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**COMPUȘI COORDINATIVI MONONUCLEARI AI NICHELULUI(II) ȘI CUPRULUI(II)  
CU LIGANDUL BAZĂ SCHIFF DERIVAT AL S-METILIZOTIOSEMICARBAZONEI  
ACETILACETONEI ȘI 8-CHINOLINALDEHIDEI**

**MONONUCLEAR NICKEL(II) AND COPPER(II) COORDINATION COMPOUNDS  
WITH SCHIFF BASE LIGAND DERIVED FROM ACETYLACETONE  
S-METHYLISOTHIOSEMICARBAZONE AND QUINOLINE-8-CARBALEDEHYDE**

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**Rezumat.** *Au fost sintetizați doi compuși coordinativi noi [NiL]I (1) și [CuLI] (2) cu ligandul tetradentat de tip bază Schiff N<sub>3</sub>O (HL), obținut prin metoda de condensare templată a S-metilizotiosemicarbazonei acetilacetonei cu 8-chinolinaldehida, în prezența ionilor de metale. Compușii au fost caracterizați utilizând analiza elementală, spectroscopia IR și spectrometria de masă pESI, iar structura cristalină a compușilor a fost determinată prin metoda difracției cu raze X pe monocristal.*

**Cuvinte-cheie:** *compuși coordinativi, Ni(II), Cu(II), S-metilizotiosemicarbazona, 8-chinolinaldehida.*

**Abstract.** *Two new coordination compounds [NiL]I (1) and [CuLI] (2) with tetradentate N<sub>3</sub>O Schiff base ligand (HL) were synthesized by direct template condensation of acetylacetone S-methylisothiosemicarbazone and quinoline-8-carbaldehyde in the presence of metal ions. These complexes were characterized by elemental analysis, IR and pESI MS spectroscopies and their crystal structures were determined by the single crystal X-ray diffraction method.*

**Key-words:** *coordination compounds, Ni(II), Cu(II), S-methylisothiosemicarbazone, quinoline-8-carbaldehyde.*

## **Introduction**

Nitrogen-containing Schiff base ligands and their coordination compounds played an important role due to the wide range of their industrial, biological, analytical, medicinal, pharmaceutical and catalytical applications [1, 2]. Metal complexes of thiosemicarbazone are well known for their pharmacological applications, while quinoline derivatives (in particular, quinoline carbaldehydes) display bactericidal, insecticidal and fungicidal properties [3]. The combination of both active fragments in one molecular complex seems promising for obtaining new biologically active compounds.

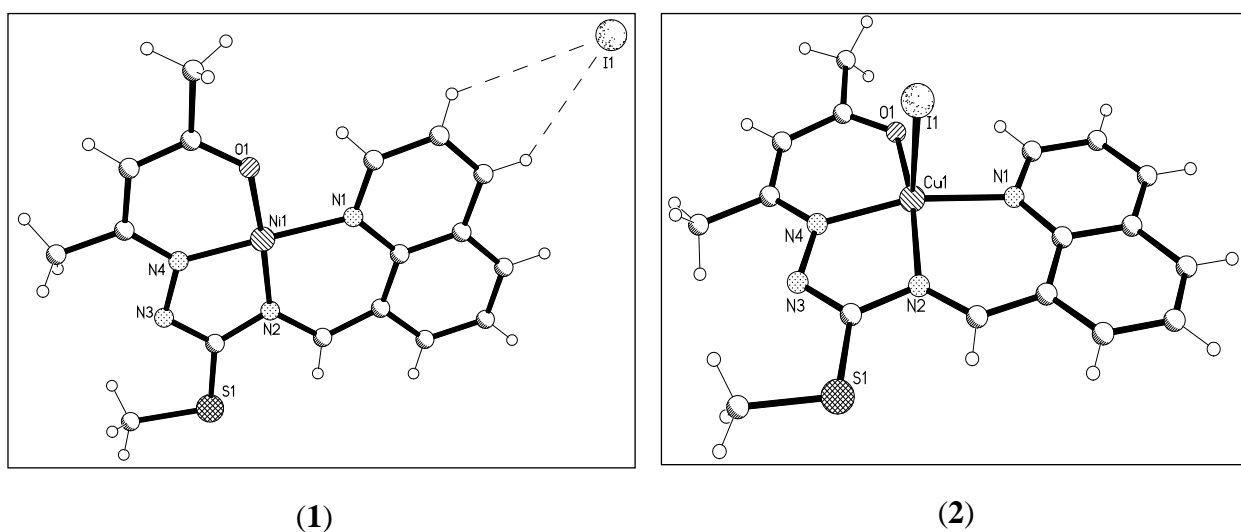
## Results and discussions

Two new complexes with unsymmetrical tetradentate Schiff base ligand HL resulting from template binding of acetylacetone S-methylisothiosemicarbazone with quinoline-8-carbaldehyde in the presence of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  in  $\text{CH}_3\text{OH}$  solvent with composition  $[\text{NiL}]\text{I}$  (**1**) and  $[\text{CuLI}]$  (**2**) have been synthesized and investigated. Complexes **1** and **2** were isolated as air-stable, dark brown crystals soluble in chloroform, DMF, DMS, and insoluble in alcohols, acetone, hexane, ether and water.

The IR spectrum of **1** and **2** show no absorption in the  $3100\text{--}3400\text{ cm}^{-1}$  region ( $\nu(\text{NH}_2)$ ) and at  $1700\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$ ), indicating the condensation of the terminal amino group of acetylacetone S-methylisothiosemicarbazone with the carbonyl group of quinoline-8-carbaldehyde.

The IR spectra of **1** and **2** complexes contain strong absorption bands at  $1550$  and  $1521\text{ cm}^{-1}$  respectively, which can be attributed to the  $\nu(\text{C}=\text{O})$  stretching vibrations of the coordinated organic ligand. The decrease of the vibration frequencies of the carbonyl group in **1** and **2** compared to the frequencies of the carbonyl group in  $\beta$ -diketones (keto form  $\sim 1720\text{ cm}^{-1}$  and enolic form  $1650\text{--}1600\text{ cm}^{-1}$ ) is explained by the resonance between  $\text{C}-\text{O}-\text{M}$  and  $\text{C}=\text{O}\cdots\text{M}$  bonds during the coordination of carbonyl group of the ligand to the metals [4].

The identity and purity of the complexes with newly prepared tetradentate  $[\text{N}_3\text{O}]$  ligands were confirmed by elemental analysis and pESI mass spectrum, which showed the presence of the molecular ion peaks  $[\text{M}-\text{I}]^+=383$  and  $[\text{M}-\text{I}]^+=388$ , for compound **1** and **2**, respectively, that suggests the presence of iodine in complexes. The lack of further fragmentation of  $[\text{M}-\text{I}]^+$  ions in the mass-spectra of both studied compound emphasizes their high stability.



**Fig. 1. View of structures 1 and 2**

The crystal structures of complexes **1** and **2** were determined by the single crystal X-ray diffraction method. The structural study reveals the formation of the mononuclear ionic coordination compound  $[\text{NiL}]\text{I}$  (**1**) and the molecular complex  $[\text{CuLI}]$  (**2**) (Figure).

The structure of compound **1** reveals the planar cationic complex in which monodeprotonated tetradentate  $\text{N}_3\text{O}$  ligand forms two six-membered and one five-membered metalocycles and outer-sphere iodide anion. The  $\text{Ni}-\text{N}$  distances are in the range  $1.788(8) - 1.929(8)\text{ \AA}$ ,  $\text{Ni}-\text{O} = 1.792(6)\text{ \AA}$ . In the crystal, the charged components are linked by weak  $\text{C}-\text{H}\cdots\text{I}$  hydrogen bonds.

Compound **2** represents a neutral square-pyramidal complex of copper (II) with tetradentate N<sub>3</sub>O ligand coordinated in basal plane in the manner similar to **1** and iodide anion in apical position. The Cu–N distances 1.929(8) – 2.052(8) Å, Cu–O = 1.916(7) Å, and Cu–I = 2.906(1) Å. The Cu (1) atom displace from the plane of four donor atoms of the ligand on 0.203 Å in the direction of coordinated iodide anion.

The organic ligand is deprotonated on oxygen atom in both compounds, resulting in bonds delocalization.

## Conclusions

The synthetic methods were developed for the preparation of two novel mononuclear nickel(II) and copper(II) coordination compounds with N<sub>3</sub>O tetradentate Schiff base ligand derived from acetylacetone S-methylisothiosemicarbazone and quinoline-8-carbaldehyde.

The single crystal X-ray diffraction study revealed the square-planar structure of Ni(II) ionic complex and square-pyramidal molecular complex of Cu(II).

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