Published in final edited form as:

Chem Commun (Camb). 2015 June 18; 51(48): 9864–9867. doi:10.1039/c5cc01827g.

Probing Cu^I in Homogeneous Catalysis using High-Energy-Resolution Fluorescence-Detected X-ray Absorption Spectroscopy

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Abstract

Metal-to-ligand charge transfer excitations in Cu^I X-ray absorption spectra are introduced as spectroscopic handles for the characterization of species in homogeneous catalytic reaction mixtures. Analysis is supported by correlation of a spectral library to calculations and to complementary spectroscopic parameters.

Global desire for a sustainable chemical industry has spurred efforts toward the substitution of earth-abundant base metal (e.g. Fe and Cu) catalysts for conventional precious metal (e.g. Rh and Pt) analogues.^{1–5} Remarkable progress has been made toward this goal, and the significance of such achievements is amplified by the difficulties intrinsic to studying these new catalysts. For example, Cu catalysts typically undergo one-electron redox; accordingly Cu-catalyzed reaction mixtures frequently contain on-path or off-path paramagnetic Cu^{II} species that complicate mechanistic study by conventional methods such as NMR. Consequently, alternative analytical approaches are required.

Our laboratory uses synchrotron-based X-ray spectroscopies to interrogate the electronic and molecular structures of transition metal species in homogeneous catalysis.^{6, 7} K-edge (Metal 1s → valence/continuum) X-ray absorption spectroscopy (XAS) in particular has found widespread use in determining physical oxidation states of transition metal centres and qualitatively defining ligand geometries about these centres.^{8–12} Weak “pre-edge” features in transition metal K-edge XAS are conventionally assigned as metal 1s → nd transitions.¹³ Time-dependent density functional theory (TD-DFT) accurately predicts the energies and intensities of these features, and thus has facilitated quantitative interpretation of their electronic structural origins.^{14, 16} Consequently, XAS is steadily evolving from a “fingerprinting” method into a tool for compound identification.

One major innovation in this regard has been the development of high-energy resolution fluorescence detection (HERFD) methods. HERFD is a collection mode for XAS,

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[†]These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: Experimental procedures, details of X-ray measurements, data analysis, and calculations. See DOI: 10.1039/c000000x/

introduced by Eisenberger and co-workers¹⁷ and later described for Dy XAS by Hämäläinen and co-workers,¹⁸ that exploits crystal analyser optics to narrowly (ca. 1 eV linewidth) monochromate X-ray fluorescence. This fluorescence is then plotted as a function of incident photon energy to facsimile XAS. This approach affords narrower spectral line widths relative to conventional total fluorescence yield (TFY) by dramatically reducing uncertainty broadening. Modern improvements to synchrotron brightness have prompted vigorous adoption of HERFD, whose use had previously been limited due to considerably lower signal-to-noise ratios per photon flux compared to TFY XAS. Significant resolution enhancements via HERFD have been noted in XAS of 3d transition metal systems, with several recent studies appearing that showcase the utility of this method towards establishing molecule and electronic structures of bioinorganic cofactors and intermediates^{19, 20} as well as abiotic catalysts^{21, 26} and nanoparticles.²⁷ The advantage of HERFD is especially pronounced in XAS of lanthanides and 4d and 5d metals, where long core-hole lifetimes dramatically broaden XAS linewidths in conventionally collected spectra.^{15, 28} Herein, we discuss the application of HERFD to the study of homogeneous Cu catalysis and report the observation and assignment of pre-edge features in the K-edge XAS of select Cu^I complexes.

To evaluate how HERFD enhances the information content of Cu K-edge XAS, we collected spectra for 9 Cu coordination compounds spanning a range of coordination environments and oxidation states (Figure 1). The K-edge XAS of **7** and **3** collected via K α_1 (2p_{3/2} → 1s) HERFD are shown in Figure 2. The ca. 8979 eV Cu 1s → 3d excitation in **7** appears as a distinct peak that is well separated from the rising edge (Figure 2a). The pre-edge regions in K-edge XAS of d¹⁰, Cu^I species necessarily lack this weak 1s → 3d pre-edge band, but typically display an intense feature at ca. 8984 eV assigned to the Cu 1s → Cu 4p transition. In the HERFD K-edge XAS of **3**, the 1s → Cu 4p is distinct from the rising edge (Figure 2b).

Remarkably, HERFD reveals additional pre-edge features near 8980 eV in the Cu K-edge XAS of closed-shell **4**, where Cu^I is coordinated by the diimine ligand 2,2'-bipyridine (bpy) (Figure 3a). Similar features are present in the XAS of Cu^I-bpy complex derivatives **5** and **6**. A recent study by Wieghardt and co-workers²⁹ describes computational assignment of similar features to Cu 1s → ligand π^* metal-to-ligand charge transfer (MLCT) excitations. By correlating the energies of these features in **4–6** to additional spectrochemical parameters, we now lend experimental credence to these assignments.

Precise energy values for these features were determined using least-squares pseudo-Voigt fitting employing a previously described Monte Carlo algorithm to minimize bias (Figure 3b).³⁰ The spectral parameters originate from 100 fits to each spectrum; the resulting values for pre-edge peak positions have fitting errors on the order of 10⁻⁵–10⁻⁶ eV. The energies of these features correlate with Hammett parameters for the bpy substituents³¹ as well as to corresponding Cu 3d → ligand π^* MLCT energies (Figure 3c). The strongly electron-donating OMe substituents of **5** strengthen N → Cu σ donation, concomitantly weakening π -acceptor characteristics. Oppositely, the more electron poor pyridyl-naphthyridines in **6** are strongly π -accepting. Thus, ligand π^* -Cu interaction energies are expected to be highest in **6** and smallest for **5**. We assume negligible differences in Cu 1s binding energies.

Consequently, Cu 1s $\rightarrow$ ligand π^* energy gaps will be governed by ligand π -acceptor capability (Figure 3d). Accordingly, we affirm assignment of the ca. 8980 eV pre-edge features in the XAS of **4–6** to Cu 1s $\rightarrow$ ligand π^* MLCT. Apart from the Wieghardt study,²⁹ such features have only otherwise been observed as shoulders obscured by the rising edge in conventional Mn K-edge XAS.³² Moreover, we have validated a prediction by DeBeer and co-workers that enhancements to XAS resolution should allow its use as a probe of ligand back-bonding characteristics.¹⁴

TDDFT calculations predict these Cu^I XAS MLCT pre-edge features. Calculated (B3LYP/def2-TZVP-ZORA) XAS pre-edge and rising-edge features for compounds **1–9** correlate strongly ($R^2 = 0.96$) to experimental data in the energy domain (Figure 4). The average absolute error between experimental and calculated peak energies is 0.4 ± 0.3 eV. Relative peak areas are less well-modelled, although here errors will necessarily arise due to intrinsic limitations of TD-DFT, specifically its inability to model XAS shakedown transitions and near-edge X-ray scattering as well as its difficulties with modelling charge-transfer excited states^{33,36} (See SI). Nevertheless, with confidence in the ability of TD-DFT to predict the number and energies of pre-edge transitions, the orbitals participating in the pre-edge features exhibited by compounds **4–6** were analyzed. The acceptor orbitals in all three cases are predominantly of ligand π^* character, lending further support to our assignment of the 8980 eV pre-edge features as MLCT bands. Band intensity may principally be attributed to an electric dipole mechanism originating from small (ca. 1 %) Cu p admixture with the bpy π^* acceptor orbitals.

The observation and assignment of MLCT pre-edge features in Cu^I K-edge XAS affords a useful, additional spectroscopic handle for compound identification within parameter spaces defined by compounds likely to be present within samples. As a preliminary demonstration, spectra were measured at various points of reagent addition and maturation for the reaction reported by Stahl and co-workers of the aerobic oxidation of benzyl alcohol to benzaldehyde by the mixture of **3**, bpy, (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), and N-methylimidazole (NMI) (Figure 5a).³⁷ The identities of the resting and catalytically active species in such reactions are controversial.³⁸

The first spectrum measured (Figure 5a, black trace) corresponds to the aerobic mixed solution of all reaction components except for NMI. Based on the observed features and calculated spectra of possible species including $[\text{Cu}(\text{bpy})(\text{MeCN})_2]^+$, this spectrum is most consistent with a mixture of primarily **4** and **3**, neither of which is catalytically competent for oxidation of benzyl alcohol (Figure 5b). After the addition of NMI and allowing 10 minutes to ensure that the reaction had achieved steady state, a second spectrum was recorded (Figure 5a, red trace). A 1 eV blue shift of the rising-edge local maximum to 8983.5 eV as well as increased absorbance past this feature was observed. The features at 8980.0 and 8983.5 eV are most consistent with the predicted spectrum of $[\text{Cu}(\text{bpy})(\text{NMI})]^+$ (Figure 5c). Importantly, this agreement excludes $[\text{Cu}(\text{bpy})(\text{NMI})(\text{MeCN})]^+$, $[\text{Cu}(\text{bpy})(\text{NMI})_2]^+$, $[\text{Cu}(\text{bpy})(\text{MeCN})]^{2+}$, and $[\text{Cu}(\text{bpy})(\text{MeCN})_2]^{2+}$ (Figure S15). We note that our results exceed the specificity that would be provided by extended X-ray absorption fine structure (EXAFS) analysis, where errors due to parameter correlation cannot with certainty define 3- versus 4-coordination in Cu, nor can it with certainty distinguish a C-donor from

and N-donor.^{39, 40} Thus, we propose that NMI shifts equilibrium toward this mono-bpy Cu^I species to produce active catalyst. We note that by XAS, Cu^I predominates in solution during catalysis in accord with observations from Stahl and co-workers concerning benzyl alcohol oxidation by this system.⁴¹ Finally, a spectrum was recorded corresponding to the spent reaction mixture (Figure 5a, gray trace). This spectrum agrees with the calculated spectrum of [Cu(bpy)(NMI)(OH)]₂²⁺ (Figure 5d), which is the species reported by Stahl and co-workers as the resting species formed following substrate depletion.⁴¹

The observation of pre-edge MLCT features in Cu^IK-edge XAS of compounds with π -accepting ligands will be a valuable tool for identifying and characterizing discrete species within reaction mixtures. Our spectroscopic studies of aerobic Cu-catalyzed oxidations are ongoing, and we intend to generalize our approach to study additional base metal-catalyzed reactions using HERFD XAS.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We are grateful to Kenneth D. Finkelstein (Cornell High Energy Synchrotron Source, CHESS) for assistance with X-ray data collection. We thank Theis Brock-Nannestad (U. Copenhagen) for mass spectrometry. K.M.L. thanks the Cornell University College of Arts and Sciences for startup funding. R.C.W. was supported by the NIH, Award Number T32GM008500 from the NIGMS. J.W.H.U. gratefully acknowledges support from an NSF Graduate Research Fellowship (DGE-1144153). This work is based in part upon research conducted at CHESS, which is supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under NSF award DMR-0936374.

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Figure 1.
Cu complexes studied in this work.

Figure 2.
HERFD Cu K-edge XAS of (a) **7** and (b) **3**.

Figure 3.

(a) HERFD Cu K-edge XAS of **4–6**. (b) Closeup of the pre-edge region of the spectra in (a), with pseudo-Voigt peaks fitted to the ca. 8980 eV features shown as dashed lines. (c) Bpy substituent Hammett coefficients (σ_p , black circles) and the electronic absorption MLCT band energies (red triangles) plotted as functions of the Cu K pre-edge energies for **4–6**. Values of σ_p are taken from Ref. 23. (d) Qualitative molecular orbital diagram displaying variations in Cu–bpy π^* backbonding interaction energies as a function of ligand substituent.

Figure 4.

(a) Correlation of experimental Cu K-edge pre-edge and rising-edge XAS peak energies with values calculated by TD-DFT (B3LYP/def2-TZVP-ZORA).

Figure 5.

(a) HERFD Cu K-edge XAS of aerobic Cu/TEMPO/NMI-driven oxidation of benzyl alcohol to benzaldehyde. Spectra were taken prior to NMI addition (–NMI), 10 minutes after NMI addition (+NMI), and after full consumption of benzyl alcohol (substrate depleted). (b) The –NMI spectrum is most consistent with a mixture of **3** and **4**. (c) The +NMI spectrum is most consistent with a $[\text{Cu}(\text{bpy})(\text{NMI})]^+$ species. (d) The substrate depleted spectrum is most representative of $[\text{Cu}(\text{bpy})(\text{NMI})(\text{OH})]_2^{2+}$. Calculated spectra were energy-corrected per the calibration reported in Figure 4.