NMR Studies of Mixed-Ligand Lanthanide (III) Complexes. Peculiarities of Molecular Structure, Dynamics and Paramagnetic Properties for Cerium Subgroup Chelates with Crown Ethers

SERGEY P. BABAILOV* and DMITRY A. MAINICHEV
*Radiospectroscopic Laboratory, Institute of Inorganic Chemistry SB RAS, pr. Lavrentyev, 3, Novosibirsk, 630090, Russia,
E-mail babaiIov@che.nsk.su*

Abstract

The molecular structure, dynamics and paramagnetic properties of the complex cations $[Ln(ptfa)_2 (18\text{-crown-}6)]^+$ in deuterated toluene were studied for Ln = La, Ce, Pr and Nd. The activation enthalpy values of 68 ± 5, 55 ± 15 and 60 ± 13 kJ mol^{-1} for the 18-crown-6 conformational inversion processes for the complex cations of Ce, Pr and Nd, respectively, were obtained. Quantitative investigation of the lanthanide-induced chemical shifts shows a monotonic change of a spatial structure and magnetic susceptibility in comparison with the Bleaney predicted dependence. The free energy of molecular inversion activation for 18-crown-6 molecules in the complex cation $[Ln(fod)_2(18\text{-crown-}6)]^+$ is 74 ± 9 kJ mol^{-1} at 363 K, which is a little more than the value of the free energy of activation 64 ± 9 kJ mol^{-1} at 363 K in the complex cation $[Ln(ptfa)_2(18\text{-crown-}6)]^+$.

Introduction

The last two decades have seen a deep interest to examine complexes of macrocyclic polyethers (MCPEs) and lanthanide cations (Ln) because MCPEs are prospective extractants and NMR analytical reagents. Besides, MCPEs are considered as model compounds for natural ionophores [1–3] by many investigators. The NMR technique allows one to solve problems of definition of molecular structure and dynamics of Ln-MCPE complexes [3] effectively. Recently special interest has been stimulated by the lack in 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].

The NMR spectra of $[La(ptfa)_2(18\text{-crown-}6)]^+$ $[La(ptfa)_4]^-(H_2O)_4$ (**I**), $[Ce(ptfa)_2(18\text{-crown-}6)]^+$ $[Ce(ptfa)_4]^-(H_2O)_4$ (**II**), $[Pr(ptfa)_2(18\text{-crown-}6)]^+$ $[Pr(ptfa)_4]^-(H_2O)_4$ (**III**) and $[Nd(ptfa)_2(18\text{-crown-}6)]^+$ $[Nd(ptfa)_4]^-(H_2O)_4$ (**IV**) complex ion pairs were characterized and interpreted in weakly polar solvents, where ptfa is 1,1,l-trifluoro-5,5-dimethyl-2,4-hexanedione [3, 6]. Intramolecular inversion of the 18-crown-6 molecule in the complex cation $[Pr(ptfa)_2(18\text{-crown-}6)]^+$ was found by a temperature dependent investigation of NMR spectral signal shapes [3].

In this article, intramolecular dynamics and properties for $[Ln(ptfa)_2(18\text{-crown-}6)]^+$ Ln = La, Ce, Pr and Nd in

d$_8$-toluene were studied to find out how the activation enthalpy and paramagnetic properties depend on Ln cation atomic numbers. Due to the recent investigation of complex stoichiometry by the ligand substitution method applied to β-diketone anions [3, 6] the definition of activation parameters for crown ether inversion in complexes where ptfa anions are substituted by some other anions (for instance, fod) is to be made to compare the results obtained. The free energy of inverse activation for the 18-crown-6 molecule in the complex cation $[Pr(fod)_2(18\text{-crown-}6)]^+$ $\Delta G^{\neq}$ (363K) $= 74 \pm 9$ kJ mol^{-1} is a little more than the value of the free energy of activation $\Delta G^{\neq}$ (363K) $= 64 \pm 9$ kJ mol^{-1} in the complex cation $[Pr(ptfa)_2(18\text{-crown-}6)]^+$.

Experimental

NMR spectra were obtained by pulse spectrometers TESLA BS-567a (^{1}H and ^{13}C, Czechoslovak manufacture), operating frequencies 100 and 25.144 MHz respectively and Bruker MSL-400 (operating frequency 400 MHz). TMS was used as internal standard in the ^{1}H and ^{13}C NMR experiments. Spin-lattice relaxation rate constants were measured by the impulse sequence 180°-τ-90° (for example [7]). Deuterium-enriched organic solvents for NMR spectroscopy CDCl$_3$, CD$_2$Cl$_2$, CD$_3$C$_6$D$_5$ produced by "Izotop" were used as solvents. 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.

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* Author for correspondence.
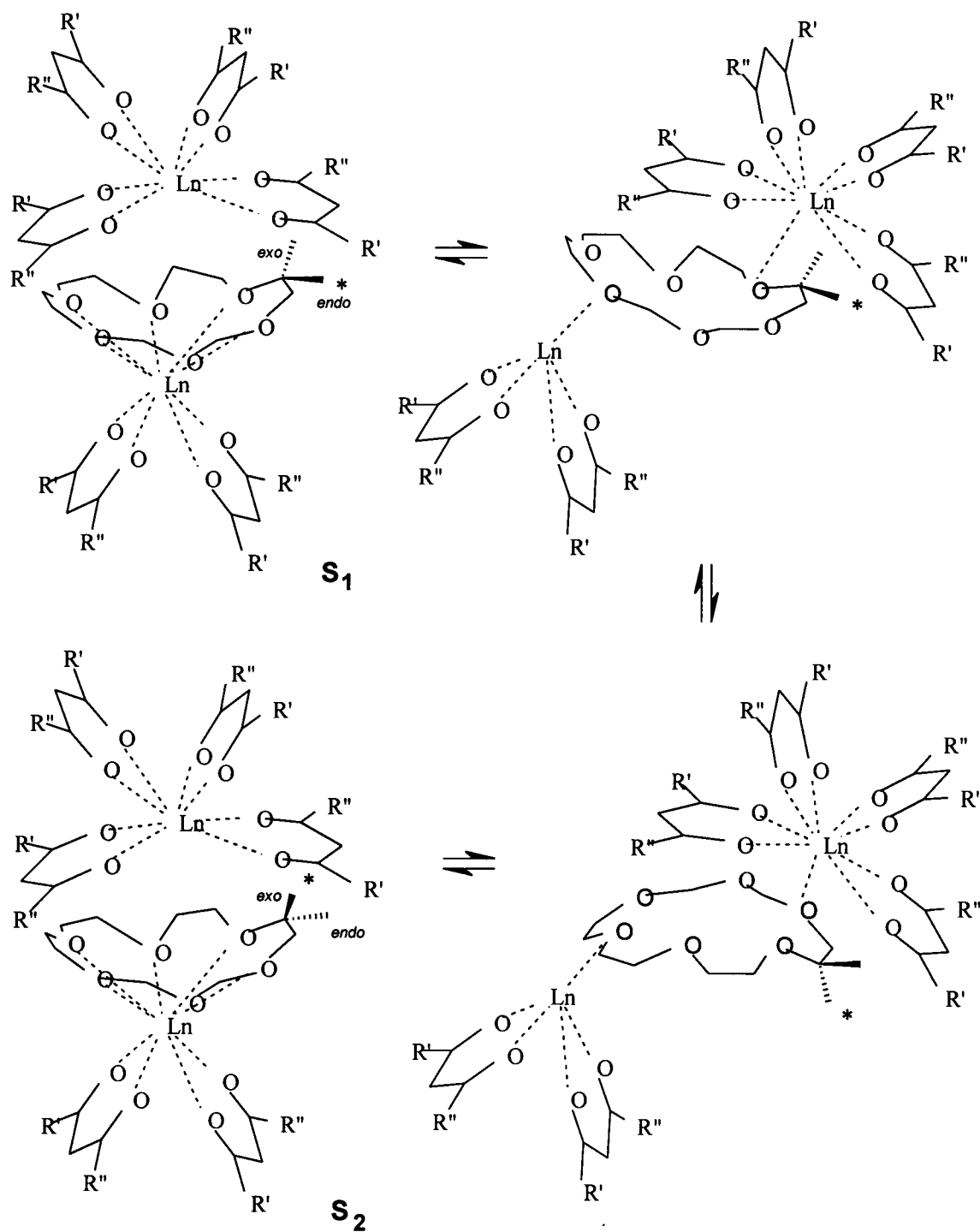
Scheme 1.

Results and discussion

The signals in the ^{1}H NMR spectra of the complex ion pairs $[Ln(ptfa)_2(18\text{-crown-}6)]^+[Ln(ptfa)_4]^-$ $(H_2O)_4$ have been examined in detail [6, 8] over a wide temperature range from 185 K to 382 K (solvents-d_8-toluene, $CDCl_3$ and CD_2Cl_2). Figure 1 shows the temperature dependence of the signals corresponding to the diastereotopic $–CH_2–$ groups protons of the 18-crown-6 molecule in the complex cation $[Ce(ptfa)_2(18\text{-crown-}6)]^+$ (Schemes 1 and 2). The signal at lower magnetic field corresponds to *exo* oriented protons of

the CH_2 groups in comparison with *endo* oriented protons signal for spectra at low temperature [9]. Probably the signal shape modification with temperature increase for stereochemically non-rigid systems is observed, being interpreted as 18-crown-6 molecule inversion (similarly the inversion of the macrocycle molecule in $[Ln(NO_3)_3(18\text{-crown-}6)]$ [8]).

Two possible mechanisms of the intramolecular dynamics in complexes **I–IV** are shown in Schemes 1 and 2. The first mechanism is related with the break of the majority of the coordination bonds between the Ln cation and the crown ether molecule (Scheme 1). However, one cannot exclude
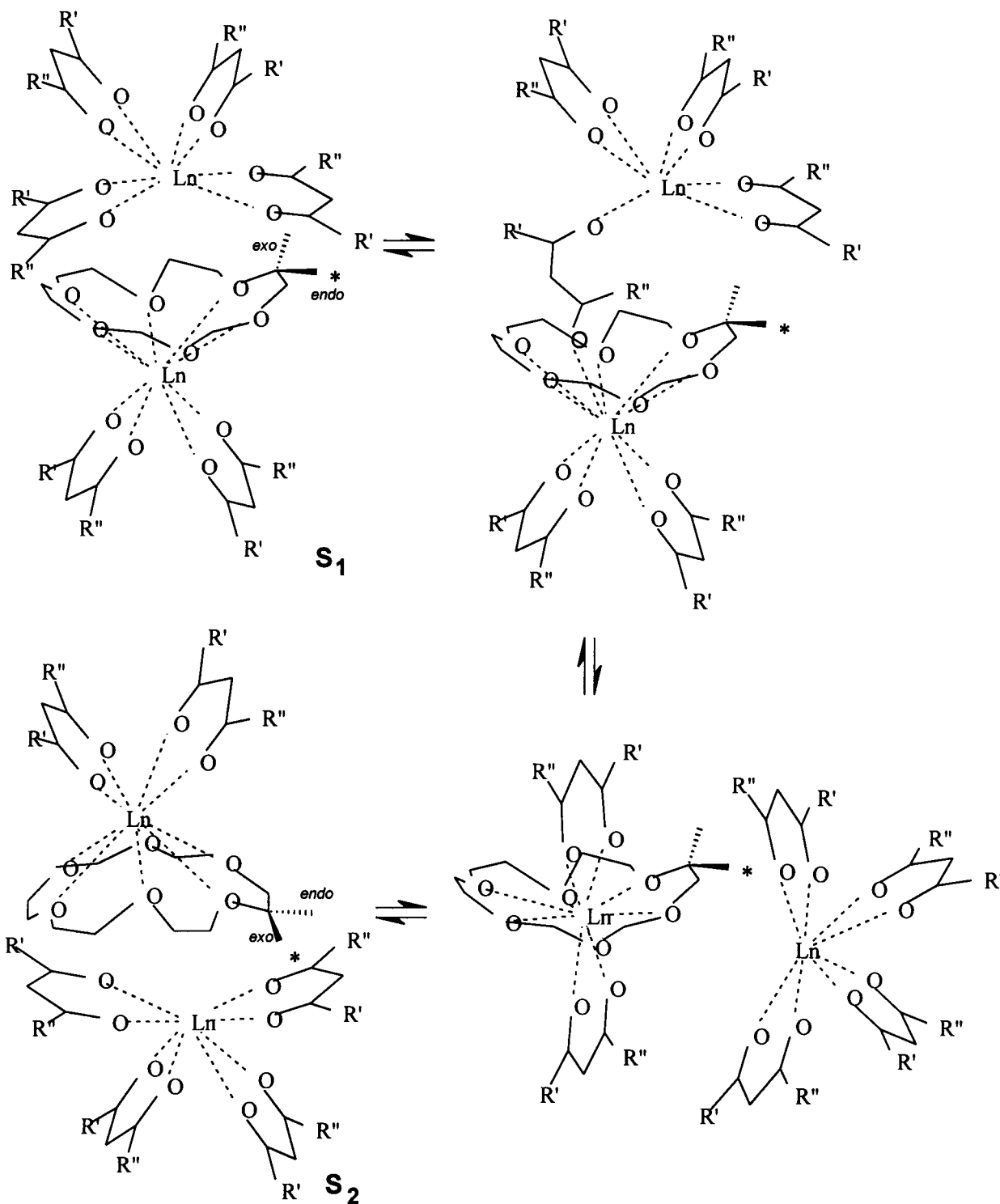
Scheme 2.

the presence of the alternative mechanism of crown ether molecule inversion without breakage of the Ln-crown ether coordination bonds (Scheme 2). In the case of the second mechanism dominating one would observe the broadening of signals of the CH and CH$_3$-group protons at high temperature (due to intermolecular exchange of β-diketonato anions). But the first mechanism is preferable because the broadening is not observed in our spectra.

As a result of the quantitative examination of the NMR signal shapes in the frame of Dynamic NMR techniques applied to chemical exchange of protons on two sites [3, 7, 8, 10] the values of the rate constants (k) of this chemical exchange (Figure 2) were estimated at various temperatures (Figure 3). In particular it was revealed that the lifetime of the conformations S_1, and S_2 of the complex cation [Nd(ptfa)$_2$(18-crown-6)]$^+$ shown on Schemes 1 and 2 $\tau = 1/k = 50$ ms at ambient temperature.
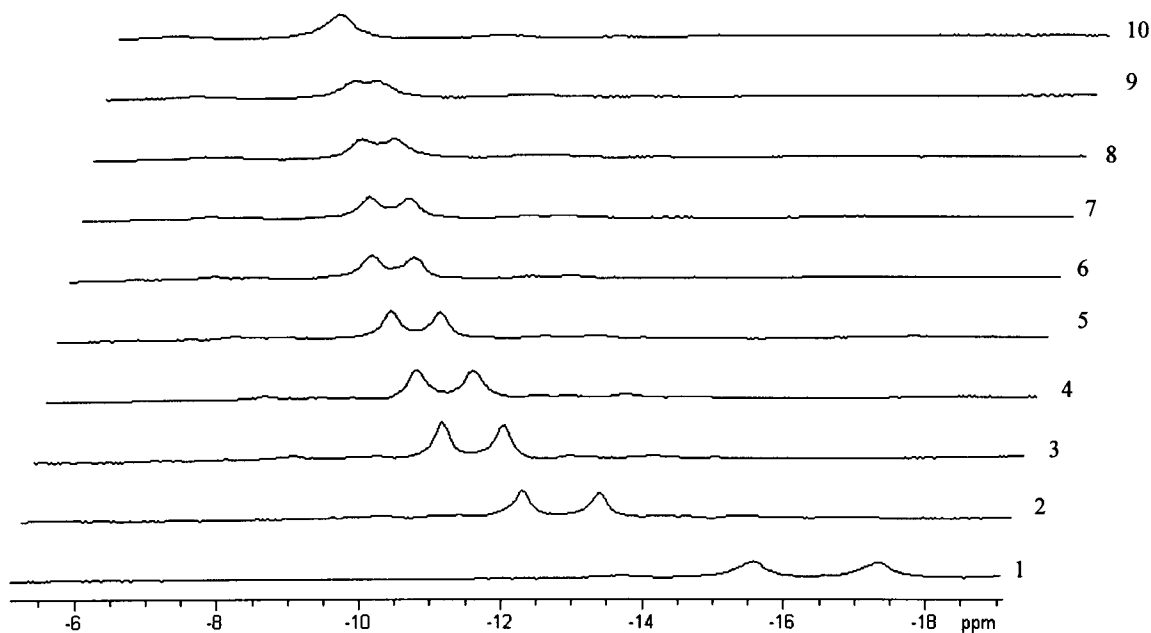
Figure 1. 100 MHz ^{1}H NMR spectra of [Ce(ptfa)$_2$(18-crown-6)]$^+$ in 8:1 composition of CDCl$_3$ and CD$_2$Cl$_2$ at various temperatures: 223 K(1), 253 K(2), 263 K(3), 273 K(4), 283 K(5), 288 K(6), 293 K(7), 298 K(8), 303 K(9), 311.5 K(10); chemical shift values are relative to TMS.
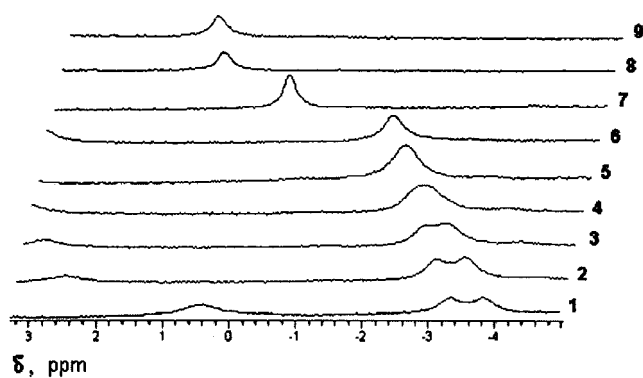

Figure 2. 100 MHz ^{1}H NMR spectra of [Nd(ptfa)$_2$(18-crown-6)]$^+$ in d_8-toluene at various temperatures: 298 K(1), 3093 K(2), 308 K(3), 313 K(4), 318 K(5), 323 K(6), 358 K(7), 377 K(8), 382 K(9); chemical shift values are relative to TMS.

By linear regression analysis of the dependence of $\ln(k/T)$ on $1/T$ using the Eyring equation [3, 8, 9]

$$\ln(k/T) = -\Delta H^{\neq}/RT + \Delta S^{\neq}/R + \ln(k_B/h) \quad (1)$$

the activation enthalpy values were obtained as $\Delta H^{\ddagger} = 68 \pm 15$ kJ mol^{-1}, 55 ± 15 kJ mol^{-1} and 60 ± 13 kJ mol^{-1} for the 18-crown-6 inversion processes respectively for the complex cations Ce, Pr and Nd in d_8-toluene (Figure 3 illustrates definition of $\Delta H^{\ddagger}$ for complex cation Nd). The activation entropy values were obtained as $\Delta S^{\ddagger} = 8 \pm 4$ J mol^{-1} K^{-1}, -27 ± 4 J mol^{-1} K^{-1} and -12 ± 4 J mol^{-1} K^{-1} respectively for the complex cations Ce, Pr and Nd.

We carried out additional examinations of the inversion process in the complex [Pr(ptfa)$_2$(18-crown-6)]$^+$ applying the biresonance spin saturation transfer technique to examine the rotation process of phenylic fragments of the paramagnetic complex DyH(oep)(tpp), where (oep) is octaethy-
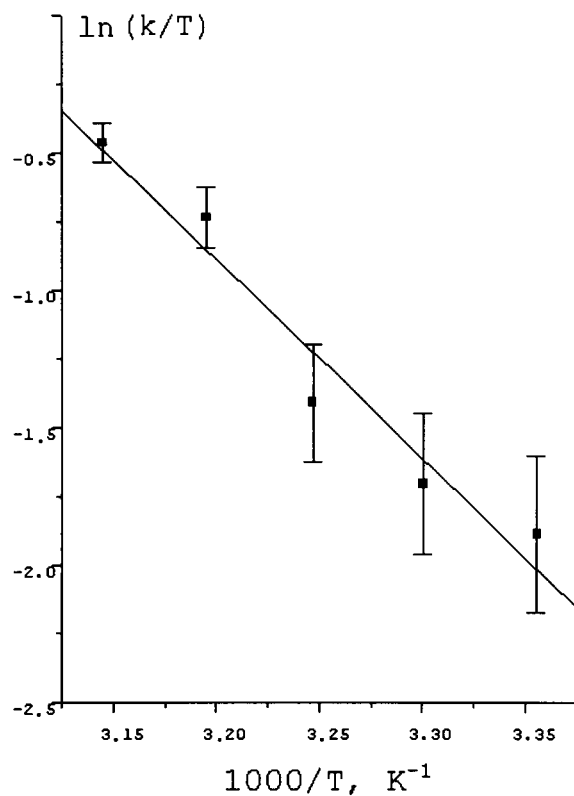
Figure 3. Dependence of $\ln(k/T)$ on $1/T$, where k is the rate constant of 18-crown-6 molecule inversion in [Nd(ptfa)$_2$(18-crown-6]$^+$; T is temperature; d_8-toluence as solvent.

porphyrin, and (tpp) is tetraphenylporphyrin. This additional investigation was undertaken to check the results obtained by the NMR signal shape temperature dependence examination technique and to improve techniques used to investigate dynamic processes in paramagnetic complexes of Ln. Dynamic NMR was utilized to a small extent for activation paramet-

ers definition of intramolecular processes in paramagnetic lanthanide complexes. That's why intramolecular dynamic processes examination and activation parameters definition techniques are not designed well in paramagnetic coordination compounds of Ln. The following relation [7,11] was utilized to estimate the chemical exchange rate constant values k_A

$$v_{\text{eff}}(\infty, v_A)/v_{\text{eff}}(\infty, v_B) = 1 - 1/(1 + T_{1A}k_A), \quad (2)$$

where $v_{\text{eff}}(\infty, v) = v_1(\infty, v) - v_2(\infty, v)$ i.e. the difference between the integrated intensities of the NMR signals at secondary rf frequencies $v_X = v_B$ and $v_X = 2v_A - v_B$; A and B are the chemical forms of chemical exchange system $A \leftrightarrow B$; v_A and v_B are the resonance signal frequencies corresponding to chemical forms A and B. The value measured appeared to be $\Delta H^{\ddagger} = 54 \pm 7$ kJ mol^{-1} in agreement with the results obtained by NMR signal shapes examination.

The activation enthalpy values obtained for complexes **II**, **III** and **IV** are equal within s.d. Also the insignificant lowering of $\Delta H^{\ddagger}$ with the Ln atomic number increase is probably caused by the so-called lanthanide contraction effect.

We took into account the temperature dependence of paramagnetic lanthanide-induced shifts (LIS) applying the Curie-Weiss approximation [3, 8] during examination of NMR signal shape temperature dependence

$$\delta_{\text{LIS}} = a + b/T. \quad (3)$$

As seen in Figure 4 experimental LIS values are approximated well by a linear dependence on $1/T$, and on the diagram the median value for *exo* and *endo* protons corresponds to the –CH$_2$– groups. The spectra at temperatures below 291 K were also examined but they are not shown in Figure 1 because they were obtained at an rf frequency value of 1 KHz less (because of essential temperature dependence of chemical shifts). The LIS values of *exo* and *endo* protons signals "without exchange" in cases of intermediate and fast exchange (on the NMR time scale [10]) were calculated as

$$\Delta\delta_i(T) = \Delta\delta_i(T_0)(1/T + A)/(1/T_0 + A), \quad (4)$$

where A is a constant defined by analysis of average LIS value for –CH$_2$– groups and T_0 = 240 K. It was assumed that at T_0 = 240 K the difference between the *exo* and *endo* protons shifts "without exchange" was equal to the experimentally defined difference, because the estimated chemical exchange rate constant is significantly less than 1 s^{-1}. Examinations of the ^{1}H NMR spectra of the complex ion pair [Pr(ptfa)$_2$(18-crown-6)]$^+$[Pr(ptfa)$_4$]$^-$ at 178 and 173 K in a 8:1 v/v mixture of CD$_2$Cl$_2$/CDCl$_3$ were made on the Bruker MSL-400 (400 MHz) spectrometer. But no –CH$_2$– groups doublet signal coupling was detected at low temperatures as in the complexes [Ln(NO$_3$)$_3$(18-crown-6)] and [Ln(NO$_3$)$_3$(DA-18-crown-6)] [3].

The following experiments were made to characterize qualitatively the dependence of the complex ion pairs

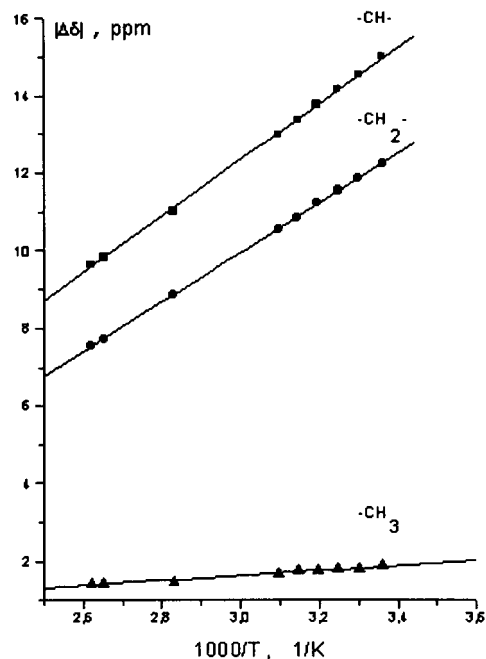*Figure 4.* Temperature dependence of the isotropic paramagnetic lanthanide-induced shifts in the 100 MHz ^{1}H NMR spectra for groups of protons of complex cations [Nd(ptfa)$_2$(18-crown-6]$^+$ relative to corresponding protons in the diamagnetic cations [La(ptfa)$_2$(18-crown-6]$^+$, d$_8$-toluene as solvent.

[Ln(ptfa)$_2$(18-crown-6)]$^+$[Ln(ptfa)$_4$]$^-$ on the Ln atomic number. In CDCl$_3$ solvent initial reagents Ln(ptfa)$_3$, Ln(ptfa)$_3$ 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 assuming that the [Ln(ptfa)$_4$] anion thermodynamic stability does not depend or weakly depends on atomic number.

The measured values of the spin-lattice relaxation rate constants for protons of diamagnetic (La) and paramagnetic complexes (Ce and Pr) were used to calculate values of dipole paramagnetic lanthanide-induced magnifications of the spin- lattice relaxation rates for protons of various groups of examined complexes (Table 1). Considerable (approximately 10 times) magnification of the relaxation rate constants for paramagnetic complexes protons in comparison with diamagnetic ones were observed. From the analysis of the paramagnetic dipole contributions in the spin-lattice relaxation rate constants made using the technique described in [7, 12] Ln-H effective distance values were obtained and Ln-H average distance values were calculated (Tables 2 and 3).

One can easily compare Ln-H effective distance values and Ln-H average distance values for protons of various groups in model compounds which are shown in Table 2 (due to X-ray analysis). The analysis of structural parameters shown in Tables 2 and 3 testifies that the molecule S and chelated anions are in the first coordination sphere of a Ln cation. Geometrical parameters obtained from lanthanide-induced spin-lattice relaxation rate constant magnification

Table 1. Spin-lattice relaxation rates (R, s^{-1}) and paramagnetic lanthanide-induced relaxation rate enhancements (R*, s^{-1}) for various protons of cation fragments of complex ion pairs at 300 K

Substance**	R(CH)	R(CH$_2$)	R(CH$_3$)	R*(CH)	R*(CH$_2$)	R*(CH$_3$)
[LaL$_2$S]$^+$[La L$_4$]$^-$	0.83	4.8	1.3	0	0	0
[Ce L$_2$S]$^+$[CE L$_4$]$^-$	30.3	43	9.5	29.5	38.2	8.2
[Pr L$_2$S]$^+$[Pr L$_4$]$^-$	19.9	36	9.1	19.1	31.2	7.8

**For diamagnetic compound [La L$_3$]2H$_2$O: R (CH$_3$) = 1.1, R (CH) = 0.95. L = ptfa, S = 18-crown-6.

Table 2. Ln–H ($\bar{r}$, Å) average distance and Ln–H effective distance values, where $r_{eff} = (1/N \sum_i^N r_i^{-6})^{-1/6}$

Substance	–CH	–CH	–CH$_3$	–CH$_3$	–CH$_2$	–CH$_2$	Literature
Pr(dpm)$_3$	5.00(2)	5.00(2)	5.76(9)	5.56(0)			[15]
La(NO$_3$)$_3$S	–	–	–	–	4.21(2)	4.05(2)	[16]
[CeL$_2$S]$^+$	5.0	5.0	5.76	5.56	4.46(3)	4.3(3)*	
[PrL$_2$S]$^+$	5.0	5.0	5.76	5.56	4.56(3)	4.4(3)*	

*Calculated assuming that effective distance to CH$_3$-group protons is 5.56 Å.

Table 3. Values of geometric parameters $r_{eff}(i)/r_{eff}(j) = \{R^*(i)/R^*(j)\}^{-1/6}$ in cations [LnL$_2$S]$^+$, where $r_{eff}(i)$ is the effective distance between the cation Ln and the ith ligand molecule kernel **

Substance	r_{eff}(CH$_3$)/r_{eff}(CH)	r_{eff}(CH$_3$)/r_{eff}(CH$_2$)
[CeL$_2$S]$^+$[CeL$_4$]$^-$	1.23 ± 0.07	1.29 ± 0.07
[PrL$_2$S]$^+$[PrL$_4$]$^-$	1.16 ± 0.07	1.26 ± 0.07

**L = ptfa, S = 18-crown-6; CH$_3$ and CH groups of ptfa, and CH$_2$ groups of 18-crown-6.

Table 4. Values of geometric parameters θ_1(CH), θ_2(CH$_2$), θ_3(CH$_3$), θ_4(CH$_3$), σ (degrees) in cations [LnL$_2$S]$^+$

Ln	θ_1	θ_2	θ_3	θ_4	σ	AF
Ce	29	105	53	30	−29	1.1×10^{-2}
Pr	36	114	50	44	−7	1.4×10^{-3}
Nd	42	117	52	51	0	1.2×10^{-3}

Here θ_i are the angles between the symmetry axis and Ln–H vectors, σ-dihedral angle between a plane of a chelated ring and the perpendicular plane in which the C$_2$ axis and a straight line transiting through the kernels Ln and H(CH) lie, AF-parameter characterizing concurrence between the calculated and experimental values of the lanthanide-induced shifts of parametric fitting by the method of least squares.

data show that the complex cations of Ce and Pr have similar spatial structures.

The experimentally found geometric parameters characterize cation ion pairs structure are shown in Tables 2 and 4. The value of parameter AF describing the concurrence of calculated and experimental LIS shows that experimental LIS values with sufficient accuracy are characterized in the frame of the geometric model used.

To compare the obtained results with the results of X-ray analysis in the crystal phase for the complexes [Ln(NO$_3$)$_3$S] we calculated parameters using data in [13]. For every neighbouring NO$_3$ groups the value of the angle between the N and the symmetry axis is 32°, the value of the parameter

similar to σ approximately equals −20° , and the value of the effective angle of the C(S)-Ln-symmetry axis is 101°. The results obtained indicate particular structural proximity for the coordination polyhedrons of the oxygen atoms in ion pair cations and in complexes [Ln(NO$_3$)$_3$ S]. It is necessary to note that values of the geometric parameters σ and θ_i, vary monotonically with Ln atomic number increase. The monotonic character of the structure modification for the co-ordination polyhedron of oxygen atoms in ion pair cations with Ln atomic number increase is probably caused by the lanthanide contraction effect.

It is interesting to analyze paramagnetic susceptibility modifications for ion pair cations caused by modification of the geometric structure in dependence on Ln. The theoretical dependence of the magnetizability anisotropy (X(Ln)) in a series of isostructural Ln complexes [14] is known (see Table 5). The ratio of the experimental susceptibility value and the theoretical one in dependence on Ln can be a parameter describing modification of the complexes geometric structure in dependence on Ln. The analysis of paramagnetic susceptibility anisotropy values (($\chi_{zz} - \chi_{av}$)/X(Ln) are normalized to 1 for Pr) shown in Table 6 confirms the conclusion made above about the monotonic modification of ion pair cations geometry with Ln atomic number increase. The violation (or deviation) of the paramagnetic susceptibility dependence (on Ln) in the complex cations [Ln(ptfa)$_2$(18-crown-6)]$^+$ from the Bleaney predicted dependence should be noted.

Using X-ray diffraction analysis data available from the literature for complexes Pr(dpm)$_3$ we calculated the parameters characterizing the relative position of dpm anion chelated rings. Half of the angle magnitude H(CH)-Ln-H(CH) (θ_1, in Table 4) is equal to 46°. The value of an angle corresponding to σ equals −31°. The value of parameters θ_i in ion pair cations is a little less than the value of the corresponding parameter in Pr(dpm)$_3$. It allows one to assume that there is a chelate spatial interaction between the chelated rings L in ion pair cations. And the degree of interaction is

Table 5. Numerical values of parameters describing paramagnetic pseudo-contact (PC) and Fermi contact (FC) contributions in isotropic lanthanide-induced shifts (LIS) in NMR spectra of lanthanide (Ln) coordination compounds

Configuration	Ln	J	g_J	$X(Ln) = g^2 J(J+1)(2J-1)(2J+3) <J \lVert \alpha \rVert J>$	PC* LIS, %	$g_J(g_J - 1)J(J+1)$	FC** LIS, %
$4f^1$	Ce^{3+}	5/2	6/7	−11.8	−6.52	−1.071	−3.40
$4f^2$	Pr^{3+}	4	4/5	−20.7	−11.44	−3.2	−10.16
$4f^3$	Nd^{3+}	9/2	8/11	−8.08	−4.46	−4.909	−15.58
$4f^4$	Pm^{3+}	4	3/5	+4.28	+0.36	−4.8	−15.24
$4f^5$	Sm^{3+}	5/2	2/7	+0.943	+0.52	−1.786	−5.67
$4f^6$	Eu^{3+}	0	–	–	–		
		1	3/2	–	–		
		2	3.2	–	–		
$4f^7$	Gd^{3+}	7/2	2	0	0	31.5	+100
$4f^8$	Tb^{3+}	6	3/2	−157.5	−87.2	31.5	+100
$4f^9$	Dy^{3+}	15/2	4/3	−181	−100	28.333	+89.95
$4f^{10}$	Ho^{3+}	8	5/4	−71.2	−39.34	22.5	+71.43
$4f^{11}$	Er^{3+}	15/2	6/5	+58.8	−32.49	15.3	+48.57
$4f^{12}$	Tm^{3+}	6	7/6	+95.3	+52.05	8.167	+25.93
$4f^{13}$	Yb^{3+}	7/2	8/7	+39.2	+21.66	2.571	+8.16

*The paramagnetic pseudo-contact contributions to LIS are normalized at −100% for Dy.

**The Fermi contact contributions to LIS are normed at −100% for Tb.

Table 6. Paramagnetic susceptibility anisotropy values $(\chi_z - \chi_{av})$ (CGSE units)/mol for cations $[LnL_2S]^+$ at 295 K

Ln	$(\chi_z - \chi_{av}) \, 10^3$	$(\chi_z - \chi_{av})/X(Ln)^*$
Ce	2.1	0.39
Pr	8.5	0.92
Nd	3.6	1

*X(Ln) – Bleaney parameters for various cations.

increased with atomic number increase (taking into account modification character of parameter σ).

Recently a stoichiometric mixture of complexes has been examined by the ligand substitution technique applied to β-diketone anions [3, 6]. Cations with composition $[Ln(hfa)_2(18\text{-crown-}6)]^+$ and $[Ln(ptfa)(hfa)(18\text{-crown-}6)]^+$ were made and characterized by the NMR technique. So, it is interesting to find the activation parameters for crown-ether inversion in complexes where ptfa anions are substituted by some other anions, for instance, fod, and to compare the results obtained. The free energy of inversion of the 18-crown-6 molecule in $[Ln(fod)_2(18\text{-crown-}6)]^+$ $\Delta G^{\ddagger}(363K) = 74.3 \pm 9$ kJ mol^{-1} is a little greater than the similar parameter $\Delta G^{\ddagger}(363K) = 63.9 \pm 9$ kJ mol^{-1} in $[Ln(ptfa)_2(18\text{-crown-}6)]^+$. This activation free energy increase can be caused by the electron-acceptor properties of fod anions being stronger than the ptfa ones or that they occupy more volume than ptfa molecules.

Acknowledgements

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