Isolation of the simplest hydrated acid

Rui Zhang, Michihisa Murata, Atsushi Wakamiya, Takafumi Shimoaka, Takeshi Hasegawa, Yasujiro Murata*

Dissociation of an acid molecule in aqueous media is one of the most fundamental solvation processes but its details remain poorly understood at the distinct molecular level. Conducting high-pressure treatments of an open-cage fullerene C70 derivative with hydrogen fluoride (HF) in the presence of H2O, we achieved an unprecedented encapsulation of H2O-HF and H2O. Restoration of the opening yielded the endohedral C70@, that is, (H2O-HF)@C70, H2O@C70, and HF@C70 in macroscopic scales. Putting an H2O-HF complex into the fullerene cage was a crucial step, and it would proceed by the synergistic effects of “pushing from outside” and “pulling from inside.” The structure of the H2O-HF was unambiguously determined by single crystal x-ray diffraction analysis. The nuclear magnetic resonance measurements revealed the formation of a hydrogen bond between the H2O and HF molecules without proton transfer even at 140°C.

INTRODUCTION

One of the most important chemical processes is dissociation of a Brønsted acid in aqueous media accompanied by proton transfer from the acid to H2O molecules and solvation of the charged fragments (1). This fundamental event plays a key role in myriad chemical reactions and biological phenomena. However, the detailed mechanism of acid dissociation (2, 3) and the nature of protons in an aqueous environment (4, 5) are rather complex, and still remain to be revealed at the distinct molecular level. Hydrogen fluoride (HF) is the smallest molecule and has been studied well, mostly in the gas phase, both theoretically and experimentally (6). One extensively discussed issue on HF is the minimum number of H2O molecules that is necessary to solvate an HF molecule resulting in the formation of the solvent-shared ion pair [H2O·HF]3 (7, 8). However, the central obstacle to resolution of this subject includes the difficulty of preparation of any of the possible HF·(H2O)n complexes in a pure form with definite components. This is because the high reactivity of HF and the strong hydrogen bond affinity of H2O often result in the formation of many types of oligomers, which are in equilibrium with others, rendering their separation and isolation almost impossible (9). To understand this fundamental process, it is highly desirable to construct an ideal system that can elucidate the intrinsic nature of the hydrated HF molecule.

To isolate reactive chemical species, the compounds should be located in an inert atmosphere, preventing interaction and/or reaction from the outer environments. These subnano-sized environments can be found inside fullerenes, which are spherical carbon clusters having a hollow cavity. Very reactive chemical species such as metal ions (10, 11), metal clusters (12), and a nitrogen atom (13) have thus far been encapsulated inside fullerenes. These well-defined supramolecular systems have provided opportunities to study the physical and chemical properties of the encapsulated species at the molecular scale and to use them as functional materials (14). However, selectivity in encapsulated species in addition to fullerene cages are difficult to control because of the reliance of most production methods on harsh conditions (12, 14). In contrast, the “molecular surgery” approach can produce molecule-encapsulating fullerenes with almost-perfect selectivities under mild conditions in solution (15). Using this method, endohedral C60 encapsulating a single molecule of H2 (16), He (17), H2O (18), and HF (19) was synthesized.

Molecular surgery can also be applied to fullerene C70 despite difficulties in characterization of products due to low symmetry. Reflecting the larger inner space in C70 compared to C60 (20, 21), two small molecules were introduced inside open-cage C70 derivatives to afford the corresponding doubly encapsulating endohedral C70 derivatives after restoration of the cage, that is, (H2O)2@C70 (22) and (H2O)2@C70 (23), respectively. Previously, we reported two open-cage C70 derivatives, α-13 mem (24) and β-13 mem (Fig. 1A) (23), both having a 13-membered ring opening with the same functional groups. These compounds were synthesized by a three-step reaction starting from the addition of a pyridazine derivative to the α- and β-bonds of C70 with total yields of 22% and 2%, respectively. Both openings were enlarged in situ into the 16-membered ring as their C60 analog (18). The opening of α-16 mem is smaller than that of β-16 mem, evidenced by the fact that only a trace amount of H2O was introduced inside α-16 mem, whereas a H2O molecule was entrapped almost quantitatively inside β-16 mem. Density functional theory (DFT) calculations also supported the smaller size of α-16 mem (23). Taking advantage of the efficient synthetic yield of α-13 mem, we envisioned that α-13 mem would be more suitable as a starting material for novel endohedral C70 derivatives. Because the size of HF is smaller than that of H2O (25), we studied encapsulation of HF into α-13 mem with initial intention to synthesize HF@C70. Here, we report facile synthesis of HF@C70 as well as unprecedented formation of (H2O-HF)@C70 and H2O@C70 using α-13 mem as a key compound despite the small size of the opening for the insertion of H2O.

As shown in Fig. 1B, after optimization of the conditions (vide infra), the high-pressure treatment of α-13 mem in the presence of 0.5 equivalence of 70% (w/w) HF in pyridine (HF-Py) (26) and a trace amount of water was conducted in chlorobenzene under 9000 atm at 120°C for 18 hours to afford guest-encapsulating α-13 mem (G@α-13 mem; G = HF, H2O-HF, and H2O) in 40% isolated yield after purification with column chromatography. The filling factors of the guests inside α-13 mem were determined by the proton nuclear magnetic resonance (1H NMR) analysis: 32% HF@α-13 mem, 11% (H2O-HF)@α-13 mem, 27% H2O@α-13 mem, and 30% empty α-13 mem, respectively. After collecting the products from several batches, closing of G@α-13 mem via two-step reactions, without considerable loss of the encapsulated species, gave the corresponding endohedral C70 derivatives, that is, expected...
HF@C\(_{70}\) and unprecedented \((\text{H}_2\text{O}-\text{HF})@C\(_{70}\) and \(\text{H}_2\text{O}@C\(_{70}\) (figs. S8 to S15).

We confirmed that HF encapsulation into \(\alpha\)-16mem did not take place in chlorobenzene under ambient pressure at 110°C, in contrast to the case for the open-cage \(C\(_{60}\) \((25)\). Thus, the high-pressure conditions were found to be critical, where the guest species are forced to be “pushed from outside” of the opening of \(\alpha\)-16mem. The experimental conditions and results are summarized in Table 1. Upon checking the time dependence (entries 1 to 4), the filling factor of HF appeared to almost reach a plateau after 14 hours, whereas that of H\(_2\)O increased slowly and that of H\(_2\)O·HF was developed rapidly at around 14 hours. These observations suggested stepwise formation of G@\(\alpha\)-13mem, that is, HF@\(\alpha\)-16mem followed by \((\text{H}_2\text{O}-\text{HF})@\alpha\)-16mem and then \(\text{H}_2\text{O}@\alpha\)-16mem. To prevent a high degree of decomposition of the starting materials and the products, a reduced amount of HF-Py at slightly higher temperature gave the better chemical yield of G@\(\alpha\)-13mem (entry 5). As described previously by Zhang et al. (23, 24), H\(_2\)O encapsulation did not occur in the absence of HF (entry 6), showing only that pushing from outside was not an effective method of inserting H\(_2\)O inside \(\alpha\)-16mem. Among the products obtained from entries 1 to 5, \((\text{H}_2\text{O})_2@\alpha\)-13mem and \(\text{H}_2\text{O}@\alpha\)-13mem were not detected.

Our experiments considered the insertion mechanisms of HF, H\(_2\)O-HF, and H\(_2\)O (as shown in Fig. 2). Because the size of the opening of \(\alpha\)-16mem, which was generated in situ from \(\alpha\)-13mem by eliminating a water molecule from the bis(hemiketal) moiety, is not large enough for water to pass through, insertion of a smaller HF initially takes place by pushing from outside to give molecular complex A. In earlier work, Gan et al. (27) reported that encapsulated H\(_2\)O inside an open-cage \(C\(_{60}\) was pulled by attractive interaction with fluoride atom being present outside the opening, resulting in the release of the H\(_2\)O. Taking into consideration the similar attractive interaction of the encapsulated HF and the H\(_2\)O near the opening, the H\(_2\)O should be introduced into \(\alpha\)-16mem by the assist of “pulling from inside,” shown as B, to yield C. Then, positional exchange of the lower HF and the upper H\(_2\)O occurs to afford D. DFT calculations at the M06-2X/6-31G(d) level showed that the required energy for the positional exchange of the HF and H\(_2\)O in C is 20.8 kcal/mol (tables S3 to S5), which should be possible to occur under the applied conditions. Finally, the resulting HF near the opening escapes to form E. During the cooling process, addition of a water molecule regenerates the \(\alpha\)-13mem cage to furnish G@\(\alpha\)-13mem.

Because of the complexities in the structures of H\(_2\)O clusters and hydrated HF, it is very difficult to evaluate energy profiles including A, B, D, and E by DFT studies. In the case of the gas-phase stabilization energy calculated at the MP2/6-311++G(3pd,3df) level, H\(_2\)O-HF gains more energy (7.3 kcal/mol) than HF dimer (3.9 kcal/mol) and H\(_2\)O dimer (3.8 kcal/mol) (tables S8 to S15). This stability is considered to play an important role for the formation of C. However, we needed to study another possibility that the presence of an acid would change...
the solvated structures of HF and H$_2$O before encapsulation to result in facile encapsulation of H$_2$O. Although a high-pressure treatment in the presence of HCl-Py, instead of HF-Py, under the same conditions was found to contain only a small amount of H$_2$O·HF, the results strongly support the hypothesis that both pushing and pulling effects are necessary to achieve encapsulation of H$_2$O·HF inside α-13mem in a remarkably high yield compared with the doubly encapsulating C$_{70}$ reported so far (22, 23).

After closure of the openings (Fig. 1B), the high-performance liquid chromatography (HPLC) analysis of the products displayed three peaks corresponding to empty C$_{70}$, a mixture of HF@C$_{70}$ and H$_2$O@C$_{70}$, and (H$_2$O·HF)@C$_{70}$ (as shown in Fig. 3A). The mono-encapsulating HF@C$_{70}$ and H$_2$O@C$_{70}$ appeared at almost the same retention time regardless of the encapsulated species. In contrast, facile separation of (H$_2$O·HF)@C$_{70}$ as a pure form was achieved in a preparative scale, showing clear differences caused by the double encapsulation. By the atmospheric pressure chemical ionization mass analysis (APCI MS), we detected (HF)$_2$@C$_{70}$ before elution of (H$_2$O·HF)@C$_{70}$, albeit in only a trace amount (fig. S16).

The $^1$H NMR analysis is a powerful tool to study the structure and dynamics of the isolated H$_2$O·HF. As shown in Fig. 3B, a signal of the singly encapsulated H$_2$O at $-27.1$ ppm [500 MHz; CDCl$_3$/CS$_2$ (1:1), 25°C] coincides with that of our previous report for H$_2$O@C$_{70}$ synthesized from different synthetic routes (23), showing strong shielding effects due to C$_{70}$ cage (22, 23). A doublet corresponding to the singly encapsulated HF was observed at $-25.0$ ppm with a coupling constant $J_{HF} = 507$ Hz, whose value is almost the same as that of HF@C$_{60}$ (19). The $^1$H NMR of (H$_2$O·HF)@C$_{70}$ displayed a singlet at $-25.3$ ppm corresponding to the H$_2$O in addition to a doublet at $-17.5$ ppm corresponding to the HF. It is noteworthy that both chemical shifts are downfield-shifted compared with those of H$_2$O@C$_{70}$ and HF@C$_{70}$, indicating more positive charges on the protons due to the formation of a hydrogen bond. The shifted value for the HF ($\Delta \delta = 7.5$) is larger than that of the H$_2$O ($\Delta \delta = 1.8$), demonstrating that this molecular complex adopts the structure H$_2$O·HF, in which the oxygen works as a hydrogen bond acceptor, rather than HF·H$_2$O, in which the fluorine works as the acceptor. In addition, the smaller value of the coupling constant $J_{HF}$ = 443 Hz also supports the structure H$_2$O·HF, the value being close to those of HF in diethyl ether and dimethyl sulfoxide solutions, $J_{HF}$ = 464 and 410 Hz, respectively (28). Hence, we concluded that this is the simplest hydrated acid. Upon heating the solution in ortho-dichlorobenzene-$d_4$ (ODCB-$d_4$), no change in the spectral shape was observed even at 140°C, revealing that no proton transfer takes place between the H$_2$O and HF on the NMR time scale.

The structure of (H$_2$O·HF)@C$_{70}$ was unambiguously determined by the single-crystal x-ray diffraction analysis for the crystals containing nickel(II) octaethylporphyrin and solvent molecules, with almost the same unit cell constants as those of empty C$_{70}$ (29) and H$_2$O@C$_{70}$ (23). As shown in Fig. 3D, the O and F atoms of the H$_2$O·HF were observed inside the C$_{70}$ located on the porphyrin. It is the first example of the x-ray structure for doubly encapsulating C$_{70}$. Here, in contrast to

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**Table 1. Encapsulation of HF, H$_2$O·HF, and H$_2$O inside α-13mem under the high-pressure conditions of 9000 atm in the chlorobenzene solution.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>HF-Py (eq.)</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
<th>Yield (%)</th>
<th>Filling factor (%)*</th>
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<tbody>
<tr>
<td></td>
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<td></td>
<td>H$_2$O·HF·HF H$_2$O</td>
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<td>6</td>
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<td>0</td>
<td>120</td>
<td>18</td>
<td>87</td>
<td>0</td>
</tr>
</tbody>
</table>

*Isolated yields of the sum of recovered α-13mem and G@α-13mem (G = HF, H$_2$O·HF, and H$_2$O) after purification with a column chromatography on silica gel.

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![Fig. 2. Insertion mechanism of HF, H$_2$O·HF, and H$_2$O into α-16mem with the synergestic effects of pushing from outside by high-pressure conditions and pulling from inside by attractive interaction of HF with the outer H$_2$O.](http://advances.sciencemag.org/)
General
The $^1$H, $^{13}$C, and $^{19}$F NMR measurements were performed with the JEOL JNM-ECA 500 and JNE-ECA 600 instruments. The NMR chemical shifts of the cage carbons near the H$_2$O are smaller than those near the HF, indicating the polarity of (H$_2$O·HF)$_{@C_{70}}$ which was shown by the gauge-independent atomic orbital (GIAO) calculations (fig. S17). However, this polarity was not obvious on reduction potentials determined by cyclic voltammetry (CV) in ODCB, the first reduction potentials for (H$_2$O·HF)$_{@C_{70}}$ and empty C$_{70}$ being $-1.04$ and $-1.06$ V versus a ferrocene/ferrocenium couple (fig. S18). The ultraviolet-visible (UV-vis) absorption in toluene is almost superimposable that of empty C$_{70}$ (fig. S19). The infrared (IR) bands for the HO–H and F–H bonds were not observed, probably due to the shielding effects of the cage, which was the same for H$_2$O$_{@C_{60}}$ (18), HF$_{@C_{60}}$ (19), and H$_2$O$_{@C_{70}}$ (23). However, interesting suppression of the characteristic IR bands of C$_{70}$ was observed for HF$_{@C_{70}}$ and (H$_2$O·HF)$_{@C_{70}}$ (fig. S20).

In summary, the simplest hydrated HF was isolated in a confined subnano space by the use of molecular surgical methods. Compared with the doubly encapsulating C$_{70}$s reported so far, a high efficiency of the encapsulation was achieved because of the synergistic effects of pushing from outside by the high-pressure conditions and pulling from inside with an attractive interaction of the encapsulated HF with the outer H$_2$O, which was supported by the stepwise formation of HF$_{@C_{70}}$, followed by (H$_2$O·HF)$_{@C_{70}}$ and then H$_2$O$_{@C_{70}}$. The NMR studies revealed the rigid structure of the H$_2$O·HF without hydrogen exchange. The single crystal x-ray analysis and theoretical calculations showed the closer contact of the oxygen with the hydrogen of HF compared with that of free H$_2$O·HF.
shifts were reported in parts per million with reference to residual protons, carbons, and fluorine of CDC$_3$ (δ 7.26 ppm in $^1$H NMR, δ 77.0 ppm in $^{13}$C NMR), tetrahydrofuran (THF-d$_8$) (δ 67.57 ppm in $^{13}$C NMR), and hexafluorobenzene ($C_6F_6$) (δ 164.90 ppm in $^{19}$F NMR). The APCI MS spectra were measured on a Bruker microTOF-Q II. High-pressure experiments were conducted by using the Hikari Koatsu high-pressure apparatus HR15-B3. The HPLC was performed with a Cosmosil Buckyprep column (4.6 × 250 mm) for analytical purpose and the same columns (two directly connected columns; 20p × 250 mm) for preparative purpose. CV was conducted in an ALS Electrochemical Analyzer Model 620C using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/0.01 M AgNO$_3$ electrode. The H+(H$_2$O)$_8$ was purchased from Sigma-Aldrich. The open-cage C$_{70}$ derivative $\text{C}_7\text{O}_4\text{H}_{8}$ was purchased from Tokyo Chemical Industry Co. Ltd. Hydrogen fluoride pyridine was purchased from ChemService.

Computational methods

All calculations were conducted with Gaussian 09 packages (31). The structures were optimized at the M06-2X/6-31G(d), MP2/6-311++G(3df,3pd), and ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)) levels without any symmetry assumptions (32). For the ONIOM method, the MP2 method was applied for the endohedral species and the M06-2X method was used for the fullerene cage. All structures including the stationary states and the transition states were confirmed by the frequency calculations at the same level. The calculated $^1$H NMR and $^{13}$C NMR chemical shifts were obtained at the GIAO-B3LYP/6-311G(d,p) level using the optimized structures at the ONIOM or M06-2X methods with a reference of tetramethylsilane calculated at the GIAO-B3LYP/6-311G(d,p)//M06-2X/6-31G(d) level. The isotropic chemical shifts were calculated for protons (32,3196 ppm) and carbons (185,7282 ppm).

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/6/e1602833/DC1

fig. S1. $^1$H NMR [500 MHz; CDCl$_3$/Cs$_2$ (1:1)] spectrum of a mixture of HF at $\alpha$-13mem, (H$_2$O)HF at $\omega$-13mem, H$_2$O at $\omega$-13mem, and empty $\alpha$-13mem.
fig. S2. $^{13}$C NMR (151 MHz; THF-d$_8$) spectrum of a mixture of HF at $\alpha$-13mem, (H$_2$O)HF at $\omega$-13mem, H$_2$O at $\omega$-13mem, and empty $\alpha$-13mem.
fig. S3. $^{19}$F NMR (470 MHz; CDCl$_3$/Cs$_2$ (1:1)) spectrum of a mixture of HF at $\alpha$-13mem, (H$_2$O)HF at $\omega$-13mem, H$_2$O at $\omega$-13mem, and empty $\alpha$-13mem.
fig. S4. $^1$H NMR [500 MHz; CDCl$_3$/Cs$_2$ (1:1)] spectrum of a mixture of HF at $\alpha$-13mem, (H$_2$O)HF at $\omega$-13mem, H$_2$O at $\omega$-13mem, and empty $\alpha$-13mem obtained under the optimized conditions (Table 1, entry 5).
fig. S5. $^1$H NMR [500 MHz; CDCl$_3$] spectrum of a mixture of HF at $\omega$-8mem, (H$_2$O)HF at $\omega$-8mem, H$_2$O at $\omega$-8mem, and empty $\omega$-8mem.
fig. S6. $^{13}$C NMR (151 MHz; CDCl$_3$) spectrum of a mixture of HF at $\omega$-8mem, (H$_2$O)HF at $\omega$-8mem, and empty $\omega$-8mem.
fig. S7. $^{19}$F NMR (470 MHz; CDCl$_3$) spectrum of a mixture of HF at $\omega$-8mem, (H$_2$O)HF at $\omega$-8mem, H$_2$O at $\omega$-8mem, and empty $\omega$-8mem.
fig. S8. $^1$H NMR [500 MHz; CDCl$_3$/Cs$_2$ (1:1)] spectrum of a mixture of HF at $\omega$-13mem, and H$_2$O at $\omega$-13mem (1:1).
fig. S9. $^{19}$F NMR (470 MHz; CDCl$_3$/Cs$_2$ (1:1)) spectrum of a mixture of HF at $\omega$-13mem, and H$_2$O at $\omega$-13mem (1:1).

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