SOME DERIVATIVES OF ETHYLENEDIAMINOBISMETHYLPHOSPHONIC ACID

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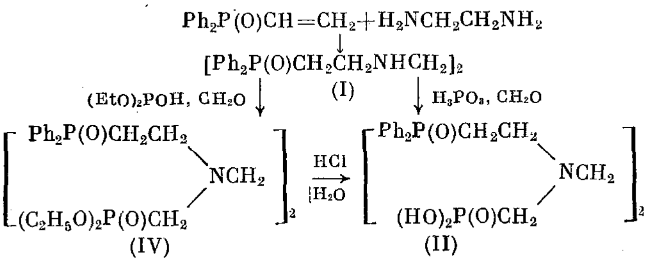
Polyaminopolyphosphonic acids [1] and polyphosphine polyoxides [2] have been extensively studied and have respectively found use as complexes and extractants. These reagents have a set of specific properties, which are determined mainly by the presence of either acid phosphonic or the so-called neutral phosphoryl groups.

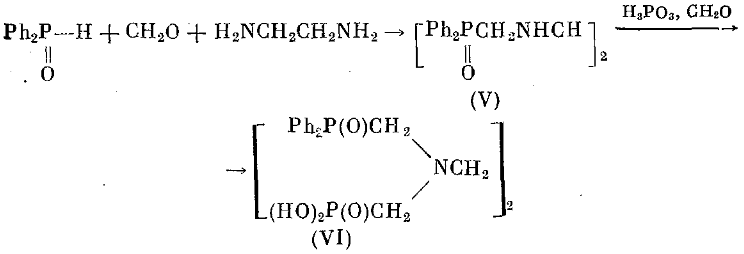
The synthesis and study of reagents that simultaneously contain fragments, which are characteristic for a complexon and for an extractant, seems of interest. A possible path for the synthesis of compounds of this type is given in the present paper.

As the starting compound we used N,N'-di(β-diphenylphosphorylethyl)ethylenediamine (I) [3]. Its condensation with formalin and phosphorous acid in HCl medium [4] gave compound (II), which contains phosphine oxide and acid phosphonic groups. It can be considered to be a derivative of the previously studied ethylenediaminobismethylphosphonic acid $[(HO)_2P(O)CH_2NHCH_2]_2$ (III) [5], which is substituted by β-diphenylphosphorylethyl groups on the nitrogen atoms.

Compound (II) was also obtained by another route, by the condensation of (I) with diethyl phosphite and paraform, followed by saponification of the thus-obtained ester (IV):



From (II) and (IV) were obtained the salts with HCl, picric acid, PbCl , and cyclohexylamine. Compound (VI), where the N and P atoms of the phosphine oxide group are separated by a methylene bridge, was obtained by an analogous route. In this case we took N,N'-bis(diphenylphosphorylmethyl)ethylenediamine (V) [3] as the starting compound and condensed it with H_3PO_3 and formalin.



The structure of acid (II) was confirmed by the elemental analysis and the IR and ^{31}P NMR spectral data. The IR spectra of (II) have bands at 1205 cm^{-1}, which are characteristic for $P(O)(OH)_2$ groups, and at 1175 cm^{-1} for $P(O)Ph_2$. The band in the 2300-2400 cm^{-1} region probably belongs to a nitrogen bearing a positive charge. The ^{31}P NMR spectra have signals at 33.3 and 12.8 ppm, which respectively belong to the P atoms of the phosphoryl and phosphonic groupings. Using the potentiometric titration method with $HClO_4$ in nitromethane, the basicity constants were determined for compound (IV). The titration curve has only two jumps of the potential: pK_a^{I} (CH_3NO_2) = 11.46; pK_a^{II} (CH_3NO_2) = 4.31.

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TABLE 1. Acid Dissociation (pK_a) of Acids (II) and (III) 25°, $\mu = 0.1$ (0.1 M KCl)

Acid	pK_1	pK_2	pK_3	pK_4
(II)	1,94	5,50	7,38	9,71
(III)	4,61	5,72	8,02	10,47

TABLE 2. Logarithms of Stability Constants* 25°, $\mu = 0.1$ (0.1 M KCl)

M	(II)		(III)
	MHL	ML	ML
Ca^{2+}	–	<2	<2
Sr^{2+}	–	<1	<1
Ba^{2+}	–	<1	<1
Mg^{2+}	–	<3	<2
Co^{2+}	6,7	10,5	10,8
Ni^{2+}	7,5	11,4	12,0
Cu^{2+}	10,4	15,4	18,6
Zn^{2+}	7,2	11,1	12,0
Mn^{2+}	4,9	7,9	7,6

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*The accuracy of determining the constants for acid (II) is on the order of ±0.1-0.2 with a reliability of 0.95.

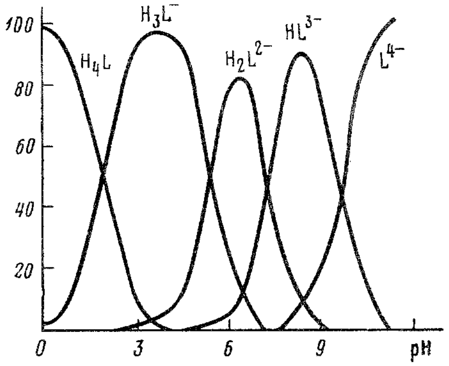

Fig. 1. Curve for distribution of ionic forms of acid (II) as a function of pH.

To study the acid–base and complexing properties of acid (I) we used the potentiometric titration method in water. The acid dissociation constants, calculated as described in [6], are given in Table 1. For comparison are given the pK_a of acid (III), which differs by the absence of diphenylethylphosphine oxide groups on the N atoms [5]. The given constants are the concentration constants. For the selected ionic strength $p[H^+] = pH - 0.11$ [7]. The accuracy of determining the pK_a of acid (II) is ±0.06 pK unit for pK_1 and ±0.04 pK unit for the other constants with a reliability of 0.95.

A comparison of the dissociation pK_a of acids (II) and (III) shows that the presence of substituents on the N atom leads to an increase in the acid properties of (II) at all of the dissociation steps. The difference in the K_1 constants is especially substantial. This is apparently due to the fact that compound (II), in contrast to (III), is not found in solution as the binary betaine, since the pK_1 value is close to the pK_a value of the completely protonated PO_3H_2 group. The absence of a binary betaine structure for (II) is possibly determined by a decrease in the basicity of the N atoms due to the inductive effect of the substituents.

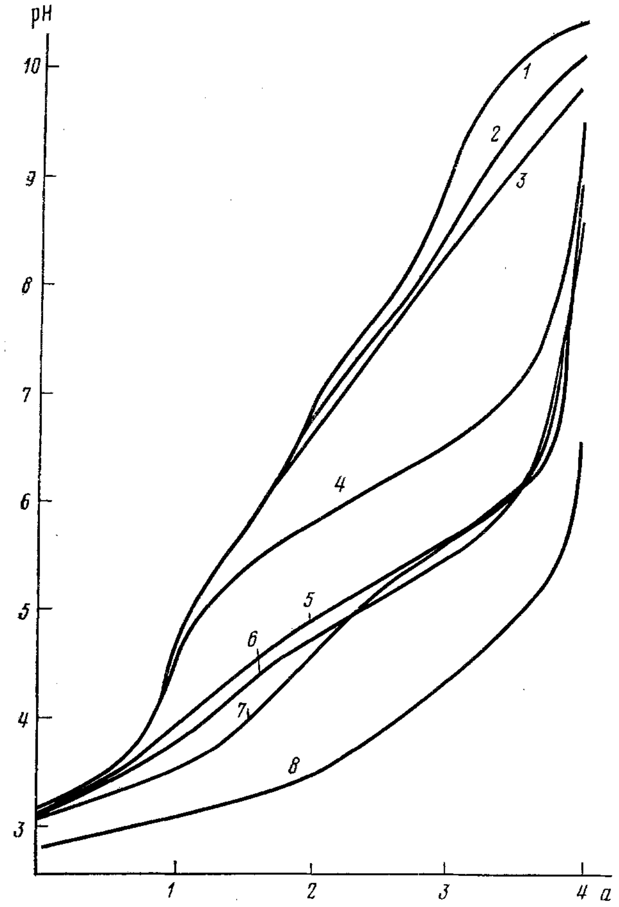

Fig. 2. Potentiometric titration curves for acid (II) at a concentration of $1 \cdot 10^{-3}$ M (1) and in the presence of $1 \cdot 10^{-3}$ M of the cations: 2) Ca^{2+}; 3) Mg^{2+}; 4) Mn^{2+}; 5) Co^{2+}; 6) Zn^{2+}; 7) Ni^{2+}; 8) Cu^{2+}. a = number of moles of KOH/mole of acid (II).

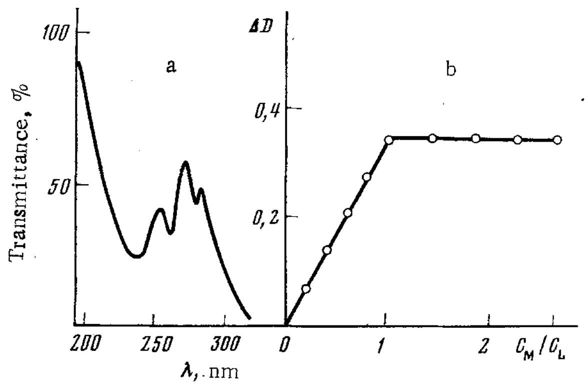

Fig. 3. Absorption spectrum of complex (II) with Cu^{2+} (a) and saturation curve (b) of $1 \cdot 10^{-4}$ M acid (II) in presence of variable Cu^{2+} concentrations (λ_{max} 266 nm, pH 7.7; 9.2; 11.0).

The data obtained on the titration of the tetraethyl ester of (II) in nitromethane also testify to a decrease in the basicity of the N atoms in (II): $pK_1 = 11.46$ and $pK_2 = 4.31$ when compared with $pK_1 = 15.3$ and $pK_2 = 8.6$ for N,N,N',N'-tetramethylethylenediamine [8]. The existence of "unsymmetrical" betaine structures in solution during the dissociation of ethylenediaminopolymethylenephosphonic acids was indicated in [9, 10]. On the basis of the obtained pK_a values of acid (II) we calculated and constructed the diagram for the distribution of the ionic forms of the acid as a function of pH (Fig. 1).

The complexing properties of acid (II) were studied relative to the ions of the alkaline-earth, transition, and rare-earth elements. With Ca^{2+}, Sr^{2+}, and Ba^{2+} are formed unstable complexes with the logarithms of the stability constants not exceeding two. With Eu^{3+}, Yb^{3+}, Nd^{3+}, and also Fe^{3+} and Th^{4+} insoluble complexes are formed. Soluble complexes are formed with the transition elements. The corresponding potentiometric titration curves are given in Fig. 2. The values of the stability constants, calculated as described in [11], are given in Table 2. For comparison are given the stability constants of the normal complexes of acid (III) with the studied cations [4, 12].

As follows from the given results, the insertion of phosphine oxide groupings into (III) fails to increase the stability constants of the complexes. The potentiometric method does not permit recording the contribution of the neutral phosphine oxide groups to the stability constant, since the cleavage of protons fails to occur during their complexing. In our opinion, in aqueous phase the phosphine oxide groupings do not make a significant contribution to the formation constant.

The composition of the formed complexes was determined spectrophotometrically on the example of complex formation with copper ions. The saturation curve, obtained at λ_{max} 226 nm and pH 7.7, 9.2, and 11.0 (borate buffers), has a break at the point corresponding to the composition M:L = 1:1 (Fig. 3).

EXPERIMENTAL

N,N'-Di(β-diphenylphosphorylethyl)ethylenediamine (I) and N,N'-di(diphenylphosphorylmethyl)ethylenediamine (V) were obtained as described in [2]; (I), mp 145-146°C; (V), mp 172-174° (cf. [2]).

Tetraethyl Ester of N,N'-Di(β-diphenylphosphorylethyl)ethylenediaminobismethylphosphonic Acid (IV). A mixture of 3.7 g (7.1 mmoles) of (I), 2.56 g (18 mmoles) of diethyl phosphite, and 18 mmoles of paraform in 15 ml of abs. benzene was heated in an ampul for 6 h at 100°. The residue from distilling off the benzene was passed through an Al_2O_3 column (eluant = 20:5 benzene:ethanol). After removing the solvent the residue was recrystallized from benzene to give 3.4 g (60%) of (IV), mp 126-127°. Found: P 15.2; N 3.4%; mol. wt. 820 (ebullioscopically). $C_{40}H_{56}N_2O_8P_4$. Calculated: P 15.4; N 3.2%; mol. wt. 816.

(IV) Hydrochloride. The passage of dry HCl into an acetone solution of (IV) gave a crystalline precipitate, mp 134-135°. Found: Cl 7.9%. $C_{40}H_{56}N_2O_8P_4 \cdot 2HCl$. Calculated: Cl 7.6%.

N,N'-Di(β-diphenylphosphorylethyl)ethylenediaminobismethylphosphonic Acid (II). A. A mixture of 1 g (1.2 mmoles) of the diethyl ester of N,N'-di(β-diphenylphosphorylethyl)-ethylenediaminobis(methylphosphonic) acid and 10 ml of conc. HCl was refluxed for 7 h. The precipitate obtained on cooling was filtered, dissolved in aqueous alcohol, and treated with propylene oxide. The volatiles were distilled off and the residue was recrystallized from alcohol to give 0.6 g (73%) of (II), mp 215-217°.

B. A mixture of 3 g (6 mmoles) of (I) and 0.98 g (12 mmoles) of crystalline H_3PO_3 in 3 ml of water and 3 ml of HCl was heated to reflux and the 2.2 g (24 mmoles) of 37% formalin solution was added to this mixture in 1 h. Then the reaction mixture was refluxed for another hour. Two layers were formed when the mixture was kept overnight. The HCl and water were removed in vacuo, and the residue was treated with a solution of propylene oxide in alcohol. After removal of the solvent the substance was recrystallized, first from abs. alcohol, and then from aqueous EtOH to give 2 g (50%) of (II), mp 215-217°. Found: C 53.2; H 6.2; P 17.2; N 3.6%. $C_{32}H_{40}N_2O_8P_4 \cdot H_2O$. Calculated: C 53.1; H 5.8; P 17.1; N 3.9%.

Cyclohexylammonium Salt of Acid (II). When a solution of cyclohexylamine in acetonitrile is added to an alcohol suspension of (II), the solution becomes clear. The solution on standing deposits the salt, mp 167-170°. Found: N 7.6%. $C_{56}H_{92}N_6O_8P_4$. Calculated: N 7.3%.

Complex of Acid (II) with $PbCl_2$. The complex was obtained by mixing aqueous solutions of the components. Found: Cl 7.8%. $C_{32}H_{40}N_2O_8P_4 \cdot PbCl_2$. Calculated: Cl 7.2%.

N,N'-Di(diphenylphosphorylmethyl)ethylenediaminobismethylphosphonic Acid (VI). Acid (VI) was synthesized using method B for (II), from 0.7 g (1.5 mmoles) of (V), 0.18 g (6 mmoles) of 37% formalin solution, 0.25 g (6 mmoles) of H_3PO_3, 0.7 ml of water, and 0.7 ml of conc. HCl. We obtained 0.65 g (70%) of (VI) as an amorphous substance that decomposes at ∿100°. Found: P 18.3%. $C_{30}H_{36}N_2O_8P_4$. Calculated: P 18.6%.

The potentiometric titration was run on a pH-262 pH meter with an accuracy of 0.01 pH unit. The electrode system was calibrated using standard buffer solutions. The starting acid concentration in the titration was $1 \cdot 10^{-3}$ M. As the titrant we used 0.1 M KOH solution, free of carbonates.

The UV absorption spectra were taken on a Specord UV-VIS instrument in a quartz cell (l = 1 cm) at ∿20°. The concentration of the metal salt solutions was determined trilonometrically [13].

CONCLUSIONS

1. Some new organophosphorus reagents were synthesized, combining in the molecule phosphonic and phosphine oxide groupings, which are characteristic for a complexon and an extractant.

2. Employing the potentiometric titration method, the acid dissociation pK_a were determined for N,N'-di(β-diphenylphosphorylethyl)ethylenediaminobismethylphosphonic acid and a study was made of its complexing with a number of cations in water. It is postulated that phosphine oxide substituents on the nitrogen atoms do not take part in the coordination with metal ions.

3. The composition (M:L = 1:1) of the formed complexes was determined on the example of complex formation with copper ions.

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