

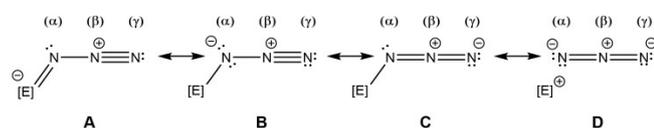
Synthesis, Solid State Structure and Bonding Analysis of the first Homoleptic Beryllium Azide

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In memoriam Prof. K. Dehnicke

Abstract: $[\text{Ph}_4\text{P}]_2[\text{Be}(\text{N}_3)_4]$ **1** and $[\text{PNP}]_2[\text{Be}(\text{N}_3)_4]$ **2** (PNP = $\text{Ph}_3\text{PNPPh}_3$) were synthesized by reaction of $\text{Be}(\text{N}_3)_2$ with $[\text{Ph}_4\text{P}]\text{N}_3$ and $[\text{PNP}]\text{N}_3$. **1** represents the first structurally characterized homoleptic beryllium azide and the electronic structure and bonding situation of the tetraazidoberyllate $[\text{Be}(\text{N}_3)_4]^{2-}$ dianion **1'** was investigated by quantum chemical calculations (NBO, ELF, LOL).

Beryllium azides tend to form predominantly ionic bonds, but are also expected to show covalent bonding contributions. However, even though $\text{Be}(\text{N}_3)_2$ ^[1] and solvent-coordinated beryllium azide complexes $\text{L}_2\text{Be}(\text{N}_3)_2$ (L = thf, pyridine)^[2] have been synthesized, their solid state structures are unknown. Only two heteroleptic beryllium azides $[\text{Ph}_4\text{P}]_2[\text{Be}_4\text{X}_4(\mu\text{-N}_3)_6]$ (X = Cl, Br) with bridging azide and two complexes with terminal azide groups ($[\text{Ph}_4\text{P}]_2[\text{Be}(\mu\text{-OSiMe}_3)(\text{N}_3)_2]_2$, (*R,R,S^N,S^N*)- $[(\text{C}_{12}\text{H}_{26}\text{N}_2)\text{BeCl}(\text{N}_3)]$) have been structurally characterized.^[3-5] $\text{N}_\alpha\text{-N}_\beta$ and $\text{N}_\beta\text{-N}_\gamma$ bond distances within the bridging azide in $[\text{Ph}_4\text{P}]_2[\text{Be}_4\text{X}_4(\mu\text{-N}_3)_6]$ (X = Cl, Br) differ significantly as is typical for covalently bonded azides (type **B**),^[3] while those of the terminal azide are almost identical, indicating high ionic bonding contributions (type **C**).^[4,5]

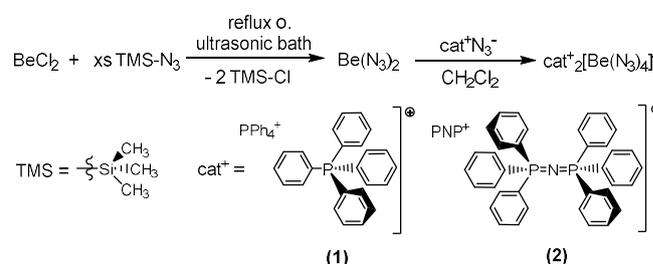


Scheme 1. Resonance structures of azide complexes.

Unfortunately, quantum chemical calculations were not provided and their bonding situation is still not finally clarified. Recently, an *ab initio* MCSCF study on $C_{\infty v}$ -symmetric HBeN_3 was reported.^[6] HBeN_3 contains a linear azide group with different $\text{N}_\alpha\text{-N}_\beta$ (1.187) and $\text{N}_\beta\text{-N}_\gamma$ (1.125) bond lengths and a substantially shorter Be-N_α bond length (1.471 Å) compared to $\text{Be}[\text{N}(\text{SiMe}_3)_2]_2$ (ED: 1.562(24) Å,^[7] XRD 1.525(2) Å^[8]) and 2,6-Mes₂C₆H₃BeN(SiMe₃)₂ (1.519(4) Å),^[9] the only structurally characterized linear beryllium amides with twofold-coordinated Be atoms. The authors suggested a π -conjugation of the covalently bonded azide group to the less electronegative Be atom (mesomeric form **A**). We herein report on the synthesis the

first homoleptic tetraazidoberyllates $[\text{Ph}_4\text{P}]_2[\text{Be}(\text{N}_3)_4]$ **1** and $[\text{PNP}]_2[\text{Be}(\text{N}_3)_4]$ **2** and the solid state structure of **1**.

1 and **2** were obtained from reactions of $\text{Be}(\text{N}_3)_2$ with two equivalents of $[\text{Ph}_4\text{P}]\text{N}_3$ and $[\text{PNP}]\text{N}_3$, respectively. Both compounds do not explode upon mechanical or thermal stress, but burn with a bright yellow flame while being heated on a metal plate with a Bunsen burner. However, care should generally be taken during the synthesis and handling of **1** and **2**.



Scheme 2. Syntheses of **1** and **2**.

The IR spectra of **1** and **2** show the expected absorption bands of the cation and the symmetric (1259 cm^{-1} **1**, 1261 cm^{-1} **2**) and anti-symmetric (2076 cm^{-1} **1**, 2071 cm^{-1} **2**) stretching vibrations of the azide group, which compare well with the anti-symmetric (2128, 2147 cm^{-1}) and symmetric stretching vibration (1255, 1263 cm^{-1}) of $\text{Be}(\text{N}_3)_2$.^[1,2] The symmetric stretching vibration is IR forbidden for the N_3^- ion, hence its appearance in the IR spectrum of $\text{Be}(\text{N}_3)_2$ indicates a covalently bonded azide.^[10] The IR spectra of donor-stabilized beryllium diazides ($\text{L}_2\text{Be}(\text{N}_3)_2$ (L = thf, pyridine) only show the anti-symmetric stretching vibration (2150 cm^{-1} (thf), 2137 cm^{-1} (pyr)), while heteroleptic complexes $[\text{Ph}_4\text{P}]_2[\text{Be}_4\text{X}_4(\mu\text{-N}_3)_6]$ (X = Cl, Br) with bridging azide groups show the anti-symmetric (Cl: 2141 cm^{-1} ; Br: 2132 cm^{-1}) and symmetric azide stretching vibration (Cl: 1297 cm^{-1} ; Br: 1299 cm^{-1}), pointing to a covalent bonding contribution.^[3] Be-N stretching vibrations (Cl: 800 cm^{-1} ; Br: 790 cm^{-1}) were observed for heteroleptic beryllium azides.

⁹Be NMR spectra of **1** and **2** in dmsO-d_6 solutions show singlet resonances at 0.05 ppm (**1**) and 0.04 ppm (**2**), which supports the symmetric tetrahedral coordination mode of the Be atom. In addition, a second species was observed for **2** at -0.13 ppm (Fig. S24), indicating the existence of an equilibrium between two beryllium azide species in solution. The ⁹Be NMR spectrum of **2** in CD_2Cl_2 shows additional beryllium species, which originate from well-established azide-halide exchange reactions.^[11] ¹⁴N NMR spectra of **1** and **2** in dmsO-d_6 each show three resonances (**1**: -139 N_β , -246 N_γ , -310 ppm N_α ; **2**: -138 N_β , -246 N_γ , -310 ppm N_α), which can be assigned to a covalently or polar-covalently bonded beryllium azide. Comparable chemical shifts were observed for $(\text{thf})_2\text{Be}(\text{N}_3)_2$ ($\delta = -135 \text{ N}_\beta$, -180 N_γ , -326

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ppm N_α) and $(\text{pyr})_2\text{Be}(\text{N}_3)_2$ ($\delta = -135 N_\beta$, $-245 N_\gamma$, -316 ppm N_α).^[1,2] Two additional signals were observed in both spectra at -131 ppm and -276 , which are caused by the presence of free N_3^- (Fig. S32).^[12] Since decomposition reactions can be excluded in $\text{dms}\text{-}d_6$, we performed temperature-dependent ^9Be and ^{14}N NMR experiments with **2**. The ^{14}N NMR spectra clearly showed the existence of an equilibrium in solution, which is fully temperature-reversible (Fig. 1). Moreover, the titration of **2** with PNP- N_3 , which was followed by ^{14}N (Fig.S40 – S58) and ^9Be NMR spectroscopy (Fig. 2), respectively, also showed the formation of an equilibrium between two major species.

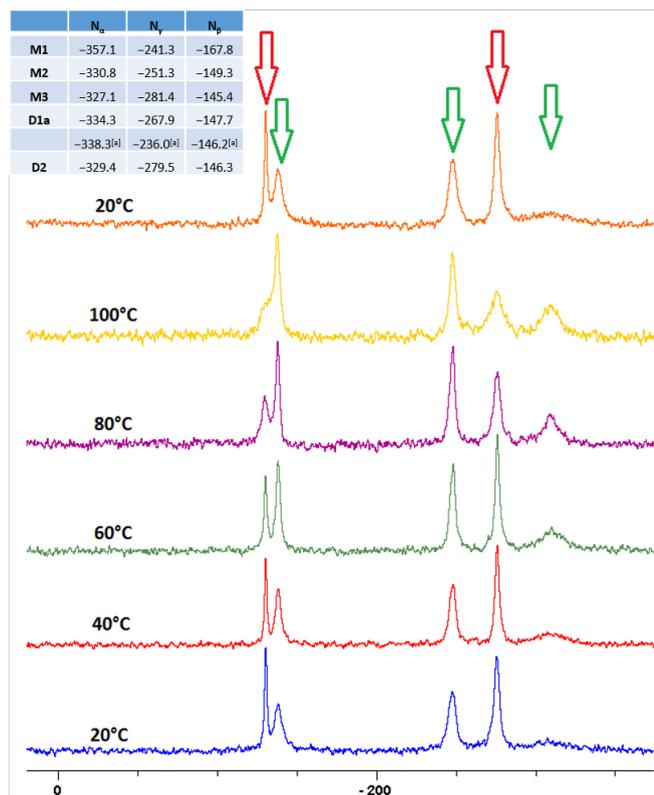


Figure 1. Temperature-dependent ^{14}N NMR spectra of **2** in $\text{dms}\text{-}d_6$; chemical shifts in ppm. Red – “free” N_3^- / Green – overlapping resonances of **D1**, **D2**, **M2**, **M3**; Table: calculated NMR shifts; ^[a] bridging azide.

The experimental findings in $\text{dms}\text{-}d_6$ solution point to the presence of an equilibrium (scheme 3) between monomeric species such as $[\text{Be}(\text{N}_3)_4]^{2-}$ (**M3**), $[\text{Be}(\text{N}_3)_3]^-$ (**M2**) and N_3^- and azide-bridged dimers, i.e. $[\text{Be}(\text{N}_3)_3]_2^{2-}$ (**D1**) or $[(\text{N}_3)_3\text{Be}-\text{N}_3-\text{Be}(\text{N}_3)_3]^-$ (**D2**). Resonances due to free azide N_3^- are present at ambient temperature, whose intensities increase upon stepwise addition of up to five equivalents of PNP- N_3 , whereas those of the beryllium azide remain almost unchanged (Fig. S38). The ^9Be NMR spectra simultaneously show the formation of **M3**, while the signal corresponding to **D1**, **D2** or **M2** is consumed. This indicates that the chemical shifts of the Be azide species **D1**, **D2**, **M2** and **M3** in the ^{14}N NMR are overlaid and cannot be differentiated without the help of other methods such as ^{15}N

NMR. The closeness of the signals is further supported by our quantum chemical calculations (Table S11).

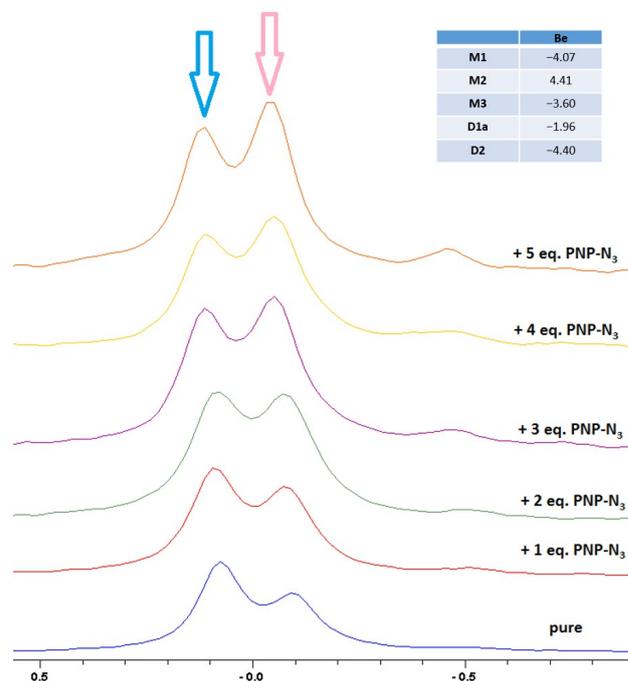
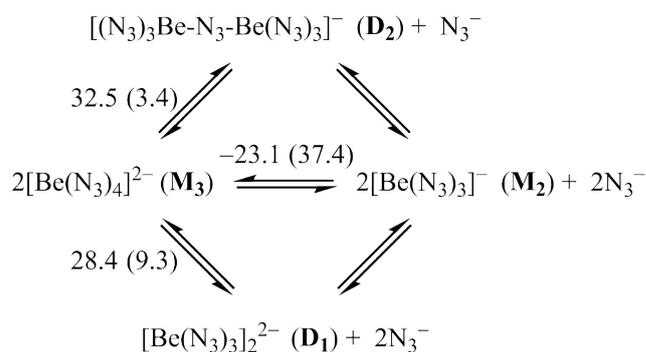


Figure 2. ^9Be NMR titration of **2** with the stepwise addition of five equivalents of PNP- N_3 in $\text{dms}\text{-}d_6$; chemical shifts in ppm. Pink - **M3** / Blue - **D1** or **D2**.

Surprisingly, the free azide is consumed upon heating (Fig. 1), showing that the entropically favored formation of **M2** + N_3^- is unlikely in solution and dimeric species like **D1** or **D2** are formed, from which **D2** is entropically favored. The energies and thermodynamical values of the compounds depicted in scheme 3 are very close in the quantum chemical calculations supporting the notion of equilibria between the species (Table S8 – S10).



Scheme 3. Postulated equilibrium of **2** in $\text{dms}\text{-}d_6$ solution; ΔH (ΔG) values in solution as obtained from calculations (Table S9 & S10).

Single crystals of **1** (Fig. 3) were obtained by diffusing toluene into a saturated CH_2Cl_2 solution of **1** within two days. **1** crystallizes in the triclinic space group $P-1$ with two $[\text{Ph}_4\text{P}]^+$

cations and one $[\text{Be}(\text{N}_3)_4]^{2-}$ dianion in the asymmetric unit.^[13] The Be atom adopts a slightly distorted tetrahedral coordination sphere as observed in tetraazidometallates of main group metals (Table S4). The Be-N bond lengths range from 1.692(2)–1.729(2) Å and the N-Be-N bond angles from 108.44(12)–111.18(12)° (**1**). The $\text{N}_\alpha\text{-N}_\beta$ bonds (1.185(2)–1.2035(19) Å) are elongated compared to the $\text{N}_\beta\text{-N}_\gamma$ bonds (1.153(2)–1.158(6) Å) as is typical for covalent azides (Tab. 1).

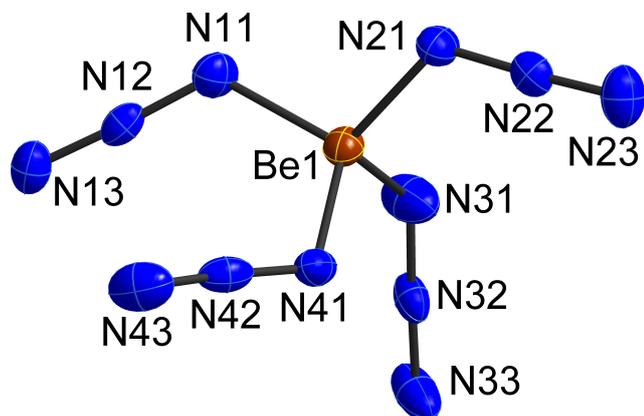


Figure 3. Molecular structure of $[\text{Ph}_4\text{P}]_2[\text{Be}(\text{N}_3)_4]$ **1**. Only the tetraazidoberyllate anion is shown, while the Ph_4P^+ cations have been omitted for clarity; displacement ellipsoids are drawn at the 50% probability level.

The conformation (i.e. N-Be-N-N torsion angles) differs significantly from the calculated model (Fig. 5), while there are also slight differences in the N-N bond lengths (see Tab.1). Since the calculated structure represents the (energetically) most favorable state without any external disturbances, the differences are most likely explained by an interplay with surrounding cations. $[\text{Ph}_4\text{P}]^+$ ions are known to form intermolecular contacts (Phenyl Embracing = PE), which notably influence the packing and are often considered to be structure determining.^[14] Two of these motifs can be found in the packing of **1** (Fig. 4). The 6PE motif is located between each of the independent cations and their respective equivalents (C1x, C2x, C3x, C1x', C2x', C3x' and C5x, C6x, C8x, C5x', C6x', C8x', numbering see SI), while distorted parallel 4PE motifs were found between the independent cations (C2x, C4x, C6x, C7x and C3x, C4x, C5x, C7x). In addition, several $\text{CH}\cdots\text{N}$ and $\text{CH}\cdots\pi$ interactions between anions and cations were found.

1 is isostructural to $[\text{Ph}_4\text{P}]_2[\text{Hg}(\text{N}_3)_4]$,^[15] but despite the unchanged packing of the cations in $[\text{Ph}_4\text{P}]_2[\text{Hg}(\text{N}_3)_4]$, the distortion of the anion is far more pronounced (Hg–N 2.184(2)–2.295(2) Å; N–Hg–N 102.97°–126.87°), most likely due to repulsive interactions due to the limited space available to the anion within the rather rigid cation network. The packing of the analogous $[\text{Ph}_4\text{P}]_2[\text{Cd}(\text{N}_3)_4]$ ^[15] is dominated by different cation-cation interactions, i.e. offset 6PE and a variation of the parallel 4PE, where the edge-to-face interactions are donated by the H in ortho and meta position instead of meta and para. Since the $[\text{Cd}(\text{N}_3)_4]^{2-}$ anion is heavily disordered, detailed structural comparison isn't possible.

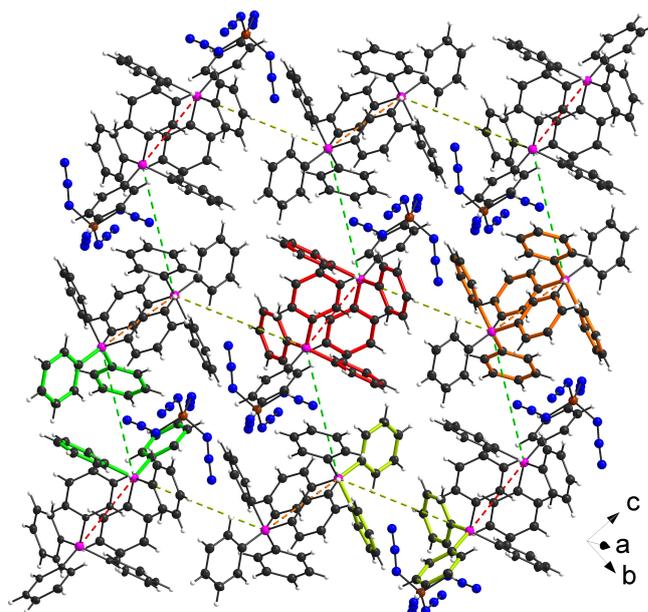


Figure 4. Illustration of the packing of **1** with PE interactions, reddish 6PE greenish parallel 4PE

Quantum chemical investigations. The gas phase structure of the $[\text{Be}(\text{N}_3)_4]^{2-}$ dianion **1'** was obtained by optimizing the geometry of a model structure using the resolution of the identity density functional theory (RI-DFT)^[16] methods with the B3-LYP functional^[17] and TZVPP basis sets.^[18,19] **1'** shows an almost tetrahedrally coordinated Be atom. The coordinating azide groups are tilted by about 42°, which breaks the tetrahedral symmetry and leads to an S_4 symmetry (Table 1). The bond lengths observed in **1'** agree well with those obtained in **1**, with minor differences in the N-N bond lengths within the azide groups, whereas the bond angles vary more significantly due to the different symmetry and structure of **1'** and **1**. However, since these differences are rather small, it is not to be expected that this reflects a different bonding situation.

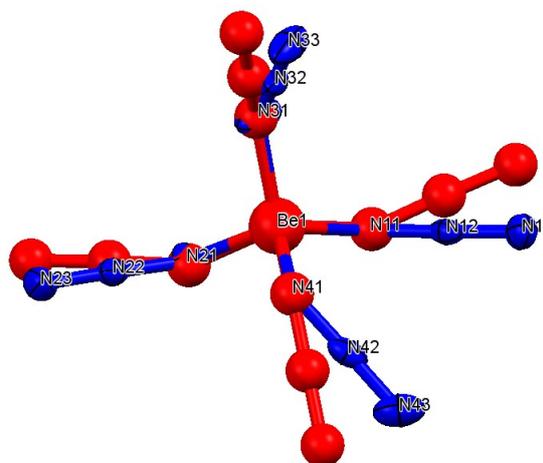
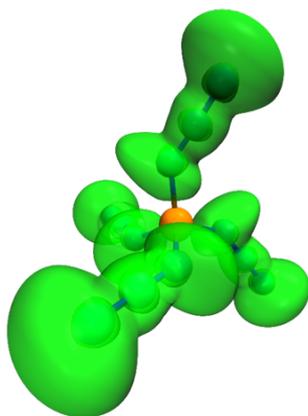
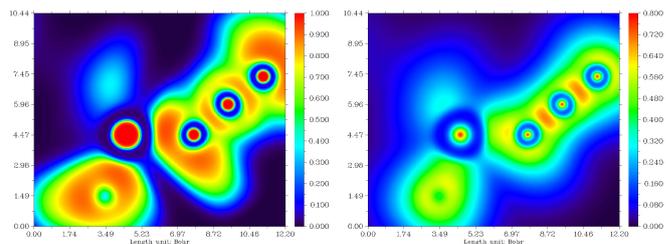


Figure 5. Overlay of observed (**1**, shown with displacement ellipsoids) and calculated (**1'**, shown in red "ball and stick" model) structure of the anion.

Table 1. Bond lengths and angles of $[\text{Be}(\text{N}_3)_4]^{2-}$ as observed/calculated in $1/1'$

	Be-N_α	$\text{N}_\alpha\text{-N}_\beta$	$\text{N}_\beta\text{-N}_\gamma$
	1.692(2)	1.1951(18)/1.182	1.1586(18)
	1.709(2)	1.2008(18)/1.182	1.1555(19)
	1.725(2)	1.185(2)/1.182	1.154(2)
	1.729(2)	1.2035(19)/1.182	1.153(2)
calculated	1.729	1.182	1.159
	$\text{Be-N}_\alpha\text{-N}_\beta$	$\text{N}_\alpha\text{-N}_\beta\text{-N}_\gamma$	$\text{N}_\alpha\text{-Be-N}_\alpha\text{-N}_\beta$
	124.81(13)	176.87(15)	-160.51(14)
	123.26(13)	177.27(16)	173.92(14)
	128.58(14)	176.07(17)	139.43(19)
	122.10(13)	176.82(16)	-141.20(14)
calculated	138.2°	176.8°	±166.9°

The nature of the Be-N bond was investigated in more detail using natural population analyses (NPA), electron localization function (ELF) and localized orbital locator (LOL) analysis.^[20] Figure 6 shows a 3D rendering of the ELF at an isovalue of 0.6, while Figure 7 shows 2D plots in the $\text{Be-N}_\alpha\text{-N}_\beta$ plane of the ELF and LOL functions. According to the NPA analysis, which shows positively charged Be (1.59) and N_β (0.21) atoms and negatively charged N_α (-0.68) and N_γ (-0.42) atoms, the Be-N bond should be regarded as polar covalent (about 80% ionic) as is expected from the large electronegativity difference between Be and N. The polar covalent nature is also illustrated in the 2D plots, which show very low values for an extended area around the Be center. The localization plots show an area of electron density at the N_α atom on the opposite side of the Be-N_α contact point, which should be considered as a free electron pair.

**Figure 6.** Rendering of the ELF at an isovalue of 0.6.**Figure 7.** Plot of the ELF (left) and the LOL (right)

To check the extent of the flexibility of the $\text{Be}(\text{N}_3)_4^{2-}$ dianion, its structure was optimized with the methods stated above and was found to end up in a different local minimum that proved to have C_s symmetry. The crystal structure **1** and the calculated C_s symmetric structure **1'** differ slightly (Fig. 5). Further investigations showed another local minimum with D_{2d} symmetry, which has higher symmetry than the S_4 structure but an energy, that falls between the two other minima (relative energies of the local minima: S_4 0 kJ/mol; D_{2d} 0.133 kJ/mol; C_s 0.933 kJ/mol). The structure of the tetraazidoberyllate anion found in the crystal structure **1** resembles that of the C_s symmetrical structure, which puts it within a few kJ/mol of the S_4 symmetrical structure. The narrowing of the Be-N-N angles in the crystal structure can thus be attributed to the packing effects explained above and the rigidity of the cationic network.

Conclusion

We synthesized the first homoleptic beryllium azides, which were characterized by IR and NMR spectroscopy. The conformation of the tetraazidoberyllate dianion **1** in the solid state differs from the calculated gas phase structure **1'**, which is most likely caused by the rigidity of the cation network, the conformational flexibility of the anion and the interactions of the hydrogen bonds of the azide ligands with the cations. The $[\text{Be}(\text{N}_3)_4]^{2-}$ dianion is dynamic in $\text{dms}\text{-}d_6$ solution and forms equilibria between different beryllium azide species and free N_3^- , as was shown by ^9Be and ^{14}N NMR spectroscopy. Quantum chemical calculations support the experimental findings.

Acknowledgements

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Keywords: main group elements • beryllium • azide • crystal structure • quantum chemical calculation

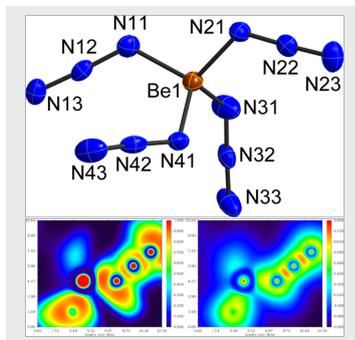
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- [13] The crystal of **1** was mounted on nylon loops in inert oil. Data were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoK α radiation, $\lambda = 0.71073$ Å). The structure of **1** was solved by Direct Methods (SHELXS-97; G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467-473) and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014; G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112-122 and shelXle, C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, 44, 1281-1284). Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The crystallographic data (without structure factors) were deposited as „supplementary publication no. 1537645“ at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).
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Reactions of $\text{Be}(\text{N}_3)_2$ with two equivalents of $[\text{Ph}_4\text{P}]\text{N}_3$ and $[\text{PNP}]\text{N}_3$ ($\text{PNP} = \text{Ph}_3\text{PNPPh}_3$) yielded $[\text{Ph}_4\text{P}]_2[\text{Be}(\text{N}_3)_4]$ **1** and $[\text{PNP}]_2[\text{Be}(\text{N}_3)_4]$ **2** containing the tetraazidoberyllate $[\text{Be}(\text{N}_3)_4]^{2-}$ dianion. **1** was structurally characterized by single crystal X-ray analysis and its electronic structure and bonding situation was studied by quantum chemical calculations. In addition, the structure of **2** in solution was studied by heteronuclear NMR spectroscopy.



*Dominik Naglav, Briac Tobey, Benjamin Lyhs, Beate Römer, Dieter Bläser, Christoph Wölper, Georg Jansen, and Stephan Schulz**

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Synthesis, Solid State Structure and Bonding Analysis of the first Homoleptic Beryllium Azide

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