

Oral Contributions

[MS24 - 05] **Organic salts: the nemesis of crystal engineering and prediction?** Peter A. Wood, Elna Pidcock, Neil Feeder, Peter T. A. Galek

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At the simplest level the difference between a given co-crystal and salt structure may be only the position of a single proton which, based on X-ray analysis at least, is a very minor element of the structure. Over the last decade or so, design principles such as Etter's H-bonding rules [1] and Desiraju's supramolecular synthon approach [2] have been shown to be very effective in prediction of co-crystal formation. In contrast however, design and prediction of organic salts has often proven to be more challenging, especially when the counterion is a halide or an alkali metal.

Recent examples include the analysis of isostructurality amongst sodium and potassium salts [3], which showed that there was very little structural consistency upon switching between counterions, and the failure to this point of extending the concept of molecular descriptor complementarity [4] to the prediction of salt formation.

Organic salts have also continued to provide a significant challenge to the crystal structure prediction (CSP) community. The most recent blind test [5] included a molecular salt for the first time (system XIX -1,8-naphthyridinium fumarate) which was correctly predicted by two out of 11 participating research groups. The energetic ranking of these ionic structures provided a significant challenge though, with one of the groups relying on comparison with a similar isostructural compound rather than energetics alone.

Here we discuss why organic salts are such a

challenge using current methodologies and some ideas of how they might be tackled differently.

[1] Etter M. C., *Acc. Chem. Res.*, 1990, 23, 120-126.

[2] Desiraju G. R., *Angew. Chem. Int. Ed.*, 1995, 32, 2311-2327.

[3] Wood P. A. et al., *CrystEngComm*, 2012, 14, 2413-2421.

[4] Fabian L., *Cryst. Growth Des.*, 2009, 9, 1436-1443.

[5] Bardwell D. A. et al., *Acta Cryst.*, 2011, B67, 535-551.

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