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THERMAL DECOMPOSITION OF RARE EARTH COMPLEXES WITH *m*-AMINOBENZOIC ACID

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The conditions of thermal decomposition of the m-aminobenzoates of Y, La, Ce(III), Pr, Nd and Sm-Lu, $Ln(C_6H_4NH_2COO)_3.nH_2O$ (n = 4-6), have been studied.

The hydrated compounds lose all molecules of crystallization water in one stage at 333-413 K. The anhydrous compounds are stable up to 570 K and are then decomposed exothermically to oxides.

This paper is a continuation of research on rare earth complexes with the aminobenzoic acid isomers. In previous papers, the lanthanide complexes with *o*-aminobenzoic acid were investigated, and the modes of coordination [1, 2] and decomposition [3] were studied.

Metal complexes of *m*-aminobenzoic acid have been studied by many authors, who considered mainly the metal - ligand coordination in the complexes. Thus, Spitzyn [4] investigated chromium(III) complexes, Aggarwal and Singh [5] those of tin(IV), Lysiak [6] and Kharotonov [7] those of thallium(I), Kukutshkin [8] those of platinum(II), and Inomata and Makiwaki [9] those of several divalent metal compounds. In these papers, the thermal stability of the compounds was not determined.

In our recent investigations, the metal - ligand coordination in the *m*-aminobenzoates of lanthanides was studied [10]. The present paper deals with the thermal decomposition of the complexes during heating in an air atmosphere.

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Experimental

The *m*-aminobenzoates of Y, La and the lanthanides were obtained by adding *m*-aminobenzoic acid solution at 363 K to freshly precipitated colloidal hydroxides of the metal ions in a molar ratio of acid to Ln^{3+} of 3:1. The crystals of the compounds were filtered off, washed with alcohol and dried to constant weight under room conditions. The contents of carbon, nitrogen and hydrogen were determined by elemental analysis, using V_2O_5 as oxidizing agent; the contents of rare earth elements were determined by ignition of the complexes to Ln_2O_3, CeO_2, Pr_6O_{11} or Tb_4O_7 at 1273 K; the contents of water were determined from the TG curves and by isothermal heating to 403 K.

These results revealed that the prepared *m*-aminobenzoates of the rare earth elements have the formula $Ln(C_6H_4NH_2COO)_3.nH_2O$, where $n = 6$ for Ln = La-Nd, Eu-Tb and Yb, $n = 5$ for Ln = Y, Sm, Dy, Er and Lu, and $n = 4$ for Ln = Ho and Tm (Table 1).

Table 1a Temperature range of decomposition of Y, La and lanthanide m-aminobenzoates

Compound	Temperature range of dehydrat., K	Loss of weight, %	
		calc.	found
$YL_3.5H_2O$	353-393	15.33	16.0
$LaL_3.6H_2O$	358-413	16.49	16.7
$CeL_3.6H_2O$	353-393	16.46	16.0
$PrL_3.6H_2O$	353-406	16.44	16.4
$NdL_3.6H_2O$	343-408	16.36	16.2
$SmL_3.5H_2O$	333-383	13.88	14.0
$EuL_3.6H_2O$	353-398	16.17	16.0
$GdL_3.6H_2O$	348-403	16.00	16.0
$TbL_3.6H_2O$	353-393	16.00	16.0
$DyL_3.5H_2O$	353-388	13.63	13.6
$HoL_3.4H_2O$	353-393	11.16	11.2
$ErL_3.5H_2O$	343-383	13.53	13.6
$TmL_3.4H_2O$	338-383	11.09	11.2
$YbL_3.6H_2O$	338-383	15.67	15.2
$LuL_3.6H_2O$	338-383	13.75	13.6

$L = C_6H_4NH_2COO$

The IR spectra of the complexes were recorded on a UR-20 spectrophotometer over the range 400-4000 cm^{-1}. The spectra indicated ions with coordination number nine coordinated to three *m*-aminobenzoate ligands through carboxyl groups forming bidentate, symmetric and chelating bonds and simultaneously to three ligands through the nitrogen atom of the amino group. The recorded diffractograms (DRON-2, Ni filtered CuK_a radiation) showed that the *m*-aminobenzoates have low symmetry, with large unit cells, and isostructural in the whole range for Y, La-Lu.

Table 1b Decomposition T, K of Y, La and lanthanide m-aminobenzoate

Compound	Temperature range of decomp., K	Loss of weight, %		T_k	Exo peak,	Endo peak,
		calc.,	found	K	K	K
$YL_3.5H_2O$	578-908	80.77	80.4	908	643-903	383
$LaL_3.6H_2O$	593-793	75.14	75.1	793	593-833	383
$CeL_3.6H_2O$	583-923	73.78	73.2	923	583-923	363
$PrL_3.6H_2O$	588-933	74.10	73.8	933	603-923	383
$NdL_3.6H_2O$	583-928	74.53	74.4	928	593-853	378
$SmL_3.5H_2O$	578-893	73.13	73.1	893	583-873	383
$EuL_3.6H_2O$	578-903	73.67	73.6	903	583-873	383
$GdL_3.6H_2O$	573-938	73.16	72.8	938	593-888	393
$TbL_3.6H_2O$	573-873	72.32	72.2	873	588-873	388
$DyL_3.5H_2O$	598-993	71.78	72.0	993	598-993	378
$HoL_3.4H_2O$	573-1023	70.72	70.4	1023	573-1023	388
$ErL_3.5H_2O$	563-968	71.27	71.4	968	593-933	373
$TmL_3.4H_2O$	633-1053	70.29	70.4	1053	633-1038	378
$YbL_3.6H_2O$	603-943	71.42	72.0	943	603-378	363
$LuL_3.5H_2O$	628-943	70.45	70.4	943	628-943	373

$L = C_6H_4NH_2COO$

The thermal stabilities of the Y, La and lanthanide complexes of *m*-aminobenzoic acid were studied. The TG, DTG and DTA curves were recorded. The measurements were made with an OD-102 derivatograph at a heating rate of 9 deg.min^{-1} up to 1173 K, in a ceramic crucible in air, with sensitivity TG = 100 mg. The results are presented in Figs 1-4. From the thermal curves of the *m*-aminobenzoates, the temperatures of thermal decomposition were evaluated (Table 1). The decomposition products obtained during heating, as deduced from the TG curves, were confirmed by recording their IR and X-ray spectra.

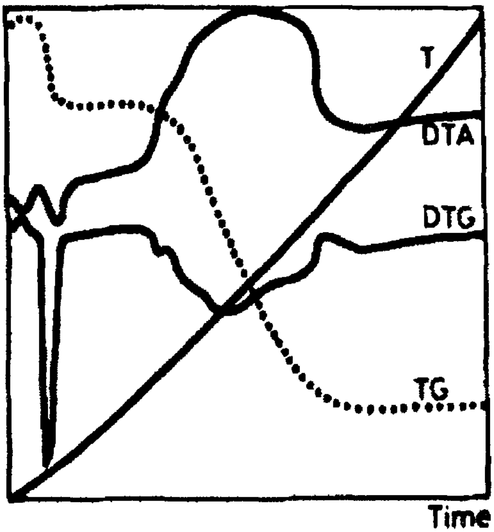

Fig. 1 TG, DTG and DTA curves of $Y(C_6H_4NH_2COO)_3.5H_2O$

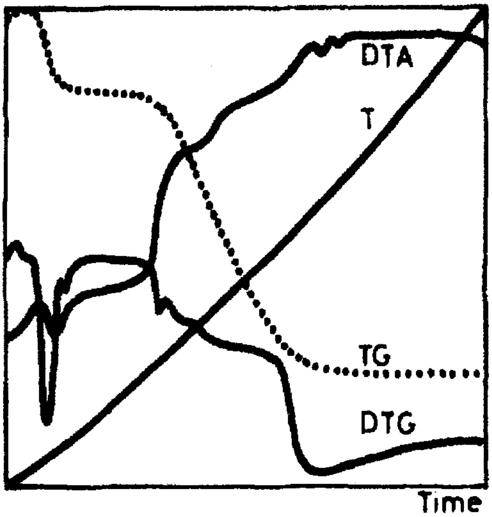

Fig. 2 TG, DTG and DTA curves of $Nd(C_6H_4NH_2COO)_3.6H_2O$

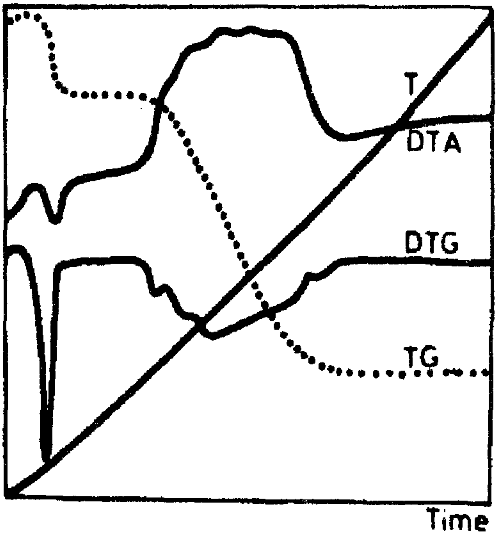

Fig. 3 TG, DTG and DTA curves of $Gd(C_6H_4NH_2COO)_3.6H_2O$

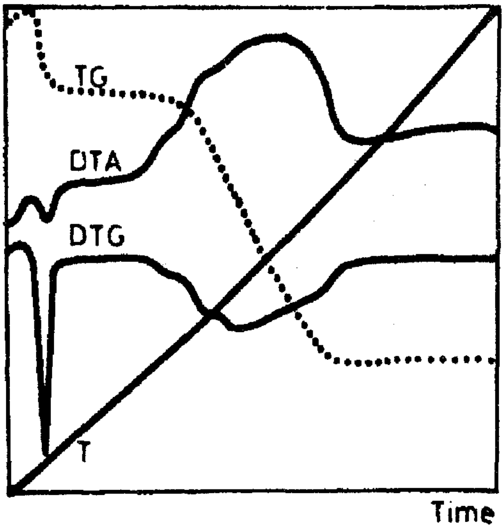

Fig. 4 TG, DTG and DTA curves of $Lu(C_6H_4NH_2COO)_3.5H_2O$

Results and discussion

The thermal analysis results indicate that the complexes of the rare earth elements with *m*-aminobenzoic acid decompose in a similar manner.

On heating the hydrated compounds first lose all the molecules of crystallization water in one stage at 333-413 K. The dehydration process is accompanied by a strong endothermic effect, with maximum at about 380 K. The comparatively low temperature of dehydration suggests the outer--sphere character of the crystallization water. Dehydration leads to the anhydrous *m*-aminobenzoates of the lanthanides, which are stable up to 570 K. Their structures are quite different from those of the hydrated compounds, as confirmed by the X-ray and IR spectra, which may also indicate different modes of metal-ligand bonding in the hydrated and anhydrous compounds [10].

When heated to above 570 K, the anhydrous *m*-aminobenzoates decomposed directly to the oxides Ln_2O_3, CeO_2, Pr_6O_{11} or Tb_4O_7. Ignition of the organic ligand is accompanied by a strong exothermic effect in the temperature range of about 600-900 K. The temperature of oxide formation varies irregularly in the lanthanide series, from 793 to 1053 K (Table 1).

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Zusammenfassung -- Es wurden die Bedingungen für die thermische Zersetzung der *m*-Aminobenzoate $Ln(C_6H_4NH_2COO)_3.nH_2O$ (n = 4-6) von Y, La, Ce(III), Pr, Nd und Sm-Lu untersucht. Alle Verbindungen geben ihr Kristallwasser in einem Schritt bei einer Temperatur zwischen 333 und 413 K ab. Die wasserfreien Verbindungen sind bis 570 K stabil und zersetzen sich dann exotherm unter Entstehung von Oxiden.