



	Experiment title: Probing the Structural and Electronic Characteristics of Dicopper Oxygen Complexes Relevant to Catalysis	Experiment number: CH-5295
Beamline:	Date of experiment: from: 20.10.18 8:00 to: 26.10.18 8:00	Date of report: 20.01.18
Shifts:	Local contact(s): Blanka Deflets	<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-oxygen motifs possessing differing copper oxidation states. Scientifically, this proposal aimed to first structurally probe the oxygen bond (or lack there of) in dicopper-peroxo and in dicopper-bis- μ -oxo complexes (Fig 1). DFT calculations of the valence-to-core XES predicted dramatic changes for the two motifs, allowing for the presence of the O-O bond in dioxygen to be directly detected by differing $K\beta''$ features (Fig 2).

The second scientific goal was to probe the origins and the mechanism of the copper edge features, particularly the ‘shakedown’ feature. 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’.

The various complexes shown in Figure 1 possess either a Cu(II) or a Cu(III) oxidation states and their monocopper precursors have a Cu(I) oxidation state, providing all three

oxidation states for RIXS. The $K\beta$ mainline of each complex was collected and unfortunately in the present study were all found to overlay. The three copper oxidation state have indistinguishable non-resonant mainline spectra (Fig 3) of the final states independent of oxidation state. Therefore, no copper fingerprint ‘oxidation-state’ mainlines are available for these complexes, making any intermediate assignments in the RIXS impossible. The $K\beta$ HERFD XAS edges do however exhibit the expected edge energies and shifts for Cu(I), Cu(II) and Cu(III) as shown in Fig 4. Further investigation by theoretical studies are necessary to understand the mainline spectra of these molecular copper complexes and why the mainline spectra are insensitive to spin-state.

Preliminary comparison of Valence-to-Core (VtC) emission spectra of $\text{Cu}_2(\mu\text{-O})_2$ and $\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$ cores (Fig 5) exhibit the predicted transitions as shown in Fig 2. The $\text{Cu}_2(\mu\text{-O})_2$ core exhibits a weak single $K\beta$ feature from the O 2s emission. $\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$ core does not have any resolved $K\beta$ features, but the calculated intensity is much less than the $\text{Cu}_2(\mu\text{-O})_2$ core. However, a shoulder to the lower energy side of the $K\beta_{2,5}$ line is apparent for the $\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$ core from the O 2s-2s* emission, signifying the presence of the O-O bond in the peroxo unit.

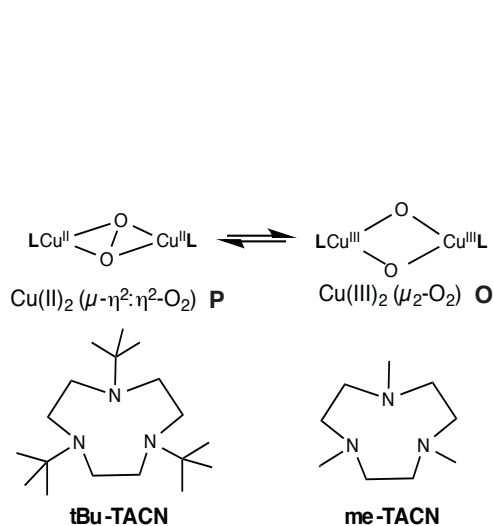


Figure 1. $\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$ (P) and $\text{Cu}_2(\mu_2\text{-O}_2)$ (O) cores with differing ligands (L), tBu- and me-TACN, respectively.

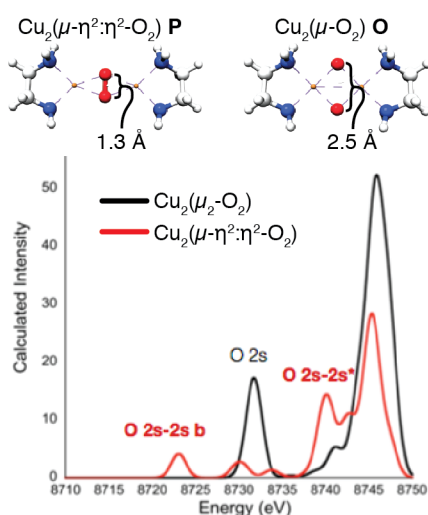


Figure 2. (Top) $\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$ (P) and $\text{Cu}_2(\mu_2\text{-O}_2)$ (O) cores with labeled O-O bond length. (Bottom) Corresponding DFT $K\beta$ XES spectra of P and O.

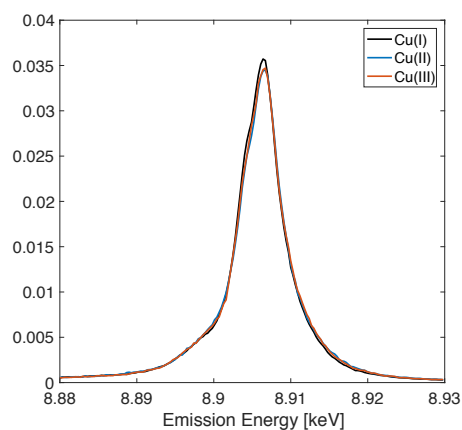


Figure 3. Cu K-beta emission mainline of copper +1, +2, +3 oxidation states

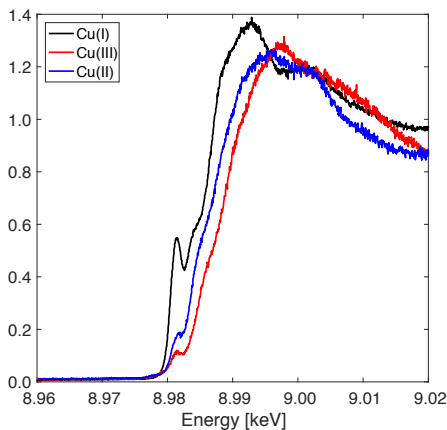


Figure 4. Cu K-beta HERFD-XAS of copper +1, +2, +3 oxidation states

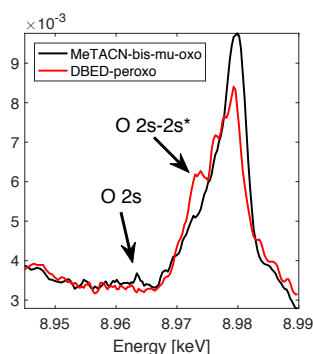


Figure 5. VtC emission spectra of $\text{Cu}_2(\mu\text{-O})_2$ (black) and $\text{Cu}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)$ (red)