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The Hexaazidosilicate(IV) Ion: Synthesis, Properties, and Molecular Structure

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Binary azides of group 14 elements form a class of rare highly endothermic compounds.[1] Synthesis and handling of these compounds afford proper experimental care to minimize unpredictable, explosive hazards resulting from exothermic decomposition by elimination of dinitrogen.[2] Therefore, it is not surprising that to date only the ions $[C(N_3)_3]^+$ [3] and $[E(N_3)_6]^{2-}$ (E = Ge-Pb)[1,4] and the primary explosive α-$Pb(N_3)_2$[5] have been isolated and structurally characterized. In comparison, structural information for analogous silicon compounds is lacking. Thus far, only $Si(N_3)_4$ has been reported to be a violently explosive substance,[6] which was prepared in situ and characterized by ^{29}Si NMR or IR spectroscopy.[7] Following our interest in main-group element azides with a high nitrogen content,[8] we describe here the synthesis and full characterization of the $[Si(N_3)_6]^{2-}$ ion.

Treatment of a solution of $SiCl_4$ in CH_3CN with an excess of $(PPN)N_3$ at 0 °C leads selectively to $(PPN)_2[Si(N_3)_6]$ (**1**) as evidenced by IR monitoring of the reaction (equation).

$$SiCl_4 + \text{ex. } PPN(N_3) \xrightarrow[PPN^+ = [(Ph_3P)_2N]^+]{\text{MeCN, 0 °C}} (PPN)_2[Si(N_3)_6] \quad (\mathbf{1})$$

The hexaazidosilicate salt **1** was separated from (PPN)X (X = Cl, N_3) after repeated recrystallization from CH_3CN and isolated as a colorless, moisture−sensitive, crystalline solid in 37−62% yields. It was characterized by elemental analysis, thermal analysis and IR, Raman, ^{29}Si, and ^{14}N NMR spectroscopies and single-crystal X-ray crystallography.[9] Compound **1** is insoluble in THF and very soluble in CH_2Cl_2 and CH_3CN to give colorless solutions, which turn immediately cloudy due to hydrolysis, when exposed to air. Hydrolysis of **1** liberates HN_3 and $(PPN)N_3$.[10] The hexazidosilicate salt **1** exhibits remarkable thermal stability, melting in vacuo without decomposition at 225 °C. Its melting point is even higher than that of the germanium analogue $(PPN)_2[Ge(N_3)_6]$ (**2**) (mp = 211 °C).[1] Simultaneous thermal analysis (TG-DTA) of **1** coupled with mass spectrometric detection of the evolved gases revealed that two distinct exothermic decomposition processes follow the endothermic melting of **1** at the extrapolated onset temperature T_{on}^{ex} = 214 °C (peak temperature T_p = 220 °C). The first process started at T_{on} = 256 °C (T_p = 296 °C) and was associated with a mass loss of 6.1%, which is mainly ascribed to elimination of N_2.[11] The second process was observed at T_{on} = 321 °C, and was accompanied by a fast mass loss and liberation of energy (T_p = 333 °C) leading to a pressure surge on the balance. This process involves degradation of the PPN cations and evolution of $Si(N_3)_4$, N_2, and some HN_3.[11] The solid-state structure of **1** was determined by single-crystal X-ray diffraction. **1** crystallizes in the space group $P\bar{1}$ and is isostructural with the hexaazidogermanate salt **2**.[1] The crystal structure of **1** consists of discrete PPN^+ cations and S_2 symmetric $[Si(N_3)_6]^{2-}$ anions (Figure 1). The mean $Si-N_{azide}$ bond length of **1** (1.871 Å, Table 1) is 6−11 pm longer than those reported for tetrahedral azidosilanes (Si−N = 1.760(3)−1.814(2) Å).[12] The mean $N_\alpha-N_\beta$ and $N_\beta-N_\gamma$ bond lengths in **1** (1.202 and 1.145 Å, Table 1) agree well with those in $(PPN)_2[Ge(N_3)_6]$ ($(N_\alpha-N_\beta)_{av}$ = 1.212 Å, $(N_\beta-N_\gamma)_{av}$ = 1.147 Å)[1] and the difference Δ(NN) between the N−N bond lengths of 5.7 pm is smaller than that found in other covalent azides.[8] All of these structural parameters suggest in agreement with the IR data and the results of the theoretical calculations the presence of polar Si−N bonds in **1**. The IR spectra of **1** in CH_3CN display at different concentrations only one very strong absorption band for the $\nu_{as}(N_3)$ vibration at 2109 cm^{-1} [13,14] and give no evidence for a dissociation of **1** to $(PPN)N_3$ and $Si(N_3)_4$.[10,15] The Raman and IR spectra of **1** are consistent with the presence of S_6 symmetric $[Si(N_3)_6]^{2-}$ ions in solution and allow in combination with the calculated vibrational spectra (Supporting Information) an assignment of most observed bands to fundamental modes of the $[Si(N_3)_6]^{2-}$ ion.[9] The ^{29}Si NMR spectrum of **1** in CH_3CN displays one sharp signal at δ = −188.7 ppm,[16] which is considerably upfield-shifted relative to that of $Si(N_3)_4$ (−75.1 ppm).[7a] The ^{29}Si chemical shift of **1** agrees well with that calculated for the $[Si(N_3)_6]^{2-}$ ion (−198.2 ppm)[16] using the GIAO-MBPT(2) method,[17] and is similar to that reported for other hexa-coordinate silicon compounds, such as $ZnSiF_6$ (δ = −185.3 ppm).[18] All these facts provide additional evidence for the presence of intact $[Si(N_3)_6]^{2-}$ ions in solution. The ^{14}N NMR spectrum of **1** in CH_3CN shows two singlet resonances at δ = −214.7 (N_γ) and −297 ppm (N_α) for the $[Si(N_3)_6]^{2-}$ ion, which agree well with the calculated values ($\delta(N_\gamma/N_\alpha)$ = −217/285 ppm).[16,19]

The electronic structure of the $[Si(N_3)_6]^{2-}$ ion was calculated using different methods and basis sets (Table 1, Supporting Information).[20,21] All geometry optimizations led to a S_6 symmetric minimum structure as the most stable $[Si(N_3)_6]^{2-}$ isomer. Moreover, a good to excellent agreement was found between the calculated and experimental bond lengths and angles.

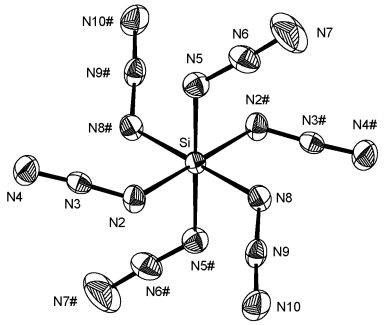

Figure 1. DIAMOND plot of the anion $[Si(N_3)_6]^{2-}$ in **1** (view down the pseudo-S_6 axis). Thermal ellipsoids are set at the 50% probability level. Selected bond lengths (Å) and angles (deg): Si−N2 1.866(1), Si−N5 1.881(1), Si−N8 1.867(1), N2−N3 1.198(2), N3−N4 1.144(2), N5−N6 1.201(2), N6−N7 1.144(2), N8−N9 1.207(2), N9−N10 1.146(2), Si−N2−N3 126.5(1), Si−N5−N6 122.6(1), Si−N8−N9 121.9(1), N2−Si−N5 90.16(6), N2−Si−N8 89.32(6), N5−Si−N8 90.30(6), N2−N3−N4 175.3(2), N5−N6−N7 176.4(2), N8−N9−N10 176.1(2).

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Table 1. Experimental and Calculated Parameters of $[Si(N_3)_6]^{2-}$ [a]

	bond lengths D [Å]			angles [°]
	Si–N_α	N_α–N_β	N_β–N_γ	Si–N_α–N_β
X-ray[b]	1.871(5)	1.202(3)	1.145(1)	124(1)
RI-MP2/TZVP	1.876	1.206	1.174	126.1
RI−BP86/TZVPP[c]	1.902	1.205	1.161	127.2
B3LYP/TZVPP[c]	1.896	1.195	1.146	127.1
HF/TZVPP[c]	1.889	1.179	1.108	124.4
	partial charges q [e]			
BP86/TZVPP	Si: +1.86	N_α: −0.58	N_β: +0.22	N_γ: −0.28

[a] Details of all theoretical calculations are found in the Supporting Information. [b] The unweighted mean x_u of the three crystallographically independent bond lengths and angles of **1** is listed. The standard deviation σ of x_u is given in parentheses and was calculated by $\sigma^2 = \sum(x_i - x_u)^2/(n^2 - n)$, x_i = individual value, $n = 3$. [c] Restrained geometry (S_6).

The best results were obtained at the RI-MP2/TZVP level (Table 1). The small difference between the calculated and experimental N_β−N_γ length ($D_c = 1.174$, $D_o = 1.145(1)$ Å) can be traced back to thermal motion in the crystal.[22] Thus, a correction of D_o with the riding model[22] led to a significant elongation of the N_β−N_γ distances (D_i(av) = 1.166(5) Å),[23] which agrees very well with the calculated length, whereas the Hirshfeld test for rigid body vibrations[24] failed with the X-ray data of **1**.[25] An NBO analysis of $[Si(N_3)_6]^{2-}$ reveals the presence of polar Si−N bonds (Table 1).[26] A second isomer of $[Si(N_3)_6]^{2-}$ with D_{3d} symmetry was also found to be a local minimum on the potential energy surface. However, this isomer is less stable than the S_6 symmetric isomer (100.3 kJ mol^{-1} at the HF/SVP level and 54.4 kJ mol^{-1} at the BP86/SVP level (zero-point vibrational energy corrected). A look at the electron density distribution suggests that an optimal orientation of the azido groups is achieved in the S_6 symmetric minimum structure to minimize the Coulombic repulsion between the lone pairs of the N_α atoms and to maximize the Coulombic attraction between the opposite charged N_α and N_β atoms in adjacent azido groups.

The anion $[Si(N_3)_6]^{2-}$ belongs to a class of very rare hypercoordinate silicon complexes with a SiN_6 coordination polyhedron,[18,27] and has the highest nitrogen content (89.98%) among the homoleptic hexaazidometalates reported thus far.[28] Further studies in this direction show that stable neutral Lewis-base adducts of $Si(N_3)_4$ are also accessible following a similar approach.

Supporting Information Available: CCDC 192397 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). Experimental Section, X-ray crystallography of **1** (CIF), thermal analysis of **1**, electronic structure calculations, calculations of NMR chemical shifts and vibrational spectra of $[Si(N_3)_6]^{2-}$, isocharge plot of calculated and experimental electron density (PDF), and Acknowledgment. This material is available free of charge via the Internet at http://pubs.acs.org

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(9) Synthesis and spectroscopic data of **1**: A solution of $SiCl_4$ (0.1 mL, 0.8 mmol) in 15 mL of CH_3CN was treated at 0 °C with a solution of (PPN)-N_3 (3.47 g, 6 mmol) in 10 mL of CH_3CN. The cooling was removed and slow stirring was continued for 4 h at ambient temperature. The slightly cloudy solution was filtered at 0 °C using a stainless steel cannula fitted with a fiberglass filter (Whatman®). The clear, colorless filtrate was concentrated in vacuo below 0 °C until crystallization started, and the resulting suspension was stored for 12 h at −28 °C. The supernatant solution was decanted off and the crystalline precipitate washed with cold CH_3CN and dried for 30 min in vacuo. The recrystallization was repeated three times to afford air-sensitive, colorless crystals of **1** in 37−62% yield from $SiCl_4$. Anal. Calcd for $C_{72}H_{60}N_{20}P_4Si$ (1357.38): C, 63.71; H, 4.45; N, 20.64. Found: C, 63.66; H, 4.37; N, 20.26%; the substance did not contain chlorine. IR (CH_3CN, cm^{-1}) ν = 2109 vs ($\nu_{as}(N_3)$, E_u and A_u), 1590 vw (ν(ar)). IR (CH_2Cl_2, cm^{-1}) 2108 vs ($\nu_{as}(N_3)$, E_u and A_u), 1590 vw (ν(ar)). IR (Nujol, cm^{-1}) 3390 vw, 3354 vw, 3055 vw, 2104 vs, 1587 vw, 1482 w, 1438 s, 1320 s, 1315 m, 1302 m(sh), 1272 m, 1184 vw, 1161 vw, 1115 s, 1026 w, 997 w, 796 w, 765 vw(sh), 750 w, 724 m, 692 s. Raman (CH_3CN, rt, cm^{-1}; p = polarized, dp = depolarized): ν([Si-$(N_3)_6]^{2-}$) = 2142 m (p, $\nu_{as}(N_3)$, A_g), 2104 w, br (dp, $\nu_{as}(N_3)$, E_g), 2079 w, br, 1329 m (p, $\nu_{sym}(N_3)$, A_g), 1316 w (dp, $\nu_{sym}(N_3)$, E_g), 702 s (p), 440 vs (p, ν(Si−N), A_g). ^{14}N NMR (21.7 MHz, CH_3CN, rt, ppm): $\delta = -214.7$ (s, $\Delta\nu_{1/2} \approx 36$ Hz, N_γ), −297 (s, $\Delta\nu_{1/2} \approx 391$ Hz, N_α). ^{29}Si NMR (49.7 MHz, CH_3CN, rt, ppm) $\delta = -188.7$ (s, $\Delta\nu_{1/2} \approx 1$ Hz). ^{14}N NMR of (PPN)N_3 (21.7 MHz, CH_3CN, rt, ppm) $\delta = -130.0$ (s, $\Delta\nu_{1/2} \approx 11$ Hz, N_β), −276.9 (s, $\Delta\nu_{1/2} \approx 28$ Hz, 2 × N_α). No ^{14}N NMR signal could be detected for the PPN cation in **1** and (PPN)X (X = Cl, N_3, solvent: CH_3-CN).
(10) Despite all attempts for vigorous air-exclusion the IR spectra of **1** in MeCN showed always two $\nu_{as}(N_3)$ bands of varying weak intensity of the hydrolysis products HN_3 (2139 cm^{-1}) and (PPN)N_3 (2005 cm^{-1}) in addition to the strong $\nu_{as}(N_3)$ absorption band of **1** at 2109 cm^{-1}.
(11) At the start of the first exothermic step only the ion $[N_2]^+$ (m/z = 28) and to less extent the ions $[N]^+$ (14) and $[HN_3]^+$ (43) appeared in the EI mass spectra of the evolved gases. The intensity of these signals followed the progress of the DTA curve from T_{on} = 256 °C. The ions $[Ph]^+$ (m/z = 77), $[Ph - C_2H_2]^+$ (51) and $[Si(N_3)_3]^+$ (154) appeared in the mass spectra at the start of the second exothermic effect. The intensity of these signals developed as the DTA curve and increased from T_{on} = 321 °C to T_p = 333 °C. Evolution of $Si(N_3)_4$ during the second exothermic process was confirmed by an independent experiment, in which a sample of **1** was heated with a rate of 30 K min^{-1} in high vacuo and the gases analyzed with a Hewlett-Packard 5995A mass spectrometer using the EI method (70 eV, positive ions). Above 318 °C the mass spectra showed signals at m/z = 70.1, 154.0, and 196.1 (based on the ^{14}N and ^{28}Si isotopes). The isotope patterns of these signals matched perfectly to those calculated for the ions $[Si(N_3)_n]^+$ (n = 1, 3, 4).
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