

# COMPLEXES WITH THE PARTICIPATION OF SALTS Cu (II), Co (II), Ni (II) WITH 2- MERCAPTOTHIAZOLINE, 2- MERCAPTOBENZOTHIAZOLE AND THIAMINE HYDROCHLORIDE

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**Annotation.:** *The article describes the conditions for the synthesis of 2-mercaptothiazoline, 2-mercaptobenzothiazole and thiamine hydrochloride complexes with Cu (II), Ni (II), and Co (II) salts. If the composition of synthesized compounds was determined using elemental analysis, the proof of identity was performed by determining the liquefaction temperatures. The coordination centers of ligands, the dentate of the central atom, were determined based on IR spectra.*

*As a result of the studies, it was found that thiazoles are connected by nitrogen and sulfur atoms in the heterocycle, in promissory notes formed by intermediate metals. In this regard, it is observed upon the transition of the hydrogen atom of the S-H group to a metal atom.*

**Keyword:** *Thiamine hydrochloride, 2-mercaptobenzothiazole, 2-mercaptothiazoline, IR, salts of copper, cobalt, nickel.*

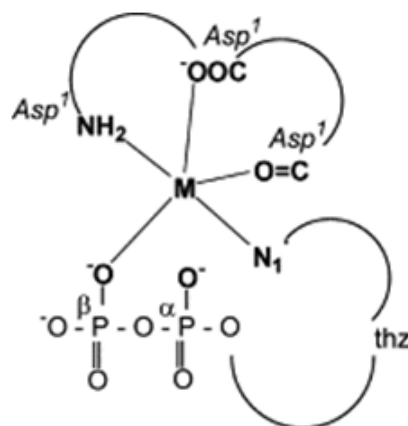
## 1.Introduction

Complexes of zinc (II) and cadmium (II) metals from thiamine pyrophosphate and 2-( $\alpha$ -hydroxyethyl) thiamine pyrophosphate were synthesized. Metal complexes are formed from thiamine pyrophosphate (TPP) as follows  $[M_2 (TPPH)_2 Cl_2] \cdot 4H_2O$  ( $M = Zn^{2+}, Cd$ ). In this case, the binding of metals to the nitrogen atom and the pyrophosphate group in the pyrimidine molecule was observed [1].

Experiments were conducted on ruthenium complex compounds with heterocyclic compounds. In this case, 2-mercaptobenzothiazole was used as a ligand from heterocyclic compounds. The research was conducted on the topic of complex compounds of rhenium with organic N, O - and S-donor ligandamide. The main feature of these complexes is the combination of a 2-mercaptobenzothiazole ligand that binds metal and boron through simple sulfur atoms [2].

B metals of group II of thiamine are mainly synthesized in  $Zn^{+2}, Cd^{+2}$  complexes in methanol solution. The effect of  $Zn^{+2}$  and  $Cd^{+2}$  metal salts on thiamine pyrophosphate was studied using NMR and IR spectroscopy. Based on the results of this analysis, it was found

that the metal binds to the first nitrogen atom and the pyrophosphate group in the pyrimidine molecule [3].



3d-metal complexes with organic ligands have high biological activity. Thiamine and thiazole are ambident ligands that form complex compounds with metals through nitrogen and sulfur atoms. Such complex compounds can be effectively used in medicine and agriculture.

Based on the foregoing, in this research work, the goal was to synthesize thiazole metal complexes (2-mercaptothiazoline (L1), 2-mercaptobenzothiazole (L2) and thiamine hydrochloride (L3)) with two valence ions of copper, cobalt, nickel and determine the structure and properties the resulting compounds.

## 2. Materials and methods

### Synthesis of thiamine hydrochloride complexes with 3d-metal.

1000 g of thiamine hydrochloride and 0.8280 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were mechanically mixed in an agate pool for 3 hours together. The mixture turned yellowish-green. The resulting powder was dissolved in water, stirring for 0.5 h to  $50^\circ\text{C}$ . As a result of recrystallization at room temperature for 24 h, yellow-green crystals were obtained.

1000 g of thiamine and 0.9300 g of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  were mixed for 3 hours at room temperature and the resulting mixture was dissolved in water, fried at  $50^\circ\text{C}$  for 0.5 hours. When it was kept at room temperature for 24 hours, the yellow crystals began to crumble.

The liquefaction temperatures of the synthesized compounds were determined (Table 1).

**Table 1. Temperatures of liquefaction of thiamine complexes with copper (II) and cobalt (II) ions**

| No | Compound                  | Liquefaction temperature |
|----|---------------------------|--------------------------|
| 1  | $\text{Cu}(\text{L}_3)_2$ | $230^\circ\text{C}$      |
| 2  | $\text{Co}(\text{L}_3)_2$ | $197^\circ\text{C}$      |
| 3  | thiamine                  | $250^\circ\text{C}$      |

### Synthesis of 2- mercaptothiazoline complexes with 3d-metals

Synthesis of complex compounds was carried out in the ratio ME:L=2:1. Initially, 1.5470 g of 2-mercaptothiazoline was dissolved in water from 0.6720 g of KOH, while the resulting potassium salt solution was gradually added to the mixing solution of the 3d metal salt using magnetic mixer, and after stirring for 0.5 h, it was filtered in a Büchner funnel using a vacuum pump [4]. The resulting precipitate was dried.

### Synthesis of coordination compounds of 2-mercaptobenzothiazole with 3d-metals

2.1710 g of 2-mercaptobenzthiazole was added to an aqueous solution containing 0.6720 g of KOH and mixed using a magnetic stirrer. An aqueous solution containing a 3d metal salt was added to the resulting potassium salt solution by mixing in large quantities (ratio 1:2).

After the mixing process takes 0.5 hours, the vacuum is filtered in a Büchner funnel using a pump [5-6]. The resulting precipitate was dried at room temperature. The liquefaction temperatures of the synthesized compounds were determined (Table 2).

**Table 2. Liquefaction temperatures of coordination compounds of 2-mercaptobenzothiazole with 3d-metals**

| No | Complex compound     | Liquefaction temperature <sup>0</sup> C |
|----|----------------------|---|
| 1  | $[(C_3H_3NS_2)_2Ni]$ | 219-220                                 |
| 2  | $[(C_3H_3NS_2)_2Co]$ | 214-215                                 |
| 4  | $[(C_7H_4NS_2)_2Co]$ | 165-166                                 |
| 5  | $[(C_7H_4NS_2)_2Cu]$ | 165-166                                 |
| 6  | $C_7H_4NS_2$         | 180                                     |
| 7  | $C_3H_3NS_2$         | 107                                     |

### 3. Results and their analysis

IR spectra were obtained to determine the structure of synthesized compounds, the coordination centers of ligands, and the coordination number of the Central ion.

The following fields were detected in the IR spectra of free ligands:

2-mercaptobenzothiazole:  $667\text{ cm}^{-1}$ (C-S),  $1282\text{ cm}^{-1}$  (C-N),  $1597\text{ cm}^{-1}$  (N = C) and  $2560\text{ cm}^{-1}$  (S-H).

2-mercaptothiazoline:  $700\text{ cm}^{-1}$ (C-S),  $1411\text{ cm}^{-1}$  and  $1230\text{ cm}^{-1}$  (C-N),  $1585\text{ cm}^{-1}$  (N = C) and  $2560\text{ cm}^{-1}$  (S-H).

As a result of the formation of a coordination compound with the metal 2-mercaptobenzothiazole, a decrease in the absorption frequency of the C-S bond was observed to be  $12-60\text{ cm}^{-1}$ . The absence of a complex absorption frequency in the  $2560\text{ cm}^{-1}$  region specific to the mercapto-group indicates that the S-H group hydrogen in the 2-mercaptobenzothiazole molecule was replaced by 3d-metal [7]. Observations of a decrease in the absorption spectrum of the N = C group by  $6-50\text{ cm}^{-1}$  indicate coordination with the nitrogen atom. An increase in the absorption spectrum of the C-N group by  $29-44\text{ cm}^{-1}$  compensates for the decrease in bond energy in the formation of this bond and indicates that this group is not involved in the complex formation (Fig. 1, Table 3). Depending on the change in the absorption spectra in the functional group, it can be said that the coordination takes place through the thio- group and the mercapto-group as well as the nitrogen atom. The result is a sandwich-type coordination compound with a coordination number of 6.

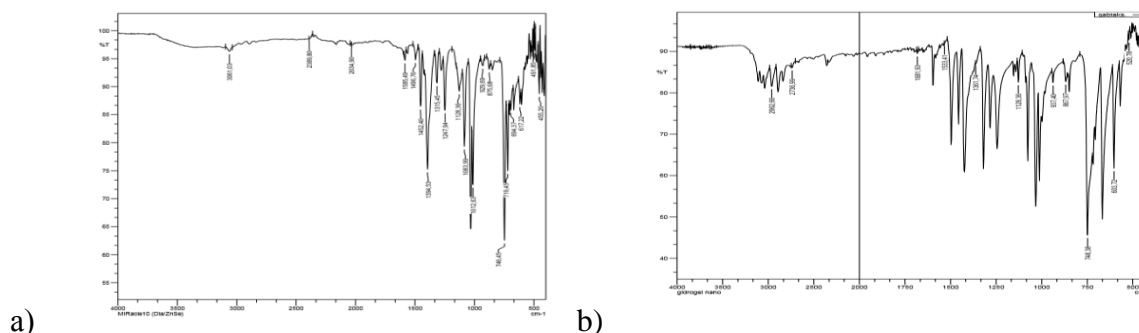


Figure 1. IR spectra of 2-mercaptobenzothiazole (a) and complex (b)  
 Table 3. IR spectra of 3d-metal complexes of 2-mercaptobenzothiazole

| Compound   | C-N  | C=N  | C-S | S-H  | S-M |
|--|------|------|-----|------|-----|
| C <sub>7</sub> H <sub>5</sub> NS <sub>2</sub>                      | 1282 | 1597 | 667 | 2560 | -   |
| [(C <sub>7</sub> H <sub>4</sub> NS <sub>2</sub> ) <sub>2</sub> Ni] | 1315 | 1585 | 617 | -    | 491 |
| [(C <sub>7</sub> H <sub>4</sub> NS <sub>2</sub> ) <sub>2</sub> Co] | 1326 | 1562 | 660 | -    | 511 |
| [(C <sub>7</sub> H <sub>4</sub> NS <sub>2</sub> ) <sub>2</sub> Cu] | 1311 | 1537 | 661 | -    | 516 |

When 2- mercaptothiazoline was coordinated with a metal ion, the following changes were observed in the IR spectra. A decrease in the absorption spectrum of the C-S bond to 10-45 cm<sup>-1</sup> is observed, as well as the absence of light absorption in the region of 2560 cm<sup>-1</sup> due to the 3d-metal exchange of hydrogen in mercapto-group. A decrease in the absorption spectrum of the N = C group to 6-64 cm<sup>-1</sup> was observed. An increase in the absorption spectrum of the C-N group to 35–83 cm<sup>-1</sup> and 5–50 cm<sup>-1</sup> was observed, which indicates that this group was not involved in the formation of the complex [8]. Based on changes in the absorption spectra of the functional groups of the ligand, it was found that coordination with the Central ion occurs through the sulfur atom in the ring and the sulfur atom in the S-H group, as well as through the nitrogen atom. Sandwich-type coordination compounds are formed in which the coordination number of the Central atom is 6.

| Compound   | C-N       | C=N  | C-S | S-H  | S-M |
|--|-----------|------|-----|------|-----|
| C <sub>3</sub> H <sub>3</sub> NS <sub>2</sub>                      | 1411 1230 | 1585 | 700 | 2560 | -   |
| [(C <sub>3</sub> H <sub>3</sub> NS <sub>2</sub> ) <sub>2</sub> Ni] | 1446 1235 | 1521 | 688 | -    | 501 |
| [(C <sub>3</sub> H <sub>3</sub> NS <sub>2</sub> ) <sub>2</sub> Co] | 1494 1257 | 1575 | 690 | -    | 445 |
| [(C <sub>3</sub> H <sub>3</sub> NS <sub>2</sub> ) <sub>2</sub> Cu] | 1489 1280 | 1579 | 655 | -    | 453 |

#### 4. Conclusion

Complex compounds of 2-mercaptotiazoline, 2-mercaptobenzthiazole and thiamine hydrochlorides with 3d metal salts were synthesized in the mechanochemical way and solution. The individuality of the obtained compounds was confirmed by the method of determining the liquefaction temperature. The elemental analysis of the synthesized complexes was carried out and gross formulas were proposed. The structure of coordination compounds and ligand coordination centers were determined by IR spectroscopy. It has been established that the sulfur and nitrogen atoms of the ligands are involved in the formation of the coordination bond.

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