

Synthesis and Characterization of Cobalt (II) And Zinc (II) Complexes with Diphenylcarbazone and Dimethylsulfoxide: Exploring Antifungal Properties

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ABSTRACT

This study investigates the synthesis of cobalt (II) and zinc (II) complexes with ligands L1 (diphenylcarbazone) and L2 (dimethylsulfoxide), specifically $[\text{CoL2}(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$, $[\text{CoL2L1}(\text{H}_2\text{O})_2]$, $[\text{ZnL2}(\text{H}_2\text{O})_2]2\text{H}_2\text{O}$ and $[\text{ZnL2L1}(\text{H}_2\text{O})_2]$. The composition of the resulting complexes is shown to depend on the ratios of the starting materials. Characterization of the complexes was conducted using elemental analysis, X-ray phase analysis, UV-VIS spectroscopy, IR spectroscopy, and thermogravimetric analysis. UV spectroscopy revealed d-d transitions in the cobalt (II) complexes at wavelengths between 460-540 nm, while the zinc (II) complex showed a peak at 238 nm. Thermogravimetric analysis indicated that the final products of thermal decomposition for all compounds are metal oxides. Additionally, the effects of these complexes on the growth of selected fungi, specifically *Candida*, were examined.

1. Introduction

In recent decades, the number of works aimed at studying the role of biogenic macro and micronutrients in biochemical processes has increased significantly. It is noted that the role of these macro and microelements is significantly increased when used together with organic ligands [1-5]. Organic ligands can play the role of metal-chelating ligands, which on this basis connect the organic ligand with its elements and effectively contribute to their habitat. allows to create drugs that provide transport [6-10]. Currently, the current scientific task is to clarify the composition and structure of compositions based on macro-, microelements and ligands at the molecular and supramolecular level, as well as their mechanism of action, and to find ways to increase the effectiveness of these compositions. The complexes of many metals with amino acids serve as a model of processes occurring in living organisms. Besides, many complexes are widely used in medicine as medicines [11-20].

The aim of this work was the synthesis of a complex of ligands(L¹-diphenylcarbazone and L²-dimethylsulphoxide) with cobalt (II) and zinc(II), the study of structures and their biological effects.

2. Materials and methods

Physical measurements

The composition and chemical structure of the synthesis products obtained are studied by physical-chemical analysis methods: X-ray phase analysis (diffractometer (Germany) D-2 Phaser firm Bruker); IR spectroscopy ("Specord M-80" brand Carl Zeiss). The spectra of the reaction solutions in the UV regions were recorded on the Evolution 60S spectrophotometer, by Thermo Scientific Spectronic (USA). Differential thermogravimetric analysis was performed on (NETZSCH STA 449F3 STA449FSA-0622-M).

Experimental part

Synthesis $[\text{ZnL}^2(\text{H}_2\text{O})_2] 2\text{H}_2\text{O}$, L¹- diphenylcarbazone

A calculated amount of the ligand (L-diphenylcarbazone) (0.01 mmol, 1.2 g) and its metal salt $\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 0.8 g) were mixed in 20 mL of ethanol (1:1) in a molar ratio. 4-5 drops of dilute NHOH were added and the mixture was refluxed continuously for 6 h. The obtained precipitate was filtered, washed with ethanol and dried in a desiccator over sulfuric acid for one week.

Synthesis $[\text{ZnL}^2\text{L}^1(\text{H}_2\text{O})_2]$ L¹- diphenylcarbazone ,L²-dimethylsulfoxide

The synthesis of a zinc (II) complex with L^1 - diphenylcarbazone , L^2 -dimethylsulfoxide was obtained by the method described above.

Synthesis $-\text{[CoL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, L^1 - diphenylcarbazone

A calculated amount of ligand(L^1 - diphenylcarbazone) (0.01 mmol, 1.2g) and the metal salt $\text{CoNO}_3 \cdot 6\text{H}_2\text{O}$ (0.01 mmol, 0.6g) were mixed in (1:1) molar ratio in 20 mL ethanol. 4–5 drops of dilute HCl were added to it and the mixture was continuously refluxed for 6 h. The resulting precipitate was filtered off, washed with ethanol and dried in a desiccator over sulfuric acid for one week.

Synthesis $-\text{[CoL}^2\text{L}^1(\text{H}_2\text{O})_2]$ L^1 - diphenylcarbazone , L^2 -dimethylsulfoxide

The synthesis of a cobalt (II) complex with L^1 - diphenylcarbazone , L^2 -dimethylsulfoxide was obtained by the method described above.

3. Results and Conclusion

Infrared Spectroscopy

The IR-spectral analysis method was used to determine the coordination nature of the complex and the ligand. The $\nu_{\text{C=O}}$ -1721.95 cm^{-1} band belonging to the carboxyl group in the ligand disappears and is not visible in both complexes. This indicates that coordination is due to ionic bonds between the ligand and the complex. $\nu_{\text{N-H}}$ -3306.48 cm^{-1} $\delta_{\text{N-H}}$ -750.73 cm^{-1} bands belonging to the amino group in the ligand are located in the complex $\nu_{\text{N-H}}$ -3320.41 cm^{-1} , $\delta_{\text{N-H}}$ -764.24 cm^{-1} , It changes to 765.35 cm^{-1} and enters coordination due to coordinative bonding. (Figure.1,2)

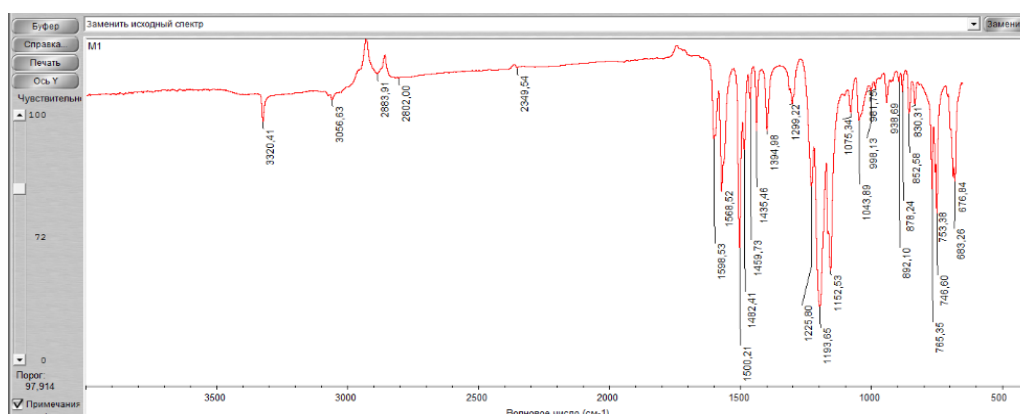


Fig.1. IR spectra of complex $-\text{[ZnL}^2 (\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, L^1 - diphenylcarbazone

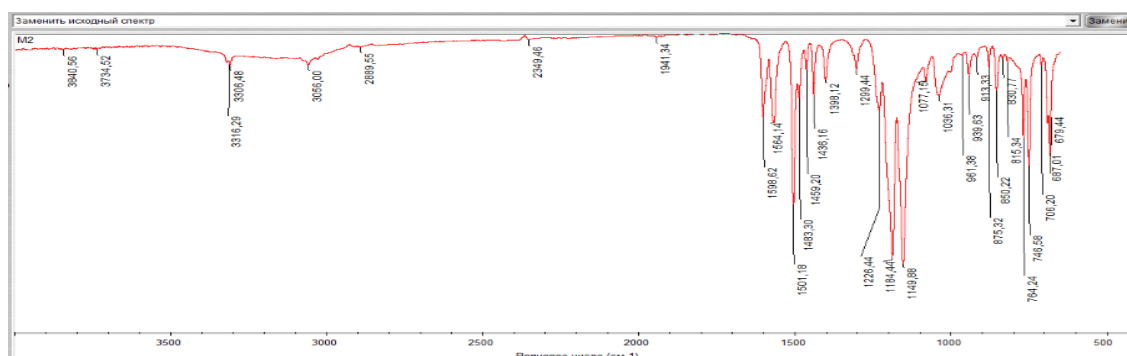


Fig.2. IR spectra of complex $[\text{ZnL}^1 \text{L}^2(\text{H}_2\text{O})_2]$, L^1 - diphenylcarbazone, L^2 -dimethylsulfoxide

UV-VIS spectroscopy

The UV-VIS spectroscopy analysis of 0.01 M of a) $[\text{CoL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, b) $[\text{CoL}^2\text{L}^1(\text{H}_2\text{O})_2]$ complex in water was made. It is clear from the specimen that the d-d passage is 490-540 nm wavelength. Figure 3

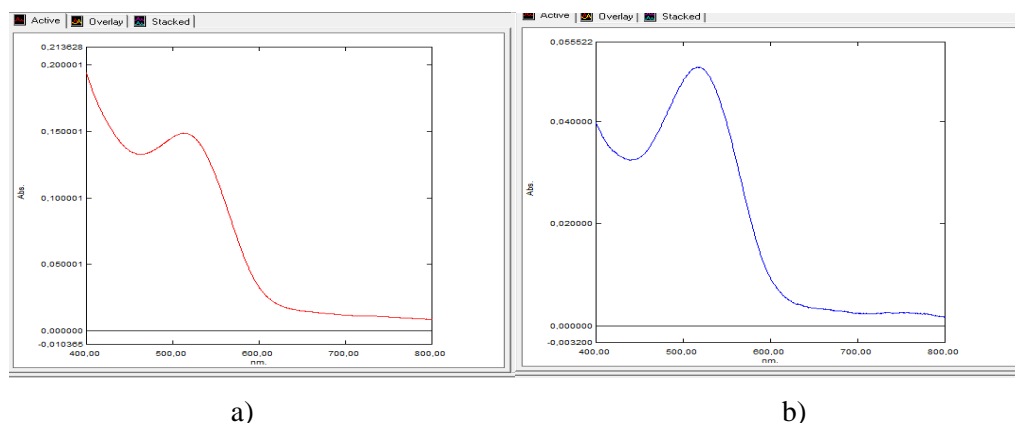


Figure 3. UV absorption spectrum of a complexes a)[CoL₂(H₂O)₂]2H₂O, b)[CoL²L¹(H₂O)₂] - diphenylcarbazone ,L²-dimethylsulfoxide

Differential Scanning Calorimetry

The thermal stability of synthesized complexes with one and different ligands was studied by means of thermogravimetric analysis method. It was determined that the complex [CoL²L¹(H₂O)₂] are stable up to 330°C. After this temperature, the decomposition of the complex occurs. In the complex with different ligands, the decomposition occurs in two stages. In stage I, the separation of two molecules of dimethylsulfoxide is likely (290°C), and in stage II, decomposition of the complex (350°C) takes place. The results of research have shown that in all cases the end product of thermal decomposition of complexes is a metal oxide. In the end, based on the results of modern physicochemical methods used in the study, it was determined that the composition and structure of the obtained complexes depend on the ratio of raw materials.

Shows the result of X-ray phase analysis of the synthesis product. The interpretation of the obtained data also confirms the formation of the [ZnL²(H₂O)₂] 2H₂O complex. Figure 4.

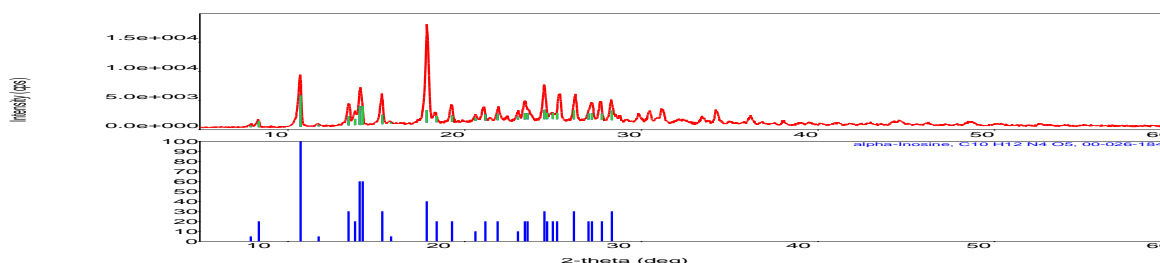


Fig.4. Diffractogram of the complex [ZnL²(H₂O)₂] 2H₂O ,L¹- diphenylcarbazone

Since the parameters of the crystalline cell differ from each other, a complex coordination Zn-diphenylcarbazone was established. Although peaks did not appear in Zn- diphenylcarbazone , almost all complexes were created through analysis.

Shows the result of X-ray phase analysis of the synthesis product. The interpretation of the obtained data also confirms the formation of the [ZnL¹L²(H₂O)₂], L¹- diphenylcarbazone, L²-dimethylsulfoxide Figure 5.

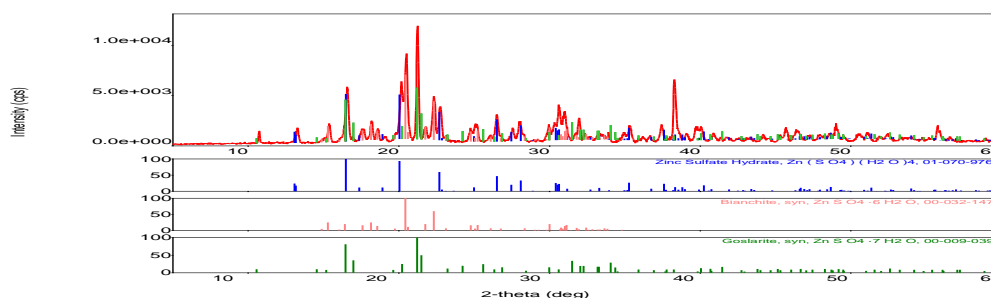


Fig.5. Diffractogram of the complex [ZnL¹L²(H₂O)₂], L¹- diphenylcarbazone, L²-dimethylsulfoxide

Elemental analysis, X-ray phase analysis, IR and UV-VIS spectral and thermometric analysis have been conducted to study the thermal stability and composition of the complexes. Our studies showed that thermal decomposition of the complexes leads to metal oxide in every case. Thus, it has been found that the composition and structure of the obtained complexes depend on the ratio of the given initial products as per the results of the analysis.

Antifungal activity of complexes

Fungi such as *Candida albicans* were used as mentioned in the studies conducted to determine the use of synthesized complex compounds such as complexes of cobalt (II) and zinc (II) with ligands (L^1 -diphenylcarbazone and L^2 -dimethylsulfoxide) $[CoL_2(H_2O)_2] \cdot 2H_2O$, $[CoL^2L^1(H_2O)_2]$ and $[ZnL_2(H_2O)_2] \cdot 2H_2O$, $[ZnL^2L^1(H_2O)_2]$ as agents with antifungal activity. From the obtained results, it was clear that the growth is either weakened or significantly inhibited depending on the fungi used as the test culture under the influence of the complex compounds tested for antifungal activity. More specifically, depending on the chemical composition of the tested complex and the biological characteristics of the test cultures, either fungostatic or fungicidal effect on the growth of fungi is observed (Table 1).

Table 1. Antifungal properties of $[M L^1 L^2]$ ($M=Ni, Mn, Zn$) complexes

Test culture	(L^1 -diphenylcarbazone and L^2 -dimethylsulfoxide)	of the lysis zone diameter mm
Candida	(Co)	16
Candida	(Zn)	15
Candida	kontrol (DMSO)	4.0

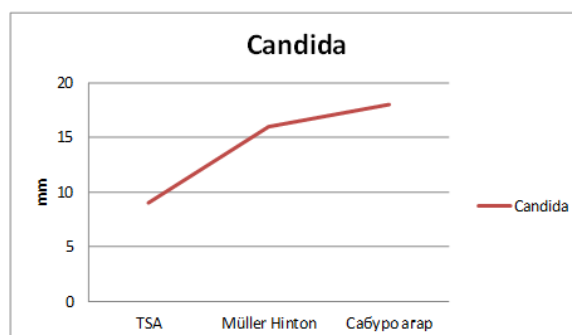


Figure 6. Graphical interpretation of the antifungal activity of the complexes

Antifungal activity of complex. Antifungal properties of *Candida* fungi were studied using complexes $[ML_2]$ ($M=Ni, Mn, Zn$). The results regarding the antifungal activity against the test culture are given in table 1. Antimicrobial activity of Ni, Mn, Zn ligand complexes was 4.2, 3.4, 3.6 times higher than the control, respectively. Maximum antimicrobial activity was observed in the Mn ligand complex. Some of the synthesized substances were also tested biologically on fungi with toxic effects (*Aspergillus* and *Penicillium*) due to their biological activity characteristics.

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