

Abstract

This dissertation thesis reports the study of several copper complexes and their reactivity in the gas phase. The complexes were analyzed using different methods, namely, electrospray ionization-mass spectrometry (ESI-MS), infrared multiphoton dissociation (IRMPD) spectroscopy and theoretical calculations.

In the first part, the complexes of redox-active ligands (catechol, maltol, and phenanthraquinone) with copper were studied under electrospray ionization conditions. $[\text{Cu}(\text{PQ})_2]^+$ (PQ = 9,10-phenanthraquinone), $[\text{Cu}(\text{maltol})(\text{maltol-H})]^+$ and $[\text{Cu}(\text{maltol})(\text{maltol-H}_2)]^+$ were produced by electrospray ionization. The copper complexes were compared with complexes of other metals (Zn, Ag, and Na), and the structures were studied by collision induced dissociation (CID) and IRMPD spectroscopy. The redox process of copper complexes was studied using the C-O stretching mode as a redox marker and using fragmentation experiments. Both the phenanthraquinone and maltol ligands showed redox activity of the studied copper complexes in the gas phase.

In the second part, negatively charged complexes of copper with pincer ligand L (L = *N,N'*-bis[2,6-diisopropylphenyl]-2,6-pyridinedicarboxamide) were investigated to show the effects of different counter-ions. The results showed that electrospray ionization of copper chlorate salt generates $[\text{Cu}^{\text{III}}(\text{L-2H})(\text{O})]^-$ complexes. Furthermore, other copper salts were also investigated to generate copper(II) complexes. Specifically, $[\text{Cu}(\text{L-2H})(\text{CH}_3\text{COO})]^-$ and $[\text{Cu}(\text{L-2H})(\text{CH}_3\text{O})]^-$. In the case of $[\text{Cu}(\text{L-2H})(\text{CH}_3\text{COO})]^-$ were studied, CID analysis showed that the acetoxy complex undergoes competitive eliminations of the acetoxy radical and acetic acid. $[\text{Cu}(\text{L-2H})(\text{CH}_3\text{O})]^-$ fragmentation shows that this complex is involved in the redox process and in the rearrangement reaction.

In the last part, the generation and reactivity of copper(III)-oxo complexes with monodentate or bidentate ligands and different copper salts were studied. Electrospray ionization of copper chlorate salts is an efficient method to generate various $[(\text{L})\text{CuO}]^+$ complexes with monodentate and bidentate ligands. The signature of these terminal copper-oxo complexes is the elimination of the oxygen atom upon collisional activation. Furthermore, these complexes reacted with water, ethane, ethylene, and 1,4-cyclohexadiene in the gas phase. The $[(\text{MeCN})\text{CuO}]^+$ complex oxidized water and performed C-H activation and hydroxylation of ethane. The complexes with bidentate ligands did not react with water

and oxidized only larger hydrocarbons. All the investigated complexes showed comparable reactivities in the oxygen-transfer reaction with ethylene.