ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 9, pp. 591–603. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © P.S. Koroteev, Zh.V. Dobrokhotova, A.B. Ilyukhin, N.N. Efimov, A.V. Gavrikov, V.M. Novotortsev, 2016, published in Koordinatsionnaya Khimiya, 2016, Vol. 42, No. 9, pp. 550–562.

Specific Features of the Structure, Reactivity, Thermolysis, and Magnetism of Cymantrenecarboxylate Complexes of Lanthanides

P. S. Koroteev*, Zh. V. Dobrokhotova, A. B. Ilyukhin, N. N. Efimov, A. V. Gavrikov, and V. M. Novotortsev
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia
**e-mail: pskoroteev@list.ru*

Received February 3, 2016

Abstract—The properties of the cymantrenecarboxylate (containing $(CO)_3Mn(\eta^5\text{-}C_5H_4CO_2^-)$ group) complexes of lanthanides obtained and studied by the authors in the years 2009–2015 are reviewed. The complexes represent a new type of heterometallic 3*d*–4*f* compounds. Both binuclear and polymer complexes of various types are synthesized. The variation of the synthesis conditions and the use of additional ligands make it possible to successively change the Mn : Ln ratio in a molecule of the compounds and to obtain the ratio equal to 3 : 1, 2 : 1, and 1 : 1. The polymeric heteroleptic derivatives, acetate and acetyacetonate cymantrenecarboxylates, are synthesized. Using the photolabile cymantrene fragment as a source of Mn^{2+} ions, polynuclear Mn–Ln heterometallic cymantrenecarboxylates are obtained under the oxidative photolysis conditions. The influence of binuclear neodymium cymantrenecarboxylate on the polymerization of dienes is studied. The structures of the complexes, their physicochemical properties, and possibilities of practical application are considered.

Keywords: cymantrenecarboxylates, synthesis, structure, magnetic properties, thermolysis, lanthanide manganites

DOI: 10.1134/S1070328416090037

Intensive research has been carried out in the recent decade in the area of synthesis and investigation of the physicochemical properties of heterometallic 3*d*–4*f* complexes in which metal ions are linked by various polydentate organic ligands, such as Schiff bases, carboxylates, amino acids, etc. [1–4]. However, the number of heterometallic 3*d*–4*f* complexes in which the transition metal is included in the organometallic fragment is comparatively low: in particular, almost exclusively the ferrocene derivatives have been known among carboxylates up to the recent time [5].

Cyclopentadienyltricarbonylmanganese (cymantrene) is an electronic analog of ferrocene and, similarly to the latter, cymantrene is chemically stable and forms numerous diverse derivatives [6]. Heterometallic compounds containing the cymantrene residue can be significantly interesting in both theoretical and practical respects. In particular, we have previously shown that the tin-containing cymantrene derivative, complex $(CO)_2Mn(C_5H_5)SnCl_2 \cdot THF$, can serve as a precursor of ferromagnetic intermetallic compound Mn_2Sn, which is the single solid product of the thermal decomposition of the complex in an inert atmosphere [7]. Examples of organometallic compounds combining lanthanide atoms and cymantrene residue have been known rather long ago [8, 9]. However, they contain the Ln–C bond and, correspondingly, are sensitive to air and water. Therefore, it seemed interesting to obtain lanthanide compounds containing cymantrene fragments as parts of stable O-ligands, for example, complexes with cymantrenecarboxylate anions $CymCO_2^-$ (Cym = $(\eta^5\text{-}C_5H_4)Mn(CO)_3$).

It should be mentioned that no information about lanthanide cymantrenecarboxylates and their physicochemical properties could be found in both Russian and foreign literature sources before the publication of our first results [10, 11], which were pioneering in this area: in essence, we consider a new class of heterometallic compounds of 3*d*–4*f* elements. These coordination compounds do not belong to the class of heterometallic 3*d*–4*f* complexes in the traditional sense. They can be considered as both lanthanide carboxylates and heterometallic 3*d*–4*f* compounds. Therefore, on the one hand, the properties characteristic of lanthanide compounds can be expected for these com-

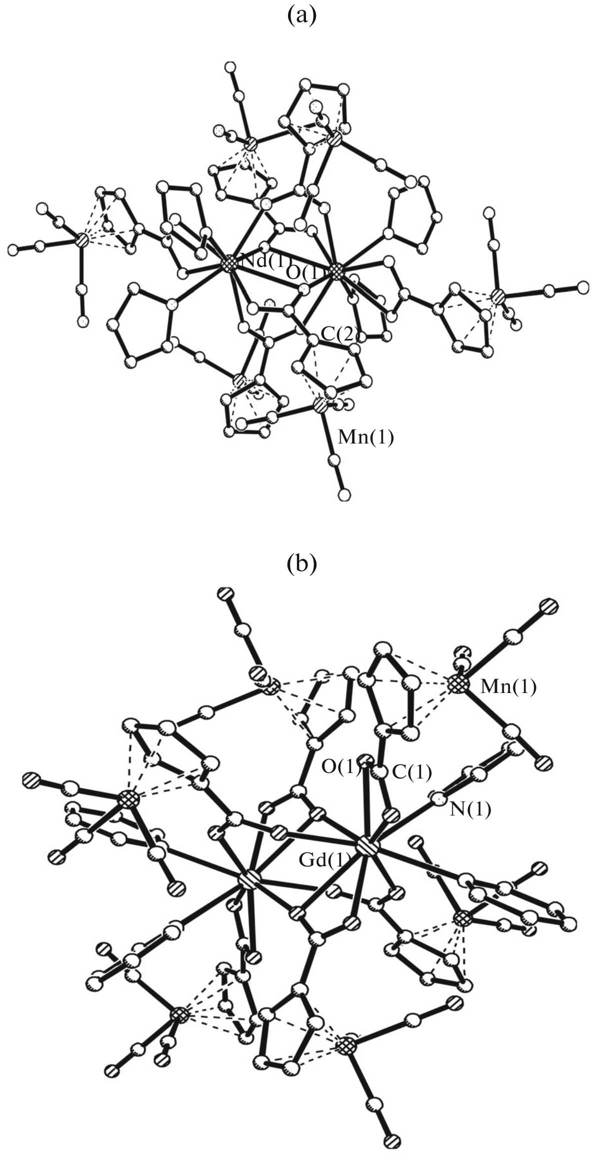

Fig. 1. Structures of the binuclear cymantrenecarboxylates: (a) Nd with THF and (b) Gd with Py.

plexes, for example, the properties of molecular magnets in the case of heavy lanthanides (Tb, Dy, Ho, and Er). On the other hand, their behavior during thermal destruction should be similar to that of classical heterometallic 3*d*–4*f* compounds.

Two similar series of heteroleptic cymantrenecarboxylates of light lanthanides, $[\mathrm{Ln_2(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\mu_2\text{-}O,O'\text{-}O_2CCym)_2(\eta^2\text{-}O_2CCym)_2L_4}] \cdot n\mathrm{L}$, containing volatile molecules of tetrahydrofuran (THF) (Ln = Nd, *n* = 0; Ln = Gd, Eu, *n* = 1; L = THF) [10, 11] and pyridine (Py) (Ln = Pr, Sm, Eu, Gd, *n* = 2, L = Py) [12] as neutral ligands were the first examples among the synthesized complexes of the type considered. The compounds were synthesized by the exchange reaction of a lanthanide salt and alkaline metal cymantrenecarboxylate in methanol followed by the evaporation of the mixture in vacuo, extraction of the product with a mixture of the corresponding solvent with toluene, and crystallization.

The obtained complexes were binuclear with two bridging, two chelate-bridging, and two chelate cymantrenecarboxylate anions. It is one of the typical structures of lanthanide carboxylates [13] (Fig. 1). All the pyridine-containing complexes are isostructural. The Eu and Gd derivatives were isostructural (among the complexes with THF), whereas the structure of the Nd complexes differed insignificantly. The Eu and Gd complexes with THF and all complexes with pyridine contained lattice molecules of the solvent.

The thermolysis of the synthesized complexes was studied in more detail. It was found that intermediates stable in a wide temperature range (100–250°C) were formed after the first stage of thermolysis comprising the removal of lattice molecules and volatile ligands. The intermediates undergo the reversible phase transition, whose temperature and heat are determined by the specificity of the metal ion only and monotonically increase with an increase in the ion radius from the Gd derivative (161°C, 21.7 kJ/mol) to the Pr derivative (205°C, 39.7 kJ/mol). As shown later, the thermolysis of polymer lanthanide cymantrenecarboxylates $[\mathrm{Ln(\eta^2\text{-}O_2CCym)_2(\mu\text{-}O_2CCym)_4Ln(ROH)_4}]_n \cdot m\mathrm{Solv}$ (Ln = Nd, Gd, Dy, Ho, Er; R = H, Me) after volatile ligands were removed also resulted in the formation of stable intermediates that underwent a similar phase transition [14]. The temperatures and thermal effects of this transition for the intermediates derived from the binuclear and polymer complexes of the same metals (Nd and Gd) differ insignificantly (Fig. 2).

In the case of the binuclear complexes, oligo- or polymerization occurs probably upon the removal of ligands, since the comparison of the IR spectra of the corresponding binuclear complexes and intermediates indicates the enhancement of the bridging function of the cymantrenecarboxylate anions [12]. For the formation of intermediates of polymer cymantrenecarboxylates, the polymer structure of the metal core is retained after the removal of neutral ligands due to a significant increase in the fraction of chelate-bridging carboxyl groups [14]. The comparison of this data suggests that the removal of neutral ligands from both polymer and binuclear cymantrenecarboxylates results in the formation of polymer isostructral tris(cymantrenecarboxylates) $[\mathrm{Ln(CymCO_2)_3}]_n$ crystallizing in the triclinic crystal system, space group $P\overline{1}$.

Thus, the idendity demonstrated for the $[\mathrm{Ln(CymCO_2)_3}]_n$ intermediates derived from the binuclear and polymer cymantrenecarboxylates made it possible to establish dependences of the onset temperature and thermal effect of the phase transition on the ion radius of lanthanides in the series Pr–Er (135.0°C, 12.5 kJ/mol) (Fig. 2).

As mentioned above, the intermediates $[Ln(Cym\text{-}CO_2)_3]_n$ are stable up to 250°C, and the destruction of the cymantrenyl fragments begins at higher temperatures. When the process is carried out in artificial air, the destruction is accompanied by an intensive oxidation process and affords a mixture of $LnMn_2O_5$ and Mn_2O_3 phases. In the case of thermolysis in an inert atmosphere, the final product contains oxides Ln_2O_3 and MnO and a considerable amount of the amorphous phase. Since manganites $LnMn_2O_5$ are the basis of promising functional materials [15] and the composition of the thermolysis product in air is determined by the Ln : Mn ratio in the initial compound, one of directions of further studies was a search for complexes with the Ln : Mn ratio of 1 : 2, which could serve as precursors of manganites $LnMn_2O_5$.

It also seemed interesting to study the volatility of the synthesized compounds to establish a possibility of using them as molecular precursors for the preparation of $LnMn_2O_5$ films by the MOCVD method. It could be assumed that the presence of the cymantrenyl fragments forming a periphery of the molecules imparts a noticeable volatility to the synthesized binuclear complexes. The volatility is characteristic of the carbonyl and cyclopentadienyl complexes of transition metals. However, the studies of the vaporization of the cymantrenecarboxylate complexes by the Knudsen method combined with mass spectral analysis of the evaporation products and traditional mass spectrometry show that these compounds are almost nonvolatile [12].

The studies of the luminescence properties of the europium cymantrenecarboxylate complexes show that the cymantrenyl fragment substantially suppresses the luminescence of the Eu^{3+} ions [16].

The cymantrenecarboxylate complexes of lanthanides can combine specific properties of the lanthanide ions and cymantrenyl moiety. It is known that cymantrene, like other carbonyl derivatives of transition metals, is catalytically active in the polymerization of unsaturated substrates when the process is initiated by UV radiation [17]. At the same time, it is also known that the polymerization of diene hydrocarbons is stereospecific in the presence of the carboxylate complexes of lanthanides, in particular, neodymium [18, 19]. Therefore, lanthanide cymantrenecaroxylates soluble in nonpolar solvents could serve as unique individual catalysts of stereospecific diene polymerization in solutions. Unfortunately, the binuclear lanthanide cymantrenecarboxylates with THF and Py easily decompose losing the volatile ligand and are insoluble in noncoordinating solvents, which did not allow their activity in homogeneous catalysis to be studied. Therefore, it seemed interesting to obtain complexes without these drawbacks.

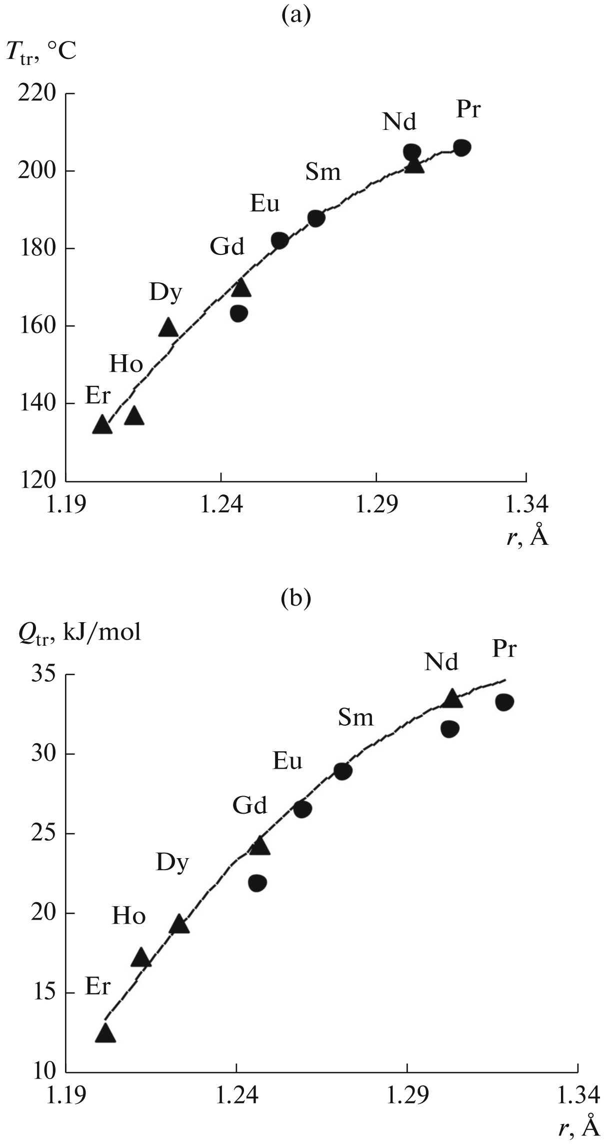

Fig. 2. Dependences of the (a) onset temperature and (b) thermal effect of the phase transition for the $[Ln(Cym\text{-}CO_2)_3]_n$ intermediates on the ion radius of lanthanides: literature data (●) [12] and (▲) [14].

A series of the binuclear complexes containing lowly volatile dimethyl sulfoxide (DMSO) as a neutral ligand, $[Ln_2(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\mu_2\text{-}O,O'\text{-}O_2CCym)_2\text{-}(\eta^2\text{-}O_2CCym)_2(DMSO)_4]$ (Ln = Ce, Nd, Eu, Gd [20]; Ln = Tb, Dy), was obtained [21]. The synthesis of the complexes included the exchange between lanthanide chloride and potassium cymantrenecarboxylate in methanol in the presence of DMSO followed by methanol removal in vacuo and the extraction of the product with boiling toluene. As in the case of the binuclear complexes described above, the compounds with DMSO have the centrosymmetric structure characteristic of binuclear lanthanide carboxylates. However, unlike two previous series of the complexes, the compounds with DMSO do not lose the neutral ligand on storage in air and are moderately soluble in

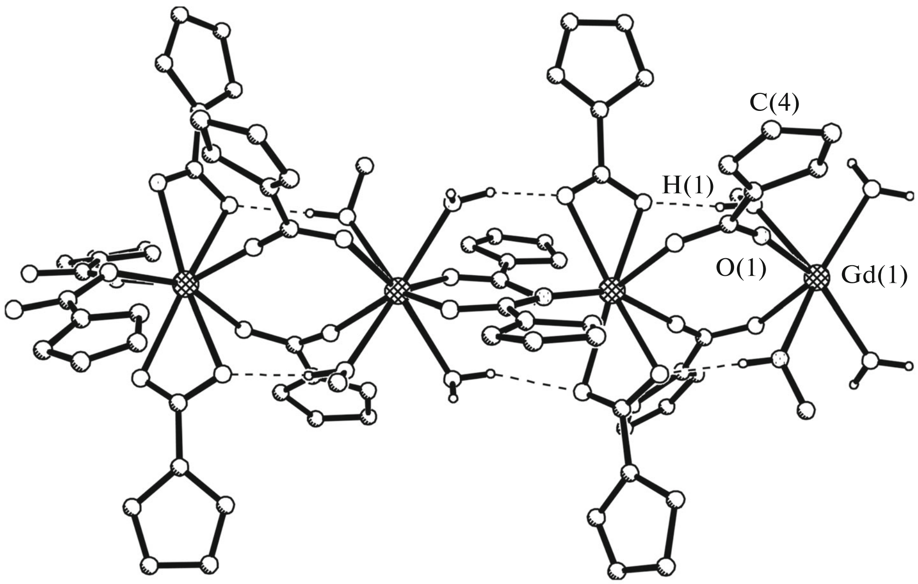

Fig. 3. Structure of complex $[Gd(\eta^2\text{-}O_2CCym)_2(\mu\text{-}O_2CCym)_4Ln(MeOH)_2(H_2O)_2]_n \cdot n MeOH \cdot 0.5n H_2O$ (here and in Figs. 4–6 and 9–11, the $Mn(CO)_3$ fragments are omitted).

aromatic solvents. The polymerization of 2,3-dimethyl-1,3-butadiene (DMB) in the presence of the Nd complex under UV irradiation in toluene was studied. A blank experiment in the absence of the complex was carried out for comparison. In the first case, the obtained product was a rubber-like substance (the conversion of the monomer was 7.16%), and a viscous oil (conversion 3.86%) was obtained in the second case. It is found using mass spectrometry and NMR and IR spectroscopy that the polymer obtained in the presence of the Nd complex is mainly built of *trans*-1,4-polydimethylbutadiene units, whereas the polymerization of DMB is irregular in the absence of the complex [20].

The thermolysis of the complexes with DMSO is more complicated than in the previous cases because of the low volatility and thermal instability of the ligand. The mass loss starts below the boiling point of DMSO, which is related to its disproportionation to $(CH_3)_2S$ and $(CH_3)_2SO_2$. The formation of these products in the gas phase was confirmed by mass spectrometry, and the disproportionation in the solid state is indicated by the data of differential scanning calorimetry (DSC). Since ligand removal occurs in a much broader temperature range than that in the case of the complexes with THF and Py, the range of existence of a possible polymer intermediate is almost absent and the destruction of the cymantrene moiety starts immediately after DMSO removal. The final thermolysis products in air in the cases of the Nd, Eu, and Gd complexes are mixtures of $LnMn_2O_5$ and Mn_2O_3. In the case of Ce, the product is a mixture of CeO_2 and Mn_3O_4. Similar mixtures are active in the oxidation of ammonia [22] and organic water contaminants [23] and, hence, are of practical interest. The $Ln–OS(CH_3)_2$ bond energy in the complexes was estimated from the obtained DSC data [20].

The series of the aforementioned polymer cymantrenecarboxylates of rare-earth elements, $[Ln(\eta^2\text{-}O_2CCym)_2(\mu\text{-}O_2CCym)_4Ln(MeOH)_x(H_2O)_{4-x}]_n \cdot m$Solv (Ln = Nd, Gd, Dy, Ho, Er), was obtained by the crystallization of the products of the exchange between $CymCO_2K$ and $LnCl_3 \cdot 6H_2O$ (ratio 3 : 1) from a mixture of water, methanol, and THF under the conditions of slow evaporation of the organic components of the solution [14]. Two types of coordination centers alternate in the polymer chain. In the first type, the Ln^{3+} ions are coordinated by the water or methanol molecules and the oxygen atoms of the bridging cymantrenecarboxylate anions. In the second type, they are coordinated by the O atoms of the bridging and chelate $CymCO_2$ anions. In both cases, the coordination number of lanthanide is 8 (Fig. 3).

The thermolysis of the polymer complexes is similar to the thermal decomposition of the complexes with THF and Py. Solvate and coordinated neutral molecules are removed and intermediate $[Ln(CymCO_2)_3]_n$ is formed at the first stage. The subsequent oxidative destruction of the intermediate in air gives a mixture of $LnMn_2O_5$ and Mn_2O_3.

In spite of similar synthesis conditions, the considered polymer complexes contain a variable number of water and methanol molecules coordinated to the Ln^{3+} ions. The maximum amount of methanol was observed in the neodymium complex ($CH_3OH : H_2O$ = 3 : 1), whereas the dysprosium complex contains only aqua ligands. To study the influence of denticity of the

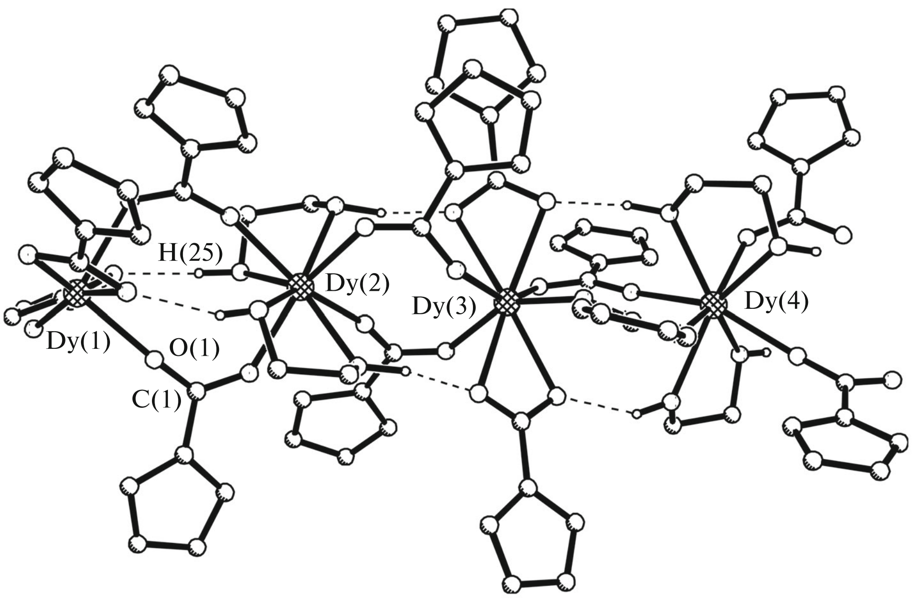

Fig. 4. Structure of complex $[Dy_4(O_2CCym)_{12}(HOCH_2CH_2OH)_{3.76}(H_2O)_{0.48}] \cdot 3THF$.

O-ligand on the structure of the product, we carried out a similar exchange reaction followed by crystallization in the presence of bidentate ethylene glycol instead of methanol. It turned out that polymer $[Dy_4(O_2CCym)_{12}(HOCH_2CH_2OH)_{3.76}(H_2O)_{0.48}]_n \cdot 3n$THF was formed in which the most part of water molecules was displaced from the coordination sphere of Dy by ethylene glycol molecules. The structure of this polymer includes four crystallographically independent Dy^{3+} ions (Fig. 4).

As mentioned above, the cymantrenecarboxylate complexes of lanthanides are interesting as precursors for mixed oxides, and the formation of manganites $LnMn_2O_5$ should be expected for the ratio Ln : Mn = 1 : 2, whereas the perovskite-like phases $LnMnO_3$ should be formed at Ln : Mn = 1 : 1. We obtained three series of the precursor complexes for $LnMn_2O_5$ and a series of the precursors for $LnMnO_3$.

The first of the series of the complexes with the ratio Ln : Mn = 1 : 2 were compounds $[Ln_2(\mu_2\text{-}O_2CCym)_2(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\eta^2\text{-}NO_3)_2(\eta^2\text{-}DME)_2]$ (Ln = Pr, Eu, Gd, Tb, Dy, Ho, Er; DME is 1,2-dimethoxyethane) [16]. These complexes were synthesized by the exchange reaction between lanthanide nitrate and potassium cymantrenecarboxylate at a ratio of 1 : 2 in methanol. Then the reaction mixture was evaporated in vacuo, the residue was extracted with THF, toluene and DME were added to the extract, and the obtained solution was left to evaporate slowly at room temperature. Under these conditions, most likely, bidentate DME completely displaces monodentate and more volatile THF from the coordination sphere of lanthanide due to the chelate effect. In the case of heavy lanthanides (Tb–Er), structural isomers with four purely bridging cymantrenecarboxylate anions $[Ln_2(\mu_2\text{-}O_2CCym)_4(\eta^2\text{-}NO_3)_2(\eta^2\text{-}DME)_2]$ were first isolated. However, is was found later that these complexes were metastable and on storage under the mother liquor for three weeks transformed into stable forms, which were isostructural with the light lanthanide complexes $[Ln_2(\mu_2\text{-}O_2CCym)_2(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\eta^2\text{-}NO_3)_2(\eta^2\text{-}DME)_2]$. The formation of binuclear complex $[Yb_2(\mu_2\text{-}O_2CCym)_4(\eta^2\text{-}NO_3)_2(\eta^2\text{-}DME)_2]$ and trinuclear complex $[Yb_3(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\mu_2\text{-}O_2CCym)_4(\eta^2\text{-}NO_3)_3(\eta^2\text{-}DME)_2\text{-}(H_2O)_2]$ in the same reaction mixture was found for ytterbium. Both compounds were isolated in a low yield and separated mechanically due to different habitus of the crystals. The last complex is a rare example of trinuclear lanthanide carboxylates (Fig. 5).

Complexes $[Ln_2(O_2CCym)_4(NO_3)_2(DME)_2]$ are built similarly to the binuclear complexes with THF, Py, and DMSO with the distinction that the role of chelating anions is played by nitrate ions and chelate DME molecules are the neutral ligands. The first stage of thermolysis of the complexes is DME removal (160–240°C). The process is impeded because of the bidentate coordination mode of the ligand and occurs in the range, the onset of which considerably exceeds the boiling point of DME (85°C). Intensive oxidative destruction starts in air immediately after DME removal and leads to the formation of $LnMn_2O_5$ phases. A pronounced exothermal effect is observed in argon which is related to the intramolecular redox process that occurs due to the reduction of the NO_3 groups by organic moieties. The thermolysis products of the complexes in argon are amorphous.

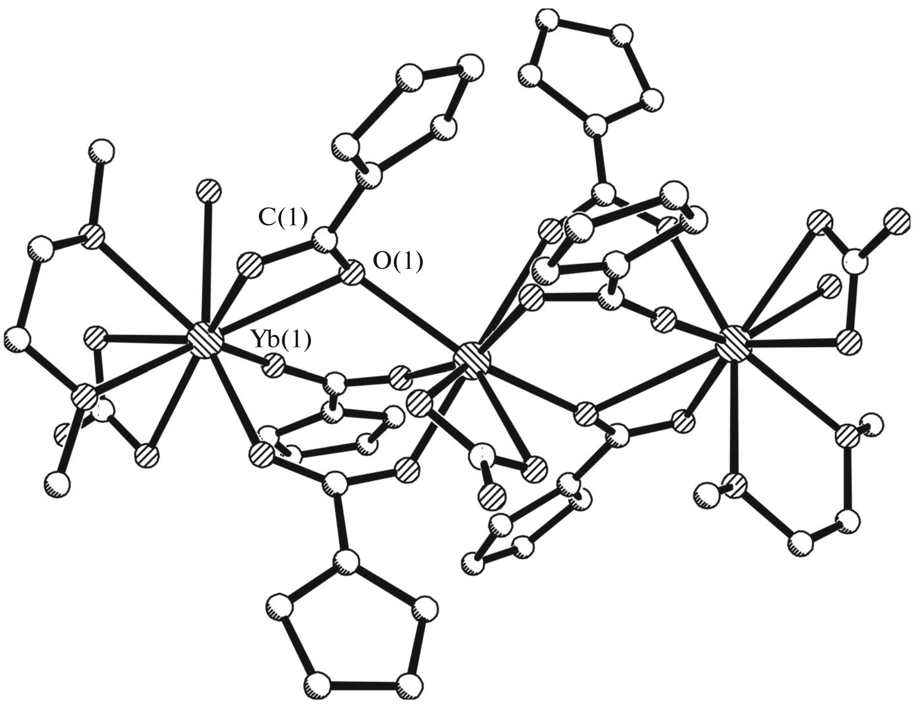

Fig. 5. Structure of complex [$Yb_3(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\mu_2\text{-}O_2CCym)_4(\eta^2\text{-}NO_3)_3(\eta^2\text{-}DME)_2(H_2O)_2$].

The magnetic properties of the phases $LnMn_2O_5$ (Ln = Gd, Ho [16]; Ln = Eu, Tb, Y [24]), which were obtained by the thermolysis of the corresponding precursor complexes in air, were studied. The yttrium precursor complex was synthesized similarly to the procedure used for lanthanides [16].

It was found in further studies that the substitution of the last NO_3 group was hindered during the formation of the binuclear cymantrenecarnoxylates of heavy lanthanides (Tb, Dy) from nitrates in the presence of DMSO, due to which complexes [$Ln_2(\mu_2\text{-}O_2CCym)_4(\eta^2\text{-}NO_3)_2(DMSO)_4$] were formed. These complexes also contain the corresponding metals in the ratio Ln : Mn = 1 : 2. Probably, this is related to the chelating effect of the bidentate NO_3 group and to steric hindrance of the cymantrenecarboxylate anion. The formed complexes are also precursors of manganites $LnMn_2O_5$ during thermolysis in air [21].

Mixed acetate cymantrenecarboxylate complexes represent another type of compounds with the Ln : Mn = 1 : 2 ratio. We found that the reactions of cymantrenecarboxylic acid with lanthanide acetates in a mixture of water, alcohols, and THF in the case of Nd, Gd, and Dy afforded isostructural polymers $[Ln(CymCO_2)_2(OAc)(MeOH)]_n$ when methanol was used. When using isopropanol, whose coordination on the Ln^{3+} ions is sterically hindered, polymers $[Nd(CymCO_2)_2(OAc)(H_2O)_2]_n \cdot 0.5n(^iPrOH) \cdot nH_2O$, $[Gd(CymCO_2)_2(OAc)(H_2O)_2]_N \cdot 2nH_2O$, and $[Dy(CymCO_2)_2(OAc)(H_2O)]_n \cdot 0.55n\text{THF} \cdot 0.45n(^iPrOH) \cdot 0.45nH_2O$ containing aqua ligands and having different structures are formed [25]. The carboxylate ligands (acetate and cymantrenecarboxylate anions) compete during the formation of complexes in the reaction mixture. The products containing the hydrophobic cymantrenyl fragments crystallize with the evaporation of the organic components of the reaction mixture because of the low solubility in water. All the polymers are characterized by the general "ladder" structure $\{Ln(OAc)\}_n$ formed by the tetradentate acetate residues and Ln^{3+} ions. The cymantrenecarboxylate residues form a periphery of the polymer chain. They act as monodentate, chelate, or bridging ligands. The variety of the coordination functions of the cymantrenecarboxylate residues determines the difference in polymer structures (Fig. 6).

In the case of heavy lanthanides (Ho, Er, Tm), binuclear complexes [$Ln_2(\mu_2\text{-}O_2CCym)_2(\eta^2\text{-}O_2CCym)_2(\eta^2\text{-}OAc)_2(H_2O)_4$] · $5H_2O$ are formed regardless of the nature of alcohol in the reaction medium. The recrystallization of the binuclear Er complex from methanol affords polymer $[Er(CymCO_2)_2(OAc)(MeOH)]_n$ isostructural to the Nd, Gd, and Dy polymers with methanol. The dimer in the structure of the binuclear complexes can be considered as a building block in the polymer compounds. The structure of the binuclear complex and the fragment of the polymer chain of the erbium derivatives are shown in Fig. 7.

The thermolysis of all the complexes occurs similarly and in stages: the first stage is the removal of lat-

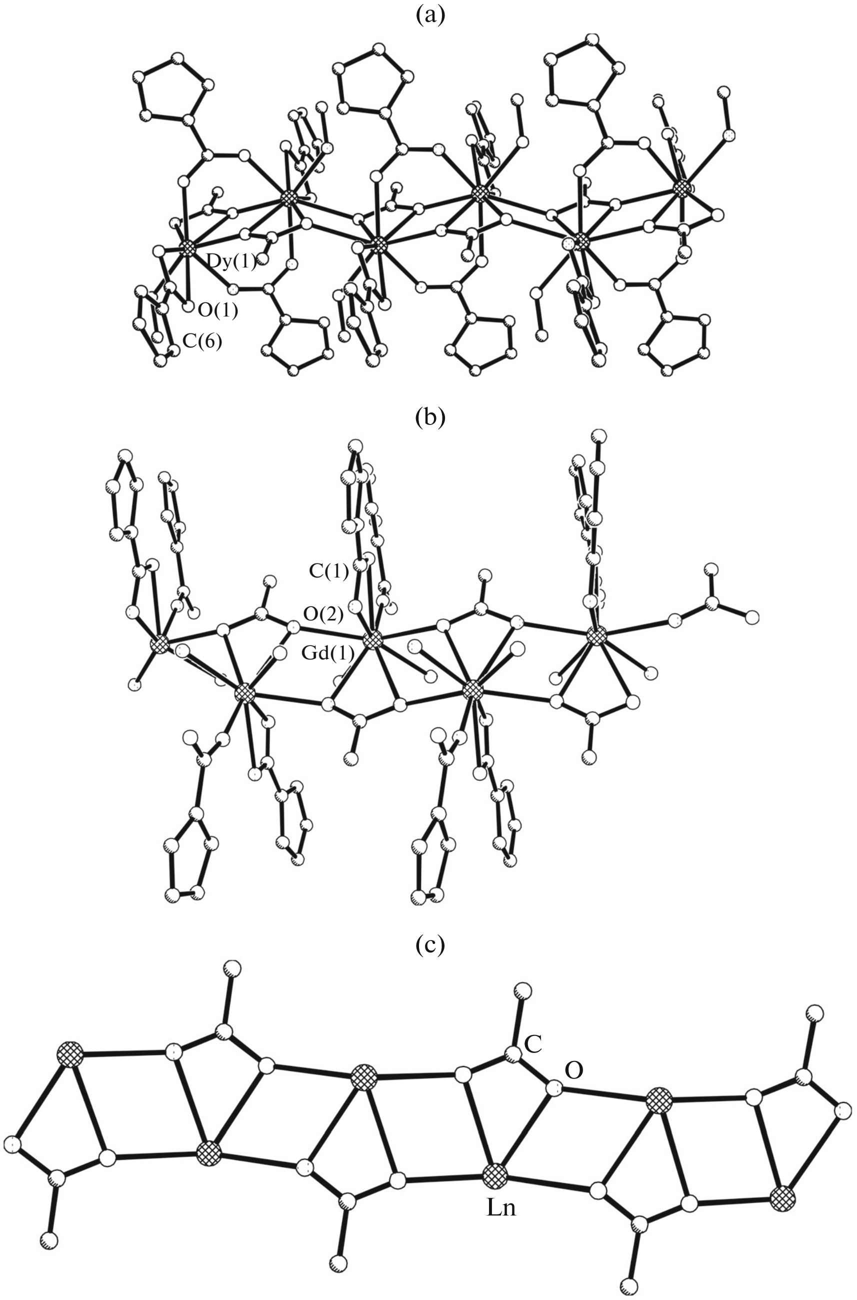

Fig. 6. Structures of complexes (a) $[Dy(CymCO_2)_2(OAc)(MeOH)]_n$ and (b) $[Gd(CymCO_2)_2(OAc)(H_2O)_2]_n \cdot 2nH_2O$; (c) the fragment of structure $\{Ln(OAc)\}_n$.

tice molecules and neutral ligands (70–140°C) and the formation of intermediates undergoing structural transformations (140–260°C). When the process is carried out in artificial air, the oxidation of the intermediates starts above 265°C and affords $LnMn_2O_5$ [25]. The product of thermal decomposition in argon is an amorphous mixture. The magnetic properties of samples of $ErMn_2O_5$ and $DyMn_2O_5$ obtained by the thermolysis of the methanol-containing polymers were studied in DC and AC fields in comparison with similar phases obtained by the thermolysis of the earlier synthesized complexes $[Ln_2(CymCO_2)_4(NO_3)_2(DME)_2]$. The $LnMn_2O_5$ phases were shown to exhibit the properties of metamagnetics, and the dependence of the magnetic properties of the dysprosium manganite samples on the crystallite size was observed.

A synthesis procedure using hydrated lanthanide acetylacetonates as the initial reactants was applied to obtain cymantrenecarboxylates with the ratio Ln : Mn = 1 : 1. The reactions of hydrated lanthanide

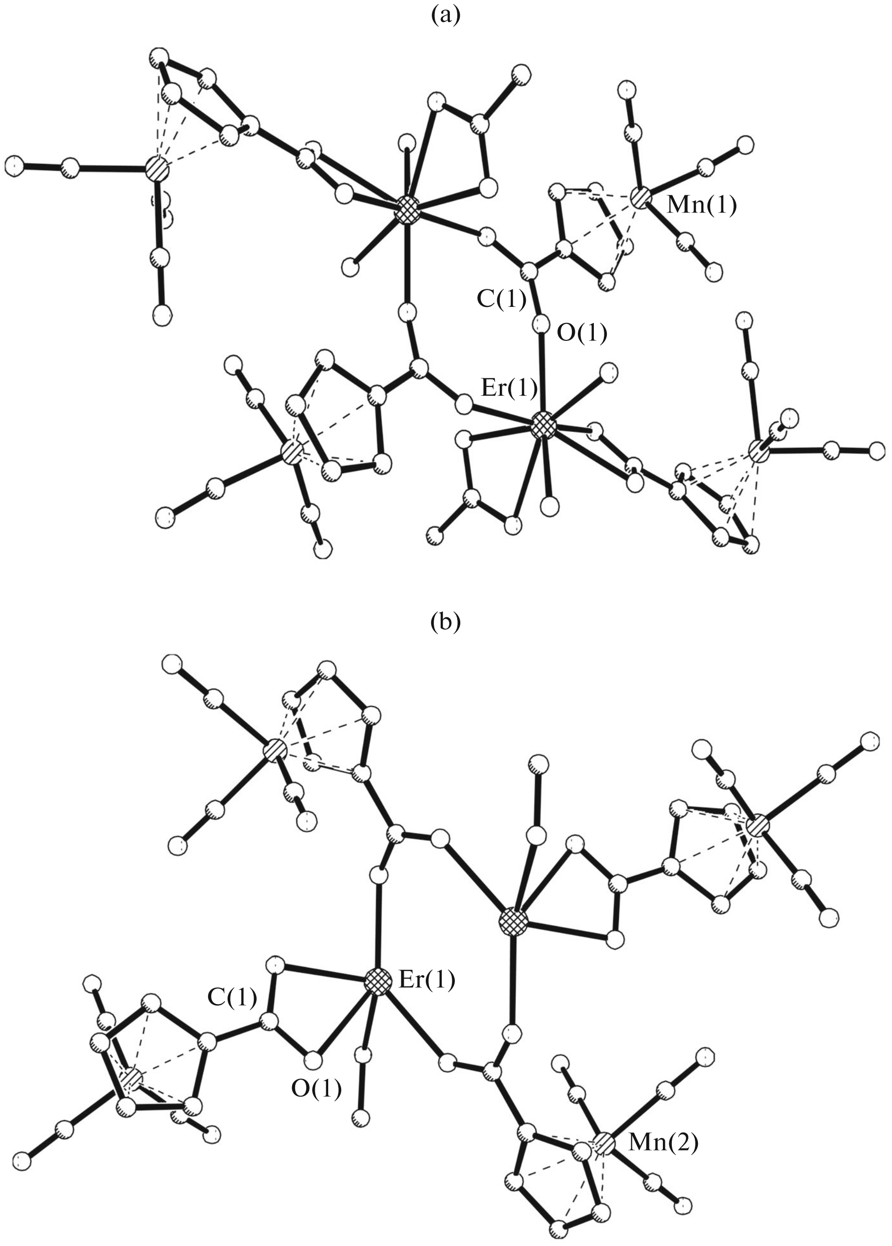

Fig. 7. (a) Structure of complex $[Er_2(\mu_2\text{-}O_2CCym)_2(\eta^2\text{-}O_2CCym)_2(\eta^2\text{-}OAc)_2(H_2O)_4]$ and (b) the fragment of polymer chain of $[Er(CymCO_2)_2(OAc)(MeOH)]_n$.

acetylacetonates with $CymCO_2H$ in a mixture of ethanol, chloroform, and water afford polymer complexes $[Ln(CymCO_2)(Acac)_2(H_2O)]_n$ (Ln = Eu, Gd, Tb, Dy, Ho, Er) crystallizing during the gradual evaporation of the reaction mixture [26]. The structures of the complexes are formed by the $[Ln(Acac)_2(H_2O)]$ fragments in which the lanthanide ion is chelated by two Acac ligands and bridging cymantrenecarboxylate anions that link the $[Ln(Acac)_2(H_2O)]$ fragments into an infinite chain. The coordination number of the Ln^{3+} ion is 7, which is fairly low for the lanthanide complexes. The chain is additionally stabilized by hydrogen bonds between the hydrogen atoms of the aqua ligands and oxygen atoms of the Acac ligands. Stacking interactions occur between the cyclopentadienyl rings of the $CymCO_2$ ligands of the adjacent chains (Fig. 8).

The cymantrenecarboxylate ligand is an unusual structural block due to the geometry of the cymantrenyl residue (piano stool) and the nature of its fragments. For example, in the case of the alkaline metal derivatives, the $CymCO_2$ ligand exhibits an unusual mode of coordination to the metal ion through the oxygen atom of the carbonyl group [27]. The $CymCO_2$

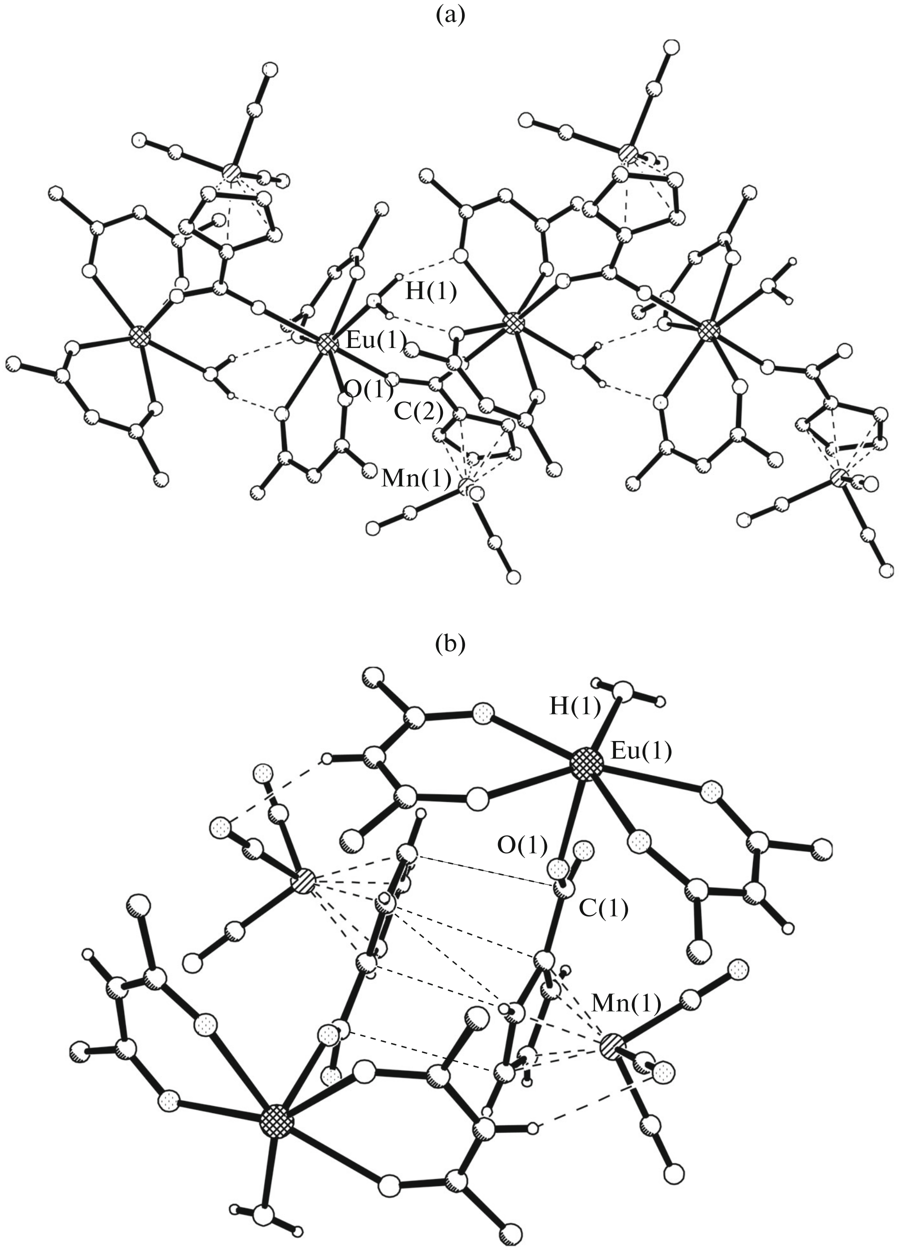

Fig. 8. (a) Chain structure of complex $[Eu(CymCO_2)(Acac)_2(H_2O)]_n$ and (b) stacking interactions between the Cp rings of the adjacent chains.

ligand behaves, as a whole, similarly to other carboxylates in lanthanide cymantrenecarboxylates and transition metal complexes [28–31]. The stacking interactions of the cyclopentadienyl rings stabilizing the structure of the polymer complexes $[Ln(CymCO_2)(Acac)_2(H_2O)]_n$ can be considered as a manifestation of the specifics of the cymantrenecarboxylate ligand.

The thermolysis of cymantrenecarboxylate acetylacetonates has an interesting feature. According to the data of thermogravimetry and mass spectrometry, the partial intramolecular hydrolysis occurs at the first stage in a range of 125–170°C along with the loss of coordinated water, due to which 1/6 of the Acac ligands present in the complex is removed in the form of acetylacetone, and intermediate $\{Ln_3(CymCO_2)_3(Acac)_5(OH)\}_n$ is formed. The complicated character of the first thermolysis stage was confirmed by the kinetic analysis of the thermoanalytical data (non-isothermal kinetics). The intermediate formed is stable up to 220°C. The further thermal destruction starts at higher temperatures and leads, in the case of the process occurring in air, to the formation of perovskites $LnMnO_3$. The properties of a series of the

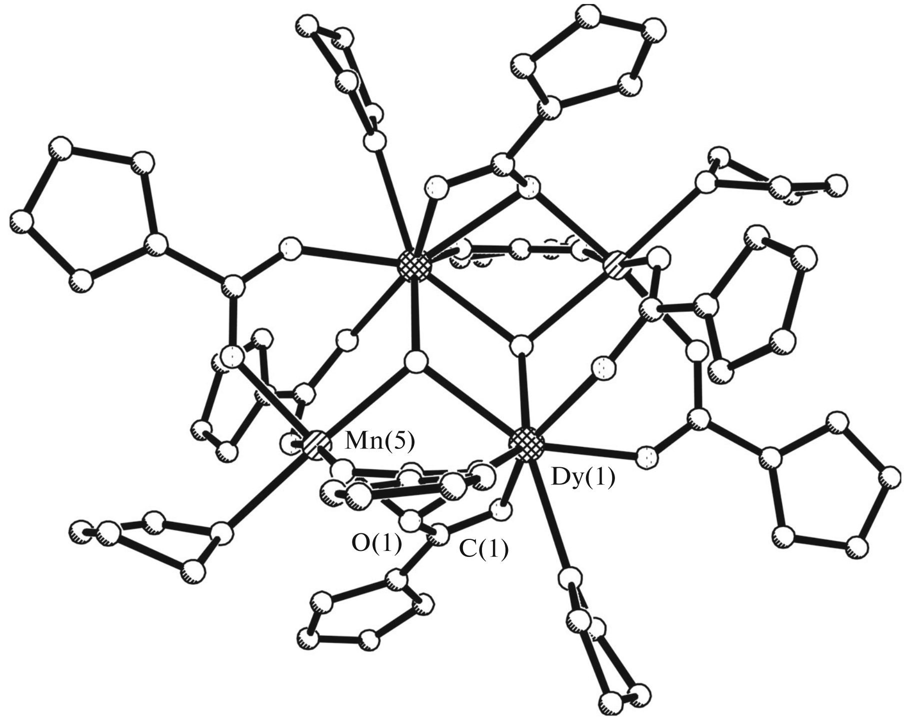

Fig. 9. Molecular structure of $[Dy_2Mn_2(\mu_3\text{-}OH)_2(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\mu_2\text{-}O_2CCym)_6(THF)_2]$.

obtained manganites (Ln = Eu, Gd, Tb, Dy) were studied. Magnetic ordering in the sublattice of Ln^{3+} ions was observed for the Gd, Tb, and Dy derivatives at temperatures of ~10 K, whereas antiferromagnetic ordering in the Mn^{3+} sublattice was observed at 50 K for $EuMnO_3$.

Although cymantrene belongs to the most stable organometallic compounds, it is photolabile and can decompose to releasing the Mn atom. We have used this property of the cymantrene moiety for the preparation of new heterometallic Mn–Ln complexes. The tetranuclear complexes $[Ln_2Mn_2(\mu_3\text{-}OH)_2(\mu\text{-}O,\eta^2\text{-}O_2CCym)_2(\mu_2\text{-}O_2CCym)_6(THF)_2]$ (Ln = Dy, Ho) containing Ln^{3+} and Mn^{2+} ions were synthesized [32]. For the preparation of these complexes, the product of the exchange reaction between $LnCl_3 \cdot 6H_2O$ and $CymCO_2K$ (carried out in methanol) was dissolved in a mixture of THF, toluene, and a minor amount of water, and the solution was UV-irradiated. The proposed scheme of cymantrenecarboxylate fragment decomposition is the following:

$$2(CO)_3Mn(C_5H_4CO_2)^- + 3H_2O + 0.5O_2$$
$$\xrightarrow{h\nu} 6CO\uparrow + 2Mn^{2+} + 4OH^- + [C_5H_5CO_2^-]_2.$$

The resulting Mn^{2+} and OH^- ions are included into the structure of the resulting complexes.

The metal and oxygen atoms in the structures of the tetranuclear complexes form two cubes each of which lacks one vertex. The cubes have the common facet $Ln_2(\mu_3\text{-}OH)_2$ (Fig. 9). A similar defect dicubane structure of the metal framework is known for both 3*d*–4*f* heterometallic and homometallic complexes [32]. The erbium and ytterbium derivatives were also obtained in a low yield.

The thermolysis of the synthesized complexes proceeds in stages. The coordinated THF molecules and OH groups (in the form of water) are removed at the first stage in a range of 140–190°C. The destruction of the cymantrene fragments starts above 200°C, and the product is a mixture of the $LnMn_2O_5$ and Mn_2O_3 phases if the process occurs in air.

Polynuclear complexes $[Er_2Mn(\mu_2\text{-}O_2CCym)_6(\eta^2\text{-}O_2CCym)_2((MeO)_3PO)_4] \cdot 2MePh$ and $[Tb_4(\mu_3\text{-}OH)_4(\mu_2\text{-}O,O'\text{-}O_2CCym)_6(H_2O)_3(THF)_4][MnCl_4] \cdot 4CH_2Cl_2 \cdot 6THF$ were isolated in low yields due to the spontaneous destruction of the $CymCO_2$ fragment in the presence of the corresponding Ln^{3+} ions in various media [21]. The structure of the former contains a unique centrosymmetric trinuclear fragment $Er(\mu_2\text{-}L)_2Mn(\mu_2\text{-}L)_2Er$ (Fig. 10). The structure of the latter is formed by cationic complexes $[Tb_4(\mu_3\text{-}OH)_4(\mu_2\text{-}O,O'\text{-}O_2CCym)_6(H_2O)_3(THF)_4]^{2+}$ (Fig. 11), $[MnCl_4]^{2-}$ anions, and solvate molecules. The complex cation is based on the cubane-like fragment $[Ln_4(\mu_3\text{-}OH)_4]^{8+}$. The structures based on a similar core are known for the carboxylate clusters of lanthanides [33, 34].

The diamagnetic nature of the cymantrene fragments distinguishes lanthanide cymantrenecarboxyl-

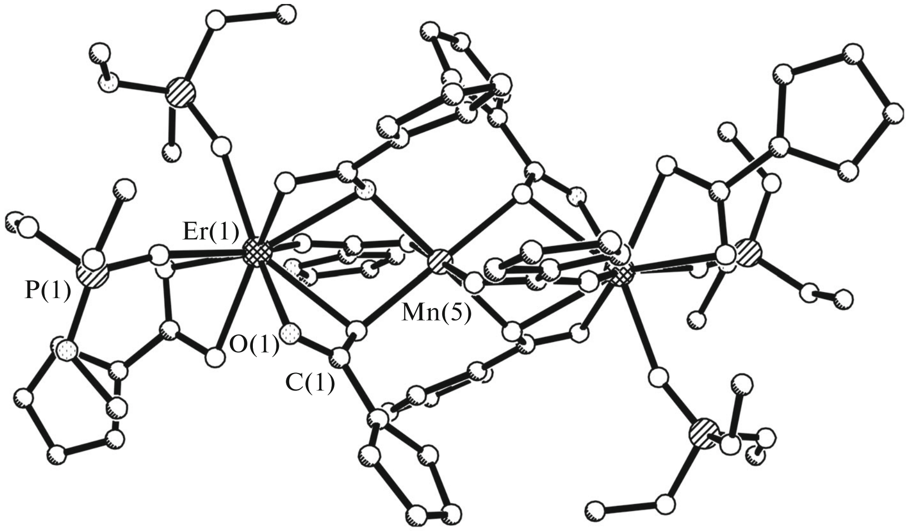

Fig. 10. Structure of complex $[Er_2Mn(\mu_2\text{-}O_2CCym)_6(\eta^2\text{-}O_2CCym)_2((MeO)_3PO)_4] \cdot 2MePh$.

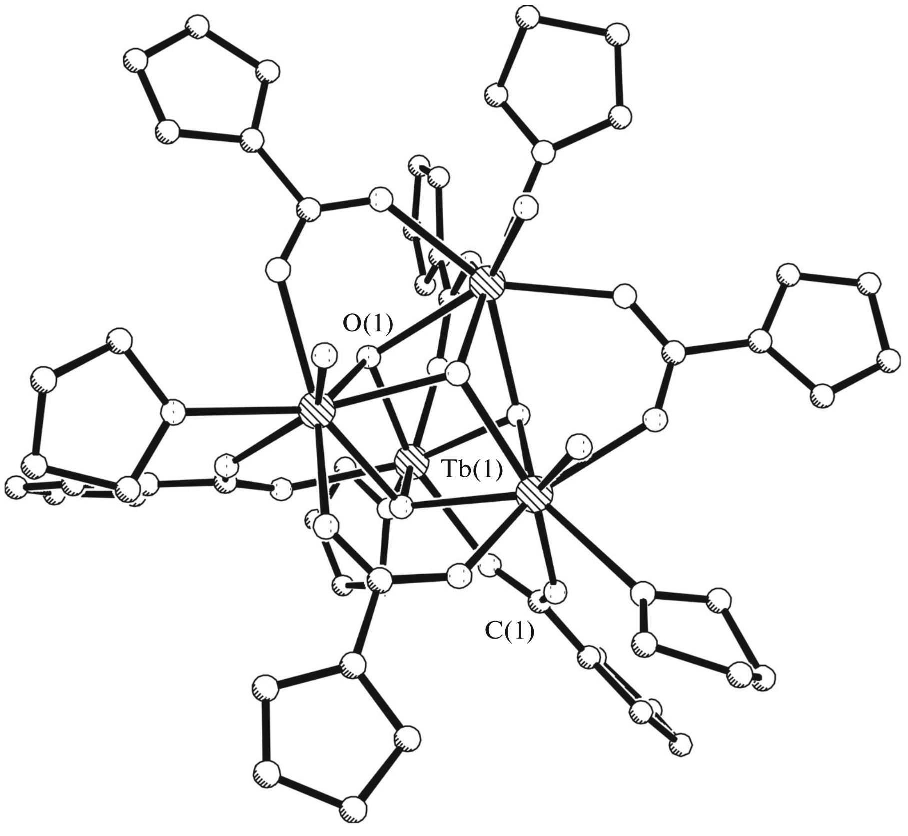

Fig. 11. Structure of the cation in complex $[Tb_4(\mu_3\text{-}OH)_4(\mu_2\text{-}O,O'\text{-}O_2CCym)_6(H_2O)_3(THF)_4][MnCl_4] \cdot 4CH_2Cl_2 \cdot 6THF$.

ates from all other heterometallic Mn–Ln complexes, since the magnetism of the cymantrenecarboxylates is caused by the contribution of Ln^{3+} ions only. The magnetic behavior of the lanthanide complexes is interesting and specific due to a high magnetic moment inherent in some of them (Gd–Er) and to a high magnetic anisotropy of certain Ln^{3+} ions, which provides possibilities of their use for the design of molecular magnets [35–39]. For the most part of the synthesized complexes, the magnetic properties were studied in a permanent field in a temperature range of 300–2 K. The data for the Gd complexes are most interesting because of the electronic structure of this ion. The Gd^{3+} ion has the maximum possible number of unpaired electrons ($S = 7/2$) among the 4*f* elements. In addition, it is an isotropic ion for which the magnetic moment contains no orbital contribution, which facilitates the mathematical description of the magnetism for the Gd^{3+} complexes.

The analysis of the magnetic properties of the binuclear cymantrenecarboxylates with THF and Py made it possible to discover antiferromagnetic interactions between the Gd^{3+} ions in both cases. These interactions were stronger for the complex with Py in which the distance between the Gd^{3+} ions was shorter. We combined these results with the literature data for 32 complexes containing the $[Gd_2O_2]$ core and established a relationship between the energy of the exchange interaction $J_{Gd-Gd'}$ and the distance between the gadolinium atoms Gd···Gd' in the structures of such complexes. The validity of the obtained relationship was confirmed for the binuclear gadolinium cymantrenecarboxylate with DMSO [40] and some other similar complexes [25, 41].

Other synthesized lanthanide cymantrenecarboxylate complexes exhibit the temperature dependences of the magnetic moment typical of lanthanide carboxylates and caused by a decrease in the population of the excited m_J levels and/or weak antiferromagnetic interactions between the lanthanide ions [42, 43]. A significant orbital contribution and anisotropy of the most part of lanthanide ions do not allow the quantitative description of the temperature behavior of the complexes to be performed. The exceptions are the europium complexes, whose magnetism is determined by the population of the nearest excited states, since the ground state of the Eu^{3+} ion is diamagnetic. In this case, the approximation of the free Eu^{3+} ion is a good model for the theoretical description of the experimental temperature dependence of the magnetic susceptibility, which was shown for the $[Eu(CymCO_2)(Acac)_2(H_2O)]_n$ complex [26].

The appearance of the Mn^{2+} ion in the defect dicubane complexes due to the photolysis of the cymantrene moiety is the "magnetic activation" of the Mn^I atom, which is present in the cymantrenyl composition and has the low-spin d^6 configuration. The compounds formed are traditional 3*d*–4*f* complexes containing metals in the ionic form. In these compounds, the magnetic interactions between the ions are considerably stronger than those in the polynuclear 4*f* complexes [37]. In addition, the 3*d*–4*f* complexes are especially interesting as potential molecular magnets [44]. The measurements of the magnetic susceptibility in a variable field made it possible to reliably establish that complex $[Dy_2Mn_2(OH)_2(O_2CCym)_8(THF)_2]$ is a single-molecule magnet. The same can be asserted with some probability for the holmium complex, since the latter demonstrates the slow relaxation of magnetization at temperatures about 2 K [32]. No slow relaxation was observed for complex $[Er_2Mn(O_2CCym)_8((MeO)_3PO)_4] \cdot 2MePh$ [21]. For all the compounds comprising Mn^{2+}, the temperature dependences of the magnetic properties in DC magnetic field exhibit no anomalies and can indicate antiferromagnetic interactions in the metal core.

Among lanthanide ions, the Dy^{3+} ion is the most appropriate for the design of molecular magnets. This ion is characterized by a high magnetic anisotropy and, in addition, it has an odd number of electrons ($n = 9$), i.e., it is Kramer's ion (its ground state is always bistable). Thus, two conditions necessary for the manifestation of molecular magnetism are optimally combined in the case of Dy^{3+} [38, 39]. The magnetic measurements in AC field revealed the properties of molecular magnets for the studied both binuclear [21] and polymer [14] Dy^{3+} cymantrenecarboxylates.

Thus, we synthesized and studied the new type of heterometallic 3*d*–4*f* compounds containing transition metal in the organometallic fragment, namely, cymantrenecarboxylates of rare-earth elements. Selecting the sources of lanthanide ions and additional ligands during the synthesis, one can vary the type of structures of the formed complexes and the stoichiometric ratio of lanthanide and manganese atoms in them. Varying this ratio, one can use various cymantrenecarboxylate complexes of lanthanides as precursors of manganites $LnMn_2O_5$ or $LnMnO_3$ having the properties of multiferroics. The partial photolysis of the cymantrene fragment during the synthesis has served as a method for the preparation of new Mn^{II}–Ln^{III} complexes. A combination of the catalytic properties of the cymantrene fragment and Ln^{3+} ions provides prospects of using lanthanide cymantrenecarboxylates as catalysts for stereoregular diene polymerization.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, project no. 14-13-00938.

REFERENCES

1. Masatomi, S., Kazuhiro, M., and Hisashi, O., *Coord. Chem. Rev.*, 2001, vols. 219–221, p. 379.
2. Andruh, M., Costes, J.-P., Diaz, C., and Gao, S., *Inorg. Chem.*, 2009, vol. 48, p. 3342.
3. Huang, Y.-G., Jiang, F.-L., and Hong, M.-Ch., *Coord. Chem. Rev.*, 2009, vol. 253, p. 2814.
4. Sharples, J.W. and Collison, D., *Coord. Chem. Rev.*, 2014, vol. 260, p. 1.
5. Koroteev, P.S., Dobrokhotova, Zh.V., Efimov, N.N., et al., *Russ. J. Coord. Chem.*, 2014, vol. 40, no. 7, p. 495.

6. Ginzburg, A.G., *Russ. Chem. Rev.*, 2009, vol. 78, no. 3, p. 195.
7. Dobrokhotova, Zh.B., Koroteev, P.S., Novotortsev, V.M., et al., *Russ. J. Inorg. Chem.*, 2007, vol. 52, no. 7, p. 1109.
8. Suleimanov, Q.Z., Petrovskii, P.V., Bogachev, Yu.S., et al., *J. Organomet. Chem.*, 1984, vol. 262, p. C36.
9. Suleimanov, G.Z., Bogatchev, Y.S., Abdullaeva, L.T., et al., *Polyhedron*, 1985, vol. 4, p. 29.
10. Koroteev, P.S., Kiskin, M.A., Dobrokhotova, Zh.V., and Novotortsev, V.M., Abstracts of Papers, *VI Vseros. konf. po khimii poliyadernykh soedinenii i klasterov* (VI All-Russian Conf. on the Chemistry of Polynuclear Compounds and Clusters), Kazan, 2009, p. 26.
11. Koroteev, P.S., Kiskin, M.A., Dobrokhotova, Zh.V., et al., *Polyhedron*, 2011, vol. 30, p. 2523.
12. Koroteev, P.S., Dobrokhotova, Zh.V., Kiskin, M.A., et al., *Polyhedron*, 2012, vol. 43, p. 36.
13. *Rare Earth Coordination Chemistry: Fundamentals and Applications*, Huang Ch., Ed., Singapore: Wiley, 2010, p. 91.
14. Koroteev, P.S., Dobrokhotova, Zh.V., Ilyukhin, A.B., et al., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 12, p. 805.
15. Akbashev, A.R. and Kaul, A.R., *Usp. Khim.*, 2011, vol. 80, no. 12, p. 1211.
16. Koroteev, P.S., Dobrokhotova, Zh.V., Ilyukhin, A.B., et al., *Polyhedron*, 2013, vol. 65, p. 110.
17. Kotlova, E.S., Pavlovskaya, M.V., Grishin, I.D., et al., *Polym. Sci.*, vol. 53, nos. 3–4, p. 108.
18. Zhang, Z., Cui, D., Wang, B., et al., *Struct. Bond.*, 2010, vol. 137, p. 49.
19. Friebe, L., Nuyken, O., and Obrecht, W., *Adv. Polym. Sci.*, 2006, vol. 204, p. 1.
20. Koroteev, P.S., Dobrokhotova, Zh.V., Ilyukhin, A.B., et al., *Russ. Chem. Bull., Int. Ed.*, 2012, no. 6, p. 1069.
21. Koroteev, P.S., Efimov, N.N., Dobrokhotova, Zh.V., et al., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 3, p. 149.
22. Imamura, S. and Doi, A., *Ind. Eng. Chem. Res.*, 1985, vol. 24, p. 75.
23. Matatov-Meytal, Y.I. and Sheintuch, M., *Ind. Eng. Chem. Res.*, 1998, vol. 37, p. 309.
24. Dobrokhotova, Zh.V., Koroteev, P.S., Kirdyankin, D.I., et al., *Russ. J. Inorg. Chem.*, 2015, vol. 60, no. 12, p. 1433.
25. Koroteev, P.S., Dobrokhotova, Zh.V., Ilyukhin, A.B., et al., *Polyhedron*, 2015, vol. 85, p. 941.
26. Gavrikov, A.V., Koroteev, P.S., Dobrokhotova, Zh.V., et al., *Polyhedron*, 2015, vol. 102, p. 48.
27. Ilyukhin, A.B., Koroteev, P.S., Kiskin, M.A., et al., *J. Mol. Struct.*, 2013, vol. 1033, p. 187.
28. Pasynskii, A.A., Shapovalov, S.S., Gordienko, A.V., et al., *Inorg. Chim. Acta*, 2012, vol. 384, p. 18.
29. Pasynskii, A.A., Shapovalov, S.S., Gordienko, A.V., and Skabitskii, I.V., *Russ. J. Coord. Chem.*, 2011, vol. 37, no. 2, p. 127.
30. Shapovalov, S.S., Pasynskii, A.A., Skabitskii, I.V., et al., *Russ. J. Coord. Chem.*, 2014, vol. 40, no. 2, p. 75.
31. Maksakov, V.A., Podberezskaya, N.V., Zavodnik, V.E., et al., *Koord. Khim.*, 1986, vol. 12, no. 8, p. 1132.
32. Koroteev, P.S., Efimov, N.N., Ilyukhin, A.B., et al., *Inorg. Chim. Acta*, 2014, vol. 418, p. 157.
33. Zheng, Z., *Chem. Commun.*, 2001, p. 2521.
34. Ma, B.-Q., Zhang, D.-Sh., Gao, S., et al., *Angew. Chem., Int. Ed. Engl.*, 2000, vol. 39, p. 3644.
35. Sorace, L., Benelli, C., and Gatteschi, D., *Chem. Soc. Rev.*, 2011, vol. 40, p. 3092.
36. Feltham, H.L.C. and Brooker, S., *Coord. Chem. Rev.*, 2014, vol. 276, p. 1.
37. Benelli, C. and Gatteschi, D., *Chem. Rev.*, 2002, vol. 102, p. 2369.
38. Peng Zhang, Yun-Nan Guo, Jinkui Tang, *Coord. Chem. Rev.*, 2013, vol. 257, p. 1728.
39. Woodruff, D.N., Winpenny, R.E.P., and Layfield, R.A., *Chem. Rev.*, 2013, vol. 113, p. 5110.
40. Koroteev, P.S., Efimov, N.N., Dobrokhotova, Zh.V., et al., *Russ. Chem. Bull., Int. Ed.*, 2013, no. 8, p. 1768.
41. Koroteev, P.S., Ilyukhin, A.B., Efimov, N.N., et al., *Polyhedron*, 2015, vol. 89, p. 238.
42. Fomina, I.G., Dobrokhotova, Zh.V., Kazak, V.O., et al., *Eur. J. Inorg. Chem.*, 2012, vol. 22, p. 3595.
43. Li Yi-Lei, Liu Qing-Yan, Liu Cai-Ming et al., *Aust. J. Chem.*, 2015, vol. 68, p. 488.
44. Piquer, L.R. and Sanudo, E.C., *Dalton Trans.*, 2015, vol. 44, p. 8771.

Translated by E. Yablonskaya