Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 1, 157–162

INFLUENCE OF PREPARATION CONDITIONS ON THERMAL PROPERTIES OF LANTHANIDE BENZENEPOLYCARBOXYLATES

M. Iwan[*]*, R. Łyszczek, A. Ostasz and Z. Rzączyńska*

Department of General and Coordination Chemistry, Faculty of Chemistry UMCS, Maria Curie Skłodowska Sq.2
20-031 Lublin, Poland

Properties of lanthanide 1,2,4-benzenetricarboxylates and lanthanide 1,2,4,5-benzenetetracarboxylates obtained by a classical synthesis method and under hydrothermal conditions were compared. Solid 1,2,4-benzenetricarboxylates and 1,2,4,5-benzenetetracarboxylates of cerium, neodymium and erbium were prepared by a classical precipitation method. The same lanthanide compounds were obtained also from hydrothermal reaction. All obtained products were examined by elemental analysis. General formulae of complexes were: $Ln(1,2,4\text{-btc})\cdot xH_2O$ and $Ln_4(1,2,4,5\text{-btec})_3\cdot yH_2O$. The thermal analysis shows that hydrothermal conditions cause the coordination of less number of water molecules to complex molecule. Because lanthanide ions exhibit the most often the coordination number equal 8 or 9 one can conclude that the coordination ability of carboxylic groups under hydrothermal conditions is different from that under mild ones. Probably, in hydrothermal conditions the carboxylic groups of 1,2,4-benzenetricarboxylate ions are able to form more coordination bonds with lanthanide ions than under normal pressure.

Keywords: *1,2,4,5-benzenetetracarboxylates, 1,2,4-benzenetricarboxylates, hydrothermal synthesis, lanthanide complexes*

Introduction

Various polycarboxylates ligands are used to prepare coordination polymer compounds of metals. Such polymers having microporous structure and open channels are applied as heterogeneous catalysts, storage or sorption materials, ion exchanger, etc. [1, 2]. By this reason the development of coordination framework materials is an area of current interest. Lanthanide coordination polymers offer attractive properties in terms of their potential application, for example as luminescent or non-linear optical materials [3–6]. High coordination numbers of lanthanide ions allow to obtain unusual structures of framework of coordination polymers that would be difficult to prepare with d-block metals [4, 7, 8]. However, lanthanide-based systems are far less known in comparison with d-block ion analogs. The obtainment of highly porous and/or highly crystalline compounds is the principle problem of synthesis of metal-organic framework. Fortunately, solvothermal or hydrothermal techniques have appeared very useful in this case [9].

Our work presents the results of influence of preparation conditions on properties of 1,2,4-benzenetricarboxylates and 1,2,4,5-benzenetetracarboxylates of chosen lanthanides (cerium(III), neodymium and erbium).

Experimental

Solid 1,2,4-benzenetricarboxylates and 1,2,4,5-benzenetetracarboxylates of cerium(III), neodymium and erbium were prepared by a classical precipitation method. Stoichiometric amounts of 0.05 M solution of ammonium benzenepolycarboxylate (pH 5.5) were added to a hot solution of lanthanide chlorides (in the case of cerium(III) a nitrate solution was used) [10]. The same lanthanide compounds were obtained also from hydrothermal reaction: water solutions of substrates were put into Teflon-lined autoclave at 140°C under autogenous pressure. After 5 days autoclaves were cooled with a rate of 5°C h^{-1} and the solid products were separated by filtration.

The compounds were identified by the method of elemental analysis (with a Perkin-Elmer CHN 2400 elemental analyzer) and on the base of IR spectra recorded over the range of 4000–400 cm^{-1} in KBr discs by using a FTIR 1725X Perkin-Elmer spectrophotometer.The X-ray diffraction patterns were taken on a Seifert-DRON automated X-ray diffractometer ($2\theta=5–80°$) at ambient temperature.

The thermal stability and decomposition of the lanthanide benzenepolycarboxylates was investigated with the aid of a Setsys 16/18 (Setaram) thermal analyzer, recording TG/DTA/DTG or TG/DSC/DTG curves. Samples (9–10 mg) were heated in ceramic crucible between 30–1000°C (30–400°C in the case of

---

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

1388–6150/$20.00

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

Table 1 Results of elemental analysis of 1,2,4-benzenetricarboxylates ($C_9H_3O_6^{3-}$) and 1,2,4,5-benzenetetracarboxylates ($C_{10}H_2O_8^{4-}$) of cerium, neodymium and erbium obtained under classical and hydrothermal conditions

Complexes	C/%		H/%		Ln/%	
	found	calc.	found	calc.	found	calc.
			Classical synthesis			
$CeC_9H_3O_6\cdot2.5H_2O$	27.50	27.54	2.00	2.04	35.29	35.73
$Ce_4(C_{10}H_2O_8)_3\cdot18H_2O$	22.46	22.03	2.96	2.57	34.44	34.29
$NdC_9H3O_6\cdot3.5H_2O$	25.97	26.07	2.67	2.41	34.98	34.82
$Nd_4(C_{10}H_2O_8)_3\cdot14H_2O$	22.66	22.80	2.00	2.15	36.14	36.54
$ErC_9H_3O_6\cdot3.5H_2O$	24.50	24.70	2.36	2.29	38.03	38.25
$Er_4(C_{10}H_2O_8)_3\cdot14H_2O$	21.50	21.54	2.11	2.03	40.05	40.04
			Hydrothermal synthesis			
$CeC_9H_3O_6$	30.00	31.11	1.00	0.86	38.10	40.37
$CeC_{10}H_2O_8\cdot2H_2O$	29.15	28.16	1.00	1.41	34.40	32.88
$NdC_9H_3O_6$	30.55	30.75	1.00	0.85	39.23	41.07
$Nd_4(C_{10}H_2O_8)_3\cdot10H_2O$	24.00	23.89	1.82	1.73	37.92	38.29
$ErC_9H_3O_6\cdot2H_2O$	26.52	26.32	1.82	1.71	39.79	40.77
$Er_4(C_{10}H_2O_8)_3\cdot10H_2O$	22.50	22.51	1.78	1.63	41.31	41.84

DSC analysis) in flowing air atmosphere (v=1 L h^{-1}) with a heating rate of 10°C min^{-1}. The products of decomposition were postulated on the basis of the TG curves. The purpose of TG/DSC/DTG analysis was to determine the enthalpy of dehydration process.

Results and discussion

The benzenepolycarboxylates of cerium(III), neodymium and erbium were obtained as crystalline compounds. The stoichiometry of compounds is given in Table 1. The elemental analysis clearly shows that complexes obtained by hydrothermal synthesis bond less water molecules than compounds synthesized under mild conditions. The results are confirmed by thermogravimetric curves (Tables 2, 3). With the exception of cerium complexes obtained hydrothermally all results of elemental and thermogravimetric analysis are in good agreement with theoretically calculated values of C, H and Ln content (Table 1). The most probable interpretation is a partial or full oxidation of cerium(III) ion to Ce(IV) caused by hydrothermal conditions.

X-ray diffraction patterns indicate that all studied complexes are crystalline. Figure 1 presents the patterns of neodymium complexes as an example. The shape and the number of peaks of X-ray diffraction patterns show that the hydrothermal technique produces higher crystalline compounds. Their structures seem to be more ordered than the structures of classically obtained compounds.

The thermal stability of complexes was studied in air atmosphere. The results are presented in Tables 2 and 3. The scheme of thermal decomposition: hydrated complex → anhydrous complex → oxide is very characteristic of lanthanide organic complexes and it was observed by many authors [11–14]. Table 4 presents the values of enthalpy of dehydration

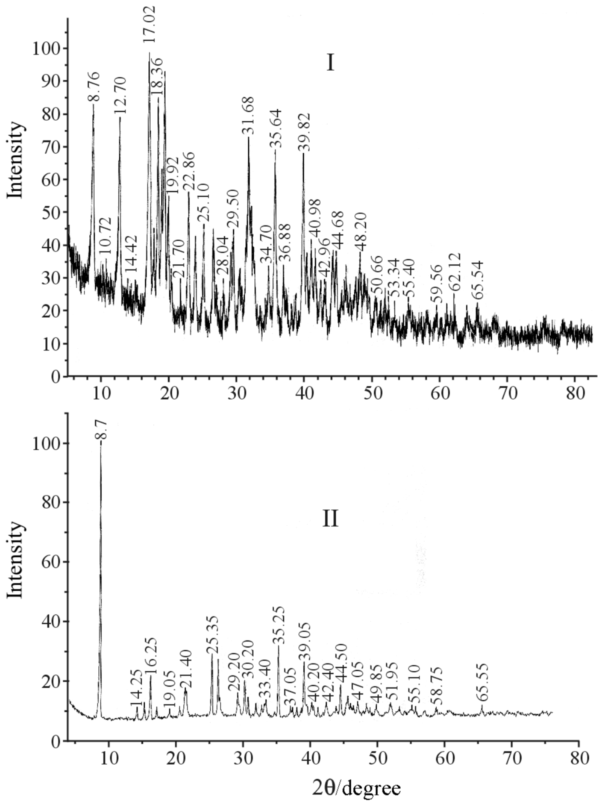

Fig. 1 X-ray diffraction patterns of neodymium 1,2,4-benzenetricarboxylate obtained by classical synthesis (I) and under hydrothermal conditions (II)

Table 2 Results of thermal decomposition of cerium, neodymium and erbium 1,2,4-benzenetricarboxylates obtained under classical and hydrothermal conditions (dynamic air atmosphere; β=10°C min^{-1})

	Classical synthesis					Hydrothermal synthesis				
	Compound	Temperature range of decomposition/°C	Mass loss/%		Product	Compound	Temperature range of decomposition/°C	Mass loss/%		Product
			found	calc.				found	calc.	
Ce	$CeL{\cdot}2.5H_2O$	40–200	6.00	6.89	$CeL{\cdot}H_2O$	CeL	250–520	53.2	50.43	CeO_2
	$CeL{\cdot}H_2O$	200–310	10.64	11.48	CeL					
	CeL	310–480	56.65	56.12	CeO_2					
Nd	$NdL{\cdot}3.5H_2O$	35–120	4.52	4.35	$NdL{\cdot}2.5H_2O$	NdL	200–750	53.43	52.14	Nd_2O_3
	$NdL{\cdot}2.5H_2O$	120–170	13.53	13.04	$NdL{\cdot}0.5H_2O$					
	$NdL{\cdot}0.5H_2O$	170–300	16.59	15.22	NdL					
	NdL	450–700	59.20	59.42	Nd_2O_3					
Er	$ErL{\cdot}3.5H_2O$	35–250	15.08	14.42	ErL	$ErL{\cdot}2H_2O$	135–250	8.50	8.78	ErL
	ErL	400–700	56.51	56.29	Er_2O_3		460–650	54.50	53.41	Er_2O_3

$L=C_9H_3O_6^{3-}$

Table 3 Results of thermal decomposition of cerium, neodymium and erbium 1,2,4,5-benzenetetracarboxylates obtained under classical and hydrothermal conditions (dynamic air atmosphere; β=10°C min^{-1})

	Classical synthesis					Hydrothermal synthesis				
	Compound	Temperature range of decomposition/°C	Mass loss/%		Product	Compound	Temperature range of decomposition/°C	Mass loss/%		Product
			found	calc.				found	calc.	
Ce	$Ce_4L'_3{\cdot}18H_2O$	35–295	20.50	19.83	$Ce_4L'_3$	$CeL'{\cdot}2H_2O$	320–425	9.68	8.45	CeL’
	$Ce_4L'_3$	320–465	57.70	57.89	CeO	CeL’	425–540	57.75	59.62	CeO_2
Nd	$Nd_4L'_3{\cdot}14H_2O$	35–360	16.06	15.97	$Nd_4L'_3$	$Nd_4L'_3{\cdot}10H_2O$	340–465	12.39	11.95	$Nd_4L'_3$
	$Nd_4L'_3$	380–760	57.85	57.41	Nd_2O_3	$Nd_4L'_3$	465–720	55.77	55.38	Nd_2O_3
Er	$Er_4L'_3{\cdot}14H_2O$	40–320	15.40	15.09	$Er_4L'_3$	$Er_4L'_3{\cdot}10H_2O$	105–320	11.63	11.26	$Er_4L'_3$
	$Er_4L'_3$	370–700	54.20	54.25	Er_2O_3	$Er_4L'_3$	320–700	52.76	52.19	Er_2O_3

$L'=C_{10}H_2O_8^{4-}$

Table 4 Values of enthalpy of dehydration process of lanthanide benzenepolycarboxylates obtained by classical and hydrothermal synthesis

	1,2,4–benzenetricarboxylates						1,2,4,5–benzenetetracarboxylates					
	classical synthesis			hydrothermal synthesis			classical synthesis			hydrothermal synthesis		
	onset point[a]/°C	ΔH^b/ J g^{-1}	ΔH^c/ kJ mol^{-1}	onset point[a]/°C	ΔH^b/ J g^{-1}	ΔH^c/ kJ mol^{-1}	onset point[a]/°C	ΔH^b/ J g^{-1}	ΔH^c/ kJ mol^{-1}	onset point[a]/°C	ΔH^b/ J g^{-1}	ΔH^c/ kJ mol^{-1}
Ce	I stage: 58.0	68.75	17.97	–	–	–	71.0	343.10	31.15	352.6	165.57	35.27
	II stage: 245.8	52.75	20.68									
Nd	I stage: 69.1	62.80	26.00	–	–	–	149.8	210.94	23.78	373.8	207.93	31.31
	II stage: 136.4	168.24	34.83									
Er	51.2	287.50	35.90	165.9	270.92	55.54	102.2	261.07	31.14	160.0	210.53	33.64

[a] onset point of endothermic peak on DSC curve
[b] enthalpy of dehydration in J per 1 gram of starting compound
[c] enthalpy of dehydration in kJ per 1 mol of loss water molecules

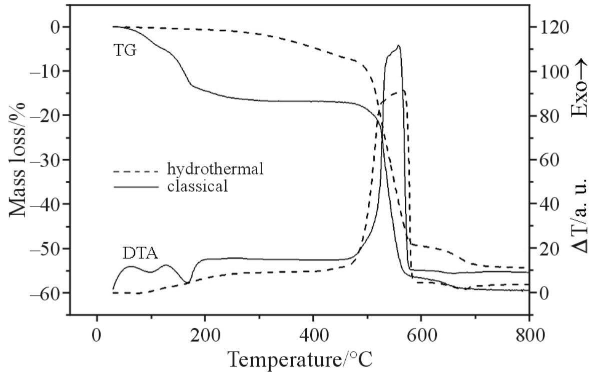

Fig. 2 TG and DTA curves of thermal decomposition of neodymium 1,2,4-benzenetricarboxylate obtained by classical and hydrothermal conditions (dynamic air atmosphere; β=10°C min^{-1})

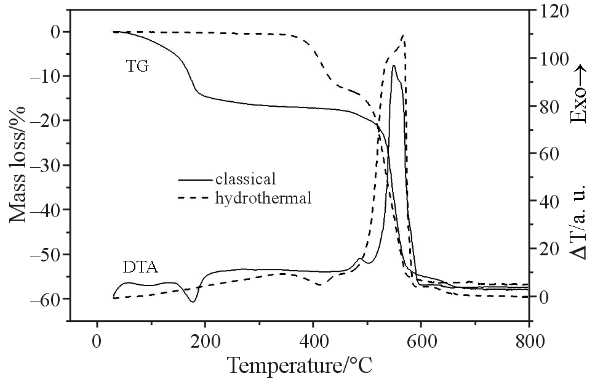

Fig. 3 TG and DTA curves of thermal decomposition of neodymium 1,2,4,5-benzenetetracarboxylate obtained by classical and hydrothermal conditions (dynamic air atmosphere; β=10°C min^{-1})

process determined by DSC method. At all cases the complexes obtained hydrothermally bond less water molecules (the cerium and neodymium 1,2,4-benzenetricarboxylates appeared anhydrous). They are much more stable than their classical analogs (see temperature ranges of decomposition in Tables 2 and 3 and values of onset point temperature of endothermic peaks of dehydration in Table 4). Figures 2 and 3 are useful to compare the thermal stability of complexes obtained under different conditions. One can conclude that hydrothermal conditions eliminate the weakly bonded water molecules, probably from outer sphere of complex.

Analyzing the thermal stability of cerium and neodymium 1,2,4-benzenetricarboxylates it is evident that the anhydrous complexes which are formed under hydrothermal conditions are less stable than the anhydrous compounds formed during thermal decomposition of classically obtained complexes (Table 2). For example the hydrothermally obtained Nd(1,2,4-btc) decomposes above 200°C and the same salt which is the intermediate of the thermal decomposition of Nd(1,2,4-btc)·3.5H_2O is stable up to 450°C. We have not succeeded in explaining this fact. Probably the different structure of both anhydrous compounds is responsible in charge of different thermal stability.

The hydrothermally obtained anhydrous 1,2,4-benzenetricarboxylates are interesting also by other reason. The carboxylates of lanthanides show the most often the existence of nine-coordinated lanthanide ions or the change of coordination number from 9 to 8 in the series from La to Lu [15]. Because the 1,2,4-benzenetricarboxylates of cerium and neodymium are anhydrous we suppose that the coordination ability of carboxylic groups under hydrothermal conditions is different from that under mild ones. In the absence of crystallization water molecules three carboxylic groups have to fill 9 coordination place. The following conclusion can be drawn: in hydrothermal conditions the carboxylic groups of 1,2,4-benzenetricarboxylate ions act as more dentate than under normal pressure. Our results are consistent with those reported by Livage *et al.* concerning the cobalt(II) succinate [16].

Conclusions

- The hydrothermal conditions probably cause the partial or full oxidation of cerium(III) ion to Ce(IV).
- The structure of hydrothermally obtained compounds is more ordered than the structure of classically synthesized ones.
- The complexes bond less water molecules under hydrothermal conditions than under mild ones. The high temperature and pressure eliminate the most weakly bonded water molecules.
- Probably, in hydrothermal reaction carboxylic groups of 1,2,4-benzenetricarboxylate ions act as more dentate than under normal pressure.

References

1 S. L. James, Chem. Soc. Rev., 32 (2003) 276.
2 D. M. Rudkevich and A. V. Leontiev, Aust. J. Chem., 57 (2004) 713.
3 J.-M. Shi, W. Xu, Q.-Y. Liu, F.-L. Liu, Z.-L. Huang, H. Lei, W.-T. Yu and Q. Fang, Chem. Commun., (2002) 756.
4 R. J. Hill, D.-L. Long, P. Hubberstey, M. Schröder and N. R. Champness, J. Solid State Chem., 178 (2005) 2414.
5 L.-N. Sun, J.-B. Yu, H.-J. Zhang, Q.-G. Meng, E. Ma, C.-Y. Peng and K.-Y. Yang, Microporous Mesoporous Mater., 98 (2007) 156.
6 P. Juan, G. Xiaotian, Y. Jianbo, Z. Yanhui, Z. Ying, W. Yunyou and S. Bo, J. Alloys Compd., 426 (2006) 363.

7 M. Lalia-Kantouri and Ch. Papadopoulos, J. Therm. Anal. Cal., 81 (2005) 375.

8 Y. Ren, S. Chen and S. Gao, J. Coord. Chem., 59 (2006) 2135.

9 J. L. C. Rowsell and O. M. Yaghi, Microporous Macroporous Mater., 73 (2004) 3.

10 Z. Rzączyńska, A. Ostasz, M. Sikorska-Iwan, H. Głuchowska, E. Olszewska and S. Pikus, J. Therm. Anal. Cal., 84 (2006) 575.

11 S. A. Sallam, K. M. Bahgat, A. Z. El-Tanany and M. A. Mahmond, J. Coord. Chem., 59 (2006) 2055.

12 R. Kurpiel-Gorgol and W. Brzyska, J. Therm. Anal. Cal., 85 (2006) 449.

13 R. Kurpiel-Gorgol and W. Brzyska, J. Therm. Anal. Cal., 82 (2005) 389.

14 A. Kula, J. Therm. Anal. Cal., 81 (2005) 381.

15 S. A. Cotton, C. R. Chimie, 8 (2005) 129.

16 C. Livage, C. Egger and G. Férey, Chem. Mater., 13 (2001) 410.

DOI: 10.1007/s10973-006-8120-2