

**ONIUM HEXAFLUROSILICATES WITH HETEROCYCLIC CATIONS:
SUPRAMOLECULAR STRUCTURE, PROPERTIES AND PHARMACEUTICAL
APPLICATION**

Vladimir O. Gelmboldt^{1,2}

¹*Odessa National Medical University, Valikhovskiy lane, 2, 65026 Odessa, Ukraine*

²*Physico-Chemical Institute of the Environment and Human Protection, Odessa, Ukraine*

e-mail: vgelmboldt@te.net.ua

Recent years demonstrate the steady interest to the various aspects of supramolecular chemistry of anions, and, in particular, fluorocomplexes anions due to their important role in chemical engineering. The high H-acceptor affinity of covalently bound fluorine in SiF_6^{2-} anions results in strong H-bonding interactions in $(\text{LH})_2\text{SiF}_6$ complexes (L = N-donor base) and affects on the structural characteristics and properties of salts. In present communication some structural aspects, properties and potential pharmaceutical application of onium hexafluorosilicates with heterocyclic cations will be discussed.

The crystalline salts with the composition $(\text{LH})_2\text{SiF}_6$ (L = $\text{RC}_5\text{H}_4\text{N}$, R = H, 2- CH_3 , 2-COOH, 3-COOH, 4-COOH, 2- NH_2 , 3- NH_2 ; L = $\text{R}_2\text{C}_5\text{H}_3\text{N}$, R_2 = 2,6- CH_3 , 2,6- CH_2OH , 2,5-COOH, 2,6-COOH, 2,6- NH_2 ; L = benzimidazole, 2-aminobenzimidazole, 3,5-diamino-1,2,4-triazole), $(\text{LH})_2\text{SiF}_6 \cdot \text{H}_2\text{O}$ (L = 2-Br-6- $\text{CH}_3\text{C}_5\text{H}_3\text{N}$) and $(\text{LH}_2)\text{SiF}_6$ (L = 2,2'-Dipy, 4,4'-Dipy) were obtained by the interaction of hexafluorosilicic acid with methanol solution of corresponding ligands. The inter-ionic interactions of the $\text{NH} \cdots \text{F}$ and $\text{OH} \cdots \text{F}$ type released in the structures of salts, and for the anion SiF_6^{2-} the symmetry deviation from the ideal octahedral one is dictated by its closest environment and an involvement of all or part of the fluoroligands in H-bonds of different strength. The common tendency for structurally characterized hexafluorosilicates exhibit a disproportionation of Si-F bond lengths depending on whether the corresponding fluoro ligand is involved in H-bonds and on the strength of the such bonds.

As it was shown for the onium hexafluorosilicates with piridinium and related heterocyclic cations, water solubility C (mol. %) of the explored salts may depend on the h parameter:

$$h = n/d(\text{D} \cdots \text{A})_{\text{av.}}$$

n – amount of short interionic H-bonds ($\text{D} \cdots \text{A} \leq 3,2 \text{ \AA}$), $d(\text{D} \cdots \text{A})_{\text{av}}$ – average donor-acceptor distance in the structure of complex. The h and C values agree with anti-exponential dependance. Similarly dependance was found between the values of C and h' parameter:

$$h' = N_{\text{H}}/pK_{\text{a}} \text{ L},$$

N_{H} – number of potential H-donors in cations, $pK_{\text{a}} \text{ L}$ – value of L basicity. Thus, cation functionalization by introduction of H-donor substituents is accompanied by amplification of interionic H-interactions and results in a lower solubility of hexafluorosilicates. The pH and NMR ^{19}F data confirm the hydrolytic instability of onium hexafluorosilicates in solutions showing equilibrium between SiF_6^{2-} , fluoride ore hydrofluoride ions, free base L and LH^+ . The potential biological activity of L was estimated with the help of PASS program. The results of calculation indicate on different types of pharmacological effects, including of antibacterial activity. It can be concluded that, taking into account the chemical behavior and biological activity of hexafluorosilicates with heterocyclic cations, this onium salts are perspective anti-carries agents.