

## Poster Sessions

charge density study on this second row metal complex with the aim of providing information about metal coordination, and interatomic bonds and interactions, beyond classical geometrical criteria.

The experimental electron density distribution of the ruthenium complex has been determined from high resolution ( $\sin\theta_{\max}/\lambda=1.05\text{\AA}^{-1}$ ) X-ray diffraction data collected at 100 K. After the conventional spherical refinement, the multipole refinement was performed using Hansen and Coppens model [1] with Mopro software [2, 3]. Electronic configuration of the ruthenium atom and a disorder in the ciclooctadiene ligand have been inspected. The deformation density model has been interpreted according to the "Quantum Theory of Atoms in Molecules" [4]. Characterization of the nature of the different metal-ligand interactions in this organometallic complex via the topological properties at the bond critical points will be discussed.

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**Keywords:** Charge density, organometallic, ruthenium.

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#### X-ray absorption spectroscopy studies of copper site in the ubiquinol oxidase

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We present recent experimental and modeling results on membrane protein studied by X-ray absorption spectroscopy (XAS) at the room temperature in solution. Heme-copper oxidases are integral membrane proteins which serve as the final electron acceptor of respiratory chains across all kingdoms of life. These integral membrane proteins accept electrons so as to reduce oxygen to water and thereby exploit the chemical energy released to pump protons. Given the complexity of these processes, it is essential to determine any effect of changes in protonation state of groups near the catalytic iron-copper centre. Such groups are likely to play essential roles in these functionally important conformational changes. Most proposed proton-pumping mechanisms involve CuB site and its histidine ligands. The existence and identity of such reorganization of the CuB geometry caused by protonation/deprotonation and/or breakage of one of the Cu-N(His) bonds is a difficult matter to either prove or disprove since CuB is spectrally silent. Since the Ubiquinol oxidase consists just one Cu site and two Fe atoms it's ideal candidat to apply X-ray absorption spectroscopy to study what happen near the Cu-site when Cu changes its oxidation state and to study pH dependence of the Cu site.

We report the X-ray absorption near edge spectroscopy (XANES) studies of the copper edge of the cytochrome bo<sub>3</sub> quinol oxidase from *Escherichia coli*. Our ab-initio calculations (non muffin-tin FDMNES [1]) and modeling (FitIt software [2]) results indicate that the Cu-site changed its associated ligands for oxidised Cu(II) and reduced Cu(I) states of the protein. However room temperature copper K-edge X-ray absorption spectra remains unchanged in the pH range 6.5-9.5 for both oxidized and reduced forms of copper correspondently, indicating that no structural changes takes place at Cu-site depending on pH.

[1] Y. Joly, *Phys. Rev. B* **2001**, *63*, 125120-125129. [2] G. Smolentsev, *Comp. Matter. Science* **2007**, *39*, 69.

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#### Ferrocene and fluorescence studies: How can we understand stereochemistry of dilute systems?

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Ferrocene is a standard for iron X-ray absorption fine structure (XAFS) and X-ray absorption near-edge structure (XANES) especially for comparison to samples in solution, both because of its well-defined structure and its sharp redox properties. Its significance is reflected by award of the Nobel prize to EO Fischer and G Wilkinson in 1973 for the elucidation of its structure [1,2]. We analyse ferrocene data collected in a cold cell at the Australian National Beamline Facility (ANBF) in Tsukuba, KEK, Japan using conventional fluorescence XAFS. A challenge for fluorescence spectra is the determination of information content or significance. With this, critical quantitative hypothesis testing can be pursued. Without this, naive hypothesis testing can be applied for simple systems, becoming fraught for complex systems, even including mixtures of two species or ionization states. We present robust standard errors from such typical datasets and illustrate their potential applied to a subtle and long-standing problem of ferrocene – that of the orientation of the two cyclo-pentadienyl rings.

Similar recent approaches have shown great potential in the comparison of crystallographic parameters to dynamical measurements [3,4,5], measuring dynamical bond lengths [6], solution of local structure in catalytic organometallics [7,8,9] and developing new theoretical and analytical approaches to structure determination [10].

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#### Conformational studies of bovine insulin

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