

Dieses Verhalten wird verständlich, wenn man bedenkt, dass wir es bei den $A^{IV}B^{IV}C_2^V$ -Verbindungen mit sp^3 -ähnlichen, relativ festen und starren Valenzen zu tun haben, während bei den $A^{IV}B^VC_2^{VI}$ -Verbindungen Bindungen vorliegen, die denen der $A^{IV}B^{VI}$ -Verbindungen (z.B. PbTe) ähnlich sein dürften (Wernick *et al.*, 1958). Diese Art der Bindung ist aber im allgemeinen weniger fest und auch nicht so sehr an starre Valenzwinkel gebunden (Krebs & Schottky, 1954; Dehlinger, 1957), wie es bei den Bindungen der Zinkblende- und Chalkopyritstrukturen der Fall ist.

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The Crystal Structure of *bis*-Acetylacetonone Beryllium

BY V. AMIRTHALINGAM, V. M. PADMANABHAN AND JAGDISH SHANKAR

Chemistry Division Atomic Energy Establishment Trombay, Bombay, India

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The crystal structure of *bis*-acetylacetonone beryllium has been determined by single-crystal X-ray diffraction. The crystals are monoclinic with

$$a = 13.49, \quad b = 11.32, \quad c = 7.76 \text{ \AA}; \quad \beta = 100^\circ 48'.$$

There are four molecules per unit cell and the space-group was fixed as $P2_1$ with two molecules forming one asymmetric unit. Inequality relations and trial-and-error methods gave the approximate structure and refinements were made by two-dimensional Fourier summation. Due to severe overlapping in electron density, the atomic co-ordinates could not be refined to a great accuracy. Oxygen co-ordination about the beryllium is tetrahedral, and the acetylacetonone radical is planar within experimental error.

Introduction

This paper is the second in a series from these laboratories dealing with the crystal structure of metallic acetylacetonates. Recently the structure and properties of metal chelates and coordination compounds have attracted the attention of many investigators. Acetylacetonone chelate is a representative of such metal chelate compounds.

The unit cell and space group of *bis*-acetylacetonone-beryllium has been determined by Bullen (1957). His values are

$$a = 13.45, \quad b = 11.30, \quad c = 7.74 \text{ \AA}; \quad \beta = 100.8^\circ.$$

The space group is $P2_1$, or $P2_1/m$ with four molecules in the unit cell.

Experimental

Bis-acetylacetonone beryllium crystallises from aqueous solution as needles elongated parallel to the c -axis. Well-developed crystals show prominent (100) planes, cleavage is perfect along the plane (110). Laue photographs with the (100) plane perpendicular to the X-ray beam show strong diffuse scattering, indicating large thermal vibrations of the atoms. Rotation and Weissenberg layer-line photographs about the b and c axes with Cu $K\alpha$ radiation gave the cell dimensions

$$a = 13.49, \quad b = 11.32, \quad c = 7.76 \text{ \AA}; \quad \beta = 100^\circ 48',$$

with four molecules per unit cell. The only systematic absence is $0k0$ when k is odd, thereby indicating the space group as $P2_1$, or $P2_1/m$ confirming the results of

Bullen. Complete intensity data for the $h0l$ and $hk0$ reflections were obtained using nickel-filtered $\text{Cu } K\alpha$ radiation and Weissenberg multi-film technique. The $h0l$ data comprise 90 reflections out of 230 that are possible and the $hk0$ data 110 reflections out of 170. All intensities were visually estimated using calibrated intensity photographs and were corrected for Lorentz and polarization effects. No correction for absorption was made since the crystals used for collecting the data were very small. The scale and temperature factors for the $h0l$ and $hk0$ reflections were determined by Wilson's method and were adjusted at each stage of structure refinement by plotting $\log F_o/F_c$ versus $\sin^2 \theta/\lambda^2$.

Structure determination

The space group was uniquely fixed as $P2_1$ from the following considerations. If the unit cell is centrosymmetric, the four molecules have to be packed between the mirror planes. This is difficult because of the short c -axis. However, if the molecule is assumed to be planar or to have mm symmetry with planar or tetrahedral Be-O co-ordination (ligand being planar),

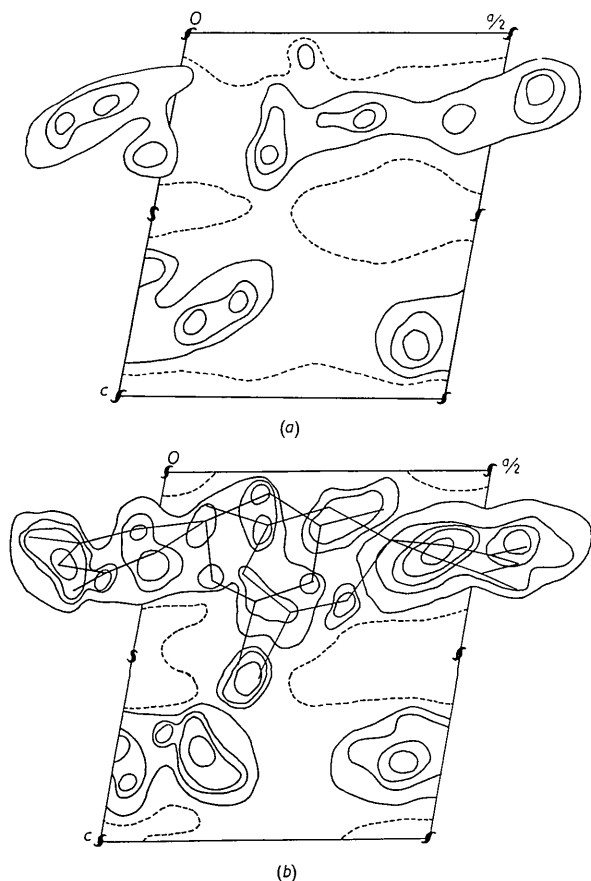


Fig. 1. (a) First projection of electron density on (010), contours drawn at arbitrary intervals. (b) Final (010) electron density. Contours drawn at intervals of $2 \text{ e.}\text{\AA}^{-2}$; one-electron line broken.

they can be placed on the mirror planes with two molecules in one asymmetric unit. Structure-factor values F_c calculated on such trial structures did not at all agree with F_o . The intensities of the $hk0$ reflections were statistically analysed for the $N(z)$ test (Howells, Phillips & Rogers, 1950). The curve obtained was found to lie between 1 and $\bar{1}$ curves. Hence the space group $P2_1/m$ was abandoned and the complete structure analysis was carried out with the space group $P2_1$, with two molecules forming one asymmetric unit.

Inequality methods were applied to the $h0l$ reflections. The largest unitary structure factor $|U_0|$ was found to be only 0.44. Then all the $|U_0|$ values were recast as $|U| = |U_0| \exp 2B (\sin^2 \theta/\lambda^2)$ with $B = 4.0 \text{ \AA}^2$ as suggested by Gillis (1948). The relations of Okaya & Nitta (1952) gave the signs of 6 reflections. Systematic application of Harker-Kasper inequalities as recast by Grison (1951) in conjunction with the signs of the 6 reflections obtained previously gave the signs for 10 more reflections and a large number of ambiguous sign relations. Cochran's (1952) equality $S(\mathbf{H}_1) = S(\mathbf{H}_2) \cdot S(\mathbf{H}_1 + \mathbf{H}_2)$ was applied to some of these relations involving $|U| \geq 1.5\sigma$ (σ is the r.m.s. value of the Unitary structure factors) and a further set of signs for 11 reflections was determined. The 27 terms whose signs were so established were used in computing the preliminary Fourier synthesis on the (010) plane. Fig. 1(a) shows the electron-density projection. The arrangement of the peaks suggested that the two molecules of the asymmetric unit are one above the other. Wire models of the molecule with tetrahedral oxygen co-ordination round beryllium, and the ligand planar with standard bond lengths and angles, were used in the trial methods which followed. The final x and z co-ordinates were obtained after a series of trials, Fourier refinements and structure-factor computations. The y co-ordinates were also simultaneously determined by trial methods and were further refined by structure-factor agreement and Fourier syntheses. All the Fourier syntheses were carried out with Beever-Lipson strips with an interval of 6° . The final electron-density projections on (001) and (010) are

Table 1. Atomic co-ordinates

Molecule I				Molecule II			
Atom	x	y	z	Atom	x	y	z
Be	0.068	0.195	0.122	Be'	0.373	0.708	0.176
O ₁	0.184	0.165	0.040	O ₁ '	0.431	0.571	0.230
O ₂	0.101	0.133	0.329	O ₂ '	0.451	0.818	0.217
O ₃	0.033	0.090	0.160	O ₃ '	0.313	0.721	0.318
O ₄	0.028	0.313	0.261	O ₄ '	0.253	0.733	0.080
C ₁	0.192	0.110	0.553	C ₁ '	0.576	0.456	0.298
C ₂	0.189	0.128	0.356	C ₂ '	0.528	0.583	0.268
C ₃	0.262	0.093	0.278	C ₃ '	0.573	0.703	0.248
C ₄	0.260	0.139	0.113	C ₄ '	0.541	0.816	0.225
C ₅	0.372	0.091	0.126	C ₅ '	0.619	0.906	0.203
C ₆	0.201	0.038	0.184	C ₆ '	0.210	0.768	0.589
C ₇	0.119	0.135	0.216	C ₇ '	0.242	0.771	0.398
C ₈	0.150	0.253	0.258	C ₈ '	0.158	0.786	0.314
C ₉	0.072	0.333	0.296	C ₉ '	0.176	0.798	0.133
C ₁₀	0.126	0.448	0.309	C ₁₀ '	0.058	0.831	0.126

Table 2. *Observed and calculated structure amplitudes and calculated phases*

<i>hkl</i>	<i>F_o</i>	<i>F_c</i>	α (°)	<i>hkl</i>	<i>F_o</i>	<i>F_c</i>	α (°)	<i>hkl</i>	<i>F_o</i>	<i>F_c</i>	α (°)	<i>hkl</i>	<i>F_o</i>	<i>F_c</i>	α (°)
020	52	59	118	640	6	6	45	001	28	40	0	50 $\bar{4}$	6	5	0
040	38	44	158	650	7	7	215	002	72	80	180	50 $\bar{5}$	5	8	0
060	22	32	162	660	18	10	230	003	28	35	180	601	5	4	180
080	13	15	320	670	12	14	54	004	5	6	180	602	28	22	0
110	44	45	38	680	11	11	80	005	5	7	180	603	5	4	0
120	34	29	129	710	13	9	115	101	58	68	180	605	5	4	180
130	75	73	130	720	17	10	115	102	5	2	0	60 $\bar{1}$	14	16	180
140	21	19	122	730	9	9	312	103	49	40	0	60 $\bar{2}$	14	8	180
150	46	44	12	740	10	10	12	104	21	28	180	603	21	20	180
160	10	13	308	750	11	12	300	10 $\bar{1}$	28	30	0	60 $\bar{5}$	16	14	0
170	14	15	10	760	5	5	355	10 $\bar{2}$	42	36	0	701	16	17	180
180	11	11	68	770	5	5	55	103	12	10	0	702	5	3	180
210	34	36	59	810	14	12	215	104	14	12	0	703	5	4	0
220	58	50	312	820	7	7	35	201	35	36	0	705	5	6	0
230	44	39	242	830	5	6	150	202	20	26	180	70 $\bar{1}$	21	19	0
240	33	32	144	840	7	7	125	203	60	52	180	70 $\bar{2}$	5	10	180
250	9	13	31	850	5	6	172	204	21	18	0	70 $\bar{3}$	14	18	180
260	16	19	24	910	16	12	325	20 $\bar{1}$	5	4	0	70 $\bar{5}$	18	16	180
270	10	10	102	920	4	4	45	20 $\bar{2}$	16	26	180	801	14	11	0
280	14	20	118	930	7	6	250	20 $\bar{3}$	12	14	0	802	5	4	180
310	35	24	334	940	11	11	335	204	5	12	0	803	5	5	180
320	19	16	173	950	12	11	220	301	28	18	180	80 $\bar{1}$	5	4	0
330	17	22	37	960	10	8	72	302	14	14	0	80 $\bar{2}$	5	6	180
340	28	20	35	070	12	12	232	303	22	26	0	80 $\bar{3}$	6	4	180
350	29	30	239	10,1,0	16	17	335	304	5	3	180	901	8	10	180
360	35	33	162	10,2,0	7	7	55	30 $\bar{1}$	56	38	180	902	5	5	0
370	10	10	38	10,3,0	13	16	75	30 $\bar{2}$	28	26	0	903	5	10	0
380	8	8	43	11,1,0	8	7	135	30 $\bar{3}$	14	10	180	904	5	4	180
410	10	8	165	11,2,0	11	12	160	304	5	5	180	90 $\bar{1}$	5	5	0
420	13	12	99	11,3,0	9	13	76	401	21	18	180	90 $\bar{2}$	21	18	180
430	28	29	160	11,4,0	12	12	140	402	5	4	0	90 $\bar{3}$	16	16	0
440	36	33	68	12,1,0	9	11	134	403	16	14	180	904	16	15	0
450	8	10	290	12,2,0	10	13	143	404	5	5	0	10,0,1	5	5	180
460	5	5	166	100	12	16	0	40 $\bar{1}$	5	4	0	10,0,2	5	6	0
470	8	9	282	200	12	13	0	40 $\bar{2}$	5	4	180	10,0,3	5	8	0
510	24	17	287	300	38	40	180	403	16	14	0	10,0, $\bar{1}$	6	5	180
520	30	18	7	400	11	10	180	404	6	5	0	10,0, $\bar{2}$	5	5	0
530	12	14	296	500	10	12	0	501	20	14	180	10,0, $\bar{3}$	9	7	0
540	9	11	155	600	9	9	180	502	14	10	0	11,0,1	5	3	0
550	8	9	134	700	21	21	0	503	16	14	180	11,0,2	5	5	0
560	8	8	121	800	5	6	180	504	5	5	0	11,0, $\bar{1}$	14	10	180
570	5	6	110	900	>5	4	180	505	20	16	0	11,0, $\bar{2}$	13	13	180
610	9	9	134	10,0,0	>5	4	180	50 $\bar{1}$	20	12	180	12,0,1	8	10	180
620	7	7	74	11,0,0	5	6	180	50 $\bar{2}$	22	20	0	12,0, $\bar{1}$	16	14	0
630	30	20	217	12,0,0	12	11	180	50 $\bar{3}$	14	12	180				

given in Figs. 1(b) and 2(a). The co-ordinates are listed in Table 1 and the complete structure factors together with the calculated phases are given in Table 2. Throughout the structure factor calculations Viervoll & Øgrim (1949) scattering factors were used, and an isotropic temperature factor $B=3.8 \text{ \AA}^2$ (for $h0l$) and 3.2 \AA^2 (for $hk0$) was employed. The reliability index R , $[\sum\{|F_o| - |F_c|\}]/\sum|F_o|$ with the atomic positions given in Table 1 was found to be 0.18 for the $h0l$'s and 0.13 for the $hk0$'s (hydrogen contribution neglected).

The co-ordinates could not be refined further because of the severe overlapping of the maxima in the projections and, needless to say, complete three-dimensional work will be more helpful. However, in order to have an indication of the accuracy of the proposed co-ordinates we have used the method by Luzzati (1952). The mean error in bond lengths was $\pm 0.04 \text{ \AA}$ and in angles $\pm 4^\circ$.

Description of the structure

Fig. 2(b) shows a projection of the structure on (001). The structure reveals the tetrahedral co-ordination of oxygen round beryllium. The bond lengths and angles obtained are given in Table 3. The slight distortion noted in the tetrahedral arrangement of oxygen should be confirmed with a three-dimensional analysis. The average Be-O bond length is 1.70 \AA . Pauling & Sherman (1934) have reported 1.65 \AA for Be-O in basic beryllium acetate.

Within experimental error the acetylacetonate radical is planar. The deviation of an atom from the plane passing through the beryllium atom and the seven atoms of the organic radical is found to be less than the probable error in atomic co-ordinates. The mean values of the bond lengths C-CH₃, C-C and C-O are 1.55 , 1.33 and 1.24 \AA respectively. These, as well as

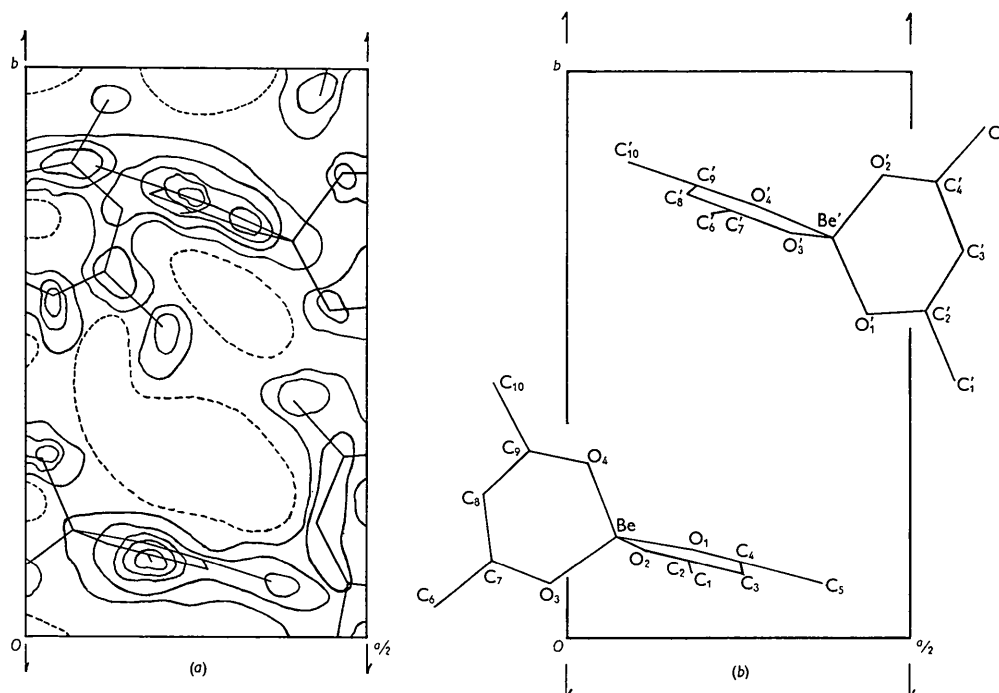


Fig. 2. (a) Final projection of the electron density on (001). Contours are drawn at intervals of $2 \text{ e.}\text{\AA}^{-2}$; one-electron line broken. (b) The crystal structure of $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ viewed down the c -axis, showing one asymmetric unit.

Table 3. *Interatomic distances and bond angles*

	Interatomic distances		Bond angles		
	Mole- cule I	Mole- cule II	Mole- cule I	Mole- cule II	
Be-O ₁	1.68 Å	1.72 Å	O ₁ -Be-O ₂	106°	104°
Be-O ₂	1.68	1.71	O ₁ -Be-O ₃	111	109
Be-O ₃	1.72	1.68	O ₁ -Be-O ₄	116	115
Be-O ₄	1.73	1.70	O ₂ -Be-O ₃	107	104
			O ₂ -Be-O ₄	112	114
			O ₃ -Be-O ₄	104	102
O ₁ -C ₄	1.21	1.22	Be-O ₂ -C ₄	129	123
O ₂ -C ₂	1.20	1.24	Be-O ₂ -C ₂	123	122
O ₄ -C ₉	1.27	1.28	Be-O ₃ -C ₇	128	128
O ₃ -C ₇	1.26	1.22	Be-O ₄ -C ₉	129	124
C ₁ -C ₂	1.55	1.54	C ₁ -C ₂ -C ₃	119	126
C ₄ -C ₅	1.55	1.51	C ₆ -C ₇ -C ₈	120	116
C ₆ -C ₇	1.56	1.55	C ₃ -C ₄ -C ₅	112	118
C ₉ -C ₁₀	1.52	1.58	C ₈ -C ₉ -C ₁₀	115	118
C ₂ -C ₃	1.30	1.36	C ₂ -C ₃ -C ₄	126	128
C ₃ -C ₄	1.33	1.31	C ₇ -C ₈ -C ₉	128	121
C ₇ -C ₈	1.36	1.32	O ₄ -C ₉ -C ₁₀	126	125
C ₈ -C ₉	1.37	1.38	O ₃ -C ₇ -C ₆	127	121
			O ₁ -C ₄ -C ₅	128	123
			O ₂ -C ₂ -C ₁	119	126

the bond angles, agree well with the values reported

in ferric acetylacetonate (Roof, 1956) and cobaltic acetylacetonate (Padmanabhan, 1958).

Bullen (1956) has observed in nickel acetylacetonate that three molecules form one asymmetric unit with short distance between metal atoms. No such short contact between metal atoms has been noticed in the present study. The closest approach between the two molecules of the asymmetric unit is 4.61 Å. The molecules are linked by normal van der Waals forces with distances varying from 3.42 to 4.61 Å.

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