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ORIGINAL PAPER

A combined extraction and DFT study on the complexation of the silver cation with dibenzo-18-crown-6

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Abstract Extraction experiments in the two-phase water/nitrobenzene system and γ-activity measurements were used to determine the stability constant of the dibenzo-18-crown-6·Ag^+ complex species in nitrobenzene saturated with water. Furthermore, the structure of the resulting complex was derived by means of theoretical calculations at the density functional level.

Keywords Crown ethers · Macrocycles · Complexation · Ab initio calculations · Complex structure

Introduction

In 1967, Pedersen published his first papers [1, 2] dealing with cyclic polyether compounds with oxyethylene groups $–CH_2–CH_2–O–$, which are called crowns owing to their structure. These electroneutral crown compounds form relatively stable complexes in nonaqueous solvents, especially with alkali and alkaline earth metal cations, which are located 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 [3]. It is the complexing properties of the crowns that have driven the rapid development of the chemistry of these cyclic polyethers witnessed in recent decades.

Recently, protonation of valinomycin, some calixarenes, dibenzo-18-crown-6, and a hexaarylbenzene-based receptor has been investigated [4–15]. On the other hand, in the current work, the stability constant of the dibenzo-18-crown-6·Ag^+ (**1**·Ag^+) complex species (Scheme 1) is determined in the organic phase of the water/nitrobenzene extraction system. In this context it is necessary to emphasize that the Ag^+ ion is one of the few transition metal cations forming complexes with crown ether ligands in nonaqueous solvents. Moreover, quantum mechanical density functional theory (DFT) calculations are used to derive the most probable structure of the above-mentioned cationic complex species.

Results and discussion

Extraction experiments

Previous results [4, 16–22] indicated that the two-phase water–$AgNO_3$/nitrobenzene–NaDCC–**1** (dibenzo-18-crown-6) extraction system (see "Experimental"), chosen for determination of the stability constant of the cationic complex **1**·Ag^+ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium (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.

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

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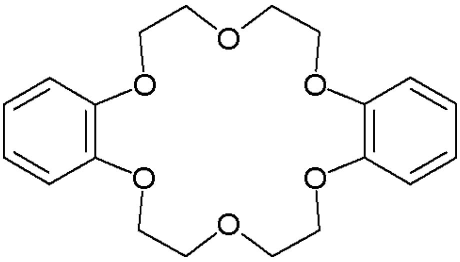

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Scheme 1

$$K_{\mathrm{ex}}(\mathrm{Ag}^+, \mathbf{1}\cdot\mathrm{Na}^+) = \frac{[\mathbf{1}\cdot\mathrm{Ag}^+]_{\mathrm{nb}}[\mathrm{Na}^+]_{\mathrm{aq}}}{[\mathrm{Ag}^+]_{\mathrm{aq}}[\mathbf{1}\cdot\mathrm{Na}^+]_{\mathrm{nb}}} \qquad (2)$$

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

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of Ag^+ and Na^+ ions at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, $D_{\mathrm{Na}} = [\mathbf{1}\cdot\mathrm{Na}^+]_{\mathrm{nb}}/[\mathrm{Na}^+]_{\mathrm{aq}}$, combined with Eq. 2, we get the final expression for the above-mentioned extraction constant, Eq. 3; $C_{\mathrm{AgNO_3}}^{\mathrm{in,aq}}$ is the initial concentration of $\mathrm{AgNO_3}$ in the aqueous phase and $C_{\mathrm{NaDCC}}^{\mathrm{in,nb}}$ denotes the initial concentration of NaDCC in the organic phase of the system under consideration.

$$K_{\mathrm{ex}}(\mathrm{Ag}^+, \mathbf{1}\cdot\mathrm{Na}^+) = \frac{1}{D_{\mathrm{Na}}}\,\frac{C_{\mathrm{NaDCC}}^{\mathrm{in,nb}}}{(1 + D_{\mathrm{Na}})C_{\mathrm{AgNO_3}}^{\mathrm{in,aq}} - C_{\mathrm{NaDCC}}^{\mathrm{in,nb}}} \qquad (3)$$

From the extraction experiments and γ-activity measurements (see "Experimental"), and by using Eq. 3, the following value of the constant K_{ex} (Ag^+, $\mathbf{1}\cdot\mathrm{Na}^+$) was determined as log K_{ex} (Ag^+, $\mathbf{1}\cdot\mathrm{Na}^+$) = 1.1. Furthermore, with respect to Refs. [4, 16–22], for the exchange extraction constant K_{ex} (Ag^+, Na^+) corresponding to the equilibrium $\mathrm{Ag}^+(\mathrm{aq}) + \mathrm{Na}^+(\mathrm{nb}) \rightleftarrows \mathrm{Ag}^+(\mathrm{nb}) + \mathrm{Na}^+(\mathrm{aq})$ and for the extraction constant K_{ex} (Ag^+, $\mathbf{1}\cdot\mathrm{Na}^+$) defined above, as well as for the stability constants of the complexes $\mathbf{1}\cdot\mathrm{Na}^+$ and $\mathbf{1}\cdot\mathrm{Ag}^+$ in nitrobenzene saturated with water, denoted by β_{nb} ($\mathbf{1}\cdot\mathrm{Na}^+$) and β_{nb} ($\mathbf{1}\cdot\mathrm{Ag}^+$), one obtains Eq. 4.

$$\log\beta_{\mathrm{nb}}(\mathbf{1}\cdot\mathrm{Ag}^+) = \log\beta_{\mathrm{nb}}(\mathbf{1}\cdot\mathrm{Na}^+) + \log K_{\mathrm{ex}}(\mathrm{Ag}^+, \mathbf{1}\cdot\mathrm{Na}^+) - \log K_{\mathrm{ex}}(\mathrm{Ag}^+, \mathrm{Na}^+) \qquad (4)$$

Using the value log K_{ex} (Ag^+, Na^+) = 1.5 inferred from Refs. [16, 17], the constant log K_{ex} (Ag^+, $\mathbf{1}\cdot\mathrm{Na}^+$) given above, log β_{nb} ($\mathbf{1}\cdot\mathrm{Na}^+$) = 7.1 [18], and applying Eq. 4, we gain the stability constant of the $\mathbf{1}\cdot\mathrm{Ag}^+$ complex in water-saturated nitrobenzene as log β_{nb} ($\mathbf{1}\cdot\mathrm{Ag}^+$) = 6.7. Beside this, Table 1 summarizes the stability constants of the cationic complexes $\mathbf{1}\cdot\mathrm{M}^+$, where $\mathrm{M}^+ = \mathrm{Li}^+$, Na^+, K^+, Rb^+, Cs^+, or Ag^+, in nitrobenzene saturated with water at 25 °C. Thus, from the data reviewed in this table it follows that the stability of the considered complexes $\mathbf{1}\cdot\mathrm{M}^+$ in the mentioned nitrobenzene medium increases in the series of $\mathrm{Li}^+ < \mathrm{Cs}^+ < \mathrm{Rb}^+ < \mathrm{Ag}^+ < \mathrm{K}^+ < \mathrm{Na}^+$.

Table 1 Stability constants of the $\mathbf{1}\cdot\mathrm{M}^+$ complexes (**1** = dibenzo-18-crown-6; $\mathrm{M}^+ = \mathrm{Li}^+$, Na^+, K^+, Rb^+, Cs^+, Ag^+) in nitrobenzene saturated with water at 25 °C

M^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
log β_{nb} ($\mathbf{1}\cdot\mathrm{M}^+$)[a]	4.5	7.1	6.9	5.8	4.9	6.7[b]

[a] Ref. [18]

[b] This work

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 [23]. The structural optimizations of **1** and its complex with Ag^+ were fully unconstrained. Although a possible influence of a polar solvent on the detailed structures of **1** and $\mathbf{1}\cdot\mathrm{Ag}^+$ could be imagined, our quantum mechanical calculations in similar cases, carried out in an analogous way, showed very good agreement of experiment with theory [24–29].

In the model calculations, we optimized the molecular geometries of the parent crown ligand **1** and its complex with Ag^+. The optimized structure of the free ligand **1** with C_2 symmetry is illustrated in Fig. 1.

In Fig. 2, the structure obtained by the full DFT-optimization of the $\mathbf{1}\cdot\mathrm{Ag}^+$ complex also having C_2 symmetry is depicted, together with the lengths of the corresponding bonds (in Å; 1 Å = 0.1 nm). In the $\mathbf{1}\cdot\mathrm{Ag}^+$ cationic complex species, which is most energetically favored, the "central" cation Ag^+ is bound by strong bond interactions to four (Ar–O–$\mathrm{CH_2}$) ethereal oxygens (2.71, 2.71, 2.71, and 2.71 Å) and two ($\mathrm{CH_2}$–O–$\mathrm{CH_2}$) ethereal oxygen atoms (2.58 and 2.58 Å) of the parent crown ligand **1**.

Finally, the interaction energy, E(int), of the $\mathbf{1}\cdot\mathrm{Ag}^+$ complex [calculated as the difference between electronic energies of the complex $\mathbf{1}\cdot\mathrm{Ag}^+$ and isolated **1** and Ag^+ species: $E(\mathrm{int}) = E(\mathbf{1}\cdot\mathrm{Ag}^+) - E(\mathbf{1}) - E(\mathrm{Ag}^+)$] was found to be −439.5 kJ mol^{-1}, which confirms the formation of the considered cationic complex $\mathbf{1}\cdot\mathrm{Ag}^+$.

Conclusions

In summary, we have demonstrated that a complementary theoretical and experimental approach can provide important information on the complexation of the crown ligand **1** with the silver cation. From the experimental investigation of the resulting complex $\mathbf{1}\cdot\mathrm{Ag}^+$ in the two-phase water/nitrobenzene extraction system, the strength of the considered $\mathbf{1}\cdot\mathrm{Ag}^+$ cationic complex species in nitrobenzene saturated with water was characterized quantitatively by the stability constant, $\log \beta_{\mathrm{nb}}\,(\mathbf{1}\cdot\mathrm{Ag}^+) = 6.7$ (for a temperature of 25 °C). By using theoretical quantum mechanical DFT calculations, the structural details of the $\mathbf{1}\cdot\mathrm{Ag}^+$ complex, such as position of the Ag^+ ion in the parent crown ligand **1** as well as the interatomic distances within the complex species under study, were obtained.

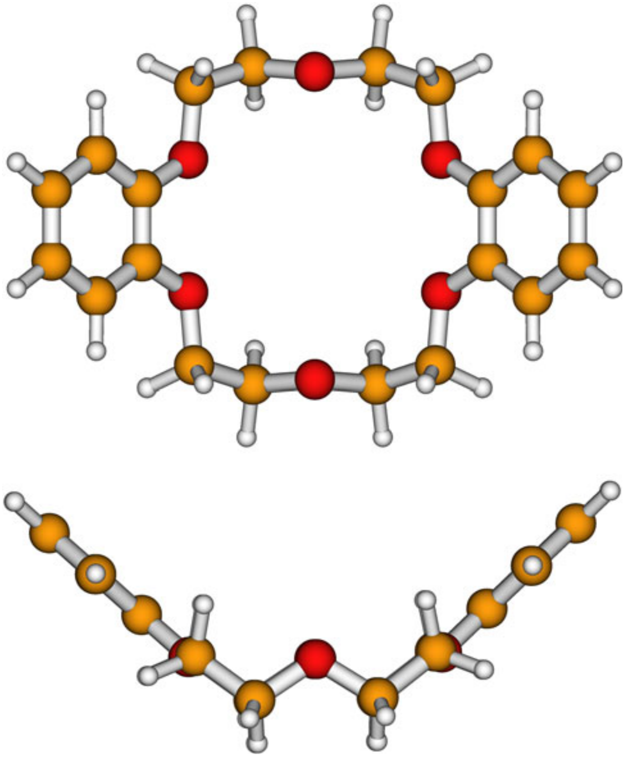

Fig. 1 Two projections of the DFT-optimized structure of free **1** (B3LYP/LanL2DZ)

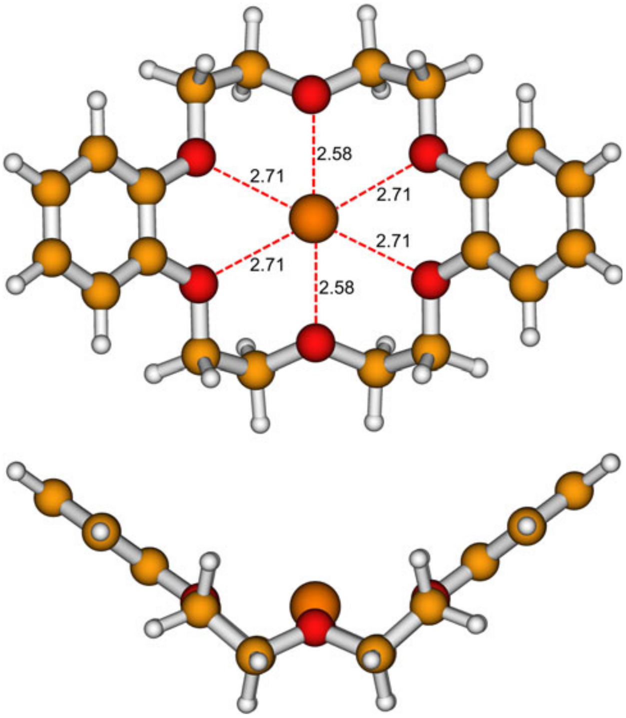

Fig. 2 Two projections of the DFT-optimized structure of the $\mathbf{1}\cdot\mathrm{Ag}^+$ complex (B3LYP/LanL2DZ)

Experimental

Dibenzo-18-crown-6 (**1**) was purchased from Fluka. Cesium dicarbollylcobaltate (CsDCC) was synthesized by means of the method published by Hawthorne et al. [30]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC) [31] was prepared from CsDCC by the procedure described elsewhere [32]. Equilibration of the nitrobenzene solution of HDCC with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 M), yielded the corresponding NaDCC solution in nitrobenzene. The radionuclide $^{22}\mathrm{Na}^+$ (DuPont, Belgium) 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 $\mathrm{AgNO_3}$ of a concentration in the range from 1×10^{-3} to 1×10^{-2} M and microamounts of $^{22}\mathrm{Na}^+$ were added to 2 cm^3 of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations also varied from 1×10^{-3} to 1×10^{-2} M (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{\mathrm{in,nb}}$, was equal to the initial concentration of NaDCC in this medium, $C_{\mathrm{NaDCC}}^{\mathrm{in,nb}}$). 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 by 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 $^{22}\mathrm{Na}^+$ in the nitrobenzene and aqueous samples.

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