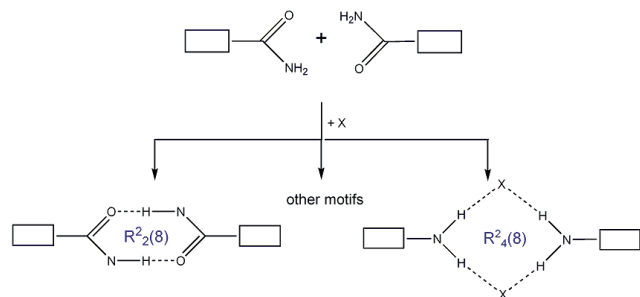


tetrameric motifs involving different accepting atoms, mostly halogens, are observed in seven of seventeen structures. Therefore, it would be of interest to determine the main factors influencing the outcome of supramolecular synthesis.

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

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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

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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,¹ the interest in frameworks containing Zinc is still high due their interesting properties and potential applications.² 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.³ 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

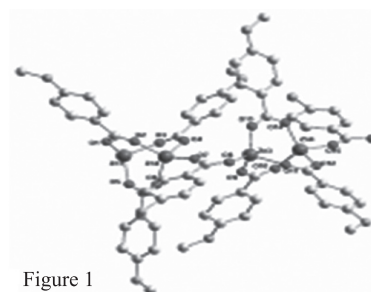


Figure 1

acid affects its coordination ability and in compound **2** the ligand only connects to the metal by the carboxylate group. In the structure it is observed a dimetallic subunit where the Zn atoms are bonded by three ligands. These units are linked by another ligand through its carboxylate fragment, rendering a disposition where the metals are bonded to four oxygen atoms in a tetrahedral geometry.

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Keywords: carboxylate, coordination, zinc

MS17.P16

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Design and crystal structures of novel lamotrigine cocrystals

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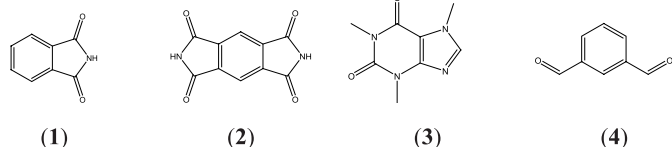
Design of cocrystals is conducted with detailed examination of selected API (Active Pharmaceutical Ingredient) molecular fragments that can be involved in supramolecular assemblies as well as with analysing similar structures available in crystallographic data bases. Exploring the potential of cocrystal formation contributes for better understanding the basic principles of supramolecular chemistry.

In this work, lamotrigine, an antiepileptic drug was chosen as a model drug to design and prepare cocrystals on the basis of the synthon types and interactions found in its crystalline structures of salts and solvates. Due to its basicity, nitrogen N2 atom of triazine ring is always protonated in lamotrigine salts.

It is well known that the N-H...N hydrogen bonds between amino groups and the N2 triazine nitrogen atom form an $R_2^2(8)$ dimer in lamotrigine structure itself [1]. These dimers are usually further connected via N-H...O hydrogen bonds between another N-H amino group and oxygen atoms of oxygen containing solvate molecules into more complex hydrogen-bonded rings.

These synthons along with the presence of chlorine atoms in lamotrigine molecule are considered as models in design of targeted lamotrigine cocrystals.

In that context, four cocrystal former molecules are chosen for lamotrigine cocrystal preparation: phthalimide (**1**) and analogous pyromellitic diimide (**2**), caffeine (**3**) and isophthalaldehyde (**4**) on the basis of their stereochemically disposable proton donors (N-H) and proton acceptors (keto groups). In cocrystal structures with (**1**), (**2**) and (**3**) molecules, the lamotrigine N-H groups and the triazine N2 atom participate into hydrogen bond formation mutually via N-H...N hydrogen bonds and with cocrystal molecule via N-H...O=C bonds. The presence of the Cl...O short contacts in (**2**), (**3**) and (**4**) structures has been confirmed.



[1] B. Sridhar and K. Ravikumar, *Acta Cryst.* **2009**, C65, o460-o464.

Keywords: cocrystal, lamotrigine, synthon

MS17.P17

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Synthesis and structural analysis of cadmium dipicolinate coordination polymers and tetramers

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Metal coordination polymers constructed with multi-carboxylate ligands have been extensively studied in supramolecular chemistry and materials chemistry due to their structural diversity and application in catalysis, ion exchange, adsorption, nonlinear optics, luminescence and magnetism. [1] Dipicolinic acid, dipicH_2 , is a versatile chelating ligand which can interact with metal ions both in anionic and protonated form. It is widely used for the preparation of the various metal complexes. It displays a large number of coordination modes due to the position of its carboxylate groups and its nitrogen atom, with the potential to act as a bidentate, tridentate and/or bridging ligand [2].

Here we report the hydrothermal preparation of two cadmium dipicolinate polymers and four tetramers. The two polymers have the formula $[\text{Cd}_2(\text{H}_2\text{O})_3(\text{dipic})_2]_n$ and are polymorphs of each other. The four tetramers can be classed into two groups of general formula $[\text{Cd}_2\text{X}(\text{H}_2\text{O})_4(\text{dipic})(\text{dipicH})]_2 \cdot 2\text{H}_2\text{O}$ and $[\text{Cd}_2\text{X}_2(\text{H}_2\text{O})_3(\text{dipicH})_2]_2 \cdot 2\text{H}_2\text{O}$, where X = Cl or Br. The structures of the compounds have been elucidated by single X-ray diffraction and their thermal behaviour characterized by thermal gravimetry and differential scanning calorimetry.

Using either the cadmium bromide or chloride salt in a 1:1 ratio with dipicolinic acid can lead to any of the above type of structures, indicating the importance of subtle differences in preparation conditions, e.g. concentration of reactants and duration of heating.

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Keywords: coordination, polymer, polymorph

MS17.P18

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Structural analysis of hexa-imidazole cobalt (II) 2-bromide tetrahydrate

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Hexa-imidazole cobalt (II) 2-bromide tetrahydrate, formulated as $\text{C}_{18}\text{H}_{32}\text{Br}_2\text{CoN}_{12}\text{O}_4$ (I), was synthesized. The crystal and molecular structure of (I) have been determined by X-ray single crystal diffraction. The compound (I) crystallizes in the triclinic, space group P-1 with unit cell parameters $a=8.8660(8)\text{Å}$, $b=9.2117(9)\text{Å}$, $c=10.7641(10)\text{Å}$, $\alpha=76.356(8)^\circ$, $\beta=83.275(8)^\circ$, $\gamma=61.527(7)^\circ$, $R_1=0.431$, and $wR_2=0.0993$.

The title compound is composed of $[\text{Ni}(\text{imidazole})]^{2+}$ complex cations, Br atoms and water molecules. The cobalt atom is located at special positions. The Co atom has octahedral coordination geometry defined by imidazole rings coordinated through N atoms.

The crystal packing is achieved by strong and moderate hydrogen bonds which play an important role in the formation of the 3D network.