[MS25-P19] Organic salts: the nemesis of crystal engineering and prediction?

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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.

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Keywords: crystal engineering, salts, crystal structure prediction