Macrocycle complexation chemistry

34*. Polyethylene glycol and glycolate complexes of Th^{4+}. Preparation and structural characterization of [ThCl$_3$(pentaethylene glycol)]Cl·CH$_3$CN and the (Th^{4+})$_4$ cluster, [Th$_4$Cl$_8$(O)(tetraethylene glycolate)$_3$]·3CH$_3$CN

Robin D. Rogers**, **Andrew H. Bond** and **Misty M. Witt**

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115 (U.S.A.)

Abstract

The reaction of pentaethylene glycol with ThCl$_4$ in 3/1 CH$_3$CN/CH$_3$OH produced [ThCl$_3$(EO5)]Cl·CH$_3$CN upon slow evaporation. The same reaction with tetraethylene glycol exhibits reduced ThCl$_4$ solubility. The only isolable product, a (Th^{4+})$_4$ cluster, is the result of ionization of the glycol and incorporation of oxide impurities, [Th$_4$Cl$_8$(O)(EO4^{2-})$_3$]·3CH$_3$CN. Both products were crystallographically characterized. [ThCl$_3$(EO5)]Cl·CH$_3$CN is monoclinic, Pc with (at 22 °C) $a = 8.857(2)$, $b = 12.364(4)$, $c = 9.685(2)$ Å, $\beta = 92.75(2)°$, $U = 1059$ Å^3, $D_{calc} = 2.05$ g cm^{-3} for $Z = 2$ formula units, and $R = 0.031$ for 1624 independent observed ($F_o \geqslant 5\sigma(F_o)$) reflections. [Th$_4Cl_8$(O)(EO4^{2-})$_3$]·3CH$_3$CN is triclinic, $P\bar{1}$ with (at 22 °C) $a = 12.277(3)$, $b = 12.404(3)$, $c = 18.738(4)$ Å, $\alpha = 73.01(2)$, $\beta = 77.71(2)$, $\gamma = 75.49(2)°$, $U = 2611.7$ Å^3, $D_{calc} = 2.45$ g cm^{-3} for $Z = 2$ formula units, and $R = 0.040$ for 5849 observed reflections. In the EO5 complex, the glycol wraps the metal ion with all six donor atoms coordinated to thorium. There are only three tight ion pairs with the fourth chloride anion accepting hydrogen bonds from the two alcoholic oxygen atoms. There are four Th^{4+} ions in the glycolate cluster bridged by a μ_4-oxide. Each of the three tetraethylene glycolate ligands wraps one Th atom and bridges it (via the terminal alkoxide) to two other Th atoms in the cluster. There are two bridging and six terminal chloride anions. The four thorium atoms are crystallographically unique, however, there are only three different Th environments.

Introduction

Structural characterization of inner sphere Th^{4+} complexes with macrocyclic crown ethers, their acyclic polyethylene glycol analogs, or even simple alkoxide ligands is nearly non-existent. Our own work with Th^{4+} and crown ethers has produced only the second sphere hydrogen bonded complexes, [Th(NO$_3$)$_4$-(OH$_2$)$_3$]·18-crown-6 [2], [ThCl$_4$(OHMe)$_2$(OH$_2$)]·15-crown-5·CH$_3$CN [3], [ThCl$_2$(OH$_2$)$_7$]Cl$_2$·18-crown-6·2H$_2$O [4], [ThCl$_4$(OHEt)$_3$(OH$_2$)]·18-crown-6·H$_2$O [5] and [ThCl(OH)(OH$_2$)$_6$]$_2$Cl$_4$·18-crown-6 [6].

This lack of structural data contrasts sharply with the fact that with an understanding of the control of metal ion coordination offered by these ligands, their use could lead to such wide ranging applications as easier solution routes to new materials doped with Th, or novel Th^{4+} extraction processes. For example, thorium doping into high T$_c$ superconductors is currently difficult [7, 8]. Soluble alkoxides are now being prepared as precursors to some of these same materials [9–14] and one report even details the use of an acyclic chelating, bridging alkoxide unit similar to polyethylene glycols for use with Cu^{2+} [13].

The lack of intensive study into the use of crown ethers and polyethylene glycols in thorium separations chemistry probably reflects the weak donor nature of these oxygen ligands. The few studies done with these ligands as extractants or synergists do show some promise but the exact nature of most of the extracted species is unknown [14–16]. Our current efforts are directed toward a fuller understanding of ligand control of metal coordination environment. This information will then direct the development of new complexing agents and separations technologies.

---

*For Part 33, see ref. 1.

**Author to whom correspondence should be addressed.

Experimental

Preparation and crystallographic characterization of [Th₄Cl₈(O)(C₈H₁₆O₅)₃]·3CH₃CN

Preparation and crystallographic characterization of $[Th_4Cl_8(O)(C_8H_{16}O_5)_3]\cdot 3CH_3CN$

1.738 mmol of $ThCl_4$ (0.6498 g) was added to 0.3 ml of tetraethylene glycol (1.738 mmol) in 15 ml of solvent (3/1 CH_3CN/CH_3OH). The reaction was heated to 60 °C for 1 h and cooled to 20 °C. A gray precipitate ($ThCl_4$) formed immediately and after six days small clear crystals of the title complex were observed mixed in with the precipitate and on the walls of the flask. *Anal.* Calc. for $[Th_4Cl_8(O)\text{-}(C_8H_{16}O_5)_3]\cdot 3CH_3CN$: C, 18.69; H, 2.98; N, 2.18. Found: C, 18.08; H, 3.05; N, 1.96%. Loss of acetonitrile from the crystals occurred at room temperature when removed from the solvent.

A transparent single crystal of the title complex was mounted in a thin walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Successful refinement of the structure was carried out in the centric space group $P\bar{1}$. A summary of data collection parameters is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to $R = 0.064$. Disorder was evident in three of the ethylene units (C(3)–C(4), C(5)–C(6) and C(19)–C(20)). Resolution of the disorder revealed two conformations of the ethylene groups. These atoms were refined isotropically in alternate least-squares cycles with 50% occupancy each. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å². The methyl hydrogen atoms were included as a rigid group with rotational freedom

TABLE 1. Crystal data and summary of intensity data collection and structure refinement

Compound	$[Th_4Cl_8(O)(C_8H_{16}O_5)_3]\cdot 3CH_3CN$	$[ThCl_3(EO5)]Cl\cdot CH_3CN$
Color/shape	colorless/parallelepiped	colorless/parallelepiped
Formula weight	1927.6	653.18
Space group	$P\bar{1}$	Pc
Temperature (°C)	22	22
Cell constants[a]		
a (Å)	12.277(3)	8.857(2)
b (Å)	12.404(3)	12.364(4)
c (Å)	18.738(4)	9.685(2)
α (°)	73.01(2)	
β (°)	77.71(2)	92.75(2)
γ (°)	75.49(2)	
Cell volume (Å³)	2611.7	1059
Formula units/unit cell	2	2
D_{calc} (g cm⁻³)	2.45	2.05
μ_{calc} (cm⁻¹)	113.1	72.23
Diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ	Enraf-Nonius CAD-4/ω-2θ
Range of relative transmission factors (%)	60/100	57/100
Radiation, graphite monochromator	Mo Kα ($\lambda = 0.71073$)	Mo Kα ($\lambda = 0.71073$)
Max. crystal dimensions (mm)	0.05×0.08×0.25	0.10×0.23×0.40
Scan width	0.80+0.35 tan θ	0.80+0.35 tan θ
Standard reflections	800; 070; 009	900; 0, 12, 0; 008
Decay of standards (%)	±2	±1
Reflections measured	9137	2087
2θ range (°)	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$
Range of h, k, l	+14, ±14, ±22	+10, +14, ±11
Reflections observed $(F_o \geqslant 5\sigma(F_o))$[b]	5849	1624
Computer programs[c]	SHELX [17]	SHELX [17]
Structure solution	SHELXS [19]	SHELXS [19]
No. parameters varied	553	218
Weights	$(\sigma(F_o)^2 + 0.0008F_o^2)^{-1}$	$(\sigma(F_o)^2 + 0.002F_o^2)^{-1}$
GOF	0.64	1.18
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.040	0.031
R_w	0.048	0.045
R inverse configuration		0.043
Largest feature final difference map	1.7 e⁻ Å⁻³ within 1 Å of Th(2)	1.3 e⁻ Å⁻³ near Th

[a]Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 18°$.   [b]Corrections: Lorentz–polarization and absorption (empirical, psi scan).   [c]Neutral scattering factors and anomalous dispersion corrections from ref. 18.

at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ Å^2). Refinement of non-hydrogen atoms with anisotropic temperature factors (except for the disordered C atoms) led to the final values of $R = 0.040$ and $R_w = 0.048$. The final values of the positional parameters are given in Table 2.

Preparation and crystallographic characterization of [ThCl$_3$(EO5)]Cl·CH$_3$CN

ThCl$_4$ (0.5301 g, 1.418 mmol) was added to 0.3 ml of pentaethylene glycol (1.418 mmol) in 15 ml of 3/1 CH$_3$CN/CH$_3$OH. The reaction mixture was heated to 60 °C for 1 h and cooled to 20 °C. A small amount of gray precipitate (ThCl$_4$) was centrifuged and removed. Slow evaporation produced copius amounts of a flaky white precipitate which contained the crystals of the title compound. *Anal.* Calc. for [ThCl$_3$(EO5)]Cl·CH$_3$CN: C, 22.07; H, 3.86; N, 2.14. Found: C, 21.45; H, 3.90; N, 1.32%.

A transparent single crystal of the title complex was mounted in a thin walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either the centric $P2/c$ or acentric Pc from the systematic absences. Successful refinement of the structure was carried out in the acentric space group Pc. A summary of data collection parameters is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to $R = 0.049$. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The alcoholic hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.031$ and $R_w = 0.045$. The final values of the positional parameters are given in Table 3.

Results and discussion

By analogy to our work comparing polyethylene glycols to crown ethers in lanthanide chloride complexation [20, 21] (where the chelate effect of the glycol is greater than the macrocyclic effect of the crown ether) we prepared the title complexes by reaction of ThCl$_4$ with the corresponding glycols in 3/1 solutions of CH$_3$CN/CH$_3$OH at 60 °C for 1 h. As observed for the lanthanide chlorides with

TABLE 2. Final fractional coordinates for [Th$_4$Cl$_8$(O)(C$_8$H$_{16}$O$_5$)$_3$]·3CH$_3$CN

Atom	x/a	y/b	z/c	B_{eq}[a]
Th(1)	0.13011(4)	0.26135(4)	0.33644(3)	1.61
Th(2)	0.43420(4)	0.32962(4)	0.23735(3)	1.70
Th(3)	0.25546(4)	0.27052(4)	0.11981(3)	1.76
Th(4)	0.37826(4)	0.01165(4)	0.28616(3)	1.60
Cl(1)	0.1357(3)	0.0255(3)	0.3358(2)	2.28
Cl(2)	0.2965(3)	0.0926(3)	0.4257(2)	2.41
Cl(3)	−0.0121(4)	0.4737(3)	0.3260(2)	3.10
Cl(4)	0.4342(4)	0.5605(3)	0.2130(2)	3.04
Cl(5)	0.6572(3)	0.3386(4)	0.1683(2)	3.05
Cl(6)	0.5251(4)	0.3052(4)	0.3663(2)	3.14
Cl(7)	0.1110(4)	0.2025(4)	0.0526(2)	3.35
Cl(8)	0.5645(4)	−0.1108(4)	0.2105(2)	3.19
O(1)	0.2931(8)	0.2072(7)	0.2530(5)	1.91
O(2)	0.2643(9)	0.3724(8)	0.3264(5)	2.36
O(3)	0.1321(9)	0.3246(8)	0.4565(5)	2.40
O(4)	−0.006(1)	0.1883(9)	0.4642(5)	2.87
O(5)	−0.0721(8)	0.2303(9)	0.3317(5)	2.60
O(6)	0.0879(8)	0.2880(8)	0.2131(6)	2.39
C(1)	0.249(2)	0.447(1)	0.3738(9)	3.28
C(2)	0.223(2)	0.384(2)	0.451(1)	4.41
C(3)	0.097(2)	0.253(2)	0.530(1)	2.2(5)[b]
C(4)	−0.023(3)	0.243(3)	0.527(2)	3.8(6)[b]
C(5)	−0.121(3)	0.166(3)	0.456(2)	4.0(7)[b]
C(6)	−0.128(3)	0.141(3)	0.386(2)	3.8(6)[b]
C(3)'[c]	0.059(4)	0.296(4)	0.526(3)	8(1)[b]
C(4)'	0.025(3)	0.198(3)	0.530(2)	4.5(7)[b]
C(5)'	−0.126(2)	0.200(2)	0.469(2)	2.8(5)[b]
C(6)'	−0.138(2)	0.173(2)	0.400(1)	2.7(5)[b]
C(7)	−0.089(1)	0.224(2)	0.2592(9)	3.21
C(8)	−0.029(1)	0.312(1)	0.200(1)	3.21
O(7)	0.282(1)	0.4244(8)	0.1602(6)	2.85
O(8)	0.1172(9)	0.4782(9)	0.0735(6)	2.78
O(9)	0.2735(9)	0.3825(9)	−0.0265(5)	2.83
O(10)	0.4138(9)	0.1801(9)	0.0174(6)	2.84
O(11)	0.4475(8)	0.2641(9)	0.1251(5)	2.44
C(9)	0.218(2)	0.538(1)	0.147(1)	3.52
C(10)	0.104(1)	0.544(1)	0.1286(9)	2.97
C(11)	0.146(1)	0.545(1)	−0.0037(9)	3.15
C(12)	0.174(2)	0.467(1)	−0.053(1)	3.53
C(13)	0.329(2)	0.319(2)	−0.0835(9)	3.99
C(14)	0.438(2)	0.253(2)	−0.061(1)	4.84
C(15)	0.521(1)	0.129(2)	0.047(1)	3.86
C(16)	0.550(1)	0.210(2)	0.083(1)	4.11
O(12)	0.5114(8)	0.1239(8)	0.2720(5)	2.19
O(13)	0.5272(9)	−0.0701(8)	0.3765(5)	2.57
O(14)	0.3710(9)	−0.1876(8)	0.3858(5)	2.79
O(15)	0.3067(9)	−0.1447(8)	0.2528(6)	2.66
O(16)	0.3111(9)	0.0675(8)	0.1674(5)	2.34
C(17)	0.622(1)	0.074(1)	0.297(1)	3.44
C(18)	0.605(1)	0.002(1)	0.3751(9)	3.36
C(19)	0.491(3)	−0.144(2)	0.451(2)	3.2(6)[b]
C(20)	0.469(3)	−0.241(3)	0.427(2)	3.4(6)[b]
C(19)'	0.535(3)	−0.178(3)	0.433(2)	4.2(7)[b]
C(20)'	0.431(3)	−0.220(3)	0.452(2)	4.2(7)[b]
C(21)	0.356(2)	−0.286(1)	0.362(1)	3.45
C(22)	0.267(2)	−0.240(1)	0.3112(8)	2.88
C(23)	0.249(1)	−0.109(1)	0.1878(8)	2.95

(continued)

TABLE 2. (continued)

Atom	x/a	y/b	z/c	B_{eq}[a]
C(24)	0.307(1)	−0.018(1)	0.1317(8)	2.56
N(1)	0.678(2)	0.477(2)	0.449(1)	6.32
C(25)	0.684(2)	0.500(2)	0.385(1)	4.34
C(26)	0.685(2)	0.522(2)	0.306(1)	4.92
N(2)	−0.144(3)	0.157(2)	−0.051(2)	10.13
C(27)	−0.133(2)	0.124(3)	0.008(2)	7.19
C(28)	−0.142(2)	0.074(3)	0.094(2)	9.11
N(3)	−0.091(3)	0.899(2)	0.291(2)	8.69
C(29)	−0.094(3)	0.833(3)	0.260(2)	7.98
C(30)	−0.113(3)	0.774(3)	0.210(2)	9.68

[a]$B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$. [b]Isotropic refinement. [c]Primed atoms are disordered. See 'Experimental'.

TABLE 3. Final fractional coordinates for [ThCl$_3$-(EO5)]Cl·CH$_3$CN

Atom	x/a	y/b	z/c	B_{eq}
Th	−0.5000	−0.75280(2)	−0.7500	1.36
Cl(1)	−0.6114(7)	−0.7377(3)	−0.4927(5)	3.07
Cl(2)	−0.5884(5)	−0.7808(3)	−1.0191(5)	2.71
Cl(3)	−0.2518(5)	−0.6884(3)	−0.8890(5)	2.37
Cl(4)	−0.1339(5)	−1.0194(3)	−0.9611(5)	2.69
O(1)	−0.280(1)	−0.7896(7)	−0.583(1)	2.51
O(2)	−0.372(1)	−0.5881(6)	−0.6186(9)	1.81
O(3)	−0.599(1)	−0.5665(6)	−0.8081(9)	1.72
O(4)	−0.789(1)	−0.7329(8)	−0.777(2)	2.63
O(5)	−0.662(1)	−0.9249(7)	−0.734(1)	2.44
O(6)	−0.369(1)	−0.9267(7)	−0.788(1)	2.27
C(1)	−0.223(2)	−0.709(1)	−0.479(2)	2.53
C(2)	−0.223(2)	−0.601(1)	−0.559(2)	3.25
C(3)	−0.392(2)	−0.485(1)	−0.682(2)	2.70
C(4)	−0.553(2)	−0.475(1)	−0.719(2)	2.53
C(5)	−0.754(2)	−0.557(1)	−0.859(2)	2.79
C(6)	−0.853(2)	−0.624(1)	−0.768(2)	2.98
C(7)	−0.880(2)	−0.814(1)	−0.716(2)	3.12
C(8)	−0.823(2)	−0.921(1)	−0.760(2)	3.19
C(9)	−0.597(2)	−1.023(1)	−0.794(2)	2.39
C(10)	−0.436(2)	−1.025(1)	−0.748(2)	2.62
N(1)	0.001(2)	−0.592(1)	−1.198(2)	4.57
C(11)	0.002(2)	−0.681(2)	−1.177(2)	3.15
C(12)	0.001(3)	−0.789(2)	−1.141(3)	4.88

EO3–EO7*, ThCl$_4$ readily complexes with the polyethylene glycols. Reaction of ThCl$_4$ with EO5 produced the neutral donor complex, [ThCl$_3$(EO5)]Cl·CH$_3$CN, while ionization of EO4 produced the Th^{4+} cluster, [Th$_4$Cl$_8$(O)(EO4^{2-})$_3$]·3CH$_3$CN.

---

*Polyethylene glycols are represented by the symbols EO with the number of ethylene linkages (e.g. EO3 = triethylene glycol, EO7 = heptaethylene glycol). The ionized forms of these ligands are represented with one or two minus superscripts (e.g. EO4$^-$ and EO4^{2-} are the ionized forms of tetraethylene glycol, C$_8$H$_{16}$O$_5$H$^-$ and C$_8$H$_{16}$O$_5$$^{2-}$, respectively).

The longer chain EO5 gave enhanced solubility of the thorium salt compared to EO4. A small (c. 1/8 of starting total) amount of gray ThCl$_4$ precipitated from the EO5 reaction. The complex itself did not crystallize until the solution was slowly evaporated. In contrast, copius amounts of ThCl$_4$ precipitated from the EO4 reaction and crystallization occurred without slow evaporation. The product itself contained an oxide ion (an impurity from the thorium salt) and an ionized form of EO4. The use of EO3 resulted only in precipitation of ThCl$_4$. We believe that we can control solubility with glycol chain length and are now investigating the use of longer chain glycols.

It is interesting to note that the eventual EO4 product (albeit a minor one) was produced by ionization of EO4. The ionizability of glycols may have profound implications in their use in extraction technologies. The glycol wrapping could provide a hydrophobic metal ion environment while the charge on the alcoholic oxygen atoms could obviate the need to transfer anions from an aqueous to organic phase in separations processes. We have also observed the ionization of glycols in the preparation and structural characterization of the Bi^{3+} complexes, [Bi(NO$_3$)$_2$(EO4$^-$)]$_2$·2CH$_3$OH [6], [Bi(NO$_3$)$_2$(EO5)]-[Bi(NO$_3$)$_2$(EO5^{2-})Bi(NO$_3$)$_3$]·2H$_2$O [6] and [Bi(NO$_3$)$_2$(EO6$^-$)]$_2$ [6].

The isolation of both the neutral donor complex and the glycolate complex allows us this opportunity to directly compare the effect of ligand ionization on structure. As shown below the wrapping effect of the glycolate ligand effectively stops polymerization which would probably have rendered this complex insoluble.

The Th^{4+} EO5 complex is depicted in Fig. 1. The glycol wraps the metal ion with all six donor atoms coordinated to thorium. There are only three tight ion pairs with the fourth chloride anion accepting hydrogen bonds from the two alcoholic oxygen atoms (O(1) and O(6)). The resulting hydrogen bonding forms zigzag chains along c (Fig. 2). One acetonitrile molecule per formula unit crystallizes in the unit cell with weak contacts between the methyl group and Cl(2), Cl(3) and Cl(4).

Thorium is nine-coordinate tricapped trigonal prismatic (Fig. 3). As we have seen with all of our nine-coordinate polyethylene glycol complexes of the lanthanide chlorides [21], the flexible glycol donors alternate between capping and prismatic sites. O(1), O(3) and O(5) are capping. Variance in the bond distances are noted which relate to coordination position. The average parameters include Th–O(alcoholic) = 2.49(1), Th–O(etheric) = 2.57(4), Th–Cl = 2.73(2), C–O = 1.45(2), C–C = 1.50(3) Å,
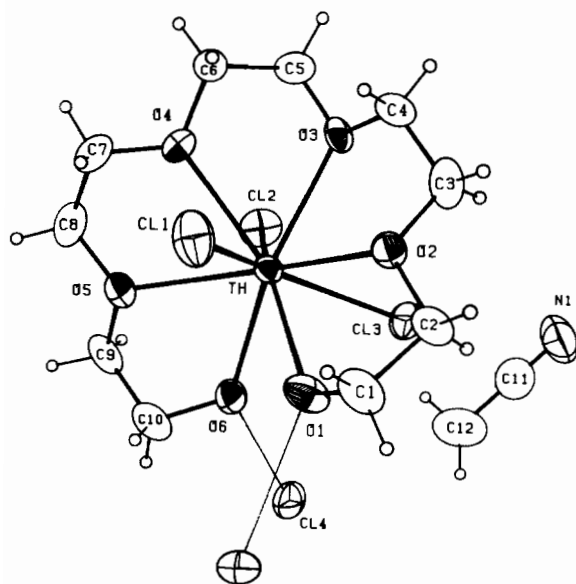
Fig. 1. ORTEP illustration of [ThCl₃(EO5)]Cl·CH₃CN represented with 50% probability ellipsoids for thermal motion. Hydrogen atoms have been arbitrarily reduced.
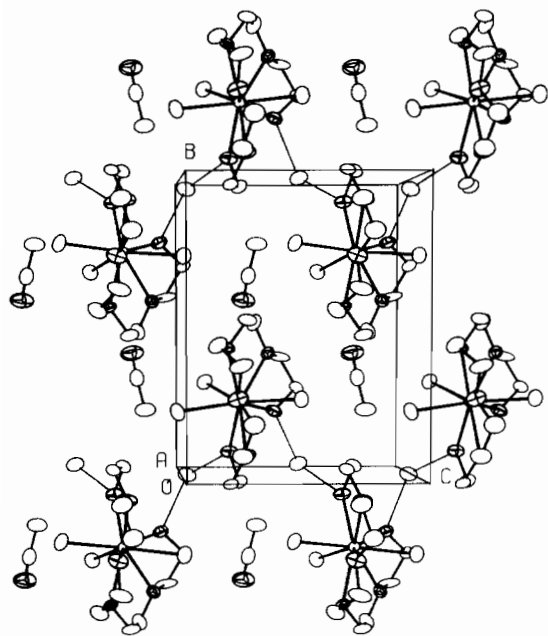

Fig. 2. Cell packing diagram for [ThCl₃(EO5)]Cl·CH₃CN.

Fig. 3. Th^{4+} ion geometry in [ThCl₃(EO5)]Cl·CH₃CN.

C–O–C = 112.0(7), C–C–O = 107(2)° (Table 4). The O–C–C–O torsion angles have the sequence g$^+$ (60°, C(1)–C(2)), g$^-$, g$^-$, g$^+$, g$^-$. All of the C–C–O–C angles are *anti* except for O(3)–C(5) which occurs between C–C angles of like sign.

The glycolate cluster is depicted in Fig. 4. There are four Th^{4+} ions in the cluster bridged by a μ_4-oxide. Acetonitrile molecules separate the clusters
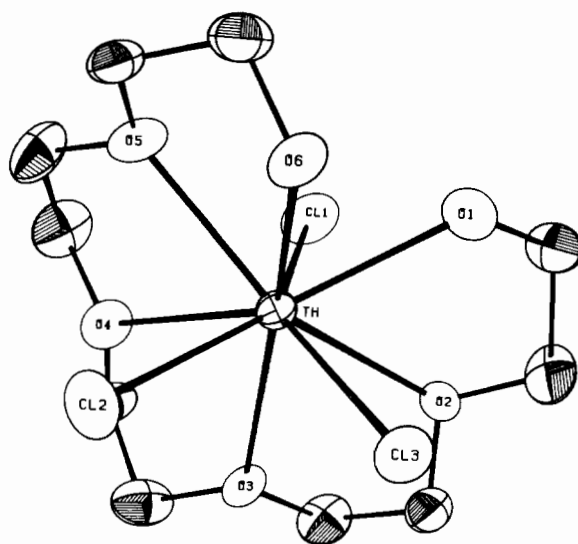
in the unit cell (Fig. 5). Each of the three tetraethylene glycolate (EO4^{2-}) ligands wraps one Th atom and bridges it (via the terminal alkoxide) to two other Th atoms in the cluster. There are two bridging and six terminal chloride anions. The four thorium atoms are crystallographically unique, however, there are only three different Th environments. Th(1) and Th(4) are nearly identical (Fig. 6(a) and (d)). Each is bridged by two asymmetric chloride bridges and has one terminal chloride ion. Both Th coordination environments are nine-coordinate tricapped trigonal prismatic with the oxide and the two etheric oxygen atoms closest to the chains' ends in capping positions. This again allows the oxygen atoms of the polyether to alternate between prismatic and capping sites. The Th–O(alkoxide bridges) distances average 2.36(3) Å, the Th–Cl bridges = 2.908(6), 2.95(1) Å, the terminal Th–Cl = 2.76(1) Å, the Th–O(etheric) distances average 2.62(3) Å, and the average Th–O(μ_4-oxide) = 2.344(3) Å (Table 5).

The glycol adopts two conformations in the disorder model. The O–C–C–O torsion angles alternate $^{\pm}$g and the C–C–O–C angles are all *anti* in one conformation of the glycols complexing both Th(1) and Th(4). This conformation is that found for a similar fragment in the common D_{3d} form of 18-crown-6. The alternate conformation in the O(2)–O(6) glycol has the sequence g$^-$, g$^-$, g$^-$, g$^+$ for the C–C angles and similarly the conformation in the O(12)–O(16) glycol has C–C angles of g$^+$, g$^+$, g$^+$, g$^-$. Each conformation has one C–C–O–C torsion angle which approaches g.

The Th(3) coordination and geometry (Fig. 6(c)) are identical to those found in Th(1) and Th(4) with the exception of having two alkoxide bridges (one

TABLE 4. Bond distances (Å) and angles (°) for [ThCl₃(EO5)]Cl·CH₃CN

Atoms	Distance	Atoms	Distance
Th–Cl(1)	2.731(5)	Th–Cl(2)	2.708(4)
Th–Cl(3)	2.751(4)	Th–O(1)	2.51(1)
Th–O(2)	2.630(8)	Th–O(3)	2.519(8)
Th–O(4)	2.57(1)	Th–O(5)	2.575(9)
Th–O(6)	2.476(9)	O(1)–C(1)	1.49(2)
O(2)–C(2)	1.43(1)	O(2)–C(3)	1.42(2)
O(3)–C(4)	1.47(2)	O(3)–C(5)	1.44(2)
O(4)–C(6)	1.46(2)	O(4)–C(7)	1.44(2)
O(5)–C(8)	1.44(2)	O(5)–C(9)	1.48(2)
O(6)–C(10)	1.43(2)	C(1)–C(2)	1.54(2)
C(3)–C(4)	1.46(2)	C(5)–C(6)	1.52(2)
C(7)–C(8)	1.49(2)	C(9)–C(10)	1.48(2)
N(1)–C(11)	1.11(2)	C(11)–C(12)	1.39(3)

Atoms	Angle	Atoms	Angle
Cl(1)–Th–Cl(2)	141.9(2)	Cl(1)–Th–Cl(3)	139.4(1)
Cl(2)–Th–Cl(3)	76.5(1)	Cl(1)–Th–O(1)	74.2(3)
Cl(2)–Th–O(1)	140.9(3)	Cl(3)–Th–O(1)	75.7(3)
Cl(1)–Th–O(2)	70.9(2)	Cl(2)–Th–O(2)	131.5(2)
Cl(3)–Th–O(2)	71.1(2)	O(1)–Th–O(2)	61.7(3)
Cl(1)–Th–O(3)	90.2(2)	Cl(2)–Th–O(3)	79.6(2)
Cl(3)–Th–O(3)	84.5(2)	O(1)–Th–O(3)	124.1(3)
O(2)–Th–O(3)	62.5(3)	Cl(1)–Th–O(4)	71.6(4)
Cl(2)–Th–O(4)	71.0(4)	Cl(3)–Th–O(4)	137.5(3)
O(1)–Th–O(4)	145.1(4)	O(2)–Th–O(4)	112.3(3)
O(3)–Th–O(4)	63.6(3)	Cl(1)–Th–O(5)	77.0(3)
Cl(2)–Th–O(5)	79.4(3)	Cl(3)–Th–O(5)	136.8(3)
O(1)–Th–O(5)	103.2(3)	O(2)–Th–O(5)	147.1(3)
O(3)–Th–O(5)	125.5(3)	O(4)–Th–O(5)	62.0(3)
Cl(1)–Th–O(6)	112.7(3)	Cl(2)–Th–O(6)	82.1(3)
Cl(3)–Th–O(6)	77.9(2)	O(1)–Th–O(6)	65.4(3)
O(2)–Th–O(6)	123.3(3)	O(3)–Th–O(6)	157.1(3)
O(4)–Th–O(6)	122.5(3)	O(5)–Th–O(6)	63.7(3)
Th–O(1)–C(1)	122.8(8)	Th–O(2)–C(2)	118.5(7)
Th–O(2)–C(3)	116.2(8)	C(2)–O(2)–C(3)	112(1)
Th–O(3)–C(4)	119.4(8)	Th–O(3)–C(5)	117.9(7)
C(4)–O(3)–C(5)	112(1)	Th–O(4)–C(6)	118.0(9)
Th–O(4)–C(7)	118.0(9)	C(6)–O(4)–C(7)	113(1)
Th–O(5)–C(8)	120.9(8)	Th–O(5)–C(9)	115.7(8)
C(8)–O(5)–C(9)	111(1)	Th–O(6)–C(10)	120.6(9)
O(1)–C(1)–C(2)	105(1)	O(2)–C(2)–C(1)	106(1)
O(2)–C(3)–C(4)	107(1)	O(3)–C(4)–C(3)	109(1)
O(3)–C(5)–C(6)	109(1)	O(4)–C(6)–C(5)	103(1)
O(4)–C(7)–C(8)	107(1)	O(5)–C(8)–C(7)	109(1)
O(5)–C(9)–C(10)	106(1)	O(6)–C(10)–C(9)	108(1)
N(1)–C(11)–C(12)	175(2)		

Fig. 4. [Th₄Cl₈(O)(EO4²⁻)₃]·3CH₃CN. The solvent molecules have been omitted for clarity.
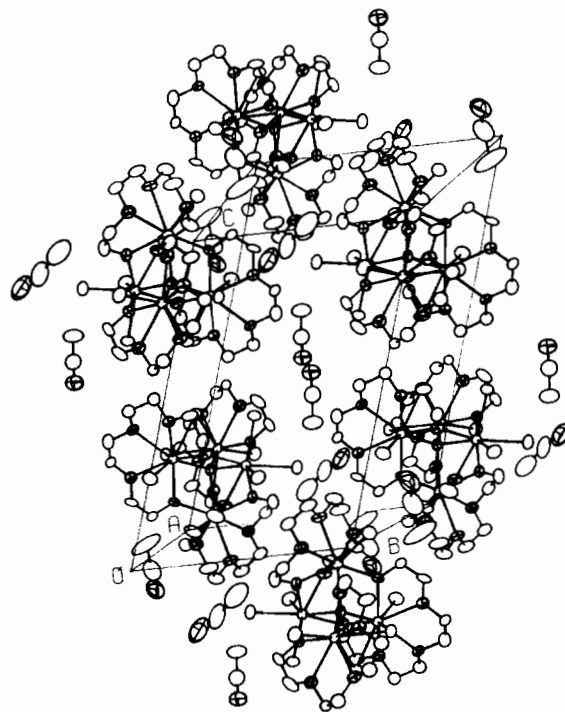
Fig. 5. Cell packing diagram for [Th₄Cl₈(O)(EO4²⁻)₃]·3CH₃CN.

each with Th(1) and Th(4)) instead of chloride bridges. The average coordination parameters include Th(3)–O(alkoxide of the ligand coordinated to Th(3)) = 2.36(1), Th(3)–O(alkoxide bridges to Th(1) and Th(4)) = 2.40(1), Th(3)–Cl = 2.787(6), Th–O-(etheric) = 2.70(2), Th(3)–O(μ_4-oxide) = 2.49(1) Å.

The glycol conformation is different from either of the alternate models for the O(2)–O(6) or O(12)–O(16) glycols. The sequence of C–C torsion
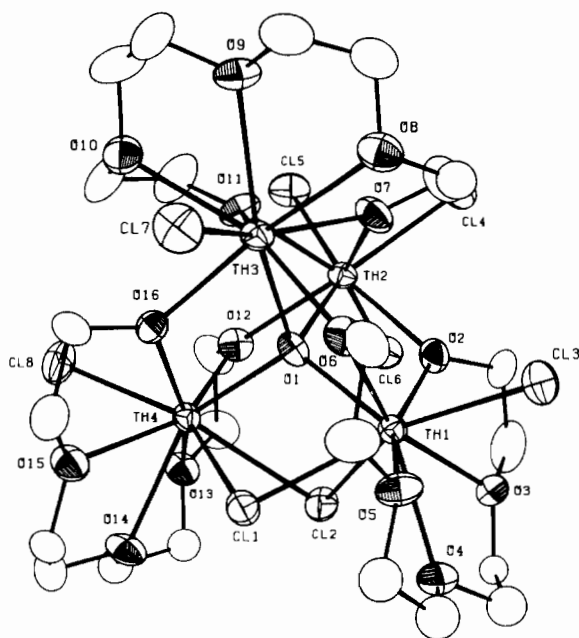
angles is g^-, g^-, g^+, g^+ and one C–O angle is distorted toward gauche between each pair of consecutive C–C angles with the same sign.

Th(2) is only eight-coordinate (Fig. 6(b)), coordinated to three terminal chloride ions and five
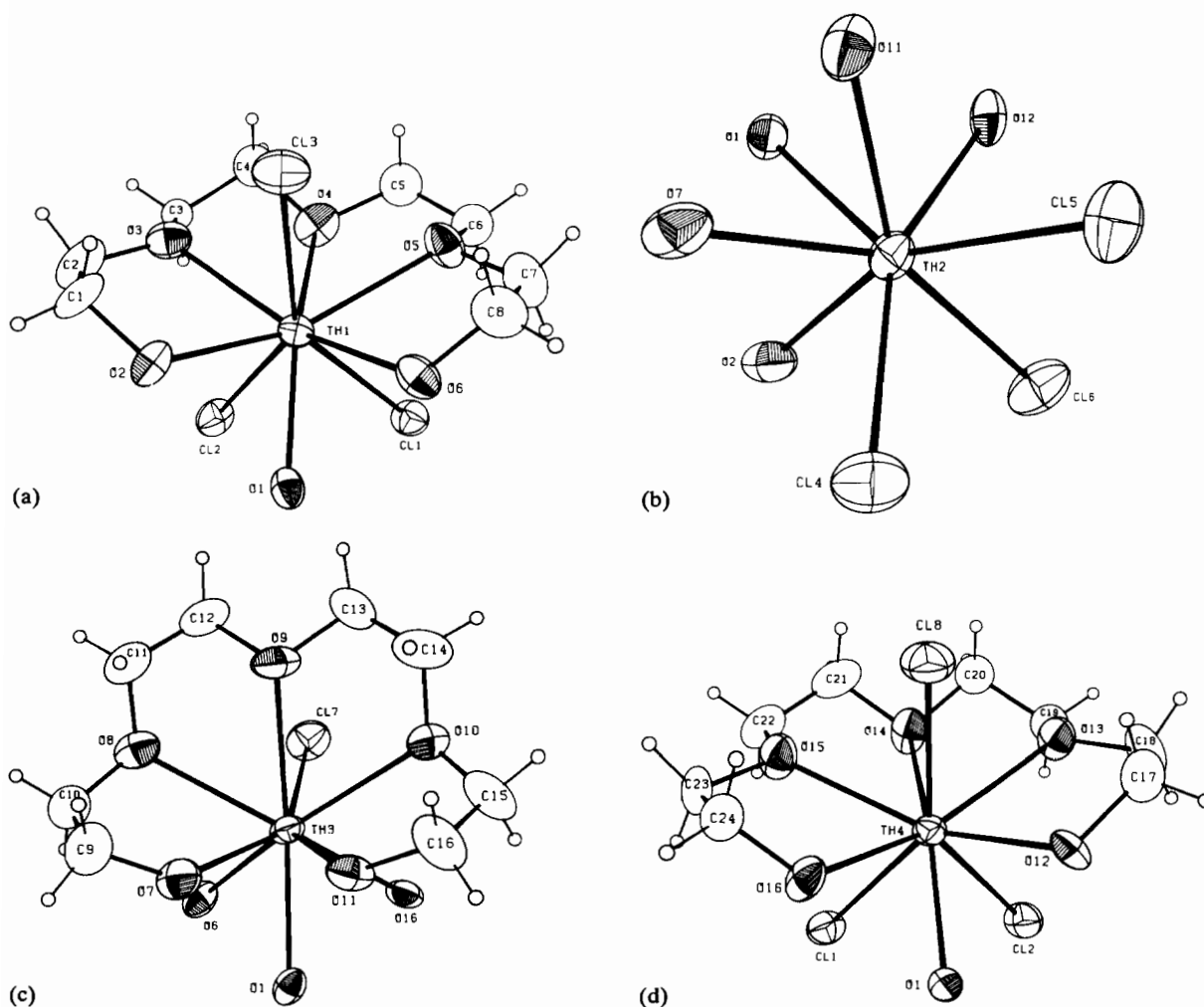
Fig. 6. The four Th⁴⁺ geometries in [Th₄Cl₈(O)(EO4²⁻)₃]·3CH₃CN.

bridging alkoxides. The square antiprismatic geometry is comprised of Cl(4), Cl(5), O(7) and O(11) as one face and Cl(6), O(1), O(2) and O(12) as the second face. The average parameters are Th(2)–Cl = 2.776(8), Th–O(alkoxide) = 2.435(9), Th–O(μ_4-oxide) = 2.50(1) Å.

The μ_4-oxide has two short distances (Th(1), Th(4) average 2.344(3) Å) and two long separations (Th(2), Th(3) average 2.50(1) Å). This is in sharp contrast to the rather symmetrical metal–oxide distances observed in several other μ_4-oxides [22–25]. All of the μ-alkoxides involving Th(2) are asymmetric. This may arise from the lower coordination number of Th(2). The alkoxide bridges between Th(3) and Th(4) (O(16)) and Th(1) and Th(3) (O(6)) are essentially identical.

The Th···Th separations range from 3.9390(7)–4.0031(6) Å except for Th(2)···Th(3) which is the shortest of all such separations at 3.7431(9) Å. For

comparison, the Th···Th separation in the hydroxy bridged [Th₂(OH)₂(aquanitrato(2,6-diacetylpyridinedisemicarbazone))₂(NO₃)₂(OH₂)][NO₃]₄·4H₂O [26], is 4.0181(6) Å and in the compartmental Schiff base complex, Mg[ThL₃]₂·6H₂O* [27], a Th···Th separation of 3.831 Å was observed. The aryl oxide bridges average 2.47 Å from each Th in the latter, while the Th–μ-OH separation in the former average 2.366 Å. We have also recently characterized the hydroxy bridged complex, [ThCl(OH)(OH₂)₆]₂Cl₄·18-crown-6 which exhibits a Th···Th separation of 3.995 Å and an average Th–μ-OH distance of 2.35(1) Å [6].

It is interesting to note that the Th(2)···Th(3) separation of 3.7431(9) Å is shorter than the U···U distances in such alkoxides as U₂(OⁱPr)₁₀ (3.789(1) Å) [28]. An even shorter U···U separation of

*L is the trianion derived by condensation of 2,6-diformyl-4-chlorophenol and o-aminophenol.

TABLE 5. Bond distances (Å) and angles (°) for $[Th_4Cl_8(O)(C_8H_{16}O_5)_3] \cdot 3CH_3CN$

Atoms	Distance	Atoms	Distance
Th(1)–Cl(1)	2.913(4)	Th(1)–Cl(2)	2.935(3)
Th(1)–Cl(3)	2.750(4)	Th(1)–O(1)	2.347(8)
Th(1)–O(2)	2.35(1)	Th(1)–O(3)	2.60(1)
Th(1)–O(4)	2.668(9)	Th(1)–O(5)	2.63(1)
Th(1)–O(6)	2.39(1)	Th(2)–Cl(4)	2.765(4)
Th(2)–Cl(5)	2.783(4)	Th(2)–Cl(6)	2.780(5)
Th(2)–O(1)	2.50(1)	Th(2)–O(2)	2.428(9)
Th(2)–O(7)	2.45(1)	Th(2)–O(11)	2.43(1)
Th(2)–O(12)	2.432(9)	Th(3)–Cl(7)	2.787(6)
Th(3)–O(1)	2.49(1)	Th(3)–O(6)	2.408(9)
Th(3)–O(7)	2.36(1)	Th(3)–O(8)	2.720(9)
Th(3)–O(9)	2.676(9)	Th(3)–O(10)	2.70(1)
Th(3)–O(11)	2.36(1)	Th(3)–O(16)	2.385(9)
Th(4)–Cl(1)	2.902(4)	Th(4)–Cl(2)	2.960(4)
Th(4)–Cl(8)	2.772(4)	Th(4)–O(1)	2.342(8)
Th(4)–O(12)	2.33(1)	Th(4)–O(13)	2.57(1)
Th(4)–O(14)	2.635(9)	Th(4)–O(15)	2.59(1)
Th(4)–O(16)	2.39(1)		

Atoms	Angle	Atoms	Angle
Cl(1)–Th(1)–Cl(2)	67.2(1)	Cl(1)–Th(1)–Cl(3)	142.3(1)
Cl(2)–Th(1)–Cl(3)	143.0(1)	Cl(1)–Th(1)–O(1)	73.4(2)
Cl(2)–Th(1)–O(1)	71.9(2)	Cl(3)–Th(1)–O(1)	128.4(2)
Cl(1)–Th(1)–O(2)	136.4(2)	Cl(2)–Th(1)–O(2)	79.1(2)
Cl(3)–Th(1)–O(2)	80.6(2)	O(1)–Th(1)–O(2)	70.3(4)
Cl(1)–Th(1)–O(3)	123.9(2)	Cl(2)–Th(1)–O(3)	70.4(2)
Cl(3)–Th(1)–O(3)	72.9(2)	O(1)–Th(1)–O(3)	124.6(4)
O(2)–Th(1)–O(3)	63.9(3)	Cl(1)–Th(1)–O(4)	77.3(3)
Cl(2)–Th(1)–O(4)	79.4(2)	Cl(3)–Th(1)–O(4)	86.7(2)
O(1)–Th(1)–O(4)	144.9(3)	O(2)–Th(1)–O(4)	123.7(4)
O(3)–Th(1)–O(4)	60.0(4)	Cl(1)–Th(1)–O(5)	68.1(2)
Cl(2)–Th(1)–O(5)	124.4(2)	Cl(3)–Th(1)–O(5)	74.3(2)
O(1)–Th(1)–O(5)	123.0(4)	O(2)–Th(1)–O(5)	154.5(3)
O(3)–Th(1)–O(5)	111.6(3)	O(4)–Th(1)–O(5)	59.9(3)
Cl(1)–Th(1)–O(6)	78.8(3)	Cl(2)–Th(1)–O(6)	133.1(2)
Cl(3)–Th(1)–O(6)	82.8(2)	O(1)–Th(1)–O(6)	68.0(3)
O(2)–Th(1)–O(6)	108.2(3)	O(3)–Th(1)–O(6)	155.2(3)
O(4)–Th(1)–O(6)	124.3(4)	O(5)–Th(1)–O(6)	64.6(3)
Cl(4)–Th(2)–Cl(5)	78.7(1)	Cl(4)–Th(2)–Cl(6)	84.1(1)
Cl(5)–Th(2)–Cl(6)	82.5(1)	Cl(4)–Th(2)–O(1)	137.7(2)
Cl(5)–Th(2)–O(1)	137.8(2)	Cl(6)–Th(2)–O(1)	115.4(2)
Cl(4)–Th(2)–O(2)	83.2(2)	Cl(5)–Th(2)–O(2)	154.6(3)
Cl(6)–Th(2)–O(2)	78.0(3)	O(1)–Th(2)–O(2)	66.5(3)
Cl(4)–Th(2)–O(7)	77.3(3)	Cl(5)–Th(2)–O(7)	117.8(2)
Cl(6)–Th(2)–O(7)	148.4(3)	O(1)–Th(2)–O(7)	67.0(3)
O(2)–Th(2)–O(7)	74.7(3)	Cl(4)–Th(2)–O(11)	115.8(2)
Cl(5)–Th(2)–O(11)	77.2(3)	Cl(6)–Th(2)–O(11)	147.5(2)
O(1)–Th(2)–O(11)	68.0(3)	O(2)–Th(2)–O(11)	127.2(4)
O(7)–Th(2)–O(11)	64.0(3)	Cl(4)–Th(2)–O(12)	155.8(3)
Cl(5)–Th(2)–O(12)	82.8(2)	Cl(6)–Th(2)–O(12)	78.1(3)
O(1)–Th(2)–O(12)	65.9(3)	O(2)–Th(2)–O(12)	108.6(3)
O(7)–Th(2)–O(12)	125.7(4)	O(11)–Th(2)–O(12)	74.5(3)
Cl(7)–Th(3)–O(1)	129.7(2)	Cl(7)–Th(3)–O(6)	81.6(3)
O(1)–Th(3)–O(6)	65.3(3)	Cl(7)–Th(3)–O(7)	143.9(3)
O(1)–Th(3)–O(7)	68.5(3)	O(6)–Th(3)–O(7)	80.7(4)
Cl(7)–Th(3)–O(8)	81.0(3)	O(1)–Th(3)–O(8)	118.6(3)

(continued)

TABLE 5. *(continued)*

Atoms	Angle	Atoms	Angle
O(6)–Th(3)–O(8)	71.1(3)	O(7)–Th(3)–O(8)	63.6(4)
Cl(7)–Th(3)–O(9)	71.5(3)	O(1)–Th(3)–O(9)	158.8(4)
O(6)–Th(3)–O(9)	126.5(3)	O(7)–Th(3)–O(9)	94.6(4)
O(8)–Th(3)–O(9)	59.8(3)	Cl(7)–Th(3)–O(10)	81.6(3)
O(1)–Th(3)–O(10)	117.0(3)	O(6)–Th(3)–O(10)	158.3(4)
O(7)–Th(3)–O(10)	120.7(4)	O(8)–Th(3)–O(10)	119.5(3)
O(9)–Th(3)–O(10)	59.7(3)	Cl(7)–Th(3)–O(11)	144.6(3)
O(1)–Th(3)–O(11)	69.1(3)	O(6)–Th(3)–O(11)	130.9(4)
O(7)–Th(3)–O(11)	66.4(4)	O(8)–Th(3)–O(11)	119.0(4)
O(9)–Th(3)–O(11)	92.8(3)	O(10)–Th(3)–O(11)	63.2(4)
Cl(7)–Th(3)–O(16)	81.7(3)	O(1)–Th(3)–O(16)	65.1(3)
O(6)–Th(3)–O(16)	94.2(3)	O(7)–Th(3)–O(16)	130.7(4)
O(8)–Th(3)–O(16)	158.7(4)	O(9)–Th(3)–O(16)	125.1(3)
O(10)–Th(3)–O(16)	69.7(3)	O(11)–Th(3)–O(16)	82.2(4)
Cl(1)–Th(4)–Cl(2)	67.0(1)	Cl(1)–Th(4)–Cl(8)	141.4(1)
Cl(2)–Th(4)–Cl(8)	143.2(1)	Cl(1)–Th(4)–O(1)	73.7(2)
Cl(2)–Th(4)–O(1)	71.4(2)	Cl(8)–Th(4)–O(1)	129.4(2)
Cl(1)–Th(4)–O(12)	137.6(2)	Cl(2)–Th(4)–O(12)	81.0(3)
Cl(8)–Th(4)–O(12)	80.3(3)	O(1)–Th(4)–O(12)	70.0(3)
Cl(1)–Th(4)–O(13)	123.4(2)	Cl(2)–Th(4)–O(13)	69.5(2)
Cl(8)–Th(4)–O(13)	73.8(2)	O(1)–Th(4)–O(13)	123.0(4)
O(12)–Th(4)–O(13)	64.2(3)	Cl(1)–Th(4)–O(14)	77.6(2)
Cl(2)–Th(4)–O(14)	80.4(2)	Cl(8)–Th(4)–O(14)	84.9(2)
O(1)–Th(4)–O(14)	145.7(3)	O(12)–Th(4)–O(14)	125.0(4)
O(13)–Th(4)–O(14)	60.7(4)	Cl(1)–Th(4)–O(15)	68.3(2)
Cl(2)–Th(4)–O(15)	125.4(2)	Cl(8)–Th(4)–O(15)	73.1(2)
O(1)–Th(4)–O(15)	122.4(3)	O(12)–Th(4)–O(15)	152.3(3)
O(13)–Th(4)–O(15)	113.8(3)	O(14)–Th(4)–O(15)	60.6(3)
Cl(1)–Th(4)–O(16)	79.4(2)	Cl(2)–Th(4)–O(16)	132.6(2)
Cl(8)–Th(4)–O(16)	83.1(2)	O(1)–Th(4)–O(16)	67.4(4)
O(12)–Th(4)–O(16)	105.5(3)	O(13)–Th(4)–O(16)	155.9(3)
O(14)–Th(4)–O(16)	124.9(4)	O(15)–Th(4)–O(16)	64.4(3)
Th(1)–Cl(1)–Th(4)	85.3(1)	Th(1)–Cl(2)–Th(4)	83.9(1)
Th(1)–O(1)–Th(2)	110.3(4)	Th(1)–O(1)–Th(3)	111.5(3)
Th(2)–O(1)–Th(3)	97.2(3)	Th(1)–O(1)–Th(4)	114.3(3)
Th(2)–O(1)–Th(4)	110.6(4)	Th(3)–O(1)–Th(4)	111.7(4)
Th(1)–O(2)–Th(2)	112.8(4)	Th(1)–O(2)–C(1)	121.5(9)
Th(2)–O(2)–C(1)	125(1)	Th(1)–O(3)–C(2)	115.0(9)
Th(1)–O(3)–C(3)	119(1)	Th(1)–O(3)–C(3)'	124(3)
Th(1)–O(4)–C(4)	120(1)	Th(1)–O(4)–C(5)	117(1)
Th(1)–O(4)–C(4)'	115(2)	Th(1)–O(4)–C(5)'	124(1)
Th(1)–O(5)–C(6)	124(1)	Th(1)–O(5)–C(7)	115.3(8)
Th(1)–O(5)–C(6)'	120(1)	Th(1)–O(6)–Th(3)	113.1(4)
Th(1)–O(6)–C(8)	120.5(9)	Th(3)–O(6)–C(8)	126.3(9)
Th(2)–O(7)–Th(3)	102.0(3)	Th(2)–O(7)–C(9)	131(1)
Th(3)–O(7)–C(9)	127(1)	Th(3)–O(8)–C(10)	108.4(8)
Th(3)–O(8)–C(11)	117.2(8)	Th(3)–O(9)–C(12)	118.1(8)
Th(3)–O(9)–C(13)	119.5(8)	Th(3)–O(10)–C(14)	119(1)
Th(3)–O(10)–C(15)	110.5(9)	Th(2)–O(11)–Th(3)	102.7(3)
Th(2)–O(11)–C(16)	127(1)	Th(3)–O(11)–C(16)	129(1)
Th(2)–O(12)–Th(4)	113.5(4)	Th(2)–O(12)–C(17)	124(1)
Th(4)–O(12)–C(17)	121.6(9)	Th(4)–O(13)–C(18)	117.8(7)
Th(4)–O(13)–C(19)	116(1)	Th(4)–O(13)–C(19)'	126(2)
Th(4)–O(14)–C(20)	117(1)	Th(4)–O(14)–C(21)	119.5(8)
Th(4)–O(14)–C(20)'	120(1)	Th(4)–O(15)–C(22)	122(1)
Th(4)–O(15)–C(23)	117.3(9)	Th(3)–O(16)–Th(4)	114.0(5)
Th(3)–O(16)–C(24)	126.2(8)	Th(4)–O(16)–C(24)	119.9(7)

3.576(1) Å in $U_3O(OC)_{10}$ was still not taken as evidence of any U$\cdots$U bonding interaction. The close approach of the two Th atoms in our compound

does, however, deserve further study. The entire Th_4 cluster may have unique properties which we can explore.

Supplementary material

Tables listing crystallographic parameters, fractional coordinates, thermal parameters, torsion angles, least-squares planes results and observed and calculated structure factors or amplitudes for both compounds (34 pages) are available from the authors on request.

Acknowledgement

References

1 R. D. Rogers, A. H. Bond and W. G. Hipple, *J. Crystallogr. Spectrosc. Res., 20* (1991) 611.
2 R. D. Rogers, L. K. Kurihara and M. M. Benning, *Acta Crystallogr., Sect. C, 43* (1987) 1056.
3 R. D. Rogers and M. M. Benning, *Acta Crystallogr., Sect. C, 44* (1988) 641.
4 R. D. Rogers, *Lanthanide Actinide Res., 3* (1989) 71.
5 R. D. Rogers, L. K. Kurihara and M. M. Benning, *J. Chem. Soc., Dalton Trans.,* (1988) 13.
6 R. D. Rogers and A. H. Bond, 1991, unpublished results.
7 E. Moran, A. I. Nazzal, T. C. Huang and J. B. Torrance, *Physica C, 160* (1989) 30.
8 M. Andersson and O. Rapp, *Physica C, 162–164* (1989) 725.
9 S.-i. Hirano, T. Hayashi, M. Miura and H. Tomonaga, *Bull. Chem. Soc. Jpn., 62* (1989) 888.
10 N. N. Sauer, E. Garcia, K. V. Salazar, R. R. Ryan and J. A. Martin, *J. Am. Chem. Soc., 112* (1990) 1524.
11 H. A. Stecher, A. Sen and A. L. Rheingold, *Inorg. Chem., 28* (1989) 3280.
12 O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting and K. G. Caulton, *Inorg. Chem., 28* (1989) 263.
13 S. C. Goel, K. S. Kramer, P. C. Gibbons and W. E. Buhro, *Inorg. Chem., 28* (1989) 3620.
14 C. Yonezawa and G. R. Choppin, *J. Radioanal. Nucl. Chem., 134* (1989) 233.
15 W.-J. Wang, Q. Sun and B. Chen, *J. Radioanal. Nucl. Chem., 110* (1987) 227.
16 W.-J. Wang, Q. Sun and B. Chen, *J. Radioanal. Nucl. Chem., 98* (1986) 11.
17 G. M. Sheldrick, *SHELX76,* a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, U.K., 1976.
18 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., Vol. IV, 1974, pp. 72, 99, 149. (Present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands.)
19 G. M. Sheldrick, SHELXS, in G. M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3,* Oxford University Press, London, 1985, pp. 175–189.
20 R. D. Rogers, A. N. Rollins and M. M. Benning, *Inorg. Chem., 27* (1988) 3826.
21 R. D. Rogers, E. J. Voss and R. D. Etzenhouser, *Inorg. Chem., 27* (1988) 533.
22 L. Hiltunen, M. Leskela, M. Makela and L. Niinistro, *Acta Chem. Scand., Ser. A, 41* (1987) 548.
23 C. Gaffney, P. G. Harrison and T. J. King, *J. Chem. Soc., Chem. Commun.,* (1980) 1251.
24 J. T. Guy, Jr., J. C. Cooper, R. D. Gilardi, J. L. Flippen-Anderson and C. F. George, Jr., *Inorg. Chem., 27* (1988) 635.
25 G. A. Zank, C. A. Jones, T. B. Rauchfuss and A. L. Rheingold, *Inorg. Chem., 25* (1986) 1886.
26 A. Bino and R. Chayat, *Inorg. Chim. Acta, 129* (1987) 273.
27 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 134* (1987) 165.
28 F. A. Cotton, D. O. Marler and W. Schwotzer, *Inorg. Chim. Acta, 85* (1984) L31.