Terminal Beryllium–Hydrogen Bonding. *X*-Ray Crystal Structure of the (2-Dimethylamino-*N*-methylethylamido)hydridoberyllium Dimer

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An *X*-ray crystal structure determination shows that in $[HBeN(Me)C_2H_4NMe_2]_2$ the hydrogen atom bound to beryllium occupies a terminal position with amido nitrogen atoms as the bridging atoms in a four-membered Be_2N_2 ring; the metal and nitrogen atoms achieve four-co-ordination *via* formation of four- and five-membered rings with the diamine.

Compounds containing hydrogen bonded to beryllium are associated and it has hitherto been believed that hydrogen occupies a bridging position between metal atoms.[1] The presence of the BeH_2Be unit has been established by *X*-ray analysis[2] for $(NaBeEt_2H{\cdot}OEt_2)_2$; the structures of main group organometallic compounds, particularly those containing bridging groups, are discussed in ref. 3. The persistence of hydrogen bridges between beryllium atoms in the presence of bases is well illustrated by the dimer $(MeBeH{\cdot}NMe_3)_2$[4] (*cf.* the monomeric $Me_2Be{\cdot}NMe_3$[5]) and by $(RBeH)_2$(tmed)[4,6] (tmed = *N,N,N′,N′*-tetramethylethane-1,2-diamine), all of which are believed to contain the BeH_2Be unit.

Beryllium hydride reacts in a 1 : 1 molar ratio with *N,N,N′*-trimethylethane-1,2-diamine eliminating hydrogen to form a well defined crystalline solid, $HBeN(Me)C_2H_4NMe_2$, which is trimeric in benzene solution.[7] I.r. data did not support the presence of the BeH_2Be unit, and in an attempt to establish the existence of the suggested six-membered Be_3H_3 ring[7] we have determined the crystal structure of this compound.

Crystal data: needles of $HBeN(Me)C_2H_4NMe_2$, crystallised from toluene–hexane, are triclinic, space group $P\bar{1}$, a = 7.463(2), b = 6.061(1), c = 8.252(2) Å, α = 104.05(2), β = 95.90(2), γ = 96.80(2)°, Z = 1 molecule of dimer, D_c = 1.04, D_m = 1.05(1) g cm^{-3}. The structure was solved by the method of symbolic addition from diffractometer data. All 14 hydrogen atoms could be identified on a difference map and full-matrix refinement with anisotropic temperature factors for Be, N, and C, isotropic temperature factors for H, and unit weights throughout converged R to 0.048 for the 958 reflections for which $I_{obs} \geq 3\sigma(I_{obs})$.‡

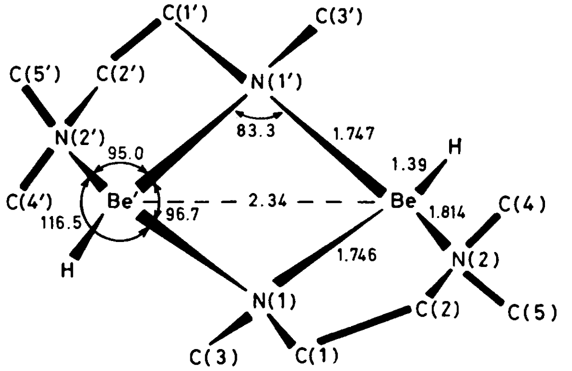

Figure 1. *X*-Ray structure of the dimer $[HBeN(Me)C_2H_4NMe_2]_2$ showing selected bond lengths (Å) and angles (°).

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‡ The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The crystal structure (Figure 1) of the title compound surprisingly is similar to that of the zinc analogue.[8] Thus the compound is dimeric in the solid state and is the first example of a compound containing a terminal Be–H bond, authenticated by crystallographic methods. Each beryllium atom is bonded to two different types of nitrogen atom, the bonds involving N(1) and N(1′) resulting in a planar four-membered Be_2N_2 ring about the centre of symmetry holding the two halves of the molecule together; the bond involving N(2) results in a puckered five-membered ring so that both metal and nitrogen atoms achieve four-co-ordination. The enhancement of the donor strength of nitrogen when it is bonded to an electropositive metal atom, relative to that of a tertiary amine, and the acceptor strength of beryllium when bonded to an electronegative nitrogen atom, relative to the metal atom in 'RBeH' accounts for nitrogen rather than hydrogen acting as the bridging atoms in the dimer units.

The Be–H distance [1.39(2) Å] is as expected shorter than the electron deficient Be···H distance [1.48(3) Å] in $(NaBeEt_2H{\cdot}OEt_2)_2$[2] and is considerably shorter than the sum of the ionic radii (2.39 Å). The atoms N(1), C(1), and C(5) lie in a plane through the origin which is almost at right angles (88.5°) to the Be_2N_2 plane. The Be–N(1)–Be′ angle [83.1(4)°] does not differ significantly from the angle [83.9(3)°] at bridging nitrogen in $[Be(NMe_2)_2]_3$[9] but is somewhat smaller than the corresponding angles in the hydridozinc [88.0(4)°][8] and methylmagnesium[10] [88.30(12) and 88.62(12)°] analogues as expected from the differing bulk of the metal atoms. The diamine moiety has bond lengths and angles similar to those found in the hydridozinc compound[8] and shows many features in common.

There is no significant interaction between dimer units and there can be no question of hydrogen bridging between beryllium atoms of different dimer units as the shortest contact between hydrogen and beryllium of neighbouring dimer units is >4 Å.

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