single crystal X-ray diffraction and by DFT calculations. The X-ray crystal structure of $C_{10}H_{12}S_3$ was studied both at 295 K and at 100 K. The Space group is C2/m at 295 K, which is transformed to $P2_1/n$ at 100 K. The mirror symmetry perpendicular to 2-fold axis disappears at low temperature. Such reduction of symmetry elements was also found in a previous study on the 2,5-dimethyl-6a-thiathiophthene[1]. The bond lengths of two S-S bonds are crystallographically the same [2.3341(8)Å] at 295K, but are significantly different [2.3274(5) and 2.3393(5) Å] at low temperature. The experimental electron density is produced according to multipole model. The theoretical electron density is calculated by DFT calculation, where the basis set of 6-31G** is used for all the atoms but an additional diffuse function is added for S atom. Results on the electron density distribution will be presented in terms of deformation density, Laplacian maps and the topological properties. Sulfur K-edge X-ray absorption spectroscopy (XAS) is also undertaken to further our knowledge on the electronic configuration of S atom.

[1] Wang Y., Wu S. Y., Cheng A. C., *Acta Cryst*. 1990, **B46**, 850.
**Keywords: charge density, XAS, DFT calculations**

## P.14.07.13
**An Examination of All the Inter-ion Interactions in $(CH_3)_2N(H)CH_2CH_2N(H)(CH_3)_2$ $(SCN)_2$**
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N,N,N'N'-tetramethylethylenediammonium $(CH_3)_2N(H)CH_2CH_2N(H)(CH_3)_2]^+$ forms a di-thiocyanate hydrogen bonded salt in space group P-1 with Z = 1. X-ray data were collected on a Saturn 70 with Mo-$K_\alpha$ radiation to $2\theta(max) = 105^o$. The multipole refinement was performed via XD [1] and all the topological interactions were then investigated. Of the 8 unique C-H hydrogen atoms, all but one forms significant interactions to the thiocyanate anion. These interactions constitute 4 (C-H…S), 2(C-H…C), 2(C-H…$\pi$(C≡N)), and 2(C-H…N) with two bifurcated C-H interactions. All 10 interactions satisfy all the eight of Koch & Popelier's criteria [2] for a weak interaction, though one interaction of a bifurcated pair is only marginally satisfactory. The N-H…N classical hydrogen bond is found to have weakened in the crystal when compared with the theoretically calculated values for an isolated ion pair.

[1] Koritsanszky T. S., Howard S., Macchi P., Gatti, C., Farrugia L. J., Mallinson P. R., Volkov A., Su Z., Richter T., Hansen N. K., *XD (version 4.10, July): A computer program package for multipole refinement and analysis of electron densities from diffraction data*, 2003. [2] a) Koch U., Popelier P. L. A., *J. Phys. Chem.* 1995, **99**, 9747; b) Popelier P., *Atoms in Molecules*, Prentice Hall, UK, 2000, 151.
**Keywords: multipole refinement, hydrogen bonding, topological properties of charge distribution**

## P.14.07.14
**$Rb_4C_{60}$ Equation of States and Electronic Density Study by Compton Scattering**
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In the family of compounds $A_nC_{60}$ (A=K, Rb and Cs; n=1,3,4 and 6), $Rb_4C_{60}$ exhibits an unusual behavior : it is a non-magnetic insulator at ambient pressure, whereas expected as a conductor, even a superconductor (cf. $Rb_3C_{60}$), by theory [1]. Furthermore $Rb_4C_{60}$ undergo an insulator to metal transition under pressure around 0.8 GPa, as observed by NMR study of $Rb_4C_{60}$ [2].
We have performed combined Compton scattering (ID15B) and diffraction experiments at ESRF (ID-30), at pressures below and above the insulator-metal transition. Our diffraction experiment exhibits, for the first time, an abrupt jump in compressibility between 0.5 GPa and 0.8 GPa. We attributed this jump to a structural phase transition preserving the initial tetragonal symmetry [3]. By *ab-initio* calculations we reproduced the experimental phase transition and studied the pressure dependence of internal coordinates. Going further, the comparison with *ab-initio* LDA calculations allowed us to quantitatively evaluate contributions due to contraction of the unit cell as well as an unexpected contraction of the $C_{60}$ molecule itself, evidenced by Compton measurements. In fact, this $C_{60}$ molecule contraction leads to a major effect on electronic density of $Rb_4C_{60}$ compound [5].

[1] Erwin S.C., *Buckminsterfullerenes*, ed. W. E. Billups M. A. Ciufolini, VCH, New York, 1993, 217. [2] Kerkoud R. *et al*, *J. Phys. Solids*, 1996, **57**, 143. [3] Sabouri-Dodaran A.A. *et al.*, *Phys. Rev.*, 2004, **B70**, 174114.
**Keywords: structural change, Compton scattering, high-pressure X-ray diffraction**

## P.14.07.15
**An Examination of All the Inter-ion Interactions in Tetraphenyl-phosphonium Squarate**
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The tetraphenyphosphonium squarate salt crystallises with a hydrogen bonded dimeric squarate anion in space group $P2_1/n$ with Z = 4. X-ray data were collected on a Saturn 70 with Mo-$K_\alpha$ radiation to $2\theta(max) = 76^o$ at $-153^oC$. The multipole refinement was performed with XD [1] and all the topological interactions were then investigated. Currently of the 20 unique C-H hydrogen atoms, all but two form significant interactions either to the squarate ion (C-H…O interactions) or among the phenyl groups C-H….H-C, or C-H…$\pi$(Ph). The two remaining 'non-interacting' (C)H atoms are adjacent *ortho* hydrogen atoms, that look as though there ought to be an intramolecular H…H interaction though this has not yet been fully characterized. The remaining interactions satisfy all the eight of Koch & Popelier's criteria [2] for a weak interaction.The O-H…O classical hydrogen bond of the squarate is found to have weakened in the crystal when compared with the theoretically calculated values for an isolated dimeric anion

[1] Koritsanszky T. S., Howard S., Macchi P., Gatti, C., Farrugia L.J., Mallinson P.R., Volkov A., Su Z., Richter T., Hansen N. K., *XD (version 4.10, July): A computer program package for multipole refinement and analysis of electron densities from diffraction data*, 2003. [2] a) Koch U., Popelier P. L. A., *J. Phys. Chem.*, 1995, **99**, 9747; b) Popelier, P., *Atoms in Molecules*, Prentice Hall, UK, 2000, 151.
**Keywords: multipole refinement, hydrogen bonding, topological properties of charge distribution**

## P.14.07.16
**X-ray Charge Density of a New Magnetic Metal Organic Framework, $Mn_3(C_8O_4H_4)_3(C_5H_{11}ON)_2$**
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A new magnetic metal organic framework material has been synthesized, $Mn_3(C_8O_4H_4)_3(C_5H_{11}ON)_2$.[1] Magnetic susceptibility measurements from 2 to 400 K reveal anti-ferromagnetic ordering at ~4 K and a total magnetic moment of 6.0 $\mu_B$. The magnetic phase transition is confirmed by heat capacity data (2 - 300 K). The crystal structure is studied by conventional single crystal X-ray diffraction data at 300, 275, 250, 225, 200, 175, 150, 125 and 100 K, and synchrotron data at 20 K. The electron distributions around the two unique Mn centers are different, and both have substantial anisotropy. Orbital population analysis reveals large electron donation (1.7 e) to each Mn atom and the maximum possible number of un-paired electrons is 3.2 for both

Mn sites. Thus, there is a considerable orbital component to the magnetic moment. Bader topological analysis shows an absence of Mn-Mn bonding and the magnetic ordering is via super-exchange through the oxygen bridges. Formal electron counting suggests mixed valence Mn sites, but this is not supported by the Bader atomic charges, Mn(1)=+0.11, Mn(2)= +0.17. The topological measures show the dominant metal-ligand interactions to be electrostatic, and a simple exponential correlation is derived between Mn-O bond lengths and the values of $\nabla^2\rho$ at the bond critical points.

[1] Poulsen R. D., Bentien A., Chevalier M., Iversen, B. B., *J. Am. Chem. Soc.*, 2005, *submitted*. [2] Poulsen R. D., Bentien, A., Graber T., Iversen B. B., *Acta Cryst.*, 2004, **A60**, 382.

**Keywords: charge density, physical properties, metallorganic framework**

**P.14.07.17**
**Charge Density of 1-phenylpropane-1,2,3-triyl Trinitrate**
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The organic esters of nitric acid, the nitrates, are a class of products widely used for the treatment of a number of cardiovascular diseases. The prototype of nitrates is glyceryl trinitrate (GTN, nitroglycerin) It is an oil endowed with potent vasodilating and explosive properties. The major limit in its therapeutical use as vasodilator is an early development of the tolerance. 1-Phenylpropane-1,2,3-triyl trinitrate, a phenyl substituted GTN is characterised by having a high lipophilicity and interesting *in vitro* vasodilating profiles assessed on rat aorta strips pre-exposed to GTN.

A multipole  analysis has been applied to the low temperature X-ray intensities of *threo* form of 1-Phenylpropane-1,2,3-triyl trinitrate (mp 40.5-41°C); the electron density distribution obtained has been analysed using the QTAIM and the topological and energetic parameters of  intra- and inter-molecular interactions have been determined. The features of experimental and *ab initio* results are in good agreement and will be discussed.

**Keywords: experimental charge density, ab initio calculations, pharmaceuticals**

**P.14.07.18**
**$Ru_3(CO)_{12}$. Why $D_{3h}$?**
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$M_3(CO)_{12}$ (M= Fe, Ru, Os) may, in theory, adopt $D_3$, $D_{3h}$, $C_{2v}$ symmetries.  Iron carbonyl has a $C_{2v}$ structure, ruthenium and osmium carbonyls have $D_{3h}$ structures and only their derivatives show the least hindered $D_3$ configuration. The $D_{3h}$ structure of $Ru_3(CO)_{12}$  has been justified theoretically using steric or electronic parameters. Only a marginal attention was paid to the deformation of axial CO groups, and it  has been attributed to steric repulsion among oxygen atoms or to a more efficient orbital superposition between Ru atoms and C atoms. X-ray intensities of a $Ru_3(CO)_{12}$ crystal have been collected at low temperature and to them a multipole  analysis  has been applied; the electron density distribution obtained has been studied with the QTAIM  and the topological and energetic parameters of  intra- and inter-molecular interactions have been determined. Significant $C_{ax}\cdots C_{ax}$ interactions have been detected. The unexpected features of experimental electron density maps will be discussed.

**Keywords: experimental charge density, ab initio calculations, ruthenium cluster**

**P.14.07.19**
**On the (Non)-Planarity of 1,2,4,5-Tetramethoxybenzene**
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The conformation of methoxy groups on phenyl rings is a long-standing problem that has been tackled in the past with a variety of structure determination techniques and at different levels of quantum chemical calculations.

1,2,4,5-tetramethoxybenzene has two sets of *ortho*-dimethoxy moieties and displays a nearly planar structure in the crystal. We obtained a high quality data set at 150 K which was suitable for multipole refinement. The charge density maps and electronic properties in the bond critical points are compared with values from high-level quantum chemical calculations. The latter reveal a large number of energy minima on the potential energy surface.

The reason for the planarity of the molecule is not evident from the experimental structure, but the calculated bond orders in the molecule indicate that the stabilizing factor off-setting the repulsion between the free electron pairs of oxygen is the participation of the latter in the π-electron system of the ring.

**Keywords: ab initio calculations, charge density, conformational studies**
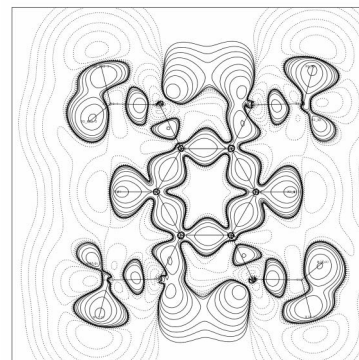
**P.14.08.1**
**On the Conditions Leading to the Gaussian Distribution of the Magnetic Moments in a Spin-glass State**
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The unperturbed ideal ferromagnetic system is described by a Hamiltonian of the Heisenberg type with the coupling constants $J_{ij}$ ($i$ and $j$ numerate the magnetic ions). The presence of dopants (or defects) affects the values of $J_{ij}$ for the magnetic ions surrounded by these dopants (or defects) in the random way. Thus the magnetic properties of such a system will depend on: the number of magnetic ions surrounding a j-th magnetic ion and interacting with it with the coupling constants $J_{ij}$,  the number of dopants (or defects) surrounding a j-th ion, the coupling constants between i-th and j-th ions in the presence of dopants (or defects), and the random probability distributions of appearance of dopants (or defects) between i-th and j-th ions. These distributions correspond – after introducing so-called "global" magnetic coupling constant (which turns out to be also random) - to the conditions of the central theorem of the theory of probability (the Lyapunov theorem). Thus the distributions of magnetic moments in such systems are Gaussian. Therefore one can use the Anderson-Edwards model of the spin-glass state in order to describe the system. Several examples of the spin-glass state are described in this approach.

**Keywords: spin glass, probability, central theorem of the theory of probability**

**P.14.08.2**
**Spin Density and Ordered Orbital of $YTiO_3$ Observed by X-ray Magnetic Diffraction**
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