



	<b>Experiment title:</b> <b>Probing the Structural and Electronic Characteristics of Dicopper Oxygen Complexes Relevant to Catalysis</b>	<b>Experiment number:</b> <b>CH-5295</b>
<b>Beamline:</b>	<b>Date of experiment:</b> from: 24.08.18 8:00 to: 28.08.18 8:00	<b>Date of report:</b> 16.02.22
<b>Shifts:</b>	<b>Local contact(s):</b> Pieter Glatzel	<i>Received at ESRF:</i>
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## Report:

The experimental objective of this beam time was to collect non-resonant x-ray emission (XES) and resonant x-ray inelastic scattering (RIXS) spectra of various copper motifs possessing differing copper oxidation states to probe the origins and the mechanism of the copper edge features, particularly the ‘shakedown’ feature and further understand the  $K\beta$  mainline of copper, which have yet to be completely assigned. The shakedown has been described as a formal 1s to 4p transition occurring at higher energy than the typical 1s to 4p transition and is combined with a ligand-to-metal charge transfer event, which is energetically favorable due to the formation of a 1s core hole on Cu. The final state yields a ligand hole (L) and for Cu(II) results in a closed-shell  $d^{10}$  ion ( $3d^{10}\underline{L}4p^1$ ).

The process of the shakedown could hypothetically be probed by RIXS spectroscopy because of the differing intermediate state possibilities. For Cu(II)  $d^9$ , two possible intermediate states are possible: *i*) 1s 4p transition which will resemble the Cu(II)  $K\beta$  mainline emission, indicating that a single electron process occurs or *ii*) a 1s 4p+‘shakedown’ transition where the final state will resemble a Cu(I) emission spectrum, as a result of a ligand to metal ‘shakedown’.

During this beamtime, we collected preliminary RIXS data and/or resonant cuts (either in the absorption or the emission directions) of the RIXS plane to assess both the feasibility of the experiment and identify differences in features correlated with oxidation state, Figure 1.

A set of  $\beta$ -diketiminato copper coordinated complexes, all in trigonal geometry, were studied with either NCMe ( $Cu^I$ ), thiol, chloride, or siloxide ligands ( $Cu^{II}$ ). The non-resonant  $K\beta$  mainline of the Cu(I) and Cu(II) complexes overlay, exhibiting no sensitivity to the oxidation state. However, as the Cu(II) is  $d^9$  and has a weak 1s $\rightarrow$ 3d pre-edge feature, comparisons of the resonant XES of the Cu(I) and Cu(II) complexes is a useful exercise. When

resonant in the pre-edge of the Cu(II) complex, a  $1s^13p^63d^{10}4p^0$  intermediate state is achieved, as compared to the rising edge of the Cu(I):  $1s^13p^63d^{10}4p^1$ . The resonant XES of the Cu(II) is spin selective as only a beta spin may be excited and refill the core-hole. However, the Cu(I) does not exhibit the same spin selectivity and either an alpha or beta may be promoted to the 4p and refill the core hole. When resonant with the pre-edge of the Cu(II), enhancement of a low-energy feature in the  $K\beta$  mainline is observed, both line sharpening of the  $K\beta$  mainline and enhancements of the  $K\beta'$  feature at  $\sim 8896$  eV is observed. The next highest energy cut at an incident energy of 8985 eV is in the rising edge of the spectrum into a formal 1s-4p transition. This absorption results in either a  $1s^13p^63d^94p^1$  or a  $1s^13p^63d^{10}4p^0\bar{L}$  intermediate state, where  $\bar{L}$  is a ligand hole due to a shake-down transition.

However, the resonant mainline here resembles that of the Cu(I) along the same 1s-4p transitions, implying that the 8985 eV absorption feature of the Cu(II) has the same d electronic configuration (d10) as copper as a result of the shakedown transition. Corresponding resonant XAS cuts are also collected and require analysis to fully corroborate this proposed mechanism. Lastly, valence-to-core RIXS was collected to determine both the resolution and feasibility of the experiment to capture and identify charge transfer and multi-electron processes. An example VtC-RIXS plane is plotted below and the multiple electron transfer features are identified, but not yet assigned with the 1s $\rightarrow$ 4p transition of the rising edge.

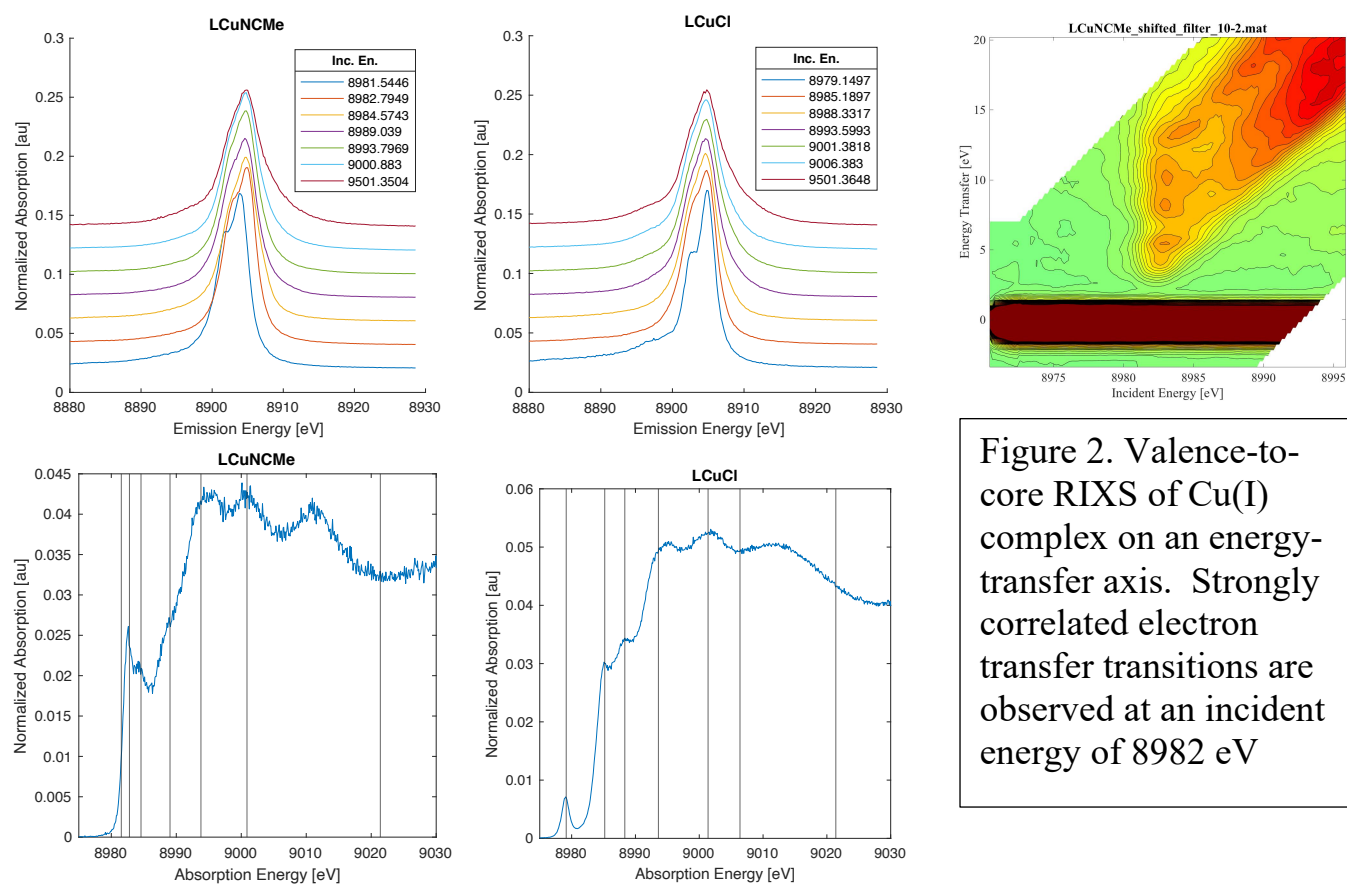


Figure 2. Valence-to-core RIXS of Cu(I) complex on an energy-transfer axis. Strongly correlated electron transfer transitions are observed at an incident energy of 8982 eV

Figure 1. (top) Resonant Cu  $K\beta$  mainline XES of Cu(I), left, and Cu(II), right at various incident energies as depicted in the XAS spectra (bottom).