

CHALLENGES OF HETEROCYCLICAL MIXED LIGAND UNIONS WITH d-METALS OF ACETAMID AND THIOSEMIKARBAZID

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Abstract: *Complex compounds of chloride, nitrate and acetate of some d-metals based on acetamide and thiosemicarbazide have been synthesized. The composition and structure were determined by methods of elemental analysis and thermal analysis.*

Keywords: *acetamide, thiosemicarbazide, thermal analysis, composition, structure, properties, complex compound.*

Introduction One of the main tasks in the chemistry of coordination compounds is to study the regularities of "composition-structure-property". The obtained information is essential for target detection and synthesis of new chemicals with predetermined specificity, composition and structure as well as other important properties. It is especially crucial for biologically active substances used in medicine.

It is known that thiosemicarbazide derivatives have a wide range of biological effects: tetanus, glypoglycemic, anti-inflammatory and antibacterial properties. Thiosemicarbazide has the ability to form coordination compounds with various ions of d-elements, thereby acting as a bidentant ligand. The study of compounds of mixed metal-ligand complexes and the study of their chemical structure is an actual problem of modern coordination chemistry.

From the literature, we can see that the composition, structure and properties of complex compounds of acetamide and thiosemicarbazide with metal salts are sufficiently studied. However, complex amino acid ligands with mixed thiosemicarbazide ligands have not been studied. The study of complex structure, composition, properties and regularities of mixed ligand compounds is vital for the enrichment of theoretical foundations of fundamental knowledge. Therefore, we reviewed the literature published to study the complex formation properties of acetamide and thiosemicarbazide.

The compounds of Co(II), Ni(II) and Cu(II) salts were synthesized with acetamide and thiosemicarbazide, their composition, structure and properties were studied, and the laws of complex formation were determined.

A complex compound of chlorides and nitrates Co(II), Ni(II) and Cu(II) with acetamide and thiosemicarbazide was developed as a method for the synthesis. Synthesis of 6 new complex compounds with mixed ligand based on acetamid-tyosemicarbazide was carried out. The composition, structure and properties of the synthesized complex compounds were studied using physico-chemical methods: elemental analysis, infrared spectra, X-ray. Methods and conditions for the synthesis of new compounds based on acetamide and thiosemicarbazide have been developed.

Experimental part: The complex compounds of acetamide and thiosemicarbazide with chlorides and nitrates Co(II), Ni(II) and Cu(II) were synthesized as follows. Accordingly, 0.59 g of acetamide (AA), (0.01 mole), 0.91 g of thiosemicarbazide (TSK) and nickel chloride (II) were mixed in 1.65 g (0.01 mole). The mixture was dark green in the mixture. The mixture was dissolved in 50 ml of ethanol and 0.30 min in the reverse refrigerator. The mixture was boiled, then filtered and poured for crystallization. After three days, the small crystals were removed, filtered and washed several times in ethanol. Output = 65%. $T_{pl}=242$ oC.

Thus, a combination of ligand complex with acetamide and thiosemicarbazide chloride and nitrate salts of Co(II) and Cu(II) was synthesized.

The content of carbon, sulfur and metals in the complex compounds was determined by atomic absorption spectrophotometer "Perkin-Elmer-432" using elemental analysis.

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

A powder diffractometer on XRD-6100 (Shimadzu, Japan) was used to identify complex compounds. $\text{CuK}\alpha$ was performed under the action of radiation (β -filter, Ni, $\lambda = 1.54178\text{ \AA}$, current and voltage 30 mA, 30 kV in the X-ray tube). The constant speed of the detector was 4 degrees/min, step 0.02° ($\omega/2\theta$), and the scanning angle was adjustable from 4° to 80° . Samples were analyzed in a rotating chamber at a rotation speed of 30 ml/min.

Results Analysis: The structure of complex compounds synthesized with acetamide and thiosemicarbazide chlorides and nitrates Co(II), Ni(II) and Cu(II) was analyzed based on IR spectra.

Table 1 and Figure 1 show the results of IR spectra of complex ligands synthesized from a mixed ligand.

The vibration spectra of thiosemicarbazide and its complexes with metals were studied by several authors [1-2]. However, due to their complexity, interpretation of these spectra presents some difficulties. According to the analysis of literature data, thiosemicarbazide is a bentate in complex compounds with different metals with sulfur atom and hydrazine nitrogen fragment at the central atom of the metal complex [3].

Anti-symmetric and symmetric valence oscillations of N-H thioamide group in the molecule of thiosemicarbazide were shown in the region $3366-3177\text{ cm}^{-1}$, with valence oscillations of analogues of the hydrazine fragment in the region 3263 cm^{-1} . High-frequency shifts of valence oscillations of N-H bonds of thioamide group in many spectra of compounds do not participate in the protonation of the nitrogen atom of this group. In the spectra of all compounds of the N-H bond of the hydrated fragment are shifted to the low-frequency part of the valence oscillation field [4].

IR spectra of free thiosemicarbazide at 1531, 1483 and 1316 cm^{-1} are explained by valence oscillations of C-N bonds [5]. In the spectrum of compounds corresponding to these vibrations, spheres appear in other circles: high-frequency components move into low-frequency circles, while low-frequency components, on the contrary, move into high-frequency circles. This indicates that the value of C-N bonds is not equal in the compounds.

Valent oscillations of C=S thioamide bonds are a severe problem in infrared spectra. Typically, the oscillations of this link are mixed with oscillations of groups NH_2 and CN. Strong librational effects can be observed in compounds associated with two nitrogen atoms of the thiocarbonyl group, and oscillations of C = S bonds are not localized. Thus, there are four oscillations in total. However, the IR spectrum of thiosemicarbazide is a strong field at 800 cm^{-1} .

The ease of embedding this field into the IR spectrum can be explained by the valence oscillations C = S bonds in the IR thiosemicarbazide spectrum in the 800 cm⁻¹ region [6].

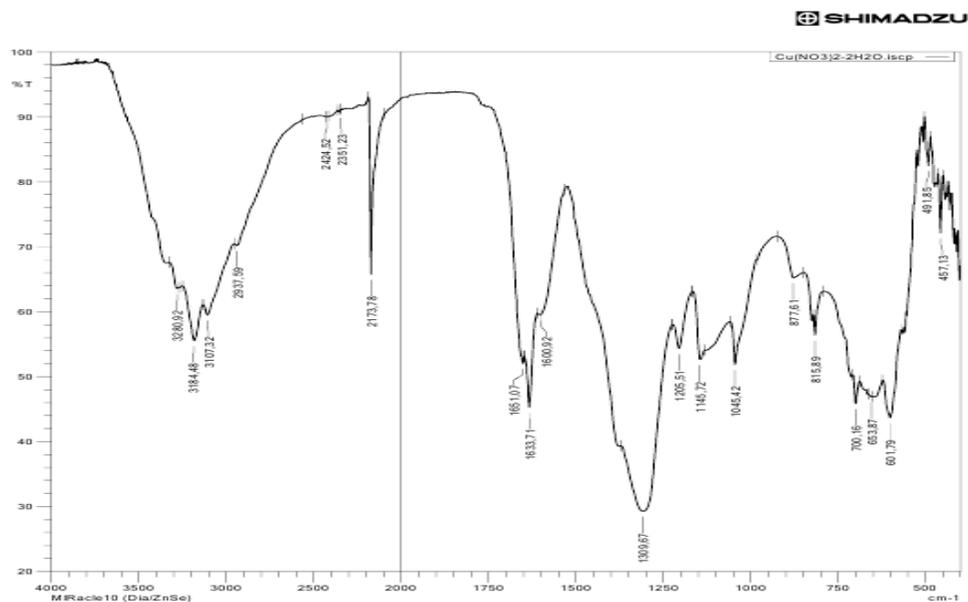
Comparison of IR absorption spectra of thiosemicarbazide and its complex compounds is observed in the spectrum of complexes, when the NH bond with a band of valence oscillations is associated with uncoordinated ligands. It was shown that such a relationship $\nu(\text{NH})$ in the low-frequency region is a link between the nitrogen atom of metal-thiosemicarbazide in the amino group. Lines in the region 1531-1290 cm⁻¹ are characterized by thiosemicarbazide oscillation $\nu(\text{CN})$ with spectrum shift to high frequency 8-40 cm⁻¹. The appearance of intensive lines in the region 813-889 cm⁻¹ was of particular interest. Literature shows that these lines are specific to the valence oscillations of CS. These lines are shifted to the region 13-89 cm⁻¹ in complex, which means that thiosemicarbazide is associated with metal sulfur [7]. Thus, the frequency reduction $\nu(\text{NH})$, $\nu(\text{C}=\text{C})$ and the frequency increase $\nu(\text{CN})$ indicate that the thiosemicarbazide sulfur atom and the hydrazine residue are associated with the formation of a metal cycle of five elements.

Significant changes were observed in infrared spectra of complex compounds containing [Ni(NO₃)₂·TSC·AA]. If in the infrared thiosemicarbazide spectra there are significant valence oscillations of C=S bonds in a strong field of 800 cm⁻¹, which is significant in the infrared spectrum, there is a complex compound, shifted up to 813 cm⁻¹. This indicates that the sulfur atom was coordinated. In addition, new absorption curves of 501 cm⁻¹ were shown in the shorter region, which corresponds to the valence oscillations coordinated by the nitrogen atom in the amino group [7]. The lines in the region $\nu(\text{NH})$ 1531 cm⁻¹ of thiosemicarbazide molecules were shifted to the high-frequency region 42 cm⁻¹ in the complex interaction spectrum.

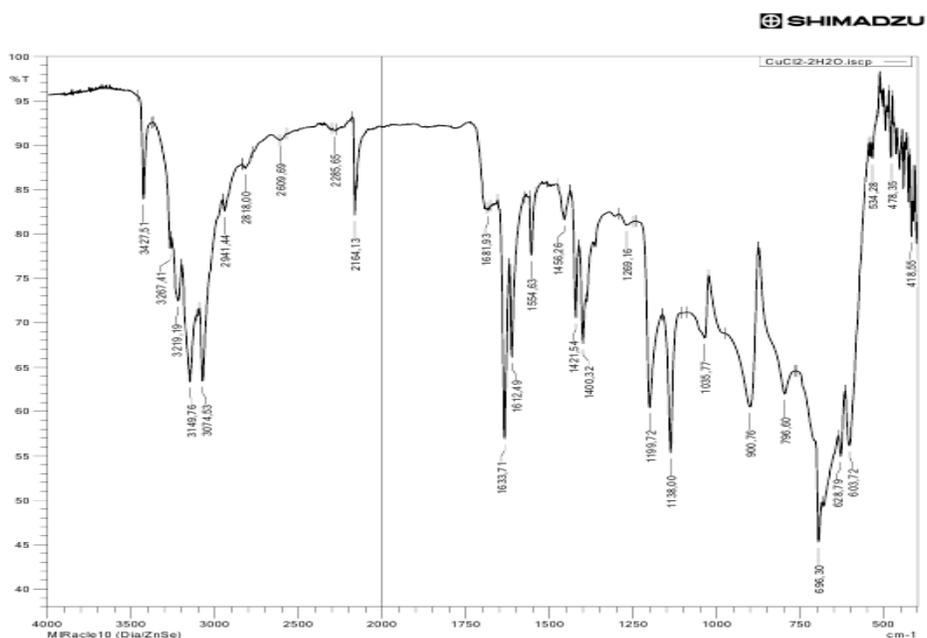
Table 1: Basic frequencies of vibration of infrared spectra of complex compounds based on acetamide and thiosemicarbazide (cm⁻¹)

Connections	ν_{as} (CO ⁻)	ν (-N-N-)	ν (NH)	ν (CN)	ν (M-S)	ν (M-O)	ν (M-N)
1	2	4	5	6	7	8	9
Thiosemicarbazide (TSC)	-	1000	3263	1531	-	-	-
Acetamide (AA)	1665	-	3210	-	-	-	-
[Co(NO ₃) ₂ ·TSC·AA]	1643	1047	3182	1643	819	597	497
[CoCl ₂ ·TSC·AA]·	1645	1082	3057	1645	866	601	468
[Ni(NO ₃) ₂ ·TSC·AA]	1633	1041	3149	1647	889	599	468
[NiCl ₂ ·TSC·AA]·	1647	1047	3147	1633	813	594	491
[Cu(NO ₃) ₂ ·TSC·AA]	1633	1045	3184	1633	815	601	457
[CuCl ₂ ·TSC·AA]·	1633	1035	3219	1633	796	534	478

In contrast to [CuCl₂·TSC·AA] connections, it was shown that the intricate connection moves upwards with symmetric and asymmetric valence oscillations of C=O connection. Thus, the data showing that the oxygen atoms of an acetamide molecule are connected with the metal atom by means of a coordinate bond are in line with the literature. In infrared spectra of complex chloride compounds in the region of 796 cm⁻¹ new oscillations were observed in contrast to ligand, and from the literature it is well known that the valence oscillations M-Cl [8]. Chloride acidoligand participates in the complex formation and occupies the inner sphere of the compound.



a)



b)

Fig.1 a) IR spectra $[\text{Ni}(\text{NO}_3)_2 \cdot \text{TSC} \cdot \text{AA}]$, b) $[\text{NiCl}_2 \cdot \text{TSC} \cdot \text{AA}]$.

Based on IR spectra of a complex $[\text{Co}(\text{NO}_3)_2 \cdot \text{TSC} \cdot \text{AA}]$, it was found out that nitrogen oxidoligand in the complex compound is in the inner sphere. According to the literature data, symmetric valence oscillations of nitrate ion 1043 cm^{-1} involved in the coordination are in the region of 2827 cm^{-1} flat deformation oscillations 1043 cm^{-1} and 262 in the region of 726 cm^{-1} .

Valent oscillations 3 are divided into two thin lines in the regions 1393 cm^{-1} and 1336 cm^{-1} . This indicates that the nitrate ion has a monodent bond with the metal atom and that the nitrate ion is in the inner sphere of the complex. Also, there are valence oscillations of the M-O

bond in the 597 cm^{-1} region. It can be concluded that the nitrate ion is in the inner sphere of the complex connection.

Based on quantum-chemical calculations, the oxygen atom in the acetamide molecule and the nitrogen atom, the sulfur atom and the amino group in the thiosemicarbazide molecule should participate in the coordination, indeed, in the reaction of these atoms in the infrared spectrum of the complexes $M\leftarrow S$, $M\leftarrow O$ and $M\leftarrow N$. The valence oscillations in the complexes were confirmed by the frequencies $697\text{-}799$, $545\text{-}560$ and $455\text{-}497\text{ cm}^{-1}$ [8]. Based on these results, it was confirmed that acetamide and thiosemicarbazide form a stable metal oxide complex with metal ion without bidentate.

The individuality of the synthesized complex compounds, their specific crystalline lattice, the distance between the planes and the sensitivity of the initial and synthesized compounds were studied by X-ray structure analysis. X-ray diagrams of complex compounds are shown in Figures 2, and results of diffractogram calculation are shown in Table 2.

Table 2 : Intensities and planes of complex compounds $[\text{NiCl}_2\cdot\text{TSC}\cdot\text{AA}]$

No	Angle; θ	Distance between the planes; d	Intensity I (%)	The intensity I/I ₀
1	5.38	16.40	9	3
2	6.13	14.39	11	4
3	8.20	10.76	8	3
4	9.35	9.44	19	7
5	11.08	7.97	9	3
6	12.25	7.06	184	67
7	13.09	6.75	66	24
8	14.90	5.94	52	19
9	16.27	5.44	73	27
10	20.02	4.43	36	13
11	28.71	3.101	15	5
12	30.12	2.964	22	8
13	38.70	2.324	19	7
14	42.14	2.142	9	0
15	44.38	2.039	13	5
16	48.893	1.861	9	3
17	50.74	1.797	11	4
18	55.33	1.658	10	4
19	59.58	1.550	19	7
20	60.71	1.524	13	5
21	70.04	1.342	13	5
22	76.18	1.248	8	3
23	77.02	1.237	177	65
24	77.40	1.231	21	8

File Name : Standard\UzMU-Kompleks-NiCl2
 Sample Name : Comment :
 Date & Time : 05-31-19 14:26:35
 Condition
 X-ray Tube : Cu(1.54060 Å) Voltage : 30.0 kV Current : 30.0 mA
 Scan Range : 4.0000 <-> 80.0000 deg Step Size : 0.0200 deg
 Count Time : 0.30 sec Slit DS : 1.00 deg SS : 1.00 deg RS : 0.30 mm

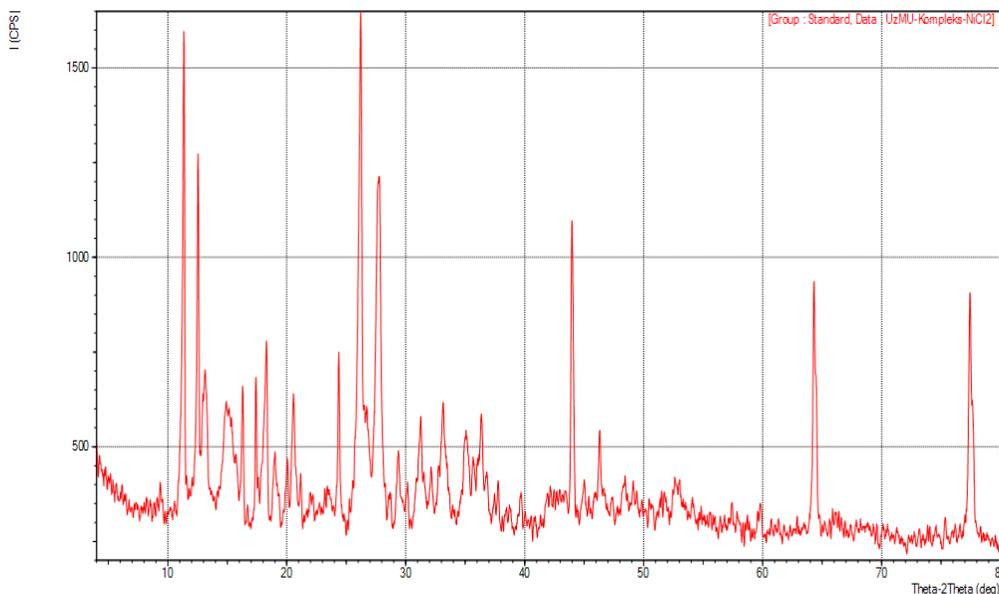


Fig 2. Complex compound X-ray $[\text{NiCl}_2 \cdot \text{TSC} \cdot \text{AA}]$.

Comparison of X-ray diffractograms of complex compounds with mixed ligands has shown that they differ. The results of the analysis obtained from the diffractogram calculation show that the synthesized complex compounds have individual crystalline lattices. X-rays have shown that the complexes are isostructured with each other [9 - 10].

Thermal analysis Thermodynamic instrument - Netzsch Simult STA 409 PG (Germany), K-type (Low RG Silver), thermal steam and aluminum crucible. All measurements were performed in an atmosphere of inert nitrogen at a speed of 50 ml/min. The temperature range of the analysis was 20-400 °C and heating was carried out at a rate of 5 K/min. The sample size in one measurement was 6-10 mg. The standard set of measurements was vibrated using KNO_3 , In, Bi, Sn, Zn, CsCl. At the same time, it was found that the sample mass, the mass decomposition of the complexes and the thermal stability of the complexes change with increasing temperature. Thus, as a result of thermal analysis, decomposition and elimination of the complex, quality and coordination of the ligand coordination, the end products of the complex [11-12].

The derivatogram obtained from $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{TSC} \cdot \text{AA}]$ is shown in Figure 1, which consists of 4 curves. The differential thermogravimetric analysis (DTGA) curve analysis (curve 2) shows that the DTGA curve mainly takes place in the range of 2 intensively degradable temperatures. The 1-degradation interval corresponds to temperatures 63-237 °C, while the 2-degradation interval corresponds to temperatures 240-680 °C [3]. The analysis shows that during the 1st decay interval the decay value is 61.95% [13-14].

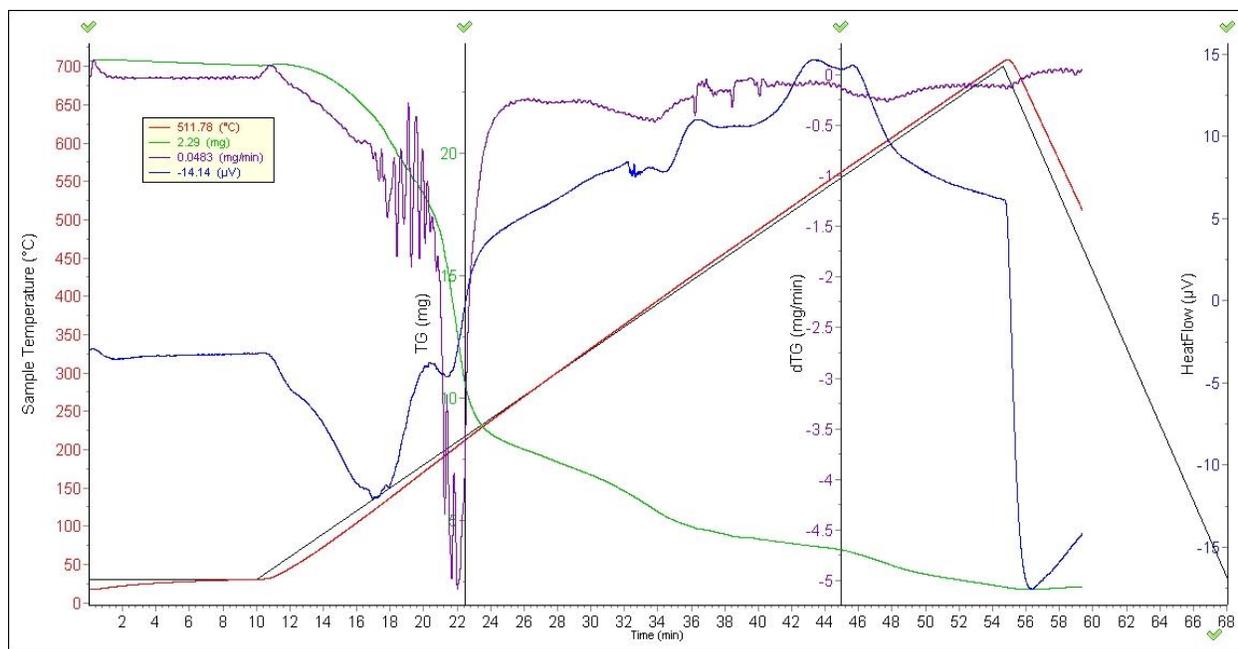


Fig. 3. Derivatogram $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{TSC} \cdot \text{AA}]$.

1 temperature curve; 2 thermogravimetric analysis curve (TGA); 3-differential thermogravimetric analysis curve (DTGA); 4-DSC curve.

Detailed analysis of the differential thermogravimetric analysis curve and the DSC curve is given in the following table.

Derivatogram $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{TSC} \cdot \text{AA}]$, subjected to mass scattering at 100-250 $^{\circ}\text{C}$ for 1 week, when 62% of the main mass, that is 15 mg, is lost. 2-degradation occurs at 260-680 $^{\circ}\text{C}$, where 18% of the mass, i.e. 5.6 mg, is lost. No change is observed after 690 $^{\circ}\text{C}$.

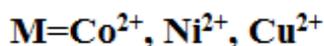
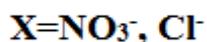
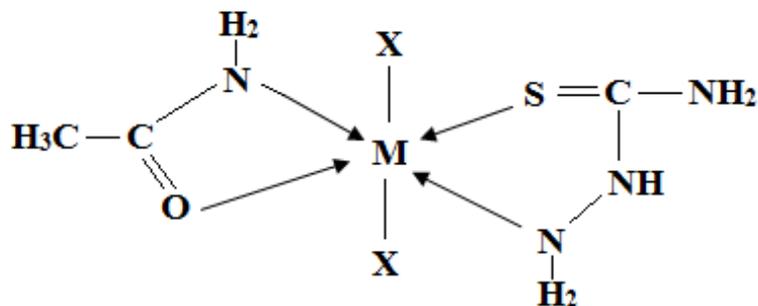
This derivatographic study shows that the loss of main mass occurs at a fragmentation of 100-50 $^{\circ}\text{C}$, equal to 1, where 62% of the main mass, i.e. 15 mg, is lost. 2-degradation occurs at 260-680 $^{\circ}\text{C}$, when 18% of mass, i.e. 5.6 mg of mass, is lost [15].

Table 3.

DTGA and DSK curve analysis results $[\text{Co}(\text{CH}_3\text{COO})_2 \cdot \text{TSC} \cdot \text{AA}]$

No	Temperature, $^{\circ}\text{C}$	Lossmass, mg(22)	Lossmass, %	Amount of energy consumption ($\mu\text{V} \cdot \text{s}/\text{mg}$)
1	50	21,603	1,802	2,45
2	100	20,309	7.68	1,91
3	200	17,609	19.92	3,09
4	300	8,36	62.0	4,08
5	400	7,896	64,10	5,93
6	500	6,696	69.68	6,07
7	600	5,996	72.74	3,70
8	700	4,42	79.9	3,32

On the basis of physical and chemical studies it was concluded that the structure of the complex compound is acetamide-metal-thiosemicarbazide in the ratio 1: 1: 1, and the structure of the synthesized complex compounds looks as follows:



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