Phosphine Oxide and Sulphoxide Complexes of Thorium(IV) and Uranium(IV) Halogenoacetates

Kenneth W. Bagnall,* Omar Velasquez Lopez, and Li Xing-fu
Chemistry Department, The University of Manchester, Manchester M13 9PL

Complexes of thorium(IV) and uranium(IV) carboxylates with phosphine oxides and sulphoxides of the types $M(O_2CR)_4 \cdot nL$ [n = 4, M = Th or U, L = Me_2SO (dmso), R = CF_3 and L = PMe_3O (tmpo), R = CCl_3 or $CHCl_2$; M = U, L = tmpo, R = CF_3; n = 3, M = Th, L = tmpo, R = CF_3 and L = PPh_3O (tppo) or dmso, R = CCl_3; M = U, L = tppo, R = CF_3 and L = dmso or Ph_2SO (dpso), R = CCl_3; n = 2, M = Th, L = tppo, R = CF_3 or $CHCl_2$ and L = dpso, R = CF_3 or CCl_3; M = U, L = dpso, R = CF_3 and L = tppo, R = CCl_3 or $CHCl_2$; n = 1, M = Th or U, L = dmso, R = $CHCl_2$] have been prepared. The i.r. and u.v.–visible spectra [uranium(IV) complexes only] of these compounds are reported and the effects of steric crowding on the possible bonding arrangements of the carboxylate groups in the complexes are discussed in terms of a cone angle approach to steric crowding about the central metal ions.

Amide complexes of thorium(IV) and uranium(IV) carboxylates have been reported,[1] and subsequently the preparation of bis-pyridine, -pyridine *N*-oxide and -triphenylphosphine oxide complexes of thorium(IV) trichloroacetate has been described.[2] In order to investigate the effects of steric crowding on the mode of bonding of the carboxylate group (bidentate, bridging, or unidentate) in complexes of the halogenoacetates, it was of interest to prepare a series of phosphine oxide and sulphoxide complexes of thorium(IV) and uranium(IV) trifluoro-, trichloro-, and dichloro-acetates, and to correlate the results by applying the cone angle approach to steric crowding which was described briefly in a recent paper.[3]

Results and Discussion

Preparation of the Complexes.—Although the halogenoacetates are insoluble in dichloromethane, they dissolve in the presence of PMe_3O (tmpo), PPh_3O (tppo), Me_2SO (dmso), or Ph_2SO (dpso) and addition of n-pentane to the resulting solution yields the appropriate complexes, the compositions of which depend on the ligand and the halogenoacetate. Thus the smallest ligand, dmso, formed tetrakis complexes with thorium(IV) and uranium(IV) trifluoroacetates, as did tmpo with the dichloro- and trichloro-acetates of both elements, and with uranium(IV) trifluoroacetate, whereas, surprisingly, thorium(IV) trifluoroacetate formed only a tris complex with tmpo. With the larger ligand, tppo, tris complexes were obtained with thorium(IV) trichloro- and uranium(IV) trifluoro-acetates, whereas bis complexes were formed with thorium(IV) trifluoro- and uranium(IV) trichloro-acetates and with the dichloroacetates of both elements; tris dmso complexes were also obtained for both trichloroacetates, although only mono dmso complexes were isolated for the dichloroacetates of the two elements. In the case of dpso, a tris complex was obtained for uranium(IV) trichloroacetate, but bis complexes were formed with both trifluoroacetates and with thorium(IV) trichloroacetate. These stoicheiometries do not appear to be related in any simple way to the bulk of the ligand and that of the halogenoalkyl group of the acid. All of the thorium complexes are white and their uranium analogues are green.

Infrared Spectra.—In all cases the shift in ν(X=O) (for X = P or S) of the ligand on complexation was quite large, and in some cases the features assigned to this mode were split into two or three components (Table 2). Thus, in the tppo complexes, both strongly [$\Delta\nu$(P=O) over 120 cm^{-1}] and weakly bonded [$\Delta\nu$(P=O) 45 to 65 cm^{-1}] ligand is present, whereas in the spectra of the tmpo complexes ν(P=O) appears as a single feature except for the spectrum of $Th(O_2CCF_3)_4 \cdot 3tmpo$ which exhibits features indicating strongly [$\Delta\nu$(P=O) 60 cm^{-1}] and weakly bonded [$\Delta\nu$(P=O) 20 cm^{-1}] tmpo. In the spectra of the sulphoxide complexes ν(S=O) was always a single feature, and $\Delta\nu$(S=O) was smaller for the dpso complexes than for their dmso analogues, which may indicate stronger bonding of the latter ligand. This may be correlated with the faster reaction of dmso with the carboxylates than was the case with dpso. It was also found that the latter did not react with thorium(IV) or uranium(IV) dichloroacetate, whereas dmso formed 1 : 1 complexes with both.

The frequencies assigned to ν_{asym}(OCO) in the i.r. spectra of the complexes are substantially greater than those reported[4] for the sodium salts of the carboxylic acids, and both ν_{asym}(OCO) and ν_{sym}(OCO) show a considerable degree of splitting in the cases of the spectra recorded as mulls of the solids, apart from those of the tmpo complexes. It has been suggested[5] that splittings of the order of 30 cm^{-1} in the (OCO) stretching modes might arise from vibrational coupling in the solid state, which might be circumvented by recording solution spectra. Spectra were obtained for several of the complexes in solution in chloroform (Table 2), and the degree of splitting was nearly always less than that observed for solid mulls.

The differences between the frequencies of ν_{asym}(OCO) and ν_{sym}(OCO) (Table 2) do not provide a reliable diagnostic guide to the bonding mode (unidentate, bidentate, bridging, or ionic) of the carboxylate group,[6] although the values of these differences appear to fall into two groups, one in the range 137—193 cm^{-1} for compounds in which bridging carboxylate may be present, and the other 245—315 cm^{-1} for compounds in which the presence of unidentate carboxylate is suspected.[1] However, the degree of splitting of these features shown in the spectra of the complexes reported here makes it uncertain as to whether the frequencies of the two modes have been correctly paired, and no firm inferences can be drawn from them. In the case of the trifluoroacetates, it has been shown[6] that values of ν_{asym}(OCO) for the unidentate carboxylate group appear in the range 1 692—1 720 cm^{-1} in the i.r. spectra of metal complexes, whereas for the bridging or bidentate carboxylate group this mode appears in the range 1 592—1 660 cm^{-1} and in alkali metal salts in the range 1 667—1 678 cm^{-1}. On these criteria, all the complexes of the thorium(IV) and uranium(IV) trifluoroacetates evidently con-

Table 1. Analytical results (%) [a]

Complex	Metal	C	H	Halogen	P or S	Yield (%)
$Th(O_2CCF_3)_4\cdot 3tmpo$	23.0 (24.2)	21.0 (21.3)	2.7 (2.8)		8.4 (9.7)	47
$U(O_2CCF_3)_4\cdot 4tmpo$	23.0 (22.5)	22.5 (22.7)	3.3 (3.4)		11.5 (11.7)	51
$Th(O_2CCCl_3)_4\cdot 4tmpo$	17.9 (18.6)	18.6 (19.2)	2.9 (2.9)		9.8 (9.9)	45
$U(O_2CCCl_3)_4\cdot 4tmpo$	19.3 (19.0)	19.7 (19.1)	3.5 (2.9)		10.3 (9.9)	59
$Th(O_2CCHCl_2)_4\cdot 4tmpo$	20.0 (20.8)	21.2 (21.6)	3.4 (3.6)		9.8 (11.2)	41
$U(O_2CCHCl_2)_4\cdot 4tmpo$	22.7 (21.3)	20.6 (21.5)	3.3 (3.6)	25.6 (25.4)	11.0 (11.1)	54
$Th(O_2CCF_3)_4\cdot 2tppo$	17.6 (18.7)	42.7 (42.6)	2.7 (2.4)		4.3 (5.0)	59
$U(O_2CCF_3)_4\cdot 3tppo$	16.1 (15.6)	48.2 (48.8)	2.5 (3.0)		6.0 (6.1)	55
$Th(O_2CCCl_3)_4\cdot 3tppo$	13.6 (13.5)	43.3 (43.4)	2.7 (2.6)		5.5 (5.4)	52
$U(O_2CCCl_3)_4\cdot 2tppo$	16.8 (16.5)	38.1 (36.6)	2.3 (2.1)	30.4 (29.5)	4.7 (4.3)	56
$Th(O_2CCHCl_2)_4\cdot 2tppo$	16.5 (17.9)	39.3 (40.6)	2.7 (2.6)		4.5 (4.8)	45
$U(O_2CCHCl_2)_4\cdot 2tppo$	17.9 (18.2)	39.4 (40.4)	2.4 (2.6)	22.3 (21.7)	4.7 (4.75)	47
$Th(O_2CCF_3)_4\cdot 4dmso$	23.0 (23.3)	18.8 (19.3)	2.2 (2.4)		12.3 (12.8)	65
$U(O_2CCF_3)_4\cdot 4dmso$	24.3 (23.8)	18.9 (19.2)	2.4 (2.4)		12.2 (12.8)	72
$Th(O_2CCCl_3)_4\cdot 3dmso$	21.2 (20.8)	14.7 (15.1)	1.5 (1.6)		8.6 (8.6)	42
$U(O_2CCCl_3)_4\cdot 3dmso$	22.3 (21.2)	14.9 (15.0)	1.5 (1.6)	36.5 (37.9)	7.2 (8.6)	58
$Th(O_2CCHCl_2)_4\cdot dmso$	28.5 (28.2)	14.7 (14.6)	1.2 (1.2)		3.9 (3.9)	48
$U(O_2CCHCl_2)_4\cdot dmso$	28.3 (28.8)	14.5 (14.5)	1.1 (1.2)	33.9 (34.3)	3.8 (3.9)	56
$Th(O_2CCF_3)_4\cdot 2dpso$	22.0 (21.3)	35.8 (35.3)	1.6 (1.8)		5.8 (5.9)	53
$U(O_2CCF_3)_4\cdot 2dpso$	22.8 (21.8)	35.6 (35.1)	2.0 (1.8)	21.2 (20.8)	6.0 (5.8)	66
$Th(O_2CCl_3)_4\cdot 2dpso$	18.2 (18.0)	29.2 (29.9)	1.5 (1.6)		4.8 (5.0)	41
$U(O_2CCl_3)_4\cdot 3dpso$	16.6 (15.9)	34.6 (35.4)	1.9 (2.0)	28.7 (28.5)	6.3 (6.4)	61

[a] Calculated values in parentheses.

Table 2. Infrared spectra (cm^{-1}) of the halogenoacetate complexes

Complex $X = O_2CCF_3$	$\nu_{asym}(OCO)$	$\nu_{sym}(OCO)$	$\nu_{asym}(OCO) - \nu_{sym}(OCO)$	$\delta(OCO)$	$\pi(OCO)$	$\rho(OCO)$	$\nu_{X=O}$	$\Delta\nu_{X=O}$ [a]
$ThX_4\cdot 2tppo$	1 730vs	1 475s	255	790s	615m	521m	1 140,	50,
	1 635s	1 410vs	225	725vs	600m		1 070	120
$UX_4\cdot 3tppo$	1 705vs	1 485w	220	795m	615vw	520m	1 140,	50,
	1 630m	1 400vs	230	788m	600w		1 050	140
				780m				
				730vs				
$UX_4\cdot 3tppo$ [b]	1 705vs	1 420m (sh)	285				1 140,	50,
		1 360s	(345)				1 050	140
$ThX_4\cdot 3tmpo$	1 750vs	1 470s	280	793s	610w	522w	1 140,	20,
	1 700vs	1 405m	295	720s	595w (sh)		1 100	60
	1 680vs		(275)					
$UX_4\cdot 4tmpo$	1 680vs	1 420vs	260	795vs	675m	520m	1 100	60
				719vs	600m			
$UX_4\cdot 4tmpo$ [b]	1 680vs	1 410vs	270					
$ThX_4\cdot 4dmso$	1 690vs, br	1 410vs	280	720vs	600s	520s	990	66
	1 580m (sh)	1 320m	260	790vs				
$UX_4\cdot 4dmso$	1 720s (sh)	1 410vs	310	790vs	600s	520m	990	66
	1 700vs	1 400vs	300	719vs				
	1 580m (sh)	1 315m	265					
$ThX_4\cdot 2dpso$	1 770s (sh)	1 470m	300	790s	605m	520m	980	58
	1 730s (sh)	1 400m	230	721s				
	1 700s (sh)		(300)					
	1 665vs		(265)					
$ThX_4\cdot 2dpso$ [b]	1 680vs	1 480m	200					
		1 420m	(260)					
$UX_4\cdot 2dpso$	1 730vs (sh)	1 475s	255	800s	610m	520m	975	63
	1 700vs	1 395s	305	790s	600m	510m		
	1 620s (sh)		(225)	720s				
$UX_4\cdot 2dpso$ [b]	1 680vs	1 475m	205					
		1 400m	(280)					
$X = O_2CCCl_3$								
$ThX_4\cdot 3tppo$	1 710vs	1 390s	320	725s		465m	1 130,	60,
	1 695vs	1 310vs	385	690s			1 065	125
	1 640vs	1 285vs	355					
$UX_4\cdot 2tppo$	1 710vs	1 390vs	320	728vs		480w	1 125,	65,
	1 622s	1 295vs	327	685vs			1 062	128
	1 610s		(315)					
$UX_4\cdot 2tppo$ [b]	1 710s	1 390vs	320					
	1 618s	1 290m	328					

Table 2 (*continued*)

Complex X = O_2CCCl_3	ν_{asym}(OCO)	ν_{sym}(OCO)	ν_{asym}(OCO) − ν_{sym}OCO)	δ(OCO)	π(OCO)	ρ(OCO)	$\nu_{X=O}$	$\Delta\nu_{X=O}$ [a]
$ThX_4\cdot$4tmpo	1 685vs	1 350m	335	725vs		450m	1 105	55
				675vs				
$UX_4\cdot$4tmpo	1 675vs	1 335vs	340	675m	620w	480m	1 100	60
$UX_4\cdot$4tmpo [b]	1 660vs	1 340s	320					
$ThX_4\cdot$3dmso	1 710vs	1 370vs	340	760vs		480m	980	76
	1 675m	1 295vs	380	725s				
	1 628vs		(333)					
$ThX_4\cdot$3dmso [b]	1 690vs	1 385s	305					
	1 625m (sh)	1 320s	305					
$UX_4\cdot$3dmso	1 710vs	1 380s (sh)	330	760vs	540w, br	480vs	1 005	51
	1 625vs	1 350vs	275	721vs				
		1 270vs	(355)					
$UX_4\cdot$3dmso [b]	1 710s (sh)	1 380vs	330					
	1 665vs		(285)					
$ThX_4\cdot$2dpso	1 720vs	1 380vs	340	765vs	655m (sh)	510m	980	58
	1 690vs	1 300vs	390	725vs				
	1 615vs		(315)					
$ThX_4\cdot$2dpso [b]	1 660vs	1 390vs	270					
	1 615m (sh)	1 300m	315					
$UX_4\cdot$3dpso	1 705vs	1 380s	325	770s	665m (sh)	505vw	970	68
	1 680s	1 290vs	390	721s				
	1 630vs		(340)					
$UX_4\cdot$3dpso [b]	1 665vs	1 380vs	285					
X = O_2CCHCl_2								
$ThX_4\cdot$2tppo	1 690vs	1 425s	265	725vs		470w	1 145	45
	1 655vs	1 395s	260	670m			1 130	60
	1 592s	1 330s	262				1 070	120
$UX_4\cdot$2tppo	1 700vs	1 415vs	285	725vs		440m	1 135	55
	1 605vs	1 315vs	290				1 060	130
	1 585vs		(270)					
$UX_4\cdot$2tppo [b]	1 700vs	1 415vs	285					
	1 635s	1 350vs	285					
	1 595m		(245)					
$ThX_4\cdot$4tmpo	1 670vs	1 340s	330	718vs		460w	1 100	60
	1 600m		(260)	675w				
$UX_4\cdot$4tmpo	1 650vs	1 340vs	310	710m		460w	1 100	60
	1 605s (sh)		(265)	675m, br				
$UX_4\cdot$4tmpo [b]	1 665vs	1 330vs	335					
	1 605s (sh)		(275)					
$ThX_4\cdot$dmso	1 690m	1 405s	285	730m		468w	1 005	51
	1 610s (sh)		(205)					
	1 580vs		(175)					
$ThX_4\cdot$dmso [b]	1 610m	1 420m	190					
$UX_4\cdot$dmso	1 690s	1 398s	292	735s		465s	995	59
	1 608s (sh)	1 320w	288	725s				
	1 580vs		(260)					

[a] X = P or S. [b] Solution in chloroform.

tain unidentate carboxylate groups, and in most of them bidentate or bridging carboxylate groups are also present.

In an attempt to investigate this further, the recently described[3] cone angle factor (c.a.f.) approach to steric crowding was applied to the new complexes of all of the carboxylates. The calculated values of Σ c.a.f. for seventeen uranium(IV) compounds, all of known structure, indicate[3] that the average value is 0.80 (σ = 0.03) and that for values of Σ c.a.f. lower than 0.77 secondary crowding, such as that caused by bulky groups R in phosphine oxides PR_3O (*e.g.* R = C_6H_5 or Me_2N), is necessary to achieve the formation of a stable complex. As a first-order approximation for the carboxylate complexes, the values of c.a.f. for unidentate and bidentate (or bridging) carboxylate groups were calculated, using the procedure outlined previously,[3] to be 0.09 and 0.18 respectively, and that for the neutral donor ligand (sulphoxide or phosphine oxide) is 0.10 (for thorium) and 0.11 (for uranium). The results for the complexes are summarised in Table 3, which shows the values of Σ c.a.f. for all possibilities of bonding of the carboxylate groups; these are expressed graphically in Figures 1 and 2.

It can be seen from Table 3 that in the tetrakis complexes $U(O_2CR)_4\cdot4L$, where L = tmpo with R = CF_3, CCl_3, or $CHCl_2$, and L = dmso, with R = CF_3, the carboxylate groups are all unidentate (Σ c.a.f. = 0.80), whereas in the thorium compounds, $Th(O_2CR)_4\cdot4L$, where L = tmpo with R = CCl_3 or $CHCl_2$ and L = dmso with R = CF_3, the carboxylate groups are probably all unidentate, but there could be three unidentate groups and one bidentate or bridging group. Similarly, for the tris complexes $U(O_2CR)_4\cdot3L$, where L = tppo with R = CF_3, and L = dpso or dmso with R = CCl_3, there are probably three unidentate carboxylate groups and one bidentate (or bridging), and in the thorium complexes $Th(O_2CR)_4\cdot3L$, where L = tmpo with R = CF_3 and L = tppo or dmso with R = CCl_3, there could be either equal numbers of unidentate and bidentate (or bridging) carboxylate groups, or three unidentate groups and one bidentate; the latter would probably be favoured for Th(O_2-

Table 3. Calculated values of Σ c.a.f.*

Complex	Bidentate or bridging : unidentate carboxylate groups					Co-ordination number	Σ c.a.f.
	4 : 0	3 : 1	2 : 2	1 : 3	0 : 4		
Th(O$_2$CCF$_3$)$_4$·2tppo	(0.92, CN10)		S.R.	(0.65, CN7)	(0.56, CN6)	8	0.74
		S.R.				9	0.83
Th(O$_2$CCF$_3$)$_4$·3tmpo	(1.02, CN11)	(0.93, CN10)		S.R.	(0.66, CN7)	8	0.75
			S.R.			9	0.84
Th(O$_2$CCCl$_3$)$_4$·3tppo	(1.02, CN11)	(0.93, CN10)		S.R.	(0.66, CN7)	8	0.75
			S.R.			9	0.84
Th(O$_2$CCCl$_3$)$_4$·4tmpo	(1.12, CN12)	(1.03, CN11)	(0.94, CN10)		S.R.	8	0.76
				S.R.		9	0.85
Th(O$_2$CCHCl$_2$)$_4$·2tppo	(0.92, CN10)		S.R.	(0.65, CN7)	(0.56, CN6)	8	0.74
		S.R.				9	0.83
Th(O$_2$CCHCl$_2$)$_4$·4tmpo	(1.12, CN12)	(1.03, CN11)	(0.94, CN10)		S.R.	8	0.76
				S.R.		9	0.85
Th(O$_2$CCF$_3$)$_4$·4dmso	(1.12, CN12)	(1.03, CN11)	(0.94, CN10)		S.R.	8	0.76
				S.R.		9	0.85
Th(O$_2$CCF$_3$)$_4$·2dpso	(0.92, CN10)		S.R.	(0.65, CN7)	(0.56, CN6)	8	0.74
		S.R.				9	0.83
Th(O$_2$CCCl$_3$)$_4$·3dmso	(1.02, CN11)	(0.93, CN10)		S.R.	(0.66, CN7)	8	0.75
			S.R.			9	0.84
Th(O$_2$CCCl$_3$)$_4$·2dpso	(0.92, CN10)		S.R.	(0.65, CN7)	(0.56, CN6)	8	0.74
		S.R.				9	0.83
Th(O$_2$CCHCl$_2$)$_4$·dmso	S.R.	(0.73, CN8)	(0.64, CN7)	(0.55, CN6)	(0.46, CN5)	9	0.82
U(O$_2$CCF$_3$)$_4$·3tppo	(1.05, CN11)	(0.96, CN10)	(0.87, CN9)	S.R.	(0.69, CN7)	8	0.78
U(O$_2$CCF$_3$)$_4$·4tmpo	(1.16, CN12)	(1.07, CN11)	(0.98, CN10)	(0.89, CN9)	S.R.	8	0.80
U(O$_2$CCl$_3$)$_4$·2tppo	(0.94, CN10)		S.R.	(0.67, CN7)	(0.58, CN6)	8	0.76
		S.R.				9	0.85
U(O$_2$CCCl$_3$)$_4$·4tmpo	(1.16, CN12)	(1.07, CN11)	(0.98, CN10)	(0.89, CN9)	S.R.	8	0.80
U(O$_2$CCHCl$_2$)$_4$·2tppo	(0.94, CN10)		S.R.	(0.67, CN7)	(0.58, CN6)	8	0.76
		S.R.				9	0.85
U(O$_2$CCHCl$_2$)$_4$·4tmpo	(1.16, CN12)	(1.07, CN11)	(0.98, CN10)	(0.89, CN9)	S.R.	8	0.80
U(O$_2$CCF$_3$)$_4$·2dpso	(0.94, CN10)		S.R.	(0.67, CN7)	(0.58, CN6)	8	0.76
		S.R.				9	0.85
U(O$_2$CCF$_3$)$_4$·4dmso	(1.16, CN12)	(1.07, CN11)	(0.98, CN10)	(0.89, CN9)	S.R.	8	0.80
U(O$_2$CCCl$_3$)$_4$·3dpso	(1.05, CN11)	(0.96, CN10)	(0.87, CN9)	S.R.	(0.69, CN7)	8	0.78
U(O$_2$CCCl$_3$)$_4$·3dmso	(1.05, CN11)	(0.96, CN10)	(0.87, CN9)	S.R.	(0.69, CN7)	8	0.78
U(O$_2$CCHCl$_2$)$_4$·dmso		S.R.	(0.65, CN7)	(0.56, CN6)	(0.47, CN5)	8	0.74
	S.R.					9	0.83

* CN = Coordination number. S.R. = Stable region.

CCl$_3$)$_4$·3tppo. In all the bis complexes, M(O$_2$CR)$_4$·2L, there appears to be an equal likelihood of there being either three bidentate carboxylate groups and one unidentate, or two bidentate and two unidentate, whereas in the complexes M(O$_2$CCHCl$_2$)$_4$·dmso (M = Th or U) the probability is that all four carboxylate groups are bidentate or bridging, although it is quite possible that the ratio of bidentate to unidentate carboxylate groups is 3 : 1, which would be consistent with the i.r. spectra.

Electronic Spectra.—The visible and near-i.r. spectra of the uranium(IV) carboxylate–phosphine oxide complexes were recorded by diffuse solid reflectance and as solution spectra [U(O$_2$CCF$_3$)$_4$·4tmpo only] in chloroform. The spectra were characteristic of U^{IV} in an environment of high co-ordination number (≥ 8) and were of no assistance in determining the symmetry of the environment of the uranium atom.

^{19}F *N.M.R. Spectra.*—The spectrum of U(O$_2$CCF$_3$)$_4$·4tmpo at −30 °C (243 K) in CDCl$_3$ showed a single resonance 8.4 p.p.m. upfield, which suggests that all four CF$_3$CO$_2$ groups are equivalent. Under identical conditions the ^{19}F n.m.r. spectrum of U(O$_2$CCF$_3$)$_4$·3tppo exhibited nine signals (at +26, −5, −35, −46, −62, −68, −72, −75, and −84 p.p.m.), consistent with the presence of a mixture of unidentate and bridging or bidentate CF$_3$CO$_2$ groups, although the result is not of diagnostic value.

Experimental

The complexes were prepared and handled as described previously.[1]

Materials.—The thorium(IV) and uranium(IV) halogenoacetates were prepared by the published method,[1] except that,

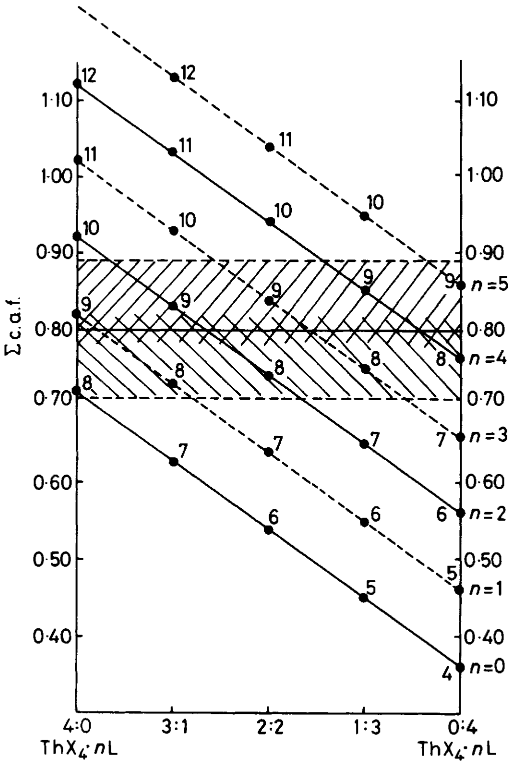

Figure 1. Σ c.a.f. and co-ordination number for thorium halogenoacetate complexes

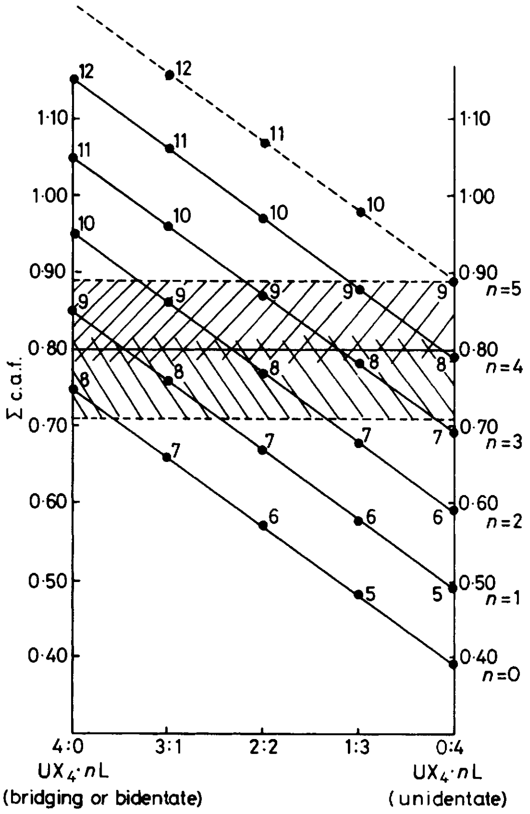

Figure 2. Σ c.a.f. and co-ordination number for uranium(IV) halogenoacetate complexes

before vacuum drying, the trifluoro- and dichloro-acetates were washed with dichloromethane (4 × 10 cm^3), followed by n-pentane (8 × 10 cm^3), and the trichloroacetates were washed with hot toluene (10 × 10 cm^3), dichloromethane (5 × 10 cm^3), and diethyl ether (8 × 10 cm^3). The ligands tppo and dpso (Aldrich) were used as supplied; tmpo was prepared by the published method [7] and dmso (B.D.H. Ltd.) was distilled, stored over dried molecular sieves (type 4A), and then redistilled before use. Chloroform was washed with dilute sulphuric acid, followed by water, then dried over calcium chloride before refluxing over phosphorus pentaoxide, after which it was distilled. Dichloromethane and n-pentane were stored over sodium wire and then distilled from calcium hydride.

Preparation of the Complexes.—(*a*) *Phosphine oxide compounds.* A solution containing an excess of the ligand in dichloromethane (3 cm^3) was added to a suspension of the halogenocarboxylate (0.5 g) in the same solvent (10 cm^3). The carboxylates dissolved on stirring within 10 min, except for the tppo complexes of the di- and tri-chloroacetates, for which complete dissolution required stirring overnight. The complexes were then precipitated by adding n-pentane until the solution became cloudy. In some cases the product separated as crystals after contact with the supernatant for up to 2 d, otherwise the oily product which first precipitated was solidified by grinding intermittently for 2—3 d in contact with the supernatant. All products were finally washed with n-pentane (2 × 10 cm^3) and vacuum-dried (6—12 h; 10^{-2} Torr).

Typically, $Th(O_2CCF_3)_4$ (0.50 g, 0.73 mmol) was suspended in dichloromethane (10 cm^3), tmpo (0.282 g, 3.07 mmol) in the same solvent (3 cm^3) was added, and the mixture was stirred for 10 min. After filtration, n-pentane was added dropwise until the solution became cloudy. Crystals of the complex had separated after 12 h, and these were washed and dried as just described.

(*b*) *Sulphoxide complexes.* The dpso complexes were prepared as described in (*a*). The trifluoroacetates dissolved rapidly, but the di- and tri-chloroacetates required overnight stirring to complete dissolution. The oily products precipitated on addition of n-pentane were solidified as in (*a*).

The dmso complexes were obtained by adding the ligand dropwise to a suspension of the halogenoacetate in dichloromethane (10 cm^3) until a clear solution was obtained. The addition of n-pentane yielded an oily precipitate which was solidified as in (*a*). Alternatively, the oily product was redissolved in dichloromethane, reprecipitated therefrom with n-pentane, and then treated as in (*a*).

Physical Measurements.—I.r. spectra were recorded using a Perkin-Elmer PE577 (4 000—200 cm^{-1}) or Pye Unicam SP 2300 (4 000—600 cm^{-1}) spectrometer with samples mounted as Nujol or hexachlorobutadiene mulls or in chloroform solution. Solid reflectance spectra were recorded using a Beckmann DK2A instrument (2 200—500 nm) with MgO as reference. Solution spectra over the same range were obtained using a Cary 14 spectrophotometer. ^{19}F N.m.r. spectra were obtained using a Bruker WP80 spectrometer (75 MHz).

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