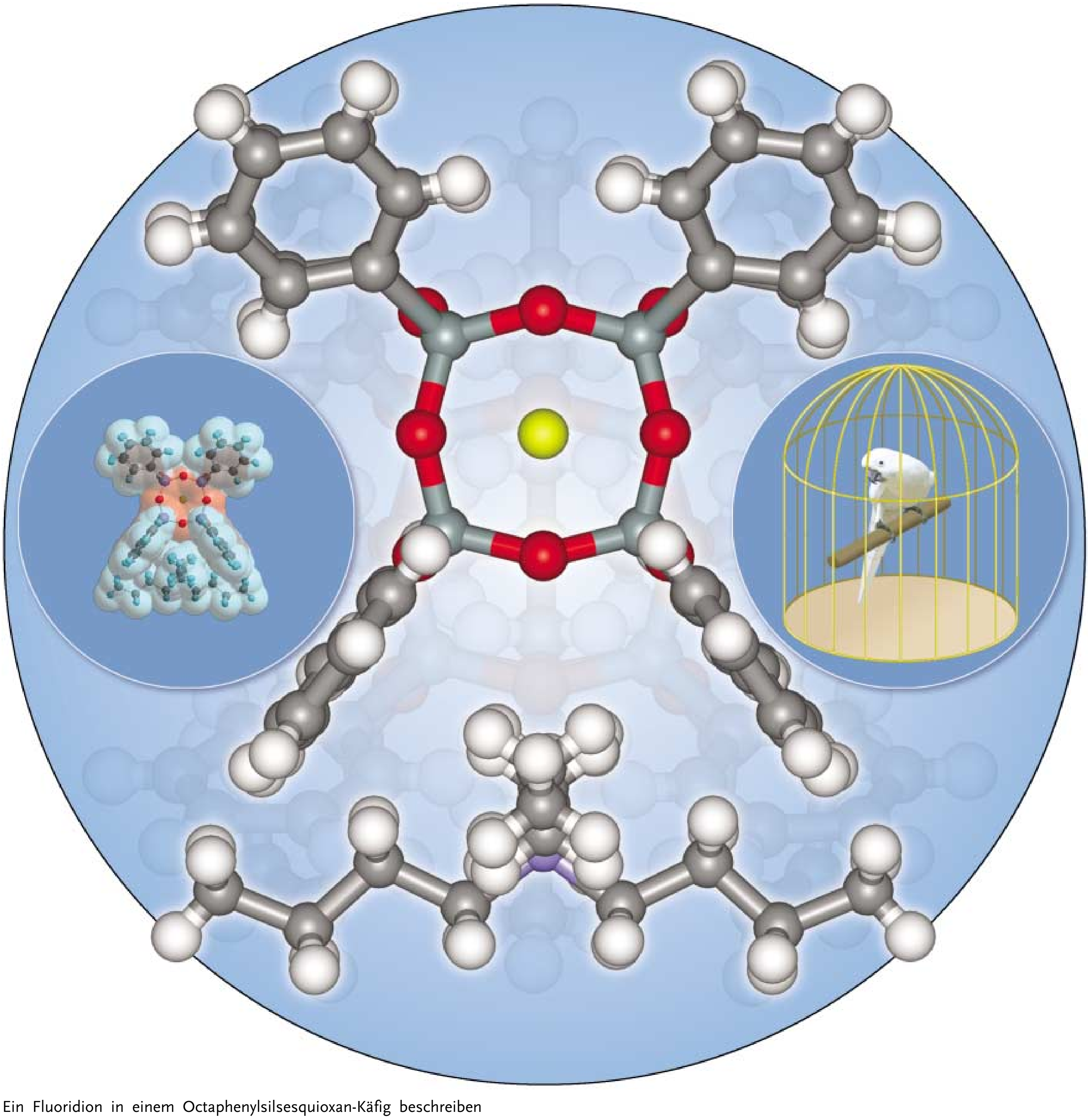
# Zuschriften



Ein Fluoridion in einem Octaphenylsilsesquioxan-Käfig beschreiben A. Bassindale, P. G. Taylor und Mitarbeiter auf den folgenden Seiten. Die Aufsicht zeigt, dass sich das Fluoridion in der Mitte seines Käfig aufhält – etwa so wie der ebenfalls abgebildete Sittich. Das Tetrabutylammonium-Gegenion nimmt einen Platz zwischen den Phenylsubstituenten ein.

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**Fluoride Ions in Cage Structures**

# Fluoride-Ion Encapsulation within a Silsesquioxane Cage

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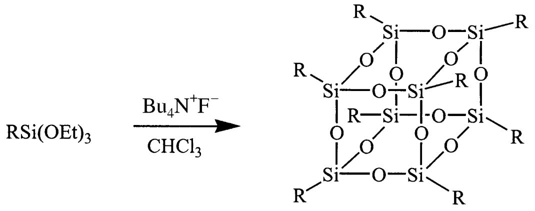
Octaspherosilicate structures have found use as scaffolds for dendrimer synthesis,[1–4] as models for aluminosilicate structures,[5] and as supports for organometallic catalysts.[6–8] Space-filling models of such cages suggest there is a void at the center of the cube, but that it is questionable whether it could be filled by an atomic species. Päch and Stosser have shown that γ-irradiation of octaalkyl octasilsesquioxane or octatrialkyl siloxyoctasilsesquioxane leads to hydrogen-encapsulated T8 or Q8 cages.[9] ESR spectroscopy confirmed that the hydrogen originated from the organic substituents of the cage.

We have recently developed a high-yield route to T8 cages based on the reaction of tetrabutylammonium fluoride with trialkoxysilanes (Scheme 1).[10] However, we have found that if instead of precipitating the cage by the addition of acetone the solvent is removed, then concentrating the quantity of tetrabutylammonium fluoride with the cage leads to a new cage structure. For example, the reaction of phenyltriethoxysilane with a 5 % solution of tetrabutylammonium fluoride in tetrahydrofuran, followed by removal of the solvent, gives a powder that can be purified by addition of chloroform leaving a white solid that is soluble in acetone. The solubility of this compound confirms that it is not phenyl T8.[11] The $^1$H NMR spectrum shows that each phenyl T8 cage is accompanied by one tetrabutylammonium cation. The $^{29}$Si NMR spectrum confirms the presence of the T8 cage and that the signal is shifted upfield by 0.9 ppm from octaphenyl octasilsesquioxane to $\delta = -80.6$ ppm, which suggests that the cage has been modified in some way. Negative-ion FAB mass spectrometry gives a single peak at $m/z = 1051.2$, with an isotope pattern corresponding to $C_{48}H_{40}Si_8O_{12}F$. These results suggest that a T8 cage associated with a fluoride ion was formed, which was confirmed by single-crystal X-ray crystallography after recrystallization from acetone. Figure 1 shows an ORTEP diagram of the crystal structure, in which the fluoride ion is essentially at the center of the cage.[12]



**Scheme 1.**

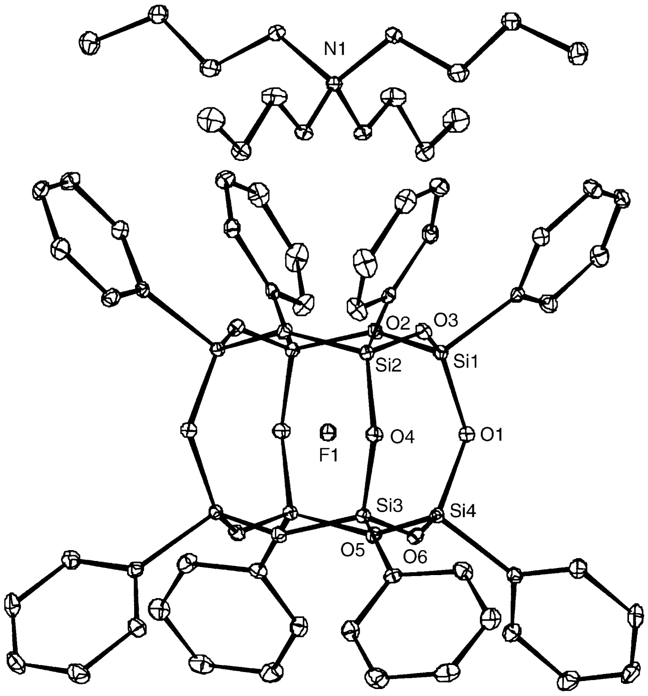


***Figure 1.*** ORTEP representation of tetrabutylammonium octaphenyl octasilsesquioxane fluoride. Selected bond lengths [Å] and angles [°] are given in Table 1.

The cages are packed together in horizontal layers with the tetrabutylammonium ions interleaved between the layers. The phenyl groups are aligned so that the butyl groups of the counterions lie in a cleft formed by the aromatic rings. This means that each cage has a tetrabutylammonium ion on two opposing faces.

Table 1 compares selected bond lengths and bond angles of the fluoride-encapsulated cage with those of the published phenyl T8 cage.[11] This reveals that the presence of the fluoride ion makes very little difference to the structure. The mean separation between the silicon atoms on opposite vertices of the cube is slightly shorter in the fluoride-encapsulated cage (5.306 Å) than in the free structure (5.381 Å) suggesting a small interaction of the fluoride ion with each of the eight silicon atoms. The Si···F separation in the fluoride cage is 2.65 Å, which is much longer than that of a full Si–F covalent bond (1.709 Å) or the Si–F bond length in a typical pentavalent species (1.675 Å).[13] The level of the fluorine–silicon interaction can be estimated by the size of the upfield shift in the $^{29}$Si NMR spectrum, which at 0.9 ppm is relatively small compared to the difference between a tetracoordinate silicon atom and the corresponding pentacoordinate silicon center associated with a fluoride ion ($\delta =$

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*Table 1:* Selected bond lengths [Å] and angles [°] of the phenyl T8 fluoride-encapsulated cage and the phenyl T8 cage.

| | Phenyl-T8 fluoride cage | Phenyl-T8 |
|---|---|---|
| Bond lengths [Å] | | |
| Si(1)–O(1) | 1.6224 | 1.613 |
| Si(1)–O(2) | 1.6213 | 1.607 |
| Si(1)–O(3) | 1.6284 | 1.614 |
| Average Si–O bond length [Å] | 1.625 | 1.612 |
| Bond angles [°] | | |
| O(4)-Si(1)-O(2) | 112.98 | 109.9 |
| O(4)-Si(1)-O(3) | 113.55 | 109.1 |
| O(2)-Si(1)-O(3) | 112.40 | 108.0 |
| Average O-Si-O angle [°] | 112.98 | 109.0 |
| Si(1)-O(1)-Si(4) | 141.11 | 144.6 |
| Si(1)-O(2)-Si(2) | 143.36 | 151.4 |
| Si(2)-O(3)-Si(1) | 139.11 | 151.4 |
| Average Si-O-Si angle [°] | 141.19 | 149.2 |

63 ppm).[13] The absence of any measurable Si–F coupling also confirms the low degree of silicon–fluoride interaction.

The mean separation between the oxygen atoms on opposite edges of the cube is slightly longer in the fluoride-encapsulated cage (5.413 Å) than in the free structure (5.396 or 5.176 Å), which suggests that the oxygen atoms are repelled by the fluoride ions. Comparison of the bond angles in Table 1 also confirms a general pulling together of the silicon atoms and pushing apart of the oxygen atoms. Closer examination of the position of the fluoride ion suggests that within experimental error it is slightly off center. This almost certainly reflects the slightly staggered packing of the cages.

The ability of fluorine atoms to cause supramolecular self-assembly and be involved in host–guest complexation has been extensively reviewed by Roesky and Haiduc, who provide evidence that fluorine can behave as a mono-, di-, tri-, or tetracoordinating species.[14] Whilst the Si–F interaction is small in the encapsulated cage, it is difficult to imagine that the fluoride ion is randomly placed in the center of the cage. Thus we are forced to conclude that in these octasilsesquioxane cages the fluorine atom is octacoordinated, as has recently been observed by Morris et al.[15] Refluxing the fluoride-ion cage in a range of solvents does not lead to the loss of the fluoride ion; this indicates that the faces of the silsesquioxane cage cannot provide a sufficiently large opening for the fluoride ion to pass through. This suggests that the fluoride ion must be acting as a template for formation of the cage and that once inside, it can only escape when the cage is broken down. Such a templating role for the fluoride ion has been proposed in molecular sieve synthesis, and Roesky et al.[16] and Mason et al.[17] have attempted to encapsulate a fluoride ion in alumino- and gallophosphonate models of the double four-ring (D4R) cage without success. However, Morris et al. have successfully used a hydrothermal synthesis involving HF to prepare the germanium oxide D4R cage containing a fluoride ion.[15] Preparations using tetrabutylammonium chloride show no evidence for encapsulation, and indeed no cage formation. This reflects the key role played by the fluoride ion as a base catalyst,[10] and the precise match between the size of the fluoride ion and the unoccupied space at the center of the cage.

Since the fluoride ion only coordinates with the silicon atoms to a small extent, it is essentially a naked fluoride ion. The $^{19}F$ NMR spectrum shows a sharp peak at $\delta = -26.4$ ppm, which is one of the highest frequencies recorded for a fluoride salt. The chemical shifts recorded for tetrabutylammonium fluoride are highly variable, ranging from $\delta = -73$ to $-146$ ppm depending upon solvent coordination and hydrogen bonding, particularly with moisture in the solvent. "Anhydrous" tetrabutylammonium fluoride has a chemical shift of $\delta = -73$ ppm.[18] The solid-state $^{19}F$ NMR spectrum is identical to that found in solution, which suggests that once inside the cage, the chemical shift of the fluoride ion is not greatly affected by its immediate environment. Recently, we reported that the change in the $^{19}F$ NMR chemical shift with the extent of Si–F bond breaking in pentacoordinate silicon complexes suggests that a value of about $\delta = -26$ ppm is in keeping with that expected for a naked fluoride ion.[19] Caullet et al. have reported the preparation of an octadecasil zeolite containing a fluoride ion in the D4R cage.[20] Whilst there is no detailed structural information reported, the solid-state $^{19}F$ NMR shows a peak at $\delta = -38$ ppm. The Si–F coordination is expected to be greater in these silicate structures since there is a Si–O bond apical to the fluoride ion, and thus the peak in the $^{19}F$ NMR spectrum should be shifted to a lower frequency compared to a naked fluoride ion. The $^{19}F$ chemical shift of a fluoride ion encapsulated in a D4R alumino- or gallophosphate cage in molecular sieves are observed further downfield at $\delta = -69$ to $-95$ ppm,[21–23] although the $^{19}F$ chemical shift of the fluoride ion encapsulated in the germanium oxide D4R cage occurs at $\delta = -15$ ppm.[15]

In conclusion, we have prepared the first fluoride ion to have been encapsulated in a silsesquioxane cage. The X-ray crystal structure and NMR data suggest very little F–Si coordination, such that the fluoride ion essentially resembles a naked fluoride ion. We are at present preparing other T8 cages containing a fluoride ion, but with different organic substituents on the silicon atoms. We are also exploring the novel properties of these molecular anions.

## Experimental Section

Tetrabutylammonium octaphenyl octasilsesquioxane fluoride: Tetrabutylammonium fluoride (1 M solution in THF, 2.5 cm$^3$ , with 5% water) was added to phenyl triethoxysilane (1.02 g, 4.2 mmol) dissolved in dry THF (20 cm$^3$). The mixture was stirred at room temperature for 24 h and a yellow viscous liquid obtained after removal of the solvent. Dry chloroform (10 cm$^3$) was added, and a white powder was obtained after filtration. Recrystallization from acetone afforded colorless crystals (1.25 g, 46%). $^1H$ NMR (300 MHz, [D$_6$]acetone, TMS): $\delta = 7.81$–$7.78$ (dd, $^3J(H_2,H_1) = 2.0$ Hz, $^3J(H_2,H_3) = 1.1$ Hz, 2H; *m*-CH), 7.79 (t, $^3J(H_3,H_2) = 1.1$ Hz, 1H; *p*-CH), 7.29 (d, $^3J(H_1,H_2) = 2.0$ Hz, 2H; *o*-CH), 3.39–3.34 (t, $^3J(H_4,H_5) = 8.26$ Hz, 2H; N-CH$_2$), 1.75–1.85 (quintuplet, $^3J(H_5,H_4) = 8.26$ Hz, $^3J(H_5,H_6) = 7.33$ Hz, 2H; CH$_2$), 1.36–1.48 (m, 2H; CH$_2$), 0.95–0.99 ppm (t, $^3J(H_7,H_6) = 7.54$ Hz, 3H, CH$_3$); $^{13}C$ NMR (75.5 MHz, [D$_6$]acetone, TMS): $\delta = 138.4$ (*p*-C), 134.9 (*m*-C), 129.7 (*i*-C), 128.1 (*o*-C), 49.8 (N-C), 24.3 (CH$_2$), 20.3 (CH$_2$), 13.8 ppm

($CH_3$); $^{19}F$ NMR (376 MHz, $CDCl_3$): $\delta = -26.4$ ppm; $^{29}Si$ NMR (79.30 MHz, $CDCl_3$, TMS): $\delta = -80.6$ ppm; IR (KBr disc): $\tilde{\nu} = 3085$ ($\nu_{C\text{-}H}$), 2990 ($\nu_{C\text{-}H}$), 2935 ($\nu_{C\text{-}H}$), 1410 (m), 1120 ($\nu_{as(Si\text{-}O\text{-}Si)}$), 1050, 1000, 750, 700, 510 ($\nu_{s(Si\text{-}O\text{-}Si)}$), 410 $cm^{-1}$ ($\delta_{(O\text{-}Si\text{-}O)}$); MS (MALDI-TOF): $m/z$ (%): 1294.5 [$M^-$], 1052.5 (35) [$M^- - C_{16}H_{36}N$], 1034 (100) [$M^- - C_{16}H_{36}NF$], 242.3 (99) [$C_{16}H_{36}N^-$], 19 [$F^-$].

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[12] Cell dimensions and intensity data were recorded using a Bruker Nonius KappaCCD area detector at the window of a molybdenum rotating anode generator following standard procedures. Crystal data: $C_{64}H_{76}NO_{12}FSi_8$, $M_W = 1294.98$, $T = 120(2)$ K, monoclinic, space group $C2/c$, $a = 23.8267(4)$, $b = 12.9976(3)$, $c = 22.1794(5)$ Å, $\beta = 108.1550(12)°$, $V = 6526.8(2)$ Å$^3$, $\rho_{calcd} = 1.318$ $g\,cm^{-3}$, $\mu = 0.228$ $mm^{-1}$, $Z = 4$, reflections collected: 16965, independent reflections: 5719 ($R_{int} = 0.0555$), final $R$ indices [$I > 2\sigma I$]: $R1 = 0.0397$, $wR2 = 0.1050$, $R$ indices (all data): $R1 = 0.0560$, $wR2 = 0.1134$. CCDC-203187 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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