

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 $[Cu_2(\text{bimb})_4Cl]^{3+}$ [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

CLC number O61 **Document code** A **Article ID** 1001-4616(2009)01-0074-05

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 $[Cu_2(\text{bimb})_4Cl]^{3+}$ 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。

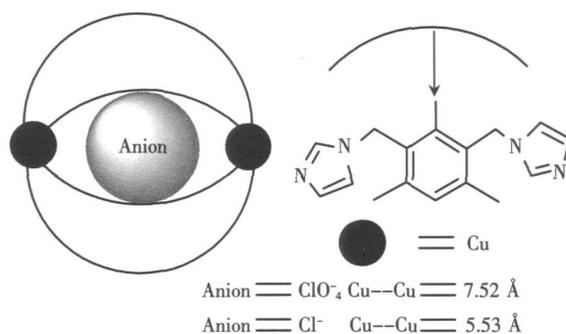
[关键词] 诱导契合机制, 阴离子受体, 柔性分子笼, 主客体化学

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^[1,2]. 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^[3-8], showed that different receptors would be obtained when the different substrates were used. For example, according to Lehn's works^[3,4], the reaction of the tris-2,2'-bipyridine ligand with $Fe(II)$ which gave a pentanuclear circular helicate^[3] 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^[4]. Dunbar^[5,6] reported that the ring-size of the metallacyclopentane can be tuned by changing the size of anions, molecular squares $[M_4(\text{bptz})_4]^{8+}$ (M: Ni, Zn; bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine) were formed in high yields with $[BF_4]^-$ and $[CD_4]^-$ anions, while in case of $[SbF_6]^-$, a molecular pentagon $[Ni_5(\text{bptz})_5]^{10+}$ 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.

Received date 2008-04-15.

Foundation item: Supported by the National Natural Science Foundation of China (20871069), Natural Science Foundation of Jiangsu Province (BK2008428), and Fund of State Key Laboratory of Coordination Chemistry.

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1 Results

Self-assembly of the M_2L_4 cage-like complexes $[Cu_2(bimb)_4Cl]Cl \cdot 12H_2O$ (1) and $[Cu_2(bimb)_4](BF_4)_4 \cdot 2CH_3OH \cdot 4H_2O$ (2): Blue block crystals were formed when the dipodal ligand *bimb*^[9] reacted with $CuCl_2 \cdot 2H_2O$ (Cu : *bimb* ratio of 1 : 2) in ethanol and water, and analyzed elementally as $[Cu_2(bimb)_4Cl]Cl \cdot 12H_2O$ (1). The FAB mass spectrum showed clearly the formation of a peak at m/z 758, which corresponds to the $[Cu_2(bimb)_2ClH]^+$ species, and a peak at m/z 723, which corresponds to the $[Cu_2(bimb)_2CH_2]^+$ species, respectively. Single crystal X-ray crystallographic analysis showed that it is an Cu_2L_4 cage-like complex with a chlorine anion encapsulated in the cage, and the structure is shown in Figure 1. Additional Cu...Cl attached to internal Cl atom locates at a distance of 2.76 Å which augments the coordination polyhedral for the two 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 Cu...Cl attached (Cl from internal anion) with a distance of 2.76 Å (Figure 1), adopts a disordered square-pyramidal $[CuN_4Cl]$ geometry. Neglecting the weak Cu—Cl interactions, the coordination geometry for Cu is square $[CuN_4]$. The encapsulated Cl anion is almost in the center of the $Cu_2(bimb)_4$ 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 Cl...Cu1 and Cl...Cu2 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...Cl hydrogen bonds between the internal chlorine anion and two internal water molecules with the same O...Cl distance of 3.22 Å.

Similar procedure is used to study the reaction of $Cu(BF_4)_2 \cdot 6H_2O$ or $Cu(CH_3CN)_4(BF_4)_4$ with *bimb*. When the *bimb* reacted with $Cu(BF_4)_2 \cdot 6H_2O$ in ethanol aqueous solution, purple crystals $[Cu_2(bimb)_4](BF_4)_4 \cdot 2CH_3OH \cdot 4H_2O$ (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^[10, 11] showed that reaction of $Pd(CH_3CN)_4Cl_2$ or $Cu(ClO_4)_2 \cdot 6H_2O$ with dipodal ligand *bimb* at M : L ratio of 1 : 2 led to M_2L_4 cage-like complexes $[Pd_2(bimb)_4]Cl_2 \cdot 2H_2O$ and $[Cu_2(bimb)_4](ClO_4)_3 \cdot H_2O$ (3); the only difference of the above two complexes is that there are no anion guest in the Pd cage, but a $[ClO_4]^-$ anion encapsulated within the cage complex 3. The results presented here showed that the reactions of $Cu(BF_4)_2 \cdot 6H_2O$, $Cu(CH_3CN)_4(BF_4)_4$ and $CuCl_2 \cdot 2H_2O$ with *bimb* at molar ratio of 1 : 2 also form two dinuclear complexes $[Cu_2(bimb)_4Cl]Cl \cdot 12H_2O$ (1) and $[Cu_2(bimb)_4](BF_4)_2(OH) \cdot 2CH_3OH \cdot 3H_2O$ (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 M_2L_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 Cu_2L_4 cage was formed by two copper(II) at-

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

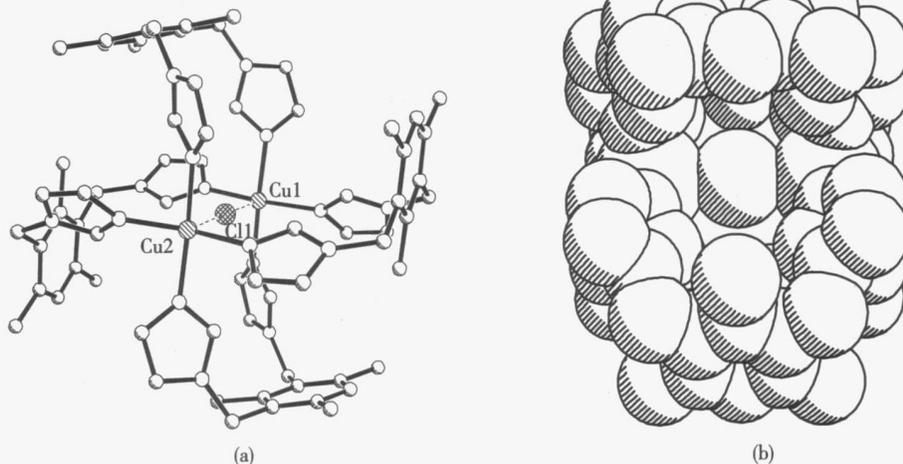


Fig.1 Crystal structure of 1. (a) Molecular structure of the Cu_2L_4 cage and its encapsulated Cl^- anion (down the Cu - Cu axis). The hydrogen atoms, three other Cl^- anions and water molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Cu-N 1.994(5) ~ 2.003(5), N-Cu-N 88.1(2) ~ 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^[9] (5.1 Å) and the dimension of the cage is 5.53 × 10.90 × 10.85 Å³. 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^[11] and the dimension of the cage is 7.49 × 10.45 × 10.42 Å³.

As shown in scheme 1, reactions of the flexible ditopic ligand 1, 3-bis(methylamino)-2,4,6-trimethylbenzene (bimb)^[9] 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(methylamino)-2,4,6-trimethylbenzene) was prepared according to the literature methods^[9]. 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 bombardment

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

4 Assembly of Cage Complexes

Synthesis of [Cu₂(bimb)₄]Cl₄ · 12H₂O (1): A solution of bimb (28 mg 0.1 mmol) in ethanol solution (5 mL) was added to an aqueous solution (5 mL) of CuCl₂ · 2H₂O (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 C₆₈H₁₀₄N₁₆Cl₄O₁₂Cu₂ ([Cu₂(bimb)₄]Cl₄ · 12H₂O, *M*_{calcd} = 1606.58): C, 50.83; H, 6.52; N, 13.94%. FAB-MS Found *m/z* 758. Calcd for [Cu₂(bimb)₂Cl₄H]⁺: 759. *m/z* 723. Calcd for [Cu₂(bimb)₂CH₂]⁺: 725.

Synthesis of [Cu₂(bimb)₄](BF₄)₄ · 2CH₃OH · 4H₂O (2): A solution of bimb (28 mg 0.1 mmol) in ethanol solution (5 mL) was added to an acetonitrile solution (10 mL) of Cu(BF₄)₂ · 6H₂O (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 C₇₀H₉₆N₁₆B₄F₁₆O₆Cu₂ ([Cu₂(bimb)₄](BF₄)₄ · 2CH₃OH · 4H₂O, *M*_{calcd} = 1731.94): C, 48.54; H, 5.59; N, 12.95%. *v* = 1084 cm⁻¹ (B-F).

Crystallography. Crystals of complex 1 was mounted on a Bruker CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) 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*_o² (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	C ₆₈ H ₁₀₄ N ₁₆ Cl ₄ O ₁₂ Cu ₂
<i>M</i> _r	1606.58
crystal size [mm]	0.35 × 0.28 × 0.24
crystal system	monoclinic
space group	P-1
<i>a</i> [Å]	13.053(3)
<i>b</i> [Å]	14.353(3)
<i>c</i> [Å]	14.399(3)
α [°]	93.59(3)
β [°]	115.84(3)
γ [°]	106.98(3)
<i>V</i> [Å ³]	2264.9(8)
<i>Z</i>	1
ρ _{calcd} [g cm ⁻³]	1.359
2θ _{max}	49.42°
μ [mm ⁻¹]	1.108
<i>T</i> [K]	293(2)
reflections collected	8962
unique reflections	7068
observed reflections	4138
parameters	454
GOF on <i>F</i> ²	1.093
<i>R</i> ₁	0.0995
<i>R</i> _w	0.2886
<i>R</i> ₁ [I > 2σ(I)]	0.1399
<i>wR</i> ₂ [I > 2σ(I)]	0.3188
Δρ _{min} /max [e Å ⁻³]	1.449 / -0.492

Table 2 Selected bond length [\AA] and angles [$^\circ$] of complex 1

$\text{Cu}_2(\text{bim b})_4\text{Cl}_4 \cdot 12\text{H}_2\text{O} (1)$			
Cu1-N11	1.994(5)	Cu1-N7	2.000(5)
Cu1-N4	2.000(6)	Cu1-N6	2.003(5)
Cu1-Cl	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-Cl	99.16(17)
N7-Cu1-Cl	93.32(18)	N4-Cu1-Cl	98.42(17)
N6-Cu1-Cl	93.95(18)	Cu1-Cu2	5.53

5 Acknowledgment

We thank the Fund of Talent Scientists (HL) and Undergraduate Research Training Programs of Nanjing Normal University for their support for this work.

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