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# Lanthanide 5-sulfosalycilates and 3-amino-5-sulfosalycilates: Synthesis and estimation of thermal stability

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ABSTRACT

Trivalent lanthanum, europium, terbium, erbium and lutetium 5-sulfosalycilates and terbium, europium and holmium 3-amino-5-sulfosalycilates have been synthesized with their composition studied using thermogravimetric, IR and quantum chemical analysis. Quantum chemical calculations were performed for anhydrous complexes. According to calculated data, coordination of La and Lu with 5-sulfosalycilic acid anion via carboxylic oxygen is more favorable compared to coordination via sulfonate oxygen, while the reverse situation is observed for Eu, Tb and Er 5-sulfosalycilates. In the case of Ho 3-amino-5-sulfosalycilate metal atom is coordinated by both groups while coordination via sulfonate group appears to be more preferable for Eu and Tb 3-amino-5-sulfosalycilates.

A good correlation ($R^2 = 0.96$) was found between calculated Ln–$O_{ligand}$ bond energy and temperature of complex decomposition, thus showing that semi-empirical methods can be used for preemptive estimation of thermal stability of lanthanide complexes. Synthesized compounds have potential as anti-exhaust additives to diesel fuel as their decomposition correspond with formation of soot particles, thus, inhibiting their growth.



## 1. Introduction

Lanthanide complexes with organic ligands are widely used as active substances of magnetic materials, catalysts and photoelectric cells [1–8]. Their potential biological activity is also a subject of intense study [9–11]. Lanthanide compounds can also be as additives to diesel fuel and lubricant oil as they allow improving ecological characteristics of diesel engines by ensuring complete combustion of soot, decreasing amount of carbon residue in oil tank and reducing concentration of hazardous and toxic products in exhaust gases [12–14]. One of the most prominently used additives is cerium dioxide [15] due to its remarkable redox properties arising from non-stoichiometric behavior. In addition, the presence of $CeO_2$ can promote the conversion of carbon monoxide (CO) into hydrocarbons and water, besides converting nitrogen oxides into $N_2$, showing very promising results [15]. Other lanthanides can also be used as efficient additives, f.e., erbium 2-sulfobenzoate, which dissolves rather well in diesel oil, reduces CO concentration in exhaust gases by 30–40% and opacity of such gases by up to 44% [16].

There are many papers dedicated to studying structure and physico-chemical properties of trivalent lanthanide (Ln) complexes both in solid state and in various solutions. However, theoretical study of such substances is performed much more rarely due to various difficulties with correct quantum chemical modeling of Ln (III) complexes, i.e. presence of partially or fully filled 4f-electron energy level, relativistic effect and high coordination numbers (usually, 8 or 9) of $Ln^{3+}$ ions [17,18]. However, according to Freire et al. [19], it is be possible to calculate structure of a substance using semi-empirical methods. His group and other researchers successfully used Sparkle approximation in order to calculate ground state geometry of lanthanide complexes [19–21]. Although, this algorithm was tested with PM6 semi-empirical basis set [19], further studies have shown that it can also be used with AM1 [20] and PM3 [21] basis sets while retaining the accuracy. Calculated geometry correlates rather well with crystallographic data and allows evaluating several practically significant physical and chemical properties of such complexes in a very short time compared to DFT methods or ab initio analysis. Therefore, our aim was to study thermal stability of lanthanide complexes with

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5-sulfosalycilic and 3-amino-5-sulfosalycilic acids using both physicochemical and quantum chemical methods.

## 2. Experimental part

### 2.1. Reagents

The following chemicals were used in this study: analytical grade 5-sulfosalycilic and 3-amino-5-sulfosalycilic acids recrystallized from aqueous solutions prior to synthesis; chemically pure lanthanide (La, Eu, Tb, Er, Ho and Lu) chlorides; 30% aqueous ammonia solution (chemically pure).

### 2.2. Synthesis of 5-sulfosalycilates

5-Sulfosalycilates were synthesized by gradually adding $10^{-2}$ moles of solid lanthanide (La, Eu, Tb, Er and Lu) chlorides or carbonates to excessive amount of 5-sulfosalycilic acid aqueous solution heated to 75 °C. After that the solution was cooled down to 25 °C and left for 1–3 days (depending on the metal) until complete precipitation of colorless sulfosalycilate crystals. The precipitates were rinsed with distilled water until negative reaction to $Cl^-$ anion (via addition of 0.1 M solution of silver (I) nitrate to the filtrate) and left for drying at room temperature.

### 2.3. Synthesis of 3-amino-5-sulfosalycilates

Holmium and terbium 3-amino-5-sulfosalycilates was obtained via ammonium salt of 3-amino-5-sulfosalycilic acid because solubility of the acid itself in water is low (less than 0.01 g/100 g of water) [22]. Ammonium salt was obtained by adding concentrated (30%) aqueous ammonia solution to the acid ($3 \cdot 10^{-2}$ moles) until its complete dissolution. Obtained solution was added to aqueous Ln chloride solution ($2 \cdot 10^{-2}$ moles) with pH monitored by pH-meter. Synthesis of Ho 3-amino-5-sulfosalycilate ended with pH = 4.1–4.4 while synthesis of Tb and Eu complexes ended with pH = 4.7 (if necessary, pH can be adjusted with hydrochloric acid aqueous solution). Solutions were then placed into a dark place for crystallization. Crystals of formed salts were rinsed with distilled water and ethanol and left for drying at room temperature.

### 2.4. Methods of characterization

Chemical composition of synthesized compounds was established using methods provided in paper [22]. Results are provided in Table 1.

Thermogravimetric analysis was performed using MOM Q-1500 D (Paulik–Paulik–Erdey) derivatograph. Sample weight was 200 mg, heating rate – 10 °C per second.

IR spectral analysis was performed using Nicolet 6700 FT-IR spectrometer.

### 2.5. Quantum chemical calculations

Geometry and electronic structure of synthesized compounds was calculated using semi-empirical SPARKLE/AM1 [19], SPARKLE/PM3 [20] и SPARKLE/PM6 [21] methods implemented in MOPAC2012 software [23,24].

## 3. Results and discussion

### 3.1. Thermogravimetric analysis

According to thermogravimetric data, character of thermal decomposition of synthesized 5-sulfosalycilates is similar, so it was decided to provide detailed description only for lanthanum compound (Fig. 1S (1) in Supporting Information). Primary thermogravimetric parameters of 1st and 2nd stages of thermal decomposition are provided in Table 1S in Supporting Information.

Synthesized lanthanum 5-sulfosalycilate is stable up to 70 °C. Derivative thermal analysis (DTA) curve shows an intensive endothermic peak at 130 °C corresponding to complex dehydration resulting in loss of 7.4 mol of water (14% weight loss). Further decomposition is accompanied with two endothermic peaks at 200 and 290 °C followed by exothermic effect (with maximum at 450 °C) corresponding to decomposition of organic ligands. Derivative thermogravimetric analysis (DTG) curve drifts at the aforementioned temperature range with peaks present at 210, 290 and 450 °C points that correlate with aforementioned DTA curve effects. Formation of complete product (lanthanum oxosulfate) occurs at 755–1000 °C temperature range while exothermic effect at 780 °C corresponding to oxidation of intermediate compound.

Thermal decomposition of synthesized 3-amino-5-sulfosalycilates is a three-stage process comprised of dehydration, decomposition of anhydrous salt accompanied by formation of intermediate products and formation of final product (lanthanide oxosulfate). Primary characteristics of 1st and 2nd stages of aforementioned process are provided in Table 2S in Supporting Information.

Dehydration of Ho 3-amino-5-sulfosalycilate starts at 30° (Fig. 1S (**2**)). DTA curve shows an endothermic effect with two peaks at 110 °C and 160 °C corresponding to two-staged complex dehydration. The similar peaks are also observed on DTG curve. Weight loss after first stage of dehydration is equal to 7% which correlates to evaporation of 3.2 mol of water with additional 4 mol of water evaporated during the second stage (16% weight loss). The TG curve does not have any defined platform corresponding to existence of anhydrous salt: endothermic dehydration

**Table 1**
Element analysis of synthesized compounds

| Chemical formula | Content (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Lanthanide | | Carbon | | Hydrogen | | Sulfur | |
| | [a] Act. | [b] Exp. | Act. | Exp. | Act. | Exp. | Act. | Exp. |
| $La(C_7H_5O_5S)_3{\cdot}9H_2O$ | 15.2 | 15.3 | 27.6 | 27.9 | 3.46 | 3.67 | 10.4 | 10.6 |
| $Eu(C_7H_5O_5S)_3{\cdot}7H_2O$ | 17.5 | 17.2 | 28.7 | 28.6 | 3.66 | 3.31 | 10.5 | 10.9 |
| $Tb(C_7H_5O_5S)_3{\cdot}7H_2O$ | 18.1 | 17.9 | 28.5 | 28.4 | 3.55 | 3.29 | 10.4 | 10.8 |
| $Er(C_7H_5O_5S)_3{\cdot}9H_2O$ | 17.8 | 17.9 | 26.8 | 27.0 | 3.32 | 3.56 | 10.0 | 10.3 |
| $Lu(C_7H_5O_5S)_3{\cdot}9H_2O$ | 18.5 | 18.6 | 26.5 | 26.8 | 3.31 | 3.53 | 9.98 | 10.2 |
| $HoH(C_7H_5O_5NS)_2{\cdot}8H_2O$ | 22.1 | 22.3 | 22.2 | 22.7 | 3.57 | 3.78 | 8.58 | 8.66 |
| $Eu_2(C_7H_5O_5NS)_3{\cdot}13H_2O$ | 25.5 | 25.7 | 21.1 | 21.3 | 3.54 | 3.49 | 7.99 | 8.13 |
| $Tb_2(C_7H_5O_5NS)_3{\cdot}13H_2O$ | 26.2 | 26.5 | 20.9 | 21.1 | 3.23 | 3.45 | 7.91 | 8.03 |

[a] Actual.
[b] Expected.