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# New Maze-Type Network Assembled by Copper(II) and 4,4′-Diaminodiphenylmethane: $\{[Cu(C_{13}H_{14}N_2)(C_3H_4O_4)Cl]Cl\}_2$

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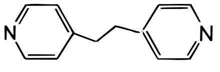
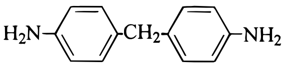
## Introduction

Self-assembly is the most efficient means for construction of highly organized structures.[1,2] Recently, transition metal directed self-assembly via coordination has emerged as a new and major motif in supramolecular architecture.[3] Application of this method to macrocyclization is quite attractive since cyclization of a large molecule by the usual synthetic method is frequently a tedious and low-yield process.[3b−f,4] To date, molecular squares or boxes with unique, well-defined shapes and geometry assembled by transition metals with square-planar geometry (such as Pd and Pt) and rigid ligands have been well studied.[3b−f,4,5] Displacement of this rigid ligand by a flexible one (**1**) caused unfavorable oligomerization rather than cyclization.[4b,5g,6] The high ability of this oligomer for molecular recognition of an electron-rich aromatic guest with high shape specificity is most attractive.[4b,6] While recognition of molecular shapes and functions is becoming an urgent problem both in organic and in inorganic chemistry, structural design or modification of the framework is still a challenge for various guest molecules, especially for low-symmetry guest molecules. This idea prompts us to choose new connector ligands with different flexibilities, electron properties, and shapes and transition metals with different coordination geometries to construct new macrocyclic molecules. Previous strategies of assembling macrocycles were mostly focused on using oligopyridines as connector ligands.[4−6] Displacement of oligopyridine by oligoaniline should lead to new structural motifs and new topologies. Here, we report a new macrocycle assembled from 4,4′-diaminodiphenylmethane (**2**) and pentacoordinated Cu(II) ions. To the best of our knowledge, this is the first example of supramolecular architecture constructed by bidentate oligoanilines. An attractive two-dimensional steric maze-type network was constructed by distorted macrocycle units through hydrogen bonds,[7] and two-dimensional network layers stacked a parallel packing also via hydrogen bonds, revealing an ever-increasing variety of framework compositions and topologies.



**1**



**2**

## Experimental Section

**Materials and Methods.** All starting materials were purchased from Aldrich or other companies and were used without further purification. Elemental analyses were carried out by Structure Research Laboratory, University of Science and Technology of China. A crystal of approximate dimensions 0.30 × 0.40 × 0.50 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS-II imaging plate area detector with graphite-monochromated Mo Kα radiation. Scattering factors were taken from Cromer and Waber. The $\omega-2\theta$ scan mode with a maximum $2\theta$ value of 50° was used to collect intensity data. A total of 2950 reflections were collected, of which 2656 had $I > 3\sigma(I)$ with 227 parameters. The data were corrected for Lorentz−polarization effects. The structure was solved by direct methods using SIR92, expanded using Fourier techniques, and refined by full-matrix least-squares calculations. The non-hydrogen atoms were refined. Hydrogen atoms were included, but their positions were not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Final $R = 0.089$, $R_w = 0.126$, goodness of fit = 5.26, max. shift/esd = 0.02. Crystal data are listed in Table 1.

**$\{[Cu(CH_2(C_6H_4NH_2)_2)(CH_2(COOH)_2)Cl]Cl\}_2$ (3).** To an aqueous solution of $CuCl_2$ (134.5 mg, 1 mmol) and malonic acid (104 mg, 1 mmol) was added an alcohol solution of 4,4′-diaminodiphenylmethane (198 mg, 1 mmol) at room temperature with stirring. The pH value was adjusted to 4.5 by using dilute NaOH and HCl solutions. The mixture was allowed to stand for several days, and the dark blue cubic crystals were isolated to yield 261 mg (0.6 mmol, 60% based on Cu). Anal. Calcd for $C_{16}H_{18}N_2O_4Cl_2Cu$: C, 43.99; H, 4.19; N, 6.41. Found.

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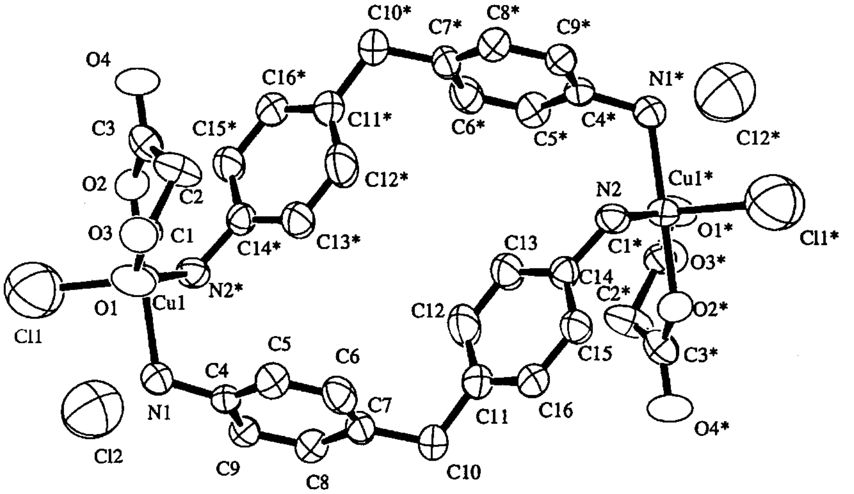

**Figure 1.** ORTEP diagram of **3** with 50% ellipsoids and labeling scheme. Selected bond lengths (Å) and angles (deg): Cu1−Cl1 2.313(5), Cu1−O1 1.960(5), Cu1−O2 1.938(5), Cu1−N1 2.023(6), Cu1−N2* 2.087(5), O1−C1 1.279(9), O2−C3 1.272(9), O3−C1 1.225(8), O4−C3 1.234(9), N1−C4 1.457(8), N2−C14 1.467(10), Cl1−Cu1−O1 101.0(2), Cl1−Cu1−O2 87.6(2), Cl1−Cu1−N1 93.5(2), Cl1−Cu1−N2* 101.7(2), O1−Cu1−O2 92.6(2), O1−Cu1−N1 86.8(2), O1−Cu1−N2* 157.3(2), O2−Cu1−N1 178.8(2), O2−Cu1−N2* 87.8(2), N1−Cu1−N2* 92.3(2), Cu1−N1−C4 114.0(4), Cu1−N2*−C14* 114.1(4), C7−C10−C11 114.7(7).

**Table 1.** Crystallographic Data for Complex **3**

| | | | |
|---|---|---|---|
| empirical formula | $C_{16}H_{18}N_2O_4Cl_2Cu$ | fw | 436.78 |
| *a* | 9.834(2) Å | space group | $P2_1/a$ |
| *b* | 11.871(5) Å | *T* | 25 °C |
| *c* | 15.368(8) Å | $\lambda$(Mo Kα) | 0.710 70 Å |
| $\beta$ | 106.833(3)° | $\rho_{calc}$ | 1.689 g cm$^{-3}$ |
| $\mu$ | 16. 07 cm$^{-1}$ | $R[F_o^2 > 2\sigma(F_o^2)]^a$ | 0.089 |
| *V* | 1717.2(10) Å$^3$ | $R_w[F_o^2 > 2\sigma(F_o^2)]^b$ | 0.126 |
| *Z* | 4 | | |

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

C, 44.01; H, 4.25; N, 6.47. Main IR bands for complex **3** were found: 577m, 763m, 814m 863m $\delta$(C═C), $\gamma$(CH); 1087s $\nu$(CN), $\rho(NH_2)$; 1222.6m, 1392m and 1440.3m $\delta$(CH), $\nu$(CN), $\rho(NH_2)$; 1508.1s, 1565.2s, $\nu$(COOH); 1611.6m $\delta(NH_2)$, $\delta$(OH); 2922.6m, 3232.8s, 3302s, 3449.6s, $\nu$(NH), $\nu$(OH). Complex **3** decomposes at 198.3 °C.

## Results and Discussion

Previous strategies of assembling macrocycles were mostly focused on using oligopyridines as connector ligands.[4−6] Displacement of oligopyridine by oligoaniline should lead to new structural motifs and new topologies. Research activities on the use of oligoaniline in the assembly of supramolecular structures are limited by its instability, as it is easily oxidized in aqueous solution and/or in air. Macrocyclic complex **3** was synthesized by carefully controlling the pH value at 4.0−4.5. The pH balance for the formation of this network was very subtle. Several kinds of side reactions can be observed: protonation of the aniline in a more acidic environment makes the aniline a poor ligand; otherwise, a more basic environment will accelerate the oxidation of aniline accompanied by complexation of copper with malonate alone.

**Description of the Structure.** The X-ray analysis reveals that complex **3** contains a distorted macrocycle, which is composed of two copper(II) ions and two ligands **2**, 4,4′-diaminodiphenylmethane. The binuclear macrocyclic structure has central symmetry. Each Cu(II) atom is in triangle-bipyramidal surroundings. The equatorial plane consists of one nitrogen atom from $(CH_2(C_6H_4NH_2)_2)$, one oxygen atom from the carbonyl group of malonic acid, and one terminal chloride atom. The four atoms $Cu_1$, $O_1$, $N_2$, $Cl_1$ are almost coplanar. The apical positions are occupied by one oxygen atom also from the carbonyl group of malonic acid and one nitrogen atom from another 4,4′-diaminodiphenylmethane. Malonic acid, as a neutral bidentate ligand, coordinates to one Cu(II) ion, forming a six-membered chelating ring and takes a boat-type structure. The bond lengths about the carbonyl group of malonic acid indicate a decrease in the carbon−oxygen double-bond character [(C═O = 1.245 Å; C−O = 1.31 Å);[8] complex mean C═O = 1.276 Å], consistent with the coordination of the oxygen atoms. Similarly, the carbon−oxygen bond lengths are too short for single-bond character (C═OH = 1.230 Å), suggesting that the electrons delocalized over the carbonyl group.

$\{[Cu(CH_2(C_6H_4NH_2)_2)(CH_2(COOH)_2)Cl]Cl\}_2$ **3** possesses a distorted macrocycle enclosed by 4,4′-methylenedianiline (Figure 1). The opposite two phenyl rings are parallel, and the torsion angle between two neighboring phenyl rings is 71.5°. The dimensions of this distorted square cavity are approximately 8.36 × 4.10 Å, measured from opposite phenyl ring to phenyl ring. It is slightly larger than Pd−ligand **1** complex, 4 × 6 Å.[4b,6] Here, the molecular box in **3** is twisted to make the enclosed cavity a small one corresponding to the flexibility of by 4,4′-methylenedianiline and the pentacoordination geometry of Cu(II) ion. It is known that the host structures generated to date all have a high degree of symmetry, which may limit the range of substrates that can be recognized. Although no solvent molecules were clathrated in the cavity of complex **3**, the distorted macrocyclic structure is still attractive in the recognition of low-symmetry guest molecules.[9]

It is interesting that malonic acid coordinates as a neutral chelating ligand, and not as malonate, and is therefore able to participate in a hydrogen-bonding network, see Figure 2. An extended two-dimensional network is constructed via hydrogen-bonding interactions between hydroxyl groups of malonic acid and amino groups of 4,4′-methylenedianiline of different binuclear macrocycle units (hydrogen bond: O3···N1 3.136(8) Å, N1−H3 0.950 Å, ∠O3−H3−N1 139.529°; O4···N2 2.851(8) Å, H6−O4 0.950 Å, ∠O4−H6−N2 153.93°). Every binuclear macrocycle stands in the network and works as a gate for

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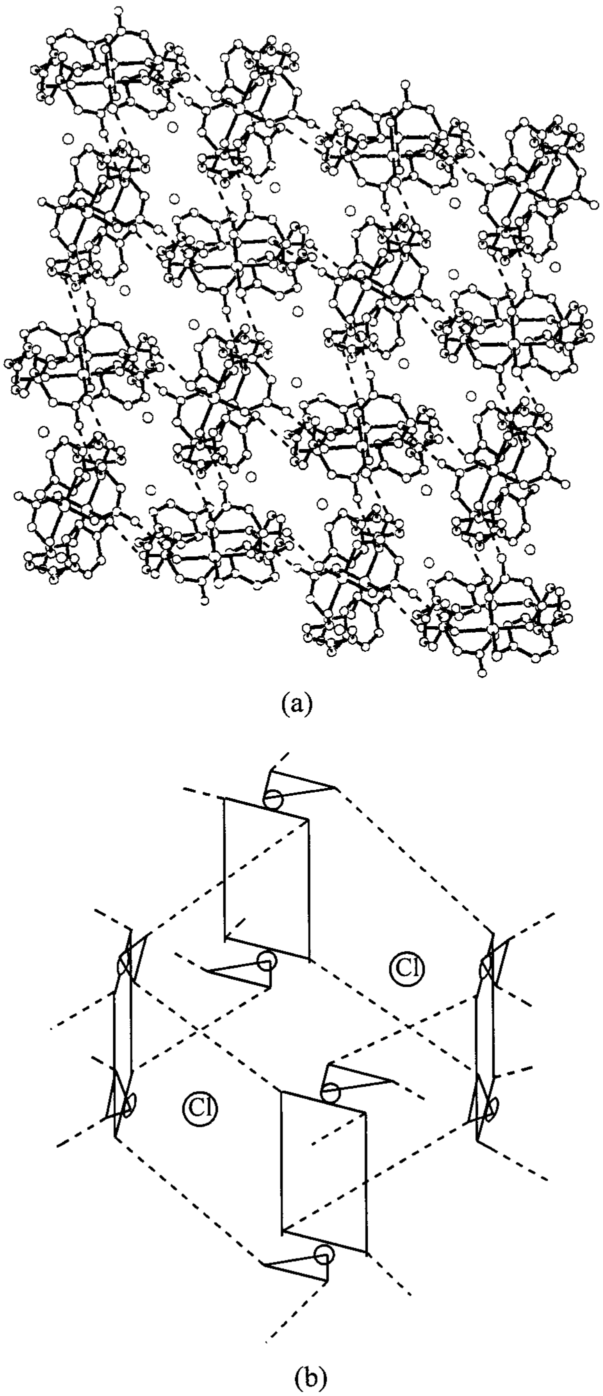

**Figure 2.** Extended crystal structure of complex **3**: (a) top view of the two-dimensional network linked by hydrogen bonds in **3**; (b) a model of the steric maze-type network in **3**. The squares represent the macrocycles enclosed by two oligoaniline connector ligands and work as gates in the maze, and triangles represent six-membered rings formed by malonic acid and Cu(II) ion (the small circle). Hydrogen bonds are shown as dotted lines. Two chloride anions are clathrated in every cylindrical cavity.

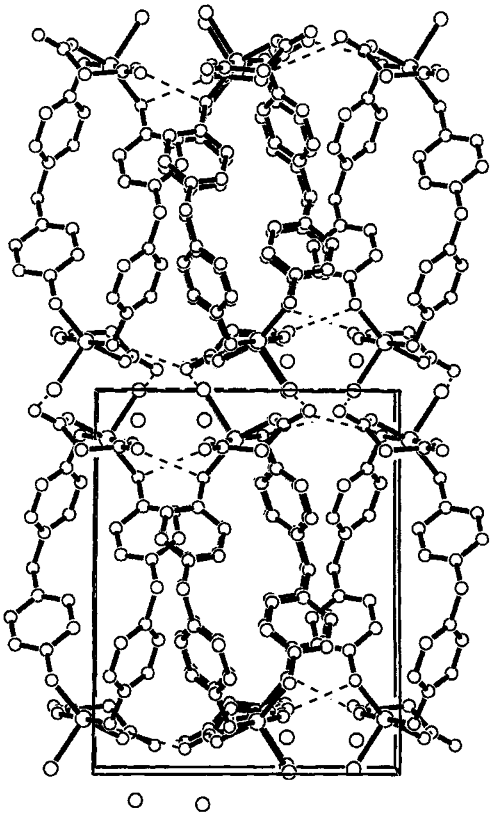

**Figure 3.** Packing diagram for **3** along the *c* axis. Hydrogen interactions are shown as dotted lines.

constructing the novel maze-type structure and as pillar to support the network. The thickness of the two-dimensional net layer is 15.36 Å. Two chloride ions are located in one cylindrical cavity. This steric maze-type network assembled through both coordinative and hydrogen bonds represents a further type of supramolecular structure.[10] Furthermore, two-dimensional network layers stack head-to-head to form a parallel packing; the three-dimensional framework is constructed through hydrogen interactions between coordinated chloride atoms and hydroxyl groups of malonic acid of the adjacent layer (Cl···O 2.96 Å, O−H 0.950 Å, ∠O−H−Cl 143.79°), see Figure 3.

Finally, it is worthy of note that supramolecular assembly constructed through multiple bonds is remarkable. Coordinative bonds form the primary-class structures, and hydrogen interactions induce and sustain secondary and/or third-class structures. It shows the general self-organization rule of natural products and also reveals an ever-increasing variety of framework compositions and topologies.

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**Supporting Information Available:** An X-ray crystallographic file in CIF format for the structure determination of $\{[Cu(CH_2(C_6H_4NH_2)_2)(CH_2(COOH)_2)Cl]Cl\}_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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