

**Experiment title:**

Investigation of redox chemistry of model Cu-complexes for direct alkanes to alcohols conversion by combined XAS-UVvis-IR spectroscopies

**Experiment****number:**

CH-5964

<b>Beamline:</b> BM31	<b>Date of experiment:</b> from: 05/05/2021 to: 10/05/2021	<b>Date of report:</b> 07/09/2023
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**Report:**

This proposal aimed at characterizing a selection of Cu-complexes by simultaneous in situ XAS, UV-vis and IR spectroscopies, to disclose the fundamentals of their redox chemistry in solution and to understand their reactivity in the direct oxidation of alkanes to alcohols. Beside the direct scientific interest in the complexes themselves, the complexes represent the starting point for the rational design of ligands to be incorporated in metal-organic frameworks (we are currently pursuing), to reproduce the outstanding catalytic performances of Cu single sites in enzymes, while circumventing the stability and scalability limitations typical of biological systems. We collected XAS data on 4 model homoleptic complexes, based on Cu<sup>+</sup> ligated by substituted 2,2'-bipyridines: CuBPA (ligand=6,6'-dimethyl-bipyridine); CuBPB (ligand=5,5'-dimethyl-bipyridine); CuBPC (ligand=6,6'-dimethoxy-bipyridine); and CuBPD (ligand=unsubstituted bipyridine). Since the samples were dissolved in dichlorometane (DCM), the resulting solution exhibited very high absorption, such as it was necessary to collect the XAS spectra in fluorescence mode. Initially, due to the pandemic, the beamline was planned in mail-in mode (local contact: Hermann Emerich), delivering liquid samples sealed in glass capillaries. However it immediately turned out that samples were subjected to severe beam damage, being unable to resist the time required to attain a reasonable S/N ratio for the spectra. In agreement with the beamline staff, we withdrew this attempt and we resorted to a beamtime in presence. To decrease the extent of the beam damage in closed sample environments, we built and tested on the beamline a recirculation setup, where a larger amount of solution (ca. 10 ml) was continuously flowed through a kapton capillary and then brought back to the reservoir. This strategy was sufficient to mitigate the extent of beam damage for 2 over 4 samples. However, due to the very long acquisition time per sample/state we finally adopted (about 4 h of total collection, through the average of ca. 200 spectra), for some samples (CuBPB and CuBPC) we verified the occurrence of beam damage despite the continuous circulation. Accordingly, we discarded these samples for further reaction steps. The circulation setup offered some further advantages, in particular: i) dosing reagents directly in the reaction environment, without solution exchange; and ii) the possibility to online monitoring the solution by complementary techniques, in our case on-line UV-vis spectroscopy. The advantage of coupling a second, higher

time resolution technique was the possibility to live check the evolution of the redox processes occurring, impossible by bare XAS data due to the poor time resolution and S/N ratio of the single spectra.

In detail, we investigated the sample in their pristine  $\text{Cu}^+$  form, their oxidized form upon interaction with an oxidant (tertbutyl hydroperoxide or  $\text{NOPF}_6$ ) and, eventually, the reaction of the oxidized form with a substrate, in our case cyclohexene. The obtained XAS spectra are shown (in the XANES region) in Figure 1.

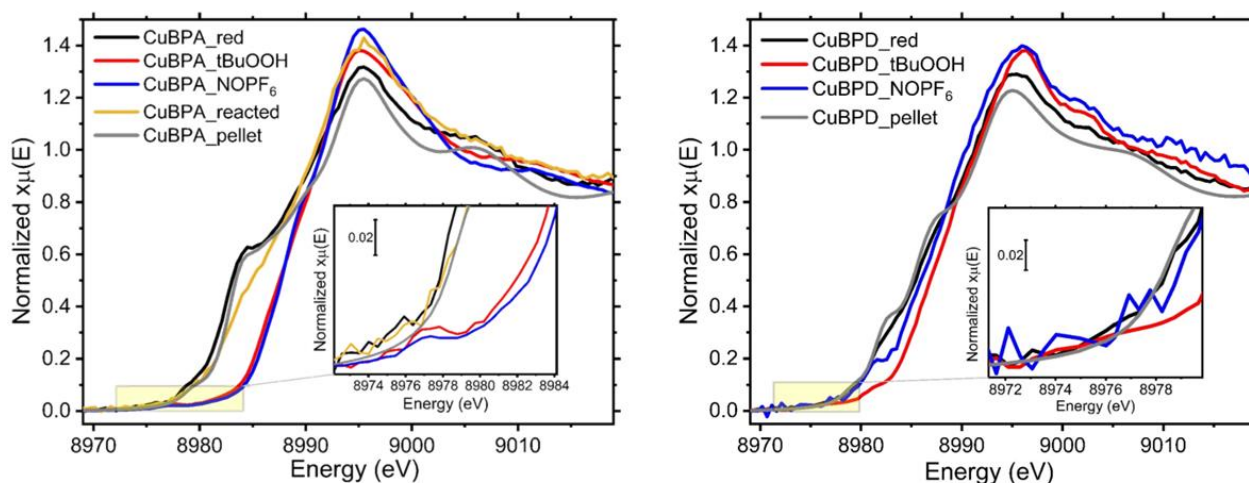


Figure 1. XANES spectra of CuBPA (left) and CuBPD (right) complexes at different reaction stages.

A clear difference in the redox reactivity of the two complexes was identified: by comparing the averaged spectra for the different states of each complex, it emerges as CuBPA has a reversible redox behaviour when oxidized with tertbutyl hydroperoxide, whereas CuBPD remains in its oxidized state regardless the adopted oxidant. We could further perform a semi-quantitative EXAFS analysis on the obtained data: due to the poor S/N, the  $k$  space was limited to a maximum value of  $10 \text{ \AA}^{-1}$  in the better cases, so we stuck on a first-shell analysis, including a path to represent the 4 N atoms coordinating the Cu ion + an additional path to a light atom L. For both paths, we optimized length and coordination number. From this analysis, it clearly resulted as the treatment of CuBPA with tertbutyl hydroperoxide is the only case where the L atom is present with coordination number 1 at a distance  $< 2.0 \text{ \AA}$ , compatible with the formation of a Cu-O species. From our data, it is however impossible to assess the exact nature of the exact functional group bound to the Cu ion, being possibly a Cu-OH, a Cu-OOH or even a  $\text{Cu-O}^\bullet$ . Further studies are ongoing to precisely assess the nature of the moiety. Apart from its exact nature, we could identify this specie as the catalytically active toward cyclohexene oxidation, as only when it is formed a partial reversion of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  is observed in the presence of substrate.

