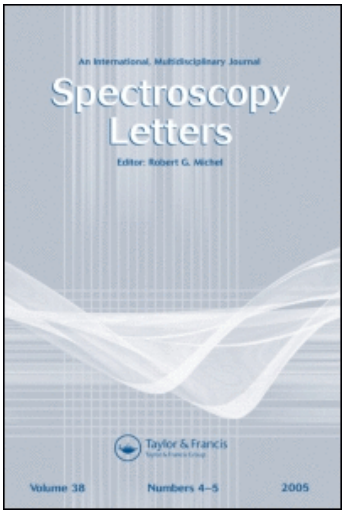

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SYNTHESIS AND IR-SPECTRAL CHARACTERIZATION OF MIXED-LIGAND SOLID STATE COMPLEXES OF SOME LANTHANOIDES WITH MONO-(2-ETHYLHEXYL) PHOSPHORIC ACID

Key words: IR-spectrometry, Lanthanoides, Solid state complexes

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Abstract

The synthesis of a new type of complexes of Y, Nd and Er with mono-(2-ethylhexyl) phosphoric acid is reported. The elemental composition, IR-spectral data and thermogravimetric analysis prove the presence of both mono- and bivalent ions of the acid as ligands as well as of NO_3^--ions. The IR-spectrum is interpreted in comparison with those of other lanthanoid complexes of the same acid.

INTRODUCTION

A few types of solid state complexes of lanthanoides (Ln) with bis-(2-ethylhexyl) phosphoric acid (HA, $A=/CH_3(CH_2)_3CH(CH_2CH_3)CH_2O/_2PO_2^{2-}$ are described in the literature [1]. Some of them possess the properties of the liquid crystals, others have been used as catalysts. Recently, the formation of Ln-solid complexes with mono-(2-ethylhexyl) phosphoric acid (H_2B, $B=CH_3(CH_2)_3CH(CH_2CH_3)CH_2OPO_3^{2-}$) was reported and a possible application of the both types of complexes for La-separation from other Ln was pointed out [2]. In the present paper the preparation of a new type of mixed-ligand solid complexes of some Ln with H_2B is reported. Its synthesis is realized under specific experimental conditions which model to some extent that, applied in the case of La-separation by precipitation [2, 3] or by liquid-membrane extraction [4] using Ln-complexes of (2-ethylhexyl) phosphoric acids. The study of these complexes is significant for the understanding of the mechanism of the separation process mentioned and for an effective application of the latter. The work was done using elements, representative for the subgroups of the light (Nd) and the heavy (Er) lanthanoides, and using Y, which, possessing a different electronic configuration, has an ionic radius very close to that of Er.

EXPERIMENTAL

Materials. The synthesis was performed using a commercially available bis-(2-ethylnexyl) phosphoric acid (Fluka), usually utilized in Ln-separation processes. According to the potentiometric titration data the acid represents a mixture of 37% H_2B and 62% HA. The other reagents were of puriss. p.a. grade.

Synthesis. To a known mass of the mentioned above commercial mixture of acids, 0.5 M NaOH was added in an amount stoichiometrically required for neutralization of 1/6 of the acids to NaA and NaHB respectively. After 30 min of agitation and a period of time which ensures the phase separation, the two

phases were separated. The synthesis methods, applied up to now, are based on the usage of the organic phase. In the present work the aqueous phase, strongly enriched with H_2B and its salt was used as starting material. Acetone solution of $Ln(NO_3)_3$ (100 $g.dm^{-3}$) was added to it, and it was treated further on following the method employed in Ref. [2].

Analysis. The contents of C, H and N in the precipitates were determined using common organic analysis methods whereas that of Ln – by ICP-AES. IR-spectra (400–4000 cm^{-1}, nujol mulls) were recorded by a FT–Bomem Michelson–100 spectrometer. The resolved spectra were obtained as an average of 50 scans. Strongly overlapping bands were subjected to a deconvolution prior to the resolving. Simultaneous TG/DTG/DTA analysis was carried out by a MOM Paulik–Paulik–Erdey derivatograph by heating 0.3 g of the samples in static air up to 723 K at a rate of 5 K min^{-1} in a synthetic corundum crucible. Al_2O_3 was used as reference. The calibration was carried out with $CaC_2O_4.H_2O$. The sensitivity was: TG – 5 mg; DTA – 1/5. The activation energies of the process stages were calculated following the method proposed in Ref. [5].

RESULTS AND DISCUSSION

The elemental compositions of the precipitates obtained are given in Table 1. On this base the compounds can be described as mixed-ligand complexes of the type $Ln_2B_2(HB)NO_3.2H_2O$. The formation of complexes namely of the H_2B is not surprising bearing in mind the greater solubility of this acid and its salts in water compared to that of HA and NaA [6]. In the aqueous phase, obtained by the partial neutralization of the starting ($HA+H_2B$)-mixture, an excess of NaOH is raised in spite of the overall excess of acids in the system as a whole (organic and water phases). Therefore B^{2-} exists in the latter (along with HB^-).

The proposed formulae of the complexes are confirmed by the IR-spectral analysis. The spectra of Y-, Nd- and Er- complexes are identical. In Fig. 1 the

TABLE 1.

Elemental composition (%) of the obtained complexes

No	Formula proposed	C		H		N		Ln	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1	$Y_2B_2(HB)NO_3.2H_2O$	31.97	31.98	6.30	6.26	1.7	1.6	19.60	19.72
2	$Nd_2B_2(HB)NO_3.2H_2O$	29.75	28.48	5.71	5.58	1.5	1.4	28.31	28.50
3	$Er_2B_2(HB)NO_3.2H_2O$	26.52	27.24	5.12	5.33	1.3	1.3	31.80	31.62

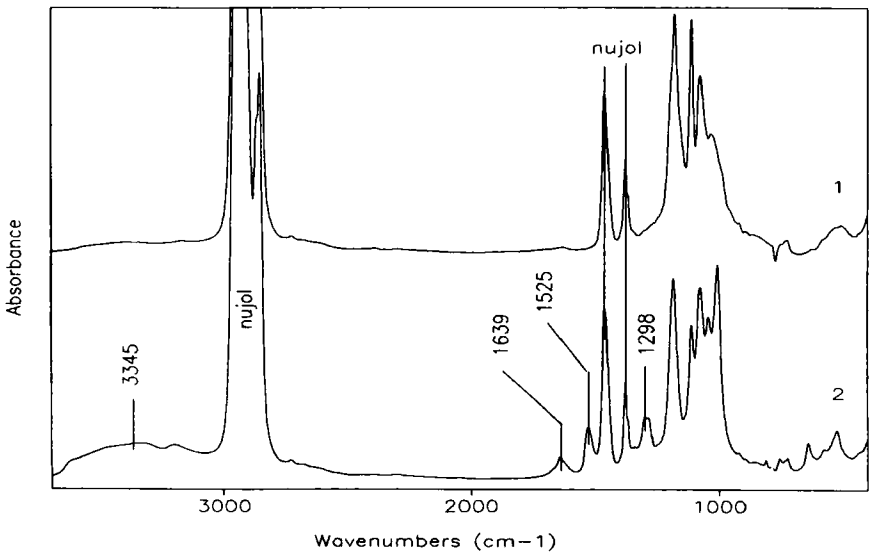

FIG. 1. IR-spectra of: YA_3 (1) and $Y_2B_2(HB)NO_3.2H_2O$

spectrum of Y-compound is shown, compared with that of the respective complex of the well-known LnA_3-type. The bands at 3345 cm^{-1} and 1639 cm^{-1} are raised by the coordinated water existence. The absorption maxima at 1525 cm^{-1} and 1298 cm^{-1} prove the presence of bidentate ONO_2-group [7]. The presence of HB^- and B^{2-} ligands in the complex presumes a mixed type of yttrium coordination namely, bridging and chelating, i.e. bands, characteristic for $Ln(HB)_3$ and Ln_2B_3 [8] have to be expected in $Ln_2B_2(HB)NO_3$-spectrum. The resolving of the spectral curve (1300−900 cm^{-1}, Fig. 2) confirms this supposition. The bands corresponding to ν^{as}_{POO-} at 1195 cm^{-1} and 1182 cm^{-1} and those corresponding to ν^{s}_{POO-} at 1112 cm^{-1} and 1077 cm^{-1} are disposed at the same wavenumbers as in the YA_3-spectrum. However, at the same time absorption maxima are also observed at 1165 cm^{-1} and 1045 cm^{-1} which are characteristic for the $Ln(HB)_3$- and Ln_2B_3- types of complexes. In the cases of $La(HB)_3.1.5H_2O$ and $La_2B_3.3H_2O$ these bands occur at 1195 cm^{-1} and 1055 cm^{-1} respectively [8]. The presence of non-deprotonized OH-group causes also the increased absorbance in the 1030−1000 cm^{-1} region of the $Y_2B_2(HB)NO_3.2H_2O$-spectrum. In more details this effect is discussed for the case of $La(HB)_3.1.5H_2O$ [8].

The presence of OH-group in $Ln_2B_2(HB)NO_3$ and the mentioned similarity of their spectra with that of $Ln(HB)_3.1.5H_2O$ give the grounds to suppose that the supramolecular structure of the former complex is stabilized (along with the alcylphosphate bridges of the type −P−O−Ln−O−P−O−Ln−) by an additional association through PO−H...O(H)−P hydrogen bonds.

The thermal decomposition behaviour of the studied complexes additionally proves the composition and structure proposed. The respective results are shown in Table 2. The decomposition proceeds without melting, thus confirming the strong bonding of the alcylphosphate bridges. The dehydration of the complexes completes at approximately the same temperature as that of $La_2B_3.3H_2O$ (433 K [9]) with small variations (400÷453 K) which depend on the Ln-nature. According to the mass loss data the dehydration is followed by a release of

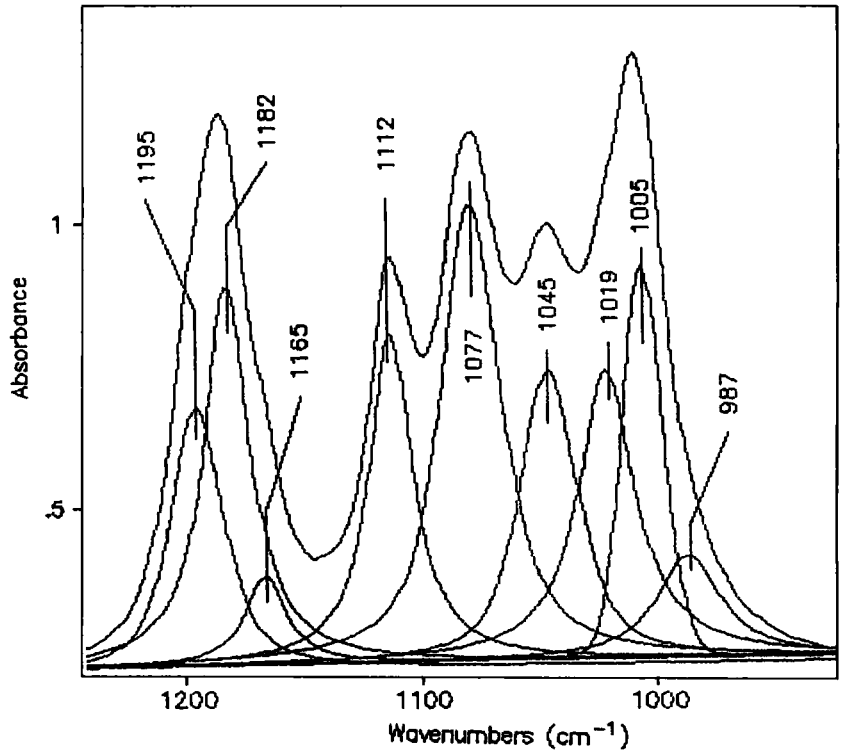

FIG. 2. Resolved IR-spectrum (1300−900 cm^{-1}) of $Y_2B_2(HB)NO_3.2H_2O$.

1 mol HNO_3/mol $Ln_2B_2(HB)NO_3$. The rate-controlling process (established by following [10]) of the HNO_3-release is a random nucleation, which is the same as the one in the case of NO_3-release from CeA_3NO_3 heated in static air [11]. As one can expect, however, the activation energies are rather different (kJ.mol^{-1}): 132 for CeA_3NO_3 [11] and 30 for $Y_2B_2(HB)NO_3$ (Table 2). On the other hand, the release of HNO_3 is analogous to the H_2O- release observed during the thermally induced condensation of $La(HB)_3$ [9].

The proceeding of the above described processes is confirmed by the IR-spectrum of the intermediate, obtained when heating $Y_2B_2(HB)NO_3.2H_2O$ up

TABLE 2

Thermal decomposition of the investigated complexes

Complex	Temperature interval according to DTA-curve, K	Probable process	Mass loss, %		DTG peak, K	Activation energy, kJ.mol^{-1}
			Found	Calc.		
$Y_2B_2(HB)NO_3.2H_2O$	<453	Release of 2 mol H_2O	4.0	4.0		
	453–523	Release of 1 mol HNO_3	7.0	7.0	483	30
	523–553	Release of 3 mol C_2H_5	9.4	9.7	546	69
	553–623	Release of 3 mol $C_6H_{12}O_{0.5}$	27.0	30.7	576	138
	623–723	Crystallization	1.3	—		
		Total [1]	48.7	51.4		
$Nd_2B_2(HB)NO_3.2H_2O$	<398	Release of 2 mol H_2O	3.4	3.6		
	398–473	Release of 1 mol HNO_3	6.1	6.2	473	82
	473–723	Release of 3 mol $C_8H_{17}O_{0.5}$	34.6	35.9	544	149
		Total [1]	44.1	45.7		
$Er_2B_2(HB)NO_3.2H_2O$	<446	Release of 2 mol H_2O	3.2	3.4	446	50
	446–513	Release of 1 mol HNO_3	6.0	6.0		
	513–723	Release of 3 mol $C_8H_{17}O_{0.5}$	33.4	34.3	562	115
		Total [1]	42.6	43.7		

[1] $Ln_2B_2(HB)NO_3.2H_2O \longrightarrow 1.5LnPO_4+0.5Ln(PO_3)_3$

to ~ 530 K. The bands corresponding to H_2O and ONO_2 seen in Fig. 1 as well as the one caused by OH at 1165 cm^{-1} disappear and the absorbance in the 1030–1000 cm^{-1} region considerably decreases. The spectrum obtained is quite similar to that of La_2B_3 (registered after the dehydration of $La_2B_3.3H_2O$ [9]).

The decomposition of the hydrocarbon chains of the Nd- and Er- complexes proceeds in a one-stage process. Random nucleation with a two-dimensional

nucleous growth is a rate-controlling reaction. In the case of Er-complex the kinetic analysis reveals also the role of the interface boundary motion (with cylindrical symmetry). Two strongly overlapping stages are observed during the hydrocarbon degradation of $Y_2B_2(HB)NO_3$. The C_2H_5-release (most probably connected with the tertiary C-atom) is followed by the release of the remaining part of the fragments. The final heating product is a mixture of $LnPO_4$ and $Ln(PO_3)_3$ (mole ratio = 3), analogously to the case of $La_2B_3.3H_2O$ heating [9]. It was proved by the total mass loss and by the elemental composition of the product.

CONCLUSION

The results reported show that the mixed-ligand NO_3-containing solid state Ln complexes of the type $Ln_2B_2(HB)NO_3.2H_2O$ can be prepared by a reaction of $Ln(NO_3)_3$ with H_2B sodium salt in aqueous-acetone solution. Most probably the supramolecular structure of these complexes is constituted by alcylphosphate bridges of the type $-P-O-Ln-O-P-O-Ln-$ and an additional association through $PO-H...O(H)P$ hydrogen bonds.

Generally, the thermal decomposition of the complexes follows the mode already determined in the cases of the other studied Ln-complexes with HA and H_2B and confirms our earlier supposition [12] that the mechanism and the quantitative parameters of the process depend on the Ln-nature and on the structure of the complex.

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