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**ACETAMIDE AND NICOTINIC ACID OF MONOTYPE LIGAND COORDINATION
COMPOUNDS OF ZINC NITRATE****Lobar Sharipova***Doctoral student Institute of General and Inorganic Chemistry
of the Academy of Sciences of the Republic of Uzbekistan,
Uzbekistan, Tashkent***Taxir Azizov***Chief scientific researcher, Institute of General and Inorganic Chemistry
of the Academy of Sciences of the Republic of Uzbekistan,
Uzbekistan, Tashkent***Mavluda Ibragimova***s.r., PhD Institute of General and Inorganic Chemistry
of the Academy of Sciences of the Republic of Uzbekistan,
Uzbekistan, Tashkent
E-mail: lobar5266@gmail.com***ОДНОРОДНОЕ КООРДИНАЦИОННЫЕ СОЕДИНЕНИЯ НИТРАТА ЦИНКА
С АЦЕТАМИДОМ И НИКОТИНОВОЙ КИСЛОТОЙ****Шарипова Лобар Акрамовна***докторант (PhD),
Институт общей и неорганической химии АН Республики Узбекистан,
Республика Узбекистан, г. Ташкент
E-mail: lobar5266@gmail.com***Азизов Тохир Азизович***гл. науч. сотр.,
Институт общей и неорганической химии АН Республики Узбекистан,
Республика Узбекистан, г. Ташкент***Ибрагимова Мавлуда Рузметовна***ст. науч. сотр. PhD
Институт общей и неорганической химии АН Республики Узбекистан,
Республика Узбекистан, г. Ташкент***ABSTRACT**

Monotype ligand coordination compounds of zinc nitrate with acetamide and nicotinic acid were obtained. 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 with high yield. The composition and individuality of the synthesized compounds were established by elemental analysis. Using vibrational spectroscopy and thermal analysis, methods for coordinating organic ligands have been proven, water molecules surroundings of the central ion and thermal behavior of the resulting complex compounds.

АННОТАЦИЯ

Получены однородные координационные соединения нитрата цинка с ацетамидом и никотиновой кислотой. Синтез осуществляется механохимическим (твердофазным) методом, который не требует применения дефицит-

ных растворителей как на стадии синтеза, так и случаях при выделении основного продукта и позволяет за короткое время синтезировать комплексы различного состава с высоким выходом. Состав и индивидуальность синтезированных соединений были установлены методом элементного анализа. С помощью колебательной спектроскопии и термического анализа были доказаны методы координации органических лигандов, окружения молекул воды центральным Ионом и теплового поведения образующихся комплексных соединений.

Keywords: monotype ligand complex compounds, mechanochemical synthesis, composition, physico-chemical methods of analysis, IR absorption spectra, personality, thermolysis.

Ключевые слова: однородные комплексные соединения, механохимический синтез, состав, физико-химические методы анализа, ИК-спектры поглощения, индивидуальность, термолиз.

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 [6, p.35].

Substances containing donor atoms, for example, amides of aliphatic, carboxylic, pyridinecarboxylic acids, in particular acetamide and nicotinic acid contribute to the formation of coordination compounds with metal ions. Anions of Organic and Inorganic Acids (acetic, benzoic, stearic, oleic, palmitic, nicotine, nitrogen, etc.) depending on the synthesis conditions, the nature of metals and the composition of complexes exhibit diverse methods of coordination [9, p.142; 11, p. 2963]. Numerous studies on the coordination compounds of p, d, and f metals with acid amides are devoted to complexes with homogeneous ligands [7 p.820;10 p.535]. There are no data in the literature of monotype ligand coordination compounds of zinc nitrate with acetamide and nicotinic acid [8, p.181]. The reasons for the competitive coordination of ligands, acid anions, and water molecules around the central atom are not shown [3, p.765; 5, p.680]. To solve these problems as complexing agents we have chosen zinc nitrate since by the change in the nature of organic ligands it is convenient to judge their ability to complexation. In connection with the above, the purpose of this work were the synthesis of monotype ligand complex compounds of zinc nitrate with acetamide and nicotinic acid and the establishment of the composition, personality methods for coordinating organic ligands and studying the thermal behavior of new compounds [4, p.430; 14, p.1950].

Experimental part. The coordination compounds of zinc nitrate with ligands were synthesized by the

mechanochemical method [13, p.370]. 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 derivatographic analysis. Sampling was carried out 18-20 times. After 17-19 reps no changes were observed in the diffraction patterns and derivatograms of the samples, which indicates the individuality of the compounds obtained.

Complex compound of the composition $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{CO}(\text{NH}_2) \cdot 2\text{H}_2\text{O}$ obtained by intensive mixing 0.003 mol of zinc hexahydrate and 0.006 mol of acetamide (L^2) in the ball mill at room temperature for 30 minutes.

The composition of the compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{NC}_5\text{H}_4\text{COOH} \cdot \text{H}_2\text{O}$ synthesized by intensive mixing 0.003 mol of zinc hexahydrate with 0.006 mol of nicotinic acid (L^7) in the ball mill at room temperature for 30 minutes.

The amount of zinc in the synthesized compounds was determined on a novAA 300 brand atomic absorption spectrophotometer from Analytik Jena AG (Germany) [15, p.250]. Nitrogen, hydrogen, carbon, and sulfur were determined on an EuroEA3000 CHNS-O Analyzer (Eurovector S.p.A., Milano, Italy) [1, p.182] (Table 1). IR absorption spectra were recorded in the region of 400-4000 cm^{-1} on an IR Fourier spectrometer IRTraser-100, company of "SHIMADZU" [12, p.34]. Thermal analysis was carried out on a F. Paulik-J. Paulik-L. Erdey system derivatograph [2, p.98] at a speed of 9 deg / min. and a weighting of 0.1-0.094 g with the sensitivity of the T-900, TG-200, DTA, DTG-1/10 galvanometers. Recording was carried out in atmospheric conditions. The holder was a platinum crucible with a diameter of 10 mm without covers. As a standard were used Al_2O_3 .

Table 1.

The results of the elementary analyzes of the synthesized coordination compounds

Compound	Zn %		N %		C %		H %	
	Found.	Counted.	Found.	Counted.	Found.	Counted.	Found.	Counted.
$\text{Zn}(\text{NO}_3)_2 \cdot 2\text{L}^2 \cdot 2\text{H}_2\text{O}$	19,03	18,95	16,27	16,33	14,05	13,99	13,97	4,08
$\text{Zn}(\text{NO}_3)_2 \cdot 2\text{L}^7 \cdot \text{H}_2\text{O}$	14,23	14,35	12,28	12,36	32,01	31,79	2,61	2,65

Results and its discussion.

The infrared absorption spectrum of a free molecule of acetamide (AA) is characterized by bands at 3377– $\nu(\text{NH}_2)$, 3191– $2\delta(\text{NH}_2)$, **1674**– $\nu(\text{C=O})$, 1612– $\delta(\text{NH}_2)$, $\nu(\text{CO})$, **1394**– $\nu(\text{CN})$, 1354– $\delta(\text{CH}_3)$, 1150– $\rho(\text{NH}_2)$, 1047– $\rho(\text{CH}_3)$, 1005– $\nu(\text{C-C})$, 872– $\nu(\text{C-C})$, 582– $\delta(\text{NCO})$ и 465– $\delta(\text{CCN})$.

IR spectrum of an uncoordinated nicotinic acid molecule has frequencies at 3446, 3072, 2360, 1883, 1694, **1595** – (NC_6H_5), 1583, 1480, 1416, 1319, 1296, 1182, 1136, 1113, 1087, 1030 – (C_6H_5), 953, 830, 810, 744, 691, 681, 639, 561, 551, 515 cm^{-1} .

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 3337, 1626, 1560, 1047, 820, 596, 530, 473, 419 cm^{-1} .

$\text{Zn}(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{CONH}_2 \cdot 2\text{H}_2\text{O}$ 3208, 2360, **1657** $\nu(\text{C=O})$, **1410** $\nu(\text{CN})$, 1587, 1312, 1132, 1042, 886, 830, 625, 582, 472 cm^{-1} .

$\text{Zn}(\text{NO}_3)_2 \cdot 2\text{NC}_5\text{H}_4\text{COOH} \cdot \text{H}_2\text{O}$ 3358, 3093, 2779, 1723, 1643, **1622** (NC_6H_5), 1587, 1536, 1479, 1381, 1284, 1195, 1099, 1054, 1008, 914, 836, 814, 750, 697, 671, 621, 503, 441 cm^{-1} .

As can be seen from the data in the IR spectra synthesized compounds in coordinated acetamide molecules frequency of the stretching vibration of the C=O group decreases by 17 cm^{-1} , respectively, and the absorption frequency of the C-N group increases by 16 cm^{-1} , which indicates the coordination of acetamide. The IR absorption spectrum of the nicotinic acid molecule has a sufficient number of frequencies and the frequency ν (rings) is observed at 1030 cm^{-1} , which in the case of the complex is significantly increased. The absorption bands at 1595- $\nu(\text{CN})$ belonging to the vibrations of the ring are split, while a simultaneous decrease and increasing frequencies. These changes may be indicative of the coordination of nicotinic acid with zinc ions through the nitrogen heteroatom of the pyridine ring.

In the IR spectrum of zinc nitrate there are bands at 1047, 1360, 820 cm^{-1} , during the formation of monotype ligand complex compounds, changes corresponding to the bidentate coordination of nitrate groups are observed.

Thus, the coordination site of zinc ion in the new coordination compounds corresponds to six-coordination complex compounds.

The appearance of the first and second endothermic effect is due to the removal of two water molecule.

The mass loss in the temperature range of 50-160 $^{\circ}\text{C}$ is 10.2 %. The nature of the subsequent thermal effects is accompanied by a stepwise decomposition of the anhydrous compound. In temperature intervals 160-255, 255-460, 460-540, 540-680, 680-800, 800-860 $^{\circ}\text{C}$ weight loss is 63.20; 0.9; 0.50; 0.6; 0.3; 0.1 %. The total weight loss in the temperature range of 50-860 $^{\circ}\text{C}$ according to the thermogravimetric curve is 75.80%.

The appearance of the first and second endothermic and exothermic effects is due to the removal of one water molecules. The mass loss in the temperature range at 60-150 $^{\circ}\text{C}$ is 4.1 %.

The heating curve of the complex compound $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{NC}_5\text{H}_4\text{COOH} \cdot \text{H}_2\text{O}$ revealed eight endothermic effects at 218, 362, 390, 615, 645, 648, 704, 728 $^{\circ}\text{C}$ and seven exothermic effects at 133, 291, 438, 441, 538, 571 and 818 $^{\circ}\text{C}$. In the temperature ranges 150-280, 280-350, 350-380, 380-418, 418-440, 440-460, 460-550, 550-580, 580-620, 620-650, 650-670, 670-718, 718-740, 740-820 $^{\circ}\text{C}$ loss of weight is 9.64; 56.63; 0.12; 0.24; 0.12; 0.12; 9.64; 0.12; 0.36; 0.12; 0.24; 0.24; 0.12; 0.12%. The total mass loss in the temperature range 60-820 $^{\circ}\text{C}$ on the TG curve is 81.93%.

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

Using the method of derivatographic analysis, the thermal behavior of the synthesized compounds was established. Intermediate thermolysis products were obtained and the composition of the compounds was established. Endothermic effects observed when heated, can be caused by such physical phenomena like melting, evaporation, changing the crystal structure, or chemical reactions of dehydration, dissociation. Transformations, which when heated are accompanied by exothermic effects, meets much less: these are oxidation processes and some structural transformations.

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