

resulting precipitates were characterized by Infrared Spectroscopy, X-ray diffraction and the morphology of crystals was observed by an optical microscope and a scanning electron microscope.

The results showed that SOM influences not only on the agglomeration, morphology, size and polymorphism of the CaCO₃ crystals but also narrows the range of calcium and carbonate critical concentrations necessary to induce nucleation, the "Crystals-Growing Space". Thus, it appears evident that in gelling environment the SOM is able to select a specific calcium and carbonate concentration. That, respecting the supersaturation laws, confines the nucleation and growth processes.

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Keywords: biomineralization, organic matrix, gelling environment

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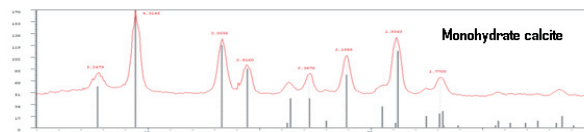
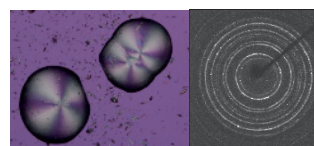
Self-assembled crystalline materials of calcium carbonate and silica

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Biom mineralization is a widespread crystalline phenomenon among living systems which provides superior microscopic and macroscopic material properties, which has aroused a great deal of interest and in vitro studies throughout the past years [1]. Moreover, the self-assembly of alkaline-earth metal carbonates in the presence of silicate is an outstanding example in biomineralization, as purely inorganic precursors cooperate in this case to constitute special structures and shapes strongly reminiscent of biological forms [2]. This kind of completely inorganic, self-assembled silica-carbonate aggregates showing a wide range of non-crystallographic, biomimetic morphologies and sizes from a much simpler system compare to living organisms [3]. However, the precipitation of calcium carbonate (CaCO₃) in basic silica has not produced the similar forms characteristic of biomorphs in the absence of any additives at room temperature until now.

Here we report an experimental study of the crystallization of calcium carbonate in silica gel at ordinary temperature and pressure. The experiments have been performed by diffusion-reaction technique in a diffusion cell, without the presence of organic additives. The concentrations of CaCl₂ and Na₂CO₃ have been varied from 0.05M to 0.2M in equimolar amounts and the gel pH value from 9.0 to 10.5. The crystals have been characterized by XRD, SEM and optical microscopy. After the screening of pH we have specially studied the crystallization at pH=10.5.

At this pH the results are the precipitation of the following crystalline phases with the increase in reagent concentrations: monohydrate calcite, calcite and aragonite. Microscopic observation of these crystalline phases reveals that monohydrate calcite is formed as peanut-like and hemispheric crystals in the liquid part of the system (see figure) whereas calcite (rhombohedral and sheaf of wheat morphologies) and aragonite (flower-like and lamellar morphology) are found out in the gel part. The formation mechanisms and specially the way in which silica interact with calcium carbonate to produce these morphologies is being deeply investigated.



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Keywords: silica gel, monohydrate calcite, calcite, aragonite

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Coordination polymers of *N,N'*-bis(pyridin-4-ylmethyl)hexanediamide (L): Ligand conformation and the effect of metal to ligand ratio

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The X-Ray crystal structures of four coordination complexes namely: [Cd(L)_{1.5}(NO₃)₂]_n **1**, {[Cd(L)(H₂O)₄](NO₃)₂(H₂O)₂]_n **2**, {[Zn₂(L)(H₂O)₅](NO₃)(H₂O)₂]_n **3** and {[Zn(L)(H₂O)₄](NO₃)₂(H₂O)₂]_n **4** are described. It was found that the ligand conformation [1] and the metal to ligand ratio [2] play an important role in determining the structure of the resulting complex. By varying the metal to ligand ratio and keeping other experimental factors constant, different coordination complexes were obtained.

Complex **1** was grown from cadmium nitrate and L (*N,N'*-bis(pyridin-4-ylmethyl)hexanediamide) in a metal ratio of 2:1. The complex consists of 2-D networks which are linked by self complementary amide hydrogen bonds. Complex **2** was grown from cadmium nitrate and L in a metal to ligand ratio of 1:1 and it consists of 1-D chains that are interlinked by hydrogen bonding via the nitrate anion. The three independent ligands in complex **2** adopt the AAA (anti-anti-anti) and GAG (gauche-anti-gauche) conformations while the ligands in complex **2** adopt the GAG conformation. Complexes **3** and **4** were grown from zinc nitrate and L in metal to ligand ratio of 1:2 and 1:1 respectively. Complex **3** consists of discrete and dinuclear units that are linked by hydrogen bonding via the coordinated water molecules. Complex **4** consists of 1-D chains that are interlinked by hydrogen bonding via the nitrate counter ions. The ligands in complex **3** are arranged in the AAA conformation while the ligands in complex **4** are arranged in the GAG conformation.

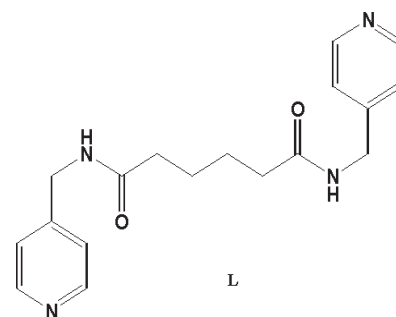


Fig 1. *N,N'*-bis(pyridin-4-ylmethyl)hexanediamide (L).