

[3] Vidal, F.; Dávila, M.^a A. San Torcuato, A.; Gómez-Sal, P. & Mosquera, M. E. G. (2013). *Dalton Trans.*, 42, 7074-7084; Mosquera, M. E. G.; Gómez-Sal, P.; Díaz, I.; Aguirre, L. M.; Ienco, A.; Manca, G. & Mealli C. (2016) *Inorg. Chem.*, 55, 283-291; Mosquera, M. E. G.; Gomez-Sal, P.; Egido, I.; Lopez Lopez, M. & Hortelano, C. (2017) *Faraday Discussions*, 203, 257-283

Keywords: XB networks, ruthenium complexes, substitution reactions

MS30-O3

Thiazoliums and selenazoliums as Chalcogen Bond donors in crystals

Patrick Scilabra¹, Konstantis F. Konidaris¹, Giancarlo Terraneo¹, Giuseppe Resnati¹

1. Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131, Milano, Italy

email: patrick.scilabra@polimi.it

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/selenazolium-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.

Fig. 1 – Crystal structures of thiamine monophosphate (right) and two model compounds showing the presence of CBs between the sulphur atom of thiazole ring and neutral and/or anionic electron-donors.



References:

- [1] Terraneo, G & Resnati, G. (2017) *Cryst. Growth Des.* 17, 4, 1439-1440
- [2] Cavallo G., Metrangolo P., Pilati T., Resnati G. & Terraneo G. (2014) *Cryst. Growth Des.* 14, 6, 2697-2702
- [3] Politzer P., Murray J. S., Clark T. & Resnati G. (2017) *Phys. Chem. Chem. Phys.*, 19, 32166-32178

Keywords: Chalcogen bond, Crystal engineering, σ -Hole interactions

MS30-O4

Chalcogen and halogen bonding in case of multiple i...i and i...s interactions with ambiguous mutual orientations

Irina Yushina¹, Natalya Tarasova², Ekaterina Bartashevich¹

- 1. Laboratory of Multiscale modelling of multicomponent materials, South Ural state University, Chelyabinsk, Russia
- 2. Theoretic and applied chemistry, South Ural State University, Chelyabinsk, Russia

email: iushinaid@susu.ru

The question of identification and characterization of non-covalent interactions lies in the center of modern crystal engineering problems. Ambiguity of geometric criteria generates the necessity to use electronic descriptors in cases with competitive interactions or unobvious orientation of nucleophilic and electrophilic sites of interacting atoms in molecule and crystals.

In this study we demonstrate several examples of multiple I...I and I...S interactions and test reliability and visibility of the series of electronic criteria. Organic crystals with polyiodide anions and S,N-containing heterocyclic cations open possibility for the design of wide row of nonlinear optical and semiconductor materials as well as dye-sensitized solar cell devices. Variety of crystal structures, available for material engineering is due to the ability of sulfur and iodine atoms form different types of noncovalent interactions, organized in various types of 3D structure motives: nets, layers, chains, cages.

Our computational approach includes solid state quantum-chemical calculations with periodic boundary conditions and atomic basis sets, implemented in CRYSTAL14 package. Electronic criteria based on characteristics of calculated electron density such as ELF distribution and superposition of atomic basin boundaries in the electron density and electrostatic potential are used (TOPOND14).

Testing these computational tools on the series of boundary cases, different types of mutual orientations of interacting atoms can increase reliability of these criteria. The central point of the work is the demonstration of possibility of computational approaches to elucidate which of the interacting atoms acts as acceptor and which as a donor and thus to assign the type of interaction: halogen or chalcogen bond.

In the unusual orientation of I-CH₂ fragment so that equatorial part of iodine atom is directed towards σ -hole region of triiodide anion leads to the situation where iodine atom of organic cation acts as the donor and acceptor of the halogen bond simultaneously. ELF distribution in the plane, containing multiple covalent interactions allows indicating the type of bonding and visualizing features of electron shells distortion due to formed noncovalent interactions. Here we discuss features of σ -hole interactions and their impact on crystal packing and properties of the polyiodide structures.