

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, (Alegria).* ^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.

- [1] Y. Katayama, M. Yokomizo, T. Miura, T. Kishi, *Electrochemistry*, **2001**, *69*, 834–836. [2] S. Kalem, *Appl. Surf. Sci.* **2004**, *236*, 336–341. [3] C. Airoldi, R.F. De Farias, *J. Fluorine Chem.* **2000**, *103*, 53–55.

Keywords: hybrid materials, single crystal, hydrogen bond

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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.

To compare the strengths of these interactions and to investigate their geometrical preferences, the approach suggested by Lommerse et al. [1], using the normalized distance R_{HX} and the spatially normalized distance vs. angle (R_{HX}^3 vs. $1 - \cos[180 - (D-H \cdots X)]$) plot, was applied.

The study implies: (1) Even if the N-H(s) were deprotonated / substituted, O-H(s) and C-H(s) in the molecules could serve as hydrogen bond donors. O-H(s) are normally better donors than N-H(s), while C-H(s) build weaker interactions. (2) No notable differences were found among F, Cl and Br in both examined criteria. (3) In general, the capability as hydrogen bond acceptor is $X^- > X-M > X-C$, which is complied with results of others [2]. (4) Important counter anions in coordination chemistry, such as BF_4^- , PF_6^- and SbF_6^- , exhibit comparable hydrogen bond acceptor capabilities like transition metal-halides. (5) Special attention is drawn to MX_4^{2-} type counter anions (templates). The several cases recorded show exclusively the formation of much stronger hydrogen bonds compared to normal metal-halides. Their possible roles in complex synthesis and nucleation are still unclear, further studies with theoretical methods would follow. (6) Although CH_2Cl_2 / $CHCl_3$ are often used and are observed in structures, X-C is seldom involved in hydrogen bonding. In the rare cases at most very weak interactions were built. While on the other hand the increased acidity of the C-H(s) makes them possible hydrogen bond donors.

[1] J.P.M. Lommerse, A.J. Stone, R. Taylor, F.H. Allen, *J. Am. Chem. Soc.* **1996**, *118*, 3108-3116. [2] L. Brammer, E.A. Bruton, P. Sherwood, *Cryst. Growth Des.* **2001**, *1*, 277-290.

Keywords: hydrogen bond, halogens, N-heterocycles

MS73.P11

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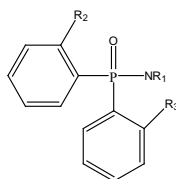
Structural investigation of phenol-phosphonic amides

C.Alicia Renison, D.Bradley.G Williams, Alfred.J Muller and Stephen.J Evans, *Research Centre for Synthesis and Catalysis, Department of Chemistry, University of Johannesburg, Auckland park, Johannesburg 2006, (South Africa)*. E-mail: aliciarenison@yahoo.com

The synthesis and use of phosphine ligands in homogeneous catalysed reactions is a field of research that is gaining more interest [1]. There is currently a special focus [2] on the synthesis of unsymmetrical ligands, for various reasons, including asymmetric catalytic transformations [3]. The stereoelectronic nature of the ligand plays a significant role in the outcome of the reaction² and, as a result, we have investigated a potentially new route to ortho-substituted arylphosphine ligands.

Several of these ligands are crystalline which enables their investigation by means of X-ray crystallography. A series of phenol-phosphonic amides was investigated as shown in Scheme 1. An interesting feature exhibited by all of these structures is that of phenol-phosphine oxide intramolecular hydrogen bonding. Packing motifs, hydrogen bonding and geometrical features of the structures were compared in this study.

Calculation of Tolman cone angles and solid angles were determined to illustrate the steric behaviour of these phosphine ligands [4]. Electrostatic potential properties such as V_{min} and d_{cp} were calculated in order to quantify the electronic effect of these ligands. The calculations were performed in Gaussian with Density functional theory (DFT) incorporating the B3LYP functional and 6-31G(d,p) basis set [5].



$R_1 = Et, Pr, Bu, R_2 = H, OH, R_3 = H, OH, PPh_2$

Scheme 1: Phenol phosphonic amides

[1] P.W.N.M. Leeuwen, P.C.J. van Kamer, J.N.H. Reek, P. Dierkes, *Chem. Rev.* **2000**, *100*, 2741-2770. [2] W. Tang, X. Zhang, *Chem. Rev.* **2003**, *103*, 3029-3069. [3] S. Jeulin, S.D. de Paule, V. Ratovelomanana-Vidal, J.P. Genêt, N. Champion, P. Dellis, *Angew. Chem. Int. Ed.* **2004**, *43*, 320-325. [4] C.A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348. [5] C.H. Suresh, N. Koga, *Inorg. Chem.* **2002**, *41*, 1573-1578.

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How many molecules can you crystallize in one experiment? the role of hydrogen bonding in chalcone-flavanone isomerization.

Miriam Rossi,^a Michelle Duong,^a Francesco Caruso,^b ^a*Department of Chemistry, Vassar College, Poughkeepsie, NY 12604 (USA)*. ^b*CNR, Istituto di Chimica Biomolecolare, c/o Università "La Sapienza", Roma, Piazzale Aldo Moro 5, 00185 Roma (Italy)*. E-mail: rossi@vassar.edu.

Chalcones, flavones and flavanones are naturally occurring compounds from plants and they have a wide range of biological activities. We are interested in studying the molecular structures using X-ray diffraction of these compounds so that a relationship between the chemical structure and the biological activities may be seen. The crystallization of $C_{16}H_{14}O_5$, 3-methoxy-4,2',5'-trihydroxyxchalcone from a mixture of ethanol-water produced *three* different types of crystals which were visually distinct. We report the results of these 3 crystal structure determinations that show, respectively, the chalcone and the flavanone isomers and a third structure showing the conformational disorder resulting from the molecular rearrangement due to the intramolecular isomerization reaction between the flavanone and the chalcone molecular structure! The role that intermolecular interactions such as hydrogen bonding and stacking play in the self assembly and biological activity of these structures is investigated.

Keywords: chalcone, flavanone, molecular rearrangement

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The hydrogen bond in supramolecular network

Marcos Flores-Alamo, Ana Laura Maldonado-Hermenegildo, Humberto Gómez-Ruiz, *Unidad de Servicios de Apoyo a la Investigación, Facultad de Química, Universidad Nacional Autónoma de México, (México D.F.) 04510*. E-mail: mfa@unam.mx

In recent years, supramolecular arrangement and intermolecular interactions have played an important role in crystal engineering. A detailed analysis of hydrogen bonds in some molecules can classify this as *I- very strong*, *II- strong* and *III-weak* [1]. An easy way to visualize the intermolecular interactions is to apply a graphical analysis of the patterns that represent these interactions [*motif* $G_d^a(r)$] [2] in crystals. In this paper we analyze the crystals of the organic substance enrofloxacin and other inorganic substances such as copper acetate, ferrous sulfate, etc. Of X-ray data, tables are constructed of lengths and hydrogen bond angles. Finally we illustrate how to classify the bond and its possible application in Crystal Engineering and / or the design of molecular devices. Below is a brief summary of this work.

Data collection X-ray diffractometer was carried out with a Gemini with Atlas area detector and two sources of radiation $\lambda_{Mo} = 0.7103$ and $\lambda_{Cu} = 1.5418 \text{ \AA}$ to 130 K.

The asymmetric unit of enrofloxacin corresponds to the moiety