

Coordination Compounds of Nickel-Nicotinate with Some Acid Amides

Mavluda Ruzmetovna Ibragimova^{1*}

¹Institute of General and Inorganic Chemistry, Academy of Sciences of the Republic of Uzbekistan.
77A-Mirzo-Ulugbek Avenue, Tashkent, Uzbekistan.

Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/25856

Editor(s):

(1) Ling Bing Kong, School of Materials Science and Engineering, Nanyang Technological University, Singapore.

Reviewers:

(1) Muhammad Asam Raza, Government College University Lahore, Pakistan.
(2) Hanan E. S. Ali, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

Complete Peer review History: <http://sciencedomain.org/review-history/14333>

Received 23rd March 2016

Accepted 16th April 2016

Published 26th April 2016

Original Research Article

ABSTRACT

Complexes of Nickel-Nicotinate with some acid amides are synthesized aiming 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 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 Nickel-Nicotinate, 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.

1. INTRODUCTION

Currently, one of the promising areas of inorganic chemistry is the synthesis and research

of properties of transition metal complexes with organic nitrogen-containing ligands that exhibit different biological activities. Molecules acetamide, carbamide, thiocarbimide,

*Corresponding author: E-mail: mavluda@gmail.com;

nicotinamide and nicotinic acid anion represent bioorganic compounds. They are involved in many biological processes. With the transition to a coordinated state of these substances greatly increase the biological activity [1,2]. Therefore, searching for the synthesis of new coordination compounds with biologically active molecules is very important. Numerous studies on research of complexed compounds p, d, and f – metals with amide acids were devoted to complexes with homogeneous ligands. However, data on mixed ligands and complexed compounds of metal carboxylates were not studied before [3,4]. The causes of competitive coordination of ligands, acid anions, and water molecule around the central atom were not shown earlier. For the solution of these problem as a complexing, we selected Nickel-Nicotinate as to change the nature organic ligands is convenient to judge their ability to the complexation. In connection with the above, the purpose of this work was synthesis of mixedamid complex compounds of Nickel-Nicotinate with acetamide, carbamide, thiocarbamide, nicotinamide and the establishment of the composition, individuality, ways to coordination organic ligands and thermal behavior of new compounds.

2. EXPERIMENTAL DETAILS

Analytically and chemically pure $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, NaOH and nicotinic acid were used for the synthesis of the coordination compounds pointed above. Analytically pure acetamide (CH_3CONH_2) (AA), carbamide ($\text{CO}(\text{NH}_2)_2$) (C), thiocarbamide ($\text{CS}(\text{NH}_2)_2$) (TC), nicotinamide ($\text{NC}_5\text{H}_4\text{CONH}_2$) (NA) were used as ligands.

The synthesis was performed by mechanochemical (enzyme) method [5]. The components required included Nickel-Nicotinate, amid 1 and amid 2. They were mixed in a ratio of 1: 2: 2 for 20 minutes at room temperature in 1liter ball mill. Thus compound $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CH}_3\text{CONH}_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2 \cdot 2\text{H}_2\text{O}$ was synthesized by triturating 0.5624 g of $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with 0.1772 g of acetamide and 0.3664 g of nicotinamide. The coordination compound $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{CS}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ was synthesized using 0.5624 g of $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.1802 g of carbamide and 0.2284 g of thiocarbamide. Complex compound $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2 \cdot 2.5\text{H}_2\text{O}$ was synthesized by triturating of 0.5624 g $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 4\text{H}_2\text{O}$ with

0.1802 g of carbamide and 0.3664 g of nicotinamide.

The metal content of the synthesized compounds was determined following the procedure described in [6], that of nitrogen was evaluated with the application of the Dumas micromethod [7], while that of carbon, hydrogen and sulfur was found through combustion in an oxygen stream. The identity of the synthesized complexes was established by on the ground of X-ray diffractograms. The latter were recorded using X-ray diffractometer DRON-2.0 with Cu-anticathode [8]. Tables provided by [9,10] were used to calculate the interplanar distances and the relative intensity of the line I/I_1 . IR absorption spectra were recorded in the range from 400 cm^{-1} to 4000 cm^{-1} on AVATAR-360 spectrometer from "Nicolet" using samples compressed with KBr. The diffuse reflectance spectrum was constructed by dividing the reflectance spectrum in the range of the halogen lamp as obtained through the direct illumination slit of the monochromator. Samples of the powders were measured by compressing them into tablets with a diameter of 1.4 cm and thickness of 0.2 cm. The measurements were performed at the Department of Thermal Physics of the Academy of Sciences of Uzbekistan.

Thermal analysis was performed on a system derivatograph Paulik-Paulik-Erdei [11] at 10°C min and 0,1 g linkage to the sensitivity of galvanometers T-900, TG-100, DTA-1/10, DTG-1/10. The recording was carried out under atmospheric conditions with a constant removal of the gaseous medium by a water pump. A platinum crucible of a diameter of 7 mm of no cover served as a holder, while Al_2O_3 was used as a reference.

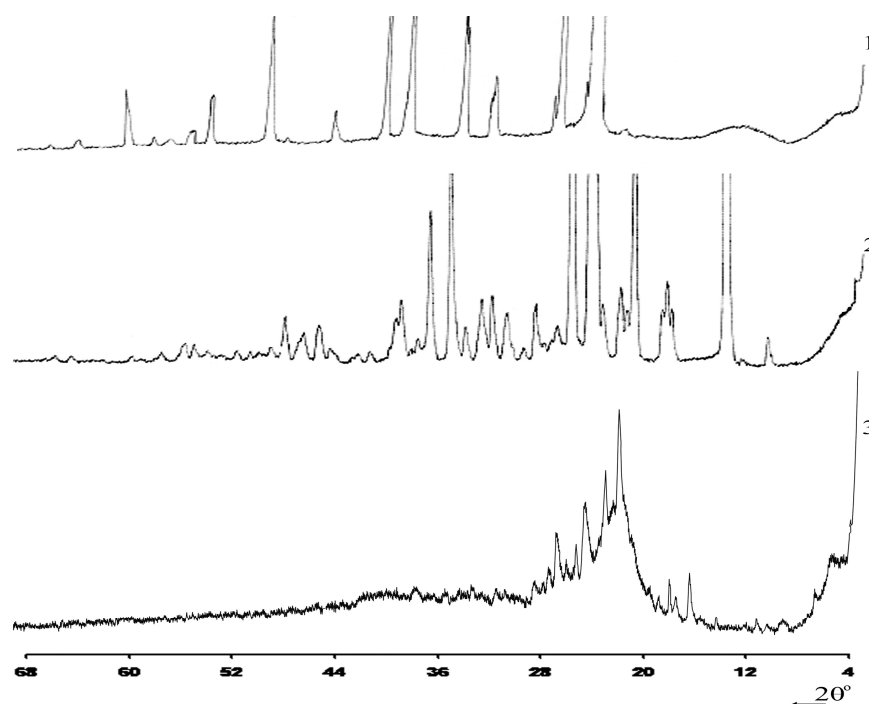
3. RESULTS AND DISCUSSION

The data obtained by the elemental analysis of the compounds synthesized is shown in Table 1.

The comparative consideration of the relative intensities and the spatial structures of nickel nicotinate, carbamide, nicotinamide and coordination compound composition $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2 \cdot 2.5\text{H}_2\text{O}$ showed that the new coordination compound significantly differ from original components. Therefore, the synthesized complex compound of Nickel-Nicotinate has an individual crystal lattice (Fig. 1).

Table 1. Elemental analysis data referring to mixed-ligand coordination compounds of Nickel-Nicotinate

Compound	Ni, %		S, %		N, %		C, %		H, %	
	Found	Count	Found	Count	Found	Count	Found	Count	Found	Count
Ni(Hκ-H) ₂ ·2AA·2NA·2H ₂ O	8,19	8,42	-	-	15,95	15,98	47,90	47,93	4,76	4,85
Ni(Hκ-H) ₂ ·2C·2TC·2H ₂ O	9,43	9,08	10,13	9,90	21,96	21,65	30,39	29,69	5,31	4,95
Ni(Hκ-H) ₂ ·2C·2NA·2,5H ₂ O	8,17	8,29	-	-	19,73	19,67	43,73	43,82	4,95	4,63

**Fig. 1. Radiographs: CO(NH₂)₂ (1), NC₅H₄CONH₂ (2), Ni(NC₅H₄COO)₂·2CO(NH₂)₂·2NC₅H₄CONH₂·2,5H₂O(3)**

The infrared absorption spectra of the free ligand molecules are characterized by the following bands (cm⁻¹) [12].

Acetamide: 3377-ν(NH₂), 3191-2δ(NH₂), 1669-ν(C=O), 1612-δ(NH₂), ν(CO), 1396- ν(CN), 1354-δ(CH₃), 1150-ρ(NH₂), 1047-ρ(CH₃), 1005-ν(C-C), 872-ν(C-C), 582-δ(NCO) and 465-δ(CCN).

Carbamide: 3448-vas(NH₂), 3348-vs(NH₂), 3263-2δ(NH₂), 1685-ν(C=O), δ(NH₂), 1623-δ(NH₂), ν(CO), 1464-ν(CN), 1153, 1061-ρ(NH₂), 1005-ν(CN), 788-2δ(NH₂), 583-δ(NCO) and 557-δ(NCN).

Thiocarbamide: 3365-vas(NH₂), 3260-vs(NH₂), 3167-2δ(NH₂), 1631-2δ(NH₂), δ(HNC), 1431-

ν(CS), 1093-ν(CN), 780-ρ(NH₂), 726-δ(CS), 621-δ(CS), δ(NCS), 485-δ(NCN) and 459-δ(NCS).

Nicotinamide: 3367-ν(NH₂), 3160-2δ(NH₂), 3053-ν(CH), 1680-ν(C=O), 1619-δ(NH₂), 1593-νκ, 1574-νκ, 1484, 1423-νκ, δ(CCN), 1397, 1340-ν(CH), δ(CCN), 1201-δ(CCN), 1154, 1123-ν(NH₂), δ(CCN), 1087-δ(CCN), ν(CO), 1028-νκ, δ(CCN), 974-ν(CC), 829- ν(CC), δ(CCC), 780, 703-δ(CCN), δ(CO), 623, 603-δ(CO), δ(CNC), 510-δ(CO), δ(CCC).

The spectra of the compounds synthesized show the following bands:

Ni(NC₅H₄COO)₂·2AA·2NA·2H₂O 701- δ(CO)+ δ(CCN)(NA), 764-δ(CO)+ δ(CCN)(NA), 1056- νκ

+ (CCN)(NA), 1100 ν_K + (CCN)(NA), 1391- $\nu_s(\text{COO}^-)$, 1427- $\nu(\text{CN})$ (AA), 1592- $\nu_{as}(\text{COO}^-)$, 1614- $\nu_K(\text{NA})$, 1666- $\nu(\text{C=O})(\text{AA})$, 3350- $\nu(\text{H}_2\text{O})$.

$\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{C} \cdot 2\text{TC} \cdot 2\text{H}_2\text{O}$ 599- $\delta(\text{CS})$, 715- $\nu(\text{CS})$, 1390- $\nu_s(\text{COO}^-)$, 1467- $\nu(\text{CN})$ (C), 1590- $\nu_{as}(\text{COO}^-)$, 1662- $\nu(\text{C=O})(\text{C})$, 3338- $\nu(\text{H}_2\text{O})$.

$\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{C} \cdot 2\text{NA} \cdot 2,5\text{H}_2\text{O}$ 700- $\delta(\text{CO})$ +
 $\delta(\text{CCN})(\text{NA})$, 764- $\delta(\text{CO})$ + $\delta(\text{CCN})(\text{NA})$, 1056- ν_K
+ (CCN)(NA), 1110- ν_K +(CCN)(NA), 1390- $\nu_s(\text{COO}^-)$, 1473- $\nu(\text{CN})$ (C), 1591- $\nu_{as}(\text{COO}^-)$,
1614- $\nu_K(\text{NA})$, 1675- $\nu(\text{C=O})(\text{C})$, 3438- $\nu(\text{H}_2\text{O})$.

The IR - spectra of the compounds synthesized show that the acetamide and carbomide frequency of the stretching vibration of C=O groups is reduced by 3 cm^{-1} and 10 - 23 cm^{-1} , respectively, while the absorption frequency of C-N group is increased by 31 cm^{-1} and 3- 9 cm^{-1} , correspondingly. This indicates coordination of acetamide and carbomide with the central atom via the carbonyl group oxygen ion. The frequency of the stretching vibrations of C-S group of thiocarbamide in the course of the transition to a coordinated state is reduced 22 cm^{-1} - 26 cm^{-1} . This change verifies the central atom coordination through the sulfur atom.

In nicotinamide oscillation frequency at 703 cm^{-1} is split with subsequent increase and decrease of the oscillation frequency of the ring by 61 cm^{-1} - 61 cm^{-1} and 2 - 3 cm^{-1} , respectively. This indicates nicotinamide coordination through the nitrogen heteroatom of the pyridine ring. The bands in the range of 3200 cm^{-1} - 3500 cm^{-1} confirm the presence of water of crystallization. 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 stretching vibrations of the carboxylate group. The value of $\Delta\nu = \nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$, found equal to 200 cm^{-1} - 201 cm^{-1} evidences [10] in favor of monodentate¹ coordination of carboxylate group.

¹ A monodentate ligand has only one donor atom used to bond to the central metal atom or ion. The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the center through only one atom. Some examples of monodentate ligands are: chloride ions (referred to as chloro when it is a ligand), water (referred to as aqua when it is a ligand), hydroxide ions (referred to as hydroxo when it is a ligand), and ammonia (referred to as ammine when it is a ligand).

Studied thermal behavior of the synthesized complexes. The heating curve compound of composition $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CH}_3\text{CONH}_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2 \cdot 2\text{H}_2\text{O}$ has four endoeffect at 98, 190, 254 and 294°C and three exothermic effect at 442, 518 and 576°C. The first two endoeffect caused by removal of available water in the synthesized substance. The loss of mass of 4.75% and 4.71% is calculated. Endoeffect at 147-190°C proper disposal molecule acetamide and top step of decomposition of nicotinamide. The nature of the subsequent effects can be explained by the decomposition of nicotinate nickel (II), the burning of thermolysis products and formation of oxygen compounds of nickel.

On the heating curve of the complex compound $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{CS}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ are four endothermic effects at 101, 138, 230 and 266°C and three exothermic effect at 300, 441 and 584°C. The appearance of the first two effects caused by the removal of two molecules of water. The weight loss in the temperature range 120-180°C on the curve thermogravimetry of 10.21% and 10.41% is calculated. Two subsequent thermal effects correspond to the coordinated elimination of the molecule thiocarbamide and stepwise degradation coordinated molecules of carbamide. The nature of the subsequent exothermic effects associated decomposition of remainder of coordinated molecules of carbamide, nicotinate groups the burning of gaseous products of thermolysis to form of nickel oxide (II). The heating curve compound of composition $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2 \cdot 2,5\text{H}_2\text{O}$ has three endoeffect at 137, 257 and 332°C, as well as two exothermic effect at 456 and 534°C. First endoeffect is caused by removing the water molecules from the synthesized coordination compound. The loss of mass is 6.39%, 6.15% is calculated. Endoeffect at 147-350°C corresponds to the decomposition of the molecule of carbamide and the beginning of stepwise decomposition of nicotinamide. Nature of the following effects can be explained by decomposition of nicotinate nickel, the thermolysis products burn out and the formation of oxygen compounds of nickel.

Registered electronic spectra of diffuse reflection of complex compounds of nicotinate nickel $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CH}_3\text{CONH}_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2 \cdot 2\text{H}_2\text{O}$, $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{CS}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$.

Octahedral complexes of nickel (II) usually give three absorption bands at intervals 8000-13000,

15000-19000 and 25000-29000 cm^{-1} . In each spectrum, there are a few kinks (Figs. 2,3). To analyze the assignment of bands selected the most intense peaks. Complex compounds are the proposed order on the three peaks in the 25576, 16142, 10228; 26738, 16314, 10766 cm^{-1} , which are related to the spin-allowed transition from ${}^3A_{2g}(F)$ на ${}^3T_{2g}(F)$, ${}^3T_{1g}(F)$ и ${}^3T_{1g}(P)$.

The values of Δ , β and p calculated according to the conventional method. The following equation was applied to calculate p :

$$[6Dq - 16(Dq)^2] + (-6Dq - p)E + E^2 = 0$$

For Ni^{2+} ion parameter $P = 15V$, where V - parameter R_{ak} , and in the case of complexes of

Ni(II) $p=15B'$. The energy difference between the states of the $3P$ and $3F$ in the complex is reduced with respect to gaseous ion difference influenced covalence, i.e. reduction $3P$ serves, inter alia, a measure of covalency.

As seen in Table 2, there is a difference between the calculated and found energy ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, which shows some of covalency bonds between the central ion and ligands. And this leads to a distorted octahedral coordination geometry node. Proceeding from the observed spectra it can be argued that in mixed-ligand coordination compounds of divalent nickel coordination number is 6, and the geometry coordinating node corresponds to octahedron.

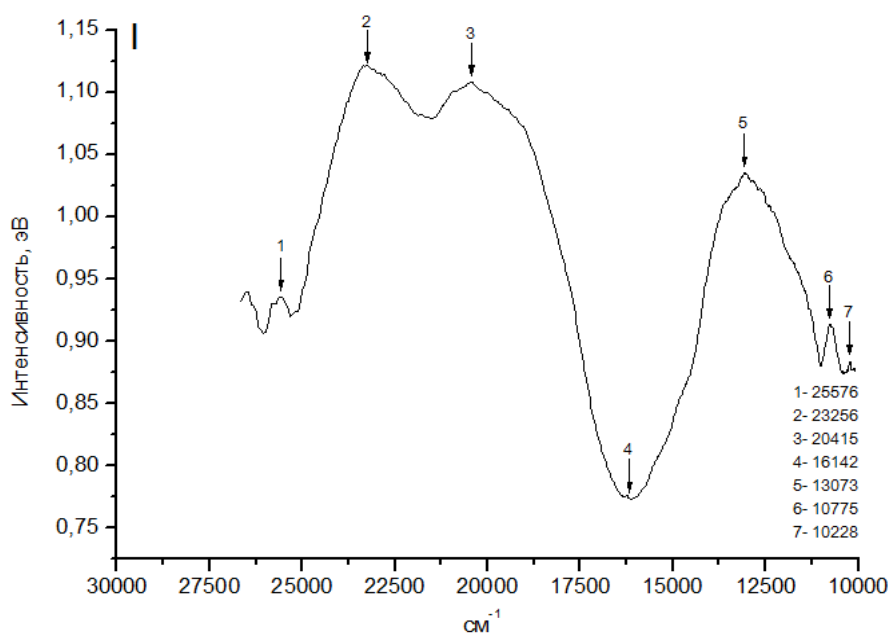


Fig. 2. Electronic diffuse reflectance spectra of $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CH}_3\text{CONH}_2 \cdot 2\text{NC}_5\text{H}_4\text{CONH}_2 \cdot 2\text{H}_2\text{O}$

Table 2. Comparing the found and calculated values of the electronic spectra of mixed-ligand coordination compounds nicotinate nickel (II)

Compounds	Found value			Calculated value			B %	$p=15B$ B-Rak parametr cm^{-1}
	${}^3A_{2g} \rightarrow {}^3T_{2g}$	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$\Delta=10Dq$		
$\text{Ni}(\text{Hk-H})_2 \cdot 2\text{AA} \cdot 2\text{NK} \cdot 2\text{H}_2\text{O}$	10228	16142	25576	16075	25576	10228	69,23	10967
$\text{Ni}(\text{Hk-H})_2 \cdot 2\text{C} \cdot 2\text{TC} \cdot 2\text{H}_2\text{O}$	10766	16314	26738	16859	26738	10766	71,33	11299

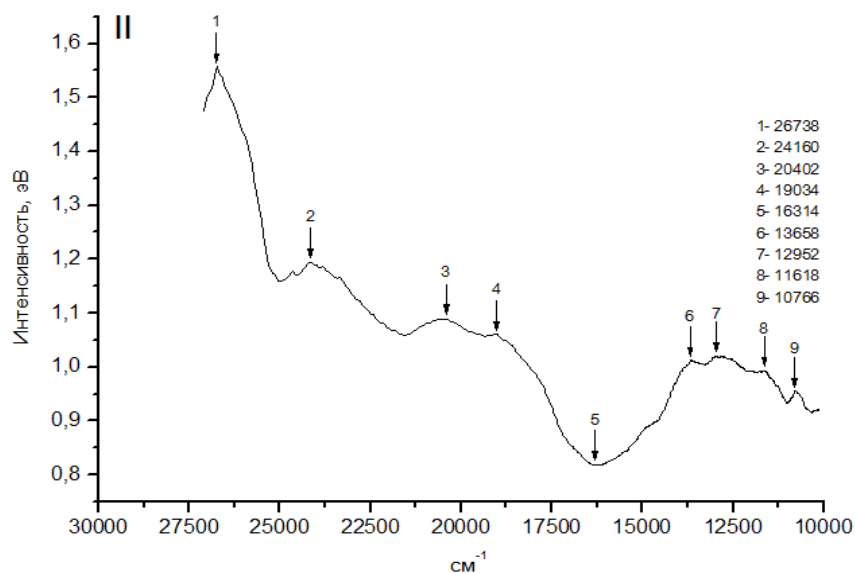


Fig. 3. Electronic diffuse reflectance spectra of $\text{Ni}(\text{NC}_5\text{H}_4\text{COO})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{CS}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$

4. CONCLUSION

Mixed-ligand coordination compounds of nickel-nicotinate are synthesized with the application of the mechanochemical method. Individuality of the synthesized compounds proved by physico-chemical methods of analysis. Coordination centres and denticity acid residue proved by IR spectroscopy. Electronic spectra of the diffuse reflection of the synthesized compounds have shown that the compounds have octahedral coordination geometry, and the coordination number of the central atom is 6. The synthesized compounds are tested as stimulators of cotton growth. The results obtained show that the plants grow faster, have heavier body mass and yield better harvest. It is concluded that the compounds synthesized can be used as environmentally non-hazardous and relatively cheap stimulators of cotton growth.

ACKNOWLEDGEMENTS

The author is thankful to her supervisor Prof. dr. Azizov Tohir Azizovich for his revision and contributions to this article as well as his continuous support. The author is also thankful to two peer reviewers for their revision, comments and suggestions.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Azizov O, Kadirova Z, Azizov T, Tolipov S, Ibragimov B. Catena-poly [[aqua(benzoato-k2O,O') (benzoic acid-kO)calcium]- μ 3-benzoato-k4O:O,O':O']. Acta Cryst. 2011; E67:m 597.
2. Ibragimova MR, Abdullaeva FA, Khasanov Sh. B, Azizov TA. Acid amide coordination compounds of magnesium nicotinate. Journal of Chemical Technology and Metallurgy. Sofia. 2016;51(1):47-52.
3. Aly AAM, Al-Fakeh MS, Ghandour MA, Abu-Zied BM. Possible sonochemical synthesis of nanosized particles mixed ligand metal coordination polymers derived from 1,3-Di(4-pyridyl)propane and Benzimidazole. Advances in Research. 2014;2(12):807-816.
4. Anandakumaran J, Sundararajan ML, Jeyakumar T, Mohammad Nasir Uddin. Transition metal complexes of 4-aminobenzenesulfonamide 1,3-benzodioxole-5-carbaldehyde: Synthesis, Characterization and Biological Activities. American Chemical Science Journal. 2016;11(3):1-14.
5. Ibdullayeva MI, Azizov TA. About nicotinate complex compound of zinc with carbamide. Actual Problems of Modern Science. M. 2011;58(2):172-173.
6. Jebentyayev AI, Jernosek AK, Tatul IE. Analytical chemistry. Chemical methods of

- analysis, Minsk, Novoe Znanie; Moscow, INFRA-M; 2011. (in Russian).
7. Bajenova LN. Quantitative elemental analysis of the organic compounds, Yekateringburg; 2008. (in Russian).
 8. Yakimov IS, Dubinin PS. Quantitative X-ray analiz. IPK SFU; 2008. (in Russian).
 9. Yegorov-Tismenko YK. Crystallography and crystal chemistry. Moscow; 2005. (in Russian).
 10. Kuzmicheva GM. Powder diffraction in materials science. Part 1, MITHT MV Lomonosov Moscow State University; 2005. (in Russian).
 11. Gabbott P, (ed.). Principles and applications of thermal analysis. Singapore, Wiley-Blackwell; 2008.
 12. Shulgin VF, Sotnik SA, Konnik OV. Synthesis spacers trinuclear complexes based trimezinate copper (II), scientific proceedings of Taurida National University named after V. Vernadsky I., Series in «Biology, Chemistry». Simferopol. 2010; 23;62(2):263-269.

© 2016 Ibragimova; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

*The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/14333>*