measurements on a non-deuterated hydroquinone clathrate sample have shown high quality positional and thermal parameters. The obtained atomic displacement parameters are investigated and compared with data from the same compound at the High Flux Isotope Reactor and an X-ray source.

The obtained positional and thermal parameters from the neutron experiment are used in combination with high quality X-ray data for a state-of-the-art charge density refinement. The investigation of these hydroquinone host-guest systems revealed significant charge redistribution of the host structure with the so-called weakly interacting guest solvent molecule.

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Keywords: clathrate, electrostatic, neutron

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Comparative study of the electron distribution in *3d*-orbitals

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In tetrakis(μ_2-Acetato)-diaqua-di-copper(II) complex for the coordinated Cu central atom only Cu-O bonds in the equatorial plane form the coordination bonds [1,2]. Contrary to very small apical Cu-O bond distance of 2.1443(1) Å, this interaction is not a coordination bond. Fully populated d_{z^2} orbital (2.019(5) e) is pointing directly to O(5) atom and accordingly the oxygen O(5) lone electron pair is repelling. The value of the O(5)-Cu-Cu* angle is 173.977(4)^o.

Comparing similar crystal structures we have found the crystal structure of Diaqua-bis(2,7-dimethyl-5-oxo-5H-pyrano(4,3-B)pyran-1-ium-4-oxalato-O,O')-copper(II) diperchlorate (YUSNIK) [3] in which the axial Cu-O(5) distance is also very short (2.160 Å), but the O(5)-Cu-O(5)* angle is exactly 180^o according to the symmetry. Preliminary B3LYP/G311G* quantum-chemical calcul-ations show highly unusual order of *d*-orbitals on the hexacoordinated central Cu atom.

In order to explain the electronic structure in YUSNIK the electronic structure study was undertaken.

The GEMINI R diffraction data at 100K will be used for electronic structure study. As the space group is a monoclinic (P 2_1/n) and the whole diffraction sphere was measured, a high redundancy was established. The multipole refinement and the results of both experimental and theoretical topological analysis will be discussed.

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Keywords: cu-complex, electronic structure, d-orbitals

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Electron density studies of magnetic di-nuclear complexes,

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In the aim to rationalise the conception of single molecular magnets the first step is to explore the interactions in molecular magnetic complexes and to understand their role. To this end we modeled the experimental electron density distributions in di-nuclear complexes. For example, we studied a cobalt(II) compound ([Co2(sym-hmp)$_2$](BPh$_4$)$_2$) which was theoretically studied by Tone *et al.* in 2007[1]. When decreasing the temperature, the magnetic susceptibility of this complex deviates from the Curie law (Fig. 1) because of the anti-ferromagnetic exchange interaction, but the susceptibility increases sharply at low temperature (< 20K). The theoretical analysis of Tone *et al.* showed that this behavior is explained by a tilt of local distortion axes around cobalt atoms and not by a paramagnetic impurity. A polarized neutron diffraction experiment was carried out in order to model the spin density and verify this hypothesis (Borta *et al.* (2011), accepted in Phys. Rev. B.)

To support this electronical approach and to better describe the metal-ligand interactions, we determined the charge density of this complex using high resolution X-ray diffraction at 100 K. We will present our multipolar model[2] and its description using various tools (Fig. 2). The different interactions will be described and comparison will be made with spin density results from polarized neutron diffraction experiments. We will finally introduce our project of a new program for joint refinements of a unique electronic model based on X-rays and polarized neutrons diffraction data.

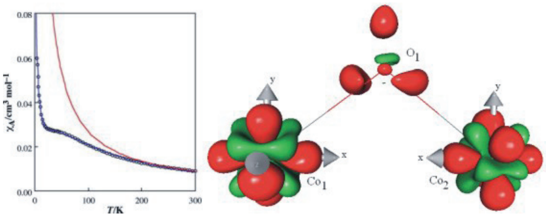

Fig.1. (left) Temperature dependencies of χ_A (O) at 100K.
Fig.2. Electron deformation density around each Co atom.

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Charge density analysis of K_2SO_4

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Despite being a common subject of chemistry textbooks, hypervalency issues are still a matter of debate. Concerning sulfur, and S-O interactions in particular, there is still an ongoing discussion on the nature of the bond. In general, two limiting pictures have been suggested. One with enhanced shared-shell features, leading in some cases to a "double bond" description, and another considering mainly "single-bonds" with enhanced polarization (closed-shell character). [1]

Here, we address this problem considering the sulfate group, SO_4^{2}, within a crystalline environment. The aim of the study is to experimentally investigate the structure and topology of K_2SO_4 and compare it with theoretical calculations on the current and on similar S-O containing compounds.

High quality, low temperature single crystal diffraction data have been collected at the ChemMatCARS beamline at the Advanced Photon Source (APS) at Argonne National Laboratory, Chicago. Extinction and absorption effects are minimized using a small crystal (~30 μm) and a high-energy (30 keV) synchrotron beam. The experimental charge density is determined by multipole least squares refinement using the program package *XD2006*. [2]

To highlight the bonding features, the topology and Laplacian of the electron density is analyzed by means of the Quantum Theory of Atoms In Molecules (QTAIM). [3] The results achieved from the inspection of these two observables have been compared with the ones obtained applying QTAIM to the density obtained from periodic *ab-initio* calculations. In order to provide a less biased and unambiguous comparison, the Source Function topologic descriptor has also been applied. [4]

To the best of our knowledge, no previous charge density analysis has been performed on a K_2SO_4 crystal. Nonetheless our results compares well with previously reported theoretical calculations on an isolated sulfate group. A polarized shared-shell (covalent) description arises, with the charge density being mainly localized in the region between the two atoms involved in the bonding interaction. [5]

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Keywords: K2SO4, charge density, source function

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Charge density of a Zn containing coordination polymer

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It is of general interest to understand how enzymes perform their catalytic activity and since many important macromolecules contain Zn^{2+} in the active site, detailed information about the electronic structure of this ion is highly desirable. One way to achieve information about this is using multipole modeling of high-resolution single-crystal X-ray data. However, due to the generally limited resolution of macromolecular X-ray diffraction data, full charge density analysis of small molecule analogs has been performed by some groups, [1-2] while others have studied Zn^{2+} in non-biological inspired molecules. [3-6] The general approach when modeling the charge density of these compounds varies between refining the 3d shell, the 4s electrons or both. Often, the analysis is complicated by anharmonic motion of the Zn-ions. [1-3, 6]

Here, we will present both experimental and theoretical charge density models of a Zn containing coordination polymer, $Zn(HCOO)_2(H_2O)_2$. The experimental CD is based on a highly redundant data set collected at 100 K on an Oxford Diffraction SuperNova (Mo) system with an Atlas CCD detector. To model the CD reliably several different approaches have been tried and few systematic differences have been observed. Contrary to many molecular Zn containing compounds this compound does not show anharmonic motion.

The best model is obtained by refining the allowed multipoles on both Zn sites along with distinct κ and κ' for the two sites. Remarkably the best fit is obtained by including the two 4s electrons on Zn. This leads to neutral atoms in the κ-formalism, but quite ionic charges using the QTAIM approach, namely 1.76 and 1.78. The d-orbitals are found to be completely filled.

The theoretical models are calculated using experimental geometry in CRYSTAL06, [7] using the B3LYP functionals. Generally, the two models agree quite well. Similarities and differences will be discussed.

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Keywords: charge density, coordination polymers, d-electrons

MS34.P11

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Hetero and homo-halogen intermolecular interactions via charge density analysis

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Halogen···halogen interactions are weak but highly directional in the formation of supramolecular assemblies in crystalline state. These manifest as $C–X_1···X_2–C$ short contacts and are characterized by three geometrical parameters, $R_{ij} = X_1···X_2$, two angles $\theta_1 = C–X_1···X_2$ and $\theta_2 = X_1···X_2–C$. Contacts with $\theta_1 \cong \theta_2$ are referred to as type I where as contacts with $\theta_1 \cong 180°$ and $\theta_2 \cong 90°$ are referred to as type II interactions. Recent charge density studies demonstrate attractive nature of interactions for type II contacts whereas type I contacts depict decreased repulsion due to polar flattening effects [1]. Fluorine atom has a relatively small size, high electronegetivity and very low polarizability than other halogens and its participation in intermolecular interactions have been subject of debate [2]. In order to decipher an interaction profiles of Cl···F and F···F intermolecular interactions, we have carried out charge density analysis of 4-fluoro benzoic acid and 4-fluoro benzamide using high resolution X-ray diffraction data ($\sin\theta/\lambda = 1.08$ Å^{-1}) collected on good quality crystals at 100 K. The nature of Cl···F and F···F intermolecular interactions has been analyzed using both experimental and theoretical charge density approaches. The topological features are derived from Bader's 'atoms in molecules' (AIM) approach [3]. Intermolecular Cl···F interaction in 2-chloro-4-fluorobenzoic acid is attractive in nature (type II interaction) while the