Supplementary Material (ESI) for Dalton Transactions

Supporting Information

For

Synthesis of fluoro(aryloxo)alkaline earth metal cages by C-F bond activation

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Contents

1. General experimental details

The compounds contained in this paper are extremely air and moisture sensitive; consequently all reactions and manipulations were performed using standard Schlenk line and dry box techniques under an atmosphere of purified nitrogen. 1,2-dimethoxyethane (dme) was dried and de-oxygenated by refluxing over, and distillation from, purple sodium benzophenone ketyl. 2,4,6-trimethylphenol (HOmes) was purchased from Aldrich and used as received. Bis(pentafluorophenyl)mercury was prepared using a literature procedure.[1] Alkaline earth metals were obtained from Aldrich as chunks or turnings which were freshly filed under purified nitrogen prior to use. Infrared spectra were recorded as Nujol mulls sandwiched between NaCl plates on a Perkin-Elmer 1600 Fourier transform infrared spectrometer. ^{1}H NMR and ^{19}F NMR spectra were obtained with a Bruker DPX 300 MHz spectrometer, using dried, de-gassed deuterated solvents. ^{1}H NMR chemical shifts are referenced to the residual ^{1}H resonances of the solvent, while ^{19}F NMR spectra were measured using $CFCl_3$ as an external reference. Microanalyses were performed in duplicate by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

1. G.B. Deacon, J.E. Cosgriff, E.T. Lawrenz, C.M. Forsyth and D.L. Wilkinson, in *Synthetic Methods of Inorganic and Organometallic Chemistry,* ed. F.T. Edelmann, G. Thieme Verlag, New York, 1996, vol. 6, p. 48.

2. X-ray crystallographic details

Intensity data were collected using a Bruker X8 Apex II CCD at 123 K with Mo-Kα radiation (λ = 0.71703 Å). Suitable crystals were immersed in viscous hydrocarbon oil and mounted on a glass fibre which was mounted on the diffractometer. Using psi and omega scans N_t (total) reflections were measured, which were reduced to N_o unique reflections, with $F_o > 2\sigma(F_o)$ being considered observed. Data were initially processed and corrected for absorption using the Bruker Apex II program suite.[2] The structures were solved using direct methods, and observed reflections were used in least squares refinement on F^2, with anisotropic thermal parameters refined for non-hydrogen atoms. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Structure solutions and refinements were performed using the programs SHELXS-97[3] and SHELXL-97[4] through the graphical interface X-Seed,[5] which was also used to generate the figures. **Variata:** The anisotropic displacement parameters of atoms C8 and C25 (methyl groups) in **1**·2dme were restrained. The anisotropic displacement parameters of atoms C19 - C27, C46 - C54, C64 - C71 and C82 - C90 in **2**·4dme were restrained. Disordered lattice dme molecules (16 dme per unit cell) could not be successfully modelled and were removed from the refinement using PLATON SQUEEZE.[6] Evidence for the diffuse nature of the dme of solvation was supported by its ready loss prior to microanalysis and ^{1}H NMR measurements which are consistent with 2·0dme.

2. *Apex II Version 2.1*, Bruker AXS Ltd., Madison, Wisconsin.

3. G.M. Sheldrick *SHELXS-97 Program for crystal structure solution*; University of Göttingen, Göttingen, Germany, 1997.

4. G.M. Sheldrick *SHELXL-97 Program for crystal structure refinement*; University of Göttingen, Göttingen, Germany, 1997.

5. L.J. Barbour, *J. Supramol. Chem.,* 2001, **1**, 189.

6. P. v.d. Sluis and A. L. Spek, Acta Crystallogr., Sect A, 1990, **46**, 194.

3. Bond distances (Å) and angles (°) for 1·2dme and 2·4dme

Table S1: Selected bond distances (Å) and bond angles (°) for **1**·2dme.

Bond distances			
Ca(1) - F(1)	2.240(2)	Ca(2) - O(6)	2.506(3)
Ca(1) - F(1)#1	2.240(2)	Ca(2) - O(7)	2.445(3)
Ca(1) - F(2)	2.237(2)	Ca(3) - F(1)	2.287(2)
Ca(1) - F(2)#1	2.237(2)	Ca(3) - F(2)#1	2.371(2)
Ca(1) - O(3)	2.145(4)	Ca(3) - F(3)	2.410(1)
Ca(2) - F(1)	2.368(2)	Ca(3) - O(1)	2.326(3)
Ca(2) - F(2)	2.297(2)	Ca(3) - O(2)#1	2.325(3)
Ca(2) - F(3)	2.381(1)	Ca(3) - O(4)	2.446(3)
Ca(2) - O(1)	2.317(3)	Ca(3) - O(5)	2.509(3)
Ca(2) - O(2)	2.334(3)		
Bond angles			
F(1) - Ca(1) - F(1)#1	127.5(1)	F(1) - Ca(3) - F(3)	70.99(8)
F(1) - Ca(1) - F(2)	78.86(8)	F(1) - Ca(3) - O(1)	76.26(8)
F(1) - Ca(1) - F(2)#1	78.83(8)	F(1) - Ca(3) - O(2)#1	141.82(9)
F(1) - Ca(1) - O(3)	116.24(6)	F(1) - Ca(3) - O(4)	87.7(1)
F(1)#1 - Ca(1) - F(2)	78.83(8)	F(1) - Ca(3) - O(5)	126.9(1)
F(1)#1 - Ca(1) - F(2)#1	78.86(8)	F(2)#1 - Ca(3) - F(3)	69.88(8)
F(1)#1 - Ca(1) - O(3)	116.24(6)	F(2)#1 - Ca(3) - O(1)	140.88(9)
F(2) - Ca(1) - F(2)#1	128.1(1)	F(2)#1 - Ca(3) - O(2)#1	74.50(9)
F(2) - Ca(1) - O(3)	115.95(6)	F(2)#1 - Ca(3) - O(4)	77.9(1)
F(2)#1 - Ca(1) - O(3)	115.95(6)	F(2)#1 - Ca(3) - O(5)	133.68(9)
F(1) - Ca(2) - F(2)	75.10(8)	F(3) - Ca(3) - O(1)	75.88(8)
F(1) - Ca(2) - F(3)	70.14(7)	F(3) - Ca(3) - O(2)#1	77.13(8)
F(1) - Ca(2) - O(1)	74.88(9)	F(3) - Ca(3) - O(4)	144.8(1)
F(1) - Ca(2) - O(2)	141.75(9)	F(3) - Ca(3) - O(5)	150.1(1)
F(1) - Ca(2) - O(6)	132.69(9)	O(1) - Ca(3) - O(2)#1	115.9(1)
F(1) - Ca(2) - O(7)	76.23(9)	O(1) - Ca(3) - O(4)	126.9(1)
F(2) - Ca(2) - F(3)	71.62(8)	O(1) - Ca(3) - O(5)	85.2(1)
F(2) - Ca(2) - O(1)	141.99(9)	O(2)#1 - Ca(3) - O(4)	107.9(1)
F(2) - Ca(2) - O(2)	75.74(9)	O(2)#1 - Ca(3) - O(5)	91.1(1)
F(2) - Ca(2) - O(6)	126.97(9)	O(4) - Ca(3) - O(5)	64.9(1)
F(2) - Ca(2) - O(7)	88.58(9)	Ca(1) - F(1) - Ca(2)	98.69(8)
F(3) - Ca(2) -O(1)	76.61(8)	Ca(1) - F(1) - Ca(3)	101.26(8)
F(3) - Ca(2) - O(2)	77.53(7)	Ca(2) - F(1) - Ca(3)	92.66(8)

F(3) - Ca(2) - O(6)	150.4(1)	Ca(1) - F(2) - Ca(2)	100.88(9)
F(3) - Ca(2) - O(7)	144.3(1)	Ca(1) - F(2) - Ca(3)#1	98.76(8)
O(1) - Ca(2) - O(2)	117.2(1)	Ca(2) - F(2) - Ca(3)#1	92.19(8)
O(1) - Ca(2) - O(6)	90.74(9)	Ca(2) - F(3) - Ca(2)#1	167.3(1)
O(1) - Ca(2) - O(7)	106.2(1)	Ca(2) - F(3) - Ca(3)	89.31(3)
O(2) - Ca(2) - O(6)	85.04(9)	Ca(2) - F(3) - Ca(3)#1	89.20(3)
O(2) - Ca(2) - O(7)	127.0(1)	Ca(2)#1 - F(3) - Ca(3)	89.20(3)
O(6) - Ca(2) - O(7)	64.82(9)	Ca(3) - F(3) - Ca(3)#1	166.5(1)
F(1) - Ca(3) - F(2)#1	75.19(8)		

Symmetry operation used to generate equivalent atoms: #1: -x + 1, y, -z + 1/2

Table S2: Selected bond distances (Å) and bond angles (°) for **2**·4dme.

Bond distances			
Sr(1) - F(1)	2.455(6)	Sr(6) - F(3)	2.468(6)
Sr(1) - F(2)	2.438(6)	Sr(6) - F(4)	2.451(6)
Sr(1) - F(5)	2.441(6)	Sr(6) - F(7)	2.448(5)
Sr(1) - F(6)	2.459(5)	Sr(6) - F(8)	2.447(5)
Sr(1) - O(1)	2.497(7)	Sr(6) - O(5)	2.484(7)
Sr(1) - O(2)	2.453(7)	Sr(6) - O(6)	2.502(7)
Sr(2) - F(1)	2.441(6)	Sr(7) - F(5)	2.425(5)
Sr(2) - F(4)	2.463(6)	Sr(7) - O(1)	2.427(8)
Sr(2) - F(5)	2.430(5)	Sr(7) - O(8)	2.430(8)
Sr(2) - F(8)	2.439(5)	Sr(7) - O(12)	2.430(7)
Sr(2) - O(11)	2.483(7)	Sr(7) - O(13)	2.657(8)
Sr(2) - O(12)	2.492(7)	Sr(7) - O(14)	2.646(8)
Sr(3) - F(2)	2.429(6)	Sr(8) - F(6)	2.423(6)
Sr(3) - F(4)	2.444(6)	Sr(8) - O(2)	2.426(7)
Sr(3) - F(5)	2.440(6)	Sr(8) - O(3)	2.433(7)
Sr(3) - F(7)	2.434(5)	Sr(8) - O(10)	2.450(7)
Sr(3) - O(7)	2.466(7)	Sr(8) - O(15)	2.627(8)
Sr(3) - O(8)	2.461(7)	Sr(8) - O(16)	2.661(8)
Sr(4) - F(2)	2.449(6)	Sr(9) - F(7)	2.426(5)
Sr(4) - F(3)	2.452(6)	Sr(9) - O(6)	2.430(7)
Sr(4) - F(6)	2.421(6)	Sr(9) - O(7)	2.412(7)
Sr(4) - F(7)	2.427(5)	Sr(9) - O(9)	2.442(7)
Sr(4) - O(9)	2.471(7)	Sr(9) - O(19)	2.667(7)
Sr(4) - O(10)	2.470(7)	Sr(9) - O(20)	2.641(7)
Sr(5) - F(1)	2.443(6)	Sr(10) - F(8)	2.418(5)
Sr(5) - F(3)	2.461(6)	Sr(10) - O(4)	2.402(8)
Sr(5) - F(6)	2.445(5)	Sr(10) - O(5)	2.455(7)
Sr(5) - F(8)	2.437(6)	Sr(10) - O(11)	2.427(7)
Sr(5) - O(3)	2.465(7)	Sr(10) - O(17)	2.669(8)
Sr(5) - O(4)	2.485(7)	Sr(10) - O(18)	2.649(8)
Bond angles			
F(1) - Sr(1) - F(2)	109.5(2)	F(5) - Sr(7) - O(12)	70.8(2)
F(1) - Sr(1) - F(5)	70.8(2)	F(5) - Sr(7) - O(13)	159.7(3)
F(1) - Sr(1) - F(6)	70.5(2)	F(5) - Sr(7) - O(14)	137.3(2)
F(1) - Sr(1) - O(1)	112.8(2)	O(1) - Sr(7) - O(8)	106.5(3)
F(1) - Sr(1) - O(2)	107.4(2)	O(1) - Sr(7) - O(12)	113.7(3)
F(2) - Sr(1) - F(5)	71.0(2)	O(1) - Sr(7) - O(13)	91.3(3)
F(2) - Sr(1) - F(6)	70.1(2)	O(1) - Sr(7) - O(14)	150.0(3)
F(2) - Sr(1) - O(1)	106.6(2)	O(8) - Sr(7) - O(12)	111.0(3)
F(2) - Sr(1) - O(2)	110.5(2)	O(8) - Sr(7) - O(13)	103.7(3)
F(5) - Sr(1) - F(6)	109.7(2)	O(8) - Sr(7) - O(14)	91.4(3)
F(5) - Sr(1) - O(1)	70.3(2)	O(12) - Sr(7) - O(13)	127.7(3)
F(5) - Sr(1) - O(2)	178.1(2)	O(12) - Sr(7) - O(14)	79.7(3)
F(6) - Sr(1) - O(1)	176.2(2)	O(13) - Sr(7) - O(14)	61.2(3)
F(6) - Sr(1) - O(2)	70.1(2)	Sr(1) - F(5) - Sr(2)	109.4(2)
O(1) - Sr(1) - O(2)	110.1(2)	Sr(1) - F(5) - Sr(3)	108.7(2)
Sr(1) - F(1) - Sr(2)	108.6(2)	Sr(1) - F(5) - Sr(7)	109.9(2)
Sr(1) - F(1) - Sr(5)	109.4(2)	Sr(2) - F(5) - Sr(3)	109.2(2)
Sr(2) - F(1) - Sr(5)	109.7(2)	Sr(2) - F(5) - Sr(7)	110.8(2)
F(5) - Sr(7) - O(1)	71.7(2)	Sr(3) - F(5) - Sr(7)	108.8(2)
F(5) - Sr(7) - O(8)	72.0(2)		

4. Molecular structures of 1·2dme and 2·4dme

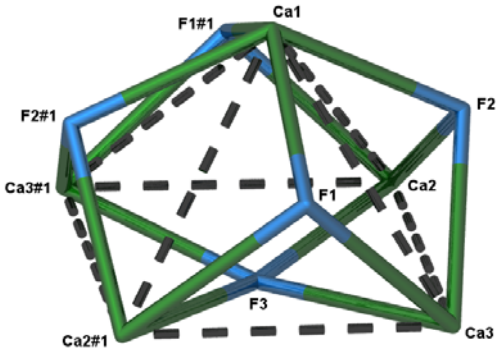

Figure S1: The pentanuclear core structure of **1**·2dme, displaying the bridging fluoride ligands. The square pyramidal arrangement of Ca atoms is denoted by the dashed lines. Symmetry operation used to generate equivalent atoms: #1: -x + 1, y, -z + 1/2

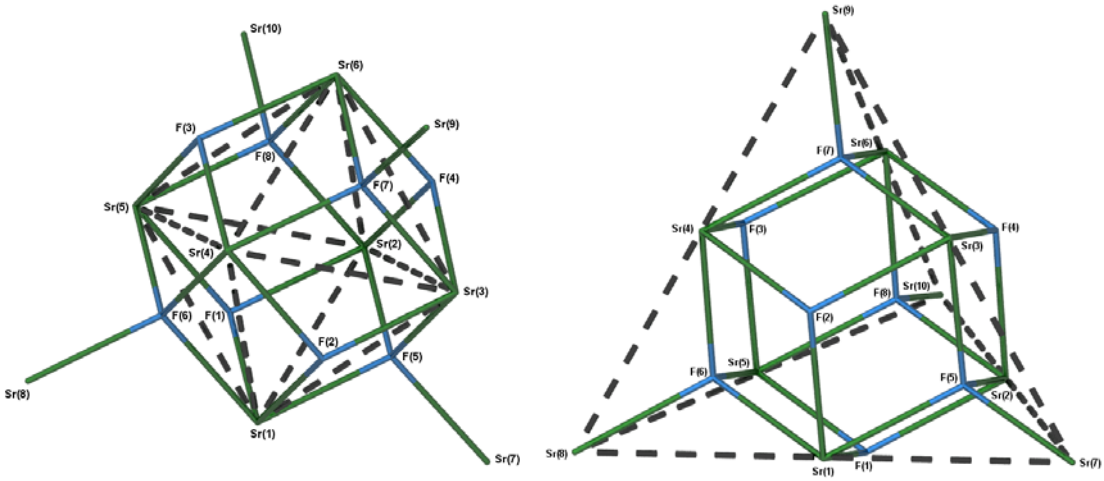

Figure S3: The core structure of **2**·4dme, displaying the bridging fluoride ligands. The octahedral arrangement of core Sr atoms (left) and tetrahedral arrangement of peripheral Sr atoms (right) is denoted by the dashed lines.