

Ammonium hexafluorosilicate salts

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Abstract

The preparation and characterization of the ammonium hexafluorosilicate salts, $2[\text{R}]^+ [\text{SiF}_6]^{2-}$ (where R = piperidinium (2), methylammonium (3), quinolinium (4), acridinium (5), 2,2,6,6-tetramethylpiperidinium (6), and propylammonium (7)) is described.

The salts were prepared from the reaction of the corresponding alkylammonium fluoride with silica gel. The compounds were characterized by NMR, IR, mass spectrometry and in the case of 1 (piperidinium fluoride), 2–4 by X-ray crystallography. Compounds 1–3 crystallize in the orthorhombic crystal system (space groups *Iba*2, *Fdd*2, and *Pnmm*, respectively), with *Z* = 8, 14, and 4, respectively. Compound 4 crystallizes in the triclinic space group *P*-1, with *Z* = 2. Compounds 1–4 exhibit hydrogen bonding. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hexafluorosilicates are used widely in research and industry, for the selective removal of surface acidity in zeolite ZSM-5 [1], in photovoltaic applications [2], as active agents in the formulation of mouthwashes and dentrifices [3], and for studying the effects of hydrogen bonding on structural properties [4–6]. One possible application of hexafluorosilicate salts is in the formation of ionic liquids. Ionic liquids have potential uses in chemical synthesis as catalysts, in nuclear fuel processing, separation technologies, and as electrolytes in batteries and solar cells. Ionic liquids also have potential as replacements for volatile organic compounds traditionally used as industrial solvents. Ionic liquids are generally comprised of nitrogen-containing organic cations and symmetric inorganic anions [7]. Despite its -2 charge, the stability and geometry (O_h) of the hexafluorosilicate anion may make it suitable as a component of an ionic liquid when paired with suitable linear or planar bases. The present work is an exploration into what results when hexafluorosilicate and amines are combined.

Thus, the preparation of the ammonium hexafluorosilicate salts, $2[\text{R}]^+ [\text{SiF}_6]^{2-}$ (where R = piperidine (2), methylamine (3), 2,2,6,6-tetramethylpiperidine (6), and propylamine

(7)), and $2[\text{R}]^+ [\text{SiF}_6]^{2-}$ (where R = quinoline (4), acridine (5)) is described. The compounds were characterized by NMR, IR, mass spectrometry and in the case of 1 (piperidinium fluoride), 2–4 by X-ray crystallography.

2. Experimental

The ^1H , ^{13}C , ^{19}F NMR spectra were recorded on a JEOL-GSX-400 spectrometer operating at 400.25 MHz (^1H), 100.52 MHz (^{13}C), 376.08 MHz (^{19}F), are reported relative to SiMe_4 (^1H and ^{13}C) and CFCl_3 (^{19}F), and are in ppm. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1} . Mass spectral data (MALDI-TOF) were obtained on a Kratos Kompact instrument.

Piperidine, hydrogen fluoride (47–49% HF in water), methylamine, propylamine, 2,2,6,6-tetramethylpiperidine, and acridine were obtained from Acros. Quinoline was obtained from aldrich. Reagents were used as received.

2.1. Synthesis of piperidinium fluoride (1) and bis[piperidinium] hexafluorosilicate (2)

A hydrogen fluoride solution (31.21 ml, 0.625 mol) was added drop wise to a plastic beaker containing piperidine (34.54 ml, 0.35 mol) at 0 °C. The solution was stirred for 2 h at 0 °C, and then allowed to warm to room temperature. A small portion of the solution was removed, and the solvent

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removed via vacuum to yield light yellow crystals of (**1**). H_2O ^1H NMR (D_2O): δ 1.45–1.54 (2H, m, CH_2), 1.53–1.67 (4H, m, CH_2), 2.97–3.00 (4H, t, CH_2). ^{13}C (D_2O): δ 16.0, 16.8, 39.1. ^{19}F (D_2O): δ 130.7 (s, F^-).

Silica gel (1.74 g, 0.029 mol) was slowly added to a solution of piperidinium fluoride (18.40 g, 0.175 mol). The mixture was stirred overnight. After stirring, the solvent was slowly evaporated from the beaker to yield a light yellow crystalline solid (**2**). ^1H NMR (DMSO): δ 1.49–1.70 (2H, m, CH_2), 1.63–1.69 (4H, m, CH_2), 2.92–2.96 (4H, t, CH_2). ^{13}C (DMSO): δ 22.7, 41.1, 44.7. ^{19}F (DMSO): δ 125.9 (s, $J = 62.5$ Hz, SiF_6). Yield 94%; mp 62–64 °C. IR (KBr) (cm^{-1}): 2760, 2513, 2413 (ν N–H); 1585 (δ N–H); 737 (ν Si–F); 481 (δ Si–F). MS (MALDI-TOF): m/z 86 [M] $^+$.

2.2. Synthesis of bis[methylammonium] hexafluorosilicate (**3**)

A solution of methylammonium fluoride was made by adding a methylamine solution (27.20 ml, 0.35 mol) drop wise and slowly to a plastic beaker containing hydrogen fluoride (31.25 ml, 0.625 mol) at 0 °C. The solution was stirred for 2 h at 0 °C, and then allowed to warm to room temperature. Silica gel (1.74 g, 0.029 mol) was slowly added to the solution of methylammonium fluoride (8.94 g, 0.175 mol). The mixture was stirred overnight. After stirring, the solvent was slowly evaporated from the beaker to yield white crystalline (**3**). ^1H NMR (CDCl_3): δ 2.13 (s, $J = 64$ Hz, CH_3). ^{13}C (CDCl_3): δ 65.4. ^{19}F (D_2O): δ 130.5 (s, $J = 54.7$ Hz, SiF_6). Yield 95%; mp 286–290 °C, solid decomposed to produce a gas and a white solid. Solid melted at 304 °C. IR (KBr) (cm^{-1}): 3274, 3219, 3060 (ν N–H); 1640, 1611, 1521, 1500; 737 (ν Si–F); 481 (δ Si–F). MS (MALDI-TOF): m/z 32 [M] $^+$.

2.3. Synthesis of bis[quinolinium] hexafluorosilicate (**4**)

A solution of quinolinium fluoride was made by adding quinoline (4.73 ml, 0.04 mol) drop wise and slowly to a plastic beaker containing hydrogen fluoride (1.78 ml, 0.08 mol) at 0 °C. The solution was stirred for 2 h at 0 °C, and then allowed to warm to room temperature. Silica gel (1.20 g, 0.02 mol) was slowly added to the solution of quinolinium fluoride (5.967 g, 0.04 mol). The mixture was stirred overnight. After stirring, the solvent was slowly evaporated from the beaker to yield a brown crystalline solid of (**4**). ^1H NMR (DMSO): δ 7.79–7.89 (2H, m, H2 & H5), 7.96–8.10 (1H, m, H6), 8.14–8.16 (1H, dd, H3), 8.18–8.21 (1H, dd, H4), 8.80–8.82 (1H, dd, H7), 9.14–9.15 (1H, dd, N–CH1). ^{13}C (DMSO): δ 122.4, 125.40, 128.86, 128.89, 129.4, 132.9, 142.2, 148.6. ^{19}F (DMSO): δ 139.16 (s, broad, SiF_6). Yield 93%; mp 160–164 °C. IR (KBr) (cm^{-1}): 2726, 2671 (ν N–H); 738 (ν Si–F); 482 (δ Si–F). MS (MALDI-TOF): m/z 130 [M] $^+$.

2.4. Synthesis of bis[acridinium] hexafluorosilicate (**5**)

Acridine (1.50g, 8.37 mmol) was dissolved in the minimum amount of boiling water in a plastic beaker, and then cooled to 0 °C. Hydrogen fluoride (8.36 ml, 16.74 mmol) was slowly added dropwise. The mixture was stirred for 2 h at 0 °C, and then allowed to warm to room temperature. A yellow solid was formed (acridinium fluoride). Silica gel (0.42 g, 6.97 mmol) was added to the yellow solid (0.834 g, 4.185 mmol) dissolved in water. The mixture was stirred overnight at room temperature. The solvent was evaporated from the solution until a greenish yellow crystalline solid was obtained. Yield 92%. The greenish yellow solid turned golden brown after being exposed to air for 2 weeks (**5**). ^1H NMR (DMSO): δ 7.78–7.82 (2H, m, H3 & H7), 8.07–8.14 (2H, m, H2 & H8), 8.25–8.28 (2H, d, H4 & H6), 8.37–8.39 (2H, d, H1 & H9), 9.6 (1H, s (broad), H5). ^{13}C (DMSO): δ 126.6, 126.7, 127.5, 129.9, 144.1. ^{19}F (DMSO): δ 134.98 (s, broad, SiF_6). Yield 93%; mp dec. 199–201 °C. IR (KBr) (cm^{-1}): 2924, 2847 (ν N–H); 743 (ν Si–F); 483 (δ Si–F). MS (MALDI-TOF): m/z 180 [M] $^+$.

2.5. Synthesis of bis[2,2,6,6-tetramethylpiperidinium] hexafluorosilicate (**6**)

A solution of [2,2,6,6-tetramethylpiperidinium] fluoride was made by adding 2,2,6,6-tetramethylpiperidine (2.025 ml, 0.012 mol) drop wise and slowly to a plastic beaker containing hydrogen fluoride (0.869 ml, 0.024 mol) at 0 °C. The solution was stirred for 2 h at 0 °C, and then allowed to warm to room temperature. Distilled water (2.0 ml) was added to dissolve some of the salt that precipitated out of solution. Silica gel (0.360 g, 0.006 mol) was slowly added to the solution of [2,2,6,6-tetramethylpiperidinium] fluoride (1.935 g, 0.012 mol). The mixture was slowly stirred overnight. After stirring, the solvent was slowly evaporated from the beaker to yield a light brown crystalline solid of (**6**). ^1H NMR (D_2O): δ 1.23 (12H, s, CH_3), 1.46–1.50 (4H, m, CH_2), 1.57–1.63 (2H, m, CH_2). ^{13}C (D_2O): δ 10.2, 21.2, 24.8, 29.0, 51.2. ^{19}F (D_2O): δ 130.6 (s, SiF_6). Yield 95%; mp at 200 °C white vapors formed. At 286–290 °C solid decomposed. IR (KBr) (cm^{-1}): 3012, 2889, 2871, 2823, 2779; 1594 (δ N–H); 744 (ν Si–F); 487 (δ Si–F). MS (MALDI-TOF): m/z 142 [M] $^+$.

2.6. Synthesis of bis[propylammonium] hexafluorosilicate (**7**)

A solution of propylammonium fluoride was made by adding propylamine (28.77 ml, 0.35 mol) drop wise and slowly to a plastic beaker containing hydrogen fluoride (31.21 ml, 0.625 mol) at 0 °C. The solution was stirred for 2 h at 0 °C, and then allowed to warm to room temperature. Silica gel (1.753 g, 0.029 mol) was slowly added to the solution of propylammonium fluoride (13.85 g, 0.175 mol). The mixture was stirred overnight. After stirring, the solvent

was slowly evaporated from the beaker to yield white crystalline (**7**). ^1H NMR (DMSO): δ 0.86–0.90 (3H, t, CH_3), 1.50–1.52 (2H, sextet, CH_2), 2.64–2.68 (2H, m, CH_2), 6.0–8.0 (very broad hump, NH_3^+). ^{13}C (DMSO): δ 11.6, 21.2, 41.4. ^{19}F (DMSO): δ 124.73 (s, SiF_6). Yield 96%; mp 292 °C. IR (KBr) (cm^{-1}): 3032, 2969 (ν N–H); 1526, 1504 (δ N–H); 738 (ν Si–F); 481 (δ Si–F). MS (MALDI-TOF): m/z 60 $[\text{M}]^+$.

2.7. Structure determinations

X-ray diffraction data were collected at 173 K on a Nonius kappaCCD diffractometer from irregular-shaped crystals. Initial cell parameters were obtained (DENZO-SMN [15]) from ten 1° frames and were refined via a least-squares scheme based on all frames (SCALEPACK, DENZO-SMN, [16]). Lorentz/polarization corrections were applied during data reduction. The structures were solved by direct methods (SHELXS97) and difference Fourier (SHELXL97, [16]).

Refinement was carried out against F2 by weighted full-matrix least-squares (SHELXL97, [16]). Hydrogen atoms were either found in difference maps or placed at calculated positions, and refined using a riding model with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography [17]. Crystal data and relevant details of the structure determinations are summarized in Table 1 and selected geometrical parameters are given in Table 2. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1,76,971 (**1**), 1,76,970 (**2**), 1,76,969 (**3**), 1,76,972 (**4**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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

	1	2	3	4
Empirical formula	$\text{C}_5\text{H}_{14}\text{FNO}$	$\text{C}_{10}\text{H}_{24}\text{F}_6\text{N}_2\text{Si}$	$\text{C}_2\text{H}_{12}\text{F}_6\text{N}_2\text{Si}$	$\text{C}_{19}\text{H}_{16}\text{F}_6\text{N}_2\text{OSi}$
Formula weight	123.17	314.39	206.21	430.43
Temperature (K)	173 (1)	173(1)	173(1)	173(1)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic
Space group	<i>Iba2</i>	<i>Fdd2</i>	<i>Pnmm</i>	<i>P-1</i>
<i>a</i> (Å)	9.5830(19)	13.8220(10)	7.181(4)	7.0780(10)
<i>b</i> (Å)	18.908(4)	19.194(2)	9.415(4)	8.6770(10)
<i>c</i> (Å)	7.3660(15)	11.010(3)	6.225(5)	14.938(2)
α (°)	90	90	90	102.062(10)
β (°)	90	90	90	91.894(10)
γ (°)	90	90	90	104.211(10)
Volume (Å ³)	1334.7(5)	2920.9(9)	420.9(4)	866.3(2)
Z	8	16	4	2
Density (calculated) (Mg/m ³)	1.226	1.430	1.627	1.650
Absorption coefficient (mm ⁻¹)	0.102	0.216	0.327	0.212
Reflections collected/unique	3213/1168	1595/1595	727/431	7831/3949
Independent reflections (R(int))	0.0253	0.000	0.0348	0.0233
Data/restraints/parameters	1168/4/80	1595/1/89	431/0/32	3949/3/260
Goodness-of-fit on F^2	1.047	1.082	1.026	1.033
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0420$ $wR_2 = 0.1064$	$R_1 = 0.0299$ $wR_2 = 0.0556$	$R_1 = 0.0430$ $wR_2 = 0.0959$	$R_1 = 0.0413$ $wR_2 = 0.1067$
<i>R</i> indices (all data)	$R_1 = 0.0461$, $wR_2 = 0.1095$	$R_1 = 0.0333$ $wR_2 = 0.0570$	$R_1 = 0.0617$ $wR_2 = 0.1027$	$R_1 = 0.0575$ $wR_2 = 0.1155$

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

	1	2	3	4
Si–F _(ave)	–	1.6815(9)	1.6816(14)	1.6852(10)
N–C _(ave)	1.493(3)	1.4795(19)	1.474(4)	1.3498(19)
F _(trans) –Si–F _(trans)	–	178.62(6)	180.00(5)	178.00(5)
F _(cis) –Si–F _(cis)	–	90.00(5)	90.00(6)	89.94(5)
C–N–C	112.40(16)	111.91(12)	–	122.93(15)
H–N–H	107.9	107.9	106.6	–

3. Results and discussion

The reaction of piperidine with a hydrogen fluoride solution gave piperidinium fluoride (**1**). The alkylammonium fluoride salts, RNH_2^+F^- ($\text{R} = \text{C}_5\text{H}_{12}$, C_9H_{18} , C_3H_8 , C_9H_7 , C_{13}H_9), $\text{CH}_3\text{NH}_4^+\text{F}^-$, $\text{C}_9\text{H}_7\text{NH}^+\text{F}^-$, and $\text{C}_{18}\text{H}_9\text{NH}^+\text{F}^-$, were reacted with silica gel to form the bis(alkylammonium) hexafluorosilicates **2–7**. They act as a source of hydrogen fluoride in these reactions. The reactions were conducted in water, were high yielding, and produced crystalline solids after evaporation of the water. The products were air stable, except for **4** which decomposed after 2 weeks. Compound **1** melts at 62°C , however, compounds **3–7** had higher melting points (160 – 292°C). Thus, these compounds could not compete with currently available room temperature ionic liquids. However, ionic liquid behavior at higher temperatures may be possible. A thermal study of these compounds is currently underway and will be the subject of a future publication.

Compounds **1–3** crystallize in the orthorhombic crystal system (space groups *Iba2*, *Fdd2*, and *Pnmm*, respectively), with $Z = 8$, 14 , and 4 , respectively. Compound **4** crystallizes in the triclinic space group *P-1*, with $Z = 2$. Crystal structure and data refinement data is given in Table 1. Bond lengths and angles are given in Table 2. Compounds **1** and **4** co-crystallized with molecules of water. The asymmetric unit of **2–4** reveals two independent protonated alkylammonium cations and one hexafluorosilicate anion (Figs. 2–4). Both of the six-membered rings of piperidinium fluoride (**1**) and hexafluorosilicate (**2**) are in a chair conformation (Figs. 1 and 2). As expected, the C–N bonds in **1** (average $1.493(3)\text{ \AA}$) are similar to the C–N bonds in **2** (average $1.4975(19)\text{ \AA}$). The C–N bond length of **3** (alkyl chain) is $1.474(4)\text{ \AA}$. The C–N bond length in the fused ring system of **4** is shorter at $1.3498(19)\text{ \AA}$. An average C=N bond is approximately 1.30 \AA [8].

The Si–F bond lengths in compounds **1** and **4** can be divided into two sets. In **4**, one set of Si–F bonds are between $1.6637(10)$ and $1.6873(11)\text{ \AA}$. The other set of Si–F bonds are slightly longer at $1.7030(10)$ and $1.7051(10)\text{ \AA}$. The fluorine atoms in the longer Si–F bond form strong hydrogen

bonds to the quinolinium cation and water molecules. For compound **2**, one set of Si–F bonds are between $1.6724(10)$ and $1.6770(7)\text{ \AA}$. The other set of Si–F bonds are $1.6951(10)\text{ \AA}$. The fluorine atoms in the longer Si–F bond form strong hydrogen bonds to both hydrogens on the nitrogen. The presence of longer and shorter Si–F bonds are also observed in *N*-methylpiperidine betaine hexafluorosilicate [9]. The fluorine atoms that form hydrogen bonds have Si–F bond lengths of $1.7159(7)$ and $1.7181(7)\text{ \AA}$, whereas those that do not form hydrogen bonds have Si–F bond lengths of $1.6699(7)$ – $1.6864(8)\text{ \AA}$. However, the relationship between Si–F bond length and hydrogen bonding is not observed in **3**. Although fluorine atoms hydrogen bond to ammonium protons from each cation, all of the Si–F bond lengths are very similar ($1.6809(11)$ – $1.6829(17)\text{ \AA}$).

The hexafluorosilicate anion in **2** and **4** shows small deviations from ideal octahedral geometry. The $\text{F}_{(\text{trans})}\text{--Si--F}_{(\text{trans})}$ angles for **2** and **4** are $178.62(12)$ and $178.00(5)^\circ$, respectively. The slight deviation in **2** and **4** can be ascribed to the previously mentioned hydrogen bonding. The SiF_6^{2-} anion in compound **3** has almost ideal octahedral geometry. The $\text{F}_{(\text{trans})}\text{--Si--F}_{(\text{trans})}$ angle is $180.00(5)^\circ$, the $\text{F}_{(\text{cis})}\text{--Si--F}_{(\text{cis})}$ angle is $90.00(6)^\circ$, and the Si–F bond lengths are all similar. This is unusual, as most hexafluorosilicates involved in hydrogen bonding deviate slightly from ideal octahedral geometry.

The C–N–C bond angle in **1** and **2** are similar, $112.40(16)$ and $111.91(12)^\circ$ respectively, despite the change from a fluoride anion to a larger, more electron repulsive hexafluorosilicate anion. The C–N–C angle in **4** is larger, $122.93(15)^\circ$, reflecting the presence of only one proton on the nitrogen, and the fused ring system. The H–N–H angle is similar for **1–3** (107.9 , 107.9 , and 106.6° , respectively).

The proton acceptor properties of a fluoride ion differ from the covalently bonded, diffusely charged fluorides in the hexafluorosilicate anion. This is reflected in the very short hydrogen bond $\text{F}\cdots\text{H--O--H}$ in **1** ($\text{D}\cdots\text{H}$ 2.302 \AA) compared to the longer hydrogen bond $\text{F}\cdots\text{H--O--H}$ in **4** ($\text{D}\cdots\text{H}$ 2.705 \AA). The $\text{F}\cdots\text{H--O--H}$ hydrogen bond for

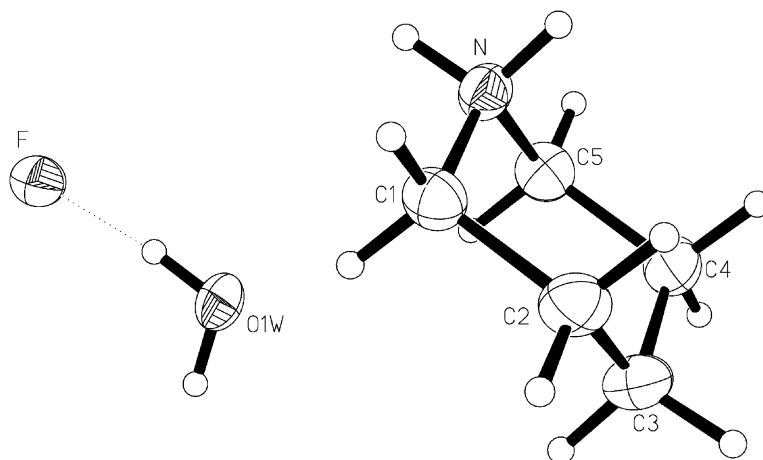


Fig. 1. Molecular structure of piperidinium fluoride-H₂O (**1**), showing hydrogen bonding.

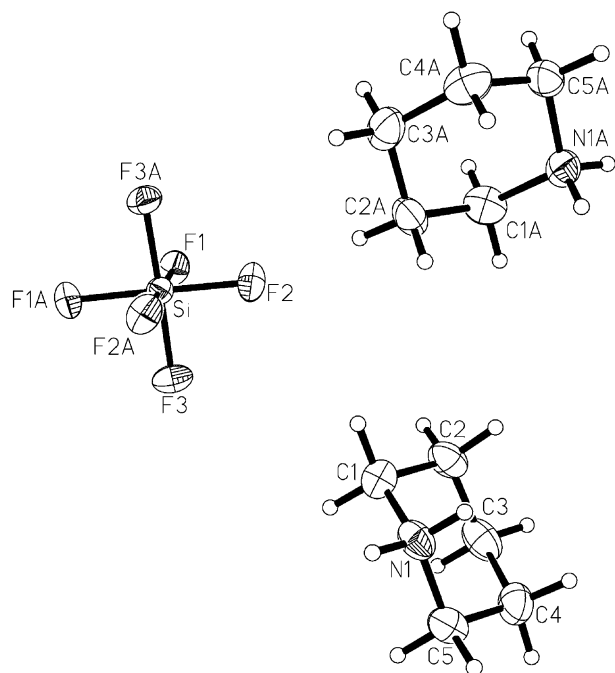


Fig. 2. Molecular structure of bis[piperidinium] hexafluorosilicate (**2**).

other alkylammonium hexafluorosilicates is usually longer (for example, 2.80 Å for acridine orange hexafluorosilicate [10]). Differing hydrogen bond lengths are also observed in **1** and **2**. For **1**, the $F \cdots N$ –HOA distance is 2.646 Å, while the $F \cdots N1$ –H1A in **2** is longer at 2.795 Å (Table 2).

A high degree of hydrogen bonding throughout the structures was expected because of the participation of electrostatic forces generated from the presence of donor and acceptor ions on oppositely charged ions. In compound **1**, a hydrogen bond is formed between the fluoride anion and a water molecule. There are also hydrogen bonds between the amine hydrogens and the fluoride ion (Fig. 1). In **2**, there are hydrogen bonds formed between both hydrogens on the nitrogen of the piperidinium cation and the fluorines of the SiF_6^{2-} anion (Fig. 2). In compound **3**, an ammonium proton from each cation forms a hydrogen bond with fluorines from symmetrically related SiF_6^{2-} anions (Table 3). Compound **4** has the most extensive hydrogen bonding interactions of all four compounds. Hydrogen bonds are formed between the SiF_6^{2-} anion, water molecules, and the quinolinium cation (Figs. 3 and 4).

The IR spectra for **2–7** exhibits bands characteristic of the octahedral SiF_6^{2-} anion. The IR bands at 737, 737, 738, 743, 744, and 738 cm^{-1} for **2–7**, respectively, can be assigned to SiF_6 (ν Si–F). These compare well to the values for *N*-methylpiperidine betaine hexafluorosilicate (757 cm^{-1}) [9], pyridinium hexafluorosilicate (735 cm^{-1}) [11], and bis(ammonium) hexafluorosilicate (725 cm^{-1}) [12]. The peaks at 481, 481, 482, 483, 487, and 481 cm^{-1} for **2–7**, respectively can be assigned to SiF_6^{2-} (δ Si–F). These compare well to the values for *N*-methylpiperidine betaine hexafluorosilicate (474 cm^{-1}), pyridinium and bis(ammonium) hexafluorosilicate (480 cm^{-1}).

Table 3
Hydrogen bonding geometry (Å, °) for **1–4**

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
1				
N–HOA \cdots F ⁱ	0.920	1.730	2.646	173.55
N–HOB \cdots F ⁱⁱ	0.920	2.116	2.847	135.49
N–HOB \cdots F ⁱⁱⁱ	0.920	2.126	2.846	134.35
O1W–H1W \cdots F	0.850	1.457	2.303	172.21
2				
N1–H1A \cdots F1 ^{iv}	0.920	2.048	2.795	137.36
N1–H1A \cdots F3 ^v	0.920	2.299	3.155	154.56
N1–H1B \cdots F2 ^{vi}	0.920	1.931	2.777	151.85
N1–H1B \cdots F1 ^{vii}	0.920	2.351	3.036	131.06
N1–H1B \cdots F3 ^{viii}	0.920	2.536	3.321	143.51
3				
N–H1N \cdots F1	0.904	1.926	2.816	167.91
N–H2N \cdots F2 ^{ix}	0.854	2.070	2.897	162.62
N–H2N \cdots F1 ^x	0.854	2.537	3.183	133.24
N–H2N \cdots F1 ^{xi}	0.854	2.537	3.183	133.24
4				
N1A–H1A \cdots F2	0.880	1.947	2.739	149.07
N1A–H1A \cdots F3	0.880	2.419	3.166	142.99
N1A–H1A \cdots F6	0.880	2.497	3.196	136.80
N1B–H1B \cdots O1W ^{xiii}	0.880	1.810	2.681	170.06
O1W–H1W \cdots F4 ^{xiii}	0.850	1.974	2.808	166.85
O1W–H2W \cdots F6	0.861	1.859	2.705	167.07
O1W–H2W \cdots F5	0.861	2.567	3.156	126.59

Symmetry codes: (i) $x, y, z + 1$; (ii) $x, -y + 1, z + 1/2$; (iii) $-x, y, z + 1/2$; (iv) $[-x, -y, z + 1]$; (v) $[x, y, z + 1]$; (vi) $[-x + 1/4, y - 1/4, z + 3/4]$; (vii) $[-x + 1/4, y - 1/4, z + 3/4]$; (viii) $[-x + 1/4, y - 1/4, z + 3/4]$; (ix) $x - 1/2, -y + 1/2, -z + 1/2$; (x) $-x + 1/2, y - 1/2, z - 1/2$; (xi) $-x + 1/2, y - 1/2, -z + 1/2$; (xii) $-x, -y + 3, -z + 1$; (xiii) $x - 1, y, z$.

For the cations, the ν N–H modes are assigned to the peaks in the range 2671–3032 cm^{-1} for **2–7** (the peaks overlap with the C–H stretches). These are lower than the values found for pyridinium hexafluorosilicate (3270 and 3200 cm^{-1}) and bis(ammonium) hexafluorosilicate (3300 cm^{-1}). The δ N–H modes are assigned to 1585, 1594, 1504–1526 cm^{-1} for **2, 6**, and **7**, respectively. These are higher than the values found for bis(ammonium) hexafluorosilicate (1410 cm^{-1}).

Mass spectrometry also confirmed the structures of compounds **2–7**. MALDI-TOF positive ion spectra confirmed the identity of the positively charged species (86, **1** and **2**; 32, **3**; 130, **4**; 180, **5**; 142, **6**; 60, **7**). Negative ion mass spectrometry shows the presence of fluoride in **1** and hexafluorosilicate in **2–7**.

The ^{19}F NMR of the hexafluorosilicates and the fluoride anion were recorded. The piperidinium fluoride anion **1** was more downfield (–130.7 ppm) than the corresponding hexafluorosilicate **2** (–125.9 ppm). The ^{19}F signals due to **3–7** were observed at –130.5, –139.2, –134.9, –130.6, and –124.7 ppm, respectively. The range of chemical shifts observed (–124.7 to –139.2 ppm) could be due to changes in sample concentration, different solvents (D_2O and *d*-DMSO), the presence or absence of water, and the differing cationic species. The peaks for the aromatic cations, **4** and **5**, were broad compared to the other hexafluorosilicates. Si–F coupling was observed in **2** ($J = 62.5$ Hz) and **3** ($J = 54.7$ Hz),

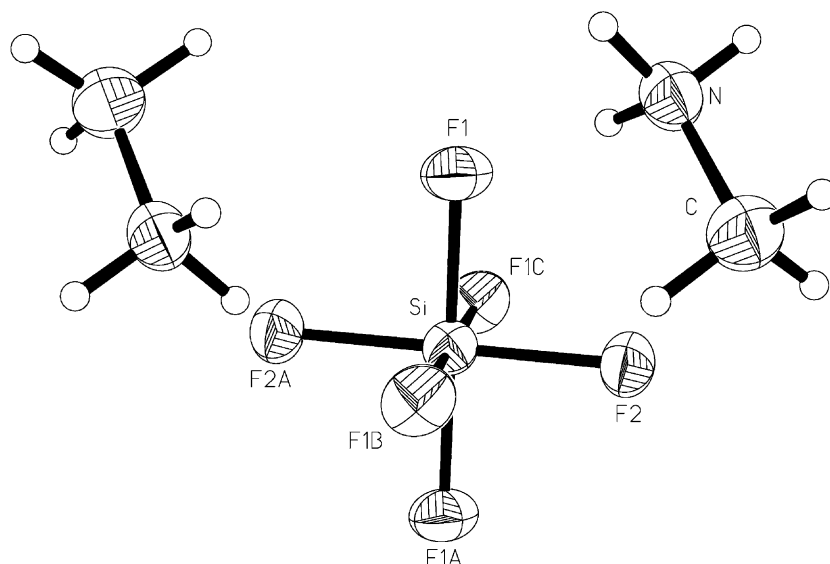


Fig. 3. Molecular structure of bis[methylammonium] hexafluorosilicate (**3**).

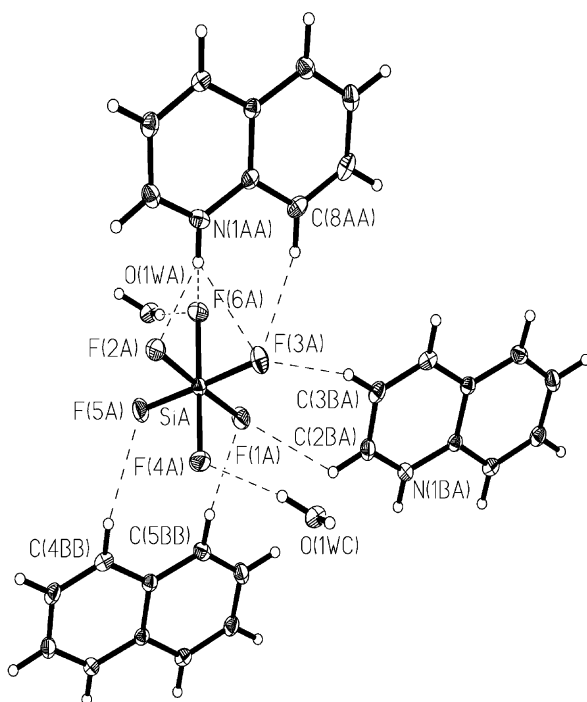


Fig. 4. Molecular structure of bis[quinolinium] hexafluorosilicate-H₂O (**4**).

however, no Si-F coupling was observed in **4–7**. The shifts for **3–5** are at lower field than those reported for the SiF₆²⁻ anion (–126 ppm [13] and –127 ppm [14]).

References

- [1] S. Hahn, D.S. Shihabi, C.D. Chang, *J. Catal.* 196 (2000) 375.
- [2] K.L. Carleton, J.M. Olson, A. Kibbler, *J. Electrochem. Soc.* 130 (1983) 782.
- [3] N. Kurtessis, K. Menzel, G. Weissflog, German Patent DD 92997, 1972.
- [4] G.J. Reiss, *Acta Cryst.* C54 (1998) 1489.
- [5] D.Y. Naumov, N.E. Kashcheeva, E.V. Boldyreva, J.A.K. Howard, *Acta Cryst.* C55 (1999) 1205.
- [6] T. Steiner, *J. Chem. Cryst.* 27 (1997) 673.
- [7] M. Freemantle, *Chem. Eng. News* 15 (2000) 37.
- [8] X. Zhang, R. Bau, J.A. Sheehy, K.O. Christe, *J. Fluorine Chem.* 98 (1999) 121.
- [9] M. Szafran, Z.D. Szafran, A. Addlagatta, M. Jaskolski, *J. Mol. Struct.* 589 (2001) 267.
- [10] C.A. Mattia, O. Ortona, R. Puliti, G. Cascarano, C. Giacovazzo, *J. Mol. Struct.* 350 (1995) 63.
- [11] R.G. Kalbandkeri, K.S. Mohamed, D.K. Padma, A.R.V. Murthy, *Polyhedron* 4 (1985) 787.
- [12] K.S. Mohamed, D.K. Padma, *Ind. J. Chem.* 27A (1988) 712.
- [13] R.K. Harris, B.E. Mann (Eds.), *NMR and the Periodic Table*, Academic Press, New York, 1978.
- [14] C.H. Dungan, J.R. Van Wazer, *Compilation of Reported ¹⁹F NMR Chemical Shifts 1951 to Mid-1967*, Wiley, New York, 1970.
- [15] Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction data collected in oscillation mode*, in: C.W. Carter Jr., R.M. Swet (Eds.), *Methods in Enzymology. Part A: Macromolecular Crystallography*, Vol. 276 Academic Press, New York, 1997, pp. 307–326.
- [16] G.M. Sheldrick, *SHELX97-Programs for Crystal Structure Solution and Refinement*, University of Göttingen, Germany, 1997.
- [17] T. Hahn (Ed.), *International Tables for Crystallography, Space Group Symmetry*, Vol. A Kluwer Academic Publishers, Holland, 1999.