

## Synthesis and Crystal Structure of Macrocyclic Cavitand Cucurbit[5]uril and Its Supramolecular Adduct with Cu(II)

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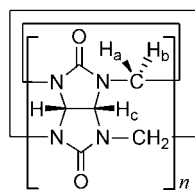
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The first supramolecular adduct  $(\text{H}_3\text{O})_2[\text{Cu}(\text{H}_2\text{O})_4](\text{SO}_4)_2 \cdot 2(\text{C}_{30}\text{H}_{30}\text{N}_{20}\text{O}_{10}) \cdot 24(\text{H}_2\text{O})$  based on cucurbit[5]uril was synthesized and characterized by single crystal X-ray diffraction analysis. In the adduct, copper ion is coordinated by four oxygen atoms from  $\text{H}_2\text{O}$ . The latter links two cucurbit[5]uril molecules due to a complicated hydrogen bonding containing lattice water molecules.

**Keywords** cucurbit[5]uril, crystal structure, supramolecular adduct

### Introduction

The cucurbit[*n*]urils (CB[*n*]s) are a kind of cyclic methylene-linked glycoluril oligomers and possess a characteristic annular shape, with two identical carbonyl-fringed portals.<sup>1-3</sup> As the most common cucurbituril, CB[6], has been widely studied in supramolecular chemistry by the groups of Mock<sup>4</sup> and Kim.<sup>5</sup> Recently, other CB[*n*] (*n*=5, 7, 8), the molecular recognition properties of which are different from those of CB[6] itself, have been extensively utilized in molecular recognition and self-assembly studies.<sup>6</sup>



*n* = 5, 6, 7, 8, 10

Metal ions and metal clusters are bound to CB[6] either via the coordination of the oxygen atoms of the portals of CB[6] to metal cations (in the case of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,<sup>7-10</sup>  $\text{Ca}^{2+}$ ,<sup>1,11</sup> and lanthanides<sup>12</sup>) or via hydrogen bonds between the oxygen atoms of the portals and the aqua ligands (in the case of  $\text{Al}^{3+}$ ,  $\text{In}^{3+}$ ,<sup>13</sup> cluster aqua complexes,<sup>14</sup> and transition metal ions<sup>15,16</sup>). The first instance of a metal halide compound within CB[7] was reported.<sup>17</sup> And a supramolecular complex based on CB[8] was synthesized by Fedin.<sup>18</sup> Recently, a new supramolecular adduct cucurbit[7]uril with  $[\text{PtCl}_6]^{2-}$  was prepared and characterized by us.<sup>19</sup> The presence of

large pores or channel with controlled size and shapes in these supramolecular complexes or adducts, is very interesting for the construction of porous materials. And they are applied widely in the separation and supramolecular catalysis.

Here we report the purification and structures of CB[5] (**1**), and its first supramolecular metal adduct  $(\text{H}_3\text{O})_2[\text{Cu}(\text{H}_2\text{O})_4](\text{SO}_4)_2 \cdot 2(\text{C}_{30}\text{H}_{30}\text{N}_{20}\text{O}_{10}) \cdot 24(\text{H}_2\text{O})$  (**2**).

### Experimental

All reagents were obtained commercially unless specially stated. Glycoluril and DCI/D<sub>2</sub>O (20%) were purchased from Acros. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Inova-600 (600 MHz) spectrometer with TMS as the internal standard. IR spectra were recorded with KBr pellets on a Testscan Shimadzu FTIR8000. FAB-MS measurements were carried out on a Finnigan MAT 95 mass spectrometer. Elemental analyses were performed using a VarioEL III elemental analyzer.

### Synthesis of the macrocyclic cavitand **1**

CB[5] was synthesized according to the reported method<sup>3</sup> with a little modification. The separation and purification of CB[5] was completed through repetitive dissolution and crystallization (yield 6.4%). The colorless single crystals, suitable for single crystal X-ray diffraction analysis, were obtained by slow addition of methanol into the aqueous solution of CB[5]. <sup>1</sup>H NMR (20% DCI/D<sub>2</sub>O)  $\delta$ : 4.45 (d, *J*=15.6 Hz, 10H, H<sub>b</sub>), 5.55 (d, *J*=15.6 Hz, 10H, H<sub>a</sub>), 5.61 (s, 10H, H<sub>c</sub>); <sup>13</sup>C NMR 50.33 (CH<sub>2</sub>), 68.94 (CH), 156.23 (CO); IR (KBr)  $\nu$ : 2993 (m), 2932 (m), 1731 (s), 1477 (s), 1418 (m), 1376

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(m) 1327 (s) 1235 (s), 1190 (s), 1148 (m), 966 (m), 802 (s), 758 (m), 673 (m)  $\text{cm}^{-1}$ ; FAB-MS  $m/z$  (%): 831  $[\text{M}+\text{H}]^+$  (25), 848  $[\text{M}+\text{OH}]^+$  (100). Anal. calcd for  $\text{C}_{30}\text{H}_{61}\text{ClN}_{20}\text{O}_{25}$ : C 31.68, H 5.41, N 24.63; found C 30.98, H 5.29, N 24.13.

### Synthesis of copper adduct 2

Slow addition of methanol into the aqueous solution of CB[5] and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  resulted in the formation of blue single crystals of **2** in 64.0% yield. Its IR spectrum of is the same to that of CB[5]. Anal. calcd for  $\text{C}_{60}\text{H}_{122}\text{CuN}_{40}\text{O}_{58}\text{S}_2$ : C 29.30, H 5.00, N 22.78; found C 28.85, H 4.87, N 22.24.

### X-ray crystal analyses

Data collections were performed on a Siemens SMART CCD diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.071073$  nm) at 293(2) K. The structures were solved by direct method (SHELXL-97) and refined against  $F^2$  in anisotropic approximation (SHELXL-97) except for the carbon atoms refined isotropically, whereas the hydrogen atoms in the CB[5] molecule were generated geometrically. The total amount of hydroxonium cations in the formula was assigned to satisfy the charge balance. The crystallographic data and other experimental details, including data collection parameters, structure solution and refinement details, are summarized in Table 1. Crystallographic data for the adduct **2** have been deposited at the Cambridge Crystallographic Data Center with the deposition number CCDC-231955.

## Results and discussion

### Synthesis of the macrocyclic cavitant 1

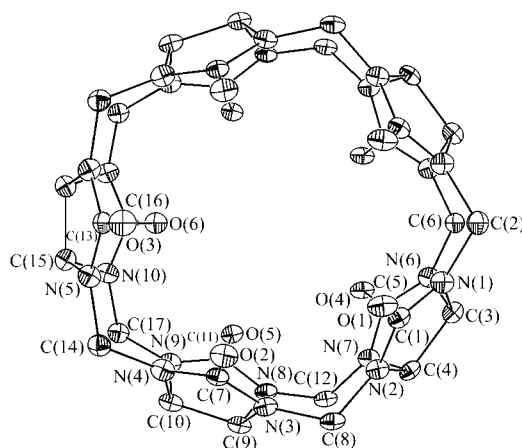
Though acid-catalyzed condensation reaction of glycoluril and formaldehyde yielded a mixture of CB[ $n$ ] ( $n=5, 6, 7, 8, 10$ ), their purification procedure was troublesome.<sup>2,3</sup> Day<sup>3</sup> reported that CB[5] was separated by fractional crystallization from the mixture of CB[5] and CB[6]. We found that among CB[ $n$ ], CB[5] has the largest solubility in water. It has a moderate solubility (about 33 g/L) even in 50% aqueous methanol solution. CB[7] has a solubility in water (about 26 g/L), but the solubility is less than 3.9 g/L in 50% methanol aqueous solution. An interesting phenomenon is that the solubility of CB[5] decreases with increasing the concentration of acid. These results are not in accordance with the conclusion reported by Buschmann.<sup>20</sup> So CB[5] was separated by dissolving it in 50% aqueous methanol. Then pure sample of CB[5] was obtained by crystallization from 20% HCl solution.

### Crystal structure of 1

Figure 1 shows the molecular structure of the macrocyclic cavitant **1**. In the crystal structure, one water molecule is encapsulated in the cavity of CB[5]. The structural parameters are the same as the results reported by Kim.<sup>2</sup>

**Table 1** Crystal data and data collection parameters for compounds **1** and **2**

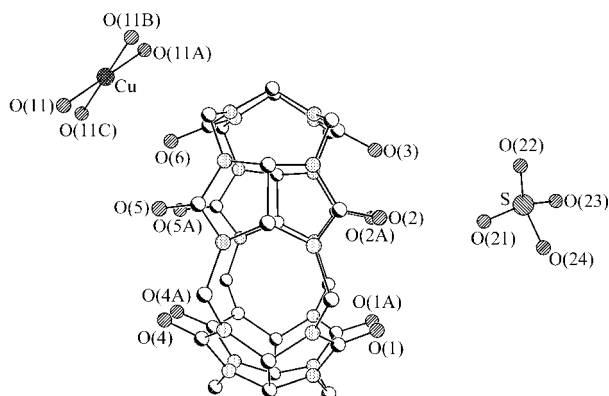
Complex	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{30}\text{H}_{61}\text{ClN}_{20}\text{O}_{25}$	$\text{C}_{60}\text{H}_{122}\text{CuN}_{40}\text{O}_{58}\text{S}_2$
$M_r$	1137.44	2459.64
Crystal size/mm	$1.12 \times 0.80 \times 0.64$	$0.80 \times 0.58 \times 0.48$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/m$
$a/\text{nm}$	2.49527(17)	2.42083(5)
$b/\text{nm}$	1.44320(10)	1.49078(2)
$c/\text{nm}$	1.47915(11)	1.53271(3)
$\alpha/^\circ$	90	90
$\beta/^\circ$	101.3490(10)	100.0810(10)
$\gamma/^\circ$	90	90
$V/\text{nm}^3$	5.2225(6)	5.44604(17)
$Z$	4	2
$D_c/(\text{g} \cdot \text{cm}^{-3})$	1.447	1.500
$\mu(\text{Mo } K\alpha) (\text{cm}^{-1})$	1.74	3.55
$F(000)$	2392	2574
Reflections collected	8105	8220
Unique reflections	4786	4915
$R_1 [I > 2\sigma(I)]$	0.1418	0.0828
$wR_2 [I > 2\sigma(I)]$	0.3634	0.2253
$R_1$ (all data)	0.1750	0.1054
$wR_2$ (all data)	0.4110	0.2560



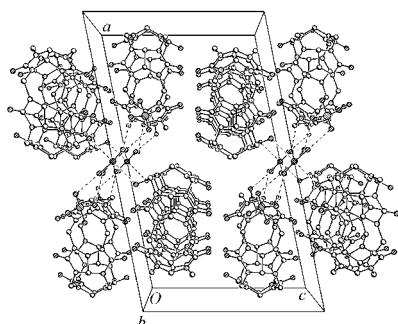
**Figure 1** Molecular structure of the macrocyclic cavitant **1** (all  $\text{H}_2\text{O}$  molecules and H atoms are omitted for clarity).

### Crystal structure of 2

Figure 2 and Figure 3 show the molecular structure of the supramolecular adduct **2** and its crystal packing. Selected bond distances and angles are summarized in Table 2. According to X-ray diffraction data, the compound **2** is a supramolecular adduct with a 2 : 1 ratio of CB[5] to copper(II) aqua complex. The cavity of CB[5]



**Figure 2** Molecular structure of **2**.



**Figure 3** Packing of structural units in crystal **2** (view along the *b*-axis). The water molecules of solvation and H atoms are omitted for clarity.

**Table 2** Selected bond lengths (nm) and angles (°) for **2**

Cu—O(11)#1	0.1951(4)	Cu—O(11)#2	0.1951(4)
Cu—O(11)	0.1951(4)	Cu—O(11)#3	0.1951(4)
O(11)#1—Cu—O(11)#2	180.0(3)	O(11)#1—Cu—O(11)	89.7(2)
O(11)#2—Cu—O(11)	90.3(2)	O(11)#1—Cu—O(11)#3	90.3(2)
O(11)#2—Cu—O(11)#3	89.7(2)	O(11)—Cu—O(11)#3	180.0(3)

Symmetry transformations used to generate equivalent atoms: #1  $-x+1, y, -z$ ; #2  $x, -y, z$ ; #3  $-x+1, -y, -z$ .

is filled with a disordered water molecule. From the Figure 3, it can be seen that the copper cation has a six-coordinated octahedral environment (two O atoms from CB[5] molecules and four O atoms from the water molecules). But in fact, the Cu—O(6)(CB[5]) bond length is 0.2665 nm, much larger than the summarization of ionic radii of Cu and O (0.236 nm). So, the interaction between them may be due to the weaker intermolecular interaction. Four oxygen atoms from water molecules are coordinated with copper(II) cation to form a similar planar square configuration. The average Cu—O(H<sub>2</sub>O) bond length is 0.1951 nm. Four oxygen atoms coordinated to Cu<sup>2+</sup> form hydrogen bonds directly with two sulfate anions; the latter are bound to CB[5] due to interactions with the lattice water molecules. CB[5] and the lattice water molecules (omitted) are combined by hydrogen bonds to form “Z” chains (Figure 3). The space between these chains is filled with

[Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and the lattice water molecules. Interestingly, in the adduct **2**, the oxygen atoms of carbonyl groups in CB[5] are neither coordinated directly to Cu<sup>2+</sup> nor form hydrogen bonds with water molecules of [Cu(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup>. This phenomenon is different from all the cases of metal complex of CB[6].

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