

"Synthesis and characterisation of transition metal complexes with polyfunctional N,S-chelating ligands"

Dipl. Chem. Andreas J. Heuwing

The objective of this Ph. D. thesis was the synthesis and analysis of complexes with polyfunctional N,S-chelating ligands as specific structural models of active centers of nickel- and copper-containing enzymes, respectively.

For these purposes precursor complexes $[\text{NiX}_2\text{btm}gp]$ were reacted with suitable arenthiolates to give synthones which by further reaction with iron carbonyl complexes gave trinuclear complexes. The latter are important structural models of $[\text{NiFeSe}]$ -hydrogenase centers. A byproduct of in these reactions was the novel trinuclear compound $[\text{Fe}(\text{btm}gp)\text{Fe}_2(\text{CO})_8]$ which exhibits a formerly unknown coordination pattern for Fe_3 complexes.

Furthermore, dinuclear nickel complexes with varying coordination numbers were prepared. The different coordination numbers could be controlled by suitable selection of the starting materials (nickel salts, chelating ligands).

In order to investigate new mixed valence copper complexes, novel multidentate ligand systems of the type $\text{N}_2^R\text{S}_x^{\text{Me}}$ ($x = 1, 2$) were developed. As a result complexes of the type $[\text{Cu}_4(\text{N}_2^R\text{S}_x^{\text{Me}})_y]$ ($y = 2, 4$) were found. Mixed valence copper complexes were formed by reaction of $[\text{Cu}_4(\text{pN}_2^{\text{Me}}\text{S}_2^{\text{Me}})_2]$ with solvents containing halogen radicals (e.g. CHCl_3) or triplet oxygen in the presence of halogen anions. Single crystal x-ray analysis proves the formation of octanuclear copper complexes of the type $[\text{Cu}_3(\text{pN}_2^{\text{Me}}\text{S}_2^{\text{Me}})_3\text{Cu}_5\text{X}_5]$ ($\text{X} = \text{Cl}, \text{Br}$). On application of the chelating ligand $e\text{N}_2^{\text{Me}}\text{S}_2^{\text{Me}}$ the novel decanuclear complex $[\text{Cu}_4(e\text{N}_2^{\text{Me}}\text{S}_2^{\text{Me}})_4\text{Cu}_6\text{I}_6]$ is formed.