

Abstract of the doctoral dissertation
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entitled *Coordination polymers based on phosphonic acids*
– *design, synthesis and structural characterization*

Nowadays, the field of coordination polymers is one of the most popular areas of crystal engineering. Coordination polymers have attracted great attention not only for their impressive structural diversity, but also for their potential applications in molecular adsorption, chemical separation, ion exchange and heterogeneous catalysis.

The aim of the thesis was to design and synthesize novel coordination polymers based on phosphonic acids, and to characterize them with respect to their structural, spectroscopic and thermal properties.

Coordination polymers are constructed from two fundamental components, namely metal ions or clusters and organic ligands. Such metal-ligand compounds can extend into one, two or three dimensions. However, the ability to predict and control the structural dimensionality of coordination polymers is seriously limited by many structure-directing factors, such as the preferable coordination geometry of the metal ion, the nature of the counter anion, the chemical structure of the ligand, the metal-to-ligand ratio, solvent system, temperature, pH value, and so on. Among these factors, the judicious selection of a well-designed organic linker appears to play a crucial role in the construction of coordination polymers with desired structures. From the crystal engineering point of view, ligand should fulfill some requirements. It should be (i) multidentate, (ii) structurally and geometrically predisposed to extend the metal ions in different directions in order to form a multidimensional coordination network, (iii) relatively rigid to allow for a certain control of steric consequences in the assembly process. Taking into account the above-mentioned considerations the following phosphonic acids have been synthesized: 4-nitrobenzylphosphonic acid (**H₂L1**), 4-carboxybenzylphosphonic acid (**H₃L2**), 1,2-bis(dihydroxyphosphorylmethyl)benzene (**H₄L3**), 1,2,4,5-tetrakis(dihydroxyphosphorylmethyl)benzene (**H₈L4**), 4-carboxyphenylphosphonic acid (**H₃L5**), 3-pyridylphosphonic acid (**H₂L6**), 5-carboxypyridin-3-ylphosphonic acid (**H₃L7**) and 3,5-pyridinediylldiphosphonic acid (**H₄L8**). The key step in the synthesis of these compounds was the formation of the C–P bond by using Arbuzov reaction or catalytic phosphorylation. The molecular structures of all phosphonic acids have been confirmed by ¹H NMR and ³¹P{¹H} NMR spectroscopy. In

addition, acids denoted as **H₂L1**, **H₃L2**, **H₄L3** and **H₈L4** have been prepared in the form of single crystals. The obtained crystals have been characterized using single-crystal X-ray diffraction, infrared and Raman spectroscopy, and their solid state organizations have been studied.

Five phosphonic acids, namely **H₃L2**, **H₃L5**, **H₂L6**, **H₃L7** and **H₄L8** have been used as organic ligands to form new coordination polymers. Twelve coordination compounds, namely [Co(H₂L2)₂(H₂O)₄] (7), [Co(C₁₀H₈N₂)(H₂O)₄]_n · 2H₂L2 · 0.188(O) (8), [Co(H₂O)₆][H(H₂L5)₂]₂ · 2H₂O (9), [Mn(L6)(H₂O)₅] (10), [Co(L6)(H₂O)₅] (11), [ZnCl(HL6)]_n (12), [Co₂(L7)(H₂L7)(H₂O)₃]_n (13), [Ca(H₃L8)₂(H₂O)]_n (14), [Co(H₂O)₆][Co(L8)(H₂O)₅] · 5(O) (15), [Co(H₃L8)₂(H₂O)₂]_n (16), [Zn(H₃L8)₂(H₂O)₂]_n (17) and [Cd(H₃L8)₂(H₂O)₂]_n (18) have been synthesized by slow evaporation of the solvent or hydrothermal method. The obtained compounds have been characterized by powder and single-crystal X-ray diffraction, infrared and Raman spectroscopy, and thermal analysis (TG-DTA-MS). Afterwards, a detailed topological analysis of polymeric coordination networks has been performed with respect to the intermolecular interactions responsible for self-organization of molecules in the solid state. Compounds 7, 9, 10, 11 and 15 are discrete coordination units, which are extended into three-dimensional supramolecular networks by multiple O–H···O hydrogen bonds. It is worth noting that compound 15 crystallizes as a non-centrosymmetric and chiral structure in one of the Sohncke space groups (*P*2₁2₁2₁). This means that coordination units of compound 15 organize themselves into the three-dimensional supramolecular network using only symmetry operation of the first kind. Compounds 8 and 12 are one-dimensional coordination polymers. Compound 8 adopts a ladder structure. The adjacent ladders are held together *via* N–H···O hydrogen bonds and offset face-to-face interactions. As regards compound 12, the cobalt(II) ions are propagated by 4,4'-bipyridine molecules to form positively charged coordination chains. The acid anions serve both to balance the charge of chains and to combine them *via* O–H···O hydrogen bonds. Compounds 13, 16, 17 and 18 exhibit layered structures. As regards compound 13, the adjacent layers are connected *via* strong O–H···O hydrogen bonds. On the other hand, in case of compounds 16–18, the neighbouring layers are linked together through N–H···O and O–H···O hydrogen bonds, and offset face-to-face interactions. In compound 14, one- and two-dimensional sublattices interweave at the calcium(II) ions to form a three-dimensional framework.