

Title: “Control of molecular organization in solid state from strong halogen, chalcogen and pnictogen bonds”

Laboratory and team: Laboratory of Crystallography, Nuclear Magnetic Resonance and Modelling - Crystal Engineering group

Website: <http://crm2.univ-lorraine.fr/lab/en/animation-scientifique/ingenierie-cristalline/>

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Project

Molecular electrophilic regions observed at halogen (Hal), chalcogen (Chalc) and pnictogen (Pnic) atoms, also called Sigma-Holes, are preferential anchored sites targeted by molecular partners bearing nucleophilic groups. Interactions involving Sigma-Holes are highly directional, while the intensities are controlled by the electrophilic/nucleophilic interactions. In the context of Supramolecular Chemistry, Crystal Engineering and Material Science, sigma-hole interactions, are much less understood than hydrogen-bonding interactions, and therefore have been less used. The use of strong and directional intermolecular interactions is of main importance in those fields of research because, driving the molecular organization in the space, sigma-hole interactions can control the properties of supramolecular entities and materials through the structure-properties relationship. To this end, we will focus on the analysis of the electron density distribution, in particular in the intermolecular regions they are involved.

In the design of sigma-hole interactions, three key points are main objectives in the project. First, the strengthening of such interactions will be investigated by (i) introduction of electron withdrawing groups, (ii) co-crystallization with Lewis bases of enhanced basicity, and (iii) the conception of cooperative systems driving main electrophilic...nucleophilic forces in the building of the crystalline space and permitting the design of novel supramolecular motifs. Second, while the electrophilic sites of sigma-holes are placed along specific molecular directions depending on the Hal, Chalc and Pnic hybridizations, they are a priori enhanced in all molecules when heavier atoms of their respective series are used. Accordingly, the synthesis of molecules bearing heavier atoms of these families permits to generate directional intermolecular electrophilic....nucleophilic interactions with increased interaction energies along specific directions. Third, the modification of intermolecular forces driving the crystalline building will permit the tuning of associated properties, such as for instance fusion enthalpies and charge transfer between molecules (either by electronic or atomic transfer).

Research Groups

The project gathers together two complementary research groups in Nancy and Rennes, collaborating in the field since 2007. In addition to the research already carried out with sigma-hole interactions involving halogen bonding, we have also initiated together the investigation of chalcogen bonding (references 1-3). Thus, in a recent paper dealing with accurate low-temperature high-resolution X-ray diffraction measurements and ab initio quantum calculations of the selenium sigma-hole in selenophthalic anhydride, we have demonstrated that chalcogen and halogen bonding can drive different geometrical preferences of molecular packing (Fig. 1). Furthermore, during this last year, we also identified that organic selenocyanates actually have a very strong tendency to self-associate in the solid state through short N•••Se interactions. These structures indicate that the selenocyanate group can actually be a very efficient chalcogen bond donor group, for its implementation in Crystal

Engineering strategies, as planned in the present project. Concerning the much less explored pnicogen bonding, sigma-holes can also appear along Pnic-series, provided these atoms bear at least one electron-withdrawing group. Accordingly, we will design and prepare systems adapted for in-depth analysis of the electron density, both theoretically and experimentally, concentrating first on phosphorus based model molecules.

PhD work

While synthesis and crystal growth will be carried out in Rennes, the analyses of experimental and theoretical electron densities (allowing for accurate descriptions of Hal-, Chalc- and Pnic-bonding patterns) and of thermodynamic properties will be performed in Nancy. The PhD candidate is expected to be quickly autonomous on the measurements of low-temperature high-resolution X-ray diffraction data, to derive the charge density models that will be used in the experimental modelling of intermolecular interactions. In addition, spectroscopic characterizations (DSC, IR,...) will complement his/her experimental work. Notions of theoretical modelling and Quantum Chemistry calculations will be appreciated.

Fellowship

Salary: 30 K€ per year (gross amount)

Contract: 3 years (2018-2021)

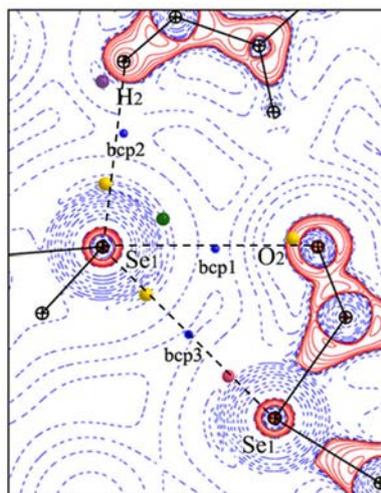


Fig 1.- The study of the topological critical points (CPs) of $\nabla^2\rho(r)$ has indicated that charge concentration (CC) and charge depletion (CD) sites found in the valence shell of atoms are driving geometric preferences of molecules in solid state. This is shown in the Figure, where directional nucleophilic...electrophilic interactions between several CC and CD sites are simultaneously involved in the relative orientation of three molecules in a crystal. The Figure shows the $L(r) = -\nabla^2\rho(r)$ map in intermolecular regions of the $C_8O_2H_4Se$ crystal structure (Reference 3): CC sites are represented by (3,-3) critical points (CPs) of L (yellow spheres), CD sites are denoted by (3,+3) (violet), (3,+1) (pink) and (3,-1) (green) CPs of L. CC...CD directions closely correspond to internuclear directions (dashed lines), which in turn almost superpose with bond path directions (bond critical points are in blue).

References

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- 2.- M. E. Brezgunova, E. Aubert, S. Dahaoui, P. Fertey, S. Lebègue, C. Jelsch, J. G. Ángyán, E. Espinosa, *Cryst. Growth Des.* 2012, 12, 5373–5386.
- 3.- M. E. Brezgunova, J. Lieffrig, E. Aubert, S. Dahaoui, P. Fertey, S. Lebègue, J. G. Ángyán, M. Fourmigué, E. Espinosa, *Cryst. Growth Des.* 2013, 13, 3283–3289.