# Synthesis, structure, thermal behavior, thermodynamic, magnetic and luminescent properties of Pr, Sm, Eu, and Gd cymantrenecarboxylates

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## ABSTRACT

New isostructural lanthanide cymantrenecarboxylates $[Ln_2(\mu\text{-}O,\eta^2\text{-}OOCCym)_2(\mu_2\text{-}OOCCym)_2(\eta^2\text{-}OOCCym)_2(py)_4]\cdot2py$, where Ln = Pr (**1**), Sm (**2**), Eu (**3**), Gd (**4**) and Cym = $(\eta^5\text{-}C_5H_4)Mn(CO)_3$, were synthesized and characterized by X-ray diffraction. The crystals of **1–4** are built of discrete binuclear molecules; the Ln atoms are nine-coordinate. The phases produced by thermal elimination of pyridine from complexes **3** and **4** are identical to the phases formed by elimination of THF from the THF-containing cymantrenecarboxylates prepared earlier. The magnetic properties of complex **4** indicate an enhancement of antiferromagnetic interactions between $Gd^{3+}$ ions due to the substitution of THF for pyridine; in the product of ligand elimination from **4**, ferromagnetic interactions were found. It was shown that the lanthanide cymantrenecarboxylates are virtually nonvolatile. The thermal decomposition of the complexes was studied by differential scanning calorimetry (DSC) and thermogravimetry (TGA). Thermolysis of **1–4** in air affords mixtures of $LnMn_2O_5$ and $Mn_2O_3$. For the earlier prepared complex $[Nd_2(\mu_2\text{-}OOCCym)_4(OOC\text{-}Cym)_2(THF)_4]$ (**5**), standard thermodynamic functions were calculated from adiabatic calorimetry data. Cymantrenecarboxylate ligands appreciably suppress $Eu^{3+}$ luminescence and determine the spectral and the fluorescent properties of the lanthanide cymantrenecarboxylates.

## 1. Introduction

In the coordination chemistry of rare-earth elements considerable attention is paid to studies of carboxylate complexes [1]. Heterometallic carboxylates of 4*f*- and 3*d*-metals, which have extraordinary magnetic [2], sorption [3], and luminescent [4] properties are of special interest. The major subjects of studies in this field have long been heterometallic 3*d*–4*f*-metal complexes in which different metal ions were connected by polydentate organic ligands (Schiff bases, amino alcohols, amino phenols, amino acids, carboxylic acids, and so on) [4a].

An interesting (but not abundant) class of heterometallic 3*d*–4*f*-metal carboxylates comprises those containing 3*d*-metal as a part of organometallic fragment [5]. This is a relatively new type of compounds; only a few examples of such complexes are known, and most of them are the carboxylate derivatives of ferrocene [5b–h]. Recently we prepared Nd, Eu, and Gd cymantrenecarboxylates with a coordinated neutral ligand (THF) and studied their solid-phase thermolysis and magnetic behavior [6].

The diamagnetism of cymantrenyl moieties distinguishes lanthanide cymantrenecarboxylate complexes from the other manganese–lanthanide heterometallic complexes since the magnetism of cymantrenecarboxylates results from the $Ln^{3+}$ ions solely. The magnetic properties of lanthanide carboxylate complexes remain insufficiently studied yet. There are several theoretical models that provide a correct interpretation of $Ln^{3+}$ exchange interactions via bridging carboxylate ligands [7]; the simplest case to be interpreted theoretically is the interaction of two paramagnetic centers.

Compounds containing $Gd^{3+}$ ion take a special place among the complexes of 4*f* elements due to peculiarities of the electronic structure of this ion. First, $Gd^{3+}$ ion has the greatest possible number of unpaired electrons ($S = 7/2$) among the 4*f*-elements. Second, this is an isotropic ion for which there is no spin–orbit coupling, and this eases the mathematical description of magnetic properties for its complexes. Despite the isotropicity of a discrete $Gd^{3+}$ ion, however, a ferromagnetic ground state has been discovered in its complexes [8], and this is one more reason for studying the magnetic properties of gadolinium compounds.

The goals of this work were: to expand the number of lanthanide cymantrenecarboxylate complexes by using pyridine as an ancillary coordinating ligand; to consider the influence of structural variations on the magnetic properties of gadolinium

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cymantrenecarboxylates; to provide a deeper insight into the thermal behavior of the newly prepared complexes and the complexes we prepared earlier [6]; and to study the volatility and the photoluminescent properties of lanthanide cymantrenecarboxylates.

## 2. Experimental

### 2.1. Materials and physical methods

The following commercially available reagents and solvents were used for the syntheses: hydrated lanthanide nitrates $Ln(NO_3)_3\cdot6H_2O$ from Alfa Aesar, cymantrene from Aldrich, and solvents (MeOH, $C_5H_5N$, and $C_6H_5Me$) from Alfa Aesar. Carboxycymantrene was prepared according to a known procedure [9]. Before use in the synthesis, the carboxycymantrene was sublimed in vacuo to remove traces of $Mn^{2+}$. All experiments with solutions of the compounds were carried out in foil-wrapped vessels to prevent photolysis. Methanol was dehydrated before use by distillation over magnesium; pyridine was distilled over KOH; toluene was successively distilled over $P_2O_5$ and sodium. Microanalyses were carried out on a Euro Vector CHN Elemental Analyser (Model EA 3000). The presence of manganese and lanthanides in the complexes and the 3:1 ratio of the metals were confirmed by ICP-AES analysis on an IRIS Advantage spectrometer. IR spectra were recorded in KBr pellets on a Spectrum-65LS (Perkin–Elmer) FT-IR instrument. Attenuated total reflection infrared (ATR-IR) spectra were recorded on a Nexus (Nicolet) FT-IR spectrometer in the range 4000–550 $cm^{-1}$ using a MIRacle (Pike) attachment. UV–Vis spectra were recorded on a Varian Cary-100 spectrophotometer in the range 200–900 nm. Photoluminescence (PL) measurements were performed on an LS55 (Perkin–Elmer) spectrometer in the range 200–900 nm at room temperature with resolution of 0.5 nm; the slit width was varied from 4 to 10 nm. An attachment for luminescence measurements in solids was used.

Vapor formation was studied by the Knudsen effusion method with mass-spectrometric analysis of the gas phase composition (hereinafter, Knudsen effusion mass spectrometry) in the temperature range 340–680 K (67–407 °C) using an MS 1301 instrument. Standard effusion cells with a ratio of the evaporation area to the effusion area of ~600 were used in this study. Temperature was measured by a Pt–Pt(Rh) thermocouple with a constant accuracy of ±1°. The mass spectra of $[Gd_2(\mu_2\text{-}OOCCym)_4(OOCCym)_2(THF)_4]\cdot THF$ and $[Eu_2(\mu\text{-}O,\eta^2\text{-}OOCCym)_4(OOCCym)_2(py)_4]\cdot2py$ (an electron impact; 70 eV) were taken on a Finnigan MAT INCOS instrument.

Magnetochemical measurements were performed on a Quantum Design MPMS-XL magnetometer (for complex **4**) and a Quantum Design PPMS-9 magnetometer (for $[LnL_3]$ (L = OOCCym, Ln = Nd or Gd) in the temperature range 2–300 K in a 5-kOe magnetic field. The paramagnetic susceptibility $\chi$ component was determined taking into account the diamagnetic contribution evaluated from Pascal's constants. The temperature-dependent effective magnetic moment was calculated as $\mu_{eff} = [(3k/N\beta^2)\cdot\chi T]^{1/2} \approx (8\chi T)^{1/2}$, where $N$ is Avogadro's number, $k$ is the Boltzmann constant, and $\beta$ is the Bohr magneton.

### 2.2. Synthesis of $[Ln_2(\mu\text{-}O,\eta^2\text{-}OOCCym)_2(\mu_2\text{-}OOCCym)_2(\eta^2\text{-}OOCCym)_2(py)_4]\cdot2py$, Ln = Pr (1), Sm (2), Eu (3), and Gd (4)

Cymantrenecarboxylic acid CymCOOH (310 mg, 1.25 mmol) and KOH (70 mg, 1.25 mmol) were dissolved in methanol (4 mL). The solution was stirred for 20 min at room temperature. Then a solution of 0.417 mmol $Ln(NO_3)_3\cdot6H_2O$ (182 mg for Ln = Pr; 185 mg for Ln = Sm; 186 mg for Ln = Eu; and 188 mg for Ln = Gd) in methanol (4 mL) was added. A precipitate formed in a few

minutes. The mixture was stirred for 20–24 h under argon atmosphere. Then the reaction mixture was concentrated to dryness in vacuo using a water-jet pump. The dry residue was treated with hot (~70 °C) pyridine (4–5 mL), toluene (5–6 mL) was added, and the mixture was filtered in vacuo through a glass filter. The resulting solution was vacuum concentrated to a volume of 3–4 mL using a water-jet pump without heating. For the europium derivative, the onset of crystallization of the product was noticed after 1-day exposure at room temperature; for the derivatives of the other lanthanides, exposure of the solution at −18°C was required. The crystallization took several days. The yield was 65–70%.

For **1**, Anal. Calc. for $C_{84}H_{54}Pr_2Mn_6N_6O_{30}$: C, 45.07; H, 2.43; N, 3.75. Found: C, 45.23; H, 2.37; N, 3.68%. IR of **1**, (KBr $cm^{-1}$): 3100 w, 2935 w, 2025 s, 1931 vs 1662 m, 1600 m, 1574 s, 1483 m, 1397 s, 1363 m, 1219 w, 1197 w, 1070 w, 1061 w, 1037 m, 1004 w, 925 w, 851 w, 800 m, 780 w, 701 w, 668 m, 633 s, 543 m, 490 w, 462 m.

For **2**, Anal. Calc. for $C_{84}H_{54}Sm_2Mn_6N_6O_{30}$: C, 44.69; H, 2.41; N, 3.72. Found: C, 44.57; H, 2.35; N, 3.65%. IR of **2**, (KBr $cm^{-1}$): 3102 w, 2939 w, 2026 s, 1930 vs, 1660 m, 1615 m, 1574 m, 1485 m, 1399 m, 1363 m, 1219 w, 1197 w, 1109 w, 1058 w, 1036 m, 927 w, 851 w, 798 m, 777 w, 696 w, 668 m, 634 s, 542 m, 491 w, 460 m.

For **3**, Anal. Calc. for $C_{84}H_{54}Eu_2Mn_6N_6O_{30}$: C, 44.62; H, 2.41; N, 3.72. Found: C, 44.54; H, 2.31; N, 3.63%. IR of **3**, (KBr $cm^{-1}$): 3114 w, 2934 w, 2021 s, 1930 vs, 1664 m, 1611 m, 1573 m, 1484 m, 1396 m, 1363 m, 1223 w, 1198 w, 1108 w, 1058 w, 1037 m, 926 w, 852 w, 799 m, 777 w, 696 w, 667 m, 634 s, 543 m, 490 w, 464 m.

For **4**, Anal. Calc. for $C_{84}H_{54}Gd_2Mn_6N_6O_{30}$: C, 44.42; H, 2.40; N, 3.70. Found: C, 44.49; H, 2.34; N, 3.66%. IR of **4**, (KBr $cm^{-1}$): 3110 w, 2935 w, 2022 s, 1934 vs, 1664 m, 1610 m, 1573 m, 1488 m, 1396 m, 1364 m, 1224 w, 1200 w, 1109 w, 1060 w, 1036 m, 924 w, 850 w, 800 m, 780 w, 700 w, 668 m, 632 s, 544 m, 488 w, 464 m.

### 2.3. X-ray data collection

X-ray data sets for complexes **1** and **4** were collected on a Bruker SMART APEX II diffractometer equipped with a CCD camera and a graphite-monochromated Mo Kα radiation source [10]. Semi-empirical absorption corrections were applied for all complexes [11]. The structures were solved by direct methods and using Fourier techniques and were refined by the full-matrix least squares against $F^2$ with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were positioned geometrically and refined using the riding model. All calculations were carried out with the use of the SHELX97 program package [12]. The crystallographic parameters and the refinement statistics are given in Table 1.

Unit cell parameters derived from XRD data for a crystal of complex **2** are as follows: triclinic $P\bar{1}$, $a = 12.002(5)$, $b = 12.803(5)$, $c = 15.961(6)$ Å, $\alpha = 75.615(7)°$, $\beta = 70.552(11)°$, $\gamma = 72.326(9)°$, $V = 2174.3(3)$ Å$^3$. Unit cell parameters derived from XRD data for a crystal of complex **3** are as follows: triclinic $P\bar{1}$, $a = 12.043(3)$, $b = 12.822(4)$, $c = 15.941(4)$ Å, $\alpha = 75.782(5)°$, $\beta = 70.707(5)°$, $\gamma = 72.017(8)°$, $V = 2181.3(1.6)$ Å$^3$.

The X-ray powder diffraction analysis of the solid products of decomposition in air was carried out on a G670 (HUBER) Guinier camera (Cu Kα1 radiation). The X-ray powder diffraction analysis of the solid products of decomposition under an inert atmosphere was carried out on an FR-552 monochromator camera (Cu Kα1 radiation) using germanium as the internal standard (X-ray diffraction patterns were processed on an IZA-2 comparator with an accuracy of ±0.01 mm).

### 2.4. Thermal analysis

The thermal decomposition of complexes **1** to **4** was studied by differential scanning calorimetry (DSC) and thermogravimetry