

Short communication

Extraction and DFT Study on the Complexation of K^+ with a Hexaarylbenzene – Based Polyaromatic Receptor

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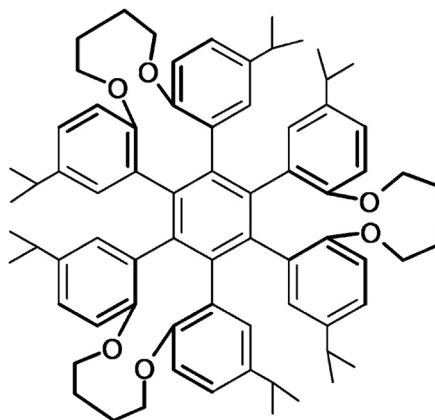
Abstract

From extraction experiments and γ -activity measurements, the exchange extraction constant corresponding to the equilibrium $K^+(aq) + \mathbf{1} \cdot Cs^+(nb)_{sipy} \rightleftharpoons \mathbf{1} \cdot K^+(nb) + Cs^+(aq)$ taking part in the two-phase water–nitrobenzene system ($\mathbf{1}$ = hexaarylbenzene – based polyaromatic receptor; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{ex}(K^+, \mathbf{1} \cdot Cs^+) = -1.0 \pm 0.1$. Further, the stability constant of the hexaarylbenzene – based polyaromatic receptor $\cdot K^+$ complex (abbrev. $\mathbf{1} \cdot K^+$) in nitrobenzene saturated with water was calculated for a temperature of 25 °C: $\log \beta_{nb}(\mathbf{1} \cdot K^+) = 5.1 \pm 0.2$. By using quantum mechanical DFT calculations, the most probable structure of the $\mathbf{1} \cdot K^+$ complex species was solved. In this complex having C_3 symmetry, the cation K^+ synergistically interacts with the polar ethereal oxygen fence and with the central hydrophobic benzene bottom via cation – π interaction. Finally, the calculated binding energy of the resulting complex $\mathbf{1} \cdot K^+$ is $-282.8 \text{ kJ mol}^{-1}$, confirming the relatively high stability of the considered cationic complex species.

Keywords: Hexaarylbenzene-based polyaromatic receptor, potassium cation, complexation, extraction and stability constants, water–nitrobenzene system, DFT, complex structure

1. Introduction

Recently, hexaarylbenzene (HAB) derivatives attract a great attention because of their unique propeller-shaped structure and potential application in molecular electronics and nanotechnology. It has been previously described by employing NMR spectroscopy and X-ray crystallography that HAB – based receptor (abbrev. $\mathbf{1}$; see Scheme 1) binds a single potassium cation because it interacts both with the polar ethereal fence and with the central benzene ring via cation – π interaction.¹ Cation – π interaction is a well-established phenomenon in gas phase, as well as in solid state,² and is known to play an important role in the stabilization of tertiary structures of various proteins.³



Scheme 1. Structural formula of a hexaarylbenzene (HAB)-based polyaromatic receptor (abbrev. $\mathbf{1}$).

Dicarbollycobaltate anion⁴ and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs⁺, Sr²⁺, Ba²⁺, Eu³⁺ and Am³⁺) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,^{5–35} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{36–38}

In the current work, the stability constant of the HAB – based receptor ·K⁺ complex species (1·K⁺) in nitrobenzene saturated with water was determined. Moreover, applying quantum mechanical DFT calculations, the most probable structure of the mentioned cationic complex was derived.

2. Experimental

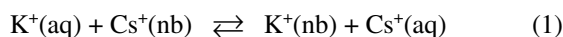
Preparation of the electroneutral HAB – based receptor **1** (see Scheme 1) is described elsewhere.¹ Cesium 3,3'-*commo*-bis(undecahydro-1,2-dicarbonyl-3-cobaltaclosododecaborate), Cs⁺{[π-(3)-B₉C₅H₁₁]₂Co(III)}⁻ (called also cesium dicarbollycobaltate, abbrev. CsDCC), was synthesized by means of the method published by Hawthorne et al.³⁹ The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radioisotope ¹³⁷Cs⁺ (Techsnaveksport, Russia) was of standard radiochemical purity.

The extraction experiments were carried out in 10 cm³ glass test-tubes with polyethylene stoppers: 2 cm³ of an aqueous solution of KCl of the concentration in the range from 1 × 10⁻³ to 3 × 10⁻³ mol dm⁻³ and microamounts of ¹³⁷Cs⁺ were added to 2 cm³ of a nitrobenzene solution of **1** and CsDCC, the concentrations of which varied also from 1 × 10⁻³ to 3 × 10⁻³ mol dm⁻³ (in all experiments, the initial concentration of **1** in nitrobenzene, C₁^{in,nb}, was always equal to the initial concentration of CsDCC in this medium, C_{CsDCC}^{in,nb}). The test-tubes filled with the solutions were shaken for 2 hours at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 cm³ samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of cesium, D_{Cs}, were determined as the ratios of the measured radioactivities of ¹³⁷Cs⁺ in the nitrobenzene and aqueous samples.

3. Results and Discussion

Regarding the results of previous papers,^{4,40} the two-phase water–KCl–nitrobenzene–CsDCC extraction system can be described by the following equilibrium

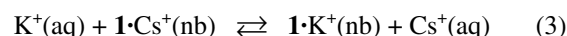


with the corresponding exchange extraction constant K_{ex}(K⁺, Cs⁺); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K_{ex}(K⁺, Cs⁺) one can write⁴⁰

$$\log K_{\text{ex}}(\text{K}^+, \text{Cs}^+) = \log K_{\text{K}^+}^i - \log K_{\text{Cs}^+}^i \quad (2)$$

where K_{K⁺}ⁱ and K_{Cs⁺}ⁱ are the individual extraction constants for K⁺ and Cs⁺, respectively, in the water–nitrobenzene system.⁴⁰ Knowing the values log K_{K⁺}ⁱ = -4.1⁴⁰ and log K_{Cs⁺}ⁱ = -2.7,⁴⁰ the exchange extraction constant K_{ex}(K⁺, Cs⁺) was simply calculated from Eq. (2) as log K_{ex}(K⁺, Cs⁺) = -1.4.

Previous results^{41–44} indicated that the two-phase water–KCl–nitrobenzene–**1** (1 = HAB – based receptor)–CsDCC extraction system (see Experimental), chosen for determination of the stability constant of the complex **1**·K⁺ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium



with the respective equilibrium extraction constant K_{ex}(K⁺, **1**·Cs⁺):

$$K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Cs}^+) = \frac{[\mathbf{1} \cdot \text{K}^+]_{\text{nb}} [\text{Cs}^+]_{\text{aq}}}{[\text{K}^+]_{\text{aq}} [\mathbf{1} \cdot \text{Cs}^+]_{\text{nb}}} \quad (4)$$

It is necessary to emphasize that **1** is a considerably hydrophobic receptor, practically present in the nitrobenzene phase only, where it forms – with K⁺ and Cs⁺ – the relatively stable complexes **1**·K⁺ and **1**·Cs⁺ in the nitrobenzene phase. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the univalent cations studied at equal volumes of the nitrobenzene and aqueous phases, as well as the measured distribution ratio of cesium, D_{Cs} = [1·Cs⁺]_{nb} / [Cs⁺]_{aq}, combined with Eq. (4), we obtain the final expression for K_{ex}(K⁺, **1**·Cs⁺) in the form

$$K_{\text{ex}}(\text{K}^+, \mathbf{1} \cdot \text{Cs}^+) = \frac{1}{D_{\text{Cs}} (1 + D_{\text{Cs}})} \frac{C_{\text{CsDCC}}^{\text{in,nb}}}{C_{\text{KCl}}^{\text{in,aq}} - C_{\text{CsDCC}}^{\text{in,nb}}} \quad (5)$$

where C_{KCl}^{in,nb} is the initial concentration of KCl in aqueous phase of the system under consideration.

In this study, from the extraction experiments and γ-activity measurements (see Experimental) by means of Eq. (5), the following value of the constant K_{ex}(K⁺, **1**·Cs⁺) was determined: log K_{ex}(K⁺, **1**·Cs⁺) = -1.0 ± 0.1.

Furthermore, with respect to previous results,^{41–44} for the extraction constants K_{ex}(K⁺, Cs⁺) and K_{ex}(K⁺, **1**·Cs⁺) defined above, as well as for the stability constants of the complexes **1**·K⁺ and **1**·Cs⁺ in nitrobenzene saturated with water, denoted by β_{nb}(**1**·K⁺) and β_{nb}(**1**·Cs⁺), respectively, one gets

$$\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{K}^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) + \log K_{\text{ex}}(\text{K}^+, \mathbf{1}\cdot\text{Cs}^+) - \log K_{\text{ex}}(\text{K}^+, \text{Cs}^+) \quad (6)$$

Using the constants $\log K_{\text{ex}}(\text{K}^+, \text{Cs}^+)$ and $\log K_{\text{ex}}(\text{K}^+, \mathbf{1}\cdot\text{Cs}^+)$ given above, the value $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) = 4.7 \pm 0.1^{45}$ and applying Eq. (6), we obtain the stability constant of the $\mathbf{1}\cdot\text{K}^+$ complex in water-saturated nitrobenzene at 25 °C as $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{K}^+) = 5.1 \pm 0.2$. In this context it should be noted that the stability constant of the complex species KL^+ , where L is 18-crown-6, in nitrobenzene saturated with water is $\log \beta_{\text{nb}}(\text{KL}^+) = 9.5$.⁴⁶ This means that in the mentioned nitrobenzene medium, the stability of the $\mathbf{1}\cdot\text{K}^+$ complex under study is substantially lower than that of the cationic complex species KL^+ (L = 18-crown-6).

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs.⁴⁷ The 6-31G(d) basis set was used and the optimizations were

unconstrained. Although a possible influence of a polar solvent on the detailed structures of **1** and the $\mathbf{1}\cdot\text{K}^+$ complex species could be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory.^{48–53}

In the model calculations, we optimized the molecular geometries of the parent HAB – based receptor **1** and its complex with K^+ . The optimized structure of a free receptor **1** having C_3 symmetry, involving a bowl – shaped cavity, which is comprised of an aromatic bottom (i. e. central benzene ring) and an ethereal fence formed by six oxygen atoms from the peripheral aryl groups, is illustrated in Fig. 1. The depth of the cavity, i. e. the distance between the mean plane of the aromatic bottom and that of the ethereal fence, is 2.15 Å (1 Å = 0.1 nm); the diameter of this cavity in **1** is 6.19 Å (see Fig. 1).

The structure obtained by the full DFT optimization

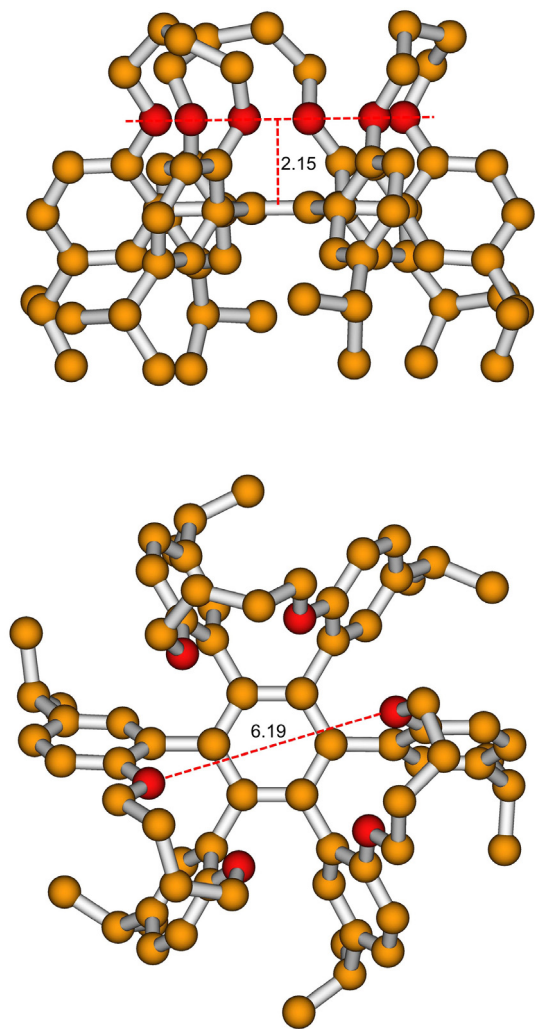


Figure 1: Two projections of the DFT optimized structure of a free HAB – based receptor **1** [B3LYP/6-31G(d)] (hydrogen atoms omitted for clarity).

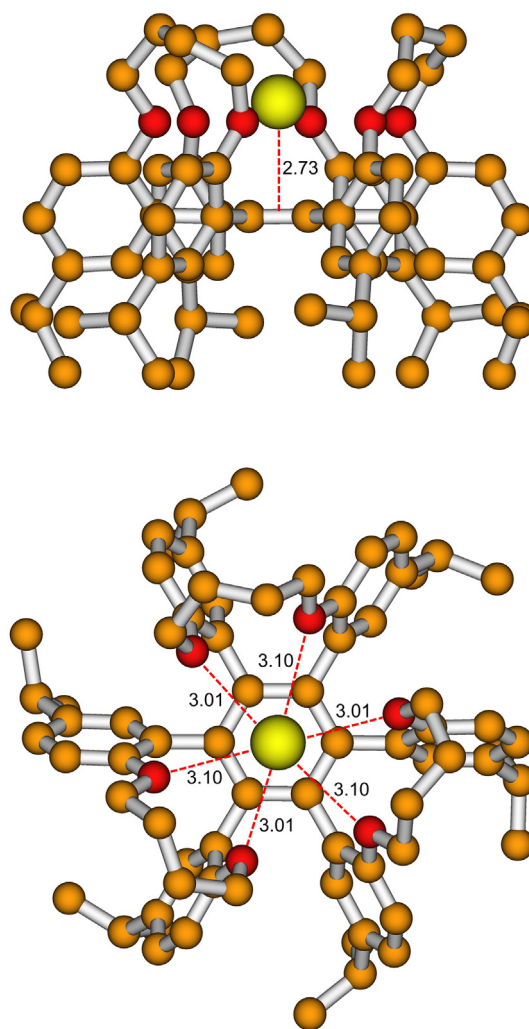


Figure 2: Two projections of the DFT optimized structure of the $\mathbf{1}\cdot\text{K}^+$ complex [B3LYP/6-31G(d)] (hydrogen atoms omitted for clarity).

of the cationic complex species $\mathbf{1}\cdot\mathbf{K}^+$ is depicted in Fig. 2. In this complex having also C_3 symmetry, the cation \mathbf{K}^+ synergistically interacts with the hydrophilic polar etheral oxygen fence (the corresponding $\mathbf{K}^+ \cdots \mathbf{O}$ distances are gradually 3.01, 3.10, 3.01, 3.10, 3.01 and 3.10 Å) and with the central hydrophobic benzene bottom via cation – π interaction (the distance between the mean plane of the bottom benzene ring and the \mathbf{K}^+ cation is 2.73 Å, as pictured in Fig. 2). At this point it should be noted that the depth of the cavity in the $\mathbf{1}\cdot\mathbf{K}^+$ complex is about 2.26 Å, while its diameter is roughly 6.04 Å. This means that the formation of the complex species $\mathbf{1}\cdot\mathbf{K}^+$ results in the small tapering of the mentioned cavity and at the same time, in its getting longer.

Finally, the interaction energy, $E(\text{int})$, of the $\mathbf{1}\cdot\mathbf{K}^+$ complex [calculated as the difference between electronic energies of $\mathbf{1}\cdot\mathbf{K}^+$ and isolated \mathbf{K}^+ and $\mathbf{1}$ species, $E(\text{int}) = E(\mathbf{1}\cdot\mathbf{K}^+) - E(\mathbf{K}^+) - E(\mathbf{1})$] was found to be $-282.8 \text{ kJ mol}^{-1}$, which confirms quite unambiguously the formation of the considered cationic complex $\mathbf{1}\cdot\mathbf{K}^+$.

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Povzetek

S pomočjo ekstrakcije in meritev γ -aktivnosti smo določili konstanto ekstrakcije $\log K_{\text{ex}}(K^+, \mathbf{1}.\text{Cs}^+) = -1.0 \pm 0.1$, za ravnotežje $K^+(\text{aq}) + \mathbf{1}.\text{Cs}^+(\text{nb}) \rightleftharpoons \mathbf{1}.\text{K}^+(\text{nb}) + \text{Cs}^+(\text{aq})$, ki ga dosežemo v dvofaznem sistemu voda-nitrobenzen ($\mathbf{1}$ = heksaaril benzen-poliaromatski receptor; aq = vodna faza, nb = faza nitrobenzena). Pri 25 °C smo določili tudi konstanto stabilnosti K^+ kompleksa ($\mathbf{1}.\text{K}^+$) v nitrobenzenu nasičenem z vodo, $\log \beta_{\text{nb}}(\mathbf{1}.\text{K}^+) = 5.1 \pm 0.2$. Z uporabo DFT kvantomehanskega računa smo določili najbolj verjetno strukturo $\mathbf{1}.\text{K}^+$ kompleksa, ki predvideva C3 simetrijo, K^+ kation pa sinergistično interagira s polarno etersko skupino in centralnim hidrofobnim benzenovim obročem preko kation- π interakcije. Izračunali smo tudi vezno energijo nastalega kompleksa, $\mathbf{1}.\text{K}^+$, ki znaša $-282.8 \text{ kJ mol}^{-1}$ in potrjuje njegovo relativno visoko stabilnost.