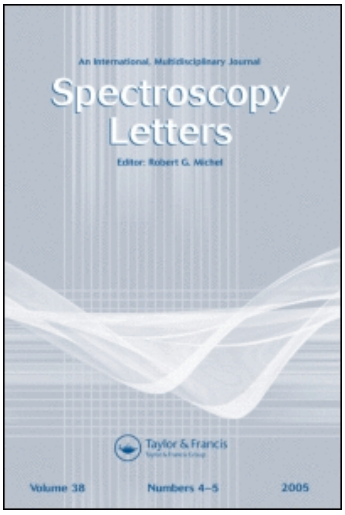

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

IR-Spectral Study of Solid State Complexes of Lanthanum with Mono-and *bis*-(2-Ethylhexyl) Phosphoric Acids

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To cite this Article Arnaudov, M. G. , Milanova, M. M. and Todorovsky, D. S.(1996) 'IR-Spectral Study of Solid State Complexes of Lanthanum with Mono-and *bis*-(2-Ethylhexyl) Phosphoric Acids', Spectroscopy Letters, 29: 5, 781 — 798
To link to this Article: DOI: 10.1080/00387019608001610
URL: http://dx.doi.org/10.1080/00387019608001610

SPECTROSCOPY LETTERS, 29(5), 781-798 (1996)

IR-SPECTRAL STUDY OF SOLID STATE COMPLEXES OF LANTHANUM WITH MONO- AND BIS-(2-ETHYLHEXYL) PHOSPHORIC ACIDS

Key words: Alcyl phosphoric acids, Infrared spectrometry, Lanthanum, Solid state complexes

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ABSTRACT

IR-spectra of the solid state lanthanum complexes with mono- and bis-(2-ethylhexyl) phosphoric acids (H_2B, resp. **HA**) are studied. It is confirmed that La coordinates **HA** as LaO_6-octahedra, connected through $-La-O-P-O-La-$ bridging bonds. The so fixed polynucleous chains form the crystal structure of the complex. The obtained IR-spectral data as well as the results of the X-ray powder diffraction analysis show that La forms shorter polymeric chains than the other rare earth complexes of the same type.

Certain methods for the synthesis of the solid state complexes of La with H_2B (studied for the first time) are considered. It is shown that the structure of La-**HB**-complexes is consituted also by LaO_6-octahedra, resp. $-La-O-P-O-La-$

polymeric chains. However they are binded through crosswise PO−H...O(H)−P hydrogen bonds, owing to the non-deprotonized hydroxo-group presented in the complex. The so formed supramolecular structure has to be more disordered than the one in the case of the complexes with **HA**. This determines the amorphous (nanocrystalline) state of the $\mathbf{H_2B}$-complexes and, probably, their abiliity to coordinate water as well.

INTRODUCTION

The preparation methods and some properties of the solid state complexes of the rare earth (**RE**) with bis-(2-ethylhexyl) phosphoric acid (**HA**, $\mathbf{A}=/CH_3CH(CH_2CH_3)(CH_2)_4O/_2PO_2^-$) of the type $(RE)A_3$ are considered in the literature[1]. Certain data especially on LaA_3 are reported in[2-5]. Some peculiarities (in comparison with the other RE complexes of the same type) of this compound, concerning the polymerization degree[2] and the solubility in specific solvents[5], have been pointed out. Some methods for synthesis of the mixed-ligand complexes $LaA(NO_3)_2.nH_2O$ (n=1, 2) and $LaA(NO_3HA)_2$ and data about their molecular structure are reported in[6], resp.[7].

From practical point of view, interesting results are obtained in the case when a commercially available mixture of **HA** and mono-(2-ethylhexyl) phosphoric acid ($\mathbf{H_2B}$, $\mathbf{B}=CH_3CH(CH_2CH_3)(CH_2)_4OPO_3^{2-}$) is used (instead of pure **HA**) for the $(RE)A_3$-preparation. Its interaction with an aqueous solution of equimolar amounts of $LaCl_3$ and $NdCl_3$ leads to formation of a precipitate, enriched with Nd[8]. The systematic study show that, under specific experimental conditions, the above mentioned commercial mixture of **HA** and $\mathbf{H_2B}$ reacts quite selectively with acetone solution of RE-nitrates: Pr, Nd and Er form solid phases of the type $(RE)A_3$, La produces solid state complexes *only* with $\mathbf{H_2B}$[9], whereas Ce precipitates as NO_3-containing complex[10]. The results briefly mentioned above stimulated the present study on the structure and IR-spectra peculiarities of the La-solid state complexes with **HA** and $\mathbf{H_2B}$, all the more that solid complexes of La with $\mathbf{H_2B}$ are not described in the literature avaliable. The existence of RE-

complexes with H_2B in liquid phase has been reported long ago[11] but the data obtained have not been analyzed thoroughly.

MATERIALS AND METHODS

Materials. $(RE)(NO_3)_3$ were obtained from the respective oxides with an assay $\geq$ 99.9 %. According to the potentiometric titration data, the acid used (Fluka) contains 62 % **HA** and 37 % H_2B. The two acids were separated following the method proposed in[12]; the so obtained acids are with an assay of 99 %. The other reagents used were of puriss. p.a. grade.

Preparation of the Complexes. The complexes were prepared by a reaction of $(RE)(NO_3)_3$ acetone solution (100 $g.dm^{-3}$) with the respective ligands, introduced into the system as acids and/or their salts. After stirring for 1 h, H_2O as desalting agent was added in volume approximately equal to that of acetone presented. A solid phase is then formed; it was separated after 24 h, washed with acetone and water and dried for 48 h in a dessicator above conc. H_2SO_4. The ligands were introduced into the system as:

a) Sodium salt of HA (NaA). To the known mass of the acid, 0.5 M NaOH was added in amount required for its neutralization. After 30 min agitation, to the so obtained NaA, $(RE)(NO_3)_3$ acetone solution was added (mole ratio $RE^{3+}/A^- = 3$) and the above described procedure was followed.

b) Hydrogen sodium salt of H_2B (NaHB). H_2B and 0.5 M NaOH were mixed in mole ratio $H_2B/NaOH = 1$. After a prolonged agitation the acetone solution of the nitrate was added in a mole ratio $NaHB/RE^{3+} = 3$.

c) Mono-(2-ethylhexyl) phosphoric acid (H_2B). The acetone solution of the nitrate and H_2B were mixed in a mole ratio $H_2B/RE^{3+} = 3$.

d) Disodium salt of H_2B (Na_2B). 0.5 M NaOH was added to H_2B in amount stoichiometrically required for a complete neutralization of the acid. After stirring, $La(NO_3)_3$ solution was added in a mole ratio $Na_2B/RE^{3+} = 3/2$.

The elemental composition of the obtained precipitates is shown in Table 1 along with the formulae proposed on this base.

TABLE 1

Composition (%) of the obtained complexes.

Preparation		Formula proposed	H		C		P		RE	
No*	Form of the ligand		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
a	NaA	LaA_3	9.26	9.32	51.98	52.26	8.3	8.4	12.8	12.6
a	NaA	NdA_3	9.17	9.28	51.52	51.96	8.2	8.4	13.4	13.1
b	NaHB	$La(HB)_3.1.5H_2O$	7.32	7.44	36.92	37.71	11.9	12.0	17.7	18.0
c	H_2B	$La(HB)_3.1.5H_2O$	7.55	7.44	38.00	37.71	12.1	12.0	17.9	18.0
d	Na_2B	$La_2B_3.3H_2O$	6.18	6.01	30.87	30.14	9.3	9.7	28.9	29.0

* According to Materials and Methods part.

Analysis. The common organic analysis methods for C, H and N, and ICP−AES for P and RE were used to determine the elemental composition of the complexes. FT-IR spectra (4000−400 cm^{-1}, nujol suspensions) were recorded by a Bomem-Michelson−100 spectrometer. The spectral curves resolving was carried out using Spectra Calc program. The positions of the absorption maxima in the regions of strongly overlapping bands were specified after a preliminary deconvolution.

RESULTS AND DISCUSSION

IR-spectra of the initial acids. IR-spectral data for **HA** are published repeatedly along with investigations of its salts' and complexes' structure. The earlier papers on this problem have been summarized by Peppard et al.[13-17]. The IR-spectrum of $\mathbf{H_2B}$ have been discussed in[13] as to find out the differences in the association type at the mono- and dibasic phosphoric acids. It is shown that whereas the diesters of the H_3PO_4 form cyclic dimmers, the respective monoesters

possess a polymeric structure. The same results are obtained from the study of phosphonic acids and their monoesters[15]. However only a general refering of the respective characteristic frequences has been done. In such a sense, the following discussion makes the literature data available more precise.

In the region 3700−400 cm^{-1} **HA** possesses bands, typical for the monobasic phosphoric acids. The formation of cyclic dimmers (stabilized by strong PO−H...O=P- hydrogen bonds) causes the absence of absorbance above 3000 cm^{-1}. The absorption maxima characteristic for OH-groups, linked in cyclic associates, are at 2640, 2325, 2180 and 1690 cm^{-1} (Fig. 1). These bands are also observed in the H_2B-spectrum along with a new band with a maximum at ~2900 cm^{-1} as well (Fig. 1), due to ν(OH)-bonded of the second type of association. It is defined as polymeric[13] and can be realized in two ways: 1) forming both cyclic and chain associates by PO−H...O=P- hydrogen bonds; 2) the separate cyclic dimmers are bonded crosswise through P−OH...O(H)−P- hydrogen bonds.

The resolving of the spectral curves in the region of 1300−900 cm^{-1} gives an additional information on the above subject. The band at 1230 cm^{-1}, correspondig to ν(P=O) dimmer[13] and the multiplet with maxima at 1080, 1036, 1010 and 982 cm^{-1} (Fig. 2.1) are typical for **HA** in this interval. The complicated nature of the second band was already considered in[18]. The ν(P−O)-vibration of the P−O(H) and P−O−C fragments give the main contribution in this band.

In the H_2B IR-spectrum the characteristic vibrations discussed above correspond to the absorption maxima at 1227, 1072, 1034, 1003 and 962 cm^{-1}. The formation of the new type of associates is revealed by an additional band at 1149 cm^{-1} causing a redistribution of the absorption maxima intensities in the 1075−960 cm^{-1} region (Fig. 2.2). The strong increase of the absorbance at 1034 cm^{-1} suggests that this band should be related to P−OH-stretching vibration. If PO−H...O=P-chain structures actually form in H_2B, the 1149 cm^{-1} absorption maximum should be connected with ν(P=O)-assoc. of this type of associates. Such an interpretation is, however, open to criticism since it follows

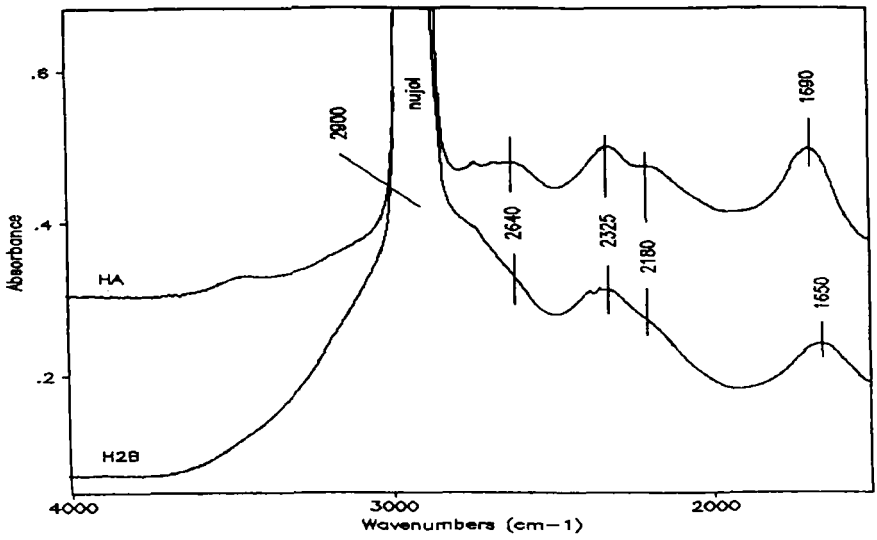


FIG. 1. IR-spectra (4000–400 cm^{-1}) of **HA** and $\mathbf{H_2B}$ (capillary).

that to the weaker hydrogen bond /weaker influenced ν(OH)/ corresponds stronger batochromic effect in the case of ν(P=O).

Our experimental results are in favour of the supposition that in $\mathbf{H_2B}$, a structure, consisting of cyclic dimmers stabilized through crosswise PO−H...O(H)−P- hydrogen bonds exists. Indeed, when studing $La(HB)_3.1.5H_2O$ thermal decomposition, it was shown that heating to 458 K leads to a condensation process accompanied by a disappearing of the absorption maximum at 1149 cm^{-1} and by a sharp decrease of the absorption in the region of 1040−1000 cm^{-1} [19]. Such a condensation can be realized provided that a suitable steric orientation of the OH-groups exists. The latter may be realised just by PO−H...O(H)−P-associates. According to the results obtained (see below) these forms remain when the La coordination takes place.

At the premise that PO−H...O(H)−P-associates do exist in $\mathbf{H_2B}$, it could be accepted that the absorption maximum at 1149 cm^{-1} is related to the out of plane

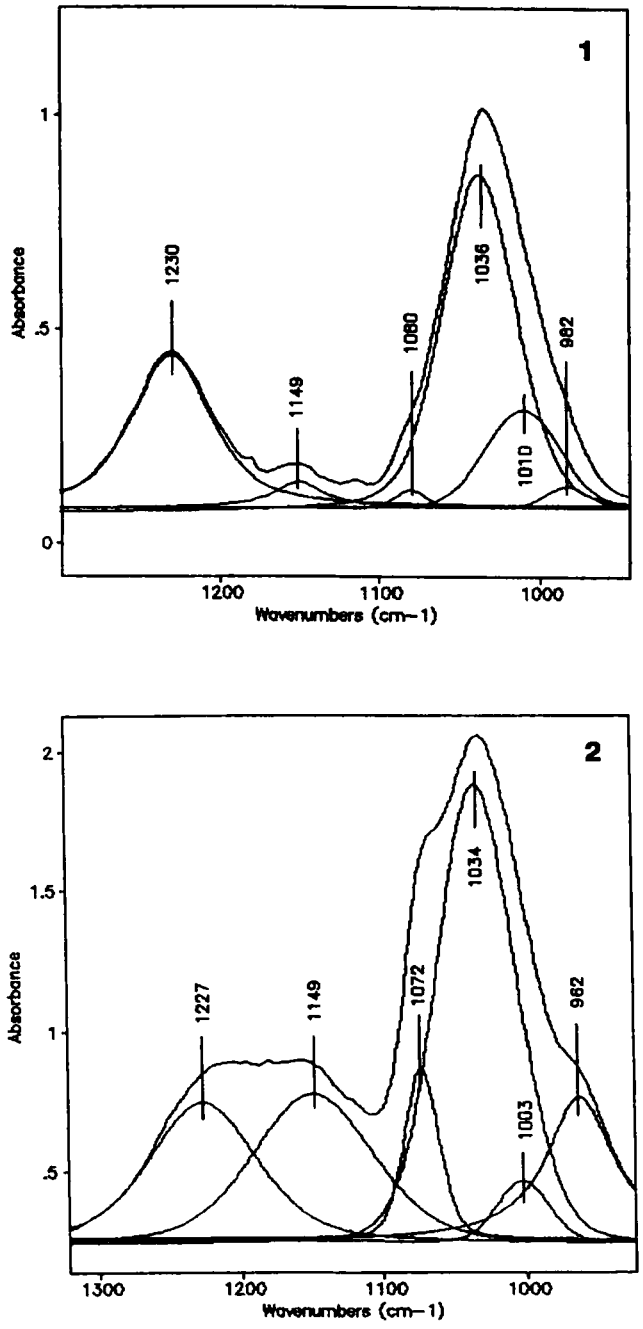


FIG. 2. Resolved IR-spectra (1300–900 cm^{-1}) of **HA** (1) and $\mathbf{H_2B}$ (2) (capillary).

γ(OH)-vibration as it is adopted when interpreting the phosphonic acids' IR-spectra[20]. This band is not characteristic for the **HA**-spectrum probably due to the fixing effect of the dimmeric cycle. A similar phenomenon is observed for the $\rho(CH_2)$-vibration band (~ 720 cm^{-1}). It is typical for the chain alkanes but is absent in the case of alicyclic hydrocarbon[21, 22].

In conclusion, it should be noted that, although with a very low intensity, the absorption maximum at 1149 cm^{-1} exists in the **HA** IR-spectrum also (Fig. 2.1). Bearing in mind that the assay of the studied sample is higher than 99 % (see Materials and Methods), it has to be accepted that P−OH...O(H)−P-association is also realized in the monobasic acid but to a very low extent. The corresponding non-associated P=O-bond absorbs at 1230 cm^{-1} [13] overlapping with the strong band of the ν(P=O)-dimmer band.

LaA_3. The complex was prepared by the method *a)* (see Materials and Methods). In contrast to the other RE-complexes of this type, it can not be obtained by the interaction of $La(NO_3)_3$ with **HA** since LaA_3 is unstable to HNO_3 at a mole ratio $HNO_3/LaA_3 \geq 3$[6].

The molecular and crystal structures of $(RE)A_3$ complexes are derived from the combined luminiscent, IR- and X-ray analyses data[23-25]. The powder diffractograms of $(RE)A_3$ (RE = La, Nd, Eu, Lu) suggests that these compounds are isostructural[24]. In such a case, the obtained so far results could be generalized as follows: the structure of $(RE)A_3$ is constituted by $(RE)O_6$-octahedra which form polynucleous chains through −RE−O−P−O−RE− bonds. The 2-ethylhexyl fragments are disposed perpendicularly to the polymeric chains, stabilizing the supramoleculear structure by Van-der-Vaals forces.

In the IR-spectra of $(RE)A_3$ complexes the described type of complexing is marked by the presence of two intensive bands for the bridging coordinated phosphate anion. They are disposed in the regions 1190−1170 cm^{-1} − $\nu_{as}(POO^-)$ and 1100−1000 cm^{-1} − $\nu_s(POO^-)$ and usually have a dublet structure[4, 23, 25, 26]. These results are in coincidence with the IR-spectral data for RE complexes with other dialkylphosphate ligands[27].

The IR-spectrum (1250−900 cm^{-1}) of LaA_3, obtained by us, is shown in Fig. 3.1, compared with that of NdA_3 (Fig. 3.2). One can see that:

− The NdA_3 spectrum is typical for the $(RE)A_3$ complexes (Fig. 3.2). Along with the bands at 1036, 1006 and 985 cm^{-1} which are characteristic for the ligand alkoxy-fragments (see also Fig. 2.1), the dublets at 1186 and 1167 cm^{-1} − $\nu_{as}(POO^-)$, respectively at 1102 and 1077 cm^{-1} − $\nu_s(POO^-)$, prove the bridging type of the coordination. The spectrum of PrA_3 (prepared under the same conditions) is analogous.

− The LaA_3 spectrum is characterized by an increase of the absorption at 1065−1020 cm^{-1} (compare Figs. 3.1 and 3.2). It is owing to the presence of additional bands in this interval which are observed when a chelating coordination at dialkylphosphate complexes takes place[28]. In order to prove this supposition we prepared the complex La_2B_3 (method *d)* in Materials and Methods; Table 1). Its stoichiometry "a priori" determinates the formation of such a "mixed" bridging−chelating structure. As can be seen in Fig. 4, the most intensive absorption maxima in La_2B_3 IR-spectrum are actually in the region 1065−1020 cm^{-1}.

The results described above are in agreement with the X-ray powder diffraction data[2] which reveal that LaA_3 forms shorter chains than the other $(RE)A_3$ complexes. The decrease of the polymeric chain length leads to an increase of the content of the chelate coordinated end La^{3+}-ions and to an appearence of the relevant bands in the IR-spectrum. Most probably, the specificity of the LaA_3 dissolving in and desalting from some solvents[5] can be ascribed to the pointed structure peculiarities.

$La(HB)_3.1.5H_2O$. The complex is prepared following the methods *b)* and *c)* (see Materials and Methods and Table 1). The first one is analogous to the common method *a)* for $(RE)A_3$ synthesis. As it was already emphasized, method *c)* is unapplicable for a preparation of LaA_3. This means that $La(HB)_3$ or, more precisely, its precursor, existing in the solution, is more stable to HNO_3. Generally speaking, one may conclude that **H_2B** behaves as a stronger complexing agent than **HA**.

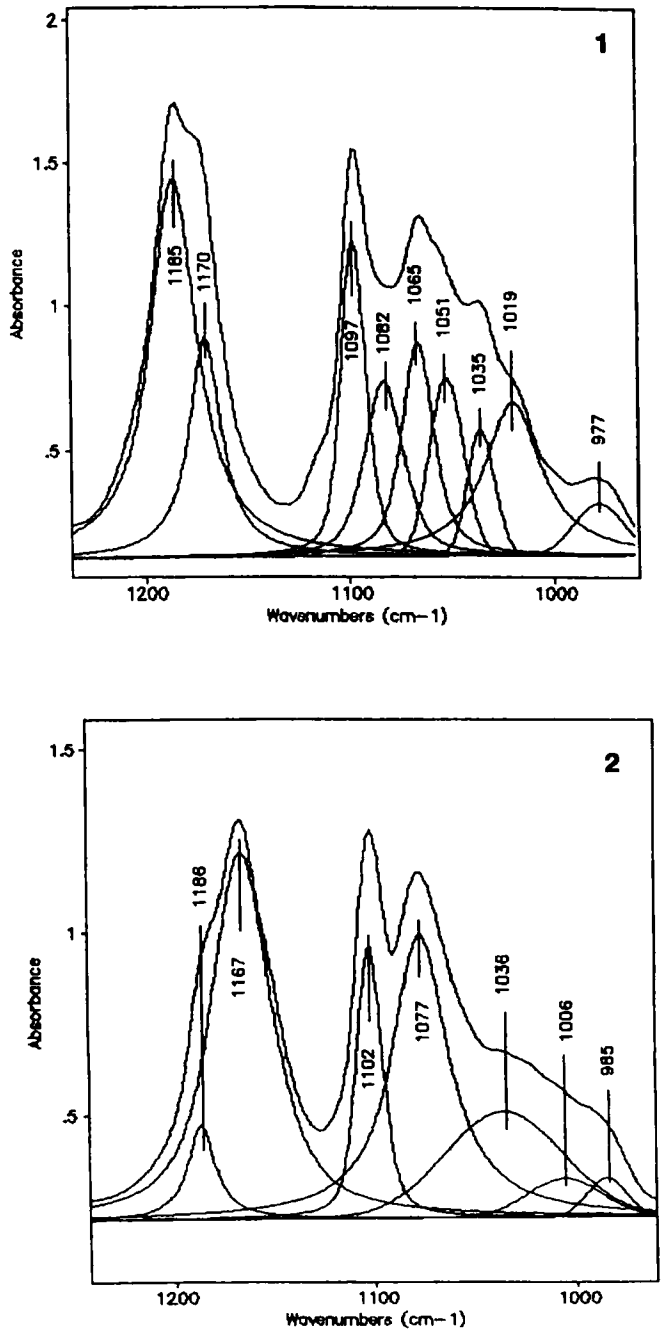


FIG. 3. Resolved IR-spectra (1300–900 cm^{-1}) of LaA_3 (1) and NdA_3 (2); nujol mulls.

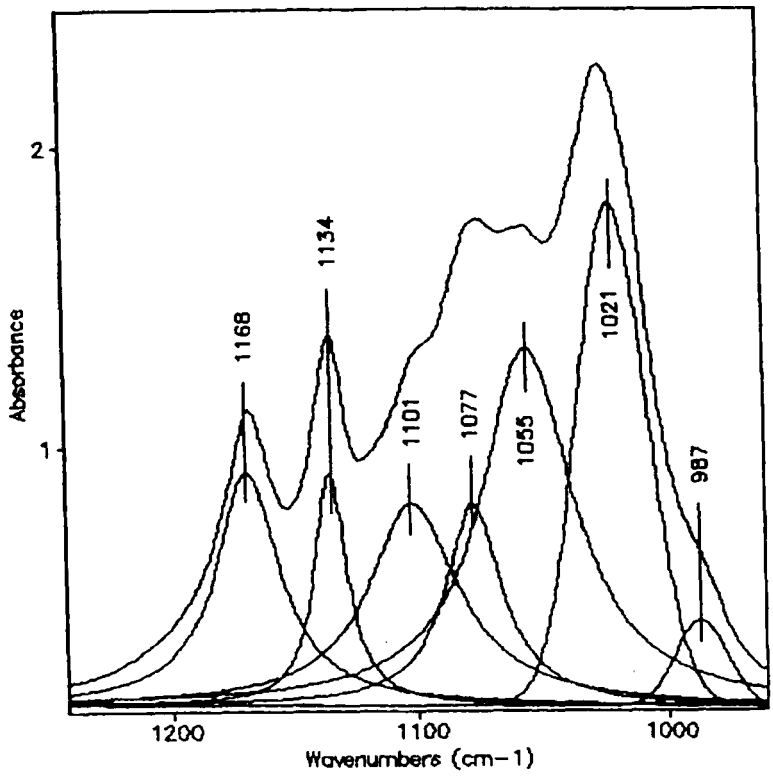


FIG. 4. Resolved IR-spectrum (1300–900 cm^{-1}) of La_2A_3; nujol mull.

The IR-spectrum of $La(HB)_3.1.5H_2O$ (Figs. 5.1 and 6.1) shows some peculiarities when comparing with those of $\mathbf{H_2B}$ and of LaA_3: 1) a band of complicated character appears in the 3700−3100 cm^{-1} region (Fig. 5.1). No absorbance in this region is seen in LaA_3-spectrum; 2) the absorption maximum at 1031 cm^{-1} has a prevailing intensity (Fig. 6.1). This band is much weaker expressed in the spectra of LaA_3 (Fig. 3.1) and of $(RE)A_3$ in general. It is however characteristic for the ligand $\mathbf{H_2B}$ (Fig. 2.2).

These data were interpreted comparing the $La(HB)_3.1.5H_2O$ spectrum with the analogous spectra of the intermediates obtained during its thermal treatment.

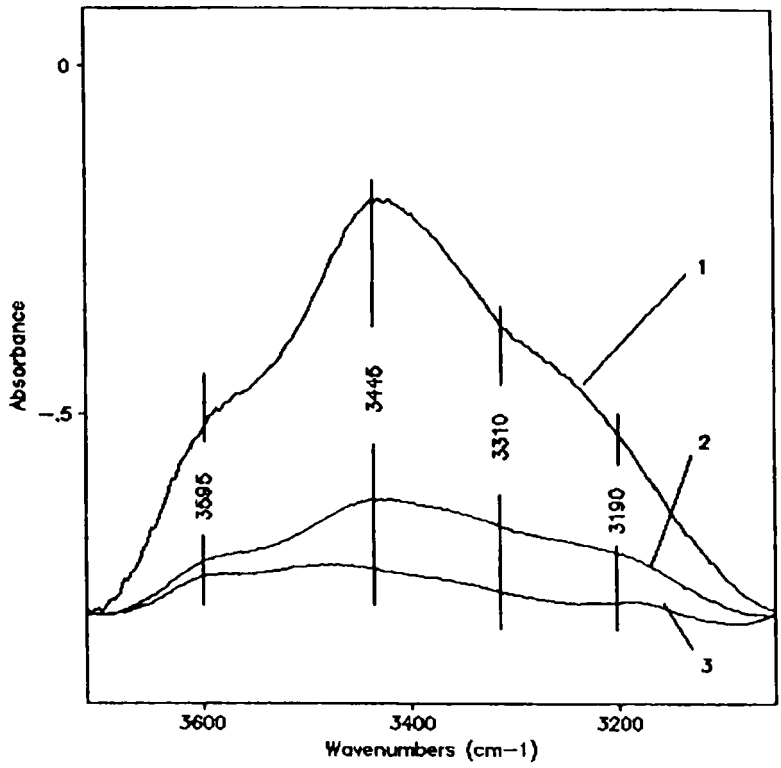


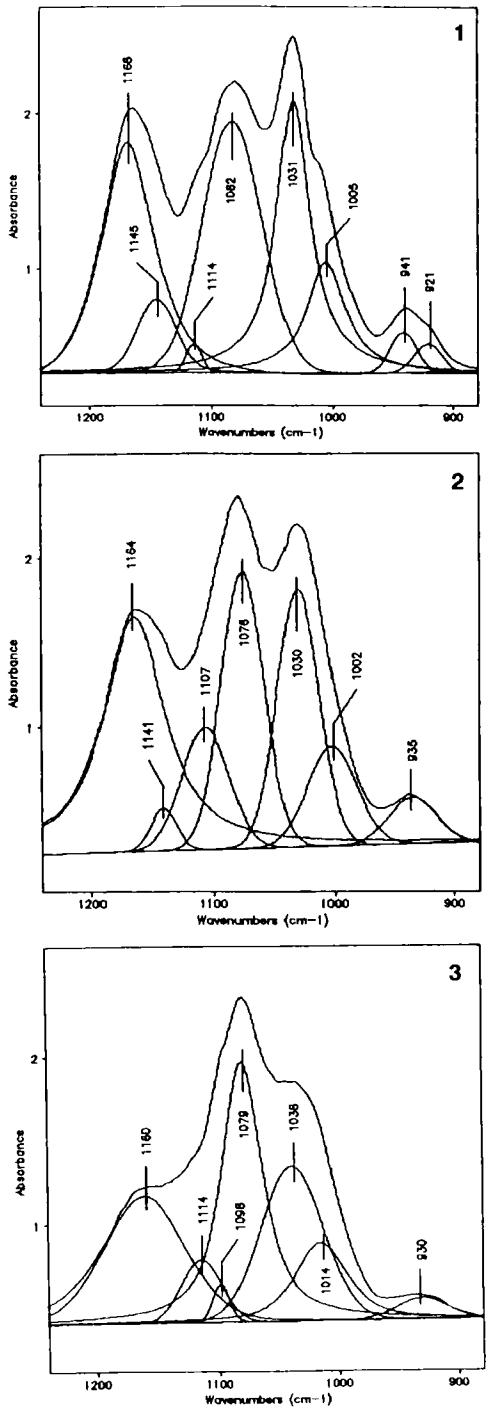
FIG. 5. Resolved IR-spectra (3700–3100 cm^{-1}) of $La(HB)_3.1.5H_2O$ (1) and of the intermediates optained during a heating to 373 K (2) and to 458 K (3); nujol mulls.

According to[19] the latter leads to the following changes of the complex'es structure: 1) disappearing of the crystalline water, completed at 383 K; 2) condensation of OH-groups, thus forming bridging diphosphate bonds. The latter effect is observed above 383 K and completes at 483 K. A destruction of the hydrocarbon part follows till the obtaining of the final heating product $La(PO_3)_3$. Figs. 5 and 6 show the characteristic spectral regions of $La(HB)_3.1.5H_2O$ and of two products obtained respectively at 373 K (at which the main part of the hydrated H_2O is removed) and at 458 K (advanced but not

completed condensation process). The spectral data show that the heating causes strong decrease of the bands intensity in the region 3650−3050 cm^{-1} (Fig. 5). The resolving of the spectra of the $La(HB)_3.1.5H_2O$ and of the product heated up to 373 K show the presence of four absorption maxima which have the averaged values shown in Fig. 5 (the data from the resolving of the IR-spectrum of the product heated up to 458 K could not be considered as a reliable since the absorbance in the discussed interval is too low). The heating up to 373 K reflects mainly on the band at 3445 cm^{-1}. It means that it is connected with the stretching vibration of the crystalline and, eventually presented, adsorbed water. The intensities of the maxima at 3595, 3310 and 3190 cm^{-1} are decreased much less but are continuing to decrease at following temperature increasing (Fig. 5.3). So these maxima have to be related to ν(OH) of the non-dissociated hydroxogroup of the $\mathbf{H_2B}$.

The dehydration and condensation cause changes in the spectral region 1300−900 cm^{-1} as well: the band's intensity at 1031 and 1005 cm^{-1} decreases and the maximum at 1145 cm^{-1} fully disappears (Fig. 6). The latter confirms our suppositions that the band at 1145 cm^{-1} corresponds to the bending OH-vibration (see the discussion on the $\mathbf{H_2B}$-spectrum) and that the P−OH-groups, associated through PO−H...O(H)P hydrogen bonds have a contribution in the absorption at 1035-950 cm^{-1}. The formation of −La−O−P−O−La− coordination bonds causes the absence of the band at 1227 cm^{-1} and leads to the appearence of the strong maxima at 1168 cm^{-1} − $\nu_{as}(POO^-)$ and 1082 cm^{-1} − $\nu_s(POO^-)$ (compare with Fig. 2.2). The second one possesses a weakly expressed dublet nature which causes the maximum at 1114 cm^{-1} (Fig. 6.1). These bands correspond to the analogous ones in the case of $(RE)A_3$ (Fig. 3).

The elemental composition and the above described IR-data show that, analogously to LaA_3, the $La(HB)_3.1.5H_2O$ structure is constituted by LaO_6 octahedra, forming polynucleous chains by the bridging −La−O−P−O−La− bonds. One of the OH-groups of the $\mathbf{H_2B}$ remains during the complex formation owing to the low value of the $\mathbf{H_2B}$ second dissociation



constants. The so formed PO−H...O(H)P-hydrogen bonds stabillize the polymeric chains and facilitate the heating promoted condensation process. Such a type of complexation supposes more disordered supramolecular structure than in the case of anhydrous $(RE)A_3$ in which the coordination takes place with a symmetrical ligand. Such a conclusion coincides with the X-ray powder diffractometry data, proving the amorphous (or nanocrystalline) state of the $La(HB)_3.1.5H_2O$[29]. The presented IR-data confirm this finding − in comparison with LaA_3 and $(RE)A_3$ in general, the bands connected with the symmetric and antisymmetric POO^--stretching vibration are with greater halfwidth. This is characteristic for solid state systems with disturbed middle order. The dublet splitting caused by the crystal field effect is also very weakly expressed (compare Figs. 3 and 6).

CONCLUSION

The results from the detailed IR-spectral study of LaA_3 are in coinsidence with the published data concerning the bridging structure of the $(RE)A_3$ type complexes. The IR-analysis however reveals that mixed type coordination of La with bis-(2-ethylhexyl) phosphoric acid takes place − additional bands are observed which characterize chelate coordination bonds as well. This result is in agreement with the fact that La forms shorter polymeric chains than the analogous complexes of the other RE.

Solid state complexes of La with mono-(2-ethylhexyl) phosphoric acid are studied for the first time. In contrast to LaA_3, $La(HB)_3.1.5\ H_2O$ can be prepared by an interaction of La^{3+} with the acid itself. As in the case of LaA_3 the structure

FIG. 6. Resolved IR-spectra (1300–900 cm^{-1}) of $La(HB)_3.1.5H_2O$ (1) and of the intermediates optained during a heating to 373 K (2) and to 458 K (3); nujol mulls.

of this complex is formed by LaO_6-octahedra, resp. $-La-O-P-O-La-$ polymeric chains. However the latter is linked with crosswise PO−H...O(H)P-hydrogen bonds due to the non-deprotonated OH-group, rested from the ligand. The so arranged supramolecular structure is more disordered than in the complexes of bis-(2-ethylhexyl) phosphoric acid. This determines the amorphous (nanocrystalline) state of the studied complex and, probably, contributs to its ability to coordinate water.

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Received: December 15, 1995
Accepted: January 29, 1996