Hexafluorosilicates of bis(carboxypyridinium) and bis(2-carboxyquinolinium)

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ABSTRACT

The preparation and characterization of three isomeric carboxypyridinium and carboxyquinolinium hexafluorosilicate salts is described. The salts of the general formulas $(LH)_2[SiF_6]$ (**I–III**, L = 2-carboxypyridine, 3-carboxypyridine, 4-carboxypyridine) and $(LH)_2[SiF_6]\cdot 2H_2O$ (**IV**, L = 2-carboxyquinoline) were prepared from the protonation reaction of the corresponding pyridine carbonic acid by the fluorosilicic acid. The compounds were characterized by IR, mass-spectrometry, thermogravimetric analysis, solubility data, and in the case of **III** by X-ray crystallography. The relationship between the salts solubility and the H-bonding system was analysed.

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1. Introduction

"Onium" hexafluorosilicates $(LH)_2[SiF_6]$ (L = ammonia, N-,O-containing organic bases) find application as chemical reagents [1–3], herbicides and fungicides [4,5], functional materials [6,7], and also can be utilised as the models for estimation of influence of interionic H-bonds on structure and physicochemical properties of the complexes [8]. In continuation of our previous examinations on relationship between structure and properties of "onium" hexafluorosilicates the preparation, spectral data, thermochemical transformations and solubility of salts of three isomeric bis(carboxypyridinium) hexafluorosilicates (**I–III**) and bis(2-carboxyquinolinium) hexafluorosilicate (**IV**) are described alongside with the crystal structure of bis(4-carboxypyridinium) hexafluorosilicate (**III**). The structural characteristics for hexafluorosilicates of the general formula $(LH)_2[SiF_6]\cdot nH_2O$ (L = 2-, 3-carboxypyridine, n = 0; L = 2-carboxyquinoline, n = 2) have been reported earlier [9,10].

2. Results and discussion

Compound **III** crystallizes in the monoclinic crystal system (space group $P2_1/n$) with Z = 2. Crystal structure and refinement data is given in Table 1. Selected bond distances and angles are given in Table 2. The asymmetric unit of **III** comprises a half of a hexafluorosilicate anion that resides on an inversion center and one 4-carboxypyridinium cation in general position (Fig. 1). The positions of pyridinium and carboxylic hydrogen atoms were found in the difference Fourier map.

In the $[SiF_6]^{2-}$ anion the Si–F bond lengths are between 1.666(1) and 1.692(1) Å. The fluorine atoms in the longer Si–F bond participates in the strongest hydrogen bond (Table 3). The F(trans)–Si–F(trans) angles are 180°, the F(cis)–Si–F(cis) angles deviate at 1.08(5)° from the right angle. Such a slightly distorted octahedral geometry is typical for $[SiF_6]^{2-}$ anion involved in the system of hydrogen bonding. The relationship between Si–F bond length and hydrogen bonding is also observed in bis(piperidinium) hexafluorosilicate, bis(quinolinium) hexafluorosilicate monohydrate, and in N-methylpiperidine betaine hexafluorosilicate [11,12] and surprisingly is not observed in bis(methylammonium) hexafluorosilicate [11]. The 4-carboxypyridinium cation in **III** has a practically planar skeleton with the twisted angle between the pyridinium ring and the carboxylic group equal to 23.7°. The C–O

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Table 1
Crystal data and structure refinement parameters for **III**

Empirical formula	$C_{12}H_{12}F_6N_2O_4Si$
Formula weight	390.33
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	7.384(2)
b (Å)	12.981(3)
c (Å)	7.738(2)
β (°)	99.24(3)
Cell volume (Å³)	732.1(3)
Z	2
D_{calc} (g/cm³)	1.771
μ (mm⁻¹)	0.255
$F(0\,0\,0)$	396
θ range for data collection (°)	3.21–25.02
Limiting indices	$0 \leq h \leq 8$
	$0 \leq k \leq 15$
	$-9 \leq l \leq 9$
Reflections collected	1243
Reflections with $I > 2\sigma(I)$	1162
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1243/0/123
Goodness-of-fit on F^2	1.107
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0308, wR_2 = 0.0750$
R indices (all data)	$R_1 = 0.0333, wR_2 = 0.0761$
Largest diff. peak and hole (e Å⁻³)	0.207/−0.154

Table 2
Selected intermolecular distances (Å) and angles (°) for **III**

Si(1)–F(1)	1.666(1)	F(1)–Si(1)–F(2)	91.08(5)
Si(1)–F(2)	1.683(1)	F(1)–Si(1)–F(3)	89.57(6)
Si(1)–F(3)	1.692(1)	F(2)–Si(1)–F(3)	90.33(6)
O(1)–C(6)	1.317(2)	O(2)–C(6)–O(1)	125.0(2)
O(2)–C(6)	1.202(2)	O(2)–C(6)–C(3)	122.6(2)
N(1)–C(5)	1.330(2)	O(1)–C(6)–C(3)	112.4(1)
N(1)–C(1)	1.331(3)	C(5)–N(1)–C(1)	123.1(2)
C(1)–C(2)	1.379(3)	N(1)–C(1)–C(2)	119.7(2)
C(2)–C(3)	1.382(2)	N(1)–C(5)–C(4)	119.6(2)
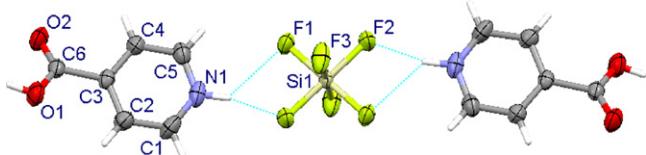
Fig. 1. ORTEP drawing for **III** showing hydrogen bonding. Only asymmetric unit is numbered.

distances essentially differ (Table 2) and are in agreement with the neutral form of carboxylic group.

Two effects are crucial for crystal packing: the hydrogen bonding between the charged species and π–π stacking interactions between the cationic units. Both pyridinium and carboxylic hydrogens participate in H-bonding with the $[SiF_6]^{2-}$ anion, each anion being connected with four closest cations. In their turn, the adjacent cations related by inversion are arranged in parallel

planes with the centroid–centroid distance of 3.765 Å that is in agreement with the value typical for π–π stacking interactions. These concerted interactions combine the charged species in the chain running along c direction. The fragment of this chain showing the environment of the $[SiF_6]^{2-}$ anion is given in Fig. 2.

The IR data for hexafluorosilicates **I**–**IV** are summarized in Table 4. The IR spectra for **I**–**III** exhibit stretching vibrations $\nu(N^+H)$ in the form of fuzzy bands of average intensity in the range 3210–3085 cm⁻¹. In spectrum for **IV** the complicated bands in the range 3420–3125 cm⁻¹ can be assigned to the $\nu(OH)$ vibrations of water molecules involved in the system of H-bonding (upfield components 3420, 3310, 3205 cm⁻¹), and $\nu(N^+H)$ vibrations for protonated quinoline–2-carbonic acid (preferred contribution in the downfield component at 3125 cm⁻¹). The presence of fuzzy absorption bands in the spectra **I**–**IV** in the field of 2720–2525 cm⁻¹ can be assigned to strong interionic OH···F hydrogen bonds [9,10]. In the field of 800–650 cm⁻¹ (Table 4) was registered the superposition of vibration bands $\nu(SiF)$ for $[SiF_6]^{2-}$ anions and deformation vibrations for the N^+H, CCH moieties (for **IV**, the vibrations for water molecule). Deformation vibrations $\delta(SiF_2)$ for the anions in the form of triplets (**I**, **II**, **IV**) or doublets of average intensity are registered in the range 490–435 cm⁻¹ free of natural oscillations of the cations. The multiple character of the $\delta(SiF_2)$ vibrations is in agreement with the X-ray data indicating the distortion of the octahedral geometry of the $[SiF_6]^{2-}$ anion in **I**–**IV** due to interionic hydrogen bonds.

The results of thermogravimetric analysis for hexafluorosilicates **I**–**IV** are summarized in Table 5. As it follows from Table 5, the thermolysis of compounds **I** and **III** is accompanied by a stage of elimination of hydrogen fluoride and silicon tetrafluoride with the subsequent decomposition of the ligands:

$$(L^{1,3}H)_2[SiF_6] \rightarrow SiF_4 + 2HF + 2L^{1,3} \tag{1}$$

$$L^{1,3} \rightarrow \text{decomposition products} \tag{2}$$
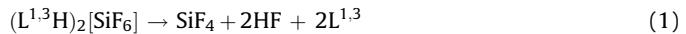
The thermal decomposition for **IV** is implemented with consecutive elimination in a gas phase of two moles H_2O, two moles HF, one mole SiF_4 and decomposition products for L^4:

$$(L^4H)_2[SiF_6] \cdot 2H_2O \rightarrow (L^4H)_2[SiF_6] + 2H_2O \tag{3}$$

$$(L^4H)_2[SiF_6] \rightarrow SiF_4 \cdot 2L^4 + 2HF \tag{4}$$

$$SiF_4 \cdot 2L^4 \rightarrow SiF_4 + 2L^4 \tag{5}$$

$$L^4 \rightarrow \text{decomposition products} \tag{6}$$
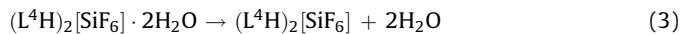
The thermolysis of compound **II** proceeds similarly to decomposition of the anhydrous phase **IV**. It is interesting to note, that in their thermal stability which in the first approximation is characterized by the values t_0 for the first endothermic effect, compounds **I**–**III** somewhat surpass the hexafluorosilicates $(C_5H_5NH)_2[SiF_6]$ and $(n\text{-}CH_3C_5H_4NH)_2[SiF_6]$; ($n = 2, 3, 4$; $t_0 = 120$–140 °C) [13], despite of higher values of basicity for pyridine and isomeric picolines (pK_a L^1–L^3 4.81–5.32; pK_a C_5H_5N 5.23; pK_a $n\text{-}CH_3C_5H_4N$ 5.68–6.02) [14,15]. Apparently, the relative stabilization of salts **I**–**III** in comparison with the hexafluorosilicates $(C_5H_5NH)_2[SiF_6]$ and $(n\text{-}CH_3C_5H_4NH)_2[SiF_6]$ is dictated by the extra

Table 3
Geometry of hydrogen bonds for **III**

D–H···A	d(D–H) Å	d(H···A) Å	d(D···A) Å	∠(DHA) (°)	Symmetry transformation for acceptor
O(1)–H(1O1)···F(3)	0.82(3)	1.77(3)	2.5869(17)	168(2)	$-x + 2, -y + 1, -z$
N(1)–H(1N1)···F(2)	0.90(3)	1.85(3)	2.7278(19)	164(2)	$-x + 1, -y + 1, -z + 1$
N(1)–H(1N1)···F(1)	0.90(3)	2.37(3)	3.014(2)	129(2)	x, y, z
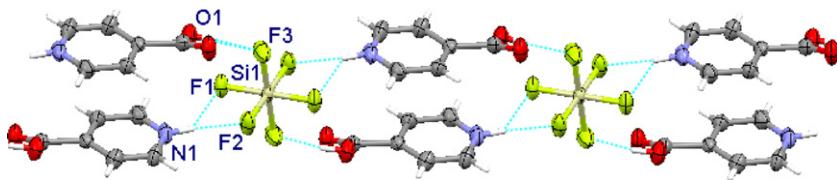
Fig. 2. Fragment of chain in **III**.

Table 4
IR spectral data (cm^{-1}) for **I–IV**

	$\nu(N^+H)$, $\nu(OH)$	$\nu(OH\cdots F)$	$\nu(C=O)$, $\delta(N^+H)$, $\delta(H_2O)$	ν_{ring}	$\nu(SiF)$, $\rho(N^+H)$, $\delta(CCH)$, $\gamma(H_2O)$	$\delta(SiF_2)$
I	3135 m,br	2710 m,br 2590 m,br	1720 m 1670 sh 1645 sh	1610 m 1560 m 1535 m 1055 m	767 sh 720 s 685 s	490 sh 475 m 435 m
II	3170 m,br 3085 m,br	2720 m,br	1715 v,s 1690 sh 1625 m	1580 s 1545 m 1040 m	745 v,s 720 sh 680 m	490 sh 465 m 435 sh
III	3210 m,br 3150 m,br	2655 m,br	1725 sh 1700 m 1635 m	1610 m 1550 m 1040 m	745 sh 720 v,s 690 sh	475 m 435 m
IV	3420 sh 3310 m,br 3205 m,br 3125 m,br	2525 sh	1720 sh 1670 m 1645 sh 1630 m	1590 s 1560 m 1500 m 1065 c 1050 sh	770 s 725 s,br	465 m 450 sh 435 sh

Note: w = weak, m = medium, s = strong, v = very, sh = shoulder, br = broad.

Table 5
Thermogravimetric data for **I–IV**

Compound	Effect (°C)			Mass loss (%)		Assignment
	Type	t_0	t_M	Found	Calcd	
$(L^1H)_2[SiF_6]$	endo	145	200	37.1	36.9	Elimination of 2 mol HF + 1 mol SiF_4
	endo	205	223	97.0	100	Decomposition of L^1
$(L^2H)_2[SiF_6]$	endo	175	207	–	10.3	Elimination of 2 mol HF
	endo	–	220	35.0	36.9	Elimination of 1 mol SiF_4
	endo	225	235	–	–	Melting of L^2
	endo	258	270	96.0	100	Decomposition of L^2
$(L^3H)_2[SiF_6]$	endo	185	241	37.4	36.9	Elimination of 2 mol HF + 1 mol SiF_4
	endo	257	308	98.0	100	Decomposition of L^3
$(L^4H)_2[SiF_6]\cdot2H_2O$	endo	100	130	9.0	6.8	Elimination of 2 mol H_2O
	endo	145	170	14.0	14.4	Elimination of 2 mol HF
	endo	176	195	29,0	27,4	Elimination of 1 mol SiF_4
	endo	211	450	96,0	100	Decomposition of L^4

intermolecular OH···F hydrogen bonds which are absent in the structures of pyridinium and pycolinium salts.

Solubility data for **I–IV** as well as for hexafluorosilicates of pyridinium, 2-methylpyridinium and several functionalized derivatives of carboxypyridinium and 2-carboxyquinolinium are summarized in Table 6. The introduction in the pyridinium cation of H-donor functional groups, -COOH, –CONHNH$_2$, –CONH$_2$, –CSNH$_2$ essentially (in some cases more than by order of magnitude) decreases the solubility of the relevant hexafluorosilicates. The observed differences in the solubility of the hexafluorosilicates can be explained by the specificity of H-bonding in the discussed compounds. So, quite apparently, that pyridinium (2-methylpyridinium) cation can function as a single H-donor (one H-bond from NH$^+$-group), whereas basing on the X-ray data in the salts the carboxypyridinium (2-carboxyquinolinium) cations donate two strong H-bonds, OH···F and NH···F (COOH and NH$^+$–groups). The embodying of auxilary interionic NH···F H-bonds (besides that formed by NH$^+$-group) with participation of NHNH$_3^+$ fragment is structurally confirmed also for the hexafluorosilicate [4-H$_3$NHN(O)CC$_5$H$_4$NH][SiF$_6$] [16]. Thus, cation functionalization by introduction of substituents with H-donor properties is accompanied by amplification of interionic H-interactions and results in a lower solubility of the relevant hexafluorosilicates. It is interesting to note, that from the point of

Table 6
Solubility of pyridinium hexafluorosilicates and its substituted derivates in water

Compound	Solubility (mol%) 25 °C
$(C_5H_5NH)_2[SiF_6]$	19.6
$(2\text{-}CH_3C_5H_4NH)_2[SiF_6]$	11.6
$[2\text{-}HO(O)CC_5H_4NH]_2[SiF_6]$	5.33
$[3\text{-}HO(O)CC_5H_4NH]_2[SiF_6]$	3.33
$[4\text{-}HO(O)CC_5H_4NH]_2[SiF_6]$	0.80
$[2\text{-}HO(O)CC_9H_6NH]_2[SiF_6]\cdot2H_2O$	1.75
$[4\text{-}H_3NHN(O)CC_5H_4NH][SiF_6]$	0.87
$[2\text{-}H_3NHN(O)CC_9H_6NH][SiF_6]$	0.24
$[3\text{-}H_2N(O)CC_5H_4NH]_2[SiF_6]$	0.39
$[2\text{-}C_2H_5\text{-}4\text{-}H_2N(S)CC_5H_3NH]_2[SiF_6]$	0.10

view of Davies's group numbers conception [17] used for a qualitative estimation of the hydrophilic–lipophilic balance (HLB) in a series of complexes of a similar composition and structure and not taking into account the effects of H-bonding, compounds [n-HO(O)CC$_5$H$_4$NH]$_2$[SiF$_6$] (n = 2, 3, 4) should differ by greater solubility in comparison with salts (RC$_5$H$_4$NH$_3$)$_2$[SiF$_6$] (R = H, CH$_3$) (within the framework of model [17] the COOH-group provides the hydrophilic contribution to the HLB of the complex against to the lipophilic contribution of CH, CH$_3$ groups). Besides, the account of effects of H-bonding allows to explain the differences in the solubility of the pyridinium (RC$_5$H$_4$NH)$_2$[SiF$_6$] and phenylammonium (RC$_6$H$_4$NH$_3$)$_2$[SiF$_6$] salts [18]: in spite of the formal concurrence of the HLB characteristics, the (RC$_6$H$_4$NH$_3$)$_2$[SiF$_6$] salts exhibit a lower solubility. It can be provoked by the ability of the RC$_6$H$_4$NH$_3^+$ cation to donate three H-bonds (without the account of effects of the substituent R) [8,18], while for the RC$_5$H$_4$NH$^+$ cation—only one hydrogen bond.

It is possible to ascertain, that in the carboxypyridinium (2-carboxyquinolinium) hexafluorosilicates the interionic H-bonds carry out the structural and stabilizing functions and noticeably influence the structural characteristics of the anions and salts properties. The sensitivity of the geometry of [SiF$_6$]$^{2-}$ anion to the effects of XH$\cdots$F (X = N, O) H-bonds is manifested in **I–III** as an antibate relationship of the Si–F and X$\cdots$F distances, and as a consequence, as an essential redistribution of the Si–F bond distances in the anion. At the same time the solubility of the pyridinium salts (RC$_5$H$_4$NH)$_2$[SiF$_6$] depends on a number of short interionic H-contacts and decreases with their increase upon introduction in the cation of the H-donor substituents. It might be concluded, that the cation functionalization can serve as a convenient tool for directional change of physicochemical properties of "onium" hexafluorosilicates.

3. Experimental

The IR-absorption spectra were recorded on a spectrophotometer Specord 75IR (range 4000–400 cm^{-1}, samples as suspension in Nujol mulls between KRS-5 windows). The mass spectra were registered on a spectrometer MX-1321 (direct input of a sample in a source, energy of ionizing electrons 70 eV). The thermogravimetric experiments were carried out on a OD-102 derivatograph of a system F. Paulik–J. Paulik–L. Erdey in ambient conditions (Al$_2$O$_3$ internal standard, heating rate of a sample 5°/min, sensitivity of DTA and DTG—1/10 or 1/5 from maximal, samples 150–200 mg). The isothermal conditions of experiments on detection of a solubility of hexafluorosilicates (t = 25 ± 0.2 °C) were provided with the help of an ultra thermostat U15.

3.1. Synthesis of bis(2-carboxypyridinium) hexafluorosilicate (I)

Pyridine-2-carbonic acid (L^1; 0.123 g, 1 mmol) was dissolved in boiling methanol (3 mL) and to the obtained solution the fluorosilicic acid (FSA, 0.9 mL, molar ratio L^1: FSA = 1:3) was added. A reaction mixture stored at ambient conditions prior to the beginning of crystallization of the reaction product, which was obtained in an approximately qualitative yield. Colourless transparent crystals of the composition (L^{1}H)$_2$SiF$_6$ (**I**) with mp 180–182 °C. Anal. found, %: Si 6,33, N 7,41, F 25,11. Calcd for C$_{12}$H$_{12}$F$_6$N$_2$O$_4$Si, Si 6,83, N 6,81, F 27,72. Mass spectrum: [ML^1]$^+$ (m/z = 123, I = 100%), SiF$_3^+$ (m/z = 85, I = 41%).

3.2. Synthesis of bis(3-carboxypyridinium) hexafluorosilicate (II)

Pyridine-3-carbonic acid (L^2, 0.123 g, 1 mmol) was dissolved in boiling ethanol (10 mL) and to obtained solution water (2 mL) and 45% FSA (0.9 mL) were added. A reaction mixture subjected to isothermal evaporation at ambient conditions. Colourless transparent crystals of composition (L^{2}H)$_2$SiF$_6$ and mp 248–250 °C were obtained in an approximately qualitative yield. Anal. found, %: Si 7,11, N 6,09, F 29,31. Calcd for C$_{12}$H$_{12}$F$_6$N$_2$O$_4$Si, Si 6,83, N 6,81, F 27,72. Mass spectrum: [ML^2]$^+$ (m/z = 123, I = 52%); SiF$_3^+$ (m/z = 85, I = 100%); [ML^2–COOH]$^+$ (m/z = 78, I = 26%).

3.3. Synthesis of bis(4-carboxypyridinium) hexafluorosilicate (III)

Pyridine-4-carbonic acid (L^3, 0.123 g, 1 mmol) was dissolved in boiling water (10 mL) and to obtained solution 45% FSA (0.9 mL) was added. A reaction mixture subjected to isothermal evaporation at ambient conditions. Colourless transparent crystals of composition (L^{3}H)$_2$SiF$_6$ with mp >220 °C (sublimation) were obtained in an approximately qualitative yield. Anal. found, %: Si 6,67, N 7,09, F 28,85. Calcd for C$_{12}$H$_{12}$F$_6$N$_2$O$_4$Si, Si 6,83, N 6,81, F 27,72. Mass spectrum: [ML^3]$^+$ (m/z = 123, I = 100%); SiF$_3^+$ (m/z = 85, I = 48%); [ML^3–COOH]$^+$ (m/z = 78, I = 41%).

3.4. Synthesis of bis(2-carboxyquinolinium) hexafluorosilicate dihydrate (IV)

Quinoline-2-carbonic acid (L^2, 1.73 g, 10 mmol) was dissolved in boiling methanol (20 mL) and to obtained solution 45% FSA (9 mL, molar ratio L^4: FSA = 1: 3) was added. A reaction mixture stored at ambient conditions prior to the beginning crystallization of the reaction product, colourless transparent crystals of composition (L^{4}H)$_2$SiF$_6$·2H$_2$O with mp >200 °C (with decomposition) were obtained in an approximately qualitative yield. Anal. found, %: Si 5,62, N 5,48, F 23,51. Calcd for C$_{20}$H$_{20}$F$_6$N$_2$O$_6$Si, Si 5,34, N 5,32, F 21,65. Mass spectrum: [ML^4]$^+$ (m/z = 173, I = 44%); [ML^4–COOH]$^+$ (m/z = 129, I = 100%); SiF$_3^+$ (m/z = 85, I = 69%).

3.5. Structure determination

The X-ray intensity data were collected at a room temperature on a Nonius Kappa CCD diffractometer equipped with graphite monochromated Mo Kα radiation using ϕ–ω rotation. Unit cell parameters were obtained and refined using the whole data set. Experimental data reduction and cell refinement were performed using DENZO [19] package. The structure solution and refinement proceeded using SHELX–97 program package [20]. Direct methods yielded all non-hydrogen atoms of the asymmetric unit which were treated anisotropically. C-bound hydrogen atoms were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while the N-bound and O-bound H-atoms were found from differential Fourier maps at an intermediate stage of the refinement and were treated isotropically. Crystallographic data (cif file) for the structural analysis of compound **III** has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 682042. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1233 336 033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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