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Condensation of isonicotinic hydrazide and acetylacetone resulted in the formation of novel V-shape organic ligand (L) that consists of a six-membered pyridine and five-membered hydroxyl, dimethyl-substituted diazole cycles joined *via* carbonyl bridge [1]. The metathesis reaction between [Co(DfgH)$_2$Br(H$_2$O)] (DfgH$_2$=diphenylglyoxime) and L resulted in mononuclear octahedral complex [Co(DfgH)$_2$BrL] (**1**) with the substitution of water molecule in apical position by L ligand (Fig. 1). The dihedral angle between the cycle units is equal 49.5° in L in **1**. The reaction starting from [Co(DmgH)$_2$Cl(H$_2$O)] (DmgH=dimethylglyoxime) and L resulted in the mononuclear octahedral Co(III) complex again with the composition [Co(DmgH)$_2$ClL´] (**2**), were unexpectedly L´ represent the dehydrated derivative of L (Fig. 2). The dihedral angle between pyridine and diazole rings is equal 88.8° in L´ in **2**. While the organic molecules L/L´ have several donor centers, both ligands act as monodentate ligands and coordinate with metal atom by nitrogen atom of pyridine fragment.

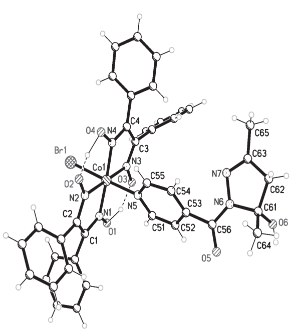

Fig. 1. The structure of [Co(DfgH)$_2$BrL] (**1**)
Co-N1 1.881(3) Å
Co-N2 1.890(3) Å
Co-N3 1.889(3) Å
Co-N4 1.893(3) Å
Co-N5 1.980(3) Å
Co-Br 2.3768(7)Å

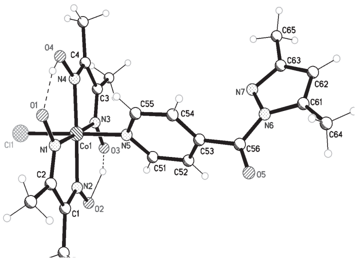

Fig. 2. The structure of [Co(DmgH)$_2$ClL´] (**2**)
Co-N1 1.884(2) Å
Co-N2 1.890(2) Å
Co-N3 1.904(2) Å
Co-N4 1.917(2) Å
Co-N5 1.969(2) Å
Co-Cl 2.2320(7) Å

Explanation of the different structure of L and L ‘in the complex requires further research.

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Keywords: cobalt(III), coordination compound, X-ray

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Influence of ligand substituent on molecular architecture; Very large changes in structural assembly and coordination geometry

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The planning in coordination crystal engineering, construction of the structures of crystalline coordination compounds, [1] depends on a number of experimental variables such as the solvent, time of reaction, reagent ratio, temperature, pH, guest molecules and counterions. In this regard, chemical structure of the organic ligand [2] -eventh slight of the substitute position- and preferred coordination geometry of the metal [3] play an important role on the formation of different molecular architecture of complexes in the assembly processes. To make progress in controlling specific interactions in the solid state of coordination compounds requires systematic investigations of the effects of different factors on the final structures. Despite to the potential utility, from crystal engineering point of view, there has been little attention to systematic studies that examine the effect of the substituent variation of the ligand on the supramolecular aggregation of coordination complexes.

In this study, *N*-(aryl)-2-pyrazinecarboxamide ligands with two different aryl groups (o-anisidyl, L1, and o-phenitidyl, L2, groups) have been employed for the synthesis of six Hg (II) complexes, [HgCl$_2$(L1)$_2$]$_n$, [HgBr$_2$(L1)]$_n$, [HgI$_2$(L1)]$_n$, [Hg$_3$Cl$_6$(L2)$_3$.HgCl$_2$(L2)], [HgBr$_2$(L2)] and [HgI$_2$(L2)] in order to get insights to the substituent effects on the molecular architecture of complexes. Structural analysis of mercury (II) halides containing L1 ligand demonstrated that the assembly process produced infinite 2D structures. For mercury (II) halides containing L2 ligand, the assembly processes are involved weak interaction between monomeric Hg(II) coordination compounds.

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Keywords: carboxamide, mercury, crystal engineering

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New supramolecular dimer and 2D-supramolecular layers formation through hydrogen bonds

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Coordination compounds with both donor A–H and acceptor B groups and forming hydrogen bonds are used as building block for construction of supramolecular networks. Some copper(II) carboxylate complexes have shown that the intermolecular H-bonds can alter their magnetic properties. We have recently published mononuclear molecular complex [1], binuclear molecular complex [2] and more coordination polymers [3,4] which exhibit similar magnetic properties. These very similar magnetic properties of mononuclear, binuclear as well as polymeric complexes could be explained by the presence of very similar H-bond systems, supramolecular synthons, that are pathway for antiferromagnetic interactions.

In this report we present new supramolecular dimer [Cu(3-Brbz)$_2$(dena)(H$_2$O)$_2$] (3-Brbz is 3-brombenzoate, dena is *N*,*N*-diethylnicotinamide as terminal ligand) and series of 1D-coordination polymers of general formula [Cu(RCO$_2$)$_2$(μ-dena)(H$_2$O)]$_n$ (RCO$_2$ are 3-chlorbenzoate, 4-chlorbenzoate or 3,5-dichlorbenzoate, and dena as bridging ligand) with similar system of hydrogen bonds and properties. The hydrogen bonds described by $R_2^2(10)$ and $R_2^2(12)$ supramolecular synthons, formed by coordinated water molecule and two carboxylic group on each Cu^{2+} ions could create supramolecular dimer of two mononuclear complex molecules or 2D-supramolecular layers of 1D-coordination polymers.

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Keywords: hydrogen bonds, supramolecular structure, N,N-diethylnicotinamide

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Synthesis, crystal structure and thermal behavior of $M(C_{16}H_{16}N_3)_2(VO_3)_4$ compounds

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The use of organic molecules for the design of new inorganic materials has allowed the preparation of compounds with major technological applications [1]. In this context, vanadium derivatives seem to be good candidates to obtain new materials because of its rich crystal chemistry [2]. For this reason, our research has been focused in the synthesis and characterization of hybrid vanadates with aromatic and aliphatic amines [3]. In this work we report the synthesis, structure and thermal properties of a family of three isostructural compounds with $M(C_6H_{16}N_3)_2(VO_3)_4$ formula, where M= Co^{2+}, Ni^{2+} and Cu^{2+}, as well as the relationship between the crystal structure and the thermal stability.

$Co(C_6H_{16}N_3)_3(VO_3)_4$, **1**, $Ni(C_6H_{16}N_3)_3(VO_3)_4$, **2** and $Cu(C_6H_{16}N_3)_3(VO_3)_4$, **3**, have been synthesized using mild solvothermal conditions. The crystal structures were solved using single-crystal X-ray diffraction data. They crystallize in the monoclinic system, space group $P2_1/c$. The cell parameters are very similar for the three phases, but they do not follow the Vegard law [4]. These compounds show a two-dimensional crystal structure, with sheets composed of $[VO_3]_n^{n-}$ chains and metal centres octahedrically coordinated chelated by two 1(2-aminoethyl)pyperazonium ligands. The cupper(II) containing phase show slight differences in the bond distances of the octahedra due to a Jahn-Teller effect.

The thermogravimetric decomposition curves of the three phases show a sequence of overlapped processes of mass loss from approximately 250 ºC to almost 500 ºC for compounds **1** and **2**, whereas, for compound **3**, these processes occur between 185 and 470 ºC. Time-resolved X-ray diffractometry show that phases **1** and **2** are stable until 270 ºC and 280 ºC, respectively, while the copper(II) phase is less stable, and its structure collapses at 180 ºC. The destruction of the crystal structure is due to the calcination of the organic ligand according to the thermogravimetric data. Above these temperatures the formation of amorphous compounds takes place.

The temperature at which the crystal structure of **3** collapses is significantly lower, comparing with the isostructural phases **1** and **2**. This fact is closely related with the presence of Cu^{2+} and the slight differences observed in the crystal structure when this metal is present.

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Keywords: organic-inorganic_materials, thermoanalysis, structure-thermal_stability_relationship

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Catalytic behaviour of two structurally related vanadyl arsenates

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Among open-framework metal phosphates, transition metal containing ones constitute an important group due to their potential activity as redox catalysts [1]. Other anionic moieties such as borates, arsenates, sulphates and selenates have been used successfully in the preparation of novel open framework structures, some of them with catalytic properties [2]. During the course of our research, we have synthesized and characterized two new fluorovanadyl-hydrogenarsenate with ethylendiamonium and piperazonium as templating agents, with formulae $(C_2N_2H_{12})_{0.5}[(VO)(HAsO_4)F]$, EnVAs, and $(C_4N_2H_{14})_{0.5}[(VO)(HAsO_4)F]$, PipVAs, [3] with catalytic properties [4].

EnVAs and PipVAs have been synthesized by mild hydrothermal conditions under autogenous pressure. The crystal structures have been solved from single-crystal X-ray diffraction data. The phases crystallize in the $P2_1/c$ monoclinic space group with cell parameters a = 7.8634(4)Å, b = 7.7658(4)Å, c = 10.4195(6)Å, β = 101.524(5)º for EnVAs and a = 6.301(1)Å, b = 10.244(1)Å, c = 10.248(1)Å and β = 95.225(1)º for PipVAs. These phases exhibit a very similar layered inorganic framework. In both cases, the structure is built from secondary building units (SBU) which are formed by $[V_2O_8F_2]$, dimmers of edge-sharing vanadyl octahedra, connected by the vertices to two hydrogenarsenate tetrahedra. The repetition of this SBU unit originates sheets along the [1 0 0] direction. The ethylenediammonium and piperazinium cations are located inside the interlayer space.

Both phases have been evaluated as catalysts for the oxidation of thioethers and alkenes, using H_2O_2 and t-butyl hydroperoxide (TBHP) as oxidants. Both phases act as heterogeneous catalysts for these reactions. The intrinsic activity of EnVAs was higher than that of PipVAs for the oxidation of sulfides. Similar results were obtained when using either H_2O_2 or TBHP as oxidants. However, the steric effects were enhanced when TBHP was used and higher selectivities towards sulfoxides were achieved with this oxidant. The different catalytic behaviour between EnVAs and PipVAs, could be explained taking into account the structural differences between them. The catalytic activity of the V-based materials in the epoxidation of simple alkenes and allylic alcohols was assessed. Upon reuse, both materials