

# Protonation constants of methyliminobis(methylenephosphonic) acid and the stability constants of its complexes

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The protonation constants of methyliminobis(methylenephosphonic) acid ( $H_4mibmp$ ) and the stability constants of its complexes with nine cations have been determined at 25°C and the ionic strength  $I(NaClO_4) = 0.1 \text{ mol dm}^{-3}$  by potentiometric titrations ( $pK_1 < 2$ ,  $pK_2 = 5.00$ ,  $pK_3 = 6.22$ ,  $pK_4 = 11.94$ ). The data were treated using the MINIQAD statistical program. It has been verified that  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$  form only the complexes of the type  $[Mmibmp]^{2-}$  ( $\log\{\beta\} = 5.00 (Mg^{2+}) - 4.21 (Ba^{2+})$ ). With the transition metal cations,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ , and  $Cd^{2+}$ , the existence of the complexes of the types  $[Mmibmp]^{2-}$ ,  $[Mmibmp_2]^{6-}$  and their protonated forms,  $[MHmibmp]^-$  and  $[M(Hmibmp)_2]^{4-}$ , has been confirmed. The  $[Mmibmp_2]^{6-}$  complex has not been found in the systems containing copper. On the basis of the results, coordination through N-atoms is assumed only for the complexes with  $Cu^{2+}$  and  $Cd^{2+}$ . The other cations are probably coordinated only through the oxygen atoms.

Посредством потенциометрического титрования проведено определение констант протонирования метилиминобис(метиленфосфоной) кислоты ( $H_4mibmp$ ), а также констант устойчивости ее комплексов с девятью катионами при 25°C и ионной силе  $I(NaClO_4) = 0,1 \text{ моль дм}^{-3}$  ( $pK_1 < 2$ ,  $pK_2 = 5,00$ ,  $pK_3 = 6,22$ ,  $pK_4 = 11,94$ ). Полученные данные были обработаны с помощью статистической программы MINIQAD. Было подтверждено, что  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  и  $Ba^{2+}$  образуют только комплексы типа  $[Mmibmp]^{2-}$  ( $\log\{\beta\} = 5,00 (Mg^{2+}) - 4,21 (Ba^{2+})$ ). В случае катионов переходных металлов  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  и  $Cd^{2+}$  было показано, что существуют комплексы типов  $[Mmibmp]^{2-}$ ,  $[Mmibmp_2]^{6-}$  и их протонированные формы  $[MHmibmp]^-$  и  $[M(Hmibmp)_2]^{4-}$ . Комплекс  $[Mmibmp_2]^{6-}$  не был обнаружен в системах, содержащих медь. На основании этих результатов можно предполагать, что координация по атомам N имеет место лишь в комплексах с  $Cu^{2+}$  и  $Cd^{2+}$ . Другие катионы, вероятно, координируются только по атомам кислорода.

Aminoalkylphosphonic acids are analogues of natural amino acids. They can be formally derived from amino acids or aminopolycarboxylic acids by substituting the carboxylic group with the  $-P(O)(OH)_2$  group. They have been

recently studied because of their biological activity and for the use as chelating agents. For the latter reason, attention has been primarily paid to analogues of edta and nta. The complexing properties of aminoalkylphosphonic and aminopolycarboxylic acids have been summarized and compared by *Szczepaniak* and *Siepak* [1] and *Redmore* [2]. In agreement with *Kabachnik et al.* [3], the authors have demonstrated that the complex stability increases with decreasing radius and increasing charge of the central atom. In contrast to aminopolycarboxylic acids, aminoalkylphosphonic acids form stable protonated complexes at pH as high as 3–6 [4]. The exceptional stability of protonated and unprotonated complexes of beryllium [5] and the stability of the complexes with lanthanoides [6] also correspond to this fact. With most studied complexes, coordination only through oxygen atoms is assumed. These conclusions are also confirmed by the recent study of the complexing properties of iminobis(methylenephosphonic) acid [7] ( $H_4ibmp$ ) and partially also of those of ethyliminobis(methylenephosphonic) acid ( $H_4eibmp$ ) with magnesium and calcium [8].

Our study of the complexing properties of  $H_4mibmp$  should contribute to knowledge of the complexation behaviour of lower aminoalkylphosphonic acids. To study these properties, the transition metals  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$  have been selected and complemented with  $Zn^{2+}$  and  $Cd^{2+}$ , and further the series of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$  has been used in view of a possible exceptional position of calcium.

## Experimental

### Chemicals

The  $H_4mibmp$  acid was prepared by the Mannich synthesis in 20 % HCl, according to *Moedritzer* and *Irani* [9], from phosphorous acid, methylamine, and formaldehyde. The phosphorous acid was prepared by hydrolysis of distilled  $PCl_3$ . The  $H_4mibmp$  was recrystallized twice and dried at 90 °C and a pressure of 2.7 kPa. The melting temperature is 203 °C; the nitrogen content was determined by  $NH_3$  distillation after sample mineralization:  $w(\text{found}) = 6.38\%$  N,  $w(\text{calc.}) = 6.39\%$  N. The stock solutions of the cations were acidified solutions of the perchlorates, prepared by dissolution of the oxides or carbonates (anal. grade) of the metals in a small excess of anal. grade perchloric acid (Merck). The metal content in the solution was determined by edta titrations and the excess of perchloric acid was found pH-metrically, using a DTS 833 titrator with a program given by the manufacturer.

### Instrumentation

The  $^1H$  NMR spectra were obtained on a Tesla BS 487 A instrument at a frequency of 80 Hz and using *tert*-butanol as the internal standard. The values obtained were recalculated to TMS using  $\delta(\textit{tert}\text{-butanol}) = 1.234$  ppm. Deuterium oxide was the sol-

vent. The potentiometric measurements were performed with a DTS 833 digital titration system (Radiometer, Copenhagen) with a GK 2401 B combined electrode from the same manufacturer. The measurements were carried out in a 150 cm<sup>3</sup> glass vessel, maintained at (25.0 ± 0.1) °C with an MLW U2C thermostat, at an ionic strength of  $I(\text{NaClO}_4) = 0.1 \text{ mol dm}^{-3}$ . An inert atmosphere was secured by continuous feeding with argon saturated with the solvent vapours. Prior to each series of measurements, the pH-meter was calibrated using borax and oxalate buffers [10]. The calibration was checked with the buffer obtained from the manufacturer; the deviation of the pH from the tabulated value was always smaller than 0.005 pH units. The calibration was always carried out so that the pH-meter directly yielded the  $-\log\{[\text{H}^+]\}$  values [11]. The following optimal instrumental parameters were found experimentally: titration program, MODE = 0.2 and the addition rate, SPEED = 15. Thus 30–40 points were obtained on each titration curve. The titrant was added sufficiently slowly, to attain equilibrium at each point. In the measurement of the stability constants for the alkaline earth metals, the titration program was adjusted to 1.2, which permitted the obtaining of the same number of points within the range of pH = 9–11. The initial solution volume was 50 cm<sup>3</sup> and the H<sub>4</sub>mibmp concentration equalled  $5 \times 10^{-4} \text{ mol dm}^{-3}$ . The metal ions concentrations were selected so that the cation-to-acid ratios were 2 : 1, 1 : 1, 2 : 3, and 1 : 2. The solutions were titrated with 0.1 M-NaOH within the range of pH = 2.7–11.5. The reversibility of the processes was verified by back-titration with 0.1 M-HClO<sub>4</sub>.

### Data handling

The  $\bar{n}$  and  $-\log\{[L]\}$  values were calculated from the experimental data ( $L$  = free ligand concentration) and plotted. The stability constants estimates obtained from the ligand were fed to the MINIQUAD statistical program [12]. The stability constants of the unprotonated complexes were refined first and then used as fixed values for the refinement of the stability constants of the protonated complexes. Finally, all the constants were refined simultaneously.

### Results and discussion

The H<sub>4</sub>mibmp acid was prepared by the Mannich synthesis according to *Moedritzer* and *Irani* [9]. The authors isolated the substance from the reaction mixture by precipitation with ethanol. However, when using this procedure, we obtained a substance with a lower temperature of melting (196 °C) than that given in the literature (210–212 °C). The product was, therefore, recrystallized twice and dried *in vacuo*, with an increase in the temperature of melting to 203 °C. The preparation purity was further checked using the <sup>1</sup>H NMR spectrum in D<sub>2</sub>O. No band, even with a very low intensity, indicating the presence of impurities, was found in addition to the doublet corresponding to the  $-\text{CH}_2-$  groups ( $\delta = 3.58 \text{ ppm}$ ,  $J_2(\text{H}, \text{P}) = 12.8 \text{ Hz}$ ) and the singlet correspond-

ing to the  $-\text{CH}_3$  group ( $\delta = 3.17$  ppm). The ratio of the areas under the doublet and singlet peaks, 4 : 3, corresponds to four protons in the two  $-\text{CH}_2-$  groups and three protons in the  $-\text{CH}_3$  group.

It has been found during the refinement of the acid protonation constants using the MINQUAD program [12] that the  $\log\{\beta_1\}$  value is relatively high and strongly depends on the ionic product of water ( $\text{p}K_{\text{W}}$ ), as demonstrated by the values  $\log\{\beta_1\} = 11.01$  for  $\text{p}K_{\text{W}} = 14.00$  and  $\log\{\beta_1\} = 12.55$  for  $\text{p}K_{\text{W}} = 13.79$ . For the experimental conditions,  $25^\circ\text{C}$  and  $I(\text{NaClO}_4) = 0.1 \text{ mol dm}^{-3}$ , the literature  $\text{p}K_{\text{W}}$  values vary from 13.77 to 13.81 [13–17]. The value found from our results and refined by the above program is  $\text{p}K_{\text{W}} = 13.82$ ; it is very close to the literature values and has been used in the calculation of the protonation and stability constants. The  $\log\{\beta\}$  values calculated for  $\text{p}K_{\text{W}} = 13.82$  are given in Table 1 ( $\text{p}K_1 < 2$ ;  $\text{p}K_2 = 5.00$ ;  $\text{p}K_3 = 6.22$ ;  $\text{p}K_4 = 11.94$ ). When comparing our values for  $\text{H}_4\text{mibmp}$  with the literature values for  $\text{H}_4\text{ibmp}$  and  $\text{H}_4\text{eibmp}$ , an increase can be seen in  $\text{p}K_4$  ( $\log\{\beta_1\}$ ) from  $\text{H}_4\text{ibmp}$  (10.79) through  $\text{H}_4\text{mibmp}$  (11.94) to  $\text{H}_4\text{eibmp}$  (12.42). In view of the fact that all the aminoalkylphosphonic acids studied so far exist as zwitterions both in the solid state and in solution and the proton bound to the N-atom exhibits the highest  $\text{p}K$  value, this trend

Table 1

Protonation constants of  $\text{H}_4\text{mibmp}$  and the stability constants of its complexes at  $25^\circ\text{C}$  and  $I(\text{NaClO}_4) = 0.1 \text{ mol dm}^{-3}$   
 $\beta_{pqr} = [\text{M}_p\text{H}_q\text{L}_r]/[\text{M}]^p[\text{H}]^q[\text{L}]^r$

Cation	<i>p</i>	<i>q</i>	<i>r</i>	$\log\{\beta\}$ ( $\sigma$ )	Cation	<i>p</i>	<i>q</i>	<i>r</i>	$\log\{\beta\}$ ( $\sigma$ )
$\text{H}^+$	0	1	1	11.93(2)	$\text{Ni}^{2+}$	1	1	1	15.63(12)
	0	2	1	18.16(4)		1	2	2	30.58(25)
	0	3	1	23.16(4)	$\text{Cu}^{2+}$	1	0	1	13.91(5)
	0	4	1	—		1	1	1	18.77(3)
				1		2	2	35.78(12)	
$\text{Mg}^{2+}$	1	0	1	5.00(4)	$\text{Zn}^{2+}$	1	0	1	8.90(9)
$\text{Ca}^{2+}$	1	0	1	4.52(2)		1	0	2	14.62(13)
$\text{Sr}^{2+}$	1	0	1	4.23(3)		1	1	1	15.46(13)
$\text{Ba}^{2+}$	1	0	1	4.21(2)		1	2	2	31.44(14)
$\text{Co}^{2+}$	1	0	1	9.47(7)	$\text{Cd}^{2+}$	1	0	1	10.15(7)
	1	0	2	13.96(10)		1	0	2	16.75(5)
	1	1	1	15.94(8)		1	1	1	14.51(12)
	1	2	2	30.71(23)		1	2	2	31.53(2)
$\text{Ni}^{2+}$	1	0	1	9.40(7)					
	1	0	2	13.23(12)					

can be explained by increasing positive induction effect of the substituent which somewhat increases basicity of the nitrogen atom. The values of the other protonation constants are very close for all the three acids.

In the study of the complexing properties of  $H_4mibmp$ , the existence of the protonated complexes  $[MHmibmp]^-$  and  $[M(Hmibmp)_2]^{4-}$  has been demonstrated for cobalt, nickel, zinc, and cadmium, in addition to the expected species  $[Mmibmp]^{2-}$  and  $[Mmibmp_2]^{6-}$ . The  $\log\{\beta\}$  values found are given in Table 1.

The distribution diagrams for these systems are similar and that for the cobalt— $H_4mibmp$  system at a concentration ratio of 1 : 2 is given in Fig. 1. The  $[Mmibmp]^{2-}$  species are present at a relatively high content and begin to appear at  $pH \sim 5$ . The  $[Mmibmp_2]^{6-}$  species begin to appear only at  $pH \sim 8$ . The content of the protonated complexes is somewhat lower.

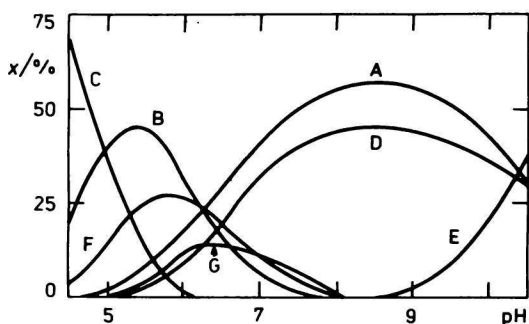


Fig. 1. Distribution curves for species A =  $[Hmibmp]^{3-}$ , B =  $[H_2mibmp]^{2-}$ , C =  $[H_3mibmp]^-$ , D =  $[Mmibmp]^{2-}$ , E =  $[Mmibmp_2]^{6-}$ , F =  $[MHmibmp]^-$ , G =  $[M(Hmibmp)_2]^{4-}$  in a solution with the Co-to- $H_4mibmp$  concentration ratio 1 : 2.

The differences in the  $\log\{\beta_{111}\}$  and  $\log\{\beta_{101}\}$  constants yield the complex protonation constant  $pK_{111}$ , where

$$K_{111} = \frac{[[Mmibmp]^{2-}][H^+]}{[[MHmibmp]^-]} \quad (1)$$

On the basis of the  $pK_{111}$  values, the complexes can be classified into two groups. The first group, in which  $pK_{111}$  lies in an interval from 6.23 to 7.06, contains the complexes of  $Co^{2+}$  (6.47),  $Ni^{2+}$  (6.23), and  $Zn^{2+}$  (7.06). In the other group ( $pK_{111} = 4.36$ —4.86) belong those of  $Cd^{2+}$  (4.36) and  $Cu^{2+}$  (4.86). This classification is in agreement with the work of *Motekaitis* and *Martell* [7] who consider  $pK_{111} = 6$  to be the borderline between the two groups. It is probable that in the first group a proton is bound to the nitrogen atom and coordination occurs only through the oxygen atoms. In the other group it can be assumed that a proton

is bound to the oxygen atom in the phosphonic group, which enables coordination of the nitrogen atoms to the central ion. This coordination type is also suggested by the  $\log\{\beta_{110}\}$  values that are higher compared with the first group of complexes (Table 1).

The system containing copper somewhat differs from the above systems, as the stability constant for the  $[\text{Cumibmp}]^{2-}$  species is exceptionally high. This has also been observed for other aminoalkylphosphonic acids [18–20]. This phenomenon can be explained by the coordination of the nitrogen atom and the formation of stable four-membered cycles due to bidentate coordination of the  $-\text{PO}_3^{2-}$  group.

A precipitate was formed when the titration was attempted in the systems with a 1:2 Cu-to- $\text{H}_4\text{mibmp}$  concentration ratio. The existence of the  $[\text{Cumibmp}_2]^{6-}$  species could not be confirmed during the treatment of the data from the titrations in the Cu- $\text{H}_4\text{mibmp}$  systems with the 1:1 and 2:3 ratios of concentrations.

It has been found already in the calculation of the  $\bar{n}$  values for the alkaline earth metal complexes that the values are not real at pH from 2.7 to 9.0 ( $\bar{n} < 0$ ). Therefore, all the other titrations were carried out only at pH from 9 to 11.5, where only the existence of the  $[\text{Mmibmp}]^{2-}$  species could be demonstrated. If the alkaline earth metal complexes with the M-to- $\text{H}_4\text{mibmp}$  concentration ratio 1:2 exist at all, then they are only formed at very high pH values and are weak. The  $\log\{\beta_{101}\}$  values found for the  $[\text{Mmibmp}]^{2-}$  species are listed in Table 1.

The values found for the stability constants correspond to the previous results of the study of aminoalkylphosphonic acids, *i.e.* the acids form more stable complexes than the analogous aminopolycarboxylic acids and the protonated complexes are formed even in the acidic region.

If the values found here for the stability constants of the complexes with  $\text{H}_4\text{mibmp}$  are compared with the analogous values for  $\text{H}_4\text{ibmp}$ , it is clear that the values for the complexes with  $\text{H}_4\text{mibmp}$  are on average greater by a unity. This fact is probably connected with a higher induction effect of the substituent on the nitrogen atom and the resultant higher basicity of this atom, as mentioned above. This is also supported by the fact that the unprotonated complexes  $[\text{Mmibmp}]^{2-}$  and  $[\text{Mmibmp}_2]^{6-}$  are formed at a pH more than one unit greater than that for the formation of the analogous complexes  $[\text{Mibmp}]^{2-}$  and  $[\text{Mibmp}_2]^{6-}$ .

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