Amide Complexes of Thorium(IV) and Uranium(IV) Carboxylates

By **Kenneth W. Bagnall** * and **Omar Velasquez Lopez**, Chemistry Department, The University of Manchester, Manchester M13 9PL

Thorium(IV) and uranium(IV) carboxylates $M(O_2CR)_4$ (R = Bu^n, Me_2CHCH_2, Me_3C, $CHCl_2$, and CH_2Cl) and $U(O_2CCCl_3)_4$ have been prepared; the investigation of the behaviour of these, and other carboxylates, with amides as ligands has led to the isolation of complexes of the types $M(O_2CR)_4{\cdot}xL$ [$x = 3$, M = Th, L = $MeCONMe_2$ (dma), R = CF_3 or CCl_3 and M = U, R = CCl_3; $x = 1$, M = Th, L = dma, R = $CHCl_2$ or CH_2Cl, and L = $MeCONPh_2$(dpa), R = $CHCl_2$; $x = 0.5$, M = U, L = dma, R = CH_3Cl] and $[M(O_2CR)_3L]_2O$ [M = Th or U, L = $Me_3CCONMe_2$(dmpa), R = CF_3, CCl_3, or $CHCl_2$; M = U, L = dma, R = CF_3 or $CHCl_2$ and L = dpa, R = $CHCl_2$]. The infrared and Raman spectra of these compounds are discussed.

ALIPHATIC monocarboxylic acid compounds of thorium(IV) and uranium(IV), $M(O_2CR)_4$ [R = H(Th,[1,2] U [3-5]), Me(Th,[6-8], U [3,9-13]), CF_3(Th,[14,15] U [11]), CCl_3(Th [16]), Et-(Th,[17] U [10,11]), Pr^i(U [10,11]), Bu^i(U [10]), n-C_5H_{11}(U [10]), n-C_6H_{13}(U [11]), and n-$CH_3(CH_2)_x$ (x = 10, 12, or 14; U [18])] have been recorded, but only one complex with a donor ligand,[19] $Th(O_2CH)_4{\cdot}SMe_2O$, appears to be known. The structure of $U(O_2CMe)_4$ consists of an infinite polymeric arrangement in which each uranium atom is ten-co-ordinate,[20] and the low solubility in water and in organic solvents of the known non-halogenated carboxylates suggests that they are probably also polymeric in nature. It was therefore of interest to prepare a set of isomeric carboxylates, $M(O_2CR)_4$ (M = Th or U, R = Bu^n, Me_2CHCH_2, and Me_3C), in order to investigate the effect of steric hindrance on the ability to form complexes with donor ligands, and to prepare the three possible chloroacetates, and the trifluoroacetates, of the two metals in order to investigate the effect of the electron-withdrawing halogen atoms for the same purpose.

RESULTS AND DISCUSSION

The Complexes.—The non-halogenated thorium(IV) and uranium(IV) carboxylates are insoluble in water and at best only slightly soluble in the common organic solvents, as found for other actinoid(IV) carboxylates. They dissolve in oxygen-donor ligands on heating [dimethylacetamide (dma), 80; SMe_2O, 100; PPh_3O or $P(NMe_2)_3O$ in acetone at 50 °C] but the original carboxylates were reprecipitated when 2-methylbutane was added to the cooled solutions.

The corresponding chloroacetates are only very slightly more soluble in water and in the common organic solvents than the acetates, but the trifluoroacetates are much more soluble, presumably because electron withdrawal by the fluorine decreases the donor ability of the carboxylate oxygen atoms, so reducing their ability to act as bridging atoms in a polymeric structure. Although the trifluoro- and trichloro-acetates are insoluble in chloroform, they dissolve when dma is added to the suspension; the addition of 2-methylbutane to the resulting solution yielded the tris dma complexes, $M(O_2CR)_4{\cdot}3dma$, in the cases of the two trichloroacetates and thorium(IV) trifluoroacetate, but with uranium(IV) trifluoroacetate the product isolated from chloroform, dichloromethane, or acetone solutions of the ligand analysed as $[U(O_2CCF_3)_3(dma)]_2O$. All three tris dma complexes are unstable, decomposing within 3 d of their preparation even when kept under nitrogen and in a refrigerator; the decomposition products were identified tentatively as species of the type $[M(O_2CR)_3L]_2O$, presumably formed by loss of the acid anhydride and some of the ligand. Complexes of this unusual stoicheiometry were also obtained for thorium(IV) and uranium(IV) trifluoro-, trichloro-, and dichloro-acetates with the more bulky ligand $Me_3C{\cdot}CONMe_2$(dmpa) and for uranium(IV) dichloroacetate with

TABLE 1

Molecular-weight determinations of selected complexes

Complex	*M*			Solvent
	Found		Calc.	
	in air	in nitrogen		
$[U(O_2CCF_3)_3(dma)]_2O$	597	1 115	1 344	CH_2Cl_2
$U(O_2CCCl_3)_4{\cdot}3dma$	477	644	1 149	CH_2Cl_2
$[U(O_2CCHCl_2)_3(dma)]_2O$	639	966	1 434	CH_2Cl_2
$[Th(O_2CCHCl_2)_3(dmpa)]_2O$	360		1 505	MeCN

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TABLE 2

Infrared and Raman spectra (cm^{-1}) of the halogenoacetates and their complexes

Compound		ν_{asym}(OCO)	ν_{sym}(OCO)	[ν_{asym}(OCO)- ν_{sym}(OCO)]	δ(OCO)	$\Delta\nu_{sym}$(CO) [a]
X = O_2CCH_2Cl						
ThX_4	I.r.	1 580vs	1 430s	150	715m	
		1 540vs	1 395s	(145)	700m	
ThX_4·dma		1 590vs	1 435vs	155	719w	39
		1 555vs	1 420s	(135)	700w, 675w	
	Raman		1 435s		715vw	
		1 560w	1 420m	(140)	680vw	
UX_4	I.r.	1 566vs	1 426s	140	718m	
		1 540vs	1 396s	(144)	698m	
UX_4·0.5dma		1 576vs	1 425vs	151	700w	
		1 556vs			662vw	
X = O_2CCHCl_2						
ThX_4	I.r.	1 590vs	1 425m	165	738m	
		1 570vs			715m	
	Raman	1 582m	1 460vs	122	736, 721s	
ThX_4·dma	I.r.	1 708s	1 440s (sh)	268	726s	52
		1 620vs	1 430s	(190)	709m, 700m	
	Raman	*b*	1 424m		721w	
			1 400vw		700m	
$[ThX_3(dpa)]_2O$	I.r.	1 718m				
		1 640s	1 420vs	220 (?)	703s	105
		1 615s			676m, 650w	
	Raman	*b*	*b*		715s	
$[ThX_3(dmpa)]_2O$	I.r.	1 690vs	1 425vs	265	715s	62
		1 660vs	1 410vs	(250)	705s	
		1 620vs				
	Raman	1 684m	1 447vs	237	718s	52
		1 643m	1 418s	(225)	707s	
		1 612m				
UX_4	I.r.	1 590vs	1 416s	174	730s, 708s	
$[UX_3(dma)]_2O$		1 680s	1 430s	250	740w	45
		1 648s	1 410s	(238)	721w, 708m	
$[UX_3(dpa)]_2O$		1 678s	1 435s	243	725m	97
		1 650vs	1 410s	(240)	715m, 701s	
$[UX_3(dmpa)]_2O$		1 673s	1 445m	228	740w	59
		1 647vs	1 416vs	(231)	720s, 710m	
X = O_2CCCl_3						
ThX_4		1 618vs	1 425s	193	740s	
			1 400s		692s	
ThX_4·3dma		1 706vs	1 410s	296	770m	47
		1 630s	1 315vs	(315)	751m	
			1 300vs		675s	
	Raman	1 715w	1 424w	291	771w (sh)	
		1 703w	1 315vw		755vs	
			1 300vw		689w	
$[ThX_3(dmpa)]_2O$	I.r.	1 690vs	1 380vs	310	715s	62
		1 645s	1 330vs	315	705s	
		1 628vs				
	Raman	*b*	*b*		715m	
UX_4	I.r.	1 610vs	1 425s	185	735s	
			1 397s		688s	
UX_4·3dma		1 716vs	1 425s	291	760s	47
		1 702vs	1 410m	(292)	728s	
		1 635vs	1 315s	(320)	680s	
$[UX_3(dmpa)]_2O$		1 690vs	1 450s	240	720m	62
		1 675vs	1 415s	(260)	685s	
		1 650m, 1 630m				
X = O_2CCF_3						
ThX_4		1 634vs	1 492s	142	727s	
ThX_4·3dma		1 745s	1 430s	315	757m	32
		1 715vs	1 415s	(300)	725s	
	Raman	1 740w	1 415m	325	758s	
		1 710w			721vw	
$[ThX_3(dmpa)]_2O$	I.r.	1 740m	1 470s	270	757m	49
		1 718vs	1 425m	(293)	732vs	
		1 680s				
		1 646m				
	Raman	*b*	1 470m		730m	
			1 420w		715m	
UX_4	I.r.	1 625vs	1 488s	137	727s	
$[UX_3(dma)]_2O$		1 740s	1 460s	280	755m	37
		1 720s	1 430m	(290)	725vs	
		1 690vs			700w	
		1 670s				
$[UX_3(dmpa)]_2O$		1 695vs	1 450s	245	725s	62
		1 640m (sh)	1 416m	(224)	695w	
					675w	

s = Strong, m = medium, w = weak, sh = shoulder, and v = very.

[a] Amide-ligand carbonyl group. [b] Obscured by fluorescence.

dma and *NN*-diphenylacetamide (dpa), whereas the corresponding thorium(IV) compound yielded the 1 : 1 complexes, $Th(O_2CCHCl_2)_4\cdot L$, with these two ligands. The monochloroacetates did not behave in the same way, but yielded 1 : 1 (Th) and 2 : 1 (U) complexes with dma and did not react with dpma, either alone, or in a suitable organic solvent. Conductivity measurements for the complexes in methyl cyanide or dichloromethane indicated that they were non-electrolytes and molecular-weight determinations (Table 1) did not resolve the question of the molecular complexity of the species of composition $[M(O_2CR)_3L]_2O$. However, the formation of such species with bulkier ligands or bulkier carboxylates suggests that the acid anhydride is probably eliminated when the environment of the metal atom becomes sterically crowded, presumably with the formation of an M–O–M bridge. Unfortunately we could not identify the M–O stretching mode for the bridge.

TABLE 3

Analytical results* and yields (%)

Compound		M		C		H		N		Halogen		Yield
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	
$Th[O_2C(CH_2)_3Me]_4$	A	36.0	36.5	37.5	37.7	5.7	5.7					93
	B	35.8	36.5	37.4	37.7	5.8	5.7					98
$U[O_2C(CH_2)_3Me]_4$	A	36.5	37.1	37.1	37.4	5.5	5.6					93
$Th(O_2CCH_2CHMe_2)_4$	A	36.5	36.5	37.9	37.7	5.8	5.7					89
	B	34.0	36.5	37.9	37.7	5.6	5.7					97
$U(O_2CCH_2CHMe_2)_4$	A	36.7	37.1	37.2	37.4	5.7	5.6					96
$Th(O_2CCMe_3)_4$	A	36.7	36.5	35.8	37.7	5.3	5.7					81
	B	36.2	36.5	37.3	37.7	5.5	5.7					98
$U(O_2CCMe_3)_4$	A	36.6	37.1	37.1	37.4	5.3	5.6					95
$Th(O_2CCF_3)_4$	A	34.5	33.9	14.0	14.0					33.0	33.3	91
$U(O_2CCF_3)_4$	A	34.5	34.5	13.4	13.9					32.1	33.1	93
$Th(O_2CCCl_3)_4$	A	26.8	26.3	10.8	10.9					48.0	48.3	92
$U(O_2CCCl_3)_4$	A	26.8	26.8	11.0	10.8					47.8	47.9	92
$Th(O_2CCHCl_2)_4$	A	31.3	31.2	12.5	12.9	0.5	0.5			37.9	38.1	89
$U(O_2CCHCl_2)_4$	A	31.8	31.7	12.8	12.8	0.4	0.5			37.4	37.8	92
$Th(O_2CCH_2Cl)_4$	A, B	37.9	38.1	16.2	15.8	1.1	1.3			23.6	23.4	87 (A), 80 (B)
$U(O_2CCH_2Cl)_4$	A	38.8	38.9	15.6	15.7	1.2	1.3			23.2	23.2	94
$Th(O_2CCF_3)_4\cdot 3dma$		25.3	24.6	25.6	25.4	2.9	2.9	4.8	4.5	24.4	24.1	77
$[Th(O_2CCF_3)_3(dmpa)]_2O$		32.3	32.8	22.3	22.0	2.2	2.1	1.8	2.0	24.1	24.2	91
$[U(O_2CCF_3)_3(dma)]_2O$		35.4	35.4	19.6	17.9	1.8	1.3	2.6	2.1	25.6	25.4	61
$[U(O_2CCF_3)_3(dmpa)]_2O$		35.5	33.3	21.5	21.9	2.2	2.1	2.5	2.0	24.6	24.0	63
$Th(O_2CCCl_3)_4\cdot 3dma$		20.4	20.3	21.3	21.0	2.4	2.4	3.8	3.7	37.3	37.2	64
$[Th(O_2CCCl_3)_3(dmpa)]_2O$		26.0	27.1	20.1	18.2	2.2	1.8	2.0	1.6	38.0	37.3	72
$U(O_2CCCl_3)_4\cdot 3dma$		20.8	20.7	20.7	20.9	2.4	2.4	3.4	3.7	37.4	37.0	68
$[U(O_2CCCl_3)_3(dmpa)]_2O$		28.1	27.6	18.5	18.1	1.8	1.7	1.6	1.6	35.3	37.0	75
$Th(O_2CCHCl_2)_4\cdot dma$		27.9	27.9	17.6	17.3	1.6	1.6	1.8	1.7	34.1	34.2	90
$Th(O_2CCHCl_2)_4\cdot dpa$		24.6	24.3	27.7	27.7	1.8	1.8	1.4	1.5	29.7	29.7	89
$[Th(O_2CCHCl_2)_3(dmpa)]_2O$		31.0	30.8	21.0	20.7	2.4	2.4	2.0	1.9	28.3	28.3	91
$[U(O_2CCHCl_2)_3(dma)]_2O$		33.4	33.2	17.1	16.7	1.9	1.7	2.0	2.0	30.3	29.7	71
$[U(O_2CCHCl_2)_3(dpa)]_2O$		27.7	28.3	30.3	28.5	2.3	1.9	1.9	1.7	26.2	25.3	88
$[U(O_2CCHCl_2)_3(dmpa)]_2O$		31.4	31.4	18.9	20.6	2.2	2.4	1.4	1.8	27.3	28.0	82
$[Th(O_2CCH_2Cl)_4\cdot dma$		33.3	33.5	21.2	20.8	2.6	2.4	1.9	2.0	20.0	20.5	93
$U(O_2CCH_2Cl)_4\cdot 0.5dma$		36.6	36.3	17.0	18.3	1.8	1.9	1.0	1.1	22.1	21.6	63

* A, Prepared by acid interchange from the tetra-acetate; B, prepared from the hydroxide and the aqueous acid.

Infrared and Raman Spectra.—In the i.r. spectra (Table 2) of the thorium(IV) and uranium(IV) halogenoacetates the asymmetric OCO frequency increased very markedly with the electron-withdrawing capacity of the halogenated methyl group, with no marked mass effect, and the i.r.- and Raman-active symmetric OCO stretching frequency decreased as the mass of the substituted methyl group increases, but was not noticeably affected by the electron-withdrawing ability of this group, thus following the reported [21] i.r. spectra of the sodium salts of these acids.

In the spectra of the complexes, the dma adducts of the monochloroacetates differed very little from those of the parent compounds, with only a slight increase in ν_{asym}(OCO), but in the cases of the complexes of the di- and tri-chloroacetates, and of the trifluoroacetates, the frequency of this mode increased to values greater than those reported [21] for the sodium salts of the acids, the largest increases being observed for the trifluoroacetate complexes. Smaller changes were also observed in the symmetric stretching frequencies. If these results are due to an increase in electron withdrawal by the halogenated methyl groups, following electron donation from the ligand to the metal atom, one would expect the shifts in carbonyl frequency of the amide ligands to increase in the same sense, but although these shifts (Table 2) are appreciably larger than those observed in the spectra of the corresponding complexes of the actinoid tetrachlorides [22,23] or tetranitrates [24] their magnitudes do not correlate with the electron-withdrawing ability of the methyl groups. It is therefore probable that the changes

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in ν_{asym}(OCO) are related to the mode of bonding of the carboxylate group. Although the frequencies of the carboxylate-stretching modes do not enable unambiguous assignment of the type of bonding (unidentate, bidentate, bridging, or ionic), it should be possible to make a tentative assignment for a series of compounds of similar metals in the same oxidation state. In a recent review [25] it has been shown that ν_{asym}(OCO) for the unidentate trifluoroacetate group appears in the range 1 692—1 720 cm^{-1} in metal complexes, whereas for the bridging or bidentate carboxylate group this mode appears in the range 1 592—1 660 cm^{-1} and in ionic species (alkali-metal salts) it appears in the range 1 667—1 678 cm^{-1}.

Taking these ranges as approximate criteria, the values of ν_{asym}(OCO) for the thorium(IV) and uranium(IV) halogenoacetates, and for the amide complexes of the monochloroacetates, and uranium(IV) dichloroacetates, suggest that in these compounds the carboxylate groups are bidentate or bridging, while in the thorium(IV) dichloroacetate complexes the presence of both high- (1 708, dma; 1 718, dpa; 1 690 cm^{-1}, dmpa) and low-frequency features (1 620, 1 640, and 1 615, 1 660 and 1 620 cm^{-1} respectively) suggests that both uni- and bi-dentate or bridging carboxylate groups are present. The presence of high- and low-frequency features in the i.r. spectra of all of the trichloro- and trifluoro-acetate complexes also suggests these two bonding modes. The differences between ν_{asym}(OCO) and ν_{sym}(OCO) (Table 2) do not provide a reliable diagnostic guide to the bonding mode,[25] although there seems to be some correlation with the tentative assignment of bonding mode in that the majority of values of [ν_{asym}(OCO) − ν_{sym}(OCO)] fall into two groups, one a range from 137 to 193 cm^{-1} for the compounds in which bridging carboxylate is suggested, and the other from 245 to 315 cm^{-1} for compounds in which the presence of unidentate carboxylate is suspected. There are also some complexes {*e.g.* $[U(O_2CCHCl_2)_3(dmpa)]_2O$} in which the value lies between these two ranges; with the extensive splitting of ν_{asym}(OCO) and ν_{sym}(OCO) it is uncertain whether the frequencies of these two modes have been correctly paired.

The Raman spectra of some of the thorium(IV) compounds were also recorded in an attempt to ascertain whether there were any differences in relative intensities which would help to resolve this problem, as is the case with nitrate complexes,[26] but no positive deductions could be made so that confirmation of the tentative assignments will have to come from *X*-ray structure determinations.

Electronic Spectra.—The visible and near-i.r. spectra of the uranium(IV) halogenoacetates and their complexes were recorded by diffuse solid reflectance and, in some cases, as solution spectra. The spectra were characteristic of U$^{\text{IV}}$ 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.

EXPERIMENTAL

The complexes were handled in a dry nitrogen atmosphere in a glove-box in order to afford protection from atmospheric moisture and to minimise oxidation of the uranium(IV) compounds.

Materials.—The halogenoacetic (monochloro, B.D.H. Ltd.; di- and tri-chloro, Hopkin and Williams, Ltd.; trifluoro, Koch–Light, Ltd.) and other carboxylic acids (B.D.H. Ltd.) and *NN*-diphenylacetamide (dpa) (Kodak Ltd.) and *NN*-dimethylacetamide (dma) (Koch–Light, Ltd.) were used as supplied; *NN*-dimethylpivalamide (dmpa) [24] and thorium(IV) [8] and uranium(IV) acetates [13] were prepared by published methods except that in the last instance the primary product was heated under reflux with glacial acetic acid–acetic anhydride–concentrated hydrochloric acid (35 : 5 : 2) for several hours in order to eliminate zinc used as reductant. The ligands and solvents were treated as described previously [24] before use.

Preparation of the Carboxylates.—The thorium(IV) and uranium(IV) carboxylates were prepared by the acid-interchange method [10] in which the tetra-acetate was heated under reflux with an excess of the carboxylic acid, either alone or in a hydrocarbon such as benzene or toluene. Thorium(IV) monochloroacetate was also prepared by dissolving freshly precipitated thorium(IV) hydroxide in the 20% aqueous acid; the product precipitated from the solution on standing. Uranium(IV) pivalate was particularly hygroscopic and was oxidised to U$^{\text{VI}}$ on storage more readily than the other uranium(IV) carboxylates.

Preparation of the Complexes.—Complexes of the trichloro- and trifluoro-acetates were prepared by adding an excess of the ligand to a suspension of the metal carboxylate in chloroform; the resulting solution was filtered and addition of 2-methylbutane to the filtrate precipitated the complex, sometimes as an oil which was induced to solidify by grinding it under 2-methylbutane. Typically, dma (1 cm^3, 11 mmol) was added to a suspension of $Th(O_2CCF_3)_4$ (1 g, 1.46 mmol) in chloroform (5 cm^3); a clear solution resulted immediately. The addition of 2-methylbutane (5—10 cm^3) precipitated a colourless oil which solidified on grinding under the hydrocarbon. The *complex*, $Th(O_2CCF_3)_4 \cdot 3dma$ was washed with 2-methylbutane (5 × 10 cm^3) and dried *in vacuo* (10^{-3} Torr, 8 h).*

The complexes of the monochloroacetates were prepared in a similar manner, using the undiluted ligand, and those of the dichloroacetates were prepared as described for the trihalogenoacetates, but using acetone as the solvent, except for $Th(O_2CCHCl_2)_4 \cdot dpa$, for which dichloromethane was used. The isolation procedure was also the same, except that $Th(O_2CCHCl_2)_4 \cdot dma$ separated from the solution rapidly, and $Th(O_2CCHCl_2)_4 \cdot dpa$ crystallised out overnight, both without addition of a hydrocarbon.

Analysis.—Thorium and uranium were determined as described previously; [26] thorium was also determined volumetrically using ethylenediaminetetra-acetic acid.[27] Carbon, H, and N were determined by combustion. Halogen was determined by potentiometric titration against silver(I) nitrate (Cl) and spectrophotometrically (F) by the

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* 1 Torr = (101 325/760) Pa.

[25] C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.

[26] P. J. Alvey, K. W. Bagnall, D. Brown, and J. Edwards, *J.C.S. Dalton*, 1973, 2308.

[27] A. I. Vogel, 'A Text-book of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961, p. 444.

Alizarin Fluorine Blue method,[28] after decomposition of the sample in a Schoniger oxygen flask and using aqueous hydrazine sulphate (Cl) and sodium hydroxide (F) as absorbents. The analytical results are summarised in Table 3.

Physical Measurements.—All physical methods used in this work were as described previously.[29]

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[28] W. C. Johnson, 'Organic Reagents for Metals and for Certain Radicals,' Hopkin and Williams Ltd., 1964, p. 3.

[29] K. W. Bagnall and M. W. Wakerley, *J.C.S. Dalton*, 1974, 889.