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THERMAL PROPERTIES OF RARE EARTH ELEMENTS COMPLEXES WITH 1,3,5-BENZENETRICARBOXYLIC ACID

Z. Rzączyńska[*], *A. Ostasz and S. Pikus*

Faculty of Chemistry, Maria Curie-Skłodowska University, M. C. Skłodowska Sq. 2, 20-031 Lublin, Poland

Rare earth elements 1,3,5-benzenetricarboxylates were prepared as solids of the general formula $Ln(C_9H_3O_6)\cdot nH_2O$, where n=6 for La–Dy and n=4 for Ho–Lu,Y. Their solubilities in water at 293 K are of the order 10^{-4}–10^{-6} mol dm^{-3}. The IR spectra of the complexes indicate that the carboxylate groups are bridging and bidentate chelates. Hydrated 1,3,5-benzenetricarboxylates lose water molecules during heating in one step (La–Tb), two steps (Y, Ho–Tm) or three steps (Dy, Yb, Lu). The anhydrous complexes are stable up to 573–742 K and decompose to oxides (Ce–Lu) at higher temperatures.

Keywords: *1,3,5-benzenetricarboxylates of rare earth elements, IR spectra, thermal analysis, X-ray powder analysis*

Introduction

The studies of the coordinating polymeric complexes, especially metal carboxylates, have developed rapidly in recent years. The results show how fascinating geometry they create and how potentially they can be used [1]. Crystalline porous metal–organic compounds have potential applications in separation, catalysis, non-linear optics and storage of gases [2]. It was found that the microporous complexes of metal dicarboxylates (copper(II) terephthalate) absorb a large amount of gases such as N_2, Ar, O_2. The investigations of the latter ability indicate that the gases are not adsorbed on the surface but occluded within the solid. The procedure of patenting of adsorption of gases on microporous complexes was undertaken [3].

Yaghi demonstrated that polydentate ligands, such as 1,3,5-benzenetricarboxylate ions, are suitable for constructing porous solids [4, 5]. This ligand has great ability to adopt different bonding modes – unidentate, bidentate or bridging sometimes in more than one way – in the same compound [4, 6]. It is possible to prepare mono-, two- and three-dimensional structures such as ladder, honeycomb, etc. [6, 7].

The examinations of the carboxylates create enormous applicative possibilities and that is why we turned our attention to the lanthanide trimesates (where trimesate stands for 1,3,5-benzenetricarboxylate, $C_6H_3(COO)_3^{3-}$).

The aim of our paper was to prepare the complexes of Y(III) and lanthanides(III) with 1,3,5-benzenetricarboxylic acid, to determine their properties and to investigate their thermal decomposition in air.

Experimental

The complexes of Y(III) and lanthanide(III) from La to Lu (except Pm) were prepared adding stoichiometric amounts of 0.1 M solution of ammonium 1,3,5-benzenetricarboxylate (pH=5.6) to the hot solution of lanthanide chlorides, in the case of cerium(III) nitrate was used. The precipitates formed were heated in mother solution for 1 h, then filtered off, washed with hot water to remove ammonium ions and dried at 303 K to a stable mass.

Elemental analyses were done using a CHN 2400 Perkin Elmer instrument. Some of the results are presented in Table 1. IR spectra of the complexes were recorded over the range 4000–400 cm^{-1} by using a FTIR 1725X Perkin Elmer spectrophotometer. The samples were dispersed in KBr (Table 2). The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss, Jena) diffractometr using Ni filtered CuK_α radiation (2θ=5–80°). The powder diffraction data of the Nd(III) and Er(III), representatives of the isostructural group of hexahydrated and tetrahydrated complexes, were collected on a Philips Xpert Pro (Holland) automated X-ray diffractometer. The experimental conditions were: Cu target X-ray tube operated at 45 kV and 30 mA, 6° take-off angle, 1° divergence slit, 0.15 mm receiving slit, curved graphite diffracted beam monochromator and scintillation counter with pulse height analyser. The powder diffraction patterns were collected by step scanning between 4 and 80° in 2θ with a step equal 0.02° and a count time of 10 s/step. The diffractometer was calibrated by using a SRM 1976 standard. Throughout the measurements, the ambient temperature was maintained at 20±1°C. The Xrayan program was used for de-

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[*] Author for correspondence: rzacz@hermes.umcs.lublin.pl

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

termining peak intensities and positions. Pattern indexing was carried out with the PC-version of TREOR program [8]. For these samples, the all 2θ peak positions were used (Table 3). The thermal stability and decomposition of the complexes in air was investigated with the aid of the SETSYS 16/18 derivatograph, recording TG, DSC and DTG curves. Samples (9–10 mg) were heated in ceramic crucible between 293–1273 K in flowing air atmosphere with a heating rate of 10 K min^{-1}. The products of decomposition were postulated on the basis of the TG curves (Table 4). Gaseous products of decomposition were identified using a Netzsch TG apparatus coupled to a Brucker FTIR IFS 66 spectrophotometer. The samples were heated in a dynamic argon atmosphere. TG curves were recorded on a Netzsch TG 209 using a ceramic crucible and heating with a rate of 10 K min^{-1} up to 1273 K.

Results and discussion

1,3,5-Benzenetricarboxylates of Y(III) and lanthanides(III) – from La(III) to Lu(III) – were obtained as crystalline hydrates. 1,3,5-Benzenetricarboxylic acid forms complexes with ions of rare elements of stoichiometric ratio metal:ligand equal to 1:1 and the general formula $Ln(C_9H_3O_6)\cdot nH_2O$ (n=6 for La–Dy and n=4 for Ho–Lu and Y). The colours of the complexes are typical of the appropriate trivalent lanthanide ions, i.e. Pr-green, Nd-violet, Sm-cream, Eu-pink, Ho-peach and the remaining complexes are white.

To study the types of bonding between the ligand and metal ions, and to elucidate the structures of the complexes obtained, their IR spectra were recorded. All the prepared complexes exhibit similar IR spectra in the solid-state. Table 2 presents the most

Table 1 The results of the elemental analysis of some 1,3,5-benzenetricarboxylate complexes

Complexes	C/%		H/%	
	calc.	found	calc.	found
$YL\cdot 4H_2O$	29.33	29.33	2.98	3.06
$LaL\cdot 6H_2O$	23.80	24.35	3.25	3.33
$NdL\cdot 6H_2O$	23.66	23.96	3.28	3.19
$GdL\cdot 6H_2O$	22.89	23.35	3.19	3.09
$DyL\cdot 6H_2O$	23.06	23.05	3.01	3.02
$HoL\cdot 4H_2O$	24.33	24.30	2.50	2.70
$ErL\cdot 4H_2O$	24.19	24.51	2.46	2.55
$Tm\cdot 4H_2O$	24.09	24.21	2.45	2.54
$Lu\cdot 4H_2O$	23.80	23.15	2.44	2.79

$L=C_9H_3O_6^{3-}$

Table 2 Bands in IR spectra of complexes of Nd(III), Er(III) and trimesic acid

Vibrations	H_3L	$NdL\cdot 6H_2O$	$ErL\cdot 4H_2O$	Na_3L
$\nu_{C_{Ar}-H}+\nu_{OH}$	3500–2400	3700–2700	3700–2800	–
$\gamma_{C_{Ar}-H}$	–	1910, 1866	1875	–
$\nu_{C=O}$	1719	–	–	–
$\nu_{C_{Ar}-C_{Ar}}$	1606	1613	1611	–
$\nu_{as(COO^-)}$	–	1558	1552	–
$\nu_{s(COO^-)}$	–	1373	1384	–
$\Delta\nu_{COO^-}$	–	185	168	198
$\beta_{C_{Ar}-C_{Ar}}$	1454	1435	1442	–
$\beta_{OH}+\nu_{C-O}$	1404	–	–	–
ν_{C-OH}	1276	–	–	–
$\beta_{C_{Ar}-H}$	1182, 1108	1109	1122, 1115	–
$\gamma_{C_{Ar}-H}+\gamma_{OH}$	918	933	942, 924	–
$\gamma_{C_{Ar}-H}$	–	–	847	–
$\gamma_{C_{Ar}-C_{Ar}}$	742, 688	761, 710	772, 739	–
$\gamma_{C_{Ar}-H}+\gamma_{C=O}$*	613	668	660, 625	–
$\gamma_{C_{Ar}-H}$	537	533	521	–

*only for acid

Table 3 The unit cell parameter for $Nd(C_9H_3O_6)\cdot 6H_2O$ and $Er(C_9H_3O_6)\cdot 4H_2O$

Complex crystal system	$Nd(C_9H_3O_6)\cdot 6H_2O$ monoclinic	$Er(C_9H_3O_6)\cdot 4H_2O$ monoclinic
a/Å	10.11	16.79
b/Å	17.95	9.91
c/Å	7.27	7.61
α/degree	90.00	90.00
β/degree	99.30	100.70
γ/degree	90.00	90.00
Volume/Å^3	1301	1244

important bands and their assignments. The following notation is used: ν=stretching vibration, β=in-plane deformation vibration, γ=out-of-plane deformation vibration and C_{Ar}=aromatic carbon atom vibration [9–12]. In the IR spectra of the complexes there are broad absorption bands relevant to ν_{OH}, with max. at 3305–3403 cm^{-1}, confirming the presence of water molecules linked by hydrogen bonds. In the range of 3700–2700 cm^{-1} there are bands characteristic for $\nu_{C_{Ar}-H}$ stretching vibrations in aromatic compounds. These bands are generally weak. The broad absorption bands of OH and the bands of $C_{Ar}H$ overlap.

When the acid is converted to salts, the stretching C=O vibration $\nu_{C=O}$ of COOH, at 1720 cm^{-1}, disappears, whereas the bands of asymmetric COO^- vibration, at 1552–1564 cm^{-1}, and symmetric COO^- vibration, at 1371–1386 cm^{-1}, appear [13, 14]. The lack of stretching C=O vibration in salts indicates that all carboxylate groups take part in coordination of metal ions. The separation of the $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ modes ($\Delta\nu_{COO^-}$) in the complexes of light lanthanides and Tb(III) and Dy(III) is similar ($\Delta\nu_{COO^-}$= 182–189 cm^{-1}, Table 2) as for the sodium salt ($\Delta\nu_{COO^-}$=198 cm^{-1}). On the basis of Nakamoto spectroscopic criteria it is possible to suggest that the carboxylate groups are bridging ones [12]. In the case of Ho(III)–Lu(III) and Y(III) the separation of the $\nu_{as(COO^-)}$ and $\nu_{s(COO^-)}$ modes ($\Delta\nu_{COO^-}$) is smaller ($\Delta\nu_{COO^-}$=168–172 cm^{-1}, Table 2) than that of the sodium salt ($\Delta\nu_{COO}$=198 cm^{-1}). Probably the carboxylate groups of tetrahydrated complexes of Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III) are bidentate chelating.

X-ray spectra of 1,3,5-benzenetricarboxylate of rare earth elements indicate that complexes belong to two groups of isostructural compounds. First group contains the compounds from La(III) to Dy(III) with six molecules of water. Second isostructural group contains tetrahydrated complexes, i.e. Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Y(III). For samples Nd(III) and Er(III), every 2θ peak position was used in the calculation. A unique solution with monoclinic cell for $Nd(C_9H_3O_6)\cdot 6H_2O$ and $Er(C_9H_3O_6)\cdot 4H_2O$ was given by the program. In Table 3 the unit cell data are presented.

Table 4 Thermoanalytical data of Y(III) and lanthanide(III)1,3,5-benzenetricarboxylates

Complexes	ΔT_1/K	Mass loss%		ΔT_2/K	Mass loss%	
		calc.	found		calc.	found
$YL\cdot 4H_2O$	327–457	19.57	20.2	705–954	69.41	69.2
$LaL\cdot 6H_2O$	323–555	23.78	23.4	930–1100	64.12	64.6
$CeL\cdot 6H_2O$	303–508	23.75	23.7	573–726	62.19	63.5
$PrL\cdot 6H_2O$	303–499	23.68	23.7	674–864	62.67	64.6
$NdL\cdot 6H_2O$	303–549	23.66	23.4	665–971	63.11	64.7
$SmL\cdot 6H_2O$	303–548	23.20	23.5	682–938	62.54	63.2
$EuL\cdot 6H_2O$	303–515	23.12	23.1	644–926	62.32	63.1
$GdL\cdot 6H_2O$	310–511	22.86	22.7	647–1051	61.62	61.3
$TbL\cdot 6H_2O$	313–470	22.79	21.8	691–1242	60.57	60.4
$DyL\cdot 6H_2O$	310–483	21.14	21.3	698–1003	60.21	60.6
$HoL\cdot 4H_2O$	313–453	16.22	16.8	710–922	57.47	57.8
$ErL\cdot 4H_2O$	329–448	16.14	16.4	709–943	57.16	57.1
$TmL\cdot 4H_2O$	336–457	16.08	16.3	723–956	56.94	56.5
$YbL\cdot 4H_2O$	306–467	15.93	16.8	716–929	56.43	56.8
$LuL\cdot 4H_2O$	313–483	15.87	15.9	742–998	56.19	56.4

$L=C_9H_3O_6^{3-}$
ΔT_1 – temperature range of dehydration process
ΔT_2 – temperature range of decomposition of anhydrous complexes or intermediates to oxides: Ln_2O_3, CeO_2, Pr_6O_{11} and Tb_4O_7

The hydrated trimesates are stable up to 303–336 K. On further heating they lose molecules of water that leads to anhydrous complexes stable up to 573–742 K. The hexahydrated complexes of La(III)–Nd(III) lose in one step all water molecules

$$LnL\cdot 6H_2O \rightarrow LnL+6H_2O$$

Sm(III), Eu(III), Gd(III) and Tb(III) dehydrate in one step but with the inflexion point seen in TG and DSC curves. Dehydration of the tetrahydrated complexes of Y(III), Ho(III), Er(III) and Tm(III) proceeds in two stages. In the first stage the compounds lose two molecules of water which is connected with the effect on the DSC curves.

The next endothermic effect on the DSC curve and relevant loss of mass is connected with release of remaining molecules of water.

$$LnL\cdot 4H_2O \rightarrow 2H_2O+LnL\cdot 2H_2O \rightarrow LnL+2H_2O$$

$DyL\cdot 6H_2O$, $YbL\cdot 4H_2O$ and $LuL\cdot 4H_2O$ dehydrate in three steps. The shape of TG and DTG curves and sharp endothermic effects in the DSC curves indicate that some water molecules present in the trimesates of Dy(III), Yb(III) and Lu(III) are weakly bonded and other are tightly bonded. Further dehydration of these compounds occurs in inseparable three steps. Therefore it is difficult to evaluate the number of water molecules released in successive steps.

The anhydrous compounds decompose on heating to oxides (Ln_2O_3, CeO_2, Tb_4O_7 and Pr_7O_{11}) – directly or with formation intermediates e.g. in the case La(III) complex. The anhydrous complexes of Ce(III)–Lu(III) and Y(III) decompose in the range 573–742 K, directly to oxides. The anhydrous complex of La(III) is stable up to about 645 K. When heated over 645 K, it decomposes with intermediate formation (in the range 645–930 K) and then La_2O_3 (between 930–1100 K). The temperature of oxide formation changes from 726 K, for (CeO_2), to 1242 K, for (Tb_4O_7). The dehydration processes are accompanied by endothermic effects, observed on the DSC curves whereas the oxidation of the organic ligand is accompanied by the exothermic effects.

IR spectra of gaseous products of decomposition of the Nd(III) complex, a representative of the isostructural group of hexahydrated compounds, and relevant TG curves are shown in Fig. 1. The characteristic valence and deformation vibrations of water molecules appear in the wavenumber ranges of 3950–3500 and 1900–1300 cm^{-1}, respectively. These spectra were observed at 403 K. The anhydrous complex is stable between 498–748 K. Above 750 K CO_2 appears in the IR spectra of gaseous products. Carbon dioxide molecules absorb in the wavenumber ranges: 2400–2250 and 750–600 cm^{-1} due to valence and deformation vibrations, respectively. At 873 K bands in the wavenumber range of 3100–3000 cm^{-1} are observed [15]. This region is characteristic of stretching =C–H vibrations. These bands are probably due to the presence of gaseous hydrocarbons. Upon further heating they disappear at 890 K. At 789 K very weak bands at 2177 and 2113 cm^{-1} can be seen. These peaks are characteristic of valence vibration, of CO. They disappear at 973 K.

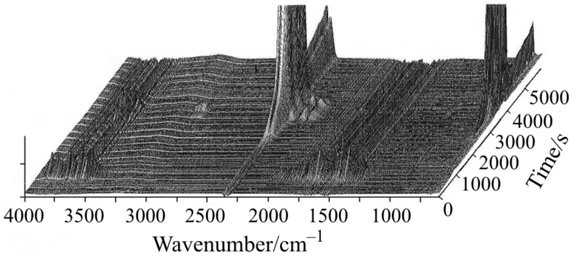

Fig. 1 FTIR spectra of gaseus products of thermal decomposition of $Nd(C_9H_3O_6)\cdot 6H_2O$

Conclusions

Complexes of Y(III) and lanthanide(III) with 1,3,5-benzenetricarboxylic acid were prepared as crystalline hydrated solids. The carboxylate groups in the complexes are bridging bidentate chelates. The powder X-ray analysis revealed that they belong to two isostructural groups. The trimesates of rare elements are hydrated. Thermoanalytical investigations indicate that some water molecules present in the complexes are weakly bonded and other tightly bonded. During heating the complexes lose water molecules in one, two or three steps. The anhydrous complexes decompose directly to oxides or through intermediate states (for La). FTIR spectra gaseous products indicate that decomposition of the compounds is accompanied by the release of CO_2, H_2O, hydrocarbons and CO.

References

1 R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi and Q. Shi, Inorg. Chem., 41 (2002) 2087.
2 L. Huang, H. Wang, J. Chen, Z. Wang, J. Sun, D. Zhao and Y. Yan, Microporous Mesoporous Mater., 58 (2003) 105.
3 C. J. Kepert, T. J. Prior and M. J. Rosseinsky, J. Sol. State Chem., 152 (2000) 261.
4 O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, Acc. Chem. Res., 31 (1998) 474.
5 C. Livage, N. Guillou, J. Marrot and G. Ferey, Chem. Mater., 13 (2001) 4387.
6 C. Daiguebonne, O. Guillou, K. Boubekeur, Inorg. Chim. Acta, 304 (2000) 161.
7 A. Dimos, A. Michaelides and S. Skoulika, Chem. Mater., 12 (2000) 3256.

8 P. E. Werner (1984). ‘TREOR, Trial and Error Program for Indexing of Unknown Powder Patterns’ University of Stockholm, S 106 91, Stockholm, Sweden.
9 M. Sikorska, R. Mrozek and Z. Rzączyńska, J. Thermal Anal., 51 (1998) 467.
10 W. Brzyska, A. Bartyzel, K. Zieniewicz and A. Zwolińska, J. Therm. Anal. Cal., 63 (2001) 493.
11 W. Ferenc and A. Walków-Dziewulska, J. Therm. Anal. Cal., 71 (2003) 375.
12 K. Nakamoto, Infrared and Raman Spectra of Inorganic Coordination Compounds, Wiley, New York 1968.
13 R. Silverstein and F. X. Webster, Spectrometric Identification of Organic Compounds, Wiley and Sons, New York 1998.
14 S. Holly and P. Sohar, Absorption spectra in the infrared region, Akadémiai Kiadó, Budapest.
15 W. Ferenc and A. Walków-Dziewulska, J. Therm. Anal. Cal., 74 (2003) 511.

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