of the synthesis of organo-alkaline earth metals compounds is their tendency to form insoluble due 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 (CH₃OCH₂CH₂OCH₃), diglyme (CH₃OCH₂CH₂OCH₃) and triglyme (CH₃OC₂H₅OC₂H₅OC₂H₅) in order to, in a fundamental way, known new ligands can 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.

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 Déniz⁵, Jorge Pasán⁵, Oscar Fabelo⁵, Laura Cañadillas-Delgado⁶, Ana Belén Lago⁵, Catalina Ruiz-Pérez⁵. “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 of d-block metal 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 (CH₃OCH₂CH₂OCH₃), diglyme (CH₃OCH₂CH₂OCH₃) and triglyme (CH₃OC₂H₅OC₂H₅OC₂H₅) in order to, in a fundamental way, known new ligands can 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.

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

FA4-MS02-P09
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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 CdSO₄•NioxH₂•bpy in the molar ratio 1:2:2 resulted in 1D polymer of the composition [{Cd(NioxH₂)(SO₄)(Bpy)}(NioxH₂)(H₂O)]ₙ, where 4,4’-bipyridine = bpy, 1,2-cyclohexanedione = NioxH₂. It crystallizes in the triclinic space group P-1 with a = 10.144(2), b = 11.814(2), c = 24.23(3) Å, α = 108.23(3), β = 93.23(3), γ = 90.65(3)° and Z = 2. The X-ray diffraction shows that each Cd(II) ion bonds two-coordimate NioxH₂ molecules, two two-coordimate sulfato-anions as basal ligands and two bpy molecules as axial ligands with the formation of a square bipyramidal N₅O₂-coordination core. In common with the sulfate anions NioxH₂ formulate the robust extended binuclear metal platform. The key feeding 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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FA4-MS02 Design and Properties of Functional Molecular Materials


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, Lilia Croitoru, Yuriy M. Chumakov, Maria Gdaniec, Barbara Wicher, Marina S. Fonari. 

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 metal is 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 [Cu₂(dmgH)(bpy)], 4dmglH(OH)(Cu₂(dphH)(bpy))DMFA, [Cu₂(Hdmg)(bpy)][Cu(dmgH)(bpy)](2H₂O)O₂Cl₂, [M₂(NioxH)(CH₃COO)](H₂O)(bpy)](CH₃CH₂OH), where M=Zn (4), Cd (5), dmgH = dimethylglyoxime, NioxH = 1,2-cyclohexanedioloxime, dphH₂ = diphenyldioxime, bpy = 4,4'-bipyridine. In 1-3 (Figure) two Cu(II) atoms have an identical N₅-environment formulated by four oxime 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 N₅O₂-environment. Its basal plane is defined by a bidentate NioxH 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 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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Keywords: design; dioxime; binuclear complexes

FA4-MS02-P11


By comparing the structural and macroscopic properties of three spin crossover solvates of iron(II) tris(2-picolylamine) 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.


Keywords: design; dioxime; binuclear complexes

FA4-MS02-P12

Growth Conditions, Point Defects and Some Properties of Langasite. Elena Tyunina, Galina Kuz’micheva, Oksana Zaharko, Alain Cousson, Viktor Rybakov, Aleksandr Dybovskiy, Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia. Laboratory for Neutron Scattering, ETZ Zurich & Paul Scherrer Institute, Switzerland. Laboratory Leon Brillouin, CEA-CNRS Saclay, France. Moscow State University, Moscow, Russia. Association “Quartz palette”, Aleksandrov, Russia.

Compounds La₉Ga₅SiO₁₄ - LGS (sp.gr. P321, z=1) is the most attractive materials for acoustic-volume (surface-