# Complexation of the Silver Cation with Dibenzo-30-crown-10: Extraction and DFT Study

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*Received: 15-02-2012*

## Abstract

From extraction experiments and $\gamma$-activity measurements, the exchange extraction constant corresponding to the equilibrium $Ag^+$(aq) + **1**·$Cs^+$(nb) $\Leftrightarrow$ **1**·$Ag^+$ (nb) + $Cs^+$(aq) taking place in the two–phase water–nitrobenzene system (**1** = dibenzo-30-crown-10; aq = aqueous phase, nb = nitrobenzene phase) was determined as log $K_{ex}$ ($Ag^+$, **1**·$Cs^+$) = –1.7 ± 0.1. Further, the stability constant of the complex **1**·$Ag^+$ in nitrobenzene saturated with water was calculated for a temperature of 25 °C: log $\beta_{nb}$ (**1**·$Ag^+$) = 6.0 ± 0.2. Finally, by using quantum mechanical DFT calculations, the most probable structure of the resulting complex **1**·$Ag^+$ was solved.

**Keywords:** Silver cation, dibenzo-30-crown-10, complexation, extraction and stability constants, water-nitrobenzene system, DFT calculations, complex structure

## 1. Introduction

In 1967, Pedersen published his first papers[1,2] dealing with cyclic polyether compounds with oxyethylene groups –$CH_2$–$CH_2$–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.[3] It is the complexing properties of the crowns that are due to the rapid development of the chemistry 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.[3–6]

The dicarbollylcobaltate anion (DCC⁻)[7] 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,[8–21] and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.[22–24]

In the current work, the stability constant of the cationic complex species **1**·$Ag^+$, where **1** denotes dibenzo-30-crown-10 (see Scheme 1), in nitrobenzene saturated
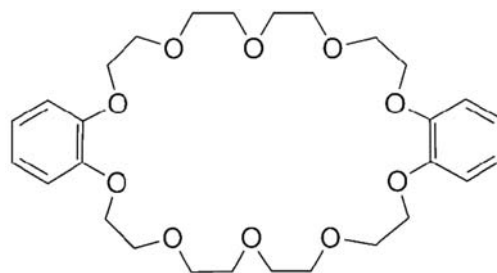


**Scheme 1.** Structural formula of dibenzo-30-crown-10 (abbrev. **1**).

with water was evaluated. Moreover, applying quantum mechanical DFT calculations, the most probable structure of the mentioned complex species was predicted.

# 2. Experimental

Dibenzo-30-crown-10 (abbrev. **1**; see Scheme 1) was purchased from Fluka. Cesium dicarbollylcobaltate (CsDCC)[7] was synthesized by means of the method published by Hawthorne et al.[25] The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The radionuclide $^{137}Cs^+$ was supplied by Techsnaveksport, Russia.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of an aqueous solution of $AgNO_3$ of a concentration in the range from $1 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/L and microamounts of $^{137}Cs^+$ were added to 2 mL of a nitrobenzene solution of **1** and CsDCC, whose initial concentrations also varied from $1 \times 10^{-3}$ to $5 \times 10^{-3}$ mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{in,nb}$, was equal to the initial concentration of CsDCC in this medium, $C_{CsDCC}^{in,nb}$). The test-tubes filled with the solutions were shaken for 2 h at $25 \pm 1$ °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their $\gamma$-activities were measured using a well-type NaI(Tl) scintillation detector connected to a $\gamma$-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of cesium, $D_{Cs}$, were determined as the ratios of the measured radioactivities of $^{137}Cs^+$ in the nitrobenzene and aqueous samples.

# 3. Results and Discussion

Previous results[26–32] indicated that the two–phase water–$AgNO_3$–nitrobenzene–**1** (dibenzo-30-crown-10) –cesium dicarbollylcobaltate (CsDCC) extraction system (see Experimental), chosen for determination of the stability constant of the complex **1·Ag⁺** in water-saturated nitrobenzene, can be characterized by the main chemical equilibrium

$$Ag^+ (aq) + \mathbf{1}\cdot Cs^+ (nb) \Leftrightarrow \mathbf{1}\cdot Ag^+ (nb) + Cs^+ (aq); \quad (1)$$
$$K_{ex} (Ag^+, \mathbf{1}\cdot Cs^+)$$
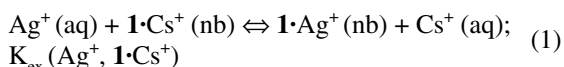
with the respective equilibrium extraction constant $K_{ex}$ $(Ag^+, \mathbf{1}\cdot Cs^+)$:

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

where the subscripts "aq" and "nb" denote the aqueous and nitrobenzene phases, respectively.

It is necessary to emphasize that **1** is a considerably hydrophobic ligand, practically present in the nitrobenzene phase only, where it forms – with $Ag^+$ and $Cs^+$ – the very stable complexes **1·Ag⁺** and **1·Cs⁺**. 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 equilibrium distribution ratio of cesium, $D_{Cs} = [\mathbf{1}\cdot Cs^+]_{nb} / [Cs^+]_{aq}$, combined with Eq. (2), we obtain the final expression for $K_{ex} (Ag^+, \mathbf{1}\cdot Cs^+)$ in the form

$$K_{ex}(Ag^+, \mathbf{1} \cdot Cs^+) = \frac{1}{D_{Cs}} \frac{C_{CsDCC}^{in,nb}}{(1 + D_{Cs}) C_{AgNO_3}^{in,aq} - C_{CsDCC}^{in,nb}} \quad (3)$$

where $C_{AgNO_3}^{in,aq}$ is the initial concentration of $AgNO_3$ in the aqueous phase and $C_{CsDCC}^{in,nb}$ denotes the initial concentration of CsDCC in the organic phase of the system under consideration.

In this study, from the extraction experiments and $\gamma$-activity measurements (see Experimental) by means of Eq. (3), the following value of the constant $K_{ex}$ $(Ag^+,$ $\mathbf{1}\cdot Cs^+)$ was determined as log $K_{ex}(Ag^+, \mathbf{1}\cdot Cs^+) = -1.7 \pm 0.1$.

Furthermore, with respect to previous results,[28–32] for the exchange extraction constant $K_{ex}$ $(Ag^+, Cs^+)$ corresponding to the equilibrium $Ag^+(aq) + Cs^+(nb) \Leftrightarrow Ag^+(nb) + Cs^+ (aq)$ and for the extraction constant $K_{ex}$ $(Ag^+, \mathbf{1}\cdot Cs^+)$ defined above, as well as for the stability constants of the complexes **1·Cs⁺** and **1·Ag⁺** in nitrobenzene saturated with water, denoted by $\beta_{nb}$ $(\mathbf{1}\cdot Cs^+)$ and $\beta_{nb}(\mathbf{1}\cdot Ag^+)$, respectively, one gets

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

Using the value log $K_{ex}$ $(Ag^+, Cs^+) = -1.8$ inferred from References 26 and 27, the constant log $K_{ex}$ $(Ag^+,$ $\mathbf{1}\cdot Cs^+)$ given above, log $\beta_{nb}$ $(\mathbf{1}\cdot Cs^+) = 5.9 \pm 0.1$,[33] and applying Eq. (4), we gain the stability constant of the **1·Ag⁺** complex in nitrobenzene saturated with water as log $\beta_{nb}(\mathbf{1}\cdot Ag^+) = 6.0 \pm 0.2$. This means that in the mentioned nitrobenzene medium, the stability constants of the cationic complex species **1·Ag⁺** and **1·Cs⁺** are comparable.

The quantum mechanical calculations were carried out at the density functional level of theory (DFT, B3LYP functional) using the Gaussian 03 suite of programs.[34] The LanL2DZ 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 03 keyword "Int = UltraFine".

Although a possible influence of a polar solvent on the detailed structures of **1** and its complex with Ag⁺ could be imagined, our quantum mechanical calculations in similar cases, performed in an analogous way, showed very good agreement of experiment with theory.[35–42]

In the model calculations, we optimized the molecular geometries of the parent crown ligand **1** and the **1**·Ag⁺ complex species. The optimized structure of the free ligand **1** with center symmetry is illustrated in Figure 1.



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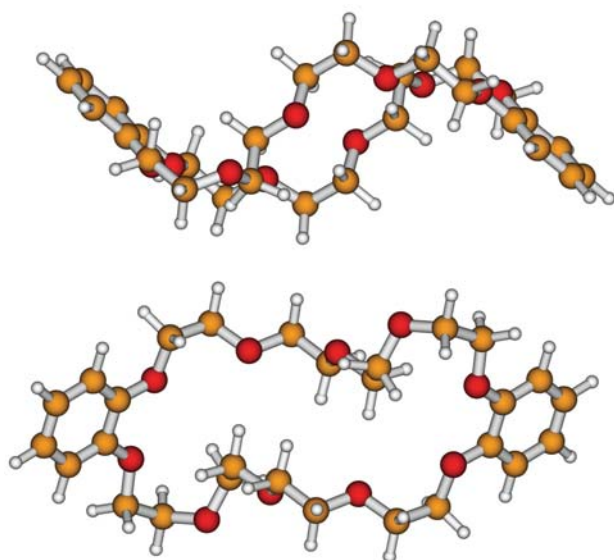


**Figure 2.** Two projections of the DFT optimized structure of the **1**·Ag⁺ complex (B3LYP/LanL2DZ).

In Figure 2, the structure obtained by the full DFT optimization of the **1**·Ag⁺ complex having a tennis-ball-seam conformation is depicted, together with the lengths of the corresponding bonds (in Å; 1 Å = 0.1 nm). In the **1**·Ag⁺ cationic complex species, which is most energetically favoured, the "central" cation Ag⁺ is bound by ten strong interactions to four (Ar–O–CH₂) ethereal oxygens (2.84, 2.78, 3.79 and 3.71 Å) and six (CH₂–O–CH₂) ethereal oxygen atoms (2.67, 2.94, 2.66, 2.83, 2.86 and 2.66 Å) of the parent crown ligand **1**.

Finally, the interaction energy, E(int), of the **1**·Ag⁺ complex [calculated as the difference between the pure electronic energies of the complex **1**·Ag⁺ and isolated **1** and Ag⁺ species: E(int) = E(**1**·Ag⁺) – E(**1**) – E(Ag⁺)] was found to be –471.0 kJ/mol, which confirms the formation of the considered cationic complex **1**·Ag⁺.

# 4. Acknowledgements

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## Povzetek

S pomočjo ekstrakcijskih eksperimentov in meritev γ-aktivnosti smo v dvofaznem sistemu voda-nitrobenzen določili konstanto ekstrakcije za ravnotežje $Ag^+(aq) + \mathbf{1} \cdot Cs^+(nb) \Leftrightarrow \mathbf{1} \cdot Ag^+(nb) + Cs^+(aq)$ (**1** = dibenzo-30-crown-10; aq = vodna faza, nb = faza nitrobenzena); $\log K_{ex}(Ag^+, \mathbf{1} \cdot Cs^+) = -1.7 \pm 0.1$. Pri temperaturi 25 °C smo v izračunali tudi konstanto stabilnosti kompleksa, $\beta_{nb}$, za $\mathbf{1} \cdot Ag^+$ v vodni fazi, nasičeni z nitrobenzenom, ki znaša $\log \beta_{nb}(\mathbf{1} \cdot Ag^+) = 6.0 \pm 0.2$. Najbolj verjetno strukturo kompleksa $\mathbf{1} \cdot Ag^+$ smo ocenili z uporabo kvantnomehanskih DFT računov