

Electronic Supplementary Information for:

An Expanded Neutral M_4L_6 Cage that Encapsulates Four Tetrahydrofuran Molecules†

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Experimental

Ligand synthesis

Ligand H_2L was prepared as previously reported.^{S1}

Complex synthesis

H_2L (0.002 mol) in dry THF (40 mL) was added to Na_2CO_3 (1.0 g, 0.01 mol) in dry THF (10 mL). The mixture was stirred for 1 h before anhydrous iron(III) or gallium(III) chloride (0.0013 mol) dissolved in dry THF (40 mL) was added dropwise. The mixture was stirred for 16 h at reflux under nitrogen, then filtered and the filtrate collected. The filtrate was taken to dryness and the crude solid obtained was washed with methanol followed by diethyl ether before recrystallisation from tetrahydrofuran; individual crystalline samples used for microanalysis were crushed and dried under vacuum over P_2O_5 prior to analysis. Yields and characterisation are given below.

[Fe₄L₆]

Yield 0.82g (90 %), red microcrystalline powder. Found: C, 68.66; H, 6.74 %. Calc. for $C_{156}H_{168}Fe_4O_{24} \cdot 5CH_3OH$: C, 68.80; H, 6.74 % UV-Vis (solid state): 370, 420, 466, 579, 655, 780 nm. Crystals suitable for X-ray analysis of composition

$[Fe_4L_6 \supset 4THF] \cdot 14THF \cdot 14Et_2O$ were grown over several months by the slow diffusion of diethyl ether into a loosely sealed container of a THF solution of $[Fe_4L_6]$.

[Ga₄L₆]

Yield 0.67g (76 %), pale yellow microcrystalline powder. Found: C, 69.33; H, 6.57 %. Calc. for C₁₅₆H₁₆₈Ga₄O₂₄: C, 69.31; H, 6.27 %. ¹H-NMR δ (400 MHz, THF-*d*₈): 8.09 (d of d, aromatic, 4H), 7.76(d of d, aromatic, 4H), 6.64 (s, -CH- enol, 2H), 1.22 (s, -CH₃, 18H). UV-Vis (solid state): 452, 675, 806 nm

Crystallography

Data were collected at 150(2) K with ω scans to approximately 56° 2 θ using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å). Data integration and reduction were undertaken with SAINT and XPREP.^{S2} Subsequent computations were carried out using the WinGX-32 graphical user interface.^{S3} Structures were solved by direct methods using SIR97.^{S4} Multi-scan empirical absorption corrections were applied to data sets using the program SADABS.^{S5} Data were refined and extended with SHELXL-97.^{S6} All non-hydrogen atoms were refined anisotropically. In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. One of the tertiary butyl groups is disordered over three equal occupancy positions and each of the carbon atoms was included with identical thermal parameters. The tetrahydrofuran guest molecules are disordered over two equal occupancy positions and a number of bond length restraints were required to facilitate realistic modelling. The crystals were highly unstable through loss of solvent and decayed at room temperature in a matter of seconds. A very rapid cold mount (less than 10 seconds at *ca* 200 K) and cryostream quenching (150 K) were required to enable satisfactory data collection to take place. Reflecting the instability of the crystals, there is a large region of smeared electron density in the lattice, some of which could be modelled as five disordered diethyl ether molecules. However, the best fit that could be achieved resulted in a high *R*-factor of the order of 16 %. The SQUEEZE function of PLATON^{S7} estimated that there were 4727 electrons associated with disordered solvent in this region, which corresponds approximately to 12 diethyl ether or tetrahydrofuran molecules per unit cell (or 28 per tetrahedron, which was

included in the formula as equal numbers of both diethyl ether and tetrahydrofuran). When this electron density was removed a significantly improved *R*-factor of ~8 % resulted.

Volume Calculations

In order to determine the size of the inner cavity of the complexes, VOIDOO calculations based on the crystal structures were performed.^{S8} A virtual probe with a radius of 1.4 Å (default, water-sized) was employed, and the following parameters were changed from their default settings:

Maximum number of volume-refinement cycles:	30
Minimum size of secondary grid:	3
Grid for plot files:	0.1
Primary grid spacing:	0.1
Plot grid spacing:	0.1

Due to the large pore size of each complex, six grapheme sheets were placed over the pores to prevent the probe from “falling out” of the inner sphere. They were placed in such a way that the van der Waals radii of their atoms touched the outermost edge of the van der Waals radii of the atoms of the complexes lining the pores. The cavities calculated are presented as a green mesh inside the crystal structures of each complex (see Figure S1). The volumes calculated corresponded to 174 Å³ for the small structure^{S9} and 834 Å³ for the larger [Fe₄L₆]·15THF·14Et₂O.

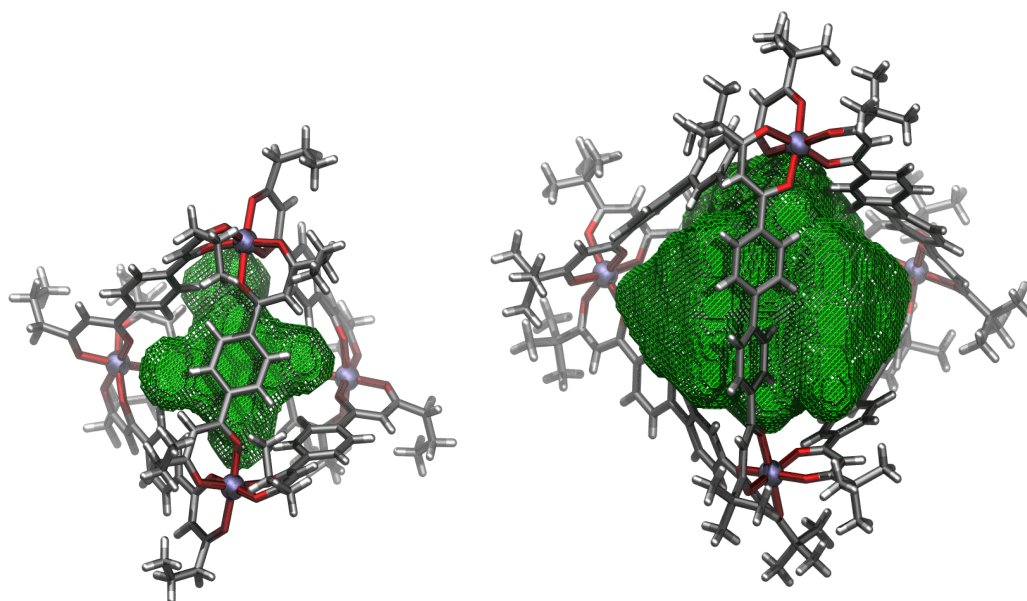


Figure S1: Voidoo calculated volumes (green mesh) inside the respective crystal structures.

References

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