

Molecular Design of Calix[4]Arene Derivatives for Uranyl Ion Extraction from Aqueous Media

D. Yüksel

Hacettepe University Department of Chemistry, Organic Chemistry Section, Beytepe 06800 Ankara, Turkey

Abstract. Uranyl ion extraction is an important part of nuclear waste reprocessing. Use of organic ligands having chelating property with uranyl ions is a promising tool in this area, because of the possibility to improve the selectivity and the affinity of the ligands towards uranyl ions.

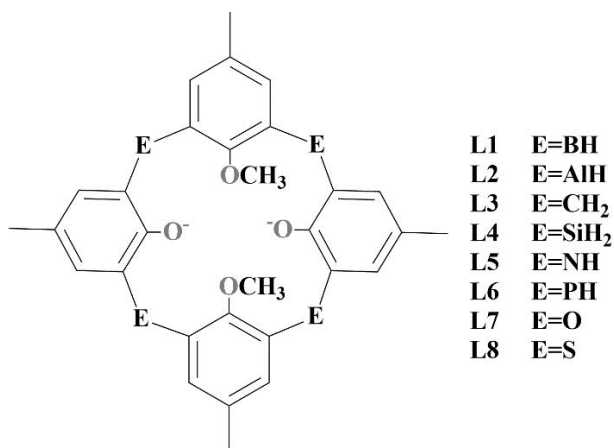
In this study, Calix[4]arene derivatives containing B, Al, C, Si, N, P, O and S elements in bridging positions were designed and their chelating energetics with uranyl cation are calculated by means of DFT methods.

Keywords: uranyl ion extraction, calixarenes, binding energy, DFT, PCM

1 Introduction

The uranyl ion, UO_2^{2+} , which is the main waste product in the nuclear industry, has high stability in aqueous media, and can be re-used in the nuclear reactors after extraction from the spent fuel. The investigations on improving the stability and the extractability of uranium (VI) complexes are very important for nuclear-waste reprocessing. Furthermore, uranyl ion extraction and removal from sea waters and ground waters is also crucial for ecological safety, because uranyl ion is toxic and possesses significant risk for aquatic organisms and other biological systems.

For all these reasons, new methods have been continually sought to design molecular or polymeric ligand systems showing high affinity and selectivity towards uranyl ions [1-5]. Among these ligand systems, calixarenes are promising macrocyclic ligands with their non-toxic structures. To date, calixarenes have been investigated in many forms such as nanoemulsions for removing uranyl contamination from the skin [6], as self-assembled cages for binding uranyl cation [7], and as selective metal binding ligands for uranyl and other metal ions [8-11].



Scheme 1. Chemical structures of the calix[4]arene ligands.

In this study, eight proposed Calix[4]arene ligands, containing B, Al, C, Si, N, P, O and S atoms in bridging positions (**L1-L8** shown in Scheme 1) were investigated theoretically on their chelating energetics with uranyl cation.

2 Computational Methods

All calculations presented in this work were performed with Gaussian 09 molecular modeling software[12] using density functional theory (DFT) [13] and hybrid functional B3LYP (Becke's three parameter exact-functional combined with gradient-corrected correlational functional of Lee, Yang and Parr), in combination with 6-31g(d) basis set. Proposed structures were characterized in both gaseous and aqueous phases. Energetics in aqueous medium were examined by applying the polarizable continuum model (PCM). All optimized geometries were also subjected to frequency analyses at the same level of optimization to verify the nature of the stationary points and to calculate thermochemistry data.

3 Results and Discussion

Optimized geometries for uranyl ion-Calix [4]arene ligand complexes **C1-C8**, are as shown in Figure 1. Calculated Uranium-Oxygen distances and complexation energetics are listed in Table 1 and in Table 2, respectively. According to the calculation results, all ligand systems (**L1-L8**) are found suitable for uranyl ion extraction, with negative reaction free energy values. Among these, the strongest binding was observed for CH_2 bridged complex in both gaseous and aqueous phases. Descending binding strength order for the complexes are as **C3>C5>C6>C4>C8>C7>C1>C2** in gaseous phase and as **C3>C4>C5>C6>C1>C7>C8>C2** in aqueous phase. It is seen that in aqueous phase binding power of silicon bridged ligand has improved with respect to that of nitrogen and phosphorus-bridged ligands. This behavior may have been

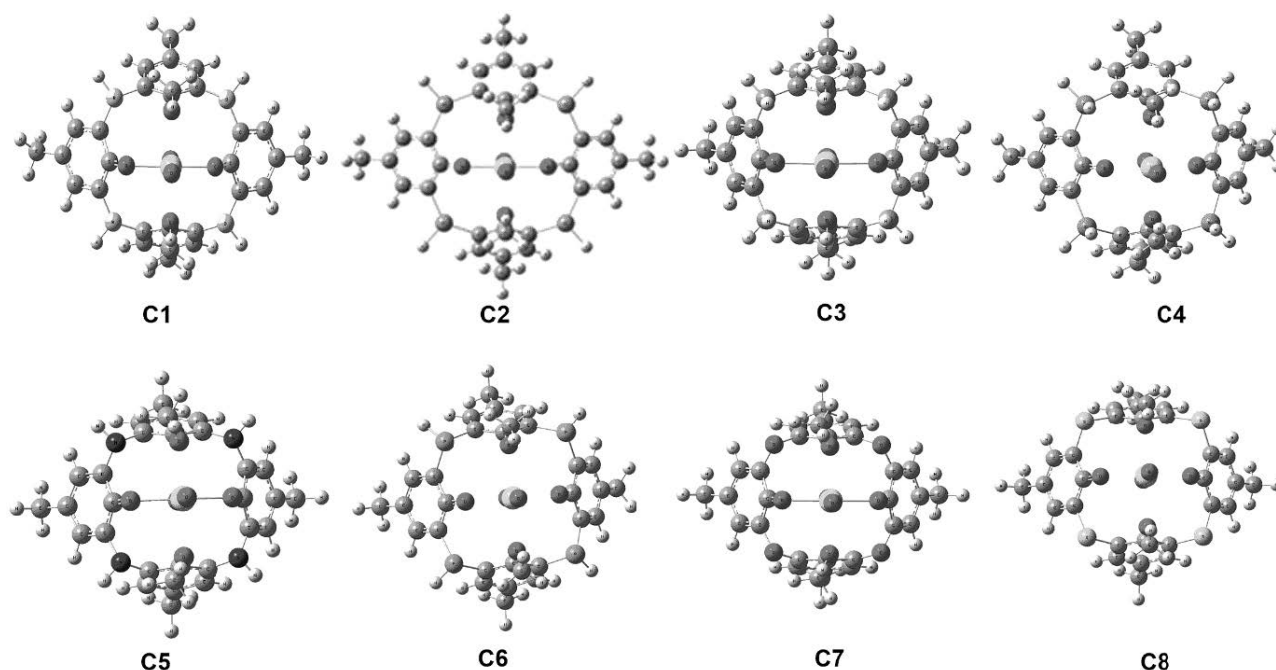


Figure 1. Optimized geometries of calix[4]arene ligand-uranyl complexes.

Table 1. Uranium-oxygen distances in uranyl complexes (Å)

	C1	C2	C3	C4	C5	C6	C7	C8
U=O(Uranyl)	1.824	1.829	1.826	1.822	1.825	1.819	1.822	1.818
U=O(Uranyl)	1.815	1.816	1.811	1.812	1.819	1.812	1.817	1.813
U-OPh	2.165	2.167	2.176	2.186	2.169	2.190	2.163	2.188
U-OPh	2.164	2.167	2.178	2.188	2.169	2.192	2.176	2.189
U-OMe	2.386	2.443	2.430	2.444	2.432	2.441	2.428	2.446
U-OMe	2.386	2.443	2.431	2.444	2.433	2.441	2.428	2.447

Table 2. Calculated relative energies, enthalpies and free energies of complex formation reactions of ligands with uranyl cation (kcal/mol) in gas and aqueous phases

	ΔE_g	ΔE_{aq}	ΔH_g	ΔH_{aq}	ΔG_g	ΔG_{aq}
$L1^{2-} + [UO_2]^{2+} \rightarrow C1$	43.1	21.5	44.0	21.7	39.9	19.2
$L2^{2-} + [UO_2]^{2+} \rightarrow C2$	113.3	76.0	114.9	76.6	108.6	75.4
$L3^{2-} + [UO_2]^{2+} \rightarrow C3$	0.0	0.0	0.0	0.0	0.0	0.0
$L4^{2-} + [UO_2]^{2+} \rightarrow C4$	11.6	7.3	11.6	7.3	11.2	8.7
$L5^{2-} + [UO_2]^{2+} \rightarrow C5$	8.1	12.2	8.2	12.1	6.3	12.2
$L6^{2-} + [UO_2]^{2+} \rightarrow C6$	10.4	16.9	10.1	16.7	11.7	17.9
$L7^{2-} + [UO_2]^{2+} \rightarrow C7$	27.3	23.1	27.5	23.3	26.2	21.9
$L8^{2-} + [UO_2]^{2+} \rightarrow C8$	12.9	24.5	12.8	24.6	12.6	23.8

originated from H-bonding property of electronegative N and P elements with water molecules, leading a decrease in the affinity of the ligand towards uranyl ions.

4 Conclusions

Computational results show that all Calix [4]arene ligands, investigated in this study were able to bind to the uranyl cation with an average distance value of 2.177 Å U-O distance, which is slightly longer than a single covalent bond (2.060 Å) within experimental results. Negative complex formation free energy values also support this finding with a range from -496.8 and -31.9 kcal/mol (C2) to -605.4

and -107.3 kcal/mol (C3) in gaseous and aqueous media, respectively.

References

- [1] Metilda P., Prasad K., Kala R., Gladis J.M., Prasada Rao T., Naidu G.R.K., Ion Imprinted Polymer Based Sensor for Monitoring Toxic Uranium in Environmental Samples, *Analytica Chimica Acta* **582** (2007) 147-153.
- [2] Tashkhouriana J., Moradi Abdolousofi L., Pakniat M., Montazerzohori M., Sodium Dodecyl Sulfate Coated Alumina Modified with a New Schiff's Base as a Uranyl Ion Selective Adsorbent, *Journal of Hazardous Materials* **187** (2011) 75-81.
- [3] Sun Y., Yang S., Chen Y., Ding C., Cheng W., Wang X.,

- Adsorption and Desorption of U(VI) on Functionalized Graphene Oxides: A Combined Experimental and Theoretical Study, *Environ. Sci. Technol.* **49** (2015) 4255-4262.
- [4] Bühl M., Sieffert N., Chaumont A., Wipff G., Water versus Acetonitrile Coordination to Uranyl. Effect of Chloride Ligands, *Inorg. Chem.* **51** (2012) 1943-1952.
- [5] Pattenau S.A., Kuehner C.S., Dorfner W.L., Schelter E.J., Fanwick P.E., Bart S.C., Spectroscopic and Structural Elucidation of Uranium Dioxophenoxazine Complexes, *Inorg. Chem.* **54** (2015) 6520-6527.
- [6] Spagnul A., Bouvier-Capely C., Adam M., Phan G., Rebière F.O., Fattal E., Quick and Efficient Extraction of Uranium from a Contaminated Solution by a Calixarene Nanoemulsion, *International Journal of Pharmaceutics* **398** (2010) 179-184.
- [7] Pasquale S., Sattin S., Escudero-Adán E.C., Martínez-Belmonte M., de Mendoza J., Giant Regular Polyhedra from Calixarene Carboxylates and Uranyl, *Nature Communications* **3** (2012) 785.
- [8] Guang-Ke L., Zhen-Xiang X., Chuan-Feng C., Zhi-Tang H., A Highly Efficient and Selective Turn-On Fluorescent Sensor for Cu²⁺ Ion Based on Calix[4]arene Bearing Four Iminoquinoline Subunits on the Upper Rim, *Chem. Commun.* (2008) 1774-1776.
- [9] Sayin S., Yilmaz M., Synthesis of a New Calixarene Derivative and its Immobilization onto Magnetic Nanoparticle Surfaces for Excellent Extractants Toward Cr(VI), As(V), and U(VI), *J. Chem. Eng. Data* **56** (2011) 2020-2029.
- [10] Asfari Z., Bilyk A.J., Dunlop W.C., Hall A.K., Harrowfield J.M., Hosseini M.W., Skelton B.W., White A.H., Subtleties with Sulfur: Calixarenes as Uranophiles, *Angew. Chem. Int. Ed.* **40** (2001) 721-723.
- [11] Schühle D.T., Peters J.A., Schatz J., Metal Binding Calixarenes with Potential Biomimetic and Biomedical Applications, *Coordination Chemistry Reviews* **255** (2011) 2727-2745.
- [12] Frish M.J. et al., GAUSSIAN 09, revision C.01; Gaussian, Inc.: Wallingford, CT (2010).
- [13] a) Hohenberg P., Kohn, W., Inhomogeneous Electron Gas, *Phys. Rev.* **136** (1964) B864-B871;
b) Kohn W., Sham L.J., Self-Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev.* **140** (1965) A1133-A1138.
c) Parr R.G., Yang W., Density-functional theory of atoms and molecules, Oxford Univ. Press, Oxford (1989).
d) Salahub D.R., Zerner M.C., The Challenge of d and f Electrons, ACS, Washington D.C. (1989).