

hydrogen bonds of the type C-H...O/N and weaker interactions of the type C-H...F and C-H... π are also considered to have important role in the building of a crystal lattice in the presence of strong hydrogen bonds [3]. Different altered modes of hydrogen bonds and weak interactions are known to generate a number of polymorphs of many compounds [4]. Polymorphism is a phenomenon of immense importance in pharmaceutical industry [5] and generation of new polymorphs, [5] cocrystals [6] and salts [7] of known APIs are possible using different modes of hydrogen bonds and weaker interactions. Study of polymorphism and cocrystal formation have gained momentum in recent years in the view of intellectual property rights (IPR) as well as in the enhancement of physicochemical properties of the drug molecules for their better formulations [8]. We are interested to investigate the possibility of the formation of new polymorphs and cocrystals of a number of well-known Active Pharmaceutical Ingredients (APIs). Our recent experiments using Fluconazole, Ciprofloxacin, Lamivudine, Lamotrigine and Voriconazole reveal that these APIs form new polymorphs or cocrystals or salts when crystallized in the presence of stoichiometric amount of a cocrystal former. The cocrystallization screening experiments have been performed by using both single crystal and powder X-ray diffraction techniques and solid state Raman spectroscopy. We shall highlight our recent results of these experiments and elucidate the crystal structures of new polymorphs of Fluconazole and Lamivudine, new salts of Fluconazole, Ciprofloxacin, Lamivudine and Lamotrigine and a new cocrystal of Voriconazole. Our studies indicate that the presence of a number of weak hydrogen bonds or weaker intermolecular interactions collectively can alter the mode of strong hydrogen bonds and generate new polymorphs, cocrystals and salts of the known APIs.

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Geometry of C-H...O interactions: case of aromatic CH donors.
D.Ž. Veljković,^a G.V. Janjić,^a V.B. Medaković,^b S.D. Zarić,^b ^a*Institut of Chemistry, Technology and Metallurgy, University of Belgrade Njegoševa 12, Belgrade, (Serbia).* ^b *Department of Chemistry, University of Belgrade (Serbia).* E-mail: vdusan@chem.bg.ac.rs

C-H...O interactions play important role in biological systems, especially in biomolecules, in stabilizing structures of proteins, in interactions with the ligands, and in recognition of host-guest systems [1,2]. Based on directionality it was shown that C-H...O interactions, although can be weak, are hydrogen bonds and not the van der Waals interaction. Directionality is one of the most important properties of hydrogen bonds [3]. Hydrogen bonds with linear or close to linear geometries are energetically more stable than bent ones.

In this paper, angular distribution of C-H...O interactions of aromatic C-H donor was studied by *ab initio* calculations and by analyzing data in the Cambridge Structural Database (CSD). Crystal structures involving C₆-H aromatic groups and oxygen atoms were

screened for intermolecular contacts. Following systems with oxygen atom were taken: HOH (non-coordinated), HOZ, Z₁OZ₂, O=CZ and O=YZ (Z, Z₁, and Z₂ are not hydrogen atoms, Y is not carbon atom). High level *ab initio* calculations were performed on three model systems: benzene-water, benzene-methanol, and benzene-acetone.

The analysis of the C-H...O interactions in crystal structures indicate that aromatic C-H donors do not show strong preference for linear contacts and that the preference depend on the type of the atom or group in o-position to the interacting C-H group. The acceptor oxygen atom has possibility for simultaneous C-H...O interactions with the hydrogen atom in o-position to the interacting C-H group. The C-H...O interactions of aromatic molecules with two hydrogen atoms in o-positions do not show preference for linear contacts. Bifurcated interactions are observed in substantial number of structures. Moreover, in the structures with a substituent in o-position there is possibility for simultaneous hydrogen bonds, depending on the nature of the substituent. The calculated energies for linear C-H...O interactions of benzene with water, methanol, and acetone are 1.28, 1.47, 1.45 kcal/mol; while for bifurcated interactions are 1.38, 1.63, and 1.70 kcal/mol, respectively. The calculations are in agreement with the results obtained by analysing crystal structure data from the CSD and show that stabilization energy is larger for bifurcated than for linear interactions. Analysis of the data in the CSD and the *ab initio* calculations indicate that the vicinity of the other possible hydrogen donors in the aromatic molecules cause small tendency for the linear contact the in C-H...O interactions. The result shows that nonlinear interactions are not energetically disfavoured because of the possibility for simultaneous interactions. This can be very important for recognizing C-H...O interaction in biomolecules containing aromatic groups, like proteins. It can also help in recognizing important C-H...O interactions, showing that nonlinear interactions are not energetically disfavoured, because of the possibility for simultaneous interactions.

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Synthesis, structural characterization and hydrogen bond of new hybrid compound based on indium.

Sofiane Bouacida,^{a,b} Ratiba Belhouas,^b Boubakeur Fantazi, Chaouki Boudren,^b Thierry roisnel,^c ^a*Département SM, Université LBM, Oum El Bouaghi, (Alegria).* ^b*Unité de recherche CHEMS, Université Constantine, (Alegria).* ^c*Centre de diffractométrie X ,UMR 6226, Université de Rennes I, (France).* E-mail: Bouacida_sofiane@yahoo.fr

The Tris(piperazine-1,4-dium) bis[hexachloridoindate(III)] tetrahydrate, 2[InCl₆]³⁻·3[C₄H₁₂N₂]²⁺·4H₂O was prepared as part of our ongoing studies of hydrogen-bonding interaction in the crystal structures of protonated amines and imines (Bouacida, 2008; Bouacida et al., 2005; 2007). we report here the synthesis and crystal structure of new hybrid compound based on indium with piperazine-1,4-dium that promises both the superior carrier mobility of inorganic semiconductors and the processability of organic materials.

It has been prepared by slow evaporation of an aqueous solution of piperazine, indium(III) chloride and hydrochloric acid in a molar ratio of 10:5:1.

The asymmetric unit consists of one and half independent piperazinium cations, an hexachloridoindiumate anion and two

molecule of water. These cations adopt a typical chair conformation and are alternate with hexachloridoindiumate complex forming layers parallel to the (10-1) plane (Fig.1). In the crystal, the components of the structure are linked via intra and intermolecular N...H...O, O-H...Cl, C-H...O and N-H...Cl hydrogen bonds to form a complex three-dimensional network. Additional stabilization within these layers is provided by weak intermolecular C-H...Cl interactions.

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Effect of the anion on cation chain geometry in hexamethylenediammonium salts

Charmaine Arderne, Gert J. Kruger, *Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park, Johannesburg, (South Africa), 2006*. E-mail: carderne@uj.ac.za

The investigation of structure-property relationships and applications of *n*-alkyldiammonium salts are of continued importance and form the basis of our ongoing studies [1], [2] of these materials. In particular, we have focused on the structural characteristics of the *n*-alkyldiammonium salts as they are precursors to layered inorganic-organic perovskite-type hybrids [3]; they are bidentate ligands in transition metal complexes that have applications in propellants, explosives and pyrotechnic compositions [4]; they have structure directing properties in the synthesis of a number of zeolites [5]; and many have biological applications [6].

This work focuses on the effect of variation of the anion in hexamethylenediammonium salts on the diammonium cation geometry. Four crystal structures are presented – the chloride, bromide, iodide and nitrate salts of hexamethylenediamine. Significant deviations from diammonium cation chain planarity become evident as the anion is varied. The smaller spherical anions (such as chloride and bromide) showed minor deviations from dication chain planarity while larger spherical anions (such as iodide) and large trigonal planar anions (such as nitrate) showed major deviations from dication chain planarity – resulting in kinked and buckled dication chain conformations.

The variation in anion type in the crystal structures resulted in significantly different types of hydrogen bonding interactions being identified. These interactions were found to be strong N–H...X bonds (X = anion type) as well as weak C–H...X bonds. All relevant bonds were found to be directly related to the observed aberration in dication chain geometry.

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New hybrid compound based on fluorosilicate with complex hydrogen-bonding scheme.

Ratiba Belhouas,^a Sofiane Bouacida,^{a,b} Chaouki Boudren,^a and Jean-Claude Daran,^c ^a*Unité de recherche CHEMS, Université Constantine, Algeria.* ^b*Département SM, Université LBM, Oum El Bouaghi, (Algeria).* ^c*Laboratoire de Chimie de Coordination, Université de Toulouse, (France).* E-mail: Belhouas_ratiba@yahoo.fr

Fluorosilicate salts involving onium cations of N- and O-containing organic bases and amino acids have practical applications as ionic liquids (Katayama et al., 2001), dielectrics with cryptocrystalline structure (Kalem, 2004) and layered organic-inorganic hybrid materials (Airoldi & De Farias, 2000). This new hybrid compound has been prepared by slow evaporation of an aqueous solution of adenine, SiO₂ and hydrofluoric acid in a molar ratio of 10:5:1.

The asymmetric unit of Bis adeninium hexafluorosilicate(VI) hydrate consists of one adeninium cation, half of a fluorosilicate anion located on inversion center and a solvent water molecule which are connected through the water molecules by N-H...O and O-H...F hydrogen bonds to the (10-1) plane. The adeninium cations are connected by N-H...N hydrogen bonds involving one H atom of the NH₂ groups and the H atom of the protonated N atom of the five membered ring forming respectively centrosymmetric R₂²(10) and R₂²(8) rings. Then these N-H...N hydrogen bonds build up an infinite planar ribbon parallel to the (1 2 2) plane. The H atoms of the water molecules interact with the F2 and F3 atoms of the fluorosilicate building R₄⁴(12) graph set motif. These O-H...F hydrogen bonds form infinite chains parallel to the [1 0 0] axis.

The adeninium ribbons and the chains formed by the water and fluorosilicate are further connected through N-H...O1W, N-H...F and O1W-H...F building a R₃³(10) graph set motif.

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D-H...X Contacts Performed by N-Heterocycles: a Practical View
Yu Sun, Werner R. Thiel, *Fachbereich Chemie, TU Kaiserslautern, 67663 Kaiserslautern (Germany)*. E-mail: sun@chemie.uni-kl.de

N-Heterocycles are important structural motifs in organic syntheses, coordination chemistry and also in various catalytically active compounds. For quite some time our group has been working on the development of novel N-heterocyclic ligands based on pyrazoles, pyrimidines and related structures.

The existence of N-H(s) groups obviously provides a good opportunity to form hydrogen bonds which in most cases would be the dominating forces in the corresponding crystal structures. As a matter of fact in many of our obtained solid state structures hydrogen bonds between different donors and halogens as the acceptors were observed. These hydrogen bond acceptors could be halide anions (X⁻), metal-halides (X-M) and carbon-halides (X-C), most of them serving at the same time as counter anions, templates and solvents.

In order to better understand the roles of these counter anions, templates and solvents in the nucleation processes and sometimes even in the synthesis procedures, a brief study of the hydrogen bonds involving halogens as the acceptors in these structures was carried out.