INTERNAL ROTATION AND PHASE TRANSITIONS IN LANTHANUM TETRAHYDROBORATES

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Using the $^1\mathrm{H}$, $^{11}\mathrm{B}$, $^{139}\mathrm{La}$ NMR and relaxation NMR methods, we have investigated the molecular dynamics in $\text{La}(\text{BH}_4)_3$ and its adduct with tetrahydrofuran $\text{La}(\text{BH}_4)_3\cdot3\text{THF}$. We have observed phase transitions connected with the change in the nature of the internal rotation (reorientation) of the $\text{BH}_4^-$ anions. We have determined the barrier to reorientation of the $\text{BH}_4^-$ anions and the THF molecules in the investigated compounds, and we have shown that the change in the mobility of the THF molecule does not lead to a phase transition.

Internal rotation of the $\text{BH}_4^-$ anions and disordering of the atoms in high-symmetry tetrahydroborates of alkali metals is closely connected with phase transition in these compounds [1]. In the transition to the low-symmetry compounds of the type $M^{\text{II}}(\text{BH}_4)_n$, the hydrogen atoms cannot be located in structurally and chemically equivalent positions. In compounds of the type $\text{Ln}(\text{BH}_4)_3\cdot\text{THF}$, according to x-ray diffraction data [2-4] the coordination interaction of the lanthanide ions $\text{Ln}^{3+}$ with the $\text{BH}_4^-$ ions is accomplished using hydrogen bridges. Reorientation of the $\text{BH}_4^-$ anions should lead to intramolecular exchange of bridge and terminal hydrogen atoms. It has remained unclear to what degree the role of dynamic effects and disordering of the hydrogen atoms is important for the structure of the given compounds.

In this work, using steady-state and pulsed NMR methods at the $^1\mathrm{H}$, $^{11}\mathrm{B}$, and $^{139}\mathrm{La}$ nuclei, we have investigated the dynamic effects in lanthanum tetrahydroborate and its adduct with tetrahydrofuran.

EXPERIMENTAL

The samples of $\text{La}(\text{BH}_4)_3\cdot3\text{THF}$ were synthesized by an exchange reaction of lanthanum chloride with sodium tetrahydroborate in tetrahydrofuran (THF) using the technique described in [5]:

$$\text{LaCl}_3 + 3\text{NaBH}_4 \rightarrow \text{La}(\text{BH}_4)_3 + 3\text{NaCl}. \quad (1)$$

For the synthesis we used NaBH$_4$ purified by recrystallization from an aqueous solution of alkali with subsequent extraction by diethyleneeglycol dimethyl ether (diglyme) and drying at 200°C under vacuum. The NaBH$_4$ content in the product obtained was not less than 99 mass %. The lanthanum chloride for carrying out the synthesis according to Eq. (1) was obtained by ether–acid drying of the crystal hydrate LaCl$_3$$\cdot$6H$_2$O and was finally dried at 190°C under vacuum. The LaCl$_3$ content in the product obtained was not less than 99 mass %. The tetrahydrofuran was dried and distilled above lithium aluminum hydride. All the operations were carried out under an atmosphere of dry inert gas.

In the starting materials and products, the lanthanum was determined complexonometrically with Trilon B using xylene orange; the boron was determined potentiometrically by
TABLE I. Calculated and Experimental Values of \( T_1(B) \) and \( T_1(H) \) at Relaxation Minima

<table>
<thead>
<tr>
<th>( T_1 ), ms</th>
<th>Isotropic reorient.</th>
<th>( C_4 )</th>
<th>( C_4 )</th>
<th>( La(BH_4)_3 )</th>
<th>( La(BH_4)_3\cdot3THF )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_1(B) )</td>
<td>14.08</td>
<td>21.1</td>
<td>21.4</td>
<td>76±15</td>
<td>110±10</td>
</tr>
<tr>
<td>( T_1(H) )</td>
<td>4.16</td>
<td>6.075</td>
<td>6.82</td>
<td>17.1±0.9</td>
<td>58.0±6</td>
</tr>
<tr>
<td>( T_1(B) )</td>
<td>3.35</td>
<td>3.47</td>
<td>3.19</td>
<td>4.4±1.0</td>
<td>2.0±0.4</td>
</tr>
</tbody>
</table>

The product obtained from reaction (1) was crystallized twice from THF and dried at room temperature under vacuum.

The La(BH_4)_3 samples were obtained by desolvation of La(BH_4)_3\cdot3THF using the technique in [6].

The IR spectra of lanthanum tetrahydroborate and its tetrahydrofuranate, taken on the SPECORD 75-IR spectrophotometer in petrolatum oil, are identical to the IR spectra of these complexes given in [7].

The nuclear magnetic resonance (NMR) spectra of the \(^1H\), \(^{11}B\), and \(^{139}La\) nuclei were obtained using a wide-line NMR spectrometer [8] based on the Jeol JNM-4H-100. The spin-lattice relaxation times for the \(^{11}B\) and \(^1H\) nuclei were measured on the modified IS-3 pulse spectrometer [9]. The sample temperature was varied by blowing nitrogen gas through the cryostats of the spectrometers.

RESULTS

The most important result of the NMR study is the fact that in the temperature dependences of the spin-lattice relaxation times of the \(^1H\) and \(^{11}B\) nuclei in La(BH_4)_3, at 210 K we observe a jumpwise change (Fig. 1) indicating the existence of a structural phase transition.

In the 95-110 K temperature region, the dependence of the logarithm of \( T_1 \) on the reciprocal temperature is linear. This means that the frequency of the reorientational jumps \( \nu_c \) of the BH_4^- anions per unit time is described by an Arrhenius law [10]:

\[
\nu_c = \nu_0 \exp \left( -\frac{E_a}{kT} \right),
\]

where \( \nu_c \) is the correlation frequency of the motion; \( E_a = 1.2 \pm 0.2 \text{ kcal/mole} \) is the activation barrier; \( \nu_0 \) is a constant. The minimum values of \( T_1(1H) \) and \( T_1(11B) \) differ substantially from those calculated for the BH_4^- ions with the intramolecular distance \( R(B-H) = 1.26 \text{ \AA} \) [11] (see Table 1). From the large width of the relaxation minima (\( \sim 90 \text{ K} \)) and taking into account the disagreement between the experimental and calculated values of \( T_1 \), we may conclude that in La(BH_4)_3 there are positions of the BH_4^- anions which are slightly different structurally and have different correlation frequencies \( \nu_c \).

In order to refine the relaxation mechanism for the \(^{11}B\) nuclei, we calculated the ratios of the minimum values of \( T_1(11B)/T_1(1H) \). As is evident from the table, the experimental ratio \( T_1(11B)/T_1(1H) \) is consistent with a purely dipole-dipole mechanism for the interaction of the nuclei within experimental accuracy limits, and the quadrupole coupling constant of the \(^{11}B\) nuclei in the low-temperature phase is less than \( \sim 1 \text{ kHz} \).