**Insight into systematic formation of hexafluorosilicate during crystallization via self-assembly in a glass vessel**†

Dongwon Kim, a Jihun Han, a Ok-Sang Jung b *a and Young-A. Lee b

Formation of the unexpected hexafluorosilicate (SiF$_6^{2-}$) anion during crystallization via self-assembly in glassware is scrutinized. Self-assembly of M(BF$_4$)$_2$ (M$^{2+} =$ Cu$^{2+}$ and Zn$^{2+}$) with tridentate N-donors (L) in a mixture solvent including methanol in a glass vessel gives rise to an SiF$_6^{2-}$-encapsulated Cu$_3$L$_4$ double-decker cage and a Zn$_2$L$_4$ cage, respectively. Induced reaction of CuX$_2$ (X$^- =$ PF$_6^-$ and SbF$_6^-$) instead of Cu(BF$_4$)$_2$, with the tridentate ligands, produces the same species. The formation time of SiF$_6^{2-}$ is in the order of anions BF$_4^-$ < PF$_6^-$ < SbF$_6^-$ under the given reaction conditions. The SiF$_6^{2-}$ anion, acting as a cage template or cage-to-cage bridge, seems to be formed from the reaction of polyatomic anions containing fluoride with the SiO$_2$ of the surface of the glass vessel.

**Introduction**

Anion-related chemistry is a rapidly burgeoning field owing to the timeliness and importance including environmental pollution, industrial chemicals, biological processes, ionic liquids, lithium batteries, templates, ion-pairing, and health.1–12 Some anions play a significant role in the construction and behaviors of desirable molecular architectures based on negative charge, size, shape, solvents, and pH.13–18 In particular, F-containing polyatomic anions such as BF$_4^-$, PF$_6^-$, and SbF$_6^-$ have been extensively employed for various purposes such as important chemical phenomena, cage-templates, coordination, and the Hofmeister series,19–26 however, they are known to be not thermodynamically stable depending on conditions27,28 relative to the F-free polyatomic anions NO$_3^-$, ClO$_4^-$, CH$_3$CO$_2$-, and SO$_4^{2-}$. For instance, the PF$_6^-$ anion could be converted to PF$_6^-[\text{OH}]_{n-}$ during the complexion of Pd(n)-L.29 Furthermore, BF$_4^-$ is known to be changed to the SiF$_6^{2-}$ anion via subsequent reaction of dissociated F$^-$ with the Si-O moieties of a glass vessel or stoneware.30–35 Hexafluorosilicate (SiF$_6^{2-}$) is a stable octahedral anion with six Si–F bond distances of 1.71 Å,36 and its solubility is significantly dependent on cations.37 Furthermore, the diatomic species have been discovered as uses: leather and wood preservation agents, fluoridation agents for drinking water, two-solution fluoride mouth rinse, commercial laundry, enamels/enamel frits for china and porcelain, opalescent glass, metallurgy of aluminum and beryllium, glue, ore flotation, insecticides and rodenticides, fluorinating agent in organic synthesis, and water fluoridation.38–47

In this context, systematic research on the unusual formation process and recognition of SiF$_6^{2-}$ is very much in demand. Thus, herein, formation of hexafluorosilicate via conversion of PF$_6^-$ and SbF$_6^-$ beside BF$_4^-$ during self-assembly or recrystallization in a glass vessel is scrutinized. This paper reports the unique SiF$_6^{2-}$-encapsulated cages constructed via self-assembly of M$^{2+}$ (M = Cu$^{2+}$ and Zn$^{2+}$) with tridentate N-donor ligands in a glass vessel. To our knowledge, this article presents clear systematic research on the formation of hexafluorosilicate by reactions of glassware with F-containing polyatomic anions.

**Experimental**

**Materials and measurements**

All of the chemicals, including copper(n) tetrafluoroborate (Cu(BF$_4$)$_2$), copper(n) nitrate (Cu(NO$_3$)$_2$), copper(n) chloride (CuCl$_2$), silver(i) hexafluorophosphate (AgPF$_6$), silver(i) hexafluoroantimonate (AgSbF$_6$), and zinc(ii) tetrafluoroborate (Zn(BF$_4$)$_2$), were purchased from Aldrich and used without further purification. ($1S,1'S,1''S,2R,2'R,2''R$)-[Benzencarboxyltris(azanediy)]tris(2,3-dihydro-1H-indene-2,1-diyl)trisonicotinate ($L^1$) and 1,3,5-tris[isonicotinoyl][methyl]benzene ($L^2$) were synthesized according to the literature,48,49 respectively. Glass vessels (Hubena Co, Seongnam, Korea) were employed in all of the self-assembly reactions. The $^1$H and $^19$F NMR spectra were recorded on a Varian Mercury Plus operating at 400 MHz. The infrared (IR) spectra were obtained on a Nicolet 380 FT-IR spectrophotometer with samples prepared as...
Method 1. A methanol solution (2.0 mL) of copper(II) tetrafluoroborate (4.7 mg, 0.02 mmol) was carefully layered onto a dichloromethane solution (2.0 mL) of L1 (18.4 mg, 0.02 mmol). After 2 weeks, blue crystals suitable for single crystal X-ray structure determination were obtained in an 83% yield.

Method 2. A methanol solution (1.0 mL) of silver(I) hexafluorophosphate (10.1 mg, 0.04 mmol) was added to copper(II) chloride (2.7 mg, 0.02 mmol) dispersed in methanol at room temperature. The reaction mixture was stirred for 30 min, after which, the precipitated silver chloride was filtered off. The methanol solution of Cu(PF6)2 was carefully layered onto a dichloromethane solution (2.0 mL) of L1 (18.4 mg, 0.02 mmol). After 4 weeks, blue crystals suitable for single crystal X-ray structure determination were obtained in a 78% yield.

Method 3. A methanol solution (1.0 mL) of silver(I) hexafluorophosphate (13.7 mg, 0.04 mmol) was added to a suspension of copper(II) chloride (2.7 mg, 0.02 mmol) dispersed in methanol at room temperature, and a methanol solution of Cu(BF4)2 was carefully layered onto a dichloromethane solution (2.0 mL) of L1 (18.4 mg, 0.02 mmol). After 1 day, blue crystals suitable for single crystal X-ray structure determination were obtained in a 62% yield.

Method 4. A methanol solution (2.0 mL) of copper(II) nitrate (2.8 mg, 0.015 mmol), a dichloromethane solution (4.0 mL) of L1 (18.4 mg, 0.02 mmol), and a methanol solution of Cu(SBF6)2 were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å). Thirty-six (36) frames of 2D diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the multi-scan method (SADABS).22 The structures were resolved using the direct method (SHELXLS) and refined by full-matrix least squares techniques (SHELXL 2018/3).23 The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1.

**Results and discussion**

**Synthesis aspects**

Self-assembly of Cu(BF4)2 with L1 in a mixture of methanol and dichloromethane produced crystals consisting of [(SiF6)@Zn(L2)4]·2C4H8O·4CH2Cl2 and [(SiF6)@Zn(L2)4]·2C4H8O·4CH2Cl2 suitable for single crystal X-ray structure determination. After 2 weeks, as shown in Scheme 1. Moreover, the reactions with Cu(PF6)2 and Cu(SBF6)2 instead of Cu(BF4)2 gave rise to the same product after significant duration, specifically 4 and 6 weeks, respectively. The reaction time may be owed to the stability of the BF4−<PF6−<SF6− anions under the given reaction conditions. As expected, self-assembly of Cu(BF4)2 with L1 in the presence of (NH4)2SiF6 produced blue crystals within 1 day. In order to investigate the metal effects, self-assembly of Zn(BF4)2 instead of Cu(BF4)2 with L2 was performed, which generated crystals of [(SiF6)@Zn(L2)4]·2C4H8O·4CH2Cl2 after 2 weeks, indicating that the central metal cation is not a significant factor in anion transformation in a glass vessel. For all of the reactions, the SiF62− anion acted...
either as a template by which to form the cage products or as a cage-to-cage bridge.

Both crystalline products are stable under anaerobic condition at room temperature. The crystals are insoluble in common organic solvents such as acetone, chloroform, toluene, benzene and tetrahydrofuran, but are partially dissociated in dimethyl sulfoxide and N,N-dimethylformamide. Their compositions and structures were confirmed by elemental analyses, IR-spectral analysis (Fig. S1 and S2†), thermal analysis (Fig. S3†), 1H NMR (Fig. S4, as dissociated in Me$_2$SO-$_d_6$), and single-crystal X-ray crystallography. The characteristic IR bands of SiF$_6^{2-}$ were easily assigned. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed [(SiF$_6$)$_2$@Cu$_3$L$_1$][SiF$_6$]-16CH$_3$OH and [(SiF$_6$)$_2$@Zn$_2$L$_2$][SiF$_6$]-2C$_4$H$_8$O·4CH$_2$Cl$_2$ to be stable up to 277 and 257 °C, respectively. Evaporation of the solvate molecules of the two kinds of crystals occurred in the 10–60 and 20–135 °C temperature ranges, respectively (Fig. S3†).

**Crystal structures**

The crystal structure of [(SiF$_6$)$_2$@Cu$_3$L$_4$][SiF$_6$]-16CH$_3$OH is depicted in Fig. 1, and its bond lengths and angles are listed in Table 1. The geometry of each copper(n) ion is an octahedral N$_4$F$_2$ coordination arrangement with four N donors from four L$_4$ and F donors from two SiF$_6^{2-}$ anions (Cu–N = 2.007(4) – 2.019(3) Å; Cu–F(encapsulated) = 2.317(2), 2.300(3) Å; Cu–F(bridged) = 2.357(3) Å) in axial positions, resulting in the formation of the Cu$_3$L$_4$ double-decker occupied by two SiF$_6^{2-}$ anions. Concomitantly, for the nestled SiF$_6^{2-}$, the equatorial Si–F bond lengths (1.637(4) Å) are slightly shorter than the axial Si–F lengths (1.733(5) – 1.746(6) Å). The intra-cage Zn–Zn distance is 8.113(2) Å. Its packing structure is in the linear cage–SiF$_6^{2-}$…cage–SiF$_6^{2-}$ mode (Fig. S5†). The solvate molecules of [(SiF$_6$)$_2$@Cu$_3$L$_1$][SiF$_6$]-16CH$_3$OH were squeezed. The volumes of solvate molecules in [(SiF$_6$)$_2$@Cu$_3$L$_4$][SiF$_6$]-16CH$_3$OH and [(SiF$_6$)$_2$@Zn$_2$L$_2$][SiF$_6$]-2C$_4$H$_8$O·4CH$_2$Cl$_2$ were 56.2% (10 282 Å$^3$/18 304 Å$^3$) and 37.8% (2093.4 Å$^3$/5539.5 Å$^3$), respectively, on the basis of a PLATON/SOLV calculation. 

**Discussion**

Formation of SiF$_6^{2-}$ during self-assembly of more than 2 weeks’ duration requires some explanation, because the anion was not added to the self-assembly solution in a glass vessel. It should

![Scheme 1](https://example.com/scheme1.png)
be noted that the SiF$_6^{2-}$ anion replaces the starting BF$_4^{-}$ anion in the self-assembly reaction and that it is formed after extracting Si$^{4+}$ from the glass vessel in methanol solvent—a rare but well-known phenomenon.$^{35}$ The generation of SiF$_6^{2-}$ by slow release of Si$^{4+}$ from the glass vessel in the methanol solution was clearly confirmed, and the resultant anions were separated as counteranions. The SiF$_6^{2-}$ anions appear to play significant roles as both encapsulator and bridge in the construction of the cage skeleton. The stable anion, by contrast, forms as a consequence of the hydrolysis of the BF$_4^{-}$ anion and subsequent reaction of F$^-$ with the Si–O moieties of the glass vessel$^{36,37}$ in which a methanol solution of M(BF$_4$)$_2$ is kept for self-assembly or crystallization. The formation of SiF$_6^{2-}$ seems to be promoted by the presence of a small quantity of H$_2$O in addition to a mixture solvent including methanol. Formation of SiF$_6^{2-}$ from BF$_4^{-}$ and PF$_6^{-}$ in a glass vessel in water has been observed by other groups,$^{30-32,56}$ but that of SiF$_6^{2-}$ from SbF$_6^{-}$ heretofore has not been recorded. The present self-assembly of MX$_2$ (M$^{2+}$ = Cu$^{2+}$, Zn$^{2+}$; X$^{-}$ = BF$_4^{-}$, PF$_6^{-}$, SbF$_6^{-}$) with each tridentate ligand in each glass vessel systematically transformed BF$_4^{-}$, PF$_6^{-}$ or SbF$_6^{-}$ into the SiF$_6^{2-}$ anion according to the following eqn (1):

$$\text{SiO}_2 + 6\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}_2\text{O}^+ $$

(1)

Of course, formation of SiF$_6^{2-}$ from CF$_3$SO$_3^{-}$ (C–F compound) could not be carried out in a similar reaction performed in a polypropylene vessel instead of a glass one; that is, the reaction did not yield crystals containing the SiF$_6^{2-}$ anion. The presence of SiF$_6^{2-}$ in Me$_2$SO-d$_6$ was confirmed by $^{19}$F NMR spectra (Fig. S6f). The SiF$_6^{2-}$ occurred as a singlet at $\delta = -134$ ppm. Spectra taken of the sample preparation one month later indicated that almost all of the original BF$_4^{-}$ anions had been converted to SiF$_6^{2-}$ anions. As regards the formation of SiF$_6^{2-}$ from PF$_6^{-}$ and SbF$_6^{-}$ anions, PF$_6^{-}$ (~70.8 ppm) and SbF$_6^{-}$ chemical shifts (~119.9 ppm) disappeared after 4 and 6 weeks, respectively, and appeared at the position of the SiF$_6^{2-}$ anion. As for construction of the coordination architecture, insight into the stability and geometry of a specific anion as a template is useful to the tuning of the shape and topology of coordination species. In the present study, the encapsulated and bridged SiF$_6^{2-}$ anions helped to stabilize the crystal structure of the cages. Certainly, transformation of polyatomic anions and their role is a topic worthy of further investigation.

Conclusions

In summary, transformation of polyatomic anions BF$_4^{-}$, PF$_6^{-}$, and SbF$_6^{-}$ into SiF$_6^{2-}$ during self-assembly or recrystallization in a glass vessel was systematically confirmed. This shows that the surface of regular laboratory glassware should be given serious consideration for long-duration reactions or self-assembly with F$^-$ species. Further studies on other means of anion-bridging or -encapsulation of cage units will contribute to the development of task-specific polyatomic anions for recognition as well as environmental molecular materials such as adsorbents and sensing materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by National Research Foundation of Korea (NRF) grants funded by the Korean Government [MEST] (2021R1A2C2005105, 2016R1A5A1009405 (OSJ)), and 2021R1I1A3059982 (YAL)). The X-ray crystallography at the PLS- II 2D-SMC beamline was supported in part by MSIP and POSTECH.

Notes and references

1 J. L. Anthony, J. L. Anderson, E. J. Maginn and J. F. Brennecke, J. Phys. Chem. B, 2005, 109, 6366–6374.
2 Z. Wang, X. Li, W. Guo and Y. Fu, Adv. Funct. Mater., 2021, 31, 2009875.
3 J. P. Carpenter, C. T. McFernan, T. K. Ronson and J. R. Nitschke, J. Am. Chem. Soc., 2019, 141, 11409–11413.
4 P. A. Gale, R. Perez-Tomas and R. Quesada, Acc. Chem. Res., 2013, 46, 2801–2813.
5 D. H. Shin, M. Kim, Y. Kim, I. Jun, J. Jung, J. H. Nam, M. H. Cheng and M. G. Lee, Pflugers Arch. - Eur. J. Physiol., 2020, 472, 1003–1018.
6 Y. Zhao, Y. Li, S. Yuan, J. Zhu, S. Houtmeyers, J. Li, R. Dewil, C. Gao and B. Van der Bruggen, J. Mater. Chem. A, 2019, 7, 6348–6356.
7 Y. Zhao, Y. Cotelle, L. Liu, J. López-Andarias, A.-B. Bornhof, M. Akamatsu, N. Sakai and S. Matile, Acc. Chem. Res., 2018, 51, 2255–2263.
8 Y. Bando, Y. Haketa, T. Sakurai, W. Matsuda, S. Seki, H. Takaya and H. Maeda, Chem. Eur. J., 2016, 22, 7843–7850.
9 S. Patnaik, D. P. Sahoo and K. Parida, Carbon, 2021, 172, 682–711.
