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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^a, Lilia Croitor^b, Yurii M. Chumakov^b, Maria Gdaniec^c, Barbara Wicher^c, Marina S. Fonari^a. ^a*Institute of Chemistry Academy of Sciences of R. Moldova, Academy str., 3 MD2028, Chisinau, Moldova.* ^b*Institute of Applied Physics Academy of Sciences of R. Moldova, Academy str., 5 MD2028, Chisinau, Moldova.* ^c*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 [Cu₂(dmgH)₄(bpy)]₂·4dmgH₂ (**1**), [Cu₂(dphH)₄(bpy)]DMFA (**2**), [Cu₂(Hdmg)₄(bpy)]·[Cu(dmgH)₂(bpy)]·2dmgH₂ (**3**) [1], [M₂(NioxH₂)₂(CH₃COO)₄(H₂O)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 N₃O₃-environment. Its basal plane is defined by a bidentate NioxH₂ 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 NioxH₂ 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.

This work was supported by the grant 09.819.05.04A (CSȘDT).

[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^a, Karl Wilhelm Törnroos^b, Hans-Beat Bürgi^c. ^a*SNBL at ESRF, 6 rue Jules Horowitz, BP 220, F-38043 Grenoble cedex 9, France.* ^b*Department of Chemistry, University of Bergen, 5007 Bergen, Norway,* ^c*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^a, Galina Kuz'micheva^a, Oksana Zaharko^b, Alain Cousson^c, Viktor Rybakov^d, Aleksandr Dybovskiy^e. ^a*Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia.* ^b*Laboratory for Neutron Scattering, ETZ Zurich & Paul Scherrer Institute, Switzerland.* ^c*Laboratory Leon Brillouin, CEA-CNRS Saclay, France.* ^d*Moscow State University, Moscow, Russia,* ^e*Association "Quartz palette", Aleksandrov, Russia.*
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Compounds La₃Ga₃SiO₁₄ - LGS (sp.gr. P321, z=1) is the most attractive materials for acoustic-volume (surface)-

waves devices. Single crystals of various properties have been grown by the Czochralski method from different melt compositions ($\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$ and $\text{La}_3\text{Ga}_4(\text{Ga}_{1.14}\text{Si}_{0.86})\text{O}_{14}$) using different conditions: the growth direction ($\langle 0001 \rangle$ -Z-crystals, $\langle 01-11 \rangle$ - $Y54^\circ$ -crystals), the growth atmosphere (Ar - colorless crystals, $99 \pm 98\% \text{Ar} + 1 \pm 2\% \text{O}_2$ -colored crystals), and post-grown treatment (vacuum or air at the 1000° ; ultraviolet or γ -irradiations). The other technology parameters ("Kristall-3M", the pulling and rotation rates - 1.2 mm/h and 1-15 rpm, respectively) did not vary. The aim of this work is to find a relationship between composition, color, microhardness, optical properties, and specific conductivity of LGS.

The peculiarities of the crystal structure and the refined composition of all samples have been determined by the diffraction methods: X-ray (the single crystals - CAD-4 diffractometer, MoK_α ; ground in powder crystals - HZG-4 diffractometer: Ni - filter, CuK_α , 2θ $10-115^\circ$), neutron (the single crystals - TriCS diffractometer: $\lambda=1.18\text{\AA}$; diffractometer located at the channel 5C2, $\lambda=0.830\text{\AA}$).

It is supposed, that color of $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_y$ is caused by the oxygen contain: $y \sim 14$ (I-colorless), $y \sim 13.7$ (II-orange), $y \sim 13.6$ (III-yellow), $y \sim 13.4$ (IV-colorless). The colorless crystals can have both the stoichiometric composition (I) and to contain a plenty of oxygen vacancies- $\text{V}_\text{O}^\bullet$ (IV). These results agree with the optical properties (spectrophotometer "Specord-M40"): the bands 28500, 26000, 25000 cm^{-1} are connected with $\text{V}_\text{O}^\bullet$ and the band 20800 cm^{-1} -with color centres. At that the crystals of like visual coloration can have a different shade of color according to the chromaticity diagrams: for example, with the increase a ratio Ga/Si in $\text{La}_3\text{Ga}_4(\text{GaSi})\text{O}_{14}$ orange crystals changes the shade of color from yellow to pale blue over pale green. It has been concluded that the increase in the concentration of oxygen vacancies is of particular value for color crystals, the microhardness, the tangent of dielectric losses and specific conductivity. The frequency and elastic coefficients depend on common crystal composition. The $Y54^\circ$ -crystals, $Y54^\circ$ -cut possess the greater value of microhardness ($MH=14.6$ GPa) and the more structural perfection (the half-width of the Bragg $02\bar{2}2$ peak is $\beta_{\text{exp}}=36.22^\circ$) in comparison with Z-crystals, Z-cut ($MH=14.3$ GPa; $\beta_{\text{exp}}=94.54^\circ$ for 0002 peak). $Y54^\circ$ -crystals, $Y54^\circ$ -cut have the greater value of activation energy ($E_a=1.01$ eV) than Z-crystals, X and Y cuts ($E_a=0.92$ eV). Obtaining of homogeneous on compositions LGS crystals is possible at partial replacement Si on Ge or at contents of Ga excesses in initial composition.

Keywords: piezoelectric; point defect; physical properties

FA4-MS02-P13

Magnetic Structure of the Molecular Compound $[\text{Co}_2(\text{bta})]_n$ (H_4bta : Pyromellitic acid). Oscar Fabelo^a, Laura Cañadillas-Delgado^a, Jorge Pasán^a, Fernando S. Delgado^a, Ines Puente-Orench^{b,c}, Javier Campo^{b,c}, Juan Rodriguez-Carvajal^c, Catalina Ruiz-Pérez^a. ^aLaboratorio de Rayos X y Materiales Moleculares,

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The design and construction of new polymeric compounds of tuneable dimensionality, through adapted synthetic routes, is of strong interest in molecular materials [1]. In particular, the hydrothermal synthesis is currently being developed in solid-state and coordination chemistry for the design of new architectures. The magnetic behaviour of $[\text{Co}_2(\text{bta})]_n$ is complex and controversial. DC magnetic measurements without applied magnetic field in the range of temperature 2-300K show different features, a maximum at 16 K which has been explained as a long-range antiferromagnetic order confirmed by a lambda-shaped maximum in the specific-heat plot. At 13 K, another maximum appears together with a maximum in the out-of-phase signal (no frequency dependent). Some authors suggest that this is a field-dependent spin-canting region. [2-4]. Along this line, we have the possibility to shed light on the magnetic properties of a cobalt(II) complex of formula $[\text{Co}_2(\text{bta})]_n$. We have performed a neutron experiment in D1B diffractometer at ILL intending to clarify this situation. We are able to discard the presence of structural phase transitions at low temperatures and to obtain, preliminarily, the antiferromagnetic structure of $[\text{Co}_2(\text{bta})]_n$ below 16K without applied field, but no traces of spin canting has been observed, including that the SC is incompatible with the magnetic space group of the AF phase.

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Keywords: molecular materials; magnetism; neutron diffraction

FA4-MS02-P14

Crystal Structures and Magnetic Properties of a Series of Copper(II)-Methylmalonate Complexes with 4,4'-Bipyridine. Jorge Pasán^a, Pau Diaz-Gallifa^a, Mariadel Déniz^a, Laura Cañadillas-Delgado^a, Oscar Fabelo^a, Joaquín Sanchiz^b, Francesc Lloret^c, Miguel Julve^c, Catalina Ruiz-Pérez^a. ^aDepartamento de Física Fundamental II, Facultad de Física, Universidad de La Laguna. La Laguna, Tenerife. Spain. ^bDepartamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Spain. ^cICMol, Departament de Química Inorgánica, Universitat de València, Valencia, Spain. E-mail: jpasang@ull.es

The construction of one-, two-, or three-dimensional (1-D, 2-D, or 3-D) coordination polymers with various architectures is based upon the directionality and control