

**MS30-P12** Novel complexes of copper(II) with  $[\text{MnCl}_4]^{2-}$  anionJuraj Kuchár<sup>1</sup>, Erika Samořová<sup>1</sup><sup>1</sup>. Institute of Chemistry, Department of Inorganic Chemistry, P. J. Šafárik University in Košice, Košice, Slovakia

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At present, hydrogen bonding mediated magnetism is a well-documented phenomenon [1] and the results of magnetic studies have shown that the exchange parameter  $J$  can reach as high values as 38.3 K [2]. The study of magnetic and thermodynamic properties of structurally 1D compound  $\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4$  ( $\text{en} = 1,2$ -diaminoethane) in the very low temperature region (below 0.5 K) corroborated its magnetically 2D character; as additional exchange paths to the covalent bonds the present HBs of the N-H...N type were suggested. The character of the magnetic exchange interactions is very weak and is in line with long exchange path through the diamagnetic -NC-M-CN- five-atomic bridge. In order to shorten this five-atomic bridge we have undertaken a study of a series copper(II) compounds in which  $[\text{M}(\text{CN})_4]^{2-}$  bridging species were replaced by  $[\text{MnCl}_4]^{2-}$  anion. The use of this anion as a bridging unit enhances the attractiveness of these Cu(II)-Mn(II) bimetallic chain systems from magnetic properties point of view. The use of ethylenediamine's methyl derivatives lead to structurally similar 1D compounds as it was in the case of  $\text{Cu}(\text{en})_2\text{Ni}(\text{CN})_4$ , in which copper(II) atoms are linked by anion species. Surprisingly the use of the macrocyclic ligand *cyclam* (*cyclam* = 1,4,8,11-tetraazacyclotetradecane) led to different structural arrangement and the crystal structure analysis reveal 3D character of the structure, where besides the expected chains of -Cu-Cl-Mn-Cl-Cu- type another chain of -Mn-Cl-Mn-Cl-Mn- type that connecting them appeared. In order to investigate this phenomena we have prepared and characterized several new derivatives of the *cyclam* and used them for preparation of new complexes. The results of the crystal structure determination have shown formation of 1D chains; the hexa-coordinated Cu(II) atoms are surrounded by one molecule of blocking ligands and two chlorine atoms in *trans* position linking Cu(II) atoms with Mn(II) atoms as it was in above mentioned compounds. Further details of the synthesis, characterization and molecular and crystal structures of all compounds will be given.

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**Keywords:** hydrogen bonds, copper and manganese compounds

**MS30-P13** Crystallographic analysis of iridium(I) N-heterocyclic carbene complexes of benzimidazol-2-ylideneMerve İzmirli<sup>1</sup>, Aytaç G. Gökçe<sup>1</sup>, Süleyman Gülcemal<sup>2</sup>, Muhittin Aygün<sup>1</sup><sup>1</sup>. Department of Physics, Dokuz Eylül University, 35160 Buca, İzmir, Turkey.<sup>2</sup>. Department of Chemistry, Ege University, 35100 Bornova, İzmir, Turkey

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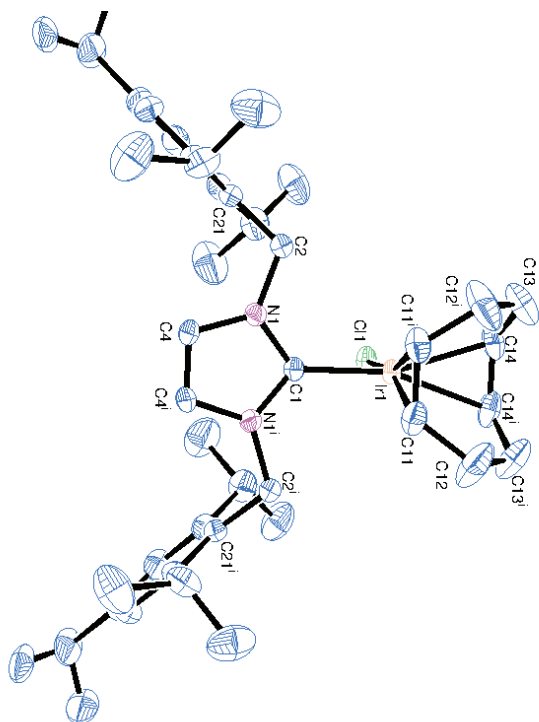
The transition metal complexes of N-heterocyclic carbenes (NHCs) based on imidazol, imidazolin and benzimidazole framework have been the focus of intense research in organometallic chemistry and homogeneous catalysis.<sup>1-4</sup> The crystal and molecular structures of Ir(I) NHC complexes have been determined by single crystal x-ray diffraction technique. In both complexes, iridium atoms lie in a slightly distorted square-planar coordination environments defined by the coordination of the metal to the two olefinic bonds of the cyclooctadiene ligand, the carbon atom of the NHC ligand and the chlorine atom (Figure 1). The iridium–NHC bond lengths agreed (COD) well with the values found in other NHC-supported [Ir(COD)Cl] complexes.

<sup>1</sup> N-heterocyclic carbenes: From laboratory curiosities to efficient synthetic tools, ed. S. Díez-González, RSC Catalysis Series No. 6, Royal Society of Chemistry, Cambridge, 2011.

<sup>2</sup> F.E. Hahn and M.C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, 47, 3122.

<sup>3</sup> W.A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, 41, 1290.

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**Figure 1.** The molecular structure of the complex with displacement ellipsoids drawn at the 30% probability level and hydrogen atoms have been omitted for clarity.

**Keywords:** N-heterocyclic carbene, Ir(I) complex, benzimidazol-2-ylidene, crystal structure

**MS30-P14** Ligand type and synthetic approach induced variability of supramolecular topologies of  $[\text{Ni}_4\text{L}_4(\text{ROH})_4]$  AND  $[\text{Ni}_4\text{L}_4(\text{ROH})_X(\text{R}'\text{OH})_Y; X+Y = 4]$

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The synthesis of polynuclear cluster compounds of the Mn, Fe, Ni, V and Co or mixed metals represents a number of challenges. Often it is difficult to predict the exact cluster structure due to potentially variable outcomes of self-assembly process. Owing to a wide range of their potential applications, e.g. in data storage, memory devices, switches and sensors, considerable attention has been devoted to the targeted synthesis of such systems. The impact of reversible release and reabsorption of both coordinated and uncoordinated solvent molecules on the cluster properties is well documented in the literature.<sup>1</sup> These processes are accompanied by the structural changes related to a cleavage/formation of the coordination bonds.<sup>2,3</sup> Among different cluster types that can exhibit those features, cubane-like clusters with  $[\text{Ni}_4(\mu_3\text{-O})_4]$  core are especially well studied class. The cubane-like core of nearly all investigated tetranuclear Ni(II) complexes consists of four identical  $\mu_3\text{-O}$  bridges originating from  $\text{-OH}$  or  $\text{-OR}$  moieties. The symmetry of  $[\text{Ni}_4\text{O}_4]$  core and the differences in the  $\text{Ni}-\mu_3\text{-O}-\text{Ni}$  angles often have a decisive role in establishing intramolecular magnetic interactions.  $[\text{Ni}_4\text{L}_4(\text{soln})_4]$  type of complexes can undergo reversible exchange of the coordinated solvent molecules ( $\text{MeOH}$  vs.  $\text{H}_2\text{O}$ ).<sup>4</sup> Although the structural alterations induced by such solvent exchange were subtle, substantial changes of the physical and chemical properties have been established. This study unveiled novel synthetic aspects and interesting structural features of a new family of Ni(II) compounds based on cubane-like clusters. Depending on reaction conditions different cubane-like clusters of the type  $[\text{Ni}_4\text{L}_4(\text{ROH})_4]$  and  $[\text{Ni}_4\text{L}_4(\text{ROH})_2(\text{R}'\text{OH})_2]$  ( $\text{H}_2\text{L}$  = tridentate Schiff base ligand,

$N$ -(2-hydroxy-5-methylphenyl)salicylideneimine,  $\text{R} = \text{-CH}_3, \text{-C}_2\text{H}_5, \text{-C}_3\text{H}_7, \text{-C}_4\text{H}_9, \text{ i } \text{-C}_5\text{H}_{11}$ ) were isolated (Fig.1). The various supramolecular phenomena such as polymorphism, conformational isomorphism and synmorphism were established. These phenomena will be discussed in detail on the basis of structure-property relationships. <sup>1</sup> H. Zheng-Ming, X.-M. Zhang, *Dalton Trans.* 2011, 40, 2092–2098. <sup>2</sup> E.-C. Yang, et. al., *Polyhedron* 2003, 22, 1727–1733. <sup>3</sup> M. Moragues-Cánovas, et. al., *Eur. J. Inorg. Chem.* 2004, 2219–2222. <sup>4</sup> A. Das, et. al., *Inorg. Chem.* 2012, 51, 8141–8149.

**Keywords:** cubane-like clusters  $[\text{Ni}_4\text{L}_4(\text{soln})_4]$ ; solv = ROH, tridentate Schiff base ligand, synthesis, supramolecular topologies