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# Coordination-directed assembly of trigonal and tetragonal molecular boxes encapsulating anionic guests†

**Cheng-Yong Su,* Yue-Peng Cai, Chun-Long Chen, Hua-Xin Zhang and Bei-Sheng Kang***

*School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, P. R. China. E-mail: cesscy@zsu.edu.cn*

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**$M_2L_3$ and $M_2L_4$ box-like complexes {[$Ag_2$(pbbimb)$_3$][$CF_3SO_3$]$_2$ 1 and [$Cu_2$(mbbimb)$_4$][$ClO_4$]$_4$ 2} with respective $S_3$ and $S_4$ symmetry, in which anionic molecular guests are accommodated, have been synthesized and structurally characterized.**

The inclusion of guest molecules into host structures has drawn much attention due to its potential importance in molecular recognition, ion exchange, chemical sensors, separation and transportation.[1] Whilst organic supramolecular systems have been well developed to mimic biological induced-fit receptors or capsules,[2] artificial inorganic species have the great advantage of incorporating magnetic, electronic, optical and catalytic properties.[3] The rational design of discrete molecular architectures with defined shape and size containing inner cavities for inclusion represents a burgeoning field, and a number of well-characterized entities have been constructed.[4] Exodentate linear or tripodal ligands, represented by various $M_2L_2$ and $M_4L_4$ molecular squares and metallacycles, have been vigorously exploited.[5] Even larger entities may include huge cages like [{Pd(en)($NO_3$)$_2$}$_{18}$(tpb)$_6$][6] [en = ethylenediamine, tpb = 1,3,5-tris(3,5-pyrimidyl)benzene], [$Ni_6$(tpst)$_8Cl_{12}$][7] {tpst = 2,4,6-tri[(4-pyridyl)sulfanylmethyl]-1,3,5-triazine}, and cuboctahedral, dodecahedral and super-adamantanoid molecular architectures.[8]

Interestingly enough, some compositionally and geometrically different but topologically identical assembly pairs, for example, $M_4L_6$[9] and $M_6L_4$,[10] $M_8L_{12}$[11] and $M_{12}L_8$,[12] have been obtained by deliberate combination of different metal ions and ligands. In contrast, the much simpler pairs, $M_2L_3$ and $M_3L_2$, $M_2L_4$ and $M_4L_2$, have scarcely been investigated, although the trigonal $M_3L_2$ cage[13] and tetragonal $M_4L_2$ cage[14] have been spectroscopically characterized. Herein we report the syntheses and structural characterization of two canonical molecular boxes: the trigonal $M_2L_3$ [$Ag_2$(pbbimb)$_3$][$CF_3SO_3$]$_2$ **1** and tetragonal $M_2L_4$ [$Cu_2$(mbbimb)$_4$][$ClO_4$]$_4$ **2**.

The ligands 1,4-bis(benzimidazol-1-ylmethyl)-2,3,5,6-tetramethylbenzene (pbbimb) and 1,3-bis(benzimidazol-1-ylmethyl)-2,4,6-trimethylbenzene (mbbimb), feature mainly in their exobidentate coordination mode with the benzene ring as the base and two free-rotating benzimidazole rings as anchors. They can be easily prepared, by a similar procedure to that reported earlier,[15] by the replacement reactions of 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene and 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene with benzimidazole. Complex **1** was prepared by the reaction of Ag($CF_3SO_3$) with ligand pbbimb in a molar ratio of 2 : 3 in MeOH–MeCN, while **2** was prepared from Cu($ClO_4$)$_2$·6$H_2O$ and ligand mbbimb in MeOH as indicated in Scheme 1.‡ Single crystals suitable for X-ray analysis§ were obtained by slow evaporation of solvent for **1** and diffusion of $Et_2O$ into the reaction mixture for **2**.

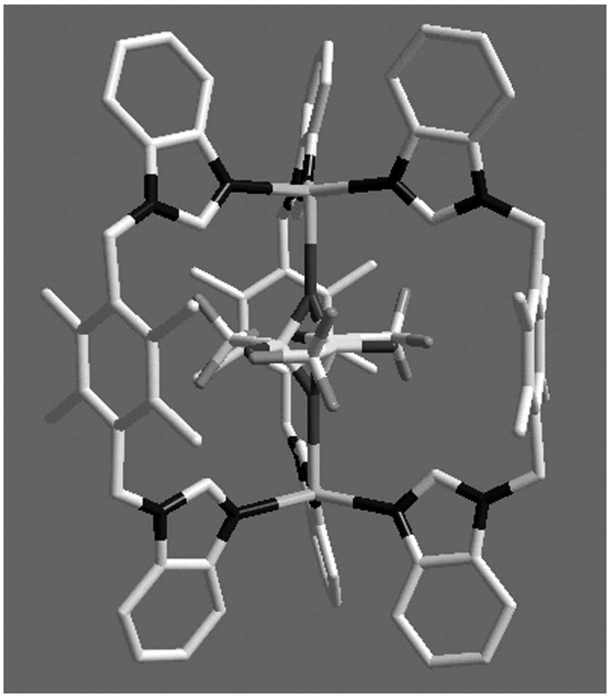

**Fig. 1** Perspective view of the [$Ag_2$(pbbimb)$_3$]$^{2+}$ cationic box.

Single-crystal structural analysis showed that the [$Ag_2$(pbbimb)$_3$]$^{2+}$ cation in **1** is a five-component molecular aggregate consisting of two silver(I) ions and three pbbimb ligands as shown in Fig. 1. Every Ag(I) ion is triangularly coordinated by three imino nitrogen atoms belonging to three $C_3$ symmetrically arranged ligands which adopt a *cis*-conformation with the two benzimidazole rings nearly perpendicular to the base phenyl ring, thus generating a trigonal prism with a triflate anion encapsulated in its center. The $C_3$ axis passes through the two Ag(I) atoms with a perpendicular mirror across the middle point, so that the trigonal box has $S_3$ symmetry. The included triflate anion shows three-fold disorder with two of the oxygen atoms lying in the $C_3$ axis and interacting with the two Ag(I) ions [2.543(3) Å]. The dimensions of the internal cavity may be described by the Ag–Ag separation (7.5 Å) and the edge length of the equilateral triangle (9.7 Å) defined by the centers of the three phenyl rings.

The [$Cu_2$(mbbimb)$_4$]$^{4+}$ cation in **2** is a cationic box as shown in Fig. 2. Four mbbimb ligands adopt a *cis*-conformation to bridge two copper(II) ions, each held by the benzimidazole arms from four different ligands *via* Cu–N coordination to metal ions in a square planar geometry. The base phenyl rings "turn up" to enclose the box within which resides a perchlorate anion. There is a crystallographically imposed $C_4$ axis passing through the two $Cu^{2+}$ ions and a $\sigma_h$ mirror across the center of the molecule, resulting in $S_4$ symmetry of the box. Along the $C_4$ axis the perchlorate anions are arranged alternately inside and outside

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† Electronic supplementary information (ESI) available: a view of the one-dimensional multicompartmental chain in 2 and colour versions of Figs. 1 and 2. See http://www.rsc.org/suppdata/dt/b0/b010118o/

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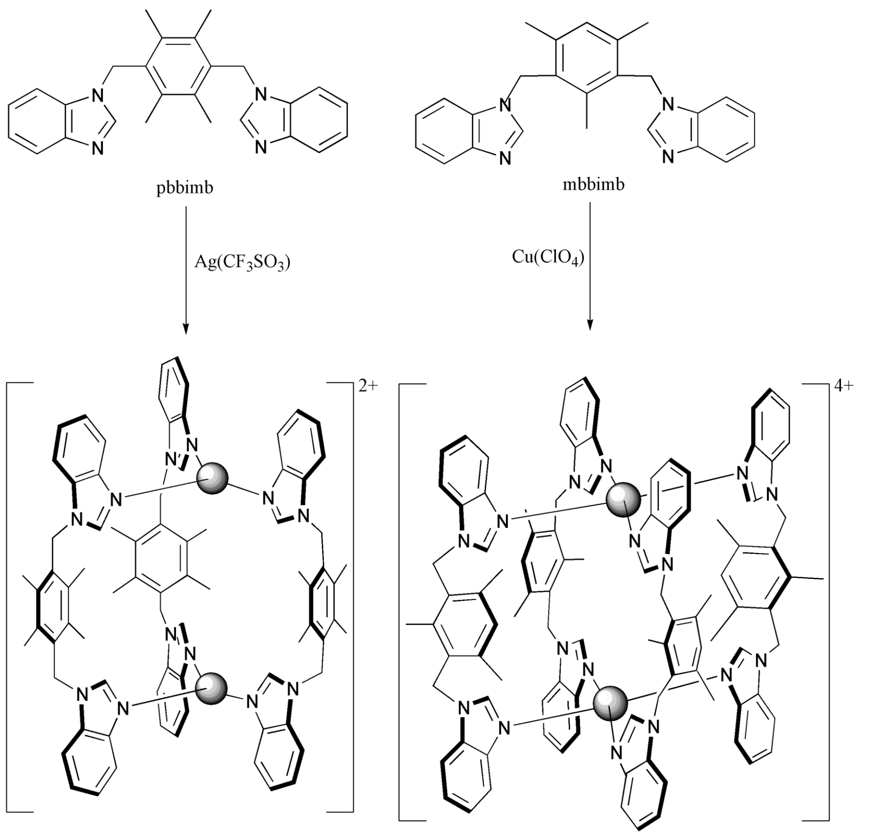

**Scheme 1** Preparation of **1** and **2**.

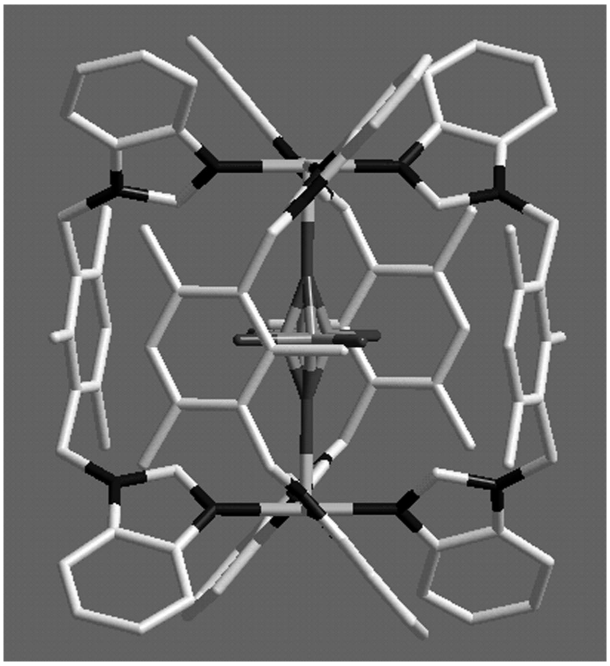

**Fig. 2** Top view of the $[Cu_2(pbbimb)_4]^{4+}$ cationic box showing its tetragonal prismatic shape.

the box, both being four-fold axially disordered around two of the oxygen atoms riding on the axis. These oxygen atoms interact with $Cu^{2+}$ ions (2.388 and 2.659 Å) to generate a one-dimensional multicompartmental column as shown in Fig. S1.† The whole crystal is stacked side-by-side in such columns leaving perchlorate anions located within or between the columns. The intermetallic distance of 7.4 Å and the vertical distance of 10.3 Å between two parallel phenyl rings defines the size of the cavity in the tetragonal box.

The trigonal prism represents the simplest and therefore the smallest three-dimensional molecular architecture.[4a] Its topological criterion is to join two 3-connecting nodes together by three node-to-node connections ($M_2L_3$ or $M_3L_2$), and similarly, that of the tetragonal prism is to link two 4-connecting nodes by four node-to-node connections ($M_2L_4$ or $M_4L_2$).[4a,12] Two strategies can be found to construct the same topology but different compositional molecular architectures. The difference lies in the fact that either the 3- or 4-connecting node is provided by the metal (as in $M_2L_3$ and $M_2L_4$) or by the ligand (as in $M_3L_2$ and $M_4L_2$). Fujita *et al.* have presented NMR and ESI-MS evidence for the presence of the $D_{3h}$ symmetric $M_3L_2$ cage using the tridentate ligand 1,3,5-tris(4-pyridylmethyl)-benzene and $Pd(en)(NO_3)_2$,[13] however, few of the reported $M_2L_3$ complexes with internal cavities have approached the normal trigonal prismatic shape observed in our study.

The most similar complex to **1** is the trigonal gold(I) cage $[Au_2(P_2Phen)_3]^{2+}$ [$P_2Phen$ = 2,9-bis(diphenylphosphino)-1,10-phenanthroline][16] which has $D_3$ symmetry but encapsulates $Tl^+$ or $Na^+$ cations. Another example may be Lehn's eleven-component "molecular cylinder" formed by two flat circular hexaphenylhexaazatriphenylene ligands that form the top and bottom and three bridging tetrapyridine groups as well as six central $Cu^+$ ions.[17] Other cases are usually helical complexes deviating from a regular trigonal prism geometry.[18] On the other hand, while an $M_4L_2$ cage with $D_{4h}$ symmetry has been prepared by Dalcanale and Jacopozzi[14] from two preformed cavitands and four square-planar metal bistriflates, the tetragonal $M_2L_4$ molecular box is scarce. Steel and McMorran have managed to construct a coordinatively saturated quadruply stranded helical cage[19] *via* combination of square-planar palladium ions and 1,4-bis(3-pyridyloxy)benzene ligands. Another $M_2L_4$ molecular box,[20] reported by Steel and O'Keefe is $[Ag_2L_4(NO_3)_2]$ [L = 2,7-bis(2-pyridyloxy)naphthalene] in which only two of the four ligands act as bidentate bridges while the other two are monodentate.

To the best of our knowledge, such $M_2L_3$ and $M_2L_4$ molecular boxes with $S_3$ and $S_4$ symmetry represent the first crystallographically characterized examples most approaching the canonical trigonal and tetragonal prisms in the solid state, respectively. The assembly process is remarkably controlled by the coordination geometries of the metal ions and facilitated by the semi-rigid exobidentate ligands. In contrast to the many molecular hosts capable of recognizing and complexing cationic or neutral guests, encapsulation of anionic molecules is usually difficult, but no less important.[19,21] The M···O interactions may play an important role in the inclusion of anionic guests by these boxes. Further investigation on the inclusion of other guests is currently in progress.

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## Notes and references

‡ Preparation of **1**: To a MeCN (10 mL) solution of silver trifluoromethanesulfonate (0.52 g, 2 mmol) was added a MeOH (10 mL) solution of pbbimb (1.2 g, 3 mmol) and the mixture was stirred for 30 min at room temperatue. After filtration, the filtrate was left standing for several days to produce colorless crystals upon slow evaporation of the solvent. Yield 0.65 g. Found: C, 56.37; H, 4.91; N, 9.84. Anal. calcd. for $C_{80}H_{78}F_6Ag_2N_{12}O_6S_2$: C, 56.61; H, 4.60; N, 9.91%. IR (KBr, $cm^{-1}$): $\nu$ 3119(m), 3046(w), 1618(m), 1431(m), 1251(vs), 1178(s), 1047(s), 810(m), 762(w), 637(m), 576(m), 518(m), 444(w).

Preparation of **2**: Copper(II) perchlorate hexahydrate (0.37 g, 1 mmol) and mbbimb (0.76 g, 2 mmol) were dissolved in 10 mL of methanol. The mixture was stirred for 3 hours at room temperature. After filtration, slow diffusion of diethyl ether into the mixture afforded blue block crystals. Yield 0.90 g. Found: C, 58.54; H, 4.93; N, 11.29. Anal. calcd. for $C_{100}H_{96}Cl_4Cu_2N_{16}O_{16}$: C, 58.65; H, 4.69; N, 10.96%. IR (KBr, $cm^{-1}$): $\nu$ 3122(w), 3067(w), 2974(w), 2916(w), 2869(w), 1612(m), 1524(m), 1462(m), 1402(m), 1325(w), 1294(m), 1240(m), 1191(m), 1087(vs), 1014(w), 924(w), 746(m), 623(m), 479(w), 428(w).

§ Crystal data for **1**: $M = 1697.4$, hexagonal, space group $P6_3/m$, $a = 14.0129(12)$, $c = 23.119(3)$ Å, $U = 3931.5(7)$ Å$^3$, $Z = 2$, $T = 293$ K, crystal size $0.23 \times 0.18 \times 0.02$ mm$^3$, 2247 unique reflections measured, final $R1 = 0.0716$ and $wR2 = 0.1935$ for 1329 observed $[I > 2\sigma(I)]$ reflections.

**2**: $M = 2046.81$, tetragonal, space group $I4/m$, $a = 18.6162(11)$, $c = 16.1840(13)$ Å, $U = 5608.8(7)$ Å$^3$, $Z = 2$, $T = 293$ K, crystal size $0.48 \times 0.17 \times 0.15$ mm$^3$, 2679 unique reflections measured, final $R1 = 0.1070$ and $wR2 = 0.2353$ for 2289 observed $[I > 2\sigma(I)]$ reflections. All anionic molecules are badly disordered in the crystal, partially responsible for relatively high *R* values. CCDC reference number 186/2322. See http://www.rsc.org/suppdata/dt/b0/b010118o/ for crystallographic files in .cif format.

1 (*a*) J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (*b*) M. M. Conn and J. Rebek, Jr., *Chem. Rev.*, 1997, **97**, 1647.

2 (*a*) O. F. Schall and G. W. Gokel, *J. Am. Chem. Soc.*, 1994, **116**, 6089; (*b*) C. M. Drain, R. Fishcher, E. G. Nolen and J.-M. Lehn, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 243; (*c*) K. Kobayashi, T. Shirasaka, K. Yamaguchi, S. Sakamoto, E. Horn and N. Furukawa, *Chem. Commun.*, 2000, 41; (*d*) B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem.*, *Int. Ed. Engl.*, 1988, **27**, 1547; (*e*) V. A. Russell, C. C. Evans, W. Li and M. D. Ward, *Science*, 1997, **276**, 575.

3 (*a*) C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289; (*b*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (*c*) B. Linton and A. D. Hamilton, *Chem. Rev.*, 1997, **97**, 1669; (*d*) J. A. R. Navarro, M. B. L. Janik, E. Freisinger and B. Lippert, *Inorg. Chem.*, 1999, **38**, 426.

4 (*a*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*b*) B. Olenyuk, A. Fechtenkötter and P. J. Stang, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1707.

5 (*a*) C. M. Drain and J.-M. Lehn, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2313; (*b*) A.-K. Duhme, S. C. Davies and D. L. Hughes, *Inorg. Chem.*, 1998, **37**, 5380; (*c*) H. M. Colquhoun, R. A. Fairman, P. Tootell and D. J. Willams, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2651; (*d*) J. Manna, J. A. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1996, **118**, 8731; (*e*) P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel and D. Fenske, *Chem. Commun.*, 1997, 2231; (*f*) M. A. Houghton, A. Bilky, M. M. Harding, P. Turner and T. W. Hambley, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2725.

6 N. Takeda, K. Umemoto, K. Yamaguchi and M. Fujita, *Nature*, 1999, **398**, 794.

7 M. Hong, Y. Zhao, W. Su, R. Cao, M. Fijita, Z. Zhou and A. S. C. Chan, *J. Am. Chem. Soc.*, 2000, **122**, 4819.

8 (*a*) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature*, 1999, **398**, 796; (*b*) B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield and P. J. Stang, *J. Am. Chem. Soc.*, 1999, **121**, 10434; (*c*) S. L. James, D. M. P. Mingos, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 2323.

9 (*a*) R. W. Saalfrank, A. Stark, K. Peters and H. G. Von Schnering, *Angew. Chem.*, *Int. Ed. Engl.*, 1988, **27**, 851; (*b*) R. W. Saalfrank, B. Horner, D. Stalke and J. Salbeck, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1197; (*c*) T. Beissel, R. E. Powers and K. N. Raymond, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 1084.

10 (*a*) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **278**, 469; (*b*) C. M. Hartshorn and P. J. Steel, *Chem. Commun.*, 1997, 541.

11 (*a*) S. Roche, C. Haslem, H. Adams, S. L. Heath and J. A. Thomas, *Chem. Commun.*, 1998, 1681; (*b*) K. K. Klausmeyer, T. B. Rauchfuss and S. R. Wilson, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1694; (*c*) J. L. Heinrich, P. A. Berseth and J. R. Long, *Chem. Commun.*, 1998, 1231.

12 B. F. Abrahams, S. J. Egan and R. Robson, *J. Am. Chem. Soc.*, 1999, **121**, 3535.

13 M. Fujita, S. Nagao and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 1649.

14 P. Jacopozzi and E. Dalcanale, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 613.

15 Z. Shi and R. P. Thummel, *J. Org. Chem.*, 1995, **60**, 5935.

16 V. J. Catalano, B. L. Bennett and H. M. Kar, *J. Am. Chem. Soc.*, 1999, **121**, 10235.

17 P. Baxter, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 69.

18 (*a*) M. Albrecht, H. Röttele and P. Burger, *Chem. Eur. J.*, 1996, **2**, 1264; (*b*) M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin and W. Errington, *Chem. Commun.*, 1997, 1807; (*c*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975.

19 D. A. McMorran and P. J. Steel, *Angew. Chem.*, *Int. Ed.*., 1998, **37**, 3295.

20 B. J. O'Keefe and P. J. Steel, *Inorg. Chem. Commun.*, 1998, **1**, 147.

21 R. D. Schnebeck, E. Freising and B. Lippert, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 168.