

## MS30 Halogen and chalcogen bonding in the solid state

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### MS30-O1

#### Chalcogen bonding in synthesis and design of arylhydrazone dyes

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Inter- and intramolecular noncovalent interactions (hydrogen, aerogen, halogen, chalcogen, pnicogen, tetrel and icosagen bonds, as well as cation- $\pi$ , anion- $\pi$ ,  $\pi$ - $\pi$  stacking,  $n$ - $\pi^*$ , agostic, anagostic, lipophilic, etc. interactions) play a crucial role in the synthesis, crystal engineering, structural organization of biochemical systems, molecular recognition, drug delivery and design, decoration of materials, electrochemical immobilization and catalysis.<sup>1</sup> Among these weak forces recently explored, chalcogen bonding has received a particular attention in view of its *directionality, hydrophobicity, tunability, donor atom size and multiplicity*.<sup>2</sup> These properties have successfully been utilized in catalysis, construction of co-crystals or ions having complementary acceptor and donor sites. Similarly to the hydrogen bonds,<sup>3</sup> the chalcogen bonds are classified into several fundamental types: negative charged assisted ( $\text{Ch}\cdots\text{D}^-$ ), positive charged assisted ( $\text{Ch}^+\cdots\text{D}$ ), conventional (or "neutral") ( $\text{Ch}\cdots\text{D}$ ) and resonance assisted chalcogen (RACHB) bonds.<sup>2</sup> In comparison to other types of chalcogen bonding the RACHB was only theoretically highlighted, concerning a kind of intramolecular Ch-bonding strengthened by a conjugated  $p$ -system in multi-membered ring(s). The lecture will demonstrate the role of RACHB in the synthesis and design of arylhydrazones of sulfamethizole.

References:

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### MS30-O2

#### Halogen-bonding mediated reactions

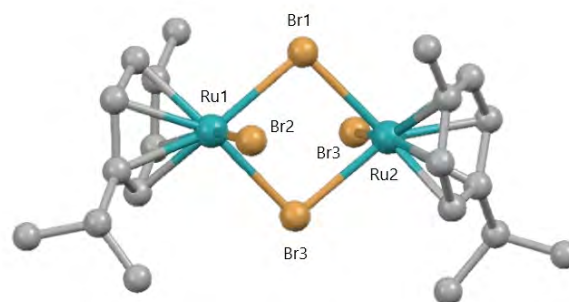
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Along this century, the importance of halogen bonding has been increasingly acknowledged specially in molecular recognition processes, as structural directing tool and in some physical properties.[1] However, an area whose influence has been less studied is its role in reactivity, even though halogen bonding interactions can be found at the starting point of some chemical processes.[2]

In our group we are interested in the preparation of halogen bonding supramolecular organometallic networks, containing either main group or transition metal complexes. In these studies, we have observed that the formation of this XB interaction is the first step to the substitution reactions of halide ligands in isocyanide transition metal complexes of the type  $[\text{Ru}(\text{X})_2(\text{CNR})_4]$  when reacted with  $\text{Br}_2$  or  $\text{I}_2$ . [3] The reaction takes place independently of which one is the halogen used and the halide ligand, although the reaction rate varies depending on the nature of the halogens. As well the electronic density on the metal influences the reaction rate. The extension of these studies to other co-ligands such as arene groups shown that the process also takes place and new species can be generated, as shown in the figure. The study of these systems has led to a whole range of XB-based networks were  $\text{Cl}\cdots\text{Br}$ ,  $\text{Cl}\cdots\text{I}$ ,  $\text{Br}\cdots\text{Br}$ ,  $\text{I}\cdots\text{I}$  and  $\text{I}\cdots\text{Br}$  are present which has allowed us to perform a comparison of the XB parameters for the different networks isolated. We have also extended this work to organic molecules, in this case a halide abstraction by halogen bonding has been detected in a process that led to the formation of new C-S bonds. The influence of halogen bonding in the reactivity, either in metallic complexes or in organic molecules, gives a dynamic picture for this interaction and expands even further its applications.



References:

- [1] Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. (2016). Chem. Rev., 116, 2478-2601; Brammer, L.; Espallargas, G. Minguez and Libri, S. (2008) CrystEngComm, 10, 1712-1727.  
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