

to extended delocalized  $\pi$ -electron systems and the intrinsic neglect of intermolecular interactions are investigated.

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**Keywords:** charge density, dipole moment, chromophore

## MS41.P22

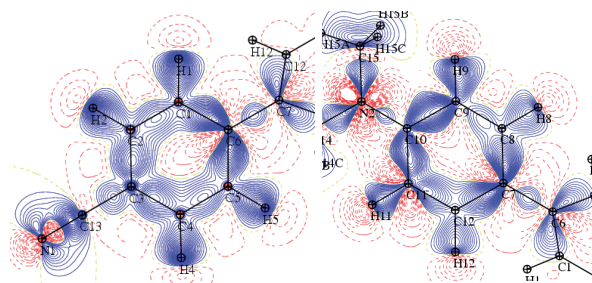
*Acta Cryst.* (2011) A67, C515

### Charge density study of an nonlinear optical compound – A combined experimental and theoretical study.

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In recent years an intense worldwide effort has been focused on the design and development of organic conjugated materials with large optical non-linearities due to their potential applications in various optical devices [1–5]. Materials with high non-linear optical (NLO) activities are useful as electro-optic switching elements for telecommunication and optical information processing.

We present here a comparative study of a quantum-chemical analysis and X-ray diffraction study of a nonlinear optical material structure. The molecular optimized and experimental geometries are obtained via B3LYP/6-31G (d, p) level and X-ray diffraction respectively. The agreement between the experimental and theoretical results was satisfactory. The multipolar refinement was performed using Hansen-Coppens model implemented in the Mopro program [6]. The molecular electron charge density distribution is described accurately. The study reveals the nature of inter-molecular interactions including charge transfer and hydrogen bonds. More results about electrostatic properties will be presented at the meeting.



charge density of the studied compound

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**Key words:** Organic compounds, nonlinear optical properties, X-ray diffraction, DFT, charge density.

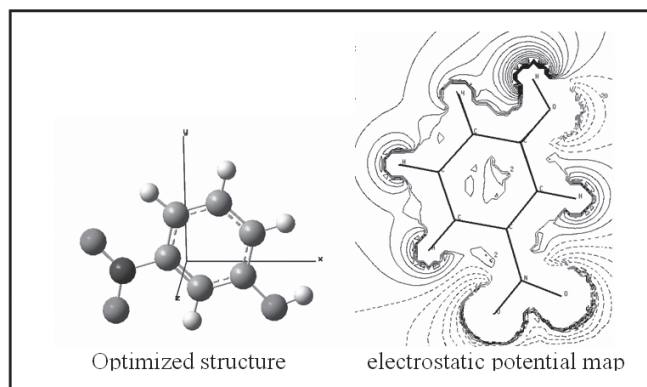
## MS41.P23

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### Topological Analysis and Charge Density Studies of m-Nitrophenol compound. A Combined Experimental and Theoretical Study.

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A combined experimental and theoretical study of the non linear optical compound, m-Nitrophenol was made on the basis of the electron density distribution and topological analysis. Accurate single-crystal diffraction data were measured on a suitable crystal with MoK $\alpha$  radiation at 125 K. Parallel MO calculations were made at UHF and DFT/UB3LYP. The agreement between experiment and theory is reasonably good. A charge density analysis, including the multipole refinement based on the Hansen – Coppens formalism [1], deformation density, topological analysis of  $\rho(r)$  according to the AIM theory [2] was carried out with the program Mopro [3]. The results of the topological analysis of  $\rho(r)$  at the bond critical points enable a quantitative description of the bonds. The chemical bonding characterization is presented in terms of the topological properties associated with bond critical points and the natural bond orbital (NBO) analysis as well. The asphericity in electron density is nicely demonstrated by the Laplacian of electron density in both experimental and theoretical results.



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**Keywords:** Structural Study, Electron charge density, m-Nph, Mopro program, nonlinear optical compound (NLO)

## MS41.P24

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### Experimental charge density study of the [RuCl( $\kappa^3$ -N,N,O-bdmpza)( $\eta^4$ -cod)] complex

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The [RuCl( $\kappa^3$ -N,N,O-bdmpza)( $\eta^4$ -cod)] (bdmpza = bis(3,5-dimethylpyrazol-1yl)acetate) complex is a versatile catalyst precursor in some specific organic reactions. We have carried out a detailed experimental

## 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.

### MS42.P01

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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.

**Keywords:** XANES, ubiquinol oxidase, Cu K-edge

### MS42.P02

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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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**Keywords:** ferrocene, fluorescence XAFS, dynamical bondlengths

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#### Conformational studies of bovine insulin

Christian Grundahl Frankær, Kenny Ståhl, Pernille Harris, *Chemistry*