Condensation of isonicotinic hydrazide and acetylactone resulted in the formation of novel V-shaped organic ligand (L) that consists of a six-membered pyridine and five-membered hydroxyl, dimethyl-substituted diazole cycles joined via carboxyl bridge [1]. The metathesis reaction between [Co(DfgH)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)$_2$CH$_2$(H$_2$O)] (DmgH$_2$=dimethylglyoxime) and 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´ 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) A
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 1.904(3) Å
Co-N1 1.904(3) Å
Co-Br 2.3768(7) Å

Fig. 2. The structure of [Co(DmgH)$_2$ClL´] (2) A
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-CI 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

MS24.P59

Influence of ligand substituent on molecular architecture; Very large changes in structural assembly and coordination geometry
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In this study, N-(aryl)-2-pyrazinecarboxamide ligands with two different aryl groups (o-anisidyl, L1, and o-phenidyl, L2, groups) have been employed for the synthesis of six Hg (II) complexes, [HgCl$_2$(L1)$_2$], [HgBr$_2$(L1)$_2$], [HgI$_2$(L1)$_2$], [HgCl$_2$(L2)$_2$], [HgBr$_2$(L2)$_2$] and [HgI$_2$(L2)$_2$] 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.


Keywords: carboxamide, mercury, crystal engineering

MS24.P60


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 and polymeric complexes could be explained by the presence of very similar H-bond systems, supramolecular synths, that are pathway for antiferromagnetic interactions.

In this report we present new supramolecular dimer [Cu(3-Brbz)$_2$(dena)(H$_2$O)$_3$] (3-Brbz is 3-bromobenzoate, dena is N$_2$-diethylaminotetramide as terminal ligand) and series of 2D-coordination polymers of general formula [Cu(RCO$_2$)$_2$(dena)(H$_2$O)$_n$] (RCO$_2$ are 3-chlorobenzoate, 4-chlorobenzoate or 3,5-dichlorobenzoate, and dena as bridging ligand) with similar system of hydrogen bonds and properties. The hydrogen bonds describe by $R_2^2(10)$ and $R_2^2(12)$ supramolecular
**Poster Sessions**

**MS24.P61**  

**Synthesis, crystal structure and thermal behavior of**  
\[ \text{M(C}_\text{H}_\text{N}_\text{O}_\text{S})_\text{Cu} \] **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 \[ \text{M(C}_\text{H}_\text{N}_\text{O}_\text{S})_\text{Cu} \] formula, where \( \text{M} = \text{Co}^2+, \text{Ni}^2+ \) and \( \text{Cu}^2+ \). As well as the relationship between the crystal structure and the thermal stability.

\( \text{Co(C}_\text{H}_\text{N}_\text{O}_\text{S})_\text{Cu} \) 1. \( \text{Ni(C}_\text{H}_\text{N}_\text{O}_\text{S})_\text{Cu} \) 2 and \( \text{Cu(C}_\text{H}_\text{N}_\text{O}_\text{S})_\text{Cu} \) 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 \( \text{VO}_4^2- \) chains and metal centres octahedrically coordinated chelated by two \( 1(2\text{-aminoethyl}) \text{pyperazinyl} \) 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 °C to almost 500 °C for compounds 1 and 2, whereas, for compound 3, these processes occur between 185 and 470 °C. Time-resolved X-ray diffraction and thermal analysis show that phases 1 and 2 are stable until 270 °C and 280 °C, respectively, while the copper(II) phase is less stable, and its structure collapses at 180 °C. 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 \( \text{Cu}^2+ \) and the slight differences observed in the crystal structure when this metal is present.

**Keywords:** hydrogen bonds, supramolecular structure, N,N-diethylaminonimidamide

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**MS24.P62**  

**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 ethyldiammonium and piperazonium as templating agents, with formulæ (C\(_3\)N\(_4\)H\(_6\))[\(\text{VO(H}_\text{AsO}_4\text{)F}\)] EnVASs, and (C\(_3\)N\(_4\)H\(_6\))[\(\text{VO(H}_\text{AsO}_4\text{)F}\)] PipVASs, [3] with catalytic properties [4].

EnVASs and PipVASs 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 \( a = 7.863(4) \text{Å}, b = 7.765(4) \text{Å}, c = 10.419(6) \text{Å}, \beta = 101.52(4)^\circ \) for EnVASs and \( a = 6.301(1) \text{Å}, b = 10.244(1) \text{Å}, c = 10.248(1) \text{Å}, \beta = 95.225(1)^\circ \) for PipVASs. Both phases exhibit a very similar layered inorganic framework. In both cases, the structure is built from secondary building units (SBU) which are formed by \( [\text{V}_2\text{O}_6\text{F}_6] \), 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 ethyldiammonium and piperazonium cations are located inside the interlayer space.

Both phases have been evaluated as catalysts for the oxidation of thioethers and alkynes, using \( \text{H}_2\text{O}_2 \) and \( \text{t}-\text{butyl hydroperoxide} \) (TBHP) as oxidants. Both phases act as heterogeneous catalysts for these reactions. The intrinsic activity of EnVASs was higher than that of PipVASs for the oxidation of sulfides. Similar results were obtained when using either \( \text{H}_2\text{O}_2 \) 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 EnVASs and PipVASs 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

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**Keywords:** organic-inorganic materials, thermoanalysis, structure-thermal_stability_relationship

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