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Bonding situation in $Be[N(SiMe_3)_2]_2$ – an experimental and computational study†

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The solid state structure of $Be[N(SiMe_3)_2]_2$ (1) was determined by *in situ* crystallisation and the bonding situation investigated by quantum chemical calculations. The Be–N bond is predominantly ionic, but some evidence for the presence of a partial Be–N double bond character was found.

Beryllium chemistry has led a cinderella-like existence compared to the heavier group 2 elements, in particular Mg, due to the toxicity of beryllium and its compounds.[1] This has changed significantly in the last decade and highly interesting compounds such as beryllium diorganyls,[2] NHC-stabilized beryllium dihalides,[3] diorganyls,[4] and hydride (i-PrNHC-Be(Me)H),[5] or the Lewis acid–base adducts $[(Cy_3P)_2Pt\text{-}Be(Cl)X]$ (X = Cl, Me) have been prepared.[6] Moreover, the search for Be(I) complexes and the use of BeF_2 as a fluoride acceptor in liquid ammonia pushed the beryllium chemistry recently.[7,8]

Aside from as-described compounds, there has been steady interest in Be–N chemistry since the Be–N bond in homoleptic, monomeric beryllium diamides $Be(NR_2)_2$ is expected to show π-bonding character due to the high electrophilic nature of the Be center and its small size. Comparable findings were reported for monomeric aminoboranes $R_2BNR'_2$, containing a B=N double bond, and monomeric iminoboranes RBNR′, showing B≡N triple bonding.[9] Alternatively, a high ionic contribution was discussed for the bonding in beryllium amides due to the high electronegativity difference. Therefore, beryllium diamides have been synthesized and structurally characterized, but they were found to almost exclusively adopt dimeric or trimeric structures in the solid state.[10] Only $Be[N(SiMe_3)_2]_2$ **1** and a very few beryllium amides as reported by Nöth and Schlosser were found to be monomeric in solution,[11,12] but their solid state structures remain unknown. However, vapor phase studies supported the presence of π-bonding in $Be[N(SiMe_3)_2]_2$ **1**.[13] The Be–N bond length of 1.562(24) Å is significantly shorter than the calculated value of a Be–N single bond (1.73 Å),[14] but slightly longer than the calculated Be=N double bond (1.50 Å),[15] respectively. In addition, Power *et al.* observed the shortest Be–N bond (1.519(4) Å) in the heteroleptic beryllium amide $(2,6\text{-}Mes_2\text{-}C_6H_3BeNSiMe_3)_2$, to the best of our knowledge the only structurally characterized beryllium amide containing a twofold-coordinated Be atom in a linear arrangement.[16] Our increasing interest in beryllium chemistry[17] prompted us to determine the solid state structure of $Be[N(SiMe_3)_2]_2$ **1** and to analyze its bonding situation by quantum chemical calculations.

1 was synthesized by reaction of $BeCl_2$ and $KN(SiMe_3)_2$.[11] ^1H, ^{13}C and ^{29}Si NMR spectra of **1** showed the expected resonances due to the trimethylsilyl groups, and the ^9Be NMR spectrum showed a resonance at 12.3 ppm in C_6D_6 (9.6 ppm in THF-d_8/ 12.4 ppm in Tol-d_8).

A single crystal of **1** was grown on the diffractometer at a temperature of 150 K using a miniature zone melting procedure with focused infrared-laser-radiation,[18,19] which we previously used for the structural characterization of small inorganic and organometallic molecules.[20,21] **1** crystallises in the monoclinic space group $P2_1/n$ with the molecule placed on the general positions (Fig. 1). The central Be atom shows an almost perfect linear coordination environment (N1–Be1–N2 178.73(16)°) and the N atoms adopt trigonal-planar coordination spheres. The flat arrangement of the N atoms and their respective neighbours (max. deviation from best plane N1: 0.0224(10), N2: 0.0012(10) Å) as well as their bond angles point to an sp^2 hybridisation, a prerequisite for the formation of Be–N π-bonding. The short Be–N bond lengths (Be1–N1 1.525(2), Be1–N2 1.519(2) Å), which are comparable to that observed in the gas phase of **1** (1.562(24) Å)[13] are identical to that reported for $2,6\text{-}Mes_2\text{-}C_6H_3BeN(SiMe_3)_2$ (1.519(4) Å),[16] and the Si–N···N–Si torsion angles of approx. 90° further support the presence of Be=N double bonds. However, analogous structural findings would also be expected for a predominantly ionic contribution and are individually considered with no experimental proof for the presence of π-bonding character in the Be–N bond.

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† Electronic supplementary information (ESI) available: Experimental procedure and characterization of **1** as well as computational details of **1a**–**7**. CCDC 1003578 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc09732g

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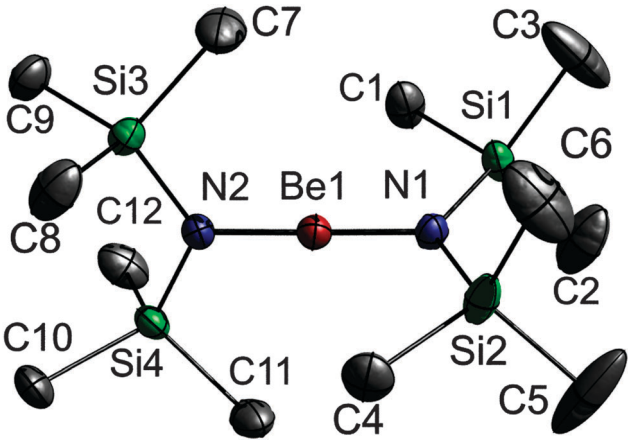

Fig. 1 Solid state structure of **1**; non-H-atoms are shown as thermal ellipsoids at 50% probability levels. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Be1–N1 1.525(2), Be1–N2 1.519(2), N1–Si1 1.7286(12), Si1–N2 1.7251(12); N1–Be1–N2 178.73(16), Si1–N1–Si2 127.20(7), Si1–N1–Be1 115.55(10), Si2N1–Be1 116.64(10); Si1–N1···N2Si3 −92.12(8), Si1–N1···N2Si4 88.32(8), Si2–N1···N2Si3 84.03(8), Si2–N1···N2Si4 −95.53(8).

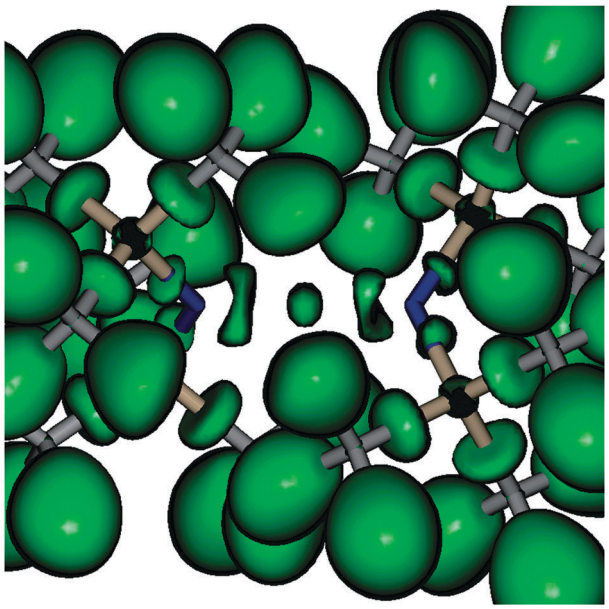

Fig. 2 ELF isosurfaces of $Be[N(SiMe_3)_2]_2$ (isovalue 0.850, Be atom in the centre).

Theoretical computations with dispersion corrected density functional theory confirm this picture.[22] Geometry optimizations lead to a S_4-symmetrical structure **1a** with a Be–N bond length of 1.525 Å and a perfectly planar environment of the N atoms (Si–N–Si angle 128.3°). The Si–N–N–Si torsion angle is 90°.

Geometry optimizations of $Be(NR_2)_2$ (R = SiH_3 **2**, Me **3**, H **4**) followed by frequency calculations resulted in D_{2d} symmetrical minimum structures with torsion angles of 90°. The nitrogen charge and the R–N–R bond angles strongly depend on the organic ligands (*cf.* Table 1), which is in line with their electronegativity and steric demand. In contrast, the charge on the Be atom in **1a**–**4** is about 1.7 *e* for all cases according to the theory of atoms in molecules (AIM).[23] Compared with other BeX_2 compounds (X = Me, OH, F; *cf.* Table 1) we note that (i) the Be charge is fairly independent of X, (ii) the density at the bond critical point $\rho(r_c)$ is inversely proportional to the Be–X distance, (iii) the Laplacian $\Delta\rho(r_c)$ correlates with the expected bond polarity, and (iv) the energy density $H(r_c)$ is positive for **7**, indicating the expected ionic interaction, while it is negative for **5**, which in combination with the positive value of $\Delta\rho(r_c)$ is indicative of mixed closed shell/shared interaction cases. While **6** has a nearly vanishing $H(r_c)$, the bond critical point parameters of **1a**–**4** resemble more closely that of the metal organic $BeMe_2$ **5** (*cf.* Table 1). Accepting the resulting picture of strongly polar covalent Be–N bonds, the bond ellipticities ε (0.07 (**1a**)–0.13 (**4**)) together with the dumbbell-shaped localization regions of the electron localization function (ELF)[24] between the Be and N atoms (*cf.* Fig. 2 and Fig. S2–S4, ESI†) indicate a certain double bond character.

The solid state structure of $Be[N(SiMe_3)_2]_2$ **1** was determined using an *in situ* crystallisation approach. Quantum chemical calculations on different beryllium diamides $Be(NR_2)_2$ with different steric and electronic properties prove that the Be–N bond is strongly polarized and should therefore be described as predominantly ionic. However, some evidence for the presence of a partial Be–N double bond character in **1** was also found.

We thank one of the referees for fruitful discussions and hinting on the possibility of an S_4 minimum structure of **1a**.

Table 1 Geometrical parameters, AIM partial charges, densities and local energy densities at the bond critical point r_c between Be and N of the calculated (DFT(BP)+D3/def2-TZVP) structures of $Be(NR_2)_2$ (R = $SiMe_3$ **1a**, SiH_3 **2**, Me **3**, H **4**) as well as of $BeMe_2$ **5** (D_{3d} symmetry), $Be(OH)_2$ **6** (C_2, O–Be–O 175.3°, H–O–O–H 96.6°), and BeF_2 **7** ($D_{\infty h}$)

	Be–N [Å]	R–N–R [°]	q(Be) [e]	q(N) [e]	$\rho(r_c)$ [au]	$\Delta\rho(r_c)$ [au]	$H(r_c)$ [au]
1a	1.525	128.3	1.69	−2.35	0.116	0.705	−0.018
2	1.528	123.0	1.70	−2.36	0.114	0.703	−0.016
3	1.517	112.5	1.67	−1.44	0.118	0.766	−0.015
4	1.522	109.4	1.71	−1.56	0.114	0.752	−0.010

	Be–X	q(Be) [e]	q(X) [e]	$\rho(r_c)$ [au]	$\Delta\rho(r_c)$ [au]	$H(r_c)$ [au]
5	1.692	1.69	−0.92	0.098	0.312	−0.030
6	1.441	1.72	−1.44	0.126	1.057	0.001
7	1.392	1.74	−0.87	0.133	1.271	0.007

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