

MS25-03 Predictable Supramolecular Motifs in Cocrystals of (Thio)urea with Ph_4P^+ Halides. Filip Topić,^a Kari Rissanen,^a ^aDepartment of Chemistry, Nanoscience Center, FIN-40014, University of Jyväskylä, Finland, E-mail: filip.f.topic@jyu.fi

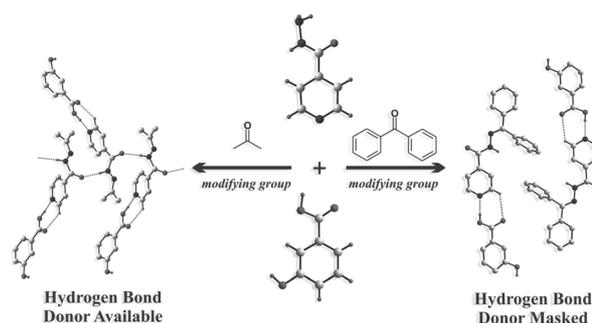
The channel-like structures of urea [1] and thiourea [2] inclusion complexes with “innocent” guests such as hydrocarbons have long ago attracted interest. These structural patterns have been extensively studied for the design of materials with interesting mechanical [3] and optical [4] properties. Also, the generally predictable hydrogen-bonding patterns have been exploited in the preparation of structurally unusual cocrystals [5], as templates in solid-state reactions [6] and in design of a hybrid hydrogen/halogen-bonded supramolecular network [7]. Combining the tetraalkylammonium salts with urea and thiourea enabled the construction of hydrogen-bonded networks consisting of oxoanion nodes bridged by thiourea [8] or halide nodes bridged by urea [9]. We envisaged that a large and rigid cation such as the tetraphenylphosphonium (Ph_4P^+) cation could template the formation of channel- or cage-like motifs in the solid state. We have therefore combined fluoride, chloride and bromide anions with urea and thiourea, while employing Ph_4P^+ as the counter-cation. Three pairs of solids were obtained, where each pair has similar structural motifs and metrics: 1) The isostructural cocrystals of $\text{Ph}_4\text{P}^+\text{Cl}^-$ and $\text{Ph}_4\text{P}^+\text{F}^-$ with urea (1:5) contain hydrogen-bonded channels formed by molecules of urea and chloride or fluoride anions, respectively; 2) Two cocrystal solvates of $\text{Ph}_4\text{P}^+\text{Cl}^-$ and thiourea with CH_3CN and CH_3NO_2 , respectively, where thiourea and chloride form channels through hydrogen-bonding. Although differing in stoichiometry, the structures possess similar hydrogen bonding patterns and metrics; 3) Two cocrystals of $\text{Ph}_4\text{P}^+\text{Cl}^-$ and $\text{Ph}_4\text{P}^+\text{Br}^-$ with thiourea (1:1) which both exhibit ribbon-like assemblies of the anions with thiourea. In all six structures, columnar assemblies of Ph_4P^+ cations were identified as a crucial structure-templating factor.

- [1] Smith, A. E. (1952). *Acta Cryst.* **5**, 224-235.
- [2] Lenné, H.-U. (1954). *Acta Cryst.* **7**, 1-15.
- [3] Hollingsworth, M. D., Peterson, M. L., Pate, K. L., Dinkelmeyer, B. D., Brown, M. E. (2002). *J. Am. Chem. Soc.* **124**, 2094-2095.
- [4] Chao, M.-H., Kariuki, B. M., Harris, K. D. M., Collins, S. P., Laundy, D. (2003). *Angew. Chem. Int. Ed.* **42**, 2982-2985.
- [5] Videnova-Adrabinska, V., Janeczko, E. (1999). *Chem. Commun.*, 1527-1528.
- [6] Bhogala, B. R., Captain, B., Parthasarathy, A., Ramamurthy, V. (2010). *J. Am. Chem. Soc.* **132**, 13434-13442.
- [7] Arman, H. D., Giesecking, R. L., Hanks, T. W., Pennington, W. T. (2010). *Chem. Commun.* **46**, 1854-1856. [8] Lam, C.-K., Mak, T. C. W. (2003). *Chem. Commun.*, 2660-2661.
- [8] Li, Q., Mak, T. C. W. (1998). *Acta Cryst.* **B54**, 180-192.

Keywords: urea compounds; isostructurality; cocrystallization and complexation of small molecules

MS25-04 Covalent Assistance to Supramolecular Synthesis: The Use of Hydrogen Bonding Modifying Groups to Control the Assembly of Co-Crystals. Andreas Lemmerer, Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, 2050, Johannesburg, South Africa. E-mail: andreas.lemmerer@wits.ac.za

The supramolecular reagent isonicotinic acid hydrazide (isoniazid) is a promising molecule in the supramolecular synthesis of multi-component molecular complexes [1]. Due to the covalent reaction of the carbonyl functional group with simple ketones and aldehydes, the hydrogen bonding functionality of isoniazid can be modified, where two of the hydrogen bond donors are replaced with hydrogen bonding “inert” hydrocarbons [2]. The ketones used are propanone, 2-butanone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, 4'-methylacetophenone and benzophenone and the aldehyde 4'-methylbenzaldehyde. The “modifiers” bonded to the isoniazid then give a measure of control of the outcome of the supramolecular synthesis with 3-hydroxybenzoic acid depending on the identity and steric size of the modifier used. The steric size itself can be used to shield or to “mask” the remaining hydrogen bonding functionality of isoniazid such that common homomeric and heteromeric interactions are prevented from taking place. This process of covalent assistance to supramolecular synthesis has been carried out in a one-pot covalent and supramolecular reaction to make six unhydrated co-crystals and five hydrated co-crystals.



- [1] Lemmerer, A., Bernstein, J. & Kahlenberg, V. (2010). *CrystEngComm*, **12**, 2856-2864.
- [2] Lemmerer, A., Bernstein, J. & Kahlenberg, V. (2011). *CrystEngComm*, **13**, 5692-5708.

Keywords: crystal and molecular structure; hydrogen bonding; crystal engineering