

Mixtures of  $\gamma$ -oryzanol and  $\beta$ -sitosterol can form transparent organogels in edible oils. This process is a nice example of molecular self-assembly, where  $\gamma$ -oryzanol and  $\beta$ -sitosterol molecules form very well-defined supramolecular entities.

Small-angle X-ray scattering (SAXS) was used to elucidate the microstructure of the building blocks of these organogels in sunflower oil [3]. The measurements were performed at the high-brilliance ID2 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, allowing collection of SAXS data in the range  $0.06 < q/\text{nm}^{-1} < 4.5$ . Differential Scanning Calorimetry (DSC) was used to study the dissolution, melting and crystallisation behaviour of these systems during a heating-cooling-heating cycle.

It was found that the  $\gamma$ -oryzanol +  $\beta$ -sitosterol system forms tubules with a diameter of  $7.2 \pm 0.1$  nm and a wall thickness of  $0.8 \pm 0.2$  nm. Tubules prepared with  $\gamma$ -oryzanol-rich structurant show the least bundle formation, and can be supercooled during formation most easily. The tubes vanish at the melting point of the gel, in agreement with the loss of structuring capacity as observed in earlier experiments.

Moreover, a number of alternative sterols (e.g. stigmasterol, cholesterol, cholestanol) can replace  $\beta$ -sitosterol in the tubules. The diameter of the tubules for these systems varies between 7.2 and 8.0 nm, the wall thickness between 0.6 and 1.1 nm. The microstructure of the sterol(esters) in emulsions differs from that in pure oil.

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**Keywords:** organogels, self-assembly, small-angle X-ray scattering

#### FA4-MS33-P07

**Synthesis and Structural Resolution of C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>S·H<sub>2</sub>O, a new Thiosemicarbazone.** Eva Fernández-Zapico<sup>a</sup>, Rafael Mendoza-Meroño<sup>a</sup>, Laura Menéndez-Taboada<sup>a</sup> and Santiago García-Granda<sup>a</sup>  
<sup>a</sup>*Department of Physical and Analytical Chemistry, University of Oviedo, Spain.*  
E-mail: fernandezeva.uo@uniovi.es

Thiosemicarbazones, a class of compounds possessing a wide spectrum of potential medicinal applications, have been studied for their antitumoral, antiviral, antibacterial, antimalarial, antifungal, anti-inflammatory and anti-HIV activities [1]. These properties are thought to arise from the metal-chelating ability of these ligands. In almost all cases, the ligands are bidentate and bind to the metal through the S and hydrazinic N atoms, although there are examples of them acting as monodentate ligands binding only through sulphur [2]. The synthesis, crystal structure and electron density topological properties for title compound C<sub>14</sub>H<sub>13</sub>N<sub>3</sub>S·H<sub>2</sub>O are reported here.

The thiosemicarbazone adopts an E conformation with a trans configuration observed about the C=N bond. The dihedral angle between benzene ring and the thiosemicarbazone moiety is  $4.67(1)^\circ$ , this value suggests that are nearly coplanar, due to the delocalized  $\pi$ -electrons in the benzaldehyde

thiosemicarbazone fragment.

The water molecules are involved in an extensive intermolecular N—H...O hydrogen bonds and O—H...S interactions, which link the molecules into chains extended along b axis. Sulphur atom is also involved in N—H...S intermolecular interactions, favouring the crystal packing in the ac plane. An intramolecular N—H...N hydrogen bond contributes to stabilize the molecular conformation. The intermolecular distance value between centroids of the planar rings in the b axis direction (6.350 Å), does not suggests  $\pi$ -stacking interactions between parallel molecules.

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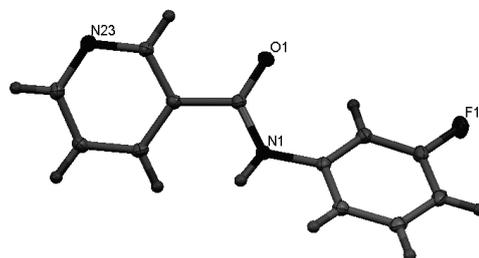
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**Keywords:** Thiosemicarbazones, Synthesis, Structural Determination, Electron Density Topology

#### FA4-MS33-P08

**Structural and systematic studies of a 3x3 isomer grid of nine N-(fluorophenyl)-pyridinecarboxamides**  
John F. Gallagher<sup>a</sup>, Pavle Mocilac<sup>a</sup> and Alan J. Lough<sup>b</sup>  
<sup>a</sup>*School of Chemical Sciences, Dublin City University, Ireland,* <sup>b</sup>*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6*  
E-mail: john.gallagher@dcu.ie

Nine N<sub>xx</sub>F isomers (x = 4-, 3- or 2-N/F substitution) were investigated and compared to determine factors underpinning (a) the roles of the F/N atom substituents on molecular conformation and overall supramolecular aggregation, (b) competition between intermolecular amide...amide (in N<sub>pp</sub>F) or intra-/intermolecular amide...pyridine hydrogen bond formation and (c) general structural and physico-chemical properties and trends.



Crystal structure analyses of the nine N<sub>xx</sub>F isomers reveal different primary interactions as N—H...N or N—H...O=C. N<sub>pm</sub>F and N<sub>po</sub>F are isomorphous and the latter is also disordered. Conformational analysis of the N<sub>xx</sub>F molecular conformations from DFT calculations differ from the crystal structure results for several isomers and highlighting the cooperative effects of intra-/intermolecular interactions in the solid state.

**Keywords:** Benzamides, Isomers, *ab initio*

#### FA4-MS33-P09

##### Planarity of tuberculostatic (aryl)heteroaryl- and heteroarocarbonimidoyl-dithiocarbazonic acid esters

Marek L. Główka<sup>a</sup>, Andrzej Olczak<sup>a</sup>, Jolanta Gołka<sup>a</sup>, Małgorzata Szczesio<sup>a</sup>, Katarzyna Gobis<sup>b</sup>, <sup>a</sup>Technical University of Łódź, Poland, <sup>b</sup>Medical University of Gdańsk, Poland

E-mail: [marekgl@p.lodz.pl](mailto:marekgl@p.lodz.pl)

A rise of the mortality rates and spread of tuberculosis also in developed countries, attributed to the emergence of multi-drug resistant strains, resulted in a search for new lead compounds. Several dithiocarbazonic acid esters obtained by Foks [1-3] have shown high activity against standard and resistant strains of *Mycobacterium tuberculosis*.

Our early crystallographic studies on type A structures (Scheme, X=N,CH) showed all of them to maintain planarity in the crystal state due to two intramolecular hydrogen bonds and extensive conjugation. Therefore we have assumed that their planarity is a prerequisite for tuberculostatic activity [4-6]. At that time the question could not be answered by inspection of CSD, as structures incapable of adopting planar conformation, for example N<sup>-</sup>-substituted, were not known.

Now, as we have solved more similar structures (Scheme), including compounds with forced twist at N-N bond through their substitution or with free ring orientation due to lack of ortho N atom, more specific conclusions have been drawn.

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**Keywords:** tuberculostatics, intramolecular interactions, SAR

#### FA4-MS33-P10

##### Structure and Magnetic properties of Manganese (III)-Schiff-Base-Hexacyanoferrate-Polymeric Compound.

Ayşe Karaoglu<sup>a</sup>, Hulya Kara<sup>a</sup>, Raif Kurtaran<sup>b</sup>, Akın Azizoglu<sup>b</sup>, Robert Hughes<sup>c</sup>, Mairi F. Haddow<sup>c</sup>, <sup>a</sup>Department of Physics, Balıkesir University, Balıkesir, Turkey, <sup>b</sup>Department of Chemistry, Balıkesir University, Balıkesir, Turkey, <sup>c</sup>School of Chemistry, University of Bristol, Department of Chemistry, Bristol University, Bristol, UK.

E-mail: [ayse\\_karaoglu84@hotmail.com](mailto:ayse_karaoglu84@hotmail.com), [aysekaraoglu84@gmail.com](mailto:aysekaraoglu84@gmail.com)

A cyano-bridged Mn(III)-Fe(III) complex, [Mn(L)]<sub>2</sub>Fe(CN)<sub>6</sub>(NEt<sub>3</sub>)(MeOH)<sub>2</sub> (**1**) (L=N,N-bis(5-bromo salicylidene)-2,2-dimethyl-1,3-diaminopropane) was prepared and characterized. The compound **1** crystallizes in Trigonal space group *P3(2)* with *a*= 28.5554, *b*= 28.5554, *c*= 19.2155 Å, γ= 120.00°. Single crystal X-ray analysis reveals that the complex assumes a cyano-bridged Mn<sub>4</sub>Fe unit. The four CN in the equatorial plane of the [Fe(CN)<sub>6</sub>]<sup>3-</sup> moiety bridge four Mn

ions, each in the *cis* position, which results in a 3D neutral layered structure giving a [-Mn-NC-Fe-CN-Mn-] linkage. The Mn ion assumes an elongated octahedral geometry, in which the equatorial sites are occupied by N<sub>2</sub>O<sub>2</sub> donor atoms of the Schiff base ligand, and the two axial positions are filled by two cyanide ion of [Fe(CN)<sub>6</sub>]<sup>3-</sup>. The magnetic measurement showed this complex to exhibit ferromagnetic behavior.

**Keywords:** cyanide complexes, molecular magnets, crystal engineering

#### FA4-MS33-P11

##### Structural and magnetic transitions in ionic fullerene complexes with metalloporphyrins. Salavat Khasanov<sup>a</sup>, Leokadia Zorina<sup>a</sup>, Dmitry Konarev<sup>b</sup>, <sup>a</sup>Institute of Solid State Physics, RAS, Russia, <sup>b</sup>Institute of Problem of Chemical Physics, RAS, Russia

E-mail: [khasanov@issp.ac.ru](mailto:khasanov@issp.ac.ru)

Ionic complexes containing C<sub>60</sub><sup>•-</sup> radical anions and metalloporphyrins coordinatively bound to *N,N'*-trimethylpiperazinium cations, {(TMP<sup>+</sup>)<sub>2</sub>M<sup>II</sup>TTP}·(C<sub>60</sub><sup>•-</sup>)<sub>2</sub>·(C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>)<sub>2</sub>·(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub> (M = Zn (**1**) and Mn (**2**)), have been obtained [1]. The crystal structures of **1** and **2** solved at 250 and 270 K, respectively, show layered packing in which fullerene layers alternate with the (TMP<sup>+</sup>)<sub>2</sub>M<sup>II</sup>TTP ones. Fullerenes form pairs in the layer with short center-to-center distance of 10.044 and 10.077 Å, respectively. The structures of **1** and **2** solved at 100 K showed the formation of singly bonded (C<sub>60</sub><sup>•-</sup>)<sub>2</sub> dimers. That results in the transition of **1** from paramagnetic to diamagnetic state accompanied by the disappearance of the EPR signal of C<sub>60</sub><sup>•-</sup> at 220-150 K. Dimerization in **2** results in decrease in magnetic moment from 6.36 to 6.00 μ<sub>B</sub> at 200-150 K and change in the shape of EPR signal. The room-temperature EPR signal shows a major broad component at *g* = 2.0678 (Δ*H* = 111.6 mT) attributed to both paramagnetic C<sub>60</sub><sup>•-</sup> and high-spin (TMP<sup>+</sup>)<sub>2</sub>Mn<sup>II</sup>TTP species having strong exchange interaction. After dimerization the signal is characteristic of isolated high-spin Mn<sup>II</sup>TTP (*g*<sub>⊥</sub> = 6 with |*A*| = 7.3 mT and *g*<sub>∥</sub> ≈ 2). Two TMP<sup>+</sup> cations can coordinate to M<sup>II</sup> in (TMP<sup>+</sup>)<sub>2</sub>M<sup>II</sup>TTP. However, a weak coordination bond is formed only with one cation with the M<sup>II</sup>...N(TMP<sup>+</sup>) distances of 2.489(2)-2.688(3) Å. As a result, metal atoms displace by ± 0.232(3) (**1**, 250 K), ± 0.231(1) (**1**, 100 K) and ± 0.4684(7) Å (**2**, 270 K) out of the porphyrin plane to be located above and below the porphyrin plane with equal occupancies for both positions. Symmetry of the crystal structure of **2** lowers from monoclinic to triclinic under cooling. That results in unequal 0.85/0.15 occupation of the Mn<sup>II</sup> positions at 100 K with the displacement of metal by 0.391(2) and 0.554(4) Å, respectively.

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