

Short communication

Experimental and Theoretical Study on the Complexation of the Thallium Cation with Dibenzo-18-crown-6

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Abstract

From extraction experiments and γ -activity measurements, the extraction constant corresponding to the equilibrium $\text{Tl}^+(\text{aq}) + \mathbf{1}\cdot\text{Na}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{Tl}^+(\text{nb}) + \text{Na}^+(\text{aq})$ taking place in the two-phase water–nitrobenzene system ($\mathbf{1}$ = dibenzo-18-crown-6; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{\text{ex}}(\text{Tl}^+, \mathbf{1}\cdot\text{Na}^+) = 2.1$. Further, the stability constant of the complex $\mathbf{1}\cdot\text{Tl}^+$ in nitrobenzene saturated with water was calculated for a temperature of 25 °C: $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Tl}^+) = 6.6$. Finally, by using quantum mechanical DFT calculations, the most probable structure of the resulting complex $\mathbf{1}\cdot\text{Tl}^+$ was solved.

Keywords: Thallium cation, dibenzo-18-crown-6, complexation, extraction and stability constants, water-nitrobenzene system, DFT, complex structure

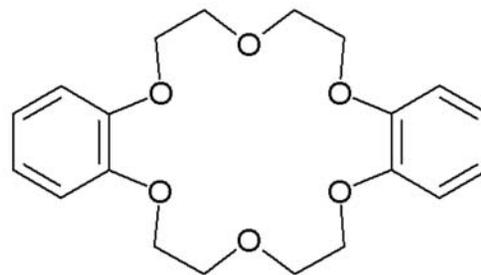
1. Introduction

The dicarbollylcobaltate anion¹ 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,^{2–23} and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{24,25}

In 1967, Pedersen published his first papers^{26,27} dealing with cyclic polyether compounds with oxyethylene groups $-\text{CH}_2-\text{CH}_2-\text{O}-$, that are called crowns owing to their structure. These electroneutral compounds form relatively stable complexes in nonaqueous solvents, especially with alkali and alkaline-earth metal cations, the cations being placed in the ligand cavities. The ratio of the size of the crown ligand cavity to the ion radius of the central cation is a decisive or at least an important factor in the stability of the complex compounds formed.²⁸ It is the complexing properties of the crowns that are due to the rapid development of the che-

mistry of these cyclic polyethers that we have witnessed in recent decades. At this point it should be noted that several reviews have covered many aspects of their chemistry.^{28–31}

In the current work, the stability constant of the cationic complex species $\mathbf{1}\cdot\text{Tl}^+$, where $\mathbf{1}$ denotes dibenzo-18-crown-6 (see Scheme 1), in nitrobenzene saturated with water was determined. Moreover, applying quantum mechanical DFT calculations, the most probable structure of the mentioned complex species was predicted.



Scheme 1. Structural formula of dibenzo-18-crown-6 (abbrev. $\mathbf{1}$).

2. Experimental

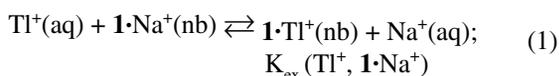
Dibenzo-18-crown-6 (abbrev. **1**; see Scheme 1) was purchased from Fluka. Cesium dicarbollylcolbaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al.³² The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcolbaltate (HDCC)¹ was prepared from CsDCC by the procedure described elsewhere.³³ The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 mol/L), yielded the corresponding NaDCC solution in nitrobenzene. The radionuclide ²²Na⁺ (DuPont, Belgium) 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 TlNO₃ of a concentration in the range from 1 × 10⁻³ to 1 × 10⁻² mol/L and microamounts of ²²Na⁺ were added to 2 mL of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations also varied from 1 × 10⁻³ to 1 × 10⁻² mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, C₁^{in,nb}, was equal to the initial concentration of NaDCC in this medium, C_{NaDCC}^{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 mL 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 sodium, D_{Na}, were determined as the ratios of the measured radioactivities of ²²Na⁺ in the nitrobenzene and aqueous samples.

3. Results and Discussion

Previous results^{34–40} indicated that the two-phase water–TlNO₃–nitrobenzene–**1** (dibenzo-18-crown-6)–NaDCC extraction system (see Experimental), chosen for determination of the stability constant of the complex **1**·Tl⁺ in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium



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

$$K_{\text{ex}}(\text{Tl}^+, \mathbf{1}\cdot\text{Na}^+) = \frac{[\mathbf{1}\cdot\text{Tl}^+]_{\text{nb}}[\text{Na}^+]_{\text{aq}}}{[\text{Tl}^+]_{\text{aq}}[\mathbf{1}\cdot\text{Na}^+]_{\text{nb}}} \quad (2)$$

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene

phase only, where it forms – with Tl⁺ and Na⁺ – the very stable complexes **1**·Tl⁺ and **1**·Na⁺. 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 sodium, D_{Na} = [**1**·Na⁺]_{nb} / [Na⁺]_{aq}, combined with Eq.(2), we obtain the final expression for K_{ex}(Tl⁺, **1**·Na⁺) in the form

$$K_{\text{ex}}(\text{Tl}^+, \mathbf{1}\cdot\text{Na}^+) = \frac{1}{D_{\text{Na}}} \frac{C_{\text{NaDCC}}^{\text{in,nb}}}{(1 + D_{\text{Na}}) C_{\text{TlNO}_3}^{\text{in,aq}} - C_{\text{NaDCC}}^{\text{in,nb}}} \quad (3)$$

where C_{TlNO₃}^{in,aq} is the initial concentration of TlNO₃ in the aqueous phase and C_{NaDCC}^{in,nb} denotes the initial concentration of NaDCC 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. (3), the following value of the constant K_{ex}(Tl⁺, **1**·Na⁺) was determined as log K_{ex}(Tl⁺, **1**·Na⁺) = 2.1.

Furthermore, with respect to previous results,^{36–40} for the exchange extraction constant K_{ex}(Tl⁺, Na⁺) corresponding to the equilibrium Tl⁺(aq) + Na⁺(nb) ⇌ Tl⁺(nb) + Na⁺(aq) and for the extraction constant K_{ex}(Tl⁺, **1**·Na⁺) defined above, as well as for the stability constants of the complexes **1**·Na⁺ and **1**·Tl⁺ in nitrobenzene saturated with water, denoted by β_{nb}(**1**·Na⁺) and β_{nb}(**1**·Tl⁺), respectively, one gets

$$\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Tl}^+) = \log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) + \log K_{\text{ex}}(\text{Tl}^+, \mathbf{1}\cdot\text{Na}^+) - \log K_{\text{ex}}(\text{Tl}^+, \text{Na}^+) \quad (4)$$

Using the value log K_{ex}(Tl⁺, Na⁺) = 2.6 inferred from References 34 and 35, the constant log K_{ex}(Tl⁺, **1**·Na⁺) given above, log β_{nb}(**1**·Na⁺) = 7.1,³⁶ and applying Eq. (4), we gain the stability constant of the **1**·Tl⁺ complex in nitrobenzene saturated with water as log β_{nb}(**1**·Tl⁺) = 6.6. Besides, Table 1 summarizes the stability constants of the cationic complexes **1**·M⁺, where M⁺ = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Tl⁺, in water-saturated nitrobenzene at 25 °C. Thus, from the data reviewed in this table it follows that the stability of the considered complexes **1**·M⁺ in the mentioned nitrobenzene medium increases in the series of Li⁺ < Cs⁺ < Rb⁺ < Tl⁺ < K⁺ < Na⁺.

Table 1. Stability constants of the **1**·M⁺ complexes (**1** = dibenzo-18-crown-6; M⁺ = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Tl⁺) in nitrobenzene saturated with water at 25 °C.

M ⁺	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Tl ⁺
log β _{nb} (1 ·M ⁺) ^a	4.5	7.1	6.9	5.8	4.9	6.6 ^b

^a Ref. 36. ^b This work.

The quantum mechanical calculations were carried out at the density functional level of theory (DFT,

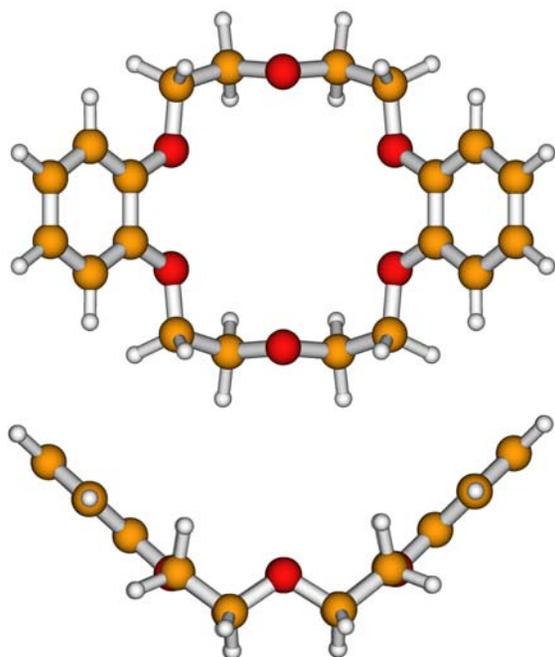


Figure 1. Two projections of the DFT optimized structure of free ligand **1** (B3LYP/LanL2DZ)

B3LYP/LanL2DZ) using the Gaussian 03 suite of programs.⁴¹ The structural optimizations of **1** and its complex with Ti^+ were fully unconstrained. Although a possible influence of a polar solvent on the detailed structures of **1** and $\mathbf{1}\cdot\text{Ti}^+$ could be imagined, our quantum mechanical calculations in similar cases, carried out in an analogous way, showed very good agreement of experiment with theory.^{42–49}

In the model calculations, we optimized the molecular geometries of the parent crown ligand **1** and its complex with Ti^+ . The optimized structure of the free ligand **1** with C_2 symmetry is illustrated in Figure 1. In Figure 2, the structure obtained by the full DFT optimization of the $\mathbf{1}\cdot\text{Ti}^+$ complex having also C_2 symmetry is depicted, together with the lengths of the corresponding bonds (in Å; 1 Å = 0.1 nm). In the $\mathbf{1}\cdot\text{Ti}^+$ cationic complex species, which is most energetically favoured, the “central” cation Ti^+ is bound by six bond interactions to four (Ar-O- CH_2) ethereal oxygens (2.91, 2.91, 2.91 and 2.91 Å) and two (CH_2 -O- CH_2) ethereal oxygen atoms (2.92 and 2.92 Å) of the parent crown ligand **1**.

Finally, the interaction energy, $E(\text{int})$, of the $\mathbf{1}\cdot\text{Ti}^+$ complex [calculated as the difference between the pure electronic energies of the complex $\mathbf{1}\cdot\text{Ti}^+$ and isolated **1** and Ti^+ species: $E(\text{int}) = E(\mathbf{1}\cdot\text{Ti}^+) - E(\mathbf{1}) - E(\text{Ti}^+)$] was found to be -334.2 kJ/mol, which confirms the formation of the considered cationic complex $\mathbf{1}\cdot\text{Ti}^+$.

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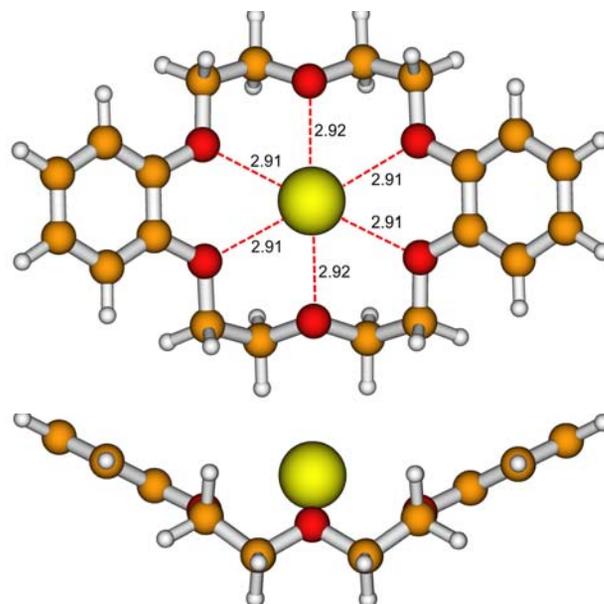


Figure 2. Two projections of the DFT optimized structure of the $\mathbf{1}\cdot\text{Ti}^+$ complex (B3LYP/LanL2DZ)

tion Society No.: CZ.1.05/1.1.00/02.0090 and by the Czech Science Foundation (Project P 205/10/2280). The computer time at the MetaCentrum (Project LM 2010005), as well as at the Institute of Physics (computer Luna/Apollo), Academy of Sciences of the Czech Republic, is gratefully acknowledged.

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Povzetek

Za ravnotežje $\text{Ti}^+(\text{aq}) + \mathbf{1}\cdot\text{Na}^+(\text{nb}) \rightleftharpoons \mathbf{1}\cdot\text{Ti}^+(\text{nb}) + \text{Na}^+(\text{aq})$ v dvofaznem sistemu voda–nitrobenzen ($\mathbf{1}$ = dibenzo-18-crown-6; aq = vodna phase, nb = nitrobenzen) smo s pomočjo podatkov za ekstrakcijo in meritev γ -aktivnosti določili konstanto ravnotežja, $\log K_{\text{ex}}(\text{Ti}^+, \mathbf{1}\cdot\text{Na}^+) = 2.1$. Ocenili smo tudi konstanto stabilnosti kompleksa $\mathbf{1}\cdot\text{Ti}^+$ v nitrobenzenu, nasičenem z vodo pri 25 °C, $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Ti}^+) = 6.6$. S pomočjo kvantno mehanskih izračunov smo določili najbolj verjetno strukturo $\mathbf{1}\cdot\text{Ti}^+$ kompleksa.