

M.A.S. Chevallier, B.B. Iversen *Journal of Solid State Chemistry* **2005**, *175*, 3342-3351.

**Keywords:** MOF, solvothermal, isotypical

## MS17.P11

*Acta Cryst.* (2011) **A67**, C317

### New low-melting molecular complexes of common solvents - crystallization, structures, packing motifs

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The structural studies of low-melting molecular complexes (LmMC), i.e. co-crystals of components which are liquid under ambient condition, attract a lot of interest in recent years [1]. These complexes are usually formed by small molecules and thus provide excellent models for theoretical chemistry as the number of possible intermolecular interactions in such systems is low.

Earlier [2] we reported crystallization and structures of several LmMC of chloroform (CF) and dichloromethane (DCM) with small cyclic ketones and amines. In continuation of these studies several new LmMC of common organic solvents such as acetone, DMSO butanone-2 with CF, DCM and 1,2-dichloroethane have been grown *in situ* on a diffractometer and structurally characterized. The obtained crystal structures are compared with the structures of pure components and of previously known LmMC. In spite of seeming simplicity of the components, the structures display a variety of types and motifs of intermolecular interactions. Alongside with (C)C-H...O contacts, which are present in all studied structures, a number of other weaker interactions have been observed. Fine balance of these interactions and different spatial arrangements of the "syntons" make such LmMC unique, curious and challenging for prediction. However it is possible to outline general tendencies and make some conclusions about the driving forces of crystallization of LmMC. Attempts to use them in the design of co-crystallization experiments will also be discussed.

[1] M.T. Kirchner, D. Blaser, R. Boese *Chem.Eur.J.* **2010**, *16*, 2131-2146. [2] D.S. Yufit, J.A.K. Howard, *CrystEngComm*, **2010**, *12*, 737-741.

**Keywords:** in-situ crystallization, molecular complexes, intermolecular interactions

## MS17.P12

*Acta Cryst.* (2011) **A67**, C317

### The Multiple Phenyl Embrace: a useful synthon in crystal engineering

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The Multiple Phenyl Embrace (MPE), first described in 1995 by I. Dance and M.L. Scudder, [1] is a supramolecular motif comprised of phenyl rings involved in multiple aromatic interactions, which can, like hydrogen bonds, form extended networks between molecules in the solid state. The MPEs are of a strong attractive nature and they could, therefore, dominate solid state structures, which might lead to the formation of networks in one, two, and three dimensions.

Our MPE analysis focuses on crystal structures of coordination

polymers based on a Cu(I)/PPh<sub>3</sub>/N-donor ligand system. [2] By varying the linker ligand (pyrazine, 4,4'-bipyridine and 3,4'-bipyridine), anion (X = BF<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>) and solvent (CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, THF) a series of coordination polymers was synthesized resulting from reactions with [Cu(MeCN)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][X] as starting material. The 18 crystallization experiments with linear N-donor ligands yielded seven crystal structures of 1D and five crystal structures of 2D coordination polymers. The nine crystallization experiments with the non-linear N-donor ligand yielded four crystal structures showing 1D coordination polymers. [3]

The first stage of our analysis comprises the search for intermolecular P-P distances and M-P---P-M colinearities, which are parameters that can identify the presence of a Multiple Phenyl Embrace. The second stage is to describe the intramolecular geometry of the PPh<sub>3</sub> group, which tells us something about the strength of the embrace.

The analysis of 23 crystal structures, 16 from the 27 crystallization experiments mentioned above and 7 comparable ones from literature, [4] showed that 71% of the independent M-PPh<sub>3</sub> groups are involved in a six-fold phenyl embrace (6PE). Strong 6PE interactions are obtained when the geometry of the PPh<sub>3</sub> group can be described as a rotor. The analysis of these groups showed that 83% of the PPh<sub>3</sub> groups have their phenyl groups in the rotor conformation. It is shown, however, that these good rotors are not necessarily involved in the 6PE, and that the 6PE can also be formed by non-rotors.

In the Cu(I)/PPh<sub>3</sub>/N-donor ligand system the 6PE interactions form an independent connection (often) perpendicular to the backbone of the coordination polymer. In many cases the 6PE increases the dimensionality of the network formed between Cu(I) and N-donor ligands. Therefore, the Multiple Phenyl Embrace seems to be a useful synthon in crystal engineering of stable networks.

[1] I. Dance, M.L. Scudder, *J. Chem. Soc., Chem. Commun.* **1995**, *10*, 1039-1040. [2] F.F.B.J. Janssen, R. de Gelder, A.E. Rowan, *in preparation*. [3] F.F.B.J. Janssen, L.P.J. Veraart, J.M.M. Smits, R. de Gelder, A.E. Rowan, *in preparation*. [4] References cited on the poster.

**Keywords:** network synthon, crystal engineering, multiple phenyl embrace

## MS17.P13

*Acta Cryst.* (2011) **A67**, C317-C318

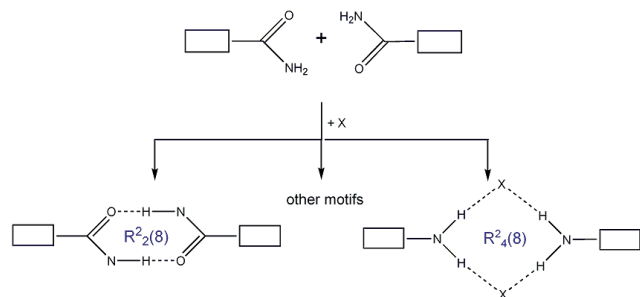
### Impact of metal coordination on amide synthons in picolinamide complexes

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Due to the abundance of the amide functionality in biological systems, the structural chemistry of the amide moieties has received considerable attention. The supramolecular behaviour of the amide functionally in organic systems is well characterized. It has become clear that it is robust and reliable supramolecular connector. It links discrete organic molecules through supramolecular R<sup>2</sup><sub>2</sub>(8) synthons at high supramolecular synthetic yield. However, relatively little work has been done in constructing predictable architectures of coordination compounds [1]. Picolinamide, having a carboxamide moiety in *ortho* position, distinctly to the other two of its isomers acts as chelating ligand, mostly through *N,O* donor set of atoms, thus imposing some restrictions on accessibility of the amide group for participation in hydrogen bonding [2], [3], [4]. The search of the CSD, confined to octahedral chelating-*N,O* dipicolinamide complexes, revealed that tetrameric motif [R<sup>2</sup><sub>4</sub>(8)] is more commonly found than the dimeric one [R<sup>2</sup><sub>2</sub>(8)]. Particularly, the dimer is observed in only one, while

tetrameric motifs involving different accepting atoms, mostly halogens, are observed in seven of seventeen structures. Therefore, it would be of interest to determine the main factors influencing the outcome of supramolecular synthesis.

With this intention here we report a series of picolinamide complexes. The complexes have been characterized using single crystal X-ray diffraction, in addition to variety of thermal and spectroscopic techniques.



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**Keywords:** hydrogen bonding, amide supramolecular synthons, crystal engineering

### MS17.P14

*Acta Cryst.* (2011) A67, C318

#### The role of metal ion choice on the structure of coordination polymer materials

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The ability to predict the nature of intermolecular forces and manipulate these in the design of property specific supramolecular entities is still a significant scientific challenge today. This quest for the design of novel functional materials has led to active study in areas such as crystal engineering and supramolecular chemistry. One of the most studied areas at the moment is the creation of novel metal-organic frameworks or coordination polymers due to the possibility of using metal ions to align molecules in desired directions. However, complexes composed of first-row transition metals and monocarboxylic acids acting as both linkers and ligands are relatively rare and as a consequence there is an interest to develop methods for the synthesis of such complexes and to study their properties [1]. One of the envisaged uses of such materials is as single-chain and single-molecule magnets.

In this work the effect of the coordination characteristics of divalent Zn, Co and Mn on structures involving monocarboxylic acids has been examined. Several 1D and 2D coordination polymers have been synthesized and their structures determined. Typical 1D structures are composed of chains in which divalent metal ions ( $Zn^{2+}$ ,  $Co^{2+}$  or  $Mn^{2+}$  for example) form a polymeric chain surrounded by carboxylate ligands. In all cases the carboxylate ligands coordinate to two metal ions and as a consequence act as a bridge between them, with the coordination environment being either tetrahedral ( $T_d$ ) or octahedral ( $O_h$ ) in some structures, or a combination of both in others. In these structures, Zn has a tendency to form complexes with either  $T_d$  or  $O_h$  coordination geometry, while Co prefers to form  $O_h$  but is also able to form  $T_d$  and other coordination geometries in between. This flexibility

in coordination usually results in 1D chains when Co or Zn are used.  $Mn^{2+}$  on the other hand, almost exclusively forms coordination sites with  $O_h$  geometry and as a consequence forms a more diverse array of structures to satisfy this requirement. This variety of coordination amongst these metals leads to a variety of structures - varying from cluster molecules to 1D chains and 2D nets - depending on the metal ion.

In addition, subtle alteration of organic ligand can significantly alter the coordination environment, and hence the structure of a material, offering further opportunities for structure manipulation. Other workers in this field have shown that in a 1D magnetic material that even very small changes in the weak interactions between the coordination polymer chains can significantly affect the properties of the material [1]. As a consequence, the effect of the systematic alteration of the organic ligands and metal ions on the crystal structures of several materials has been examined and will be presented.

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**Keywords:** crystal engineering, coordination polymer, crystal structure

### MS17.P15

*Acta Cryst.* (2011) A67, C318-C319

#### Effect of ligand functionality in the structure of $Zn^{II}$ 1D coordination polymers

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Although  $Zn^{II}$  metal-organic framework's are within the first examples of this kind of compounds to be prepared,<sup>1</sup> the interest in frameworks containing Zinc is still high due their interesting properties and potential applications.<sup>2</sup> Because of its spherical  $d^{10}$  configuration the  $Zn^{II}$  ion has a flexible coordination environment than can lead to zinc complexes with variable dimensionality.<sup>3</sup> Hence an appropriate synthetic strategy can result in new Zn MOF's with 1D, 2D or 3D dimensionalities

One of our research areas is focused on the synthesis of MOF containing  $Zn(II)$ . In this contribution we report the synthesis and structural description of three 1D  $Zn^{II}$  coordination polymers using as organic linkers amino-carboxylate ligands derived from functionalized benzoic acid.

The reaction of the appropriate  $Zn(II)$  precursors ( $Zn(NO_3)_2 \cdot 6H_2O$  or  $Zn(CH_3COO)_2 \cdot 2H_2O$ ) with 4-aminobenzoic acid (4-abaH), 4-(methyl)aminobenzoic acid (4-mabaH) and 3,4-diaminobenzoic acid (3,4-dabaH) generates the species  $\{[Zn(4-aba)_2(H_2O)] \cdot (H_2O)\}_n$  [1],  $\{[Zn_2(\mu-4-maba)_3] (\mu-4-maba)\}_n$  [2], and  $\{[Zn(3,4-daba)_2(H_2O)_2] \cdot (H_2O)\}_n$  [3].

These three compounds show a 1D structure 1D where the metal centres are linked by amino-carboxylate ligands. Both **1** and **3** consist of one-dimensional chains in which the metals have similar environments. Two of the ligands are bonded by the amino group and the other two by the carboxylate group. However the presence of a methyl group in the amino moiety of 4-(methyl)aminobenzoic

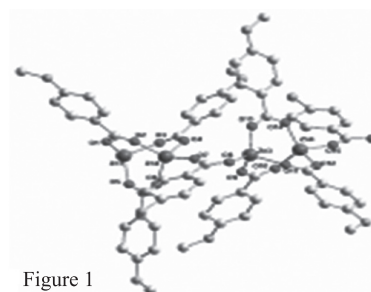


Figure 1