Research Article

Jun Zheng, Lin Zhang, Xinan Yang, Yanmei Jin, Jie Gao, and Peihua Ma*

A study on the coordination of cyclohexanocucurbit[6]uril with copper, zinc, and magnesium ions

<https://doi.org/10.1515/gps-2021-0074>
received July 10, 2021; accepted November 02, 2021

Abstract: Herein, we report the supramolecular complexes of cyclohexanocucurbit[6]uril ($\text{CyH}_6\text{Q}[6]$) with $\text{Cu}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, and $\text{Mg}(\text{ClO}_4)_2$ in formic acid solution. The crystal structure was determined using single crystal X-ray diffraction. The analysis results showed that $\text{CyH}_6\text{Q}[6]$ formed a one-dimensional supramolecular chain with $\text{Cu}(\text{ClO}_4)_2$ and formed a supramolecular assembly with a mixture ratio of 2:3 with $\text{Zn}(\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$. In this system, ClO_4^- induced $\text{CyH}_6\text{Q}[6]$ and metal ions to form supramolecular complexes through ion–dipole interactions.

Keywords: $\text{CyH}_6\text{Q}[6]$, crystal structure, ion–dipole interaction, supramolecular complexes

1 Introduction

Cucurbit[n]uril [1–13] is the fourth generation of macrocyclic compounds after cyclodextrin, crown ether, and calixarene. In 1905, German chemists Behrend et al. obtained a white solid compound through the reaction of glycoluril and paraformaldehyde under acidic conditions [14]. However, because of the problem of solubility, it had not been further studied. It was not until 1981, when the Mock team determined its structure using single crystal X-ray diffraction, that the structure of substance was known [11]. It is a ring compound with a hydrophobic cavity having a neutral potential, two carbonyl ports with a negative potential,

and an outer surface with a positive potential. Since then, various cucurbit[n]uril have been discovered one after another and are still being explored [15–18].

However, because the cucurbit[n]uril itself can dissolve only in solutions of formic acid, concentrated acid, and concentrated alkali, the development of cucurbit[n]uril is greatly limited. Through the efforts of some researchers, some modified cucurbit[n]urils such as methyl-, hydroxyl-, cyclopentyl-, and cyclohexyl-substituted cucurbit[n]urils have been reported [19–25]. In the presence of inducers, it is easy to form complexes with various metal ions due to the effect of the outer surface of cucurbit[n]uril [26]. Moreover, cyclohexyl alkyl groups have a stronger ability to bind metal ions due to their electron-pushing effects. Therefore, it leads to an increase in electron cloud density in the ports and an increase in electrostatic repulsion. This increases the cavity of the cucurbit[n]uril and has better performance than ordinary cucurbit[n]uril and the solubility is greatly improved. Therefore, cyclohexyl-substituted cucurbit[n]uril is a kind of cucurbit[n]uril with great generalizing significance. Kim's research group, which was the first to introduce cyclohexyl into cucurbit[n]uril, reported a series of fully substituted cyclohexyl cucurbits. The experimental results show that fully substituted cyclohexyl cucurbit[5]uril and fully substituted cyclohexyl cucurbit[6]uril have good water solubility [27]. In the Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, a series of $\text{Ln}-\text{CyH}_5\text{Q}[5]$ complexes formed by the interaction of fully substituted cyclohexyl cucurbit[5]uril with rare earth metal ions has been reported [28]. A series of $\text{Ln}-\text{CyH}_6\text{Q}[6]$ complexes formed by the interaction of fully substituted cyclohexyl cucurbit[6]uril with rare earth metal ions has been reported [29]. There are few studies on the supramolecular complexes constructed by $\text{CyH}_6\text{Q}[6]$ and metal perchlorates.

In this study, $\text{CyH}_6\text{Q}[6]$ (Figure 1) was used as the ligand with $\text{Cu}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, and $\text{Mg}(\text{ClO}_4)_2$ to construct three kinds of supramolecular complexes in formic acid solution. Finally, their structures were determined using single crystal X-ray diffraction.

* Corresponding author: Peihua Ma, Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China, e-mail: phma@gzu.edu.cn, tel: +86-13368690478

Jun Zheng, Lin Zhang, Xinan Yang, Yanmei Jin, Jie Gao: Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China

Figure 1: Crystal structure of $\text{CyH}_6\text{Q}[6]$: (a) top view and (b) side view.

2 Experimental

2.1 General materials

All materials and reagents are analytically pure and purchased on the Aladdin platform, used without any further purification. The cyclohexanocucurbit[6]uril ($\text{CyH}_6\text{Q}[6]$) was prepared and purified in accordance with a literature method [24]. The synthesis process of $\text{CyH}_6\text{Q}[6]$ is shown in Scheme 1.

2.2 Preparation of complexes

A mixture of $\text{CyH}_6\text{Q}[6]$ (10 mg, $7.58\ \mu\text{mol}$) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (5 mg, $13.49\ \mu\text{mol}$) in 3 mL of formic acid was heated until dissolution. The resultant solution was left to stand at room temperature. A week later, colorless prismatic crystals of complex **1** ($\text{C}_{60}\text{H}_{84}\text{Cl}_2\text{CuN}_{24}\text{O}_{26}$) were obtained in 40% yield (based on $\text{CyH}_6\text{Q}[6]$). The crystals of complex **2** ($\text{C}_{40}\text{H}_{56}\text{Cl}_2\text{ZnN}_{16}\text{O}_{20}$) and complex **3** ($\text{C}_{40}\text{H}_{56}\text{Cl}_2\text{MgN}_{16}\text{O}_{20}$) were obtained following the method described above for

complex **1**. The yield of complex **2** was about 50% and of complex **3** was about 46% based on $\text{CyH}_6\text{Q}[6]$.

2.2.1 Instrument characterization methods and test conditions

We selected crystals of an appropriate size and fixed them to a glass filament with Vaseline. Crystal data were collected using a Bruker D8 Venture X-ray single-crystal diffraction machine in scan mode using a graphite monochromatic Mo-K ray ($\lambda = 0.71073\ \text{\AA}$, $\mu = 0.828\ \text{mm}^{-1}$) in ω -scan mode. Lorentz polarization and absorption corrections were applied. Structural solutions and full-matrix least-squares refinements based on F^2 were performed using the SHELXT-14 and SHELXL-14 program packages, respectively. All non-hydrogen atoms were refined anisotropically. Analytical expressions for the neutral-atom scattering factors were used and anomalous dispersion corrections were incorporated. Most of the water molecules in the compounds were omitted using the SQUEEZE option in the PLATON program. The main crystal structure parameters are shown in Table 1.

Scheme 1: The synthesis process of $\text{CyH}_6\text{Q}[6]$.

Table 1: Crystallographic parameters of complexes 1–3

Complex	1	2	3
Empirical formula	C ₆₀ H ₈₄ Cl ₂ CuN ₂₄ O ₂₆	C ₄₀ H ₅₆ Cl ₂ ZnN ₁₆ O ₂₀	C ₄₀ H ₅₆ Cl ₂ MgN ₁₆ O ₂₀
Formula weight	1691.95	1217.27	1176.21
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	12.972(3)	12.755(4)	12.762(2)
<i>b</i> [Å]	15.551(3)	15.431(7)	15.463(3)
<i>c</i> [Å]	19.921(4)	21.533(7)	21.530(4)
α [°]	98.692(6)	91.857(16)	91.961(6)
β [°]	92.474(5)	98.189(9)	98.121(6)
γ [°]	105.477(6)	103.915(14)	103.958(6)
<i>V</i> [Å ³]	3813.7(13)	4062(3)	4071.6(12)
<i>Z</i>	2	3	3
<i>D</i> _{calcd.} [g·cm ^{−3}]	1.473	1.493	1.439
<i>T</i> [K]	273.15	273.15	273.15
μ [mm ^{−1}]	0.451	0.641	0.220
Parameters	1,031	1,073	1,075
<i>R</i> _{int}	0.1037	0.0572	0.1069
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0999	0.0814	0.1073
<i>wR</i> [<i>I</i> > 2 σ (<i>I</i>)] ^b	0.2698	0.2424	0.3042
<i>R</i> (all data)	0.1493	0.0993	0.1565
<i>wR</i> (all data)	0.2980	0.2581	0.3417
GOF on <i>F</i> ²	1.081	1.041	1.203

^aConventional *R* on *Fhkl*: $\sum||F_o| - |F_c||/\sum|F_o|$; ^bWeighted *R* on *Fhkl*: $\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Figure 2: Crystal structure of complex 1: (a) asymmetric unit, (b) coordinate bond, (c) ion–dipole interaction, and (d) two-dimensional structure viewed along the *a*-axis.

3 Results and discussion

3.1 Description of the crystal structure of complexes 1–3

Complex **1** exhibited the triclinic $P\bar{1}$ space group. The asymmetric unit structure contained one $\text{CyH}_6\text{Q}[6]$ molecule, two counter ClO_4^- ions, two central Cu^{2+} ions, and four coordinating water molecules (Figure 2a). One central Cu^{2+} ion of the complex was coordinated by one carbonyl oxygen atom (O1) and two water molecules (O1W and O2W) from the ligand $\text{CyH}_6\text{Q}[6]$ molecule. The coordination bond length of Cu1–O1 was 2.356 Å. In addition, the coordination bond lengths of Cu1–O1W and Cu1–O2W were 1.975 and 1.978 Å, respectively. Another central Cu^{2+} ion of the complex was coordinated by one carbonyl oxygen atom (O7) and two water molecules (O3W and O4W) from the ligand $\text{CyH}_6\text{Q}[6]$ molecule. The coordination bond length of Cu2–O7 is 2.288 Å. In addition, the coordination bond lengths of Cu2–O3W and Cu2–O4W were 1.980 and 1.971 Å, respectively. The bond angle around Cu^{2+} was between 86.74° and 91.97° (Figure 2b).

The port of $\text{CyH}_6\text{Q}[6]$ and Cu^{2+} was bridged by coordination bonds to form a one-dimensional supramolecular chain (Figure 2b). The ion–dipole interaction between counter ClO_4^- ions and the positive potential outer surface of the $\text{CyH}_6\text{Q}[6]$ leads to distance of 2.589–2.700 Å (Figure 2c). Complex **1** formed a two-dimensional stacking model in the presence of coordination and ion dipoles as shown in Figure 2d.

Complex **2** exhibited the triclinic $P\bar{1}$ space group. The asymmetric unit structure contained one $\text{CyH}_6\text{Q}[6]$ molecule, three counter ClO_4^- ions, two central Zn^{2+} ions, five coordinating water molecules, and one coordinating chloride ion (Figure 3a). One central Zn^{2+} ion of the complex was coordinated by one carbonyl oxygen atom (O1) and two water molecules (O4W and O5W) from the ligand $\text{CyH}_6\text{Q}[6]$ molecule. The coordination bond length of Zn1–O1 was 2.146 Å. In addition, the coordination bond lengths of Zn1–O4W and Zn1–O5W were 2.027 and 2.074 Å, respectively. Another central Zn^{2+} ion of the complex was coordinated by two carbonyl oxygen atoms (O7 and O8), one chloride ion (Cl14), and three water molecules (O1W, O2W, and O3W) from the ligand $\text{CyH}_6\text{Q}[6]$ molecule. The coordination bond lengths of Zn2–O7 and Zn2–O8 were 2.077 and

Figure 3: Crystal structure of complex **2**: (a) asymmetric unit, (b) coordinate bond, (c) ion–dipole interaction, and (d) two-dimensional structure viewed along the *b*-axis.

Figure 4: Crystal structure of complex **3**: (a) asymmetric unit, (b) coordinate bond, (c) ion–dipole interaction, and (d) two-dimensional structure viewed along the *b*-axis.

2.153 Å, respectively. The coordination bond length of Zn2–Cl14 was 2.187 Å. In addition, the coordination bond lengths of Zn2–O1W, Zn2–O2W, and Zn2–O3W were 2.108, 2.033, and 2.043 Å, respectively. The bond angle around Zn²⁺ was between 84.20° and 98.66° (Figure 3b). In fact, because of this outer surface interaction of the cucurbit[*n*] uril, the ion–dipole interaction between counter ClO₄[−] ions and the positive potential outer surface of the CyH₆Q[6] produces distance of 2.388–3.179 Å (Figure 3c). Complex **2** formed a two-dimensional stacking model in the presence of coordination and ion dipoles as shown in Figure 3d. Complex **2** was different from complexes **1** and **3** in that it not only coordinates with carbonyl oxygen and water molecules but also with chloride ions.

Complex **3** exhibited the triclinic $P\bar{1}$ space group. The asymmetric unit structure contained one CyH₆Q[6] molecule, three counter ClO₄[−] ions, two central Mg²⁺ ions, and six coordinating water molecules (Figure 4a). One central Mg²⁺ ion of the complex was coordinated by one carbonyl oxygen atom (O1) and two water molecules (O1W and O2W) from the ligand CyH₆Q[6] molecule. The coordination bond length of Mg1–O1 was 2.092 Å. In addition, the

coordination bond lengths of Mg1–O1W and Mg1–O2W were 2.033 and 2.068 Å, respectively. Another central Mg²⁺ ion of the complex was coordinated by two carbonyl oxygen atoms (O7 and O12) and four water molecules (O3W, O4W, O5W, and O6W) from the ligand CyH₆Q[6] molecule. The coordination bond lengths of Mg2–O7 and Mg2–O12 were 2.062 and 2.113 Å, respectively. In addition, the coordination bond lengths of Mg2–O3W, Mg2–O4W, Mg2–O5W, and Mg2–O6W were 2.080, 2.070, 2.045, and 2.033 Å, respectively. The bond angle around Mg²⁺ was between 85.59° and 92.47° (Figure 4b). In fact, because of this outer surface interaction of CyH₆Q[6], the ion–dipole interaction between counter ClO₄[−] ions and the positive potential outer surface of CyH₆Q[6] results in distance of 2.419–3.215 Å (Figure 4c). Complex **3** formed a two-dimensional stacking model in the presence of coordination and ion dipoles (Figure 4d). The coordination configurations of complexes **3** and **2** were similar. The difference was that the central Mg²⁺ of complex **3** did not form coordination bonds with chloride ions, whereas the central Mg²⁺ of complex **2** formed coordination bonds with chloride ions.

4 Conclusion

Complexes **1–3** were constructed using $\text{CyH}_6\text{Q}[6]$ and $\text{Cu}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, and $\text{Mg}(\text{ClO}_4)_2$, respectively, in formic acid aqueous solution. The experimental results showed that complex **1** formed a two-dimensional stacking model in the presence of coordination and ion–dipole interaction. The coordination configurations of complexes **3** and **2** were similar. The difference was that the central Mg^{2+} of complex **3** did not form coordination bonds with chloride ions, whereas the central Zn^{2+} of complex **2** formed coordination bonds with chloride ions. Complex **2** was different from complexes **1** and **3** in that it not only coordinated with carbonyl oxygen and water molecules but also with chloride ions. This study further helped to fill the research gap of $\text{CyH}_6\text{Q}[6]$. At the same time, it provided a theoretical basis for cucurbit[*n*]urils in the fields of carrier catalyst, collection, precipitation, adsorption, enrichment, and recovery.

Funding information: This work was supported by the National Natural Science Foundation of China (Grant No. 21762011), Guizhou Science and Technology Planning Project (Guizhou Science and Technology Cooperation Platform Talent [2017]5788) and the Guizhou Province Graduate Education Innovation Project (No. YJSCXJH [2020] 188).

Author contributions: Jun Zheng: writing – original draft, writing – review and editing, methodology, formal analysis; Lin Zhang: writing – original draft, formal analysis; Xinan Yang: visualization, project administration; Yanmei Jin: resources, writing – review and editing, supervision, data curation; Jie Gao: resources, writing – review and editing, supervision, data curation; Peihua Ma: writing – review and editing.

Conflict of interest: Authors state no conflict of interest.

Data availability statement: The X-ray crystallographic data for structures reported in this study have been deposited in the Cambridge Crystallographic Data Center under accession numbers CCDC: 2055928 (**1**), 2055951 (**2**), and 2055947 (**3**). These data can be obtained free of charge via https://www.ccdc.cam.ac.uk//data_request/cif.

References

- [1] Lagona J, Mukhopadhyay P, Chakrabarti S, Isaacs L. The cucurbit[*n*]uril family. *Angew Chem Int Edit*. 2005;44:4844–70.

- [2] Lee JW, Samal S, Selvapalam N, Kim HJ, Kim K. Cucurbituril homologues and derivatives: new opportunities in supramolecular chemistry. *Acc Chem Res*. 2003;36:621–30.
- [3] Gerasko OA, Samsonenko DG, Fedin VP. Supramolecular chemistry of cucurbiturils. *Russ Chem Rev*. 2002;71:741–60.
- [4] Elemans JAAW, Rowan AE, Nolte RJM. Self-assembled architectures from glycoluril. *Ind Eng Chem Res*. 2000;39:3419–28.
- [5] Cintas P. Cucurbituril: supramolecular perspectives for an old ligand. *J Incl Phenom Mol Recogn Chem*. 1994;17:205–20.
- [6] Yang RY, Deng XY, Huang Y, Zhang YQ, Tao Z. Recognition of lanthanide metal cations by t-DSMI@alkyl-substituted cucurbit[6]uril probes. *Chem*. 2020;5:8649–55.
- [7] Lin RL, Li R, Shi H, Zhang K, Meng D, Sun WQ, et al. Symmetrical-tetramethyl-cucurbit[6]uril-driven movement of cucurbit[7]uril gives rise to heterorowheel [4]pseudorotaxanes. *J Org Chem*. 2020;85:3568–75.
- [8] Day A, Arnold AP, Blanch RJ, Snushall B. Controlling factors in the synthesis of cucurbituril and its homologues. *J Org Chem*. 2001;66:8094–100.
- [9] Jansen K, Buschmann HJ, Wego A, Dopp D, Mayer C, Drexler HJ, et al. Cucurbit[5]uril, decamethylcucurbit[5]uril and cucurbit[6]uril. synthesis, solubility and amine complex formation. *J Incl Phenom Macro*. 2001;39:357–63.
- [10] Kim J, Jung IS, Kim SY, Lee E, Kang JK, Sakamoto S, et al. New cucurbituril homologues: syntheses, isolation, characterization, and x-ray crystal structures of cucurbit[*n*]uril (*n* = 5, 7, and 8). *J Am Chem Soc*. 2000;122:540–1.
- [11] Freeman WA, Mock WL, Shih NY. Cucurbituril. *J Am Chem Soc*. 1981;103:7367–8.
- [12] Xu HP, Lin D, Zhang B, Huo Y, Lin SF, Liu C, et al. Supramolecular self-assembly of a hybrid ‘hyalurosomes’ for targeted photothermal therapy in non-small cell lung cancer. *Drug delivery*. 2020;27:378–86.
- [13] Day AI, Blanch RJ, Arnold AP, Lorenzo S, Lewis GR, Dance I. A cucurbituril-based gyroscane: a new supramolecular form. *Angew Chem Intedit*. 2002;41:275–7.
- [14] Behrend R, Meyer F, Rusche F. Condensation products from glycoluril and formaldehyde. *Justus Liebigs Ann Chem*. 1905;339:1–37.
- [15] Zheng J, Zhao WW, Meng Y, Jin YM, Ma PH. Supramolecular self-assembly of cyclopentyl substituted cucurbit[*n*]uril with Fe^{3+} , Fe^{2+} , and HClO_4 based on outer surface interaction. *Cryst Res Technol*. 2021;56:2000183.
- [16] Liu SM, Ruspice C, Mukhopadhyay P, Chakrabarti S, Zavalij PY, Isaacs L. The cucurbit[*n*]uril family: prime components for self-sorting systems. *J Am Chem Soc*. 2005;127:15959–67.
- [17] Isaacs L, Park SK, Liu SM, Ko YH, Selvapalam N, Kim Y, et al. The inverted cucurbit[*n*]uril family. *J Am Chem Soc*. 2005;127:18000–1.
- [18] Zhao YJ, Xue SF, Zhu QJ, Tao Z, Zhang JX, Wei ZB, et al. Synthesis of a symmetrical tetrasubstituted cucurbit[6]uril and its host-guest inclusion complex with 2,2′-bipyridine. *Chin Sci Bull*. 2004;49:1111–6.
- [19] Flinn A, Hough GC, Stoddart JF, Williams DJ. Decamethylcucurbit[5]uril. *Angew Chem Int Edit*. 1992;31:1475–7.
- [20] Zhao JH, Kim HJ, Oh JH, Kim SY, Lee JW, Sakamoto S, et al. Cucurbit[*n*]uril derivatives soluble in water and organic solvents. *Angew Chem*. 2001;113:4363–5.

- [21] Wu F, Wu LH, Xiao X, Zhang YQ, Xue SF, Tao Z, et al. Locating the cyclopentano cousins of the cucurbit[*n*]uril family. *J Org Chem*. 2012;77:606–11.
- [22] Tian ZC, Ni XL, Xiao X, Wu F, Zhang YQ, Zhu QJ, et al. Interaction models of three alkyl substituted cucurbit[6]urils with a hydrochloride salt of 4,4'-dipyridyl guest. *J Mol Struct*. 2007;888:48–54.
- [23] Jon SY, Selvapalam N, Oh DH, Kang JK, Kim SY, Jeon YJ, et al. Facile synthesis of cucurbit[*n*]uril derivatives via direct functionalization: expanding utilization of cucurbit[*n*]uril. *J Am Chem Soc*. 2003;125:10186–87.
- [24] Isobe H, Sato S, Nakamura E. Synthesis of disubstituted cucurbit[6]uril and its rotaxane derivative. *Org Lett*. 2002;4:1287–9.
- [25] Jin YM, Huang TH, Zhao WW, Yang XN, Meng Y, Ma PH. A study on the self-assembly mode and supramolecular framework of complexes of cucurbit[6]urils and 1-(4-methoxyphenyl)piperazine. *RSC Adv*. 2020;10:37369–73.
- [26] Chen K, Kang YS, Zhao Y, Yang JM, Lu Y, Sun WY. Cucurbit[6]uril-based supramolecular assemblies: possible application in radioactive cesium cation capture. *J Am Chem Soc*. 2014;136:16744–7.
- [27] Zhao J, Kim HJ, Oh J, Kim SY, Lee JW, Sakamoto S, et al. Cucurbit[*n*]uril derivatives soluble in water and organic solvents. *Angew Chem Int Ed Engl*. 2001;40:4233–5.
- [28] Liu JX, Hu YF, Lin RL. Coordination complexes based on pentacyclo-hexano-cucurbit[5]uril and lanthanide(III) ions: lanthanide contraction effect induced structural variation. *Cryst Eng Comm*. 2012;14:6983–9.
- [29] Qin X, Ni XL, Hu JX, Chen K, Zhang YQ, Redshaw C, et al. Macrocyclic-based metal ion complexation: a study of lanthanide contraction effect towards hexacyclo-hexanocucurbit[6]uril. *Cryst Eng Comm*. 2013;15:738–44.