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Binuclear Cu(II) Dioximates and Zn(II) and Cd(II) Dioximes Mediated by 4,4'-Bpy. Eduard B. Coropceanu^a, Lilia Croitor^b, Yurii M. Chumakov^b, Maria Gdaniec^c, Barbara Wicher^c, Marina S. Fonari^a. ^aInstitute of Chemistry Academy of Sciences of R. Moldova, Academy str., 3 MD2028, Chisinau, Moldova. ^bInstitute of Applied Physics Academy of Sciences of R. Moldova, Chademy str., 5 MD2028, Chisinau, Moldova. ^cFaculty of Chemistry, Adam Mickiewicz University, Poznań, Poland. E-mail: ecoropceanu@yahoo.com

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 homoor heterometallic one-dimensional zigzag chains or onedimensional 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 $[Cu_2(dmgH)_4.(bpy)]_2.4dmgH_2(1), [Cu_2(dphH)_4(bpy)]DMFA$ (2), $[Cu_2(Hdmg)_4.(bpy)].[Cu(dmgH)_2.(bpy)](bpy).2dmgH_2$ (3) [1], $[M_2(NioxH_2)_2(CH_3COO)_4(H_2O)_2(bpy)]$, where M=Zn (4), Cd (5); dmgH₂ = dimethylglyoxime, NioxH₂ = 1,2-cyclohexanedionedioxime, dphH₂ = 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 N₂O₂-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 fivemembered 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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Structural Disorder and Spin Crossover: how weak Interactions Affect the Spin State of a Molecular Fe(II) Complex. <u>Dmitry Chernyshov</u>^a, Karl Wilhelm Törnroos^b, Hans-Beat Bürgi^c. ^aSNBL at ESRF, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble cedex 9, France. ^bDepartment of Chemistry, University of Bergen, 5007 Bergen, Norway, ^cUniversity of Berne, 3012 Berne, Switzerland.

E-mail:dmitry.chernyshov@esrf.fr

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.

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Growth Conditions, Point Defects and Some Properties of Langasite. <u>Elena Tyunina</u>^a, Galina Kuz'micheva^a, Oksana Zaharko^b, Alain Cousson^c, Viktor Rybakov^d, Aleksandr Dybovskiy^e. ^aLomonosov State Academy of Fine Chemical Technology, Moscow, Russia. ^bLaboratory for Neutron Scattering, ETZ Zurich & Paul Scherrer Institute, Switzerland. ^cLaboratory Leon Brillouin, CEA-CNRS Saclay, France. ^dMoscow State University, Moscow, Russia, ^eAssociation "Quartz palette", Aleksandrov, Russia. E-mail: <u>tyunina_elena@mail.ru</u>

Compounds $La_3Ga_5SiO_{14}$ - *LGS* (sp.gr. *P321*, *z*=1) is the most attractive materials for acoustic-volume (surface)-