

range 5-300 K. A combination of the polarized Raman spectra and single-crystal X-ray diffraction data allowed us to correlate the geometry and the energy for the selected hydrogen bonds.

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**Keywords: hydrogen bonds, amino-acid salts, low temperatures**

#### FA4-MS30-P04

**Halogen...Halogen interactions from experimental charge density analysis.** Enrique Espinosa<sup>a</sup>, Thai Thanh Thu Bui<sup>a</sup>, Slimane Dahaoui<sup>a</sup>, Claude Lecomte<sup>a</sup> and Gautam R. Desiraju<sup>b</sup>, <sup>a</sup>Laboratoire de Cristallographie, Résonance Magnétique et Modélisations (UMR 7036), Université Henri Poincaré – Nancy 1, Vandoeuvre-lès-Nancy, France, <sup>b</sup>School of Chemistry, University of Hyderabad, Hyderabad, India  
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Directional intermolecular interactions of diverse strengths[1,2] are favorite tools of crystal engineering, since the orientation of molecules in the solid state can be predicted with a reasonable degree of accuracy. Two such interactions stand out: hydrogen bonding and halogen bonding. The marked directionality of the hydrogen bond (HB) is well established and is the basis for efficient and reliable topologies of intermolecular motifs. The strength of the hydrogen bond can be estimated from high resolution X-ray diffraction as proposed by our group[3,4] and this method based on the topological analysis of the electron density at the HB critical point is now widely used. On the other hand, the *halogen bonding* interaction has been much less investigated. It occurs in the systems  $\text{CHal}\cdots\text{X}$  ( $\text{X} = \text{L}, \text{Hal}$ ) where an organic halogen atom approaches either a Lewis base (L) or a halogen atom (Hal). Halogen bonding can be as effective as hydrogen bonding for driving highly specific crystal packing motifs, as synthons. It finds its origin in the anisotropy of the electron density around the halogen nucleus, leading to a smaller effective atomic radius along the extended  $\text{CHal}$  bond axis than in the direction perpendicular to this axis, a feature called polar flattening. In a recent experimental charge density analysis of hexachlorobenzene ( $\text{C}_6\text{Cl}_6$ )[5] we have confirmed the anisotropy of the electron distribution around the chlorine nuclei, which leads to the formation of electrophilic and nucleophilic sites in the valence-shell charge concentration region of Cl-atoms. In the crystal structure of  $\text{C}_6\text{Cl}_6$ , main halogen...halogen interactions are thus electrophilic-nucleophilic in nature, being established between oppositely polarized regions in front of each other within a  $\text{Cl}_3$ -synthon. The Atoms in Molecules theory[6] developed by Bader and co-workers has been applied to this crystalline system, demonstrating all these features and indicating that the electron density properties at the halogen...halogen bond critical points correlate with the strength of the observed interactions.

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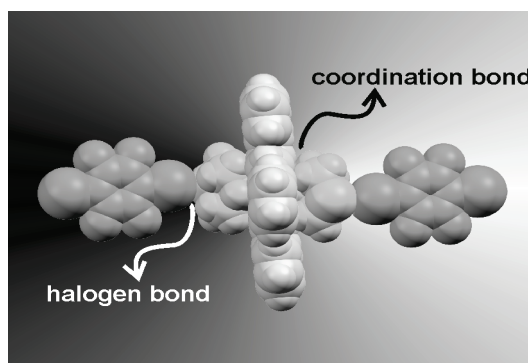
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**Keywords: halogens, charge density study, topological properties of charge distribution**

#### FA4-MS30-P05

**Halogen bonds: mechanosynthesis, unusual acceptors and metal-organic materials.** Tomislav Friščić, William Jones, *Department of Chemistry, University of Cambridge, United Kingdom*  
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The past decade has witnessed an explosive growth of interest of chemists, materials scientists and biochemists in halogen bonds. As a result of such intensive research, halogen bonding is now becoming recognised as a versatile design element in crystal engineering. The presentation will provide a brief overview of the current status of halogen bonding in crystal engineering, and highlight several halogen-bonded systems that are being studied in our laboratory. We will describe the application of halogen bonding and isostructurality for the construction of cocrystal-based materials with controllable properties,[1] with particular attention given to systems involving halogen bond acceptors that are not compatible with hydrogen bonding, such as sulfur groups. The application of solid-state mechanochemistry for the synthesis of halogen-bonded architectures will be described,[2] and we will illustrate how the study of mechanochemical cocrystallisation using halogen bonds led to a better understanding of the mechanosynthesis of hydrogen-bonded cocrystals. Finally, the presentation will address our efforts towards the development of designs to construct halogen-bonded metal-organic materials.



[1] Cinčić, D., Friščić, T., Jones W., *Chem. Eur. J.*, 2008, 14, 747. [2] Cinčić, D., Friščić, T., Jones W., *J. Am. Chem. Soc.* 2008, 130, 7524.

**Keywords: halogen bonding, cocrystals, metal-organic compounds**