Ab Initio Investigating the Bonding and Electronic Structure in Bismuth Calixarene Complexes

Liwei Zhao and Hua-Jun Fan

ABSTRACT

The geometric and electronic structures of calixarene bismuth(III) complexes have been investigated by ab initio method in this study. Three conformations (cone shape conformation with C\(_{2v}\) symmetry, 1,2-alternative conformation with C\(_{2h}\) symmetry and 1,3-alternative conformation) are investigated as possible binding modes between bismuth fragment and calixarene fragment. The optimized geometries are then compared with the recent reported crystal structure. Two bis-muth(III) fragments are needed to bind with calixarene ligand due to the inert-pair effect. Co-crystalized LiCl-DMSO fragment plays a crucial role in stabilizing the bismuth calixarene crystal, where the binding energy \(\Delta H\) is estimated to be 55.3 kcal/mol or 56.1 kcal/mol with zero-point energy correction. The estimated \(\Delta G\) is -28.2 kcal/mol for the complex, which is consistent with the strong HC\(_4\)Bi-ClLi interactions. The trans effect is evidenced by two slight longer Bi-O bond lengths.

INTRODUCTION

Recently, the calixarenes and related macrocycles have been receiving increased attention because of their polydentate ability to bind metals, as well as its selectivity and flexibility in binding to various metals [1-3]. As shown in the diagram, calixarenes can change not only the R-group, but also the oxygen to ester to accommodate the different oxidation states of metals. As a result, chemists have been focusing on synthesis, fine-tuning, and structural characterization of new metallocalixarenes for their potential applications in homogeneous catalysts and novel materials with transition metals and heavy main group elements [4-7]. While the bismuth complex with aryloxides and alkoxides demonstrated their extensive applications in catalysts, medicine, superconductor and ferroelectric materials [8-10], the recent work by Hanna et al. showed the different kind of binding mode of bismuth Calixarenes complexes and their chemistry properties are quite different from that of their lighter congeners[2,11-15]. Previous studies have shown that most
of the metal-calix[4] arene system usually binds in a tetradentate, cone-like fashion with square pyramidal complex [16,17]. Hanna et al. reported the synthesis and characterization of the heavy main group complex (bismuth (III) and antimony (III)) with calixarenes (where R=H, tert-butyl, allyl, respectively) that bind in alternative and partial cone mode with calixarenes [2,14,15]. Their study has provided unique opportunity for theoretical exploration on the structural and electronic difference comparison of these complexes in different binding modes. In this study, Hartree-Fock theory (HF) method will be employed to study the structural and electronic properties of Bismuth-Calixarene complex. The factors that contribute to the stability, bonding structure and geometry preference will be closely examined.

**COMPUTATIONAL DETAILS**

The ground state structures in this study all have been optimized using Hartree Fock methods included in Gaussian 09, Revision A.02 [18]. Due to the large size of the interested molecule and interested in the time and cost, standard basis set 6-31G was used for carbon, hydrogen and oxygen, LANL2DZ with ECP basis set was used for bismuth and chlorine during the geometry optimization [19]. Frequency calculations were also carried out to verify that the optimized geometries were indeed at the minimum. The energy terms and electronic structure calculations of aforementioned optimized geometries were obtained using HF/6-311G**//HF/6-31G model chemistry by performing separated single point calculations using 6-311G** basis set for carbon, hydrogen and oxygen, and Stuttgart Relativistic Large Core ECP basis set for bismuth and chlorine [19]. Additionally, the original calixarene is used where R=H (HC₄) to search the various conformation and binding modes of the complexes. Comparison between the tBu-calixarene ligand (R=tBu) and the original calixarene (R=H) shows little impact on electronic and structural properties. The co-crystallized LiCl and solvent were not used in the binding modeling probe, but was later used in charge decomposition and molecular orbital analysis. This pruned model was chosen for its size to reduce the computational cost but still yield important electronic and geometric representation of the original complex. Maximum symmetry has been preserved for the cone-shape (a local Cᵥ₂ symmetry) and 1,3-alternative (a local Cᵥ₂h symmetry) though the comparison between the higher symmetry with lower symmetry is made structurally and electronically.

**RESULTS AND DISCUSSIONS**

When Lattman et al. compared phosphorus and arsenic calixarene complexes, a few important differences were noticed [20]. Vigalok et al. found the similar dimetallic binding pattern of zinc-calixarene complexes [21]. Similar to the antimony- and bismuth-calixarenes complexes, the reaction conditions such as temperature and reaction stoichiometry can lead to either alternate flattened cone or conic inclusion conformations. The estimated covalent radii of zinc, antimony and bismuth is 131, 138 and 146 pm, respectively, verse those of phosphorous and arsenic are 106 and 109 pm, respectively [22]. Other studies showed that changing Sb(III) to Bi(III) in the sulfide compound expanded the basic building block and
contraction of intervals between these building blocks [23]. For example, the inert-pair effect dominant the oxidation and reaction in the group, such as the decreasing hydrolyze reaction rate from P to Bi for trihalides compounds [24,25]. The origin of this inert-pair effect was first discussed by Jorgensen in 1971 as the relativistic origin [26]. However, to reproduce this inert-pair effect or relativistic contributions computationally were deemed to be hard if not impossible. For example, the calculated energy gap between the s- and p-orbital increases from 7.5 eV of P to 9.4 eV for Bi, however, it is hard to claim that such small amount of increased energy gap is due to either the stabilization of s-orbital or destabilization of p-orbital. Though experimentally, this inert-pair effect is consistent with the recent synthesis of bismuth(III) and antimony(III) calixarene complexes [2].

In the interest of clarity, a schematic cup-type formation of calixarene is used in the following drawing, where Latin calix means “cup” (see Fig. 1). Each circle represents a benzene ring from the calixarene ligand. It is worth pointing out that this cup-formation is particularly of interests to medical application because such cup-formation can be used to model the active site of enzyme, where the metal at the bottom of the cup mimic the cofactors in the enzyme [27]. In this study, three conformations of calixarene were identified according to the arrangement of four arene rings and their corresponding local symmetry: the cone shape conformation (A in the Fig. 1), which has C$_{2v}$ locally symmetry; followed by the 1,2-alternative conformation (B) with C$_{2h}$ symmetry and 1,3-alternative conformation (C) (no symmetry with Bi$_2$Cl$_2$ fragment). Each conformation was optimized with the methods stated in “Computational Details” section and confirmed with frequency calculations.

![Figure 1. Schematic representation of three modeling conformations of calixarene ligand.](image)

One can see from the optimized geometry parameters in Table 1, conformation A is the worst for HC$_4$Bi$_2$Cl$_2$. This is almost exclusively due to the deformation energy needed to distort the complex in order to maintain the C$_{2v}$ symmetry computationally. Additionally, with C$_{2v}$ symmetry, the bismuth(III) would lose the agnostic interaction from the third oxygen, which would help to stabilize the conformation (i.e., the weak interaction between Bi(2) with O(2) in Fig. 2). As such, the conformation A is 26.4 kcal/mol higher in energy than that of conformation B. It is interesting to point out that, by relaxing the conformation B from C$_{2h}$ symmetry can offer a third Bi-O bond. This relaxation further stabilizes the conformation B 23.90kcal/mol. This relaxed geometry is the closest to the crystal structure [2,14,15].
While the numerical discrepancy of conformation B and C is small when comparing with crystal structure of HC₄Bi₂Cl₂, the position of two bismuth atoms and relative stability of two conformations are drastically different. Conformation B has O(1) (ether oxygen atom in ring 1) and O(4) bind to Bi(1), O(2) and O(3) bind to Bi(2). Their bond lengths are 2.024 Å and 2.079 Å. A third Bi-O bond between Bi(1) and O(2) (similarly between Bi(2) and O(4)) with bond length of 2.341 Å is identified in conformation B. This Bi-O bond is trans to Cl, which explains the lengthening Bi-O bond due to trans effect. This trans effect was originally used to describe a phenomenon that one ligand tends to weaken the other ligand bonded trans to itself [16, 25, 26, 28]. Unlike the model molecules, the crystal structure shows one relative short Bi-O bond (2.124 Å) and two relative long Bi-O bonds (2.300 and 2.362 Å). This discrepancy can be justified by not taking the co-crystalized LiCl•DMSO fragment into the modeling. The Cl from LiCl fragment is situated endohedrally in the partial cone space where is trans to one of the Bi-O bond, such as the space opposite of O(2) and O(4). Consequently, the Bi-Cl distance in the reported crystal structure (2.607 Å) is slightly longer than that of BiCl₃, which is 2.424 Å [29].

![Figure 2](image_url)

The optimized geometry of conformation B (right) and C (left) of HC₄Bi₂Cl₂. Hydrogen is omitted for clarity. The each ring is labeled for indexing.

The bonding and geometry arrangement for conformation C is much different from that of conformation B. As shown in Fig. 2, Bi(1) is bridged to bond O(1) and O(3), while Bi(2) is bridged to bond O(2) and O(4). However, due to the trans effect from Cl situated across of O(2) and O(4), Bi(1) forms three strong Bi-O bond with O(1) 1.986, O(2) 2.103, and O(3) 2.057 Å, while Bi(2) forms two relative weak Bi-O bonds with O(4) 2.381 and O(2) 2.580 Å. As such, this conformation is 44.8 kcal/mol less stable in energy than conformation B. The Bi-Bi distances of these conformations (A: 3.833 Å, B: 3.695 Å and C: 4.096 Å) are still much longer than reported Bi-Bi single bond (2.99 Å [30]) and Bi=Bi double bond (2.82 Å [31]). The reported crystal Bi-Bi distance is 3.922 Å.
The optimized geometry parameters of $^{1}\text{BuC}_4\text{Bi}_3\text{Cl}_2$ basically trace those of $\text{HC}_4\text{Bi}_2\text{Cl}_2$ as expected. The discrepancy in one of the Bi-O bond length most likely is due to the crystal packing. Additionally, when closely examining the crystal structure, it reveals that the LiCl•DMSO is serving more than role of the solvent. Firstly, the bond length between Li atom and oxygen atom from DMSO is 1.933 Å (optimized bond length is 1.919 Å) is comparable to other crystal structure such as LiBr•Dimethyl ether, but is much longer than that in Li$_2$O (1.689 Å) [32]. In order to understand the interaction between LiCl•DMSO fragment and $\text{HC}_4\text{Bi}_2\text{Cl}_2$ fragment, the crystal structures of these two fragments are investigated. The Li-Cl bond length is 2.367 Å in the crystal structure, which is slight longer than the typical Li-Cl compound (2.021 Å). The crystal structure shows this Cl from LiCl also serves as agonistic interaction with bismuth(III), which is energetically favorable. The calculated formation energy of these two fragments is 55.3 kcal/mol, or 56.1 kcal/mol with zero-point energy correction. The calculated ΔG energy is 28.2 kcal/mol favored to form the complex, which is consistent with the strong $\text{HC}_4\text{Bi}$-ClLi interactions.

**SUMMARY**

In summary, we investigated the geometric and electronic structures of three conformations of calixarene bismuth(III) complexes. The calculation indicated, co-crystalized LiCl-DMSO fragment plays a crucial role in stabilizing the bismuth calixarene crystal, where the binding energy ΔH is estimated to be 55.3 kcal/mol or 56.1 kcal/mol with zero-point energy correction. The estimated ΔG is -28.2 kcal/mol for the complex, which is consistent with the strong $\text{HC}_4\text{Bi}$-ClLi interactions. This work highlights an efficient strategy for ligand design, which could potentially be applied to the organic and oxidation catalysis, medicine and other oxide based materials.

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