

Currently we are exploring the use of N-heterocyclic carbenes in the chemistry of rhodium complexes. Our idea is to increase the stability of potential rhodium catalysts by incorporating this sort of electron-rich ligands, whereas we try to direct selectivity by introducing bulky substituents exerting steric control over the interaction of substrates with catalysts [2].

We have chosen the 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene (IPr) ligand in the synthesis of a family of rhodium complexes of the types $[\text{RhCl}(\text{IPr})\text{PyL}]$ or $[\text{RhCl}(\text{IPr})\text{L}]_2$ (Py = pyridine or substituted pyridines; L = ethylene, cyclo-octene, oxygen) (see figure). The additional presence in all these complexes of an unsaturated labile ligand L confers them a good suitability to be used as catalyst precursors in different processes [3]. In the present communication, we will discuss the structural features of these complexes trying to understand the relationships between these features with their chemical and catalytic behavior.

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Molecular iodine trapped as alternating layers with amphiphilic salts

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Halogen bonding is a term used to describe a non-covalent interaction between a halogen atom acting as a Lewis acid and a Lewis base.¹ As the bonding parameters of this interaction are very predictable halogen bonding can be exploited to create some intriguing solid state structures using both halogen containing hydrocarbons (aliphatic or aromatic) and dihalogen species (eg. I₂).

We have investigated the insertion of molecular iodine (I₂) to amphiphilic salts where mono-alkylated DABCO (1,4-diazabicyclo[2.2.2]octane) moiety acts as the cationic species and the halogen bond acceptor. The solid state structures of the I₂⋯DABCO complexes will be presented in addition to the complexation reactions which include crystallization of the complexes from solutions as well as solid state complexation.

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Keywords: halogen bonding, x-ray diffraction, amphiphilic salts

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Crystal Structure of PrAgAlGe_{3-x}

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A systematic investigation of the Pr-Ag-Al-Ge system led to the

discovery of a new quaternary compound.

An alloy of the nominal composition Pr_{0.125}Ag_{0.250}Al_{0.250}Ge_{0.375} was synthesized by arc-melting of the constituent elements under argon atmosphere. For homogenization the sample was annealed in an evacuated silica tube at 873 K for 720 h and subsequently quenched into cold water. X-ray powder diffraction data were collected on a diffractometer PANalytical (Cu K α radiation). The profile and structural parameters were refined using the WinCSD [1] program package.

X-ray phase analysis of the alloy indicated a three-phase sample. It contained: PrAgAlGe_{3-x} (87.32%), Ag₃Ge (9.26%) and Ge (3.42%). Automatic indexing of the peaks of the phase PrAgAlGe_{3-x} resulted in an *I*-centered tetragonal unit-cell with the parameters $a \approx 0.423(1)$ and $c \approx 2.489(1)$ nm. The crystal structure of the quaternary compound was solved in the space group *I4/mmm*. It was established that its crystal structure belongs to a new type. For the refined composition PrAg_{0.94}(¹)Al_{1.06(2)}Ge_{2.17(2)} (Pearson symbol *tI32-8.70*, space group *I4/mmm*) the unit-cell parameters are: $a = 0.42332(2)$, $c = 2.4902(1)$ nm. The final values of the reliability factors ($R_1 = 0.1068$, $R_p = 0.1690$, $R_{wp} = 0.1449$, $R_{dbw} = 0.0763$) were obtained for the following distribution of atoms: Pr $4e$ 0 0 0.14281(9) ($B_{iso} = 0.43(3) \cdot 10^{-2}$ nm²), 0.440(6)Ag + 0.560(6)Al $4d$ 1/2 0 1/4 ($B_{iso} = 0.68(4) \cdot 10^{-2}$ nm²), Ge1 $4e$ 0 0 0.4141(5), occ. 0.354(8), ($B_{iso} = 0.84(4) \cdot 10^{-2}$ nm²), 0.500(9)Ag + 0.500(9)Al $4e$ 0 0 0.3150(2) ($B_{iso} = 0.70(4) \cdot 10^{-2}$ nm²), Ge2 $16n$ 1/2 0.063(2) 0.0474(2), occ. 0.455(2), ($B_{iso} = 1.04(4) \cdot 10^{-2}$ nm²).

The crystal structure of PrAgAlGe_{3-x} is a quaternary substitution derivative of the closely-related types ScNi₂Si₃ [2] and UNi₂Si₃ [3] with splitting of one small-size atom site. The structure types ScNi₂Si₃ and UNi₂Si₃ differ by the distribution of the small-size atoms. In ScNi₂Si₃ the small-size atoms are distributed in an orderly manner, whereas in UNi(Ni,Si)₂Si₂ both $4e$ sites are occupied by a statistical mixture of Ni and Si atoms in the ratio 1:1. In comparison with these prototypes, in the structure of PrAgAlGe_{3-x} splitting of the $8g$ site takes place; the new $16n$ site is occupied by Ge atoms. Moreover, another kind of small-size atom distribution is observed. The crystal structure of PrAgAlGe_{3-x} (like the ScNi₂Si₃ and UNi₂Si₃ structure types) is an intergrowth of structural segments of the simple type BaAl₄ (or its ordered ternary variant CeAl₂Ga₂), which are separated along the crystallographic [001] axis by segments of the α -Po type.

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Synthesis and crystal structure of mer-[Co(C₈H₄O₄)(C₃H₄N₂)₃(H₂O)₂] H₂O

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The design and synthesis of metal-organic frameworks (MOFs) have received attention in recent years due to their potential applications in diverse areas such as electrical conductivity, magnetism, host-guest chemistry, molecular separation, gas storage, sensors and catalysis [1][2].

Recently, great success has been achieved by the combination

of aromatic dicarboxylic acids and N-donors such as imidazole ligands, which resulted in compounds having 1D to 3D frameworks with interesting physicochemical properties. A large number of novel architectures assembled through the combination of 1,4-benzenedicarboxylic acid (terephthalic acid) and imidazole ligand have been reported [3][4][5][6].

In our course to obtain extended structures with mixed ligands, a mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, terephthalic acid and imidazole was heated at 60°C . Pink single crystals were isolated after several days. Unfortunately, no polymeric structure was obtained but monomeric complex $[\text{Co}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_3\text{H}_4\text{N}_2)(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ was isolated. It has three isomers: *fac*, *trans*, *mer* and *cis*, *mer*. The structure of the title compound is the latter, with two aqua ligands *cis* and three N-coordinated imidazole ligands meridional, relative to the $\text{Co}(\text{II})$ center.

The asymmetric unit of the neutral complex contains one Co^{II} ion, two coordination water molecules, three imidazole ligands, one fully deprotonated terephthalate ligand and one free water molecule. The $\text{Co}(\text{II})$ center is coordinated by one oxygen atom from one monodentate terephthalato ligand and two water molecules and three nitrogen atoms from three imidazole ligands, in a slightly distorted octahedral coordination geometry. The imidazole molecules act as typical monodentate ligands terminally coordinated to the metal center. Notably, only one of two carboxylates of terephthalato ligand coordinates to the central $\text{Co}(\text{II})$ atom in monodentate mode and the second one, which is deprotonated, remains free of coordination. The two carboxylate groups are respectively inclined at $18.76(15)^\circ$ to each other. In the former (O1-C1-O2) the carboxylate group is almost coplanar with the plane of its parent aromatic ring, and the other is rotated out of this plane by $17.27(20)^\circ$. The dihedral angles between imidazole co-ligands are $45.90(7)^\circ$, $61.58(6)^\circ$ and $76.56(7)^\circ$, respectively.

The geometry of the complex is constrained by one intramolecular O-H...H bond formed between one hydrogen atom of an aqua ligand, and adjacent terephthalic carbonyl oxygen atom.

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Polymorphic crystallization and kinetic pathways of triacylglycerols

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The kinetic properties of crystallization and structural transformation are important, particularly for the application of polymorphic crystal systems in pharmaceutical, biomedical, food technology, and other applications.

Triacylglycerols (TAGs) are the main components of alimentary fats and oils. Fat structures and compositions determine their physical properties (e.g., rheology, morphology, and texture), where polymorphism exerts a strong influence. There are different

polymorphic forms of TAGs: the most general ones (in increasing stability) are: α form, which crystallizes in the hexagonal system, β' form (orthorhombic system) and β form (triclinic system).

In this study, several techniques, like Synchrotron Radiation X-Ray Diffraction, Thermal Analysis and Thermo-optical Microscopy, were used in order to characterize the polymorphism under the kinetic point of view of some TAGs present in edible oils and fats. Therefore, the role of some kinetic parameters (e.g. cooling and heating rates) is highlighted.

Keywords: fat, polymorphism, nucleation rate

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Conformational polymorphism and order-disorder phase transition in Enalapril-Zn complex

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Polymorphism is the capacity of a substance to exist in more than one crystalline form [1]. When different conformers of the same molecule occur in different crystal forms, the phenomenon is named conformational polymorphism. A classical example of this polymorphism is observed in ferrocene which presents one room-temperature disordered phase and two low-temperature ordered crystalline forms [2,3]. Conformational polymorphs crystals may or not interconvert through a phase transition.

Some crystals of the enalapril-Zn complex were analyzed by X-ray diffraction at room temperature (298 K) and low temperature (150 K). This analysis was performed on a Oxford GEMINI A-Ultra diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). The structure was solved and refined by means of SHELXL-97 program [4]. These crystal structures showed the presence of conformational polymorphism. Significant differences in molecular conformation are essentially localized in torsion angles. These polymorphs interconverted to each other by a phase transition. Figure 1 shows the crystal structure of complex formed at low and room temperature, respectively. Order-disorder phase transition is observed in these crystals, since the crystalline structure of enalapril-Zn complex is ordered at low temperature but presents occupational disorder at room temperature.

Crystal data are summarized next.

Enalapril-Zn (room temperature): orthorhombic, C222, Z=2, $a=24.870(2)$, $b=21.002(2)$, $c=9.230(2) \text{ \AA}$, $R=0.067$, $wR=0.184$, $s=1.044$, for 2911 reflections.

Enalapril-Zn (low temperature): orthorhombic, P2₁2₁2₁, Z=4, $a=23.655(2)$, $b=20.840(2)$, $c=17.519(2) \text{ \AA}$, $R=0.037$, $wR=0.098$, $s=1.022$, for 12453 reflections.

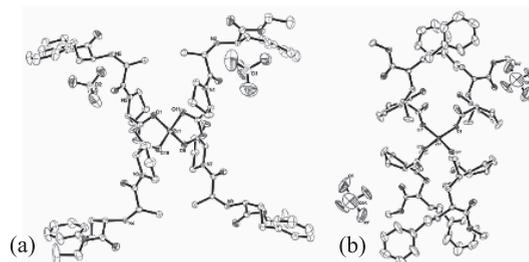


Figure 1: Crystal structure of the enalapril-Zn complex (a) low temperature and (b) room temperature. Symmetry codes: (i) $-x, -y, z-1$; (ii) $x, -y, -z$; (iii) $-x, -y, z$; (iv) $-x, y, -z$; (v) $-x+1/2, -y+1/2, z$; (vi) $x-1/2, y-1/2, z-1$.