The cation dimensions are similar to those in $[(Ph_3P)_2N][HOs_5(CO)_{15}]$ (Guy & Sheldrick, 1978*b*), with staggered PPh_3 groups.

We thank the Science Research Council for financial support. The calculations were performed on the Cambridge University IBM 370/165 computer with programs written by Dr G. M. Sheldrick; the figure was drawn with *PLUTO* written by Dr W. D. S. Motherwell.

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Tetrakis(acetylacetonato)thorium(IV) Hemibenzene

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Abstract. $Th(C_5H_7O_2)_4.\frac{1}{2}C_6H_6$, triclinic, $P\bar{1}$, a = 11·591 (4), b = 14·153 (2), c = 9·229 (3) Å, α = 94·20 (2), β = 106·50 (2), γ = 113·51 (2)°, FW = 667·6, Z = 2, D_x = 1·670 Mg m^{-3}, R = 0·037, 4181 observed reflections. The inner coordination polyhedron around the Th atom is a square antiprism (D_{4d}-$\bar{8}2m$). Of the four acetylacetonate ligands, two have a fold angle of about 16° over the line joining the two O atoms within the ligand, while the corresponding angle for the remaining two ligands is close to 3°.

Introduction. During investigations of the coordination of Th in chelate complexes with β-diketones, the title compound has been synthesized and its structure investigated. A preliminary structure analysis, with the results of IR measurements, has been published (Allard, 1976). This is the only reported organic solvate of a tetravalent metal acetylacetonate. It is of interest to find out if the benzene molecules influence the coordination around Th.

The complex, $Th(AA)_4$, was precipitated by mixing aqueous solutions of $Th(NO_3)_4$, ammonia and acetylacetone. The precipitate was recrystallized from benzene at room temperature.

The diffraction data were collected on a Syntex $P2_1$ computer-controlled four-circle diffractometer. The parameters of the cell were determined by a least-squares procedure from the coordinates of 15 reflections. The intensities of 4501 independent reflections were measured up to 2θ = 50° with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·71069 Å). A standard reflection, measured after every 25 reflections, gave no indication of crystal decay. The intensities were corrected for Lorentz and polarization effects but not for absorption. 4181 reflections had intensities $>3\sigma$. The Th atom was located from a Patterson synthesis and the remaining non-hydrogen atoms by a subsequent Fourier synthesis. The structure was refined by a block-diagonal least-squares method (Lindgren, 1977) with anisotropic thermal parameters and an overall scale factor. The final R was 0·037. Scattering factors were those of Doyle & Turner (1968) for C and O, and for Th those of Cromer & Waber (1965). Correction for the real part of the anomalous dispersion was made (*International Tables for X-ray Crystallography*, 1962). Atomic positions are given in Table 1.* The structure factors were weighted according to $w = (a + F_o + cF^2_o)^{-1}$ (Cruickshank, 1965) with a = 80·0 and c = 0·003.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publications No. SUP 33922 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* ($\times 10^5$) *for* $Th(AA)_4.\frac{1}{2}C_6H_6$

	x	*y*	*z*
Th	−1466 (2)	24758 (2)	23949 (3)
O(1)	−24149 (55)	18900 (52)	17916 (74)
O(2)	−9341 (53)	34478 (47)	6733 (67)
O(3)	−10190 (61)	11798 (45)	448 (66)
O(4)	−6675 (62)	7729 (47)	29292 (71)
O(5)	16184 (53)	30668 (52)	12982 (71)
O(6)	19428 (54)	26262 (49)	41866 (72)
O(7)	10336 (60)	42848 (47)	37909 (66)
O(8)	−4688 (57)	26219 (52)	48302 (65)
C(1)	−48551 (105)	14333 (122)	9138 (180)
C(2)	−34607 (83)	20752 (86)	9071 (114)
C(3)	−32536 (91)	28267 (86)	−150 (119)
C(4)	−20150 (81)	34695 (73)	−719 (96)
C(5)	−19306 (111)	42699 (90)	−10929 (137)
C(6)	−20335 (102)	−2450 (83)	−21243 (114)
C(7)	−14927 (75)	1983 (76)	−3834 (106)
C(8)	−16153 (83)	−4985 (72)	6238 (114)
C(9)	−12295 (82)	−1874 (72)	22072 (116)
C(10)	−14703 (131)	−10065 (89)	31991 (156)
C(11)	35497 (104)	38634 (106)	5913 (156)
C(12)	28791 (81)	34722 (76)	17712 (117)
C(13)	36832 (92)	35883 (91)	32560 (140)
C(14)	31660 (90)	31451 (79)	44129 (124)
C(15)	41369 (124)	32845 (116)	60259 (157)
C(16)	24687 (109)	59187 (85)	55942 (131)
C(17)	14878 (85)	47540 (74)	52026 (108)
C(18)	11401 (95)	42836 (86)	63794 (105)
C(19)	1699 (83)	32549 (87)	61370 (96)
C(20)	−2129 (121)	28190 (109)	74867 (124)
C(21)	60745 (153)	6584 (133)	46718 (204)
C(22)	56875 (162)	10341 (138)	57947 (194)
C(23)	53656 (151)	−3989 (156)	38849 (181)

Discussion. A stereoscopic view (*ORTEP*, Johnson, 1965) of the cell is shown in Fig. 1, where the benzene molecules, of which only half of each belongs to the cell, are completed. The O coordination polyhedron of the $Th(AA)_4$ molecule is a near-perfect square antiprism (D_{4d}–$\bar{8}2m$). The angle between the two square planes of the antiprism is 3·3°, compared with the ideal value of 0°; the angles at the corners of the squares are all very close to 90°. Fig. 2 shows the coordination polyhedron around the Th atom. The ligand attachment in the notation of Hoard & Silverton (1963) is II*a*–*ssss*, with an average bite distance of 2·732 Å.

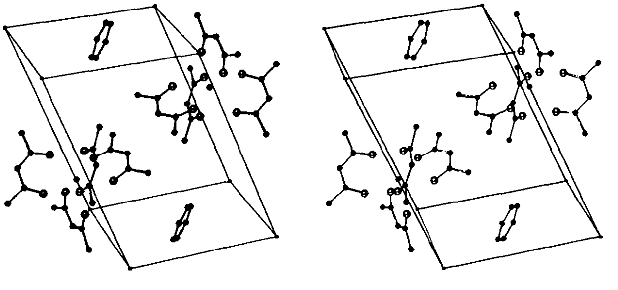

Fig. 1. A stereoview of the unit cell.

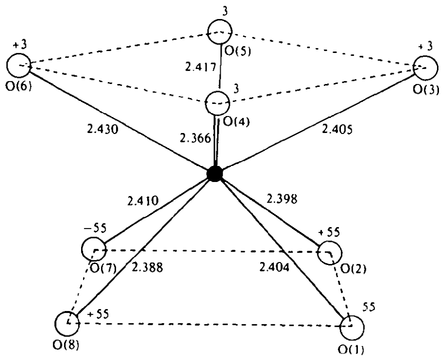

Fig. 2. The oxygen coordination in $Th(AA)_4.\frac{1}{2}C_6H_6$ with the bond lengths (Å) and the deviations from the least-squares planes (Å $\times 10^3$).

The geometry of the AA ligands is shown in Fig. 3, which also includes the numbering of the atoms. Bond distances and angles are given in Table 2. The acetylacetonate ligands show the expected geometry, with C–CH and C–O bonds of marked double-bond character. The ligand rings are nearly planar, and folded over the O···O line from the plane of the Th atom with the two O atoms of each ligand, as is common in this type of compound. This fold angle is usually, within a few degrees, of the same order of magnitude for all the four ligands in related compounds (Allard, 1972; Soling, 1975, 1976). For this compound, however, two of the acetylacetonate ligands exhibit a fold angle of about 3°, while the remaining two ligands are folded

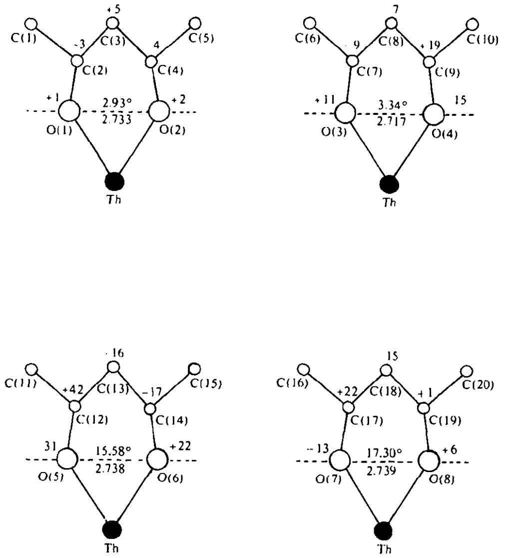

Fig. 3. The numbering of the atoms in the four AA ligands. The deviations (Å $\times 10^3$) from the least-squares planes for the atoms of the five-membered ligand rings are given. The ligand bite distances (Å) and the magnitudes of the fold over the O···O line in each ligand are noted.

Table 2. *Bond distances* (Å) *and angles* (°)

Th–O(1)	2·404 (5)	C(6)–C(7)	1·528 (14)
Th–O(2)	2·398 (6)	C(7)–C(8)	1·398 (13)
Th–O(3)	2·405 (6)	C(8)–C(9)	1·381 (14)
Th–O(4)	2·366 (6)	C(9)–C(10)	1·517 (16)
Th–O(5)	2·417 (6)	C(11)–C(12)	1·524 (16)
Th–O(6)	2·430 (6)	C(12)–C(13)	1·376 (15)
Th–O(7)	2·410 (6)	C(13)–C(14)	1·433 (15)
Th–O(8)	2·388 (6)	C(14)–C(15)	1·533 (17)
O(1)–C(2)	1·300 (11)	C(16)–C(17)	1·525 (14)
O(2)–C(4)	1·260 (10)	C(17)–C(18)	1·388 (13)
O(3)–C(7)	1·255 (11)	C(18)–C(19)	1·392 (15)
O(4)–C(9)	1·277 (11)	C(19)–C(20)	1·529 (14)
O(5)–C(12)	1·260 (10)		
O(6)–C(14)	1·254 (11)		
O(7)–C(17)	1·273 (11)	C(21)–C(22)	1·390 (24)
O(8)–C(19)	1·269 (11)	C(21)–C(23)	1·401 (26)
C(1)–C(2)	1·508 (14)	C(22)–C(23)	1·324 (23)
C(2)–C(3)	1·399 (15)	C(21)–O(1)	3·695 (18)
C(3)–C(4)	1·378 (13)	C(22)–C(6)	3·923 (20)
C(4)–C(5)	1·517 (15)	C(23)–C(1)	3·935 (24)

O(1)–O(2)–O(7)	88·2 (2)	O(1)–C(2)–C(3)	124·2 (8)
O(2)–O(1)–O(8)	91·8 (2)	C(2)–C(3)–C(4)	123·8 (9)
O(1)–O(8)–O(7)	88·4 (2)	C(3)–C(4)–O(2)	124·8 (8)
O(2)–O(7)–O(8)	91·3 (2)	O(3)–C(7)–C(8)	124·0 (9)
O(3)–O(4)–O(6)	91·4 (2)	C(7)–C(8)–C(9)	124·0 (9)
O(4)–O(3)–O(5)	89·0 (2)	C(8)–C(9)–O(4)	124·0 (9)
O(3)–O(5)–O(6)	90·2 (2)	O(5)–C(12)–C(13)	125·2 (9)
O(4)–O(6)–O(5)	89·4 (2)	C(12)–C(13)–C(14)	123·0 (8)
O(1)–Th–O(2)	69·4 (2)	C(13)–C(14)–O(6)	123·8 (9)
O(3)–Th–O(4)	69·4 (2)	O(7)–C(17)–C(18)	124·7 (9)
O(5)–Th–O(6)	68·8 (2)	C(17)–C(18)–C(19)	123·8 (9)
O(7)–Th–O(8)	69·6 (2)	C(18)–C(19)–O(8)	124·4 (8)

approximately 16°. This uncommon feature might be due to the presence of the benzene molecules in the crystal. The distances between the benzene C atoms and the rigid C–CH–C parts of the AA ligands show that the C_6H_6 molecule is somewhat closer to ligands 1 and 2 although none of these intramolecular distances is <3·7 Å.

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Structure du [1–6-η-(Benzoate de méthyle)]dicarbonylsélénocarbonylchrome*

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Abstract. $Cr(C_8H_8O_2)(CO)_2(CSe)$, $C_{11}H_8CrO_4Se$, triclinic, $P\bar{1}$, $a = 7{\cdot}259$ (3), $b = 10{\cdot}519$ (7), $c = 8{\cdot}536$ (5) Å, $\alpha = 89{\cdot}50$ (6), $\beta = 96{\cdot}00$ (4), $\gamma = 105{\cdot}10$ (6)°, $Z = 2$, $d_x = 1{\cdot}78$ Mg m^{-3}. The structure was solved by the direct method. Full-matrix least-squares refinement converged at $R = 0{\cdot}111$ and $R'' = 0{\cdot}108$ for 2135 independent reflexions. It is shown that CSe is a stronger ligand than CS and CO.

Introduction. Cette structure se situe dans le cadre de l'étude de composés du type $CH_3CO_2(C_6H_5)Cr(CO)_2(CX)$ (X = O, S, Se), les structures correspondant à X = O et S ayant été déjà publiées (Carter, McPhail & Sim, 1967; Saillard & Grandjean, 1976; Saillard, Le Borgne & Grandjean, 1975). Les échantillons étudiés ont été préparés suivant la méthode de Butler, Cozak & Stobart (1975). 4239 réflexions ont été mesurées sur diffractomètre Nonius CAD-4 avec: anticathode Mo, monochromateur au graphite, balayage

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* Etude Structurale de Dérivés du Chrome (0). V.