

STUDY OF MIXED AMIDE COORDINATION COMPOUNDS OF COPPER (II) NICOTINATE

Abstract. Complexes of copper(II) nicotinate with acid amides were synthesized in order to vary the composition and the individual properties of the compounds obtained through coordination of the nicotinate group to acetamide, carbamide, thiocarbamide and nicotinamide. The coordination of the organic ligands, the environment of the central ion and the thermal behaviour of the synthesized compounds were elucidated by vibrational spectroscopy and thermal analysis. The relative intensities and the spatial structures of copper(II) nicotinate and the synthesized complexes showed that the new coordination compounds differ from each other and the original components, as they have unique crystal lattices. X-ray phase analysis was used to obtain diffraction patterns of free molecules of ligands, copper nicotinate, and synthesized coordination compounds. The thermal behaviour of the synthesized compounds was investigated and the thermolysis products were identified. The stepwise decomposition of the synthesized compounds was found with several endo - and exo effects correspond to the decomposition of the constituent parts of the complexes. Based on the intensity of the electronic spectrum of diffuse reflection and the values of the bands, the six-coordination environment of Cu (II) the synthesized complexes was proven.

Keywords: coordination compounds, synthesis, IR spectroscopy, X-ray analysis, thermal behaviour.

Introduction

Worldwide, large amounts of mixed-ligand complex compounds of transition metals are synthesized. Among them, Cu(II)-containing complexes play a key role in pharmaceuticals, supramolecular materials, crystal engineering and other industries [1, 2, 3]. In addition to Cu(II)-containing hydrogels in the form of carboxymethyl groups, chitosan (CMCh) nanocomposites have been revealed as good antibacterial candidates against *Staphylococcus aureus* and *Escherichia coli* [4]. However, Cu, along with other 3d metals, can form centres with extended materials and biological systems during the molecular recognition process. In other words, Cu complexes with N,O-donor centres in a ligand environment occupy a special place in modern coordination chemistry, especially in agricultural chemistry. In this case, biologically active substances with donor atoms, such as mixed amid carboxylate complexes of metals, can better stimulate plant growth. To accelerate and increase the productivity of the main crops, much attention is given to stimulants, particularly to the groups of metal complexes.

New species of metal complexes are formed over time due to the specific effect of their environment on the stereochemistry of polyhedra. They are good models for studying competitive coordination in the chemistry of complex compounds.

In this regard, it is important and urgent to search for ways to perform directed synthesis of polydentate ligands and metal complexes of a certain composition and structure that contain such ligands for solving theoretical and practical tasks, such as creating new materials with

predetermined properties. The synthesis of new, effective complex compounds for increasing crop yields and their widespread use in agriculture remains an urgent issue.

Therefore, coordination compounds of **Cu(II)nicotinate** with other **amide** ligands have academic and engineering importance. Many studies have been devoted to isonicotinic acid adducts $[\text{Ru}(\text{g}3:\text{g}3\text{-C}_{10}\text{H}_{16})\text{Cl}_2(\text{p-NC}_5\text{H}_4\text{CO}_2\text{H})]$ 1 and nicotinate and isonicotinate bridged binuclear complexes $[\text{Ru}_2(\text{g}3:\text{g}3\text{-C}_{10}\text{H}_{16})_2\text{Cl}_3(1\text{-jN},\text{O},\text{O}0\text{-NC}_5\text{H}_4\text{CO}_2)]$ [5].

Additionally, solid-state $\text{M}(\text{L})_2 \cdot n\text{H}_2\text{O}$ compounds, where M stands for bivalent transition metals (Mn, Fe, Co, Ni, Cu and Zn), L is nicotinate and $n = 0\text{--}4.5$, have been synthesized [1].
~~cross check—reference~~

However, metal complexes obtained in previous studies [1 and 5] were prepared using organic or inorganic solvents that cause pollution.

In the 1990s, the idea of green chemistry emerged against the background of soil and water pollution, and the disappearance of useful flora and fauna as a result of human activities was very relevant. Based on the green chemistry principle of rejection of solvents during chemical synthesis, we chose mechanochemical synthesis to obtain coordination compounds. This method allows us to completely abandon the use of solvents, has a high product yield, eliminates the formation of reaction **by-products**, and does not require purification of the final product. These factors, in turn, lead to significant cost savings compared to other methods [6].

The aim of the present work is to study of mixed amide coordination compounds of copper (II) nicotinate with amides such as acetamide (AA), carbamide (C), thiocarbamide (TC) and nicotinamide (NAM) based on mechanochemical methods.

Experimental

The synthesis of coordination compounds of metal nicotinate with amides was carried out by the mechanochemical (solid-phase) method. The mechanochemical interaction of the initial components was carried out by intensive grinding of a mixture of copper nicotinate: **amide1: amide2**
~~clarify which amide~~ in a molar ratio of 1: 2: 2 and for 30 minutes at room temperature in a ball mill with a working fluid (mill volume 100 ml). Working body weight 67 grams.

The duration of one stirring session was 30 sec. Three such mixes make up one cycle. After each cycle, the device rests for 2-3 seconds. Samples were taken periodically after each cycle for X-ray phase and derivatographic analysis. This operation was repeated 18-20 times. After 17-19 repetitions, no changes were observed in the diffractograms and derivatograms of the samples, which shows the individuality of the obtained compounds.

For the synthesis of coordination compounds, $\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot \text{HO}$ was chosen as a complex former, and CH_3CONH_2 (AA), $\text{CO}(\text{NH}_2)_2$ (C), $\text{CS}(\text{NH}_2)_2$ (TC), and

NC₄H₅CONH₂(NAM) as ligands. Synthesis of Cu(NC₅H₄COO)₂ · 2CO(NH₂)₂ · 2NC₅H₄CONH₂ compound in a ball mill 0.4755 g Cu(NC₅H₄COO)₂ · H₂O with 0.1802 g urea and 0.3664 g nicotinamide for 30 min at room temperature.

The coordination compound Cu(NC₅H₄COO)₂ · 2CH₃CONH₂ · 2CS(NH₂)₂ was synthesized using 0.4755 g of Cu(NC₅H₄COO)₂ · H₂O, 0.1772 g of acetamide, and 0.2284 g of thiocarbamide. A mixture of copper (II) nicotinate with amides was ground in a ball mill at room temperature for 30 min.

A compound with the composition Cu(NC₅H₄COO)₂ · 2CS(NH₂)₂ · 2NC₅H₄CONH₂ was synthesized using 0.4755 g of Cu(NC₅H₄COO)₂ · H₂O, 0.2284 g of thiocarbamide, and 0.3664 g of nicotinamide. A mixture of copper (II) nicotinate with amides was ground for 30 minutes in a ball mill at room temperature.

The amount of metals in the synthesized compounds was determined on a novAA 300 atomic absorption spectrophotometer from Analytik Jena AG (Germany) [7]. Nitrogen, hydrogen, carbon, and sulfur were determined on an EA-1108 elemental analyzer from Carlo Erba [8]. To establish the individuality of the synthesized complex compounds, X-ray diffraction patterns were taken on a Panalytical Empyrean X-ray diffractometer equipped with a Cu tube (Kα₁ = 1.5406 Å) [9]. To calculate the interplanar distances, tables [10, 11] were used, and the relative intensity of I / I₁ line was determined as a percentage of the most pronounced reflection at the maximum.

IR absorption spectra were recorded in the range of 400-4000 cm⁻¹ on a Perkin Elmer System-2000 IR Fourier spectrometer using the method of pressing samples with KBr.

Electronic diffuse reflectance spectra (EDRS) were recorded on a SHIMADZU-2400.

The diffuse reflectance spectrum was constructed by dividing the measured reflectance spectrum by the spectrum of the halogen lamp obtained by direct illumination of the monochromator slit. Powder samples were measured by pressing them into tablets with a diameter of 1.4 cm and a thickness of 0.2 cm.

Thermal analysis was carried out on a Paulik-Paulik-Erdey system derivatograph [12] at a speed of 10 deg / min and a sample of 0.1 g at the sensitivity of the T-900, TG-100, DTA-1/10, DTG-1/10 galvanometers. The recording was carried out under atmospheric conditions with constant removal of the gaseous medium using a water-jet pump. A platinum crucible 7 mm in diameter without a lid served as a holder. Al₂O₃ was used as a reference.

Table 1

Elemental analysis results for mixed-ligand coordination compounds of copper (II) nicotinate

Compound	Cu, %	S, %	N, %	C, %	H, %
----------	-------	------	------	------	------

	found	count	found	count	found	count	found	count	found	count
$\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CS}(\text{NH}_2)_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2$	9.30	9.03	9.12	9.10	20.01	19.90	44.80	44.35	4.00	3.98
$\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2$	9.60	9.46	-	-	20.45	20.85	46.37	46.46	4.12	4.17
$\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CH}_3\text{CONH}_2 \cdot 2\text{CS}(\text{NH}_2)_2$	11.03	11.00	11.14	11.08	19.33	19.39	37.63	37.40	4.35	4.50

The physical properties of the synthesized compounds were established by conventional techniques and are shown in Table 2.

Table 2

Product yields and some physical properties of the synthesized mixed-ligand coordination compounds of copper (II) nicotinate

Compound	Yield, %	Product colour	t_{boil} , °C	Solubility, g/100 g		
				Water	Methanol	Ethanol
1	2	3	4	5	6	7
$\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{TC} \cdot 2\text{NAM}$	85	Bright blue	108	0.02	0.01	0.03
$\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{K} \cdot 2\text{NAM}$	80	Blue green	distillation	0.03	0.01	0.03
$\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{AA} \cdot 2\text{TC}$	87	Blue green	106	0.03	0.01	0.02

The product yield was determined as the ratio of the calculated and experimental masses after the obtained complex compounds were washed, filtered, and dried to a constant weight. All the obtained compounds were first washed with distilled water twice and then with methanol since the starting copper nicotinate was dissolved in methanol.

Results and discussion

The results of elemental analysis of the synthesized compounds are shown in Table 1.

We carried out an X-ray phase analysis of free molecules of carbamide, thiocarbamide, copper nicotinate, and a compound of the composition $\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2$. Comparison of the diffraction patterns of free ligand molecules and the synthesized coordination compound showed a discrepancy between the diffractograms, which indicates that the new coordination compound has a unique crystal lattice that is different from those of the initial substances (Fig. 1).

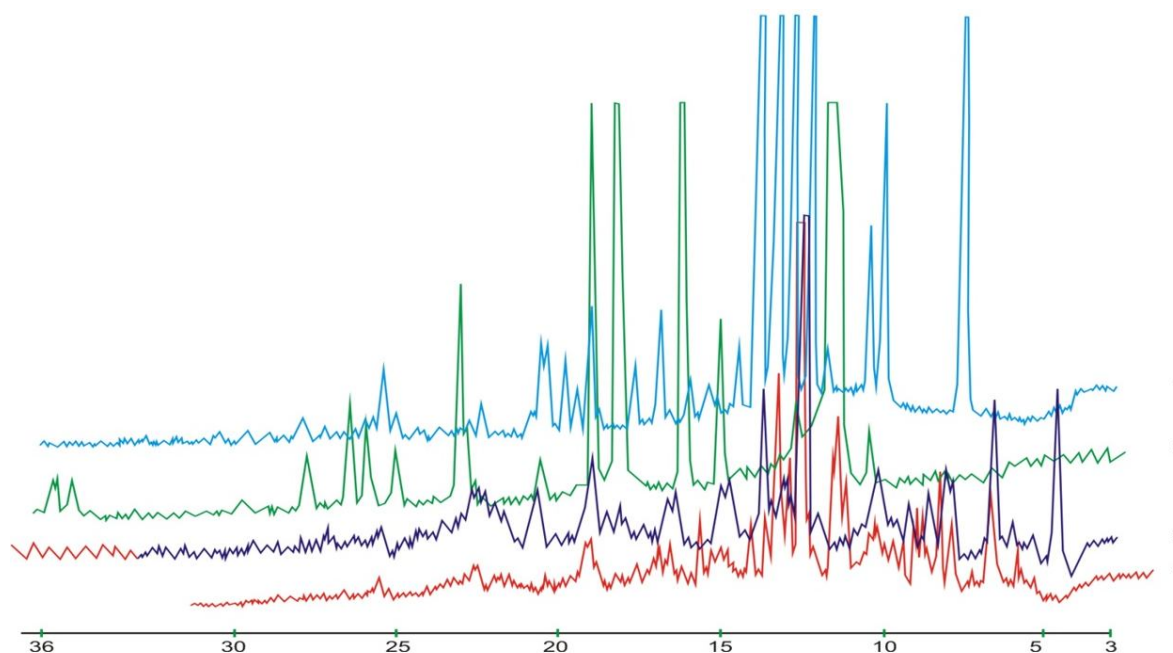


Fig. 1. X-ray diffraction patterns of $\text{NC}_5\text{H}_4\text{CONH}_2$ (1), $\text{CO}(\text{NH}_2)_2$ (2), $\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2\cdot\text{H}_2\text{O}$ (3), $\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2\cdot 2\text{CO}(\text{NH}_2)_2\cdot 2\text{NC}_5\text{H}_4\text{CONH}_2$ (4)

The IR absorption spectrum of free ligand molecules is characterized by the following bands (cm^{-1}):

Acetamide: 3377- $\nu(\text{NH}_2)$, 3191- $2\delta(\text{NH}_2)$, 1669- $\nu(\text{C} = \text{O})$, 1612- $\delta(\text{NH}_2)$, $\nu(\text{CO})$, 1396- $\nu(\text{CN})$, 1354- $\delta(\text{CH}_3)$, 1150- $\rho(\text{NH}_2)$, 1047- $\rho(\text{CH}_3)$, 1005- $\nu(\text{C}-\text{C})$, 872- $\nu(\text{C}-\text{C})$, 582- $\delta(\text{NCO})$ and 465- $\delta(\text{CCN})$.

Carbamide: 3448- $\nu_{\text{as}}(\text{NH}_2)$, 3348 $\nu_{\text{s}}(\text{NH}_2)$, 3263- $2\delta(\text{NH}_2)$, 1685- $\nu(\text{C} = \text{O})$, $\delta(\text{NH}_2)$, 1623- $\delta(\text{NH}_2)$, $\nu(\text{CO})$, 1464- $\nu(\text{CN})$, 1153, 1061- $\rho(\text{NH}_2)$, 1005- $\nu(\text{CN})$, 788- $2\delta(\text{NH}_2)$, 583- $\delta(\text{NCO})$ and 557- $\delta(\text{NCN})$.

Thiocarbamide: 3365- $\nu_{\text{as}}(\text{NH}_2)$, 3260- $\nu_{\text{s}}(\text{NH}_2)$, 3167- $2\delta(\text{NH}_2)$, 1631- $2\delta(\text{NH}_2)$, $\delta(\text{HNC})$, 1431- $\nu(\text{CS})$, 1093- $\nu(\text{CN})$, 780 - $\rho(\text{NH}_2)$, 726- $\delta(\text{CS})$, 621- $\delta(\text{CS})$, $\delta(\text{NCS})$, 485- $\delta(\text{NCN})$ and 459- $\delta(\text{NCS})$.

Nicotinamide: 3367- $\nu(\text{NH}_2)$, 3160- $2\delta(\text{NH}_2)$, 3053- $\nu(\text{CH})$, 1680- $\nu(\text{C}=\text{O})$, 1619- $\delta(\text{NH}_2)$, 1593- ν_{r} , 1574- ν_{r} , 1484, 1423- ν_{r} , $\delta(\text{CCN})$, 1397, 1340- $\nu(\text{CH})$, $\delta(\text{CCN})$, 1201- $\delta(\text{CCN})$, 1154, 1123- $\nu(\text{NH}_2)$, $\delta(\text{CCN})$, 1087- $\delta(\text{CCN})$, $\nu(\text{CO})$, 1028- ν_{r} , $\delta(\text{CCN})$, 974- $\nu(\text{CC})$, 829- $\nu(\text{CC})$, $\delta(\text{CCC})$, 780, 703- $\delta(\text{CCN})$, $\delta(\text{CO})$, 623, 603- $\delta(\text{CO})$, $\delta(\text{CNC})$, 510- $\delta(\text{CO})$, $\delta(\text{CCC})$.

For the synthesized compounds, the following are observed:

$\text{Cu}(\text{NC}_5\text{H}_4\text{COO})_2\cdot 2\text{CO}(\text{NH}_2)_2\cdot 2\text{NC}_5\text{H}_4\text{CONH}_2$: 694- $\delta(\text{CO})$ + $\delta(\text{CCN})$ (NAM), 717- $\delta(\text{CO})$ + $\delta(\text{CCN})$ (NAM), 1050- ν_{k} + (CCN) (NAM), 1092- ν_{k} + (CCN) (NAM), 1418- $\nu_{\text{s}}(\text{COO}^-)$, 1474- $\nu(\text{CN})$ (C), 1595- $\nu_{\text{as}}(\text{COO}^-)$, 1614- ν_{k} (NAM), 1673- $\nu(\text{C} = \text{O})$ (C).

Cu(NC₅H₄COO)₂·2CH₃CONH₂·2CS(NH₂)₂: 585- δ (CS), 717- ν (CS), 1385- ν_s (COO⁻), 1416- ν (CN) (AA), 1587- ν_{as} (COO⁻), 1656- ν (C = O) (AA).

Cu(NC₅H₄COO)₂·2CS(NH₂)₂·2NC₅H₄CONH₂: 601- δ (CS), 688- δ (CO) + δ (CCN) (NAM), 695- ν (CS), 720- δ (CO) + δ (CCN) (NAM), 1049- ν_r + (CCN) (NAM), 1010- ν_k + (CCN) (NAM), 1387- ν_s (COO⁻), 1561- ν_{as} (COO⁻), 1614- ν_k (NAM).

As shown in the IR spectra of the synthesized compounds in the coordinated acetamide and carbamide molecules, the frequency of the stretching vibration of the C = O group decreases by 12 and 13 cm⁻¹, respectively, and the absorption frequency of the C-N group increases by 10 cm⁻¹ and 20 cm⁻¹, which indicates the coordination of acetamide and carbamide with the central ion through the oxygen atom of the carbonyl group. The frequency of stretching vibrations of the C-S group in thiocarbamide during the transition to the coordinated state decreases by 6-9 cm⁻¹ and 20-36 cm⁻¹, respectively. These data are evidence that the central atom is coordinated with the sulfur atom.

In the IR spectrum of the uncoordinated nicotinamide molecule, the ring frequency is observed at 1593 cm⁻¹, which in the case of a complex compound is increased by 21 cm⁻¹. At 703 cm⁻¹, 1028 cm⁻¹, there is a simultaneous increase and decrease in the vibration frequencies of the ring by 17-21 cm⁻¹ and 15-18 cm⁻¹, respectively, due to the ring splitting. This means that in nicotinamide, coordination with the central ion is carried out through the nitrogen atom of the pyridine ring.

The IR spectra of the complexes exhibit two intense bands with absorption maxima in the range of 1561-1595 cm⁻¹ and 1385-1418 cm⁻¹, corresponding to asymmetric and symmetric stretching vibrations of the carboxylate group. The value $\Delta\nu = \nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$ is equal to 176-177 cm⁻¹ and testifies in favor of monodentate coordination of the carboxylate group [13].

On the curve of differential thermal analysis of the Cu(NA-H)₂ · 2AA · 2TC compound, three endothermic effects are observed at 72, 178, 260 °C and four exothermic effects at 320, 444, 520, 597 °C. The nature of endothermic effects is associated with the removal of coordinated acetamide molecules and the onset of decomposition of the thiocarbamide molecule. A further increase in temperature leads to the simultaneous decomposition and combustion of the products of thermal decomposition of the nicotinate copper complex with the formation of first copper (II) sulfate and subsequent decomposition and the formation of copper (II) oxide, as evidenced by the appearance of three exothermic effects at 444, 520 and 597 °C (Fig. 2).

The derivatogram of Cu (NA-H)₂ · 2C · 2NAM has three endothermic effects at 160, 275, and 286 °C, as well as three exothermic effects at 402, 546 and 664 °C.

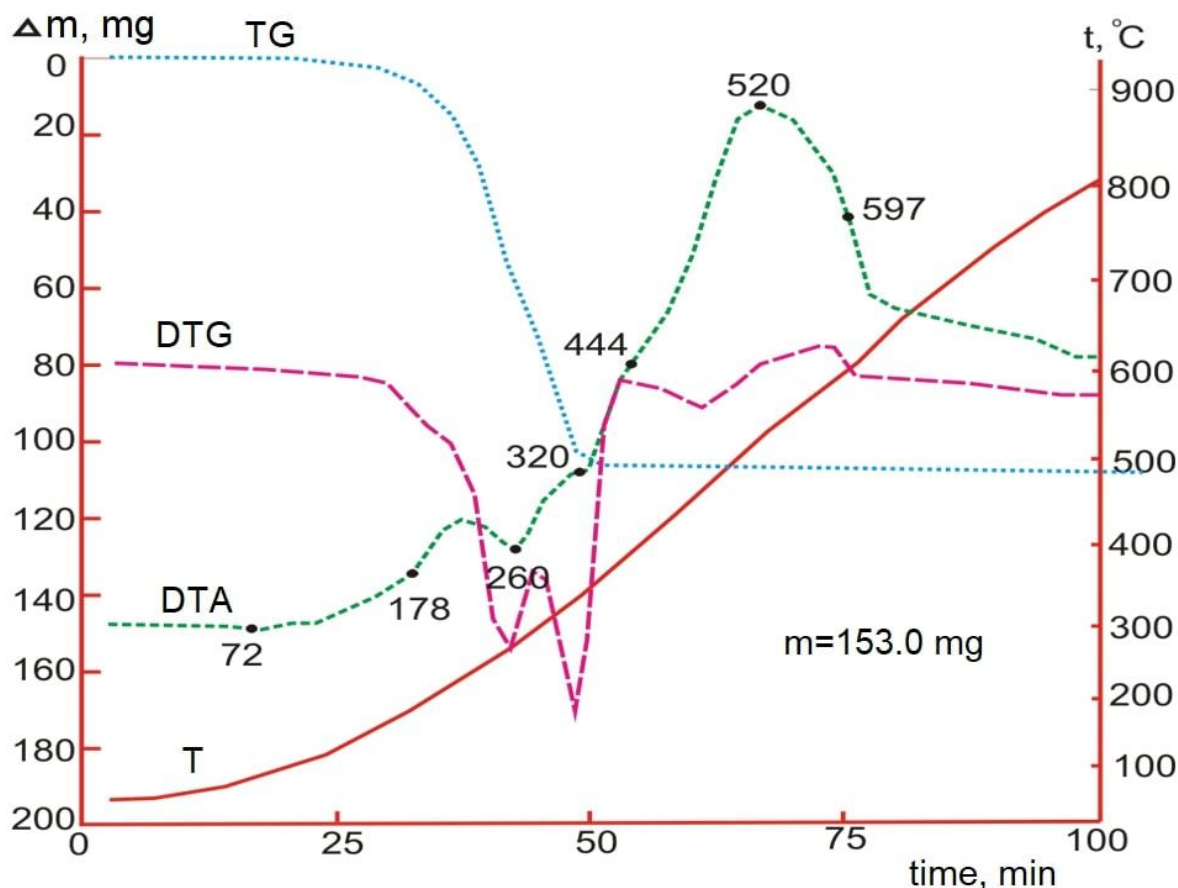


Fig.2. Derivatogram of Cu(NA-H)₂·2AA·2TC

Endoeffects at 147-350 °C correspond to the decomposition of the carbamide molecule and the beginning of the stepwise decomposition of nicotinamide. The nature of the subsequent effects can be explained by the decomposition of copper (II) nicotinate, combustion of thermolysis products, and the formation of copper oxygen compounds.

The heating curve of Cu(NA-H)₂ · 2TC · 2NAM is characterized by three endothermic effects at 138, 280 and 342 °C and three exothermic effects at 450, 512 and 586 °C. Three thermal effects correspond to the cleavage of the coordinated nicotinamide molecule and stepwise decomposition of the coordinated thiocarbamide molecule. The nature of the subsequent exothermic effects is associated with the decomposition of the remaining part of the coordinated thiocarbamide molecule, nicotinate groups, and combustion of gaseous thermolysis products.

Thermal analysis of the obtained mixed-ligand coordination compounds shows that when heated to 80-140 °C, melting or polymorphic transformations of complex compounds occurs. In acetamide and carbamide coordination compounds, when heated to 150-250 °C, the decomposition of coordination compounds and a stepwise removal of acetamide and carbamide molecules take place. In thiocarbamide compounds, when heated above 200 °C, the

thiocarbamide molecule decomposes to H_2S , CS_2 , NH_2CN and copper sulfide is formed. In the coordination compounds of nicotinamide, endothermic effects are observed at 250-300 °C, which corresponds to the decarboxylation of the nicotinamide molecule. Further heating of these compounds leads to the stepwise decomposition of nicotinamide molecules.

Upon further heating, decomposition of copper nicotinate occurs combustion of thermolysis products and the formation of copper oxide, as evidenced by exothermic effects above 400 °C.

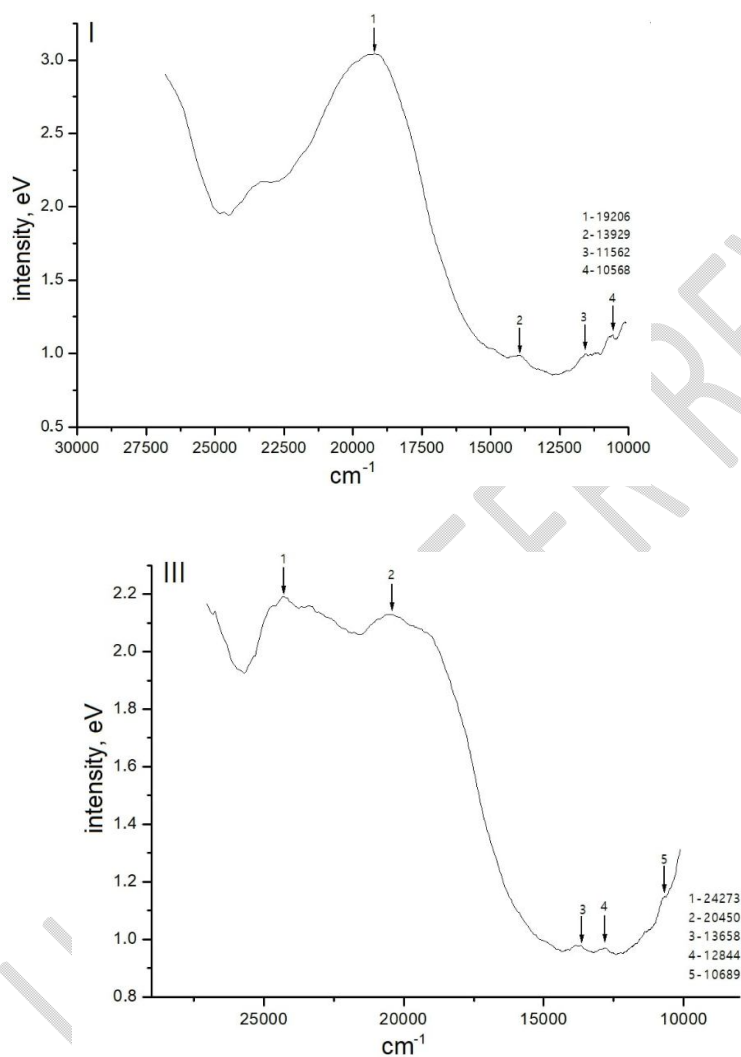


Fig.3. EDRS: I - $\text{Cu}(\text{NA-H})_2 \cdot 2\text{AA} \cdot 2\text{TC}$, II - $\text{Cu}(\text{NA-H})_2 \cdot 2\text{C} \cdot 2\text{NAM}$; III - $\text{Cu}(\text{NA-H})_2 \cdot 2\text{TC} \cdot 2\text{NAM}$.

The electronic spectra of the compound of the composition $\text{Cu}(\text{NA-H})_2 \cdot 2\text{AA} \cdot 2\text{TC}$ are characterized by two maxima at 13929, 19206 cm^{-1} .

The EDRS of the coordination compound with the composition $\text{Cu}(\text{NA-H})_2 \cdot 2\text{C} \cdot 2\text{NAM}$ has two bands with maxima at 13693 and 20501 cm^{-1} . The EDRS of the coordination compound with the composition $\text{Cu}(\text{NA-H})_2 \cdot 2\text{C} \cdot 2\text{NAM}$ has two bands with maxima at 13693

and 20501 cm^{-1} , which correspond to the transition $Z^2 \rightarrow X^2 - Y^2$ and $XY, XZ, YZ \rightarrow X^2 - Y^2$ of the six-coordinated complex Cu(II).

Compound $\text{Cu}(\text{NA-H})_2 \cdot 2\text{TC} \cdot 2\text{NAM}$ in the diffuse reflectance spectrum has bands with maxima at 13658 and 20450 cm^{-1} .

Similar data for six-coordination coordination compounds Cu(II) are given in [14], [15]. Electronic diffuse reflectance spectra of mixed-ligand coordination compounds of copper(II) nicotinate are shown in Fig.3.

Conclusion

The optimal ratios of the components and the reaction time have been established. The composition of the synthesized compounds was established by the method of elemental analysis.

X-ray phase analysis was used to obtain diffraction patterns of free molecules of ligands, copper nicotinate, and synthesized coordination compounds. The thermal behaviour of the synthesized compounds was investigated and the products of thermolysis were identified. It was established that the stepwise decomposition of the synthesized compounds with several endo- and exo effects corresponding to the decomposition of the constituent parts of the complexes. Based on the intensity of the electronic spectrum of diffuse reflection and the values of the bands, the six-coordination environment of Cu(II) for the synthesized complexes was proved.

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