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ORIGINAL PAPER

Experimental and theoretical study of the complexation of the thallium cation with a hexaarylbenzene-based receptor

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Abstract From extraction experiments in the two-phase water/nitrobenzene system and γ-activity measurements, the stability constant of a hexaarylbenzene-based receptor. Tl^+ complex species dissolved in nitrobenzene saturated with water was determined. By using the quantum-mechanical density functional level of theory calculations, the most probable structure of this complex was derived.

Keywords Receptors · Macrocycles · Complexation · DFT · Structure

Introduction

The dicarbollylcobaltate anion (DCC^-) [1] and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs^+, Sr^{2+}, Ba^{2+}, Eu^{3+}, and Am^{3+}) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes [2–25], and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [26, 27].

Hexaarylbenzene (HAB) derivatives attract a great deal of attention because of the unique propeller-shaped structure and potential applications in molecular electronics and nanotechnology. It has been described previously by employing NMR spectroscopy and X-ray crystallography that the HAB-based receptor **1** (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 [28]. Cation–π interaction is a well-established phenomenon in gas phase and in solid state [29–31], and is known to play an important role in the stabilization of tertiary structures of various proteins [32].

Recently, protonation of valinomycin, some calixarenes, dibenzo-18-crown-6, and the mentioned HAB-based receptor **1** has been investigated [33–44]. On the other hand, in the current work, the stability constant of the HAB-based receptor $\mathbf{1}\cdot Tl^+$ complex species is determined in the organic phase of the water/nitrobenzene extraction system. In this context it is necessary to emphasize that the Tl^+ ion is one of few metal cations forming the complexes with the HAB-based receptor **1** in nonaqueous solvents. Moreover, by applying quantum-mechanical density functional level of theory (DFT) calculations, the most probable structure of the above-mentioned cationic complex species is derived.

Results and discussion

Extraction experiments

Previous results [33, 45–51] indicated that the two-phase water-$TlNO_3$/nitrobenzene-CsDCC-**1** (HAB-based

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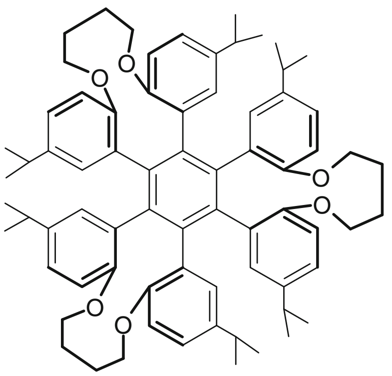

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Scheme 1

receptor) extraction system (see “Experimental”), chosen for determination of the stability constant of the cationic complex $\mathbf{1}{\cdot}\mathrm{Tl}^+$ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (Eq. 1) to which the equilibrium extraction constant (Eq. 2) corresponds; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively.

$$\mathrm{Tl}^+(\mathrm{aq}) + \mathbf{1}{\cdot}\mathrm{Cs}^+(\mathrm{nb}) \rightleftarrows \mathbf{1}{\cdot}\mathrm{Tl}^+(\mathrm{nb}) + \mathrm{Cs}^+(\mathrm{aq}); \quad K_{\mathrm{ex}}(\mathrm{Tl}^+, \mathbf{1}{\cdot}\mathrm{Cs}^+) \tag{1}$$

$$K_{\mathrm{ex}}(\mathrm{Tl}^+, \mathbf{1}{\cdot}\mathrm{Cs}^+) = \frac{[\mathbf{1}{\cdot}\mathrm{Tl}^+]_{\mathrm{nb}}[\mathrm{Cs}^+]_{\mathrm{aq}}}{[\mathrm{Tl}^+]_{\mathrm{aq}}\,[\mathbf{1}{\cdot}\mathrm{Cs}^+_{\mathrm{nb}}]} \tag{2}$$

It is necessary to emphasize that **1** is a considerably hydrophobic receptor, practically present in the nitrobenzene phase only, where this receptor forms—with Tl^+ and Cs^+—the relatively stable complexes $\mathbf{1}{\cdot}\mathrm{Tl}^+$ and $\mathbf{1}{\cdot}\mathrm{Cs}^+$.

Taking into account the conditions of electroneutrality in the aqueous and organic phases of the system under study, the mass balances of Tl^+ and Cs^+ ions at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of cesium, $D_{\mathrm{Cs}} = [\mathbf{1}{\cdot}\mathrm{Cs}^+]_{\mathrm{nb}}/[\mathrm{Cs}^+]_{\mathrm{aq}}$, combined with Eq. (2), we get the final expression for the above-mentioned extraction constant (Eq. 3); $C_{\mathrm{TlNO_3}}^{\mathrm{in,aq}}$ is the initial concentration of $\mathrm{TlNO_3}$ in the aqueous phase, and $C_{\mathrm{CsDCC}}^{\mathrm{in,nb}}$ denotes the initial concentration of CsDCC in the organic phase of the system under consideration.

$$K_{\mathrm{ex}}(\mathrm{Tl}^+, \mathbf{1}{\cdot}\mathrm{Cs}^+) = \frac{1}{D_{\mathrm{Cs}}}\frac{C_{\mathrm{CsDCC}}^{\mathrm{in,nb}}}{(1 + D_{\mathrm{Cs}})C_{\mathrm{TlNO_3}}^{\mathrm{in,aq}} - C_{\mathrm{CsDCC}}^{\mathrm{in,nb}}} \tag{3}$$

From the extraction experiments and γ-activity measurements (see “Experimental”), and by using Eq. (3), the following value of the constant K_{ex} (Tl^+, $\mathbf{1}{\cdot}\mathrm{Cs}^+$) was determined: $\log K_{\mathrm{ex}}$ (Tl, $\mathbf{1}{\cdot}\mathrm{Cs}^+$) = 0.1 ± 0.1.

Furthermore, with respect to Refs. [33, 45–51], for the exchange extraction constant K_{ex} (Tl^+, Cs^+) corresponding to the equilibrium $\mathrm{Tl}^+(\mathrm{aq}) + \mathrm{Cs}^+(\mathrm{nb}) \rightleftarrows \mathrm{Tl}^+(\mathrm{nb}) + \mathrm{Cs}^+(\mathrm{aq})$ and for the extraction constant K_{ex} (Tl^+, $\mathbf{1}{\cdot}\mathrm{Cs}^+$) defined above, as well as for the stability constants of the complexes $\mathbf{1}{\cdot}\mathrm{Cs}^+$ and $\mathbf{1}{\cdot}\mathrm{Tl}^+$ in nitrobenzene saturated with water, denoted by β_{nb} ($\mathbf{1}{\cdot}\mathrm{Cs}^+$) and β_{nb} ($\mathbf{1}{\cdot}\mathrm{Tl}^+$), one obtains Eq. (4).

$$\log \beta_{\mathrm{nb}}(\mathbf{1}{\cdot}\mathrm{Tl}^+) = \log \beta_{\mathrm{nb}}(\mathbf{1}\cdot\mathrm{Cs}^+) + \log K_{\mathrm{ex}}(\mathrm{Tl}^+, \mathbf{1}{\cdot}\mathrm{Cs}^+) - \log K_{\mathrm{ex}}(\mathrm{Tl}^+, \mathrm{Cs}^+) \tag{4}$$

Using the value $\log K_{\mathrm{ex}}$ (Tl^+, Cs^+) = −0.7 inferred from Refs. [45, 46], the constant $\log K_{\mathrm{ex}}$ (Tl^+, $\mathbf{1}{\cdot}\mathrm{Cs}^+$) given above, $\log \beta_{\mathrm{nb}}$ ($\mathbf{1}{\cdot}\mathrm{Cs}^+$) = 4.7 ± 0.1 [52], and applying Eq. (4), we obtain the stability constant of the $\mathbf{1}{\cdot}\mathrm{Tl}^+$ complex in water-saturated nitrobenzene at 25 °C as $\log \beta_{\mathrm{nb}}$ ($\mathbf{1}{\cdot}\mathrm{Tl}^+$) = 5.5 ± 0.2. This means that in the mentioned nitrobenzene medium, the stability of the $\mathbf{1}{\cdot}\mathrm{Tl}^+$ complex under study is somewhat higher than that of the cationic complex species $\mathbf{1}{\cdot}\mathrm{Cs}^+$.

Quantum-mechanical calculations

The quantum-mechanical calculations were performed at the density functional level of theory (DFT, B3LYP/LanL2DZ) using the Gaussian 03 suite of programs [53]. The structural optimization of **1** and its complex with Tl^+ were fully unconstrained. Although a possible influence of a polar solvent on the detailed structures of **1** and $\mathbf{1}{\cdot}\mathrm{Tl}^+$ could be imagined, our quantum-mechanical calculations in similar cases, carried out in an analogous way, showed very good agreement of experiment with theory [54–59].

In the model calculations, we optimized the molecular geometries of the parent HAB-based receptor **1** and its complex with Tl^+. The optimized structure of a free receptor **1** having C_3 symmetry, involving a bowl-shaped cavity 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 2.14 Å (1 Å = 0.1 nm); the diameter of this cavity in **1** is 6.30 Å (Fig. 1).

The structure obtained by the full DFT optimization of the cationic complex species $\mathbf{1}{\cdot}\mathrm{Tl}^+$ is depicted in Fig. 2. In this complex having also C_3 symmetry, the cation Tl^+ synergistically interacts with the hydrophilic polar ethereal oxygen fence (the corresponding $\mathrm{Tl}^+\cdots\mathrm{O}$ distances are gradually 3.09, 3.17, 3.09, 3.17, 3.09, and 3.17 Å) and with the central hydrophobic benzene bottom via cation–π

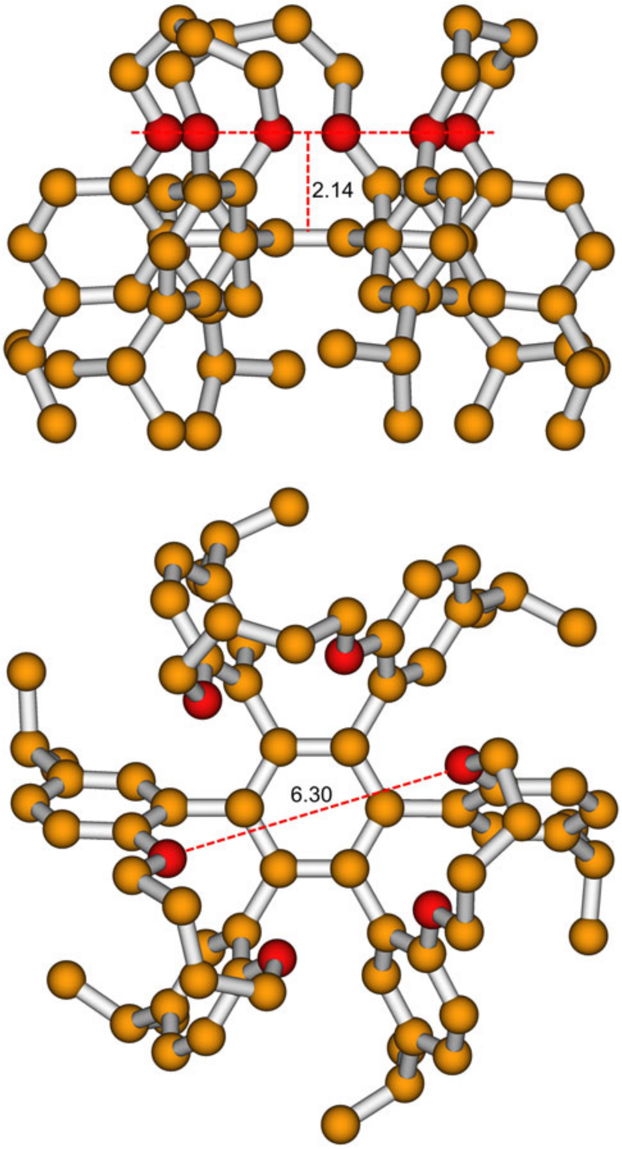

Fig. 1 Two projections of the DFT-optimized structure of free **1** (B3LYP/LanL2DZ) (hydrogen atoms omitted for clarity)

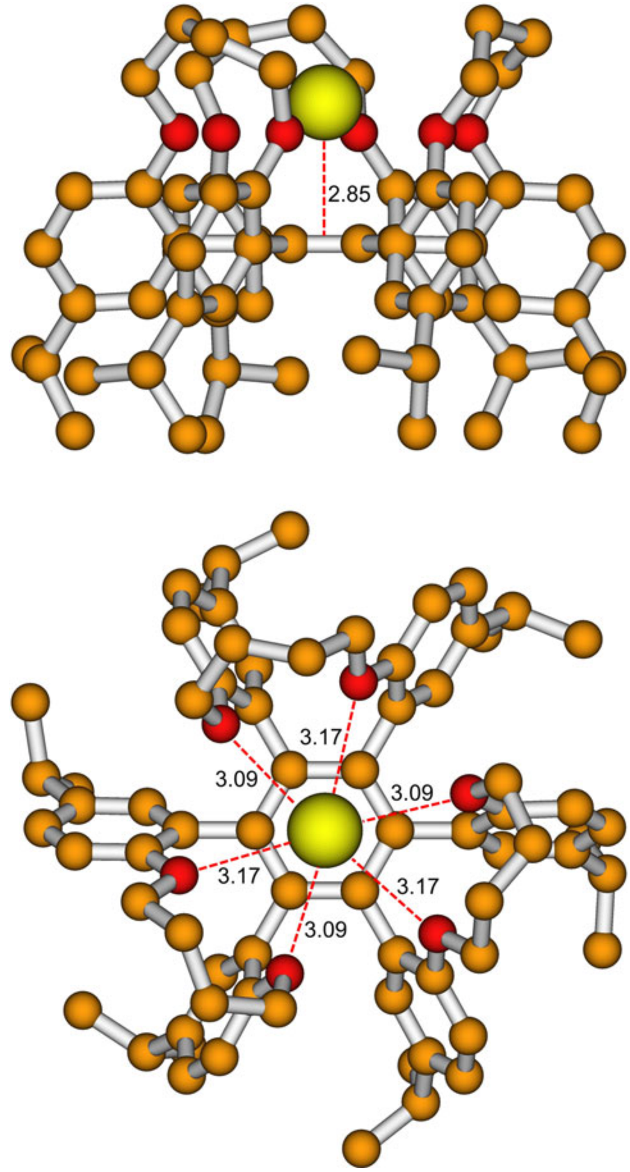

Fig. 2 Two projections of the DFT-optimized structure of the **1**·Tl^+ complex (B3LYP/LanL2DZ) (hydrogen atoms omitted for clarity)

interaction (the distance between the mean plane of the bottom benzene ring and the Tl^+ cation is 2.85 Å, as pictured in Fig. 2). At this point it should be noted that the depth of the cavity in the **1**·Tl^+ complex is about 2.24 Å, while its diameter is roughly 6.14 Å. This means that the formation of the complex species **1**·Tl^+ 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 **1**·Tl^+ complex (calculated as the difference between the electronic energies of **1**·Tl^+ and isolated Tl^+ and **1** species: $E(\text{int}) = E(\mathbf{1}\cdot\text{Tl}^+) - E(\text{Tl}^+) - E(1)$) was found to be −332.9 kJ/mol, which confirms the formation of the considered cationic complex **1**·Tl^+.

Conclusions

In summary, we have demonstrated that a complementary theoretical and experimental approach can provide important information on the HAB-based receptor **1** complexation with the thallium cation. From the experimental investigation of the resulting complex **1**·Tl^+ in the two-phase water/nitrobenzene extraction system, the strength of the considered **1**·Tl^+ cationic complex species in nitrobenzene saturated with water was characterized quantitatively by the stability constant, $\log \beta_{\text{nb}}$ (**1**·Tl^+) = 5.5 ± 0.2 (for a temperature 25 °C). By using theoretical quantum-mechanical DFT calculations, the structural details of the **1**·Tl^+ complex, such as the position of the

Tl^+ ion in the parent HAB-based receptor **1** as well as the interatomic distances within the complex species under study, were obtained.

Experimental

Preparation of the electroneutral HAB-based receptor **1** (Scheme 1) is described elsewhere [28]. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [60]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{137}Cs^+$ (Techsnaveksport, Russia) was of standard radiochemical purity.

The extraction experiments were carried out in 10 cm^3 glass test tubes with polyethylene stoppers: 2 cm^3 of an aqueous solution of $TlNO_3$ of a concentration in the range from 1×10^{-3} to 3×10^{-3} M and microamounts of $^{137}Cs^+$ were added to 2 cm^3 of a nitrobenzene solution of **1** and CsDCC, whose initial concentrations also varied from 1×10^{-3} to 3×10^{-3} M (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{\mathrm{in,nb}}$, was equal to the initial concentration of CsDCC in this medium, $C_{\mathrm{CsDCC}}^{\mathrm{in,nb}}$). 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 cm^3 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 $^{137}Cs^+$ in the nitrobenzene and aqueous samples.

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