MS30 Halogen and chalcogen bonding in the solid state

Chairs: Dr. Guillermo Minguez, Prof. Giuseppe Resnati

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-π, anion-π, π-π stacking, n-π*, 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.[1] 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.*[2] 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,[3] the chalcogen bonds are classified into several fundamental types: negative charged assisted (Ch···D^-), positive charged assisted (Ch^+···D), conventional (or "neutral") (Ch···D) and resonance assisted chalcogen (RAChB) bonds.[2] 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.

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Keywords: Chalcogen bonding, Noncovalent interactions, Hydrazone dyes

MS30-O2

Halogen-bonding mediated reactions

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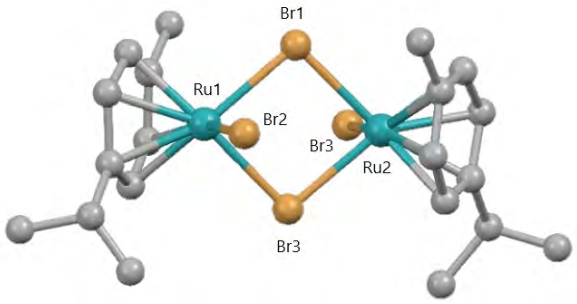
Along this century, the importance of halogen bonding has been increasingly acknowledged specially in molecular recognition processes, as structural directing tool and in some physical properties.[1] However, an area whose influence has been less studied is its role in reactivity, even though halogen 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 [Ru(X)2(CNR)4] when reacted with Br2 or I2.[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 Cl···Br, Cl···I, Br···Br, I···I and I···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.



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MS30-O3

Thiazoliums and selenazoliums as Chalcogen Bond donors in crystals

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In-depth understanding of weak bonds, commonly named interactions, is essential in designing and tailoring of a wide variety of properties in supramolecular chemistry, crystal engineering, materials science, and biology. A detailed comprehension is available for some noncovalent interactions, and this is the case, for instance, for the well-known Hydrogen (HB) and Halogen bonds (XB). A substantially more limited set of information is available for some other weak bonds. The ongoing *IUPAC project n° 2016-001-2-300* (https://iupac.org/projects/project-details/?project_nr=2016-001-2-300) aims to register the emerging consensus on proposals suggesting to use terms Chalcogen, Pnictogen, and Tetrel bonds exclusively for interactions wherein Groups 14-16 elements are the electrophile sites [1]. The purpose of this research is to partially fill this dearth of information by exploring the potential of Chalcogen Bond (CB) which is the attractive interaction wherein an element of Group 16 is the electrophilic site [2]. While there is a plethora of papers examining CB from the theoretic point of view, the experimental studies on this weak bond are lacking. Modeling supports the understanding of the CB as a case of σ-hole bonds [3]. Halogen Bond (XB) also belongs to the family of σ-hole interactions. A decisive contribution to the stereoelectronic understanding of the XB was given by computational studies on the distribution of the electron density in halogen atoms. These studies demonstrated the anisotropic charge distribution on halogen atoms forming one covalent bond and paved the way to the definition of the σ-hole: a region of depleted and often positive electrostatic potential on the surface of halogen atoms. We based our strategy to investigate CB on this robust experimental background available for XB, the parent interaction of the family. Taking into account the mindset promoted by XB, we designed a series of thiazolium/selenazolium-containing molecules, as models to study CB in systems of increasing structural and functional complexity (Fig. 1). These systems are chosen in order to profile the interactional landscape accessible to molecules important in biological systems and as molecular materials. Specifically, these model compounds are expected to give information of the preferred interactions formed, among others, by Thiamine (Fig. 1, vitamin B1) and related cofactors, by Thioflavin T, a standard dye for amyloids structures, and by thiazolium/selenazoliun-containing cyanine dyes. Close contacts between sulphur/selenium and an electron-donor group will be discussed in several systems, thiamine and cyanine dyes included, as *bona fide* cases of CBs.