

FA4-MS34-P25

Two novel ammin complexes of copper(II) with [Pd(CN)₄]²⁻ anion. Juraj Kuchár^a, Veronika Suchá^a, Klaus Harms^b, Juraj Černák^a, ^a*Institute of Chemistry, Department of Inorganic Chemistry, P. J. Šafárik University in Košice, Slovakia,* ^b*Fachbereich Chemie der Philipps Universität, Hans–Meerwein–Str., D-35043 Marburg, Germany*
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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 exhibiting composition Cu(L_N)₂M(CN)₄ (L_N = N-methyl-derivates of ethane-1,2-diamine, M = Ni, Pd) [1,2]. As a continuation we have investigated the aqueous systems Cu²⁺–L_N–[Pd(CN)₄]²⁻ (L_N = N,N,N',N'-tetraethyl-ethane-1,2-diamine and buthane-1,4-diamine), where excess of ammonia was used to dissolve the precipitate formed during reaction. As a byproduct we have obtained and structurally characterized two novel ammin complexes of copper(II) with tetracyanidopalladate(II) anion, [Cu(NH₃)₄Pd(CN)₄] (1) and [Cu₄(NH₃)₁₂(μ₂-CN)₈-Pd₄(CN)₈] (2). Both complexes exhibit molecular structure built up of [Cu(NH₃)_x]²⁺ cations (x = 2, 4) and square [Pd(CN)₄]²⁻ anions. While 1 is binuclear complex in which Cu(II) and Pd(II) atoms are linked by one bridging cyanido ligand, the structure of 2 contains octanuclear planar molecules in which two cyanide ligands in *cis*-positions among four of the complex anions exhibit bridging character. In both compound Cu(II) atoms is pentacoordinated with respective τ parameters 0 (1), 0 and 29 % (2), resp. Hydrogen bonds link the complex molecules in both 1 and 2 and lead to 3D arrangements of molecules.

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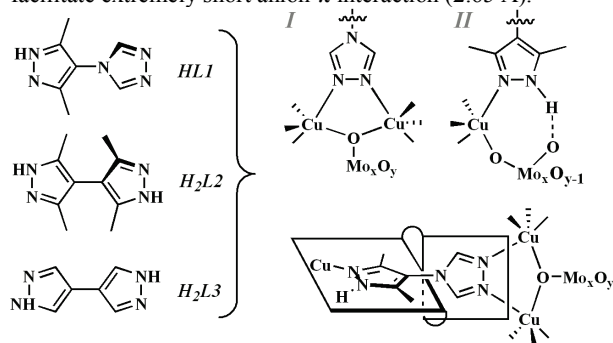
Keywords: copper compounds, cyanide complexes, ammonia complexes

FA4-MS34-P26

New heterometallic Cu(I,II)/Mo(VI) oxide coordination polymers. Liliána Lukashuk^a, Andrey Lysenko^a, Konstantin Domasevitch^a, ^a*Kiev National Taras Shevchenko University, Ukraine*
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The design and synthesis of new hybrid organic/inorganic coordination polymers based upon polyoxomolybdates attract a great deal of attention due to their wide-ranging application in catalysis, magnetochemistry 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 (*tr*) groups acting as multiple donors (Scheme 1) for construction of stiff mixed-metal Cu^{I/II}/Mo^{VI}-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 ((Mo₈O₂₆)⁴⁻, (P₂Mo₅O₂₃)⁶⁻, (Mo₅O₁₇)⁴⁻) and polymeric ((Mo₃O₁₀)_n²ⁿ⁻) anions. We have demonstrated that the 1,2,4-*tr* fragment (**HLI**) behaves as a short *N*ⁱ,*N*^j-bridge between two closely situated Cu^{I/II} centers (secondary metal-ligand subunits) in the geometry variety of the clusters possessing either discrete trinuclear [Cu^{II}₃(η²-*tr*)₂(μ-P₂Mo₅O₂₃)] or polymeric [Cu^{II}(η²-*tr*)(μ-Mo₃O₁₀)_n], [Cu^I₂(η²-*tr*)₂(μ-Mo₈O₂₆)_n] 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 polyoxomolybdate 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 Cu^I – Mo^{VI} oxides decorated by **HLI** ligand are attractive systems for sustaining anion-π interaction. Such situation is established for [Cu₄(OH)₄(H₂O)₂(**HLI**)₄(Mo₈O₂₆)₂·2H₂O and [Cu₃(H₂O)(**HLI**)₃(P₂Mo₅O₂₃)₃·8H₂O], where discrete high charge (Mo₈O₂₆⁴⁻, P₂Mo₅O₂₃⁶⁻) anions being closely located to electron deficient *tr*-centroid facilitate extremely short anion-π interaction (2.65 Å).



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

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New Imido-Pyridine Ti(IV) Anions. Marta E. G. Mosquera, Pilar Gómez-Sal, Sergio Pedrosa, *Dpto de Química Inorgánica, Universidad de Alcalá, Madrid, Spain.*

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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 metalloligands for the construction of ordered supramolecular structures.

Treatment of $[\text{Ti}(\text{C}_5\text{Me}_5)\text{Cl}_3]$ with the appropriate lithiated amino-pyridine species (RNHLi) results in the formation of new amido compounds $[\text{Ti}(\text{C}_5\text{Me}_5)(\text{NHR})_3]$. It is possible to deprotonate one of the amido ligands with a lithiated base, generating the mixed imido-amido derivatives $[\text{Ti}(\text{C}_5\text{Me}_5)(=\text{NR})(\text{NHR})_2]$ that show unusual structures. Interestingly, very few titanocene imido-amido species have been reported.[2] In this contribution we describe the synthesis, characterization and reactivity of these new imido compounds.

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Keywords: catalysis, organometallics, titanium

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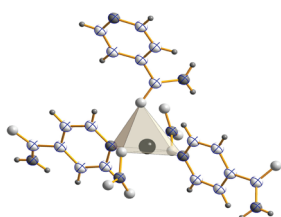
Additional Ligand in the Ru Coordination Sphere the Hoveyda-type Catalysts. Aleksandra Pazio^a, Anna Makal^a, Anna Szadkowska^b, Karol Greła^{b*} and Krzysztof Woźniak^{a*}, ^aDepartment of Chemistry, Warsaw University, Poland, ^bInstitute of Organic Chemistry, Polish Academy of Science, Warsaw, Poland
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A metathesis is a bimolecular process formally involving the exchange of a bond (or bonds) between similar interacting chemical species so that the bonding affiliations 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. Greła'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.

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Keywords: crystal structure analysis, metalloorganic catalysts, metathesis

FA4-MS34-P29

Isonicotinamide as bridging ligand in the coordination polymer $\text{Cu}(\text{Ina})_2(\text{NO}_3)_2$. Ines Pinkert, Gerd Meyer Department für Chemie, Universität zu Köln, Germany
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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 Cu^{2+} cations.

For the synthesis of $\text{Cu}(\text{Ina})_2(\text{NO}_3)_2$, Ina and $\text{Cu}(\text{NO}_3)_2$ 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. $\text{Cu}(\text{Ina})_2(\text{NO}_3)_2$ crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19), $a = 1489.4(2)$, $b = 1354.0(2)$, $c = 787.43(7)$ pm, $Z = 4$.

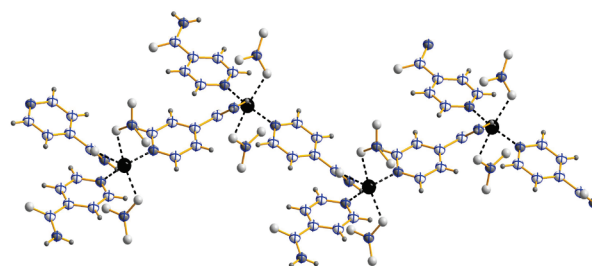


Fig. 1. Coordination sphere of Cu(II) in $\text{Cu}(\text{Ina})_2(\text{NO}_3)_2$ (top) and the connection to a zig-zag chain (bottom).

In $\text{Cu}(\text{Ina})_2(\text{NO}_3)_2$, Cu^{2+} is surrounded by three Ina and two nitrate ligands with $2\text{N}+2\text{O}+1\text{O}$ ligand 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, $\text{Cu}(\text{Ina})_2(\text{NO}_3)_2$ is a coordination polymer, according to $\text{Cu}(\text{Ina})_{1/1}(\text{NO}_3)_{2/1}(\text{Ina})_{2/2}$. 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.

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Keywords: Copper, Isonicotinamide, Coordination polymer