

THE COORDINATION CHEMISTRY OF THE ACTINIDE HALIDES

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(Received March 28th, 1967)

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A. INTRODUCTION

Although comprehensive reviews of the chemistry of the actinide halides are available^{1,2} and much detailed information about the halides has been given by Katz and Seaborg³, there has been only one review dealing specifically with the coordination chemistry of the actinides as a group⁴. The present review includes the stereochemistry of the halides themselves but, as will be seen, structural data are lacking for almost every donor complex recorded here.

B. GENERAL SURVEY

The earlier members of the actinide group, up to americium, exhibit a greater variety of valence states (Table 1) than the higher actinides, which appear to be predominantly lanthanide in character, but very little is known about the complexing properties of any of the trivalent actinides.

TABLE 1

OXIDATION STATES^a OF ELEMENTS 89-95

Element Atomic No.	Ac 89	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cationic species in aqueous solution
	3			3	3	3	3	M ³⁺
		4	4	4	4	4	4	M ⁴⁺
			5	5	5	5	5	MO ₂ ⁺ (except Pa)
				6	6	6	6	MO ₂ ⁺⁺

^a The most stable oxidation state in aqueous solution is italicised.

Unlike the lanthanides, in which the 4f electrons are not accessible for bonding, the 5f orbitals of the actinides extend spatially into the outer, valence regions of the atom; they are less effectively shielded by the outer electrons, and have relatively lower binding energies, than is the case with the 4f orbitals. Because of these factors, and in marked contrast to the lanthanides, the actinides form a wide variety of complex species in which hybridization must involve the normally unoccupied higher energy orbitals (6d, 7s, 7p) and this can be expected only with the more strongly coordinating ligands. Thus stable complexes, other than the hydrated cations in solution, are formed most commonly with ligands which contain highly electronegative donor atoms, such as oxygen. Although f orbitals are obviously not as important as d orbitals in bonding, the contribution of the former to bonding cannot be neglected. For example, the stability of the oxygenated ions MO₂⁺ and MO₂⁺⁺ is attributed to f orbital participation⁵.

Although there is still some doubt about the electronic configuration of the lighter actinides, largely because the 6d and 5f electron-binding energies are very

similar even at uranium, magnetic studies of uranium trichloride in lanthanum chloride are consistent with a $5f^3$ configuration⁶ and similar studies of the higher actinides accord with a $5f^n$ configuration⁷.

The actinide cations, whatever the oxidation state, are, like the lanthanide cations, large compared with d-transition element cations and are therefore appreciably more basic in character. Since the actinide cations decrease in size with increasing atomic number—the actinide contraction—the electrostatic attraction between actinide ions and ligands will increase in magnitude for a given oxidation state as the cation radius decreases, and for a given element as the cation charge increases. Thus in the trivalent state, halide complexing of the earlier members of the group in aqueous solution is relatively weak, although there is evidence for the chlorocomplex species MCl^{2+} and $MCl_2^{+8,9}$, and it is evident that halide ions will only displace the hydration water from actinide(III) ions in very concentrated halide solutions. Americium(III) forms anionic chlorocomplexes in aqueous solution⁹ and salts of these can be obtained with little difficulty at high chloride concentrations¹⁰. Bromide ion complexes the terpositive actinides more weakly than chloride ion, and the general complexing behaviour of the actinides in all valence states indicates that they are Chatt-Ahrland A-class elements.

The shapes of the f orbitals, unlike those of the s, p and d orbitals, are not commonly depicted in the standard textbooks, but they have been described in the literature^{11,12}; their transformation properties under the operations of the common symmetry groups have also been tabulated¹³.

All of the actinides are radioactive and are therefore extremely toxic; because of this, work with all of these elements, excepting natural thorium and uranium, must be carried out in glove-boxes and, since the quantities available of the transcurium elements are very small, work with them is restricted to microscale studies. The techniques used for such work have been described in the reviews of the chemistry of the actinides^{1,3}.

C. THE TERVALENT ACTINIDES

(i) *Trihalides*. The anhydrous trifluorides (Ac, U-Cm) have the hexagonal LaF_3 structure^{1,14} in which the metal ion lies on a two-fold axis and has 9 nearly equidistant neighbours¹⁵. The trichlorides (Ac, U-Cm, Cf) are also of hexagonal symmetry^{1,14,16}, but in this UCl_3 structure type 9 coordination is achieved in the form of a trigonal prism with three chlorine atoms situated above the centres of the three tetragonal faces¹⁷. $AcBr_3$, UBr_3 and $\alpha-NpBr_3$ also have this structure¹, but $\beta-NpBr_3$, $PuBr_3$, $AmBr_3$, and $CmBr_3$ have the orthorhombic $PuBr_3$ structure in which the metal ion is 8-coordinate, the coordination arrangement being the same as in the UCl_3 structure but with only two of the bromine atoms situated above tetragonal faces of the prism¹⁷. The change in structure is due to

the decrease in radius of the M^{3+} ions with increasing atomic number and a similar structure change occurs with the triiodides. UI_3 , NpI_3 and PuI_3 ^{1,18} have the orthorhombic $PuBr_3$ structure, whereas AmI_3 and CmI_3 are of hexagonal symmetry¹⁴ and the coordination arrangement is uncertain. Thorium triiodide is not isomorphous with UI_3 and is probably more correctly formulated as $Th^{4+}(e^-)(I^-)_3$; both forms of thorium diiodide may also be of this type¹⁹.

(ii) *Oxyhalides*. Apart from $AcOF$, which appears to have the 8-coordinate cubic fluorite structure²⁰, all other known oxyhalides have the tetragonal $PbFCl$ structure²⁰⁻²⁴, a layer structure in which the metal is also 8-coordinate. The only known imidochloride, $U(NH)Cl$, also possesses this structure²⁵.

(iii) *Complexes*. Fluorocomplexes of the type $NaMF_4$ ($M = Pu, Am$) have been made by solid state reactions; they are²⁶ of hexagonal symmetry but although they are said to have the β_2 - Na_2ThF_6 structure, the $NaNbF_4$ structure seems more likely²⁷; in both structures the environment of the 9-coordinate metal ion^{17,27} is similar to that of the metal ion in the UCl_3 structure type. Studies of fused salt systems have produced evidence for species such as $PuCl_5^{2-}$ ^{28,29}, $PuCl_9^{6-}$ ³⁰, $PuCl_6^{3-}$ ^{28,29} and $Pu_2Cl_7^{2-}$ ²⁹, but only the hexachlorocomplex, $Cs_3PuCl_6 \cdot 2H_2O$, has been isolated from aqueous solution³¹; no structural data are available for any of these species. The $AmCl_6^{3-}$ ion is known from spectral studies to be of octahedral symmetry³² and it is probable that the anion in $Cs_2NaAmCl_6$, obtained from aqueous solution, is also octahedral; the anion in $CsAmCl_4 \cdot 2H_2O$ is probably not octahedral, the crystal apparently containing lattice water which is not coordinated to the metal in the anion. The $Am-Cl$ stretching vibrations appear at 240 cm^{-1} and 214 cm^{-1} respectively in $Cs_2NaAmCl_6$ and Cs_3AmCl_6 ¹⁰, the latter isolated from ethanol solution. To date there is no evidence for the existence of any similar bromo- and iodo-complexes; the only other recorded complex is $UBr_3 \cdot 6NH_3$, the structure of which is unknown³³.

D. THE TETRAVALENT ACTINIDES

(i) *Tetrahalides*. The tetrafluorides ($Th-Cm$) are all of monoclinic symmetry, the UF_4 structure consisting of 8 fluorine atoms arranged around the metal atom in a slightly distorted antiprism³⁴, whereas the tetrachlorides ($Th-Np$), in which the metal is still 8-coordinate, are of tetragonal symmetry with, in the case of uranium, each metal atom having the four nearest (2.41 \AA) halogen atoms at the apices of an almost flat tetrahedron (or at the corners of a distorted square) and four more distant chlorine atoms at 3.09 \AA ³⁵. Thorium tetrabromide is dimorphic and the high temperature form, with which protactinium tetrabromide is isomorphous³⁶, may be isostructural with uranium tetrachloride³⁷. Thorium tetraiodide

is of monoclinic symmetry and has a layer structure in which the metal is surrounded by 8 iodine atoms in a deformed square antiprism³⁸. X-ray powder data are available for the other tetrabromides and tetraiodides, but their stereochemistry is unknown. Some infrared data are given in Table 2.

(ii) *Oxyhalides*. The infrared spectra of all the known oxodihalides, MOX_2 , indicate that they are oxygen bridged polymers²; one of them, ThOF_2 , was thought to have the LaF_3 structure²³ but subsequent work indicates that the compound is a fluorite type mixed crystal containing randomly distributed oxygen and fluorine atoms³⁹.

(iii) *Halocomplexes*. A wide variety of fluorocomplexes have been recorded; genuine compounds of the type LiMF_5 ($\text{M} = \text{Th}-\text{Cm}$) are of tetragonal symmetry but where the radius ratio A^+/M^{4+} lies between 0.99 and 1.59, compounds reported to be of this type but of rhombohedral symmetry actually have the composition $7 A^+F \cdot 6 MF_4$ ($\text{Th}-\text{Cm}$); however, where the radius ratio A^+/M^{4+} lies between 1.59 and 1.68, both types of compound can exist⁴⁰. The coordination polyhedron around the actinide ion in the 7:6 complexes will be as that in the zirconium compound, $\text{Na}_7\text{Zr}_6\text{F}_{31}$, with which the actinide compounds are isostructural; this is an 8-coordinate array, six M^{4+} ions being arranged in a polyhedron which contains the "extra" fluorine atom⁴¹.

The U^{4+} ion in LiUF_5 has a 9-coordinate environment similar to that found for UCl_3 ⁴² and a similar 9-coordinate array has been reported for U_2F_9 ⁴³, for complexes of the type $A^+M_2F_9$ (Th , U - Pu)^{17,44} and for the hexafluorocomplexes of the β_2 - Na_2ThF_6 and β_1 - K_2UF_6 structure types¹⁷, whereas compounds such as BaMF_6 (Th , U) have a disordered LaF_3 structure²³. The U^{4+} ion in α - K_2UF_6 and γ - Na_2UF_6 is 8-coordinate, the former being a disordered²³ and the latter a slightly deformed¹⁷ fluorite structure. In both Na_3UF_7 ¹⁷ and K_3UF_7 (which is dimorphic⁴⁵) the metal is 7-coordinate, at the centre of a pentagonal bipyramid. Octafluorocomplexes, $A^+M_2F_8$ (Pa ⁴⁶, U - Pu ^{47,48}, Am ⁴⁹) exist but the structure of the anion is not known.

Halogens of higher atomic number do not appear to give rise to such a variety of complexes as does fluorine, the common type being $A^+_2MX_6$ (Th - Pu ,

TABLE 2

METAL-HALOGEN STRETCHING FREQUENCIES IN COMPLEXES OF THE TYPE $A^+_2MX_6$

	cm^{-1}	Reference		cm^{-1}	References
Th-Cl	251-258	55	Th-Br	177-179	55
Pa-Cl	257-266	103	Pa-Br	180-182	103
U-Cl	253-259	55	U-Br	178-181	55
Np-Cl	265-267	55, 56			

X = Cl, Br; Th-U, X = I). X-ray crystallography has shown that the anion is of octahedral symmetry in the chlorocomplexes⁵⁰, a result confirmed by spectroscopic⁵¹ and magnetic susceptibility⁵² studies. Similar studies^{51, 53, 54} indicate that the anion retains this symmetry in the hexabromo- and hexaiodo-complexes. The mixed halocomplex ion, $\text{UCl}_4\text{Br}_2^{2-}$, has the *trans* octahedral configuration⁵⁴. Some infrared data are given in Table 2.

A number of other thorium chlorocomplexes have been reported, including hydrated and anhydrous A^+ThCl_5 ⁵⁷, hydrated KTh_2Cl_9 ⁵⁸ and anhydrous A^+ThCl_8 ⁵⁹. These systems have not been investigated since the compounds were first prepared and they are clearly worth further study.

(iv) *Oxygen donor complexes.* The only known adducts of the tetrafluorides are the hydrates, such as $\text{MF}_4 \cdot 2.5 \text{H}_2\text{O}$ (Th^{60, 61}, U⁶², Pu⁶³) and the hydrate systems of the other tetrahalides appear to be more complicated (*e.g.* $\text{UCl}_4 \cdot 4.5\text{--}9 \text{H}_2\text{O}$ ⁶⁴). 1:2 and 1:4 complexes of the actinide tetrahalides with monodentate ligands are quite common, but their stereochemistry, and the coordination number of the M^{4+} ion, as with the hydrates, are often unknown. Some infrared data are given in Table 3.

The 1:2 complexes $\text{ThCl}_4 \cdot 2 \text{L}$ (L = ethanol⁶⁵, acetaldehyde⁶⁶, cinnamaldehyde⁶⁷, $\text{UCl}_4 \cdot 2 \text{L}$ (L = tri-*n*-butylphosphate⁶⁸), $\text{ThBr}_4 \cdot 2 \text{L}$ (L = ethylace-

TABLE 3

METAL-HALOGEN STRETCHING FREQUENCIES AND LIGAND SHIFTS IN SOME COMPLEXES OF THE TETRAHALIDES

Compound	M-Cl (cm^{-1})	Ligand shift (cm^{-1})	References
ThCl_4^a	245	—	55
UCl_4	254	—	55
$\text{ThCl}_4 \cdot 4 \text{DMA}$	—	$\Delta\nu(\text{C}=\text{O})$ 44	75
$2 \text{UCl}_4 \cdot 5 \text{DMA}$	245, 259	$\Delta\nu(\text{C}=\text{O})$ 29	80, 89
$(\text{U}_2\text{Cl}_7 \cdot 5 \text{DMA})_2$	254	$\Delta\nu(\text{C}=\text{O})$ 54	80
$\text{ThCl}_4 \cdot 4 \text{MeCN}$	256	$\Delta\nu(\text{C}=\text{N})$ 24	55, 79
$\text{PaCl}_4 \cdot 4 \text{MeCN}$	—	$\Delta\nu(\text{C}=\text{N})$ 26	36
$\text{UCl}_4 \cdot 4 \text{MeCN}$	262	$\Delta\nu(\text{C}=\text{N})$ 29	55, 79
$\text{UCl}_4 \cdot 2 \text{Ph}_3\text{PO}$	267	$\Delta\nu(\text{P}=\text{O})$ —	54
Compound	M-Br (cm^{-1})	Ligand shift (cm^{-1})	References
$\text{ThBr}_4 \cdot 4 \text{DMA}$	176	$\Delta\nu(\text{C}=\text{O})$ 34	79
$\text{UBr}_4 \cdot 4 \text{DMA}$	180	$\Delta\nu(\text{C}=\text{O})$ 34	79
$\text{ThBr}_4 \cdot 4 \text{MeCN}$	188	$\Delta\nu(\text{C}=\text{N})$ 24	55, 79
$\text{PaBr}_4 \cdot 4 \text{MeCN}$	—	$\Delta\nu(\text{C}=\text{N})$ 25	36
$\text{UBr}_4 \cdot 4 \text{MeCN}$	193	$\Delta\nu(\text{C}=\text{N})$ 27	55, 79

^a The M-F stretching frequency appears at 520 cm^{-1} in the case of gaseous ThF_4 ¹¹⁶ and at 400 cm^{-1} in the case of solid PaF_4 ¹¹⁷. DMA = *N,N*-dimethylacetamide.

tate⁶⁹), and $\text{MX}_4 \cdot 2 \text{L}$ ($\text{M} = \text{Th}, \text{U}^{70}, \text{Pa}^{36}$; $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{hexamethylphosphoramide}$) may be *trans*-octahedral like the phosphine oxide complexes, $\text{UX}_4 \cdot 2 \text{R}_3\text{PO}$ ($\text{X} = \text{Cl}^{54,72}, \text{Br}^{54}$).

Thorium tetrachloride forms 1:4 complexes with cinnamaldehyde⁷³, acetophenone, benzophenone⁷⁴, *N,N*-dimethylacetamide (DMA)⁷⁵, *N,N*-dimethylformamide (DMF)⁷⁶ and aliphatic alcohols⁶⁵. Uranium tetrachloride also forms 1:4 complexes with alcohols⁷⁷, *N*-methylacetamide⁷⁵ and with phosphorus oxytrichloride⁷⁸. Both thorium tetrabromide and uranium tetrabromide form 1:4 complexes with DMA⁷⁹, as does uranium tetraiodide⁸⁰, which also forms a similar complex with DMF⁸¹, and thorium tetrabromide forms 1:4 complexes with ethanol and with benzaldehyde⁶⁹.

A number of 1:3 complexes of the tetrahalides have been recorded and in all cases the coordination number of the metal atom is uncertain. Thorium and uranium tetrachlorides form such complexes with tetrahydrofuran⁸² and dioxan^{83,84}, whilst uranium tetrachloride also forms 1:3 complexes with tri-*n*-butylphosphate⁸⁵, trimethyl phosphine oxide⁸⁶, acetone⁸⁴, diphenylsulphoxide⁸⁷ and dimethylsulphoxide^{70,224}. Although the last is monomeric in methyl cyanide, it is possible that the uranium atom is 8-coordinate in a chlorine bridged dimeric structure in the solid state; similarly, $\text{ThCl}_4 \cdot 5 \text{DMSO}$ may involve 10-coordinate thorium⁷⁰. The $\text{S}=\text{O}$ shifts in the infrared spectra of the DMSO complexes are between 102 and 112 cm^{-1} ⁷⁰. A plutonium tetrachloride complex with DMSO, $\text{PuCl}_4 \cdot 3 \text{DMSO}$, has also been reported²²⁴. Thorium tetrabromide forms 1:3 complexes with ethyl benzoate⁶⁹ and with hexamethylphosphoramide, the latter being monomeric in benzene but a 1:1 electrolyte in nitromethane⁷⁰. The $\text{P}=\text{O}$ shift in the infrared spectrum of $\text{ThBr}_4 \cdot 3 \text{HMPA}$ is only 130 cm^{-1} , as compared with shifts of 159–174 cm^{-1} in the 1:2 complexes⁷⁰.

Uranium tetrachloride has been reported to form the complex $\text{UCl}_4 \cdot 3 \text{DMF}^{81}$ but other work⁸⁸ indicates that the complex has the stoichiometry $2 \text{UCl}_4 \cdot 5 \text{DMF}$, the same as that found⁸⁹ for the DMA complexes, $2 \text{MCl}_4 \cdot 5 \text{DMA}$ ($\text{U}, \text{Np}, \text{Pu}$); the structure probably involves the 8-coordinate metal atom with one ligand and two chlorine bridges⁹⁰.

Thorium tetrabromide forms a complex of unusual stoichiometry with acetophenone⁶⁹, $2 \text{ThBr}_4 \cdot 7 \text{L}$, and 1:6 complexes of the tetrahalides with acetamide⁸⁹, $\text{MCl}_4 \cdot 6 \text{L}$ ($\text{U}, \text{Np}, \text{Pu}$), dimethylsulphoxide⁷⁰, $\text{MBr}_4 \cdot 6 \text{L}$ (Th, U) and *N,N*-dimethylacetamide⁸⁰, $\text{ThI}_4 \cdot 6 \text{DMA}$, are also known.

Complexes with bidentate oxygen donors include the apparently simple 1:1 complexes of uranium tetrachloride with methylene and ethylene bis-(diphenylphosphine) oxides⁸⁶ and *N,N,N',N'*-tetramethyl- α,α -dimethylmalonamide (HMMA)⁹⁰, the 2:3 complexes of thorium and uranium tetrachloride with the corresponding glutaramides, thorium tetrachloride with HMMA and uranium tetrachloride with *N,N,N',N'*-tetramethylmalonamide, which forms a 1:2 complex with thorium tetrachloride. Most of these complexes are probably ligand bridged poly-

mers⁹⁰. A 1:2 complex of uranium tetrachloride with 1,2 dimethoxyethane is also known⁹¹.

(v) *Nitrogen donor complexes.* 1:4 primary amine complexes of thorium tetrachloride⁹², thorium tetrabromide^{69,93} and uranium tetrachloride⁹⁴, and 1:4 complexes of uranium tetrachloride with ammonia^{87,95}, piperidine⁸⁷ and, somewhat surprisingly, with ethylenediamine⁸⁷ are also known; the structure of the ethylenediamine complex is well worth investigation. Uranium tetrachloride forms a 1:6 adduct with hydrazine⁹⁴ and thorium tetrachloride is said to form a hexamine⁹², but the thorium tetrabromide-ammonia system is less well defined, amines in the composition range $\text{ThBr}_4 \cdot 8\text{--}20 \text{NH}_3$ being reported. Uranium tetrachloride is also reported to form 1:2 complexes with ammonia and primary amines⁹⁴ and a 1:2 *o*-phenanthroline complex with thorium tetrachloride is known⁸⁸.

Pyridine forms the complexes $\text{ThBr}_4 \cdot 3 \text{py}$ ⁶⁹ and $\text{UCl}_4 \cdot 2 \text{py}$ ⁸⁷, and 1:3 stoichiometry had been reported for the thorium tetrachloride-toluidine complex⁹². 1:1 complexes of thorium tetrachloride with α -picoline⁹⁷ and of uranium tetrachloride with primary amines⁹⁴ are also known.

Methyl cyanide complexes of the tetrahalides are nearly all of 1:4 stoichiometry (ThCl_4 ^{79,83}; PaCl_4 ⁷¹; UCl_4 ⁷⁹; ThBr_4 ^{69,79}; PaBr_4 ⁷¹; UBr_4 ⁷⁹; ThI_4 ⁵³), as is the benzyl cyanide complex, $\text{ThCl}_4 \cdot 4 \text{PhCN}$ ⁸³, although the 1:2 complexes $\text{ThCl}_4 \cdot 2 \text{PhCN}$ ⁹⁸ and $\text{UCl}_4 \cdot 2 \text{MeCN}$ ⁸⁴ have also been recorded. The metal ions are presumably 8-coordinate in the complexes of 1:4 stoichiometry, but molecular weight and conductivity data are not available, in many cases because the compounds are not appreciably soluble in any suitable solvent.

No complexes of the actinide tetrahalides with monodentate phosphines are known, the complexes supposed to be of this type being phosphine oxide adducts⁹⁹, but a 1:1 adduct of uranium tetrachloride with tetra-*P*-methylenediphosphine⁹¹ is probably a genuine complex.

(vi) *Sulphur donor complexes.* There is little evidence for the existence of complexes with monodentate sulphur donors, thioacetamide⁸⁹ and phosphine sulphides⁸⁶ failing to form complexes with uranium tetrachloride. The only known complex seems to be that with 1,2 dimethylthioethane, $\text{UCl}_4 \cdot 2 \text{L}$, in which the uranium is thought to be 8-coordinate⁹¹.

(vii) *Cyclopentadienylhalides.* Tris(cyclopentadienyl)chlorides of thorium and uranium are known^{100,101}, the structure of the uranium compound being an approximately tetrahedral arrangement of the three cyclopentadiene rings and the chlorine atom about the central uranium atom¹⁰².

E. THE PENTAVALENT ACTINIDES

(i) *Pentahalides*. Simple compounds are known only for protactinium and uranium; protactinium pentafluoride¹⁰⁴ is isostructural with the low temperature (β) form of uranium pentafluoride, in which the uranium atom is thought to be 7-coordinate in a pentagonal bipyramidal arrangement in which vertices are shared at four positions in the pentagon¹⁰⁵; a somewhat similar 7-coordinate arrangement has been established for protactinium pentachloride¹⁰⁶. The structure of α -UF₅, the high temperature form, consists of an infinite chain of octahedra linked by opposite corners¹⁰⁵, whereas in UCl₅ edges of the octahedron are shared to form a dimeric unit¹⁰⁷. No structural data are available for PaBr₅⁷¹, PaI₅¹⁰⁸ or UBr₅^{109,110}, the only other known actinide pentahalides; intermediate fluorides of the type U₂F₉ and U₄F₁₇ have distorted UF₄ structures and uranium in the former is 9-coordinate⁴³.

(ii) *Oxyhalides*. Compounds of the type M₂OX₈ (M, X: Pa, F¹¹¹; U, F¹¹²; Pa, Cl), are dimorphic¹¹³ and well established, and although there is some evidence for the existence of UOF₃¹¹⁴ and PaOCl₃¹¹³, the only compounds of the type MOX₃ which are known with any certainty are UOCl₃^{115,116}, which also forms a 1:1 adduct with ethanol¹¹⁷, PaOBr₃⁷¹, UOBr₃^{110,118,119}, PaOI₃¹⁰⁸ and NpOF₃ · x H₂O¹²⁰. Structural data are available only for PaOBr₃, in which protactinium is 7-coordinate in a pentagonal bipyramidal arrangement¹²¹.

A few dioxahalides are also known; NpO₂F¹²⁰, PaO₂Cl¹¹³, PaO₂Br⁷¹, UO₂Br¹²² and PaO₂I¹⁰⁸ have been reported, but the infrared spectrum of UO₂Br differs most markedly from those recorded for other actinide oxahalides (Table 4) and further work on this compound is desirable. The compound Pa₂O₃Cl₄¹¹³, like all the other oxahalides, is probably an oxygen bridged polymer.

Oxohalocomplex salts of the types A¹²MOCl₅ (U¹¹⁷, Np⁵⁶), A¹MO₂F₂ (Np, Pu, Am^{123,124}) and A¹MO₂Cl₄ (Np⁵⁶, Am¹²⁵) have been prepared and infrared data for some of these, and other actinide(V) halide species, are given in Table 4.

TABLE 4

INFRARED SPECTRA OF THE PENTAHALIDES, OXYHALIDES AND SOME OXYHALOCOMPLEXES

Compound	M-X (cm ⁻¹)	M-O (cm ⁻¹)	References	Compound	M-X (cm ⁻¹)	M-O (cm ⁻¹)	References
Pa ₂ OF ₈	450	790, 740, 690	111	Cs ₂ NpO ₂ Cl ₄	264	810, 794	56
NpO ₂ F	476, 385, 277	800	120	Cs ₂ AmO ₂ Cl ₄	—	800	125
PaCl ₅	323, 362	—	113	PaOBr ₃	—	513, 364, 298(?)	71
α Pa ₂ OCl ₈	326, 370	460, 500	113	PaO ₂ Br	—	642, 576, 376	71
β Pa ₂ OCl ₈	324, 370	458, 506	113	UO ₂ Br	—	940, 890, 850	122
Pa ₂ O ₃ Cl ₄	342, 378	426, 540	113	PaOI ₃	—	480, 339, 276	108
PaO ₂ Cl	396	520, 624	113	PaO ₂ I	—	555, 469, 386, 281	108
(Ph ₄ As) ₂ NpOCl ₂	271	907	56				
Cs ₂ NpOCl ₄	275	921	56				

(iii) *Halocomplexes.* Fluorocomplexes of the types $A^I MF_6$ ($Pa^{127-131}$; $U^{132-140}$; Np^{141} ; Pu^{142}), $A^I_2 MF_7$ ($Pa^{130,143,144}$; U^{145} ; Np^{141} ; Pu^{142}) and $A^I_3 MF_8$ ($Pa^{130,146,147}$; $U^{145,148,149}$; Np^{120}) are now known; some infrared data are given in Table 5.

TABLE 5

METAL-HALOGEN STRETCHING FREQUENCIES IN ACTINIDE(V) HALOCOMPLEXES

Compound	$M-X$, (cm^{-1})	References	Compound	$M-X$, (cm^{-1})	References
$KPaF_6$	523, 454	130	$A^I_2 PaF_7$	430-438, 356-357	130
$CsUF_6$	503	150	$A^I_3 PaF_8$	395-404 ^b	130
$NOUF_6$	550, 509 ^a	135	$A^I_3 NpF_8$	—	120
$A^I PaCl_6$	305-310	151	$(NMe_4)_3 PaCl_6$	290	151
$A^I UCl_6$	305-310	152			
$A^I PaBr_6$	215-216	153			

^a $NOUF_6$; 550, 509 cm^{-1} , but the intensities of the two bands are interchanged as compared with $NOUF_6^{136}$. ^b $Nu_3 PaF_8$; 468, 422 cm^{-1} .¹³⁰

Lithium and sodium hexafluorouranates(V) are known to have the $LiSbF_6$ structure, and a second form of the sodium salt has the $NaTaF_6$ structure; $CsMF_6$ (U, Np, Pu) have the $KOsF_6$ structure, and in all these compounds the metal atom is in octahedral coordination. The protactinium atom in K_2PaF_7 is 9-coordinate, the coordination polyhedron being close to a trigonal prism with three additional fluorine atoms in the equatorial plane¹⁵⁴. The rubidium heptafluoro-complex salts, Rb_2MF_7 (U, Np, Pu) are isostructural with K_2NbF_7 in which the metal ion is 7-coordinate in the crystal, six fluorines being at the apices of a trigonal prism and the seventh above the centre of one of the tetragonal faces. The structures of the other fluoro complexes are not yet known.

Hexachlorometallates(V), $A^I MCl_6$ (Pa^{151} ; U^{152}) and the analogous protactinium bromides¹⁵³ and iodides¹⁵⁶ have been prepared, but stable octachloro-complex salts are formed only with the tetramethylammonium ion (Pa^{151} ; U^{152}); no structural data are available for these compounds.

(iv) *Oxygen donor complexes.* The nature of hydrated protactinium pentafluoride, $PaF_5 \cdot 2 H_2O^{104}$, is uncertain and no definite hydrates of the other pentahalides have been recorded. Phosphine oxides form 1:1 complexes, $MCl_5 \cdot R_3PO$ (Pa^{157} ; U^{158}) which are remarkable for the large $P=O$ shift (over 200 cm^{-1}) observed in their infrared spectra. They do not react with an excess of the ligand, to form oxychloride complexes, unlike their niobium and tantalum analogues, which exhibit an equally large $P=O$ shift and which form complexes of the type $MOCl_3 \cdot 2 R_3PO^{157}$. A peculiar complex of uranium pentachloride with trichloroacryloyl chloride (TAC), $5 UCl_5 \cdot TAC$, has been recorded¹⁵⁹.

(v) *Nitrogen donor complexes.* The only nitrogen donor complex known is $\text{PaBr}_5 \cdot 3 \text{CH}_3\text{CN}$ ⁷¹, the Pa-Br stretching frequency appearing¹⁵³ at 216 cm^{-1} , and there is no record of any complex with a sulphur donor ligand.

F. THE HEXAVALENT ACTINIDES

(i) *Hexahalides.* Uranium¹⁶⁰⁻¹⁶³, neptunium^{164, 165} and plutonium^{164, 165} hexafluorides are all of regular octahedral symmetry and uranium hexachloride is of near octahedral symmetry¹⁶⁶.

(ii) *Halocomplexes.* Heptafluoro- and octafluorouranates(VI), $\text{A}^{\text{I}}\text{UF}_7$ ^{136, 167-171} and $\text{A}^{\text{I}}_2\text{UF}_8$ ¹⁷¹⁻¹⁷³ are well established, but the enneafluorocomplexes, $\text{A}^{\text{I}}_3\text{UF}_9$, although reported on many occasions (*e.g.* 174-176), seem to be rather doubtful. The uranium atom in Na_2UF_8 is 8-coordinate¹⁷¹ and it is possible that the UF_7^- ion has a pentagonal bipyramidal structure. A complex of composition $2 \text{NaF} \cdot \text{UF}_6 \cdot \text{HF}$ has also been reported¹⁷⁷ and compounds with metal fluorides, such as $\text{PbF}_4 \cdot \text{UF}_6$, are also known^{178, 179}, but no structural information is available. Halocomplexes derived from neptunium and plutonium hexafluorides, and uranium hexachloride, are as yet unknown.

(iii) *Oxyhalides.* Actinide (VI) oxyhalides of the type MO_2X_2 are quite well known; the fluorides (U, Np, Pu) are isostructural, and the recently prepared americium compound will probably conform to this structure. The uranyl compound has a linear O-U-O group and six fluorine atoms are bonded to the metal (2.50 Å), but the structure is not a hexagonal bipyramid, for the fluorine atoms are arranged around the uranium atom in much the same manner as the carbon atom in the chair form of cyclohexane¹⁸⁰. Only two chlorides (U, Pu) have been recorded, but their structures have not been determined, and the only actinide (VI) bromides and iodides known are the uranyl compounds, the former of which is not very stable at room temperature and the latter is so unstable that it has never been isolated other than in complexes. Some infrared data are given in Table 6.

TABLE 6

INFRARED SPECTRA OF THE ACTINIDE(VI) OXYHALIDES, MO_2X_2

Compound	$M=O$ (cm^{-1})	$M-X$ (cm^{-1})	References
UO_2F_2	990	—	120, 181
NpO_2F_2	980	446, 277, 255	120
PuO_2F_2	975	—	182
UO_2Cl_2	905, 948	—	183
UO_2Br_2^a	905, 930	—	183

^a ν_3 , 852 cm^{-1} .

(iv) *Oxyhalocomplexes.* Fluorocomplexes of the types $A^I\text{MO}_2\text{F}_3$ (hydrated, U^{184} ; Np^{120} ; Pu^{185}), $A^I_3(\text{UO}_2)_2\text{F}_7^{184}$, $A^I\text{UO}_3\text{F}^{186,187}$ and $A^I_3\text{UO}_2\text{F}_5$ are known, the stereochemistry of the anion in the last being a pentagonal bipyramid¹⁸⁸. A compound of composition $\text{UO}_2\text{Cl}_2 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}^{189}$ has been recorded and this may possibly be the hydrated acid HUO_2Cl_3 , but no salts derived from such an acid are known and the halocomplexes formed with chlorine (and the other halogens) are nearly all of the type $A^I_2\text{MO}_2\text{Cl}_4$ ($\text{U}^{189,190,191}$; $\text{Np}^{56,191}$; $\text{Pu}^{190,191}$; Am^{125}), a type not formed with fluorine. It has been established that the $\text{UO}_2\text{Cl}_4^{2-}$ ion is near octahedral in the caesium salt¹⁹², as it is in the corresponding bromocomplex¹⁹³, although it was observed in both cases that the linear O-U-O group did not appear to be quite normal to the equatorial plane. Similar uranyl bromocomplexes have been prepared¹⁹⁴⁻¹⁹⁶, but only one iodocomplex salt, $(\text{Ph}_3\text{BuP})_2\text{UO}_2\text{I}_4$, is known¹⁹⁶. Salts such as $\text{K}_2\text{UO}_3\text{Cl}_2^{197,198}$, $\text{K}_2\text{UO}_3\text{Br}_2^{198}$ and CsUO_3Cl are also known, the structure of the anion in the last being a distorted pentagonal bipyramid¹⁹⁹. Some infrared data are given in Table 7.

TABLE 7

INFRARED SPECTRA OF THE ACTINIDE(VI) OXYHALO COMPLEXES

Compound	M-O (cm^{-1})	M-X (cm^{-1})	References
CsUO_2F_3	935, 895		120
CsNpO_2F_3	935		120
$\text{K}_3\text{UO}_2\text{F}_5$	863, 789		225
$\text{Cs}_3\text{NpO}_2\text{F}_5$	870, 840	357, 294	120
$(\text{Ph}_3\text{BuP})_2\text{UO}_2\text{I}_4$	925		196
<i>Anion</i>			
$\text{UO}_2\text{Cl}_4^{2-}$	904-930	270	196
$\text{UO}_2\text{Cl}_2\text{Br}_2^{2-}$	912	260 (U-Cl)	196
$\text{NpO}_2\text{Cl}_4^{2-}$	919	271	56
$\text{AmO}_2\text{Cl}_4^{2-}$	902		125
$\text{UO}_2\text{Br}_4^{2-}$	921-934	—	196

(v) *Complexes of the oxyhalides with oxygen donors.* The existence of complexes of the uranyl halides is well documented, but structural data are generally lacking, and no work seems to have been done on the analogous neptunyl, plutonyl and americyl systems. The uranyl halides commonly form 1:2 complexes with oxygen donors; phosphine oxide adducts of the chloride⁸⁶, bromide^{84,99,196,200} and iodide^{99,196} have the *trans*-octahedral configuration¹⁹⁶. Some infrared data are given in Table 8.

Uranyl chloride also forms 1:2 complexes with *N,N*-dimethylacetamide⁷⁹, 1,3 dimethylurea and tetramethylurea²⁰¹, 1,5 diphenyl- and 1,5-bis(*p*-methoxyphenyl)-3-pentadienone, dibenzal- and dianisyl-acetone²⁰², 4-methoxy- and 4-nitro-pyridine-*N*-oxide²⁰³, ethanol²⁰⁴, diethylether²⁰⁸ and acetamide, but in this case monohydrated²⁰⁵. There is also spectroscopic evidence for the formation of

TABLE 8

INFRARED DATA FOR OXYGEN DONOR COMPLEXES OF THE URANYL HALIDES

Compound	M=O (cm ⁻¹)	M-X (cm ⁻¹)	Ligand (cm ⁻¹)	References
UO ₂ Cl ₂ · 2 Ph ₃ PO	921	274	1070 (P=O)	99, 196
UO ₂ Br ₂ · 2 Ph ₃ PO	931	—	1060 (P=O)	99, 196
UO ₂ I ₂ · 2 Ph ₃ PO	943	—	1060 (P=O)	99, 196
UO ₂ Cl ₂ · 3 DMSO	922	231	995 (S=O)	215
UO ₂ Br ₂ · 4.5 DMSO	922	—	995 (S=O)	215
UO ₂ Cl ₂ · 2 DMA	924, 918	—	1613 (C=O)	79
UO ₂ Br ₂ · 2 DMA	922	—	1608 (C=O)	79
UO ₂ Cl ₂ · MeCN	962	—	2280 (C≡N)	79
UO ₂ Cl ₂ · H ₂ O	958	—	—	79

a 1:2 complex with tri-*n*-butylphosphate (TBP) in ligand solutions of uranyl chloride²⁰⁶. A few uranyl bromide analogues have been recorded; 1:2 complexes are formed with *N,N*-dimethylacetamide⁷⁹, tri-*n*-butylphosphate²⁰⁶, acetic anhydride (described as a black solid²⁰⁷), diethylether²¹⁶, 1,5-bis(*p*-methoxyphenyl)-3-pentadienone, 2,6-dimethylpyran-4-one and acetophenone²⁰⁸. Apart from the phosphine oxide complexes mentioned earlier, uranyl iodide does not appear to form 1:2 complexes.

A number of 1:4 complexes have been recorded; uranyl chloride forms such complexes with 1,3-dimethylurea (which is also reported to form a 1:5 complex²⁰¹), 4-chloropyridine *N*-oxide²⁰³ and urea²⁰⁵; hydrated 1:2 and 1:3 complexes with urea have also been isolated²⁰⁹. Uranyl bromide forms 1:4 complexes with phenacetin and aminopyrine²¹⁰, presumably coordinated by way of the carbonyl oxygen in both cases, and uranyl iodide⁸¹ forms a 1:4 complex with *N,N*-dimethylformamide (DMF). Since the corresponding 1:3 complexes of uranyl chloride⁸¹ and uranyl bromide²¹¹ with DMF ionise as (UO₂X · 3 L)⁺X⁻²¹², as does the 1:3 uranyl chloride complex with dimethyl sulphoxide²¹³, it is probable that the uranyl iodide complex will be found to be a 2:1 electrolyte. Some infrared data²¹⁵ are given in Table 8.

Uranyl chloride also yields 1:3 complexes with ethylurea, 1,3 diethylurea²⁰¹, 4-methylpyridine *N*-oxide²⁰³ and there is spectroscopic evidence for the existence of UO₂Cl₂ · 3 TBP in solution²¹⁴. Curiously, the uranyl bromide complex, UO₂Br₂ · 4.5 DMSO, ionises as a 1:1 electrolyte²¹³ and is obviously worth further investigation.

A few 1:1 complexes of uranyl chloride are known; the benzophenone²⁰⁸ and acetyl chloride²¹⁷ complexes would be expected to be 1:2 compounds. Crystallographic data are also available for uranyl chloride monohydrate²¹⁸. Uranyl chloride complexes with *N,N,N',N'*-tetramethyldicarboxylic acid amides are of 2:3 or 1:1 stoichiometry and are probably polymeric⁷⁹.

(vi) *Complexes of the oxyhalides with nitrogen donors.* Uranyl halide amines of 1:2 (F^{219} ; $Cl^{220, 221}$; Br^{219}), 1:3 (F^{219} ; Cl^{222} ; Br^{219}) and 1:4 (F , Br^{219}) stoichiometry have been recorded. The 1:2 and 1:3 complexes with alkyl amines, and the 1:4 complex with hydrazine²²² are also known. 1:1 complexes of uranyl chloride with methyl cyanide⁷⁹, 2,2-dipyridyl (dihydrated²²³) and both 1:1 and 1:2 complexes with 1,10-phenanthroline²²³ have been reported. As usual, no structural data are available for any of them.

The so-called 1:2 triphenylphosphine complexes of uranyl chloride, bromide and iodide are now known to be the phosphine oxide adducts^{99, 196}.

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