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The Crystal Structure of Cerium(IV) Acetylacetonate

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The atomic co-ordinates of cerium(IV) acetylacetonate have been obtained by the heavy-atom method with the help of electron-density projections along [010] and [100] making use of the isomorphism to the analogous thorium compound. The co-ordination polyhedron of oxygen atoms around the cerium atom is a slightly distorted Archimedean antiprism, the Ce–O distance being 2·40 ± 0·03 Å and the O–Ce–O bond angle 72 ± 1°. The atoms of the acetylacetonate ring are coplanar. The mean values of the O · · · O distances within an acetylacetonate ring are 2·81 Å, and the distances between the adjacent rings are 2·95 and 2·97 Å along the edge of the triangular or square faces, respectively.

Introduction

Recent results in the series of acetylacetonates of quadrivalent metals defined by formula $M^{\mathrm{iv}}(C_5H_7O_2)_4$, where M^{iv} = Zr, Ce, Th, U, Pu, may be summarized as follows:

(i) Thorium(IV) acetylacetonate is dimorphic. In the α-modification it is isomorphous with cerium(IV) and uranium(IV) acetylacetonates, but in the β-modification with zirconium(IV) acetylacetonate. The occurrence of two crystallographic modifications has been explained by different packing arrangements of the otherwise identically built molecules (Grdenić & Matković, 1959). These results should be valid also for plutonium(IV), since its acetylacetonate is isomorphous with β-thorium acetylacetonate (Comyns, 1960).

(ii) Thorium(IV) acetylacetonate, as established by means of structure analysis of its α-modification (Grdenić & Matković, 1958), consists of molecules in which a thorium atom is surrounded by eight oxygen atoms in a nearly regular Archimedean antiprism. The complex belongs to the isomer with the symmetry D_2 (among three possible isomers involving plane chelate rings) in which the square edges of the antiprism are bridged by the acetylacetone rings.

(iii) Octaco-ordination in cerium(IV) tetradibenzoylmethane is effected in a trigonal dodecahedron (Wolf & Bärnighausen, 1960) which proves that the Archimedean antiprism as a co-ordination polyhedron is not a fixed property of these metals, but is liable to alteration under the influence of structural details not understandable so far.

The closeness of crystallographic constants for isomorphous cerium, thorium and uranium acetylacetonates (α-modification) permits a common treatment of the stereochemistry of these compounds on the basis of the structure analysis of only one of them. Although the structure analysis of the thorium compound (Grdenić & Matković, 1958) gave all necessary information, the high atomic number of thorium had prevented the attainment of a desirable accuracy of the light-atom parameters. For this reason the structure analysis of isomorphous cerium(IV) acetylacetonate was undertaken. It made a satisfactory location of oxygen and carbon atoms possible, as seen from the results which are reported in the present paper.

Experimental

Single crystals of cerium(IV) acetylacetonate were obtained directly from the reaction mixture (Job & Goissedet, 1913). The crystallographic data are those as reported in a previous paper (Grdenić & Matković, 1959), *i.e.*

$$a = 11{\cdot}70,\ b = 12{\cdot}64,\ c = 16{\cdot}93\ \text{Å};\ \beta = 112°\ 15'.$$

Measured density: $D_m = 1{\cdot}53$ g.cm^{-3}.
Number of molecules in the unit cell: $Z = 4$ (calculated density: $D_x = 1{\cdot}54$ g.cm^{-3}).
Space group: C_{2h}^5–$P2_1/c$ (from systematically absent reflexions: $h0l$ with l odd, $0k0$ with k odd).

Particular attention was paid to the absorption correction ($\mu = 171$ cm^{-1}). For this purpose the specimens intended for the determination of the intensity of reflexions were made cylindrical by grinding in a jet of dolomite powder applied tangentially to the rotating crystal (Pepinsky, 1953). Two cylindrical specimens (along [100] and [010] axes) were chosen and used for collecting the intensity data on multiple-film integrating Weissenberg photographs (Cu $K\alpha$-radiation). Both specimens, along [100] and along [010], were adequately thin, with a diameter of 0·14 mm and 0·17 mm, respectively.

The relative intensities were determined from the optical densities measured at the centre of each spot by means of a microdensitometer. The corrections for absorption and for polarization and Lorentz factors were made in the usual way.

Structure determination

The [010] and [100] projections of the electron density distribution were computed using signs defined only by the cerium-atom position, the co-ordinates being taken as those found for thorium in the isomorphous thorium compound (Grdenić & Matković, 1958), *i.e.* $x=0{\cdot}191$, $y=0{\cdot}146$, $z=0{\cdot}200$. Both projections (Figs. 1 and 2) gave a sharp cerium peak; the light-atom peaks were partly well resolved but partly concealed in broad maxima. All these peaks were much better defined than in the corresponding projections for thorium acetylacetonate.

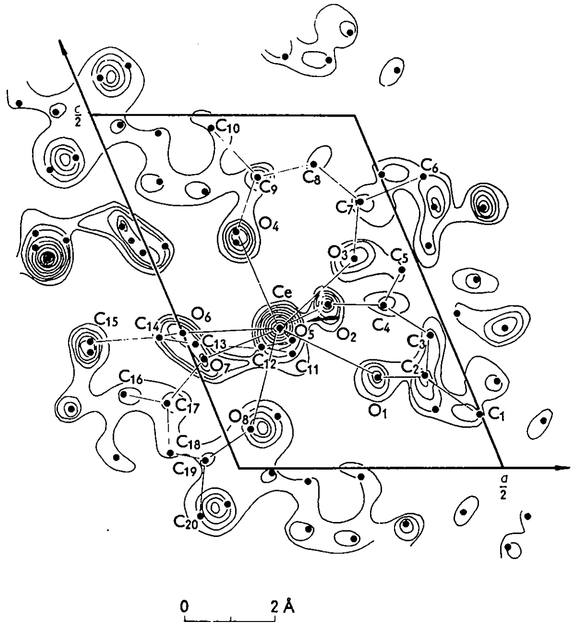

Fig. 1. Electron-density projection on (010) with the acetylacetonate rings projected on the same plane. The contours are drawn at intervals of 2 e.Å^{-2} with the lowest contour at 5 e.Å^{-2}, except round the cerium atom where the contours are taken at arbitrary intervals.

The molecules are oriented in the crystal structure in such a way that the plane of one of four chelate rings is almost parallel to the (010) plane. All atoms O_3, C_7, C_8, C_9, O_4 belonging to this ring are well resolved in the [010] projection. The bond lengths and angles obtained from the position of these peaks were used for the location of those light atoms whose peaks were not resolved in either projection. The position of one oxygen (O_5) and two carbon (C_{11} and C_{12}) atoms, whose maxima were overlapped by the cerium atom in the [010] projection, were determined from the [100] projection and from difference Fourier synthesis [010] (Fig. 3). The final atomic co-ordinates of all atoms, except hydrogen, are given in Table 1.

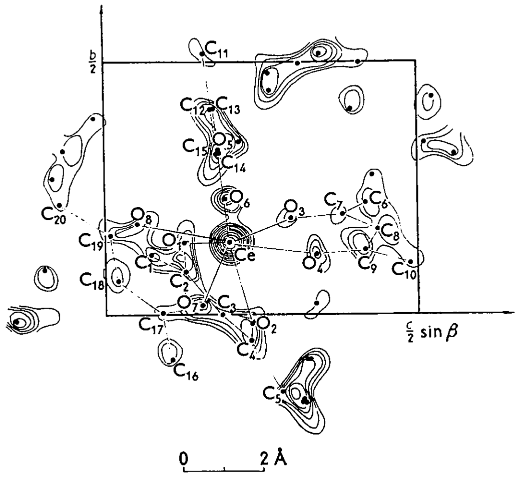

Fig. 2. Electron-density projection on (100) with the acetylacetonate rings projected on the same plane. The contours are drawn at intervals of 2 e.Å^{-2} with the lowest contour at 5 e.Å^{-2}, except round the cerium atom where the contours are taken at arbitrary intervals.

Table 1. *Atomic co-ordinates expressed as fractions of unit-cell edges*

	x	*y*	*z*
Ce	0·190	0·145	0·200
O_1	0·332	0·145	0·128
O_2	0·300	−0·019	0·235
O_3	0·387	0·192	0·299
O_4	0·188	0·121	0·338
O_5	0·211	0·330	0·184
O_6	0·005	0·232	0·194
O_7	0·022	0·018	0·155
O_8	0·054	0·182	0·054
C_1	0·497	0·120	0·075
C_2	0·425	0·085	0·130
C_3	0·466	−0·001	0·187
C_4	0·404	−0·052	0·233
C_5	0·466	−0·154	0·282
C_6	0·581	0·225	0·416
C_7	0·442	0·200	0·380
C_8	0·386	0·170	0·435
C_9	0·268	0·129	0·416
C_{10}	0·221	0·102	0·486
C_{11}	0·194	0·521	0·163
C_{12}	0·139	0·412	0·173
C_{13}	0·019	0·412	0·177
C_{14}	−0·045	0·323	0·186
C_{15}	−0·180	0·321	0·180
C_{16}	−0·158	−0·090	0·106
C_{17}	−0·082	0·002	0·093
C_{18}	−0·119	0·067	0·021
C_{19}	−0·056	0·158	0·009
C_{20}	−0·114	0·222	−0·073

The cerium atom co-ordinates differed so slightly from the preliminary values that the difference was without any influence on the sign of the structure factors. The comparison between F_o and F_c is given

Table 2. *Observed and calculated structure factors*

$h0l$

$h\ l$	F_o	F_c	$h\ l$	F_o	F_c	$h\ l$	F_o	F_c	$h\ l$	F_o	F_c
1 0	151	139	12 2	< 8	−15	11 6	< 6	−4	3 12	85	67
2 0	64	−49	13 2	< 6	10	0 8	144	−175	4 12	64	54
3 0	173*	−178	0 4	< 16	−4	1 8	30	−10	5 12	20	−26
4 0	32	29	1 4	221*	216	2 8	99	84	6 12	46	−39
5 0	192*	212	2 4	68	72	3 8	55	49	7 12	< 8	−7
6 0	73	94	3 4	118	−117	4 8	84	−84	8 12	29	36
7 0	55	−45	4 4	112	−119	5 8	103	−112	0 14	34	18
8 0	120	110	5 4	< 15	−13	6 8	< 11	−19	1 14	78	53
9 0	31	−23	6 4	86	67	7 8	74	47	2 14	54	51
10 0	76	70	7 4	61	47	8 8	29	21	3 14	47	−34
11 0	47	40	8 4	< 11	−23	9 8	21	−18	4 14	44	−38
12 0	< 8	−15	9 4	63	−60	10 8	38	−36	5 14	< 8	−1
13 0	39	−38	10 4	< 6	−2	0 10	131	135	6 14	33	25
14 0	< 12	−17	11 4	49	31	1 10	< 27	34	7 14	< 12	16
0 2	241*	−245	12 4	31	18	2 10	57	−27	0 16	< 16	32
1 2	137*	−133	0 6	82	102	3 10	69	−71	1 16	49	−30
2 2	69	49	1 6	62	−16	4 10	< 11	−11	2 16	47	−33
3 2	112	130	2 6	152	−170	5 10	88	86	3 16	< 8	11
4 2	24	24	3 6	26	12	6 10	34	24	4 16	36	41
5 2	138	−145	4 6	133	141	7 10	34	−22	5 16	19	30
6 2	138	−158	5 6	86	98	8 10	53	−44	0 18	31	−33
7 2	44	−54	6 6	30	−4	9 10	< 6	5	1 18	< 6	7
8 2	85	84	7 6	93	−89	0 12	72	−43	2 18	34	34
9 2	69	47	8 6	< 16	−20	1 12	45	−20	3 18	< 12	8
10 2	51	−65	9 6	58	59	2 12	28	14	0 20	22	19
11 2	63	−60	10 6	43	34						

$h0\bar{l}$

$h\ l$	F_o	F_c	$h\ l$	F_o	F_c	$h\ l$	F_o	F_c	$h\ l$	F_o	F_c
1 2	92	94	8 6	69	−49	12 10	< 8	−5	3 16	35	−31
2 2	158	174	9 6	83	−69	13 10	36	−20	4 16	71	−70
3 2	101	87	10 6	36	−23	14 10	15	−17	5 16	< 16	−2
4 2	89	−116	11 6	62	51	15 10	< 12	15	6 16	58	48
5 2	185*	−194	12 6	36	32	1 12	< 25	28	7 16	48	46
6 2	65	−60	13 6	26	−16	2 12	84	62	8 16	37	−32
7 2	96	100	14 6	26	−32	3 12	< 25	−3	9 16	49	−50
8 2	78	75	15 6	< 12	−7	4 12	85	−77	10 16	10	−19
9 2	48	−30	1 8	161	−166	5 12	107	−90	11 16	28	10
10 2	67	−40	2 8	25	−10	6 12	< 25	−7	12 16	33	41
11 2	27	−26	3 8	186	179	7 12	69	72	13 16	< 6	5
12 2	49	40	4 8	92	58	8 12	47	36	1 18	34	−22
13 2	41	29	5 8	89	−103	9 12	50	−27	2 18	< 6	−2
14 2	< 6	−3	6 8	122	−123	10 12	67	−50	3 18	48	40
1 4	173*	−192	7 8	< 25	19	11 12	< 7	−13	4 18	26	22
2 4	171	−176	8 8	81	59	12 12	42	35	5 18	34	−31
3 4	88	96	9 8	92	112	13 12	31	26	6 18	52	−51
4 4	168*	171	10 8	40	−52	14 12	< 6	3	7 18	< 6	−12
5 4	84	53	11 8	95	−75	1 14	82	−86	8 18	28	21
6 4	70	−90	12 8	20	−9	2 14	85	−80	9 18	25	18
7 4	117	−128	13 8	31	33	3 14	38	30	10 18	< 8	−19
8 4	< 25	2	14 8	36	45	4 14	83	64	11 18	28	−35
9 4	73	49	15 8	< 12	−1	5 14	53	25	12 18	< 6	−23
10 4	59	54	1 10	59	41	6 14	52	−56	1 20	7	12
11 4	30	−39	2 10	121	−120	7 14	81	−72	2 20	14	−12
12 4	67	−71	3 10	127	−146	8 14	< 16	27	3 20	31	−27
13 4	13	−9	4 10	44	42	9 14	57	45	4 20	< 8	18
14 4	22	10	5 10	103	89	10 14	48	51	5 20	36	39
1 6	202	217	6 10	87	67	11 14	< 6	−4	6 20	21	24
2 6	121	118	7 10	45	−49	12 14	40	−40	7 20	14	−24
3 6	160*	−155	8 10	52	−51	13 14	11	−19	8 20	27	−31
4 6	114	−101	9 10	40	−42	14 14	23	25	9 20	< 6	−13
5 6	94	121	10 10	56	32	1 16	49	40	10 20	16	24
6 6	136	161	11 10	58	41	2 16	49	36	11 20	< 12	23
7 6	82	75									

Table 2 (*cont.*)

0*kl*

k l	F_o	F_c
2 0	42	−57
4 0	188*	−189
6 0	158*	171
8 0	79	66
10 0	51	−64
12 0	<20	18
14 0	49	52
16 0	<13	−17
1 1	68	84
2 1	195*	−188
3 1	<6	−1
4 1	95	114
5 1	11	5
6 1	106	109
7 1	48	50
8 1	84	−81
9 1	<13	−11
10 1	48	−63
11 1	<17	−23
12 1	62	68
13 1	21	28
14 1	<14	0
15 1	<16	12
16 1	24	−39
0 2	241*	−246
1 2	120*	−121
2 2	20	1
3 2	55	−83
4 2	55	73
5 2	100	117
6 2	115	−113
7 2	<13	−26
8 2	56	−52
9 2	61	−56
10 2	55	68
11 2	<17	50
12 2	<20	−2
13 2	<16	9
14 2	38	−38
15 2	<16	−26
16 2	<13	13
1 3	65	−57
2 3	61	−35
3 3	34	3
4 3	49	−30
5 3	<6	32
6 3	41	−58
7 3	102	−120
8 3	35	19
9 3	<13	−7
10 3	<17	16
11 3	70	66
12 3	57	−46
13 3	48	−48
14 3	<14	6
15 3	<16	−17
16 3	<13	20
0 4	<6	−3
1 4	213*	236
2 4	34	−12
3 4	49	40
4 4	31	−28
5 4	118	−139
6 4	38	33
7 4	<13	0
8 4	<13	−1
9 4	83	83
10 4	39	−43
11 4	42	−61
12 4	<20	0
13 4	27	−24
14 4	<14	9
15 4	31	46
16 4	<13	−4
1 5	52	51
2 5	44	−21
3 5	88	−81
4 5	38	43
5 5	<13	3
6 5	<13	14
7 5	107	114
8 5	<13	17
9 5	42	−26
10 5	<17	39
11 5	67	−92
12 5	<16	−3
13 5	46	47
14 5	<14	2
15 5	<16	25
0 6	82	103
1 6	161*	−170
2 6	<6	5
3 6	44	−38
4 6	52	−64
5 6	131	138
6 6	<13	32
7 6	<13	−10
8 6	<13	8
9 6	60	−69
10 6	<17	−16
11 6	52	47
12 6	<16	15
13 6	25	30
14 6	<14	7
15 6	27	−30
1 7	72	−77
2 7	70	−79
3 7	83	87
4 7	<13	6
5 7	<13	20
6 7	<13	32
7 7	69	−72
8 7	54	−52
9 7	<17	−7
10 7	<20	−33
11 7	51	46
12 7	33	32
13 7	24	−42
14 7	<16	−4
15 7	<13	−15
0 8	145	−178
1 8	60	28
2 8	79	87
3 8	<13	26
4 8	79	79
5 8	89	−93
6 8	65	−81
7 8	<13	−16
8 8	35	−32
9 8	65	60
10 8	48	45
11 8	<16	−19
12 8	<16	−5
13 8	24	−22
14 8	29	−24
15 8	<13	15
1 9	71	74
2 9	85	84
3 9	45	−34
4 9	67	−58
5 9	<13	−29
6 9	65	−63
7 9	<17	35
8 9	64	62
9 9	<20	−17
10 9	45	41
11 9	<16	−10
12 9	49	−54
13 9	<14	18
14 9	<14	−1
0 10	126	142
1 10	<13	1
2 10	61	−60
3 10	<13	4
4 10	96	−96
5 10	<13	12
6 10	62	58
7 10	<17	10
8 10	35	39
9 10	<20	−19
10 10	46	−56
11 10	<16	9
12 10	<14	4
13 10	<16	13
14 10	24	40
1 11	<13	−14
2 11	93	−96
3 11	23	−4
4 11	57	46
5 11	<17	−1
6 11	52	40
7 11	<17	34
8 11	57	−41
9 11	<20	5
10 11	<16	−10
11 11	<14	−20
12 11	46	55
13 11	<16	16
0 12	74	−51
1 12	59	−63
2 12	45	44
3 12	<17	−5
4 12	66	66
5 12	46	40
6 12	55	−45
7 12	<20	—16
8 12	<16	−10
9 12	34	−36
10 12	44	46
11 12	<14	26
12 12	<16	2
13 12	<13	12
1 13	39	−36
2 13	65	69
3 13	62	63
4 13	30	−36
5 13	35	30
6 13	<20	−23
7 13	58	−54
8 13	<16	28
9 13	<16	5
10 13	<14	−8
11 13	32	35
12 13	<16	−15
0 14	35	21
1 14	79	82
2 14	<20	−16
3 14	51	35
4 14	<20	−24
5 14	67	−63
6 14	<16	16
7 14	<16	−1
8 14	<16	17
9 14	41	54
10 14	<16	−21
11 14	<16	−23
1 15	36	44
2 15	<20	−20
3 15	72	−75
4 15	<16	−10
5 15	<16	−21
6 15	<16	5
7 15	51	54
8 15	<14	−1
9 15	<16	−8
10 15	<16	0
0 16	<16	34
1 16	43	−41
2 16	<16	−24
3 16	36	−31
4 16	<16	−21
5 16	48	44
6 16	<14	5
7 16	<14	−5
8 16	<16	−5
9 16	29	−47
10 16	<13	−9
1 17	<16	−29
2 17	41	−43
3 17	34	39
4 17	<14	10
5 17	<14	7
6 17	<16	9
7 17	31	−32
8 17	<16	−13
0 18	41	−41
1 18	<14	14
2 18	<14	15
3 18	<14	4
4 18	29	25
5 18	<16	−16
6 18	<16	−19
7 18	<13	5
1 19	<16	4
2 19	<16	38
3 19	<16	−20
4 19	<16	−18
5 19	<13	1
0 20	22	27
1 20	<13	5
2 20	<13	−9

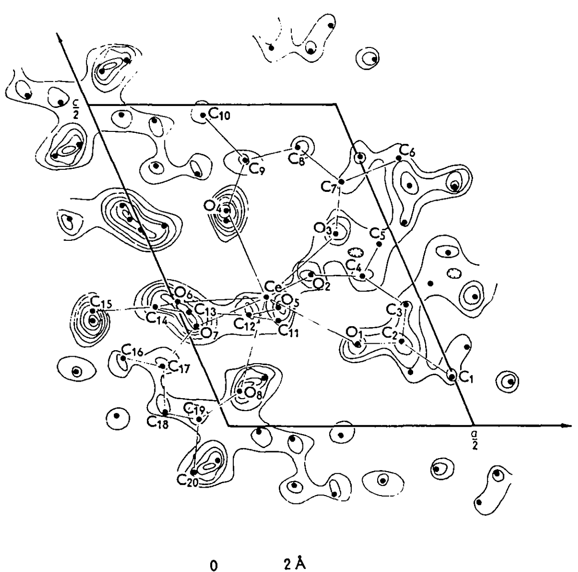

Fig. 3. Electron-density projection on (010), difference map, with the acetylacetonate rings projected on the same plane. The contours are drawn at intervals of 2 e.Å^{-2} with the lowest contour at 5 e.Å^{-2}.

in Table 2. For evaluating F_c the atomic scattering factors from *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) were used. The following temperature factors were obtained: $B=3\cdot1$ Å^2 for $F(h0l)$ and $B=2\cdot5$ Å^2 for $F(0kl)$ for cerium, and $B=3\cdot1$ Å^2 for the light atoms. The values of B were obtained both by Wilson's method (1942) and from the ratios of the observed structure factors to those calculated using the cerium contributions only. For the $h0l$ reflexions both methods gave almost the same value of B, while for the $0kl$ reflexions there was a small difference; the mean value was taken. The extinction correction was necessary only for some of the strongest reflexions (denoted in Table 2 by an asterisk) and it was applied according to the method described by Pinnock, Taylor & Lipson (1956).

The reliability indices $R(h0l)$ and $R(0kl)$, with $R=\Sigma||F_o|-|F_c||/\Sigma F_o$, included the unobserved reflexions; as proposed by Hamilton (1955), each unobserved structure factor which was estimated according to this method but which was weaker than or equal to the calculated value F_c was not used. The values obtained in this way are: $R(h0l)=0\cdot16$, $R(0kl)=0\cdot17$. When the calculated structure factors are based on the heavy atom only, the values for the reliability indices are: $R(h0l)=0\cdot25$, $R(0kl)=0\cdot29$. It is interesting that all but four weak structure factors have the sign of the cerium atom contribution although only 21·5% of the total number of electrons in the structure belongs to cerium.

From the comparison of the present data with the data obtained for thorium(IV) acetylacetonate, as well as for the acetylacetonates of other heavy metals, the accuracy of the Ce–O bond length is estimated to be ±0·03 Å. The accuracy of the co-ordinates of the C-atoms is also satisfactory since they give correctly the general position and orientation of the molecule with the values of C–C and C–O distances and relevant angles as expected according to the known stereochemical facts.

Description of the structure

The interatomic distances and bond angles which resulted from the co-ordinates in Table 1 are listed in Tables 3, 4 and 5. The geometry of the co-ordination polyhedron is best understood from Table 3, since the edges of the antiprism, which in ideal cases should be equal, are actually defined by the oxygen-to-oxygen distances. The observed values are classified as (*b*) the O · · · O distances within an acetylacetonate ring, with the mean values of 2·81 Å, (*c*) the O · · · O distances between two adjacent rings along the edge

Table 3. *The bond lengths in the co-ordination polyhedron*

(*a*)	(*b*)	(*c*)	(*d*)
$Ce–O_1=2\cdot40$ Å	$O_1–O_2=2\cdot87$ Å	$O_1–O_8=3\cdot05$ Å	$O_1–O_3=2\cdot78$ Å
$Ce–O_2=2\cdot39$	$O_3–O_4=2\cdot80$	$O_2–O_7=3\cdot05$	$O_1–O_5=3\cdot06$
$Ce–O_3=2\cdot36$	$O_5–O_6=2\cdot77$	$O_3–O_5=2\cdot84$	$O_2–O_3=2\cdot91$
$Ce–O_4=2\cdot37$	$O_7–O_8=2\cdot80$	$O_4–O_6=2\cdot92$	$O_2–O_4=3\cdot10$
$Ce–O_5=2\cdot38$			$O_4–O_7=3\cdot24$
$Ce–O_6=2\cdot40$			$O_5–O_8=2\cdot94$
$Ce–O_7=2\cdot43$			$O_6–O_8=2\cdot72$
$Ce–O_8=2\cdot43$			$O_6–O_7=2\cdot81$

Table 4. *The bond lengths in the acetylacetonate ring*

$C_1–C_2=1\cdot54$ Å	$C_2–C_3=1\cdot41$ Å	$O_1–C_2=1\cdot32$ Å
$C_4–C_5=1\cdot56$	$C_3–C_4=1\cdot41$	$O_2–C_4=1\cdot30$
$C_6–C_7=1\cdot54$	$C_7–C_8=1\cdot38$	$O_3–C_7=1\cdot28$
$C_9–C_{10}=1\cdot52$	$C_8–C_9=1\cdot39$	$O_4–C_9=1\cdot30$
$C_{11}–C_{12}=1\cdot56$	$C_{12}–C_{13}=1\cdot43$	$O_5–C_{12}=1\cdot30$
$C_{14}–C_{15}=1\cdot54$	$C_{13}–C_{14}=1\cdot39$	$O_6–C_{14}=1\cdot27$
$C_{16}–C_{17}=1\cdot53$	$C_{17}–C_{18}=1\cdot40$	$O_7–C_{17}=1\cdot29$
$C_{19}–C_{20}=1\cdot51$	$C_{18}–C_{19}=1\cdot42$	$O_8–C_{19}=1\cdot26$

Table 5. *The bond angles in the acetylacetonate ring*

$Ce–O_1–C_2=135°$	$O_1–C_2–C_3=122°$	$C_1–C_2–C_3=121°$
$Ce–O_2–C_4=134$	$O_2–C_4–C_3=123$	$C_3–C_4–C_5=116$
$Ce–O_3–C_2=138$	$O_3–C_7–C_8=122$	$C_6–C_7–C_8=119$
$Ce–O_4–C_9=136$	$O_4–C_9–C_8=122$	$C_8–C_9–C_{10}=121$
$Ce–O_5–C_{12}=135$	$O_5–C_{12}–C_{13}=126$	$C_{11}–C_{12}–C_{13}=117$
$Ce–O_6–C_{14}=142$	$O_6–C_{14}–C_{13}=120$	$C_{13}–C_{14}–C_{15}=126$
$Ce–O_7–C_{17}=140$	$O_7–C_{17}–C_{18}=120$	$C_{16}–C_{17}–C_{18}=125$
$Ce–O_8–C_{19}=134$	$O_8–C_{19}–C_{18}=125$	$C_{18}–C_{19}–C_{20}=119$
$O_1–C_2–C_1=117°$	$C_2–C_3–C_4=128°$	$O_1–Ce–O_2=73°$
$O_2–C_4–C_5=120$	$C_7–C_8–C_9=129$	$O_3–Ce–O_4=73$
$O_3–C_7–C_6=118$	$C_{12}–C_{13}–C_{14}=126$	$O_5–Ce–O_6=71$
$O_4–C_9–C_{10}=116$	$C_{17}–C_{18}–C_{19}=126$	$O_7–Ce–O_8=71$
$O_5–C_{12}–C_{11}=117$		
$O_6–C_{14}–C_{15}=114$		
$O_7–C_{17}–C_{16}=115$		
$O_8–C_{19}–C_{20}=115$		

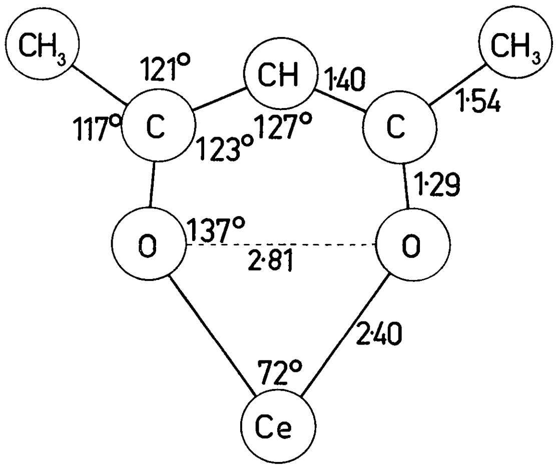

Fig. 4. Average bond lengths and angles in an acetylacetone ring.

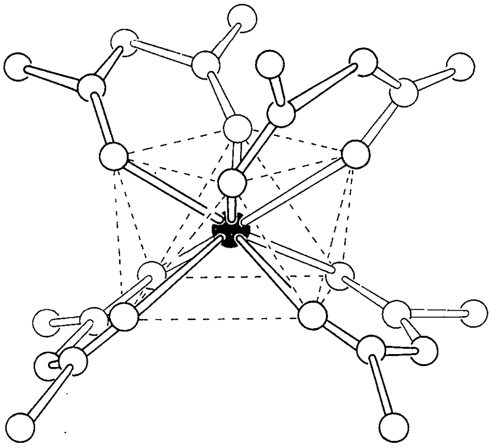

Fig. 5. A view of the model of the cerium(IV) acetylacetonate molecule.

of the square faces, with the mean value of 2·97 Å and (*d*) the O · · · O distances between two adjacent rings along the edges of the triangular faces with the mean value of 2·95 Å. The greatest variations from the mean value occur just in the last group, showing a departure from the parallelism of the square faces. The difference between the O · · · O distance within the ring and the mean distance of the (*c*) group is not so significant. If one takes the Ce–O bond length of 2·40 Å for granted, the ideal Archimedean antiprism will have an edge of 2·92 Å and an OCeO bond angle of 75°. The observed mean values are 2·81, 2·97, 2·95 Å and 72°, respectively.

The atoms of each acetylacetonate ring are almost coplanar. The bond lengths and angles within the ring (Tables 4 and 5) are in good agreement with the previously reported values, *e.g.* in Roof (1956), Bullen (1959), Amirthalingam, Padmanabhan & Jagdish, (1960), Lippert & Truter (1960), and Dodge, Templeton & Zalkin (1961) for C–C and C–O distances and bond angles, and in Cromer & Larson (1956) for Ce–O distances (Table 3). The closest approaches between non-bonded atoms are: 3·50 Å between two methyl groups, 3·11 Å between oxygen and methyl group, 3·41 Å between methyl group and CH carbon, 3·55 Å between two CH-carbon atoms.

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