# CrystEngComm

Accepted Manuscript






ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/crystengcomm

Journal Name

RSCPublishing

ARTICLE

# Dual modes of binding on hexafluorosilicate anion by a $C_3v$ symmetric flexible tripodal amide ligand in solid state

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

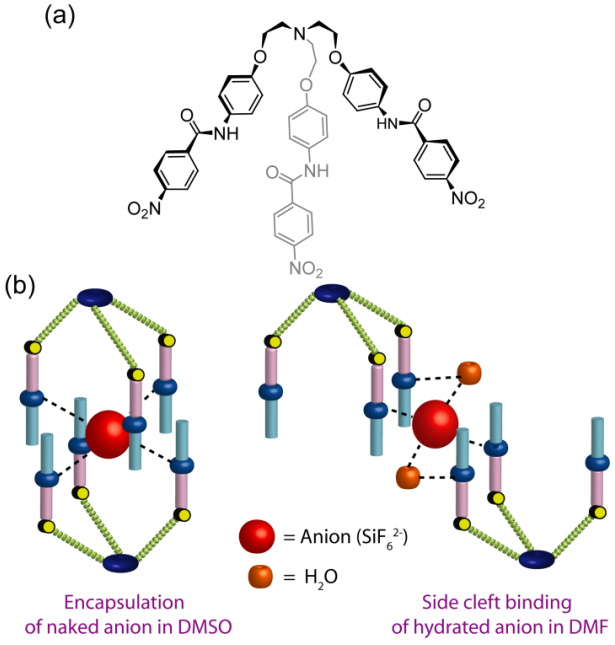
Arghya Basu, Romen Chutia, and Gopal Das*

A *para*-nitrophenyl functionalized $C_{3v}$ symmetric flexible tripodal amide ligand, **L**, shows remarkable solvent dependent dual binding behaviour towards the octahedral hexafluorosilicate anion in solid state. In DMSO solvent the ligand encapsulates a hexafluorosilicate anion within its dimeric capsular assembly, whereas in case of DMF solvent the ligand stabilizes the hexafluorosilicate anion *via* side cleft binding. The binding dissimilarities of hexafluorosilicate anion in the complexes are also confirmed by Hirshfield Surface analysis.

## Introduction

The field of anion coordination has developed rapidly in recent years and continues to expand because anions play important roles in many biological, environmental, and chemical processes.[1,2] Studies have shown that the coordination behavior of the anions less-well defined, therefore designing new receptors for anions is always challenging.[2] Further, it has already been established that, apart from the charge density of the anionic species, the spatial arrangement of the binding motif(s) in the receptor and geometry of the anions are play crucial role in the receptor–anion binding efficiency and specificity. One of the important criteria for recognition of anionic guest is to create a suitable cavity/cleft in the receptor designing to overcome the high solvation energy of anions. Although, recognition of hydrated anions is also important because in nature, anions exist mostly as its hydrated form.[3] Among the various anions, the binding and recognition of fluorosilicate is comparatively less well explored in literature.[4] However, recently selective binding and recognition/ encapsulation of fluorosilicate anions receives a special attention due to their immense environmental and biomedical impact.[5-7]

On the other hand, self-assembled supramolecular capsules that provide an isolated nanocavity have attracted much attention in recent years for unusual guest encapsulation.[8] Within the area of hydrogen bonding triggered self-assembly, numerous molecular capsules have been constructed by different laboratories *via* the self-assembly of various hydrogen bonding motifs such as calixarenes, glycoluril, resorcinarenes and tripodal derivatives, commonly in the presence of a ionic or neutral guests.[9] But, hydrogen-bonding interactions are weak noncovalent interactions that are strongly affected by external stimules like pH, nature of guest and solvent.[10] Therefore, by varying the solvent/pH/guest it should in principle be possible to reorient or rupture the self-assembled structure. [11]



**Scheme 1** (a) Molecular structure of $C_{3v}$ symmetric conformationally flexible tripodal amide ligand **L**; (b) Schematic representation of solvent dependent binding discrepancy of hexafluorosilicate anion by tripodal ligand **L**.

In our recent communication, we have shown encapsulation of chloride/bromide water cluster within the dimeric capsular assembly of the 4-nitrophenyl functionalized tripodal ligand, **L**.[3k] In a continuation of our previous effort, herein we have shown serendipitous solvent dependent dual binding modes on octahedral dianionic hexafluorosilicate anion by the same tripodal amide ligand **L** (Scheme 1). In case complex **1a**, obtained from DMSO solvent, the hexafluorosilicate anion is encapsulated within highly symmetric dimeric capsular assembly of the protonated ligand. While for complex **1b**, obtained from DMF solvent, side cleft binding of di-hydrated $SiF_6^{2-}$ anion with the ligand(s) is observed. To the best of our knowledge this report shows the first solid state structural evidence of solvent dependent binding dissimilarity of hexafluorosilicate anion by a simple tripodal ligand.

## Results and discussion

### Single Crystal X-ray Structural Analysis

**Hexafluorosilicate complex $[(LH)_2^+.SiF_6^{2-}]$ (1a).** Silicon hexafluoride salt **1a** was obtained on reaction of the tripodal ligand **L** with HF in DMSO, presumably as a result of glass corrosion (eq 1). The complex crystallizes in trigonal crystal system with centrosymmetric space group *R-3* with Z=3. Structural elucidation reveals that two units of protonated ligand $\mathbf{LH}^+$ which are flipped inward toward each other in a face-to-face fashion (dN1···N1 = 19.330 (8) Å) with both the ligands coordinating hexafluorosilicate anion exactly identical fashion and thereby, creating a caged supramolecular structure (Fig. 1). In complex **1a** all the three arms of the protonated ligand ($\mathbf{LH}^+$) are projected in one direction.

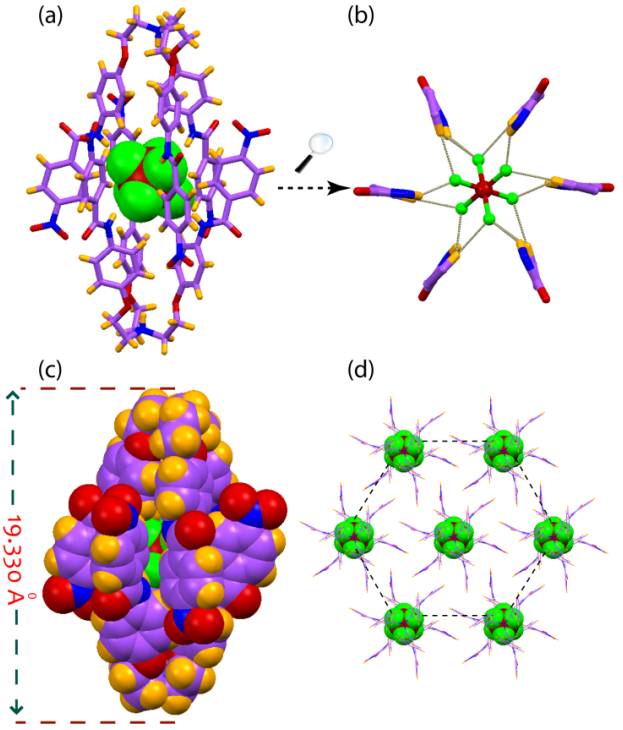



**Fig.1**(a) Hexafluorosilicate anion encapsulation by the crystalline self-assembled capsules $\mathbf{LH}^+$, Two molecules of $\mathbf{LH}^+$, shown as stick models, and hexafluorosilicate anion is shown as a space-filling model; (b) Magnified view showing coordination of $SiF_6^{2-}$ with six amide –NH and C–H···F (*ortho*-aryl hydrogen of nitro phenyl ring) within the dimeric capsule; (c) Space-filling representation depicting full encapsulation of the hexafluorosilicate anion; (d) Crystal packing in complex **1a**, as viewed down the crystallographic c axis.

$$6HF+SiO_2 = H_2SiF_6+2H_2O \quad (1)$$

The O-atoms of each aliphatic branch are equidistant (~2.71Å) from centrally bridged N-atom, indicative of hydrogen bonding interactions between the proton attached to central N-atom and O-atoms of each aliphatic branch. These hydrogen bonding interactions actually organizes the flexible arms in one direction. One *ortho*-hydrogen atom of the aromatic ring attached to ethereal oxygen atom of each branch are connected to similar aromatic ring of neighbouring arm through C−H···π interactions in a twisted edge-to-face fashion. The unidirectional arms of $\mathbf{LH}^+$ creates a perfect $C_3$ symmetric tripodal cavity and two symmetry independent molecules of $\mathbf{LH}^+$ with opposite orientation form a capsular nanocavity that encapsulates a dianionic hexafluorosilicate anion in its centre *via* H-bonds . Figure 1a and 1c represents $SiF_6^{2-}$ encapsulation within dimeric assembly of hexafluorosilicate anion behaves as a trifurcated hydrogen bond acceptor and each tripodal arm donates one N−H···F and two C−H···F (from *ortho* aryl hydrogen of nitro phenyl ring) hydrogen bonds resulting in eighteen H-bonds with an average donor-to-acceptor distance of 3.112 Å (Table 1). A similar type of hexaflurosilicate anion encapsulation by a Tris(2-aminoethyl)amine (tren) based pentafluorophenyl-substituted tripodal amine ligand was previously shown by Ghosh and co-worker.[4b] Interestingly, the hexafluorosilicate encapsulated dimeric cages are interlinked with one another through hydrogen-bonding interactions between the oxygen atom of a nitro group and one of the aryl hydrogen atoms of the phenyl ring attached to ethereal oxygen, with a separation distance of 2.48 Å, and which subsequently form a 1D chain capsular assembly along the crystallographic b axis. Two such 1D arrays of capsular assemblies are further interconnected with one another *via* similar C−H···O (nitro) interactions, and generate hexagonal networks of hexafluorosilicate encapsulated dimeric cages around each capsular unit along the c axis (Fig. 1d).

**Hexafluorosilicate complex, $[(L_3H)_2^+.SiF_6^-]\cdot 2DMF,4H_2O$ (1b).** Interestingly, another hexafluorosilicate complex with different cell parameter was grown from DMF solvent. Complex **1b** crystallizes in the triclinic space group *P-1* with two protonated ligand moieties along with one hexafluorosilicate anion, and two DMF and four water molecules as the solvents of crystallization (Fig. 2). The structural elucidation reveals a 2:1 ligand–anion stoichiometric

salt formation confirming the $SiF_6^{2-}$ complex of protonated **L**. Although, all the three arms of the protonated ligand ($\mathbf{LH}^+$) are projected in one direction, but the protonated ligand does not able to create $C_3$ symmetric tripodal cavity (Fig. S7 ESI†), which is evident from the difference in basal N···N distances of nitro groups (N3···N5=6.93Å, N5···N7=12.09Å, and N3···N7= 17.46Å) and, the $SiF_6^{2-}$anions in complex **1b** is located outside the

**Table 1** Hydrogen bonding contacts in complexes **1a** and **1b**.

| Complexes | D-H···O | *d*(H···O)/Å | *d*(D···O)/Å | ∠D-H···O/° |
|---|---|---|---|---|
| **1a** | N2H···F1 | 2.07 | 2.847(6) | 148.8(3) |
| | C15H···F1 | 2.41 | 3.210(8) | 144.0(4) |
| | C15H···F1 | 2.51 | 3.290(1) | 140.9(0) |
| **1b** | N4H···F1 | 2.08 | 2.820(4) | 156.0(3) |
| | C30HA···F1 | 2.65 | 3.511(4) | 152.9(2) |
| | C30HA···F3 | 2.47 | 3.306(5) | 148.8(2) |
| | C30HA···F2 | 2.66 | 3.424(4) | 139.3(2) |
| | C31HA···F1 | 2.50 | 3.371(3) | 149.1(2) |
| | C16HA···F2 | 2.25 | 3.057(4) | 139.3(2) |
| | C16HA···F3 | 2.60 | 3. 364 (5) | 135.3(2) |
| | O14H15O···F2 | 2.46 | 2.974(3) | 114.0(4) |
| | O14H15O···F3 | 2.07 | 3.010(4) | 171.0(5) |

tripodal cavity and stabilized mainly by N−H···F and C−H···F hydrogen bonds from the four ligand cations (Fig. 2b). Apart from these hydrogen bonds with the ligand cations, the hexafluorosilicate anion also forms O−H···F hydrogen bonds with two same symmetric lattice water molecules (O14). This water molecule (O14) further forms hydrogen bond with an amide function of $\mathbf{LH}^+$ and gets stabilized. The coordination environment of the $SiF_6^{2-}$ in complex **1b** is shown in Figure 2b. The detail coordination environment of $SiF_6^{2-}$ suggests that, it is stabilized *via* eighteen hydrogen bonding interactions with four ligand cations and two crystallizing water molecules, comprised of two N–H···F, four O–H···F (lattice water O14), 6-

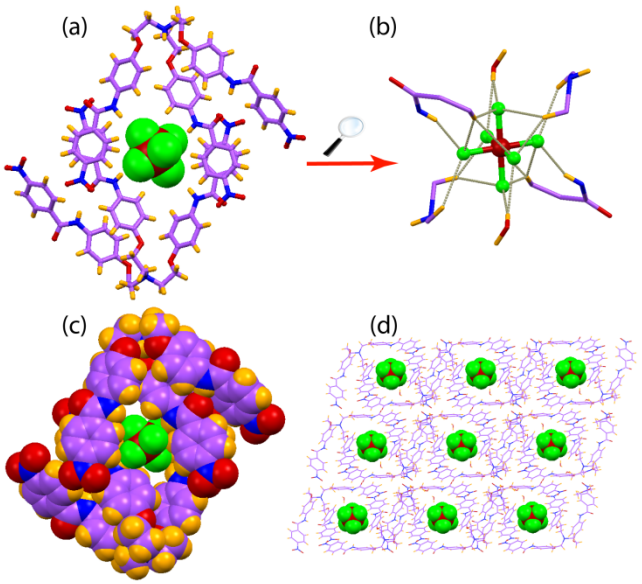



**Fig.2** (a) Showing molecular structure of hexafluorosilicate complex **1b**.Two molecules of $\mathbf{LH}^+$, shown as stick models, and hexafluorosilicate anion is shown as a space-filling model. Solvent molecules are omitted for clarity; (b) Magnified view showing coordination of hexafluorosilicate anion with four $\mathbf{LH}^+$ (only the interacting parts of the protonated ligands are shown) and two lattice water molecules; (c) Space-filling representation of complex **1b** depicting side cleft binding of $SiF_6^{2-}$ anion; (d) Crystal packing in complex **1b**, as viewed down the crystallographic c axis.

-$C_{Ar}$–H···F (*ortho* hydrogen of the nitro phenyl ring) and 6 $C_{Alp}$–H···F (from the acidic $-CH_2$ group, adjacent to the bridgehead protonated nitrogen atom of two neighbouring ligands) bonds having an average donor-to-acceptor distance of 3.18 Å (Table S1 ESI†). The $C_{Alp}$–H···F hydrogen bonding interactions from two neighbouring ligands eventually lead polymeric assembly of complex **1b** along crystallographic 'c' axis (Fig. 2d). Similar outer capsular binding of hexafluorosilicate anion by amide and urea based tripodal ligands were previously shown by Ghosh[4fg] and Hossain[4h] respectively. Interestingly, in complex **1b** one out of three amidic –NH protons of a $\mathbf{LH}^+$ moiety is neither involved in hydrogen bonding interactions with $SiF_6^{2-}$ anion nor with solvent molecules. Instead, it forms hydrogen bonds with the oxygen atom of an amide function of the next side arm of the same ligand molecule. Probably insertion of crystallizing solvent molecule (DMF and water) in complex **1b** prevents the formation of $SiF_6^{2-}$ encapsulated dimeric capsular assembly of protonated ligand $\mathbf{LH}^+$, as observed in complex **1a**. It is important to mention here that efforts have also been made to crystallize the fluoride complex of the ligand from Teflon vial, but in spite of several attempts, we were unable to form crystals.

Thus, by a mere change of crystallizing solvent, we have been able to isolate two structurally different $SiF_6^{2-}$ complexes (**1a** and **1b**). In complex **1a** $SiF_6^{2-}$ anion is encapsulated with in highly symmetric dimeric capsular assembly of $\mathbf{LH}^+$. It is important to note that the height of the capsule of **1a** is less compared to the previously reported halide (chloride and bromide) water cluster encapsulated capsular complexes of the same ligand (Fig. S6, ESI†).[3k] This suggest that the hexafluorosilicate anions fits better within the dimeric capsular assembly of **L**, compared to the halide water clusters. Whereas in case of **1b** the $SiF_6^{2-}$ anion is located outside the tripodal cavity and stabilized mainly by N−H···F and C−H···F hydrogen bonds from the four ligand cations. It is important to note in both the $SiF_6^{2-}$complexes (**1a** and **1b**) the $SiF_6^{2-}$ anion is present in its complementary octahedral environment and stabilized *via* 18 H-bonds, therefore it can be concluded that the optimal coordination number for $SiF_6^{2-}$ is 18 H-bonds.

The bulk phase purity of both the complexes was confirmed from PXRD data. The diffraction patterns of **1a** and **1b** are completely different and match closely with their individual simulated PXRD patterns, obtained from single crystal X-ray structures (Fig. S7 ESI†). Moreover, in FT-IR spectra the small but significant difference in Si−F stretching frequencies between complex **1a** and complex **1b** also suggest the hydrogen bonding coordination modes of $SiF_6^{2-}$ anion in the complexes are not identical (Fig. S2 and S4 ESI†).

### Hirshfield Surface Analysis of 1a and 1b

The binding dissimilarities of $SiF_6^{2-}$ anion between complex **1a** and complex **1b** have also been visualized by Hirshfeld surface analysis, which is a useful tool to describe the surface properties of molecules.[12] Hirshfeld surfaces basically offer a unique way of visualizing intermolecular interactions by colour-coding short or long contacts the colour intensity indicating the relative strength of the interactions. While, two dimensional fingerprint plots complement these surfaces, quantitatively summarizing the type and nature (strong or weak) of intermolecular interactions experienced by the molecules in the crystal as ''contact contribution''.

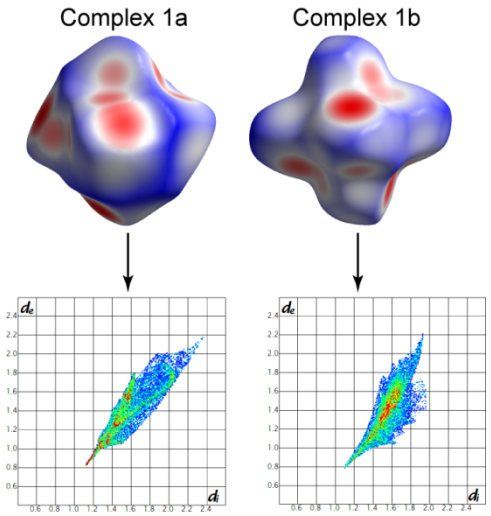



**Fig. 3** Hirshfeld surface analysis of complex **1a** and complex **1b**, showing the dnorm surfaces of the hexafluorosilicate anion and the corresponding 2D fingerprint plots with the H···F interactions.

Figure 3 represents the Hirshfeld surfaces of the hexafluorosilicate anion mapped with $d_{norm}$ for complex **1a** and **1b**, and the corresponding 2D fingerprint plots for the H···F close contacts. In the case of complex **1a** the large dark red spots on the $d_{norm}$ surface can be attributed to N−H···F interaction which appears as a sharp spike ($d_i$ −1.117 and $d_e$ − 0.831) in the fingerprint plot. Beside these dark spots the presence of faint red spots of the Hirshfeld surface can be assigned to weak C−H···F interactions. It is important to mention the symmetric distribution of the red spots over the Hirshfeld surface of hexafluorosilicate anion clearly indicates that the $SiF_6^{2-}$ anion present in highly symmetrical environment in which hydrogen bonding coordination modes of all the fluorine atoms are identical. For complex **1b** the presence of three large dark red spots on the $d_{norm}$ surface can be assigned for N−H···F and O−H···F (from water) interactions which together appear as a sharp spike ($d_i$ − 1.097 and $d_e$ − 0.786) in the fingerprint plot. Apart from that the presence of faint red spots of the Hirshfeld surface can be assigned to weak C−H···F interactions. Thus the detail comparison of the Hishfield surfaces and corresponding fingerprint plots of hexafluorosilicate anion between the two complexes clearly indicates that the hydrogen bonding coordination mode of hexafluorosilicate anion in complex **1a** is completely different than in complex **1b**.

## Conclusions

In conclusion, we have structurally authenticated the solvent dependent dual binding modes on hexafluorosilicate anion by a $C_{3v}$ symmetric tripodal amide ligand **L**, where solvent polarity and flexible ligand geometry play critical role. X-ray crystallography analyses revealed the formation of $SiF_6^{2-}$ encapsulated dimeric capsular assembly of the ligand only when the complex was crystallized from DMSO solvent. Whereas, crystallizing the $SiF_6^{2-}$ complex from DMF solution showed side cleft binding of di-hydrated $SiF_6^{2-}$ anion. The detailed Hirshfeld surface analysis of the hexafluorosilicate anion in the complexes also supports the solvent dependent dual binding behaviour of the ligand towards $SiF_6^{2-}$ anion. Thus, ligand **L** provides an ideal example of a $SiF_6^{2-}$ binding ligand which has unique ability to change its binding mode towards $SiF_6^{2-}$ anion according to the crystallizing environment.

## Experimental section

### Materials and methods

All reagents and solvents were obtained from commercial sources and used as received without further purification. Tetrabutylammonium (*n*-TBA) salts used were purchased from Sigma-Aldrich and used as received. Solvents for synthesis and crystallization experiments were purchased from Merck-India and used as received. $^1$H NMR spectra were recorded on a Varian FT-400 MHz instrument, and chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) or residual solvent peak as a reference, and $^{13}$C spectra were recorded at 100 MHz on the same instrument. The FT-IR spectra of air-dried samples were recorded on a Perkin-Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000−450 cm$^{-1}$.

### X-ray Crystallography

In each case, a crystal of suitable size was selected from the mother liquor and immersed in silicone oil, and it was mounted on the tip of a glass fibre and cemented using epoxy resin. The intensity data was collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) at 298 K, with increasing $\omega$ (width of 0.3° per frame) at a scan speed of 5 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP[13] software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.[14] Structures were solved by direct methods using SHELXS-97[15] and refined with full-matrix least-squares on $F^2$ using SHELXL-97.[16] Graphics are generated using MERCURY 3.0.[17] In all cases, non-hydrogen atoms are treated anisotropically.

Wherever possible, the hydrogen atoms are located on a difference Fouriermap and refined. In other cases, the hydrogen atoms are geometrically fixed. PLATON/SQUEEZE[18] was performed to refine the host framework in **1a** excluding the disordered solvent electron densities.Usually, temperature factors of H-atoms attached to carbon atoms are refined by restraints −1.2 or −1.5 Uiso (C), although the isotropic free refinement is also acceptable. Parameters for data collection and crystallographic refinement details of isolated anion complexes are summarized in Table 2. It is important to mention that the wR2 value of complex **1a** is comparatively higher. The high wR2 value (31%) for complex **1a** is due to poor data quality. The situation did not improve even after recrystallization and fresh data collection. However, the reported data is the best possible data set for complex **1a**.

**Table 2** Crystallographic parameters and refinement details.

| Parameters | Complex **1a** | Complex **1b** |
|---|---|---|
| CCDC | 973073 | 973074 |
| Formula | $C_{90}H_{80}F_6N_{14}O_{24}Si$ | $C_{96}H_{102}F_6N_{16}O_{30}Si$ |
| Fw | 1883.77 | 968.76 |
| Crystal system | Trigonal | Triclinic |
| Space group | *R -3* | *P-1* |
| a/Å | 13.3641(7) | 13.1197(5) |
| b/Å | 13.3641(7) | 13.1321(6) |
| c/Å | 45.517(3) | 15.7929(6) |
| α/° | 90.00 | 108.655(2) |
| β/° | 90.00 | 105.033(2) |
| γ/° | 120 | 92.632(2), |
| V/Å$^3$ | 7040.2(6) | 2464.94(17) |
| Z | 3 | 1 |
| Dc/g cm$^{-3}$ | 1.333 | 1.416 |
| μ Mo $K_α$/mm$^{-1}$ | 0.118 | 0.125 |
| T/K | 298(2) | 298(2) |
| θ max. | 20.79 | 20.99 |
| Total no.of reflections | 10351 | 30365 |
| Independent reflections | 3736 | 11455 |
| Observed reflections | 2030 | 9244 |
| Parameters refined | 206 | 708 |
| $R_1$, I > 2σ(I) | 0.0472 | 0.0608 |
| $wR_2$ (all data) | 0.3140 | 0.1831 |
| GOF ($F^2$) | 1.057 | 0.830 |

**Synthesis and Characterization**

See reference no. 3k for the synthesis of the ligand, **L**.

**Hexafluorosilicate complex $[(LH)_2^+.SiF_6^{2-}]$ (1a).** Hexafluorosilicate encapsulated complex of the ligand was obtained by adding 0.5 mL of 40% hydrofluoric acid (HF) to a 5 mL dimethylsulfoxide (DMSO) solution of **L** (100 mg, 0.12 mmol). After the addition of HF, the solution was stirred for about 1 hr and was allowed to slowly evaporate at room temperature, which yielded dark yellow block shaped crystals suitable for XRD analysis within a week. Yield 66%.

Melting point: 165-166°C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ (ppm): 10.44 (s, 3N–H), 8.33 (d, $J$ = 7.2 Hz, 6H), 8.14 (d, $J$ = 7.6 Hz, 6H), 7.66 (d, $J$ = 7.2 Hz 6H), 6.96 (d, $J$ = 7.2 Hz, 6H) 4.18 (s (br), 6H) and 3.30 (s (br), 6H) FT-IR (ν, cm$^{-1}$): 1345 ($NO_2$), 1671 (C=0), 3286 (N–H) and 719 (Si−F).

**Hexafluorosilicate complex, $[(LH)_2^+.SiF_6^-]\cdot 2DMF,4H_2O$ (1b).** Another hexafluorosilicate complex of the ligand was obtained by adding 0.5 mL of 40% hydrofluoric acid (HF) to a 5 mL dimethylformamide (DMF) solution of **L** (100 mg, 0.12 mmol). After the addition of HF, the solution was stirred for about 1 hr and was allowed to slowly evaporate at room temperature, which yielded dark yellow block shaped crystals suitable for XRD analysis within a week. Yield 69%.

Melting point: 165-166°C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ (ppm): 10.44 (s, 3N–H), 8.33 (d, $J$ = 8.4 Hz, 6H), 8.15 (d, $J$ = 8.8 Hz, 6H), 7.94 (s, 1H, DMF solvent), 7.66 (d, $J$ = 7.6 Hz, 6H), 6.95 (d, $J$ = 7.4 Hz, 6H), 4.08 (s (br), 6H), 3.07 (s (br), 6H) 2.88 (s, 3H, DMF solvent) and 2.72 (s, 3H, DMF solvent). FT-IR (ν, cm$^{-1}$): 1339 ($NO_2$),1653 (C=O) and 711 (Si−F).

## Acknowledgements

G.D. gratefully acknowledges Council of Scientific and Industrial Research (01/2727/13/EMR-II) and Science & Engineering Research Board (SR/S1/OC-62/2011), New Delhi, India, for financial support. We thank CIF, IIT Guwahati and DST-FIST for providing instrument facilities. A.B. thanks IIT Guwahati for fellowship.

## Notes and references

[a] *Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India. Fax: +91 0361 2582349; Tel: +91 361 258231 E-mail: gdas@iitg.ernet.in;*

† Electronic Supplementary Information (ESI) available: Characterization spectra of the complexes, optical images of the crystals and crystallographic figures. See DOI: 10.1039/b000000x/

1 (*a*) J. L. Sessler, P. A. Gale and W.-S. Cho, Anion Receptor Chemistry, Cambridge, 2006; (*b*) P. D. Beer and P. A. Gale, *Angew. Chem*., 2001, **113**, 502–532; *Angew. Chem. Int. Ed*., 2001, **40**, 486–516; (*c*) P. A. Gale, *Acc. Chem. Res*., 2006, **39**, 465–475; (*d*) E. A. Katayev, Y. A. Ustynyuk and J. L. Sessler, *Coord. Chem. Rev*., 2006, **250**, 3004–3037; (*e*) P. A. Gale, S. E. García-Garrido, J. Garric, *Chem. Soc. Rev*., 2008, **37**, 151–190; (*f*) for recent reviews on anion chemistry, see a thematic issue: *Chem. Soc. Rev*. 2010, 3581 –4008.

2 (*a*) J. M. Lehn, *Acc. Chem. Res*., 1978, **11**, 49–57; (*b*) J. M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995; (*c*) K. Bowman-James, *Acc. Chem. Res*. 2005, **38**, 671–678; (d) Anion Coordination Chemistry (Eds.: K. Bowman-James, A. Bianchi, E. García-Espaňa) Wiley-VCH, Weinheim, 2011.

3 (*a*) M. Cametti and K. Rissanen, *Chem. Commun*., 2009, 2809–2829; (*b*) T.W. Hudnall, C.-W. Chiu and F. P. Gabbai, *Acc. Chem. Res*., 2009, **42**, 388–397; (*c*) M. Cametti and K. Rissanen, *Chem. Soc. Rev*., 2013, **42**, 2016−2038. (*d*) Q.-Q. Wang, V. W. Day and K. Bowman-James, *J. Am. Chem. Soc*., 2013, **135**, 392−399; (*e*) Q.-Q.Wang,V. W. Day and K. Bowman-James, *Angew. Chem*., *Int. Ed*., 2012, **51**, 2119−2123; (*f*) M. A. Saeed, A. Pramanik, B.M. Wong, S. A. Haque, D. R. Powell, D. K. Chand and M. A. Hossain, *Chem. Commun*., 2012, **48**, 8631−8633; (*g*) M. A. Hossain, M. A. Saeed, A. Pramanik, B. M. Wong, S. A. Haque and D. R. Powell, *J. Am. Chem. Soc*., 2012, **134**, 11892−11895; (*h*) M. Arunachalam and P. Ghosh, *Chem. Commun*., 2011, **47**, 6269−6271; (*i*) M. Arunachalam and P. Ghosh, *Chem. Commun*., 2009, 5389−5391; (*j*) S. Dalapati, M. A. Alam, R. Saha, S. Jana and N. Guchhait, *CrystEngComm*, 2012, **14**,

1527−1530; (*k*) A.Basu and G.Das, *Chem. Commun*., 2013, **49**, 3997−3999; (*l*) M. N. Hoque, A. Basu, and G. Das *Cryst. Growth Des*., 2012, **12**, 2153–2157; (*m*) . N. Hoque, A. Basu, and G. Das *Supra. Chem*., doi:10.1080/10610278.2013.844811.

4 (*a*) A. S. Degtyarenko, E. B. Rusanov, A. Bauzá, A. Frontera, H. Krautscheid, A. N. Chernega, A. A. Mokhire and K. V. Domasevitch, *Chem. Commun*., 2013, **49**, 9018−9020 (*b*) P. Bose, I. Ravikumar, and P. Ghosh, *Inorg. Chem*., 2011, **50**, 10693−10702; (*c*) I. Ravikumar, P. S. Lakshminarayanan, E. Suresh, and P. Ghosh *Beilstein J. O. Chem.,* 2009, **5**, 1−8; (*d*) Y-P. Xie, S. A. Al-Thabaiti and T. C.W. Mak, *J. Mol.Sturct*., 2013, **1048**, 121−123; (*e*) M. Maekawa, S. Kitagawa, T. K.-Sowac and M. Munakata, *Chem. Commun*., 2006, 2161−2163; (f) I. Ravikumar, P.S. Lakshminarayanan and P. Ghosh *Inorg. Chim. Acta*., 2010, **310**, 2886-2895; (g) P. S. Lakshminarayanan, E. Suresh, and P. Ghosh *Inorg. Chem*., 2006, **45**, 10693−10702; (h) A. Pramanik, D. R. Powell, B. M. Wong, and Md. A. Hossain *Inorg. Chem*., 2012, **51**, 4274−4784.

5 (*a*) N. T. Crosby, *J. Appl. Chem*., 1969, **19**, 100−102; (*b*) R. D. Masters and M. J. Coplan, *Int. J. Environ. Stud*., 1999, **56**, 435−449.

6 (*a*) A. Knappwost and J. Westendorf, *Naturwissenschaften*, 1974, **61**, 274; (*b*) B. Machalinski, M. Baskiewicz-Masiuk, B. Sadowska, A. Machalinska, M. Marchlewicz, B. Wiszniewska and I. Stecewicz, *Fluoride*, 2003, **36**, 231−240.

7 E. T. Urbansky, *Chem. Rev*., 2002, **102**, 2837−2854.

8 (*a*) F. Hof, S. L. Craig, C. Nuckolls and J. Rebek, Jr., *Angew. Chem*., *Int. Ed*., 2002, **41**, 1488−1508; (*b*) S. R. Seidel and P. J. Stang, *Acc. Chem. Res*., 2002, **35**, 972−983; (*c*) M. Fujita, M. Tominaga, A. Hori and B. Therrien, *Acc. Chem. Res*., 2005, **38**, 369−378; (*d*) Y. Yamauchi and M. Fujita, *Chem. Commun*., 2010, **46**, 5897−5899; (*e*) K. Ikemoto, Y. Inokuma and M. Fujita, *Angew. Chem*., *Int. Ed*., 2010, **49**, 5750−5752; (*f*) M. Yoshizawa, J. K. Klosterman and M. Fujita, *Angew. Chem*., *Int. Ed*., 2009, **48**, 3418−3438.

9 (*a*) T. Martin, U. Obst and J. Rebek, Jr., *Science*., 1998, **281**, 1842−1845; (*b*) J. Rebek, Jr., *Chem. Commun*., 2000, 637−643; (*c*) B. M. O'Leary, T. Szabo, N. Svenstrup, C. A. Schalley, A. Lutzen, M. Schafer and J. Rebek, Jr., *J. Am. Chem. Soc*., 2001, **123**, 11519−11533; (*d*) M.W. Heaven, G. W. V. Cave, R. M. McKinlay, J. Antesberger, S. J. Dalgarno, P. K. Thallapally and J. L. Atwood, *Angew. Chem*., *Int. Ed*., 2006, **45**, 6221−6224; (*e*) M. Alajarin, R.-A. Orenes, J. W. Steed and A. Pastor, *Chem. Commun*., 2010, **46**, 1394−1403; (*f*) M. Alajarin, A. Pastor, R.-A. Orenes, A. E. Goeta and J. W. Steed, *Chem. Commun*., 2008, 3992−3994; (*g*) H. Mansikkamaki, M. Nissinen and K. Rissanen, *Chem. Commun*., 2002, 1902−1903; (*h*) R. Custelcean, P. Remy, P. V. Bonnesen, D.-E. Jiang and B. A. Moyer, *Angew. Chem*., *Int. Ed*., 2008, **47**, 1866−1870; (*i*) C. Jia, B. Wu, S. Li, X. Huang, Q. Zhao, Q.-S. Li and X.-J. Yang, *Angew. Chem*., *Int. Ed*., 2011, **50**, 486−490; (*j*) N. Busschaert, M. Wenzel, M. E. Light, P. Iglesias-Hernandez, R. Perez-Tomas and P. A. Gale, *J. Am. Chem. Soc*., 2011, **133**, 14136−14148; (*k*) S. K. Dey and G. Das, *Dalton Trans*., 2011, **40**, 12048−12051;(*l*) A. Basu and G. Das, *Dalton Trans*., 2012, **41**, 10792–10792; (*m*) S. K. Dey and G. Das, *DaltonTrans*., 2011, **41,** 8960–8972; (n) A. Basu and G. Das, *J.Org.Chem*., DOI: 10.1021/jo500102e.

10 J. M. Lehn, Supramolecular Chemistry Concepts and Perspectives, VCH, Weinheim, 1995.

11 (*a*) M. Arunachalam and P. Ghosh *Chem. Commun*., 2009, 3184–3186; (*b*) A. S. Singh and S-S. Sun *Chem. Commun*., 2011, **47**, 8563–8565.

12 (*a*) M. A. Spackman and P. G. Byrom, *Chem. Phys. Lett*., 1997, **267**, 215–220; (*b*) J. J.McKinnon, A. S. Mitchell and M. A. Spackman, *Chem.–Eur. J*., 1998, **4**, 2136–2141; (*c*) T. E. Clark, M. Makha, A. N. Sobolev and C. L. Raston, *Cryst. Growth Des*., 2008, **8**, 890–896; (*d*) J. J. McKinnon, D. Jayatilaka and M. A. Spackman, *Chem. Commun*., 2007, 3814–3816; (*e*) P. A. Wood, J. J. McKinnon, S. Parsons, E. Pidcock and M. A. Spackman, *CrystEngComm*., 2008, **10**, 368–376.

13 SAINT and XPREP, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, **1995**. Sheldrick, G. M.

14 SADABS, empirical absorption Correction Program; University of Göttingen: Göttingen,Germany, **1997**.

15 G. M. Sheldrick, SHELXTL Reference Manual: Version 5.1; Bruker AXS: Madison, WI, **1997**.

16 G. M. Sheldrick, SHELXL-97: Program for Crystal Structure Refinement; University ofGöttingen: Göttingen, Germany, 1997.

17 Mercury 2.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 20011-20012.

18 P. Van der Sluis and A. Spek, L. ActaCrystallogr.1990, A46, 194.

