

methionine sulfoxide}platinum(II) (Freeman, 1977). Although the longer Pt—Cl bond length being *trans* to S suggests a possible *trans* effect, a trend was not observed when *cis* and *trans* Pt—Cl bond lengths for a series of compounds were compared.

[Pt{CH₃(SO)CH₂CH₂NH₂}Cl₂] is designed to specifically target GpA sequences in DNA (Ling, Allen & Hambley, 1991) with a hydrogen bond between the sulfoxide oxygen and the —NH₂ group of the adenine promoting the binding. Thus, the hydrogen bonding of the sulfoxide O is of some relevance. In the present structure, the sulfoxide O makes two hydrogen bonds with N(1), one of which is intramolecular [O(1)⋯N(1) 3.000, O(1)⋯H(1B) 2.28, O(1)⋯N(1) 2.938, O(1)⋯H(1B) 2.30 Å], con-

firmed its propensity to hydrogen bond to amine groups.

References

- ALLAIN, A., KUBIAK, M., JEZOWSKA-TREBIATOWSKA, B., KOZŁOWSKI, H. & GŁOWIAK, T. (1980). *Inorg. Chim. Acta*, **46**, 127–133.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- FREEMAN, W. A. (1977). *Acta Cryst.* **B33**, 191–194.
- HAMBLEY, T. W. (1991). *Inorg. Chem.* **30**, 937–942.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- LING, E. C. H., ALLEN, G. W. & HAMBLEY, T. W. (1991). Unpublished data.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1992). **C48**, 1199–1201

Structure of [ThCl(OH)(OH₂)₆]₂Cl₄·18-Crown-6·2H₂O

BY ROBIN D. ROGERS* AND ANDREW H. BOND

Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, USA

(Received 12 August 1991; accepted 27 November 1991)

Abstract. Bis[hexaqua(chloro)hydroxothorium(IV)] tetrachloride–18-crown-6–water (1/1/2), [ThCl(OH)(OH₂)₆]₂Cl₄·C₁₂H₂₄O₆·2H₂O, *M_r* = 1227.3, triclinic, *P* $\bar{1}$, *a* = 9.227 (3), *b* = 10.599 (3), *c* = 11.089 (2) Å, α = 74.01 (2), β = 67.36 (2), γ = 77.02 (2)°, *V* = 953.6 Å³, *Z* = 1, *D_x* = 2.14 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 85.5 cm⁻¹, *F*(000) = 584, *T* = 295 K, final *R* = 0.044 for 2552 observed [*F_o* ≥ 5σ(*F_o*)] reflections. The structure consists of hydroxide bridged thorium dimers hydrogen bonded to uncoordinated chloride ions and water molecules and to 18-crown-6 molecules. Each Th is nine-coordinate tricapped trigonal prismatic which includes two hydroxide bridges, one terminal chloride ion, and six water molecules. The 18-crown-6 molecules reside around centers of inversion and accept eight hydrogen bonds.

Introduction. Reaction of hydrated thorium salts with crown ethers in nonaqueous solvents has led to a variety of compounds with one common feature: the crown ether resides in the thorium ion's second coordination sphere, hydrogen bonded to coordinated solvent or water molecules. Structurally characterized complexes include [Th(NO₃)₄(OH₂)₃].18-crown-6 (Rogers, Kurihara & Benning,

1987), [ThCl₂(OH₂)₇]Cl₂·18-crown-6·2H₂O (Rogers, 1989), [ThCl₄(OHEt)₃(OH₂)₂].18-crown-6·H₂O (Rogers, Kurihara & Benning, 1988), and [ThCl₄(OHMe)₂(OH₂)₂].15-crown-5·CH₃CN (Rogers & Benning, 1988). The title complex is the first we have isolated of this type in which hydrolysis has taken place and this allows us to compare the hydrogen-bonding environment of a larger dimer to the previously characterized monomeric cations.

Experimental. The title complex was isolated from the same reaction scheme that led to the isolation of [ThCl₂(OH₂)₇]Cl₂·18-crown-6·2H₂O (Rogers, 1989). Clear parallelepipeds grown from THF. *D_m* not determined. Crystal 0.08 × 0.15 × 0.15 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *K* α radiation, ω –2 θ scans. Cell constants from setting angles of 25 reflections ($\theta > 15^\circ$). Corrections for Lorentz–polarization effect and for absorption (empirical, ψ scans), range of relative transmission factors 45/100%. θ_{\max} = 25°; *h* 0 to 10, *k* –12 to 12, *l* –13 to 13. Standard reflections 500, 060, 003 measured every 3600s of data collection time, variation ± 1.5%. 3361 reflections measured, 2552 independent observed reflections [*F_o* ≥ 5σ(*F_o*)], *R_{int}* = 0.0015. Structure solved via *SHELXS* (Sheldrick, 1985). Crown ether H atoms placed 0.95 Å from the bonded C atom with a fixed isotropic

* To whom correspondence should be addressed.

thermal parameter $B = 5.5 \text{ \AA}^2$ and allowed to ride with the C—H distance fixed; remaining H atoms not included. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 72, 99, 149); structure refined with *SHELX76* (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma(F_o)^2 + 0.002F_o^2]^{-1}$, 190 parameters varied. $R = 0.044$, $wR = 0.055$, $S = 0.55$. Δ/σ in final least-squares refinement cycle < 0.01 , $\Delta\rho < 1.8 \text{ e \AA}^{-3}$ near Th position in final difference map.*

Discussion. Fractional coordinates and B_{eq} values are given in Table 1, distances and angles in Table 2, and *ORTEP* illustrations (Johnson, 1976) of the atom labelling and hydrogen bonding around the dimeric cation in Fig. 1 and around the crown ether in Fig. 2.

The dimeric cation consists of two nine-coordinate tricapped trigonal prismatic Th atoms bridged by two hydroxide ions and resides around a crystallographic center of inversion. Each Th atom's coordination environment is completed by one chloride ion and six water molecules. The longer of the two hydroxide bridges [O(1)^a for Th] and two water molecules [O(3) and O(7)] occupy the capping positions.

The two Th—OH separations, 2.361 (8) [O(1)] and 2.340 (8) Å [O(1)^a] differ by only 0.021 Å, just within 3σ . The Th...Th separation is 3.9955 (9) Å. Similar Th—OH distances were observed in other hydroxide bridged dimers of Th including [Th(NO₃)₃(OH)(OH₂)₃]₂·2H₂O (Johansson, 1968: CN = 11, Th—OH = 2.36 Å, Th...Th = 3.99 Å) and [Th(NO₃)(2,6-di-acetylpyridinedisemicarbazone)(OH)(OH₂)₂][NO₃]₄·4H₂O (Bino & Chayat, 1987: CN = 10, Th—OH = 2.366 Å, Th...Th = 4.0181 Å). A somewhat longer Th—OH separation of 2.46 Å was observed in the trinuclear [Th₃(C₄₄H₂₈N₄)₃(OH)₆(OH₂)₂]₃·3C₇H₁₆ (Kadish, Liu, Anderson, Charpin, Chevrier, Lance, Nierlich, Vigner, Dormond, Belkalem & Guilard, 1988: Th...Th = 3.960 Å).

Of the several compounds of this type we have structurally characterized, [ThCl₂(OH₂)₇]₂Cl₂·18-crown-6·2H₂O has the most similar environment to the title complex. The Th atom is also nine-coordinate tricapped trigonal prismatic; however, there are only two tight ion pairs (both chloride ions) whereas there are three (one chloride ion and two

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters (Å²)*

$$B_{\text{eq}} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$$

	x	y	z	B_{eq}
Th	0.08934 (5)	0.90772 (4)	0.34698 (4)	1.38
Cl(1)	0.3362 (4)	0.8144 (3)	0.4458 (3)	2.32
Cl(2)	0.3324 (4)	1.2106 (4)	-0.0664 (3)	2.86
Cl(3)	0.2181 (4)	0.7513 (3)	-0.0572 (3)	2.87
O(1)	0.040 (1)	1.1047 (7)	0.4211 (8)	1.94
O(2)	0.300 (1)	0.7887 (9)	0.1758 (9)	2.62
O(3)	0.323 (1)	1.0383 (8)	0.2125 (9)	2.35
O(4)	0.050 (1)	0.6723 (8)	0.4561 (8)	2.27
O(5)	0.056 (1)	1.068 (1)	0.1413 (9)	2.80
O(6)	-0.203 (1)	0.967 (1)	0.3908 (9)	3.06
O(7)	-0.023 (1)	0.7965 (9)	0.2249 (9)	2.73
O(8)	0.142 (1)	0.451 (1)	0.6724 (9)	2.93
O(9)	0.281 (1)	0.469 (1)	0.386 (1)	3.74
O(10)	0.125 (1)	0.3535 (9)	0.2684 (9)	3.21
O(11)	-0.374 (1)	1.000 (1)	0.231 (1)	3.12
C(1)	0.307 (2)	0.435 (2)	0.597 (2)	3.30
C(2)	0.339 (2)	0.377 (1)	0.480 (1)	2.85
C(3)	0.351 (2)	0.453 (2)	0.252 (2)	5.15
C(4)	0.300 (2)	0.346 (2)	0.233 (2)	4.58
C(5)	0.060 (3)	0.439 (2)	0.172 (2)	5.43
C(6)	-0.107 (2)	0.473 (2)	0.229 (2)	4.24

Table 2. *Bond distances (Å) and angles (°)*

Th—Cl(1)	2.771 (3)	Th—O(1)	2.340 (8)
Th—O(2)	2.518 (9)	Th—O(3)	2.554 (8)
Th—O(4)	2.495 (8)	Th—O(5)	2.523 (9)
Th—O(6)	2.507 (9)	Th—O(7)	2.608 (9)
Th—O(1) ^a	2.361 (8)	O(8)—C(1)	1.42 (2)
O(8)—C(6) ^b	1.43 (2)	O(9)—C(2)	1.40 (2)
O(9)—C(3)	1.42 (2)	O(10)—C(4)	1.49 (2)
O(10)—C(5)	1.42 (2)	C(1)—C(2)	1.49 (2)
C(3)—C(4)	1.42 (3)	C(5)—C(6)	1.43 (3)
Cl(1)—Th—O(1)	90.9 (2)	Cl(1)—Th—O(2)	75.1 (2)
O(1)—Th—O(2)	139.4 (3)	Cl(1)—Th—O(3)	68.7 (2)
O(1)—Th—O(3)	71.0 (3)	O(2)—Th—O(3)	68.4 (3)
Cl(1)—Th—O(4)	76.7 (2)	O(1)—Th—O(4)	135.5 (3)
O(2)—Th—O(4)	78.9 (3)	O(3)—Th—O(4)	137.0 (3)
Cl(1)—Th—O(5)	135.1 (2)	O(1)—Th—O(5)	81.5 (3)
O(2)—Th—O(5)	82.4 (3)	O(3)—Th—O(5)	66.9 (3)
O(4)—Th—O(5)	136.2 (3)	Cl(1)—Th—O(6)	149.0 (2)
O(1)—Th—O(6)	79.1 (3)	O(2)—Th—O(6)	130.1 (3)
O(3)—Th—O(6)	132.5 (3)	O(4)—Th—O(6)	89.9 (3)
O(5)—Th—O(6)	72.8 (3)	Cl(1)—Th—O(7)	130.1 (2)
O(1)—Th—O(7)	138.9 (3)	O(2)—Th—O(7)	66.1 (3)
O(3)—Th—O(7)	119.7 (3)	O(4)—Th—O(7)	66.4 (3)
O(5)—Th—O(7)	69.8 (3)	O(6)—Th—O(7)	64.9 (3)
Cl(1)—Th—O(1) ^a	77.2 (2)	O(1)—Th—O(1) ^a	63.6 (3)
O(2)—Th—O(1) ^a	143.5 (3)	O(3)—Th—O(1) ^a	121.7 (3)
O(4)—Th—O(1) ^a	71.9 (3)	O(5)—Th—O(1) ^a	134.1 (3)
O(6)—Th—O(1) ^a	72.1 (3)	O(7)—Th—O(1) ^a	118.5 (3)
C(1)—O(8)—C(6) ^b	111 (1)	C(2)—O(9)—C(3)	117 (1)
C(4)—O(10)—C(5)	116 (1)	O(8)—C(1)—C(2)	111 (1)
O(9)—C(2)—C(1)	110 (1)	O(9)—C(3)—C(4)	112 (2)
O(10)—C(4)—C(3)	116 (2)	O(10)—C(5)—C(6)	112 (1)
O(8) ^a —C(6)—C(5)	110 (2)		

Symmetry code: (a) $-x, 2-y, 1-z$; (b) $-x, 1-y, 1-z$.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares-planes results and a figure of the hydrogen-bonding network within the unit cell have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54911 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0073]

hydroxide ions) in the title compound, and thus the average distances are somewhat shorter than we observe for the hydroxide: Th—Cl = 2.750 (6) [ThCl₂(OH₂)₇]₂Cl₂·18-crown-6·2H₂O} vs 2.771 (3) Å (title complex); Th—OH₂ (capping) = 2.544 (5) vs 2.58 (3) Å (title complex); Th—OH₂ (prismatic) = 2.503 (7) vs 2.51 (1) Å (title complex).

H atoms for the water and hydroxide molecules were not located; however, geometric considerations of the O...O and O...Cl contacts (Table 3) give clear indication of the hydrogen-bonding network. The uncoordinated chloride ions and water molecule are hydrogen bonded to the coordinated water molecules. Both Cl(2) and Cl(3) accept four hydrogen bonds, while the uncoordinated water molecules accept two and donate two to uncoordinated chloride anions. There is one intramolecular hydrogen bond donated by a water molecule on one Th and accepted by the chloride ion coordinated to the second Th in the dimer. Interestingly, the hydrogen bonding is confined to organic regions (approximately in xz zones) separated by layers of crown ethers.

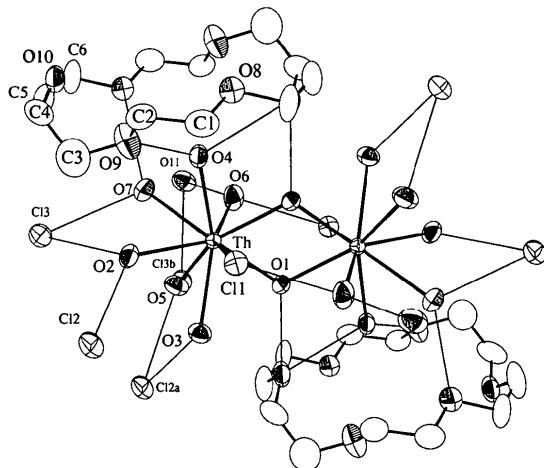


Fig. 1. ORTEP illustration of the hydrogen-bonding environment of the dimeric cation. 50% probability ellipsoids for thermal motion, H atoms omitted, H bonds represented as thin lines. Symmetry code: (a) $1 - x, 2 - y, -z$; (b) $-x, 2 - y, -z$.

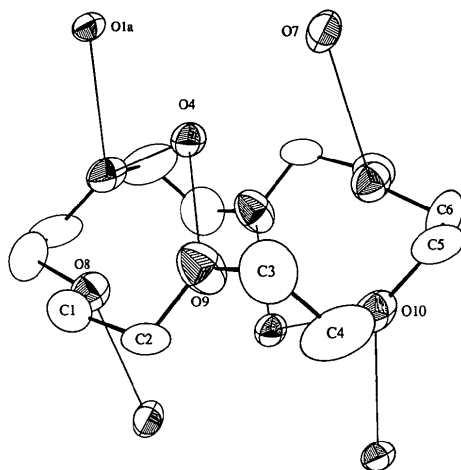


Fig. 2. The hydrogen-bonding environment around the crown ether. Symmetry code: (a) $-x, 2 - y, 1 - z$. The crown ether resides around a crystallographic center of inversion. O(4) and O(7) are coordinated water molecules, O(1) is the bridging hydroxide anion.

Table 3. Hydrogen-bonding contact geometries ($\text{\AA}, ^\circ$)

O(1)...O(10) ^a	2.81 (1)	O(2)...Cl(3)	3.10 (1)
O(2)...Cl(2) ^b	3.14 (1)	O(3)...Cl(2)	3.109 (9)
O(3)...O(11)	2.81 (2)	O(4)...O(10) ^c	2.82 (1)
O(4)...O(9)	2.71 (1)	O(5)...Cl(3) ^d	3.09 (1)
O(5)...Cl(2)	3.066 (9)	O(6)...Cl(1) ^e	3.08 (1)
O(6)...O(11)	2.71 (2)	O(7)...Cl(3)	3.154 (9)
O(7)...O(8) ^f	2.84 (1)	O(11)...Cl(3) ^d	3.08 (1)
O(11)...Cl(2) ^d	3.13 (1)		
Cl(2) ^b ...O(2)...Cl(3)	105.7 (3)	O(11)...O(3)...Cl(2)	109.1 (3)
O(9)...O(4)...O(10) ^f	115.9 (4)	Cl(2)...O(5)...Cl(3) ^d	98.8 (3)
O(11)...O(6)...Cl(1) ^e	108.1 (4)	O(8) ^f ...O(7)...Cl(3)	99.9 (4)
Cl(2) ^d ...O(11)...Cl(3) ^d	113.0 (3)		

Symmetry code: (a) $x, 1 + y, z$; (b) $1 - x, 2 - y, -z$; (c) $-x, 1 - y, 1 - z$; (d) $-x, 2 - y, -z$; (e) $-x, 2 - y, 1 - z$.

The hydrogen bonding to the crown ethers is unusual. The 18-crown-6 molecule resides around a crystallographic center of inversion and actually accepts eight hydrogen bonds. Each side accepts four from one cation dimer: one from a hydroxide ion, two from one water molecule and one from a second water molecule. O(10) and O(10)^b both accept two hydrogen bonds (Fig. 2).

We have observed single crown O atoms accepting two hydrogen bonds, but not often. In $[\text{ThCl}_4(\text{OHMe})_2(\text{OH}_2)_2] \cdot 15\text{-crown-5} \cdot \text{CH}_3\text{CN}$, 15-crown-5 accepts six hydrogen bonds and in $[\text{Dy}(\text{OH}_2)_8]\text{Cl}_3$, 18-crown-6 accepts seven hydrogen bonds. The resulting crown ether conformation in the title complex is a rarely observed one with O—C—C—O torsion angles of $g^+, g^+, g^+, g^-, g^-, g^-$. Whenever there are two consecutive O—C—C—O angles of like sign, one of the C—O—C—C angles is forced toward *gauche*. The four such angles average 77° . This is the same 18-crown-6 conformation found in $[\text{Th}(\text{NO}_3)_4(\text{OH}_2)_3] \cdot 18\text{-crown-6}$ and for one of the disordered conformations in $[\text{ThCl}_2(\text{OH}_2)_7]\text{Cl}_2 \cdot 18\text{-crown-6} \cdot 2\text{H}_2\text{O}$.

References

- BINO, A. & CHAYAT, R. (1987). *Inorg. Chim. Acta*, **129**, 273–276.
 JOHANSSON, G. (1968). *Acta Chem. Scand.* **22**, 389–398.
 JOHNSON, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KADISH, K. M., LIU, Y. H., ANDERSON, J. E., CHARPIN, P., CHEVRIER, G., LANCE, M., NIERLICH, M., VIGNER, D., DORMOND, A., BELKALEM, B. & GUILARD, R. (1988). *J. Am. Chem. Soc.* **110**, 6455–6462.
 ROGERS, R. D. (1987). *Inorg. Chim. Acta*, **133**, 347–352.
 ROGERS, R. D. (1989). *Lanthanide Actinide Res.* **3**, 71–81.
 ROGERS, R. D. & BENNING, M. M. (1988). *Acta Cryst.* **C44**, 641–644.
 ROGERS, R. D., KURIHARA, L. K. & BENNING, M. M. (1987). *Acta Cryst.* **C43**, 1056–1058.
 ROGERS, R. D., KURIHARA, L. K. & BENNING, M. M. (1988). *J. Chem. Soc. Dalton Trans.* pp. 13–16.
 SHELDRIK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRIK, G. M. (1985). SHELX586. In *Crystallographic Computing 3*, edited by G. M. SHELDRIK, C. KRÜGER, & R. GODDARD, pp. 175–189. Oxford Univ. Press.