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Interaction of $LnCl_3 \cdot 6H_2O$ Crystal Hydrates with the Alkoxy Derivatives of Aluminum in Organic Solvents

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Abstract—The interaction of $LnCl_3 \cdot 6H_2O$ (Ln = Pr, Nd, and Tb) with the alkoxy derivatives of aluminum $(RO)_nAlCl_{3-n}$ (where R = Et or iso-Bu; n = 1–3) in organic solvents was studied. It was found that the reaction of the crystal water of $LnCl_3 \cdot 6H_2O$ with $(RO)_nAlCl_{3-n}$ resulted in the partial dehydration of the crystal hydrates with the formation of an alcohol (ROH) and the $LnCl_3 \cdot 3H_2O \cdot 3(RO)_mAl(OH)Cl_{2-m}$ complex (m = 1, 2). The solid colloidal particles of this complex and a solvent form a lanthanide-containing gel. The physicochemical (including luminescence) and catalytic properties of the complex in butadiene polymerization and 1,1-*gem*-dibromo-2-phenylcyclopropane dehalogenation were studied.

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INTRODUCTION

Alkoxides like $(RO)_3Al$ are used as catalysts for the polymerization reactions of epoxides, isocyanates, unsaturated compounds, aldehydes, esters, and CSF_2 [1], as well as for the Meerwein–Ponndorf reduction of aldehydes and ketones [2]. It is also well known that $LnCl_3 \cdot 6H_2O$ crystal hydrates actively react with organoaluminum compounds like R_3Al, and the products of these reactions are efficient catalysts for the polymerization of dienes [3] and nitrogen heterocycles [4]. According to published data [5, 6], the $(RO)_3Al$ alkoxides also react with water. In this case, $Al(OH)_3$ or partial hydrolysis products like $(HO)_xAl(OR)_{3-x}$ (x = 1–3) and an alcohol (ROH) are formed. This reaction forms the basis for the commercial production of higher fatty alcohols from alkylaluminums (Alfol process) [7]. The examples of the use of the alkoxy derivatives of aluminum $(RO)_nAlCl_{3-n}$ in combination with lanthanide complexes in catalysis have not been described in the scientific literature, and the interaction of the crystal hydrates with the alkoxy derivatives of aluminum has not been studied previously. At the same time, the reactions of the alkoxy derivatives of aluminum with the crystal water of the crystal hydrates can result in the formation of new lanthanide complexes with dehydrated alkoxide derivatives, and these complexes can exhibit catalytic activity in chemical reactions.

In this work, we studied the interaction of the crystal hydrates with the alkoxy derivatives of aluminum in organic solvents with the use of the following techniques: UV and IR spectroscopy, X-ray diffraction (XRD) analysis, gas–liquid chromatography (GLC), gravimetric and differential thermal analysis (TG DTA), photoluminescence, and τ-metry (the measurement of the lifetime of the Tb^{3+*} ion). The efficiency of luminescence techniques for studying synthesis reactions and the action of Ziegler–Natta catalysts was demonstrated previously [3, 8, 9], and the properties of catalysts based on other metal compounds were considered in [10].

Terbium was chosen from the lanthanide series because of its relatively bright *f–f* luminescence [11], and neodymium and praseodymium were chosen because of their high catalytic activity in the preparation of polydienes [12] and nitrogen heterocycles [13].

EXPERIMENTAL

The crystal hydrates of chemically pure grade and commercial gasoline solutions of the following organoaluminum compounds were used in this study: Et_3Al (98%), iso-Bu_3Al (91%), iso-Bu_2AlH (73%), and iso-Bu_2AlCl (95%). 1,1-*gem*-Dibromo-2-phenylcyclopropane was prepared according to a published procedure [14], and butadiene was purified in accordance with a procedure described elsewhere [3]. The crystal hydrates were ground in a mortar; sieve analysis was performed, and fractions of <63 μm were taken. Benzene, toluene, ethylbenzene, cumene, and hexane of reagent grade were purified in accordance with a published procedure [15] followed by distillation from sodium metal. Argon was passed through a gas absorbing apparatus, and air and O_2 were passed through a purification system, which was described elsewhere [16]. The alkoxy derivatives of aluminum were prepared in Schlenk vessels by the oxidation of solutions of corresponding organoaluminum compounds with air and O_2 according to Korneev [5].

The reactions of the crystal hydrates with the alkoxy derivatives of aluminum at 20°C in an argon atmosphere were performed in a thermostated glass reactor, which was equipped with a magnetic stirrer. A crystal hydrate (0.25 mmol) was loaded in the reactor; a solution of an alkoxy derivative of aluminum was added (the ratios between the alkoxy derivative of aluminum and the crystal hydrate were 3, 6, and 9; the total volume was 5 ml), and the contents were stirred for 20 min. Next, a solvent (0.5 ml) was added, and the stirring of the solution was continued until the complete disappearance of the solid crystal hydrate and the formation of a gel. A 4.5-ml portion of the solvent was added for analytical purposes, and the mixture was separated into two phases (a solution and a gel) by centrifugation. The gel was washed with the solvent, which was then removed in a vacuum (10 Torr; 20 min) to obtain a loose powder (Cat-Ln). The solution, the gel, and Cat-Ln were analyzed to determine the concentrations of Ln^{3+} and Al^{3+} by trilonometry [17]. The water contents of the crystal hydrates and reaction products were determined by the Karl Fischer method [17], and ROH was determined by GLC. The UV–visible absorption spectra and the photoluminescence of the gel and Cat-Ln were measured in airtight quartz cells or ampules in an atmosphere of Ar. In the measurement of XRD patterns, the samples of Cat-Ln were pelleted. The TG DTA of Cat-Ln samples was performed in an atmosphere of air in accordance with standard procedures. The polymerization of butadiene and the dehalogenation of 1,1-*gem*-dibromo-2-phenylcyclopropane were performed in accordance with procedures described in [3] and [18], respectively, with the use of Cat-Ln as catalysts.

The alcohol was analyzed on a Tsvet 500M chromatograph (2-m steel column 3 mm in diameter packed with 30.5% SE as a stationary liquid phase on Chromaton N-AW HMDS; FID) with temperature programming from 50 to 270°C at a heating rate of 8 K/min. The elemental analysis of Cat-Ln was performed on a Carlo Erba 106 analyzer. The IR, ^{13}C NMR, and photoluminescence spectra were measured on a Specord 75IR spectrophotometer, a JEOL FX90Q spectrometer, and an Aminco Bowman spectrofluorimeter, respectively. The XRD patterns were measured on a Philips PW-1800 diffractometer with CuK_{α} radiation; survey parameters: step, 0.05° 2θ; time step, 2 s; sample revolution, 1 rps. The TG DTA curves were obtained on a Mettler Toledo Star instrument. The specific surface area of Cat-Tb was measured on a Carlo Erba Monosorb analyzer. The lifetime of the Tb^{3+*} ion (τ) was measured on a τ-metric system including an LGI-23 pulsed nitrogen laser ($\lambda_{excitation}$ = 337 nm). The error in the measurement of τ was 10%, and the determination limit was 10 μs.

RESULTS AND DISCUSSION

Interaction of $LnCl_3 \cdot 6H_2O$ *Crystal Hydrates with* $(RO)_nAlCl_{3-n}$

The crystal hydrates are insoluble in the test aromatic solvents (benzene, toluene, ethylbenzene, and cumene). On the addition of the alkoxy derivatives of aluminum to a crystal hydrate suspension in a solvent, the heterogeneous reaction of the crystal water of the crystal hydrate with the alkoxy derivatives of aluminum results in the disappearance of the solid crystal hydrate phase and in the formation of a gel. Visually, the solution after reaction (S-1) seems homogeneous and exhibits clearly pronounced opalescence. Upon centrifugation, S-1 is easily separated into two phases: a gel (a heavier phase) and a solution (S-2). The formation of two phases also occurs upon keeping S-1 for a day. The gel has the color of the corresponding lanthanide crystal hydrate (white, green, or pink for Tb, Pr, or Nd, respectively), whereas S-2 is transparent and colorless. The resulting gel is a two-phase heterogeneous structure.

The results of chelatometric analysis indicate that Ln^{3+} ions completely pass into the gel regardless of the ratios between the alkoxy derivative of aluminum and the crystal hydrate equal to 3, 6, and 9; therefore, these ions are absent from S-2. Unlike Ln^{3+} ions, the presence or absence of Al^{3+} ions in S-2 depends on the ratio between the alkoxy derivative of aluminum and the crystal hydrate. Thus, at the above ratio equal to 3, Al^{3+} ions completely pass into the gel, whereas they partially remain in S-2 at the ratios equal to 6 and 9. The residual amounts of the alkoxy derivatives of aluminum were 50 and 67% (at the ratios between the alkoxy derivative of aluminum and the crystal hydrate equal to 6 and 9, respectively). They were monitored by measuring characteristic NMR signals. ^{13}C NMR (C_6D_6) δ (ppm): 18.85 (q, $3(\underline{C}H_3CH_2O)$, 58.71 (t, 3 $(CH_3\underline{C}H_2O)$). ^1H NMR (C_6D_6; *J*, Hz): 1.44 (t, 9H, $3(C\underline{H}_3CH_2O)$, ^3J = 7.3 Hz), 4.18 (br signal, 6H, $3(CH_3C\underline{H}_2O)$, $W_{1/2} \approx 20$ Hz).

The corresponding alcohol ROH was identified by GLC as the reaction product of the crystal hydrate with the alkoxy derivative of aluminum in S-2. The amount of the resulting ROH suggests that only three molecules of crystal water from the crystal hydrate participate in the formation of ROH regardless of the ratio between the alkoxy derivative of aluminum and the crystal hydrate equal to 3, 6, or 9.

Thus, regardless of the ratio between the alkoxy derivative of aluminum and the crystal hydrate, only a strictly specified amount of the alkoxy derivative of aluminum enters into the reaction of hydrolysis, which corresponds to a ratio of Ln to the alkoxy derivative of aluminum equal to 1/3.

If the gel is subjected to evacuation (10 Torr; 20 min), a finely dispersed loose powder is formed (which retained the color of the Cat-Ln gel), which is insoluble in the above solvents, as well as in hexane, isopropanol, ethanol, methanol, chloroform, and water.

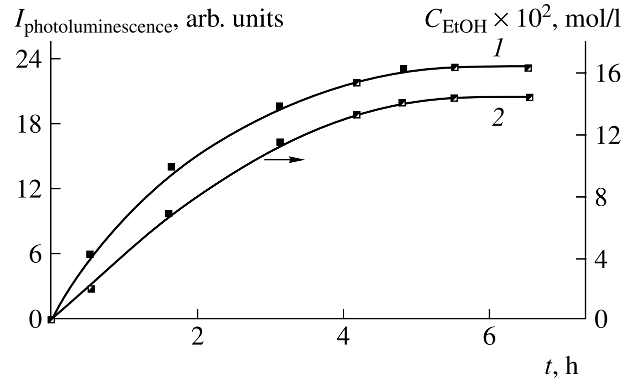


Fig. 1. Changes in (*1*) the photoluminescence intensity of the Tb^{3+*} ion at a maximum with $\lambda_{max} = 490$ nm and (*2*) the concentration of EtOH in the interaction of $TbCl_3 \cdot 6H_2O$ (0.25 mmol) with $(EtO)_3Al$ (0.75 mmol) in toluene: (*1*) $\lambda_{excitation} = 365$ nm; $T = 300$ K.

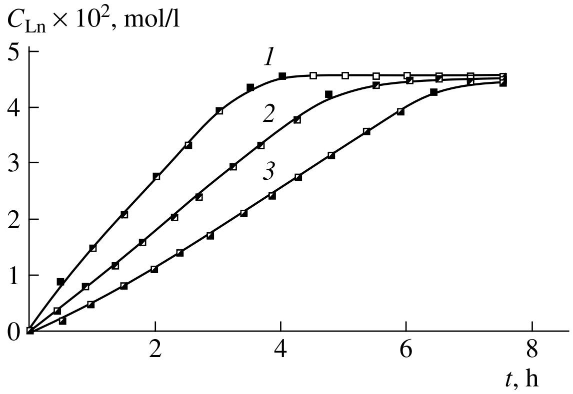


Fig. 2. Effect of the nature of the lanthanide on the rate of formation of a lanthanide-containing gel in the interaction of $LnCl_3 \cdot 6H_2O$ (0.25 mmol) with $(EtO)_3Al$ (0.75 mmol) in toluene: (*1*) Nd, (*2*) Tb, and (*3*) Pr. $T = 300$ K.

Based on the results of the Karl Fischer analysis, the Cat-Ln samples contain three water molecules per mole of a lanthanide. The amount of the remaining water is independent of the nature of the alkoxy derivative of aluminum, the lanthanide, and the solvent. The Ln/Cl and Ln/Al ratios in Cat-Ln are both 1/3. In addition to the above analyses, elemental analysis of Cat-Ln was also performed. According to the results of all of the analyses, the composition of Cat-Ln corresponds to the empirical formula $LnCl_3 \cdot 3H_2O \cdot 3(RO)_mAl(OH)Cl_{2-m}$. For example, for Cat-Tb obtained in the reaction of $TbCl_3 \cdot 6H_2O$ with $(EtO)_3Al$, found (%): Tb, 21.87; Al, 11.05; Cl, 14.28; C, 20.44; H, 5.62; O, 26.74. For $TbCl_3 \cdot 3H_2O \cdot 3(EtO)_2Al(OH)$ anal. calcd. (%): Tb, 22.03; Al, 11.23; Cl, 14.76; C, 19.96; H, 5.40; O, 26.62.

Cat-Ln could be an individual compound or a mixture of two well-known compounds, $LnCl_3 \cdot 3H_2O$ [19] and $(RO)_mAl(OH)Cl_{2-m}$ [1, 6], which readily react with water to form $LnCl_3 \cdot 6H_2O$ and $Al(OH)_3$, respectively, along with ROH. To determine the nature of Cat-Ln, it was exposed to water (stirring at 20°C for a day). In this case, no visible changes were observed. In the analysis of an aqueous phase, Ln^{3+} and Al^{3+} ions were not detected. The qualitative color reaction with a benzene solution of vanadium hydroxyquinolinate [20] showed that EtOH was also absent from the aqueous phase. The Karl Fischer analysis of the solid phase suggests that the water content of this phase remained unchanged.

Thus, Cat-Ln are individual compounds in which the $(RO)_mAl(OH)Cl_{2-m}$ ligand is tightly bound to the Ln^{3+} ion. This conclusion will be supported below by the results of spectroscopic measurements.

The experimental results allowed us to propose a simplified scheme (Scheme 1) for the reactions of the crystal hydrates with the alkoxy derivatives of aluminum. The reaction of an alkoxy derivative of aluminum with the crystal water of a crystal hydrate (reaction (1)) resulted in the formation of an alcohol (ROH) and $LnCl_3 \cdot 3H_2O_s \cdot 3(RO)_xAl(OH)Cl_{2-x}$, the solid colloidal particles of which and the solvent formed a gel (reaction (2)).

$$[LnCl_3 \cdot 6H_2O]_s + 3(RO)_nAlCl_{3-n} \longrightarrow [LnCl_3 \cdot 3H_2O \cdot 3(RO)_mAl(OH)Cl_{2-m}]_s + 3ROH, \quad (1)$$

$$x[LnCl_3 \cdot 3H_2O \cdot 3(RO)_mAl(OH)Cl_{2-m}]_s + yS \longrightarrow \{[LnCl_3 \cdot 3H_2O \cdot 3(RO)_mAl(OH)Cl_{2-m}]_x \cdot S_y\}_{gel} + (y-x)S, \quad (2)$$

where S is the solvent.

Scheme 1.

The formation of ROH and the lanthanide transfer to a gel occurred simultaneously; these processes were monitored using GLC analysis and measuring an increase in the maximum intensity (545 nm) in the photoluminescence spectrum of the gel, respectively (Fig. 1). The rate of gel formation does not depend on temperature (20–60°C) but does depend on the nature of the lanthanide, the alkoxy derivative of aluminum, and the solvent in accordance with orders **I–III**.

Nd > Tb > Pr **I**

$(EtO)_3Al > (iso\text{-}Bu)_2AlCl > (iso\text{-}Bu)_3Al$ **II**

benzene > toluene > ethylbenzene > cumene **III**

These orders were obtained in a study of the concentration of Ln^{3+} ions in the gel as a function of the reaction time for the crystal hydrates with the alkoxy derivatives of aluminum (Figs. 2–4). The effects of the nature of the metal and the solvent were studied using the interactions of the crystal hydrates and $TbCl_3 \cdot 6H_2O$ with $(EtO)_3Al$, respectively, as examples, and the effect of the nature of the alkoxy derivatives of aluminum was studied with the $TbCl_3 \cdot 6H_2O$ crystal hydrate. Note that, unlike alkylaluminums, there are no published

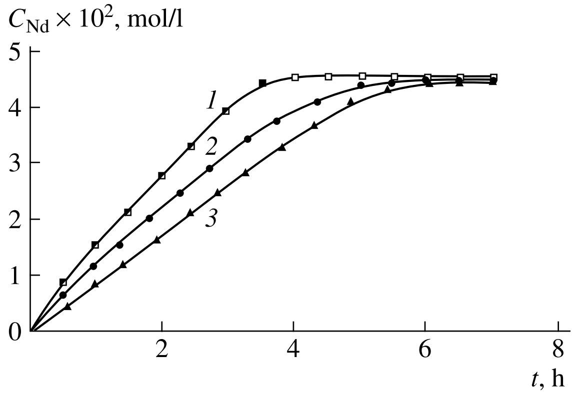


Fig. 3. Effect of the nature of the alkoxy derivative of aluminum on the rate of formation of a lanthanide-containing gel in the interaction of $NdCl_3 \cdot 6H_2O$ (0.25 mmol) with $(RO)_nAlX_{3-n}$ (0.75 mmol) in toluene: (*1*) $(EtO)_3Al$, (*2*) $(iso\text{-}BuO)_2AlCl$, and (*3*) $(iso\text{-}BuO)_3Al$. $T = 300$ K.

data on the effects of the nature of the lanthanide, the alkoxy derivatives of aluminum, and the solvent on the rates of hydrolysis of the alkoxy derivatives of aluminum.

It was found that order I is somewhat different from the well-known order of Ln–H_2O bond strengths [19]: Tb < Pr < Nd. At the same time, according to published data [5, 21], the rate of reaction of the crystal water of $CuSO_4 \cdot 5H_2O$ and $LnCl_3 \cdot 6H_2O$ with organoaluminum compounds depends strongly on the Ln–H_2O bond strength. Currently, it is difficult for us to explain the reason for the inconsistency of the above lanthanide orders. We can only hypothesize that the rate of Tb transfer to a gel is higher than that of Pr transfer because the step of gel formation (reaction (2)) exerts a greater effect on this process. Order **II** is consistent with the order of changes in the reactivity of alkylaluminums toward hydrolysis [5, 21]. Order **III** also correlates with a well-known order [5, 21] of decreasing reactivity of alkylaluminums, which depends on the solvation of these compounds by solvent molecules.

An analysis of orders **II** and **III** suggests that, as in the case of the hydrolysis of R_3Al, the rate of hydrolysis of the alkoxy derivatives of aluminum is higher for compounds containing smaller numbers of carbon atoms in the alkyl fragments and for solvents having greater coordinating ability. Moreover, the efficiency of gel formation in aromatic solvents is limited to a greater degree by the rate of hydrolysis of the alkoxy derivatives of aluminum, that is, reaction (1) in Scheme 1.

Physicochemical Properties of a Lanthanide-Containing Gel and Cat-Ln

Absorption spectra of a neodymium-containing gel. The absorption spectra of gels were studied using a neodymium-containing gel (Nd^{3+}) as an example because maximums in the absorption spectra of well-known Tb^{3+} and Pr^{3+} compounds [11] occur in the region that is strongly masked by the absorption of solvents. Unlike these lanthanides, Nd^{3+} compounds exhibit absorption maximums in the region 514–840 nm [11], which is not covered by aromatic solvents. Figure 5 shows the absorption spectrum of a toluene neodymium-containing gel. It differs from the absorption spectra of the aqua ion Nd^{3+}_{aq} in a bathochromic shift by 5–10 nm. This relatively large shift (for *f*–*f* transitions) suggests a considerable change in the coordination environment of Nd^{3+} upon passing from the crystal hydrate to the gel. With consideration for the similar chemical properties of Ln^{3+} ions, it is safe to assume that analogous changes in the coordination environment also occur in other lanthanide ions. The experimental spectroscopic data and the results of

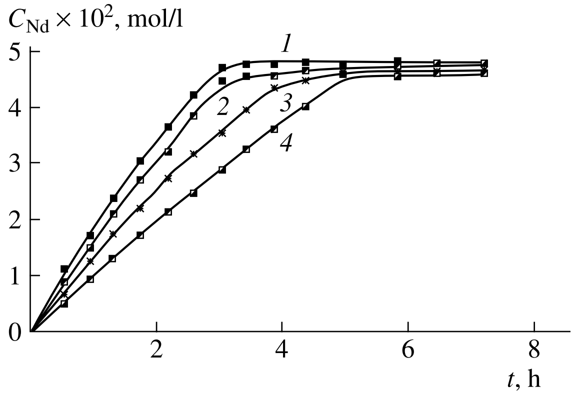


Fig. 4. Effect of the nature of the solvent on the rate of formation of a lanthanide-containing gel in the interaction of $NdCl_3 \cdot 6H_2O$ (0.25 mmol) with $(EtO)_3Al$ (0.75 mmol): (*1*) benzene, (*2*) toluene, (*3*) ethylbenzene, and (*4*) cumene. $T = 300$ K.

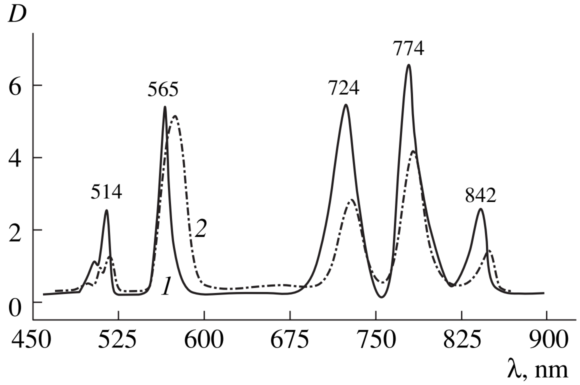


Fig. 5. Absorption spectra of (*1*) an aqueous solution of $NdCl_3 \cdot 6H_2O$ and (*2*) a toluene solution of a neodymium-containing gel obtained by the interaction of $NdCl_3 \cdot 6H_2O$ (0.25 mmol) with $(EtO)_3Al$ (0.75 mmol). $C_{Nd} = 5 \times 10^{-2}$ mol/l.

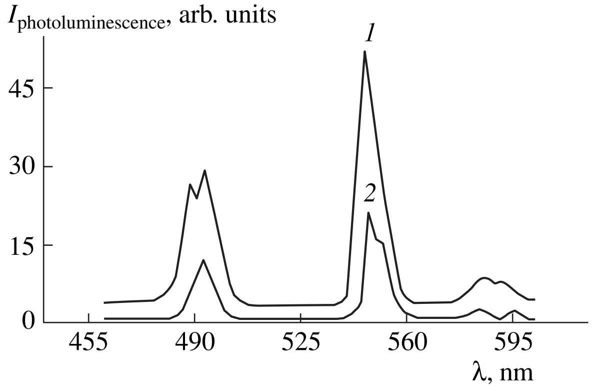


Fig. 6. Photoluminescence spectra (298 K): (*1*) $TbCl_3 \cdot 6H_2O$ and (*2*) Cat-Tb. $\lambda_{excitation}$ = 365 nm.

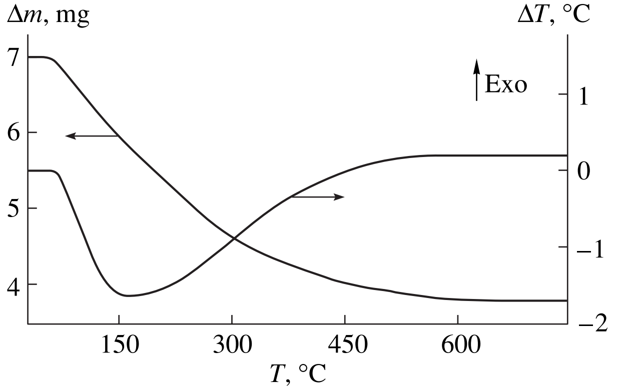
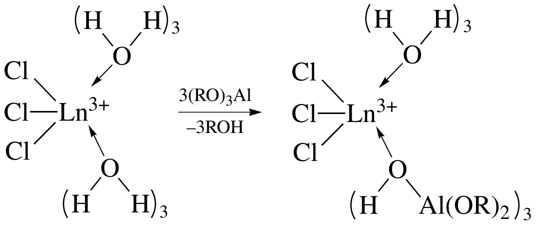


Fig. 7. TG DTA curves for Cat-Tb samples.

the chemical identification of products allowed us to propose the following scheme for changes in the coordination environment of Ln^{3+} in the reactions of the crystal hydrates with the alkoxy derivatives of aluminum:



Scheme 2.

The active RO–Al bond of an alkoxide is hydrolyzed by the crystal water of a crystal hydrate with the abstraction of a hydrogen atom from water and the formation of $(RO)_2Al(OH)$. We believe that, in this case, the oxygen atom of the water molecule, which participates in the reaction, retains its coordination bond with the Ln^{3+} ion.

Luminescence properties of a terbium-containing gel and Cat-Tb. The photoluminescence spectra of a toluene terbium-containing gel and Cat-Tb (Fig. 6) exhibit maximums at 493, 546, 586, and 593 nm and a shoulder at 550 nm, the positions of which differ only slightly from the maximums of parent $TbCl_3 \cdot 6H_2O$ (488, 493, 545, 586, and 591 nm). However, well-known data on the photoluminescence of terbium compounds [11] allowed us to ascribe the photoluminescence of the gel and Cat-Tb to *f–f* transitions ($^5D_4$–$^7F_6$, $^5D_4$–$^7F_5$, and $^5D_4$–$^7F_4$). As a result of the dehydration of $TbCl_3 \cdot 6H_2O$ under the action of $(EtO)_3Al$, τ increased from 425 ($TbCl_3 \cdot 6H_2O$) to 900 μs for the gel and Cat-Tb. The increase in τ was due to a decrease in the number of water molecules in the coordination sphere of the lanthanide ion as a result of the interaction of the crystal hydrate with the alkoxy derivative of aluminum. According to Ermolaev and Sveshnikova [22], water molecules are the luminescence quenchers of Ln^{3+*}. Note that τ in the gel remained unchanged in the course of the interaction of $TbCl_3 \cdot 6H_2O$ with the alkoxy derivative of aluminum. In turn, this suggests the formation of only a single complex species of terbium. The photoluminescence intensity of Cat-Tb samples is somewhat lower than that of the corresponding crystal hydrate. Because it is difficult to maintain identical conditions of passing the exciting light and luminescence through solid samples in the measurement of the photoluminescence spectra of powdered crystal hydrate and Cat-Ln samples, we believe that the decrease of the photoluminescence intensity was due to an internal filter effect. The positions of maximums in the photoluminescence spectra and the value of τ are independent of the nature of the solvent in which the dehydration of the crystal hydrate occurred. By this is meant that solvent molecules do not enter into the first coordination sphere of the Ln^{3+} ion because otherwise luminescence parameters will be changed [22].

We failed to detect the photoluminescence of the $PrCl_3 \cdot 6H_2O$ crystal hydrate and Cat-Pr. This was due to a low quantum yield of the photoluminescence of the Pr^{3+} ion in crystalline matrices [11], which is much lower than that for the intensely luminescent aqua ion of praseodymium in aqueous solutions [11]. The long-wavelength photoluminescence (800–1100 nm) of the $NdCl_3 \cdot 6H_2O$ crystal hydrate and Cat-Nd could not be measured on the FEU-39 photomultiplier tube (sensitivity region 200–650 nm) used in this work.

TG DTA. Two segments can be recognized in the TG DTA curves of the Cat-Tb sample (Fig. 7), which was prepared by the interaction of $TbCl_3 \cdot 6H_2O$ with $(EtO)_3Al$. In the range 30–145°C, a decrease in the weight of Cat-Ln (7.5%) occurred, which quantitatively corresponds to the endothermic process of the removal of residual crystal water. Note that, according to von Brauer [23], the complete dehydration of the $TbCl_3 \cdot 6H_2O$ crystal hydrate occurred in the range 65–250°C. In our case, it was complete at lower temperatures. This was likely due to the fact that the coordination of three $(RO)_2Al(OH)$ molecules, which occupied

Dependence of the yield and molecular characteristics of polybutadiene on the Al/Nd ratio in butadiene polymerization on the Cat-Nd–(iso-Bu)$_3$Al catalyst

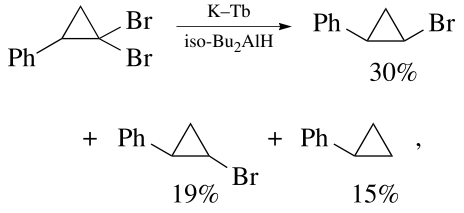
Al/Nd	Yield, %	Microstructure			$M_w \times 10^{-5}$	$M_n \times 10^{-4}$	M_w/M_n
		1,4-*cis*	1,4-*trans*	1,2-			
20*	0.3	–	–	–	–	–	–
40*	3.2	91.0	5.9	3.1	–	–	–
60*	7.8	–	–	–	–	–	–
80*	9.5	91.4	5.8	2.8	–	–	–
100*	10	–	–	–	–	–	–
20	5.7	88.2	7.1	4.7	4.61	6.35	7.3
40	23.1	86.3	8.4	5.3	–	–	–
60	33.3	89.2	7.3	3.5	–	–	–
80	39.0	–	–	–	2.20	7.9	27.8
100	41.6	88.4	8.6	3.0	–	–	–

Note: $C_{Nd} = 2 \times 10^{-3}$ and $C_{butadiene} = 2.0$ mol/l; 25 and 60°C; 4 h; solvent, toluene.
* Polymerization temperature of 25°C.

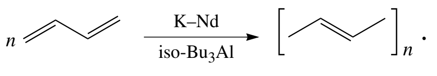
the places of three water molecules, which participated in the hydrolysis of the alkoxy derivative of aluminum, decreased the binding energy of the remaining water molecules with Ln^{3+}. Based on published data [1], we believe that, on the subsequent heating starting with 150°C, the exothermic decomposition of $(RO)_2Al(OH)$ occurred as a result of reaction with water vapor formed in the dehydration of Cat-Tb and with air moisture. According to Penkos [1], the thermal decomposition of the alkoxy derivatives of aluminum is accompanied by the formation of $Al(OH)_3$ and ROH followed by conversion into C_nH_{2n}, H_2O, and Al_2O_3. It is likely that this decomposition occurs simultaneously with the consecutive processes of formation of the oxychlorides $2TbCl_3 \cdot TbOCl$ and TbOCl, which are well known [23] for $TbCl_3 \cdot 6H_2O$. According to von Brauer [23], the formation of Tb_4O_7 occurs at temperatures of >715°C.

XRD analysis. It follows from X-ray diffraction patterns that, unlike crystalline $TbCl_3 \cdot 6H_2O$, Cat-Tb is an amorphous substance. The specific surface area of Cat-Tb is small and equal to 20 m^2/g.

Catalytic properties of Cat-Ln. The Cat-Ln samples were tested for catalytic activity in reaction (I) of 1,1-*gem*-dibromo-2-phenylcyclopropane dehalogenation (Ln = Tb) and in reaction (II) of butadiene polymerization (Ln = Nd).



(I)



(II)

Note that reaction (I) on lanthanide catalysts was performed for the first time. We found that, in this reaction, the same products were formed as with the use of the well-known $(n\text{-BuO})_4Ti$ catalyst [18]: *cis*-1-bromo-2-phenylcyclopropane, *trans*-1-bromo-2-phenylcyclopropane, and phenylcyclopropane. Cat-Tb exhibited lower catalytic activity (64% conversion) than that of the most efficient $(n\text{-BuO})_4Ti$ catalyst (96% conversion). At the same time, Cat-Ln was found to be a more selective catalyst because with the use of it the ratio of *cis*- and *trans*-1-bromo-2-phenylcyclopropanes, which are most important practically, to phenylcyclopropane is equal to 3/1, whereas the corresponding ratio was 1/3 in the case of $(n\text{-BuO})_4Ti$.

The Cat-Nd samples exhibited a certain catalytic activity in butadiene polymerization in the presence of (iso-Bu)$_3$Al. The dependence of the polymer yield on the (iso-Bu)$_3$Al/Nd ratio has the shape of a saturation curve. This curve flattened out at relatively high concentrations of (iso-Bu)$_3$Al. The molecular weight of the polymer decreased with an increasing (iso-Bu)$_3$Al/Nd ratio, whereas polydispersity increased in this case (see table). An analysis of data given in the table indicates that, as compared with the well-known $NdCl_3 \cdot 3TBP$–(iso-Bu)$_3$Al catalyst [9], the Cat-Nd catalyst ranks below it in efficiency and the molecular weight of polybutadiene, although the latter catalyst exhibits high stereospecificity in the formation of 1,4-*cis*-polybutadiene.

We found that the intense release of iso-BuH (the reaction product of the water molecules of Cat-Tb with (iso-Bu)$_3$Al) occurred on the addition of (iso-Bu)$_3$Al to Cat-Tb at the ratio (iso-Bu)$_3$Al/Tb ≥ 20. The solid phase formed in this case exhibited τ (≤10–20 μs) much shorter that τ in Cat-Tb (1000 μs). An analogous decrease in τ in the interaction of the $TbCl_3 \cdot 3TBP$ complex with (iso-Bu)$_3$Al was described by Bulgakov et al. [9] and explained by the displacement of TBP molecules from the coordination sphere of the lanthanide and the formation of bridging structures with Tb–Cl–Tb and Tb–Alk units. In this case, Monakov et al. [24] hypothesized the formation of various structurally different catalytically active centers containing Tb–Cl–Tb and Tb–Alk units. We believe that coordinatively unsaturated lanthanide ions formed as a result of the dehydration of Cat-Tb also form analogous units. At the same time, the results of polymerization indicate that the catalytically active centers formed in this case are structurally different from those in the case of the $TbCl_3 \cdot 3TBP$ complex.

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