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Self-assembly of hydrogen-bonded supramolecular structures based on hexafluorosilicate anion

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ABSTRACT

Interesting hydrogen-bonded supramolecular patterns have been achieved by hexafluorosilicate anion in the crystal structures of bis(thiabendazole) hexafluorosilicate dihydrate **1** and bis(pyrimethamine) hexafluorosilicate **2**. In compound **1**, the nitrogen atom of the benzimidazole ring rather than that of the thiazole ring is protonated. Water molecule is hydrogen-bonded with SiF_6^{2-} anion through O–H···F hydrogen bonds to form a twelve membered cyclic hydrogen-bonded cluster. This cluster is self-organized to form a supramolecular chain. In the crystal structure of compound **2**, the asymmetric unit contains two crystallographically independent protonated pyrimethamine (PMN) cations and a hexafluorosilicate SiF_6^{2-} anion. The combination N–H···F and N–H···N hydrogen bonds results in the formation of complementary DADA (D and A represent donor and acceptor, respectively) array motif. It confirms that DADA array motif is a robust synthon in the crystal structures of diaminopyrimidine salts.

1. Introduction

Fluorosilicic acid and sodium fluorosilicate are commonly used to fluoridate drinking water and as an additive in fluoridated mouth rinse in many countries [1,2]. Diamine silver fluoride [AgF:$(NH_3)_2$AgF] has been used clinically in Japan to reduce dental caries and dentin hypersensitivity [3]. The AgF present in this compound stains the teeth black due to silver precipitation. It has been proposed recently that replacement of diamine silver fluoride by ammonium hexafluorosilicate [SiF:$(NH_4)_2(SiF_6)$] prevents the staining and SiF has good potential as anticariogenic agent [4,5]. Hexafluorosilicate salts are used for the selective removal of surface acidity in Zeolite ZSM-5 [6]. They have also been used in photofunctional and conductivity materials [7]. One possible application of hexafluorosilicate salts is ionic liquids formation. Ionic liquids are generally comprised of nitrogen containing organic cations and symmetric inorganic anions [8,9]. They have potential uses in chemical synthesis as catalysts, in nuclear fuel processing, separation technologies, and as electrolytes in batteries and solar cells.

In recent years, different anions are used in supramolecular design strategy. The anions add versatility to the supramolecular designs since they display various directional preferences as hydrogen bond acceptors. The hydrogen bond acceptor capability of halides has attracted the attention of scientists in fields as diverse as supramolecular chemistry, biochemistry, coordination chemistry and organometallic chemistry [10–21]. The recent study suggests models for water-ion networks in ionic shells and membrane channels as well as challenges for designed approaches to employ water molecules and halide ions to build functional supramolecular architectures [22].

Identifying hydrogen-bonded supramolecular motifs involving different anions of drug salts are of current interest. Thiabendazole [2-(thiazole-4-yl)-1H-benzimidazole] (TB) is used as an anthelmintic in the treatment of parasitic diseases and also as a fungicide [23]. Pyrimethamine [2,4-diamino-5-(4-chlorophenyl)-6-ethyl-pyrimidine] (PMN) is an antimalarial drug, which selectively inhibits the parasitic dihydrofolate reductase enzyme (DHFR) through several hydrogen bonds [24,25]. The recurring hydrogen bonding motifs involving different anions with diaminopyrimidinium cations have been reported from our laboratory [26–33]. We have already demonstrated the metal chelating ability as well as hydrogen bonding patterns with different anions of thiabendazole molecule in different crystalline environments [34,35]. The octahedral shaped hexafluorosilicate anion (SiF_6^{2-}) has six fluoride ions, all of which have very good acceptor capability [36–38]. Our objective is to understand the role played by SiF_6^{2-} anion in achieving the same or different supramolecular architecture. In this communication, we are reporting a few interesting hydrogen-bonded motifs and supramolecular patterns involving SiF_6^{2-} anion

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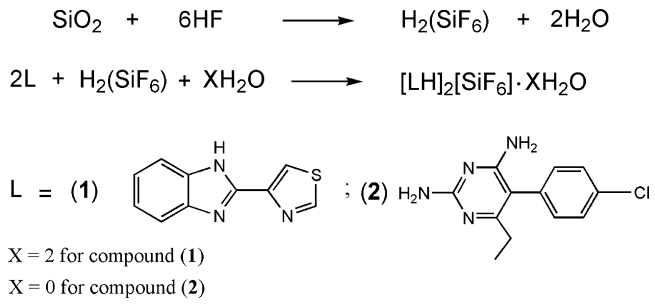

Scheme 1.

in the crystal structures of bis(thiabendazole) hexafluorosilicate dihydrate **1** and bis(pyrimethamine) hexafluorosilicate **2**.

2. Results and discussion

Hydrofluoric acid has the ability to dissolve by reacting with SiO_2, the major component of most glasses. The hexafluorosilicate compounds (**1** and **2**) were formed by reactions in Scheme 1. These

Table 1
Crystallographic parameters for **1** and **2**.

	1	2
Formula	$2(C_{10}H_8N_3S),SiF_6, 2(H_2O)$	$2(C_{12}H_{14}O_6N_4), SiF_6$
Formula weight	582.65	641.53
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	7.0471(14)	11.495(14)
b [Å]	9.4657(19)	11.733(6)
c [Å]	9.980(3)	12.399(15)
α [°]	65.336(17)	80.05(6)
β [°]	76.022(19)	63.52(9)
γ [°]	81.405(16)	69.26(7)
V [Å^3]	586.2(2)	1400(3)
Z	1	2
Observed reflections	1573	3646
Independent reflections	2056	4907
R_1 [$I > 2\sigma(I)$]	0.0378	0.0601
R_1 for all data	0.0574	0.0824
wR_2 [$I > 2\sigma(I)$]	0.0946	0.1633
wR_2 for all data	0.1039	0.1808
GOF (F^2)	1.048	1.045

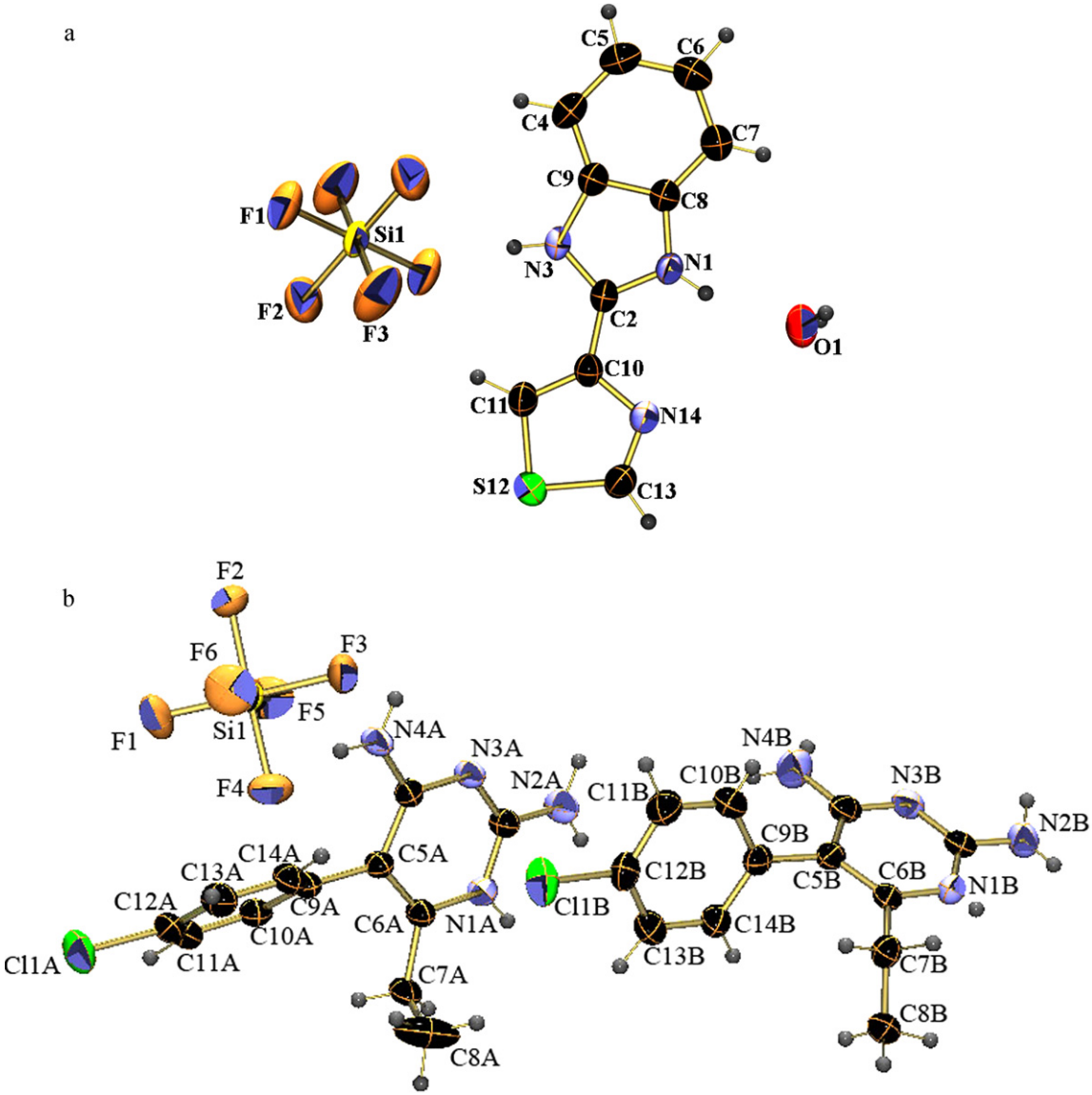

Fig. 1. (a and b) ORTEP view of **1** and **2**, Ellipsoids for non-hydrogen atoms are drawn at the 50% probability level (CCDC-210448 for **1** and CCDC-210449 for **2**). Labeled atoms are in the asymmetric unit.