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Report on the doctoral thesis

*“Coordination polymers based on phosphonic acids –
design, synthesis and structural characterization*

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Coordination polymers (CPs) are compounds composed of metal ions or clusters that are connected in one, two or three dimensions by ligands. Especially crystalline CPs have been in the focus of many investigation since the systematic variation of metal ions and linker molecules open up the possibility to change the structure and properties of these compounds. Most impressive results have been reported for a subclass of CPs the metal-organic frameworks (MOFs), which are CPs with potential porosity. The connection of well-defined inorganic building units (IBUs, often also called secondary building units) by rigid organic molecules, like aryl dicarboxylates, leads to three dimensional frameworks. The pore size as well as the pore surface chemistry can be tuned by using organic linker molecules of different sizes and functionalized linker molecules. The “predictability” of the final structures is mainly due to the fact that the carboxylate groups are restricted in their coordination modes. Hence the chemistry of metal carboxylate CPs is very well developed.

Organic linker molecules containing other functional groups such as $-\text{Ge}(\text{OH})_3$, $-\text{PO}_3\text{H}_2$ or $-\text{SO}_3\text{H}$ have been less frequently employed in the synthesis of CPs. This is due to the fact that the larger number of coordinating O-atoms at each functional group leads to a larger structural variability. Hence, different predictable IBUs are only rarely observed and thus the tuning of CP structures is not possible. Nevertheless the use of linker molecules containing $-\text{PO}_3\text{H}_2$ groups is of special interest in the synthesis of CPs since there exists a large number of synthetic routes to obtain (poly)phosphonic acids. In addition, metal phosphonates are often chemically and thermally more stable compared to metal carboxylates, which is due to the higher charge of the fully deprotonated group ($-\text{PO}_3^{2-}$ vs $-\text{COO}^-$) as well as the larger number of coordinating O-atoms.

The dissertation of Ms Wilk-Kozubek deals with the topic of metal phosphonate CPs. The synthesis of phosphonic acids containing different numbers of $-\text{PO}_3\text{H}_2$ groups or additional functional groups such as $-\text{COOH}$, NO_2 or pyridyl units, and their detailed characterization as well as their use in the synthesis of new metal phosphate coordination polymers is reported. All compounds were characterized in great detail mainly using spectroscopic as well as X-ray diffraction methods and the crystal structures were topologically analyzed.

In the introduction (Chapter 1) the topic of the dissertation is very well introduced. The definitions are summarized and the most important synthesis methods of phosphonic acids and metal phosphonates are presented.

After the objectives of the work are shortly summarized in Chapter 2, the syntheses of the compounds and their characterization is covered in Chapter 3. The phosphonic acids (4-nitrophenyl)methylphosphonic acid (**H₂L1**), (4-phosphonomethyl)benzoic acid (**H₃L2**) as well as the pseudopolymorphs $\text{H}_2\text{L}\cdot 0.5\text{C}_4\text{H}_8\text{O}_2$, $2\text{H}_2\text{L}\cdot \text{C}_2\text{H}_5\text{OH}$ and $\text{H}_2\text{L}\cdot \text{H}_2\text{O}$, 1,2-phenylenbis(methylphosphonic acid) **H₄L3**, 1,2,4,5-benzenetetrayltetrakis(methylphosphonic) acid (**H₈L4**), 3-pyridinylphosphonic acid (**H₂L6**), 5-phosphono-3-pyridinecarboxylic acid (**H₃L7**) and 3,5-pyridinediylbisphosphonic acid (**H₄L8**) were obtained and characterized by ^1H -, $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy to confirm phase purity. Room temperature crystal growth experiments resulted in crystals that were suitable for structure determination by single-crystal X-ray diffraction.

The phosphonic acids were employed in the synthesis of CPs using Co-, Zn-, Cd- and Ca-salts. Room temperature synthesis (slow evaporation of the solvent) as well as solvothermal reactions employing autoclaves were carried out to obtain single crystals. These investigations led to the compounds $[\text{Co}(\text{H}_2\text{L2})_2(\text{H}_2\text{O})_4]$, $[\text{Co}(4,4'\text{-bpy})(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{L2}\cdot 0.188(\text{O})$, $[\text{Co}(\text{H}_2\text{O})_6][\text{H}(\text{H}_2\text{L5})_2]_2\cdot 2\text{H}_2\text{O}$, $[\text{M}(\text{L6})(\text{H}_2\text{O})_5]$ (with $\text{M} = \text{Mn}$, Co), $[\text{ZnCl}(\text{HL6})]_n$, $[\text{Co}_2(\text{L7})(\text{H}_2\text{L7})(\text{H}_2\text{O})_3]_n$, $[\text{Ca}(\text{H}_3\text{L8})_2(\text{H}_2\text{O})]_n$, $[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{L8})(\text{H}_2\text{O})_5]\cdot 5(\text{O})$ and $[\text{M}(\text{H}_3\text{L8})_2(\text{H}_2\text{O})_2]_n$ (with $\text{M} = \text{Co}$, Zn , Cd). Sometimes only minute amounts of the compounds were obtained and further characterization could not be carried out for these compounds. In the other cases they were analyzed regarding the elemental composition, and the simulated PXRD patterns were compared to the experimental ones. In addition, the thermal stabilities were determined by thermogravimetric measurements and the IR/Raman spectra were recorded and interpreted.

The results of the structure determinations and the results of the characterization measurements of the phosphonic acids and the metal phosphonates are presented in Chapter 4. This chapter starts off with a summary of coordination modes that have been observed in metal phosphonates and a list of compounds (CSD reference codes) that have been obtained in previous studies when the phosphonic acid derivatives of this thesis were employed. Subsequently the results of the structure determinations are presented in great detail taking into account coordination environments, hydrogen bonding and P=O π interactions. The intermolecular interactions of the phosphonic acid molecules in the crystal structures were determined by Hirshfeld surface analysis.

Due to the large number of crystal structures certain conclusions were drawn, which confirm trends observed in previous studies. Thus, in most of the compounds the metal ions are octahedrally surrounded, the exception being Zn^{2+} , which has a tetrahedral coordination environment in $[ZnCl(HL6)]_n$. Different coordination modes were observed for the phosphonate groups and the carboxyl and carboxylate groups were involved in hydrogen-bonding interactions. In contrast to Ca^{2+} which was only surrounded by O-atoms, in the compounds containing Mn^{2+} , Co^{2+} and Zn^{2+} ions coordination of the N-atoms was also observed. Counter ions and solvent molecules either complete the coordination sphere of the metal ions or occupy space in the structure and both are involved in hydrogen bonding.

The thesis of Ms Wilk-Kozubek is very well written. It is a very systematic work that involves synthesis and characterization at a high scientific level. The data is of high quality and presented accordingly. The results have been summarized in seven publications in different pre-reviewed international journals. In addition, they have been presented at various conferences mainly as poster presentations, but also as oral presentations. Nevertheless there are also some parts that could be further improved. Thus additional measurements for example, temperature dependent PXRD investigations or the determination of proton conductivity would have been very interesting. Discussion and comparison to literature data could also be improved in order to set the newly obtained results in a better context. Taking all these points into account the thesis definitely fulfills the requirements for receiving a PhD in Chemistry. It was a pleasure reading the thesis and learning more about metal phosphonates.



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