DFT Study on the Complexation of Bambus[6]uril with the Perchlorate and Tetrafluoroborate Anions

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Abstract

By using quantum mechanical DFT calculations, the most probable structures of the bambus[6]uril·ClO₄⁻ and bambus[6]uril·BF₄⁻ anionic complex species were derived. In these two complexes having C₃ symmetry, each of the considered anions, included in the macrocyclic cavity, is bound by 12 weak hydrogen bonds between methine hydrogen atoms on the convex face of glycoluril units and the respective anion.

Keywords: Bambus[6]uril; perchlorate and tetrafluoroborate anions; complexation; DFT calculations; complex structures

1. Introduction

Cucurbit[n]urils are macrocyclic compounds consisting of n glycoluril units connected by 2n methylene bridges. The shape of the macrocycle resembles a hollow barrel with a hydrophobic interior and partially negative charged rims of carbonyls on both sides of the macrocycle. This structure makes the macrocycles suitable to bind organic guests bearing one or more positive charges in their structures.¹⁻³

Cucurbit[6]uril (abbrev. CB[6]) is the oldest and the most accessible representative of the CB family of macrocycles and its supramolecular interactions with various guests have been extensively investigated.¹,² The ability of CB[6] to behave as a synthetic receptor was described in detail by Mock and co-workers together with the discovery of the macrocyclic structure of the molecule.⁴ Guest positioning and complex stability strongly depended on the length of alkyl chain of the guest.⁵⁻⁸ Since then the complexation between CB[6] and many organic guests has been studied, including polyamines,⁹,¹⁰ viologen derivatives,¹¹ organic dyes,¹² polypeptides,¹³ amino acids, and dipeptides.¹⁴

New macrocycles prepared by the acid-catalyzed condensation of ethyleneurea and formaldehyde were named hemicucurbit[n]urils (n = 6,12),¹⁵,¹⁶ as their structures resemble the motif obtained when the corresponding cucurbit[n]uril is cut in half along the equator. In contrast to cucurbit[n]urils, hemicucurbit[n]urils are soluble in nonpolar solvents, such as chloroform. Furthermore, hemicucurbit[n]urils form complexes with anions, but no interaction with common metal cations was observed in an aqueous solution.¹⁷,¹⁸

Recently, the synthesis of a cyclic hexamer, bambus[6]uril (abbrev. BU[6]; see Scheme 1), which combi-
nes the structural features of both cucurbit[n]urils and he-  
monicucurbit[n]urils, was described. An acid-catalyzed  
condensation between 2,4-dimethylglycoluril and formal-  
dehyde in HCl resulted in the mentioned macrocycle  
\( \text{BU}[6] \), in which the glycoluril units are connected  
through methylene bridges (Scheme 1). This macrocycle  
was isolated as a white powder in a maximum yield of  
30%, when the reaction was carried out in 5.4 M HCl at  
room temperature. Further, it is necessary to emphasize  
that \( \text{BU}[6] \) showed a good affinity for halide anions; the  
crystal structure of the anionic complex \( \text{BU}[6] \cdot \text{Cl}^- \)  
was presented as well. On the other hand, in the current  
work, applying quantum mechanical DFT calculations,  
the most probable structures of the \( \text{BU}[6] \cdot \text{ClO}_4^- \)  
and \( \text{BU}[6] \cdot \text{BF}_4^- \) anionic complex species are solved.

## 2. Results and Discussion

The quantum mechanical calculations were carried  
out at the density functional level of theory (DFT, B3LYP  
functional) using the Gaussian 03 suite of programs. The  
6-31G(d) basis set was used and the optimizations  
were unconstrained. In order to increase the numerical  
accuracy and to reduce oscillations during the molecular  
geometry optimization, two-electron integrals and their  
derivatives were calculated by using the pruned (99,590)  
integration grid, having 99 radial shells and 590 angular  
points per shell, which was requested by means of the  
Gaussian 03 keyword “\text{Int = UltraFine}”.

Although a possible influence of a polar solvent on  
the detailed structures of \( \text{BU}[6] \), \( \text{BU}[6] \cdot \text{ClO}_4^- \) and \( \text{BU}[6] \cdot \text{BF}_4^- \) could be imagined, our quantum mechanical calcula- 
tions in similar cases, performed in an analogous way,  
showed very good agreement of experiment with theo- 
ry.

In the model calculations, we optimized the molecular  
geometries of the parent macrocycle \( \text{BU}[6] \) and its  
anionic complex species with \( \text{ClO}_4^- \) and \( \text{BF}_4^- \). The optimized  
structure of the free macrocyclic receptor \( \text{BU}[6] \) with  
\( C_3 \) symmetry is illustrated in Figure 1. At this point it  
should be noted that the six glycoluril units in the conside- 
red macrocycle adopt alternate conformations; the methi- 
ne hydrogen atoms on the convex face of each unit point  
into the cavity – its diameter is alternately 8.42 and 8.55 Å  
(see Figure 1). This macrocycle can be divided into two  
identical parts by a plane defined by the carbon atoms of

![Figure 1](image1.png)

**Figure 1.** Two projections of the DFT optimized structure of free  
macrocycle \( \text{BU}[6] \) \( \text{B3LYP/6-31G(d)} \). The diameter of the cavity  
in \( \text{BU}[6] \) is alternately 8.42 and 8.55 Å.

![Figure 2](image2.png)

**Figure 2.** Two projections of the DFT optimized structure of the  
\( \text{BU}[6] \cdot \text{ClO}_4^- \) complex \( \text{B3LYP/6-31G(d)} \). Each of the three oxy- 
gen of \( \text{ClO}_4^- \) is bound by four weak hydrogen bonds (2.44, 2.98,  
2.77, and 2.42 Å) with four methine hydrogens on the convex face  
of glycoluril units; the diameter of the cavity in \( \text{BU}[6] \cdot \text{ClO}_4^- \) is  
alternately 8.14 and 8.26 Å.
the six methylene bridges, and besides, the carbons of six carbonyl groups are arranged alternately above and below the mentioned plane in a “zigzag” manner.

Finally, the interaction energies of the BU[6] · ClO₄⁻ and BU[6] · BF₄⁻ complexes, involving the Boys-Bernardi counterpoise corrections, were found to be -158.6 and -182.1 kJ/mol, respectively, confirming the formation of the considered anionic complex species.

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4. References


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