



The variations in hydrogen bonding in hexafluorosilicate salts of protonated methyl substituted pyridines and tetramethylethylenediamine

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ABSTRACT

The synthesis and spectroscopic characterization of hexafluorosilicate salts with organic cations $(R)_2[SiF_6]$ (where R = 2-picolinium (**1**), 2,6-lutidinium (**2**) and 2,4,6-collidinium (**3**)) and $R[SiF_6] \cdot 2H_2O$ (where R = tetramethylethylenediammonium (**4**)) are reported. The salts were prepared by the reaction of methyl substituted pyridines or tetramethylethylenediamine with hydrogen fluoride solution and subsequent addition of silica. The crystal structures of **1**, **2** and **4** have been determined by single-crystal X-ray diffraction analysis. The effect of hydrogen bonding on the elongation of the Si–F bonds is discussed.

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1. Introduction

The compounds with hexafluorosilicate anions $[SiF_6]^{2-}$ and protonated nitrogen bases as cations found application as hybrid functional materials [1], ionic liquids [2] and in zeolite synthesis [3]. The electrostatic attractive forces between these cations and the anions $[SiF_6]^{2-}$ facilitates the formation of extensive N–H...F hydrogen-bond interactions [4–14]. The hydrogen bonds between ions are much stronger than between molecules and can play dominant roles in crystal structures [15]. This hydrogen-bonding network is prone to incorporate during the crystallization the water molecules which participate in hydrogen bonding [4,9,12–14].

The ionic compounds with heterocyclic aromatic cation and $[SiF_6]^{2-}$ anion are relatively rare [4,9,10]. Protonated methyl substituted pyridines have been shown to serve as efficient counterions in organofluorometalates [16,17], aquafluoromanganate(III) [18], aquafluorooxovanadate(IV) [19], magnesiate thiolate [20], fluoroaluminate [21] and fluoroarsenate [22].

This contribution reports the preparation and characterization of three hexafluorosilicates with monocations $(R)_2[SiF_6]$ (where R = 2-picolinium (**1**), 2,6-lutidinium (**2**) and 2,4,6-collidinium (**3**)) and a hydrate with dication $R[SiF_6] \cdot 2H_2O$ (where R = tetramethylethylenediammonium (**4**)). The compounds were characterized by 1H and ^{19}F NMR and IR spectro-

scopy and the compounds **1**, **2** and **4** also by X-ray crystallography. Hydrogen bonding with different topologies was found in the structures of **1**, **2** and **4**.

2. Results and discussion

The reaction of methyl substituted pyridines or tetramethylethylenediamine with hydrogen fluoride solution and subsequent addition of silica at 0 °C produces ionic hexafluorosilicates **1–4**. The compounds **1**, **2** and **4** crystallize as colorless crystals in monoclinic (space group $P2_1/c$ for **1** and $C2/m$ for **2**) and triclinic (space group $P-1$ for **4**) crystal systems. Crystallographic data and associated experimental details are given in Table 1. Selected bond lengths and angles are given in Table 2.

The asymmetric units of **1** and **2** reveal half of the hexafluorosilicate anion and the picolinium or the lutidinium cation. The structure of **1** is built from hydrogen-bonded units consisting of two cations and the anion (Fig. 1). The orientation of the aromatic rings in **1** suggests the aromatic stacking along the $[001]$ direction with the inter-ring distance of 4.013 Å. The planes of these rings are inclined to each other with the angle of 14.05°. The fluorine atoms in $[SiF_6]^{2-}$ can be divided into two sets according to the bond lengths. Two apical Si–F bonds are longer (1.703 Å) than four equatorial Si–F bonds (1.644 Å). Four fluorine atoms of each $[SiF_6]^{2-}$ anion in **1** are involved in four bifurcated N–H...F hydrogen bonds with protonated nitrogens of two 2-picolinium cations. Two fluorine F1 atoms in apical positions form strong and two equatorial F2 fluorine atoms form weak hydrogen bond to the picolinium cations (Table 3).

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Table 1
Experimental data for the X-ray diffraction studies on compounds **1**, **2** and **4**

	1	2	4
Formula	C ₁₂ H ₁₆ F ₆ N ₂ Si	C ₁₄ H ₂₀ F ₆ N ₂ Si	C ₆ H ₂₂ F ₆ N ₂ O ₂ Si
Fw (g mol ⁻¹)	330.36	358.41	296.35
Crystal size (mm)	0.75 × 0.50 × 0.50	0.10 × 0.25 × 1.00	0.20 × 0.20 × 0.10
Crystal color	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 ₁ /c	C2/m	P-1
a (Å)	6.8401 (2)	15.8171 (4)	6.3753 (2)
b (Å)	13.3041 (4)	6.4567 (2)	7.6256 (2)
c (Å)	7.9192 (2)	8.5075 (2)	7.8004 (3)
α (°)	90	90	117.849 (2)
β (°)	91.499 (2)	114.694 (1)	104.368 (2)
γ (°)	90	90	91.689 (2)
V (Å ³)	720.41 (4)	789.39 (4)	320.10 (2)
Z	2	2	1
Calcd density (g cm ⁻³)	1.523	1.508	1.537
F(0 0 0)	340	372	156
θ Range (°)	2.98–27.51	3.46–27.48	3.07–27.36
No. of collected reflns	3047	1759	2470
No. of independent reflns	1647	973	1428
R _{int}	0.018	0.016	0.023
No. of reflns used	1404	903	1248
No. parameters	122	74	92
R[I > 2σ(I)] ^a	0.0390	0.0324	0.0337
wR ₂ (all data) ^b	0.1128	0.0910	0.0857
Goof, S ^c	1.027	1.093	1.044
Maximum/minimum residual electron density (e Å ⁻³)	+0.25/−0.23	+0.17/−0.21	+0.19/−0.25

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

$$^c S = \{ \sum [(F_o^2 - F_c^2)^2] / (n/p) \}^{1/2} \text{ where } n \text{ is the number of reflections and } p \text{ is the total number of parameters refined.}$$

The chains composed of alternating cations and anions along *b*-axes can be found in the crystal structure of **2** (Fig. 2). Within the chain, the lutidinium cations and [SiF₆]²⁻ anions are linked by bifurcated N–H···F hydrogen bonds. In contrast to compound **1** only two fluorine atoms from each [SiF₆]²⁻ anions are involved in the formation of hydrogen bond. The protonated nitrogen of the cation is a donor of two hydrogen bonds to the two neighboring [SiF₆]²⁻ anions in the chain. The Si–F bond distance to the fluorine atoms involved in hydrogen-bonding system is slightly longer than the other two Si–F bond distances in [SiF₆]²⁻ anion (Table 2). The interring distance of two aromatic rings in the chain is 6.4567(2) Å and is too long for the interaction. The rings from the neighboring chains do not exhibit any interactions.

The hexafluorosilicate **4** is composed of the [SiF₆]²⁻ anion and the double-protonated tetramethylethylenediammonium cation, and one water molecule (Fig. 3). Four of the [SiF₆]²⁻ fluorine atoms

are involved in the O–H···F hydrogen bonding with four water molecules. Each of the water molecules acts also as hydrogen-bond acceptors towards the cation, via N–H···O hydrogen bond. These hydrogen-bonding interactions result in two dimensional layers which are perpendicular to the *c*-axis in the crystal structure. Two fluorine atoms of [SiF₆]²⁻, involved in hydrogen bonds, exhibit slightly longer Si–F bonds (Table 2).

Although the Si–F bond lengths in the [SiF₆]²⁻ anions in the structures of **1**, **2** and **4** increase due to hydrogen bonding, the F–Si–F angles within [SiF₆]²⁻ octahedral are close to 90° and 180°. Such unperturbed octahedral geometry of the [SiF₆]²⁻ anion can also be found in some other complexes with [SiF₆]²⁻ anion, as observed previously [9,12,14].

The elongation of Si–F bonds of the [SiF₆]²⁻ fluorine atoms involved in D–H···F hydrogen bond was observed and correlated with hydrogen bond strength [23]. Most of the known structures with [SiF₆]²⁻ exhibit extensive hydrogen-bonding networks that mainly incorporate all fluorine atoms of [SiF₆]²⁻ [4–14,23]. The nitrogen bases used in syntheses of **1**, **2**, and **4** are sterically demanding due to methyl groups on the basic nitrogen atom (**4**) or

Table 2
Selected bond lengths (Å) and angles (°) for **1**, **2** and **4**

	1	2	4
Si–F1	1.7030(9)	1.697(1)	1.6845(9)
Si–F2	1.644(3)	1.6763(9)	1.6657(9)
Si–F3	1.644(3)	1.668(1)	1.6836(9)
N–C1	1.332(2)	1.336(3)	1.496(2)
N–C2			1.486(2)
N–C3			1.493(2)
N–C5	1.341(2)	1.340(3)	
N–H1	0.86(2)	0.84(2)	0.85(2)
C1–C1a			1.516(3)
O–H1w			0.85(3)
O–H2w			0.76(3)
F1–Si–F2	89.11(8)	90.0	89.97(5)
F1–Si–F1a	180.00(7)	180.0	180.0
C1–N–C5	123.8(2)	125.5(2)	
C1–N–C2			113.1(1)
C1–N–C3			109.8(1)
C2–N–C3			110.6(1)

Table 3
Hydrogen bonding geometry for **1**, **2** and **4**

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°	Symmetry transformation for acceptors
1					
N–H1···F1	0.86(1)	1.89(2)	2.735(2)	169(2)	
N–H1···F2a	0.86(1)	2.36(2)	2.922(3)	123(2)	−x + 1, −y, −z
2					
N–H1···F1	0.84(2)	2.14(1)	2.786(1)	133.8(4)	x + 1/2, y + 1/2, z + 1
N–H1···F1a	0.84(2)	2.14(1)	2.786(1)	133.8(4)	−x + 1/2, −y − 1/2, −z + 2
4					
O–H1w···F1	0.85(3)	1.91(3)	2.752(2)	167(2)	
O–H2w···F3b	0.76(3)	2.02(3)	2.759(2)	163(3)	−x + 1, −y + 1, −z
N–H1···O	0.85(1)	1.90(2)	2.737(2)	168(2)	−x + 1, −y + 2, −z + 1

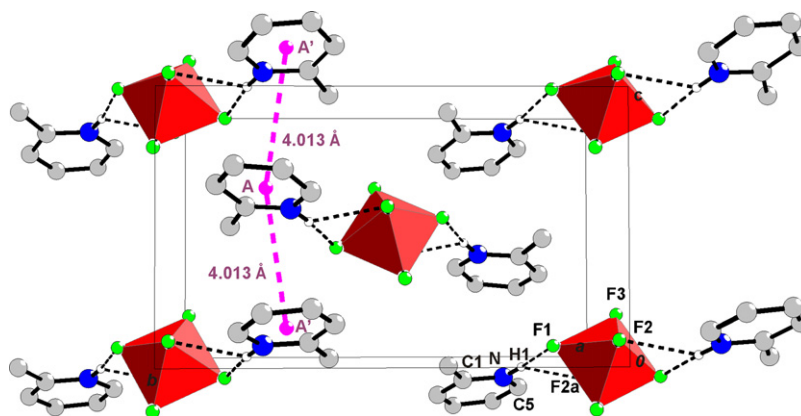


Fig. 1. Stacking diagram and atom numbering scheme of **1** along the [1 0 0] direction evidencing the $\pi \cdots \pi$ interactions between the 2-picolinium cations. The centroid A \cdots centroid A' distance is 4.013 Å. The hydrogen atoms on methyl groups and aromatic rings have been removed for clarity.

on the pyridine ring (**1**, **2**). The bulkiness of the protonated bases in compounds **1**, **2** and **4** apparently diminishes the number of cations that interact with $[\text{SiF}_6]^{2-}$. Consequently, some fluorine atoms of $[\text{SiF}_6]^{2-}$ do not participate in hydrogen bonding: four atoms in **2** and two atoms in **1** and **4**. The difference in the Si–F bond length of the fluorines with and without hydrogen bonds could therefore

serve as a measure of the strength of the particular hydrogen bond. The compound **1** with cation–anion N–H \cdots F hydrogen bonding and 2.735 Å N \cdots F distance and 169° N–H \cdots F angle exhibits 0.059 Å difference in the Si–F bond lengths. The compound **2** has similar cation–anion interaction with 2.786 Å N \cdots F distance and 133.8° N–H \cdots F angle. In this case, the difference in the Si–F bond lengths

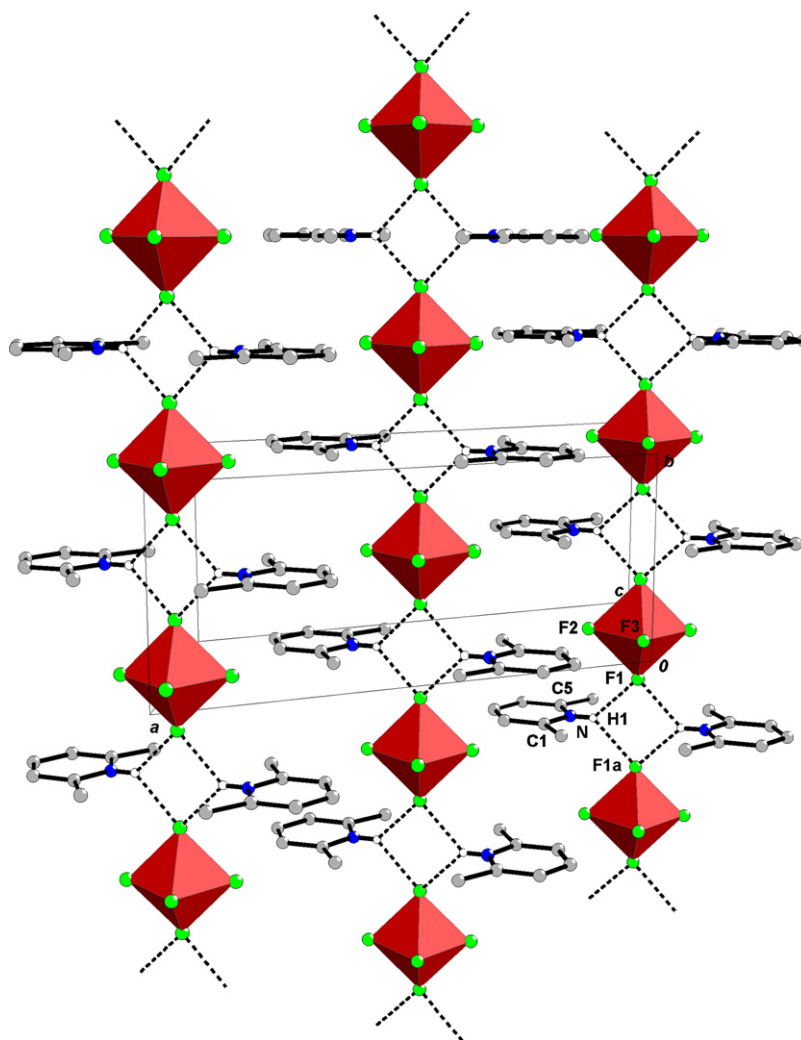


Fig. 2. Packing diagram and atom numbering scheme of **2** along the [0 0 1] direction. The hydrogen atoms on methyl groups and aromatic rings have been removed for clarity.

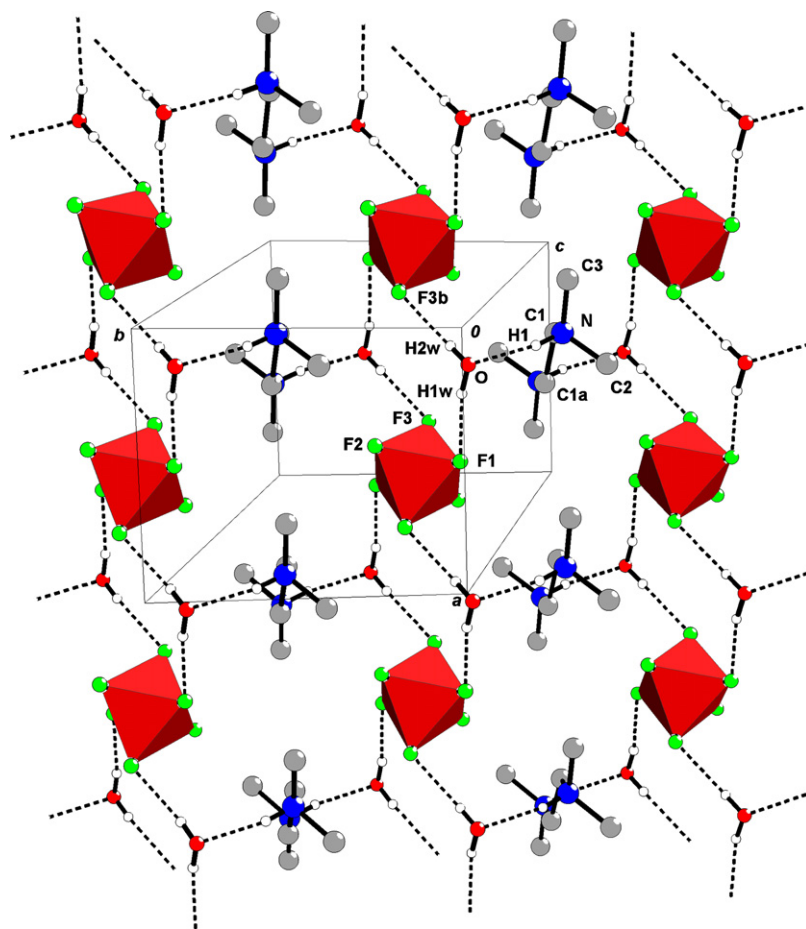


Fig. 3. 2-D layered structure of **4** in [001] direction. The hydrogen atoms on methyl and methylene groups have been removed for clarity.

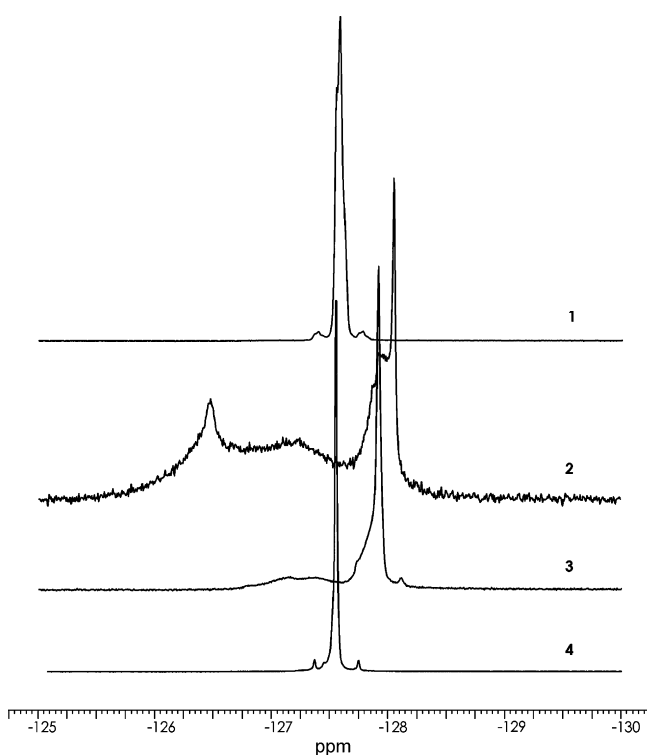


Fig. 4. ^{19}F NMR spectra of **1–4** in D_2O at 302 K.

of 0.029 Å suggests weaker hydrogen bonding in **2** than in **1**. Weaker hydrogen bonding can be explained by smaller N–H···F angle and larger H···F distance. In both **1** and **2** each nitrogen-bonded hydrogen atom forms two hydrogen bonds. The anions $[\text{SiF}_6]^{2-}$ and water molecules are hydrogen-bonded with two slightly different bonds in the structure of **4**. The geometry of the O–H···F hydrogen bond is similar as in **1**: 2.755 Å O···F distance and 165° O–H···F angle (average of two hydrogen bonds). The difference in the Si–F bond lengths is 0.019 Å and suggests weaker hydrogen bonding in **4** than in **1**. Weaker hydrogen bonding is attributed to interaction of water molecule and $[\text{SiF}_6]^{2-}$ in **4**, in comparison to the cation– $[\text{SiF}_6]^{2-}$ interaction in **1**.

The ^1H and ^{19}F NMR spectra of compounds **1–4** in D_2O were recorded (see Fig. 4. for ^{19}F NMR spectra). The resonances for the nitrogen-bonded proton of the cations were not observed in the ^1H NMR spectra due to the fast exchange with solvent deuterons in D_2O solutions. The other ^1H NMR resonances of the cations were observed as expected. The ^{19}F NMR spectrum of **4** shows a single resonance at -127.50 ppm accompanied by two silicon satellites with coupling constant $J(^{29}\text{Si}, ^{19}\text{F}) = 108$ Hz. The resonance is in accordance with the published chemical shifts for $[\text{SiF}_6]^{2-}$ anions [9]. The ^{19}F NMR resonance with two satellites ($J(^{29}\text{Si}, ^{19}\text{F}) = 107$ Hz) is also in the spectrum of **1**, however the resonance and satellites are broader and composed from three unresolved bands. The ^{19}F NMR spectra of compounds **2** and **3** have one sharp and additional broad resonance. It is not likely that the equilibrium between free ions and ion pairs $[\text{R}]^+ [\text{SiF}_6]^{2-}$ in the solution should be slow enough to give separate resonances of free ions and ion pairs. Therefore the plausible explanation for the

additional resonances in the ^{19}F NMR spectra of **2** and **3** is slow-exchange hydrolytic equilibrium between $[\text{SiF}_6]^{2-}$ and $[\text{SiF}_5\text{H}_2\text{O}]^-$ [24,25] coupled with protonation and deprotonation equilibria of organic base and fluoride (Eqs. (1)–(3)).



IR spectra for compounds **1–4** reveal two extensive absorption bands in the region about 730 and 470 cm^{-1} for stretching and bending Si–F, respectively. This is also in accordance with the other compounds with $[\text{SiF}_6]^{2-}$ anions [26]. Absorption bands for N–H stretching and N–H bending in cations were found in the region from 3200 to 3500 cm^{-1} and about 1640 cm^{-1} . This compare well with the values reported for other ammonium hexafluorosilicate salts [9].

3. Conclusions

In summary, we described new hexafluorosilicates with nitrogen-containing organic cations. The variations in hydrogen-bonding interactions result in the formation of discrete cation–anion unit (compound **1**), chain structure (**2**) and polymeric layer (**4**) in the crystal. The elongation of Si–F bonds of fluorine atoms forming the hydrogen bond have been observed.

4. Experimental

4.1. General experimental procedures

Infrared spectra (Nujol) were recorded on a PerkinElmer FT-1720X spectrometer. NMR spectra were recorded on a Bruker DPX 300 spectrometer operating at 300 MHz (^1H) and 282 MHz (^{19}F). Elemental analyses were carried out on a PerkinElmer 2400 CHN analyzer at the University of Ljubljana (Department of Organic Chemistry). The chemicals were used as purchased: HF (BDH Chemicals), SiO_2 (Carl Roth), ethanol (Riedel-de Haen), pyridine (Kemika), 2-picoline (Janssen Chemica), 2,6-lutidine (Aldrich), 2,4,6-collidine (Aldrich), tetramethylethylenediamine (Bio Chemica).

4.2. Synthesis of bis[2-methylpyridinium] hexafluorosilicate (1)

A hydrogen fluoride solution (10.4 mL; 0.29 mol) was slowly added to a plastic beaker containing 2-picoline (11.5 mL; 0.12 mol) at 0 °C. The solution was stirred for 2 h at 0 °C and then silicon dioxide (1.16 g; 0.019 mol) was slowly added. The mixture was stirred overnight and then filtered. After filtration, the solvent was slowly evaporated from the beaker to yield colorless crystalline product in five days. The crystals were washed with ethanol and dried in air. IR (Nujol) (cm^{-1}): 3253, 1634, 1539, 721, 624, 541, 476. ^1H NMR (300 MHz, D_2O): δ = 8.67 (d, 1H, *o*-ArH); 8.51 (td, 1H, *p*-ArH); 7.92 (m, 2H, *m*-ArH); 2.84 (s, 3H, *o*-CH₃) ppm. ^{19}F NMR (282 MHz, D_2O): δ = –127.58 (s, SiF_6) ppm. Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{F}_6\text{N}_2\text{Si}$: C, 43.63; H, 4.88; N, 8.48. Found: C, 43.92; H, 5.10; N, 8.62.

4.3. Synthesis of bis[2,6-dimethylpyridinium] hexafluorosilicate (2)

A hydrogen fluoride solution (10.4 mL; 0.29 mol) was slowly added to a plastic beaker containing 2,6-lutidine (13.6 mL; 0.12 mol) at 0 °C. The solution was stirred for 2 h at 0 °C and then

silicon dioxide (1.16 g; 0.019 mol) was slowly added. The mixture was stirred overnight and then filtered. After filtration, the solvent was slowly evaporated from the beaker to yield colorless crystalline product in three days. The crystals were washed with ethanol and dried in air. IR (Nujol) (cm^{-1}): 3457, 1655, 1615, 1280, 1178, 822, 737, 667, 558, 471, 418. ^1H NMR (300 MHz, D_2O): δ = 8.35 (t, 1H, *p*-ArH); 7.71 (d, 2H, *m*-ArH); 2.80 (s, 6H, *o*-CH₃) ppm. ^{19}F NMR (282 MHz, D_2O): δ = –128.03 (s, SiF_6) ppm. Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{F}_6\text{N}_2\text{Si}$: C, 46.92; H, 5.62; N, 7.82. Found: C, 43.91; H, 6.14; N, 7.39.

4.4. Synthesis of bis[2,4,6-trimethylpyridinium] hexafluorosilicate (3)

A hydrogen fluoride solution (10.4 mL; 0.29 mol) was slowly added to a plastic beaker containing 2,4,6-collidine (15.4 mL; 0.12 mol) at 0 °C. The solution was stirred for 2 h at 0 °C and then silicon dioxide (1.16 g; 0.019 mol) was slowly added. The mixture was stirred overnight and then filtered. After filtration, the solvent was slowly evaporated from the beaker to yield colorless solid product in six days. The solid product was washed with ethanol and dried in air. IR (Nujol) (cm^{-1}): 3303, 1641, 1280, 1048, 985, 925, 761, 724, 647, 596, 520, 469. ^1H NMR (300 MHz, D_2O): δ = 7.52 (s, 2H, *m*-ArH); 2.72 (s, 6H, *o*-CH₃); 2.59 (s, 3H, *p*-CH₃) ppm. ^{19}F NMR (282 MHz, D_2O): δ = –127.92 (s, SiF_6) ppm. Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{F}_6\text{N}_2\text{Si}$: C, 49.73; H, 6.26; N, 7.25. Found: C, 49.44; H, 6.46; N, 7.47.

4.5. Synthesis of tetramethylethylenediamonium hexafluorosilicate dihydrate (4)

A hydrogen fluoride solution (10.4 mL; 0.29 mol) was slowly added to a plastic beaker containing tetramethylethylenediamine (8.8 mL; 0.058 mol) at 0 °C. The solution was stirred for 2 h at 0 °C and then silicon dioxide (1.16 g; 0.019 mol) was slowly added. The mixture was stirred overnight and then filtered. After filtration, the solvent was slowly evaporated from the beaker to yield colorless crystalline product in four days. The crystals were washed with ethanol and dried in air. IR (Nujol) (cm^{-1}): 3445, 3049, 2561, 1645, 1505, 1009, 984, 722, 476. ^1H NMR (300 MHz, D_2O): δ = 3.73 (s, 4H, CH_2CH_2); 3.08 (s, 12H, CH_3) ppm. ^{19}F NMR (282 MHz, D_2O): δ = –127.50 (s, SiF_6) ppm. Anal. Calcd. for $\text{C}_6\text{H}_{22}\text{F}_6\text{N}_2\text{O}_2\text{Si}$: C, 24.32; H, 7.48; N, 9.45. Found: C, 24.67; H, 8.05; N, 9.43.

4.6. X-ray crystallography

The X-ray intensity data were collected at room temperature on a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 [27] and refined against F^2 on all data by a full-matrix least squares with SHELXL-97 [28]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model. The other hydrogen atoms were located in the difference Fourier synthesis and refined freely (O–H) and in the case of N–H bonds with the help of distance restraints. In **1** the fluorine atoms F2 and F3 are disordered over two orientations in the equatorial plane and were refined with the use of PART instruction. The occupancy of F2a and F2b refined to a ratio of 62% and 38%, the ratio of F3a and F3b was found to be 61–39%.

Crystallographic data (excluding structure factors) for the structures **1**, **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 680933, 680934 and 680935. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or

from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK.

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