Investigation of Complexes between Calix[4]arene and Molybdenum/Tungsten: a Theoretical Approach

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Abstract

These days Calixarenes are widely investigated as container agents. They can carry Alkali metals, transition metals and some drugs and viruses. In this work, interactions between calix[4]arene and Molybdenum/Tungsten are investigated. The free energies, enthalpies and thermal energies are calculated by B3LYP/LANL2DZ level. The obtained results show that the reactions are irreversible and exothermic. They are more stable than the single agents. The double bond properties of $W=O_{54}$ and $Mo=O_{53}$ are proved. NBO analysis displays that some donor-acceptor interactions between LP of Oxygen atom and π^*orbitals of metals can make the structures more stable.

Keywords: Calixarene, Molybdenum, Tungsten, DFT, NBO.

Introduction

Calix[n]arenes are macrocyclic molecules made of n phenol units connected by ortho methylene groups [1].The simplest and most common family has four phenolic residues and thus they are known as Calix[4]arenes [2] and resembles cup with a defined upper and lower rim and a central annulus. The upper and lower rims are possible to prepare various derivatives with differing selectivity for various questions and small molecules [3]. They have been studied in the context of electrochemical switches sensors [4] and liquid crystals [5]. They are important in molecular recognition as molecular filters [6] and in many other applications [7].

Thus four phenoxyl groups in the Calix[4]arenes reactions with transition metal complex can produce alkoxides with substitution of from one to four hydrogen atoms [8].

The Calixarenes can be organized through their conformational flexibility with shape-specific π-rich cavities capable of metal…π-arene interactions as well as the metal to oxygen centre interplay [9]. In the unsubstituted form, Calix[4]arenes display four distinct structural conformation at room temperature, these are identifed as cone , partial cone, 1-2alternate,1-3 alternate [10]. In the con scheme metal ions con bind to the phenolate oxygen centres either by residing inside or outside of the calixarene cavity, endo and exo, respectively [9]. Ion may

interact with the(π)-faces of the aromatic groups whilst simultaneously interaction with the calix[4]arene phenol oxygen, whereas in the exo case a metal ion cone is unfavourable [9]. Between metals which intract by calixarenes tungsten and molybdenum are in the most important groups. Several oxo and chloro tungasten(VI)complexes with calix[4]arenes have been prepared and used (W(eg)3)(eg=1,2-ethanediolato dianion) in the preparation material for new tungesten(VI)complexes.The eg ligsnds are randomly distributed in a 1:1 ratio over W(VI)atoms of the complex in the unit cell [11].The first molybdenum complex derived from a large calixarene was raedily prepared from the imido-alkoxie complex (MO(NAr)2(oBut)2)(Ar=2,6-Pr2C6H3) via alkoxide and imide displacement reactions. Lettman has demonstrated the ability of the calix(5)arene ligand to accommodate both a main group ligand [12].

Because of the importance of these intractions between molybdenum/tungsten and calixarenes, in this work a theoretical investigation of these complexes is performed.

Computational method

All of the calculations are carried out by a pc computer which has Intel (R) Pentium Dual CPU with 2GB RAM. The Calix[4]arene includes 56 atoms (4 O),(25 H),(27 C) which reacts with tungsten/molybdenum. Geometry optimization is performed by Gaussview [13] and Gaussian 03 [14] softwares by DFT/B3LYP method [15] and LANL2DZ basis set. The selected calix[4]aren is made by Gaussview and optimized by Gaussian 03 by B3LYP/LANL2DZ method (Fig. 1). Then composites between calix[4]arene and molybdenum/tungsten are formed and optimized by B3LYP/LANL2DZ method (Fig. 2,3). For optimized molecules, bond angles and bond lengths are calculated. Natural bond orbital (NBO) calculations have been also performed for all structures using the standard LANL2DZ basis set.
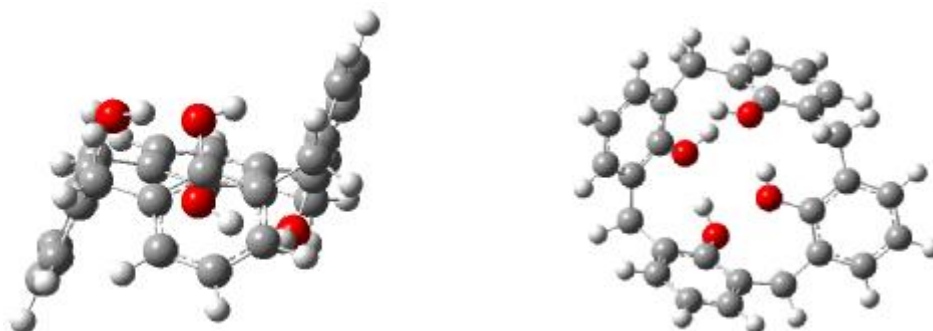

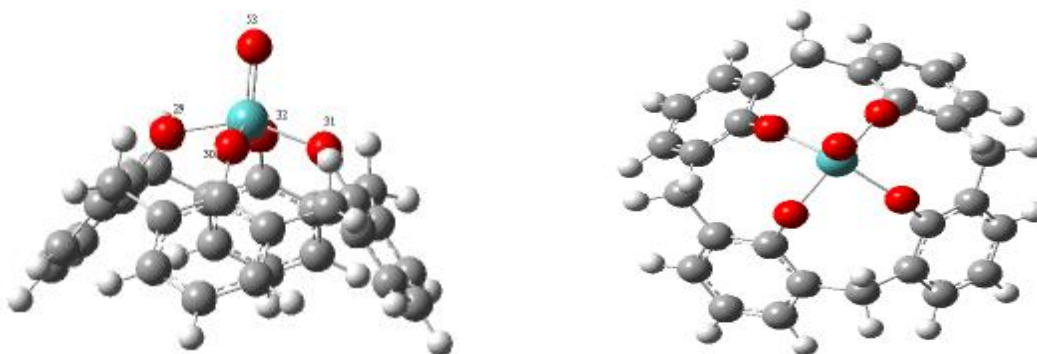Fig. 1. Two images of Calix[4]arene

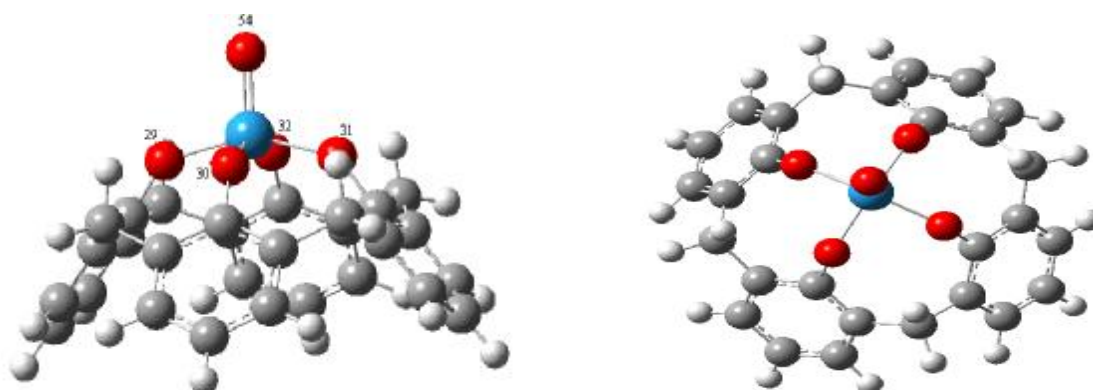Fig. 2. Complex between Molybdenum and Calix[4]arene

Fig. 3. Complex between Tungsten and Calix[4]arene

Results and Discussion

The obtained free energies, enthalpies and thermal energies in 298K are shown in table 1.

Agent	ΔG^0 / kcal mol^{-1}	ΔH^0 / kcal mol^{-1}	ΔE^0 / kcal mol^{-1}
Calixarene-Tungsten	-1001272.304	-1001198.353	-1001198.353
Calixarene-molybdenum	-1001011.37	-1000937.464	-1000938.058

Table 1. Obtained energies calculated by B3LYP/LANL2DZ level

In which ΔG^0, ΔH^0 and ΔE^0 are the changes in energies of following two reactions:

1) Calixarene +Mo → Complex 1
2) Calixarene+W→ Complex2

By evaluating the energies of these reaction, it is clear that both of these reaction are irreversible ($\Delta G^0 < 0$) and exothermic ($\Delta H^0 < 0$).

Also by investigating of these reactions, it is understandable that the complexes between calix[4]arene and the named metals are more stable than the single agents.

Table 2 shows the obtained bond lengths and bond angles.

Agent	Metal-O$_{54/53}$ Bond length/Å	Metal-O$_{29}$ Bond length/Å	O$_{29}$-Metal-O$_{54/53}$ Bond Angel	C$_{22}$-O$_{29}$-Metal Bond Angel
Calixarene -Tungsten	1.729	1.90	104.6	139.9
Calixarene-molybdenum	1.721	1.92	104.3	138.6

Table 2. Obtained parameters calculated by B3LYP/LANL2DZ level.

From the obtained results, it is shown that the bond lengths of W−O$_{54}$ and O$_{29-31}$−W are different.It can confirm the double bond of W=O$_{54}$. For the complex 1, it is the same, too.

From the bond angle, it is clear that the O−Metal−O$_{53-54}$ angle is tetrahedral.

Also NBO calculation results are shown in table3.

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Calixarene-Tungsten		Calixarene-molybdenum	
Donor $\rightarrow$ Acceptor	E_2/ kcalmol^{-1}	Donor $\rightarrow$ Acceptor	E_2/ kcalmol^{-1}
$LP_{(3)\,O29} \rightarrow \pi^*_{W\text{-}O54}$	38.64	$LP_{(3)\,O29} \rightarrow \pi^*_{O53\text{-}Mo}$	39.32
$LP_{(3)\,O30} \rightarrow \pi^*_{W\text{-}O54}$	38.41	$LP_{(3)\,O30} \rightarrow \pi^*_{O53\text{-}Mo}$	39.25
$LP_{(3)\,O31} \rightarrow \pi^*_{W\text{-}O54}$	38.41	$LP_{(3)\,O31} \rightarrow \pi^*_{O53\text{-}Mo}$	39.25
$LP_{(3)\,O32} \rightarrow \pi^*_{W\text{-}O54}$	38.64	$LP_{(3)\,O32} \rightarrow \pi^*_{O53\text{-}Mo}$	39.32

Table3.The second – order perturbation energy $E_{(2)}$ (donor$\rightarrow$acceptor) calculated by B3LYP/LANL2DZ level.

In this context, a study of hyperconjugative interactions has been completed. Hyperconjugation may be given as a stabilizing effect that arises from an overlap between an occupied orbital when these orbitals are properly oriented. This noncovalent bonding – antibonding interaction can be quantitatively described in term of the NBO approach that is experessed by means of the second-order perturbation interaction energy(E_2). This energy represents the estimate of the off-diagonal NBO Fock matrix element [16-18]. Here we are interested in the interactions between the Oxygen lone pairs orbitals as donor and some acceptor orbitals that the most important of them are as follow: In calixarene-W composite hyperconjugation in $LP_{(3)O29\text{-}31} \rightarrow \pi^*_{W\text{-}O54}$ have maximum energy. In calixarene-Mo composite the most important transfers are $LP_{(3)O29\text{-}31} \rightarrow \pi^*_{Mo\text{-}O53}$.

Conclusions
In this Work the results show the complexes between calixarene and Mo/W are more stable than the single agents. These reactions are irreversible and exothermic. The double bond properties of $W=O_{54}$ and $Mo=O_{53}$ are proved.
NBO analysis displays that some donor-acceptor interactions between LP of Oxygen atom and π^* orbitals of metals can make the structures more stable.

References
[1] F . A . Cotton , G . Wilkinson , C . A . Murillo , G . Bochmann , Advanced Inorganic Chemistry 6th ., wile – Interscience , New York , 1999 , P . 475.
[2] F . Albert Cotton , lee M . Daniel , chun lin , carlos A . Murillo , Inorganica Chimica Acta , 2003 . p , 1-8
[3] Gillian Mc Mahan , Shane O‚malley , and Kieran Molan , Arkivoc 2003(vii)23-31.
[4] p . L . boulas , m . Gomez-Caifer , L . Echegoyen , Angew . Chem ., Int . Ed . Engl . 37(1998)216.
[5] C . mieser , C . B . Dieleman , D . Matt , Coord . Chem . Rev . 165(1997)93.
[6] A. Ikeda , s . shinkai , chem . Rev . 97(1997)1713 .
[7] R . Ludwig , Fresenius‚ J .Anal . chem367(2000)103.
[8] V . Böhmer , Angew . Chem ., Int. Ed . Engl . 34(1995)533.

[9] Antonella J . Petrella , colinaL . Raston , Journal of organometallic Chemistry 689 (2004)4125-4136

[10] C . D . Gutsche , Calixarenes Revisited , Royal Society of Chemistry , Cambridge , 1998.

[11] Ari Lehtonen and Reijo Sillanpää , Polyhedron Vol . 17 , No . 19 , pp . 3327-3330 , 1998.

[12] Carl Redshaw , Coordination Chemistry Reviews 244 (2003) 45-70.

[13] A .Frisch , A . B . Nielsen and A . J . Holder , Gaussianview users Manual, Gaussian Inc (2000).

[14] M . J . Frisch et al . Gaussian 03 , Revision D.01, Gaussian In c ,Walling Ford ct (2004).

[15] A . D . Becke , J .Chem . Phys . 98 (1993) 785.

[16] L.Padmaja 1, M. Amalanathan, C. Ravikumar, I.Hubert Joe, Spectrochimic Acta A 74 (2009)349.

[17] E. Zahedi , M . Aghaie , K . zare , J . Mol . struct . (THEOCHEM), 905 (2009)101 .

[18] S . Sebastian , N . sundaraganesan ,J . Spectrochimica Acta A, 75(2010)941.

مطالعه تشکیل کمپلکس بین کلیکس آرن (4) و فلزات تنگستن/ مولیبدن به روش محاسباتی

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چکیده:

در سالهای اخیر استفاده از کلیکس آرنها به عنوان مواد حامل مواد بسیار وسیع شده است. این گونه از مواد می توانند فلزات قلیایی و واسطه، داروها و برخی از ویروس ها را در حفره درونی خود حمل کنند. در این مقاله بر هم کنش بین کلیکس آرن (4) با فلزات مولیبدن و تنگستن بررسی شده است. انرژی آزاد گیبس، آنتالپی و انرژی گرمایی واکنش تشکیل کمپلکس بین مواد نامبرده به روش تئوری تابعیت دانسیته و سطح B3LYP/LANL2DZ محاسبه شده است. نتایج بدست آمده نشان می دهد که این واکنش ها خودبخودی و گرمازا بوده و کمپلکس تشکیل شده پایدارتر از هر یک از مواد به تنهایی می باشند. همچنین خصلت دو گانه پیوند بین فلز و کلیکس آرن مورد نظر اثبات می شود. محاسبات NBO انجام شده دلیل پایداری این کمپلکس را فوق مزدوج شدن بین الکترونهای غیر پیوندی اکسیژن کلیکس و اربیتال π^* فلز معرفی می کند.

واژههای کلیدی : کلیکس آرن (4) ، مولیبدن، تنگستن، DFT،NBO .