# SYNTHESIS AND STUDY OF COMPLEXING PROPERTIES OF

XYLYLENEDIAMINOTETRA (METHYLPHOSPHONIC) ACIDS

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The insertion of fragments, which increase the conformational rigidity of the compound, into a complexon molecule, leads to an increase in the complexing selectivity [1]. Thus, replacing the flexible ethylene bridge in ethylenediamino-bis(alkylphosphonic) acids by the relatively rigid xylylene bridge increases the selectivity of their action. In contrast to acids with a flexible bridge, the m- and p-xylylenediamino-bis(isopropylphosphonic) acids [2] form stable chelates of composition  $MH_2L$  only with cations with a large radius  $(UO_2^{2+})$ . It seemed interesting to study some polydentate complexons that contain two --CH\_2N(CH\_2PO\_3H\_2)\_2 groups in different positions of the benzene ring.

For this purpose we synthesized the m- (I) and p-isomer (II) of xylylenediaminotetra-(methylphosphonic) acid by the general method given in [3]

$$H_{2}NCH_{2} \longrightarrow H_{2}O_{3}PCH_{2}O_{2}NCH_{2} \longrightarrow H_{2}O_{3}PCH_{2}O_{2}NCH_{2} \longrightarrow H_{2}O_{2}OCH_{2}OC$$

To compare the complexing properties we obtained butylenediaminotetra(methylphosphonic) acid (III) [3] in a similar manner, which has a flexible alkylene bridge between the nitrogen atoms, whereas in acids (I) and (II) the bridges contain 5 and 6 C atoms, which lie in one plane:

## $(H_2O_3PCH_2)_2NCH_2CH_2CH_2CH_2N(CH_2PO_3H_2)_2$ (III).

The acid—base and complexing properties of the synthesized compounds (I)-(III) were studied by potentiometric titration in water. The neutralization curves of the acids practically coincide (the maximum deviations do not exceed 0.05 pH units), which testifies to the same mutual electronic effect of the iminodi(methylphosphonic) groupings on each other, or more accurately to the absence of this effect due to the great distance of the dissociating groups.

Actually, on the example of diphosphonic acids of general formula  $H_2O_3P(CH_2)_nPO_3H_2$  it was shown [4, 5] that the mutual effect of the phosphonic groups on each other is negligibly small when  $n \ge 3$ . This conclusion evidently can also be assigned to the discussed iminodi-(methylphosphonic) groupings.

The neutralization curves of acids (I), (II), and (III) have three buffer regions:  $0 < \alpha < 2$ ,  $2 < \alpha < 6$ ,  $6 < \alpha < 8$  ( $\alpha$  is the number of moles of KOH per mole of acid). The cleavage of only two H<sup>+</sup> ions in the first buffer region apparently testifies to the zwitter-ion structure of the acids in solution, and also to the realization of a binary betaine structure (in the opposite case three H<sup>+</sup> ions would be cleaved in the first buffer region).

TABLE 1. Dissociation Constants of Acid (I) 25°,  $\mu$  =0.1 (0.1 M KC1)

$pK_3$	$pK_4$	$\mathrm{p}K_{5}$	p <b>K</b> 6	pK₁
$4,52{\pm}0,03$	5,13±0,03	6,09±0,03	$6,94{\pm}0,03$	11,08±0,04

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TABLE 2.\* Logarithms of Stability Constants of Complexes for Acid (I) (25°,  $\mu = 0.1$ )

Complex	Ca²+	Cu²+	Co²+	Hg²+
$egin{array}{c} MH_4L \\ MH_3L \\ MH_2L \\ MHL \\ ML \end{array}$	- - $3,87\pm0,02$ $4,26\pm0,10$	$5,85\pm0,05$ $7,51\pm0,07$ $9,02\pm0,08$ $13,51\pm0,09$ $15,36\pm0,10$	$3,26\pm0,03$ $4,21\pm0,04$ $5,11\pm0,04$ $9,01\pm0,05$ $10,31\pm0,07$	$4,61\pm0,04$ $4,01\pm0,04$ $5,14\pm0,05$ $8,98\pm0,05$ $9,78\pm0,10$

\*The given errors were determined the same as in Table 1.

Since the titration curves of acids (I)-(III) practically coincide, the dissociation constants were calculated only for acid (I).

The constants, calculated using the programs given in [6] on a BÉSM-6 electronic computer (Table 1), are concentration constants.

The  $pK_1$  and  $pK_2$  values are too low, while the  $pK_8$  value is too high to be determined by the potentiometric method at the given concentration. To calculate the stability constants of the complexes we arbitrarily took  $pK_8 = 12.00$ .

The errors given in Table 1 were found as the average of the deviations that were obtained when the titration curve is shifted by the possible error of the pH meter, which is equal to  $\pm 0.01$  pH units.

The complexing properties of compounds (II)-(III) were determined with respect to  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Hg^{2+}$ , and also  $Ca^{2+}$ . Insoluble complexes are formed with the rare-earth elements,  $UO_2^{2+}$ ,  $Th^{4+}$ , and  $Pb^{2+}$ . Fe<sup>3+</sup> and  $Zn^{2+}$  also give precipitates.

The studied acids form complexes of the same stability with each of the indicated cations, as is evidenced by the coinciding (within the limits of 0.1 pH unit) of the neutralization curves of the acids in the presence of these cations. This result can be explained by the same structure of the complexes for all of the acids, which is possible in the case of forming complexes with a chain structure. Such a coordination of the metals is probably the consequence of the high dentate character of compounds (I)-(III). The studied diphos-phonic acids [2] can apparently form a chelate ring with the cation only when both phosphonic groups are involved. In contrast to the diphosphonic acids, for tetra(methylphosphonic) acids each of the iminodi(methylphosphonic) fragments of compounds (I)-(III) is independently capable of forming a chelate ring with the cations. Consequently, the position of the compound, which is actually observed. As a result, a rigid fastening of the iminodi(methylphosphonic) groupings in the benzene ring does not lead in this case to the expected selectivity of action and compounds (I)-(II) exhibit the same complexing properties as does acid (III) with a flexible alkylene bridge.

The composition of the complexes, formed in solution, was determined conductometrically on the example of (I) with  $Cu^{2+}$  ions. A study of the change in the electrical conductivity of the salt of the acid (I) anion ( $L^{8-}$ ) reveals that only one complex with a 1:1 composition is formed in solution. The formation of complexes of composition M:L = 2:1 is not observed. An insoluble compound is formed in solution when the M:L ratio = 2.5:1.

The stability constants of the complexes (Table 2) were calculated for (I) using the program given in [6], on the assumption that complexes of composition  $MH_{iL}$  are formed. The stability constants of the complexes of acids (II) and (III) have the same values.

#### EXPERIMENTAL

The potentiometric titration was run on a pH-242 pH meter with an accuracy of  $\pm 0.01$  pH units at 25°C, an ionic strength of  $\mu = 0.01$  (0.1 M KCl), and an acid concentration of 0.002 M. The activity coefficients under the selected conditions are  $p\gamma_{H} + = p\gamma_{OH} - = 0.11$  [7].

The electrical conductivity was measured on an OK-101/1 instrument (Hungary). The concentration of the metal cations was established by trilonometric titration [8].

The <sup>31</sup>P NMR spectra were taken on a Bruker HX-90 spectrometer at an operating frequency of 36.43 MHz under Fourier-transform conditions\* (external standard = 85% H<sub>3</sub>PO<sub>4</sub>).

m-Xylylenediaminotetra(methylphosphonic) acid (I). To 5 g of cooled m-xylylenediamine was added 20 ml of 1:1 HCl solution. To the obtained solution were added 10 ml of conc. HCl and 13.3 g of  $H_3PO_3$ , and the solution was heated to 110-120°. With stirring, 20 ml of formalin was added in 2.5 h to the refluxing solution; the reaction mixture was kept for 1.5 h at 110-120°, the solvent was distilled off and, adding water, the residue was evaporated several times until the test for halogen was negative. The oily residue was reprecipitated several times with alcohol and acetone, dissolved in a little water, filtered, the filtrate was evaporated to dryness, and the white powder was dried in vacuo for 1 h at 100° to give 5.3 g of m-xylylenediaminotetra(methylphosphonic) acid (43.3% yield). Found: P 23.7; N 5.4%. C12H24N2O12P4. Calculated: P 24.2; N 5.5%. Neutralization equivalent: found 380, calculated 384. The <sup>31</sup>P NMR spectrum of the neutral Na salt of the acid in water has one signal at  $\delta + 16.75$  ppm.

p-Xylylenediaminotetra(methylphosphonic) acid (II). To 5.3 g of cooled p-xylylenediamine was added 20 ml of 1:1 HCl solution. To the obtained solution were added 14 g of H<sub>3</sub>PO<sub>3</sub> and 10 ml of conc. HCl, the solution was heated to 110-120° and, with stirring, 25 ml of formalin was added in 1.5 h. The reaction mixture was kept for 1 h at 110-120°. The obtained white suspension was cooled, and the powder was filtered, washed several times with water, and dried for 1 h in vacuo to give 10.9 g (80%) of p-xylylenediaminotetra(methylphosphonic) acid. Found: C 28.0; H 4.7; N 5.4; P 23.9%. C12H24N2O12P4. Calculated: C 28.1; H 4.7; N 5.5; P 24.2%. Neutralization equivalent: found 381, calculated 384. The <sup>31</sup>P NMR spectrum of a water solution of the neutral Na salt has one signal at  $\delta + 16.48$  ppm.

Tetramethylenediaminotetra (methylphosphonic) acid (III) was obtained in a similar manner from tetramethylenediamine in 82% yield, mp 229-231° (decompn.), cf. [3]. Neutralization equivalent: found 347, calculated 348.

### CONCLUSIONS

1. We synthesized some members of the polydentate organophosphorus complexons, and specifically the m- and p-isomers of xylylenediaminotetra(methylphosphonic) acid, and we calculated their dissociation pK<sub>a</sub> and the stability constants of the complexes with a number of metal cations.

2. For the m- and p-isomers of xylylenediaminotetra(methylphosphonic) acid the position of the complexing groupings in the benzene nucleus has no effect on the acid-base and complexing properties of these compounds.

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<sup>\*</sup>The <sup>31</sup>P NMR spectra were taken with noise suppression of the protons. The signals downfield relative to H<sub>3</sub>PO<sub>4</sub> are designated by a positive sign.