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# Interaction of Terbium Acetylacetonate with Diethylaluminum Chloride

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**Abstract**—The interaction of terbium acetylacetonate $Tb(acac)_3 \cdot H_2O$ with $Et_2AlCl$ in toluene was studied by spectroscopic techniques (photoluminescence, IR, and UV–visible spectroscopy) with the use of GLC, volumetric, and chemical analysis.

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## INTRODUCTION

It is well known that catalytic systems based on lanthanide β-diketonates (including acetylacetonates) and organoaluminum compounds exhibit catalytic activity in the reactions of diene polymerization [1, 2]. At the same time, data on the mechanism of catalytic polymerization on these systems are very scarce. The presence or absence of catalytic activity in the polymerization of dienes on the $Ln(acac)_3 \cdot H_2O$–$Et_2AlCl$–*i*-$Bu_3Al$ and $Ln(acac)_3 \cdot H_2O$–*i*-$Bu_3Al$ systems remained unexplained [1]. The reasons for the dependence of the efficiency of isoprene polymerization under the action of the $Ln(acac)_3 \cdot H_2O$–$Et_2AlCl$–*i*-$Bu_3Al$ system on the Cl/Ln ratio were not determined [3]. In this case, the system exhibited a maximum efficiency at the ratio Cl/Ln = 2.2. There are no published data on the mechanism of formation and the nature of catalytically active complexes in the interaction of lanthanide acetylacetonates with organoaluminum compounds. Therefore, a study of $Ln(acac)_3 \cdot H_2O$–organoaluminum compound systems is of considerable current interest for extending the concepts of Ziegler–Natta catalysts and from the standpoint of studying the reactivity of lanthanide complexes.

In this work, we studied for the first time the interaction of $Tb(acac)_3 H_2O$ with $Et_2AlCl$ in toluene with the use of a wide range of physicochemical (including luminescence) techniques. The efficiency of luminescence techniques for studying the synthesis reactions and the action of lanthanide Ziegler–Natta catalysts has been demonstrated previously [4–8]. The complex of Tb was chosen from the lanthanide series because it exhibits bright photoluminescence in solution and a solid phase [9].

## EXPERIMENTAL

Terbium acetylacetonate was prepared and recrystallized in accordance with a published procedure [10]. A commercial diethylaluminum chloride solution (95%) in gasoline was subjected to vacuum distillation [11]. Toluene was purified by distillation from sodium metal [12]. Argon was passed through a gas absorber apparatus.

The interaction of terbium acetylacetonate with diethylaluminum chloride was performed at 20°C in an atmosphere of argon in a thermostated glass reactor equipped with a magnetic stirrer and connected to a gas burette for measuring the volume of the released gas. Terbium acetylacetonate (0.08 mmol) was loaded in the reactor, and toluene (20 ml) was added; the contents were stirred until the complete dissolution of terbium acetylacetonate, and diethylaluminum chloride was added ($Et_2AlCl/Tb(acac)_3 \cdot H_2O = 2.2$). The reaction mixture was stirred until the completion of gas evolution and then centrifuged; the liquid phase was separated from the solid phase (K-Tb). Then, K-Tb was washed with the solvent (3 × 10 ml), and the solvent residue was removed by evacuation (10 Torr; 20 min) to obtain loose powder.

The liquid phase and K-Tb were analyzed for $Tb^{3+}$ by trilonometry [13], and $Al^{3+}$ was determined in accordance with a published procedure [13] and by atomic absorption spectrometry. The water content of terbium acetylacetonate and the absence of water from K-Tb were determined by the Fischer method [13], whereas ethane formed in the reaction was determined by GLC analysis. The presence and amount ($N$) of metal–carbon bonds in K-Tb were determined from the volume of ethane released upon hydrolysis with a 10% aqueous solution of HCl. The photoluminescence, IR, and UV–visible absorption spectra of the liquid phase and K-Tb were measured in hermetically sealed cells or ampules in an atmosphere of argon. In the measurement of XRD patterns, the samples of

K-Tb were pelletized in an atmosphere of argon and then impregnated with a toluene solution of 4508 rubber adhesive in order to prevent contact with air. The thermogravimetric analysis of the samples of K-Tb was performed in accordance with standard procedures in an atmosphere of air.

Ethane was determined on KARLO ERBA GC 6000 chromatographs (a 3-m column 4 mm in diameter; stationary liquid phase, 15% PEG 6000 on Chromaton). The elemental analysis of K-Tb 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. The photoluminescence spectra were measured on an AMINKO-BOWMAN spectrofluorimeter. The analysis of samples for Al was performed on a SHIMADZU GFA-4B atomic absorption spectrophotometer (atomizer: a graphite cuvette). The XRD patterns were measured on a PHILIPS PW-1800 diffractometer using Cu$K_\alpha$ radiation. The following measurement parameters were used: step, 0.05° (2θ); step time, 2"; and sample rotation rate, 1 rps. The TGA–DTA curves were obtained on a METTLER TOLEDO STAR TGA-851E derivatograph. The lifetime of the $Tb^{3+*}$ ion ($\tau$ $Tb^{3+*}$) was measured using a system with an LGI-23 pulse nitrogen laser ($\lambda_{ex}$ = 337 nm; measurement error, 10%; determination limit $\tau$ = 10 μs).

## RESULTS AND DISCUSSION

### *Volumetric Measurements*

The interaction of terbium acetylacetonate with diethylaluminum chloride in toluene (Al/Tb = 2.2; $T$ = 300 K) resulted in gas evolution (Fig. 1) and the separation of the system into liquid and solid phases (LP and K-Tb, respectively). It was found that K-Tb is insoluble in aromatic and aliphatic solvents. According to the results of the GLC analysis of gas and liquid phases, the released gas was ethane (EtH), the amount of which is consistent with the stoichiometry of reaction (I). Because thoroughly dried toluene was used in this work, the only source of the formation of EtH in the test system was the reaction of diethylaluminum chloride with the coordination water of the complex terbium acetylacetonate.

$$H_2O + Et_2AlCl \longrightarrow Et(OH)AlCl + EtH, \quad (I)$$

$$Et(OH)AlCl + Et_2AlCl \longrightarrow EtH + (EtAlCl)_2O. \quad (II)$$

According to published data [14], the interaction of diethylaluminum chloride with free $H_2O$ (not coordinated to metal ions) in organic solvents at the ratios of $Al/H_2O \geq 2$ occurred through the formation of an Et(OH)AlCl intermediate by reactions (I) and (II). Assuming that coordinated water also interacted by reactions (I) and (II) and taking into account the fact that the amount of EtH (1 mol) released in the reaction of diethylaluminum chloride with terbium acetylacetonate (at Al/Ln = 2.2) was lower than a stoichiometric amount by a factor of 2, we can hypothesize that coordinated water reacted with only one diethylaluminum chloride molecule. In this case, the remaining amount of diethylaluminum chloride was unreacted or participated in another reaction unaccompanied by ethane formation.

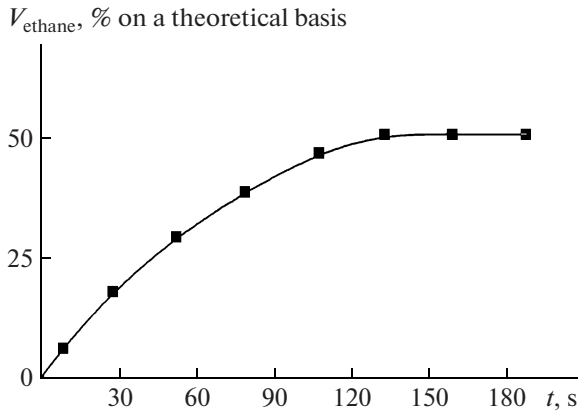



**Fig. 1.** Kinetics of gas evolution in the interaction of $Tb(acac)_3 \cdot H_2O$ with $Et_2AlCl$ in toluene. [Tb] = $4 \times 10^{-3}$ M; Al/Tb = 2.2; $T$ = 293 K.

### *Analysis of the Liquid Phase*

The data of chelatometric analysis indicated that $Tb^{3+}$ ions were absent from the liquid phase, and the liquid phase contained only $Al^{3+}$ and $Cl^-$ ions in a ratio of 1 : 0.14. This conclusion was also supported by the absence of the green photoluminescence of $Tb^{3+*}$ even at 77 K, although this photoluminescence can be easily observed in a solution of terbium acetylacetonate in toluene at room temperature.

The IR spectrum of the liquid phase contained the following bands ($cm^{-1}$): 1581 ($\nu_{C=O}$), 1527 ($\nu_{C=C}$), 1380, 1295 ($\nu_{C-H+C-C}$), 1187, and 1100 ($\delta_{Al-C-H}$ + $\nu_{C-CH_3}$). According to Nindakova et al. [15], these absorption bands can be assigned to the absorption of $Et_2Al(acac)$. The formation of $Et_2Al(acac)$ is not surprising because it was found previously [16, 17] that $Et_2Al(acac)$ is a product of the interaction of Ti and V acetylacetonates with diethylaluminum chloride. In addition to the above absorption bands, the spectrum contained low-intensity bands at 490, 500 ($\nu_{Al-Cl}$), 630, and 654 ($\nu_{Al-C}$) $cm^{-1}$, which were hypothetically attributed to an EtAlClOH intermediate of the reaction of diethylaluminum chloride with coordination water.

The UV–visible absorption spectrum of the complex terbium acetylacetonate in toluene exhibited a diffuse maximum at 293.0 ± 0.5 nm ($\varepsilon$ = 40000 l $cm^{-1}$ $mol^{-1}$) [15]. The absorption spectrum of the liquid phase exhibited a new peak at 310.0 ± 0.5 nm ($\varepsilon$ = 5000 l $cm^{-1}$ $mol^{-1}$) in place of the above maximum. At the same time,

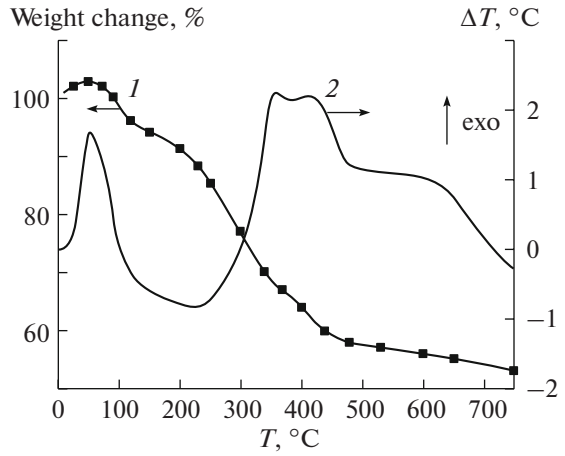



**Fig. 2.** (*1*) TG and (*2*) DTA curves for K-Tb obtained by the interaction of $Tb(acac)_3 \cdot H_2O$ with $Et_2AlCl$. Al/Tb = 2.2.

according to Sager at al. [10], absorbance in the region of 280–340 nm is characteristic of various metal acetylacetonates, and it is due to the intraligand $\pi \longrightarrow \pi^*$ transition of the carbonyl group of the acac ligand. However, taking into account that only $Al^{3+}$ ions were present in the liquid phase, we related the absorption maximum at 310 nm to the absorption of the acac ligand of the $Et_2Al(acac)$ complex. This was supported by data published by Dmitrieva et al. [18], who attributed a maximum at 314 nm to the absorption of the $Et_2Al(acac)$ complex in benzene. We related a difference in the positions of the compared peaks to different natures of the solvents.

*Analysis and Properties of the Solid Phase (K-Tb)*

Because $Tb^{3+}$ ions were not detected in the liquid phase, the lanthanide entirely transferred to K-Tb. As a result of chelatometric analysis (for $Al^{3+}$ and $Tb^{3+}$) and Volhard titration ($Cl^-$), the following ratio between the elements in K-Tb was found: Al/Tb/Cl = 0.8 : 1 : 2. In the hydrolysis of K-Tb with a 10% $HNO_3$ solution, EtH was released; this suggests the presence of compounds with metal–Et bonds in K-Tb. The concentration of these compounds found from the amount of released EtH was equal to the concentration of $Al^{3+}$ ions. Thus, we assume that these compounds contain the Al–Et rather than Tb–Et bond. This conclusion was supported by published data [3], according to which the product of the reaction of terbium acetylacetonate with diethylaluminum chloride (which was not identified in [3]) does not exhibit catalytic activity in the reaction of isoprene polymerization; that is, it does not contain the Tb–Et bond.

The IR spectrum of a crystalline sample of terbium acetylacetonate contained the following absorption bands ($cm^{-1}$): 1602 ($\nu_{C=O}$); 1518 ($\nu_{C=C}$); 915 and 1020 ($\nu_{C-C(=O)-C}$); 1382, 1187, 1068, 1014, and 1216 ($\nu_{C-H+C-C}$); 789, 766, 749, 722, and 646 ($\nu_{Tb-O}$); 422, 529, and 551 ($\nu_{ring}$); and 3250–3500 ($\nu_{OH}$) [19]. This spectrum was different from the spectrum of K-Tb. Thus, bands at 915, 1020, 1260, and 1602 $cm^{-1}$ in the spectrum of terbium acetylacetonate underwent a high-frequency shift with a decrease in the intensity to 925, 1025, 1290, and 1610 $cm^{-1}$, respectively. In place of a spectrum with sharp peaks at 789, 766, 749, 722, and 646 $cm^{-1}$, a diffuse maximum is formed, which is likely a superposition of the absorption bands of various complex compounds. In the region of 3200–3600 $cm^{-1}$, a broad diffuse maximum was observed; this maximum was smaller than that in the initial terbium acetylacetonate by a factor of 1.5. This maximum suggests the presence of OH groups in K-Tb; these groups remain after the interaction of terbium acetylacetonate with diethylaluminum chloride. The only reaction product of terbium acetylacetonate with diethylaluminum chloride containing OH groups is the EtAlClOH intermediate. It is likely that this intermediate occurred both in the liquid phase and in K-Tb. Gorelik et al. [14] characterized the EtAlClOH intermediate as a stable compound. Note that the intensity of absorption bands in the range of 800–1700 $cm^{-1}$ (the absorption region of the acac ligand) also decreased as compared with the intensity of absorption bands in the spectrum of the initial terbium acetylacetonate. The reason for the decrease in the intensity of absorption bands due to the acac ligand in K-Tb can be the elimination of these ligands from terbium acetylacetonate and transfer to the liquid phase as the $Et_2Al(acac)$ complex.

The TGA–DTA studies of K-Tb demonstrated that a small increase in weight (~2.5%) occurred in the range of 30–100°C (Fig. 2). This was due to the oxidation of a compound containing the Al–Et bond to an alkoxy derivative with a higher molecular weight. Quantitatively, the increase in the sample weight was consistent to the transformation of the Al–Et bond into Al–O–Et, and it began even before heating was turned on. The oxidation of organoaluminum compounds is an exothermic process, which is reflected as a diffuse maximum in the DTA curve. The TGA–DTA curves of the samples of the initial complex terbium acetylacetonate did not exhibit an increase in weight in the region of 30–145°C [20]. According to published data [21], a decrease in the weight of the sample of K-Tb in the range of 125–230°C can be due to the endothermic process of the removal of acac ligands and hydroxyl groups.

X-ray diffraction analysis showed that K-Tb was an amorphous substance (Fig. 3) unlike the initial crystalline terbium acetylacetonate. It is most likely that the amorphism of K-Tb results from several factors, one of which is the dehydration of terbium acetylacetonate with the degradation of its crystal structure. Previously [20], it was found that anhydrous $Ho(acac)_3$ also exhibits an amorphous structure, whereas the crystal hydrate $Ho(acac)_3 \cdot H_2O$ exhibits a crystalline structure.

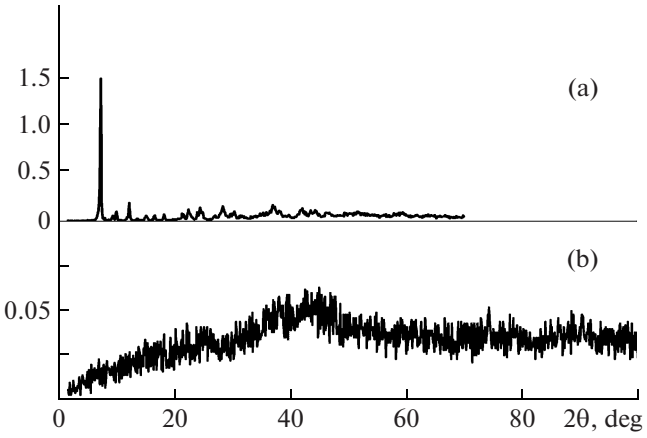



**Fig. 3.** Diffraction patterns of (a) $Tb(acac)_3 \cdot H_2O$ and (b) K-Tb.

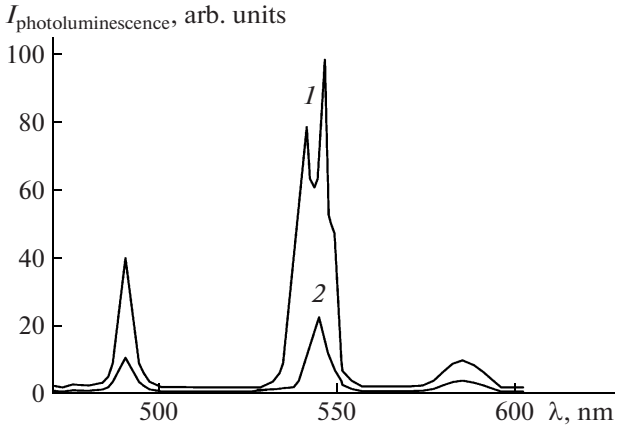
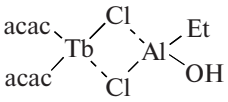



**Fig. 4.** Photoluminescence spectra: (*1*) $Tb(acac)_3 H_2O$ ($T = 293$ K) and (*2*) K-Tb ($T = 77$ K); $\lambda_{ex} = 365$ nm.

The photoluminescence intensity of $Tb^{3+}$ and the value of $\tau\ Tb^{3+*}$ in K-Tb decreased by a factor of 5 and by 120 μs, respectively, as compared with those of the initial terbium acetylacetonate (740 μs). The less structured photoluminescence spectrum of K-Tb contained maximums at 491, 546, and 584 nm, whose positions almost coincide with the maximums of the photoluminescence spectrum of terbium acetylacetonate (Fig. 4).

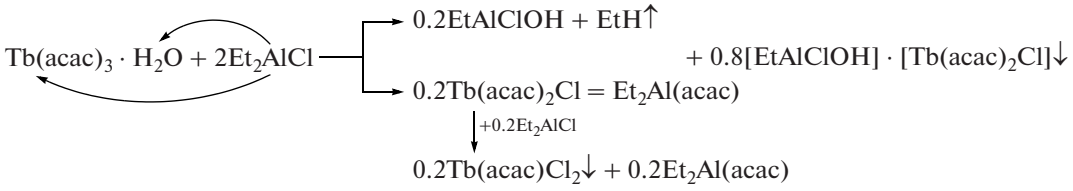
According to chelatometric, photoluminescence, and elemental analysis data, the following empirical formula of K-Tb was found: $TbCl_2Al_{0.8}C_{10.6}H_{17.6}O_{4.4}$. Found (%): Tb, 34.08; Al, 4.65; Cl, 15.22; C, 27.23; H, 3.73; O, 15.09. Calculated (%): Tb, 34.12; Al, 4.61; Cl, 15.25; C, 27.22; H, 3.68; O, 15.12. The stoichiometric ratios between the elements in K-Tb did not allow us to identify it as an individual compound. This assumption is consistent with published data [15, 22], which indicate that the interaction of $Ti(acac)_3$ or $Ce(naph)_3$ with diethylaluminum chloride resulted in the replacement of acac and naph groups by chlorine atoms with the formation of mixed titanium and cerium halides, respectively, which are insoluble in hydrocarbon solvents. In this case, the published ion ratio Al/Ce = 0.6–0.7 [22] is consistent with our results of the analysis of K-Tb (Al/Tb = 0.8). We believe that K-Tb is a mixture of two complexes, $Tb(acac)Cl_2$ and $Tb(acac)_2Cl \cdot EtAlClOH$. Indeed, according to calculations, the above empirical formula of K-Tb can result from the addition of the mole fractions of the elements that constitute these complexes only in this case.

We believe that the complex $Tb(acac)_2Cl \cdot EtAlClOH$ has the following structure:




**A**

Based on the experimental results and published data on the reactions of titanium acetylacetonates and cerium naphthenates with diethylaluminum chloride, the interaction of terbium acetylacetonate with diethylaluminum chloride can be described by the following reaction scheme:




**Scheme.**

According to the scheme, diethylaluminum chloride attacks two fragments of the complex terbium acetylacetonate: coordination water and the acac ligand. As a result of the former attack, EtAlClOH and EtH are formed, whereas the latter attack resulted in $Tb(acac)_2Cl$ and $Et_2Al(acac)$. Then, $Tb(acac)_2Cl$ is bound to EtAlClOH to form the complex $[Tb(acac)_2Cl \cdot EtAlClOH]$ insoluble in toluene. In addition, the interaction of $Tb(acac)_2Cl$ with diethylaluminum chloride resulted in the formation of the complex $Tb(acac)Cl_2$, which is also insoluble in toluene and forms a precipitate.

It is well known [1] that the product of the reaction of terbium acetylacetonate with diethylaluminum chloride exhibits a catalytic activity in the reactions of diene polymerization only in the presence of a large excess of $i$-$Bu_3Al$ (Tb/Al = 1 : 10–20). As demonstrated above, a solid product of the interaction of terbium acetylacetonate with diethylaluminum chloride is complex **A** with a bridged structure. It is likely that this structure serves as a primary building block, which provides the basis for the formation of new catalytically active bridged structures containing Tb–alkyl–Al units, upon the addition of a large excess of $i$-$Bu_3Al$. These units are catalytically active sites for polymerization. The scheme allowed us to explain the well-known dependence [1] of the catalytic activity of the terbium acetylacetonate–diethylaluminum chloride–triisobutyl aluminum ternary system on the diethylaluminum chloride/terbium acetylacetonate ratio in the reaction of isoprene polymerization. This dependence is bell-shaped with a maximum at Cl/Tb = 2.2. At $3 \le Cl/Tb \le 1$, the above system is catalytically inactive [1, 3]. Based on the results of the analysis of reaction products in the terbium acetylacetonate–diethylaluminum chloride system, we assume that, at the ratios of $Cl/Tb \le 1$, the initial diethylaluminum chloride attacks only coordination water to form EtAlClOH and EtH, which are inactive in diene polymerization. In the range of the ratios of $1 \le Cl/Tb \le 3$, diethylaluminum chloride reacts with both coordination water and the acac ligand to form the complex [$Tb(acac)_2Cl \cdot EtAlClOH$], which is converted into a catalytically active center for polymerization upon the addition of $i$-$Bu_3Al$. At the ratio of $Cl/Tb \ge 3$, catalytically inactive $Tb(acac)Cl_2$ is formed as a product.

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