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Detailed investigation of the charge density distribution in concomitant polymorphs of 3-acetylcoumarin [1] in terms of experimental and theoretical densities show significant differences in the intermolecular features when analyzed based on the topological properties via the quantum theory of atoms in molecules [2]. The two forms, triclinic (form **A**) and monoclinic (form **B**) crystallize in centrosymmetric space group, form **A** in  $P\bar{1}$  ( $Z'=2$ ) and form **B** in  $P2_1/n$  ( $Z'=1$ ) and pack in the crystal lattice via weak C-H...O and C-H... $\pi$  interactions. The electron density maps in two forms demonstrate the differences in the nature of the charge density distribution in general. The net charges derived based on the population analysis via multipole refinement and also the charges evaluated via integration over the atomic basins and the molecular dipole moments show significant differences between the two forms. The lattice energies evaluated at the HF and DFT (B3LYP) methods with 6-31G\*\* basis set for the two forms clearly suggest that form **A** is thermodynamically stable compared to form **B**. Mapping of electrostatic potential over the molecular surface showing dominant variations in the electronegative region bring out the differences between the two forms.

[1] Munshi P., Venugopala K. N., Jayashree B. S., Guru Row T. N., *Cryst. Growth Des.*, 2004, **4**(6), 1105. [2] Bader R. F. W., *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, UK, 1990.

**Keywords:** charge density distribution, polymorphs, lattice energy calculations

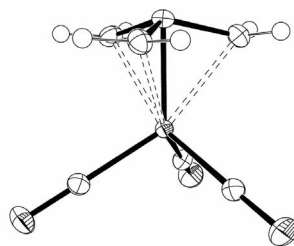
#### P.14.06.2

*Acta Cryst.* (2005). A61, C424

#### Experimental and Theoretical Charge Densities of $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)$

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Topological analysis of the experimental charge density of  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)$  (1) based on high resolution X-ray diffraction data collected at 100K is presented. The nature of the metal-ligand interaction is examined using the Atoms in Molecules (AIM) approach. The interaction between the iron atom and the carbon atoms of the trimethylenemethane ligand has been explored in depth. Theoretical DFT studies on the molecule calculated at the B3LYP/6-311++G(2p,2d) level show close agreement with the experimental results.



ORTEP diagram of  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)$

**Keywords:** experimental charge density, DFT, carbonyl

#### P.14.06.3

*Acta Cryst.* (2005). A61, C424

#### Multipole-Refined Charge Density Study of Diopside

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The electron density distribution of diopside at ambient conditions has been determined by X-ray diffraction and refined through the multipole model of electron density, following the formalism of Stewart [1].

The final multipole refinement includes two extinction parameters, according to the Sabine model, and two kappa expansion/contraction parameters (one for O and the other for Si, Ca and Mg valence monopoles). The expansions over the spherical

harmonics were truncated at the octopole level.

Topological analyses of the electron density and its Laplacian distributions [2] reveal that the bonding character of the four Si–O bonds is intermediate between ionic and covalent, as previously found for stishovite and coesite. As expected, the Mg–O and Ca–O bonds are definitely ionic. Determination of the atomic basins results in charges of +3.2(2)  $e$  for Si and –1.6(1)  $e$ , on average, for the oxygen atoms. The charges calculated for Mg and Ca are very close to the formal values. Our atomic charges are then more ionic than the corresponding ones determined by Sasaki et al. [3].

The program VALTOPO [4] was used for refinements and topological analysis of the experimental density.

[1] Stewart R. F., *Acta Crystallogr. Sect. A*, 1976, **32**, 565. [2] Bader R. F. W., *Atoms in Molecules - A Quantum Theory*, Oxford University Press, Oxford, 1994. [3] Sasaki S., Fujino K., Takéuchi Y., Sadanaga R., *Acta Cryst. Sect. A*, 1980, **36**, 904. [4] Bianchi R., Forni A., *J. Appl. Crystallogr.*, 2005, **38**, 232.

**Keywords:** charge density distribution, topological properties of charge distribution, silicates

#### P.14.06.4

*Acta Cryst.* (2005). A61, C424

#### Topological Analysis of Bio-molecules

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Intra and intermolecular interactions of bio-molecules are investigated in terms of topological analyses. Ultra high resolution data helped us to determine the more accurate positions of atoms in protein and nucleic acid. We could find the hydrogen atoms in the difference Fourier maps. We also introduce the bio-molecule databank to the macromolecule and describe the more exact electron density of the structures. The electron density could be transferred to macromolecules as a multipole model which may be used to derive some physical properties including bond orders, electrostatic potential, hydrogen bond energies, bond paths, and atomic domains, atomic or fragment charges and their possible delocalization. When we build an adequate databank of the electron densities, it will be useful to refine more accurately the lower resolution crystal structures. The electron densities are obtained both from X-ray diffraction data at low temperature and from a periodic density functional theory calculation. The features of the deformation densities, Laplacian distributions, bond paths, and atomic domains are shown to describe the variety of bonding. All the interactions are verified by the location of the bond critical point and its associated topological properties.

**Keywords:** charge density studies, multipole model, topological properties of charge density

#### P.14.06.5

*Acta Cryst.* (2005). A61, C424-C425

#### Charge Density and Topological Properties of Chosen Aromatic Nitramines

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Aromatic nitramines rearrange under the influence of elevated temperature or diluted mineral acids. The migration is entirely intramolecular, *i.e.* the *N*-nitro group shifts three or five atoms from its original position, still remaining bound to the aromatic residue [1]. The mechanism of the nitramine rearrangement remains still unclear. Analysis of charge density distribution in aromatic nitramines could bring the grounds for electron reasons of their interesting properties *viz.* structure–reactivity relationships and the role of an acidic catalyst. Charge density of chosen aromatic nitramines have been studied to understand those special properties. Conjugation between  $\pi$ -electron systems should divert the charge distribution within the  $\text{NNO}_2$  group and give rise to some observable changes in its geometry and

chemical properties of the nitramine [2].

In the communication will be shown results of structure determination together with a charge density analysis of N-phenyl-N-methylnitramine together with 1-nitroindoline. Topological properties associated with the bond critical points (BCP), molecular geometry, crystal packing and topological properties of those compounds will also be presented.

[1] Daszkiewicz Z., Zaleski J., Nowakowska E., Kyzioł J., *Pol. J. Chem.*, 2002, 76, 1113. [2] Anulewicz R., Krygowski T., Gawinecki R., Rasała D., *J. Phys. Org. Chem.*, 1993, 6, 257.

**Keywords:** charge density, nitramines, topological analysis

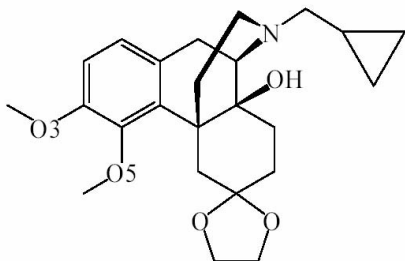
#### P.14.06.6

*Acta Cryst.* (2005). A61, C425

##### Rapid Charge Density Data Collection

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A charge density study has been completed on 17-Cyclopropylmethyl-4,14-dihydroxy-3-methoxymorphinan-6-ethylene ketal, a member of an important class of opioid compounds. The two methoxy groups of this compound exhibit unexpected chemical reactivity. Addition reactions strongly favor the more sterically hindered O5 position rather than the O3 position.



Data were collected on an R-Axis Rapid Curved Image Plate. The statistical analysis of the data set as well as the complete results of the multipole refinement will be presented. This will include topological analysis as well as an analysis of the electrostatic potential.

**Keywords:** electron density distribution, charge density, chemical reactivity and structure

#### P.14.07.1

*Acta Cryst.* (2005). A61, C425

##### Experimental Electron Density of [Cu(phen)<sub>2</sub>Cl](NO<sub>3</sub>)(H<sub>2</sub>O)

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The electron density of the title complex was obtained from a high resolution (0.55Å) X-ray diffraction experiment at 100 K, with a KappaCCD diffractometer. Experimental data were collected with MoK $\alpha$  radiation. 11199 independent reflections were used in the refinements. The charge density model was obtained from the Hansen-Coppens formalism. R(F)=0.0368, wR(F)=0.0406.

The copper ion presents coordination between trigonal bipyramidal and square pyramidal. The chlorine atom and one phenantroline nitrogen are in the equatorial plane. Deformation density maps around the copper ion and its d-orbital occupations can be explained in terms of crystal field theory and the  $\pi$ -donating effect of chlorine. Two hydrogen bonds with the water oxygen stabilize the crystalline complex: [Cl $\cdots$ H1–O(w) and O(w)–H2 $\cdots$ O(nitrate)].

Bader's<sup>1</sup> topological analysis of the electron density was performed. (3,-1) critical points were found in all chemical bonds. This analysis shows that the Cu–N and Cu–Cl bonds are ionic, and that the hydrogen bonds are electrostatic. The C–C, C–N and C–H

bonds, on the other hand, are covalent. (3,+1) critical points are present approximately in the center of each phenantroline ring, as well as in the center of the rings containing the copper atom.

[1] Bader R. F. W., *Atoms in Molecules – A Quantum Theory*, Oxford University Press, Oxford, 1994.

**Keywords:** copper compounds, crystal field theory, multipole refinements

#### P.14.07.2

*Acta Cryst.* (2005). A61, C425

##### Phase Transition and Charge Density Study of the m-carboxy-phenyl ammonium phosphite

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Hybrid materials resulting from the association of amino acids with phosphorous acid have a great importance in industry (frequency doubling; can be used as infrared detector and pyroelectric devices). The structure determination, thermal behaviour and the charge density of a new hybrid material of this family (m-carboxy phenyl ammonium monohydrogenphosphite C<sub>7</sub>H<sub>8</sub>NO<sub>2</sub><sup>+</sup>, H<sub>2</sub>PO<sub>3</sub><sup>-</sup> (m-CPAMP) at low and high temperature phases (LTP) and (HTP) respectively will be presented and discussed. This study will improve the understanding of the phase transition mechanism

Crystals of m-CPAMP, space group P2<sub>1</sub>/c, grown from aqueous solution undergo a reversible phase transition as evidenced by the behaviour of the unit-cell parameters versus temperature and by DSC measurements at about T<sub>c</sub> = 246  $\pm$  2 K. The reported phase transition appears to be first order type according to the thermal hysteresis, 3.6 K, and the observed abrupt jumps of the unit-cell parameters.

Using accurate X-ray single crystal investigations between 100 and 320 K, we were able to describe the transition by the rotation of both cations and anions by ca 4.6° around the crystallographic b axis induced by their translation along the b direction. We also will show how the precise description of the electron charge density and its topology modelled from high resolution X-ray diffraction helps in the description of the phase transition.

**Keywords:** hybrid materials, phase transitions, charge density

#### P.14.07.3

*Acta Cryst.* (2005). A61, C425-C426

##### Experimental Charge Density Study of Salicylaldehyde Thiosemicarbazone

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Thiosemicarbazones and their metal complexes are studied due to their wide biological activities spectrum, analytical applications and specific chemical and structural properties [1]. Up to date almost a thousand thiosemicarbazide based crystal structures have been reported, among them over one hundred were structures containing salicylaldehyde thiosemicarbazone (Sal-TSC) structural fragment. Sal-TSC and its derivatives have been recently reported as a potential thrombopoietin mimic agents [2], and two thiosemicarbazone based molecules are in clinical phase I due to their inhibitor activity against ribonucleotide reductase [3]. Here, we present an experimental charge density study of one of the most simple compound [4] of this family, in order to characterize the electronic and electrostatic properties of this potent pharmacophore fragment.

[1] Casas J.S., *et al*, *Coord. Chem. Rev.*, 2000, 209, 197. [2] Duffy K. J., *et al*, *J. Med. Chem.*, 2002, 45, 3573. [3] Finch R. *et al*, *Advan. Enzyme regul.*, 1999,