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Terminal Beryllium—Hydrogen Bonding in Dimeric (2-Dimethylamino-*N*-methylethylamido)hydridoberyllium,* $[Be_2(C_5H_{13}N_2)_2H_2]$

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Abstract. $M_r = 222\cdot38$, triclinic, $P\bar{1}$, $a = 7\cdot463$ (2), $b = 6\cdot061$ (1), $c = 8\cdot252$ (2) Å, $\alpha = 104\cdot05$ (2), $\beta = 95\cdot90$ (2), $\gamma = 96\cdot80$ (2)°, $U = 356\cdot17$ Å^3, $Z = 1$, $D_m = 1\cdot05$ (1), $D_x = 1\cdot04$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0\cdot067$ mm^{-1}, $F(000) = 124$, $T = 293$ K. Final $R = 0\cdot048$ for 958 observed diffractometer data. Although the compound is trimeric in solution, it is dimeric in the solid state, with the two halves of the dimer being linked by a centrosymmetric four-membered Be_2N_2 ring. Be achieves a coordination number of four by formation of a dative Be←N bond involving the second N atom of the ligand resulting in the formation of five-membered rings. This represents the first example of the structural characterization of a compound containing a terminal Be—H bond.

Introduction. Compounds of the type RMN(Me)C_2H_4NMe$_2$ (R = alkyl) have been reported for M = Be (Coates & Green, 1962; Coates & Roberts, 1968), Mg (Coates & Heslop, 1968) and Zn (Coates & Ridley, 1965). All are dimeric in benzene solution and doubtless have structures similar to that found for [MeMgN(Me)C_2H_4NMe$_2$]$_2$ (Magnuson & Stucky, 1969). The zinc hydride analogue has a similar structure with a terminal Zn—H bond (Bell, Moseley, Shearer & Spencer, 1980) and is dimeric in solution whereas the Be analogue is trimeric in solution (Bell & Coates, 1968). Since an H bonded to Be generally occupies a bridging rather than a terminal position (Bell, 1982), a structure containing a six-membered Be_3H_3 ring system was proposed and we therefore decided to establish whether such a structure existed in the solid state. A preliminary report of this structure has been published (Bell, Coates, Schneider & Shearer, 1983).

Experimental. Preparation by heating beryllium hydride and *N,N,N'*-trimethylethylenediamine under nitrogen in a sealed tube (Bell & Coates, 1968), recrystallization from toluene/hexane, D_m by flotation in fluorobenzene/pentafluorobenzene, colourless needles, crystal 0·2 × 0·3 × 0·4 mm sealed in a Pyrex capillary tube under dry nitrogen, unit-cell dimensions by least-squares refinement of ten strong reflections; data collected on a Hilger & Watts four-circle diffractometer, three reference reflections monitored every 50 reflections, intensities corrected for 7% variation, 1406 independent reflections, $2\theta \leq 52°$, 958 (h, −9→ +9; k, 0→ +7; l, −10→ +9) with $I \geq 3\sigma(I)$ used for structure refinement, intensities corrected for Lorentz and polarization effects but no absorption corrections applied. Structure solved by symbolic addition, H atoms located on a difference map, atomic scattering factors from *International Tables for X-ray Crystallography* (1962), least-squares refinement on F^2, anisotropic temperature factors for Be, N, C, isotropic for H, $R = 0\cdot048$, unit weights throughout, mean $\Delta/\sigma = 0\cdot33$, largest features on final difference map $\pm0\cdot2$ e Å^{-3}. Computer programs used were those of Ahmed (1968).

Table 1. *Fractional positional parameters* ($\times 10^4$) *and isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B(Å^2)
Be(1)	1373 (3)	−409 (4)	556 (3)	2·49 (13)*
N(1)	−676 (2)	−134 (2)	1379 (2)	2·61 (9)*
N(2)	2713 (2)	1972 (2)	2159 (2)	3·17 (10)*
C(1)	−400 (3)	1963 (3)	2780 (2)	2·64 (12)*
C(2)	1319 (3)	3468 (3)	2656 (3)	3·38 (13)*
C(3)	4320 (3)	3331 (5)	1774 (3)	3·67 (14)*
C(4)	3327 (4)	962 (5)	3547 (3)	4·67 (18)*
C(5)	−1642 (3)	−2046 (4)	1890 (3)	4·55 (16)*
H(1)	2111 (22)	−2434 (29)	408 (21)	3·64 (37)
H(11)	−278 (22)	1535 (28)	3894 (23)	3·12 (37)
H(12)	−1470 (26)	2879 (30)	2750 (22)	3·98 (42)
H(21)	1107 (24)	4264 (31)	1749 (26)	4·08 (43)
H(22)	1777 (26)	4579 (33)	3731 (27)	4·71 (47)
H(31)	3950 (33)	4251 (41)	960 (35)	7·10 (65)
H(32)	5125 (31)	2286 (39)	1293 (28)	5·88 (61)
H(33)	5007 (33)	4280 (40)	2815 (32)	6·53 (60)
H(41)	2280 (32)	−77 (37)	3740 (26)	5·89 (60)
H(42)	3779 (28)	2160 (37)	4619 (29)	5·27 (50)
H(43)	4385 (34)	104 (40)	3189 (31)	7·41 (66)
H(51)	−995 (26)	−2195 (31)	3050 (27)	4·64 (45)
H(52)	−1642 (23)	−3538 (33)	1075 (23)	3·63 (42)
H(53)	−2929 (31)	−1830 (33)	2045 (24)	4·94 (49)

* B_{eq} values calculated by reference to Willis & Pryor (1975).

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* Bis[μ-(2-dimethylamino-*N*-methylethylamido)-*N'*,μ-*N*]-bis(hydridoberyllium).

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Discussion. Final atomic parameters are in Table 1.*

Compounds containing H bonded to Be are associated and it has hitherto been believed that H occupies a bridging position between Be atoms (Bell, 1982). This has been conclusively established for $(NaHBeEt_2.OEt_2)_2$ by X-ray analysis (Adamson, Bell & Shearer, 1981) and the persistence of H bridges between Be atoms in the presence of bases is illustrated by the dimer $(MeBeH.NMe_3)_2$, formulated from IR studies as a BeH_2Be bridged species which cannot be cleaved by excess amine (Bell & Coates, 1965), whereas $Me_2Be.NMe_3$ is monomeric (Coates & Huck, 1952) and forms a weak 2:1 complex with excess amine (Bell & Coates, 1966).

The structure of the beryllium hydride complex of *N,N,N'*-trimethylethylenediamine (Fig. 1) surprisingly is identical to the Zn analogue. Thus, the compound is dimeric in the solid state and this represents the first authenticated example of a compound containing a terminal Be—H bond. One half of the molecule is related by a centre of symmetry to the other. The molecule possesses a planar four-membered ring containing two metal atoms bridged by two N atoms. Each trimethylethylenediamine moiety acts as a bidentate ligand, with one N atom, N(1), located in the bridge and the other, N(2), forming a coordinate bond to the metal atom resulting in a puckered five-membered ring. In this way, both metal and N atoms achieve four-coordination.

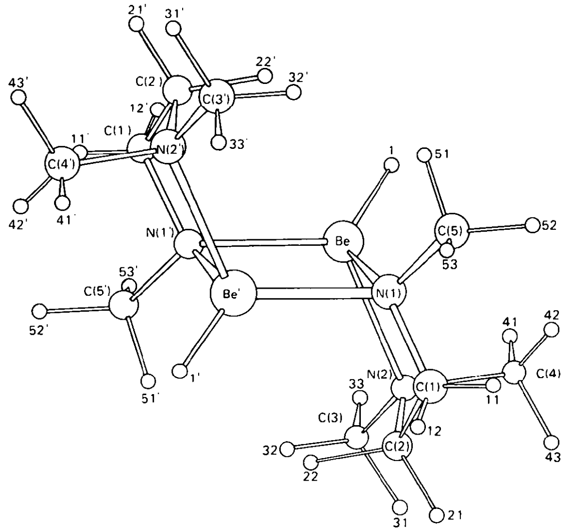

Fig. 1. Structure of $[HBeN(Me)C_2H_4NMe_2]_2$.

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

Symmetry code: (i) $-x, -y, -z$.

Be—H(1)	1·39 (2)	N(1)—C(5)	1·464 (3)
Be—N(1)	1·746 (3)	N(2)—C(2)	1·485 (3)
Be—N(1$^{\rm i}$)	1·747 (3)	N(2)—C(3)	1·479 (3)
Be—N(2)	1·814 (3)	N(2)—C(4)	1·482 (3)
N(1)—C(1)	1·473 (2)	C(1)—C(2)	1·511 (3)
N(1)—Be(1)—N(1$^{\rm i}$)	96·9 (4)	Be(1$^{\rm i}$)—N(1)—C(1)	112·1 (4)
N(1)—Be(1)—N(2)	95·5 (4)	C(1)—N(1)—C(5)	109·6 (5)
N(1$^{\rm i}$)—Be(1)—N(2)	116·6 (4)	C(2)—N(2)—C(4)	110·6 (5)
N(1)—Be(1)—H(1)	120·0 (5)	C(2)—N(2)—C(3)	110·1 (5)
N(1$^{\rm i}$)—Be(1)—H(1)	113·6 (4)	C(3)—N(2)—C(4)	108·0 (5)
N(2)—Be(1)—H(1)	112·3 (4)	C(2)—N(2)—Be(1)	101·7 (4)
Be(1)—N(1)—Be(1$^{\rm i}$)	83·1 (4)	C(3)—N(2)—Be(1)	121·0 (5)
Be(1)—N(1)—C(5)	120·3 (5)	C(4)—N(2)—Be(1)	105·1 (5)
Be(1)—N(1)—C(1)	108·6 (4)	C(2)—C(1)—N(1)	108·7 (5)
Be(1$^{\rm i}$)—N(1)—C(5)	120·6 (5)	N(2)—C(2)—C(1)	108·4 (5)

The enhancement of the donor strength of N when it is bound to an electropositive metal, relative to that of a tertiary amine, and the acceptor strength of Be when bound to an electronegative N atom, relative to the metal in R_2Be or *R*BeH, accounts for N rather than H acting as the bridging atoms in the dimeric unit.

Bond lengths and angles are listed in Table 2. The metal—N(1) distances 1·746 (3) and 1·747 (3) Å in the four-membered ring are the same within experimental error and can be compared to that found in $[Be(NMe_2)_2]_3$, 1·785 (4) Å, which also contains Be_2N_2 ring systems (Atwood & Stucky, 1969). The bridging distances in the present complex are significantly shorter than the Be—N(2) distance, 1·814 (3) Å, an effect also found in the methylmagnesium (Magnuson & Stucky, 1969) and hydridozinc (Bell *et al.*, 1980) analogues, although this difference is smaller in the Be compound. The Be—H distance of 1·39 (2) Å is, as expected, shorter than the average Be—H (bridge) distance of 1·48 (3) Å found in $(NaHBeEt_2.OEt_2)_2$ (Adamson *et al.*, 1981) and is close to values (1·28–1·38 Å) obtained from MO calculations on some hydrido compounds of Be (Dewar & Rzepa, 1978; Würthein, Krogh-Jespersen & Schleyer, 1981) but it is considerably smaller than the sum of the ionic radii (2·39 Å) (Pauling, 1960). N(1), C(1) and C(5) and the symmetry-related N(1$^{\rm i}$), C(1$^{\rm i}$), C(5$^{\rm i}$) all lie within 0·016 (1) Å of a plane through the origin which is almost at right angles [88·5 (3)°] to the Be_2N_2 plane. Details of these planes have been deposited.*

The Be—N(1)—Be$^{\rm i}$ angle [83·1 (4)°] does not differ significantly from the angle of 83·9 (3)° found in $[Be(NMe_2)_2]_3$ (Atwood & Stucky, 1969) but it is somewhat smaller than the analogous angles in the hydridozinc compound [88·0 (4)°] (Bell *et al.*, 1980) and in the methylmagnesium compound [88·30 (12) and 88·62 (12)°] (Magnuson & Stucky, 1969) as expected for the differing bulk of the metal atoms.

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes' data and bonds and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39067 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

The N—Be—N angles in the four-membered Be_2N_2 rings in $[Be(NMe_2)_2]_3$ are $91\cdot2\,(2)^\circ$ for the four-coordinate Be and $101\cdot0\,(3)^\circ$ for the three-coordinate Be atoms (Atwood & Stucky, 1969). In the structure described herein, although Be is four-coordinate, the N(1)—Be—N(1^i) angle lies intermediate [$96\cdot9\,(4)^\circ$] between these two values. The trimethylethylenediamine moiety has bond lengths and angles similar to those found in the hydridozinc analogue (Bell *et al.*, 1980) and the C—C and C—N bond distances are essentially the same in the two compounds and show many features in common. The Be—Be^i non-bonding contact of $2\cdot316\,(3)$ Å is similar to the short Be···Be distances found with other three-electron bridging ligands (O'Neill & Wade, 1982).

There is no evidence of any significant interdimer interactions, the only contacts less than 4 Å being C(2)···C(3) and C(3)···C(5) of $3\cdot816\,(10)$ and $3\cdot815\,(10)$ Å respectively and thus there can be no question of H acting as a bridging group between Be atoms in this compound.

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π-Bonding Around Three-Coordinate Beryllium in Tetra-*μ*-*tert*-butoxo-dichlorotriberyllium, $[Be_3Cl_2(C_4H_9O)_4]$

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Abstract. $M_r = 390\cdot4$, orthorhombic, *Cmcm*, $a = 13\cdot91\,(2)$, $b = 12\cdot19\,(2)$, $c = 13\cdot71\,(2)$ Å, $U = 2324\cdot7$ Å^3, $Z = 4$, $D_m = 1\cdot12\,(1)$, $D_x = 1\cdot11$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu = 0\cdot304$ mm^{-1}, $F(000) = 840$, $T = 293$ K. Final $R = 0\cdot054$ for 720 observed reflections. The molecule lies at the intersection of two perpendicular mirror planes in the unit cell. The two Cl and three Be atoms lie along the intersection of these mirror planes and are collinear. Adjacent Be atoms are linked by two bridging *tert*-butoxy groups and the two $Be(\mu\text{-}OBu^t)_2Be$ units are at right angles to one another so that the central Be atom is four-coordinate and has an approximately tetrahedral distribution of surrounding O atoms. The terminal Be atoms are trigonal planar and involved in π-bonding to the surrounding O and Cl atoms.

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