

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

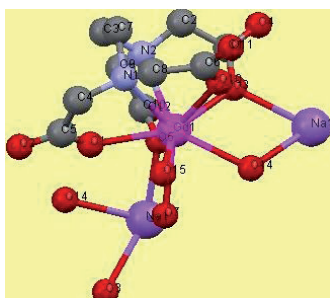
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Synthesis, characterization, structural analysis and biological activities of new transition metal complexes

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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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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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Keywords: Bioinorganic, Copper, Complex

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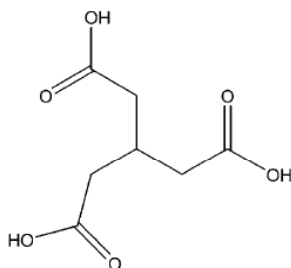
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Discrete and Polymeric Metal-Organic Systems Based on the Methanetriacetic Acid

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The construction of multidimensional frameworks and the design of infinite MOF'S with transition metal ions and lanthanides is a field of great interest due to the applications that can be developed from these new materials. Carboxylic acids with specific geometries can be used to generate topological networks by design. In this work we have focused on the methanetriacetic acid, a tricarboxylate with a C₃-symmetry whose arms can coordinate to different number of metal nuclei as it has been recently reported in a series of gadolinium(III) complexes [1]. However, now we have turned our attention not only to the design of polymeric systems based on the methanetriacetic acid, but also to discrete systems taking into account the tritopic nature of the ligand to coordinate with three elements and using blocking ligands.

Here we present a series of copper(II) complexes of different dimensionalities that show the coordination chemistry that can be done with the methanetriacetate ligand. The conditions of the synthesis, mainly the stoichiometry of the reaction, afforded Cu(II) compounds whose crystal structure and magnetic properties have been investigated.



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Keywords: copper, crystal structure, carboxylic acids.

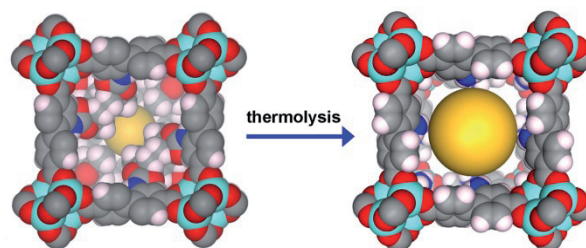
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Creating nothing out of something: thermolabile groups in metal-organic frameworks (MOFs)

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We are interested in the 'reverse' post-synthetic modification of MOFs, *viz* the expulsion of functional groups whilst conserving framework crystallinity and enhancing porosity [1, 2]. This can be accomplished using specifically designed thermolabile and photolabile ligand side-arms. In this talk I will outline our recent results in this area. We have found that when thermo/photolabile groups are tethered to various biphenyl-4,4'-dicarboxylate ligands, we observe several interesting and useful outcomes, for example (i) the suppression of network interpenetration (catenation), (ii) the expansion of cavities and apertures within the framework, (iii) the unmasking of useful functional groups that are located on the surface of this void space, and (iv) the synthesis of MOFs that cannot be prepared directly. This methodology has been extended to the preparation of chiral, catalytically-active MOFs.



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The structural chemistry of nano-crystalline ferrihydrite

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Nano-crystalline oxyhydroxides are implicated in a variety of processes, including toxic metal sequestration, sorption, acid-mine drainage, and the global iron and sulfur cycles [1,2]. The composition, single-phase nature and atomic arrangements in nano-crystalline ferrihydrite have been controversial for at least 50 years [3-6]. Contrary to previous reports [5], the scattering data from nano-crystalline ferrihydrite is consistent with a single-phase model [6], greatly simplifying modeling of local and global cycles. Considerable debate still surrounds the atomic arrangement in ferrihydrite [5-8]. A growing body of evidence, gleaned from a combination of structural and thermal probes, confirms the composition of ferrihydrite is close to Fe₁₀O₁₄(OH)₂ and that a single-phase model suffices for explanation of the atomic arrangement in inorganically and biologically derived 2- and 6-line varieties.

The kernel of the debate over appropriate structural models for ferrihydrite boils down to the presence [4,6,7], or not [5,8], of iron(III) in the tetrahedral environment. Real space modeling of the pair distribution function (PDF) derived from analysis of the total high-energy elastic x-ray and neutron scattering has been particularly instructive in this regard. While multi-phase models [5,8] have been used in the past, there are features in the PDF of ferrihydrite, that are inconsistent with both single and multiphase models that do not include a component of tetrahedral coordination for Fe(III). In particular a 3.44Å peak in the X-ray PDF is observed in ferrihydrite. Only the x-ray PDFs for minerals containing tetrahedral Fe(III), maghemite and magnetite, contain peaks close to this value of *r*. Multi-phase models containing only octahedral Fe(III) cannot produce a strong 3.44Å