# NMR, potentiometric and ESI-MS combined studies on the zinc(II) magnesium(II) and calcium(II) complexation by (morpholin-1-yl)methane-1,1-diphosphonic acid and its thio-analog.

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Streszczenie

The crystal structures of the two derivatives of aminomethane-1,1-diphosphonic acid with morpholinyl- (**1**) and thiomorpholinyl- (**2**) side chains were determined by single crystal X-ray diffraction and discussed with respect to molecular geometry and solid state organization. The protonation equilibria, solution behavior and complex-formation equilibria in solutions of **1** and **2** with the Zn(II), Mg(II) and Ca(II) ions were studied by means of NMR, pH-potentiometry and ESI-MS methods.

As the pK(NH)protonation constants of**1** and **2** are high (11.65 and 11.91, respectively) two different approaches were used to evaluate the pH-potentiometric data. The first approach disregarded the proton-dissociation from the $NH^+$ group. In the second one, all the p$K_a$ values were considered in the M(II):ligand formation equilibria. For **1**, the accuracy of the determination was shown to be sufficient to calculate reliable stability constants of metal complexes with the use of both approaches. For **2**, only approach neglecting the

protonation constant was shown to be correct.

The studied acids form dinuclear, $[M_2L_3H_x]$, $[M_2L_2H_x]$ and mononuclear $MLH_x$ and $ML_2H_x$ complexes with different degree of ligand protonation. Tendency to undergo some oligomerization with the increase in the metal and ligand concentration was demonstrated for the [CaLH] complex of **1** and **2**. As far as **1** and **2** remain protonated, the Zn(II), Mg(II) and Ca(II) ions are coordinated exclusively through oxygen atoms of the phosphonate groups. The metal promoted proton dissociation from the $NH^+$ ring atom takes place in alkaline pH.

Słowa kluczowe

Bisphosphonates, X-ray structures, Complex-formation equilibria, NMR, potentiometry, ESI-MS

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