

Supramolecular assembly of ternary complexes and their analysis using X-ray diffraction and vibrational spectroscopy.

University Analytical Centre

Darren Andrew Whitaker

Aim

This project aims to investigate the feasibility of creating multi-component complexes, containing both organic and inorganic components. This was done with a view of stabilising and controlling bonding between components of these complexes by exploiting different bonding motifs such as charge transfer interactions, π - π stacking of aromatic systems and hydrogen bonding. The overall aim is to create a crystal structure with organic framework on the outside of a central metal charge channel (*Figure 1*).

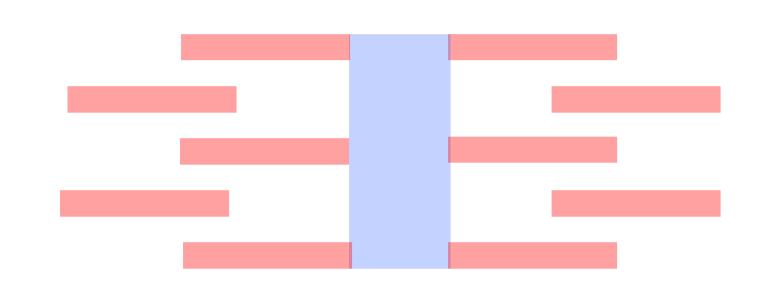


Figure 1 – Red represents the organic framework, and blue represents the metal channel.

Crystal Engineering & Polymorphism

Crystal engineering describes the exploitation of noncovalent bonding to allow control of the arrangement of molecules and ions in relation to one another in the solid state. Much of the early work in this area was purely organic in nature and focused for the most part on hydrogen bonding. When research was moved into the inorganic arena it was found that the coordination bond was also a powerful tool. Of the available intramolecular forces the two most commonly used are hydrogen bonding and co-ordination, however alternative noncovalent forces such as π . . . π , halogen . . . halogen and Au . . . Au interactions have been studied. Systems that are held together by these types of forces are known as supermolecules or supramolecular assemblies. The process by which they form is known as molecular self-assembly, this concept is key to crystal engineering. One of the key problems in crystal engineering is polymorphism. This describes the situation when the same chemical compound exists in a variety of different crystal forms.

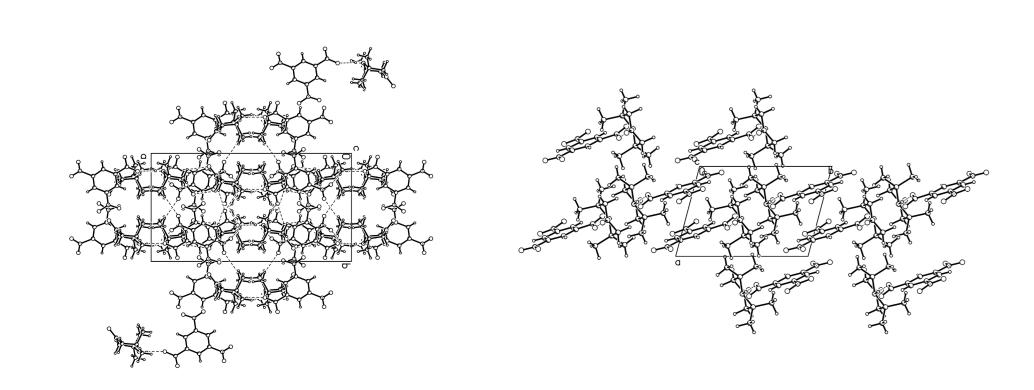


Figure 2 – Two polymorphic forms of [(TRA)(3,5-DNBA)]

(Viewed along *c*-axis)

Overview

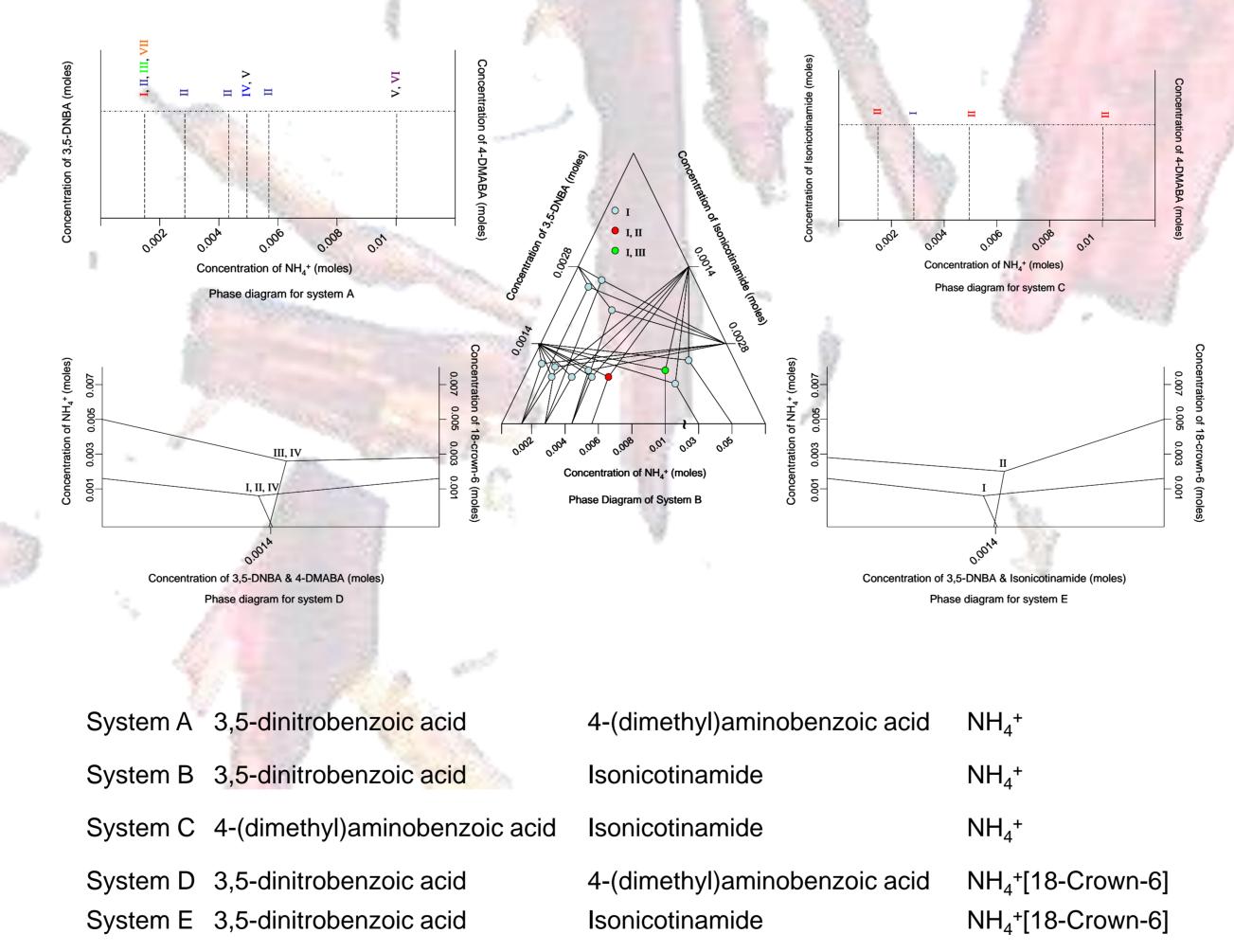
In order to complete the aims a variety of systems were investigated. These were;

- •Co-crystal systems between; 3,5-dinitrobenzoic acid & 4-(dimethyl)aminobenzoic acid, 3,5-dinitrobenzoic acid & isonicotinamide and 4-(dimethyl)aminobenzoic acid.
- •Ternary systems where each co-crystal system was complexed with an ammonuim ion.
- •Ternary systems including the benzoic acids with an metallocrown ether.

Experimental

Each system was attempted with a number of different concentrations of starting materials. The phase diagrams below outline the conditions and the different products obtained.

The basic scheme used was to use a suitable solvent to dissolve the starting materials in, and then allow to crystallise via solvent evaporation.



Results

From system A, Phase I was analysed by single crystal x-ray diffraction. The resulting structure was the following complex $[(3,5-DNBA)(4-DMABA)(NH_4^+)]$ (Figures 2 & 3)

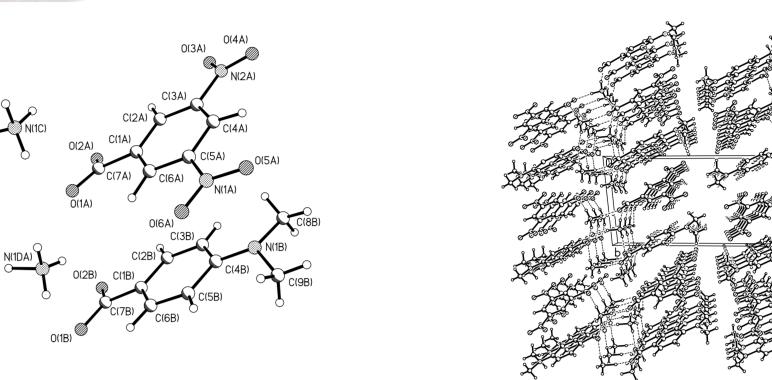


Figure 2 - Asymmetric Unit [(3,5-DNBA)(4-DMABA)(NH4+)]

Figure 3 - [(3,5-DNBA)(4-DMABA)(NH4+)] (Viewed down *b*-axis)

A co-crystal of [(3,5-DNBA)(4-DMABA)] was also isolated from system A. (*Figures 3 & 4*)

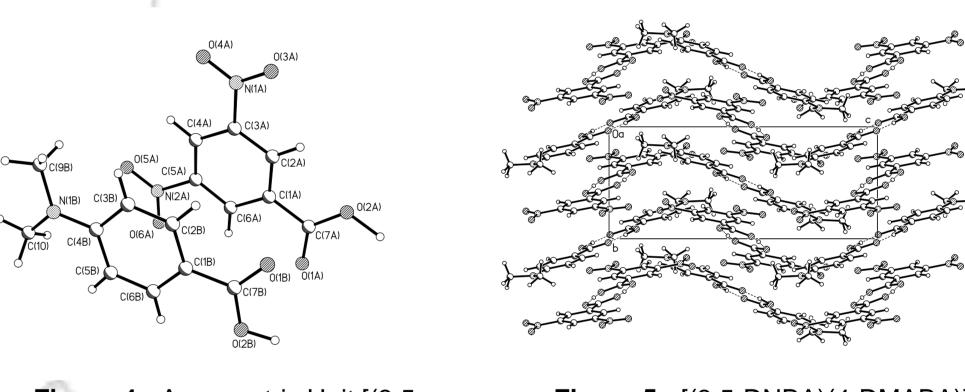


Figure 4 - Asymmetric Unit [(3,5-DNBA)(4-DMABA)]

Figure 5 - [(3,5-DNBA)(4-DMABA)] (Viewed down *b*-axis)

System D yielded [(3,5-DNBA)(18-crown-6)(NH₄+)]. (*Figures 6 & 7*)

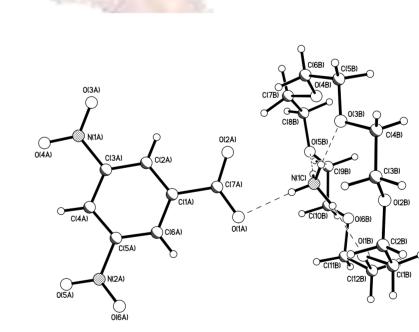


Figure 6 - Asymmetric Unit [(3,5-DNBA)(18-crown-6)(NH4+)].

Figure 7 - [(3,5-DNBA)(18-crown-6)(NH4+)]. (Viewed down *b*-axis)

Conclusion

From the work carried out it can be concluded with strong certainty that in these systems changing the relative amounts of the starting materials does not afford control of which form of the system is created. It would therefore require experimentation with other variables to determine if/how this control can be gained.

Acknowledgements

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