The Crystal and Molecular Structure of α -Tetrakis (acetylacetonato)thorium(IV)

BERT ALLARD

Department of Nuclear Chemistry, Chalmers University of Technology, Fack, S-402 20 Göteborg 5, Sweden

The crystal and molecular structure of α -tetrakis-(acetylacetonato)thorium(IV), molecular formula $[\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4]$, has been determined from three-dimensional X-ray intensity data. The unit cell is monoclinic and belongs to the space group $P2_1/c$ with the lattice parameters $a = 11.768(2)$ Å, $b = 12.792(2)$ Å, $c = 17.039(3)$ Å, $\beta = 112.24(2)^\circ$ and $Z = 4$. The structure determination was based on 1358 reflexions which were collected with the Weissenberg multiple-film technique. The structure was refined to a final R -value of 0.078. The coordination polyhedron around the thorium atom is a distorted dodecahedron ($D_{2d}-42m$). The Th–O bond distances range from 2.35 to 2.43 Å with a mean value of 2.38 Å. In contrast to most other dodecahedral structures involving bidentate ligands, the ligands, in this structure span adjacent vertices between the two orthogonal trapezoids in the dodecahedron. The over-all D_2 symmetry is nearly achieved. The ligands are folded 18° about the line joining the oxygen atoms within the ligand.

As a part of a systematic study of the properties of tetravalent actinide acetylacetonates^{1–3} the α -form of thorium(IV) acetylacetonate (in this report denoted by $\alpha\text{-Th}(\text{AA})_4$) has been synthesized and investigated. Based on previous structure investigations,³ theoretical considerations⁴ and solution experiments⁵ it has been suggested, that a change from a predominantly antiprismatic coordination (for the β -form) to a dodecahedral coordination (for the α -form) of the tetrakis acetylacetonates tend to occur with increasing radius of the central atom. The thorium complex would be the best choice for the study of such an effect, since thorium is the largest atom of the actinides and group IVb elements in the tetravalent state. Preliminary structure

data from electron density projections have been previously given for $\alpha\text{-Th}(\text{AA})_4$,^{6,7} but these data do not conclusively establish the nature of the inner coordination polyhedron. Lattice parameters and ligand configuration have also been suggested for the isomorphous $\alpha\text{-Ce}(\text{AA})_4$.⁸

EXPERIMENTAL

Preparation of the crystals. $\alpha\text{-Th}(\text{AA})_4$ was prepared by precipitation from an aqueous thorium nitrate acetylacetone solution, by addition of ammonia,⁹ or by an extractive procedure previously used for $\beta\text{-Np}(\text{AA})_4$.¹⁰ By recrystallization from an organic solvent at room temperature, the α -form was almost exclusively formed. The β -form could sometimes be obtained from polar solvents at elevated temperature or by vacuum sublimation carried out just below the melting point. Recrystallization from benzene, however, yielded a solvate with the composition $\text{Th}(\text{AA})_4 \cdot \frac{1}{2}\text{C}_6\text{H}_6$, which will be described in a following communication. For the complex $\alpha\text{-Th}(\text{AA})_4$ the metal content was determined radiometrically (α -counting using liquid scintillation technique) and the purity was checked by comparing recorded infrared spectra with spectra obtained from the literature.¹²

X-Ray methods. The structure investigation was based on single crystal X-ray diffraction measurements using an integrated Weissenberg equi-inclination multiple-film technique. A freshly prepared crystal with the dimensions $0.09 \times 0.11 \times 0.31$ mm³ was mounted along the longest crystal axis denoted as the c -axis in a 0.2 mm glass capillary. Weissenberg photographs of the layers $hk0$ – $hk13$ were taken, using $\text{CuK}\alpha$ radiation. The intensities were measured with an optical densitometer. The intensities of the four films recorded for each layer were brought to a common scale by a least squares procedure and were corrected

for Lorentz and polarization effects. When a preliminary structure had been found, a correction for absorption was performed.

The unit cell dimensions were obtained from X-ray powder photographs by using a Guinier focusing camera with $\text{CuK}\alpha$ radiation and an internal standard of potassium chloride.

The computations were carried out on an IBM 360/65 computer. The programs used were POWDER, SCALE, DATAP2, DRF, BLOCK, LALS, LINUS, DISTAN, PLANEFIT and ORTEP.¹³

STRUCTURE DETERMINATION AND REFINEMENT

The lattice parameters were obtained by a least-squares refinement of powder data. Preliminary values from single crystal measurements were used as starting parameters.

Cell parameters are given in Table 1. The systematic absences corresponded to the space group $P2_1/n$. After the refinement, the atomic parameters and unit cell dimensions were transferred to $P2_1/c$ in order to facilitate direct comparison with the isomorphous $\alpha\text{-Ce}(\text{AA})_4$. (Values given in Table 3 and Fig. 2 correspond to $P2_1/c$).

The positions of the thorium atoms were deduced from the three-dimensional Patterson synthesis. From a three-dimensional electron density difference synthesis the positions of the eight chelated oxygen atoms were found. A difference synthesis based upon the positions of the atoms located revealed the positions

of the carbon atoms. The positions of the hydrogen atoms were not determined.

The inter-layer scale factors and preliminary parameters were improved by full-matrix least-squares refinement. The quantity $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w = (a + |F_o| + c|F_o|^2)^{-1}$ chosen according to Cruickshank.¹⁴ Only reflexions with $0.70 < |F_o|/|F_c| < 1.40$ were refined. The scattering factors given by Cromer and Waber¹⁵ were used for thorium and those of Doyle and Turner¹⁶ for oxygen and carbon. An analysis of the weighting scheme is given in Table 2.

After refinement with only the thorium atom localized the conventional discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ had a value of 0.21, which indicates the dominance of the heavy atom. Refinement with all non-hydrogen atoms localized without correction for absorption and with isotropic thermal parameters gave the value $R = 0.09$. After correction for absorption the value $R = 0.078$ was obtained. When allowance was made for anisotropic thermal parameters and with an over-all scale factor refinement, the value $R = 0.72$ was obtained, but since the ratio between the number of reflexions and the number of refined parameters in this case was low (5.2) very high values of the standard deviations were obtained. In Table 3 only the isotropic thermal parameters are given.

An attempt to introduce correction for extinction and anomalous scattering in the

Table 1. Crystallographic data for $\alpha\text{-Th}(\text{AA})_4$.

Unit cell: ^a	Monoclinic with $a = 16.664(2)$ Å $b = 12.792(2)$ Å $c = 17.039(3)$ Å $\beta = 40.88(2)^\circ$ $V = 2374.0(8)$ Å ³ $Z = 4$
Formula weight:	$M = 628.48$
Density:	$\rho_{\text{obs}} = 1.74$ g cm ⁻³ $\rho_{\text{calc}} = 1.758$ g cm ⁻³
Systematic absences:	$h0l$ when $h + l = 2n + 1$ $0k0$ when $k = 2n + 1$
Space group:	$P2_1/n$
General point positions:	$4c: \pm(x, y, z); \pm(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$
Linear absorption coefficient:	$\mu_{\text{CuK}\alpha} = 220$ cm ⁻¹

^a For $P2_1/c$ the lattice parameters $a = 11.768(2)$ Å, $b = 12.792(2)$ Å, $c = 17.039(3)$ Å and $\beta = 112.24(2)^\circ$ are obtained.

Table 2. Analysis of the weighting scheme $w = (20.0 + |F_o| + 0.016 |F_o|^2)^{-1}$.

F_o interval	$w\Delta^2$	Number of reflexions	$\sin\theta$ interval	$w\Delta^2$	Number of reflexions
0–24	0.71	132	0.00–0.46	1.50	351
24–29	0.71	133	0.46–0.59	1.22	324
29–33	0.89	136	0.59–0.67	0.93	246
33–37	1.01	135	0.67–0.74	1.20	166
37–43	0.92	134	0.74–0.79	1.15	119
43–49	1.03	134	0.79–0.84	1.31	79
49–56	0.72	134	0.84–0.88	1.00	44
56–64	1.20	132	0.88–0.93	1.51	6
64–79	1.21	131	0.93–0.96	0	0
79–195	1.41	134	0.96–1.00	0	0

Table 3. Atomic coordinates, expressed as fractions of unit cell edges, and isotropic thermal parameters with their standard deviations (in parenthesis) for α -Th(AA)₄.

Atom	x	y	z	$B, \text{\AA}^2$
Th	0.1903(1)	0.1464(1)	0.2003(1)	3.25(1)
O1	0.0618(25)	0.1791(21)	0.0562(19)	5.7(6)
O2	0.0398(19)	0.0150(18)	0.1535(17)	4.0(5)
O3	0.2108(22)	0.3323(16)	0.2005(18)	4.2(5)
O4	0.0098(19)	0.2219(18)	0.2061(14)	3.3(5)
O5	0.1888(23)	0.1200(19)	0.3379(16)	4.1(5)
O6	0.3885(22)	0.1914(21)	0.3011(15)	4.6(6)
O7	0.3010(17)	–0.0141(17)	0.2275(15)	3.3(4)
O8	0.3297(20)	0.1361(19)	0.1256(20)	5.0(5)
C1	–0.0858(34)	0.2295(20)	–0.0668(25)	4.2(8)
C2	–0.0514(28)	0.1637(22)	–0.0007(17)	2.4(5)
C3	–0.1182(35)	–0.0761(32)	0.0196(28)	5.5(9)
C4	–0.0645(28)	0.0118(25)	0.0991(26)	3.4(7)
C5	–0.1623(33)	–0.0773(31)	0.0967(29)	4.5(8)
C6	0.1837(36)	0.5057(26)	0.1704(30)	4.9(8)
C7	0.1377(29)	0.4091(33)	0.1865(30)	5.9(9)
C8	–0.0018(37)	0.4048(30)	0.1633(29)	5.7(9)
C9	–0.0524(36)	0.2988(34)	0.1811(28)	4.9(8)
C10	–0.1971(32)	0.3070(38)	0.1699(22)	5.2(9)
C11	0.2233(41)	0.0994(39)	0.4882(30)	5.1(9)
C12	0.2597(35)	0.1093(28)	0.4078(31)	5.0(8)
C13	0.3880(27)	0.1353(34)	0.4352(29)	4.0(7)
C14	0.4339(26)	0.1844(46)	0.3667(31)	5.0(9)
C15	0.5737(43)	0.1931(45)	0.4095(41)	5.4(9)
C16	0.4478(45)	–0.1447(38)	0.2789(26)	5.1(9)
C17	0.4071(28)	–0.0492(35)	0.2303(26)	4.8(8)
C18	0.4571(33)	–0.0010(31)	0.1776(32)	5.0(8)
C19	0.4270(28)	0.0811(26)	0.1329(25)	3.6(7)
C20	0.4842(33)	0.1256(33)	0.0735(31)	5.4(8)

refinement afforded no improvement. The parameters obtained in the last cycle of refinement are given in Table 3. Observed and calculated structure factors are available on

request. A final difference synthesis, calculated by using the refined parameters given in Table 3 did not show any unexpected maximum or minimum.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The coordination polyhedron composed of eight chelated oxygen atoms around the thorium atom in α -Th(AA)₄ is a distorted dodecahedron ($D_{2d}42m$) as shown in Fig. 1. The ligand rings are essentially planar, while the thorium atom is displaced from this plane, producing a fold with an average value of 18° across the O—O line of the 6-membered ring. The packing of the molecules is illustrated in Fig. 2.

From the parameters in Table 3 distances and angles defining the geometry of the α -Th(AA)₄ molecule were calculated and are given in Table 4. The geometry of one ligand with average geometrical parameters is shown in Fig. 3. These average values are in line with previously obtained parameters for other acetylaceton-

ates,¹⁻³ indicating a C—C single bond and C—CH and C—O bonds with significant double bond character.¹⁷ The C—CH bonds seem, however, to be unexpectedly long.

The differences between measured and average values are sometimes large and are in cases larger than 3σ . There is, however, no systematic deviation which would indicate a lower ligand symmetry than the expected C_{3v} . Discrepancies in bond lengths and angles must be interpreted as indicative of systematic errors in the data, such as uncorrected absorption, rather than an actual distortion of the molecule. Another reason for the poor accuracy can be the unfavourable proportion between the heavy and light atoms in the molecule. The single thorium atom constitutes 37 % of the total molecular weight and the $Z_{\text{heavy}}^3/\Sigma Z_{\text{light}}^2$ ratio is 6.4. Moreover, the complex

Fig. 1. The α -Th(AA)₄ formula unit (stereoscopic drawing).

Fig. 2. The unit cell of α -Th(AA)₄ (stereoscopic drawing).

Table 4. Distances and angles for α -Th(AA)₄ (in Å and °) with their standard deviations (in parenthesis). The notation is in accordance with Fig. 1.

Distance		Angle	
Th-O1	2.38(2)	O1-Th-O2	70.9(9)
Th-O2	2.35(2)	Th-O1-C2	143(2)
O1-C2	1.33(4)	Th-O2-C4	134(2)
O2-C4	1.23(4)	O1-C2-C3	115(3)
C1-C2	1.34(4)	O2-C4-C3	128(3)
C2-C3	1.48(5)	C2-C3-C4	123(3)
C3-C4	1.50(5)	O1-C2-C1	115(3)
C4-C5	1.60(5)	O2-C4-C5	123(3)
O1-O2	2.75(3)	C1-C2-C3	131(3)
Th-C3	3.87(4)	C3-C4-C5	109(3)
Th-O3	2.39(2)	O3-Th-O4	71.6(8)
Th-O4	2.37(2)	Th-O3-C7	135(2)
O3-C7	1.27(4)	Th-O4-C9	139(3)
O4-C9	1.21(4)	O3-C7-C8	127(4)
C6-C7	1.41(5)	O4-C9-C8	124(4)
C7-C8	1.53(6)	C7-C8-C9	116(3)
C8-C9	1.55(6)	O3-C7-C6	116(4)
C9-C10	1.64(5)	O4-C9-C10	124(4)
O3-O4	2.79(3)	C6-C7-C8	116(4)
Th-C8	3.91(4)	C8-C9-C10	113(3)
Th-O5	2.38(2)	O5-Th-O6	72.1(8)
Th-O6	2.38(2)	Th-O5-C12	138(3)
O5-C12	1.18(5)	Th-O6-C14	136(3)
O6-C14	1.15(5)	O5-C12-C13	124(4)
C11-C12	1.58(6)	O6-C14-C13	130(3)
C12-C13	1.44(5)	C12-C13-C14	117(3)
C13-C14	1.58(5)	O5-C12-C11	124(4)
C14-C15	1.53(6)	O6-C14-C15	122(4)
O5-O6	2.80(3)	C11-C12-C13	110(4)
Th-C13	3.79(3)	C13-C14-C15	107(4)
Th-O7	2.38(2)	O7-Th-O8	68.1(8)
Th-O8	2.43(2)	Th-O7-C17	139(2)
O7-C17	1.31(4)	Th-O8-C19	136(3)
O8-C19	1.31(4)	O7-C7-18	117(4)
C16-C17	1.45(6)	O8-C19-C18	123(4)
C17-C18	1.39(6)	C17-C18-C19	131(4)
C18-C19	1.26(5)	O7-C17-C16	114(3)
C19-C20	1.52(6)	O8-C19-C20	109(3)
O7-O8	2.70(3)	C16-C17-C18	128(4)
Th-C18	3.80(3)	C18-C19-C20	128(3)

slowly disintegrated by X-ray irradiation.

For the dodecahedral coordination three different stereoisomers corresponding to different ligand attachments are possible for bidentate ligands with a fixed ring span. These are, with the notations given by Hoard,⁴ *Id-mmmm*, *IId-gggg* and *IIId-gggg* where *g* and *m* denotes edges of the polyhedron according to Fig. 4. Only *Id* and *IIId* have the overall *D₄* symmetry, which makes formation of poly-

hedron hydrides with antiprismatic coordinated isomers possible. So far only eight-coordinate chelates with dodecahedral configuration of type *Id* and *IIId* are known. The isomer *Id* seems to be by far the most common configuration,¹⁸ although lately β -diketonates of type *IIId* have been found.^{19,20} The configuration of α -Th(AA)₄ corresponds to isomer *IIId* although a significant antiprismatic feature is observed. (Previously, α -Ce(AA)₄ has been denoted as

Fig. 3. The geometry of the acetylacetonate ligand in α -Th(AA)₄ (average values with standard deviations, in Å and °).

Fig. 4. The dodecahedron ($D_{2d}\bar{4}2m$). Notations according to Hoard.⁴

Table 5. Distances between oxygen atoms within the dodecahedral coordination polyhedron for α -Th(AA)₄ (average values, in Å), with III d configuration, and distances in the most favourable polyhedron,⁴ calculated for Th—O = 2.38 Å. Notations according to Fig. 4.

Polyhedron edge	Measured values	Calculated values (most favourable polyhedron)		
		III d	Id	II a
a	2.91(2)	2.79	3.55	3.00
b_1^a	3.80(20)	3.55	4.90	4.00
b_2	3.30(7)	3.55	2.79	3.00
m	2.85(9)	2.79	2.95	2.84
g_1^b	2.76(5)	2.95	2.79	2.84
g_2	3.01(16)	2.95	2.95	3.00

^a The edges b_1 and b_2 are unequal. This is consistent with a distortion towards the antiprismatic isomer II a , when b_1 corresponds to a diagonal of the square face, giving $b_1 > b_2$. ^b The edge spanned by ligands.

predominantly antiprismatic.⁹) In Table 5 distances between the oxygen atoms in the coordination polyhedron are given.

For the dodecahedron orthogonality between the two trapezoids is required.¹¹ This criterion is very poorly fulfilled. Nevertheless description of the coordination as dodecahedral seems appropriate since the individual shape parameters, not the average values, for the whole polyhedron show the best correspondence with isomer III d when compared with values of the most favourable polyhedron.⁴ This is, however, surprising, since the Id isomer should be more probable if ligand atom repulsion is considered as having the main influence on the choice of configuration.¹² Moreover, the β -form of tetravalent acetylacetonates, which is antiprismatic in the II a configuration,³ show dodecahedral distortion towards Id, as would be expected, and not towards III d . This steric divergence between the two forms may be due to different bonding interaction, or intermolecular interaction due to a fortuitous packing in the solid state of the α -form. Different bond strength in the two forms, *e.g.* caused by various degrees of π overlap between ligand and metal, would be likely to influence the ligand geometry and would cause changes in the infrared spectrum. No significant differences between α - and β -Th(AA)₄ indicating such an effect have, however, been found.¹³ Packing relations could be the main factor determining the preferred coordination polyhedron. Any short intermolecular distances indicating interaction between adjacent molecules have not been found. The closest intermolecular distances

between non-bonded atoms are 3.32 Å (C4—C2) and 3.45 Å (C2—O2).

For acetylacetonates with the small central atoms zirconium and hafnium only the β -form is known,²² while for thorium acetylacetonate, which has the largest central atom of all possible tetravalent acetylacetonates, the α -form is far more easily prepared than the β -form, which decomposes rapidly at room temperature. This is an indication that the size of the central atom has a marked influence on the choice of coordination polyhedron. For the more bulky dibenzoylmethanates only one form is known for different tetravalent metals.²³ The inner coordination corresponds to the dodecahedral *Id* isomer, which is completely in agreement with the predicted most favourable polyhedron.²² The effect of substituting the acetylacetonate ligand with the still larger dipivaloylmethanate ligand on the inner coordination would be of considerable interest, and a structure investigation of thorium dipivaloylmethanate is in progress.

Acknowledgements. The X-ray measurements were performed at the Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg. I am greatly indebted to Professor G. Lundgren and Professor N.-G. Vannerberg for all facilities put at my disposal and for helpful encouragement. Thanks are also due to Professor J. Rydberg and Doc. O. Lindqvist for stimulating interest and advice. I am also indebted to Mrs. B. Hjorth for skilful experimental help and never failing optimism. The English text was revised by E. Ratti-Moberg. Support by the Swedish Atomic Research Council is gratefully acknowledged.

REFERENCES

1. Titze, H. *Acta Chem. Scand.* **23** (1969) 399.
2. Titze, H. *Acta Chem. Scand.* **24** (1970) 405.
3. Allard, B. *Acta Chem. Scand.* **26** (1972) 3492.
4. Hoard, J. L. and Silverton, J. V. *Inorg. Chem.* **2** (1963) 235.
5. Liljenzin, J. O. and Rydberg, J. *Physico-Chemie du Protactinium*. Editions du C. N. R. S. No 154, Paris 1966, p. 255.
6. Grdenić, D. and Matković, B. *Croat. Chem. Acta* **30** (1958) 95.
7. Grdenić, D. and Matković, B. *Nature (London)* **182** (1958) 465.
8. Titze, H. *Acta Chem. Scand. A* **28** (1974) 1079.
9. Young, R. C. and Kovitz, J. *Inorg. Syn.* **2** (1946) 123.
10. Titze, H. and Allard, B. *Acta Chem. Scand.* **24** (1970) 715.
11. Allard, B. *Acta Chem. Scand. A* **30** (1976) 381.
12. Yoshimura, T., Miyake, C. and Imoto, S. *Bull. Chem. Soc. Jpn.* **46** (1973) 2096.
13. Computer programs available in the program library of the Department of Inorganic Chemistry, Göteborg.
14. Cruickshank, D. W. J. In Rollet, S. J., Ed., *Computing Methods in Crystallography*, Pergamon, Glasgow 1965, p. 99.
15. Cromer, D. T. and Waber, J. T. *Acta Crystallogr.* **13** (1965) 104.
16. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* **24** (1968) 390.
17. *Table of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London 1965.
18. Lippard, S. J. *Progr. Inorg. Chem.* **8** (1967) 109.
19. Lalancette, R. A., Cefola, M., Hamilton, W. C. and La Placa, S. J. *Inorg. Chem.* **6** (1967) 2127.
20. Bennet, M. J., Cotton, F. A., Ledzins, P. and Lippard, S. J. *Inorg. Chem.* **7** (1968) 1770.
21. Lippard, S. J. and Russ, B. J. *Inorg. Chem.* **7** (1968) 1686.
22. Allard, B. *J. Inorg. Nucl. Chem. In press.*
23. Wolf, L. and Bärnighausen, H. *Acta Crystallogr.* **13** (1960) 778.

Received October 31, 1975.