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2001 Russ. Chem. Rev. 70 865

(http://iopscience.iop.org/0036-021X/70/10/R03)

Russian Chemical Reviews **70** (10) 865 – 884 (2001)

DOI 10.1070/RC2001v070n10ABEH000646

State-of-the-art coordination chemistry of radioactive elements

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Contents

Abstract. Modern procedures for the synthesis of coordination and organometallic compounds of actinides and technetium and the properties of these compounds are surveyed. Experimental techniques, including methods for the synthesis of actinide and technetium complexes from elemental metals (oxidative dissolution and direct electrosynthesis), salts and halide, carbonyl and other complexes are generalised. The bibliography includes 283 references.

I. Introduction

Among compounds of natural and artificial radioactive elements (Tc, Pm, Po, Fr, Ra, Ac and actinides), only organometallic compounds and complexes of technetium and actinides (An) have been well studied. Complexes of these metals attract interest because technetium, which is available in multikilogram quantities, is widely used for medical and technical purposes and actinides find application in nuclear industry and power engineering. Over a period of the last two decades, a large number of experimental studies, reviews and monographs were devoted to Tc and An complexes.[1–16] The aim of the present review is to give a comprehensive survey of modern synthetic procedures for the preparation of coordination and organometallic compounds of radioactive elements. The data are systematised according to the nature of the ligands in these complexes.

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Received 22 December 2000
Uspekhi Khimii **70** (10) 974 – 995 (2001); translated by T N Safonova

II. General notion of technetium and actinide complexes

Actinium (atomic number 89) and all elements with atomic numbers from 90 to 103 (actinides) are radioactive.[17] Only four actinides (Th – Np) and actinium by itself were found in nature, whereas the remaining elements were prepared artificially by irradiation of U and other elements with neutrons or by bombardment with heavy atoms. Actinides are analogues of lanthanides. They belong to the same IIIB Group but reside in the next row.

Technetium (atomic number 43) has several isotopes two of which are characterised by large half-lifes (2.12×10^5 and 1.5×10^6 years for ^{99m}Tc and ^{98}Tc, respectively) and is a rhenium analogue.[18]

The electronic states of the actinide atoms and ions differ substantially from those of the lanthanide atoms and ions. In both series, the *f* level is successively filled up to the f^{14} configuration; however, this filling in actinides begins with Th only formally because Th does not bear *f* electrons and is an electronic analogue of hafnium.[16] In contrast to lanthanides, actinides can exist in various oxidation states. Actinides in the oxidation state +3 are analogues of lanthanides, whereas actinides in the oxidation state +4 are analogues of Hf(IV) and Ce(IV).

Actinides produce the An^{m+} ($m = 2-4$) and AnO_2^{m+} ($m = 1$ or 2) ions whose highest occupied level is filled only with *f* electrons. In the series of the An^{3+} anions, the actinide contraction is observed, this contraction changing in parallel with the lanthanide contraction. The 5*f* and 6*d* energy levels of the An^{m+} ions as well as the 4*f* and 5*d* energy levels of the Ln^{m+} ions correlate with each other. The difference in the correlations for the An^{3+} and Ln^{3+} ions leads to the noticeable difference in the magnetic properties and electronic spectra of their compounds.[17] Technetium (the $4s^24p^64d^55s^2$ or $4s^24p^64d^65s^1$ electronic configuration) exists in the oxidation states from +1 to +7, the oxidation states from +4 to +7 being most stable.[18]

Spin – orbit coupling (J) in the An^{3+} ions is very strong (2000 – 4000 cm^{-1}) and it is ~1000 cm^{-1} stronger than J in the Ln^{3+} ions. In contrast to lanthanides, the splitting due to spin – orbit coupling in actinides is comparable with the crystal field splitting and, hence, the J value is no longer a good quantum number. Since the 5*f* and 6*d* orbitals have close energies and the thermally accessible excited states of actinides are filled, the equation for the effective magnetic moment

$$\mu_e = g[J(J+1)]^{1/2}$$

is less appropriate than in the case of lanthanides.[17, 19]

Actinide organometallic complexes contain actinide–carbon π bonds, actinide–carbon σ bonds or bonds of both types. Organometallic complexes of all early actinide elements from thorium to californium are known.[20] However, most data have been obtained for the chemistry of organometallic compounds of Th and U due to the extremely large half-lifes of natural ^{232}Th and ^{238}U (1.41×10^{10} and 4.468×10^{9} years, respectively). The first actinide organometallic compound, *viz*., Cp_3UCl, was isolated by Reynolds and Wilkinson in 1956.[21]

The actinide atoms possess rather large atomic and ionic radii and large (up to 14) coordination numbers.[22] Examples of actinide compounds characterised by various coordination numbers and oxidation states are listed in Table 1.

The maximum coordination numbers were found for polymeric uranium hydroborates, whereas the presence of bulkier ligands, for example, of NPh_2, leads to a decrease of the maximum coordination number to 5 or even to 4.[17] Like lanthanides, the spherical An^{3+} and An^{4+} ions have the highest coordination numbers (generally, 8 or 9) and often form isomorphous complexes in which the polyhedron type is determined by repulsions between the ligands (steric factors) or packing factors rather than by the electronic effects.[23] For example, the square antiprism in the rhodanide complexes $Cs_4An(NCS)_8$ and $U(NCS)_4(Ph_3PO)_4$ is transformed into the dodecahedron in the case of $Th(NCS)_4[(Me_2N)_2CO]_4$ or into the cube in the case of $(NEt_4)_4An(NCS)_8$.[17]

The nature of the bond between the π-donor ligand and the actinide centre has been discussed.[24, 25] The authors emphasised that there is no simple answer to the question as to the nature of the bond in organoactinide complexes. Examples of almost completely ionic binding of the Cp^- anions or cyclooctatetraene (COT) with U^{4+} (see Ref. 26) as well as of covalent binding of the metal atom with the aromatic ring of the ligand in uranocene accompanied by essential ligand-to-metal electron transfer are available in the literature.[24, 27, 28] It was concluded[24, 29] that the

Table 1. Coordination numbers (CN) and coordination polyhedra in actinide compounds.[17]

Oxidation state	CN	Coordination polyhedron	Examples of compounds
+7	6	octahedron	$Li_5(AnO_6)$ (An = Np, Pu)
+6	6	octahedron	$(NEt_4)(PaOCl_5)$, AnF_6 (An = U, Np, Pu), *trans*-$UO_2Cl_2(OPPh_3)_2$
	7	pentagonal bipyramid	$[UO_2Cl_2(acac)_2] \cdot Hacac$, $PuO_2(C_2O_4) \cdot 3H_2O$, $K_3UO_2F_5$
	8	hexagonal bipyramid	$Cs_2[AnO_2(MeCO_2)_3]$ (An = Np, Pu, Am), $(UO_2)(NO_3)_2(H_2O)_2$
+5	6	octahedron	$CsAnF_6$ (An = U, Np, Pu)
	7	pentagonal bipyramid	$PaCl_5$
	8	cube	$Na_3(AnF_8)$ (An = Pa, U, Np)
	9	tricapped trigonal prism	$M_2(PaF_7)$ (M = NH_4, K, Rb, Cs)
+4	4	tetrahedron	$U(OAr)_4 \cdot [N(SiMe_3)_2]_3 \cdot THF$
	5	trigonal bipyramid	$U_2(NEt_2)_8 \cdot [Li(THF)_4] \cdot [U(OAr)_5]$
	6	octahedron	Na_2PuCl_6, *cis*-$UCl_4 \cdot 2Ph_3PO$, *trans*-$UBr_4 \cdot 2Ph_3PO$, $UCl_4 \cdot 2HMPA$
		trigonal prism	$U_4(dmed)_3$
	7	pentagonal bipyramid	UBr_4, K_3UF_7
		monocapped octahedron	$[UCl(TMPO)_6]Cl_3$
	8	dodecahedron	$Np(HCOO)_4$, $Th(tta)_4$, $An(S_2CNEt_2)_4$ (An = Th, U, Np, Pu)
		square antiprism	$K_7Th_6F_3$, $An(acac)_4$ (An = Th, U)
+4	8	cube	$(NEt_4)_4[An(NCS)_8]$ (An = Th, Pa, U, Np)
		bicapped trigonal prism	$Th(acac)_4$
		bicapped octahedron	$[UCl_2(Me_2SO)_6](UCl_6)$
	9	tricapped trigonal prism	$(NH_4)_3(ThF_7)$, $LiUF_5$, $Th(tta)_4 \cdot TOPO$
		monocapped square antiprism	Li_3ThF_7, $Th(tfa)_4 \cdot 2H_2O$, $[C(NH_2)_3]_5[Th(CO_3)_3F_3]$
	10	bicapped square antiprism	$U(C_2H_3O_2)_4 \cdot 2H_2O$, $An(MeCO_2)_4$ (An = Th, U), $Na_6[Th(CO_3)_5] \cdot 2H_2O$
	11	irregular structure	$An(NO_3)_4 \cdot 5H_2O$ (An = Th, Pu)
	12	icosahedron	$(PPh_4)[Th(NO_3)_5(OPMe_3)_2]$, $An(BH_4)_4$ (An = Np, Pu)
	14	bicapped hexagonal antiprism	$[An(BH_4)_4]_n$ (An = Th, U)
+3	5	trigonal bipyramid	$[K(THF)_2]_2[U(NHAr)_5] \cdot THF$
	6	octahedron	$[UCl_6]^{3-}$
	8	dodecahedron	$UCl_3 \cdot 3DMSO$
		bicapped trigonal prism	$AnBr_3$ (An = Pu, Am, Cm, Bk), AnI_3 (An = Pa, U, Np, Pu)
	9	tricapped trigonal prism	$NaPuF_4$, $AnCl_3$ (An = U, Np, Pu, Am, Cm), $Am(sal)_3 \cdot H_2O$
+2	6	framework structure	Th_6Br_{12}
0	8	cube	$U(bipy)_4$

Note: acac is acetylacetonate, Hacac is acetylacetone, HMPA is hexamethylphosphoramide, dmed is *N*,*N*′-dimethylethylenediamine, TMPO is trimethylphosphine oxide, tta is thenoyltrifluoroacetonate, TOPO is tri-n-octylphosphine oxide, tfa is trifluoroacetylacetonate, sal is salicylate, bipy is bipyridyl.

covalent binding of the metal atom with the ligand in $U(COT)_2$ involves primarily the 6*d* orbitals of uranium, while the 5*f* orbitals are of secondary importance.

As mentioned above, actinides show various oxidation states in aqueous solutions. Stable oxidation states vary from +3 for Ac to +6 for U and Np and then gradually decrease to +3 for Am and the following elements, except for No (+2). For Ac, Th, Pa, U, Md and Lr, the maximum oxidation states are stable; Np and Pu can occur in the oxidation state +7; Am can exist in the oxidation state +6; Cm, Bk, Cf, Es and Fm can occur in the oxidation state +4; the oxidation state +3 is possible for No. In aqueous solutions, virtually all actinides can exist in the unstable oxidation state +2.[17] The hydrated An^{2+}, An^{3+}, An^{4+}, AnO^{2+} and AnO_2^{2+} ions behave as Brönsted acids.[30]

$$An^{n+} + H_2O \longrightarrow An(OH)^{(n-1)+} + H^+.$$

The An^{4+} ions are typical of actinides from thorium to californium (however, U^{4+} is readily oxidised). As for Th, only Th^{4+} ions exist in solutions. The acidity decreases in the series $Pa^{4+} \gg U^{4+} > Pu^{4+} > Np^{4+} > Th^{4+}$.[17] Individual ions occur only in very dilute solutions. These ions tend to form polynuclear species as the concentration increases

$$m An^{4+} + n H_2O \rightleftharpoons An_m(OH)_n^{(4m-n)+} + n H^+ .$$

The acidity of the An^{n+} ions depends on their charge and radius. The An^{4+} and AnO_2^{2+} ions are much stronger acids than the An^{3+} and AnO_2^+ ions, respectively.[17] The redox behaviour of actinides is complicated by their high radioactivity, which, in particular, results in the formation of hydrogen peroxide in aqueous solutions.

The data on the complex formation of the actinide ions An^{3+}, An^{4+}, AnO_2^+ and AnO_2^{2+} (An = U, Np or Pu) with chlorides were surveyed in several comprehensive reviews.[30–32] The results of recent studies of hydrated and chloride complexes of UO_2^{2+}, NpO^{2+}, Np^{4+}, Pu^{3+}, *etc.* by XAFS (X-ray absorption fine structure) spectroscopy were covered in Refs 33 and 34. In particular, using hydrated ions and fluoride complexes of U(IV) and Th(IV) as examples, it was demonstrated that the coordination number of these hydrated ions is 10 and the M–O distances for U(IV) and Th(IV) are in the ranges of 2.42 ± 0.01 and 2.45 ± 0.01 Å, respectively.[34] The results of physical and chemical studies of hydrated complexes of uranium were published in the literature.[35,36]

Mössbauer spectroscopy is very convenient to use for studying the oxidation states and the symmetry of the ligand environment. The Mössbauer effect is observed for ^{232}Th, ^{231}Pa, ^{238}U, ^{240}Pu, ^{243}Am and, particularly, ^{237}Np generated upon the ^{237}U β^--decay. The maximum isomer shifts (up to -70 mm s^{-1}) are observed for Np(VII) compounds; for Np(III) compounds, these shifts decrease to $+30$ mm s^{-1} (see Ref. 37).

III. Actinide alkoxides and other oxygen-containing complexes and salts

Uranium alkoxides are similar to alkoxides of transuranium elements. Their chemistry has been surveyed in the recent review.[37] Homoleptic alkoxides $An(OR)_n$ are known for $n = 3$ (U and Pu), 4 (Th, U, Np and Pu), 5 (Pa and U) and 6 (U). A great quantity of such U and Th compounds are available, whereas only a few Pa and Pu complexes were prepared. Alkoxides of uranium in the the oxidation states +3, +4, +5 and +6 are known. Complexes characterised by mixed oxidation states, such as $[U(OPh)_3(THF)]_2[UO_2(THF)_2]_2(\mu\text{-}OPh)_4(\mu_3\text{-}O)_2$, were also prepared.[38] Compounds of U(IV) are analogous to Th(IV) compounds.

Most actinide alkoxides are oligomeric {like $[U_3O(OBu^t)_{10}]$}. However, derivatives of bulky alcohols and 2,6-disubstituted phenols are monomeric,[17] for example, $U(OCHBu^t_2)_4$,[39] $U(OEt)_5$,[37] $U(OMe)_6$, $U_2(OEt)_{10}$, $U(OAr)_4$ and $U(OAr)_3$ (Ar = 2,6-$Bu^tC_6H_3$).[37,40,41] The influence of electronic factors on the structure and stability of complexes of uranium tri-*tert*-butylmethoxide was examined.[42]

Monomeric alkoxides can react with each other[43]

$$U(OEt)_4 + U(OEt)_6 \xrightarrow{C_6H_{14}} U_2(OEt)_{10} .$$

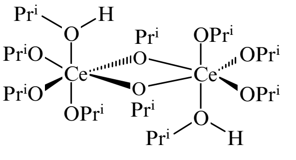
Anionic alkoxide complexes, such as $(Bu^t_4N)[U_2(OBu^t)_9]$ and $[Li(THF)_4][U(OAr)_5]$, were also obtained.[44] Treatment of $[U(COT)(BH_4)_2]$ with alcohols ROH (R = Et, Pr^i or Bu^t) afforded the alkoxide derivatives $[U(COT)(BH_4)(OR)]$.[45]

In a toluene solution of the $Th(OCHPr^i_2)_4$ complex, a monomer–dimer equilibrium occurs; however, only the dimeric form crystallises (with trigonal-bipyramidal geometry).[46]

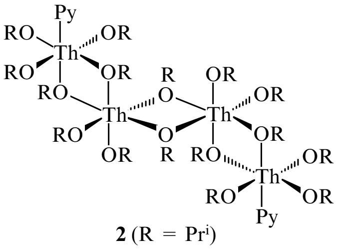
Actinide alkoxides are very readily hydrolysed[17]

$$3\,U_2(OBu^t)_8(HOBu^t) + 2\,H_2O \xrightarrow{PhMe} 2\,U_3O(OBu^t)_{10} + 7\,HOBu^t.$$

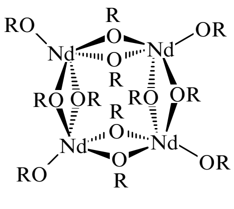
The actinide ions have large radii and, consequently, high coordination numbers, which are often responsible for oligomerisation of homoleptic alkoxide complexes of *f* metals[37,47–49] giving rise to dinuclear (**1**), tetranuclear (**2**, **3**) or higher oligomers.[47]



1

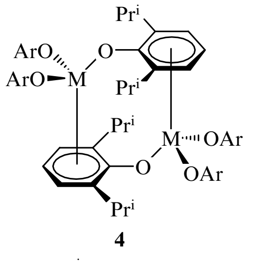


2 (R = Pr^i)



3 (R = CH_2Bu^t)

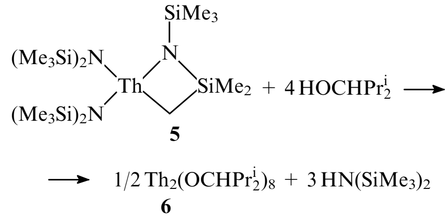
Dimeric actinide complexes are exemplified by the $\{U[O(2,6\text{-}Pr^i_2C_6H_3)]_3\}_2$ complex (**4**), which contains the unusual π-arene bridge and is sterically hindered due to the presence of the isopropyl groups.[47,49] This complex is stabilised through π-arene interactions both in the solid state and in solution.



4

Ar = 2,6-$Pr^i_2C_6H_3$; M = La, Nd, Sm, Er, U.

Some actinide complexes can occur both in the monomeric and dimeric forms. Thus treatment of metallacycle **5** with isopropyl alcohol afforded the homoleptic $Th_2(OCHPr^i_2)_8$ complex.



5

$$\longrightarrow 1/2\,Th_2(OCHPr^i_2)_8 + 3\,HN(SiMe_3)_2$$

6

In the solid state, the latter exists as dimer **6** (the coordination number of thorium is 5) consisting of two ThO_5 fragments (with trigonal-bipyramidal geometry), which are linked *via* a shared axial-equatorial edge.[44] At room temperature, this complex in non-coordinating solvents exists as monomer **7**.[46,47]

$$\underset{\mathbf{6}}{\mathrm{Th_2(OCHPr^i_2)_8}} \rightleftharpoons \underset{\mathbf{7}}{2\,\mathrm{Th(OCHPr^i_2)_4}}$$

The dimeric halide-alkoxide complex $Th_2I_4(OPr^i)_4(HOPr^i)_2$ was prepared by the reaction of metallic thorium with 2 equivalents of iodine in isopropyl alcohol.[50] This reaction provides an example of the direct synthesis from elemental metals. The $Th_2I_4(OPr^i)_4(HOPr^i)_2$ complex (the triclinic system, space group $P\bar{1}$) has a bioctahedral structure (the octahedra are linked *via* a shared edge), the isopropyloxy anions occupying the bridging positions. This complex is isostructural to its uranium analogue $U_2I_4(OPr^i)_4(HOPr^i)_2$ (see Ref. 51) and is structurally similar [50] to a number of alkoxide and halide-alkoxide compounds of lanthanides and early transition metals, such as $M_2(OPr^i)_8(HOPr^i)_2$ (M = Zr or Ce) [52] and $Ti_2Cl_4(OR)_4(HOR)_2$ ($R = CH_2CH_2Cl$).[53] It was assumed that the $[AnI(OPr^i)_2(HOPr^i)_4]I$ intermediates (An = U or Th) were initially formed, which then underwent dimerisation.[50] Other alkoxide complexes of actinides, for example $Th_2(OBu^t)_8(HOBu^t)$,[54] $(TBA)U_2(OBu^t)_9$ (TBA is tetrabutylammonium) and $KU_2(OBu^t)_9$,[55] were also characterised. It was demonstrated that the K^+ cations in the latter complex in solutions remain associated with the dimeric anions, the structures of the molecular unit in the crystalline state and solution being, apparently, identical.

Oxidation of the uranium(III) aryloxide complex $U(OAr)_3$ (**8**) (OAr is 2,6-di-*tert*-butylphenoxide) afforded various oxide and halide-oxide complexes of U(IV).[50]

$$\begin{tikzcd}
\mathrm{FU^{IV}(OAr)_3} & & \mathrm{BrU^{IV}(OAr)_3} \\
\mathrm{I_2U(OAr)_2} & \underset{\mathbf{8}}{\mathrm{U(OAr)_3}} \arrow[ul, "a"'] \arrow[l, "b"'] \arrow[dl, "c"] \arrow[ddl, "d"] \arrow[ur, "e"] \arrow[r, "f"] \arrow[dr, "g"'] \arrow[ddr, "h"'] & \mathrm{(ArO)_3USU(OAr)_3}\ (\mathbf{10}) \\
\mathrm{ClU^{IV}(OAr)_3} & & \mathrm{IU^{IV}(OAr)_3} \\
\mathrm{U(OAr)_4} & & \mathrm{(ArO)_3UOU(OAr)_3}\ (\mathbf{9})
\end{tikzcd}$$

(*a*) $AgBF_4$ or $AgPF_6$; (*b*) CI_4; (*c*) PCl_5; (*d*) O_2; (*e*) AgBr, CBr_4 or PBr_5; (*f*) COS or $Ph_3P{=}S$; (*h*) N_2O, NO, Me_3NO or pyridine *N*-oxide.

In the presence of an appropriate source of chalcogenide, oxidation gave rise to bridged binuclear uranium(IV) complexes **9** or **10**.[50]

Alkoxide complexes of cyclooctatetraenyluranium(IV) were synthesised by the reactions of cyclooctatetraenyluranium precursors with alcohols.[56]

The unusual monomeric complex $U(OTeF_5)_6$ can be considered as an analogue of metal alkoxides.[57] In spite of the large molecular weight, this complex sublimes at 333 K (1.3 Pa).[57]

Actinide alkoxides are generally prepared from dialkylamides and alcohols.[44] The homoleptic $UX_4(MeCN)_n$ complex can serve as a precursor in the synthesis of mixed halide-alkoxide compounds of uranium. The coordination environment in the reaction product depends on the nature of the halogen. Thus the reaction of $UBr_4(MeCN)_4$ with 2 equivalents of KOAr in THF afforded the $Br_2U(OAr)_2(THF)\cdot 4THF$ complex, whereas UCl_4 produced the anionic $[K(THF)_4][UCl_3(OAr)_2]$ complex. In solution, mixed halide-aryloxide complexes do not undergo ligand exchange. Light halides of uranium(IV) are reagents of choice in the metathesis because $UI_4(MeCN)_4$ is thermally unstable.[58] A series of aryloxides and alkoxides of (triamidoamine)uranium(IV) were described.[59]

One of the approaches to the synthesis of methoxide derivatives of actinides of type **11** involves the reactions of $Cp^*_2MH_2$ (Cp^* is pentamethylcyclopentadienyl; M = U or Th) with trimethyl phosphite in pentane.[60]

$$\mathrm{Cp^*_2ThH_2} \xrightarrow[-\mathrm{H_2}]{\mathrm{P(OMe)_3}} \mathrm{Cp^*_2Th(OMe)_2} + \underset{\mathbf{11}}{[\mathrm{Cp^*_2Th(OMe)_2}](\mu\text{-PH})}$$

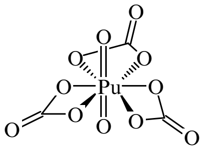
The corresponding thorium derivatives can also be prepared by alcoholysis of alkyl complexes, for example, of $Cp^*_2ThMe_2$, the reactions of $Cp^*_2ThCl_2$ with alkali metal hydroxides, the insertion of ketones at the Th−Alk bond (see the review [37] and references cited therein)

$$\mathrm{Cp^*_2ThCl(Me)} + \mathrm{Me_2CO} \xrightarrow{\mathrm{PhMe}} \mathrm{Cp^*_2ThCl(OCMe_3)}\,,$$

and hydrogenation of η^2-acyl complexes [37]

$$\mathrm{Cp^*_2ThCl(\eta^2\text{-}OCCH_2Bu^t)} \xrightarrow{\mathrm{H_2}} \mathrm{Cp^*_2ThCl(\eta^2\text{-}OCH_2CH_2Bu^t)}.$$

Crystallisation of a Pu(IV) salt (0.15 mol litre^{-1}) from a solution of Na_2CO_3 (2.6 mol litre^{-1}) afforded single crystals of $[Na_6Pu(CO_3)_5]_2\cdot Na_2CO_3\cdot 33\,H_2O$ (the space group is $P2_1/c$).[61] In the solid state, the asymmetric unit contains a complex framework consisting of $[Pu(CO_3)_5]^{6-}$ anions and Na^+ cations linked through interactions between the CO_3^{2-} ligands and the H_2O molecules. The $[Pu(CO_3)_5]^{6-}$ anion can be considered as a pseudohexagonal bipyramid with three carbonate ligands in the equatorial plane and two carbonate ligands in the axial positions. Its structural unit is very similar to that of the related $[Th(CO_3)_5]^{6-}$ anion involved in the crystal structures of $Na_6[Th(CO_3)_5]\cdot 12\,H_2O$ and $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot 4\,H_2O$ (see Ref. 61 and references cited therein). Clark *et al.*[61] believed that the well-known coordination polyhedron (hexagonal bipyramid) in the $[PuO_2(CO_3)_3]^{4-}$ complex (**12**) [62–64] is analogous to that of the $[Pu(CO_3)_5]^{6-}$ anion (**13**).



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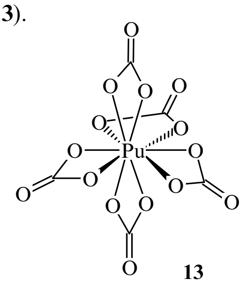


13

The structure of yet another carbonate complex, *viz.*, $(Me_4N)_4[NpO_2(CO_3)_3]\cdot 8\,H_2O$, consists of alternating anionic and cationic layers.[65] The water molecules of crystallisation are involved in the formation of the $\{[NpO_2(CO_3)_3]\cdot 8\,H_2O\}_n^{4n-}$ anionic layers. Analogous uranium and uranyl complex ions in carbonate,[66,67] sulfate,[68] nitrate,[69] phosphate,[70] silicate [70] and citrate complexes [71] as well as in other oxygen-containing compounds were also studied. In particular, the behaviour of carbonate complexes of uranium in $CO_2-HCO_3^-$ solutions of various ionic strengths (I = 0.5, 1.0, 2.0 or 3.0 mol litre^{-1} of $NaClO_4$) at 25 °C was examined by UV/Vis spectrophotometry.[65] The authors believed that tetracarbonate complexes exist in an equilibrium with pentacarbonate complexes

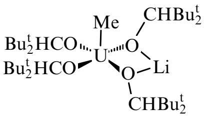
$$[\mathrm{U(CO_3)_4}]^{4-} + \mathrm{CO_3^{2-}} \rightleftharpoons [\mathrm{U(CO_3)_5}]^{6-}\,.$$

Citric acid forms mixed Fe and U complexes analogous to the citrate complex of uranium. The mixed Fe−U citrate complex is stable to biodegradation.[71]

Among other oxygen-containing actinide compounds, uranium peroxo complexes with various ligands, *viz.*, with tri- and tetradentate Schiff's bases,[72] amines or aminocarboxylic acids,[73] were described. The einsteinium(II) complexes with crown ethers $[Es(18\text{-}C\text{-}6)]L_2$ ($L = ClO_4^-$ and BF_4^-, BPh_4^-) were prepared.[74] The behaviour of einsteinium(II) in THF was examined by co-crystallisation. It was found that the coefficients of co-crystallisation of Es(II) with solid $[Sr(18\text{-}C\text{-}6)]I_2$ in THF depend on the ClO_4^- and BF_4^- ions as additives and are independent of the presence of the BPh_4^- ions.

Very stable actinide complexes with β-diketones [for example, with $An(acac)_4$ or $AnO_2(acac)_2$] are used for isolation and separation of actinides by extraction. These complexes are prepared by the reactions of metal or actinyl halides with the

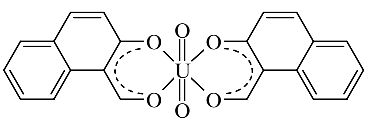
Table 2. Preparation of actinide alkoxides and related oxygen-containing complexes.

Starting compound or metal	Reaction system	Products	Ref.
Synthesis from elemental metals			
U anode	Hbac, O_2 or N_2 (see [a])	$UO_2(bac)_2(Hbac)_{0.5}$, $UO_2(bac)_2$	84
	Hacac, O_2 or N_2 (see [a])	$U(acac)_4$, $UO_2(acac)_2 \cdot Hacac$	84
Synthesis from salts			
$UO_2(MeCO_2)_2$	Hacac Hdbm HBTF in EtOH	$UO_2(Hacac)_2$ $UO_2(Hdbm)_2$ $UO_2(HBTF)_2$	75–77, 85
$ThCl_4$	$NaOPr^i$, $HOPr^i$	$Th(OPr^i)_4(HOPr^i)_x$	37, 38, 86
$PaCl_5$	NaOEt, EtOH	$Pa(OEt)_5$	37, 87
$NpCl_4$	LiOR, ROH (R = Me, Et)	$Np(OR)_4$	37, 88
Synthesis from halide complexes			
$UBr_4(MeCN)_4$	KOAr	$Br_2U(OAr)(THF) \cdot (THF)_4$	89
$ThBr_4(THF)_4$	$2,6\text{-}Bu^t_2C_6H_3OK$ (see [b])	$ThBr_2(OAr)_2(THF)_2$	44, 90
Py_2PuCl_6	NH_3, PhH, Pr^iOH [c]	$Pu(OPr^i)_4$, $Pu(OPr^i)_4(Py)$	91
Synthesis from β-diketonates or alkoxides			
$U(OCHBu^t_2)_4$	MeLi		92
$Th(acac)_4$	electrochemical reduction [d]	$[Th(acac)_4]^-$	93
Synthesis from π-complexes			
$(MeCp)_3U(THF)$	alcohols or thiols	$(MeCp)_3UR$ (R = OMe, OPr^i, OPh, SPr^i)	94, 95
Cp^*_3UH	EtOH	Cp^*_3UOEt	96
$HU(C_5H_4Bu^t)_3$	EtOH	$(C_5H_4Bu^t)_3UOEt$	96
$HU(C_5H_4SiMe_3)_3$	EtOH	$(C_5H_4SiMe_3)_3UOEt$	96

[a] Direct electrochemical synthesis; [b] alkylation of the product afforded $Th(OAr)_2(CH_2SiMe_3)_2$; [c] recrystallisation from hot isopropyl alcohol gave rise to $Pu(OPr^i)_4(HOPr^i)$; [d] the product lost $acac^7$ to form $Th(acac)_3$; the known Th(III) complexes are few in number.

corresponding diketone in the presence of a base. In the case of An(IV) actinides, only fluorine-containing diketonates form complexes with Lewis bases; diketonates of actinyls AnO_2 (An = Np or Pu) generally exhibit the Lewis acid properties and are stabilised through the formation of adducts. The fluorinated complex $UO_2(hfa)_2$ (hfa is hexafluoroacetylacetonate) exhibits pronounced acidic properties and its adducts with water and alcohols can be sublimed without decomposition.[17]

Uranyl acetylacetonate,[75,76] other actinide β-diketonates[77] and uranyl complexes with 2-hydroxy-1-naphthaldehyde (**14**)[78] and 2-hydroxybenzaldehyde[79] were studied in detail by spectroscopic methods. These investigations made it possible to establish the structure of the complex **14** synthesised previously.[80]

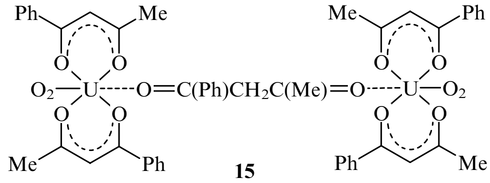


14

Based on the data on the electronegativities obtained earlier (see references cited in the study[78]), the U–O bond orders in the complexes **14**, $UO_2(acac)_2$, $UO_2(Hdbm)_2$ and $UO_2(HBTF)_2$ (Hdbm is dibenzoylmethane, HBTF is 1,1,1-trifluoropentane-2,4-dione) were calculated. The results of the calculations indicated that the equatorially coordinated 2-hydroxy-1-naphthaldehyde ligand exerts a pronounced effect on the oxygen atoms of the UO_2^{2+} anion.[78]

Based on the spectra of neptunium β-diketonates,[77] the Np(IV) complexes with acetylacetonate, dibenzoylmethane, benzoylacetone (Hbac), benzoyltrifluoroacetone (Hbtfa) and thenoyltrifluoroacetone (Htta) can be divided into two groups according to the type of coordination polyhedron about the central atom. In $Np(acac)_4$, $Np(dbm)_4$ and $Np(tta)_4$, the coordination polyhedron is a tetragonal antiprism, whereas $Np(bac)_4$ and $Np(btfa)_4$ (dbm is dibenzoylmethanate, bac is benzoylacetonate and btfa is benzoyltrifluoroacetonate) have bitetrahedral structures. Apparently, when Np(IV) β-diketonates are dissolved in benzene, the bidentate ligands are oriented about the central atom so that the oxygen atoms form the tetragonal-pyramidal coordination.[77]

It should be noted that uranium β-diketonates were also prepared by direct electrochemical synthesis using a dissolving anode. Thus electrochemical oxidation of uranium in the presence of β-diketones afforded chelate complexes of the UL_4 or UO_2L_2 type (L is diketonate).[81–83] The reaction with benzoylacetone gave rise to a compound with composition $UO_2(bac)_2(Hbac)_{0.5}$ along with the above-mentioned complexes.[82] In our opinion, the structure **15**, which was assigned to this compound on the basis of the IR spectroscopic data, needs further investigation.



15

Selected methods for the synthesis of actinide alkoxides are listed in Table 2.

IV. Halide complexes of actinides

Light actinides (U, Np and Pu) react with iodine or bromine in donor solvents[97,98] to give complexes of trivalent actinides AnX_3L_4 (X = Br or I).

$$U + 1.5\,I_2 + n\,L \xrightarrow{0\ ^\circ C} \underset{\mathbf{16a-c}}{UI_3L_n}$$

$n = 2$, L = DME (**a**); $n = 4$, L = THF (**b**), Py (**c**).

This reaction is a convenient and highly efficient procedure for the preparation of halide complexes of actinides in quantitative yields, which does not require special equipment.

Complexes of uranium triiodide with Lewis bases are used as intermediates in the synthesis of other trivalent uranium compounds. For example, the $UI_3(THF)_4$ adduct (**16b**), which can be prepared in large amounts, is a soluble form of UI_3 convenient for subsequent use in synthesis.[98] Reactions involving solvate complexes of other uranium halides or alkoxides can be complicated, for example, by the formation of mixtures of products.

The mononuclear complex $UI_3(THF)_4$ (**16b**) crystallises in the space group $P2_1/c$. The coordination environment about the central U atom is a pentagonal prism. The complex **16b** is stable up to 75 °C. At a higher temperature, the THF molecules are successively eliminated; at 162 °C, UI_3 is finally formed.

Other adducts of uranium halides UX_3 were also described.[99–103]

Actinide tetrahalides readily react with Lewis bases to give complexes containing two or four donor atoms. The compositions of some resulting products differ from usual $AnCl_4 \cdot 2\,L$ or $AnCl_4 \cdot 4\,L$. For example, the $AnCl_4 \cdot n\,L$ complexes, where $n = 2.5$, 5 [L is *N*,*N*-dimethylacetamide (DMA)] or 6 (L = DMSO or TMPO), were prepared. Complexes with composition $AnCl_4 \cdot 2\,HMPA$ (An = Th or U) are extremely volatile.[17] The coordination polyhedron typical of the $AnCl_4 \cdot 2\,L$ complexes is a *trans*-octahedron.[17]

The cationic uranium(IV) complexes $UX_2L_4Y_2$ [X = Cl, Br or I; L is a bulky neutral O-donor ligand, such as tris(pyrrolidin-1-yl)phosphine oxide; Y = ClO_4 or BPh_4] were described.[102]

The reactions of UI_4 with a series of sulfoxide donor ligands in non-aqueous media were investigated. The behaviour of UI_4 was compared with that of UCl_4 and UBr_4 in the presence of the same ligands. It was demonstrated that UI_4 was readily oxidised with dimethyl or diisobutyl sulfoxide at ~20 °C. Only complexes with compositions $UI_4(DMSO)_8$ and $UI_4(DIBSO)_6$ (DIBSO is diisobutyl sulfoxide) appeared to be stable and were isolated.[104]

All actinide halides tend to accept Hal^- ions to form anionic complexes. The stability of the complexes decreases in the series $F \gg Cl > Br \gg I$. Adducts of actinide trihalides are ionised to a large extent. Thus uranium trichloride crystallises from dimethyl sulfoxide as the solvate $UCl_3 \cdot 3\,DMSO$. Its structure consists of the dodecahedral $[U(OSMe_2)_8]^+$ cations and the octahedral $[UCl_6]^-$ anions. X-ray diffraction study demonstrated that americium chloride hexahydrate has an ionic structure built of the $[AmCl_2(H_2O)_6]^+$ cations and $[Cl(H_2O)_6]^-$ anions, which are linked *via* hydrogen bridges.[17]

Uranium and protactinium pentahalides generate complexes of the $AnX_5 \cdot L$ type (X = Cl or Br; L = R_3PO or HMPA). Dissolution of UO_3 in thionyl chloride afforded the $UCl_5 \cdot SOCl_2$ adduct, whereas dissolution of Pa(V) hydroxide gave rise to the ionic complex $(SO)(PaCl_6)_2$. Generally, actinide hexahalides do not react with Lewis bases (except for the $UCl_6 \cdot bipy$ complex), whereas actinyl halides readily form complexes with composition $AnO_2X_2 \cdot n\,L$ (n = 1, 1.5, 2, 3 or 4).[17]

Uranium fluorides UF_5 and UF_6 give complexes with 2-fluoropyridine (F-Py) or bipy.[105] Thus UF_6 in CH_2Cl_2 produced the $UF_4 \cdot (F\text{-}Py)$ and $U_2F_{12} \cdot bipy$ complexes, respectively. However, in the case of the UF_6–bipy system, reduction of UF_6 was the predominating process and the formation of $U_2F_{12} \cdot bipy$ {the authors believed that this complex has the structure $[UF_4(bipy)_2]^{2+} \cdot [UF_7]_2^- \cdot UF_6$} can be considered as the first stage of this reduction.

In the case of UF_5, two products were obtained and structurally characterised. These are the extremely moisture-sensitive $UF_5 \cdot bipy$ and the ionic derivative $[(bipy)_2H]^+[UF_6]^-$.

The $AnX_3(THF)_4$ complexes serve as synthetic precursors of a number of inorganic and organometallic complexes due, in particular, to their high solubility in toluene and THF. The use of $UI_3(THF)_4$ can also provide a convenient approach to the synthesis of many other compounds of trivalent uranium.[97]

Salts of organic ligands with alkali metals react with $AnX_3(THF)_4$ to give the corresponding aryloxides, amides, *etc.* This reaction can serve as a highly efficient procedure for the preparation both of the known and new complexes of trivalent actinides. Thus reduction of uranium tetrachloride with NaH or Na/Hg in THF afforded poorly soluble $UCl_3(THF)_n$.[106] This compound is sometimes used for the synthesis of other uranium complexes. However, this procedure is of limited application due to the formation of by-products. For example, the synthesis of $U[N(SiMe_3)_2]_3$ from $UCl_3(THF)_n$ and $NaN(SiMe_3)_2$ often give rises[97] to a mixture of a U(III) complex and a uranium(IV) derivative, *viz.*, the metallacycle $[(Me_3Si)_2N]_2\overline{U(CH_2SiMe_2N}SiMe_3)$.[107]

Selected procedures for the synthesis of halide complexes of actinides are listed in Table 3.

Table 3. Synthesis of halide complexes of actinides.

Starting compound or metal	Reaction system	Products	Ref.
Synthesis from elemental metals			
U	X_2 (X = Cl, Br, I), THF	$UX_3(THF)_4$	97, 98
Th	X_2 (X = Br, I), THF	$ThX_4(THF)_4$	44
Th anode[a]	Br_2, MeCN	$ThBr_4(MeCN)_4$	108
U	$HgCl_2$, THF	$UCl_4(THF)_3$ (see [b])	109
An (U, Np, Pu)	Br_2 or I_2, THF	$AnX_3(THF)_4$ (see [c])	97
Synthesis from salts or halide complexes			
UI_4	DMSO	$UI_4(DMSO)_n$ (n = 6, 8)	104
	DIBSO	$UI_4(DIBSO)_n$ (n = 6, 8)	104
UCl_4	NaH	$UCl_3 \cdot n\,THF$	44
$ThBr_4(THF)_4$	$KNPh_2$, THF KNMePh, THF	$Th(NPh_2)_4 \cdot THF$ $K[Th(NMePh)_5]$	110
$ThBr_4(THF)_4$	Cp*MgBr(THF)	$Cp^*ThBr_3(THF)_3$	111
$UI_3(THF)_4$	KCp*, THF	$Cp^*UI_2(THF)_3$	20, 98
$AnI_3(THF)_4$ (An = U, Np, Pu)	$NaN(SiMe_3)_2$, THF	$An[N(SiMe_3)_2]_3$	97, 112

[a] Direct electrochemical synthesis; [b] a large amount of a uranium amalgam was obtained as a by-product; [c] air-sensitive.

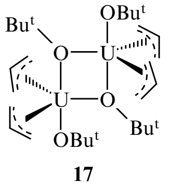
V. Actinide π-complexes with allyl, cyclopolyene, arene and related ligands

Considerable recent attention has been given to actinide complexes with allyl, cyclopolyene and arene ligands, particularly, with cyclopentadiene and its derivatives (see review[20]).

Allyl complexes can be synthesised from $AnCl_4$ and the Grignard reagent[44]

$$AnCl_4 + AllMgCl \xrightarrow[<0\ ^\circ C]{Et_2O} An(\eta^3\text{-}All)_4\,.$$

According to the data of low-temperature NMR spectroscopy,[20] the allyl groups in these complexes are η^3-coordinated and can be replaced under the action of HX or alcohols to produce, for example, $U(C_3H_5)_3X$ or $[U(C_3H_5)_3(OR)]_2$.[44] Thus the dimeric *tert*-butyloxyallyl complex $[U(C_3H_5)_3(OR)]_2$ (**17**) was synthesised.[20]



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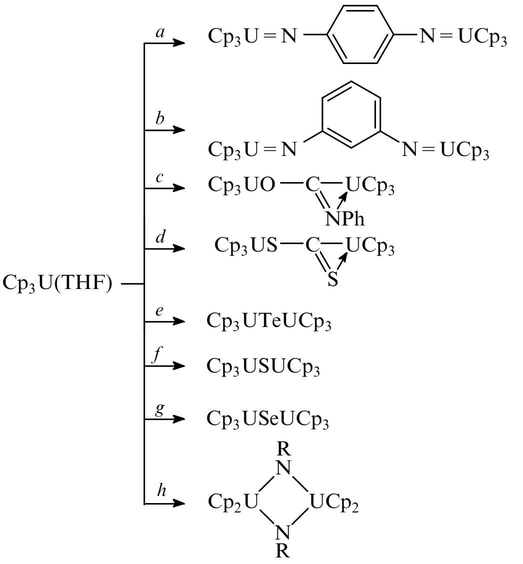
Of actinide π-complexes, the uranium(III, IV) and thorium(III, IV) complexes with cyclopentadiene and its derivatives were obtained in the widest range.

Uranium(V, VI) complexes[20] and neptunium(VI) and californium(III) sandwich complexes were also prepared.[44] These complexes can be compositionally divided into the following groups: Cp_nAn (n = 3 or 4), Cp_nAnX (n = 2 or 3), Cp_2AnX_n (n = 1 or 2) and $CpAnX_n$ (n = 2 or 3), X being generally Hal. The corresponding cyclopentadienyl alkyls, carbonyls, alkoxides, *etc.* are also known.[20] All Cp_4An complexes are poorly soluble in organic solvents. The U–C distances in the Cp_4U complex are 2.81(2) Å. The bonds between the An atom and the ligand are covalent in character.[20, 44]

The Cp_3An complexes are strong Lewis acids and form complexes with various Lewis bases (see Ref. 24 and references cited therein).

The Cp_3UCl complex, which was the first synthesised organoactinide compound,[21, 44] serves as a precursor of compounds containing the non-bridging metal–metal bond between, for example, uranium and iron or ruthenium [$Cp_3U-MCp(CO)_2$, M = Fe or Ru] or between uranium and germanium (Cp_3UGePh_3).[20, 113] The first organouranium(III) complexes,[24, 114, 115] *viz.*, tris[(cyclopentadienyl)uranium] and some its derivatives of the Cp_3UL type, are also used for the synthesis of bimetallic compounds.[24]



(*a*) 1,4-$(N_3)_2C_6H_4$; (*b*) 1,3-$(N_3)_2C_6H_4$ (*c*) PhNCO; (*d*) CS_2; (*e*) $TePBu_3$; (*f*) COS or $Ph_3P=S$; (*g*) $Ph_3P=Se$; (*h*) $Cp_3U=NR$; R = Ph, $SiMe_3$.

Voltammetric studies[116] demonstrated that oxidation of $(RC_5H_4)_3UCl$ (R = H, Me, Bu^t or Me_3Si) was accompanied by disproportionation. NMR studies revealed electron transfer and ligand exchange in Cp_3UX (X = Hal, BH_4 or Alk).[24, 117]

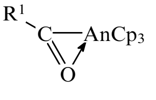
$$Cp_3UX \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} Cp_3UX^-,$$

$$Cp_3UX + Cp_3U^*(THF) \rightleftharpoons Cp_3U^*(THF) + Cp_3U^*X,$$

$$Cp_3UX^- + Cp_3U^*(THF) \rightleftharpoons Cp_3U^*(THF) + Cp_3U^*X^-.$$

The equilibrium constants of the ligand exchange in complexes with substituted cyclopentadienyl ligands were determined.[24, 118] It was found that binding of ligands with $(MeCp)_3U$ is reduced in the series of the ligands PMe_3 > $P(OMe)_3$ > Py > tetrahydrothiophene > THF > quinuclidine > CO, whereas binding of $(Me_3SiC_5H_4)_3U$ with the EtNC ligand is stronger than with the EtCN ligand, which is indicative of substantial π-back bonding with uranium in the case of π-acceptor ligands.[24] The results of calculations of the electronic structure of the model $Cp_3U(CO)$ complex showed substantial back bonding between the 5*f* orbitals of U and the 2π orbitals of CO, which leads to stabilisation of the 5*f* atomic orbitals of uranium.[20, 119] Some uranium complexes containing carbonyl ligands were described in the study.[120] The relativistic effective core potentials of tris(cyclopentadienyl) actinide complexes were calculated by the *ab initio* quantum-chemical method. These complexes were examined also by gas-phase UV photoelectron spectroscopy.[121, 122]

The Cp_3AnR^1 complexes tend to incorporate the CO, CO_2 and CNR^2 ligands to form η^2-acyl (**18**), η^2-carboxylate (**19**) and η^2-iminoalkyl (**20**) complexes, respectively.[20]



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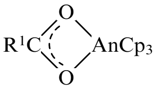

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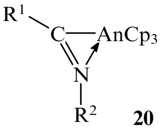

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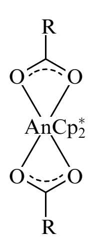
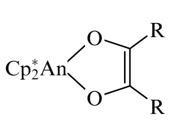
The Cp_3UX compounds containing the U–P, U–N, U–Si, U–Sn or U–Ge bonds were prepared from Cp_3UCl by the replacement of the chloride ligand.[24] In the crystal structures of $Cp_3U(OPh)$ and $Cp_3U(OSiPh_3)$, which were established by X-ray diffraction analysis, the U–O distances are shortened [2.119(7) and 2.135(8) Å, respectively] and the U–O–C and U–O–Si angles are 159.4(5)° and 172.6(6)°, respectively. These geometric parameters are indicative of strong π-bonding between the U and O atoms in oxygen-containing uranium complexes.[24] The bimetallic oxygen-bridged complex, *viz.*, μ-*O*-bis[tris(cyclopentadienyl)uranium(IV)] was investigated.[123] The absolute enthalpies of the cleavage of the uranium–ligand bonds in complexes containing the U–S bonds of the L_3U-SR type (L = $C_5H_4Bu^n$, $C_5H_4SiMe_3$ or $C_9H_6SiMe_3$; R = Et or Bu) were determined.[124] The heteroatomic compound $UCp_2(\mu\text{-}Cl)_2Li[(Me_2NCH_2CH_2)_2.NMe]$ containing two chloride bridges provides yet another example of bimetallic complexes.[125]

The electronic structure and configuration of the ground state of the monomeric alkyl uranium(III) complex η^5-$Cp_2^*UCH(SiMe_3)_2$ were studied.[126] The ground state of the molecule is $4A''[(a')^1(a'')^1(a'')^1]$, which corresponds to the $5f^3$ configuration of the uranium atom; its energy is close to that of the higher-lying $4A''(5f^26d^1)$ state. The uranium(III) ions free of ligands can adopt two different electronic configurations, *viz.*, $5f^3$ and $5f^2d^1$ (see Ref. 126 and references cited therein). The ground state of the U^{3+} ions in the gaseous phase has the $5f^3$ configuration. According to the results of an EPR study of the $Th[\eta^5\text{-}C_5H_3(SiMe_3)_2]_3$ complex in the gaseous state, Th(III) in the ground state adopts the $6d^1$ configuration, whereas the free ion has the $5f^1$ configuration.[127]

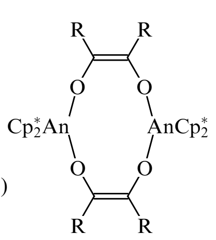
The insertion of CO or CO_2 into the An–R bond in the $Cp_2^*AnR_2$ complexes gave rise to complexes **21**–**23** or carbene-like η^2-acyl complexes $Cp_2^*An(COR)_2$ (**24**, R = Alk).[20, 128–130]



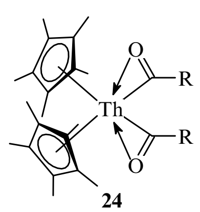
21 (R = Me)



22 (R = CH_2SiMe_3)

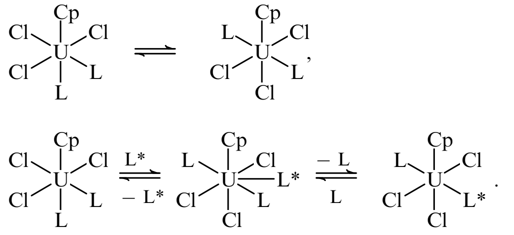


23 (R = Me, Bn)



24

The dynamic behaviour of $CpUCl_3L_2$ in solutions was examined.[24, 131] In toluene, rapid isomerisation and the ligand exchange were observed.[24]



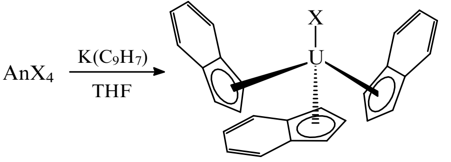
The tribromide complex $Cp^*ThBr_3(THF)_3$ (see Ref. 111 and Table 3) is a convenient compound for studying the chemistry of mono(pentamethylcyclopentadienyl) derivatives of thorium. Treatment of this complex with bases or Grignard reagents afforded aryloxide or alkyl derivatives.[111]

$$Cp^*ThBr_3(THF)_3 + KOAr \xrightarrow[18\ h]{THF} Cp^*ThBr_2(OAr)(THF) + KBr,$$

$$Cp^*ThBr_3(THF)_3 + 2\,KOAr \xrightarrow[18\ h]{THF} Cp^*ThBr_2(OAr)_2 + 2\,KBr,$$

$$Cp^*ThBr_2(OAr)_2 + MeMgBr \longrightarrow Cp^*MeTh(OAr)_2 + MgBr_2.$$

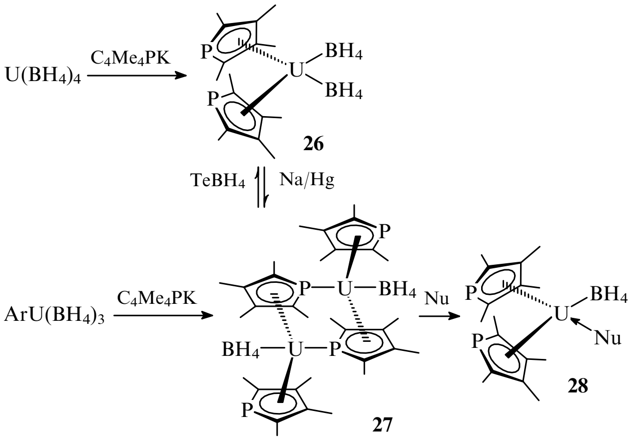
In 1971, the first indenyl derivative of actinides was prepared upon treatment of uranium tetrachloride with indenyl anions.[132] The indenyl uranium(III) complex $U(C_9H_7)_3$ was synthesised from UCl_3 and indenylsodium.[133] Indenyl actinide(IV) complexes **25** were prepared from the corresponding halides and indenylpotassium.[20]



25

An = Th, U, Np; X = Hal.

Uranium complexes **26**–**28** containing phosphacyclopentadienyl ligands were described.[24, 134]



Nu = THF, $OPPh_3$.

The structure of the first cycloheptatrienyl sandwich complex $[K(18\text{-}C\text{-}6)][U(\eta\text{-}C_7H_7)_2]$ was established.[135] The authors believed that the cycloheptatrienyl ligand can be formally considered as $C_7H_7^{3-}$ and the uranium atom occurs in the oxidation state +5.[135, 136] It was demonstrated that the C_7H_7 ligands in this compound are planar and are located parallel to each other and perpendicular to the axis passing through the uranium atom and the centres of the rings.[135]

Generally, cyclooctatetraene complexes of actinides have the composition $(COT)_2An$ or $(COT)AnX_2$ (X = Hal). Compounds of the mixed type (COT)AnCp can also be obtained. Some of these complexes contain solvent molecules, for example, THF.[20] Compounds of this type can be prepared, for example, according to the following procedures:

$$AnCl_4 + 2\,K_2(COT) \longrightarrow An(COT)_2 + 4\,KCl,$$

An = Th, Pa, U, Np;

$$(PyH)_2PuCl_6 + 2\,K_2(COT) \longrightarrow Pu(COT)_2 + 4\,KCl + 2\,PyHCl,$$

$$ThCl_4 + Th(COT)_2 \longrightarrow 2\,(COT)ThCl_2(THF)_2,$$

$$UCl_4 + COT + 2\,NaH \longrightarrow (COT)UCl_2(THF)_2 + 2\,NaCl + H_2.$$

Cyclooctatetraene complexes of uranium, thorium, protactinium, neptunium and plutonium $[(\eta\text{-}COT)An(\mu\text{-}SPr)_2]_2$ with

Table 4. Selected actinide complexes with allyl, cyclopolyene, arene, alkyl and carbonyl ligands.

Starting compound	Reagent	Reaction product	Ref.
Allyl complexes			
$AnCl_4$	C_3H_5MgCl, Et_2O	$An(C_3H_5)_4$	20, 44
$U(C_3H_5)_4$	HOR, Et_2O	$[U(C_3H_5)_2(OR)_2]_2$	20
Cyclopentadienyl complexes			
Cp_3AnCl	$NaC_{10}H_8$, THF or Na/Hg, THF	$Cp_3An(THF)$	24, 140
MX_4 (M = Th, U, Np; X = Cl, Br, I)	M′Cp, DME (M′ = Na, K, Tl)	Cp_3AnX	20, 44, 141
$(MeC_5H_4)_3UBu^t$	C_2H_4 or CO in PhMe	$(MeC_5H_4)_3U(Bu^t)L$ (L = C_2H_4, CO)	142
Cp_3UCl	LiL (L = PPh_2, NEt_2, $SiPh_3$)	Cp_3UL	143–145
Cp_3UX (X = NEt_2, PPh_2, $SiPh_3$)	2,6-$Me_2C_6H_3NC$	$Cp_3U\cdot[\eta^2\text{-}C(X){=}N\cdot C_6H_3Me_2\text{-}2{,}6]$	20, 145, 146
$Cp_3U(NEt_2)$	$HSnPh_3$	$Cp_3U(SnPh_3)$	24
$Cp_3U{=}C(H)PPh_2Me$	$HC{\equiv}CPh$	$Cp_3UC{\equiv}CPh$	24
Cyclopentadienyl complexes			
$(MeCp)_3U(THF)$	Me_3SiN_3 or PhN_3	$(MeCp)_3U = NR$ (R = Me_3Si, Ph)	20
L_3UH, (L = Cp*, $C_5H_4Bu^t$, $C_5H_4SiMe_3$)	I_2	L_3UI	96
Cp_3AnCl (An = Th,U,Np)	RMgX in THF or RLi in Et_2O	Cp_3AnR	20
Cp_4U, Cp_3UBu^n or Cp_3UBu^i	Bu^nCl, Bu^tCl, BnCl	Cp_3UBu^n, $Cp_3UCH_2CMe_2Cl$, Cp_3UBn, Cp_3UCl or $CpUBn_3$	147
$Cp_2^*ThX_2$ (X = Cl, Br)	$CpRu(CO)_2Na$	$Cp_2^*(X)Th\cdot Ru(Cp)(CO)_2$	24
$Cp_2^*AnCl_2$	LiR, Et_2O	$Cp_2^*AnR_2$ (R = Alk)	20
$(Me_3Si)_2C_5H_3UX_2$	Na/Hg, THF	$(Me_3Si)_2C_5H_3\cdot UX(THF)$	20
$BkCl_3$	Cp_2Be	$[Cp_2BkCl]_2$	20

Table 4 (continued).

Starting compound	Reagent	Reaction product	Ref.
Arene complexes			
UCl_4	C_6Me_6, $AlCl_3$, Al	$[U_3(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_3\cdot(\mu_1,\eta^2\text{-}AlCl_4)_3\cdot(\eta^6\text{-}C_6Me_6)_3](AlCl_4)$	24
	Al, $AlCl_3$, PhH	$(PhH)U(AlCl_4)_3$	98
	Zn, $AlCl_3$, C_6Me_6	$[(C_6Me_6)_2U_2Cl_7]^+\cdot[AlCl_4]^-$	98
Alkyl complexes			
UCl_4	LiR, L (L = THF, Et_2O)	$Li_2UR_6L_8$	20
$ThCl_4$	LiMe, TMEDA, Et_2O	$[Li(TMEDA)]_3\cdot ThMe_7\cdot TMEDA$ [a]	148
Cycloheptatriene complexes			
UCl_4	C_7H_8, THF	$[U(\eta\text{-}C_7H_7)_2]^-$	96
UX_4 (X = NEt_2, BH_4)	$K(C_7H_9)$	$K[X_3U\cdot(\mu\text{-}\eta^7{:}\eta^7\text{-}C_7H_7)UX_5]$	149
Cyclooctatetraene complexes			
UCl_4	$K_2(COT)$	$U(COT)_2$	150, 151
AnX_3 (An = U, Np, Pu, Am)	$K_2(COT)$, solvent (solv)	$[K(solv)][An(COT)_2]$	152, 153
$AnCl_4$ (An = U, Th)	COT, NaH	$(COT)AnCl_2(THF)_2$	24
$U(BH_4)_4$	COT	$(COT)U(BH_4)_2$	24
$(PyH)_2PuCl_6$	$K_2(COT)$, THF	$Pu(COT)_2$	20
$(COT)ThCl_2(THF)_2$	$Cp^*MgCl(THF)$, PhMe	$(COT)ThCp^*Cl(THF)$	154
$UI_3(THF)_4$	1) KCp^*, THF 2) $K_2(COT)$	$Cp^*U(COT)(THF)$	155
Carbonyl complexes			
U (vapour)	CO, Ar (4 K)	$U(CO)_x$	156
$[(Me_3Si)_2C_5H_3]U$	CO	$[(Me_3Si)_2C_5H_3]U(CO)$	20
Cp_3MR (M = U, Th, Np)	CO	$Cp_3M(CO)R$	44, 157

[a] In this complex, six of seven CH_3 groups are involved in coordination to the $Li(TMEDA)^+$ cations, two groups being coordinated to each of the cations; TMEDA is tetramethylenediamine.

mixed ligands were prepared by treatment of $An(COT)(BH_4)$ with thiol.[137] Mono(cyclooctatetraene) amide uranium complexes $K[U(COT)(NEt_2)_2]$ and $U(COT)(NEt_2)_2(THF)$ were synthesised from tetrakis(diethylamine)uranium and bis(cyclooctatetraene)uranium, respectively. Oxidation of these complexes afforded a series of uranium(V) derivatives.[138]

As can be seen from Table 4, actinide π-complexes containing the cyclopolyene or arene ligands (see also Ref. 139) are more abundant than actinide complexes with other ligands.

VI. Hydride and hydroborate complexes of actinides

The first organoactinide hydrides were prepared by hydrogenation of $Cp^*_2AnR_2$.[20]

$$Cp^*_2AnR_2 + H_2 \longrightarrow Cp^*_2AnH_2 + 2\,RH$$

Both monomeric and oligomeric hydride complexes of actinides are available. Generally, these complexes contain OAlk, 1,2-bis(dimethylphosphino)ethane (dmpe) or cyclopentadienyl as additional ligands. Thus uranium and thorium tetrahydroborates are polymeric compounds, whereas neptunium and plutonium tetrahydroborates are monomeric. Methyltrihydroborate derivatives $An(MeBH_3)_4$ always occur as monomers.

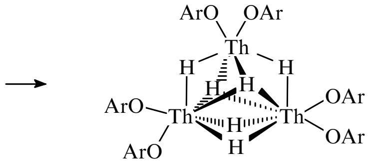
$$AnF_4 + 2\,Al(BH_4)_3 \xrightarrow{0\ ^\circ C} An(BH_4)_4 + 2\,AlF_2(BH_4)$$

The volatility of the complexes increases and their stability decreases on going from thorium to plutonium.[17]

Thorium, neptunium, plutonium and protactinium hydroborates and uranium tris(tetrahydroborate) possess similar properties. However, Th, Np, Pu and Pa hydroborates have a number of characteristic structural features.[44] The $UH(BH_4)_3(DME)$ complex contains the U−H bond. The $U(BH_4)_3[Ph_2P(Py)]_2$ complex was also described in the cited study.[44]

Trimeric thorium complex **29** provides a rare example of hydride complexes of early actinides, which are stabilised only by the aryloxide ligands.[90]

$$Th(OAr)_2(CH_2SiMe_3)_2 \xrightarrow[-\,SiMe_4]{H_2,\ PhP,\ 1.5\ atm,\ 7\ days}$$

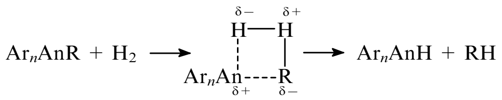


29

Ar = $C_6H_3Bu^t_2$-2,6

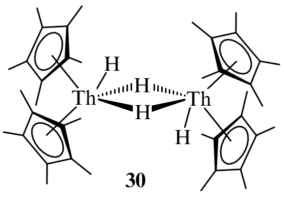
The complex **29** exhibits moderate catalytic activity in hydrogenation of hex-1-ene.[158] Alkoxide tetrahydroborate complexes of uranium(IV) were also described.[159]

Organoactinide hydrides are formed from the Ar_nAnR complexes through metathesis of σ-bonds.[20]



$$Ar_nAnR + H_2 \longrightarrow \begin{array}{c} \overset{\delta-}{H}\!-\!\overset{\delta+}{H} \\ \vdots \quad\ | \\ \underset{\delta+}{Ar_nAn}\cdots\underset{\delta-}{R} \end{array} \longrightarrow Ar_nAnH + RH$$

The structure of complex **30** was established.[20] The geometric parameters [the H−Th−Th and Th−H−Th angles are 58(1)° and 122(4)°, respectively; the distance between the thorium atoms is 4.007(8) Å] indicate that the metal−metal interaction in this complex is weak.



30

The unusual electron-deficient cyclopentadienyl complexes $(C_5H_4PPh_2)_2U(BH_4)_2$ and $(C_5H_4BH_3)_2U(BH_4)_2$ were described.[160]

Other cyclopentadienyl and related hydroborate complexes, for example, $[Na(THF)_6][Cp^*U(BH_4)_3]_2$,[161] were also synthesised.[161, 162]

Selected examples of hydride and hydroborate complexes of actinides are listed in Table 5.

Table 5. Selected hydride and hydroborate complexes of actinides.

Starting compound	Reagent	Reaction product	Ref.
UH_3	B_2H_6, THF	$U(BH_4)_3(THF)_3$	44
$U(BH_4)_4$	thermal decomposition in solution	$U(BH_4)_3$	44
	THF	$U(BH_4)_4(THF)_2$	44
	Et_2O	$[U(BH_4)_4(Et_2O)]_\infty$	44
ThX_4 (X = Cl, Br)	$Li_2C_2B_9H_{11}$	$[Li(THF)_4]_2\cdot Th(\eta^5\text{-}C_2B_9H_{11})_2X_2$	163
$ThBr_4(THF)_4$	CpMgBr(THF)	$CpThBr_3(THF)_3$	164
$Th(OAr)_2\cdot(CH_2SiMe_3)_2$	H_2	$Th_3(\mu_3\text{-}H)_2(\mu_2\text{-}H)_4\cdot(OAr)_6$	90
$UBr_4(MeCN)_2$	$Li_2C_2B_9H_{11}$, MeCN	$Li_2[U^{IV}(\eta^5\text{-}C_2B_9H_{11})_2\cdot Br_2]$	165
$UI_3(THF)_4$	$Li_2C_2B_9H_{11}$, TMEDA	$[Li(TMEDA)]\cdot[U(C_2B_9H_{11})I_2(THF)_2]$	165
$Cp_2^*UH_2$	dmpe	$Cp_2^*U(H)Cl$	20
$(Me_3XC_5H_4)_3UCl$ (X = C, Si)	$KHBEt_3$	$(Me_3XC_5H_4)_3UH$	166
Cp_3^*UH	Ph_3PBH_3	$Cp_3^*UBH_4$	96
$(C_5H_4Bu^t)_3UH$	Ph_3PBH_3	$(C_5H_4Bu^t)_3UBH_4$	96
$(C_5H_4SiMe_3)_3UH$	Ph_3PBH_3	$(C_5H_4SiMe_3)_3UBH_4$	96
$[U(\eta\text{-}C_5Me_5)_2\cdot Cl(THF)]$ or $[U(\eta\text{-}C_5H_4R)_3Cl]$ (R = H, Bu, $SiMe_3$)	$[K(THF)_2]\cdot[ReH_6(PPh_3)_2]$	$K[Cl(\eta\text{-}C_5Me_5)_2UH_6\cdot Re(PPh_3)_2]$ or $[U(\eta\text{-}C_5H_4R)_3UH_6\cdot Re(PPh_3)_2]$	167
Cp_2MR_2 (M = U, Th)	H_2	$Cp_2M(H)(\mu\text{-}H)_2\cdot M(H)Cp_2$	44
$[(\eta^5\text{-}C_2B_9H_{11})_2\cdot U^{IV}Br_2]\cdot 2[Li(THF)_4]$	electrochemical reduction and reduction with Na/Hg	$[(\eta^5\text{-}C_2B_9H_{11})_2U^{III}Br\cdot(THF)]\cdot 2[Li(THF)_x]$ ($x = 2-4$)	168

VII. Actinide complexes with macrocyclic ligands

Data on several actinide complexes with crown ethers and other macrocyclic ligands were published in the literature. Thus treatment of uranium and thorium tetrakis(diethylamides) $[An(NEt_2)_4]$ with free porphyrin (TPP) afforded the diporphyrin non-planar sandwich complexes $An(TPP)_2$.[17] Ultrafast electronic deactivation and the vibrational dynamics for the excited states of the uranium(IV) porphyrin sandwich complexes were examined.[169]

General procedures for the preparation of actinide complexes with macrocyclic Schiff's bases involve direct binding of the metal ion with the corresponding ligand and cyclisation in the presence of the metal ion. Thus phthalodinitrile reacted with anhydrous uranyl dichloride in DMF to give a 'superphthalocyanine' uranyl complex. Condensation of ethylenediamine with 2,6-dicarbonylpyridine in the presence of UO_2^{2+} gave rise to a hexaazamacrocyclic complex.[17] When irradiated with neutrons, the phthalocyanine complex $ThPc_2$ (Pc is phthalocyanine) entered into the nuclear reaction to give the corresponding protactinium(IV) complex.[17]

$$^{232}ThPc_2(n,\gamma)^{233}ThPc_2 \longrightarrow {}^{233}PaPc_2$$

The phthalocyanine complexes $AnPc_2$ were described in detail in a number of publications.[170–173]

Complexes with other polydentate ligands, for example, with chelating agents, can be used for efficient binding of actinide ions. These complexes are soluble both in water and organic solvents.[17] The higher the dentation of the ligand the more stable the complex. In the An^{4+}(EDTA) complexes (EDTA is ethylenediaminetetraacetic acid), the ligand is hexadentate and adopts a twist conformation.[17] Binding of plutonium and other radionuclides can be carried out with the use of cyclic and linear catecholamines.[174]

Actinide complexes with crown ethers are generally prepared from actinide salts. Complexes only with tri- and tetravalent actinide ions are known {for example, $[UCl_3(18\text{-}C\text{-}6)]_2\cdot[UO_2Cl_3(OH)H_2O]$}. The hydrogen bonds between the oxygen atoms of the ether and the water molecules of coordination were found in the UO_2^{2+} complexes.[17] The IR spectra and the isotope effects for uranium complexes with crown ethers and the crystal structures of some of these compounds were published in the literature.[175]

Actinide complexes with crown ethers can be prepared also from organometallic compounds. Thus Cp_3UCl reacted with 18-C-6 in the presence of a sodium amalgam in THF to yield $(Cp_3UCl)[Na(18\text{-}C\text{-}6)]$ (see Ref. 24 and references cited therein).

VIII. Actinide complexes with nitrogen-containing ligands

Most of N-donor bases possess low affinity for actinides and act predominantly as proton acceptors. The An–N bonds with mono- and even bidentate N-donor ligands are rather weak.[17] The complex $UO_2(hfa)_2$ exhibiting high acidity forms a 1 : 1 complex only with ammonia. Like actinide alkoxides, actinide amides occur generally in the associated form. For example, these compounds react with chelating *N*,*N*′-dimethylethylenediamine to give the linear trimeric $[U(dmed)_2]_3$ complex and the square tetrameric $[U(dmed)_2]_4$ complex.[17, 176] Dialkylamide and related complexes, such as $U[N(SiMe_3)_2]_3$, $[U(NEt_2)_3]BF_4$, $U(NPh_2)_4$, $UO_2[N(SiMe_3)_2]_2\cdot(OPPh_3)_2$ and $UO_2CrO_4\cdot 2\,MeCONEt_2$, were described in the literature.[97, 177–182]

The structure of the $U[N(SiMe_3)_2\{N(SiMe_3)[SiMe_2-CH_2B(C_6F_5)_3]\}]$ complex was established by X-ray and neutron diffraction analysis. It was demonstrated that the electron deficiency on the uranium atom is effectively compensated by the formation of multicentre bonds between the U atom and the $SiCH_2$ groups of the amine ligands. The X-ray diffraction data are unambiguously indicative of μ^3-coordination of the BH_4 groups.[183] The structure of the unusual uranium(III) complex with a tripodal aromatic amine, *viz.*, tris[(2,2′-bipyridin-6-yl)]amine, was established by X-ray diffraction analysis.[184]

Protolysis of the U–N bond in amide complexes of uranium affords cationic complexes. This procedure was used for the synthesis of compounds containing the cations $[U(\eta\text{-}Cp)_3(THF)]^+$, $[U(\eta\text{-}Cp^*)(NEt_2)_2(THF)_2]^+$, $[(U\text{-}\eta\text{-}C_5R_5)_2\cdot(NEt_2)(THF)]^+$, $[U(\eta\text{-}C_5R_5)(\eta\text{-}COT)(THF)_2]^+$ (R = H, Me),[185] $[U(NEt_2)_3]^+$, $[U(NEt_2)_2(THF)_3]^{2+}$, *etc.*[177] The resulting Th and U complexes with the silylated $N(CH_2CH_2NSiMe_3)_3$ ligand contain bonds between the metal atoms and the chlorine, carbon, hydrogen or oxygen atoms.[186] Chloro, pentamethylcyclopentadienyl and tetrahydroborate complexes of uranium containing the $N(CH_2CH_2NSiMe_3)_3$ ligand were characterised by the X-ray diffraction method.[186] The reactions of actinide amides were surveyed in a recent review.[187]

Only several imide complexes of actinides are known: $Me_3SiN=U^V[N(SiMe_3)_2]_3$, $Me_3SiN=U^{VI}F[N(SiMe_3)_2]_3$, $Cp_2.U(NC_6H_2Bu^t_3\text{-}2,4,6)$ and $U[N(CHMeCH=PPh_2Me)]Cp_3$.[188, 189] In complexes of the $(C_5H_4Me)_3U=NR$ type (R = Ph or $SiMe_3$), both lone electron pairs of nitrogen are involved in binding with uranium.[24, 190] Of the simplest nitrogen-containing ligands, the azide anion gives very stable complexes with uranium ($K_{diss} = 5\times10^{-3}$). The stabilities of the latter complexes are comparable with those of fluoride complexes.[17] The binuclear (U – Mo) heterocomplexes with N_2 were prepared.[191] IR spectroscopic and quasirelativistic theoretical studies of the coordination and activation of N_2 with the uranium and thorium atoms were carried out virtually at the same time.[192]

The mononuclear $UCp^*_2(NHR)_2$ complexes (R = 2,6-$Me_2C_6H_3$, Et or Bu) were synthesised, their structures were established and these complexes were demonstrated to catalyse hydroamination of terminal alkynes with ammonia.[193] The data on complex formation of uranium(VI) with neutral N-donors in DMSO were reported. [194]

An analogue of the uranyl ion was found in the crystal structure of the red complex $PPh_4^+\{UOCl_4[NP(C_6H_4Me\text{-}3)_3]\}^-$ (**31**).[195] The air-stable complex **31** was prepared from compound **32** by the replacement of the chloride ligand in the $[UOCl_5]^-$ anion accompanied by elimination of Me_3SiCl.

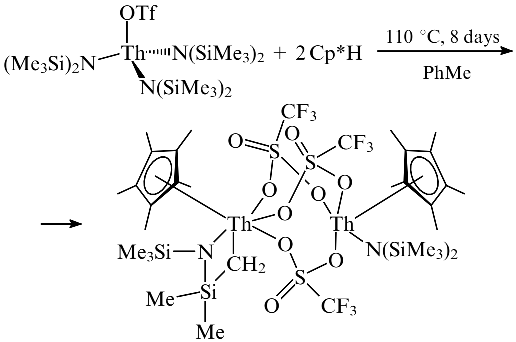
$$PPh_4^+[UOCl_5]^- + \underset{\mathbf{32}}{Me_3Si[NP(C_6H_4Me\text{-}3)_3]} \xrightarrow[-Me_3SiCl]{CH_2Cl_2}$$

$$\longrightarrow \underset{\mathbf{31}}{PPh_4^+\{UOCl_4[NP(C_6H_4Me\text{-}3)_3]\}^-}$$

According to the data of X-ray diffraction analysis, the $\{UOCl_4[NP(C_6H_4Me\text{-}3)_3]\}^-$ ion contains the linear O = U = N group coordinated by four chlorine atoms.[195] The U – O distance (1.76 Å) is typical of the uranyl ion (see Ref. 195 and references cited therein). The U – N distance (1.90 Å) indicates that the bond order is no less than 2. The U – N – P group is nearly linear (171.9 °), which suggests that the π electrons of the nitrogen atom are completely involved in bonding with uranium. The orders of the bonds between the uranium atom and each of the oxygen atoms in the uranyl ion can be equal to 3 due to the fact that the uranium atom bears simultaneously *f* and *d* valence orbitals.[195, 196]

Other anionic actinide complexes can be prepared immediately from salts. For example, UF_5 and UF_6 react with nitrogen bases to give molecular or ionic compounds, such as $[(bipy)_2H]^+[UF_6]^-$, $UF_4(2\text{-}FC_5H_4N)$ and $U_2F_{12}(bipy)$.[197]

Thermolysis of the thorium derivative $Th(OSO_2CF_3).[N(SiMe_3)_2]_3$ in the presence of 1 equiv. of pentamethylcyclopentadiene afforded binuclear complex **33**.[111]



33

The actinide complex with 1,4-di-*tert*-butyl-1,4-diazabutadiene (DAB) **34** was prepared for the first time from the complex containing $N(CH_2CH_2NHSiMe_3)_3$ (tren) as a ligand.[198]

$$[(tren)ThCl]_2 + 2\,Li[Bu^t_2(DAB)_2] \xrightarrow[-80\ ^\circ C]{THF}$$

$$\longrightarrow \underset{\mathbf{34}}{2\,(tren)Th[Bu^t_2(DAB)]} + 2\{Li[Bu^t_2(DAB)]\}Cl$$

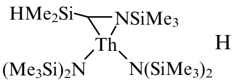
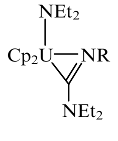
The complex **34** was obtained as red paramagnetic crystals (monoclinic, the space group is $P2_1/n$). The $N(CH_2CH_2NHSiMe_3)_3$ ligand ensures the optimum spatial environment for stabilisation of this complex. Since thorium(IV) compounds are diamagnetic, the diazabutadiene ligand in the paramagnetic complex **34** is subjected to one-electron reduction, *i.e.*, this ligand is present as the $[Bu^t_2DAB]^{-\bullet}$ radical anion.

The complex formation of neptunium(VI) with 3,3′-bis(diaziridine) derivatives [199] and of uranium(VI) with 8-hydroxyquinoline and its 5-halogen derivatives was studied.[200] In the latter case, the UO_2L and UO_2L_2 complexes (where L is a 8-hydroxyquinoline derivative) were obtained.[200]

Considerable recent attention has been given to uranium complexes with Schiff's bases (see, for example, the review [201]). Uranium(VI) complexes with Schiff's bases are used as organic oxidants (the catalytic modifications of these reactions were also developed).[202] Polystyrene-supported chelating resins incorporating U(VI) complexes with Schiff's bases are available.[203, 204] Salicylaldehyde [205] and triethylenetetramine,[203] 3-formylsalicylic acid and *o*-hydroxybenzylamine [204] or salicylaldehyde and 1-amino-2-hydroxynaphthalene-4-sulfonic acid [206] were used as precursors of Schiff's bases. Uranium(VI) complexes with Schiff's bases exhibit photochromic properties. The kinetics and the mechanisms of photochromic conversions were examined.[207]

Examples of actinide complexes with nitrogen-containing ligands are given in Table 6.

Table 6. Selected actinide complexes with nitrogen-containing ligands.

Starting compound	Reagents	Reaction products	Ref.
UO_2Cl_2	$KN(SiMe_3)_2$, THF	$UO_2[N(SiMe_3)_2]_2\cdot(THF)_2$	208
$ThBr_4(THF)_4$	KNR_2	$Th(NPh_2)_4(THF)$ or $K[Th(NMePh_5)]$	44, 110
$UCl_3(THF)_3$	$NaN(SiMe_3)_2$, THF	$U[N(SiMe_3)_2]_3$	112
$U(NPh_2)_4$	L (L = Py, Et_2O, THF, $(EtO)_3PO$)	$U(NPh_2)_4\cdot L$	180
$(NSiMe_2)_2U\cdot CH_2SiMe_2NSiMe_3$	Ph_2NH	$U(NPh_2)_4$	44
UCl_4	$LiNEt_2$	$U(NEt_2)_4$	44
	HNMePh	$Th[N(SiMe_3)_2]_2\cdot(NMePh)_2$	110
$(Me_3Si)_2N[ThN\cdot(SiMe_3)\cdot(SiHMe_2CH)]$	1) CF_3SO_3H 2) CpH	$Cp[(Me_3Si)_2N]Th\cdot(\mu_2\text{-}OSO_2CF_3)_3\cdot Th[N(SiMe)_3\cdot(SiHMe_2CH)]Cp$	208
$Cp_3U=C(H)PPh_2Me$	$HNPh_2$	Cp_3UNPh_2	24
$(C_5H_4Me)_3U(THF)$	RN_3 (R = Me_3Si, Ph)	$(C_5H_4Me)_3U=NR$	190
$Cp_2U(NEt_2)_2$	RNC		44

IX. Complexes with phosphorus-containing ligands

A large number of actinide complexes, which bear oxygen-containing phosphorus ligands and in which the metal atom is coordinated by the oxygen atom, are available.[17] Examples of phosphine complexes containing the An$-$P bond are few in number.[209] Thus thorium(IV) and uranium(IV) tetrahalides react with trimethylphosphine to give the 1 : 2 complexes $MCl_4(PMe_3)_2$ (M = U or Th).[17, 210] The $U[Me_2PCH_2CH_2PMe_2]_4$ complex containing an eight-coordinate uranium atom, which is isostructural to the thorium analogue, was described.[211] Uranium complexes with phosphorus donor ligands, procedures for their synthesis, structures and properties were considered in the study.[212]

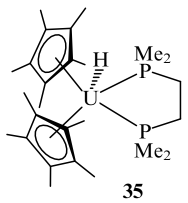
Ligands of the phosphacyclopentadienyl type serve as bridges, for example, in the dimeric uranium(III) complex **27**.[24, 134, 213]

The reactions of lithium salts of the potentially tridentate diphosphinoamide ligands $N(CH_2CH_2PR_2)^{2-}$ (R = Et or Pr^i) with uranium or thorium tetrachlorides afforded diphosphinoamide complexes of actinides. Ligands of this type are suitable for the preparation of various complexes of uranium(IV) (for example, $\{UCl_2[N(CH_2CH_2PEt_2)_2]_2\}_2$), uranium(V) and thorium(IV). Depending on the reaction conditions, these ligands can be mono-, bi- and tridentate. The character of the coordination compounds can be radically changed by varying the substituents at the neutral phosphine centre.[214]

Thorium and uranium complexes with diphosphazane dioxides were synthesised.[215] The crystal structure of the $UO_2(NO_3)_2[Ph_2P(O)N(Ph)P(O)Ph_2]$ complex was established. It was demonstrated that the metal atom is coordinated by diphosphazane dioxide in a bidentate fashion. Some other organophosphorus and related compounds of uranium were described in the studies.[216–219]

Actinide complexes containing simultaneously the phosphine and cyclopentadienyl ligands are few in number. Only the $Cp_2ThX_2(Me_2PCH_2CH_2PMe_2)$ complexes (X = Cl, Me or Bn)[179] and monomeric hydride complex of uranium(III) **35** were prepared.[220]

$$Cp_2^*UR_2 + Me_2PCH_2CH_2PMe_2 \xrightarrow[\text{autoclave, } -20\ ^{\circ}\text{C}]{\text{PhMe, } H_2}$$



R = Me, CH_2SiMe_3 .

35

The reactions of $U(BH_4)_3(THF)_x$ with some diphosphine ligands afforded the $U(BH_4)_3(L)_2$ complexes [L is dimethylphosphinoethane[221] or 2-(diphenylphosphino)pyridine[222]]. In these compounds, dynamic transformations are observed within the NMR time scale even at low temperature.

Table 7. Selected actinide complexes with phosphorus-containing ligands.

Substrate	Reagent	Product	Ref.
$AnCl_4$	$MP(CH_2CH_2PMe_2)_2$ M = Li, K	$An[P(CH_2CH_2PMe_2)_2]_4$ An = Th, U	211, 214
$ThCl_4$	$[N(CH_2CH_2PPr^i_2]^{2-}\cdot Li_2^+$	$ThCl_2[NCH_2CH_2PPr^i_{0.5}]_2$	211, 214
UCl_4	$[N(CH_2CH_2PEt_2]^{2-}\cdot Li_2^+$	$\{UCl_2[N(CH_2\cdot CH_2PEt_2)_2]_2\}_2$	211, 214
$[UOCl_5]^-$	$Me_3Si[NP\cdot (C_6H_4Me\text{-}3)_3]$	$[UOCl_4NP\cdot (C_6H_4Me\text{-}3)_3]^-$ (see [a])	189
$UO_2Cl_2\cdot (Ph_3PO)_2$	$KOBu^t$	$UO_2(OBu^t)_2\cdot (Ph_3PO)_2$	181
	$NaN(SiMe_3)_2$	$UO_2[N(SiMe_3)_2]_2\cdot (Ph_3PO)_2$	181
$Cp_2^*UCl_2$	$HNPPh_3$	$Cp_2^*UCl_2(HNPPh_3)$ [b]	223

[a] The red salt containing the Ph_4P^+ cation is air-stable and is soluble in CH_2Cl_2 and MeCN; [b] the first complex of the *f* element with the phosphineimino ligand.

Examples of actinide complexes with phosphorus-containing ligands are given in Table 7.

X. Sulfur-containing actinide complexes

Being hard acids, actinides usually do not form stable complexes with S-donor ligands, which are soft bases. Only a few examples of complexes with sulfur-containing ligands are available in the literature, *viz*., $UCl_4(dmte)_2$ (dmte is 1,2-dimethylthioethane), $An(S_2CNEt_2)_4$ (An = Th, U, Np or Pu), $(NEt_4)[Np(S_2CNEt_2)_4]$, $(NMe_4)[UO_2(S_2CNEt_2)_3]$,[17] $U(SBu^n)_4$, $[U(SBu^n)_6]^{2-}$ and $[U(SPh)_6]^{2-}$;[224] $[Na(18\text{-}C\text{-}6)\cdot (THF)][U(COT)(C_4H_4S_4)_2]$ is the only known uranium(V) complex containing the metal$-$sulfur bond.[225] The reaction of UCl_4 with $Li_2(SCH_2CH_2S)$ in dimethoxyethane afforded[226] the first homoleptic dithiolate complex of an *f* element (**36**; the space group is $P2_1/n$).

$$UCl_4 + 4\,Li_2(SCH_2CH_2S) \xrightarrow{\text{DME}} \underset{\mathbf{36}}{[Li(DME)]_4[U(SCH_2CH_2S)_4]\cdot DME}$$

The nature of the U$-$S bond in the complex **36** was estimated by the semiempirical Hückel method. It was found that the 6*d*, 7*s* and 7*p* orbitals of uranium are responsible for interactions with sulfur-containing ligands. The involvement of 5*f* orbitals is insignificant, and hence, the π interaction between uranium and sulfur is weak.[226] The authors also gave a brief review of the state of the art in the chemistry of actinide ions with sulfur-containing ligands.[226]

Derivatives of uranium(IV) tetrathiolate were prepared by treatment of $U(NEt_2)_4$, $U(BH_4)_4$ or $U(SBu^n)_4$ with thiols and by oxidation of metallic uranium with disulfides.[227] It was found that the reactions of the $U(SBu^i)_4$ complex with acids, I_2 and CS_2 proceeded at the U$-$S bond.[227]

The neptunium(V) complex with DMSO with composition $[(NpO_2)_2(DMSO)_7(H_2O)_2](ClO_4)_2\cdot H_2O$ was structurally characterised.[228] The structure contains the dimeric complex $[(NpO_2)_2(DMSO)_7(H_2O)_2]^+$ cations, perchlorate anions, coordinated water molecules and water molecules of crystallisation. The IR and electronic spectra are indicative of the non-equivalence of the dioxo cations. Thus $Np(1)O_2^+$ acts as a monodentate ligand, whereas $Np(2)O_2^+$ serves as the coordination centre.[228]

Treatment of the $U(COT)(BH_4)_2$ complex with thiols or sodium thiolates (RSH or RSNa, where R = Bu^n, Pr^i or Bu^t) afforded first organouranium compounds containing the bridging disulfide $\{[U(COT)(\mu\text{-}S)_2]_2\}$ and thiolate $\{[U(COT)(\mu\text{-}SR)_2]_2\}$ groups. The structures of these compounds differ from those of their alkoxide analogues, which contain only two bridging OR groups.[229]

The reaction of $U(NEt_2)_4$ with Pr^iSH and $OP(NMe_2)_3$ gave rise to the first structurally characterised tetrathiolate complex of uranium $U(SPr^i)_4[OP(NMe_2)_3]_2$.[229] The uranium sulfur cluster $U_3(\mu_3\text{-}S)(\mu_3\text{-}SBu^t)(\mu_2\text{-}SBu^t)_3(SBu^t)_6$ was also described.[230]

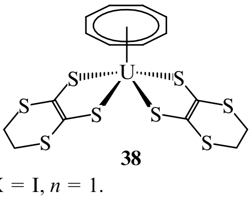
The $Cp_2^*U(dddt)$ complex (dddt is 5,6-dihydro-1,4-dithiin-2,3-dithiolate)[231] and the homoleptic uranium(IV) complexes $(THF)_3Na(\mu\text{-}SR)_3U(\mu\text{-}SR)_3Na(THF)_3$ (R = Bu^t or Ph) were synthesised.[232]

Recently, the first heteroleptic uranium(V) complex **38** was prepared by oxidation of complex **37** with $AgBPh_4$ in THF.[233]

$$(COT)UX_2(THF)_n + Na_2(dddt) \longrightarrow$$

$$\longrightarrow \underset{\mathbf{37}}{[(COT)U^{IV}(dddt)_2][Na(18\text{-}C\text{-}6)]_2} \xrightarrow[\text{THF}]{AgBPh_4}$$

$\longrightarrow$



38

X = BH_4, n = 0; X = I, n = 1.

Notwithstanding the fact that the available sulfur-containing actinide complexes are few in number, these compounds are of great interest in the coordination chemistry[230] and can find use for extraction of actinides.[232]

Examples of sulfur-containing uranium complexes are given in Table 8.

Table 8. Selected sulfur-containing uranium complexes.

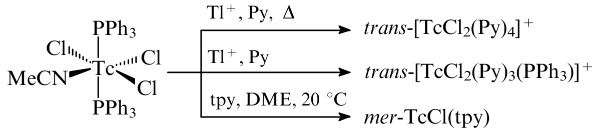
Starting compound	Reagents	Product	Ref.
UCl_4 or $U(BH_4)_4$	NaSR (R = Bu^t, Ph), THF	$(THF)_3Na(\mu\text{-}SR)_3U\cdot(\mu\text{-}SR)_3Na(THF)_3$	232
UI_4	DMSO DIBSO	$UI_4(DMSO)_n$ (n = 6, 8) $UI_4(DIBSO)_n$ (n = 6, 8)	104
$Cp_2^*UCl_2$	$Na_2(dddt)$	$Cp_2^*U(dddt)$	230
$U(NEt_2)_4$	Pr^iSH, $(Me_2N)_3PO$	$U(SPr^i)_4[OP(NMe_2)_3]_2$	233

XI. Technetium complexes

The chemistry of technetium becomes increasingly important, particularly, due to the fact that the short-lived ($T_{1/2}$ 6.015 h, γ irradiator) nuclide ^{99m}Tc is used in diagnostic medicine. This nuclide has been used over many years in bone scanning. Recently, ^{99m}Tc has found use in the treatment of various diseases of the heart, brain, kidney, liver and other organs as well as of tumour tissues. Technetium complexes are also of interest in the radiopharmaceutical industry.[234] Owing to the ideal energy of γ radiation (140 keV), lack of particulate radiation dose, the small half-life $T_{1/2}$ and the fact that ^{99m}Tc is readily accessible, this isotope is a radionuclide of choice for obtaining images in diagnostic nuclear medicine.[235, 236]

1. Complexes with nitrogen-containing ligands

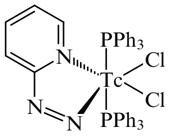
Complexes of Tc(III), Tc(II) and Tc(I) with pyridine ligands were prepared.[237] The authors were interested to prepare a coordinatively unsaturated low-valence electron-rich Tc metal centre surrounded by very weak π-donor ligands.



tpy is terpyridine.

The $TcCl_2(Py)_4$, $TcCl_3(PPh_3)_2(TMEDA)$, $TcCl_3[Bu_3^t(tpy)]$ and $[Tc(tpy)(Py)_3]Cl$ compounds were characterised by electrochemical and spectroscopic methods and by X-ray diffraction analysis.[237] According to the data of this investigation, π-back bonding is observed in the Tc(II) and Tc(I) complexes, unlike the Tc(III) complexes. In particular, the Tc−N bonds in pyridine complexes of Tc(II) are shortened by 0.04−0.06 Å and the Tc−N(internal) bonds in terpyridine complexes of Tc(I) are shortened by 0.09 Å compared to those in the analogous Tc(III) complexes.[237] These effects are favourable for stabilisation of low oxidation states of the metal atoms. The pyridine Tc(III) complexes give Knight-shifted ^{1}H NMR spectra. The visible regions of the spectra show transitions, which were empirically assigned to ligand-to-metal charge transfer transitions; multiple reversible electrochemical redox couples were found.[237]

Reduction of pertechnates (as well as perrhenates or permolybdates) with 2-hydrazinopyridine hydrochloride in methanol afforded complexes containing the $M(\eta^1\text{-}NNC_5H_4NH_x)(\eta^2\text{-}HNNH_yC_5H_4N)$ core (M = Tc, Re or Mo).[238] In particular, the $TcCl_3(NNC_5H_4NH)(HNNC_5H_4N)$ complex was prepared. The latter was used for the synthesis of the $Tc(C_5H_4NS)_2.(NNC_5H_4N)(HNNC_5H_4N)$ complex (C_5H_4NS is pyridine-2-thiolate), which is a precursor of ^{99m}Tc-containing peptide reagents for medical investigations. The bifunctional hydrazine ligands used in the study[238] are efficient and versatile linkers for labelling antibodies and protein fragments. Other organic hydrazine complexes of ^{99m}Tc were also prepared. The reactions of $[TcOCl_4]^-$ with hydrazine hydrochloride (PhMe, 20 °C or CH_2Cl_2, 36 °C) gave rise to $[TcCl_2(C_8H_5N_4)(PPh_3)_2]\cdot 0.75\,PhMe$ and $[TcNCl_2(PPh_3)_2]\cdot 0.25\,CH_2Cl_2$, respectively.[239] The exchange reaction of $Tc(MeCN)(PPh_3)_2Cl_3$ with 2-hydrazinopyridine afforded Tc(III) complex **39**.[240]



39

Complexes with compositions *mer*-$[Cl_3(pic)_3Tc]$ and *mer*-$[Cl_3(pic)(PMe_2Ph)_2Tc]$ (pic is 4-picoline) were prepared by the reactions of $[TcOCl_4]^-$ with a series of phosphine ligands in 4-picoline. The process was accompanied by the oxygen atom migration. The resulting compounds were characterised by spectroscopic methods and X-ray diffraction analysis.[241]

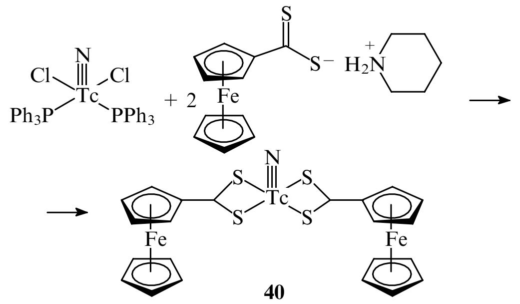
Complexes of high oxidation state technetium containing the $[Tc\equiv N]^{2+}$ core are more stable than the corresponding complexes of technecyl $[Tc=O]^{3+}$ and their properties resemble those of technecyl derivatives.

The technetium(V) complex $[TcN(L)(H_2O)]\cdot 2H_2O$ (L is the tetraazamacrocycle) was prepared by the reaction of $TcNCl_2(PPh_3)_2$ with the tetraazamacrocycle.[242] A complex with the $[Tc\equiv N]^{2+}$ core was synthesised using ancillary polydentate phosphorus- and nitrogen-containing ligands. The reaction of $[TcNBr_4]^-$ with 2,2′-bipyridyl in ethanol afforded the *cis*-octahedral $[TcNBr(bipy)_2]_2(TcBr_4)$ complex with the $[Tc\equiv N]^{2+}$ core containing the tetrahedral tetrabromo technetate(II) cation.[243]

Other chelate nitride complexes of technetium(V) with the N_2S_2 ligand and the $[Tc\equiv N]^{2+}$ core were prepared by the reactions of $TcNCl_2(PPh_3)_2$ with $(HSCR_2CH_2NRCH_2)_2$ (R = Me or Et).[244]

Since the chemical behaviour of the Mo^VO complexes is similar to that of the $Tc^{VI}N$ complexes, pertechnate complexes can be synthesised according to the procedure developed for the preparation of analogous Mo^VO complexes. Thus chelate nitride complexes of technetium(V) with ligands of the N_2S_2 type and the $[Tc\equiv N]^{2+}$ core, *viz*., $[TcN(S_2CNEt_2)]_2(\mu\text{-}O)_2$, $[TcN.(S_2CNC_4H_8)]_2(\mu\text{-}O)_2$, $(AsPh_4)_2\{[TcN(CN)]_2(\mu\text{-}O)_2\}$ and $(AsPh_4)_2.\{[TcN(edt)]_2(\mu\text{-}O)_2\}$ [edt = $S(CH_2)_2S$], were prepared by the reactions of $\{[TcN(OH_2)_3]_2(\mu\text{-}O)_2\}^{2+}$ or $Cs_2(TcNCl_5)$ with precursors of the corresponding ligands in solutions of $Na_4P_2O_7$.[245]

The reaction of $TcNCl_2(PPh_3)_2$ with the piperidinium ferrocenyldithiocarboxylate gave rise to nitride complex **40**. According to the data of cyclic voltammetry,[246] two iron(II) atoms in the complex **40** act as independent redox centres linked through the $[Tc\equiv N]$ core. Chelate complexes **41** and **42** containing the same $[Tc\equiv N]$ core were also synthesised.[247]



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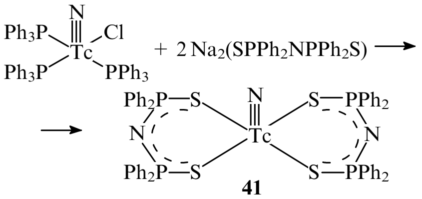


41

$$\mathrm{TcNCl_2(PPhMe_2)_2} \xrightarrow{\mathrm{NaN(SPPh_2)_2}} \mathrm{TcN(Cl)(PPhMe_2)[N(SPPh_2)_2]}$$

42

The possibility of radiopharmaceutical application of nitride technetium complexes with nitrogen-substituted amino acids, *viz.*, derivatives of 2,5-dimethyldithiocarbamic acid, was reported.[248] Complexes with composition $\mathrm{TcN(L^{\mathit{n}})(PPh_3)}$, where L^n = Z-Gly-dtc ($n = 1$), Z-Ala-dtc ($n = 2$), Z-Phe-dtc ($n = 3$), Z-Val-dtc ($n = 4$) or Z-Leu-dtc ($n = 5$), were synthesised. All these complexes were characterised by spectral methods and X-ray diffraction analysis.

Binuclear complexes of Tc(VII) **43** and Tc(VI) **44** were synthesised by reduction of complexes **45** and **46**, respectively, with sodium.[249]

$$\underset{\mathbf{45}}{\mathrm{Tc(NC_6H_3Me_2\text{-}2,6)_3I}} \xrightarrow{\mathrm{Na}} \underset{\mathbf{43}}{\mathrm{Tc_2(NC_6H_3Me_2\text{-}2,6)_4(\mu\text{-}NC_6H_3Me_2\text{-}2,6)_2}}$$

$$\underset{\mathbf{46}}{\mathrm{Tc(NC_6H_3Pr^i_2\text{-}2,6)_3I}} \xrightarrow{\mathrm{Na}} \underset{\mathbf{44}}{\mathrm{Tc(NC_6H_3Pr^i_2\text{-}2,6)_6}}$$

The crystal structure of the complex **43** consists of tetrahedra linked *via* shared edges, whereas the complex **44** has an 'ethylene-like' structure.[249] The reaction of the pertechnate ion with the salt of 3,6-bis(2′-pyridyl-1,2,4,5-tetrazine) (bptz · 2 HCl) in methanol or ethanol afforded binuclear complexes of the general formula $\mathrm{(\mu\text{-}bptz)(TcO_3X)_2}$ (X = Cl, OMe or OEt) containing Tc(VII), Tc(V) and the bridging bptz ligand. 4-Phenyl-3,6-bis(2′-pyridyl)-pyridazine (pppz) was used as a ligand for the preparation of mononuclear complexes from pertechnate and $\mathrm{TcOCl_4}$ in an aqueous-ethanolic solution of HCl.[250] The binuclear polypyridyl oxo-bridged technetium(III) complex $\mathrm{\{(tpy)[Me_2(bipy)]Tc-O-Tc(tpy)[Me_2(bipy)]\}(OTf)_4}$ was prepared by the reaction of $\mathrm{TcCl_3(tpy)}$ with thallium triflate in the presence of water.[251]

The synthesis of diazene technetium complexes was described.[252] Thus the $\mathrm{TcCl(NNR)_2(PPh_3)_2}$ complex ($\mathrm{R = C_6H_4Cl\text{-}4}$), which was prepared from $\mathrm{TcOCl_4^-}$ and monosubstituted hydrazine $\mathrm{RNHNH_2}$ in methanol, reacted with the bidentate $\mathrm{S_2CNR_2}$ ligand and maltol to give $\mathrm{Tc(NNR)L_2(PPh_3)}$ and $\mathrm{TcCl(NNR)L(PPh_3)}$ ($\mathrm{L = S_2CNR_2}$) in high yields.[252]

The template synthesis from tetrabutylammonium pertechnate $\mathrm{(NBu_4)(TcOCl_4)}$ or $\mathrm{(NH_4)_2(TcXO)}$ (X = Cl or Br) followed by reduction by divalent tin afforded seven-coordinate Tc(III) complexes, for example, such as the monocapped adduct of boric acid with technetium(III) trisdioximate or $\mathrm{TcX(dioxime)_3BR}$ (X = Cl or Br; dioxime = dimethylglyoxime or cyclohexanone dioxime; R = Me or Bu).[253]

A technetium(III) complex containing acetonitrile, *viz.*, $\mathrm{TcCl_3(MeCN)(PR_3)_2}$ ($\mathrm{R = Ph}$ or $\mathrm{C_6H_4Me\text{-}3}$), was prepared by reduction of $\mathrm{TcCl_4(PPh_3)_2}$ with zinc in acetonitrile in the presence of $\mathrm{PPh_3}$. This complex is a convenient intermediate in the synthesis of other Tc(III) compounds. Its reactions with bipy, 1,10-phenanthroline (phen) and tpy afforded dicationic Tc(III) complexes, *viz.*, $\mathrm{[Tc(bipy)_3]^{2+}}$, $\mathrm{[Tc(phen)_3]^{2+}}$ and $\mathrm{[Tc(tpy)_3]^{2+}}$, respectively, as salts with $\mathrm{BPh_4^-}$ or $\mathrm{PF_6^-}$.[254]

2. Complexes with sulfur- and oxygen-containing ligands

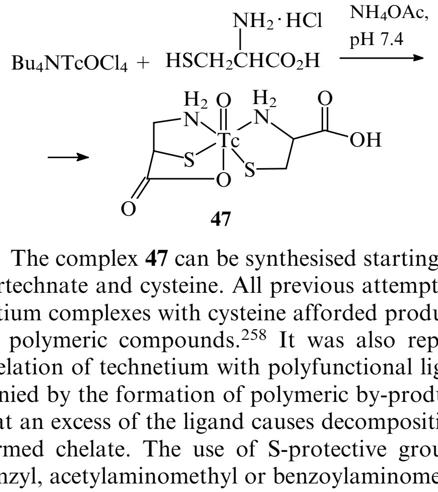
Reduction of $\mathrm{[Tc(OH)O(dmpe)_2]^{2+}}$ in the presence of an excess of toluene-3,4-dithiol ($\mathrm{H_2tdt}$) gave rise to the thiolate Tc(IV) complex $\mathrm{[Tc(tdt)(dmpe)_2](PF_6)}$ ($\mathrm{tdt = MeC_6H_3S_2\text{-}3,4}$).[255] Its structure was established by spectroscopic methods and X-ray diffraction analysis. The coordination polyhedron about technetium is intermediate between the octahedron and the trigonal prism [the Tc−S and Tc−P distances are 2.318(6) Å and 2.902(7) Å, respectively; the S−Tc−S angle is 84.49(4) °].

Refluxing of the salt $\mathrm{(NBu_4)(TcOCl_4)}$ in alcoholic solution with dihydrooxazoles and dihydrothiazoles, for example, with 2-(2-hydroxyphenyl)-4,5-dihydrooxazole, 2-(2-hydroxy-3-methylphenyl)-4,5-dihydrooxazole or 2-(2-hydroxyphenyl)-4,5-dihydrothiazole, yielded the six-coordinate complexes $\mathrm{TcOClL_2}$ (L is the corresponding (hydroxyphenyl)dihydrooxazole or -thiazole).[256]

The reaction of ammonium pertechnate with 3,5-di-*tert*-butylpyrocatechol (DBCat) in methanol afforded a mixture of the $\mathrm{Tc^{VI}(DBCat)_3}$ and $\mathrm{Tc^{VI}(DBCat)_2(DBAP)}$ complexes (DBAP is the amidophenoxide ligand).[257] The amidophenoxide ligand is formed through condensation of ammonia (from ammonium pertechnate) with pyrocatechol to give the Schiff's base. According to the data of EPR spectroscopy and X-ray diffraction analysis, technetium in the complex exists in oxidation state +6, which is very untypical. The DBCat ligand serves both as a reducing and chelating agent.

3. Complexes with nitrogen- and sulfur-containing ligands

The $\mathrm{HTcO(cysteine)_2}$ complex (**47**) and its barium salt $\mathrm{Ba[TcO(cysteine)_2]_2}$ were synthesised.[258] These compounds are of importance in biology and medicine. The properties of these complexes were studied.



47

The complex **47** can be synthesised starting from ammonium pertechnate and cysteine. All previous attempts to prepare technetium complexes with cysteine afforded products contaminated by polymeric compounds.[258] It was also reported[259–263] that chelation of technetium with polyfunctional ligands was accompanied by the formation of polymeric by-products. It is believed that an excess of the ligand causes decomposition of the initially formed chelate. The use of S-protective groups (for example, benzyl, acetylaminomethyl or benzoylaminomethyl) prevents the formation of undesirable polymeric products.[258]

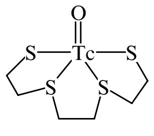
The technetium ($\mathrm{^{99m}Tc}$) analogue of oxorhenium bis-cysteinate possesses valuable biological properties. In particular, it is accumulated in kidneys,[264] which is useful in diagnostics of the morphological status of this organ.[258]

Potential radiopharmaceuticals for diagnostics of the renal function were synthesised with the use of chelating carboxyl-containing ligands bearing N- and S-centres . The carboxyl groups favour the renal uptake of these compounds.[264] The $\mathrm{^{99}TcO(ECH_3)}$ complex was prepared based on the ammonium salt $\mathrm{NH_4(TcOX_4)}$ (X = Hal) and (2*R*,7*R*)-2,7-dicarboxy-3,6-diaza-1,8-octanedithiol ($\mathrm{ECH_3}$). In the isostructural rhenium(V) complex, one of the carboxyl groups in the *trans* position with respect to the oxo ligand is coordinated in an unexpected fashion.[265]

The choice of other ligands, *viz.*, Schiff's bases, was governed by their tendency to be coordinated to technetium in various unusual oxidation states. The chemistry of technetium(I) complexes is poorly known. Only a few compounds were identified and characterised. The reaction of $\mathrm{(PPh_3)_2(CO)_3Cl}$ with the lithium salt of Schiff's base, *viz.*, *N*-*ortho*-hydroxybenzylidene-2-thiazolylimine, in boiling THF gave rise to the Tc(I) complex with composition $\mathrm{Tc(PPh_3)_2(CO)_2[(C_3H_2NS)N=CHC_6H_4O]}$. This six-coordinate complex has a distorted octahedral structure with *trans*-$\mathrm{PPh_3}$ and *cis*-CO groups and one chelating bidentate anion.[266]

Complexes containing biologically active molecules, such as peptides, proteins or antibodies, as ligands can be used as unique target-specific radiopharmaceuticals in diagnostics. The reaction of $[TcO_4]^-$ with $SnCl_2$, sodium gluconate and RP 294 produced the $^{99}Tc(V)$ oxo complex with RP 294, which exists as the *syn* and *anti* isomers. The study of the crystal structure of the isostructural rhenium(V) complex demonstrated that the isomerism results from the positions of the CH_2OH groups in the serine residues. At room temperature, the isomers in solution undergo interconversion. The ^{99m}Tc and rhenium complexes with RP 294 exhibit similar chemical properties.[267]

The ^{99}Tc and ^{99m}Tc complexes with new tetradentate N_2S_2 and NS_2 ligands were prepared by refluxing a methanolic solution of $(TcOCl_4)(NBu_4)$ with the corresponding NS_3H_3 proligands. The technetium(V) complex $[TcO(NS_3)](NBu_4)$ (**48**) was obtained in high yield. However, compounds of this type are unstable and decompose in a matter of several hours or days. By analogy with the crystal structure of the related rhenium oxo complex, these compounds can be considered as square-pyramidal complexes containing the oxygen atom in the apical position.[268]



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4. Complexes with phosphorus-containing ligands

Phosphine ^{99m}Tc-labelled derivatives can be used for obtaining images of internal organs, for example, heart images. Complexes of the $[TcO_2(PR_3)_3](BPh_4)$ (R = Et or Pr) type[234] have distorted trigonal-bipyramidal structures with two oxo ligands located in a single plane. Salts of the $[TcO_2(PR_3)_3]^+$ cations are convenient starting compounds for the synthesis of other complexes with mixed ligands.

$$[TcO_2(PR_3)_2]^+ \xrightarrow[\text{MeOH}]{\text{Py}} [TcO_2(PR_3)_2(Py)_2]^+$$

The trimethylphosphine derivative $[TcO_2(PMe_3)_2(Py)_2]^+$ can be prepared according to a one-pot procedure directly from pertechnates $[TcO_4]^-$. Apparently, this procedure can be adapted for the preparation of ^{99m}Tc radiopharmaceuticals in hospitals.

$$NH_4(TcO_4) \xrightarrow[\text{MeOH}]{\text{Py, PMe}_3} [TcO_2(PMe_3)_2(Py)_2]^+$$

The $[TcO_2(PR_3)_2(Py)_2]^+$ derivatives are diamagnetic, which is indicative of a noticeable deviation of their geometry from the ideal octahedron.[234]

The reactions of pertechnate with derivatives of phosphinocarboxylic acids afforded the TcL_3 complexes [L is 2-(diphenylphosphino)benzoic acid, 3-(diphenylphosphino)propionic acid or (diphenylphosphino)acetic acid]. According to the results of spectroscopic studies and X-ray diffraction analysis, these complexes possess a distorted octahedral geometry with the *mer* configuration in which the donor atoms of the same type are in *trans* positions with respect to each other and the phosphorus atom is in the *trans* position with respect to the oxygen atom.[269]

Complexes of the short-lived ^{99m}Tc isotope were prepared analogously. Their physical and chemical properties are similar to those of ^{99}Tc complexes. Biological assays revealed significant brain uptake of these compounds.

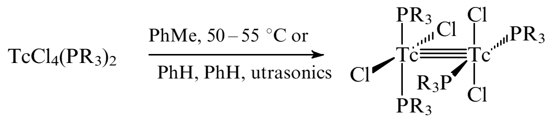
Chelate technetium(V) complexes with bis(*o*-hydroxyphenyl)-phenylphosphine and (*o*-hydroxyphenyl)diphenylphosphine were prepared by metathesis of the corresponding Tc(V) precursors or by reduction – ligand exchange with ammonium pertechnate.[270] These complexes combine a soft phosphine donor site and two hard phenoxide centres. It was expected that this fact would stabilise technetium in intermediate oxidation states.

The $[Tc(tu\text{-}S)_6]Cl_3 \cdot 4\,H_2O$ complex (tu-S is thiourea) was used as the precursor of $[Tc(dppe)_2(Bu^tNC)_2](PF_6)$ (dppe is diphenylphosphinoethane).[271] This complex can be prepared by mixing both ligands and a source of technetium(III) in ethanol followed by refluxing of the reaction mixture. This procedure is more convenient than the method involving a sodium amalgam, dppe and $TcCl_4(PPh_3)_2$. In the $[Tc(tu\text{-}S)_6]Cl_3 \cdot 4\,H_2O$ complex, the coordination polyhedron about the technetium atom is a distorted tetrahedron, the isocyanide ligands being in *trans* positions with respect to each other.

Treatment of $[TcO_4]^-$ with an excess of the corresponding S,P-bidentate phosphinothiolate ligands, such as 2-(diphenylphosphino)ethanedithiolate, 2-(diphenylphosphino)propanethiolate or 2-(diphenylphosphino)thiophenoxide, yielded neutral technetium(III) complexes.[272] These complexes have a trigonal-bipyramidal geometry, two phosphorus donor centres (consisting of two chelate rings) occupying axial positions and being in *trans* positions with respect to each other.

5. Complexes with the metal – metal bond, carbonyl complexes

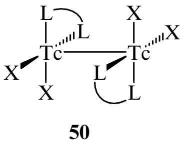
The data on complexes containing multiple Tc – Tc bonds are scarce. Thus several diamagnetic phosphine ditechnetium(II) complexes of the $Tc_2Cl_4(PR_3)_4$ type (**49**) were described.[160] These complexes contain a triple bond between the metal atoms and provide the first examples of phosphine complexes possessing a multiple technetium – technetium bond.



PR$_3$ = PEt$_3$, PPr$^n_3$, PMePh$_2$, PMe$_2$Ph.

49 (> 90%)

The polymeric chain structure of $[Tc_2Cl_6]_n^{2n-}$ also contains triple metal – metal bonds.[273] The triple Tc ≡ Tc bond was found in the α and β forms of the $Tc_2Cl_4(dppe)_2$ complex.[274] The α isomer **50** adopts an eclipsed conformation; the Tc – Tc distance is 2.15(1) Å. In the β isomer **51**, the twist angle is 35(2)° and the Tc – Tc distance is 2.117(1) Å. These isomeric complexes were prepared by refluxing $Tc_2Cl_4(PR_3)_4$ (PR$_3$ = PEt$_3$ or PMe$_2$Ph) in toluene in the presence or in the absence of an excess of dppe, respectively.



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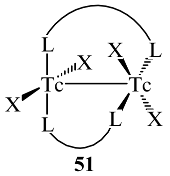


51

L = dppe, X = Cl.

Complexes containing the multiple Tc – Tc bond of order 3.5 were synthesised in high yields by one-electron chemical oxidation of the $Tc_2Cl_4(PMe_2Ph)_4$ complex with ferrocenium hexafluorophosphate in acetonitrile.[275] In this study, the cationic $[Tc_2Cl_4(PMe_2Ph)_4](PF_6)$ complex was prepared.[275] Oxidation in the presence of bis(triphenylphosphine)iminium produced the neutral $Tc_2Cl_5(PMe_2Ph)_3$ complex.[275] The complexes $Tc_2Cl_4(PR_3)_4$ **49** (PR$_3$ = PEt$_3$, PMePh$_2$ or PMe$_2$Ph) reacted with molten diphenyl- or di-*p*-tolylformamidine to give mixtures of formamidine-bridged complexes of the general formula $Tc_2(L)_4Cl_n$ (n = 1 or 2) in moderate yields.[276] Complexes with the triple Tc ≡ Tc bond, for example $[Tc_2(MeCN)_{10}](BF_4)_4$,[277] in an acetonitrile solution can undergo photodissociation to give the $[Tc(MeCN)_6]^{2+}$ ions in almost quantitative yields.[278] A decaacetonitrile binuclear complex with the triple Tc ≡ Tc bond was obtained in good yield by acidification of a solution of $Tc_2Cl_4(PR_3)_4$ in a mixture of acetonitrile and dichloromethane using $HBF_4 \cdot Et_2O$.[277] The $[Tc_2Cl_8]^{n-}$ (n = 2, 3 or 4) and

$[Mo_2Cl_8]^{m-}$ (m = 4 or 5) clusters were studied by theoretical methods.[279]

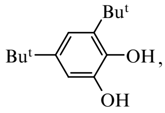
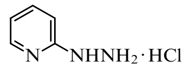
Of other types of Tc complexes, noteworthy are Tc carbonyl derivatives.[280–282] The $Tc(CO)_5I$ complex, which is isostructural to the $Mn(CO)_5I$ complex, exists as orthorhombic crystals. Its crystal structure consists of $Tc(CO)_5I$ molecules. The crystals of $[Tc(CO)_4I]_2$ are monoclinic and are also built of individual $[Tc(CO)_4I]_2$ molecules. Complexes with composition $[M(CO)_4X]_2$ (M = Mn, Tc or Re; X = Cl, Br or I) are isostructural. The main types of technetium complexes are given in Table 9.

* * *

In spite of the difficulties associated with operations with radioactive elements, their complexes are being studied intensively. The development of the coordination chemistry of these compounds, particularly, of those containing radioactive elements in unusual oxidation states,[24] is dictated both by the possibility of their practical use and theoretical interest. Thus considerable recent attention has been given to bimetallic complexes of 5*f* elements in connection with a search for new unusual properties and molecular structures. Investigations and a search for new uranium(V) complexes remain to be of great importance. Information[166, 167] on the unique activities of alkylcyclopentadienyl derivatives $Cp_2^*AnR_2$ (An = Th or U; R = H or Alk) as catalysts of alkene hydrogenation and polymerisation gave impetus to studies in this field of chemistry. These compounds proved to be ten times more active than traditional Pt/SiO_2 catalysts. Hence, actinide complexes are of interest from the viewpoint of extension of the scope of their use in catalysis, as the starting compounds in organometallic synthesis[17, 24] and for separation and extraction of actinides.[283]

We are grateful to Professor M Ephritikhine (Service de Chimie Moleculaire, France) for permission to reproduce schemes from his articles and Professors A D Garnovskii (Rostov State University, Russia) and S S Berdonosov (Moscow State University, Russian Federation) for valuable advice.

Table 9. Synthesis of technetium complexes with oxygen-, sulfur-, nitrogen- and phosphorus-containing ligands.

Starting compound	Reagent and reaction conditions	Products	Ref.
Complexes with oxygen- and sulfur-containing ligands			
$KTcO_4$	 , MeOH	$Tc(DBCat)_3$, $Tc(DBCat)_2(DBAP)$	257
$Tc(PPh_3)_2(CO)_3Cl$	$LiOC_6H_4CH{=}N(CSNC_3H_2)$, THF	$Tc(PPh_3)_2(CO)_2\cdot$ $[(C_3H_2NSC)N{=}CHC_6H_4O]$	266
$Tc(CO)_5X$ (X = Cl, Br, I)	H_2O	$[Tc(CO)_3(H_2O)_3]^+$	282
Complexes with nitrogen-containing ligands			
$Tc_2Cl_4(PR_3)_4$ (PR_3 = PEt_3, PMe_2Ph, $PMePh_2$)	(1) Bu_3SnH or Zn (2) MeCN, HBF_4	$[Tc_2^{II}(MeCN)_{10}](BF_4)_4$ (see[a])	277
$[TcCl_6]^{2-}$	(1) Bu_3SnH or Zn (2) MeCN, HBF_4	$[Tc_2^{II}(MeCN)_{10}](BF_4)_4$	277
$(Bu_4N)(TcOCl_4)$	Cys[b]	$HTcO(Cys)_2$	258
$TcCl_3(PPh_3)_2(MeCN)$	$Bu_3^t(tpy)$, DME	$TcCl_3[Bu_3^t(tpy)]$	237
NH_4TcO_4	 , MeOH	$TcCl_3(\eta^1\text{-}NNC_5H_4NH)(\eta^2\text{-}HNNC_5H_4N)$	238
Complexes with phosphorus-containing ligands			
$Tc_2Cl_4(PMe_2Ph)_4$	$(Cp_2Fe)(PF_6)$	$[Tc_2Cl_4(PMe_2Ph)_4](PF_6)$[c]	275
$NH_4(TcO_4)$	PR_3, MeOH (R = Et, Pr) (see[d])	$[TcO_2(PR_3)_3]^+$	234
$[TcO_2(PR_3)_3]^+$ (R = Et, Pr)	PR_3, MeOH, Py (R = Et, Pr)	$[TcO_2(PR_3)_3(Py)_2]^+$	234
$TcCl_3(PPh_3)_2(MeCN)$	TMEDA, PhMe, DME	$TcCl_3(PPh_3)_2(TMEDA)$	237
	Py	*mer*-$TcCl_3(Py)_2$	241
$TcCl_4(PPh_3)_2$	PR_3 (R = Et, Pr^n), THF	$TcCl_4(PR_3)_2$	160
$TcCl_4(PEt_3)_2$	Zn, PhH, utrasonics	$Tc_2Cl_4(PEt_3)_4$	160

[a] The yield was 50%, the Tc–Tc multiple bond is present; [b] Cys is an aqueous solution of cysteine chloride monohydrate; [c] the multiple Tc–Tc bond is present; [d] the yield was 60%–70%; a ~10-fold excess of the ligand was used; there was no need for the use of reducing agents; the reaction was accompanied by the formation of NH_3.

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[a] — *Radiochemistry (Engl. Transl.)*
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