# Intramolecular Dynamics and Molecular Structure of Europium(III) Chelate Complexes with Crown Ethers as Studied by NMR Spectroscopy

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## Abstract

Earlier the intramolecular inversion of the 18-crown-6 molecules was found in the complex ion pairs [Ln(ptfa)$_2$ (18-crown-6)]$^+$ [Ln(ptfa)$_4$]$^-$ (H$_2$O)$_4$ where Ln = La (**1**), Ce (**2**), Pr (**3**), Nd (**4**), and ptfa is 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione. In this work the peculiarities of the molecular structure and dynamics were studied for [Eu(ptfa)$_2$ (18-crown-6)]$^+$ [Eu(ptfa)$_4$]$^-$ (H$_2$O)$_4$ (**5**) by NMR spectroscopy techniques. Through VT-NMR spectra analysis the temperature dependence was obtained for the rate constant. The free energy $\Delta G^{\ddagger}(320)$ of 18-crown-6 ring inversion activation was found to be 65 ± 5 kJ mol$^{-1}$ for **5** in CDCl$_3$. This result is comparable with the earlier data [S.P. Babailov and D.A. Mainichev: *J. Inclusion Phenom. Macrocyclic Chem.* **43**, 187–193 (2002)] for complexes **2**, **3**, **4** in deuterated toluene ($\Delta G^{\ddagger}(320)$ = 65 ± 9, 64 ± 9, 64 ± 9 kJ mol$^{-1}$ respectively). It was found by relaxation NMR spectroscopy that the effective distance between Ln and protons of the crown molecule is 4.5 ± 0.2 Å. The analysis of structural parameters testifies that the crown ether and chelated anions are in the first coordination sphere of a Ln cation. Obtained geometrical parameters show that the complex cations of Eu, Ce and Pr have similar spatial structures.

## Introduction

The last two decades have shown a deep interest in examining complexes of macrocyclic polyethers (MCPEs) and lanthanide cations (Ln) since MCPEs are prospective extractants and NMR analytical reagents. Besides, MCPEs are considered as model compounds for natural ionophores [1, 2] by many investigators. The NMR technique allows to solve problems of definition of molecular structure and dynamics of Ln – MCPE complexes [2] effectively. Recently special interest has been stimulated by the lack of investigations of molecular dynamic processes in Ln β-diketonates – MCPE complexes to be used as photo resists [3] and possible applications of photosensitive phthalocyanine, styryl and other MCPE derived compounds in molecular electronics [4, 5].

A sufficient number of studies on intramolecular dynamic kinetic processes in complexes containing the macrocycle and the diamagnetic lanthanide cation have been reported in the literature. And only a few of them are devoted to determination of enthalpy and entropy of activation for intramolecular dynamic processes in paramagnetic coordination compounds of Ln using NMR spectroscopy techniques [2, 6–10]. Earlier some tris–β-diketonates of Ln and MCPEs interaction thermodynamics was studied [11, 12]. Recently the complex stoichiometry for the ion pairs was investigated by the ligand and metal-cationic substitution methods applied to β-diketone anions [2, 13].

We have already qualitatively found that thermodynamic stability of ion pairs [Ln(ptfa)$_2$ (18-crown-6)]$^+$ [Ln (ptfa)$_4$]$^-$(H$_2$O)$_4$ decreases in a row Ln = La–Nd. And for yttrium subgroup lanthanides these ion pairs were not found at all [14]. But the quantitative characterization of thermodynamic stability of the ion pairs have not been made yet. In some works [2, 15] Gd is characterized as the element on which the physicochemical properties jump occurs ('gadolinium break' [15]). The position of Eu is closer to Gd although Eu is contained in the Ce subgroup. It appears that complex ion pairs with Eu can exist. Therefore, the case of Ln = Eu situated in the central part of lanthanide row is dramatically interesting. Besides, europium complexes are poorly investigated by relaxation NMR spectroscopy techniques.

In this report we used the dynamic NMR approach [2, 16] to obtain the activation parameters for the

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intramolecular inversion of the (18-crown-6) molecule in the complex cation [Eu(ptfa)$_2$ (18-crown-6)]$^+$. The NMR spectra of complex ion pairs **5** in weakly polar solvents were characterized and interpreted. The thermodynamic stability and the crown molecule ring inversion mechanism of the complex ion pairs **5** were studied in detail. We also compared the values of splittings of diastereotopic protons of CH$_2$-groups in **5** obtained in this paper with that found for the other complexes of crown ethers with lanthanides presented in literature.
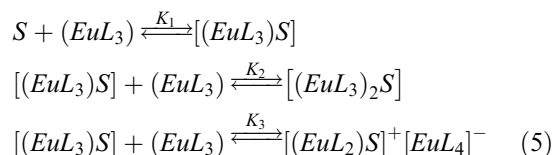
## Experimental

Samples for NMR spectroscopy were prepared by dissolving [Eu(ptfa)$_3$] and (18-crown-6) in deuterated chloroform. $^1$H-NMR spectra were recorded using MSL 200 and CXP 300 Bruker spectrometers operating at 200 and 300 MHz Larmor frequencies, respectively. The spectra were calibrated by assigning the residual chloroform signal at 298 K to a shift from TMS of $\delta = 7.24$. 1,4,7,10,13,16-hexaoxacyclo-octadecane (18-crown-6) produced by Cherkasskiy firm (mark 'Che', TU 6-09-09-190-83) was used.

Spin–lattice relaxation rate constants were measured using the pulse sequence 180$^o$-$\tau$-90$^o$ (e.g., publications [17–19]). The $T_1$ values were obtained from two-parameter fit of the data to an exponential recovery function. Fourier-transformed spectra were subjected to the complete line shape analysis [16] to obtain rate data for **5**.

Complex formation thermodynamics of system [Eu(ptfa)$_3$]-(18-crown-6) was analyzed in the framework of model (Scheme 1) which was described by thermodynamic Equations (5). Here $L$ is ptfa and $S$ is (18-crown-6).

$$S + (EuL_3) \xrightleftharpoons{K_1} [(EuL_3)S]$$

$$[(EuL_3)S] + (EuL_3) \xrightleftharpoons{K_2} [(EuL_3)_2S]$$

$$[(EuL_3)S] + (EuL_3) \xrightleftharpoons{K_3} [(EuL_2)S]^+[EuL_4]^- \quad (5)$$

Our assumption for this model was that the relative chemical shift of CH$_2$-group protons of the 2:1 complex [(EuL$_3$)$_2$S], $\Delta\delta_{2:1}$, was twice as much as the relative chemical shift of CH$_2$-group protons of the 1:1 complex [(Eu L$_3$)S], $\Delta\delta_{1:1}$, considering that both shifts were taken relative to the shift of crown ether CH$_2$-group protons $\delta_S = 3.61$. Thus, $\Delta\delta_{2:1} = 2\,\Delta\delta_{1:1}$ where $\Delta\delta_{2:1} = \delta_{2:1} - \delta_S$ and $\Delta\delta_{1:1} = \delta_{1:1} - \delta_S$. We assumed $K_1 = K_2$ for the simplified estimate.
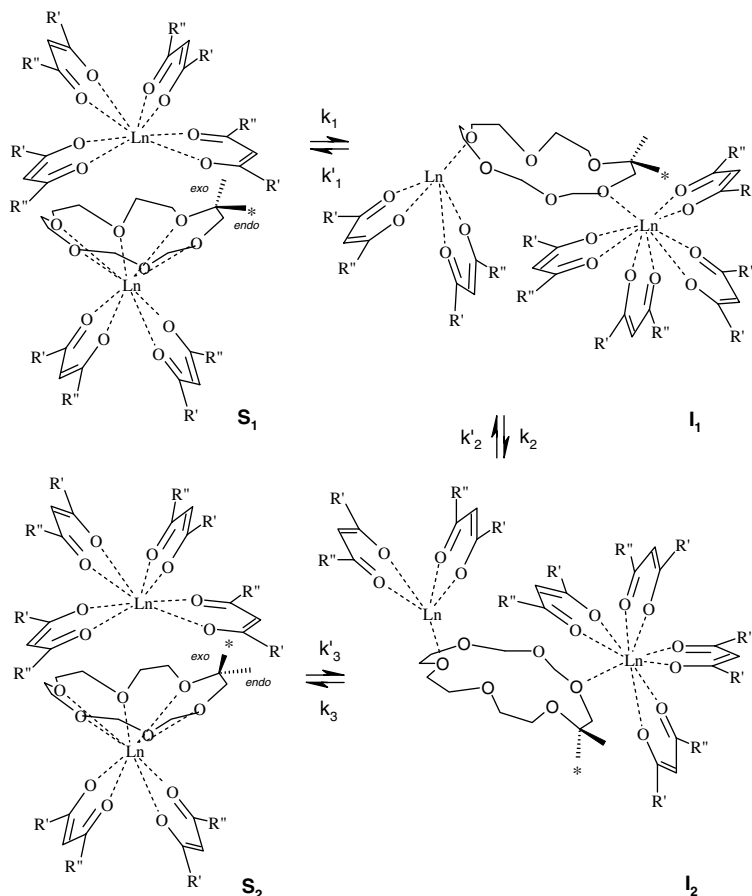


Scheme 1. R$'$=CF$_3$, R$''$=C(CH$_3$)$_3$. The dotted lines denote the coordination bonds.

It is supposed that complexes 1:1 and 2:1 are kinetically instable. So, we observe a broad signal chemical shift $\delta_{out}$ for $CH_2$-group protons out of ion pairs (which are in $S$ and in complexes 1:1 and 2:1 analogously to [20] for complexes $[Ln(L)_3 \, (18\text{-}C\text{-}6)]$ of the yttrium subgroup) given by the next equation:

$$\delta_{out} = \frac{\delta_S C_S + \delta_{1:1} C_{1:1} + \delta_{2:1} C_{2:1}}{C_S + C_{1:1} + C_{2:1}}$$

The equations of material balance can be written as

$$C_S + C_{1:1} + C_{2:1} + C_{IP} = C_{S\Sigma}$$
$$C_K + C_{1:1} + 2C_{2:1} + 2C_{IP} = C_{Eu\Sigma}$$

$C_S$ is the concentration of S, $C_K$ is the concentration of $[EuL_3]$, $C_{1:1}$ is the concentration of 1:1 complex $[(EuL_3)S]$ and $C_{2:1}$ is the concentration of 2:1 complex $[(EuL_3)_2S]$. $C_{S\Sigma}$ and $C_{Eu\Sigma}$ are the initial concentrations of S and Eu obtained by weighing $[EuL_3]$ and (18-crown-6). The concentration of ion pairs 5, $C_{IP}$, was found using the simple equation for integral intensities of signals corresponding to $CH_2$-group protons in and out of ion pairs ($I_{in}$ and $I_{out}$) obtained from the observed $^1$H-NMR spectra.

$$C_{IP} = \frac{I_{in}}{I_{in} + I_{out}} C_{S\Sigma}$$

Special homemade LabVIEW 6 program was applied for solving the system of eight equations we have got. With known parameters $\delta_{out}$, $\delta_S$, $C_{IP}$, $C_{S\Sigma}$ and $C_{Eu\Sigma}$, considering $\delta_{1:1}$ as the unknown parameter we obtained the sets of eight numbers $\delta_{1:1}$, $\delta_{2:1}$, $C_S$, $C_K$, $C_{1:1}$, $C_{2:1}$, $K_1$, $K_2$, $K_3$ for every concentration ratio $C_{S\Sigma}/C_{Eu\Sigma}$. The optimal value of $\delta_{1:1}$ was found to be $7.70 \pm 0.05$ using the optimization analysis of the set of functions $K_1$ and $K_3$ versus $\delta_{1:1}$. The best value of $\delta_{1:1}$ corresponds to the minimum of the $K_1$ mean square error normalized to mean $K_1$ as function of $\delta_{1:1}$.

## Results and discussion

### Intramolecular dynamics

The schematic representation of the complex dynamics is illustrated in Scheme 2. The mechanism is accompanied by the break of the majority of the coordination bonds between the Ln cation and the crown ether molecule. The intramolecular ring inversion rate for complex 5 was determined from the measurements of the temperature dependence of its $^1$H-NMR spectra. $^1$H-NMR spectra of complex 5 at different temperatures are shown in Figure 1. The analysis of the temperature dependence of paramagnetic lanthanide-induced shifts (LIS) in Figure 2 shows that the Curie–Weiss approximation [2] $\delta_{LIS} = a + b/T$ is good for 5 (like for 2, 3, 4 [8]). This dependence was taken into account during the investigation of intramolecular dynamics and thermodynamics. $^1$H-NMR signals corresponding to *endo* and *exo* protons are broadened with an increase in temperature that is consistent with (18-crown-6) molecule inversion (Scheme 1).

The first-order rate constant $k$ for the intramolecular exchange process was determined by the comparison of calculated and observed $^1$H-NMR spectra using the home-made LabVIEW 6 program. Activation parameters were determined using the Eyring kinetic
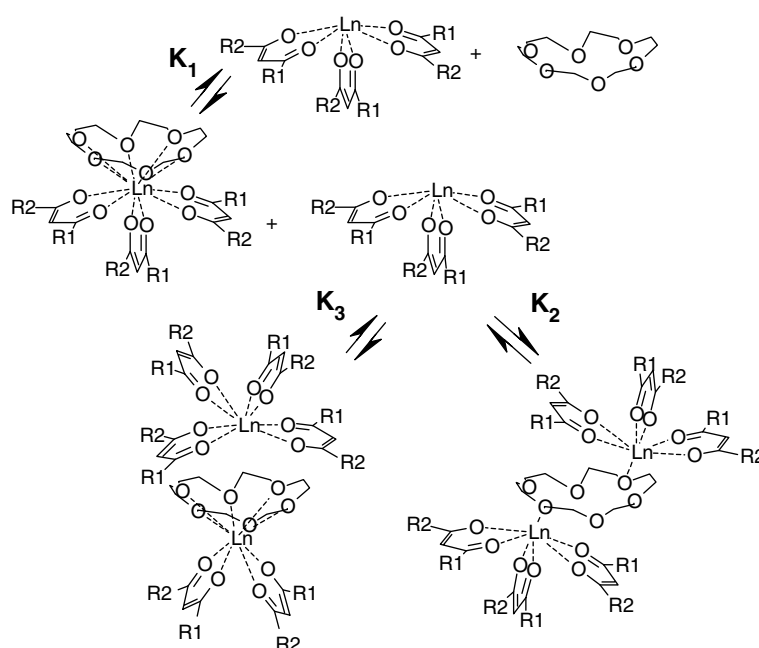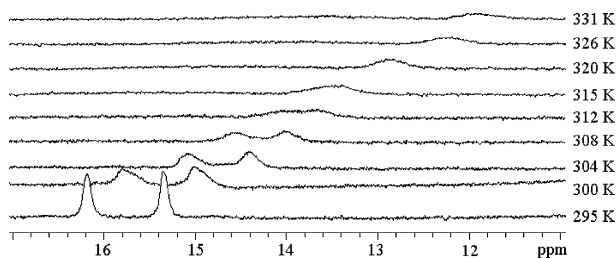


*Scheme 2.*

*Figure 1.* Variable temperature dependence of 200 MHz $^1$H-NMR spectra of [Eu(ptfa)$_2$ (18-crown-6)]$^+$ in CDCl$_3$; chemical shifts values are relative to TMS.



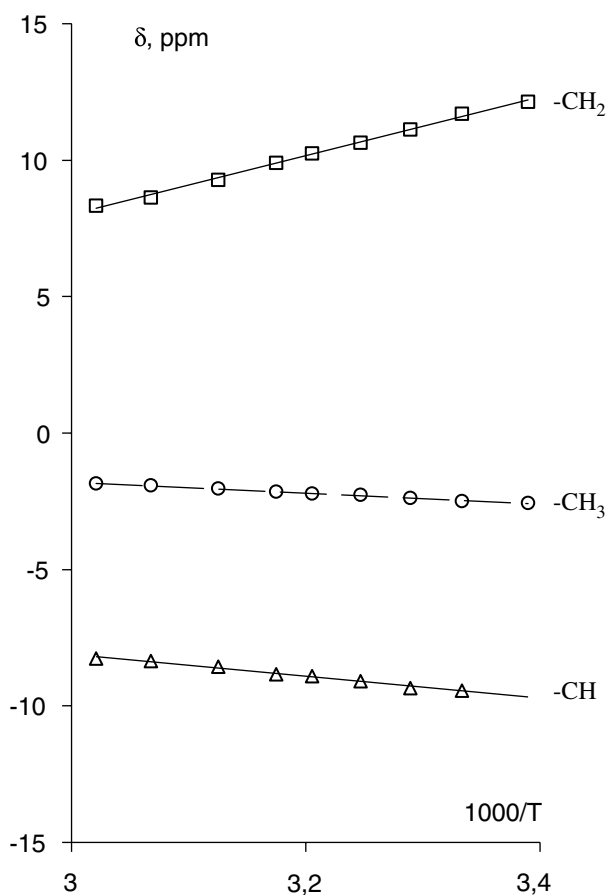*Figure 2.* Temperature dependence of the isotropic paramagnetic lanthanide-induced shifts in the 200 MHz $^1$H-NMR spectra for groups of protons of complex cations [Eu(ptfa)$_2$(18-crown-6)]$^+$ in CDCl$_3$ relative to corresponding protons in the diamagnetic cations [La(ptfa)$_2$(18-crown-6)]$^+$.

Equation (1) from weighted least squares $\{\ln[k(T)/T$ versus $1/T\}$ where $R$ is the gas constant, $k_B$ is the Boltzmann constant and $h$ is the Planck constant.

$$\ln\left[\frac{k(T)}{T}\right] = -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{h}\right) \qquad (1)$$

The activation enthalpy and activation entropy of the intramolecular ring inversion for **5** were found to be $\Delta H^{\ddagger} = 56 \pm 5$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -22 \pm 12$ J mol$^{-1}$ K$^{-1}$, respectively, with $k(295$ K$) = 40$ s$^{-1}$.

*Table 1.* Values of effective distance between the cation Ln and CH$_2$-group proton $r_{eff}$(CH$_2$) and geometric parameter $r_{eff}$(CH$_3$)/ $r_{eff}$(CH$_2$) calculated assuming that effective distance to CH$_3$-group proton $r_{eff}$(CH$_3$) is 5.56 Å[1]

| Substance | $r_{eff}$(CH$_2$), Å | $r_{eff}$(CH$_3$)/$r_{eff}$(CH$_2$) |
|---|---|---|
| [Ce (ptfa)$_2$(18-crown-6)]$^+$ | 4.3 ± 0.3 | 1.29 ± 0.07 |
| [Pr (ptfa)$_2$(18-crown-6)]$^+$ | 4.4 ± 0.3 | 1.26 ± 0.07 |
| [Eu (ptfa)$_2$(18-crown-6)]$^+$ | 4.5 ± 0.2 | 1.24 ± 0.04 |

[1]$r_{eff}$ was obtained in [8] by taking into account rotation about C—C bonds.

We have also calculated the free energy of activation $\Delta G^{\ddagger} = 65 \pm 5$ kJ mol$^{-1}$ in **5** at 320 K in CDCl$_3$ in order to compare it with the data previously reported for **2, 3, 4** [8]. The value obtained for the ring inversion activation free energy in **5** is in good agreement with that found for the complexes **2, 3, 4** in deuterated toluene [8] ($\Delta G^{\ddagger}(320) = 65 \pm 9$, $64 \pm 9$, $64 \pm 9$ kJ mol$^{-1}$ respectively).

Let $k$ be the effective rate constant for the direct reaction $S_1 \rightarrow S_2$, $k'$ is the same for the reverse reaction $S_1 \leftarrow S_2$. For the mechanism (Scheme 1) $S_1 \leftrightarrow I_1 \leftrightarrow I_2 \leftrightarrow S_2$ with intermediate states $I_1$ and $I_2$ between forms $S_1$ and $S_2$ there are rate constants $k_1$ and $k_1'$, $k_2$ and $k_2'$, $k_3$ and $k_3'$ for direct and reverse reactions correspondingly. The thermodynamic equivalence of $S_1$ and $S_2$ and stationarity ($k = k'$, $k_1 = k_1' = k_3 = k_3'$, $k_2 = k_2'$) cause the relation (2) between rate constants.

$$k = \frac{k_1 k_2}{k_1 + 2k_2} \qquad (2)$$

Due to the independence (within the limits of error) of the activation enthalpy on the Ln cation, it is just the crown molecule inversion ($I_1 \leftrightarrow I_2$) that is the rate-limiting step of intramolecular dynamics reaction ($k_1 \gg k_2$).

*Complex cation structure in solution*

We analyzed the available $^1$H-NMR and structural data on **5** using Equation (3).

$$\frac{r_{eff}(CH_3)}{r_{eff}(CH_2)} = \left[\frac{T_1(CH_3)}{T_1(CH_2)}\right]^{\frac{1}{6}} \qquad (4)$$

The results (Table 1) obtained by using lanthanide-induced enhancements of longitudinal relaxation rates experienced by some protons of complex cations [Ce (ptfa)$_2$ (18-crown-6)]$^+$, [Pr (ptfa)$_2$ (18-crown-6)]$^+$ and [Eu(ptfa)$_2$(18-crown-6)]$^+$ reveal that the structures of complexes are very similar, with only a slight decrease in geometric parameter $r_{eff}$(CH$_3$)/$r_{eff}$(CH$_2$) of distances between the cation Ln and the resonating protons upon an increase in the atomic number of the lanthanide ions. The observed small differences between three complex

*Table 2.* Lanthanide-induced splittings ($\Delta\delta$, ppm) of the $^1$H-NMR signals of diastereotopic protons of the CH$_2$-groups of macrocyclic polythers and the structural type of molecules in Ln complex compounds at room temperature

| Compound | Ln | Solvent | Inclusion type structure | Kinetic stability | $\Delta\delta$ | Refs. |
|---|---|---|---|---|---|---|
| [Ln(ClO$_4$)$_3$ (12-C-4)] | Tm | CD$_3$CN | + | + | 215 | [21] |
| [Ln(NO$_3$)$_3$ (DCH-18-C-6)] | Pr | CD$_3$CN/ CDCl$_3$ | + | + | 5 | [22] |
| [Ln(NO$_3$)$_2$ (DA-18-C-6)] | Eu | CDCl$_3$ | + | + | 57 | [23] |
| [Ln(NO$_3$)$_3$ (DA-18-C-6)] | Pr | CDCl$_3$/ CD$_2$Cl$_2$ | + | + | 2 | [6] |
| | Nd | CDCl$_3$/ CD$_2$Cl$_2$ | | | 3 | [7] |
| [Ln(L)$_2$ (18-C-6)]$^+$ | Pr | CDCl$_3$; CD$_2$Cl$_2$ | + | + | 2 | [24] |
| | Nd | | | | 0.7 | [25] |
| | Eu | | | | 0.8 | |
| [Ln(L)(L$'$) (18-C-6)]$^+$ | Pr | CDCl$_3$; CD$_2$Cl$_2$ | + | + | 0 | [13] |
| [Ln(L$'$)$_2$ (18-C-6)]$^+$ | Pr | CDCl$_3$; CD$_2$Cl$_2$ | + | + | 0 | [13] |
| [Ln(NO$_3$)$_3$ (18-C-6)] | Pr | CD$_3$CN; CDCl$_3$ | + | + | 10 | [6] |
| | Ce | CDCl$_3$/ CD$_2$Cl$_2$ | | | 6 | [26] |
| [Ln(L)$_2$ (DB-18-C-6)]$^+$ | Pr | CDCl$_3$ | + | + | 6.7 | [13] |
| [Ln(L)$_3$ (18-C-6)] | Gd-Yb | CDCl$_3$ | – | – | 0 | [20] |
| [Ln(FOD)$_3$ (18-C-6)] | Pr, Eu | CDCl$_3$ | – | – | 0 | [11, 27, 28] |

Here L – PTFA anion, L$'$ – HFA anion.

cation structures can be due either to an error in determination of $T_1$ values or to minor structural differences.

The analysis of structural parameters testifies that the crown ether and chelated anions are in the first coordination sphere of a Ln cation. Geometrical parameters obtained show that the complex cations of Eu, Ce and Pr have similar spatial structures.

The splitting of chemical shifts of CH$_2$-group protons in the 200 MHz $^1$H-NMR spectrum at 295 K of [Eu(ptfa)$_2$ (18-crown-6)]$^+$ in CDCl$_3$ (Figure 1) conditioned by diastereotopy of *endo* and *exo* protons analogously to crown ether complexes with other lanthanide cations previously studied by us [2, 6–8]. We analyzed the diastereotopic splittings (Table 2) in the different complexes of crown ethers with lanthanides presented in literature for comparison with our data.

Table 2 lists several Ln complexes with MCPE whose spatial structure in solution was studied in detail. Based on the data presented in the table, it was concluded that detecting lanthanide-induced splittings of the signals of diastereotopic protons of the −CH$_2$− groups of MCPE molecules in complexes with Ln cations is enough for identifying kinetically stable complexes with an inclusion type structure.

*Thermodynamics of complex formation*

The NMR spectroscopy techniques have been often successfully used for the investigation of complex formation thermodynamics in solution including lanthanide complexes [11, 15, 29–33]. The following additional experiments were made to characterize qualitatively the dependence of the complex ion pairs [Ln(ptfa)$_2$(18-crown-6)]$^+$ [Ln (ptfa)$_4$]$^-$ on the Ln atomic number. In CDCl$_3$ solvent initial reagents La(ptfa)$_3$,

Ln(ptfa)$_4$ and 18-crown-6 were added in equal molar quantities. We carried out relative comparisons of the NMR signal integrated intensities for cationic fragments with various Ln and found that [Ln(ptfa)$_2$(18-crown-6)]$^+$ thermodynamic stability decreases with the atomic number increasing in the row La < Ce < Pr < Nd < Eu assuming that the [Ln(ptfa)$_4$]$^-$ anion thermodynamic stability does not depend or weakly depends on atomic number.

Optimal values for the constants of equilibrium were found for the model described in the Experimental section. The variable–temperature dependence (4) of the constants of equilibrium allowed us to obtain the calorific effect of complex formation reaction.

$$\ln K = a - \frac{\Delta Q}{RT} \qquad (4)$$

The constant of equilibrium $K_1$ of [(Eu(ptfa)$_3$)(18-crown-6)] complex formation is 470 $\pm$ 130 as we supposed $K_1$ equal to constant of equilibrium $K_2$ of [(Eu(ptfa)$_3$)$_2$(18-crown-6)] complex formation. The constant of equilibrium $K_3$ of complex formation is 23 $\pm$ 4 for **5**. We can see that $K_3 < K_1$ and so the concentration of ion pairs is much less than the concentrations of other components of the system. The calorific effect of complex formation reaction $\Delta Q_1 = \Delta Q_2$ is 121 $\pm$ 35 kJ mol$^{-1}$ for [(Eu(ptfa)$_3$)(18-crown-6)] and [(Eu(ptfa)$_3$)$_2$(18-crown-6)], $\Delta Q_3$ is 67 $\pm$ 30 kJ mol$^{-1}$ for **5**.

The chemical shift $\delta_{1:1}$ of CH$_2$-group protons of the 1:1 complex [(Eu (ptfa)$_3$)(18-crown-6)] is one of the parameters used for description of NMR spectra of thermodynamic system under investigation. The optimal value of $\delta_{1:1}$ was found to be 7.70 $\pm$ 0.05. In order to estimate it in other way we analyzed Fermi contact and pseudo contact contributions to the lanthanide-induced

shift, $\delta^{FC}$ and $\delta^{PC}$, using data in the previous publication [14] considering the proposed similarity of [(Eu(ptfa)$_3$)(18-crown-6)] and [(Ln(ptfa)$_3$)(18-crown-6)] structures, Ln = Gd, Tb, Dy, Ho, Er and Yb (calculated analogously to publications [14, 15]). The predicted value of $\delta_{1:1}$ is $6.3 \pm 1.4$ ($\delta^{FC} = 4.2 \pm 0.7$ and $\delta^{PC} = -1.5 \pm 0.7$). The optimal value of $\delta_{1:1}$ and its predicted value are in good agreement.

## Conclusion

Sequential experimentation for [Ln(ptfa)$_2$(18-crown-6)]$^+$ [Ln(ptfa)$_4$]$^-$ (H$_2$O)$_4$, Ln = Ce, Pr, Nd, Eu, shows that though thermodynamic stability of complex ion pairs decreases in the lanthanide row the complex cation [Eu(ptfa)$_2$(18-crown-6)]$^+$ has the concentration enough to be detected in the $^1$H-NMR spectra.

The activation enthalpy of crown ether inversion in the cationic fragment of the complex ion pairs [Ln(ptfa)$_2$(18-crown-6)]$^+$ [Ln(ptfa)$_4$]$^-$ (H$_2$O)$_4$ where Ln = Ce, Pr, Nd, Eu does not change in the lanthanide row, even near the point of the 'gadolinium break'.

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