Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.088$
$S = 1.047$
10206 reflections
596 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 5.4307P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.877$ e Å^{-3}
$\Delta\rho_{\min} = -0.746$ e Å^{-3}
Extinction correction: *SHELXL*96
Extinction coefficient: 0.00058 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

Sn1—N111	2.226 (4)	Sn2—N112	2.244 (5)
Sn1—N211	2.371 (4)	Sn2—N212	2.343 (4)
Sn1—C111	2.144 (4)	Sn2—C112	2.131 (5)
Sn1—C211	2.131 (4)	Sn2—C212	2.131 (5)
Sn1—C311	2.129 (4)	Sn2—C312	2.131 (5)
N111—N121	1.137 (5)	N112—N122	1.094 (6)
N121—N131	1.145 (7)	N122—N132	1.137 (7)
N211—N221	1.186 (5)	N212—N222	1.165 (6)
N221—N231	1.139 (5)	N222—N232	1.156 (6)
N111—Sn1—N211	177.54 (14)	N112—Sn2—N212	175.7 (2)
N121—N111—Sn1	123.4 (3)	N122—N112—Sn2	126.7 (4)
N221—N211—Sn1	121.5 (3)	N222—N212—Sn2	125.1 (3)
C111—Sn1—C211	123.70 (14)	C112—Sn2—C212	118.3 (2)
C111—Sn1—C311	120.83 (15)	C112—Sn2—C312	117.91 (19)
C211—Sn1—C311	115.28 (15)	C212—Sn2—C312	123.58 (18)
C111—Sn1—N111	89.73 (16)	C112—Sn2—N112	86.7 (2)
C211—Sn1—N111	92.24 (16)	C212—Sn2—N112	93.21 (18)
C311—Sn1—N111	92.41 (16)	C312—Sn2—N112	94.1 (2)
C111—Sn1—N211	88.17 (15)	C112—Sn2—N212	90.53 (19)
C211—Sn1—N211	87.88 (14)	C212—Sn2—N212	85.14 (17)
C311—Sn1—N211	89.76 (14)	C312—Sn2—N212	90.16 (18)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N41—H41···N211^{i}	0.91	1.93	2.838 (5)	172.2
N51—H51···N231	0.91	2.26	2.949 (6)	132.0
N51—H51···N232^{i}	0.91	2.43	3.140 (7)	135.3

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

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *SHELXL*96; molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1297). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1794–1797

Dibromobis(η^5-pentamethylcyclopentadienyl)thorium(IV)

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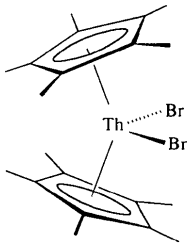
Abstract

The title compound, $[ThBr_2(\eta^5\text{-}C_{10}H_{15})_2]$ or $Cp^*_2ThBr_2$ [$Cp^* = \eta^5\text{-}C_5(CH_3)_5$], presents a pseudo-tetrahedral 'bent-metallocene' geometry in the solid state, with the

Th atom binding to two pentamethylcyclopentadienyl ligands and two bromide ligands. The Th—Br bond length is 2.800 (2) Å, whereas the Th—C distances are in the range 2.77 (1)–2.782 (9) Å.

Comment

Thorium tetrahalides ThX_4 (X = Cl, Br, I) have been the standard starting materials in organothorium chemistry despite their polymeric structure and low solubility in common organic solvents. However, the recent introduction of discrete species displaying improved solubility and reactivity such as $ThBr_4(thf)_4$ (Clark, Frankcom, Miller & Watkin, 1992), has stimulated new studies in the inorganic and organometallic chemistry of thorium. The bis(pentamethylcyclopentadienyl)thorium complex $Cp^*_2ThBr_2$, (I), prepared as described below, is isostructural with both the thorium and uranium dichloro analogs, $Cp^*_2MCl_2$ (Spirlet, Rebizant, Apostolidis & Kanellakopulos, 1992). As such, it presents two π-bonded Cp* ligands and two σ-bonded bromide ligands, with an overall pseudo-tetrahedral environment around the Th atom (Fig. 1). The site symmetry is *mm*2.



(I)

The Th—Br distances [2.800 (2) Å] are slightly shorter than those observed in the few other structurally characterized complexes containing terminal Th—Br bonds: 2.829 (3) Å in $ThBr_4[OC(Me)N^iPr_2]_2$ and 2.834 (4) Å in $ThBr_4[OC(NEt_2)_2]_2$ (Al-Daher, Bagnall, Benetollo, Polo & Bombieri, 1986), 2.833 (2)–2.876 (3) Å in $ThBr_4(thf)_4$ (Clark *et al.*, 1992), 2.895 (2) Å in $Cp^*_2Th(thf)Br_2$ (Edelman, Hitchcock, Hu & Lappert, 1995), 2.821 (2) Å in $Cp^*ThBr(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)_2$ (Butcher, Clark, Grumbine, Scott & Watkin, 1996), and 2.863 (1) and 2.874 (1) Å in $[Li(thf)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2Br_2]$ (Rabinovich, Chamberlin, Scott, Nielsen & Abney, 1997). The shorter bonding contacts observed for (I) are probably the result of the relatively reduced crowding about the metal center. The Th—C distances [2.77 (1)–2.782 (9) Å] are within the values expected for Th—Cp* interactions [see, for example, Butcher *et al.* (1996), and references therein]. Similarly, the Th—centroid distances and centroid—Th—centroid angle in $Cp^*_2ThBr_2$ (2.51 Å and 137.1°) are very close to the values reported for other Th—Cp* complexes [*e.g.* 2.53 Å and 128° in $Cp^*_2ThCl_2$ (Spirlet *et al.*, 1992), and 2.54 Å and 133° in $Cp^*_2Th(thf)Br_2$ (Edelman *et al.*, 1995)]. Finally, all C—C bond distances [1.39 (1)–1.52 (2) Å] and angles [ring: 107.0 (6)–109.4 (9)°; exocyclic: 122 (1)–128 (1)°] within the Cp* ligand (for examples and leading references, see Butcher *et al.*, 1996; Edelman *et al.*, 1995; Spirlet *et al.*, 1992) are also typical, considering the different types of hybridization of the atoms involved. There are no unusual intermolecular contacts (Fig. 2).

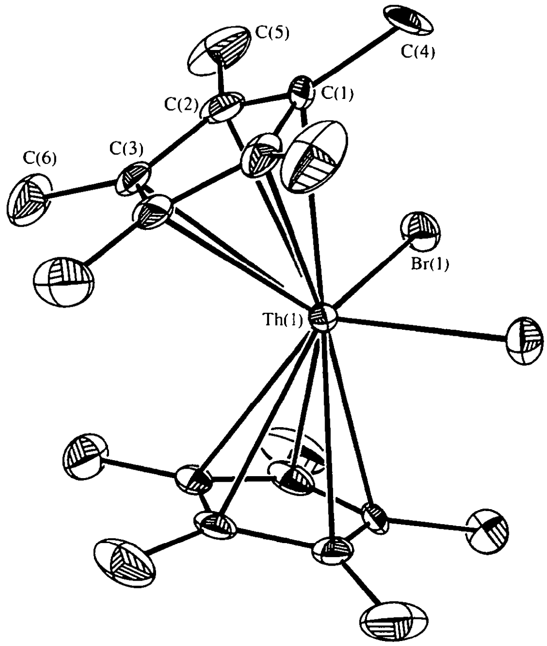


Fig. 1. The molecular structure of $Cp^*_2ThBr_2$. H atoms have been omitted for clarity and displacement ellipsoids are at the 35% probability level.

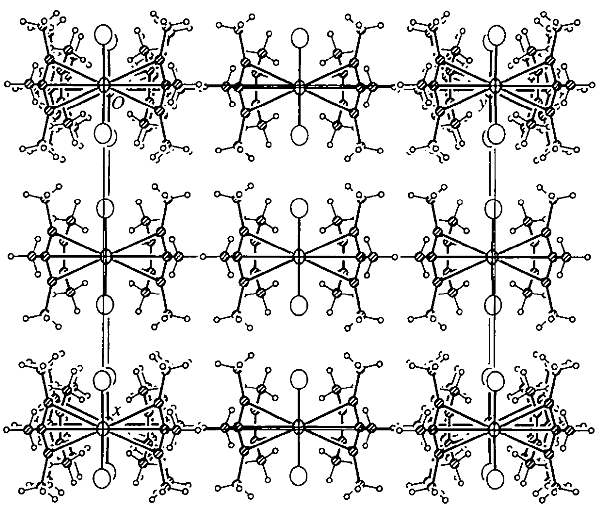


Fig. 2. A view of the unit cell of (I) parallel to the *c* axis, with 35% displacement ellipsoids for Th atoms, Br atoms as boundary ellipsoids and C atoms as striped spheres.

Experimental

The preparation of (I) was achieved by reacting ThBr$_4$(thf)$_4$ with a slight excess (2.2 equivalents) of Cp*MgCl.THF in toluene for 1 d at 373 K. After filtration, the solvent was removed under reduced pressure to give Cp$^*_2$ThBr$_2$ as a white microcrystalline solid (87% yield). Crystals of Cp$^*_2$ThBr$_2$ used in this structure determination were obtained from a concentrated toluene solution at 247 K.

Crystal data

[ThBr$_2$(C$_{10}$H$_{15}$)$_2$]
$M_r = 662.3$
Orthorhombic
*Fmm*2
$a = 15.018\,(7)$ Å
$b = 17.517\,(4)$ Å
$c = 8.226\,(4)$ Å
$V = 2164\,(1)$ Å^3
$Z = 4$
$D_x = 2.033$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.66$–$14.10°$
$\mu = 10.59$ mm^{-1}
$T = 150$ K
Parallelepiped
$0.14 \times 0.12 \times 0.10$ mm
Colorless

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.21$, $T_{\max} = 0.35$
1024 measured reflections
1024 independent reflections

1022 reflections with $F > 4\sigma(F)$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 20$
$l = -9 \rightarrow 9$
3 standard reflections every 100 reflections intensity decay: 0.3%

Refinement

Refinement on *F*
$R = 0.031$
$wR = 0.034$
$S = 2.28$
1022 reflections
60 parameters
H atoms riding, overall *U* for H atoms refined: 0.10 (2) Å^2

$w = 1/[\sigma^2(F) + 0.005F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 3.6$ e Å^{-3}
$\Delta\rho_{\min} = -4.3$ e Å^{-3}
Extinction correction: none
Scattering factors from Cromer & Waber (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Th(1)	0	0	0	0.020 (1)
Br(1)	0.1417 (1)	0	0.2215 (2)	0.040 (1)
C(1)	0	−0.1574 (7)	0.025 (2)	0.028 (4)
C(2)	0.0743 (7)	−0.1410 (6)	−0.069 (1)	0.038 (3)
C(3)	0.0466 (6)	−0.1129 (5)	−0.222 (1)	0.032 (3)
C(4)	0	−0.1892 (9)	0.192 (2)	0.073 (9)
C(5)	0.1709 (7)	−0.1587 (7)	−0.031 (2)	0.072 (6)
C(6)	0.106 (1)	−0.0985 (6)	−0.368 (2)	0.064 (5)

Table 2. *Selected geometric parameters (Å, °)*

Th(1)—Br(1)	2.800 (2)	C(1)—C(4)	1.48 (2)
Th(1)—C(1)	2.77 (1)	C(2)—C(3)	1.42 (1)
Th(1)—C(2)	2.77 (1)	C(2)—C(5)	1.52 (2)
Th(1)—C(3)	2.782 (9)	C(3)—C(6)	1.52 (2)
C(1)—C(2)	1.39 (1)	C(3)—C(3$^{\rm i}$)	1.40 (2)
Br(1)—Th(1)—Br(1$^{\rm ii}$)	98.9 (1)		

Symmetry codes: (i) $-x, y, z$; (ii) $-x, -y, z$.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined anisotropically and H atoms were located from difference Fourier maps and then set with ideal geometries [d(C—H) = 0.96 Å and 109.5°] and refined with a group displacement parameter as riding groups. Major peaks in the final difference Fourier map were located near the Th atom. The apparent thermal motion of C(4) is quite anisotropic. In an attempt to improve this situation, C(4) was moved off the mirror plane and fixed at half occupancy. This model would simulate a wagging motion of the methyl group, yet still allow the mirror symmetry to be satisfied by the rest of the molecule. Unfortunately, all such refinements with this model would not converge; thus, the model with C(4) on the mirror plane is reported. Because *Fmm*2 is a non-centrosymmetric space group, the structure was also refined as the other enantiomorph. The final residuals obtained for the incorrect absolute structure were $R = 0.048$ and $wR = 0.055$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXTL-Plus* (Sheldrick, 1990). Molecular graphics: *SHELXTL-Plus*.

This work was performed under the auspices of the Divisions of Chemical Science and Technology and Materials Science and Technology, Los Alamos National Laboratory, which is operated by the University of California for the US Department of Energy under contract W-7405-ENG-36. The structure was analyzed in conjunction with an undergraduate faculty development workshop in PC Based X-ray Crystallography, conducted at Clemson University. We gratefully acknowledge the Camille and Henry Dreyfus Foundation Special Grant Program in the Chemical Sciences for funding of this workshop. We also thank Drs Steven K. Grumbine and John G. Watkin (LANL) for a generous gift of ThBr$_4$(thf)$_4$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1342). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1797-1799

Disodium Hexadecahydrate Diprotonated Form of 1,4,8,11-Tetra(2-carboxy)ethyl-1,4,8,11-tetraazacyclotetradecane $(H_2TETP)^{2-}$ at 110 K†

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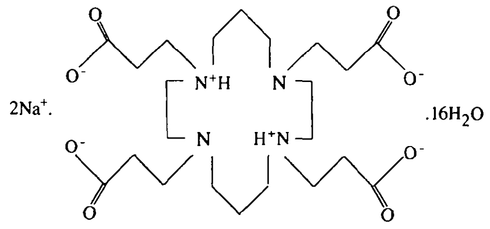
Abstract

The diprotonated $(H_2TETP)^{2-}$ macrocycle in the title compound, $2Na^+.C_{22}H_{38}N_4O_8^{2-}.16H_2O$ or $2Na^+.(H_2TETP)^{2-}.16H_2O$, possesses a [3434] conformation, the propionate arms all being deprotonated. Two are extended and the other two are folded towards two protonated N atoms. The crystal structure is stabilized by a complex hydrogen-bonding scheme since the unit cell contains 16 water molecules.

Comment

The structure of the diprotonated form of 1,4,8,11-tetra(2-carboxy)ethyl-1,4,8,11-tetraazacyclotetradecane, $(H_2TETP)^{2-}$, (I), has been investigated as part of a study of the different conformations of the TETP ligand according to its protonation state (Dahaoui-Gindrey *et al.*, 1995; Dahaoui-Gindrey, 1995).



(I)

As in other TETP forms, the structure is centrosymmetric so only half of the atoms of the chemical formula are unique (Fig. 1). Atoms N1 and N1′ in *trans* positions are protonated, the N—C bond distances of these N atoms being on average longer than those involving the non-protonated N2 and N2′ atoms [1.503 (4) and 1.470 (4) Å, respectively]. The C—O bond lengths, which are statistically equal [1.254 (1)–1.270 (1) Å], are appropriate for deprotonated carboxyl groups. Thus, the TETP ligand is diprotonated bearing two negative charges, and consequently is formulated as $(H_2TETP)^{2-}$. Both negative charges of the ligand are neutralized by the positive charges of two Na^+ ions.

The cyclam skeleton of this compound has a [3434] conformation according to Dale's nomenclature (Dale, 1980), with a methylene group located at each corner of the macrocycle to give an endodentate geometry, as was also reported for H_4TETP and H_5TETP^+ (Dahaoui-Gindrey *et al.*, 1995). $(H_2TETP)^{2-}$ has two of the propionate groups extended outside of the ring and two others folded inside forming an intramolecular three-centre hydrogen bond between the HN1—N1 donor group, and the O3 and N2 acceptors. The sum of the intramolecular angles involving the HN1 atom as the central atom is exactly 360°. The $(H_2TETP)^{2-}$ torsion angles (Table 1) are close to those found in H_4TETP except for the extremity of the folded propionate chain: in particular, the O3 and O4 atoms of $(H_2TETP)^{2-}$ exhibit perfect *cis* and *trans* positions, respectively, with regard to the C10—C11 bond [whereas in H_4TETP, the N2—C9—C10—C11, C9—C10—C11—O3 and C9—C10—C11—O4 torsion angles are −49.8 (7), −45.9 (9) and 132.3 (6)°, respectively].

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† Alternative name: disodium 4,11-diaza-1,8-diazoniatetradecane-1,4,8,11-tetrayltetrakis(3-propionate) hexadecahydrate.