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Structure of Chlorotris(1–3-η-1-ethylindenyl)thorium(IV)

By M. R. Spirlet* and J. Rebizant

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

S. Bettonville† and J. Goffart‡

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

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Abstract. [Th($C_{11}H_{11}$)$_3$Cl], $M_r = 697{\cdot}12$, monoclinic, $P2_1/c$, $a = 7{\cdot}651$ (4), $b = 11{\cdot}750$ (6), $c = 30{\cdot}23$ (1) Å, $\beta = 94{\cdot}18$ (7)°, $V = 2711$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}708$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 58{\cdot}104$ cm^{-1}, $F(000) = 1352$, $T = 295$ (1) K, $R = 0{\cdot}055$ for 2611 reflections [$I > 3\sigma(I)$]. The coordination about thorium is a slightly distorted tetrahedron with three trihapto indenyl rings and one σ-bonded Cl ligand. The ethyl substituents on the indenyls seem to orient themselves preferentially in the planes of the indenyl rings, except when packing hindrance occurs. In the present complex, statistical disorder leads to two possible orientations for the terminal ethyl C atom of one ethylindenyl ligand; one orientation is rotated by 102 (3)° with respect to the other.

Introduction. The present work forms part of our investigations on the bonding and stereochemistry in organoactinide complexes of the indenyl ligand. In the series of tris(indenyl)-halogeno complexes of thorium and uranium, structural data have been reported for: [U(C_9H_7)$_3$Cl] (Burns & Laubereau, 1971), [UBr(C_9H_7)$_3$)] (Spirlet, Rebizant & Goffart, 1987), [U(C_9H_7)$_3$I] (Rebizant, Spirlet, Van den Bossche & Goffart, 1988), [Th($C_{12}H_{13}$)$_3$Cl] (Spirlet, Rebizant & Goffart, 1982), and [U($C_{12}H_{13}$)$_3$Cl] (Meunier-Piret & Van Meerssche, 1984). The characterization and structure analysis, by single-crystal X-ray diffraction, are reported here for the first ethylindenyl derivative.

Experimental. Compound synthesized by reaction of ethylindenyl sodium with thorium tetrachloride in tetrahydrofuran at room temperature. Recrystallization from tetrahydrofuran. Selected specimen (0·27 × 0·20 × 0·18 mm) sealed in a thin-walled glass capillary under an inert atmosphere. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation using θ–2θ scans. Cell parameters refined by least squares from angle data of 25 reflections in range $11 < 2\theta < 23°$. Space group established from systematic absences. Data collected in range $2 < 2\theta < 23°$; h 0–10, k 0–14, l −33–33: 3705 reflections collected, corresponding to 3433 unique reflections. 2611 with $I > 3\sigma(I)$ used in refinement. Intensities of three standard reflections measured at 30 min intervals showed no deviations from mean. Intensities corrected for Lorentz–polarization effects: empirical absorption corrections using the program *DIFABS* (Walker & Stuart, 1983). Transmission coefficients $T_{\min} = 0{\cdot}6247$ and $T_{\max} = 1{\cdot}2918$. Structure solved by direct methods and refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$: $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I) + (AI)^2]^{1/2}/\mathrm{Lp}$, where A, the ignorance factor, is 0·06. Only the thermal motions of the Th and Cl atoms were treated anisotropically. H atoms were not included in refinement. No extinction correction. $R = 0{\cdot}055$. $wR = 0{\cdot}069$. $S = 1{\cdot}806$. Final $(\Delta/\sigma)_{\max} = 0{\cdot}03$. Max. and min. heights in final difference Fourier map: 1·57 and −1·40 e Å^{-3} (near the Th position). Atomic factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1986) *SDP* programs.

Discussion. The molecular structure is illustrated in Fig. 1. The packing is illustrated by Fig. 2 which shows the content of two unit cells. Final atomic coordinates are given in Table 1;§ selected distances

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* On secondment from University of Liège, Belgium.

† Research Assistant, FNRS, Brussels.

‡ Research Associate, IISN, Brussels.

§ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52739 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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and angles are listed in Table 2. The coordination polyhedron of the Th atom is a slightly distorted tetrahedron as shown by the angles between the Th–Cl direction and the Th–centre-of-ring (designated as Ind. I, Ind. II and Ind. III) directions (Table 2). The Th—Cl bond length of 2·673 (3) Å corresponds to the value expected for a single covalent bond (2·64 Å). A similar value [2·664 (1) Å] has been previously reported for the Th—Cl bond in [Th($C_{12}H_{13}$)$_3$Cl] (Spirlet, Rebizant & Goffart, 1982). The Th—C distances (Table 2) indicate a trihapto mode of bonding of the indenyl rings (bonding through the non-bridging C atoms) as also observed in other tris- and tetrakis-indenyl thorium and uranium compounds: [Th{$C_9H_4(CH_3)_3$}$_3$Cl] (Spirlet, Rebizant & Goffart, 1982), [UBr(C_9H_7)$_3$] (Spirlet, Rebizant & Goffart, 1987), [U(C_9H_7)$_3$I] (Rebizant, Spirlet, Van den Bossche & Goffart, 1988), [Th(C_9H_7)$_4$] (Rebizant, Spirlet, Kanellakopulos & Dornberger, 1986). In the present case, a lengthening of Th—C is

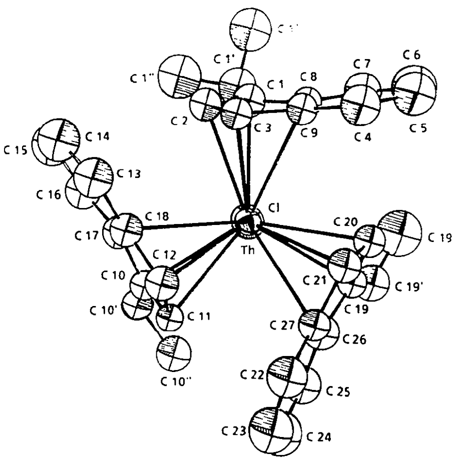

Fig. 1. The molecular structure. Thermal ellipsoids are at the 50% probability level (Johnson 1976).

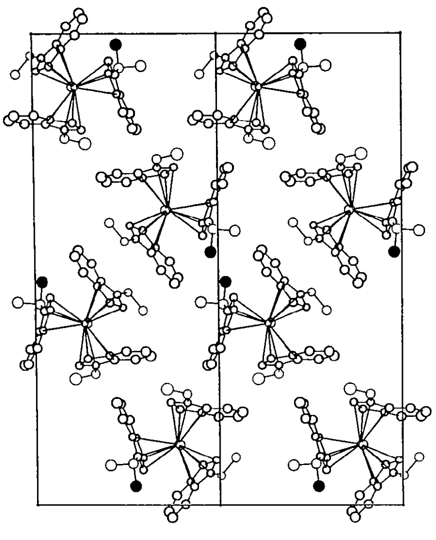

Fig. 2. The content of two unit cells as a projection along the *a* axis; *b* is horizontal from left to right. Black circles represent the C(1″) atom positions.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Th	0·13160 (6)	0·23077 (4)	0·11411 (2)	2·80 (1)
Cl	0·4809 (5)	0·2148 (4)	0·1189 (2)	4·9 (1)
C(1)	0·248 (2)	0·451 (1)	0·0897 (6)	4·6 (4)
C(2)	0·105 (2)	0·418 (1)	0·0588 (5)	4·2 (3)
C(3)	−0·046 (2)	0·417 (1)	0·0818 (5)	3·6 (3)
C(4)	−0·109 (2)	0·492 (2)	0·1614 (6)	5·6 (4)
C(5)	−0·022 (2)	0·542 (2)	0·1976 (7)	6·5 (5)
C(6)	0·157 (3)	0·559 (2)	0·2031 (8)	8·1 (6)
C(7)	0·264 (2)	0·530 (2)	0·1707 (6)	5·9 (4)
C(8)	0·179 (2)	0·478 (1)	0·1311 (5)	3·5 (3)
C(9)	−0·006 (2)	0·459 (1)	0·1257 (5)	3·6 (3)
C(10)	0·198 (2)	0·051 (1)	0·0537 (5)	3·6 (3)
C(11)	0·056 (2)	0·021 (1)	0·0788 (5)	3·0 (3)
C(12)	−0·093 (2)	0·092 (1)	0·0660 (5)	4·2 (3)
C(13)	−0·141 (2)	0·237 (2)	−0·0002 (6)	5·6 (4)
C(14)	−0·053 (3)	0·280 (2)	−0·0335 (7)	6·7 (5)
C(15)	0·114 (3)	0·262 (2)	−0·0421 (7)	6·9 (5)
C(16)	0·217 (2)	0·190 (2)	−0·0124 (6)	5·5 (4)
C(17)	0·135 (2)	0·139 (1)	0·0239 (6)	4·3 (3)
C(18)	−0·044 (2)	0·160 (1)	0·0308 (5)	4·1 (3)
C(19)	0·224 (2)	0·174 (1)	0·2047 (5)	3·8 (3)
C(20)	0·095 (2)	0·264 (1)	0·2030 (5)	3·9 (3)
C(21)	−0·071 (2)	0·216 (1)	0·1850 (5)	4·1 (3)
C(22)	−0·171 (2)	0·006 (2)	0·1669 (6)	5·8 (4)
C(23)	−0·104 (3)	−0·101 (2)	0·1689 (7)	7·2 (5)
C(24)	0·070 (3)	−0·128 (2)	0·1815 (7)	7·6 (5)
C(25)	0·193 (2)	−0·043 (2)	0·1913 (6)	5·7 (4)
C(26)	0·135 (2)	0·071 (2)	0·1908 (6)	5·1 (4)
C(27)	−0·046 (2)	0·096 (1)	0·1781 (5)	3·8 (3)
C(1′)	0·437 (2)	0·474 (2)	0·0786 (7)	6·7 (5)
C(1″)	0·462 (6)	0·460 (4)	0·031 (2)	9 (1)
C(1‴)	0·489 (6)	0·594 (4)	0·076 (2)	9 (1)
C(10′)	0·374 (2)	−0·008 (1)	0·0520 (5)	4·4 (3)
C(10″)	0·417 (2)	−0·089 (2)	0·0918 (6)	5·9 (4)
C(19′)	0·407 (2)	0·174 (2)	0·2266 (6)	6·0 (4)
C(19″)	0·465 (4)	0·284 (2)	0·238 (1)	10·7 (8)

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

Th—Cl 2·673 (3)

Ind. I		Ind. II		Ind. III	
Th—C(1)	2·85 (1)	Th—C(10)	2·86 (1)	Th—C(19)	2·86 (1)
Th—C(2)	2·76 (1)	Th—C(11)	2·73 (1)	Th—C(20)	2·75 (1)
Th—C(3)	2·72 (1)	Th—C(12)	2·71 (1)	Th—C(21)	2·74 (1)
Th—C(8)	2·97 (1)	Th—C(17)	2·94 (1)	Th—C(26)	2·98 (1)
Th—C(9)	2·91 (1)	Th—C(18)	2·89 (1)	Th—C(27)	2·91 (1)
Th-Ind.I	2·57 (1)	Th-Ind.II	2·55 (1)	Th-Ind.III	2·70 (1)

Cl—Th-Ind.I	99·8 (3)	Ind.I-Th-Ind.II	117·2 (3)
Cl—Th-Ind.II	100·6 (3)	Ind.I-Th-Ind.III	124·6 (4)
Cl—Th-Ind.III	92·0 (3)	Ind.II-Th-Ind.III	113·3 (4)

Ind. I		Ind. II	
C(8)—C(1)—C(1′)—C(1″)	− 168 (3)	C(17)—C(10)—C (10′)—C(10″)	+ 173 (1)
C(8)—C(1)—C(1′)—C(1‴)	− 66 (3)	C(11)—C(10)—C(10′)—C(10″)	− 18 (2)
C(2)—C(1)—C(1′)—C(1″)	0 (3)	Ind. III	
C(2)—C(1)—C(1′)—C(1‴)	+ 102 (3)	C(26)—C(19)—C(19′)—C(19″)	− 179 (2)
		C(20)—C(19)—C(19′)—C(19″)	− 14 (3)

Table 3. *Short intra- and intermolecular distances* (Å)

Cl···C(1)	3·38 (1)	C(3)···C(18)	3·39 (2)
Cl···C(10)	3·41 (1)	C(4)···C(20)	3·30 (2)
Cl···C(19)	3·40 (1)	C(4)···C(21)	3·33 (2)
Cl···C(10′)	3·37 (2)	C(5)···C(20)	3·38 (2)
Cl···C(10″)	3·68 (2)	C(9)···C(20)	3·32 (2)
Cl···C(19′)	3·38 (2)	C(11)···C(27)	3·28 (2)
Cl···C(19″)	3·71 (2)	C(11)···C(22)	3·29 (2)
C(2)···C(13)	3·28 (2)	C(11)···C(23)	3·39 (2)
C(2)···C(14)	3·38 (2)	C(12)···C(27)	3·38 (2)
C(2)···C(18)	3·33 (2)	C(12)···C(22)	3·31 (2)
C(3)···C(13)	3·30 (2)		
Intermolecular distances			
C(13)···C(10′)	3·53 (2)	C(1″)···C(1″)	2·21 (8)
C(15)···C(1‴)	3·68 (4)	C(1‴)···C(10″)	3·80 (4)
C(1′)···C(1″)	3·55 (5)	C(10′)···C(10′)	3·81 (2)
C(1″)···C(1‴)	3·34 (6)		

observed for the bond to the ethyl-substituted C atom of the indenyl ring. A slight bending is also observed between the five- and six-membered portions of the indenyl rings [8 (2), 8 (3) and 6 (3)° respectively for rings I, II and III]. This bending results from steric crowding in the coordination sphere of the Th atom. Indeed, there appear to be several non-bonded intramolecular contacts (Table 3) shorter than normal van der Waals values (Pauling, 1960). The ethyl substituents on two of the indenyl ligands (II and III) are almost in plane with the indenyl rings, as shown by torsion angles reported in Table 2, but on the third indenyl ligand (I) the ethyl groups appear with two possible orientations. These correspond to a statistical disorder of the terminal ethyl carbon position [C(1″) or C(1‴)] and correspond to a 102° rotation about the C—C ethyl–indenyl bond. This disorder results from stacking hindrance between the two positions of C(1″) which are symmetrically related by inversion through a center of symmetry [2(*d*) or 2(*c*)]. These two positions are only 2·21 (8) Å apart (Table 3).

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Structure of a Cu^I Complex with a Saturated N_2S_2 Macrocycle

By Karappulli P. Balakrishnan, Andreas Riesen, Andreas D. Zuberbühler and Thomas A. Kaden

Institute of Inorganic Chemistry of Basel, CH-4056 Basel, Switzerland

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Abstract. (1,5-Dithia-9,13-diazacyclohexadecane-*S*,*S*′,*N*,*N*′)copper(I) tetrafluoroborate, $[Cu(C_{12}H_{26}N_2S_2)][BF_4]$, $M_r = 412{\cdot}82$, monoclinic, $P2_1/c$, $a = 13{\cdot}077\ (5)$, $b = 8{\cdot}997\ (3)$, $c = 16{\cdot}502\ (3)$ Å, $\beta = 112{\cdot}78\ (3)°$, $V = 1790{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}532$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}413$ mm^{-1}, $F(000) = 856$, $T = 298$ K, $R = 0{\cdot}063$ for 2120 reflections with $I \geq 2\sigma(I)$. The Cu^I is coordinated by the two amino nitrogens and by the two thioether sulfurs of 1,5-dithia-9,13-diazacyclohexadecane in a slightly distorted tetrahedral geometry. The Cu—S bonds (2·25–2·26 Å) are distinctly longer than the Cu—N bonds (2·05–2·06 Å) and the angles N—Cu—S for the N and S atoms *trans* to each other are somewhat larger (117–121°) than the tetrahedral angle.

Introduction. The structure determination of plastocyanin in its oxidized (Guss & Freeman, 1983) and reduced (Guss, Harrowell, Murata, Norris & Freeman, 1986) form and the observation that both Cu^{2+} and Cu^+ (at high pH) are tetrahedrally coordinated by two imidazole nitrogens, a methionine thioether and a cysteine thiolate has generated great interest in Cu–N_2S_2 systems. The spectral, EPR, electrochemical and structural properties of Cu^{2+}

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