

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)][•], are investigated, namely [CpNi(tfd)][•] (tfd=1,2-bis(trifluoromethyl) ethene-1,2-dithiolate) (**1**), [CpNi(mnt)][•] (mnt=maleonitriledithiolate) (**2**) and [CpNi(adt)][•] (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 NiS₂ moiety and, more importantly, up to 20% of $s(\mathbf{r})$ 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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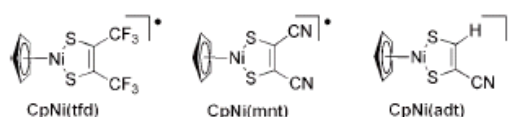


Figure 1.

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