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Short Review

Molecular λ^5-silicates: synthesis, structure and properties of zwitterionic λ^5-organospirosilicates and λ^5-organofluorosilicates *

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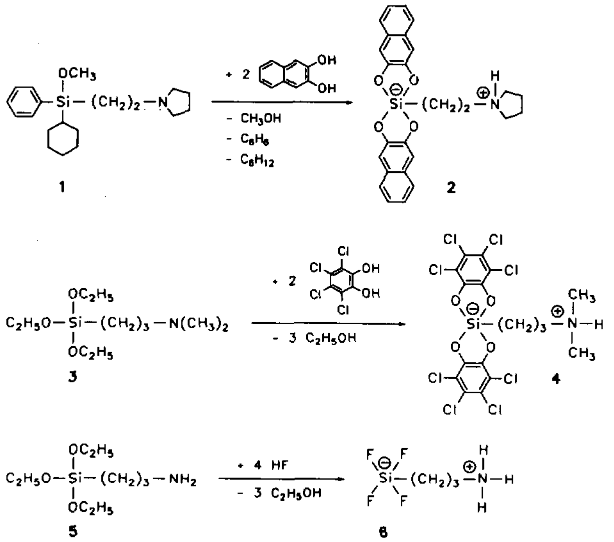
Abstract

In contrast to the well established chemistry of ionic λ^5-organosilicates, the chemistry of zwitterionic λ^5-organosilicates is virtually unexplored. In this paper, the synthesis, structure and properties of a series of zwitterionic λ^5-organospirosilicates and λ^5-organofluorosilicates are described.

1. Introduction

In recent years, numerous papers on the synthesis, structure and properties of ionic λ^5-organosilicates have been published [1,2]. In contrast, the chemistry of zwitterionic λ^5-organosilicates is virtually unexplored. In the late 1980s, we came across this class of compounds by accident when we studied reactions of the silane **1** (a precursor of the muscarinic antagonist sila-procyclidine [3]) with *vic*-diols of the pyrocatechol type. To our great surprise, reaction of **1** with 2,3-dihydroxynaphthalene in acetonitrile at room temperature gave the zwitterionic λ^5-organospirosilicate **2**, which was isolated as the acetonitrile solvate **2** · CH_3CN (Scheme 1) [4]; not only a Si–OC cleavage (formation of methanol), but also two totally unexpected Si–C cleavage reactions (formation of benzene and cyclohexane) were observed. To the best of our knowledge, **2** · CH_3CN is the first zwitterionic λ^5-organosilicate whose structure was determined in the solid state (single-crystal X-ray analysis) and in solution (^1H, ^{13}C and ^{29}Si NMR studies). When we were about to publish these results, we became aware of unpublished results of Schomburg and Krebs [5] concerning the synthesis of the zwitterionic λ^5-organospirosilicate **4** · CH_3CN. This compound, however, was only characterized in the solid state [5]. As outlined in Scheme 1, **4** (isolated as **4** · CH_3CN) was prepared by reaction of the silane **3** with 3,4,5,6-tetrachloro-1,2-dihydroxybenzene in acetonitrile [5], following the classical route [2a] for the preparation of ionic λ^5-organospirosilicates. In this context, it should be mentioned that the existence of zwitterionic λ^5-organosilicates was postulated nearly two decades ago by Müller and Dathe [6], who concluded that the product obtained from the reaction of the silane **5** with hydrogen fluoride may be the zwitter-



Scheme 1.

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* Dedicated to Professor M.G. Voronkov in recognition of his distinguished contributions to organosilicon chemistry.

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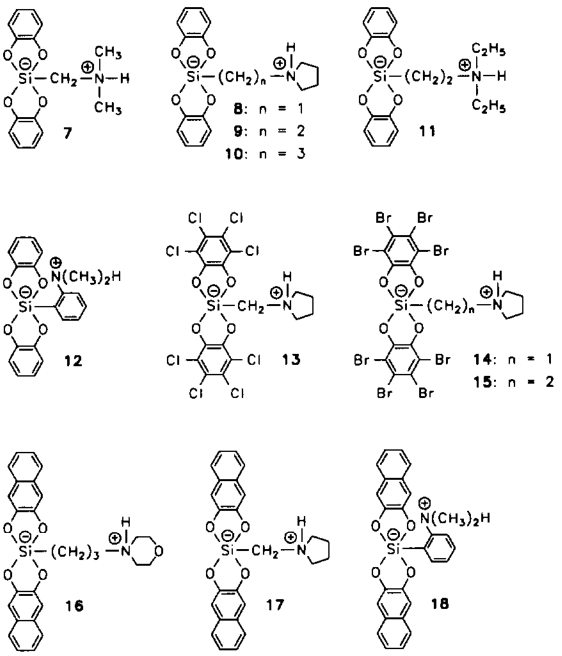
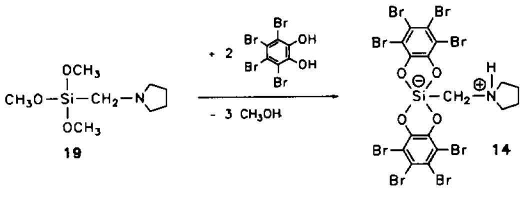


Scheme 2.

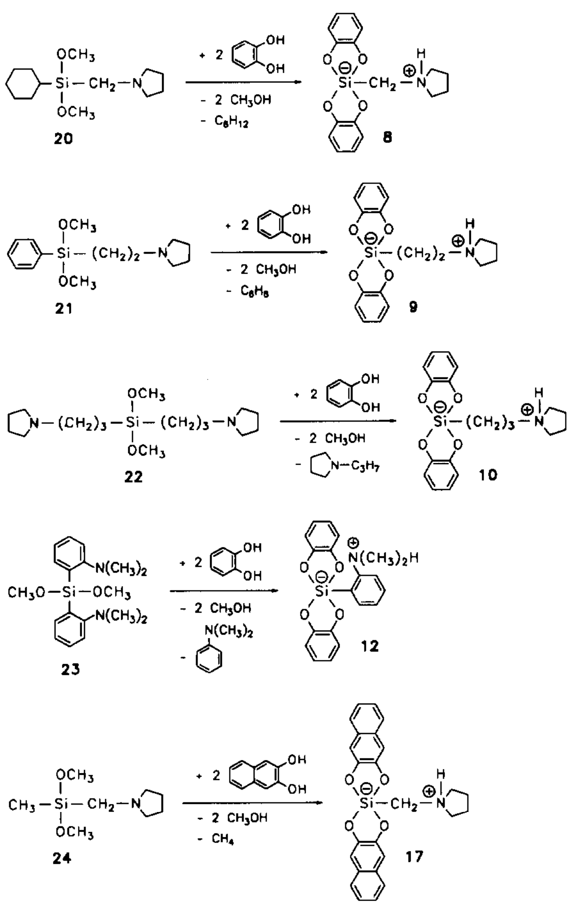
ionic λ^5-organofluorosilicate **6** (Scheme 1), but **6** was identified only by elemental analysis and thus its structure has remained uncertain until now. Thus an extensive investigation of zwitterionic λ^5-organosilicates appeared to us to be worth while, and we decided to study this virtually unexplored field of silicon chemistry systematically. This short review describes some of our results obtained in this area in the past three years.

2. Syntheses

Scheme 2 shows a selection of the zwitterionic λ^5-organospirosilicates synthesized in our laboratory, some of which were isolated and characterized as solvates (**7** [7], **8** [8], **9** [8], **10** [9], **11** [10], **12** [11], **13** [12], **14** · CH_3CN [13], **15** [7], **15** · H_2O [7], **16** · $\frac{1}{2}CH_3CN$ [14], **17** · CH_3CN [15], **18** · $\frac{1}{2}CH_3CN$ [11,16]). As demonstrated in Scheme 3 for the reaction **19** → **14** (isolated as **14** · CH_3CN) [13], these compounds were obtained from the corresponding (aminoalkyl)trimethoxysilanes [$(CH_3O)_3Si(CH_2)_nNR_2$; $n = 1, 2, 3$] by reaction with the appropriate pyrocatechol derivatives or 2,3-dihydroxynaphthalene (Method I). These reactions were carried out in acetonitrile at room temperature. In nearly all cases the products precipitated spontaneously, and were isolated in high yields (*ca.* 80–90%) as crystalline solids.

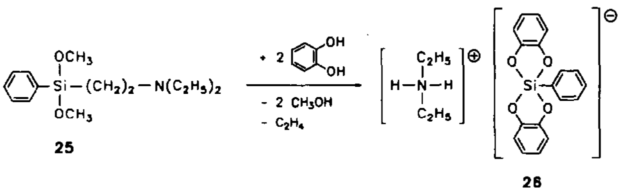


Scheme 3.



Scheme 4.

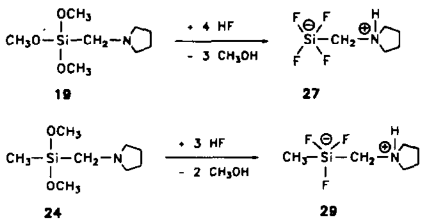
Some of the compounds listed in Scheme 2 were also synthesized by Si–C cleavage reactions (Method II). Examples of this alternative approach are shown in Scheme 4 (reactions **20** → **8** [8], **21** → **9** [8], **22** → **10** [9], **23** → **12** [11], **24** → **17** (isolated as **17** · CH_3CN) [15]). The crystalline products were isolated in high yields (*ca.* 75–85%), indicating a high degree of chemoselectivity for these conversions (selective Si–C cleavage). Generally, the quality of the crystals obtained by this method was significantly better than those obtained by Method I. This is due to the relatively low rates of the Si–C cleavage reactions, which control the kinetics of the crystallization process. In several cases, suitable single crystals for X-ray diffraction studies were isolated directly from the reaction mixtures. In contrast, under similar conditions, Method I yields micro-crystalline products. However, it should be pointed out that Method II cannot be generally applied. As exemplified



Scheme 5.

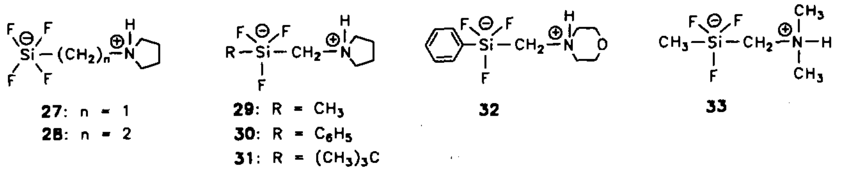
by reaction **25** → **26** in Scheme 5, undesirable Si-C cleavage reactions (inverse selectivity) can dominate [8]; thus, whereas the silane **21** reacts with pyrocatechol to give the zwitterionic λ^5-silicate **9** in high yield (see Scheme 4), the reaction of the structurally related silane **25** with pyrocatechol yields the ionic λ^5-silicate **26** as the main product. This difference in behaviour between silanes **21** and **25** cannot yet be explained.

The λ^5-organospirosilicates shown in Scheme 2, and also their solvates, are high-melting crystalline solids, reflecting the zwitterionic nature of these species. As expected, the compounds are almost insoluble in non-polar organic solvents and also exhibit a very low solubility in polar organic solvents. For solution NMR studies (see below), dimethyl sulphoxide (DMSO) was used as the solvent. Interestingly, compound **11** is the most soluble of all the λ^5-organospirosilicates studied, and even dissolves to a significant extent in acetonitrile.



Scheme 7.

Scheme 6 shows a selection of the zwitterionic λ^5-organofluorosilicates synthesized and characterized in our laboratory (**27** [17], **28**–**30** [18], **31**–**33** [19]). As demonstrated in Scheme 7 for the reactions **19** → **27**



Scheme 6.

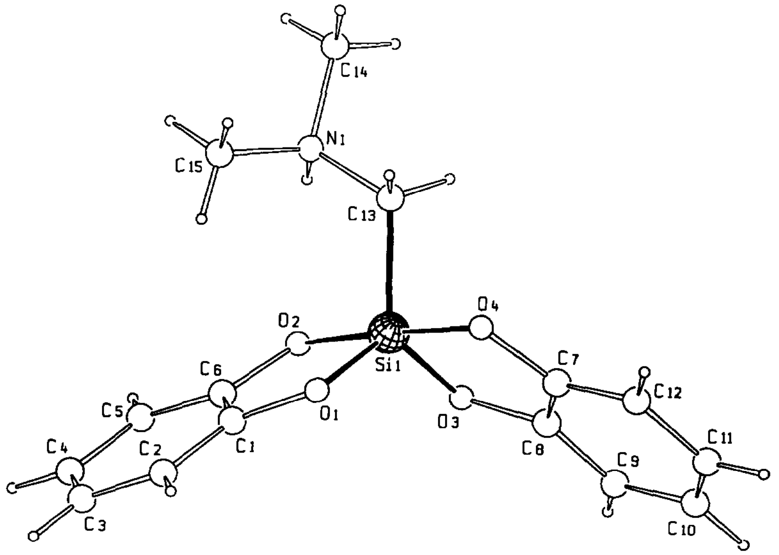


Fig. 1. Structure of one of the two crystallographically independent molecules in the crystal of 7. Selected bond distances (Å) and angles (deg): Si(1)–O(1) 1.695(2), Si(1)–O(2) 1.791(2), Si(1)–O(3) 1.714(2), Si(1)–O(4) 1.765(2), Si(1)–C(13) 1.890(2); O(1)–Si(1)–O(2) 89.69(6), O(1)–Si(1)–O(3) 118.86 (6), O(1)–Si(1)–O(4) 90.64(6), O(1)–Si(1)–C(13) 120.39(7), O(2)–Si(1)–O(3) 87.70(6), O(2)–Si(1)–O(4) 176.75(6), O(2)–Si(1)–C(13) 93.95(6), O(3)–Si(1)–O(4) 89.31(6), O(3)–Si(1)–C(13) 120.74(7), O(4)–Si(1)–C(13) 88.67(7).

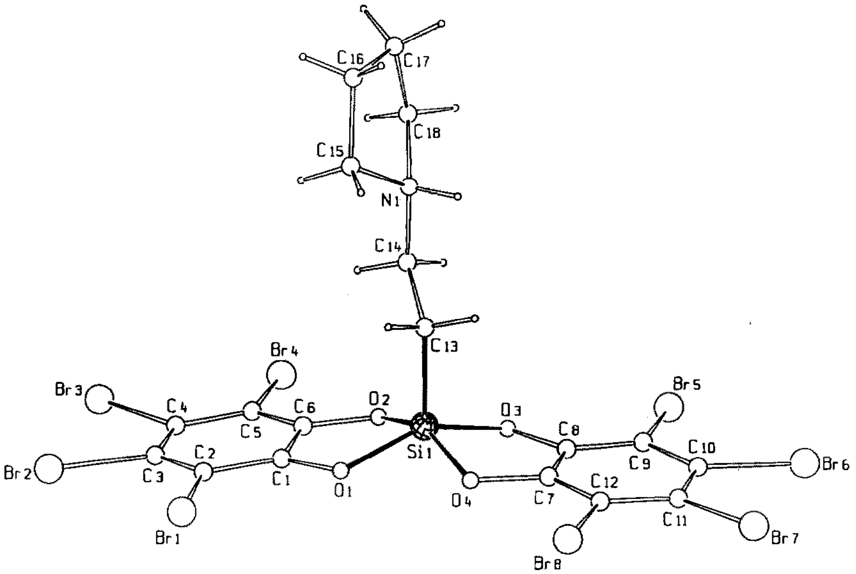


Fig. 2. Structure of one of the two crystallographically independent zwitterions in the crystal of **15** · H_2O. Selected bond distances (Å) and angles (deg): Si(1)–O(1) 1.78(2), Si(1)–O(2) 1.78(2), Si(1)–O(3) 1.75(2), Si(1)–O(4) 1.75(2), Si(1)–C(13) 1.87(3); O(1)–Si(1)–O(2) 87.9(8), O(1)–Si(1)–O(3) 151(1), O(1)–Si(1)–O(4) 84.8(9), O(1)–Si(1)–C(13) 105(1), O(2)–Si(1)–O(3) 84.3(9), O(2)–Si(1)–O(4) 152(1), O(2)–Si(1)–C(13) 106(1), O(3)–Si(1)–O(4) 89.1(9), O(3)–Si(1)–C(13) 104(1), O(4)–Si(1)–C(13) 102(1).

[17] and **24** → **29** [18], **27–33** were prepared from the corresponding (aminoalkyl)trimethoxysilanes [$(CH_3O)_3Si(CH_2)_nNR_2$; $n = 1,2$] and (aminomethyl)alkyl- or (aminomethyl)aryldimethoxysilanes [$R(CH_3O)_2SiCH_2NR_2$] by reaction with hydrogen fluoride in ethanol/hydrofluoric acid at 0°C. The products were obtained in good yields (*ca.* 70–90%) as crystalline solids. The zwitterionic nature of these species is again reflected in high melting points and low solubilities in organic solvents. However, the melting points are generally lower and the solubilities are somewhat better than those observed for the above-mentioned λ^5-organo-

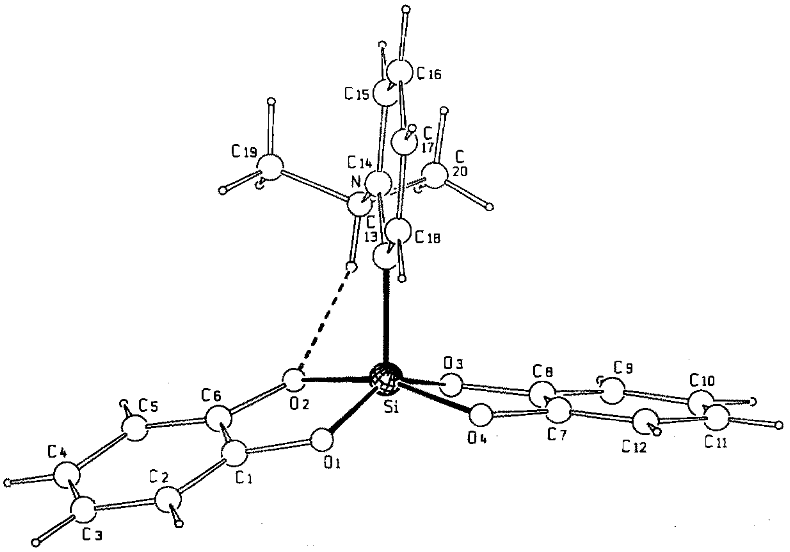


Fig. 3. Crystal structure of **12** showing the intramolecular N–H ··· O hydrogen bond. Hydrogen bonding parameters: N ··· O(2) 2.856 Å, NH ··· O(2) 2.042 Å, N–H ··· O(2) 145.1°.

spirosilicates. For solution NMR studies of the λ^5-organofluorosilicates (see below), acetonitrile and methanol were suitable solvents.

3. Structures

The crystal structures of most of the zwitterionic λ^5-organosilicates shown in Schemes 2 and 6 were studied by X-ray diffraction (**7** [7], **10** [9], **12** [11], **14** · CH_3CN [13], **15** [7], **15** · H_2O [7], **16** · $\frac{1}{2}CH_3CN$ [14], **17** · CH_3CN [15], **18** · $\frac{1}{2}CH_3CN$ [16], **27** [17], **28–30** [18], **32** [19]). In the series of the λ^5-organospirosilicates, the coordination polyhedrons around the silicon atoms were found to vary continuously from trigonal-bipyramidal to square-pyramidal geometry. In contrast, the structures of the λ^5-organofluorosilicates can be uniformly described as nearly ideal trigonal-bipyramidal. The Si–O and Si–F bond lengths in the zwitterionic λ^5-organospirosilicates and λ^5-organofluorosilicates are similar to those obtained for related ionic silicates (see, *e.g.*, [2e,g,p] for Si–O and [2m,n,w] for Si–F).

To illustrate the range of the structural chemistry of the zwitterionic λ^5-organospirosilicates in the solid state, the structures of **7** and **15** · H_2O are discussed. In the crystal lattice of **7**, there are two crystallographically independent molecules with very similar structures. As shown for one of these molecules in Fig. 1, the coordination polyhedrons around the silicon atoms can be described as nearly ideal trigonal bipyramids. In the crystal lattice of **15** · H_2O, two crystallographically independent zwitterions were also found, as well as two crystallographically independent water molecules. As shown for one of these zwitterions in Fig. 2, the coordination geometries of these species can be described as slightly distorted square pyramids.

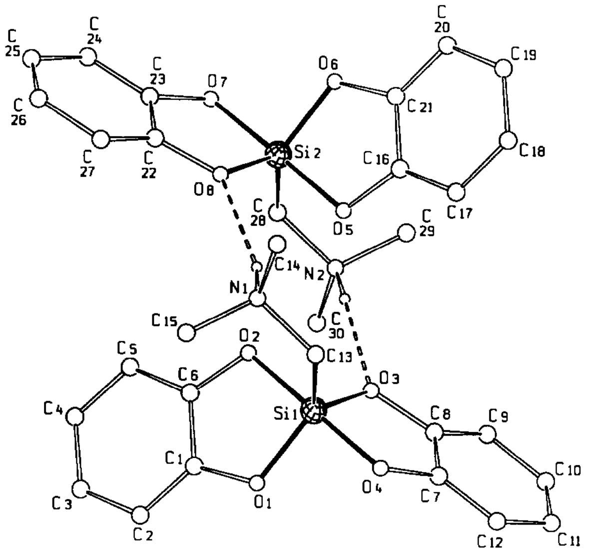


Fig. 5. Crystal structure of **7** showing the intermolecular N–H · · · O hydrogen bonds between the two crystallographically independent molecules. Except for NH, the hydrogen atoms are omitted. Hydrogen bonding parameters: N(1) · · · O(8) 2.946 Å, N(1)H · · · O(8) 2.069 Å, N(1)–H · · · O(8) 149.2°; N(2) · · · O(3) 2.906 Å, N(2)H · · · O(3) 1.988 Å, N(2)–H · · · O(3) 153.3°.

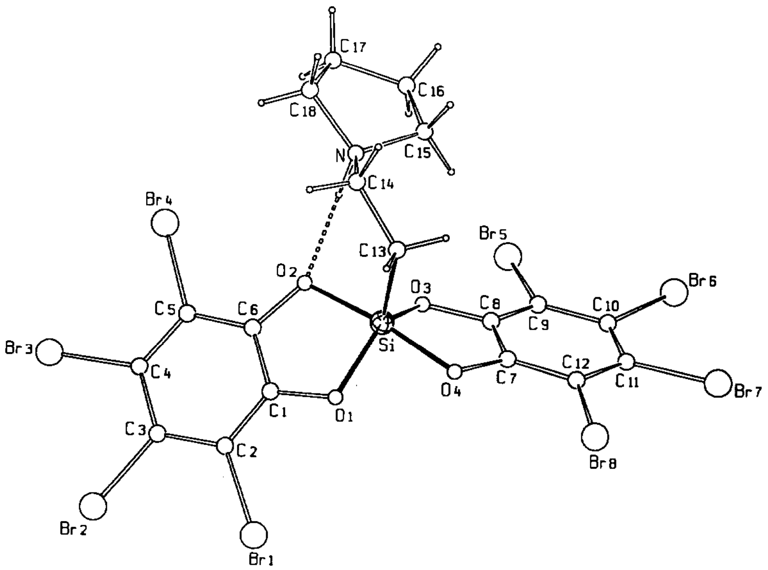


Fig. 4. Crystal structure of **15** showing the intramolecular N–H · · · O hydrogen bond. Selected bond distances (Å) and angles (deg): Si–O(1) 1.706(9), Si–O(2) 1.783(9), Si–O(3) 1.712(9), Si–O(4) 1.754(9), Si–C(13) 1.880(10); O(1)–Si–O(2) 88.8(4), O(1)–Si–O(3) 122.2(5), O(1)–Si–O(4) 85.0(4), O(1)–Si–C(13) 126.9(6), O(2)–Si–O(3) 87.9(4), O(2)–Si–O(4) 171.4(5), O(2)–Si–C(13) 93.4(5), O(3)–Si–O(4) 90.4(4), O(3)–Si–C(13) 110.8(5), O(4)–Si–C(13) 95.1(5). Hydrogen bonding parameters: N · · · O(2) 2.683 Å, NH · · · O(2) 1.819 Å, N–H · · · O(2) 148.3°.

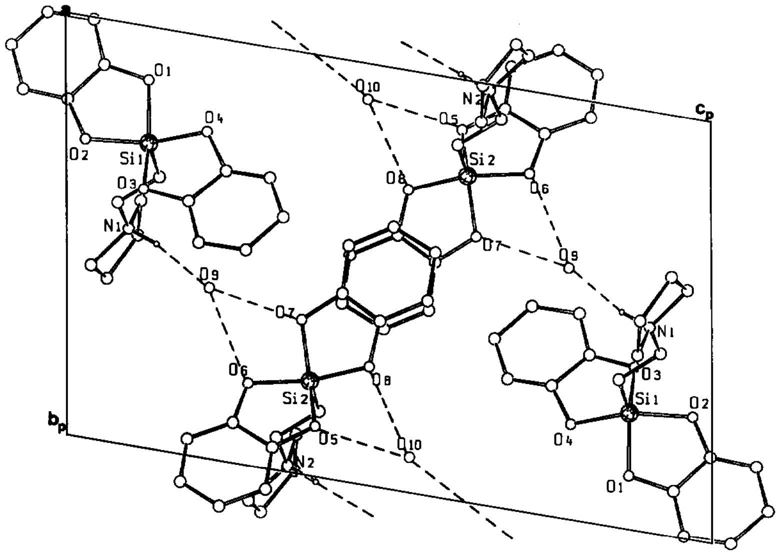


Fig. 6. Intermolecular N–H ··· O and O–H ··· O hydrogen bonds in the crystal of **15** · H_2O ([100] projection). Except for NH, the hydrogen atoms and all bromine atoms are omitted. O(9) and O(10) represent the oxygen atoms of the two crystallographically independent water molecules.

A detailed analysis of the crystal structures of the zwitterionic λ^5-organospirosilicates reveals that the structural chemistry of this class of compounds is significantly influenced by intramolecular (examples: **12** and **15**; Figs. 3 and 4) or intermolecular hydrogen bonding (examples: **7** and **15** · H_2O; Figs. 5 and 6). This becomes particularly clear from a comparison of the structures of **15** (Fig. 4; intramolecular N–H ··· O hydrogen bond) and **15** · H_2O (Figs. 2 and 6; intermolecular N–H ··· O and O–H ··· O hydrogen bonds between the zwitterions and the water molecules). In contrast to the slightly distorted square-pyramidal geometry observed for **15** · H_2O, the coordination polyhedron around the silicon atom of **15** can be described as a distorted trigonal bipyramid. Obviously, the geometry of the coordination polyhedrons is influenced not only by the electronic and steric parameters of the ligands, but also, strongly, by intra- or intermolecular hydrogen bonding.

To illustrate the structural chemistry of the zwitterionic λ^5-organofluorosilicates in the solid state, the structure of **28** is shown in Fig. 7. As observed for **27**,

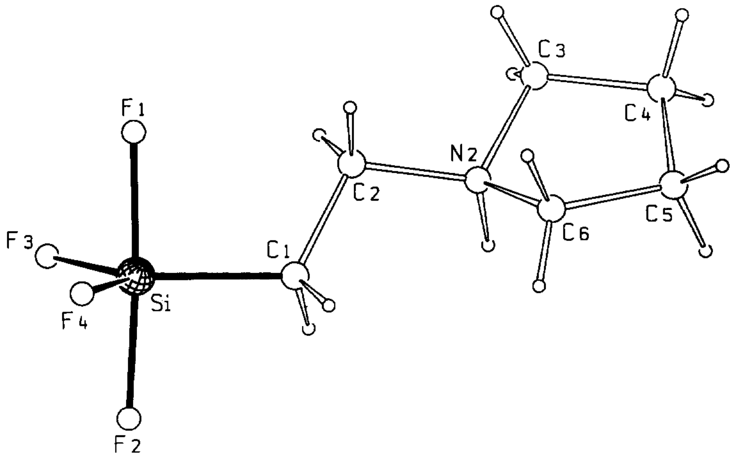
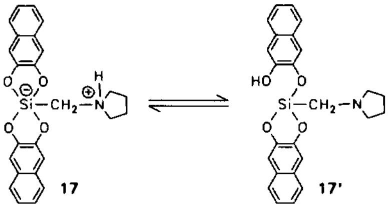


Fig. 7. Crystal structure of **28**. Selected bond distances (Å) and angles (deg): Si–F(1) 1.708(2), Si–F(2) 1.667(2), Si–F(3) 1.607(2), Si–F(4) 1.627(2), Si–C(1) 1.872(4); F(1)–Si–F(2) 174.8(1), F(1)–Si–F(3) 89.7(1), F(1)–Si–F(4) 86.3(1), F(1)–Si–C(1) 92.6(1), F(2)–Si–F(3) 91.1(1), F(2)–Si–F(4) 88.7(1), F(2)–Si–C(1) 91.4(1), F(3)–Si–F(4) 117.9(1), F(3)–Si–C(1) 119.9(1), F(4)–Si–C(1) 122.2(1).



Scheme 8.

29, **30** and **32**, the geometry of the coordination polyhedron around the silicon atom is a nearly ideal trigonal bipyramid.

NMR spectroscopic investigations (^{1}H, ^{13}C, ^{29}Si) of the λ^5-organospirosilicates have shown that the zwitterions also exist in solution ([D$_6$]DMSO). In most of the cases studied, the ^{29}Si NMR shifts observed for these solutions agree well with the data obtained for the solid state (^{29}Si CP/MAS NMR), and clearly confirm the presence of pentacoordinate silicon atoms (examples (δ values, solution/solid state): $-85.9/-84.8$ (**7**), $-88.6/-88.6$ (**12**), $-79.1/-80.0$ (**15**), $-76.4/-75.5$ ($\mathbf{16}\cdot\frac{1}{2}CH_3CN$), $-90.2/-88.7$ ($\mathbf{18}\cdot\frac{1}{2}CH_3CN$)). The existence of equilibria between these zwitterions and related tautomeric silane structures (see the hypothetical example $\mathbf{17} \rightleftharpoons \mathbf{17'}$ in Scheme 8) cannot be totally ruled out; but if such tautomeric silane species play any role at all in solution, the zwitterionic structures must clearly dominate the equilibria.

NMR spectroscopic investigations (^{1}H, ^{13}C, ^{19}F, ^{29}Si) of the zwitterionic λ^5-organofluorosilicates have demonstrated that these zwitterions also exist in solution (CD_3OD, CD_3CN). For example, ^{29}Si NMR shifts of δ -122.9 (solution in CD_3CN) and δ -121.0 (solid state) were observed for compound **27**, clearly indicating the presence of pentacoordinate silicon.

4. Concluding remarks

In conclusion, the chemistry of zwitterionic λ^5-organospirosilicates and zwitterionic λ^5-organofluorosilicates represents an extension and interesting enrichment of the chemistry of pentacoordinate silicon. In the investigations described here we have concentrated mainly on the synthesis and structure of these molecular λ^5-organosilicates. In the future, research efforts should be focused to a much greater extent on their chemical properties. Furthermore, studies of the hitherto unknown class of zwitterionic λ^6-organosilicates would be of interest. Further explorations of the field of zwitterionic organosilicates seem well justified, and will remain one of our major research activities in silicon chemistry.

Acknowledgments

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