

# A New Approach to the Preparation of Lanthanide Catalysts for the Synthesis of 2-Propyl-3-Ethylquinoline Based on the Reactions of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ Crystalline Hydrates with Triisobutylaluminum

R. G. Bulgakov<sup>a</sup>, S. P. Kuleshov<sup>a</sup>, A. R. Makhmutov<sup>a</sup>, R. R. Vafin<sup>a</sup>, D. S. Karamzina<sup>a</sup>,  
M. T. Golikova<sup>a</sup>, Ya. V. Shestopal<sup>a</sup>, S. M. Usmanov<sup>b</sup>, and U. M. Dzhemilev<sup>a</sup>

<sup>a</sup> Institute of Petrochemistry and Catalysis, Academy of Sciences of Bashkortostan, Ufa Scientific Center,  
Russian Academy of Sciences, Ufa, 450075 Bashkortostan, Russia

<sup>b</sup> Birsk State Pedagogical Institute, Birsk, 452320 Bashkortostan, Russia

Received March 11, 2005

**Abstract**—A new approach to the preparation of lanthanide catalysts for the synthesis of nitrogen heterocycles (exemplified by 2-propyl-3-ethylquinoline) was developed based on the reactions of  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  crystalline hydrates with alkylaluminums. It was found that the interaction of  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ce}, \text{Pr}, \text{Tb}, \text{and Eu}$ ) with iso- $\text{Bu}_3\text{Al}$  in aromatic solvents ( $20^\circ\text{C}$ ) resulted in the formation of soluble (isobutane and the alumoxane (iso- $\text{Bu}_2\text{Al}_2\text{O}$ ) and insoluble products (with the empirical formula  $\text{LnCl}_3 \cdot x\text{H}_2\text{O} \cdot y(\text{iso-}\text{Bu}_2\text{Al})_2\text{O}$  ( $x = 0.4–0.7$ ;  $y = 0.04–0.07$ )). The physicochemical properties of  $\text{LnCl}_3 \cdot x\text{H}_2\text{O} \cdot y(\text{iso-}\text{Bu}_2\text{Al})_2\text{O}$  were studied, and these compounds were found to be highly efficient catalysts for the reaction of aniline condensation with butyraldehyde to form 2-propyl-3-ethylquinoline.

**DOI:** 10.1134/S0023158406040136

## INTRODUCTION

Lanthanide trichlorides  $\text{LnCl}_3$  are efficient catalysts in the syntheses of nitrogen heterocycles [1] and, in combination with organoaluminum compounds, polydienes [2]. However, the well-known methods for the preparation of  $\text{LnCl}_3$  imply the interaction of the crystalline hydrates  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  with corrosion-active reagents ( $\text{HCl}$  and  $\text{SOCl}_2$ ) at high temperatures ( $90–500^\circ\text{C}$ ) for long times (48–110 h) [3]. Based on the above and taking into account that catalytic compositions based on lanthanide compounds frequently include organoaluminum compounds [2, 4], we developed a new approach to the preparation of lanthanide catalysts, which is characterized by the use of organoaluminum compounds for the dehydration of the crystalline hydrates. Thus, it was found that an efficient homogeneous catalyst for butadiene polymerization can be easily prepared by the interaction of the crystalline hydrates with organoaluminum compounds in toluene in the presence of  $(\text{BuO})_3\text{PO}$  at room temperature in a few minutes [5].

In this work, we studied the preparation of lanthanide catalysts for the synthesis of nitrogen heterocycles by the interaction of the crystalline hydrates with iso- $\text{Bu}_3\text{Al}$  (TIBA). As an example, we used the synthesis of 2-propyl-3-ethylquinoline by the reaction of

aniline condensation with butyraldehyde. In order to study the above interaction and to characterize the physicochemical properties of the resulting catalysts, we used the following techniques: volumetry; UV and IR spectroscopy; X-ray phase analysis and X-ray diffraction analysis (XRD); gas–liquid chromatography (GLC); gravimetric and differential thermal analysis (TG DTA); photoluminescence; chemiluminescence; and  $\tau$ -metry (the measurement of the lifetime of the  $\text{Tb}^{3+*}$  ion). The efficiency of luminescence techniques for studying synthesis reactions and the action of Ziegler–Natta catalysts was demonstrated previously [5–7]. The properties of catalysts based on other metal oxides ( $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{MgO}$ ) and containing no organoaluminum compounds were described elsewhere [8].

The lanthanides  $\text{Tb}$ ,  $\text{Eu}$ , and  $\text{Ce}$  were chosen because of their relatively bright  $f-f$  and  $f-d$  luminescence [9]. In addition, using  $\text{Eu}^{3+}$ , which can be reduced to  $\text{Eu}^{2+}$  [10], as an example, we studied the effect of the lanthanide oxidation number on the composition of products in the reaction of the crystalline hydrate with TIBA and on the catalytic activity of the products of this reaction. Praseodymium was chosen because of its high catalytic activity in the preparation of substituted quinolines [1].

## EXPERIMENTAL

The crystalline hydrates of chemically pure grade were used in this study; all of the other reagents and solvents were of reagent grade. A commercial gasoline solution of TIBA (90%) was subjected to vacuum distillation according to Korneev [11]; the concentration of the alkoxy derivatives of aluminum in TIBA was no higher than 1% (according to  $^1\text{H}$  NMR data). Aniline was distilled in a vacuum (10 Torr; 70°C), and butyraldehyde was distilled from hydroquinone [12];  $\text{Ph}_3\text{P}$  was used without purification. Solvents were purified in accordance with published procedures [12]: benzene, toluene, ethylbenzene, and cumene were purified with the subsequent distillation from sodium metal, whereas dimethylformamide (DMF) was distilled from  $\text{BaO}$ . Argon was passed through a gas absorbing apparatus.

The reactions of the crystalline hydrates with TIBA at 20°C in an argon atmosphere were performed in a thermostated glass reactor, which was equipped with a magnetic stirrer and connected to a gas burette for measuring the volume of released gases. A crystalline hydrate (0.54 mmol) was loaded in the reactor, and a solvent and TIBA were added (crystal water/TIBA ratios of 1/2 and 1/20; total volume of 10 ml). The reaction mixture was stirred to the completion of gas liberation and centrifuged; the solution was separated from a solid phase. The solid phase was washed with the solvent, which was then removed by evacuation (10 Torr; 20 min) to obtain a loose powder (henceforth denoted by Cat-Ln).

The condensation of aniline with butyraldehyde was performed in a steel autoclave ( $V = 17 \text{ cm}^3$ ) in an atmosphere of argon. The autoclave was successively loaded with aniline (20 mmol), butyraldehyde (44 mmol), and DMF (6 ml). Next, a solution of Cat-Ln (0.54 mmol) in DMF (1 ml) in the absence or in the presence of  $\text{Ph}_3\text{P}$  (1.2 mmol) was added. The autoclave was heated with continuous stirring for 4–6 h at 80–100°C and then cooled. The reaction mass was three times extracted with diethyl ether (50 ml), and the combined extracts were dried with anhydrous  $\text{MgSO}_4$ . The solvent was distilled off, and the residue was fractionated in a vacuum.

The solution after the reaction of a crystalline hydrate with TIBA and Cat-Ln was analyzed to determine the concentrations of  $\text{Ln}^{3+}$  and  $\text{Al}^{3+}$  by trilonometry and atomic absorption spectrometry, respectively, in accordance with published procedures [13]. The water contents of the crystalline hydrates and reaction products were determined by the Karl Fischer method [13]. The presence and number ( $N$ ) of metal–carbon bonds in Cat-Ln were determined from the volume of isobutane released in hydrolysis with 10% aqueous  $\text{HNO}_3$ . The following equation was used for calculations:  $N = V/22400$  (where  $V$  is the volume of isobutane with consideration for its water solubility (ml), and 22400 ml is the volume of a mole of isobutane at 20°C). Alumoxane ( $(\text{iso-Bu}_2\text{Al})_2\text{O}$ ) was identified using IR spectra according to Boleslawski and Serwatowski [14], and isobu-

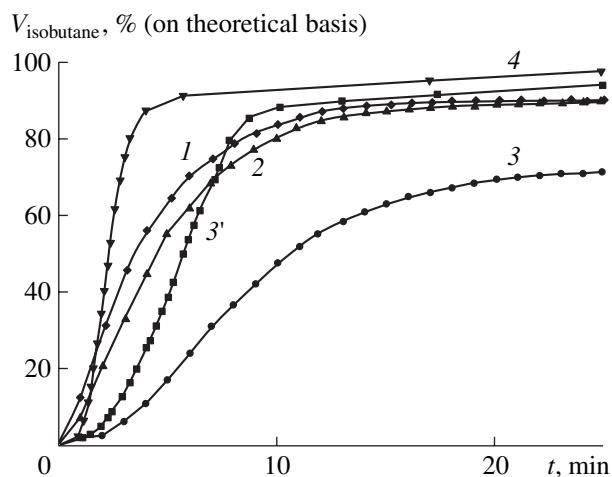
tane was identified by GLC. The IR, UV, visible absorption, and photoluminescence spectra of solutions and solid Cat-Ln were measured in airtight cells or ampules in an atmosphere of Ar. Chemiluminescence was generated by oxygen puffing onto the surface of Cat-Ln, which was uniformly scattered at the optically transparent bottom of a quartz cell. In the measurement of XRD patterns, the samples of Cat-Ln were pelleted in an atmosphere of argon and then impregnated with a toluene solution of rubber adhesive (4508) in order to exclude contact with air. The TG DTA of Cat-Ln samples was performed in an atmosphere of air in accordance with standard procedures.

Isobutane and the products of aniline condensation with butyraldehyde were analyzed on Karlo Erba GC 6000 (3-m column 4 mm in diameter; stationary liquid phase, 15% PEG 6000 on Chromaton) and Chrom 5 (3-m column 4 mm in diameter; stationary liquid phase, 30.5% SE-30 on Chromaton N-AW HMDS) chromatographs. The elemental analysis of Cat-Ln was performed on a Karlo Erba 106 analyzer. The absorption spectra in the IR and UV–visible regions were measured on Specord 75IR and Specord M40 spectrophotometers, respectively. The photoluminescence spectra were measured on an Aminco Bowman spectrofluorimeter. The analysis of samples for aluminum was performed on a Shimadzu GFA-4B atomic absorption spectrophotometer (graphite cell atomizer). The XRD patterns were measured on a Philips PW-1800 diffractometer with  $\text{CuK}_\alpha$  radiation using the following parameters: step,  $0.05^\circ$ ; 2θ; time step, 2"; sample revolution, 1 rps. The TG DTA curves were obtained on a Mettler Toledo Star TGA-851E derivatograph. The lifetime of the  $\text{Tb}^{3+*}$  ion ( $\tau_{\text{Tb}^{3+*}}$ ) was measured on a τ-metric system including an LGI-23 pulsed nitrogen laser ( $\lambda_{\text{excitation}} = 337 \text{ nm}$ ; measurement error of 10%). The determination limit was  $10 \mu\text{s}$ ; therefore, the measurement of the much shorter value of  $\tau$  for  $\text{Ce}^{3+*}$  was impossible. The system and the procedure used for chemiluminescence measurements were described previously [15].

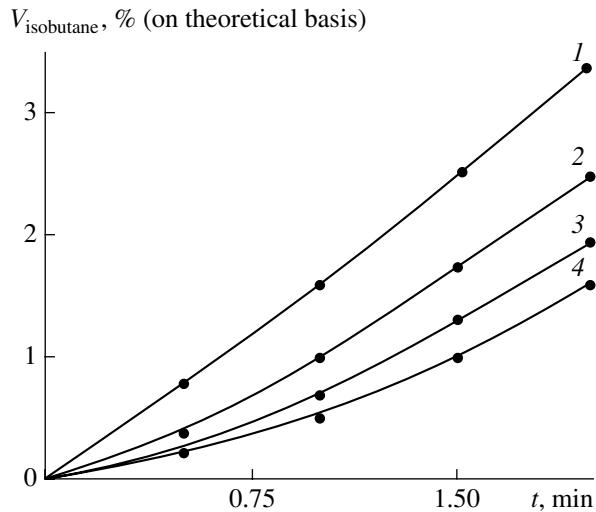
## RESULTS AND DISCUSSION

*Interaction of Crystalline Hydrates with TIBA*

**Liquid and gaseous products.** The crystalline hydrates are insoluble in aromatic solvents. Upon the addition of TIBA to a crystalline hydrate suspension in a solvent, intense gas release occurred. According to the results of the GLC analysis of liquid and gas phases, this gas was isobutane. Alumoxane was identified as the second soluble product based on IR spectra [14]: absorption at 680, 620, and  $1460 \text{ cm}^{-1}$  (stretching and deformation vibrations of  $\text{CH}_2$  groups at the Al atom) and in the region  $780$ – $810 \text{ cm}^{-1}$  (asymmetrical deformation vibrations of the Al–O bond). Chelatometric and fluorescence analysis demonstrated that  $\text{Ln}^{3+}$  ions were absent from the solution after the reaction of a crystalline hydrate with TIBA; that is, the lanthanide



**Fig. 1.** Effect of the nature of the lanthanide on the kinetics of isobutane release (20°C) in the interaction of  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  (0.54 mmol) with iso- $\text{Bu}_3\text{Al}$  in toluene.  $\text{Ln} = (1) \text{Ce}$ , (2) Pr, (3) Tb, and (4) Eu.  $\text{Ln/iso-Bu}_3\text{Al} = (1-4) 1/12$  or (3')  $1/20$ .

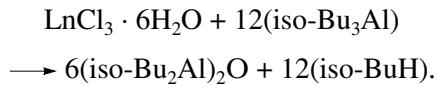


**Fig. 2.** Effect of the nature of the solvent on the kinetics of isobutane release (20°C) in the interaction of  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (0.54 mmol) with iso- $\text{Bu}_3\text{Al}$  (6.48 mmol): (1) benzene, (2) toluene, (3) ethylbenzene, and (4) cumene.

remained completely in a solid phase. Thus, the vigorous reaction of the crystal water of a crystalline hydrate with TIBA occurred not only in toluene at elevated temperatures, as reported previously [5], but also in various aromatic solvents at room temperature.

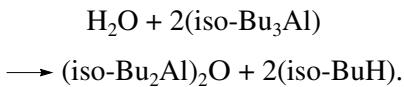
The rate of isobutane release depends on the nature of the lanthanide, its ability to change the oxidation number, the solvent, and the TIBA/crystalline hydrate ratio. Figure 1 demonstrates the effect of the nature of the lanthanide. This effect can be due to the following two main factors: the strength of the bond of a lanthanide ion with crystal water and the type of the crystal lattice of the crystalline hydrate. The test crystalline

hydrates exhibited the same crystal structure: monoclinic system; space group  $P_{2/c}-C_{2h}^4$  [16]. Changes in the rates of reactions of the crystalline hydrates with TIBA at the beginning of the process (to 2 min) are characterized by the following order: Ce > Pr > Eu > Tb. Therefore, we related the effect of the nature of the lanthanide on the rate of dehydration of the crystalline hydrate in this time interval to different bond strengths of crystal water with  $\text{Ln}^{3+}$  ions. According to Ukrainseva et al. [17], the bond strengths of crystalline hydrates increased with the atomic number of the element. After the second minute, the rate of isobutane release decreased in the order Eu > Ce > Pr > Tb. We related the maximum rate of dehydration of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  in this order to the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  as a result of an attack of TIBA, which leads to a decrease in the coordination number of europium. Note that, previously [5], the effect of the nature of the lanthanide on the rate of isobutane release was not found in the dehydration of crystalline hydrates at temperatures of  $\geq 40^\circ\text{C}$ . It is likely that at higher temperatures this effect was compensated by an increase in the rate of reaction with temperature. The effect of the nature of the solvent (Fig. 2) is characterized by the following order: benzene > toluene > ethylbenzene > cumene, which correlates with the well-known order [11] of decreasing reactivity of alkylaluminums due to their solvation with solvent molecules. The rate of isobutane release increased with the TIBA/crystalline hydrate ratio (Fig. 1). The total amount of released isobutane was found to be smaller than the stoichiometric amount determined by the reaction



This fact suggests that 2.7–4.5% of unreacted crystal water remained in Cat-Ln.

Thus, the interaction of crystalline hydrates with TIBA resulted in the formation of the same soluble products as in the well-known reaction of free water with TIBA [11]



On this basis, we believe that the mechanism of formation of these products is the same in the reactions of TIBA with free and crystal water; that is, the presence of a lanthanide ion does not affect the mechanism of reaction between the above reactants, as is often the case with other reactions. According to published data [11], the interaction of TIBA with water is a two-step process. At the first step, isobutane and iso- $\text{Bu}_2\text{AlOH}$  are formed. At the second step, iso- $\text{Bu}_2\text{AlOH}$  reacts with another TIBA molecule to form alumoxane and isobutane.

**Solid products.** According to the Karl Fischer analysis, the samples of Cat-Ln contained 0.4–0.7 water

molecules, which corresponds to the amount of formed isobutane. The amount of unreacted crystal water after the termination of isobutane release was independent of the nature of the solvent and the lanthanide and its ability to undergo reduction. The residual crystal water cannot be removed even with a 20-fold excess of TIBA with respect to crystal water and with thoroughly ground samples of the crystalline hydrates. We believe that the incomplete dehydration of the crystalline hydrates was due to heterogeneous interactions, which resulted in the passivation of the solid phase.

Along with water, Cat-Ln contained Ln and Cl ( $\text{Ln}/\text{Cl} = 1/3$ ), as well as Al ( $\text{Ln}/\text{Al} = 1/0.04\text{--}0.07$ ). In the hydrolysis of Cat-Ln with a 10%  $\text{HNO}_3$  solution, isobutane was released; this fact was indicative of the presence of an organometallic compound in Cat-Ln. In this case, the concentration of iso-Bu–metal fragments in Cat-Ln determined from the amount of released isobutane was lower than the concentration of the lanthanide by more than two orders of magnitude and greater than the concentration of aluminum by a factor of more than 2. It is well known that a tenfold (or higher) excess of TIBA [2] and an alumoxane amount greater by two orders of magnitude [18] are required for the alkylation of lanthanide chlorides. In the interactions of the crystalline hydrates with TIBA, more than 90% of TIBA was consumed in the reaction with crystal water. Taking into account these circumstances, we can exclude the alkylation of  $\text{Ln}^{3+}$  with TIBA molecules and conclude that the organometallic compound is  $(\text{iso-Bu}_2\text{Al})_2\text{O}$ . Small amounts of  $(\text{iso-Bu}_2\text{Al})_2\text{O}$  contained in Cat-Ln did not allow us to detect it by IR spectra. Based on elemental analysis data, the results of hydrolysis, and analysis for water, we found the empirical formula of Cat-Ln:  $\text{LnCl}_3 \cdot (0.4\text{--}0.7)\text{H}_2\text{O} \cdot (0.04\text{--}0.07)(\text{iso-Bu}_2\text{Al})_2\text{O}$ . For example, for Cat-Tb we found the following (%): Tb, 54.83; Al, 0.92; Cl, 36.84; C, 3.41; H, 0.98; O, 3.02; Al–C/Al = 2. For  $\text{TbCl}_3 \cdot x(\text{H}_2\text{O}) \cdot y(\text{iso-Bu}_2\text{Al})_2\text{O}$  (where  $x = 0.5$ ;  $y = 0.05$ ; average values obtained in six experiments are given). Calcd. (%) Tb, 54.93; Al, 0.93; Cl, 36.81; C, 3.32; H, 0.97; O, 3.04; Al–C/Al = 2.

#### Physicochemical Properties of Cat-Ln

**Absorption spectra of Cat-Ln solutions.** The absorption spectra (visible region) of the solutions of Cat-Ln (Ln = Ce, Pr, or Tb) in HCl (0.65 M) contained maximums characteristic [9] of  $\text{Ln}^{3+}$  ions (not given). By contrast, the absorption spectrum of an analogous solution of Cat-Eu (Fig. 3) exhibits new diffuse and more intense maximums at 250 and 325 nm, which are characteristic of  $\text{Eu}^{2+}$  compounds [19], in place of narrow maximums of  $\text{Eu}^{3+}$ . Thus, of all of the lanthanides tested, only  $\text{Eu}^{3+}$  was reduced to  $\text{Eu}^{2+}$  because of the interaction of the crystalline hydrate with TIBA. The reduction of  $\text{Eu}^{3+}$  as a constituent of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  under the action of organoaluminum compounds was

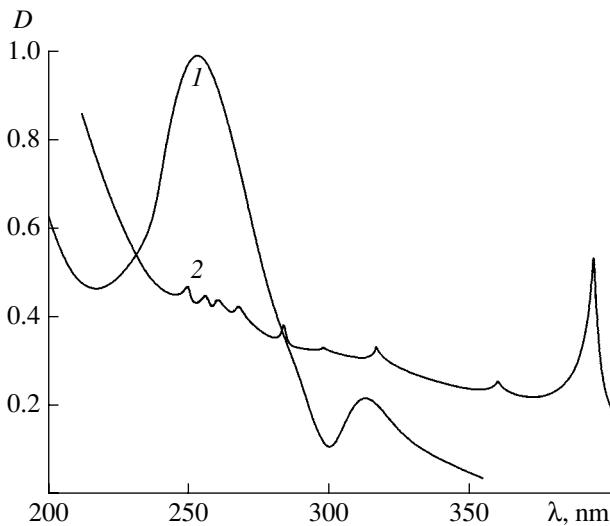


Fig. 3. Absorption spectra of the solutions of (1) Cat-Eu and (2)  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  in 0.65 M HCl;  $[\text{Cat-Eu}] = 10^{-3}$  mol/l;  $[\text{EuCl}_3 \cdot 6\text{H}_2\text{O}] = 2 \times 10^{-1}$  mol/l.

Photoluminescence intensity, arb. units

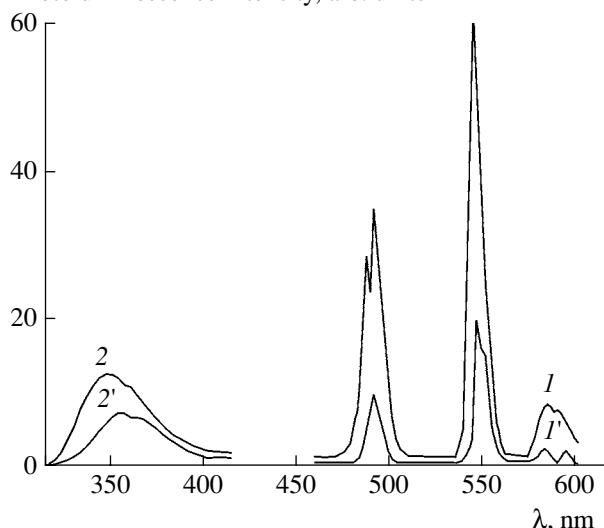
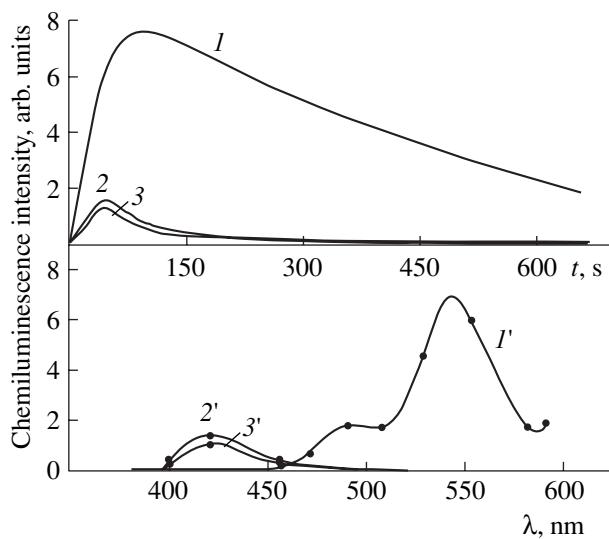


Fig. 4. Photoluminescence spectra ( $20^\circ\text{C}$ ) of (1)  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ , (1') Cat-Tb, (2)  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ , and (2') Cat-Ce.  $\lambda_{\text{excitation}} = (1, 1') 365$  or (2, 2') 300 nm.

not described previously. At the same time, the reduction of  $\text{Eu}^{3+}$  as a constituent of organic lanthanide complexes with alkylaluminums is well known [10].

**Luminescence properties of Cat-Ln.** The photoluminescence spectra of Cat-Tb (Fig. 4) contain maximums at 493, 546, 586, and 593 nm and a shoulder at 550 nm, and the spectra of Cat-Ce contain a diffuse maximum at 356 nm and a shoulder at 368 nm, the positions of which are slightly different from those in the spectra of parent  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (488, 493, 545, 586, and 591 nm) and  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$  (351 nm and a shoulder at 365 nm). Despite the above difference between the



**Fig. 5.** (1–3) Kinetic curves and (I'–3') chemiluminescence spectra measured on oxygen puffing onto the surface of Cat-Ln (20°C). Ln = (1, I') Tb, (2, 2') Ce, and (3, 3') Pr. (A set of boundary light filters was used).

photoluminescence spectra of Cat-Ln and the crystalline hydrates and with consideration for well-known data on the photoluminescence of terbium and cerium compounds [9], we can state that the photoluminescence of Cat-Tb is due to  $f-f$  transitions ( $^5D_4-^7F_6$ ,  $^5D_4-^7F_5$ , and  $^5D_4-^7F_4$ ), whereas the photoluminescence of Cat-Ce is due to transitions from the lower level  $^2D$  to the sublevels  $^2F_{7/2}$  and  $^2F_{5/2}$ . The peak positions and intensities in the photoluminescence spectra of Cat-Tb and Cat-Ce did not depend on the nature of the solvent in which the dehydration of crystalline hydrates occurred. As a result of the dehydration of  $TbCl_3 \cdot 6H_2O$ , the value of  $\tau$  for  $Tb^{3+*}$  decreased from 425 to 100  $\mu$ s for Cat-Tb. The photoluminescence intensities of Cat-Tb and Cat-Ce were lower than the photoluminescence intensities of the crystalline hydrates. We related these changes to a decrease in the number of water molecules in the coordination sphere of lanthanide ions and to structural changes in the crystal lattices of the crystalline hydrates.

In the case of Cat-Eu, red photoluminescence, which is characteristic of  $Eu^{3+*}$  [9], was not detected because of the reduction of  $Eu^{3+}$  to  $Eu^{2+}$  as a result of the interaction of  $EuCl_3 \cdot 6H_2O$  with TIBA. The photoluminescence intensities of  $PrCl_3 \cdot 6H_2O$  and Cat-Pr were very weak; because of this, luminescence measurements in praseodymium compounds were not performed in this study.

In addition to the release of isobutane in the course of hydrolysis, chemiluminescence (Fig. 5), which was detected upon oxygen puffing onto the surface of powdered Cat-Ln (Ln = Tb, Ce, and Pr), evidenced the presence of  $(iso-Bu_2Al)_2O$  in Cat-Ln. Note that the value of

$\tau$  for  $Tb^{3+*}$  before and after the oxidation of Cat-Tb with oxygen remained unchanged. This additionally evidenced that Cat-Ln does not contain Ln-alkyl bonds because otherwise the value of  $\tau$  for  $Tb^{3+*}$  would increase as a result of the appearance of Tb-O-alkyl bonds, which are characterized [6, 7] by longer values of  $\tau$  for  $Tb^{3+*}$ . The intensity and shape of spectra and the nature of chemiluminescence emission centers depend on the nature of the lanthanide. Thus, the following maximum chemiluminescence intensities were obtained (photon  $s^{-1} ml^{-1}$ ):  $6.4 \times 10^7$  (Cat-Tb),  $1.5 \times 10^7$  (Cat-Pr), and  $1.6 \times 10^7$  (Cat-Ce); that is, chemiluminescence intensities were almost equal in the cases of Cat-Pr and Cat-Ce, whereas the chemiluminescence intensity of Cat-Tb was much higher. In the case of Cat-Tb, the  $Tb^{3+*}$  ion is the emitter of chemiluminescence ( $\lambda_{max} = 490$  and 545 nm), whereas the excited triplet state of isobutyraldehyde ( $^3BA^*$ ) was identified as a chemiluminescence emitter ( $\lambda_{max} = 420$  nm) in the oxidation of Cat-Ce and Cat-Pr. Based on the spectroscopic and brightness parameters of chemiluminescence and published data on chemiluminescence activation in the autoxidation of  $(iso-Bu_2Al)_2O$  with terbium complexes [20], we propose the following mechanism of chemiluminescence excitation: The primary emitter  $^3BA^*$  results from the oxygen oxidation of  $(iso-Bu_2Al)_2O$ , which is a constituent of all of the Cat-Ln species. In the case of the oxidation of Cat-Ce and Cat-Pr, the emitter  $^3BA^*$  is deactivated with the emission of short-wavelength chemiluminescence ( $\lambda_{max} = 420$  nm). In the oxidation of Cat-Tb, energy is transferred from  $^3BA^*$  to the terbium ion, which is converted into the excited state  $Tb^{3+*}$ ; then, it emits brighter long-wavelength chemiluminescence ( $\lambda_{max} = 490, 545$  nm). This mechanism was supported by the absence of  $^3BA^*$  emission from the chemiluminescence spectra of Cat-Tb samples.

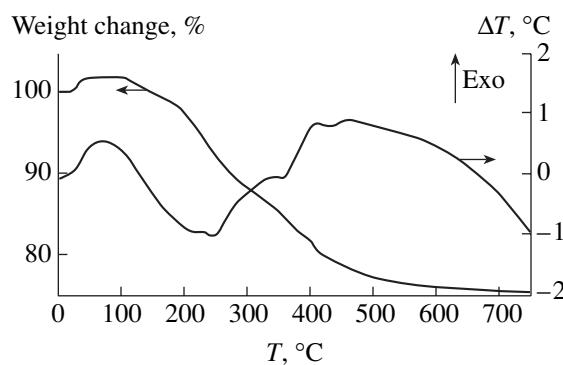
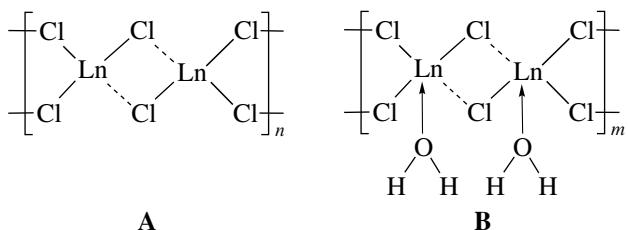
The absence of  $Ce^{3+*}$  emission from chemiluminescence in the oxidation of Cat-Ce was due to a higher energy of the emitting level of  $Ce^{3+*}$  (350 nm, 4.2 eV), as compared with that of  $^3BA^*$  (420 nm, 3 eV). It is well known [9] that the photoluminescence spectra of the solutions of  $Pr^{3+}$  compounds contain maximums at 246, 260, 271, 395, and 480 nm. However, short-wavelength excitation is required for the detection of these emission bands ( $\lambda_{excitation} = 213$  nm, 5.8 eV). Therefore, the absence of  $Pr^{3+}$ , as well as  $Ce^{3+}$ , emission from the chemiluminescence spectrum of Cat-Pr is due to an energy deficiency.

**TG DTA.** The TG DTA curves of a Cat-Tb sample (Fig. 6) exhibited four segments. In the range 30–145°C, a small weight increase (1.2%) occurred. We related this increase to the oxidation of  $(iso-Bu_2Al)_2O$  to an alkoxy derivative, which has a greater molecular weight than that of  $(iso-Bu_2Al)_2O$ . The increase in the sample weight was quantitatively consistent with the formation of  $(iso-Bu_2OAl)_2O$ , and it began even before

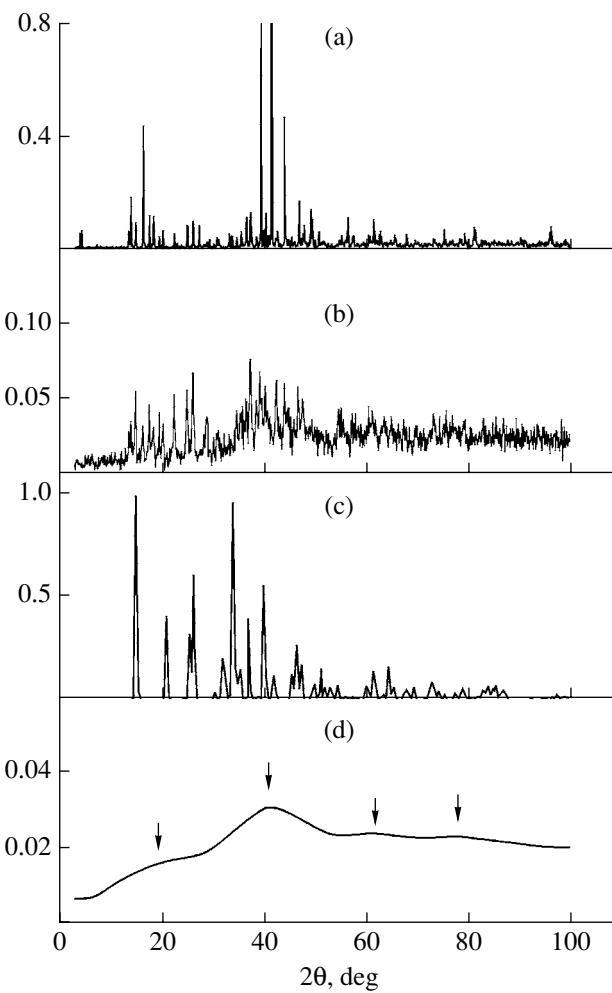
the heating was turned on. The oxidation of  $(\text{iso-Bu}_2\text{Al})_2\text{O}$ , as well as other organoaluminum compounds, is an exothermic process [11], which manifests itself as a diffuse maximum in the DTA curve. The TG DTA curves of crystalline hydrate samples did not exhibit an increase in the weight over the segment 30–145°C [21]. The weight loss in a Cat-Tb sample over the range 145–200°C was due to an endothermic process of the removal of residual crystal water (5%), whereas the weight loss in the range 200–250°C was due to the complete combustion of organics (5%) as a result of the exothermic oxidation of the hydrocarbon fragments of  $(\text{iso-Bu}_2\text{OAl})_2\text{O}$  with the formation of water and  $\text{CO}_2$ . In the region 250–750°C, the TG DTA curves of the Cat-Tb sample reflect the successive formation of the mixed oxychloride  $\text{TbOCl} \cdot 2\text{TbCl}_3$  and the oxychloride  $\text{TbOCl}$ ; it is well-known that these processes occur in the crystalline hydrate [21].

**XRD analysis.** Figure 7 shows the XRD patterns of Cat-Tb and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (well-crystallized substance). The intensity ratio between reflections and the positions of their centers in the diffraction patterns of Cat-Tb do not coincide with the corresponding parameters of  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{TbCl}_3$  as a possible product of the reaction of  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  with TIBA. Moreover, the diffraction pattern of Cat-Tb allowed us to conclude that the ordered substance occurred in two forms: crystalline and amorphous. XRD analysis suggests that the crystalline phase of Cat-Tb has the structural type of the  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  lattice (monoclinic system; space group  $P_{2/c}-C_2h^4$ ) but another lattice spacing. The estimated average block diameters of the crystalline phase of Cat-Tb and  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  are 600 and 700 Å, respectively (mean-square microdeformations of 0.35 and 0.2%, respectively). Based on quantitative XRD analysis, the phase composition of Cat-Tb was calculated assuming a two-phase system. The volume fractions of crystalline and amorphous phases were equal to ~40 and ~60%, respectively. The amorphous component, the smoothed X-ray spectrum of which is shown in Fig. 7 (smoothing parameters: rectangular window; window halfwidth, 50), exhibited a certain ordering. The amorphous phase hypothetically crystallized in an orthorhombic system, space group  $Cmmn$ .

The empirical formula of Cat-Ln and the XRD data for the Cat-Tb sample allowed us to propose the following most probable structures (**A** and **B**) of compounds that form the basis of the amorphous and crystalline Cat-Ln phases (where  $\text{Ln} = \text{Ln}^{3+}$ ):



**Fig. 6.** TG DTA curves for Cat-Tb.



**Fig. 7.** Diffraction patterns of (a)  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ , (b) Cat-Tb, and (c)  $\text{TbCl}_3$ ; (d) smoothed spectrum of an amorphous component of Cat-Tb.

Bridging units, in which lanthanide ions are bound to each other through chlorine atoms, are the main common elements of these structures. Amorphous structure **A** fully consists of these units. Despite the complete dehydration of the lanthanide ion with the

Activity of Cat-Ln in the reaction of aniline condensation with butyraldehyde

Catalytic system	Yield of <b>I</b> , %	Aniline conversion, %	Yield of resinous products, %
PrCl <sub>3</sub> –Ph <sub>3</sub> P*	61	80	7
Cat-Pr–Ph <sub>3</sub> P	78.6	98	10
Cat-Ce–Ph <sub>3</sub> P	68.0	80.1	20
Cat-Tb–Ph <sub>3</sub> P	57.2	98	21
Cat-Eu <sup>2+</sup> –Ph <sub>3</sub> P	58.7	98	14
Cat-Pr	81.6	98.5	4
Cat-Ce	69.3	80.4	13
Cat-Tb	59	98	15
Cat-Eu <sup>2+</sup>	71.3	98	7

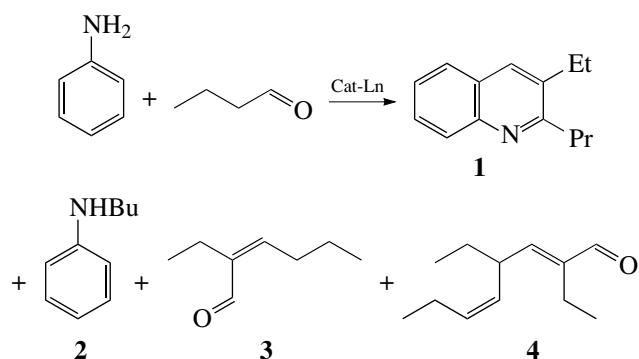
Note: Condensation conditions:  $T = 80^\circ\text{C}$ ; 4 h; autoclave; solvent, DMF.

\* Well-known PrCl<sub>3</sub>–Ph<sub>3</sub>P catalyst [1]. Condensation conditions:  $T = 100^\circ\text{C}$ ; 6 h; autoclave; solvent, DMF.

formation of structure **A**, the formation of the crystalline form of LnCl<sub>3</sub> did not occur. Previously, the formation of an amorphous phase of LnCl<sub>3</sub> as a result of the interaction of LnCl<sub>3</sub> · 3TBP with TIBA was found [2]. Unlike **A**, crystal structure **B** contained residual water molecules (unreacted with TIBA) coordinated to the lanthanide ion. Based on the low alumoxane content of Cat-Ln (5.0–5.5%), its presence can be due to the trapping of alumoxane molecules in the dehydration of crystalline hydrates and the transformation of the crystal lattices of crystalline hydrates into the new crystal lattice of structure **B**. It is likely that these small alumoxane amounts had no effect on the formation of structures **A** and **B**.

### Catalytic Properties of Cat-Ln

The samples of Cat-Ln (Ln = Ce, Pr, Tb, and Eu) were tested for catalytic activity in the reaction of aniline condensation with butyraldehyde. The following reaction scheme represents the composition of identified products:



As the predominant product, 2-propyl-3-ethylquinoline (**1**) was formed in a high yield. The structure of compound **1** was found based on the <sup>13</sup>C and <sup>1</sup>H NMR spectra, a comparison with an authentic sample [1], and the results of elemental analysis. <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 161.33 (s, C<sup>2</sup>), 134.7 (s, C<sup>3</sup>), 133.2 (d, C<sup>4</sup>), 127.0 (d, C<sup>5</sup>), 126.48 (d, C<sup>6</sup>), 128.1 (d, C<sup>7</sup>), 125.15 (d, C<sup>8</sup>), 146.07 (s, C<sup>9</sup>), 125.05 (s, C<sup>10</sup>), 37.22 (t, C<sup>11</sup>), 23.4 (t, C<sup>12</sup>), 13.91 (q, C<sup>13</sup>), 24.7 (t, C<sup>14</sup>), 14.0 (q, C<sup>15</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 1.03 (t, <sup>3</sup>J = 7.3 Hz, CH<sub>3</sub> (C<sup>15</sup>)), 1.23 (t, <sup>3</sup>J = 7.4 Hz, CH<sub>3</sub> (C<sup>13</sup>)), 1.8 (m, <sup>3</sup>J = 7.5 Hz, CH<sub>2</sub> (C<sup>12</sup>)), 2.7 (q, <sup>3</sup>J = 7.4 Hz, CH<sub>2</sub> (C<sup>14</sup>)), 2.9 (t, <sup>3</sup>J = 7 Hz, CH<sub>2</sub> (C<sup>11</sup>)), 7.3 (t, <sup>3</sup>J = 7.3 Hz, H (C<sup>6</sup>)), 7.5 (t, <sup>3</sup>J = 7.6 Hz, H (C<sup>7</sup>)), 7.66 (d, <sup>3</sup>J = 8 Hz, H (C<sup>5</sup>)), 7.8 (s, H (C<sup>4</sup>)), 8.04 (d, <sup>3</sup>J = 8.4 Hz, H (C<sup>8</sup>)). For C<sub>14</sub>H<sub>17</sub>N anal. calcd. (%): C, 84.5; H, 8.5; N, 7.0. Found (%): C, 84.2; H, 8.4; N, 7.4.

As by-products, *N*-butyylaniline (**2**) and oligomerization products (**3**) and (**4**) of the parent aldehyde were identified. Unidentified resinous products were also formed in the reaction.

The table summarizes the results of testing the efficiency of Cat-Ln, as compared with the well-known most active and selective PrCl<sub>3</sub>–Ph<sub>3</sub>P catalyst [1]. It was found that Cat-Pr was superior to the PrCl<sub>3</sub>–Ph<sub>3</sub>P catalyst in all parameters (2-propyl-3-ethylquinoline yield, aniline conversion, and by-product amount). Moreover, the reaction effectively occurred on Cat-Ln at lower temperatures and in a shorter time. The nature of the lanthanide insignificantly affected the conversion of aniline and the yield of 2-propyl-3-ethylquinoline. The most active catalyst was Cat-Pr. Note that Cat-Ln efficiently operated in the absence of Ph<sub>3</sub>P, which is an activator frequently used in catalysis. Moreover, the addition of Ph<sub>3</sub>P decreased the yield of the target product and increased the amount of resinous products. The consideration of the operation mechanism of Cat-Ln is beyond the scope of this paper because this is the subject matter of our further studies.

Thus, we developed a simple procedure for the preparation of a highly efficient lanthanide catalyst for the reaction of aniline condensation with butyraldehyde to form 2-propyl-3-ethylquinoline. A new approach to the preparation of lanthanide catalysts for the synthesis of nitrogen heterocycles was proposed based on the reactions of LnCl<sub>3</sub> · 6H<sub>2</sub>O crystalline hydrates with organoaluminum compounds.

### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 05-03-97906).

### REFERENCES

1. Selimov, F.A., Dzhemilev, U.M., and Ptashko, O.A., *Metallocopleksnyi kataliz v sinteze piridinovykh osnovanii*, Naukova Dumka, Kiev, 1988.

*vanii* (Metal Complex Catalysis in the Synthesis of Pyridine Bases), Moscow: Khimiya, 2003, p. 304.

2. Monakov, Yu.B. and Tolstikov, G.A., *Kataliticheskaya polimerizatsiya 1,3-dienov* (Catalytic Polymerization of 1,3-Dienes), Moscow: Nauka, 1990, p. 211.
3. *Handbuch der preparativen anorganischen Chemie*, von Brauer, G., Ed., Stuttgart: Ferdinand Enke, 1981.
4. Bochkarev, M.N., Kalinina, G.S., Zakharova, L.N., and Khoroshev, S.Ya., *Organicheskie proizvodnye redkozemel'nykh elementov* (Organic Derivatives of Rare-Earth Elements), Moscow: Nauka, 1989, p. 212.
5. Bulgakov, R.G., Kuleshov, S.P., Zuzlov, A.N., Mullagaleev, I.R., Khalilov, L.M., and Dzhemilev, U.M., *J. Organomet. Chem.*, 2001, vol. 636, p. 56.
6. Kuleshov, S.P., Bulgakov, R.G., Sharipov, G.L., Bikbaeva, G.G., Safonova, L.A., Gavrilova, A.A., and Sharapova, L.I., *Izv. Akad. Nauk, Ser. Khim.*, 1996, no. 8, p. 1907.
7. Bulgakov, R.G., Kuleshov, S.P., Zuzlov, A.N., Vafin, R.R., Rusakov, S.V., Mullagaliev, I.R., Dzhemilev, U.M., and Monakov, Yu.B., *Kinet. Katal.*, 2003, vol. 44, no. 5, p. 783 [*Kinet. Catal.* (Engl. Transl.), vol. 44, no. 5, p. 718].
8. Yarovoi, P.N., Ovchinnikova, O.V., Skornikova, S.A., and Chistoforova, N.V., *Lyuminestsentsiya katalizatorov pri lazernom vozbuždenii* (Laser-Excited Luminescence of Catalysts), Angarsk: AGTA, 2003.
9. Poluektov, N.S., Koronenko, L.I., Efryushina, N.P., and Bel'tyukova, S.V., *Spektrofotometricheskie i lyuminesentsiye metody opredeleniya lantanidov* (Spectrophotometric and Luminescence-Based Methods for Lanthanide Determination), Kiev: Naukova Dumka, 1989, p. 28.
10. Shen, Z., Ouyang, J., Wang, F., Hu, Z., Yu, F., and Qian, B., *J. Polymer Sci., Part A: Polymer Chem.*, 1980, vol. 18, p. 3345.
11. Korneev, N.N., *Khimiya i tekhnologiya alyuminiiorganicheskikh soedinenii* (Organoaluminum Compounds: Chemistry and Technology), Moscow: Khimiya, 1979.
12. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., *Technics of Organic Chemistry*, vol. 7: *Organic Solvents: Physical Properties and Methods of Purification*, New York: Wiley, 1955.
13. Charlot, G., *Les methodes de la chimie analytique*, Paris: Masson, 1961.
14. Boleslawski, M. and Serwatowski, J., *J. Organomet. Chem.*, 1983, vol. 254, p. 159.
15. Bulgakov, R.G., Musavirova, A.S., Abdurakhmanov, A.M., Nevyadovskii, E.Yu., Khursan, S.L., and Razumovskii, S.D., *Zh. Prikl. Spektrosk.*, 2002, vol. 69, no. 2, p. 192.
16. Panushin, V.T., Afanas'ev, Yu.A., Khanaev, E.I., and Garnovskii, A.D., *Lantanoidy: proste i kompleksnye soedineniya* (Lanthanides: Ordinary and Complex Compounds), Rostov-on-Don: Rostov. Univ., 1980, p. 296.
17. Ukrainseva, E.A., Sokolova, N.P., and Logvinenko, V.A., *Radiokhimiya*, 1989, vol. 31, no. 1, p. 6.
18. Porri, L., Giarrusso, A., and Ricci, G., *Makromol. Chem., Macromol. Symp.*, 1993, vol. 66, p. 231.
19. Bulgakov, R.G., Kazakov, V.P., and Korobeinova, V.N., *Opt. Spektrosk.*, 1973, vol. 35, no. 5, p. 856.
20. Bulgakov, R.G., Kuleshov, S.P., Zuzlov, A.N., Khalilov, L.M., and Vafin, R.R., *Izv. Akad. Nauk, Ser. Khim.*, 2002, no. 5, p. 831.
21. Wendlandt, W.W., *J. Inorg. Nucl. Chem.*, 1959, vol. 9, p. 136.