DSCM 4P "ONIUM" HEXAFLUOROSILICATES AS NEW POTENTIAL CARIES PROTECTIVE AGENTS

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In recent years, the possible usage of ammonium hexafluorosilicate (AHF) as caries-protector and hyposensitive agent in the practice of dentistry was demonstrated [1, 2]. According to [1, 2] silica, as a product of hydrolysis of AHF, acts as a non-trivial catalyst promoting the deposition of calcium phosphate or fluorapatite from saliva; silica is present in sediment that is formed on the dentin surface, thus providing prolonged dentin tubule occlusion. It is supposed that the other "onium" hexafluorosilicates, for example, with bioactive heterocyclic cations must have similar effect. In present communication we describe some results of synthesis, the study of the structure and properties of "onium" hexafluorosilicates – the fluoride containing salts with heterocyclic cations, exhibiting antibacterial, anti-inflammatory and sialagogue activity, as new potential caries protective agents.

The compounds with the compositions $(L^1)_2SiF_6$ (L^1 = cetylpyridinium, **I**), $(L^2)_2SiF_6$, $(L^2H)_2SiF_6$ (L^2 = 4,5-*bis*(hydroxymethyl)-2-methylpyridine-3-ol, **II**), $(L^3H)_2SiF_6$ (L^3 = 2-pyridineacetic acid, **III**), $(L^4H)_2SiF_6$ (L^4 = 3-pyridineacetic acid, **IV**), and $(L^5H)_2SiF_6$ (L^5 = 4-pyridineacetic acid, **V**) where obtained by the interaction of corresponding "onium" chlorides in methanol solution with fluorosilicic acid H_2SiF_6 (45 %) in molar ratios 1 : 3 [3, 4]:

$$2(LH)Cl_{(MeOH)} + H_2SiF_{6\,(aq)} \rightarrow (LH)_2SiF_6 + 2HCl.$$

The compounds $(L^6)_2SiF_6$ (L^6 = 2,6-*bis*(hydroxymethyl)pyridine, **VI**) and $(L^7)_2SiF_6$ (L^7 = 2-amino-4,6-dihydroxypyrimidine, **VII**) were obtained by the interaction of corresponding free bases in methanol solution with H_2SiF_6 (45 %) in molar ratios 1 : 3. All compounds were characterized by elemental analysis, IR, NMR ^{19}F and mass-spectrometry, solubility data, and X-ray crystallography (**II – VII**). The structural study revealed the details of the anion binding and solid state supramolecular architectures provided by the combination of the plethora of intermolecular interactions including strong charge assisted and conventional hydrogen bonds of NH···F, OH···F types along with π-π interactions. For complexes **II** and **VI** the involvement of hydroxyl groups in the cation – anion H-binding was demonstrated for the first time. The hexafluorosilicate salts revealed a tendency toward solubility decrease with increase of H-donors number in the cations moieties. In dilute water solutions ($1\cdot10^{-4}$ M), salts underwent practically quantitative hydrolysis with formation of fluoride-ions and soluble form of silicon dioxide, which catalyzed the process of formation of calcium phosphate sediment from saliva. The results of the experimental toxicity study in rats for **I** (oral route) show that cetylpyridinium hexafluorosilicate refers to the toxicity class III (204,43 mg/kg, moderately toxic compound). All hexafluorosilicates significantly improve biochemical parameters in dental pulp of animals and their ability to mineralize, reduce the depth and the number of dental caries, and provide efficiency of caries prevention up to 80 %. Taking into account the higher caries preventive activity of hexafluorosilicates, superior to similar activity of sodium fluoride by 35–36 %, it can be assumed that these drugs will take a worthy place in the arsenal of measures for the prevention of dental caries.

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