ADVANCES IN INORGANIC CHEMISTRY, VOL. 34

COMPOUNDS OF THORIUM AND URANIUM IN LOW (<IV) OXIDATION STATES

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I. Introduction

Much new information about compounds of the lower oxidation states of uranium and thorium has accumulated during the last decade, and the rapid development of the organometallic chemistry of these elements has enhanced interest in this topic.

Simple compounds of trivalent uranium have a long history; thus, in this review the emphasis is on the developments since the Gmelin Uranium (*1*) supplementary volumes (*1a–j*). However, reference is made to earlier work if it facilitates understanding and avoids a disjointed account. A compact account of most of the earlier work can be found in the second edition of *The Chemistry of the Actinide Elements* (*2*). Solid compounds, for which oxidation state concepts are inappropriate, have usually been excluded.

For thorium and the organometallic compounds, a different policy has been followed. The literature in these areas is limited and contains sufficient discrepancies to justify an attempt at complete coverage.

II. Solution Chemistry

A. THERMODYNAMIC AND RELATED DATA ON THE TRIVALENT IONS (*1b,g*)

Very little new data based on experimental work has appeared since the I.A.E.A. publication on the aqueous actinide ions (*3a,b*). The current situation has been reviewed in refs. (*4b, 8c*).

An earlier analysis of the crystallographic data suggested an ionic radius for U^{3+} of 102.5 pm in a 6-coordinate environment (*4a*). A more recent examination of all the available data gave 102.8 and 116 pm in

6- and 8-coordination, respectively (*4b*). An estimate for Th^{3+} of 108 and 122 pm, for the same coordination numbers, was also made (*4b*).

There is not much information on the hydration of these trivalent cations. Estimates made on the basis of the calculated entropies of hydration suggest a hydration number of about 7 (*5, 6a*). But an estimate made by extrapolation of data for electrophoretic transport measurements on the M^{3+} ions of some heavier actinides indicate a hydration number of about 12.7, with nine water molecules in the first coordination sphere (*6b*).

The polarizabilities of the Th^{3+} and U^{3+} ions have been calculated to be 1.98 and 1.86 10^{-24} cm^3, respectively (*7*).

There is still only the early direct measurement of the formal reduction potential for $U^{4+} + e^- \rightarrow U^{3+}$, −0.631 V (*8a*). Standard values are less accurate, because of uncertainties in the necessary activity corrections or extrapolation; values of −0.607 and −0.596 V (*8b*) have been estimated; but a larger value of −0.52 V has been proposed as more compatible with data on the enthalpies of formation of the hydrated U^{3+} and U^{4+} and their standard entropies (*8c*).

For thorium there are only estimates of the corresponding potential. An early estimate, of −2.4 V, was based on a relation between this quantity and the frequency of the first electron transfer absorption band in the UV spectrum of an aqueous thorium perchlorate solution (*9*). However, the spectral measurements did not quite reach the absorption maximum, and the necessary extrapolation introduced some uncertainty. Another value, −3.6 V, was based on the RESPET treatment of Jørgensen (*10, 11*). The adjustable parameters in the RESPET equation were fixed using experimental values for other actinide elements (*12*). This method yields a value of −0.69 V for U(IV)/(III). Another rather simple method correlates this potential with the number of 5*f* electrons for the element and gives −3.41 V for thorium and −0.54 V for uranium (*13*). A more sophisticated estimate (*14*), using a method proposed by Nugent *et al.* (*12*) (described later), gave −3.8 V for thorium.

The U(III)/(0) standard potential is −1.66 V, and the thorium value has been estimated as −1.17 V. (*14*)

The experimental values of the conventional $\Delta H_f^\circ U^{3+}$, $\Delta G_f^\circ U^{3+}$, and $\Delta S_f^\circ U^{3+}$ at 298 K are −489.1 ± 3.8 kJ mol^{-1}, −480.7 ± 4.6 kJ mol^{-1}, and −26.8 J K^{-1} mol^{-1}, respectively (*3b, 4b, 15*) (For predictions of these properties see ref. 16.) But it must be noted that these quantities involve the U(IV)/(III) potential, the enthalpy change for the reaction $U^{3+} + H^+ \rightarrow \frac{1}{2} H_2 + U^{4+}$ in 0.5-M perchloric acid (*17*), and the enthalpy of formation of U^{4+}. Now it has been reported that the oxidation of U^{3+} in perchloric acid solution does not produce hydrogen (see Section II,E), so there is some uncertainty about these values. The value of $\Delta S_f^\circ U^{3+}$ implies that $S^\circ U^{3+} = -174.9$ J K^{-1} mol^{-1} at 298 K (but see ref. *4b*).

All the data for Th^{3+} are empirical estimates. An early example using an experimental value for Pu^{3+}, allowing electronic contributions to the entropy of $R\ln(2J + 1)$ and supposing that the other contributions are displaced by 25.9 J mol^{-1} from the corresponding lanthanide values, give -171.1 J K^{-1} mol^{-1} for S_{298}° for Th^{3+} (*18*). A more recent estimate gave $-S_{298}^\circ M^{3+}$ values of 176.1 and 177.8 J K^{-1} mol^{-1} for the trivalent aquated ions of Th and U (*19*).

A more extensive investigation (*14*) follows the method of Nugent *et al.* (*20*) and evaluates the function $P(M)$ for those actinides for which the necessary data are available. $P(M)$ is defined as the difference in the energy of the lowest f^n configuration of the aqueous M^{3+} ion and the energy of the lowest $f^n s^2 d$ configuration of the gaseous M atom. Thus $P(M) + -\Delta H_f^\circ M^{3+} + \Delta H_{subl}^\circ M_{(s)}$ if an $f^n s^2 d$ configuration is the ground state of the gaseous M atom. Otherwise, an additional term ΔE, equal to the difference between the energy of the ground state of the M atom and the lowest-lying $f^n s^2 d$ state, must be added.

This function proves to be a linear function of Z. This approach yields the following estimates: $\Delta H_f^\circ M^{3+}$ for Th and U is -347.3 and -489.1 kJ mol^{-1}, respectively. Entropies were estimated in a similar manner to ref. (*19*). The values obtained were -172.8 and -172.4 J K^{-1} mol^{-1} for Th^{3+} and U^{3+}, respectively, the latter value to be compared with the value of -174.9 J K^{-1} mol^{-1}, based on the experimental value for Pu^{3+}. The method seems to be more reliable for the later actinides than for the earlier members of the group.

The changes in enthalpy and Gibbs free energy associated with the hydration of the gaseous M^{3+} ions have also been calculated: $\Delta H_{hyd}^\circ = -3125.4$ and -3188.2 kJ mol^{-1} and $\Delta G_{hyd}^\circ = -3267.7$ and -3332.1 kJ mol^{-1} for thorium and uranium, respectively (*21, 22*). However, a recent examination of the data suggests values of $\Delta H_{hyd}^\circ = -3262$ and -3376 kJ mol^{-1} for Th^{3+} and U^{3+}, respectively (*4b*).

B. U^{3+} AND TH^{3+} BY PULSE RADIOLYSIS

Pulse radiolysis of U^{4+} solutions produces U^{3+}, which can be detected by its absorption spectrum. Varying the concentrations of hydrogen and U^{4+} ions has shown that the rate constant for $e^-\,(aq) + U^{4+} \rightarrow U^{3+}$

is 4.4 times the value for e^- (aq)$^+$ $H^+ \rightarrow \frac{1}{2} H_2$. Using the accepted value for the latter reaction gives a value of 3.6×10^{11} for the reduction of the U^{4+} (*23*).

Uranium (IV) can also be reduced to U(III) photochemically. Irradiation of a solution of UCl_4 in methanol at 248 nm gave up to 85% reduction with a quantum yield of 0.17. The U(III) produced could be stabilized as its (18-crown-6) complex (*24a*).

A solution of uranium (IV) chloride and an olefin (stilbene, diphenylethylene, or acenaphthylene) in tetrahydrofuran (THF) can be reduced by pulse radiolysis to give U(III) (*24b*). The reaction may proceed through an anionic complex.

Pulse radiolysis also leads to the production of Th^{3+} in perchlorate solution. This is the first clear evidence for Th^{3+}. The Th^{4+} reacts with the $e_{aq}{}^-$ more rapidly than with $ThOH^{3+}$ or $Th(OH)_2{}^{2+}$ (*25a,c*). But in sulphate solution, $ThSO_4{}^+$ is produced (*25b*).

C. SPECTRAL DATA (*1a*)

The theoretical basis for treating absorption spectal data for the *f*-shell elements was established many years ago (see, e.g., (*26–29*).

1. *Solution Studies*

The earlier data were analyzed by Jørgensen, who drew conclusions about the complexing of U^{3+} by some simple ligands (*30, 31*).

The main features of the absorption spectra are as follows. At frequencies below about 17,000 cm^{-1}, the bands are rather sharp and arise from $f \leftrightarrow f$ transitions. In this region, although the spans of different multiplets overlap, the individual levels are often well separated, and a fine structure due to ligand interactions can often be resolved. At higher frequencies, the broad and much higher intensity $f \leftrightarrow fd$ transitions lead to spectra that are hard to analyze, but they sometimes give hints about structure on a "fingerprint" or comparative basis. At still higher frequencies, the intense electron transfer spectra dominate. Some useful information can be obtained from the lower frequency region and sometimes from the $f \leftrightarrow fd$ region.

In the $f \leftrightarrow f$ region, the molar extinction coefficients range from 2 to 12. In the intermediate coupling treatments, which have had considerable success in the quantitative analysis of the spectra (see, e.g., 32), J remains a good quantum number, and the absorption bands correspond to excitations from the $\frac{9}{2}$ ground state (formally a $^4I_{9/2}$ state) to other J values. But each J state suffers a small splitting into a number of levels that are determined by the symmetry of the ligands, the magnitude of the splitting depending on the ligand-field interaction. Such splitting commonly amounts to some hundred wave numbers, and the linewidths and vibronic effects often permit some resolution of the splitting.

In addition to this level splitting, the ligands may shift the center of gravity of the level due to nephelauxetic effects of the ligands. These can change the frequencies by some small percentage.

Both these effects provide some information about the interaction of U^{3+} ion with its surroundings. On this basis one might expect all U^{3+} solution spectra to appear superficially similar. However, this is not quite true, partly because of hypersensitivity effects leading to anomalously strong absorptions.

The absorption spectrum of U^{3+} in anhydrous formic acid is a typical example (Table I).

A number of solution spectra have been measured (Table II). Unfortunately, in most of them the U^{3+} environment is not securely established.

TABLE I

ABSORPTION SPECTRUM OF U^{3+} IN ANHYDROUS FORMIC ACID[a]

Formal description of level[b]	Center of gravity of band (cm^{-1})	Intensity[c]
$^4I_{11/2}$	4500	m
$^4F_{3/2}$	7200	—
$^4I_{13/2}$	8200	s
$^2H_{9/2}$[d]	9600	—
$^4F_{5/2}$	9900	—
$^4S_{3/2}$	11,100	s
$^4I_{15/2}$	11,310	s
$^4G_{5/2}$[d]	11,600	—
$^4F_{7/2}$	11,650	—
$^4G_{7/2}$	13,600	s

[a] Data from refs. *32* and *33*.

[b] Overlapping bands are in brackets.

[c] s, Strong; m, medium.

[d] Bands especially liable to hypersensitive intensification.

TABLE II

SOME SOLUTION SPECTRA THAT HAVE BEEN MEASURED

Solution	Ref.	Other details (band data in cm^{-1})
1. Aqueous perchlorate	*34*	Extinction coefficients and analysis of spectrum
2. Sulphate and halide solutions	*35*	Conclusions re complexing; strong band around 18,300 in strong halide solutions
3. Anhydrous acetic acid; UCl_3 and UI_3 solutes	*36*	$f \leftrightarrow fd$ region
4. Dilute mineral acids	*37*	Spectra all the same
5. Sulphate and chloride solutions	*38*	Strong band at 18,300 in concentrated chloride
6. 1-M mineral acids	*39*	As in solution 4
7. Anhydrous formic acid	*32*	Detailed analysis of spectrum
8. Rb_2UCl_5 in hexamethylphosphoramide	*40*	Extinction coefficients much lower than for U^{3+} or UCl_3
9. UCl_3 in CH_3OH, and $(CH_3)_2NOCH$, with thiocyanate in CH_3OH	*41*	Intense band at 15,100 in thiocyanate solution; intense band near 18,300 in chloride solution.
10. U trihalides in hexamethylphosphoramide	*42*	$f \leftrightarrow fd$ region; crystal field effects Cl > Br > I
11. As in solution 10	*43*	$f \leftrightarrow f$ region bands assigned
12. U(III) in AsF_5/HF	*44*	—
13. UCl_3 made *in situ* in CH_3NHOCH, $(C_2H_5)_2NOCH$, and H_2NOCH	*45*	Hypersensitivity effects

A number of investigators have noted that contamination by U(IV) gives an absorption at about 6500 cm^{-1} (*31, 39*), but it is not a very sensitive test for the presence of U(IV).

2. *Melts*

The spectrum of UCl_3 in a LiCl/KCl melt has been recorded and analyzed in detail. The spectrum is not much different in the low-frequency region from that of U^{3+} (*46, 47*). There are also data for fluoride melts. Interference from U(IV), whose extinction coefficients are about three times as large as those of U(III), could not be avoided. It is interesting to note that U(III) in LiF/BeF_2 gives a yellow melt, but that in LiF/KF a red melt is obtained. The chloride melts are similar (*48*). Data have been reported for UCl_3 in $AlCl_3$ (60%)/NaCl (40%) (*49a*).

TABLE III

OTHER STUDIES OF SOLID SPECTRA

Solid	Ref.	Other details
1. UCl_3	*52*	Transmission data; microscopic method
2. UF_3	*53*	Microscopic method
3. U^{3+} in CaF_2	*54*	U(IV) impurity.
4. UF_3 in Teflon	*55*	Transmission data
5. Sulphate complexes	*38*	Reflectance data
6. Red and green NH_4UCl_4	*39*	Reflectance data
7. U^{3+} in CaF_2	*56*	—
8. UX_3 (X = Cl, Br, or I)	*57*	Reflectance data
9. UCl_37H_2O	*58*	Transmission data
10. U^{3+} in $LaCl_3$	*50, 59.*	—

3. *Crystal Spectra*

U(III) in an alkaline earth fluoride matrix was one of the earlier laser materials (*49b*). As might be expected with crystalline substances, the splitting of the various *J* levels can be completely resolved, especially at low temperatures. Thus the polarized absorption spectrum of U^{3+} in a lanthanum chloride matrix (C_{3h} environment) has been measured from 5600 to 25,000 cm^{-1} and analyzed in detail. The $\frac{9}{2}$ ground state yields 5 sublevels in this symmetry, the $\frac{11}{2}$ state yields 6 sublevels, and 20 lines result from the combination of these two levels (*50, 51*).

Table III shows a number of other studies of solid spectra.

U(III) spectra have been discussed in various reviews (*60–62*).

4. *Luminescence*

Emission during the U^{3+}–UO_2 reaction has been reported (*63*). An emission at 18,388 cm^{-1} can be excited in $U^{3+}/LaBr_3$ crystals (*64, 65*).

D. COMPLEXES OF URANIUM(III)

Until the late 1960s only one or two reports of U(III) complexes made in aqueous systems existed, and no complex had been properly characterized. But the next decade saw the identification and characterization of several species.

Although most aqueous solutions of U^{3+} salts are unstable with respect to oxidation by hydrogen ions, this reaction is rather slow; so if the ligands are resistant to reduction, then preparation of complexes in aqueous systems ought to be possible. Oxidation of U^{3+} by dissolved air is always quite rapid, and preparations must be conducted in completely air-free systems (*38, 66, 67*). The solid products are also more or less air sensitive, especially in moist air.

Very few solid simple salts have been made. However, reduction by Zn/Hg of a solution of UCl_4 in acetonitrile containing water and propionic acid gives a solution from which $UCl_3 \cdot 7H_2O$ can be crystallized. It forms ink-blue triclinic crystals, isostructural with $LaCl_3 \cdot 7H_2O$, space group $P\bar{1}$. The compound can be dehydrated *in vacuo* without oxidation. It obeys the Curie–Weiss law over the temperature range 10–300 K with $\mu_{eff} = 2.95\ \mu_B$ and $\theta = -32.7$ (*58*).

1. Anionic Complexes

An hydrated sulphate can be obtained by evaporating an electrolytically reduced uranyl sulphate solution. It is a very soluble, olive-green solid that yields a characteristically red-green U^{3+} solution (*38, 66, 67*). At first the sulphate frequencies in the IR spectrum and the absence of nephelauxetic shifts in the reflectance spectrum, in comparison with the absorption spectrum of U^{3+}, led to the conclusion that the compound contained hydrated U^{3+} ions and free sulphate ions. Its analysis corresponded to the formulation $U_2(SO_4)_3 \cdot 8H_2O$. More recently it has been shown to be hexagonal, belonging to the space group $P6_3/m$ and to be isomorphous with $La_2(SO_4)_3 \cdot 9H_2O$. Thus it contains both 12-coordinate uranium atoms, bound to 6 bidentate sulphate groups, and 9-coordinate uranium, bound monodentately to 3 sulphate groups and to 6 water oxygens. The remaining three waters are accommodated in the lattice (*68*). The compound should be formulated with $9H_2O$. However, some water can be removed without oxidation of the uranium, and an orange dihydrate is reported (*38*).

Several sulphatouranate(III) salts have been described: the first, $K_5U(SO_4)_4\ xH_2O$ has not been confirmed in later work (*38, 69*). Most of these compounds belong to the family $MU(SO_4)_2 \cdot nH_2O$ ($M = NH_4$, Na, K, Rb with $n = 4$; $M = Cs$ with $n = 5.5$) (*67*). $K_3U(SO_4)_3\ xH_2O$ has also been reported. $NH_4U(SO_4)_2 \cdot 4H_2O$ has now been shown to be isomorphous with $NH_4La(SO_4)_2 \cdot 4H_2O$. It is monoclinic and belongs to the space group $P2_1/c$. The cell parameters are $a = 670.65$, $b = 1903.28$, and $c = 883.05$ pm; $\beta = 97.337°$, $Z = 4$. The uranium atoms are 9-coordinate, being attached bidentately to two sulphate groups, monodentately to two more sulphate groups, and to three water molecules. There is one noncoordinated water (*68*).

It appears that the nephelauxetic effects of coordinated sulphate and water are very similar and that the spectral characteristics of the sulphato complexes are not very different from those of $U_{aq}{}^{3+}$.

The halouranate(III) salts are particularly interesting. The sulphate just described dissolves in concentrated hydrochloric acid at 273 K to give an intensely colored purple solution. This solution displays the intense absorption at about 18,000 cm^{-1} noted by other workers (*31*, *35*) and decomposes very easily with oxidation of the U(III). But adding potassium, rubidium, or ammonium chloride to the ice-cold solution yields the red $MUCl_4 \cdot 5H_2O$ salts. They are deliquescent and cannot be dehydrated without oxidation of the U(III). If, however, the ice-cold mixture is saturated with HCl gas for about an hour, an olive-green complex of approximately the same composition as the red compound is obtained. The two compounds and the purple solution show much the same spectrum in the region above 10,000 cm^{-1}, the solids being examined by reflectance methods (*39*). But the green compound does not show the 18,000 cm^{-1} band. Moreover, the nephelauxetic shifts of the bands seen at 10,220 and 13,680 cm^{-1} with U^{3+} are slightly different for the two compounds. In the IR the red compounds show absorptions at 230 and 196 cm^{-1} that are not seen in the spectra of the green compounds. Magnetic susceptibilities of the two sets of compounds are virtually the same (*39*).

Presumably, the difference between the two groups of compounds is due to differences in the coordination of water and chloride to the U(III). The authors regard the red compound as containing a chlorouranate(III) anion. Analogous bromo compounds could not be obtained though a strong absorption at about 18,300 has been reported for U^{3+} in concentrated lithium bromide solution (*35*).

These paramagnetic compounds obey the Curie–Weiss relation down to about 100 K. But the effective magnetic moment of the uranium complex varies from about 3.37 μ_B at room temperature to about 2.76 μ_B at 87 K. It is always less than the 3.62 μ_B expected for simple Russell–Saunders coupling without crystal field effects.

An hydrated fluoride, $UF_3 \cdot H_2O$, can be precipitated from solution (*57*). Its structure is unknown, and it cannot be dehydrated without oxidation.

The limitations to the preparation of U(III) complexes in aqueous solutions can be judged from the observation that the addition of phosphate, carbonate, nitrate, nitrite, sulphite, thiosulphate, or carboxylic acid anions to a U(III) sulphate solution all lead to rapid oxidation of the uranium, though color changes that suggest complex formation may occur (*57*).

Further information about such complex formation has been obtained by spectroscopic methods, observing the nephelauxetic shifts in the solutions in relation to the U^{3+} bands at 10,220, 11,300, and 13,680 cm^{-1} (*70*).

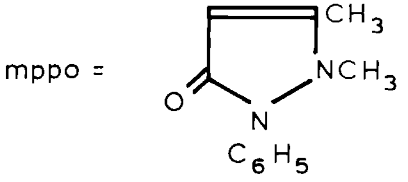
Such experiments show that oxalate, tartrate, and citrate give fairly strong complexes, and indeed these mixtures do not suffer quite such rapid oxidation as the other systems (*57, 70*). Stability constants for the complexing of U(III) by acetate, 2-hydroxy-2-methylpropionate, nitriloacetate, *trans*-cyclohexyl-1,2-diaminotetraacetate, ethylenediamine tetraacetate, and diethylenetriamine pentaacetate have been reported, but no pure compounds have been isolated (*71*). Thiocyanate also accelerates oxidation of the uranium, but the blue complex that is formed can be extracted with triethyl phosphate, tributyl phosphate, or better, trioctyl phosphine oxide; the organic extract decomposes only slowly (*45, 72*).

Addition of ferrocyanide to an alcoholic solution of $NH_4UCl_4{\cdot}5H_2O$ precipitates a dark green solid of composition $HUFe(CN)_6$ and unknown structure. Even the dry solid slowly decomposes (*78*).

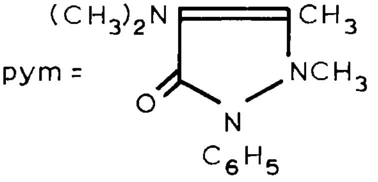
If a solution of UCl_4 in anhydrous formic acid is reduced with Zn/Hg crystals of U(III) formate separate. They are rhombohedral, belonging to the space group R3m, like Gd formate. Their magnetic susceptibility follows the Curie–Weiss expression in the temperature interval 50–250 K. The data yield μ_{eff} of 3.70 μ_B (*79, 80*). It is antiferro-magnetic below 12 K.

2. *Cationic Complexes*

Some early reports (*73–75*) described lilac hexathiocyanatochromate(III) salts of the complex cations $U(pyridine)_6^{3+}$, $U(mppo)_6^{3+}$, $U(DMF)_6^{3+}$, and $U(pym)_3^{3+}$, in which mppo = 2,3-dimethyl-1-phenyl-pyrazol-5-one (**1a**) and pym = 4-dimethylamino-2,3-dimethyl-1-phenyl-pyrazol-5-one (**1b**).



(1a)



(1b)

However, it has subsequently been shown that both $Cr(NCS)_6^{3-}$ and pyridine (pyr) are reduced quite rapidly by U(III), and it is unlikely that pure products could have been obtained.

Nonetheless, these cationic complexes exist, and the pure tetraphenylborate salts have been made (*39*). The red $NH_4UI_4\cdot 5H_2O$ is a valuable reagent for the synthesis of these complexes because it dissolves in methyl and ethyl alcohols as well as dimethylacetamide and DMF. The solutions are reasonably stable (up to about 1 day). The lilac complex salts $U(mppo)_6(BPh_4)_3$ and $U(pym)_4(BPh_4)_3$ can be made by mixing solutions of $NH_4UCl_4\cdot 5H_2O$ and the ligand in alcohol and adding sodium tetraphenylborate (*39, 70*). The ligand pym is probably bidentate as it is in other complexes. It is also possible to obtain the purple $U(MPPO)_6Cl_3$, but it is less stable (*39*). Salts of $U(DMF)_6$ can also be made.

A similar preparation has been used to obtain UL_4X_3 with $L = (CH_2)_n(CONR_2)_2$, $R = CH_3$ or C_2H_5, and $n = 1–4$, or $L = (CH_3)_2C(CH_2CONR_2)_2$, $R = CH_3$ or C_2H_5, and $X = PF_6$ or $B(C_6H_5)_4$.

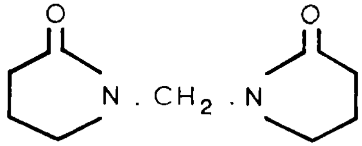
Analyses and spectra from 5000 to 50,000 cm^{-1} were recorded. These complexes are green, mauve, or black solids. At least five absorption bands were seen in the $f \leftrightarrow d$ region, suggesting a low-symmetry environment for the uranium. In the $f \leftrightarrow f$ region, all the spectra were similar. The C—O stretch in the IR decreased 30–80 cm^{-1} on complex formation, suggesting bonding to the uranium through the carbonyl oxygens. The magnetic susceptibility of the tetramethyl malonamide complex corresponds to $\mu_{eff} = 2.97$ BM. These complexes contain a UO_8 chromophore (*76, 77*).

A complex of the fully *N*-methylated ethylenediamine-tetraacetamide has also been mentioned (*85*).

A number of other U(III) complexes have been obtained by essentially the same method. $U(teep)_4(BPh_4)_3$ is lilac-mauve and $U(ompa)_4(BPh_4)_3$ is pink. The PF_6 salts are darker and redder in color. A red $U(cmp)_4(PF_6)_3$ and a darker purple $U(mbpo)_4(PF_6)_3$ have also been made (*78*). There is no structural or other information available on these compounds, beyond the observation of shifts in the $\nu_{P=O}$ or $\nu_{C=O}$ frequencies. The ligands are probably bidentate and the uranium 8-coordinate. They all show substantial nephelauxetic shifts (*77*).

teep = $(C_2H_5O)_2P(O)CH_2CH_2P(O)(OC_2H_5)_2$
ompa = $((CH_3)_2N)_2P(O)O(O)P(N(CH_3)_2)_2$
cmp = $(C_2H_5O)_2P(O)CH_2CON(CH_3)_2$

mbpo = (**2**)

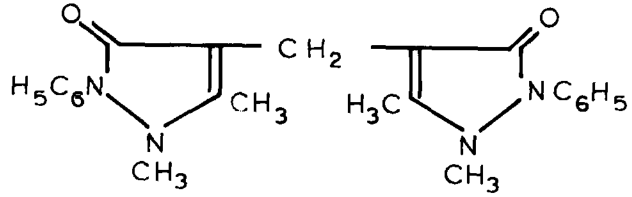


(2)

However, the red $U(temp)_3(PF_6)_3$, $U(mbp)_3(PF_6)_3$, and $U(mppo)_6(BPh_4)_3$ may contain 6-coordinate uranium. Steric reasons could account for the lower coordination number with the mbp and mppo complexes but seem less reasonable for the teep complex.

temp = $(C_2H_5O)_2P(O)CH_2CH_2CH_2(O)P(OC_2H_5)_2$

mbp = (3)



(3)

There is also evidence for complexes with hexamethylphosphoramide, 4-aminophenazone, and N-methyl and N-dimethyl acetamide. But an earlier report of a cupferron complex was not confirmed (*39*).

3. *Macrocycle Complexes*

Crown ether complexes can be precipitated by the addition of a solution of the ether to a solution of UCl_3 in the same solvent. Suitable solvents are THF and acetonitrile. The latter solutions were prepared by the reduction of a solution of UCl_4 in the solvent by zinc amalgam (*41, 79, 81*), sodium hydride (*82*), sodium naphthalenide (*83, 285*), or better, sodium carbide (*83*). The UCl_3 remains in solution, probably as an adduct of the solvent. The U(III) complexes precipitate, any U(IV) remains in solution. The complexes can also be prepared using a solution of $NH_4UCl_4 \cdot 5H_2O$ in alcohol (*78*).

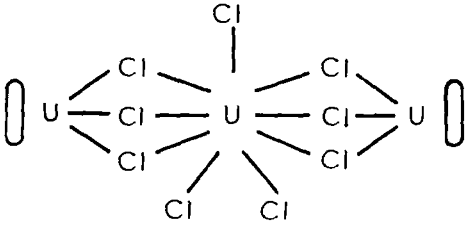
Earlier workers found difficulty in obtaining products of stoichiometric composition. This may be due, in part, to the formation of polynuclear species, solvent adducts, and in the presence of other anionic components, mixed species. Thus (18-crown-6) was reported to yield U(18-crown-6)Cl_3 (*78, 82, 85*). But more recent work shows that U_3(18-crown-6)$_2Cl_9$ is obtained (*81*) whatever the proportions of the reactants. An analogous compound is said to be obtained using a solution of $U(BH_4)_3$ in toluene, which is obtained by the thermal decomposition of $U(BH_4)_4$ in toluene solution at 423 K, the BH_4 analog precipitates with the addition of a solution of the ether in toluene (*84*).

The ligands (15-crown-5) (*78, 83, 85*) and cyclohexyl(15-crown-5) (*81*) are both reported to give complexes of composition $ULCl_3$, and a hydrated form of the first complex can be obtained, $ULCl_3 \cdot H_2O$ (*78, 85*). Benzo(15-crown-5) was first reported to give $ULCl_3$ (*83*), but more recent work suggests that in acetonitrile an adduct of $U_3L_2Cl_9$ is precipitated (*81*). This loses the solvent *in vacuo* at 383 K. An analogous complex was obtained from dibenzo(18-crown-6) and (15-crown-5) using a preparation from $U(BH_4)_3$ in toluene (*84*), but no details of these products were given. The product from dicyclohexyl(18-crown-6) in the presence of sodium tetraphenylborate has been given as $ULCl_2(BPh_4)$ (*78*). However, using a solution of $U(BH_4)_3$ in toluene, $U_3L_2(BH_4)_9$ was obtained (*84*). On the other hand, with the cis–syn–cis ligand and only chloride as anionic component, the product precipitating from acetonitrile was the pentanuclear $(UCl_3)_5L_3$ [(*81*); see also (*208, 345*)].

Finally, $U(18\text{-crown-}6)_2(PF_6)_3$ has been reported (*78, 85*), and spectrophotometric evidence for a U(III) complex of (21-crown-7) has appeared (*24*). It is possible that the precipitation of the complex depends on both the anionic component and the solvent used.

The complexes are of various shades of red or orange and are of very limited solubility in the solvents. The borohydrides tend to be slightly more soluble. Crystals of these complexes are hard to obtain, and no structures are available. In many solvents, solution is accompanied by replacement of the ether by the solvent.

The IR spectra suggest that the uranium is indeed bound to the ring oxygens. The asymmetric stretch frequency associated with the $CH_2CH_2OCH_2CH_2$ system shifts to lower frequency by about 20–40 cm^{-1} in the complexes (*81*). It has been suggested that the polynuclear complexes are chlorine bridged, 4.



(4)

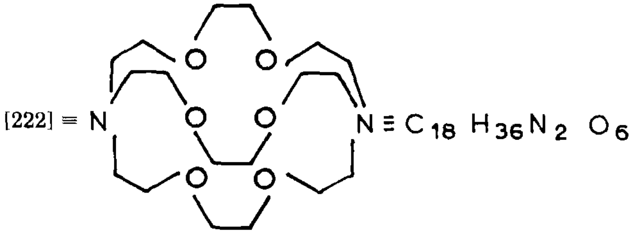
The general pattern of the UV/vis absorption spectra of all these complexes resembles that of U^{3+} (in perchloric acid), but apparently corresponding peaks are shifted by about 4% in frequency, very much the same as in the red UCl_4^- salts. Data on the magnetic susceptibilities and effective magnetic moments for the uranium in these complexes are conflicting. On the one hand, a series of rather low μ_{eff}

values, from 2.67 to 2.91 μ_B at room temperature, have been reported (*81*). But another paper gives 3.1 μ_B for the $U_3(18\text{-crown-}6)_2(BH_4)_9$ complex (*84*).

Some preliminary NMR data for $U_3(18\text{-crown-}6)_2(BH_4)_9$ dissolved in CH_2Cl_2 has appeared. It contains two kinds of BH_4 units in the ratio of 5 : 4. The chemical shifts are large and support interaction of the uranium with ring oxygens [(*84*); see also (*345*)].

U(IV) does not appear to give a related (18-crown-6) complex (*24*).

Three cryptates derived from [222] **5** have been made: $U[222]Cl_3$ (black) and $U[222]Cl_2PF_6$ (mauve), using alcoholic solutions of $NH_4UCl_4 \cdot 5H_2O$, and $U[222](BH_4)_3$ from a solution of $U(BH_4)_3$ in toluene (*78, 84, 85*).



(5)

The IR spectra again indicate a direct interaction of the uranium with the oxygens of the ligand. The NMR data indicate a C_{2v} environment for the uranium and bonding to the cryptate oxygens (*84*).

E. KINETIC STUDIES WITH AQUA U(III) (1g)

The formal reduction potential U^{4+}/U^{3+} is sufficiently negative to make U(III) a strong reducing agent, and there has been a stream of reports of kinetic studies with this reagent. The subject was reviewed in 1975 (*86b*) and again more recently (*86c*).

1. Oxidation by Aquo-cations, Radical Species, and Halogens

Most U^{3+} solutions are unstable with respect to reduction of hydrogen ions and release of hydrogen. As seen in Section II,D, oxidation by dissolved air is a more rapid process though quantitative studies have not been reported. A recent paper (*86a*) shows that pure U(III) solutions may suffer oxidation by hydrogen ions much less readily than previously supposed. Using air-free solutions, the half-life for oxidation in 0.2-*M* hydrochloric acid was found to be 5400 hr. Naturally, the half-life decreases as the hydrogen-ion concentration increases, and in 5.3-*M* acid it is reported to be 1200 hr. A value of ~1000 hr was found in 0.5-*M* sulphuric acid. But these systems are very sensitive to transition metal ion catalysis. Copper and lead ions, even in micromolar concentrations, accelerate the oxidation of U(III). At higher concentrations even Zn^{2+} shows catalytic activity. Such catalysis may explain the differences from the earlier work. In perchlorate solutions, hydrogen is not evolved, even at a perchloric acid concentration of 0.15 *M*; presumably the perchlorate is reduced. Indeed, in 0.5-*M* perchloric acid solution, the pseudo first-order rate constants for reduction of perchlorate ions and of hydrogen ions are reported to be $1.8\ 10^{-5}\ \mathrm{sec}^{-1}$ and $1.8\ 10^{-7}\ \mathrm{sec}^{-1}$ respectively (*87*).

For this reason perchlorate media may not be the most suitable for studies of U(III) reductions [see also (*88*)].

Early studies concerned the oxidation of U^{3+} by Fe^{3+}, V^{3+}, and VO^{2+} (*89a*).

In the oxidation by Tl^{3+} and Cr^{3+}, the rate depends on the first power of the U^{3+} and oxidant concentrations, but it is also pH dependent (*89b*). The data agree with the rate-controlling steps involving

$$U^{3+} + [TlOH]^{2+} \rightarrow [U(OH)Tl]^{5+}$$

and

$$U^{3+} + [Cr(OH)_2]^{+} \rightarrow [U(OH)_2Cr]^{4+}$$

The reduction of Eu^{3+} by U^{3+} has also been investigated:

$$\frac{-d[U^{3+}]}{dt} = (k' + k''[H^+])\cdot[U^{3+}]\cdot[Eu^{3+}]$$

which suggests a similar rate-controlling step to the Tl^{3+} reaction. Activation parameters for all three oxidations were evaluated (*90*).

The oxidation by iodine follows the rate law

$$\frac{-d[U^{3+}]}{dt} = k'[U^{3+}]\cdot[I_2] + k''[U^{3+}]\cdot[I_3^-]$$

With bromine, only the first term of the right-hand side of the equation is needed. Both reactions seem to take place by an outer-sphere mechanism, and the rates agree with the Marcus theory (*91*).

The rate of oxidation by a number of radical species has been studied, generating the radicals by pulse radiolysis and following the reactions spectrophotometrically. The rate constants for Cl_2^-,$Br_2^-I_2^-$, and $(NCS)_2^-$ range from 1.2 to 4.2×10^9 $dm^3\ mol^{-1}\ sec^{-1}$. The hydroxyl radical gives a rate constant of 4.1×10^8 $dm^3\ mol^{-1}\ sec^{-1}$, and the slower oxidation by hydrogen peroxide, $k = 2 \pm 1 \times 10^5$, can be seen in the same acid solution. Oxidation by $\dot{C}H_2COOH$, $\dot{C}H_2OH$, and $\dot{C}(CH_3)_2OH$ produced in acid solutions of acetic acid, methanol, or isopropanol, gave rate constants of 12, >2, and $>1 \times 10^7$ $dm^3\ mol^{-1}\ sec^{-1}$. Oxidation by $\dot{C}H_3$ was investigated, generating the radicals by

$$(CH_3)_2SO + \dot{O}H \rightarrow (CH_3)_2\dot{S}OOH \rightarrow \dot{C}H_3 + CH_3SOOH$$

with $k = 1.5 \times 10^9$. These reactions do not fit the Marcus treatment and are probably not simple outer-sphere processes. They may involve hydrogen abstraction from the ligand water or perhaps a short-lived adduct of increased uranium coordination number (*92*).

2. *Reduction of Hydroxylamine and Halo-Carboxylic Acids*

U^{3+} reduces hydroxylamine quantitatively to yield ammonia. The rate is pH dependent and follows the relation:

$$\text{rate} = [U^{3+}]\cdot[NH_2OH]\left[\frac{(k' + k''K_p[H^+])}{(1 + K_p[H^+])}\right]$$

where K_p is the protonation constant for hydroxylamine, $k'' \ll k'$, showing as expected that the protonated form reacts less readily (*93*).

The reduction of halo-carboxylic acids by U^{3+} is an interesting reaction:

$$2U^{3+} + H^+ + CH_nX_{3-n}COOH \rightarrow 2U^{4+} + X^- + CH_{n+1}X_{2-n}COOH$$

The rate $= [U^{3+}](k'[CH_nX_{3-n}COO] + k''[CH_nX_{3-n}COOH])$. In this case $k' > k''$, showing that the reaction with the anionic form proceeds more easily. An outer-sphere mechanism is suggested. Activation parameters are given (*94–96*).

The reaction has also been examined in various solvent mixtures. In t-BuOH/H_2O mixtures a plot of log k against the mole fraction of the alcohol shows a minimum at low values. The authors suggested that such minima are always shown by outer-sphere redox reactions (*97*).

3. *Complex Cationic Oxidants*

Earlier data (*98a,b*) on the reduction of $[Co(NH_3)]^{3+}$, $[Co(NH_3)_5X]^{2 \text{ or } 3+}$, and $[Cr(H_2O)_5X]^{2 \text{ or } 3+}$ have been extended to the analogous ruthenium compounds. The interpretation of the results might be simpler because of the absence of a low-spin–high-spin change accompanying the reduction of the Co(III). For $[Ru(NH_3)_6]^{3+}$, and probably $[Ru(NH_3)_5H_2O]^{3+}$ and $[Ru(NH_3)_5OH]^{2+}$, outer-sphere mechanisms are involved. The halo-substituted species $[Ru(NH_3)_5X]^{2+}$ react much faster, especially the iodo compound, and an inner-sphere mechanism is proposed. Activation parameters are given (*99*).

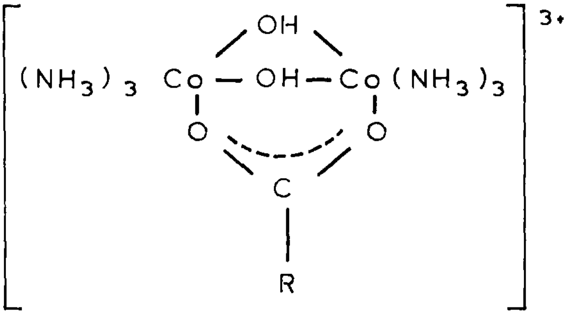
A series of papers by Gould and collaborators compares reductions by U^{3+}, Cr^{2+}, Eu^{2+}, V^{2+}, and $[Ru(NH_3)_6]^{2+}$. They establish that U^{3+} reduces both by outer- and inner-sphere mechanisms. Using $[Coen_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, and $[Co(NH_3)_5R]^{3+}$ as oxidants (R = imidazole, pyrazole, pyr, or DMF), an outer-sphere mechanism was involved. The log-k values for U^{3+} as reductant were linearly related to the analogous values for Cr^{2+}, V^{2+}, Eu^{2+}, and $[Ru(NH_3)_6]^{2+}$, agreeing with the Marcus model (*100, 101*). When R is a carboxylato species, an inner-sphere mechanism is involved.

U^{3+} is highly reactive but also selective in its kinetic behavior. The authors suggest that the structure of the intermediate complex is such that the f_{xz} orbital, containing the third $5f$ electron of the U^{3+} in D_{3h} symmetry, cannot overlap the π acceptor orbital of the carbonyl without distortion. In the analogous Cr^{2+} reduction intermediate, the different symmetry of the d orbitals premits such overlap, and very different rates of electron transfer ensue.

When the oxidant is a chromium complex $[Cr(NH_3)_5Carb]^{2+}$ and the carboxylato group is pyruvato, maleato, or pyridine carboxylato, Cr^{2+} and U^{3+} behave quite differently. The Cr^{2+} leads to stoichiometric reduction, but the U^{3+} reduces the ligand, as is shown by the NH_3 remaining attached to the chromium (*101*).

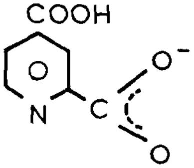
Pyridine derivatives of the type known to catalyze the outer-sphere reduction of Co(III) catalyze the reduction of $[Coen_3]^{3+}$ by U^{3+}. The catalysis is inhibited by U^{4+}, and the catalyst is slowly consumed (*102*). The catalyst, for example, isonicotinamide, is reversibly reduced by an inner-sphere reaction with the U^{3+}.

In another group of papers, it is shown that U^{3+} can bring about reduction by an inner-sphere mechanism involving attachment that is remote from the cobalt atom. The oxidants were dinuclear complexes of the type of **6**.



(6)

The slow step in the reduction is the reduction of the first cobalt atom. When the R group contained no other conjugated coordination site, the rates of reduction by U^{3+}, Cr^{2+}, Eu^{2+}, and $[Ru(NH_3)_6]^{3+}$ were of similar magnitude. But if a remote conjugated carbonyl was present, for instance, with the ligand **7**,



(7)

the U^{3+}, Cr^{2+}, and Eu^{2+} rate constants were 10^2–10^7 times greater than for the $[Ru(NH_3)_6]^{2+}$. Thus, the U^{3+} can effect reduction by an inner-sphere mechanism at a remote conjugated site (*103, 104*).

A similar fast reduction was found with such ligands even if the remote carboxyl group was converted to the amide. Since the rate constants were not appreciably pH dependent, it is unlikely that the U^{3+} attack was at the ring nitrogen, which would be protonated. The reduction by U^{3+} is stoichiometric with these ligands, but the Eu^{2+} reduces the ligands to some extent (*104*).

A comparison of several oxidant pairs of the type

$$[(CH_3)_3C{\cdot}CH_2COO{\cdot}Co(NH_3)_5]^{2+}$$

and

$$[NH_3{\cdot}CH_2COO{\cdot}Co(NH_3)_5]^{3+}$$

showed that increased positive charge reduces the rate constant in these reductions (*105*).

Not suprisingly, the reduction by U^{3+} of the caged Co(III) complexes, with ligands such as 1, 3, 6, 8, 10, 13, 16, and 19, octaazabicyclo-6,6,6-eicosane takes place by an outer-sphere mechanism (*106a*).

The reduction of benzaldehyde and salicylaldehyde by U^{3+} has also been explored (*106b*).

The trivalent uranium ion is a very reactive, but selective, reductant.

III. The Halides

A. LOWER HALIDES OF THORIUM

The di- and tri-iodides of thorium are well characterized, but the analogous compounds with the other halogens are still somewhat uncertain. So the iodides are treated first.

1. *Iodides*

a. ThI_3. A compound of this composition was described by Anderson and D'Eye (*107*) and by Hayek and Rehner (*108*), independently, in 1949. The compound is obtained by the reaction of stoichiometric amounts of ThI_4 and finely divided thorium metal at 823 K (*109, 110*). It is a black solid, showing blue-green dichroism. It loses iodine to yield β ThI_2 at 1019 K.

ThI_3 is dimorphic (*111*). The α modification is obtained by heating ThI_4 with thorium metal in a sealed tantalum tube at 957 K. (The hot, lower halides of thorium corrode glass or silica rather quickly above about 773 K.) This form is pseudoorthorhombic with $a = 787.0$, $b = 2699$, and $c = 3149.2$ pm. It belongs to the space group B2/b or Bb, both monoclinic groups, but $\gamma \approx 90^\circ$ (*111*).

Prolonged heating of the α form converts it to the β form, which has a brassy luster and an interesting structure, shown in Fig. 1. It is orthorhombic, belonging to the space group Cccm, with $a = 873.5$, $b = 2029.7$, and $c = 1466.1$ pm, $Z = 16$. The thorium atoms are 8-coordinate with three environments, one cubic and two square-antiprismatic arrangements of iodine atoms. The figure shows only the arrangement of the thorium atoms. In the long chains, as seen in the center of the figure, cubic and square-antiprismatic arrangements of the iodine neighbors alternate, and the thorium–thorium distance is 366.5 pm.

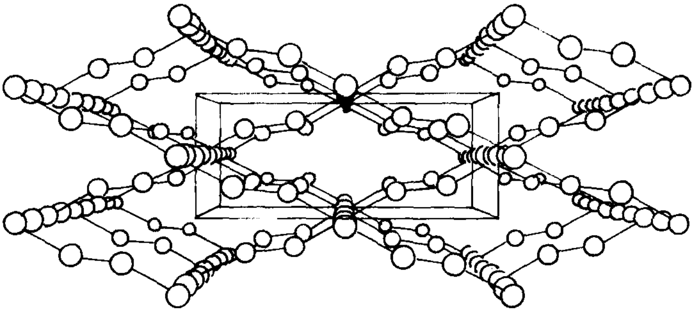


FIG. 1. Framework of Th atoms in β ThI_3, viewed along [0,0,1] *(111)*.

These chains are cross-linked by thorium–thorium pairs. The thorium–thorium distance, chain to pair, is 380.0 pm, and the pair separation is 346.0 pm, which is less than in thorium metal (360.0 pm). Clearly there is metal–metal bonding in these units. Along the chains, the distance between thorium atoms is short enough to yield a conduction band, and this variety of ThI_3 can be regarded as a one-dimensional metal, with the thorium bonded pairs normal to this dimension *(111)*.

The thorium–iodine distances (330, 322, and 325 pm) are similar to those in ThI_4 (313–329 pm) and ThI_2·(see later).

The compound reacts rapidly with aqueous solutions, yielding hydrogen.

b. ThI₂. Thorium di-iodide can also be obtained by heating stoichiometric amounts of ThI_4 and thorium metal in a tantalum tube at 773–973K *(107, 112)* or by thermal decomposition of ThI_3 at 1019 K *(110)*. It is also dimorphic.

The black, lower-temperature α form slowly changes to the β form in the temperature range 873–973 K. Above the latter temperature, decomposition, probably giving thorium metal or, possibly, a monoiodide, takes place. There is some disagreement about the crystal parameters of this hexagonal form *(107, 110, 113)*. The closest fit to the diffraction data appears to be obtained with $a = 800$ and $c = 787$ pm *(110)*.

The high-temperature β form is also hexagonal, belonging to the space group $P6_3/mmc$. The cell constants are $a = 397$ and $c = 3175$ pm *(114)*. The thorium is 6-coordinate with layers of trigonal prismatic and antiprismatic iodine coordination. The Th–I distance is 320 pm, very similar to the values for ThI_4 and ThI_3. The Th–Th distance is 397 pm.

It is a metallic conductor and diamagnetic (*112*). It reacts with water in a similar manner to the tri-iodide.

Recently a simpler preparation of ThI_2 has been described. A thorium metal anode is used to electrolyze a solution of iodine and tetraethylammonium iodide in acetonitrile. Addition of ether to the electrolyzed solution precipitates $ThI_2(CH_3CN)_2$ (*115*). This adduct loses the acetonitrile at 363 K *in vacuo*. The product is a yellow powder.

ThI_2 takes up hydrogen between 473 and 748 K, at modest pressures of hydrogen, yielding compounds containing from 0.7 to 1.8 hydrogen atoms per thorium atom (*116*).

c. Complexes of ThI_2. In the last section an adduct with acetonitrile was described. A similar anodic oxidation of thorium metal by iodine in acetonitrile in the presence of α,α-bipyridyl or 1,10-orthophenanthroline leads to the precipitation of complexes of these ligands, of composition ThI_2L_2, on addition of ether (*115*).

d. The Thorium–Iodine Phase Diagram. Two investigations have provided some information. The earlier effort combined differential thermal analysis with analytical data on Th–ThI_4 mixtures, equilibrated at chosen temperatures and then analyzed after quenching (*110*). More recently Th–ThI_4 mixtures have been equilibrated in a Knudsen cell. The rate of effusion from the cell gave the total gas pressure in the cell, and the proportions of iodine and thorium tetraiodide in the vapor were determined mass spectrometrically (*117*). The two sets of data are generally consistent though the more recent authors find no evidence for the two forms of ThI_2. They do, however, find some possibility of the existence of ThI. The main features of the system are shown in Fig. 2. The peritectic reaction, $ThI_2 \rightarrow ThI$ (or Th) + ThI_3, takes place at 803 K. At 1019 K, $ThI_3 \rightarrow ThI$ (or Th) + ThI_4(melt), and at 1137 K, one obtains Th + ThI_4·(melt) (*117*).

It is noteworthy that the Th–I distances in all these compounds and in ThI_4 are not very different, and neither compound should be regarded as a simple Th(II) or Th(III) derivative.

2. *$ThCl_2$*

At the present time there are two incompatible groups of papers. On the one hand, it has been denied that thorium metal shows any solubility in, or reaction with, molten $ThCl_4$ (*118–120*). Activity coefficient anomalies in the system are ascribed to contamination with $ThOCl_2$. On the other hand, Smirnov and collaborators report evidence for

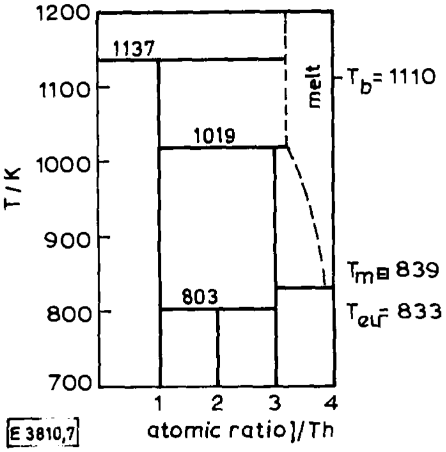


FIG. 2. Phase diagram for Th–I system (*117*).

$ThCl_2$ and, rather less convincingly, $ThCl_3$ (*121–126*). A recent pair of papers summarize much of this work (*127, 128*). These authors find that thorium metal dissolves in alkali chloride–thorium tetrachloride melts up to the composition $ThCl_2$. Very little solution of thorium takes place in the absence of the thorium tetrachloride. On slow cooling, the $ThCl_2$ disproportionates and a thorium metal mirror may ensue (*127*). If the melt is quickly quenched, the solid containing $ThCl_2$ is reported to be diamagnetic (*126*). This product is said to dissolve in water without rapid evolution of hydrogen. However, a quenched material with a composition indicating that it contains $ThCl_3$ dissolves with evolution of hydrogen. The color of these products is not mentioned.

An estimate of the IV/III reduction potential for thorium in a NaCl/$AlCl_3$ melt, using the RESPET treatment (*6, 7*), gave a value of -1.78 V. The parameters for the RESPET equation were evaluated from experimental data for the other actinides (*129*).

Further investigation of these systems seems very desirable.

3. *Oxyhalides*

Heating a stoichiometric mixture of ThF_4, ThO_2, and thorium metal for four days at 1473 K in a nickel tube has been reported to produce ThOF. A powder X-ray diffraction pattern suggested a face-centered cubic structure with $a = 568$ pm and a disordered anionic occupation. It is antiferromagnetic, stable in moist air, *in vacuo*, and in an inert gas atmosphere, up to 1673 K (*130*).

B. THE LOWER HALIDES OF URANIUM

All attempts to prepare solid compounds of composition UX_2 have failed, but there is some information on matrix-isolated UCl_2.

1. UCl_2

This compound can be matrix-isolated by the reaction of uranium vapor and chlorine or hydrogen chloride, followed by trapping in an argon matrix. The molecule is bent, with a Cl-U-Cl angle of about 100°. Infrared data showed $\nu_1 = 311\ \text{cm}^{-1}$ and $\nu_3 = 295\ \text{cm}^{-1}$. The U—Cl distance is 255 pm (*131*).

2. *Gaseous UX and UX_2*

a. Fluorides. These species can be produced at high temperatures in a graphite reaction chamber. The gas emerging from such a chamber was examined mass spectrometrically, and the pressure in the chamber was deduced from the rate of effusion. Equilibria such as the following have been investigated:

$$\text{U} + \text{BaF} = \text{UF} + \text{Ba (gas phase)}$$
$$\log k_{\text{i}} = -(0.655 \pm 0.061) + (3881 \pm 144)/T$$
$$\text{UF} + \text{BaF} = \text{UF}_2 + \text{Ba (gas phase)}$$
$$\log k_{\text{ii}} = (0.121 \pm 0.057) - (1057 \pm 127)/T$$

These data yield (*132*):

Gaseous species	ΔH_f° (298)	S° at 2300 K
UF	-48.5 ± 8.4 kJ mol^{-1}	347.7 J K^{-1}
UF_2	-540.6 ± 10.5 kJ mol^{-1}	454.4 J K^{-1}

These values are in rather good agreement with earlier estimates (133, 134). From these values one obtains bond dissociation energies of 656.9 kJ for UF and 569.0 kJ for UF_2. A similar method has been used to explore the dissociation equilibria for UF_4 (*136*).

b. Chlorides. An investigation using essentially the same technique has provided data for the analogous chlorides. Thus:

$$\mathrm{UCl + CaCl = UCl_2 + Ca} \quad \text{(gaseous phase)}$$
$$\log k_{\mathrm{i}} = -(1.293 \pm 0.111) + (4471 \pm 238)/T$$

$$\mathrm{U + CaCl = UCl + Ca} \quad \text{(gaseous phase)}$$
$$\log k_{\mathrm{ii}} \approx 1 \quad \text{at 2300 K}$$

From such data one obtains:

Gaseous species	ΔH_f° (298)	S° at 2300
UCl	202.5 kJ $\mathrm{mol^{-1}}$	358.6 J $\mathrm{K^{-1}}$
UCl_2	−166.1 kJ $\mathrm{mol^{-1}}$	452.7 J $\mathrm{K^{-1}}$

and bond dissociation energies of 452 ± 8 kJ for UCl and 490 ± 8 kJ for UCl_2 (*136*).

For all these compounds, electronic contributions to the entropy are significant.

C. URANIUM TRIHALIDES (*1d, e*)

All four trihalides have been known for many years.

1. *Uranium (III) Fluoride (1d)*

UF_3 is the most difficult of the trihalides to obtain in the pure state. It can be obtained by the reduction of uranium(IV) fluoride by aluminum (*137*), hydrogen (*138–141*), or uranium metal (*139, 141–144*). Reduction by aluminum can be carried out at 1173 K, when the aluminum fluoride can be sublimed off as the monofluoride. But the product is not very pure.

The reduction by hydrogen or finely divided uranium metal is complicated by the slow reverse disproportionation reaction $4UF_3 \rightleftharpoons U + UF_4$, which goes from left to right above about 1073 K (*140, 144, 145, 146*). In addition there is a eutectic in the UF_3/UF_4 system, melting at about 1138 K (*147*). At low temperatures the reduction is very slow, and some compromise in the choice of reaction temperature is unavoidable. Using the very fine uranium metal from the decomposition of UH_3, satisfactory reduction has been obtained in the temperature range 1073–1173 K (*140, 144*). Enthalpies and entropies of activation for the reduction reaction of 112 kJ $\mathrm{mol^{-1}}$ and −228 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ have been reported (*140*); but the disproportionation is also slow, and higher temperatures have been used (*142, 143*). Scrupulously air- and water-free materials and systems must be used. Nickel or tantalum containers are most satisfactory.

Uranium(III) fluoride can also be prepared by the reaction of uranium metal with various transition metal fluorides—CuF_2, ZnF_2, CdF_2, MnF_2, NiF_2, and CoF_2—as well as with PbF_2 and BiF_3. A reaction temperature of 1073–1223 K is required (*148*).

Finally, a Japanese patent describes a preparation by heating UF_4 with UN or U_2N_3 at 1123 K (*149*).

It is not possible to dehydrate the compound obtained by precipitation from U(III) solutions.

UF_3 has been described as a black (*137*) or grey (*141*) solid. These were impure products. The description as violet-red microcrystals (*143*) seems more reasonable.

Uranium(III) fluoride is isomorphous with LaF_3, and the coordination number of the uranium is 11. The arrangement of the fluorine atoms around the uranium is that of a fully capped trigonal prism. Unfortunately, notwithstanding measurements by both X-ray (*150–154*) and neutron diffraction methods (*153–157*), there is still some uncertainty about the space group of the crystals. Laveissière (*158*) finds equally good agreement of the data with the hexagonal group $P6_3cm$ and the trigonal group $P\bar{3}cl$. For either group the fluoride prism is somewhat distorted. If only the data due to fluorine scattering are selected, there is a preference for the former structure. The two space groups yield different U—F distances. For $P6_3cm$ there are two U—F distances of 253 pm, two of 281 pm, and one each of 245 and 308 pm. For the other structure, the values are two at 248, two at 263, and two at 301 pm. Figures illustrating these two possibilities are to be found in a detailed review by Taylor (*159*).

Uranium(III) fluoride is insoluble in water and surprisingly resistant to aerial oxidation and hydrolysis.

The sublimation and disproportionation of UF_3 have recently been reinvestigated. In one study, the UF_3 was heated in a molybdenum effusion cell, and the composition of the effusing gas was examined mass spectrometrically (*160*). The data give $\Delta H_{\text{sub}}^{\circ}$ (at 298 K) = 440 ± 12 kJ mol^{-1} with

$$\log p\ UF_3\ (\text{atmos}) = -\frac{(20.04 \pm 0.62)10^3}{T} + (8.40 \pm 0.46)$$

and for the UF_4 vapor from the disproportionation,

$$\log p\ UF_4\ (\text{atmos}) = -\frac{(17.35 \pm 1.18)10^3}{T} + (8.55 \pm 0.90)$$

Both expressions relate to the temperature interval 1252–1468 K.

In another investigation (*140, 161, 162*), the two reactions $4UF_3 = 3UF_4 + U$ and $2UF_4 + H_2 = 2HF + 2UF_3$ have been explored. There is an odd feature of this work. The earlier paper (*140*) takes account of the UF_3/UF_4 eutectic (*147*), but the second paper states that there are no phase data on this system! Using a hydrogen carrier gas transpiration method, researchers have reported the enthalpy and entropy of sublimation of UF_3 as 328.7 ± 1.3 kJ mol^{-1} and 193.9 ± 0.9 J K^{-1} mol^{-1}, respectively, at 298 K. The measurements were made in the temperature interval 1229–1367 K. Agreement between the two methods is poor.

In view of the disproportionation reaction, the melting points given for UF_3, 1768 K (*143*) and 1753 K (*147*), are approximate.

The first ionization potential of the UF_3 molecule is $8.0 + 0.2$ eV (*160*), and the electron affinity is $1.5 + 0.5$ eV (*163*).

A recent value for ΔH_f° $UF_3(298)$ is -1085 kJ mol^{-1}, slightly more negative than earlier values (*133*). This value relates to the gaseous molecule. A fairly direct value for the solid compound, based on the heat of solution of UF_3 in a ceric–boric acid solution, gave -1502.0 ± 5 kJ mol^{-1} (*164*), $\Delta G_f^\circ = -1433.4 \pm 5$ kJ mol^{-1}, and $S^\circ = 123.4 \pm 0.4$ J K^{-1} mol^{-1} (*4b, 8c*).

With this enthalpy of formation, the lattice energy of UF_3 has been calculated as 4780 kJ mol^{-1} (*165*).

A new measurement of the magnetic susceptibility of UF_3 (*166*) confirms that it obeys the Curie–Weiss relation over the temperature range 100–300 K and gives a Weiss constant of -12 K compared with earlier values of -98 K (*142*), -32.2 K (*167*), and -110 K (*168*). A lower effective magnetic moment is reported, 3.30 μ_B, compared with 3.66 (*142*), 3.50 (*167*) and 3.62 (*168*). These differences very probably reflect differences in the purity of the UF_3 used (*142, 167*).

2. *UCl_3, UBr_3, and UI_3 (1e, 3c)*

There is not much new information about these compounds beyond improved thermodynamic data and preparative methods.

All three compounds can be prepared by heating the U(IV) compound with zinc metal. The excess zinc and the zinc halide can be sublimed off (*169a*). It is also possible to obtain pure products by heating UH_3 in a stream of HX.

UCl_3 can be obtained conveniently by thermal decomposition of the violet-red $NH_4UCl_4 \cdot 4H_2O$. The latter compound was prepared by Zn/Hg reduction of a solution of UCl_4 in acetonitrile in the presence of small amounts of water and propionic acid. Excess water must be avoided or another product will ensue. The decomposition proceeds at first between 298 and 353 K but should be finished at 673 K. Pure olive-green UCl_3 is obtained (*169b*).

The THF adduct of UI_3 has been made by reacting mercury(II) iodide with excess uranium metal in THF (*169c*).

It has long been known that UCl_3 and UBr_3 are isostructural, with 9:3 coordination (*170*). Each uranium atom is surrounded by a trigonal prism arrangement of halogen atoms, with three further halogen atoms capping the quadrilateral faces. Neutron diffraction studies of both UCl_3 (*171*) and UBr_3 (*172*) have been made. For the iodide, also explored by neutron diffraction (*173*), the uranium is 8-coordinate in a bicapped trigonal prismatic arrangement of halogen atoms. The crystal structure of UCl_3 has recently been reexamined (*174*). It belongs to space group $P6_3/m$, with $Z = 2$, $a = 744.5$, and $c = 431.4$ pm. The U—Cl distance is 294.1 pm.

A measurement of the enthalpy of formation of UCl_3, based on a calorimetric determination of the heat of solution (accompanied by oxidation of the uranium(III) by hydrogen ions) of the compound in dilute sulphuric acid, gave ΔH_f° UCl_3 (298 K) $= -862.1 \pm 3.2$ kJ mol^{-1} (*175*). The enthalpy of formation of UBr_3, determined in a similar manner, was ΔH_f° $UBr_3 = -697.0 \pm 4$ kJ mol^{-1} (*176*). An earlier value due to the same group was -762.3 ± 2.1 kJ mol^{-1} (*177*). Values of -877.2 ± 3.3 and -748.3 ± 7.4 kJ mol^{-1} for UCl_3 and UBr_3, respectively, have also been given [(*178*); see also (*4b, 8c*), for best values]. The standard entropies at 298 K are 159.0 ± 1.3, 192.5 ± 8.4, and 221.7 ± 8.4 J K^{-1} mol^{-1} for UCl_3, UBr_3, and UI_3 respectively (*8c*).

Thermodynamic data on these compounds have been reviewed by Chirkst (*179*).

Neutron diffraction data show long-range antiferromagnetic ordering in UCl_3 below 6.5 K (*180*) and in UI_3 below 2.8 K (*181*).

Nothing new has been reported about the mixed halides for many years. However, phase studies on the UCl_3/UF_4 and UCl_3/ThF_4 systems have been made (*182–184*). The UCl_3/UCl_4 system has a large, solid solution area and a eutectic for 83 mole percent UCl_3 (*185, 186*). Surface tension and viscosity data have been reported for this system (*186*).

3. *Electron Spectroscopy for Chemical Analysis (ESCA) and X-ray Photoelectron Spectroscopy (XPS) Studies*

Data have appeared for UF_3, UCl_3, and UBr_3 (Table IV) (*187, 188*). Values given in the two papers for UCl_3 differ slightly, possibly due to calibration difficulties, since the $4f_{5/2}$ $4f_{7/2}$ separations are nearly the

TABLE IV

DATA FOR UF_3, UCl_3, AND UBr_3[a]

Compound	Binding energy (eV)	
	$4f_{5/2}$	$4f_{7/2}$
UF_3	390.9	379.9
UCl_3	388.9	378.1
UBr_3	388.9	378.2

[a] Source: *187*, *188*

same. The 1*s* binding energy of the fluorine in UF_3 is higher than in UF_4 or UF_6, and the 5*f* level of the uranium is lower than in the chloride or bromide (0.6 eV for UF_3, and 1.1 and 1.0 for the chloride and bromide, respectively). These and other data lead the authors to conclude that UF_3 is more covalent than the chloride or bromide! The data lend support to participation of the 5*f* electrons in the bonding.

Further discussion of the data can be found in ref. *189*.

The same technique has been applied to examine the condensate from UF_4 vapor and to obtain evidence for UF_3 formed by dissociation (*190*). Similarly, an examination of the film produced on uranium metal by exposure to iodine vapor probably contains UI_3 since electrons corresponding to the $4f_{7/2}$ shell are found at 379.0 eV (*191*). In uranium metal this shell lies at 377.0 eV.

D. OXYHALIDES OF URANIUM(III) (*1d,e*)

Although ThOF and PuOF have been described, there is no information about UOF.

The dark red UOCl was reported several years ago (*192*), the researcher having obtained it accidentally while subliming UCl_3, probably owing to the reaction of the hot uranium trichloride with silica or some other oxide.

A number of other papers mention this compound (*193–196*), but a recent book states that attempts to obtain a pure product have all been unsuccessful (*2*). However, another paper (*197*) gives crystallographic and other data for UOCl, UOBr, and UOI. The compounds were prepared by heating mixtures of UX_4, U, and U_3O_8 in amounts calculated to give rather less oxygen than corresponds to the composition UOX. The products were acknowledged to be appreciably contaminated with

TABLE V

CELL PARAMETERS OF CRYSTALS OF UOCl, UOBr, AND UOI

Compound	a (pm)	b (pm)	E_u(cm^{-1})	A_{2u}(cm^{-1})	μ_{eff}(μ_B)	θ(K)
UOCl	403.4	689.2	500	340	3.90	−145
UOBr	406.3	744.7	500	320	3.67	−140
UOI	406.2	920.8	490	315	3.56	−150

UO_2 and UX_3. The crystallographic data reported are in good agreement with those given in the first report of UOCl (*192*).

The crystals are tetragonal, belonging to space group P4nmm, with the cell parameters shown in Table V.

The uranium is 9-coordinate (*159*), in a monocapped square antiprism, like PbClF. The fourth and fifth columns in the table give U—O stretching frequencies seen in the IR.

The enthalpy of formation of UOCl has been calculated from the heat of solution, with oxidation, in aqueous sulphuric acid, ΔH_f° UOCl (298 K) = −833.87 ± 4.23 kJ mol^{-1}; but the UOCl sample used was impure, so the value should be regarded as tentative (*198, 199*).

The compounds are paramagnetic, obeying the Curie–Weiss relation above about 230 K. The Weiss constants (θ) and effective magnetic moments (μ_{eff}) are given in Table V. Below 190 K they show weak ferromagnetic ordering. The ESCA data have given the following binding energies (*188*):

Compound	Binding energy (eV)	
	$4f_{5/2}$	$4f_{7/2}$
UOCL	390.5	379.8
UOBr	390.7	379.9

E. COMPLEXES OF UX_3 (*1h*)

1. *Simple Adducts of UX_3*

This section includes adducts of the trihalides with neutral ligands, generally made in nonaqueous systems.

Although adducts of both UCl_3 and UBr_3 with ammonia have been known for a long time (*200, 201*), complete phase studies have not been made. It seems probable that UCl_3 forms a number of such adducts (*202, 203*).

The lattice energies of the trihalides are so large that it is often difficult to prepare the adducts directly from the solid UX_3 and the ligand. Thus, UCl_3 needs prolonged heating with acetonitrile to obtain the adduct. During this process some oxidation and/or degradation often occurs (*204*). By treating a solution of the $UCl_3(THF)_n$ adduct with an excess of acetonitrile, pure $UCl_3(CH_3CN)_2$ can be obtained as a brown solid. The $\nu_{C\text{-}N}$ stretch is at 2270, compared with 2250 cm^{-1} in the free ligand. A pink pyridine adduct can be made in a similar way (*205*).

Quite recently an unusual adduct, $UCl_3\cdot CH_3CN\cdot 5H_2O$, has been described (*206*). There are no analogous lanthanide or actinide compounds. The preparation is essentially similar to that of $UCl_37\cdot H_2O$ (see Section II,D), but different proportions of reactants are used. It forms monoclinic crystals, $a = 1226$, $b = 1298$, and $c = 662$ pm, $\beta = 101.7°$. It follows the Curie–Weiss law from 65–300 K with $\mu_{eff} = 3.39$ μ_B and $\theta = -65.7$ K. It is antiferromagnetic below 12 K.

Solutions of adducts can often be obtained by reduction of a solution of the more soluble UCl_4 in the ligand. Thus, the preparatively valuable solution of a THF adduct of UCl_3 can be made by reduction of a solution of UCl_4 in THF with NaH (*207*), sodium naphthalenide (*285*), sodium carbide (*83*), or Zn/Hg (*81, 206*). On evaporation of the THF solution obtained after removal of the sodium chloride and excess sodium hydride, purple crystals of $UCl_3(THF)_{1\text{ or }2}$ have been obtained. A monosolvate can be precipitated by the addition of ether to the concentrated solution (*207*). With $LiAlH_4$ in THF, the solvate $LiU_2Cl_7\ \frac{9}{2}C_4H_8O$ is said to separate as a purple solid. This is a rather surprising result (see later). In dimethoxyethane, a solvate $UCl_3\ \frac{3}{2}(C_4H_{10}O_2)$ was obtained (*208*). Such solutions catalyze hydrogenation reactions (*209, 210a,b*).

Brief mention has been made of complexes of UCl_3 with 1,10-phenanthroline and 2,2′-bipyridyl (*81, 208*).

2. *Halo-Anions*

Mention has already been made of those that can be obtained in aqueous systems (see Section II,D). The isolation of salts of these anions usually demands fairly large cations; the sodium and lithium salts have not been fully characterized.

a. Fluoroanions. Salts of the UF_4^-, UF_5^{2-}, UF_6^{3-}, and $U_2F_9^{3-}$ anions have been described, and several structures have been determined.

TABLE VI

COMPOUNDS OF M_3UF_6

Compound	a (pm)	b (pm)	Z
K_3UF_6	945	957	4
Rb_3UF_6	958	988	4
Cs_3UF_6	1010	1070	4

The compounds M_3UF_6 (M = K, Rb, Cs) are tetragonal and isostructural with β K_3YF_6 (Table VI).

K_2UF_5 and $K_3U_2F_9$ are cubic with $a = 662$ and 600 pm, respectively. KUF_4 is orthorhombic, isostructural with β $KCeF_4$, $a = 631$, $b = 3810$, $c = 1562$ pm, $Z = 4$. But $RbUF_4$ is hexagonal like $KTlF_4$, with $a = 854$ and $c = 1072$ pm, $Z = 6$. Finally, RbU_3F_{10} is also hexagonal like β KYb_3F_{10}, with $a = 826$ and $c = 1339$, $Z = 4$ (*211*).

The standard enthalpy of formation of the UF_4^- anion has been given as -1725 kJ mol^{-1} at 298 K (*212, 213*).

Phase studies have been reported on some $MF–UF_3$ systems (M = K, Rb, Cs) (*214*). The potential of an uranium electrode in a lithium–potassium chloride melt containing lithium fluoride has been studied as a function of the fluoride concentration (*215*).

b. Chloroanions. Chloride melts have attracted attention, mostly in the USSR, because of the possibility of electrochemical refining of uranium metal.

i. Preparation. The compound Cs_2NaUCl_6 was made by direct reaction of the chlorides at 1223 K several years ago. A detailed study of its magnetic susceptibility has been made. A Curie–Weiss plot shows a break at 20 K, $\mu_{eff} = 2.92\ \mu_B$ above 20 and $2.49\ \mu_B$ below 20 K. The data have been interpreted in terms of a slightly distorted octahedral environment for the U(III); but as yet there are no direct structural data though analogous lanthanide and actinide compounds are known to be octahedral (*216*).

There are some crystal data on these salts. K_2NaUCl_6 is hexagonal like K_2LiAlF_6, Rb_2NaUCl_6 is orthorhombic, and Cs_2NaUCl_6 is cubic (*217*).

The best-known chloroanion is UCl_5^{2-}. Anhydrous salts of this anion can be prepared conveniently by reduction of M_2UCl_6 or UCl_4 in acetonitrile with Zn/Hg in the presence of the alkali chloride (*218*) (M = K, Rb, NH_4 but not Li or Na) (Table VII). Solutions in hexamethylphosphoramide can be made in a similar way (*40, 41*).

TABLE VII

ANHYDROUS SALTS OF UCl_5^{2-} [a]

Compound	$\mu_{eff}(\mu_B)$	Temperature range (K)	$T_{Néel}$(K)
K_2UCl_5	3.99	20–130	13.2
	3.77	130–300	
Rb_2UCl_5	3.57	16–150	8.6
	3.44	150–300	
$(NH_4)_2UCl_5$	3.54	17–220	7.8
	3.47	220–300	

[a] Source: *220*.

A similar preparation in the presence of more alkali chloride, Ph_4AsCl or Ph_4PCl, gives the related salts of the $U_2Cl_7^-$ anion (*219*). The violet-purple M_2UCl_5 salts are stable in dry air. They are antiferromagnetic at low temperature (Table VII).

The reduction of UCl_4 to prepare these compounds can also be effected by sodium in hexamethylphosphoramide solution (*43*).

ii. Structures. K_2UCl_5 and Rb_2UCl_5 belong to the orthorhombic system, space group Pnma, $Z = 4$. The uranium is 7-coordinate in a monocapped trigonal prism of chlorines. Two rectangular prism edges are shared in each coordination sphere (Table VIII).

The last compound in the table is also orthorhombic and isostructural with $RbDy_2Cl_7$ (*222*).

The phase diagrams for the MCl/UCl_3 systems, with M = K, Rb, and Cs, provide evidence for M_3UCl_6 and M_2UCl_5 when M = K or Rb. For M = Rb, the MU_2Cl_7 species appears; and for Cs, a more complex diagram, including $CsUCl_4$, is found. The last compound is reported to be cubic (*221*).

TABLE VIII

CRYSTAL PARAMETERS OF UCL_5^{2-} SALTS

Compound	*a* (pm)	*b* (pm)	*c* (pm)
K_2UCl_5	852	923	1125
Rb_2UCl_5	874	946	1149
Cs_2UCl_5	937	976	1203
RbU_2Cl_7	993	1028	1099

[a] Source: *174, 221*.

Diffraction data have recently been reported for $(K/Rb)_2NaUCl_6$, which is isostructural with Cs_2NaCrF_6 (*222*).

Drozdzynski has reviewed the information on these complexes (*223, 224*).

iii. Thermochemical data. Heats of formation of several of these salts are available. They are based on calorimetric measurements of the heat of solution of the compounds, with oxidation of the uranium, in an aqueous medium, (Table IX) (*178*).

Using lattice energies calculated for K_2UCl_5 and $CsUCl_4$ (1678 and 435 (?) kJ mol^{-1}) the U—Cl bond energies in the two compounds were estimated at 314 and 516(?) kJ mol^{-1}.

The relation between the heats of addition of chloride ion and the coordination number of the uranium has been discussed by Chirkst (*226–228*). Some earlier data are reviewed in (*179, 229*). Infrared data give two U—Cl stretching frequencies in $RbUCl_4 \cdot 5H_2O$ at 196 and 230 cm^{-1} (*230*).

iv. Studies with melts. The smaller cations generally only give eutectics in their phase diagrams for two component systems with UCl_3. This is the case for $CaCl_2$–UCl_3 (*231–233*), MgCl–UCl_3 (*231–233*), LiCl–UCl_3 (*234–237*), and NaCl–UCl_3 (*234, 235, 238*).

With larger cations, evidence for the chlorouranate(III) anions can be found, for example, K_2UCl_5 (*236–239*), Sr–$BaUCl_5$ (*233*), and $CsUCl_4$ (*221, 237*).

In the UCl_3–$ThCl_4$ system there is evidence for $Th(UCl_4)_4$ (*240, 241*). The same species is also present in the three component melts with $MgCl_2$ (*241*), $CaCl_2$ (*242*), LiCl (*243*), and KCl (*244*).

A large number of somewhat repetitious papers have appeared in this area by Desyatnik and his collaborators. In a number of melts they have measured the surface tension, by a gas bubble method, the viscos-

TABLE IX

HEATS OF FORMATION FOR SOME CHLOROURANATE SALTS

Compound	$-\Delta H_f^\circ$ (298 K) from elements (kJ mol^{-1})	$-\Delta H_r^\circ$ (298 K) from the chlorides (kJ mol^{-1})
K_2UCl_5	1793.4	25.5
Rb_2UCl_5	1804.7	39.7
Cs_2UCl_5	1821.5	42.3
$CsUCl_4$	1374.6	37.7
K_2NaUCl_6	2184.4	23.0
Rb_2NaUCl_6	2174.7	25.1
Cs_2NaUCl_6	1967.1	24.1

ity, and particularly, the density of the melt as a function of its composition.

In the two component systems, MCl–UCl_3, evidence of chloroanion formation from excess molar volume changes was obtained when the cation M was large, M = K, Rb, or Cs (*245–248*), but not with M = Li or Na (*248–251*).

Several studies concerned three-component melts MCl–$M'Cl$–UCl_3 (*252–256*). Since these studies were oriented toward a possible uranium-refining process, they also included several three- (or more) component systems with UCl_3 and UCl_4 (*257–263*). Phase diagrams for such systems (*264, 265*), as well as for MCl–UCl_3–ThF_4 systems, have been reported (*266, 267*). For similar reasons the diffusion of U(III) in various chloride melts has been investigated (*268–270*), and the compressibility of a $NaCl$–KCl–UCl_3 melt has been explored by measuring the velocity of sound in the melt (*271*). There are also more viscosity data for $CaCl_2$–UCl_3 and $MgCl_2$–UCl_3 melts (*272, 273*).

v. Other data on melts. An early measurement gave the U(III)–U(0) potential as −2.34 V with respect to a 1-M Pt(II)–Pt(0) electrode in a melt of UCl_3 in Na–KCl (*47*).

Some cell measurements on UCl_3–UCl_4 in Na–KCl and Li–KCl eutectics and $MgCl_2$–Li–KCl melts show that U(III) complexes chloride much less readily than U(IV) (*274*). A cell based on the reaction $UCl_3 + AgCl \leftrightarrows UCl_4 + Ag$ in the last of the above melts has an EMF of 0.973 V at 723 K and 0.845 V at 823 K (*275*), whence,

$$\Delta G_f^{\text{melt}}\ UCl_3 = -838{,}000 + 147\ T \quad \text{J mol}^{-1}$$

The equilibrium $2UCl_3 + 2Al \leftrightarrows Al_2Cl_6 + 2U$ has been investigated in KCl–$AlCl_3$ melts. The maximum reduction of UCl_3 seems to take place when KCl–$AlCl_3 \sim 1$. The authors concluded that substantial formation of $Al_2Cl_7^-$ and UCl_6^{3-} took place (*276, 277*). Another study of $AlCl_3$–KCl–UCl_3 melts led to a suggestion of $U(Al_2Cl_7)_3$ (*49, 278*).

c. Bromoanions. Like the pentachlorouranate(III) anion, the UBr_5^{2-} species does not readily attach another bromide ion. However, MBr–UBr_3 phase studies provide evidence for UBr_6^{3-} as well as UBr_5^{2-} and, probably, $U_2Br_7^-$ (*279, 280*). Indeed, face-centered cubic rubidium and caesium salts of UBr_6^{3-} have been made (*279*). As for the chloro species, large cations are required to stabilize these complexes. M_2NaUBr_6 (M = K or Cs) analogous to the chloro compounds are known; the potassium salt is tetragonal, but the caesium salt is cubic (*217, 281*).

TABLE X

CRYSTAL PARAMETERS OR SALTS OF UBr_5^{2-} [a]

Compound	*a* (pm)	*b* (pm)	*c* (pm)
K_2UBr_5	917	945	1204
Rb_2UBr_5	937	954	1231
Cs_2UBr_5	967	985	1280

[a] Source: *221, 222, 282.*

TABLE XI

HEATS OF FORMATION FOR SEVERAL BROMOURANATE SALTS

Compound	$-\Delta H_f^\circ$ (298 K) from elements (kJ mol^{-1})	$-\Delta H_r^\circ$ (298 K) from bromides (kJ mol^{-1})	Ref.
K_2UBr_5	1636	40.6	*177*
Rb_2UBr_5	1653	42.7	*177*
K_2NaUBr_6	2014.2	47.2	*178*
Cs_2NaUBr_6	—	42	*178* *284*

The dark violet M_2UBr_5 salts (M = K, Rb, and Cs) are orthorhombic (Table X). The IR bands associated with U—Br stretching occur at 110, 124, and 155 cm^{-1} in the K, Rb, and Cs salts, respectively (*230, 283*).

Heats of formation have been measured for several bromouranate(III) salts (Table XI). The data have been reviewed by Chirkst (*179*), who also calculated the enthalpy changes for successive bromide additions (*228*).

3. *Amido Compounds*

The dark red, volatile, tris[bis(trimethylsilyl)amido] uranium(III) can be made from a solution of UCl_3THF_n and the sodium bis(trimethylsilyl)amide. It is monomeric and contains 3-coordinate uranium (*285*). It has no tendency to act as an acceptor, but it reacts with trimethylamine oxide or oxygen to yield the uranium(V) compound $OU[N(SiMe_3)_2]_3$.

It is a paramagnetic compound, obeying the Curie–Weiss law from 10–70 K with $\mu_{eff} = 2.51\ \mu_B$ and $\theta = 10.5$ K. Its IR spectrum is very close to that of the lanthanide analogs. Crystals large enough for a detailed structure have not been obtained, but it appears that the compound is isostructural with the neodymium analog (space group P3cl). The cell constants are $a = 1656$ and $c = 843$ pm, very similar to those of $[(Me_3Si)_2N]_3ThH$. The nitrogens are not coplanar with the uranium, as is the case for the lanthanide analogs (*286, 287*).

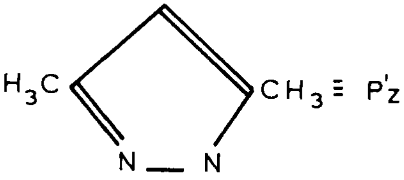
4. *Polypyrazolyl Borates*

Recently, various mixed ligand U(III) polypyrazol-1-yl borates have been made. UCl_3THF reacts with KH_2BPz_2 or $KHBPz_3$ in THF at room temperature, giving lilac $UCl_2H_2BPz_2THF$ or blue-green UCl_2HBPz_3THF, where Pz denotes pyrazole, $C_3H_3N_2$. Analogous derivatives were obtained with Pz′ = 3,5-dimethyl pyrazole (*288*). The compounds were characterized by analysis, UV/vis and IR spectra, ^1H and ^{11}B NMR spectra. Excess of pyrazole borate in the preparation did not yield compounds with further replacement of chlorine; but following the reaction by means of NMR suggested that some other U(III) compounds might be formed. U(IV) compounds, a potential impurity whose NMR spectra were known from earlier work (*289*), could easily be detected when present.

The THF in $UCl_2H_2BPz_2THF$ could easily be replaced by pyridine, giving a dark blue compound. Treatment of a solution of the THF complex in toluene with sodium cyclopentadienyl gave a red-brown solution whose UV/vis spectrum was different from that of the U(III)cyclopentadienyl THF adduct though still characteristic of a U(III) compound. The same reaction in THF solution, however, did yield a $U(C_5H_5)_3THF$ solution (*290*).

The $UCl_2HBPz_3'THF$ compound with Pz′ = 3,5-dimethylpyrazole **8** has also been made by the reduction of UCl_3HBPz_3' by sodium naphthalenide in THF (*291*). An analogous preparation yields $UClN[Si(CH_3)_2]HBPz_3'$.

Analyses, IR, and NMR data were given for all these compounds.



(8)

IV. Hydrido and Related Species

A. HYDRIDES (*1c, 3d, 292*)

1. *Thorium*

In a rather formal way the hydrides of thorium and uranium fall within the scope of this review. The thorium hydrides have been known for many years. They are obtained by the direct reaction of the metal with hydrogen.

a. ThH_2. A somewhat nonstoichiometric tetragonal phase of this composition has a structure like ZrH_2, with a = 573.5 and c = 497.1 pm, Z = 2. Hydrogen-deficient samples sometimes contain a face-centered cubic phase of similar composition, a = 548.9 pm.

The thorium hydrides are thermally more stable than uranium hydride, and thus the dissociation pressure of hydrogen over ThH_2 is 9228.4 Pa at 1000 K.

b. Th_4H_{15}. This compound has attracted much attention because it is a metallic conductor at room temperature and becomes a superconductor below 7.5 K. It has a unique cubic structure, space group $I\bar{4}3d$, Z = 4, and a = 911 pm. The shortest Th—Th distance in the structure is 384.6 pm, compared with 359 pm in thorium metal (*293*).

c. Recent Work on the Thorium Hydrides. By carrying out the preparation at high temperature, 1150 K, and under a high pressure of hydrogen, one can obtain a massive, dense form. Evidence for a tetragonally distorted, nonsuperconducting form, as well as two forms differing in their temperature range for the transition to the superconducting state, was also reported (*294*).

A phase study of the Th–H_2 system has provided more p_{H_2}-T-*composition data* (*295*).

Measurements of the temperature dependence of the hydrogen pressure in equilibrium with the two hydrides (*296, 297*) and heat capacity measurements at low temperatures (*296*) have yielded standard enthalpies and entropies of formation for the two compounds at 298 K.

The first of these papers gives standard enthalpies of formation at 298 K of -150 ± 9 and -221 ± 13 kJ mol^{-1} for ThH_2 and Th_4H_{15}, respectively. The entropies of formation of the two hydrides are given as -133.23 and -243.8 J K^{-1} mol^{-1}.

The second paper gives enthalpies of formation of -145.6 ± 1 and -215.8 ± 4.5 kJ mol^{-1} for the ThH_2 and Th_4H_{15}, respectively. The data are also discussed in refs. *3d* and *4b*. The standard entropies of ThH_2 and Th_4H_{15} are given as 50.73 and 54.42 J K^{-1} mol^{-1}, respectively (*2*).

Mixed hydrides with Zr and Ti were reported several years ago. It has now been shown that substantial replacement of thorium by lanthanum is possible in Th_4H_{15}. The temperature at which superconduction appears falls as the lanthanum content rises (*298*).

Th_4H_{15} has preparative applications, the reaction with nitrogen providing a convenient synthesis of pure Th_3N_4 and ThN (*299*). But compounds of the type ThH_xX_y, with X = C or N, $x < 2$, and $y < 1$ (*300*), and $ThN_{3-x}H_x$ have also been reported (*301*).

The electronic structure, band characteristics, and phonon distributions of both hydrides have been studied experimentally by XPS and theoretically (*302–306*). The bands arising from the bonding electrons are similar in the two hydrides, but Th_4H_{15} gives a narrow *d*-like band, half-width ≈ 0.6 eV, within 1.5 eV of the Fermi level. This band is separated from the bonding bands by about 2 eV. In ThH_2, the corresponding band is much broader and the separation from the bonding bands less marked. No evidence for a 5*f* band was obtained (*303, 306*).

A number of NMR studies of the hydrides have appeared (*307–310*). Several have measured the relaxation times as a function of temperature and extracted the energy of activation for diffusion of the hydrogen. In one report, a value of 61.5 kJ mol^{-1} is reported (*309*), but another finds 45.6 kJ mol^{-1} below 350 K and a mean value of 71.7 at 390 K (*308*). The data do not suggest much occupation of 5*f* electrons near the Fermi level. Some measurements have been extended to 4.2 K (*311*). In addition, Knight shifts at the proton have been reported for ThH_x, $x = 0 - 3.61$ (*312*).

Diffusion in thorium hydride has also been explored using an emanation measurement technique (*313*).

A further study of the decomposition kinetics of thorium hydride has been made (*314*).

2. *Uranium*

Uranium metal combines directly with hydrogen to give UH_3. Although nonstoichiometric regions of the phase diagram are found at high and low hydrogen contents, particularly at high temperatures, the dissociation pressure of hydrogen at room temperature is practically constant from about 5 to 95% UH_3 content. The kinetics of both the formation and the decomposition of UH_3 are very sensitive to impurities, as indeed are some other properties of the compound.

Two cubic crystal modifications are known. Both belong to the space group Pm3n and both contain 12-coordinate uranium. The α form, obtained by the reaction of uranium and hydrogen at 200–240 K, has $Z = 2$ and $a = 416$ pm. The commoner β form, obtained at higher temperatures, has $Z = 8$ and $a = 664.5$ pm. Formation of the hydride usually leads to a powdered product, but reacting uranium and hydrogen at 873–973 K and about 130 atmospheres of hydrogen gives macrocrystalline β UH_3. It is still uncertain whether there is a temperature range in which the α form is stable.

The β form is an excellent metallic conductor. It is paramagnetic and suffers ferromagnetic ordering below 177 K.

a. Recent Work. Recent work has added some thermodynamic data on UH_3. The specific heat of the β form has been measured from 4–298 K (*315*). Measurement of the dissociation pressure as a function of the temperature (*316a,b*) from 450–720 K combined with the previous data yielded:

$$\Delta G_f^\circ UH_3(T) = 720.7T - 182.6 \times 10^3 - 70.34T\text{Ln}T \quad \text{J mol}^{-1}$$

$$\Delta H_f^\circ UH_3(T) = -182.6 \times 10^3 + 70.34\ T \quad \text{J mol}^{-1}$$

Reproducibility in the system was good, but various uncertainties limit the precision of the data. For instance, the solid phase probably contained both α and β UH_3. The enthalpy difference between these species is unknown, and the heat capacity data for UH_3 does not extend to the relevant temperature range (*316a*). Recent analyses of all the data suggest best values of -126.99 and -72.61 kJ mol^{-1} for the standard enthalpy and Gibbs function changes on formation at 298 K and an S° value of 63.67 J K^{-1} mol^{-1} for UH_3 (*3d, 316b*).

Although the reaction of the hydride with air or water at room temperature can be spectacularly vigorous, there was surprisingly little information on the other reactions of the hydride. Some additional data have now appeared.

Ammonium chloride is reported to react with the hydride at 523 K to form $(NH_4)_2UCl_6$. This is a somewhat surprising result, and one awaits further details (*317*).

In fact, UH_3 proves disappointingly unreactive with a wide variety of compounds (*318, 319*). Thus, although the C_6H_5X (X = Cl, Br, or I) give benzene and diphenyl plus the U(III) halide, nitrobenzene is reduced to give azo and azoxy benzene, C_6H_5F, p-$(NO_2)_2C_6H_4$, C_6H_5CHO,

C_5H_5Tl, and $(C_6H_5)_3PO$ do not react. Only compounds containing acidic hydrogen or those that can function as oxidizing agents seem to react readily with UH_3. It is much less effective as a hydrogenation catalyst than the Zr or Ti hydrides (*320*).

The electronic structures of the two forms continue to claim attention. An XPS examination of macrocrystalline β UD_3, which incidentally is not spontaneously flammable in air, showed a large density of states near the Fermi level. The *f* electrons appear in both localized and delocalized orbitals. There are two uranium sites in the cell: One kind appears responsible for the metallic conduction and the other, with localized *f* orbitals, for the paramagnetism (*315, 321*).

A detailed analysis of the structural and other data on the hydride leads to similar conclusions (*322*). As Table XII shows, bond lengths are not unusually short.

Inelastic scattering of neutrons from magnetically ordered UH_3 gives a hyperfine splitting of 0.08 eV (*323*). Neutron scattering by UD_3 gives energy-loss lines at 20 meV and 40 meV. These have been attributed to crystal field transitions (*324*). A recent NMR study of UH_3 in the ferromagnetic region, from 4.2 to 85 K gave a line at 19.5 MHz and a uranium magnetic moment of 1.45 BM (*325*).

Several later studies of the kinetics of both the formation and the decomposition of the hydride have appeared. For the powdered hydride, the decomposition is zero order in the temperature range 473–573 K, with an energy of activation of 39.7 kJ. The formation from powdered uranium between 323 and 523 K depends on the $\frac{2}{3}$ power of the hydrogen pressure at 13.3 kPa, changing to a first-power dependence at 26.6 kPa. Impurities have a profound effect on the induction period. The apparent energy of activation is negative, and an adsorption rate controlling step is proposed (*326*). Studies of the hydriding of

TABLE XII

HYDRIDE BOND LENGTHS

Bond	Bond length (pm)	
	α	β
H—H	208	208
	254	216
U—H	232	232
H—H	360	332
		370

massive uranium, including topographical details, have been reported (*327, 328*). The data can be treated in the manner devised by Avrami (*329*). The reaction has also been investigated cinematically on a hot microscope stage (*330*).

The dissociation pressure of UH_3 is about twice that of UD_3 at 673 K, and formation and decomposition of the hydride shows promise for the separation of the isotopes (*331–335*).

Many of the papers appearing about uranium hydride in the last few years are concerned with technical problems arising from the possibility of its use for storing tritium as UT_3 in connection with nuclear fusion devices. Several papers on these topics can be found in ref. (*336*). From the chemical point of view, perhaps the most interesting study was the demonstration, using ^{3}He NMR, that the ^{3}He formed by tritium decay soon forms microscopic gas bubbles rather than being trapped in octahedral interstitial sites. The two situations can be expected to lead to very different relaxation times (*337–340*).

From time to time, reports have appeared of some reactive hydrido species being formed by the reaction of uranium and thorium metals with aqueous mineral acids. A Russian report suggests the formation of a black $UH(OH)_2$ (*341*).

B. Borohydrides

The formation of a U(III) borohydride by thermal decomposition of $U(BH_4)_4$ was first reported many years ago. But, although solutions of U(III) borohydride were used in preparative work, the compound was inadequately characterized (*342*). More recently, involatile red-brown $U(BH_4)_3$ has been made by the thermal decomposition of the related U(IV) compound at 373 K. The IR spectrum was recorded (*343*). The ^{1}H and ^{11}B NMR of solutions in THF, prepared by heating a solution of the U(IV) compound at 400 K, have been studied. In both spectra, three lines are seen, and the intensity ratio of two of the lines was constant at 4 : 5. The ratio of the intensity of the third line to either of these varied with the temperature. One of the ^{1}H lines was a quartet with $J_{\text{H-B}}$ = 87 Hz. It was suggested that the following equilibrium was involved:

$$3U(BH_4)_3 \rightleftharpoons U(BH_4)_5^{2-} + 2U(BH_4)_2^{+}$$

However no direct evidence of ionized species was provided (*344*).

Some crown-ether U(III) borohydride complexes have already been described (Section II,D). The compound $U_3(BH_4)_9$(dicyclohexyl 18-

crown-6)$_2$ (*84*) can be partially oxidized by oxygen in dichloromethane solution to give a brown, mixed valence compound

$$[\mathrm{U(III)}\ (\mathrm{BH_4})_2\ \text{dicyclohexyl 18-crown-6}]_2\ \mathrm{U(IV)Cl_5BH_4}$$

The crystals of this compound are tetragonal, space group P$\bar{4}$, $Z = 2$, $a = 1822.7$, $c = 975.7$ pm. Extended XAFS data show that the U(III) atoms are interacting with all the crown-ether oxygens (*345*).

U(III) borohydride is a Lewis acid, and a number of adducts are known. The crystal structure of $\mathrm{U(BH_4)_3THF{\cdot}MTHFE}$ has been described. (MTHFE = methyltetrahydrofurfurylether) (*346*).

Adding $\mathrm{(CH_3)_2PCH_2CH_2P(CH_3)_2}$ (DMPE) to a solution of the THF adduct of $\mathrm{U(BH_4)_3}$ yields a dichroic olive-red adduct containing two phosphine moieties per uranium atom. The crystals are tetragonal, space group I$\bar{4}$2d, $Z = 8$, with $a = 1450.9$ and $c = 2442.6$ pm (*347*). The phosphine ligand exhibits conformational disorder. Differences in the U—B bond lengths indicate two tridentate and one bidentate $\mathrm{BH_4}$ units, the latter lying on the twofold axis (*348*). The stereochemistry around the uranium is similar to that of the next complex (Fig. 3). The IR spectrum is complex.

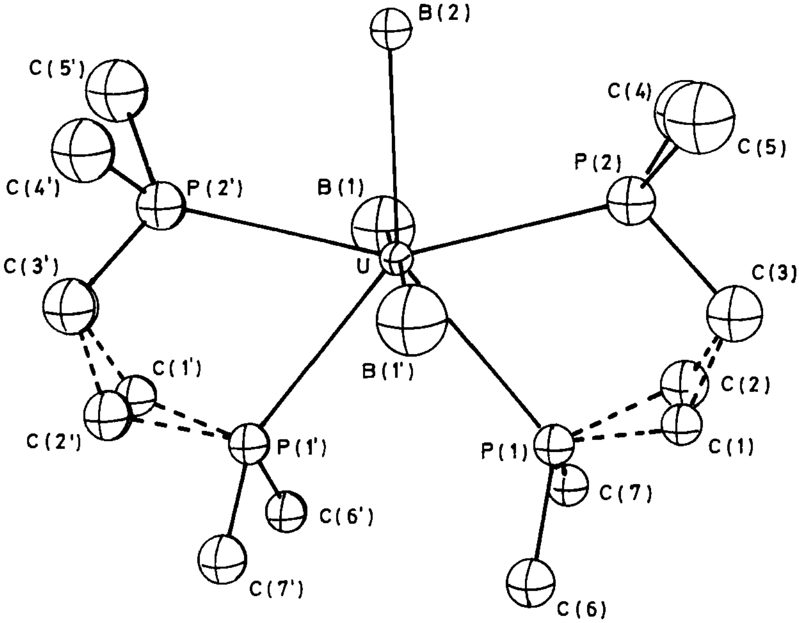


FIG. 3. Structure of $\mathrm{U(BH_4)_3(DMPE)_2}$ (*347*).

A similar preparation leads to $U(BH_4)_3L_2$, in which L = 2-(diphenylphosphino)pyridine (*349*). The crystal structure shows that this ligand is bidentate. The crystals are monoclinic, space group C2/c, $Z = 4$, which $a = 1948.2$, $b = 1217.6$, $c = 1852.9$ pm, and $\beta = 109.71°$. The stereochemistry is shown in Fig. 4.

There are two slightly different U—B bond lengths, but IR data indicate only tridentate BH_4 units (*348*, *350*). In both these complexes the uranium is quasi 7-coordinate, with a pentagonal bipyramidal arrangement.

Uranium and thorium seldom accept monodentate phosphine ligands. However, U(III) borohydride attaches two $P(C_2H_5)_3$ or $PC_6H_5(C_2H_5)_2$ molecules. The red-brown complexes were prepared in toluene and excess ligand and solvent removed *in vacuo*. Satisfactory analyses and IR spectra were reported for the first of these complexes, and detailed ^1H, ^{11}B, and ^{31}P NMR confirmed the identity of both adducts (*351*).

A DMPE adduct of $U(BH_3CH_3)_3$ has been described. It contains two molecules of phosphine per uranium atom. The complex is tetragonal, space group $P4_32_12$, $Z = 4$, with $a = 1129.7$ and $b = 2303$ pm. The H_3BCH_3 units are tridentate and the phosphines bidentate. The stereochemistry around the uranium is effectively a pentagonal bipyramid.

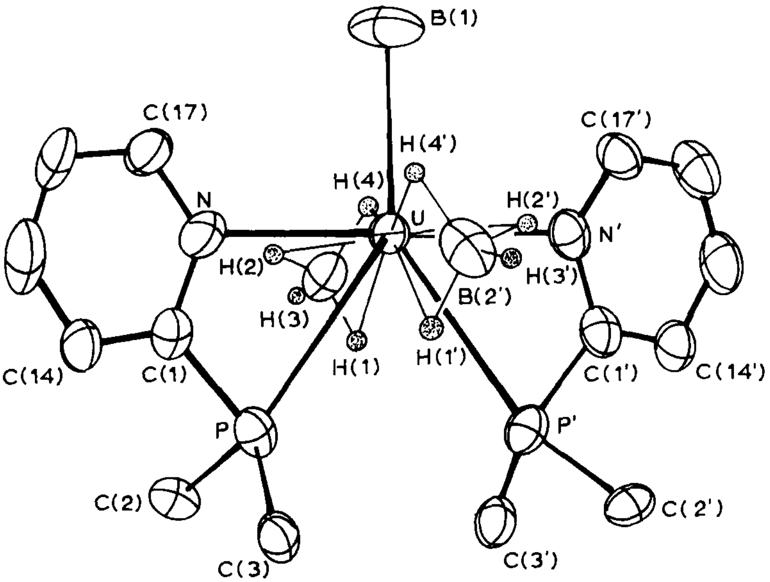


FIG. 4. Structure of di-2-diethylphosphino pyridine adduct of $U(BH_4)_3$ (*349*).

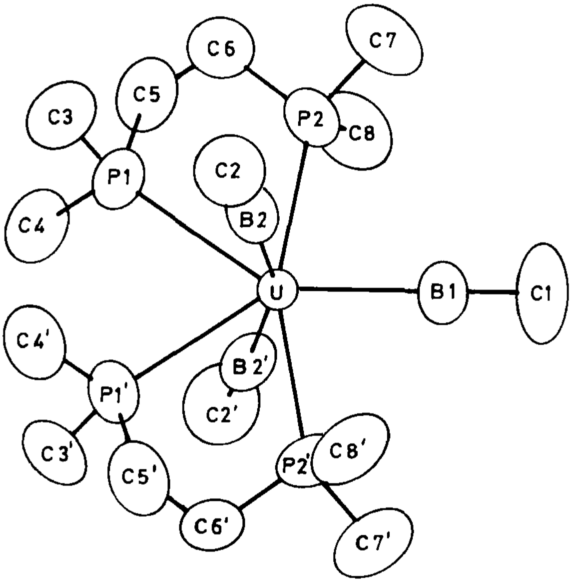


FIG. 5. Structure of $U(BH_3CH_3)_3(DMPE)_2$ (*352*).

It is interesting to note that the U—P length in this compound is shorter than in the U(IV) analog (*352*). The structure is shown in Fig. 5.

V. Organometallic Compounds (*1j, 353–358*)

A. URANIUM

1. *Uranium(III) Cyclopentadienyl $U(C_5H_5)_3$ ($\equiv UCp_3$)*

a. Preparation. The reduction of $U(C_5H_5)_3Cl$ by Li/Hg was mentioned in a dissertation at Munich in 1962, but the product was not fully characterized (*359*). Two years later an Australian patent application described the preparation of UCp_3 by the dry reaction of $MgCp_2$ with UCl_3. Again the product was not characterized (*360*). In the same year an attempted synthesis from UCl_3 and sodium cyclopentadienyl in THF yielded only Cp_3UOBu (*361*).

In 1970, however, UCp_3 was prepared by two reactions:

UCl_3 + KCp in benzene
UCp_4 +K in benzene

The product was characterized by its infrared spectrum and by mass spectrometry (*362*).

Since that time several other preparations have been explored because it is difficult to obtain a high yield of UCp_3. Earlier workers failed to obtain a reaction between finely divided uranium powder, obtained by the thermal decomposition of the hydride, and HCp; but it was subsequently reported that a 30% yield could be obtained if uranium recovered from its amalgam was used. This preparation was on a rather small scale (*363, 364*).

The reduction of UCp_3Cl by sodium hydride in benzene has also been used (*365, 366*). The compound is also formed by the photolysis, or thermal decomposition, of solutions of Cp_3UR (R = CH_3, iPr, *n*Bu, etc.) in toluene. Other U(III) compounds are also formed (*367–369*) (see also Section V,B).

b. Physical Properties. UCp_3 is a yellow-brown volatile solid, extremely sensitive to air or moisture and only very sparingly soluble in common organic solvents. The infrared spectrum is rather simple, resembling those of $PuCp_3$ or $AmCp_3$ (*362*). The analysis of such a spectrum can be found in ref. *370*. The crystal structure has not been investigated and the complexity of the structures of the lanthanide analogs makes prediction very uncertain (*371*).

The ring protons of UCp_3 give a single line in the NMR spectrum at 10.5 ppm upfield in relation to those on benzene (*364*).

The complex near-IR/UV/vis spectrum of a solution of UCp_3 in the weakly complexing solvent benzene has been reported (*365*) (see also next section).

c. The Adducts. UCp_3 is a strong Lewis acid. It forms adducts with THF, l-nicotine, cyclohexyl isocyanide, and many other donors (*362*).

The THF adduct is especially useful because it is quite soluble in THF and other solvents, so solutions can be prepared directly. The adduct cannot, however, be desolvated without decomposition of the UCp_3 (*372*).

Solutions can be prepared by

a. Reduction of a solution of UCp_3Cl in THF by sodium naphthalenide, made *in situ* (*372*);

b. reaction of UCl_3 with NaCp in THF (*207*); and
c. reduction of UCp_3Cl in THF by $LiAlH_4$, but not by $LiBH(C_2H_5)_3$ (*373*).

By reacting $UN[Si(C_2H_5)_3]_2Cl_2$ with NaCp in THF, filtering, concentrating, and then cooling the solution for several days, suitable crystals of UCp_3THF for crystallographic study were obtained (*374*). It is monoclinic, space group $p2_1/c$, $Z = 4$, with $a = 824.8$, $b = 2432.2$, and $c = 835.7$ pm, $\beta = 101.29°$. The distribution of the ligands around the uranium is approximately tetrahedral (*375*). The compound is isostructural with the various $LnCp_3THF$ (*376, 377*).

The reduction of UCp_3Cl by $LiAlH_4$ in THF involves one or more intermediate compounds. When one follows the reaction by NMR, the line at 16.3 ppm yields, first, a line between 21.2 and 21.8 ppm and, finally, the line at 28.4 ppm, which arises from the adduct (all upfield in relation to the benzene protons.) The intermediate may be the anionic species Cp_3UCl^- (*373*) (see Section V,A,4).

Near-IR/vis spectra of the adducts with $(C_2H_5)_2O$, THF, $C_6H_{11}NC$, and 1-nicotine show the expected small shifts in the $f \leftrightarrow f$ bands (*362, 366*). In the IR, $\nu_{C\text{-}N}$ shifts about 25 cm^{-1} higher on formation of the adduct (*378*).

The magnetic susceptibility of the THF adduct obeys the Curie–Weiss relation in the temperature range 2.5–22 K, with $\mu_{eff} = 1.69\ \mu_B$, $\theta = 2.9$, and also in the range 22–55 K with $\mu_{eff} = 1.08\ \mu_B$, $\theta = 10$. It was suggested that a crystal field splitting of the $\frac{9}{2}$ ground state by about 15 cm^{-1} might account for these data (*372*).

An interesting binuclear adduct is formed by the reaction of UCp_3THF with pyrazine. Powder X-ray diffraction data, as well as the mass spectrum, suggest that it is isostructural with the known $(YbCp_3)_2C_4H_4N_2$ (*381*). It is rather insoluble in common solvents, so NMR data could not be obtained (*379, 380*).

The bonding and electronic structure of these adducts have been explored using X α SW molecular orbital calculations. These indicate that back-bonding, perhaps from the $5f$ orbitals on the uranium, may be of some importance, at least in the case of the carbonyl (*382*). (For other reactions of UCp_3, see Section V,A,3.)

2. *Substituted Cyclopentadienyls*

a. Methyl Cyclopentadienyl. Black crystalline $U(C_5H_4{\cdot}CH_3)_3THF$ ($\equiv UCp_3'THF$) can be obtained by the reaction of UCl_3THF with NaCp′ in 33% yield (*383*). Several other adducts have been made and the sequence for ligand replacement reactions and order of decreasing stability is (*384*):

$$P(CH_3)_3 > P(OCH_3)_3 > NC_5H_5 > SC_4H_8 \sim THF > N(CH_2CH_2)_3CH > CO$$

It is noteworthy that the phosphine diplaces the oxygen and nitrogen donors, suggesting that for π accepting ligands, back-bonding from the uranium may be significant (*382, 384*).

The equilibrium

$$(RC_5H_4)_3UL' + L'' \rightleftharpoons (RC_5H_4)_3UL'' + L'$$

has been studied in solution with $R = H$, CH_3, or $(CH_3)_3Si$; L' = pyridine and $L'' = P(CH_3)_3$. The equilibrium constants were $R = CH_3$, 180; $R = H$, 80; and $R = (CH_3)_3Si$, 0.1. So substitution of $R = H$ by the electron-donating methyl enhances the coordinative affinity of the phosphine ligand for the U(III) whereas an increase in the steric demands on the metal coordination sphere ($R = Si(CH_3)_3$) shifts the equilibrium in favor of the smaller pyridine ligand (*384*).

Black crystals of $Cp_3'USC_4H_8$ have been made in an analogous way to the THF compound (*366*). They are orthorhombic, space group Pbca, $Z = 8$, with $a = 1514.6$, $b = 275.9$, $c = 991.1$ pm (*385*). A pyrazine derivative, $(UCp_3')_2C_4H_4N_2$, analogous to the Cp compound has also been made (*380*).

Unlike the reactions with the sulphur and selenium analogs, $(C_6H_5)_3PO$ forms an adduct, $UCp_3'L$. The dark red monoclinic crystals belong to the space group $p2_1/n$, $Z = 4$, with $a = 1626.8$, $b = 1794.8$, and $c = 1090.0$ pm, and $\beta = 105.02°$ (*386*).

The red trimethyl phosphine adduct, $Cp_3'UP(CH_3)_3$, is also monoclinic, space group Cc, $Z = 4$, with $a = 1394.9$, $b = 928.0$, and $c = 1619.4$ pm, $\beta = 104.09°$. The U—P distance is 297.2 pm. Infrared and NMR data were reported (*387*).

The 4-dimethylaminopyridine adduct, made in a similar fashion, is triclinic $P\bar{1}$, $Z = 4$, with $a = 1554.1$, $b = 1715.5$, and $c = 1030.3$ pm, $\alpha = 106.83°$, $\beta = 106.52°$, and $\gamma = 67.04°$. The pyridine N donates to the uranium (*388*).

b. Trimethylsilyl Cyclopentadienyl. This green compound, $[(CH_3)_3Si\,C_5H_4]_3U$, can be made from UCl_3THF in a similar way to its analogs (*389*), or by the reduction of $[(CH_3)_3SiC_5H_4]_3UCl$ by Na/Hg in toluene or, more conveniently, by Lit·Bu in hexane (*398*). The relative stability of the adducts has been explored by using displacement reactions. It is interesting to find the C_2H_5NC adduct stronger than the C_2H_5CN. Both $P(OCH_3)_3$ and the isocyanide give strong adducts, suggesting that the uranium may be π back-donating. This is supported by the formation of a red carbon-monoxide adduct, the first actinide carbonyl that can be handled at room temperature. Such an effect should reduce the $\nu_{C\text{-}N}$ and $\nu_{C\text{-}O}$ stretching frequencies. In both $[(CH_3)_3SiC_6H_4]_3UCNC_2H_5$ and $Cp_3UCNC_6H_{11}$, $\nu_{C\text{-}N}$ shows some increase on complex formation; but for the solid $[(CH_3)_3SiC_6H_4]_3UCO$, $\nu_{C\text{-}O}$ falls by 169 cm^{-1} on complex formation (*382, 389*).

The crystal structure of the C_2H_5NC adduct shows a quasitetrahedral arrangement of the ligands around the uranium. The U-C-N bond angle is large (173°) but not linear (*389*).

c. Tris η^5 Indenyl Uranium. The indenyl analog of UCp_3, $U(C_9H_7)_3$, has been made and characterized (*390*). It is triclinic, space group $P\bar{1}$, $Z = 2$, with $a = 1502.9$, $b = 875.7$, $c = 865.9$ pm, $\alpha = 120.07°$, $\beta = 83.72°$, and $\gamma = 100.33°$ (*391*).

d. Other Substituted Cyclopentadienyls. Derivatives of two others are known: $[(CH_3)_3Si]_2C_5H_3$ and $(CH_3)_5C_5$ (see next section).

3. *Reactions and Derivatives of the Cyclopentadienyls*

Like most actinide organometallic compounds, the ligands in these compounds are labile and the compounds reactive. For instance NMR shows a rapid exchange of THF with Cp_3UTHF (*373*). In the system UCp_3–UCp_3Cl in THF, variable temperature NMR studies reveal a second-order intermolecular exchange of UCp_3 groups. The kinetic data are compatible with chlorine atom transfer by a $Cp_3U^{(III)}\text{–}Cl\text{-}U^{(IV)}Cp_3$ intermediary. Other evidence for such species has been given (*368*). The rate constant obtained is much greater than for similar exchanges with transition metal complexes (*392*).

a. Reactions of the Cyclopentadienyls. Homolytic scission of the U—Cp bond by HCN gives Cp_2UCN. Very little information about this compound has appeared. It is paramagnetic but does not obey the Curie–Weiss law; $\nu_{C\text{-}N}$ is found at 2112 cm^{-1} (*393*).

UCp_3 reacts with both acetyl and benzoyl chloride. The reaction has been described as an oxidative addition, but the products were not very well characterized. The same paper reports cyclic voltametric evidence for a 1-electron reduction of UCp_3 dissolved in benzene, with $(C_4H_9)_4NClO_4$ as supporting electrolyte (*394*).

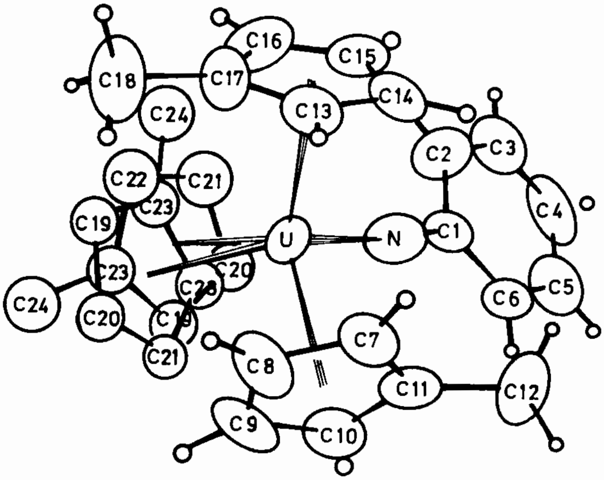


FIG. 6. Structure of $(CH_3C_5H_4)_3UNC_6H_5$ (*383*).

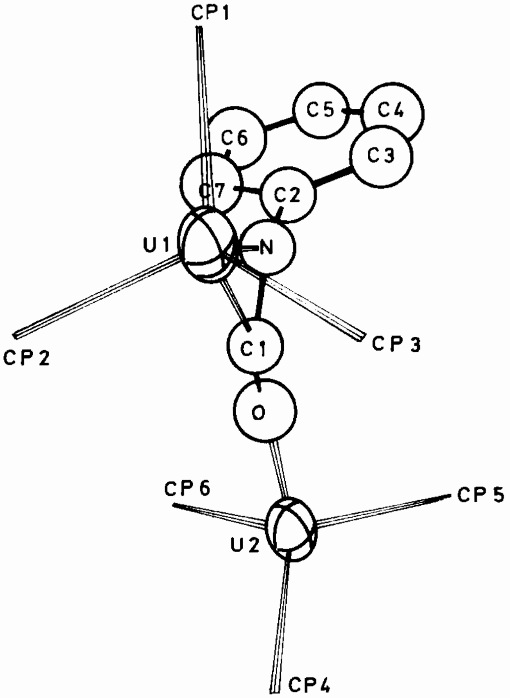


FIG. 7. Structure of $[(CH_3C_5H_4)_3U]_2[\mu,\eta^1,\eta^2\text{-}C_6H_5NCO]$ (*383*).

The THF adducts of both UCp_3 and UCp_3' react with RN_3 [R = C_6H_5 or $(CH_3)_3Si$] giving imido complexes of U(V) and nitrogen (*383*), The products were characterized by analysis, NMR, and mass spectra. The stereochemistry of $Cp_3'UNC_6H_5$ is shown in Fig. 6.

The length of the U—N bond, 201.9 pm, one of the shortest found for a pseudo U(IV) compound, and the near linearity of the U-N-C system (angle 167.4°) suggests that both lone pairs on the nitrogen may be involved in the bonding of the metal to the $N\text{-}C_6H_5$ moiety (*383*).

By contrast, although UCp_3' reacts with C_6H_5NCO and other isocyanates, CO is not formed. The product is $(Cp_3'U)_2[\mu\eta^1\ \eta^2(C_6H_5NCO)]$. The stereochemistry of the compound is shown in Fig. 7. The ligand behaves as $(C_6H_5NCO)^{2-}$, bridging the two uranium atoms. One metal atom is attached to the oxygen and the other to both the carbon and nitrogen atoms. The U—N distance (236 pm) is similar to the mean value for the pyrazolate complexes of the type $UCp_3(C_3H_3N_2)$ (*395*), the U—C distance is close to that found for $Cp_3Un\text{-}Bu$ (*396*), and the U—O distance is rather larger than in $[Cp_2U(OCH_3)]_2PH$ (*397*). Accordingly, it was suggested that the uranium is effectively U(IV), and the ligand behaves as $C_6H_5—N—C^-—O^-$ (*383*).

$Cp_3'UTHF$ and $[(CH_3)_3SiC_5H_4]_3U$ suffer oxidation by CS_2 to yield a binuclear U(IV) complex, $[(RC_5H_4)_3U]_2\ \mu\eta^1\eta^2CS_2$, with R = CH_3 or $Si(CH_3)_3$. The R = CH_3 compound is monoclinic, space group $p2_1/n$, Z =

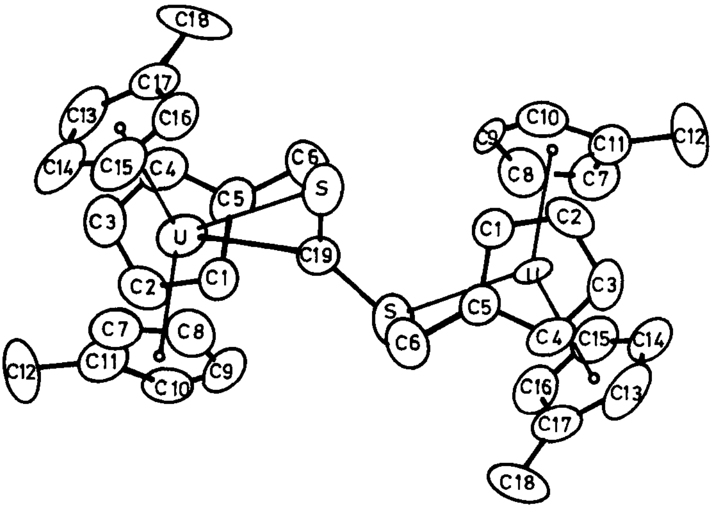
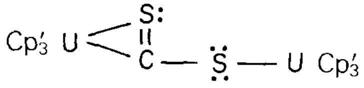


FIG. 8. Structure of $[(CH_3C_5H_4)U]_2[\mu,\eta^1,\eta^2\cdot CS_2]$ (*398*).

2, with $a = 1412.7$, $b = 1418.2$, and $c = 812.3$ pm, $\beta = 92.36°$. The stereochemistry is shown in Fig. 8.

It was suggested that the bonding can be represented as



(9)

The C—S distance for the η^2 portion is 146.4 and for the η^1 portion 183.1 pm. The central carbon atom is disordered about the center of symmetry of the system. The bridging ligand functions as CS_2^{2-} (*398*). No IR features could be assigned to the CS_2 moiety in the complex.

The complex $Cp_3'U$ also suffers oxidation by COS and $EP(C_6H_5)_3$, with E = S, Se, or Te, in diethyl ether with the formation of $(Cp_3'U)_2E$. The products have been characterized by analysis, IR, and NMR. The sulphur compound is monoclinic, space group $p2_1/c$, $Z = 4$, with $a = 1974.0$ $b = 830.2$, and $c = 2160.2$ pm, $\beta = 97.28°$ (*386*). (Other oxidation reactions appear in Section V,A,3,b.)

b. Derivatives. Simple derivatives of the type Cp_2UX or $Cp_2'UX$ have been inadequately characterized.

UCl_3THF reacts with TlCp, and it was suggested that Cp_2UCl might have been formed (*207*). It has been reported that "Cp_2UCl_2" reacts with excess $NaBH_4$ to give Cp_2UBH_4, but since "Cp_2UCl_2" is now known to disproportionate, this seems unlikely (*399*).

With the more extensively substituted bulky cyclopentadienyls, however, several monosubstituted derivatives are known; indeed, the homoleptic U(III) compounds of these cyclopentadienyls have not so far been reported.

i. Bis(1,3-trimethylsilyl) cyclopentadienyl derivatives (≡Cp″). Reduction of $Cp''UCl_2$ (*400*) by Na/Hg in toluene at room temperature gives $[Cp_2''U(\mu Cl)]_2$ (*401*). Unlike the corresponding Cp compound the $Cp_2''UCl_2$ does not disproportionate, and the related bromo and iodo compounds can be obtained by treatment of the chloro compound with BBr_3 or BI_3. Reduction of the chlorine compound by Lin·Bu in hexane at room temperature yields the dimeric Cl compound referred to previously, a similar bromo compound and a polymeric iodo compound. (MP 264–266, 253–255, and 225–228, respectively). The compounds were characterized by analysis and NMR (*401*).

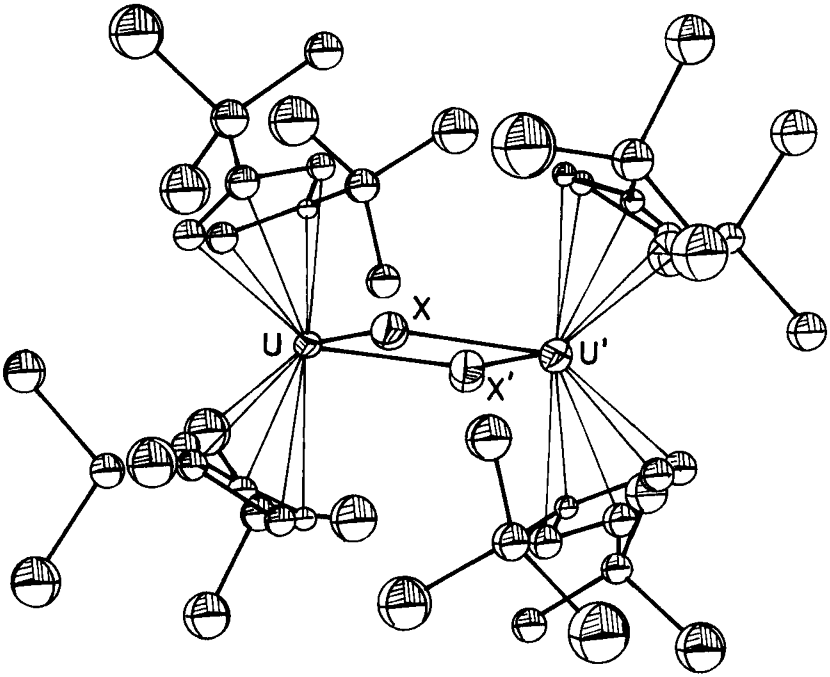


FIG. 9. Structure of $[Cp_2''U(\mu Cl)]_2$ (*401*).

The structure of $(Cp_2''UX)_2$, X = Cl or Br, is shown in Fig. 9. If one imagines the dienyl unit as monodentate, the uranium is in a 4-coordinate environment.

Reduction of $[Cp_2''U(\mu BF_4)(\mu F)]_2$, which is obtained by treating $Cp_2''UCl_2$ with silver fluoborate (*402*), gives $[Cp_2''UF]_n$ (MP 273–276) (*401*).

If the reduction of $Cp_2''UCl_2$ is made with Na/Hg or Lin·Bu in the presence of donors such as THF, tetramethylethylene diamine (TMEDA), or pentamethyldiethylene triamine (PMDETA), monomeric compounds of the general formula $Cp_2''U(\mu Cl)_2ML$ are obtained, where for M = Na, L = $(THF)_2$ or TMEDA, and for M = Li, L = $(THF)_2$, TMEDA, or PMDETA. The structures of two of these compounds are shown in Figs. 10 and 11. (Other examples of anionic U(III) organometallic compounds can be found in Section V,A,4.)

Again, if the cyclopentadienyl rings are considered to occupy only one coordination site, the uranium environment is tetrahedral 4-coordinate in these compounds (*403*).

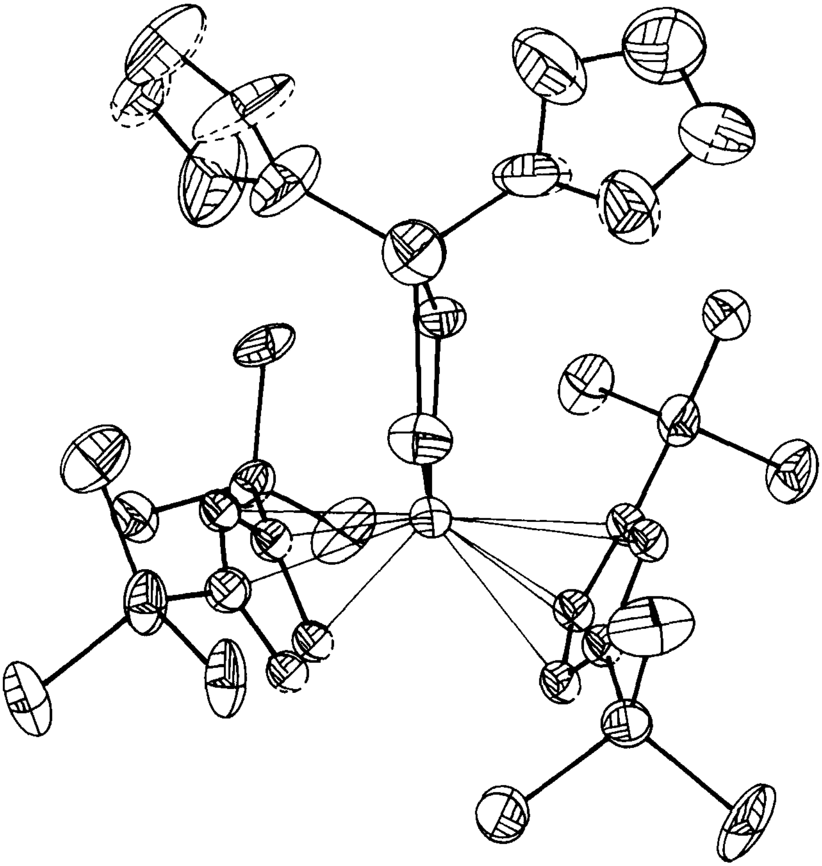


FIG. 10. Structure of $Cp_2''U(\mu Cl)_2Li(THF)_2$ (*403*).

The compound $Cp_2''U(\mu Cl)_2Li(THF)_2$ can also be made by treating the dimer $[Cp_2''U(\mu Cl)]_2$ with LiCl and THF.

Another group of quasitetrahedral monomers can be obtained by treating $[Cp_2''U(\mu Cl)]_2$ with THF, tmeda or pmdeta (=L) to obtain $Cp_2''UClL$ (*403*). Treatment of the THF adduct with LiCl in THF provides an alternative route to $Cp_2''U(\mu Cl)_2Li(THF)_2$.

The reduction of $Cp_2''UClX$, X = $N[Si(CH_3)_3]_2$ or SC_6H_2-2,4,6-*t*-Bu, by Na/Hg in hexane gives only $[Cp_2''U(\mu Cl)]_2$. But if X = OR, with R = C_6H_3-2,6-$(C_6H_5)_2$ or C_6H_3-2,6-$(iC_3H_7)_2$, green and blue $[Cp_2''UOR]_n$, respectively, are obtained. These compounds also give THF adducts. The same compounds can be obtained by the reaction of $[Cp_2''U(\mu Cl)]_2$ with LiOR in THF (*401*).

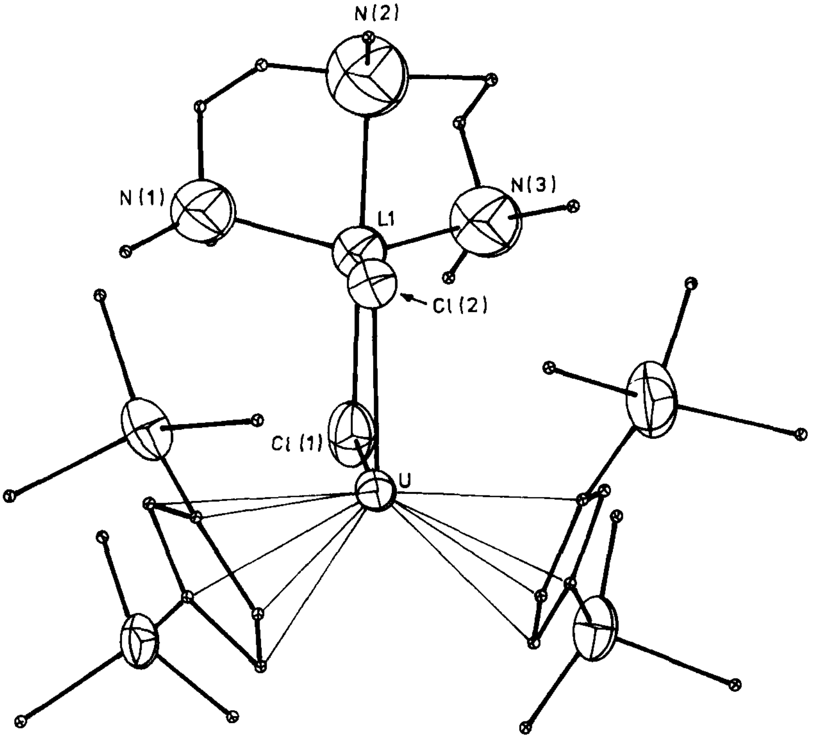


FIG. 11. Structure of $Cp_2''U(\mu Cl)_2$ Li Pmdeta *(403)*.

The green borohydride $Cp_2''UBH_4THF$ can be obtained by the reaction of the dimer chloro compound with $NaBH_4$ in THF.

The dimer adds $P(C_6H_5)_4X$ ($X = Cl$ or Br) in toluene to give $P(C_6H_5)_4Cp_2''UClX$. Like UCp_3 and UC_3' it reacts with $(CH_3)_3SiN_3$ to give $Cp_2''UClNSi(CH_3)_3$.

All these reactions have good yields ($\geqslant 60\%$). A somewhat surprising reaction is the oxidation by $Sn(NR_2)_2$, $R = Si(CH_3)_3$, to give $Cp_2''UClNR_2$ *(403)*.

A summary of these reactions is shown in Fig. 12.

ii. Pentamethyl cyclopentadienyl derivatives. The actinide derivatives of $(CH_3)_5C_5$ ($\equiv Cp^*$) have been studied rather extensively.

The trimeric $(UCp_2^*\mu Cl)_3$ has been made by the reduction of UCp_2^*ClR ($R = CH_3$ or $CH_2Si(CH_3)_3$) with hydrogen in toluene at room temperature, by reduction of $Cp_2^*UCl_2$ with Lit·Bu in ether at 195 K and by the reaction of the rather unstable $[Cp_2^*U(\mu H)H]_2$ *(404)*

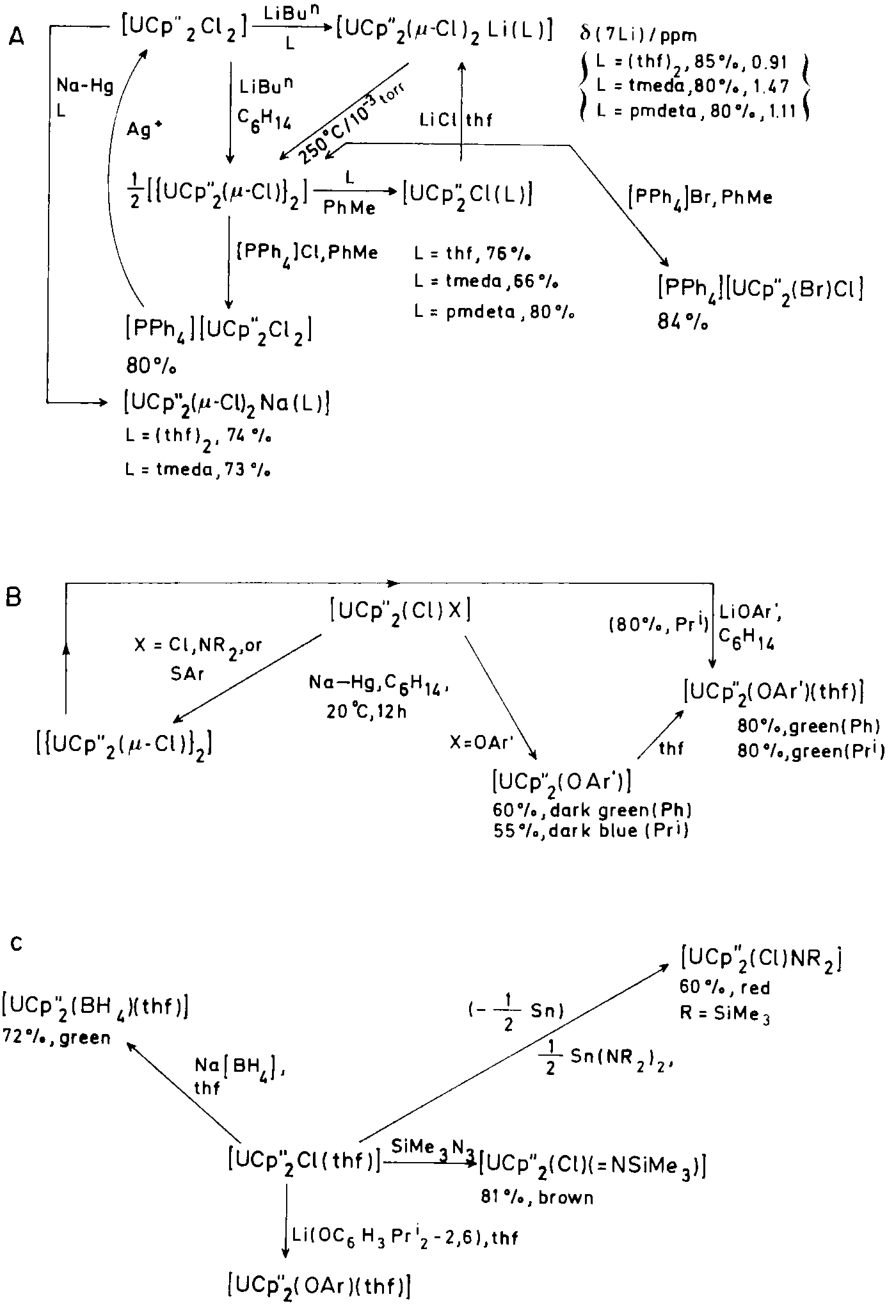


FIG. 12. Reaction schemes *(403)*.

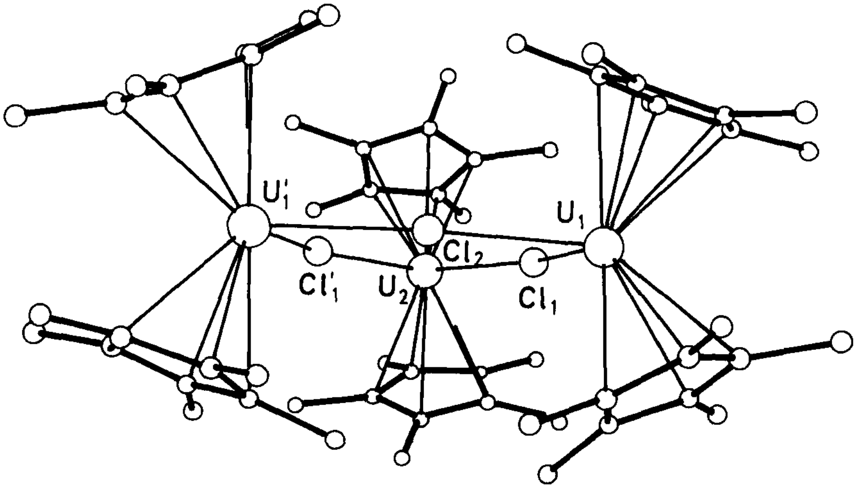


FIG. 13. Structures of $[(C_5(CH_3)_5)_2UCl]_3$ (*405*).

with $Cp_2^*UCl_2$ (*405*). Bearing in mind their data for analogous thorium compounds (*404*), the authors believe $[Cp_2^*U(\mu H)Cl]_2$ may be an intermediate in these preparations; this species is unstable, losing hydrogen to yield the trimer. This instability reflects the easier reduction of uranium compared with thorium (*367, 368*).

The trimer forms monoclinic crystals, space group C2/c, $Z = 4$, with $a = 2188.6$, $b = 1423.6$, and $c = 2451.7$ pm, $\beta = 128.65°$. The stereochemistry is shown in Fig. 13. Each U(III) atom has a pseudotetrahedral arrangement of neighbors, with two bridging chlorines (*405, 406*).

The trimer is almost insoluble in hydrocarbon solvents but forms adducts and dissolves in Lewis base solvents:

$$(Cp_2^*UCl)_3 + 3xL \rightarrow 3Cp_2^*UClL_x$$

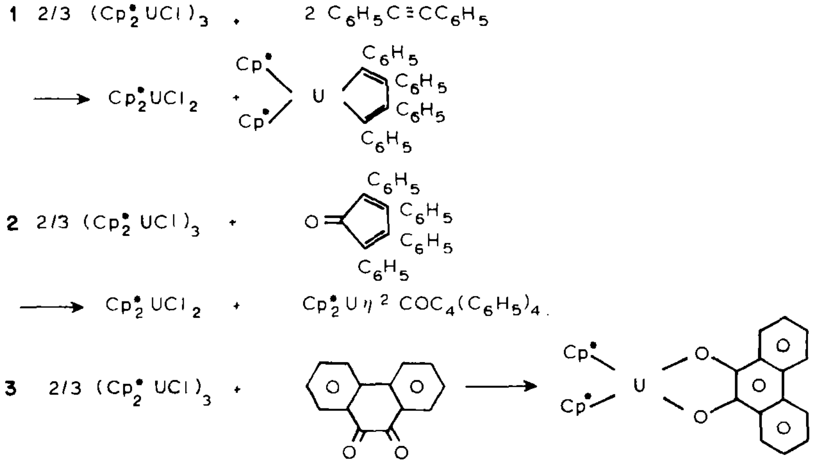
For L = pyridine, the product is dark blue and $x = 1$; THF gives a green adduct also with $x = 1$. Less-stable green adducts are obtained with diethyl ether and trimethyl phosphine (*405*).

Some alkyl derivatives of the type Cp_2^*UR [R = C_6H_5, $CH[Si(CH_3)_3]_2$, or $CH_2Si(CH_3)_3$] have been prepared, but the only stable one at room temperature was $UCp_2^*CH[Si(CH_3)_3]_2$ (*405, 406*). This seems to be in agreement with other observations that this alkyl stabilizes low oxidation states (*407, 408*).

Another stable derivative of a similar kind is the compound $Cp_2^*UN[Si(CH_3)_3]_2$ (*405, 406*).

The reduction of $Cp_2^*UCl_2$ with Na/Hg in THF does not give the trimer but the related compound $Cp_2^*U(\mu Cl)_2Na(THF)_x$, which resembles the behavior of the Cp″ compounds (*406*). Analogous species had already been isolated with the lanthanides [(*409, 410*); see also (*355, 411*)].

The trimer participates in some interesting reactions in which it undergoes oxidation (*406*). Three of these, with diphenylacetylene, tetraphenylcyclopentadienone, and 9,10-phenanthraquinone, are shown in Scheme 1.



SCHEME 1

The low solubility of the phenanthraquinone complex prevented a determination of its molecular weight, and the IR and ^1H NMR data are compatible with both a monomeric (a) and a dimeric (b) form (Fig. 14).

The trimer reacts with alkyl and aryl halides, RX, according to the following equation (*412*):

$$(UCp_2^*Cl)_3 + RCl \xrightarrow[\text{toluene}]{} UCp_2^*Cl_2 + UCp_2^*RCl$$

where $R = CH_3$ or C_6H_5.

The mechanism of these oxidative addition-type reactions (not the same usage of the term as in transition metal chemistry) has been explored by NMR (*412*). The complex UCp_2^*ClTHF reacted upon mixing with alkyl or aryl halides at an unprecedented rate. The rate of

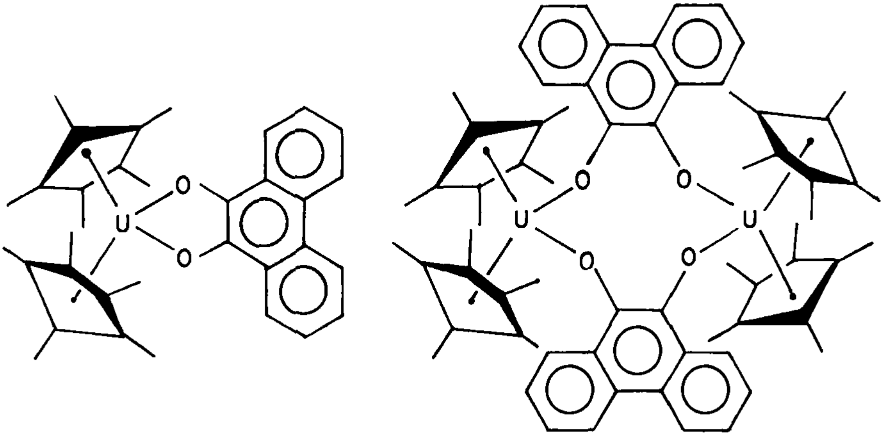
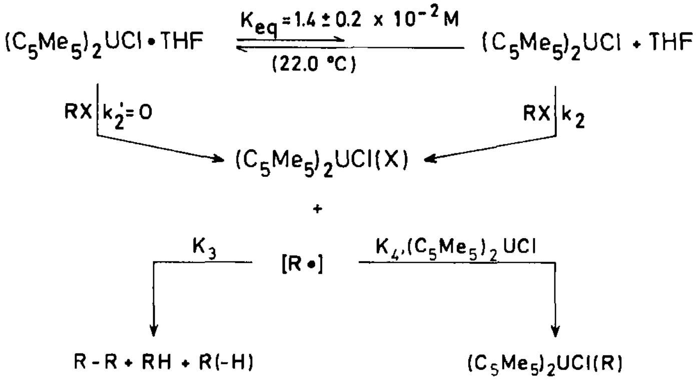


FIG. 14. Possible structures of UCp$_2$* phenanthraquin-one (*405*).

disappearance of UCp$_2$*ClTHF and RX and the appearance of UCp$_2$*Cl$_2$, UCp$_2$*ClR, as well as R—R, RH, and the olefin R(—H), was followed by NMR. The stoichiometry of the overall reaction was also established. The RX used were for X = Cl, R = $C_6H_5CH_2$, $(CH_3)_3CCH_2$, $(CH_3)_3C$, *n*-Bu, $CH_2CH_2CHCH_2$, and $CH_2 = CHCH_2CH_2$; for X = Br, R = CH_3; and for X = I, R = CH_3 or $C_6H_5CH_2$. Oxidative addition of the bromides and iodides also gave some other products containing all the possible halide combinations, such as UCp$_2$*X$_2$, UCp$_2$*XCl, and UCp$_2$*XR. It was considered that these products arise from the reasonably facile halogen and/or R exchange taking place after the initial oxidative addition reaction (*413*).

The following radical and atom abstraction mechanism was proposed.



SCHEME 2

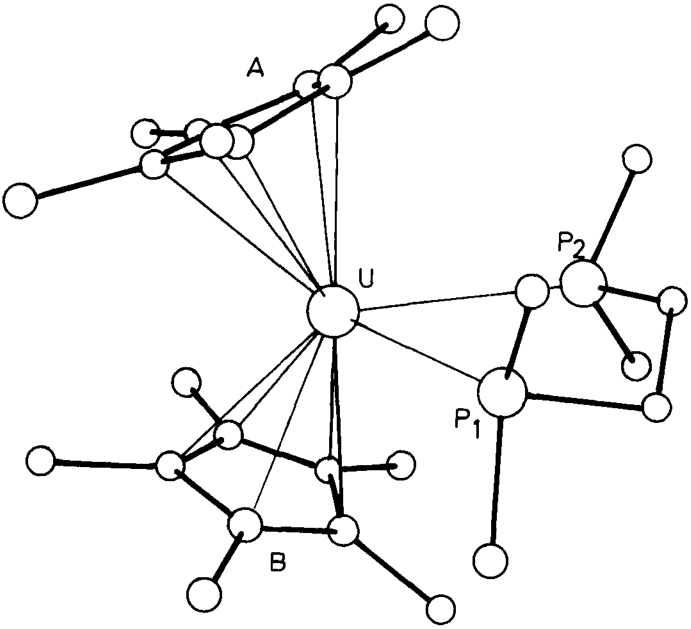


FIG. 15. Structure of $UCp_2{}^*H(DMPE)$ *(416)*.

Evidence for the radical species was obtained and the rate constants for the reactions established, as well as their dependence on the THF concentration (see also *414*).

Hydrido species can also be made. An indication of their existence can be found in the reaction of Lit·Bu with UCl_4, but the products were not clearly identified *(415)*. They may well be intermediaries in some reduction reactions *(405, 411)*.

However the hydrido complex $UCp_2{}^*HDMPE$ (DMPE = dimethylphopsphinoethane) was made by the reaction of hydrogen with $UCp_2{}^*R_2$ in the presence of excess DMPE ($R = CH_3$ and $CH_2Si(CH_3)_3$) *(416)*. The black crystals belong to the orthorhombic system, space group $Pca2_1$, $Z = 4$, with $a = 1505.5$, $b = 1105.2$, and $c = 1691.5$ pm. The stereochemistry is shown in Fig. 15.

The uranium(III) is bonded to the rings, which have the usual "bent sandwich" configuration. Naturally the lone hydrogen was not located in the diffraction study. It was thought to lie on or near a line passing through the uranium atom, parallel to the planes of the two rings.

The ^1H NMR showed no evidence of the lone hydrogen, but the IR showed a strong line at 1219 cm^{-1}, which moved to 870 cm^{-1} on deuteration.

^1H NMR studies at different temperatures showed the existence of intramolecular exchange processes, which at higher temperatures led to magnetic equivalence of the protons of the methyl and methylenic groups of the ligand DMPE, as well as those of the ring methyls.

The DMPE was suprisingly labile and could be replaced by THF, CO, and N_2. These reactions produced a mixture of U(III) and U(IV) compounds.

Solutions of the hydrido compound were paramagnetic and indicated a $\mu_{eff} = 3.47\ \mu_B$, a rather high value for U(III) compounds (*416*).

An attempt has been made to synthesize a hydrido complex containing $P(OCH_3)_3$ by treating $Cp_2{}^*U(CH_3)_2$ with hydrogen in the presence of the phosphite; but no U(III) apecies could be isolated. The products were $Cp_2{}^*U(OCH_3)_2$ and $[Cp_2{}^*U(OCH_3)]_2PH$. The former compound was also prepared from $Cp_2{}^*UCl_2$ and sodium methoxide in dimethoxyethane (*397*).

4. *Anionic U(III) Organometallics*

a. Cyclopentadienyls. The possible role of Cp_3UCl^- in the reduction of Cp_3UCl by $LiAlH_4$ has already been mentioned (*373*). Direct evidence for this species has been obtained in electrochemical experiments. A study of the electrochemical reduction of Cp_3UCl in THF, with $n\text{-}Bu_4NPF_6$ as supporting electrolyte, indicates Cp_3UCl^- formation (*417*). The NMR data in this paper do not seem compatible with those in the previous work.

Both Cp_3UCl and Cp_3UR, when treated with excess $LiCH_3$ in THF, give solutions containing $Cp_3UCH_3\text{-}Li(THF)_n$ (*418*). Although the presence of this compound was supported by ESR and ^7Li NMR measurements, a pure solid could not be obtained. It was noted, however, that a brownish-red solid separated on addition of the cryptand [221], $(C_{14}H_{28}N_2O_4)$; and a few years later, crystals of $Cp_3U\mathit{n}\cdot BuLi$ [221] were obtained (*419*). They are monoclinic, space group $p2_1/n$, $Z = 4$, with $a = 887.3$, $b = 2659.4$, and $c = 1417.5$ pm, $\beta = 93.01°$.

The lithium salt of $Cp_3UCH_3{}^-$ has been reported to catalyze the reduction of N_2 by sodium naphthalenide (*420*).

It is also possible to make these compounds by the reaction of LiR with Cp_3UTHF (*421*). Spin saturation transfer experiments suggest the equilibrium:

$$Cp_2UR + LiCp \rightleftharpoons Cp_3URLi \rightleftharpoons Cp_3U + LiR$$

where

$$R = CH_3,\ n\text{-}C_4H_9,\ \text{or}\ C_5H_{11}.$$

It may be noted that LiCp does not react with UCp_3THF to give a UCp_4^- derivative.

These anionic species are more reactive and the R ligand more labile than in the Cp_3UR compounds.

$LiCp_3UCH_3$ does not react with 1-pentene, but with hydrogen it gives methane and Cp_3U. Deuterium gives CH_3D. $LiCp_3Un\text{-}C_4H_9$, which can undergo a β elimination reaction, reacts with 1-pentene to give $LiCp_3UC_5H_{11}$ (*421*). Cp_3URLi reacts with hydrogen in the presence of a terminal olefin (R'[—H]) to give $Cp_3UR'Li$ (*422*). The authors suggest:

$$Cp_3UnBuLi \xrightarrow[+LiCp]{-LiCp} Cp_2UnBu \xrightarrow[+C_4H_8]{-C_4H_8} Cp_2UH \xrightarrow[-C_5H_{10}]{+C_5H_{10}} Cp_2UC_5H_{11} \xrightarrow[LiCp]{+LiCp} Cp_3UC_5H_{11}Li$$

but no more direct evidence for the hydrido species was obtained.

The THF in Cp_3UTHF can be displaced by diphenyl acetylene, the first adduct of this kind (*422, 423*). The product reacts readily with LiR to give $LiCp_3UR$.

Anionic derivatives have already been described for the substituted cyclopentadienyls (see Sections V,A,3,b,i and ii).

$Cp_2^*UCl_2$ undergoes reversible 1-electron reduction during cyclic voltametry in acetonitrile or THF. The $E_{1/2}$ are -1.30 and -1.22 V, respectively, measured against a standard calomel electrode (*424*).

b. Cyclooctatetraene Derivatives. An early attempt at a synthesis of $U(COT)_2^-$ by the reaction of UI_3 or UBr_3 with K_2COT was unsuccessful; only the U(IV) compound was obtained (*425*). Nor could the U(III) compound be obtained by reduction of $U(COT)_2$ by Na/Hg or sodium naphthalenide. Both reactions led to metallic uranium.

However, subsequent attempts at reducing $U(COT)_2$, in solution in THF, by slowly adding lithium naphthalenide, have been successful. The progress of the reaction can be monitored in solution by UV/vis absorbtion spectroscopy or by ^1H NMR. The reduction is complete when the stoichiometric amount of the lithium naphthalenide has been added. The compound can also be prepared by the reaction of UCl_3THF with K_2COT (*426*).

The reducing properties of the $U(COT)_2^-$ can be seen in the reactions with $Ti(Oi\text{-}C_3H_7)_4$ and Cp_3UCl, which produce $U(COT)_2$ and Ti(III) or U(III) compounds.

The reduction of bis(bicyclooctatetraenyl)diuranium (= biuranocenylene (*427*) by potassium in THF has been investigated using ^{1}H NMR. The results for the partly reduced system suggest a fast electron exchange, on the NMR time scale, between the remaining biuranocenylene and the reduction product. The reduced product appears to be a mixed valence compound with one U(IV) and one U(III) atom in the molecule (*428*).

5. Other Ligands

a. Benzene and Its Derivatives. By refluxing UCl_4, $AlCl_3$, aluminium powder, and benzene for a long time and concentrating the liquid

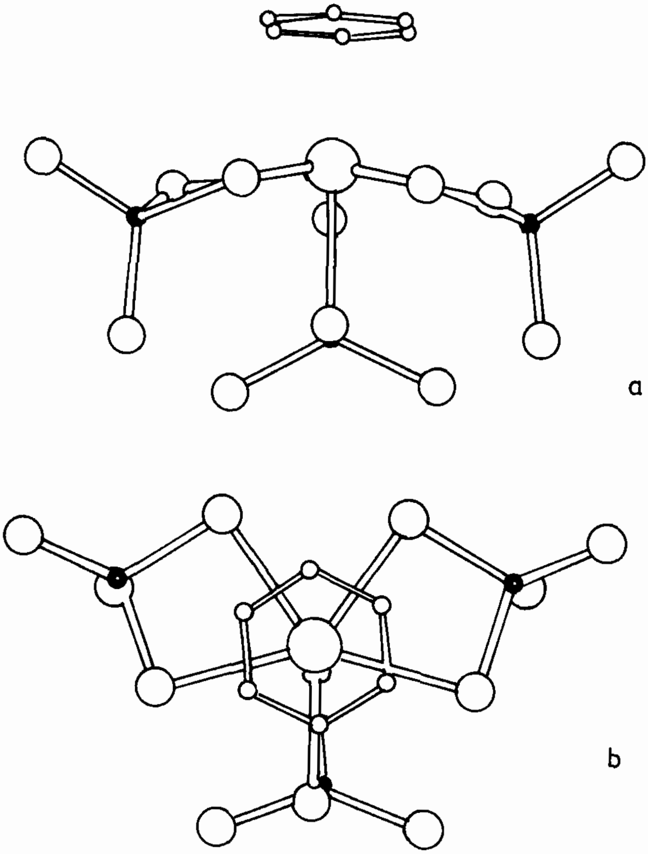


FIG. 16. Structure of $UC_6H_6(AlCl_4)_3$ (*429*).

phase, researchers have obtained the complex $U(C_6H_6)(AlCl_4)_3$ (*429*). The crystals are triclinic, space group $P\bar{1}$, $Z = 2$, with $a = 947$, $b = 1081$, and $c = 1679$ pm, $\alpha = 98.7°$, $\beta = 86.5°$, $\gamma = 122.9°$. The stereochemistry is shown in Fig. 16.

Two other arene derivatives of U(III) have recently been made. Under reducing Friedel–Crafts conditions, a similar mixture to that used to prepare the previous compound but with hexamethylbenzene instead of benzene, a trinuclear complex $[U_3(\mu^3Cl)_2(\mu^2Cl)_3(\mu^1\eta^2\text{-}AlCl_4)_3(\eta^6C_6(CH_3)_6)_3][AlCl_4]$ was obtained. It forms red-brown crystals, soluble in acetonitrile (*430*). The stereochemistry is shown in Fig. 17. With a large excess of $AlCl_3$, a similar preparation gave $U(\eta^6C_6(CH_3)_6)(AlCl_4)_3$, analogous to the benzene compound. A similar samarium compound was also prepared (*431*). The maroon-colored crystals of the uranium compound are triclinic, space group $P\bar{1}$, with $Z = 2$, $a = 981.6$, $b = 1791.8$, and $c = 973.0$ pm, and $\alpha = 96.09°$, $\beta =$

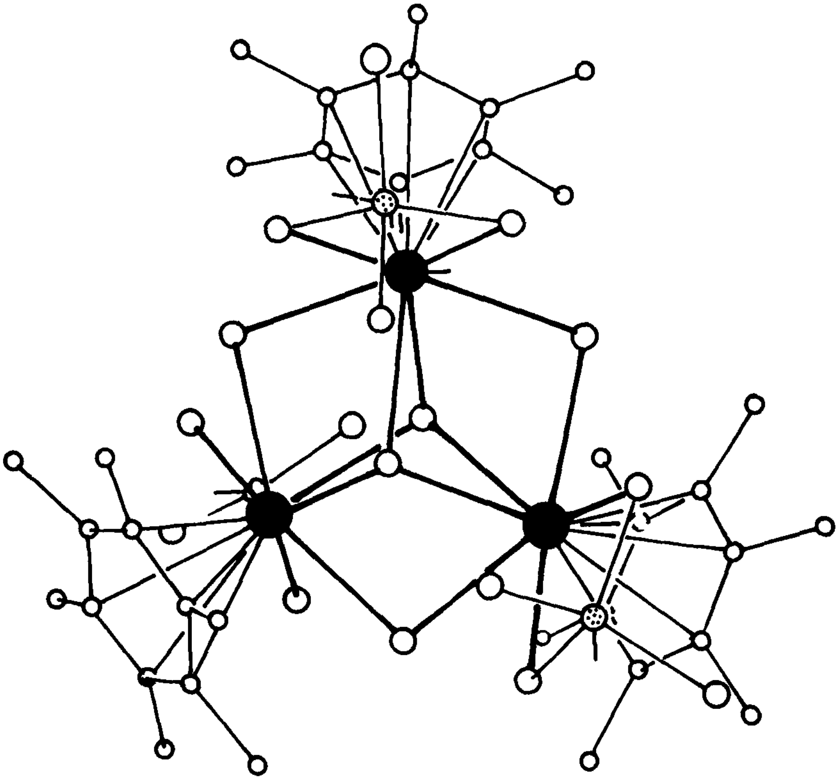


FIG. 17. Structure of $U_3Cl_5(AlCl_4)_3[C_6(CH_3)_6]_3^+$ (*430*).

118.91°, $\gamma = 80.98°$. The stereochemistry of the molecule is like that of the benzene compound. Comparing the metal–ligand bond lengths in the samarium and uranium compounds suggested that $5f$ orbitals are not substantially involved in the bonding of the arene.

The uranium is hapto coordinated to the benzene and joined by two chlorine bridges to each $AlCl_4$ unit. The coordination environment of the uranium is approximately a pentagonal bipyramid, considering the benzene to occupy only one site. The compound decomposes in polar solvents.

b. 2,4-Dimethylpentadiene. By reacting UCl_3THF with potassium 2,4-dimethylpentadienyl, one can obtain a red-brown pyrophoric solid. The compound, $U(\eta^5C_7H_{11})_3$, is not very soluble in nonreacting solvents, but it was possible to characterize it by ^1H NMR using a solution in C_6D_6. It is decomposed by dichloromethane. Unlike UCp_3 it does not readily form adducts (*432*). An analogous compound of neodymium has been made (*433*).

B. THORIUM(III) ORGANOMETALLICS

$ThCp_3$ was first prepared by the reduction of $ThCp_3Cl$ with sodium naphthalenide in THF solution (*434*). The violet-red complex, like the uranium analog, is a Lewis acid and forms 1:1 adducts with donors such as THF and cyclohexylisonitrile (*434*). The magnetic moment of this complex was found to be very low at room temperature, $\mu_{eff} = 0.403\ \mu_B$. This $ThCp_3$ was reported to react with ammonium chloride to give the brown $ThCp_2Cl$, but few details of this last compound have appeared (*435*). The powder diffraction pattern of this compound was similar to that found for other MCp_3.

An apparently different form of $ThCp_3$ is obtained by the photolysis of a solution of $ThCp_3i\text{-}C_3H_7$ in benzene at 278 K. This compound is a dark green solid. The Cp* and Cp′ compounds can be made in a similar manner. The low solubility of this form of $ThCp_3$ in common solvents has prevented its examination by ^1H NMR, and it has been characterized by elemental analysis, IR, Raman, UV/Vis, and mass spectroscopies.

The magnetic moment of this form of $ThCp_3$ was first reported as 2.10 BM at room temperature, a much larger value than that found for the violet compound (*436*), but a revised value of 0.40 BM has since appeared (*369*). This value is not very different from that of the violet compound. The moment is strongly temperature dependent, falling to

0.1 μ_B at 4 K. The green compound did not react with ammonium chloride (*369*).

The mechanism of the photolysis of the actinide hydrocarbyls has been investigated in some detail using isotopically labeled compounds. $Th(C_5E_5)_3R$, with E = H or D and R = CH_3, i-C_3H_7, and n-C_4H_9; $Th(C_5H_4CH_3)_3n$-C_4H_9; Th(indenyl)$_3n$-C_4H_9; and $U(C_5E_5)_3R$ with E = H or D, and R = CH_3, i-C_3H_7, n-C_4H_9, or s-C_4H_9 have been studied (*367–369*).

For the thorium cyclopentadienyls with R = CH_3, photolysis in aromatic solvents produces 1 : 1 mixtures of alkene and alkanes and the trivalent thorium complex $Th(C_5E_5)_3$. It was proposed that the reaction takes place by a photoinduced beta-elimination to give a hydrido complex and olefin followed by a bimolecular reductive elimination of the alkane. Schematically it can be represented by the following equations:

$$Th(C_5E_5)_3CHRCH_2R' \xrightarrow{h\nu} Th(C_5E_5)_3H + RCH = CHR'$$

$$Th(C_5E_5)_3H + Th(C_5E_5)_3CHRCH_2R' \longrightarrow Th(C_5E_5)_3 + CH_2RCH_2R'$$

This mechanism can be contrasted with that proposed for the photolysis and thermal decomposition of the uranium compounds. In their case, spin trapping and other data support a free radical homolytic scission mechanism [(*367–369*); see also (*437*)]. Possibly both mechanisms are operative with uranium compounds.

In the case of the thorium indenyl compound, photolysis produces Th(indenyl)$_3$ and the alkane, the added hydrogen being derived from the indenyl ligand. This new compound of Th(III) is orange-red and soluble in hydrocarbons.

One other piece of evidence bears on the difference between the two $ThCp_3$ compounds. The green compound releases a half a molecule of hydrogen per thorium atom when treated with methyl alcohol (*369*), whereas the violet compound is reported to yield only $\frac{1}{4}$ of a molecule of hydrogen per thorium atom (*355*). On this evidence it has been suggested that the violet compound should be

$$\eta^5Cp_3Th(\mu\eta^1\eta^5C_5H_4)Th\ \eta^5Cp_2$$

[See (*355*), p. 243]. The green compound is oxidized by iodine and chloroform to give $ThCp_3X$, X = I and Cl, respectively. Prolonged refluxing with ammonium chloride in THF gave a small amount of $ThCp_3O$-n-C_4H_9 arising from ring opening. A similar reaction has been found with the uranium compound.

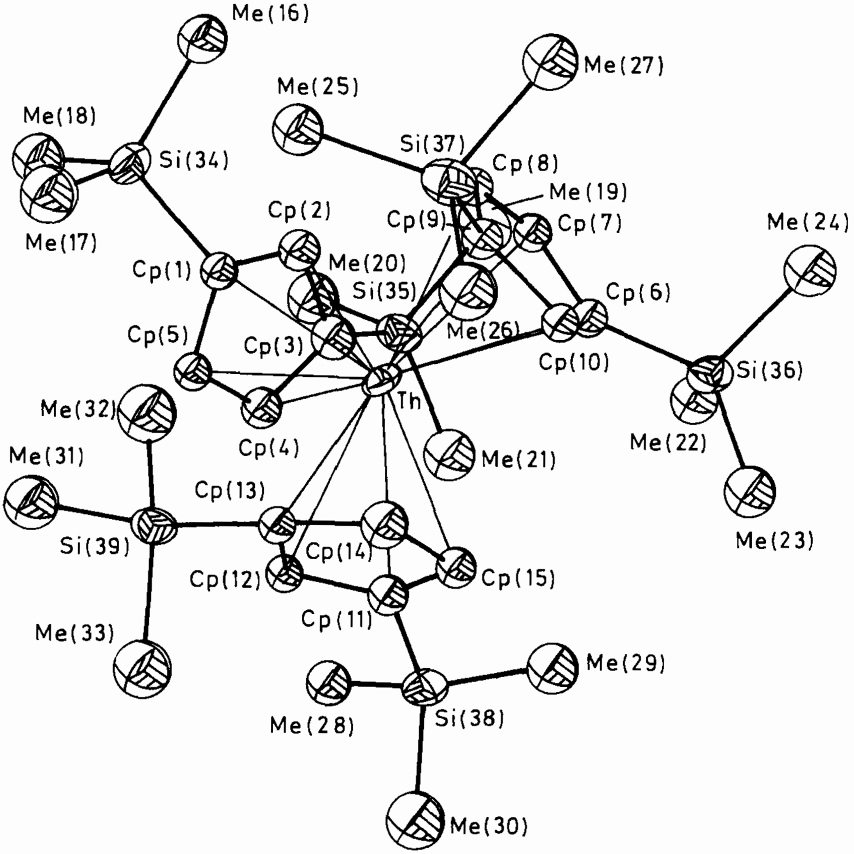


FIG. 18. STRUCTURE OF THCp$_3''$ (*438*).

Reduction of ThCp$_2''$Cl$_2$ by Na/K alloy in toluene gives the blue, hydrocarbon soluble, ThCp$_3''$, possibly formed by ThCp$_2''$. The crystals are monoclinic, space group p2$_1$/c., $Z = 4$, with $a = 1800.6$, $b = 1378.3$, and $c = 1935.9$ pm, $\beta = 112.83°$. The coordination environment of the thorium can be described as trigonal planar (*438*). The structure is shown in Fig. 18.

Attempts to reduce thorocene(IV) chloride by Na/K in toluene fail, even after prolonged reflux.

The ThCp$_3''$ reacts with C$_4$H$_9$Cl in pentane to yield the thorium(IV) compound ThCp$_3''$Cl.

It has been observed that for corresponding Th(IV) and U(IV) compounds, the difference in energies for the metal-to-ligand bonds amounts to about 40 kJ. There is as yet insufficient evidence to decide if a similar difference is to be found for the Th(III) and U(III) pairs (*439*).

VI. Conclusion

Although new information has accumulated on this aspect of the chemistry of the earlier actinide elements, there still are many uncertainties that ought to be resolved. The area is intrinsically interesting because these elements have chemistries that combine lanthanide and ordinary transition metal characteristics, the latter being more marked in these low oxidation states. Work in the next few years will probably lead to a much clearer picture.

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