

Fig. 1. The metallacycle with bond lengths (Å) and angles.

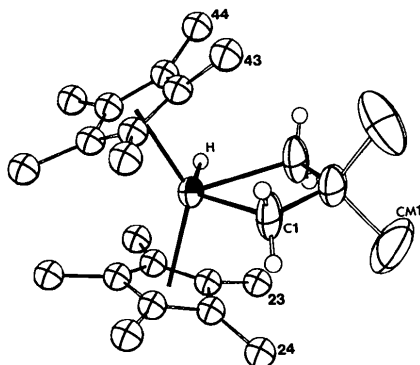


Fig. 2. General view of the title complex, with atom numbering indicated.

each case the internal  $L$  (lateral)–Zr– $L$  (central) angles are approximately  $65^\circ$ , whereas the  $L$ –Zr– $L$  angle in  $\text{Cp}_2\text{ZrL}_2$ -type compounds is approximately  $95^\circ$ ; this suggests that there is some compression of the ligands in the equatorial wedge.

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## Structure of the Extraction Complex Bis[(dicyclohexano-18-crown-6)oxonium]\* Hexanitratothorate(IV) Isomer A

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**Abstract.**  $[(\text{H}_3\text{O})(\text{C}_{20}\text{H}_{36}\text{O}_6)]_2[\text{Th}(\text{NO}_3)_6]$ ,  $M_r = 1483.22$ , m.p. = 432 K, triclinic,  $P\bar{1}$ ,  $a = 10.713$  (1),

\* Dicyclohexano-18-crown-6 = 2,5,8,15,18,21-hexaoxatricyclo-[20.4.0.0<sup>9,14</sup>]hexacosane.

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anion Th(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup>, the Th atom is surrounded by twelve O atoms from six NO<sub>3</sub><sup>-</sup> groups forming a nearly regular icosahedron. In the complex cations, each H<sub>3</sub>O<sup>+</sup> ion is anchored in the crown-ether cavity by three strong OH...O hydrogen bonds.

**Introduction.** Macrocyclic compounds have received much attention as new types of extractants and ligands. Many papers on complexes of uranium and crown ethers have been reported in connection with solvent extraction and separation (Rozen, Nikolotova, Kartasheva, Lukyanenko & Bogatskii, 1982; Wang, Chen, Jin & Wang, 1983; Yakshin, Filippov, Belov, Arklipova, Abashkin & Laskrin, 1977; Zhang & Xu, 1984). Dicyclohexano-18-crown-6 is a good extraction agent in some extraction systems (Wang, Chen, Zheng, Wang & Wang, 1986; Wang, Lin, Shen, Zheng, Wang & Wang, 1986). However, a few studies have been carried out on the complexation and extraction of thorium with crown ethers (Costes, Folgher, Plupien & Rigny, 1976), but the structure of an extraction complex has hitherto been lacking. In this work, we report the structure of the crystalline extraction complex of thorium with dicyclohexano-18-crown-6 isomer *A* (Ia) from nitric acid solution.

**Experimental.** Colourless crystal approximately 0.08 × 0.08 × 0.1 mm; Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation; determination of the lattice parameters with 25 reflections ( $2\theta < 30^\circ$ ). Three standard reflections ( $\bar{7}51$ ,  $\bar{2}72$  and 533) were monitored every hour and used to correct the intensity data for decay. 5809 independent reflections within  $0 \leq 2\theta \leq 54^\circ$ ,  $h = 0$  to 13,  $k = -15$  to 15,  $l = -15$  to 15, 4087 reflections with  $F^2 > 3\sigma(F^2)$  used in the refinement. Empirical correction for absorption. No systematic absences, space group  $P\bar{1}$ . The positional parameters of the Th atom were obtained by direct and Patterson methods. Non-H atoms were located by subsequent difference Fourier syntheses. No attempts were made to locate H atoms. Atomic parameters and anisotropic thermal parameters refined by full-matrix least-squares method on  $F$ . In the final stage, 362 variables, all  $\Delta/\sigma \leq 0.01$ , isotropic extinction coefficient =  $4.92 \times 10^{-7}$ ,  $R = 0.055$ ,  $wR = 0.068$  where  $w = 1$  for  $F^2 > 3\sigma(F^2)$ ,  $w = 0$  for  $F^2 < 3\sigma(F^2)$ . Max. value in final difference density map 1.354 e  $\text{\AA}^{-3}$  located near Th atom. All calculations were performed on a PDP 11/44 computer with Enraf-Nonius (1983) SDP program system. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974).

The extracted complex was found to be 1:2 (metal/crown) from direct determination. Anal: calcd for [(Ia)(H<sub>3</sub>O)<sub>2</sub>][Th(NO<sub>3</sub>)<sub>6</sub>]: C, 38.87%; H, 5.30%; N, 5.66%; found: C, 38.60%; H, 5.91%; N, 5.43%.

Table 1. Atomic coordinates and thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + abc\cos\gamma B(1,2) + accos\beta B(1,3) + bccos\alpha B(2,3)].$$

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Th	0.500	0.500	0.500	3.36 (1)
O(1)	0.4588 (7)	0.4450 (6)	0.6775 (5)	5.1 (2)
O(2)	0.5225 (7)	0.3134 (6)	0.5372 (6)	5.4 (2)
O(3)	0.4937 (9)	0.2821 (7)	0.6966 (6)	7.2 (2)
O(4)	0.3302 (7)	0.5955 (6)	0.6149 (6)	5.5 (2)
O(5)	0.5275 (7)	0.6819 (6)	0.6873 (6)	5.5 (2)
O(6)	0.3720 (9)	0.7471 (8)	0.7775 (7)	7.8 (3)
O(7)	0.2807 (7)	0.3443 (6)	0.4708 (6)	5.2 (2)
O(8)	0.2894 (7)	0.4568 (6)	0.3717 (6)	5.4 (2)
O(9)	0.1122 (8)	0.3211 (8)	0.3582 (7)	7.3 (3)
O(10)	-0.092 (1)	0.2241 (8)	-0.1954 (7)	9.0 (3)
O(11)	0.1506 (8)	0.3850 (6)	-0.0748 (6)	5.5 (2)
O(12)	0.0150 (7)	0.3997 (6)	-0.2592 (6)	5.5 (2)
O(13)	-0.1589 (8)	0.1984 (6)	-0.4260 (6)	5.8 (2)
O(14)	-0.2780 (8)	0.0455 (7)	-0.3281 (7)	6.1 (2)
O(15)	-0.2310 (9)	0.0600 (7)	-0.0976 (7)	7.2 (2)
O(16)	-0.0190 (9)	0.2524 (7)	0.0178 (6)	6.5 (2)
N(1)	0.4910 (9)	0.3435 (8)	0.6399 (7)	5.0 (2)
N(2)	0.4097 (9)	0.6771 (7)	0.6961 (7)	4.9 (2)
N(3)	0.2217 (8)	0.3723 (7)	0.3981 (7)	4.8 (2)
C(1)	0.177 (1)	0.404 (1)	0.045 (1)	7.4 (4)
C(2)	0.322 (2)	0.439 (2)	0.081 (1)	9.7 (5)
C(3)	0.388 (2)	0.341 (2)	0.010 (1)	12.6 (7)
C(4)	0.322 (2)	0.218 (2)	0.019 (1)	11.6 (6)
C(5)	0.174 (2)	0.182 (1)	-0.017 (1)	8.3 (4)
C(6)	0.117 (1)	0.283 (1)	0.0547 (9)	6.4 (3)
C(7)	0.174 (1)	0.495 (1)	-0.094 (1)	7.9 (4)
C(8)	0.151 (1)	0.458 (1)	-0.225 (1)	7.6 (4)
C(9)	-0.021 (2)	0.390 (1)	-0.378 (1)	7.9 (4)
C(10)	-0.159 (1)	0.318 (1)	-0.412 (1)	7.9 (4)
C(11)	-0.283 (1)	0.113 (1)	-0.481 (1)	6.6 (4)
C(12)	-0.288 (2)	0.078 (2)	-0.615 (1)	9.2 (5)
C(13)	-0.174 (2)	0.023 (2)	-0.661 (1)	9.6 (5)
C(14)	-0.184 (2)	-0.087 (1)	-0.631 (1)	8.8 (5)
C(15)	-0.179 (1)	-0.057 (1)	-0.498 (1)	6.7 (4)
C(16)	-0.287 (1)	0.004 (1)	-0.454 (1)	5.8 (3)
C(17)	-0.333 (1)	-0.052 (1)	-0.289 (1)	7.8 (4)
C(18)	-0.356 (1)	0.010 (1)	-0.164 (1)	8.0 (4)
C(19)	-0.233 (1)	0.138 (1)	0.019 (1)	8.5 (4)
C(20)	-0.096 (2)	0.181 (1)	0.077 (1)	8.5 (4)

**Discussion.** The atomic parameters are given in Table 1. The structure is shown in Fig. 1. Table 2 gives bond distances and angles for the complex.\*

The Th atom is situated at the centre of symmetry and does not bind directly to the O atoms of the crown ether. The twelve O atoms of six NO<sub>3</sub><sup>-</sup> groups coordinate to the Th atom forming a nearly regular icosahedral complex anion Th(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> shown in Fig. 2. The bond distances of Th—O range from 2.551 to 2.587 Å. The bond angles of the adjacent O atoms about the Th atom range from 49.2 to 68.3°. They are similar to those of (NH<sub>4</sub>)<sub>2</sub>[Ce(NO<sub>3</sub>)<sub>6</sub>] (Beineke & Delgandio, 1968), but are different from those of Mg[Th(NO<sub>3</sub>)<sub>6</sub>].8H<sub>2</sub>O (Scavnicar & Prodic, 1965) and [Th(NO<sub>3</sub>)<sub>3</sub>(PMe<sub>3</sub>O)<sub>4</sub>]<sub>2</sub>[Th(NO<sub>3</sub>)<sub>6</sub>] (Alcock, Esperas, Bagnall & Wang, 1978) in which the bond distances range from 2.50 and 2.34 to 2.80 and 2.75 Å, respectively. The O...O nonbonded distances between

\*Lists of observed and calculated structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51106 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Th—O(1)	2.551 (4)	O(14)—C(17)	1.459 (10)
Th—O(2)	2.563 (5)	O(15)—C(18)	1.442 (11)
Th—O(4)	2.578 (5)	O(15)—C(19)	1.431 (9)
Th—O(5)	2.551 (4)	O(16)—C(6)	1.442 (10)
Th—O(7)	2.587 (5)	O(16)—C(20)	1.466 (9)
Th—O(8)	2.575 (5)	C(1)—C(2)	1.523 (14)
O(1)—N(1)	1.300 (7)	C(1)—C(6)	1.534 (12)
O(2)—N(1)	1.276 (7)	C(2)—C(3)	1.55 (2)
O(3)—N(1)	1.209 (7)	C(3)—C(4)	1.56 (2)
O(4)—N(2)	1.267 (7)	C(4)—C(5)	1.56 (2)
O(5)—N(2)	1.259 (7)	C(5)—C(6)	1.516 (12)
O(6)—N(2)	1.222 (7)	C(7)—C(8)	1.532 (13)
O(7)—N(3)	1.281 (7)	C(9)—C(10)	1.504 (13)
O(8)—N(3)	1.271 (7)	C(11)—C(12)	1.558 (12)
O(9)—N(3)	1.197 (7)	C(11)—C(16)	1.498 (12)
O(11)—C(1)	1.441 (9)	C(12)—C(13)	1.548 (15)
O(11)—C(7)	1.422 (9)	C(13)—C(14)	1.510 (15)
O(12)—C(8)	1.444 (9)	C(14)—C(15)	1.563 (13)
O(12)—C(9)	1.473 (9)	C(15)—C(16)	1.530 (10)
O(13)—C(10)	1.422 (9)	C(17)—C(18)	1.523 (12)
O(13)—C(11)	1.466 (9)	C(19)—C(20)	1.515 (14)
O(14)—C(16)	1.460 (9)		
O(1)—Th—O(2)	50.2 (2)	O(5)—N(2)—O(6)	122.7 (6)
O(1)—Th—O(4)	67.5 (4)	O(7)—N(3)—O(8)	114.6 (5)
O(1)—Th—O(5)	66.4 (2)	O(7)—N(3)—O(9)	121.8 (6)
O(1)—Th—O(7)	68.0 (2)	O(8)—N(3)—O(9)	123.5 (6)
O(1)—Th—O(8)	67.8 (2)	O(11)—C(1)—C(2)	111.2 (7)
O(2)—Th—O(4)	67.4 (2)	O(11)—C(1)—C(6)	105.1 (6)
O(2)—Th—O(5)	68.1 (2)	C(2)—C(1)—C(6)	108.7 (9)
O(2)—Th—O(7)	67.3 (3)	C(1)—C(2)—C(3)	112.4 (9)
O(2)—Th—O(8)	68.3 (2)	C(2)—C(3)—C(4)	110 (1)
O(4)—Th—O(5)	49.5 (2)	C(3)—C(4)—C(5)	111 (1)
O(4)—Th—O(7)	67.9 (2)	C(4)—C(5)—C(6)	109 (1)
O(4)—Th—O(8)	67.6 (2)	O(16)—C(6)—C(1)	106.8 (7)
O(5)—Th—O(7)	67.8 (2)	O(16)—C(6)—C(5)	109.5 (7)
O(5)—Th—O(8)	67.1 (2)	C(1)—C(6)—C(5)	114.2 (8)
O(7)—Th—O(8)	49.2 (2)	O(11)—C(7)—C(8)	105.4 (7)
Th—O(1)—N(1)	97.5 (4)	O(12)—C(8)—C(7)	107.2 (7)
Th—O(2)—N(1)	97.6 (4)	O(12)—C(9)—C(10)	107.6 (7)
Th—O(4)—N(2)	96.2 (4)	O(13)—C(10)—C(9)	105.4 (7)
Th—O(5)—N(2)	97.8 (4)	O(13)—C(11)—C(12)	109.3 (7)
Th—O(7)—N(3)	97.7 (4)	O(13)—C(11)—C(16)	106.2 (6)
Th—O(8)—N(3)	98.5 (4)	C(12)—C(11)—C(16)	108.6 (8)
C(1)—O(11)—C(7)	112.2 (6)	C(11)—C(12)—C(13)	110.7 (8)
C(8)—O(12)—C(9)	110.0 (6)	C(12)—C(13)—C(14)	109 (1)
C(10)—O(13)—C(11)	111.7 (6)	C(13)—C(14)—C(15)	112.1 (8)
C(16)—O(14)—C(17)	111.7 (6)	C(14)—C(15)—C(16)	107.7 (7)
C(18)—O(15)—C(19)	113.7 (7)	O(14)—C(16)—C(11)	104.9 (6)
C(6)—O(16)—C(20)	111.6 (7)	O(14)—C(16)—C(15)	110.1 (7)
O(1)—N(1)—O(2)	114.6 (6)	C(11)—C(16)—C(15)	114.4 (7)
O(1)—N(1)—O(3)	123.9 (6)	O(14)—C(17)—C(18)	105.2 (7)
O(2)—N(1)—O(3)	121.5 (7)	O(15)—C(18)—C(17)	106.4 (7)
O(4)—N(2)—O(5)	116.4 (5)	O(15)—C(19)—C(20)	107.3 (8)
O(4)—N(2)—O(6)	120.8 (6)	O(16)—C(20)—C(19)	106.7 (8)

the O atoms in the icosahedron range from 2.80 to 2.89 Å except for those in the same NO<sub>3</sub><sup>-</sup> group. Because of the bidentate coordination of each NO<sub>3</sub><sup>-</sup> group, the *D*<sub>3h</sub> symmetry of unbound nitrate ions is reduced to *C*<sub>2v</sub>. The mean N—O distance involving a coordinated O atom is 1.276 Å and that to a noncoordinated O atom is 1.209 Å.

The H<sub>3</sub>O<sup>+</sup> cation is anchored in the crown-ether cavity by three strong hydrogen bonds [O(10)···O(12,14,16) distances of 2.59, 2.61 and 2.63 Å, respectively], and further stabilization may arise from ion-dipolar interactions [O(10)···O(11,13,15) distances of 2.88, 2.84 and 2.86 Å, respectively]. This bonding is analogous to that found by Behr, Dumas & Moras (1982) and Zheng, Wang, Wang, Wu, Wang & Lin (1988). The six O atoms of the crown ether are above and below their mean plane, and the H<sub>3</sub>O<sup>+</sup> cation is nearly placed on the plane (0.04 Å), which is

different from those structures reported by Behr *et al.* (1982) and Zheng *et al.* (1988) (0.2–0.4 Å).

For each cyclohexane of the crown ether, one O substituent is equatorial, and the other axial, forming a *cis-syn-cis* isomer (isomer *A*) (Mercer & Truter, 1973). The angle between two cyclohexyl mean planes is about 70°. Both planes are nearly vertical to the ether O-atom mean plane (98 and 81°, respectively). Thus the crown ether takes a boat conformation. In the crown ether, the average bond distance of C—O is 1.447 Å, C—C in the cyclohexyl is 1.538 Å, C—C in the ether ring is 1.519 Å. The average bond angles are O—C—C 107.1, C—O—C 111.8, C—C—C 110.7°. All these are similar to our previous studies (Wang, Zheng, Zhang, Chen, Shen & Yang, 1987; Zheng *et al.*, 1988).

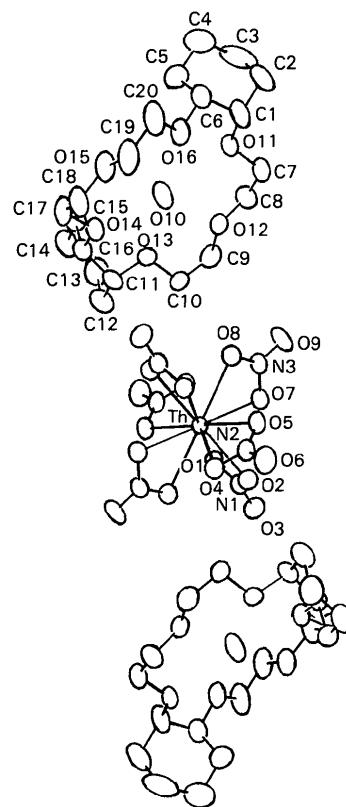


Fig. 1. View of the title compound with the atomic numbering scheme.

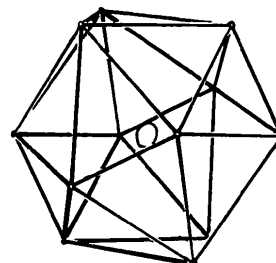
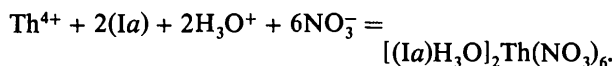


Fig. 2. The icosahedral coordination of the Th atom.

The complex anion is surrounded by six complex cations where the distances between oxonium ions and Th atoms are 7.78–8.38 Å. Besides Coulomb forces, there are van der Waals forces among complex anions and cations. The crystal is stabilized by these forces. The present structure suggests that the process of extraction of thorium(IV) from nitric acid solution with dicyclohexano-18-crown-6 isomer *A* in 1,2-dichloroethane is described as



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## The Structure of the Palladium(II) and Zinc(II) Complexes of $\alpha,\beta,\gamma,\delta$ -Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin

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**Abstract.** (I)  $\text{C}_{76}\text{H}_{92}\text{N}_4\text{O}_4\text{Pd}\cdot 3\text{C}_6\text{H}_{12}$ ,  $M_r = 1484.49$ , monoclinic,  $C2/c$ ,  $a = 28.004$  (4),  $b = 26.871$  (7),  $c = 21.267$  (2) Å,  $\beta = 131.18$  (2)°,  $V = 12\,045$  (10) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  not measured,  $D_x = 0.819$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.186$  mm<sup>-1</sup>,  $F(000) = 3192$ ,  $T = 293$  K. Final  $R = 0.086$  for 6308 reflections with  $I \geq 3\sigma(I)$ . (II)  $\text{C}_{76}\text{H}_{92}\text{N}_4\text{O}_4\text{Zn}\cdot 4\text{C}_6\text{H}_{12}$ ,  $M_r = 1527.63$ , monoclinic,  $C2/c$ ,  $a = 27.966$  (7),  $b = 26.847$  (4),  $c = 21.275$  (2) Å,  $\beta = 131.09$  (3)°,  $V = 12\,038$  (11) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  not measured,  $D_x = 0.843$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.245$  mm<sup>-1</sup>,  $F(000) = 3320$ ,  $T = 293$  K. Final  $R = 0.10$  for 4307 reflections with  $I \geq 2\sigma(I)$ . The structures are crystallographically isomorphous and have an unusual solvent of crystallization, cyclohexane, which is

readily lost from the lattice, destroying the order. The structures also show excellent pseudo-orthorhombic symmetry which made the structure solution non-trivial.

**Introduction.** We have recently been investigating the chemistry of phenolic porphyrins and their metal complexes (Traylor, Nolan & Hildreth, 1983; Milgrom, 1983; Golder, Nolan, Povey & Milgrom, 1988), and have observed that the ease of oxidation of these complexes by air in basic solution is strongly dependent on the central metal cation. Hence, whereas cobalt(II), nickel(II), iron(III) and zinc(II) complexes of *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin ( $\text{H}_2\text{t}^b\text{hpp}$ ) are readily oxidized in basified