

Complexation of the cesium cation with lithium ionophore VIII: extraction and DFT study

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Abstract From extraction experiments and γ -activity measurements, the extraction constant corresponding to the equilibrium $\text{Cs}^+(\text{aq}) + \mathbf{1}\cdot\text{Na}^+(\text{nb}) = \mathbf{1}\cdot\text{Cs}^+(\text{nb}) + \text{Na}^+(\text{aq})$ taking place in the two-phase water-nitrobenzene system ($\mathbf{1}$ = lithium ionophore VIII; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{\text{ex}}(\text{Cs}^+, \mathbf{1}\cdot\text{Na}^+) = -0.5 \pm 0.1$. Further, the stability constant of the $\mathbf{1}\cdot\text{Cs}^+$ complex in nitrobenzene saturated with water was calculated for a temperature of 25 °C: $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Cs}^+) = 4.8 \pm 0.2$. Finally, by using quantum mechanical DFT calculations, the most probable structure of the cationic complex species $\mathbf{1}\cdot\text{Cs}^+$ was derived. In the resulting complex, the “central” cation Cs^+ is bound by six bond interactions to the corresponding six oxygen atoms of the parent ligand $\mathbf{1}$.

Keywords Cesium cation · Lithium ionophore VIII · Complexation · Extraction and stability constants · Water-nitrobenzene system · DFT calculations · Structures

Introduction

Organic complexing agents with the prevailing hydrophobic character have been widely used as components for ion-selective electrodes involving predominantly liquid membranes. Theory and many applications of the ion-selective electrodes have been summarized especially in excellent reviews by Koryta [1–8], Buck [9], as well as by Horvai et al. [10].

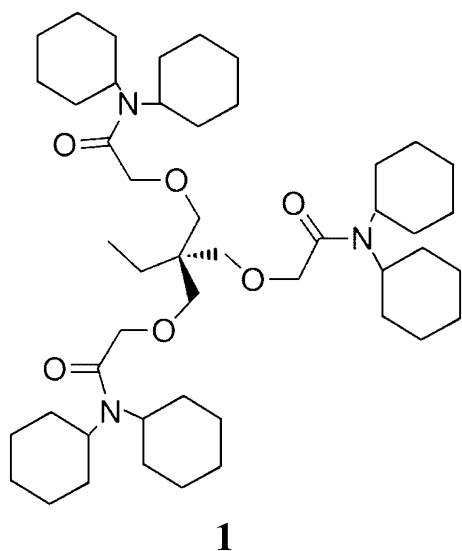
By using quantum mechanical calculations, the theoretical structures of the valinomycin complexes with Li^+ , K^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} have been solved [11–15]. Further, the interactions of Cs^+ with dibenzo-21-crown-7, dibenzo-30-crown-10, nonactin, 1,3-*alternate*-25,27-bis(1-octyoxy)calix[4]arene-crown-6, and beauvericin have been investigated [16–20]. Besides, the complexation of Sr^{2+} and Ba^{2+} with beauvericin have also been reported [21, 22].

Bocheńska and Gdaniec [23] have studied especially the interaction of lithium ionophore VIII (abbrev. $\mathbf{1}$; see Scheme 1) with lithium bromide. The main goal of this paper was to investigate whether all six oxygen binding sites of the mentioned ionophore take part in coordination of the Li^+ cation [23]. On the other hand, in the current work, the solvent extraction of Cs^+ into nitrobenzene by means of a synergistic mixture of sodium dicarbollyl cobaltate (NaDCC) and lithium ionophore VIII was studied. Moreover, the stability constant of the proved $\mathbf{1}\cdot\text{Cs}^+$ complex species in the organic phase of the water-nitrobenzene extraction system

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Scheme 1 Structural formula of lithium ionophore VIII (abbrev. **1**)

was determined. Finally, applying quantum mechanical DFT calculations, the most probable structure of this cationic complex species was predicted.

Experimental

N,N,N',N',N'',N''-Hexacyclohexyl-4,4',4''-propylidynetris(3-oxabutylamide), called also lithium ionophore VIII (puriss., $\geq 99\%$; abbrev. **1**; see Scheme 1), was supplied by Fluka and it was employed as received. Cesium dicarbollylcobaltate, CsDCC, was synthesized by means of the method published by Hawthorne et al. [24]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC) [25] was prepared from CsDCC by the procedure described elsewhere [26]. The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.20 mol/L), yielded the corresponding NaDCC solution in nitrobenzene. The radionuclide $^{22}\text{Na}^+$ was obtained from DuPont, Belgium; its radionuclidic purity was 99.9 %.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of CsNO_3 of a concentration in the range from 6×10^{-3} to 1×10^{-2} mol/L and 10 kBq of $^{22}\text{Na}^+$ were added to 2 mL of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations varied also from 6×10^{-3} to 1×10^{-2} mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{\text{in,nb}}$, was equal to the initial concentration of NaDCC in this medium, $C_{\text{NaDCC}}^{\text{in,nb}}$).

The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °C, using a laboratory shaker. Under these conditions, the equilibria in the system under study were established after ~ 20 min of shaking.

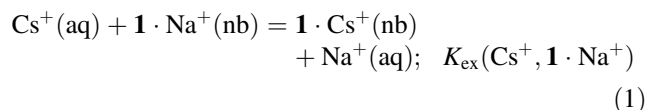
Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ -activities were measured by means of a well-type NaI(Tl) scintillation detector connected to a γ -analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of sodium, D_{Na} , were determined as the ratios of the corresponding measured radioactivities of $^{22}\text{Na}^+$ in the nitrobenzene and aqueous samples.

Results and discussion

Extraction experiments

From previous results [27–29] it follows that the two-phase water- CsNO_3 -nitrobenzene-**1** (lithium ionophore VIII)-NaDCC (sodium dicarbollylcobaltate) extraction system (see “Experimental” section), chosen for determination of the stability constant of the **1**· Cs^+ complex in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium



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

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

At this point it should be noted that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms—with Cs^+ and Na^+ —the relatively stable complexes **1**· Cs^+ and **1**· Na^+ , as given below.

Employing the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of Cs^+ and Na^+ at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, $D_{\text{Na}} = [\mathbf{1} \cdot \text{Na}^+]_{\text{nb}} / [\text{Na}^+]_{\text{aq}}$, combined with Eq. (2), we gain the final expression for $K_{\text{ex}}(\text{Cs}^+, \mathbf{1} \cdot \text{Na}^+)$ in the form

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

where $C_{\text{CsNO}_3}^{\text{in, aq}}$ is the initial concentration of CsNO_3 in the aqueous phase and $C_{\text{NaDCC}}^{\text{in, nb}}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

In this work, from the extraction experiments and γ -activity measurements (see “Experimental” section) by means of Eq. (3), the following value of the constant K_{ex} (Cs^+ , $1\cdot\text{Na}^+$) was determined: $\log K_{\text{ex}}(\text{Cs}^+, 1\cdot\text{Na}^+) = -0.5 \pm 0.1$ (see Table 1).

Furthermore, with respect to [27–29], for the exchange extraction constant $K_{\text{ex}}(\text{Cs}^+, \text{Na}^+)$ corresponding to the equilibrium $\text{Cs}^+(\text{aq}) + \text{Na}^+(\text{nb}) = \text{Cs}^+(\text{nb}) + \text{Na}^+(\text{aq})$ and for the extraction constant $K_{\text{ex}}(\text{Cs}^+, 1\cdot\text{Na}^+)$ defined above, as well as for the stability constants of the complexes $1\cdot\text{Na}^+$ and $1\cdot\text{Cs}^+$ in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(1\cdot\text{Na}^+)$ and $\beta_{\text{nb}}(1\cdot\text{Cs}^+)$, respectively, one gets

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

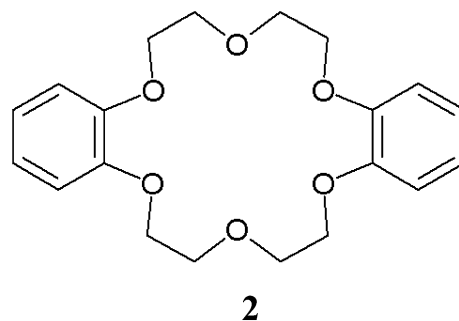
Using the value $\log K_{\text{ex}}(\text{Cs}^+, \text{Na}^+) = 3.3$ inferred from [27], the constant $\log K_{\text{ex}}(\text{Cs}^+, 1\cdot\text{Na}^+)$ given above, $\log \beta_{\text{nb}}(1\cdot\text{Na}^+) = 8.6 \pm 0.1$ [30], determined from the distribution of sodium picrate in the water-nitrobenzene system containing also the investigated ligand **1**, and applying Eq. (4), we obtain the stability constant of the $1\cdot\text{Cs}^+$ complex in water-saturated nitrobenzene at 25 °C as $\log \beta_{\text{nb}}(1\cdot\text{Cs}^+) = 4.8 \pm 0.2$. This means that in the mentioned nitrobenzene medium, the stability of the complex $1\cdot\text{Cs}^+$ is substantially lower than that of the cationic species $1\cdot\text{Na}^+$. In this context it is necessary to emphasize that the stability constant of the complex $2\cdot\text{Cs}^+$, where **2** denotes dibenzo-18-crown-6 (see Scheme 2), in nitrobenzene saturated with water is $\log \beta_{\text{nb}}(2\cdot\text{Cs}^+) = 4.9$ [31]. Thus, in this medium, the stabilities of the considered cationic complexes $1\cdot\text{Cs}^+$ and $2\cdot\text{Cs}^+$ are comparable.

Quantum mechanical calculations

The theoretical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) [32,

Table 1 Experimental data concerning determination of $\log K_{\text{ex}}(\text{Cs}^+, 1\cdot\text{Na}^+)$ on the basis of Eq. (3)

$C_{\text{CsNO}_3}^{\text{in, aq}}$ (mol/L)	$C_{\text{NaDCC}}^{\text{in, nb}}$ (mol/L)	D_{Na}	$\log K_{\text{ex}}(\text{Cs}^+, 1\cdot\text{Na}^+)$
6×10^{-3}	6×10^{-3}	1.64	−0.4
7×10^{-3}	7×10^{-3}	1.75	−0.5
8×10^{-3}	8×10^{-3}	1.63	−0.4
9×10^{-3}	9×10^{-3}	1.81	−0.5
1×10^{-2}	1×10^{-2}	1.89	−0.6



Scheme 2 Structural formula of dibenzo-18-crown-6 (abbrev. **2**)

33], employing the Gaussian 09 suite of programs [34]. The 6-31G(d,p) basis set was used for all atoms of the ligand **1**; on the other hand, for Cs^+ , quasirelativistic effective core pseudopotentials MW46 [34] were applied. 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 09 keyword “Int = UltraFine”.

Although a possible influence of a polar solvent on the detailed structures of **1** and the $1\cdot\text{Cs}^+$ complex species could be imagined, our theoretical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory [35, 36].

In the model calculations, we optimized the molecular geometries of the parent ligand **1** and its complex with Cs^+ . The optimized structure of the free ligand **1** is illustrated in Fig. 1.

In Fig. 2, the structure obtained by the full DFT optimization of the $1\cdot\text{Cs}^+$ complex is depicted, together with the lengths of the corresponding bonds (in Å). In the resulting $1\cdot\text{Cs}^+$ cationic complex species, which is most energetically favoured, the “central” cation Cs^+ is bound

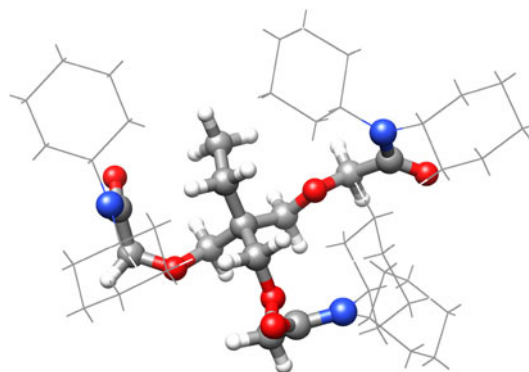


Fig. 1 The DFT optimized structure of free ligand **1** [B3LYP/6-31G(d,p)] (for lucidity, the cyclohexyl groups are illustrated by means of the “wireframe” models)

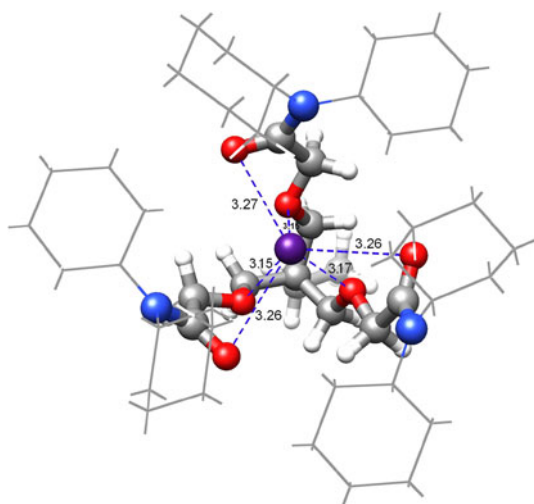


Fig. 2 The DFT optimized structure of the 1-Cs^+ complex [B3LYP/6-31G(d,p)/MW46] (for lucidity, the cyclohexyl groups are illustrated by means of the “wireframe” models)

by six relatively strong bond interactions to three ethereal oxygen atoms (3.15, 3.15, and 3.17 Å) and to three carbonyl oxygens from the corresponding amide groups (3.26, 3.27, and 3.26 Å) of the parent ligand **1** (see Fig. 2).

Finally, the interaction energy, $E(\text{int})$, of the complex 1-Cs^+ under study [calculated as the difference between the pure electronic energies of the complex 1-Cs^+ and isolated **1** and Cs^+ species: $E(\text{int}) = E(1\text{-Cs}^+) - E(1) - E(\text{Cs}^+)$] was found to be -258.9 kJ/mol, which confirms the formation of the considered cationic complex species 1-Cs^+ as well.

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