

Synthesis and Properties of Solid Complexes of Lanthanum, Cerium, Neodymium and Erbium with N-Phosphonomethylglycine

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Received: November 9, 2000

Accepted: February 15, 2001

Abstract

Water-soluble complexes of lanthanum(III), cerium(III), neodymium(III) and erbium(III) with N-Phosphonomethylglycine (glyphosate, NPMG) of the general formulae: $\text{LaC}_3\text{H}_5\text{NO}_5\text{P}\cdot\text{H}_2\text{O}$, $\text{CeC}_3\text{H}_5\text{NO}_5\text{P}\cdot\text{H}_2\text{O}$, $\text{NdC}_3\text{H}_5\text{NO}_5\text{P}\cdot 1.5\text{H}_2\text{O}$, $\text{ErC}_3\text{H}_5\text{NO}_5\text{P}\cdot 2\text{H}_2\text{O}$ were synthesized. Their solubility in water was determined. Thermal, diffractometric and IR spectrophotometric analyses were carried out. It was found that the lanthanide ions are bonded to N-phosphonomethylglycine through the oxygen atoms of the carboxylic and phosphonate groups and the nitrogen atom of the amine group. The final products of thermal decomposition at 900°C were determined.

Keywords: lanthanides; complexes of N-Phosphonomethylglycine; synthesis; IR; thermal studies.

Introduction

N-Phosphonomethylglycine (glyphosate, NPMG) is an active component of the frequently used herbicide Roundup. It exhibits strong phytocidal action involving disturbance of enzymatic processes in plants. In the soil glyphosate is microbiologically degraded and deactivated. This process is inhibited by binding glyphosate by cations of metals present in the soil. The strong complexing properties of glyphosate are due to three functional groups (amine, carboxylate and phosphonate) which may coordinate with metal ions. The studies on complexes of some metals with N-Phosphonomethylglycine were cited earlier [1]. Except for the work of Pangunoori and Ram [2], who determined the stability constants of complexes of type Me-NPMG (Me = Pr(III), Nd(III), Ga(III)) and Legendziewicz et al., who analyzed by X-ray diffraction methods $\text{EuL}_2(\text{H}_2\text{O})_8(\text{ClO}_4)_4$ (L = NPMG) and characterized it by IR and electron spectroscopy methods [3].

The authors of this paper did not find literature data concerning the formation of the complexes of lanthanides with glyphosate.

The content of lanthanides in uncultivated soil is usually low. However, it may be a few times higher in areas close to deposits of lanthanides, quarries or factories producing artificial fertilisers. From the soil lanthanides are transported to lakes, rivers and ground water and consequently to the plants growing in the area, animals and humans, where their different amounts are accumulated in different tissues. It has been found that in the human organism higher amounts of lanthanides accumulate in cancer cells than in healthy ones, which may mean that lanthanides could be used in diagnosing cancer and its treatment. Studies on eliminating of lanthanides from animal organisms has been studied using strong complexing agents such as N-Phosphonomethylglycine. The effect of lanthanides on cultivated plants and fruit trees has also been investigated. The results show that the presence of lanthanides in plant tissues increases absorption of nitrogen, phosphorus and potassium, thus ac-

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celerating the process of ripening of plants and increasing the growth of their mass; the colour of the vegetables and fruit is more intense, their taste is better and their nutritive value higher. The positive effect of lanthanides on plants has given rise to increasing interest in studies on their use as a supplement to artificial fertilisers [4].

Experimental

Chemicals

- N-Phosphonomethylglycine ($C_3H_8NO_5P$, Glyphosat, NPMG) was purified by double crystallization from aqueous solution;
 - Lanthanum (III) nitrate ($La(NO_3)_3 \cdot 6H_2O$) - Loba-Chemie, Wien-Fischamend;
 - Cerium (III) nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) - VEB Laborchemie Apolda;
 - Neodymium (III) oxide (Nd_2O_3) - Johnson, Matthey Co., Ltd.;
 - Erbium (III) oxide (Er_2O_3) - Koch-Light Laboratories Ltd.;
 - Hydrochloric acid (HCl);
 - Sodium hydroxide (NaOH);
 - Ethylenediamine tetraacetic acid (EDTA);
 - Arsenoazo(III);
- All reagents used were of analytical grade.

Apparatus

X-Ray diffraction patterns were recorded on a Siemens D 5000 diffractometer. Thermal analysis curves were plotted using an TG/DTA-SET SYS-16/8 thermoanalyser with Themostar mass spectrometer in air atmosphere within the temperature range of $20 \div 1000^\circ C$ at a heating rate of $10^\circ C/min$. IR spectra were recorded on a Shimadzu 8501 FTIR instrument in the $4400 \div 400\text{ cm}^{-1}$ region using KBr discs. Elemental analyses were performed using a Carlo-Erba 1108 CHN analyser.

Synthesis of Complexes

La(III), Ce(III), Nd(III) and Er(III) N-phosphonomethylglycine complexes were precipitated from hydroxides of the respective lanthanides, maintaining the molar ratio M:L = 1:2 and 1:3. The hydroxides were

obtained by adding a slight molar excess NaOH to the solution of the respective lanthanide salt. $Nd(OH)_3$ and $Er(OH)_3$ were obtained in the following way: oxides of these metals were solved in hot HCl (1:1), and equimolar amount of NaOH was added after the solution was neutralised. The hydroxides were filtered through a soft filter, washed and transferred into a beaker. Fifty millilitres of water were added and the suspension was heated. Hot glyphosate solution was added to the hot colloidal solution of hydroxide. The precipitates obtained were placed in the bath and heated for seven days. Then the precipitate was filtered, washed with water and dried in air. Each of the complexes had a different colour: in the case of La-NPMG the precipitate was white, Ce-NPMG was greyish, Nd-NPMG was slightly violet and Er-NPMG was pink. The yield exceeded 90% in all cases (99% for La and Nd, 93% for Ce and 98% for Er).

Analysis of Complexes

Lanthanides were determined by a spectrophotometric method by means of arsenazo(III) [5] and by titration by means of EDTA against xylene orange [6]. The content of carbon, hydrogen and nitrogen was established by elemental analysis.

Solubility of the complexes in water at room temperature was examined. About 0.4000 g of the complex were weighed, 10 ml of water were added, and the mixture was shaken for 6 hours and left for a further 48 hours to establish equilibrium. Then the precipitate was filtered off and the content of lanthanides in the filtrate was examined by spectrophotometric method with arsenazo(HI) [5].

Results and Discussion

The complexes were synthesized at two different molar ratios M:L (1:2 and 1:3). The precipitates obtained differ in colour (Table 1) and are sparingly soluble in water and ethyl alcohol but readily soluble in mineral acids and ammonium buffer. The yield of syntheses was higher than 90%. Table 1 presents theoretical and determined amounts of the metals, C, H and N in the complexes precipitated. The analyses demonstrated that N-Phosphonomethylglycine lanthanide complexes are formed at ratio 1:1 and have the following formulae: $LaC_3H_5NO_5P \cdot H_2O$, $CeC_3H_5NO_5P \cdot H_2O$, $NdC_3H_5NO_5P \cdot 1.5 H_2O$ and $ErC_3H_5NO_5P \cdot 2H_2O$.

Table 1. Results of C, H, N and metal determination (molar ratio NPMG : Ln = 1:1), synthesis yield and colour of complexes.

Compound	%C		%H		%N		%Ln		Yield	Colour
	Calcul.	Found	Calcul.	Found	Calcul.	Found	Calcul.	Found		
$LaC_3H_5NO_5P \cdot H_2O$	11.2	11.5	1.9	2.9	4.3	4.4	43.0	41.2	99%	white
$CeC_3H_5NO_5P \cdot H_2O$	11.1	11.2	1.9	2.5	4.3	4.3	43.2	39.2	93%	greyish
$NdC_3H_5NO_5P \cdot 1.5H_2O$	10.7	10.9	2.4	2.1	4.2	4.1	42.8	41.6	99%	violetish
$ErC_3H_5NO_5P \cdot 2H_2O$	10.0	9.9	2.5	2.4	3.9	3.7	46.4	45.6	98%	pink

Solubility in water at room temperature of La-NPMG, Ce-NPMG, Nd-NPMG and Er-NPMG was examined (Table 2).

Erbium with NPMG forms well-formed fine crystals. The other complexes precipitate as powders. The X-ray diffraction patterns of the complexes are presented in Fig. 1a-e.

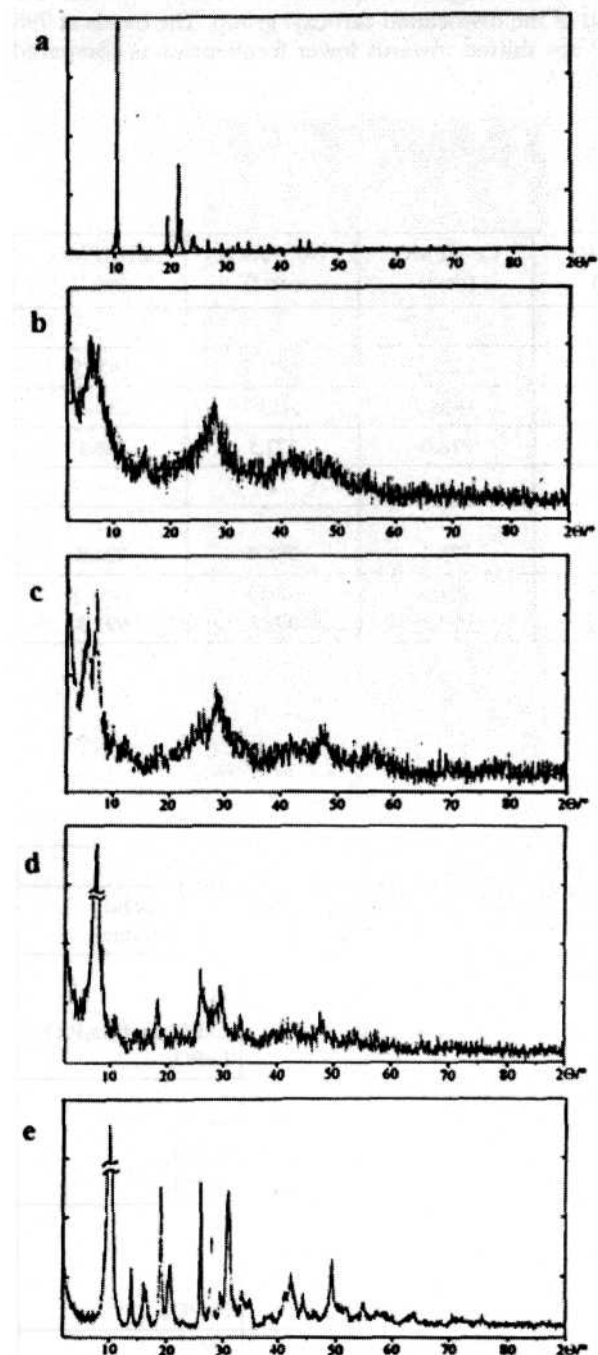


Fig. 1. X-Ray diffraction patterns of glyphosate (a), La-NPMG (b), Ce-NPMG (c), Nd-NPMG (d) and Er-NPMG (e).

Table 2. Solubility of metal - glyphosate complexes in water.

Complex	Solubility S (mol · dm ⁻³)
LaC ₃ H ₅ NO ₃ P · H ₂ O	7.46x10 ⁻⁴
CeC ₃ H ₅ NO ₃ P · H ₂ O	3.45x10 ⁻⁴
NdC ₃ H ₅ NO ₃ P · 1.5H ₂ O	2.87x10 ⁻⁴
ErC ₃ H ₅ NO ₃ P · 2H ₂ O	2.27x10 ⁻⁴

IR Spectroscopy

The IR spectra of N-phosphonomethylglycine and the complexes of N-phosphonomethylglycine with La, Ce, Nd and Er are presented in Fig. 2a-e.

In solid state NPMG has a structure of a dual ion [7].

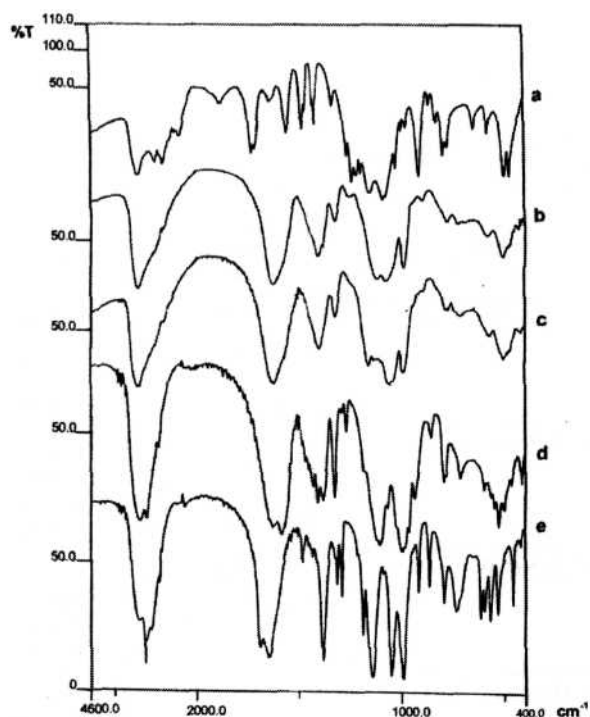
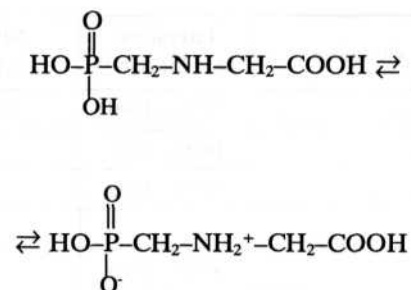


Fig. 2. The IR spectrum of NPMG (a), La-NPMG (b), Ce-NPMG (c), Nd-NPMG (d) and Er-NPMG (e).

The spectrum of the NPMG does not show a band at 3350-3320 cm^{-1} , attributed to the stretching vibrations of the amine group =NH. The bands at 1558.4 cm^{-1} and 798 cm^{-1} , on the other hand, are related to deformation vibrations of =NH²⁺ group present in the structure of the dual ion. Table 3 and Fig. 2a-e present the frequencies of vibrations for N-phosphonomethylglycine and its complexes with lanthanum, cerium, neodymium and erbium [8].

As shown in Table 3, the stretching band of the undissociated carboxyl group $\nu(\text{C}=\text{O})$ which occurs in glyphosate at 1732 cm^{-1} , does not occur in the spectra of the complexes. Instead, two new stretching bands appear: $\nu(\text{C}=\text{O})_{\text{sym}}$ and $\nu(\text{C}=\text{O})_{\text{asym}}$ originating from the dissociated carboxyl group. Calculating $\Delta\nu$ as a difference of the

asymmetric and symmetric vibration frequencies of the dissociated carboxyl group and comparing the position of the bands $\nu(\text{C}=\text{O})_{\text{asym}}$ and $\nu(\text{C}=\text{O})_{\text{sym}}$ in the complexes with the band of sodium acetate it was found that the carboxyl group in the compounds under study is monofunctional [9]. In the investigated complexes, two stretching bands $\nu(\text{P}=\text{O})$ characteristic of phosphonate are shifted towards lower frequencies as compared with the position of these bands in the NPMG molecule. The bands of deformation vibrations $\delta(\text{NH}_2^+) = 1558.5 \text{ cm}^{-1}$ do not occur in the spectra of complexes and are probably shifted towards higher frequencies, overlapping with the band of the dissociated carboxyl group. The bands at 798 cm^{-1} are shifted towards lower frequencies as compared

Table 3. Principal IR bands.

Group vibrations	Literature date [5] (cm^{-1})	NPMG (cm^{-1})	La-NPMG (cm^{-1})	Ce-NPMG (cm^{-1})	Nd-NPMG (cm^{-1})	Er-NPMG (cm^{-1})
$\nu(\text{C}=\text{O})_{\text{COOH}}$	1760 – 1690	1732	–	–	–	–
$\nu(\text{C}=\text{O})_{\text{COO} - \text{asym}}$	1610 – 1550	–	1635.9	1624.0	1591.2	1652.9
$\nu(\text{C}=\text{O})_{\text{COO} - \text{sym}}$	1420 – 1300	–	1409.9	1406.0	1413.7	1384.8
$\Delta\nu$	–	–	216.0	218.0	177.5	268.1
$\nu(\text{N-H})$	3350 – 3320	–	–	–	–	–
$\delta(\text{N}^+\text{H}_2)_{\text{aminoacid}}$	~ 1565 ~ 800	– 798.5	– 775.3	– 775.3	– 786.9	– 734.8
$\nu(\text{P}=\text{O})_{\text{phosphonate}}$	1100 – 960 two bands	1093.6 1031.8	1074.3 989.4	1060.8 993.3	1004.8 972.1	1051.1 991.3

Table 4. Results of thermal analysis

Complex	Decomposition date					
	Stage	Temperature range	Loss of mass	Thermal effect	Gaseous products	Solid products
$\text{LaC}_3\text{H}_5\text{NO}_3\text{P} \cdot \text{H}_2\text{O}$	I	50-210°C	14.5%	Endo-, peak at 136°C	H ₂ O	*
	II	210-520°C	17.2%	Exo-, peak at 380°C	H ₂ , CO ₂ , NO, NO ₂	**
	III	520-790°C	11.2%	Exo-, peak at 625°C	CO ₂ , NO, NO ₂	LaPO ₄ and La ₂ P ₄ O ₁₃
	IV	790-1000°C	3.2%	Endo-, peak at 870°C	–	LaPO ₄
$\text{CeC}_3\text{H}_5\text{NO}_3\text{P} \cdot \text{H}_2\text{O}$	I	60-190°C	9.6%	Endo-, peak at 134°C	H ₂ O	*
	II	190-540°C	15.3%	Exo-, peaks at 280, 377°C	H ₂ , H ₂ O, CO ₂ , NO, NO ₂	**
	III	540-715°C	3.5%	Exo-, peaks at 580, 660°C	CO ₂ , NO	CePO ₄
	IV	715-1000°C	6.0%	Exo-, peak at 870°C	CO ₂ , NO, NO ₂	CePO ₄
$\text{NdC}_3\text{H}_5\text{NO}_3\text{P} \cdot 1.5\text{H}_2\text{O}$	I	80-215°C	3.5%	Endo-, peak at 145°C	H ₂ O	***
	II	215-560°C	17.2%	Endo-, peak at 236°C	H ₂ , H ₂ O, CO ₂ , NO, NO ₂	**
	III	560-1000°C	7.6%	Exo-, peaks at 393, 436°C	CO ₂ , NO, NO ₂	NdPO ₄
$\text{ErC}_3\text{H}_5\text{NO}_3\text{P} \cdot 2\text{H}_2\text{O}$	I	45-180°C	2.2%	Endo-, peak at 145°C	H ₂ O	***
	II	180-350°C	5.5%	Endo-, peak at 264°C	H ₂ O, CO ₂	*
	III	350-630°C	14.0%	Exo-, peaks at 389, 473°C	H ₂ O, H ₂ , CO ₂ , NO, NO ₂	**
	IV	630-1000°C	5.4%	Exo-, peak at 800°C	CO ₂ , NO, NO ₂	ErPO ₄

* Compound dehydrated and partially decomposed; ** Compound not exactly identified; *** Compound partially dehydrated;

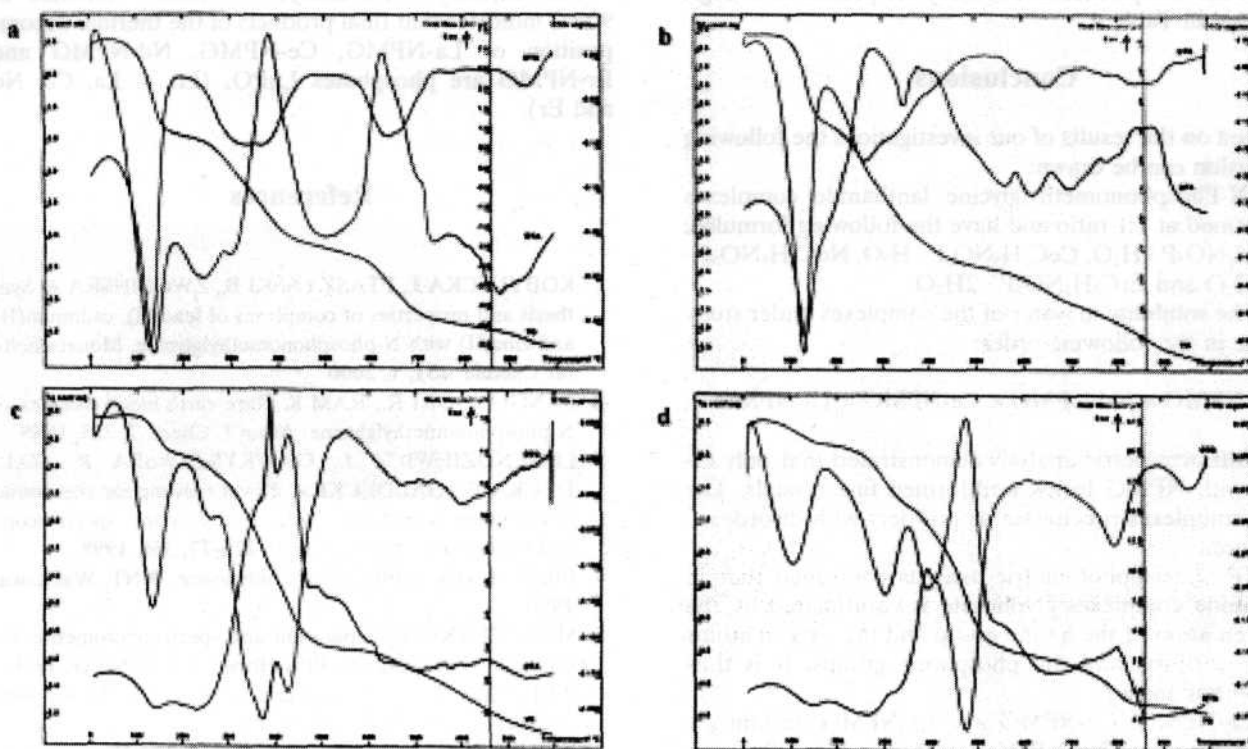


Fig. 3. Thermoanalytical curves of La-NPMG (a), Ce-NPMG (b), Nd-NPMG (c) and Er-NPMG (d).

with the position of these bands in the NPMG molecule. This results from the fact that in the complexes the lanthanide ions are also bound by the nitrogen atom.

Thermal Analysis

Thermal analysis of La-NPMG, Ce-NPMG, Nd-NPMG and Er-NPMG was carried out with the use of a thermoanalyser coupled with a mass spectrometer which analyses the gaseous products of decomposition. Derivatographic investigation was performed in air atmosphere at a temperature range from 25 to 1000°C at a heating rate 10°C/min. The mass of the samples used for the analysis was 10 mg (Figs. 3a-d and Table 4).

Nd-NPMG decomposes in three stages (Fig. 3c). The first stage of rapid decomposition (a clear DTG peak), with a 3.5% loss of mass occurs in the temperature range 80-215°C. The process is accompanied by a slight endothermic effect with a peak on DTA at 145°C. TG analysis and the mass spectrum of the gaseous products demonstrates that this stage involves partial loss of crystallisation water. Three overlapping processes take place in the second stage of decomposition in the temperature range 215-560°C. The onset of this stage is accompanied by an endothermic peak on the DTA curve at 236°C, related to the release of the remaining water of crystallisation. The other two peaks on the DTA curve at 393

and 436°C correspond with a strong exothermic effect connected with the oxidation of intermediate products leading to the release of CO₂, NO, NO₂, H₂ and H₂O. The loss of mass in this stage is 17.2%. The third stage of decomposition occurs in the temperature range 560-1000°C and proceeds very slowly (blurred DTG peaks). It is associated with a 7.6% loss of mass and a weak exothermic effect on the DTA curve at 860°C. This stage involves further oxidation of intermediate products, accompanied by the release of NO, NO₂ and CO₂. The diffractometric analysis of the sinter obtained at 900°C indicates that final product of the thermal decomposition of Nd-NPMG is phosphate NdPO₄.

Thermal decomposition of La-NPMG, Ce-NPMG and Er-NPMG compounds decompose in four stages. The first stage is dehydration process which for La-NPMG and Ce-NPMG is accompanied by a rapid loss of mass. In the case of Er-NPMG the release of crystallisation water is slow and occurs in both the first and the second stages of decomposition. The dehydration is accompanied by the endothermic peaks on the DTA curves. The second, third and fourth stages of the decomposition are connected with the exothermic oxidation processes of intermediate products, accompanied by the release of CO₂, NO and NO₂. The diffractometric analysis of sinters obtained at 900°C indicates that final products of the thermal decomposition of La-NPMG, Ce-NPMG and Er-NPMG are phosphonates LnPO₄ (Ln = La, Ce and Er).

The exact information about the thermal decomposi-

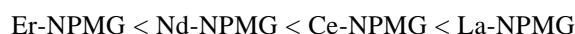
tion of the compounds under study are presented in Figs. 3a-d and in Table 4.

Conclusions

Based on the results of our investigations the following conclusion can be drawn:

1. N-Phosphonomethylglycine lanthanide complexes are formed at 1:1 ratio and have the following formulae: $\text{LaC}_3\text{H}_5\text{NO}_5\text{P} \cdot \text{H}_2\text{O}$, $\text{CeC}_3\text{H}_5\text{NO}_5\text{P} \cdot \text{H}_2\text{O}$, $\text{NdC}_3\text{H}_5\text{NO}_5\text{P} \cdot 1.5 \text{H}_2\text{O}$ and $\text{ErC}_3\text{H}_5\text{NO}_5\text{P} \cdot 2\text{H}_2\text{O}$.

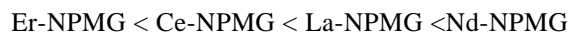
2. The solubility in water of the complexes under study change in the following order:



3. Diffractometric analysis demonstrated that only erbium with NPMG forms well-formed fine crystals. The other complexes precipitate as powders with disordered structure.

4. IR spectrophotometry analysis confirmed that in lanthanide complexes glyphosate is coordinated by the nitrogen atom of the amine group and the oxygen atoms of the carboxyl and the phosphone groups. It is thus a tridentate ligand.

5. La-NPMG, Ce-NPMG and Er-NPMG decompose in four stages and Nd-NPMG - in three stages. The mass spectrum analysis and TG curves indicate that each of the complexes contains crystallisation water and their decomposition involves the release of CO_2 , NO, NO_2 , H_2O and H_2 . The thermal stability of the anhydrous complexes measured from TG curves by the temperature at which the decomposition starts increases slightly in the sequence:



The diffractometric analysis of sinters obtained at 900°C indicates that final products of the thermal decomposition of La-NPMG, Ce-NPMG, Nd-NPMG and Er-NPMG are phosphates LnPO_4 (Ln = La, Ce, Nd and Er).

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