

## High-nuclearity Homoleptic and Heteroleptic Coordination Cages Based on Tetra-Capped Truncated Tetrahedral and Cuboctahedral Metal Frameworks

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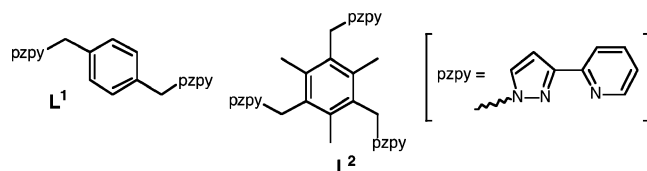
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Three-dimensional coordination cages have achieved recent prominence due to a combination of (i) their aesthetically appealing polyhedral structures, (ii) the insight they give into understanding how control of self-assembly processes can afford elaborate structures from simple constituents, and (iii) the host–guest chemistry that results from incorporation of small molecules or anions in their central cavities.<sup>1–8</sup>

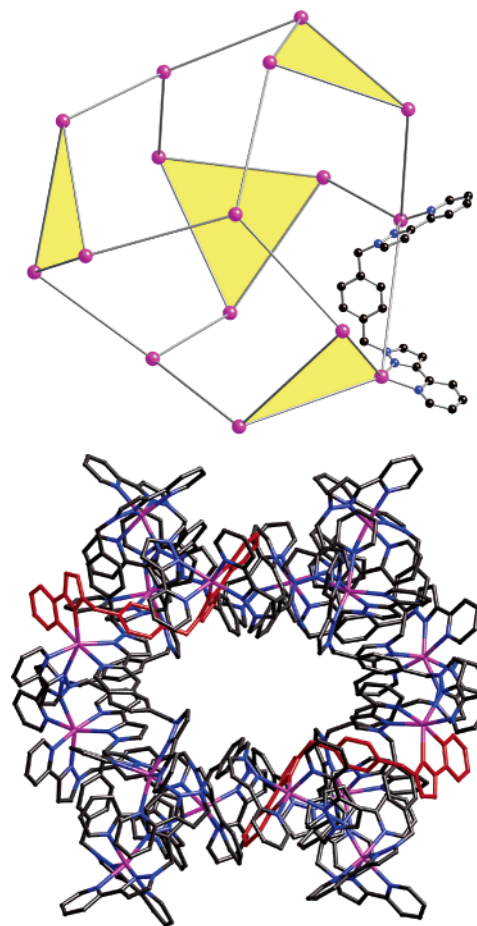
A common class of cage complexes is based on bridging ligands containing bidentate chelating termini, and labile six-coordinate metal ions. Bis-bidentate bridging ligands, providing four donors, react with six-coordinate metal ions to afford complexes whose stoichiometry is  $M_2L_3$  or some higher multiple, as shown by  $M_4L_6$  tetrahedral cages with a metal ion at each vertex and a bridging ligand spanning each edge.<sup>2</sup> Larger polyhedral structures based on the same principles, include an  $M_8L_{12}$  cube<sup>3</sup> and an  $M_{12}L_{18}$  truncated tetrahedron.<sup>4</sup> In contrast, a tris-bidentate ligand will cap one triangular face of a metal polyhedron, and—since it provides six donor atoms—will generate 1:1 complexes with octahedral metal ions. This can lead to formation of cages with the same number of triangular faces as vertexes, as exemplified by  $M_4L_4$  tetrahedra.<sup>5</sup> With very few exceptions,<sup>6,7</sup> such cage complexes are homoleptic (i.e. all ligands the same), which necessarily limits the range of polyhedral cage structures that can emerge. Use of a mixture of edge-bridging and face-capping ligands, however, could allow access to previously unavailable structural types.<sup>6,7</sup>

We report here the syntheses and structures of two polyhedral cage complexes with unusual topologies. The homoleptic cages  $[M_{16}(\mu-L^1)_{24}]X_{32}$  ( $M = Zn, X = BF_4$ ;  $M = Cd, X = ClO_4$ ) have a tetra-capped truncated-tetrahedral core. In contrast, heteroleptic cages  $[M_{12}(\mu-L^1)_{12}(\mu^3-L^2)_4]X_{24}$  ( $M = Cu, Co, X = BF_4$ ) have a cuboctahedral metal core,<sup>7,8</sup> containing a combination of edge-bridging and face-capping ligands selected during the assembly process (Chart 1).

### Chart 1. Structures of the Ligands $L^1$ and $L^2$



Reaction of a 3:2 molar ratio of  $L^1$  and  $Cd(ClO_4)_2$  in MeCN afforded crystals of  $[Cd_{16}(\mu-L^1)_{24}](ClO_4)_{32}$  (Figure 1).<sup>†</sup> The metal polyhedron may be described as a tetra-capped truncated tetrahe-



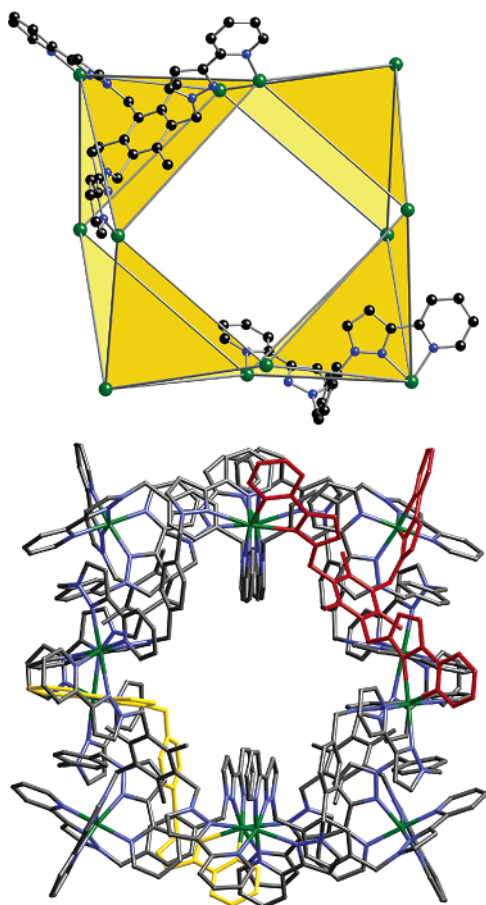
**Figure 1.** Structure of  $[Cd_{16}(\mu-L^1)_{24}](ClO_4)_{32} \cdot 23MeCN$ . (Top): Capped truncated-tetrahedral core, with one edge-bridging ligand included (the faces colored yellow are those notionally derived from truncating the parent tetrahedron). (Bottom): View showing all atoms in the cage, with two bridging ligands colored red (Cd), purple: N, blue).

dron. Each apex of a tetrahedron is sliced off to reveal a triangular face (colored yellow in the figure); the resulting truncated tetrahedron has 12 vertexes, with four triangular faces and four hexagonal faces.<sup>1d,4</sup> All triangular faces are then twisted in the same sense, such that the mirror planes through the truncated tetrahedron are removed but the  $C_3$  axes are retained. Finally, a capping atom is added to the center of each of the original four faces. This  $M_{16}$  polyhedral array, with (noncrystallographic)  $T$  symmetry, has a bridging ligand  $L^1$  along each of the 24 edges, providing the necessary 2:3  $Cd:L^1$  stoichiometry and making each  $Cd(II)$  ion (connected to three edges) six-coordinate. The large central cavity ( $\sim 700 \text{ \AA}^3$ ) contains eight  $[ClO_4]^-$  anions and six MeCN molecules.

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**Figure 2.** Two views of the structure of  $[\text{Cu}_{12}(\mu\text{-L}^1)_{12}(\mu^3\text{-L}^2)_4](\text{BF}_4)_{24} \cdot 20\text{MeNO}_2$ . (Top): Cuboctahedral core, with one face-capping and one edge-bridging ligand included. (Bottom): View showing all of the atoms in the cage, with one face-capping ligand  $\text{L}^2$  colored in red and one edge-bridging ligand  $\text{L}^1$  colored in yellow (Cu, green; N, blue).

In contrast to the behavior observed with much smaller cages,<sup>2</sup> this is a very “open” structure with the anions clearly not completely encapsulated by the cage superstructure.

The Cd(II) centers display a mix of facial and meridional tris-chelate geometries; the 12 Cd(II) centers associated with the four triangular faces of the truncated tetrahedron have a meridional arrangement, and the four “capping” metal centers [Cd(13)–Cd(16)] are facial. Remarkably, all 16 metal centers have the same optical configuration, which appears to be essential for the closed cage to form; thus, the assembly has occurred with correct control of 96 metal–ligand bonds. The crystal is racemic. This structure is not a kinetic artifact of crystallization but retains its integrity in solution as shown by ES mass spectrometry, with a series of peaks from  $m/z$  2780 to 1500 corresponding to the species  $\{[\text{Cd}_{16}(\mu\text{-L}^1)_{24}](\text{ClO}_4)_{(32-n)}\}^{n+}$  ( $n = 5\text{--}9$ ). ESMS evidence confirms formation of the similar structures  $[\text{M}_{16}(\mu\text{-L}^1)_{24}]\text{X}_{32}$  ( $\text{M} = \text{Cd}$ ,  $\text{X} = \text{BF}_4$ ;  $\text{M} = \text{Zn}$ ,  $\text{X} = \text{ClO}_4$ ; and  $\text{M} = \text{Zn}$ ,  $\text{X} = \text{BF}_4$ ) with different metal cations and counterions, and crystallographic evidence also confirms formation of the isostructural cage  $[\text{Zn}_{16}(\mu\text{-L}^1)_{24}](\text{BF}_4)_{32}$  (see Supporting Information).

Reaction of  $\text{Cu}(\text{BF}_4)_2$  with  $\text{L}^1$  and  $\text{L}^2$ , in a 3:3:1 ratio in nitromethane afforded green crystals of  $[\text{Cu}_{12}(\mu\text{-L}^1)_{12}(\mu^3\text{-L}^2)_4](\text{BF}_4)_{24}$  (Figure 2) which has a cuboctahedral metal framework containing eight triangular and six square faces (see Supporting

Information). The complex lies on a  $C_2$  axis. Four of the eight triangular faces are capped by a triply bridging ligand  $\text{L}^2$ , and the remaining vacant edges are spanned by doubly bridging ligands  $\text{L}^1$  (see Supporting Information). All 12 tris-chelate metal centers have meridional geometry, and again all have the same chirality, indicating that the same chiral configuration at each metal center is necessary for the closed cage to form. The crystal is racemic. The central cavity ( $\sim 450 \text{ \AA}^3$ ) contains a disordered mixture of  $[\text{BF}_4]^-$  anions and  $\text{MeNO}_2$  solvent molecules. Again, ESMS confirms the existence of the cage in solution, with a sequence of peaks from  $m/z$  2393.5 to 1015.6 corresponding to  $\{[\text{Cu}_{12}(\mu\text{-L}^1)_{12}(\mu^3\text{-L}^2)_4](\text{BF}_4)_{24-x}\}^{x+}$  ( $x = 4\text{--}9$ ). ESMS also confirmed formation of isostructural cages with other cations [Co(II), Cd(II)] and anions  $[\text{BF}_4^-]$ ,  $[\text{ClO}_4^-]$  (see Supporting Information). These spectra contain no peaks corresponding to traces of the homoleptic cages  $[\text{M}_{16}(\mu\text{-L}^1)_{24}]\text{X}_{32}$ , indicating that in the presence of a mixture of two types of ligand,  $\text{L}^1/\text{L}^2$  recognition leads to the cuboctahedral cage as the only product. Use of a different (nonideal) ratio of  $\text{L}^1:\text{L}^2$  also afforded the same product but in a reduced yield.

The difference between the two structural types illustrates how a mixture of ligands with different binding modes (face capping vs edge bridging) can give access to polyhedral structures different from those obtained using just one type of ligand.<sup>7</sup> With our bridging ligands no homoleptic complex could generate a cuboctahedral framework, as the cuboctahedron contains neither a 3:2 edge:vertex ratio (for edge-bridging ligands), nor a 1:1 face:vertex ratio (for face-capping ligands). In addition, the chirality of both complex cages, with 16 and 12 homochiral metal centers, respectively, suggests that if they can be resolved they would make interesting hosts for chiral anionic guests.

**Supporting Information Available:** Crystallographic details and CIF files for the two structures in this paper; details of syntheses and characterization of the ligands and complexes, including sample ES mass spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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