

One strategy of synthesis concerns the use of rigid, chemically-stable, and usually large building blocks (the so-called Secondary Building Units – SBUs) to construct MOFs. This modular approach has been successfully employed to design remarkable structures [1]. Our research group has been actively working both in the preparation and study of coordination polymers and in crystalline phases of cyclodextrins (CDs) as remarkable examples of supramolecular host-guest systems for inclusion compounds. Recently, we introduced a new concept [2]: a CD-based SBU, by including 4,4'-biphenyldicarboxylate into β -CD, a bridging ligand capable of forming porous MOFs.

Following our interest in preparing new SBUs, we present the study of the inclusion compound β CD·PPNO, (PPNO = 4-phenylpyridine-*N*-oxide) which was prepared by treating stepwise an aqueous solution of β CD with PPNO at 60 °C. Two different phases were obtained: while phase II was obtained after 1 day of slow cooling to ambient temperature, phase I was obtained by slow evaporation of the solvent after several days. The two phases show diffraction patterns similar to models described in the review of Cairra [3], which correspond to specific crystal packings of the hosts, and were ultimately confirmed by single crystal X-ray diffraction. Phase I crystallises in the monoclinic *C2* space group while phase II crystallises in the triclinic *P1* space group. In phase I the cavities are aligned forming the so-called “channel packing”, and in phase II the host dimers form a supramolecular packing named “intermediary packing” in which the cavities are isolated from each other. In both structures the guests are included in to the CD cavities. We serendipitously discovered that samples of phase II readily transform by at least two ways into phase I, but never the opposite: i) the milling of crystals of phase II for about one minute produces a phase I powder; ii) crystals of phase II transform into crystals of phase I in a few days. This latter phenomenon was monitored by X-ray diffraction: a specific crystal was indexed as belonging to phase II and two days later it was indexed as the lower crystallinity phase I.

Two different phases of β CD·PPNO were readily prepared, with the remarkable ability of fast conversion of one into the other. The use of either phase as SBU model for the synthesis of MOFs is the following step of the present work.

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Keywords: cyclodextrins, secondary building units, metal-organic frameworks

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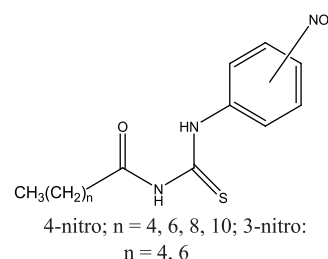
Crystal packing in a series of *N*-nitrophenylcarbomothioyl-alkylamides

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The structures of a number of 4- and 3-nitrophenyl

carbomothioylalkylamides will be reported and the effect on the crystal packing of varying the position of the nitro-substituent and the length of the alkyl chain will be examined. In each molecule intramolecular N—H...O contacts effect the molecular conformations. Centrosymmetric dimers resulting from N—H...S



hydrogen bonds dominate the crystal packing. These are augmented by a variety of C—H...O(S) contacts that vary with the substitution in the benzene ring and the length of the alkyl chain.

Keywords: packing, chains, carbomothioylalkylamides

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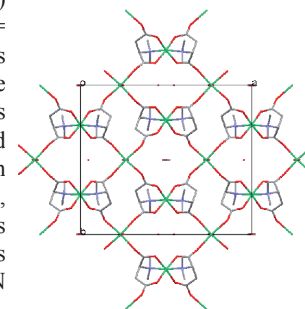
Solvothermal synthesis of metal organic framework structures in Zn- Cd- Ni-OAc -DMF system

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Synthesis and characterization of porous metal organic frameworks (MOFs) has prompted considerable interest because of the possibility for designing networks, where both pore size and physical/chemical properties can be manipulated by suitable selection of the basic components. Several synthetic pathways have been exploited for MOF construction. Significant interest has arisen in organic and coordination chemistry for the design and synthesis of novel coordination polymers with ligands generated in situ at relatively low temperatures.

In this work, we have chosen DMF as solvent in the solvothermal synthesis, of metal-organic framework compounds in the system Zn-Cd- Ni-OAc with different dicarboxylate acids. It is known that during solvothermal synthesis DMF decomposes to formate ions which are easily incorporated in MOF's [1], [2]. Thus we investigated the effect of the temperature variation of this decomposition on MOF structure generation.

The obtained MOFs are characterized by single-crystal X-ray diffraction, X-ray powder diffraction, TG analyses and IR spectroscopy analyses. Preliminary X-ray single crystal diffraction results show that at least two different types of structures may be produced in function of the temperature. The Zn- and Cd- structures crystallizes in the hexagonal R-3c, with respective parameters of $a = 8.1901(6)$, $c = 22.151(7)$ Å and $a = 8.5112(4)$, $c = 23.015(6)$ Å. The Ni- crystallizes in the monoclinic *C2/m* with $a = 14.1421(7)$, $b = 16.5006(4)$, $c = 6.7254(2)$ Å $\beta = 109.096(4)$. The Zn and Cd structures could be considered as isotypical. The difference in the unit cell parameters of Zn and Cd MOFs is explained by the difference of coordination capability of the cations. In contrast, even though Ni also coordinates octahedrally its structure consists of a mixture of Ni-O and Ni-O/N octahedra (Fig. 1).



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

Keywords: MOF, solvothermal, isotypical

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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.

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

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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)/PPh₃/N-donor ligand system. [2] By varying the linker ligand (pyrazine, 4,4'-bipyridine and 3,4'-bipyridine), anion (X = BF₄⁻, ClO₄⁻ and PF₆⁻) and solvent (CH₂Cl₂, CHCl₃, THF) a series of coordination polymers was synthesized resulting from reactions with [Cu(MeCN)₂(PPh₃)₂][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 PPh₃ 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-PPh₃ groups are involved in a six-fold phenyl embrace (6PE). Strong 6PE interactions are obtained when the geometry of the PPh₃ group can be described as a rotor. The analysis of these groups showed that 83% of the PPh₃ 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)/PPh₃/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.

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Keywords: network synthon, crystal engineering, multiple phenyl embrace

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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 R²₂(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 [R²₄(8)] is more commonly found than the dimeric one [R²₂(8)]. Particularly, the dimer is observed in only one, while