systematic errors and how to correct the problems with the way least squares refinement is currently undertaken.

An initial model is used to partition the information in an observation $|\mathbf{Y}(\mathbf{h})|^2 = \Sigma_{m=1,M} |F(\mathbf{h})_m|^2$ where the background is $|F(\mathbf{h})_M|^2$. $\mathbf{Y}(\mathbf{h})$ can be regarded as a vector in an M dimensional space with components $F(\mathbf{h})_m$ $\mathbf{i}_m$. The assumption that there is a direction of interest in Y-space for the description of $\mathbf{Y}obs(\mathbf{h}) - \mathbf{Y}calc(\mathbf{h})$ is a constraint that creates a partial observation and a partial residual should the directions of $\mathbf{Y}obs(\mathbf{h})$ and $\mathbf{Y}calc(\mathbf{h})$ not coincide, eg the back-ground is not refined. This constraint creates residuals $\Delta_{\mathbf{h}m} = |F obs(\mathbf{h})_m - F calc(\mathbf{h})_m|$ for a minor component of $\mathbf{Y}obs(\mathbf{h})$ that are much smaller than the variance based estimates using an estimate of the variance-covariance matrix. This should be interpreted as the refinement of $\Sigma_{\mathbf{h}} f_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$ rather than $\Sigma_{\mathbf{h}} w_{\mathbf{h}}' \Delta_{\mathbf{h}}^2$ with $\Sigma_{\mathbf{h}} f_{\mathbf{h}}$ the effective number of observations associated with the refined parameters and $\Sigma_{\mathbf{h}} (1-f_{\mathbf{h}}) w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$ is the unrefined component of $\Sigma_{\mathbf{h}} w_{\mathbf{h}} \Delta_{\mathbf{h}}^2$. Both $f_{\mathbf{h}}$ and $w_{\mathbf{h}}$ can change each refinement cycle.

The concept can be extended so that $f_{\mathbf{h}} = \Sigma_j f_{\mathbf{h}j} = \Sigma_m f_{\mathbf{h}m}$ where $f_{\mathbf{h}j}$ is the fraction of the residual assigned to the jth variable and $f_{\mathbf{h}m}$ is the fraction assigned to the mth component. This allows the scaling of the variance-covariance matrix one variable at a time and the evaluation of the effective number of observations associated with a particular component of the structure factors, a particular variable, or a particular set of variables.

For pseudo symmetric structures one can create symmetrized components of the structure factors and one needs to isolate classes of reflections and differences between pseudo symmetric reflections in these classes to check on the reliability of the minor components that may have errors in their relative phases, imposed symmetry and choice of initial model as well as intrinsic problems involving stacking faults and twinning. Differences between pseudo equivalent reflections are unavailable from powder data as these reflections now coincide and this makes the relative phases of symmetrized components unconfirmable and uncorrectable.

Keywords: partial observations, least squares, refinement

MS59.P01

Polyioidide salts of thioamides

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Structural properties of (poly)iodide salts of 2-mercaptopyrimidine (PMT) and its non-aromatic analogue, 3,4,5,6-tetrahydropyrymidinthione (tHPMT) have been studied by means of middle- and high-resolution X-ray diffraction.

The reaction of PMT with hydroiodic acid in a molar ratio of 1:1 produced the mixture of PMT^+I^- **(1)** and $PMT^+(I_4^{2-})_{0.5}$ **(2)**, while tHPMT reacts with diiodine in the presence of HI and (in 1:1:1 molar ratio) forms the ionic complex $[(tHPMT)_2I^-(I_4^{2-})_{0.5}]$ **(3)**. On the other hand this latter compound in the presence of HCl reacts with diiodine and, depending on the molar ratio, forms either $[(((tHPMT)_2)^{2+})_3(Cl^-)_{1.5}(I^-)_2(I^{3-})_{2.5}]$ **(4)** for a molar ratio 1:1:1 or $[((tHPMT)_2)^{2+}(I_3^-)(I_3^-)_{0.5}(Cl^-)_{0.5}]$ **(5)** for 1:1:2.

The crystal structures of all these compounds have been determined by standard X-ray diffraction method; for **(2)** also high resolution data are collected and preliminary results of the deformation electron density analysis are promising. Additionally, some of the compounds were also spectroscopically studied.

In the salts we have observed the rare forms of polyiodides i.e. tetra- and hexaiodides and the huge variety of different intermolecular

interactions including strong and weak hydrogen bonds, halogen bonds, sulfur···halogen and coulombic interactions. Some examples of the interactions found are shown below:
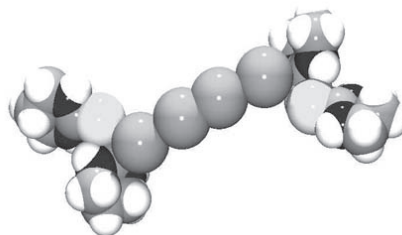

Figure 1. A view of the tetraiodide interacting with the disulfide bridge.

Keywords: polyiodides, thioamides, intermolecular interactions

MS59.P02

Anion···π, lone pair···π, and F···F interactions in nucleobase derivatives

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Hydrophobic interactions in nucleobase derivatives substituted with long aliphatic chains favors the formation of layers of nucleobases and, in the case of salts, anions separated by the aliphatic chains, giving rise to crystal packings that reminds of lipid bilayers (Figure). Although the strongest intermolecular interaction inside the nucleobase layer is hydrogen bonding, other interactions such as π···π stacking, anion···π, lone pair···π and fluorine···fluorine play a fundamental role in determining the conformation of the nucleobases inside the layers. The complex interplay between these interactions gives rise to features that have been analyzed by theoretical calculations, such as the formation of anion···π / π···π / π···anion assemblies [1], the stabilization of planar layers of fluorinated molecules by F···F interactions [2], or the favoring of lp···π over π···π interactions when electron-withdrawing substituents are present [3]. Results stresses the importance of these interactions, that should be taken into account in crystal engineering and crystal structure prediction efforts with nucleobases and other N-substituted heterocycles.
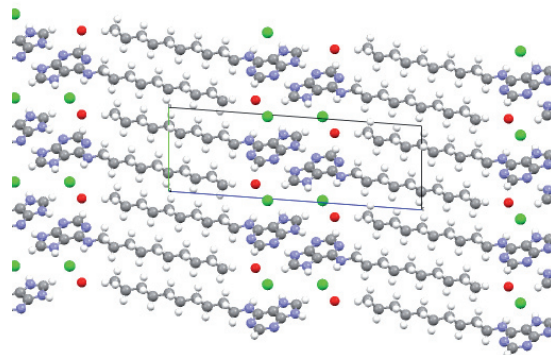
Crystal structure of N⁶-decyladenine·HCl hydrate

[1] A. García-Raso, F.M. Albertí, J.J. Fiol, Y. Lagos, M. Torres, E. Molins, I. Mata, C. Estarellas, A. Frontera, D. Quiñonero, P.M. Deyà, *Eur. J. Org. Chem.* **2010** 5171-5180 [2] M. Barceló-Oliver, C. Estarellas, A. García-Raso, A. Terrón, A. Frontera, D. Quiñonero, I. Mata, E. Molins, P.M. Deyà, *CrystEngComm* **2010**, *12*, 3758-3767 [3] M. Barceló-Oliver, C. Estarellas, A. García-Raso, A. Terrón, A. Frontera, D. Quiñonero, E. Molins, P.M. Deyà, *CrystEngComm* **2010**, *12*, 362-365.

Keywords: non-covalent interactions, nucleobase, crystal engineering

MS59.P03

Supramolecular assembly of hetero-halogen (F···X) or Homo-Halogen (X···X, X = F, Cl, Br, and I) interactions in substituted benzanilides

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A series of mixed halogen (F, Cl, Br, and I) substituted benzanilide crystal structures have been analyzed to evaluate the role of halogen involving interctions in regulating the molecular conformation and supramolecular packing [1-2]. The N-H···O H-bond is a key structure directing element acting in conjunction with C-H···O and C-H···π interactions in this series of compounds. It has been also observed that the halogen-halogen interaction plays a crucial role for polymorphic modification. It is of importance to note that organic fluorine prefers Type I F···F contacts, whereas Cl, Br and I prefer Type II contacts [3-4]. Hetero halogen···halogen interactions on the other hand are predominantly of Type II geometry and this is due to the greater polarizability of the electron density associated with the heavier halogens [4-5]. This presentation will provide the importance to evaluate the contributing role of these interactions in crystal structure packing and the co-operativity associated with such interactions in the solid state.

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Keywords: halogen, supramolecular, interaction

MS59.P04

Halogen bonding towards assembling phosphorescent cocrystals and probing specific solvent effect

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The abstract consists of two parts, one describes assembly of phosphorescent cocrystals by halogen bonding with other noncovalent interaction, and another is amid to exploring possible specific solvent effect as encountering halogenated solvent.

Part one: two supramolecular cocrystals **1**, pyrene/1,4-diiodotetrafluorobenzene (1,4-DITFB) and **2**, pyrene/1,2-diiodotetrafluorobenzene (1,2-DITFB) have been assembled by synergistical C-I···I interaction, π-π stacking and C-H···F contact. The x-ray single crystal diffraction data reveal the structural characteristics of two crystals and function of position of iodine atom in regulating cocrystal structure. Two cocrystals were also well characterized by element analysis, x-ray powder diffraction for homogeneity of samples, UV-vis absorption and FTIR. Furthermore, two cocrystals phosphoresce with well defined fine structure due to iodine acting as heavy atom perturber. They have 10^3 to 10^1 s^{-1} phosphorescence decay rate.

Part two: halide and a dual fluorescence molecule 4-dimethylaminobenzonitrile (DMABN) are used to probe possible specific solvent effect, halogen bonding between halogen donor part (Cl-C) of the solvent and acceptor group (cyano-N) of the probe molecule or halide. The experiment and calculation show cyano-N···Cl-C and halide···Cl-C are compatible to cyano-N···H-C (hydrogen donor part of the solvent) and halide···H-C. The results enlighten that the halogen bonding as one specific effect parallel to hydrogen bonding should be considered habitually in explaining interaction between solute and halogenated solvent molecule.

Keywords: halogen bonding, phosphorescence, specific solvent effect.

MS60.P01

Reversible Order-Disorder Phase Transition in a New Polymeric Metavanadate: $\{[Zn(Im)_4][V_2O_6]\}_n$

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DSC measurements show that this compound undergoes a reversible first-order phase transition at 274.84 K (exothermic transition) and at 277.05 K (endothermic transition) with a hysteresis of ~2 K with the enthalpy ΔH = ~1 kJ mol^{-1} and entropy ΔS = ~4 J mol^{-1}K^{-1} upon cooling and heating rate of 5 °C min^{-1}. Single crystal X-ray diffraction shows an ordered triclinic P–1 phase at 100 (2) K and a disordered triclinic P–1 phase at 293 (2) K (the c axis half of 100 K). The structure consists of infinite anionic polymeric metavanadate chains which composed of the corner-sharing of VO$_4$ tetrahedra and the [Zn(Im)$_4$]$^{2+}$ complex cations occupied between the anions. The 3-D supramolecular network between cations and anions through hydrogen bonding interactions.

As temperature increasing, the small reorientation of the polymeric anions with small expansion of their skeleton along c axis are driving force to the small rearrangement of a 3-D supramolecular network of the cations through observed significantly different weak C–H···O hydrogen bonding interactions between cations and anions and concerted aryl embraces of weaker *off* N–H···π, *off* C–H···π and *ef* C–H···π hydrogen bond interactions among the cations themselves. Good agreement with significantly different of infrared spectra at RT and at temperature of liquid nitrogen. In summary the order-disorder of polymeric anions can controll the behavior of a phase transition in this work.

Keyword: reversible order-disorder phase transition, polymeric metavanadate, hydrogen bond interactions