

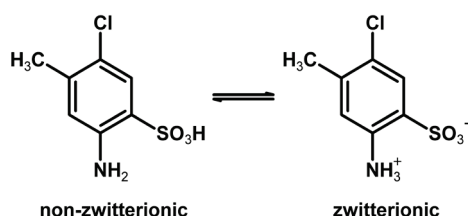
FA4-MS30-P01

Tautomerism from X-ray powder data? The challenging case of CLT acid, C₇H₈ClNO₃S. Sándor L. Bekö^a, Silke D. Thoms^a, Jürgen Brüning^a, Edith Alig^a, Jacco van de Streek^b, Andrea Lakatos^c, Clemens Glaubitz^c, Martin U. Schmidt^a, ^aGoethe-University,

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CLT acid is an industrial intermediate in the synthesis of laked red azo pigments used for newspaper printing [1] and industrially produced in an amount of several 10,000 t per year. Up to date no solid state structure of this compound is known.

The compound can exist in two tautomers:



The crystal structure was solved from laboratory X-ray powder diffraction data by means of real-space methods using the program *DASH 3.1* [2]. Subsequently the structure was refined by the Rietveld method with *TOPAS 4.1* [3].

The compound crystallises in the monoclinic space group *Ia*, *Z* = 4 with *a* = 5.49809(7) Å, *b* = 32.8051(5) Å, *c* = 4.92423(7) Å, β = 93.5011(7)° and *V* = 886.50(2) Å³ [4].

The Rietveld refinements revealed on the basis of *R*-values as well as by refining the occupancies of the H atoms that the compound exists as the zwitterionic tautomer in the solid state. The tautomeric state was confirmed by solid-state NMR and IR spectroscopy. Finally the structure was confirmed by lattice-energy minimisations using dispersion-corrected density-functional calculations [5] with the program *GRACE* [6].

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Keywords: X-ray powder diffraction, tautomerism, dispersion-corrected DFT calculations

FA4-MS30-P02

Halogen bonding in DABCO-I₂ complexes and *N*-substituted 3-iodopyridinium halides. Arto Valkonen, Kari Rissanen, *Department of Chemistry, Nanoscience*

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Predicting and designing non-covalently bound supramolecular complexes and assemblies is difficult because of the weakness of the interactions involved, most recent of these being the interaction between polarized iodine atoms and nucleophilic atoms (N, O, S) or anions (iodide, bromide, etc.), viz. the halogen bonding [1]. Our research interest has been focused on the studies of weak non-covalent intermolecular, viz. supramolecular interactions as the driving force in self-assembly and molecular recognition, especially in the solid state by single crystal X-ray diffraction. In addition to studies of well-known non-covalent forces (e.g., hydrogen bonds), recognition, characterization and understanding of less-studied halogen bonding [2,3] and derived systems is also one of our aims. The presentation will show some of our recent results on halogen bonding in DABCO-iodine (I₂, 2I₂) complexes and *N*-substituted 3-iodopyridinium halide salts.

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Keywords: halogen bonds, amines, pyridinium halides

FA4-MS30-P03

Investigation of hydrogen bonds at low temperatures using polarized Raman spectroscopy and single-crystal X-ray diffraction. Boris A. Zakharov^{a,c},

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The properties of strong hydrogen bonds are widely discussed in recent literature. This interest is related to the role of these bonds in the processes of enzymatic catalysis, in the interactions between drugs and biological molecules, and in determining the properties of molecular materials for non-linear optics. Besides, the formation of hydrogen bonds determines the secondary structure of proteins, the structure of molecular crystals, and can account for delivery of drugs to the desired area of the cell, using the mechanisms of molecular recognition.

Strong hydrogen bonds are present in many of the crystalline amino-acid salts. From this class of compounds, for the present study we have selected bis(DL-serinium) oxalate dihydrate and DL-alaninium semioxalate hydrate. Geometry of hydrogen bonds (D-A distance and angles of the bonds) was studied using single-crystal X-ray diffraction in the temperature range 100-300 K. Considering this data, polarized Raman spectra with polarization along crystallographic axes have been measured for the single crystals in the temperature

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.

This work was supported by grants from RFBR (09-03-00451), BRHE (RUX0-008-NO-06), by the Integration Projects No. 13 and 109 of the Siberian Branch of RAS, and a FASI Grant P2529.

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

FA4-MS30-P04

Halogen...Halogen interactions from experimental charge density analysis. Enrique Espinosa^a, Thai Thanh Thu Bui^a, Slimane Dahaoui^a, Claude Lecomte^a and Gautam R. Desiraju^b, ^aLaboratoire de Cristallographie, Résonance Magnétique et Modélisations (UMR 7036), Université Henri Poincaré – Nancy 1, Vandoeuvre-lès-Nancy, France, ^bSchool 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 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 (C_6Cl_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 C_6Cl_6 , main halogen...halogen interactions are thus electrophilic-nucleophilic in nature, being established between oppositely polarized regions in front of each other within a 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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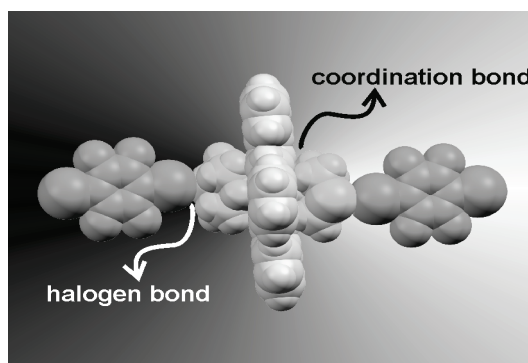
2009, 48, 3838. [6] Bader, R. F. W. *Atoms in Molecules- a Quantum Theory*; Clarendon Press: Oxford; New York, 1990.

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.



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Keywords: halogen bonding, cocrystals, metal-organic compounds