

In this thesis a pyrazolate based dicopper(I) complex featuring a constrained substrate binding pocket was reacted with dioxygen to form a dicopper(II) peroxy complex which shows the peroxide anion in an unusual *cis-μ-η¹:η¹* binding mode (^cP). Such O₂-binding is assumed to be relevant during initial stages on the trajectory of O₂ reduction in type III copper active sites.^{1,2} This abnormally bound peroxide was found to interact with alkali metal ions that affect the Cu-O-O-Cu torsion angle of this ^cP species, causing a significant change of the electronic structure of the Cu₂/O₂ core. The peroxide thereby functions as a Lewis base, which interacts with the different Lewis acidic alkali metal ions. This host-guest complex formation was studied in detail by means of UV/vis absorption spectroscopy for which binding constants could be derived, showing that the strength of adduct formation is a function of Lewis acidity of the coordinating alkali metal ion. The influence of redox-inactive metal ions on the electronic structure of metal oxo and peroxy intermediates is receiving great attention because it may play a key role in natural or chemical systems for the modulation of redox potential and reactivity.³ While previously seen in iron(III) peroxy chemistry³, such interaction has been unprecedented in copper peroxy systems. This thesis thus furthermore focused on the electrochemical properties of the dicopper(II) peroxy intermediate and its alkali adducts. Detailed electrochemical studies revealed the reversible formation of a dicopper(II) superoxy complex of which a solid state structure could be determined. Following studies of the corresponding alkali metal adducts showed that this superoxy species can also be generated electrochemically from these species. The redox potential of the corresponding oxidation was thereby observed to increase upon alkali metal binding, whereas the total shift in redox potential is a function of Lewis acidity of the coordinating alkali metal ion. This work thus provides first spectroscopic evidence for modulation of redox potential of a dicopper(II) peroxy core by interaction with redox inert metal ions.

Kinetic studies with the superoxy compound were performed upon which a dicopper(II) hydroperoxy complex is formed *via* H-atom transfer from the substrate TEMPO-H. This hydroperoxy compound can also be directly generated from the dicopper(II) peroxy intermediate by protonation with e.g. 2,6-lutidinium triflate. Detailed UV/vis titration experiments allowed the determination of the pK_a value for the hydroperoxy species for which a Bond Dissociation Free Energy could be calculated.

No matter which of the above discussed Cu₂/O₂ complexes is considered, all are forming the same decomposition product over time, where the two Cu^{II} ions are bridged by a hydroxide and an additional water molecule (denoted as H₃O₂ bridge). Until to date this species has been discarded when formed which is rather unsatisfactory, since the corresponding ligand is generated in a multi-step synthesis under a high consumption of resources. With respect to “green chemistry” the “recycling” of this decomposition product *via* e.g. generating the dicopper(I) complex which again can be selectively reacted into the corresponding dioxygen complexes, was studied. This thesis shows that the decomposition product can be selectively transformed into all above mentioned Cu₂/O₂ complexes. Furthermore the H₃O₂ bridged compound was studied towards electrocatalytic water oxidation. First results show the formation of molecular dioxygen whereas the potential water oxidation catalyst stays intact during catalysis.

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