

at ~120-130 K observed using X-ray powder diffraction. Unusual thermal properties have been observed in the 2:1 complex of urea and fumaric acid in which hydrogen ADP trends may play a role in potential negative thermal expansion along one of the crystallographic axes. Proton transfer has also been observed in a series of complexes of urea with bromanilic acid. All of these studies have benefited from our approach of multiple condition diffraction studies of structural evolution.

[1] A. Parkin, S. Harte, A. Goeta, C.C. Wilson, *New J. Chem.* **2004**, 28, 718-721

**Keywords:** hydrogen-bonding, neutron, laue

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### Design and control of hydrogen bonding in DMAN proton sponge complexes

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1,8-bis(dimethylamino)naphthalene (DMAN) is commonly known as a proton sponge and is often observed to accept a proton from acidic materials into an N-H...N intramolecular hydrogen bond. We have been using co-crystallisation with a series of benzoic acid derivatives to explore the charge assisted hydrogen bonding induced both within the DMAN and between benzoic acid molecules. X-ray diffraction has been used extensively to determine the resulting crystal structures, with a particular emphasis on attempting to determine accurate hydrogen atom parameters and to define the hydrogen bonding schemes.

In general, DMAN and halogen substituted benzoic acid co-crystals form in a 1:2 ratio where the DMAN molecule deprotonates one benzoic acid molecule taking the hydrogen into a short strong intramolecular hydrogen bond. To compensate for this, the two halogen substituted benzoic acid molecules then form a short, strong, charge assisted hydrogen bond between themselves to stabilise this loss of a proton by forming a single hydrogen bonded dimer motif and with the protonated DMAN molecule acting as building blocks of the complex. This dimer motif is present across almost the entire series of halogen substituted benzoic acid and DMAN molecular complexes with divergence present between the benzoic acids relative position to each other caused mainly by the halogen-halogen interactions occurring in these complexes. Increasing the competition for hydrogen bonds by using hydroxybenzoic acids as the co-molecule induces a different composition ratio and behaviour of the benzoic acid in the complex formed. The 3-hydroxy and 4-hydroxy benzoic acids co-crystallise with DMAN in a hydrated 2:2:1 ratio where the stabilisation of charge takes place through two medium strength intermolecular hydrogen bonds – one to a hydroxy group of a neighbouring molecule and one to a water molecule. The single hydrogen bonded dimer motif is no longer present in the complex hence there are no distinctive building blocks in the structure. The benzoic acid molecules instead form extended chain like structures where the water molecules take part in the interactions both within the chains and between the layers of benzoic acids creating a framework between which DMAN molecules are sandwiched. The water thus plays an important role in the structure as a whole.

The effect of hydration has been studied further by introducing water as a third component in DMAN and halogen-substituted benzoic acid molecular complexes; the DMAN to benzoic acid ratio is reversed in this case (2:1, DMAN to BA) and the single hydrogen bonded benzoic acid dimer motifs are not present. Stabilisation of the lost hydrogen on the benzoic acid is achieved in this case through two water

molecules creating a hydrogen bonded ring involving four molecules. The DMAN and the ring of two water and two benzoic acid molecules thus become the building units of this molecular complex. Unusually, in this case DMAN appears in both its protonated and unprotonated forms, a consequence of the crystallization ratio and the resulting molecular complex stoichiometry.

**Keywords:** hydrogen bonding, proton transfer, proton sponge

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### Organic and inorganic halogens as HB acceptors in halopyridine complexes of Cu<sup>II</sup>

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Although interactions involving halogen acceptors have been reported from the early years of hydrogen bonding (HB) research, the primary attention was paid on the oxygen and nitrogen acceptors [1]. Furthermore, due to large partial negative charges in their complexes, fluorine and chlorine are more frequently observed as HB acceptors than less electronegative heavier halogens, e.g. bromine and iodine. The information retrieved from X-ray studies on hydrogen bonding are geometry details of the D—H...A—Y moiety. While the linear D—H...A angles are statistically favoured over bent ones, the preference for the bent angles at accepting halogen atoms originates in the highly anisotropic electron density around the halogen nucleus known as 'polar flattening' [2].

Here we report the preparation and characterization of a series of halopyridine complexes of copper(II) with intention to examine the geometry details of weak hydrogen bonding involving organic and inorganic halogens as HB acceptors. In addition to thermal and spectroscopic techniques, the complexes have been characterized using single crystal X-ray diffraction as well.

[1] A. Kovács, Z. Varga, *Coord. Chem. Rev.* **2006**, 150, 710-727. [2] S.C. Nyburg, C.H. Faerman, *Acta Crystallogr.* **1985**, B41, 274-279.

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### Structural systematics of fluoro-*N*-(pyridyl)benzamides and related isomer grids

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A 3x3 isomer grid of nine fluoro-*N*-(pyridyl)benzamides (C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>O<sub>F</sub>) as **Fxx** (x = *para*-/*meta*-/*ortho*-) was studied to evaluate and correlate structural relationships from both *ab initio* calculations and the solid-state. The effect of fluoro (**Fx**) and pyridine N atom (**x**) substitution patterns on molecular conformations from calculations and in terms of molecular organization was evaluated.

Eight isomers are forming N-H...N hydrogen bonds and only one isomer (**Fom**) is found to have exclusively N-H...O=C interactions. However, the **Fpm** isomer was found in two polymorphs, **Fpm\_N** and **Fpm\_O**, both in the same space group (P2<sub>1</sub>/n) but with different