

## PhD thesis summary

### *Synthesis and properties of the coordination compounds based on the new bisphosphonates*

Recent years have shown the increase of demand for functional materials with a wide application potential, which requires engagement and cooperation of numerous branches of chemistry. This leads to the increased importance of the coordination chemistry which offers compounds based on stable metal-ligand bonds of diverse physicochemical properties. In this group of compounds, coordination polymers are of special interest due to their unusual structural and functional diversity, as a result of which they can successfully be used as gas storage and separators, sorbents, probes, drug carriers, as well as materials showing catalytic, antineoplastic, magnetic, and luminescent properties.

The term coordination polymers is used to name compounds combining metal ions or their clusters and organic ligands which, together, create a system of coordination bonds propagated in one, two or three dimensions. Individual characteristics of these components determine the way they are bound, and the properties of the end product are strictly related to its structure in a solid state. However, the possibilities of planning and controlling the coordination polymer structure to the point of obtaining a material of desired characteristics are significantly limited due to numerous factors including, for example, geometric preferences and the charge of the metal centre, as well as the method and conditions of a synthesis process (pH, metal:ligand molar ratio, temperature, reaction time). It is especially important to select a proper ligand, in which its capability to create coordination compounds is related to its structure and stereochemical requirements, as well as to the availability, number, and orientation of potential donor atoms in the molecule. That is why, polydentate bisphosphonic acids with a general formula of  $(R)H_2C_\alpha-C(PO_3H_2)_2(OH)$  have attracted an interest of chemists in recent years. What is more, a tetrahedral geometry of their phosphonic groups creates perfect conditions for the formation of coordination bonds in every dimension.

Taking into account the above considerations, the subject of this thesis is the study new bisphosphonic acids with regard to their predispositions to form coordination bonds with selected *d*-block metal ions. For this purpose, four compounds have been synthesized which are analogues of the zoledronic acid ( $H_4zoOH$ ), and in which the  $C_\alpha$  carbon atom is additionally functionalized with two methyl groups ( $H_4dmtzolOH$ ) or included in the aliphatic cyclopropane ( $H_4cppzolOH$ ), cyclobutane ( $H_4cbtzolOH$ ) or cyclopentane ( $H_4cptzolOH$ ) ring. What is more, each of them have been obtained in the single-crystal form and characterized

using single-crystal X-ray diffraction, which allowed to analyse their structure, conformational preferences and crystal network organization. It is shown that H<sub>4</sub>dmtzolOH crystallizes in the anhydrous form (**L1**), while the other bisphosphonic acids crystallize as hydrates: H<sub>4</sub>cppzolOH·H<sub>2</sub>O (**L2**), H<sub>4</sub>cbtzolOH·H<sub>2</sub>O (**L3**) and H<sub>4</sub>cptzolOH·4H<sub>2</sub>O (**L4**).

The main assumption of conducted studies was to check how the size and chemical nature of the steric hindrance located on the C<sub>α</sub> carbon atom determines the tendency of **L1-L4** ligands to form coordination compounds, including coordination polymers, with selected *d*-block metal ions. As a result, for every ligand, the study included planning, carrying out and, eventually, optimizing the synthesis of coordination compounds with Cu(II), Ni(II), and Co(II) ions in strictly specified conditions (pH, temperature, duration of the reaction, stoichiometric ratio of M(II):L) of the hydrothermal reaction. This way, sixteen compounds (**K1-K16**) in the single-crystal form were obtained and characterized by single-crystal X-ray diffraction which enabled a detailed analysis of their structure and intermolecular interactions in crystal network. Three compounds [Cu(H<sub>3</sub>dmtzolOH)<sub>2</sub>(H<sub>2</sub>O)]·8H<sub>2</sub>O (**K1**), [Cu(H<sub>3</sub>cbtzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**K2**) and [Cu(H<sub>3</sub>cptzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (**K3**) are isolated as mononuclear coordination units, and the other ten have a polymeric structure, of which eight compounds are 1D coordination polymers with formula: [Co(H<sub>2</sub>cppzolOH)(H<sub>2</sub>O)]·H<sub>2</sub>O (**K4**), [Ni(H<sub>2</sub>cppzolOH)(H<sub>2</sub>O)]·H<sub>2</sub>O (**K5**), [Co(H<sub>2</sub>cbtzolOH)(H<sub>2</sub>O)]·H<sub>2</sub>O (**K6**), [Ni<sub>3</sub>(HdmtzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]·6H<sub>2</sub>O (**K7**), [Co<sub>3</sub>(HdmtzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]·6H<sub>2</sub>O (**K8**), [Co<sub>3</sub>(HcppzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]·6H<sub>2</sub>O (**K9**), [Co<sub>3</sub>(HcbtzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]·6H<sub>2</sub>O (**K10**) and [Co<sub>3</sub>(HcptzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O (**K11**), and two extend in the second dimension [Co<sub>3</sub>(HdmtzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(4,4'-bpy)]·0.2NaOH·9.8H<sub>2</sub>O (**K12**) and [Co<sub>3</sub>(HcbtzolOH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(4,4'-bpy)]·10H<sub>2</sub>O (**K13**). The last group are tetranuclear clusters (H<sub>3</sub>O)[Ni<sub>4</sub>(HcbtzolOH)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]·13.8H<sub>2</sub>O (**K14**), (H<sub>3</sub>O)[Ni<sub>4</sub>(HcptzolOH)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]·16.8H<sub>2</sub>O (**K15**) and (H<sub>3</sub>O)[Co<sub>4</sub>(HcptzolOH)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]·10.5H<sub>2</sub>O (**K16**).

The explanation of how the additional group attached to the C<sub>α</sub> carbon atom affects ligands' tendency to form coordination compounds of a specific structure was based on the analysis of their conformation preferences in a solid state, conducted based on quantum-chemical calculations and conformer energy profiles prepared based on those calculations. The characteristics of obtained materials was supplemented with infrared spectroscopic (FT-IR) and thermal stability (TG-DTA, DSC) studies.