NMR Studies of Mixed-Ligand Lanthanide Complexes in Solution: Pseudorotation and Ring Inversion of 18-Crown-6 Molecule in Cerium Subgroup Chelates

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Abstract

^{1}H and ^{13}C NMR measurements are reported for the $CDCl_3$ and CD_2Cl_2 solutions of [La(NO$_3$)$_3$(18-crown-6)] (**I**), [Pr(NO$_3$)$_3$(18-crown-6)] (**II**) and [Ce(NO$_3$)$_3$(18-crown-6)] (**III**) complexes. Temperature dependencies of the ^{1}H NMR spectra of **II** have been analyzed using the dynamic NMR methods for multi-site exchange. Two types of conformational dynamic processes in **II** were identified (the first one with activation enthalpy $\Delta H^{\ddagger} = 26 \pm 4$ kJ/mol is conditioned by interconversion of complex enantiomeric form and pseudorotation of macrocycle molecule upon the C_2 symmetry axis, the second one with $\Delta H^{\ddagger} = 46 \pm 5$ kJ/mol is conditioned by macrocycle molecule inversion). Studies of the values of the lanthanide-induced shifts revealed that the structure of complexes in solution is similar to that reported for the complex **I** in the crystal state.

Introduction

The lanthanide (Ln) salt complexes of the cerium subgroup with 18-membered macrocyclic polyethers are 'classical' compounds, for which the possibility of forming coordination saturated 12-coordinated inclusion complexes of the lanthanides has been found [1–3]. Presently, the thermodynamic, structural and electronic properties of 18-membered macrocyclic ether complexes with the lanthanide cations are well known both in solution and in the solid state [3–9]. On the other hand, the paramagnetic properties [2, 5, 7] and dynamics of these complexes in solution have been poorly studied until recently [5, 6, 10–12]. The investigation of the dynamic properties of these complexes represents an interesting area in the chemistry of inclusion compounds and attracts the interest of researchers [6, 10–12].

Although we reported in a letter to editor our preliminary results [10] of NMR investigation of [Ln(NO$_3$)$_3$(18-crown-6)] complexes dynamic properties in solution (where Ln = La (**I**) and Pr (**II**)), the detailed model of conformational dynamics in **II** was not published. In the present work the structure of the kinetically stable complexes **II** and [Ce(NO$_3$)$_3$(18-crown-6)] (**III**) in CDCl$_3$ and CD$_2$Cl$_2$ solutions is investigated by ^{1}H and ^{13}C NMR. The molecular dynamics of complex **II** is studied in detail by dynamic ^{1}H NMR spectroscopy. It has been found that the dynamics was conditioned by two dynamic processes. The first one with activation enthalpy $\Delta H^{\ddagger} = 26 \pm 4$ kJ/mol is conditioned by interconversion of complex enantiomeric forms and pseudorotation of macrocycle molecule upon the C_2 symmetry axis. The second one with $\Delta H^{\ddagger} = 46 \pm 5$ kJ/mol is conditioned by macrocycle molecule inversion. It should be noted that an investigation of this kind is of interest both for the coordination chemistry and for the organic chemistry since a pseudorotation of 18-crown-6 molecule studied in detail in the paper represents a first experimental investigation of this phenomenon for the crown ethers. Moreover the complex **II** represents a model system of the multi-site (concretely 12-site) exchange for dynamic NMR.

Experimental

Complexes **I**, **II** and **III** were prepared by methods similar to [1, 2]. The ^{1}H and ^{13}C NMR spectra were recorded by a TESLA BS-567 (at 100.02 and 25.14 MHz, respectively) and a Bruker CXP-300 (at 300 MHz and 75.42 MHz, respectively) spectrometers. Solutions were 0.01 M in D-chloroform and CD$_2$Cl$_2$ for NMR spectroscopy with TMS internal standard. Temperature calibration was carried out using ethylene glycol and methanol samples.

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The isotropic lanthanide-induced shifts (δ_{LIS}) in NMR spectra on ligand nuclei and resulting from association of the ligand with the paramagnetic cation were expressed as the sum of diamagnetic shifts (δ^{dia}) and paramagnetic shifts (δ^{para}_{calc}) [13, 14]:

$$\delta_{LIS} = \delta^{dia} + \delta^{para}_{calc} \qquad (1)$$

The paramagnetic shifts were expressed as the sum of pseudo-contact contributions (δ_{PC}) and Fermi contact contributions (δ_{FC}) by the equality:

$$\delta^{para}_{calc} = \delta_{PC} + \delta_{FC} \qquad (2)$$

The pseudo-contact contributions to the LIS were calculated from Equation (3) [11, 14]:

$$\delta_{PC} = 10^{30}\{(\chi_Z - \chi_{av})<(3\cos^2\theta - 1)/r^3> \\ + (\chi_X - \chi_Y)<\sin^2\theta\cos 2\varphi/r^3>\}/2N_A \qquad (3)$$

where δ_{PC} is expressed in ppm, r in A and χ_i in cgs units. The Fermi contact contributions to the LIS were expressed [11, 13–17]:

$$\delta_{FC} = \frac{2\pi\beta}{3kT\gamma}\frac{A}{h}\langle S_Z\rangle = F\langle S_Z\rangle \qquad (4)$$

where β is the Bohr magneton, k is the Boltzmann constant, γ is the gyromagnetic ratio, A/h is the hyperfine coupling constant in frequency units, F is a metal-independent parameter of each nucleus for a series of isostructural complexes, and $\langle S_Z\rangle$ is the electron-spin expectation value, which has been tabulated for each Ln ion.

In calculating the paramagnetic LIS of **II** at 179 K the Fermi contact contributions were neglected compared with pseudo-contact contributions (because of predicted domination of pseudo-contact contributions) [5, 11, 12, 13, 18, 19]. The diamagnetic contributions to the LIS were allowed for by means of the diamagnetic La complexes [5, 11, 14, 18, 19]. The values of ($\chi_Z-\chi_{av}$), ($\chi_X-\chi_Y$) and α were treated as parameters and were fitted using Equation (5) to the observed shift values (δ^{para}_{obs}) for proton of the CH_2 groups using values of r, φ and θ for the atomic co-ordinates which were obtained from the X-ray structure [2] of solid $[La(NO_3)_3(18\text{-crown-}6)]$ [5, 10,14, 18, 19]:

$$AF = (\Sigma_{W_i}(\delta^{para}_{calc} - \delta^{para}_{obs})^2/\Sigma_{W_i}(\delta^{para}_{obs})^2)^{0.5} \qquad (5)$$

where w_i are the reciprocals of squares of the experimental errors. A procedure of so-called 'permutation of the pseudocontact shifts' was used at assignment of the peaks in spectrum to their respective atoms [19, 20].

The rate constants of the intramolecular dynamics were evaluated by the complete bandshape method [21] for a multi-site exchange [4, 10, 11]:

$$V_{(v)} = \text{Im} - [iC_0\mathbf{l}(i2\pi v E_n - i\Omega + \mathbf{R} + \mathbf{X})^{-1}\mathbf{P}] \qquad (6)$$

Here Ω and $\mathbf{R}$ are diagonal matrices (of the dimensions n = 12) with elements $w_i = 2\pi v_i$ and T^{-1}_{2i} respectively, and $\mathbf{X}$ is the exchange matrix. $\mathbf{P}$ is a column vector of the fractional populations. The temperature dependence of LIS was taken into account by extrapolation [21] of the low-temperature dependence to the intermediate and fast-exchange region according to the Curie–Weiss law [11, 14, 19]. We took into account temperature dependence of lanthanide-induced shifts applying Curie–Weiss approximation [11, 14, 19] during examination of NMR signal shape temperature dependence:

$$\delta_{LIS} = a + b/T \qquad (7)$$

As it could be seen on Figure 5 experimental LIS values are approximated well by linear dependence on 1/T, and on the diagram average value for $a_1, a_2, \ldots, f_2$ protons is corresponding to the $-CH_2-$ groups. Required for NMR signal shapes analysis LIS values of $a_1, a_2, \ldots, f_2$ protons signals 'without exchange' in cases of intermediate and fast exchange (NMR time scaling [19]) were calculated as

$$\Delta\delta_i(T) = \Delta\delta_i(T_0)(1/T + A)/(1/T_0 + A), \qquad (8)$$

where A is constant defined by analysis of average LIS value for $-CH_2-$ groups, $T_0 = 179$ K. All calculations were made on a IBM PC computer by a homemade set of programs [17, 19, 22].

3. Results and discussion

NMR spectra qualitative interpretation

In the ^{1}H NMR spectrum of II at 183 K (Figure 1) there are eleven signals (two signals coincide) corresponding to protons of CH_2 groups. The slow-exchange ^{1}H NMR spectrum of II (at 183 K in Figure 1) testifies that it has zero order [13, 23]. This phenomenon can be explained by considering that the J_{HH} values are smaller with respect to broadening of these signals due to lanthanide-induced enhancements of the relaxation rates [11, 17–19, 24] (values of relaxation rates are found to be 34(19) S^{-1}). It was assumed that the complexes in solution have C_2 symmetry (analogosly to [5]) and a structure similar to that found in crystal state (see Figure 2). Two steps increase of effective symmetry of spin system are observed at rising of temperature. Two signals are observed at 273 K (it appears an effective C_{6v} symmetry due to dynamic process of the first type). And additional plane of effective symmetry perpendicular to the axis of symmetry appears at high temperature (at 303 K).

It was assumed that NMR spectra correspond to the dynamic system, being characterized by twelve structure forms, which are presented in Figures 3 and 4. These structure forms (with schemes of the knots of the co-ordinational bonds) are depicted in Figure 4 in the plane perpendicular to the axis of symmetry. Ingredients of
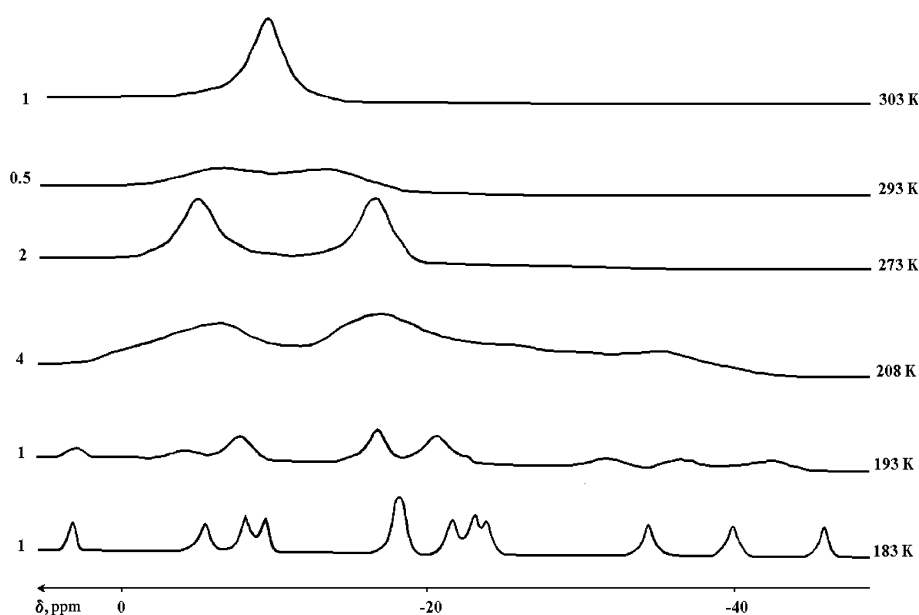
Figure 1. Variable temperature dependence of 100 MHz ^{1}H NMR spectra of the [Pr(NO$_3$)$_3$(18-crown-6] in CD$_2$Cl$_2$; chemical shifts values are relative to TMS.

o = C
O = N
O = O
O = Ln

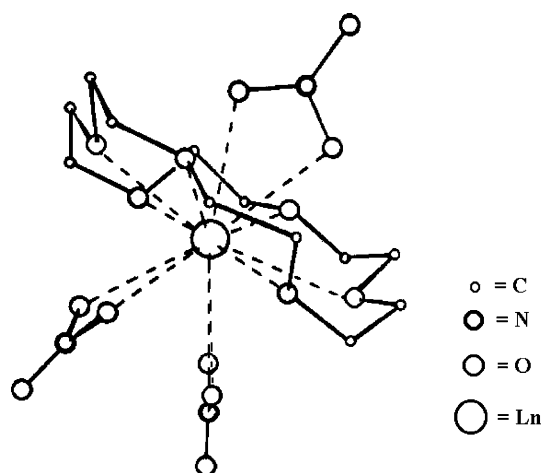*Figure 2.* Molecular structure of the [Ln(NO$_3$)$_3$(18-crown-6)]; here coordination bonds are denoted by dashed lines.

racemate are known to be indistinguishable by NMR spectroscopy at 'frozen' molecular dynamics but the presence can be identified at 'defreezing' of the molecular dynamics (due to the characteristic change of the NMR bandshape as a function of temperature) [19]. For the system studied the interconversion of the enantiomers is accompanied by exchange of proton sites which are marked in Figure 3 as a$_1$,a$_2$,...,f$_2$. For example the permutations of methylene protons a$_1'$, a$_2'$, b$_1'$, b$_2'$ between set of sites a$_1$, a$_2$, b$_1$, b$_2$ and set of sites f$_1$, f$_2$, e$_1$, e$_2$ are shown in Figure 3 (analogosly to dynamic processes in [Pr(NO$_3$)$_3$(diaza-18-crown-6)] [19]).

We did not found in the literature any experimental investigations of the pseudorotation phenomenon occurred in the free crown ether molecules or in their complexes with Ln cations (with the exception of

publications [10, 11]). Usually the term 'pseudorotation' is used in literature for the description of specific conformational dynamic processes in cyclic organic molecules (for example, in cyclohexane). In this connection let us define more precisely what is meant by «pseudorotation» of 18-crown-6 molecules in the coordination compound [Ln(NO$_3$)$_3$(18-crown-6)]. The basic conformational state of 18-crown-6 molecules is shown in Figure 2. With this conformational state of 18-crown-6 molecules in complexes [Ln(NO$_3$)$_3$ (18-crown-6)] the tensor of paramagnetic susceptibility anisotropy is associated. Z-axis of this tensor coincides with the symmetry axis C_2 and passes through Ln and N atoms of NO$_3$-group shown in [Ln(NO$_3$)$_3$(18-crown-6)] above. The orientation of X and Y axes are shown in Figures 3 and 4. The molecule 18-crown-6 can reach the short-living transition excited state characterized by a certain whole of «twist» distortions in the chain of single bonds (in 18-crown-6 molecule) in comparison with the basic conformational state of these molecules. The return in the basic conformational state can be accompanied by the change of mutual proton orientation (see, for instance, the transition of S_1 to S_2 in Figure 4). We have to remark that during the transition from S$_1$ to S$_2$ it is realized the change of proton orientation relatively to «fixed» nitrate group of **II** molecules and according to it relatively to axes of the complex molecules tensor of paramagnetic susceptibility.

The interconversion of the enantiomers and pseudorotation of macrocycle molecule upon the C_2 symmetry axis (dynamic process of the first type) lead to chemical exchange between molecular forms S_1, S_2, S_3, S_4, S_5 and S_6 (see Figure 4). Marks of proton sites a$_1$,a$_2$,...,f$_2$ are omitted in Figure 4. The supposed kinetic scheme of the reactions can be presented as:
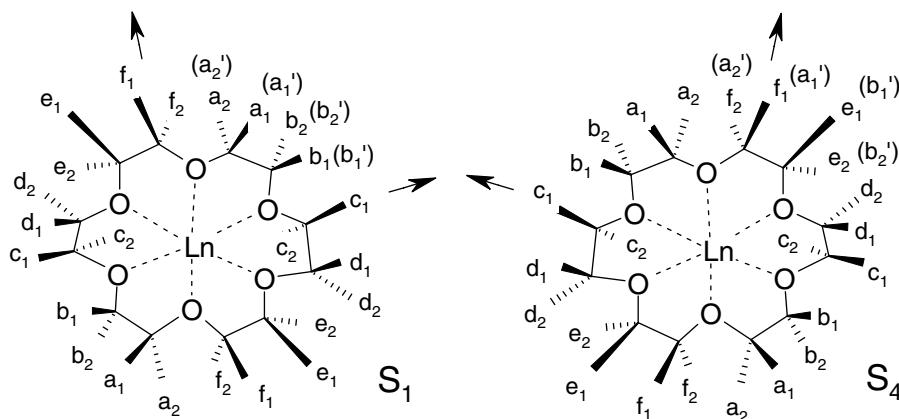
Figure 3. Scheme of enantiomeric isomer (S_1 and S_4) interconversion in [Ln(NO$_3$)$_3$ (18-crown-6)]. The plane perpendicular to the C_2 axis of symmetry.

$$S_i \xrightarrow{k_1} S^* \xrightarrow{k_1'} S_k \qquad (9)$$
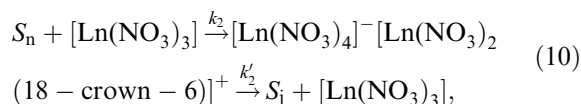
where i, $k = 1 \div 6$; S^* is a transition state.

Thus, the intramolecular dynamics of the first type causes effective exchange between sites within following two gropes: a_1, b_1, c_1, d_1, e_1, f_1 (*exo* sites) and a_2, b_2, c_2, d_2, e_2, f_2 (*endo* sites).

^{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 (see spectrum obtained at 293 K of Figure 1). The supposed kinetic scheme of the reactions can be presented as:

$$S_n + [Ln(NO_3)_3] \xrightarrow{k_2} [Ln(NO_3)_4]^- [Ln(NO_3)_2$$
$$(18 - crown - 6)]^+ \xrightarrow{k_1'} S_j + [Ln(NO_3)_3], \qquad (10)$$

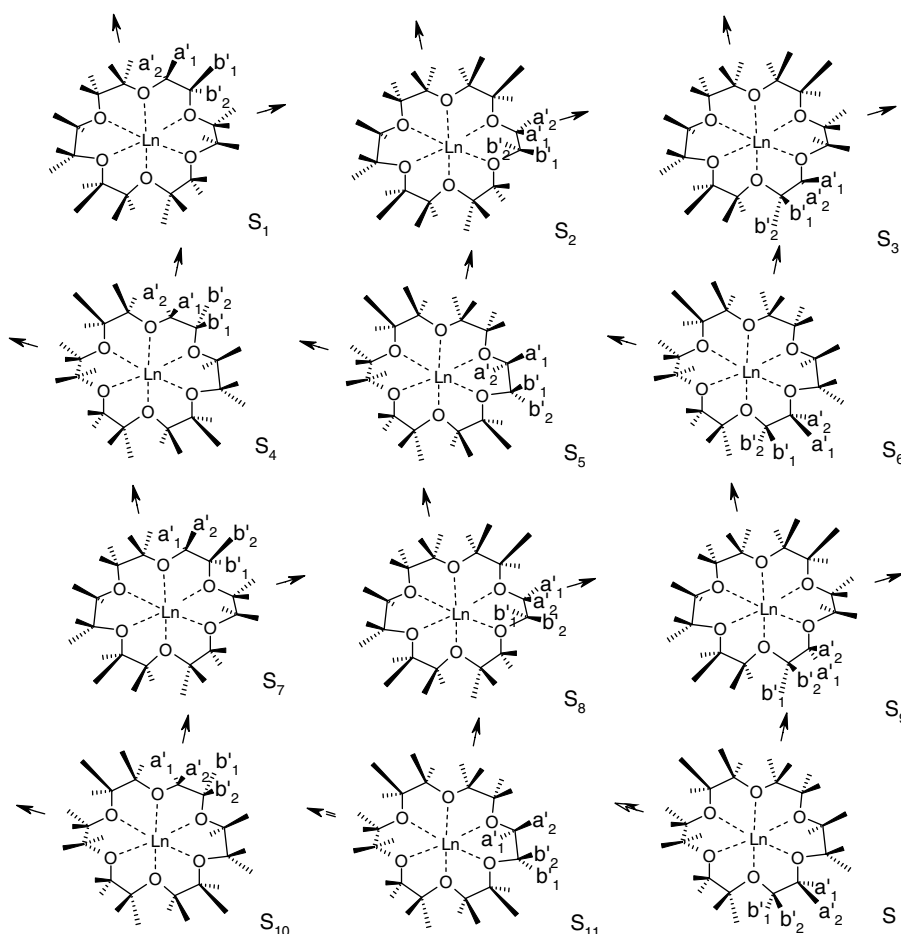if $n = 1 \div 6$ then $j = 7 \div 12$, else if $n = 7 \div 12$ then $j = 1 \div 6$.

Figure 4. Structure forms of [Pr(NO$_3$)$_3$(18-crown-6)] dynamic system.

Thus, as we see from the reaction scheme 9 and 10 and the designation of different structural forms S_j of molecule 18-crown-6 (Figure 4) the determination of reaction rate constants describing the dynamic processes in the system **II** is reduced to obtaining of rate constants values for effective twelve-site proton exchange.

Structure in solution by quantitative analysis of LIS

The results of investigating LIS in **II** at the 'frozen' chemical exchange (on the time scale of NMR) are presented in Table 1. It is proposed that the Fermi contact values related for CH_2 groups of the complexe **II** (Table 1) are comparable with those observed for protons (with spin delocalization at the distance of three chemical bonds) in related lanthanide complexes [15, 19, 20, 25]. It is awaited that the Fermi contact values not exceeding few ppm. A comparison of the calculated paramagnetic LIS for the protons of CH_2 groups with those observed (Table 1) shows a good fit for **II** (see for example results and discussions in [5, 15, 19, 20]). Thus, it may be concluded that the structure of **II** in solution is rather similar to that reported for $[La(NO_3)_3(18\text{-crown-}6)]$ in the crystal state [2] although not identical. The values of α indicate that the principal magnetic axes x and y are rotated 8.4° from the molecular x_0 and y_0 axes.

In order to obtain further support for the structure of the complexes **II** and **III**, we have investigated dependence of lanthanide-induced shifts relative to the Ln atomic number (Table 2). A theoretical ratio has been previously reported for the variation of the pseudo-contact shifts in a series of isostructural Ln complexes [26]. In order to compare the lanthanide-induced shifts of **II** with corresponding values of **III** (Table 2), the parameters $\Delta\delta/B(Ln)$, where $B(Ln)$ is the Bleaney's constant [28, 29, 33], were calculated. Analyzing Table 2, it can be concluded that there is a correlation between the corresponding values of these parameters for complexes **II** and **III**. The comparison of the calculated values of the structural parameter $\Delta\delta/B(Ln)$ for **II** and **III** reveals that the corresponding values in both complexes are rather similar although not identical. It means that the structures of complexes **II** and **III** in solution are similar. The Fermi contact values obtained for CH_2 groups (Table 2) are comparable with those observed for protons (with spin delocalization at the distance of three chemical bonds) in related lanthanide complexes [17, 19].

Table 2. Values of ^1H NMR chemical shifts (δ, ppm) of the $[Ln(NO_3)_3(18\text{-crown-}6)]$ in CD_2Cl_2 at T = 293 K relative to TMS

Ln	δ	$\Delta\delta$	$\Delta\delta/B(Ln)$	$\Delta\delta_{PC}$	$\Delta\delta_{FC}$
Ce	−3.5	−7.2	0.60	−7.9	0.7
Pr	−10.0	−13.7	0.66	−13.9	0.2

Isotropic paramagnetic lanthanide-induced shifts ($\Delta\delta$, ppm) relative to $[La(NO_3)_3(18\text{-crown-}6)]$ and their ratios to the Bleaney's constants $B(Ln)^a$; calculated pseudo-contact (Δ_{PC}) and Fermi contact (Δ_{FC}) contributions to the lanthanide-induced shifts.
$B(Pr) = -20.7; B(Ce) = -11.8$ [17].
$\langle S_Z \rangle = -3.2$ and -1.071 for Ce and Pr, respectively [17].

Molecular dynamics

We have investigated the bandshape of the zero-order ^1H NMR spectra of II over a wide temperature range (T = 179–303 K) in order to evaluate the magnitude of the activation enthalpy of the degenerate molecular dynamics of $[Pr(NO_3)_3(18\text{-crown-}6)]$. Found values of activation parameters resulted from the variable temperature analysis of reaction rate constants dependence (see Equation (6)) in the frame of Eyring theory [21], (Figure 4) are correspondingly for reactions of the first and second types $\Delta H_1^\ddagger = 26 \pm 4$ kJ/mol, $\Delta S_1^\ddagger = -60 \pm 19$ J mol^{-1}K^{-1}; $\Delta H_2^\ddagger = 46 \pm 5$ kJ/mol, $\Delta S_2^\ddagger = -19 \pm 11$ J mol^{-1}K^{-1}. Discussing the obtained values of the activation enthalpy for 18-crown-6 molecular dynamics in the complexes under investigation we have to note the following. The discovered magnitude of the activation enthalpy of the first type is commensurable with the values of the energetic barriers of conformational transitions in 18-membered macrocyclic polyethers molecules and their alkali complexes [28], and is approximately 20% more than the magnitude of the analogous parameter in $[Pr(NO_3)_3(\text{diaza-18-crown-}6)]$ [19].

The concentration of **II** appeared to have no influence on the rate constant of the first type molecular dynamics (studied between 10^{-3} and $1.2 \cdot 10^{-2}$ mol·dm^{-3}), i.e. the interconversion of enantiomeric forms and pseudorotation of macrocycle molecule upon the C_2 symmetry axis of complexes **II** is obviously a first-order reaction. It was found experimentally that the rate constant of the dynamic process of the second type was decreasing with the decrease of complex **II** concentration. We have to mention that the possibility of $[Pr(NO_3)_2(18\text{-crown-}6)]^+$ cation formation in weakly polar solvents was found in [9].

Table 1. Values of experimental ($\Delta\delta_{obs}$, ppm) and calculated ($\Delta\delta_{calc}$, ppm) isotropic paramagnetic lanthanide-induced shifts (of 100 MHz ^1H NMR spectra) of the $[Pr(NO_3)_3(18\text{-crown-}6)]$ in CD_2Cl_2 at T = 179 K relative to $[La(NO_3)_3(18\text{-crown-}6)]$

LIS, ppm	a_1	a_2	b_1	b_2	c_1	c_2	d_1	d_2	e_1	e_2	f_1	f_2
$\Delta\delta_{obs}$	−25.9	−28.1	−12.2	−39.2	−9.62	−27.6	−22.5	−51.0	−13.4	−45.0	−0.4	−22.3
$\Delta\delta_{calc}$	−23.7	−30.3	−17.0	−35.4	−3.8	−27.6	−22.3	−54.7	−18.0	−40.7	−1.3	−23.7

Found optimal values of $(x_R - \bar{x})$ and $(x_x - x_y)$ are equal to 3.21×10^{-3} and 1.66×10^{-3} (CGSE unit)/mol respectively; $\alpha = 8.4°$.

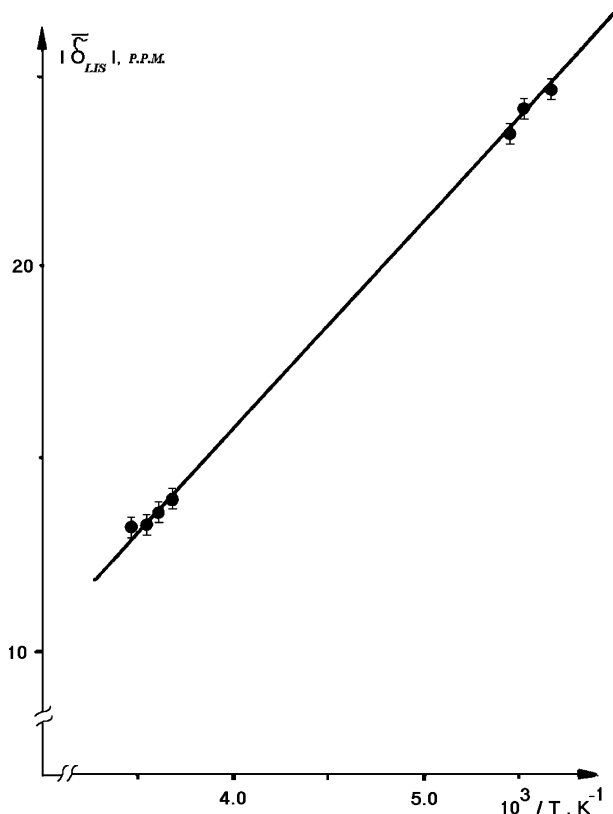*Figure 5.* Temperature dependence of average paramagnetic lanthanide-induced shifts in ^{1}H NMR spectra for -CH${}_2$- protons of [Pr(NO${}_3$)${}_3$(18-crown-6)].

The analysis of the temperature dependence of paramagnetic lanthanide-induced shifts in Figure 5 shows that the Curie–Weiss approximation (see

Equation (7)) is good for **II** (like for [Ln(ptfa)${}_2$(18-crown-6)]${}^+$ [11, 12, 25], [Ln(NO${}_3$)${}_3$(diaza-18-crown-6)] [19] and [LnH(oep)(tpp)] [27] where ptfa is 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione, tpp is tetraphenylporphyrin and oep is octaethylporphyrin).

Conclusion

The results of the present work demonstrate that there are two types of conformational dynamic processes in [Pr(NO${}_3$)${}_3$(18-crown-6)] complex (the first one with activation enthalpy $\Delta H^{\ddagger} = 26 \pm 4$ kJ/mol is conditioned by interconversion of complex enantiomeric forms and pseudorotation of macrocycle molecule upon the C_2 symmetry axis, the second one with $\Delta H^{\ddagger} = 46 \pm 5$ kJ/mol is conditioned by macrocycle molecule inversion). The [Pr(NO${}_3$)${}_3$(18-crown-6)] complex represents a model system of the effective twelve-site exchange for dynamic NMR. Studies of the values of the lanthanide-induced shifts (see Table 1) revealed that the structure of complexes in solution is similar to that reported for the [La(NO${}_3$)${}_3$(18-crown-6)] complex in the crystal state.
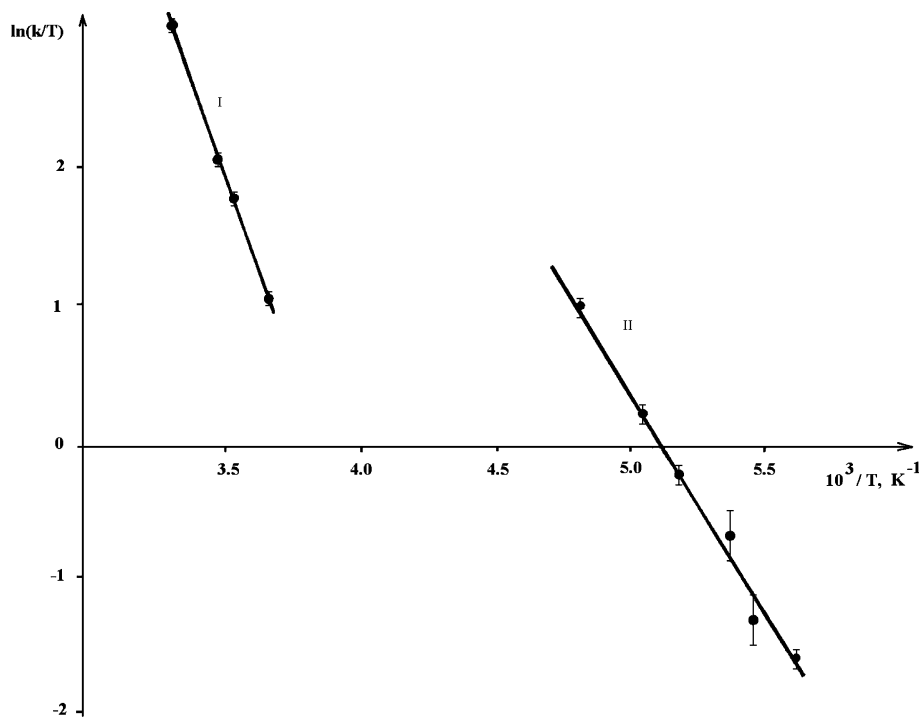
Acknowledgement

Figure 6. Dependence of ln(k/T) on 1/T, where *k* is the rate constant of 18-crown-6 molecular dynamic processes in [Pr(NO${}_3$)${}_3$(18-crown-6)]; T is temperature; CD${}_2$CI${}_2$ as solvent.

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