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[$Cu(C_{24}H_{22}N_4O_3)$]·CH_2Cl_2: A Discrete Breathing Metallamacrocycle Showing Selective and Reversible Guest Adsorption with Retention of Single Crystallinity

Yu-Bin Dong,* Qiang Zhang, Li-Li Liu, Jian-Ping Ma, Bo Tang,* and Ru-Qi Huang

College of Chemistry, Chemical Engineering and Materials Science, Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Shandong Normal University, Jinan 250014, P.R. China

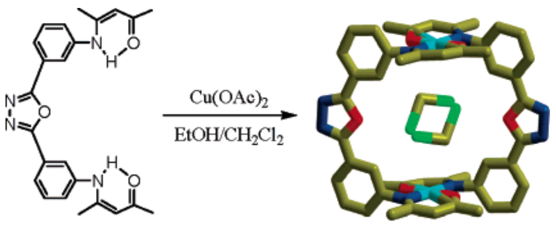
Received October 14, 2006; E-mail: yubindong@sdnu.edu.cn

The design and synthesis of discrete molecular metallamacrocyclic rings or cages with differently sized and shaped cavities capable of encapsulating guest moieties has attracted much recent interest.[1] Such materials have great application potential for separation processes, recognition, catalysis, and sensor technologies. During the past decades, numerous synthetic host−guest systems potentially useful as selective capsules for molecular recognition and separation have come into being.[2] Compared to polymeric metal−organic framework materials which are able to retain their single crystallinity after chemical reaction, guest exchange, temperature change, or some other physical stimulus,[3] exploration into single-crystallinity-maintained discrete metallamacrocycles is rarer. To date, single-crystallinity-maintained discrete metallamacrocycles which can both shrink and swell in response to different sizes, shapes, and numbers of guests have, to our knowledge, never been described. A few metallamacrocycles which can retain single crystallinity after solid-state photoreaction have appeared in the literature very recently.[4] The scarcity of such systems is probably due to inherent difficulties in harmonizing the subtle relationship between "robustness" and "flexibility" in discrete macrocyclic coordination complexes.

As we know, discrete metallamacrocycles may be synthesized on the basis of a rational ligand-directed approach.[5] We have recently designed and synthesized a series of bent oxadiazole and triazole bridging spacers which are end-capped by pyridine, phenylamine, or benzonitrile for construction of coordination polymers.[6] Considering the bent geometry of such spacers, we wondered if these ligands could be used as "organic clips"[5] to bind transition metal ions into neutral bimetallic macrorings or cages. In this contribution, we report a neutral, breathing binuclear Cu(II) macrocyclic host $Cu_2\mathbf{L}_2$ based on a new bent organic ligand **LH** which can adapt itself to different guests at ambient temperature while retaining single crystallinity.

As shown in Scheme 1, metalation of **LH** with $Cu(OAc)_2$ in an EtOH/CH_2Cl_2 mixed-solvent system at room temperature afforded the neutral metallamacrocycle $Cu_2\mathbf{L}_2$·$2CH_2Cl_2$ in high yield (Supporting information). The single-crystal structure[7] (Figure S1) of **1** revealed that two deprotonated **LH** ligands act as the desired organic clips to bind two square-coordinated Cu(II) ions through two pairs of terminal N/O chelating sites into a novel neutral bimetallic distorted rectangular cage. As shown in Figure 1, the opposite Cu···Cu and $O_{oxadiazole}$···$O_{oxadiazole}$ distances in the cage are 8.1 and 8.6 Å, respectively. A side view of **1** reveals that the two parallel bridging 2,5-bis (3-phenyl)-1,3,4-oxadiazole ridges are offset by ~3.9 Å along the direction perpendicular to the ring plane. The other two sides of the rectangular cage are effectively closed by the two planar Schiff-base Cu(II) moieties. Two CH_2Cl_2 guest molecules are trapped inside the cage through weak C−H···Cl interactions (Figure S2). Thermogravimetry (TGA) revealed that the two CH_2Cl_2 guests could be sequentially removed in the temperature ranges of 34−126 °C and 252−297 °C, respectively (Figure S2). Single crystals of **1** lose crystallinity after loss of the second CH_2Cl_2 guest. In the solid state, the $Cu_2\mathbf{L}_2$ macrorings arrange in an ABAB fashion along the crystallographic^{011} direction to generate channels containing the guest columns (Figures 1 and S3).

Scheme 1. Synthesis of $Cu_2\mathbf{L}_2$ Macrocycle



LH **1**

Remarkably, compound **1** retains its single crystallinity after guest loss and even after exchange of different guests. When a single crystal of **1** was allowed to stand in air for 3 days at room temperature, the transparent crystal $Cu_2\mathbf{L}_2$·CH_2Cl_2 (**2**) was produced (Figure 2). The single-crystal structure revealed that one of the two CH_2Cl_2 guests escaped and the remaining one moved by ~1.8 Å from the edge to the center of the ring with a rotation along the Cu···Cu axis. There is an interesting change in the unit cell parameters upon the removal of one CH_2Cl_2 guest. The cell volume decreases by 4.9% but does so in an anisotropic way. The shorter *a*-axis expands, while the long *b*- and *c*-axes contract. Upon exposure of the desolvated sample of **2** to CH_2Cl_2 vapor for 3 days at room temperature, the X-ray single-crystal analysis indicated that the escaped CH_2Cl_2 came back and the structure of **1** was regenerated. Interestingly, when a single crystal of **1** was exposed to $CHCl_3$ vapor for about 3 days, both CH_2Cl_2 guests in **1** were replaced by two $CHCl_3$ molecules, generating a new host−guest system $Cu_2\mathbf{L}_2$·$2CHCl_3$ (**3**). In addition, **3** could also be obtained

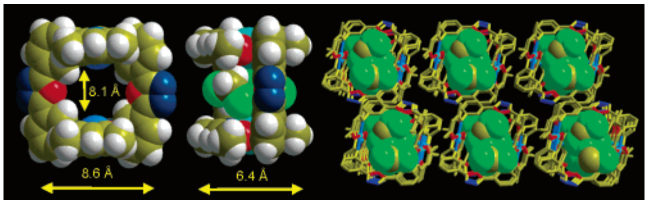


Figure 1. Top (left) and side (middle) views of the neutral Cu(II)-bimetallic macroring in space-filling mode. The CH_2Cl_2 guest molecules are omitted for clarity in the left view. The crystal packing of **1** is shown in the right view. (The guest molecules are shown in space-filling mode.)

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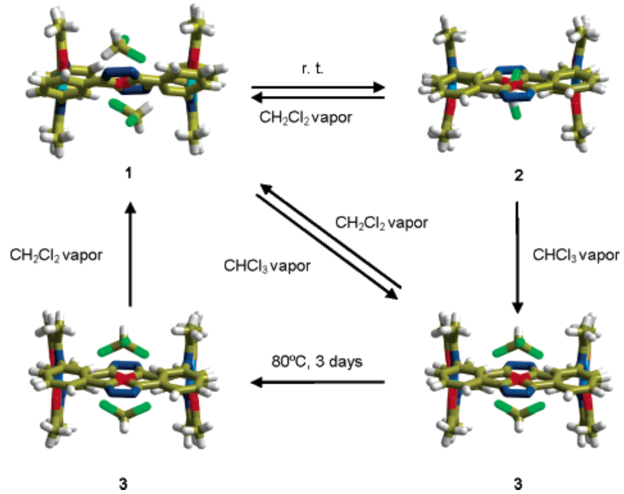

Figure 2. Stick representation of the guest exchange between **1**−**3**.

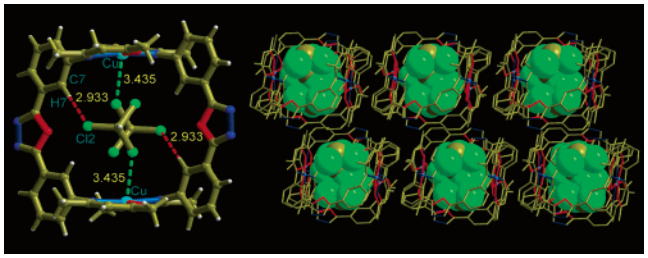

Figure 3. Stick representation of **3** encapsulating CHCl$_3$ guests (left) and its solid-state arrangement (right). The guest molecules are shown in space-filling mode.

by exposure of **2** to CHCl$_3$ vapor for 3 days. From **2** to **3**, the cell volume increases as expected upon increasing the guest size and number. The unit cell volume increases by 6.8%. As shown in Figure 2, the two CHCl$_3$ molecules are well ordered and symmetrically fixed in this molecular saddle by C−H···Cl ($d_{\mathrm{C\cdots Cl}}$ = 3.8 Å and ∠C−H···Cl = 161°) hydrogen bonds. In addition, these two CHCl$_3$ molecules weakly coordinate to the Cu(II) centers with a long Cu···Cl contact distance of 3.435 Å, less than the sum of the van der Waals radii of Cu and Cl (3.7 Å) (Figure 3). The crystal packing of **3** is the same as that in **1** and **2** (Figures 3 and S3). The CHCl$_3$ guest molecules in crystals of **3** cannot be removed even by heating at 80 °C in air for 3 days. The TGA curve of **3** (Figure S4) indicates the release of the CHCl$_3$ guest molecules around 100 °C, accompanied by loss of single crystallinity. It is noteworthy that the two CHCl$_3$ molecules in **3** can be replaced by CH$_2$Cl$_2$ molecules again by exposure of single-crystalline **3** to CH$_2$Cl$_2$ vapor for 3 days, which is confirmed by the X-ray single-crystal analysis completely (Figure 2). Thus, the Cu$_2$**L**$_2$ herein is a robust and reversible, sponge-like, dynamic framework which can shrink and expand in response to guest molecules of different size, shape, and number.

We measured the adsorption properties of single-crystalline **1** with different guest molecules to study its selectivity for other adsorbates. After exposure of a single crystal of **1** to CCl$_4$, THF, ClCH$_2$CH$_2$Cl vapor, or CO$_2$ gas for about two weeks, crystal-structure determinations revealed no degradation of crystal quality, and that no corresponding guests were encapsulated. However, one of the two CH$_2$Cl$_2$ molecules in **1** was lost, generating **2**. This indicates that the Cu$_2$**L**$_2$ host system can recognize CH$_2$Cl$_2$ guests among these common organic and gas molecules. We also examined the selective adsorption of single crystals of **1** with CH$_2$Cl$_2$ and CHCl$_3$ guests. When crystals of **1** or **3** were exposed to a mixed CH$_2$Cl$_2$/CHCl$_3$ vapor (molar ratio 1:1) for about 3 days, single-crystal structure analysis indicated that only CHCl$_3$ molecules were selectively adsorbed. Thus, compound **1** exhibits a significant affinity to CHCl$_3$ guests. Because all the guest-exchange processes are carried out in the presence of solvent vapors or gas, we believe that no dissolution of the complexes occurs.

In summary, we have synthesized an unusual Cu$_2$**L**$_2$ cage-like host complex whose framework can "breathe"[8] without bond cleavage or metal-coordination-mode change. Most importantly, **1** can selectively recognize CH$_2$Cl$_2$ and CHCl$_3$ molecules and adsorb and desorb them depending on their size, shape, and number with retention of single crystallinity. Such a property is definitely important for certain devices. Work is in progress to obtain new discrete macrocyclic and cage-like hosts generated from other bent ligands and transition metals.

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Supporting Information Available: Crystallographic data, synthesis of **L** and **1**, and TGA traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) X-ray data for **1**: Monoclinic, $P2_1/c$, $a = 12.826(3)$, $b = 14.413(3)$, $c = 14.939(3)$ Å, $\beta = 111.948(3)°$, $V = 2561.5(9)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.460$ g/cm^3, R_1 ($I > 2\sigma(I)$) = 0.0603, wR_2 ($I > 2\sigma(I)$) = 0.1773. For **2**: $P2_1/c$, $a = 12.8545(18)$ Å, $b = 14.052(2)$ (11) Å, $c = 14.440(2)$ Å, $\beta = 110.881(2)°$, $V = 2436.9(6)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.419$ g/cm^3, R_1 ($I > 2\sigma(I)$) = 0.0512, wR_2 ($I > 2\sigma(I)$) = 0.1353. For **3**: Monoclinic, $P2_1/c$, $a = 13.045(2)$ Å, $b = 14.520(2)$ Å, $c = 14.917(2)$ Å, $\beta = 112.884(2)°$, $V = 2603.1(7)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.524$ g/cm^3, R_1 ($I > 2\sigma(I)$) = 0.0704, wR_2 ($I > 2\sigma(I)$) = 0.1911.

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