

THERMAL BEHAVIOUR OF LANTHANIDE COMPLEXES OF 1,3-PROPANEDIAMINE-TETRAMETHYLENEPHOSPHONIC ACID

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Abstract

1,3-propanediaminotetramethylenephosphonic acid (PDTMP, H₈L) was prepared and its complexes with some lanthanide ions (La(III), Eu(III), Gd(III) and Sm(III)) were isolated. The IR spectra and thermal stabilities of PDTMP and its complexes were studied. All the complexes contain physically and coordinately bound water molecules, which are released from the solid samples below 370°C. On heating PDTMP decomposes to phosphorus oxides, while its anhydrous complexes decompose to lanthanide oxides, and cyclic and linear polyphosphates between 400 and 1000°C.

Keywords: aminophosphonates, IR spectra, NMR contrast agent, 1,3-propanediaminotetramethylenephosphonic acid, thermoanalytical studies

Introduction

Magnetic resonance imaging (MRI) has become one of the primary imaging modalities in modern medicine. This widespread use of MRI has led to the demand for efficient paramagnetic contrast agents, used to enhance the differences between normal and diseased tissue, or to indicate specific organ functions. Complexes of some paramagnetic ions of transition metals and some rare earth metals have been considered as potential contrast agents [1, 2].

The complexes mentioned in [3–10] are coordination compounds of polyaminopolycarboxylic acids. Replacement of the carboxylic groups by organophosphonic acid groups determines the specific nature of the polyaminopolyphosphonic acids, due to the presence of tetrahedral phosphonic groups and the greater polarizability of the PO bond [11, 12]. On the other hand, the investigation of the thermoanalytical behaviour of lanthanide complexes has got more interest in the last years [13, 14].

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In the present work, the complexes of 1,3-propanediamine-tetramethylene-phosphonic acid (PDTMP, H_8L) with certain lanthanide ions (Eu(III), La(III), Gd(III) and Sm(III)) were isolated. Their IR spectra and thermal stabilities were studied in order to determine their compositions and the binding mode of the water molecules. The results were compared with the similar data on the complexes of ethylenediamine-tetramethylenephosphonic acid (EDTMP) with the same metal ion [15].

Experimental

Preparation of PDTMP

Similarly to EDTMP, PDTMP was obtained by the Mannich condensation of 1,3-propanediamine with phosphorous acid and formaldehyde according to Eq. (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 hydrochloric acid (p.a.) was added drop by drop to 0.125 mole 1,3-propanediamine, followed slowly by 0.5 mole phosphorous acid dissolved in water. The mixture was refluxed for 30 min and 1 mole 38% aqueous formaldehyde solution was added dropwise, over 2 h. The reaction was refluxed for a further 3 h, and then allowed to cool. On standing for some days in the refrigerator, crystals precipitated out. They were filtered off and recrystallized twice from ethanol solution. The yield was ca. 60%. It was found that high acidity increased the rate of the reaction and improved the yield. The white crystalline material had $m.p. = 277-279^\circ C$.

Preparation of complexes

The method of preparation of the complexes was the same as for the complexes of EDTMP (method II in [15]).

A solution of 0.02 mole PDTMP (acid form) dissolved in water was adjusted to pH 8 by the addition of NaOH solution. 0.02 mole 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 $60^\circ C$. The complexes are very soluble in water. The lanthanum, samarium, europium and gadolinium complexes were prepared in this way.

Compositions of complexes

Metal ion (Na^+ and Ln^{3+}) analysis supported the general formula $Na_5LnL \cdot xH_2O$ ($L = PDTMP^{8-}$). All the complexes contained water molecules. The water content of the complexes proved dependent on the conditions of storage. When the complexes were stored under laboratory conditions (at room temperature, in air), the water content of

the complexes was 20–25%. Lower water contents and even anhydrous compounds could be prepared by storing the complexes over P_2O_5 in a desiccator for several days.

IR study

The IR spectra of PDTMP, its complexes, stored under laboratory conditions and over P_2O_5 in a desiccator, and the final decomposition products were taken in the UV-VIS Laboratory of the University of Szeged with Biorad instruments. The KBr disk 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 $\alpha\text{-Al}_2\text{O}_3$. To determine the decomposition scheme, the IR spectra of the final decomposition products were recorded.

Results and discussion

The IR spectrum of PDTMP

The characteristic IR bands of PDTMP are shown in Table 1. The observed absorption bands are assigned to the quaternary nitrogen atom ($\equiv\text{NH}^+$), the OH groups (of the water molecules and of the phosphonic groups), the $\text{P}(\text{O})(\text{OH})_2$ groups and the different CH_2 groups.

Broadening of the bands and many local maxima could be observed in the ranges 2000–4000 cm^{-1} , due to the presence of the strong hydrogen-bonding network, assigned to the phosphonic OH groups and to the water molecules. Two peaks

Table 1 Characteristic bands of PDTMP and their assignments

Range/ cm^{-1}	Band maximum/ cm^{-1}	Assignment
2000–4000	3372s	$\nu(\text{OH, water})$
	3024s, 3005s	$\nu(\equiv\text{NH}^+)$
	2950s, 2921s, 2849s	ν_{as} and ν_{s} of CH_2
	2773sh, 2612sh, 2288sh	$\nu(\text{OH, POH})$
1500–2000	1657br	$\delta(\text{OH, water})$
1300–1500	1485m, 1437m, 1427m, 1411m, 1344m	$\nu(\text{CH}_2)$ or/and $\nu(\text{C-N})$
700–1300	1248s, 1167s, 1050s, 980s, 944s	$\nu(\text{P=O, P-O})$
400–700	602m, 585m, 548m, 512m, 482m	$\nu(\text{P=O, P-O})$

are assigned to the quaternary N atom, which means that the two N atoms are not equivalent in the hydrogen-bonding sense.

The band at 1657 cm^{-1} supports the presence of water molecules in the PDTMP sample, as in the case of EDTMP [15].

Similarly as for EDTMP [15], 5 peaks of medium intensity could be observed in the range $1300\text{--}1500\text{ cm}^{-1}$, assigned to $((\text{CH}_2)$ or/and $(\text{CN}))$ vibrations. This is not surprising if we take into consideration the similar structures of EDTMP and PDTMP.

In the ranges $700\text{--}1300$ and $400\text{--}700\text{ cm}^{-1}$, broad peaks could be observed, with 5 defined local maxima and several shoulders, which could be assigned to the $(\text{P}(\text{O})(\text{OH})_2)$ groups. The expected symmetry of the $(\text{P}(\text{O})(\text{OH})_2)$ groups is C_{2v} , and consequently 3 peaks are expected in each of these wavenumber ranges. The number of peaks and shoulders indicated that there are at least two types of $(\text{P}(\text{O})(\text{OH})_2)$ groups in different surroundings. The shoulders are caused by hydrogen-bonding with different strengths.

After drying of the sample over P_2O_5 in a desiccator, the IR spectrum was not changed. The mass loss in the course of drying was approximately 1%, which means that the sample contains a small amount of physically adsorbed water, in support of the similarity of the spectra of the original and the dried samples.

The IR spectra of the complexes

The characteristic IR bands of the original and the dried complexes are shown in Tables 2 and 3, respectively.

A broad band could be observed between 2000 and 3600 cm^{-1} in the spectra of all the complexes, with maximum at around 3440 cm^{-1} . There were several shoulders on the lower wavenumber side of the peak. This band was assigned to the water molecules hydrogen-bonded to the ligand and/or coordinately bound to the metal ion. The shoulders are caused by hydrogen-bonds of different strengths.

In the spectra of the complexes, two bands could be observed in the interval $1500\text{--}2000\text{ cm}^{-1}$, with maxima at around 1700 and 1650 cm^{-1} . This means that the complexes contain hydrogen-bonded (1700 cm^{-1}) and coordinately bound (1650 cm^{-1}) water molecules.

Instead of 5 bands (spectrum of PDTMP), only 2 peaks of medium intensity were observed in the range $1300\text{--}1500\text{ cm}^{-1}$ (the skeletal vibrations $(\nu(\text{CH}_2)$ or/and $\nu(\text{CN}))$). Since the intensity of the bonding vibration is much stronger than the deformation vibration, these two peaks could be assigned to the $\nu(\text{CN})$ vibrations. Accordingly, the two N atoms in the complexes are in different surroundings.

The bands in the ranges $700\text{--}1300$ and $400\text{--}700\text{ cm}^{-1}$ are assigned to the $-\text{P}(\text{O})(\text{O}^-)_2$ groups. In the cases of C_{3v} and C_{2v} symmetry, 2 or 3 bands can be observed in these ranges. For the investigated complexes, 5 and 2 bands were detected in these ranges, respectively, which can be interpreted in terms of the presence of two or more different $-\text{P}(\text{O})(\text{O}^-)_2$ tetrahedra with different symmetries.

The IR spectra of the dried complexes were different from those of the original samples only in the range $1500\text{--}4000\text{ cm}^{-1}$. The relative intensity of the band at

Table 2 Characteristic IR bands of original complexes

Range/cm ⁻¹	PDTMP	La	Sm	Eu	Gd	Assignment
2000–4000	3372	3437	3440	3438	3439	v(OH, water)
1500–2000	1657	1696	1745	1713	1751	δ(OH, water)
		1641	1641	1641	1641	
1300–1500	1485	1565	1565	1566	1565	
	1437	1414	1414	1414	1413	δ(CH ₃) or/and v(C–N)
	1427					
	1411					
	1344					
700–1300	1248	1140	1128	1134		
	1167	1076	1079	1092		v(P=O)
	1059	974	985	995		P((O)OH)
	999	822	822	816	822	v(C–P)
	944	768	758	768	768	
	844					
	808					
	763					
	749					
	723					
400–700	585	572	567	573	567	v(P=O)
	548	503	515	515	502	P((O)OH)
	512					
	482					

around 3440 cm⁻¹ was decreased. From this, it could be concluded that the complexes were very hygroscopic and most of their water content (the original sample) was physically adsorbed weakly hydrogen-bonded water molecules. This is supported by the fact that in the spectra of the dried samples only one band could be observed in the range 1500–1700 cm⁻¹. The band at around 1700 cm⁻¹, assigned to the hydrogen-bonded water molecules, disappeared during drying.

This means that the physically adsorbed water molecules could be removed by storing the sample over P₂O₅ in a desiccator.

Thermal behaviour of PDTMP

The thermal analysis suggests the presence of 7.0% water content, which is approximately equivalent to 2 water molecules per PDTMP molecule. The sample loses its water content in three steps (between 85 and 140°C, between 140 and 180°C, be-

Table 3 Characteristic IR bands of the dried complexes

Range/cm ⁻¹	PDTMP	La	Sm	Eu	Gd	Assignment
2000–4000	3359	3457	3440	3438	3426	v(OH, water)
1500–2000	1642	1640	1696	1657	1641	δ(OH, water)
1300–1500	1470, 1443	1566	1566	1579	1579	v(CH ₂) or/and
	1333	1415	1413	1428	1422	v(C–N)
700–1300	1243, 1168	1127	1128	1127	1128	
	1050, 980	1079	1079	1083	1081	v(P=O)
	945, 808	986	983	995	996	P((O)OH)
	763, 749	760	926	924	822	v(C–P)
	723		822	757	759	
			755			
400–700	575, 547	650	645	649	649	v(P=O)
	512	572	570	574	574	P((O)OH)
	482	521	523	482	485	

tween 180 and 250°C). The mass losses are accompanied by an endothermic effect. These water molecules may be bound to the ligand (PDTMP) 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 1650 cm⁻¹.

Between 250 and 290°C there is no change in mass. On increase of the temperature to 420°C, the PDTMP sample loses mass continuously, with 3 peaks in the DTG curve, the masses corresponding to 1, 1 and 2 water molecules, the process being accompanied by an endothermic effect.

The remaining sample loses further mass, accompanied by an exothermic effect, in one step, between 420 and 750°C. The suggested final product is P₄O₈ (= (PO₂)₄).

The thermal decomposition of PDTMP is similar to that of EDTMP. The final decomposition product is (PO₂)_x. There is one difference between the thermal decompositions of the two ligands: in the case of PDTMP, P₄O₁₀ could not be observed as a transitional decomposition product, the decomposition proceeding continuously to the lower oxides of phosphorus. The decomposition scheme is shown by Eq. (2):



Thermal behaviour of the complexes

The thermal behaviour is similar for all of the complexes. Typical thermoanalytical curves are shown in Fig. 1.

The complexes lose their water content in two steps: in the temperature range below 150°C and between 150 and 330°C (Sm), 150 and 350°C (Eu), 150 and 360°C (Gd), or

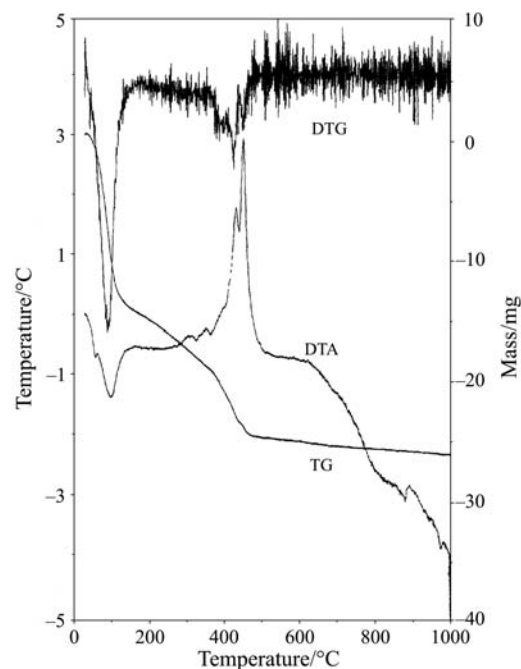


Fig. 1 Typical thermoanalytical curves of the decomposition of PDTMP complexes

150 and 370°C (La). These steps are accompanied by an endothermic heat effect. This supports the conclusion drawn from the IR spectra concerning the presence of differently bound water molecules (two bands in the wavenumber range 1500–1700 cm^{-1} , Table 2).

The endothermic effects indicated that the complexes La, Eu, Gd and Sm complexes contain 16, 16, 23 and 23 water molecules, respectively, per molecule of complex. In the course of the decomposition, in the first step 13, 13, 18 and 18 water molecules, respectively are removed from the solid samples. The remaining 3 or 5 water molecules are released from the solid phase in the second decomposition step, between 150 and 330, 350, 360 and 370°C, respectively.

The weakly bound water molecules (bound only by hydrogen-bonding) could be removed by storing the samples in a desiccator over P_2O_5 for 1 day. In the IR spectra of these dried samples, only one peak was observed in the wavenumber range 1500–1700 cm^{-1} with maximum at around 1650 cm^{-1} .

The anhydrous complexes decompose in two overlapping steps between 330 and 410°C (Sm), 350 and 480°C (Eu), 360 and 440°C (Gd), 370 and 410°C (La), accompanied by an exothermic effect. There are differences between the complexes in the ratio of the mass losses in the two steps. For the case of La and Eu complexes, the first decomposition step is accompanied by the stronger peak in the DTA curves, while for the other complexes the second step is accompanied by the stronger DTA peak.

The measured masses indicate that the La and Eu complexes decompose to the pyrophosphate ($\text{LnNa}_5(\text{P}_2\text{O}_7)_2$) in the first decomposition step, and $\text{LaNa}_5\text{P}_4\text{O}_{12}$ or

$\text{EuNa}_5\text{P}_4\text{O}_{12.5}$ could be suggested as the final decomposition product after the second decomposition step. Similarly, $\text{GdNa}_5\text{P}_4\text{O}_{11.5}$ and $\text{SmNa}_5\text{P}_4\text{O}_{12.5}$ could be suggested as decomposition products, but the formation of pyrophosphate as intermediate product could not be observed owing to the overlapping of the two decomposition steps. On further increase of the temperature, only small changes in the mass were observed.

Compositions of the final decomposition products of the ligand and its complexes

To determine the compositions of the final decomposition products, some theoretical considerations were taken and the IR spectra of the final products were recorded. The characteristic IR bands are presented in Table 4.

Table 4 Characteristic IR bands of the thermal decomposition products of the complexes

Range/cm ⁻¹	PDTMP	La	Sm	Eu	Gd	Assignment
700–1500	1272	1122	1122			
	1160	1095	1095	1092	1095	
	955	1052	1051	1055	1062	$\nu_2(\text{PO}_4^{3-})$
		1024	1019	1022	1027	
		986	985	995	988	
		958	963	953	955	
700–900	774					
	724					
400–700			605	605	607	
			582	580	580	$\nu_4(\text{PO}_4^{3-})$
		572	564	562	562	
	494	503	546	545	545	

The bands observed could not be assigned to P_2O_5 or anions such as PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$ or $\text{P}_3\text{O}_{10}^{5-}$ as in the case of the EDTMP complexes [15]. In the IR spectra of the final decomposition products, 2 or 3 (in the case of PDTMP) broad bands with some maxima could be observed.

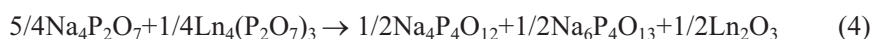
The bands of the decomposition product of PDTMP had very low intensity, which supports the suggestion of P_4O_8 as decomposition product. The oxides, P_4O_x ($x = 6-10$) have low symmetry and small dipole moments, which leads to IR bands with low intensity.

The decomposition products of the complexes gave 2 very broad bands with 5–6 and 4–5 local maxima in the wavenumber range 700–1500 and in the 400–700 cm^{-1} , respectively. These bands point to the presence of PO_4 groups in different surroundings.

The simple orthophosphate anion (PO_4^{3-}) can form different polyphosphate anions via linear coupling of the phosphate anion ($(\text{P}_x\text{O}_{3x+1})^{(x+2)-}$) or by forming cyclic polyphosphates, e.g. tetrapolyphosphate ($[\text{P}_4\text{O}_{12}]^{4-}$) [16]. The relative charge (related to one P atom) on the anions decreases with increasing degree of polymerization.

To determine the compositions of the final decomposition products, the charges on the polyphosphate anions have to be considered. The 8 positive charges (Ln^{3+} and 5Na^+) must be compensated by the phosphate and polyphosphate ions, containing 4 phosphorus atoms per unit. This requirement can be fulfilled by two $\text{P}_2\text{O}_7^{4-}$ ions. ($1/4\text{Ln}_4(\text{P}_2\text{O}_7)_3$ and $5/4\text{Na}_4\text{P}_2\text{O}_7$). Therefore, the expected decomposition product for the investigated complexes is a mixture of $\text{Ln}_4(\text{P}_2\text{O}_7)_3$ and $\text{Na}_4\text{P}_2\text{O}_7$ in a ratio of 1:5. This was observed for the La and Eu complexes.

Decomposition of the samples at higher temperature could be interpreted in terms of the formation of Ln_2O_3 and cyclic ($[\text{P}_4\text{O}_{12}]^{4-}$) and linear ($[\text{P}_4\text{O}_{13}]^{6-}$) tetrapolyphosphates in a ratio of 1:1 ratio. In this case the positive charge of the 5Na^+ is compensated by the polyphosphate ions. The suggested decomposition scheme is shown in Eqs (3) and (4):



Conclusions

EDTMP and PDTMP, which differ from one to other in one CH_2 group between the nitrogen atoms in the carbon chain, exhibit similar IR spectra and thermal behaviour. Both of them bind 2 water molecules under common conditions via hydrogen-bonding with 2 or 3 different strengths, respectively. EDTMP loses its water content in 2 steps between 50 and 150°C, 150 and 200°C, while in the case of PDTMP the 2 water molecules are released from the solid phase in 3 steps in the temperature ranges 85–140, 140–180, 180–250°C.

The complexes of EDTMP and PDTMP have similar thermal behaviour and IR spectra. However, there are several differences between the thermoanalytical curves of complexes of these ligands. The complexes of PDTMP lose their organic part between 330 and 480°C, while the complexes of EDTMP do that above 500°C. This fact refer to the moderate stability of the complexes of PDTMP, comparing to the stability of the complexes of EDTMP. It is not surprising, if we take in consideration of the supposed structure of the complexes. It is supposed that the EDTMP – similarly to the ethylenediamine tetraacetic acid (EDTA) – form a chelate ring with two nitrogen atoms (5 members of chelate ring), while the same chelate ring with PDTMP is much weaker (6 members ring).

The smaller stability of complexes causes that the complexes decompose earlier in time (at lower temperature) in the course of heating (there is enough time to decompose to the final products). This is the reason why we could observe more clearly the intermediate and the end products (pyrophosphate and the cyclic polyphosphates) in the case of the PDTMP complexes.

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