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THERMAL PROPERTIES OF LANTHANIDE(III) COMPLEXES WITH 5-AMINO-1,3-BENZENEDICARBOXYLIC ACID

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The complexes of yttrium(III) and lanthanides(III) with 5-amino-1,3-benzenedicarboxylic acid form two isostructural series of compounds and have the general formula $Ln_2(C_8H_5O_4N)_3 \cdot nH_2O$, where n=13 for Y, La–Er and n=9 for Tm, Yb, Lu. They are insoluble in water and stable at room temperature. On heating in air or inert gas atmosphere they lose all water molecules in several steps. The anhydrous compounds are stable to about 400°C and next decompose to oxides.

Keywords: *5-amino-1,3-benzenedicarboxylates, 5-aminophthalates, lanthanide complexes, TG/DTA analysis, X-ray powder analysis*

Introduction

The combination of metal-organic coordination network based on the complexes of transition metals and polyfunctional bridging ligands is a new group of materials [1]. They form the interesting network topologies by formation of the open channels and because of that they have the potential applications in host-guest chemistry [2, 3], catalysis, electrical conductivity [4] and magnetism [5]. The design and synthesis of new supramolecular networks by coordinative covalent interactions have resulted in a variety of such frameworks with fascinating structural forms. The polycarboxylate ligands have been used to prepare the coordination polymer compounds [6, 7] of transition metals [8–10] and lanthanides [11–13]. Lanthanide(III) ions in polycarboxylic complexes have the high coordination number 8 or 9 and first of coordinate all with the oxygen atoms of carboxylate groups.

5-amino-1,3-benzenedicarboxylic ligand (5-aminoisophthalic) forms covalent bonds with metal ions, especially with transition metals through nitrogen atom of amino group as well as oxygen atoms of carboxylic groups [8–10] and with lanthanide ions as strong Pearsons acids through oxygen atoms of carboxylic groups [14]. Carboxylic groups of acid have a great ability to form infinite connection with metal ions and remarkable versatility in adopting different modes of bonding – from unidendate, chelating and bridging, sometimes in more than one way in the same compound [13]. Two carboxylate groups in 1- and 3-positions may be a bridging ligand for two, three or four metal ions by chelating or/and bridging character of carboxylate groups. Additionally, this ligand can form strong hydrogen bonds as a proton donor by amino groups and as proton acceptor by carboxylic groups of 5-aminoisophthalate ligand. Because of the benzene ring in the acid structure, the stacking interaction in the network of the complex structure is possible [14, 15].

In this paper we report on the syntheses and thermal properties of the lanthanide(III) complexes with 5-aminoisophthalic acid.

Experimental

Preparation of $Ln_2(C_8H_5O_4N)_3 \cdot nH_2O$

Because of insolubility of 5-aminoisophthalic acid in water, we prepared its ammonium salt (pH=6.5) to obtain the soluble form of the ligand. Ammonium salt of the acid was added to an aqueous solution of lanthanide chloride while stirring. The resulting precipitate of the compound was stirred for an hour at room temperature for recrystallization of powder crystal compound. Then the complex was filtered, washed with hot water to remove ammonium ions (Nessler control) and dried at 30°C to constant mass for 2 days. The yield of this synthesis was about 98%. All reagents were used in the commercial form. Lanthanide oxides (with 99.9% purity) and 5-aminoisophthalic acid (with 94% purity) were obtained from Aldrich.

The C, H and N elemental analysis was performed for all complexes using the Perkin-Elmer 2400 instrument (data for: $Gd_2L_3 \cdot 13H_2O$ as representative for first isostructural group compounds Calc.: C, 26.32; H, 3.76; N, 3.87. Found: C, 26.5; H, 3.9; N, 3.8% and $Tm_2L_3 \cdot 9H_2O$ as representative for the second isostructural group compounds Calc.: C, 27.76; H, 3.18; N, 4.05. Found: C, 28.2; H, 3.3; N, 4.0%).

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The FTIR spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} by using a FT-IR 1725X Perkin Elmer spectrometer.

The X-ray diffraction patterns were taken on a Seifert – DRON automated X-ray diffractometer in the range 2θ=5–72° at the ambient temperature. Pattern indexing was carried out with the PC – version of TREOR program [16].

The thermal stability of the complexes was investigated with the aid of a Setsys 16/18 (Setaram) thermal analyzer as well the HR TA Instruments TG 2950 analyser in air or inert atmosphere (N_2, He), recording TG, DTA and DTG curves. The 5–10 mg samples were heated in a ceramic crucible from 30 to 1000°C with the heating rate of 100°C min^{-1}. The dehydration process was studied in detail by the TG technique on the CAHN TG-121 thermobalance, analyzer in the range 20–200°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 dynamic argon atmosphere using a ceramic crucible with a rate of 200°C min^{-1} up to 1000°C.

Results and discussion

5-amino-1,3-benzenedicarboxylates of Y(III) and lanthanides(III) from La to Lu were obtained as crystalline compounds with the metal:ligand ratio of 2:3 and the general formula of $Ln_2(C_8H_5O_4N)_3\cdot nH_2O$, where n=13 for the first isostructural series from La to Er and n=9 for the second of Tm, Yb and Lu(III) complexes. Figure 1 shows the X-ray diffraction patterns for both series of complexes and Table 1 gives the unit cell parameters of Gd(III) and Tm(III) complexes as representative for the two series.

The representative of isomorphic series of La–Er complexes is $Gd_2L_3\cdot 13H_2O$. The complex gadolinium(III) crystallizes in the monoclinic crystal system with the elemental cell parameters of a=17.73; b=10.66; c=11.35 Å and β=121.810°, volume of elemental cell is equal to 1823 Å^3. The stability of this framework is very weak and during dehydration at 250°C lanthanide-organic framework is destroyed. The anhydrous complex is amorphous.

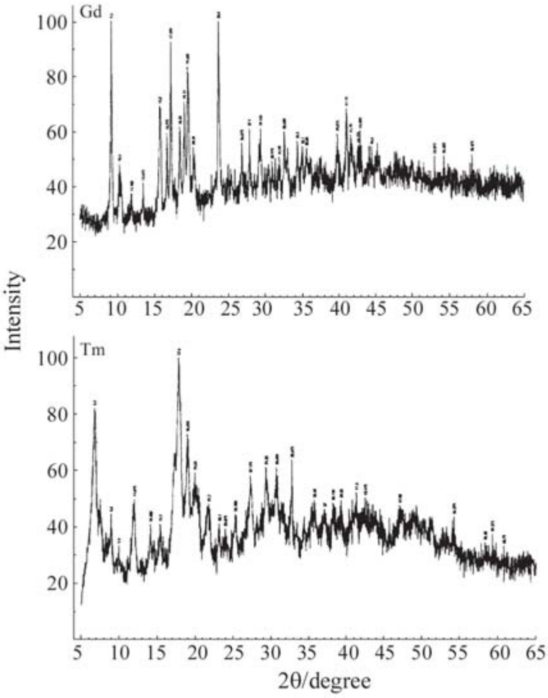

Fig. 1 X-ray powder diffraction patterns of $Gd_2L_3\cdot 13H_2O$ and $Tm_2L_3\cdot 9H_2O$ (L=$C_8H_5NO_4^{2-}$)

Table 1 The unit cell parameter for hydrated gadolinium and thulium (L=$C_8H_5NO_4^{2-}$)

Crystal system	$Gd_2L_3\cdot 13H_2O$	$Tm_2L_3\cdot 9H_2O$
	monoclinic	monoclinic
a/Å	17.73	21.84
b/Å	10.66	6.75
c/Å	11.35	12.30
α/°	90.00	90.00
β/°	121.81	100.28
γ/°	90.00	90.00
Volume/Å^3	1823	1785

The representative of isomorphic series of Tm–Lu complexes is $Tm_2L_3\cdot 9H_2O$. The complex thulium(III) crystallizes in the monoclinic crystal system with the elemental cell parameters a=21.84; b=6.75; c=12.30 Å and β=100.28°. The elemental cell volume is equal to 1785 Å^3. This compound heated to 200°C also loses all molecules of water and as before is destroyed resulting in an amorphous compound.

The complexes were characterized by FTIR spectroscopy. The spectra of complexes were compared with those of free acid and its sodium salt (Table 2). The 5-aminoisophthalic acid crystallized in the centrosymmetric space group C2/c as a zwitterion, one of carboxyl protons transferred to N atom of the amino group. Each acid molecule is directly linked to five acid molecules and to two water molecules by eight hydrogen bonds [17]. The characteristic carboxyl vibrations in the free 5-aminoisophthalic acid are found at 1700 cm^{-1} as strong and broad vibrations of the protonated carboxylic group COOH and also strong bands at 1400 and 1548 cm^{-1} assigned to the symmetric and asymmetric ν_{C-O} stretching vibrations of the other deprotonated carboxylic group of acid. Due to proton transfer from the carboxylic to the amino group and zwitterionic molecule formation in the IR spectrum the stronger bands assigned to NH_3^+ group with 2620 cm^{-1} were observed.

Table 2 Frequencies for characteristic absorption bands in the IR spectra of lanthanides(III), Y and Na(I) complexes with 5-aminoisophthalic acid (L=$C_8H_5NO_4^{2-}$)

Complex	ν_{OH}	ν_{COOH}	δ_{H_2O}	$\nu_{as(COO)}$	$\nu_{C–O}$	$\nu_{C\cdots C}$	$\nu_{C\cdots C}$	$\nu_{s(COO^-)}$	$\nu_{C–N}$	$\nu_{M–O}$	$\Delta\nu$
H_2L	3200–2500	1700	1628	1548	1592, 1452			1400	800, 752		
Na_2L	3392s			1568				1400			168
$La_2L_3\cdot13H_2O$	3392s		1608	1524		1480	1448	1392	776, 748	430	132
$Ce_2L_3\cdot13H_2O$	3432s			1536				1396	776		138
$Pr_2L_3\cdot13H_2O$	3344s		1608	1536		1480	1452	1396	776	440	138
$Nd_2L_3\cdot13H_2O$	3352s		1608	1524		1480	1448	1400	776, 748	440	124
$Sm_2L_3\cdot13H_2O$	3352s		1608	1532			1452	1400	776, 748	440	132
$Eu_2L_3\cdot13H_2O$	3352s		1608	1532		1480	1452	1400	776, 752	440	132
$Gd_2L_3\cdot13H_2O$	3344s		1608	1532		1480	1452	1400	776, 752	440	132
$Tb_2L_3\cdot13H_2O$	3344		1608	1524		1480	1460	1400	776, 752	450	124
$Dy_2L_3\cdot13H_2O$	3344		1612	1536			1464	1400	776, 752	450	136
$Ho_2L_3\cdot13H_2O$	3344		1608	1536			1456	1404	776, 752	450	132
$Er_2L_3\cdot13H_2O$	3344		1608	1532			1464	1404	776, 752	450	128
$Tm_2L_3\cdot9H_2O$	3384			1544				1400	780, 744	450	144
$Yb_2L_3\cdot9H_2O$	3416			1524			1464	1400	776, 744	450	124
$Lu_2L_3\cdot9H_2O$	3400			1536				1400	744	450	136
$Y_2L_3\cdot9H_2O$	3352		1608	1524		1464		1404	776, 752	440	120

In the spectra of the complexes, NH_3^+ band disappeared, and was replaced by NH_2 stretching bands at the 3300 cm^{-1}. During coordination of metal ions, also the bands at 1700 cm^{-1} disappear in the spectra of complexes and only symmetric and asymmetric bands of the COO^- groups appear. The single asymmetric vibration bands of COO^- groups are present at 1524–1536 cm^{-1} and symmetric vibration bands of COO^- groups are at 1392–1404 cm^{-1}. The $\Delta\nu_{COO^-}$ values for each complex of monoclinic La–Er(III) group are smaller than those of sodium salt and suggest the chelating character of carboxylate groups [18].

The splitting of asymmetric COO^- bands (about 1540 and 1570 cm^{-1}) in the spectra of Tm, Yb and Lu(III) complexes indicate that carboxylic groups in those complexes possess different coordination modes. For each complex of monoclinic Tm–Lu(III) group, there are two values of $\Delta\nu$ one of the same value as sodium salt and the other smaller than $\Delta\nu$ of sodium salt. It suggests bridging and chelating modes of coordination [19, 20]. Specific preference of lanthanide(III) ions for oxygen atoms as well as zwitterionic form of 5-aminophthalic ligands point to the fact, that the coordination of metal ion can occur only through oxygen atoms of COO^- groups but not through nitrogen atoms.

In a high energy region in the IR spectra there are the bands in the range 3500–3000 cm^{-1}, which indicates absorption peaks due to ν_{O-H} bonds of water molecules and ν_{N-H} bonds of amino group. These bands are associated with hydrogen bonds formation and change their positions with changing the hydrogen bond energy. In this case, shifting of these bands in the red region compared to the acid spectrum points to stronger and shorter hydrogen bonds in the complexes than those registered in the acid structure.

Thermogravimetric analyses were performed to investigate the thermal stability of the complexes under consideration. The results are presented in Table 3. The complexes include a great number of water molecules: six molecules of water on one metal ion. Taking into consideration a general rule in lanthanide complex binding, by the coordination number 8 or 9 of lanthanide(III) ions, only five or six coordination sites are saturated with oxygen atoms of acid anions but two or three sites can be saturated with water oxygens. So, the inner coordination sphere can include two or three water molecles and the others are in the hydrogen bonded outer coordination sphere of complex. The energy of coordination water molecules bonding is higher than that of hydrogen bonded water molecules in the second coordination sphere. This way of coordination in some cases affects the way of dehydration process – the complexes lose the hydrogen bonded water molecules in the first step and the covalent bonded water molecules from the first coordination sphere in the next one [21]. In most cases of 5-aminoisophthalate complexes the dehydration process occurs in several steps as confirmed by existing of two different kinds of water molecules in the complex structure [22].

The hydrated complexes of light lanthanides from La to Er (except Gd) heated in air lose all water molecules in two steps. The loss coordinated water molecules of yttrium and gadolinium complexes occur in one step. The results of investigations concern-

Table 3 Thermal decomposition of lanthanides(III) and Y complexes with 5-aminoisophthalic acid (air atmosphere)

Complexes	M_{mol}	ΔT_1/°C	Mass loss/%		T_b/°C	Temp. of oxide formation/°C	Residue/%	
			calcd.	found			calcd.	found
$La_2L_3\cdot13H_2O$	1049.27	30–220	22.30	22.0	390	790	31.05	31.0
$Pr_2L_3\cdot13H_2O$	1953.27	30–220	22.17	22.0	370	690	32.32	32.0
$Nd_2L_3\cdot13H_2O$	1059.93	30–220	22.08	22.0	340	710	31.75	32.0
$Sm_2L_3\cdot13H_2O$	1072.15	30–210	21.83	22.0	350	700	32.53	32.0
$Eu_2L_3\cdot13H_2O$	1075.37	30–200	21.76	22.0	300	650	32.73	33.0
$Gd_2L_3\cdot13H_2O$	1085.95	30–250	21.55	21.4	340	760	33.38	33.4
$Tb_2L_3\cdot13H_2O$	1089.29	30–220	21.48	22.0	360	620	35.79	36.0
$Dy_2L_3\cdot13H_2O$	1096.45	30–210	21.34	21.5	350	720	34.02	34.0
$Ho_2L_3\cdot13H_2O$	1101.31	30–200	21.25	21.0	350	720	34.31	34.0
$Er_2L_3\cdot13H_2O$	1105.97	30–210	21.16	21.0	400	720	34.59	34.0
$Tm_2L_3\cdot9H_2O$	1038.13	30–200	16.18	16.0	370	745	37.25	37.7
$Yb_2L_3\cdot9H_2O$	1045.53	30–210	16.07	16.0	400	720	37.69	38.0
$Lu_2L_3\cdot9H_2O$	1049.39	30–220	16.01	16.0	370	740	37.92	38.0
$Y_2L_3\cdot9H_2O$	887.27	30–250	18.93	19.0	365	760	25.45	25.5

ΔT_1 – temperature range of dehydration process, T_b – temperature of beginning of decomposition

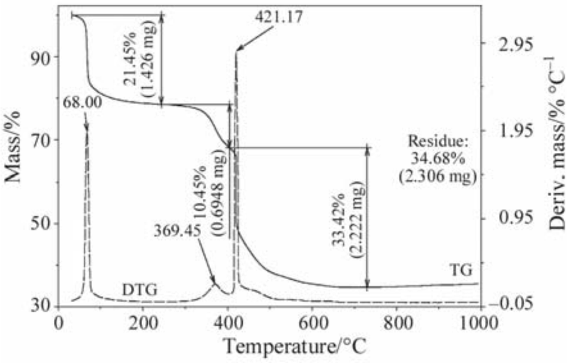

Fig. 2 High resolution TG and DTG curves of $Gd_2L_3 \cdot 13H_2O$ (L=$C_8H_5NO_4^{2-}$, air atmosphere)

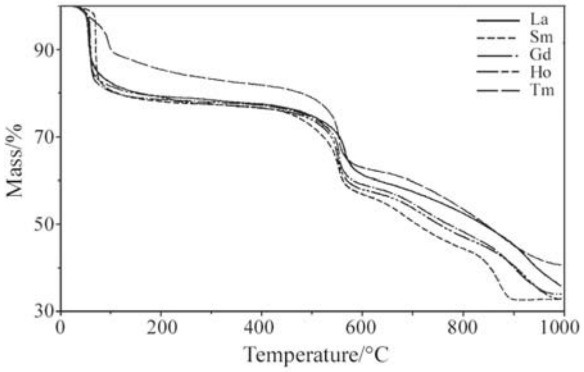

Fig. 3 TG curves of $Ln_2L_3 \cdot 13H_2O$ Ln=(La, Sm, Gd, Ho) and $Ln_2L_3 \cdot 9H_2O$ Ln=(Tm), (L= $C_8H_5NO_4^{2-}$, N_2 atmosphere)

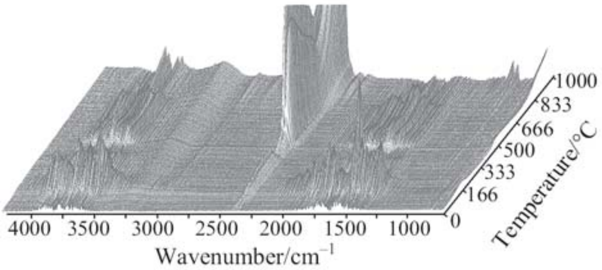

Fig. 4 FTIR spectra of gaseous products of thermal decomposition of $Gd_2(C_8H_5NO_4)_3 \cdot 13H_2O$

ing one step dehydration are in excellent agreement with those obtained by high resolution TA method (Fig. 2). Dehydration of the nonahydrated complexes of Tm, Yb and Lu occurs in three overlapping stages. A shape of DTG and DTA curves indicate the presence of three stage of dehydration. This way of dehydration process is connecting with different way of water molecules bonding in the complex structure: the part of water molecules is hydrogen bonded in the second coordination sphere and is removed in the first of dehydration process. The next steps of dehydration in higher temperatures are connecting with coordinated water removing. Additionally, the stepwise dehydration process was confirmed by the DTG curves in helium atmosphere The anhydrous compounds are stable up to about 350°C in air atmosphere and decompose on heating directly to the oxides; Ln_2O_3, Tb_4O_{10} and Pr_6O_{11}. In the case of lanthanum(III) complex the decomposition process runs through intermediate products, but finally oxide is formed. The temperature of oxide formation is in the range of 620–790°C. The anhydrous compounds are more stable in nitrogen atmosphere of heating (Fig. 3) comparatively to air heating atmosphere (Fig. 2).

The decomposition process connected with the gas product analysis was carried out for gadolinium(III) complexes as the representative complex for all isostructural compounds of La–Er group complexes. The FTIR spectrum of gaseous products is presented in Fig. 4. These spectra confirm, that at first dehydration but not deamination takes place. As follows from Fig. 4 in the spectrum of gaseous products of decomposition, in the ranges of 3750–3500 and 1900–1300 cm^{-1} stretching and deformation vibrations appear due to H_2O molecules absorption. These bands disappear above 185°C when the anhydrous compound is formed. The anhydrous compound is stable up to 400°C. When the complex is heated above 400°C, the subsequent decomposition of the compound with degradation of organic ligand takes place. The first step of decomposition of organic ligand results in release of CO_2 which is reflected in the FTIR spectra recordered at 445°C. Carbon dioxide molecules absorb in the wave number in the ranges 2300–2250 and 750–600 cm^{-1} due to deformation and valence vibration [23]. Release of carbon dioxide above 445°C is simultaneous to deamination as confirmed by characteristic double peaks of deformation vibrations of gaseous NH_3 with the maxima at 966 and 923 cm^{-1}.

Conclusions

In conclusion, the novel coordination lanthanide(III) complexes with 5-aminoisophthalic acid have been synthesized and characterized. The solid complexes crystallize in the two isostructural series: tridecahydrated compounds from La to Er and nonahydrated compounds of Tm, Yb and Lu(III). Both series are characterized by monoclinic system but differ significantly in unit cell parameters. The coordination metal ion-ligand occurs through oxygen atoms of carboxylic groups but not by the nitrogen atom of amino group. The compound disclose small framework stability. During dehydration the lanthanide-organic framework is destroyed and the formed anhydrous complex are amorphous. Tm, Yb and Lu(III) compounds heated also lose all molecules of water and as before are destroyed resulting in amorphous compounds. The anhydrous compounds of both series are stable to about 350°C, heated decompose to oxides. On the basis of this work further syntheses in different conditions to obtain the stable framework of coordination carboxylates are under way.

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