

Sulphur K-edge XANES study of Cu complexes with novel 1,2,4-triazole-3-thione ligands - potent inhibitors of metal enzymes and RNA-dependent DNA polymerase

M.T. Klepka, A. Drzewiecka, A. Wolska and B. Miroslaw¹

Institute of Physics Polish Academy of Sciences, al. Lotnikow 32/46, PL-02668 Warsaw, Poland

¹Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

New copper complexes with derivatives of 1,2,4-triazole-3-thione have been studied. The organic ligands have common S=C-N-C=N-N molecular fragment (see Figure 1) and possess ability to bind metal ions through the S atom. The analysed samples were divided into two groups according to the similar synthesis conditions. In the first group (**I**) the synthesis was conducted through the direct reaction of ligand with copper metal powder (Cu^0) in liquid medium. There were three samples in this group (**mpp**, **mp5**, **mp2**) (see Figure 1). In the second group (**II**) the complexes were obtained through the conventional synthesis with copper(II) perchlorate (**mpp**, **mp5**, **mp9** and **mpo**) (see Figure 1).

The aim of the study was to establish whether the S donor atoms are present in the coordination environment of the Cu cation. This question can be resolved by using the selectivity and sensitivity of the XAFS technique. The measurements were performed at the A1 station. XANES spectra were gathered at room temperature using fluorescence mode of detection. The analysis provides information about chemical state of elements and may provide suggestions about the local atomic order.

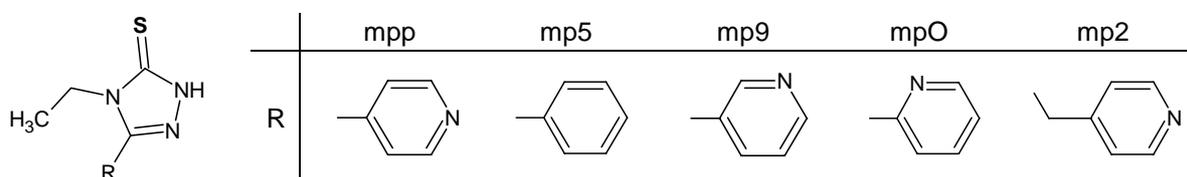


Figure 1: Molecular structure of ligands.

First, the spectra of compounds were compared with the spectrum of the parental ligand (**mp5**) in order to explore whether the complexation process was successful and whether the S atom is coordinated directly to the Cu ion. Few distinct sulphur absorption lines are marked at Figures 2 a-c and 3 a-b [1,2]. Region A between 2471 and 2472 eV (see Figure 2a) is characteristic for free ligand molecules. Peak in the area B from 2472 to 2473 eV (see Figure 2 a-c, 3 a-b) most probably results from the superposition of the C-S and S-H bonds. Region C (2475–2477 eV) is associated with C-S⁺ bond (see Figures 2a-c, 3a). Pronounced peak in a region D (~2482 eV) corresponds to inorganic sulphate anion and confirms the presence of S⁺⁶.

The direct synthesis starting from zero valent Cu in the group **I**, was successful for **mp5Cu** and **mp2Cu** samples. The spectrum of **mppCu** reproduces the shape of the initial ligand **mp5** spectrum, indicating that no chemical reaction occurred (see Figure 1a). The complex **mp5Cu** does not contain the inorganic part, while the complex **mp2Cu** does.

In case of the group **II**, the complexation reaction was successfully performed for all samples. The shape of the XANES spectra for **mpoClO₄**, **mp5ClO₄** and **mp9ClO₄** samples are similar to each other, but different from **mppClO₄**. The last one is most likely a mixture of obtained new complex and unreacted substrates.

In summary, six new copper complexes with derivatives of 1,2,4-triazole-3-thione have been obtained. The differences observed in the region C for the complexes: **mp5Cu**, **mp2Cu**, **mpoClO₄**, **mp5ClO₄** and **mp9ClO₄** can be connected with the change in the C-S bond lengths indicating that the S donor atoms are coordinating directly to the Cu cation. However, this conclusion still should be confirmed by the XAFS measurements at the Cu K-edge on these compounds.

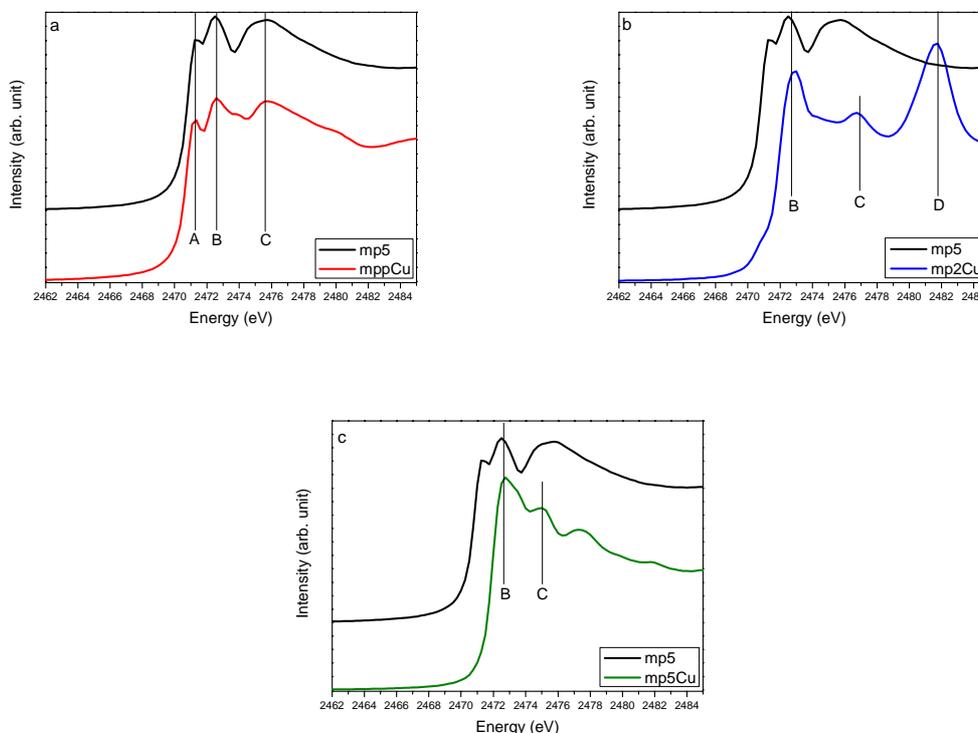


Figure 2: S K-edge XANES spectra of the samples from group I: a) **mp5Cu**; b) **mp2Cu**; c) **mp5Cu**, compared with initial ligand.

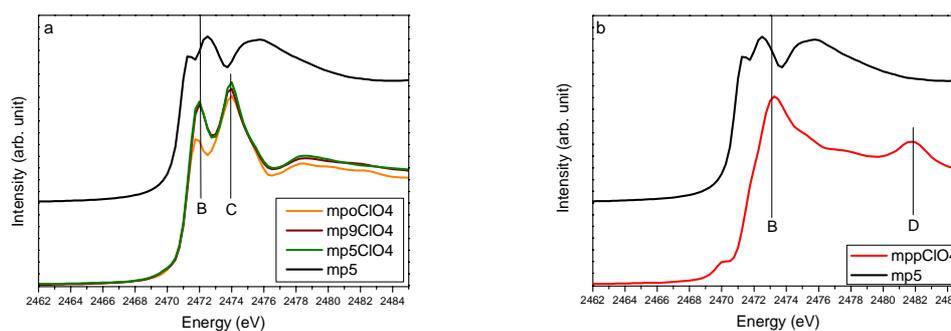


Figure 3: S K-edge XANES spectra of the samples from group II: a) **mpoClO₄**, **mp5ClO₄**, **mp9ClO₄**; b) **mppClO₄**, compared with initial ligand:

References

- [1] <http://www.esrf.eu/UsersAndScience/Experiments/Imaging/ID21/php>
- [2] H. Lichtenberg, et al. Journal of Physics: Conference Series **190** (2009)