An octanuclear coordination cage with a 'cuneane' core – a topological isomer of a cubic cage

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Supporting information: synthetic details

Synthesis of 1,4-bis(bromomethyl)naphthalene

1,4-dimethylnaphthalene (2.00 g, 13 mmol) was brominated by reaction with *N*-bromosuccinimide (5.00 g, 28 mmol) in carbon tetrachloride (80 cm^3). The mixture was refluxed for 1 hour at 90 °C in the presence of azobisisobutyronitrile (AIBN) (0.02 g) as a radical catalyst and was activated using a tungsten lamp. Progress of the reaction was monitored by thin-layer chromatography on silica eluting with hexane:dichloromethane (80:20 v/v). The insoluble succinimide was filtered off and the remaining solution dried using magnesium sulphate. The solvent was removed under vacuum, and then the solid was recrystallised from a minimum amount of hot toluene. The solid was then filtered, washed with cold toluene and dried resulting in a white powder (2.31 g, 7.4 mmol, 57 %).

Synthesis of $L^{1,4naph}$

A mixture of 1,4-bis(bromomethyl)naphthalene (1.00 g, 3.2 mmol) and 3-(2-pyridyl)pyrazole (0.93 g, 6.4 mmol; 2 equivalents) in THF (60 cm^3) containing aqueous NaOH (2.57g in 5 cm^3 H_2O) was heated to reflux for 20 hours. After cooling the solution was filtered, dried with $MgSO_4$ and reduced to dryness to yield a white powder which was washed with diethyl ether and dried (1.10 g, 2.5 mmol, 78 %).

^1H NMR (400MHz, $CDCl_3$): δ8.65 (2H, ddd, J = 5.2, 1.2 and 0.8 Hz, pyridyl H^6), 8.10 (2H, m, naphthyl $H^{5\ \mathrm{or}}$ H^6), 8.00 (2H, dt, J = 7.9 and 1.0, pyridyl H^3), 7.75 (2H, td, J = 7.9 and 1.8, pyridyl H^4), δ.57 (2H, m, naphthyl $H^{5\ \mathrm{or}}$ H^6), 7.32 (2H, d, J = 2.3 Hz, pyrazolyl H^5), 7.27 (2H, s, naphthyl H^2), 7.23 (2H, m, pyridyl H^5), 6.90 (2H, d, J = 2.3 Hz, pyrazolyl H^4), 5.90(4H, s, CH_2). Anal. Calcd for $C_{28}H_{22}N_6$: C 76.0; H, 5.0; N, 19.0%. Found: C, 75.9; H, 4.9; N, 18.9%. ESMS: *m/z* 443 $(M + H)^+$, 465 $(M + Na)^+$

Synthesis of $[Ni_8(L^{14naph})_{12}](BF_4)_{16}$

A solution of $Ni(BF_4)_2$ (0.026 g, 0.075 mmol) in MeOH (7 cm^3) was added to a solution of L^{14naph} (0.050 g, 0.11 mmol) in CH_2Cl_2 (7 cm^3). The mixture was stirred at room temperature for 24 h, and the resultant precipitate was filtered off, washed with both MeOH and CH_2Cl_2, and dried in vacuo to give $[Ni_8(L^{14naph})_{12}](BF_4)_{16}$ as a purple powder in 78% yield. X-ray quality crystals were grown by slow diffusion of isopropyl ether into a solution of the complex in acetonitrile. ESMS: *m/z*; 2303.3, $\{[Ni_8(L^{14naph})_{12}][BF_4]_{13}\}^{3+}$; 1705.2, $\{[Ni_8(L^{14naph})_{12}][BF_4]_{12}\}^{4+}$; 1346.8, $\{[Ni_8(L^{14naph})_{12}][BF_4]_{11}\}^{5+}$; 1108.1, $\{[Ni_8(L^{14naph})_{12}][BF_4]_{10}\}^{6+}$; 937.5, $\{[Ni_8(L^{14naph})_{12}][BF_4]_9\}^{7+}$ (in every case the isotopic spacing in the peak cluster was consistent with the charge). A sample for elemental analysis was vacuum-dried. Anal. Calcd for $C_{336}H_{264}B_{16}F_{64}N_{72}Ni_8$: C 56.3; H, 3.7; N, 14.1%. Found: C, 56.0; H, 3.5; N, 14.0%.