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THE DEHYDRATION BEHAVIOUR OF RARE EARTH COMPLEXES OF *m*-NITROBENZOIC ACID

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Abstract

Rare earth complexes of *m*-nitrobenzoic acid ($LnL_3{\cdot}2H_2O$, *Ln* = La-Lu and Y, except Pm, HL = *m*-nitrobenzoic acid) were synthesized and characterized by elemental analysis, chemical analysis, IR spectroscopy and X-ray diffraction analysis. The dehydration behaviour of these complexes was studied in detail by means of TG-DTA and DSC. Dehydration occurs over the temperature range 76–215°C, and the temperature of formation of the anhydrous complexes decreases with increasing atomic number of the rare earth. The activation energies and enthalpy changes for the dehydration were obtained.

Keywords: complexes, DTA-TG-DSC, IR, luminescent materials, rare earth complexes of *m*-nitrobenzoic acid, X-ray

Introduction

Rare earth complexes of carboxylic acids have unusual structures and interesting luminescence properties [1–3]. For example, the erbium complex of pyromellitic acid has a polymeric network structure; neodymium and erbium phenylacetates have infinite chain and dipolymeric structures, respectively. Some rare earth complexes of benzoic acid, as luminescent materials, have been applied in agriculture. The thermodynamic parameters for rare earth complexes of *m*-nitrobenzoic acid were determined by Choppin [4] and solid complexes were prepared and characterized by Wieslawa [5]. As a continuation of our own work [1–3, 6], rare earth complexes of *m*-nitrobenzoic acid have been prepared and their dehydration behaviour has been studied systematically by means of thermal analysis techniques.

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Experimental

An aqueous solution of $LnCl_3$ (*Ln* = La-Lu and Y, except Pm) (5.0 mmol) was added to an aqueous solution of *m*-nitrobenzoic acid (15.0 mmol). The *pH* of the resulting solution was adjusted to about 5 with aqueous ammonia solution, followed by stirring for 2 hours on a water bath (50°C). After filtration, the filtrate was kept in air for a few days. The solid complex that separated out was collected by filtration, washed with alcohol and dried over phosphorus(V) oxide in a vacuum desiccator.

Elemental analysis of the complexes was performed with a Company Model 1106 elemental analyzer. IR spectra (400 –4000 cm^{-1}) were recorded on a Perkin-Elmer 580B IR spectrophotometer using the KBr pellet method. The X-ray diffraction patterns were taken on a PW 1700 diffractometer.

TG-DTA curves were recorded on a Shimadizu Model DT-30 thermal analyzer. A sample mass of 10 mg and a dynamic air atmosphere with 50 $ml\cdot min^{-1}$ flow rate were used. The heating rate was 10 $deg\cdot min^{-1}$. DSC was performed with a Perkin-Elmer DSC-7 thermal analyzer in a dry N_2 atmosphere (flow rate 50 $ml\cdot min^{-1}$) and a heating rate of 10 $deg\cdot min^{-1}$. Indium metal was used as the calibration material for DSC.

Results and discussion

Characterization of complexes

The results of elemental analysis and chemical analysis are listed in Table 1. On the basis of the results, the composition of these complexes is considered to be $LnL_3\cdot 2H_2O$, (*Ln* = La-Lu and Y, except Pm, HL = *m*-nitrobenzoic acid).

The IR spectra of these complexes are similar. Coordination of the ligand with the rare earth leads to loss of the –COOH absorption band at 1700 cm^{-1} and the appearance of two bands arising from symmetric and asymmetric vibrations of $-COO^-$ (ν^s, ν^{as}, at 1400–1420 cm^{-1} and 1590–1600 cm^{-1}, respectively. As compared with the $\Delta\nu$ ($\nu^{as}-\nu^s$) value of 233 cm^{-1} for sodium *m*-nitrobenzoate, the values for the present complexes are only 180–188 cm^{-1}. The ligand is coordinated to the rare earth cation via the $-COO^-$ group, and the coordination bonds in these complexes have some covalent character. An absorption band at 3100–3200 cm^{-1} indicates the presence of water in the complexes.

Table 1 Elemental analysis data

Complex	% RE		% C		% H		% N	
	found	calc.	found	calc.	found	calc.	found	calc.
$LaL_3{\cdot}2H_2O$	20.71	20.63	37.31	37.36	2.31	2.40	6.15	6.24
$CeL_3{\cdot}2H_2O$	20.62	20.77	37.55	37.46	2.35	2.39	6.30	6.23
$PrL_3{\cdot}2H_2O$	20.90	20.87	37.08	37.35	2.30	2.39	6.26	6.22
$NdL_3{\cdot}2H_2O$	21.31	21.25	36.53	37.17	2.20	2.38	6.22	6.19
$SmL_3{\cdot}2H_2O$	21.90	21.95	36.49	36.84	2.27	2.36	6.24	6.14
$EuL_3{\cdot}2H_2O$	22.21	22.14	36.22	36.75	2.27	2.35	6.03	6.12
$GdL_3{\cdot}2H_2O$	22.77	22.74	36.50	36.47	2.38	2.33	5.95	6.08
$TbL_3{\cdot}2H_2O$	22.85	22.93	36.54	36.38	2.40	2.33	6.01	6.06
$DyL_3{\cdot}2H_2O$	23.40	23.32	36.40	36.21	2.23	2.31	6.14	6.03
$HoL_3{\cdot}2H_2O$	23.63	23.59	36.07	36.07	2.29	2.31	5.95	6.01
$ErL_3{\cdot}2H_2O$	23.79	23.83	35.62	35.95	2.26	2.30	5.84	5.99
$TmL_3{\cdot}2H_2O$	24.15	24.02	35.27	35.86	2.20	2.29	5.79	5.97
$YbL_3{\cdot}2H_2O$	24.51	24.46	35.49	35.65	2.22	2.28	5.94	5.94
$LuL_3{\cdot}2H_2O$	24.65	24.67	34.97	35.56	2.19	2.27	5.75	5.92
$YL_3{\cdot}2H_2O$	14.20	14.26	40.02	40.47	2.43	2.59	6.58	6.74

L=*m*-Nitrobenzoic acid ($C_7H_5NO_4$)

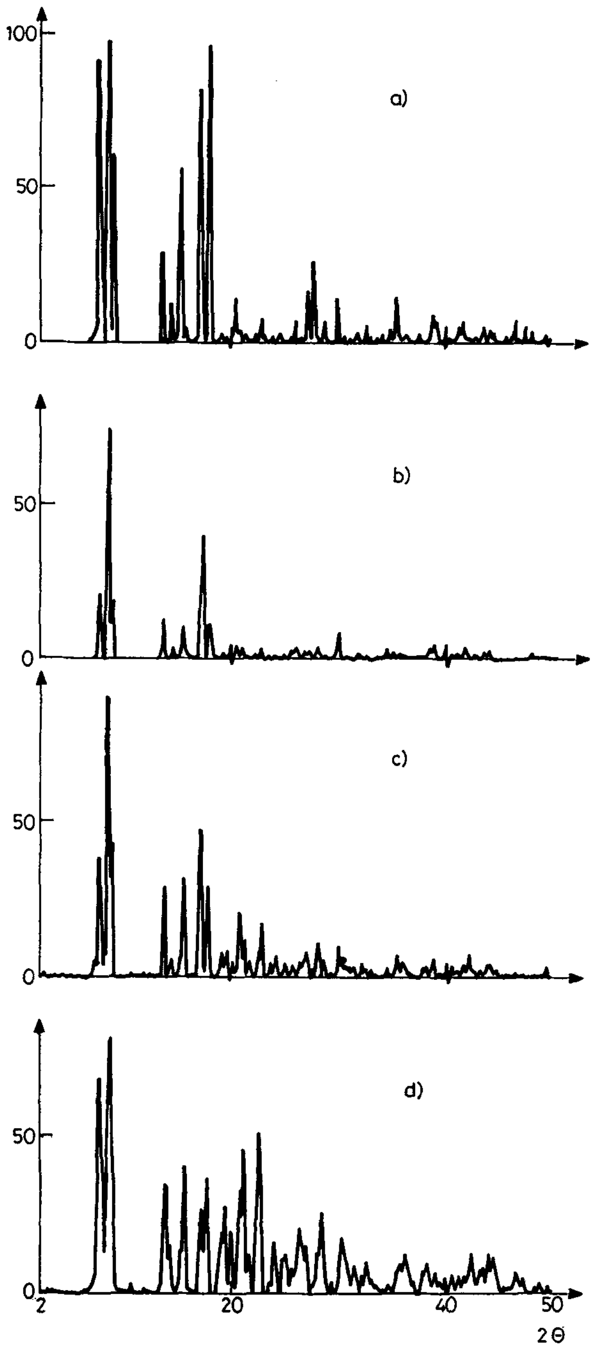

Fig. 1 X-ray diffraction patterns of rare earth complexes of *m*-nitrobenzoic acid; a) $LaL_3 \cdot 2H_2O$, b) $PrL_3 \cdot 2H_2O$, c) $SmL_3 \cdot 2H_2O$, d) $LuL_3 \cdot 2H_2O$

The X-ray spectra for the complexes (Fig. 1) reveal that the *m*-nitrobenzoates of the rare earths are isostructural and have quite a large unit cell, the crystals of all complexes belonging in the triclinic system [6].

Mechanism of dehydration of RE complexes of m-nitrobenzoic acid

Figure 2 shows the TG-DTA curves of these complexes in air atmosphere. Well-defined mass losses occur over the temperature range 76–215°C, and corresponding endothermic processes are noted in the DTA curves. The experimental mass loss accords with the theoretically calculated water content of the complexes, as shown in Table 2.

Table 2 TG data of RE complexes of *m*-nitrobenzoic acid

Complex	Dehydration temperature range / °C			Mass loss / %	
	onset	peak	offset	calc.	found
$LaL_3 \cdot 2H_2O$	90.1	152.2	215.0	5.3	5.2
$CeL_3 \cdot 2H_2O$	104.1	145.0	206.0	5.3	5.3
$PrL_3 \cdot 2H_2O$	95.0	144.4	204.8	5.3	5.5
$NdL_3 \cdot 2H_2O$	94.2	144.5	204.0	5.3	5.2
$SmL_3 \cdot 2H_2O$	90.6	144.0	176.8	5.3	5.0
$EuL_3 \cdot 2H_2O$	85.2	140.0	164.8	5.2	5.0
$GdL_3 \cdot 2H_2O$	90.0	133.3	161.4	5.2	5.4
$TbL_3 \cdot 2H_2O$	86.5	134.2	160.0	5.2	5.2
$DyL_3 \cdot 2H_2O$	78.4	125.3	156.0	5.2	5.0
$HoL_3 \cdot 2H_2O$	76.0	123.3	155.0	5.2	4.9
$ErL_3 \cdot 2H_2O$	76.2	123.7	150.4	5.1	5.1
$TmL_3 \cdot 2H_2O$	76.0	110.0	140.0	5.1	5.2
$YbL_3 \cdot 2H_2O$	76.0	106.0	135.2	5.1	5.1
$LuL_3 \cdot 2H_2O$	76.5	103.2	132.0	5.1	5.2
$YL_3 \cdot 2H_2O$	78.1	118.0	146.0	5.8	5.7

The temperatures of dehydration of these complexes are unusually high, and the corresponding DTA peaks are broad in character. Hence, it is concluded that the water in the complexes is coordination water rather than crystal water, which is in contrast with the viewpoint in the literature [5]. The crystal structures of these complexes [6] also indicate that all the water molecules in the

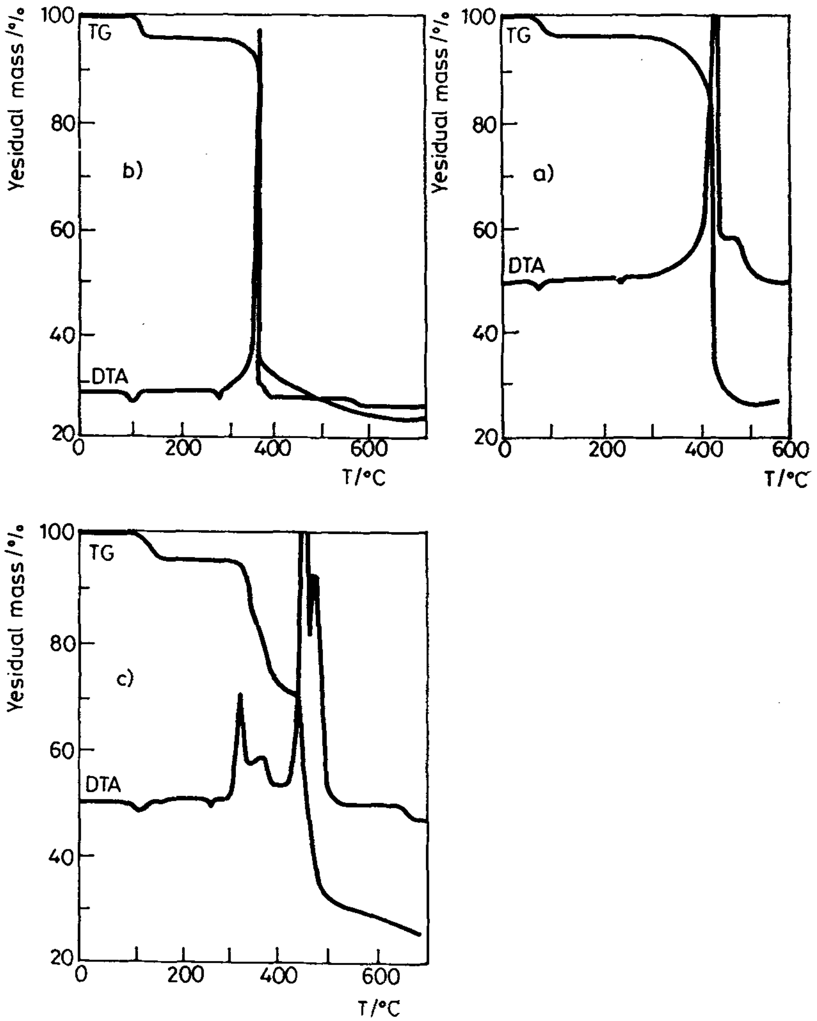

Fig. 2 TG-DTA curves of RE complexes of *m*-nitrobenzoic acid; a) $LuL_3 \cdot 2H_2O$, b) $NdL_3 \cdot 2H_2O$, c) $LaL_3 \cdot 2H_2O$

complexes are coordination water, which confirms the conclusion based on the thermal analysis results.

Figure 2 shows the relationship between dehydration temperature and rare earth atomic number. The temperatures of formation of the anhydrous complexes decrease with increasing atomic number of the rare earth, which agrees with previous studies [7]. In these complexes, the coordination number of each rare earth ion is nine, but the ionic radius decreases with increase in atomic number of the rare earth. The repulsion between the ligands and also the steric hindrance therefore increase, which results in the decreasing stability of these complexes, as shown in Fig. 2.

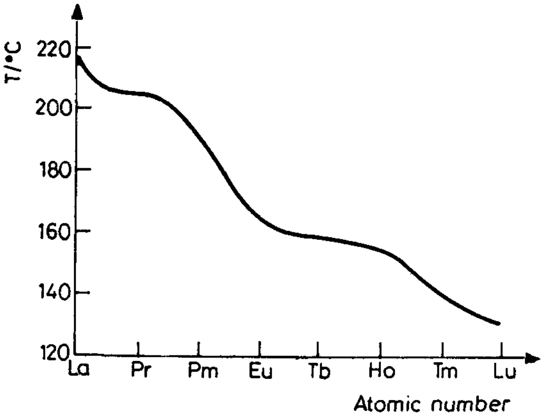

Fig. 3 Atomic number dependence on the dehydration temperature of the RE complexes

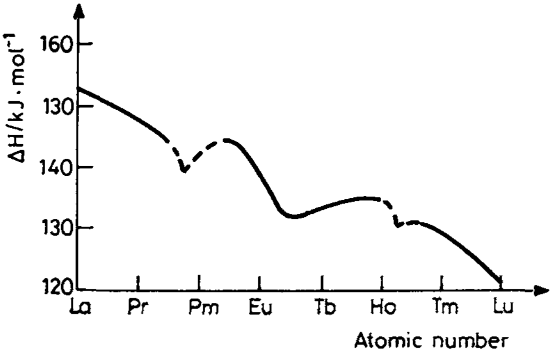

Fig. 4 Relationship between enthalpy of dehydration and atomic number for RE complexes

Activation energies and enthalpy changes for dehydration of rare earth complexes of m-nitrobenzoic acid.

The water molecules in these complexes are coordinated to the rare earth cations, and the dehydration of $LnL_3 \cdot 2H_2O$ is an endothermic process. The enthalpy changes for dehydration of the complexes were determined by means of DSC and the corresponding activation energies were calculated by the Freeman-Carroll method [8] according to the equation

$$\Delta \lg(d\alpha/dT)/\Delta \lg(1-\alpha) = -E\Delta(1/T)/(2.3R\Delta \lg(1-\alpha)) + n$$

where $d\alpha/dT$ = reaction rate, R = universal gas constant, E = activation energy, T = absolute temperature, α = degree of conversion, and n = order of reaction. A plot of $\Delta\lg(d\alpha/dT)/\lg(1-\alpha)$ *vs.* $(1/T)\lg(1-\alpha)$ should result in a straight line with slope $-E/2.3R$, and thus the activation energies can be obtained. The enthalpy change and activation energy data are listed in the Table 3. It is seen that the activation energy data vary with the rare earth cation, but there is no regularity. Figure 4 shows the relationship between the dehydration enthalpy and the atomic number of the rare earth element. The enthalpy changes exhibit a decreasing trend as the atomic number of the rare earth increases. In addition, an apparent 'tetrad effect' is observed, which is related to the electronic structure of the rare earth cation.

Table 3 The dehydration activation energies and enthalpy changes

Complex	E / kJ·mol^{-1}	ΔH / kJ·mol^{-1}
$LaL_3 \cdot 2H_2O$	89.1	152.4
$CeL_3 \cdot 2H_2O$	87.0	150.2
$PrL_3 \cdot 2H_2O$	93.4	147.7
$NdL_3 \cdot 2H_2O$	91.5	143.0
$SmL_3 \cdot 2H_2O$	97.7	146.2
$EuL_3 \cdot 2H_2O$	91.9	137.7
$GdL_3 \cdot 2H_2O$	84.6	132.0
$TbL_3 \cdot 2H_2O$	93.5	13401
$DyL_3 \cdot 2H_2O$	108.8	134.4
$HoL_3 \cdot 2H_2O$	100.1	135.6
$ErL_3 \cdot 2H_2O$	106.3	132.5
$TmL_3 \cdot 2H_2O$	93.7	128.5
$YbL_3 \cdot 2H_2O$	103.3	128.3
$LuL_3 \cdot 2H_2O$	104.0	119.4
$YL_3 \cdot 2H_2O$	98.5	128.6

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Zusammenfassung — Seltenerdenkomplexe von *m*-Nitrobenzoesäure (LnL_32H_2O, *Ln* = La-Lu und Y, mit Ausnahme von Pm, HL = *m*-Nitrobenzoesäure) wurden synthetisiert und mittels Elementaranalyse, chemischer Analyse, IR-Spektroskopie und Röntgendiffraktionsanalyse charakterisiert. Mit Hilfe von TG-DTA sowie DSC wurde das Dehydratationsverhalten dieser Komplexe im Detail untersucht. Die Dehydratation findet im Temperaturbereich 76–215°C statt und die Temperatur für die Bildung des wasserfreien Komplexes sinkt mit anwachsender Ordnungszahl des Seltenerdenelementes. Für die Dehydratation wurden auch Aktivierungsenergien und Enthalpieänderungen ermittelt.