

## Covalently Grafted, Silica Gel Supported C-protected Cysteine or Cystine Copper Complexes – Syntheses, Structure and Possible Surface Reaction Studied by FT-IR Spectroscopy

A. Aranyi, Z. Csendes, J.T. Kiss, I. Pálinkó

*Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*

In order to satisfy the need for novel highly active, and, even more importantly, highly selective catalysts various strategies may be followed. One promising way may be to mimic the active sites of enzymes [1]. To ease the work-up procedure as well as facilitating the recovery of the catalyst, immobilising these active site mimics looks advantageous. In this contribution we describe such a biomimetic approach: our work concerns the covalent anchoring of Cu(II)–C-protected L-cysteine or C-protected cystine complexes onto a modified silica gel support. Previously, we applied for anchoring of various copper–amino acid complexes onto silica gel [2] and montmorillonite [2-4] hydrogen bonding and ionic interactions, respectively. Although immobilization was successful, we hoped for a better control of synthesis using covalent grafting. Our initial results with N-protected tyrosine and chloropropylated silica gel were encouraging [5].

The components of the anchored complexes [L-cysteine or L-cystine methylester, Cu(NO<sub>3</sub>)<sub>2</sub>, chloropropylated silica gel (SG)] and the isopropanol solvent were commercial products. Covalent grafting was performed at the N-terminal of the amino acid (N-alkylation-like transformation) with the chlorine of the chloropropylated SG. Complexation followed the anchoring, applying either ligand-poor conditions (only the immobilised protected amino acids were available for coordination) or circumstances abundant in non-anchored protected amino acid molecules. Structural information on each step of the synthesis procedure was obtained by mid-range infrared spectroscopy, measuring diffuse reflectance (4000–400 cm<sup>-1</sup> wavenumber range, BIO-RAD Digilab Division FTS-65 A/896 FT-IR spectrophotometer, 2 cm<sup>-1</sup> resolution, 126 scans, the Win-IR package).

It was found that covalent anchoring was successful with both amino acids. The primary coordination site was found to be the thiolate or the disulfide sulphur for cysteine and cystine, respectively. The other site available for coordination is the carbonyl oxygen. The nitrogen was not accessible due to its direct participation in surface grafting. The cysteine methylester acted as bidentate ligand, i.e., two amino acids satisfied the fourfold coordination of the Cu(II) ion under ligand-poor conditions, while one surface-bound cystine could do the same. Ligand excess did not change the coordination mode for cysteine methylester, while for the cystine methylester the sulphur atoms of the excess amino acids molecules expelled the carbonyl oxygens from the coordination sphere. Comparing the spectra of anchored complexes revealed that there was no cysteine → cystine transformation neither under ligand-poor nor ligand-excess conditions.

- [1] A.J. Kirby, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 706-724.
- [2] I. N. Jakab, K. Hernadi D. Méhn, T. Kollár, I. Pálinkó, *J. Mol. Struct.* 651-653 (2003) 109-114.
- [3] K. Hernadi, I. Pálinkó, E. Böngyik, I. Kiricsi, *Stud. Surf. Sci. Catal.* 135, 366; CD-ROM edition 27P10 (2001).
- [4] I. Szilágyi, I. Labádi, K. Hernadi, T. Kiss, I. Pálinkó, *Stud. Surf. Sci. Catal.* 158 (2005) 1011-1018.
- [5] I. N. Jakab, K. Hernadi, J. T. Kiss, I. Pálinkó, *J. Mol. Struct.* 744-747 (2005) 487-494.

**Acknowledgement:** This work was supported by the National Science Fund of Hungary through grant K62288. The financial help is highly appreciated.