

Structural Chemistry of Actinide Compounds with Different Coordination Numbers: The Crystal and Molecular Structures of Tetrachlorotrakis(*N,N*-diethylpropionamide)thorium(IV) and Tetra-*N*-thiocyanatoTetrakis(*N,N*-dimethylpropionamide)thorium(IV)

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The crystal and molecular structures of $\text{ThCl}_4(\text{depa})_3$ (1) (*depa* = *N,N*-diethylpropionamide) and $\text{Th}(\text{NCS})_4(\text{dmpa})_4$ (2) (*dmpa* = *N,N*-dimethylpropionamide) have been determined from three-dimensional X-ray diffraction data. The compounds crystallize in space group $P2_1/n$ (1) and $P2_1/a$ (2), with $a = 18.107(5)$, $b = 10.347(3)$, $c = 17.867(5)$ Å, $\beta = 108.5(1)^\circ$, $Z = 4$ (1) and $a = 22.759(6)$, $b = 13.763(4)$, $c = 11.910(3)$ Å, $\beta = 91.4(1)^\circ$ and $Z = 4$ (2). Full matrix least-squares refinement of both structures gave for (1) with 3126 intensity data $R = 0.046$ and $R_w 0.046$ and for (2) with 3480 intensity data $R = 0.050$, $R_w 0.054$. The different steric constraints imposed by the ligand give rise to different coordination numbers. In (1) the coordination polyhedron about the seven co-ordinate thorium atom is a pentagonal bipyramid with two chlorine atoms in the axial positions, an unusual geometry for Th(IV) species. The average bonding distances are $\text{Th}-\text{O} = 2.340(9)$, $\text{Th}-\text{Cl}_{\text{eq}} = 2.754(3)$ and $\text{Th}-\text{Cl}_{\text{ax}} = 2.692(3)$ Å.

In (2) the less hindering *dmpa* ligand favours the presence of four of them in the metal coordination sphere in a distorted square antiprismatic coordination geometry. $\text{Th}-\text{O}$ and $\text{Th}-\text{N}$ average 2.37(1) and 2.49(2) Å respectively.

Introduction

Amide complexes of thorium tetrachloride often adopt a different stoichiometry to that formed by

the same ligand with uranium tetrachloride, a difference which can be ascribed to the smaller radius of the U(IV) centre compared with that of Th(IV). For example, with the amide *depa* (= EtCONEt_2) the complexes $2\text{UCl}_4 \cdot 5\text{depa}$ [1] and $\text{ThCl}_4 \cdot 3\text{depa}$ [2] are obtained. The former has been shown [1] to be ionic, $[\text{UCl}_3(\text{depa})_4]^+[\text{UCl}_2(\text{depa})]^-$, with the 7-coordinate uranium atom in the cation adopting the rather unusual pentagonal bipyramidal geometry which had already been observed [3] in the neutral complex $\text{U}(\text{NCS})_4(\text{dmiba})_3$ (*dmiba* = $\text{Me}_2\text{CHCONMe}_2$). It was therefore of interest to determine the structure of $\text{ThCl}_4 \cdot 3(\text{depa})$ in order to ascertain whether the coordination geometry was again pentagonal bipyramidal, and also to investigate the structure of the probably 8-coordinate complex $\text{Th}(\text{NCS})_4 \cdot 4\text{dmpa}$ (*dmpa* = EtCONMe_2), the preparation of which has also been reported recently [2].

Experimental

The complexes were prepared by the published methods [2].

X-ray Measurements and Structure Determination

The crystal and refinement data are summarized in Table I. $\text{ThCl}_4(\text{depa})_3$ (1) and $\text{Th}(\text{NCS})_4(\text{dmpa})_4$ (2) are in the form of colourless transparent prisms. They are very sensitive to atmospheric moisture and were therefore mounted in thin-walled Lindemann glass capillaries in an inert atmosphere glove box. The X-ray intensity data were collected with graphite monochromated $\text{MoK}\alpha$ radiation. The unit cell parameters were determined on the basis of 25 strong

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TABLE I. Crystal Data.

Compound	ThCl ₄ (depa) ₃	Th(NCS) ₄ (dmpa) ₄
Formula	C ₂₁ Cl ₄ H ₄₅ N ₃ O ₃ Th	C ₂₄ H ₄₄ N ₈ O ₄ S ₄ Th
M	761.5	821.0
Space group	P2 ₁ /n	P2 ₁ /a
Crystal system	monoclinic	monoclinic
<i>a</i> /Å	18.107(5)	22.759(6)
<i>b</i> /Å	10.347(3)	13.763(4)
<i>c</i> /Å	17.867(5)	11.910(3)
β /°	108.5(1)	91.41
<i>U</i> /Å ³	3175	3729
<i>Z</i>	4	4
<i>D_c</i> /g cm ⁻³	1.59	1.46
F(000)	1496	1720
Radiation (λ /Å)	MoK α (0.7107)	MoK α (0.7107)
μ /cm ⁻¹	48.2	40.6
Reflections measured	6409	7663
Scan method	$\theta/2\theta$	$\theta/2\theta$
Scan speed/min ⁻¹	1.8	1.8
Scan width/°	1.20	1.20
Background counts/s	10	10
$2\theta_{\max}$ /°	52	52
σ limit	$n = 3$	$n = 2.5$
$ I > n\sigma(I) $		
Unique observed reflections	3126	3480
Weighting scheme <i>w</i>	$2.2072[\sigma^2(F_o) + 0.00532(F_o)^2]^{-1}$	$1.9277[\sigma^2(F_o) + 0.00109(F_o)^2]^{-1}$
<i>R</i> ($R = \sum F_o - F_c / \sum F_o $)	0.046	0.050
<i>R_w</i> ($R_w = \left[\frac{\sum w F_o - F_c ^2}{\sum w F_o ^2} \right]^{1/2}$)	0.046	0.054

reflections found by mounting the crystal at random, varying the orientation angles ϕ and χ in the range of 120° each with the detector position varying between $\theta = 6^\circ$ and $\theta = 10^\circ$. For the determination of precise lattice parameters 20 strong reflections with $9^\circ \leq \theta \leq 14^\circ$ were considered. The intensities of two standard reflections, monitored at 180 reflection intervals, showed no greater fluctuation than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects, and for absorption following the method of North *et al.* [4]. The structures were solved using three-dimensional Patterson and Fourier techniques and refined by full matrix least-squares. Structure (1) was refined with anisotropic thermal parameters assigned to all the non hydrogen atoms.

Structure (2) was refined with anisotropic thermal parameters assigned to the Th(NCS)₄O₄ moiety and isotropic to the remaining non hydrogen atoms. Some difficulty was experienced in the refinement of terminal ethyl groups, one of which was refined with an imposed C(42)–C(43) bond distance (1.53(2)

Å because of apparent disorder). In both the refinements the weighting scheme used showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect both to F_o and to $(\lambda^{-1} \sin\theta)$.

Hydrogen atoms were not observed and not included in the refinement.

The anomalous dispersion terms [5] for Th were taken into account in the refinement. Atomic scattering factors for the non-hydrogen atoms were from ref. 6. Data processing and computation were carried out using the SHELX 76 program package [7]. Final positional parameters for (1) and (2) are presented in Tables II and III. Thermal parameters, observed and calculated structure factors ($\times 10^3$) for both compounds are available as Supplementary material.

Results and Discussion

ThCl₄(EtCONEt₂)₃

A view of the molecule down *a* is shown in Fig. 1 together with the atom numbering scheme and the

TABLE II. Atomic Coordinates ($\times 10^4$) with E.s.d.s in Parentheses for (1).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Th	5046.6(3)	3260.7(5)	2604.0(3)
Cl(1)	3860(2)	4039(4)	3103(3)
Cl(2)	6145(3)	2424(5)	2002(3)
Cl(3)	5850(3)	2096(5)	4010(3)
Cl(4)	4858(3)	5486(4)	1715(3)
O(1)	4525(6)	1190(9)	2565(6)
O(2)	4181(6)	2764(10)	1347(6)
O(3)	5866(7)	4813(11)	3397(7)
N(11)	4068(11)	-675(14)	2681(10)
C(11)	4454(11)	5(22)	2515(10)
C(12)	4950(11)	-888(16)	2063(10)
C(13)	5743(10)	-1144(19)	2668(13)
C(14)	3899(9)	-2117(14)	2711(11)
C(15)	3182(11)	-2489(20)	2002(15)
C(16)	3541(10)	287(21)	3182(12)
C(17)	3958(13)	254(22)	4047(14)
N(21)	3722(12)	3181(16)	75(12)
C(21)	3589(14)	3055(15)	708(15)
C(22)	2774(10)	3206(23)	787(13)
C(23)	2501(12)	1835(27)	911(16)
C(24)	4579(13)	3135(20)	63(12)
C(25)	4744(11)	1722(20)	-103(11)
C(26)	3042(13)	3422(23)	-710(12)
C(27)	2981(20)	4866(32)	-831(17)
N(31)	6785(8)	5986(16)	4009(14)
C(31)	6272(11)	5492(21)	4002(20)
C(32)	6037(17)	5752(25)	4751(13)
C(33)	5365(15)	6610(20)	4559(13)
C(34)	7253(13)	7045(27)	4534(15)
C(35)	8021(23)	6541(45)	4945(27)
C(36)	7063(13)	5769(21)	3102(14)
C(37)	7574(14)	4683(23)	3246(16)

packing diagram is in Fig. 2. Bond distances and angles are reported in Table IV. The coordination polyhedron is a slightly distorted pentagonal bipyramid with two chlorine atoms occupying the axial positions; the equatorial pentagon is rather puckered and the six atoms which define the plane are out

TABLE III. Atomic Coordinates ($\times 10^4$) with E.s.d.s in Parentheses for (2).

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Th	3779.8(2)	2211.3(4)	3140.4(4)
S(1)	5421(3)	2843(6)	6170(6)
S(2)	5511(3)	2666(5)	432(8)
S(3)	2043(3)	393(5)	1272(5)
S(4)	2905(3)	773(5)	6803(4)
N(1)	4499(6)	2480(9)	4687(13)
N(2)	4567(6)	2177(12)	1720(13)
N(3)	3032(6)	1050(11)	2413(11)
N(4)	3417(5)	1350(10)	4850(11)
C(1)	4870(8)	2608(12)	5361(15)
C(2)	4955(8)	2372(13)	1192(15)
C(3)	2622(7)	780(11)	1929(14)
C(4)	3198(7)	1127(12)	5639(13)
O(1)	3294(4)	2828(8)	1481(8)
O(2)	4131(5)	3841(8)	2950(8)
O(3)	4299(4)	733(8)	3201(9)
O(4)	3018(4)	3141(7)	3886(8)
N(11)	2504(6)	3033(9)	428(11)
C(11)	3016(7)	2687(12)	559(12)
C(12)	3307(8)	2112(13)	-342(14)
C(13)	3645(10)	2783(16)	-1049(19)
C(14)	2223(8)	3577(14)	1255(16)
C(15)	2156(9)	2946(14)	-719(18)
N(21)	4915(8)	4690(13)	2406(14)
C(21)	4366(8)	4478(13)	2308(13)
C(22)	3978(8)	4939(14)	1389(15)
C(23)	3554(10)	5584(17)	1868(18)
C(24)	5281(11)	4268(18)	3298(20)
C(25)	5209(9)	5404(16)	1689(17)
N(31)	5084(11)	-29(18)	2903(20)
C(31)	4604(12)	46(20)	2666(21)
C(32)	4235(9)	-615(16)	1858(18)
C(33)	4246(14)	-218(27)	758(30)
C(34)	5362(11)	-905(21)	2171(21)
C(35)	5480(11)	564(19)	3703(20)
N(41)	2212(7)	3163(11)	4894(12)
C(41)	2732(7)	3481(13)	4706(14)
C(42)	2966(11)	4139(20)	5584(21)
C(43)	3991(14)	4656(27)	5292(31)
C(44)	1933(9)	2395(15)	4224(18)
C(45)	1888(9)	3547(17)	5891(18)

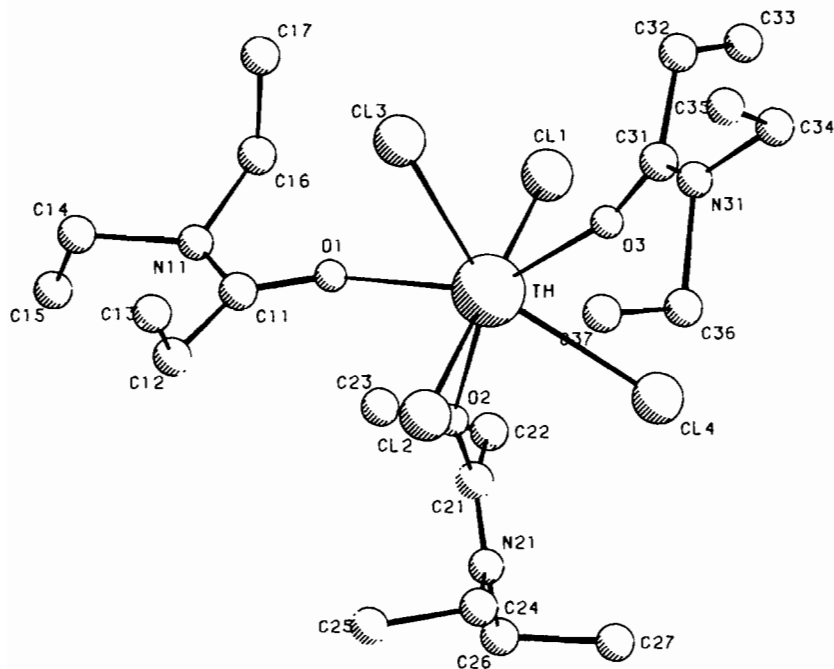
TABLE IV. Bond Distances (Å) and Angles ($^\circ$) with Estimated Standard Deviations in Parentheses for $[\text{Th}(\text{Cl}_4(\text{depa})_3)]$.

a) Thorium environment					
Th-Cl(1) _{ax.}	2.696(3)	Th-Cl(4)	2.757(3)	Th-O(2)	2.352(9)
Th-Cl(2) _{ax.}	2.687(3)	Th-O(1)	2.333(8)	Th-O(3)	2.336(9)
Th-Cl(3)	2.751(3)				
O(1)-Th-Cl(1)	85.8(2)	O(2)-Th-Cl(1)	91.2(2)	O(3)-Th-Cl(1)	90.8(2)
O(1)-Th-Cl(2)	92.1(2)	O(2)-Th-Cl(2)	84.3(2)	O(3)-Th-Cl(2)	93.2(3)
O(1)-Th-Cl(3)	73.5(2)	O(2)-Th-Cl(3)	140.9(2)	O(3)-Th-Cl(3)	72.3(3)
O(1)-Th-Cl(4)	140.8(2)	O(2)-Th-Cl(4)	73.1(2)	O(3)-Th-Cl(4)	73.4(3)

(continued overleaf)

TABLE IV. (continued)

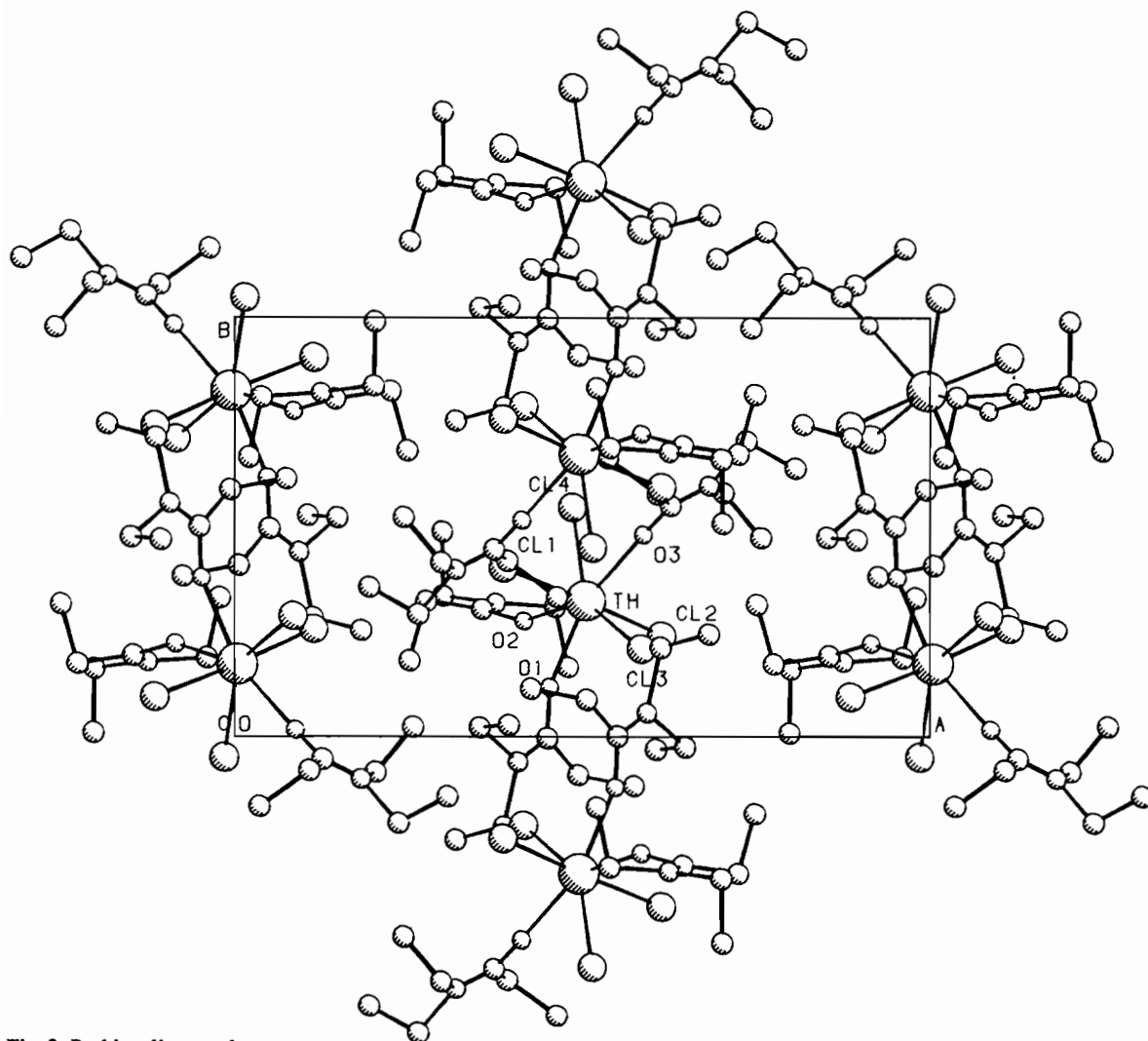
Cl(1)–Th–Cl(2)	175.5(1)	Cl(1)–Th–Cl(4)	88.6(1)	Cl(2)–Th–Cl(4)	90.6(1)
Cl(1)–Th–Cl(3)	94.3(1)	Cl(2)–Th–Cl(3)	88.9(1)	Cl(3)–Th–Cl(4)	145.6(1)
O(1)–Th–O(2)	68.3(3)	O(1)–Th–O(3)	145.3(3)	O(2)–Th–O(3)	146.3(3)
b) depa Ligands					
C(11)–O(1)	1.23(2)	C(21)–O(2)	1.33(2)	C(31)–O(3)	1.30(2)
C(11)–C(12)	1.66(2)	C(21)–C(22)	1.54(2)	C(31)–C(32)	1.55(3)
C(12)–C(13)	1.52(2)	C(22)–C(23)	1.54(2)	C(32)–C(33)	1.46(2)
N(11)–C(11)	1.10(2)	N(21)–C(21)	1.24(2)	N(31)–C(31)	1.06(2)
N(11)–C(14)	1.53(2)	N(21)–C(24)	1.56(2)	N(31)–C(34)	1.52(2)
N(11)–C(16)	1.80(2)	N(21)–C(26)	1.57(2)	N(31)–C(36)	1.86(3)
C(14)–C(15)	1.55(2)	C(24)–C(25)	1.54(2)	C(34)–C(35)	1.45(4)
C(16)–C(17)	1.49(2)	C(26)–C(27)	1.51(3)	C(36)–C(37)	1.43(2)
N(11)–C(14)–C(15)	110(1)	N(21)–C(24)–C(25)	107(1)	N(31)–C(34)–C(35)	108(2)
N(11)–C(16)–C(17)	109(1)	N(21)–C(26)–C(27)	107(2)	N(31)–C(36)–C(37)	106(2)
N(11)–C(11)–C(12)	105(2)	N(21)–C(21)–C(22)	123(2)	N(31)–C(31)–C(32)	113(3)
N(11)–C(11)–O(1)	133(2)	N(21)–C(21)–O(2)	118(2)	N(31)–C(31)–O(3)	122(3)
O(1)–C(11)–C(12)	122(2)	O(2)–C(21)–C(22)	119(2)	O(3)–C(31)–C(32)	125(2)
C(11)–C(12)–C(13)	107(1)	C(21)–C(22)–C(23)	106(1)	C(31)–C(32)–C(33)	110(2)
C(11)–N(11)–C(14)	142(2)	C(21)–N(21)–C(24)	120(2)	C(31)–N(31)–C(34)	132(3)
C(11)–N(11)–C(16)	105(2)	C(21)–N(21)–C(26)	121(2)	C(31)–N(31)–C(36)	114(2)
C(14)–N(11)–C(16)	112(1)	C(24)–N(21)–C(26)	120(2)	C(34)–N(31)–C(36)	112(1)

Fig. 1. View of the $\text{ThCl}_4(\text{EtCONEt}_2)_3$ molecule down a .

of the plane respectively Th -0.007 , Cl(3) 0.100 , Cl(4) -0.031 , O(1) -0.144 , O(2) 0.123 and O(3) -0.041 Å.

This kind of geometry is common in seven-coordinate dioxouranium(VI) complexes but rather unusual for U(IV) compounds. The only known examples are

$\text{U}(\text{NCS})_4(\text{dmiba})_3$ [3] where two NCS groups are in the apical position and the complex cation $[\text{UCl}_3(\text{depa})_4]^{+1}$ where, in the apical positions in this case are two chlorine atoms, the third being in an equatorial position. While in the first case the differences between bond lengths U–N equatorial and U–N

Fig. 2. Packing diagram down *c*.TABLE V. Ligand Arrangement around the Thorium Ion in $\text{ThCl}_4(\text{depa})_3$.


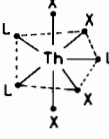
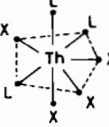
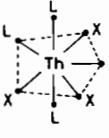
Isomer	$\Sigma\text{FA}_{\text{axial}}$	$\Sigma\text{FA}_{\text{equatorial}}$	$\Delta\Sigma\text{FA}$
1. 	168	196	28
2. 	168	196	28
3. 	160	204	44

TABLE V. (continued)

Isomer	$\Sigma\text{FA}_{\text{axial}}$	$\Sigma\text{FA}_{\text{equatorial}}$	$\Delta\Sigma\text{FA}$
4. 	160	212	52
	152		60

axial are not significant, being 2.39(3) and 2.34(3) Å in the two cases respectively, in the complex cation the $\text{U}-\text{Cl}_{\text{apical}}$ 2.62(2) Å is shorter with respect to the equatorial one 2.72(4) Å.

For thorium(IV) mononuclear derivatives this is the first example of this type of geometry.

Fan angle (FA) calculations on the four possible isomers (Table V) indicate that the first and second are the more likely. (The fan angle is used to assess

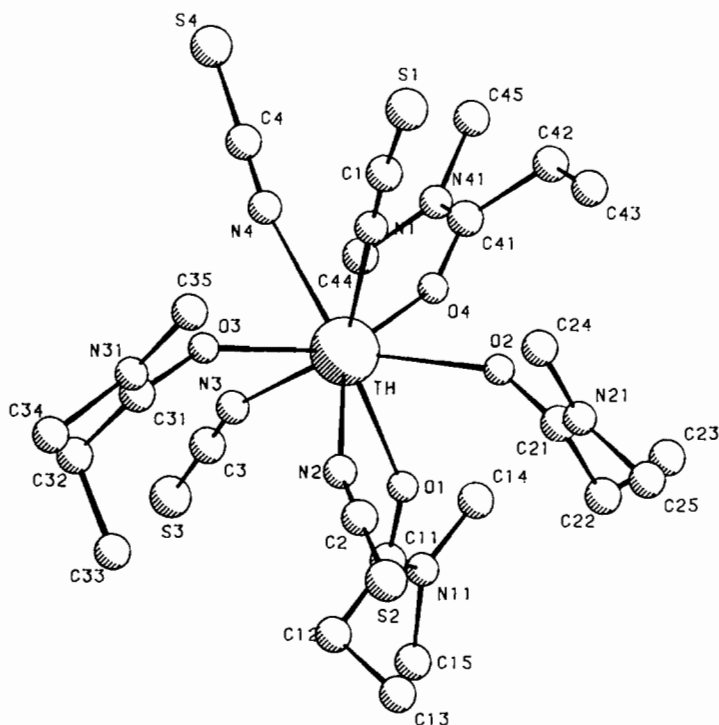
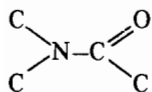


Fig. 3. View down a of $\text{Th}(\text{NCS})_4(\text{EtCONMe}_2)_4$.

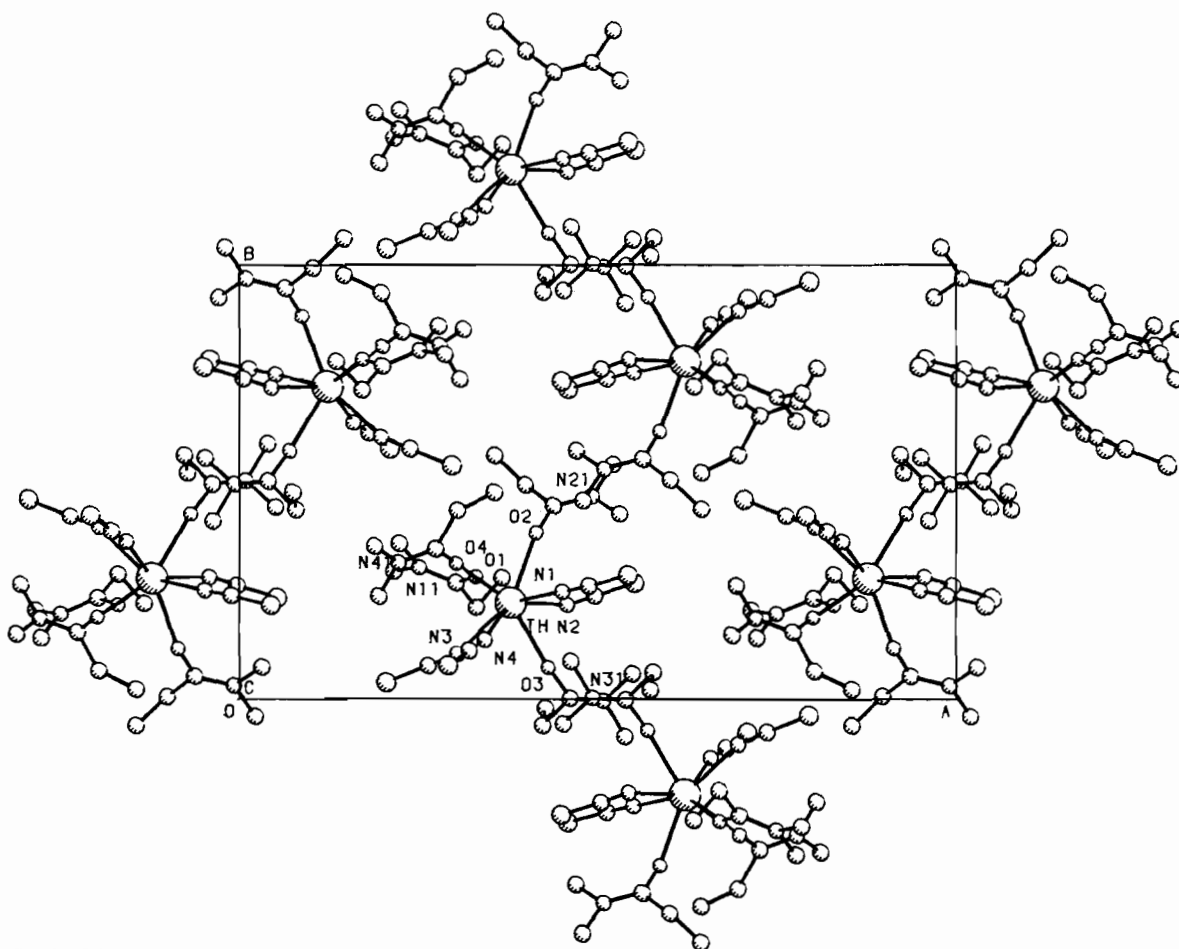
the steric crowding in the metal coordination sphere and is the angle subtended by the primary co-ordinating atom in the various symmetry planes [8]. Another term is also used, the cone angle factor (CAF) which is the solid angle of the cone comprising the metal centre at the apex and the primary co-ordinating atom or the whole ligand (CAFS) divided by 4π . The values of ΣFA (axial) of 168 and FA (equatorial) 196 allow a minimum of 28° in the 'fan' angle difference, axial to equatorial, indicating that isomer 1 and 2 structures are the more likely. The isomer 2 structure has been found here and consequently it appears to be the less sterically crowded. This kind of isomer has been found also in the $\text{U}(\text{NCS})_4(\text{dmiba})_3$ [3] derivative where the nitrogens are in the chlorine positions. The CAF summation which gives a measure of the steric crowding is 0.793, in the range expected (0.80 ± 0.02) for compounds of Th(IV) and U(IV) of stable structure (the individual CAF values for the ligands are $\text{Th}-\text{Cl}_{\text{ax}}$ 0.1284, $\text{Th}-\text{Cl}_{\text{eq}}$ 0.1216, $\text{Th}-\text{O}$ 0.0992). Mean plane calculations through the depa ligands show that the



fragment is planar within the limit of error and that the planar parts of the three neutral ligands (1, 2 and 3) are inclined with respect to the equatorial mean

plane by 85.9 , 73.5 and 63.1° respectively and with respect to the plane formed by the axial atoms ($\text{Th}-\text{Cl}(1)$, $\text{Cl}(2)$) by 67.9 , 33.5 and 38.3° respectively.

The $\text{Th}-\text{Cl}$ axial bond distance averaging $2.691(3)$ and $\text{Th}-\text{Cl}$ equatorial averaging $2.754(3)$ Å show a significant shortening for the axial one. A similar trend has been noticed also in $[\text{UCl}_3(\text{depa})_4]^+$ although due to high e.s.d.s in the bond distances it did not appear significant. The $\text{Th}-\text{Cl}_{\text{eq}}$ bond distance is comparable to the values of 2.757 and 2.759 Å reported for $\text{ThCl}_4(\text{Ph}_2\text{SO})_4$ [9] where the thorium atom is eight-coordinate with a dodecahedral geometry. The $\text{Cl}(1)-\text{Th}-\text{Cl}(2)$ angle is $175.5(1)^\circ$. The ligands (depa) are oxygen bonded to the thorium atom and form $\text{Th}-\text{O}-\text{C}$ angles ranging from $152(1)$ and $163(1)^\circ$ (average $159(1)^\circ$) not too different from the value of $164(2)^\circ$ found in $[\text{UCl}_3(\text{depa})_4]^+$. The three $\text{Th}-\text{O}$ bond distances in the equatorial plane are equal within the limit of error, being $\text{Th}-\text{O}(1)$ $2.333(8)$, $\text{Th}-\text{O}(2)$ $2.352(9)$ and $\text{Th}-\text{O}(3)$ $2.336(9)$ Å. A fruitful comparison of the ligand geometry in this compound and in the $[\text{UCl}_3(\text{depa})_4]^+$ complex cation cannot be made because of the very high thermal motion in the ligand atoms in the present compound and the poor quality of the crystal in the uranium derivative. However, within this limitation the average values of the $\text{O}-\text{C}$ $1.29(3)$, $\text{N}=\text{C}$ $1.13(3)$, $\text{N}-\text{C}$ $1.54(4)$ and $\text{C}-\text{C}$ $1.52(4)$ bond distances are still comparable to the respective values $1.34(5)$, $1.18(5)$, $1.51(12)$ (for both $\text{N}-\text{C}$ and $\text{C}-\text{C}$)

Fig. 4. Unit cell content down *c*.

found in the uranium derivative as well as the O–C–N and C–N–C ($120(4)^\circ$), C–C–C $108(1)^\circ$ angles with $120(4)^\circ$ and $109(1)^\circ$ found in the uranium compound.

Th(NCS)₄(EtCONMe)₄

A view down *a* of the molecule with the atom numbering scheme is shown in Fig. 3 and the unit

cell content viewed down *c* is in Fig. 4. Bond distances and angles are in Table VI. The structure consists of discrete $\text{Th}(\text{NCS})_4(\text{dmpa})_4$ molecules separated by Van der Waals contacts. Within a molecule the stereochemistry around the thorium conforms approximately to a square antiprism. Each of the 'square' faces contains two oxygen and two nitrogen atoms. In one 'square', atoms of the same type are

TABLE VI. Bond Distances (Å) and Bond Angles ($^\circ$) with Estimated Standard Deviations in Parentheses for $\text{Th}(\text{NCS})_4(\text{dmpa})_4$.

a) Thorium environment

Th–N(1)	2.46(2)	Th–O(1)	2.40(1)
Th–N(2)	2.50(2)	Th–O(2)	2.39(1)
Th–N(3)	2.48(2)	Th–O(3)	2.35(1)
Th–N(4)	2.51(1)	Th–O(4)	2.35(1)
N(1)–Th–N(2)	92.0(6)	O(2)–Th–O(1)	74.8(4)
N(1)–Th–N(3)	142.9(5)	O(3)–Th–N(1)	77.4(4)
N(1)–Th–N(4)	71.9(5)	O(3)–Th–N(2)	68.6(5)
N(2)–Th–N(3)	104.5(6)	O(3)–Th–N(3)	78.1(4)
N(2)–Th–N(4)	142.8(5)	O(3)–Th–N(4)	75.1(4)

(continued overleaf)

TABLE VI. (continued)

N(3)–Th–N(4)	75.1(5)	O(3)–Th–O(1)	123.6(4)				
O(1)–Th–N(1)	148.1(5)	O(3)–Th–O(2)	130.1(4)				
O(1)–Th–N(2)	76.8(5)	O(4)–Th–N(1)	96.8(5)				
O(1)–Th–N(3)	68.9(5)	O(4)–Th–N(2)	144.7(5)				
O(1)–Th–N(4)	132.9(4)	O(4)–Th–N(3)	88.7(5)				
O(2)–Th–N(1)	73.3(4)	O(4)–Th–N(4)	72.0(4)				
O(2)–Th–N(2)	72.9(5)	O(4)–Th–O(1)	77.8(4)				
O(2)–Th–N(3)	143.1(4)	O(4)–Th–O(2)	77.0(4)				
O(2)–Th–N(4)	129.5(4)						
b) Ligands							
N(1)–C(1)	1.16(2)	N(2)–C(2)	1.13(2)	N(3)–C(3)	1.15(2)	N(4)–C(4)	1.12(2)
C(1)–S(1)	1.60(2)	C(2)–S(2)	1.62(2)	C(3)–S(3)	1.61(2)	C(4)–S(4)	1.63(2)
O(1)–C(11)	1.27(2)	O(2)–C(21)	1.29(2)	O(3)–C(31)	1.34(3)	O(4)–C(41)	1.28(2)
C(11)–C(12)	1.50(2)	C(21)–C(22)	1.53(2)	C(31)–C(32)	1.56(3)	C(41)–C(42)	1.47(3)
C(12)–C(13)	1.48(3)	C(22)–C(23)	1.44(3)	C(32)–C(33)	1.42(4)	C(42)–C(43)	1.44(2)
N(11)–C(11)	1.26(2)	N(21)–C(21)	1.28(2)	N(31)–C(31)	1.13(3)	N(41)–C(41)	1.29(2)
N(11)–C(14)	1.40(2)	N(21)–C(24)	1.46(3)	N(31)–C(34)	1.62(3)	N(41)–C(44)	1.46(3)
N(11)–C(15)	1.57(3)	N(21)–C(25)	1.47(3)	N(31)–C(35)	1.53(3)	N(41)–C(45)	1.51(3)
Th–N(1)–C(1)	175(2)	C(14)–N(11)–C(15)	115(2)	C(31)–C(32)–C(33)	109(3)		
N(1)–C(1)–S(1)	173(2)	C(12)–C(11)–O(1)	119(2)	C(31)–N(31)–C(34)	109(3)		
Th–N(2)–C(2)	163(2)	N(11)–C(11)–C(12)	122(2)	C(31)–N(31)–C(35)	131(4)		
N(2)–C(2)–S(2)	179(2)	Th–O(2)–C(21)	147(1)	C(34)–N(31)–C(35)	120(2)		
Th–N(3)–C(3)	158(2)	O(2)–C(21)–C(22)	118(2)	N(31)–C(31)–O(3)	117(3)		
N(3)–C(3)–S(3)	179(2)	C(21)–C(22)–C(23)	111(2)	N(31)–C(31)–C(32)	127(4)		
Th–N(4)–C(4)	167(2)	C(21)–N(21)–C(24)	121(2)	Th–O(4)–C(41)	152(1)		
N(4)–C(4)–S(4)	177(2)	C(21)–N(21)–C(25)	124(2)	O(4)–C(41)–C(42)	126(2)		
Th–O(1)–C(11)	150(1)	C(24)–N(21)–C(25)	115(2)	C(41)–C(42)–C(43)	115(3)		
O(1)–C(11)–C(12)	119(2)	N(21)–C(21)–C(22)	121(2)	C(41)–N(41)–C(44)	123(2)		
C(11)–C(12)–C(13)	109(2)	N(21)–C(21)–O(2)	121(2)	C(41)–N(41)–C(45)	119(2)		
C(11)–N(11)–C(14)	123(2)	Th–O(3)–C(31)	149(2)	C(44)–N(41)–C(45)	118(2)		
C(11)–N(11)–C(15)	122(2)	O(3)–C(31)–C(32)	116(2)	N(41)–C(41)–C(42)	114(2)		
				N(41)–C(41)–O(4)	120(2)		

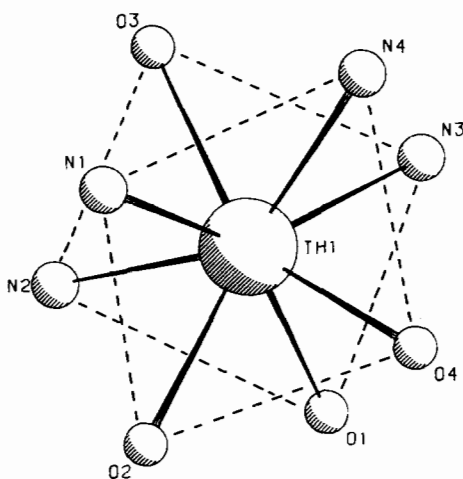


Fig. 5. Coordination polyhedron.

in adjacent positions (N(1), N(4), O(2), O(4)) and they deviate significantly from planarity in the tetrahedral direction with deviations in the interval ± 0.27

Å; in the second 'square' (O(1), N(2), O(3), N(3)) nitrogen and oxygen atoms are *trans* to each other, and the deviations from their mean plane are lower, being ± 0.20 Å. The two planes are practically parallel (the angle between them is 2°), the thorium is in the centre at a distance of 1.32 Å from each plane (Fig. 5). (The deviations of the polyhedron from a regular dodecahedron as an alternative description of the coordination around thorium, are rather high, the θ_A and θ_B values being respectively 50° and 63° versus the theoretical values [10] of 35.2 and 73.5° respectively).

The Σ CAF value for this polyhedron is 0.780, again in the range expected for stable compounds (the CAF values of Th–N (NCS) and Th–O (dmpa) are 0.1011 and 0.0951 respectively). A study of theoretically stable ligand arrangements with this coordination number for compounds of the type MX_4Y_4 using the cone packing model is still in progress.

The mean of the Th–O distance is 2.37(1) while that for Th–N is 2.49(2) Å. These values are close

to those reported for Th(NCS)₄(tetramethylurea)₄ [11], Th—O_{av.} 2.37(1) and Th—N_{av.} 2.52(1) Å. This last compound has a distorted dodecahedral coordination geometry with oxygen and nitrogen donor atoms equally distributed between the A and B sites. The hindrance of the neutral ligands is not too different from that of the neutral ligands in the present compound. For this reason the kind of compound obtained is the same and the type of coordination geometry is also comparable, there being on energetic grounds very little difference in stability between a square antiprismatic geometry and that of a dodecahedral one.

With respect to the ThCl₄(depa)₃ compound, the difference in Th—O bond lengths is, as expected, significant being shorter in the heptacoordinate derivative (av. 2.340(9) Å). This is related to the difference in crowding around the metal ion due to the different coordination number and consequently to the different steric hindrance of the coordinated ligands.

The isothiocyanate groups are essentially linear and the Th—N—C angles range from 158 to 175° as in the tetramethyl derivative [11]. The dmpa ligand has the expected geometry; bond lengths and angles are comparable to those of the depa ligand.

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