Stellated polyhedral assembly of a topologically complicated Pd₄L₄ ‘Solomon cube’
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1. Synthesis
All chemicals were obtained from Sigma-Aldrich Chemical Company or Alfa Aesar and were used
without further purification. Microanalyses were obtained on a Carlo Erba Elemental Analyser
MOD 1106 instrument. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer and
samples analysed as solids. Mass spectra of organic compounds were obtained using a micrOTOF
spectrometer using time-of-flight electrospray analysis.

Preparation of 3-(3-pyridyl)benzoic acid
Prepared according to literature methods (Gong, Y.; Pauls, H. W. Synlett 2000, 829-831) with
minor modifications.
Pd(PPh₃)₄ (0.24 g, 0.21 mmol) was added to a degassed solution 3-carboxybenzene boronic acid
(0.675 g, 4.07 mmol) and 3-bromopyridine (0.643 g, 4.07 mmol) in 0.4 M Na₂CO₃ solution (30 mL)
and acetonitrile (30 mL). The mixture was heated at 90°C under N₂ for 16 hours. The hot
suspension was filtered. The filtrate was acidified with 1 M HCl and the volume reduced by half in vacuo and the mixture colled in the fridge overnight. The white solid was collected by filtration to give 3-(3-pyridyl)benzoic acid as the hydrochloride salt. Yield 0.81 g, 84 %. ¹H NMR (500 MHz, d₆-DMSO): δ (ppm) 9.29 (1H, d, pyridyl H², J = 2.1 Hz), 8.90 (1H, dd, pyridyl H⁶, J = 5.6, 1 Hz), 8.85 (1H, dt, pyridyl H⁴, J = 8.1, 1 Hz), 8.37 (1H, t, phenyl H², J = 1.3 Hz), 8.14 (1H, m, phenyl H⁴ or H⁶), 8.06-8.11 (2H, m, phenyl H⁴ or H⁶, pyridyl H⁵), 7.72 (1H, t, phenyl H⁵, J = 7.7 Hz). ¹³C NMR (75 MHz, d₆-DMSO): δ (ppm) 167.1, 143.2, 141.7, 141.1, 138.1, 134.9, 132.3, 132.2, 130.6, 130.1, 128.5, 127.4. Found C 58.80, H 4.20, N 5.45; C₁₂H₉NO₂(HCl)(H₂O)₀.₅ requires C 58.90, H 4.53, N 5.72 %.

Preparation of 3-(3-pyridyl)benzoyl chloride hydrochloride. 3-(3-Pyridyl)benzoic acid
hydrochloride (2.07 g, 8.78 mmol) was refluxed under N₂ in thionyl chloride (10 mL) containing a
few drops of DMF for 24 hours. The thionyl chloride was removed in vacuo and the off-white solid
washed with diethyl ether to give 3-(3-pyridyl)benzoyl chloride hydrochloride as an off-white powder. Yield 1.90 g, 85 %.
2. NMR studies

**DOSY NMR measurements:** DOSY NMR measurements were made on a Varian Inova 500 MHz spectrometer operating under regulated temperature conditions (20 °C), with a 5 mm probe. The pulse sequence employed was a bipolar pulse pair simulated echo (BPPSTE) operating in the ONESHOT experiment. A diffusion delay of 0.06 s was used for the ligand compared to 0.11 s for the complex. Additional parameters: number of different gradient levels, 15; gradient stabilisation delay, 0.002 s; gradient length, 0.005 s; relaxation delay, 10 s; Kappa (unbalancing factor), 0.2. Spectra were recorded for a 4 mM solution of ligand with added Pd(NO₃)₂.2H₂O (1:1 metal/ligand ratio) and for a 4 mM solution of ligand by itself. A DOSY spectrum is shown in Figure S3 below.

**Other NMR measurements:** ¹H Nuclear Magnetic Resonance spectra were recorded using a Bruker Avance 500 instrument. ¹³C Nuclear Magnetic Resonance spectra of the organic compounds were recorded using a Bruker DPX 300 instrument. ¹H spectra are referenced to tetramethylsilane and chemical shifts given in parts per million downfield from TMS. All other spectra were recorded at 20°C (other than the VT) on a Varian Unity Inova 500 MHz spectrometer. For the 2D data sets States hypercomplex phase cycling was used, with 256 pairs of increments collected in 2048 data points. The data were processed with -1Hz line broadening in each dimension and a Gaussian factor of 0.06 and 0.03 in the F2 and F1 dimensions respectively.

All NMR spectra were run on d₆-DMSO solutions containing a mixture of Pd(NO₃)₂ and ligand 1 in 1:1 proportions.
Figure S1: $^1$H NMR spectra of ligand 1 (upper) and a 1:1 mixture of Pd(NO$_3$)$_2$ and ligand 1 (lower) in $d_6$-DMSO with (b) showing an expansion of the aromatic area. Desymmetrisation of the ligand spectrum is observed on complex formation which is consistent with formation of the [Pd$_4$(1)$_4$(NO$_3$)$_2$(H$_2$O)$_2$](NO$_3$)$_6$ Solomon’s cube where all three phenyl-pyridyl side-arms of the ligand are in different orientations.
**Figure S2**: 500 MHz $^1$H NMR spectra for [Pd$_4$(1)$_4$(NO$_3$)$_2$(H$_2$O)$_2$]$^{6+}$ as a function of temperature. The lack of changes in the spectra on heating supports there being only one species in solution.
Analysis of DOSY results

\[ D_{\text{complex}} = 0.61 \times 10^{-10} \text{ m}^2\text{s}^{-1} \]
\[ D_{\text{ligand}} = 1.08 \times 10^{-10} \text{ m}^2\text{s}^{-1} \]

Measured \( \frac{D_{\text{complex}}}{D_{\text{ligand}}} = 0.56 \)

Using the relationship \( \frac{D_1}{D_2} = \frac{\sqrt[3]{M_2}}{\sqrt[3]{M_1}} \) allows estimation of the expected \( \frac{D_{\text{complex}}}{D_{\text{ligand}}} \) ratio and/or of the molecular mass of the species in solution using the measured \( \frac{D_{\text{complex}}}{D_{\text{ligand}}} \) ratio. These calculations assume a spherical species hence will be an approximation in this case.

Expected \( \frac{D_{\text{complex}}}{D_{\text{ligand}}} \) ratio for [Pd₄(1)₄(NO₃)₂(H₂O)₂]⁶⁺ = 0.60.

Calculated \( Mr \) for species in solution is 4976 compared with 4394 for [Pd₄(1)₄(NO₃)₂(H₂O)₂]⁶⁺. Note that the species in solution will have associated NO₃⁻ anions and DMSO guest molecules not accounted for here. For example, species with one DMSO guest per ligand and all counter-anions required for charge balance (some presumably in the second coordination sphere) has a \( Mr \) of 5078.
Figure S4. 500 MHz $^1$H NOESY spectrum for the complex. Crosspeaks are the same phase as the diagonal (the nOes are thus negative). A mixing time of 400 ms was used for nOe buildup. 1D nOe spectra for the ligand display negative nOes from the CH$_2$ group to cavitand aromatic protons. Multiples of such connections can be seen in the NOESY spectrum of the complex (the CH$_2$ group(s) protons resonate at 5ppm and around 4.8ppm and display cross peaks to protons over the range 7.4-8 ppm. Similarly two sets of signals for the methyl of the methoxy group are resolved (at 3.7 and 3.3ppm) each displaying nOes to both the CH$_2$ group(s) and the aromatic protons. These are all through space connections and not exchange phenomena (as proven with the ROESY spectrum below)
**Figure S5.** 500 MHz $^1$H DQFCOSY spectrum of the complex. The singlet resonances for the cavitand core are filtered out in this experiment. All that is detected are the through bond interactions involving the CH$_2$ of the cavitand (ca. 5 and 3.8ppm) and the connections amongst the protons of the ‘arms’. It is clear that the symmetry of the cavitand is lost in the complex.
Figure S6. Section of the ROESY spectrum for the complex. The red crosspeaks are the through space connections. Three – ‘blue’ exchange cross peaks are visible. A 400 ms spin lock time was used for rOe build up. As is typical fewer through space connections are seen compared with the NOESY data set, but the importance of the ROESY spectrum is in supporting the VT experiments in establishing that chemical exchange is not the reason for the complicated spectrum, it is the asymmetry of the complex.
3. Mass spectrometry

**Electrospray MS measurements:** The electrospray mass spectrum of [Pd₄(1)₄(NO₃)₂(H₂O)₂](NO₃)₆ was collected at the University of Huddersfield and was measured on a Bruker MicroTOF-Q instrument in positive ion mode. A sample of [Pd₄(1)₄(NO₃)₂(H₂O)₂](NO₃)₆ was prepared at a concentration of ca. 5 mM in DMSO and analysed by direct infusion using a Cole Parmer syringe pump at a flow rate of 3 ml/min. Spectra were acquired over an m/z range of 50 – 4000; several scans were averaged to provide the final spectrum. The charge of each species (n⁺) was confirmed by the spacing between the isotope components, which were (1/n) mass units.

The electrospray mass spectrum for a 1:1 mixture of Pd(NO₃)₂ and ligand 1 is shown in Figure S7, together with assignments. It indicates that there is a mixture of species within the spectrometer in the gas phase. The mononuclear species {Pd(1)(NO₃)}⁺ and the dinuclear species {Pd₂(1)₂(NO₃)₂}²⁺ show evidence of fragmentation occurring within the mass spectrometer. The additional peaks are therefore attributed to fragmentation or species forming in the mass spectrometer. NMR is a more direct probe of that solution state than is MS and NMR unequivocally shows that there is a single major species in solution.

![Figure S7: The electrospray mass spectrum of [Pd₄(1)₄(NO₃)₂(H₂O)₂]⁶⁺.](image-url)