Sulphoxide Complexes of Actinoid Tetrahalides

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Complexes of actinoid tetrachlorides with sulphoxides MCl_4,xR_2SO [R = Et, x = 4(Th), 3(Th, U, or Np), and 2·5(Np or Pu); R = Ph, x = 4(Th, U, or Np) and 3(U, Np, or Pu); R = $C_{10}H_7$, x = 3(Th or U)] have been prepared. I.r. spectra, including tentative assignments for metal–halogen stretching frequencies in these complexes and the uranium tetrabromide complexes UBr_4,yR_2SO (R = Me, y = 8 and 6; R = Et, y = 5; R = Ph, y = 4), are reported. *X*-Ray powder diffraction data are also presented and the electronic spectra of the uranium tetrachloride complexes are discussed.

ANHYDROUS complexes of uranium tetrachloride with sulphoxides UCl_4,xR_2SO [$x = 2$, R = $C_{10}H_7$(naphthyl); [1] $x = 3$, R = Me,[2,3] Et,[1] Pr^n,[1] or Ph; [1,4] $x = 4$, R = Bu^n [1] or Ph; [1,5] $x = 5$ and 7, R = Me [2]] and the analogous thorium complexes (R = Me [2], x = 3, 5, 8, or 10; R = Ph,[6,7] $x = 4$) have been reported, but only dimethyl sulphoxide (dmso) complexes have been recorded for neptunium [2] and plutonium [2,3] tetrachlorides. In the series of actinoid tetrachloride complexes with dmso, the pentakis complexes become easier to degrade to the tris analogues as the actinoid(IV) radius decreases across the series to plutonium, for which the pentakis complex could not be obtained.[2] It was therefore of interest to examine the complexes formed by actinoid tetrachlorides with more bulky sulphoxide ligands in order to ascertain whether similar changes in stoicheiometry occurred as the actinoid(IV) radius decreased. Uranium tetrabromide complexes with dmso, diphenyl sulphoxide (dpso), and diethyl sulphoxide (deso) have also been prepared in an attempt to assign metal–halogen and –oxygen vibrations in the i.r. spectra of the various complexes.

RESULTS AND DISCUSSION

Diethyl Sulphoxide (*deso*) *Complexes*.—The complexes (Table 1) were prepared by reaction of the tetrachloride (Th or U) or hexachlorometallate(IV) complex $Cs_2[MCl_6]$ (M = U, Np, or Pu) with the ligand deso, either alone or in acetone or ethyl acetate. The hygroscopic thorium complex, $ThCl_4$,4deso, was obtained from ethyl acetate solution in the presence of an excess of the ligand, but this complex slowly lost deso when exposed to a vacuum for a prolonged period. The uranium tetrakis complex could not be isolated, even when the tris complex was recrystallised from deso. The complex $ThCl_4$,3deso is hygroscopic, and picks up water continuously when exposed to moist air. However, when the complex was prepared on the open bench, a non-hygroscopic hydrated complex appeared to be formed. The uranium and neptunium tetrachloride tris complexes are not hygroscopic, and the latter degrades to a product of composition close to $NpCl_4$,2·5deso when ground with carbon tetrachloride. This product is not isomorphous with the two crystal modifications of $PuCl_4$,2·5deso, one form of which was obtained from the oily primary product by crystallisation from acetone and the other by treating the oil with carbon tetrachloride. There was no evidence of formation of a plutonium tetrachloride tris complex. The complex UCl_4,3deso has previously been prepared [1] by precipitating it from a solution of the tetrachloride in deso with carbon tetrachloride.

TABLE 1

Sulphoxide complexes, MCl_4,xR_2SO

Ligand	Stoicheiometry for $ThCl_4$	UCl_4	$NpCl_4$	$PuCl_4$
Diethyl sulphoxide	1 : 4	[a]	[a]	[a]
	1 : 3	1 : 3	1 : 3	[a]
			γ-1 : 2·5	α-1 : 2·5
				β-1 : 2·5
Diphenyl sulphoxide	1 : 4	1 : 4	1 : 4	[a]
	[b]	1 : 3	1 : 3	1 : 3
Di(1-naphthyl) sulphoxide	1 : 3	1 : 3	[c]	[d]

[a] Complex of this stoicheiometry not obtained with the various preparative conditions investigated. [b] Not obtained under the various conditions which yielded other 1 : 3 complexes. [c] Products of variable composition (1 : 2·7 to 1 : 3·6) obtained. [d] Not investigated.

Partial *X*-ray powder diffraction results are given in Table 2 for the complexes $ThCl_4$,4deso and $NpCl_4$,3deso. Powder patterns of the remaining 1 : 3 complexes were of poor quality and, although they do resemble that of $NpCl_4$,3deso, it is not certain that the complexes are all isostructural. None of the 1 : 2·5 phases (Table 1) gave good powder photographs but, on the evidence available, each possesses a unique structure.

Diphenyl Sulphoxide (*dpso*) *Complexes*.—Reaction of the hexachlorometallate(IV) complex $Cs_2[MCl_6]$ (M = U, Np, or Pu) with dpso is very slow in organic solvents and the complexes formed are too insoluble in these solvents for a satisfactory separation from the residual caesium chloride. Addition of dpso to the actinoid tetrachloride in nitromethane yields the complexes $ThCl_4$,4dpso and MCl_4,3dpso (M = U or Np), whereas dpso precipitates the tetrakis complexes MCl_4,4dpso (M = Th, U, or Np)

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[1] P. Gans and J. Marriage, personal communication.

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[5] N. Gründüz, B. C. Smith, and M. A. Wassef, *Comm. Fac. Sci. Univ. Ankara, ser. B.*, 1969, 31.

[6] B. C. Smith and M. A. Wassef, *J. Chem. Soc.* (*A*), 1968, 1817.

[7] V. V. Savant and C. C. Patel, *J. Less-Common Metals*, 1971, **24**, 459.

and the tris complex $PuCl_4$,3dpso from a solution of actinoid(IV) in 6M-hydrochloric acid. The complex $PuCl_4$,3dmso has been prepared previously in this way.[3] The complex $ThCl_4$,4dpso recrystallised unchanged from nitromethane, but UCl_4,4dpso degraded to the tris complex when recrystallization was attempted. The complexes $ThCl_4$,4dpso and UCl_4,4dpso have previously been prepared from the components in ethanol,[6,7] ethyl acetate,[6] acetone,[7] and methyl cyanide [5] respectively; UCl_4,3dpso is reported to be formed in the reaction of the components in benzene.[4]

TABLE 2

Partial X-ray powder diffraction results for the complexes $ThCl_4$,4deso and $NpCl_4$,3deso

$ThCl_4$,4deso		$NpCl_4$,3deso	
sin$^2\theta$(obs.)	I(est.)	sin$^2\theta$(obs.)	I(est.)
0·0084	s	0·0075	s
0·0094	s	0·0088	s
0·0101	m	0·0093	s
0·0162	w+	0·0095	w
0·0256	m	0·0099	s
0·0306	m	0·0113	w−
0·0334	w+	0·0126	m
0·0372	w+(d)	0·0134	m
0·0407	m−	0·0146	w
0·0426	m	0·0155	w
0·0520	w+	0·0165	w+
0·0583	w+	0·0170	w+(d)
0·0614	w+	0·0194	m−
0·0652	w	0·0211	w
0·0669	w+	0·0256	w
0·0753	m(d)	0·0269	w−
0·0821	w+	0·0276	w−
0·0850	m−	0·0286	w
0·0917	m−	0·0322	w+
0·0988	m−	0·0328	m
0·1066	m(d)	0·0340	m
0·1153	w+	0·0352	w−
0·1189	w+	0·0380	m(d)
0·1551	w+	0·0405	m−
0·1583	w	0·0408	w
0·1644	w+(d)	0·0440	w+(d)
0·1707	w	0·0455	w−
0·2295	w+	0·0468	w−
		0·0482	w−
		0·0484	w
		0·0490	w+
		0·0516	w−
		0·0520	w−
		0·0657	w−

s = Strong, m = medium, and w = weak.

Partial X-ray powder data for selected 1 : 4 and 1 : 3 complexes are shown in Table 3. The complex $PuCl_4$,3dpso appears to possess a different structure from its U and Np analogues, which are isostructural. The 1 : 4 complexes (Th, U, and Np) appear to form an isostructural series.

Di(1-*naphthyl*) *Sulphoxide* (*dnso*) *Complexes*.—As with dpso, reaction of dnso with the hexachlorometallate(IV) complex was also slow, presumably for steric reasons in both cases. The complex $ThCl_4$,3dnso was precipitated when dnso was added to a solution of the tetrachloride in hot ethyl acetate; the corresponding uranium tetrachloride complex resulted when nitromethane was added to a mixture of solid UCl_4 and dnso, and when a solution of dnso in dichloromethane was mixed with a solution of uranium(IV) in a mixture of 6—9M-HCl and acetone. Reaction of dnso with neptunium tetrachloride in nitromethane yielded products of variable composition ($NpCl_4$,2·7—3·6dnso) and no pure products could be obtained. The bis complex UCl_4,2dnso, reported [1] to be formed in the reaction of dnso with hexachlorouranate(IV) in dry ethanolic hydrogen chloride, was not formed from aqueous media or from dichloromethane solution.

I.r. Spectra.—Shifts in the S=O stretching frequency of the ligand in all the sulphoxide complexes indicate that the ligands are bonded to the metal through the sulphoxide oxygen atom; the relevant parts of the i.r. spectra are summarised in Table 4. The shift in frequency of the S=O stretching mode in the tris deso complexes increased along the series from thorium to neptunium, as one might expect from the increase in polarising power of the actinoid metal ion with decreasing radius due to the actinoid contraction. The shift also increased as the ligand content of the complexes decreased in the thorium tetrachloride complexes and similarly, but to a less marked extent, in those of neptunium tetrachloride, behaviour which is consistent with a decrease in co-ordination number of the metal atom. However, in the corresponding dmso complexes,[2] the changes in $\Delta\nu$(S=O) between the complexes MCl_4,3dmso and MCl_4,5dmso are in the opposite sense to those observed here for the deso complexes, which suggests that co-ordination arrangements in the dmso complexes differ from those in the deso and dpso complexes.

TABLE 3

Partial X-ray powder diffraction results for selected diphenyl sulphoxide complexes

UCl_4,4dpso*		UCl_4,3dpso†		$PuCl_4$,3dpso	
sin$^2\theta$(obs.)	I(est.)	sin$^2\theta$(obs.)	I(est.)	sin$^2\theta$(obs.)	I(est.)
0·0051	s	0·0055	s	0·0050	w
0·0061	s	0·0059	m+	0·0052	w
0·0066	s	0·0088	m	0·0060	s
0·0073	w+	0·0093	m+	0·0064	s
0·0114	w	0·0105	s(d)	0·0092	m(d)
0·0134	w+	0·0140	m−	0·0104	m−(d)
0·0190	m−	0·0147	w	0·0111	s−
0·0197	w	0·0151	w	0·0117	w
0·0219	w+	0·0156	m−	0·0128	w+
0·0258	w	0·0191	m−	0·0157	m
0·0268	w	0·0235	w	0·0184	s−
0·0346	w−	0·0254	w	0·0206	w
0·0384	w−	0·0259	w	0·0229	w
0·0428	w−	0·0281	w	0·0254	w
0·0515	w−	0·0312	w	0·0265	w
0·0561	w−	0·0372	w	0·0302	w
0·0681	w+	0·0437	w	0·0367	w
0·0796	w−	0·0514	w	0·0523	w(d)
0·0841	w−	0·0561	w		
0·1175	w−	0·0691	w		
		0·0762	w		
		0·1025	w		

Abbreviations as in footnote to Table 2.

* Th and Np analogues are isostructural. † Np analogue is isostructural.

The shifts in the S=O stretching mode in the tris dpso complexes were likewise greater than those in the tetrakis complexes, although in both these series of complexes the mode was split, unlike that in the deso complexes, although it is possible that the higher-frequency band of the two assigned to the S–O stretching mode may be an aromatic rocking mode. The magnitude of the shift in the tris dpso complexes also varied somewhat irregularly with increasing atomic number, whereas it increased in the same direction in the spectra of the dnso complexes.

TABLE 4

Wavenumbers (cm^{-1}) for S=O and M–X stretching vibrations of the actinoid tetrahalide R_2SO complexes

Compound	Colour	ν(S=O)	Δν(S=O)	ν(M–X)*
dmso		1 056s		
UCl_4,3dmso	Green	945s	111	262s
UBr_4,8dmso	Green	945s, 1 049m	111, 117	190s
UBr_4,6dmso	Green	935s	121	
deso		1 059s		
UBr_4,5deso	Green		170s	
$ThCl_4$,4deso	White	961s	98	
$ThCl_4$,3deso	White	952s	107	261s, 248s
$ThCl_4$, 3deso,$x$$H_2O$	White	959s, 938s	100, 121	
UCl_4,3deso	Green	945s	114	255s
$NpCl_4$,3deso	Pink	935s	124	266m
$NpCl_4$,2·5deso	Pink	932s	127	
α-$PuCl_4$,2·5deso	Red-brown	930s	129	
β-$PuCl_4$,2·5deso	Red-brown	932s	127	265s, 251s
dpso		1 038s		
$ThCl_4$,4dpso	White	985, 959	53, 79	
UCl_4,4dpso	Green	985, 974	53, 64	
UBr_4,4dpso	Green	973, 940	65, 98	160s
$NpCl_4$,4dpso	Pink	983, 972	55, 66	
UCl_4,3dpso	Green	961, 939	71, 99	
$NpCl_4$,3dpso	Red	958, 941	80, 97	
$PuCl_4$,3dpso	Orange-brown	974, 951	64, 87	
dnso		1 042s		
$ThCl_4$,3dnso	White	985, 959	57, 83	
UCl_4,3dnso	Green	978, 942	64, 100	264s
$NpCl_4$,3dnso	Pale brown	974, 938	68, 104	252s

* The limit of the instrument used for other than the uranium complexes was 225 cm^{-1} and, therefore, low-wavelength assignments are more complete for the uranium complexes which were examined down to *ca.* 50 cm^{-1}.

This difference in behaviour is unexpected in view of steric similarity of the immediate environment of the metal atoms in the complexes of these two ligands.

The metal–halogen modes in the spectra of most of the complexes were assigned by examining the spectra of the tetrachloride and tetrabromide complexes of the same ligand. For this purpose the complexes UBr_4,8dmso, UBr_4,4dpso, and UBr_4,5deso were prepared by methods similar to those used to obtain the tetrachloride analogues. The presence of a band at 1 049 cm^{-1} in the spectrum of the complex UBr_4,8dmso suggests that some of the ligand molecules are bonded only very weakly, or are held in the lattice. These observations are similar to those reported previously [2] for actinoid tetrachloride complexes MCl_4,7dmso.

Spectra of dpso, UCl_4,3dpso, UCl_4,4dpso, and UBr_4,4dpso in the region 330—150 cm^{-1} are shown in Figures 1 and 2. Comparison of the free-ligand spectrum (Figure 1) with those of the complexes UCl_4,4dpso and

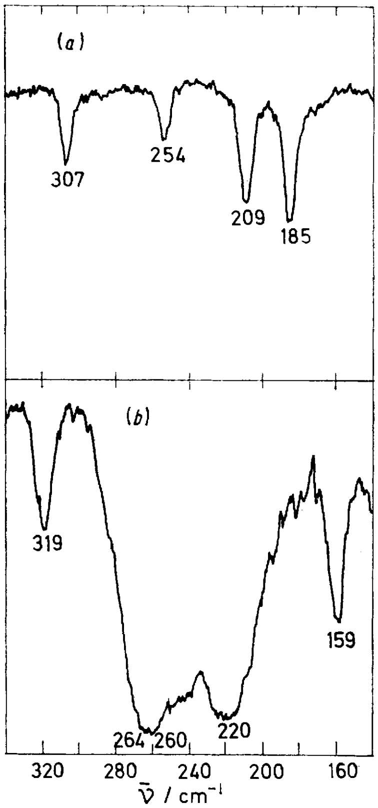

FIGURE 1 I.r. spectra of (*a*) dpso and (*b*) UCl_4,3dpso

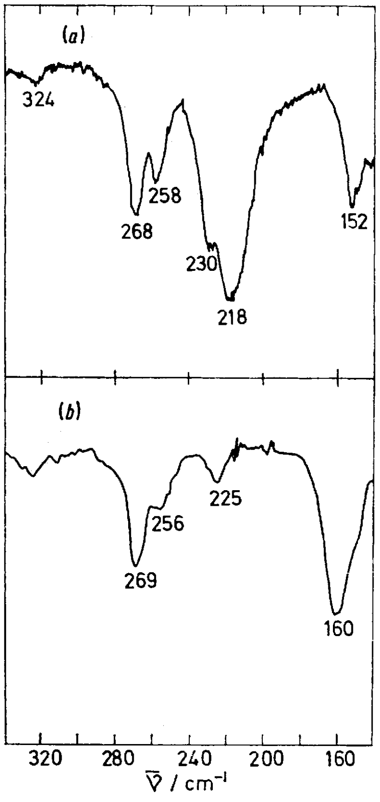

FIGURE 2 I.r. spectra of (*a*) VCl_4,4dpso and (*b*) UBr_4,4dpso

UBr_4,4dpso suggests that the strong band at 160 cm^{-1} (UBr_4,4dpso) can be assigned to the M–Br stretching vibration. The disappearance of the band at 185 cm^{-1} (dpso) may be associated with the new band in the spectra of the complexes at 152 (m, UCl_4,4dpso) and 150 cm^{-1} (sh, UBr_4,4dpso). Medium-intensity bands at 268 and 269 cm^{-1} in the respective spectra of these complexes, and very strong bands at 220 and 260 cm^{-1} in the spectrum of the complex UCl_4,3dpso are not assigned, since one cannot be certain which are associated with metal–halogen vibrations and which with M–O vibrations. The thorium, neptunium, and plutonium tetrachloride dpso complexes gave virtually identical spectra to those illustrated for their uranium tetrachloride analogues. The spectra of the complexes exhibited only minor changes relative to that of the free ligand in the region 700—400 cm^{-1}.

Although reasonably reliable metal–halogen assignments can be made for the dmso, deso, and dnso series of complexes (Table 4), it is not possible to identify M–O stretching vibrations in the spectra of these complexes without assuming, for example in the deso complexes, that this band is coincident with the M–Cl vibration. Consequently no M–O assignments were made. Obviously it would be valuable to have structural data for these complexes, particularly since $ThCl_4$,5dmso was recently shown [8a] to be ionic in the solid state, $[ThCl_3,5dmso]^+Cl^-$.

U.v.–Visible Spectra.—Spectra (Table 5 and 6) of the uranium complexes $UCl_4,3R_2SO$ (R = Me, Et, or Ph) in the solid state and in solvents other than the ligand were very similar, indicating that the species present have close structural similarity. Although the solid-state spectrum of UCl_4,4dpso differed somewhat from that of the tris complex, the spectrum of its solution in dichloromethane was the same as that of the tris complex, which indicates dissociation of the tetrakis complex in that solvent.

TABLE 5

Bands (nm) in the u.v.–visible spectra of UCl_4 dmso and deso complexes (400—700 nm)

UCl_4,3dmso			UCl_4,3deso		
	Solution*			Solution*	
Solid	in $MeNO_2$	in dmso	Solid	in CH_2Cl_2	in deso
405	401(3)		404	401(3)	
440					
448	450(13)	441(15)	448	454(18)	443(12)
492	491(11)	494(30)	495	492(10)	493(19)
559	557(6)	560(23)	558	553(4)	561(15)
588			588		
594	592(5)		593	593(6)	
601			600		
637	634(9)			631(7)	
651	651(19)	651(51)	649	650(11)	652(31)
678	677(24)	678(65)	678	671(17)	678(32)

* Absorption coefficients (l mol^{-1} cm^{-1}) in parentheses.

Spectra of the complexes UCl_4,3dmso and UCl_4,3deso in solution in the appropriate ligand differed markedly from those of the solid or solutions in other solvents. The weak bands at *ca.* 401, 592, and 631—634 nm disappeared when the ligand was used as the solvent and there were marked increases in the intensities of the bands at *ca.* 490, 560, 650, and 677 nm. Octahedral uranium(IV) species, such as the UCl_6^{2-} ion,[8b] exhibit weak bands in the region of 400, 590, and 630 nm, as well as a band at *ca.* 450 nm, which also appears in spectra of eight-co-ordinate uranium(IV) species, such as [9] $U(NCS)_4$,4dma (dma = *NN*-dimethylacetamide). It is therefore probable that the bands at 401, 592, and 631—634 nm can be assigned to electronic transitions of a six-co-ordinate uranium(IV) species, and that the increased intensities of the remaining bands are due to an increase in concentration of an eight-co-ordinate uranium(IV) species resulting from the interaction of the six-co-ordinate species with the excess of ligand.

TABLE 6

Bands (nm) in the u.v.–visible spectra of the UCl_4 dpso complexes (400—700 nm)

UCl_4,3dpso		UCl_4,4dpso	
Solid	Solution* in CH_2Cl_2	Solid	Solution* in CH_2Cl_2
	402(3)		402(3)
416			
439	445(8)	435	444(9)
458	455(15)	445	457(16)
498	495(11)	500	493(12)
559	554(6)	562	556(6)
602	593(8)	603	594(8)
648	631(11)	638	632(12)
675	654(21)	653	654(22)
683	672(28)	678	674(30)

* Absorption coefficients (l mol^{-1} cm^{-1}) in parentheses.

The structure of the complex $ThCl_4$,5dmso has now been shown [8a] to be an ion-pair, $[Th(dmso)_5Cl_3]^+Cl^-$. Changes in the visible spectra of the tris dmso complexes on dissolution in dmso become explicable if the tris complex is represented as $[U(dmso)_5Cl_3]^+[U(dmso)Cl_5]^-$ This formulation is consistent with the observed equivalent conductivity of the complex in nitromethane, which increases from 52·1 Ω^{-1} cm^2 $equiv.^{-1}$ for solutions of concentration $1{\cdot}2 \times 10^{-3}$ equiv. l^{-1} to 72·4 Ω^{-1} cm^2 $equiv.^{-1}$ at $7{\cdot}92 \times 10^{-5}$ equiv. l^{-1}, behaviour which might be expected of a 1 : 1 electrolyte with extensive ion-pairing. The excess of ligand molecules would simply displace two more chloride ions from the anion, so converting the tris complex to the known pentakis complex. It is possible that the structures of the corresponding deso and dpso complexes involve similar configurations to the dmso complex, although steric effects may lead to somewhat different arrangements of the ligands.

It is uncertain whether the same considerations apply to the neptunium and plutonium complexes, for in their visible spectra (Table 7) the more intense bands expected to arise from electronic transitions within the six-co-ordinate neptunium(IV) ion (684, 718, 817, 887, 922, and 1 006 nm) can equally well be assigned to transitions

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[8] (*a*) M. B. Hursthouse, personal communication; (*b*) J. L. Ryan, *Inorg. Chem.*, 1964, **3**, 211.

[9] K. W. Bagnall, D. Brown, and R. Colton, *J. Chem. Soc.*, 1964, 2527.

within an eight-co-ordinate neptunium(IV) ion, such as[10] $Np(NCS)_4$,4tmpo, and the same applies to known plutonium(IV) spectra.

TABLE 7

Bands (nm) in the visible–near i.r. spectra of neptunium and plutonium complexes (400—1 300 nm)

$NpCl_4$,3deso Solution* in CH_2Cl_2	$PuCl_4$,3dmso Solid†	$PuCl_4$,2·5deso Solid†	$PuCl_4$,3dpso Solid†
418(7)		452s	
432(11)	458s	462s	
441(8)	472m	488s	
473(4)		496s	494s
482(5)	511m	515m	512s
490(5)		533m	528s
509(9)		541s	542s
523(13)		552m	556s
536(12)	566m	564m	
574(7)	572m	569m	
588(4)	607w	608w	
627(8)	638m	635m	639m
660(9)	661m		
	700s	686s	688s
684(9)	730m	727m	723w
718(22)	760m	747m	753w
759(40)	777m		791s
817(24)		799s	803s
841(20)	822m	818s	
868(18)			854w
887(22)	905m	891m	884w
922(26)		953w	
1 006(15)		1 022w	1 019m
1 212(13)	1 067m		1 067m
1 269(8)		1 093m	1 092s
	1 118m	1 128s	1 151m

* Absorption coefficients ($l\ mol^{-1}\ cm^{-1}$) in parentheses. † Relative intensities, s = strong, m = medium, and w = weak.

EXPERIMENTAL

The complexes were prepared and handled in inert (nitrogen or argon) atmosphere dry-boxes because of the hygroscopic nature of the actinoid tetrachlorides (Th, U, or Np) and also because of the radioactive hazards associated with the α-emitting nucleides ^{237}Np and ^{239}Pu used in this work.

Materials.—Thorium,[11,12] uranium,[13] and neptunium[14] tetrachlorides, UCl_4,3dmso,[2] and the hexachlorometallate(IV) complexes[15] $Cs_2[MCl_6]$ were prepared by published methods. The ligands dmso and dpso were obtained commercially from B.D.H. Ltd. and Ralph N. Emmanuel Ltd., respectively; deso was prepared by the oxidation of the sulphide with sodium periodate[16] and dnso was prepared by reaction of (1-naphthyl)magnesium bromide with thionyl chloride and recrystallised from chloroform.[1] All organic solvents, dmso, and deso were distilled, freed from dissolved oxygen by purging with nitrogen, and stored over molecular sieves (type 5A).

Diethyl Sulphoxide (*deso*) *Complexes.*—deso (0·54 cm³, 6·65 mmol) was added to a hot solution of anhydrous thorium tetrachloride (356·9 mg, 0·95 mmol) in ethyl acetate (2 cm³) with stirring. The oil that separated on cooling was left in contact with the supernatant liquid for 14 days, and the white, hygroscopic crystalline *product*, $ThCl_4$,4deso, was vacuum dried (10^{-4} Torr) for 10 h (yield 90%). A similar procedure, but with a smaller excess of ligand (deso 0·18 cm³, 2·23 mmol; $ThCl_4$ 164·6 mg, 0·44 mmol) yielded an oil which, when washed with ethyl acetate (1 cm³) and ground under ethyl acetate, yielded white, hygroscopic *crystals* of $ThCl_4$,3deso. These were washed with ethyl acetate (1 cm³) and vacuum dried as before (yield 90%). The complex UCl_4,3deso was prepared from deso (0·4 cm³, 4·96 mmol) and the tetrachloride (478·7 mg, 1·26 mmol) in acetone; the complex separated on setting aside at 0 °C (yield 80%). Alternatively, deso (0·61 cm³, 7·56 mmol) was added to a suspension of $Cs_2[UCl_6]$ (768·2 mg, 1·07 mmol) in acetone (2 cm³) and the mixture was boiled for 10 min. The hot solution of the complex was separated from the precipitated caesium chloride, which was washed with acetone and the washings were combined with the filtrate. The complex separated, as before, on setting aside at 0 °C. In both cases the crystals were washed with 2-methylbutane (2 cm³) and vacuum dried (10^{-4} Torr) for 3 h (yield 75%).

The neptunium complex was prepared from $Cs_2[NpCl_6]$ in the same way but did not crystallise out on setting aside; a pink oil was precipitated when 2-methylbutane was added to the acetone solution. This oil was dissolved in dichloromethane and slow evaporation of the solution yielded pink crystals of the *complex* $NpCl_4$,3deso, which were vacuum dried as above (yield 82%). When the pink oil produced as a primary product was triturated with carbon tetrachloride (1 cm³), a pink solid *product* of composition close to $NpCl_4$,2·5deso resulted (yield 65%). This procedure gave the *complex* β-$PuCl_4$,2·5deso (yield 80%) as product of the reaction between deso and $Cs_2[PuCl_6]$ in acetone; this product was recovered unchanged when treated with boiling ethyl acetate. When dichloromethane (2 cm³) and 2-methylbutane (5 cm³) were added to the initial acetone solution of the product of reaction between deso and $Cs_2[PuCl_6]$, to which the methyl cyanide washings of the residual caesium chloride had been added, a brown oil separated which, when crystallised from acetone, yielded the crystallographically distinct *complex* designated α-$PuCl_4$,2·5deso (yield 60%). The two products were washed with acetone (0·5 cm³) and carbon tetrachloride (1 cm³) respectively, and vacuum dried (10^{-4} Torr) for 8—10 h.

Diphenyl Sulphoxide (*dpso*) *Complexes.*—A solution of dpso (299·8 mg, 1·48 mmol) in nitromethane (2 cm³) was added to a solution of anhydrous thorium tetrachloride (184·7 mg, 0·49 mmol) in the same solvent. The complex $ThCl_4$,4dpso was precipitated as a white, non-hygroscopic, crystalline solid. The crystals were washed with nitromethane (2 × 2 cm³) and vacuum dried (5×10^{-5} Torr) for 1 day (yield, based on dpso, 90%). Alternatively, a solution of thorium tetrachloride (209·6 mg, 0·56 cm³) in 6M-HCl (2 cm³) was added to a hot solution of dpso (340·3 mg, 1·68 mmol) in the same solvent (2 cm³) and the mixture was heated on a water-bath. The precipitated complex $ThCl_4$,4dpso was washed with 6N-HCl (2 × 3 cm³) or with methyl cyanide, followed by 2-methylbutane, and vacuum dried (10^{-4} Torr) for 24 h (yield, based on dpso, 90%). The complex was recovered unchanged when recrystallised from acetone or treated with benzene at room temperature. The complex UCl_4,4dpso

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was prepared in the same way from 6M-HCl (yield 73%). The neptunium *complex* $NpCl_4$,dpso (yield 90%) and the plutonium *complex* $PuCl_4$,3dpso (yield 85%) were prepared by adding 6M-HCl (1 cm^3) to a mixture of dpso and the solid hexachlorometallate(IV) complex $Cs_2[MCl_6]$. After heating for 10 min, the precipitated complexes were left in contact with 6M-HCl for 3 days, washed with 6M-HCl (2 × 5 cm^3), and vacuum dried (10^{-4} Torr) for 1 day. The ligand dpso was not completely soluble in the quantities of acid that were used and when hot the mixture tended to separate into two layers, comprising a solution of dpso in aqueous acid and dpso as an oil.

The complex UCl_4,3dpso separated on setting aside from the dark green solution obtained by heating nitromethane (5 cm^3) with a mixture of uranium tetrachloride (399·6 mg, 1·05 mmol) and dpso (1·083 g, 5·35 mmol). The crystals were washed with nitromethane (5 cm^3) and vacuum dried (10^{-4} Torr) for 1 day (yield 90%). The neptunium analogue was prepared by adding a hot solution of the tetrachloride (104·2 mg, 0·28 mmol) in nitromethane (5 cm^3) to dpso (166·9 mg, 0·83 mmol); the solution was centrifuged and the supernatant liquid was vacuum evaporated to 0·5 cm^3, whereupon red crystals of the tris *complex* separated. These were washed with nitromethane (2 × 0·5 cm^3) and vacuum dried as above (yield 90%).

Di(1-naphthyl) Sulphoxide (dnso) Complexes.—The complex $ThCl_4$,3dnso was precipitated on addition, with stirring, of dnso (373·8 mg, 1·24 mmol) in hot ethyl acetate (10 cm^3) to a solution of thorium tetrachloride (154·0 mg, 0·41 mmol) in the same solvent. The non-hygroscopic *complex* was washed with ethyl acetate (2 × 2 cm^3) and vacuum dried (yield 70%). The analogous uranium complex was obtained by heating a mixture of the tetrachloride (489·9 mg, 1·29 mmol) and dnso (1·170 g, 3·87 mmol) with nitromethane (7 cm^3). A green, oily product separated at 0 °C which yielded a green, non-hygroscopic solid when set aside under 2-methylbutane for 3 days. The *product* was washed with 2-methylbutane (2 cm^3) and vacuum dried (yield 71%). Attempted preparation of the complex $NpCl_4$,3dnso from nitromethane solutions of the components yielded pale brown products of composition from $NpCl_4$,2·7dnso to $NpCl_4$,3·6dnso. Treatment of the ligand-rich products (which, from the i.r. spectra, contained free ligand) with hot ethyl acetate reduced the ligand content to $NpCl_4$,2·7dnso (yield 80%). This is presumably a mixture of the tris complex with a second complex containing less ligand, as all the ligand is co-ordinated.

The complex UCl_4,3dnso was also obtained when the tetrachloride (373·8 mg, 0·98 mmol) in 6—9M-HCl (2 cm^3) was added to dnso (1·191 g, 3·94 mmol) in warm dichloromethane (5 cm^3). Acetone (2 cm^3) was added to render the two phases partially miscible; this procedure is necessary because the ligand is almost insoluble in 6—9M-HCl. The mixture was heated on a water-bath, which removed the organic solvents, and the resulting green gum yielded the crystalline *complex* when washed with acetone–2-methylbutane (1 : 3 v/v), followed by 2-methylbutane (yield 60%). The same procedure with neptunium(IV) and plutonium(IV) in aqueous hydrochloric acid was unsuccessful.

Uranium Bromide Complexes.—The complexes UBr_4,8dmso, UBr_4,4dpso,[1] and UBr_4,5deso were precipitated when the appropriate ligand, dissolved in ethyl acetate, was added to a solution of uranium tetrabromide in the same solvent. The precipitates were vacuum dried (yields ranged from 30 to 40%). The complex UBr_4,8dmso degrades to the known [17] hexakis complex when stored under carbon tetrachloride.

Analyses.—Thorium and uranium were weighed as ThO_2 and U_3O_8, respectively, after ignition of the hydroxides obtained by hydrolysing the complexes with an aqueous acetone solution of ammonia. Neptunium and plutonium were determined by α-assay of aliquot portions of a solution prepared by dissolving the hydroxide in dilute nitric acid [specific activity $^{237}Np = 1·562 \times 10^6$ α-disintegrations mg^{-1} min^{-1}; Pu (calculated from isotopic analysis of the sample used) $= 1·739 \times 10^8$ α-disintegrations mg^{-1} min^{-1}]. Hydrolysis of the dpso and dnso complexes produced organic material insoluble in the alkaline medium. This did not affect the thorium and uranium determinations since combustion was complete, but it affected the analyses for neptunium and plutonium, preventing complete dissolution of the hydroxides of these two elements. The organic material was therefore leached from the precipitated hydroxides by washing them with large quantities of acetone. Halide (X) in the supernatant solution was precipitated and weighed as AgX. Carbon, hydrogen, and sulphur (selected thorium and uranium complexes only) were determined by combustion. The analytical results are summarised in Tables 8 and 9.

TABLE 8

Analytical results

	Found (%)		Calc. (%)		
Complex	M	Halogen	M	Halogen	M.p.(t/°C)
UBr_4,8dmso	20·5	27·5	20·9	27·7	
UBr_4,6dmso	23·3	31·0	23·8	31·6	
UBr_4,5deso	22·8	29·5	21·9	29·4	
$ThCl_4$,4deso	29·6	17·5	29·1	17·8	
$ThCl_4$,3deso	33·5	20·3	33·5	20·5	
UCl_4,3deso	34·0	20·2	34·1	20·2	110 *
$NpCl_4$,3deso	33·3	20·9	33·9	20·3	
$NpCl_4$,2·5deso	37·7	22·6	36·8	22·1	
α-$PuCl_4$,2·5deso	36·8	22·4	37·0	21·9	
β-$PuCl_4$,2·5deso	37·2	22·2	37·0	21·9	
$ThCl_4$,4dpso †	19·5	11·8	19·6	12·0	195d
UCl_4,4dpso	20·3	12·1	20·0	11·9	120d
UBr_4,4dpso	18·0	23·3	17·4	23·4	
$NpCl_4$,4dpso	20·0	12·0	20·0	11·9	
UCl_4,3dpso	24·1	14·4	24·1	14·4	114d
$NpCl_4$,3dpso	24·1	14·1	24·0	14·4	
$PuCl_4$,3dpso	23·5	14·2	24·2	14·4	
$ThCl_1$,3dnso	17·8	10·7	18·1	11·1	167
UCl_4,3dnso	18·7	10·9	18·5	11·0	109d
'$NpCl_4$,3dnso' ‡	19·6	11·7	18·4	11·0	

d = With decomposition ($U^{IV} \longrightarrow U^{VI}$ in the case of uranium complexes).

* Oxidised to U^{VI} at 125 °C. † Prepared from 6M-HCl. ‡ Analyses close to $NpCl_4$, 2·7dnso.

TABLE 9

Carbon, hydrogen, and sulphur analyses

	Found (%)			Calc. (%)		
Complex	C	H	S	C	H	S
UCl_4,3deso	20·3	4·3	13·8	20·6	4·3	13·8
UCl_4,3dpso	43·6	2·9	10·0	43·8	3·0	9·8
UCl_4,4dpso	47·7	3·2	10·8	48·5	3·4	10·8

Physical Measurements.—I.r. spectra were recorded with Infrascan, Perkin-Elmer PE421, 257 or 157 spectrometers (4 000—625 cm^{-1}) with samples mounted as mulls in Nujol, hexachlorobutadiene, or Fluorolube between potassium

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bromide or sodium chloride plates. A Grubb–Parsons DM4 spectrometer was used for spectra in the range 680—225 cm^{-1}; spectra in the range below 225 cm^{-1} were recorded with a Beckmann IR 11 spectrometer by Mr. P. J. Jones of Southampton University using Nujol mulls mounted between Polythene plates. Visible and near i.r. spectra (400—1 300 nm) were recorded using a Carey 14 spectrophotometer with samples as solutions in 1 cm silica cells or as solids in the form of mulls in Voltalef 901 grease between silica plates.[18] Visible transmission spectra in solution (400—800 nm) were recorded using SP 200 or PE 402 spectrophotometers. Solid reflectance spectra (400—800 nm) were recorded using a Beckmann DK2a spectrophotometer. For all spectral studies samples of radioactive materials were enclosed in Perspex boxes, fitted with the appropriate windows. *X*-Ray powder diffraction patterns were obtained using either Debye–Scherrer 19 or 11 cm cameras, or a Guinier focussing camera, with filtered Cu-K_α radiation ($\lambda_{\alpha_1} = 1{\cdot}5405$ Å). Conductivities were determined for nitromethane solutions of the complexes using a cell with platinum electrodes and a Philips conductivity bridge PR 9500.

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