„Oxygen activation and transfer mediated by copper(I) complexes with polyfunctional bisguanidine ligands”

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In this thesis in the field of Bioinorganic Chemistry, biological relevant copper complexes were synthesised which are capable to activate and transfer molecular oxygen.

As ligand systems, substituted guanidines were used because the N donor functions of these ligands resemble the basic δ imin donor functions of the histidine residues which contribute to copper coordination in almost all copper enzymes.

In order to approach the functionality of tyrosinase and catechol oxidase, a synthetic protocol was developed which allows the unrestricted modification of the spacer as well as of the guanidine unit. By using this modular principle, a library of bisguanidine ligands was built up. This ligand library contains members with total flexibility of the guanidine-connecting spacers as well as of the substitution pattern of the guanidine moieties. Via modification of this spacer, it is possible to change the denticity, the bite angle and the coordination geometry, whereas via modification of the guanidine moities, the σ-donating and π-accepting properties of the N_{imine} atom can directly be influenced. The reaction of the obtained bisguanidines with copper(I) salts yielded copper(I) bisguanidine complexes which were investigated towards their ability to activate molecular oxygen. As result, the observed ability to bind oxygen under formation of Cu_2O_2 adduct complexes was correlated with the degree of conjugation within the guanidine units.

The ligand matrix was screened regarding the oxidation capability of its $Cu(II)/Cu(III)O_2$ complexes. The possibility of controlling the oxidation selectivity of these $Cu(II)/Cu(III)O_2$ species by peripheric modifications is a particularly attractive feature of this ligand design.

The studies presented in the following may contribute to a better understanding of oxygen transport and activation in biological systems. Furthermore, this information can support the directed oxygenation of organic substrates.