

## STUDY OF STRUCTURE OF HETEROLYGAND COMPLEX COMPOUNDS OF 3D-METAL SALTS

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### *Abstract*

Glycine and acetamide-based mixed ligand complex compounds with some intermediate metals were synthesized and a synthesis method was developed. The composition, structure and properties of the synthesized complex compounds were determined by physicochemical methods IR-spectrum, elemental analysis, X-ray phase, thermal analysis. The electronic and spatial structure of ligand molecules and complex compounds was studied by the method of quantum chemical calculation.

**Key words:** Glycine, acetamide, 3d-metal, heteroligand, element analysis, IR spectrum, thermal analysis, chelate, dehydration, deactivation, inner sphere, coordination compound.

### **Introduction**

One of the main tasks in the chemistry of coordination compounds is the study of the laws between "composition-structure-property". The results of the research are important for the targeted detection and synthesis of new chemicals with predetermined properties, composition and structure, as well as other important properties.

Amide group-containing ligands tend to form complexes with metals and have different biological activity [1, 2]. Due to the different coordination of amide groups and their role in biological processes, interest in them is high. All this allows for the targeted synthesis of metal structures with specific structure and properties. It is known from the literature that the coordination compounds of metals containing various ligands are poorly understood.

Part of the experiment. In order to study the reactivity and complex-forming properties of ligands held by the glycine and acetamide molecule, salts of some 3d-metals were obtained and several synthesis studies were carried out with them. As a result, the synthesis of heteroligand complex compounds of Cu(II), Zn(II), Ni(II) and Co(II) nitrates with glycine and acetamide was carried out.

For the synthesis of the complex compound  $[ML'L'' \cdot NO_3 \cdot H_2O]$ , an aqueous solution of glycine (Gly-L') (0.001 mol) was added to an alcoholic solution of acetamide (AA-L'') (0.001 mol) and a salt of MX(II) (0.001 mol). an aqueous solution (L':M:L:1:1:1ratio) was added. The mixture was heated in a reverse cooler for 0.5 h, then filtered while hot and removed for crystallization. After 3 days, small white crystals fell, the s were filtered and washed several times in ethanol.

The color, yield, liquefaction temperatures, element analysis results, and solubility in solvents of complex compounds were studied.

The absorption IR spectra of the compounds were studied in the 400-4000  $\text{cm}^{-1}$  field range using Avatar System 360 FT-IR and Rrotege 460 Magna-IR technology from Nicolet Instrument Corporation (USA) using a 7 mm diameter sample in the form of a KBr tablet and 4  $\text{cm}^{-1}$ .

Thermal analysis was performed on a thermodynamic instrument - Netzsch Simultaneous Analyzer STA 409 PG (Germany), K-type (Low RG Silver) thermocouple and aluminum crucible. All measurements were made at a nitrogen flow rate of 50ml/min in an inert nitrogen atmosphere. The temperature range of the analysis was 20-400°C, heating was carried out at a rate of 5K / min. The amount of sample in one measurement was 6-10 mg. The measuring system was vibrated using a standard set of substances  $\text{KNO}_3$ , In, Bi, Sn, Zn, CsCl. Simultaneously, the mass of the sample, the decomposition mass of the complexes, and the thermal stability are determined to change with increasing temperature. Thus, as a result of thermal analysis, the decomposition and liquefaction of the complex, the coordination quality of the ligand and the final products of the complex were studied.

### Results and discussion

The structure of complex compounds of 3d-metal salts synthesized with acetamide and glycine was analyzed on the basis of the results of elemental analysis, IR-spectrum, thermal analysis [3].

The study of the composition and structure of complex compounds formed by a metal atom with the same ligand in the composition of complex compounds requires several studies. The structure of complex compounds of Cu(II), Zn(II), Ni(II) and Co(II) salts synthesized with acetamide and glycine was analyzed based on the results of IR spectra [4].

Acetamide obtained as a ligand has several functional groups. In the IR spectrum of the acetamide molecule, symmetrical oscillation frequencies were observed in the 1665  $\text{cm}^{-1}$  region [5]. Asymmetric valence oscillations of the amino group were observed in the 3210  $\text{cm}^{-1}$  region. The valence oscillation of the C-N bond is located at 1552  $\text{cm}^{-1}$ . The glycine molecule has the following functional groups: C=O,  $\text{NH}_2$ , C-N. In the IR spectral analysis of glycine, symmetrical valence oscillations of the carbonyl group were observed in the area of 1611  $\text{cm}^{-1}$ , symmetrical valence oscillations of the amino group in the area of 3169  $\text{cm}^{-1}$ , valence oscillations of the C-N bond in 1522  $\text{cm}^{-1}$ , and valence oscillations of the OH group in the area of 3397  $\text{cm}^{-1}$  [6].

Analysis of the IR spectra of mixed ligand complexes showed that the valence oscillations of the C=N group in the acetamide molecule varied sharply from 1552 to 1495  $\text{cm}^{-1}$ . The asymmetric valence oscillations of the amino group in acetamide were almost unchanged from 3210  $\text{cm}^{-1}$  to 3263  $\text{cm}^{-1}$  in the complexes. The valence oscillation frequencies of the amino group in glycine ranged abruptly from 3169 to 3347  $\text{cm}^{-1}$ . Characteristic valence oscillations of the -COOH group in the glycine molecule were observed in complex compounds from 2899 to 2924  $\text{cm}^{-1}$  without abrupt changes.

### Conclusion

The coordination bond with the metal complexing agent in mixed ligand complexes confirms the theoretical possibility that the glycine molecule travels through the nitrogen atom in the amino group and the acetamide molecule through the oxygen in the carbonyl group and the nitrogen atom in the

amino group. Another proof that the formation of a complex occurs precisely through nitrogen atoms is the appearance of new absorption lines not observed in the spectrum of ligands in the 559-690  $\text{cm}^{-1}$  region in the IR spectrum of the complexes. In contrast to the spectrum of ligands, new absorption lines also appeared in the spectrum of the complexes in the 412–597  $\text{cm}^{-1}$  region. The fact that these lines belong to the absorption lines of chloride, nitrate, and sulphates, which are mainly bound to the literature [7], indicates that these acid residues are located in the inner sphere.

In the IR spectrum of a complex compound containing  $[\text{ZnL}'\text{L}''\cdot\text{Cl}\cdot\text{H}_2\text{O}]$ , in contrast to ligands, it was observed that the absorption lines of symmetrical and asymmetric valence oscillations of the C=O bond shifted to the upper field, indicating that the metal ion was involved in coordination through the oxygen atom in the acetamide molecule. The valence oscillations of the amino group in this complex were observed in the area of 3198  $\text{cm}^{-1}$ , and the deformation oscillations in the area of 1409  $\text{cm}^{-1}$ . The shift of the valence oscillation frequencies belonging to the amino group of the complex to a lower field relative to the ligand indicates that the coordination went through the nitrogen atom in the amino group. The appearance of new absorption lines in the 562  $\text{cm}^{-1}$  and 512  $\text{cm}^{-1}$  fields indicates that nO-M and N-M are related to valence oscillations, and that the metal atom is coordinated by oxygen atoms in the amino group nitrogen and carbonyl groups in the glycine and acetamide molecules [9]. In the chloride complex compounds of the IR spectrum, in contrast to the ligand, new oscillations were observed in the area of 673  $\text{cm}^{-1}$ , and it is known from the literature that this refers to the valence oscillations of n (M-Cl). Chloride is involved in the formation of acidoligand complex and is located in the inner sphere of the complex compound.

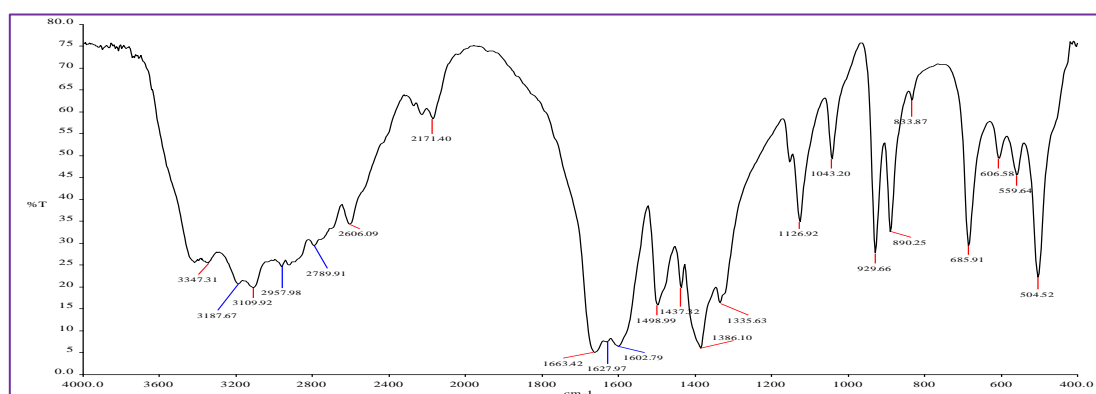
Based on the results of the IR spectrum of the complex containing  $[\text{CoL}'\text{L}''\cdot\text{NO}_3\cdot\text{H}_2\text{O}]$ , it was observed that the nitric acididolygand in the complex is located in the inner sphere. According to the literature,  $\nu_1$  symmetrical valence oscillations of the nitrate ion involved in coordination are observed in the 1042  $\text{cm}^{-1}$ ,  $\nu_2$  non-lying valence oscillations in the 827  $\text{cm}^{-1}$  and  $\nu_4$  flat deformation oscillations in the 679  $\text{cm}^{-1}$  domains. The 3 valence oscillations are divided into two fine lines in the 1395 and 1332  $\text{cm}^{-1}$  areas. This indicates that the nitrate ion is attached to the metal atom as a monodentant and that the nitrate ion is located in the inner sphere of the complex. In addition, valence oscillation frequencies corresponding to the M-O bond are observed in the 679  $\text{cm}^{-1}$  area. It can be concluded that the nitrate ion is located in the inner sphere of the complex [9].

**Table 1** Vibration frequencies of IR spectra of complex compounds ( $\text{cm}^{-1}$ )

Compound	$\nu$ (C=O)	$\nu$ (C=N)	$\nu_{\text{as}}$ (NH <sub>2</sub> )	$\nu$ (M-Cl)	$\nu$ (M-O)	$\nu$ (M-N)
L'	1611	1522	3169	-	-	-
L''	1665	-	3397	-	-	-
$[\text{ZnL}'\text{L}''\cdot\text{Cl}\cdot\text{H}_2\text{O}]$	1660	1495	3429	673	562	512
$[\text{NiL}'\text{L}''\cdot\text{Cl}\cdot\text{H}_2\text{O}]$	1661	1468	3356	751	586	412
$[\text{CuL}'\text{L}''\cdot\text{Cl}\cdot\text{H}_2\text{O}]$	1656	1608	3344	791	576	458
$[\text{CoL}'\text{L}''\cdot\text{Cl}\cdot\text{H}_2\text{O}]$	1619	1516	3429	673	612	520
$[\text{NiL}'\text{L}''\cdot\text{NO}_3\cdot\text{H}_2\text{O}]$	1663	1498	3347	-	559	504
$[\text{NiL}'\text{L}''\cdot\text{NO}_3\cdot\text{H}_2\text{O}]$	1663	1512	3355	-	690	597

[CuL'L''·NO <sub>3</sub> ·H <sub>2</sub> O]	1669	1504	3431	-	669	534
[CoL'L''·NO <sub>3</sub> ·H <sub>2</sub> O]	1662	1502	3358	-	679	578
[CuL'L''·SO <sub>4</sub> ·H <sub>2</sub> O]	1666	1608	3333	-	614	458
[CoL'L''·SO <sub>4</sub> ·H <sub>2</sub> O]	1630	1353	3433	-	668	514

Thus, in metal acetates, the metal ion with the oxygen atom of the acetate group is involved in the formation of the complex. In the complex compound, oscillations of the M-O bond were observed in the area of 606 cm<sup>-1</sup>. Furthermore, the observation of new absorption lines 506 cm<sup>-1</sup> in the short field relates to the NM valence oscillations, indicating that the metal ion is coordinated by the nitrogen atom in the amino group (Table 1).



**Figure 1. IR spectrum of a complex compound [ZnL'L''·NO<sub>3</sub>·H<sub>2</sub>O]**

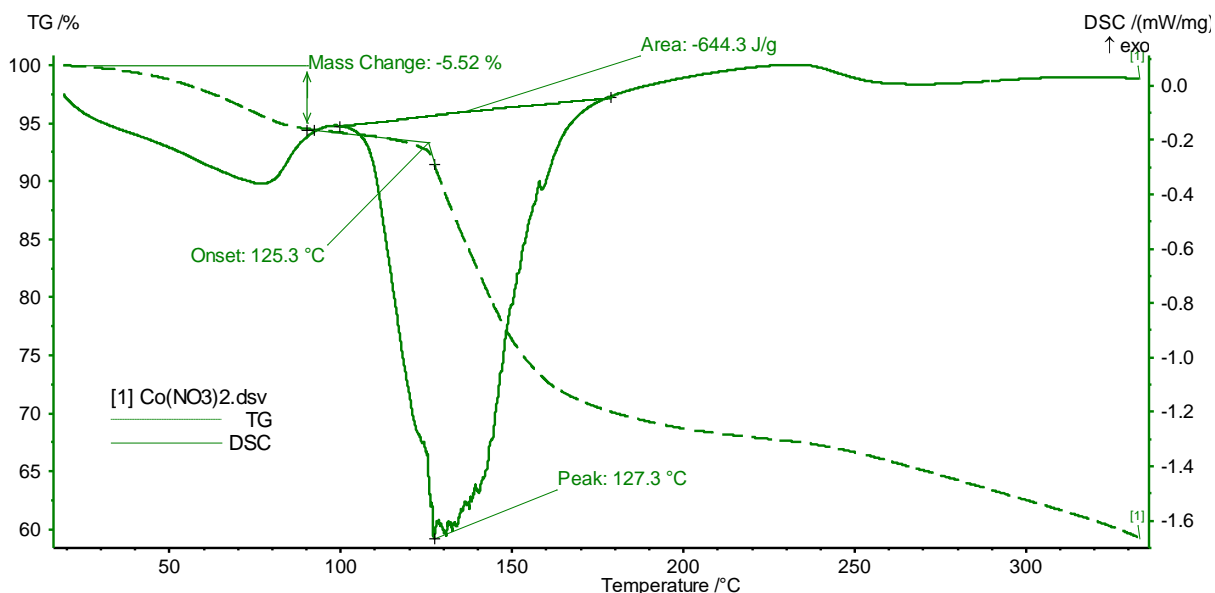
Spectral results summarized the presence of water molecules in the complex compounds of Cu(II), Zn(II), Ni(II) and Co(II) salts synthesized with acetamide and glycine.

Based on these results, the formation of a stable metallohelate complex with a metal ion without acetamidemonodentate was confirmed. It was concluded that glycine-metal-acetamide forms a Gly:M:AA complex compound in a 1: 1: 1 ratio, and this was confirmed to be the same as the data in the literature.

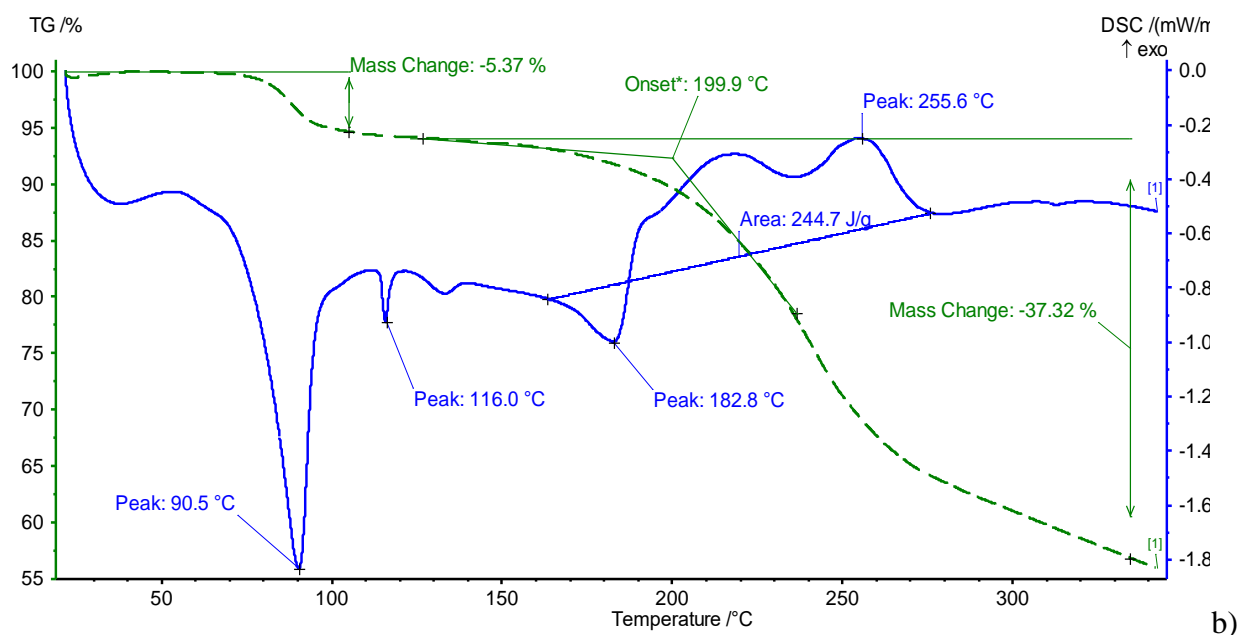
The results of derivatography were analyzed to determine the thermal stability of complex compounds and the presence of water molecules in their composition. The results of the thermal analysis show the nature of the thermal effects, the observation of the thermal decomposition of the compounds, the temperature range of the effects and its nature, as well as the mass loss in percentages in the same effect range (Table 2). The dehydration process takes place at a slightly higher temperature than dewatering. This is because working against the Van der Waals force requires less energy than a coordination bond break. The separation of water in the inner sphere takes place over a slightly wider temperature range. Therefore, it is practically impossible to determine the temperature at which water begins to separate. For the studied complexes, the course of the decomposition process was observed in the range of 90–103°C and 136–140 °C. This corresponds to water molecules in the outer and inner spheres of complex compounds [10].

**Table 2 Results of thermal analysis of synthesized mixed ligand complex compounds**

Compounds	Thermoeffect temperature °C	Thermoeffect nature exo +, endo-	Lost mass,%	Thermolysis product
1	2	3	4	5
[ZnL'L''·NO <sub>3</sub> ·H <sub>2</sub> O]	103	-	2.02	ZnO
	136	-	10.2	
	210	-	20.72	
	220	-	23.38	
	310	+	59.5	
	360	+	65.88	
	440	+	77.04	
[ZnL'L''·Cl·H <sub>2</sub> O]	90	-	2,56	ZnCl <sub>2</sub>
	140	-	11.04	
	188	-	21.38	
	260	-	34.28	
	340	+	60.42	
	520	+	72.04	
	650	+	85.98	



a)



**Figure 2. a) [CoL'L''·NO<sub>3</sub>·H<sub>2</sub>O], b) [CuL'L''·Cl·H<sub>2</sub>O] derivatogram of a complex compound.**

Mass loss in two stages was observed in the temperature range of 20-400 °C of the complex containing [CoL'L''·NO<sub>3</sub>·H<sub>2</sub>O]. In this case, the first stage corresponds to the loss of adsorbed water at 60-80 °C ( $\Delta m = -5.52\%$ ). The second stage corresponds to the decomposition of the sample at 125–170 °C ( $\Delta m = -32.32\%$ ). On the DSK curve, the first peak corresponds to the water outlet at 76.8 °C (enthalpy  $\Delta Q = -51.8$  J/g), the second peak corresponds to the liquefaction of the complex at 127.3 °C, and the sample (3.5% / min) rapidly) decomposes. The total enthalpy of decomposition is  $\Delta Q = -644.3$  J/g

The change in the complex of [CuL'L''·NO<sub>3</sub>·H<sub>2</sub>O] DTA was observed in the range of 20-400 °C, with mass loss in two stages - the first stage corresponds to the loss of 6 molecules of water at 85-95 °C ( $\Delta m = -5.37\%$ ). The second stage - ( $\Delta m = -37.32\%$ ) corresponds to the decomposition of the sample in the temperature range of 199–400 °C. The first vibration on the DSK curve corresponds to the output of a water molecule of 90.5 °C (process enthalpy  $\Delta Q = -155.2$  J/g), the second vibration corresponds to the liquefaction of the sample at 116 °C (process enthalpy  $\Delta Q = -5$  J/g), the other two vibrations the endothermic effect (182.8 °C) and the exothermic effect (255.6 °C) correspond to the decomposition of the sample. The total decomposition enthalpy is  $\Delta Q = 244.7$  J / g [11].

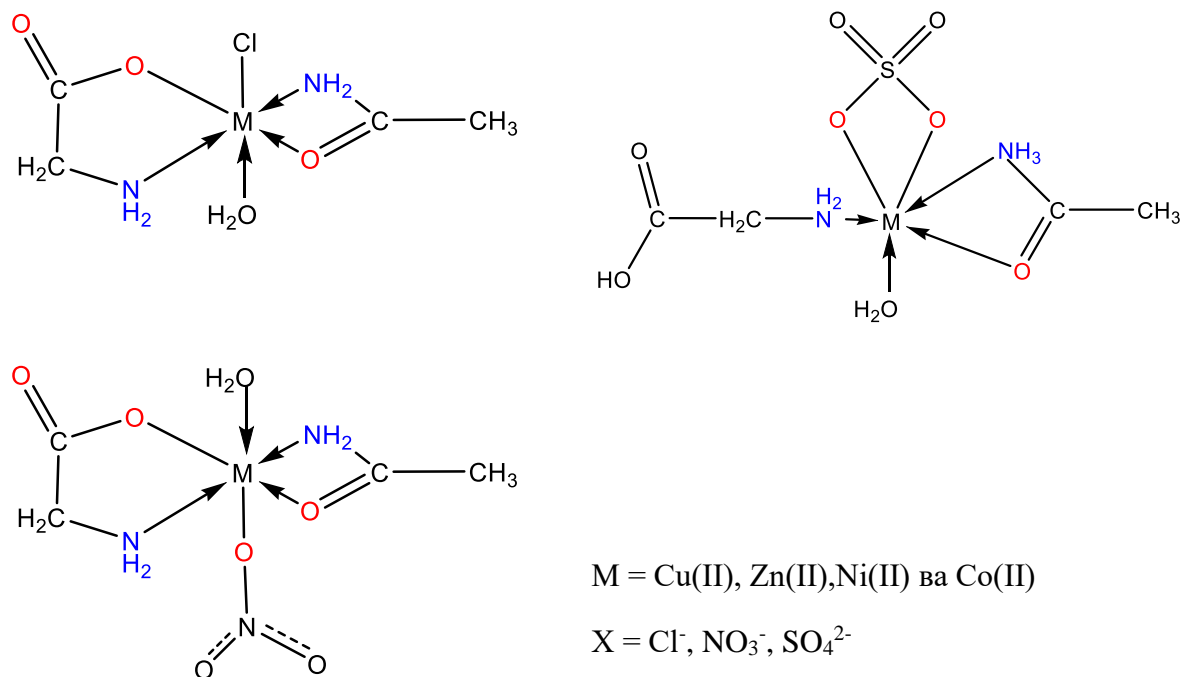
As a result of thermal analysis, endothermic and exothermic effects were studied. According to the results of thermal analysis, it was determined that the complex compounds contain crystal hydrate and crystallization water molecules. Thermolysis revealed metal oxide and chloride residues.

According to the results of IR spectroscopy, elemental, thermal and X-ray phase analysis, the synthesized mixed ligand complex compounds bidant metal ions acetamide and glycine molecules. However, it has been shown that acidoligands and the water molecule bind to the metal atom in the inner sphere to form a stable metallohelate.

In summary, the formation of new absorption lines in the glycine and acetamide molecules of ligands in the 559–690 cm<sup>-1</sup> and 412–597 cm<sup>-1</sup> regions in the IR spectra of mixed ligand complexes

indicates that there are valence oscillations corresponding to the O-M and N-M bonds. This confirms the theoretical possibility that the coordination of the ligand to the central ion in the ligand molecule by the quantum chemical method is the donor center through the nitrogen atom in the amino group of the glycine molecule and the nitrogen atom in the carbonyl group of the acetamide molecule.

The structure of complex compounds on the basis of physicochemical studies was recommended as follows:



It was concluded that the structure of complex compounds with mixed ligands is a combination of glycine - metal - acetamide in a ratio of 1: 1: 1.

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