The packing of oxygens has each O–H group centering a tetrahedron of the four nearest oxygens at about 2·70 A., and a rectangular antiprism of the eight next nearest at about 3·06 A.

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The Structure of Dimethylberyllium*

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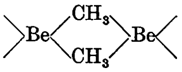
Dimethylberyllium is body-centered orthorhombic, with $a_0 = 6{\cdot}13$, $b_0 = 11{\cdot}53$, $c_0 = 4{\cdot}18$ A., and a structure similar to SiS_2. In the



chains, the C–Be–C angle within the four-membered ring is somewhat greater than tetrahedral, and the Be–C–Be angle is only 66°. The electron-deficient Be–C bonds are 1·93 A. in length.

This structure is in agreement with the rule that electron-deficient bonding results from the tendency of metals, with fewer valence electrons than low-energy orbitals, to use all their low-energy orbitals in forming bonds, even though combined with elements or groups containing no unshared pairs.

Introduction

Compounds in which the number of bonds exceeds the number of electron pairs, historically limited to the boron hydrides and other third-group hydrides and alkyl compounds, have presented a difficult problem in chemical valence. The discovery of similar electron-deficient bonding in tetramethylplatinum (Rundle & Sturdivant, 1947) made it clear that this valence anomaly was not limited to compounds involving third-group elements. It has been suggested, and given some theoretical justification (Rundle, 1947, 1949), that metals tend to use all their low-energy orbitals in bond formation, even if this requires delocalization of bonding, so that one electron pair serves for more than one interatomic link. This rule not only accounts for the known 'electron-deficient' compounds, but predicts that metals with more low-energy orbitals than valence electrons should form 'electron-deficient' compounds when combined with elements or groups containing no unshared pairs.

Beryllium has four low-energy orbitals, one 2*s* and three 2*p* orbitals, and only two valence electrons. It might be expected to form four tetrahedral interatomic links, even in dimethylberyllium. As a test of the above rule we have determined the structure of dimethylberyllium by X-ray diffraction.

Structure determination

Preparation of the compound

Dimethylberyllium was prepared by the method of Gilman & Schulze (1927), reacting methyl Grignard and anhydrous beryllium chloride in ether solution. The compound, obtained as the ether complex, was freed of ether by subliming repeatedly in a vacuum system.

Dimethylberyllium reacts violently with moisture and air, so that crystals have to be kept in sealed containers. Crystals for single-crystal examination were prepared by subliming excess dimethylberyllium into a thin-walled capillary attached to a vacuum system, sealing off the capillary, and then growing a number of single crystals within the capillary by sublimation under a temperature gradient. In favorable cases this method yielded isolated single crystals suitable for diffraction purposes.

Physical and X-ray data

Dimethylberyllium is a white solid subliming at 200° C. As mentioned above, it forms a crystalline complex with ether. These properties are in agreement with those reported by Gilman & Schulze.

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In our experience, the first sublimation of dimethylberyllium leads to apparently isotropic crystals with triangular and square faces, which transform readily to another form upon standing. We were unable to retain this apparently cubic modification long enough to confirm its nature by X-ray diffraction.

The stable form of dimethylberyllium consists of fibrous needles with a density of $0{\cdot}88 \pm 0{\cdot}1$ g.cm.$^{-3}$ as determined by the flotation method using cyclohexane ($\rho = 0{\cdot}78$) and chlorocyclohexane ($\rho = 0{\cdot}98$).

Single-crystal X-ray data, obtained with a Weissenberg camera and Cu radiation, and a Buerger (1944) precession camera and Mo radiation, reveal the crystals to be orthorhombic with

$$a_0 = 6{\cdot}13 \pm 0{\cdot}02,\ b_0 = 11{\cdot}53 \pm 0{\cdot}02,\ c_0 = 4{\cdot}18 \pm 0{\cdot}02\ \text{A}.$$

From the density, there are 4 $(CH_3)_2Be$ per unit cell.

Reflections (hkl) are absent unless $h+k+l=2n$. Reflections ($0kl$), observable to $k=12$, $l=5$, were absent unless $k=2n$, $l=2n$. Reflections ($h0l$), observable to $h=6$, $l=5$, were absent unless $h=2n$, $l=2n$ (reflections ($00l$) were observed to $l=8$). Possible space groups are, then, D_{2h}^{26}–*Ibam* and C_{2v}^{21}–*Iba*.

Intensities of Weissenberg reflections were obtained visually by the multiple-film technique, using five films. Precession data were obtained from sets of films using timed exposures, with an exposure ratio of two between films in the set. A few intensities were obtained using a precession camera and the multiple-film technique, using thin silver foil to bring the film factor to 5·3. For zones where only single films were available, intensities were determined by comparison with two different series of films whose relative intensities had been determined by the multiple-film technique. Because of the difficulty of handling dimethylberyllium crystals, the combination of Weissenberg and precession cameras, making it possible to get ($hk0$), ($h0l$), and ($0kl$) data from one mounting of a crystal, was particularly advantageous.

Intensities of Weissenberg films were corrected for Lorentz and polarization factors in the usual manner. The Lorentz-factor correction for zero- and higher-layer-line precession films were made as described by Buerger (1944). Absorption by glass capillaries was sometimes significant, but no corrections were attempted.

Atom positions

Reflections (hkl) with l odd require, for the space group *Ibam*, that the carbon positions be

$$8(j){:}\ (0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) \pm x,y,0;\ x,\bar{y},\tfrac{1}{2}.$$

In *Iba*, the $8(c)$ positions are identical with these if z is set equal to zero, which can be done without loss of generality. The beryllium positions are then

$$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) + 0,0,z;\ 0,0,\tfrac{1}{2}+z,$$

where $z=\frac{1}{4}$ if the space group is *Ibam*. Reflections ($00l$) were examined out to $l=8$, and since $I_{(008)} > I_{(006)}$, it can be shown that $z = 0{\cdot}25 \pm 0{\cdot}03$. We presume, therefore, that the space group is actually *Ibam*. In any case the structure can deviate from this only by a shift in the beryllium position along c_0 of at most 0·12 A.

To the approximation that hydrogen positions can be ignored, the problem remaining involves two parameters for carbon. These are most easily found by trial-and-error methods, and a first comparison gave $x_C = 0{\cdot}18 \pm 0{\cdot}01$, $y_C = 0{\cdot}099 \pm 0{\cdot}003$. Signs of structure factors were determined from these parameters and a Fourier projection on to (001) was made using ($hk0$) data. The result (Fig. 1) was confirmatory, leading to $x_C = 0{\cdot}183$, $y_C = 0{\cdot}100$.

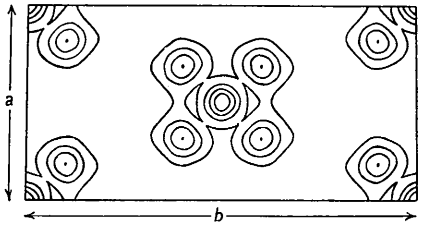


Fig. 1. Fourier projection of dimethylberyllium on to (001).

Temperature factor

Parameter refinement requires consideration of two other factors. First, hydrogen contributions to the X-ray scattering are far from negligible, and finally, the temperature factor is high and obviously anisotropic. It is easily seen, for example, that reflections ($00l$) are observed at far higher angles than either ($h00$) or ($0k0$).

Consideration of the reflections ($hk0$) indicates that the temperature factor is essentially isotropic for these reflections. A temperature factor of the form

$$T_{hkl} = \exp[-(C\cos^2\phi_{hkl} + B)\sin^2\theta/\lambda^2].$$

was chosen, where $C = A - B$, A is a temperature coefficient evaluated for the ($00l$) reflections, ϕ_{hkl} is the angle between (001) and the normal to (hkl), and B is the temperature coefficient evaluated for the ($hk0$) reflections. A and B, evaluated ignoring hydrogen contributions, and re-evaluated after hydrogen contributions were included, were $A = 2{\cdot}87 \times 10^{-16}$, $B = 5{\cdot}88 \times 10^{-16}$ cm.^{2}.

Hydrogen contributions

Several different attempts to take into account the hydrogen contributions were made. The scattering factor for methyl was approximated by using that for fluorine, by adding to the form factor of carbon the difference between calculated values for N^{3-} and N, and by the method of James & Brindley (1931). All of these approximations assume a spherically symmetrical carbon atom, and, though helpful, did not remove all the discrepancies at low angles.

The geometry of the structure suggests that the methyl group is tetrahedral, with one tetrahedral orbital directed symmetrically between two beryllium atoms. There are two tetrahedral arrangements of hydrogen about carbon consistent with the apparent symmetry of the structure, so that half a hydrogen atom was placed in each position. In the first trial, the C–H distance was taken as 1·09 A., but it was found that lowering the effective C–H distance improved the intensity agreement. This is not unreasonable, since the scattering of hydrogen is by the electrons in the covalent bond, and the center of the electron density should lie between carbon and the hydrogen nucleus rather than at the latter. This has been noted in other structures (Shoemaker, Donohue, Schomaker & Corey, 1950). The intensity agreement is not especially sensitive to the assumed C–H distance. For the calculated structure factors of Table 1, the C–H distance was taken as 0·9 A.

The hydrogen parameters chosen were:

	x_1	y_1	z_1	x_2	y_2	z_2
8 (*j*)	0·322	0·077	—	0·137	0·174	—
16 (*k*)	0·154	0·144	0·176	0·262	0·088	0·176

This asymmetric methyl group gave better agreement between calculated and observed intensities than any other approximation tried by us.

Parameter refinement

Trial-and-error refinements of the carbon parameters were carried out using data corrected for the temperature factor, as noted above. In one the above hydrogen positions were used, and in the other, based upon reflections at comparatively high angles where hydrogen contributions were negligible, the hydrogen atoms were omitted. In both cases the result was the same:

$$x_C = 0{\cdot}182 \pm 0{\cdot}002, \quad y_C = 0{\cdot}101 \pm 0{\cdot}002,$$

in good agreement with parameters obtained from the Fourier projection.

Table 1. *Comparison of observed and calculated structure factors for dimethylberyllium*

(*hkl*)	F_o	F_c	F_c*
020*a*	6·0	6·0	5·6
040*a*	4·8	−4·7	−2·9
002*abg*	3·5	2·8	2·9
022*a*	0	−0·2	−0·1
060*ad*	1·7	−1·5	−1·4
042*a*	3·2	4·0	3·8
080*ad*	1·6	1·4	1·5
062*a*	2·7	−2·7	−2·7
082*a*	0	−0·2	−0·1
0,10,0*ad*	2·1	1·7	1·7
004*abg*	2·8	2·5	2·5
024*a*	1·0	1·2	1·2
110*bc*	6·4	6·2	5·9
130*d*	0	0·1	1·1
121*e*	7·0	−6·8	−5·3
141*ef*	2·4	−2·3	−2·1
112*f*	0	−0·2	−0·1
150*f*	0	−0·2	−0·3
132*f*	1·7	−1·7	−1·7
161*f*	1·3	1·5	1·5
170*df*	0·9	0·9	0·7
152*f*	1·8	−1·8	−1·8
181*ef*	1·5	1·5	1·5
123*f*	1·4	−1·9	−2·1
190*df*	1·1	1·1	1·1
172*f*	0·9	−1·2	−1·2
143*f*	1·0	−1·0	−1·0
163*f*	0·6	0·8	0·9
1,10,1*f*	0	0	0
192*f*	0	−0·1	−0·1
114*cf*	1·3	1·3	1·3
1,11,0*df*	0·7	0·7	0·7
134*f*	0	0·4	0·4
183*f*	0·8	0·9	0·9
154*f*	0	0	0
1,10,3*f*	0	0	0
174*f*	0·6	0·3	0·3
194*f*	0·9	0·5	0·5
200*g*	4·0	−3·8	−2·0
220*bd*	0	0·2	0·6
211*ce*	2·8	−2·5	−2·1
240*d*	3·9	3·8	3·2
231*e*	2·5	−2·6	−2·6
202*g*	3·1	−3·2	−3·3
251*e*	0·5	0·3	0·1
222*b*	1·8	−1·7	−1·8
242*h*	—	—	—
260*d*	2·4	2·5	2·2
271*c*	1·3	1·5	1·4
213*ci*	0·7	−0·9	−1·0
280*i*	0·7	1·1	1·1
262*i*	0	0·2	0·2
233*i*	1·3	−1·3	−1·4
291*i*	0	0·4	0·5
253*i*	0	0·1	0·1
282*i*	0·7	−1·0	−1·0
2,10,0*i*	0	−0·3	−0·3
273*i*	0·9	0·9	0·9
204*i*	0	−0·3	−0·4
224*i*	0	0·3	0·3
293*i*	0	0·4	0·4
264*i*	1·0	0·9	0·9
284*i*	0	0	0
310*cd*	1·6	−2·0	−1·5
330*b*	2·2	3·0	2·4
321*e*	0·7	0·9	0·8
341*e*	1·3	0·6	0·4
350*d*	3·5	3·0	3·0
312*c*	2·9	−2·6	−2·7
332*b*	0	−0·1	−0·2
361*e*	0	−0·3	−0·3
370*d*	1·0	1·1	1·1
381*e*	0	−0·5	−0·4
323*j*	0	0·4	0·5
372*j*	0	−0·2	−0·2
390*j*	0	−0·4	−0·4
343*j*	0	0·2	0·3
363*j*	0	−0·2	−0·2
3,10,1*j*	0	0	0
392*j*	1·0	−1·1	−1·1
3,11,0*d*	0	−0·2	−0·2
314*j*	0	−0·2	−0·2
334*j*	0·6	0·8	0·8
383*j*	0	−0·2	−0·2
354*j*	1·1	1·2	1·2
3,10,3*j*	0	0	0
374*j*	0	0·4	0·4
400*g*	0·6	0·5	0·6
420*d*	1·0	0·9	0·8
411*ce*	1·4	1·2	1·2
431*e*	2·0	1·6	1·7
440*bd*	0·7	1·0	0·9
402*g*	1·3	−1·0	−0·9
451*e*	0	0·2	−0·1
422*h*	—	—	—
460*d*	0	0·6	0·7
442*b*	0	−0·4	−0·4
471*e*	1·7	−1·0	−1·0
480*d*	0	0·3	0·3
462*h*	—	—	—
431*c*	0	0·9	0·9
491*e*	0	0·4	0·4
404*g*	0	0·2	0·2
424*h*	—	—	—
444*b*	0	0	0
510*cd*	1·4	0·9	1·0
530*d*	0	−0·4	−0·4
521*e*	1·3	0·7	0·6
600*g*	1·1	1·2	1·1

a (0*kl* precession data).
b (*hhl* precession data).
c (*h*1*l* Weissenberg data).
d (*hk*0 precession data).
e (*hk*1 Weissenberg data).
f (1*kl* precession data).
g (*h*0*l* precession data).
h (Data not obtained).
i (2*kl* precession data).
j (3*kl* precession data).

* Does not include hydrogen contributions.

In order to set limits on the x and y parameters, intensity data from ($hk0$) precession diagrams were used. Intensities were estimated by visual comparison of a series of timed exposures. In the trial-and-error determination the specific intensity ratios used were assumed to be accurate within 20%. Rough intensity considerations had shown that the ranges

$$x = 0{\cdot}168 - 0{\cdot}192 \quad \text{and} \quad y = 0{\cdot}88 - 0{\cdot}112$$

certainly contained all possible values of the x and y parameters. Table 2 gives examples of the intensity ratios considered, the limits used, and the conditions on parameter values set by these limits within the range of x and y parameters given above.

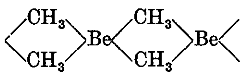
The two sets of calculated structure factors of Table 1 are corrected by the same temperature factors and are given both with and without hydrogen contributions. The observed values include data from several sources, as noted, put on the same relative scale by comparison of reflections common to several sources. The table includes 63 observed reflections for which

$$R = \Sigma \,||F_o| - |F_c|| \div \Sigma\, |F_o|$$

is 0·13, if only reflections observed to be present are included; $R = 0{\cdot}21$, if all reflections are included. These R values are computed from F values which include hydrogen contributions. If the hydrogen positions are not included, and if only reflections observed to be present are considered, $R = 0{\cdot}18$, which is a significantly poorer value than if the hydrogen positions are included. The inclusion of hydrogen positions most appreciably affects the six reflections appearing at the lowest angles [(020), (110), (130), (200), (121), and (040), respectively].

Discussion

The structure of dimethylberyllium, isostructural with SiS_2 (Zintl & Loosen, 1935; also Büssem, Fischer & Gruner, 1935), consists of linear chains



where the methyl groups are tetrahedrally arranged about beryllium. The packing of the chains, approximating the close-packing of circular cylinders, is illustrated in Fig. 2 and in the projection on to (001), Fig. 3.

The Be–C distance in the electron-deficient bonds is 1·93 ± 0·02 A., versus 1·84 calculated using Pauling's rule (1947*a*), assuming the bond number of the Be–C bonds to be one-half, and accepting Pauling's single-bonded radii of beryllium and carbon, 0·89 and 0·77 A., respectively. The C–Be–C angles within the four-membered rings of the chain are 114 ± 1°, significantly larger than the ideal angle of 109° 28′. The Be–C–Be angle within the ring is, then, only 66°.

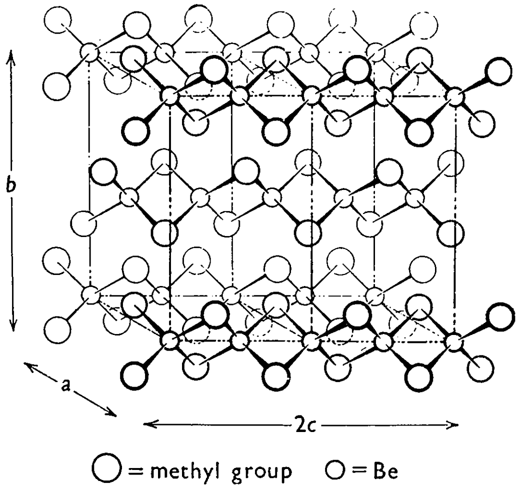


Fig. 2. Structure of dimethylberyllium. Two unit cells are shown.

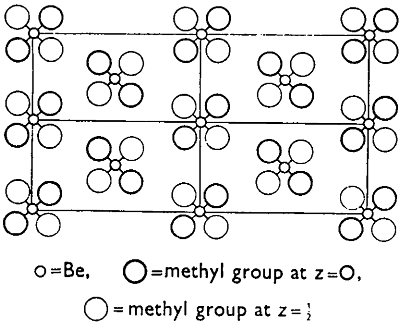


Fig. 3. Projection of four unit cells of dimethylberyllium on to (001). All beryllium atoms are at $z = \frac{1}{4}$ and $\frac{3}{4}$.

Table 2. *Parameter field*

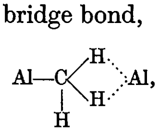
Reflections compared	Observed ratio, $\|F\|/\|F\|$	Corrected ratio*	Acceptable calculated ratio	Parameter limits
(080)/(440)	1·53	1·37	1·09–1·84	For $x = 0{\cdot}180$, $y \geqslant 0{\cdot}099$ For $x = 0{\cdot}168$–180, $y > 0{\cdot}096$ For $y = 0{\cdot}088$–$0{\cdot}100$, $x \geqslant 0{\cdot}180$
(080)/(420)	1·64	1·64	1·31–1·97	$y < 0{\cdot}104$ for all x For $y = 0{\cdot}100$, $x \geqslant 0{\cdot}180$ For $y = 0{\cdot}100$–$0{\cdot}104$, $x > 0{\cdot}180$
(510)/(190)	1·04	1·09	0·83–1·37	For $x = 0{\cdot}180$, $y < 0{\cdot}103$ For all y, $x < 0{\cdot}184$ For $x = 0{\cdot}176$–$0{\cdot}192$, $y > 0{\cdot}096$
(0,10,0)/(420)	1·83	2·84	1·46–3·41	For $y = 0{\cdot}100$, $x < 0{\cdot}184$

* Corrected by temperature factor.

It seems reasonable to interpret the bonding in terms of a tetrahedral methyl group in which one tetrahedral orbital is directed symmetrically between the two neighboring beryllium atoms. This type of methyl group was first suggested by Mullikan (1947). The carbon orbital would then overlap orbitals from the two beryllium atoms, the three orbitals combining to form one molecular orbital containing one electron pair. The sharp Be–C–Be angle could be explained in terms of achieving the best overlap with the carbon orbital, which would increase as the angle became more acute. It could also be explained in terms of residual Be–Be binding and repulsion of methyl groups within the four-membered ring.

It has been suggested that in electron-deficient bonding there is a tendency for metal–metal binding and for the ligancy of the metal to exceed the number of low-energy orbitals of the metal (Pauling, 1947*b*) (Pauling attributes the suggestion to V. Schomaker). Though this is clearly not the case in tetramethylplatinum, where Pt–Pt distances are very large (Rundle & Sturdivant, 1947), the importance of metal–metal binding in dimethylberyllium is of interest. Pauling's rule and radii give bond numbers of 0·35 and 0·31 for the Be–C and Be–Be links, respectively. This suggests that Be–Be bonding is significant. Clearly the rule is rough, however, since by its use the calculated number of electrons in the four-membered ring is 3·5, whereas the correct value must be 4. From the relative electronegativities of carbon and beryllium, one would expect to find fewer electrons in the Be–Be, more in the Be–C ligands, than given by Pauling's rule. It seems reasonable to assume that the short Be–Be bond is a result of the required geometry of the four-membered bridge and the tetrahedral C–Be–C angles, though the close approach of the metal atoms may lead to some further delocalization of bonding as a secondary, rather than a primary, consideration. In the case of the tetramethylplatinum tetramer, for example, where the geometry of the molecule leads to large Pt–Pt distances, no distortion to provide for better Pt–Pt binding is indicated.

Pitzer & Gutowsky (1946) have proposed a very asymmetric type of bridge bond,



for the trimethylaluminum dimer. Clearly the largest permitted deviation of the beryllium parameter in the present structure would not permit bonds analogous to those suggested by Pitzer & Gutowsky. Since aluminum and beryllium are rather closely related metals it seems most probable that the bridge bonds in trimethylaluminum are also symmetrical, as has been suggested (Rundle, 1947).

Goubeau & Rodewald (1949) have presented boiling-point and Raman data indicating that diethylberyllium is polymeric. They were unable to establish the nature of the bonding, but suggested four- or six-membered rings. The structure is undoubtedly similar to that of dimethylberyllium, but steric effects must interfere with polymerization, leading to polymer fragments and a liquid, rather than to essentially infinite chains and crystallization in the neighborhood of room temperature. This is quite analogous to the relation between trimethylaluminum and triethylaluminum, where the former forms a more stable dimer than the latter (Pitzer & Gutowsky, 1946).

The physical properties of dimethylberyllium crystals are compatible with the determined structure. The weak van der Waals forces between chains allow large vibrational amplitudes perpendicular to the c_0 axis which account for the large temperature factor in these directions. Methyl–methyl distances between chains are 4·1 A., normal van der Waals distances. The bonding along the chain is more rigid, leading to a lower temperature factor in this direction. The bonding in the a_0 and b_0 directions is similar enough to account for the pronounced tendency of this compound to form twinned crystals along the fiber axis.

The determination of this structure extends the region of the periodic table where metal atoms are known to form electron-deficient compounds of the type considered here. (Strictly metallic structures may be considered as electron-deficient (Rundle, 1948, 1949), but until recently were not considered as such.) The only suggestion in accord with electron-deficient bonding in all known cases is the one first suggested by one of us (Rundle, 1947, 1949), that such bonding results from the tendency of a metal to use all of its low-energy orbitals in bond formation even when these exceed the number of valence electrons.

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