

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 ($\sim 30 \mu\text{m}$) 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

MS34.P10

Acta Cryst. (2011) **A67**, C447

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, $\text{Zn}(\text{HCOO})_2(\text{H}_2\text{O})_2$. 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

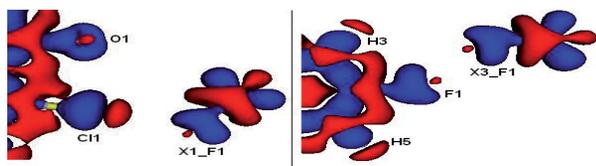
Acta Cryst. (2011) **A67**, C447-C448

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 $\text{C}-\text{X}_1 \cdots \text{X}_2-\text{C}$ short contacts and are characterized by three geometrical parameters, $R_{ij} = \text{X}_1 \cdots \text{X}_2$, two angles $\theta_1 = \text{C}-\text{X}_1 \cdots \text{X}_2$ and $\theta_2 = \text{X}_1 \cdots \text{X}_2-\text{C}$. Contacts with $\theta_1 \cong \theta_2$ are referred to as type I where as contacts with $\theta_1 \cong 180^\circ$ and $\theta_2 \cong 90^\circ$ 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 electronegativity 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 $\text{Cl} \cdots \text{F}$ and $\text{F} \cdots \text{F}$ 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 ($\sin\theta/\lambda = 1.08 \text{ \AA}^{-1}$) collected on good quality crystals at 100 K. The nature of $\text{Cl} \cdots \text{F}$ and $\text{F} \cdots \text{F}$ 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 $\text{Cl} \cdots \text{F}$ interaction in 2-chloro-4-fluorobenzoic acid is attractive in nature (type II interaction) while the

nature of F...F interactions in 4-fluorobenzamide show indication of a minor decrease in repulsion (type I interaction), though the extent of polarization on the fluorine atom is limited [4].



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Keywords: charge density, halogen interaction, organic fluorine

MS34.P12

Acta Cryst. (2011) **A67**, C448

Experimental and theoretical charge density studies and topological analysis of 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile: case of antiparallel cyano-cyano interaction

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High resolution diffraction data were collected on laboratories diffractometers for 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile, as part of our studies on intermolecular interactions in 4-nitro-1H-imidazole derivatives series.

The standard data processing within the Independent Atom Model (IAM) approximation, where the atoms are treated as 'spherical balls' in their ground state ie free, neutral and non interacting with neighbors does not take into account the density moved to the bonding regions and the charge transfer related to intermolecular interactions.

More realistic picture of the charge density distribution in crystals, which allows for inter- and intramolecular analysis can be derived from the Hansen-Coppens formalism [1] and Atoms-In-Molecule approach topological analysis [2]. The multipole model implemented in MoPro program suite [3] allows electrostatic and topological calculations either for small molecules or biological molecules at subatomic resolution.

The communication presents the experimental charge density analysis of the title compound, supported with the theoretical calculations. The standard resolution crystal structure was published some time ago [4], however no detailed analysis of the substituent's effect on the imidazole ring was performed. 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile consists of two strongly electronegative and withdrawing groups, and the main interactions in its crystal structure are four weak hydrogen bonds (C-H...N; C-H...O) and interesting antiparallel cyano-cyano interactions. This dipole dipole interaction is found to be the most common type of C≡N...C≡N contacts (which in fact are similar to C=O...C=O interaction), and will be analyzed in details by means of experimental data and theoretical calculations.

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Keywords: 4-nitro-1H-imidazole derivatives, multipole, refinement, antiparallel cyano interactions

MS34.P13

Acta Cryst. (2011) **A67**, C448

Observation of a conserved "selenium bond synthon" involving Se...O interaction

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Organoselenium compounds have gained extreme importance in recent years due to their diverse biological, medicinal and catalytic activities which essentially stem from the presence of a seemingly divalent selenium atom. An in depth understanding of the non bonded Se...X interactions (X=heteroatom like N, O etc) becomes essential as they play crucial role in enzyme-mimetic reactions and protein engineering [1,2]. Three polymorphs of the organoselenium antioxidant drug *m-Ebselenol*, 2-(3-hydroxyphenyl)-1,2-benzisoxazol-3(2H)-one [3] have been generated by tuning the solvent polarity and their crystal structures have been analyzed. Polymorph I, which crystallizes in a noncentrosymmetric space group *Pna2₁* has O-H...O hydrogen bond chains propagating in a catemeric fashion whereas polymorphs II and III which crystallize in centrosymmetric space groups, *Pbcn* and *P2₁/c* respectively form centrosymmetric O-H...O hydrogen bond dimers. In all polymorphic forms as well as in the original drug *Ebselen* [4] and its derivatives we have identified a new conserved "selenium bond synthon". This is formed by strong Se...O and a surrogate C-H...O interaction which is conserved in all the structures as shown in Figure 1. The intricate nature of the Se...O interactions analyzed by both experimental and theoretical charge density analysis will be presented[5].

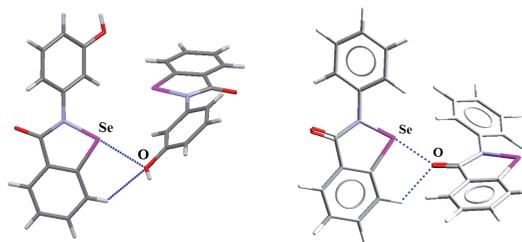


Figure1. Conserved "selenium bond" interactions in m-ebselenol and ebselen

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Keywords: Se...O interaction, Selenium bond synthon, crystal engineering

MS34.P14

Acta Cryst. (2011) **A67**, C448-C449

Non-Covalent Interactions descriptor using experimental electron densities

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