

MS29-P3 Theoretical insights into the Rh...Rh interactionsFerdi G. Groenewald¹, Andreas Roodt¹

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Our theoretical investigation focuses on Rh...Rh interactions with the first observation of this metallophilic interactions dates back to 1975. We theoretically investigate numerous Rh(I) structures, synthesised in our group, containing Rh...Rh interactions that yield infinite 1D chains brought upon by the directionality of these interactions. The neutral crystal structures exhibit Rh...Rh distances ranging from 3.254(3) Å to 3.617(3) Å, with ligands ranging in steric bulk and electronic properties. Our aim is to characterise these interactions and to determine why these differences in the Rh...Rh separations occur. In particular, we shed light onto if these geometrical changes are brought upon by changes in the electronic state of the metal center influenced by the coordinating ligands, the energies of the orbitals or due to changes in intermolecular interactions between adjacent ligands. Characterisation of the Rh...Rh interactions were determined from the properties of the Bond Critical Point (BCP) calculated with the Atoms in Molecules (AIM) theory. Electrostatic Surface Potentials were calculated to evaluate the electrostatic properties of the complexing monomers that could give additional insight into packing preferences in the solid state. Noncovalent Interactions (NCI) plots were utilised to shed light on additional interactions. This is to better our understanding of the influence of ligands on the Rh...Rh distances. Furthermore, these interactions yield interesting optical properties which is dependent on the Rh...Rh interactions that can induce shifts in the UV visible spectra as the interaction strength changes. Our work seem to bare commonalities with Pt(II) packing in the solid state. A summary of our work thus far will be presented and correlated with solid state X-ray crystallographic and spectroscopic data for a range of complexes wherein the electron donating properties of the ligands were systematically varied.

Keywords: Computational Chemistry, Metallophilic, Atoms in Molecules, Interaction

MS29-P4 The Crystalline Sponge Method for the Unambiguous Structural Determination of Non-Crystalline Compounds: Reproducibility, Reliability and Versatility.Lilian M. Hayes¹, Dr Caroline E. Knapp¹, Dr Neil J. Press², Prof Derek A. Tocher¹, Prof Claire J. Carmalt¹

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The crystalline sponge method, first introduced by Fujita and co-workers in 2013,¹ provides a revolutionary way of investigating the structures of liquid and amorphous compounds previously not amenable to single-crystal X-ray diffraction studies. It involves the encapsulation of non-crystalline compounds of interest into the pores of a specific crystalline sponge – the metal-organic framework (MOF) $\{[(ZnL)_3(\text{tris}(4\text{-pyridyl})\text{-}1,3,5\text{-triazine})_2 \cdot x(\text{solvent})]_n\}$. Through the formation of guest – host interactions the guest may be rendered regularly ordered and thus capable of contributing to Bragg peaks and a diffraction pattern. As such, its structure may be solved alongside that of its host. Whilst implementation of the technique has not been without its difficulties, its applicability has been tested and its value clearly demonstrated. However, in order for the method to be applied routinely to compounds with a broad range of functionalities and size we must gain more understanding as to why this MOF acts so successfully as a crystalline sponge and apply these findings to the design and synthesis of alternative host frameworks.

Here we present a systematic study detailing the encapsulation of a range of chemically simple functionalised aromatic molecules and assess how guest – host and guest – guest interactions vary with specific functionality of guest molecules, such as aldehyde, halogen and nitrile groups. These include the formation of hydrogen bonds, pi – pi and CH – pi interactions and those involving halogens. We also discuss the reproducibility of guest positioning within the void space and why certain positions may be favoured.

(1) Inokuma, Y.; Yoshioka, S.; Ariyoshi, J.; Arai, T.; Hitora, Y.; Takada, K.; Matsunaga, S.; Rissanen, K.; Fujita, M. *Nature* **2013**, *495* (7442), 461–466.

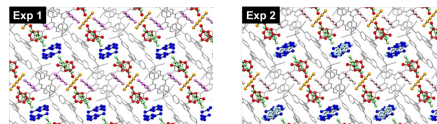


Figure 1. Plot of X-ray crystal structures of repeat encapsulation experiments with 1,3-dichlorobenzene. Guest molecules coloured to show the reproducibility of their locations in the framework (shown in grey).

Keywords: Crystalline Sponge, pi – pi interactions, guest – host complexes, metal organic frameworks