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Synthesis and Properties of Complexes of Lead(II), Cadmium(II), and Zinc(II) with N-Phosphonomethylglycine

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Summary. Sparingly water soluble complexes of lead(II), cadmium(II), and zinc(II) with N-phosphonomethylglycine (glyphosate, N*PMG*) of the general formulae $C_3H_6O_5NPPb$, $C_3H_6O_5NPCd \cdot 2H_2O$, and $C_3H_6O_5NPZn$ were synthesized. The complexes were also precipited from a dilute Roundup solution, and their solubility in water was determined. Thermal, diffractometric, and IR spectrophotometric analyses were carried out. It was found that the metal is bonded to glyphosate through the oxygen atoms of the carboxylic and phosphonate groups; metal-nitrogen binding is absent in the above compounds. Studying the complexing behaviour in solution by UV spectrophotometry pointed out that a complex of the composition Pb(II) : N*PMG* = 1:1 with an absorption band at 232 nm is formed. Its stability constant as determined by *Job*'s method is $\log K = 5.9 \pm 0.1$. Using potentiometric techniques, the dissociation constant of N-phosphonomethylglycine and the stability constants of its complexes with cadmium (II) and zinc (II) were determined.

Keywords. Lead(II); Cadmium(II); Zinc(II); Complexes; N-Phosphonomethylglycine; Synthesis; IR; UV; Thermal studies.

Synthese und Eigenschaften von Blei(II)-Cadmium(II)- und Zink(II)-Komplexen mit N-Phosphonomethylglycin

Zusammenfassung. Die schwer wasserlöslichen Blei(II)-, Cadmium(II)- und Zink(II)-Komplexe mit N-Phosphonomethylglycin (Glyphosat, N*PMG*) der allgemeinen Formeln $C_3H_6O_5NPPb$, $C_3H_6O_5NPCd \cdot 2H_2O$ und $C_3H_6O_5NPZn$ wurden hergestellt. Die Komplexe wurden auch aus einer verdünnten *Roundup*-Lösung niedergeschlagen, und ihre Löslichkeit in Wasser wurde bestimmt. Die Komplexe wurden thermochemisch, diffraktometrisch und spektrophotometrisch untersucht. Es wurde gefunden, daß das Metall mit Glyphosat über die Sauerstoffatome der Carboxyl- und Phosphonatgruppen gebunden wird und daß keine Metall-Stickstoff-Bindung vorliegt. Aus UV-spektrophotometrischen Untersuchungen zur Komplexbildung in Lösung geht hervor, daß im Fall der Blei(II)-Verbindung ein Komplex der Zusammensetzung Pb(II):N*PMG* = 1:1 mit einer Absorptionsbande bei 232 nm ensteht. Seine nach der *Job*'schen Methode ermittelte Stabilitätskonstante beträgt $\log K = 5.9 \pm 0.1$. Auf Grund der potentiometrischen Messungen wurden die Dissoziationskonstanten des N-Phosphonomethylglycins und die Stabilitätskonstanten seiner Komplexe mit Cd(II) und Zn(II) bestimmt.

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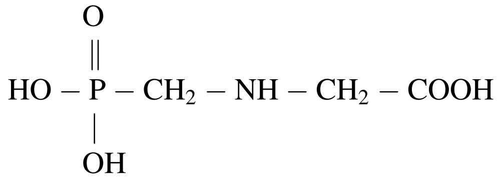
Introduction

N-Phosphonomethylglycine (glyphosate) is one of the best and the most frequently used herbicides. It was introduced to the market in 1971 by Monsanto, an American company, in the form of a solution under the trade name Roundup. Its active component is a salt of glyphosate with isopropylamine. Glyphosate is a non-selective post-emergence herbicide, exhibiting strong phylocidal action involving disturbance of enzymatic processes in plants. Absorbed by the leaves, it is quickly transported throughout the plant, destroying all its parts including the roots and rhizomes. Glyphosate is harmless to people and animals. In the soil it is microbiologically degraded and consequently deactivated. This process is inhibited by adsorption of glyphosate on soil particles and has been explained by binding of the phosphonate group of glyphosate by metal ions present in the soil [1, 2]. *Sprankle et al.* [3] have confirmed this by demonstrating that addition of iron(III) and aluminum(III) cations to the soil evidently decreases the degradation of glyphosate. These cations form new active sites in the soil which bind glyphosate and make it more resistant to biodegradation.

Studies carried out during the past two decades indicate that glyphosate has strong complexing properties. It has three functional groups (amine, carboxylate, and phosphonate) which may coordinate with metal ions. Depending on the *pH* of the reaction medium, *i.e.* the degree of deprotonation, glyphosate may be coordinated as a tridentate ligand through the amine group nitrogen, the carboxylate group oxygen, and the phosphonate group oxygen or as tetradentate ligand when the phosphonate group coordinates through two oxygen atoms.



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-CH_2-NH-CH_2-COOH$$

The first studies on complexes of metals with glyphosate appeared in late seventies. *Madsen et al.* [4] used potentiometric methods to determine the stability constants of glyphosate complexes with Cu(II), Zn(II), Mn(II), Ca(II), and Mg(II). *Glass* [5] used differential pulse polarography as well as UV and IR spectrophotometry to investigate complexes of glyphosate with Cu(II), Cd(II), and Fe(III). *Motekaitis* and *Martell* [6] obtained a number of complexes of N-phosphonomethylglycine with ions of di- and trivalent metals and determined their stability constant by potentiometry. Potentiometric methods were also used by *Pangunoori*, *Ram*, and *Rao* who have published four studies of glyphosate complexes with the following metals: Cu(II), Co(II), Ni(II) [7], Mg(II), Ca(II), Sr(II) [8], Pr(III), Nd(III), Gd(III) [9], and Be(II), Zn(II), Cd(II) [10]. Formation of complexes of Fe(III) and Cu(II) with glyphosate within a wide *pH* range and at different metal-ligand molar ratios was investigated by *McBride* and *Kung* [11, 12] who employed electron spin resonance.

Subramanian and *Hoggard* [13] obtained glyphosate complexes with Fe(III), Cu(II), Ni(II), Ca(II), and Mg(II) in the solid form and examined them by IR and X-ray methods. On the basis of their analyses they proposed that glyphosate used for spraying of the plants will not get into underground waters because of the formation of sparingly soluble complexes with metals when passing through the soil. Other authors [14] have investigated the solubility of analogous complexes and found that it decreases in the following order: Mg(II) $\approx$ Ca(II) > Mn(II) > Zn(II) > Cu(II) > Fe(III).

Piccolo et al. [15, 16] examined reactions of glyphosate with humic acids (HA) and with Fe(III)-HA complexes. They found that these may be important substrates for binding of the herbicide in the soil. Similar studies (reaction of glyphosate with copper bound in a complex with humic acids) were carried out by *Undabeytia et al.* [17].

The authors of the present work did not find literature data concerning the formation of complexes of lead(II) with glyphosate.

Results and Discussion

Investigations in solutions

Figure 1 presents UV spectra recorded for aqueous solutions of lead(II) perchlorate (curve 1), N*PMG*(curve 9), and mixtures containing a constant amount of lead and increasing amounts of glyphosate (curves 2–8). N*PMG* does not absorb over the examined wavelength range (200–300 nm), whereas $Pb(ClO_4)_2$ exhibits a maximal absorbance at 209 nm ($\varepsilon = 8.7 \times 10^3 dm^3 \cdot mol^{-1} \cdot cm^{-1}$). As increasing amounts of

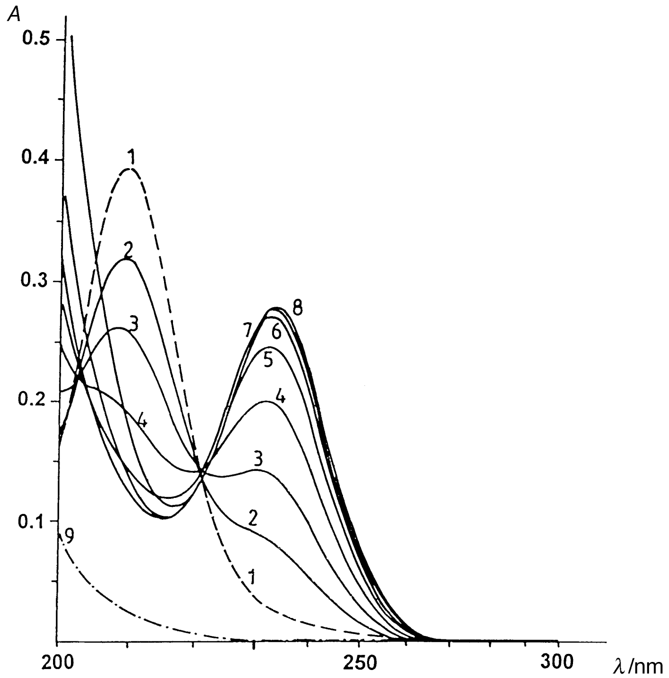


Fig. 1. Influence of the N*PMG*:Pb(II) molar ratio on the UV spectra of the Pb(II)-N*PMG* complex; 1) $Pb(ClO_4)_2$, $c = 4.48 \times 10^{-5} mol \cdot dm^{-3}$; 2–8) [N*PMG*]:[Pb(II)] = 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0; 9) N*PMG*, $c = 4.48 \times 10^{-5} mol \cdot dm^{-3}$, $pH = 7.0$

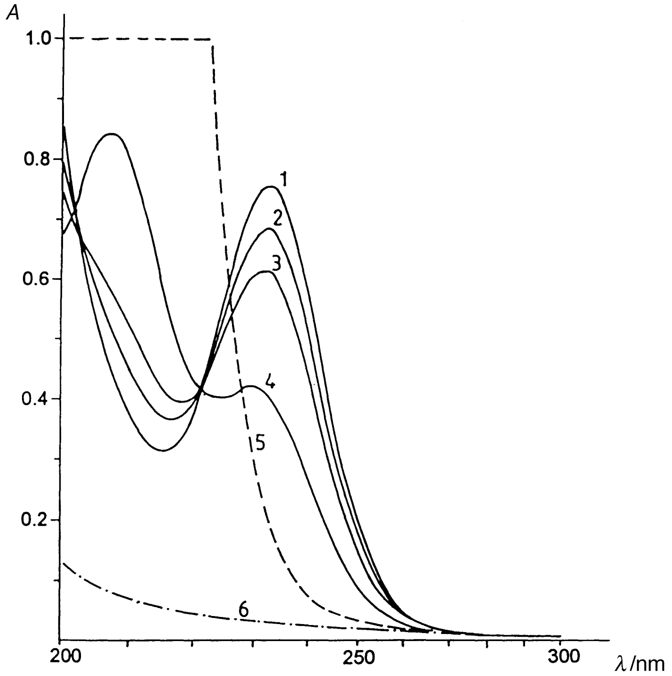


Fig. 2. Influence of *pH* on the UV spectra of the Pb(II)-N*PMG* complex; 1–4) Pb(II)-N*PMG*, $c = 1.3 \times 10^{-4}\,\mathrm{mol \cdot dm^{-3}}$, $pH = 6.5$–9.5, 6.0, 5.5, 5.0; 5) $Pb(NO_3)_2$, $c = 1.3 \times 10^{-4}\,\mathrm{mol \cdot dm^{-3}}$, $pH = 4$–7; 6) N*PMG*, $c = 1.3 \times 10^{-4}\,\mathrm{mol \cdot dm^{-3}}$, $pH = 5$–9.5

N*PMG* are added to the solution of the lead salt, the intensity of the band at 209 nm decreases and disappears when the molar ratio N*PMG*:Pb(II) reaches a value of about 0.8 (curve 5). These changes are accompanied by the appearance of a new band at 232 nm whose intensity increases with increasing amount of glyphosate and reaches its maximum when the molar ratio of N*PMG*:Pb is about 1 (curve 6); it remains practically unchanged, independent of further increase of the amount of glyphosate (curves 7 and 8, $\varepsilon = 6.1 \times 10^3\,\mathrm{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$). This band indicates the formation of a complex of the composition Pb(II):N*PMG* = 1:1. The method of isomolar series used in the present work confirmed the composition of the complex and allowed to determine its stability constant $\log K_{\mathrm{Pb(II)-N}PMG} = 5.90 \pm 0.1$. Figure 2 presents the influence of the *pH* value on the absorpition spectra of the Pb(II)-N*PMG* complex. It exhibits a constant absorbance at 232 nm within the *pH* range of 6.5–9.5 (curve 1). As the solution is acidified, the intensity of the band decreases, and at $pH < 5$ the band disappears, whereas at 209 nm a band characteristic of the Pb(II) ion appears. This investigation shows that the Pb(II)-N*PMG* complex is stable in aqueous solution at $pH > 6.5$.

UV spectrophotometry is not suitable for the investigation of Cd(II) and Zn(II) complexes as in the wavelength range of 200–300 nm no absorption bands appear for their solution. N-Phosphonomethylglycine is a weak triprotonated acid; its aqueous solution as well as solutions containing glyphosate and $CdCl_2$ or $ZnCl_2$ in a molar ratio of N*PMG*: metal = 1:1 were titrated potentiometrically (Fig. 3). From the titration curve of N-phosphonomethylglycine its dissociation constants were

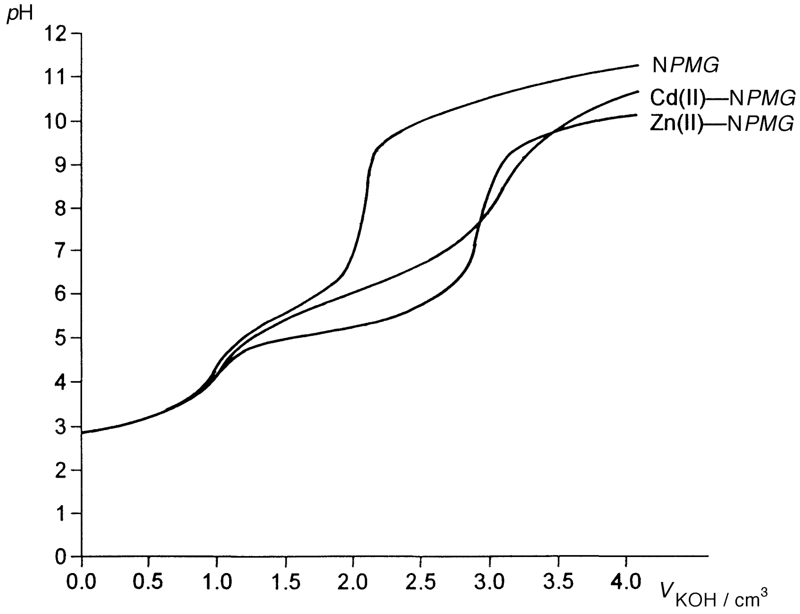


Fig. 3. Potentiometric titration curves of glyphosate, and its complexes with Cd(II) and Zn(II)

determined by a method described in the literature [4]. Their average values are $pK_1 = 2.53$, $pK_2 = 5.68$, and $pK_3 = 10.25$. Different shapes of the titration curves of glyphosate and N*PMG*-metal solutions indicate compound formation. The formation of the complex of cadmium(II) with glyphosate starts at $pH = 5$, whereas that of zinc(II) starts at $pH = 4$. Using a method described elsewhere [18], the stability constants of the complexes were determined. The values amount to $\log K_{\mathrm{Cd(II)-N}PMG} = 4.94$ and $\log K_{\mathrm{Zn(II)-N}PMG} = 7.61$.

The potentiometric titration of the lead complex in the *pH* region above 6 is not possible, because at the concentrations used in the study a precipitate appears.

Investigations in the solid state

Complexes of lead(II), cadmium(II), and zinc(II) with glyphosate in the solid state have not been investigated until now.

The complex Pb(II)-N*PMG* was obtained according to the method described in Ref. [13] for other metals. It precipitates immediately from the weakly alkaline (*pH* about 8) solution of N-phosphonomethylglycine in 90% yield. Diffractometric analysis indicated that in alkaline medium zinc and cadmium form solid mixtures with glyphosate containing, besides the metal(II)-N*PMG* complex, compounds of unknown composition. A new procedure was therefore developed to synthesize these complexes in slightly acid medium. Cd(II)-N*PMG* and Zn(II)-N*PMG* precipitate slowly in 70 and 90% yield, respectively. The content of metal(II) in compounds precipitated from N-phosphonomethylglycine as well as elemental analysis results (Table 1) indicate that lead(II), cadmium(II), and zinc(II) react with glyphosate at a molar ratio of metal(II):N*PMG* = 1:1 and form compounds of the formulae $C_3H_6O_5NPPb$,$C_3H_6O_5NPCd \cdot 2H_2O$, and $C_3H_6O_5NPZn$.

Table 1. Results of C, H, N and metal determination (molar ratio N*PMG*:*Me*(II) = 1:1)

Compound	%C		%H		%N		%M	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_3H_6O_5NPPb$	9.62	9.70	1.60	1.59	3.74	3.75	55.37	54.24
$C_3H_6O_5NPCd \cdot 2H_2O$	11.42	11.75	3.20	3.22	4.44	4.37	35.65	35.10
$C_3H_6O_5NPZn$	15.50	15.44	2.61	2.65	6.03	5.82	28.14	27.91

Table 2. Yields of *Me*(II)-N*PMG* complexes from Roundup

Dilution of Roundup	Amounts of reactants				Masses of precipitates		
	Roundup (cm^3)	$Pb(NO_3)_2$ (g)	$CdCl_2$ (g)	$ZnCl_2$ (g)	Calculated (g)	Found (g)	Yield (%)
100	100	0.260			0.600	0.250	41.7
	100		0.360		0.442	0.417	94.3
	100			0.215	0.367	0.237	64.7
250	100	0.104			0.240	0.070	29.2
	100		0.144		0.177	0.117	66.5
	100			0.086	0.147	0.101	69.1
500	100	0.052			0.120	0.025	20.8
	100		0.072		0.088	0.043	48.4
	100			0.043	0.073	–	–
1000	100	0.026			0.060	–	–
	100		0.036		0.044	–	–
	100			0.021	0.037	–	–

The studied complexes can be also precipitated from Roundup. The yield of the process depends on the degree of dilution of Roundup (Table 2). The contents of metal in precipitates from Roundup are in good accordance with that determined in complexes obtained by the method described earlier.

X-Ray diffraction patterns of N-phosphonomethylglycine and its compounds with lead(II), cadmium(II), and zinc(II) are presented in Fig. 4. The compounds are crystalline and sparingly soluble in water (Table 3).

Thermal analysis

Thermal analysis curves demonstrate that Pb(II)-N*PMG* contains no crystallization water (Fig. 5a). The compound is stable up to about 330°C. With further increase of temperature (up to about 600°C) it decomposes in several stages. The decomposition corresponds with DTA peaks (an endothermic peak at 340°C and two exothermic peaks at 400 and 570°C) associated with oxidation of the products of thermal decomposition of the compound. The final product of decomposition is lead(II) pyrophosphate, which was identified by diffractometric analysis of the

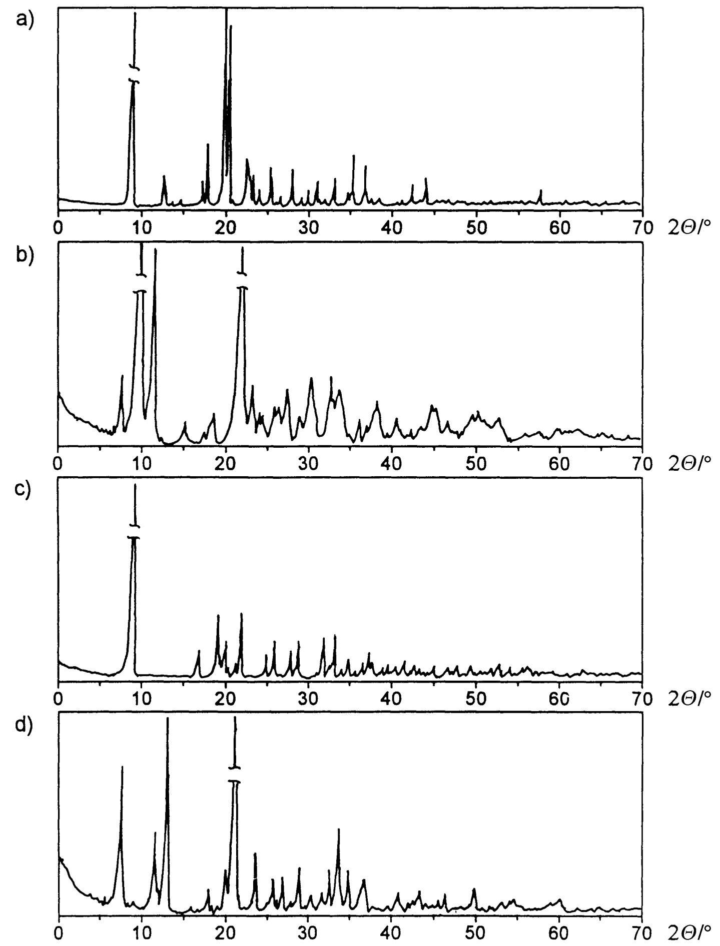


Fig. 4. X-Ray diffraction patterns of glyphosate (a), Pb(II)-N*PMG* (b), Cd(II)-N*PMG* (c), and Zn(II)-N*PMG* (d)

Table 3. Solubility of metal-glyphosate complexes in water (molar ratio N*PMG*:*Me*(II) = 1:1)

Complex	Solubility ($\mathrm{mol \cdot dm^{-3}}$)
Pb(II)-N*PMG*	7.28×10^{-5}
Cd(II)-N*PMG* · $2H_2O$	2.55×10^{-3}
Zn(II)-N*PMG*	8.81×10^{-4}

sinter obtained by heating Pb(II)-N*PMG* up to 650°C and confirmed by the presence of a sharp endothermic peak on the DTA curve at 825°C (melting point of $Pb_2P_2O_7$: 824°C).

The TG curve of the Cd(II)-N*PMG* complex indicates the presence of two molecules of crystallization water (Fig. 5b). The compound decomposes in three stages. In the first one (80–140°C endothermic), water is liberated. In the second stage (340–410°C), a fast loss of mass is observed. It corresponds with an

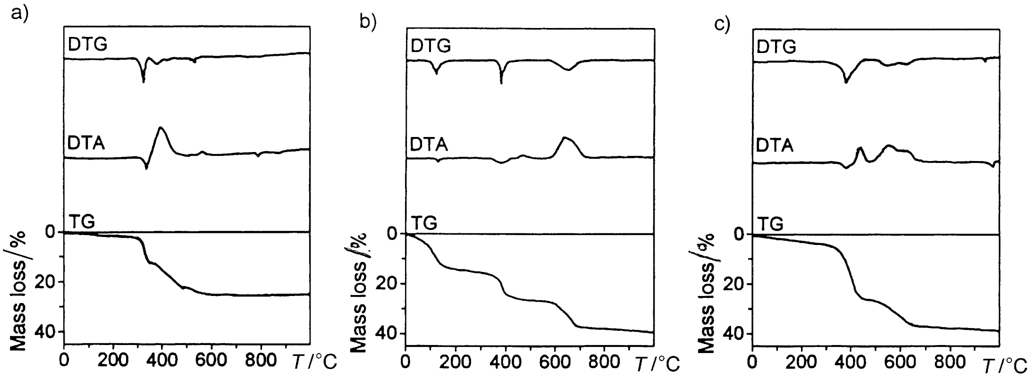


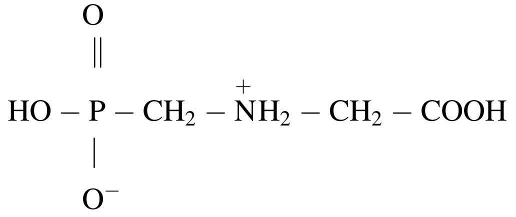
Fig. 5. Thermoanalytical curves of Pb(II)-N*PMG* (a), Cd(II)-N*PMG* (b), and Zn(II)-N*PMG* (c)

endothermic DTA peak at 390°C. The third (exotermic) stage, occuring within the temperature range of 560–680°C, is associated with the oxidation of the intermediate products of decomposition. The final product of thermal decomposition of the Cd(II)-N*PMG* complex was not identified.

The complex of zinc(II) with N-phosphonomethylglycine does not contain crystallization water as confirmed by TG, DTG, and DTA curves (Fig. 5c). It decomposes in two stages. The first one (endothermic), takes place within the temperature range of 370–440°C. In the second stage (550–680°C), further decomposition occurs, accompanied by oxidation of the intermediate products. Appropriate exothermic DTA peaks appear at 460, 570, and 650°C. The diffractometric analysis of the sinter obtained by heating the Zn(II)-N*PMG* complex up to 700°C indicates that the final product of decomposition is a mixture of $Zn_3(PO_3)_2$ and $Zn_2P_2O_7$.

IR spectroscopy

Table 4 lists the vibration frequencies characteristic for the functional groups of glyphosate and its complexes with lead(II), cadmium(II), and zinc(II) [19]. In the IR spectrum of glyphosate there is no band at 3350–3320 cm^{-1} corresponding with stretching vibration of the $=NH$ group, but there are bands at 1558.4 and 798.5 cm^{-1} attributed to deformation vibrations of this moiety which is present in the structure of the zwitterion as stated earlier by *Krawczyk* and *Bartczak* who determined the crystal structure of glyphosate [20]. Analogous bands occur also in the spectra of Pb(II)-N*PMG*, Cd(II)-N*PMG*, and Zn(II)-N*PMG*.



$$\mathrm{HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^{-}}{|}}{P}}-CH_2-\overset{+}{N}H_2-CH_2-COOH}$$

In the investigated compounds, the stretching bands of the phosphonate group are shifted towards lower vibration frequencies compared with those in the

Table 4. Principal IR bands of the investigated compounds

Group vibrations	Literature data [19] (cm^{-1})	N*PMG* (cm^{-1})	Pb(II)–N*PMG* (cm^{-1})	Cd(II)–N*PMG* (cm^{-1})	Zn(II)–N*PMG* (cm^{-1})
$\nu(C{=}O)_{COOH}$	1760–1690	1732.0	–	–	–
$\nu(C{=}O)_{COO}$-asym	1610–1550	–	1635.5	1635.5	1618.2
$\nu(C{=}O)_{COO}$-sym	1420–1300	–	1386.7	1379.0	1407.9
ν(N–H)	3350–3320	–	–	–	–
$\delta(N^+H_2)_{aminoacid}$	~1565	1558.4	1558.4	1558.4	1560.3
	~800	798.5	798.5	783.0	792.7
$\nu(P{=}O)_{physphonate}$	1100–960	1093.6	1143.7	1070.4	1099.3
	two bands	1031.8	1012.6	991.3	1008.7

spectrum of glyphosate. The stretching vibration band of the nondissociated carboxylic group at 1732 cm^{-1} present in the spectrum of glyphosate is not visible in the spectra of the complexes; instead, stretching vibration bands arising from the dissociated carboxylic group appear. This results from the fact that lead(II), cadmium(II), and zinc(II) are bonded with N-phosphonomethylglycine through the oxygen atoms of the carboxyl and phosphonate groups and that there is no metal-nitrogen bond. *Smith* and *Raymond* [21] reported a similar behaviour for the complex of glyphosate with calcium which has a polymeric structure. The authors consider this to be possible also in the case of the presently studied compounds.

Experimental

Chemicals

N-Phosphonomethylglycine ($C_3H_8O_5NP$, N*PMG*) was purified by double crystallization from aqueous solutions. Commercial Roundup (Monsanto Europe S.A.) containing 360 $g \cdot dm^{-3}$ N-phosphonomethylglycine in the form of its isopropylamine salt was used. Lead(II) nitrate (Merck), cadmium(II) chloride (P.O.Ch.), and zinc(II) chloride (Fluka AG) were used for the synthesis of the examined compounds. All other chemicals were of analytical grade and used without further purification.

Apparatus

The potentiometric measurements were performed using a Mettler Delta 350 *pH*-meter. X-Ray diffraction patterns were recorded on a Siemens D 5000 diffractometer. Thermal analysis curves were plotted using an OD-102/1500 derivatograph in air atmosphere within the temperature range of 20–1000°C at a heating rate of 5°C $\cdot$ min^{-1}. IR spectra were recorded on a Shimadzu 8501 FTIR instrument in the 4400–400 cm^{-1} region using KBr discs. Electronic spectra were recorded on Specord M 40 UV/VIS spectrophotometer. Elemental analyses were performed using a Carlo-Erba 1108 CHN analyser.

Procedures in solutions

The stability constant of the Pb(II)-N*PMG* complex was determined by *Job*'s method. The series of isomolar solutions was prepared from $Pb(ClO_4)_2$ and N-phosphomethylglycine solutions (both

$1.05 \cdot 10^{-4} mol \cdot dm^{-3}$). Constant ionic strength (0.1) was obtained by addition of appropriate amounts of $1 mol \cdot dm^{-3}$ KCl solution. The *pH* range of the solutions was 6.5–7. The UV absorption spectra (Fig. 1) were recorded in the 200–300 nm region using water as reference. logK of the complex Pb(II)-N*PMG* was calculated from the absorbance at 232 nm according to a method described in the literature [18].

To investigate the influence of *pH* on the absorption spectra of the complexes, a series of solutions was prepared by dissolution of weighed portions of the complex in the solid state in distilled water with addition of NaOH (0.025 g of Pb(II)-N*PMG* in a $500 cm^3$ measuring flask corresponds to a concentration of $1.3 \cdot 10^{-4} mol \cdot dm^{-3}$). Prior to filling the flask to the mark, the appriopriate *pH* value was fixed using a *pH*-meter. The UV absorption spectra (Fig. 2) were recorded in the 200–300 nm region against water as a reference. Attempts of recording these spectra using solutions obtained by mixing solutions of $Pb(NO_3)_2$ and N*PMG* in concentrations of $1.3 \cdot 10^{-4} mol \cdot dm^{-3}$ failed.

Mixtures A–C were prepared for the determination of equilibrium constants of N*PMG* as well as Cd(II)-N*PMG* and Zn(II)-N*PMG* complexes:

(A) $10 cm^3$ N*PMG* ($0.01 mol \cdot dm^{-3}$)+$5 cm^3$ KCl ($1 mol \cdot dm^{-3}$) +$35 cm^3$ H_2O
(B) $10 cm^3$ N*PMG* ($0.01 mol \cdot dm^{-3}$)+$10 cm^3$ $CdCl_2$ ($0.01 mol \cdot dm^{-3}$)+$5 cm^3$ KCl ($1 mol \cdot dm^{-3}$) +$25 cm^3$ H_2O
(C) $10 cm^3$ N*PMG* ($0.01 mol \cdot dm^{-3}$)+$10 cm^3$ $ZnCl_2$ ($0.01 mol \cdot dm^{-3}$)+$5 cm^3$ KCl ($1 mol \cdot dm^{-3}$) +$25 cm^3$ H_2O

Mixtures A–C were titrated potentiometrically with a standard KOH solution ($0.1000 mol \cdot dm^{-3}$). The acid dissociation constants of N-phosphomethylglycine were determined by titrating mixture A. The stability constants of Cd(II) and Zn(II) complexes with N*PMG* in solution were determined by titration of the mixtures B and C. The calculations were performed according to a method desribed in the literature [18].

Synthesis of solid complexes

The solid lead(II), cadmium(II), and zinc(II) complexes of N-phosphomethylglycine were prepared by precipitation from N*PMG* (a) and Roundup (b) solutions.

(a) To prepare the Pb(II)-N*PMG* complex, an aqueous solution of $Pb(NO_3)_2$ was added to a weak alkaline (*pH*~8) aqueous solution of N*PMG* in molar proportions of 1:1 and 1:2. In each case, a white precipitate appeared immediately. After 24 h it was filtered off, washed with water, and dried in air. Yields were about 70%. Results of chemical analyses indicated that at both proportions of Pb:N*PMG* mentioned above the same compound was obtained. The complexes of Cd(II) and Zn(II) with N-phosphomethylglycine precipitated slowly from the solutions of metal chloride and N*PMG* in molar proportions of 1:1 at *pH* 5 (Cd(II)-N*PMG* and 4(Zn(II)-N*PMG*. The white precipitates were recrystallized on the water bath, filtered off, washed with water, and dried in air. Yields were about 70% for cadmium and 90% for zinc complexes.

(b) The appropriate amounts of $Pb(NO_3)_2$, $CdCl_2$, and $ZnCl_2$ (molar rations of N*PMG* to metal: 1:1) were added to $100 cm^3$ of 100-, 250-, 500-, and 1000-fold diluted Roundup solutions (*pH* about 4.7). In the 100–500-fold diluted solutions white precipitates appeared. They were filtered off, washed with water, and dried in air. Yields depended upon the degree of dilution (Table 2). In the case of 1000-fold dilution of Roundup (500× for Cd(II)-N*PMG*), the solution became only turbid.

Analysis of solid complexes

Metals were determined by titration with *EDTA* against eriochrome black T (Pb(II) in the presence of tartaric acid (*pH* = 8-10), Cd(II) and Zn(II) in the presence of ammonium buffer (*pH* = 10)) [22].

Tests with standard solutions demonstrated that a N*PMG*:metal molar ratio of 2:1 does not interfere with the complexometric determination of Pb(II), Cd(II), and Zn(II). The carbon, hydrogen, and nitrogen contents were determined by elemental analyses; the corresponding data are given in Table 1. The solubility of complexes of Pb(II), Cd(II) and Zn(II) with N*PMG* in water at 21°C was determined. In saturated solutions prepared under isothermic conditions, the metals were determined spectrophotometrically with 4-(2-pyridylazo) resorcinol [23–25] (Table 3).

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