

Acta Cryst. (1993). **C49**, 1138–1140

Tris[(1,2,3- η)-1-ethylindenyl]methylthorium(IV)

MARIE-ROSE SPIRLET† AND JEAN REBIZANT

Commission of the European Communities, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe, Germany

SERGE BETTONVILLE‡ AND JEAN GOFFART§

Laboratoire de Chimie Analytique et Radiochimie, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

(Received 26 May 1992; accepted 7 December 1992)

Abstract

The asymmetric unit contains two mononuclear molecules. The coordination around each Th atom is a slightly distorted tetrahedron with three π -bonded indenyl rings and one σ -bonded methyl ligand. Th—C(indenyl) distances range from 2.69 (2) to 3.04 (2) Å and indicate a trihapto mode of bonding of the indenyl rings (through the outer, non-bridging C atoms) as previously observed in other tris(indenyl) complexes of thorium and uranium. The Th—C bonds to ethyl-substituted indenyl C atoms [2.83 (2)–2.94 (3) Å] are longer than the other Th—C(non-bridging) bonds [2.69 (2)–2.78 (2) Å]. Th—C(methyl) distances average 2.49 (3) Å. In one molecule each CH₂—CH₃ bond is approximately normal to the plane of the indenyl ring to which it is attached, while in the other molecule only two of the ethylindenyl ligands adopt this conformation; in the third ligand, the ethyl group lies in the plane of the indenyl ring. The crystal is stabilized by van der Waals interactions.

Comment

The characterization and crystal-structure analysis of the title compound by single-crystal X-ray diffraction forms part of our investigations on the bonding and stereochemistry in organoactinide complexes of the indenyl ligand. Structural data for several tris(indenyl) and tris(methylindenyl) complexes of thorium(IV) and uranium(IV) have been reported: [U(C₉H₇)₃Cl] (Burns & Laubereau, 1971), [U(C₉H₇)₃Br] (Spirlet, Rebizant & Goffart, 1987), [U(C₉H₇)₃I] (Rebizant, Spirlet, Van den Bossche & Goffart,

1988), [Th(C₁₂H₁₃)₃Cl] (Spirlet, Rebizant & Goffart, 1982), [U(C₁₂H₁₃)₃Cl] (Meunier-Piret & Van Meerssche, 1984); but only one (ethylindenyl) complex is known: the chloro complex [Th(C₁₁H₁₁)₃Cl] (Spirlet, Rebizant, Bettonville & Goffart, 1990). The title complex, [Th(C₁₁H₁₁)₃CH₃], is the corresponding methyl derivative. It was prepared by reaction of chlorotris(ethylindenyl)thorium, [Th(C₁₁H₁₁)₃Cl], with methyl lithium in tetrahydrofuran at 195 K with recrystallization from tetrahydrofuran. A selected single crystal was sealed in a thin-walled glass capillary under an inert atmosphere.

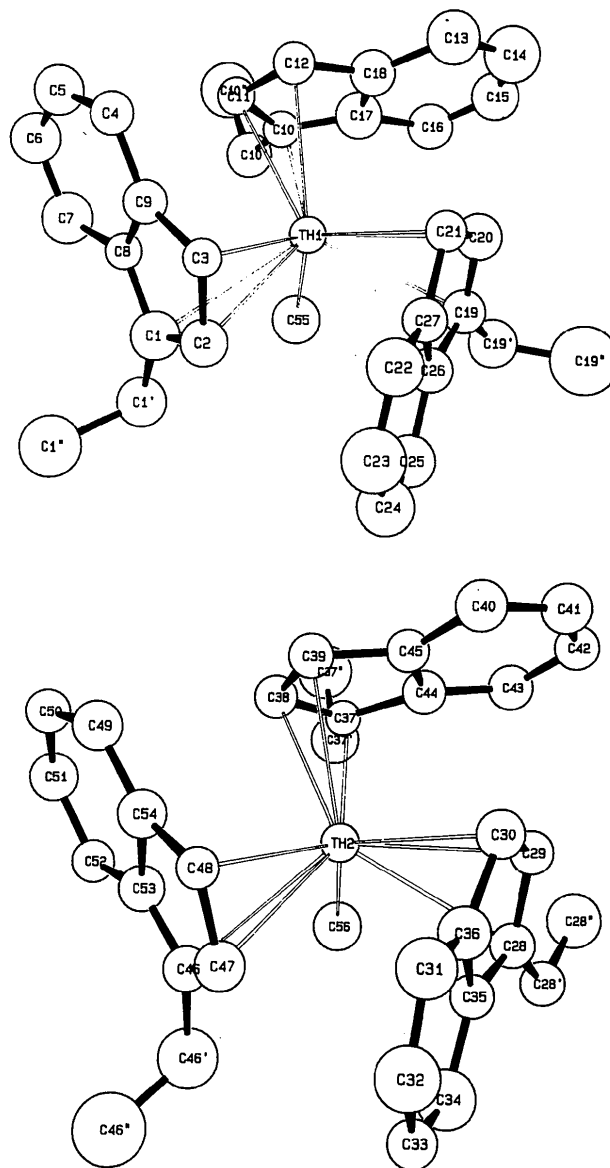


Fig. 1. The structures of the two independent molecular units with the atom-numbering scheme. Note the different orientation of one ethyl substituent in the Th2 molecule. Displacement ellipsoids enclose 30% probability.

† On leave from University of Liège, Belgium.

‡ Research Assistant, FNRS, Brussels, Belgium.

§ Research Associate, IISN, Brussels, Belgium.

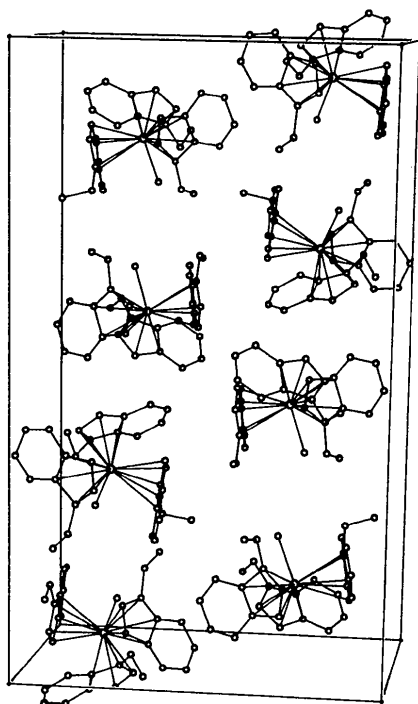


Fig. 2. The crystal packing; c is horizontal from left to right, b is vertical.

The structures of the two molecular units are illustrated in Fig. 1. The packing is illustrated in Fig. 2. The distortion of the coordination polyhedron is reflected by the angles subtended at the Th atom. The different orientations of the ethyl substituents with respect to the indenyl rings are shown by the torsion angles reported in Table 2.

Experimental

Crystal data

[Th(C₁₁H₁₁)₃CH₃]

M_r = 676.7

Monoclinic

*P*2₁/*c*

a = 9.914 (3) Å

b = 30.95 (1) Å

c = 18.145 (5) Å

β = 95.2139 (4)°

V = 5554 (6) Å³

Z = 8

D_x = 1.618 Mg m⁻³

Mo *K*α radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 8–22°

μ = 5.570 mm⁻¹

T = 298 K

Prismatic

0.4 × 0.3 × 0.3 mm

Brown

Crystal source:

[Th(C₁₁H₁₁)₃Cl] + MeLi
in thf at 195 K

Data collection

Enraf-Nonius CAD-4

diffractometer

ω -2 θ scans

3289 observed reflections

[*I* > 3 σ (*I*)]

θ_{\max} = 22.5°

Absorption correction:
empirical, using a set of
reflections with χ values
close to 90°
*T*_{min} = 88.50, *T*_{max} =
99.95%
6980 measured reflections
6980 independent reflections

h = 0 → 10
k = 0 → 33
l = -19 → 19
3 standard reflections
frequency: 30 min
intensity variation:
<0.02%

Refinement

Refinement on *F*

Final *R* = 0.053

wR = 0.068

S = 1.595

3289 reflections

292 parameters

H atoms not included

$w = 1/[\sigma(F_o)]^2 \{ \sigma(F_o) =$

$\sigma(F_o^2)/2F_o; \sigma(F_o^2) =$

$[\sigma(I) - (0.07I)^2]^{1/2}/Lp\}$

(Δ/σ)_{max} = 0.01

$\Delta\rho_{\max} = 2.35 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.51 \text{ e \AA}^{-3}$

Extinction correction: *F_c* =

$F_c/[1 + g(F_c)^2 Lp]$

Extinction coefficient: *g* =

2.71×10^{-9}

Atomic scattering factors
from *International Tables*
for *X-ray Crystallogra-*
phy (1974, Vol. IV) (also
for anomalous-dispersion
corrections)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²)

Only the Th1 and Th2 atoms were refined anisotropically, for which

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> / <i>U</i> _{eq}
Th1	-0.17026 (9)	0.16406 (3)	0.74886 (5)	2.80 (2)
Th2	-0.29769 (9)	0.05920 (3)	0.21755 (5)	2.48 (2)
C1	-0.418 (3)	0.1363 (9)	0.660 (2)	5.0 (7)
C2	-0.307 (2)	0.1138 (9)	0.644 (1)	4.3 (6)
C3	-0.261 (2)	0.0849 (7)	0.706 (1)	2.7 (5)
C4	-0.372 (2)	0.0721 (8)	0.831 (1)	3.5 (5)
C5	-0.480 (3)	0.0857 (9)	0.865 (2)	4.9 (6)
C6	-0.572 (3)	0.1138 (9)	0.840 (2)	5.4 (7)
C7	-0.560 (3)	0.137 (1)	0.774 (2)	5.7 (7)
C8	-0.443 (2)	0.1237 (7)	0.733 (1)	2.7 (5)
C9	-0.355 (2)	0.0915 (8)	0.761 (1)	3.7 (6)
C10	-0.245 (2)	0.2104 (8)	0.873 (1)	3.2 (5)
C11	-0.273 (2)	0.1659 (8)	0.886 (1)	3.1 (5)
C12	-0.144 (2)	0.1453 (8)	0.898 (1)	3.7 (6)
C13	0.108 (3)	0.173 (1)	0.919 (2)	6.0 (8)
C14	0.179 (3)	0.213 (1)	0.920 (2)	7.1 (8)
C15	0.119 (3)	0.250 (1)	0.902 (2)	5.4 (7)
C16	-0.009 (3)	0.2551 (9)	0.882 (2)	5.1 (7)
C17	-0.107 (3)	0.2181 (9)	0.882 (1)	5.2 (7)
C18	-0.039 (3)	0.1767 (8)	0.898 (1)	4.5 (6)
C19	0.043 (2)	0.2057 (8)	0.682 (1)	4.1 (6)
C20	0.102 (3)	0.1787 (8)	0.739 (1)	4.4 (6)
C21	0.081 (2)	0.1358 (7)	0.730 (1)	3.1 (5)
C22	0.012 (3)	0.0925 (9)	0.608 (2)	5.5 (7)
C23	-0.041 (3)	0.098 (1)	0.537 (2)	7.0 (9)
C24	-0.070 (3)	0.141 (1)	0.505 (2)	6.1 (8)
C25	-0.055 (3)	0.1768 (9)	0.547 (7)	5.4 (7)
C26	0.001 (2)	0.1715 (8)	0.623 (1)	4.0 (6)
C27	0.034 (2)	0.1308 (8)	0.655 (1)	3.7 (6)
C28	-0.252 (2)	0.1085 (8)	0.087 (1)	3.4 (5)
C29	-0.214 (2)	0.0651 (7)	0.078 (1)	3.1 (5)
C30	-0.326 (2)	0.0380 (8)	0.072 (1)	3.5 (5)
C31	-0.592 (3)	0.0553 (9)	0.057 (1)	4.7 (6)
C32	-0.669 (3)	0.0917 (9)	0.053 (2)	5.4 (7)
C33	-0.631 (2)	0.1342 (8)	0.066 (1)	3.4 (5)
C34	-0.490 (3)	0.144 (1)	0.081 (2)	5.5 (7)
C35	-0.397 (2)	0.1084 (8)	0.082 (1)	3.0 (5)
C36	-0.445 (2)	0.0663 (8)	0.071 (1)	4.0 (6)
C37	-0.041 (2)	0.0343 (7)	0.293 (1)	2.4 (5)
C38	-0.144 (2)	0.0114 (8)	0.319 (1)	3.4 (5)
C39	-0.196 (2)	-0.0191 (8)	0.263 (1)	3.4 (5)

C40	-0.121 (2)	-0.0411 (9)	0.136 (1)	4.3 (6)	Ind. III
C41	-0.016 (3)	-0.0302 (8)	0.093 (1)	4.3 (6)	C53—C46—C46'—C46'' -88 (3)
C42	0.082 (2)	0.0013 (8)	0.109 (1)	3.6 (6)	C47—C46—C46'—C46'' 77 (3)
C43	0.088 (2)	0.0266 (8)	0.171 (1)	3.9 (6)	
C44	-0.018 (2)	0.0189 (8)	0.221 (1)	3.6 (5)	
C45	-0.118 (2)	-0.0156 (7)	0.202 (1)	3.1 (5)	
C46	-0.494 (2)	0.1011 (8)	0.297 (1)	3.5 (5)	
C47	-0.563 (2)	0.0801 (8)	0.236 (1)	3.8 (6)	
C48	-0.552 (2)	0.0345 (7)	0.248 (1)	2.6 (5)	
C49	-0.449 (2)	-0.0103 (8)	0.365 (1)	3.9 (6)	
C50	-0.392 (2)	-0.0054 (8)	0.438 (1)	3.3 (5)	
C51	-0.353 (2)	0.0361 (9)	0.464 (1)	4.2 (6)	
C52	-0.380 (2)	0.0747 (8)	0.425 (1)	3.3 (5)	
C53	-0.447 (2)	0.0716 (8)	0.349 (1)	3.6 (5)	
C54	-0.485 (2)	0.0249 (8)	0.320 (1)	3.7 (6)	
C55	-0.276 (3)	0.231 (1)	0.694 (2)	5.6 (7)	
C56	-0.190 (3)	0.1277 (9)	0.266 (1)	4.6 (6)	
C1'	-0.497 (3)	0.1693 (9)	0.610 (2)	5.4 (7)	
C1''	-0.624 (3)	0.140 (1)	0.569 (2)	8.0 (9)	
C10'	-0.349 (3)	0.246 (1)	0.869 (2)	5.3 (7)	
C10''	-0.392 (3)	0.258 (1)	0.946 (2)	8.2 (9)	
C19'	0.054 (3)	0.252 (1)	0.664 (2)	5.5 (7)	
C19''	0.201 (4)	0.263 (1)	0.645 (2)	11 (1)	
C28'	-0.159 (2)	0.1467 (8)	0.087 (1)	3.6 (5)	
C28''	-0.014 (3)	0.137 (1)	0.094 (2)	5.8 (7)	
C37'	0.054 (3)	0.0620 (9)	0.336 (2)	5.0 (6)	
C37''	0.175 (3)	0.040 (1)	0.382 (2)	6.7 (8)	
C46'	-0.502 (3)	0.150 (1)	0.305 (2)	6.3 (8)	
C46''	-0.636 (4)	0.166 (1)	0.331 (2)	9 (1)	

Table 2. Selected distances (Å), angles (°) and torsion angles (°)

Ind. denotes the centroid of the five-membered indenyl ring

Molecule Th1			
Th1—C55	2.48 (3)		
Ind. I			
Th1—C1	2.94 (3)	Ind. II	
Th1—C2	2.73 (2)	Th1—C10	2.83 (2)
Th1—C3	2.70 (2)	Th1—C11	2.78 (2)
Th1—C8	2.97 (2)	Th1—C12	2.77 (2)
Th1—C9	2.92 (2)	Th1—C17	2.96 (3)
		Th1—C18	2.92 (3)
Th1—Ind. I	2.59 (3)	Th—Ind. II	2.58 (3)
		Th—Ind. III	2.58 (3)
C55—Th1—Ind. I	98.0 (8)	Ind. I—Th1—Ind. II	116.0 (7)
C55—Th1—Ind. II	100.1 (8)	Ind. I—Th1—Ind. III	118.0 (7)
C55—Th1—Ind. III	99.4 (8)	Ind. II—Th1—Ind. III	118.6 (7)
Ind. I			
C8—C1—C1'—C1''	-85 (3)		
C2—C1—C1'—C1''	96 (3)		
Ind. II			
C17—C10—C10'—C10''	-90 (3)		
C11—C10—C10'—C10''	75 (3)		
Ind. III			
C26—C19—C19'—C19''	-90 (3)		
C20—C19—C19'—C19''	65 (4)		
Molecule Th2			
Th2—C56	2.50 (3)		
Ind. I			
Th2—C28	2.89 (2)	Ind. II	
Th2—C29	2.74 (2)	Th2—C37	2.89 (2)
Th2—C30	2.72 (2)	Th2—C38	2.72 (2)
Th2—C35	2.98 (2)	Th2—C39	2.72 (2)
Th2—C36	2.92 (2)	Th2—C44	3.04 (2)
		Th2—C45	2.95 (2)
Th2—Ind. I	2.58 (2)	Th2—Ind. III	2.57 (3)
C56—Th2—Ind. I	99.7 (8)	Ind. I—Th2—Ind. II	116.1 (6)
C56—Th2—Ind. II	98.8 (7)	Ind. I—Th2—Ind. III	118.1 (7)
C56—Th2—Ind. III	97.3 (8)	Ind. II—Th2—Ind. III	119.3 (6)
Ind. I			
C35—C28—C28'—C28''	179 (3)		
C29—C28—C28'—C28''	-13 (3)		
Ind. II			
C44—C37—C37'—C37''	-83 (3)		
C38—C37—C37'—C37''	81 (3)		

Space group $P2_1/c$ was indicated by the systematic absences. Data were corrected for Lp effects. The structure was solved by direct methods and subsequent $\Delta\rho$ maps. The maximum and minimum excursions of density in the final difference map were close to the Th atom. Refinement was performed by full-matrix least-squares techniques. Only the thermal motions of the Th atoms were refined. H atoms were not included in the refinement. Computer programs used were from the Enraf-Nonius (1986) SDP, including ORTEPII (Johnson, 1976).

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55908 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1017]

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Acta Cryst. (1993). **C49**, 1140–1142

Structure of $[\text{Cu}_2(\text{dmpe})_3\text{Cl}_2]_n \cdot 2\text{CH}_2\text{Cl}_2$

JOSEPH H. REIBENSPIES, DONALD J. DARENSBOURG
AND ELISABETH M. LONGRIDGE

*Department of Chemistry, Texas A & M University,
College Station, Texas 77843, USA*

(Received 2 October 1992; accepted 9 December 1992)

Abstract

Recrystallization of the product obtained from the reaction of copper(I) acetate and 1,2-bis(dimethylphosphino)ethane (dmpe) from methylene chloride and hexane resulted in the formation of the air-stable colorless polymeric compound *catena*-poly[(chlorocopper)-bis- μ -{1,2-