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Complexes of Lanthanides with Triethanolamine

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Abstract—Reactions of equimolar amounts of Cp_3Er or amides $[(Me_3Si)_2N]_3Ln$ (Ln = Y, Nd) with triethanolamine lead to the formation of insoluble products of the composition $Ln(OC_2H_4)_3N$. Naphthalene complex of Eu(II), $Cl_{10}H_8Eu(THF)_3$, reacts with triethanolamine also with the formation of insoluble compound of trivalent europium $Eu(OC_2H_4)_3N$. Erbium aminoalkoxide $Er(OC_2H_4)_3N$ actively reacts with carbon dioxide at room temperature and atmospheric pressure in THF to form the adduct $Er[OC(O)OC_2H_4]_3N$. In the reaction of triethanolamine with the excess of $[(Me_3Si)_2N]_3Ln$ (Ln = Y, Eu) in THF soluble binuclear complexes of the composition $[(Ne_3Si]_2NLn(OC_2H_4)_3NC_2H_4OLn[N(SiMe_3)_2]_2(THF)$ are formed. The reaction of triethanolamine with $[(Me_3Si)_2N]_3Y$ in 3:1 ratio in THF gives the compound $Y[OC_2H_4N(C_2H_4OH)_2]_3$. The composition and structure of obtained complexes was established by elemental analysis and the IR and NMR spectroscopy.

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Homo- and heterometallic alkoxides including aminoalkoxides of *d*- and *f*-elements attract significant interest as potential precursors of ceramic materials having variable application [1]. It can be expected that polyalkoxides, in particular of rare earth elements, can exhibit high catalytic activity in polymerization of olefins and in activation of carbon dioxide and epoxides [2, 3]. Lanthanoid aminoalkoxides of the composition $(i\text{-}C_3H_7O)_2LnOC_2H_4NH_2$, $i\text{-}C_3H_7OLn\cdot(OC_2H_4NH_2)_2$, $Ln(OC_2H_4NH_2)_3$, $i\text{-}C_3H_7OLn(OC_2H_4)_2NH$, $Ln_2[(OC_2H_4)_2NH]_3$, $Ln[(OC_2H_4)_2NH][OC_2H_4N(H)\cdot C_2H_4OH]$ [4], $ClLn(OC_2H_4)_2NH$ [5], $Ln(OC_2H_4)_3N$ [4, 6], and $La[(OC_2H_4)_2NC_2H_4OH][OC_2H_4N(C_2H_4OH)_2]$ [7] are known.

Practically all these compounds were prepared by the reaction of aminoalcohol with isopropoxide $(i\text{-}C_3H_7O)_3Ln$ in an appropriate ratio. Chlorine derivatives $ClLn(OC_2H_4)_2NH$ were isolated from reaction mixtures resulting from the interaction of $LnCl_3$ with diethanolamine. By the reaction of $La[(OC_2H_4)\cdot NC_2H_4OH][OC_2H_4N(C_2H_4OH)_2]$ with niobium isopropoxide $(i\text{-}C_3H_7O)_3Nb$ a heterometallic complex $La[(OC_2H_4)_3N]_2[Nb(OC_3H_7\text{-}i)_4]_3$ was synthesized. It is the only known soluble lanthanide derivative of triethanolamine [7]. X-ray analysis of these compound showed that $Nb(OC_3H_7\text{-}i)_4$ fragments were bound with the lanthanum atom through oxygen atoms of the bridge groups $–OC_2H_4NC_2H_4O–$ resulting in the presence of a symmetry axis of the pseudothird order. All the rest lanthanide aminoalkoxides (unlike the derivatives of non-transition and d-transition metals) are insoluble indicating their polymeric structure. The aim of the present investigation is the search for new methods for preparing soluble metalatranes of rare earth elements. Besides the above-mentioned application areas of these substances they also can be convenient starting substances for preparing new class of substances, lanthanide-containing dendrimers with the rare earth metal atoms in the branching centers of chains.

It was found that the reaction of equimolar amounts of triethanolamine and the amide or cyclopentadiene complexes of yttrium, niobium, or erbium easily proceeded in THF solutions. But similarly to the reaction with $(i\text{-}C_3H_7O)_3Ln$ in this case the insoluble products of the composition $Ln(OC_2H_4)_3N$ were formed.

$$R_3Ln + (HOC_2H_4)_3N \rightarrow Ln(OC_2H_4)_3N + 3RH,$$

$$R = (Me_3Si)_2N,\ Ln = Y\ (\mathbf{I}),\ Nd\ (\mathbf{II});\ R = Cp,\ Ln = Er\ (\mathbf{III}).$$

Compounds were separated from the solution as colorless (Y), light blue (Nd), or light pink (Er) amorphous precipitates in 85–90% yield. The reaction of tricyclopentadienylerbium with triethanolamine in liquid ammonia gives the same product in high yield. While heating above 250°C the obtained complexes decompose without melting. Their IR spectra coincide with the spectra of the previously prepared praseodymium and neodymium metalatranes [4].

While performing the reaction of triethanolamine with the europium naphthalene complex $C_{10}H_8Eu\cdot(THF)_3$ containing the bivalent metal it was expected that in the formed complex europium would retain its oxidation state giving a metalatrane of a new type. But in this case aminoalkoxide $Eu(OC_2H_4)_3N$ **IV** was isolated as a bright yellow insoluble powder. The lack of absorption bands of the OH groups in the range 3300–3400 cm^{-1} in the IR spectrum shows that all three hydroxy groups of triethanolamine take part in the reaction. Considering the equimolar ratio of reagents in the starting mixture it may be concluded that the third OH group takes part in the oxidation of europium to Eu^{3+}. This stage of the reaction is confirmed by the liberation of hydrogen.

The magnetic moment of the complex is 4.0 MB which corresponds to the trivalent state of the metal $\{\mu_{eff}$ for Eu(III) compounds is 4.0 MB [8]$\}$.

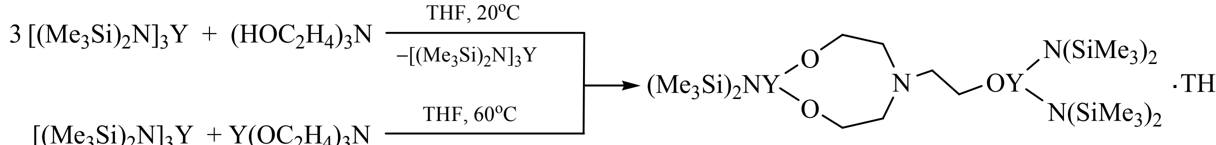
$$C_{10}H_8Eu(THF)_3 + (HOC_2H_4)_3N$$

$$\rightarrow [Eu(OC_2H_4)_2NC_2H_4OH] + C_{10}H_8 + H_2$$

$$[Eu(OC_2H_4)_2NC_2H_4OH] \rightarrow \underset{\textbf{IV}}{Eu(OC_2H_4)_3N} + 1/2H_2.$$

By an example of the erbium complex it was found that aminoalkoxides $Ln(OC_2H_4)_3N$ similarly to the derivatives of monohydric alcohols reacted under mild conditions (20°C, 1 at, THF) with carbon dioxide which inserted into the Ln–O bond to form adduct $Ln[OC(O)OC_2H_4]_3N$ **V**.

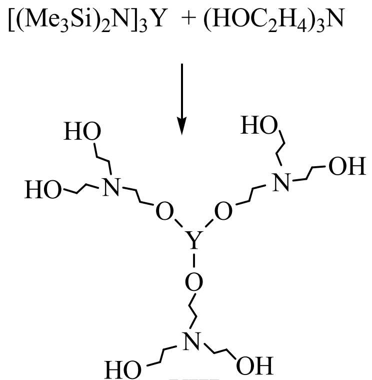
A soluble rare earth metal aminoalkoxide was prepared by the reaction of triethanolamine with the excess of $[(Me_3Si)_2N]_3Y$. Elemental analysis data, IR and NMR spectra of the product correspond to the formula $(Me_3Si)_2NY(OC_2H_4)_2NC_2H_4OY[N(SiMe_3)_2]_2\cdot(THF)$ **VI**. The same complex was isolated in 81% yield from the products of the reaction of $[(Me_3Si)_2N]_3Y$ with the aminoalkoxide $Y(OC_2H_4)_3N$ that proceeded unexpectedly easily.



VI

Note that despite of the excess of yttrium amide in both cases the binuclear complex is formed instead of the trinuclear one, $N\{C_2H_4OY[N(SiMe_3)_2]_2\}_3$ which could be used for the synthesis of yttrium dendrimer by the divergent method. Compound **VI** is isolated as a colorless amorphous substance soluble in THF, moderately soluble in 1,2-dimethoxyethane, and insoluble in toluene and hexane. Reaction of europeum(III) amide with the excess of triethanolamine in THF proceeds analogously. The obtained complex $(Me_3Si)_2NEu\cdot(OC_2H_4)_2NC_2H_4OEu[N(SiMe_3)_2]_2(THF)$ **VII** was isolated as an orange yellow amorphous powder in 93% yield.

In contrast to the easily proceeding conproportionation between $[(Me_3Si)_2N]_3Y$ and $Y(OC_2H_4)_3N$ the reaction of the latter with triethanolamine does not take place even under the prolonged heating at 80°C. The expected compound $Y[OC_2H_4N(C_2H_4OH)_2]_3$ **VIII** containing six terminal OH groups was prepared according to another pathway by the reaction of triethanolamine with $[(Me_3Si)_2N]_3Y$ in 3:1 ratio. Similarly to the reactions with the excess of amide the product formed remains dissolved even after the completion of the reaction. Nevertheless, after isolation from the solution and drying in a vacuum this substance looses the solubility. At the same time the liberation of some amount of triethanolamine was marked. Evidently under these conditions intermolecular reaction leading to partial elimination of triethanol-amine and crosslinking of yttrium product due to formation of $–OCH_2CH_2N\cdot(CH_2CH_2OH)CH_2CH_2O–$ bridges takes place.



VIII

Aminoalkoxide **VIII** is a colorless amorphous powder decomposing while heating above 220°C. Its structure was confirmed by the data of elemental analysis, IR and ^{1}H NMR spectroscopy (see the table). The presence of six hydroxy groups on the periphery of compound **VIII** permits to use this compound for the synthesis of organometallic dendrimers.

Hence, it was shown that the reaction of triethanolamine with cyclopentadienyl, amide, or naphthalene complexes of rare earth elements leads to the formation of insoluble aminoalkoxides $Ln(OC_2H_4)_3N$ having evidently the structure of a crosslinked polymer. But while using the excess of one of reagents it becomes possible to prepare monomeric metalatranes containing terminal amide, $Ln–N(SiMe_3)_2$, or hydroxy groups. The presence of these functions opens the possibility of obtaining lanthanide and heterometallic aminoalkoxides of dendrimer structure. It was found that amino oxides $Ln(OC_2H_4)_3N$ easily enter in the reaction of conproportionation with the amide complexes $[(Me_3Si)_2N]_3Ln$ forming soluble complexes $(Me_3Si)_2NLn(OC_2H_4)_2NC_2H_4OLn[N(SiMe_3)_2]_2(THF)$.

EXPERIMENTAL

All reactions and the isolation of products were carried out excluding the contact with air using Schlenk technique. IR spectra were recorded on the Specord M80 and Perkin Elmer 577 spectrophotometers from mulls in mineral oil. NMR spectra were taken on a Bruker DPX-200 spectrometer. Magnetic measurements were carried out at room temperature as described before [9].

Synthesis of $Y(OC_2H_4)_3N$ (I). To a solution of 2.12 g of $Y[N(SiMe_3)_2]_3$ in 30 ml of THF a solution of 0.56 g of triethanolamine in 20 ml of THF was added. The obtained white amorphous precipitate was filtered off on a glass frit filter, washed with THF (2×24 ml), and dried in a vacuum at 50°C. Compound **I**, 0.80 g (91%), was obtained. IR spectrum ν, cm^{-1}: 1290 w, 1260 m, 1150 m, 1100 s, 1090 s, 1040 s, 1010 s, 950 s, 920 s, 880 s, 730 m, 690 m, 550 w.

Complex **II** was synthesized analogously in 82% yield. Its IR spectrum is identical to the spectrum of yttrium analog.

Synthesis of $Er(OC_2H_4)_3N$ (III). To a solution of Cp_3Er in 40 ml of liquid ammonia a solution of 0.9 g of triethanolamine in 30 ml of pyridine was added at –60°C under vigorous stirring. The immediate formation of the amorphous light pink precipitate was observed. Liquid ammonia was evaporated and the suspension left was filtered through a glass frit filter. The precipitate obtained was washed with pyridine and dried in a vacuum at 70°C. Yield of product **III** 1.7 g (90%). Its IR spectrum is identical to that of yttrium analog.

Synthesis of $Eu(OC_2H_4)_3N$ (IV). To a solution of 0.14 g of triethanolamine in 20 ml of THF a suspension of 0.4 g of $C_{10}H_8Eu·(THF)_2$ in 25 ml of THF was added slowly under vigorous stirring. The liberation of hydrogen and dissolution of black precipitate of naphthalene complex of europium was observed. Simultaneously a bright yellow precipitate of product **IV** was formed. This precipitate was filtered off, washed with THF, and dried in a vacuum. Yield of compound **IV** 0.27 g (96%). IR spectrum ν, cm^{-1}: 1280 w, 1250 m, 1150 w, 1090 s, 1060 s, 1030 s, 1010 s, 900 m, 880 s, 860 w, 790 m, 710 m, 600 w. In the filtrate 0.12 g (100%) of naphthalene was found by GLC.

Reaction of compound III with CO_2. An ampule containing 0.63 g of compound **III** dissolved in 30 ml of THF was connected with the gas burette filled with dry carbon dioxide. A vigorous absorption of CO_2 was

Elemental analysis data of the lanthanides complexes with triethanolamine

Comp. no.	Compound	Found, %			Formula	Calculated, %		
		C	H	Ln		C	H	Ln
I	$Y(OC_2H_4)_3N$	30.68	5.98	37.90	$C_6H_{12}NO_3Y$	30.66	5.14	37.82
II	$Nd(OC_2H_4)_3N$	25.56	5.09	48.80	$C_6H_{12}NNdO_3$	24.82	4.16	49.67
III	$Er(OC_2H_4)_3N$	23.12	4.15	54.00	$C_6H_{12}ErNO_3$	22.99	3.86	53.37
IV	$Eu(OC_2H_4)_3N$	24.66	5.11	51.40	$C_6H_{12}EuNO_3$	24.17	4.05	50.97
V	$Er(OC(O)OC_2H_4)_3N$	24.84	3.55	38.10	$C_9H_{12}ErNO_9$	24.26	2.71	37.54
VI	$(Me_3Si)_2NY(OC_2H_4)_2NC_2H_4OY[N(SiMe_3)_2]_2(THF)$	37.50	7.26	21.10	$C_{28}H_{74}N_4O_4Si_6Y_2$	38.34	8.49	20.26
VII	$(Me_3Si)_2NEu(OC_2H_4)_2NC_2H_4OEu[N(SiMe_3)_2]_2(THF)$	33.03	8.44	30.28	$C_{28}H_{74}Eu_2N_4O_4Si_6$	33.52	7.38	30.32
VIII	$Y[OC_2H_4N(C_2H_4OH)_2]_3$	41.21	7.54	16.40	$C_{18}H_{42}N_3O_9Y$	40.53	7.93	16.67

observed at room temperature. After 30 min the reaction stopped, 128 ml of CO_2 was absorbed. The precipitate became looser. The product was filtered off on a glass frit filter, washed with THF (2×25 ml), and dried in a vacuum at 50°C over 2 h. Complex **V**, 0.66 g (78%) was obtained. IR spectrum ν, cm^{-1}: 1620 s, 1305 m, 1270 m, 1170 m, 1110 s, 1090 s, 1050 m, 1020 w, 920 m, 900 s, 850 w, 820 w, 610 w.

Synthesis of $(Me_3Si)_2NY(OC_2H_4)_2NC_2H_4OY\cdot[N(SiMe_3)_2]_2$ (VI). To a solution of 1.38 g of $[(Me_3Si)_2N]_3Y$ in 30 ml of THF a solution of 0.12 g of triethylamine in 15 ml of THF was added. After the completion of the reaction the solvent and volatile products were removed in a vacuum, the solid residue was washed with hexane (2×20 ml), and dried in a vacuum to give 0.68 g (97%) of product **VI**.

IR spectrum ν, cm^{-1}: 1290 w, 1270 w, 1235 s, 1170 m, 1090 s, 1070 s, 1020 w, 1000 m, 960 s, 915 m, 880 w, 850 w, 820 s, 770 m, 650 w, 590 m, 550 w.

^1H NMR spectrum (C_5D_5N, 25°C) δ, ppm: 0.213 br.s (18H, $SiMe_3$), 0.599 br.s (36H, $SiMe_3$), 1.593 m (4H, THF), 2.1–3.5 br.m (6H, CH_2N), 3.634 m (4H, THF), 3.8–5.1 br.m (6H, CH_2O). ^{13}C NMR spectrum (50 MHz, C_5H_5N, 25°C) δ_C, ppm: 7.27, 7.372, 7.506, 26.162, 50–60 br.m, 68.184.

Compound **VII** was obtained analogously, yield 94%. Its IR spectrum is identical to that of compound **VI**.

Synthesis of $Y[OC_2H_4N(C_2H_4OH)_2]_3$ (VIII). A solution of 1.4 g of $[(Me_3Si)_2N]_3Y$ in 30 ml of THF was added slowly under vigorous stirring to a solution of 1.1 g of triethanolamine in 30 ml of THF. The obtained insignificant amount of loose precipitate was filtered off, and the filtrate was treated with 40 ml of hexane. White precipitate was obtained. The solvent was decanted, the residue was washed with hexane (2×25 ml) and dried in a vacuum over 2 h at 50°C. Compound **VIII** was obtained, yield 1.15 g (88%). IR spectrum ν, cm^{-1}: 3300 s, 1290 s, 1260 m, 1150 m, 1090 s, 1060 s, 1040 w, 1010 m, 900 s, 880 m, 790 w, 730 m, 660 w. ^1H NMR spectrum (C_5D_5N, 25°C) δ, ppm: 2.3–3.0 br.m (18H, CH_2N), 3.9-4.7 br.m (18H CH_2O), 6.0 br.s (6H, OH).

Reaction of compound I with $[(Me_3Si)_2N]_3Y$. To a suspension of 0.32 g of compound **I** in 30 ml of THF a solution of 1.55 g of $[(Me_2Si)_2N]_3Y$ in 20 ml of THF was added. The reaction mixture was stirred at 60°C for 4 days until the complete dissolution of compound **I**. The solvent was removed in a vacuum, the residue was washed with hexane (2×20 ml) and dried at a reduced pressure to give 0.67 g (91%) of compound **VI**. Elemental analysis data, IR and NMR spectra of the product agree with the characteristics of compound presented above. In the hexane extracts 0.69 g of starting $[(Me_3Si)_2N]_3Y$ was found.

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