

## Disodium Di- $\mu$ -hydrido-bis(diethylberyllate) Diethyl Ether Solvate

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### Abstract

$\text{Na}_2[\text{Be}_2(\text{C}_2\text{H}_5)_4\text{H}_2] \cdot 2\text{C}_4\text{H}_{10}\text{O}$ ,  $\text{C}_8\text{H}_{22}\text{Be}_2^- \cdot 2\text{Na}^+ \cdot 2\text{C}_4\text{H}_{10}\text{O}$ ,  $M_r = 330.51$ , is monoclinic,  $P2_1/c$ , with  $a = 5.044$  (6),  $b = 11.17$  (2),  $c = 20.90$  (3) Å,  $\beta = 101.25$  (16)°,  $U = 1154.93$  Å<sup>3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å, Cu  $K\alpha$ ,  $\lambda = 1.5418$  Å,  $Z = 2$ ,  $D_m = 0.95$  (2),  $D_c = 0.95$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.06$ ,  $\mu(\text{Cu } K\alpha) = 0.69$  mm<sup>-1</sup>,  $F(000) = 368$ . Final  $R = 0.117$  for 1094 observed reflections. The structure consists of  $[\text{Be}_2\text{Et}_4\text{H}_2]^{2-}$  ions with pairs of  $\text{Na}^+$  ions, each coordinated to one disordered ether molecule, lying about alternate centres of symmetry along  $a$ . Each Be is surrounded by a pseudotetrahedral arrangement of two H and two C atoms while the bridging H atoms are surrounded by an approximately tetrahedral arrangement of two Na and two Be atoms.

### Introduction

The title compound was prepared (Coates & Cox, 1962) by the reaction between sodium hydride and diethylberyllium in diethyl ether. Spectroscopic studies (Bell & Coates, 1965) of this and a number of related compounds showed the presence of  $\text{BeH}_2\text{Be}$  bridges, and the present work was undertaken to provide further information about these. A preliminary report (Adamson & Shearer, 1965) of the crystal structure has been published. Since this work was completed, structural data about compounds containing H in bridging positions between Be and B have appeared (Calabrese, Gaines, Hildebrandt & Morris, 1976; Marynick & Lipscomb, 1972; Morosin & Howatson, 1979).

### Experimental

The compound crystallizes from solution in diethyl ether as needles elongated along  $a$ . The crystals lose ether readily, the dissociation pressure being 2.3 kPa at

293 K, and inflame on exposure to air. Suitable specimens were picked from the solution in which they were grown and sealed immediately into thin-walled capillary tubes in an atmosphere of dry nitrogen. The crystal used for data collection was a tapering needle of mean cross-section  $0.35 \times 0.44$  mm. The density was determined by flotation in a mixture of benzene and trifluorobenzene. The cell constants were determined from precession photographs taken with Zr-filtered Mo radiation.

The nets  $0kl-4kl$  were recorded photographically with the equi-inclination Weissenberg method and Ni-filtered Cu radiation, and the nets  $h0l-h3l$  by the precession technique and Zr-filtered Mo radiation. The intensities were estimated visually, corrected for Lorentz and polarization factors and for spot length for the upper-level Weissenberg data. The structure factors were placed on a common scale by least squares from common reflections.

### Structure determination and refinement

The positions of the Na, O and Be atoms and of the C atoms in the ethyl groups attached to Be were determined from the sharpened Patterson function by superposition methods. Positions for the ether C atoms were obtained from an electron density map, where the relevant peaks were broad and of height about  $2.0 \text{ e } \text{Å}^{-3}$ . These positions were chosen on the basis of an ordered arrangement for the ether molecules. The structure was refined by Fourier methods and by least squares, with the block-diagonal approximation, to  $R = 0.186$ . At this stage, anisotropic temperature factors had been assigned to all the atoms included in the refinement but the dimensions obtained for the ether molecule departed considerably from the expected values.

A difference map then showed the positions of the alkyl and bridging H atoms in the  $[\text{Be}_2\text{Et}_4\text{H}_2]^{2-}$  ions. The peak heights lay between 0.3 and 0.6  $\text{e } \text{Å}^{-3}$  and the height of the peak due to the bridging H atom was about 0.5  $\text{e } \text{Å}^{-3}$ . The difference map also showed features consistent with there being two possible sites for each of the C atoms in the ether molecule and atoms were placed in all these sites, with occupation

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factors of one half. The H atoms in the ether molecule were not located.

The positional and anisotropic thermal parameters of all the atoms, except those of the C atoms of the ether molecule and the alkyl H atoms, were refined by block-diagonal least squares. The coordinates and anisotropic thermal parameters of the ether C atoms were refined separately by full-matrix least squares. In these calculations, the H atoms in the ethyl groups attached to Be were included at their observed positions and were given isotropic temperature factors of 0.15 (CH<sub>3</sub>) and 0.11 Å<sup>2</sup> (CH<sub>2</sub>). A final difference map showed no pronounced features.

The final value of *R* was 0.117 and that of the weighted residual *R'* was 0.026 for the 1094 observed reflections. The weighting function had the form

$$W^{1/2} = 1.0 / (32.0 + |F_o| + 2.4 |F_o|^2)^{1/2}$$

and the unobserved reflections were given zero weight. Scattering factors were those given for H, H<sup>-</sup>, Be, C, O, Na<sup>+</sup> in *International Tables for X-ray Crystallography* (1962). The final values of the atomic parameters are given in Table 1.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35597 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional positional parameters* [Na, O, C, H(11) and Be × 10<sup>4</sup>, H × 10<sup>3</sup>] with *e.s.d.*'s in parentheses

|                | <i>x</i>   | <i>y</i>  | <i>z</i>  | <i>B</i> <sub>eq</sub> <sup>*</sup><br>(× 10 <sup>4</sup> Å <sup>2</sup> ) |
|----------------|------------|-----------|-----------|--|
| Na             | 851 (4)    | 1190 (2)  | 592 (1)   | 73 (1)   |
| O              | 1102 (9)   | 2585 (4)  | 1444 (2)  | 79 (2)   |
| C(1)           | 7239 (13)  | 1257 (6)  | -1469 (3) | 80 (3)   |
| C(2)           | 5181 (10)  | 509 (5)   | -1183 (3) | 62 (3)   |
| C(3)           | 5474 (10)  | 2252 (4)  | -39 (3)   | 59 (2)   |
| C(4)           | 3445 (12)  | 3137 (6)  | -422 (3)  | 78 (3)   |
| C(5 <i>a</i> ) | 463 (64)   | 1569 (38) | 2353 (24) | 109 (13)   |
| C(5 <i>b</i> ) | 1921 (73)  | 1567 (44) | 2460 (26) | 131 (14)   |
| C(6 <i>a</i> ) | 1041 (88)  | 2609 (40) | 2109 (17) | 137 (18)   |
| C(6 <i>b</i> ) | -283 (58)  | 2187 (57) | 1914 (15) | 143 (21)   |
| C(7 <i>a</i> ) | 370 (46)   | 3857 (26) | 1230 (22) | 108 (12)   |
| C(7 <i>b</i> ) | 2213 (111) | 3688 (25) | 1510 (17) | 168 (18)   |
| C(8 <i>a</i> ) | 2963 (48)  | 4618 (28) | 1383 (16) | 110 (13)   |
| C(8 <i>b</i> ) | 1382 (108) | 4446 (35) | 1128 (15) | 119 (16)   |
| Be             | 5171 (10)  | 734 (6)   | -347 (3)  | 50 (3)   |
| H(1)           | 699        | 120       | -196      | 118  |
| H(2)           | 924        | 88        | -133      | 118  |
| H(3)           | 700        | 212       | -133      | 118  |
| H(4)           | 337        | 76        | -150      | 87   |
| H(5)           | 512        | -37       | -134      | 87   |
| H(6)           | 725        | 262       | -7        | 87   |
| H(7)           | 549        | 237       | 45        | 87   |
| H(8)           | 149        | 276       | -41       | 118  |
| H(9)           | 375        | 400       | -32       | 118  |
| H(10)          | 374        | 301       | -91       | 118  |
| H(11)          | 3002 (63)  | 0 (25)    | -104 (17) | 18 (13)  |

\* Defined according to Willis & Pryor (1975).

## Discussion

As shown in Fig. 1, two Na<sup>+</sup> ions are grouped together by the centre of symmetry at (0,0,0) and two Be atoms by that at (½,0,0). The bridging H atoms lie near the *a* axis and each is surrounded by two Na and two Be atoms which lie at the corners of a distorted tetrahedron. An ether molecule is coordinated to each Na<sup>+</sup> ion and two ethyl groups are attached to each Be atom. The structure can be most simply described as made up of [NaOEt<sub>2</sub>]<sup>+</sup> and [Be<sub>2</sub>Et<sub>4</sub>H<sub>2</sub>]<sup>2-</sup> ions, which lie in chains parallel to *a*, the interactions between the chains arising from van der Waals forces. Bond distances and angles are reported in Tables 2 and 3 respectively and some non-bonding distances in Table 4.

The Be—Be'' distance of 2.219 Å is not significantly different from the 2.225 Å in beryllium metal (*International Tables for X-ray Crystallography*, 1962); it is greater than the 2.11 Å in solid dimethylberyllium (Snow & Rundle, 1951), suggesting that the direct Be—Be interaction is weaker when the Be atoms are

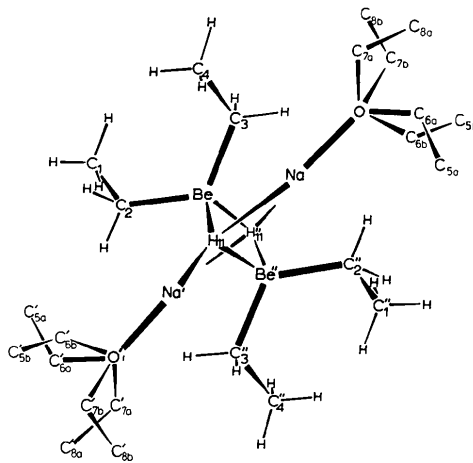


Fig. 1. Perspective view of Na<sub>2</sub>[Be<sub>2</sub>Et<sub>4</sub>H<sub>2</sub>].2Et<sub>2</sub>O showing the numbering of the atoms.

Table 2. *Bond distances* (Å) with *e.s.d.*'s in parentheses

|                               |           |            |          |
|-------------------------------|-----------|------------|----------|
| Na—O                          | 2.350 (5) | Be—H(11)   | 1.53 (3) |
| Na—H(11)                      | 2.38 (3)  | Be''—H(11) | 1.44 (3) |
| Na'—H(11)                     | 2.41 (3)  | C(1)—H(1)  | 1.01     |
| O—C(6 <i>a</i> )              | 1.40 (4)  | C(1)—H(2)  | 1.08     |
| O—C(6 <i>b</i> )              | 1.39 (4)  | C(1)—H(3)  | 1.02     |
| O—C(7 <i>a</i> )              | 1.51 (3)  | C(2)—H(4)  | 1.07     |
| O—C(7 <i>b</i> )              | 1.35 (3)  | C(2)—H(5)  | 1.03     |
| C(1)—C(2)                     | 1.542 (8) | C(3)—H(6)  | 1.00     |
| C(3)—C(4)                     | 1.532 (8) | C(3)—H(7)  | 1.03     |
| C(2)—Be                       | 1.766 (8) | C(4)—H(8)  | 1.08     |
| C(3)—Be                       | 1.810 (8) | C(4)—H(9)  | 0.99     |
| C(5 <i>a</i> )—C(6 <i>a</i> ) | 1.32 (6)  | C(4)—H(10) | 1.07     |
| C(5 <i>b</i> )—C(6 <i>b</i> ) | 1.59 (6)  |            |          |
| C(7 <i>a</i> )—C(8 <i>a</i> ) | 1.54 (4)  |            |          |
| C(7 <i>b</i> )—C(8 <i>b</i> ) | 1.18 (5)  |            |          |

Symmetry code: none *x, y, z*; (')  $-x, -y, -z$ ; (")  $1 - x, -y, -z$ .

Table 3. Bond angles (°) with e.s.d.'s in parentheses

|                 |           |                  |            |
|-----------------|-----------|------------------|------------|
| Na'-Na-O        | 167.2 (2) | C(4)-C(3)-H(7)   | 108        |
| O-Na-H(11)      | 150.3 (8) | Be-C(3)-H(6)     | 112        |
| O'-Na'-H(11)    | 127.3 (8) | Be-C(3)-H(7)     | 117        |
| H(11)-Na-H(11') | 81.9 (11) | H(6)-C(3)-H(7)   | 100        |
| Na-O-C(6a)      | 139 (2)   | C(3)-C(4)-H(8)   | 105        |
| Na-O-C(6b)      | 111 (2)   | C(3)-C(4)-H(9)   | 117        |
| Na-O-C(7a)      | 115 (2)   | C(3)-C(4)-H(10)  | 102        |
| Na-O-C(7b)      | 130 (2)   | H(8)-C(4)-H(9)   | 119        |
| C(6a)-O-C(7a)   | 103 (3)   | H(8)-C(4)-H(10)  | 106        |
| C(6b)-O-C(7b)   | 119 (3)   | H(9)-C(4)-H(10)  | 107        |
| C(2)-C(1)-H(1)  | 114       | O-C(6a)-C(5a)    | 114 (4)    |
| C(2)-C(1)-H(2)  | 110       | O-C(6b)-C(5b)    | 106 (3)    |
| C(2)-C(1)-H(3)  | 106       | O-C(7a)-C(8a)    | 108 (2)    |
| H(1)-C(1)-H(2)  | 100       | O-C(7b)-C(8b)    | 120 (5)    |
| H(1)-C(1)-H(3)  | 110       | C(2)-Be-C(3)     | 118.0 (4)  |
| H(2)-C(1)-H(3)  | 117       | C(2)-Be-Be''     | 123.9 (4)  |
| C(1)-C(2)-Be    | 116.0 (4) | C(3)-Be-Be''     | 118.1 (4)  |
| C(1)-C(2)-H(4)  | 100       | H(11)-Be-H(11'') | 83.4 (17)  |
| C(1)-C(2)-H(5)  | 112       | Na-H(11)-Na'     | 98.1 (11)  |
| Be-C(2)-H(4)    | 114       | Na-H(11)-Be      | 110.1 (15) |
| Be-C(2)-H(5)    | 116       | Na-H(11)-Be''    | 103.2 (18) |
| H(4)-C(2)-H(5)  | 95        | Na'-H(11)-Be     | 136.3 (20) |
| C(4)-C(3)-Be    | 114.6 (4) | Na'-H(11)-Be''   | 108.9 (15) |
| C(4)-C(3)-H(6)  | 103       | Be-H(11)-Be''    | 96.6 (18)  |

Table 4. Some non-bonding distances (Å)

The position of the second atom is indicated by the operation shown in parentheses.

|                  |           |                  |           |
|------------------|-----------|------------------|-----------|
| Na-Na'           | 3.620 (4) | Na-H(2'')        | 2.79      |
| Na-Be            | 3.245 (4) | Na-H(8)          | 2.80      |
| Na-Be''          | 3.051 (4) | Na-C(2')         | 2.86      |
| Na'-Be           | 3.675 (4) | Na-H(7) (-1,0,0) | 2.97      |
| Na'-Be''         | 3.183 (4) | Na-C(3) (-1,0,0) | 3.02      |
| Na-H(5'')        | 2.49      | Na-C(3')         | 3.13      |
| Na-H(6) (-1,0,0) | 2.60      | Be-Be''          | 2.219 (3) |
| Na-H(7)          | 2.75      |                  |           |

bridged by H atoms than when they are bridged by methyl groups.

The Be-H distances of 1.53 and 1.44 Å are equal within experimental error and their mean value is 1.49 (2) Å. In solid beryllium borohydride (Marynick & Lipscomb, 1972) an X-ray diffraction study has shown that the Be-H bridging distances have a mean value of 1.54 Å for bonds outside the polymeric chain and average 1.63 Å within the chain. In [Be<sub>2</sub>(Bu'O)<sub>4</sub>(BH<sub>4</sub>)<sub>2</sub>] and [Be(B<sub>3</sub>H<sub>6</sub>)<sub>2</sub>] where H also has a bridging role between Be and B, the average Be-H $\mu$  distances are 1.55 (Morosin & Howatson, 1979) and 1.504 Å (Calabrese, Gaines, Hildebrandt & Morris, 1976) respectively. The Be atoms are attached to six bridging H atoms in beryllium borohydride and some allowance would have to be made for the changes in coordination number before comparing the lengths in these compounds. Moreover, the distances in beryllium borohydride are thought to be subject to an anomalous shortening of about 0.1 Å, arising mainly from the use of spherical atoms in the refinement but

also due to the neglect of torsional oscillation. In the present work, the H atoms are four-coordinate and such effects would be expected to be smaller but any correction which leads to a lengthening of the Be-H bonds would decrease the Na-H distances.

The Be-C lengths of 1.766 (8) and 1.810 (8) Å differ significantly from one another. An explanation of this is difficult to find unless the difference arises through an underestimate of the coordinate e.s.d.'s due to the use of the block-diagonal approximation. The Be-C lengths can be compared with the 1.84 Å in lithium tetramethylberyllate (Weiss & Wolfrum, 1968), where the Be is bonded to four C atoms, and with the 1.75 and 1.71 Å for terminal Be-C bonds in dimeric methyl(propynyl)beryllium-trimethylamine (Morosin & Howatson, 1971) and tetrameric methyl(trimethylsilylato)beryllium (Mootz, Zinnius & Böttcher, 1969) respectively. They are shorter than the bridging 1.93 Å in polymeric dimethylberyllium (Snow & Rundle, 1951), but longer than the 1.698 and 1.699 Å in monomeric dimethylberyllium (Almenningen, Haaland & Morgan, 1969) and di-*tert*-butylberyllium (Almenningen, Haaland & Nilsson, 1968) where the Be atoms are two-coordinate. The C-Be-C angle of 118° is similar to the terminal H-B-H angle of 121° in diborane (Smith & Lipscomb, 1965). The C-H lengths in the alkyl groups which are bonded to the Be atoms lie between 0.99 and 1.08 Å.

Atoms Be, C(2), C(3) are coplanar with those related by the centre of symmetry at ( $\frac{1}{2}$ ,0,0) within experimental error, the largest deviation being 0.002 Å. The angle between this plane and that defined by Be, Be'', H(11) and H(11'') is 86.25°.

The Na-Na' distance of 3.620 Å is shorter than the 3.716 Å in metallic sodium (*International Tables for X-ray Crystallography*, 1962) but longer than the 3.078 Å in Na<sub>2</sub> in the gas phase (Herzberg, 1957). The four Na-Be distances range from 3.051 to 3.675 Å whereas the sum of the metallic radii (*International Tables for X-ray Crystallography*, 1962) is 2.97 Å. The Na-H distances of 2.38 and 2.41 Å are not significantly different from each other or the 2.440 Å in sodium hydride (Brewer & Mastick, 1951). The Na-H-Na' and Be-H-Be'' angles of 98.1 and 96.6° do not differ significantly from one another nor do the H-Na-H and H-Be-H angles of 81.9 and 83.4°. The Na-O distance of 2.350 Å is equal to the sum of the ionic radii (Pauling, 1960). Each Na<sup>+</sup> ion thus has as near neighbours a further Na<sup>+</sup> ion at 3.620 Å, two bridging H atoms at 2.38 and 2.41 Å and an O atom at 2.350 Å. Na, Na', O, O', H(11) and H(11'') are nearly coplanar. In addition, the Na<sup>+</sup> ion has six alkyl H atoms closer than 3.0 Å, the shortest of these distances being 2.49 Å.

The four C-O distances arising from the disorder in the ether molecule do not differ significantly from the 1.416 Å in dimethyl ether (Kimura & Kubo, 1959).

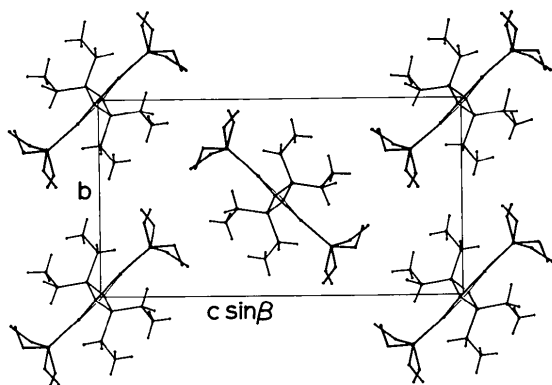


Fig. 2.  $\text{Na}_2[\text{Be}_2\text{Et}_4\text{H}_2] \cdot 2\text{Et}_2\text{O}$ : [100] projection.

However, the C—C distances differ markedly from the expected value. The disordered model used in the refinement is thus not completely satisfactory but no indication of how the model could be improved was found from the difference maps.

There are no significant intermolecular interactions, as shown in the packing diagram (Fig. 2). The structure is thus considered as being made up of  $[\text{NaOEt}_2]^+$  and  $[\text{Be}_2\text{Et}_4\text{H}_2]^{2-}$  ions. The anions are isoelectronic with  $\text{B}_2\text{Et}_4\text{H}_2$  and contain  $\text{Be} \cdots \text{H} \cdots \text{Be}$  three-centre electron-pair bonds analogous to those in boron hydrides. In the anions, the negative charge would be expected to be most closely associated with the bridging H atoms so that these would carry a negative charge and interact with the ether-solvated  $\text{Na}^+$  ions. The similarity in environment of the bridging H atoms with respect to Be and Na suggests that the  $\text{Na} \cdots \text{H}$  and  $\text{Be} \cdots \text{H}$  interactions may be similar in character.

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#### References

- ADAMSON, G. W. & SHEARER, H. M. M. (1965). *Chem. Commun.* p. 240.
- ALMENNINGEN, A., HAALAND, A. & MORGAN, G. L. (1969). *Acta Chem. Scand.* **23**, 2921–2922.
- ALMENNINGEN, A., HAALAND, A. & NILSSON, J. E. (1968). *Acta Chem. Scand.* **22**, 972–976.
- BELL, N. A. & COATES, G. E. (1965). *J. Chem. Soc.* pp. 692–699.
- BREWER, L. & MASTICK, D. F. (1951). *J. Am. Chem. Soc.* **73**, 2045–2050.
- CALABRESE, J. C., GAINES, D. F., HILDEBRANDT, S. J. & MORRIS, J. H. (1976). *J. Am. Chem. Soc.* **98**, 5489–5492.
- COATES, G. E. & COX, G. F. (1962). *Chem. Ind. (London)*, p. 269.
- HERZBERG, G. (1957). *Molecular Spectra and Molecular Structure*, Vol. I. Princeton: Van Nostrand.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KIMURA, K. & KUBO, M. (1959). *J. Chem. Phys.* **30**, 151.
- MARYNICK, D. S. & LIPSCOMB, W. N. (1972). *Inorg. Chem.* **11**, 820–823.
- MOOTZ, D., ZINNIUS, A. & BÖTTCHER, B. (1969). *Angew. Chem. Int. Ed. Engl.* **8**, 378–379.
- MOROSIN, B. & HOWATSON, J. (1971). *J. Organomet. Chem.* **29**, 7–14.
- MOROSIN, B. & HOWATSON, J. (1979). *J. Inorg. Nucl. Chem.* **41**, 1667–1670.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- SMITH, H. W. & LIPSCOMB, W. N. (1965). *J. Chem. Phys.* **43**, 1060–1064.
- SNOW, A. I. & RUNDLE, R. E. (1951). *Acta Cryst.* **4**, 348–352.
- WEISS, E. & WOLFRUM, R. (1968). *J. Organomet. Chem.* **12**, 257–262.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.