Bismuth–Nitrogen Cations

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A Blue Homoleptic Bismuth–Nitrogen Cation**

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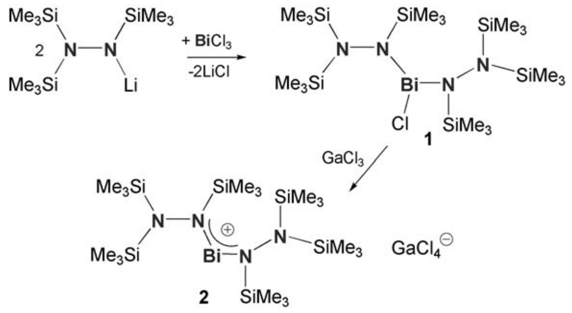
As early as 1834 the first nitrogen–phosphorus compounds were reported by Rose and Liebig.[1] Ever since, the chemistry of nitrogen–pnictogens, in particular the heavier homologues, has attracted considerable interest. More recently, low-coordinated P–N, As–N, and Sb–N species have been isolated and fully characterized.[2–4] An interesting aspect of the chemistry of the heavier Group 15 elements, in terms of both structure and reactivity, that continues to receive significant attention, is the area of cationic compounds with low coordination numbers.[4] In the case of bismuth, only a few neutral homoleptic Bi^{III}–N compounds[5] are known, and to the best of our knowledge only one cationic dicoordinated cyclic Bi–N species, $(CH_3)_2Si(N\mathit{t}Bu)_2Bi^+\,AlCl_4^-$ (**A**),[6] has been reported. Typical approaches to stabilize heavy-element double bonds (low coordination numbers) and positive charges are the introduction of bulky groups, charge delocalization, and charge transfer by means of bases such as DMAP (4-(*N*,*N*-dimethylamino)pyridine).[2b,h,3,7,8]

In this study, we employed silylated hydrazine units to stabilize the first acyclic homoleptic dicoordinated bismuth–nitrogen cation with a Bi=N double bond (see Scheme 1). Formally, this cation can also be regarded as a 3-bisma-2-pentazenium cation $[R_2N{-}N(R){-}Bi{=}N(R){-}NR_2]^+$ ($R = (CH_3)_3Si$) and represents a new member of the class of nitrogen-rich pentapnictogenium cations of the type $R_6E_5^+$ (E = pnictogen).

Our two-step synthesis starts with lithium *N*,*N*′,*N*′-tris(trimethylsilyl)hydrazide (Scheme 1), which we assumed to be an easily accessible source for a N-N-Bi unit. Hence, a solution of the hydrazide (5.5 mmol) in toluene was added dropwise at −50 °C to a suspension of $BiCl_3$ (5.0 mmol) in toluene. Removal of the solvent at −10 °C yielded a black residue, which was extracted with *n*-hexane. This orange solution was stored at −40 °C for 20 h and orange crystals formed (yield 40 %). The crystal structure determination (see Figure 1) in combination with elemental analysis and ^1H, ^{13}C, and ^{29}Si NMR studies clearly demonstrated the formation of chlorobis[*N*,*N*′,*N*′-tris(trimethylsilyl)hydrazino]bismutane (**1**; Figure 1) instead of dichloro[*N*,*N*′,*N*′-tris(trimethylsilyl)hydrazino]bismutane. It is impossible to isolate the monosubstituted product in toluene, even when the reaction is carried out with a large excess of $BiCl_3$. Apparently as a result of the low solubility of $BiCl_3$ in toluene, there is always an excess of lithium hydrazide in solution and double substitution always results.



Scheme 1. Synthesis of **1** and **2**.

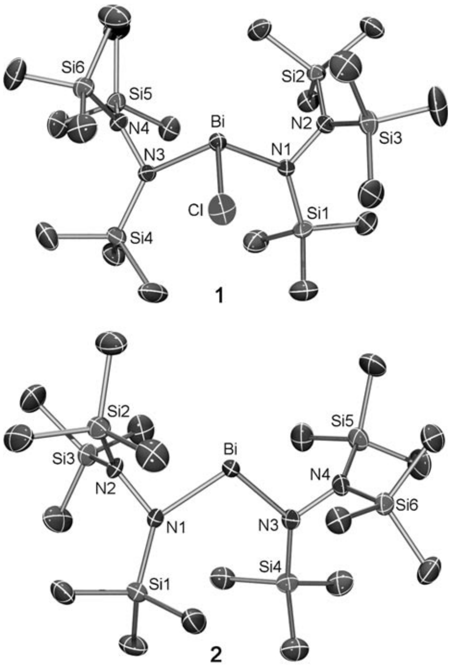


Figure 1. ORTEP drawings of the molecular structures of **1** and **2** in the crystal. Thermal ellipsoids are at 50% probability at 173 K (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: **1**: Bi–N1 2.164(2), Bi–N2 2.949(2), Bi–N3 2.160(2), Bi–Cl 2.5252(9), N1–N2 1.473(3); N3-Bi-N1 112.45(9), N3-Bi-Cl 99.00(7), N2-N1-Bi 106.8(2); **2**: Bi–N1 2.150(3), Bi–N2 2.794(4), Bi–N3 2.115(3), N1–N2 1.481(5), N3–N4 1.467(5), N1-Bi-N3 111.9(1), N2-N1-Bi 99.0(2), N1-Bi-N2 31.6(1).

Pure dry chlorodihydrazinobismutane **1** is stable at ambient temperature for a short period ($T_{dec} = 74\,°C$) but

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decomposes within 5 min in polar solvents (formation of elemental bismuth) as shown by ^1H and ^{29}Si NMR experiments. Hence, **1** must be stored under an argon atmosphere at $T < -30\,^\circ C$. Moreover, **1** displays thermochromic behavior: at $-196\,^\circ C$ it is pale yellow, at $25\,^\circ C$ deep orange.

The formation of **1** prompted us to attempt to abstract the chloro substituent with a Lewis acid. For this reason, a solution of $GaCl_3$ (1.1 mmol) in CH_2Cl_2 was added dropwise at $-60\,^\circ C$ to a solution of **1** (1.0 mmol) in CH_2Cl_2, leading to a dark blue solution. Slow removal of CH_2Cl_2 at $-10\,^\circ C$ yielded deep blue crystals (black appearance, yield 95%) of **2** (see Scheme 1 and Figure 1). It is interesting to note that **1** can be recovered from **2** simply by addition of THF which forms a $THF{\cdot}GaCl_3$ adduct.

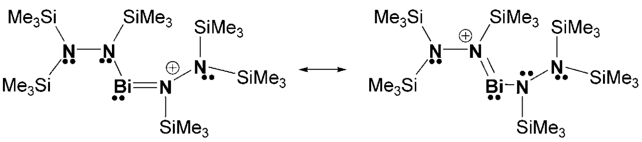
The blue salt **2** is, like **1**, air and moisture sensitive but stable under argon atmosphere over a long period as a solid and in CH_2Cl_2 solution at low temperature ($T < -60\,^\circ C$). The dark blue color of **2** vanishes rapidly when traces of H_2O are present. Compounds **1** and **2** are easily prepared in bulk and are infinitely stable when stored in sealed tubes and kept cool at $-80\,^\circ C$ in the dark. The bismuth salt **2** is considerably less stable than **1**, and it decomposes rapidly at ambient temperature.

^1H, ^{13}C, and ^{29}Si NMR spectroscopy are particularly well-suited to distinguish between **1** and **2**. The spectra show three resonances for compound **1** (all three silyl groups are chemically inequivalent) and two resonances for **2** (the silyl groups of the terminal N atoms are chemically equivalent). The downfield shift upon chloride abstraction is largest in the ^{29}Si NMR spectra (**1**: $\delta = 9.8$, 11.1 and 27.2 ppm vs. **2**: $\delta = 15.8$ and 43.8 ppm).

Compound **1** crystallizes in the monoclinic space group *C*2/*c* and **2** in the triclinic space group *P*1. The Bi center of **1** adopts a trigonal-pyramidal coordination geometry (sum of angles at Bi = 312.4°, cf. 296–297° in $Bi(NPh_2)_3$)[5d] without any significantly short intermolecular contacts. As depicted in Figure 1, the main structural motif of **1** is the W-shaped arrangement of the NNBiNN moiety which is not planar; the torsion angle between the two NNBi planes is 150.0°. This arrangement is slightly distorted, with two short Bi–N bonds (Bi–N1 = 2.164(2) and Bi–N3 = 2.160(2); cf. $Bi(NPh_2)_3$: 2.1–2.2 Å[5d] and $\Sigma r_{cov} = 2.2$ Å)[9] and two rather short $Bi{\cdots}N_{terminal}$ distances (Bi–N2 = 2.949(2) and Bi–N4 = 2.856(2) Å). For comparison, the sum of the van der Waals radii of N and Bi is 4.0 Å;[9] thus the two $Bi{\cdots}N_{terminal}$ distances indicate strong intramolecular $Bi{\cdots}N_{terminal}$ contacts.

The X-ray crystal structure of **2** displays features very similar to those of **1**: 1) The NNBiNN moiety also adopts a W-shaped configuration, with a torsion angle between the two NNBi planes of 154.2°. 2) As expected, all Bi–N distances with 2.150(3)/2.115(3) and 2.794(4)/2.817(4) Å, respectively, are slightly shorter than those in **1** (cf. 2.08–2.09 Å in the cyclic cation of salt **A**).[6] However, the difference between the two short Bi–N bonds in **2** is significantly greater than in **1** (**1**: 0.004 vs. **2**: 0.075 Å) indicating a stronger π-bond character in Bi–N3 than in Bi–N1 bond (Figure 2). The N-Bi-N angle in **2** (cf. **1**: 112.45(9)°) is considerably larger than that in A (111.9(1) vs. 72.9(4)°).[6] The N–N and Si–N bond lengths and all angles within the hydrazine fragment do not change much upon chloride abstraction.

The NBO analysis[10] of **1** shows three σ bonds and one lone pair of electrons localized at the Bi atom, while only two σ bonds, one lone pair, and one Bi–N double bond are found in **2**. In the VB picture the π bond can be best described by the two resonance shown in Scheme 2.[10e] The π bond can thus be classified as a four-electron, three-center bond.



Scheme 2. Lewis representation of **2** according to NBO analysis.

All Bi–N/Bi–Cl bonds are highly polarized.[10] For example only 15% of the Bi=N double bond in **2** is localized at the bismuth atom. The σ and π orbitals in **1** and **2** are mainly composed of p-type atomic orbitals (< 5% s AOs), while the lone pair of electrons on Bi possesses 89% (**1**) and 92% (**2**) s character. Upon chloride abstraction, only very small changes occur in the hybrid orbitals involved in bonding. In compound **1**, the Bi–Cl bond and the p-type lone pairs (p-LPs) at the adjacent nitrogen atoms are almost parallel; hence intramolecular donor–acceptor interactions between the nitrogen p-LP and the antibonding Bi–Cl σ* bond are found (hyperconjugative energies $\Delta E^{(2)}_{\sigma\sigma*} = 10.3$ and 5.5 kcal mol^{-1} for N1 and N3, respectively).[10] This interaction introduces a small amount of Bi–N π bonding and weakens the Bi–Cl σ bonds (see Figure S5 in the Supporting Information).[10e]

One of the major characteristics of the chloride abstraction in **1** is the total intramolecular charge transfer Q_{ct}. Interestingly, upon chloride abstraction the Bi atom becomes slightly less positive ($\Delta Q_{Bi} = q(Bi(\mathbf{2}) - q(Bi(\mathbf{1}) = -0.03$ e); the same holds for the silicon atoms. The positive charge is stabilized by the formation of the Bi–N double bond, which can also be considered to be a highly polarized intramolecular donor–acceptor bond. It is interesting to note that a considerable amount of the intramolecular charge transfer stems from the 18 methyl groups of the six silyl groups ($\Delta Q_{methyl} = 0.42$ e, Table S6 in the Supporting Information).[10e]

According to TD-B3LYP calculations (Figure S4 and Table S5 in the Supporting Information)[10e] the blue color arises from the n→π* electronic transitions (HOMO→LUMO and HOMO-1→LUMO) in the cation. The two occupied MOs describe mainly lone pairs localized at the four N atoms (Figure S4 in the Supporting Information).[10e] A closer inspection of the orbital coefficients shows rather large coefficients for the Bi atom in the LUMO (representing a Bi–N π* orbital), while the HOMO-3 describes mainly the Bi–N π bond delocalized over the N-Bi-N moiety (Figure 2).

We have described the first example of a homoleptic acyclic dicoordinated bismuth–nitrogen cation with an interesting W-shaped N-N-Bi-N-N structural motif. Two short Bi–N bonds and two $Bi{\cdots}N_{terminal}$ interactions are found in this highly labile nitrogen-rich pentapnictogenium cation.

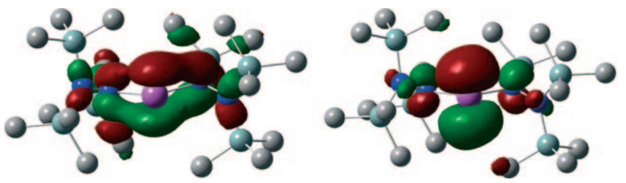


Figure 2. Molecular orbitals of **2**: left HOMO-3, right LUMO. Color code: Bi violet, N blue, Si light blue, C gray (H atoms are omitted).

According to NBO analysis, Bi contributes almost exclusively p-AOs to the Bi−X bonds (X = N, Cl), while the lone pair of electrons is located in primarily in an s-type AO.

Experimental Section

Synthesis of **1:** To a stirred suspension of $BiCl_3$ (1.734 g, 5.0 mmol) in toluene (40 mL), a solution of lithium *N,N′,N′*-tris(trimethylsilyl)hydrazide (1.273 g, 5.5 mmol) in toluene (20 mL) was added dropwise at −50 °C over a period of 15 min. The resulting brownish suspension was stirred at −40 °C for 10 min and was then warmed slowly to −10 °C over a period of 30 min, resulting in a black suspension. The solvent was removed in vacuo, and the resulting black residue was extracted with *n*-hexane (25 mL) and filtered (F4) to give a clear orange solution. The solution was concentrated in vacuo until crystallization started at −20 °C. Storage at −40 °C over a period of 20 h resulted in the deposition of orange crystals. Removal of supernatant by syringe and short drying in vacuo yielded 0.743 g (1.0 mmol, 40 %) of **1** as an orange, crystalline solid. Storage at −30 °C. M.p. 74 °C (decomp.). Anal. calcd % (found): C 29.23 (28.83), H 7.36 (7.12), N 7.58 (7.50). ^{29}Si NMR (25 °C, CD_2Cl_2, 59.6 MHz): $\delta =$ 9.8 (m, $N(Si(CH_3)_3)_2$), 11.1 (m, $N(Si(CH_3)_3)_2$), 27.2 ppm (m, $NSi(CH_3)_3$). ^1H NMR (25 °C, CD_2Cl_2, 300.13 MHz): $\delta = 0.28$ (s, 18H), 0.35 (s, 18H), 0.37 ppm (s, 18H). $^{13}C\{^1H\}$ NMR (25 °C, CD_2Cl_2, 75.5 MHz): $\delta = 4.24$ (s, $N(Si(CH_3)_3)_2$), 4.56 (s, $N(Si(CH_3)_3)_2$), 5.43 ppm (s, $NSi(CH_3)_3$). IR (ATR): $\tilde{\nu} = 2976$ (w), 2953 (w), 2898 (w), 1403 (w), 1296 (w), 1243 (s), 989 (m), 922 (s), 901 (m), 830 (s), 815 (s), 778 (s), 752 (s), 672 (m), 649 (m), 620 (m). Raman (25 mW, 25 °C, 42 scans, cm^{-1}): $\tilde{\nu} = 2961$ (5), 2904 (10), 2828 (2), 2756 (2), 1405 (1), 1011 (1), 835 (1), 799 (1), 760 (1), 685 (1), 653 (2), 521 (2), 370 (1), 260 (2), 181 (1). MS (EI, positive, 70 eV, > 10 %): *m*/*z*: 43 (10), 45 (18), 73 (100) $[Si(CH_3)_3]^+$, 77 (20), 118 (13), 130 (47), 132 (87), 145 (55) $[(Si(CH_3)_3){-}N{=}Si(CH_3)_2]^+$, 160 (16), 204 (13), 217 (19), 232 (10), 233 (35), 247 (43) $[(Si(CH_3)_3)_2N{=}N{-}Si(CH_3)_3]^+$, 248 (94) $[(Si(CH_3)_3)_2N{=}NHSi(CH_3)_3]^+$.

Synthesis of **2:** To a stirred solution of **1** (2.184 g, 1.0 mmol) in CH_2Cl_2 (20 mL), $GaCl_3$ (0.634 g, 1.1 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −60 °C over a period of 10 min. The resulting dark blue solution was stirred at −50 °C for 30 min and filtered (F4). The solvent was removed in vacuo at −10 °C to give a black, crystalline residue, which was washed with cold (−50 °C) *n*-hexane (10 mL) and dried in vacuo at −10 °C to yield 0.870 g (0.95 mmol, 95 %) of **2** as black crystals. Storage at −80 °C. M.p. 59 °C (decomp.). Anal. calcd. % (found): C 23.61 (21.82), H 5.94 (4.85), N 6.12 (4.35). ^{29}Si NMR (−75 °C, CD_2Cl_2, 79.5 MHz): $\delta = 15.8$ (m, $N(Si(CH_3)_3)_2$), 43.8 (m, broad, $NSi(CH_3)_3$). ^1H NMR (−75 °C, CD_2Cl_2, 400.13 MHz): $\delta = 0.25$ (s, 36H, $N(Si(CH_3)_3)_2$), 0.39 ppm (s, 18H, $NSi(CH_3)_3$). $^{13}C\{^1H\}$ NMR (−75 °C, CD_2Cl_2, 100.6 MHz): $\delta = 4.38$ (s, $N(Si(CH_3)_3)_2$), 5.24 ppm (s, $NSi(CH_3)_3$). IR (ATR): = 2957 (w), 2902 (w), 1574 (w), 1498 (w), 1407 (w), 1252 (s), 1060 (m), 1001 (m), 964 (m), 900 (s), 812 (s), 758 (s), 730 (s), 683 (s). MS (FAB^+, Cs, 20 keV, *p*-NBA matrix): *m*/*z*: 247 $[(Si(CH_3)_3)_2N{=}N{-}Si(CH_3)_3]^+$, 703 $[M]^+$.

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