

Short communication

# Extraction and DFT Study on the Complexation of the TRIS<sup>+</sup> Cation with a Hexaarylbenzene-Based Receptor

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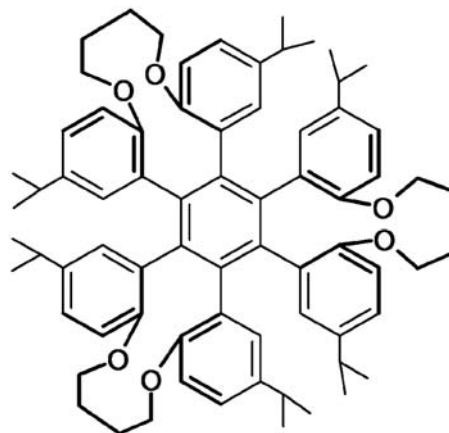
## Abstract

From extraction experiments and  $\gamma$ -activity measurements, the exchange extraction constant corresponding to the equilibrium  $\text{TRIS}^+(\text{aq}) + \mathbf{1}\cdot\text{Cs}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{TRIS}^+(\text{nb}) + \text{Cs}^+(\text{aq})$  taking place in the two-phase water–nitrobenzene system ( $\text{TRIS}^+ = (\text{HOCH}_2)_3\text{C-NH}_3^+$ ,  $\mathbf{1}$  = hexaarylbenzene – based receptor; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as  $\log K_{\text{ex}}(\text{TRIS}^+, \mathbf{1}\cdot\text{Cs}^+) = -2.0 \pm 0.1$ . Further, the stability constant of the hexaarylbenzene – based receptor  $\cdot\text{TRIS}^+$  complex (abbrev.  $\mathbf{1}\cdot\text{TRIS}^+$ ) in nitrobenzene saturated with water was calculated for a temperature of 25 °C :  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{TRIS}^+) = 6.0 \pm 0.2$ . By using quantum mechanical calculations, the most probable structure of the  $\mathbf{1}\cdot\text{TRIS}^+$  complex species was solved. In this complex having  $C_3$  symmetry, the cation  $\text{TRIS}^+$  synergistically interacts with the polar ethereal oxygen fence and with the central hydrophobic benzene bottom via cation –  $\pi$  interaction.

**Keywords:** TRIS<sup>+</sup>, hexaarylbenzene – based receptor, complexation, extraction and stability constants, water–nitrobenzene system, DFT, complex structure

## 1. Introduction

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 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>



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

The dicarbollylcobaltate anion<sup>6</sup> and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs<sup>+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Eu<sup>3+</sup> and Am<sup>3+</sup>) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes,<sup>7–23</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>24,25</sup>

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

## 2. Experimental

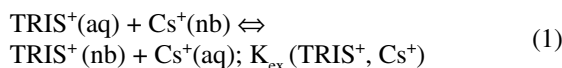
Preparation of the electroneutral HAB – based receptor **1** (see Scheme 1) is described elsewhere.<sup>1</sup> Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al.<sup>26</sup> Tris(hydroxymethyl)aminomethane hydrochloride, (HOCH<sub>2</sub>)<sub>3</sub>C–NH<sub>3</sub><sup>+</sup>Cl<sup>–</sup> (abbrev. TRIS<sup>+</sup>Cl<sup>–</sup>), was supplied by Fluka. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide <sup>137</sup>Cs<sup>+</sup> was purchased from Technaveksport, Russia.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of TRIS<sup>+</sup>Cl<sup>–</sup> (1 × 10<sup>–3</sup> to 3 × 10<sup>–3</sup> mol/L) and microamounts of <sup>137</sup>Cs<sup>+</sup> were added to 2 mL of a nitrobenzene solution of **1** and CsDCC, whose initial concentrations varied also from 1 × 10<sup>–3</sup> to 3 × 10<sup>–3</sup> mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, C<sub>1</sub><sup>in,nb</sup>, was equal to the initial concentration of CsDCC in this medium, C<sub>CsDCC</sub><sup>in,nb</sup>). The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of cesium, D<sub>Cs</sub>, were determined as the ratios of the measured radioactivities of <sup>137</sup>Cs<sup>+</sup> in the nitrobenzene and aqueous samples.

## 3. Results and Discussion

Regarding the results of previous papers,<sup>6,27,28</sup> the two-phase water–TRIS<sup>+</sup>Cl<sup>–</sup>–nitrobenzene–cesium dicarbollylcobaltate (CsDCC) extraction system can be described by the following equilibrium

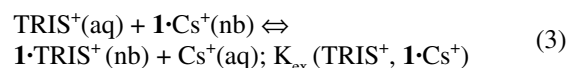


with the corresponding exchange extraction constant K<sub>ex</sub>(TRIS<sup>+</sup>, Cs<sup>+</sup>); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K<sub>ex</sub>(TRIS<sup>+</sup>, Cs<sup>+</sup>) one can write<sup>27,28</sup>

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

where K<sub>TRIS<sup>+</sup></sub><sup>i</sup> and K<sub>Cs<sup>+</sup></sub><sup>i</sup> are the individual extraction constants for TRIS<sup>+</sup> and Cs<sup>+</sup>, respectively, in the water–nitrobenzene system.<sup>27,28</sup> Knowing the values log K<sub>TRIS<sup>+</sup></sub><sup>i</sup> = –6.0<sup>28</sup> and log K<sub>Cs<sup>+</sup></sub><sup>i</sup> = –2.7,<sup>27</sup> the exchange extraction constants K<sub>ex</sub>(TRIS<sup>+</sup>, Cs<sup>+</sup>) was simply calculated from Eq. (2) as log K<sub>ex</sub>(TRIS<sup>+</sup>, Cs<sup>+</sup>) = –3.3.

Previous results<sup>29–31</sup> indicated that the two-phase water–TRIS<sup>+</sup>Cl<sup>–</sup>–nitrobenzene–**1** (HAB – based receptor)–CsDCC extraction system (see Experimental), chosen for determination of the stability constant of the complex 1·TRIS<sup>+</sup> in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium



with the respective equilibrium extraction constant K<sub>ex</sub>(TRIS<sup>+</sup>, 1·Cs<sup>+</sup>):

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

It is necessary to emphasize that **1** is a considerably hydrophobic receptor, practically present in the nitrobenzene phase only, where it forms – with TRIS<sup>+</sup> and Cs<sup>+</sup> – the relatively stable complexes 1·TRIS<sup>+</sup> and 1·Cs<sup>+</sup>. 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<sub>Cs</sub> = [1·Cs<sup>+</sup>]<sub>nb</sub> / [Cs<sup>+</sup>]<sub>aq</sub>, combined with Eq. (4), we gain the final expression for K<sub>ex</sub>(TRIS<sup>+</sup>, 1·Cs<sup>+</sup>) in the form:

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

where C<sub>TRIS<sup>+</sup>Cl<sup>–</sup></sub><sup>in,aq</sup> is the initial concentration of TRIS<sup>+</sup>Cl<sup>–</sup> in the aqueous phase and C<sub>CsDCC</sub><sup>in,nb</sup> denotes the initial concentration of CsDCC in the organic 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<sub>ex</sub>(TRIS<sup>+</sup>, 1·Cs<sup>+</sup>) was determined as log K<sub>ex</sub>(TRIS<sup>+</sup>, 1·Cs<sup>+</sup>) = –2.0 ± 0.1.

Furthermore, with respect to previous results,<sup>29–31</sup> for the extraction constants  $K_{\text{ex}}(\text{TRIS}^+, \text{Cs}^+)$  and  $K_{\text{ex}}(\text{TRIS}^+, \mathbf{1}\cdot\text{Cs}^+)$  defined above, as well as for the stability constants of the complexes  $\mathbf{1}\cdot\text{TRIS}^+$  and  $\mathbf{1}\cdot\text{Cs}^+$  in nitrobenzene saturated with water, denoted by  $\beta_{\text{nb}}(\mathbf{1}\cdot\text{TRIS}^+)$  and  $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+)$ , respectively, one gets

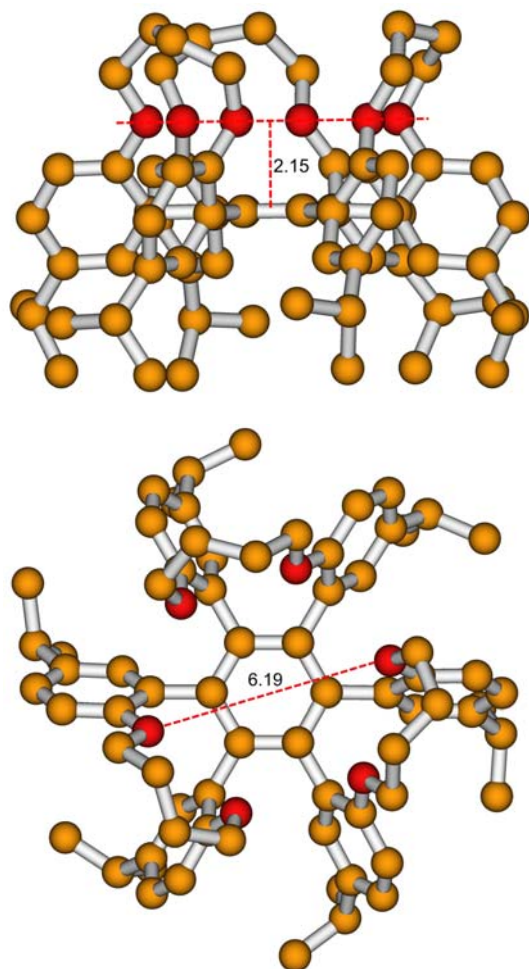
$$\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{TRIS}^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) + \log K_{\text{ex}}(\text{TRIS}^+, \mathbf{1}\cdot\text{Cs}^+) - \log K_{\text{ex}}(\text{TRIS}^+, \text{Cs}^+) \quad (6)$$

Using the constants  $\log K_{\text{ex}}(\text{TRIS}^+, \text{Cs}^+)$  and  $\log K_{\text{ex}}(\text{TRIS}^+, \mathbf{1}\cdot\text{Cs}^+)$  given above, the value  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) = 4.7 \pm 0.1$ ,<sup>32</sup> and applying Eq. (6), we obtain the stability constant of the  $\mathbf{1}\cdot\text{TRIS}^+$  complex in water-saturated nitrobenzene at 25 °C as  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{TRIS}^+) = 6.0 \pm 0.2$ . This means that in the mentioned nitrobenzene medium, the stability of the  $\mathbf{1}\cdot\text{TRIS}^+$  complex under study is somewhat higher than that of the cationic complex species  $\mathbf{1}\cdot\text{Cs}^+$ .

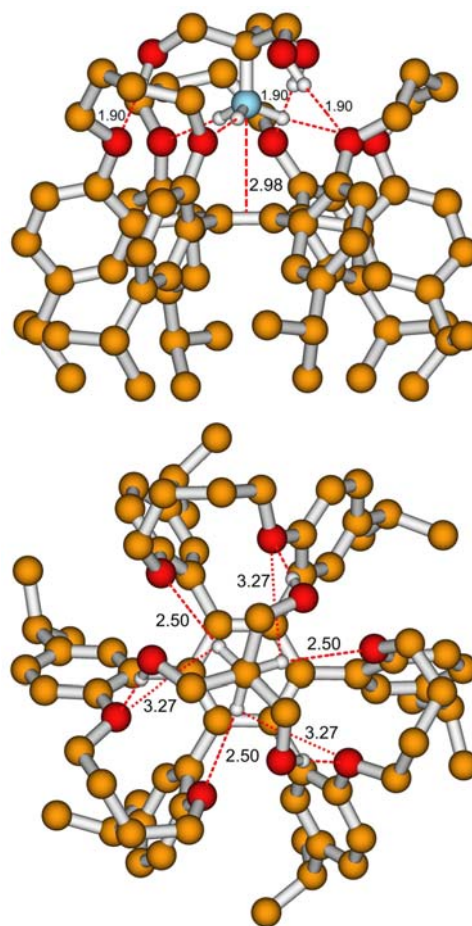
The quantum mechanical calculations were carried

out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs.<sup>33</sup> 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  $\mathbf{1}$  and the  $\mathbf{1}\cdot\text{TRIS}^+$  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>34–41</sup>

In the model calculations, we optimized the molecular geometries of the parent HAB – based receptor  $\mathbf{1}$  and its complex species with  $\text{TRIS}^+$ . The optimized structure of the free receptor  $\mathbf{1}$  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



**Figure 1.** Two projections of the DFT optimized structure of free receptor  $\mathbf{1}$  (B3LYP/6-31G(d), hydrogen atoms omitted for clarity). The depth of the cavity in  $\mathbf{1}$ : 2.15 Å; the diameter of the cavity in  $\mathbf{1}$ : 6.19 Å.



**Figure 2.** Two projections of the DFT optimized structure of the  $\mathbf{1}\cdot\text{TRIS}^+$  complex (B3LYP/6-31G(d), hydrogen atoms omitted for clarity except those of  $\text{TRIS}^+$ ). The distance between the mean plane of the bottom benzene ring and the nitrogen atom of  $\text{TRIS}^+$  in the  $\mathbf{1}\cdot\text{TRIS}^+$  complex: 2.98 Å; H-bond ( $\text{OH}\cdots\text{O}$ ) lengths of  $\text{TRIS}^+$  to the three corresponding oxygens of the ethereal fence of  $\mathbf{1}$ : 1.90, 1.90 and 1.90 Å; the lengths of the three two-center bond interactions in the  $\mathbf{1}\cdot\text{TRIS}^+$  complex: 3.27, 2.50, 3.27, 2.50, 3.27 and 2.50 Å; the depth of the cavity in  $\mathbf{1}\cdot\text{TRIS}^+$ : 1.99 Å; the diameter of the cavity in  $\mathbf{1}\cdot\text{TRIS}^+$ : 6.91 Å

groups, is illustrated in Figure 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 (Figure 1).

The structure obtained by the full DFT optimizations of the cationic complex species **1**·TRIS<sup>+</sup> is depicted in Figure 2, together with the lengths of three strong OH...O hydrogen bonds and the corresponding three two-center bond interactions (in Å). In this complex having also C<sub>3</sub> symmetry, the cation TRIS<sup>+</sup> synergistically interacts with the hydrophilic polar ethereal oxygen fence and with the central hydrophobic benzene bottom via cation – π interaction (the distance between the mean plane of the bottom benzene ring and the nitrogen atom of TRIS<sup>+</sup> in the resulting complex **1**·TRIS<sup>+</sup> is 2.98 Å, as pictured in Figure 2. At this point it is necessary to emphasize that the formation of the complex species **1**·TRIS<sup>+</sup> results in the extending of the respective cavity and at the same time, in its getting shorter, as follows from comparison of Figure 1 with Figure 2.

Finally, the interaction energy, E(int), of the **1**·TRIS<sup>+</sup> complex [calculated as the difference between the pure electronic energies of **1**·TRIS<sup>+</sup> and isolated TRIS<sup>+</sup> and **1** species: E(int) = E(**1**·TRIS<sup>+</sup>) – E(TRIS<sup>+</sup>) – E(**1**)] was found to be –106.4 kJ/mol, which confirms the formation of the considered cationic complex species **1**·TRIS<sup>+</sup>.

## 4. Conclusions

In summary, we have demonstrated that a complementary theoretical and experimental approach can provide important information on the HAB – based receptor (**1**) complex – formation with the TRIS<sup>+</sup> cation. From the experimental investigation of the resulting complex **1**·TRIS<sup>+</sup> in the two-phase water–nitrobenzene system, the strength of the considered **1**·TRIS<sup>+</sup> cationic complex species in nitrobenzene saturated with water was characterized quantitatively by the stability constant,  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{TRIS}^+) = 6.0 \pm 0.2$  (for a temperature of 25 °C). By using theoretical quantum mechanical DFT calculations, the structural details of the **1**·TRIS<sup>+</sup> complex, such as position and orientation of the TRIS<sup>+</sup> ion in the cavity of the parent HAB – based receptor **1** as well as the significant interatomic distances within the complex species under study, were obtained.

## 5. Acknowledgements

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## Povzetek

Z uporabo ekstrakcijskih eksperimentov in meritev  $\gamma$ -aktivnosti smo v dvofaznem sistemu voda-nitrobenzen raziskovali ravnotežje  $\text{TRIS}^+(\text{aq}) + \mathbf{1}\cdot\text{Cs}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{TRIS}^+(\text{nb}) + \text{Cs}^+(\text{aq})$  ( $\text{TRIS}^+ = (\text{HOCH}_2)_3\text{C-NH}_3^+$ ,  $\mathbf{1}$  = heksaarilbenzen,  $\text{aq}$  = vodna faza,  $\text{nb}$  = faza nitrobenzena). Določili smo konstanto ekstrakcije,  $\log K_{\text{ex}}(\text{TRIS}^+, \mathbf{1}\cdot\text{Cs}^+) = -2.0 \pm 0.1$  in konstanto stabilnosti kompleksa  $\mathbf{1}\cdot\text{TRIS}^+$ ,  $\beta_{\text{nb}}$ , v vodni fazi, nasičeni z nitrobenzenom,  $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{TRIS}^+, 25\text{ }^\circ\text{C}) = 6.0 \pm 0.2$ . Z uporabo kvantnomehanskih računov smo ocenili najbolj verjetno strukturo kompleksa  $\mathbf{1}\cdot\text{TRIS}^+$ , ki ima  $\text{C}_3$  simetrijo. Izkazalo se je, da kation  $\text{TRIS}^+$  interagira sinergistično s polarno etrsko skupino in centralnim hidrofobnim benzenovim obročem preko kation- $\pi$  interakcij.