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Short Communication

Complexation of the strontium cation with a macrocyclic lactam receptor: Experimental and theoretical study

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ABSTRACT

On the basis of extraction experiments and γ-activity measurements, the extraction constant corresponding to the equilibrium $Sr^{2+}(aq) + 2A^-(aq) + \mathbf{1}(nb) \rightleftarrows \mathbf{1}\cdot Sr^{2+}(nb) + 2A^-(nb)$ occurring in the two-phase water–nitrobenzene system (A^- = picrate, **1** = macrocyclic lactam receptor — see Scheme 1; aq = aqueous phase, nb = nitrobenzene phase) was evaluated as $\log K_{ex}(\mathbf{1}\cdot Sr^{2+}, 2A^-) = -4.0 \pm 0.1$. Further, the stability constant of the $\mathbf{1}\cdot Sr^{2+}$ cationic complex in nitrobenzene saturated with water was calculated for a temperature of 25 °C: $\log \beta_{nb}(\mathbf{1}\cdot Sr^{2+}) = 5.1 \pm 0.1$. Finally, applying quantum mechanical DFT calculations, the most probable structure of the cationic complex species $\mathbf{1}\cdot Sr^{2+}$ was derived. In the resulting complex, which is most energetically favored, the "central" cation Sr^{2+} is bound by five bonding interactions to two ethereal oxygen atoms and two carbonyl oxygens, as well as to one carbon atom of the corresponding benzene ring of the parent macrocyclic lactam receptor **1** via cation–π interaction.

1. Introduction

Macrocyclic polyethers [1–6], polyoxalactones [7,8], polyazalactones [9], and cryptands [10–12] form stable inclusion complexes with various cations especially in nonpolar solvents. The ratio of the size of the ligand cavity to the ionic radius of the central cation is an important factor in the stability of the complex species formed [13]. It is the complexing properties of the macrocyclic electroneutral species that are due to the rapid development of the chemistry of these compounds that we have witnessed in recent decades. At this point it should be noted that several reviews have covered many aspects of their chemistry [13–17]. In general, fundamental forces in supramolecular chemistry, responsible for forming the stable complexes, are predominantly the following noncovalent bonding interactions: ion–ion interactions, ion–dipole interactions, dipole–dipole interactions, hydrogen bonding, cation–π interactions, π–π stacking, van der Waals forces, close packing in the solid state, or hydrophobic effects, respectively [18].

Several years ago, a novel macrocyclic lactam receptor (abbrev. **1**; see Scheme 1) for alkali or transition metal cations (e.g., Li^+, Na^+, K^+, Co^{2+}, Hg^{2+}, Pb^{2+}) has been synthesized [19]. However, up to now, interaction of this lactam receptor **1** with Sr^{2+} has not been investigated. In this context it is necessary to emphasize that the Sr^{2+} ion is a typical representative of the divalent metal cations with a large radius; besides, the radionuclide $^{85}Sr^{2+}$ used (see Section 'Experimental') enables relatively fast and very accurate physical–chemical measurements. Thus, this cation was chosen for the present study. Therefore, in the current work, the solvent extraction of strontium picrate (abbrev. SrA_2) from water into nitrobenzene by means of the mentioned electroneutral receptor **1** was studied. Furthermore, the stability constant of the proven $\mathbf{1}\cdot Sr^{2+}$ cationic complex species in the organic phase of the water–nitrobenzene extraction system was determined. Finally, employing DFT calculations, the most probable structure of this cationic complex was solved.

2. Experimental section

2.1. Chemicals

The electroneutral macrocyclic lactam receptor **1** (see Scheme 1) was synthesized by the method described elsewhere [19]; the corresponding IR and NMR spectra, as well as the respective elemental analysis and melting point of **1** were also presented in the mentioned work [19]. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A solution of strontium picrate, SrA_2, in water was prepared by dissolving a stoichiometric amount of picric acid in an aqueous solution of $Sr(OH)_2$. The carrier-free radionuclide $^{85}Sr^{2+}$ was supplied by DuPont, Belgium; its radionuclidic purity was 99.9%.

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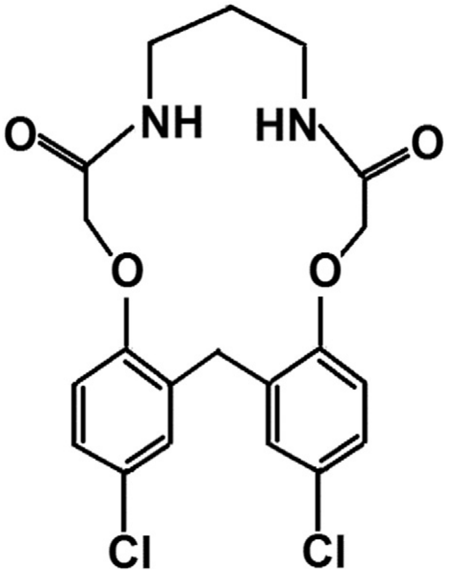

Scheme 1. Structural formula of 2,18-dichloro-9,10,11,12-tetrahydro-6*H*, 20*H*-dibenzo[*l,o*] [1,11,4,8]dioxadiazacyclohexadecine-7,13(8*H*, 14*H*)-dione (abbrev. **1**).

2.2. Extraction

The extraction experiments were carried out in 10 mL polypropylene test-tubes with polypropylene stoppers: 2 mL of an aqueous solution of SrA_2 (1×10^{-4} to 3×10^{-4} mol/L) and 10 kBq of $^{85}Sr^{2+}$ were added to 2 mL of a nitrobenzene solution of **1**, the initial concentration of which varied from 1×10^{-3} to 3×10^{-3} mol/L (in all experiments, the initial concentration of **1** in nitrobenzene, $C_1^{in,nb}$, was always higher than the initial concentration of SrA_2 in water, $C_{SrA_2}^{in,aq}$). The test-tubes filled with the solutions were shaken for 3 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Finally, 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 Triathler (Hidex, Turku, Finland).

The equilibrium distribution ratios of strontium, D_{Sr}, were determined as the ratios of the corresponding measured radioactivities of $^{85}Sr^{2+}$ in the nitrobenzene and aqueous samples.

3. Results and discussion

3.1. Extraction experiments

Regarding the results of previous papers [20–22], the two-phase water–SrA_2 ($A^- =$ picrate)–nitrobenzene extraction system can be described by the following equilibrium

$$Sr^{2+}(aq) + 2A^-(aq) \rightleftarrows Sr^{2+}(nb) + 2A^-(nb); \quad K_{ex}\left(Sr^{2+},\ 2A^-\right) \tag{1}$$

with the corresponding extraction constant K_{ex} (Sr^{2+}, $2A^-$); aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively. For the constant K_{ex} (Sr^{2+}, $2A^-$) one can write [20,22]

$$\log K_{ex}\left(Sr^{2+},\ 2A^-\right) = \log K_{Sr^{2+}}^{i} + 2\log K_{A^-}^{i} \tag{2}$$

where $K_{Sr^{2+}}^{i}$ and $K_{A^-}^{i}$ are the individual extraction constants for Sr^{2+} and A^-, respectively, in the water–nitrobenzene system [20,22]. Knowing the values $\log K_{Sr^{2+}}^{i} = -10.7$ [22] and $\log K_{A^-}^{i} = 0.8$ ($A^- =$ picrate) [22], the extraction constant K_{ex} (Sr^{2+}, $2A^-$) was simply calculated from Eq. (2) as $\log K_{ex}(Sr^{2+}, 2A^-) = -9.1$.

Our previous results [23,24] indicated that the two-phase water–SrA_2 ($A^- =$ picrate)–nitrobenzene–**1** (macrocyclic lactam receptor) extraction system (see Section 2), chosen for determination of the stability constant of the complex $\mathbf{1} \cdot Sr^{2+}$ in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium

$$Sr^{2+}(aq) + 2A^-(aq) + \mathbf{1}(nb) \rightleftarrows \mathbf{1} \cdot Sr^{2+}(nb) + 2A^-(nb); \quad K_{ex}\left(\mathbf{1} \cdot Sr^{2+},\ 2A^-\right) \tag{3}$$

to which the equilibrium extraction constant

$$K_{ex}\left(\mathbf{1} \cdot Sr^{2+}, 2A^-\right) = \frac{[\mathbf{1} \cdot Sr^{2+}]_{nb}[A^-]_{nb}^2}{[Sr^{2+}]_{aq}[A^-]_{aq}^2[\mathbf{1}]_{nb}} \tag{4}$$

corresponds. It is necessary to emphasize that **1** is a considerably lipophilic receptor, practically present in the nitrobenzene phase only, where this receptor forms — with the Sr^{2+} cation — the relatively stable complex $\mathbf{1} \cdot Sr^{2+}$, as given below.

Employing the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of **1** and SrA_2 at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of strontium, $D_{Sr} = [\mathbf{1} \cdot Sr^{2+}]_{nb}/[Sr^{2+}]_{aq}$, combined with Eq. (4), we gain the final expression for the extraction constant K_{ex} ($\mathbf{1} \cdot Sr^{2+}$, $2A^-$):

$$K_{ex}\left(\mathbf{1} \cdot Sr^{2+}, 2A^-\right) = D_{Sr}^3 \Big/ \left\{ C_1^{in,nb} - \frac{D_{Sr}}{1 + D_{Sr}} C_{SrA_2}^{in,aq} \right\} \tag{5}$$

where $C_{SrA_2}^{in,aq}$ is the initial concentration of SrA_2 in the aqueous phase and $C_1^{in,nb}$ denotes the initial concentration of **1** in the organic phase of the system under consideration.

In this work, from the extraction experiments and γ-activity measurements (see Section 2) by means of Eq. (5), the following value of the constant K_{ex} ($\mathbf{1} \cdot Sr^{2+}$, $2A^-$) was determined: $\log K_{ex}$ ($\mathbf{1} \cdot Sr^{2+}$, $2A^-$) $= -4.0 \pm 0.1$ (see Table 1). This constant experimentally proves the justifying of the extraction mechanism and the presentation of the corresponding species, expressed by the two-phase chemical equilibrium (3).

Moreover, with respect to previous results [23,24], for the extraction constants K_{ex} (Sr^{2+}, $2A^-$) and K_{ex} ($\mathbf{1} \cdot Sr^{2+}$, $2A^-$) defined above, as well as for the stability constant of the complex $\mathbf{1} \cdot Sr^{2+}$ in nitrobenzene saturated with water, denoted by β_{nb} ($\mathbf{1} \cdot Sr^{2+}$), corresponding to the equilibrium $\mathbf{1}(nb) + Sr^{2+}(nb) \rightleftarrows \mathbf{1} \cdot Sr^{2+}(nb)$, one gets

$$\log\beta_{nb}\left(\mathbf{1} \cdot Sr^{2+}\right) = \log K_{ex}\left(\mathbf{1} \cdot Sr^{2+},\ 2A^-\right) - \log K_{ex}\left(Sr^{2+},\ 2A^-\right) \tag{6}$$

Using the constants $\log K_{ex}$ (Sr^{2+}, $2A^-$) and $\log K_{ex}$ ($\mathbf{1} \cdot Sr^{2+}$, $2A^-$) given above, and employing Eq. (6), we obtain the stability constant of the $\mathbf{1} \cdot Sr^{2+}$ complex in water-saturated nitrobenzene at 25 °C as $\log \beta_{nb}$ ($\mathbf{1} \cdot Sr^{2+}$) $= 5.1 \pm 0.1$. In this context it should be noted that the stability constant of the complex species $\mathbf{2} \cdot Sr^{2+}$, where **2** denotes valinomycin (see Scheme 2), in nitrobenzene saturated with water is $\log \beta_{nb}$ ($\mathbf{2} \cdot Sr^{2+}$) $= 5.4$ [25]. This means that in the mentioned nitrobenzene medium, the stabilities of the considered complexes $\mathbf{1} \cdot Sr^{2+}$ and $\mathbf{2} \cdot Sr^{2+}$ are nearly comparable.

Table 1
Experimental data concerning determination of $\log K_{ex}$ ($\mathbf{1} \cdot Sr^{2+}$, $2A^-$) on the basis of Eq. (5).

$C_{SrA_2}^{in,aq}$ (mol/L)	$C_1^{in,nb}$ (mol/L)	D_{Sr}	$\log K_{ex}$ ($\mathbf{1} \cdot Sr^{2+}$, $2A^-$)
1.0×10^{-4}	1.0×10^{-3}	0.0050	−3.9
1.5×10^{-4}	1.5×10^{-3}	0.0056	−3.9
2.0×10^{-4}	2.0×10^{-3}	0.0060	−4.0
2.5×10^{-4}	2.5×10^{-3}	0.0063	−4.0
3.0×10^{-4}	3.0×10^{-3}	0.0062	−4.1