but the mixture was stirred for 1 h before the solvent was taken off under vacuum. The white solid residue was taken up in hot 1,4-dioxane and crystals (0.43 g, 91%) suitable for the crystallographic study separated on cooling.

Crystal data

[LiI(C$_4$H$_8$O$_2$)$_2$]	Mo $K\alpha$ radiation
$M_r = 310.05$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 7.726\,(2)$ Å	$\theta = 7-10°$
$b = 10.220\,(2)$ Å	$\mu = 2.698$ mm^{-1}
$c = 15.169\,(3)$ Å	$T = 173\,(2)$ K
$\beta = 99.67\,(2)°$	Block
$V = 1180.7\,(4)$ Å^3	$0.30 \times 0.30 \times 0.25$ mm
$Z = 4$	Colourless
$D_x = 1.744$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf-Nonius CAD-4 diffractometer	2178 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$R_{int} = 0.023$
Absorption correction:	$\theta_{max} = 27.97°$
ψ scan (MolEN; Fair, 1990)	$h = 0 \rightarrow 10$
	$k = 0 \rightarrow 13$
$T_{min} = 0.46$, $T_{max} = 0.51$	$l = -20 \rightarrow 19$
3030 measured reflections	2 standard reflections
2837 independent reflections	frequency: 120 min
	intensity decay: 0.5%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 1.157$ e Å^{-3} (at
$R[F^2 > 2\sigma(F^2)] = 0.034$	centre of a dioxane ring)
$wR(F^2) = 0.084$	$\Delta\rho_{min} = -0.634$ e Å^{-3}
$S = 1.005$	Extinction correction:
2837 reflections	SHELXL93
123 parameters	Extinction coefficient:
H atoms riding	0.0091 (6)
$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	International Tables for
$(\Delta/\sigma)_{max} = -0.001$	Crystallography (Vol. C)

Table 1. *Selected geometric parameters* (Å, °)

Li—I	2.640 (6)	Li—O1	1.923 (6)
Li—O3	1.944 (6)	Li—O4^i	1.940 (6)
O1—Li—I	111.1 (3)	O3—Li—I	112.3 (3)
O4^i—Li—I	119.5 (3)	O1—Li—O3	109.0 (3)
O1—Li—O4^i	101.4 (3)	O4^i—Li—O3	102.6 (3)

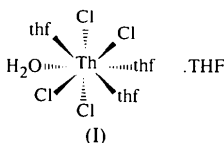Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *CAMERON* (Watkin & Pearce, 1993). Software used to prepare material for publication: *SHELXL93*.

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Aquatetrachlorotris(tetrahydrofuran-*O*)-thorium(IV) Tetrahydrofuran Solvate (1/1)

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Abstract

The title compound, [ThCl$_4$(C$_4$H$_8$O)$_3$(H$_2$O)].C$_4$H$_8$O, is eight-coordinate with a distorted square-antiprismatic metal-atom geometry; pairs of O or Cl atoms are located at opposite vertices of the square planes.

Comment

The structural chemistry of thorium(IV) chloride adducts is relatively well understood with both seven- and eight-coordinate geometries known. Differentiation between these would seem to be a function of the steric effects invoked by the donor ligands. Typical examples include, with coordination number (CN) = 7, [ThCl₄{O=C(NPhMe)₂}₃] (Bagnall, Al-Daher, Bombiere & Benetollo, 1986), [ThCl₄(NMe₃)₃] (Willey & Drew, 1984) and [ThCl₄(OPPh₃)₃] (Van den Bossche, Rebizant, Spirlet & Goffart, 1988), and with CN = 8, [ThCl₄{(Me₂N)₂P(O)-O-(O)P(NMe₂)₂}₂] (Kepert, Patrick & White, 1983), [ThCl₄(EtOH)₃-(H₂O)].(18-crown-6).H₂O (Rodgers, Kurihara & Benning, 1988) and [ThCl₄(OSPh₂)₄] (Rickard & Woolard, 1980).

Our interest in lanthanide (Ln) and actinide (An) tetrahydrofuran adducts stems from their use as suitable precursors for cationic species, e.g. LnCl₂⁺, Ln = Pr (Willey, Meehan, Salter & Drew, 1996) and Gd (Willey, Meehan, Rudd, Clase & Alcock, 1994), as generated in situ by halide abstraction using SbCl₅. In this instance, conventional treatment of the hydrated salt ThCl₄.xH₂O (x = 7–9) with an excess of thionyl chloride in tetrahydrofuran as the bulk solvent provided the 'mixed' solvate [ThCl₄(thf)₃(H₂O)].THF, (I). Incomplete dehydration with retention of one molecule of water per metal centre is presumably the result of insufficient heating at reflux.

$$thf\diagdown \overset{Cl}{\underset{Cl}{\overset{\text{Cl}}{\vert}}}\diagup Cl$$

$$H_2O\cdots Th\cdots thf \quad .THF$$

$$Cl\diagup \underset{Cl}{\vert}\diagdown thf$$

(I)

The molecular structure of the title compound is illustrated in Fig. 1. The coordination geometry is best described as that of a distorted square antiprism; see Fig. 2, which shows more clearly the positions of the donor atoms relative to the metal. The Th—Cl bond distance, mean 2.714 (6) Å, appears to be marginally shorter than those of corresponding eight coordinate, e.g. [ThCl₄{(Me₂N)₂P(O)-O-(O)P-(NMe₂)₂}₂] [2.749 (8) Å], and seven coordinate, e.g. [ThCl₄(OPPh₃)₃] [2.736 (4) Å], species. The sole exception is the trimethylamine complex [ThCl₄(NMe₃)₃] (Willey & Drew, 1984), where the Th—Cl bond distance, mean 2.661 (12) Å, is perceptibly shorter than that of the title compound, (I). Interestingly the parent ThCl₄ (Mucker, Smith, Johnson & Elson, 1969) is eight coordinate and has two sets of Th—Cl bond distances of 2.718 (8) and 2.903 (7) Å, based upon a dodecahedral geometry.

The Th—O(thf) bond distances range from 2.541 (3) to 2.622 (3) Å, mean 2.58 (3) Å, and the Th—O(H₂O) bond distance of 2.437 (3) Å is comparable with Th—O
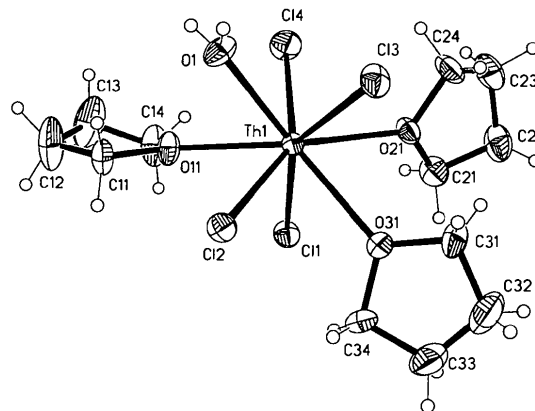

Fig. 1. View of the molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.
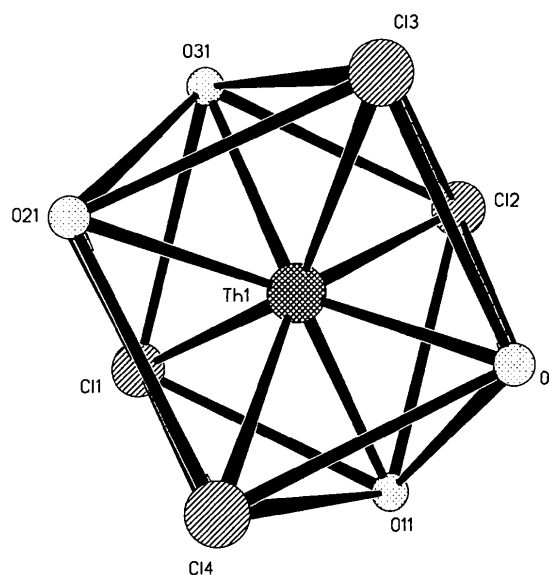

Fig. 2. Distorted square-antiprismatic coordination geometry around the metal atom.

linkages in similar systems, e.g. [ThCl₄(OSPh₂)₄], mean 2.46 (1) Å, and [ThCl₄(OPPh₃)₃], mean 2.376 (8) Å. The best correlation comes, not surprisingly, from the hydrated ethanol complex [ThCl₄(EtOH)₃(H₂O)].(18-crown-6).H₂O, which has a mean Th—O(ethanol) distance of 2.517 (8) Å and a Th—O(H₂O) distance of 2.453 (7) Å.

Experimental

The title compound was obtained from the ThCl₄.xH₂O (x = 7–9 as purchased)/SOCl₂/THF system following by heating at reflux for 24 h. After removal of the solvent in vacuo, the resulting solid was washed with diethyl ether (2 × 25 ml) to give an off-white powder. Recrystallization from THF gave colourless block crystals.

Crystal data

[ThCl4(C4H8O)3-
　(H2O)].C4H8O
$M_r = 680.27$
Monoclinic
$C2/c$
$a = 29.0856\,(13)$ Å
$b = 9.7417\,(4)$ Å
$c = 21.1140\,(9)$ Å
$\beta = 126.8530\,(10)°$
$V = 4787.1\,(4)$ Å^3
$Z = 8$
$D_x = 1.888$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192
　reflections
$\theta = 1.75-26.00°$
$\mu = 6.698$ mm^{-1}
$T = 180\,(2)$ K
Block
$0.26 \times 0.20 \times 0.16$ mm
Colourless

Data collection

Siemens SMART diffractom-
　eter
ω scans
Absorption correction:
　multi-scan SADABS
　(Sheldrick, 1996a)
　$T_{min} = 0.466$, $T_{max} = 0.694$
12 793 measured reflections
4697 independent reflections

3900 reflections with
　$I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 26.00°$
$h = -38 \rightarrow 33$
$k = -13 \rightarrow 8$
$l = -21 \rightarrow 28$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.050$
$S = 1.026$
4697 reflections
243 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2$
　$+ 4.467P]$
　where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.007$
$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ e Å^{-3}
Extinction correction: none
Scattering factors from
　International Tables for
　Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Th1—O1	2.437 (3)	Th1—Cl1	2.7038 (10)
Th1—O21	2.541 (3)	Th1—Cl2	2.7159 (10)
Th1—O11	2.590 (3)	Th1—Cl4	2.7158 (11)
Th1—O31	2.622 (3)	Th1—Cl3	2.7198 (10)
O1—Th1—O21	128.10 (10)	Cl1—Th1—Cl2	95.57 (3)
O1—Th1—O11	67.79 (10)	O1—Th1—Cl4	75.35 (9)
O21—Th1—O11	138.51 (9)	O21—Th1—Cl4	72.91 (7)
O1—Th1—O31	137.17 (10)	O11—Th1—Cl4	76.62 (7)
O21—Th1—O31	67.47 (9)	O31—Th1—Cl4	139.64 (7)
O11—Th1—O31	131.32 (9)	Cl1—Th1—Cl4	91.29 (4)
O1—Th1—Cl1	141.02 (8)	Cl2—Th1—Cl4	147.27 (3)
O21—Th1—Cl1	79.60 (7)	O1—Th1—Cl3	71.72 (8)
O11—Th1—Cl1	73.57 (7)	O21—Th1—Cl3	76.41 (7)
O31—Th1—Cl1	74.59 (7)	O11—Th1—Cl3	138.33 (7)
O1—Th1—Cl2	79.35 (9)	O31—Th1—Cl3	75.73 (7)
O21—Th1—Cl2	139.81 (7)	Cl1—Th1—Cl3	147.21 (3)
O11—Th1—Cl2	74.77 (7)	Cl2—Th1—Cl3	88.68 (3)
O31—Th1—Cl2	72.76 (7)	Cl4—Th1—Cl3	102.52 (3)
O11—Th1—O21—C21	−57.8 (4)	Cl1—Th1—O21—C21	−7.7 (3)
O31—Th1—O21—C21	69.8 (3)	Cl2—Th1—O21—C21	78.6 (3)

The temperature of the crystal was controlled using the Oxford
Cryosystems Cryostream Cooler (Cosier & Glazer, 1986).
Data were collected over a hemisphere of reciprocal space,
by a combination of three sets of exposures. Each set had

a different φ angle for the crystal and each exposure of 10
s covered 0.3° in ω. The crystal-to-detector distance was
5.01 cm. Coverage of the unique set was over 99% complete to
at least 26° in θ. Crystal decay was monitored by repeating the
initial frames at the end of the data collection and analyzing
the duplicate reflections. H atoms were added at calculated
positions and refined using a riding model; those associated
with the water molecule were inserted from the electron-
density map and the H—O distances restrained to be equal.
Anisotropic displacement parameters were used for all non-
H atoms. The U_{iso} parameters for the water H atoms were
allowed to refine, while for the methylene groups $U_{iso}(H) =$
$1.2U_{eq}(C)$.

Data collection: SMART (Siemens, 1994). Cell refinement:
SAINT (Siemens, 1995). Data reduction: SAINT. Program(s)
used to solve structure: SHELXTL/PC (Sheldrick, 1995).
Program(s) used to refine structure: SHELXL96 (Sheldrick,
1996b). Molecular graphics: SHELXTL/PC. Software used to
prepare material for publication: SHELXTL/PC.

We wish to acknowledge the use of the EPSRC's
Chemical Database Service at Daresbury Laboratory
(Fletcher, McMeeking & Parkin, 1996) for access to
the Cambridge Structural Database (Allen & Kennard,
1993).

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