

DSC/TGA thermal analysis. FT-IR spectra of the compounds indicates the nature of the metal-ligand coordination environment. Presence of $\nu(\text{O-H})$ shifted to lower energy indicated H-bonded carboxylic acid, while $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ splitting show both monodentate and bidentate carboxylate coordination [2]. Monodentate SO_4^{2-} (C_{3v}) and bidentate bridging SO_4^{2-} (C_{2v}) modes can also be inferred from infrared spectral analysis.

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Keywords: metal-picolinate complexes, carboxylic acid, spectroscopy

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Inverse opal-like systems: correlating mesoscale structure and magnetic properties

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A new class of the three-dimensional mesoscale ferromagnetic structure, Inverse Opal-Like Structures (IOLS), is investigated by means of microradian X-ray Diffraction (XRD) and polarized Small-Angle Neutron Scattering (SANS). The samples are synthesized by filling the voids of artificial opals with cobalt or nickel precursors and subsequent removing the initial template in order to leave three-dimensionally ordered porous films consisting of quasi-tetrahedra and quasi-cubes which are connected by vertices.

The microradian XRD reveals the type and degree of imperfection of opal-like structures. It was shown that the inverse OLS ordered in the twin FCC structures with the lattice constant of 640 ± 10 nm but also with clear tendency to the random hexagonal close-packed (RHCP) structure along the [111] axis.

The magnetic properties of IOLS were studied by polarized SANS technique with the analysis of the magnetic contribution and nuclear-magnetic interference of the diffraction peaks. The complex magnetic structure appears upon application of the magnetic field with non-homogeneous distribution of magnetization density. Such distribution is determined by the combined effect of the easy-plane geometry of the film and the principal axes of the opal-like structure with respect to the applied field direction.

Keywords: opal-1, magnetism-2, SANS-3

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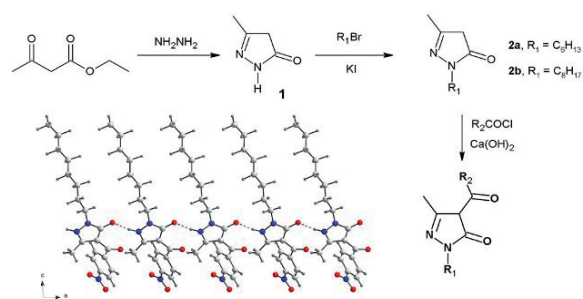
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A supramolecular approach to the analysis of the crystal structures of some 1-Alkyl-3-methyl-4-acyl-5-pyrazolone derivatives

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For theoretical and practical reason pyrazolones are an important group of nitrogen heterocyclic organic compounds. They find applications as analgesic and anti-inflammatory drugs, dyes, chelating extractants for numerous metal ions [1]. Pyrazolones have also attracted much attention because they exhibit prototropic tautomerism and they have been extensively studied both in solution and in the crystalline phase. Pyrazolones have also been studied as photochromic and luminescent materials. Coordination chemistry of pyrazolones is also very important; consequently considerable effort has been devoted to have a better knowledge of both ligands and metal complexes based on pyrazolone derivatives.

Most 3-methyl-4-acyl-pyrazolones reported to date are 1-aryl derivatives, in some few cases it is possible to found 1-alkyl examples like methyl or t-butyl, but the 1-n-alkyl-pyrazolones are scarce. On the other side, it was shown that 5-pyrazolone can be easily alkylated at N-1 with primary alkyl halides yields being very good [2]. Alkylpyrazolones underwent electrophilic substitution at C-4 the same way 1-arylpyrazolones do. Thus, 1-n-alkylpyrazolones can be acylated following the procedure reported by Jensen [3]. The 1-aryl-4-acylpyrazolones are isoelectronic with β -diketones and their coordination chemistry is very well known. The coordination chemistry and tautomeric behaviour of some 1-n-alkyl-4-acylpyrazolones is even less known. In this presentation the synthesis and crystallographic data of 1-alkyl-3-methyl-4-acyl-5-pyrazolones and their Cu(II) complexes are discussed.



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Keywords: crystal engineering, acylpyrazolones, Cu-complexes

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Amide to amide interactions: from strong to weak hydrogen bonds in bis-(quinoxaline-carboxamide) functionality

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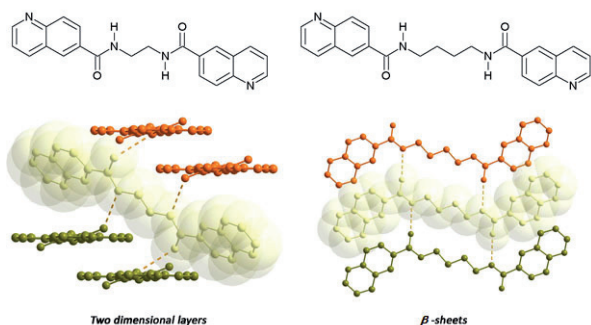
Deliberate design of molecules to build supramolecules in crystals with particular properties has become a very attractive area of research. A productive strategy in crystal engineering is to consider the molecules with functional groups that form robust synthons [1]. Crystal packing is the result of the optimization of various possible intermolecular interactions between the molecules. Structures including carboxylic

acid and amides functional groups are usually known to form robust synthons in absence of other strong hydrogen bonding functional groups.

The primary goal of crystal engineering is the prediction of supramolecular arrangements for a given molecular structure. Such predictions are more difficult for molecules featuring multiple hydrogen functional groups as well as flexibility [2].

We have explored the crystal structures of homologous series of *bis*-(quinoline-carboxamido)-alkane in which the amide moieties are separated by even number of $-(CH_2)_n-$ groups. The *bis*-amides show an "anti" conformation, in spite of the modification from quinoline-2-carboxamido to quinoline-6-carboxamido. Other authors have made important efforts to understand the occurrence of amide-amide hydrogen bonds in presence of nitrogen-heterocycles moieties [3]. In this contribution, we present the geometric molecular analyses versus hydrogen bonding formation in the compounds. The nature of the hydrogen bond is strongly determined by the molecular geometry [3]. Changes in the dihedral angle defined between the quinoline ring and the amide groups allow the interactions from weak $Csp^2-H\cdots O$ to strong $N-H\cdots O$. A rare exchange between the 2D-layers and β -sheets occur with the extension of the alkyl chain in our quinoline-6-carboxamide derivatives [4]. Subtle variations in some geometric parameters would account for this change but a more systematic research is necessary to have a better understanding in these systems.

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Keywords: H-bonding, amide interaction, crystal engineering.

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The inclusion of substituted acetophenones in cyclodextrins: an X-ray diffraction and solution NMR spectroscopy study

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2-hydroxy-4-methoxy acetophenone (2H4M), known as paeonol, is a naturally occurring phytoalexin which has been found to have analgesic and antibacterial properties. 4-hydroxy-3-methoxy acetophenone (4H3M), commonly known as acetovanillone, is also plant-derived and possesses anti-inflammatory activity. The use of these drugs is limited by their low solubility in water [1]. A method commonly used to improve drug solubility is cyclodextrin inclusion. The inclusion complexes were formed in the solid state between the

guest molecules and various cyclodextrins (CDs), namely the native hosts γ -CD and β -CD, as well as the derivatised CDs heptakis(2,3,6-tri-*O*-methyl)- β -CD (TMB), heptakis(2,6-di-*O*-methyl)- β -CD (DMB) and hexakis(2,3,6-tri-*O*-methyl)- α -CD (TMA). These inclusion complexes were characterised using X-ray diffraction methods (single crystal XRD and powder XRD), thermal analysis (DSC, TGA and HSM) and proton nuclear magnetic resonance spectroscopy (¹H NMR) [2]. Solubility studies were carried out using UV-Vis spectrophotometry. The isomers 2-hydroxy-5-methoxy acetophenone (2H5M) and 2-hydroxy-6-methoxy acetophenone (2H6M) were also studied for comparative purposes.

Inclusion complexes were formed between each of the four guest molecules and β -CD and γ -CD, respectively. The single crystal XRD data showed that two of the four inclusion complexes, namely 2H4MBCD and 2H5MBCD, were isostructural with a known isostructural series which crystallises in the monoclinic space group C2. The remaining two complexes 2H6MBCD and 4H3MBCD are isostructural with a known isostructural series which occurs in the triclinic space group P1. The inclusion compounds formed between each of the four guest molecules and γ -CD crystallise in the tetragonal space group P4₂, 2₁. ¹H NMR spectroscopy was used to determine the stoichiometry.

Single crystal inclusion complexes were only formed between TMB and 2H4M, 2H5M and 4H3M, between 4H3M and DMB and between 2H5M and TMA. The structures of 2H4MTMB and 4H3MTMB were found to be isostructural with one another, occurring in the orthorhombic space group P2₁, 2₁. The 2H5MTMB complex crystallised in the triclinic space group P1. The crystal 4H3MDMB belongs to the orthorhombic space group P2₁, 2₁ while the 2H5MTMA complex crystallised in the hexagonal space group P6₃.

In a complementary study, the association between the guest molecules and the native cyclodextrin β -CD was studied using ¹H NMR spectroscopy. By analysing the proton chemical shift changes in aqueous solution as a function of concentration, the stoichiometry of inclusion complexes formed was assessed by Job Plot analysis and the association constants were calculated. In each case, the Job Plots of the proton chemical shifts of both host and guest revealed a 1:1 host to guest ratio. The association constants were found to be of the order of 10² for each complex, indicating weak host-guest interactions.

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Keywords: cyclodextrin, paeonol, acetovanillone

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The influence of solidification direction on the CET in Zn-base alloys

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Zinc gravity casting alloys can be used for general industrial applications where strength, hardness, wear resistance or good pressure tightness is required. Zinc alloys are often used to replace cast iron because of their similar properties and higher machinability ratings.

The composition of hypoeutectic alloys is close to 4%wtAl and their aluminum content is greater than that of eutectic alloys (5%wtAl). All zinc casting alloys have dendritic/eutectic microstructures. However, hypoeutectic alloys solidify with zinc-rich dendrites, whereas