A Seven-co-ordinate Actinoid Complex: Crystal and Molecular Structure of Tetrachlorotris(trimethylamine)thorium(IV) [*]

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The title compound $[ThCl_4(NMe_3)_3]$ has been prepared by the reaction of anhydrous thorium(IV) chloride with trimethylamine. Crystals are monoclinic, space group $P2_1/a$, $Z = 4$, with $a = 15.336(8)$, $b = 8.320(9)$, $c = 15.263(11)$ Å, and $\beta = 101.0(1)°$. 1 557 Above-background reflections were collected on a diffractometer and the structure refined to R 0.085. The structure comprises discrete molecules of $[ThCl_4(NMe_3)_3]$. The metal atom is seven-co-ordinate in a capped-octahedral environment with one chlorine in the capping position [Th–Cl 2.678(10) Å], three nitrogens occupying the capped face [Th–N 2.79(3), 2.83(3), and 2.66(4) Å], and three chlorines the uncapped face [Th–Cl 2.642(9), 2.637(12), and 2.685(11) Å].

Numerous complexes of thorium(IV) halides are well established, certainly on a chemical basis.[1] *X*-Ray structural confirmation is limited to two examples both of which feature eight-co-ordination, *viz.* $[ThCl_4(SOPh_2)_4]$ where the co-ordination of the metal is a slightly distorted dodecahedron with the O-donors in the A sites and the halogens in the B sites[2] and $[ThCl_4\{(Me_2N)_2(O)POP(O)(NMe_2)_2\}_2]$ in which the metal environment is again dodecahedral with the halogens occupying the B sites.[3]

We have investigated the reaction of thorium(IV) chloride with trimethylamine only to find that it is the tris adduct $[ThCl_4(NMe_3)_3]$, (1), that is formed. This is a genuine seven-co-ordinate actinoid complex based on the MA_4B_3 stoicheiometry (A, B = unidentate ligand).[†] The ' obvious ' example of $UCl_4{\cdot}3SOMe_2$ does not belong to this set. Bagnall *et al.*[9] reported an ionic structure comprising $[UCl_2(SOMe_2)_6]^{2+}$-$[UCl_6]^{2-}$ in which the co-ordination geometries for the uranium cation and anion are distorted dodecahedral and regular octahedral respectively. However, two recent examples of MA_4B_3 stoicheiometry have been established as having pentagonal-bipyramidal structures, namely $[U(NCS)_4L_3]$[10] (L = *N*,*N*-diethylpropionamide) and $[UCl_3L_4]$[11] (L = *N*,*N*,2-trimethylpropionamide). Apart from these two recent structures it would appear that the only validated examples of this particular MA_4B_3 formulation incorporate the transition metals molybdenum and tungsten, *viz.* $[MoBr_4(PMe_2Ph)_3]$,[12] $[MoCl_4(PMe_2Ph)_3]{\cdot}EtOH$,[13] and $[NEt_4][WBr_3(CO)_4]$.[14]

In this paper we report and discuss the structure of $[ThCl_4(NMe_3)_3]$.

Experimental

Anhydrous thorium(IV) chloride (1.0 g) was treated with an excess (20 cm³) of anhydrous trimethylamine in a sealed double-ampoule vessel. Vigorous bubbling denoted the immediate onset of reaction. When bubbling ceased, decantation of the mother-liquor through the sinter followed by slow back distillation of amine gave colourless hexagonal crystals of the title compound. These were washed with n-hexane (3 × 15 cm³), dried by pumping *in vacuo* for several hours at room temperature, and sealed in glass ampoules under a nitrogen atmosphere (Found: C, 19.2; H, 4.2; Cl, 25.3; N, 7.3. Calc. for $C_9H_{27}Cl_4N_3Th$: C, 19.6; H, 4.9; Cl, 25.7; N, 7.6%).

Infrared spectra (4 000—200 cm^{-1}) were recorded using a Perkin-Elmer 580 B spectrophotometer with samples as Nujol mulls squeezed between CsI plates. For the 200—50 cm^{-1} region a Fourier FS720 instrument was used with samples mounted as Nujol mulls between polyethylene plates. Proton n.m.r. spectra were obtained using a Bruker WH90 spectrometer with deuteriochloroform solutions. Microanalyses were determined commercially and chloride was evaluated using the Volhard titration method.

X-*Ray Crystal Structure of* $[ThCl_4(NMe_3)_3]$, (1).—*Crystal data.* $C_9H_{27}Cl_4N_3Th$, $M = 551.05$, monoclinic, $a = 15.336(8)$, $b = 8.320(9)$, $c = 15.263(11)$ Å, $\beta = 101.0(1)°$, $U = 1\,911.58$ Å^3, $D_m = 1.91$, $Z = 4$, $D_c = 1.88$ g cm^{-3}, $F(000) = 1\,040$, $\mu(Mo\text{-}K_\alpha) = 121.3$ cm^{-1}, $\lambda = 0.7107$ Å.

Systematic absences $h0l$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$ were observed on precession photographs, establishing the space group as $P2_1/a$.

A crystal of size 0.50 × 0.80 × 0.24 mm was mounted on a Stoe STADI2 diffractometer and data were collected *via* variable-width ω scans. Background counts were 20 s and the scan rate of 0.033° s^{-1} was used with a width of $(1.5 + \sin \mu/\tan \theta)$. 2 741 Independent reflections were measured, of which 1 557 with $I > 3\sigma(I)$ were used in subsequent calculations. An absorption correction was applied using SHELX,[15] with transmission factors ranging from 0.10 to 0.01. The structure was solved by the Patterson method and the positions of non-hydrogen atoms found from the Fourier syntheses. The CH_3 groups were refined as rigid groups which were allowed to rotate around the N–C bond. The hydrogen atoms in each group were given a common

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[*] *Supplementary data available* (No. SUP 23829, 16 pp.): thermal parameters, H-atom co-ordinates, ligand dimensions, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

[†] There are many apparent MA_4B_3 complexes in the literature, *e.g.* $ThCl_4{\cdot}3CO(NMe_2)_2$,[4] $ThBr_4{\cdot}3POPh_3$,[5] and $ThCl_4{\cdot}3NMeEtCO_2Et$,[6] but all are without any structural confirmation of the exact ligand arrangements. A seven-co-ordinate capped-octahedral metal environment has been noted for one actinoid cation $[UCl(tmpo)_6]^{3+}$ (tmpo = trimethylphosphine oxide) in a compound of stoicheiometry $UCl_4{\cdot}6POMe_3$.[7] Recently[8] some further complexes of formulation MCl_4L_3 have been prepared. It seems likely that some of these are also seven-co-ordinate.

Table 1. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Th(1)	3 101(1)	5 443(2)	7 719(1)	C(3)	4 689(25)	3 929(50)	6 464(37)
Cl(1)	1 569(6)	5 891(13)	8 233(8)	C(4)	1 744(32)	8 141(65)	6 189(35)
Cl(2)	3 710(7)	3 860(15)	9 208(8)	C(5)	1 007(31)	5 621(73)	6 009(34)
Cl(3)	3 955(7)	7 646(13)	6 922(9)	C(6)	2 329(31)	6 030(73)	5 373(30)
Cl(4)	2 493(7)	2 673(12)	6 927(9)	N(3)	3 451(20)	7 770(48)	8 933(28)
N(1)	4 626(18)	3 886(37)	7 418(24)	C(7)	3 003(28)	9 354(48)	8 577(36)
N(2)	1 895(22)	6 364(48)	6 156(25)	C(8)	4 428(27)	8 115(64)	9 184(33)
C(1)	5 489(26)	4 800(47)	7 961(35)	C(9)	3 162(31)	7 480(54)	9 777(33)
C(2)	4 733(25)	2 224(62)	7 602(34)				

Table 2. Dimensions in the co-ordination sphere: distances in Å, angles in °

Th(1)–Cl(1)	2.642(9)	Cl(1)–Th(1)–Cl(2)	90.2(3)	Cl(2)–Th(1)–N(1)	74.9(7)	N(1)–Th(1)–N(2)	114.9(10)
Th(1)–Cl(2)	2.637(12)	Cl(1)–Th(1)–Cl(3)	125.3(3)	Cl(3)–Th(1)–N(1)	75.2(6)	Cl(1)–Th(1)–N(3)	76.3(7)
Th(1)–Cl(3)	2.678(10)	Cl(2)–Th(1)–Cl(3)	127.6(3)	Cl(4)–Th(1)–N(1)	75.9(6)	Cl(2)–Th(1)–N(3)	76.9(9)
Th(1)–Cl(4)	2.685(11)	Cl(1)–Th(1)–Cl(4)	90.2(3)	Cl(1)–Th(1)–N(2)	74.7(7)	Cl(3)–Th(1)–N(3)	76.5(9)
Th(1)–N(1)	2.787(29)	Cl(2)–Th(1)–Cl(4)	89.7(3)	Cl(2)–Th(1)–N(2)	158.1(8)	Cl(4)–Th(1)–N(3)	160.7(9)
Th(1)–N(2)	2.83(3)	Cl(3)–Th(1)–Cl(4)	122.7(4)	Cl(3)–Th(1)–N(2)	74.3(8)	N(1)–Th(1)–N(3)	112.9(9)
Th(1)–N(3)	2.66(4)	Cl(1)–Th(1)–N(1)	159.5(6)	Cl(4)–Th(1)–N(2)	74.8(8)	N(2)–Th(1)–N(3)	113.7(10)

(and refined) thermal parameter. The structure was refined by full-matrix least squares with a weighting scheme $w = 1/[\sigma^2(F) + 0.003 F^2]$. The final R value was 0.085 ($R' = 0.090$).

Calculations were carried out using SHELX 76 at the University of Manchester Computing Centre. Atomic scattering factors and dispersion corrections were taken from ref. 16. Atomic parameters are given in Table 1, dimensions around the metal atom in Table 2.

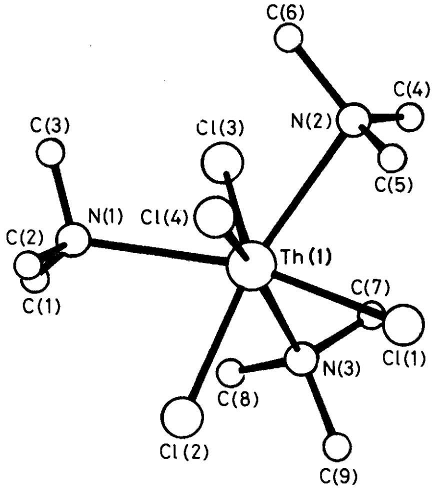

Figure. The structure of $[ThCl_4(NMe_3)_3]$

Results and Discussion

The structure consists of discrete molecules of $[ThCl_4(NMe_3)_3]$ which are illustrated in the Figure together with the atomic numbering scheme. The thorium atom is seven-co-ordinate [17,18] being bonded to four chlorines and three nitrogens making up the rare MA_4B_3 (A,B = unidentate ligand) stoicheiometry. The geometry of the co-ordination sphere is very close to that of an ideal capped octahedron with a chlorine in the capping position [Th–Cl(3) 2.678(10) Å], three nitrogens in the capped face [Th–N(1) 2.79(3), Th–N(2) 2.83(3), and Th–N(3) 2.66(4) Å], and three chlorines in the uncapped face [Th–Cl(1) 2.642(9), Th–Cl(2) 2.637(12), and Th–Cl(4) 2.685(11) Å]. Using our method [17] of fitting co-ordination geometry to ideal polyhedra, we obtain a small root mean square (r.m.s.) value of 0.02 Å for the distortion from C_{3v} symmetry.

The bond lengths in the structure fall within the expected ranges. There are no unusual intramolecular contacts.

Other examples of this stoicheiometry, namely $[MoX_4(PMe_2Ph)_3]$ (X = Br [12] or Cl [13]) and $[WBr_4(CO)_3]^-$ [14] have similar structures. The first two molecules contain four halides and three bulky ligands. As in compound (1) the three bulky ligands occupy the capped face which is estimated as the least crowded site of the capped octahedron with the halogens in the unique capping position and the uncapped face. A similar geometry is found for $[WBr_4(CO)_3]^-$ with the carbonyls in the capped face but here the reason for the choice of geometry may be electronic rather than steric.

On the basis that Th^{IV} behaves chemically much like Zr^{IV} and Hf^{IV} and often U^{IV}, each of which reacts with trimethylamine to give a six-co-ordinate bis adduct,[19-21] the formation of the tris adduct with Th^{IV} is unexpected. The colourless crystals can be stored indefinitely under an inert atmosphere but exposure to air causes immediate decomposition/hydrolysis. There is good solubility in benzene and chlorinated hydrocarbons. The i.r. spectrum includes one broad, intense metal–halogen vibration at 256 cm^{-1} (with evidence of a shoulder on the high-energy side at *ca.* 290 cm^{-1}) and a much weaker band at 109 cm^{-1} most likely associated with a deformational halogen-bending mode.[22] An intense band at 491 cm^{-1} is assigned to a ν(Th–N) stretching mode. Bands at 1 234 [$\nu_{asym}(NC_3)$], 987 [$\rho(CH_3)$], and 811 cm^{-1} [$\nu_{sym}(NC_3)$] are typical for co-ordinated trimethylamine. The room-temperature ^1H n.m.r. spectrum shows one sharp singlet emphasising equivalent amine environments: δ_H (90 MHz, solvent $CDCl_3$, standard $SiMe_4$) 2.47 (s, 3 H, CH_3). Even on cooling to 210 K this sharp singlet remains unchanged and there is no evidence of any other species present and thus no evidence for the transformations, pentagonal bipyramid $\rightleftharpoons$ capped octahedron $\rightleftharpoons$ capped trigonal prism. Retention of the solid-state capped-octahedral structure in solution, which seems chemically reasonable, is substantiated further by the fact that the solution and Nujol-mull i.r. spectra are identical to within 1 cm^{-1}.

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