tetravalent disubstituted compounds, this would be expected to be at the high end of the series. This argument is, of course, predicated on the original MO reasoning of Meyer and coworkers mentioned above[15] but removes the need for separate MO schemes for each compound. Somewhat similar reasoning has been used to explain the differences in folding observed in the phenoxarsine series, but the emphasis was mainly on delocalization through the arsenic, and it was admitted that there was "no ready explanation" for the 20° difference between the Cl and S derivatives.[22-25]

An interesting use of this theory might be the determination of relative electronegativities of unusual substituents, e.g., the observation that trifluoroacetate would be essentially equal to chlorine on the basis of the dihedral angle. One would predict that the difluoro compound would have an angle between 145 and 151°, and we hope to be able to investigate this in the near future.

Acknowledgment. J.D.K. and I.B. thank the U.S. National Science Foundation for the funds used in purchasing the diffractometer and for operational support and also the Robert A. Welch Foundation for research funds through Grant E-594.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of Two Crystalline Forms of (Cyclooctatetraene)thorium(IV) Dichloride-Bis(tetrahydrofuran)

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$Th(C_8H_8)Cl_2(OC_4H_8)_2$ crystallizes in two modifications. The α form, space group $P2_1/n$, has dimensions $a = 8.589$ (4) Å, $b = 27.222$ (10) Å, $c = 7.950$ (4) Å, $\beta = 96.92$ (5)°, $Z = 4$, and $d_x = 1.99$ g/cm^3. The β form, space group $P2_1/c$, has dimensions $a = 13.036$ (6) Å, $b = 11.601$ (6) Å, $c = 24.598$ (10) Å, $\beta = 102.90$ (5)°, $Z = 8$, and $d_x = 2.02$ g/cm^3. The α form has one molecule in the asymmetric unit whereas the β form has two which are chemically equivalent but crystallographically different. The study thus yields three independent determinations of the same molecular structure. Thorium is bonded to the cyclooctatetraene ring, to two chlorine atoms, and to two oxygen atoms from the tetrahydrofuran moieties. Significant distances (averaged) are Th-Cl = 2.69 Å, Th-O = 2.57 Å, and Th-to-plane of C_8H_8 = 2.02 Å.

Introduction

Since the first synthesis of uranocene, bis(π-cyclooctatetraene)uranium(IV),[2] a large number of related compounds have been prepared.[3] The bis(cyclooctatetraene) compounds of all the lower actinides are now known, including thorocene, bis(π-cyclooctatetraene)thorium(IV).[4] X-ray crystal structures have been determined at Berkeley for several of these compounds.[5] All show the central metal atom in the center of two parallel planar eight-member rings.

We recently reported the preparation of mono(cyclooctatetraene)thorium(IV) dichloride and diborohydride.[6] In this paper we report the crystal structure of the dichloride which was isolated as the bis(tetrahydrofuran) compound, $C_8H_8ThCl_2{\cdot}2C_4H_8O$, **1**, by the reaction of thorocene with thorium tetrachloride in THF. Compound **1** is more soluble in THF than is thorocene itself.

Experimental Section

(Cyclooctatetraene)thorium Dichloride-Bis(tetrahydrofuran). A suspension of 1.3 g (3.0 mmol) of thorocene and 1.7 g (4.5 mmol) of thorium tetrachloride in tetrahydrofuran (THF) was stirred at reflux under argon until the yellow color of thorocene disappeared (ca. 1 week). The mixture was degassed and taken into the glovebox, and the solid was separated by centrifugation. The THF-soluble portions were combined, and the solvent was removed by vacuum transfer. Crystals were grown from hot saturated THF solutions. Anal. Calcd for $C_{16}H_{24}ThCl_2O_2$: C, 34.86; H, 4.39; Cl, 12.86. Found: C, 34.65; H, 4.38; Cl, 12.22.

X-ray Diffraction. White crystals of the compounds, because of their extreme sensitivity to the atmosphere, were sealed inside thin-walled quartz capillaries for the X-ray experiments. Weissenberg photography showed the material to be monoclinic, later designated as the β form. Upon investigating a different crystal on a Picker

Table I. Summary of Crystal Data Intensity Collection and Least-Squares Refinement Statistics

	α-$C_8H_8ThCl_2$-$(OC_4H_8)_2$	β-$C_8H_8ThCl_2$-$(OC_4H_8)_2$
fw	551.31	551.31
a, Å	8.589 (3)	13.036 (4)
b, Å	27.22 (2)	11.601 (3)
c, Å	7.950 (3)	24.598 (8)
β, deg	96.92 (4)	102.90 (4)
V, Å^3	1845	3626
space group	$P2_1/n$	$P2_1/c$
Z	4	8
d(calcd), g/cm^3	1.985	2.020
color	white	white
cryst size, mm	parallelepiped, 0.1 × 0.2 × 0.3	0.15 × 0.15 × 0.3
cryst vol, mm^3	0.007	0.007
μ, cm^{-1}	288	293
T, °C	22	21
no. of scans (including stds)	5679	11 573
decay cor range	1.0-1.05	1.0-1.05
no. of unique data	2740	5390
no. data $F^2 > 3\sigma$ used in least-squares	2242	3914
extinction factor k ($F_{cor} = (1 + kI)F_o$)	5×10^{-7}	7×10^{-7}
ignorance factor, p, in weighting expression $w = [(\sigma(F^2))^2 + (pF^2)^2]^{-1}$	0.04	0.06
no. of variables in least squares	190	331
$R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$	0.045	0.054
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$ ($F^2 > 3\sigma$)	0.036	0.045
R for all data	0.044	0.064
goodness of fit	1.24	1.16

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0020-1669/80/1319-2560$01.00/0

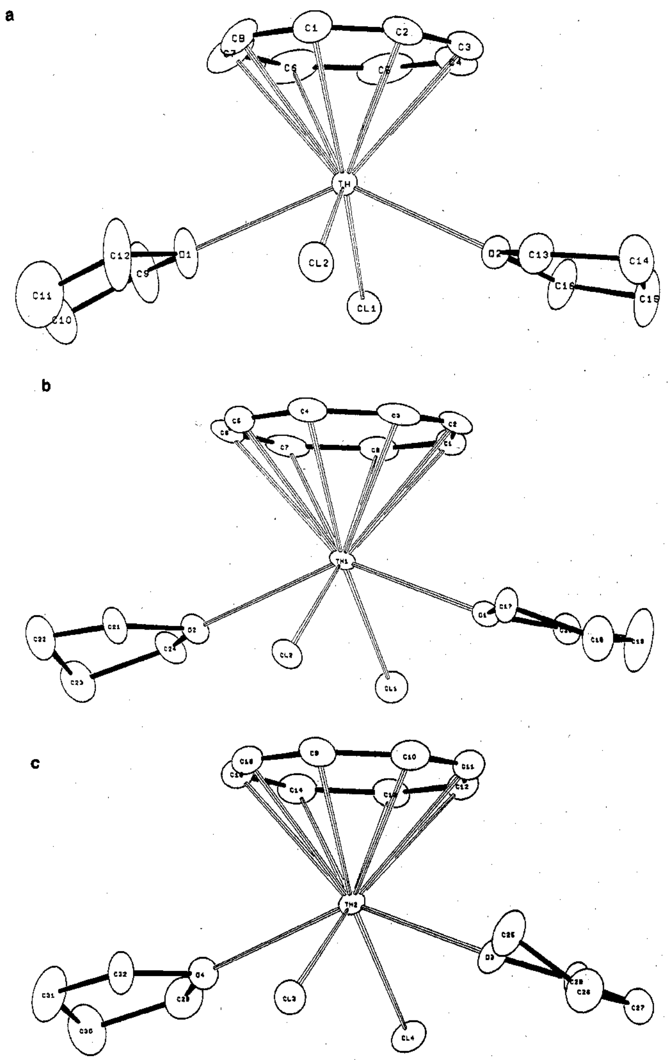

Figure 1. ORTEP drawing of the $C_8H_8ThCl_2(OC_4H_8)_2$ molecules: (a) α form; (b) β form, molecule 1; (c) β form, molecule 2.

FACS-I automated diffractometer, which was equipped with a graphite monochromator and a copper X-ray tube, we found it to be monoclinic with cell dimensions different from those of the first crystal. This new form was designated as the α form, and a set of intensity data was collected from it. A third crystal from the same preparation was investigated and observed to be the β form, and a set of intensity data was collected from it.

In both cases, setting angles of 12 reflections where $95° < 2\theta < 106°$ ($\lambda(\mathrm{Cu}\ K\alpha_1) = 1.54056$ Å) were used for least-squares adjustment of the cell dimensions. Cell dimensions and other crystal data are given in Table I.

Table II. Positional Parameters[a]

atom	*x*	*y*	*z*
		α Form	
Th	0.46399 (4)	0.13344 (1)	0.05714 (3)
Cl(1)	0.5612 (3)	0.08843 (9)	−0.2128 (3)
Cl(2)	0.2512 (3)	0.0769 (1)	0.1868 (3)
O(1)	0.223 (1)	0.1350 (3)	−0.169 (1)
O(2)	0.6250 (8)	0.0622 (2)	0.1857 (7)
C(1)	0.393 (2)	0.2010 (4)	0.292 (1)
C(2)	0.530 (2)	0.1810 (4)	0.360 (1)
C(3)	0.677 (2)	0.1714 (4)	0.305 (2)
C(4)	0.740 (2)	0.1799 (4)	0.156 (2)
C(5)	0.689 (2)	0.2004 (4)	0.000 (2)
C(6)	0.547 (2)	0.2202 (4)	−0.073 (2)
C(7)	0.400 (2)	0.2291 (4)	−0.017 (2)
C(8)	0.336 (2)	0.2207 (4)	0.133 (2)
C(9)	0.230 (2)	0.1477 (6)	−0.344 (2)
C(10)	0.072 (2)	0.1397 (5)	−0.429 (2)
C(11)	−0.032 (3)	0.1411 (7)	−0.293 (3)
C(12)	0.063 (2)	0.1387 (7)	−0.138 (2)
C(13)	0.603 (2)	0.0395 (4)	0.347 (1)
C(14)	0.758 (2)	0.0174 (5)	0.414 (2)
C(15)	0.838 (2)	0.0101 (6)	0.265 (2)
C(16)	0.768 (2)	0.0425 (5)	0.126 (2)
		β Form	
Th(1)	0.08705 (4)	0.17124 (4)	0.33807 (2)
Th(2)	0.41202 (4)	0.26318 (4)	0.62281 (2)
Cl(1)	−0.0870 (3)	0.0453 (3)	0.3322 (2)
Cl(2)	0.2072 (3)	0.0214 (3)	0.2963 (1)
Cl(3)	0.2107 (3)	0.1956 (3)	0.5916 (2)
Cl(4)	0.4755 (3)	0.2098 (4)	0.5290 (1)
O(1)	0.0054 (8)	0.1715 (7)	0.2337 (4)
O(2)	0.1444 (8)	0.0169 (8)	0.4139 (4)
O(3)	0.4190 (8)	0.0417 (8)	0.6268 (4)
O(4)	0.3192 (8)	0.4179 (8)	0.5532 (4)
C(1)	−0.017 (1)	0.372 (1)	0.3352 (7)
C(2)	0.055 (2)	0.393 (1)	0.3044 (7)
C(3)	0.160 (2)	0.372 (1)	0.3073 (7)
C(4)	0.243 (1)	0.332 (1)	0.3487 (8)
C(5)	0.251 (1)	0.290 (1)	0.4002 (8)
C(6)	0.185 (2)	0.274 (1)	0.4368 (7)
C(7)	0.075 (2)	0.290 (1)	0.4316 (7)
C(8)	−0.005 (1)	0.331 (1)	0.3897 (8)
C(9)	0.383 (1)	0.309 (2)	0.7264 (6)
C(10)	0.454 (2)	0.217 (2)	0.7333 (7)
C(11)	0.549 (2)	0.198 (1)	0.7187 (7)
C(12)	0.612 (1)	0.253 (2)	0.6858 (7)
C(13)	0.606 (1)	0.362 (2)	0.6600 (6)
C(14)	0.533 (2)	0.454 (1)	0.6541 (6)
C(15)	0.441 (2)	0.477 (1)	0.6715 (7)
C(16)	0.380 (1)	0.416 (2)	0.7002 (7)
C(17)	0.067 (1)	0.187 (1)	0.1905 (6)
C(18)	−0.016 (2)	0.191 (2)	0.1385 (7)
C(19)	−0.117 (2)	0.214 (3)	0.1500 (8)
C(20)	−0.107 (1)	0.196 (1)	0.2110 (6)
C(21)	0.252 (1)	−0.021 (1)	0.4339 (6)
C(22)	0.259 (1)	−0.069 (2)	0.4895 (8)
C(23)	0.152 (2)	−0.100 (2)	0.4922 (7)
C(24)	0.085 (1)	−0.013 (1)	0.4558 (6)
C(25)	0.364 (2)	−0.023 (1)	0.6620 (8)
C(26)	0.370 (2)	−0.144 (2)	0.6432 (9)
C(27)	0.467 (2)	−0.155 (2)	0.6226 (7)
C(28)	0.497 (1)	−0.032 (1)	0.6138 (7)
C(29)	0.369 (2)	0.485 (2)	0.5167 (7)
C(30)	0.286 (2)	0.569 (2)	0.487 (1)
C(31)	0.213 (2)	0.575 (2)	0.520 (1)
C(32)	0.221 (1)	0.471 (1)	0.5549 (7)

[a] Estimated standard deviation of the least significant digit is given in parentheses in this and the following tables.

A θ–2θ scan technique with a scan speed of 2°/min was used to collect the intensities in the range of $4° < 2\theta < 120°$; backgrounds were measured for 4 s at the beginning and end of each scan. ω scans of several low-angle reflections showed widths at half-peak height of 0.13–0.15°. Three standard reflections were measured after each 200th scan to monitor for crystal decay, instrumental stability, and crystal alignment. A decay of 5% was observed in the intensities of the standards of both data sets, and the data were adjusted accordingly. Correction for absorption was made by an analytical integration

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Table III. Interatomic Distances (*D*, Å)[a]

α		β(molecule 1)		β(molecule 2)	
atoms	*D*	atoms	*D*	atoms	*D*
Th-Cl(1)	2.690 (2)	Th(1)-Cl(1)	2.676 (4)	Th(2)-Cl(3)	2.681 (4)
-Cl(2)	2.688 (3)	-Cl(2)	2.692 (3)	-Cl(4)	2.691 (3)
-O(1)	2.58 (1)	-O(1)	2.55 (1)	-O(3)	2.57 (1)
-O(2)	2.53 (1)	-O(2)	2.57 (1)	-O(4)	2.59 (1)
-C(1)	2.74 (1)	-C(1)	2.69 (2)	-C(9)	2.71 (1)
-C(2)	2.73 (1)	-C(2)	2.71 (2)	-C(10)	2.70 (2)
-C(3)	2.73 (1)	-C(3)	2.69 (2)	-C(11)	2.73 (2)
-C(4)	2.72 (1)	-C(4)	2.73 (2)	-C(12)	2.72 (2)
-C(5)	2.73 (1)	-C(5)	2.71 (2)	-C(13)	2.74 (2)
-C(6)	2.71 (1)	-C(6)	2.75 (2)	-C(14)	2.73 (2)
-C(7)	2.71 (1)	-C(7)	2.72 (2)	-C(15)	2.75 (2)
-C(8)	2.72 (1)	-C(8)	2.68 (2)	-C(16)	2.70 (2)
C(8)-C(1)	1.40 (2)	C(8)-C(1)	1.40 (2)	C(16)-C(9)	1.40 (3)
C(1)-C(2)	1.35 (2)	C(1)-C(2)	1.35 (2)	C(9)-C(10)	1.40 (3)
C(2)-C(3)	1.41 (2)	C(2)-C(3)	1.37 (3)	C(10)-C(11)	1.38 (2)
C(3)-C(4)	1.39 (2)	C(3)-C(4)	1.39 (3)	C(11)-C(12)	1.43 (2)
C(4)-C(5)	1.38 (2)	C(4)-C(5)	1.34 (2)	C(12)-C(13)	1.40 (2)
C(5)-C(6)	1.39 (2)	C(5)-C(6)	1.38 (3)	C(13)-C(14)	1.41 (2)
C(6)-C(7)	1.41 (2)	C(6)-C(7)	1.43 (3)	C(14)-C(15)	1.39 (2)
C(7)-C(8)	1.39 (2)	C(7)-C(8)	1.38 (3)	C(15)-C(16)	1.37 (2)
C-C(av)	1.39 ± 0.02	C-C(av)	1.38 ± 0.03	C-C(av)	1.40 ± 0.02
O(1)-C(9)	1.44 (1)	O(1)-C(17)	1.48 (2)	O(3)-C(25)	1.45 (2)
-C(12)	1.43 (2)	-C(20)	1.47 (2)	-C(28)	1.42 (2)
O(2)-C(13)	1.46 (1)	O(2)-C(21)	1.44 (2)	O(4)-C(29)	1.45 (2)
-C(16)	1.47 (1)	-C(22)	1.46 (2)	-C(32)	1.43 (2)
C(9)-C(10)	1.46 (2)	C(17)-C(18)	1.48 (2)	C(25)-C(26)	1.48 (3)
C(10)-C(11)	1.48 (2)	C(18)-C(19)	1.43 (3)	C(26)-C(27)	1.47 (3)
C(11)-C(12)	1.40 (3)	C(19)-C(20)	1.49 (2)	C(27)-C(28)	1.51 (3)
C(13)-C(14)	1.50 (2)	C(21)-C(22)	1.46 (2)	C(29)-C(30)	1.52 (3)
C(14)-C(15)	1.45 (2)	C(22)-C(23)	1.46 (3)	C(30)-C(31)	1.39 (3)
C(15)-C(16)	1.49 (2)	C(23)-C(24)	1.49 (2)	C(31)-C(32)	1.47 (2)
Cl(1)-Cl(1)	4.396	Cl(1)-Cl(2)	4.132	Cl(3)-Cl(4)	4.084
O(1)-O(2)	4.635	O(1)-O(2)	4.749	O(3)-O(4)	4.793
Cl(1)-O(1)	3.232	Cl(1)-O(1)	3.280	Cl(3)-O(3)	3.203
Cl(1)-O(2)	3.230	Cl(1)-O(2)	3.248	Cl(3)-O(4)	3.184
Cl(2)-O(1)	3.222	Cl(2)-O(1)	3.241	Cl(4)-O(3)	3.305
Cl(2)-O(2)	3.237	Cl(2)-O(2)	3.177	Cl(4)-O(4)	3.297

[a] Average of six Th-Cl values = 2.686 ± 0.006 Å. Average of six Th-O values = 2.57 ± 0.02 Å. Average of 24 Th-C values = 2.72 ± 0.02 Å. Average of 24 C-C values = 1.39 ± 0.02 Å.

Table IV. Selected Angles (Deg)

α		β(molecule 1)		β(molecule 2)	
atoms	angle	atoms	angle	atoms	angle
Cl(1)-Th-Cl(2)	109.6 (1)	Cl(1)-Th(1)-Cl(2)	100.7 (1)	Cl(3)-Th(2)-Cl(4)	99.0 (3)
O(1)-Th-O(2)	130.6 (2)	O(1)-Th(1)-O(2)	136.0 (3)	O(3)-Th(2)-O(4)	136.5 (3)
Cl(1)-Th-O(1)	75.7 (2)	Cl(1)-Th(1)-O(1)	77.7 (2)	Cl(3)-Th(2)-O(3)	75.1 (3)
Cl(1)-Th-O(2)	76.4 (1)	Cl(1)-Th(1)-O(2)	76.4 (2)	Cl(3)-Th(2)-O(4)	74.4 (2)
Cl(2)-Th-O(1)	75.5 (2)	Cl(2)-Th(1)-O(1)	76.4 (2)	Cl(4)-Th(2)-O(3)	77.8 (2)
Cl(2)-Th-O(2)	76.7 (2)	Cl(2)-Th(1)-O(2)	74.2 (2)	Cl(4)-Th(2)-O(4)	77.3 (2)
Cl(1)-Th-C(5)	83.1 (3)	Cl(1)-Th(1)-C(8)	86.6 (4)	Cl(3)-Th(2)-C(9)	89.5 (4)
Cl(2)-Th-C(1)	84.6 (2)	Cl(2)-Th(1)-C(4)	89.8 (3)	Cl(4)-Th(2)-C(13)	86.9 (3)
O(1)-Th-C(7)	73.0 (4)	O(1)-Th(1)-C(2)	71.9 (3)	O(3)-Th(2)-C(11)	71.2 (4)
O(2)-Th-C(3)	73.2 (3)	O(2)-Th(1)-C(6)	70.2 (4)	O(4)-Th(2)-C(15)	70.1 (4)
C(8)-C(1)-C(2)	135 (1)	C(8)-C(1)-C(2)	131 (2)	C(16)-C(9)-C(10)	133 (2)
C(1)-C(2)-C(3)	136 (1)	C(1)-C(2)-C(3)	138 (2)	C(9)-C(10)-C(11)	135 (2)
C(2)-C(3)-C(4)	134 (1)	C(2)-C(3)-C(4)	135 (2)	C(10)-C(11)-C(12)	137 (2)
C(3)-C(4)-C(5)	136 (1)	C(3)-C(4)-C(5)	134 (2)	C(11)-C(12)-C(13)	133 (2)
C(4)-C(5)-C(6)	135 (1)	C(4)-C(5)-C(6)	137 (2)	C(12)-C(13)-C(14)	134 (2)
C(5)-C(6)-C(7)	135 (1)	C(5)-C(6)-C(7)	133 (2)	C(13)-C(14)-C(15)	136 (2)
C(6)-C(7)-C(8)	135 (1)	C(6)-C(7)-C(8)	134 (2)	C(14)-C(15)-C(16)	134 (2)
C(7)-C(8)-C(1)	135 (1)	C(7)-C(8)-C(1)	138 (2)	C(15)-C(16)-C(9)	138 (2)

method.[7] During refinement, effects of extinction were evident in the data, and an empirical isotropic correction was applied; see Table I. Atomic scattering factors of Cromer and Waber[8] were used for Th, of Doyle and Turner[9] for Cl, O, and C, and of Stewart, Davidson, and Simpson[10] for hydrogen. Anomalous scattering corrections of Cromer and Liberman[11] were applied.

Determination of Structures. Three-dimensional Patterson maps indicated the positions of the Th atoms. Subsequent least-squares

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Table V. Least-Squares Planes and Distances (Å) of Atoms from the Planes

Plane: C(1)–C(8) in the α Compound
$2.367x + 24.583y + 2.336z = 6.542$

C(1)	0.014	C(5)	0.015	Th	−2.03
C(2)	0.004	C(6)	−0.005	Cl(1)	−3.54
C(3)	−0.013	C(7)	−0.001	Cl(2)	−3.62
C(4)	−0.003	C(8)	−0.010	O(1)	−3.09
				O(2)	−3.10

Plane: C(1)–C(8) in the β Compound, Molecule 1
$1.334x + 10.740y + 8.166z = 6.739$

C(1)	−0.028	C(5)	−0.019	Th(1)	−2.02
C(2)	0.045	C(6)	0.023	Cl(1)	−3.66
C(3)	−0.019	C(7)	0.000	Cl(2)	−3.81
C(4)	0.003	C(8)	−0.004	O(1)	−2.98
				O(2)	−2.98

Plane: C(9)–C(16) in the β Compound, Molecule 2
$4.408x + 4.739y + 18.471z = 16.586$

C(9)	−0.018	C(13)	−0.011	Th(2)	−2.02
C(10)	−0.012	C(14)	−0.004	Cl(3)	−3.80
C(11)	0.044	C(15)	0.025	Cl(4)	−3.72
C(12)	−0.021	C(16)	−0.003	O(3)	−2.96
				O(4)	−2.98

refinements and difference Fourier maps readily revealed all of the nonhydrogen atoms. All of the atoms, with the exception of the hydrogen atoms, were assigned anisotropic thermal parameters in the final refinements. For the β compound, because the thermal tensor for one of the C_8H_8 carbon atoms was not positive-definite, the thermal parameters of the opposing carbons in the C_8H_8 ring were constrained to be equal. Hydrogen atom parameters were estimated from the geometry at C–H distances of 0.95 Å and included in the least-squares calculations but not refined. The full-matrix least-squares program minimizes the function $\sum w(\Delta F)^2/\sum wF_o^2$. After the last cycle of refinement the largest shift of a parameter was 0.02 and 0.24 of its esd for the α and the β compound, respectively. *R* factors and other statistical results of the least-squares refinements are given in Table I.

Positional parameters are given in Table II. Tables of the anisotropic thermal parameters, the calculated hydrogen positions, and the lists of observed structure factors are given as supplementary material. Distances and angles are given in Tables III and IV, with atom numbers as in Figure 1.

Discussion

The Th atom is bonded to the cyclooctatetraene (COT) ring, to two chloride ions, and to the oxygen atoms of the two THF molecules; see Figure 1. The COT ring is centrally located on the Th atom with its plane at a distance of 2.02 Å. The chloride ions and THF molecules are alternatively disposed on the opposite side, with Th–Cl and Th–O distances of 2.686 ± 0.006 and 2.57 ± 0.02 Å, respectively. The Cl and the O atoms are very nearly equidistant from the COT plane; see Table V. The comparable Th-to-ring distance in thorocene[5b] is 2.00 Å, and the Th–Cl distances in these structures are just slightly under the 2.72 and 2.90 Å reported for $ThCl_4$.[12] The Cl–Cl vector is orthogonal to the O–O vector (see Figure 2) and both are from 4 to 9° from an eclipsed orientation with the COT carbon atoms.

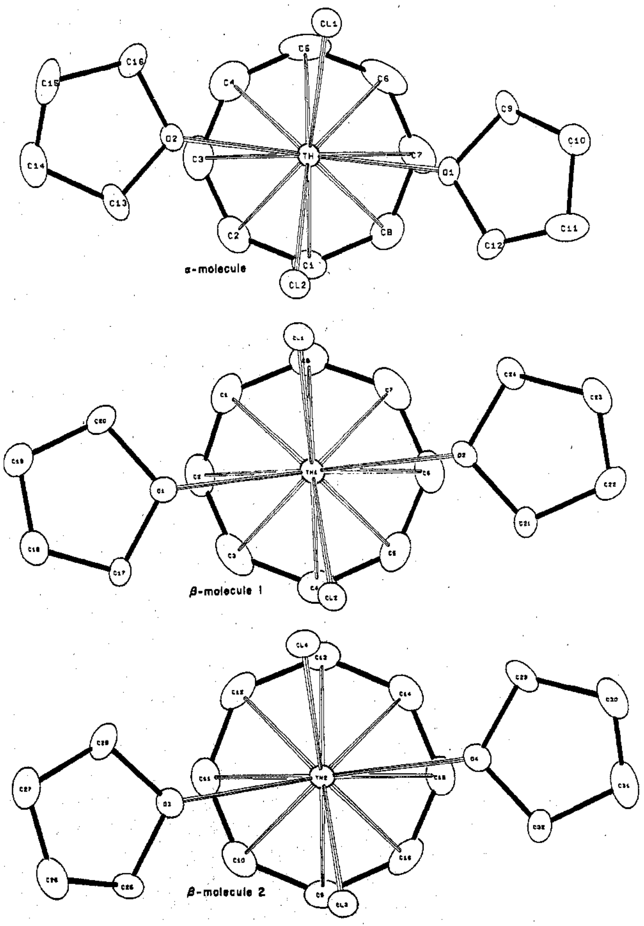

Figure 2. ORTEP drawing perpendicular to the COT ring showing the orientation of the Cl atoms and THF molecules to the COT ring.

The three molecular structures determined in this study are chemically identical with essentially identical bond distances. About the only significant geometrical difference between the α and β forms is the larger Cl–Th–Cl and smaller O–Th–O angles that the α form exhibits, which is probably a packing effect. Nothing in the experiments reported here gives any information concerning what fosters the crystallization of one form rather than the other.

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Registry No. 1, 73652-04-7; thorocene, 12702-09-9.

Supplementary Material Available: A list of anisotropic thermal parameters, a list of estimated hydrogen positional parameters, and a listing of observed structure factors (35 pages). Ordering information is given on any current masthead page.

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(12) Mucker, K.; Smith, G. S.; Johnson, Q.; Elson, R. E. *Acta Crystallogr., Sect. B* **1969**, *B25*, 2362.