

## FA4-MS34-P25

**Two novel ammin complexes of copper(II) with [Pd(CN)<sub>4</sub>]<sup>2-</sup> anion.** Juraj Kuchár<sup>a</sup>, Veronika Suchá<sup>a</sup>, Klaus Harms<sup>b</sup>, Juraj Černák<sup>a</sup>, <sup>a</sup>*Institute of Chemistry, Department of Inorganic Chemistry, P. J. Šafárik University in Košice, Slovakia,* <sup>b</sup>*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<sub>N</sub>)<sub>2</sub>M(CN)<sub>4</sub> (L<sub>N</sub> = N-methyl-derivates of ethane-1,2-diamine, M = Ni, Pd) [1,2]. As a continuation we have investigated the aqueous systems Cu<sup>2+</sup>–L<sub>N</sub>–[Pd(CN)<sub>4</sub>]<sup>2-</sup> (L<sub>N</sub> = 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(NH<sub>3</sub>)<sub>4</sub>Pd(CN)<sub>4</sub>] (1) and [Cu<sub>4</sub>(NH<sub>3</sub>)<sub>12</sub>(μ<sub>2</sub>-CN)<sub>8</sub>-Pd<sub>4</sub>(CN)<sub>8</sub>] (2). Both complexes exhibit molecular structure built up of [Cu(NH<sub>3</sub>)<sub>x</sub>]<sup>2+</sup> cations (x = 2, 4) and square [Pd(CN)<sub>4</sub>]<sup>2-</sup> 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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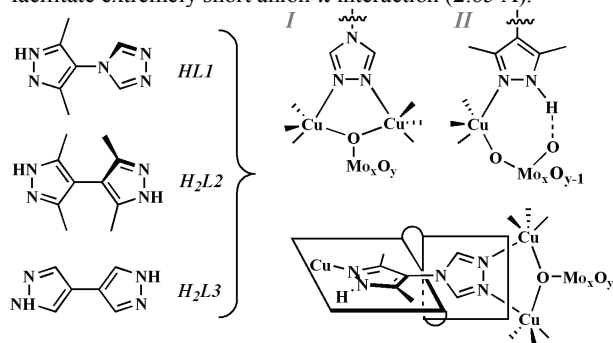
**Keywords: copper compounds, cyanide complexes, ammonia complexes**

## FA4-MS34-P26

**New heterometallic Cu(I,II)/Mo(VI) oxide coordination polymers.** Liliána Lukashuk<sup>a</sup>, Andrey Lysenko<sup>a</sup>, Konstantin Domasevitch<sup>a</sup>, <sup>a</sup>*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<sup>I/II</sup>/Mo<sup>VI</sup>-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 ((Mo<sub>8</sub>O<sub>26</sub>)<sup>4-</sup>, (P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub>)<sup>6-</sup>, (Mo<sub>5</sub>O<sub>17</sub>)<sup>4-</sup>) and polymeric ((Mo<sub>3</sub>O<sub>10</sub>)<sub>n</sub><sup>2n-</sup>) anions. We have demonstrated that the 1,2,4-*tr* fragment (**HLI**) behaves as a short *N*<sup>i</sup>,*N*<sup>j</sup>-bridge between two closely situated Cu<sup>I/II</sup> centers (secondary metal-ligand subunits) in the geometry variety of the clusters possessing either discrete trinuclear [Cu<sup>II</sup><sub>3</sub>(η<sup>2</sup>-*tr*)<sub>2</sub>(μ-P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub>)] or polymeric [Cu<sup>II</sup>(η<sup>2</sup>-*tr*)(μ-Mo<sub>3</sub>O<sub>10</sub>)<sub>n</sub>], [Cu<sup>I</sup><sub>2</sub>(η<sup>2</sup>-*tr*)<sub>2</sub>(μ-Mo<sub>8</sub>O<sub>26</sub>)<sub>n</sub>] 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<sup>I</sup>–Mo<sup>VI</sup> oxides decorated by **HLI** ligand are attractive systems for sustaining anion-π interaction. Such situation is established for [Cu<sub>4</sub>(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(**HLI**)<sub>4</sub>(Mo<sub>8</sub>O<sub>26</sub>)<sub>2</sub>·2H<sub>2</sub>O and [Cu<sub>3</sub>(H<sub>2</sub>O)(**HLI**)<sub>3</sub>(P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub>)<sub>3</sub>·8H<sub>2</sub>O, where discrete high charge (Mo<sub>8</sub>O<sub>26</sub><sup>4-</sup>, P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub><sup>6-</sup>) 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**

## FA4-MS34-P27

**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.