Selective guest recognition by a self-assembled paramagnetic cage complex

Simon Turega, Martina Whitehead, Benjamin R. Hall, Mairi Haddow, Christopher A. Hunter and Michael D. Ward

Supporting Information

Figure S1 View of the complex cation of $[Co_8(L^{1,5\text{-naph}})_{12}](ClO_4)_{16}$•3MeCN•$2H_2O$ with only four ligands around one face shown.

Figure S2 Alternative view of the complex cation of $[Co_8(L^{1,5\text{-naph}})_{12}](ClO_4)_{16}$• 3MeCN•$2H_2O$ with only four ligands shown for clarity.

Figure S3 A fragment of the crystal structure of $[Co_8(L^{1,5\text{-naph}})_{12}](BF_4)_{16}$•6MeOH (from ref. 3b) showing the hydrogen-bonding interaction between a MeOH molecule in the central cavity and some of the inwardly-directed CH groups at one of the vertices.

Figure S4 A fragment of the crystal structure of $[Co_8(L^{1,5\text{-naph}})_{12}](ClO_4)_{16}$•3MeCN•$2H_2O$ (this work) showing the hydrogen-bonding interaction between a water molecule in the central cavity and some of the inwardly-directed CH groups at one of the vertices.

Figure S5 ^{1}H NMR spectrum of $[Co_8(L^{1,5\text{-naph}})_{12}][BF_4]_{16}$ (0.2 mM) in d_3-acetonitrile at 298K.

Comments on crystal structure solution and refinement

Measurement of association constants

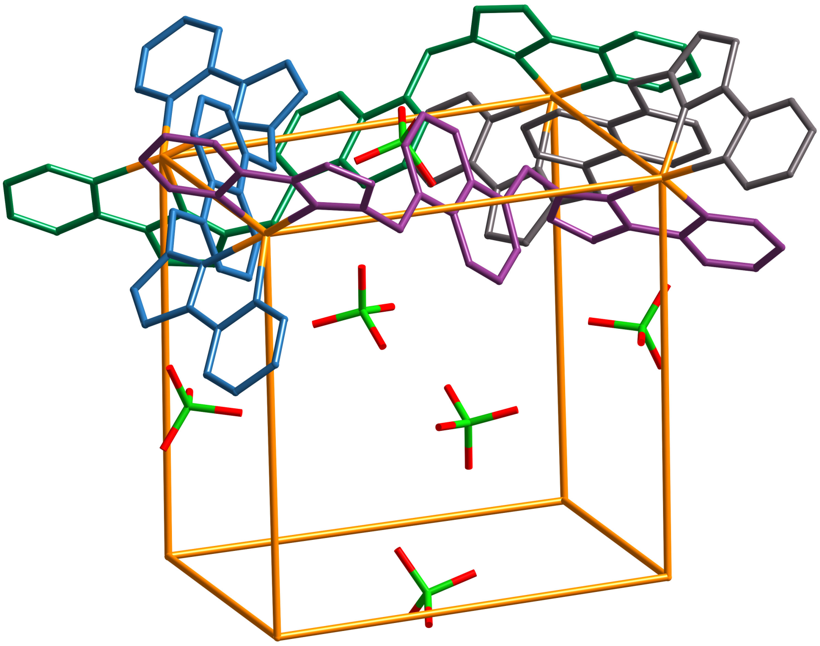

Fig. S1. View of the complex cation of $[Co_8(L^{1,5\text{-naph}})_{12}](ClO_4)_{16}$•3MeCN•$2H_2O$ with only four ligands around one face shown. The array of eight metal cations forms a basically cubic arrangement with Co•••Co separations of 11.19 or 11.30 Å along the edges; a perchlorate anion lies over the centre of eaxh of the six faces. The central cavity contains only two water molecules that could be located.

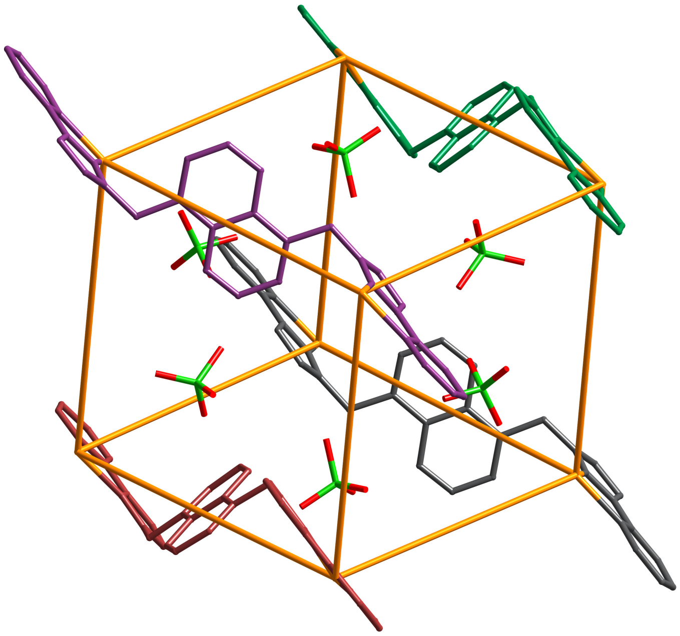

Fig. S2. Alternative view of the complex cation of $[Co_8(L^{1,5\text{-naph}})_{12}](ClO_4)_{16}$•3MeCN•$2H_2O$ with only four ligands shown for clarity. This view emphasises the conformation of the bridging ligands in which the naphthyl groups are involved in π-stacking interactions with pyrazolyl-pyridine fragments of other ligands; see ref. 3b for more details of the isostrucural tetrafluoroborate analogue.

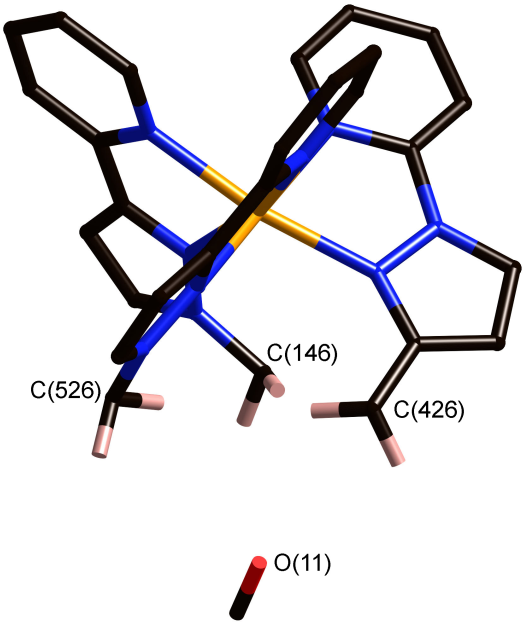

Figure S3. A fragment of the crystal structure of $[Co_8(L^{1,5\text{-naph}})_{12}](BF_4)_{16}$•6MeOH (from ref. 3b) showing the hydrogen-bonding interaction between a MeOH molecule in the central cavity and some of the inwardly-directed CH groups at one of the *fac* tris-chelate vertices. H atoms of the MeOH molecule were not located but the C•••O separations are indicative of weak CH•••O hydrogen bonds [*e.g.* C(426)–O(11), 3.47 Å]

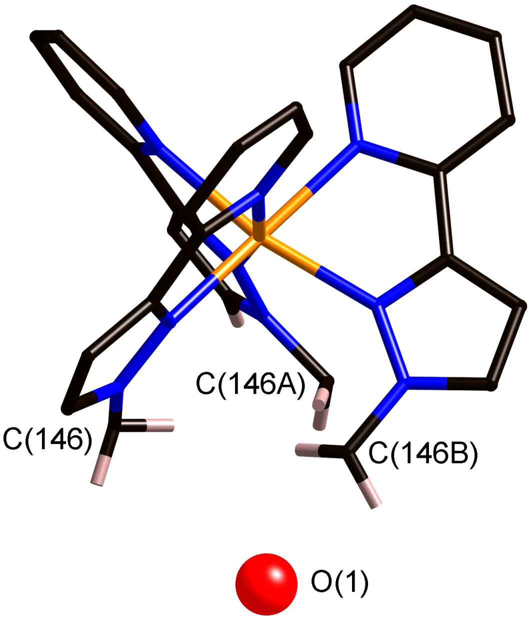

Figure S4. A fragment of the crystal structure of $[Co_8(L^{1,5\text{-naph}})_{12}](ClO_4)_{16}$•3MeCN•2$H_2O$ (this work) showing the hydrogen-bonding interaction between a water molecule in the central cavity and some of the inwardly-directed CH groups at one of the *fac* tris-chelate vertices. H atoms of the water molecule were not located but the C•••O separations are indicative of weak CH•••O hydrogen bonds [C(146)–O(1), 3.56 Å]

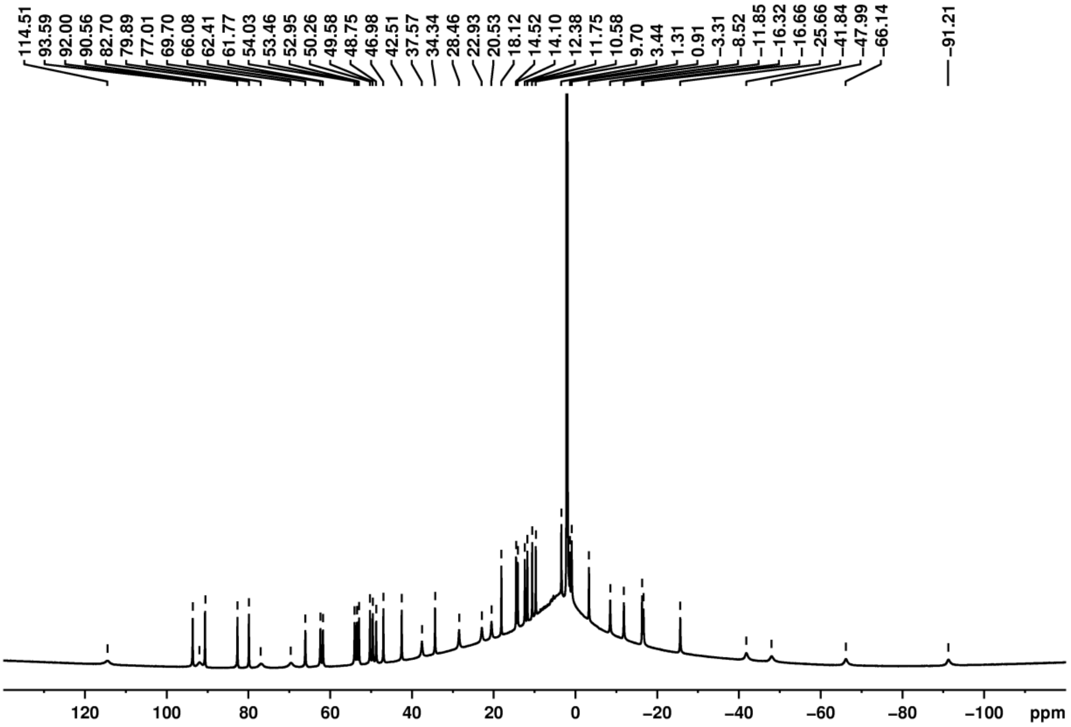

Fig. S5. ^{1}H NMR spectrum of $[Co_8(L^{1,5\text{-naph}})_{12}][BF_4]_{16}$ (0.2 mM) in d$_3$-acetonitrile at 298K.

Comments on crystal structure solution and refinement

As is typical for large cage complexes the crystals scattered weakly necessitating use of a rotating-anode source and Cu(Kα) radiation. One sixth of the molecule lies in the asymmetric unit with the remainder generated by a combination of a threefold axis and an inversion centre; one Co(II) ion is in a general position and the other on the threefold axis. Two of the perchlorate anions could not be located and are assumed to be disordered. Large regions of diffuse electron density were removed using the SQUEEZE function in PLATON. The structure is the same as that of the fluoroborate analogue (ref. 3b); see Figures above.

Measurement of association constants

Association constants were measured by integration of signals in slow exchange in the ^{1}H NMR spectrum. The guest is always present in a large excess, and so this concentration is known from the concentration and volume added. The ratio of the concentrations of the host and host•guest complex were determined from the integrals of several well-resolved signals in the NMR spectrum, and this allowed us to calculate the association constant using Equation S1. The errors are estimated based on the variation in the ratio [host•guest]/[host] measured using different signals and guest concentrations.

$$K_a = [\text{host}\bullet\text{guest}] / [\text{host}][\text{guest}] \qquad \text{eqn. S1}$$