



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 $\text{O}-\text{H} \cdots \text{F}$ 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 $\text{N}-\text{H} \cdots \text{F}$ and $\text{N}-\text{H} \cdots \text{N}$ 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.

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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 [$\text{AgF}:(\text{NH}_3)_2\text{AgF}$] 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 [$\text{SiF}:(\text{NH}_4)_2(\text{SiF}_6)$] 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

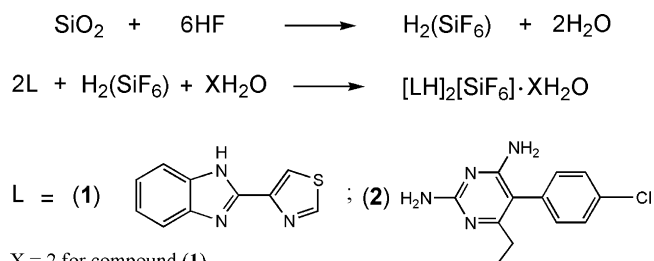
designs since they display various directional preferences as hydrogen bond acceptors. The hydrogen bond acceptor capability of halides has attracted the attention of scientists in fields as diverse as supramolecular chemistry, biochemistry, coordination chemistry and organometallic chemistry [10–21]. 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-ethylpyrimidine] (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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X = 2 for compound (1)

X = 0 for compound (2)

Scheme 1.

in the crystal structures of bis(thiabenzazole) 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	$2(\text{C}_{10}\text{H}_8\text{N}_3\text{S})\cdot\text{SiF}_6 \cdot 2(\text{H}_2\text{O})$	$2(\text{C}_{12}\text{H}_{14}\text{O}_6\text{N}_4) \cdot \text{SiF}_6$
Formula weight	582.65	641.53
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> [Å]	7.0471(14)	11.495(14)
<i>b</i> [Å]	9.4657(19)	11.733(6)
<i>c</i> [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)
<i>V</i> [Å ³]	586.2(2)	1400(3)
<i>Z</i>	1	2
Observed reflections	1573	3646
Independent reflections	2056	4907
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0378	0.0601
<i>R</i> ₁ for all data	0.0574	0.0824
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0946	0.1633
<i>wR</i> ₂ for all data	0.1039	0.1808
GOF (<i>F</i> ²)	1.048	1.045

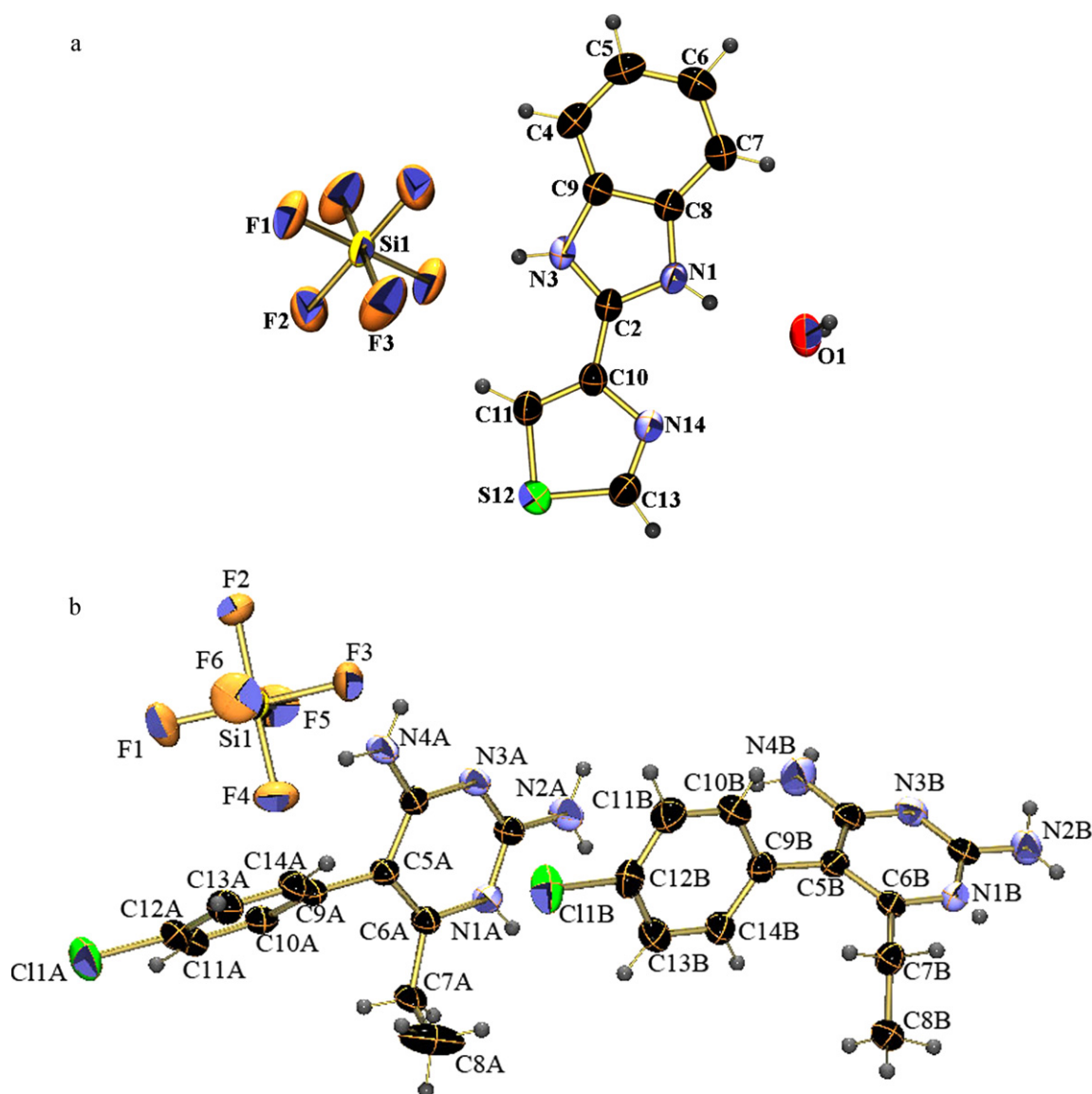


Fig. 1. (a and b) ORTEP view of **1** and **2**, Ellipsoids for non-hydrogen atoms are drawn at the 50% probability level (CCDC-210448 for **1** and CCDC-210449 for **2**). Labeled atoms are in the asymmetric unit.

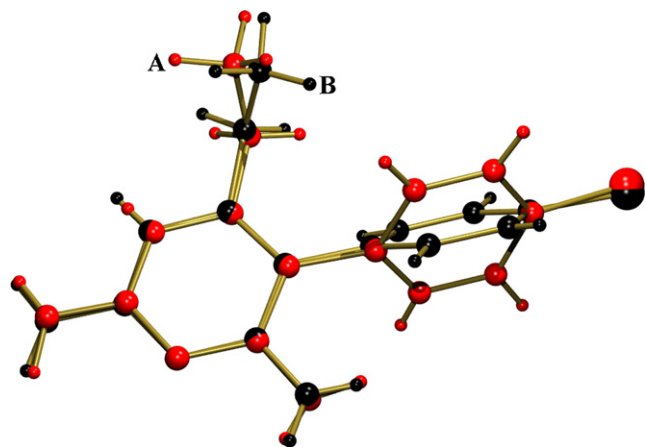


Fig. 2. View of superimposed pyrimidine rings of molecule A and B in compound **2** (molecule A is colour coded in red and molecule B in black. All the bonds are showed in bronze metallic colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

compounds (**1** and **2**) were crystallized in the triclinic system. The crystal data for the compounds are given in Table 1. ORTEP [40] views of the compounds (**1** and **2**) are shown in Fig. 1. In compound **1**, the asymmetric unit consists of a protonated TB moiety, a water molecule and one half of the SiF_6^{2-} anion. The nitrogen atom of the benzimidazole ring (N1) rather than that of the thiazole ring is protonated. The protonation leads to equalization of the bond angles at the two nitrogen atoms (N1 and N3) of the benzimidazole group in contrast to the benzimidazole group present in the crystal structure of free TB where the two angles are different [42]. The internal angle at N1, C2–N1–C8 has increased to $109.2(2)^\circ$ as compared to $103.8(1)^\circ$ in neutral TB [42]. The dihedral angle between the benzimidazole and thiazole ring planes is $2.20(1)^\circ$. This value indicates that, as in neutral TB, the protonated ligand also maintains a near coplanar geometry. The C–C distance of the bond connecting the two rings systems (C2–C10) has a value of $1.441(4) \text{ \AA}$ as in neutral TB where the corresponding value is $1.442(1) \text{ \AA}$. This value which is shorter than the ideal C–C bond length of $1.521(6) \text{ \AA}$ suggests appreciable delocalisation across this bond.

In compound **2**, the asymmetric unit contains two crystallographically independent protonated PMN cations and a hexafluorosilicate SiF_6^{2-} anion. The atom label with suffix A is PMN molecule A and with suffix B is PMN molecule B. Both the PMN moieties are protonated at N1 of the pyrimidine ring. The internal angles at N1 positions have increased as compared to neutral PMN moiety [from $116.3(2)$ (molecule A) and $116.1(2)$ (molecule B) in neutral PMN to $122.2(3)^\circ$ (molecule A) and $122.4(4)^\circ$ (molecule B) in compound **2**] [45]. This enhancement of the internal angle at N1 due to protonation compared to that of the neutral molecule has been observed in other crystals of pyrimethamine salts [26,27].

The two angles, torsion and dihedral, are important for the conformation of PMN moieties. The torsion angle, C5–C6–C7–C8, represents the deviation of the ethyl group from the pyrimidine plane and the values are $-78.8(6)$ and $104.5(4)^\circ$ for molecule A and molecule B, respectively. These values clearly indicate the flexibility of ethyl group in the present crystal structure. The dihedral angle between pyrimidine and phenyl rings is $58.1(2)^\circ$ in molecule A, and the corresponding angle in molecule B is $68.5(2)^\circ$. The flexibility of ethyl and phenyl groups in PMN moieties is shown in Fig. 2. In order to find the flexibility of ethyl and phenyl groups, we have analysed distribution of the related torsion and dihedral angles available in the CSD version 5.29 (November 2007) [43]. The histograms shown in Fig. 3 imply the ethyl and phenyl groups have different conformations. The torsion angle values

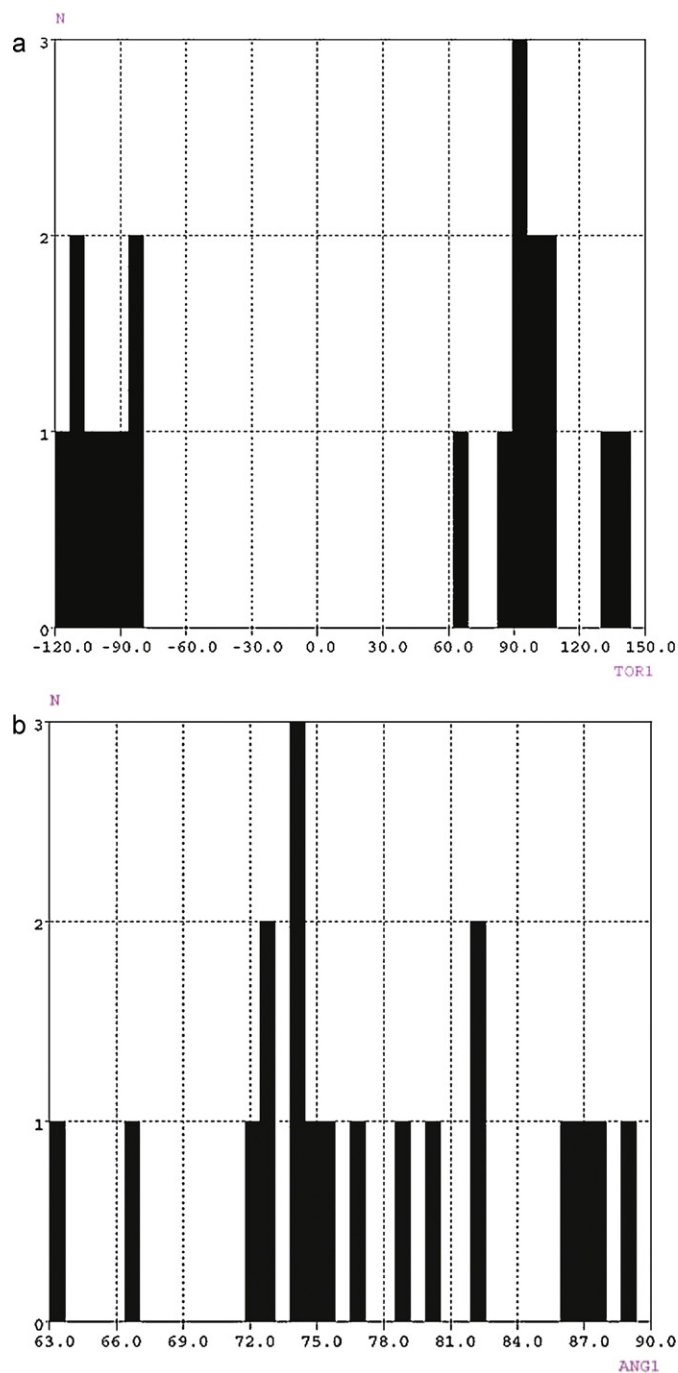


Fig. 3. Histograms showing distribution of torsion (C5–C6–C7–C8) (a) and dihedral (b) angles of pyrimethamine moieties retrieved from CSD.

range from -75° to -120° and 62° to 140° and the dihedral angle values range from 63 to 89° . Modeling studies of DHFR–PMN complexes indicate that only the dihedral angle plays an important role in proper docking of the drug molecule in the active site of the enzyme [44]. They also found that the orientation of the ethyl group does not affect the over all binding energy of the enzyme drug complex. In the recently reported crystal structure of PMN–DHFR complex, the dihedral angle between pyrimidine and phenyl rings is 66.9° and the ethyl torsion angle is -108.5° . This dihedral angle value is in close agreement with the conformation of molecule B in the present crystal structure [25].

The Si–F bond lengths are particularly equal and adopt the values 1.695 \AA , $1.655(2) \text{ \AA}$ and $1.669(3) \text{ \AA}$ in compound **1** and the

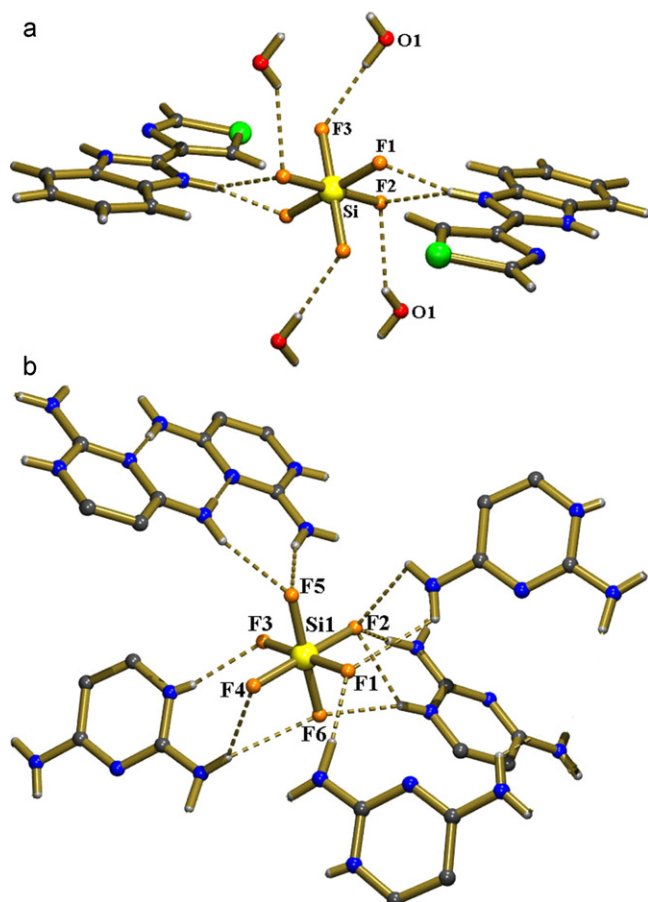


Fig. 4. (a) SiF_6^{2-} anion holding four water molecules and two TB cations in compound **1** (b) SiF_6^{2-} anion holding six pyrimethamine moieties in compound **2** (ethyl and phenyl groups are omitted for clarity).

values range from 1.657 to 1.692 Å in compound **2**. These values are very similar to the recently reported hexafluorosilicate anion containing crystal structures [36–38]. The SiF_6^{2-} anion in **1** and **2** shows small deviations from ideal octahedral geometry. This small

Table 2
Bond lengths (Å) and angles (°) of SiF_6 moiety for **1** and **2**.

Compound (1)		Compound (2)	
F(1)–Si(1)	1.695(2)	F(1)–Si(1)	1.671(3)
F(2)–Si(1)	1.655(2)	F(2)–Si(1)	1.692(3)
F(3)–Si(1)	1.669(2)	F(3)–Si(1)	1.685(3)
F(2)–Si(1)–F(3)	90.86(13)	F(4)–Si(1)	1.657(3)
F(2)–Si(1)–F(1)	89.33(10)	F(5)–Si(1)	1.664(3)
F(3)–Si(1)–F(1)	90.74(10)	F(6)–Si(1)	1.685(3)
		F(4)–Si(1)–F(5)	93.38(16)
		F(4)–Si(1)–F(1)	91.19(16)
		F(5)–Si(1)–F(1)	91.31(16)
		F(4)–Si(1)–F(3)	89.80(15)
		F(5)–Si(1)–F(3)	89.39(17)
		F(1)–Si(1)–F(3)	178.75(14)
		F(4)–Si(1)–F(6)	89.24(16)
		F(5)–Si(1)–F(6)	177.29(14)
		F(1)–Si(1)–F(6)	89.35(15)
		F(3)–Si(1)–F(6)	89.91(16)
		F(4)–Si(1)–F(2)	177.42(13)
		F(5)–Si(1)–F(2)	88.63(16)
		F(1)–Si(1)–F(2)	90.38(15)
		F(3)–Si(1)–F(2)	88.61(14)
		F(6)–Si(1)–F(2)	88.74(16)

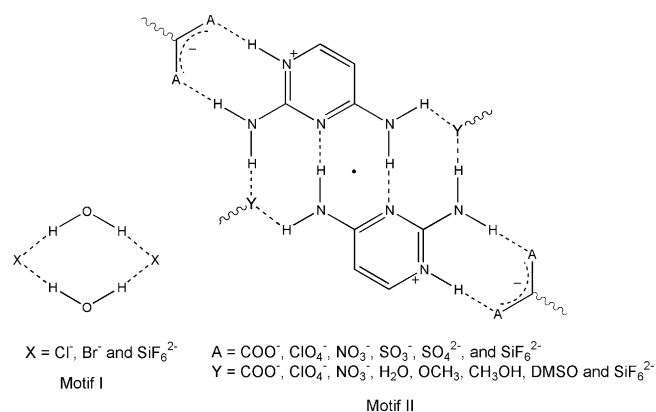


Fig. 5. Schematic representation of predominant hydrogen-bonded motifs observed in compounds **1** and **2** [motif I; X=Cl[−] or Br[−]; 8-membered cyclic hydrogen-bonded cluster, X= SiF_6^{2-} ; 12-membered cyclic hydrogen-bonded cluster, motif II; complementary DADA array of supramolecular motif in 2,4-diaminopyrimidine salts].

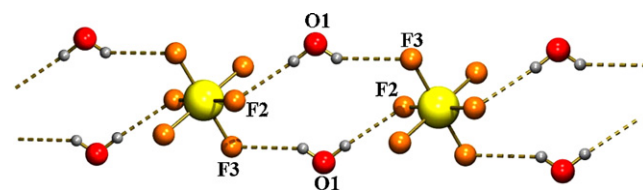


Fig. 6. Hydrogen-bonded supramolecular chain in compound **1**.

distortion of SiF_6^{2-} is due to the involvement of all the fluorine atoms in hydrogen bonding (Fig. 4). The bond lengths and angles of SiF_6 anion are shown in Table 2.

In the crystal structure of **1**, a water molecule and a half of the SiF_6^{2-} anion are the building blocks. Here SiF_6^{2-} anion lies at the inversion center. 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 [with graph set notation $R_4^4(12)$] [motif I (X = SiF_6^{2-})] (Fig. 5). The recent Cambridge Structural Database (CSD) study reveals predominant cyclic hydrogen bonded clusters [motif I (X = Cl and Br)] leading to channel hydrates [46]. This cluster yielded 390 and 72 hits for X = Cl and Br, respectively. Even though the size of SiF_6^{2-} anion is bigger than the halide ions, this motif was observed in compound **1**, which is more interesting for crystal engineering. Since SiF_6^{2-} has very good acceptor capability, the hydrogen bonded cluster motif I (X = SiF_6^{2-}) is self-organized to form a supramolecular chain (Fig. 6). Whereas in the previous study, the cyclic hydrogen-bonded cluster motif I (X = Cl[−] or Br[−]) is involved to form hydrogen-bonded quadrilaterals, pentagons and alternate quadrilaterals-hexagons [46,47]. The formation of supramolecular chain involving SiF_6^{2-} anion and water molecules has already been observed in hexafluorosilicate salts [48,49]. In compound **1**, two such chains are interconnected by inversely related protonated TB cations arranged in an alternate manner by N–H...O hydrogen bonds leading to a supramolecular 2D-layered pattern. A view of this hydrogen bonding pattern observed in **1** is shown in Fig. 7. The almost same type of 2D-layered structure has also been observed in the crystal structure of tetramethylethylenediammonium salt [48]. The only difference is that two chains are interconnected by inversely related tetramethylethylenediammonium ions instead of TB cations.

The crystal structure of compound **2** was studied for an important reason, which is as follows. In general, the 2,4-diaminopyrimidine salts have been stabilized by oxygen-mediated DADA (D and A represent donor and acceptor, respectively) array

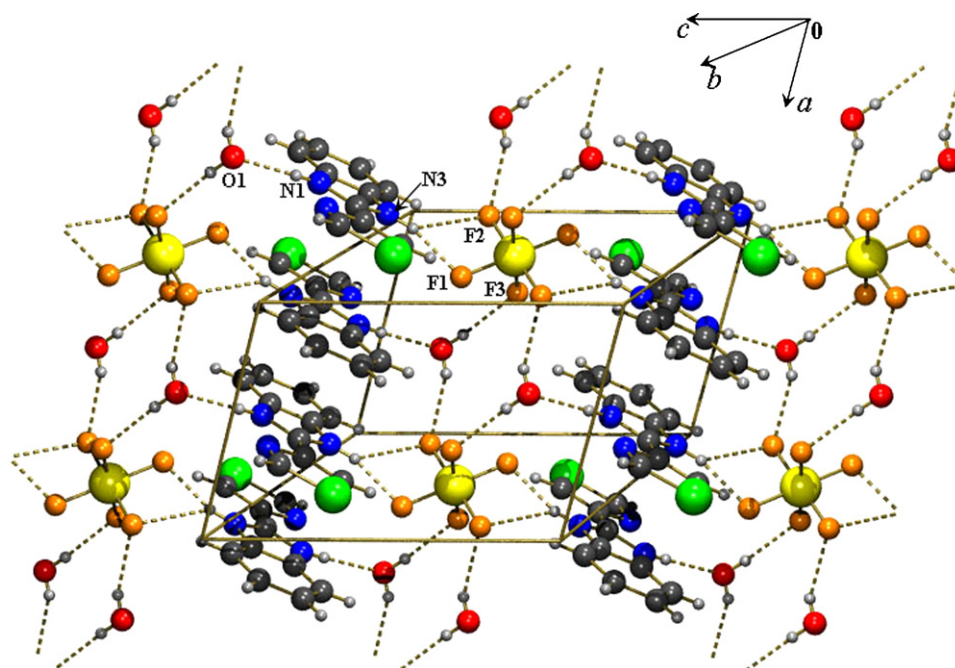


Fig. 7. Hydrogen-bonded supramolecular pattern in compound **1** (view along *ab* plane).

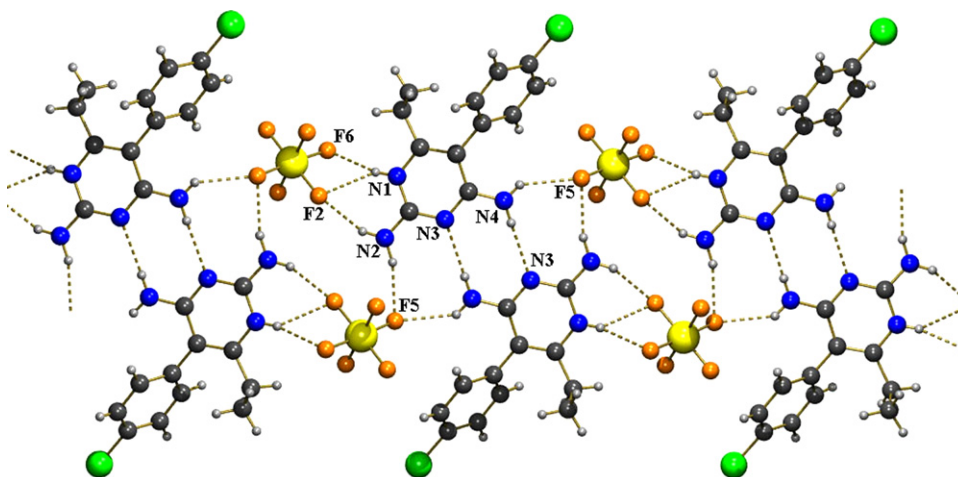


Fig. 8. Hydrogen-bonded supramolecular ladder involving pyrimethamine moiety A and SiF_6^{2-} anion in compound **2** (view along *a* axis).

motif II (Fig. 5) with combination of $\text{N-H} \cdots \text{N}$ and $\text{N-H} \cdots \text{A}$ [A may be a oxygen atom of groups like $\text{COO}^-/\text{ClO}_4^-/\text{NO}_3^-/\text{SO}_3^-/\text{SO}_4^{2-}/\text{BF}_4^-$] and $\text{N-H} \cdots \text{Y}$ [Y may be a oxygen atom of groups like $\text{COO}^-/\text{ClO}_4^-/\text{NO}_3^-/\text{H}_2\text{O}/\text{OCH}_3/\text{CH}_3\text{OH}/\text{DMSO}$] hydrogen bonds, which is a robust synthon [26–28,33,50]. Our aim is to investigate the A and Y atoms could be fluorine (F) atoms of the SiF_6^{2-} anion or not. Interestingly in the crystal structure of compound **2**, the same type of DADA array has been achieved. As a result, the presence of this DADA array motif again confirms that it is a robust synthon in the crystal structures of diaminopyrimidine salts [26–28,33].

It is interesting to note that two types of novel supramolecular 2D layers have been observed in **2**. One layer is made up of pyrimethamine moieties A and SiF_6^{2-} anions through $\text{N-H} \cdots \text{F}$ and $\text{N-H} \cdots \text{N}$ hydrogen bonds (Fig. 8). Alternatively it can be viewed as a self-organization of DADA motifs (Motif II). This layer contains a number of ring motifs, which can be represented by the graph set notation [$\text{R}_2^2(8)$, $\text{R}_1^2(4)$, $\text{R}_3^2(8)$, $\text{R}_2^2(8)$, $\text{R}_3^2(8)$ and $\text{R}_4^4(12)$]. These ring motifs are the building blocks of the first supramolecular 2D layer. The second layer is made up of pyrimethamine moieties B

and SiF_6^{2-} anions through $\text{N-H} \cdots \text{F}$ hydrogen bonds (Fig. 9). This layer contains a number of ring motifs, which can be represented by the graph set notation [$\text{R}_2^2(8)$, $\text{R}_1^2(4)$, $\text{R}_2^2(6)$, $\text{R}_4^2(16)$, and $\text{R}_4^4(12)$]. Thus, these ring motifs are the building blocks of the second supramolecular 2D layer. These two supramolecular layers criss-cross one another to form a 3D-network of hydrogen bonding pattern. The hydrogen-bonding geometries are given in Table 3. In addition, the π – π interaction also stabilizes the crystal structure of compound **1**. The distance between two benzimidazole rings is 3.531(2) Å. This interaction was not observed in compound **2**.

In general, SiF_6^{2-} has preferences as hydrogen bond acceptors and hence the compounds containing SiF_6^{2-} anion have several potential applications such as fluoridating agent in drinking water, conductivity of polymer electrolytes in batteries, and catalytic activity of porous materials in chemical synthesis [2,5,8,51–53]. In most of the compounds, the free SiF_6^{2-} anion acts either as guest or host lattice [51–53]. Thus, it can be predicted that the enhancement of further studies in identifying hydrogen bonded motifs and supramolecular patterns on SiF_6^{2-} containing compounds will

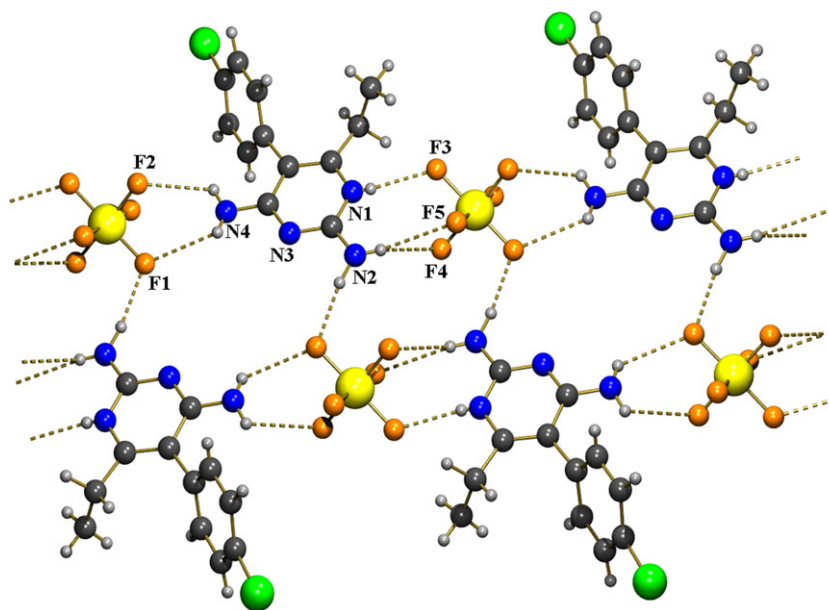


Fig. 9. Hydrogen-bonded supramolecular ladder involving pyrimethamine moiety B and SiF_6^{2-} anion in compound **2** (view along *b* axis).

Table 3
Geometries of the hydrogen bonds in **1** and **2**.

Compound no.	D–H...A	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	∠(D–H...A) (°)
1	N1–H1...O1	1.92(3)	2.718(4)	164(3)
	O1–H1A...F3 ^a	2.05(5)	2.832(4)	176(5)
	O1–H1B...F2 ^b	2.27(4)	2.881(5)	143(5)
	N3–H3...F1 ^c	1.95(3)	2.764(3)	164(3)
	N3–H3...F2 ^c	2.46(3)	3.092(3)	132(3)
	C11–H11...F1 ^c	2.37(3)	3.198(4)	143(2)
2	N1A–H1A...F2 ^d	2.33(4)	2.966(5)	135(4)
	N1A–H1A...F6 ^d	2.17(5)	2.959(6)	162(4)
	N1B–H1B...F3 ^e	2.13(5)	2.711(7)	168(6)
	N2A–H2A1...F2 ^d	2.19(4)	2.925(5)	145(5)
	N2A–H2A2...F5 ^c	2.16(4)	3.069(5)	164(4)
	N2B–H2B1...F4 ^e	2.42(4)	3.058(6)	137(3)
	N2B–H2B1...F6 ^e	2.53(5)	3.311(7)	165(3)
	N2B–H2B2...F1 ^f	2.00(5)	2.943(6)	170(5)
	N4A–H4A1...N3A ^c	2.30(4)	3.147(6)	172(4)
	N4B–H4B1...F2 ^c	2.53(6)	2.891(7)	106(5)
	N4A–H4A2...F5	2.26(5)	2.928(6)	140(4)
	N4B–H4B2...F1 ^c	2.49(8)	2.954(7)	118(6)
	C8B–H8B1...F3 ^e	2.48(6)	3.240(6)	132(4)

^a *x*, *y*, *−1* + *z*.

^b *1* + *x*, *y*, *−1* + *z*.

^c *−x*, *1* − *y*, *1* − *z*.

^d *x*, *1* + *y*, *z*.

^e *1* − *x*, *1* − *y*, *1* − *z*.

^f *x*, *1* + *y*, *1* + *z*.

bring forth a number of potential supramolecular synthons and interesting supramolecular patterns.

3. Conclusion

The two crystal structures (**1** and **2**) are dominated by the presence of fluorine mediated novel hydrogen bonding motifs. In compound **1**, the supramolecular chain has been achieved by twelve member cyclic hydrogen-bonded clusters. Two such chains are interconnected by inversely related protonated TB cations arranged in an alternate manner by N–H...O hydrogen bonds leading to a supramolecular 2D-layered pattern. Interestingly in the crystal structure of compound **2**, the DADA array motif (II) has been achieved similar to earlier reports. As a result, the presence of this DADA array motif again confirms that it is a robust synthon in

the crystal structures of diaminopyrimidine salts. In order to find out potential supramolecular synthons, further efforts will be directed to identifying hydrogen-bonded motifs in compounds containing SiF_6^{2-} anion with cations of different geometries. The knowledge base so evolved may be very useful for the design of novel functional materials.

4. Experimental

4.1. Preparation

Compounds **1** and **2** were prepared by adding a slightly excess quantity of aqueous hydrofluoric acid (HF) to a hot methanolic solution of thiabendazole (Merck, Sharp & Dohme Inc., USA) or pyrimethamine (Lupin Laboratories Ltd., India) taken in a glass beaker (hydrofluorosilicic acid was produced *in situ* by the reaction of HF with silica of glass). The solutions were allowed to cool to room temperature. Within few hours, colourless crystals were obtained.

4.2. X-ray crystallography

The data for compounds **1** and **2** were collected at 293 K on a Enraf-Nonius CAD4 diffractometer. In both the compounds, non-hydrogen atoms were located from a Fourier map and refined anisotropically. In compound **1**, all the hydrogen atoms were located from the difference Fourier map and were refined isotropically. In compound **2**, the ethyl hydrogen atoms of the PMN moiety B were fixed geometrically and refined using a riding model. All other hydrogen atoms were located from the difference Fourier map and were refined isotropically. Structure solution and refinement were carried out using the SHELX program [39]. The geometric parameters were calculated by the PLATON97 program [41].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.07.027.

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