„Biomimetic copper complexes with sulphur guanidine ligands“

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In this thesis covering a field of Bioinorganic Chemistry, biological relevant copper complexes with sulphur-containing guanidine ligands were synthesised. These ligands combine thioether- or thiolate S donor functions with basic N_{Imin} functionalities of CN_3 guanidine units.

The synthesis and characterisation of sulphur-containing guanidines is the main focus of the first part of the thesis. Multidentate (NS- resp. N_2S_2-Donorsets) and tripodal (N_3S-Donorsets) thioether-guanidines as well as molecules with redox-active disulfid units (NSSN-Donorset) were synthesised. In the second part of the thesis, the coordination properties of these guanidines towards Cu are investigated. The reaction of thioether-guanidines and copper(I) salts yielded numerous copper(I) thioether-guanidine complexes with novel and uncommon coordination properties. When trityl-thioether- or disulfide-guanidines were used, thiolate-bridged oligomeric complexes including binuclear copper(II), tri- and hexanuclear mixed valent copper(I/II) and trinuclear copper(I) complexes containing 2-(guanidino)benzolthiolate ($Gua_{ph}S^-$) as ligands were obtained. In case of reactions of Cu(I) with disulfide-guanidines, di-, tetra- and octanuclear disulfide complexes are obtained as well. Further investigations based on spectroscopic, electrochemical and magnetochemical techniques were carried out using selected copper complexes. As a result, the physical and chemical properties indicate some structural and/or functional model character for active Cu protein sites like type 1 ('blue') copper and Cu_A.

Among various observations during the synthesis of novel sulphur-copper complexes, a unique reversible 'thiolat-disulfide-thiolate' interchange reaction has been identified and explored. This type of reaction is a rare example in copper-sulphur chemistry and possesses model character for the important reversible disulfid cleavage in biological systems (e.g. reaction of glutathione to glutathione disulfide).

The studies presented here contribute to a better understanding of structure, function and physical properties of sulphur containing metalloproteins.