

Abstract

In this dissertation 15 new coordination polymers and one new coordination complex with *para*-aminobenzonitrile (4ABN) are presented. Their structures were determined by X-ray crystallography; furthermore the compounds were investigated by vibrational spectroscopy. The focus of research was on the influence of the anion on the self-assembly process. An additional focal point was the determination of the dominating resonance structure of *para*-aminobenzonitrile.

There are three different topologies of the coordination polymers: $\infty^n\{[\text{Ag}(\text{4ABN})_{4/2}]^+\}$ ($n=1,2$), $\infty^1\{[\text{M}(\text{4ABN})_{4/2}(\text{H}_2\text{O})_{2/1}]^{2+}\}$ ($\text{M}=\text{Cu}^{2+}$, Zn^{2+} , Cd^{2+} and Co^{2+}) and $\infty^2\{[\text{M}(\text{4ABN})_{4/2}\text{X}_{2/1}]\}$ ($\text{X}=\text{NO}_3^-$ and $\text{M}=\text{Cd}^{2+}$ as well as $\text{X}=\text{Cl}^-$ and $\text{M}=\text{Ni}^{2+}$). A comparison of the crystal structures shows a significant influence of the anion on the self-assembly process, as the anion requires empty space. A higher dimensional cross-linking is not practicable. So the presence of anions with larger sizes leads to one dimensional chain structures, while smaller anions support the formation of two dimensional networks. The latter will also be achieved if no coordinating water molecules are present in the structure as this enables an interaction of the anion with the metal. As a result two-dimensional cross-linking is facilitated.

Systematic investigations on the C-N_{amin}- and C-N_{cyano}-bonds show a notable influence of the coordinating mode on C-N-bond length. Both resonance structures known for 4ABN, cyanoaniline and iminoquinone, are in equilibrium. Due to the coordination of the linker to a metal, the equilibrium is shifted. If the linker is terminally bonded (*via* NH₂ group), the equilibrium is moved to the cyanoaniline structure. For a terminal bond *via* the C≡N-group the equilibrium is shifted in the opposite direction to the iminoquinone structure. The bridging coordination mode is also observed: here an equilibrium point in-between is found. For free 4ABN the iminoquinone structure clearly dominates. The spectroscopic results are in agreement with these findings.

Additionally the coordination polymers $\infty^1[\text{M}^{\text{II}}(\text{4ABN})_{4/2}(\text{H}_2\text{O})_{2/1}](\text{BF}_4)_2$ with $\text{M}=\text{Cu}(\text{II})$ and $\text{Co}(\text{II})$ were investigated by UV-vis spectroscopy. A high ligand field energy Δ_0 is found. Therefore, *para*-aminobenzonitrile is classified as a strong σ -donor and π -acceptor ligand. The latter is achieved solely through the cyano group.