

Experimental and theoretical study on complexation of Li⁺ with lithium ionophore VIII

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Abstract From extraction experiments in the two-phase water/nitrobenzene system and γ -activity measurements, we determined the stability constant of the lithium ionophore VIII-Li⁺ cationic complex dissolved in nitrobenzene saturated with water. By using quantum-mechanical calculations, the most probable structure of this complex species was predicted.

Keywords Ionophores · Macrocycles · Complexation · DFT calculations · Structures

Introduction

Electrically neutral lipophilic organic complexing agents are widely used as components for ion-selective electrodes [1–3]. Sensors for lithium [4], sodium [5], potassium [1, 2, 6–8], ammonium [9, 10], calcium [11], strontium [12], and barium [13–16] are based on such molecules. Besides, considerable effort has been directed toward the design of selective and stable potentiometric as well as optical silver ion-selective sensors with subnanomolar detection limits [17].

The dicarbollylcobaltate anion [18] and some of its halogen derivatives are very useful reagents for the

extraction of various metal cations (especially Cs⁺, Sr²⁺, Ba²⁺, Eu³⁺, and Am³⁺) from aqueous solutions into a polar organic phase, both under laboratory conditions for purely theoretical or analytical purposes [19–27] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste [28–30].

Recently, protonation of valinomycin, some calixarenes, dibenzo-18-crown-6, and a hexaarylbenzene-based receptor has been investigated in detail [31–40]. Further, the theoretical structures of the valinomycin complexes with Li⁺, K⁺, NH₄⁺, and Mg²⁺ have been solved [41–44]. Besides, the interactions of benzo-18-crown-6 with NH₄⁺ as well as dibenzo-18-crown-6 with Ag⁺ and Cs⁺ have also been reported [45–47].

In the current work, the solvent extraction of Li⁺ into nitrobenzene by means of a synergistic mixture of sodium dicarbollylcobaltate (NaDCC) and lithium ionophore VIII (**1**, Scheme 1) was studied. Moreover, the stability constant of the proved 1·Li⁺ complex species in the organic phase of the water–nitrobenzene extraction system was determined. Finally, applying quantum-mechanical DFT calculations, the most probable structure of this cationic complex species was predicted on the basis of the thorough conformational analysis (i.e., different initial mutual positions of the ligand **1** and the Li⁺ cation were considered during the geometry optimization) and the respective vibrational frequency calculations.

Results and discussion

Extraction experiments

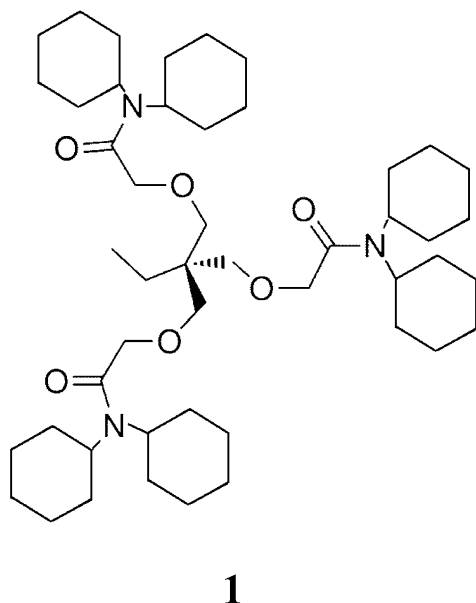
Previous results [18, 48–52] indicated that the two-phase water-LiNO₃/nitrobenzene-**1** (lithium ionophore VIII)-

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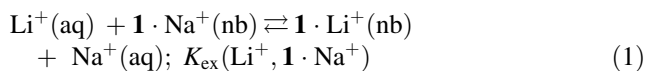
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Scheme 1



sodium dicarbollylcobaltate extraction system (see “Experimental”), chosen for determination of the stability constant of the cationic complex $\mathbf{1}\cdot\text{Li}^+$ in nitrobenzene saturated with water, can be characterized by the main 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.



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

At this point, it is necessary to emphasize that $\mathbf{1}$ is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where this ligand forms—with Li^+ and Na^+ —the very stable complexes $\mathbf{1}\cdot\text{Li}^+$ and $\mathbf{1}\cdot\text{Na}^+$, as given below.

Employing the conditions of electroneutrality in the aqueous and organic phases of the system under study, the mass balances of Li^+ 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 get the final expression for the above-mentioned extraction constant [Eq. (3)]; $C_{\text{LiNO}_3}^{\text{in, aq}}$ is the initial concentration of LiNO_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.

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

In this work, from the extraction experiments and γ -activity measurements (see “Experimental”) by means of Eq. (3), the following value of the constant $K_{\text{ex}}(\text{Li}^+, \mathbf{1}\cdot\text{Na}^+)$ was determined: $\log K_{\text{ex}}(\text{Li}^+, \mathbf{1}\cdot\text{Na}^+) = 3.6 \pm 0.1$.

Furthermore, with respect to [18, 48–52], for the exchange extraction constant $K_{\text{ex}}(\text{Li}^+, \text{Na}^+)$ corresponding to the equilibrium $\text{Li}^+(\text{aq}) + \text{Na}^+(\text{nb}) \rightleftharpoons \text{Li}^+(\text{nb}) + \text{Na}^+(\text{aq})$, and for the extraction constant $K_{\text{ex}}(\text{Li}^+, \mathbf{1}\cdot\text{Na}^+)$ defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot\text{Na}^+$ and $\mathbf{1}\cdot\text{Li}^+$

in nitrobenzene saturated with water, denoted by $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+)$ and $\beta_{\text{nb}}(\mathbf{1}\cdot\text{Li}^+)$, one obtains Eq. (4).

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

Using the value $\log K_{\text{ex}}(\text{Li}^+, \text{Na}^+) = -0.7$ inferred from [48], the constant $\log K_{\text{ex}}(\text{Li}^+, \mathbf{1}\cdot\text{Na}^+)$ given above, $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Na}^+) = 8.6 \pm 0.1$ [53], determined from the distribution of sodium picrate in the water-nitrobenzene system also containing the investigated ligand $\mathbf{1}$, and applying Eq. (4), we get the stability constant of the $\mathbf{1}\cdot\text{Li}^+$ complex in water-saturated nitrobenzene at 25 °C as $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Li}^+) = 12.9 \pm 0.2$. This means that in the mentioned nitrobenzene medium, the stability of the complex $\mathbf{1}\cdot\text{Li}^+$ is substantially higher than that of the cationic species $\mathbf{1}\cdot\text{Na}^+$. In this context, it is necessary to emphasize that the stability constant of the complex $\mathbf{2}\cdot\text{Li}^+$, where $\mathbf{2}$ denotes *p-tert*-butylcalix[4]arenetetrakis(*N,N*-diethylacetamide) (see Scheme 2), in nitrobenzene saturated with water is $\log \beta_{\text{nb}}(\mathbf{2}\cdot\text{Li}^+) = 10.0$ [54]. Thus, in this medium, the stability of the $\mathbf{1}\cdot\text{Li}^+$ complex under study is also essentially higher than that of the cationic complex species $\mathbf{2}\cdot\text{Li}^+$.

Quantum-mechanical calculations

The theoretical calculations were performed at the density functional level of theory (DFT, B3LYP functional) [55, 56], employing the Gaussian 09 suite of programs [57]. The 6-31G(d,p) 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 09 keyword “Int = UltraFine”.

Although a possible influence of a polar solvent on the detailed structures of **1** and the $\mathbf{1}\cdot\text{Li}^+$ complex species could be imagined, our theoretical calculations in similar cases, performed in an analogous way, showed very good agreement of the experiment with theory [58–63].

In the model calculations, we optimized the molecular geometries of the parent ligand **1** and its complex with Li^+ . 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 $\mathbf{1}\cdot\text{Li}^+$ complex is depicted, together with the lengths of the corresponding bonds (in Å). In the resulting $\mathbf{1}\cdot\text{Li}^+$ cationic complex species, which are most energetically favored, the “central” cation Li^+ is bound by six evidently very strong bond interactions to three ethereal

Scheme 2

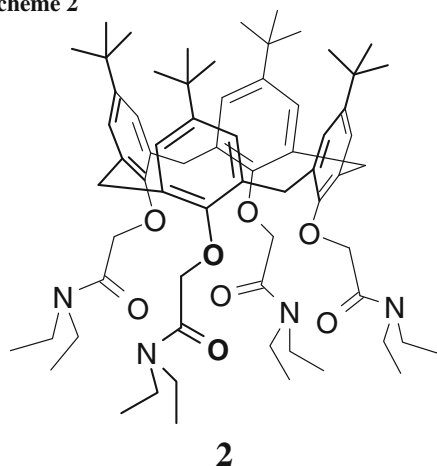
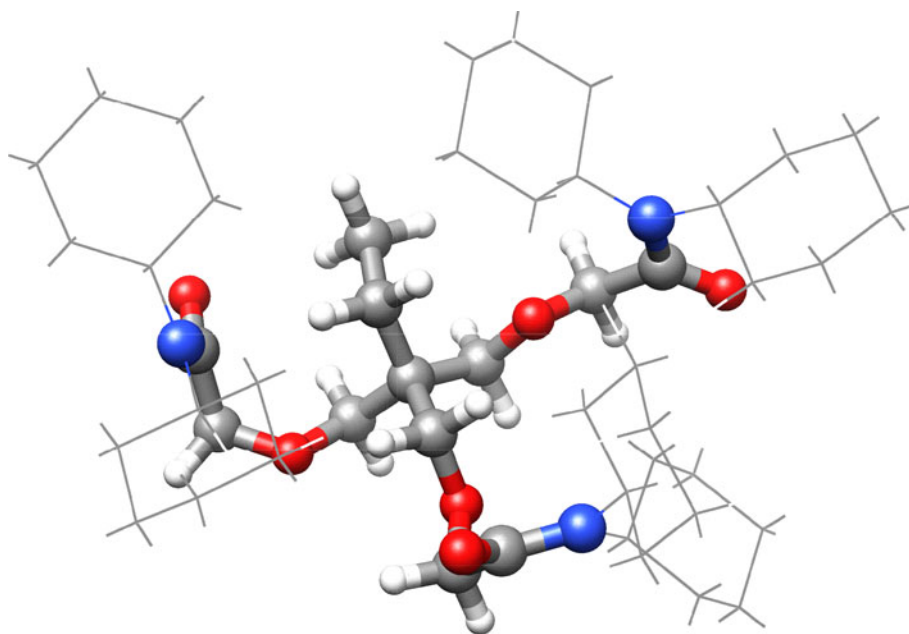


Fig. 1 The DFT optimized structure of free ligand **1** [B3LYP/6-31G(d,p)] (for lucidity, the cyclohexyl groups are illustrated by means of the “wireframe” models)



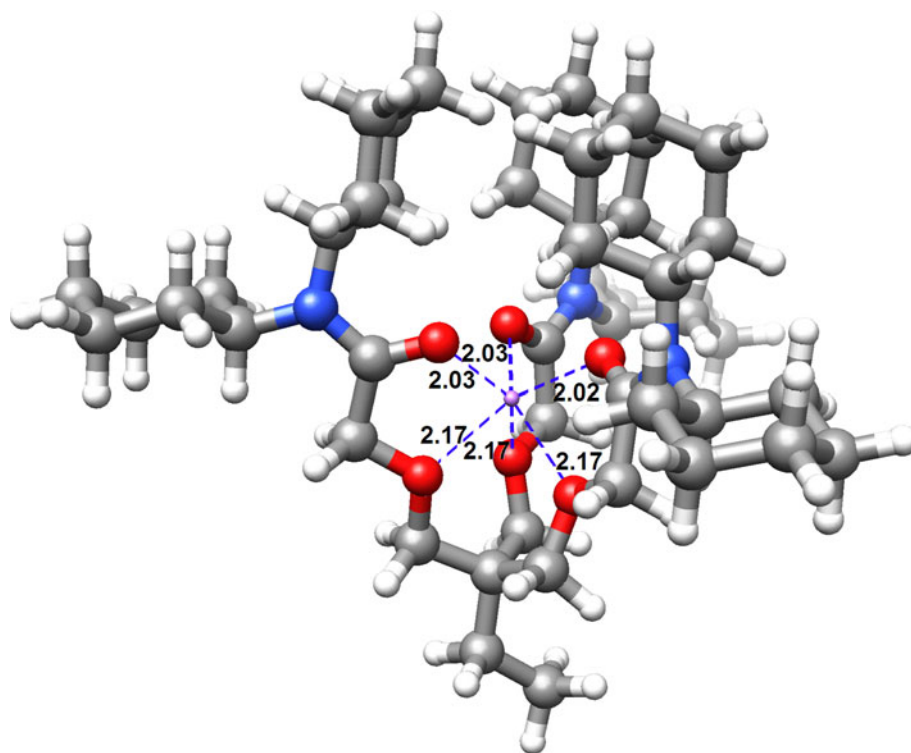
oxygens (2.17, 2.17, and 2.17 Å) and to three carbonyl oxygens from the corresponding amide groups (2.03, 2.03, and 2.02 Å) of the parent ligand **1** (see Fig. 2).

Finally, the interaction energy, $E(\text{int})$, of the complex $\mathbf{1}\cdot\text{Li}^+$ under study [calculated as the difference between the pure electronic energies of the $\mathbf{1}\cdot\text{Li}^+$ complex and isolated **1** and Li^+ species: $E(\text{int}) = E(\mathbf{1}\cdot\text{Li}^+) - E(\mathbf{1}) - E(\text{Li}^+)$] was found to be $-595.8 \text{ kJ mol}^{-1}$, which also confirms the formation of the considered cationic complex species $\mathbf{1}\cdot\text{Li}^+$.

Conclusions

In this study, we have shown that the combination of an experimental extraction method and theoretical quantum-mechanical DFT calculations can provide relevant data on the noncovalent bond interactions of the lithium ionophore VIII ligand (**1**) with the lithium cation Li^+ . From the experimental investigation of the resulting complex $\mathbf{1}\cdot\text{Li}^+$ in the two-phase water/nitrobenzene extraction system, the strength of the considered $\mathbf{1}\cdot\text{Li}^+$ cationic complex species in nitrobenzene saturated with water was characterized quantitatively by the stability constant, $\log \beta_{\text{nb}}(\mathbf{1}\cdot\text{Li}^+) = 12.9 \pm 0.2$ ($t = 25 \text{ }^\circ\text{C}$). Further, by applying the mentioned DFT calculations, the most probable structure of this $\mathbf{1}\cdot\text{Li}^+$ complex was predicted. In the resulting $\mathbf{1}\cdot\text{Li}^+$ cationic complex, which is most energetically favored, the “central” cation Li^+ is bound by six evidently very strong bond interactions to three ethereal oxygens and to three carbonyl oxygens from the corresponding amide groups of the parent ligand **1**.

Fig. 2 The DFT optimized structure of the **1**-Li⁺ complex [B3LYP/6-31G(d,p)]; distances/Å



Experimental

N,N,N',N',N'',N''-Hexacyclohexyl-4,4',4''-propylidynetris(3-oxabutylamide), also called lithium ionophore VIII (puriss., $\geq 99\%$; **1**, Scheme 1), was supplied by Fluka and was employed as received. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [64]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC) [18] was prepared from CsDCC by the procedure described elsewhere [65]. The equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.20 M), 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-cm³ glass test tubes with polyethylene stoppers: 2 cm³ of an aqueous solution of LiNO₃ of a concentration in the range from 6×10^{-3} to 1×10^{-2} M and 10 kBq of $^{22}\text{Na}^+$ were added to 2 cm³ of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations also varied from 6×10^{-3} to 1×10^{-2} M (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 approximately 20 min of shaking. Then the phases were separated by centrifugation. Afterwards, 1-cm³ 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.

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