

The Structure of Tetrakis(thenoyltrifluoroacetato)thorium(IV)

BY MAGNUS LENNER AND OLIVER LINDQVIST

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Gothenburg,
PO Box, S-402 20 Göteborg, Sweden

(Received 25 September 1978; accepted 1 November 1978)

Abstract

$\text{Th}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_4$ is orthogonal but the lattice is disordered along a . One MDO structure, with $a = 17.631$ (8), $b = 10.606$ (4), $c = 20.474$ (14) Å, has been determined from 1324 family reflexions, measured at 173 K, and refined to a final R of 0.049. The inner coordination polyhedron around Th is a distorted dodecahedron with a mean Th–O length of 2.397 Å. The four bidentate ligands span the legs of the two perpendicular trapezoids of the dodecahedron.

Introduction

To study the properties of tetravalent Th chelate complexes with β -diketones, $\text{Th}(\text{TTA})_4$ has been synthesized and investigated. Although a study (Leipoldt, Wessels & Bok, 1975) of the nine-coordinated adduct $\text{Th}(\text{TTA})_4 \cdot (\text{C}_8\text{H}_{17})_3\text{PO}$ has been published, most previous structure investigations (Titze & Allard, 1970; Allard, 1972) of actinide chelate complexes have dealt with acetylacetonates. This work aims to study the effects of the introduction of the asymmetric ligand TTA.

Experimental

Crystals were obtained from an aqueous solution of 6.5 g of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ mixed with a benzene solution of 8.9 g of HTTA. The pH was adjusted to 5.5 by addition of ammonia, and some petroleum ether was added to lessen the solubility of the complex in the organic phase which was then allowed to evaporate (~48 h). The residue was recrystallized from benzene.

Crystal data

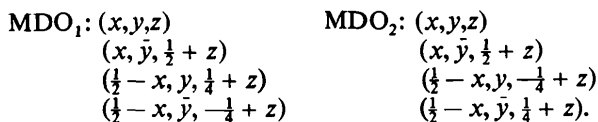
$\text{Th}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_4$, FW = 1112.8, crystallizes with a disordered structure, $a = 17.631$ (8), $b = 10.606$ (4), $c = 20.474$ (14) Å, $\alpha = \beta = \gamma = 90^\circ$, $D_x = 1.892$ Mg m^{-3} , $Z = 4$, $\lambda = 0.7107$ Å. The crystal was $0.10 \times 0.15 \times 0.16$ mm.

The intensities of 2648 independent reflexions were measured on a Syntex $P2_1$ four-circle diffractometer, equipped with a liquid-nitrogen cooling device to maintain a temperature of 173 K. Intensities were measured up to $2\theta = 53^\circ$ with graphite-monochromatized Mo $K\alpha$ radiation. After every 25 reflexions, a standard reflexion was measured, the intensity of which underwent no significant change. The intensities were corrected for Lorenz and polarization effects, and for absorption. $\mu(\text{Mo } K\alpha)$ for Th was obtained from Roof (1959).

Determination and refinement of the structure

Weissenberg films of the layers $h0l$ – $h5l$ proved the structure to be disordered, showing discrete reflexions for hkl , $l = 2n$, and diffuse streaks linking the reflexions hkl , $l = 2n + 1$ along a^* (Fig. 1). Disregarding the streaks, the systematic absences $h0l$, $l = 2n$ and $hk0$, $h = 2n$ indicated space groups $P2_1ca$ and $Pmca$. The coordinates of Th were derived from a Patterson synthesis. From successive Fourier syntheses it was possible to determine the positions of the 56 remaining non-hydrogen atoms in $P2_1ca$. When this set of parameters was refined, however, R was as high as 0.12, and the interatomic distances were clearly not right.

An inspection of the parameters proved the $\text{Th}(\text{TTA})_4$ molecule to possess an extra twofold axis along $[0, y, \frac{3}{4}]$, not inherent in $P2_1ca$. The streaks along a^* indicate ordered bc layers placed in a disordered manner along a . Since the first attempted solution gave an R as low as 0.12, the Th atoms are unaffected by the disorder. It appears that the true structure is a mixture of two possible MDO structures, the symmetry elements of which are:



Thus, each ordered bc layer has a thickness $a/2$ and the mirror image along a (at $x = 0.25$) is translated either $\frac{1}{4}$ or $-\frac{1}{4}$ along c .

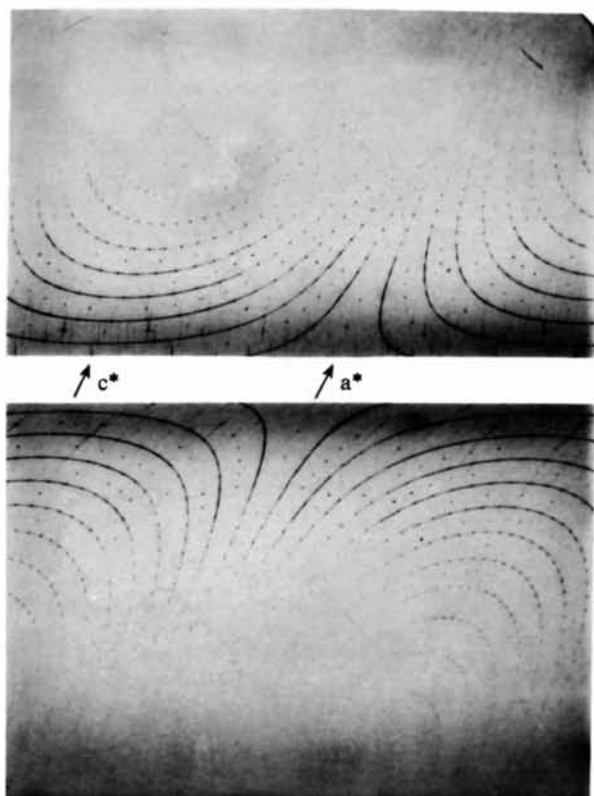


Fig. 1. A Weissenberg photograph of the $h1l$ layer of $\text{Th}(\text{TTA})_4$.

The family reflexions hkl , $l = 2n$ coincide for the two structures. With only the family reflexions, the structure of one of the two MDO models could be refined, regardless of the mixture of MDO_1 and MDO_2 . The structure was refined by a full-matrix least-squares method. This refinement converged to $R = 0.049$. The scattering factors used for C, O, F and S were those of Doyle & Turner (1968) and for Th those of Cromer & Waber (1965). Correction for the real part of the anomalous dispersion was included (*International Tables for X-ray Crystallography*, 1962). The final positional and thermal parameters are listed in Table 1.* The observations were weighted according to $w = (a + |F_o| + c|F_o|^2)^{-1}$ (Cruickshank, 1965) with $a = 80.0$ and $c = 0.001$.

Description and discussion of the structure

A stereoscopic picture of the molecule is shown in Fig. 2 (ORTEP, Johnson, 1965). In the propeller-like

* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34081 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters for $\text{Th}(\text{TTA})_4$ ($\times 10^4$, $\times 1$ for isotropic B)

	x	y	z	B (\AA^2)
Th	0000	2275 (1)	7500	anisotropic*
O(1)	0502 (9)	2901 (11)	6484 (6)	2.64 (29)
O(2)	0496 (11)	0465 (13)	6940 (7)	2.47 (33)
O(3)	0856 (10)	3948 (13)	7790 (6)	3.11 (30)
O(4)	1031 (12)	1510 (17)	8178 (9)	2.80 (49)
F(1)	0738 (9)	2662 (13)	-5204 (7)	4.77 (34)
F(2)	0232 (11)	4070 (15)	-4625 (7)	4.75 (38)
F(3)	1388 (17)	3840 (22)	-4564 (10)	5.73 (47)
F(4)	1072 (11)	6217 (15)	8330 (8)	7.47 (44)
F(5)	1978 (10)	5820 (14)	7700 (7)	6.72 (39)
F(6)	2108 (14)	5738 (19)	8736 (9)	5.86 (44)
C(1)	0774 (16)	3203 (18)	-4621 (9)	3.47 (38)
C(2)	0648 (15)	2277 (18)	-4068 (9)	2.52 (40)
C(3)	0709 (13)	1090 (33)	-4183 (7)	2.53 (52)
C(4)	0628 (15)	0097 (17)	6343 (9)	2.96 (37)
C(5)	0770 (14)	-1138 (17)	-3809 (8)	2.19 (35)
C(6)	1065 (17)	-1727 (21)	-4423 (11)	1.86 (50)
C(7)	1132 (18)	-3050 (23)	-4285 (12)	3.57 (59)
C(8)	0955 (5)	-3463 (6)	6329 (3)	4.35 (14)
C(9)	1620 (29)	5601 (24)	8247 (12)	2.85 (61)
C(10)	1301 (16)	3969 (21)	8155 (10)	4.47 (44)
C(11)	1715 (16)	3236 (19)	8616 (10)	3.13 (44)
C(12)	1519 (19)	1961 (25)	8569 (13)	2.98 (65)
C(13)	2021 (16)	1090 (18)	8979 (9)	5.11 (41)
C(14)	2599 (14)	1388 (28)	9454 (9)	2.62 (59)
C(15)	2709 (15)	0159 (16)	9709 (8)	4.03 (35)
C(16)	2372 (5)	-0982 (6)	9486 (3)	1.90 (16)
S(1)	0646 (10)	-2262 (13)	6799 (7)	4.27 (30)
S(2)	1615 (9)	-0527 (15)	8969 (7)	4.82 (34)

* $B_{11} = 22$ (1)
 $B_{12} = 0$

$B_{22} = 43$ (1)
 $B_{13} = -4$ (1)

$B_{33} = 15$ (0)
 $B_{23} = 0$

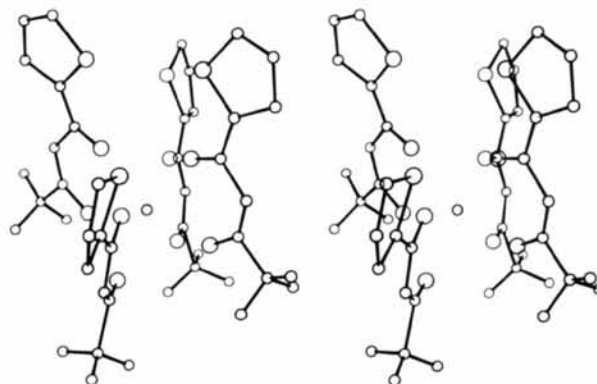


Fig. 2. A stereoscopic picture of the $\text{Th}(\text{TTA})_4$ molecule.

molecule, the CF_3 groups of all four ligands are situated on the same side of a plane through the centre of the molecule and perpendicular to its central axis. Consequently the thienyl groups are all on the other side of that plane. The inner coordination polyhedron, composed of eight chelated O atoms surrounding Th, is a distorted dodecahedron ($D_{2d}-42m$). The ligand attachment, in the notation of Hoard & Silverton (1963), is $Id-mmmm$, i.e. each ligand span is a leg of one of the

trapezoids in the dodecahedron. The angle between the trapezoids is 94.5° , compared with the ideal value of 90° . Fig. 3 shows the coordination polyhedron.

The TTA ligand is nearly planar, except for the F atoms and the thienyl ring. The thienyl ring itself is planar, and the angle between the thienyl and ligand rings has a mean value of 10.4° . The ligand plane is folded from the Th atom over the O...O line, as is common in this type of molecule. The mean value of this fold for $\text{Th}(\text{TTA})_4$ is 13.7° . The geometry of the TTA ligand is shown in Fig. 4. Bond distances and some angles are given in Table 2. The C—CH bonds of the ligand ring show the expected double-bond character. The fact that the C—C bond adjacent to the CF_3 group is shorter than the one near the thienyl group is consistent with the findings in related compounds (Soling, 1975, 1976).

The differences between measured and average values of bond lengths are sometimes quite large. One explanation of these discrepancies is the unfavourable

Table 2. Bond distances (\AA) and angles ($^\circ$)

Th—O(1)	2.357 (14)	Th—O(3)	2.404 (15)
Th—O(2)	2.401 (13)	Th—O(4)	2.427 (16)
O(1)—C(2)	1.333 (24)	O(3)—C(10)	1.206 (35)
O(2)—C(4)	1.303 (24)	O(4)—C(12)	1.269 (30)
C(1)—F(1)	1.326 (26)	C(9)—F(4)	1.178 (33)
C(1)—F(2)	1.325 (31)	C(9)—F(5)	1.307 (29)
C(1)—F(3)	1.283 (34)	C(9)—F(6)	1.328 (29)
C(1)—C(2)	1.516 (30)	C(9)—C(10)	1.750 (36)
C(2)—C(3)	1.286 (28)	C(10)—C(11)	1.365 (38)
C(3)—C(4)	1.513 (38)	C(11)—C(12)	1.399 (32)
C(4)—C(5)	1.369 (46)	C(12)—C(13)	1.530 (38)
C(5)—C(6)	1.499 (27)	C(13)—C(14)	1.443 (40)
C(6)—C(7)	1.436 (30)	C(14)—C(15)	1.417 (34)
C(7)—C(8)	1.366 (34)	C(15)—C(16)	1.423 (34)
C(5)—S(1)	1.736 (20)	C(13)—S(2)	1.858 (29)
C(8)—S(1)	1.686 (27)	C(16)—S(2)	1.770 (25)
O(1)—Th—O(2)	70.6 (4)	O(3)—Th—O(4)	70.4 (4)
O(1)—C(2)—C(3)	131.1 (20)	O(3)—C(10)—C(11)	136.8 (20)
C(2)—C(3)—C(4)	122.8 (21)	C(10)—C(11)—C(12)	115.6 (23)
C(3)—C(4)—O(2)	118.4 (18)	C(11)—C(12)—O(4)	125.1 (18)

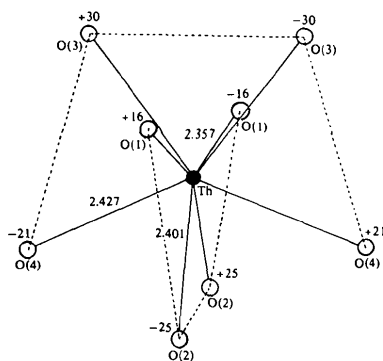


Fig. 3. The oxygen coordination in $\text{Th}(\text{TTA})_4$, with the bond lengths (in \AA) and the deviations (in $\text{\AA} \times 10^2$) from the least-squares planes through the two trapezoids.

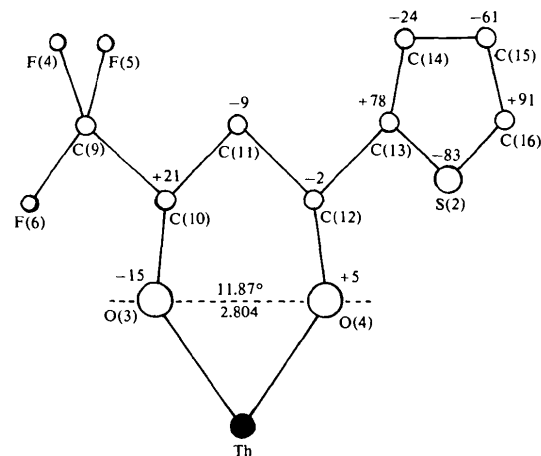
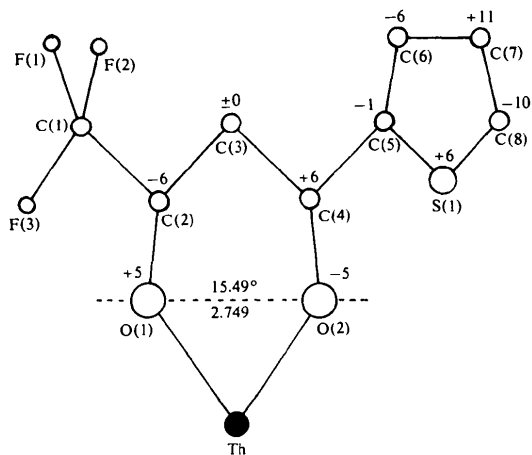


Fig. 4. The geometry of the two independent TTA ligands. The ligand bite distance (in \AA), the fold angle over the O...O line and the deviations (in $\text{\AA} \times 10^3$) from the least-squares planes of the ligand ring and the thienyl ring are given.

proportion between heavy and light atoms. The high thermal motion of the atoms in the outer parts of the ligands is another factor that affects the accuracy of the measured bond lengths.

The authors thank Dr Ove Lindgren for valuable discussions and Dr Bert Allard who prepared the crystals. The English text was revised by Dr John Wood. This work has been supported by the Swedish Natural Science Research Council (NFR Contract No. 2318).

References

- ALLARD, B. (1972). *Acta Chem. Scand.* **26**, 3492–3504.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, p. 114. Oxford: Pergamon Press.

- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* **2**, 235–243.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LEIPOLDT, J. G., WESSELS, G. F. S. & BOK, L. D. C. (1975). *J. Inorg. Nucl. Chem.* **37**, 2487–2490.
- ROOF, R. B. JR (1959). *Phys. Rev.* **113**, 820–825.
- SOLING, H. (1975). *Acta Chem. Scand. Ser. A*, **29**, 523–527.
- SOLING, H. (1976). *Acta Chem. Scand. Ser. A*, **30**, 163–170.
- TITZE, H. & ALLARD, B. (1970). *Acta Chem. Scand.* **24**, 715.

Acta Cryst. (1979). **B35**, 603–608

The Crystal and Molecular Structures of Trichlorobis(η^5 -cyclopentadienyl)- μ -hydroxo-di- μ -methanethiolato-dimolybdenum Hemitoluene Solvate and Observations on the Structure of a Possible Trichlorobis(η^5 -cyclopentadienyl)-tri- μ -methanethiolato-dimolybdenum

BY CLAIRE COULDWELL, BERNARD MEUNIER AND KEITH PROUT

Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England

(Received 27 September 1978; accepted 7 November 1978)

Abstract

The crystal structures of trichlorobis(η^5 -cyclopentadienyl)- μ -hydroxo-di- μ -methanethiolato-dimolybdenum hemitoluene solvate [$\text{Mo}_2(\text{C}_5\text{H}_5)_2(\text{CH}_3\text{S})_2\text{Cl}_3(\text{OH}) \cdot \frac{1}{2}\text{C}_7\text{H}_8$, $\text{C}_{12}\text{H}_{17}\text{Cl}_3\text{Mo}_2\text{OS}_2 \cdot \frac{1}{2}\text{C}_7\text{H}_8$], compound (I) [orthorhombic, $a = 22.115$ (2), $b = 16.020$ (2), $c = 11.226$ (6) Å, $Z = 8$, space group $C222_1$, 2231 reflexions, $R_w = 0.049$] and trichlorobis(η^5 -cyclopentadienyl)-tri- μ -methanethiolato-dimolybdenum [$\text{Mo}_2(\text{C}_5\text{H}_5)_2(\text{CH}_3\text{S})_3\text{Cl}_3$, $\text{C}_{13}\text{H}_{19}\text{Cl}_3\text{Mo}_2\text{S}_3$], compound (II) [monoclinic, $a = 15.441$ (5), $b = 15.678$ (4), $c = 7.257$ (1) Å, $\beta = 97.80$ (2)°, $Z = 4$, space group $P2_1/n$, 1935 reflexions, $R_w = 0.084$] have been determined. Each molecule consists of a $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2$ moiety and a $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}$ moiety linked by three ligands: one hydroxo and two methanethiolato bridges in (I), and three methanethiolato bridges in (II), where problems of disorder and partial hydrolysis were encountered. The $\text{Mo}\cdots\text{Mo}$ distances of 2.726 (1) and 2.852 (2) Å in (I) and (II), respectively, suggest a direct $\text{Mo}-\text{Mo}$ bond.

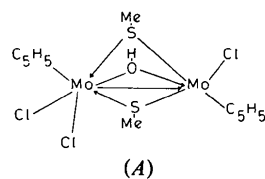
Introduction

The reaction of (η^5 -cyclopentadienyl)molybdenum tetrachloride with methanethiol in diethyl ether yielded at first (II) in the form of orange cube-shaped crystals which were examined by X-ray diffraction. The X-ray analysis ran into difficulties and attempts were made to

repeat the preparation. However, all subsequent attempts gave (I) as orange needles (Green & Bunker, 1978). Analytical and spectroscopic data indicate that (I) and (II) are similar and contain η^5 -cyclopentadienyl, methanethiolato, and chloride residues, but give little guidance as to their true nature. Here we report the X-ray structure analyses.

Results and discussion

(I) was readily identified as the hemitoluene solvate of trichlorobis(η^5 -cyclopentadienyl)- μ -hydroxo-di- μ -methanethiolato-dimolybdenum (A). The final atomic positional parameters are given in Table 1,* bond lengths and angles with e.s.d.'s calculated from the variance-covariance matrix in Table 2 and details of important molecular planes in Table 3. A projection of the molecule is shown in Fig. 1. The asymmetric unit contains one molecule in a general position in the unit



* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34088 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.