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., Kyziol 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

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Rapid Charge Density Data Collection

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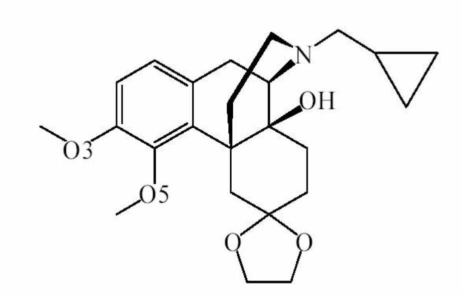
A charge density study has been completed on 17-Cyclopropylmethyl-4,14-dihydroxy-3-methoxymorphinan-6-ethylene ketal, a member of an important class of opioid compounds. The two methoxy groups of this compound exhibit unexpected chemical reactivity. Addition reactions strongly favor the more sterically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

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Experimental Electron Density of [Cu(phen)$_2$Cl](NO$_3$)(H$_2$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 MoKα 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 π-donating effect of chlorine. Two hydrogen bonds with the water oxygen stabilize the crystalline complex: [Cl···H1–O(w) and O(w)–H2···O(nitrate)].

Bader's[1] 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

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Phase Transition and Charge Density Study of the m-carboxyphenyl 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 $C_7H_8NO_2^+$, $H_2PO_3^-$ (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 $P2_1/c$, 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_c = 246 ±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

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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 derivates have been recently reported as a potential thrombopoetin mimic agents [2], and two thiosemicarbazone based molecules are in clinical phase I due to 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,

39, 3. [4] Chattopadhyay D. *et al*, *Acta Cryst.*, 1988, **C44**, 1025.

Keywords: electron density, electrostatic properties, structure-activity relationships

P.14.07.4

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Interactions in Selected Dicarboxylic Acids Derived from Electron Charge Density

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High-resolution X-ray diffraction data were collected for tartaric acid, malic acid and its adduct with urea at 80 K to obtain accurate crystal data and experimental electron density. The measurements were performed on Nonius KappaCCD difractometer equipped with Oxford Cryosystems 700 Series Cryostream Cooler. The quality of tartaric acid data was compared with that of the data obtained using a point detector at 105 K.

Data was interpreted using the multipole formalism [1] to derive the electron density and related properties such as the electrostatic potential and atomic moments. The electron density and its Laplacian extracted from the data were analyzed in terms of the topological properties of covalent bonds and non-bonded interactions [2].

Charge density and topological properties for the studied crystal structures were carried out to explore the character and role of both inter- and intra-molecular hydrogen bonds.

The interesting features related to the differences of electron density distribution were found for the same functional groups (hydroxyl and/or carboxyl). The differences caused by molecular interactions have influence on the molecular symmetry. The results are compared to those obtained for analogous molecules.

[1] Hansen N. K., Coppens P., *Acta Cryst.*, 1978, **A34**, 909. [2] Bader R. F. W., *Atoms in Molecules: A Quantum Theory*, Oxford, Calderon Press, 1995.

Keywords: electron charge density, dicarboxylic acids, interactions

P.14.07.5

Acta Cryst. (2005). A**61**, C426

Experimental Electron Density Distribution of Bis(thiosemicarbazide)-Zinc(II) Dinitrate

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Over three hundred transition metal complexes with thiosemicarbazide-based (TSC) ligand have been characterized by classical X-ray diffraction and seem to play a role in supramolecular chemistry [1]. In addition, a great number of TSC derivates present a very wide of potent pharmacological application [2, 3], while two of them (3-AP) and (5-HP) are used in clinical phase I or II against ribonucleotide reductase [4]. Understanding the interactions between the organic part and the divalent cation is essential in that case, since the mechanism involves a chelate compound with a divalent cation. Here, we present the electronic and electrostatic properties of the most simple TSC ligand coordinated with zinc(II). Cation behavior will be discussed in comparison with a zinc aspirinate compound [5].

[1] Babb J. *et al*, *Polyhedron*, 2003, **22**, 673. [2] Kasuga N.C. *et al*, *J. Inorg. Biochem.*, 2003, **96**, 298. [3] Beraldo H., *Quim. Nova*, 2004, **3**, 461. [4] www.vionpharm.com/treatmentp05.html [5] Spasojevic-de Biré A. *et al*, *J. Phys. Chem. A*, 2002, **106**, 12170.

Keywords: electron density, electrostatic properties, structure-activity relationships

P.14.07.6

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Electron Density, the Driving Tool towards Dynamics and Reactivity of Systems ?

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The fast development of photo-induced and time resolved diffraction leads to fundamental questioning about the proper modelisation of systems out of equilibrium.

Based on the role of Hellmann-Feynman force and its impact onto molecular dynamics, we have modelled the evolution of the charge density of simple molecules along a reaction path. Moreover, we have addressed the change of charge density in a molecular chain undergoing strong distortions, such as those initiating na soft mode transition.

The planned developments are strongly connected with the Cluster Partitioning Model recently developed in our group [1,2] which allows for a description of one particle density matrix of complex systems through a superposition of local contributions taking into account realistic environmental effects.

[1] Ragot S., Gillet J.M., Becker P., *Physical Review*, 2002, **B 65**, 235115. [2] Gillet J.M., Becker P., *J. Phys. Chem. Solids*, 2004, **65**, 2017.

Keywords: electron density, dynamics of molecules, reactivity

P.14.07.7

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Estimating ADP's of Hydrogen Nuclei for Charge Density Analysis

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Charge density analysis of X-ray diffraction data requires accurate treatment of the motion of all nuclei in order to deconvolute nuclear motion from the electron distribution. Presently, nearly 80% of charge density studies on molecular crystals assume isotropic motion of hydrogen nuclei, in large part due to the difficulty of performing accurate neutron diffraction studies on all systems of interest. However, failure to model the motion correctly not only alters the topology of the electron density close to the nuclei where the thermal motion has been simplified, but also in the vicinity of neighbouring nuclei [1].

Methods for approximating hydrogen atom ADP's based on a combination of rigid-body analysis and allowances for internal modes have been shown to be quite successful [1,2]. We have recently developed a new method for estimating hydrogen atom ADP's from first principles, using two layer “ONIOM” calculations [3] which mimic the effects of the crystal field and yield internal (high frequency) and external (low frequency) contributions to the nuclear motion. Results obtained for small molecules are consistent with neutron experiments at a variety of temperatures.

[1] Madsen A. O., Sorensen H. O., Flensburg C., Stewart R. F., Larsen S., *Acta Cryst.*, 2004, **A60**, 550. [2] Roversi P., Destro R., *Chem. Phys. Lett.*, 2004, **386**, 472. [3] Dapprich S., Komaromi I., Byun K. S., Morokuma, K., Frisch M. J., *J. Mol. Struct. (Theochem)*, 1999, **462**, 1.

Keywords: charge density analysis, vibrational analysis, ab-initio calculations

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Bonding in 5-Membered Cyclic Alkynes: Charge Density in 1-Zirconacyclopent-3-yne

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Small cyclic alkynes are, in general, unstable because of ring strain. Recently, 1-zirconacyclopent-3-yne complexes, *viz* 5-membered cyclic alkynes, were synthesized.[1] The bonding nature