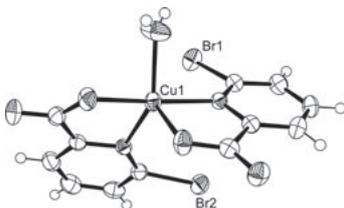


P07.01.10

Acta Cryst. (2008). A64, C402**Copper(II) complexes with derivatives of picolinic acid. Synthesis, structural and magnetic study**Boris-Marko Kukovec¹, Zora Popovic¹, Nives Kitanovski², Zvonko Jaglicic³, Gordana Pavlovic⁴

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Metal complexes of hydroxy derivatives of picolinic acid are of a great interest in terms of chemical and biological properties. Other substituents in the pyridine ring, methyl group or halide atom, may lead to significant electronic and steric effects enlarging the structural diversity. We have prepared and fully characterized copper(II) complexes with 6-methylpicolinic (6-MepicH) and 6-bromopicolinic acid (6-BrpicH): [Cu(6-Mepic)₂(H₂O)], **1**, [Cu(6-Mepic)₂(py)], **2** (py = pyridine) and [Cu(6-Brpic)₂(H₂O)], **3**. Both **1** and **3** were prepared in aqueous solution by reaction of copper(II) sulfate and appropriate acid, while **2** was prepared by recrystallization of **1** from pyridine solution. X-ray crystal structure analysis revealed square-pyramidal coordination of copper(II) in **1** and trigonal-bipyramidal in **2** and **3** and *N,O*-chelated coordination mode of 6-Mepic and 6-Brpic ligands. All prepared complexes were characterized by spectroscopic (IR, EPR) and thermal methods (TGA/DTA). The magnetic susceptibility data for **1** and **2** revealed paramagnetic behaviour, while **3** is paramagnetic only above 100 K. At lower temperature, **3** exhibits antiferromagnetic interaction.



Keywords: copper coordination compounds, carboxylate complexes, magnetic behaviour

P07.01.11

Acta Cryst. (2008). A64, C402**Structural and oxidation state study of two novel mixed-valence binuclear copper complexes**Laura Rocés¹, Santiago Garcia-Granda¹, Jesus Garcia Lopez², Victor Yanez Rodriguez², Alfredo Guevara-Garcia⁵, Ana Martinez^{3,4}, Fernando Lopez Ortiz²

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We have stereoselectively synthesized a novel binuclear Cu(I)-Cu(III) mixed-valence complex **I** stable to air upon reaction of a C_α, C_{ortho} dilithiated phosphazene with CuI. The crystal structure of this compound, as studied by single crystal X-ray diffraction, reveals two ligands bridged through two copper centres. The first Cu atom is squareplanar coordinated to four carbanionic centers and

the second one binds linearly to two nitrogen atoms. The distance between the two Cu atoms of the complex (2.73 Å) is shorter than the sum of the correspondent van der Waals radii, which suggests that there exists a Cu-Cu interaction. The X-ray absorption near the K-edge (XANES) spectrum confirmed that the dimer is a unique species containing a Cu(I)-Cu(III) bimetallic complex. In addition, when **I** reacts with Ph₃P a new complex **II** is obtained in which the triphenylphosphine ligand is bonded to the Cu(I) atom. Significantly, the X-ray structure shows that the intermetallic distance in complex **II** increases to 3.45 Å. DFT calculations on **I** reveal the existence of a copper-copper interaction. The theoretical distance between the two Cu atoms is 2.86 Å, in agreement with the experimental value. Experimental electron density on the Cu-Cu interaction on **I** and **II** has been topologically analysed [2]. There is no precedent in the literature for such mixed-valence derivatives. The intricate aspects of the structural and oxidation state study of this novel Cu(I)-Cu(III) complex will be explained in detail in this presentation.

[1] García-López, J.; Fernández, I.; Serrano-Ruiz, M.; López-Ortiz, F. *Chem. Commun.* 2007, 4674.

[2] Menendez-Velazquez, A.; Garcia-Granda, S. *J. Appl. Cryst.* (2003), 36, 193-205.

Keywords: mixed-valence compounds, copper complexes, XANES

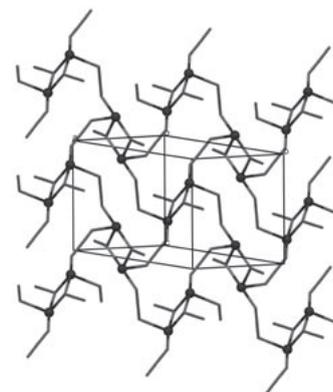
P07.01.12

Acta Cryst. (2008). A64, C402**The isonicotinamide complexes of copper(II) with N₃⁻, SCN⁻ and SO₄²⁻ as bridging ligands**Marijana Đaković¹, Zora Popovic¹, Zvonko Jaglicic², Bojan Kozlevcar³

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Recently, the rational design, synthesis and characterisation of polymeric metal-organic coordination networks has been an active area due to its application in many fields. The utilization of N- or O-donor ligands is an effective strategy in the construction of these types of complex networks [1]. We will present three Cu(II) complexes: [Cu(N₃)₂L]_n **1**, [Cu(SCN)₂L₂]_n **2**, and [Cu(SO₄)(H₂O)L₂·2H₂O]_n **3** (L = isonicotinamide), and discuss the structural features in each case. The complexes **2** and **3** were prepared in situ from aqueous solution, and **1** was synthesized hydrothermally. The X-ray structure determinations reveal that the **1** and **2** are 2D- and **3** 1D-polymers. The magnetic susceptibility data for **2** and **3** revealed paramagnetic behaviour, while **1** is paramagnetic only above 100 K. At lower temperature, **1** exhibits ferromagnetic interaction.

[1] Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101** 1629-1658.



Keywords: copper(II) coordination polymers, crystal structure, magnetic properties