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ORIGINAL PAPER

Solvent extraction of silver trifluoromethanesulfonate from water into nitrobenzene in the presence of silver ionophore IV

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Abstract From extraction experiments in the two-phase water/nitrobenzene system, the stability constant of the silver ionophore IV (i.e., 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-(methylthio)ethoxy]calix[4]arene)–Ag^+ complex in nitrobenzene saturated with water was determined. Furthermore, the most probable structure of the resulting complex was derived by means of density functional level of theory calculations.

Keywords Calixarenes · Macrocycles · Complexation · Ab initio calculations · Complex structure

Introduction

Calix[*n*]arenes are a well-known family of macrocyclic molecules with many potential applications in various branches of chemistry. Because of their one-pot preparation, easy derivatization, and unique complexation abilities, calix[*n*]arenes are widely used as building blocks for the constructions of more sophisticated molecular systems. Their unique three-dimensional (3D) pre-organization makes them very attractive as receptors for complexation of cations, anions, and even neutral molecules. Calix[*n*]arenes find applications as selective binders and carriers, analytical sensors, catalysts, and model structures for biomimetic studies [1, 2]. In the field of host–guest chemistry, many studies have focused on the binding ability of calixarene derivatives with carbonyl groups at their lower rims toward metal ions, predominantly alkali and alkaline earth, but also transition and heavy metal cations [3–11], and even toward H_3O^+ [12–19].

Silver-selective electrodes based on thioether-functionalized calix[4]arenes have been investigated by Malinowska et al. [20]. The best results have been obtained with membranes containing 5,11,17,23-tetra-*tert*-butyl-25,27-bis [2-(methylthio)ethoxy]calix[4]arene, also called silver ionophore IV (**1**, Scheme 1). However, to date, neither the precise composition of the complex Ag^+–**1** nor its structure have been known. Therefore, in the current work, the extractive distribution of silver trifluoromethanesulfonate ($AgCF_3SO_3$) in the water/nitrobenzene system involving the above-mentioned ligand **1** was studied in order to determine this composition. Furthermore, applying DFT calculations, the most probable structure of the mentioned complex species was derived.

Results and discussion

Extraction experiments

Regarding the previous results [21–23], the two-phase water–AgA ($A^- = CF_3SO_3^-$)/nitrobenzene extraction system can be described by the following equilibrium (1) with the corresponding extraction constant $K_{ex}(Ag^+, A^-)$; "aq" and "nb" denote the presence of the species in the aqueous and nitrobenzene phases.

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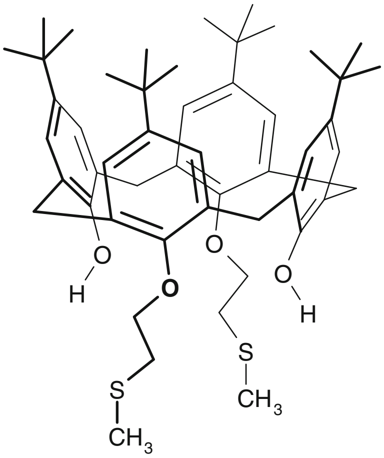

Scheme 1

$$Ag^+(aq) + A^-(aq) \rightleftarrows Ag^+(nb) + A^-(nb); K_{ex}(Ag^+,\ A^-). \quad (1)$$

The constant log $K_{ex}(Ag^+, A^-)$ can be written [21–23] as shown in Eq. 2, where $K^i_{Ag^+}$ and $K^i_{A^-}$ are the individual extraction constants for Ag^+ and A^- ions in the water/nitrobenzene system [21–23].

$$\log K_{ex}(Ag^+, A^-) = \log K^i_{Ag^+} + \log K^i_{A^-}. \quad (2)$$

Knowing $\log K^i_{Ag^+} = -4.5$ [23] and $\log K^i_{A^-} = 0.9$ (unpublished results), the extraction constant $K_{ex}(Ag^+, A^-)$ was simply calculated from Eq. 2 as log $K_{ex}(Ag^+, A^-) = -3.6$.

In terms of previous papers [24, 25], the two-phase water–AgA ($A^- = CF_3SO_3^-$)/nitrobenzene–**1** extraction system, chosen for determination of the stability constant of the complex **1**·Ag^+ (see "Experimental"), can be characterized by the main equilibrium (3) to which the equilibrium extraction constant (Eq. 4) corresponds.

$$Ag^+(aq) + A^-(aq) + \mathbf{1}(nb) \rightleftarrows \mathbf{1} \cdot Ag^+(nb) + A^-(nb);\ K_{ex}(\mathbf{1} \cdot Ag^+, A^-) \quad (3)$$

$$K_{ex}(\mathbf{1} \cdot Ag^+, A^-) = \frac{[\mathbf{1} \cdot Ag^+]_{nb}[A^-]_{nb}}{[Ag^+]_{aq}[A^-]_{aq}[\mathbf{1}]_{nb}}. \quad (4)$$

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^+—the relatively stable **1**·Ag^+ complex species.

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of **1** and AgA at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of silver, $D_{Ag} = [\mathbf{1}{\cdot}Ag^+]_{nb}/[Ag^+]_{aq}$, combined with Eq. 4, we get the final expression for the above-mentioned extraction constant (Eq. 5); $C^{in,aq}_{AgA}$ is the initial concentration of AgA in the aqueous phase and $C^{in,nb}_{\mathbf{1}}$ denotes the initial concentration of **1** in the organic phase of the system under consideration.

$$K_{ex}(\mathbf{1} \cdot Ag^+, A^-) = D^2_{Ag} \Big/ \left\{ C^{in,nb}_1 - \frac{D_{Ag}}{1 + D_{Ag}} C^{in,aq}_{AgA} \right\}. \quad (5)$$

From the extraction experiments and the AAS measurements (see "Experimental") and using Eq. 5, the following value of the constant $K_{ex}(\mathbf{1}{\cdot}Ag^+, A^-)$ was determined: log $K_{ex}(\mathbf{1}{\cdot}Ag^+, A^-) = 3.2 \pm 0.1$.

Moreover, with respect to [24, 25], for the stability constant of the **1**·Ag^+ complex in water-saturated nitrobenzene corresponding to the equilibrium **1**(nb) + Ag^+(nb) ⇄ **1**·Ag^+(nb), as well as for the extraction constants $K_{ex}(Ag^+, A^-)$ and $K_{ex}(\mathbf{1}{\cdot}Ag^+, A^-)$ defined above, one can formulate Eq. 6.

$$\log\beta_{nb}(\mathbf{1} \cdot Ag^+) = \log K_{ex}(\mathbf{1} \cdot Ag^+, A^-) - \log K_{ex}(Ag^+, A^-). \quad (6)$$

Using the constants log $K_{ex}(Ag^+, A^-)$ and log $K_{ex}(\mathbf{1}{\cdot}Ag^+, A^-)$ given above, and applying Eq. 6, we obtain the stability constant of the considered cationic complex species **1**·Ag^+ in nitrobenzene saturated with water at 25 °C as log $\beta_{nb}(\mathbf{1}{\cdot}Ag^+) = 6.8 \pm 0.1$. In this context it should be noted that, in the 2-nitrophenyl octyl ether (*o*-NPOE) medium, Szigeti et al. [26] determined the stability constant of the same metal cation complex **1**·Ag^+ as log $\beta_{org}(\mathbf{1}{\cdot}Ag^+) = 9.93 \pm 0.04$. Since the formation of an arbitrary complex is assumed to be accompanied by competition for the respective cation between solvent molecules and ligand bonding sites, the presented results are obviously a consequence of the decrease in basicity and solvating power of the medium as one proceeds from nitrobenzene saturated with water to *o*-NPOE.

Quantum-mechanical calculations

Quantum-mechanical calculations were performed at the density functional level of theory (DFT, B3LYP/6-31G(d) + LanL2DZ) using the Gaussian 03 suite of programs [27]. 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 the **1**·Ag^+ complex could be imagined, our quantum-mechanical calculations in similar cases, carried out in an analogous way, showed very good agreement of experiment with theory [28–32].

In the model calculations, we optimized the molecular geometry of the parent calix[4]arene ligand **1** and its complex with Ag^+. The optimized structure of **1** is depicted in Fig. 1, together with the lengths of the two strong OH···O hydrogen bonds (1.83 Å). From this figure it

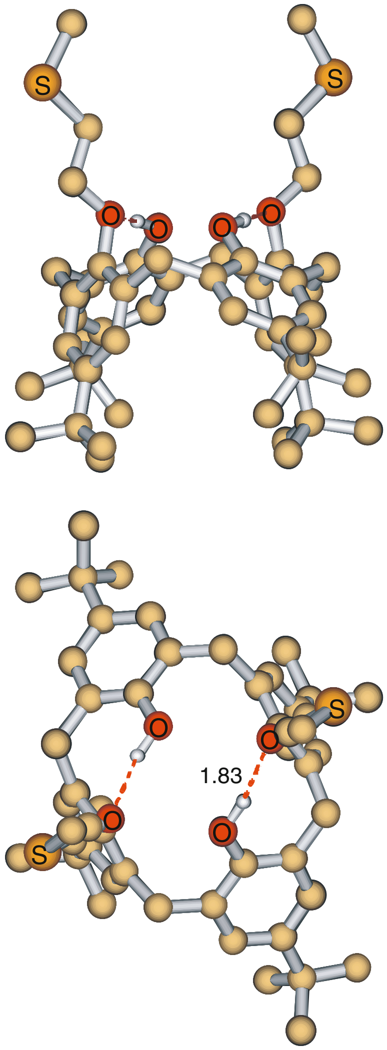

Fig. 1 Two projections of the DFT optimized structure of free **1** [B3LYP/6-31G(d) + LanL2DZ]; hydrogen atoms omitted for clarity except two hydrogens taking part in two internal OH···O hydrogen bonds (1.83 Å)

follows that the most stable conformation of **1**, stabilized by the mentioned hydrogen bonds, forms a pinched cone structure [2] with C_2 symmetry.

On the other hand, Fig. 2 illustrates the most stable structure of the considered **1**·Ag^+ complex. Analogously to the free molecule **1**, the conformation of the calixarene part of the complex **1**·Ag^+ is stabilized by two strong OH···O hydrogen bonds (1.86 and 1.90 Å) so that its structure is very close to C_2 symmetry. At this point it is necessary to note that the "central" cation Ag^+ is bound to pairs of sulfur and oxygen atoms of **1** (Fig. 2); however, the position of Ag^+ in the resulting complex is slightly asymmetric. This fact is demonstrated by the differences in both the Ag^+···O bond lengths (2.62 and 2.85 Å) and Ag^+···S bond lengths (2.61 and 2.63 Å).

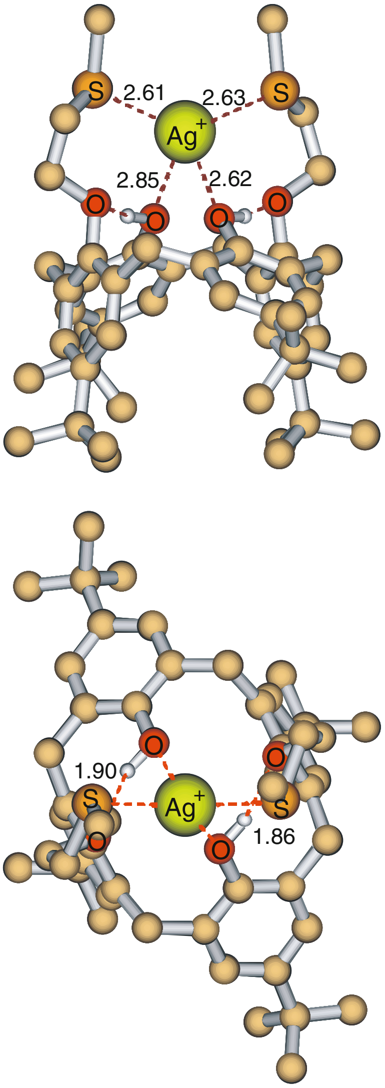

Fig. 2 Two projections of the DFT optimized structure of the **1**·Ag^+ complex [B3LYP/6-31G(d) + LanL2DZ]; hydrogen atoms omitted for clarity except two hydrogens taking part in two internal OH···O hydrogen bonds (1.86 and 1.90 Å)

Finally, the calculated stabilization energy of the **1**·Ag^+ cationic complex species is -285.1 kJ mol^{-1}, which confirms the relatively high stability of this complex.

Conclusions

This study proved that, in the nitrobenzene medium, the cation Ag^+ forms with the silver ionophore IV ligand (**1**) the resulting complex **1**·Ag^+. The conformation of the calixarene part of the **1**·Ag^+ complex is stabilized by two strong OH···O hydrogen bonds, so that its structure is very close to C_2 symmetry. Besides this, the "central" cation Ag^+ is bound to pairs of sulfur and oxygen atoms of **1**; however, the position of Ag^+ in the considered complex is slightly asymmetric.

Experimental

Silver trifluoromethanesulfonate ($AgCF_3SO_3$) and the electroneutral macrocycle 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-(methylthio)ethoxy]calix[4]arene, also called silver ionophore IV (**1**, Scheme 1), were supplied by Fluka, Buchs, Switzerland. Other chemicals used (Lachema, Brno, Czech Republic) were of reagent-grade purity.

Extraction experiments were carried out in 10-cm^3 glass test-tubes with polyethylene stoppers: 2 cm^3 of an aqueous solution of silver trifluoromethanesulfonate (AgA) of a concentration in the range from 1×10^{-3} to 1×10^{-2} M were added to 2 cm^3 of a nitrobenzene solution of **1** and NaDCC, whose initial concentrations varied from 2×10^{-3} to 2×10^{-2} M (in all experiments, the initial concentration of **1** in nitrobenzene, $C_{\mathbf{1}}^{\mathrm{in,nb}}$, was always higher than the initial concentration of AgA in water, $C_{\mathrm{AgA}}^{\mathrm{in,nb}}$). The test-tubes filled with the solutions were shaken for 24 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1-cm^3 sample was taken from the equilibrium aqueous phase, and the equilibrium concentration of silver in this phase was determined by the AAS method (Spectr AA 880, Varian) at 328.1 nm (flame: acetylene-air). On the other hand, the concentration of silver in the equilibrium organic phase was calculated from the respective mass balance of this element in the system under consideration. Finally, the equilibrium distribution ratios of silver, D_{Ag}, were determined as the ratios of the corresponding equilibrium concentrations of silver in the nitrobenzene and aqueous samples.

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