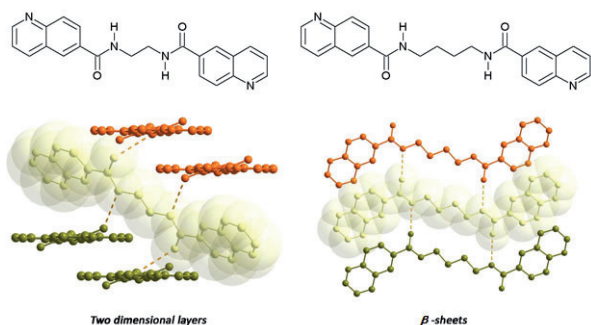


acid and amides functional groups are usually known to form robust synthons in absence of other strong hydrogen bonding functional groups.

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

MS24.P84

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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

hypereutectic alloys solidify with aluminum-rich dendrites.

In a solidification process, the microstructure depends on the alloy characteristics and is mainly a function of the temperature evolution ahead the solid/liquid interphase [1-3].

Among the several phenomena occurring during solidification, like solute segregation or morphology stability, one of the most important ones is dendritic growth. The most important dendrite parameters are the primary, secondary and tertiary arm spacings due to their influence on mechanical properties.

An efficient method to examine the evolution of the dendrite arms is related to the application of steady-state directional solidification with an imposed growth rate, V , and a thermal gradient, G , at the solid/liquid interphase.

In this work, Zn-Al (wt%) alloys were solidified under unidirectional solidification in a device cooled with water, in a vertical upward direction (0°), inclined at 30° and 45° to the vertical and in a horizontal upward direction (90° to the vertical). We determined the position of the transition from columnar to equiaxed structure (CET) through macro and micro-analysis, and significant thermal parameters by recording temperature-time data. The results show that the direction of dendrite growth is about that of the heat extraction and that the angle of inclination of the columnar grains with the longitudinal axis of the alloy sample coincides approximately with the angle of inclination of the furnace.

The relevance of the problem under study is justified on the basis that the solidification variables, including natural convection, affect the structures of the solid and the formation of defects. The solidification variables are also important for modeling prediction of the structure and property of a given cast piece [3-11]. The results also allow a better understanding of the conditions and mechanisms operating in a solidification with different directions.

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Keywords: solidification, Zn base alloys, CET

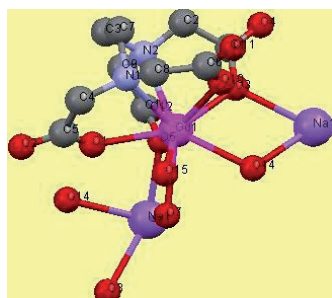
MS24.P85

Acta Cryst. (2011) **A67**, C390

Synthesis, characterization, structural analysis and biological activities of new transition metal complexes

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In this research, some of the new inorganic complexes of transition metals were synthesized. Complexes were characterized by FT-IR and UV spectra, X-ray diffraction, ¹HNMR, ¹³CNMR, techniques and some physical properties. Different properties of these new compounds such as biological properties including antitumor and antibacterial activities were studied. The antitumor activity of some complexes against a panel of human tumor cell lines were determined by MTT(3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyl-tetrazolium bromide) assay. These data suggest that some of these compounds pro-



vide good models for the further design of potent antitumor compounds [1], [2].

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Keywords: inorganic, complexes, crystals.

MS24.P86

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Two New Hydroxybenzophenone Complexes of Copper (II)

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Copper (II) complexes with non-steroidal anti-inflammatory drugs (NSAIDs) shows enhanced anti-inflammatory activity and reduced gastrointestinal toxicity compared with their uncomplexed parent drug [1]. Is known that some hydroxybenzophenones acts as NSAIDs and have antimicrobial activity [2], so is necessary to study the coordination of copper (II) to these molecules and the molecular and supramolecular structure of these complexes since the structure affects directly in these biological activities.

Complexes of bis-2-benzophenonate copper (II) – (B2BC) – and bis-2,2'-hydroxybenzophenonate copper (II) – (B22HBC) – were synthesized from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2-hydroxybenzophenone and 2,2'-dihydroxybenzophenone reaction with a 2:1 stoichiometry (ligand: metal) and their crystal were obtained from solvent slow evaporation, ethyl acetate/chloroform for B2BC and methanol for B22HBC. These complexes were characterized by single crystal XRD (Gemini, MoK α , 100K, Direct Method and Least square of full matrix) and their molecular structures were analyzed using MOGUL.[3] The main crystallographic parameters of B2BC are C2/c space group, $a = 18,695(1) \text{ \AA}$, $b = 5,7548(3) \text{ \AA}$, $c = 19,920(1) \text{ \AA}$, $\beta = 114,209(7)^\circ$, $R1 = 0,0797$ and $wR2 = 0,2517$, and of B22HBC are P21/n space group, $a = 7,077(5) \text{ \AA}$, $b = 11,037(5) \text{ \AA}$, $c = 13,138(5) \text{ \AA}$, $\beta = 100,643(5)^\circ$, $R1 = 0,0473$ and $wR2 = 0,1677$.

Both complexes have a square planar geometry with the copper atom in the plane of oxygen, since it is present in the structure's inversion center. This coordination is interesting to some biological activities. The presence of the second hydroxyl in ortho position affects the molecular geometry, especially the dihedral angle and the carbonyl bond length. These geometric features can affect the anti-inflammatory and antimicrobial activities, due to changing in the H• donation and, consequently, in the anti-oxidant properties. Many of biological functions have been attributed to free-radical-scavenging and anti-oxidation properties.[4] No intramolecular hydrogen bonding for both complexes.

In terms of supramolecular structure, the crystal packing of B2BC does not show intermolecular hydrogen bond, being stabilized only by weak VDW interactions, while B22HBC is stabilized by one classical intermolecular hydrogen bonding, forming an infinite network along the [010] and [101] directions. $\pi \cdots \pi$ staking interactions help also to stabilize the B22HBC's packing. Structure-activity relationship (SAR) of B2BC and B22HBC is being carried out parallel to the biological activity studies.

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