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Coordination compounds of copper(II) based on the coordinating agent 1,5-*bis*(2-hydroxy-1-naphthaldehyde)carbohydrazone

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Abstract. Upon the interaction of copper(II) nitrate with 1,5-*bis*(2-hydroxy-1-naphthaldehyde)carbohydrazone (H_4L^1), by modifying the solvent system, two coordination compounds were synthesized: the tetranuclear complex $[Cu_2(HL^1)(MeOH)_2(NO_3)]_2$ (**1**) and the polymeric structure $[Cu_2(HL^1)(HCOO)]_n \cdot H_2O$ (**2**). The chemical composition and structural features of complexes **1** and **2** were determined by single-crystal X-ray diffraction and IR spectroscopy.
Keywords: coordination agent, Cu(II) complex, 1,5-*bis*(2-hydroxy-1-naphthaldehyde) carbohydrazone, X-ray diffraction.

Compuși de coordinare ai cuprului(II) în baza agentului de coordinare 1,5-*bis*(2-hidroxi-1-naftaldehidă)carbohidrazonă

Rezumat. La interacțiunea azotatului de cupru(II) cu 1,5-*bis*(2-hidroxi-1-naftaldehidă)carbohidrazona (H_4L^1), prin modificarea sistemului de solvenți, au fost sintetizați doi compuși de coordinare: un compus tetranuclear $[Cu_2(HL^1)(MeOH)_2(NO_3)]_2$ (**1**) și unul cu structură polimerică $[Cu_2(HL^1)(HCOO)]_n \cdot H_2O$ (**2**). Compoziția chimică și caracteristicile structurale ale compușilor **1** și **2** au fost determinate prin difracție cu raze X pe monocristal și spectroscopie IR.
Cuvinte-cheie: agent de coordinare, complex Cu(II), 1,5-*bis*(2-hidroxi-1-naftaldehidă) carbohidrazonă, difracție cu raze X.

1. Introduction

The coordination ligands obtained from the condensation of carbohydrazide with salicylaldehyde and its derivatives (Figure 1) show coordination versatility and have been used for the synthesis of various 3d metal complexes, namely: V(V), Ni(II), Zn(II), Cu(II) [1]–[8].

These ligands are potentially pentadentate, but as in the case of the corresponding hydrazides, they exhibit the phenomenon of keto-enol tautomerism. The enol tautomer can exist in the form of the *syn* or *anti* geometric isomer, and they can be potentially hexadentate with two nonequivalent coordination sets ONO and ONN (Figure 1).

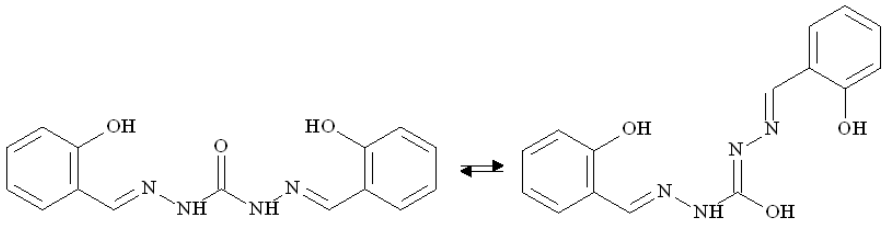

Figure 1. The phenomenon of tautomerism in the case of carbohydrazone ligands

The most numerous compounds based on 1,5-*bis*(2-hydroxybenzaldehyde)carbohydrazone were obtained upon its interaction with copper(II) ions, and the nature of the anion in the initial salt and the solvent used greatly influenced the composition and structure of the resulting coordination compounds [5]–[8]. Anions or weakly coordinated solvent molecules can be easily replaced by bridging ligands, which led to the formation of coordination polymers or high-nuclearity aggregates [9], [10].

The aim of this study was to determine the impact of the two benzene rings in the carbonyl component condensed with the carbohydrazide on the composition and structure of the corresponding copper(II) coordination compounds. Analysis of the Cambridge structural database showed the lack of such structures and the existence of only one binuclear coordination compound of tin(IV) $[Ph_4Sn_2(L^2)]$ structurally characterized with 1,5-*bis*(2-hydroxy-naphthaldehyde)thiocarbohydrazone (H_4L^2), the sulfur derivative of this class of ligands [11]. The *in vitro* antibacterial activity of the ligand and the complex $[Ph_4Sn_2(L^2)]$ was evaluated against Gram-positive (*B. subtilis* and *S. aureus*) and Gram-negative (*E. coli* and *P. aeruginosa*) bacteria and compared with standard drugs. The results showed that the ligand had no antibacterial effect against all tested bacteria, while the coordination compound $[Ph_4Sn_2(L^2)]$ significantly inhibited bacterial growth.

The present study analyzes the experimental results obtained from the synthesis of two coordination compounds of Cu(II) with 1,5-*bis*(2-hydroxy-1-naphthaldehyde)carbohydrazone, which differ in the nature of the used solvent, while the copper(II) salt involved in the synthesis process and the reaction conditions were identical.

2. Results and discussion

Recently, the synthesis of Cu(II) coordination compounds of 1,5-*bis*(2-hydroxy-1-naphthaldehyde)thiocarbohydrazone (H_4L^2) [11] with various antibacterial properties was reported. Under similar reaction conditions, a tetranuclear complex $[Cu_2(HL^1)(MeOH)_2(NO_3)]_2$ (**1**), and a polymeric structure $[Cu_2(HL^1)(HCOO)]_n \cdot H_2O$ (**2**) were obtained, based on

the Schiff base coordinating agent, 1,5-*bis*(2-hydroxy-1-naphthaldehyde)carbohydrazone) (H_4L^1), the synthesis reaction scheme is shown in Figure 2.

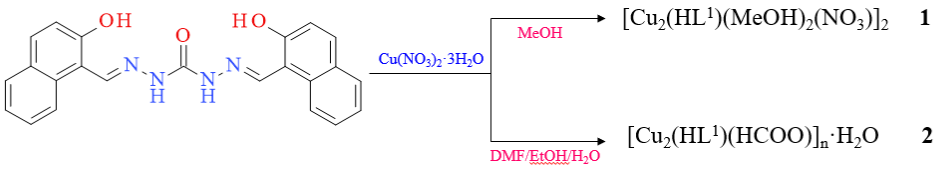

Figure 2. Scheme of the synthesis reaction of Cu(II) coordination compounds based on 1,5-*bis*(2-hydroxy-1-naphthaldehyde)carbohydrazone

Coordination compounds **1** and **2** were studied by single crystal X-ray diffraction. The crystallographic data, structure parameters for **1** and **2** are presented in Table 1.

Both syntheses start from the same precursors, namely the $Cu(NO_3)_2{\cdot}3H_2O$ salt and the 1,5-*bis*(2-hydroxy-1-naphthaldehyde)carbohydrazone (H_4L^1) ligand, but differ significantly in the nature of the solvent, crystallization time and final yield.

In the first synthesis, the copper(II) salt was dissolved directly in methanol and the solid ligand was added later. Complete dissolution of the ligand required stirring – a process accompanied by the formation of a dark green solution. Crystallization occurred slowly, over about two months, leading to the formation of crystals in the shape of rectangular prisms. This method allowed obtaining of a larger amount of product, with a mass of 0.012 g and a yield of 38%, calculated relative to the copper(II) salt.

In the second synthesis, the ligand was initially dissolved in a mixture of dimethylformamide/ethanol (1:2), and the $Cu(NO_3)_2{\cdot}3H_2O$ salt, dissolved in a minimum volume of water, was subsequently added. Unlike the first synthesis, crystallization occurred in a shorter time frame, approximately one month, but the amount of product obtained was lower, the isolated mass being 0.008 g, with a yield of 28%.

The single crystal X-ray diffraction study, revealed a discrete tetranuclear architecture in the case of compound **1** and a polymeric structure in the case of compound **2**, determined by the bridging coordination of the formate ion. In accordance with the characteristic behavior of the carbohydrazone coordinating agent described in the literature previously, it coordinates *bis*-tridentately, involving the ONN and ONO donor sets, in the trideprotonated form $(HL^1)^{3-}$. The structural representation of compound **1** is shown in Figure 3. This structure is composed of four copper(II) ions, two $(HL^1)^{3-}$ ligands, two monodentately coordinated nitrate anions and two methanol molecules.

Table 1. Crystallographic data and structure parameters for the complexes $[Cu_2(HL^1)(MeOH)_2(NO_3)]_2$ **(1)** and $[Cu_2(HL^1)(HCOO)]_n \cdot H_2O$ **(2)**

Complex	**1**	**2**
Empirical formula	$C_{50}H_{46}Cu_4N_{10}O_{16}$	$C_{24}H_{18}Cu_2N_4O_6$
M ($g \cdot mol^{-1}$)	1297.13	585.50
Temperature (K)	100(0)	293(2)
Singonia	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$Pbca$
a (Å)	9.6622(4)	17.9651(7)
b (Å)	18.1407(7)	12.0076(5)
c (Å)	28.3871(12)	21.8273(11)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	4975.7(4)	4708.54
Z	4	8
D_{calc} (mg/mm^3)	1.732	1.652
μ (mm^{-1})	1.772	1.855
GOF^c	0.984	1.071
R_1 ($I > 2\sigma(I)$)	0.0546	0.0645
wR_2	0.1015	0.2514

The Cu1 and Cu4 atoms, coordinated by the ONN set of the ligand (HL^1), present an O_3N_2 coordination sphere, while for the Cu2 and Cu3 atoms, involved in the ONO set, the O_4N type is found. The Cu1 and Cu4 metal centers adopt a distorted pyramidal-tetragonal geometry, being coordinated by one oxygen atom and two nitrogen atoms coming from the ligand (HL^1), as well as by two oxygen atoms belonging to two methanol molecules.

Similarly, the Cu2 and Cu3 atoms are found in a distorted pyramidal-tetragonal environment, completed by two oxygen atoms and one nitrogen atom of the ligand, an oxygen atom belonging to a second ligand, as well as the oxygen atom of the nitrogen ion, positioned axially. The intramolecular distance Cu2$\cdots$Cu3 has the value of 2.966 Å, being obviously smaller compared to the distances Cu1$\cdots$Cu2 and Cu3$\cdots$Cu4, which are 4.766 Å and 4.772 Å, respectively.

In the case of compound **2**, both copper atoms have a coordination number of four, and the coordination polyhedra are completed by the involvement of additional oxygen

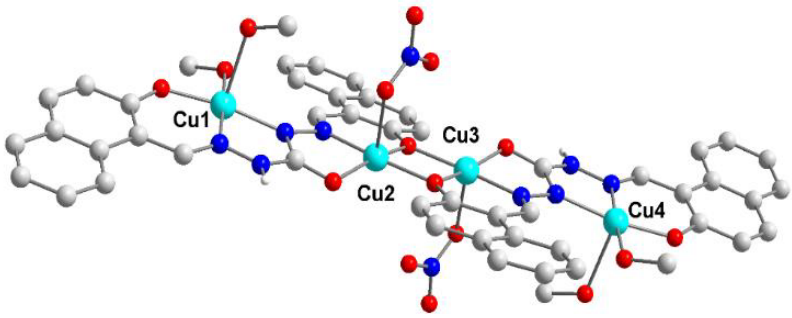

Figure 3. Structure of the compound $[Cu_4(HL^1)_2(MeOH)_4(NO_3)_2]$ (1) (hydrogen atoms of benzene rings atoms are omitted for clarity)

atoms from the formate anion (Figure 4). The $HCOO^-$ ligand functions as a μ_2-type bridging ligand, connecting two neighboring Cu(II) ions, the Cu(II)$\cdots$Cu(II) distance being 5.749 Å, which leads to the generation of a one-dimensional polymeric structure. The previously reported mononuclear Cu(II) complex with 2-hydroxi-1-naphthaldehyde semicarbazone [12], a related ligand, was also obtained from nitarte salt. The Cu(II) atom also is four-coordinated with water molecule completing the coordination environment. The appearance of the formate anion can be attributed to the hydrolysis process of dimethylformamide in the presence of water, a reaction catalyzed by Cu(II) ions [13].

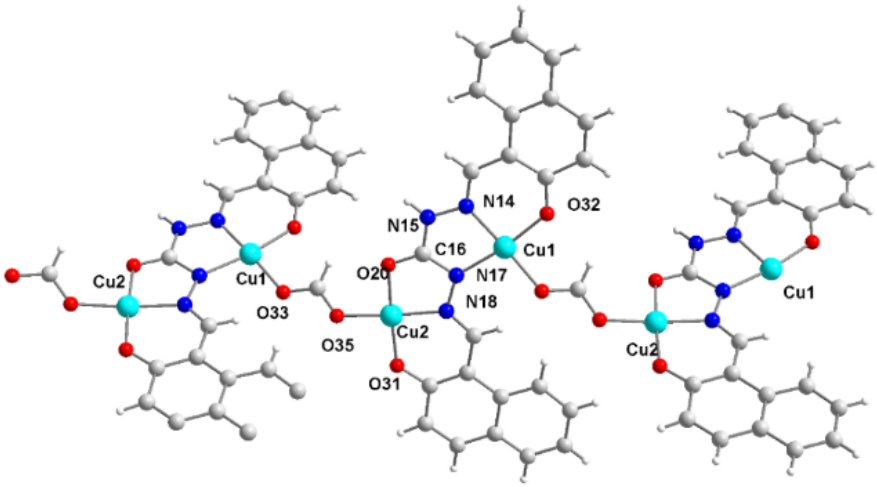

Figure 4. Fragment of the polymer structure of the compound $[Cu_2(HL^1)(HCOO)]_n \cdot H_2O$ in **(2)**

The analysis of the IR spectra [14] of compounds **1** and **2**, highlights the fact that the vibrational band ν(C=O), present in the spectrum of the free ligand at 1676 cm^{-1}, no longer appears in the spectra of the corresponding complexes. In contrast, the intense bands observed at 1600 cm^{-1} for compound **1** and 1614 cm^{-1} for compound **2** are located at values too far away to be attributed to the coordinated carbonyl group, being rather associated with the characteristic vibrations of the azomethine group involved in the coordination. These observations indicate that the ligand participates in the coordination in the enolic form.

The presence of low intensity bands in the region of approximately 3200 cm^{-1} is attributed to N–H stretching vibrations in compounds **1** and **2**, confirming the existence of an amide hydrogen atom. Also, the weak bands identified at 3053 cm^{-1} (**1**) and 3042 cm^{-1} (**2**), together with the intense bands at 736 cm^{-1} (**1**) and 747 cm^{-1} (**2**), are characteristic of aromatic ν(C–H) vibrations.

Direct comparison of the N–C and C=O bond lengths in the –N–C=O fragment between the free ligand and the coordination compounds **1** and **2** cannot be performed due to the absence of a crystallographic structure for the H_4L^1 ligand. However, analysis of the structural parameters obtained for the complexes, indicates an electronic delocalization in this structural fragment, supported by elongation of the C–O bond, and shortening of the C–N bond.

The presence of nitrate and formate ions is supported by the characteristic ν(N–O) bands of the nitrate ion, observed at 1433 cm^{-1} for compound **1**, as well as by the vibrational bands $\nu_{asym}(COO^-)$ and $\nu_{sim}(COO^-)$, identified at 1561 cm^{-1} and 1340 cm^{-1} for compound **2**, respectively.

3. Conclusion

Two coordination compounds of Cu(II) with a Schiff base ligand 1,5-*bis*(2-hydroxy-1-naphthaldehyde)carbohydrazone (**H_4L^1**), were synthesized and investigated. Crystallographic studies by single crystal X-ray diffraction, together with IR spectroscopic analysis, confirmed the structure of these compounds. In the syntheses, only the nature of the solvent was varied, while the copper(II) salt used and the initial reaction conditions (room temperature and stirring) were identical. However, the final products show distinct architectures: compound **1** is tetranuclear in nature, and compound **2** forms a polymeric structure.

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