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# COORDINATION COMPOUNDS OF NICEL SULFATE WITH SOME ACID AMIDES

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**Annotatsiya.**Sulfat guruhini atsetamid, karbamid, tiokarbamid va nikotinamid bilan koordinatsiyalash orqali olingan birikmalarning tarkibi va individual xossalarini o‘zgartirish maqsadida nikel sulfatning ba’zi kislota amidlari bilan komplekslari sintez qilindi. Organik ligandlarning koordinatsiyasi, markaziy ionning atrofi va sintez qilingan birikmalarning termik xususiyatlari tebranish spektroskopiyasi va termik tahlil usullari yordamida o‘rganildi. Nikel sulfat va sintez qilingan komplekslarning nisbiy intensivliklari va fazoviy tuzilishini qiyosiy ko‘rib chiqish shuni ko‘rsatadiki, yangi koordinatsion birikmalar bir-biridan va dastlabki komponentlardan farq qiladi, chunki ular individual kristall panjaralarga ega. Sintez qilingan birikmalarning diffuz qaytish elektron spektrlari ikki valentli nikelning koordinatsion birikmalari oktaedrik geometriyaga ega ekanligini ko‘rsatdi. Sintez qilingan birikmalardan g‘o‘zaning o‘sishini tezlashtiruvchi stimulyator sifatida foydalanish mumkinligi tajribada tasdiqlangan.

**Kalit so‘zlar:** koordinatsion birikmalar, sintez, IQ-spektroskopiya, rentgen tuzilish tahlili, termik xatti-harakatlar, diffuz aks ettirishning elektron spektrlari

**Аннотация.**Синтезированы комплексы сульфата никеля с некоторыми амидами кислот с целью варьирования состава и индивидуальных свойств соединений, полученных путем координации сульфатной группы с ацетамидом, карбамидом, тиокарбамидом и никотинамидом. Координация органических лигандов, окружение центрального иона и термическое



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поведение синтезированных соединений изучены методами колебательной спектроскопии и термического анализа. Сравнительное рассмотрение относительных интенсивностей и пространственных структур сульфата никеля и синтезированных комплексов показывает, что новые координационные соединения отличаются друг от друга и от исходных компонентов, так как имеют индивидуальные кристаллические решетки. Электронные спектры диффузного отражения синтезированных соединений показали, что координационные соединения двухвалентного никеля имеют октаэдрическую геометрию. Экспериментально подтверждено, что синтезированные соединения могут быть использованы в качестве стимуляторов роста хлопчатника.

**Ключевые слова:** координационные соединения, синтез, ИК-спектроскопия, рентгеноструктурный анализ, термическое поведение, электронные спектры диффузного отражения.

**Abstract.** Complexes of nickel sulfate with some acid amides are synthesized aiming to vary the composition and the individual properties of the compounds obtained through coordination of the sulfate group to acetamide, carbomide, thiocarbomide and nicotinamide. The coordination of the organic ligands, the environment of the central ion and thermal behavior of the synthesized compounds are elucidated by vibrational spectroscopy and thermal analysis. The comparative consideration of the relative intensities and the spatial structures of magnesium sulfate, and the complexes synthesized shows that the new coordination compounds differ from each other and the original components as they have individual crystal lattices. Electronic spectra of the diffuse reflection of the synthesized compounds have shown that coordination compounds of divalent nickel have an octahedral geometry. It is experimentally verified that the compounds synthesized can be used as cotton growth stimulators.

**Keywords:** coordination compounds, synthesis, IR spectroscopy, X-ray analysis, thermal behavior, electronic spectra of the diffuse reflection.

## INTRODUCTION.

Currently, one of the promising directions of inorganic chemistry is the synthesis and study of the properties of complexes of transition metals with organic nitrogen-containing ligands exhibiting various biological activity. The molecules of acetamide, carbamide, thiocarbimide, nicotinamide, and nicotinic acid anion are bioorganic compounds. They participate in many biological processes. When transitioning to a coordinated state, the biological activity of these substances increases significantly [1,2]. Therefore, finding ways to synthesize new coordination compounds with biologically active molecules is of great importance.



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Numerous studies of complex compounds of p-, d-, and f-metals with amido acids have been devoted to complexes with homogeneous ligands. However, data on mixed ligands. Complex compounds of metal carboxylates were not known until the beginning of our research. Previously, the reasons for the specific coordination of ligands, acid anions, and water molecules in the atom's coordination environment were not clarified. To solve this problem, we chose nickel sulfate as the complexing agent. Because the nature of the mixed amide and complex compounds of nickel sulfate can be judged by their ability to form complexes. In connection with the above, the purpose of this study is to synthesize mixed and complex compounds of nickel sulfate with acetamide, carbamide, thiocarbamide, nicotinamide, to establish their composition and individuality by the coordination method of organic ligands, as well as to investigate the thermal behavior of new compounds.

For the synthesis of the above-mentioned coordination compounds, analytically and chemically pure Ni $(SO_4)_2 \cdot 6H_2O$ and NaOH were used. Analytically pure acetamide ($CH_3CONH_2$) (AA), carbamide ($CO(NH_2)_2$) (C), thiocarbamide ($CS(NH_2)_2$) (TC), nicotinamide ($NC_5H_4CONH_2$) (NA) were used as ligands. The synthesis was carried out by mechanochemical (enzymatic) method [3]. The necessary components included nickel sulfate, amide1, and amide2. They were mixed in a 1:2:2 ratio for 20 minutes at room temperature in a ball mill with a volume of 1 liter. Thus, the compound Ni (SO4) $2 \cdot 2CH_3CONH_2 \cdot 2NC_5H_4CONH_2 \cdot 2H_2O$ was synthesized by grinding 0.5624 g of Ni $(SO_4)_2 \cdot 4H_2O$ with 0.1772 g of acetamide and 0.3664 g of nicotinamide. The coordination compound $Ni(SO_4)_2 \cdot 2CO(NH_2)_2 \cdot 2CS(NH_2)_2 \cdot 4H_2O$ was synthesized using 0.5624 g of $Ni(SO_4)_2 \cdot 4H_2O$, 0.1802 g of carbamide, and 0.2284 g of thiocarbamide. The complex compound $Ni(SO_4)_2 \cdot 2CO(NH_2)$ $2 \cdot 2NC_5H_4CONH_2 \cdot 2.5H_2O$ was synthesized by grinding 0.5624 g of $Ni(SO_4)$ $_2 \cdot 4H_2O$ with 0.1802 g of carbamide and 0.3664 g of nicotinamide. The metal content in the synthesized compounds was determined using the method described in [5], the nitrogen content was assessed using the Dumas micro-method [6], and the carbon, hydrogen, and sulfur content was determined by burning in a stream of oxygen. The identity of the synthesized complexes was established based on radiographs. The latter were recorded using a DRON-2.0 X-ray diffractometer with a Cu-anticathode [8]. IR absorption spectra were recorded in the range from 400 cm-1 to 4000 $cm^{-1}$ on a "Nicolet" AVATAR-360 spectrometer using samples pressed with KBr. The diffuse reflection spectrum was constructed by dividing the reflection spectrum in the range of the galogen lamp obtained through the slit of the monochromator's direct illumination. Powder samples were measured by



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pressing them into tablets with a diameter of 1.4 cm and a thickness of 0.2 cm. The measurements were carried out at the Department of Heat Physics of the Academy of Sciences of Uzbekistan. Thickness 0.2 cm.Thermal analysis was carried out on a Paulik-Paulik-Erdey system derivatograph [10] at a heating rate of 10°C/min and the sensitivity of the T-900, TG-100, DTA-1/10, DTG-1/10 galvanometers at a coefficient of 0.1. Registration was carried out under atmospheric conditions with constant removal of the gaseous medium by a water pump. A 7 mm diameter platinum crucible without a lid was used as the holder, and $Al_2O_3$ served as the standard.

**Table 1.**

**Data of elemental analysis of mixed-ligand coordination compounds of nickel sulfate.**

| Compounds | Ni, % | | S, % | | N, % | | C, % | | H, % | |
|---|---|---|---|---|---|---|---|---|---|---|
| | found | calculated | found | calculated | found | calculated | found | calculated | found | calculated |
| $Ni(SO_4)_2 \cdot 2AA \cdot 2NA \cdot 2H_2O$ | 8,19 | 8,42 | - | - | 15,95 | 15,98 | 47,90 | 47,90 | 4,76 | 4,85 |
| $Ni(SO_4)_2 \cdot 2C \cdot 2TC \cdot 4H_2O$ | 9,43 | 9,08 | 10,13 | 9,9 | 21,9 | 21,6 | 30,3 | 29,6 | 5,3 | 4,9 |
| $Ni(SO_4)_2 \cdot 2C \cdot 2NA \cdot 2,5H_2O$ | 8,17 | 8,29 | - | - | 19,73 | 19,67 | 43,73 | 43,82 | 4,95 | 4,63 |

The data of elemental analysis of the synthesized compounds are presented in Table 1.

Comparative analysis of the relative intensities and spatial structures of nickel sulfate, carbamide, nicotinamide, and the coordination compound $Ni(SO_4)_2 \cdot 2CO(NH_2)_2 \cdot 2NC_5H_4CONH_2 \cdot 2.5H_2O$ showed that the new coordination compound differs significantly from the initial components. Consequently, the synthesized complex compound of nickel sulfate has an individual crystal lattice (Fig. 1).



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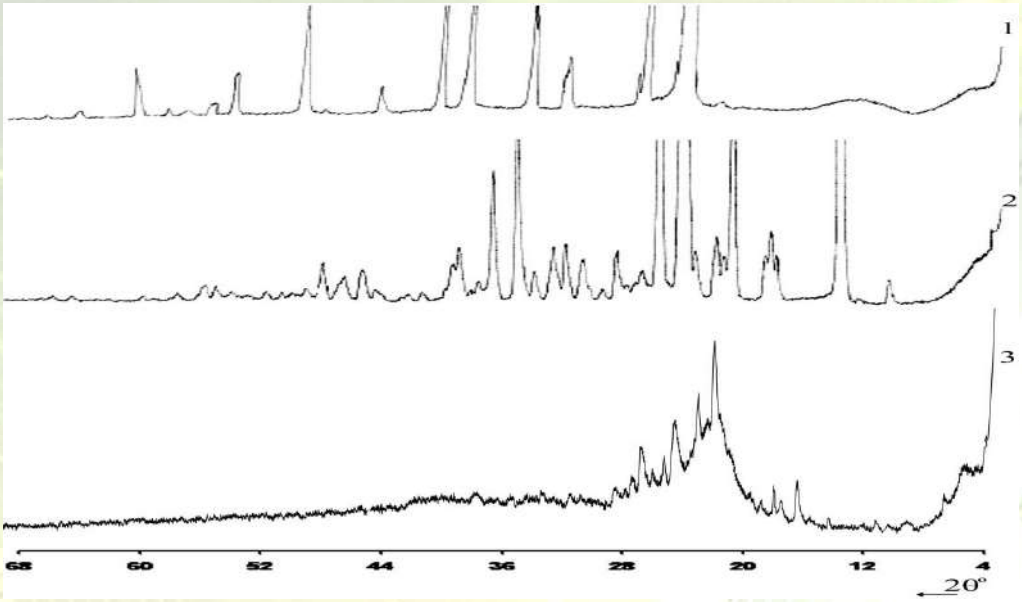



**Fig. 1. X-rays: $CO(NH_2)_2$ (1), $NC_5H_4CONH_2$ (2), $Ni(SO_4)_2$ $CO(NH_2)_2 \cdot 2NC_5H_4CONH_2 \cdot 2.5H_2O$ (3)**

The infrared absorption spectra of free ligand molecules are characterized by the following bands ($cm^{-1}$) [11].

Acetamide: 3377-ν ($NH_2$), 3191-2δ ($NH_2$), 1669-ν (C=O), 1612-δ ($NH_2$), ν (CO),

1396-ν (CN), 1354-δ ($CH_3$), 1150-ρ ($NH_2$), 1047-ρ ($CH_3$), 1005-ν (C-C), 872-ν (C-C), 582-δ (NCO), and 465-δ (CCN).

Carbamide: 3448-νas ($NH_2$), 3348-νs ($NH_2$), 3263-2δ ($NH_2$), 1685-ν (C=O), δ ($NH_2$), 1623-δ ($NH_2$), ν (CO), 1464-ν (CN), 1153, 1061-ρ ($NH_2$), 1005-ν (CN), 788-2δ ($NH_2$), 583-δ (NCO) and 557-δ (NCN).

Thiocarbamide: 3365-νas ($NH_2$), 3260-νs ($NH_2$), 3167-2δ ($NH_2$), 1631-2δ ($NH_2$), δ (HNC), 1431-ν (CS), 1093-ν (CN), 780-ρ ($NH_2$), 726-δ (CS), 621-δ (CS), δ (NCS), 485-δ (NCN) and 459-δ (NCS).

Nicotinamide: 3367-ν ($NH_2$), 3160-2δ ($NH_2$), 3053-ν (CH), 1680-ν (C=O), 1619-δ ($NH_2$), 1593-νk, 1574-νk, 1484, 1423-νk, δ (CCN), 1397, 1340-ν (CH),δ (SCN), 1201-δ (SCN), 1154, 1123-ν ($NH_2$), δ (SCN), 1087-δ (SCN), ν (CO), 1028-νk, δ (CCN), 974-ν (CC), 829-ν (CC), δ (CCC), 780, 703-δ (CCN), δ (CO), 623, 603-δ (CO), δ (CCN), 510-δ (CO), δ (CCC).

The spectra of the synthesized compounds show the following bands: $Ni(SO_4)_2 \cdot 2AA.2NA.2H_2O$ 701- δ (CO) + δ (CCN) (NA), 764-δ (CO) + δ (CCN) (NA), 1056- νK + (CCN) (NA), 1100 νK + (CCN) (NA), 1391-vs (COO-),1427- ν (CN) (AA), 1592- ν (COO-), 1614- νK (NA), 1666- ν (C=O) (AA), 3350- ν ($H_2O$).Ni (SO4) 2·2C·2TC·4H2O 599- δ (CS), 715- ν (CS), 1390- ν (COO-), 1467- ν (CN) (C), 1590- ν (COO-), 1662- ν (C=O) (C), 3338- ν ($H_2O$). $Ni(SO_4)_2 \cdot 2C \cdot 2NA \cdot 2.5H_2O$ 700-δ (CO) +δ (CCN) (NA), 764-δ (CO) +δ (CCN) (NA), 1056-



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νK + (CCN) (NA), 1110- νK + (CCN) (NA), 1390-νs (COO-),1473-ν (CN) (C), 1591- νas (COO-), 1614- νK (NA), 1675- ν (C=O) (C), 3438-ν ($H_2O$).

The IR spectra of the synthesized compounds show that the valence vibration frequency of the C=O groups of acetamide and carbamide decreases by 3 $cm^{-1}$ and 10-23 $cm^{-1}$, while the absorption frequency of the C-N group increases by 31 $cm^{-1}$ and 3-9 $cm^{-1}$, respectively. This indicates the coordination of acetamide and carbamide with the central atom through the oxygen atom of the carbonyl group. The valence vibration frequency of the C-S group of thiocarbamide during the transition to a coordinated state decreases by 22 $cm^{-1}$ - 26 $cm^{-1}$. This change confirms the coordination of the central atom through the sulfur atom.

At a vibrational frequency of 703 $cm^{-1}$, nicotinamide decomposes, subsequently increasing and decreasing the vibrational frequency of the ring by 61 $cm^{-1}$ - 61 $cm^{-1}$ and 2-3 $cm^{-1}$, respectively. This indicates the coordination of nicotinamide through the nitrogen heteroatom of the pyridine ring.

Bands in the range of 3200 $cm^{-1}$ - 3500 $cm^{-1}$ confirm the presence of crystallization water. The IR spectra of the complexes exhibit two intense absorption bands with peaks in the ranges of 1590 $cm^{-1}$ - 1592 $cm^{-1}$ and 1390 $cm^{-1}$ - 1391 $cm^{-1}$. They correspond to the asymmetric and symmetric valence vibrations of the carboxylate group. The value Δν = νas (COO-) -νs (COO-), found to be 200 $cm^{-1}$ - 201 $cm^{-1}$, indicates [10] in favor of monodentate coordination of the carboxylate group.

The thermal behavior of the synthesized complexes was studied. On the heating curve of a compound with the composition $Ni(SO_4)_2 \cdot 2CH_3CONH_2 \cdot 2NC_5H_4CONH_2 \cdot 2H_2O$, four endothermic effects are observed at 98, 190, 254, and 294°C, and three exothermic effects at 442, 518, and 576°C.

The first two endoeffects are caused by the removal of the water present in the synthesized substance. Mass loss is 4.75%, the calculated value is 4.71%. The endothermic effect at 147-190 °C corresponds to the removal of the acetamide molecule and the highest stage of nicotinamide decomposition. The nature of the subsequent effects can be explained by the decomposition of nickel (II) sulfate, the combustion of the thermolysis products, and the formation of nickel oxygen compounds. In the heating curve of the complex compound $Ni(SO_4)_2 \cdot CO(NH_2)_2 \cdot CS(NH_2)_2$, four endothermic effects are observed at 101, 138, 230, and 266°C, and three exothermic effects at 300, 441, and 584°C. The appearance of the first two effects is caused by the removal of two water molecules. Mass loss in the temperature range of 120-180°C on the thermogravimetric curve is 10.21%, the calculated value is 10.41%. The following two thermal effects correspond to the



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coordinated removal of the thiocarbamide molecule and the stepwise degradation of the coordinated carbamide molecules. The nature of subsequent exothermic effects is related to the decomposition of the remaining coordinated carbamide molecules, sulfate groups, and the combustion of gaseous products of thermolysis with the formation of nickel (II) oxide. The heating curve of a compound with the composition $Ni(SO_4)_2 \cdot 2CO(NH_2)_2 \cdot 2NC_5H_4CONH_2 \cdot 2.5H_2O$ has three endothermic effects at 137, 257, and 332°C, and two exothermic effects at 456 and 534°C. The first endothermic effect is caused by the removal of water molecules from the synthesized coordination.

Registered diffuse reflection electron spectra of $Ni(SO_4)_2 \cdot 2CH_3CONH_2 \cdot 2NC_5H_4CONH_2.2H_2O$, $Ni(SO_4)_2 \cdot CO(NH_2)_2 \cdot CS(NH_2)_2$ complex compounds of nickel sulfate.

Nickel (II) octahedral complexes usually give three absorption bands in the intervals of 8000-13000, 15000-19000 and 25000-29000 $cm^{-1}$. Each spectrum has several bends (Fig. 2, 3). For the analysis of band references, the most intense peaks were selected. Complex compounds have the proposed order of three peaks: 25576, 16142, 10228; 26738, 16314, 10766 $cm_{-1}$, which are related to the spin-resolved transition from 3A2g (F) to 3T2g (F), 3T1g (F), and 3T1g (P).

The values of, and p are calculated using the generally accepted methodology. The following equation was used to calculate p:

[6Dqr - 16 (Dq) 2] + (-6Dq-r) E + E2 = 0

For the Ni2+ ion, the parameter is P = 15V, where V is the Rakh parameter, and in the case of Ni (II) complexes, p = 15B'. The energy difference between the states of 3P and 3F in the complex decreases relative to the difference for the gas ion under the influence of covalence, i.e., the decrease in 3P serves, among other things, as a measure of covalence.

As can be seen from Table 2, there is a difference between the calculated and experimental 3A2g→3T1g (F) transition energies, indicating some covalent bonding between the central ion and ligands. This leads to distortion of the octahedral coordinate geometry node. Based on the observed spectra, it can be stated that in mixed-ligand coordination compounds of divalent nickel, the coordination number is 6, and the geometry of the coordination node corresponds to an octahedron.



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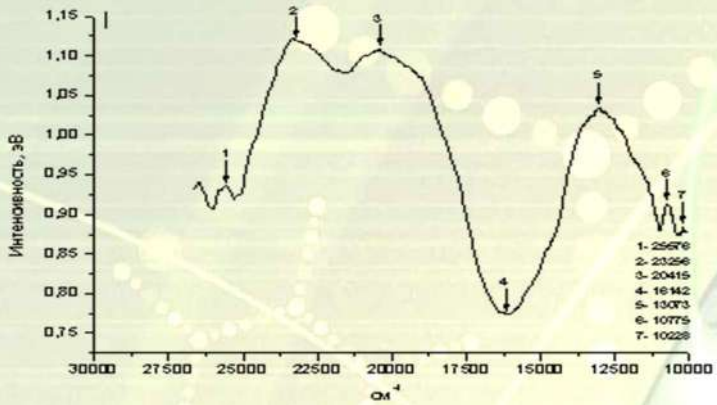



Fig.2. Electron spectra of diffuse reflection $Ni(SO_4)_2 \cdot 2CH_3CONH_2$ $2NC_5H_4CONH_2$ $2H_2O$.

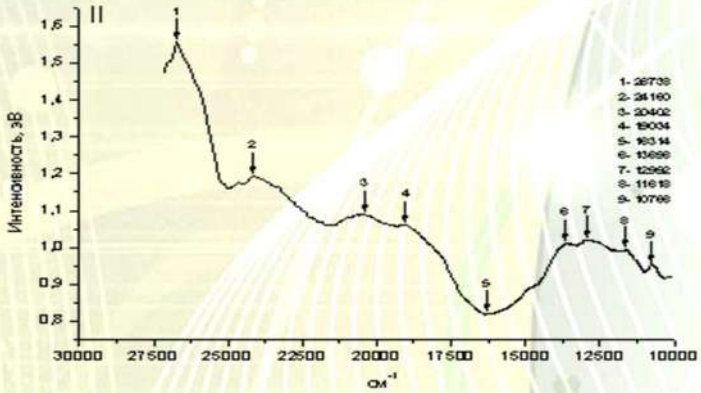



Fig.2. Electron spectra of diffuse reflection $Ni(SO_4)_2 \cdot CO(NH_2)_2 \cdot CS(NH_2)_2$.

**Table-2**

**Comparison of the found and calculated values of the electron spectra of mixed-ligand coordination compounds of nickel (II) sulfate.**

| Compounds | found value | | | calculated value | | | B % | p=15B Rakaki parameter $см^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | A2g →3T 2g | 3A2g→ 3T1g (F) | 3A2g →3T 1g (P) | 3A2g →3T1 g (F) | 3A2g →3T1 g (P) | =10Dq | | |
| $Ni(SO_4)_2 \cdot 2AA \cdot 2NK \cdot 2H_2O$ | 10228 | 16142 | 25576 | 16075 | 25576 | 10228 | 69,23 | 10967 |
| $Ni(SO_4)_2 \cdot 2C \cdot 2TC \cdot 4H_2O$ | 10766 | 16314 | 26738 | 16859 | 26738 | 10766 | | 11299 |

Conclusions and suggestions.Mixed-ligand coordination compounds of nickel sulfate are synthesized using a mechanochemical method. The individuality of the synthesized compounds has been proven by physicochemical analysis methods. The coordination centers and the dentation of the acid residue were confirmed by IR spectroscopy. The diffuse reflection electron spectra of the



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synthesized compounds showed that the compounds have an octahedral coordination geometry, and the coordination number of the central atom is 6. The synthesized compounds are being tested as cotton growth stimulants. The obtained results show that plants grow faster, have greater biomass, and yield higher yields. It was concluded that the synthesized compounds can be used as environmentally safe and relatively inexpensive cotton growth stimulants.

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