J Incl Phenom Macrocycl Chem (2008) 62:263–267
DOI 10.1007/s10847-008-9466-9

ORIGINAL ARTICLE

# A novel one-dimensional supramolecular inclusion compound linked by hydrogen bonding interaction

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Received: 15 April 2008 / Accepted: 16 May 2008 / Published online: 14 June 2008
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**Abstract** Crystal structure analysis shows the cucurbit[6]uril host and its tetrahydrofuran (THF) guest in the $Pmn2_1$ crystal lattice. The crystal data and refinement parameter for the title compound are: a = 14.027(3), b = 11.807(3), c = 16.760(4) Å, V = 2774.7(9) Å$^3$. For Z = 2 and Mw = 1529.52, the calculate density Dcal = 1.825 g/cm$^3$. Hydrogen bonding interaction assembled the adjacent $\{[La(H_2O)_6Cl](C_4H_8O@C_{36}H_{36}N_{24}O_{12})\}^{2+}$ cations into a novel one-dimensional superamolecular chain.

**Keywords** Cucurbit[6]uril · Hydrogen bonding interaction · X-ray crystallography · Supramolecular compound

## Introduction

Cucurbit[6]uril (Fig. 1) is a barrel-shaped macrocyclic cryptand with $D_{6h}$ symmetry, having a hollow core of ~5.5 Å diameter and one identical carbonyl-fringed portals on each side [1, 2]. During the past two decades, cucurbit[6]uril has received much interest as many functional molecular devices since its polarized carbonyl groups and rigid, hollow structure, and many works about supramolecular compounds of cucurbit[6]uril with metal complexes have been published [3–6]. Due to the unique structure of cucurbit[6]uril, it can form inclusion compounds with organic molecules and supramolecular associates with metal aqua complexes. According to the theoretic, we synthesized an interesting coordination complex, in which a THF molecule is encapsulated. More interestingly, the coordination complex serves as large building block for the construction of a novel one-dimensional supramolecular compound.

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## Experimental

### Synthesis

Chemicals, such as HCl, THF and lanthanide nitrate were of commercial quality and used without further purification. Cucurbit[6]uril was synthesized by following published procedures [7].

Cucurbit[6]uril (2.0 g, 2.0 mmol) was first dissolved in 100 mL 3.0 M HCl. To this solution (5 mL) was added nitrate of lanthanum (0.5 mL, 0.5 M). THF vapor was allowed to diffuse into the mixture solution at room temperature for a month to produce X-ray quality crystals of $\{[La(H_2O)_6Cl](C_4H_8O@C_{36}H_{36}N_{24}O_{12})\}(H_2O)_2(NO_3)_2$.

### Crystallography

Preliminary examination and data collection were performed with Mo–$K\alpha$ radiation on the Bruker Smart Apex 2000 diffractometer equipped with a graphite crystal incident beam monochromator ($\lambda$ = 0.71073 Å) in $\omega/2\theta$ scan mode at 173 K. The data were corrected for absorption by SADABS program in BrukerAXS program package. The structure of the title inclusion compound was solved by direct methods and refined by full-matrix least squares on

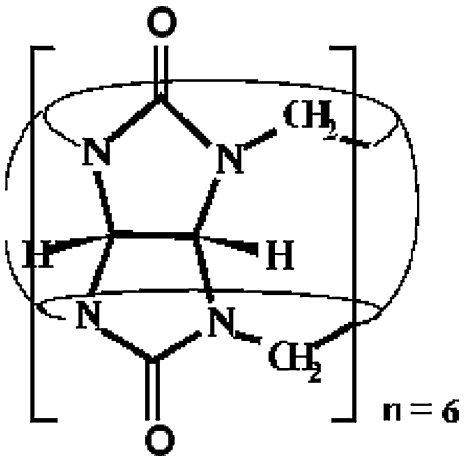


**Fig. 1** Structures of the cucurbit[n = 5–8]urils

**Table 1** Selected bond lengths (Å) and bond angle (°) for the title compound

| | |
|---|---|
| Identification code | Title compound |
| Empirical formula | $C_{40}N_{26}O_{28}H_{62}$ La Cl |
| Formula weight | 1529.5 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Orthorhombic, Pmn2(1) |
| Unit cell dimensions | a = 14.027(3) Å, alpha = 90° |
| | b = 11.807(3) Å, beta = 90° |
| | c = 16.760(4) Å, gamma = 90° |
| Volume | 2774.7(9) $Å^3$ |
| Z, Calculated density | 2, 1.831 $Mg/m^{-3}$ |
| Absorption coefficient | 0.936 $mm^{-1}$ |
| F(000) | 1,564 |
| Crystal size | 0.46 × 0.37 × 0.25 mm |
| Theta range for data collection | 1.89–26.00° |
| Limiting indices | $-16 \le h \le 17$, $-14 \le k \le 14$, $-20 \le l \le 20$ |
| Reflections collected/unique | 19,632/2,801 [R(int) = 0.0317] |
| Completeness to theta = 26.00 | 95.80% |
| Absorption correction | Multi scan |
| Max. and min. transmission | 0.8276 and 0.7351 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 2,801/20/467 |
| Goodness-of-fit on $F^2$ | 1.069 |
| Final R indices [I > 2sigma(I)] | R1 = 0.0478, wR2 = 0. 1192 |
| R indices (all data) | R1 = 0.0481, wR2 = 0.1197 |
| Absolute structure parameter | 0(10) |
| Largest diff. peak and hole | 1.902 and −0.613 e. $Å^{-3}$ |

$F^2$. About 2,801 observations with $I > 2\text{sigma}(I)$, out of 19,632 unique reflections measured ($R_{int} = 0.0317$) were used in the analysis. About 467 parameters have been refined. All non-hydrogen atoms were treated anisotropically. All hydrogen atoms were positioned at their calculated positions and were assigned common isotropic temperature factors. All calculations have been performed on a personal computer with the SHELX program package [8]. A summary of the crystallographic data, data collection and refinement parameters for the title compound is given in Table 1. The distance and angles from donor to acceptor are shown in Table 2.

**Table 2** Hydrogen bonds for the title compound (Å and °)

| D–H…A | d(D–H) | d(H…A) | d(D…A) | <(DHA) |
|---|---|---|---|---|
| O(1W)–H(1WB)…O(2) | 0.85 | 1.93 | 2.733(7) | 157 |
| O(1W)–H(1WA)…O(4 W) | 0.85 | 2.15 | 2.749(5) | 127 |
| O(2W)–H(2WB)…O(3) #1 | 0.85 | 2.06 | 2.768(4) | 139.9 |
| O(2W)–H(2WA)…O(4) #1 | 0.85 | 2.02 | 3.694(4) | 136.2 |
| O(3W)–H(3WB)…O(2) | 0.85 | 2.54 | 3.297(3) | 148.1 |
| O(4W)–H(4WB)…O(8) | 0.85 | 1.98 | 2.768(6) | 152.8 |
| O(4W)–H(4WA)…O(11) #1 | 0.85 | 2.22 | 2.880(5) | 135.1 |
| O(5W)–H(5WA)…O(9) | 0.85 | 2.35 | 3.099(19) | 162.7 |
| O(6W)–H(6WB)…O(9) | 0.85 | 2.36 | 3.19(4) | 147.5 |

Symmetry transformations used to generate equivalent atoms: #1 $x$, $y-1$, $z$

## Results and discussion

In the present study, slow vapor diffusion of THF into an aqueous solution containing $La(NO_3)_3$ and cucurbit[6]uril results in formation of crystals of the title compound, $\{[La(H_2O)_6Cl](C_4H_8O@C_{36}H_{36}N_{24}O_{12})\}(H_2O)_2(NO_3)_2$ (see the Experimental Section). The X-ray crystal structure of the title compound (Fig. 2) reveals that the lanthanum ion "lean" toward the portal of cucurbit[6]uril, being coordinated to only two carbonyl oxygen atoms (O1, O1A) at the portal. Still six water molecules (O1W, O1WA, O2 W, O2WA, O3 W and O6 W) and a chloride (Cl2) ion are coordinated to the lanthanum ion. The bond lengths of $La–O_{cucurbit[6]uril}$, $La–O_{water}$ and La–Cl are 2.600(2), 2.513(4)–2.589(3) and 2.9323(15) Å, respectively. The bond lengths of $La–O_{cucurbit[n]uril}$, $La–O_{water}$ are comparable to those of 2.563(3)–2.594(3) and 2.533(3)–2.619(5) Å in nine-coordinated La(III)/cucurbit[6]uril complex [4b]. Similar to the structure of $[(C_{36}H_{36}N_{24}O_{12})K_2(OH)_2(C_4H_8O)]9(H_2O)$ [5d], one disordered organic THF molecule is trapped in the cavity of cucurbit[6]uril the oxygen atom of the THF molecule point toward the 'equator' of cucurbit[6]uril. Thus, a "lean" lanthanum ion and a cucurbit[6]uril molecule formed an opened molecular capsule, in which a THF molecule is encapsulated. Most notable, the cucurbit[6]uril and the encapsulated THF molecule, as well as the La and one coordinated chlorine

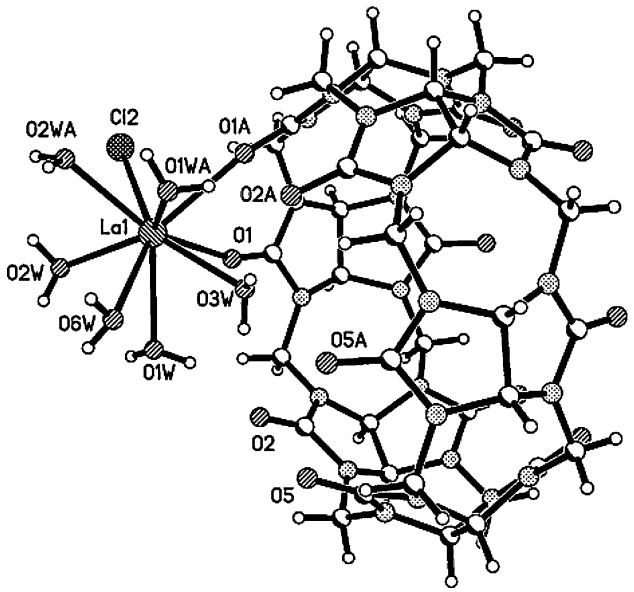


**Fig. 2** Coordination geometry of the lanthanum ion in $\{[La(H_2O)_6Cl](C_4H_8O@C_{36}H_{36}N_{24}O_{12})\}(H_2O)_2(NO_3)_2$; Solvate water molecules, THF molecules and anions are omitted for clarity

ions, one coordinated water molecule and one free water molecule lie on special positions of site symmetry *m*.

Normally, cucurbit[6]uril is a rigid cryptand with $\boldsymbol{D_{6h}}$ symmetry, having two identical carbonyl-fringed portals of $\sim$6.918 Å diameter[2]. However, the cucurbit[6]uril of the title compound shows a severe ellipsoidal distortion (Fig. 3). In the title compound, this distortion is manifested in the uneven distances: two of the six carbonyl oxygen atoms (O2 and O2A) are much shorter (6.345 Å) than the four other carbonyl oxygen atoms (O1 and O5A, O5 and O1A), which mean value is 7.243 Å. Obviously, the distortion of the cucurbit[6]uril molecules in the complex due to the coordination of lanthanum ion to the portal oxygen atoms.

Viewed along *a* axis, cucurbit[6]uril-based capsules formed a novel one-dimensional supramolecular cationic chain, in which neighboring inclusion complex link one another through O–H…O hydrogen bonding interaction (Fig. 4). Moreover, hydrogen-bonding interaction can be observed between two neighboring chains. As a result, they form a two-dimensional network structure layer on the *ac* plane (Fig. 5) with a distance between two contacting chains of 14.004 Å. Furthermore, the interchain space is filled with nitrate anions and water molecules that form a complicated hydrogen-bonding network among themselves.

In conclusion, we have prepared a new coordination complex, in which a THF molecule is encapsulated. Obviously, If we use suitable guests, which can be encapsulated in the cavity of cucurbit[6]uril, such host–guest complex has many promising applications in the area of catalysis, gas adsorption and chemicals separation. Moreover, cucurbit[6]uril-based capsules formed a novel one-dimensional supramolecular chain via hydrogen-bonding interaction. The result indicated that hydrogen-bonding interaction should be considered for the molecular design, likely leading to unusual supramolecular structure.

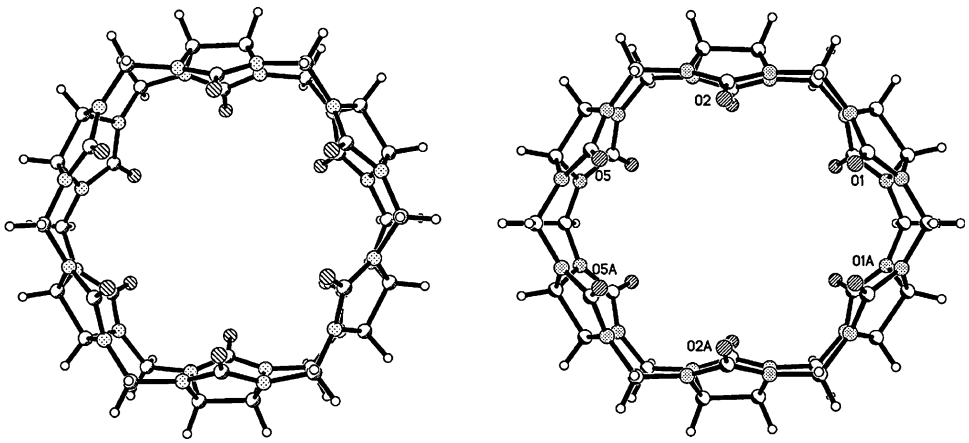


**Fig. 3** Normal cucurbit[6]uril (**a**) and ellipsoidal distorted cucurbit[6]uril of the title compound (**b**)

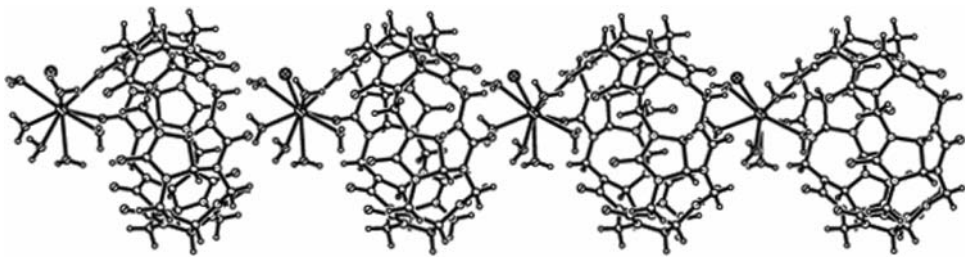

**Fig. 4** One-dimensional supramolecular cationic chain in $\{[La(H_2O)_6Cl](C_4H_8O@C_{36}H_{36}N_{24}O_{12})\}(H_2O)_2(NO_3)_2$; viewed along *a* axis

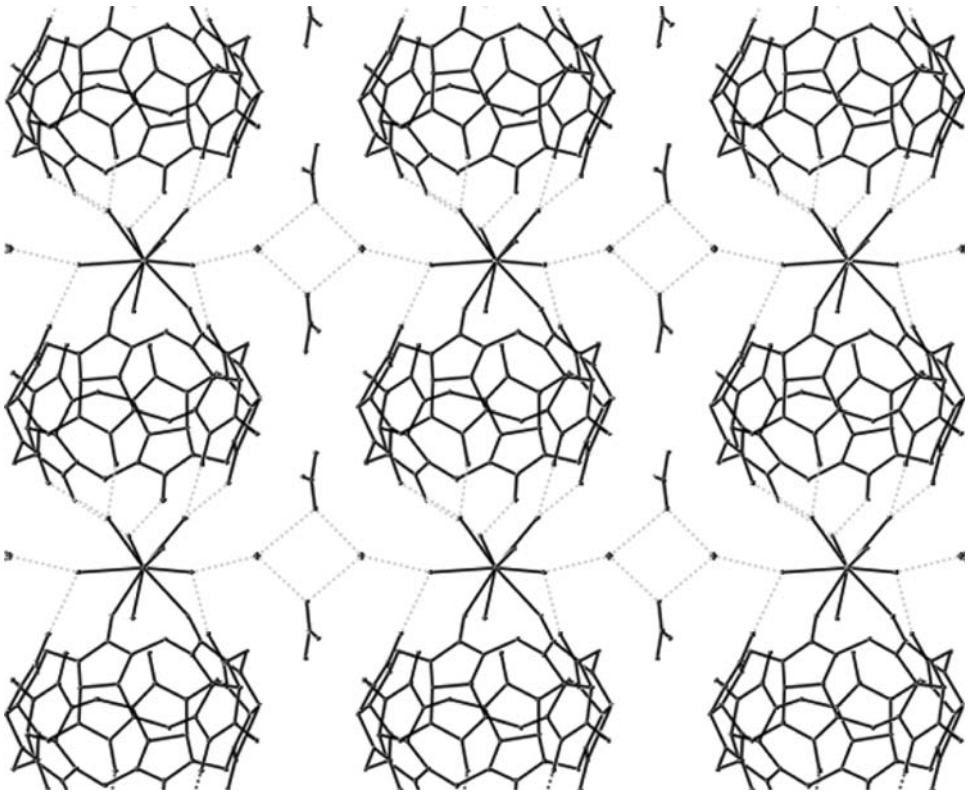

**Fig. 5** Two-dimensional network structure layer in $\{[La(H_2O)_6Cl](C_4H_8O@C_{36}H_{36}N_{24}O_{12})\}(H_2O)_2(NO_3)_2$ on the *ac* plane

**Acknowledgement** This work was supported by NNSFC (Grant Nos. 20471050, 20771003 and 20423002) for the financial support.

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