FA4-MS34-P25


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Studies of various phenomena associated with magnetism are of current interest of chemists and physicists. It is well known that besides covalent bonds also hydrogen bonds (HBs) may play an important role in mediating magnetic exchange interactions. Previously, in order to study the correlation between structural and magnetic dimensionality, and the role of hydrogen bonds, we have isolated several compounds between structural and magnetic dimensionality, and the role of current interest of chemists and physicists. It is well known that studies of various phenomena associated with magnetism are of current interest of chemists and physicists. It is well known that studies of various phenomena associated with magnetism are of current interest of chemists and physicists.

Keywords: copper compounds, cyanide complexes, ammonia complexes

FA4-MS34-P26

New heterometallic Cu(II)/Mo(VI) oxide coordination polymers. Liliana Lukashuk A., Andrey Lysenko A., Konstantin Domasevitch A., Kiev National Taras Shevchenko University, Ukraine

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The design and synthesis of new hybrid organic/inorganic coordination polymers based upon polyoxometalates attract a great deal of attention due to their wide-ranging application in catalysis, magnetocochemistry and photochemistry. Attaining to the desirable functional properties requires also the possibility of rational control of the inorganic oxide microstructure that can be achieved by exploiting bifunctional ligand approach. In the present study we introduce a series of bitopic azole ligands bearing pyrazolyl (Hpz) and 1,2,4-triazolyl (trz) groups acting as multiple donors (Scheme 1) for construction of stiff mixed-metal Cu13Mo13-oxide frameworks. Hydrothermal conditions, namely aqueous media under high temperature and pressure getting over the problems of reactants solubility were found to be the key to successful syntheses of the target compounds with discrete ([Mo6O24]4−, [P2Mo5O23]6−, [Mo10O39]5−) and polymeric ([Mo13O40]6−) anions. We have demonstrated that the 1,2,4-trz fragment (HL1) behaves as a short N−,N2-bridge between two closely situated CuII centers (secondary metal-ligand subunits) in the geometry variety of the clusters possessing either discrete trigonuclear [Cu4(η-trz)(μ3-P2Mo5O23)]2− or polymeric [Cu5(μ-trz)3(P2Mo5O23)]6− motifs. Whilst the pyrazolyl group in the synthesized complexes displays mostly the N-single donor behavior towards copper cations, its characteristic H-donor function affords efficient interaction with polyoxometalate matrix as a negatively charged H-acceptor platform. The synergistic effect between 1,2,4-triazole/pyrazole bridges and mixed-metal oxides provides sufficient thermal stability of the prepared MOFs (up to ~350°C). The mixed CuII–MoIII oxides decorated by HL1 ligand are attractive systems for sustaining anion-π interaction. Such situation is established for [Cu2(OH)4(H2O)2(HL1)(Mo13O40)2]3·1.35H2O and [Cu2(OH)4(HL1)(P2Mo5O23)]·1.35H2O, where discrete high charge (Mo13O40)7−, P2Mo5O23)6− anions being closely located to electron deficient tr-centroid facilitate extremely short anion-π interaction (2.65 Å).

Keywords: polyoxometalates, 1,2,4-triazole/pyrazole bridges, metal-organic framework

FA4-MS34-P27


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Titanium imido derivatives have attracted broad interest due to their role in various catalytic processes, and many imido complexes with alkyl or aryl substituents have been reported in the literature.[1] Our studies are focused on species containing imido ligands which possess functionalized substituents as we are interested in analysing the effect of the additional functionality on the coordination behaviour of these derivatives and on their reactivity. As well the presence of an additional donor atom in the ligand would enhance the capacity of the species synthesized to behave as metalloidligands for the construction of ordered supramolecular structures.
Treatment of [Ti(C₅Me₅)Cl₂] with the appropriate lithiated amino-pyridine species (RNHLi) results in the formation of new amido compounds [Ti(C₅Me₅)(NHR)₃]. It is possible to deprotonate one of the amido ligands with a lithiated base, generating the mixed imido-amido derivatives [Ti(C₅Me₅)(=NR)(NHR)]²⁻ that show unusual structures. Interestingly, very few titanocene imido-amido species have been reported. In this contribution we describe the synthesis, characterization and reactivity of these new imido compounds.


**Keywords:** catalysis, organometallics, titanium

### FA4-MS34-P28

**Additional Ligand in the Ru Coordination Sphere the Hoveyda-type Catalysts. Aleksandra Pazio**, Anna Makal*, Anna Szadkowska*, Karol Grela* and Krzysztof Woźniak*, †Department of Chemistry, Warsaw University, Poland, ‡Institute of Organic Chemistry, Polish Academy of Science, Warsaw, Poland E-mail: apazio@chem.uw.edu.pl

A metathesis is a bimolecular process formally involving the exchange of a bond (or bonds) between similar interacting chemical species so that the bonding affinities in the products are identical (or closely similar) to those in the reactants [1]. The reaction takes place in presence of some special type catalysts. One of the most popular catalyst is ruthenium-alkylidene complex: II generation Hoveyda-type catalyst [2]. It is stable in presence of oxygen and moisture, it has a good reaction profile: long reaction time, high thermal stability and it is recyclable after reaction. For these reasons the catalyst has become the base for research that aims in its activity improvement.

During structural research on sulphoxide derivatives synthesized in K. Grela’s group an additional ligands, water molecule, were found in ruthenium coordination sphere of some compounds [3]. They can coordinate ruthenium atom in solution or insert into coordination sphere during the crystallization. The additional ligands do not appear in other Hoveyda-type complexes. The presence of water molecule, as an additional ligand, is probably stimulated by basicity of other ligands and it leads to formation of dimers stable in the solid state. Such dimers are a very first example of a repeatable structural unit in crystalline metathesis catalysts.


**Keywords:** Copper, Isonicotinamide, Coordination polymer

### FA4-MS34-P29

**Isonicotinamide as bridging ligand in the coordination polymer Cu(Ina)₂(NO₃)₃** Ines Pinkert, Gerd Meyer Department für Chemie, Universität zu Köln, Germany E-mail: ipinkert@uni-koeln.de

Isonicotinamide (Ina) has been employed as a ligand for supramolecular assemblies in several Cu(II) complexes in which the amide moiety forms N-H-O hydrogen bonds resulting in infinite coordination polymers [1-3]. However, none of them seems to feature Ina as a direct bridging ligand for two Cu²⁺ cations. For the synthesis of Cu(Ina)₂(NO₃)₃, Ina and Cu(NO₃)₂ were dissolved in a 1:1 ratio in 40 mL of ethanol. After three days blue rhomboedric crystals grew by slow evaporation of the solvent at ambient temperature. Cu(Ina)₂(NO₃)₃ crystallizes in the orthorhombic space group P2₁2₁2₁ (no. 19), a = 1489.4(2), b = 1534.0(2), c = 873.43(7) pm, Z = 4.

**Fig. 1.** Coordination sphere of Cu(II) in Cu(Ina)₂(NO₃)₃ (top) and the connection to a zig-zag chain (bottom).

In Cu(Ina)₂(NO₃)₃, Cu²⁺ is surrounded by three Ina and two nitrte ligands with 2N+2O+1O ligator atoms constituting the coordination polyhedron, roughly an elongated tetragonal pyramid, see Fig. 1, with Cu–O/N distances in the base of about 200 pm and an apical Cu–O distance of 232 pm. All five ligands surrounding Cu(II) are monodentate ligands of which the nitrate ligands and one Ina ligand are terminal. Two Ina ligands are bridging with the acetamide-O and the ring-N atoms acting as the ligating atoms. Thus, Cu(Ina)₂(NO₃)₃ is a coordination polymer, according to Cu(Ina)₁(NO₃)₁(Ina)₂. The zig-zag chain is not formed by supramolecular (hydrogen) bonding, but by “normal” coordinative bonds, ...Cu–O•••N–Cu•••... with O•••N symbolizing the isonicotinamide ligands.


**Keywords:** Copper, Isonicotinamide, Coordination polymer