

# Controlling the Size of an $M_2L_4$ Cage-Like Receptor by Internal Anions

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**Abstract** The X-ray structure of a  $M_2L_4$  anion-encapsulated cage complex  $[Cu_2(bimb)_4Cl]^{3+}$  [ $bimb=1,3$ -bis(imidazol-1-yl)ethyl)-2,4,6-trimethylbenzene] and previous work showed that the Cu...Cu separations of the cages changed from 7.52 Å to 5.53 Å when the anions were altered from  $[CD_4]^-$  to  $Cl^-$ , which indicated that the host-guest interactions between the receptor and encapsulated anions mimic the induced-fit process well.

**Key words** induced-fit process; anion receptor; flexible cage; host-guest chemistry

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## 应用阴离子调控 $M_2L_4$ 型超分子笼体积大小的研究

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**[摘要]**  $M_2L_4$  型超分子笼状配合物  $[Cu_2(bimb)_4Cl]^{3+}$  的单晶结构及以前的工作发现当笼状分子中所包入的阳离子从  $CD_4^+$  换成  $Cl^-$  时, 其 Cu...Cu 距离从 7.52 Å 缩短到 5.53 Å, 表明笼状分子与包入的阴离子之间的主客体相互作用很好地模拟了诱导契合机制。

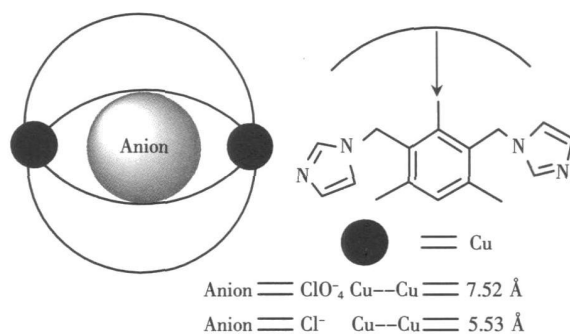
**[关键词]** 诱导契合机制, 阴离子受体, 柔性分子笼, 主客体化学

The biological enzymes can change the shape and size of their recognition sites when reacting with unsuitable substrate molecules, generating the most suitable one to fit their substrates, this phenomenon is named as induced-fit process by Koshland in 1963<sup>[1,2]</sup>. Modeling such a system is very important not only to understand the mechanism of molecular recognition, but also to develop a new receptor design wherein artificial receptors are flexible and capable to recognize guests of different size and shape. Several previous reports, which dealt with the induced-fit control of receptor linkage<sup>[3-8]</sup>, showed that different receptors would be obtained when the different substrates were used. For example, according to Lehn's works<sup>[3,4]</sup>, the reaction of the tris-2,2'-bipyridine ligand with  $Fe(II)$  which gave a pentanuclear circular helicate<sup>[3]</sup> with the  $Cl^-$  as counter anions, while in the case of  $[SO_4]^{2-}$ , a hexanuclear circular helicate was formed. Furthermore, in the case of  $Br^-$ , both of pentanuclear and hexanuclear circular helicates were generated<sup>[4]</sup>. Dunbar<sup>[5,6]</sup> reported that the ring-size of the metallacyclopentane can be tuned by changing the size of anions, molecular squares  $[M_4(bptz)_4]^{8+}$  ( $M: Ni, Zn$ ;  $bptz=3,6$ -bis(2-pyridyl)-1,2,4,5-tetrazine) were formed in high yields with  $[BF_4]^-$  and  $[ClO_4]^-$  anions, while in case of  $[SbF_6]^-$ , a molecular pentagon  $[Ni_5(bptz)_5]^{10+}$  was obtained. Present results showed that the receptors of the same composition would be obtained when the substrates of different size and shape are used, but the size and shape of the receptor are remarkably controlled by the substrates.

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## 1 Results

Self-assembly of the  $\text{M}_2\text{L}_4$  cage-like complexes  $[\text{Cu}_2(\text{bimb})_4\text{Cl}]\text{Cl} \cdot 12\text{H}_2\text{O}$  (1) and  $[\text{Cu}_2(\text{bimb})_4](\text{BF}_4)_4 \cdot 2\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$  (2): Blue block crystals were formed when the dipodal ligand bimb<sup>[9]</sup> reacted with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Cu : bimb ratio of 1 : 2) in ethanol and water, and analyzed elementally as  $[\text{Cu}_2(\text{bimb})_4\text{Cl}]\text{Cl} \cdot 12\text{H}_2\text{O}$  (1). The FAB mass spectrum showed clearly the formation of a peak at  $m/z$  758, which corresponds to the  $[\text{Cu}_2(\text{bimb})_2\text{Cl}_2\text{H}]^+$  species, and a peak at  $m/z$  723, which corresponds to the  $[\text{Cu}_2(\text{bimb})_2\text{CH}_2]^+$  species, respectively. Single crystal X-ray crystallographic analysis showed that it is an  $\text{Cu}_2\text{L}_4$  cage-like complex with a chlorine anion encapsulated in the cage, and the structure is shown in Figure 1. Additional  $\text{Cu} \cdots \text{Cl}$  attached to internal Cl atom locates at a distance of 2.76 Å which augments the coordination polyhedral for the two  $\text{Cu}^{2+}$  cations. Cu atom is coordinated by four N atoms with Cu—N bond length from 1.994 Å to 2.003 Å, and one weak  $\text{Cu} \cdots \text{Cl}$  attached (Cl from internal anion) with a distance of 2.76 Å (Figure 1), adopts a disordered square-pyramidal  $[\text{CuN}_4\text{Cl}]$  geometry. Neglecting the weak Cu—Cl interactions, the coordination geometry for Cu is square  $[\text{CuN}_4]$ . The encapsulated Cl anion is almost in the center of the  $\text{Cu}_2(\text{bimb})_4$  cage, for the distances from Cl atom to the two pairs of co-facial phenyl rings are slightly different, that is 5.87 Å and 5.67 Å, respectively; the dihedral angle between the two pairs co-facial phenyl rings is 72.4°, and the distances of  $\text{Cl} \cdots \text{Cu}1$  and  $\text{Cl} \cdots \text{Cu}2$  are equal (2.76 Å). The height of the cage in 1, namely the distance between the two Cu cations, is 5.53 Å. The four phenyl rings form a parallelogram, with lateral lengths of 8.91 Å and 7.32 Å. There are two O—H  $\cdots$  Cl hydrogen bonds between the internal chlorine anion and two internal water molecules with the same O  $\cdots$  Cl distance of 3.22 Å.

Similar procedure is used to study the reaction of  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Cu}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$  with bimb. When the bimb reacted with  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  in ethanol aqueous solution, purple crystals  $[\text{Cu}_2(\text{bimb})_4](\text{BF}_4)_4 \cdot 2\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$  (2) are formed immediately, which is further confirmed by the elemental analysis. However, the single crystals are not suitable for X-ray crystallographic analysis.

## 2 Discussion and Conclusion

Previous works<sup>[10-11]</sup> showed that reaction of  $\text{Pd}(\text{CH}_3\text{CN})_4\text{Cl}_2$  or  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with dipodal ligand bimb at M : L ratio of 1 : 2 led to  $\text{M}_2\text{L}_4$  cage-like complexes  $[\text{Pd}_2(\text{bimb})_4]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}_2(\text{bimb})_4](\text{ClO}_4)_4 \cdot (\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$  (3); the only difference of the above two complexes is that there are no anion guest in the Pd cage, but a  $[\text{ClO}_4]^-$  anion encapsulated within the cage complex 3. The results presented here showed that the reactions of  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$  and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with bimb at molar ratio of 1 : 2 also form two dinuclear complexes  $[\text{Cu}_2(\text{bimb})_4\text{Cl}]\text{Cl} \cdot 12\text{H}_2\text{O}$  (1) and  $[\text{Cu}_2(\text{bimb})_4](\text{BF}_4)_2(\text{OH}) \cdot 2\text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$  (2), and the molecular formulae were confirmed by FAB-mass spectra and elemental analyses. X-ray structure analysis showed that complex 1 is also a  $\text{M}_2\text{L}_4$  cage. Each bimb ligand is in a cis-cis-conformation and attaches to two copper(II) atoms with its two imidazolyl arms, and each copper(II) atom is of square-planar geometry coordinated by four bimb ligands, thus a  $\text{Cu}_2\text{L}_4$  cage was formed by two copper(II) at-

ons and four bimb ligands (Figure 1). Looked down the Cu—Cu axis, this  $M_2L_4$  cage is like a paddlewheel (Figure 1a).

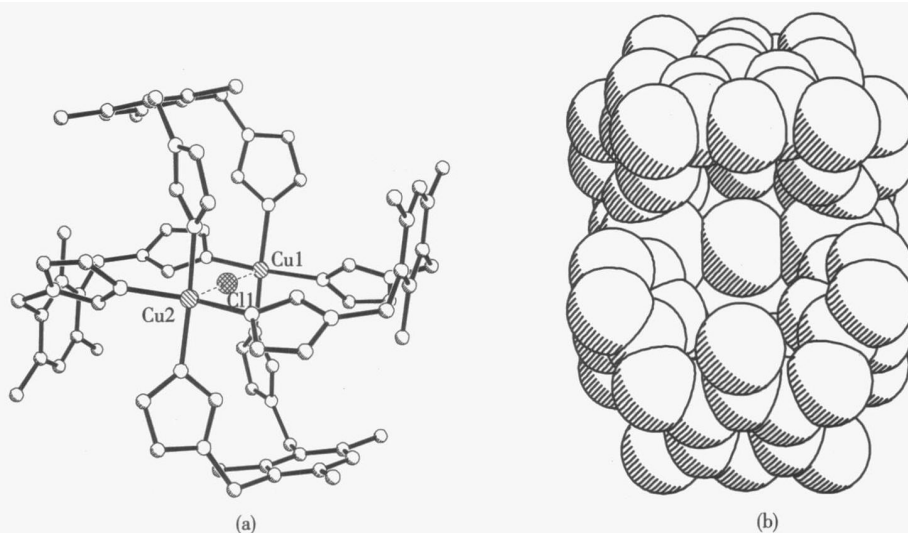


Fig.1 Crystal structure of 1. (a) Molecular structure of the  $Cu_2L_4$  cage and its encapsulated  $Cl^-$  anion (down the Cu—Cu axis). The hydrogen atoms, three other  $Cl^-$  anions and water molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Cu—N 1.994(5) ~ 2.003(5), N—Cu—N 88.1(2) ~ 90.4(2) / 162.4(2) ~ 172.7(2), N—Cu—Cl 93.32(18) ~ 99.16(17), Cu—Cl—Cu 180.00(11); Cu1 ... Cu2 5.53, Cu—Cl 2.76. (b) Space-filling diagram of the cage with the encapsulated anion (side view)

It is interesting that an anion is encapsulated in each cage. While in complex 1, a spherical  $Cl^-$  anion is encapsulated, external to the cage are three other  $Cl^-$  anions (not shown) and 12 water molecules (not shown) (Figure 1). The Cu...Cu separation is 5.53 Å which is slightly longer than that in  $Pd_3bimb_4$  twin-cage<sup>[9]</sup> (5.1 Å) and the dimension of the cage is 5.53 × 10.90 × 10.85 Å<sup>3</sup>. The Cu...Cu separation is 7.49 Å which is slightly shorter than that in  $Cu_2bimb_4$  cage 3 in which a  $[CD_4]^-$  is encapsulated<sup>[11]</sup> and the dimension of the cage is 7.49 × 10.45 × 10.42 Å<sup>3</sup>.

As shown in scheme 1, reactions of the flexible ditopic ligand 1, 3-bis(4-methyl-1-ylmethyl)-2,4,6-trimethylbenzene (bimb)<sup>[9]</sup> with Cu(II) give the same  $Cu_2L_4$  cage when the counter anion altered from  $[ClO_4]^-$  to  $Cl^-$  and in each cage an anion is encapsulated. The Cu...Cu separations of this receptor are shortened more than 26% when the anions are changed from tetrahedral  $[ClO_4]^-$  to spherical  $Cl^-$ , from 7.52 to 5.53 Å. Considering the size and the shape parameters of three anions:  $Cl^-$  with radius of 1.80 Å, 2.08 Å and 2.24 Å for  $[ClO_4]^-$  and  $[BF_4]^-$ , respectively, the host-guest interactions between this flexible cage receptor and encapsulated anions mimic the induced-fit process well. The results described here represent one of important goals in the field of molecular recognition.

The results described here not only mimic the induced-fit process well but also showed that this anion-encapsulated  $Cu_2L_4$  cage receptor can selectively “recognize” substrates of different size and shape, although this phenomenon was observed only in the solid state.

### 3 Experimental Section

**Caution:** perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled carefully.

**Physical Measurements:** Solvents such as acetonitrile and methanol were dried and purified by distillation before use. Other reagents were commercially available and used as received without further purification. The ligand bimb (bimb = 1, 3-bis(4-methyl-1-ylmethyl)-2,4,6-trimethylbenzene) was prepared according to the literature methods<sup>[9]</sup>. Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer. Infrared (IR) spectra were recorded on a Nicolet FT-IR 170SX spectrophotometer using KBr disks. Fast atom bombard-

(FAB) mass spectra were measured on a VG ZAB-MS instrument

4 Assembly of Cage Complexes

Synthesis of  $[\text{Cu}_2(\text{bimb})_4]\text{Cl} \cdot 12\text{H}_2\text{O}$  (1): A solution of bimb (28 mg 0.1 mmol) in ethanol solution (5 mL) was added to an aqueous solution (5 mL) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (9 mg 0.05 mmol) at room temperature with stirring. Standing the deep blue filtrate at room temperature for about two weeks results in the cubic blue crystals, yield 27 mg (73%). Found C, 50.81; H, 6.47; N, 13.88%. Calcd for  $\text{C}_{68}\text{H}_{104}\text{N}_{16}\text{ClO}_{12}\text{Cu}_2$  ( $[\text{Cu}_2(\text{bimb})_4\text{Cl}]\text{Cl} \cdot 12\text{H}_2\text{O}$ ,  $M_{\text{calcd}} = 1606.58$ ): C, 50.83; H, 6.52; N, 13.94%. FAB-MS Found  $m/z$  758. Calcd for  $[\text{Cu}_2(\text{bimb})_2\text{ClH}]^+$ : 759.  $m/z$  723. Calcd for  $[\text{Cu}_2(\text{bimb})_2\text{CH}_2]^+$ : 725.

Synthesis of  $[\text{Cu}_2(\text{bimb})_4](\text{BF}_4)_4 \cdot 2\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$  (2): A solution of bimb (28 mg 0.1 mmol) in ethanol solution (5 mL) was added to an acetonitrile solution (10 mL) of  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (17 mg 0.05 mmol) at room temperature with stirring. Standing the purple filtrate at room temperature for about a week resulted in the formation of purple crystals, yield 82%. Found C, 48.53; H, 5.63; N, 12.90%. Calcd for  $\text{C}_{70}\text{H}_{96}\text{N}_{16}\text{B}_4\text{F}_{16}\text{O}_6\text{Cu}_2$  ( $[\text{Cu}_2(\text{bimb})_4](\text{BF}_4)_4 \cdot 2\text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ ,  $M_{\text{calcd}} = 1731.94$ ): C, 48.54; H, 5.59; N, 12.95%.  $\nu = 1084\text{ cm}^{-1}$  (B-F).

Crystallography. Crystals of complex 1 was mounted on a Bruker CCD diffractometer with graphite-monochromated  $\text{Mo-K}\alpha$  ( $\lambda = 0.71073\text{ \AA}$ ) radiation and the intensity data were collected at room temperature. All absorption corrections were performed using the SADABS program. The structure was solved by the direct methods (SHELXS) and refined by the full-matrix least-squares method against  $F_o^2$  (SHELXL-97). All non-hydrogen atoms were refined anisotropically whereas the hydrogen atoms were generated geometrically.

Details of the crystal parameters, data collection and refinement for 1 is listed in Table 1, and selected bond length and angles in Table 2.

Table 1 Summary of crystal data and refinement results for complex 1

	1
formula	$\text{C}_{68}\text{H}_{104}\text{N}_{16}\text{Cl}_4\text{O}_{12}\text{Cu}_2$
$M_r$	1606.58
crystal size [mm]	$0.35 \times 0.28 \times 0.24$
crystal system	monoclinic
space group	$P-1$
$a$ [ $\text{\AA}$ ]	13.053(3)
$b$ [ $\text{\AA}$ ]	14.353(3)
$c$ [ $\text{\AA}$ ]	14.399(3)
$\alpha$ [ $^\circ$ ]	93.59(3)
$\beta$ [ $^\circ$ ]	115.84(3)
$\gamma$ [ $^\circ$ ]	106.98(3)
$V$ [ $\text{\AA}^3$ ]	2264.9(8)
$Z$	1
$\rho_{\text{calcd}}$ [ $\text{g cm}^{-3}$ ]	1.359
$2\theta_{\text{max}}$	$49.42^\circ$
$\mu$ [ $\text{mm}^{-1}$ ]	1.108
$T$ [K]	293(2)
reflections collected	8962
unique reflections	7068
observed reflections	4138
parameters	454
GOF on $F^2$	1.093
$R_1$	0.0995
$R_w$	0.2886
$R_1$ [ $> 2s(I)$ ]	0.1399
$wR_2$ [ $> 2s(I)$ ]	0.3188
$\Delta\rho_{\text{min/max}}$ [ $\text{e \AA}^{-3}$ ]	1.449 / -0.492

Table 2 Selected bond length [ Å ] and angles [ Å ] of complex 1

Cu <sub>2</sub> ( bim b ) <sub>4</sub> Cl <sub>4</sub> • 12 H <sub>2</sub> O ( 1 )			
Cu1 – N11	1. 994( 5)	Cu1 – N7	2. 000( 5)
Cu1– N4	2. 000( 6)	Cu1 – N6	2. 003( 5)
Cu1 – C II	2. 765( 12)	N11– Cu1– N4	162. 4( 2)
N11– Cu1– N7	89. 3( 2)	N11– Cu1– N6	89. 9( 2)
N7– Cu1– N4	90. 4( 2)	N4– Cu1– N6	88. 1( 2)
N7– Cu1– N6	172. 7( 2)	N11 – Cu1– C II	99. 16( 17)
N7– Cu1– C II	93. 32( 18)	N4– Cu1– C II	98. 42( 17)
N6– Cu1– C II	93. 95( 18)	Cu1 – Cu2	5. 53

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