Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010

Supporting Information for:

Encapsulation, storage and controlled release of sulfur hexafluoride from a metal-organic capsule

Imogen A. Riddell, Maarten M. J. Smulders, Jack K. Clegg and Jonathan R. Nitschke*

University of Cambridge, Department of Chemistry,
Lensfield Road, Cambridge, UK CB2 1EW
E-mail: jrn34@cam.ac.uk

Table of Contents

1 Experimental S2
1.1 General S2
1.2 Preparation of **1**, $(NMe_4)_4[Fe_4L_6]\cdot Me_2CO\cdot 15H_2O$ S2
1.3 Preparation of $SF_6\subset$**1** S2
1.4 Controlled release of SF_6 by opening of **1** S3
2 X-ray S4
3 Derivation and determination of the binding constant K_a S5
4 Volume and Pressure Calculations S6
4.1 Fit of Guest in Host Void Space....................S6
4.2 Estimation of Pressure Felt by SF_6 when Bound in Host Void Space S7
4.3 Maximum Total Concentration of SF_6 in Water in the Presence of **1**....................S7
5 References....................S8

1 Experimental

1.1 General

SF_6 and 1,4-dioxane were supplied from Sigma-Aldrich and used without further purification. NMR solvents were supplied from Fluorochem. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer using DMSO for reference. ^{13}C NMR spectra were recorded on a Bruker BB500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm).

1.2 Preparation of 1, $(NMe_4)_4[Fe_4L_6]\cdot Me_2CO\cdot 15H_2O$

1 was synthesised *via* an adaption of the previously published procedure.[S1]

4,4′-diaminobiphenyl-2,2′-disulfonic acid (purity 70%, balance water, 1 g, 2.03 mmol), 2-formylpyridine (502 μL, 527 mmol), tetramethylammonium hydroxide pentahydrate (958.1 mg, 5.28 mmol) and iron(II) sulfate heptahydrate (451.2 mg, 1.62 mmol) were added to a 100 mL Schlenk flask containing degassed water (25 mL). The reaction was stirred at 323 K for 20 hours before being concentrated through evaporation of approximately 5 mL of water. The product was then induced to crystallise through slow vapour diffusion of acetone into the reaction mixture. After one week the mother liquors were decanted yielding the final compound as dark purple crystals (0.85 g, 63%) which were washed with heptane and collected. NMR data was consistent with that previously published; elemental analysis calcd (%) for $C_{160}H_{144}N_{28}Fe_4O_{36}S_{12}\cdot Me_2CO\cdot 15(H_2O)$: C 49.29, H 4.57, N 9.88; found C 49.41, H 4.60, N 9.43.

1.3 Preparation of $SF_6\subset$1

A J-Young NMR tube was loaded with **1** (7 mg, 1.76 mmol) dissolved in D_2O (0.7 mL). SF_6 was bubbled through the solution for five minutes, the tube was then sealed under an atmosphere of SF_6 and heated at 323 K. After three hours two sets of resonances were clearly visible: those due to **1** and those due to $SF_6\subset$**1**. After three days the ratio of **1** : $SF_6\subset$**1** was observed to plateau. Signals corresponding to both the empty host and the host-guest species were present in both ^{1}H and ^{13}C NMR, however, for clarity only signals attributed to the host-guest complex are given below. ^{1}H NMR (400 MHz; 298 K; D_2O): δ 5.96 (12 H, d, 5,5′-benzidine), 6.45 (12H, s, 3,3′-benzidine), 7.20 (12H, d, 6,6′-benzidine), 7.63 (12H, d, 6-pyridine), 7.80 (12 H, t, 5-pyridine), 8.38 (12H, t, 4-pyridine), 8.74 (12H, d, 3-pyridine), 9.47 (12 H, s, imine). ^{13}C NMR (100.61 MHz; 298 K; D_2O): δ 176.6, 158.5, 156.8, 151.4, 144.1, 140.7, 136.8, 133.7, 133.0, 131.3, 122.6, 121.7, 56.0. ^{19}F NMR (376 MHz; 300 K; D_2O) δ 58.14 (1F, s, $^{32}SF_6$free), 61.77 (1F, s, $^{34}SF_6$bound), 61.79 (15F, s, $^{32}SF_6$bound). Purple crystals of SF_6⊂**1** were obtained through slow vapour diffusion of 1,4-dioxane into an aqueous solution of SF_6⊂**1**, which were used for the crystallographic studies.

1.4 Controlled release of SF_6 on decomposition of 1

Controlled decomposition of the cage occurred following the addition of tris(2-ethylamino)amine or following the addition of acid, in keeping with previously reported procedures.[S1] The breakdown of **1** was observed through ^{1}H NMR and the loss of SF_6 from solution by ^{19}F NMR. As noted in the main text, release of the SF_6 guest could also be achieved through heating a solution of **1** that was open to the atmosphere, which resulted in the disappearance of the ^{19}F signals.

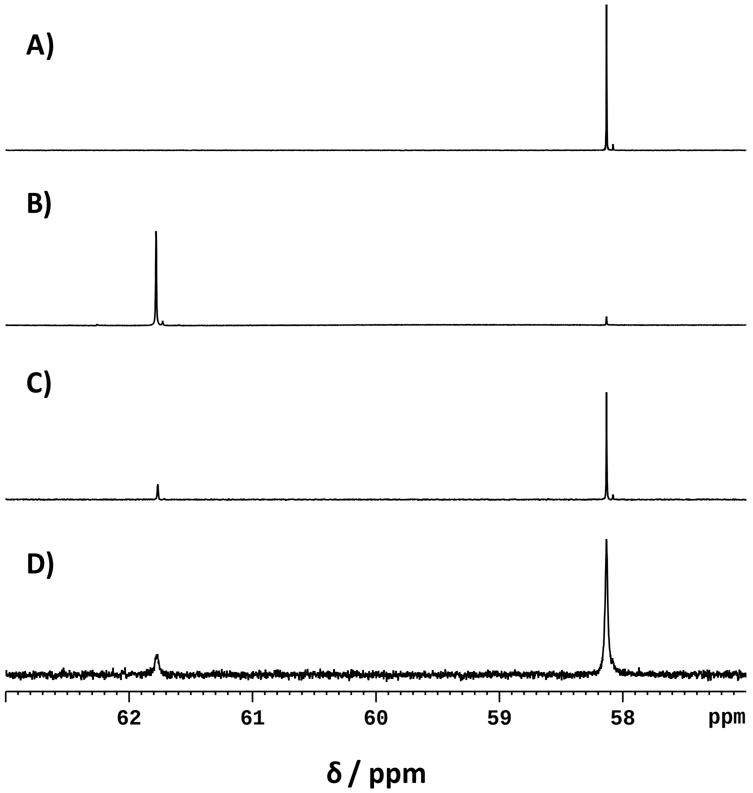

Figure S1.1: NMR spectra showing encapsulated and free SF_6 in D_2O: A) Free SF_6; B) [SF_6⊂**1**] and free SF_6; C) Remaining [SF_6⊂**1**] and free SF_6 after breakdown of **1** with tris(2-ethylamino)amine; D) Remaining [SF_6⊂**1**] and free SF_6 after breakdown of **1** with acid.

2 X-ray

Data for $(NMe_4)_4[(SF_6)_{0.5}\subset\mathbf{1}]\cdot 15H_2O$ were collected on a Nonius Kappa FR590 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a sealed tube (0.71073 Å) with ω and ψ scans at 180(2) K.[S2] Data integration and reduction were undertaken with HKL Denzo and Scalepack.[S3] Subsequent computations were carried out using the WinGX-32 graphical user interface.[S4] The structure was solved by direct methods using SIR97.[S5] Multi-scan empirical absorption corrections, when applied, were applied to the data set using the program SORTAV.[S6] Data were refined and extended with SHELXL-97.[S7] All atoms heavier than nitrogen of greater than 50 % occupancy were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. The crystals employed in this study were small and poor diffractors and rapidly suffered solvent loss. Despite rapid handling times and a low temperature collection no reflection data were observed at better than 1.0 Å resolution and none collected at better than 1.3 Å. In addition the crystals appeared to decay further during data collection resulting in lower than ideal completeness and redundancy. Nevertheless, the quality of the data is more than sufficient for establishing the connectivity of the structure and the encapsulation of the guest molecule. The SF_6 molecule is disordered over four positions and modelled with a total occupancy of 0.5. A number of bond length restraints were required to facilitate realistic modelling of the guests and the guest's atoms were all refined with identical thermal parameters as were the phenyl rings of the cage and sulfonate oxygens. In addition to the complex modelled there was a second chemically identical species present in the asymmetric unit. It was extremely disordered both positionally and by symmetry (over more than six positions). Despite numerous attempts at modelling with numerous rigid-body and bond length restraints, no satisfactory model could be found for this region (best R-factor > 30 %). In addition the cations and water solvent molecules were significantly disordered and could not be appropriately modelled. Therefore the SQUEEZE function of PLATON[S8] was employed to remove the contribution of the electron density associated with the disorder from the model (nearly 70 % of the unit cell volume), which resulted in far more satisfactory residuals.

3 Derivation and determination of the binding constant K_a

Formation of the host-guest complex was observed by both ^{1}H NMR and ^{19}F NMR spectrometry. In each case, both free and bound host and guest were observed which in conjunction with an accurate concentration of **1** allowed calculation of the binding constant for SF$_6$$\subset$**1**.

By integration of the ^{19}F NMR spectrum, the ratio p of free guest $[G]_F$ to host-guest $[HG]$ complex can be determined:

$$p = \frac{[G]_F}{[HG]} \tag{S3.1}$$

Analogously, from ^{1}H NMR, the ratio q of empty host $[H]_F$ to host-guest complex can be determined:

$$q = \frac{[H]_F}{[HG]} \tag{S3.2}$$

The total host concentration, $[H]_0$, is equal to the concentration of the empty host plus that of the host-guest complex:

$$[H]_0 = [H]_F + [HG] \tag{S3.3}$$

Therefore, combining equation S3.2 and S3.3 gives:

$$[HG] = \frac{[H]_F}{q} = \frac{[H]_0 - [HG]}{q} = \frac{[H]_0}{q+1} \tag{S3.4}$$

By inserting the known total concentration of host, $[H]_0$ and the q value determined from NMR integration in equation S3.4 the free host-guest complex concentration, $[HG]$, can be calculated, which can then be inserted in equation S3.1 to determine the free guest concentration, $[G]_F$. From the mass balance for the guest, it follows that the total guest concentration, $[G]_0$, is the sum of the free guest concentration, $[G]_F$ and the host-guest complex concentration, $[HG]$.

The final unknown parameter, the free host concentration, $[H]_F$, can be calculated in a similar manner to $[G]_F$ using the relationship: $[H]_F = q \times [HG]$.

$$[G]_0 = [G]_F + [HG] \tag{S3.5}$$

Finally, the binding constant for the equilibrium between host H and guest G, is calculated from:

$$H + G \rightleftharpoons HG$$

$$K = \frac{[HG]}{[H]_F[G]_F} \tag{S3.6}$$

Which, in this case, can be simplified to the following equation:

$$K = \frac{1}{q \times [G]_F} \tag{S3.7}$$

For three different experiments, in which the amount of guest added to the reaction mixture was varied, the following data were obtained (Table S3.1):

Table S3.1: Values obtained on integration of ^{1}H NMR and ^{19}F NMR using the equations given above (S3.1–S3.7).

Exp.	***p***	***q***	**$[H]_0$ / M**	**$[G]_0$ / M**	**K_a / M^{-1}**
IR 2.014	0.083	0.75	2.52×10^{-3}	1.56×10^{-3}	1.1×10^4
IR 2.020	0.063	0.59	2.72×10^{-3}	1.82×10^{-3}	1.6×10^4
IR 2.023	0.092	0.61	2.30×10^{-3}	1.56×10^{-3}	1.3×10^4

4 Volume and Pressure Calculations

4.1 Fit of Guest in Host Void Space

The void space of **1** was previously reported as 141 Å^3.[S1] The volume of SF_6 was calculated using SPARTAN[S10] as 74.61 Å^3.

4.2 Estimation of Pressure Felt by SF_6 when Bound in Host Void Space

Assuming **1** to be a static system and SF_6 to behave as an ideal gas, we can apply the Ideal Gas Equation to calculate the pressure felt by one molecule of SF_6 within the void cavity of **1**.

$$p = \frac{nRT}{V} \tag{S4.1}$$

The calculated pressure is found to be 288 atmospheres when $n = 1.6605 \times 10^{-24}$ mol and $V = 1.41 \times 10^{-28}$ m^3 at 298 K.

4.3 Maximum Total Concentration of SF_6 in Water in the Presence of 1

Based on the maximum solubility of **1** (8.57×10^{-3} M) and SF_6 (2.2×10^{-4} M) in water, a theoretical maximum total concentration for SF_6 could be calculated as shown below.

The following equation holds for 1:1 host-guest complexes:[S11]

$$\frac{[HG]}{[H]_0} = \frac{K_a[G]_F}{1 + K_a[G]_F} \tag{S4.2}$$

Rearranging equation S4.2 and inserting the calculated binding constant, $K_a = 1.3 \times 10^4\ M^{-1}$, and the concentration for the maximum solubility of SF_6 in water, $[G]_F = 2.2 \times 10^{-4}$ M, gives:

$$[HG] = \frac{K_a[G]_F}{1 + K_a[G]_F} \times [H]_0 \tag{S4.3}$$

$$[HG] = 0.74 \times 8.57 \times 10^{-3} = 6.35 \times 10^{-3}\ M$$

Where $[HG]$ is the concentration of the SF_6 in solution, the total concentration of SF_6 therefore is simply given by the addition of $[HG]$ to the maximum concentration of SF_6 which can be solubilised in water.

$$[G]_0 = 6.57 \times 10^{-3}\ M$$

5 References

S1. P. Mal, D. Schultz, K. Beyeh, K. Rissanen and J. R. Nitschke, *Angew. Chem., Int. Ed.*, 2008, **47**, 8297-8301.

S2. Nonius BV, *COLLECT*, (1998) Nonius BV, Delft, The Netherlands.

S3. Z. Otwinowski and W. Minor, *Methods in Enzymology*, 1997, **276**, 307-326.

S4. L. Farrugia, *J. Appl. Cryst.*, 1999, **32**, 837-838.

S5. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giocavazzo, A. Gaugliardi, G. C. Moliterni, G. Polidori and S. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.

S6. A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Cryst.*, 1994, **27**, 435.

S7. R. H. Blessing, *Acta Cryst.*, 1995, **A51**, 33-38.

S8. G. M. Sheldrick, *SHELXL-97: Programs for Crystal Structure Analysis, University of Göttingen, Germany*, 1997.

S9. A. L. Spek, *Acta Cryst.*, 1990, **A46**, C34.

S10. Wavefunction, *SPARTAN '04 for Windows*, (2004), 18401 Von Karman Ave., Irvine, CA 92612, USA.

S11. K. A. Connors, *Binding Constants: The Measurements of Molecular Complex Stability*, John Wiley + Sons, 1987.