Some Urea and Phosphine Oxide Complexes of Thorium(IV) and Uranium(IV) Trihalogenoacetates

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Complexes of thorium(IV) and uranium(IV) trifluoro- and trichloro-acetates of the types $M(O_2CR)_4 \cdot nL$ [n = 4, M = Th or U, L = $CO(NHMe)_2$, R = CCl_3 and M = Th, L = $CO(NHMe)_2$, R = CF_3; n = 3, M = Th or U, L = $PMePh_2O$ or PMe_2PhO, R = CF_3 or CCl_3 and M = U, L = $CO(NHMe)_2$, R = CF_3; n = 2.5, M = Th or U, L = $CO(NMe_2)_2$, R = CCl_3; n = 2, M = Th or U, L = $CO(NMe_2)_2$, R = CF_3] 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.

The preparation of bis-pyridine, -pyridine *N*-oxide, and -triphenylphosphine oxide complexes of thorium(IV) trichloroacetate,[1] and of amide,[2] PMe_3O (tmpo), PPh_3O (tppo), Me_2SO, and Ph_2SO [3] complexes of thorium(IV) and uranium(IV) halogenoacetates has been described. Because of the variation in the reported stoicheiometries of the complexes formed with tmpo and tppo, $M(O_2CR)_4 \cdot nL$ (n = 4, M = Th or U, L = tmpo, R = CCl_3 and M = U, R = CF_3; n = 3, M = Th, L = tmpo, R = CF_3 and L = tppo, R = CCl_3, and M = U, L = tppo, R = CF_3; n = 2, L = tppo, M = Th, R = CF_3 and M = U, R = CCl_3) it was of interest to prepare complexes of the trifluoro- and trichloro-acetates with the alkylaryl phosphine oxides, PMe_2PhO (dmppo) and $PMePh_2O$ (mdppo), and to investigate the formation of complexes of these carboxylates with *N,N'*-dimethyl- (dmu) and tetramethyl-urea (tmu), correlating the results by applying the cone angle approach to steric crowding described in recent papers.[3,4]

Results and Discussion

Preparation of the Complexes.—The halogenoacetates, suspended in dichloromethane, dissolved on addition of the ligand as described previously.[3] $Th(O_2CCF_3)_4 \cdot 4dmu$, $U(O_2CCF_3)_4 \cdot 3dmu$, and $M(O_2CCCl_3)_4 \cdot 4dmu$ (M = Th and U) precipitated as solids on stirring the dichloromethane solution overnight and the other complexes were obtained as oils on vacuum evaporation of the dichloromethane solution. These oils became solid on trituration with n-pentane. Two of the complexes [$M(O_2CCF_3)_4 \cdot 3mdppo$, M = Th or U] crystallised when a thf solution of the crude compound was treated with a small amount of n-pentane and the solution was allowed to stand overnight.

Tris-complexes, $M(O_2CR)_4 \cdot 3L$, were obtained for both thorium(IV) and uranium(IV) with R = CF_3 or CCl_3 and L = dmppo or mdppo, and for uranium(IV) with R = CF_3 and L = dmu, whereas tetrakis-complexes, $M(O_2CR)_4 \cdot 4L$, were obtained for M = Th, R = CF_3, and L = dmu, and for M = Th and U with R = CCl_3 and L = dmu. In the case of the more bulky urea, tmu, bis-complexes, $M(O_2CR)_4 \cdot 2L$, were obtained for M = Th and U with R = CF_3, but the unusual stoicheiometry $M(O_2CR)_4 \cdot 2.5tmu$ resulted for M = Th and U with R = CCl_3. All of the thorium(IV) complexes are white and the uranium(IV) analogues are green. Analytical data are in Table 1.

Infrared Spectra.—In all cases the shift in $\nu(X{=}O)$ (X = C or P) of the ligand (Table 2) was comparable with the shifts observed for complexes with the metal tetrachlorides [*e.g.* $ThCl_4 \cdot 6dmu$,[5] $\Delta\nu(C{=}O)$ = 60 cm^{-1}; $ThCl_4 \cdot 3dmppo$,[6] $\Delta\nu(P{=}O)$ = 90 cm^{-1}]. The degree of splitting of $\nu_{asym}(OCO)$ in the spectra of the complexes in Nujol mulls was reduced appreciably in the spectra in tetrahydrofuran (thf) solutions of those complexes which were sufficiently soluble in thf for the

Table 1. Analytical results (%) *

Complex	Metal	C	H	Halogen	N or P	Yield (%)
$Th(O_2CCF_3)_4 \cdot 4dmu$	22.0 (22.4)	23.2 (23.2)	3.1 (3.1)	21.6 (22.0)	10.5 (10.8)	75
$U(O_2CCF_3)_4 \cdot 3dmu$	25.0 (24.9)	21.1 (21.4)	2.5 (2.5)	22.7 (23.9)	8.2 (8.8)	70
$Th(O_2CCCl_3)_4 \cdot 4dmu$	19.3 (18.8)	18.8 (19.5)	2.4 (2.6)	34.1 (34.5)	8.9 (9.1)	70
$U(O_2CCCl_3)_4 \cdot 4dmu$	19.1 (19.2)	19.2 (19.4)	2.6 (2.6)	34.0 (34.4)	9.2 (9.0)	68
$Th(O_2CCF_3)_4 \cdot 2tmu$	25.3 (25.3)	23.2 (23.6)	2.4 (2.6)	24.8 (24.9)	5.8 (6.1)	40
$U(O_2CCF_3)_4 \cdot 2tmu$	26.5 (25.8)	22.9 (23.4)	2.7 (2.6)	25.4 (24.7)	5.7 (6.1)	42
$Th(O_2CCCl_3)_4 \cdot 2.5tmu$	20.0 (19.8)	21.4 (21.0)	2.6 (2.6)	35.8 (36.3)	6.3 (6.0)	45
$U(O_2CCCl_3)_4 \cdot 2.5tmu$	20.5 (20.2)	21.1 (20.9)	2.8 (2.6)	36.9 (36.2)	6.0 (5.9)	43
$Th(O_2CCF_3)_4 \cdot 3dmppo$	20.1 (20.2)	33.7 (33.5)	3.1 (2.9)	20.5 (19.9)	8.1 (8.1)	50
$U(O_2CCF_3)_4 \cdot 3dmppo$	20.1 (20.7)	33.5 (33.3)	2.8 (2.9)	18.9 (19.8)	7.6 (8.1)	55
$Th(O_2CCCl_3)_4 \cdot 3dmppo$	16.8 (17.3)	29.1 (28.6)	2.8 (2.5)	31.3 (31.7)	6.7 (6.9)	50
$U(O_2CCCl_3)_4 \cdot 3dmppo$	17.3 (17.6)	28.9 (28.4)	2.2 (2.4)	30.8 (31.6)	7.5 (6.9)	42
$Th(O_2CCF_3)_4 \cdot 3mdppo$	16.9 (17.4)	42.0 (42.3)	2.9 (2.9)	16.5 (17.1)	6.9 (7.0)	45
$U(O_2CCF_3)_4 \cdot 3mdppo$	18.1 (17.8)	41.7 (42.1)	2.9 (2.9)	17.6 (17.0)	6.8 (7.0)	40
$Th(O_2CCCl_3)_4 \cdot 3mdppo$	14.6 (15.2)	37.5 (36.9)	2.8 (2.6)	27.4 (27.8)	6.0 (6.1)	45
$U(O_2CCCl_3)_4 \cdot 3mdppo$	15.1 (15.5)	37.3 (36.7)	2.7 (2.5)	27.2 (27.7)	6.0 (6.1)	48

* Calculated values in parentheses.

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

Complex [a]	ν_{asym}(OCO)	ν_{sym}(OCO)	ν_{asym}(OCO) − ν_{sym}(OCO)	ν(Y=O) [b]	$\Delta\nu$(Y=O) [b]
ThX_4·4dmu	1 675s			1 610s	50
UX_4·3dmu	1 680s			1 600s	60
ThX_4·2tmu	1 760m, 1 725 (sh), 1 700w, 1 680s			1 560s	100
UX_4·2tmu	1 755s, 1 715s, 1 695s, 1 685 (sh)			1 550s	110
UX_4·2tmu [c]	1 695vs, 1 625m	1 400m	295, 225	1 550s	110
ThX_4·3dmppo	1 740s, 1 720m, 1 700s, 1 680m, 1 635 (sh)			1 098s	77
ThX_4·3dmppo [c]	1 680s	1 420m	260	1 090s	85
UX_4·3dmppo	1 680s			1 090s	85
ThX_4·3mdppo	1 725m, 1 695s, 1 660s	1 412m	313, 283, 248	1 080s, 1 070s	95, 105
UX_4·3mdppo	1 720s, 1 695s			1 060s	115
UX_4·3mdppo [c]	1 700s	1 390m	290	1 085s, 1 070s	90, 105
ThX'_4·4dmu	1 685s			1 600s	60
UX'_4·4dmu	1 685s	1 390m, 1 315s	295, 370	1 595s	65
ThX'_4·2.5tmu	1 702m, 1 696s, 1 640m			1 565s	95
UX'_4·2.5tmu	1 700s			1 550s	110
ThX'_4·3dmppo	1 690s br, 1 670s			1 100s	75
ThX'_4·3dmppo [c]	1 660s	1 440m	220	1 090s	85
UX'_4·3dmppo	1 670s, 1 660s			1 095s	80
UX'_4·3dmppo [c]	1 662vs	1 360m, 1 322s	302, 340	1 088s	87
ThX'_4·3mdppo	1 690s, 1 635m			1 088s	87
ThX'_4·3mdppo [c]	1 680vs	1 440m	240	1 080s	95
UX'_4·3mdppo	1 690s, 1 660s			1 095s	80
UX'_4·3mdppo [c]	1 658s	1 350m	308	1 080s	95

[a] X = O_2CCF_3, X′ = O_2CCCl_3. [b] Y = C or P. [c] Solution in dichloromethane; s = strong, m = medium.

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

Complex	Bidentate or bridging: unidentate carboxylate groups 4 : 0	3 : 1	2 : 2	1 : 3	0 : 4	Co-ordination number	Σ c.a.f.
$Th(O_2CCF_3)_4$·4dmu $Th(O_2CCCl_3)_4$·4dmu	1.12(CN12)	1.03(CN11)	0.94(CN10)	0.85(CN9)	S.R.	8	0.76
$Th(O_2CCF_3)_4$·3dmppo $Th(O_2CCF_3)_4$·3mdppo $Th(O_2CCCl_3)_4$·3dmppo	1.02(CN11)	0.93(CN10)	S.R.		0.66(CN7)	9	0.84
$Th(O_2CCCl_3)_4$·3mdppo				S.R.		8	0.75
$Th(O_2CCF_3)_4$·2tmu $U(O_2CCF_3)_4$·2tmu	0.92(CN10)	S.R.	0.74(CN8)	0.65(CN7)	0.56(CN6)	9	0.83
$U(O_2CCCl_3)_4$·4dmu	1.12(CN12)	1.03(CN11)	0.94(CN10)	0.85(CN9)	S.R.	8	0.76
$U(O_2CCF_3)_4$·3dmu	1.02(CN11)	0.93(CN10)	S.R.	0.75(CN8)	0.66(CN7)	9	0.84
$U(O_2CCF_3)_4$·3dmppo $U(O_2CCF_3)_4$·3mdppo $U(O_2CCCl_3)_4$·3dmppo $U(O_2CCCl_3)_4$·3mdppo	1.05(CN11)	0.96(CN10)	0.87(CN9)	S.R.	0.67(CN7)	8	0.78

* CN = Co-ordination number. S.R. = Stable region.

spectra to be recorded (Table 2). In many cases ν_{sym}(OCO) could not be identified. When both ν_{asym}(OCO) and ν_{sym}(OCO) could be assigned, the differences ν_{asym}(OCO) − ν_{sym}(OCO) were in the range 225—370 cm^{-1}, suggestive of unidentate carboxylate groups, but this is not a reliable diagnostic guide to the bonding mode (unidentate, bidentate, bridging, or ionic) in carboxylates.[7] In the case of trifluoroacetates, it has been shown that the values of ν_{asym}(OCO) for the unidentate carboxylate group are usually in the range 1 692—1 720 cm^{-1}, the range found for the complexes reported here.

Application of the cone angle factor (c.a.f.) approach described in previous papers [3,4] suggests that the carboxylate groups in the complexes $M(O_2CR)_4$·4dmu (M = Th, R = CF_3 or CCl_3 and M = U, R = CCl_3) are most likely to be unidentate (Table 3), whereas in the remaining complexes a mixture of uni- and bi-dentate carboxylate groups appears to be present, involving eight- or nine-co-ordinate metal centres, using the previously reported values for the 'stable' regions found for known complexes of thorium(IV) and uranium(IV).[3,4]

Electronic Spectra.—The diffuse-reflectance visible and near-i.r. spectra of the uranium(IV) halogenoacetate-urea and -phosphine oxide complexes were characteristic of uranium(IV) in a high (⩾8) co-ordination number environment but did not provide any indication of the symmetry.

Experimental

The complexes were prepared and handled as described previously.[2]

Materials.—The thorium(IV) and uranium(IV) halogenoacetates were prepared by the modification [3] of the published method.[2] The ligands dmu and tmu (B.D.H. Ltd.) were used as supplied; dmppo was prepared from $PPhCl_2O$ (Aldrich) by the standard method [8] and mdppo was prepared by heating $[PMePh_3]I$ with 20% aqueous NaOH.[9] The phosphonium salt was obtained in the usual way, by reaction of MeI with PPh_3 in toluene under reflux.

Preparation of the Complexes.—(*a*) $Th(O_2CCF_3)_4$·3dmppo. An excess of dmppo (0.61 g, 3.96 mmol) was added to a suspension of $Th(O_2CCF_3)_4$ (0.53 g, 0.77 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 30 min the solution was centrifuged and the supernatant was vacuum evaporated to an oil which solidified when triturated with n-pentane. The solid *product* was then washed several times with thf–n-pentane (1 : 1 v/v), and vacuum dried for 6 h. $U(O_2CCF_3)_4$·3dmppo, $M(O_2CCF_3)_4$·2tmu, $M(O_2CCCl_3)_4$·2.5tmu (M = Th or U) and $M(O_2CCCl_3)_4$·3L (M = Th or U, L = dmppo or mdppo) were prepared in the same way.

(*b*) $Th(O_2CCF_3)_4$·3mdppo. This was prepared as described in (*a*) except that the final solid product was dissolved in thf (10 cm^3) and a few drops of n-pentane were added. The complex separated as colourless needles on standing overnight. $U(O_2CCF_3)_4$·3mdppo was also prepared in this way.

(*c*) $Th(O_2CCF_3)_4$·4dmu. An excess of dmu (0.30 g, 3.41 mmol) was added to $Th(O_2CCF_3)_4$ (0.47 g, 0.69 mmol) suspended in CH_2Cl_2 (30 cm^3). A clear solution was obtained after stirring for 30 min, but continued stirring overnight led to precipitation of the complex. The solid was washed with CH_2Cl_2 (3 × 5 cm^3) and vacuum dried (6 h). $U(O_2CCF_3)_4$·3dmu and $M(O_2CCCl_3)_4$·4dmu (M = Th or U) were also obtained by this route.

Physical Measurements.—I.r. spectra were recorded using Perkin-Elmer P.E. 257 (4 000—625 cm^{-1}) or P.E. 577 (4 000—200 cm^{-1}) spectrometers with samples mounted as Nujol mulls or in dichloromethane solution. Solid reflectance spectra were recorded using a Beckmann DK2A instrument (2 200—500 nm) with MgO as reference.

Acknowledgements

We thank Mr. M. A. Hart for the microanalyses (C, H, N, P, F, Cl, Th, and U) and the Commonwealth Scholarships Commission for the award of a scholarship (to I. A.).

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Received 24*th October* 1983; *Paper* 3/1888