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# THERMAL PROPERTIES OF LANTHANIDE(III) COMPLEXES WITH 2-AMINOTEREPHTHALIC ACID

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The complexes of yttrium(III) and lanthanides(III) with 2-aminoterephthalic acid form the isostructural series of triclinic compounds with a space group $P\bar{1}$ from La to Lu and they have the general formula of $Ln_2(C_8H_5O_4N)_3{\cdot}8H_2O$. On heating in air or inert gas atmosphere they lose all water molecules in the temperature range 50–200°C in one or two steps. The anhydrous compounds are stable from 360 to 435°C and then decompose to oxides.

***Keywords:*** *2-aminoterephthalates, lanthanide complexes, powder analysis, TG/DTA analysis, X-ray*

## Introduction

Coordination polymers known as metal-organic coordination networks or metal-organic frameworks are the compounds that extend infinitely into one, two or three dimensions. The ligands used in the construction of coordination polymers should be bridging metal ions, which usually requires multidentate ligands [1–4]. One of the types of multidentate ligands for constructing coordinated polymers are polycarboxylic aromatic acids or additionally, one or two amino groups attached to the aromatic ring [5, 6]. The carboxylic groups may bond the metal ions in different modes – chelating, bridging, mono-, bi-, tri- or tetradentate [7–9].

Lanthanide ions display diverse coordination modes, which result in their high and variable coordination numbers and can construct high-dimension coordination polymers. A few lanthanide coordination polymers have been successfully synthesized [8, 10–12]. Recently the problem of synthesis the coordination polymers capable of a selective gas sorption has met with great interest [13, 14].

2-aminoterephthalic acid, as good organic building block for construction of extended open framework, was used to obtain the coordination polymer with the lanthanide ions. The crystals of some lanthanide complexes were obtained under hydrothermal conditions and the structures of Pr(III), Eu(III), Tb(III) [10], Nd(III) [12] and Dy(III) [11] 2-aminoterephthalate, were reported. In the structure of complexes only carboxylate groups of 2-aminoterephthalic acid take part in metal bonding. Some carboxylate anions chelate metal ions to form 1D chains and others bridge metal ions to link the adjacent layer. These ligands linking lanthanide ions construct one-dimension channels [10–12]. In the coordination sphere of each lanthanide ion there are eight oxygen atoms, six from organic ligands and two from water molecules. So two water molecules are bonded to lanthanide ions to complete the coordination sphere to eight and the others are hydrogen bonded in the outer coordination sphere of complex. The amino group, which cannot coordinate a metal ion in this polymer, is of importance for the channel structure of complexes. The amino group asymmetrically attached to ligand increases steric hindrance leading to the open framework [11]. The amino group favors formation of hydrogen bonds with water molecules, resulting in hydrogen bonded water (guest water molecule) accommodating in channels to decrease surface energy of the channel structure and enhance the stability of the open framework [11].

The aim of this paper is to obtain the series of lanthanide complexes with 2-aminoterephthalic acid under the standard conditions to produce complexes in order to investigate their dehydration process and the range of anhydrous complexes thermal stability.

## Experimental

### *Synthesis*

The complexes of all lanthanides(III) from La to Lu (except Ce) were prepared in the reaction of 0.1 M solution of 2-aminoterephthalic acid ammonium salt added dropwise into 0.1 M the lanthanide chloride solutions with constant stirring; in the case of cerium(III) the nitrate solution was used. The temperatures of

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reacting solutions were always in the range of 80–90°. The resulting light brown precipitates were stirred in the mother solution maintaining those temperatures for an hour, then filtered off, washed with hot water to remove ammonium ions and dried at 30°C to a constant mass. All reagents were used in the commercial form. Lanthanide oxides and 2-aminoterephthalic acid were Aldrich products.

### *Methods*

The C, H and N elemental analysis was performed for all complexes using the Perkin–Elmer 2400 instrument. The contents of lanthanide were found by the TG method. The analytical data for some of $Ln_2(C_8H_5O_4N)_3\cdot 8H_2O$ complexes are: Sm: Calc. C=29.32; H=3.16; N=4.28; Sm=30.62. Found: 31.0; 3.3; 4.4; 31.0 Gd: Calc. C=28.92; H=3.11; N=4.22; Gd=31.58. Found: 29.0; 3.2; 4.3; 32.5 Tm: Calc. C=28.25; H=3.04; N=4.12; Sm=33.14. Found: 28.5; 3.0; 4.2; 33.6

IR spectra of the complexes were recorded over the range of 4000–400 $cm^{-1}$ by using a FTIR 1725X Perkin Elmer spectrophotometer. The samples were dispersed in KBr discs (2.5 mg of sample in 50 mg of KBr).

X-ray diffraction patterns were taken on a Seifert-DRON automated X-ray diffractometer ($2\theta=5–72°$) at ambient temperature. Pattern indexing was carried out with the PC-version of TREOR program [15].

Thermal stability of the complexes was investigated by means of a Setsys 16/18 (Setaram) thermal analyzer, recording TG, DTA and DTG curves. The samples (9–10 mg) were heated in the ceramic crucible at 30–1000°C in the flowing air atmosphere ($\nu=1$ $dm^3$ $h^{-1}$) with a heating rate of 10°C $min^{-1}$. The products of decomposition were determined from the TG curves. The dehydration process of complexes was studied in detail by the TG technique on the CAHN TG-121 thermobalance, in the range 20–400°C in helium atmosphere.

Gaseous products of decomposition were identified using a Netzsch TG 209 apparatus coupled to a Brucker FTIR IFS 66 spectrophotometer. The samples were heated in a dynamic argon atmosphere using a ceramic crucible and heating with a rate of 10°C $min^{-1}$ up to 600°C.

## Results and discussion

### *Synthesis*

Solid complexes of lanthanide(III) 2-aminoterephthalates were obtained as light brown, crystalline compounds with the metal:ligand ratio of 2:3 and the general formula $Ln_2(C_8H_5O_4N)_3\cdot 8H_2O$. Their resulting precipitates are very sensitive to the conditions of reaction synthesis. It was stated, that the complexes obtained at a temperature below 80°C are characterized by changing, unstable hydration degree and retain great amounts of ammonia from the solution. Ammonia molecules are so strongly linked in the structure, that it is impossible to remove them during precipitates washing with water. They may only be removed from the complex structure when heated above 160°C. Complete removal of ammonia occurs at 340°C, however at this temperature the decarboxylation process begins. Preparation of 2-aminoterephthalates from water solutions at a temperature higher than 80°C cannot permit to bind ammonia molecules and in the channels of complex structures there are only hydrogen bonded water molecules.

### *X-ray diffraction analysis*

All lanthanide 2-aminoterephthalates, light as well as heavy ones, crystallize in the triclinic type of structure (Table 1). In this series of complexes only elemental cell volume decreases from 874 $Å^3$ for the La(III) complex to 832 $Å^3$ for the Tm(III) complex. Maybe, the same structure of complexes results from the symmetric position of carboxylate groups in the organic ligand as well as from the presence of amino group. As follows from the general structural investigations the complexes are of polymeric character due to organic ligand having two carboxylic groups that may coordinate lanthanide ions in different ways [7–9]. The structure of some lanthanide complexes with 2-aminoterephthalic acid was described by Haitao *et al.* [10]. It is interesting that both carboxyl groups of each ligand are in the same coordination fashion. Some carboxylate anions chelate metal ions to form 1D chains along the x-axis, others bridge metal ions to link the adjacent layers along the y-axis. These ligands linking lanthanide ion centers construct

**Table 1** The unit cell parameter for hydrated 2-aminoterephthalates of lanthanum, gadolinium and thulium ($L=C_8H_5O_4N^{2-}$)

| | $La_2L_3\cdot 8H_2O$ | $Gd_2L_3\cdot 8H_2O$ | $Tm_2L_3\cdot 8H_2O$ |
|---|---|---|---|
| Crystal system | triclinic | triclinic | triclinic |
| $a$/Å | 9.43 | 9.54 | 9.35 |
| $b$/Å | 10.82 | 10.23 | 10.64 |
| $c$/Å | 10.87 | 10.40 | 10.83 |
| α/degree | 117.26 | 110.70 | 119.70 |
| β/degree | 106.12 | 95.46 | 107.62 |
| γ/degree | 117.12 | 109.89 | 116.86 |
| Volume ($Å^3$) | 874 | 865 | 832 |

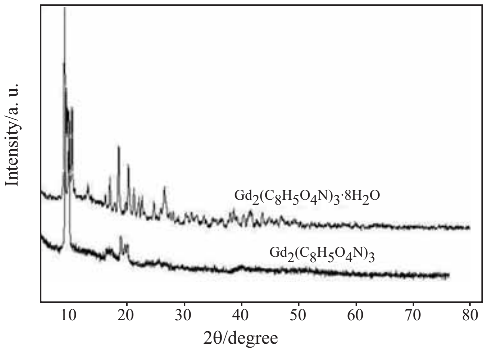

**Fig. 1** X-ray powder diffraction patterns of hydrated and anhydrous 2-aminoterephthalate of gadolinium

one-dimension channels (12Å·7Å) pending function groups linking external water molecules via the hydrogen bond along the y-axis. So the complex structures contain chelating and bridging carboxyl groups. The coordination number in these structures is eight for each lanthanide ion through six oxygen atoms from the organic ligand and two from water molecules. Next two water molecules are in the external coordination sphere [10].

In order to determine the structural changes during dehydration the hydrated lanthanide 2-aminoterephthalates were heated in air up to 150°C with a heating rate of 5°C $min^{-1}$. The anhydrous compounds were obtained. Figure 1 shows the X-ray diffractogram of anhydrous 2-aminoterephthalate of Gd(III), as a representative for all isostructural groups of lanthanide complexes. As follows from the diffractograms in Fig. 1 the anhydrous complex is not isostructural with the 8-hydrate complex and has a smaller degree of crystallinity. The small amounts of diffractogram peaks do not permit to determine the structure of anhydrous complex.

### *Thermal analysis*

The complexes are stable at room temperature and heated in air decompose at 50°C. The complexes after dehydration which is over in the range 160–200°C are stable to the range 320–440°C. At first the dehydration process takes place and the TG curve shows loss of mass by about 14–15% which corresponds to loss of eight water molecules per a dimeric unit of polymeric structure (Table 2). After the loss of all water molecules at 160–200°C anhydrous compounds are formed and the TG curve shows plateau till 320–440°C that indicates a wide range of stability of anhydrous compounds. On the DTG curve one can distinguish two steps – the first peak at a lower temperature is due to the loss of external, more weakly bonded hydrogen water molecules and it is associated with small endoeffect on the DTA curve at 105°C. The second peak on the DTG curve originates from the loss of four coordination water molecules associated with stronger endoeffect on the DTA curve at 135°C (Fig. 2). The two steps of dehydration process are clearly visible in the case of lanthanum complex decomposition and fade in the lanthanide series. The samarium complex loses hydrogen bonded and

**Table 2** Thermal decomposition of lanthanides(III) and Y(III) complexes with 2-aminoterephthalic acid (air atmosphere)

| Complex | $M_{mol}$ | $\Delta T$/°C | Loss of mass/% | | $T_b$/°C | $T_o$/°C | Residue/% | |
|---|---|---|---|---|---|---|---|---|
| | | | Calcd. | Found | | | Calcd. | Found |
| $La_2L_3 \cdot 8H_2O$ | 958.8 | 50–160 | 15.02 | 15.3 | 320 | 857 | 33.96 | 33.3 |
| $Ce_2L_3 \cdot 8H_2O$ | 561.24 | 50–165 | 14.98 | 15.2 | 340 | 820 | 34.13 | 33.9 |
| $Pr_2L_3 \cdot 8H_2O$ | 962.8 | 50–175 | 14.96 | 14.6 | 345 | 810 | 35.35 | 35.6 |
| $Nd_2L_3 \cdot 8H_2O$ | 969.48 | 50–175 | 14.85 | 14.5 | 345 | 810 | 34.69 | 35.0 |
| $Sm_2L_3 \cdot 8H_2O$ | 981.72 | 50–200 | 14.67 | 14.4 | 385 | 820 | 35.51 | 35.5 |
| $Eu_2L_3 \cdot 8H_2O$ | 984.92 | 50–170 | 14.62 | 14.4 | 375 | 810 | 35.72 | 36.0 |
| $Gd_2L_3 \cdot 8H_2O$ | 995.5 | 50–165 | 14.46 | 14.0 | 375 | 810 | 36.40 | 36.3 |
| $Tb_2L_3 \cdot 8H_2O$ | 998.86 | 50–165 | 14.42 | 14.2 | 375 | 840 | 37.41 | 37.2 |
| $Dy_2L_3 \cdot 8H_2O$ | 1006 | 50–160 | 14.31 | 14.2 | 380 | 810 | 37.06 | 37.5 |
| $Ho_2L_3 \cdot 8H_2O$ | 1010.8 | 50–165 | 14.25 | 14.3 | 395 | 810 | 37.36 | 37.5 |
| $Er_2L_3 \cdot 8H_2O$ | 1015.5 | 50–160 | 14.18 | 14.1 | 400 | 800 | 37.65 | 37.9 |
| $Tm_2L_3 \cdot 8H_2O$ | 1018.86 | 50–170 | 14.13 | 14.0 | 435 | 800 | 37.85 | 37.0 |
| $Yb_2L_3 \cdot 8H_2O$ | 1027 | 50–175 | 14.02 | 14.2 | 435 | 810 | 38.35 | 38.5 |
| $Lu_2L_3 \cdot 8H_2O$ | 1030.94 | 50–175 | 13.96 | 14.1 | 440 | 800 | 39.98 | 39.7 |
| $Y_2L_3 \cdot 8H_2O$ | 858.82 | 50–160 | 16.77 | 17.0 | 320 | 750 | 26.45 | 27.0 |

$\Delta T$ – temperature range of dehydration process; $T_b$ – temperature of beginning of decomposition; $T_o$ – temperature of oxide formation

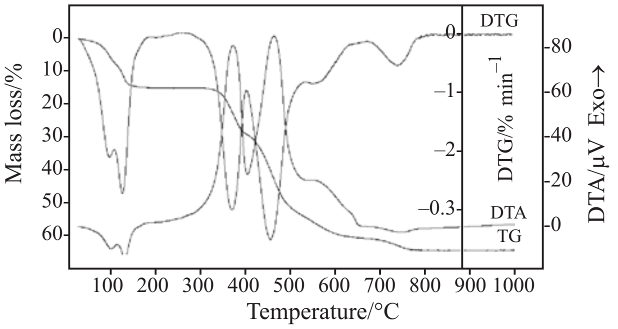

**Fig. 2** TG, DTG and DTA curves of $La_2(C_8H_5O_4N)_3·8H_2O$, (β=10°C min$^{-1}$, air atmosphere)

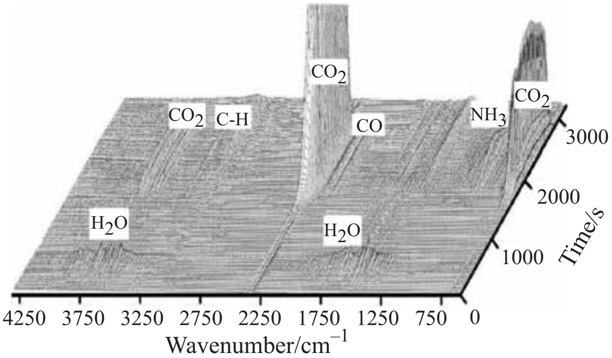

**Fig. 3** FTIR spectra of gaseous products of thermal decomposition of $Gd_2(C_8H_5O_4N)_3·8H_2O$

coordination water molecules with endoeffects at 110 and 125°C but in the thulium complex the first step is very poorly visible but the second one is well seen at 120°C on the DTA curve. The dehydration process was investigated also in neutral gases like helium and argon. The DTG curves show also two steps of dehydration process. The anhydrous complexes are stable in air up to 320–440°C and when heated decompose to lanthanide oxides at above 800°C.

Gaseous products of complex decomposition in the argon atmosphere were identified by the IR spectra analysis that was carried out for gadolinium complex of the formula $Gd_2(C_8H_5O_4N)_3·8H_2O$, representative for the isostructural series. As follows from Fig. 3 at

**Table 3** Frequencies for characteristic absorption bands in the IR spectra of some lanthanide(III) complexes with 2-aminoterephthalic acid ($L=C_8H_5O_4N^{2-}$)

| $H_2L$ | $La_2L_3·8H_2O$ | $Gd_2L·8H_2O$ | $Tm_2L_3·8H_2O$ | |
|---|---|---|---|---|
| 3507 | | | | $\nu_{as}(NH_2)$ |
| | 3600–2500 | 3600–2500 | 3600–2500 | ν(OH), ν(NH), ν(CH) |
| 3392 | | | | $\nu_s(NH_2)$ |
| 3200–2200 | | | | ν(OH), ν(CH) |
| 1690 | | | | ν(C=O) |
| | 1622 | 1624 | 1620 | δ(NH), $\delta(H_2O)$ |
| 1593 | | | | $\nu(CC)_{ar}$ |
| | 1547 | 1544 | 1555 | $\nu_{as}(COO^-)$ |
| 1555 | | | | δ(NH) |
| 1495, 1455 | 1500 | 1500 | 1500 | $\nu(CC)_{ar}$ |
| 1419 | | | | $\nu(CC)_{ar}$ |
| | 1420 | 1425 | 1430 | $\nu_s(COO^-)$ |
| | 1377 | 1381 | 1385 | $\nu_s(COO^-)$ |
| 1317 | 1335 | 1335 | 1330 | ν(CN) |
| 1234 | 1253 | 1254 | 1253 | ν(CN), ν(CO)* |
| 1160, 1122 | 1153 | 1155 | 1155 | $\beta(C_{ar}H)$ |
| | 961 | 963 | 966 | φ(CC) |
| 918 | | | | γ(OH) |
| 882, 832 | 894, 841 | 895, 848 | 895, 853 | $\gamma(C_{ar}H)$ |
| | 815 | 819 | 837 | γ(CH) |
| 783, 754 | 771 | 771 | 773 | δ(NH), $\gamma(C_{ar}H)$ |
| 691, 677 | 695 | 693 | 698 | φ(CC) |
| 588 | 580 | 581 | 585 | φ(CC) |
| 492 | 502 | 500 | 508 | φ(CC) |

*only for acid

first only dehydration process occurs which is reflected in the FTIR spectra of gaseous decomposition products. Characteristic valence and deformation vibration bands of water molecules appear in the range of 4000–3500 and 1750–1250 $cm^{-1}$, respectively. After removal of water the anhydrous complex is stable and heated does not release any gaseous products and the TG curve shows plateau. At 420°C large peaks for $CO_2$ in the range 2900–2250 and 750–600 $cm^{-1}$ appear. Release of $CO_2$ is due to decarboxylation of ligands and ends abruptly at 750°C. Simultaneously with carbon dioxide release the small amounts of CO are formed and characteristic bands of carbon oxide at 2160 and 2095 $cm^{-1}$ appear. Above 500°C the deamination of ligands occurs and the bands for $NH_3$ are observed in the range 750–1200 with characteristic double peak bands with the maxima at 966 and 931 $cm^{-1}$ (Fig. 3). At the same time, in the range 3000–2700 $cm^{-1}$ the bands of C–H hydrocarbons appear due to degradation of phenyl ring of ligand.

### *FTIR spectroscopy*

All the complexes were characterized by FTIR spectroscopy and compared with those of free acid and its sodium salt (Table 3). The whole series of 2-aminoterephthalate complexes is isostructural so the parameters of the absorption bands in the IR region are the same for all complexes. Small differences in the frequencies of IR bands equal to a few $cm^{-1}$ may be an effect of increasing ionic potential in the series from light to heavy lanthanides (2.83 for La to 3.53 for Lu).

During complex formation characteristic bands at 1690 $cm^{-1}$ for the protonated carboxylate groups disappear and the IR spectra of compounds show characteristic bands at 1564–1544 $cm^{-1}$ for the asymmetric vibrations and at 1430–1418 and 1386–1377 $cm^{-1}$ for the symmetric vibrations of carboxylate anions. The splitting of $\nu_s(COO^-)$ into two bands confirms that carboxylate groups have different coordination modes, chelating and bridging [16–20]. It was stated that increasing bond covalence in the lanthanide series is associated with decreasing $\Delta\nu$, (differences in $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ ). In the isostructural series of complexes, in which lanthanide ions have the same environments in each structure, the values of $\Delta\nu$ are 123–130 and 160–170 $cm^{-1}$ and do not show any evident decrease or increase in the lanthanide series.

Two sharp stretching asymmetric and symmetric vibrations of $NH_2$ group ($\nu_{as}NH_2$ and $\nu_sNH_2$) occur at 3507 and 3392 $cm^{-1}$ for free acid. The IR spectra of complexes show broad absorption bands in the range 2500–3600 $cm^{-1}$. These frequencies of complexes correspond to the OH stretching vibrations. These bands confirm the presence of water molecules linked by hydrogen bonds in complexes [12, 13]. In the case of strong hydrogen bonds the ν(N–H) and ν(OH) bands become very broad and intense. As in the case of OH stretching, the frequency of NH stretching is reduced by hydrogen bonding. The shifting of the frequency of the $\nu NH_2$ vibrations may indicate the presence of stronger hydrogen bonds in the complexes in comparison with those in the free acid [14].

## Conclusions

Concluding, the series of lanthanide complexes from La to Lu was obtained in the simple preparation way. It was stated that the whole series crystallizes in the triclinic system but differ in unit cell parameters. The complexes crystallize with eight water molecules, which are lost in one or two steps during heating in air or inert gas atmosphere. After the dehydration process, the anhydrous compounds are characterized by a wide stability range. They may become promising materials in further investigations on microporous coordination polymers.

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