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[12] Crystal data for [Fe(PaPy$_3$)(NO)][ClO$_4$]$_2\cdot$CH$_3$CN (**2**$\cdot$CH$_3$CN): red plates, $0.48 \times 0.40 \times 0.02$ mm^3, orthorhombic, space group *Pbca*, $a = 7.740(3)$, $b = 21.990(9)$, $c = 30.634(11)$ Å, $V = 5214(3)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.713$ Mg m^{-3}, $2\theta_{\max} = 60°$, $\mu(\text{Mo}_{\text{K}\alpha}) = 0.855$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; the data were collected at 91(2) K on a Bruker SMART 1000 diffractometer; a total of 69800 reflections were measured, of which 7591 were independent ($R_{\text{int}} = 0.051$) and included in the refinement; min./max. transmission = 0.684/0.983; solution by direct methods (SHELXL-97, Sheldrick, **1990**); refinement by full-matrix least-squares based on F^2 (SHELXL-97, Sheldrick, **1997**); 380 parameters, $R1 = 0.0628$, $wR2 = 0.1270$ for all data; $R1 = 0.0476$ computed for 6082 observed data ($I > 2\sigma(I)$).

[13] A cuvette containing a 0.4 mM solution of **2** in CH$_3$CN was placed 5 cm from a 50 W tungsten lamp for 30 s intervals and the absorption spectra were monitored on a Cary 50 spectrophotometer in fast-scan mode (spectra shown in Figure 2). The rate of NO release was slower ($t_{1/2} = 1.5$ min) when a 20 W tungsten lamp was used. NO release upon illumination was also observed with solutions of **2** in DMF and water. In the solid state, **2** is very stable towards light (no observed decomposition over a period of months).

[14] a) Crystal data for [Fe(SBPy$_3$)(CH$_3$CN)][BF$_4$]$_2\cdot\frac{1}{3}$Et$_2$O$\cdot\frac{2}{3}$CH$_3$OH (**4**$\cdot\frac{1}{3}$Et$_2$O$\cdot\frac{2}{3}$CH$_3$OH): magenta-colored platelike crystals, $0.44 \times 0.29 \times 0.05$ mm^3, monoclinic, space group *C*2/*c*, $a = 38.398(15)$, $b = 11.859(5)$, $c = 12.783(5)$ Å, $\beta = 103.422(8)°$, $V = 5662(4)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.520$ Mg m^{-3}, $2\theta_{\max} = 61°$, $\mu(\text{Mo}_{\text{K}\alpha}) = 0.616$ mm^{-1}, ω scans, $\lambda = 0.71073$ Å; the data were collected at 91(2) K on a Bruker SMART 1000 diffractometer; a total of 37587 reflections were measured, of which 8565 were independent ($R_{\text{int}} = 0.067$) and included in the refinement; min./max. transmission = 0.773/0.970; solution by direct methods (SHELXL-97, Sheldrick, **1990**); refinement by full-matrix least-squares based on F^2 (SHELXL-97, Sheldrick, **1997**); 372 parameters, $R1 = 0.1023$, $wR2 = 0.1759$ for all data; $R1 = 0.0607$ computed for 5681 observed data ($I > 2\sigma(I)$); b) CCDC-181941 (complex **2**) and CCDC-181942 (complex **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Assembly of a Truncated-Tetrahedral Chiral $[\text{M}_{12}(\mu\text{-L})_{18}]^{24+}$ Cage**

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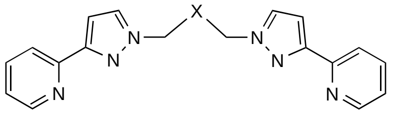
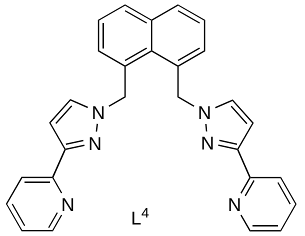
One of the most active areas of research in metallo-supramolecular chemistry at present is the assembly of polyhedral cage complexes from labile metal centers and multidentate bridging ligands.[1] Apart from the intrinsic appeal of the structures, they are of interest both for understanding the mechanisms of the assembly process which lead to their formation and for the host–guest chemistry associated with their large central cavities.[1]

Tetradentate ligands with two bidentate chelating termini are commonly used in this area. When these coordinate to octahedral metal centers in the absence of any other ligands, the resulting complex must have a metal:ligand ratio of 2:3, as found in dinuclear triple helicates with three bridging ligands.[2] The next member of this series is the M$_4$L$_6$ tetrahedron, in which a bridging ligand spans each edge of a tetrahedral array of metal ions. This type of structure has been extensively studied recently,[3–6] and there is a well-developed host–guest chemistry based on the binding of counterions or solvent molecules in the tetrahedral cavities. The only three-dimensional cage of which we are aware with a higher nuclearity but with the same M$_2$L$_3$ ratio is the cube [Ni$_8$(tab)$_{12}$]$^{16+}$ (tab = 1,2,3,4-tetraaminobutane);[7] in 1997 we described a (two-dimensional) circular M$_8$L$_{12}$ helicate with an anion encapsulated in the central cavity.[8]

Our recent work in this area is based on ligands such as L^1–L^3 which contain two bidentate pyrazolylpyridine units linked to an aromatic core through two methylene spacers.[3, 9] With cobalt(II) ions these ligands form [Co$_4$L$_6$]$^{8+}$ cages which bind



L^1 X = 1,2-C$_6$H$_4$
L^2 X = 2,3-naphthalenediyl
L^3 X = 3,3'-biphenyl



L^4

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anions in the central cavity. With the shorter ligands L^1 and L^2 the central anion (perchlorate or tetrafluoroborate) is completely encapsulated and tightly bound in the central cavity, and in fact acts as a template for the assembly of the cage around it.[3] With the larger bridging ligand L^3, in contrast, the anions in the cavity exchange freely with those outside through large cavities in the center of each face.[9] In seeking to prepare a related tetrahedral cage with a cavity of intermediate size, for the purposes of investigating the size selectivity of anion binding, we prepared ligand L^4 in which the spacer is a 1,8-naphthyl unit. Unexpectedly, this reacts with cobalt(II) and zinc(II) ions to generate dodecanuclear cage complexes $[M_{12}(\mu\text{-}L^4)_{18}]X_{24}$ (where X = perchlorate or tetrafluoroborate) in which each of the 18 bridging ligands spans an edge of a truncated-tetrahedral M_{12} array.

The ligand L^4 was prepared[10] by reaction of 1,8-bis(bromomethyl)naphthalene with 3-(2-pyridyl)pyrazole by using the procedure we have described before for related ligands.[3, 9] Reaction of L^4 with $Co(O_2CCH_3)_2 \cdot 4\,H_2O$ in MeOH in a 3:2 ratio afforded an orange solution from which a precipitate was obtained on addition of aqueous $NaBF_4$. Crystallization by diffusion of ethyl acetate vapor into a solution of the complex in DMF/MeCN afforded X-ray quality crystals of a material whose elemental analysis, as expected, was consistent with the empirical formula $[Co_2(L^4)_3][BF_4]_4$.

The crystal structure is shown in Figures 1-3.[11] The core of the structure is a truncated tetrahedral array of 12 metal ions; this polyhedron is generated by truncating each of the four vertices of a tetrahedron to reveal a triangular face. Each of the four faces of the initial tetrahedron therefore becomes a hexagon, and the polyhedron accordingly contains four triangular and four hexagonal faces (Figure 1). This is a very rare structural type in metal cage complexes: discrete $[Sn_{12}]^{12-}$ ionic clusters of this structure occur in the Zintl compounds $CaNa_{10}Sn_{12}$ and $SrNa_{10}Sn_{12}$,[12] and a dodacnuclear "capsule" with this arrangement of metal ions was formed by hydrogen-bonding association of four approximately planar triangular, trinuclear complex units.[13]

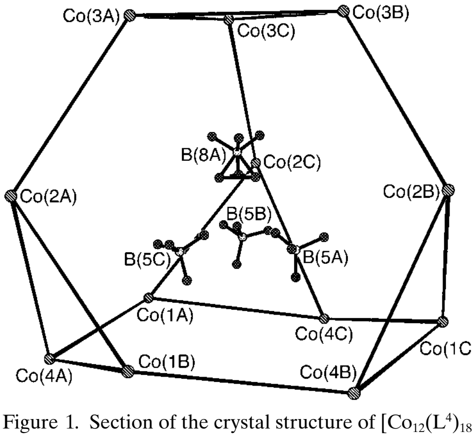

Figure 1. Section of the crystal structure of $[Co_{12}(L^4)_{18}][BF_4]_{24}$ showing the dodecanuclear cage of Co^{II} ions and the four encapsulated anions.

The Co ··· Co separations along each of the 18 edges lie in the range 9.22 – 9.36 Å. Every cobalt(II) ion is coordinated by a meridional arrangement of three pyridyl and three pyrazolyl donors from the three bidentate chelating units. All Co–N bonds are in the range 2.1 – 2.2 Å. All twelve cobalt(II) centers within each complex molecule have the same chirality; the crystal as a whole is, however, racemic. The space-filling view (Figure 2) emphasises how the ligands are entwined around each other, with extensive aromatic π-stacking interactions between overlapping naphthyl units of the ligands; columnar stacks of eight naphthyl units occur around the periphery of the complex. In the solid state the complex has only one threefold axis, but the idealized symmetry is *T*, similar to those of the M_4L_6 tetrahedral cages in which all four metal ions are homochiral.[3, 14]

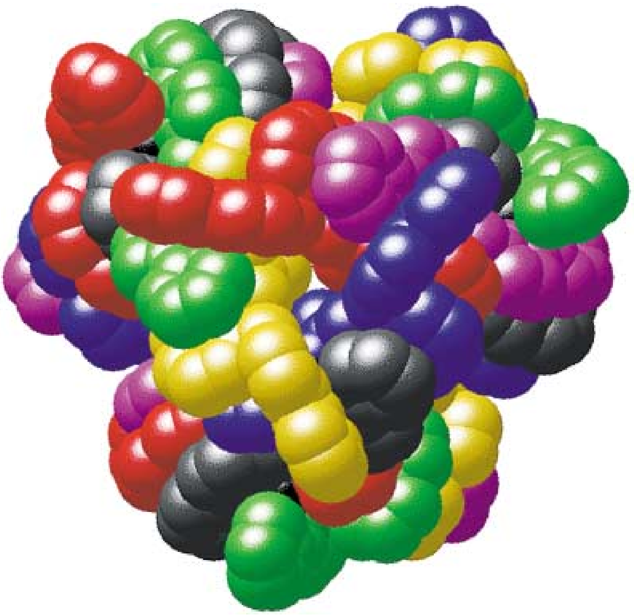

Figure 2. Space-filling view of the complex cation of $[Co_{12}(L^4)_{18}][BF_4]_{24}$.

The central cavity of the cage contains four tetrafluoroborate anions (of which one is disordered, with six F atom positions evident with a site occupancy of two-thirds in each; Figure 1). The boron atoms of these four anions describe an approximate tetrahedron with B ··· B separations of about 5.3 Å. The proximity of these anions results in F ··· F contacts between adjacent anions of 3.25 Å (based on the three ordered anions only). In addition, the two-dimensional cavities at the center of the triangular and hexagonal faces all contain a tetrafluoroborate anion (Figure 3). This situation results in nonbonded F ··· C separations of 3.0 – 3.3 Å, possibly involving weak C–H ··· F hydrogen-bonding interactions.[15] Counterions are often found occupying the two-dimensional cavities at the center of circular helicate complexes[7, 16] and the three-dimensional cavities at the center of cage complexes;[1, 3–6, 17] with anions bound in both two-dimensional (on the surface) and three-dimensional (at the center) cavities, $[Co_{12}(\mu\text{-}L^4)_{18}][BF_4]_{24}$ displays both types of behavior. Whether these anions are acting as templates without which the $[Co_{12}(\mu\text{-}L^4)_{18}]^{24+}$ cage could not form is not yet known.

Electrospray mass spectra (at a variety of cone voltages) of a solution of redissolved crystals of the complex in DMF

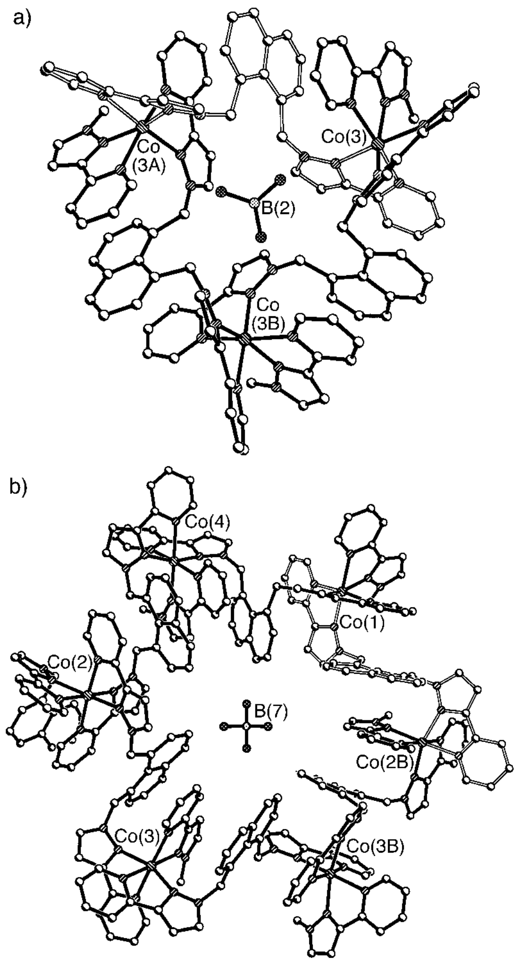

Figure 3. Sections of the crystal structure of $[Co_{12}(L^4)_{18}][BF_4]_{24}$ showing a) the view looking onto a triangular face, and b) the view looking onto a hexagonal face. One ligand has been shaded differently in each figure for clarity. In each case there is a $[BF_4]^-$ ion in the cavity at the center of the face.

showed only peaks at low m/z values, most of which were not readily assignable. Decomposition of the complex in solution under these conditions was clear from some signals (for example $[HL^4]^+$ at m/z 443, and $[Co(L^4)]^{2+}$ at m/z 250). MALDI-TOF and Fourier transform ion cyclotron resonance (FT-ICR) spectra gave similar results and also failed to show any peaks consistent with retention of the cage structure. ^1H NMR spectroscopy provided further evidence that the cage structure dissociates in solution. The intact cage has two different types of edge (12 around the triangular faces, and the remaining 6 on the hexagonal faces), with each edge having twofold symmetry. We would therefore expect to see two independent ligand halves, that is, 22 proton environments for the intact cage. The spectrum recorded at $-20\,^{\circ}C$ in $[D_6]DMSO/CD_3CN$ shows at least 36 paramagnetically shifted proton environments in the range $\delta = 10-110$ ppm, which is characteristic of the ligands coordinated to cobalt(II) ions,[18] as well a signals in the $\delta = 6-10$ ppm region characteristic of free ligand. The spectrum becomes even more complicated at higher temperatures. Fragmentation of the cage clearly occurs in this strongly coordinating solvent; the cage is not soluble in less well-coordinating solvents.

Finally, we note that we have observed essentially identical structures with zinc(II) in place of cobalt(II) ions, and also with a perchlorate as counterion in place of tetrafluorborate. Details of these structural determinations, and studies on whether alternative (nontetrahedral) guest anions give similar cages, will be reported in due course.

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[10] A mixture of 1,8-bis(bromomethyl)naphthalene (1.049 g, 3.3 mmol), 3-(2-pyridyl)pyrazole (1.02 g, 7.03 mmol), aqueous nBu_4OH (40 % wt/wt, 0.16 mL), aqueous NaOH (2.34 g dissolved in 5.5 cm^3 of water), and toluene (35 cm^3) was heated with vigorous stirring at $85\,^{\circ}C$ for 24 h. After cooling, the organic layer was separated, washed with water, and dried over $MgSO_4$. Removal of solvent yielded a brown oil which was purified by recrystallization from dichloromethane/hexane to yield L^4 as an off-white solid (yield: 0.52 g, 36 %). EIMS: m/z: 442 $[M^+]$. ^1H NMR ($CDCl_3$): $\delta = 8.56$ (2H, d; pyridyl H^6), 7.86 (2H, d; naphthyl H^2/H^7 or H^4/H^5), 7.84 (2H, d; pyridyl H^3), 7.64 (2H, m; pyridyl H^4), 7.39 (2H, t; naphthyl H^3/H^6), 7.19 (2H, d; naphthyl H^4/H^5 or H^2/H^7), 7.12 (2H, m; pyridyl H^5), 7.07 (2H, d; pyrazolyl H^5), 6.80 (2H, d; pyrazolyl H^4), 5.87 pm (4H, s; CH_2). Elemental analysis calcd for $C_{28}H_{22}N_6$: C 76.3, H 4.9, N 19.3 %; found: C 76.0, H 5.0, N 19.0 %.

[11] Crystal data for $\{[Co_4(L^4)_6][BF_4]_8 \cdot 0.5\,EtOAc \cdot 2\,DMF \cdot 12\,MeCN \cdot 0.33\,H_2O\}_3$: $M_r = 12822.57$, trigonal, space group $R\bar{3}$, $a = 41.167(5)$, $c = 82.016(9)$ Å, $V = 120374(23)$ Å^3, $Z = 6$; $\rho_{calcd} = 1.061$ g cm^{-3}; crystal dimensions $0.5 \times 0.45 \times 0.4$ mm^3; $\mu(Mo_{K\alpha}) = 0.318$ mm^{-1}. 175784 data were collected ($2\theta_{max} = 45^{\circ}$) at 123 K on a Bruker-AXS SMART diffractometer with a CCD area detector; after merging these gave 34966 unique data ($R_{int} = 0.0922$). An empirical absorption correction

was applied using SADABS. The structure was solved and refined using the SHELX-97 suite of programs[19]; refinement of 2418 parameters converged at $R_1 = 0.129$, $wR_2 = 0.359$. The complex lies on a threefold axis such that only four of the metal ions are unique. The metal ions and the ligand C and N atoms were refined with anisotropic thermal parameters, as were some of the $[BF_4]^-$ counterions; the remaining counterions and all of the (largely disordered) solvent atoms were refined isotropically. Of the expected eight $[BF_4]^-$ ions in the asymmetric unit, six were well defined; two are on threefold axes such that only one-third of the anion is in the asymmetric unit (and in one of these the F atom positions are disordered); and one only refined adequately with site occupancies of 50% for all atoms, making 7.166 anions. The remainder could not be located and it is assumed that they are in the regions of the crystal where there is extensive disorder of lattice solvent molecules; the formulation given above for solvent molecules is necessarily an approximation. CCDC-181453 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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