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Summary

The design and synthesis of metal–organic coordination polymers (CP) from versatile organic bridging ligands and metal ions is a rapidly expanding area of research. This is not only because of the immense structural diversity of the coordination polymers, but also because they are promising candidates for many significant applications including molecular absorption, chemical separation, heterogeneous catalysis or ion exchange. The crystal engineering of coordination polymers has remained under intensive research investigation for almost three decades, which was described in detail in Chapter 1.

The structural novelty of CP and their potential application as functional materials serve as an inspiration for undertaking the endeavor to study CPs. The presented dissertation is focused on the design and synthesis of new coordination polymers based on sulfonic and sulfocarboxylic acids and includes the results of my original research of those compounds. The accomplished researches include also a study of the coordination preferences and an extensive topological analysis of the obtained networks as well as a characterization of physicochemical properties, including spectroscopic and thermal properties.

The basic components of coordination compounds are metal ions or metal clusters and organic ligands. Such metal-ligand compounds can extend into one, two or three-dimensional networks. However, it still remains a great challenge to rationally design and construct desired coordination compounds fully controlling all factors that affect their structures. The formation of the coordination polymer is influenced by a variety of chemical and physical factors, the most important of which are: the chemical affinity and geometric preferences of the metal ion, the chemical and topological predispositions of the organic ligand, the metal-to-ligand ratio, the presence of (an) auxiliary ligand(s), the applied solvent and the reaction conditions (pH, temperature, pressure), etc.

Among the whole realm of possible organic linkers, the aromatic polycarboxylates appear to be the most widely applied and studied ligands, and a variety of interesting networks have been obtained with them. Based on a careful analysis of aromatic polycarboxylates we decided to use a new class of ligands, namely sulfonic and sulfocarboxylic acids. Reports on metal carboxylate–sulfonates were still rare at the time when the project started. The sulfonic and sulfocarboxylic acids satisfy the most important conditions for formation of coordination polymer: the ligand should be relatively rigid and multidentate, i.e. chemically and geometrically predisposed to extend the structure in different

directions (in order to form a multidimensional coordination network). In chapters 3 and 4 are described four sulfonic and sulfo-carboxylic acids selected (by us) to act as ligands. An extensive search is made with the use of Cambridge Structural Data Base to retrieve all structures in which the chosen ligands were applied. An attempt to classify the networks of all reported sulfonato-carboxylato compounds is also undertaken in chapter 4.

Chapters 5-9 are dedicated to the description of 18 original coordination compounds that were synthesized by slow evaporation technique or hydrothermal method.

(1) $[Cd_4(L1)_4(1,4-HDAB)_4](H_2O)_6$, (2) $[Cu_2(\mu_2-OH_2)_2(HL1)_2(H_2O)_6]$,[270]

(3) $[[Co_2(L1)(\mu_3-OH)(DMF)_3(H_2O)_2](H_2O)_2(DMF)]_n$, (4) $[Cd(L1)(H_2O)_2(HPDPA)]_n$,

(5) $[Cd(L1)(H_2O)_2(HBPA)]_n$, (6) $[[Zn(L1)(H_2O)_2(HPDPA)](H_2O)]_n$,

(7) $[Zn(L1)(H_2O)_2(HBPA)]_n$, (8) $[[Zn(4,4'-BPY)(H_2O)_4](HL3)(H_2O)_2]_n$,

(9) $[[Cd(4,4'-BPY)(H_2O)_2](L4)_{1/2}]_n$, (10) $[[Zn(4,4'-BPY)(H_2O)_2](L4)_{1/2}]_n$,

(11) $[NaCd(L1)(DMF)_2(H_2O)_2]_n$,[271]

(12) $[[NaCd_2(L1)_2(DMF)_2(H_2O)_2], HDETA,2H_2O]_n$,[271]

(13) $[[Cd_2(L1)(2,2'-BPY)_2(HCOO)(H_2O)]DMF]_n$ (14) $[[Cu_2(HL3)_2(PHE)_2]H_2O]_n$,

(15) $[Cd(HL3)(4,4'-BPY)(DMF)](H_2O)_2]_n$, (16) $[K_2Cd(L4)_4(H_2O)_6]_n$,[271]

(17) $[Na_2(HL1)]_n$,(18) $[Na(H_2L1)(DMF)]_n$.

The obtained compounds were characterized by single-crystal X-ray diffraction, infrared and Raman spectroscopy, and thermal analysis. For selected compounds magnetic and photoluminescent measurements were also made. Afterwards, a detailed topological analysis of the coordination and supramolecular network was performed. The analysis reveals that compounds **(1)** and **(2)** consist of coordination complex, which are further linked by hydrogen bonds to form a supramolecular network. Compounds **(3)** to **(10)** are constructed from 1D coordination structures which are hydrogen bonded into 3D network. Compounds **(11)** to **(15)** display 2D infinite coordination layer structures and **(16)** to **(18)** display 3D infinite coordination networks (Chapter 6).

The obtained research material allowed to carry out an in-depth comparative analysis of the obtained structures (Chapter 7). In Chapter 9 (Summary and conclusions) the coordination preferences of functional groups, the role of metal ions in the obtained structures, the observed coordination modes and the effects of reaction conditions on the coordination preferences of the ligands are highlighted and stressed.