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LANTHANIDE COMPLEXES OF ETHYLENEDIAMINOTETRAMETHYLENE-PHOSPHONIC ACID

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Abstract

Ethylenediaminotetramethylenephosphonic acid (EDTMP, H_8L) was prepared and its complexes with some lanthanide ions (La, Eu, Gd and Sm) were isolated under various conditions. IR spectra and thermal stabilities of EDTMP and its complexes were studied. The experimental conditions of the preparation influence to the composition of the complexes were shown. In alkaline solution (pH=8) deprotonated ($P(O)(O^-)_2$), and in acidic solution (pH=3–4) deprotonated and partly protonated ($P(O)(O^-)(OH)$) and non-protonated ($P(O)(OH)_2$) phosphonic groups are present in the complexes. All the complexes contain coordinated water molecules. The complexes containing a protonated phosphonic group contain coordinated and hydrogen-bonded water molecules.

Keywords: aminophosphonates, ethylenediaminotetramethylenephosphonic acid, IR spectra, NMR contrast agent, thermoanalytical studies

Introduction

The development of nuclear magnetic resonance (NMR) imaging techniques as a clinical diagnostic modality has prompted the need for a new class of pharmaceuticals. These drugs would be administrated to a patient in order to (a) enhance the image contrast between normal and diseased tissue and/or (b) indicate the status of organ function or blood flow. The intensity of the ^{1}H NMR images, largely composed of the NMR signal of the water protons, is dependent on the nuclear relaxation times. Complexes of paramagnetic transition metal and lanthanide ions, which can decrease the relaxation times of nearby nuclei via dipolar interactions, have received most attention as potential contrast agents, and numerous complexes of polyaminopolycarboxylic acid with these metal ions have been studied from this respect [1–5]. The structural similarities between the polyaminopolycarboxylic and polyaminopolyphosphonic acids (replacement of the carboxylic acid groups by organophosphonic acid groups) generally make them more selective towards cations with an enhanced coordination capacity [6]. The specific nature

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of such chelating agents is due to the presence of the tetrahedral phosphonic group as compared to the planar carboxylic group and the greater polarizability of the P–O bond [7].

In the present work, the complexes of ethylenediaminotetramethylenephosphonic acid (EDTMP) with lanthanide ions were isolated and their IR spectra and thermal stabilities were studied. The aims of the work were to determine the effects of the method of preparation on the compositions of the complexes, and on the type of binding of the water molecules, and to choose the most appropriate method of preparation of the desired complexes.

Experimental part

Preparation of EDTMP

EDTMP was obtained via a Mannich reaction of ethylenediamine with phosphorous acid and formaldehyde according to Eq. (1).

$$C_2H_8N_2+4H_3PO_3+4CH_2O=4H_2O+EDTMP \qquad (1)$$

The optimum result was obtained when the reaction was carried out at low pH, e.g. in the presence of concentrated hydrochloric acid. Concentrated HCl p.a. was added dropwise to 0.125 mol 1,2-ethanediamine, followed slowly by 0.5 mol phosphorous acid dissolved in water. The mixture was refluxed for 30 min and 1 mol 38% aqueous formaldehyde solution was added dropwise, over a 2 h period. The reaction was refluxed for a further 3 h, and then allowed to cool and stand at room temperature. For crystallization, ethanol was added to this solution. The crystals that precipitated out were filtered off and recrystallized twice from ethanol solution. The yield was ca 60%. It was found that high acidity increased the rate of reaction and improved the yield. The white crystalline material had *m.p.*: 213/215°C.

Preparation of complexes

Method I

EDTMP (or its Na salt) and metal nitrate or acetate were mixed in a ratio of 1:1 or 1:2, under continuous heating. No pH adjustment was used. (After the mixing, a white precipitate was formed immediately). The precipitate was removed from the solution by suction, washed with ethanol, dried and stored under laboratory conditions. Lanthanum (samples **1** and **2**) and samarium (samples **4** and **5**) complexes were prepared in this way. According to the literature [8–10], the compositions of these complexes are $LnH_5L\cdot xH_2O$ (**1** and **4**) and $Ln_4(H_4L)_3\cdot xH_2O$ (**2** and **5**) (H_8L=ligand). The water contents of complexes were dependent of the storage conditions.

Method II

A solution of 0.02 mol EDTMP (acid form) dissolved in water was adjusted to pH=8 by the addition of NaOH solution. 0.02 mol lanthanide salt (nitrate or acetate) was then added, the solution was heated for a short time, the pH was adjusted to pH=8 with NaOH solution and heating was continued for a further 1 h. The complex precipitated on the addition of absolute methanol. The solid product was washed with acetone and then dried at 80°C. The complexes are very soluble in water. Lanthanum (**3**), samarium (**6**), europium (**7**) and gadolinium (**8**) complexes were prepared in this way.

Compositions of complexes

Metal ion (Na^+ and Ln^{3+}) analysis supported the compositions $LnH_5L\cdot xH_2O$ and $Ln_4(H_4L)_3\cdot xH_2O$ for samples **1**, **2** and **4**, **5** (method I), and the general formula $Na_5LnL\cdot xH_2O$ for samples **3**, **6**, **7** and **8** (method II). All complexes contained water molecules.

IR spectra showed a little contamination of the lanthanum (samples **1**–**3**) and samarium (sample **6**) complexes with nitrate and acetate ions, respectively.

IR study

IR spectra of EDTMP and its complexes were taken in the JATE UV-VIS Laboratory of the University of Szeged with Biorad instruments. The KBr disc method was used.

Thermal analysis

Thermal analysis was performed with a computer-controlled MOM derivatograph (Q-1500 D), using 50–100 mg samples. The measurements were made between room temperature and 600, 800 or 1000°C by a dynamic technique, with a 5°C min^{-1} heating rate, using ceramic crucibles and air atmosphere. The reference substance was α-Al_2O_3. To determine the decomposition scheme, the IR spectra of the final decomposition products were recorded.

IR study

IR spectrum EDTMP

The characteristic IR bands of EDTMP (prepared according to the above procedure) are shown in Table 1. The observed absorption bands are assigned to the hydrogen bound to the protonated quaternary nitrogen atom ($\equiv NH^+$), to the OH groups, binding to the P=O group with hydrogen bond, to the free P=O group and two different CH_2 groups. It could be observed also the hydrogen bound water molecules.

Broadening of the bands could be observed in the ranges 2000–4000 and 1000–1400 cm^{-1}, which can be interpreted by the presence of (many) strong hydrogen-bonds.

Table 1 Characteristic bands of EDTMP and their assignments

Band maximum (cm^{-1})	Assignment
3402s, 3246s	ν(OH, water)
3026s, 3014s	ν(≡NH$^+$)
2954s, 2924vs, 2854s	ν_{as} and ν_{sym} of CH_2
2767m, 2611m, 2308m	ν(OH, POH)
1653m, broad	δHOH
1461m, 1438m, 1413w, 1379, 1321w	δCH_2 or/and ν(C–N)
1261s, 1207s, 1121vs, 1008vs, 953vs	ν(P=O, P–O(H)
838w, 792w, 776w, 748w	ν(C–P)
573m, 532m, 487m	ν(OH, POH)

IR spectra of complexes

The characteristic IR bands of the investigated complexes are shown in Tables 2 and 3.

Table 2 Characteristic IR bands of complexes prepared by method I

EDTMP	**1**	**2**	**4**	**5**	Assignment
3402, 3246	3403	3379	3397	3385	ν(OH)
3026, 3014	3011, 3007	3007		3006	ν(≡NH$^+$)
2767, 2611	2760, 2627	2775, 2627	–	2330	ν(OH, POH)
2308	2345	2310	2331	2626	
1652	1640	1658	1641	1648	δ(HOH)
1461, 1438	–	–	–	1437	δCH_2 or/and ν(C–N)
1412, 1322	1436	1440	1436	–	
1261, 1207	1171	1167	1169	1170	ν(=O, P–O(H))
1121, 1088	1080	1083	1087	1085	
1036, 1008	–	–	–	–	
951	–	945	936	941	
838, 792	838	850	–	–	ν(C–P)
776, 746	750	752	764	–	
742	–	–	–	734	
574	557	552	552	551	ν(P=O, P–O(H))
531	–	–	463	455	
487	–	–	–	–	

2000–4000 cm^{-1} range

In this wavenumber range, similarly as in the IR spectrum of EDTMP, ν(OH) was observed in the spectra of all the complexes. This band points to the presence of water molecules in the complexes, as suggested by the elemental analysis. The ν(≡NH$^+$) and νOH(PO) bands were observed only in the spectra of complexes **1**, **2**, **4** and **5** (prepared by method **I**), and not those complexes **3**, **6**, **7** and **8** (prepared by method **II**), which supports the suggested compositions.

Table 3 Characteristic IR bands of complexes prepared by method II

EDTMP	**3**	**6**	**7**	**8**	Assignment
3402	3415	3428	3419	3404	
3426	–	–	–	–	ν(OH)
3026	–	–	–	–	ν(≡NH$^+$)
3014	–	–	–	–	
2767					
2611	–	–	–	–	ν(OH, POH)
2308					
1652	1651	1640	1648	1660	δ(HOH)
1461	–	1475	1461	1461	
1438		–	–	–	δCH_2 or/and ν(C–N)
1412		1413	–	–	
1322			–	–	
1261	–	–	–	–	
1207	1157	–	–	–	
1121, 1088	–	1110	1114	1112	
1036	1085	–	–	–	ν(P=O, P–O(H)
1008	–	–	1054	1055	
951	–	992	983	982	
–	994	–	–	–	
				–	
838	–	–	–	–	
792	773	–	784	–	
776	–	772	–	–	ν(C–P)
746	–	–	–	771	
742	–	–	–	–	
				–	
574	588	580	581	569	
531	–	–	483	475	ν(P=O, P–O(H)
487	–	–	–	–	

1300–1800 and 700–950 cm^{-1}

One or two bands at around 1550 and 1700 cm^{-1} range support the presence of water molecules in the complexes. The band at around 1650 cm^{-1} points to the presence of water molecules, bound by one coordination bond or one coordination bond and one hydrogen bond. The band at higher wavenumber (or the shoulder on the band at 1650 cm^{-1}) refers to the presence of a water molecule bound by hydrogen-bond only. The absence of a band in the range 1500–1600 cm^{-1} demonstrates the absence of a water molecule bound by two coordination bonds.

The skeletal vibration (δCH_2 or/and ν(V–N) and ν(C–P) bands were observed for all the complexes, as in the IR spectrum of EDTMP.

950–1300 and 400–700 cm^{-1} wavenumber range

Relatively to the IR spectrum of EDTMP, the numbers of band's maxima for the complexes in these ranges decreased drastically. The reason for this phenomenon is the change in the hydrogen-bonding network. In the EDTMP molecule, there are many possibilities to form intra- and intermolecular hydrogen-bonds between the nitrogen atom and the HO(O)P group, and between the P=O oxygen and the P(O)OH groups. In the complexes **3**, **6**, **7** and **8**, the OH in the phosphonic groups is deprotonated, so the possibility to form a hydrogen-bond via this OH group is virtually zero.

The bands in this range are assigned to the P–O bonds, the number of bands is dependent on the $-P(O)(OH)_2)$, $-P(O)(OH)O^-$, $-P(O)(O^-)_2$ structures. In the case of C_{3v} and C_{2v} symmetry of a $-P(O)(O^-)_2$ tetrahedron, 2 or 3 bands can be observed in the ranges 950–1300 and 400–700 cm^{-1}. For the investigated complexes, 3 or 4 bands and 1 or 2 bands with shoulders were detected in these ranges, respectively, which can be interpretate by the presence of two or more different $-P(O)(O^-)_2$ tetrahedra with different symmetries.

Thermal study

Thermal behaviour of EDTMP

The thermal analysis suggests the presence of ≈8% water content, which is approximately equivalent to 2 water molecules per EDTMP molecule in a stoichiometric sense. The sample loses its water content in two steps (below 150°C and between 150 and 200°C); the ratio of the mass losses in two steps is 3 to 1. The mass loss is accompanied by an endothermic effect (Fig. 1).

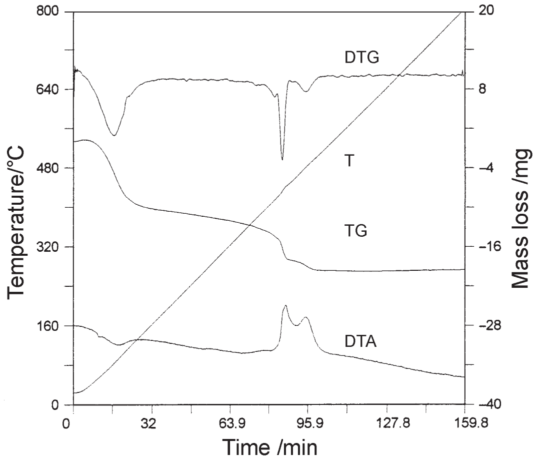

Fig. 1 Thermoanalytical curves of decomposition of EDTMP

Between 200 and 490°C, EDTMP sample loses mass continuously, with 3 peaks in the DTG curve, and the process is accompanied by an exothermic effect. The mass losses are equivalent to approximately 1, 1 and 2 water molecules. The remaining sample lost its mass accompanied by an exothermic effect, in two steps between 490 and 700°C. The suggested final product is P_2O_5 (in the first step) and $(PO_2)_x$ in the second step (Eq. (2)). The exact determination of the decomposition scheme is complicated by the sublimation of P_2O_5 at higher temperature.

$$\mathrm{EDTMP{\cdot}2H_2O \rightarrow EDTMP{\cdot}0.5H_2O \rightarrow EDTMP \rightarrow P_2O_5 \rightarrow (PO_2)_x} \qquad (2)$$

The water molecules can be bound to EDTMP via hydrogen-bonds. The thermal behaviour of the water molecules reflects the existence of a medium and a very strong hydrogen-bond. These bonds are responsible for the broad IR band with maximum at 1653 cm^{-1}. A similar IR band can be observed for hydrated inorganic compounds in which the water molecules are coordinated to the metal ion by one coordination bond.

Thermal behaviour of complexes

From the point of view of the thermal behaviour, the investigated complexes could be divided into two groups (**A** and **B**), consisting of the complexes prepared by method **I** and **II**, respectively. The thermoanalytical curves characteristic of groups **A** and **B** are shown in Figs 2 and 3. The main differences between the complexes in groups **A** and **B** are the thermal behaviour of the water molecules, the stability of the anhydrous complexes between 250 and 500°C and the IR spectra of the final products.

Thermal behaviour of water molecules in complexes

The complexes in groups **A** and **B** lose their water content in two (group **A**) or one step (group **B**), in the temperature ranges 50–150, 150–250 and 50–154°C, respectively, which shows the presence (or formation in the course of heating) of differently

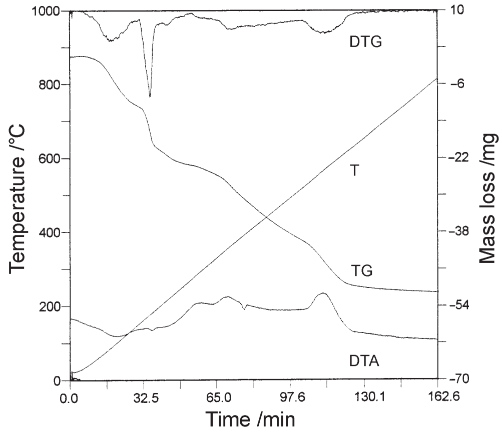

Fig. 2 Thermoanalytical curves of the decomposition of complex 1 (decomp. type **A**)

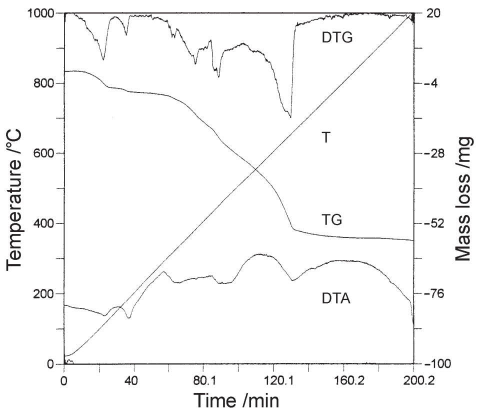

Fig. 3 Thermoanalytical curves of the decomposition of complex 6 (decomp. type **B**)

bonded water molecules in the complexes. Similar thermal behaviour was observed in the case of EDTMP.

The water molecules released from the metal complexes in the range 50–150°C are bound by hydrogen-bounding or by one coordination bond. The water molecules released at higher temperature (between 200 and 300°C) are bound to the metal ions by two coordination bonds or a very strong hydrogen-bond, as in the case of EDTMP. The water molecules of different types give different IR spectra in the range 1500–1800 cm^{-1}. The IR spectra of compounds containing water molecules bound by weak hydrogen-bonds only, with one or two coordination bonds, contain absorption bands in the ranges 1700–1800, 1600–1700 and 1500–1600 cm^{-1}, respectively. One strong hydrogen-bond and coordination bond result in approximately the same IR bands in the range 1600–1700 cm^{-1}.

In the IR spectra of EDTMP and all the investigated complexes, a medium strong band could be observed in the range 1600–1700 cm^{-1} (Tables 1–3), which reflects the presence of water molecules bound by a strong hydrogen-bond (EDTMP) or one coordination bond in all the investigated complexes and these water molecules are released in the temperature range 50–150°C.

In EDTMP and complexes **1**, **2**, **4** and **5** (which contain P(OH)OH groups), there are water molecules which give IR bands in the range 1600–1700 cm^{-1} (bound by a hydrogen-bond or one coordination bond) which are released above 150°C (150–200 and 150–250°C). A strong hydrogen-bond could be suggested between the hydrogen-bonded or coordinated water molecule and the free POH group, which did not change the IR spectrum of this water molecule in the range 1600–1700 cm^{-1}, but increased the temperature range of water release from the solid phase. In complexes **3**, **6**, **7** and **8**, which do not contain P(O)OH groups, all the water molecules are released between 50 and 150°C.

Thermal behaviour of complexes between 250 and 500°C

The complexes containing P(O)OH groups (group **A**) decompose continuously with a relatively small loss of mass, while the complexes in group **B** show no change in the TG curves in this temperature range. The loss of mass for complexes **A**, similarly as for EDTMP, is assigned to the release of water molecules from the P(O)OH groups.

Thermal behaviour of complexes above 500°C

The anhydrous complexes decompose in two overlapping steps above 500°C, accompanied by exothermic effect.

Final decomposition products of complexes

An important difference between the investigated complexes (as regards composition) is the ratio of the charges of all metal ions to the number of phosphorus atoms in the molecule. The complexes (**1**, **2**, **4** and **5**) prepared by method **I** (group **A**) contain partly protonated ligand (H_5L^{3-} or H_4L^{4-}) as complex-forming agent and the lanthanide metal ion. The ratio of the metal ion charge to the number of phosphorus atoms is 3 to 4 or 12 to 12. The complexes (**3**, **6**, **7** and **8**) prepared by method **II** (group **B**) contain the fully deprotonated ligand (L^{8-}) and sodium and lanthanide ions, the ratio of the total metal ion charge to the number of phosphorus atoms is 8 to 4.

On the basis of both theoretical considerations and the earlier experimental observations [11–13] lanthanide and sodium phosphates, linear or cyclic polyphosphates, could be suggested as the final decomposition products of the investigated complexes. The compositions of the different inorganic phosphates, linear polyphosphates, cyclic metaphosphates and ratio of the total metal ion charge to the number of phosphorus atoms (*R*) are shown in Table 4.

Table 4 Compositions of inorganic phosphates, linear polyphosphates, cyclic metaphosphates and ratio of total metal ion charge to number of phosphorus atoms (*R*)

Composition	Name	*R*
Na_3PO_4 or $LnPO_4$	sodium or lanthanum phosphate	3:1
$Na_4P_2O_7$ or $Ln_4(P_2O_7)_3$	sodium or lanthanum pyrophosphate	4:2
$Na_5P_3O_{10}$ or $Ln_5(P_3O_{10})_3$	sodium or lanthanum tripolyphosphate	5:3
$Na_6P_4O_{11}$ or $Ln_2(P_4O_{11})$	sodium or lanthanum tetrapolyphosphate	6:4
$Na_3(PO_3)_3$ or $Ln_2(PO_3)_3$	sodium or lanthanum trimetaphosphate	3:3
$Na_4(PO_3)_4$ or $Ln_{4/3}(PO_3)_4$	sodium or lanthanum tetrametaphosphate	4:4
$Na_5(PO_3)_5$ or $Ln_{5/3}(PO_3)_5$	sodium or lanthanum pentametaphosphate	5:5
$Na_6(PO_3)_6$ or $Ln_2(PO_3)_6$	sodium or lanthanum hexametaphosphate	6:6

It can be seen that for simple phosphates and linear polyphosphates $R>1$, while for cyclic methaphosphates $R=1$. On the basis of *R*, the final products in the decomposition of the investigated complexes can be suggested to be cyclic lanthanide metaphosphates (**2** and **5**), cyclic lanthanide metaphosphates and P_2O_5 (**1** and **4**), sodium and lanthanum pyrophosphates (*R*=2) or a mixture of Na_3PO_4 or $LnPO_4$ and their linear polyphosphates ($Na_4P_2O_7$, $La_3(P_2O_7)_3$, $Na_5P_3O_{10}$, $Ln_5(P_3O_{10})_3$ (**3**, **6**, **7** and **8**).

To determine the compositions of the final decomposition products of the investigated complexes, the IR spectra of the final products of thermal analysis of the complexes and of some inorganic phosphate derivatives were recorded. The experimentally found characteristic IR bands and some literature data are presented in Tables 5 and 6.

Table 5 Characteristic IR bands of decomposition products of complexes

1	2	4	5	3	6	7
135sh	1357s	1363s	1362s	–	–	–
1313s	1300s	1300s	1300s	–	–	–
1277s	1278s	1279s	1280s	–	–	–
1173m	1172m	–	1172sh	–	–	–
1160m	1150	1156	1153	1152	1152	–
1146m	–	–	1146	–	–	sh
–	1116	1125	–	1124	1129	1124
–	–	–	–	1090	–	–
1043	–	–	–	1056	1067	1062
–	1018	1016	1022	1017	1022	1029
980	981	–	986	988	–	988
–	–	960	–	–	964	965
–	–	–	–	908	908	908
793	–	sh	805	–	–	–
760	762	775	767	–	–	–
–	748	–	750	–	–	–
–	712	715	716	734	734	734
691	–	708	700	–	–	–
–	–	–	–	622	634	628
–	–	–	–	618	–	618
–	–	–	–	576	574	575
–	–	–	–	–	558	560
–	–	–	–	–	523	522
–	–	–	–	492	492	492
–	–	–	–	–	426	428

There are many similarities and differences between the IR spectres of the final decomposition products of the complexes prepared by methods **I** and **II**.

a. The final decompositions products of the complexes prepared by method **I** (group **A** of complexes) give absorption bands above 1200 cm^{-1}.

b. In the range 950–1200 cm^{-1} all the decomposition products give many bands.

c. The decomposition products of the complexes prepared by method **II** have a strong absorption band at around 908 cm^{-1}.

d. In the range 650–900 cm^{-1}, many IR bands are observed for the complexes prepared by method **I**, but only one band for the complexes prepared by method **II**.

e. Below 650 cm^{-1}, only the decomposition products of complexes **B** furnish absorption bands. The linear polyphosphates have 4-4 absorption bands in each of the ranges 950–1200 and 400–700 cm^{-1} and 1 band each at around 910 and 740 cm^{-1}. This behaviour is close to the case for the decomposition products of the complexes prepared by method **II**, and it supports the hypothesis that the decomposition products of these complexes are sodium and lanthanide pyrophosphate or a mixture of phosphate, pyrophosphate and tripolyphosphate.

Table 6 Characteristic IR bands of inorganic phosphate derivatives

$P_2O_7^{4-}$	$P_3O_{10}^{5-}$	$(PO_3^-)_6$
–	–	1277
–	1221	–
–	1176	1153
1117	1124	–
1110	–	–
–	1085	1095
1023	–	–
995	–	984
922	903	–
–	–	878
734	758	773
–	–	721
–	665	–
637	611	–
576	569	–
494	503	505
475	470	497

Cyclic sodium hexametophosphate has a band at 1277 cm^{-1}, but no band between 900 and 950 cm^{-1}. This is characteristic of the decomposition products of the complexes prepared by method **I**. These facts support the hypothesis that the decomposition products are different cyclic metaphosphates and P_2O_5.

Composition and decomposition schemes of EDTMP and its lanthanide complexes

On the basis of the thermoanalytical curves and IR spectra of the complexes and their decomposition products, the following decomposition schemes can be suggested for the complexes **1**, **4** and **2**, **5** and **3**, **6**, **7**, **8** Eqs (3), (4) and (5), respectively.

$$LnH_5L\cdot(x+y)H_2O \rightarrow LnH_5L\cdot xH_2O \rightarrow LnH_5L \rightarrow Ln(PO_3)_3+1/4P_2O_5 \qquad (3)$$

$$Ln_4(H_4L)_3\cdot(x+y)H_2O \rightarrow Ln_4(H_4L)_3\cdot xH_2O \rightarrow Ln_4(H_4L)_3 \rightarrow 4Ln(PO_3)_3 \qquad (4)$$

$$LnNa_5L\cdot yH_2O \rightarrow LnNa_5L \rightarrow 5/4Na_4P_2O_7+1/4Ln_4(P_2O_7)_3 \qquad (5)$$

According to the IR spectra and the thermal behaviour, two different types of water molecules are present in EDTMP and its complexes: One of them is bound by a hydrogen-bond or one coordination bond (EDTMP and the **B** complexes) and is released from the solid phase below 150°C. The second type of water molecules is bound by a strong hydrogen-bond (probably a double hydrogen-bond in the case of EDTMP) or by one coordination bond and a hydrogen-bond via a P(O)OH group. This kind of water molecule is released from the solid phase between 150 and 250°C.

The TG curves of the complexes give the possibility to determine the amounts of both kinds of water in the complexes. For the complexes prepared by methods **I** and **II**, the mass of the sample at 250 and 150°C is considered the mass of the anhydrous compounds.

Conclusions

It has been shown that the pH of the solution in which the preparation is performed, determines the compositions of the complexes and the type of binding the water molecules. If deprotonated phosphonic groups are present in the complexes, the water molecules bind weakly to the lanthanide ion. In the presence of a protonated phosphonic group in the complexes, the water molecules bind to the lanthanide ion in two different ways. The OH group gives a possibility for the coordinated water molecule to form a hydrogen-bond too. This phenomenon is caused by the protonation process of the ligand. EDTMP has 8 dissociable protons, with different *pK* values. The *pK* values, depending on the pH, determine the speciation of the ligand and consequently the compositions of the complexes.

In this way, the pH of the solution may determine the type of binding of the water molecules in the complexes in both solution and the solid phase. Different behaviour of these water molecules can be suggested if the complexes are used as contrast agents in NMR relaxation experiments.

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