



Intramolecular Dynamics of Lanthanide(III) Tetraoxadiaza Macrocyclic Complexes in Solution as Studied by NMR

S.P. BABAILOV*, L.D. NIKULINA and J.H. KRIEGER

Radiospectroscopic Laboratory, Institute of Inorganic Chemistry SB RAS, pr. Lavrentyev, 3, Novosibirsk, 630090, Russia

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Abstract

^1H and ^{13}C NMR and ^1H NMR relaxation spectroscopy (RS) measurements are reported for the CDCl_3 and CD_2Cl_2 solutions of $[\text{La}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$ (**I**), $[\text{Pr}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$ (**II**) and $[\text{Nd}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$ (**III**) complexes. Temperature dependencies of the ^1H NMR spectra of **II** have been analyzed using the dynamic NMR methods for multi-site exchange. Enantiomeric isomer interconversion in **II** is characterized by $\Delta H^\ddagger = 21.5 \pm 4 \text{ kJ mol}^{-1}$. Studies of the values of the lanthanide-induced shifts and the longitudinal relaxation rate enhancement revealed that the structure of complexes in solution is similar to that reported for the $[\text{La}(\text{NO}_3)_3(18\text{-crown-6})]$ complex in the crystal state. Nevertheless, it appears that the principal values of the molar paramagnetic susceptibility tensor (χ_i) significantly differ in complexes **II** and **III**. The possible reasons for the different characteristics of these complexes are discussed.

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 has 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 the $[\text{Pr}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$ complex was partially investigated by ^1H NMR, signals of the NH groups and intramolecular dynamic processes were not found [7]. In the present work the structure of the kinetically stable complexes $[\text{Ln}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$, where Ln = La (**I**), Pr (**II**) and Nd (**III**) in CDCl_3 and CD_2Cl_2 solutions is investigated by ^1H , ^{13}C NMR and ^1H relaxation spectroscopy. The intramolecular dynamics of complex **II** is studied by dynamic ^1H NMR spectroscopy. It has been found that the dynamics was conditioned by processes of the molecular enantiomeric isomer interconversion. It should be noted that an investigation of this kind is of interest both for coordination chemistry and for spectroscopic techniques since a combined study [11, 14] (using the data of lanthanide-induced shifts (LIS) [15] and longitudinal relaxation rate

enhancements [16]) of the structure of lanthanide containing complexes attracts renewed attention from investigators [17, 18]. Moreover, the complexes investigated represent a model system of the multi-site exchange for dynamic NMR.

Experimental

$[\text{Ln}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$ (where Ln = La, Pr, Nd) were prepared by methods similar to [7]. The ^1H and ^{13}C NMR spectra were recorded by a TESLA BS-567 spectrometer at 100.02 and 25.14 MHz, respectively. Solutions were 0.01 M in CDCl_3 and CD_2Cl_2 for NMR spectroscopy with HMDS internal standard. The longitudinal relaxation rates (^1H) were measured with the use of the $180^\circ - \tau - 90^\circ$ inversion recovery pulse sequence [11, 19, 22, 23]. The relaxation rates were obtained from 16 or 20 data points that were fitted to an exponential dependence using a non-linear least-squares procedure. Temperature calibration was carried out using ethylene glycol and methanol samples.

2D COSY spectra were obtained for Ln = Pr and Nd by a Bruker MSL-400 spectrometer (operating frequency 400 MHz) at 183 K. Cross peaks were observed for each pair of geminal protons analogously to [17, 31].

The isotropic lanthanide-induced shifts (δ_{LIS}) in NMR spectra of 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 ($\delta_{\text{calc}}^{\text{para}}$) [20, 21]:

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

* Author for correspondence.

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

$$\delta_{\text{calc}}^{\text{para}} = \delta_{PC} + \delta_{FC}. \quad (2)$$

The pseudo-contact contributions to the LIS were calculated from Equation (3) [11, 21]:

$$\delta_{PC} = 10^{30} \{ (\chi_Z - \chi_{\text{av}}) \langle (3 \cos^2 \theta - 1) / r^3 \rangle + (\chi_X - \chi_Y) \langle \sin^2 \theta \cos 2\psi / r^3 \rangle \} / 2N_A, \quad (3)$$

where δ_{PC} is expressed in ppm, r in Å and χ_i in cgs units. The Fermi contact contributions to the LIS were calculated from Equation (4) [11, 18, 20, 21, 30]:

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

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 (to a first approximation) the paramagnetic LIS of **II** the Fermi contact contributions were neglected compared with pseudo-contact contributions, because of the predicted domination of pseudo-contact contributions [5, 11, 12, 20]. The diamagnetic contributions to the LIS were allowed for by means of the diamagnetic La complexes [5, 11, 21]. The values of $(\chi_Z - \chi_{\text{av}})$, $(\chi_X - \chi_Y)$ and α were treated as parameters and were fitted using Equation (5) to the observed shift values ($\delta_{\text{obs}}^{\text{para}}$) for protons of the CH₂ groups using values of r , ψ and θ for the atomic co-ordinates which were obtained from the X-ray structure [2] of solid [La(NO₃)₃(18-crown-6)] [5, 10, 21]:

$$AF = (\sum w_i (\delta_{\text{calc}}^{\text{para}} - \delta_{\text{obs}}^{\text{para}})^2 / \sum w_i (\delta_{\text{obs}}^{\text{para}})^2)^{0.5}, \quad (5)$$

where w_i are the reciprocals of squares of the experimental errors. In the model oxygen atoms O(2) and O(5) [2] were replaced by nitrogen atoms. A procedure of so-called ‘‘permutation of the pseudocontact shifts’’ was used in assignment of the peaks in the spectrum to their respective atoms, taking in account results of 2D COSY [17].

The final optimal $(\chi_Z - \chi_{\text{av}})$, $(\chi_X - \chi_Y)$ and α values in **II** and **III** were obtained from an eleven-parameter fit of the paramagnetic LIS, using a previously described procedure for separating Fermi contact shifts from the LIS values [11, 14, 17, 18] and assuming that **II** and **III** are isostructural complexes.

The relaxation rates obtained were corrected for any diamagnetic contributions by using the corresponding relaxation rates of diamagnetic [La(NO₃)₃(diazia-18-crown-6)] [22]. Then with the use of Equation (3) ‘‘averaged’’ structural parameters r_i/r_j were calculated analogously to [23, 26]:

$$r_i/r_j = (R_j/R_i)^{1/6} \quad (6)$$

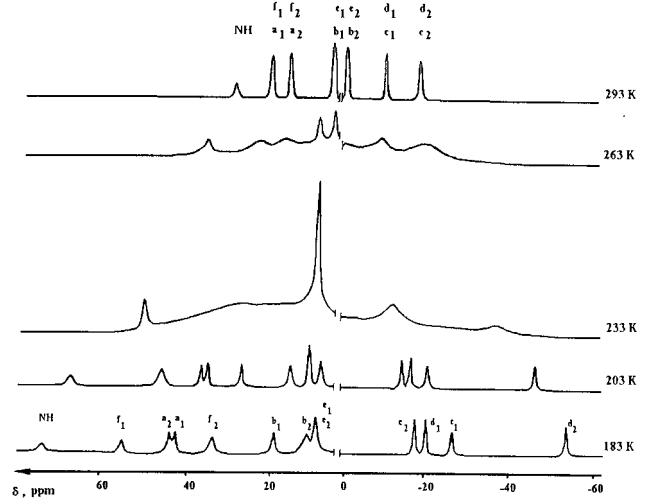


Figure 1. ¹H NMR spectra of [Pr(NO₃)₃ diaza-18-crown-6] in CD₂Cl₂ as a function of temperature at 100.02 MHz. Enthalpy of activation $\Delta H^\ddagger = 21.5 \pm 4$ kJ/mol. Signals of solvent and uncomplexed diaza-18-crown-6 molecules are omitted.

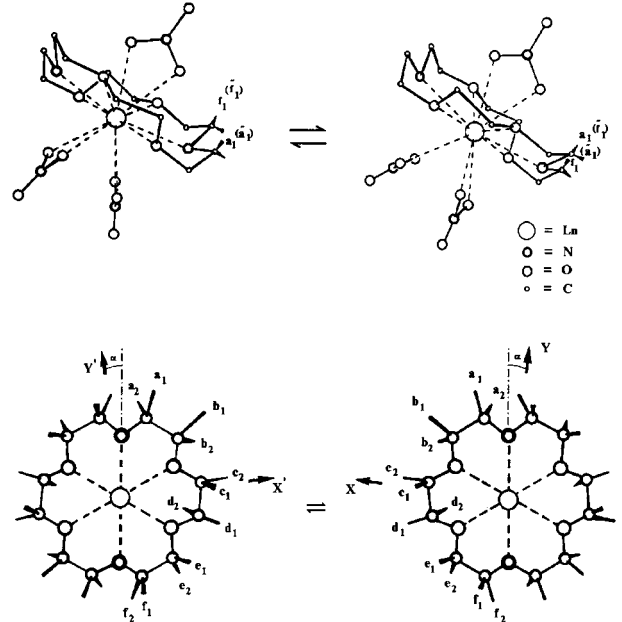


Figure 2. Scheme of enantiomeric isomer interconversion in [Ln(NO₃)₃ diaza-18-crown-6]. The plane parallel to the C₂ axis of symmetry (top) and the plane perpendicular to the C₂ axis of symmetry (bottom).

where R_i and R_j are the lanthanide-induced spin-lattice relaxation rate, r_i and r_j are distances to the corresponding nuclei i and j . The rate constants of the intramolecular dynamics were evaluated by the complete bandshape method [19] for a multi-site exchange [4, 10, 11]:

$$V(\nu) = \text{Im} - [iC_0 l (i2\pi\nu\mathbf{E}_n - i\Omega + \mathbf{R} + \mathbf{X})^{-1} \mathbf{P}]. \quad (7)$$

Here Ω and \mathbf{R} are diagonal matrices (of dimensions $n = 12$) with elements $w_i = 2\pi\nu_i$ and T_{2i}^{-1} 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 [19] of the low-temperature

Table 1. Experimental ($\Delta\delta_{\text{obs}}$, ppm) and calculated ($\Delta\delta_{\text{calc}}$, ppm) isotropic paramagnetic lanthanide-induced shifts (LIS), and calculated Fermi contact ($\Delta\delta_{\text{FC}}$, ppm) contributions to the LIS for the various nuclei of $[\text{Ln}(\text{NO}_3)_3(\text{dianza-18-crown-6})]$ at $T = 303$ K with reference to $[\text{La}(\text{NO}_3)_3(\text{dianza-18-crown-6})]$; solvent – CD_2Cl_2

| Ln | Nucleus | Commentary | NH^b | $\Delta\delta$ | | | | | |
|----|-----------------|------------------|---------------|---------------------|------------|---------------------|------------|------------|------------|
| | | | | N-CH ₂ - | | O-CH ₂ - | | | |
| | | | | a_1, f_1 | a_2, f_2 | b_1, e_1 | b_2, e_2 | c_1, d_1 | c_2, d_2 |
| Pr | ¹ H | obs | 28.5 | 17.9 | 13.4 | 2.5 | -3.6 | -13.1 | -21.8 |
| | ¹ H | calc | 29.2 | 18.3 | 13.2 | 2.9 | -3.4 | -12.8 | -22.0 |
| | ¹ H | FC | -8.3 | 1.4 | -0.5 | -0.5 | -1.0 | 1.2 | 0.2 |
| Nd | ¹ H | obs | 21.1 | 16.2 | 12.2 | 3.1 | -0.5 | -8.8 | -14.0 |
| | ¹ H | calc | 20.3 | 15.8 | 12.3 | 2.7 | -0.8 | -9.1 | -13.9 |
| | ¹ H | FC | -12.7 | 2.1 | -0.7 | -0.8 | -1.5 | 1.8 | 0.3 |
| | ¹³ C | obs ^a | - | 49.0 | | 48.6 | | 12.2 | |
| La | ¹ H | obs ^a | 2.38 | 2.99 | | | 3.70 | | |

^a The observed shifts with reference to HMDS.

^b This nucleus was not included in the optimization procedure.

Table 2. Optimum values of the anisotropy of the paramagnetic susceptibility ($\chi_z - \chi_{\text{av}}$), ($\chi_x - \chi_y$) in cgs units per mole and their ratios to the Bleaney constants $B(\text{Ln})^a$; α^b in degrees and agreement factor (AF) for $[\text{Ln}(\text{NO}_3)_3(\text{dianza-18-crown-6})]$ at $T = 303$ K

| Ln | $10^3 (\chi_z - \chi_{\text{av}})$ | $10^3 (\chi_x - \chi_y)$ | $10^3 (\chi_z - \chi_{\text{av}})/B(\text{Ln})$ | $10^3 (\chi_x - \chi_y)/B(\text{Ln})$ | α | AF |
|----|------------------------------------|--------------------------|---|---------------------------------------|----------|------|
| Pr | 0.26 | 1.8 | -0.0126 | -0.087 | 5(2) | 0.01 |
| Nd | -0.03 | 1.4 | 0.0037 | -0.173 | 5(2) | 0.02 |

^a $B(\text{Pr}) = -20.7$; $B(\text{Nd}) = -8.08$.

^b Angle of the displacement between the X axis of the tensor of the anisotropy of the paramagnetic susceptibility and the X axis of the complex.

dependence to the intermediate and fast-exchange region according to the Curie-Weiss law [11, 21]. All calculations were made on a IBM PC computer by a homemade set of programs.

Results and discussion

NMR spectra qualitative interpretation. In the ¹H NMR spectrum of **II** at 183 K (Figure 1) there are eleven signals (b_2 and e_2 coincide) corresponding to protons of CH₂ groups and the most broadened signal corresponding to NH groups. The slow-exchange ¹H NMR spectrum of **II** at 183 K in Figure 1 as well as the fast-exchange spectrum (on the NMR time scale) at 293 K testify that they have zero order [16, 20]. 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, 24]. It was assumed that: (a) NMR spectra correspond to the dynamic system, being characterized by two structural forms which are optical isomers, (b) the complexes have C₂ symmetry (analogously to [5]). The structures of the enantiomers and schemes of the knots of the co-ordination bonds are depicted in Figure 2 in the plane parallel to the axis of symmetry and the plane perpendicular to the axis of symmetry, respectively. Components of racemates 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. For the system studied the interconversion of the enantiomers is accompanied by exchange of proton sites which are marked in Figure 2 as a_1, a_2, \dots, f_2 . For example the permutations of methylene protons a'_1 and f'_1 between sites a_1 and f_1 are shown in Figure 2. Thus the intramolecular dynamics of complexes **II** cause exchange in pairs of the following sites: $a_1 \leftrightarrow f_1$, $a_2 \leftrightarrow f_2, \dots, c_2 \leftrightarrow d_2$. An effective increase in symmetry of the spin system is a consequence of the fast exchange, that is the additional plane of symmetry passing through the axis of symmetry and nitrogen atoms of diaza-18-crown-6 molecule appear. In the ¹³C NMR spectra of **II** and **III** at room temperature there are only three peaks corresponding to various CH₂ groups of diaza-18-crown-6 (see Table 1). It should be noted that this confirms the presence of the diastereotopic protons of the CH₂ groups in the ¹H NMR spectra of **II** and **III** [11, 12]. This is in agreement with the previous results on the kinetically stable lanthanide complexes with other macrocyclic polyethers [5, 10–12, 14].

Structure in solution by LIS and the relaxation-rate enhancements. The results of investigating LIS in **II** and **III** at the fast exchange (on the time scale of NMR) of the enantiomeric forms of the complexes (Figure 2) are presented in Tables 1 and 2. A comparison of the calculated paramagnetic LIS for the protons of CH₂ groups with those observed (Table 1) shows a good fit (Table 2) both for **II** and **III** (see for example results and discussions in [5, 17, 18]). Thus, it may be concluded that the structure of **II** and **III** in solution

Table 3. Paramagnetic lanthanide-induced longitudinal relaxation-rate enhancements (R_i , S^{-1}) and comparison of experimental and calculated distance ratios (r_i/r_{c1}) for protons of $[\text{Ln}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$; solvent CD_2Cl_2 , $T = 303 \text{ K}$

| Ln | Parameters | -NH | -N-CH ₂ - | | -O-CH ₂ - | | | |
|-------|-----------------|---------|----------------------|------------|----------------------|------------|------------|------------|
| | | | a_1, f_1 | a_2, f_2 | b_1, e_1 | b_2, e_2 | c_1, d_1 | c_2, d_2 |
| Pr | R_i | 56(16) | 12.5(2) | 11.2(2) | 9.9(2) | 0.9(2) | 8.9(2) | 9.1(2) |
| | (r_i/r_{c1}) | 0.74(7) | 0.95(6) | 0.96(6) | 0.98(6) | 0.98(6) | 1.00(6) | 1.00(6) |
| Nd | R_i | 330(9) | 81.3(16) | 70.(14) | 47.8(9) | 46.8(9) | 37.8(8) | 42.8() |
| | (r_i/r_{c1}) | 0.70(7) | 0.88(5) | 0.90(5) | 0.96(6) | 0.96(6) | 1.00(6) | 0.98(6) |
| Model | (r_i/r_{c1}) | 0.77 | 0.921 | 0.928 | 0.956 | 0.926 | 1 | 0.956 |
| | $r_i, \text{Å}$ | 3.35 | 3.99 | 4.02 | 4.14 | 4.01 | 4.33 | 4.14 |

is rather similar to that reported for $[\text{La}(\text{NO}_3)_3(18\text{-crown-6})]$ in the crystal state [2], although not identical. The values of α indicate that the principal magnetic x and y axes are rotated 5° from the molecular x and y axes. The Fermi contact values obtained for CH_2 groups (Table 1) are comparable with those observed for protons (with spin delocalization at a distance of three chemical bonds) in related lanthanide complexes [14, 17, 18]. It should be noted that there is a comparatively large contact effect for protons of the NH groups (two chemical bonds).

In order to obtain further support for the structure of complexes **II** and **III**, we have investigated ^1H lanthanide-induced relaxation-rate enhancements of these complexes (Table 3). We have assumed that the dipolar term in the lanthanide-induced enhancements of spin-lattice relaxation rates on the ligand nuclei for **II** and **III** dominates. The comparison of the calculated values of the structural parameter (Table 1, Equation (3)) for **II** and **III** and the model reveals that the corresponding values in both complexes are rather similar although not identical. The observed small differences between two complexes can be either due to an error in the determination of T_1 values or to minor structural differences.

A theoretical ratio has been, previously, reported for the variation of the pseudo-contact shifts in a series of isostructural Ln complexes [28]. In order to compare the molar paramagnetic susceptibility tensor (χ_i) of **II** with corresponding values of **III** (Table 2), the parameters $(\chi_z - \chi_{\text{av}})/B(\text{Ln})$ and $(\chi_x - \chi_y)/B(\text{Ln})$, where $B(\text{Ln})$ is the Bleaney constant [28–29], were calculated. Analyzing Table 2, it can be concluded that there is no correlation between the corresponding values of these parameters for complexes **II** and **III**. It means that the principal values (χ_i) of the molar paramagnetic susceptibility tensor change dramatically in passing from **II** to **III**, while only minor structural differences between these complexes were evidenced from the obtained data. This behavior can be rationalized as due to both the effect of lanthanide contraction [29–30] and the macrocyclic nature (as basicity, conformational lability, etc.) of the ligand. The results obtained are in rather good agreement with the study of complexes of porphyrin [29] and macrocyclic polyether 18-crown-6 with paramagnetic lanthanide cations [11, 12]. The values of the $(\chi_z - \chi_{\text{av}})/B(\text{Ln})$ parameters are found

to change monotonically three times with increase in the atomic number of Ln for Ln = Ce, Nd and Pr with minor changes in the effective angle H–(18-crown-6)-Ln with the C_2 axis of symmetry of the complexes.

Molecular dynamics. We have investigated the bandshape of the zero-order ^1H NMR spectra of **II** over a wide temperature range ($T = 179\text{--}303 \text{ K}$) in order to evaluate the magnitude of the activation enthalpy of the degenerate molecular dynamics of $[\text{Pr}(\text{NO}_3)_3(\text{diaza-18-crown-6})]$. The discovered magnitude of the activation enthalpy of the interconversion of the enantiomers ($\Delta H = 21.5 \pm 4 \text{ kJ/mol}$) is commensurable with the values of the energetic barriers of conformational transitions in 18-membered macrocyclic polyether molecules and their alkali complexes [25], and is approximately 20% less than the magnitude of the analogous parameter in $[\text{Pr}(\text{NO}_3)_3(18\text{-crown-6})]$ [10].

The concentration of **II** appeared to have no influence on the rate constant of molecular dynamics (studied between 10^{-3} and $1.4 \times 10^{-2} \text{ mol dm}^{-3}$), i.e. the interconversion of enantiomeric forms of complexes **II** is obviously a first-order reaction.

Conclusion

NMR relaxation spectroscopy proves once more to be a suitable technique for the determination of the structure not only for kinetically unstable complexes of Gd(III) [26, 27, 30], but also for kinetically stable complexes of other paramagnetic lanthanide cations. The combined method of study by LIS and longitudinal relaxation rate enhancements is one of the successful methods of the structural study of complexes of the lanthanides in solutions. The results of the present work demonstrate that there is a mutual transformation of the enantiomeric forms of the lanthanide complexes of the cerium subgroup with 18-membered macrocyclic ethers.

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