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THERMAL PROPERTIES OF COMPLEXES OF LANTHANIDES(III) AND SOME OF *d*-BLOCK ELEMENTS WITH 5-CHLORO-2-METHOXYBENZOIC ACID

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Abstract

The thermal properties of 5-chloro-2-methoxybenzoates of lanthanides(III) and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were studied in air and nitrogen atmospheres. The complexes were obtained as mono-, di-, tetra- and pentahydrates with a metal to ligand ratio of 1:3 (in the case of lanthanides(III)) and 1:2 (in the case of *d*-block elements). They have colours typical for Ln^{3+} and M^{2+} ions. All complexes are polycrystalline compounds. When heated they dehydrate to form anhydrous salts which next in air are decomposed to the oxides of the respective metals while in nitrogen to the mixtures of metal oxides, oxychlorides and carbon.

Keywords: 5-chloro-2-methoxybenzoates, complexes of *d*-block elements, complexes of lanthanides(III), thermal stability of compounds in air and nitrogen atmospheres

Introduction

5-Chloro-2-methoxybenzoic acid is a white crystalline solid sparingly soluble in cold water. Its melting point temperature changes from 77 to 98°C depending on the solvents used for its crystallization. The complexes of lanthanides(III) and some of *d*-block elements with 5-chloro-2-methoxybenzoic acid have not been prepared and investigated so far. Therefore we decided to obtain them as solids, to examine and compare some of their physico-chemical properties. In our previous papers [1–6] we characterised the complexes of 5-chloro-2-methoxybenzoic acid with lanthanides(III) and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) by elemental analysis, FTIR and Far-IR spectra, X-ray diffraction, thermogravimetric studies and magnetic measurements. Taking into account the kind of cation we decided to compare the thermal properties of 5-chloro-2-methoxybenzoates of *f*-block and of some of *d*-block elements in air and nitrogen during heating to 1273 K (air) and 1173 K (nitrogen) in order to investigate the influence of central ion on the properties of complexes.

Experimental

The complexes of 5-chloro-2-methoxybenzoic acid with lanthanides(III) and Mn(II), Co(II), Ni(II), Cu(II), Zn(II) were prepared by the addition of equivalent quantities of

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0.1 M ammonium 5-chloro-2-methoxybenzoate (pH ~5) to a hot aqueous solution containing the nitrates of those elements and crystallizing at 293 K. The solids were filtered off, washed with hot water and methanol to remove ammonium ions and dried at 303 K.

The thermal stability and decomposition of the prepared complexes were determined using Paulik–Paulik–Erdey Q-1500D derivatograph with Derill converter, recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The samples were heated in platinum crucibles in static air to 1273 K. TG sensitivity was 100 mg, DTG and DTA sensitivities were regulated by a Derill computer programme. The initial mass of samples used in measurements were equal to 100 mg. The measurements in nitrogen were made on an OD-102 derivatograph at a heating rate of 10 K min^{-1}. The samples were heated to 1173 K at the following sensitivities: TG–100 mg, DTA–1/10, DTG–1/5. The nitrogen flowed through gas washers filled with pyrogallol and silica gel at a rate of 115 cm^3 min^{-1}.

The thermogravimetric analysis of DSC/TG was performed at temperatures 293–973 K using a differential thermoanalyser Netzsch STA 409 C 3F at a heating rate of 1 K min^{-1}. The experiments were carried out under argon flow of 75 cm^3 min^{-1}.

The gaseous decomposition products were analysed in argon atmosphere over the range 4000–400 cm^{-1} using the Bruker IFS 66 spectrometer.

Results and discussion

The complexes of 5-chloro-2-methoxybenzoic acid with lanthanides(III) were obtained as crystalline products with a metal to ligand ratio of 1:3 and a general formula $Ln(C_8H_6ClO_3)_3 \cdot nH_2O$ (where *Ln*=La–Lu, and *n*=5 for La–Nd, *n*=1 for Sm–Gd, *n*=2 for Tb, Dy and *n*=4 for Ho–Lu). The complexes of 5-chloro-2-methoxybenzoates of some of *d*-block elements were obtained also as crystalline products but with a metal to ligand ratio of 1:2 and a general formula $M(C_8H_6ClO_3)_2 \cdot nH_2O$, where *M*=Mn, Co, Ni, Cu, Zn and *n*=4 for Mn(II), *n*=5 for Co(II), Ni(II), *n*=1 for Cu(II) and *n*=2 for Zn(II).

The thermal stability of the 5-chloro-2-methoxybenzoates of lanthanides(III) and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) was studied in air and nitrogen atmospheres (Table 1, Figs 1, 2). The complexes were found to be hydrates. Heated in air they decompose in two or three steps. 5-Chloro-2-methoxybenzoates of lanthanides(III) in air are stable up to 338–413 K. The complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 5-chloro-2-methoxybenzoic acid in air are stable up to 338–403 K. Next at 338–413 K (complexes of *f*-block elements) and 338–433 K (complexes of *d*-block elements) they lose the water molecules in one step forming anhydrous compounds. The mass losses calculated from TG curves are equal to 2.64–11.33% (in the case of lanthanides(III)) and 3.96–17.16% (in the case of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)). The theoretical values are 2.50–11.00% (complexes of *f*-block elements) and 3.98–17.32% (complexes of *d*-block elements). These values correspond to the release of 1, 2, 4 or 5 molecules of water. Using the DSC technique the values of enthalpy of the dehydration process of 5-chloro-2-methoxybenzoates of lanthanides(III) and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), ΔH, were determined. These values are proportional to the energy of the bonding of

Table 1 Temperature range of thermal stability values of 5-chloro-2-methoxybenzoates of lanthanides(III) and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air and nitrogen atmospheres and the values of enthalpy for dehydration process

Complex	T_1 / K	Mass loss/%		n	Air(A) N_2	ΔH / kJ mol^{-1}	ΔT_2 / K	T_k / K	Ref.
		calcd.	found						
$LaL_3{\cdot}5H_2O$	348–388	11.46	11.33	5	A	265.30	523–777	1435	1, 3
	333–383		11.50		N_2		513–733		
$CeL_3{\cdot}5H_2O$	343–378	11.44	11.32	5	A	262.10	493–763	763	1
	323–373		11.00		N_2		513–733		
$PrL_3{\cdot}5H_2O$	343–383	11.43	11.33	5	A	261.90	523–770	1498	1
	333–373		11.00		N_2		513–733		
$NdL_3{\cdot}5H_2O$	338–393	11.38	11.32	5	A	265.60	518–784	1498	1
	333–383		11.00		N_2		513–733		
$SmL_3{\cdot}H_2O$	398–408	2.48	2.64	1	A	50.60	518–763	1358	1
	383–403		2.50		N_2		513–733		
$EuL_3{\cdot}H_2O$	388–408	2.46	2.64	1	A	54.85	513–728	1190	1
	383–403		2.50		N_2		513–733		
$GdL_3{\cdot}H_2O$	398–413	2.46	2.64	1	A	52.91	513–777	1316	1, 3
	393–413		2.50		N_2		513–733		
$TbL_3{\cdot}2H_2O$	348–388	4.80	4.95	2	A	103.09	493–883	1193	2
	353–383		4.75		N_2		513–713		
$DyL_3{\cdot}2H_2O$	363–393	4.77	4.67	2	A	115.97	508–923	1218	2
	353–383		5.00		N_2		503–703		

Table 1 Continued

Complex	ΔT_1 / K	Mass loss/%		n	Air(A) N_2	ΔH / kJ mol^{-1}	ΔT_2 / K	T_2 / K	Ref.
		calcd.	found						
$HoL_3{\cdot}4H_2O$	343–378	9.07	8.99	4	A	204.07	498–923	1208	2
	333–373		9.24		N_2		493–713		
$ErL_3{\cdot}4H_2O$	348–378	9.05	9.24	4	A	227.90	518–923	1113	2
	333–373		8.94		N_2		513–693		
$TmL_3{\cdot}4H_2O$	353–373	9.03	9.24	4	A	214.59	533–958	1103	2
	343–373		8.98		N_2		523–713		
$YbL_3{\cdot}4H_2O$	353–378	8.92	8.67	4	A	182.85	533–923	1083	2
	343–373		9.00		N_2		523–723		
$LuL_3{\cdot}4H_2O$	348–378	8.96	8.91	4	A	250.12	533–893	1033	2, 3
	343–373		8.78		N_2		523–723		
$MnL_2{\cdot}4H_2O$	353–398	14.46	14.07	4	A	246.48	533–1273	1273	4–6
	333–393		13.70		N_2		533–1153		
$CoL_2{\cdot}5H_2O$	338–383	17.30	17.16	5	A	260.92	543–913	892	4–6
	333–373		17.56		N_2		533–928		
$NiL_2{\cdot}5H_2O$	348–398	17.32	17.16	5	A	262.96	568–868	868	4–6
	343–393		17.03		N_2		553–873		
$CuL_2{\cdot}H_2O$	403–433	3.98	3.96	1	A	74.67	483–983	963	4–6
	393–428		4.13		N_2		473–973		
$ZnL_2{\cdot}2H_2O$	343–378	7.62	7.26	2	A	175.26	483–913	892	4–6
	353–383		7.82		N_2		493–892		

ΔT_1=temperature range of dehydration process; n=number of crystallization water molecules being lost in one endothermic step;
ΔH=enthalpy for dehydration process; ΔT_2=temperature range of the anhydrous complex decomposition; T_k=temperature of the oxide formation

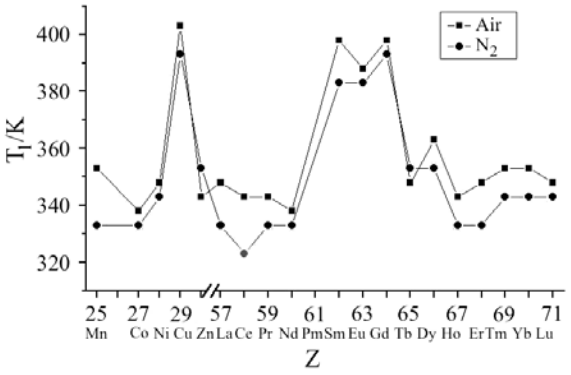

Fig. 1 Relationships between the temperature of initial dehydration of complexes (T_1) (in air and nitrogen) and Z

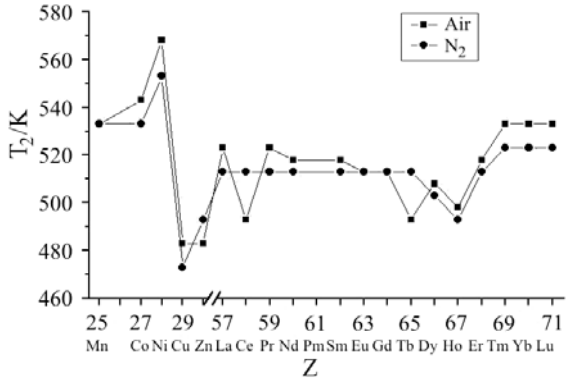

Fig. 2 Relationships between the temperature of decomposition of anhydrous complex (T_2) (in air and nitrogen) and Z

respective 1, 2, 4 or 5 of water molecules in the appropriate complexes and they are equal to: 50.60–74.67 kJ mol^{-1} for monohydrates of Sm(III), Eu(III), Gd(III) and Cu(II); 103.09–175.26 kJ mol^{-1} for dihydrates of Tb(III), Dy(III) and Zn(II); 182.85–250.12 kJ mol^{-1} for tetrahydrates of Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Mn(II); 260.92–265.3 kJ mol^{-1} for pentahydrates of La(III), Ce(III), Pr(III), Nd(III), Co(II) and Ni(II) (Table 1).

The anhydrous complexes of lanthanides(III) in air are stable up to 493–533 K and next in the temperature range 493–1435 K they decompose to the oxides of appropriate lanthanides with intermediate formation of LnOCl (with the exception of cerium(III) complex that directly decomposes to CeO_2). The temperatures of oxide formations change from 1498 K (Pr_6O_{11}, Nd_2O_3) to 763 K (CeO_2).

The anhydrous complexes of 5-chloro-2-methoxybenzoates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in air are stable up to 483–568 K and heated further to 1273 K they decompose to the respective oxides: Mn_3O_4, Co_3O_4, NiO, ZnO and a mixture of Cu_2O, CuO. In air the anhydrous 5-chloro-2-methoxybenzoates of Mn(II)

and Cu(II) decompose with the intermediate formation of Mn_2OCl_2 and Cu_2OCl (Table 1). The intermediate and final products of decomposition were identified by X-ray powder diffraction, elemental and IR spectra analyses.

The dehydration process is connected with an endothermic effect seen on DTA curves whereas the combustion of the organic ligand with exothermic one.

In the nitrogen atmosphere, similarly as in the air, the complexes of La(III), Ce(III), Pr(III), Nd(III), Co(II) and Ni(II) were found to be pentahydrates. The 5-chloro-2-methoxybenzoates of Ho(III), Er(III), Tm(III), Yb(III), Lu(III) and Mn(II) are tetrahydrates. The complexes of Tb(III), Dy(III) and Zn(II) were found to be dihydrates while those of Sm(III), Eu(III), Gd(III) and Cu(II) are monohydrates. 5-Chloro-2-methoxybenzoates of *f*- and of chosen *d*-block elements heated in nitrogen are stable up to 323–393 K (Table 1). Next they dehydrate in one step losing all molecules of crystallization water and form the anhydrous compounds. During the further heating the anhydrous complexes decompose in the range 473–1173 K. The final products of decomposition of 5-chloro-2-methoxybenzoates of lanthanides(III) and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in nitrogen are the mixtures of the carbon, metal oxides or metal oxychlorides.

The thermal stability of the obtained hydrates (T_1) do not change regularly (Table 1, Fig. 1). Monohydrates of 5-chloro-2-methoxybenzoates of Sm(III), Eu(III), Gd(III) and Cu(II) are the most thermally stable (in air T_1=388–403 K and in nitrogen T_1=383–393 K), which indicates that the water molecules are the most strongly bounded in these complexes. The rests of the hydrates for which the values of initial temperature of dehydration being equal to T_1=338–363 K (in air) and T_1=323–353 K (in nitrogen) have the similar thermal stability.

In the series of an anhydrous 5-chloro-2-methoxybenzoates of *f*- and of some of *d*-block elements the most thermally stable in air and nitrogen is the complex of Ni(II). Its initial temperatures of decomposition in air and in nitrogen, T_2, are equal to 568 K and 553 K, respectively. The weakest thermally stable in air are complexes of Cu(II) and Zn(II) (T_2=483 K) but in nitrogen only the complex of Cu(II) (T_2=473 K). Other anhydrous complexes (except those of Mn(II) and Co(II)) whose values of initial temperatures of decompositions are equal to T_2=493–533 K (in air) and T_2=493–523 K (in nitrogen) have the similar stability (Table 1, Fig. 2).

The FTIR spectra of gaseous products evolved during decomposition of 5-chloro-2-methoxybenzoates of lanthanides(III), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were presented in Table 2. The first product of decomposition of 5-chloro-2-methoxybenzoates of studied *d*- and *f*-block elements are molecules of H_2O. The bands at 4000–3500, 2000–1350 and 1820–1330 cm^{-1} characteristic for stretching and bending vibrations of OH confirm their presence in these complexes. The further heating of anhydrous compounds leads to the decomposition of the organic ligand. This process is connected with the release of a large amounts of CO_2 molecules whose valence and deformation vibrations absorb in the wavenumber ranges 2400–2200 and 700–670 cm^{-1}, respectively. The bands appearing at 3800–3500 cm^{-1} may be also connected with the valence vibrations of CO_2 molecules. In the FTIR spectra at 3059–2650 cm^{-1} the weak bands characteristic for stretching vibrations of HCl molecules releasing at a higher temperature are also observed. The bands at

2220–2060 cm^{-1} are connected with valence vibrations of CO molecules. In the FTIR spectra the bands in the ranges 3100–1420, 1000 and 915 cm^{-1} are characteristic for CH stretching vibrations which is connected with the occurrence of the gaseous hydrocarbon molecules [7–12].

Conclusions

On the basis of the obtained results it appears that 5-chloro-2-methoxybenzoates of some of *d*- and *f*-block elements are hydrated, crystalline complexes. When heated in air and in inert atmospheres they decompose in two (in the case of Ce(III), Co(II), Ni(II) and Zn(II) complexes) or three steps. The enthalpy values of the dehydration process are proportional to the energy of the bonding of respective water molecules in the appropriate complexes. The complexes are more stable in air than in nitrogen atmosphere. The monohydrates of 5-chloro-2-methoxybenzoates of Cu(II), Sm(III), Eu(III) and Gd(III) are the most thermally stable of complexes under study in air and nitrogen. The molecules of H_2O, HCl, CO_2, CO and hydrocarbons are the gaseous products evolved during decomposition of 5-chloro-2-methoxybenzoates of *d*- and *f*-block elements.

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