Scientific paper

Structural Diversity of Different Aminomethylpyridinium Hexafluoridosilicates

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Abstract

A series of new aminomethylpyridinium hexafluoridosilicate salts with the formula $(RH)_2[SiF_6]$ (where R = 2-amino-3-methylpyridine (**1**), 2-amino-4-methylpyridine (**2**), 2-amino-5-methylpyridine (**3**) and 2-amino-6-methylpyridine (**4**)) were prepared by the reaction of various methyl-substituted 2-aminopyridines with hydrogen fluoride solution of silica. The crystal packing of these ionic salts is compared with respect to the position of the methyl group on the aromatic ring. The crystal structures are dominated by the non-covalent interactions: the N–H···F hydrogen bonds and π-π interactions between aromatic rings. The potential of the corresponding ionic salts to enable supramolecular associations was investigated. Compounds **1**–**4** were also characterized by ^1H, ^{19}F NMR and IR spectroscopy.

Keywords: hexafluoridosilicate, hydrogen bond, X-ray crystal structure, aminomethylpyridine, π-π interaction

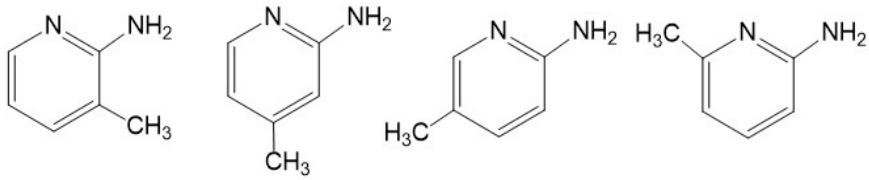
1. Introduction

Supramolecular chemistry is concerned with the research and utilization of non-covalent bonding forces. The interaction between charges is a well-known type of non-covalent interaction in common salts consisting of metal cations and halide anions. When an organic molecule plays the role of the cation and the anion is a polyatomic species, the formation of ion pairs can be directional and not just involve interactions between spherical ions.[1]

In such systems, the mutual interaction of the reaction partners is controlled by non-covalent interactions. These interactions mainly include hydrogen bonds and π–π interactions between aromatic rings. It is known from crystallographic and *ab initio* studies that the hydrogen bonding of the pyridine nitrogen significantly influences the pyridine stacking interactions.[2]

The electrostatic attractive forces in ionic compounds with the formula $(pyH)_2[SiF_6]$ between the cations of the protonated pyridines and the hexafluoridosilicate anions $[SiF_6]^{2-}$ enable the formation of extensive N–H···F hydrogen bonds and π–π interactions. The overview of the crystal structures archived in the CSD (release November 2024, version 5.32)[3] shows several hits for ionic compounds with the formula $(RH)_2[SiF_6]$, where R stands for pyridine or pyridine- related compounds.[4–9] Ionic hexafluoridosilicates with methyl[10], amino[11,12], carboxy[13,14], carboxymethyl[15], hydroxymethyl[16,17] and nicotinamide[18] substituents on the pyridine ring are well documented in the literature. In some of them, pyridine is substituted with several substituents, one of which is a methyl group.[19] Some pyridinium hexafluoridosilicates can be used as potential caries of prophylactic agents.[20]

In the present study, the crystal structures of hexafluoridosilicates with methyl-substituted 2-aminopyridinium cations (Scheme 1) were determined and structurally compared. This was accompanied with the investigation of non-covalent interactions in these sys-



Scheme 1. **1** **2** **3** **4**

tems to gain further insight into the effects of small structural variations in closely related cations on crystal packing. Two effects appear to be crucial for crystal packing: the N–H···F hydrogen bonding interactions between the charged species and the π–π stacking between the cationic units. Spectral data (NMR and IR) were also obtained for compounds **1**–**4**.

2. Experimental

General Experimental Procedures. The chemicals were used as purchased: HF (BDH Chemicals and Aristar), SiO_2 (Carl Roth), aminomethylpyridines (Fluka). Elemental analyses (C, H, N) were performed using a Perkin-Elmer 2400 Series II CHNS/O analyzer. NMR spectra were measured with a Bruker Avance III 500 spectrometer at 500 MHz (^{1}H) and 471 MHz (^{19}F). The chemical shifts are given on the δ scale (ppm). Infrared spectra (Nujol mull or solid sample support in Specac Golden Gate Diamond ATR) were recorded with a Perkin-Elmer Spectrum 100 FT-IR spectrometer.

General Synthesis. Silicon dioxide (1.00 g; 16.6 mmol) was slowly added to a plastic beaker containing hydrofluoric acid (20 mL, 48%) while stirring. After clarification of the solution aminomethylpyridine (3.61 g, 33.3 mmol) was added slowly. The mixture was stirred for 2 hours and then filtered. After filtration, the solvent was slowly evaporated from the beaker to yield a colorless crystalline product after a few days. The crystals were filtered from the mother liquor and dried in air.

Bis(2-amino-3-methylpyridinium) hexafluoridosilicate (1).

Yield 1.34 g, 22%. Anal. Calcd for $C_{12}H_{18}F_6N_4Si$: C, 39.99; H, 5.03; N, 15.55. Found: C, 39.71; H, 5.06; N, 15.47. ^{1}H NMR (500 MHz, D_2O) δ 7.76 (d, 1H, Ar*H*), 7.67 (d, 1H, Ar*H*), 6.84 (t, 1H, Ar*H*), 2.20 (s, 3H, CH_3) ppm. ^{19}F NMR (471 MHz, D_2O) δ –129.88 (s, SiF_6) ppm. IR (Nujol) (cm^{-1}): 3408, 3337, 3212, 3106 [ν(N$^+$H), ν(NH_2)], 1665, 1624, 1573 [δ(NH_2)], 724 [ν(SiF)], 474, 452 [δ(SiF_2)].

Bis(2-amino-4-methylpyridinium) hexafluoridosilicate (2).

Yield 0.60 g, 10%. Anal. Calcd for $C_{12}H_{18}F_6N_4Si$: C, 39.99; H, 5.03; N, 15.55. Found: C, 39.93; H, 4.98; N, 15.55. ^{1}H NMR (500 MHz, D_2O) δ 7.63 (d, 1H, Ar*H*), 6.79 (s, 1H, Ar*H*), 6.75 (d, 1H, Ar*H*), 2.35 (s, 3H, CH_3) ppm. ^{19}F NMR (471 MHz, D_2O) δ –129.97 (s, SiF_6) ppm. IR (Nujol) (cm^{-1}): 3407, 3356, 3231, 3108 [ν(N$^+$H), ν(NH_2)], 1674, 1636 [δ(NH_2)], 723 [ν(SiF)], 474, 452 [δ(SiF_2)].

Bis(2-amino-5-methylpyridinium) hexafluoridosilicate (3).

Yield 0.67 g, 11%. Anal. Calcd for $C_{12}H_{18}F_6N_4Si$: C, 39.99; H, 5.03; N, 15.55. Found: C, 40.10; H, 5.24; N, 15.72. ^{1}H NMR (500 MHz, D_2O) δ 7.77 (d, 1H, Ar*H*), 7.57 (s, 1H, Ar*H*), 6.92 (d, 1H, Ar*H*), 2.19 (s, 3H, CH_3) ppm. ^{19}F NMR

Table 1. Crystal data and structure refinement details for **1**–**4**.

	1	**2**	**3**	**4**
formula	$C_{12}H_{18}F_6N_4Si$	$C_{12}H_{18}F_6N_4Si$	$C_{12}H_{18}F_6N_4Si$	$C_{12}H_{18}F_6N_4Si$
Fw (g mol^{-1})	360.39	360.39	360.39	360.39
crystal size (mm)	0.20 × 0.10 × 0.08	0.20 × 0.10 × 0.05	0.25 × 0.15 × 0.08	0.50 × 0.25 × 0.25
crystal color	colourless	colourless	colourless	colorless
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*P b c n*	*C* 2/*c*	*P* 2_1/*c*	*C c*
a (Å)	14.4210(5)	8.728(5)	6.6383(2)	20.6043(4)
b (Å)	7.4652(2)	12.658(5)	12.6481(5)	20.6970(4)
c (Å)	13.9865(5)	14.892(5)	9.3048(3)	15.5669(3)
β (°)	90	97.073(5)	99.129(2)	109.4270(10)
V (Å3)	1505.73(9)	1632.7(13)	771.35(5)	6260.5(2)
Z	4	4	2	16
F(000)	744	744	372	2976
no. of collected reflns	3177	3305	3432	13644
no. of independent reflns	1721	1728	1759	13636
R_{int}	0.0178	0.0264	0.0207	0.0118
no. of reflns observed	1292	1203	1377	8149
no. of parameters	116	117	116	910
$R[I > 2\sigma(I)]^a$	0.0415	0.0451	0.0349	0.0477
wR_2 (all data)^b	0.1232	0.1225	0.0923	0.1164
Goof , S^c	1.038	1.054	1.045	1.036
Largest diff. peak/hole (e Å^{-3})	+0.30/–0.33	+0.25/–0.21	+0.17/–0.26	+0.23/–0.23

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

(471 MHz, D_2O) δ –129.93 (s, SiF_6) ppm. IR (Nujol) (cm^{-1}): 3355, 3198 [ν(N^+H), ν(NH_2)], 1674, 1629, 1559 [δ(NH_2)], 722 [ν(SiF)], 469, 439 [δ(SiF_2)].

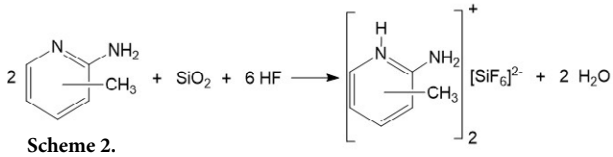
Bis(2-amino-6-methylpyridinium) hexafluoridosilicate (4).

Yield 1.41 g, 23%. Anal. Calcd for $C_{12}H_{18}F_6N_4Si$: C, 39.99; H, 5.03; N, 15.55. Found: C, 40.09; H, 5.15; N, 15.61. ^1H NMR (500 MHz, D_2O) δ 7.76 (t, 1H, Ar*H*), 6.78 (d, 1H, Ar*H*), 6.69 (d, 1H, Ar*H*), 2.43 (s, 3H, C*H*$_3$) ppm. ^{19}F NMR (471 MHz, D_2O) δ –129.77 (s, SiF_6) ppm. IR (Nujol) (cm^{-1}): 3397, 3363, 3227 [ν(N^+H), ν(NH_2)], 1680, 1637, [δ(NH_2)], 750 [ν(SiF)], 475, 464 [δ(SiF_2)].

X-ray Crystallography. The crystal data and refinement parameters of compounds **1**–**4** are listed in Table 1. X-ray intensity data were collected using a Nonius Kappa CCD diffractometer equipped with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at room temperature. The data were processed using DENZO.[21] The structures were solved by direct methods using SHELXT[22] and refined against F^2 on all data by a full-matrix least-squares procedure with SHELXL.[23] 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 hydrogen atoms bound to nitrogen were localized in the difference map and refined with the distance restraints (DFIX) with N-H = 0.86 and with U_{iso}(H) = 1.2U_{eq}(N). Compound **4** crystallizes in the non-centrosymmetric space group *Cc*. The value of the Flack parameter 0.44(5) indicates possible racemic twinning.

3. Results and Discussion

The preparation of methy-substituted aminopyridinium hexafluoridosilicates were carried out in a simple manner by reacting the corresponding pyridine with silicon dioxide in hydrofluoric acid. Hydrofluoric acid serves simultaneously as reagent and solvent in these reactions. The molar ratios between SiO_2 and the corresponding methylaminopyridine were 1:2 in all cases (Scheme 2). In all cases, colorless crystalline products were obtained by slow evaporation of the solvent at room temperature. The crystal structures of these compounds consist of methyl-substituted 2-aminopyridinium cations and hexafuoridosilicate anions. Selected bond lengths and angles for all compounds **1**–**4** are listed in Table 2. The Si–F distances in the $[SiF_6]^{2-}$ anions of compounds **1**–**4** are between 1.65 and 1.69 Å, and the bond angles within the anions are close to 90° and 180°. Such an undistorted octahedral geometry is also found in some other ionic compounds with $[SiF_6]^{2-}$ anion and heterocyclic nitrogen cation, e. g. pyrimidinium hexafluoridosilicates.[24]



Scheme 2.

The characteristic hydrogen bonds observed in **1**–**4** are listed in Table 3. These components are bound by a network of charge-assisted N–H···F hydrogen bonds. The protonated nitrogen on the pyridine ring and the amino group are potential donors of one and two hydrogen bonds, respectively. All six fluorine atoms in hexafuoridosilicate anions are capable of accepting hydrogen bonds.

2-Aminopyridinium hexafluorosilicate has already been synthesized and crystallographically characterized.[11] When investigating the crystal structures with an additional methyl substituent on the pyridine rings, we can use the influence of the interionic hydrogen bonds on the structure as a model. We expected a different crystalline architecture due to supramolecular interactions in the structure of the corresponding hexafluoridosilicate.

Table 2. Selected bond lengths (Å) and angles (°) of compounds **1**–**4**.[a]

1			
Si1–F1	1.6934(10)	F1–Si1–F2	89.19(5)
Si1–F2	1.6856(11)	F1–Si1–F3	90.22(5)
Si1–F3	1.6773(11)	F2–Si1–F3	179.02(6)
2			
Si1–F1	1.6937(12)	F1–Si1–F2	89.64(5)
Si1–F2	1.6835(19)	F1–Si1–F3	89.26(6)
Si1–F3	1.6581(16)	F1–Si1–F4	90.36(5)
Si1–F4	1.6781(19)	F2–Si1–F3	89.40(6)
3			
Si1–F1	1.6927(9)	F1–Si1–F2	90.03(5)
Si1–F2	1.6774(9	F1–Si1–F3	90.60(5)
Si1–F3	1.6778(9)	F1–Si1–F1^i	180.00(7)
4			
Si1–F1	1.678(3)	F1–Si1–F2	90.26(16)
Si1–F2	1.683(3)	F1–Si1–F3	179.4(2)
Si1–F3	1.686(3)	F1–Si1–F4	89.81(16)
Si1–F4	1.684(3)	F1–Si1–F5	90.39(19)
Si1–F5	1.646(3)	F1–Si1–F6	89.7(2)
Si1–F6	1.658(3)	F2–Si1–F4	179.14(19)

[a] Symmetry transformation used to generate equivalent atoms: (i) –x+2, –y+1, –z+1.

X-ray analysis of compound 1. Compound **1** with 2-amino-3-methypyridinium cation crystallizes in the orthorhombic space group *Pbcn* (Figure 1). The asymmetric unit consists of one half of the $[SiF_6]^{2-}$ anion which is located on a 2-fold rotation axis and one of 2-amino-3-methylpyridinium cation. All fluorine atoms of each $[SiF_6]^{2-}$

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

D – H ··· A	d(D – H)/ Å	d(H ··· A)/ Å	d(D ··· A)/ Å	<(DHA)/ °	Symmetry transformation for acceptors
1					
N1–H1N···F1	0.902(14)	1.851(15)	2.7231(16)	162.2(17)	
N2–H2E···F2	0.867(15)	1.996(16)	2.8477(19)	167(2)	
N2–H2D···F3	0.858(16)	2.211(17)	3.0172(19)	156.4(19)	x–1/2, y–1/2, –z+3/2
2					
N1–H1N···F1	0.871(16)	1.894(17)	2.750(2)	167(2)	
N2–H2D···F2	0.891(18)	2.14(2)	2.925(3)	146(3)	
N2–H2D···F3	0.891(18)	2.31(2)	3.085(3)	145(3)	
N2–H2E···F4	0.865(18)	1.97(2)	2.816(3)	166(3)	x–1/2, y+1/2, z
3					
N1–H1N···F1	0.857(15)	1.892(15)	2.7452(16)	173.9(18)	
N2–H2D···F2	0.879(15)	1.952(16)	2.8296(18)	177(2)	
N2–H2E···F3	0.882(15)	1.985(15)	2.8576(17)	170(2)	
4					
N1–H1N···F1	0.85(3)	1.90(3)	2.748(5)	171(5)	
N2–H2D···F2	0.87(3)	2.06(4)	2.874(6)	154(6)	
N2–H2E···F23	0.88(3)	2.02(3)	2.868(6)	163(6)	x–1/2, y+1/2, z
N3–H3N···F3	0.88(3)	1.87(3)	2.740(5)	169(5)	
N4–H4D···F4	0.87(3)	2.11(4)	2.875(6)	147(6)	
N4–H4E···F11	0.88(3)	2.03(3)	2.861(5)	158(6)	x–1/2, y+1/2, z
N5–H5N···F7	0.86(3)	1.91(3)	2.754(5)	168(5)	
N6–H6D···F8	0.87(3)	2.21(4)	2.985(6)	149(6)	
N6–H6E···F17	0.86(3)	1.98(3)	2.829(5)	171(6)	
N7–H7N···F9	0.88(3)	1.87(3)	2.749(5)	174(5)	
N8–H8D···F10	0.87(3)	2.21(3)	3.050(6)	160(6)	
N8–H8E···F2	0.86(3)	1.96(3)	2.815(6)	171(6)	
N9–H9N···F13	0.91(3)	1.85(3)	2.734(5)	166(4)	
N10–H10D···F14	0.89(3)	2.38(3)	3.231(6)	161(5)	
N10–H10E···F10	0.85(3)	2.11(3)	2.911(6)	158(6)	x–1/2, y–1/2, z
N11–H11N···F15	0.89(3)	1.85(3)	2.729(5)	172(5)	
N12–H12D···F18	0.87(3)	2.11(4)	2.896(6)	150(6)	
N12–H12E···F20	0.88(3)	2.05(3)	2.911(6)	166(6)	x–1/2, y+1/2, z
N13–H13N···F19	0.87(3)	1.87(3)	2.736(5)	175(5)	
N14–H14D···F20	0.84(3)	2.28(3)	3.075(6)	158(6)	
N14–H14E···F4	0.85(3)	1.97(3)	2.811(5)	173(6)	x, y–1, z
N15–H15N···F21	0.85(3)	1.95(3)	2.777(5)	165(5)	
N16–H16D···F22	0.87(3)	2.19(4)	2.984(6)	151(6)	
N16–H16E···F17	0.84(3)	1.99(3)	2.833(5)	174(6)	

anion are involved in N–H···F hydrogen bonding. The protonated heterocyclic nitrogen atom, together with the amino nitrogen and one of the amino hydrogen atoms, forms eight-membered rings (N–C–N–H···F–Si–F···H) with two fluorine ligands from $[SiF_6]^{2-}$ octahedron. This can be designated by the graph-set[25] notation $R_2^2(8)$. Four fluorine ligands from each $[SiF_6]^{2-}$ octahedron are involved in two eight-membered ring formations. The second hydrogen atom of the amino group is involved in N–H···F hydrogen bonding interactions, with the graph-set motif $R_8^8(24)$, where four $[C_6H_9N_2]_2[SiF_6]$ synthons linked to form a 24-membered ring, resulting in a two-dimensional layer perpendicular to the *c*-axis of the crystal structure. The layer is stabilized by non-covalent π–π interactions with the centroid-to-centroid separation distance of 3.741 Å (Table S1).

X-ray analysis of compound 2. Changing the position of the methyl group on the aromatic ring leads to drastic changes of hydrogen bonding interactions and crystal structure in compounds with hexafluoridosilicate anion. Compound **2** crystallizes in the monoclinic space group *C*2/*c*, in which one silicon and two fluorine atoms of the $[SiF_6]^{2-}$ anion are located in a special position of the 2-fold rotation axis. The protonated pyridine nitrogen atom and one of the amino hydrogen atoms are involved in N–H···F hydrogen-bonding interactions

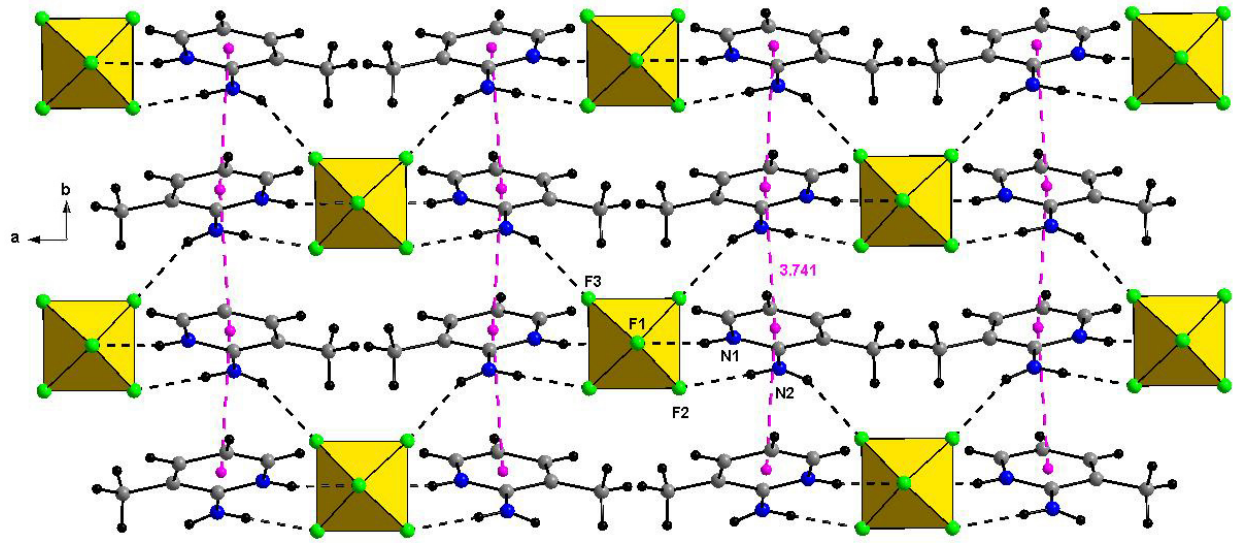


Figure 1. Crystal structure of **1** showing the atom numbering scheme, the N–H···F hydrogen bonding interactions between cations and anions and the π–π stacking between pyridine rings.

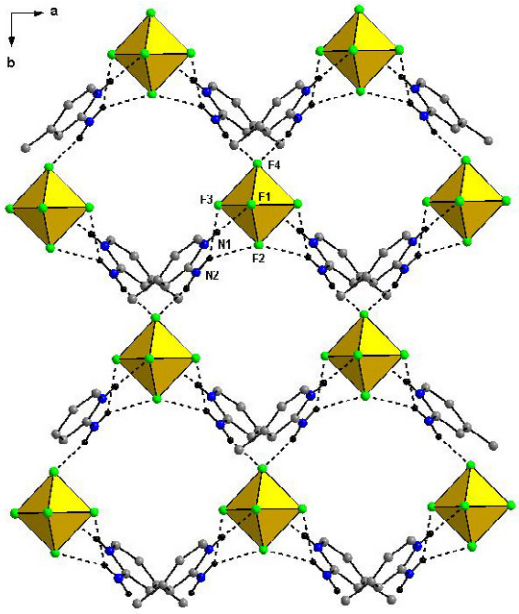


Figure 2. Layer formation in **2** by N–H···F hydrogen bonds. The hydrogen atoms on the aromatic rings and the methyl group have been removed for clarity.

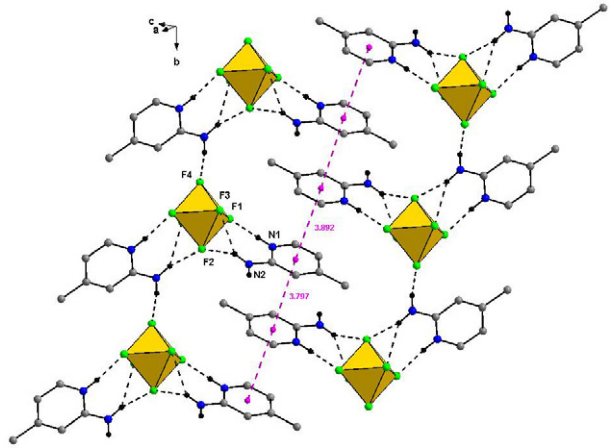


Figure 3. Fragment of crystal packing of **2** with π–π stacking between pyridine rings. The hydrogen atoms on the aromatic rings and the methyl groups have been removed for clarity.

with three fluorine acceptors of the $[SiF_6]^{2-}$ anion in the *fac* position (Figure 2). The nitrogen atom of the amino group is the donor of one bifurcated N–H···F hydrogen bond and one N–H···F hydrogen bond to the neighboring $[SiF_6]^{2-}$ anion, thus forming 20-membered rings [represented by graph-set notation $R_8^6(20)$] and a 2D layer perpendicular to the *c*-axes. These layers are packed into a supramolecular 3D architecture by the assistance of non-covalent π–π interactions between the aromatic rings with two different centroid-to-centroid separation distances of 3.797 and 3.892 Å (Figure 3 and Table S1).

X-ray analysis of compound 3. Compound **3** crystallizes in the monoclinic $P2_1/c$ space group. The formation of an eight-membered N–C–N–H···F–Si–F···H ring between one cation and one anion as well as 24-membered ring between four cations and four anions with the graph-set notations of $R_2^2(8)$ and $R_8^8(24)$ is reminiscent of the crystal structure of compound **1** (Figure 4). However, the N–H···F interactions of the 2-amino-5-methylpyridinium cations according to $[SiF_6]^{2-}$ anion in **3** are in the *trans* position. These hydrogen-bonding interactions lead to a two-dimensional zigzag layered network extending along the *bc* plane. The shortest distance between two aromatic rings is 4.863 Å and is too long for the interaction.[26]

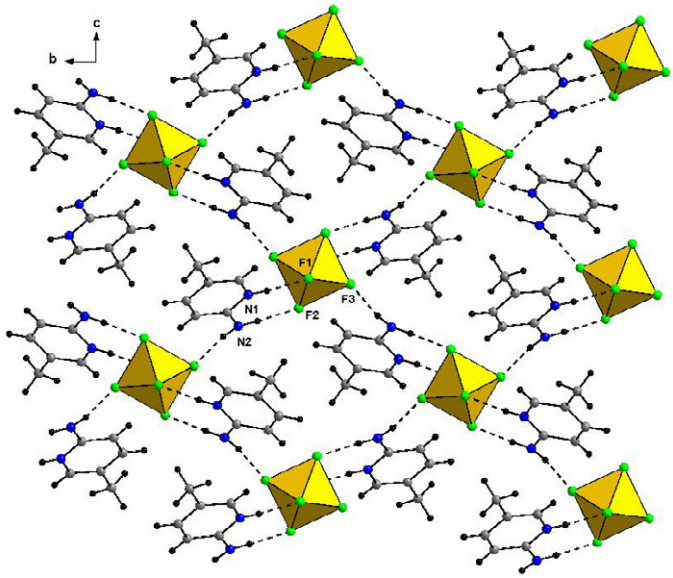


Figure 4. Crystal structure of **3** showing the atom numbering scheme and the N–H···F hydrogen bonding interactions between cations and anions.

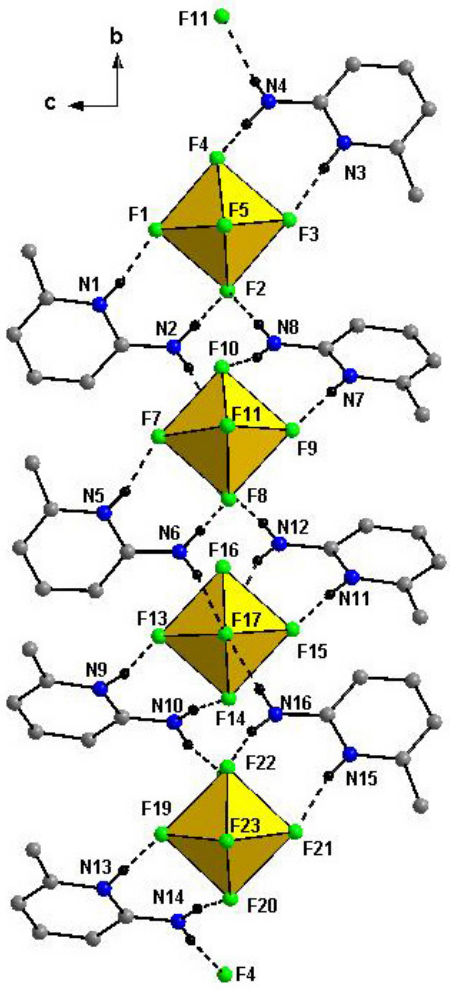


Figure 5. Fragment of crystal packing in **4** with N–H···F hydrogen bond contacts. The hydrogen atoms on aromatic rings and methyl groups have been removed for clarity.

X-ray analysis of compound 4. Compound **4** crystallizes in the non-centrosymmetric space group *Cc* with four crystallographically different $(C_6H_9N_2)_2[SiF_6]$ formula units (Figure 5). Cations and anions are connected by intense N–H···F hydrogen bonds and π–π interactions forming 3D network. In all four crystallographically different $[SiF_6]^{2-}$ anions four fluorine atoms are acceptors of four N–H···F hydrogen bonds of two 2-amino-6-methylpyridinium cations forming eight-membered N–C–N–H···F–Si–F···H rings with a graph-set motif $R_2^2(8)$. The amino group of the cations is responsible for the connection of the $(C_6H_9N_2)_2[SiF_6]$ synthons. The arrangement of the 2-amino-6-methylpyridinium cations in an asymmetric unit suggests intense π–π interactions between the aromatic rings in the range from 3.65 to 3.74 Å (Figure 6 and Table S1).

NMR and IR spectra. The ^1H and ^{19}F NMR spectra of compounds **1**–**4** were recorded in D_2O. The resonances for the nitrogen-bonded proton of the cations were not observed in the ^1H NMR spectra due to rapid exchange with deuterons of the solvent in D_2O solutions. The other ^1H NMR resonances of the cations were observed as expected. The ^{19}F NMR spectrum of **1**–**4** shows a strong singlet signal at 130 ppm with two satellites due to the spin-spin interactions ^{29}Si–^{19}F J(SiF) =106 Hz. (See Figures S1–S8)

The IR spectra of compounds **1**–**4** reveal two extensive regions for absorption bands of N–H stretching and N–H bending in cations from 3100 to 3500 cm^{-1} and about 1640 cm^{-1}, respectively. Absorption bands for Si–F stretching and bending can be found in the range of about 730 and 470 cm^{-1}. Of the five normal vibrations expected for the $[SiF_6]^{2-}$ anion, only two are infrared active.[27] This is also in accordance with the other ammonium hexafluoridosilicate salts.[28] (See Figures S9–S16)

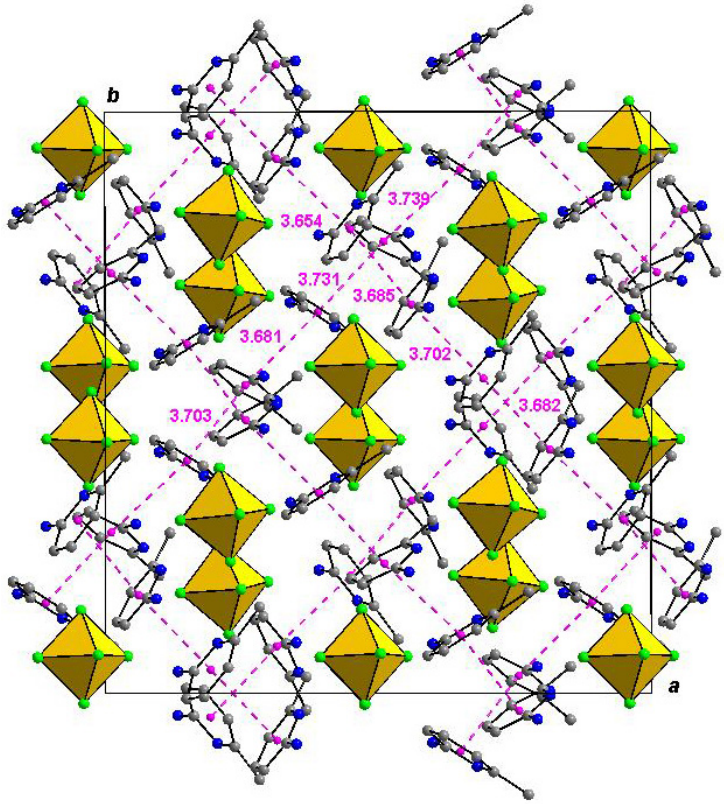


Figure 6. Fragment of crystal packing in **4** with π–π stacking between pyridine rings. The hydrogen atoms on the aromatic rings and the methyl groups have been removed for clarity.

4. Conclusion

In summary, four different crystalline compounds **1**–**4** were found in the product of the reactions between silicon dioxide and 2-aminomethylpyridine with the methyl substituent at different positions of the aromatic ring. The variations in the hydrogen bonds lead to the formation of a supramolecular layered structure. The additional non-covalent *π*–*π* interactions enable a 3D network structure. Each aminomethylpyridinium unit in compounds **1**–**4** functions as a two-connecting node, bridging two SIF_6^{2-} anions, with the hydrogen-bonded layers adopting a square lattice (sql) network topology. However, two distinct hydrogen-bonding synthons are observed. Synthon I contains an N(py)–H···F hydrogen bond (where the pyridine nitrogen is the donor) along with the single N–H···F hydrogen bond of the amino group whereas synthon II involves only an N–H···F hydrogen bond from the amino nitrogen. The NMR spectroscopy results for the **1**–**4** compounds showed their stability and purity in solution.

Supplementary Material

The Supporting Information is available: numerical parameters for π–π interactions, IR, ^{1}H NMR and ^{19}F NMR spectra of compunds **1**–**4**.

CCDC 2420167–2420170 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Povzetek

Pri reakcijah med silicijevim dioksidom, raztopljenim v fluorovodikovi kislini in štirimi različnimi 2-aminometilpiridini, kjer je metilna skupina na štirih različnih mestih piridinskega aromatskega obroča, so nastali štirje različni kristalinični ionski produkti. Sprememba položaja metilne skupine vpliva na arhitekturo vodikovih vezi med aminometilpiridinijevimi kationi in heksafluoridosilikatnimi anioni. Tvorijo se lahko verižne strukture ali polimerne plasti. Dodatne nekovalentne π–π interakcije pa prispevajo k trodimenzionalni strukturi.

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