

**MS32-O2** Recent results with halogen bonds in crystal engineeringGautam R. Desiraju<sup>1</sup><sup>1</sup>. Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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In a halogen bond, an electrophilic halogen atom makes an attractive contact with a negatively polarized species. Halogen bonds are somewhat similar and somewhat different from hydrogen bonds. They are similar because the protagonist atoms—halogen and hydrogen—are both electrophilic in nature. They are different because the size of a halogen atom is not negligible, unlike the small hydrogen atom in a hydrogen bond. In terms of crystal structure design, halogen bonds offer a unique opportunity in terms of the strength, size of halogens and a gradation of interactions. These gradations may be used in the design of ternary and possibly higher cocrystals. The specific directionality of the halogen bond makes it a good tool to achieve interaction orthogonality. Although halogen bonds have been mostly used in crystal engineering as if they were exactly like hydrogen bonds, this may be the right time to look at the *differences* between these two interaction types and exploit them in more subtle ways in crystal engineering. With a formal IUPAC definition in place and explosive growth in halogen bond research during the past few years, one may expect rapid growth in this area,

**Keywords:** crystal engineering**MS32-O3** Implication of halogen bonding in ligand substitution reactions: solid state studiesMarta E.G. Mosquera<sup>1</sup>, Pilar Gomez-Sal<sup>1</sup>, Francisco Fernández-Palacio<sup>1</sup>, Lina M. Aguirre<sup>1</sup><sup>1</sup>. Department of Organic Chemistry and Inorganic Chemistry, University of Alcalá

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The studies on the Halogen Bonding (XB) interaction have grown exponentially since the beginning of the century. Although XB interaction has been known for a long time, its importance has been particularly acknowledged in the last two decades.[1] In fact, the interest on XB keeps growing due to the broad array of areas where its influence has been observed, ranging from material science to biology.[2] In this context, one of our research areas is focused in the preparation of supramolecular organometallic networks, containing either main group or transition metal complexes using the versatility of the XB interaction.[3] In particular, the coordination compound [Ru(X)<sub>2</sub>(CNR)<sub>4</sub>] is an interesting building block for the preparation of such networks and depending on the species involved in the interaction we can reach the formation of networks with different topology. As such, when the XB donor is IC<sub>6</sub>F<sub>4</sub>I it is observed the generation of the *synthon* M—Cl...X—C that renders the formation of a monodimensional zig-zag arrangement (figure 1 right). Changing the XB donor to X<sub>2</sub> it is possible to generate the bidimensional honey-comb network shown in figure 1 left. In the course of these studies we encountered an unexpected substitution reaction on the ruthenium coordination sphere where the chloride ligands are substituted by iodides. This is an unusual process since the only source of iodide in the reaction media was iodine. The isolation of several intermediates with different substitution degree and showing XB interactions in the solid state network gave us clues on the reaction mechanism and evidenced the clear influence of the XB species in this unusual reaction process.

**References**

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Figure 1.

**Keywords:** Halogen Bonding, Substitution Reactions**MS32-O4** Engineering ternary cocrystals by orthogonal hydrogen and halogen bondsFilip Topić<sup>1</sup>, Kari Rissanen<sup>1</sup>

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In the still maturing field of halogen bonding, we have been especially interested in discovering new halogen bonding motifs [1,2] and applying them in crystal engineering [3].

The particular robustness of C–I...S halogen bond with thioureas has recently been highlighted, persisting even in solution [4]. In addition to that, the orthogonality of such interaction to hydrogen bonds has also been demonstrated [5], offering the possibility of constructing complex systems where the two can operate independently.

Also knowing that the crown ethers reliably cocrystallize with thioureas [6,7], this prompted us to combine thioureas with crown ethers and various (aromatic and non-aromatic) perfluorinated halogen bond donors, resulting in a large number of ternary cocrystals with high supramolecular yield. Besides the success of the strategy and the aesthetically appealing structures, these systems present other intriguing aspects, such as differing behavior of bromine- and iodine-based donors, tunable metrics and, finally, the possibility of constructing porous materials.

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