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Synthesis and structure of (O→Si)-chelate fluorosilane, a novel complex of pentacoordinate silicon with *N*-acetylvaline

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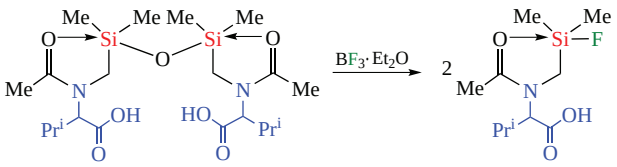
A novel organosilicon complex of *N*-acetylvaline was synthesized by the reaction of the relative disiloxane derivative with BF_3 etherate. According to X-ray and NMR data, the silicon atom of the final product is pentacoordinated in both the solid state and solution. The coordination state of silicon was correctly predicted by quantum-chemical calculations.



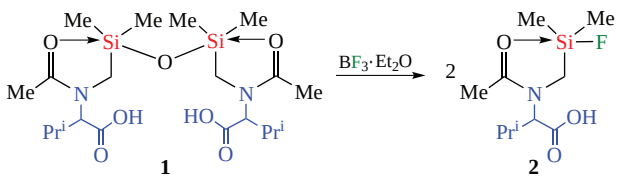
Keywords: organosilicon compounds, amino acids, valine, fluorosilanes, synthesis, pentacoordinate silicon, X-ray diffraction study, quantum-chemical analysis.

Compounds of hypercoordinated silicon are the focus of intense research due to the diversity of their structures, enhanced reactivity, biological activity and stereodynamic behaviour.[1–5] Fluorides of penta- and hexacoordinated silicon[1–7] are of particular interest because they are more stable and less susceptible to hydrolysis than other halogenosilanes. Therefore, such fluorides are commonly used as model compounds in various studies.

Recently, we have reported the synthesis and X-ray diffraction study of *N*-acetylvaline-derived complex disiloxane **1**.[8] As a continuation of this work, we now report the synthesis and structure of a novel pentacoordinate silicon complex, (O→Si)-chelate fluorosilane **2**. This unusual compound was prepared with a yield of 80% by refluxing disiloxane **1** with BF_3 etherate in acetonitrile (Scheme 1).

The IR spectrum of compound **2** shows two strong absorptions at 1740 and 1576 cm^{-1} produced by the carboxyl group and coordinating oxygen atom of the amido group, respectively. The pentacoordination of silicon in it (Figure 1) in both solid state and in solution is confirmed by X-ray† and ^{29}Si NMR data (see Online Supplementary Materials).

The Si atom in fluorosilane **2** has a distorted trigonal-bypiramidal (TBP) environment with three equatorial carbon atoms and axial fluorine and oxygen atoms. The Si(1)–O(1) bond length is 2.2792(19) Å, which is slightly longer than the coordination bonds in similar organosilicon derivatives of amino acid amides.[11] The reason for that could be the formation of a hydrogen bond between the O(1) atom of one molecule and the carboxyl group fragment O(3′)–H(3′) of another molecule (see Figure S1).



Scheme 1 *Reagents and conditions*: $BF_3{\cdot}Et_2O$, MeCN, reflux, 3 h.

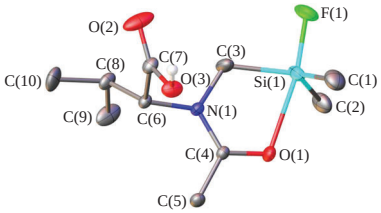


Figure 1 X-ray structure of fluorosilane **2**. Hydrogen atoms (except that of the carboxy group) are omitted.

† *Crystal data for* **2**. $C_{10}H_{20}FNO_3Si$ (M = 249.36), space group $Pca2_1$ at 120 K: a = 12.7206(8), b = 7.4105(5) and c = 14.9746(10) Å, V = 1411.60(16) $Å^3$, Z = 4, d_{calc} = 1.173 g cm^{-3}, μ = 1.72 cm^{-1}, $F(000)$ = 536. Total of 17538 reflections were collected (4363 independent reflections) and used in the refinement, which converged to wR_2 = 0.0982, GOF = 1.025 for all independent reflections [R_1 = 0.0411 was calculated for 3466 reflections with $I > 2\sigma(I)$].

The X-ray diffraction analysis was carried out on a Bruker Apex II diffractometer in Center for molecule composition studies of INEOS RAS. All calculations were performed using the SHELTXL[9] and OLEX2[10] software. The structure was solved by the direct method and refined by full-matrix technique against F^2 in the anisotropic-isotropic approximation.

CCDC 914A contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

The ^{29}Si NMR spectrum of fluorosilane **2** shows a singlet at –12.7 ppm, which confirms the pentacoordinate state of silicon in solution.[3,4] The correlation between the O→Si bond length and $\delta(^{29}\text{Si})$ observed for *N*′-(dimethylfluorosilylmethyl)-*N*′-methyl-*N*-(organosulfonyl)prolinamides[11] with a similar coordination environment of silicon suggests that the length of coordination bond in compound **2** in solution is similar to that in crystal (2.28 Å), which is somewhat longer than typical O→Si distances in monofluorides of pentacoordinate silicon. The same conclusion can be drawn from the correlational analysis of structurally similar bromides and triflates.[12] Such elongation of the O→Si bond might be caused by hydrogen bonding with the solvent (chloroform), which has been reported in literature.[13]

Possible effects of hydrogen bonding on the coordination environment of silicon were studied by quantum-chemical calculations (see Online Supplementary Materials, Figures S2–S4). The chemical shifts were calculated using three distinct models: a single molecule (**2-A**), a dimer observed in the crystal packing (**2-B**) and an associate of a single molecule of **2** with one molecule of chloroform (**2-C**). The effects of nonspecific solvation in chloroform were taken into account using the polarized continuum model (PCM) method.

The geometry optimization for the above models produced the O→Si bond lengths of 2.230, 2.388/2.218 and 2.300 Å, respectively, and the $\delta(^{29}\text{Si})$ values of –18.0, 2.4/–19.6 and –9.2 ppm, respectively. The O→Si distance in the isolated molecule **2-A** was somewhat shorter than that observed in crystal. The large difference (over 20 ppm) between the two ^{29}Si chemical shifts produced by the dimer model **2-B** reflected the difference between the calculated O→Si bond lengths. Model **2-C** gave the most accurate prediction of the experimental data, with the differences in the O→Si bond length and $\delta(^{29}\text{Si})$ chemical shift of 0.02 Å and 3.5 ppm, respectively.

Overall, the O→Si bond lengths in models **2-A**, **2-B** and **2-C** varied within a 0.15 Å range. The relationship between the bond length and the strength of coordination in fluorosilane **2** was studied using Bader's Theory of Atoms in Molecules (AIM), which is commonly applied to compounds of penta- and hexacoordinate silicon.[5] The topological analysis of the calculated electron density distribution function $\rho(r)$ showed the presence of critical points BCP (3,–1) for all expected covalent and coordination bonds as well as some weak intra- and intermolecular interactions, including hydrogen bonds O–H···O and C–H···O in **2-B** and C–H···Cl in **2-C**. The values of topological parameters $\rho(r)$, their Laplacians $\nabla^2\rho(r)$, densities of local electron energy and its potential components $H^e(r)$ and $V(r)$ are given in Tables S2–S4. Molecular graphs for models **2-A**, **2-B** and **2-C** are shown in Figures S2–S4 (Online Supplementary Materials).

The O–H···O bond energy in **2-B** determined from the Espinosa–Molins–Lecomte (EML) correlation[14] was –15.4 kcal mol^{-1} (Table S2). This value is almost twice as large as the dimerization energy (8.3 kcal mol^{-1}) calculated as the difference between the energy of **2-B** and doubled energy of **2-A**. In addition, the calculations for **2-B** suggest the presence of other weak intermolecular interactions. Apparently, the EML theory overestimates significantly the energy of strong hydrogen bonds.[15] In the case of the C–H···O interaction involving chloroform in **2-C**, the difference in energy is much lower: –4.9 and 3.7 kcal mol^{-1} (Table S3). At the same time, the calculated interval for the O→Si bond energy was only ~5 kcal mol^{-1} (from –13.0 to –7.9 kcal mol^{-1}). Such differences in the O→Si bond energy caused by the dimerization or hydrogen bonding can be detected by NMR spectroscopy using the structural models obtained from X-ray diffraction studies and quantum-chemical calculations.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.011.

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