

of the synthesis of organo-alkaline earth metals compounds is their tendency to form insoluble due on one hand to their low metal oxidation state (II) which only allows two anionic ligands, and on the other hand, their large ionic radii which demand a high coordination number. A parry to prevent a high degree of oligomerization is the use of neutral Lewis-coordinating ligands such as monodentate THF or multidentate polyether ligands which avoid any further "metal-metal contacts" via bridging ligands, saturating the metal cation. However, the chemistry of such metal halide or pseudo-halide adducts with neutral Lewis-coordinating ligands (usually non-polar aprotic solvents) is still not systematically studied. In this context, we have synthesized and characterized some new molecular compounds using polydentate neutral Lewis-coordinating ligands such as DME ( $\text{CH}_3\text{OC}_2\text{H}_4\text{OCH}_3$ ), diglyme ( $\text{CH}_3(\text{OC}_2\text{H}_4)_2\text{OCH}_3$ ) and triglyme ( $\text{CH}_3(\text{OC}_2\text{H}_4)_3\text{OCH}_3$ ) in order to, in a fundamental way, know and understand better the chemistry of d-block metal halides in aprotic solvents. Secondly, we were interested in the study of the influence of the size of the ligand on the coordination sphere of the metal cation using monodentate (THF), bidentate (DME), tridentate (diglyme) and finally tetradentate (triglyme) O-donor ligands.

[1] W. Maudez, M. Meuwly, K. M. Fromm, *Chem. Eur. J.* **13**, 29, 8302-8316, **2007**. [2] K. M. Fromm, E. D. Gueneau, A. Y. Robin, W. Maudez, J. Sague, R. Bergougnant, *Z. Anorg. Allg. Chem.* **631**, 1725-1740, **2005**. [3] K. M. Fromm, *Dalton Trans.* **43**, 5103-5112, **2006**.

**Keywords:** polyether coordination chemistry; single-crystal structure determination; transition-metal compounds

#### FA4-MS02-P08

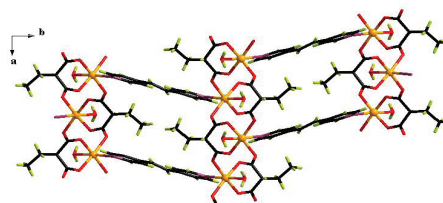
**Design, Synthesis, Structural and Magnetic Properties of Pillared MN(II) Ethylmalonate Complexes.** Mariadel Déniz<sup>a</sup>, Jorge Pasán<sup>a</sup>, Oscar Fabelo<sup>a</sup>, Laura Cañadillas-Delgado<sup>a</sup>, Ana Belén Lago<sup>a</sup>, Catalina Ruiz-Pérez<sup>a</sup>. <sup>a</sup>*Laboratorio de Rayos X y Materiales Moleculares, Departamento de Física Fundamental II, Facultad de Física, Universidad de La Laguna, Tenerife, Spain.*

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Metal-organic frameworks (MOF) have been studied in recent years due to their potential applications in a wide variety of research fields, such as magnetism, molecule adsorption, catalysis, etc [1]. The rational design of these coordination polymers can provide of efficient synthesis. The flexibility of polycarboxylic acids is well known for the diversity of their connecting modes that lead from discrete entities to 3D networks [2]. Moreover, rigid rod-like spacer molecules like 4,4'-bipyridyl (4,4'-bpy) or 1,2-bis(4-pyridyl)ethylene (bpe) can be used for the construction of controlled structures [3], in particular, as pillars to connect 2D networks leading to 3D complexes [4].

We present the synthesis and structural properties of a novel 1D Mn(II)-based coordination framework as well as 3D complexes built up by the connection of Mn(II)-

ethylmalonate layers through rigid rod-like bridging molecules such as bpe or 4,4'-bpy (Fig. 1). The layer separation can be controlled by the length of the organic spacer.



**Figure 1.**

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#### FA4-MS02-P09

**Crystal Structure of New 1D Polymer  $\{[\text{Cd}(\text{NioxH}_2)(\text{SO}_4)(\text{Bpy})](\text{NioxH}_2)(\text{H}_2\text{O})_3\}_n$ .** Lilia Croitor<sup>a</sup>, Eduard B. Coropceanu<sup>b</sup>, Yurii M. Chumakov<sup>a</sup>, Marina S. Fonari<sup>a</sup>. <sup>a</sup>*Institute of Applied Physics, Academy of Sciences of R. Moldova, Academy str., 5, MD2028, Chisinau, Moldova.* <sup>b</sup>*Institute of Chemistry, Academy of Sciences of R. Moldova, Academy str., 3, MD2028, Chisinau, Moldova.*

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The recent surge of research activity in the area of coordination polymers has been motivated by the ability of metal-ligand coordination in providing a facile approach to the controlled assembly of one-, two-, and three-dimensional extended solids. Incorporation of active groups into coordination polymers presents an excellent opportunity for the construction of functional materials with interesting properties [1]. We have favored the strategy of 'metal dioxime building block' for the construction of new generation of coordination polymers. Interaction in the system  $\text{CdSO}_4 + \text{NioxH}_2 + \text{bpy}$  in the molar ratio 1:2:2 resulted in 1D polymer of the composition  $\{[\text{Cd}(\text{NioxH}_2)(\text{SO}_4)(\text{bpy})](\text{NioxH}_2)(\text{H}_2\text{O})_3\}_n$ , where 4,4'-bipyridine = bpy, 1,2-cyclohexanedionedioxime = NioxH<sub>2</sub>. It crystallizes in the triclinic space group P-1 with  $a = 10.144(2)$ ,  $b = 11.814(2)$ ,  $c = 12.423(3)$  Å,  $\alpha = 108.23(3)$ ,  $\beta = 93.23(3)$ ,  $\gamma = 90.65(3)^\circ$  and  $Z = 2$ . The X-ray diffraction shows that each Cd(II) ion binds one two-coordinate NioxH<sub>2</sub> molecule, two two-coordinate sulfato-anions as basal ligands and two bpy molecules as axial ligands with the formation of a square bipyramidal N<sub>4</sub>O<sub>2</sub>-coordination core. In common with the sulfate anions NioxH<sub>2</sub> formulate the robust extended binuclear metal platform. The key finding of this study is a definite availability of a metal dioxime building block for the construction of a new generation of coordination polymers.

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[1] Wang Zh., Xiong R.-G., Foxman B. M., Wilson S. R., Lin W., *Inorg. Chem.* **1999**, 38, 1523.

**Keywords:** 1D polymer; Cd(II) dioxime; 4,4'-bipyridine

#### FA4-MS02-P10

**Binuclear Cu(II) Dioximates and Zn(II) and Cd(II) Dioximes Mediated by 4,4'-Bpy.** Eduard B. Coropceanu<sup>a</sup>, Lilia Croitor<sup>b</sup>, Yurii M. Chumakov<sup>b</sup>, Maria Gdaniec<sup>c</sup>, Barbara Wicher<sup>c</sup>, Marina S. Fonari<sup>a</sup>. <sup>a</sup>*Institute of Chemistry Academy of Sciences of R. Moldova, Academy str., 3 MD2028, Chisinau, Moldova.* <sup>b</sup>*Institute of Applied Physics Academy of Sciences of R. Moldova, Academy str., 5 MD2028, Chisinau, Moldova.* <sup>c</sup>*Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland.*  
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It is well known that the oximate group (=N-O-) can function as a bridging ligand to link two metal ions through the imine N atom and the deprotonated O atom, thus resulting in the simplest topological types of coordination arrays, polynuclear homo- or heterometallic clusters and homo- or heterometallic one-dimensional zigzag chains or one-dimensional helix. Of particular concern in this context is the development of such directed routes in which the metals are connected by 'robust' ligands so that fragmentation of the complexes in their subsequent reactions is inhibited. The advantage of such 'metalloligands' is the possibility to use either the free coordination sites of the ligand or to manipulate by the axial ligand in order to bind a second metal of the same or different kind. We have favored the strategy of 'metal oximate' building blocks for design and synthesis of multinuclear complexes in a controlled fashion. Herein we report a series of homometallic binuclear Cu, Zn, and Cd complexes of a wheel-and-axle shape of the compositions [Cu<sub>2</sub>(dmgH)<sub>4</sub>(bpy)]<sub>2</sub>·4dmgH<sub>2</sub> (**1**), [Cu<sub>2</sub>(dphH)<sub>4</sub>(bpy)]DMFA (**2**), [Cu<sub>2</sub>(Hdmg)<sub>4</sub>(bpy)]·[Cu(dmgH)<sub>2</sub>(bpy)](bpy)·2dmgH<sub>2</sub> (**3**) [1], [M<sub>2</sub>(NioxH<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(bpy)], where M=Zn (**4**), Cd (**5**); dmgH<sub>2</sub> = dimethylglyoxime, NioxH<sub>2</sub> = 1,2-cyclohexanedionedioxime, dphH<sub>2</sub> = diphenyldioxime, bpy = 4,4'-bipyridine. In 1-3 (Figure) two Cu(II) atoms have an identical N5-environment formulated by four oximic nitrogen atoms of two monodeprotonated ligands in a slightly distorted square planar mode and the nitrogen atom of the bridging bpy molecule in the apical position. In the binuclear units **4**, **5** the cation is hexacoordinated into a shape of a square bipyramid in the N<sub>3</sub>O<sub>3</sub>-environment. Its basal plane is defined by a bidentate NioxH<sub>2</sub> molecule and two monodentate acetate anions, water molecule and bidentate.bpy ligand occupy the apical sites, bpy mediating the symmetry-related metal atom. The neutral NioxH<sub>2</sub> coordinates in a typical bidentate mode through their oxime nitrogen atoms, thus leading to the formation of a five-membered chelating ring around the metal core. The key finding of this study is a definite availability of a 'metal dioxime' building block for the rational crystal design.

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[1]. Coropceanu E., Croitor L., Gdaniec M., Wicher B., Fonari M. *Inorg. Chim. Acta* **2009** doi: 10.1016/j.ica.2008.09.047.

**Keywords:** design; dioxime; binuclear complexes

#### FA4-MS02-P11

**Structural Disorder and Spin Crossover: how weak Interactions Affect the Spin State of a Molecular Fe(II) Complex.** Dmitry Chernyshov<sup>a</sup>, Karl Wilhelm Törnroos<sup>b</sup>, Hans-Beat Bürgi<sup>c</sup>. <sup>a</sup>*SNBL at ESRF, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble cedex 9, France.* <sup>b</sup>*Department of Chemistry, University of Bergen, 5007 Bergen, Norway,* <sup>c</sup>*University of Berne, 3012 Berne, Switzerland.*  
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By comparing the structural and macroscopic properties of three spin crossover solvates of iron(II) tris(2-picolyamine) dichloride, two being EtOH or 2-PrOH, and the third being a mixture of the two, we demonstrate how solvent disorder affects the spin crossover scenario. This mixed solvate shows a new spin crossover regime, where ordering of spin states is suppressed, the transition temperature is shifted, and cooperativity reduced relative to the parent solvent compounds. Together with a previously observed coupling of the ordering processes and spin conversion, these findings illustrate that modification of also weak but numerous van der Waals contacts may drastically change the physical properties. We also show how these and similar observations can be parameterized within a multi-sublattice Ising-like model, accounting for a coupling between spin conversion and a structural ordering processes.

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#### FA4-MS02-P12

**Growth Conditions, Point Defects and Some Properties of Langasite.** Elena Tyunina<sup>a</sup>, Galina Kuz'micheva<sup>a</sup>, Oksana Zaharko<sup>b</sup>, Alain Cousson<sup>c</sup>, Viktor Rybakov<sup>d</sup>, Aleksandr Dybovskiy<sup>e</sup>. <sup>a</sup>*Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia.* <sup>b</sup>*Laboratory for Neutron Scattering, ETZ Zurich & Paul Scherrer Institute, Switzerland.* <sup>c</sup>*Laboratory Leon Brillouin, CEA-CNRS Saclay, France.* <sup>d</sup>*Moscow State University, Moscow, Russia,* <sup>e</sup>*Association "Quartz palette", Aleksandrov, Russia.*  
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Compounds La<sub>3</sub>Ga<sub>3</sub>SiO<sub>14</sub> - LGS (sp.gr. P321, z=1) is the most attractive materials for acoustic-volume (surface)-