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-dimethyl naphthalene (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 $L_{14\text{naph}}$

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 (2.57 g in 5 cm$^3$ H$_2$O) 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%).

$^1$H NMR (400MHz, CDCl$_3$): $\delta$ 8.65 (2H, ddd, $J = 5.2, 1.2$ and $0.8$ Hz, pyridyl H$^6$), 8.10 (2H, m, naphthyl H$^5$ 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$^4$), $\delta$ 7.57 (2H, m, naphthyl H$^5$ or H$^6$), 7.32 (2H, d, $J = 2.3$ Hz, pyrazolyl H$^5$), 7.27 (2H, s, naphthyl H$^3$), 7.23 (2H, m, pyridyl H$^3$), 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 $[\text{Ni}_8(L_{14\text{naph}})_{12}][\text{BF}_4]_{16}$

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$_{14\text{naph}}$ (0.050 g, 0.11 mmol) in CH$_2$Cl$_2$ (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$_2$Cl$_2$, and dried in vacuo to give $[\text{Ni}_8(L_{14\text{naph}})_{12}][\text{BF}_4]_{16}$ 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, $\{[\text{Ni}_8(L_{14\text{naph}})_{12}][\text{BF}_4]_{13}\}^{3+}$; 1705.2, $\{[\text{Ni}_8(L_{14\text{naph}})_{12}][\text{BF}_4]_{12}\}^{4+}$; 1346.8, $\{[\text{Ni}_8(L_{14\text{naph}})_{12}][\text{BF}_4]_{11}\}^{5+}$; 1108.1, $\{[\text{Ni}_8(L_{14\text{naph}})_{12}][\text{BF}_4]_{10}\}^{6+}$; 937.5, $\{[\text{Ni}_8(L_{14\text{naph}})_{12}][\text{BF}_4]_{9}\}^{7+}$ (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%. 

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