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Short communication

Synthesis, crystal structure, IR-spectral data and some properties of 3,5-diamino-1,2,4-triazolium tetrafluoroborate and hexafluorosilicate

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ABSTRACT

3,5-Diamino-1,2,4-triazolium tetrafluoroborate (LH)BF_4 and hexafluorosilicate $(LH)_2SiF_6$ have been isolated and characterized by single-crystal X-ray structure determination, IR spectroscopy, mass spectrometry, solubility data, potentiometry. The N–H···F and N–H···N hydrogen bonds play an important role in a formation of 3-D structures of two compounds. The relationship between the salts structure and some properties is discussed.

1. Introduction

Functionalized derivatives of 1,2,4-triazole, particularly 3,5-diamino-1,2,4-triazole (L), attract an interest and are actively studied as ligands in the synthesis of d-metals complexes [1–3], precursors of condensed N-heterocyclic systems [4,5], corrosion inhibitors [6,7], biologically active compounds with a wide range efficiency [8,9] and as high-energy compounds [10–12]. On the other hand, ionic complexes with protonated form of N-containing organic bases, including 3,5-diamino-1,2,4-triazole, and complex fluoro-anions such as SiF_6^{2-}become convenient models to study an influence of interionic N–H···F bonds on the structural characteristics and properties of these compounds [13–16]. As it has been noted [15,16], the high H-acceptor affinity of covalently bound fluorine in SiF_6^{2-}anion result in a strong H-bonding interactions in complexes $(AmH)_2SiF_6$ (Am–N–donor base) that is affected on the disproportionation of Si–F bond lengths, solubility and thermal stability of salt. In present communication we are describing some results of synthesis, X-ray structure determination and physico-chemical investigations of two new salts – 3,5-diamino-1,2,4-triazolium tetrafluoroborate (LH)BF_4 and hexafluorosilicate $(LH)_2SiF_6$.

2. Results and discussion

2.1. Crystal structure

In the structure of (LH)BF_4 (I) five from six H atoms from each LH moiety participate in a formation of strong (1.98–2.33 Å) N–H···F hydrogen bonds. The sixth hydrogen atom, which belongs to one of the amino-groups, forms N–H···N bond with the non-protonated N4 atom from another LH unit. A pair of such N–H···N bonds connects two LH moieties, mutually oriented in “head-to-tail” manner, into a dimer (Fig. 1). The N3–H3···F4 contact, involving pyridine-type nitrogen atom, appears to be the shortest hydrogen bond in this structure (Table 1). These bonds connect each LH cation to four BF_4^- anions. The F4 atom acts as a μ_3-bridge, being bound to two hydrogen atoms from two different LH units, each of other fluorine atoms are connected to one H-atom. In turn, each anion is bound to $4LH^+$ units.

Such bridging role of both anions and cations, and the planar geometry of LH resulting in a formation of layered three-dimensional structure (Fig. 2). Three fluorine atoms from each BF_4^- – anion are bound with three LH units belonging to one layer, and the forth F atom is connected to the LH cation from the next layer. Because of small size of BF_4^- moieties the distance of 3.2 Å

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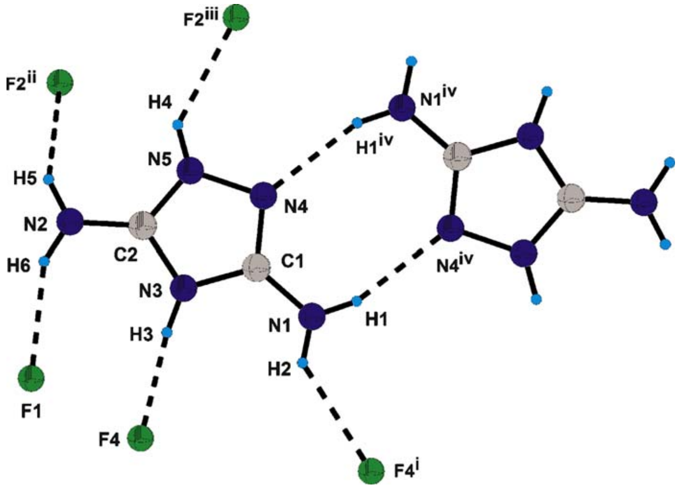

Fig. 1. Coordination of LH^+ moiety in structure of I.

between the closest LH units from two neighboring layers appears to be rather short.

In the structure of $(LH)_2SiF_6$ (II) the organic cation acts similar as in I role. Five hydrogen atoms are bonded to four SiF_6^{2-} anions (Fig. 3). Because of slightly higher than that in BF_4^- fluorine atom charge the distances H···F appear to be moderately shorter (1.90–2.11 Å) in comparison with $(LH)BF_4$. Possibly because of more "spherical" shape of SiF_6^{2-} anions and, therefore, higher spatial accessibility of fluorine atoms, all N–H···F bond lengths in II lie in a narrow range (Table 1). Similarly to that in I, the H-atom connected to the pyridine-type nitrogen forms the shortest N–H···F bond. Two F atoms act as μ_3-bridges, other four as μ_2-bridges, resulting in a connection of each SiF_6^{2-} anion to 8 organic moieties (Fig. 4). Inorganic anions and organic cations are interconnected into slightly puckered double layers, whereas further association of these layers occurs by non-valence interactions. Contrary to I, in the structure II the N–H···N bond involves removed from the N4 atom amino-group. It leads to an additional chain-like bonding of LH units within each layer.

It is interesting to compare the geometry of neutral and protonated forms of guanazole. In the structure of molecular 3,5-diamino-1,2,4-triazole one may observe a noticeable asymmetry of $C–NH_2$ bonds. It can be attributed to the difference in the surrounding of both carbon atoms. The C1 atom is connected to two–N–groups, and C2 one is bound to –N–and–NH–groups. In the structure of molecular guanazole the $C1–NH_2$ distance is 1.353 Å, and the $C2–NH_2$ one is 1.376 Å [17]. Such a tendency appears also in LH units: $C1–NH_2$ bond lengths are 1.341(4) Å in BF_4^- and 1.352(3) Å in SiF_6^{2-} derivatives respectively, and $C2–NH_2$ distances are 1.320 Å in both guanazolium salts. Similar values of 1.341(9) and 1.320(9) Å were found recently in the structure of guanazolium picrate [18]. It was also observed, that strictly identical in the structure of neutral guanazole N3–C1 and N3–C2 bond lengths of 1.363 Å become markedly different in its protonated form. Respective values appear to be 1.372(5) and 1.352(4) Å for tetrafluoroborate, 1.384(4) and 1.352(3) in hexafluorosilicate, 1.372(8) and 1.343(1) in picrate respectively. Also the protonation leads to a small deformation of the whole triazole cycle, with increasing the C–N–C angle from 102.7° in the neutral molecule to 107–108° in cationic form, and decreasing of both N–C1–N angle from 110° to 106°, and N–C2–N one from 116° to 111–112°.

Table 1
Parameters of hydrogen bonds in compounds I (top) and II (bottom).

Atoms	D–H	H···A	D···A	<(DHA)
$N1–H2\cdots F4^{i}$	0.86	2.33	3.015(4)	136.3
$N3–H3\cdots F4$	0.86	1.98	2.836(3)	173.3
$N2–H6\cdots F1$	0.86	2.13	2.927(3)	153.1
$N2–H5vF3^{ii}$	0.86	2.29	2.922(4)	130.7
$N5–H4\cdots F2^{iii}$	0.86	2.24	2.925(3)	136.0
$N1–H1\cdots N4^{iv}$	0.86	2.16	2.983(5)	160.9
	D–H	H···A	D···A	<(DHA)
Atoms				
$N1–H2\cdots F3^{i}$	0.86	2.11	2.918(4)	156.9
$N1–H1\cdots F1^{ii}$	0.86	2.02	2.849(5)	160.2
$N3–H3\cdots F1^{iii}$	0.86	1.90	2.703(4)	154.6
$N2–H5\cdots F3^{iv}$	0.86	2.00	2.833(5)	162.9
$N5–H4\cdots F2^{v}$	0.86	2.01	2.751(4)	143.1
$N2–H6\cdots N4^{vi}$	0.86	2.17	3.019(5)	167.8

Symmetry transformations: (i) $3-x$, $2-y$, $-z$ (ii) x, $y-1$, z (iii) $x-1$, $y-1$, z (iv) $2-x$, $1-y$, $-z$.
Symmetry transformations: (i) x, y, $z-1$, (ii) $x-1$, y, $z-1$, (iii) x, y, $z-1$, (iv) $x+1$, $y+1$, z, (v) x, $y+1$, z, (vi) $x+1$, y, z, (vii) $x-1$, y, z.

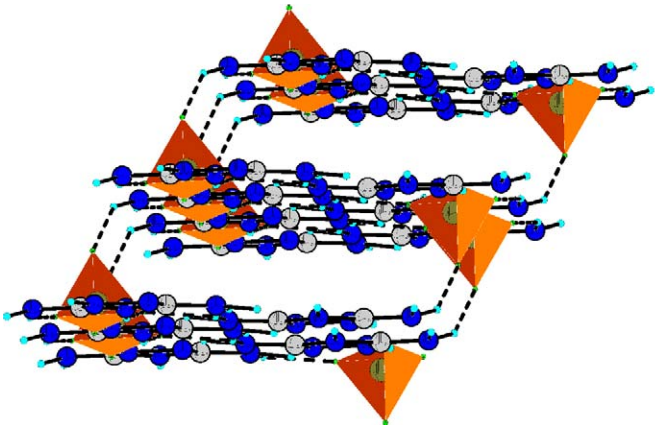

Fig. 2. Layered structure of I.

2.2. Results of IR spectroscopy

In the IR spectrum of the ligand (Table 2) vibrations of amino- and the NH-groups of the triazole cycle $\nu_{as,s}(NH_2)$ and $\nu(NH)$ appeared as a row of absorption bands with maxima at 3400, 3365, 3310, 3238, 3119 cm^{-1}. In the spectra of salts these bands were found at 3395, 3330, 3142 cm^{-1} (I) and the 3350, 3162 cm^{-1} (II). The observed transformation of the spectra appears because of protonation of one of the N–pyridine-type nitrogen atoms and the

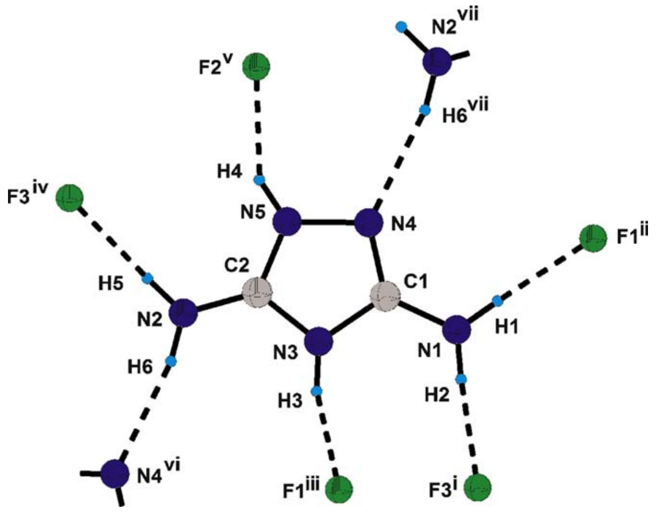

Fig. 3. Coordination of LH^+ moiety in structure of II.