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Complexation of U(VI) with Cucurbit[5]uril: Thermodynamic and Structural investigation in aqueous medium

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ABSTRACT

The assessment of cucurbituril (CBn) for selective removal of actinides from nuclear waste streams requires comprehensive understanding of binding parameters and coordination of these complexes. The present work is the first experimental report on complexation of actinide ion with Cucurbit[5]uril (CB5) in solution. The thermodynamic parameters (ΔG, ΔH and ΔS) for complexation of CB5 with U(VI) in formic acid water medium were determined using microcalorimetry and UV-Vis spectroscopy. The enthalpy and entropy of complexation revealed the partial binding of U(VI) to CB5 portal. The partial binding was confirmed by spectroscopic techniques viz. extended X absorption fine structure spectroscopy (EXAFS), ^{1}H and ^{13}C NMR. The EXAFS $\chi(r)$ versus r spectra for U-CB5 complex has been fitted from 1.4 to 3.5 Å with two oxygen shells and a carbon shell. The presence of three carbon atom in secondary shell shows the involvement of only three carbonyl oxygens directly bonding to U(VI) which is in contrast to that calculated from gas phase DFT calculation of unhydrated system. The combined effect of hydration and formic acid encapsulation led to the enhanced stability of partially bound U(VI) to CB5. In the present work the binding of formic acid has also been studied by fluorescence spectroscopy. ESI-MS data shows the unusual stabilization of U(VI) by CB5 in gas phase.

1. Introduction

Cucurbiturils (CBn) are the macrocyclic ligands with unique structure which comprise of two hydrophilic portals and a hydrophobic cavity. The carbonylated portals interact with polar moieties and metal ions whereas the hydrophobic cavity stabilizes the hydrophobic moieties. The depth of the cavity is about 7.4–7.8 A° and the width of the cavity varies from 4.4–8.8 A° depending on the number of monomers forming CBn i.e. n value (for CB5, Fig. 1) [1–6]. The presence of cyclic portal and cavity in the molecular structure leads to constrictive binding of the guest molecules. This property of CBn has been extensively used for variety of applications like catalytic processes, molecular containers, supramolecular switches, catenanes, as fluorescent materials, decontaminants for water or air and as analogue of biomolecules [7,8].

The inclusion complexes of CBn with small organic compounds viz. amine, diamines, alkylammonium salts, benzylammonium salts and dyes etc. have been extensively studied using X-ray diffraction, nuclear magnetic resonance (NMR), fluorescence, calorimetry, UV–Vis spectroscopy [9–12]. These studies with tetra alkylammonium salts revealed the inclusion of charged alkyl ammonium nitrogen into the portal and incorporation of hydrophobic alkyl part into the cavity [13,14]. The metal ion complexation with CBn have been extensively investigated with alkali, alkaline earth, group (III) and transition metal ions [15–18]. Wang et al. illustrated the formation of metal ion bottomed molecular bowls with Cs-CB6 system where metal ion can reversibly bind to four of the carbonyl groups of the cavity [19]. The metal ion bottom may serve as a lewis acid site for substrate activation and chemical catalysis. In case of K and Rb, the CB6 portal is bound to two bridging binuclear aqua complexes forming organic-inorganic mixed polymer [20]. Different crystal structures of metal CBn complexes obtained by variety of metal ion in various conditions have been described in literature [17,18]. The group III metal ions and some of the lanthanide ions were also found to form outer sphere complexes with CBn.

Designing of novel ligands for selective binding of actinide has been topic of current research due to its potential application in nuclear waste management, decontamination, recovery of uranium from sea water etc. Few studies on actinide complexation with CBn deals with

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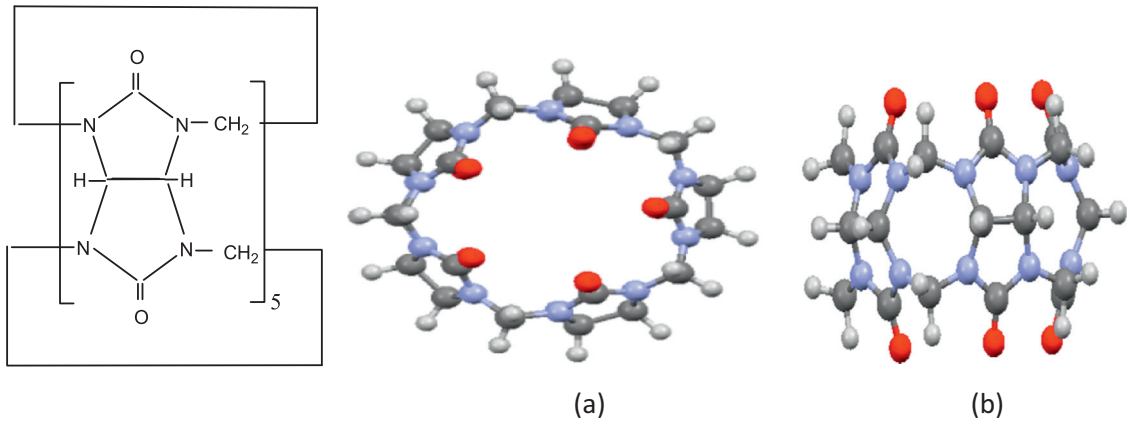

Fig. 1. Structure of cucurbit[5]uril a) Top view b) side view (red colour – oxygen, purple – nitrogen, grey – carbon, white – hydrogen). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

crystal structures of Th(IV)-CBn and U(VI)-CBn [21–23]. Fedin et al. have reported binding of Th(IV) to three adjacent carbonyl groups of CB6 [24] whereas crystallization in presence of perrhenic acid resulted in the formation of outersphere Th(IV)-CB5 complex [25]. Similarly U (VI) also reported to form inner as well as outer sphere complexes with CB5 [26,27].

In case of U(VI) ion, the coordinating ligand can bind through equatorial plane only. Therefore, the preorganised macrocyclic ligand, like CB5, having binding moieties in a plane and at optimum distance is expected to form a stable U(VI) complexes which is evident from the crystal structure report [23] wherein U(VI) is bound symmetrically to both the portals of CB5 molecule. Selective uptake of U(VI) on CB5 imprinted palm shell powder was also attributed to perfect binding offered by two portals of CB5 [23]. In view of the application of CB5 in nuclear industry, it is important to understand their speciation, coordination behavior and energetic of complexation with metal ion in solution. The understanding of mechanism of CB5 complexation with U(VI) is not only important to understand basic actinide chemistry but also helps in designing ligands with improved affinity and selectivity. The present work is the first experimental report on complexation of actinide ion with CB5 in solution.

The comprehensive understanding about the driving force in complexation phenomenon is obtained from thermodynamic parameters, which provide deeper insight about the bonding and hydration of species involved in the process. In present work, thermodynamic parameters of U(VI) complexation with CB5 were determined by UV-Vis and calorimetry. The molecular level information about the structure of the complexes was obtained by extended X ray absorption fine structure (EXAFS), ESI-MS, ^{1}H NMR and ^{13}C NMR studies. The thermodynamic and spectroscopic data were rationalized and corroborated using density functional theory calculations (DFT).

The present studies have been carried out in formic acid (FAH)-water medium 50 wt%, the preferred medium for studying CBn complexation in literature [15], due to poor solubility of CBn in aqueous solutions. The variation in the thermodynamic parameters for CB6 complexation with alkali and alkaline earth metals ions in FAH-water medium containing different volume % of FAH has been discussed in terms of interaction of proton with CB6. In order to have better comparison of thermodynamic parameters of metal ion complexation, particularly with another f block element, Eu(III) [28], with CBn, the present studies have been carried out in the same medium. Very few studies on interaction of counter anions with CBn and metal-CBn complexes have been reported [28,29]. Jing-Xin Liu demonstrated higher affinity of nitrate for CB5 compared to chloride using fluorescence spectroscopy [29]. In our previous report, on Eu(III) complexation with CB5 and CB7 in FAH-water 50 wt%, theoretical calculations has shown the important role of anion encapsulation in the cavity in stabilization of the complex [28]. Therefore in present studies, the mechanism of interaction of FAH with CB5 using fluorescence spectroscopy was investigated that was helpful in complete understanding of U(VI)-CB5 complexation in FAH-water medium.

2. Materials and Methods

CB5 of Sigma Aldrich (>98% purity) and FAH of sigma (Assay > 98%) make was used in the present work. Millipore water of resistivity (18 M Ω cm^{-1}) is used to prepare all the solutions.

2.1. Preparation of Uranium Stock

2 g of U_3O_8 was dissolved in concentrated perchloric acid and the solution was made up to 50 ml using perchloric acid solution (pH 2). The concentration of uranium is standardized by redox titrimetry using biamperometry for end point detection. To prepare uranyl ion solution in FAH-water 50 wt%, uranium stock solution was evaporated to dryness and FAH-water 50 wt% was added to obtain required concentration.

2.2. UV–Vis Spectroscopic Titration

The spectrophotometric titration was carried out by titrating 1.5 ml of Uranyl ion solution (5×10^{-3} M) with CB5 (0.02 M) solution in FAH-water 50 wt%. The spectra were recorded in the range 360–520 nm after each injection using a JASCO spectrophotometer. The absorbance, (A^i (λ)) at a particular wavelength (λ) for ith injection can be related to equilibrium concentrations of different absorbing species (j) using Lambert Beer's law:

$$\boldsymbol{A^i}(\boldsymbol{\lambda}) = l\sum \varepsilon_j(\lambda)C^i_j \tag{1}$$

where C^i_j is the concentration of jth species at ith injection, $\varepsilon_j(\lambda)$ is the molar absorbance of jth species at wavelength (λ). The matrix A(I, Λ) for I titration points and Λ spectral points obtained during the spectrophotometric titration is solved in conjunction with the mass balance Eqs. (3) and (4) for the total metal ion and ligand respectively to obtain the free concentrations of the species and thereby the equilibrium constant. The data was analysed using software Hyperquad 2006 [30].

$$xM + yL == M_xL_y \tag{2}$$

$$C^i_{MT} = \left[C^i_M + \sum x\beta_{xy}{C^i_M}^x{C^i_L}^y\right] \tag{3}$$

$$C^i_{LT} = \left[C^i_{ML} + \sum y\beta_{xy}{C^i_M}^x{C^i_L}^y\right] \tag{4}$$