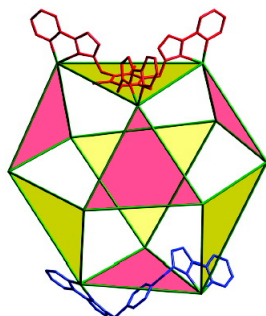


Mixed-Ligand Molecular Paneling: Dodecanuclear Cuboctahedral Coordination Cages Based on a Combination of Edge-Bridging and Face-Capping Ligands

Nawal K. Al-Rasbi, Ian S. Tidmarsh, Stephen P. Argent, Harry Adams, Lindsay P. Harding, and Michael D. Ward

J. Am. Chem. Soc., **2008**, 130 (35), 11641-11649 • DOI: 10.1021/ja803847w • Publication Date (Web): 08 August 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



Yellow faces:
capped by tritopic ligands

Pink faces:
edge-bridged by ditopic ligands

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



Mixed-Ligand Molecular Paneling: Dodecanuclear Cuboctahedral Coordination Cages Based on a Combination of Edge-Bridging and Face-Capping Ligands

Nawal K. Al-Rasbi,[†] Ian S. Tidmarsh,[†] Stephen P. Argent,[†] Harry Adams,[†]
Lindsay P. Harding,[‡] and Michael D. Ward^{*†}

*Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K., and Department of
Chemical and Biological Sciences, University of Huddersfield, Huddersfield HD1 3DH, U.K.*

Received May 22, 2008; E-mail: m.d.ward@sheffield.ac.uk

Abstract: Reaction of a tris-bidentate ligand L^1 (which can cap one triangular face of a metal polyhedron), a bis-bidentate ligand L^2 (which can span one edge of a metal polyhedron), and a range of M^{2+} ions ($M = Co, Cu, Cd$), which all have a preference for six coordination geometry, results in assembly of the mixed-ligand polyhedral cages $[M_{12}(\mu^3-L^1)_4(\mu-L^2)_{12}]^{24+}$. When the components are combined in the correct proportions $[M^{2+}:L^1:L^2 = 3:1:3]$ in $MeNO_2$, this is the sole product. The array of 12 M^{2+} cations has a cuboctahedral geometry, containing six square and eight triangular faces around a substantial central cavity; four of the eight M_3 triangular faces (every alternate one) are capped by a ligand L^1 , with the remaining four M_3 faces having a bridging ligand L^2 along each edge in a cyclic helical array. Thus, four homochiral triangular $\{M_3(L^2)_3\}^{6+}$ helical units are connected by four additional L^1 ligands to give the mixed-ligand cuboctahedral array, a topology which could not be formed in any homoleptic complex of this type but requires the cooperation of two different types of ligand. The complex $[Cd_3(L^2)_3(ClO_4)_4(MeCN)_2(H_2O)_2](ClO_4)_2$, a trinuclear triple helicate in which two sites at each Cd(II) are occupied by monodentate ligands (solvent or counterions), was also characterized and constitutes an incomplete fragment of the dodecanuclear cage comprising one triangular $\{M_3(L^2)_3\}^{6+}$ face which has not yet reacted with the ligands L^1 . 1H NMR and electrospray mass spectrometric studies show that the dodecanuclear cages remain intact in solution; the NMR studies show that the Cd_{12} cage has four-fold (D_2) symmetry, such that there are three independent Cd(II) environments, as confirmed by a ^{113}Cd NMR spectrum. These mixed-ligand cuboctahedral complexes reveal the potential of using combinations of face-capping and edge-bridging ligands to extend the range of accessible topologies of polyhedral coordination cages.

Introduction

Three-dimensional coordination cages are an attractive target in the field of supramolecular coordination chemistry, for several reasons.^{1–9} Most obviously, they can have aesthetically appealing high-symmetry polyhedral structures which, in some cases, are reminiscent of the self-assembled structures formed by virus

coat proteins.¹ More subtly, although their structures in many cases arise serendipitously, several rational syntheses have provided insight into how the control of self-assembly processes

[†] University of Sheffield.

[‡] University of Huddersfield.

- (1) Reviews on coordination cages: (a) Swieggers, G. F.; Malefetse, T. J. *Coord. Chem. Rev.* **2002**, *225*, 91. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369. (c) Fiedler, D.; Leung, D. H.; Bergman, R. G.; Raymond, K. N. *Acc. Chem. Res.* **2005**, *38*, 349. (d) Hamilton, T. D.; MacGillivray, L. R. *Cryst. Growth Des.* **2004**, *4*, 419. (e) Ward, M. D. In *Organic Nanostructures*; Atwood, J., Steed, J., Eds.; Wiley: New York, 2008. (f) Garay, A. L.; Pichon, A.; James, S. L. *Chem. Soc. Rev.* **2007**, *36*, 846. (g) Alvarez, S. *Dalton Trans.* **2006**, 2209. (h) Saalfrank, R. W.; Uller, E.; Demleitner, B.; Bernt, I. *Struct. Bonding (Berlin)* **2000**, *96*, 149. (i) Stang, P. J.; Seidel, S. R. *Acc. Chem. Res.* **2002**, *35*, 972. (j) Saalfrank, R. W.; Demleitner, B. In *Perspectives in Supramolecular Chemistry*; Sauvage, J.-P., Ed.; John Wiley & Sons Ltd.: Chichester, U.K., 1999; Vol. 5, pp 1–51.
- (2) (a) Sun, X. K.; Johnson, D. W.; Caulder, D. L.; Raymond, K. N.; Wong, E. H. *J. Am. Chem. Soc.* **2001**, *123*, 2752. (b) Fujita, M.; Umamoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. (c) Caulder, D. A.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185.

- (3) (a) Davis, A. V.; Fiedler, D.; Seeber, G.; Zahl, A.; van Eldik, R.; Raymond, K. N. *J. Am. Chem. Soc.* **2006**, *128*, 1324. (b) Johnson, D. W.; Raymond, K. N. *Inorg. Chem.* **2001**, *40*, 5157. (c) Paul, R. L.; Bell, Z. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4883. (d) Brassey, T.; Scopelliti, R.; Severin, K. *Chem. Commun.* **2006**, 3308. (e) Hiraoka, S.; Kubota, Y.; Fujita, M. *Chem. Commun.* **2000**, 16, 1509.
- (4) (a) Yamaguchi, T.; Fujita, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2067. (b) Nishioka, Y.; Yamaguchi, T.; Yoshizawa, M.; Fujita, M. *J. Am. Chem. Soc.* **2007**, *129*, 7000. (c) Takaoka, K.; Kawano, M.; Ozeki, T.; Fujita, M. *Chem. Commun.* **2006**, 1625. (d) Yoshizawa, M.; Fujita, M. *Pure Appl. Chem.* **2005**, *77*, 1107. (e) Koblenz, T. S.; Wassenaar, J.; Reek, J. N. H. *Chem. Soc. Rev.* **2008**, *37*, 247. (f) Kleij, A. W.; Reek, J. N. H. *Chem. Eur. J.* **2006**, *12*, 4219. (g) Leung, D. H.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2006**, *128*, 9781.
- (5) (a) Saalfrank, R. W.; Burak, R.; Breit, A.; Stalke, D.; Herbst-Irmer, R.; Daub, J.; Porsch, M.; Bill, E.; Muther, M.; Trautwein, A. X. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1621. (b) Fleming, J. S.; Mann, K. L. V.; Carraz, C.-A.; Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 1279. (c) Paul, R. L.; Argent, S. P.; Jeffery, J. C.; Harding, L. P.; Lynam, J. M.; Ward, M. D. *Dalton Trans.* **2004**, 3453. (d) Clegg, J. K.; Lindoy, L. F.; Moubaraki, B.; Murray, K. S.; McMurtrie, J. C. *Dalton Trans.* **2004**, 2417. (e) Davis, A. V.; Fiedler, D.; Ziegler, M.; Terpin, A.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 15354.

can afford elaborate structures from simple constituents if the symmetry issues are properly addressed.² From a functional point of view, many cages exhibit host–guest chemistry involving their central cavities.^{3,4} At a simple level this can involve binding of counterions or solvent molecules, and in some cases there is evidence that the guest species acts as a template for cage formation, with a differently sized or shaped guest templating a different cage structure from the same component parts.³ In addition, the host–guest chemistry of some cages has become much more sophisticated, with bound guests displaying unusual forms of reactivity and generating products that would not otherwise be accessible, such that the cages act as “microreactors”.⁴

The vast majority of such cages are homoleptic, meaning that they contain one type of ligand in combination with a labile metal cation. Commonly these ligands are “edge-bridging” (spanning two metal ions, and hence lying along an edge of a polyhedral cage) or “face capping” (spanning three metal ions, and hence lying over a triangular face of a polyhedral cage). These result in cages with different stoichiometries. For example, a tetradentate bridging ligand (bis-bidentate, with two compartments) may combine with a metal ion having octahedral geometry to give M_4L_6 tetrahedral cages,⁵ with a metal ion at each vertex and a bridging ligand along each edge. The same metal ion with a hexadentate bridging ligand (tris-bidentate, with three compartments) may instead give an M_4L_4 tetrahedron in which the ligands cap all four triangular faces of the tetrahedron.⁶ Thus, the nature of the ligand (edge-bridging or face-capping) defines the stoichiometry and limits the range of cages available. We have observed many $2M:3L$ cages based on bis-bidentate bridging ligands and octahedral metal ions, having the structures of M_4L_6 tetrahedra,^{5b,c} M_8L_{12} cubes,⁷ $M_{12}L_{18}$ truncated tetrahedra,⁸ and $M_{16}L_{24}$ capped truncated tetrahedra;⁹ any other examples that may arise must necessarily be a member of this series of polyhedra which have a 2:3 vertex:edge ratio, given the stoichiometric limitations.

An interesting possibility to extend the structures of available polyhedral cage complexes is to use a mixture of edge-bridging and face-capping components. We reported an example of this a while ago (Figure 1),¹⁰ in the form of a trinuclear Mn(II) complex in which a tris-bidentate ligand connected all three metal ions in a triangular array, and three bis-bidentate ligands around the edges of the triangle completed the octahedral coordination geometry. The resulting complex $[Mn_3(L^A)(L^B)_3]^{2+}$, with a 3:1:3 ratio of metal ions:face-capping ligands:edge-bridging ligands, is the simplest example of this type that can be envisaged by combining edge-bridging and face-capping ligands in a single structure. It was a purely serendipitous discovery (arising in low yield from a reaction involving an impure batch of ligand L^A which contained traces of L^B), but it

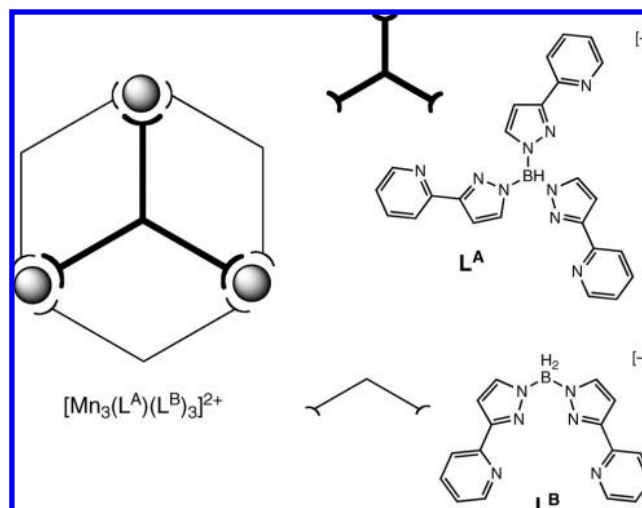


Figure 1. A mixed-ligand complex based on a combination of face-capping tritopic and edge-bridging ditopic ligands with a six-coordinate metal ion.¹⁰

suggested that this might be a phenomenon worth investigating more thoroughly. It is still the case that only a very small number of mixed-ligand cages have been prepared in this way.¹¹

In this paper we report the syntheses, structures, and solution properties of a new series of mixed-ligand cages which combine both edge-bridging (tetradentate) and face-capping (hexadentate) ligand components, combined with six-coordinate metal ions in an unusual 12-nuclear cuboctahedral array. Although the cuboctahedron has regularly arisen as a structural motif in cluster chemistry,¹² we are only aware of two other examples of coordination cages based on this polyhedral shape.^{11d,13} Mass spectrometric and ¹H NMR studies confirm the integrity of the cages in solution and provide interesting insights into the symmetry properties of the cages. Part of this work has been published recently as a preliminary communication.⁹

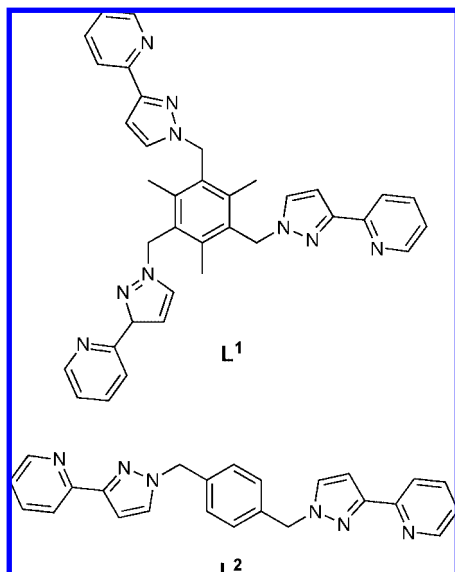
Results and Discussion

Synthesis and Crystal Structure Studies. The ligands used are L^1 and L^2 , shown in Scheme 1. L^1 is a tris-bidentate ligand with three bidentate pyrazolyl-pyridine arms radiating from a central phenyl ring; L^2 is a tetradentate (bis-bidentate) analogue with the two pyrazolyl-pyridine chelating units on either side of a 1,4-phenylene spacer. In each case the chelating units are separated from the central aromatic group by methylene “hinges”. The flexibility of these precludes any attempts to design or predict the structures of the resultant complexes: examples of self-assembled cages which have been the result

- (6) (a) Amoroso, A. J.; Jeffery, J. C.; Jones, P. L.; McCleverty, J. A.; Thornton, P.; Ward, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1443. (b) Albrecht, M.; Janser, I.; Burk, S.; Weis, P. *Dalton Trans.* **2006**, 2875. (c) Yeh, R. M.; Xu, J.; Seeber, G.; Raymond, K. N. *Inorg. Chem.* **2005**, *44*, 6228.
- (7) (a) Bell, Z. R.; Harding, L. P.; Ward, M. D. *Chem. Commun.* **2003**, 2432. (b) Argent, S. P.; Adams, H.; Harding, L. P.; Ward, M. D. *Dalton Trans.* **2006**, 542.
- (8) (a) Bell, Z. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 2515. (b) Argent, S. P.; Adams, H.; Riis-Johannessen, T.; Jeffery, J. C.; Harding, L. P.; Mamula, O.; Ward, M. D. *Inorg. Chem.* **2006**, *45*, 3905.
- (9) Argent, S. P.; Adams, H.; Riis-Johannessen, T.; Jeffery, J. C.; Harding, L. P.; Ward, M. D. *J. Am. Chem. Soc.* **2006**, *128*, 72.
- (10) Ward, M. D.; McCleverty, J. A.; Jeffery, J. C. *Coord. Chem. Rev.* **2001**, *222*, 252.

- (11) (a) Hiraoka, S.; Kubota, Y.; Fujita, M. *Chem. Commun.* **2000**, 1509. (b) Hiraoka, S.; Shiro, M.; Shionoya, M. *J. Am. Chem. Soc.* **2004**, *126*, 1214. (c) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, *5*, 102. (d) Olenyuk, B.; Whiteford, J. A.; Fechtenkötter, A.; Stang, P. J. *Nature* **1999**, *398*, 796.
- (12) (a) Steden, F.; Schmidt, P.; Wahl, B.; Isaeva, A.; Ruck, M. Z. *Anorg. Allg. Chem.* **2008**, *634*, 69. (b) Yang, Y. Y.; Huang, Z. Q.; He, F.; Chen, X. M.; Ng, S. W. Z. *Anorg. Allg. Chem.* **2004**, *630*, 286. (c) Ruck, M.; Hampel, P. *Polyhedron* **2002**, *21*, 651. (d) Watari, N.; Ohnishi, S. *Phys. Rev. B* **1998**, *58*, 1665. (e) Blake, A. J.; Gould, R. O.; Grant, C. M.; Milne, P. E. Y.; Parsons, S.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1997**, 485. (f) Hosmane, N. S.; Zhang, H. M.; Maguire, J. A.; Wang, Y.; Thomas, C. J.; Gray, T. G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1000. (g) Campana, C. F.; Chen, Y.; Day, V. W.; Klemperer, W. G.; Sparks, R. A. *J. Chem. Soc., Dalton Trans.* **1996**, 691.
- (13) Aoki, S.; Shiro, M.; Kimura, E. *Chem. Eur. J.* **2002**, *8*, 929.

Scheme 1



of rational design are based on rigid bridging ligands whose conformations are, to a large extent, predictable in advance.² Conversely, as we have seen in other work with ligands of this type, the flexibility of the ligands is also an advantage as it allows formation of quite unexpected and structurally elaborate products which could never realistically have been planned.^{7–9}

Combination of a metal perchlorate or tetrafluoroborate salt [of Co(II), Cu(II), or Cd(II)] with L^1 and L^2 in nitromethane afforded in each case a clear solution from which large prismatic crystals grew following slow diffusion of di-isopropyl ether vapor into the solution. Initially we used a 1:1:1 ratio of components, but once the crystal structures of the cages had been established (see below) we used the correct 3:1:3 ratio, upon which the crystalline products were obtained as the sole product in high yield in each case.

Although large and well-formed, these crystals scattered X-rays very weakly; in some cases scattering was almost nonexistent, even using synchrotron radiation. However, we managed to obtain reasonable data sets in two cases, with Cu(II) and Cd(II). We will focus the main discussion and analysis of the structure on the Cd(II) complex, for which single-crystal X-ray diffraction studies revealed formation of the mixed-ligand dodecanuclear cage $[\text{Cd}_{12}(\mu^3\text{-}L^1)_4(\mu\text{-}L^2)_{12}](\text{ClO}_4)_{24} \cdot \text{MeNO}_2$. The structure is shown in Figures 2 and 3.

The complex cage (Figure 2) has an approximately cuboctahedral framework of 12 metal cations, containing eight triangular and six square faces. This polyhedron may be considered as being derived from a cube, with the eight corners truncated to reveal triangular faces whose vertices meet exactly in the center of what used to be an edge of the cube (Figure 3). Since the cuboctahedron is based on two types of regular polygons, triangles and squares, which meet at (noncrystallographically) identical vertices, it is a member of the set of Archimidean solids.¹ The cage has no internal crystallographic symmetry such that all 12 Cd(II) ions are crystallographically independent.

The stoichiometry of the complex is easy to rationalize. Four ligands L^1 provide 24 nitrogen donor atoms; 12 ligands L^2 provide an additional 48 donors, giving 72 in total, exactly what is required by 12 six-coordinate metal cations. Each metal vertex is coordinated by three bidentate pyrazolyl-pyridine arms from

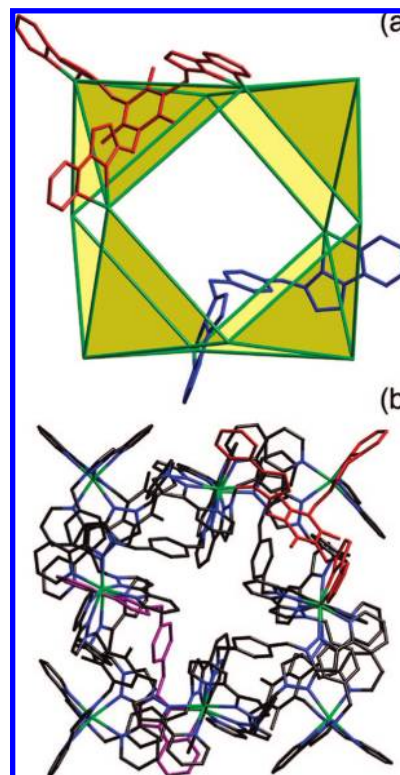


Figure 2. Two views of the structure of $[\text{Cd}_{12}(\mu^3\text{-}L^1)_4(\mu\text{-}L^2)_{12}](\text{ClO}_4)_{24} \cdot \text{MeNO}_2$. (a) The cuboctahedral Cd_{12} core, with one face-capping (L^1) ligand and one edge-bridging (L^2) ligand included; the eight triangular faces are shaded yellow, and the six square faces are not colored. (b) The complete structure, again with one ligand of each type highlighted (L^1 , red; L^2 , purple).

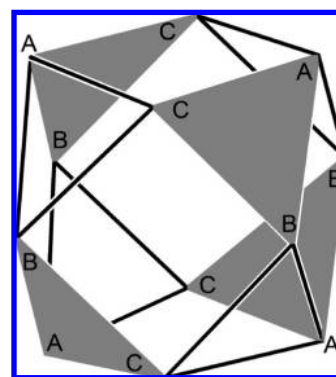


Figure 3. Diagrammatic representation of the symmetry of the cuboctahedral cage in solution. The gray solid triangles represent the four face-capping ligands L^1 , which span four of the eight triangular faces; the black lines represent the edge-bridging ligands L^2 , which bridge the edges of the remaining four triangular faces. The letters A, B, and C refer to the different environments of the metal vertices, which are inequivalent due to the nonsymmetrical coordination of the triangular ligands (see Figure 4a). This arrangement has three C_2 axes (through the open square faces), and hence the structure has D_2 symmetry.

three different ligands (one L^1 and two different L^2 ligands) and is in an irregular “pseudo-octahedral” tris-chelate coordination geometry with Cd–N bond distances in the range 2.14–2.42 Å. The Cd–N distances and the bond angles around the Cd(II) centers are individually unremarkable. The polyhedron is fairly irregular, with nearest-neighbor Cd···Cd separations along the edges of the polyhedron lying in the range 9.5–10 Å along the edges spanned by L^2 ligands, and between 10 and 12.4 Å around those triangular faces that are capped by L^1 ligands.

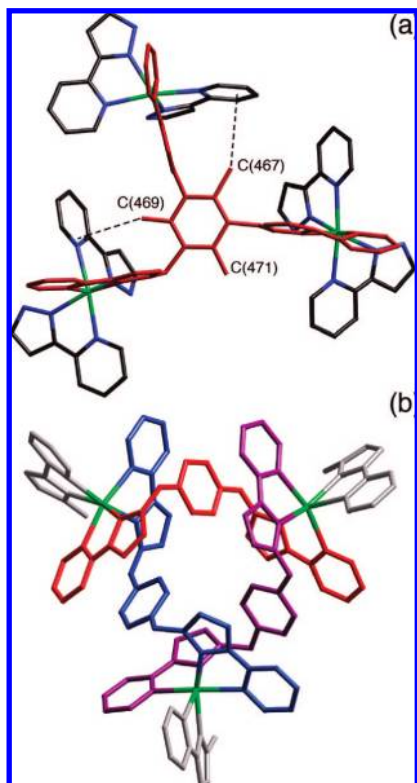


Figure 4. Two views of parts of the structure of $[\text{Cd}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{ClO}_4)_{24}\cdot\text{MeNO}_2$. (a) One of the triangular faces capped by an L^1 ligand (in red), showing the nonsymmetrical coordination of the ligand and the $\text{CH}\cdots\pi$ interactions that result in the three $\text{Cd}(\text{II})$ ions (A, B, and C in Figure 3) being inequivalent. (b) One of the alternate triangular faces in which the three $\text{Cd}\cdots\text{Cd}$ edges are each spanned by a ligand L^2 giving a circular helical structure; the ligand fragments in gray are parts of L^1 ligands.

Four of the eight triangular faces—every alternate one, which together define an approximately tetrahedral subset of the structure—are capped by a triply bridging ligand L^1 which sits over the center of triangular face and donates one bidentate arm to each metal vertex (Figure 4a). The remaining 12 edges are spanned by the bis-bidentate bridging ligands L^2 . These are arranged in four sets of three around the alternate set of four triangular faces (i.e., those triangular faces that are not capped by a single L^1 ligand). Each of these $\text{Cd}_3(\mu\text{-L}^2)_3$ triangular units has the arrangement of a cyclic helicate (Figure 4b), in which each $\text{Cd}(\text{II})$ center is coordinated two ligands L^2 . This occupies four of the six coordination sites, with the remaining two sites at each metal center being taken up by coordination to one arm of an L^1 ligand (shown in gray in Figure 4b) in each case.

Within these cyclic helical $\text{Cd}_3(\mu\text{-L}^2)_3$ subunits, the central phenyl ring of each ligand L^2 is sandwiched in a π -stacking interaction between two coordinated pyrazolyl-pyridine units from each of the other two ligands. Such aromatic stacking appears to be an important feature of all of the large cages that we have isolated.^{7–9} The aromatic stacking interaction is strengthened when it involves alternating electron-rich/electron-deficient layers,¹⁴ as is the case here: each relatively electron-

rich phenyl ring (with two alkyl substituents) is sandwiched between two pyrazolyl-pyridine units, which are made more electron-deficient by virtue of being coordinated to $2+$ metal centers.

It is significant that the formation of this polyhedral structure would not be possible if it relied on one type of ligand alone (i.e., a homoleptic complex). The vertex:edge ratio of 12:24 does not match the 2:3 stoichiometry required for complexes based solely on edge-bridging ligands (M_4L_6 tetrahedra, M_8L_{12} cubes, etc). Further, since the cuboctahedron contains a mixture of square and triangular faces, rather than just one type of face as in the Platonic solids, it could not be formed by triangular face-capping ligands alone unless the metal ions were four-coordinate: one can imagine an $\text{M}_{12}(\text{L}^1)_8$ structure based on eight face-capping tris-bidentate ligands, in which each metal ion would be bound by only two bidentate pyrazolyl-pyridine units from adjacent L^1 ligands. We note that the cuboctahedral cage reported by Stang a few years ago also relied on a mixture of ditopic and tritopic ligands.^{11d}

The absence of any other products in solution (confirmed by mass spectrometry and NMR studies, see later) implies that there is something about this mixed-ligand structure that is particularly thermodynamically favorable with respect to separate homoleptic complexes of L^1 and L^2 , such that a mixture of ligands is preferentially selected. For example, there is no sign in the ES mass spectra of homoleptic M^{2+}/L^2 cages of the form $[\text{M}_{16}(\text{L}^2)_{24}]^{32+}$.⁹ Since there is nothing remarkable about the coordination geometry around the $\text{Cd}(\text{II})$ centers, this in turn implies interligand interactions that are more effective here than they would be in a mixture of homoleptic complexes, otherwise there would be no driving force for the different ligands to combine in a single assembly in this way against the dictates of entropy. One possible candidate is the aromatic stacking between the L^2 ligands around the periphery of the complex; there are 12 such three-layer stacks (cf. Figure 4b), although this occurs also in homoleptic cages $[\text{M}_{16}(\text{L}^2)_{24}]^{32+}$.⁹ Another possible candidate is the interaction shown in Figure 4a, in which two of the three methyl groups on the central aromatic ring of each L^1 ligand are oriented such that they lie above pyridyl rings of L^2 ligands: thus, C(467) and C(469) lie 3.60 and 3.55 Å, respectively, from the mean planes of adjacent pyridyl rings. This constitutes a weak attractive $\text{CH}\cdots\pi$ interaction between L^1 and L^2 fragments¹⁵ which could not be present in homoleptic complexes.

Apart from the basic polyhedral structure which is in itself very unusual in coordination chemistry, several additional details of the structure are worth commenting on. All 12 metal centers have the same meridional coordination geometry, with one axis having two pyridyl donors, the second having two pyrazolyl donors, and the third having both pyridyl and pyrazolyl donors. This could, in principle, generate two further geometric isomers, because one pyrazolyl-pyridine unit (attached to L^1) is different from the other two (attached to L^2), so the two pyrazolyl donors from the L^2 ligands could be *trans* to the L^1 donors, or the two pyridyl donors from the L^2 ligands could occupy those positions. However, only the former of these two possible geometric isomers occurs, at every metal center.

In addition, all 12 metal centers have the same optical configuration; this is something we have noticed before in many large coordination cages and appears to be necessary for the curved surface to close.^{5b,8,9} This is manifested, for example,

(14) (a) Cockroft, S. L.; Perkins, J.; Zonta, C.; Adams, H.; Spey, S. E.; Low, C. M. R.; Vinter, J. G.; Lawson, K. R.; Urch, C. J.; Hunter, C. A. *Org. Biomol. Chem.* **2007**, *5*, 1062. (b) Cockroft, S. L.; Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 8594. (c) Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 2* **2001**, 651.

(15) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

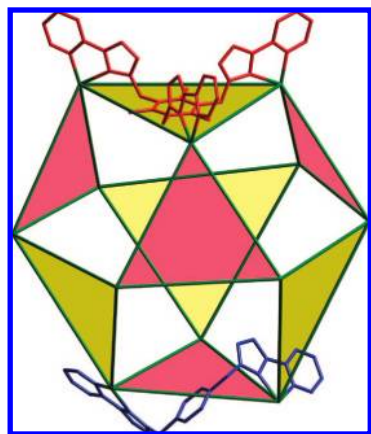


Figure 5. A view of part of the structure of $[\text{Cu}_{12}(\mu\text{-L}^1)_{12}(\mu^3\text{-L}^2)_4](\text{BF}_4)_{24}\cdot 20\text{MeNO}_2$, which is isostructural to the Cd(II) analogue in Figures 2–4. This view emphasizes the cuboctahedral cage structure differently from the way shown in Figure 2, with the four triangular faces capped by tridentate ligands L^1 shaded yellow, and the alternate four (bridged by bidentate ligands L^2) shaded pink.

in the observation that the four triangular cyclic helical fragments (Figure 4b) all have the same sense of helical twist. The bulk sample of course is racemic, but each cage is homochiral, which suggests interesting possibilities for stereoselective uptake of chiral anions into the large central cavity. This cavity has an approximate accessible volume of ca. 500 \AA^3 in which six perchlorate anions and one nitromethane solvent molecule could be located. The sizes of the “windows” in the faces (see the space-filling diagram, Figure S1, Supporting Information) are such that facile ingress and egress of small molecules is expected, and we found no evidence in the NMR spectrum for different environments for “internal” and “external” solvent molecules.

We also obtained an X-ray structure of $[\text{Cu}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{BF}_4)_{24}$, which is isostructural with the Cd(II)/perchlorate complex: it has the same basic cuboctahedral core as the Cd(II) complex, with the same arrangement of ligands (Figure 5). The complex lies on a two-fold rotation axis such that only half of the cage [six Cu(II) ions] is crystallographically unique. The dimensions are generally similar, with $\text{Cu}\cdots\text{Cu}$ separations on the $\{\text{Cu}_3(\text{L}^2)_3\}$ faces being in the range $9.87\text{--}10.18 \text{ \AA}$ and the separations on the larger $\{\text{Cu}_3(\mu^3\text{-L}^1)\}$ faces being $10.57\text{--}12.30 \text{ \AA}$. $\text{Cu}\text{--}\text{N}$ separations lie in the range $1.98\text{--}2.41 \text{ \AA}$, with each Cu(II) ion showing the usual pattern of four shorter bonds and two (*a trans*-related pair) longer bonds due to the Jahn–Teller effect. This irregularity can clearly be accommodated without disrupting the cuboctahedral assembly. This example was presented in the initial communication,⁹ and all of the points mentioned in the discussion above of the Cd(II) complex apply to this example also.

Solution Mass Spectrometry and NMR Studies. Electrospray mass spectrometry was very helpful at providing information on the structural integrity of the complexes in solution, and also in confirming that those crystals that did not diffract sufficiently well for a structural determination [of e.g. the Co(II) analogue] are nevertheless of the same structural type. For $[\text{Cd}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{ClO}_4)_{24}$ we observed a series of peaks at m/z 3504.5, 2606.3, and 2063.4 which corresponds to the species $\{[\text{Cd}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{ClO}_4)_{24-n}\}^{n+}$ ($n = 3, 4, 5$), formed by loss of perchlorate ions from the intact assembly. There are also numerous more intense peaks at lower m/z values corresponding to much smaller fragments, which could occur either from

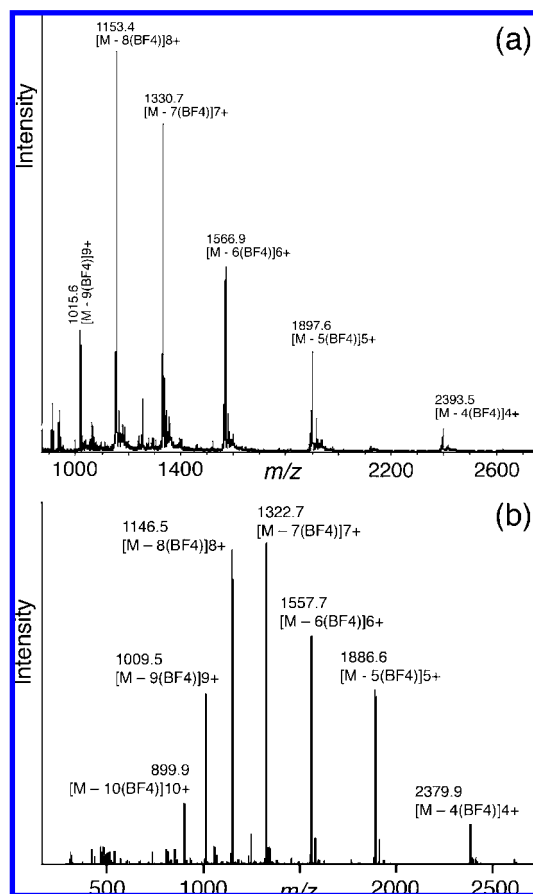


Figure 6. Electrospray mass spectra of (a) $[\text{Cu}_{12}(\mu\text{-L}^1)_{12}(\mu^3\text{-L}^2)_4](\text{BF}_4)_{24}$ and (b) $[\text{Co}_{12}(\mu\text{-L}^1)_{12}(\mu^3\text{-L}^2)_4](\text{BF}_4)_{24}$ (for details, see Experimental Section).

fragmentation of the cage in the mass spectrometer or—in principle—from dissociation of the cage in solution, although this possibility can be ruled out on the basis of NMR spectroscopic studies (below). Intense and clear mass spectra were also obtained for $[\text{M}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{BF}_4)_{24}$ ($\text{M} = \text{Co}, \text{Cu}$) which are shown in Figure 6: in each case, a clear sequence of peaks is available corresponding to $\{[\text{M}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{BF}_4)_{24-n}\}^{n+}$ ($n = 4, 5, 6, 7, 8, 9, 10$) with, in these cases, relatively little occurrence at low m/z values of peaks from small fragments and no evidence of peaks corresponding to possible homoleptic cages, such as $\{[\text{M}_{16}(\text{L}^2)_{24}]\text{X}_{32-n}\}^{n+}$, which are known products from reaction of M(II) salts with L^2 .⁹

¹H NMR spectroscopic studies on the diamagnetic complex $[\text{Cd}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{ClO}_4)_{24}$ provided complete confirmation of the structural integrity of this cage in solution and also yielded some interesting information about the symmetry of the cage in solution (Figure 7). In brief, the spectrum is *only* consistent with the molecule having four-fold symmetry in solution, such that all four L^1 ligands are equivalent to one another but with no internal symmetry, such that their three arms are different—an example of symmetry breaking.¹⁶ The 12 ligands L^2 split into three sets of four equivalent ligands (again with no internal symmetry, such that their ends are different). The reasons for this are addressed below, but for now we assign the spectrum based on this.

(16) (a) Olivier, C.; Solari, E.; Scopellitti, R.; Severin, K. *Inorg. Chem.* **2008**, *47*, 4454. (b) Präsang, C.; Whitwood, A. C.; Bruce, D. W. *Chem. Commun.* **2008**, 2137. (c) Mikami, K.; Yamanaka, M. *Chem. Rev.* **2003**, *103*, 3369.

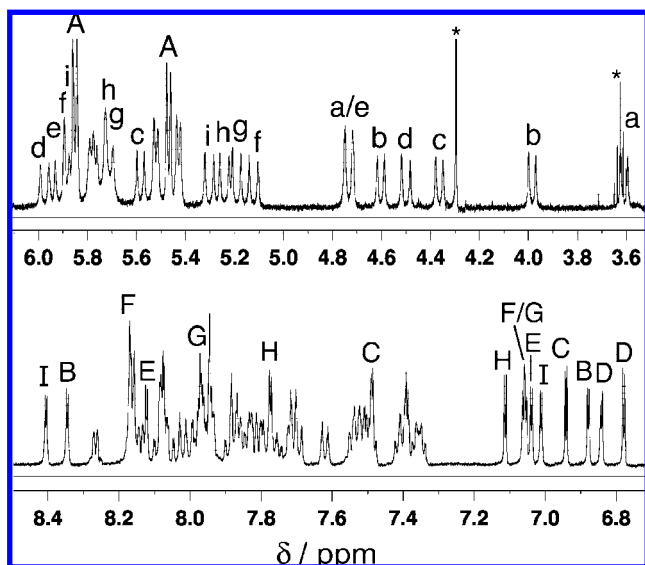


Figure 7. Part of the 500 MHz ^1H NMR spectrum of $[\text{Cd}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{ClO}_4)_{24}$ in CD_3NO_2 . The peaks labeled * are from residual protons in the solvent and/or trace water. Letters A–I are the signals arising from the 18 independent pyrazolyl protons (two on each ring, hence the two occurrences of each letter denote the coupled pair of protons on one pyrazolyl ring); likewise, lowercase letters a–i denote the 18 independent methylene protons which occur in nine coupled pairs. These assignments were made on the basis of a COSY spectrum.

The fact that the face-capping ligands L^1 have no internal symmetry is immediately apparent from the presence of three different signals for the methyl groups attached to the central aromatic ring, at 0.52, 0.90, and 2.73 ppm. The low chemical shifts of the first two are indicative of them being shielded by the ring current of nearby aromatic rings from different ligands, and in fact this is apparent in the crystal structure, as shown earlier (Figure 4a). The third methyl group [C(471) in Figure 4a, and its equivalents on the other ligands L^1] has no such interaction with a pyridyl ring, and these are the protons whose signal will be at 2.73 ppm. An essential consequence of this absence of symmetry for the face-capping ligands L^1 is that there must, in solution, be three different Cd(II) environments, and this is confirmed by the ^{113}Cd NMR spectrum which shows three sharp signals of equal intensity between -440 and -450 ppm (Figure 8).

From this, and the fact that the 12 ligands L^2 split into three sets of four equivalent ligands with all protons magnetically inequivalent in each set, we can calculate the expected number of signals in the proton NMR spectrum. There should be 18 independent methylene proton environments: six from L^1 and 12 from the three independent L^2 ligands which contribute four methylene environments each (in a chiral environment, the two protons in each CH_2 group are diastereotopic and therefore inequivalent). Likewise, there will be 18 pyrazolyl proton environments (six from L^1 and 12 from three different L^2 ligand environments which contribute four each) and 36 pyridyl proton environments (12 from L^1 and 24 from three different L^2 ligand environments which contribute eight each). Finally, there will be 12 inequivalent aromatic CH protons from the *p*-phenylene spacers of three different L^2 ligand environments which contribute four such protons each. All aromatic or methylene proton signals will have the same intensity, because every one arises from four equivalent H atoms in the complex due to the four-fold symmetry.

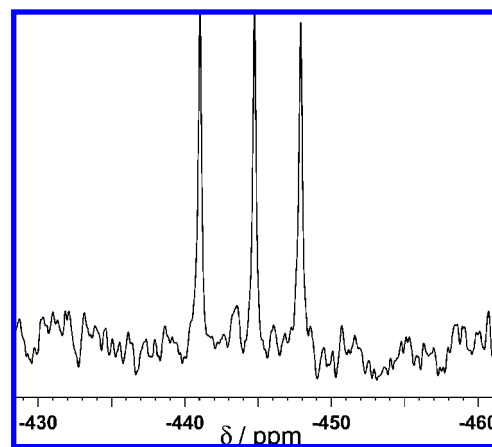


Figure 8. ^{113}Cd NMR spectrum of $[\text{Cd}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{ClO}_4)_{24}$ in CD_3NO_2 showing three peaks of equal intensity arising from the three different Cd(II) environments (Figures 3 and 4a).

Figure 7 shows the coupled pairs of doublets between 3.8 and 6.0 ppm arising from diastereotopic protons of nine inequivalent CH_2 groups in a chiral environment, with a total of 18 protons (9 pairs), as required; the pairings were assigned on the basis of a COSY spectrum. Also in this region are the phenyl protons from the L^2 ligands, which have undergone substantial upfield shifts compared to free L^2 (to ca. 5.5 ppm) as a consequence of the aromatic stacking observed in the solid state that was mentioned earlier. The pyrazolyl protons—easy to spot because they have small coupling constants and occur in pairs in the COSY spectrum—are observed between 6.7 and 8.4 ppm. Figure 7 shows these 18 protons of the nine inequivalent pyrazole rings, with couplings between the nine pairs again confirmed by the COSY spectrum. This region also contains many of the pyridyl signals (36 in total) which we have not attempted to assign individually because of their extensive overlap with each other and with other signals, but the overall number of signals (as determined from integrals) is correct.

Thus, on the basis of the numbers of signals of each type, their chemical shifts in some cases (indicative of aromatic stacking), and the chirality of the structure (given the inequivalence of the two CH_2 protons in each pair), it is clear that a single chiral four-fold symmetric structure exists in solution. The reason for *four-fold* symmetry—and hence the consequent facts that each L^1 has no internal symmetry and there are three different environments for L^2 —is not immediately obvious: one might expect, for example, three-fold axes through the triangular faces of the cuboctahedron which would result in *T* symmetry for the cage, a common consequence of removing planes of symmetry in cubic, tetrahedral, or icosahedral assemblies.¹⁷

The only way to rationalize this is shown in Figure 3, in which the shaded triangles are the four capping ligands L^1 and the lines are the 12 edge-bridging ligands L^2 . Given that there is no internal symmetry in each L^1 ligand (i.e., there are no three-fold axes), we can arbitrarily label the vertices of one L^1 ligand as A, B, and C, corresponding to the three different Cd(II) environments. Since all four L^1 ligands must be the same as one another (from the NMR spectrum), we can label the A, B, and C vertices of the other three L^1 ligands in such a way that

(17) Cotton, F. A.; Murillo, C. A.; Yu, R. *Dalton Trans.* **2005**, 3161.

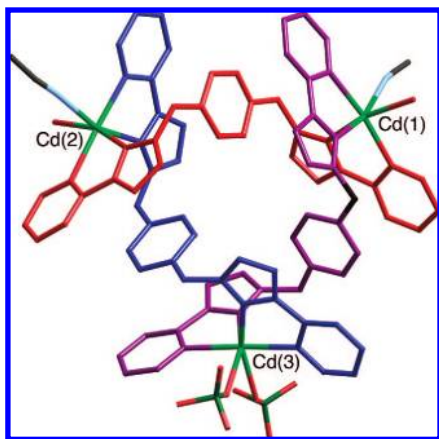


Figure 9. Structure of the complex cation of $[\text{Cd}_3(\text{L}^2)_3(\text{ClO}_4)_4(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{MeCN}$ with each of the three ligands in the cyclic helical array shaded differently for clarity. Note the similarity with the view of the $\text{Cd}_3(\text{L}^2)_3$ triangular face of the cuboctahedral cage shown in Figure 4b. Cd(1) and Cd(2) both have one water ligand and one MeCN ligand attached; Cd(3) has two perchlorate anions as monodentate ligands.

all four A vertices are connected by two-fold rotations, as are all four B vertices and all four C vertices. Thus, for each L^1 ligand, the sequence ABC is in a clockwise sense when viewed from the outside. Now we can see why the 12 bridging ligands L^2 split into four sets of three equivalent ligands, and why they have no internal symmetry. The polyhedron has four AB edges, four AC edges, and four BC edges, each edge type corresponding to one L^2 environment; given that the two ends of each edge are inequivalent, there can be no internal symmetry within the L^2 ligands. It follows from this that the cage, in solution, must have three mutually orthogonal C_2 axes through the square faces (but no mirror planes because of the chirality); i.e., it has D_2 symmetry in solution.

Structure of a “Partially Assembled” Intermediate. As mentioned earlier, when the two ligands and a metal salt were combined in MeNO_2 in the correct proportion, the 12-nuclear cage was the only product as crystalline blocks. We repeated the reaction of L^1 , L^2 , and $\text{Cd}(\text{ClO}_4)_2$ (1:3:3) in the less powerful solvent MeCN and found in this case that, in addition to crystals of the cuboctahedral Cd_{12} cage, we obtained a small number of crystals of a clearly different needle-like habit. Crystallographic analysis revealed these to be $[\text{Cd}_3(\text{L}^2)_3(\text{ClO}_4)_4(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{MeCN}$, a trinuclear circular helicate in which three bridging ligands L^2 span the three edges of a Cd_3 triangle (Figure 9). This 1:1 $\text{Cd}:\text{L}^2$ ratio only provides four donor atoms per Cd(II) center, so the remaining two coordination sites at each metal center are taken up by whatever monodentate ligands are available (MeCN, water, or perchlorate anions) to give the product that crystallizes best.

Small cyclic helicates of this sort are now well known,^{8b,18} so this structure is in itself of no major significance. However,

it is of interest here due to its close relationship to the structure of the M_{12} cuboctahedral cages: it can be considered as a fragment of an M_{12} cage based on one of the four triangular helical $\{\text{M}_3(\text{L}^2)_3\}$ faces (Figure 4b), and the resemblance between Figure 9 and Figure 4b is obvious. If this $\{\text{M}_3(\text{L}^2)_3\}$ fragment is “extracted” from the cuboctahedron by breaking the bonds to the three L^1 ligands with which it is associated, and the resultant two vacancies in the coordination sphere of each metal center are filled by adventitious monodentate ligands, a structure of this type would be the result. We note that the $\text{Cd}\cdots\text{Cd}$ separations in this trinuclear complex (average, 9.89 Å) are comparable to those around the $\{\text{M}_3(\text{L}^2)_3\}$ helical triangular faces of the cuboctahedron. Likewise, the pattern of interligand aromatic stacking, whereby the phenyl group of each ligand is sandwiched between coordinated pyrazolyl-pyridine fragments of the two other ligands L^2 , is exactly the same as we observed around each triangular face of the complete Cd_{12} cage (Figure 4b). $[\text{Cd}_3(\text{L}^2)_3(\text{ClO}_4)_4(\text{MeCN})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 3\text{MeCN}$ can therefore be considered as a trapped $\{\text{Cd}_3(\text{L}^2)_3\}^{6+}$ intermediate en route to full assembly of $[\text{Cd}_{12}(\mu^3\text{-L}^1)_4(\mu\text{-L}^2)_{12}](\text{ClO}_4)_{24}$, but use of the less powerful solvent MeCN in place of MeNO_2 has resulted in premature crystallization of small amounts of this component rather than allowing it to remain in solution and complete the cage assembly by further reaction with L^1 .

Conclusion

Combination of triangular (face-capping) and linear (edge-bridging) ligands L^1 and L^2 , respectively, with M^{2+} cations having a preference for octahedral coordination geometry results in formation of unusual dodecanuclear cuboctahedral cage complexes based on a mixture of the two types of ligand. In other words, formation of this structure is a cooperative process requiring selection of two types of ligand from a mixture in preference to formation of alternative homoleptic complexes. The resulting polyhedral architecture, a member of the set of Archimidean solids, would not be accessible with one type of ligand on its own. The cage retains its structural integrity in solution with D_2 symmetry and has a large central cavity which will be investigated for its host–guest chemistry with large anionic species.

Experimental Section

General Details. Ligand L^1 ¹⁹ and 3-(2-pyridyl)pyrazole²⁰ were prepared according to previously published methods. ¹H NMR spectra and 2-D COSY spectra were recorded at 500 MHz on a Bruker DRX-500 spectrometer; ¹¹³Cd NMR spectra were recorded on a Bruker Avance-2 400 spectrometer. Mass spectra were measured on a Bruker MicroTOF mass spectrometer in electrospray positive ion mode. Samples were prepared at a concentration of ca. 2 mg/cm³ in MeNO_2 or MeCN and analyzed by direct infusion using a Cole-Parmer syringe pump at a flow rate of 3 $\mu\text{L}/\text{min}$. Spectra were acquired over an m/z range of 50–3000; several scans were averaged to provide the final spectrum.

Synthesis of L^2 . A mixture of 1,4-bis(bromomethyl)benzene (2.00 g, 7.60 mmol), 3-(2-pyridyl)pyrazole (2.43 g, 16.7 mmol), aqueous NaOH (10 M, 20 cm³), toluene (50 cm³), and Bu_4NOH (40% aqueous solution, 3 drops) was stirred at 60 °C for 1 h. The mixture was diluted with H_2O (100 cm³), and the organic layer

(18) (a) Hasenknopf, B.; Lehn, J.-M.; Kneisel, B. O.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1838. (b) Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Dupont-Gervais, A.; van Dorsselaer, A.; Kneisel, B.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 10956. (c) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Commun.* **1999**, 195. (d) Tuna, F.; Hamblin, J.; Jackson, A.; Clarkson, G.; Alcock, N. W.; Hannon, M. J. *Dalton Trans.* **2003**, 2141. (e) Jones, P. L.; Byrom, K. J.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Chem. Commun.* **1997**, 1361. (f) Mamula, O.; von Zelewsky, A.; Brodard, P.; Schlapfer, C. W.; Bernardinelli, G.; Stoekli-Evans, H. *Chem. Eur. J.* **2005**, *11*, 3049. (g) Al-Rasbi, N. K.; Adams, H.; Harding, L. P.; Ward, M. D. *Eur. J. Inorg. Chem.* **2007**, 4770.

(19) Bell, Z. R.; McCleverty, J. A.; Ward, M. D. *Aust. J. Chem.* **2003**, *56*, 665.

(20) Amoroso, A. J.; Cargill Thompson, A. M. W.; Jeffery, J. C.; Jones, P. L.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Chem. Commun.* **1994**, 2751.

Table 1. Crystal Parameters, Data Collection, and Refinement Details for the Structures in This Paper

	complex		
	[Cd ₁₂ (μ ³ -L ¹) ₄ (μ ³ -L ²) ₁₂](ClO ₄) ₂₄ ·MeNO ₂	[Cu ₁₂ (μ-L ¹) ₁₂ (μ ³ -L ²) ₄](BF ₄) ₂₄ ·20MeNO ₂	[Cd ₃ (L ²) ₃ (ClO ₄) ₄ (MeCN) ₂ (H ₂ O) ₂](ClO ₄) ₂ ·3MeCN
formula	C ₄₃₃ H ₃₇₅ Cd ₁₂ Cl ₂₄ N ₁₀₉ O ₉₈	C ₄₅₂ H ₄₃₀ B ₁₀ Cu ₁₂ F ₄₀ N ₁₂₈ O ₄₀	C ₈₂ H ₇₉ Cd ₃ Cl ₃ N ₂₃ O ₂₆
molecular weight	10 873.02	9925.82	2352.58
<i>T</i> , K	100(2)	150(2)	100(2)
crystal system	monoclinic	monoclinic	triclinic
space group	<i>C</i> 2	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	37.220(7)	24.840(7)	17.2620(16)
<i>b</i> , Å	37.220(7)	50.544(13)	17.9425(17)
<i>c</i> , Å	43.770(9)	48.629(12)	18.4478(17)
α , °	90	90	70.614(6)
β , °	90.10(3)	102.003(5)	82.359(5)
γ , °	90	90	63.121(5)
<i>V</i> , Å ³	60 636(21)	59 720(27)	4806.5(8)
<i>Z</i>	4	4	2
ρ , g cm ⁻³	1.191	1.104	1.626
crystal size, mm ³	0.32 × 0.32 × 0.19	0.55 × 0.25 × 0.13	0.24 × 0.24 × 0.06
μ , mm ⁻¹	0.587	0.493	0.911
data, restraints, parameters	102 364, 568, 1801	39 038, 5183, 1430	16 727
final <i>R</i> 1, <i>wR</i> 2 ^a	0.134, 0.381	0.0968, 0.2943	0.1095, 0.3300

^a The value of *R*1 is based on ‘observed’ data with *I* > 2σ(*I*); the value of *wR*2 is based on all data.

was separated, dried over MgSO₄, and concentrated before purification by alumina column (5% THF/dichloromethane) to give L² as a white solid (yield: 2.83 g, 95%). ¹H NMR (270 MHz, CDCl₃): δ 8.61 (2H, ddd, *J* = 4.9, 1.8, 0.9 Hz, pyridyl H⁶), 7.92 (2H, ddd, *J* = 7.9, 1.2, 0.9 Hz, pyridyl H³), 7.69 (2H, td, *J* = 7.9, 1.8 Hz, pyridyl H⁴), 7.39 (2H, d, *J* = 2.4 Hz, pyrazolyl H⁵), 7.22 (4H, s, phenyl), 7.18 (2H, ddd, *J* = 7.9, 4.9, 1.2 Hz, pyridyl H⁵), 6.90 (2H, d, *J* = 2.1 Hz, pyrazolyl H⁴), 5.36 (4H, s, CH₂). EIMS: *m/z* 392 (*M*⁺). Found: C, 72.9; H, 5.0; N, 21.3. Required for C₂₄H₂₀N₆: C, 73.4; H, 5.1; N, 21.2.

Syntheses of Complexes [M₁₂(μ-L¹)₄(μ³-L²)₁₂]*X*₂₄. A mixture of L¹, L², and the appropriate metal salt MX₂ [Cu(BF₄)₂, Co(BF₄)₂, Cd(ClO₄)₂] in a 1:3:3 molar ratio was dissolved in MeNO₂. Slow diffusion of ¹Pr₂O into these solutions afforded a good crop of substantial single crystals in >80% yield.

ESMS data for [Cu₁₂(μ-L¹)₁₂(μ³-L²)₄](BF₄)₂₄: *m/z* [observed (calculated)] 2393.5 (2393.8), 1897.6 (1897.7), 1566.9 (1566.9), 1330.7 (1330.7), 1153.4 (1153.5), 1015.6 (1015.7), corresponding to {[Cu₁₂(μ-L¹)₁₂(μ³-L²)₄](BF₄)_{24-x}]^{x+} (*x* = 4, 5, 6, 7, 8, 9, respectively). Found: C, 48.5; H, 4.2; N, 15.4. Required for C₄₃₂B₂₄Cu₁₂H₃₇₂N₁₀₈F₉₆·20MeNO₂ (cf. the crystal structure): C, 48.7; H, 3.9; N, 16.1.

ESMS data for [Co₁₂(μ-L¹)₁₂(μ³-L²)₄](BF₄)₂₄: *m/z* [observed (calculated)] 2379.9 (2379.9), 1886.6 (1886.6), 1557.7 (1557.7), 1322.7 (1322.8), 1146.5 (1146.6), 1009.5 (1009.5), 899.6 (899.9), corresponding to {[Co₁₂(μ-L¹)₁₂(μ³-L²)₄](BF₄)_{24-x}]^{x+} (*x* = 4, 5, 6, 7, 8, 9, 10, respectively). Found: C, 50.8; H, 4.0; N, 14.8. Required for Co₁₂C₄₃₂H₂₇₉N₈₁Cl₂₄O₉₆·5(MeCN): C, 50.2; H, 3.7; N, 15.0.

ESMS data for [Cd₁₂(μ-L¹)₁₂(μ³-L²)₄](ClO₄)₂₄: *m/z* [observed (calculated)] 3504.5 (3504.6), 2603.5 (2603.6), 2062.9 (2063.0), 1702.6 (1702.6), 1445.0 (1445.1), corresponding to {[Cd₁₂(μ-L¹)₁₂(μ³-L²)₄](ClO₄)_{24-x}]^{x+} (*x* = 3, 4, 5, 6, 7, respectively). Found: C, 45.3; H, 3.7; N, 13.2. Required for Cd₁₂C₄₃₂H₂₇₉N₈₁Cl₂₄O₉₆·5(NO₂Me)·4(H₂O): C, 45.7; H, 3.4; N, 13.8.

When the preparation of [Cd₁₂(μ-L¹)₁₂(μ³-L²)₄](ClO₄)₂₄ was repeated exactly as above but using MeCN as solvent instead of MeNO₂, in addition to the Cd₁₂ cage a few needle-like crystals of [Cd₃(L²)₃(ClO₄)₄(MeCN)₂(H₂O)₂](ClO₄)₂·3MeCN were also isolated and structurally characterized; see main text.

X-ray Crystallography. Crystals were removed from the mother liquor, coated with oil, and transferred to a stream of cold N₂ on the diffractometer as quickly as possible to prevent decomposition due to solvent loss. In both cases the complexes formed large, well-shaped crystals which however scattered weakly, due to the extensive disorder of anions and solvent

molecules. After integration of the raw data and merging of equivalent reflections, an empirical absorption correction was applied (SADABS)²¹ based on comparison of multiple symmetry-equivalent measurements. The structures were solved by direct methods and refined by full-matrix least-squares on weighted *F*² values for all reflections using the SHELX suite of programs.²² Pertinent crystallographic data are collected in Table 1. Lists of bond distances and angles in the metal ions’ coordination spheres are given in the Supporting Information.

For both M₁₂cages (M = Cu, Cd), the large size of the structure, weak diffraction, and extensive disorder in the anion- and solvent-filled cavities resulted in a data set of limited quality. In order to minimize the number of parameters in the refinement, all atoms except the metals were refined with isotropic thermal parameters. To reduce the computational time taken for each refinement cycle, “blocks” were used to refine the anions and solvent molecules, and several overlapping portions of the complex cation, separately. Geometric similarity restraints were applied to all pyrazolyl, pyridine, and phenyl rings and to tetrahedral anions and (where located) solvent moieties.

For [Cu₁₂(μ-L¹)₁₂(μ³-L²)₄](BF₄)₂₄·20MeNO₂, only 10 of the 24 tetrafluoroborate anions could be located, the rest being assumed to be mixed up with disordered solvent molecules; this problem was severe for this complex because the anion contains only light atoms (B, F) which have atomic masses similar to those of the solvent atoms. A “Squeeze” function (from PLATON²³) was applied to the data to remove the scattering contributions of several small moieties which could not be satisfactorily modeled as anions or solvent. For [Cd₁₂(μ³-L¹)₄(μ-L²)₁₂](ClO₄)₂₄·MeNO₂, likewise four of the anions were too disordered to be located. One solvent molecule (nitromethane) was located and was reasonably well behaved during refinement. Additional extensive areas of residual electron density which could not sensibly be modeled as solvent or anions were removed via application of the “Squeeze” function in PLATON.²³ Although the unit cell parameters suggest higher symmetry than monoclinic (see Table 1), all attempts at structure solution and refinement in higher symmetries failed, with the refinements rapidly becoming unstable; at the end of the successful refinement in *C*₂, PLATON checks did not suggest that any higher symmetry had been missed. [Cd₃(L²)₃(ClO₄)₄(MeCN)₂(H₂O)₂](ClO₄)₂·3MeCN presented no significant problems beyond weak

(21) Sheldrick, G. M. *SADABS: A program for absorption correction with the Siemens SMART system*; University of Göttingen, Germany, 1996.

(22) *SHELXTL program system version 5.1*; Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.

(23) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

scattering and some disordered lattice solvent molecules which were approximated as three MeCN molecules.

Acknowledgment. We thank the following agencies for financial support: the Government of the Sultanate of Oman, the University of Sheffield, and EPSRC (UK).

Supporting Information Available: Bond distances associated with the metal coordination spheres for the crystal structures; crystallographic CIF files for the new structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA803847W