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THE COORDINATION CHEMISTRY OF THE ACTINIDE HALIDES

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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 Seaborg[3], there has been only one review dealing specifically with the coordination chemistry of the actinides as a group[4]. 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 tervalent 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^+ (exceptPa)
				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 MO_2^+ and MO_2^{++} is attributed to f orbital participation[5].

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 $5f^3$ configuration[6] and similar studies of the higher actinides accord with a $5f^n$ configuration[7].

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 tervalent 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 solution[9] and salts of these can be obtained with little difficulty at high chloride concentrations[10]. 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 tabulated[13].

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 neighbours[15]. 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 faces[17]. $AcBr_3$, UBr_3 and α-$NpBr_3$ also have this structure[1], but β-$NpBr_3$, $PuBr_3$, $AmBr_3$, 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 prism[17]. 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 symmetry[14] 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 type[19].

(ii) Oxyhalides. Apart from AcOF, which appears to have the 8-coordinate cubic fluorite structure[20], all other known oxyhalides have the tetragonal PbFCl structure[20–24], a layer structure in which the metal is also 8-coordinate. The only known imidochloride, U(NH)Cl, also possesses this structure[25].

(iii) Complexes. Fluorocomplexes of the type $NaMF_4$ (M = Pu, Am) have been made by solid state reactions; they are[26] of hexagonal symmetry but although they are said to have the β_2-Na_2ThF_6 structure, the $NaNdF_4$ structure seems more likely[27]; 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 $Pu_2Cl_7^-$ [29], but only the hexachlorocomplex, $Cs_3PuCl_6 \cdot 2H_2O$, has been isolated from aqueous solution[31]; no structural data are available for any of these species. The $AmCl_6^{3-}$ ion is known from spectral studies to be of octahedral symmetry[32] 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 unknown[33].

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 antiprism[34], 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 Å) 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 Å[35]. Thorium tetrabromide is dimorphic and the high temperature form, with which protactinium tetrabromide is isomorphous[36], may be isostructural with uranium tetrachloride[37]. 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 antiprism[38]. 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 polymers[2]; one of them, $ThOF_2$, was thought to have the LaF_3 structure[23] but subsequent work indicates that the compound is a fluorite type mixed crystal containing randomly distributed oxygen and fluorine atoms[39].

(iii) Halocomplexes. A wide variety of fluorocomplexes have been recorded; genuine compounds of the type $LiMF_5$ (M = Th–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 $7\,A^IF \cdot 6\,MF_4$ (Th–Cm); however, where the radius ratio A^+/M^{4+} lies between 1.59 and 1.68, both types of compound can exist[40]. The coordination polyhedron around the actinide ion in the 7:6 complexes will be as that in the zirconium compound, $Na_7Zr_6F_{31}$, 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 atom[41].

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 $A^IM_2F_9$ (Th, U–Pu[17,44]) and for the hexafluorocomplexes of the β_2-Na_2ThF_6 and β_1-K_2UF_6 structure types[17], whereas compounds such as $BaMF_6$ (Th, U) have a disordered LaF_3 structure[23]. The U^{4+} ion in α-K_2UF_6 and γ-Na_2UF_6 is 8-coordinate, the former being a disordered[23] and the latter a slightly deformed[17] fluorite structure. In both Na_3UF_7 [17] and K_3UF_7 (which is dimorphic[45]) the metal is 7-coordinate, at the centre of a pentagonal bipyramid. Octafluorocomplexes, $A^I_4MF_8$ (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 $A^I_2MX_6$ (Th–Pu,

TABLE 2

METAL-HALOGEN STRETCHING FREQUENCIES IN COMPLEXES OF THE TYPE $A^I_2MX_6$

	cm⁻¹	*References*		*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 chlorocomplexes[50], a result confirmed by spectroscopic[51] and magnetic susceptibility[52] studies. Similar studies[51, 53, 54] indicate that the anion retains this symmetry in the hexabromo- and hexaiodo-complexes. The mixed halocomplex ion, $UCl_4Br_2^{2-}$, has the *trans* octahedral configuration[54]. Some infrared data are given in Table 2.

A number of other thorium chlorocomplexes have been reported, including hydrated and anhydrous A^IThCl_5 [57], hydrated KTh_2Cl_9 [58] and anhydrous $A^I_4ThCl_8$ [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 $MF_4 \cdot 2.5\ H_2O$ (Th[60, 61], U[62], Pu[63]) and the hydrate systems of the other tetrahalides appear to be more complicated (*e.g.* $UCl_4 \cdot 4.5$–$9\ H_2O$[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 $ThCl_4 \cdot 2\ L$ (L = ethanol[65], acetaldehyde[66], cinnamaldehyde[67], $UCl_4 \cdot 2\ L$ (L = tri-*n*-butylphosphate[68]), $ThBr_4 \cdot 2\ L$ (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
$ThCl_4 \cdot 4\ DMA$	—	$\Delta\nu(C{=}O)$ 44	75
$2\ UCl_4 \cdot 5\ DMA$	245, 259	$\Delta\nu(C{=}O)$ 29	80, 89
$(UI_2Cl_2 \cdot 5\ DMA)_2$	254	$\Delta\nu(C{=}O)$ 54	80
$ThCl_4 \cdot 4\ MeCN$	256	$\Delta\nu(C{=}N)$ 24	55, 79
$PaCl_4 \cdot 4\ MeCN$	—	$\Delta\nu(C{=}N)$ 26	36
$UCl_4 \cdot 4\ MeCN$	262	$\Delta\nu(C{=}N)$ 29	55, 79
$UCl_4 \cdot 2\ Ph_3PO$	267	$\Delta\nu(P{=}O)$ —	54
Compound	*M–Br (cm⁻¹)*	*Ligand shift (cm⁻¹)*	*References*
$ThBr_4 \cdot 4\ DMA$	176	$\Delta\nu(C{=}O)$ 34	79
$UBr_4 \cdot 4\ DMA$	180	$\Delta\nu(C{=}O)$ 34	79
$ThBr_4 \cdot 4\ MeCN$	188	$\Delta\nu(C{=}N)$ 24	55, 79
$PaBr_4 \cdot 4\ MeCN$	—	$\Delta\nu(C{=}N)$ 25	36
$UBr_4 \cdot 4\ MeCN$	193	$\Delta\nu(C{=}N)$ 27	55, 79

[a] The M–F stretching frequency appears at 520 cm^{-1} in the case of gaseous ThF_4[128] and at 400 cm^{-1} in the case of solid PaF_4[111]. DMA = *N,N*-dimethylacetamide.

tate[69]), and $MX_4 \cdot 2\,L$ (M = Th, U[70], Pa[36]; X = Cl, Br; L = hexamethylphosphoramide) may be *trans*-octahedral like the phosphine oxide complexes, $UX_4 \cdot 2\,R_3PO$ (X = Cl[54,72], Br[54]).

Thorium tetrachloride forms 1:4 complexes with cinnamaldehyde[73], acetophenone, benzophenone[74], *N*,*N*-dimethylacetamide (DMA)[75], *N*,*N*-dimethylformamide (DMF)[76] and aliphatic alcohols[65]. Uranium tetrachloride also forms 1:4 complexes with alcohols[77], *N*-methylacetamide[75] and with phosphorus oxytrichloride[78]. Both thorium tetrabromide and uranium tetrabromide form 1:4 complexes with DMA[79], as does uranium tetraiodide[80], which also forms a similar complex with DMF[81], and thorium tetrabromide forms 1:4 complexes with ethanol and with benzaldehyde[69].

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 tetrahydrofuran[82] and dioxan[83,84], whilst uranium tetrachloride also forms 1:3 complexes with tri-n-butylphosphate[85], trimethyl phosphine oxide[86], acetone[84], diphenylsulphoxide[87] 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, $ThCl_4 \cdot 5$ DMSO may involve 10-coordinate thorium[70]. The S=O shifts in the infrared spectra of the DMSO complexes are between 102 and 112 cm^{-1} [70]. A plutonium tetrachloride complex with DMSO, $PuCl_4 \cdot 3$ DMSO, has also been reported[224]. Thorium tetrabromide forms 1:3 complexes with ethyl benzoate[69] and with hexamethylphosphoramide, the latter being monomeric in benzene but a 1:1 electrolyte in nitromethane[70]. The P=O shift in the infrared spectrum of $ThBr_4 \cdot 3$ HMPA is only 130 cm^{-1}, as compared with shifts of 159–174 cm^{-1} in the 1:2 complexes[70].

Uranium tetrachloride has been reported to form the complex $UCl_4 \cdot 3$ DMF[81] but other work[88] indicates that the complex has the stoicheiometry $2\,UCl_4 \cdot 5$ DMF, the same as that found[89] for the DMA complexes, $2\,MCl_4 \cdot 5$ DMA (U, Np, Pu); the structure probably involves the 8-coordinate metal atom with one ligand and two chlorine bridges[80].

Thorium tetrabromide forms a complex of unusual stoicheiometry with acetophenone[69], $2\,ThBr_4 \cdot 7\,L$, and 1:6 complexes of the tetrahalides with acetamide[89], $MCl_4 \cdot 6\,L$ (U, Np, Pu), dimethylsulphoxide[70], $MBr_4 \cdot 6\,L$ (Th, U) and *N*,*N*-dimethylacetamide[80], $ThI_4 \cdot 6$ 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) oxides[86] 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 polymers[90]. A 1:2 complex of uranium tetrachloride with 1,2 dimethoxyethane is also known[91].

(v) Nitrogen donor complexes. 1:4 primary amine complexes of thorium tetrachloride[92], thorium tetrabromide[69, 93] and uranium tetrachloride[94], and 1:4 complexes of uranium tetrachloride with ammonia[87, 95], piperidine[87] and, somewhat surprisingly, with ethylenediamine[87] are also known; the structure of the ethylenediamine complex is well worth investigation. Uranium tetrachloride forms a 1:6 adduct with hydrazine[94] and thorium tetrachloride is said to form a hexammine[92], but the thorium tetrabromide–ammonia system is less well defined, ammines in the composition range $ThBr_4 \cdot 8\text{–}20\ NH_3$ being reported. Uranium tetrachloride is also reported to form 1:2 complexes with ammonia and primary amines[94] and a 1:2 *o*-phenanthroline complex with thorium tetrachloride is known[88].

Pyridine forms the complexes $ThBr_4 \cdot 3\ py$[69] and $UCl_4 \cdot 2\ py$[87], and 1:3 stoicheiometry had been reported for the thorium tetrachloride–toluidine complex[92]. 1:1 complexes of thorium tetrachloride with α-picoline[97] and of uranium tetrachloride with primary amines[94] are also known.

Methyl cyanide complexes of the tetrahalides are nearly all of 1:4 stoicheiometry ($ThCl_4$[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, $ThCl_4 \cdot 4\ PhCN$[83], although the 1:2 complexes $ThCl_4 \cdot 2\ PhCN$[98] and $UCl_4 \cdot 2\ MeCN$[84] have also been recorded. The metal ions are presumably 8-coordinate in the complexes of 1:4 stoicheiometry, 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 adducts[99], but a 1:1 adduct of uranium tetrachloride with tetra-*P*-methylenediphosphine[91] is probably a genuine complex.

(vi) Sulphur donor complexes. There is little evidence for the existence of complexes with monodentate sulphur donors, thioacetamide[89] and phosphine sulphides[86] failing to form complexes with uranium tetrachloride. The only known complex seems to be that with 1,2 dimethylthioethane, $UCl_4 \cdot 2\ L$, in which the uranium is thought to be 8-coordinate[91].

(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 atom[102].

E. THE PENTAVALENT ACTINIDES

(i) Pentahalides. Simple compounds are known only for protactinium and uranium; protactinium pentafluoride[104] 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 pentagon[105]; a somewhat similar 7-coordinate arrangement has been established for protactinium pentachloride[106]. The structure of α-UF_5, the high temperature form, consists of an infinite chain of octahedra linked by opposite corners[105], whereas in UCl_5 edges of the octahedron are shared to form a dimeric unit[107]. No structural data are available for $PaBr_5$[71], PaI_5[108] or UBr_5[109,110], the only other known actinide pentahalides; intermediate fluorides of the type U_2F_9 and U_4F_{17} have distorted UF_4 structures and uranium in the former is 9-coordinate[43].

(ii) Oxyhalides. Compounds of the type M_2OX_8 (M, X: Pa, F[111]; U, F[112]; Pa, Cl), are dimorphic[113] and well established, and although there is some evidence for the existence of UOF_3[114] and $PaOCl_3$[113], the only compounds of the type MOX_3 which are known with any certainty are $UOCl_3$[115,116], which also forms a 1:1 adduct with ethanol[117], $PaOBr_3$[71], $UOBr_3$[110,118,119], $PaOI_3$[108] and $NpOF_3 \cdot x\,H_2O$[120]. Structural data are available only for $PaOBr_3$, in which protactinium is 7-coordinate in a pentagonal bipyramidal arrangement[121].

A few dioxohalides are also known; NpO_2F[120], PaO_2Cl[113], PaO_2Br[71], UO_2Br[122] and PaO_2I[108] have been reported, but the infrared spectrum of UO_2Br differs most markedly from those recorded for other actinide oxohalides (Table 4) and further work on this compound is desirable. The compound $Pa_2O_3Cl_4$[113], like all the other oxohalides, is probably an oxygen bridged polymer.

Oxohalocomplex salts of the types $A^I{}_2MOCl_5$ (U[117], Np[56]), $A^IMO_2F_2$ (Np, Pu, Am[123,124]) and $A^I{}_3MO_2Cl_4$ (Np[56], Am[125]) 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_2OF_8	450	790, 740, 690	111	$Cs_3NpO_2Cl_4$	264	810, 794	56
NpO_2F	476, 385, 277	800	120	$Cs_3AmO_2Cl_4$	—	800	125
$PaCl_5$	323, 362	—	113	$PaOBr_3$	—	513, 364, 298(?)	71
αPa_2OCl_8	326, 370	460, 500	113	PaO_2Br	—	642, 576, 376	71
βPa_2OCl_8	324, 370	458, 506	113	UO_2Br	—	940, 890, 850	122
$Pa_2O_3Cl_4$	342, 378	426, 540	113	$PaOI_3$	—	480, 339, 276	108
PaO_2Cl	396	520, 624	113	PaO_2I	—	555, 469, 386, 281	108
$(Ph_4As)_2NpOCl_5$	271	907	56				
Cs_2NpOCl_5	275	921	56				

(iii) Halocomplexes. Fluorocomplexes of the types A^IMF_6 ($Pa^{127-131}$; $U^{132-140}$; Np^{141}; Pu^{142}), $A^I_2MF_7$ ($Pa^{130,143,144}$; U^{145}; Np^{141}; Pu^{142}) and $A^I_3MF_8$ ($Pa^{130,146,147}$; $U^{145,148,149}$; 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	$A^I_2PaF_7$	430–438, 356–357	130
$CsUF_6$	503	150	$A^I_3PaF_8$	395–404[b]	130
$NOUF_6$	550, 509[a]	135	$A^I_3NpF_8$	—	120
A^IPaCl_6	305–310	151	$(NMe_4)_3PaCl_8$	290	151
A^IUCl_6	305–310	152			
A^IPaBr_6	215–216	153			

[a] $NOUF_7$; 550, 509 cm^{-1}, but the intensities of the two bands are interchanged as compared with $NOUF_6$[136]. [b] Na_3PaF_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 plane[154]. The rubidium heptafluorocomplex 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^IMCl_6 (Pa^{151}; U^{152}) and the analogous protactinium bromides[153] and iodides[156] have been prepared, but stable octachlorocomplex 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 recorded[159].

(v) Nitrogen donor complexes. The only nitrogen donor complex known is $PaBr_5 \cdot 3\,CH_3CN$[71], the Pa-Br stretching frequency appearing[153] at 216 cm^{-1}, and there is no record of any complex with a sulphur donor ligand.

F. THE HEXAVALENT ACTINIDES

(i) Hexahalides. Uranium[160–163], neptunium[164, 165] and plutonium[164, 165] hexafluorides are all of regular octahedral symmetry and uranium hexachloride is of near octahedral symmetry[166].

(ii) Halocomplexes. Heptafluoro- and octafluorouranates(VI), $A^{I}UF_7$[136,167–171] and $A^{I}_2UF_8$[171–173] are well established, but the enneafluorocomplexes, $A^{I}_3UF_9$, although reported on many occasions (*e.g.* 174–176), seem to be rather doubtful. The uranium atom in Na_2UF_8 is 8-coordinate[171] and it is possible that the UF_7^- ion has a pentagonal bipyramidal structure. A complex of composition $2\,NaF \cdot UF_6 \cdot HF$ has also been reported[177] and compounds with metal fluorides, such as $PbF_4 \cdot UF_6$, 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 cyclohexane[180]. 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_1, 852 cm^{-1}.

(iv) Oxyhalocomplexes. Fluorocomplexes of the types $A^{I}MO_2F_3$ (hydrated, U[184]; Np[120]; Pu[185]), $A^{I}_3(UO_2)_2F_7$[184], $A^{I}UO_3F$[186,187] and $A^{I}_3UO_2F_5$ are known, the stereochemistry of the anion in the last being a pentagonal bipyramid[188]. A compound of composition $UO_2Cl_2 \cdot HCl \cdot 2\,H_2O$[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 $A^{I}_2MO_2Cl_4$ (U[189,190,191]; Np[56,191]; Pu[190,191]; Am[125]), a type not formed with fluorine. It has been established that the $UO_2Cl_4^{2-}$ ion is near octahedral in the caesium salt[192], as it is in the corresponding bromocomplex[193], 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 prepared[194–196], but only one iodocomplex salt, $(Ph_3BuP)_2UO_2I_4$, is known[196]. Salts such as $K_2UO_3Cl_2$[197,198], $K_2UO_3Br_2$[198] and $CsUO_3Cl$ are also known, the structure of the anion in the last being a distorted pentagonal bipyramid[199]. 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
$K_3UO_2F_5$	863, 789		225
$Cs_3NpO_2F_5$	870, 840	357, 294	120
$(Ph_3BuP)_2UO_2I_4$	925		196
Anion			
$UO_2Cl_4^{2-}$	904–930	270	196
$UO_2Cl_2Br_3^{2-}$	912	260 (U–Cl)	196
$NpO_2Cl_4^{2-}$	919	271	56
$AmO_2Cl_4^{2-}$	902		125
$UO_2Br_4^{2-}$	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 chloride[86], bromide[84,99,196,200] and iodide[99,196] have the *trans*-octahedral configuration[196]. Some infrared data are given in Table 8.

Uranyl chloride also forms 1:2 complexes with *N,N*-dimethylacetamide[79], 1,3 dimethylurea and tetramethylurea[201], 1,5 diphenyl- and 1,5-bis(*p*-methoxyphenyl)-3-pentadienone, dibenzal- and dianisyl-acetone[202], 4-methoxy- and 4-nitro-pyridine-*N*-oxide[203], ethanol[204], diethylether[208] and acetamide, but in this case monohydrated[205]. 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*
$UO_2Cl_2 \cdot 2\,Ph_3PO$	921	274	1070 (P=O)	99, 196
$UO_2Br_2 \cdot 2\,Ph_3PO$	931	—	1060 (P=O)	99, 196
$UO_2I_2 \cdot 2\,Ph_3PO$	943	—	1060 (P=O)	99, 196
$UO_2Cl_2 \cdot 3$ DMSO	922	231	995 (S=O)	215
$UO_2Br_2 \cdot 4.5$ DMSO	922	—	995 (S=O)	215
$UO_2Cl_2 \cdot 2$ DMA	924, 918	—	1613 (C=O)	79
$UO_2Br_2 \cdot 2$ DMA	922	—	1608 (C=O)	79
$UO_2Cl_2 \cdot$ MeCN	962	—	2280 (C≡N)	79
$UO_2Cl_2 \cdot H_2O$	958	—	—	79

a 1:2 complex with tri-n-butylphosphate (TBP) in ligand solutions of uranyl chloride[206]. A few uranyl bromide analogues have been recorded; 1:2 complexes are formed with *N,N*-dimethylacetamide[79], tri-n-butylphosphate[206], acetic anhydride (described as a black solid[207]), diethylether[216], 1,5-bis(*p*-methoxyphenyl)-3-pentadienone, 2,6-dimethylpyran-4-one and acetophenone[208]. Apart from the phosphine oxide complexes mentioned earlier, uranyl iodide does not appear to from 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 complex[201]), 4-chloropyridine *N*-oxide[203] and urea[205]; hydrated 1:2 and 1:3 complexes with urea have also been isolated[209]. Uranyl bromide forms 1:4 complexes with phenacetin and aminopyrine[210], presumably coordinated by way of the carbonyl oxygen in both cases, and uranyl iodide[81] forms a 1:4 complex with *N,N*-dimethylformamide (DMF). Since the corresponding 1:3 complexes of uranyl chloride[81] and uranyl bromide[211] with DMF ionise as $(UO_2X \cdot 3\,L)^+X^-$[212], as does the 1:3 uranyl chloride complex with dimethyl sulphoxide[213], it is probable that the uranyl iodide complex will be found to be a 2:1 electrolyte. Some infrared data[215] are given in Table 8.

Uranyl chloride also yields 1:3 complexes with ethylurea, 1,3 diethylurea[201], 4-methylpyridine *N*-oxide[203] and there is spectroscopic evidence for the existence of $UO_2Cl_2 \cdot 3$ TBP in solution[214]. Curiously, the uranyl bromide complex, $UO_2Br_2 \cdot 4.5$ DMSO, ionises as a 1:1 electrolyte[213] and is obviously worth further investigation.

A few 1:1 complexes of uranyl chloride are known; the benzophenone[208] and acetyl chloride[217] complexes would be expected to be 1:2 compounds. Crystallographic data are also available for uranyl chloride monohydrate[218]. Uranyl chloride complexes with *N,N,N',N'*-tetramethyldicarboxylic acid amides are of 2:3 or 1:1 stoicheiometry and are probably polymeric[79].

(vi) Complexes of the oxyhalides with nitrogen donors. Uranyl halide ammines of 1:2 (F[219]; Cl[220,221]; Br[219]), 1:3 (F[219]; Cl[222]; Br[219]) and 1:4 (F, Br[219]) stoicheiometry have been recorded. The 1:2 and 1:3 complexes with alkyl amines, and the 1:4 complex with hydrazine[222] are also known. 1:1 complexes of uranyl chloride with methyl cyanide[79], 2,2-dipyridyl (dihydrated[223]) and both 1:1 and 1:2 complexes with 1,10-phenanthroline[223] 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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