

Short communication

# A Combined Experimental and DFT Study on the Complexation of the Hydrazinium Cation with a Hexaarylbenzene – Based Receptor

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## Abstract

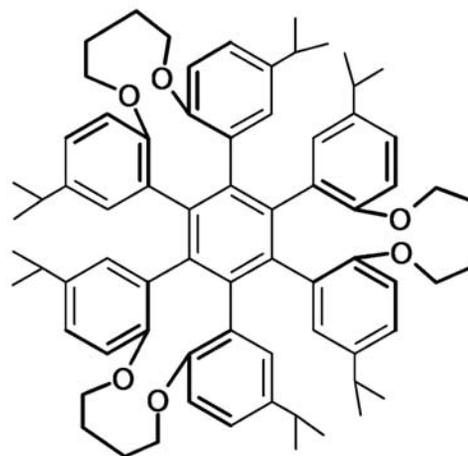
From extraction experiments and  $\gamma$ -activity measurements, the exchange extraction constant corresponding to the equilibrium  $N_2H_5^+(aq) + \mathbf{1}\cdot Cs^+(nb) \rightleftharpoons \mathbf{1}\cdot N_2H_5^+(nb) + Cs^+(aq)$  taking place in the two-phase water–nitrobenzene system ( $\mathbf{1}$  = hexaarylbenzene – based receptor; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as  $\log K_{ex}(N_2H_5^+, \mathbf{1}\cdot Cs^+) = -1.2 \pm 0.1$ . Further, the stability constant of the hexaarylbenzene – based receptor  $\cdot N_2H_5^+$  complex (abbrev.  $\mathbf{1}\cdot N_2H_5^+$ ) in nitrobenzene saturated with water was calculated for a temperature of 25 °C:  $\log \beta_{nb}(\mathbf{1}\cdot N_2H_5^+) = 5.6 \pm 0.2$ . By using quantum mechanical DFT calculations, the most probable structure of the  $\mathbf{1}\cdot N_2H_5^+$  complex species was solved. In this complex, the cation  $N_2H_5^+$  synergistically interacts with the polar ethereal oxygen fence and with the central hydrophobic benzene bottom via cation –  $\pi$  interaction. Finally, the calculated binding energy of the resulting complex  $\mathbf{1}\cdot N_2H_5^+$  is –270.5 kJ/mol, confirming the relatively high stability of the considered cationic complex species.

**Keywords:** Hexaarylbenzene – based receptor,  $N_2H_5^+$  cation, complexation, extraction and stability constants, water–nitrobenzene system, DFT, complex structure

## 1. Introduction

Hexaarylbenzene (HAB) derivatives attract a great attention because of 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 a 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 –  $\pi$  interaction.<sup>1</sup> Cation –  $\pi$  interaction is a well-established phenomenon in gas phase, as well as in solid state,<sup>2–4</sup> and is known to play an important role in the stabilization of tertiary structures of various proteins.<sup>5</sup>

The dicarbollylcobaltate anion<sup>6</sup> and some of its halogen derivatives are very useful reagents for the extrac-



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

tion of various metal cations (especially  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2-}$ ,  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$ ) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,<sup>7–44</sup> and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.<sup>45,46</sup>

Recently, the interaction of the  $\text{K}^+$  cation with the HAB – based receptor **1** has been investigated by the extraction method in the water-nitrobenzene system and by using DFT calculations.<sup>19</sup> On the other hand, in the current work, the stability constant of the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  cationic complex species 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

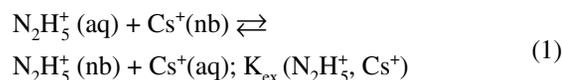
Preparation of the electroneutral HAB – based receptor **1** (see Scheme 1) is described elsewhere.<sup>1</sup> Cesium dicarbollylcobaltate (abbrev. CsDCC) was synthesized by means of the method published by Hawthorne et al.<sup>47</sup> Hydrazinium chloride ( $\text{N}_2\text{H}_5^+\text{Cl}^-$ ) was supplied by Aldrich. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide  $^{137}\text{Cs}^+$  (Technaveksport, Russia) was of standard radiochemical purity.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of  $\text{N}_2\text{H}_5^+\text{Cl}^-$  of the concentration in the range from  $1 \times 10^{-3}$  to  $3 \times 10^{-3}$  mol/L and microamounts of  $^{137}\text{Cs}^+$  were added to 2 mL of a nitrobenzene solution of **1** and CsDCC, the concentrations of which varied also from  $1 \times 10^{-3}$  to  $3 \times 10^{-3}$  mol/L (in all experiments, the initial concentration of **1** in nitrobenzene,  $C_1^{\text{in,nb}}$ , was equal to the initial concentration of CsDCC in this medium,  $C_{\text{CsDCC}}^{\text{in,nb}}$ ). The test-tubes filled with the solutions were shaken for 2 hours at  $25 \pm 1$  °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their  $\gamma$ -activities were measured using a well-type NaI(Tl) scintillation detector connected to a  $\gamma$ -analyzer NK 350 (Gamma, Budapest, Hungary).

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

## 3. Results and Discussion

Regarding the results of previous papers,<sup>6,48,49</sup> the two-phase water– $\text{N}_2\text{H}_5^+\text{Cl}^-$ –nitrobenzene–cesium dicarbollylcobaltate (CsDCC) extraction system can be described by the following equilibrium

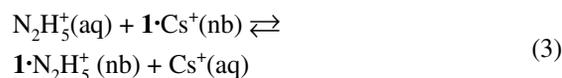


with the corresponding exchange extraction constant  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+)$ ; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+)$  one can write<sup>48</sup>

$$\log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+) = \log K_{\text{N}_2\text{H}_5^+}^i - \log K_{\text{Cs}^+}^i \quad (2)$$

where  $K_{\text{N}_2\text{H}_5^+}^i$  and  $K_{\text{Cs}^+}^i$  are the individual extraction constants for  $\text{N}_2\text{H}_5^+$  and  $\text{Cs}^+$ , respectively, in the water–nitrobenzene system.<sup>48,49</sup> Knowing the values  $\log K_{\text{N}_2\text{H}_5^+}^i = -4.8^{49}$  and  $\log K_{\text{Cs}^+}^i = -2.7^{48}$ , the exchange extraction constant  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+)$  was simply calculated from Eq. (2) as  $\log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+) = -2.1$ .

Previous results<sup>50–54</sup> indicated that the two-phase water– $\text{N}_2\text{H}_5^+\text{Cl}^-$ –nitrobenzene–**1** (**1** = HAB – based receptor)–CsDCC extraction system (see Experimental), chosen for determination of the stability constant of the complex  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium



with the respective equilibrium extraction constant  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+)$ :

$$K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+) = \frac{[\mathbf{1}\cdot\text{N}_2\text{H}_5^+]_{\text{nb}}[\text{Cs}^+]_{\text{aq}}}{[\text{N}_2\text{H}_5^+]_{\text{aq}}[\mathbf{1}\cdot\text{Cs}^+]_{\text{nb}}} \quad (4)$$

It is necessary to emphasize that **1** is a considerably hydrophobic receptor, practically present in the nitrobenzene phase only, where it forms – with  $\text{N}_2\text{H}_5^+$  and  $\text{Cs}^+$  – the relatively stable complexes  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  and  $\mathbf{1}\cdot\text{Cs}^+$ . 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,  $D_{\text{Cs}} = [\mathbf{1}\cdot\text{Cs}^+]_{\text{nb}} / [\text{Cs}^+]_{\text{aq}}$ , combined with Eq. (4), we obtain the final expression for  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+)$  in the form

$$K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+) = \frac{1}{D_{\text{Cs}} \left( (1 + D_{\text{Cs}}) C_{\text{N}_2\text{H}_5^+\text{Cl}^-}^{\text{in, aq}} - C_{\text{CsDCC}}^{\text{in, nb}} \right)} \quad (5)$$

where  $C_{\text{N}_2\text{H}_5^+\text{Cl}^-}^{\text{in, aq}}$  is the initial concentration of  $\text{N}_2\text{H}_5^+\text{Cl}^-$  in the aqueous phase and  $C_{\text{CsDCC}}^{\text{in, nb}}$  denotes the initial concentration of CsDCC in the organic phase of the system under consideration.

In this study, from the extraction experiments and  $\gamma$ -activity measurements (see Experimental) by means of

Eq. (5), the following value of the constant  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+)$  was determined as  $\log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+) = -1.2 \pm 0.1$ .

Furthermore, with respect to previous results,<sup>50–54</sup> for the extraction constants  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+)$  and  $K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+)$  defined above, as well as for the stability constants of the complexes  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  and  $\mathbf{1}\cdot\text{Cs}^+$  in nitrobenzene saturated with water, denoted by  $\beta_{\text{nb}}(\mathbf{1}\cdot\text{N}_2\text{H}_5^+)$  and  $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+)$ , respectively, one gets

$$\begin{aligned} \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{N}_2\text{H}_5^+) &= \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) + \\ \log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+) &- \log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+) \end{aligned} \quad (6)$$

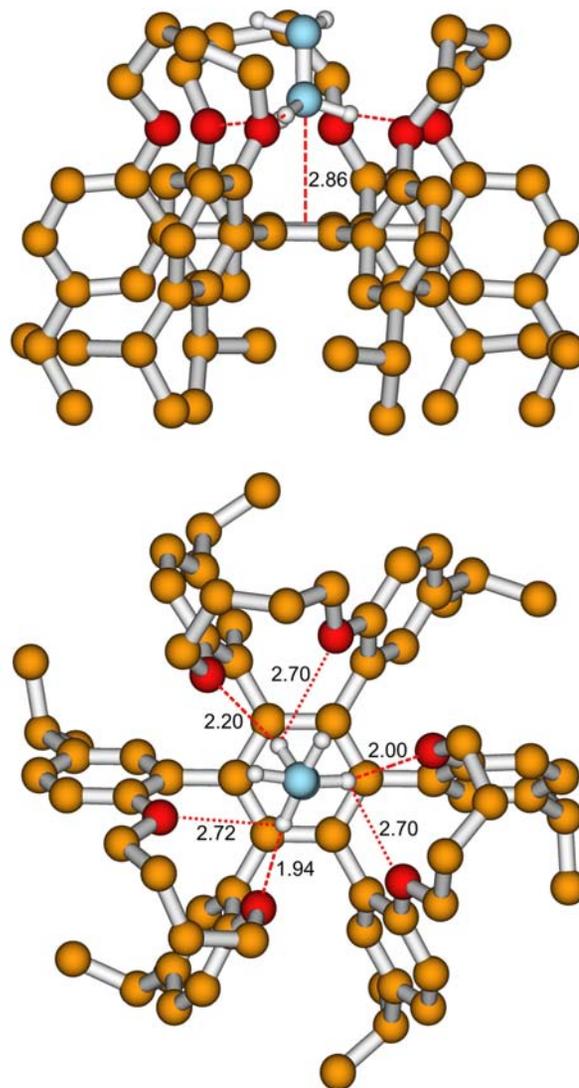
Using the constants  $\log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \text{Cs}^+)$  and  $\log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+)$  given above, the value  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) = 4.7 \pm 0.1$ ,<sup>62</sup> and applying Eq. (6), we obtain the stability constant of the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  complex in water-saturated nitrobenzene at 25 °C as  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{N}_2\text{H}_5^+) = 5.6 \pm 0.2$ . This means that in the mentioned nitrobenzene medium, the stability of the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  complex under study is somewhat higher than that of the cationic complex species  $\mathbf{1}\cdot\text{Cs}^+$ .

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs.<sup>55</sup> The 6–31G(d) basis set was used and the optimizations were unconstrained. In order to increase the numerical accuracy and to reduce oscillations during the molecular geometry optimization, two-electron integrals and their derivatives were calculated by using the pruned (99,590) integration grid, having 99 radial shells and 590 angular points per shell, which was requested by means of the Gaussian 03 keyword “Int = UltraFine”. Although a possible influence of a polar solvent on the detailed structures of **1** and the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  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.<sup>56–61</sup>

In the model calculations, we optimized the molecular geometries of the parent HAB – based receptor **1** and its complex with  $\text{N}_2\text{H}_5^+$ . 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 presented in our previous work.<sup>19</sup> 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.<sup>19</sup>

The structure obtained by the full optimization of the cationic complex species  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  is depicted in Figure 1, together with the lengths of the three two-center hydrogen bonds (in Å). In this complex, the cation  $\text{N}_2\text{H}_5^+$  synergistically interacts with the hydrophilic polar ethereal oxygen fence and with the central hydrophobic benzene bottom via cation –  $\pi$  interaction (the distance between the mean plane of the bottom benzene ring and the “near”

nitrogen atom of  $\text{N}_2\text{H}_5^+$  in the resulting complex  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  is 2.86 Å, as pictured in Figure 1). At this point it is necessary to emphasize that the formation of the complex species  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  results in the small getting longer of the respective cavity, as follows from comparison of Figure 1 with our previous results.<sup>19</sup>



**Figure 1:** Two projections of the DFT optimized structure of the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  complex [B3LYP/31G(d)] (hydrogen atoms omitted for clarity except those of  $\text{N}_2\text{H}_5^+$ ). The distance between the mean plane of the bottom benzene ring and the “near” nitrogen atom of  $\text{N}_2\text{H}_5^+$  in the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  complex: 2.86 Å; the lengths of the three two-center H-bonds in the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  complex: 1.94, 2.72, 2.20, 2.70, 2.00, and 2.70 Å; the depth of the cavity in  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$ : 2.22 Å.

Finally, the interaction energy,  $E(\text{int})$ , of the  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  complex [calculated as the difference between electronic energies of  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  and isolated  $\text{N}_2\text{H}_5^+$  and **1** species:  $E(\text{int}) = E(\mathbf{1}\cdot\text{N}_2\text{H}_5^+) - E(\text{N}_2\text{H}_5^+) - E(\mathbf{1})$ ] was found to be –270.5 kJ/mol, which confirms quite unambiguously the formation of the considered cationic complex  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$ .

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## Povzetek

S pomočjo ekstrakcije in meritev  $\gamma$ -aktivnosti smo za konstanto ekstrakcije za ravnotežje  $\text{N}_2\text{H}_5^+(\text{aq}) + \mathbf{1}\cdot\text{Cs}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{N}_2\text{H}_5^+(\text{nb}) + \text{Cs}^+(\text{aq})$  v dvo faznem sistemu voda-nitrobenzen ( $\mathbf{1}$  = heksaarilbenzen – receptor; aq = vodna faza, nb = nitrobenzen) določili vrednost  $\log K_{\text{ex}}(\text{N}_2\text{H}_5^+, \mathbf{1}\cdot\text{Cs}^+) = -1.2 \pm 0.1$ . Pri 25 °C smo določili tudi konstanto stabilnosti kompleksa heksaaril  $\text{N}_2\text{H}_5^+(\mathbf{1}\cdot\text{N}_2\text{H}_5^+)$  v nitrobenzen, nasičenem z vodo, ki znaša  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{N}_2\text{H}_5^+) = 5.6 \pm 0.2$ . S pomočjo kvantomehanskih DFT izračunov smo predvideli najbolj verjetno strukturo  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$  kompleksa. Izkazalo se je, da kation  $\text{N}_2\text{H}_5^+$  sinergistično interagira s polarno etrsko skupino in centralnim hidrofobnim benzenovim obročem preko kation –  $\pi$  interakcij. Izračunali smo tudi vezno energijo nastalega kompleksa  $\mathbf{1}\cdot\text{N}_2\text{H}_5^+$ , ki znaša –270.5 kJ/mol in potrjuje njegovo relativno visoko stabilnost.