IR-SPECTROSCOPIC ANALYSIS OF THE COORDINATION COMPOUNDS OF ZINC NITRATE WITH BENZAMIDE AND UREA

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Abstract. *Monotype ligand coordination compounds of zinc nitrate with benzamide and urea were synthesized. The synthesis is carried out by mechanochemical (solid-phase) method, which does not require the use of scarce solvents as in the synthesis stage, so and cases when highlighting the main product and allows for a short time to synthesize complexes of various compositions. The composition and individuality of the synthesized compounds were established by elemental analysis. Using vibrational spectroscopy method resulting for coordinating organic ligand have been proven, water molecules surroundings of the central ion of the complex compounds. Based on the data of IR spectroscopy, it was found that the molecules of benzamide and urea coordinated with the central atom through an oxygen atoms, and anions of nitric acid are coordinated by two oxygen atoms of the nitro group – bidentantly.*

Keywords: *ligand, complex compound, IR-spectroscopy, bond nature, polyhedron, central atom, mechanochemical synthesis.*

Introduction. Actual task of modern chemistry is the search new environmentally clean methods for the synthesis of chemical compounds and based on them materials. One of these methods is mechanochemical. Besides the fact that mechanochemical activation in the absence of solvents is at the synthesis stage, the generated mechanical energy leads to the breaking of bonds and the formation of certain intermediate products, which cannot be formed in the presence of a solution, therefore, often as a result of mechanochemical reactions, new compounds are formed, which cannot be obtained under the conditions of use of solvents. Today, theoretical and practical information about the conditions for obtaining coordination compounds based on mechanochemical synthesis, which is considered a low-cost, simple and convenient method that does not require various solvents, is increasing more [1].

Literature Review:

The search for new environmentally friendly methods of synthesis of chemical compounds and materials based on them is an urgent issue of modern chemistry. One of these methods is the mechanochemical method, which does not require different solvents either at the synthesis stage or in cases of extraction of the main product. As a result of plastic deformation of a solid body, its shape and size change and this leads to its physicochemical properties to vary. Mechanically processed solids have an activation process, that is, during the grinding process, the particle size approaches a specific critical size. Mechanical activation not only increases the surface of the object, but also leads to the accumulation of defects in the entire volume of the crystal. It is necessary to use special mechanical activation methods (reaction medium, impact energy, reaction time, temperature) to change many physico-chemical properties and reaction abilities of solid bodies in the desired direction, because according to the mechanisms, chemical reactions of solid bodies depend on various defects in the crystal [2].

The mechanical energy produced during mechanochemical activation at the synthesis stage prevents the formation of some intermediate products that are formed in solution, in addition to breaking bonds, so mechanochemical reactions lead to the formation of new compounds without the use of solvents. Many of these solvents can inhibit the interaction of reagents or strongly bind to the product, changing its structure and reactivity [3].

There are mechanochemical methods of obtaining substances in nano- and micro-scale form. While obtaining powders of passive metals is not a problem, obtaining nanopowders of active metals is complicated (oxidation, reaction with other substances, etc.). Nanopowders of such metals are obtained in an inert organic liquid in an inert gas environment. For example, to obtain finely dispersed metals, their organic salts are thermally decomposed in an organic liquid that boils at a high temperature and has reducing properties. The use of liquid, on the one hand, keeps the temperature of the decomposed substance uniform, and on the other hand, resists oxidation and agglomeration of the formed metal particles. Most importantly, nano-sized substances are obtained in an easy and convenient way. Using this method, ultradispersed powders of nickel, copper, bismuth and cobalt from 50 nm to 1 μm were obtained [4].

Experimental part

The coordination compounds of zinc nitrate with ligands were synthesized by the mechanochemical method. Mechanochemical interaction of the starting components carried out by intensive grinding Zinc nitrate: amide mixtures in a 1:2 molar ratio and for 30 minutes at room temperature in a ball mill with a working part (mill volume 100 ml). The duration of one stirring is 30 seconds. Three such mixes make up one cycle; the time between cycles is 2-3 seconds. Periodically after each cycle, samples were taken for x-ray phase analysis. Sampling was carried out 18-20 times. After 17-19 reps no changes were observed in the diffraction patterns of the samples, which indicates the individuality of the compounds obtained. Monotype ligand complexes of zinc with ligands was obtained by the above method [5, 6].

The composition of the compound $\mathbf{Zn(NO_3)_2 \cdot 2C_6H_5CONH_2 \cdot H_2O}$ synthesized by intensive mixing 0.003 mol of zinc hexahydrate with 0.006 mol of benzamide in the ball mill at room temperature for 30 minutes.

The composition of the compound $\mathbf{Zn(NO_3)_2 \cdot 2CO(NH_2)_2 \cdot H_2O}$ synthesized by intensive mixing 0.003 mol of zinc hexahydrate with 0.006 mol of urea in the ball mill at room temperature for 30 minutes.

$$\mathbf{Zn(NO_3)_2 \cdot 6H_2O + 2C_6H_5CONH_2 \rightarrow [Zn \cdot 2C_6H_5CONH_2 \cdot (NO_3)_2] \cdot H_2O + 5H_2O}$$

$$\mathbf{Zn(NO_3)_2 \cdot 6H_2O + 2CO(NH_2)_2 \rightarrow [Zn \cdot 2CO(NH_2)_2\ (NO_3)_2] \cdot 2H_2O + 4H_2O}$$

The product yield was found as the ratio of the determined and calculated masses after washing, filtering, and drying the complex compounds to constant mass. Based on the solubility of the synthesized coordination compounds in solvents, the obtained complex compounds were purified by washing. The solubilities of the synthesized compounds in various solvents are presented in Table 1. Water, ethanol, methanol, acetone, toluene were used as solvents.

Table 1.

Some physical properties of synthesized coordination compounds

№	Compounds	Output product	Compound color	T liq	Dissolution of complex compounds in various solvents				
					Water	Ethanol	methanol	acetone	toluene
1	2	3	4	5	6	7	8	9	10

2	$[ZnL^3{}_2(NO_3)_2]\cdot 2H_2O$	73	White	90	W	W	W	H	H
3	$[ZnL^8{}_2(NO_3)_2]\cdot H_2O$	69	White	120	S	W	S	S	H

Note: W - It dissolves well in solvent, S - slightly soluble in solvent, H - hardly soluble in solvent

Absorption areas of IR spectra were recorded on a spectrometer IR Tracer-100 (500-4000 cm^{-1}) of "SHIMADZU" company. [7].

The amount of metal in the synthesized complex compounds was recorded in the novAA 300 atomic absorption spectrophotometer of Analytic Jena AG (Germany) [8], and the amount of elements in the EuroEA3000 CHNS-O Analyzer (Eurovector S.p.A., Milano, Italy) element analyzer [9] (Table 2).

Table 2.

The results of the elementary analyzes of the synthesized coordination compounds.

Compound	Zn %		N %		C %		H %	
	Found	Count	Found.	Count	Found	Count	Found	Count
$[Zn\cdot 2C_6H_5CONH_2(NO_3)_2]\cdot H_2O$	21,12	20,97	13,61	13,55	26,96	27,09	2,32	2,26
$[Zn\cdot 2CO(NH_2)_2(NO_3)_2]\cdot 2H_2O$	18,72	18,84	24,23	24,35	7,04	6,96	3,54	3,48

Results and its discussion

In the study of the structure of complex compounds, IR-spectroscopy (vibrations of the atoms in the molecule in the area $\lambda=10^{-4}–10^{-2}$ cm) is used. IR-spectrum data is used in the analysis of the structure of the obtained complexes due to the possibility of drawing conclusions about new interactions and bonds based on the differences in the spectrum of the complex with the original components [10].

In the IR spectrum of the complex compound $[Zn\cdot 2C_6H_5CONH_2\cdot(NO_3)_2]\cdot H_2O$, it can be seen that the frequency of the C=O valence vibration of the benzamide molecule has decreased from 1659 cm^{-1} to 1643 cm^{-1}. And the frequency of C–N bond valence vibration in benzamide molecule increased from 1450 cm^{-1} to 1486 cm^{-1}. Hence, it showed that the benzamide molecule is coordinated through the oxygen atom of the carbonyl group. In the IR spectrum of the uncoordinated benzamide molecule, the ring vibration is observed at 1577 cm^{-1}, which increased to 1604 cm^{-1} in the complex state (Fig.1). In the region of 3350 cm^{-1}, an absorption line corresponding to the crystallization water molecule in the complex compound was observed.

In the IR spectrum of the $[Zn\cdot 2CO(NH_2)_2\cdot(NO_3)_2]\cdot 2H_2O$ complex compound, the high-intensity valence vibration frequency of the C=O bond of the urea molecule shifted from 1682 cm^{-1} to the lower frequency region of 1665 cm^{-1}. And the frequency of valence vibration of the C–N bond in the urea molecule is observed in the higher region from 1450 cm^{-1} to 1487 cm^{-1}. Hence, the urea molecule was coordinated with the oxygen atom of the CO bond. In the IR spectrum of the complex compound, a vibrational line characteristic of a new Zn-L bond was recorded at 533 cm^{-1}. At 1317 cm^{-1} there are intense bands of nitrate ion $\nu_{as}(NO_3)$ and less intense bands of $\nu_s(NO_3)$ at 1047 cm^{-1}. Asymmetric and symmetric bands of $\nu(NN_2)$ group were observed at 3344 and 3238 cm^{-1}, respectively. Absorption lines in the region of 3439 cm^{-1} are characteristic of the valence vibration of crystallization water molecules (Fig. 2).

Figure 1.

IR spectrum of complex compound $[Zn{\cdot}2C_6H_5CONH_2{\cdot}(NO_3)_2]{\cdot}H_2O$

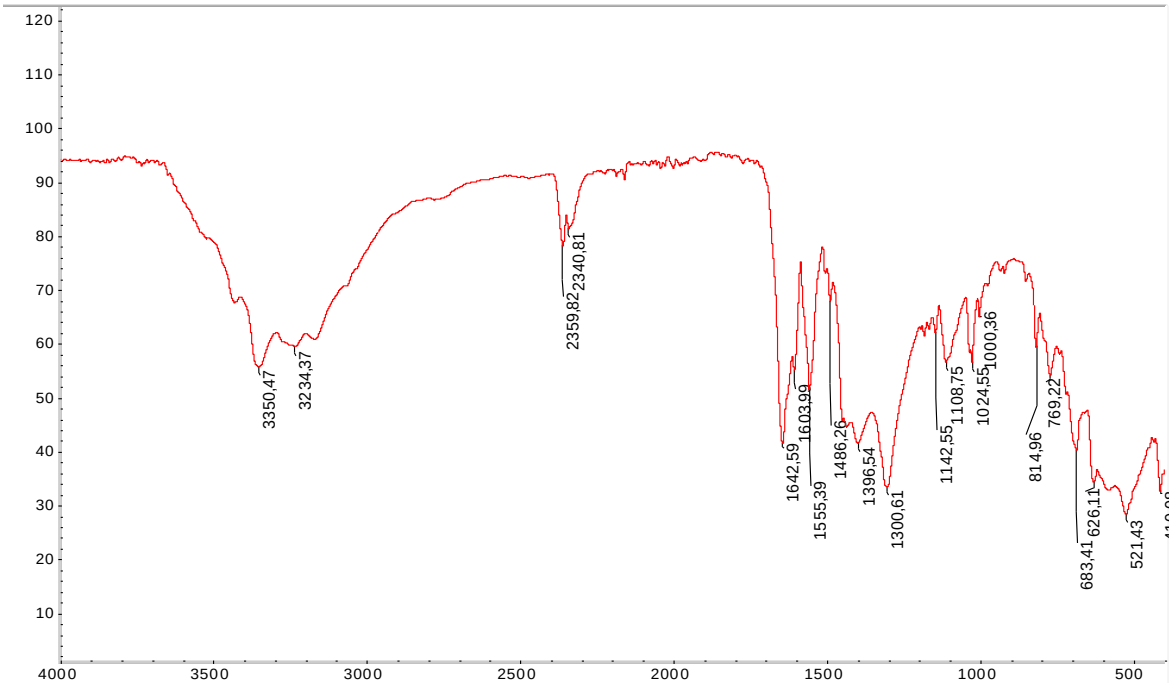
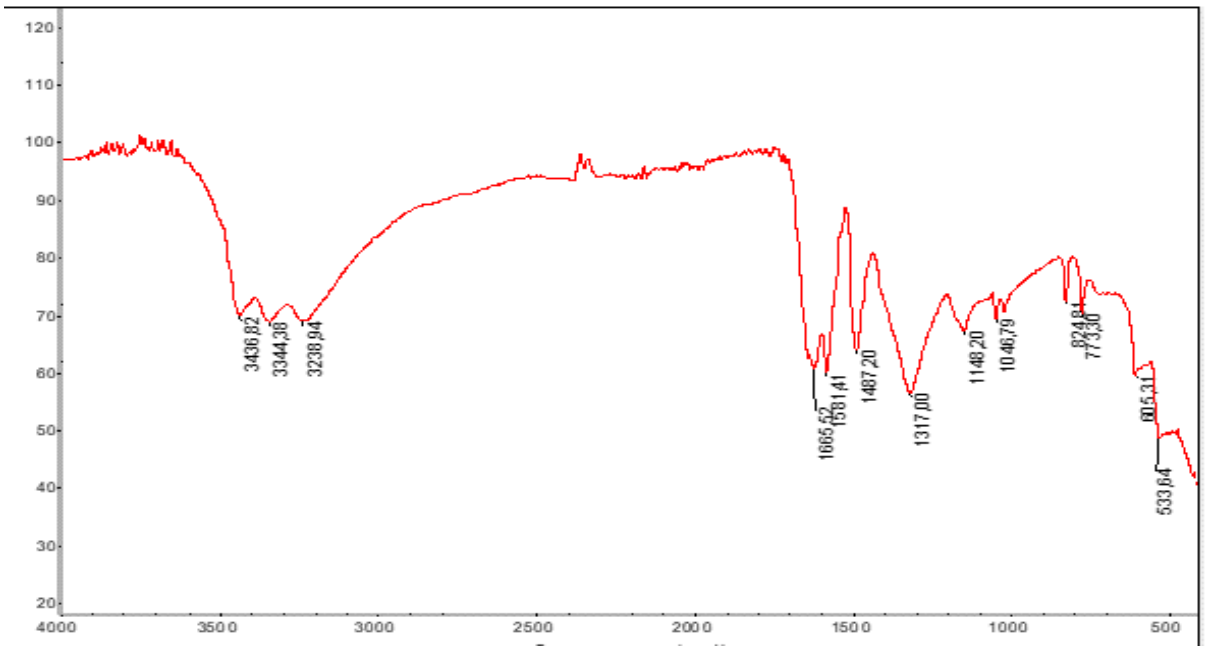


Figure 2.

IR spectrum of complex compound $[Zn{\cdot}2CO(NH_2)_2{\cdot}(NO_3)_2]{\cdot}2H_2O$



Conclusion. Synthesis conditions have been developed, isolated in the solid state of monotype ligand coordination compounds of zinc nitrate with benzamide and urea. The composition, individuality, methods for the coordination of ligand and water molecules coordination compounds are established. A relationship between the valence and deformation vibrations of the functional groups has established ligand coordination centers.

The result of IR-spectroscopy shows that in the composition of the complex compounds, the benzamide and urea molecules is coordinated through the oxygen atoms of the CO bond, with the zinc atom in a monodentate state through the oxygen atoms of the carbonyl group. Nitric acid

anions are bound to zinc atoms in a bidentate state. Water molecules are located in the outer sphere. The zinc atom has an octahedral structure with ligands.

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