J. Phys. Chem., 67 (1963) 1.
256 D. Greatorex, R.J. Hill, T.J. Kemp and T.J. Stone, J. Chem. Soc. Faraday I, 68 (1972) 2059.
257 E. Bauer and A. Rebmann, Helv. Chim. Acta, 5 (1922) 221.
258 W.G. Leighton and G.S. Forbes, J. Am. Chem. Soc., 52 (1930) 3139.
259 D.H. Volman and J.R. Seed, J. Am. Chem. Soc., 86 (1964) 5095.
260 L.J. Heidt, J. Phys. Chem., 46 (1942) 624.
261 C.A. Parker and C.G. Hatchard, J. Phys. Chem., 63 (1959) 22.
262 O. Traverso and S. Sostero, Atti Accad. Sci. Ferrara, 51 (1973—1974) 1.
263 B.F. Mentzen, J.P. Puaux and H. Loiseleur, Acta Crystallogr., Sect. B, 33 (1977) 1848.
264 E.R. Russel and M.L. Hyder, Inorg. Nucl. Chem. Lett., 12 (1976) 247.
265 J. Howatson, D.M. Grev and B. Morosin, J. Inorg. Nucl. Chem., 37 (1975) 1933.
266 N.C. Jayadevan, K.D. Singh Mudher and D.M. Chackraburtty, Acta Crystallogr., Sect. B, 31 (1975) 2277.

267 J.P. Legros and Y. Jeannin, Acta Crystallogr., Sect. B, 32 (1976) 2497.
268 R.N. Shchelokov, V.I. Belomestnykh and I.M. Orlova, Dokl. Chem., 184—186 (1969) 430.
269 V.M. Vdovenko, V.A. Vodovatov, L.G. Mashirov and D.N. Suglobov, Proc. Moscow Symp. Chem. Transuranium Elem., 1976, p. 123.
270 V.A. Vodovatov, V.B. Kolokoltsov, T.V. Kavalena, L.G. Moshirov, D.N. Suglobov and V.G. Sles, Proc. 4th Int. Symp. Transplutonium Elem., 1975, (1976) p. 247.
271 D.S. Gorbenko-Germanov and R.A. Zenkova, Russ. J. Inorg. Chem., 11 (1966) 282.
272 K.W. Bagnall, Int. Rev. Sci., Ser. 2, 7 (1975) 41.
273 G. Bandoli, R. Graziani and B. Zarli, Acta Crystallogr., Sect. B., 24 (1968) 1129.
274 A. Ferrari, L. Cavalca and M.E. Tani, Ann. Chim. (Rome), 48 (1958) 1230.
275 R. Graziani, B. Zarli and G. Bandoli, Ric. Sci., 37 (1967) 984.
276 L. Magon, G. Tomat, A. Bismondo, R. Portanova and U. Croatto, Gazz. Chim. Ital., 104 (1974) 967.