The Chemistry
of the Transuranium Elements

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9. Chemistry of the actinides in aqueous solution

9.1. Stability of the individual oxidation states

The various actinide ions show in some cases remarkably different behavior in aqueous solution in comparison with the solid state. Data concerning stability to oxidation-reduction reactions, disproportionation and characteristic autoradiation effects for the individual ions are presented below:

Ac(III): stable

Th(III): unknown in solution, the reaction of ThI_3 with dilute acids leads to the formation of Th^{4+} with evolution of hydrogen

Th(IV): stable

Pa(III): unknown in solution

Pa(IV): stable in the absence of air, rapidly oxidized to Pa(V) by oxygen. can be prepared from Pa(V) using strong reducing agents such as Zn dust or Cr(II) salts or by electrolytic reduction

Pa(V): stable, can be reduced to Pa(IV) with strong reducing agents, shows a marked tendency to irreversible hydrolysis, Pa^{5-} and the distinct "yl" ion PaO_2^+ are unknown as ionic species

U(III): reduces water to hydrogen. can be prepared from U(IV) with strong reducing agents, e. g. Zn dust or by electrolytic reduction

U(IV): stable in the absence of air, otherwise slowly oxidized to UO_2^{2+}, obtainable from UO_2^{2+} solutions with medium-strength reducing agents such as Na-dithionite, lead (Pb reductor) or, better, by electrolytic reduction

UO_2^+: unstable, disproportionates rapidly to U(IV) – U(VI). most stable at pH 2−4

UO_2^{2+}: stable, a strong tendency to hydrolysis is observed above pH 3

Np(III): stable in the absence of oxygen. otherwise slowly oxidized to Np(IV): can be prepared from Np(IV) with medium-strength reducing agents. e. g. Pt/H_2

Np(IV): stable. undergoes very slow oxidation to NpO_2^+ by oxygen

NpO_2^+: stable. disproportionates only at high acidities. e. g. > 8 M HNO_3. to Np(IV) + Np(VI)

NpO_2^{2+}: stable, but can be reduced readily. e. g. by complexing agents such as 8-hydroxyquinoline. acetylacetone. and even by ion exchange resins

NpO_2^{3+}: stable in alkaline solutions. unstable in acid ones: prepared by oxidation of NpO_2^{2+} in alkaline solution with ClO^-, $S_2O_8^{2-}$. or O_3

Pu(III): stable. slowly oxidized to Pu(IV) under the action of the α radiation of the Pu isotopes

Pu(IV): stable in concentrated acid. but disproportionates to Pu(III) – Pu(VI) in weakly acid solutions free from complexing agents

PuO_2^-: stable only at pH $2-6$. disproportionates to Pu(IV) – Pu(VI) at higher and lower pH values

PuO_2^{2-}: stable. slowly reduced under the action of the α-radiation of the Pu isotopes: the rate of reduction depends on the chemical composition of the solution

PuO_2^{3-}: known only in alkaline solution: prepared by oxidation of PuO_2^{2-} in alkaline solution with $S_2O_8^{2-}$

Am(III): stable. can be oxidized to Am(V) and Am(VI) only with strong oxidizing agents. oxidation to Am(IV) is possible only in concentrated phosphoric acid solutions

Am(IV): stable only in concentrated hydrofluoric and phosphoric acid solutions. disproportionates immediately to Am(III) + Am(VI) in other solutions

AmO_2^-: stable. like NpO_2^+ disproportionation occurs only in strong acid solutions. reduced rapidly to Am(III) under the action of the α activity of the Am isotopes

AmO_2^{2-}: stable. strong oxidizing agent (like MnO_4^-). the α activity of Am isotopes causes their rapid autoreduction to Am(III) (about 4%/h for ^{241}Am)

Am(VII): Am(VI) is postulated to disproportionate in strong alkaline solutions to Am(V) – Am(VII). seems to be extremely unstable

Cm(III): stable

Cm(IV): fairly stable only in 15 M CsF solution. reduced very rapidly to Cm(III) under the action of the α-radiation of the Cm isotopes

Bk(III): stable. can be transformed into Bk(IV) only with strong oxidizing agents such as $KBrO_3$

Bk(IV): stable. strong oxidizing agent (like Ce(IV)). rapid radiolytic self-reduction to Bk(III)

Cf(II): unstable (?). obtainable from Cf(III) by reduction with amalgam (?)

Cf(III): stable

Es(II): unstable (?). obtainable from Es(III) by reduction with amalgam

Es(III): stable

Fm(II): unstable (?). obtainable from Fm(III) by reduction with amalgam

Fm(III): stable

Md(II): fairly stable. can be prepared from Md(III) with strong reducing agents (Cr(II). Eu(II). Zn)

Md(III): stable

No(II): stable. can be oxidized to No(III) only with strong oxidizing agents

No(III): stable. strong oxidizing agent with an oxidation potential of No(II)/No(III) = -1.4 V. i. e. similar to BrO_3^- or $Cr_2O_7^{2-}$

Lr(III): stable.

9.2. Complex chemistry

Numerous studies on the formation and stability of actinide complexes have been reported. In the case of the transuranium elements most data were obtained using partition measurements with unweighable amounts. Substantial discrepancies are often observed between the stability constants found for the same compound by various authors, especially when working on the tracer level. The differences result from the difficulties in the preparation of solutions with radioactive tracers of uniform oxidation state, the limited precision of radioactive concentration determinations and the fact that different stability constants are often obtained when different methods of calculation are used.

The use of computers programmed for error compensation yields mathematically perfect results, but we have not progressed to the point where the prevailing state of affairs could be described as entirely satisfactory. One problem that remains is the vast amount of time and effort called for by existing experimental procedures, a hundred or more measuring points frequently being required to investigate a complex system. The situation may be alleviated by the use of semi-automatic methods, for example the "AKUFVE"*) extraction machine developed in Sweden and used in conjunction with a computer.

Since the activity coefficients of the actinide ions and those of the complexing agents are usually unknown, and since their determination would involve more effort than could be justified in the investigation of a complex compound, a constant ionic strength μ is generally employed. Although the activity coefficients are still unknown, they are constant and the results of the investigations can be validly compared. It is, nevertheless, preferable not to confuse the results obtained by different research teams, since many of the stability constants cited in the literature must be regarded as relative rather than absolute. Most of the stability constants known today were determined using extraction and ion-exchange techniques. More recently increasing use has been made of potentiometric, spectrophotometric and other methods for the study of complex equilibria of transuranium elements.

A distinction has to be drawn between inner sphere and outer sphere complexes, which are formed by strong and weak complexing agents respectively. The reaction mechanism leading to these two types of complexes may be represented as follows:
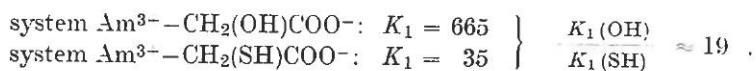

Free hydrated ions → Outer sphere complex → Transition complex → Inner sphere complex

⊖ Anion   ● H$_2$O   ⊕ Cation
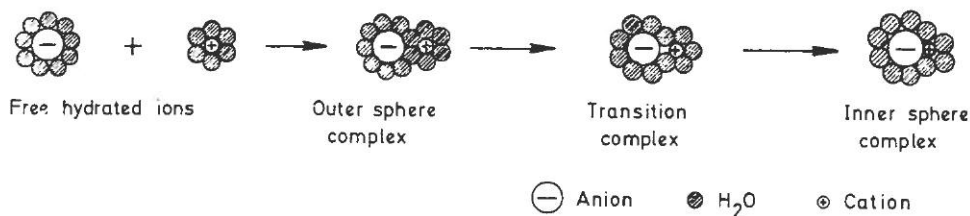
Spectrophotometric measurements provide first and foremost information concerning

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* Swedish abbreviation for "apparatus for continuous measurement of distribution factors in solvent extraction" [1].

the inner sphere complexes, since the absorption of light by the actinides is affected primarily by interactions in the inner coordination sphere. Partition methods, which rely mainly on the charge and radius of the metal ions, supply information about outer sphere complexes. Changes of entropy and enthalpy in the complex-forming reaction also provide a guide to the nature of the complex; for instance, a high positive reaction entropy can be due to displacement of water molecules from the first shell of hydration and thus point to an inner sphere complex. The entropy of the free ions is always more negative than the entropy of the complex ion, because the number of translational and rotational degrees of freedom of the ions is diminished by complex formation.

The actinides are Chatt-Ahrland A-type ions. Therefore, they coordinate preferably with, e. g. the OH-group rather than with the SH-group: the 1:1-complex of trivalent americium with the glycolate ion is much more stable than that with the thioglycolate ion as may be deduced from the stability constant K_1 ($\mu = 0.5$ (Na.H) ClO$_4$. 20°C)*):

$$\text{system } Am^{3-}-CH_2(OH)COO^-: \quad K_1 = 665 \quad \left.\right\} \quad \frac{K_1(OH)}{K_1(SH)} \approx 19 \; .$$
$$\text{system } Am^{3-}-CH_2(SH)COO^-: \quad K_1 = 35$$

The same effect is to be observed when comparing adduct chelates ($\beta_i^* = [ML_n \cdot iS]/[ML_n][S]^i$), e. g. with 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) [1a] ($\mu = 0.1$, 25.0°C. CHCl$_3$):

$$\text{system } Am(PMBP)_3\text{-tri-n-octylphosphine oxide} : \quad \beta_2^* = 3.98 \times 10^7$$
$$\text{system } Am(PMBP)_3\text{-tri-n-octylphosphine sulfide} : \quad \beta_2^* = 0.1.$$
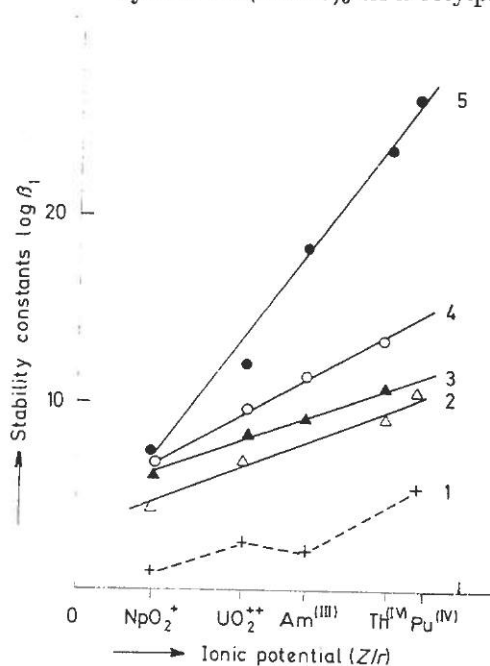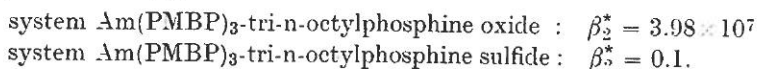

Figure 9.1. Stability constants of complexes of Am(III, Th(IV), Pu(IV), NpO$_2^+$, and UO$_2^{2+}$ as representatives of the trivalent through hexavalent actinides with acetic acid (1), acetylacetone (2), N-hydroxyethyliminodiacetic acid (3), nitrilotriacetic acid (4), and ethylenediaminetetraacetic acid (5) (S. H. Eberle, personal communication).

* The dimension of the stability constants is: $K_i = [1 \cdot mol^{-1}]$ and $\beta_i = [1^i \cdot mol^{-i}]$.

The stability of actinide element complexes in solution decreases in the sequence $M(IV) > M(III) \geqslant M(VI) > M(V)^*$. In other words, the tetravalent actinides form the strongest complexes and the pentavalent actinides, as formally monovalent "yl" ions, the weakest ones (Fig. 9.1). However, the stability of MO_2^{2+} and MO_2^+ complexes is higher than is normally found in comparable divalent or monovalent cations. Owing to the noble-gas like electronic configurations of many actinide ions, their coordination compounds are predominantly electrostatic in nature. Consequently, the stability depends primarily on the ionic potential Z/r (where Z is the charge and r the radius of the ion). This is illustrated in Figs. 9.2 and 9.3 for chelates
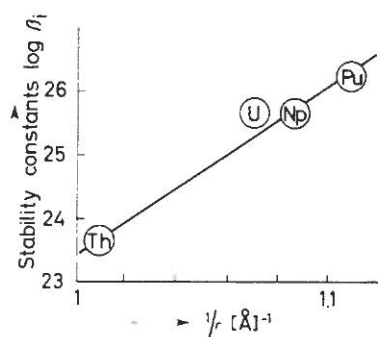

Figure 9.3. Stability constants of chelates of tetravalent actinides with ethylenediaminetetraacetic acid (S. H. Eberle, personal communication).

Figure 9.2. Stability constants of chelates of trivalent actinides and lanthanides with aminopolycarboxylic acids (H$_5$DTPA: diaminotetraethylenepentaacetic acid, H$_4$DCTA: diaminocyclohexanetetraacetic acid, H$_3$NDAP: nitrilodiaceticmonopropionic acid, H$_3$NTA: nitrilotriacetic acid) [2].
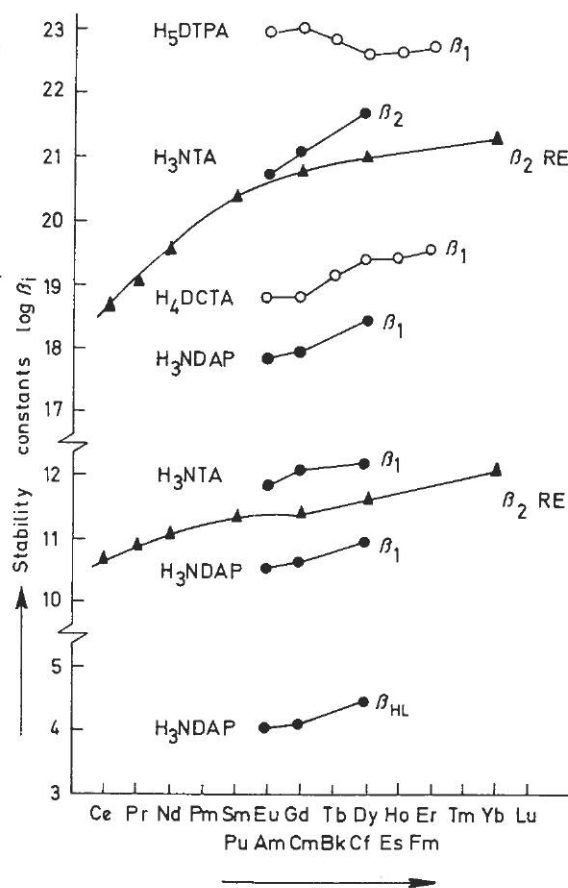
of trivalent and tetravalent actinides with aminopolycarboxylic acids, whose stability constants increase with increasing ionic potential, i. e. with increasing atomic number. For the same ionic potential, the complexes and chelates of actinide(III) ions

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* For a detailed discussion of the chemistry of actinide ions in aqueous solution see [1b, 1c].

are somewhat more stable than those of the lanthanide(III) ions. This phenomenon is attributed to the participation of $5f$ electrons in the complex bonding.

The situation is less clear for complexes of metal dioxo cations of pentavalent and hexavalent actinides. In some cases we find an increase, in others a decrease in the stability constants with increasing atomic number, and no definite pattern has emerged so far. To quote an example, with ethylenediaminetetraacetic acid the chelate of PuO_2^+ is more stable than that of NpO_2^-, while the reverse is true with aminoacetic and iminodiacetic acids.

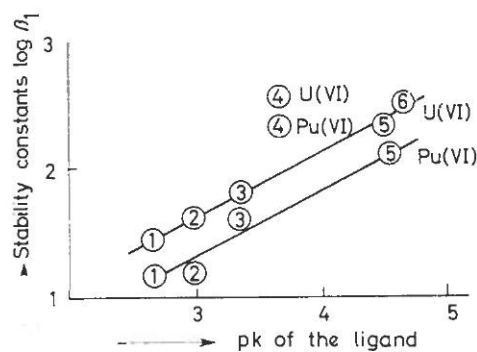The stability of complexes with similar ligands mostly increases linearly with

Figure 9.4. Stability constants of complexes of hexavalent uranium and plutonium with derivatives of acetic acid: 1 = monochloroacetic acid, 2 = furan-2-carboxylic acid, 3 = thiophen-2-carboxylic acid, 4 = glycolic acid, 5 = acetic acid, and 6 = propionic acid (S. H. Eberle, personal communication).

the pK of the ligands. This is shown in Fig. 9.4 for a series of complexes with aliphatic carboxyl ligands. If a complex does not fall into this series then a different type of bonding has to be postulated for it. This is demonstrated for the complexes with glycolic acid (Fig. 9.4); the phenomenon is explained in terms of participation of the hydroxyl group in the complex bonding: formation of a chelate instead merely of a complex.

The following sequences of decreasing tendency to complex formation may be written for the actinides:

Monovalent ligands:
OH^- > aminophenols (e. g. 8-hydroxyquinoline) > 1,3-diketones > α-hydroxycarboxylic acids > acetic acid > thiocarboxylic acids > $H_2PO_4^-$ > SCN^- > NO_3^- > > Cl^- > Br^- > I^-.

Divalent ligands:
Iminodicarboxylic acids > CO_3^{2-} > $C_2O_4^{2-}$ > HPO_4^{2-} > α-hydroxydicarboxylic acids > dicarboxylic acids > SO_4^{2-}.
Sometimes, however, these sequences are not strictly followed. The highest stability constants are found in the 8-hydroxyquinoline 1:4 chelates of tetravalent actinides, e. g. $\beta_4 \approx 10^{46}$ with $Np(IV)$-tetrakis-(5,7-dichloro-8-hydroxyquinolate) [1d].

Chelate systems with five-membered rings are normally more stable than those with six-membered rings, as may be ascertained by comparing the stability constants of $Am(III)$ acetylacetonates (Table 9.1) which form a six-membered chelate ring, with that of $Am(III)$ β-isopropyltropolonate (log $\beta_3 = 21.37$ for $\mu = 0.5$ and

Table 9.1. Stability constants of trivalent actinide chelates with 2-thenoyltrifluoroacetone (HTTA), benzoyltrifluoroacetone (HBTA), and naphthoyltrifluoroacetone (HNTA) ($\mu = 0.1$; 25°C; determined by extraction with CHCl$_3$ and 0.5 M chelating agent) [3].

Actinide ion	Stability constant $\log \beta_3$ ($= 0.1-0.3$)		
	HTTA	HBTA	HNTA
Ac^{3-}			14.63
Am^{3-}	13.3	14.48	18.31
Cm^{3-}	13.4	15.15	18.17
Cf^{3-}	14.94	16.06	18.83

25°C) [3]. β-Isopropyltropolone which may be considered as the enolform of a 1.2-diketone, forms a chelate with a five-membered ring (Fig. 9.5). Similarly, the five-membered ring chelate of α-picolinic acid with hexavalent plutonium ($\log \beta_1 = 4.58$ for $\mu = 0.1$ and 25°C) is more stable than the six-membered ring chelate of α-pico-

chelate system of
1,3-diketones

chelate system of
β-isopropyltropolone

chelate system of
squaric acid

chelate system of
α-picolinic acid

chelate system of
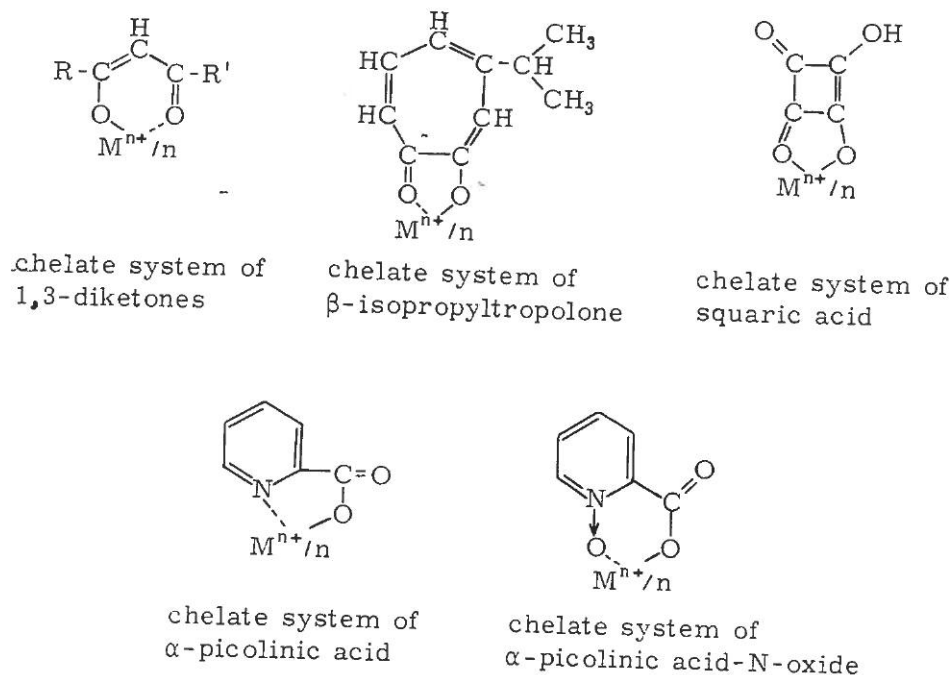α-picolinic acid-N-oxide

Figure 9.5. The ring systems of some actinide metal chelates.

linic acid-N-oxide ($\log \beta_1 = 3.33$ for $\mu = 0.1$ and 25°C) [4]. Steric hindrance of ring formation by bulky substituents or strong ring strain can reverse the stability relationships, as shown by the example of the chelates of uranium(VI) with acetylacetone ($\log \beta_1 = 8.87$ for $\mu = 0.1$ and 25°C) [5] and with squaric acid ($\log \beta_1 = 2.53$ for $\mu = 0.1$ and 25°C) [6]. In substituted 1.3-diketones of the type $R_1-COCH_2COCF_3$

the stability of the chelates decreases in the substituent sequence R_1 = naphthyl > > phenyl > thenyl > furyl (Table 9.1).

In the series of complexes of hexavalent uranium with simple fatty acids or with α-hydroxycarboxylic acids the stability rises with increasing length of the aliphatic chain (Table 9.2), and the number of complexes formed also increases with

Table 9.2. Stability constants of some complexes of hexavalent uranium with aliphatic mono-carboxylic acids ($\mu = 1.0$; 20°C; determined by potentiometric titration) [7].

Complexing agent	Stability constant K_i			
	K_1	K_2	K_3	K_4
Formic acid	77.6	12	–	–
Acetic acid	252	106	88	–
Propionic acid	340	142	64	58
Lactic acid	270	116	73	–

the chain length of the fatty acid, from two for formic acid to four for propionic acid [7]. However, the stability of the complex does not invariably increase with the chain length of the acid. For example, an alternating stability was observed in the system NpO_2^+/α-hydroxycarboxylic acids [8]. It is interesting to note that in the series of the chelates of Am(III) with nitrilotricarboxylic acids the replacement of an acetate group in nitrilotriacetic acid by propionate, butyrate, etc., leads to a decrease in the complex stability. The tendency to chelate formation diminishes as a result of the increased size of the ring system [12].

Actinide elements show a marked tendency toward complex formation with certain types of organic phosphorus compounds, as shown by the preferential extraction or the synergistic effects with phosphoric and phosphonic esters and phosphine oxides. It is therefore rather surprising that aminoalkylpolyphosphonic acids, like ethylenediamine-bis-methylenephosphonic acid [9] and ethylenediamine-bis-isopropylphosphonic acid [10], form less stable complexes than aminopolycarboxylic acids (Table 9.3). Aminosulfonic acids also exhibit very little tendency toward chelate formation with trivalent actinides.

Table 9.3. Stability constants of complexes of trivalent americium with ethylenediamine-bis-methylenephosphonic acid (H_4EDMP) and ethylenediamine-bis-isopropylphosphonic acid (H_4EDIP) ($\mu = 0.1$ M KNO_3; 25°C; determined by electrophoresis).

Complexing agent	Actinide element	Stability constant $\log \beta_1$ for			
		$M(H_3A)^{2+}$	$M(H_2A)^+$	$M(HA)$	MA^-
Ethylenediamine-bis-methylenephosphonic acid (H_4A)	Am^{3+}	6.3	8.5	12.3	16.5
	Cm^{3+}	6.2	7.9	12.2	16.5
Ethylenediamine-bis-isopropylphosphonic acid (H_4A)	Am^{3+}	6.26	8.94	13.95	18.00
	Cm^{3+}	6.26	9.04	13.85	17.70

A linear increase in the stability ($\log \beta_1$) with the number of bound donor atoms of the ligand is observed in the chelates of trivalent and tetravalent actinide ions with aminopolycarboxylic acids (Fig. 9.6), i. e., the increase in stability per
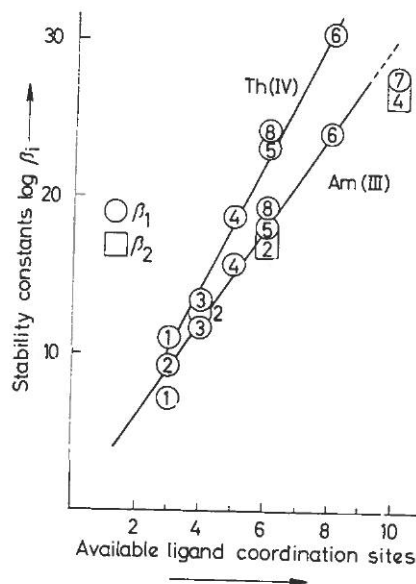
Figure 9.6. Stability constants of chelates of trivalent americium and of tetravalent thorium with various aminopolycarboxylic acids as a function of the number of available coordination sites of the chelating agent (1 = iminodiacetic acid, 2 = N-hydroxyethyliminodiacetic acid, 3 = nitrilotriacetic acid, 4 = N-hydroxyethylethylenediaminetriacetic acid, 5 = ethylenediaminetetraacetic acid, 6 = diethylenetriaminepentaacetic acid, 7 = triethylenetetraminehexaacetic acid, 8 = diaminocyclohexanetetraacetic acid) ([11] supplemented).

coordination site is constant. If a chelating agent does not fit into this linear relationship, then we may deduce that not all the coordination sites of the ligand participate in complex formation. Furthermore, Fig. 9.6 shows that, as has already been mentioned, the tetravalent actinides form more stable chelates than do trivalent ones, the difference increasing with the coordination number of the chelate.

As shown in Fig. 9.7 for the case of the NpO_2^+ ion, in pentavalent actinides the
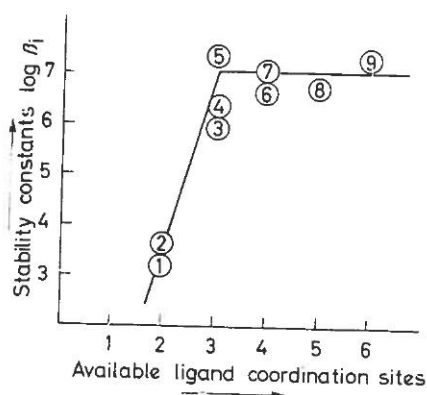
Figure 9.7. Stability constants of chelates of the NpO_2^+ ion with various aminopolycarboxylic acids as a function of the number of available coordination sites of the chelating agent (1 = aminoacetic acid, 2 = α-picolinic acid, 3 = N-hydroxyethyliminodiacetic acid, 4 = iminodiacetic acid, 5 = N-methyliminodiacetic acid, 6-nitrilotriacetic acid, 7 = nitrilodiaceticmonopropionic acid, 8 = N-hydroxyethylethylenediaminetriacetic acid, 9 = ethylenediaminetetraacetic acid) (S. H. Eberle, personal communication).

chelate stability also increases with the number of the donor atoms but only up to the limiting value of three; beyond that the stability of the chelate is independent

of the multidentate character of the ligand. In the case of the Np(V)-aminopoly-
carboxylic acids system, for example, we find a maximum value of 7 for $\log \beta_1$.
The "yl" ions can add ligands only in its equatorial plane; in pentavalent actinides a
total of four donor atoms are normally located in these positions. However, amino-
polycarboxylic acids bond only with three sites, since the oxygen atoms of the "yl"
group prevent them from being embraced on all sides, which would be required for
the addition of further groups. The still free fourth coordination site can be occupied
by an OH^--ion, giving rise to a chelate hydroxide. With nitrilotriacetic acid H_3NTA,
Np(V) thus forms the $[NpO_2(NTA)(OH)]^{3-}$-complex ion. The coordination position
occupied by the OH^--ion can also be occupied by other anions, which gives rise
to mixed 1:1:1 complexes, such as $[NpO_2(NTA)(CH_3COO)]^{3-}$ with acetic acid
replacing the OH-group [1 b].

With monobasic uni- or bidentate ligands the pentavalent transuranium
elements form complexes of the MeO_2L and MeO_2L^- types. The crystalline 1:1 com-
pounds of NpO_2^+ with acetic acid, glycolic acid, α-picolinic acid, 8-hydroxyquinoline
(HOXIN) etc., have the composition $NpO_2L \cdot 2H_2O$. In the case of $NpO_2(OXIN) \cdot 2H_2O$ the water molecules can be replaced by dimethyl sulfoxide, which gives rise
to the compound $NpO_2(OXIN) \cdot 2OS(CH_3)_2$.

The behavior of pentavalent protactinium is completely different from that
of the other pentavalent actinides, since Pa(V) does not exist as the "yl" ion PaO_2^-.
The ionic species of Pa(V) postulated in non-complexing aqueous solutions are
$PaOOH^{2-}$ and $PaO(OH)_2^+$, i. e., pentavalent protactinium occurs both as a formally
divalent and as a monovalent ion, but not as Pa^{5+}. Since other hydrolysis reactions
of the Pa(V) species are possible, it is not surprising that numerous complex species
exist and that a wide range of stability constants is given by different authors for
Pa(V) complexes [12]. The possible reactions of citric acid with Pa(V) are given in
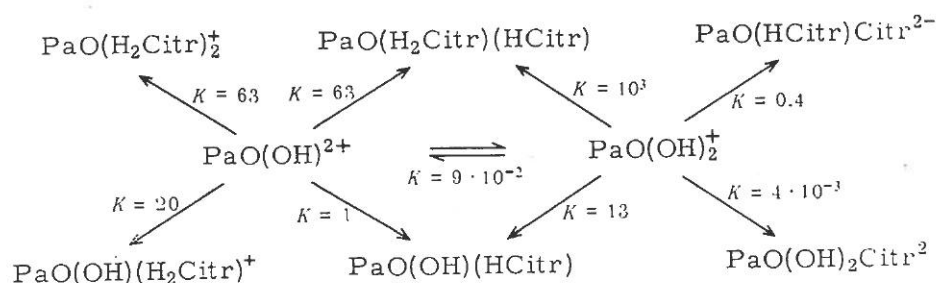Fig. 9.8 by way of illustration.

Figure 9.8. Complex formation of pentavalent protactinium with citric acid ($\mu = 3; 10^{-3} \cdot 3M$ H :
1M H_3Citr.). The equilibrium constants quoted refer to the reaction of $Pa(OH)_x^{3-x}$ with H_3Citr.

The following generalizations are valid for the stability constants of ethylene-
diamine tetraacetatechelates (Fig. 9.9) and also for most of the other cation-anion
complexes not stabilized by π-bonds:
a) The cations can be subdivided into groups on the basis of the oxidation state, elec-
tron configuration, and stability of their complexes. For each oxidation state, the

tendency of the actinides and lanthanides, as well as of the elements of the first and second main groups to form complexes, is less than that of the transition elements.
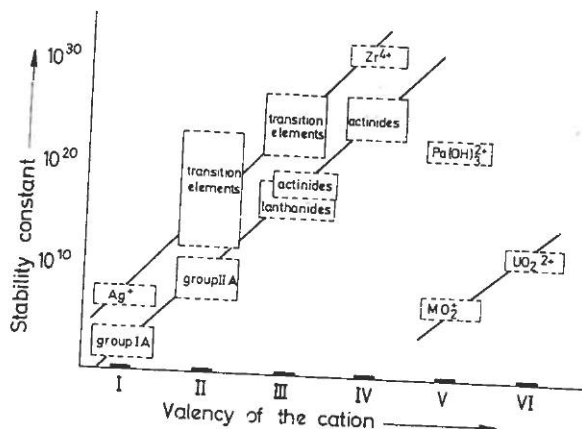

Figure 9.9. Stability of EDTA-chelates with various metal ions [*S. H. Eberle*, private communication].

b) The "average" stability constant increases, to a first approximation, in proportion to the ionic charge for cation groups of the same or of a similar electron configuration.

c) "yl" ions are a special type of cations as regards complex chemistry. The stability constant of their complexes is much lower than would correspond to the valency of the central atom and slightly higher than would correspond to the charge of the "yl" ion.

d) Pa(V) does not resemble the other pentavalent actinides, since it forms no "yl" ions.

Numerous complexes and chelates are prepared in solid form; unfortunately, very few comprehensive structural investigations have been reported. Those available include the structures of the chloroform solvate of uranyl tris-8-hydroxyquinolate [13] and of the diethyldithiocarbamates of trivalent and tetravalent actinides [14]. In the monoclinic $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ ($a = 20.76$ Å, $b = 8.75$ Å, $c = 15.625$ Å, $\beta = 97.5°$, space group $P2_1/n$) two ligand molecules are present as bidentate ligands, while the third molecule occupies only one coordination site at the central uranium atom (via the oxygen), so that the uranium exhibits sevenfold coordination with

1	2.30 Å	U–O
2	2.51 "	U–N
3	2.25 "	U–O
4	2.32 "	U–O
5	2.58 "	U–N
6	2.79 "	N–O

$\alpha = 66.0°$
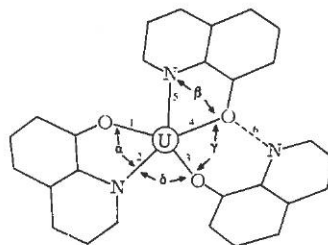$\beta = 62.6°$
$\gamma = 78.1°$
$\delta = 80.2°$

Figure 9.10. Arrangement of the equatorial ligands in uranyl tris-8-hydroxyquinolate [13].

pentagonal bipyramid as the coordination polyhedron (Fig. 9.10). The distance between uranium and oxygen in the uranyl group is about 1.50 Å, between uranium and the three oxygen atoms of the complexing agent 2.25–2.32 Å, and between uranium and the two nitrogen atoms of the bidentately bound ligands 2.51–2.58 Å. The U–N distance to the third ligand is appreciably greater, namely 4.07 Å. The different bond lengths between the three ligands and the central atom had been predicted on the basis of thermodynamic measurements even before the structure of this complex was elucidated. The five coordination sites of the ligands are arranged approximately in a plane perpendicular to the uranyl group. The chloroform molecule cocrystallized only as the solvent is slightly distorted in comparison with pure chloroform.

In monoclinic Th(IV)-tetradiethyldithiocarbamate Th($C_5H_{10}NS_2$)$_4$ ($a = 19.16$ Å, $b = 11.74$ Å, $c = 16.11$ Å, $\beta = 116.42°$, space group C2/c) the thorium atom is surrounded by the eight sulfur atoms of the four $-C{\overset{S}{\underset{S^-}{}}}$ groups in the form of a slightly distorted dodecahedron (Fig. 9.11). On the other hand, a coordination polyhedron for C. N. = 8 such as is found in the monoclinically crystallizing chelate of trivalent neptunium [(CH_3)$_4$N]Np($C_5H_{10}NS_2$)$_4$ ($a = 11.68$ Å, $b = 20.49$ Å,
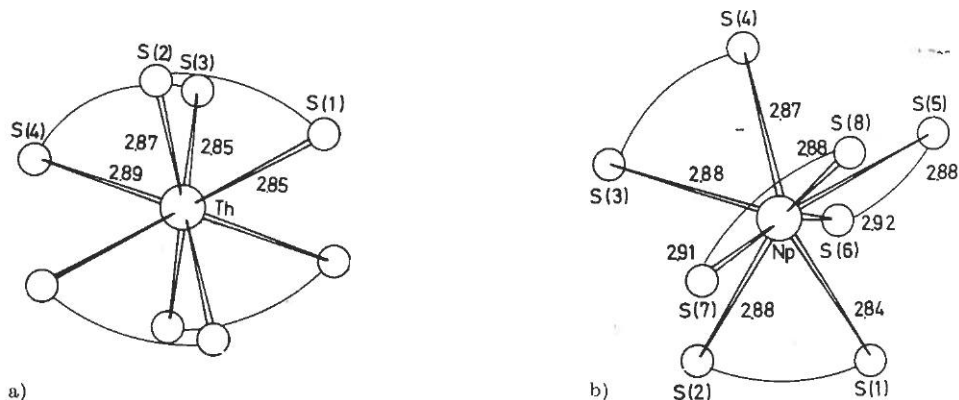

Figure 9.11. Coordination polyhedra in Th(IV)-tetradiethyldithiocarbamate (a) and in tetramethylammonium Np(III) tetradiethyldithiocarbamate (b) [14].

$c = 16.11$ Å, $\beta = 116.5°$, space group P2$_1$/c) has not been reported hitherto. It can best be described as a pentagonal arrangement of five sulfur atoms (S(1)–S(5)) with one sulfur atom (S(6)) below and two sulfur atoms (S(7) and S(8)) above this pentagon. The neptunium atom is situated somewhat above the plane formed by the five sulfur atoms.

An arrangement of three $-C{\overset{S}{\underset{S^-}{}}}$ groups about a central atom is found in the orthorhombic tetramethylammoniumuranyl trisdiethyldithiocarbamate [(CH_3)$_4$N]UO$_2$($C_5H_{10}NS_2$)$_3$ ($a = 19.03$ Å, $b = 17.21$ Å, $c = 9.41$ Å, space group Pna2$_1$)

[15]. The six sulfur atoms show a puckered arrangement with respect to the plane perpendicular to the UO_2^{2+} axis. In contrast. the six oxygen atoms of the three acetate groups in $NaUO_2(CH_2COO)_3$ have a planar hexagonal-bipyramidal arrangement. In the monoclinic uranyl bisdiethyldithiocarbamate-triphenylarsine oxide adduct $UO_2(C_5H_{10}NS_2)_2 \cdot OAs(C_6H_5)_3$ ($a = 18.280$ Å, $b = 9.128$ Å, $c = 22.242$ Å, $\beta = 118.67°$. space group $P2_1/c$) each uranium atom is surrounded by the four sulfur atoms of the two $-C\underset{S^-}{\overset{S}{\diagup}}$ groups and the oxygen of the triphenylarsine oxide, giving rise to a distorted pentagonal bipyramid (C. N. = 7) [16].

A detailed description of the crystal structure of U(IV)-β-tetrakisacetylacetonate is given by *Titze* [17, 18]. In the monoclinic unit cell each uranium atom is coordinated by eight oxygen atoms in the form of an Archimedean antiprism with a mean uranium-oxygen distance of 2.32 Å. The acetylacetonate rings are bent about a line joining the oxygen atoms. The lattice constants of hitherto known actinide(IV) acetylacetonates are summarized in Table 9.4. Single-crystal studies have been reported for a few actinide chelates with 2-thenoyltrifluoroacetone. but no complete structural investigations have been carried out [19, 20]. The various modifications of $UO_2(TTA)_2 \cdot H_2O$ are due to different stacking sequences of the layer lattice.

9.3. Hydrolysis reactions

The hydrolysis of metal ions, i. e. their complexation with OH^- ions. is one of the most important reactions in aqueous solution. As the OH^- ion is one of the strongest complexing agents. hydrolysis effects should always be taken into account when considering processes in aqueous solution. The hydrolysis of metal ions can be suppressed only by a high hydrogen ion concentration, i. e. a low OH^- concentration. or at elevated pH by extremely strong complexing agents such as aminopolycarboxylic acids. However, most hydrolysis equilibria are not exactly known. and this is true also of the actinides [21]. Most metal cations undergo a variety of hydrolytic processes, and polymeric hydrolysis products are sometimes found in addition to monomeric species.

The first stage of hydrolysis is usually thought to be

$$M^{n+} - H_2O \rightleftharpoons MOH^{(n-1)-} + H^+$$

with the equilibrium constant (hydrolysis constant)

$$K_{(H)1} = \frac{[MOH^{(n-1)+}] [H^-]}{[M^+]} \quad .$$

The following first hydrolysis constants $K_{(H)1}$ were obtained for the three- and tetravalent actinides:

trivalent actinides: Pu^{3-}: $K_{(H)1} = 1.1 \times 10^{-7}$ ($\mu = 5 \times 10^{-2}$).

Am^{3-}: $K_{(H)1} = 1.2 \times 10^{-6}$ ($\mu = 0.1$: 23 °C).

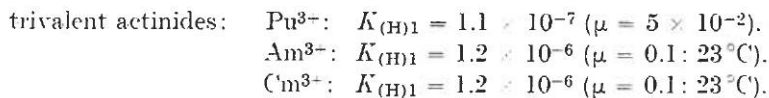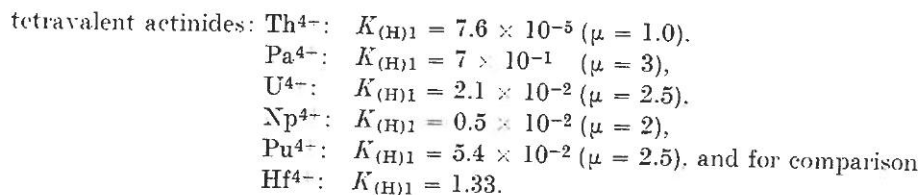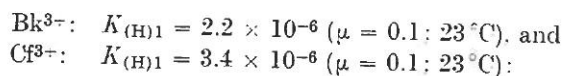Cm^{3+}: $K_{(H)1} = 1.2 \times 10^{-6}$ ($\mu = 0.1$: 23 °C).

Table 9.4. Structural data for chelates of tetravalent and hexavalent actinides with 2-thenoyltrifluoroacetone (HTTA) and acetylacetone [HAa].

Compound	Color	Lattice symmetry	Space group	No. of molecules per unit cell	Lattice constants			
					a [Å]	b [Å]	c [Å]	β [°]
Th(TTA)₄	yellowish	orthorhombic	P2₁2₁2 or Pma2	4	17.842	20.630	10.968	
U(TTA)₄	brown	orthorhombic	P2₁2₁2 or Pma2	4	17.701	20.446	10.736	
Pu(TTA)₄	brown	orthorhombic	P2₁2₁2 or Pma2	4	17.53	20.72	10.71	
Zr(TTA)₄	colorless	orthorhombic	P2₁2₁2 or Pma2	4	17.271	20.422	10.779	
Ce(TTA)₄	red-brown	orthorhombic	P2₁2₁2 or Pma2	4	17.532	20.719	10.710	
UO₂(TTA)₂ · H₂O (I)	red*)	orthorhombic	P2₁2₁2₁ or Pmn2₁	8	11.392	51.078	7.384	
UO₂(TTA)₂ · H₂O (II)	yellow-red-brown*)	monoclinic		6	38.35	7.39	11.38	92.58
UO₂(TTA)₂ · H₂O (III)	yellow-red-brown*)	orthorhombic	P2₁2₁2₁ or Pmn2₁	4	11.387	25.577	7.370	
UO₂(TTA) · C₂H₅OH	yellow-orange*)	monoclinic	B2 or Bm or B2/m	8	27.846	17.064	9.694	94.50
α-Th(Aa)₄		monoclinic	P2₁/c	4	11.72	12.76	17.02	112.25
α-U(Aa)₄		monoclinic	P2₁/c	4	11.65	12.08	16.95	112.25
α-Ce(Aa)₄		monoclinic	P2₁/c	4	11.70	12.64	16.93	112.25
β-Th(Aa)₄**)		monoclinic	C2/c	4	21.90	8.52	14.56	115.77
β-U(Aa)₄		monoclinic	C2/c	4	22.02	8.39	14.49	115.72
β-Np(Aa)₄		monoclinic	C2/c	4	22.06	8.38	14.42	116.23
β-Ce(Aa)₄		monoclinic	C2/c	4	22.01	8.38	14.37	115.78

* The compounds show pleochroism.

** D. Grdenic, B. Matkovic Acta Cryst. 12, 817 (1959).

Bk^{3+}: $K_{(H)1} = 2.2 \times 10^{-6}$ ($\mu = 0.1$; 23 °C). and
Cf^{3+}: $K_{(H)1} = 3.4 \times 10^{-6}$ ($\mu = 0.1$; 23 °C):

tetravalent actinides: Th^{4+}: $K_{(H)1} = 7.6 \times 10^{-5}$ ($\mu = 1.0$).
Pa^{4+}: $K_{(H)1} = 7 \times 10^{-1}$ ($\mu = 3$),
U^{4+}: $K_{(H)1} = 2.1 \times 10^{-2}$ ($\mu = 2.5$).
Np^{4+}: $K_{(H)1} = 0.5 \times 10^{-2}$ ($\mu = 2$),
Pu^{4+}: $K_{(H)1} = 5.4 \times 10^{-2}$ ($\mu = 2.5$). and for comparison
Hf^{4+}: $K_{(H)1} = 1.33$.

It will be noted that the hydrolysis constant does not exhibit a clear dependence on the atomic number. i. e. on the ionic potential. The slight tendency of thorium to hydrolysis is surprising. while the hydrolysis behavior of Pa(IV) is more like that of hafnium than of the other tetravalent actinides.
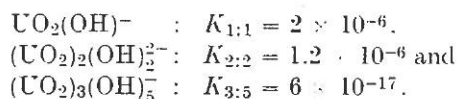
The hydrolysis of Th^{4+} was thoroughly investigated by *Baes* et al. [22] by means of potentiometric measurements and the results were subsequently evaluated on a computer. For the purpose of the analysis it was assumed that the most probable reaction path was that which exhibited the best agreement between experimental and calculated values. The conclusion was that the hydrolysis of Th^{4+} proceeds via five stages, with the compositions $Th(OH)^{3+}$ (1:1). $Th(OH)_2^{2+}$ (1:2). $Th_2(OH)_2^{6+}$ (2:2), $Th_4(OH)_8^{8+}$ (4:8), and $Th_6(OH)_{15}^{9+}$ (6:15); the corresponding equilibrium constants ($\mu = 1.0$; 25 °C) are $K_{1:1} = 7.6 \times 10^{-5}$, $K_{1:2} = 1.55 \times 10^{-8}$, $K_{2:2} = 1.45 \times 10^{-5}$, $K_{4:8} = 1.0 \times 10^{-19}$, and $K_{6:15} = 1.74 \times 10^{-37}$. Unexpectedly, the enthalpy and entropy changes per bound OH group in the polymeric species are fairly constant.

X-ray diffraction studies of aqueous solutions of Thorium(IV) oxyperchlorate established the presence of polynuclear species containing clusters of four thorium atoms [23]. A coordination number of eleven for thorium is indicated which leads to a complex species $Th_4(OH)_6^{10+}$. The thorium atoms are linked together by hydroxo bridges. Infinite linear complexes $Th[Th(OH)_2]_n$ such as are found in some basic salts. i. e., $Th(OH)_2SO_4$ and $Th(OH)_2CrO_4 \cdot H_2O$ are not evident in the thorium(IV) oxyperchlorate solution. Thorium(IV) perchlorate in acid media is found to contain mononuclear species.

Isolated dinuclear complexes with hydroxo bridges $[Th\langle^{OH}_{OH}\rangle Th]^{6+}$ have been found in basic thorium nitrate solutions with low Th:OH-ratios and in the crystalline compound $Th(OH)(NO_3)_3 \cdot 4H_2O$ (space group $P2_1/c$; $a = 6.772$ Å, $b = 11.693$ Å. $c = 13.769$ Å. $\beta = 102.63°$) [24]. Three nitrate groups, acting as bidendate ligands. three water molecules and two hydroxo groups of the hydroxo bridge are coordinated to each thorium atom (coordination number eleven). A similar dinuclear complex also exists in the dibasic salt $Th(OH)_2(NO_3)_2 \cdot aq$ [25]. The shortest Th—Th distance in the dinuclear and in the polynuclear complexes is close to 4.0 Å and is independent of the anion present.

The hydrolysis of the UO_2^{2+} ion likewise proceeds via polymeric species. as reported by a number of authors [26—29]. The observed hydrolysis species in perchloric acid solution with the corresponding hydrolysis constants (at 25 °C) are:

$$UO_2(OH)^- \quad : \quad K_{1;1} = 2 \times 10^{-6}.$$
$$(UO_2)_2(OH)_2^{2-}: \quad K_{2;2} = 1.2 \cdot 10^{-6} \text{ and}$$
$$(UO_2)_3(OH)_5^- \quad : \quad K_{3;5} = 6 \cdot 10^{-17}.$$

In addition. a 3:4 species $(UO_2)_3(OH)_4^{2+}$ ($K_{3;4} = 4.7 \times 10^{-13}$) was found in hydrochloric acid solutions ($\approx$ 1 M Cl⁻).

The hydrolysis of UO_2^{2+} depends strongly on the uranium concentration of the solution. It is a very rapid process [30], the rate constant k_2 of the reaction

$$2\,UO_2^{2-} - 2\,H_2O \xrightarrow{k_2} (UO_2)_2(OH)_2^{2+} - 2\,H^-$$
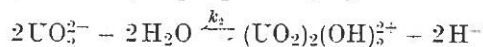
being $k_2 = 116$ mol^{-1} s^{-1} at 25 °C.

The following thermochemical data on uranyl hydrolysis were obtained in 3 M NaClO₄ [31]:

	$\Delta G_{298 °K}$ [kcal/mol]	$\Delta H_{298 °K}$ [kcal/mol]	$\Delta S_{298 °K}$ [cal/mol degree]
$2\,UO_2^{2-} - 2\,H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2-} - 2\,H^-$	8.21 ± 0.03	9.5 ± 0.1	4.3 ± 0.3
$3\,UO_2^{2-} - 5\,H_2O \rightleftharpoons (UO_2)_3(OH)_5^- + 5\,H^-$	22.56 ± 0.04	24.4 ± 1.5	6 ± 5

The entropy changes associated with the hydrolytic reactions are small: the position of the equilibria are almost entirely determined by the enthalpy terms. The values of $\Delta H_{2;2}$ and $\Delta H_{3;5}$ suggest a constancy of ΔH per OH⁻ bound (or H⁺ ion produced) of about 5 kcal/mol for the uranyl hydroxocomplexes.

Hydrolysis was found not to affect the transition frequencies observed for uranyl ion in acidic media [32]. However. the intensities and half widths of all the bands were observed to increase with hydrolysis. This information supports the idea that hydrolysis of the uranyl ion involves the water of hydration in the equatorial positions. A hydration number of four was found in perchlorate solutions at temperatures in the range −50 °C to −100 °C using the proton magnetic resonance technique [32a].
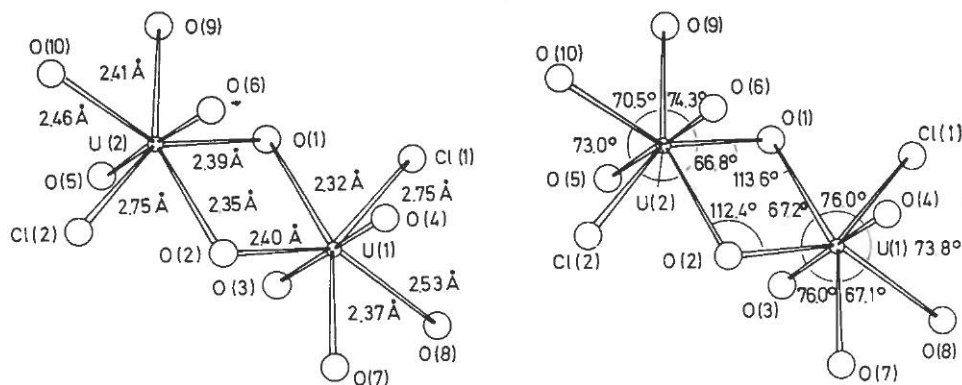

Figure 9.12. Atomic arrangement and interatomic distances in basic uranyl chloride-hydrate $(UO_2)_2(OH)_2Cl_2(H_2O)_4$. The atoms marked O(1) and O(2) are the oxygens of the OH bridge; O(3)–O(6) are those of the two uranyl groups. an O(7)–O(10) are the oxygen atoms of the water of hydration [33].

The 2:2 product $(UO_2)_2(OH)_2^{2+}$ is found not only in aqueous solution but also in crystalline compounds. It is the structural unit in the monoclinic basic uranyl chloride-hydrate $[(UO_2)_2(OH)_2Cl_2(H_2O)_4]$ ($a = 17.743$ Å, $b = 6.136$ Å, $c = 10.725$ Å, $\beta = 95.52°$, space group P2$_1$/n) [33]. Each UO_2^{2-} group is surrounded by one chlorine and four oxygen atoms. Two such pentagonal bipyramids are connected via the two

oxygens of the OH groups to form a dimer (Fig. 9.12). The $UO_2\!\!\overset{OH}{\underset{OH}{\diagup\!\!\diagdown}}\!\!UO_2$ bridge is

not symmetric. The dimer molecules are held together in the crystal lattice by hydrogen bonds.

The dihydroxo-uranium(IV) sulphate $U(OH)_2SO_4$ is isostructural with the corresponding thorium compound [34]. The crystals are built up of infinite $U(OH)_2^{2-}$ zig-zag chains linked together by sulfate ions. The orthorhombic unit cell dimensions are (space group Pnma, Z = 4)

$U(OH)_2SO_4$	$Th(OH)_2SO_4$
$a = 11.572$ Å	11.733 Å
$b = 5.926$ Å	6.040 Å
$c = 6.969$ Å	7.059 Å.

In the crystal structure of the other basic uranium(IV) sulphate $U_6O_4(OH)_4(SO_4)_6$ a rather unusual arrangement of the metal ions is obtained [35]. The structure of this body centered tetragonal compound ($a = 10.741$ Å, $c = 10.377$ Å, space group I4/m, Z = 2) is built up of sulphate ions and separate groups $[U_6O_4(OH)_4]^{12-}$. The uranium atoms form regular octahedra with $U-U$ distances of about 3.84 Å, nearly the same as in UO_2. The uranium octahedra are surrounded by 4 O^{2-} and 4 OH^- ions forming a cube. This arrangement resembles remotely the $Mo_6Cl_8^{4+}$ ions found in several molybdenum compounds. In contrast to the molybdenum-chlorine cluster the bonds within the $[U_6O_4(OH)_4]^{12-}$ clusters are mainly ionic and not metallic. In the crystals, the $[U_6O_4(OH)_4]^{12-}$ groups are joined together by sulphate ions so that the coordination of oxygen around the uranium atoms is eightfold in the shape of a square Archimedean antiprism.

The hydrolysis of pentavalent protactinium is extremely complicated and has by no means been fully cleared up. The stability of Pa(V) solutions depends not only on their concentration but also on their age. For freshly prepared solutions without complexing agents the hydrolysis equilibria
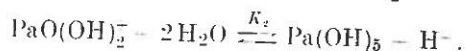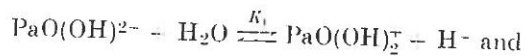
$$PaOOH^{2-} \xrightleftharpoons{K_1} PaO(OH)_2^+ \xrightleftharpoons{K_2} Pa(OH)_5$$
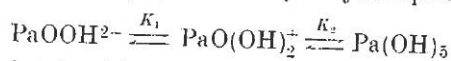
are postulated, with equilibrium constants ($\mu = 3$) [12]

$$K_1 = \frac{[PaO(OH)_2^-]\,[H^-]}{[PaO(OH)^{2-}]} = 9 \times 10^{-2} \text{ and}$$

$$K_2 = \frac{[Pa(OH)_5]\,[H^-]}{[PaO(OH)_2^-]} = 3.2 \times 10^{-5}$$

for the individual reactions

$$PaO(OH)^{2-} - H_2O \xrightleftharpoons{K_1} PaO(OH)_2^- - H^- \text{ and}$$

$$PaO(OH)_2^- - 2H_2O \xrightleftharpoons{K_2} Pa(OH)_5 - H^-.$$

Since the Pa=O group has been shown to be relatively stable the partially hydrolyzed products are probably present as oxohydroxo complexes and not as pure hydroxy complexes [36]. The proportion of the relevant ionic species as a function of the solution pH is shown in Fig. 9.13.
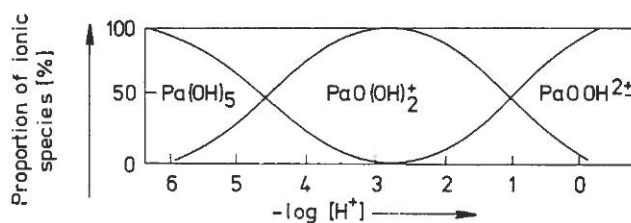

Figure 9.13. Proportions of hydrolyzed ionic species of protactinium in aqueous solutions of various hydrogen-ion concentrations [12].

In the course of extraction measurements it was found that the proportion of Pa(V) that can be extracted diminishes with time, while the proportion of Pa(V) colloids increases. This condensation is reversible in its initial steps, but the more highly condensed type of ion can no longer be depolymerized by acid treatment, or at the most only to a very limited extent.

9.4. Reduction-oxidation potentials

The values for the different reduction-oxidation potentials for the actinide elements in aqueous solution are summarized in Table 9.5. Most of the measured data are formal potentials and refer to the potential of the hydrogen electrode in the given medium, mostly in 1 M $HClO_4$.
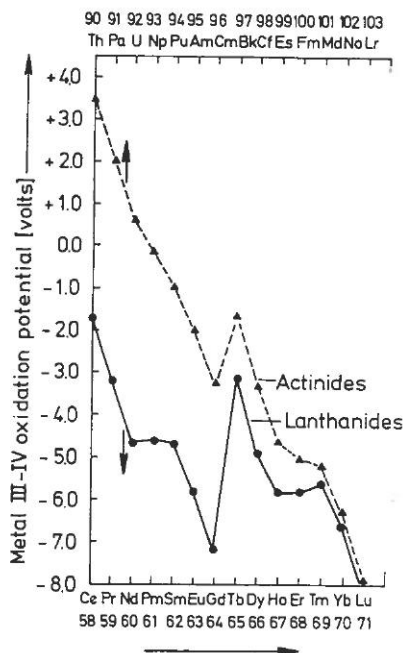

Figure 9.14. Metal (III–IV) oxidation potentials versus atomic number for the lanthanides and actinides (after [41]).

Table 9.5. Oxidation potentials of the actinides in volts.

Element	M(0)/M(III)	M(0)/M(IV)	M(II)/M(III)	M(III)/M(IV)	M(IV)/M(V)	M(V)/M(VI)	M(VI)/M(VII)	M(III)/M(V)	M(III)/M(VI)	M(IV)/M(VI)
Actinium	+2.6[1]									
Thorium		+1.899								
Protactinium		+0.9		+2.0[2]	+0.1[1]					
Uranium	+1.789			+0.631	0.58	0.063				
Neptunium	+1.83			−0.155	−0.739	−1.137	−0.61[4]	−0.477	−0.677	−0.938
Plutonium	+2.031			−0.9819	−1.1702	−0.9164			−1.0228	−1.0433
Americium	+2.320		+2.6[2]	−2.0[2]	−1.5[2]	−1.60		−1.74	−1.69	
Curium			+5.0[2]	−3.1						
Berkelium			+3.4[2]	−1.56[3]						
Californium			+1.9[5]	−3.3[2]						
Einsteinium			+1.6[5]	−4.6[2]						
Fermium			+1.3[2]	−5.0[2]						
Mendelevium			+0.1[5]	−5.2[2]						
Nobelium			−1.4[5]	−6.3[2]						

1 estimated;   2 calculated (after [37-40]);   3 for 6 M HNO₃;   4 for 1 M KOH;   5 determined by tracer experiments.

A comparison of these potentials reveal several interesting features. The actinide (II—III) potentials increase going from americium to curium and then decrease thereafter up to nobelium [37]. This is to be expected when considering the stability of the divalent actinide elements which is known to increase going from californium to nobelium. The actinide (III—IV) potentials decrease with the atomic number but show a distinct maximum at curium: the similarity between the actinide (III—IV) and the lanthanide (III—IV) potentials is strikingly apparent in Fig. 9.14 [38, 39].

Most of the values in Table 9.5 were obtained by direct measurement but some of the potentials, however, had to be estimated because of the instability of some valence states in aqueous solutions. The estimated values were obtained by using linear unit-slope relationships between the standard oxidation potentials and the photon energy of the first electron-transfer bands [40] or the first $f \rightarrow d$ bands of actinide (III, IV) complexes, mainly hexahalide complexes. It was shown that one unit-slope line calibrates the lanthanide series and another calibrates the actinide series: the calibration shift of $+0.8$ V for the lanthanide(IV)-actinide(IV) series can be explained as arising from the greater covalency of the actinide(IV) hexahalide complexes. This is twice the value of the corresponding actinide(III)-lanthanide(III) calibration shift.

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