

Two novel Cu(II) complexes with tetraimine 2,6-diacetylpyridine derivatives – Synthesis, Characterization, and Crystal Structure

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The reactions of methanolic solutions of 2,6-diacetylpyridine-*bis*(hydrazone), and copper(II)-chloride in the presence of 2,3-/2,4-dihydroxybenzaldehyde in molar ratio 1:1:2 yielded single crystals of the complexes of with the formulae [Cu(L)Cl₂] \cdot *n*MeOH (*n* = 1, 2). In both complexes, the condensation of the free amino groups of 2,6-diacetylpyridine-*bis*(hydrazone) with 2,3-dihydroxybenzaldehyde (L1) or 2,4-dihydroxybenzaldehyde (L2) took place, and the tetraimine ligand was obtained and coordinated to the metal center in an NNN tridentate manner. The complexes crystallized with one (**1**) and two MeOH molecules (**2**). Complexes are crystalline products stable in air and poorly soluble in water, alcohols, acetone, and acetonitrile but well soluble in DMF. The molar conductivity of their DMF solutions (**1**: 22 S \cdot cm² \cdot mol⁻¹; **2**: 16 S \cdot cm² \cdot mol⁻¹ for **2**) suggested their non-electrolytic nature but also indicated the partial substitution of chlorido ligands by the solvent molecules. The IR spectra and elemental analysis confirmed the composition and purity of the complexes, while SC-XRD proved their structure (Fig. 1).

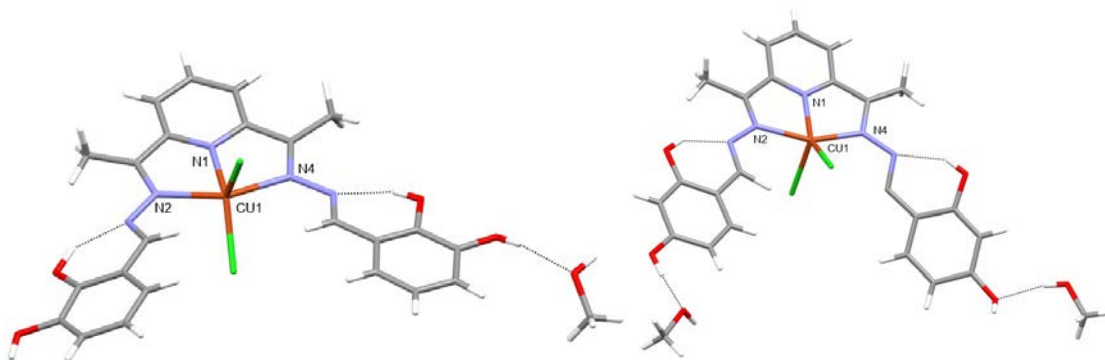


Figure 1. The molecular structures and with selected H-bonds in [Cu(L1)Cl₂] \cdot MeOH (**1**, left) and [Cu(L2)Cl₂] \cdot 2MeOH (**2**, right).

Cu(II) is situated in a distorted environment (**1**: $\tau_5 = 0.23$; **2**: 0.17) of two azomethine nitrogen atoms and a pyridine nitrogen atom of the chelating ligand, as well as two chlorido ligands. This results in the forming of two fused five-membered metallocycles. These results enable the comparative analysis of two similar structures to estimate the influence of the OH-group position. As expected, in both structures, intramolecular H-bonds are formed between hydrazine nitrogen atoms as H-acceptors and OH-groups in position 2 as H-donors. Interestingly, an additional H-bond is formed between the OH-group in position 3 of the one 2,3-dihydroxybenzaldehyde derivative and the MeOH molecule in **1**. In contrast, in **2**, a MeOH molecule is H-bonded to one of each OH-groups in position 4.

[1] M. Radanović M and Barta Holló B (2023) Some Aromatic Schiff Bases and Their Metal Complexes. Schiff Base in Organic, Inorganic, and Physical Chemistry. IntechOpen. Available at: <http://dx.doi.org/10.5772/intechopen.107405>.

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