

**科学研究費助成事業 研究成果報告書**

平成 27 年 5 月 24 日現在

機関番号：11301

研究種目：基盤研究(C)

研究期間：2012～2014

課題番号：24550172

研究課題名(和文) 環境中の放射性セシウム137の検出と除去を行う新規レセプターの計算化学による設計

研究課題名(英文) Design by computational chemistry of a new receptor for the detection and removal of radioactive cesium-137 in the environment

研究代表者

Pichierri Fabio (Pichierri, Fabio)

東北大学・工学(系)研究科(研究院)・准教授

研究者番号：40374920

交付決定額(研究期間全体)：(直接経費) 4,300,000円

研究成果の概要(和文)：Cs<sup>+</sup>イオンとククルビトリル、カリックスアレーン、スルホランそれぞれとの結合について、これら大環状化合物の結晶構造を用いてDFT計算することにより調査した。ククルビトリルは、二つのCs<sup>+</sup>イオンと結合することができるカボチャの形の分子である。計算結果は、水和したCs<sup>+</sup>イオンのククルビトリルへの結合が弱いCs-OH<sub>2</sub>結合によって好まれることを示していた。カリックスアレーンへのCs<sup>+</sup>イオンの結合は、対イオンの重要性を示していた。スルホランを用いることの利点は、この分子が常温で液体であることである。さらに、硫酸塩やアンモニウムイオンと結合したCs<sup>+</sup>イオンを含むクラスターの構造についても研究した。

研究成果の概要(英文)：Using DFT calculations and the crystal structures of selected macrocycles we investigated the binding of Cs<sup>+</sup> ion to cucurbituril, calixarene, and sulfolane. Cucurbituril is a molecule with the shape of a pumpkin which can bind two Cs<sup>+</sup> ions. The calculations indicate that binding of hydrated Cs<sup>+</sup> ions to cucurbituril is favored by the weak Cs-OH<sub>2</sub> bond. The binding of Cs<sup>+</sup> ions to calixarene showed the importance of counterions. The advantage of using sulfolane is that this molecule is liquid at room temperature. Finally, we studied the structures of clusters containing Cs<sup>+</sup> ions bonded to sulfate and ammonium ions.

研究分野：量子化学計算

キーワード：有害化学物質 計算化学 イオン認識

## 1. 研究開始当初の背景

In the aftermath of Fukushima Dai-ichi (福島第一) nuclear reactor plant accident, a large amount of radioactive nuclides ( $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{131}\text{I}$ ) were detected in eastern Japan, particularly in the Tohoku (東北) region which comprises the prefectures of Miyagi, Aomori, Yamagata, Fukushima, and Iwate. Other neighboring prefectures (Saitama, Chiba) also were contaminated. A recent analysis carried out by the Ministry of the Environment (環境省) resulted in the construction of a detailed map about  $^{137}\text{Cs}$  distribution in the above prefectures. Because the half-life of  $^{137}\text{Cs}$  is ~30 years, this element poses a special danger to human health in a long time span. Hence, this radioactive element should be efficiently removed from the contaminated environment so as to reestablish a safe and livable environment. So far, many different types of organic macrocycles (artificial receptors) have been synthesized by research chemists and tested in the laboratory. The first examples of macrocycles which are able to detect  $\text{Cs}^+$  ions are calixarenes strapped with crown-ethers which have been proposed for the first time in 1994 by Ungaro and coworkers (Ungaro et al., *Angew. Chem. Int. Ed.* 33 (1994) 1506). Despite these receptors are capable of binding cesium, they are expensive to synthesize and they can be easily degraded by sunlight and other environmental effects if used in the contaminated environment. It is therefore important to develop a new, robust receptor which can be produced

cheaply and in large quantity.

## 2. 研究の目的

The purpose of the research is to design very efficient and highly selective artificial receptors for the detection of  $\text{Cs}^+$  in the environment with the aid of quantum chemical calculations. In order to achieve this goal, it is necessary to study the structures of the  $\text{Cs}^+$ /receptor complexes and calculate their binding energies. This must be done not only for cesium but also for other alkali metal ions ( $\text{Li}^+$ ~ $\text{Rb}^+$ ) which also can bind the receptor and therefore interfere with  $\text{Cs}^+$  binding. As the starting point, we decided to investigate the complex between  $\text{Cs}^+$  and the cucurbituril macrocycle whose structure was determined by Kim's group using single-crystal x-ray diffraction analysis (Whang et al., *Angew. Chem. Int. Ed.* 37 (1998) 78). In addition, we also investigated the interaction of  $\text{Cs}^+$  with sulfolane, which is a solvent at room T, and with a calixarene receptor. Finally, we investigated the structures of molecular clusters containing  $\text{Cs}^+$ , sulfate anions ( $\text{SO}_4^{2-}$ ), and ammonium cations ( $\text{NH}_4^+$ ). Recent experiments (Niimura et al., *J. Environ. Radioactivity*, 139 (2015) 234) indicated that  $\text{Cs}^+$  and the above molecular ions form nanoparticles which are not soluble in water. Information about the structure of these nanoparticles is important in order to develop new strategies for the removal of radioactive  $^{137}\text{Cs}$  from the contaminated environment.

### 3 . 研究の方法

Different research methods were employed during the project. First, we used the Cambridge Structure Database (CSD) which contains the crystal structures of organic and organometallic molecules characterized by single-crystal x-ray diffraction analysis. By searching the CSD we selected the molecular structures of Cs<sup>+</sup>/receptor complexes which have been characterized so far. These crystal structures were subsequently used as the starting geometries for density functional theory (DFT) calculations. DFT is a theoretical method based on the use of functions of the electronic density of atoms and molecules. This approach is very efficient for the calculation of large molecules containing metal atoms or ions. Also, when using large basis sets it is possible to obtain molecular structures which are in very good agreement with experiments. The effect of the solvent was modeled in two ways: first we used explicit water molecules bonded to Cs<sup>+</sup> and to the other ions. Second, we employed the polarization continuum model (PCM) of Tomasi which simulates the effect of the solvent with a continuum electrostatic field placed around the molecule. The inclusion of the solvent effect is important for obtaining more realistic results.

### 4 . 研究成果

We started our study from the cucurbituril macrocycle in complex with Cs<sup>+</sup>. Cucurbituril is a macrocycle that has the shape of a pumpkin. This macrocycle has been synthesized in large

quantity and it can be used for binding radioactive <sup>137</sup>Cs. The calculation results indicate that the Cs<sup>+</sup> ion binds the macrocycle by forming four or five Cs–O interactions. Also, water molecules are attached to the Cs<sup>+</sup> ion while a chloride anion (Cl<sup>-</sup>) is present inside the macrocycle's cavity (Fig. 1). This means that the aquaion Cs<sup>+</sup>(H<sub>2</sub>O)<sub>8</sub> loses a few water molecules so as to bind the carbonyl groups of cucurbituril.

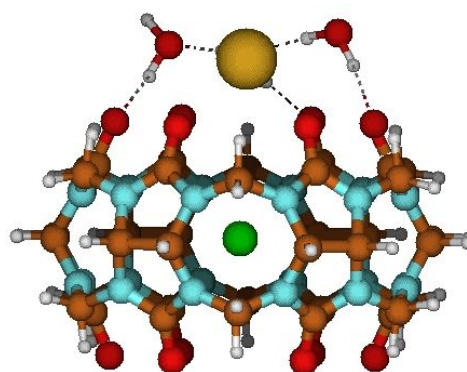


Fig. 1. Coordination of Cs<sup>+</sup>(H<sub>2</sub>O)<sub>3</sub> to cucurbit[6]uril. A chloride anion (Cl<sup>-</sup>) is present inside the macrocycle's cavity.

The competition for binding cucurbituril by other alkali metal ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>) also was investigated with DFT calculations. The results indicate that Li<sup>+</sup> is quite small and hence it can form only two Li–O interactions with the carbonyl groups. On the other hand, the other metal ions can bind cucurbituril as Cs<sup>+</sup> does. However, because the bond of these ions with water (M<sup>+</sup>–OH<sub>2</sub>) is much stronger than that with Cs<sup>+</sup> (17.1 kcal/mol), it is much easier to remove water from Cs<sup>+</sup> than removing it from the other alkali metal ions. This means that binding of Cs<sup>+</sup> to cucurbituril is favored with respect to the binding of

other alkali metal ions. Another advantage in using cucurbituril is the possibility of having two binding sites, one above and another below the macrocycle. A third advantage is that the size of the macrocycle can be changed by synthesizing smaller or larger macrocycles such as cucurbit[5]uril and cucurbit[7]uril, respectively. The larger macrocycle has a larger binding energy toward  $\text{Cs}^+$  meaning that it can bind the metal ion strongly than cucurbit[6]uril. In summary, this macrocycle could be used to remove  $\text{Cs}^+$  from water solutions containing this radioactive element. The solubility of the macrocycle in water, however, can be improved by chemical modifications.

Next I investigated the interaction of  $^{137}\text{Cs}$  with two molecules, a calixarene made of eight benzene rings and sulfolane which contains the  $\text{SO}_2$  group. Both molecules have been synthesized in gram quantities and their structures determined by x-ray crystallography. The calixarene has a cavity with the right size to accommodate a single  $\text{Cs}^+$  ion. Smaller ions such as  $\text{Li}^+$  and  $\text{Na}^+$  bind the OMe groups of only three benzene rings and therefore they are not selected by this macrocycle. On the other hand, the larger  $\text{K}^+$  and  $\text{Rb}^+$  ions can occupy the entire cavity of the macrocycle therefore competing with  $\text{Cs}^+$  for binding. The binding energy for binding  $\text{Cs}^+$  corresponds to 71.1 kcal/mol. This energy, however, changes when a counterion (anion) is present near the macrocycle. I investigated the effect of three anions ( $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{ClO}_4^-$ ) on the binding of the

corresponding ion pairs  $\text{Cs}^+/\text{X}^-$ . The calculations indicate that the  $\text{Br}^-$  anion provides the largest binding energy (59.2 kcal/mol) in comparison to  $\text{Cl}^-$  (51.6 kcal/mol) and  $\text{ClO}_4^-$  (58.8 kcal/mol). The reason for this result is due to the formation of additional  $\text{CH}\cdots\text{Br}^-$  interactions that are established with the calixarene molecule. Therefore the  $\text{Cs}^+/\text{Br}^-$  ion pair (Fig. 2) has the highest binding energy.

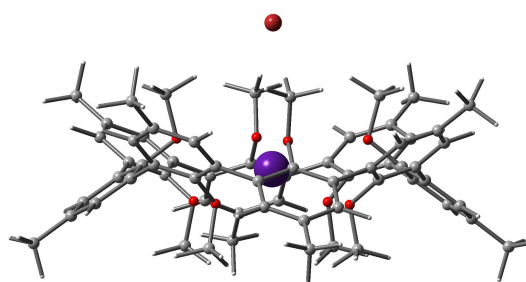


Fig. 2. Coordination of the  $\text{Cs}^+/\text{Br}^-$  ion pair to calixarene.

Sulfolane ( $\text{C}_4\text{H}_8\text{SO}_2$ ) possesses a large dipole moment of 4.7 Debye. This means that the dipole moment will favor the interaction with cations which will coordinate the  $\text{SO}_2$  moiety of sulfolane (Fig. 3).

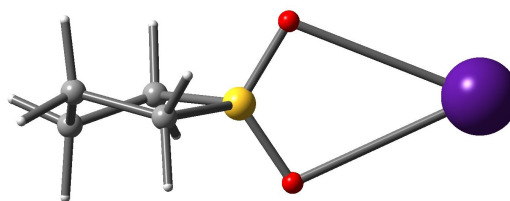


Fig. 3. Coordination of  $\text{Cs}^+$  by the sulfolane molecule.

The calculations of different sulfolane/ $\text{M}^+$  complexes ( $\text{M}^+ = \text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ) indicate that the binding energy

decreases from  $\text{Li}^+$  to  $\text{Cs}^+$ . However, the larger the ion the more sulfonate molecules can coordinate a single alkali metal ion. Because  $\text{Cs}^+$  has the largest ionic radii among the five alkali metal ions investigated, the coordination of  $\text{Cs}^+$  should be quite favorable when the concentration of this ion in solution is relatively high.

In a recent study by Niimura et al. (*J. Environ. Radioactivity*, 139 (2015) 234) it was discovered that  $^{137}\text{Cs}$  emitted by the Fukushima Dai-ichi nuclear plant is present in the soil in combination with sulfate ( $\text{SO}_4^{2-}$ ) and ammonium ( $\text{NH}_4^+$ ) ions. The resulting granular material is soluble in strong acids ( $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ ) but not in weak acid ( $\text{CH}_3\text{COOH}$ ). Using DFT calculations I have therefore investigated the structures of the clusters made of  $\text{Cs}^+$  ions bonded to sulfate and ammonium ions. Both charged and neutral clusters were considered. However, the neutral clusters are more important because they are less soluble in water than the charged clusters. The simplest neutral cluster does contain one sulfate group and two  $\text{Cs}^+$  ions and no ammonium ions (Fig. 4). Therefore, binary-type neutral clusters can be obtained by combining  $n$  sulfate groups and  $2n$   $\text{Cs}^+$  ions.

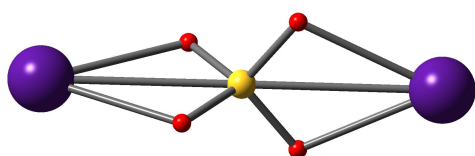


Fig. 4. Molecular structure of the neutral cluster  $\text{Cs}_2\text{SO}_4$ .

Another type of neutral clusters results from the combination of one  $\text{Cs}^+$  ion, one sulfate ion, and one ammonium ion (Fig. 5). Therefore, ternary-type neutral clusters can be obtained by combining  $n$   $\text{Cs}^+$  ions,  $n$  sulfate groups, and  $n$  ammonium ions (where  $n$  is an integer number).

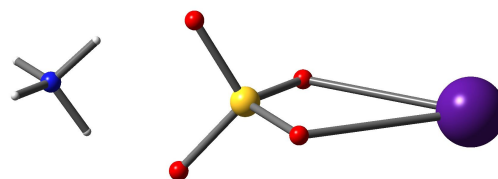


Fig. 5. Molecular structure of the neutral cluster  $\text{Cs}(\text{NH}_4)(\text{SO}_4)$ .

Hence, the DFT calculations suggest the possibility that granular cesium materials can arise from two family of neutral clusters: binary-type clusters  $(\text{Cs}^+)_{2n}(\text{SO}_4^{2-})_n$  and ternary-type clusters  $(\text{Cs}^+)_n(\text{SO}_4^{2-})_n(\text{NH}_4^+)_n$ . The latter group of clusters are stabilized by intramolecular hydrogen bonds between the sulfate and ammonium groups. The spectroscopic properties of these clusters calculated with DFT methods can be helpful in the characterization of the  $^{137}\text{Cs}$  granular materials that have been investigated experimentally.

#### 5 . 主な発表論文等

( 研究代表者、研究分担者及び連携研究者には下線 )

[ 雑誌論文 ] ( 計 1 件 )

- 1) PICHIERRI Fabio, DFT study of caesium ion complexation by cucurbit[n]urils ( $n=5-7$ ), Dalton Transactions, 査読有, 42, 2013, 6083–6091.  
DOI: 10.1039/c2dt32180g

[ 学会発表 ] ( 計 5 件 )

- 1) PICHIERRI Fabio, Complexation of Cs-137 by molecular cavitands, International

Symposium of Metal Complexes (ISMEC2013), 2013年6月20日, プルゴス大学 (スペイン)

- 2) PICHIERRI Fabio, Solvation of alkali metal ions by sulfolane, 33-rd International Conference on Solution Chemistry, 2013年7月10日, 京都テルサ (京都)
- 3) PICHIERRI Fabio, Bragg's Law and the birth of chemical crystallography, 9-th International Conference for the History of Chemistry, 2013年8月22日, ウップサラ大学 (スウェーデン)
- 4) PICHIERRI Fabio, Atomic structure of granular cesium materials, Computational Science Workshop (CSW2014), 2014年8月20日, つくば国際会議場 (つくば市)
- 5) PICHIERRI Fabio, Computational chemistry studies of cesium ion complexation by cucurbituril macrocycles, International Symposium on Chemical-Environmental-Biomedical Technology (isCEBT2014), 2014年9月12日, Chang Gung Health and Culture Village (台湾).

〔その他〕  
ホームページ等

#### 6. 研究組織

##### (1) 研究代表者

ピキエリ ファビオ (PICHIERRI FABIO)  
東北大学・大学院工学研究科・准教授  
研究者番号：40374920

##### (2) 研究分担者

( )

研究者番号：

##### (3) 連携研究者

( )

研究者番号：