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Some New Complexes of Thorium Tetrachloride with Substituted Ureas; the Crystal and Molecular Structure of Tris(*N*,*N*′-dimethyl-*N*,*N*′-diphenylurea)-tetrachlorothorium(IV)

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Abstract

Thorium tetrachloride forms a 1:3 complex, ThCl$_4$·3L, with *N*,*N*-diethyl *N*′,*N*′-dimethylurea (dedmu); and 1:2 complexes with dedmu, *N*,*N*-diisopropyl *N*′,*N*′-dimethyl (dibdmu), *N*,*N*-diisobutyl-*N*′,*N*′-dimethyl (dibdmu), *N*,*N*-diisopropyl *N*′,*N*′-diphenyl (dipdpu), *N*,*N*,*N*′,*N*′-tetramethyl (tmu) and *N*,*N*,*N*′,*N*′-tetraethylurea (teu) have been obtained. A dichloromethane solvate, ThCl$_4$·3L·CH$_2$Cl$_2$, where L = *N*,*N*′-dimethyl-*N*′,*N*-diphenylurea (dmdpu), has also been obtained. The crystal and molecular structure of ThCl$_4$(dmdpu)$_3$·n-pentane has been determined from three dimensional X-ray diffraction data. The cell is triclinic, space group $P\bar{1}$, with $a = 16.826(3)$, $b = 16.019(3)$, $c = 12.131(2)$ Å, $\alpha = 110.4(1)$, $\beta = 106.6(1)$ and $\gamma = 59.4(1)°$ and $Z = 2$. Full matrix least-squares refinement with 7963 intensity observations reached convergency with $R = 0.053$ and $R_w = 0.058$. The coordination polyhedron about the seven-coordinate thorium atom is a pentagonal bipyramid with two chlorine atoms in apical positions. The average bonding distances are Th–O = 2.392(5), Th–Cl$_{eq}$ = 2.743(3) and Th–Cl$_{ax}$ = 2.696(3) Å. The IR spectra of the complexes are also reported.

Introduction

The only recorded complexes of thorium tetrachloride with substituted ureas appear to be ThCl$_4$·3{(Me$_2$N)$_2$CO}, ThCl$_4$·3{(MePhN)$_2$CO}, ThCl$_4$·4{(Me$_2$N)(MeNH)CO} and ThCl$_4$·6{(MeNH)$_2$CO} [1]; uranium tetrachloride forms bis complexes with the first two ligands and tetrakis complexes with the last two [1]. It was therefore of interest to investigate the possible formation of complexes with more bulky substituted ureas, in the expectation of obtaining bis complexes, and to attempt to prepare bis analogues of the known tris complexes.

The ligands investigated, and the abbreviations used for them in this work, are shown below:

R^{1}R^{2}N·CO·NR^{3}R^4

R^1 = R^2 = R^3 = R^4 = Me	tmu
R^1 = R^2 = R^3 = R^4 = Et	teu
R^1 = R^3 = Me, R^2 = R^4 = Ph	dmdpu
R^1 = R^2 = Et, R^3 = R^4 = Me	dedmu
R^1 = R^2 = Pr^i, R^3 = R^4 = Me	dipdmu
R^1 = R^2 = Pr^i, R^3 = R^4 = Ph	dipdpu
R^1 = R^2 = Bu^i, R^3 = R^4 = Me	dibdmu

The Complexes

ThCl$_4$·2dedmu and ThCl$_4$·2dibdmu were obtained by treating a suspension of thorium tetrachloride in dichloromethane with an excess of the ligand in the same solvent, followed by evaporation of the resulting solution to dryness and dissolution of the oily residue in ethyl acetate; n-pentane was then added until the solution became cloudy and the solution was left to crystallise. ThCl$_4$·2teu, ThCl$_4$·2dipdpu and ThCl$_4$·2dipdmu were obtained in a similar manner from tetrahydrofuran solutions of the reagents, whereas ThCl$_4$·2tmu separated as a solid on vacuum evaporation of a dichloromethane solution containing the stoicheiometric quantitites of the tetrachloride and tmu.

ThCl$_4$·2dedmu crystallised on standing from a solution of the tris complex in dichloromethane to which n-pentane had been added until a cloudiness developed, followed by dropwise addition of dichloromethane until the solution cleared. The same

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procedure with the known complex ThCl$_4$·3dmdpu yielded the solvate ThCl$_4$·3dmdpu·CH$_2$Cl$_2$, the ^{1}H NMR spectrum of which (in CD$_3$CN) showed 3 resonances, at 3.56 ppm (singlet, 18H, CH$_3$ protons), 5.36 ppm (singlet 2H, CH$_2$Cl$_2$) and 6.94 ppm (multiplet, 30H, C$_6$H$_5$ protons). The attempted preparation of ThCl·2dmdpu from the stoicheiometric quantities of the tetrachloride and dmdpu was unsuccessful.

The bis complexes were, in general, much more hygroscopic than ThCl$_4$·3dedmu and ThCl$_4$·3dmdpu, and the two tris complexes were much more soluble in dichloromethane than the bis complexes.

IR Spectra

The shifts in the C=O stretching frequencies of the ligands on complex formation (Table I) are large, as reported [1] for analogous complexes with other substituted ureas. The IR spectra of the bis complexes in tetrahydrofuran indicated complete (dipdpu) or appreciable dissociation of the ligand in that solvent, whereas in dichloromethane solution only ThCl$_4$·2dipdpu appeared to dissociate appreciably. The tris complexes, ThCl$_4$·3dedmu, ThCl$_4$·3dmdpu and ThCl$_4$·3dmdpu·CH$_2$Cl$_2$ also appear to dissociate partially in tetrahydrofuran and in dichloromethane.

The Structure of ThCl$_4$·3dmdpu

The crystal structure of the title compound consists of well separated molecules of ThCl$_4$(dmdpu)$_3$ which are packed in the triclinic cell together with disordered pentane molecules (see 'Experimental'). A view of a single molecule down *b* is shown in Fig. 1, together with the atom numbering scheme, a packing diagram is shown in Fig. 2. (The disordered pentane molecules are omitted for clarity).

Bond distances and angles are given in Table II. The thorium ion is seven-coordinated to four chlorine and three oxygen atoms belonging to the dmdpu ligands. The coordination geometry is a pentagonal bipyramid in which two chlorines are in axial and two in equatorial positions together, with three dmdpu ligands coordinated through the oxygens. This kind of geometry, which was considered rather

TABLE I. IR Spectra (cm^{-1}); Nujol Mull (a), Dichloromethane Solution (b) and Tetrahydrofuran Solution (c)

Complex	Solvent	$\nu_{C=O}$^{a}	$\Delta\nu_{C=O}$	ν_{Th-Cl}^{a}
ThCl$_4$·2tmu	a	1579s	58	260s
	b	1567s	70	
	c	1645w, 1560s	−8, 67	
ThCl$_4$·2teu	a	1539s	101	263s
	b	1532s, sh	108	
	c	1637m, 1531s, sh	3, 109	
ThCl$_4$·3dmdpu	a	1536s	108	262m, 236w, sh
	b	1642w, 1528s	2, 116	
	c	1650s, 1533m	−6, 111	
ThCl$_4$·3dmdpu·CH$_2$Cl$_2$	a	1531s	113	250m, 233w, sh
	b	1645vw, 1528s, sh	−1, 116	
	c	1651s, 1537s, sh	−7, 107	
ThCl$_4$·2dedmu	a	1566s	77	259s
	b	1564s	79	
	c	1639w, 1550s, sh	4, 93	
ThCl$_4$·3dedmu	a	1544s, sh	99	243m, 228m, sh
	b	1634w, sh, 1553s, sh	9, 90	
	c	1643m, 1543s, sh	0, 100	
ThCl$_4$·2dipdmu	a	1540s	101	261s
	b	1544s	97	
	c	1640s, 1545m	1, 96	
ThCl$_4$·2dipdpu	a	1555s	106	263s
	b	1656w, 1551s	5, 110	
	c	1660s	1	
ThCl$_4$·2dibdmu	a	1560s	82	260s
	b	1559s	81	
	c	1643m, 1543s, sh	−1, 99	

[a] s = strong; m = medium; w = weak; v = very; sh = shoulder.

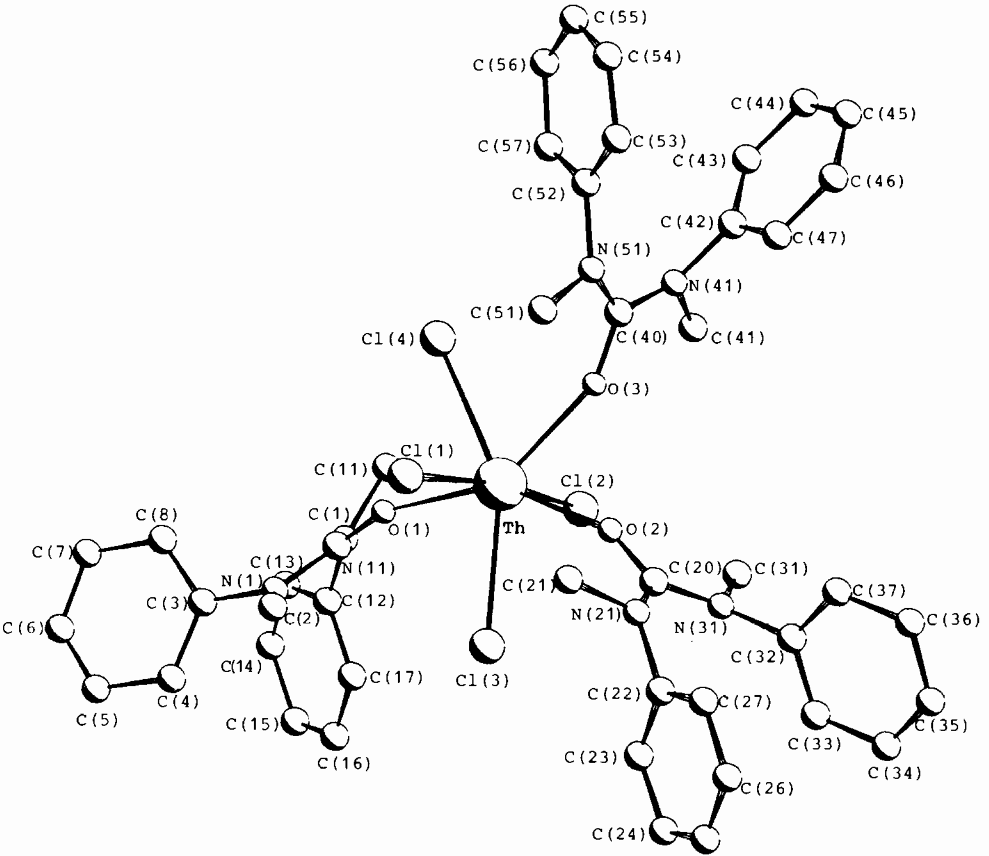

Fig. 1. View down *b* of the $ThCl_4(dmdpu)_3$ molecule.

unusual for Th(IV) derivatives, seems fairly common for MX_4L_3 derivatives (M = U, Th), (X = halide or pseudohalide, L = substituted amide or urea) and it is closely related to the bulk of either the anionic and/or the neutral ligands. Recently we have also determined the analogous structure of [$ThCl_4$(*N,N*-diethylpropionamide)$_3$] [2]; of the possible isomers, the most likely seems to be the one with two anionic ligands in axial positions, two neutral ligands in adjacent positions in the equatorial plane and two anionic ligands which comprise between them the third neutral ligand. It has been also found in the complex [$U(NCS)_4(dmiba)_3$] [3].

The pentagonal equatorial plane is rather irregular with deviations from planarity ranging between 0.12(1) to −0.18(1) Å from the best weighted mean plane calculated with the five coordinated atoms; the Th atom is −0.004(9) Å from this plane.

The Cl(1)–Th–Cl(2) angle of 171.8(1)° deviates significantly from linearity. The $Th-Cl_{ax}$ bond distances average 2.696(3) Å and are significantly shorter with respect to the $Th-Cl_{eq}$ which average 2.743(3) Å, indicating either more covalency in the Th_{ax} bond distances or less steric hindrance in these positions with respect to the equatorial ones. The first hypothesis could be reminiscent of the behaviour of the UO groups in the uranyl compounds with the same coordination geometry [4].

The Th–O in the equatorial plane are close to each other, but the two adjacent Th–O(1) (2.370(5)) and Th–O(2) (2.413(5) Å) are slightly different, while Th–O(1) is practically equal to Th–O(3) (2.375(5) Å). A comparison with [$ThCl_4$(*N,N*-diethylpropionamide)$_3$] [2], which has the same coordination geometry and is the same isomer, shows analogous values and analogous differences between $Th-Cl_{ax}$ and $Th-Cl_{eq}$ (being on average 2.692(3) and 2.754(3) Å, respectively). This could substantiate a higher covalency in the $Th-Cl_{ax}$ bond lengths, as the different hindrance of the neutral ligands in the equatorial plane seems not to influence the Th–Cl equatorials. In the complex [$Th-Cl_4(depa)_3$] [2] the Th–O bond distances are equal in the limit of the errors, and their average 2.34(1) Å is in any case shorter with respect to the averaged value of 2.386(5) Å found in the [$ThCl_4$-$(dmdpu)_3$] derivative. This suggests that the bulk of the dmdpu ligands does not influence the Th–O bond distances and that the steric factors are predominant on the Th–O bond lengths and probably

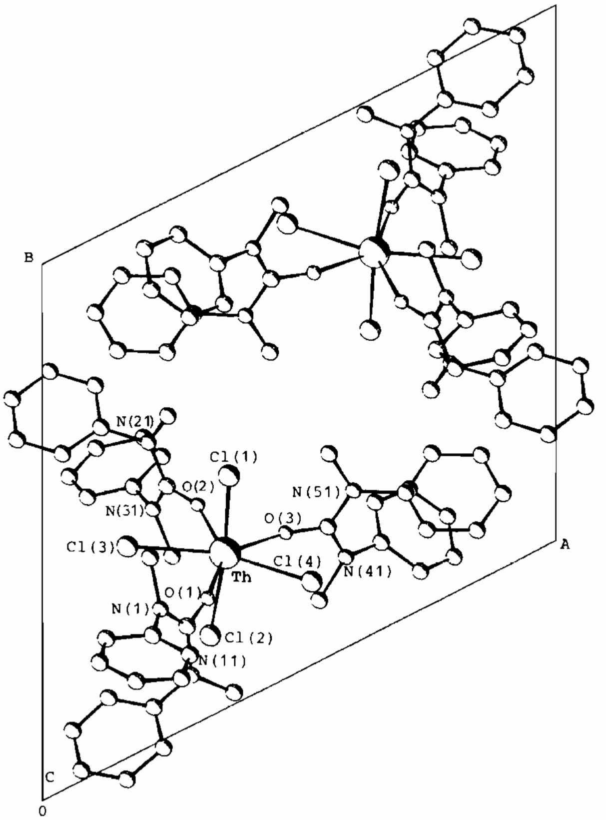

Fig. 2. Unit cell content viewed down *c* (n-pentane molecules are omitted for the sake of clarity).

on the bending of the Cl–Th–Cl axial angle. In fact, in the less-crowded [$ThCl_4(depa)_3$] the Cl(1)–Th–Cl(2) angle (axial) is 175.5(1)° with less pronounced deviation from linearity, and also the pentagonal equatorial plane is less puckered with deviations from the best mean plane ranging from –0.144 to 0.100 Å.

Some selected structural parameters in analogous actinide compounds with the same coordination geometry are reported in Table III. It can be seen that the trend for which $M–X_{axial}$ bond distances are shorter compared with the equatorial ones is independent of the hindrance of the neutral ligand in the equatorial plane.

Experimental

The drying of solvents and the handling of air- and moisture-sensitive products was carried out as described previously [6]. $ThCl_4$ was prepared by the published method [7] and the substituted ureas were obtained as follows: tmu from B.D.H. Limited, teu from Fluka and dmdpu from K. and K. Laboratories, Inc. The remaining ligands were prepared by reaction of the carbamoyl chloride with the appropriate amine. IR [8] and ^1H NMR [9] spectra were obtained as reported previously.

TABLE II. Distances (Å) and Principal Angles (°) for $ThCl_4 \cdot 3dmdpu$[a]

Distances					
(a) Thorium coordination polyhedron					
Th–Cl(1)	2.695(3)	Th–O(1)	2.370(5)		
Th–Cl(2)	2.696(3)	Th–O(2)	2.413(5)		
Th–Cl(3)	2.729(2)	Th–O(3)	2.375(5)		
Th–Cl(4)	2.758(3)				
Mean Th–Cl	2.720(3)	Mean Th–O	2.386(5)		
(b) dmdpu ligands					
O(1)–C(1)	1.24(1)	O(2)–C(20)	1.24(1)	O(3)–C(40)	1.27(1)
C(1)–N(1)	1.36(1)	C(20)–N(21)	1.35(1)	C(40)–N(41)	1.35(1)
C(1)–N(11)	1.37(1)	C(20)–N(31)	1.36(2)	C(40)–N(51)	1.34(2)
N(1)–C(2)	1.47(1)	N(21)–C(21)	1.46(2)	N(41)–C(41)	1.46(2)
N(1)–C(3)	1.43(1)	N(21)–C(22)	1.44(1)	N(41)–C(42)	1.44(1)
N(11)–C(11)	1.46(1)	N(31)–C(31)	1.45(1)	N(51)–C(51)	1.47(1)
N(11)–C(12)	1.42(1)	N(31)–C(32)	1.45(1)	N(51)–C(52)	1.46(1)
$C(3) \rightarrow C(8)_{(Ph)}$	1.36(2)	C(22)–C(23)	1.35(1)	$C(42) \rightarrow C(47)_{(Ph)}$	1.38(2)
$C(12) \rightarrow C(17)_{(Ph)}$	1.38(2)	$C(32) \rightarrow C(37)_{(Ph)}$	1.38(2)	$C(52) \rightarrow C(57)_{(Ph)}$	1.38(2)
Angles					
(a) Thorium environment					
Cl(1)–Th–Cl(2)	171.8(1)	Cl(1)–Th–O(1)	87.6(2)		
Cl(1)–Th–Cl(3)	87.0(1)	Cl(1)–Th–O(2)	90.2(2)		
Cl(1)–Th–Cl(4)	88.0(1)	Cl(1)–Th–O(3)	99.1(2)		

(Continued on facing page)

TABLE II *(continued)*

Cl(2)–Th–Cl(3)	86.8(1)	Cl(2)–Th–O(1)	85.7(2)		
Cl(2)–Th–Cl(4)	94.6(1)	Cl(2)–Th–O(2)	93.2(2)		
Cl(3)–Th–Cl(4)	150.0(1)	Cl(2)–Th–O(3)	89.1(2)		
		Cl(3)–Th–O(1)	76.9(2)		
O(1)–Th–O(2)	150.0(2)	Cl(3)–Th–O(2)	73.1(1)		
O(1)–Th–O(3)	144.4(2)	Cl(3)–Th–O(3)	138.0(1)		
O(2)–Th–O(3)	65.5(2)	Cl(4)–Th–O(1)	73.4(2)		
Th–O(1)–C(1)	160.3(8)	Cl(4)–Th–O(2)	136.5(1)		
Th–O(2)–C(20)	154.8(5)	Cl(4)–Th–O(3)	72.0(1)		
Th–O(3)–C(40)	155.8(6)				
(b) dmdpu ligands					
O(1)–C(1)–N(1)	120.1(9)	O(2)–C(20)–N(21)	121(1)	O(3)–C(40)–N(41)	118(1)
O(1)–C(1)–N(11)	121.6(8)	O(2)–C(20–N(31)	119.2(8)	O(3)–C(40)–N(51)	120.0(8)
N(1)–C(1)–N(11)	118.2(7)	N(21)–C(20)–N(31)	119.8(7)	N(41)–C(40)–N(51)	121.5(7)
C(1)–N(1)–C(2)	118.3(7)	C(20)–N(21)–C(21)	118.5(8)	C(40)–N(41)–C(41)	118.7(8)
C(1)–N(1)–C(3)	122.8(7)	C(20)–N(21)–C(22)	123(1)	C(40)–N(41)–C(42)	122(1)
C(2)–N(1)–C(3)	116.8(8)	C(21)–N(21)–C(22)	114.6(8)	C(41)–N(41)–C(42)	116.2(9)
N(1)–C(3)–C(4)	119.4(7)	N(21)–C(22)–C(23)	119.8(7)	N(41)–C(42)–C(43)	119.4(7)
N(1)–C(3)–C(8)	120.5(8)	N(21)–C(22)–C(27)	119.8(9)	N(41)–C(42)–C(47)	121.0(6)
C(1)–N(11)–C(11)	116.7(8)	C(20)–N(31)–C(31)	118.8(8)	C(40)–N(51)–C(51)	118.7(7)
C(1)–N(11)–C(12)	123.3(6)	C(20)–N(31)–C(32)	124.9(8)	C(40)–N(51)–C(52)	121.4(7)
C(11)–N(11)–C(12)	119.1(9)	C(31)–N(31)–C(32)	112.7(9)	C(51)–N(51)–C(52)	116.8(9)
N(11)–C(12)–C(13)	119.5(8)	N(31)–C(32)–C(33)	119.2(7)	N(51)–C(52)–C(53)	117.7(6)
N(11)–C(12)–C(17)	120.5(8)	N(31)–C(32)–C(37)	120.0(8)	N(51)–C(52)–C(57)	120.1(8)
$C–C–C_{(C3 \rightarrow C8)}$	120.1(8)	$C–C–C_{(C22 \rightarrow C27)}$	120.0(9)	$C–C–C_{(C42 \rightarrow C47)}$	119.8(9)
$C–C–C_{(C12 \rightarrow C17)}$	120(1)	$C–C–C_{(C32 \rightarrow C37)}$	120(1)	$C–C–C_{(C52 \rightarrow C57)}$	120(1)
$C–C–C_{av}$	120(1)				

[a]Estimated standard deviations in parentheses.

TABLE III. Selected Structural Parameters in Pentagonal Bipyramidal Actinide Derivatives

	$M–X_{ax}$[a]	$M–X_{eq}$	M–O	X–M–X
$ThCl_4(EtCONEt_2)_3$ [2]	2.696(3) 2.687(3)	2.751(1) 2.757(3)	2.333(8) 2.352(9) 2.336(9)	175.5(1)
$ThCl_4(PhMeNCONMePh)_3$	2.695(3) 2.696(3)	2.729(2) 2.758(3)	2.370(5) 2.413(5) 2.375(5)	171.8(1)
$U(NCS)_4(Me_2CHCONMe_2)_3$ [3]	2.36(3) 2.32(2)	2.43(3) 2.34(3)	2.30(2) 2.29(2) 2.32(2)	177.4(9)
$[UCl_3[EtCONEt_2]_4]^+$ [5]	$2.62(2)_{av}$	$2.72(4)_{av}$	2.29(5)	not reported

[a]X is the anionic ligand.

Preparations

(a) Tris(N,N-diethyl-N'N'-dimethylurea)tetrachlorothorium(IV), $ThCl_4$·3dedmu

An excess of dedmu (0.8 g, 5.56 mmol) in dichloromethane (5 cm^3) was added to a suspension of thorium tetrachloride (0.5 g, 1.34 mmol) in the same solvent (10 cm^3). The solution became clear after stirring for *ca.* 10 min; any insoluble material was discarded and the supernatant was evaporated to dryness, leaving an oily residue which was dissolved in ethyl acetate (5 cm^3). n-Pentane was then added until the solution became cloudy and the product crystallised on standing overnight. The crystals were washed with n-pentane (3 × 3 cm^3) and vacuum dried (8 h). $ThCl_4$·2dibdmu was prepared in the same way.

(b) Bis(N,N,N′,N′-tetramethylurea)tetrachlorothorium(IV), $ThCl_4 \cdot 2tmu$

The stoicheiometric quantity of tmu (0.31 g, 2.67 mmol) in dichloromethane (5 cm^3) was added to a suspension of thorium tetrachloride (0.5 g, 1.34 mmol) in the same solvent (10 cm^3). After stirring overnight, the solution was filtered, and the insoluble material was extracted with dichloromethane (3 × 5 cm^3), after which the combined extracts and the filtrate were vacuum evaporated to *ca.* 5 cm^3, whereupon the white solid product separated. This was washed with n-pentane (2 × 3 cm^3) and vacuum dried (5 h).

(c) Bis(N,N,N′,N′-tetraethylurea)tetrachlorothorium(IV), $ThCl_4 \cdot 2teu$

An excess of teu (0.5 g, 2.9 mmol) was added to a solution of thorium tetrachloride (0.5 g, 1.34 mmol) in tetrahydrofuran (10 cm^3). After stirring for 1 h the solution was vacuum evaporated to dryness and the oily residue was dissolved in toluene (5 cm^3). n-Pentane was added until the solution became cloudy and large colourless crystals of the product separated on standing overnight; these were washed with n-pentane (2 × 3 cm^3) and vacuum dried (6 h). The known complex [1] $ThCl_4 \cdot 3dmdpu$ was prepared in the same way except that the product crystallised from toluene solution without addition of n-pentane.

(d) Bis(N,N-diisopropyl-N′,N′-dimethylurea)tetrachlorothorium(IV), $ThCl_4 \cdot 2dipdmu$

An excess of dipdmu (1.0 g, 5.81 mmol) in tetrahydrofuran (3 cm^3) was added to a solution of thorium tetrachloride (0.5 g, 1.34 mmol) in the same solvent (10 cm^3). After stirring for 1 h the solution was vacuum evaporated to small bulk (2 cm^3) whereupon the product separated as white crystals. These were washed with n-pentane (2 × 3 cm^3), ground to powder, rewashed with n-pentane (2 × 3 cm^3) and vacuum dried (8 h). $ThCl_4 \cdot 2dipdpu$ was prepared in a similar manner, except that the tetrahydrofuran solution was vacuum evaporated to dryness, leaving an oil which was dissolved in ethyl acetate (10 cm^3). Vacuum evaporation of the solution to *ca.* 3 cm^3 yielded the product as a white crystalline solid which was then washed and dried as above.

(e) Bis(N,N-diethyl-N′,N′-dimethylurea)tetrachlorothorium(IV), $ThCl_4 \cdot 2dedmu$

n-Pentane was added to a solution of $ThCl_4 \cdot 3dedmu$ (0.6 g, 0.74 mmol) in dichloromethane (5 cm^3) until the solution became cloudy. The solution was then cleared by dropwise addition of dichloromethane and, on standing overnight, large, colourless prismatic crystals of the product separated. These were washed with n-pentane (2 × 3 cm^3) and vacuum dried (5 h). The same procedure with $ThCl_4 \cdot 3dmdpu$ yielded the dichloromethane solvate, $ThCl_4 \cdot 3dmdpu, CH_2Cl_2$.

The analytical results are summarised in Table IV which includes the yields.

X-ray Measurements and Structure Determination

The crystal and refinement data are summarized in Table V. $ThCl_4((OC(NMePh)_2)_3$ is in the form of white transparent regular square bipyramidal prisms.

A single crystal (0.25 × 0.12 × 1.10 mm) was lodged in a Lindemann glass capillary. It was centered on a four-circle Philips 1100 automated diffractometer with graphite monochromated Mo Kα radiation. The orientation matrix and preliminary unit cell dimensions were determinated from 25 reflections found by mounting the crystal at random, varying the orientation angles ψ and χ in the range of 120°, each the detector position varying between $\vartheta = 6$ and $\vartheta = 9$. For the determination of precise lattice parameters 25 strong reflections with $8 < \vartheta < 16$ were considered.

The intensities of the two standard reflections 3 1 2 and 5 4 1 were monitored every 180 min. There was no significant fluctuation in intensities than those expected Poisson statistic.

The intensity data were corrected for Lorentz-polarization effects, and for absorption following the method of North *et al.* [10]. The structure was

TABLE IV. Analytical Data (%)[a] and Yields of Complexes

Complex	Th	C	H	N	Cl	Yield (%)
$ThCl_4 \cdot 2tmu$	37.9(38.3)	20.4(19.8)	4.1(4.0)	9.4(9.2)	23.1(23.4)	52
$ThCl_4 \cdot 2teu$	32.2(32.3)	29.9(30.1)	5.7(5.6)	7.7(7.8)	19.6(19.8)	41
$ThCl_4 \cdot 3dmdpu \cdot CH_2Cl_2$	20.0(19.7)	46.7(46.8)	4.2(4.2)	7.1(7.1)	18.4(18.1)	75
$ThCl_4 \cdot 2dedmu$	35.3(35.0)	25.7(25.4)	5.3(4.8)	8.6(8.5)	21.7(21.5)	45
$ThCl_4 \cdot 3dedmu$	28.8(28.8)	31.2(31.3)	6.1(6.0)	10.3(10.4)	17.4(17.6)	70
$ThCl_4 \cdot 2dipdmu$	32.7(32.3)	30.0(30.1)	5.8(5.6)	7.9(7.8)	19.4(19.8)	73
$ThCl_4 \cdot 2dipdpu$	23.6(24.0)	47.1(47.2)	5.1(5.0)	5.7(5.8)	14.5(14.7)	65
$ThCl_4 \cdot 2dibdmu$	30.0(30.1)	34.1(33.7)	6.2(6.2)	7.2(7.3)	18.3(18.0)	65

[a] Calculated values are given in parentheses.

TABLE V. Crystal Data

Formula	$C_{50}H_{60}O_3N_6Cl_4Th$
M	1166.9
Space group	$P\bar{1}$
Crystal system	triclinic
a (Å)	16.826(3)
b (Å)	16.019(3)
c (Å)	12.131(2)
α (°)	110.4(1)
β (°)	106.6(1)
γ (°)	59.4(1)
U (Å^3)	2614.5
Z	2
D_c (Mg m^{-3})	1.48
F(000)	1168
Radiation (λ (Å))	(Mo Kα (0.7107))
Reflections measured	10529
Scan method	$\theta/2\theta$
Scan speed (° min^{-1})	1.80
Scan width (°)	1.2
Background counts(s)	10
2θ max (°)	52
σ limit $[I \geqslant n\sigma(I)]$	3
Unique observed reflections $[I \geqslant 3\sigma(I)]$	7936
Weighting scheme w	$1.5464/[\sigma^2(F_o) + 0.002527(F_o)^2]$
$R = (\Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|)$	0.053
$R_w = \left[\dfrac{\Sigma w\|F_o\| - \|F_c\|^2}{\Sigma w\|F_o\|^2}\right]^{1/2}$	0.058
μ(Mo Kα) (cm^{-1})	29.43

solved using three-dimensional Patterson and Fourier syntheses and refined by full matrix least-squares with anisotropic thermal parameters only for the atoms belonging to the Th coordination polyhedron and isotropic for the remaining non-hydrogen atoms. Hydrogen-atom contributions (for the phenyl and methyl groups) were introduced in calculated positions ($d_{C-H} = 0.95$ Å and $Th_{iso} = 0.07$ Å). Some difficulties were experienced in the last stages of the refinement. In fact the refinement of the $ThCl_4(dmdpu)_3$ molecule reached convergency to $R = 0.086$. At this point a Fourier difference map failed to reveal the CH_2Cl_2 atom positions as expected from the analytical formulation of the compound; instead about 10 residuals of the order of 2–3 e/Å^3 were observed. They were interpreted as statistically distributed n-pentane molecules. The introduction of carbon atoms in the positions indicated by the electron density residuals with population factors of 0.5 gave the most significant lowering of the R values: $R = 0.053$ and $R_w = 0.058$ but probably a more complex statistical distribution could be present, if the presence of disordered CH_2Cl_2 molecules seems to be excluded. (Attempts to interpret the residuals in terms of disordered CH_2Cl_2 were unsuccessfull). An explanation for this result is that the crystals suitable for X-ray study were recrystallized from CH_2Cl_2 and n-pentane in a quantity not sufficient for a microanalysis of the compound which has been analysed through its crystal structure determination. The anomalous dispersion terms [11] for Th were taken into account in the refinement. Atomic scattering factors were from ref. 11.

Data processing and computation were carried out using the SHELX 76 program package [12].

Final positional parameters are presented in Table VI.

TABLE VI. Fractional Coordinates (×10^4)^a

	x	y	z
Th	3542.6(2)	2896.5(2)	3490.6(2)
Cl(1)	3629(2)	4305(2)	2869(2)
Cl(2)	3260(2)	1503(2)	3847(2)
Cl(3)	1651(2)	3942(2)	3050(3)
Cl(4)	5234(2)	1549(2)	2677(3)
O(1)	3210(5)	2218(4)	1441(5)
C(1)	2810(6)	1893(6)	495(8)
N(1)	2291(5)	2468(5)	−295(6)
C(2)	2089(7)	3525(7)	82(10)
C(3)	2138(6)	2055(6)	−1541(8)
C(4)	1243(7)	2427(8)	−2146(10)
C(5)	1119(9)	2047(8)	−3409(11)
C(6)	1814(9)	1360(9)	−3950(13)
C(7)	2699(10)	983(10)	−3405(12)
C(8)	2862(7)	1343(7)	−2138(9)
N(11)	2892(5)	950(5)	204(6)
C(11)	3721(7)	219(8)	764(10)
C(12)	2161(6)	706(6)	−436(8)
C(13)	2349(7)	−152(7)	−1329(8)
C(14)	1637(8)	−399(9)	−1934(11)
C(15)	757(10)	199(9)	−1666(12)
C(16)	589(9)	1029(9)	−804(12)
C(17)	1286(7)	1305(8)	−167(10)
O(2)	3017(4)	4064(4)	5336(5)
C(20)	2422(5)	4705(6)	6002(7)
N(21)	2061(5)	5687(5)	6072(6)
C(21)	2441(9)	5993(9)	5423(12)
C(22)	1145(6)	6409(6)	6377(7)
C(23)	396(7)	6283(7)	5728(9)
C(24)	−483(8)	6969(8)	6039(11)
C(25)	−576(9)	7771(9)	6950(11)
C(26)	152(8)	7931(9)	7607(11)
C(27)	1032(7)	7243(7)	7311(9)
N(31)	2144(5)	4405(5)	6677(6)
C(31)	2518(8)	3341(7)	6556(10)
C(32)	1771(5)	5011(5)	7787(7)
C(33)	886(6)	5247(7)	7872(9)
C(34)	531(7)	5800(7)	8961(9)
C(35)	1051(8)	6068(9)	9897(11)
C(36)	1968(8)	5819(8)	9858(11)
C(37)	2324(7)	5300(7)	8757(9)
O(3)	4723(4)	2701(4)	5157(5)

(continued overleaf)

TABLE VI *(continued)*

	x	y	z
C(40)	5552(5)	2416(5)	5688(7)
N(41)	5899(5)	1686(5)	6253(6)
C(41)	5381(8)	1132(8)	6054(10)
C(42)	6588(6)	1624(6)	7294(7)
C(43)	7352(7)	714(8)	7370(10)
C(44)	8009(8)	667(9)	8394(11)
C(45)	7880(8)	1493(8)	9317(11)
C(46)	7141(8)	2366(8)	9241(10)
C(47)	6466(7)	2442(7)	8240(9)
C(51)	5575(7)	3774(7)	5273(9)
N(51)	6049(5)	2864(5)	5712(6)
C(52)	7060(5)	2330(5)	5786(7)
C(53)	7575(6)	2805(7)	6630(8)
C(54)	8535(8)	2308(9)	6653(11)
C(55)	8961(8)	1393(8)	5936(10)
C(56)	8455(8)	949(8)	5129(10)
C(57)	7476(7)	1434(7)	5021(9)

[a]Estimated standard deviations in parentheses.

Supplementary Material

Thermal parameters, observed and calculated structure factors (×10) are available from the authors on request.

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