



## Hexafluorosilicates of *bis*(aminopyridinium). The relationship between H-bonding system and solubility of salts

Vladimir O. Gelmboldt<sup>a</sup>, Eduard V. Ganin<sup>b</sup>, Marina S. Fonari<sup>c,\*</sup>, Larisa V. Koroeva<sup>a</sup>, Yurii Ed. Ivanov<sup>d</sup>, Mark M. Botoshansky<sup>e</sup>

<sup>a</sup> Physico-Chemical Institute of Environment and Human Protection of Ministry of Education and Science of Ukraine and National Academy of Sciences of Ukraine, Preobrazhenskaya str., 3, 65082, Odessa, Ukraine

<sup>b</sup> Odessa State Environmental University of Ministry of Education and Science of Ukraine, Lvovskaya str., 15, 65016, Odessa, Ukraine

<sup>c</sup> Institute of Applied Physics, Academy of Sciences of Moldova, Academy str., 5, MD2028 Chisinau, Republic of Moldova

<sup>d</sup> A.V. Bogatsky Physico-Chemical Institute of National Academy of Sciences of Ukraine, Lustdorfskaya Doroga, 86, 65080, Odessa, Ukraine

<sup>e</sup> Schulich Faculty of Chemistry, Technion-Israel Institute of Technology, Technion City, 32000 Haifa, Israel

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### ABSTRACT

Pyridinium hexafluorosilicates of the composition  $(LH)_2[SiF_6]$  (**I**, **II**, **IV**, L = 2-aminopyridine, 3-aminopyridine, and 2,6-diaminopyridine) and  $(LH)_2[SiF_6] \cdot H_2O$  (**III**, L = 4-aminopyridine) were separated as crystalline products of interaction of fluorosilicic acid with relevant aminopyridines. The compounds were characterized by IR, mass-spectrometry, potentiometry, solubility data, and in the case of **I** and **IV** by X-ray crystallography. The relationship between the salts structure and some physical properties is discussed.

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## 1. Introduction

Anion co-ordination or recognition is an area that has been receiving increased attention in the past two decades [1,2] with particular emphasis on the thermodynamics of interactions between the anions and a wide variety of synthetic hosts where pre-organization and cooperative effects are of a crucial importance [3]. Contrary to the “classic” complexes of transition metals generated due to coordinative covalent bonds the coordination chemistry of anions [4] is based on interionic H-bonds with synthetic organic receptors. The wide range of recently developed anion receptors include amides and thioamides, pyrroles and indoles, ureas and thioureas, ammonium, guanidinium, imidazolium, as well as the receptors with hydroxyl groups [5,6]. Apparently, H-bonds should definitely influence on the geometry of anion (in the case of complex anion) and on physicochemical properties of complex in a whole; moreover, the effects of H-bonds

have appeared to be decisive in synthetic chemistry, for example, for the stabilization of the poor stable anions of the type  $[H_{n-1}F_n]^-$  ( $n = 3-5$ ) [7–9],  $[SiF_5(H_2O)]^-$  [10] and  $[GeF_5(H_2O)]^-$  [11]. The high H-acceptor affinity of fluoride-anion [12], which is substantially preserved also by a covalently bound fluorine in complex fluoro-containing anions such as  $[SiF_6]^{2-}$  [13], makes “onium” hexafluorosilicates attractive models to clarify the features that influence on the interionic H-bonds and on the structural properties of the complexes. For the naked halides the host containing NH moieties has been known as good binding agent and as Mascall has underlined [14] the most effective H-bond donor is the  $[N-H]^+$  functionality that promotes interactions with halides through a combination of electrostatic interactions and hydrogen bonding. Earlier we have demonstrated the ways of binding of  $[SiF_6]^{2-}$  anions by protonated aza-macrocycles [10] as well as by aromatic molecules, derivatives of benzoic or pyridinecarboxylic acids [15,16]. The present communication continues the previous investigations and is devoted to the study of relationship between the composition and some properties of aminopyridinium hexafluorosilicates. Both 2-aminopyridine and 2,6-diaminopyridine are very popular co-crystal formers in supramolecular chemistry of anions [17,18]. In contrast to *para*-aminopyridine, it is found that *ortho*-aminopyridines (2-aminopyridine and 2,6-diaminopyridine)

\* Corresponding author. Tel.: +373 22 73 81 54; fax: +373 22 72 58 87.  
E-mail addresses: [eksvor@ukr.net](mailto:eksvor@ukr.net) (V.O. Gelmboldt), [edganin@yahoo.com](mailto:edganin@yahoo.com) (E.V. Ganin), [fonari.xray@phys.asm.md](mailto:fonari.xray@phys.asm.md), [fonari.xray@gmail.com](mailto:fonari.xray@gmail.com) (M.S. Fonari), [ivanov\\_yu@ukr.net](mailto:ivanov_yu@ukr.net) (Y.Ed. Ivanov), [botoshan@tx.technion.ac.il](mailto:botoshan@tx.technion.ac.il) (M.M. Botoshansky).

**Table 1**  
Crystal data and structure refinement parameters for **I** and **IV**.

	<b>I</b>	<b>IV</b>
Empirical formula	(C <sub>5</sub> H <sub>7</sub> N <sub>2</sub> ) <sub>2</sub> [SiF <sub>6</sub> ]	(C <sub>5</sub> H <sub>8</sub> N <sub>3</sub> ) <sub>2</sub> [SiF <sub>6</sub> ]
Formula weight	332.34	362.38
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P $\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	13.916(3)	6.841(1)
<i>b</i> (Å)	10.623(2)	7.473(1)
<i>c</i> (Å)	9.833(2)	7.670(2)
$\alpha$ (°)	90.0	97.65(3)
$\beta$ (°)	111.46(3)	105.86(3)
$\gamma$ (°)	90.0	102.35(3)
Cell volume (Å <sup>3</sup> )	1352.8(5)	360.72(12)
<i>Z</i>	4	1
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.632	1.668
$\mu$ (mm <sup>-1</sup> )	0.243	0.239
<i>F</i> (0 0 0)	680	186
$\theta$ range for data collection (°)	2.48–25.91	2.82–25.02
Limiting indices	0 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 12 −11 ≤ <i>l</i> ≤ 10	0 ≤ <i>h</i> ≤ 8 −8 ≤ <i>k</i> ≤ 8 −9 ≤ <i>l</i> ≤ 8
Reflections collected	1258	1261
Reflections with <i>I</i> > 2σ( <i>I</i> )	964	1059
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	1243/0/123	1261/0/126
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.096	1.087
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]		
<i>R</i> <sub>1</sub>	0.0484	0.0380
<i>wR</i> <sub>2</sub>	0.1351	0.1003
<i>R</i> indices (all data)		
<i>R</i> <sub>1</sub>	0.0646	0.0463
<i>wR</i> <sub>2</sub>	0.1433	0.1032
Largest diff. peak and hole (e Å <sup>-3</sup> )	0.423/−0.275	0.268/−0.309

support bent pathways of supramolecular assembly through H-bond formation as the amino and pyridinium groups together form a kind of “angle joint” [17] and serve as an efficient molecular tecton for the intermolecular assembly supported by hydrogen bonding and in some cases can lead to noncentric cocrystalline salts.

The crystal structures of hexafluorosilicate salts presented herein demonstrate the influence of subtle modification of the cation that induces distinctive lattice structure formation. The preparation, spectral data and solubility data for four aminopyridinium hexafluorosilicates (LH)<sub>2</sub>[SiF<sub>6</sub>] (**I**, **II**, **IV**, L = 2-aminopyridine, 3-aminopyridine, and 2,6-diaminopyridine) and (LH)<sub>2</sub>[SiF<sub>6</sub>].H<sub>2</sub>O (**III**,

**Table 2**  
Selected intermolecular distances (Å) and angles (°) for **I** and **IV**.

	<b>I</b>	<b>IV</b>	<b>I</b>	<b>IV</b>
Si(1)–F(1)	1.689(1)	1.689(1)	F(1)–Si(1)–F(2)	90.23(8)
Si(1)–F(2)	1.666(2)	1.689(1)	F(1)–Si(1)–F(3)	89.28(9)
Si(1)–F(3)	1.655(2)	1.663(2)	F(2)–Si(1)–F(3)	89.09(11)
N(1)–C(4)	1.348(3)	1.358(3)	C(4)–N(1)–C(5)	122.6(3)
N(1)–C(5)	1.356(3)	1.359(3)	C(5)–C(1)–C(2)	119.3(3)
N(2)–C(4)	1.326(4)	1.331(3)	C(3)–C(2)–C(1)	120.3(3)
C(1)–C(5)	1.344(5)	1.382(3)	C(2)–C(3)–C(4)	120.1(3)
C(1)–C(2)	1.393(4)	1.381(4)	N(2)–C(4)–N(1)	119.1(3)
C(2)–C(3)	1.352(4)	1.374(4)	N(2)–C(4)–C(3)	123.2(3)
C(3)–C(4)	1.403(4)	1.393(3)	N(1)–C(4)–C(3)	117.6(2)
N(3)–C(5)	–	1.350(3)	C(1)–C(5)–N(1)	120.1(3)
			N(3)–C(5)–N(1)	–
				116.5(2)

L = 4-aminopyridine) alongside with the crystal structures for **I** and **IV** are described.

## 2. Results and discussion

All compounds were obtained by interaction of the proper aminopyridine with an aqueous solution of fluorosilicic acid. Binary compounds **I** and **IV** crystallize in monoclinic (space group C2/c with *Z* = 4) and triclinic (space group P $\bar{1}$  with *Z* = 1) crystal systems, respectively. Crystal structure and refinement data for **I** and **IV** is given in Table 1. Selected bond distances and angles are given in Table 2, hydrogen bonding geometry is summarized in Table 3. The asymmetric units of **I** and **IV** reveal half of the hexafluorosilicate anion and the 2-aminopyridinium or 2,6-diaminopyridinium cation. Both structures are built from the hydrogen-bonded units consisting of the anion and two cations (Fig. 1). The positions of N-bound hydrogen atoms were found in the difference Fourier map. Proton transfer to the pyridine nitrogen atom is clearly revealed by the widened C–N–C bond angle in the aromatic ring (Table 2). In **I** two donor centers of 2-aminopyridinium cation act in a chelate mode resulting in a non-planar R<sub>2</sub><sup>2</sup>(8) hydrogen-bonding ring [19], with the twisted angle between the planes of equatorial fluorine atoms (F1 and F2) and planar H1N–N1–C4–N2–H2N2 fragment of the aromatic cation equal to 28.4°. In **IV** the H-donor area of the cation enriched by the additional aminogroup provides the set of four short NH...F contacts (two single and one bifurcated H-bonds) that formulate three shared H-bonded rings, R<sub>2</sub><sup>1</sup>(6), R<sub>2</sub><sup>1</sup>(4), R<sub>2</sub><sup>1</sup>(6) sequence in graph set notation. The twisted angle between two six-membered H-bonded rings is equal to 15.3°.

The second hydrogen atom of amino-group in **I** is involved in bifurcated NH...F hydrogen bonding with apical F3 and equatorial F1 atoms of the anion. Thus, each [SiF<sub>6</sub>]<sup>2−</sup> anion in the crystal is

**Table 3**  
Geometry of hydrogen bonds for **I** and **IV**.

D–H...A	<i>d</i> (D–H)/Å	<i>d</i> (H...A)/Å	<i>d</i> (D...A)/Å	∠(DHA)/°	Symmetry transformation for acceptor
<b>I</b>					
N(1)–H(1N)···F(1)	0.90(3)	1.81(3)	2.706(3)	173(3)	− <i>x</i> + 1/2, − <i>y</i> + 1/2, − <i>z</i> + 1
N(2)–H(1N2)···F(3)	0.89(3)	2.00(4)	2.856(3)	163(3)	<i>x</i> , − <i>y</i> , <i>z</i> − 1/2
N(2)–H(1N2)···F(1)	0.89(4)	2.49(3)	3.165(3)	133(3)	<i>x</i> , − <i>y</i> , <i>z</i> − 1/2
N(2)–H(2N2)···F(2)	0.82(4)	2.05(4)	2.846(4)	164(3)	<i>x</i> , <i>y</i> , <i>z</i>
<b>IV</b>					
N(1)–H(1N1)···F(1)	0.87(3)	1.92(3)	2.760(3)	161(2)	<i>x</i> , <i>y</i> , <i>z</i>
N(1)–H(1N1)···F(2)	0.87(3)	2.63(3)	3.322(3)	138(2)	<i>x</i> , <i>y</i> , <i>z</i>
N(2)–H(1N2)···F(3)	0.86(3)	1.98(3)	2.835(3)	174(3)	<i>x</i> , <i>y</i> + 1, <i>z</i>
N(2)–H(2N2)···F(2)	0.84(4)	2.07(3)	2.891(3)	165(3)	<i>x</i> , <i>y</i> , <i>z</i>
N(3)–H(1N3)···F(1)	0.88(3)	2.25(3)	3.026(3)	147(3)	<i>x</i> , <i>y</i> , <i>z</i>
N(3)–H(2N3)···F(2)	0.84(3)	2.12(3)	2.955(3)	173(3)	<i>x</i> , <i>y</i> , <i>z</i> + 1
N(3)–H(2N3)···F(1)	0.84(3)	2.57(3)	3.050(3)	117(2)	− <i>x</i> , − <i>y</i> , − <i>z</i> + 1

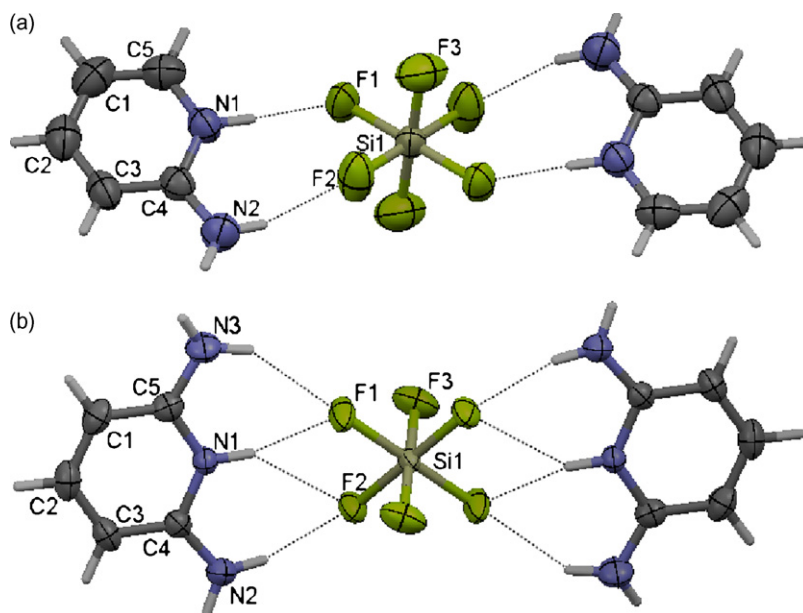


Fig. 1. ORTEP drawing for **I** (a) and **IV** (b) showing hydrogen bonding. Only asymmetric unit is numbered.

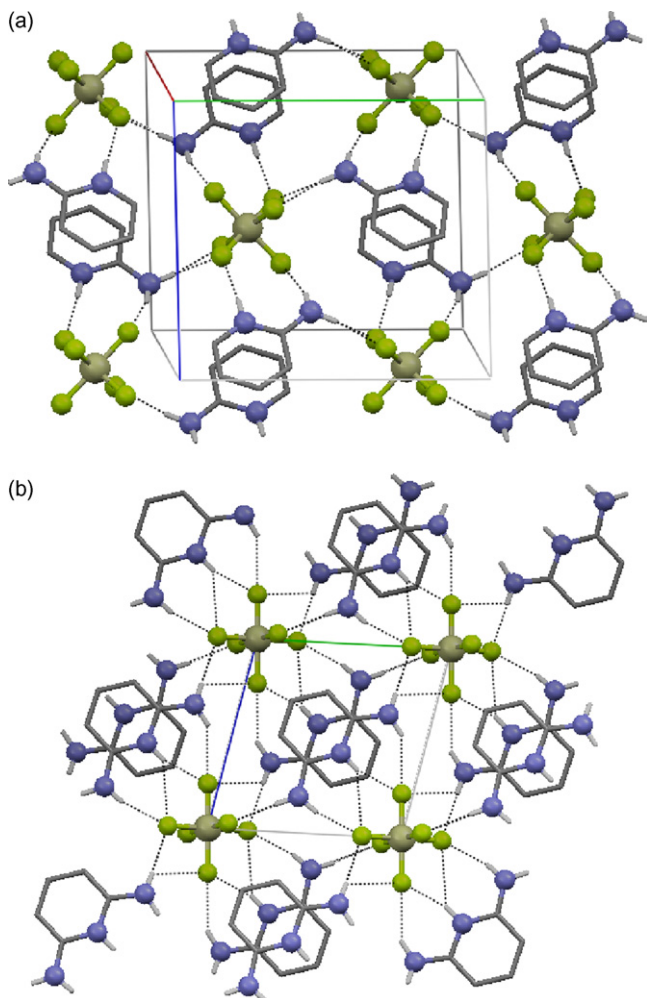


Fig. 2. Fragment of the layer in **I** (a) and **IV** (b). Axes: *a* – red, *b* – green, *c* – blue. C-bound H-atoms are omitted for clarity.

surrounded by four cations (Fig. 2a) being involved in eight hydrogen bonds, each cation bridging two [SiF<sub>6</sub>]<sup>2-</sup> anions. In **IV** due to the second amino-group we observe the more extended system of hydrogen bonding where each [SiF<sub>6</sub>]<sup>2-</sup> anion is surrounded by six cations being involved in 14 hydrogen bonds, each cation being bound with 3 closest anions (Fig. 2b). In both cases these concerted hydrogen-bonding interactions majority of which include the equatorial (F1 and F2) fluorine atoms join the charged species into two-dimensional layers which develop in the *bc* plane.

In both structures all fluorine atoms are involved in the hydrogen-bonding system. The structures exhibit the same effect marked earlier: the longest Si–F bond length corresponds to the shortest hydrogen bond and vice versa. Following [20] in spite of distribution in Si–F distances we do not observe the pronounced distortion in F–Si–F angles which remain close to the right and open values. Packing of the layers in **I** and **IV** also demonstrates the common features: the  $\pi$ – $\pi$  stacking interactions between the cationic units is observed both within and between the layers. Fig. 3 shows the packing of the layers and distances between the centroids of the overlapping pyridinium rings, which are in an agreement with the values typical for  $\pi$ – $\pi$  stacking interactions.

The IR data for **I–IV** are summarized in Table 4. The protonation of the heterocyclic nitrogen atom of aminopyridines proved by X-ray data in the case of complexes **I** and **IV**, is concerted with the IR data, in particular, with high-frequency shift of the bands  $\nu(\text{CC})$ ,  $\nu(\text{CN})$  ( $\nu_{\text{ring}}$ ) and pulsating vibrations of a cycle ( $\nu_{\text{puls}}$ ) in comparison with positions of these bands in the spectra of initial ligands [21]. The spectra **I–IV** in the region 800–650 cm<sup>-1</sup> are complicated by superposition of vibration bands of cations and  $\nu(\text{SiF})$  vibrations of [SiF<sub>6</sub>]<sup>2-</sup> anion, that impedes the assignment of the last ones. The  $\delta(\text{SiF}_2)$  vibrations in a disclosed area of spectra are registered by a band of an average intensity and a shoulder at 470 ± 5 cm<sup>-1</sup> for **I**, by two shoulders for **III** and **IV**, and by a doublet band at 450 and 475 cm<sup>-1</sup> for **II**. The multiple character of  $\delta(\text{SiF}_2)$  vibrations indicates the decrease of symmetry of [SiF<sub>6</sub>]<sup>2-</sup> anion with regard to *O<sub>h</sub>* and is concerted with the X-ray data.

Table 5 summarises the solubility data and pH values for 0.001 M solutions of **I–IV** in comparison with other hexafluorosilicates of

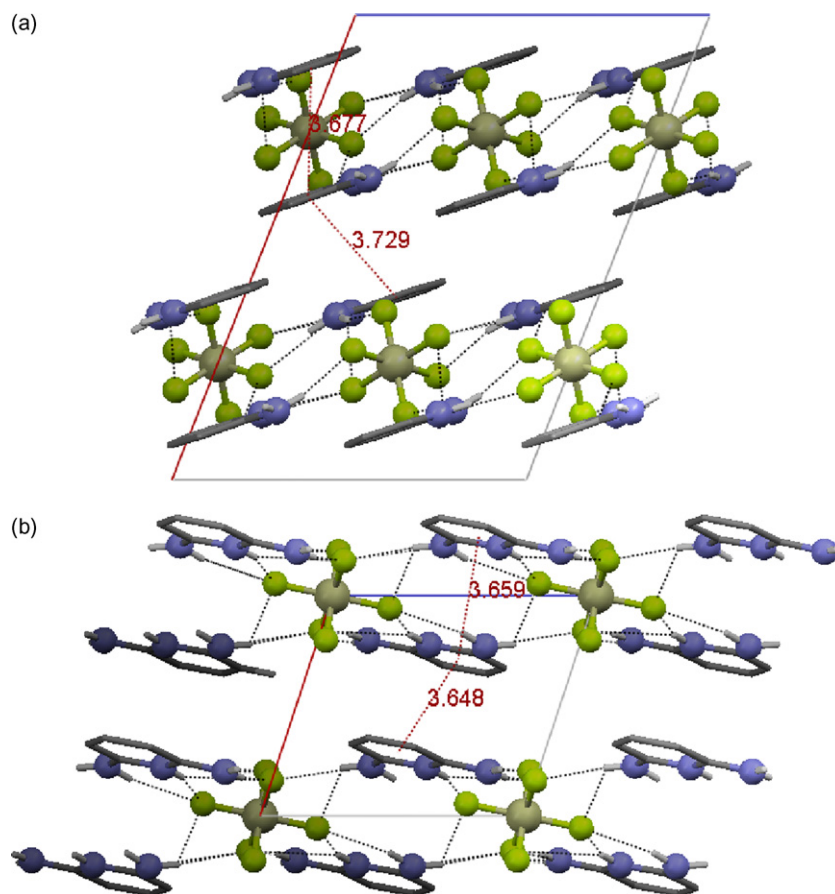


Fig. 3. Packing of the layers in I (a) and IV (b). View along *b* axis. Axes: *a* – red, *c* – blue. C-bound H-atoms are omitted for clarity.

functionalized pyridinium cations. As it has been previously noted [16], the tendencies in change of solubility of pyridinium hexafluorosilicates cannot be interpreted within the Davies's group numbers conception [25] that operates by characteristics of the hydrophilic–lipophilic balance (HLB) of compounds (in our case of pyridinium cations). In particular, a transition from  $[\text{HO}(\text{O})\text{CC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$  to  $[(\text{HOOC})_2\text{C}_5\text{H}_3\text{NH}]_2[\text{SiF}_6]$  should be accompanied by increase in solubility due to increase of the number of hydrophilic carboxylic groups in the final salt. The opposite effect

(Table 5) is actually observed. The similar situation is also observed for compounds  $[\text{H}_2\text{NC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$  and  $[(\text{H}_2\text{N})_2\text{C}_5\text{H}_3\text{NH}]_2[\text{SiF}_6]$ . At the same time attention has been drawn [16] to a relationship between the solubility of pyridinium hexafluorosilicates and a number of interionic H-bonds in the salt structure: the propagation of a number of short interionic contacts of a  $\text{XH} \cdots \text{F}$  ( $\text{X} = \text{N}, \text{O}$ ) type is accompanied, as a rule, by a diminution of solubility of relevant hexafluorosilicates. To estimate the effects of interionic H-bonds on the solubility of salts we have suggested utilizing the

**Table 4**  
IR spectral data ( $\text{cm}^{-1}$ ) for hexafluorosilicates I–IV.

Complex	$\nu(\text{N}^+\text{H}), \nu(\text{NH}_2), \nu(\text{OH})$	$\nu(\text{CC}), \nu(\text{CN}), \delta(\text{N}^+\text{H}), \delta(\text{NH}_2), \delta(\text{H}_2\text{O})$	$\nu_{\text{puls}}$	$\nu(\text{SiF}), \rho(\text{N}^+\text{H}), \delta(\text{CCH}), \delta(\text{CNC}), \gamma(\text{H}_2\text{O})$	$\delta(\text{SiF}_2)$
<b>I</b>	3370 m. 3340 m. 3190 m.br. 3080 sh.	1655 m. 1620 s. 1565 m. 1500 s.	1000 m.	770 sh. 745 v.s.br.	470 m. 425 sh.
<b>II</b>	3370 m.br. 3190 m.br. 3060 m.	1640 m. 1590 s. 1500 s.	1015 m.	740 v.s.br.	475 m. 450 m.
<b>III</b>	3400 sh. 3380 m. 3305 m. 3220 m. 3130 m. 3080 sh.	1650 m. 1635 m. 1620 s. 1560 s. 1505 s.	1010 m.	765 sh. 740 v.s. 670 sh.	490 sh. 475 m. 425 sh.
<b>IV</b>	3375 m.br. 3315 m.br. 3070 sh.	1630 v.s. 1550 sh. 1500 s.	1010 m.	750 v.s.br.	465 m. 440 sh. 420 sh.

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



**Table 5**  
Solubility of pyridinium hexafluorosilicates in water and pH of salts solutions.

Compound	Solubility/mol.%, 25 °C	$h/\text{Å}^{-1}$	pH of 0.001 M solutions	Reference
$[\text{C}_5\text{H}_5\text{NH}]_2[\text{SiF}_6]$	19.60 <sup>a</sup>	–	3.20	
$[2\text{-CH}_3\text{C}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$ <sup>b</sup>	11.60 <sup>a</sup>	0.71	3.27	[20]
$[2\text{-HO(O)CC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$ <sup>b</sup>	5.33 <sup>a</sup>	0.76	–	[22]
$[3\text{-HO(O)CC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$ <sup>b</sup>	3.33 <sup>a</sup>	1.09	–	[23]
$[4\text{-HO(O)CC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$ <sup>b</sup>	0.80 <sup>a</sup>	1.08	–	[16]
$[2,5\text{-(HOOC)}_2\text{C}_5\text{H}_3\text{NH}]_2[\text{SiF}_6]$	0.07	–	–	
$[2,6\text{-(HOOC)}_2\text{C}_5\text{H}_3\text{NH}]_2[\text{SiF}_6]$	0.02	–	–	
$[2\text{-H}_2\text{NC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$ <sup>b</sup>	5.60	1.38	3.30	
$[3\text{-H}_2\text{NC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]$	1.86	–	3.35	
$[4\text{-H}_2\text{NC}_5\text{H}_4\text{NH}]_2[\text{SiF}_6]\cdot\text{H}_2\text{O}$	3.88	–	3.09	
$[2,6\text{-(H}_2\text{N)}_2\text{C}_5\text{H}_3\text{NH}]_2[\text{SiF}_6]$ <sup>b</sup>	0.06	2.35	3.33	
$[4\text{-H}_3\text{NHN(O)CC}_5\text{H}_4\text{NH}][\text{SiF}_6]$ <sup>b</sup>	0.87 <sup>a</sup>	1.80	3.23	[24]

<sup>a</sup> Data [9].

<sup>b</sup> X-ray characterized compounds.

parameter  $h$  (Eq. (1)):

$$h = \frac{n}{d(\text{D} \cdots \text{A})_{\text{av}}} \quad (1)$$

where  $n$  is a number of short interionic contacts ( $\text{D} \cdots \text{A} \leq 3.2 \text{ Å}$ , strong and moderate H-bonds following the classification [13]),  $d(\text{D} \cdots \text{A})_{\text{av}}$  is an average donor–acceptor distance in the complex structure. The calculated  $h$  values for the structurally characterized compounds are given in Table 5, and the graphical dependence of solubility values  $C$  upon parameter  $h$  is given in Fig. 4. As it follows from these data the propagation of  $h$  values, reflecting the magnification of intensity of interionic H-interactions, results in exponential diminution of solubility of the relevant hexafluorosilicates. The potentiometric data given in Table 5, confirm the repeatedly marked fact of hydrolytic instability of “onium” hexafluorosilicates. The pH values of solutions of pyridinium hexafluorosilicates are close to the similar values for anilinium hexafluorosilicates [26], however, against to anilinium analogs, for pyridinium salts the relationship between the pH of salt solutions and  $\text{pK}_a$  of the relevant pyridine ligands is not observed. The aptitude of hydrolytic equilibrium expressed by Eq. (2) can be promoted by a weakening of a number of Si–F bonds of  $[\text{SiF}_6]^{2-}$  anions due to the participation of relevant fluoroligands in strong interionic H-bonds.



The known X-ray data, including presented herein, are adjusted with such opportunity. Concluding, we should stress that the interionic H-bonds in pyridinium hexafluorosilicates result in a disproportionation of Si–F bond lengths of anion that is affected on the salt properties. In particular, quite probable the relation-

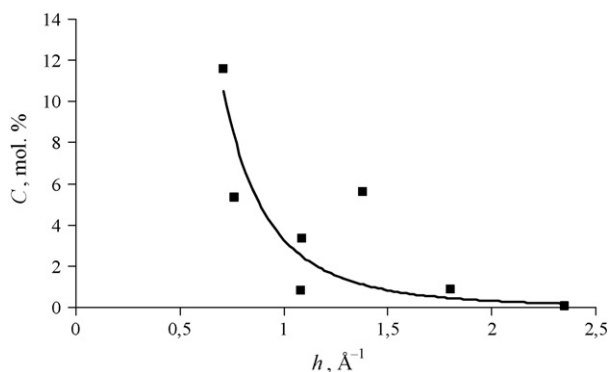


Fig. 4. Relationship between  $C$  and  $h$  values.

ship between the hydrolytic instability of salts and weakening of a part of Si–F bond lengths in the studied structures is demonstrated. On the other hand, the effects of H-bonds essentially influence the salt solubility: functionalization of pyridinium cation by introduction of the H-donor groups allows directionally varying (to decrease) a solubility of relevant hexafluorosilicates. Thus the solubility values can serve as a simple test for a qualitative estimation of a degree of interionic H-bonding in pyridinium hexafluorosilicates.

### 3. Experimental

The IR-absorption spectra were recorded on a spectrophotometer Specord 75IR (range 4000–400  $\text{cm}^{-1}$ , 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 isothermal conditions of experiments on detection of a solubility and hydrolysis of hexafluorosilicates ( $t = 25 \pm 0.2 \text{ °C}$ ) were provided with the help of an ultra thermostat U15.

#### 3.1. Synthesis of bis(2-aminopyridinium) hexafluorosilicate (I)

Pyridine-2-amine (0.094 g, 1 mmol) was dissolved in boiling methanol (5 mL) and to the obtained solution the fluorosilicic acid (FSA, 45%, 9 mL, molar ratio  $\text{L}^1:\text{FSA} = 1:3$ ) 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 quantitative yield. Colorless transparent crystals of the composition  $(\text{L}^1\text{H})_2\text{SiF}_6$  (I) with m.p.  $> 240 \text{ °C}$  (with decomposition). Anal. found, %: Si 8.28, N 16.31, F 35.11. Calcd for  $\text{C}_{10}\text{H}_{14}\text{F}_6\text{N}_4\text{Si}$ , Si 8.45, N 16.86, F 34.30. Mass spectrum:  $[\text{ML}^1]^+$  ( $m/z = 94$ ,  $I = 100\%$ ),  $[\text{ML}^1\text{-HCN}]^+$  ( $m/z = 67$ ,  $I = 69\%$ ),  $\text{SiF}_3^+$  ( $m/z = 85$ ,  $I = 11\%$ ).

#### 3.2. Synthesis of bis(3-aminopyridinium) hexafluorosilicate (II)

Pyridine-3-amine (0.094 g, 1 mmol) was dissolved in boiling methanol (5 mL) and to the obtained solution the fluorosilicic acid (FSA, 45%, 9 mL, molar ratio  $\text{L}^2:\text{FSA} = 1:3$ ) 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 quantitative yield. Colorless transparent crystals of the composition  $(\text{L}^2\text{H})_2\text{SiF}_6$  (II) with m.p.  $> 210 \text{ °C}$  (with decomposition). Anal. found, %: Si 8.16, N 17.02, F 34.57. Calcd for  $\text{C}_{10}\text{H}_{14}\text{F}_6\text{N}_4\text{Si}$ , Si 8.45, N 16.86, F 34.30. Mass spectrum:  $[\text{ML}^2]^+$  ( $m/z = 94$ ,  $I = 100\%$ ),  $[\text{ML}^2\text{-HCN}]^+$  ( $m/z = 67$ ,  $I = 31\%$ ),  $\text{SiF}_3^+$  ( $m/z = 85$ ,  $I = 4\%$ ).

### 3.3. Synthesis of bis(4-aminopyridinium) hexafluorosilicate monohydrate (III)

Pyridine-4-amine (0.094 g, 1 mmol) was dissolved in boiling methanol (5 mL) and to the obtained solution the fluorosilicic acid (FSA, 45%, 9 mL, molar ratio  $L^3:FSA = 1:3$ ) 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 quantitative yield. Colorless transparent crystals of the composition  $(L^3H)_2SiF_6 \cdot H_2O$  (III) with m.p.  $> 210$  °C (with decomposition). Anal. found, %: Si 8.02, N 15.71, F 33.10. Calcd for  $C_{10}H_{16}F_6N_4OSi$ , Si 8.02, N 15.99, F 32.54. Mass spectrum:  $[ML^3]^+$  ( $m/z = 94$ ,  $I = 100\%$ ),  $[ML^3-HCN]^+$  ( $m/z = 67$ ,  $I = 37\%$ ),  $SiF_3^+$  ( $m/z = 85$ ,  $I = 7\%$ ).

### 3.4. Synthesis of bis(2,6-diaminopyridinium) hexafluorosilicate (IV)

Pyridine-2,6-diamine (0.109 g, 1 mmol) was dissolved in boiling methanol (15 mL) and to the obtained solution the fluorosilicic acid (FSA, 45%, 9 mL, molar ratio  $L^4:FSA = 1:3$ ) 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 quantitative yield. Colorless transparent crystals of the composition  $(L^4H)_2SiF_6$  (IV) with m.p.  $> 230$  °C (with decomposition). Anal. found, %: Si 7.92, N 23.38, F 33.19. Calcd for  $C_{10}H_{16}F_6N_6Si$ , Si 7.75, N 23.19, F 31.46. Mass spectrum:  $[ML^4]^+$  ( $m/z = 109$ ,  $I = 100\%$ ),  $[ML^4-HCN]^+$  ( $m/z = 82$ ,  $I = 36\%$ ),  $SiF_3^+$  ( $m/z = 85$ ,  $I = 9\%$ ).

### 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-K $\alpha$  radiation using  $\phi$ - $\omega$  rotation. Unit cell parameters were obtained and refined using the whole data set. Experimental data reduction and cell refinement were performed using DENZO [27] package. The structure solution and refinement proceeded using SHELX-97 program package [28]. 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 H-atoms were found from differential Fourier maps at an intermediate stage of the refinement and were treated isotropically. Crystallographic data (cif files) for **I** and **IV** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 713403 and 713404. 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 www: <http://www.ccdc.cam.ac.uk>).

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