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Unusual Silicon Coordination Polyhedra: Non-VSEPR Structures of Zwitterionic λ^5-Si Silicon(IV) Complexes with an SiS_2N_2C or SiS_2O_2C Skeleton**

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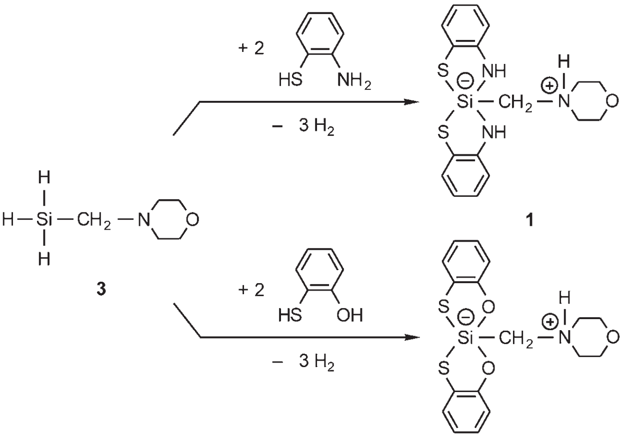
The chemistry of higher-coordinate silicon is currently one of the main areas of research in silicon chemistry.[1] Our systematic studies on zwitterionic λ^5-Si compounds that contain a pentacoordinate (formally negatively charged) silicon atom and a tetracoordinate (formally positively charged) nitrogen atom have led to a large variety of structures with different Si coordination polyhedra.[1d] We have recently reported on the synthesis of zwitterionic λ^5-Si complexes with Si–S bonds, demonstrating that sulfur atoms can also act as ligand atoms in pentacoordinate silicon compounds.[2] In most cases, the Si coordination polyhedra of zwitterionic λ^5-Si compounds with an SiS_4C or SiS_2O_2C skeleton are somewhat distorted trigonal bipyramids, with the carbon atom and two sulfur atoms in the three equatorial positions. We have now succeeded in synthesizing the first zwitterionic λ^5-Si complex with an SiS_2N_2C skeleton (**1**) and the zwitterionic λ^5-Si complex **2** with an SiS_2O_2C skeleton, in which sulfur atoms occupy axial positions. This arrangement of ligand atoms is contradictory to VSEPR predictions. We are aware of only a few other pentacoordinate silicon complexes with a non-VSEPR distribution of the ligand atoms with respect to their electronegativity ($F > O > N$).[3] However, in all of these other cases, the preferred bite angle of the chelate ligands appears to dictate the distribution. Thus, it was of interest to investigate the structures of **1** and **2** by computational studies.

Compounds **1** and **2** were synthesized according to Scheme 1 by treatment of (morpholinomethyl)silane (**3**)[2c] with 2 molar equivalents of 2-mercaptoaniline and 2-mercaptophenol, respectively, at 20 °C in acetonitrile (**1**) or tetrahydrofuran (**2**). After recrystallization from acetonitrile, both products were isolated as crystalline solids (yields: **1**, 65 %; **2**, 52 %), and their identities were established by elemental analyses, solid-state NMR spectroscopy, and single-crystal X-ray diffraction.



Scheme 1. Syntheses of the zwitterionic λ^5-Si compounds **1** and **2**. For details, see Experimental Section.

Compound **1** crystallizes in the space group $P2_1/c$ with one zwitterion in the asymmetric unit.[4] As can be seen from Figure 1, the Si coordination polyhedron of **1** is a distorted trigonal bipyramid (transition trigonal bipyramid→square pyramid: 15.1 %; pivot atom C1),[5] in which each bidentate ligand spans one axial and one equatorial site. The two sulfur atoms (S1, S2) occupy the axial positions, whereas the two nitrogen atoms (N1, N2) and the carbon atom (C1) are found in the equatorial positions. This structure is quite surprising, as one would expect the more electronegative nitrogen atoms to occupy the axial sites. The Si–S bond lengths range from 2.2842(6) to 2.3853(6) Å and are quite similar to those of the axial Si–S bonds in related zwitterionic λ^5-Si compounds with SiS_4C skeletons and trigonal-bipyramidal Si coordination polyhedra.[2b,c] The Si–N distances (1.7261(13) and 1.7339(13) Å) are similar to those observed for related zwitterionic λ^5-Si complexes with an SiO_2N_2C skeleton, in which the nitrogen atoms also occupy the equatorial positions of a trigonal-bipyramidal Si coordination polyhedron.[6] Compound **1** forms an intramolecular N3–H···S1 hydrogen bond,[7] resulting in an elongation of the Si–S1 bond compared to the other axial Si–S2 bond.

Compound **2** crystallizes in the space group *Pbca* with one zwitterion in the asymmetric unit.[4] The Si coordination polyhedron of **2** (Figure 2) is a slightly distorted trigonal bipyramid (transition trigonal bipyramid→square pyramid: 8.0 %; pivot atom C1)[5] with one sulfur atom (S1) and one

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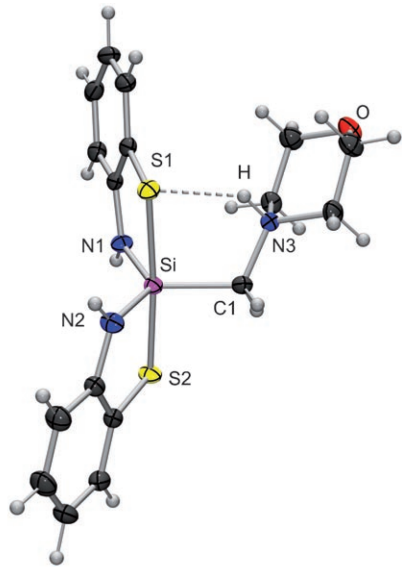


Figure 1. Molecular structure of **1** (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–S1 2.3853(6), Si–S2 2.2842(6), Si–N1 1.7339(13), Si–N2 1.7261(13), Si–C1 1.9214(14); S1-Si-S2 175.25(2), S1-Si-N1 85.93(4), S1-Si-N2 88.00(5), S1-Si-C1 91.04(5), S2-Si-N1 94.18(4), S2-Si-N2 88.08(5), S2-Si-C1 93.20(5), N1-Si-N2 125.71(6), N1-Si-C1 115.47(6), N2-Si-C1 118.54(6). The dashed line indicates the presence of an intramolecular N3–H⋯S1 hydrogen bond: N3–H 0.900(17), H⋯S1 2.230(17), N3⋯S1 3.0029(13); N3-H⋯S1 143.7(15).

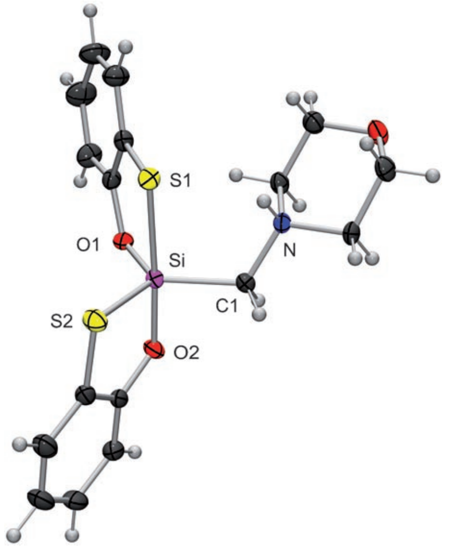


Figure 2. Molecular structure of **2** (probability level of displacement ellipsoids 50%). Selected bond lengths [Å] and angles [°]: Si–S1 2.3831(5), Si–S2 2.1510(6), Si–O1 1.6935(12), Si–O2 1.7423(11), Si–C1 1.9047(15); S1-Si-S2 86.72(2), S1-Si-O1 87.71(4), S1-Si-O2 176.61(4), S1-Si-C1 94.18(5), S2-Si-O1 122.01(4), S2-Si-O2 90.79(4), S2-Si-C1 121.46(5), O1-Si-O2 91.67(5), O1-Si-C1 116.50(6), O2-Si-C1 89.08(6).

oxygen atom (O2) in the axial positions, whereas the equatorial sites are occupied by a sulfur (S2), oxygen (O1), and carbon (C1) atom. Compared to related λ^5-Si compounds with an SiS_2O_2C skeleton and both oxygen atoms in the axial positions,[2a,d] this asymmetric arrangement of ligand atoms is quite unusual. The axial Si–S1 bond length (2.3831(5) Å) is significantly longer than the equatorial Si–S2 distance (2.1510(6) Å), which is in good agreement with the Si–S distances observed for related zwitterionic λ^5-Si compounds with SiS_4C skeletons.[2b,c] Likewise, the axial Si–O2 bond (1.7423(11) Å) is longer than the equatorial one (1.6935(12) Å). Compound **2** forms a bifurcate N–H⋯S1/S1A hydrogen bond,[7] which leads to the formation of centrosymmetric dimers in the crystal (Figure 3).

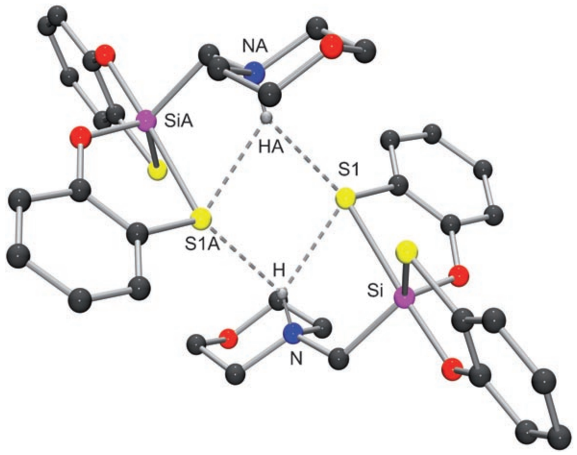
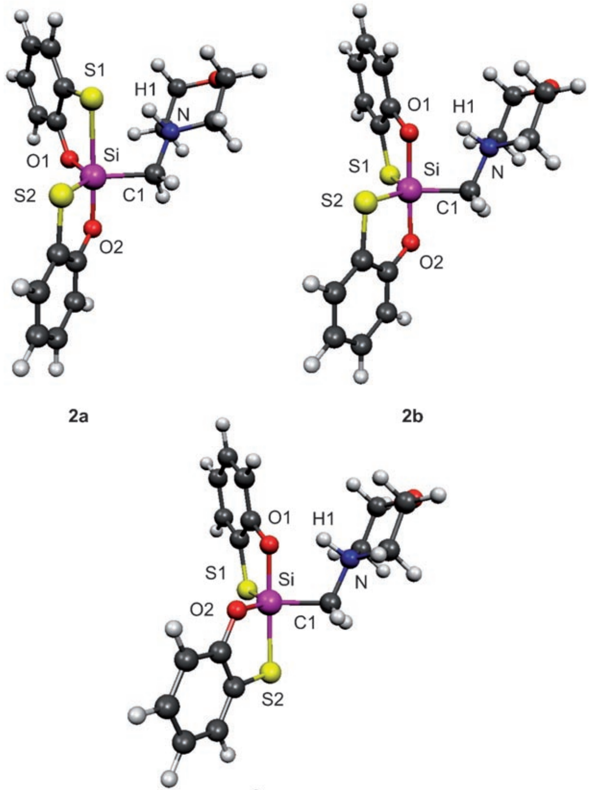


Figure 3. Hydrogen-bonding system in the crystal of **2**. The dashed lines indicate bifurcate N–H⋯S/S hydrogen bonds, with an intra- and intermolecular interaction leading to the formation of centrosymmetric dimers. The hydrogen atoms (except for the NH atoms) are omitted for clarity. Bond lengths [Å] and angles [°]: N–H 0.86(2), H⋯S1 2.420(19), N⋯S1 3.0493(13), H⋯S1A 2.82(2), N⋯S1A 3.5401(13); N-H⋯S1 130.1(15), N-H⋯S1A 141.8(16), S1⋯H⋯S1A 74.3(5).

Compounds **1** and **2** were characterized by solid-state ^{13}C, ^{15}N, and ^{29}Si NMR spectroscopy (see Experimental Section).[8] The NMR spectra obtained are in agreement with the crystal structures of **1** and **2**. All attempts to characterize these compounds by solution NMR spectroscopy failed owing to poor solubility and/or decomposition upon dissolution.

Structures and relative energies for **1**, **2**, and the dimer of **2** were studied by quantum chemical calculations at the DFT and MP2 level (see Computational Details). For compound **1**, the experimentally observed structure (cf. Figure 1) corresponds to a minimum on the potential-energy surface. Both the B3LYP and the MP2 structure agree well with the experimental structure. Rotation of the morpholinio group by approximately 90° around the C1–N3 bond provides a second minimum, with a different intramolecular hydrogen bond (N3–H⋯N2), which is higher in energy than the first minimum by 25 kJ mol^{-1} (22 kJ mol^{-1}) at the B3LYP (MP2) level. All attempts to locate a minimum with the atoms N1 and N2 in the axial positions led back to the experimentally observed structure. Thus, we have no evidence for a minimum of **1** that would follow the VSEPR predictions. When the N_{ax}–Si–C_{eq}–N dihedral angle was fixed at the value of the S_{ax}–Si–C_{eq}–N dihedral angle in the minimum structure during a partial optimization of a "VSEPR-conforming" structure, an energy of 38.5 kJ mol^{-1} above the initial minimum was computed (B3LYP).

For compound **2**, the VSEPR rules would predict a structure with the two oxygen atoms in axial positions, in contrast to the experimental finding (cf. Figure 2 and Figure 3). MP2 and B3LYP optimizations provided minima for both the non-VSEPR structure observed experimentally (cf. **2a** in Figure 4) and the structure predicted by the VSEPR concept (cf. **2b** in Figure 4). Indeed, the latter minimum, **2b**, is lower than **2a** by 6.5 kJ mol^{-1} (6.1 kJ mol^{-1}) at the B3LYP (MP2) level. The optimized structure for **2a** exhibits a relatively long Si–S1 bond (0.1 Å (0.06 Å) above the experimental value at the B3LYP (MP2) level). An even more stable structure **2c** might be expected with a strong N–H1···O1 hydrogen bond (Figure 4; the O1···H1 distance is 1.720 Å at the B3LYP level). While this arrangement is also a minimum, its energy is computed to be 8.3 kJ mol^{-1} (10.1 kJ mol^{-1}) above that of **2a** at the B3LYP (MP2) level. To see whether the energetic preferences are altered upon formation of hydrogen-bonded dimers (cf. Figure 3), we have also optimized the dimeric structures of **2a** and **2b** at the B3LYP level. The energy of the VSEPR-conforming dimer of **2b** is still slightly (7.0 kJ mol^{-1}) above that of **2a**. The energy differences between the isomers of **2** (monomers and dimers) are extremely small. This result suggests that the preference for crystallization of one or the other isomer may well be governed by small effects arising from the crystal packing. Alternatively, formation of dimeric **2a** may be favored kinetically during the crystallization process. There is no possibility to prove this suggestion at the moment, so it might be helpful to synthesize further comparable compounds to study their crystallization behavior.



2a **2b**

2c

Figure 4. B3LYP-optimized minima of **2**.

The VSEPR concept predicts that the more electronegative substituents would be found in the axial positions of a trigonal bipyramid. Why then is the energy difference between VSEPR and non-VSEPR structures small enough to allow crystallization of the latter for **2**, and why can the VSEPR-conforming structure not even be located as a minimum on the potential-energy surface for **1**? If we disregard transition-metal systems (and d^0 systems encompassing some formal main-group cases[9]) or the question of stereochemically active/inactive lone pairs,[10] the remaining counterexamples to the VSEPR concept are typically seen when steric effects start to dominate.[11] This situation does not apply to **1** or **2**, as the sulfur atom is not only less electronegative than the nitrogen or oxygen atom but also larger. Steric effects, if present, should thus enhance the VSEPR preferences. How much energy gain should more electronegative substituents in axial positions "normally" provide? In the model system $[SiF_3H_2]^{2-}$, B3LYP gives a preference of approximately 20 kJ mol^{-1} for the isomer with two axial fluoro ligands over that with two axial hydrogen atoms. This value is reduced to only a few kJ mol^{-1} for **2** and potentially reversed for **1**. We actually see the order predicted by electronegativity differences, which according to Pauling are about 1.8 for F versus H, 0.8 for S versus O, and 0.4 for S versus N. Thus, while population analyses (not shown) clearly indicate that sulfur bears less negative charge than coordinated nitrogen or oxygen in **1** and **2**, respectively, the driving force for placing sulfur in an axial position is either very small or has vanished.

Apart from ligand electronegativity, the size of ligand atoms in relation to the orbitals at silicon may affect the preferred position within the trigonal bipyramid: More p-character is expected in the silicon hybrid orbitals directed towards the axial ligand atoms, consistent with longer bonds. This situation might indeed favor sulfur over oxygen in the axial position. Other cases of violation of Bent's rule or VSEPR are known, in which the relative sizes of orbitals on the central atom and on the ligand atoms may overrule electronegativity considerations.[12] We suggest that the relatively small energy differences computed between **2a** and **2b**, and the exclusive observation of the non-VSEPR arrangement for **1** may partly reflect such size effects when comparing ligand atoms from different rows of the periodic table.

Experimental Section

1: Compound **3**[2c] (131 mg, 998 μmol) was added at 20 °C to a stirred solution of 2-mercaptoaniline (250 mg, 2.00 mmol) in acetonitrile (10 mL), and the mixture was stirred at 20 °C for 1 h (evolution of hydrogen). The resulting precipitate was redissolved in the mother liquor by heating, and the resulting solution was kept undisturbed at 20 °C for 8 days. The precipitate that formed was isolated by filtration, washed with *n*-pentane (20 mL), and dried in vacuo (0.1 mbar, 20 °C, 2 h) to give **1** in 65 % yield as a colorless crystalline solid (244 mg, 650 μmol); m.p. 144–146 °C (decomp.); ^{13}C VACP/MAS NMR (ν_{rot} =

6.5 kHz):[8] $\delta = 55.9$ (2 C) and 61.7 (NCH_2C, SiCH_2N), 66.1 (OCH_2C), 66.7 (OCH_2C), 112.2, 113.8, 118.7, 119.7, 123.9 (2 C), 126.4, 127.6, 128.7, 129.3, 145.3, and 145.9 ppm (C_6H_4); ^{15}N VACP/MAS NMR ($\nu_{rot} = 6.5$ kHz):[8] $\delta = -275.5$ (SiNHC), -278.6 (SiNHC), -311.7 ppm (CN(H)C_2); ^{29}Si VACP/MAS NMR ($\nu_{rot} = 6.5$ kHz):[8] $\delta = -76.2$ ppm; elemental analysis (%) calcd for $C_{17}H_{21}N_3OS_2Si$ ($M_r = 375.59$): C 54.36, H 5.64, N 11.19, S 17.07; found: C 54.23, H 5.61, N 10.83, S 16.69.

2: Compound **3**[2c] (263 mg, 2.00 mmol) was added at 20 °C to a stirred solution of 2-mercaptophenol (504 mg, 3.99 mmol) in tetrahydrofuran (2 mL), and the mixture was stirred at 20 °C for 2 h (evolution of hydrogen). The solution was then covered with a layer of *n*-pentane (5 mL) and kept undisturbed at 20 °C for 9 days. The resulting precipitate was isolated by filtration, washed with *n*-pentane (20 mL), and dried in vacuo (0.1 mbar, 20 °C, 2 h). The crude product (691 mg) was recrystallized from hot acetonitrile (2 mL, cooling to 20 °C and crystallization within 13 days). The resulting precipitate was isolated by filtration, washed with *n*-pentane (20 mL), and dried in vacuo (0.1 mbar, 20 °C, 2 h) to give **2** in 52 % yield as a colorless crystalline solid (390 mg, 1.03 mmol); m.p. 162–163 °C (decomp.); ^{13}C VACP/MAS NMR ($\nu_{rot} = 7$ kHz):[8] $\delta = 53.6$, 55.4, and 56.0 (NCH_2C, SiCH_2N), 64.3 (OCH_2C), 65.1 (OCH_2C), 110.8, 114.5, 120.3, 121.2, 124.3, 125.5, 127.0, 128.5, 130.0, 133.3, 153.4, and 155.4 ppm (C_6H_4); ^{15}N VACP/MAS NMR ($\nu_{rot} = 5.5$ kHz):[8] $\delta = -314.8$ ppm. ^{29}Si VACP/MAS NMR ($\nu_{rot} = 5.5$ kHz):[8] $\delta = -68.0$ ppm; elemental analysis (%) calcd for $C_{17}H_{19}NO_3S_2Si$ ($M_r = 377.56$): C 54.08, H 5.07, N 3.71, S 16.99; found: C 53.95, H 5.00, N 3.65, S 16.95.

Computational Details. All molecular structures were optimized at the B3LYP[13] DFT and MP2 level using the Turbomole 5.8[14] program system and TZVP[15] basis sets. Stationary points on the potential-energy surface were characterized by harmonic vibrational frequency analyses. Unless noted otherwise, structures were optimized without symmetry constraints.

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Keywords: ab initio calculations · density functional calculations · S ligands · silicon · zwitterions

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[4] Crystal structure analyses of **1** and **2**: Suitable single crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97). For the CH hydrogen atoms, a riding model was employed. The positions of the NH hydrogen atoms were localized in difference Fourier syntheses and refined freely. CCDC-647513 (**1**) and CCDC-647514 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected data for **1**: single crystal of dimensions 0.5 × 0.5 × 0.2 mm obtained by crystallization from acetonitrile at 20 °C, $C_{17}H_{21}N_3OS_2Si$, $M_r = 375.58$, analysis at 173(2) K, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.415(2)$, $b = 13.1368(17)$, $c = 11.3397(17)$ Å, $\beta = 103.870(18)°$, $V = 1795.5(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.389$ g cm^{-3}, $\mu = 0.373$ mm^{-1}, $F(000) = 792$, $2\theta_{max} = 56.24°$, 23 244 collected reflections, 4345 unique reflections ($R_{int} = 0.0379$), 226 parameters, $S = 1.009$, $R1 = 0.0313$ ($I > 2\sigma(I)$), $wR2$ (all data) = 0.0825, max./min. residual electron density +0.318/−0.211 e Å^{-3}. Selected data for **2**: single crystal of dimensions 0.5 × 0.3 × 0.3 mm obtained by crystallization from acetonitrile at 20 °C, $C_{17}H_{19}NO_3S_2Si$, $M_r = 377.54$, analysis at 173(2) K, orthorhombic, space group *Pbca* (no. 61), $a = 19.1266(17)$, $b = 9.1883(8)$, $c = 19.6856(15)$ Å, $V = 3459.9(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.450$ g cm^{-3}, $\mu = 0.393$ mm^{-1}, $F(000) = 1584$, $2\theta_{max} = 56.24°$, 43 407 collected reflections, 4197 unique reflections ($R_{int} = 0.0411$), 220 parameters, $S = 1.036$, $R1 = 0.0338$ ($I > 2\sigma(I)$), $wR2$ (all data) = 0.0863, max./min. residual electron density +0.578/−0.318 e Å^{-3}.

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