

Experiment Report Form



	Experiment title: In situ XAS studies of structural transformations in the formation pathways of multinuclear copper(pyalk) oxo-cluster complexes	Experiment number:
Beamline: BM31	Date of experiment: from: 29 June 2021 to: 05 July 2021	Date of report: 26.10.2022
Shifts: 12	Local contact(s): Wouter Van beek	<i>Received at ESRF:</i>
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Report:

Background

Coordination complexes (CCs) find major applications in a broad spectrum of fields ranging from catalysis and chemical biology to energy conversion materials.^[1-2] Among these, multinuclear metal oxo-cluster complexes have been widely employed as potential candidates for artificial photosynthesis and chemical fuel production such as methane to methanol conversion.^[3] Even today, the assembly mechanisms and formation pathways of these metal oxo-clusters are not well understood. A detailed understanding of the same would lead to acquiring control over their nuclearity and coordination environment, which would ultimately help a chemist in tuning the structural features of CCs for appropriate applications and thereby making it possible for the targeted synthesis of such inorganic metal oxo-complexes.^[4] We herein demonstrate the counter anion-driven structural & coordination evolution of Cu oxo-clusters via *in-situ* XAS under their solution synthesis condition.

In-situ X-ray Absorption Spectroscopy under synthesis conditions:

In-situ Cu K-edge XAS experiments under the synthesis conditions of respective Cu complexes were performed at the BM31 beamline. *Ex-situ* measurements were carried out on Cu reference samples dispersed in cellulose and pressed into pellets. For all *in-situ* measurements, a in-house built glass cell with kapton windows, capable

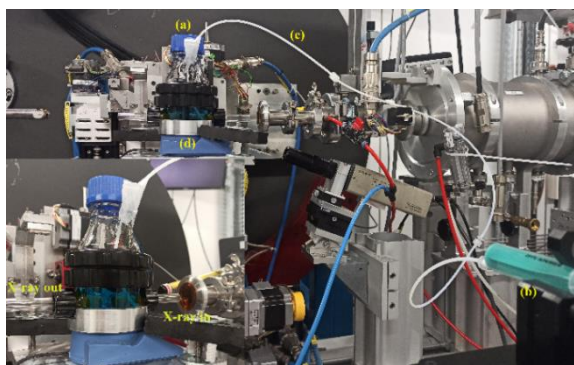


Fig.1: (a) In-situ cell, (b) Syringe Pump setup, (c) Tubings, mounted at BM31. *Inset:* Enlarged Cell

in water solvent were only limited to k ranges from 3 to 9 Å⁻¹.

Results:

At first, *in-situ* XAS was carried on methanolic solution of Cu(BF₄)₂ via dropwise ligand addition to track the formation of Cu₇-oxo the cluster and understand its EXAFS signatures. *In-situ* XANES indicated Cu₇-oxo cluster formation after completion of ligand addition, and *in-situ* EXAFS signals indicated the evolution of Cu-O coordination shell at 2.04 Å & Cu-Cu shell at 2.47 Å respectively (**Fig.2**). The same set of *in-situ* experiments was carried out with Cu(ClO₄)₂ and Cu(SO₃CF₃)₂ salts to capture the presence of Cu₇-oxo clusters. Secondly, the structural evolution of Cu-oxo clusters was studied in the presence of electronically tuned Borate anions, namely NaBPh₄ and BARF. *In-situ* XAS was recorded while dropwise addition of methanolic borate solution into Cu₇-oxo cluster solution placed in the reaction cell. *In-situ* data strongly suggested that the Cu₇-oxo cluster is greatly influenced by counter-anion charge density. Specifically, the addition of BPh₄⁻ anions indicated that the Cu₇-oxo cluster transformed to a monomer Cu complex, evidenced by the evolution of shoulder peak at 8976 eV in XANES (*also confirmed with Cu-monomer reference signal*) (**Fig.2, bottom**). Similarly, *in-situ* EXAFS

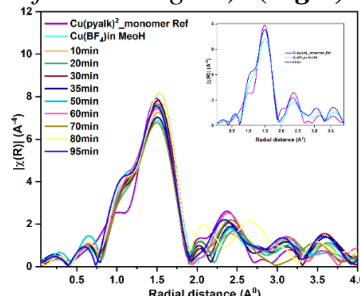


Fig3: *In-situ* EXAFS signals in presence of BPh₄⁻ anions & Cu-monomer reference

signals of the *in-situ* reaction of Cu₇ and BPh₄⁻ were in good agreement with the EXAFS signals of reference Cu monomer complex (**Fig.3**). Whereas, in the presence of BARF anion, the Cu₇ signals were not altered, confirming that the Cu₇-oxo clusters are being stabilized by BARF anion. Finally, the methanolic Cu₇-oxo cluster solution was titrated with pure distilled water, and *in-situ* XAS were measured to track the impact of H₂O molecules on the cluster size and structure. This indicated that the Cu₇-oxo clusters transformed to Cu-oxo dimers in the presence of H₂O molecules.

Conclusions & Outlook:

The *in-situ* XANES & EXAFS data suggest that the structural & electronic features of Cu-oxo clusters are greatly impacted by the counter anion used in their synthesis. Specifically, the use of electronically tuned borate anions have been found to selectively tune the cluster size of Cu-oxo clusters from Cu₇ to Cu₁. Additionally, presence of water molecules in the organic reaction indicated the transformation of Cu₇ clusters to Cu₂, which suggests the importance of solvent contribution. Further correlations are to be drawn from DFT calculations, so as to completely confirm the optimized geometry and electronic states of each cluster.

References:

- [1] *Chem. Sci.*, 2021, **12**, 1964–1981.
- [2] *Dalton Trans.*, 2022, **51**, 4199–4201.
- [3] *J. Phys. Chem. A* 2022, **126**, 4941–4951.
- [4] *Chem. Rev.* 2021, **121**, 9927–10000.

of adjusting the path length was used (**Fig.1**). In addition, an automated (*programmable*) syringe pump equipped with PTFE tubings connected to the *in-situ* cell was placed in vicinity of the cell, for ligand addition (**Fig.1**). Each synthesis experiments lasted 2-4 hours and XAS signals were collected periodically, by synchronising with ligand drops addition (from the syringe pump) time. Data treatment was carried with *Athena* software package. The k₃-weighted Fourier transform (FT) for all the *in-situ* EXAFS data was conducted in the k-ranges of 0 to 11 Å⁻¹. Since the experiments were conducted in solution conditions, the ones where water was used as the solvent were extremely challenging to acquire high quality EXAFS data. Therefore, the investigations of Cu K-edge EXAFS data

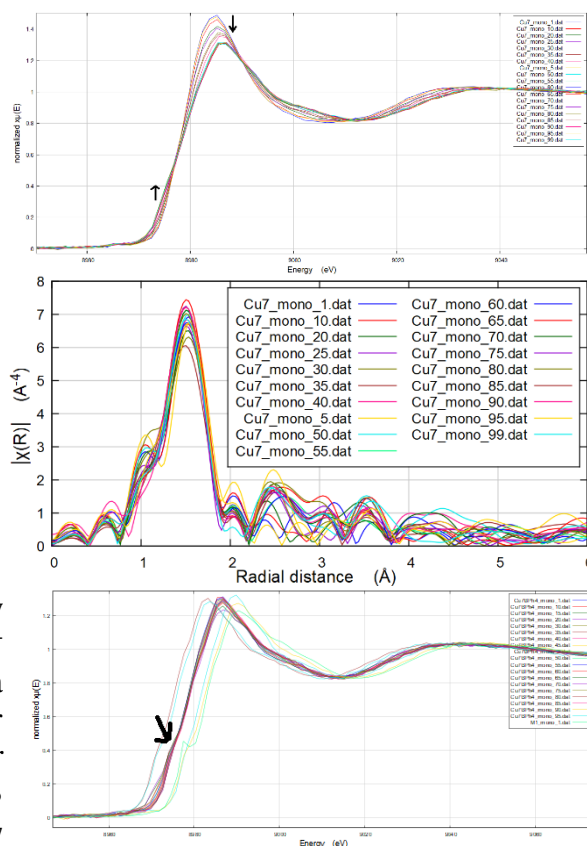


Fig.2: (top) *In-situ* XANES OF Cu₇ formation from CuBF₄ salt MeOH solution, (Mid) *in-situ* EXAFS of Cu coordination evolution in Cu₇. (Bottom) *in-situ* XANES of Cu-monomer formation with the addition of NaBPh₄