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Structural, Vibrational, Thermal, Phase Transitions, and Properties Review of Alkylammonium, Alkylenediammonium, and Aminoacid Hexafluorosilicate Salts

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Abstract—The present paper aims to review and discuss structural, thermal, phase transitions, solubility, catalytical, anticaries and toxicity properties of alkylammonium $[R_{4-n}NH_n]_2SiF_6$, alkylenediammonium $NH_3(CH_2)_nNH_3SiF_6$, and amino acid hexafluorosilicate salts, which have been previously published. Structural comparative analyses are made on the crystal structures, which have been determined for these compounds. The effect of hydrogen bonding on the Si···F elongation bonds is reviewed in terms of solid-state relationship. For the solution event, the hydrogen bonds are discussed in relation to the hexafluorosilicate compounds solubility. The vibrational and thermal properties of the hexafluorosilicates are reviewed and discussed, which lead us to highlight as well as the mechanisms and the characters of the phase transitions undergone by these compounds. The $NH_3(CH_2)_nNH_3SiF_6$ ($n = 4, 6$) and $(N_2H_5)_2SiF_6$ salts are found to be highly efficient novel catalysts in the synthetic protocols for organic compounds such as benzimidazoles, benzothiazole and benzoxazole, 3,4-dihydropyrimidin-2-ones/thiones and quinoxalines derivatives, which is considered as a novel tendency in the hexafluorosilicate researchs, particularly in the green chemistry field. The toxicological and anticaries properties of some hexafluorosilicate compounds are reviewed. Besides, the identification and quantification methods of new potential medical substances based on these salts are discussed.

Keywords: alkylenediammonium, alkylammonium, amino acid, hexafluorosilicates, IR, Raman spectra, hydrogen bonding, site symmetry, phase transitions, catalysis, solubility, toxicity, anticaries

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INTRODUCTION

Hexafluorosilicate compounds of the general formula $[R_{4-n}NH_n]_2SiF_6$ (R = alkyl, $n = 0–3$) studied over the two last decades [1–19] have been found to present interesting crystal dynamic and phase transitions involving as well as hydrogen bonds and reorientational motions of alkylammonium cations [1–8]. The temperature-dependent phase transitions of such compounds [3–5, 16–18] have been studied by DSC, dielectric, and Raman spectra at different temperatures. The alkylenediammonium salts $NH_3(CH_2)_n$-NH_3SiF_6 constitute a new important family of hexafluorosilicate compounds [20–27]. Among this family, the $NH_3(CH_2)_2NH_3SiF_6$ is the first compound to be studied [20]. More recently, research reporting X-rays, DSC-TGA, vibrational, DFT modeling, and catalytical properties have been developped on $NH_3(CH_2)_nNH_3SiF_6$ ($n = 3, 4, 6$) compounds [22–27]. The research interest in the hexafluorosilicates becomes to shift to the catalysts, optical materials, fluorinating agents, and pharmaceutical substances fields.

The first serious review study, which leads to summarize and systematize the research results published mainly after 2000 on the synthetic protocols, structure and spectral characteristics, solubility and hydrolysis, properties and the practical application aspects of the hexafluorosilicate salts has been developed by Gelmboldt et al. [13]. The review study reflected the various aspects state of chemistry and applied use of hexafluorosilicate salts obtained up 2019: modifiers of zeolite catalysts, fluoridating agents, activating additives and catalysts, preparation of amorphous silica, ionic liquids, and electro-optical materials.

The important work review has focused mainly on the synthesis and the properties of hexafluorosilicate salts [13]. Nevertheless, the structural data, vibrational characteristics, phase transitions, and thermal properties have not been fully reviewed and detailed for these compounds. Hence, the present review aims to highlight the structural, vibrational, thermal, and catalytical, toxicological, and anticaries studies, which have been developped up to now on alkylammonium, alkylenediammonium, and amino acid hexafluorosilicate compounds. The vibrational spectroscopy is used as a powerful tool to describe the behaviour of the cations, particularly in terms of their ability to form hydrogen bonds, and their contribution to the distortion of the SiF_6^{2-} octahedral geometry from its free symmetry O_h in the crystals.

EXPERIMENTAL

Synthesis methods. We give here just the principle of the synthesis methods via some examples, because of a detailed review study on the different synthesis methods of the hexafluorosilicate compounds was developed in [13]. Indeed, the alkylammonium hexafluorosilicate $[R_{4-n}NH_n]_2SiF_6$ crystals were obtained generally by slow evaporations at room temperature of aqueous solutions containing stoichiometric amounts of organic alkylamine (or hydroxide alkylammonium) and H_2SiF_6 acid [1–5]. Another synthesis method of these compounds consists to prepare firstly a solution of alkylammonium fluoride by adding an alkylamine drop wise and slowly to hydrogen fluoride. Secondly, the silica gel was slowly added to the stirred alkylammonium fluoride solution. After straining the mixture solution, the solvent was slowly evaporated, which yield crystalline salts [14]. Alkylenediammonium $NH_3(CH_2)_nNH_3SiF_6$ crystals were obtained by slow evaporation at room temperature of aqueous solutions containing stoichiometric amounts of the appropriate alkylenediamine and the H_2SiF_6 acid [20–24, 27].

Structural data analysis. The crystallographic data established elswhere on alkylammonium [1–5, 11, 12, 14–18, 28–30] and alkylenediammonium [20–23, 27, 29, 31–35] hexafluorosilicate compounds are shown in Tables S1 and S2, respectively. The crystal structures characteristics are discussed for these compounds.

Alkylammonium salts review. The crystal structures have not been fully determined for several alkylammonium hexafluorosilicate salts given in the Table S1 [1–5, 12, 15–18]. Only the crystallographic data of the unit cells are determined for the cited compounds. However, the structures of some hexafluorosilicate salts with nitrogen-containing organic cations are determined and well described [11, 28–30]. The Table S1 regroups hexafluorosilicate compounds as well as with aliphatic [1–5, 11, 12, 14–16] and cyclic cations [14, 17, 18, 28, 29].

The tetramethylammonium hexafluorosilicate $[(CH_3)_4N]_2SiF_6$ has been studied by X-ray diffraction, IR and Raman analyses [1]. Its structure was purposed at ambient temperature in the faces-centred cubic (antifluorite structure type) with the space group $Fm3m$ ($Z = 4$) and parameter: $a = 11.172$ Å [1]. The SiF_6^{2-} anions were expected to occupy the O_h sites symmetry, while the $(CH_3)_4N^+$ cations were assumed to have the T_d symmetry. The octahedral anions and the tetrahedral cations have been considered as not distorted from their ideal symmetries.

When one $-CH_3$ group of $[(CH_3)_4N]_2SiF_6$ is substitued by a hydrogen atom, then the obtained compound $[(CH_3)_3NH]_2SiF_6$ crystallized in the cubic system with space group $P4_132$ ($Z = 2$) and the parameter $a = 11.688$ Å, which is slightly increased rather than that observed in the $[(CH_3)_4N]_2SiF_6$ compound. Based on structural phase transitions develooped theoretically in the crystal with $Fm3m$ symmetry [36], the $[(CH_3)_3NH]_2SiF_6$ structure may be considered as derived by a possible structural phase transition taken place at the W-point of the Brillouin zone in the $[(CH_3)_4N]_2SiF_6$ of $Fm3m$ symmetry.

The substitution of all $-CH_3$ groups by $-C_2H_5$ gives rise to the tetraethylammonium hexafluorosilicate $[(C_2H_5)_4N]_2SiF_6$ compound, crystallizing in the monoclinic system of with the space group $P2_1$ ($Z = 2$) and the parametrs: $a = 13.430$ Å, $b = 13.825$ Å, $c = 12.940$ Å, $\beta = 90.894°$ [3, 5]. The space group $P2_1$ is considered as a sub-group of $Fm3m$, implying that the $[(C_2H_5)_4N]_2SiF_6$ crystal structure may be derived by a structural phase transition taken place at the X-point of the Brillouin zone of the $[(CH_3)_4N]_2SiF_6$ compound [36]. In $[(C_2H_5)_4N]_2SiF_6$ structure, as well the SiF_6^{2-} anions and $(C_2H_5)_4N^+$ cations were expected to occupy the C_1 sites symmetry, meaning that the anions and the cations were extensively distorted in this crystal [3, 5].

The diethylammonium hexafluorosilicate $[(C_2H_5)_2NH_2]_2SiF_6$ crystallized in the $P2_1$ space group ($a = 7.22$ Å, $b = 10.27$ Å, $c = 11.70$ Å, $\beta = 102.90°$) [16]. It is clearly noted that a, and β parametrs changed more remarkably, when passing from tetraethylammonium to diethylammonium structures, all monoclinic ($P2_1$ space group).

Concerning hexafluorosilicates containing monoalkylammoniums with $-NH_3$ group, the $[(C_2H_5)NH_3]_2SiF_6$ and $[(C_4H_9)NH_3]_2SiF_6$ compounds have too the trigonal symmetry: $P\overline{3}m$; $a = 10.429$, $c = 10.065$ Å [15] and $P321$ ($Z = 1$); $a = 8.861$, $c = 5.038$ Å [2, 16], respectively. Since the $P321$ is a sub-group of the $P\overline{3}m$ space group, then there is relationship symmetry between the two monoalkylammonium structures. So, the butylammonium salt structure may be derived from the ethylammonium structure by losing the m mirror, and the c parameter passes from 10.065 Å in ethylammonium structure to 5.038 Å in the derived butylammonium structure.

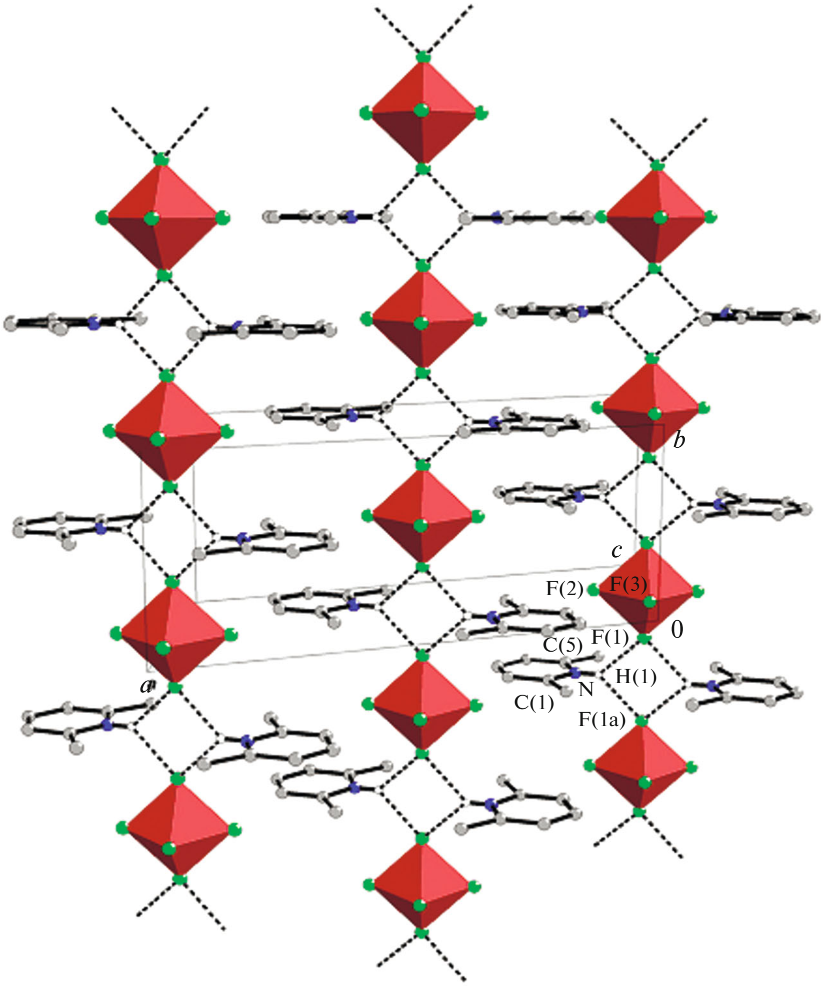

Fig. 1. The crystal structure scheme of $[(CH_3)_2C_5H_3NH]_2SiF_6$ viewed along the [0 0 1] direction. The hydrogen atoms on methyl groups and aromatic rings have been removed for clarity [29].

For the aromatic-alkylammoniums hexafluorosilicate, the $[C_6H_5NH_3]_2SiF_6$ compound is crystallized in the orthorhombic system with *Pmmm* ($Z = 2$) as space group and parametrs: $a = 5.540$, $b = 9.196$, $c = 17.165$ Å, $\beta = 90.894°$ [17, 18]; the others aromatic-compounds given in Table S1 are crystallized in the monoclinic and triclinic systems [28, 29]. As an example, the $[C_3H_6N]_2SiF_6$ was found to be monoclinic of space group $P2_1/C$ ($Z = 4$) and parameters: $a = 9.444(1)$, $b = 11.511(1)$, $c = 10.167(2)$ Å, $\beta = 100.62(4)°$ [28].

The hexafluorosilicate salts of protonated methyl substituted pyridines, R_2SiF_6 (R = 2-picolinium and 2,6-lutidinium) have been studied, especially their structural and vibrational characterisations. The 2,6-lutidinium $[(CH_3)_2C_5H_3NH]_2SiF_6$ compound is crystallized in the monoclinic system with the space group $C2/m$ ($Z = 2$; $a = 15.8171(4)$, $b = 6.4567(2)$, $c = 8.5075(2)$ Å, $\beta = 114.694(1)°$) [29]. In the cationic part of this compound, there are two $-CH_3$ groups linked to the aromatic ring, C_5H_3NH. Besides, they are found chains consisting of alternating 2,6-lutidinium cations and SiF_6^{2-} anions along *b*-axes (Fig. 1). Within these chains, the cations and anions were linked by bifurcated N–H···F hydrogen bonds of 2.14(1) Å order (for H···F lengths). Noting that only two fluorine atoms of each SiF_6^{2-} anion is involved in the hydrogen bond with the protonated nitrogen of the cations in this compound.

The 2-picolinium $[(CH_3)C_5H_4NH]_2SiF_6$ salt containing one $-CH_3$ group linked to the aromatic-ring was found to be crystallized in the monoclinic system, but with a different space group $P2_1/c$ ($Z = 2$) and the following parameters: $a = 6.8401(2)$, $b = 13.3041(4)$, $c = 7.9192(2)$ Å, $\beta = 91.499(2)°$ [29]. The structure of this compound is built from hydrogen-bonded units consisting of two cations and the anion, as illustrated in the Fig. 2. In contrast to the 2,6-lutidinium compound, four fluorine atoms of each SiF_6^{2-} anion are

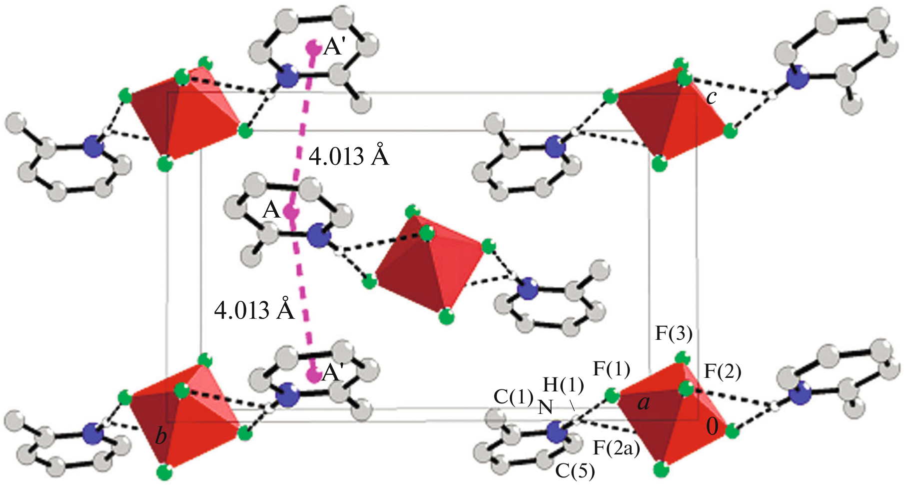

Fig. 2. The crystal structure scheme of $[(CH_3)C_5H_4NH]_2SiF_6$ along the [1 0 0] direction highlighting the π-π interactions between the 2-picolinium cations (with $A{-}A_0$ length = 4.013 Å). The hydrogen atoms on methyl groups and aromatic rings have been removed for clarity [29].

involved in four bifurcated $N{-}H\cdots F$ hydrogen bonds with two 2-picolinium cations, in the way that two fluorine atoms considered in apical positions F(1) form strong (1.89(2) Å) and two equatorial F(2) fluorine atoms form weak (2.735(2) Å) hydrogen bonds to the picolinium cations.

The structural change between these two compounds is accompanied by an important distortion of the β angle from 91.499(2)° in the compound with one $-CH_3$ group to 114.694(1)° in the compound with two $-CH_3$ groups. The distortion is traduced by the lowering symmetry when passing from the $C2/m$ ($Z = 2$) phase to the $P2_1/c$ ($Z = 2$) one, accordingly to the modification of the Bravais lattice symmetry of C to P.

Recently, we have synthesised and characterised by X-ray, IR, and Hirshfeld surfaces analyses a novel hexafluorosilicate based on hydrazinium (1+), $(N_2H_5)_2SiF_6$ [11]; the crystal structure of this compound is formed by two $(N_2H_5)_2^{2+}$ cations and an anion SiF_6^{2-}, which are linked together through hydrogen bonds $N{-}H\cdots F$. The surface analysis (2D fingerprint plot,) showed that the $F\cdots H/H\cdots F$ intermolecular interactions occupy the important area of the total Hirshfeld surfaces (75.5%), which implied that hydrogen bonds are predominant as intermolecular contacts in the crystal [11].

Comparative study of alkylenediammonium salts. The crystal structures of the reviewed alkylenediammonium hexafluorosilicate salts were completely determined [21–23], which allows us to make such comparative study between the determined compounds' crystal structures. The comparative study concerns mainly the compounds of general formula $NH_3(CH_2)_nNH_3SiF_6$ ($n = 0, 2, 3, 4, 6$). The crystallographic data of these hexafluorosilicate are given in Table S2.

The hydrazinium (2+) hexafluorosilicate $NH_3NH_3SiF_6$ crystallizes at room temperature in the orthorhombic system with the space group $Pbca$ ($Z = 4$) and the parametrs: $a = 7.603$, $b = 7.594$, $c = 8.543$ Å [20, 31]. Its structure consists of centrosymmetric $N_2H_6^{2+}$ and SiF_6^{2-}, ions arranged in a NaC1-type packing and connected by hydrogen bonds $N{-}H\cdots F$ ranging from 1.889 to 2.207 Å, and forming three-dimensional hydrogen-bonding networks [31]. The SiF_6^{2-} anions are observed in inversion centres compatibly to the Wyckoff positions 4a (1/2, 0, 1/2) of the space group $Pbca$. For the hydrazinium $^{+}NH_3NH_3^{+}$ cation, the bond N(1)–Ni centre is situated on the crystallographic inversion centre, corresponding to the 4b Wyckoff positions.

The ethylendiammonium hexafluorosilicate $NH_3(CH_2)_2NH_3SiF_6$ [21] crystallized in the monoclinic structure $P2_1/n$ ($Z = 2$, $a = 7.351(3)$, $b = 8.732(3)$, $c = 5.819(2)$ Å, $\beta = 93.84(1)°$), which is consisted of SiF_6^{2-} octahedra located on inversion centres corresponding to the Wyckoff positions: 2d (1/2, 1/2, 0); 2c (0, 0, 1/2) and ethylendiammonium cations either placed on inversion centres: 2a (0, 0, 0); 2b (1/2, 1/2, 1/2).

In the structure of $NH_3(CH_2)_4NH_3SiF_6$, crystallized in the triclinic system ($P\overline{1}$, $Z = 1$, $a = 5.796(1)$, $b = 5.889(1)$, $c = 7.774(2)$ Å, $\alpha = 87.02(1)°$, $\beta = 82.15(1)°$, $\gamma = 61.87(1)°$), the SiF_6^{2-} anion is observed on an inversion center $C_i(1)$ compatibly with Wyckoff the position 1d (1/2, 0, 0), the centre of the bond

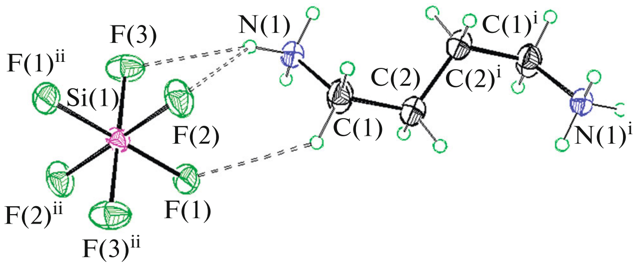

Fig. 3. The molecular structure of the $NH_3(CH_2)_4$-NH_3SiF_6 compound with the atom-labeling scheme. Symmetry codes : (i) $-x - 1, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z$ [22].

C(2)–C(2i) of the butylammonium cation is situated on another crystallographic inversion centre [22].

The crystal structure of $NH_3(CH_2)_6NH_3SiF_6$ monoclinic $P\bar{1}$ ($Z = 2$, $a = 5.8965(2)$, $b = 13.6946(5)$, $c = 14.4945(5)$ Å, $\alpha = 91.379(2)°$, $\beta = 92.797(2)°$, $\gamma = 90.906(2)°$), is built up from two SiF_6^{2-} anions and two organic cations $^{+}NH_3(CH_2)_6NH_3^{+}$ [23]. An anion Si(1) observed in the general position, i.e. in the Wyckoff position (x, y, z) corresponding to C_1 symmetry and two moiety of anions located at inversion centres of the $P\bar{1}$ space group: Si(2) on the Wyckoff position 1g (0, 1/2, 1/2) and Si(3) on 1a (0, 0, 0). The unit cell contains one organic cation and two halves of cations located about an inversion centre.

It is mentioning that the monoclinic structure (with $n = 2$) becomes triclinic of space group $P\bar{1}$ with $Z = 1$ and $Z = 2$, when n is equal to 4 and 6, respectively. In the $P2_1/n$ space group, there are four sets of non-equivalent inversion centres $4C_i(2)$, while in the $P\bar{1}$ there are night nonequivalents inversion centres $8C_i(1)$.

In all $NH_3(CH_2)_nNH_3SiF_6$ structures, as well as $^{+}NH_3(CH_2)_nNH_3^{+}$ cations and SiF_6^{2-} anions were linked with N–H···F hydrogen bonding, ensuring the three-dimensional cohesion of the crystals. Indeed, four significant N–H···F hydrogen bonding (2.864(2), 2.890(2), 3.017(2), 3.134(2) Å) have been determined by X-ray's study for the compound ($n = 4$) [22]. When n increases to 6, the compound presents 17 N–H···F hydrogen bonding ranging from 2.832(3) to 3.095(3) Å [23]. Hence, the compound ($n = 6$) presents several and strong hydrogen bonds rather than the compound with $n = 4$. The hydrogen bonding scheme illustrations in the two compounds are given in the Figs. 3 and 4.

For the compounds containing aliphatic alkylenediammonium, the V/Z variation (V: unit cell volume, Z: number of motifs per unit cell) versus the $-CH_2$ groups' number (n = 0, 2, 4, 6) in the H_3N-$(CH_2)_nNH_3SiF_6$ compounds drawn and given in Fig. 5. The curve variation is not linear; the V/Z value decreases from 124 Å^3 for n = 0 (orthorhombic) to 74 Å^3 for n = 2 (monoclinic). When passing to the triclinic system, the V/Z value increases to reach 234 Å^3 when n = 4, and 580 Å^3 at n = 6. The number of CH_2 groups impact of on the unit cell parametrs and volume values is clearly shown. The observed change takes place when passing from the orthorhombic system (n = 0) to the monoclinic one (n = 2), and from the monoclinic to the triclinic system (n = 4).

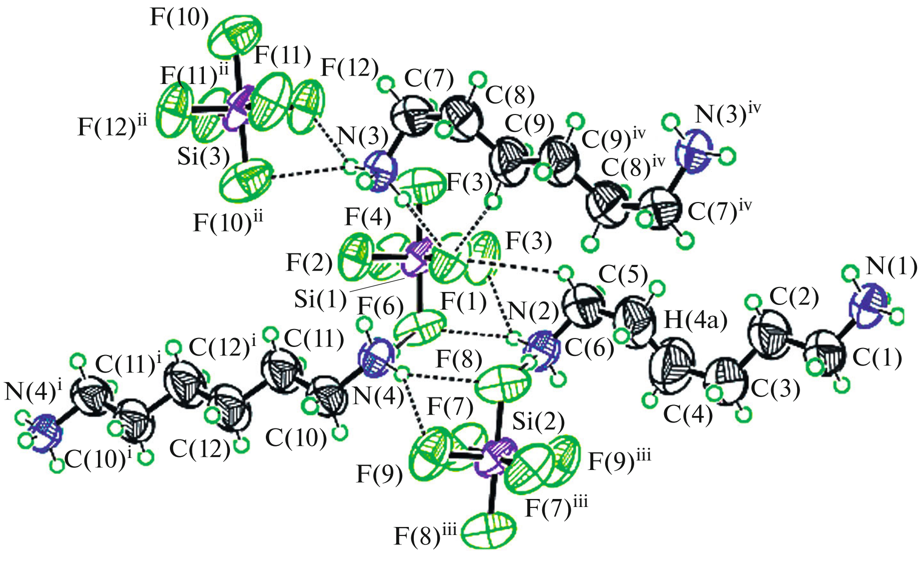

Fig. 4. The molecular structure of the $NH_3(CH_2)_6NH_3SiF_6$ compound with the atom-labeling scheme. Symmetry codes : (i) $-x, 1 - y, -z$; (ii) $-x, 2 - y, -z$; (iii) $-x, 1 - y, 1 - z$; (iv) $-x, 2 - y, 1 - z$ [23].

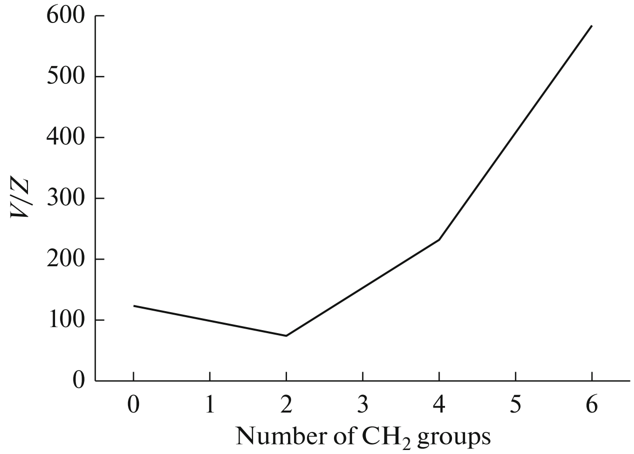

Fig. 5. The variation of the unit cell volume (*V*)/number of motifs per cell (*Z*) versus the number of CH_2 groups in the hexafluorosilicate $NH_3(CH_2)_nNH_3SiF_6$ ($n = 0, 2, 4, 6$).

Recently, a primary single crystal X-ray diffraction characterization made at ambient temperature showed that the $NH_3(CH_2)_3NH_3SiF_6$ compound crystallizes in the monoclinic system with the space group $P2_1/c$ ($Z = 4$) and parametrs : $a = 18.871(4)$, $b = 5.879(2)$, $c = 17.345(3)$ Å; $\beta = 117.331(3)°$ [27]. The full crystal structure is not yet determined.

The phenylenediammonium hexafluorosilicate has been synthetised by studying the interactions in the H_2SiF_6–*o*-phenylenediamine–H_2O (FSA–PDA–H_2O) system at 25°C, using the isothermal solubility method [32]. The solid phase obtained in this system, formulated as (o-PDAH$_2$)SiF$_6$ (23.70–44.60 wt % H_2SiF_6), crystallized in the orthorhombic, with the space group *Pmmn* ($Z = 2$), and the parametrs: $a = 5.5269(6)$, $b = 7.6648(7)$, $c = 11.2594(9)$ Å. In this structure, the *o*-PDA cations and the SiF_6^{2-} anions were linked through hydrogen bonds of NH···F type (N···F: 2.865(2)–2.967(2) Å) to form a two-dimensional network.

The crystal structure of $(C_4N_2H_{12})SiF_6$, monoclinic ($C2/c$ ($Z = 4$); $a = 10.577(5)$, $b = 7.317(5)$, $c = 11.598(5)$ Å, $\beta = 99.168(5)°$), consisted of isolated SiF_6^{2-} octahedra anions and di-protonated piperazine cations, which are connected to each other via hydrogen bonds to form a three-dimensional network [33].

The hexafluorosilicate salts $[2,2'(C_5H_4)_2(NH)_2]SiF_6$ and $[4,4'(C_5H_4)_2(NH)_2]SiF_6$ [34] crystallized in the centrosymmetric monoclinic $I2/a$ ($Z = 4$, $a = 12.396(4)$, $b = 6.6042(7)$, $c = 13.475(3)$ Å, $\beta = 92.46(4)°$) and orthorhombic *Pbcn* ($Z = 4$; $a = 11.897(2)$, $b = 7.188(2)$, $c = 12.882(3)$ Å) space groups, respectively. As observed, the *a*, *b*, and *c* parametrs are not greatly changed between the two compounds structures. The passage from the orthorhombic to the monoclinic system was done by a slight distortion, traduced by the 92.46(4)° value of β in the monoclinic structure of $[2,2'(C_5H_4)_2(NH)_2]SiF_6$. In these structures, the SiF_6^{2-} anions occupied inversion centres positions, and the bipyridinium ligands resided on the two-fold axes that cross the middle of single C–C bonds of the dications. The SiF_6^{2-} anions in these structures were distorted from octahedron geometry, with the Si-F distances varying from 1.658(2) to 1.706(2) Å. The anionic and cationic species were held together via strong N–H···F hydrogen bonds, of 1.77(3) Å in $[2,2'(C_5H_4)_2(NH)_2]SiF_6$ and 1.82(3) Å in $[4\text{-}4'(C_5H_4)_2(NH)_2]SiF_6$ compounds. These compounds have been characterized by the high tendency to hydrolysis in dilute aqueous solutions with the formation of silica and fluoride anions that allowed considering these salts as potential caries-protected agents [34].

The crystallographic data of $[(CH_3)_2NH(CH_2)_2NH(CH_3)_2]SiF_6 \cdot 2H_2O$ [29], which is an example of hexafluorosilicate salts of protonated methyl substituted pyridines and tetramethylethylenediamine is given in the Table S2. This compound crystallized in the triclinic system $P\bar{1}$ ($Z = 1$), with the parameters $a = 6.3753(2)$, $b = 7.6256(2)$, $c = 7.8004(3)$ Å, $\alpha = 117.849(2)°$, $\beta = 104.368(2)°$, $\gamma = 91.689(2)°$.

The crystal structure of the *N*,*N*-dimethylbiguanidinium hexafluorosilicate salt $[(CH_3)_2NC(NH_2)NHC(NH_2)NH_2]SiF_6$ has been determined and studied [35]. This compound is of monoclinic system with the space group $P2_1/c$ ($Z = 4$) and the parameters: $a = 7.4346(10)$, $b = 12.7628(10)$, $c = 11.0828(10)$ Å, $\beta = 104.080(10)°$. The crystal structure of this salt is consisted of SiF_6^{2-} anions and *N*,*N*-dimethylbiguanidinium cations, which are combined in a framework by medium to strong interionic H-bonds of N–H···F type, varying from 1.85(4) to 2.27(3) Å for the N–H···F bonds.

Others hexafluorosilicate salts. The present study is interested not only in alkylammonium and alkylenediammonium hexafluorosilicate compounds, but it aims also to extend reviewing to other interesting topic of hexafluorosilicates [8, 14, 37–47].

The crystal structures of an important class containing over 40 hexafluorosilicate salts of amino acids have been established and studied [43–47]. Indeed, the crystal structure of *N*-methylpiperidine betaine hexafluorosilicate has been determined at 100 K in monoclinic system with space group $P2_1/c$ ($Z = 4$, $a = 15.038(3)$, $b = 10.688(2)$, $c = 13.950(3)$ Å, $\beta = 112.93(3)°$) [43]; it consisted of two protonated betaines and one SiF_6^{2-} anion. In the cations, the piperidinium ring was found to be of chair conformations, but the CH_2COOH group is axial in one cation and equatorial in the other. In the crystal, two medium-strong hydrogen bonds of O–H···F type with d(O···F)

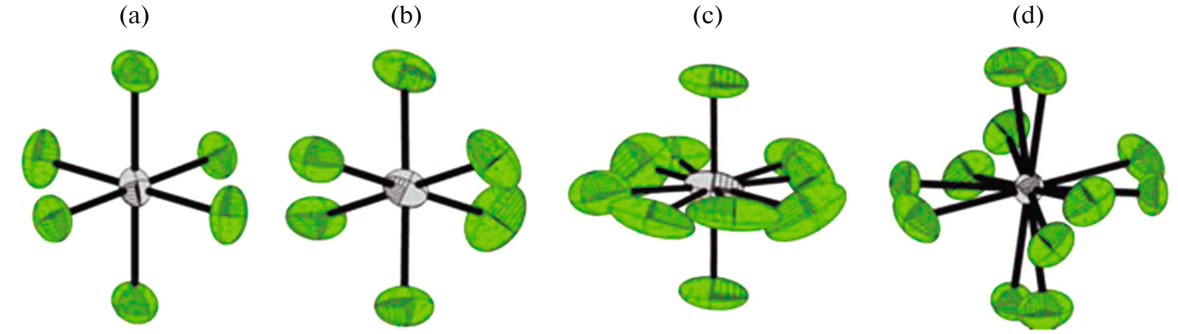

Fig. 6. The SiF_6^{2-} anions in amino acids: ordered and centrosymmetric, e.g. in (b-Ala)$_2H_2SiF_6$ (a); ordered, but non symmetric, e.g. in (L-Leu)$_2H_2SiF_6\cdot 2H_2O$ (b); rotational disorder, e.g. in (L-Ala)$_2H_2SiF_6\cdot 3H_2O$ (c); complete disorder in (Gly)$_2H_2SiF_6\cdot 2H_2O$ [46] (d).

equal to 2.565(1) and 2.617(Å) were taken place between the two protonated betaines and SiF_6^{2-} anion.

The hexafluorosilicate salts of α-alanine have investigated in [44]. Both L-alanine (L-Ala) and DL-alanine (DL-Ala) form hexafluorosilicate salts according to the main $2A^+SiF_6^{2-}$ type: 2L-Ala$^+SiF_6^{2-}\cdot 3H_2O$ and 2DL-Ala$^+SiF_6^{2-}\cdot 2H_2O$. The L-alanine formed a new $A^+(A\cdots A^+)SiF_6^{2-}$ salt type: L-Ala$^+$(L-Ala···L-Ala$^+$)$SiF_6^{2-}\cdot H_2O$, where $A\cdots A^+$ is dimeric cation held together by a strong hydrogen bond. The structural and vibrational spectroscopic propreties have been described and discussed for these amino-acid hexafluorosilicate salts [44].

Three types of salts of amino acid hexafluorosilicates with singly charged cations have been also investigated in [45]: (i) $2A^+SiF_6^{2-}$ (2Gly$^+SiF_6^{2-}$, 2L-Phe$^+$-SiF_6^{2-}, 2L-Val$^+SiF_6^{2-}$, 2L-Glu$^+SiF_6^{2-}$, 2L-His$^+$-SiF_6^{2-}), (ii) $A^{2+}SiF_6^{2-}$ (L-His$^{2+}SiF_6^{2-}$, L-Lys$^{2+}SiF_6^{2-}$, L-Orn$^{2+}SiF_6^{2-}$), and (iii) $2(A^+\cdots A)SiF_6^{2-}$ (2(Bet···Bet$^+$)SiF_6^{2-}), where A is an amino acid in zwitterionic state, A^+ is a singly charged cation, A^{2+} is a doubly charged cation and $(A\cdots A^+)$ is a dimeric cation with a short hydrogen bond. The indicated amino acids are: glycine (Gly), L-phenylalanine (L-Phe), L-valine (L-Val), L-glutamine (L-Glu), L-histidine (L-His), L-lysine (L-Lys), L-ornithine (L-Orn), betaine (Bet).

Single crystal data of eight hexafluorosilicate salts of amino acids: β alanine (β-Ala), betaine (Bet), L-ornithine (L-Orn), L-serine (L-Ser), L-leucine (L-Leu), L-isoleucine (L-Ile), L-methionine (L-Met) and L-aspartic acid (L-Asp) have presented and discussed in [46]. The corresponding crystals obtained are 2(β-AlaH)SiF_6, 2(BetH)SiF_6, 2(L-OrnH)SiF_6, 2(L-SerH)SiF_6, 2(L-LeuH)$SiF_6\cdot 2H_2O$, 2(L-IleH)$SiF_6\cdot 2H_2O$, 2(L-MetH)$SiF_6\cdot H_2O$, and 2(L-AspH)$SiF_6\cdot 2H_2O$. Among these salts, four structures were found anhydrous, and other four ones were hydrated. Analysing the structural properties of these compounds and 22 other amino acid hexafluorosilicates [46], the authors have found that the SiF_6^{2-} anions, generally ordered, are in octahedral coordination in the majority of the studied and reviewed salts. The SiF_6^{2-} anions possess more or less octahedral geometry with well-defined fluorine positions. In some cases, the ordered and centrosymmetric anions are located on special positions, which are expressed in their local symmetry (Fig. 6a), however, the most anions, ordered and non-centrosymmetric, were located on general positions with point symmetry C_1 (Fig. 6b). Nevertheless, the rotational disorder behaviour occurred in four cases (2(L-AlaH)$SiF_6\cdot 3H_2O$, 4(BetH)SiF_6, 2(L-OrnH)SiF_6, 2(L-ValH)-SiF_6) for the equatorial fluorine atoms (Fig. 6c). For the (Gly)$_2H_2SiF_6\cdot 2H_2O$ compound, the disorder was found for all atoms as shown in the Fig. 6d.

It was concluded that the majority of salts of amino acids with SiF_6^{2-} anion belong to the $2A^+SiF_6^{2-}$ type; such compounds tend to form crystal hydrates, and the SiF_6^{2-} anion is often disordered within the structures [45, 46]. Analysing all structural data obtained on amino acid hexafluorosilicates, it has been showed that the disorder correlates with the degree of hydrogen bonding [46], so that more hydrogen bonds stabilize the fluorine positions and lead to ordered structures. The authors revealed that the amount of hydrogen bonding towards the SiF_6^{2-} anion is an indication of disorder; they concluded that in all crystals with 0.6 or less hydrogen bond per fluorine atom are disordered.

Three hexafluorosilicate salts belonging to the sarcosine–H_2SiF_6–H_2O system, which are 2Sar$^+SiF_6^{2-}$, Sar$^+$(Sar···Sar$^+$)$SiF_6^{2-}\cdot 2H_2O$ and 2(Sar···Sar$^+$)SiF_6^{2-} have synthesized and studied in [47]. The crystal structures at 296 K as well as the thermal expansion of

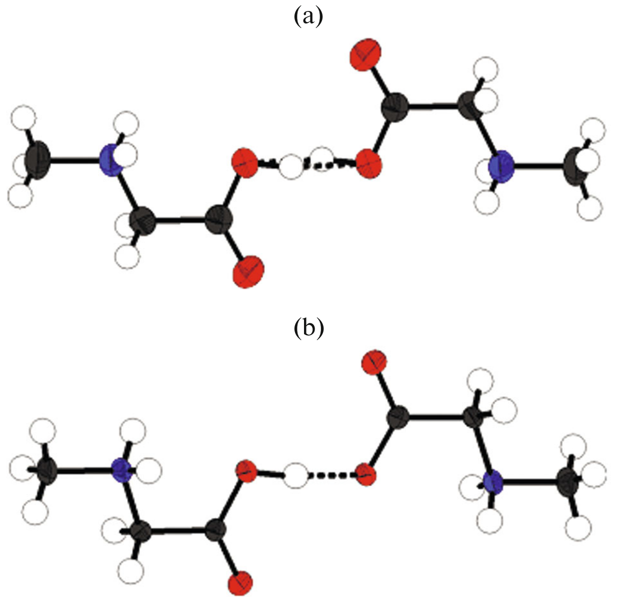

Fig. 7. View of the hydrogen bond arrangement in $Sar^+(Sar...Sar^+)SiF_6^{2-} \cdot 2H_2O$ at 296 (a) and 150 K (b) [47].

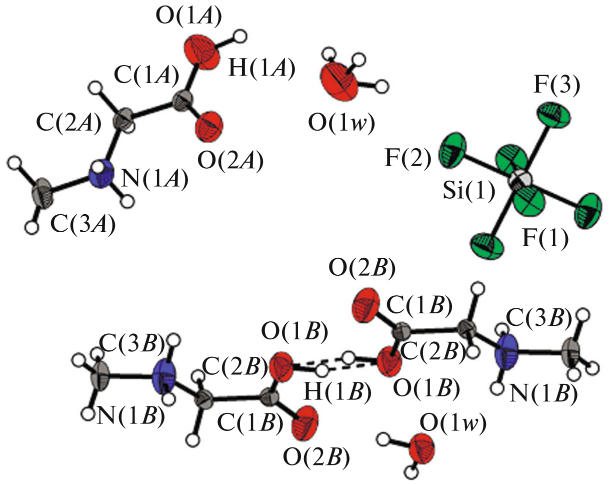

Fig. 8. Atom labelling in the molecular structure of $Sar^+(Sar...Sar^+)SiF_6^{2-} \cdot 2H_2O$. The disorder is observed for the hydrogen atom H(1*B*) in the dimeric unit and for the O(2*w*) hydrogen atom [47].

the three crystals have been determined. The compounds crystallized in the system monoclinic $P2_1/n$ ($Z = 2$), orthorhombic *Pnma* ($Z = 4$), and monoclinic $P2_1/c$ ($Z = 2$) respectively. The structure of the second compound is beside determined at 150 K in the system orthorhombic, but with the space group $P2_12_12_1$ ($Z = 4$). In the structure of $Sar^+(Sar...Sar^+)SiF_6^{2-} \cdot 2H_2O$, the disorder was observed in all three carboxyl groups between the protonated –COOH and deprotonated $-COO^-$ states. Thus, the symmetry-related pair of two moieties (Fig. 7b) comprise a dimeric sarcosinium/sarcosine pair, whereas the third sarcosinium moiety (Fig. 7a) extends its O–H hydrogen bond toward a water molecule. Determining the structure of the dihydrate hexafluorosilicate salt at 150 K, it was established [47] that this compound had a lower symmetry (space group $P2_12_12_1$, $Z = 4$), where occurred the lower temperature ordering of the disordered hydrogen, which means that a phase transition occurred to a lower symmetry structure. Although the atom positions remain in their place, the disorder of the acid hydrogen atom of the dimeric unit disappears. The disordered water molecule O(2*w*) also was found to be ordered at 150 K, and placed slightly off the mirror plane in the respective higher space group. A comparison of the hydrogen bond situation at 296 and 150 K is shown in the Fig. 8.

Recently, the synthesis, the crystal structure studies, the physicochemical properties, and anticaries activity of novel potential anticaries hexafluorosilicate substances are developped [48, 49]. The 2-amino-4,6-dihydroxypyrimidinium hexafluorosilicate $(L^1H)_2SiF_6$) crystallized in the monoclinic system ($I2/a$, $Z = 4$). The structure of this salt was constructed on the basis of two L^1H^+ pyrimidinium cations and an SiF_6^{2-} anion, which are linked by the NH···F and CH···F hydrogen bond contacts [48].

The structures of three pyridinium hexafluorosilicate compounds $(LH)_2SiF_6$ (L = 2-,3-,4-carboxymethylpyridine) with the general formula $(C_{14}H_{16}N_2O_4)SiF_6$ have been studied [49]. The X-ray results showed that the compound with 2-,3-,4-carboxymethylpyridine crystallized in the ($P2_1/n$, $Z = 2$), ($P2_1/c$, $Z = 2$), and ($I2/a$, $Z = 4$), respectively. The SiF_6^{2-} anion occupied positions on inversion centres in 2-,3-carboxymethylpyridine compounds, and on a two-fold axis in 4-carboxymethylpyridine salt. These compounds were stabilized by the interplay of intermolecular interactions including strong charge assisted and conventional hydrogen bonds of NH···F and OH···O types along with CH···F contacts and π–π stacking interactions. The different supramolecular motifs in these compounds are due to the different arrangement of the principal binding sites in the isomeric carboxymethylpyridines, as shown in the Fig. 9. These hexafluorosilicate salts have been found to be efficient in caries prevention [49].

Hydrogen bonding in hexafluorosilicate salts. The specificity of these compounds lies in the dominant H-bonds role in the formation of hexafluorosilicate salt structures with alkylammonium, alkylenediammonium and amino acid cations. It was concluded that the high H-acceptor ability of the SiF_6^{2-} anions leads to a noticeable influence of the H-bond effects

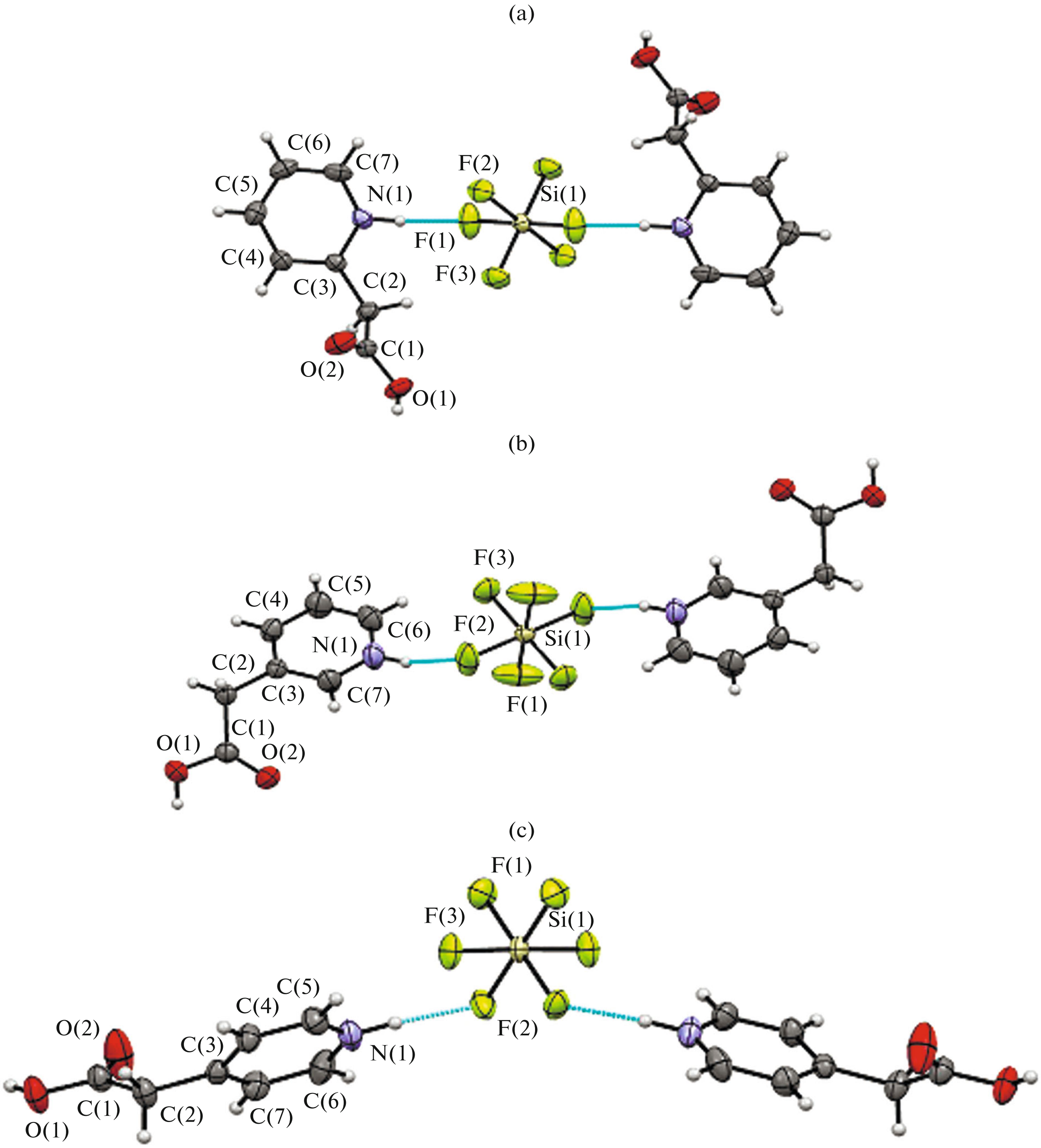

Fig. 9. Ortep plots with labeling scheme of the formula units in the $(LH)_2SiF_6$ ((a, b, c), where L = 2-,3-,4-carboxymethylpyridine) compounds [49].

on macroscopic properties of hexafluorosilicates, as water solubility and thermal stability [13].

The most known hexafluorosilicate structures with nitrogen-containing organic cations exhibit extensive hydrogen-bonding networks that incorporate all fluorine atoms of SiF_6^{2-} [13, 29, 37, 38, 48, 49]. The variations in hydrogen bonding interactions in these salts result in the formation of discrete cation–anion unit in the crystal such as in the $[(CH_3)C_5H_4NH]_2SiF_6$ compound, the formation of chain structure as in $[(CH_3)_2C_5H_3NH]_2SiF_6$, and the formation of polymeric layer as in $[(CH_3)_2NH(CH_2)_2NH(CH_3)_2]SiF_6 \cdot 2H_2O$ [29].

The elongation of Si–F bonds as a result of participation of the fluorine atoms in the hydrogen bond D–H···F have been observed and correlated with hydrogen bond strength. Even if the Si–F bond lengths in the SiF_6^{2-} anions in these compound structures increase due to hydrogen bonding, the FSF angles of the octahedral anions are found to be closed to 90° and 180° [29]. The unperturbed octahedral geometry of SiF_6^{2-} anion was also found in some hexafluorosilicate complexes with alkylammonium cations and with other organic cations [14, 37, 39].

In the pyridinium hexafluorosilicates $(LH)_2SiF_6$ (L = 2-,3-,4-carboxymethylpyridine) [49], the ionic components are held together via a couple of charge-assisted NH···F hydrogen bonds, for which N···F distances vary in the 2.683(2)–2.825(4) Å range. While each anion binds four cations, each cation bridges two SiF_6^{2-} anions acting besides the hydrogen bonds of NH···F type, also via COOH···F hydrogen bonds, for which the O···F distances vary between 2.583(3) and 2.6525(18) Å. These motifs are realized as three-dimensional H-bonded network in $(LH)_2SiF_6$ (L = 2-carboxymethylpyridine), as one-dimensional double tapes in the compound with (L = 3-carboxymethylpyridine) and as two-dimensional layers in the salt (L = 4- carboxymethylpyridine).

Thermal, vibrational, and phase transitions properties. As mentioned in the structural part, the crystal structures of several hexafluorosilicate compounds are not yet fully determined [1–5, 12, 15–18, 27]. The structural characteristics of these compounds, such as the hydrogen bonding, the anions and cations symmetry in the crystals, and the phase transitions, have been investigated using the IR and Raman spectra [1–5, 12, 15–18, 27]. The assignment of the observed bands has been discussed for the studied compounds, showing that the cations and anions, weakly to strongly hydrogen-bonded to each other, are generally distorted inside the crystals, from their free symmetries.

In the infrared spectra of the hexafluorosilicate compounds [1–5, 12, 15–18, 27], weak to medium bands were observed generally at lower frequencies of NH and CH stretching spectral regions, which have been assigned to the combination and overtone modes. In several cases, these non-fundamental bands normally possess appreciable intensities, due to the Fermi resonance. The observation of these bands was considered as indication of the presence of medium to strong hydrogen bonds in the hexafluorosilicate compounds, connecting the cations and the anions. Generally, the CH stretching frequencies are lower than NH ones; the formation of N–H...F hydrogen bonding causes shifting of NH stretching toward lows frequencies, which make it difficult to distinguish between NH and CH stretching modes [12].

The vibrational studies of the alkylammonium hexafluorosilicate compounds spectra were made on the basis of theoretical group analyses, which have developped on the supposed sites symmetry of anions and cations compatibly with the space groups determined by X-ray diffraction studies (Table 1), which lead to interpretate and discuss the vibrational spectra of these hexafluorosilicate compounds. The IR and Raman spectra of the compounds $NH_3(CH_2)_nNH_3$-SiF_6 (n = 0, 4, 6) with fully determined structures are interpreted knowing exactly the local symmetry of anions and cations [20, 24], as indicated in the Table 1. The site symmetry of the anions and cations are recently predicted in the $NH_3(CH_2)_3NH_3SiF_6$ structure [27].

As an example, the tetramethylammonium hexafluorosilicate IR and Raman spectra have been interpreted in terms of symmetry O_h for SiF_6^{2-} anions and T_d for $(CH)_4N^+$ cations, compatibly with the highly symmetric space group $Fm3m$, which means that as well as the anions and the cations are considered as preserving their free symmetry in the crystal belonging to the antifluorite cubic structure type [1]. In other study based on the electron paramagnetic resonance spectroscopy at room temperature, it is concluded that the radicals induced by δ-irradiation in the on the $[(CH_3)_4N]_2SiF_6$ compound is $(CH_3)_3N^+$ [9]. So, each methyl groups rotate around the C_{3v}-axis, and they also rotate around the C_{3v}-axis of $(CH_3)_3N^+$ radical, which rotate around the c-axis of the crystal since the EPR spectra did not change in the (a, b) plane.

It is to note that the octahedral SiF_6^{2-} anions are considered of O_h symmetry and their internal vibrational modes are described as: $1A_{1g}$(Ra) $+1E_g$(Ra) + $1F_{2g}$(Ra) + $2F_{1u}$(IR) + $1F_{2u}$(In). For an isolated anion, the vibrational modes (A_{1g}, E_g, F_{2g}) are theoretically Raman-active, the vibrational modes of F_{1u} symmetry are IR active and should appear as single bands. The symmetry lowering take place generally when going from the ions considered as isolated to the ions inside the crystal structures, which gives in terms of spectroscopy the splitting of the characteristic degenerate vibrational modes of SiF_6^{2-} octahedron, particularly in the Raman spectra of hexafluorosilicate compounds [1–5, 12, 15–18]. The inactive T_{2u} modes could be Raman and (or) infrared actives in particular situations with the lowering symmetry of the hexafluorosilicate.

The infrared spectra of the SiF_6^{2-} anion (O_h symmetry) are characterized by the presence of two F_{1u} vibrations $\nu_3(\nu_{as}$ Si–F) and $\nu_4(\delta_{as}$ FSiF) observed around 730 and 470 cm^{-1}; while the Raman spectra are known by three characteristic active vibrations $\nu_1(\nu_s$ Si–F, $A_{1g})$, $\nu_2(\nu_{as}$ Si–F, $E_g)$ and $\nu_5(\delta_s$ FSiF) (F_{2g}) observed generally around 660, 470 and 400 cm^{-1} [1]. In the hexafluorosilicate crystals, the SiF_6^{2-} anions are generally distorted and their symmetry is lowered from O_h to a determined site-symmetry (Table 1). For example, in the case of the $[(CH_3)_3NH]_2SiF_6$ compound, the symmetry of the anion becomes (D_3) in the site group [12], which results in splitting of the degen-

Table 1. Point group and site group correlations considered for anions and cations in the assignment of vibrational bands of hexafluorosilicate salts

Compound	Point group (site group) symmetry		References
	SiF_6^{2-}	cation	
$[(CH_3)_4N]_2SiF_6$	O_h (O_h)	T_d (T_d)	[1]
$[(CH_3)_3NH]_2SiF_6$	O_h (D_3)	C_{3v} (C_3)	[12]
$[(C_2H_5)_4N]_2SiF_6$	O_h (C_1)	D_{2d} (C_1)	[3, 5]
$[(C_2H_5)_2NH_2]_2SiF_6$	O_h (C_1)	C_{2v} (C_1)	[16]
$[C_2H_5NH_3]_2SiF_6$	O_h (C_i)	C_s (C_{3v}: statistical symmetry due to cations disorder)	[15]
$[C_4H_9NH_3]_2SiF_6$	O_h (distorted anions, symmetry not proposed)	C_s (statistical symmetry higher than C_s: disordered cations)	[2, 16]
$[C_6H_5NH_3]_2SiF_6$	O_h (distorted anions, symmetry not proposed)	C_s (statistical symmetry C_{2v}: disordered cations)	[17, 18]
$[(CH_2OD)_3CND_3]_2SiF_6$	O_h ($C_{3i} = S_6$)	C_3 (C_3)	[8]
$NH_3NH_3SiF_6$	O_h (C_i)	D_{3d} (C_i)	[20]
$NH_3(CH_2)_4NH_3SiF_6$	O_h (C_i)	C_i (C_i)	[24]
$NH_3(CH_2)_6NH_3SiF_6$	O_h (C_i, C_1) Non-equivalent anions	C_i (C_i, C_1) Non-equivalent cations	[24]
$NH_3(CH_2)_3NH_3SiF_6$	O_h (C_i)	C_{2v} (C_1)	[27]

erate vibrational modes $\nu_5(\delta_s$ FSiF) into two components observed at 360 and 345 cm^{-1}. The band observed at 760 cm^{-1} in the Raman spectrum of $[(CH_3)_3NH]_2SiF_6$ includes the IR vibrational modes $\nu_4(\delta_{as}$ FSiF), which becomes active in the Raman spectrum as a result of lowering symmetry of the anion SiF_6^{2-} inside the crystal. More details about the lowering symmetry site and its effect on the splitting and the activation of vibrational modes as well as in infrared and Raman spectra are available for the hexafluorosilicate compounds [1, 3, 5, 8, 12, 15–18, 20, 24].

For the majority of hexafluorosilicate studied by us [3, 12, 15–17, 24], the experimental IR and Raman frequencies have been compared to semi-empirical PM3 and DFT calculations. The optimal geometries and full thermodynamic properties of these compounds are also characterized, particularly for the alkylammoniums hexafluorosilicates. For the compounds [16, 17], the thermodynamic properties have been calculated using PM3 frequencies, where T (temperature in K), S (entropy in J mol^{-1} K^{-1}), C_p (heat capacity at constant pressure in kJ mol^{-1} K^{-1}), and $\Delta H = H° - H^{\circ}_{298.15}$ (enthalpy content, in kJ mol^{-1}), T_1 = 100 K, T_2 = 298.15 K, and T_3 = 1000 K. In the Table 2, we give the computational methods used, the energy ionisation (IE), and the band gap (BG) calculated for some hexafluorosilicates. The ionization energy of the $[C_6H_5NH_3]_2SiF_6$ system was calculated at 10.41 eV (PM3) and 7.25 eV (DFT), its band gap was determined at 9.51 eV (PM3) and 6.614 eV (DFT). These values are considered as indicative of a well delocalized aromatic-type of system [17], which is considered as more stable than $[C_4H_9NH_3]_2SiF_6$, $[C_3H_7NH_3]_2SiF_6$, and $[C_2H_5)_2NH_2]_2SiF_6$ [16].

The IR and Raman spectra of $NH_3(CH_2)_nNH_3$-SiF_6 (n = 4, 6) in solid state, where three-dimensional N–H···F hydrogen bonds network is formed, are interpreted on the basis of periodic DFT calculations of the model complexes, at fixed unit cell parameters [24] as found from XRD determination, which leads to suggest stronger N-H···F hydrogen bonding (HB) for n = 6 in comparison to n = 4 in agreement with the crystallographic finding [22, 23]. The vibrational frequencies of these compounds were calculated using the density functional perturbation theory (DFPT) (linear response (LR) theory), developed for crystal and determining the Hessian matrix of the second derivatives of the energy with respect to the atomic positions [24]. The Gaussian set of programs computes directly infrared intensities and infrared wavenumbers. The simulated Raman spectra using the calculated Raman scattering activity coefficient, which are not the real intensities, could not be compared to the experimental Raman spectra. Hence, the calculated Raman activities were converted into Raman scattering intensities (comparable with the experimental Raman intensities) with the help of Chemcraft program [24].

Table 2. Computational methods used, band gap (BG), and ionisation energy (IE) calculated for some hexafluorosilicate salts

Compound	Method			BG, eV	IE, eV	References
	MNDO	PM3	DFT			
$[(CH_3)_3NH]_2SiF_6$	+					[12]
$[(C_2H_5)_4N]_2SiF_6$	+					[3]
$[(C_2H_5)NH_3]_2SiF_6$	+					[15]
$[(C_2H_5)_2NH_2]_2SiF_6$		+	B3LYP	**5.70** (DFT)	**7.44** (DFT)	[16]
$[(C_3H_7)NH_3]_2SiF_6$		+	B3LYP	**5.89** (DFT)	**7.59** (DFT)	[16]
$[(C_4H_9)NH_3]_2SiF_6$		+	B3LYP	**6.11**(DFT)	**7.55** (DFT)	[16]
$[C_6H_5NH_3]_2SiF_6$		MP3		**9.51**	**10.4**	[17]
			B3LYP	**6.614** (DFT)	**7.25** (DFT)	
$[(CH_2OD)_3CND_3]_2SiF_6$			RB3LYP			[8]
$NH_3(CH_2)_4NH_3SiF_6$			Periodic DFT			[24]
$NH_3(CH_2)_6NH_3SiF_6$			Periodic DFT			[24]

* Periodic DFT: means that the crystal model was calculated based on the CIF file containing structural information details.

The HB interactions effect on the geometrical and vibrational characteristics of the ions in these compounds was studied. Indeed, the stretching Si–F modes frequencies could be used as characteristic spectroscopic data to estimate the HB relative strength in the alkylenediammonium hexafluorosilicate compounds.

In hexafluorosilicate-based phase transition materials, the phase transitions are caused generally by cations or protons, and sometimes by the SiF_6^{2-} anions considered as structurally ordered. Indeed, the $[C_4H_9NH_3]_2SiF_6$ compound showed a phase transition at 268/261 K, studied by DSC (heating/cooling) and Raman spectroscopy at different temperatures [2]. The observed phase transition is interpretate as a first order transition of order-disorder character, due to the tetrabutylammonium cations dynamic in the system. The changes observed in the Raman spectra at different temperatures for the majority of the internal vibrations of cations indicated that the disordered butylammonium cations exhibit reorientational motions at high temperatures. The butylammonium becomes ordered at low temperatures, and their motions are found to be frozen below phase transition temperature [2].

The $[C_3H_7NH_3]_2SiF_6$ compound exhibited a first order structural phase transition at around 229/216 K, which was detected by DSC (heating/cooling) and Raman spectroscopy [4, 16]. It is important to note the splitting of the DSC peaks observed as well as in heating and cooling, and the 229/216 K are considered as the centres of the observed doublets. This phenomenon is up to now inexplicable since the crystal structure of this compound is not yet determined. However, important changes are observed for the majority of the propylammonium internal vibrations observed in the Raman spectra at different temperatures near and below the phase transition temperature. The reorientational motions of these cations were considered as the contributor in the mechanism of the observed order–disorder phase transition in this hexafluorosilicate compound [2].

The $[(C_2H_5)_4N]_2SiF_6$ compound exhibited three structural phase transitions, which have been studied by DSC, Raman spectroscopy, and dielectric measurements [3, 5]. The phase transitions are observed in DSC (heating/cooling) at 30/15, 72/40, and 195/186°C. However, only two-phase transitions were detected by dielectric measurements at 30 and 195°C. The Raman spectra at different temperatures showed that the change in the dynamical state of the tetraethylammonium cations and SiF_6^{2-} anions contributed to the order-disorder mechanism of the observed phase transitions [5].

The $[C_6H_5NH_3]_2SiF_6$ compound presents two phase transitions at low temperatures (286/280 and 230/226 K), which have been studied by DSC (heating/cooling) and Raman spectroscopic at different temperatures [18]. The transition observed at 286 K is considered as a second-order phase transition, whereas that observed at 230 K is interpretate as a first-order character. From the Raman spectroscopy as function of temperature, it was concluded that as well as the hexafluorosilicate SiF_6^{2-} and the phenylammonium cations contribute in the first-order phase transition observed at 230/226 K; but only the cationic motions contribute to the mechanism of the second-order phase transition observed at 286/280 K [18].

The $[(CH_2OD)_3CND_3]_2SiF_6$ ferroic crystal undergone a solid-solid phase transition of the first order at

185 K, which has been investigated by the optical (linear birefringence) and thermal (DSC) measurements [8]. The infrared spectra of this compound were studied in the temperature domain (308–33 K). The temperature changes of frequencies, width, position and intensity of the IR bands were analyzed to clarify the phase transition mechanism and the contribution of SiF_6^{2-} and CH_2OD groups to the phase transition [8]. The Raman spectra of $[(CH_2OD)_3CND_3]_2SiF_6$ at room temperature were discussed on the basis of the theoretical calculations made based on DFT [8].

In the $[(CH_2OH)_3CNH_3]_2SiF_6$ salt, trigonal of space group $P\overline{3}$ ($a = 7.699(1)$, $c = 7.818(2)$ Å) at room temperature, the SiF_6^{2-} anions located in large cavities formed by hydrogen bonded cations are strongly disordered [7]. The DSC measurements revealed a first-order phase transition at low temperature (177 K), which was confirmed by a sharp increase of the linear birefringence below the phase transition temperature. The domain structure observed in the low temperature phase under a polarizing microscope, and the temperature dependent changes of birefringence indicate that this hexafluorosilicate salt has potential ferroelastic properties. The mechanism of the first-order phase observed in this compound is related to the freezing of the reorientational motions of the SiF_6^{2-} anions below the temperature phase transition 177 K.

The hexafluorosilicate moiety has been used to assemble the phase transitions in others hybrid materials based on amino acids [40, 47]. The bis(betainium)hexafluorosilicate bi(betaine) [40] is an example, which well illustrates the SiF_6^{2-} anions motions during the order-disorder phase transition since its structure has been determined at two different temperatures. At room temperature, the crystal is orthorhombic with space group *Fddd* (a = 13.2237, b = 19.3136, c = 22.0443 Å, V = 5630.05 Å^3), where the SiF_6^{2-} part exhibits partial disorder originated from a uniaxial wheel-like rotation [40]. When the temperature decreases, a total freeze of this wheel-like motion results in a second-order phase transition at 250 K, and the low temperature phase becomes monoclinic with $C2/c$ space group (a = 13.022, b = 21.9525, c = 11.4831 Å, β = 123.5238°, V = 2736.6 Å^3). The DSC measurements, variable temperature single-crystal X-ray diffractions, and theoretical computation of potential energies for the wheel-like motion confirmed that the solid-state phase transition is derived by the order-disorder transformation of the anionic rotor. The basic structural unit of this compound consists of one SiF_6^{2-} anion and two dimeric (betaine-H-betaine)$^+$ cations, which are well illustrated in the two phases in Fig. 10. During the phase transition, the small variation in O–H···O the hydrogen bonding interactions changing from 2.429 to 2.432 Å, indicates that proton dynamic is unrelated to the phase transition. Further detailed structural changes concerning the order-disorder transformation of the wheel-like motion in this compound is illustrated in the Fig. 11. The dynamic changes of the crystalline in-plane rotor give rise to anisotropic and switchable dielectric constants.

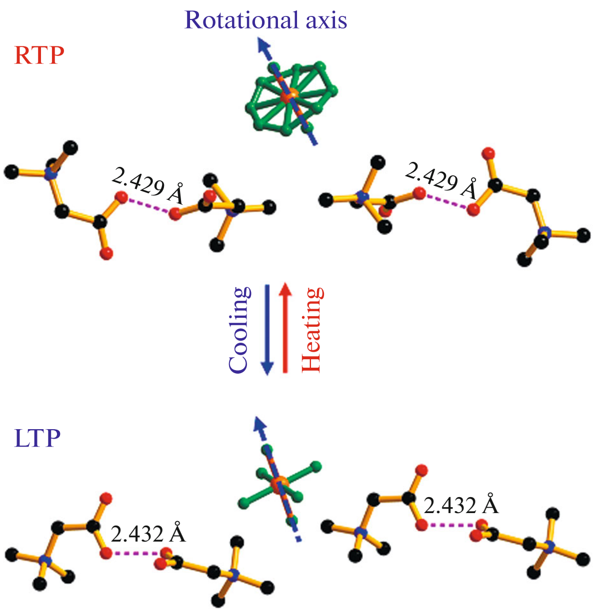

Fig. 10. Molecular structures of the bis(betainium)hexafluorosilicate bi(betaine) at room temperature (RTP) and low (LTP) temperature phases [40].

The tetraalkylammonium hexafluorosilicates were used as precursors for silicon films. The electrochemical methods of silicon coatings deposition from low-temperature ion-organic melts have been discovered for the first time by Gudymenko et al. [10]. For this goal, the authors have synthesized the hexafluorosilicate salts $[(CH_2)_2(C_2H_5)_2N)]_2SiF_6$, $[(CH_2)_3(C_3H_7)N]_2SiF_6$ and $[(CH_2)(C_2H_5)_3N]_2SiF_6$, which have studied their structure by X-rays diffraction, IR, NMR spectroscopy, and also by DTA/DSC methods. The studied tetraalkylammonium salts showed their stability enough to be suit able for electrochemical deposition of silicon coatings under temperatures at least up to 200°C. The temperatures of the beginning of thermal decomposition of the studied complexes were close to each other (~270–280°C) which means that energies of the cation-anion ionic bonds are practically identical and do not depend on the structure of the cation. The initial complex composition change during the thermal decomposition leads to the formation of the binary system (tetraalkylammonium fluoride-tetraalkylammonium fluorosilicate), which results in the formation of lower temperature melts. The use of background melts to produce silicon coatings at

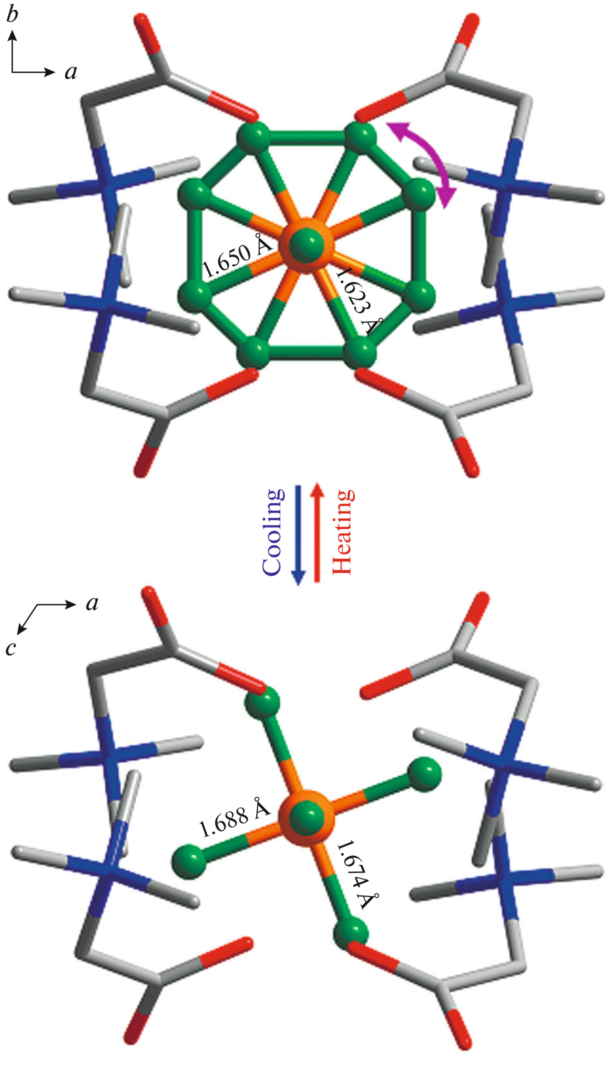

Fig. 11. Structural changes during the order–disorder transition of the wheel-like motion in bis(betainium) hexafluorosilicate bi(betaine) [40].

temperatures up to 200°C is possible by their respective thermal stability.

For the $NH_3(CH_2)_3NH_3SiF_6$ crystal recently characterized [27], the DSC and TGA-dTGA techniques recorded in the 25–250°C temperature domain showed the compound decomposition above 30°C, which is described by as the following equation:

$$NH_3\,(CH_2)_3\,NH_3SiF_{6\,(s)} \rightarrow SiF_{4(s)} + 2HF_{(g)} + N_{2\,(g)} + 3C_{(g)} + 5H_{2(g)}.$$

Water solubility. The relationship between the hexafluorosilicate structures and solubility was studied in several works [30, 41, 49] and reviewed for the majority of hexafluorosilicate compounds in [13]. As an example, the relationship between the solubility and the structure of the pyridinium $(C_5H_5NH)_2SiF_6$, 2-methylpyridinium $(2\text{-}CH_3C_5H_4NH)_2SiF_6$, and others hexafluorosilicates with substituted pyridinium cations was discussed [41]. The solubility has been investigated in relation to the number of interionic H-bonds in the salt structures [40], which implied that the propagation of a number of short interionic contacts of X–H···F (X = N, O) type is accompanied by a diminution of solubility of relevant hexafluorosilicates.

For a comparative assessment of the effect of interionic H-bonds on the solubility of pyridinium hexafluoridosilicates, an empirical parameter *h* was purposed [28]. Indeed, the interionic H-bond effects on the solubility of hexafluorosilicate salts have been estimated by using a parameter *h*, expressed as:

$$h = \frac{n}{d(\mathrm{D}\cdots\mathrm{A})_{\mathrm{av}}},$$

where n is a number of short interionic contacts $\mathrm{D}\cdots\mathrm{A} \le 3.2$ Å, $d(\mathrm{D}\cdots\mathrm{A})_{\mathrm{av}}$ is an average donor-acceptor distance in the complex structure; the strong and moderate H-bonds following the classification [30]. The solubility data and pH values for 0.001 M solutions of the hexafluorosilicate compounds, $(LH)_2SiF_6$ (L: 2-aminopyridine, 3-aminopyridine, 2,6-diaminopyridine) and $(LH)_2SiF_6 \cdot H_2O$ (L: 4-aminopyridine) in comparison with other hexafluorosilicate salts of functionalized pyridinium cations have been studied by means of calculated *h* parameters [30].

Generally, the calculated *h* values for structurally characterized hexafluoridosilicates with pyridinium cations as well as related heterocyclic cations containing pyridine nitrogen atoms are reviewed [13], which conclude that an increase in *h* values, reflecting an increase in the intensity of interionic H-interactions in salt structures, leads to an exponential decrease in the solubility of the corresponding ammonium hexafluoridosilicates. Furthermore, the solubility of arylammonium hexafluorosilicates in water and *h* values is reported in the review study [13], which claimed that the tendency to decrease in solubility of hexafluoridosilicates where cations bear additional H-donor groups or for hydrated forms.

Catalytical properties. The hexafluorosilicate of $NH_3(CH_2)_2NH_3SiF_6$ ($n = 4, 6$) are found to be highly efficient solid catalysts in the easy synthetic protocols for benzimidazoles, benzothiazole and benzoxazole, 3,4-dihydropyrimidin-2-ones/thiones and quinoxalines derivatives [25, 26]. The advantages of the hexafluorosilicate catalysis methods are: no solvent; mild conditions (room temperature); use of recyclable catalyst, easy work-up procedure, short reaction times (2–7 min), low catalyst content (1 mol %), scalability, solvent free conditions, excellent yields of target products (90–99%), easy reusability, and use of an eco-friendly catalyst. These obvious advantages are the important and significant attributes and of the practical features of the protocols using the two novel hexafluorosilicates compounds in catalysis field [25, 26].

Recently, the new hybrid crystal $(N_2H_5)_2SiF_6$ is used as a heterogeneous catalyst, in a simple, effective, green and non-toxic protocol, for the Knoevenagel condensation and the biscoumarin derivatives synthesis [19]. This compound examined for five successive cycles without significant loss of catalytic activity, presents several advantages such as a short reaction time and exceptional catalytic activity.

Anticaries and toxicity properties. The caries prophylactic efficacy (CPE) of some fluoride-containing solids has been determined in experiments developped on rats [47, 48]. It is worthy to note that the CPE was calculated as: $CPE = [(A - B)/A] \times 100\%$, where A is the number of caries lesions to the teeth in rats receiving the CID (caries-inducing diet) and B is the number of caries lesions in rats receiving the CID + a fluorinated compound [48].

The CPE results obtained for fluorinated compounds showed that $(NH_4)_2SiF_6$ and the 2-amino-4,6-dihydroxypyrimidine hexafluorosilicate $(L^1H)_2SiF_6$ decreased significantly the caries lesions numbers, by 22.7 and 45.5%, respectively [48]; the $(L^1H)_2SiF_6$ compound had a high CPE, five times greater than that of sodium fluoride NaF (9.1%). In contrast to NaF and $(NH_4)_2SiF_6$, the compound $(L^1H)_2SiF_6$ has significant differences in terms of its mechanism of biological activity, and then showed significant increase in alanine aminotransferase (ALT) activity (39%), considered as an evidence of a hepatotoxic action [48]. The disadvantage of this compound as a caries prophylactic agent is the presence of a hepatotoxic action, linked with the specific effects of the pyrimidinium cation.

However, the use of carboxymethylpyridinium hexafluorosilicates results in the significant decrease in the carious lesions number, in the following order: $(LH)_2SiF_6$ (L = 2-carboxymethylpyridine) by 6.8%, $(LH)_2SiF_6$ (L = 3-carboxymethylpyridine) by 11.4%, and $(LH)_2SiF_6$ (L = 4-carboxymethylpyridine) by 45.5%. The latest compound showing the highest CPE, also being 5 times higher than that of NaF, reduce the depth and the number of dental caries and provide efficiency of caries prevention [49]. The findings showed that these fluoride compounds devoid of hepatotoxic effect, which implies that the $(LH)_2SiF_6$ (L = 4-carboxymethylpyridine) salt is particularly of interest as a promising anti-caries agent.

It has been stated that the sodium hexafluorosilicate Na_2SiF_6, hexafluorosilicic acid H_2SiF_6 and NaF compounds have similar toxicity of fluoridation [50]. Although the effects of the fluoride compounds have been found to be varied among the 3 biological endpoints, no differences were found between the three compounds, relative to the fluoride ion concentration, in any of the assays. Furthermore, the hexafluorosilicic H_2SiF_6 acid and the ammonium hexafluorosilicate $(NH_4)_2SiF_6$ are toxic chemicals [51, 52]. The $(NH_4)_2SiF_6$ compound is known by the following toxicological informations [52]:

Health hazard: the inhalation of $(NH_4)_2SiF_6$ dust can cause pulmonary irritation and can be fatal in some cases; the ingestion may also prove fatal. Contact with dust causes irritation of eyes as well as irritation or ulceration of the skin.

Hazard statement: the $(NH_4)_2SiF_6$ has been characterised by: H301 (Toxic if swallowed), H311 (Toxic in contact with skin), and H331 (Toxic if inhaled).

In regard to the catalysis field undertaken recently with the alkylenediammonium $NH_3(CH_2)_nNH_3SiF_6$ ($n = 4, 6$) [25, 26] and hydrazinium [19] hexafluorosilicates, it seems important to study the toxicity of these compounds, for which any toxicological study has not yet done. Since these compounds are belonging to the hexafluorosilicate salts, then these novel catalysts, could present such toxicological properties as in $(NH_4)_2SiF_6$, since the silicofluorides compounds have generally similar toxicity of fluoridation.

Thus, the structural, vibrational, thermal properties, and phase transitions of alkylammonium, alkylenediammonium, and amino acid hexafluorosilicate salts are reviewed and discussed. For the alkylenediammonium salts $NH_3(CH_2)_nNH_3SiF_6$, the structural comparative analysis is developped on the determined crystal structures ($n = 0, 2, 4, 6$). The effect of hydrogen bonding is discussed as well as on the elongation of the Si–F bonds, and in relation to the solubility of hexafluorosilicate compounds. As a novel tendency in the hexafluorosilicate field research, $NH_3(CH_2)_nNH_3SiF_6$ ($n = 4, 6$) salts are found to be as highly efficient novel catalysts in the synthetic protocols for organic compounds such as benzimidazoles, benzothiazole and benzoxazole, 3,4-dihydropyrimidin-2-ones/thiones and quinoxalines derivatives.

As a perspective of this review, it seems very important to study as well as the acute toxicity of the hexafluorosilicate compounds and the development of methods for identification and quantification of new potential medical substances of hexafluorosilicates.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

SUPPLEMENTARY INFORMATION

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ADDITIONAL INFORMATION

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