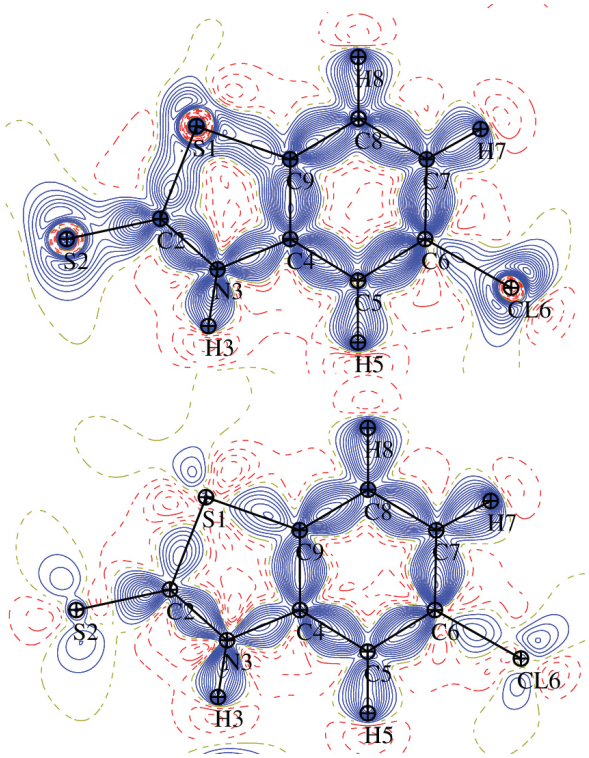

Figure 1. The static deformation density map of CMBZT, obtained from different data.

Keywords: charge density, thioamide, sulfur

MS28-P9 Charge density studies on polymorphic co-crystals

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Polymorphism is a widely-studied phenomena, and of huge importance especially in pharmaceutical industries, as well as a factor to consider in crystal engineering and solid-state studies. That a compound can exhibit different crystalline structures, often with differing physical properties, is remarkable, as well as the fact that the origin of such behaviour is often unknown. Multi-component systems, too, are widely studied and such systems can also exhibit this behaviour. We present the results of comparative studies of two polymorphic forms of the analgesic drug ethenzamide 1:1 co-crystallised with saccharin. The aim of this work is to further understanding of the differences between the structures and their related properties by investigating the electronic distributions, and the properties thereof, in the solid state.

Two polymorphs of the 1:1 co-crystal of ethenzamide (2-ethoxybenzamide, EA) and saccharin (SAC) have previously been reported [1]. Form I crystallises in the triclinic P-1 space group, whilst form II is monoclinic, P21/n. Both polymorphs display the primary carboxy-amide–imide heterosynthon interaction between molecules. However, it is at the second level of hydrogen bonding, extending the hydrogen bonding network through the structure, where polymorphic variation can be seen. Here extended 1D linear tapes are present in form I, generated via N-H•••O hydrogen bonding interactions, whilst form II exhibits stacked tetrameric motifs which utilise both N-H•••O hydrogen bonds and C-H•••O interactions. Thus, the polymorphs can be classified as synthon polymorphs at the second level of hydrogen bonding.

To investigate these structures further, high-resolution charge density distribution analysis has been carried out to enable differences in electronic structures to be determined and ascertain how these differences relate to the polymorphic behaviour. The Hansen-Coppens formalism [2] and Bader's AIM theory [3] provide a quantitative analysis and determination of both intra- and intermolecular interactions, in terms of their nature and role in these systems.

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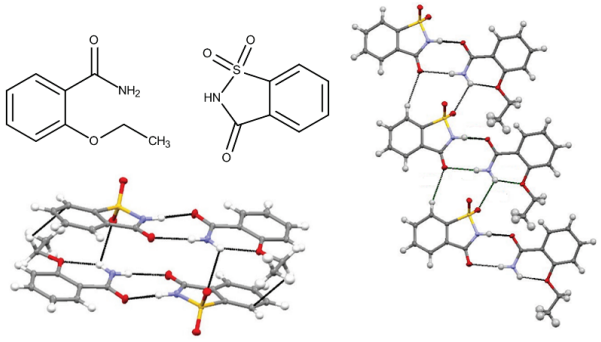

Figure 1. Top left: Structure of EA:SAC co-crystal, right: linear ID tape motif in form I, bottom left: tetrameric motif in form II.

Keywords: charge density, polymorphism, co-crystal, structure, interactions

MS28-P10 Non-Innocent role of ligands in some Ni organometallic complexes as viewed through the Spin Density Source Function

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A key feature of the non innocent metal ligand complexes is that the oxidation state of the central metal atom and the electronic structure of the ligands can not be *a priori* and unambiguously determined.[1] In this work we apply the recently introduced Spin Density Source Function[2] to a series of Ni metal complexes to get insight on the factors that lead to ferro- or anti-ferro magnetic coupling behaviour and to quantitatively distinguish whether the ligands play a innocent or non-innocent role. Three neutral Ni radical organometallic complexes, of general formula [CpNi(dithiolene)]$^{\bullet}$, are investigated, namely [CpNi(tfd)]$^{\bullet}$ (tfd=1,2-bis(trifluoromethyl) ethene-1,2-dithiolate) (**1**), [CpNi(mnt)]$^{\bullet}$ (mnt=maleonitriledithiolate) (**2**) and [CpNi(adt)]$^{\bullet}$ (adt=acrylonitrile-2,3-dithiolate) (**3**). They are all known to exist in doublet state (S = 1/2) and to show, in their dimeric forms, a strong anti-ferromagnetic coupling that can not be explained solely by short S···S intermolecular contacts[3]. In fact DFT calculations showed that spin density is strongly delocalized on the NiS_2 moiety and, more importantly, up to 20% of s(**r**) is delocalized on the Cp ring. As a result, the intermolecular Cp···Cp and Cp···dithiolene overlap interactions lead to anti-ferromagnetic couplings mediated by ligands that are commonly classified as innocent. The Source function enables to quantify to which extent the spin density is delocalized over the metal center and the Cp and dithiolene ligands, and to assess the role played by the π-stacking in the exchange interaction between molecules in their dimers. Finally, with the help of solid state quantum mechanical simulations it allows to detect quantitatively the effect of crystal packing on the spin density delocalization mechanism and on the resulting magnetic coupling in the solid state.

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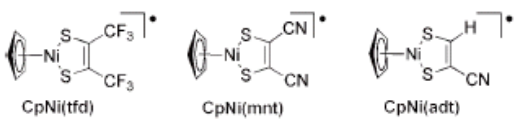

Figure 1.

Keywords: Non Innocent Ligands, Source Function, Spin Density, Magnetic Interactions