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СИНТЕЗ, КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА, МОНОЯДЕРНОГО КОМПЛЕКСА НИКЕЛЯ С ЛИГАНДОМ- ВОССТАНОВЛЕННЫМ ТИОСЕМИКАРБАЗОНОМ ГЛИОКСАЛЕВОЙ КИСЛОТЫ (H_2TAA)

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В данной работе синтезированы комплексы Ni (II) с потенциально тридентатным лигандом 2-[2- (аминотиоксометил) гидразинил] уксусной кислотой (H_2TAA). Новый комплекс Ni (II) (1) синтезировали путем взаимодействия нитрата никеля с востановленным боргидридом натрия тиосемикарбазоном глиоксалевой кислоты - 2- [2- (аминотиоксометил) гидразинил] уксусной кислоты (H_2TAA). Строение синтезированных координационных соединений никеля исследованы методами ИК и электронной абсорбционной спектрометрий, элементным анализом и термогравиметрией. Молекулярная структура комплекса $Ni(C_3H_6N_3O_2S)_2$ (1) охарактеризована методом кристаллической дифракции рентгеновских лучей. Рентгеноструктурные исследования показали, что комплекс 1 является моноядерным, в котором координация вокруг металла имеет октаэдрическую геометрию, состоящую из двух атомов серы тиольной группы, двух атомов азота азометиновой группы и двух атомов кислорода карбоксильной группы от двух лигандов. Асимметричная единица комплекса 1 состоит из одного иона Ni (II) и одного лиганда 2- [2- (аминотиоксометил) гидразинил] уксусной кислоты (H_2TAA). Термический анализ был проведен методом ТГА/ДТА. ТГА и ДТА кривые комплекса были получены в атмосфере азота. Термограмма 1 комплекса показывает пять стадий разложения в интервале температур 22–990 °С с разложением при температурах 95–990 °С. Магнитный момент (3,04 Б.М.) комплекса Ni (II) также свидетельствует об октаэдрической геометрии. Электронный спектр комплекса Ni (II) показывает три полосы при 10200 см$^{-1}$, 11000 см$^{-1}$, 16475 см$^{-1}$. H_2TAA ведет себя как двухосновный тридентатный лиганд, координирующий через карбоксилатный кислород, азометиновый азот и тиоловую серу с ионами металлов.

Ключевые слова: тиосемикарбазоны, комплексы никеля (II), кристаллическая структура

SYNTHESIS, CRYSTAL STRUCTURE OF NICKEL MONONUCLEAR COMPLEX WITH REDUCED THIOSEMICARBAZONE OF GLYOXYLIC ACID (H_2TAA)

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Ni (II) complex with potentially tridentate ligand, 2-[2-(aminothioxomethyl) hydrazinyl]acetic acid (H_2TAA), was synthesized. The ligand was obtained via reduction of the corresponding thiosemicarbazone of glyoxylic acid by borohydride. The structure of the synthesized nickel complex coordination compounds has been studied by the methods of IR and electronic absorption spectrometry, elemental analysis, and thermogravimetry. The molecular structure of the complex 1 has been characterized by crystal X-ray diffraction. X-ray diffraction studies have shown that the $Ni(C_3H_6N_3O_2S)_2$ (1) complex is mononuclear, in which the coordination around the metal is octahedral coordination geometry of nickel, made up of two sulfur atoms of thiolic, two nitrogen atoms

of the azomethine group and two oxygen atoms of carboxylate from two ligands. The asymmetric unit of the complex 1 consists of one Ni(II) ion and one 2-[2-(aminothioxomethyl)hydrazinyl]acetic acid (H_2TAA) ligand. The thermal properties of the synthesized complex were investigated by TGA/DTA. TGA and DTA curves of the complex was obtained in the nitrogen atmosphere.The thermogram of 1 complex shows five decomposition steps within the temperature range of 22–990 °C with decomposition steps in the temperature range of 95–990 °C. The magnetic moment (3.04 B.M.) of the Ni(II) complex is indicative of the octahedral geometry. The electronic spectrum of the Ni(II) complex shows three bands at 10.200 cm^{-1}, 11.000 cm^{-1}, 16.475 cm^{-1}.

Key words: thiosemicarbazones, nickel(II) complex, crystal structure

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INTRODUCTION

Thiosemicarbazones and its derivatives have been the subject of interest of researchers in various syntheses. The structures possessing O, N and S atoms leads to various coordination chemistryin the presence of thiosemicarbazones molecules.Metal complexes with these ligands may have a mononuclear, binuclear and polymeric structure [1-3]. Thiosemicarbazones are of great importance because of biological, medicinal, pharmacological and analytical properties [4-14]. In these compounds properties change depending on the metal atom, coordination modes, connected aldehyde or ketone and substituents on aldehyde-ketone [15-19]. Metal complexes with these ligands may have a mononuclear, binuclear and polymeric structure [20]. Mononuclear and binuclear structures are known for complexes of Ni(II) with similar ligands [21]. Monodentate [22], bidentate [23] and polymeric [24] structures are known for Ni(II) complexes with other ligands.

In this study, we have synthesised a new complex of Ni(II) with the H_2TAA ligand obtained as the result of the hydrogenation of hydrazone derived from thiosemicarbazone of glyoxalic acid. Coordination around the metal is octahedral, consisting of two sulfur atoms, two nitrogen atoms, and two oxygen atoms of two ligands. The structure and its properties of this compound are studied. X-ray diffraction studies have shown that the $Ni(C_3H_6N_3O_2S)_2$ complex is mononuclear tridentate. The structure of the synthesized complex has full from structural the connection received in nickel nitrate interaction with thiosemicarbazone of glyoxylic acid (H_2GAT) [1].

EXPERIMENTAL

All reactants and solvents were of reagent grade. The ligand H_2TAA was prepared according to the procedure described earlier [2]. Carbon, nitrogen, hydrogen and sulfur analyses were performed using Perkin Elmer 2400 Series H Elemental Analyser. IR spectra were recorded on a NicoletIS10 Spectrometer using KBr discs in the range of 4000-400 cm^{-1}. Magnetic moments at 25 °C were determined using the Faraday method with $Hg[Co(SCN)_4]$ as calibrant.

Synthesis of the ligand $C_3H_5N_3SO_2$-H_2GAT

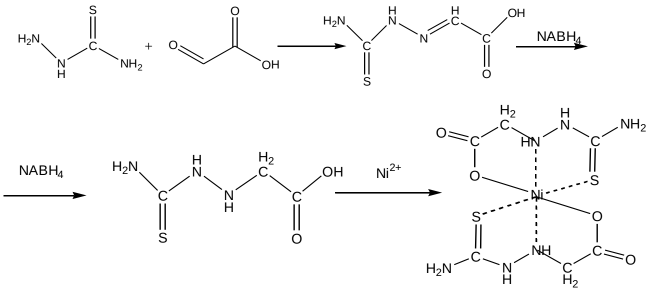
0.69 g (0.01 mol) of glyoxylic acid dissolved in 30 ml of water was added to a solution of 1.45 g (0.01 mol) of thiosemicarbazide in 30 ml of water. The obtained solution was stirred for 2 min, after which a yellow microcrystalline powder was precipitated. Analytical Found: C, 24.48; H, 3.43; N, 28.57; S, 21.76; O, 21.76%. Calc. for $C_3H_7N_3SO_2$: C, 24.45; H, 3.46; N, 28.55; S, 21.77; O, 21.77%. M.p. 165 °C. IR (KBr, cm^{-1}): 3626(m), 3324(ms), 3282(s), 3171(vs), ν(NH), ν(OH); 1760(s), 1630(as), ν(C=O), ν_{as}(COO); 1599(s), (CN); 1463(ms), ν_s(COO); 1377(vs), 1312(ms), 1272(ms), ν(C–OH); 1202(vs), ν(NCS); 723(vs), 708(s), ν(C=S).

Synthesis of the ligand $C_3H_7N_3SO_2$-H_2TAA

The ligand H_2GAT 1.47 g (0.01 mol) was dissolved in 5 ml water by mixing it in a magnetic stirrer, and $NaBH_4$ was added in the appropriate proportions. The pH was neutralised and stored for one day to settle in the refrigerator. After which a white microcrystalline 2-[2-(aminothioxomethyl)hydrazinyl]acetic acid (H_2TAA) powder was precipitated. The product was filtered, washed and dried in air. Analytical Found: C, 24.48; H, 3.43; N, 28.57; S, 21.76; O, 21.76%. Calc. for $C_3H_7N_3SO_2$: C, 24.45; H, 3.46; N, 28.55; S, 21.77; O, 21.77%. M.p. 130 °C. IR (KBr, cm^{-1}): 3626(m), 3324(ms), 3282(s), 3171(vs), ν(NH), ν(OH); 1760(s), 1630(as), ν(C=O), ν_{as}(COO); 1599(s), (CN); 1463(ms), ν_s(COO); 1377(vs), 1312(ms), 1272(ms), ν(C–OH); 1129(vs), ν(NCS); 721(vs), 788(s), ν(C=S).

Synthesis of the complex $Ni(C_3H_6N_3O_2S)_2$

$Ni(NO_3)_2·4H_2O$ (molar ratio Ni:H_2TAA 1:1) dissolved in 20 ml of water was added to a solution of 0.15 g (1 mmol) of 2-[2-(aminothioxomethyl)hydrazinyl]acetic acid (H_2TAA) dissolved in 20 ml of water. The resulting blue solution was stirred at room temperature for 5 min and then was allowed to stand. Blue crystals were grown by slow evaporation (Scheme1**)**. Analytical and spectroscopic data correspond to the minimal formula $Ni(C_3H_6N_3O_2S)_2$Analytical Found: C, 20.28; H, 3.38; N, 23.66; S, 18.02%. Calc. for $NiC_6H_{12}N_6O_4S_2$: C, 20.61; H, 3.13; N, 21.98; S, 17.58%. IR (KBr, cm^{-1}): 3544(m), 3412(ms), 3293(s), ν(NH), ν(OH); 1685(s), ν(C=O), ν_{as}(COO); 1603(s), ν(CN); 1462(ms), ν_s(COO); 1377(vs), 1340(ms), 1279(ms), ν(C−OH); 1196(vs), ν(NCS); 911(vs), 825(s), ν(C=S).



Scheme 1. Synthesis of Ni(II) complex with 2-[2-(aminothioxomethyl)hydrazinyl]acetic acid (H_2TAA)

Схема 1. Синтез комплекса Ni(II) с 2- [2- (аминотиоксометил) гидразинил] уксусной кислотой (H_2TAA)

X-Ray diffraction analysis

Suitable crystal of **1** was selected for data collection which was performed on a D8-QUEST diffractometer equipped with graphite-monochromatic Mo-K_α radiation at 296 K. The structure was solved by direct methods using SHELXS-2013 [25] and refined by full-matrix least-squares methods on F^2 using SHELXL-2013 [26]. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of C atom were located from different maps and then treated as riding atoms with a C-H distance of 0.97 Å. The other H atoms were located in a difference map refined freely. The following procedures were implemented in our analysis: data collection: Bruker APEX2 [27]; program used for molecular graphics were as follow: MERCURY programs [28]; software used to prepare material for publication: WinGX [29]. Details of data collection and crystal structure determinations are given in Table 1.

RESULTS AND DISCUSSION

Infrared Spectra

The interpretation of IR spectra provides valuable information regarding the nature of functional group attached to the metal atom and helped in confirmation of bond formation. In order to study the bonding mode of Schiff base ligand to the central metal atom, IR spectra of the free ligand was compared with the spectra of the complex.The IR spectrum of H_2TAA shows the band at 1760 cm^{-1}, which is attributed to ν(C=O) of the carboxylate group. In the IR spectra of complex, this band is absent.The ν(C–N) band at 1599 cm^{-1} in H_2TAA shifts to a lower frequency in the complex indicating the involvement of azomethine nitrogen in connection with metal ions. Two strong of ν(C=S) bands at 1129 cm^{-1} and 721-788cm^{-1} in H_2TAA disappeared in the complex. This observation involves the hydrogenation of the Schiff base and the coordination of thiol sulfur to the metal ions. In his complex, two new bands observed in the 694-475 cm^{-1} and 448-432 cm^{-1} are tentatively assigned to ν(M–N) and (M–O), respectively. ν(M–S) expected at 350-390 cm^{-1} is not obtained with KBr sample preparing. The most significant Shifts are observed in the 1700-1500 cm^{-1} region; in particular, only one absorption, at 1685 cm^{-1}, is observed in the spectrum of $Ni(HTAA)_2$ ($\Delta\nu$ = 35 cm^{-1} with respect to the free H_2TAA), where the ligand is deprotonated. As far as the involving the CN and CS groups are concerned, the variations of the frequency values upon coordination suggest an ONS terdentate ligand behavior, in agreement with previously reported data [30, 31].

Magnetic moment and electronic spectra

The magnetic moment (3.04 B.M.) of the Ni(II) complex is indicative of the octahedral geometry [32]. The electronic spectrum of the Ni(II) complex shows three bands at 10200 cm^{-1}, 11000 cm^{-1}, 16475 cm^{-1}, which are assigned to $^3A_{2g} \rightarrow {}^1E$, $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A \rightarrow {}^3T_1$ transitions, respectively and support the octahedral structure of the complex. H_2TAA behaves as a dibasic tridentate ligand coordinating through the carboxylate oxygen, azomethine nitrogen and thiol sulfur to the metal ions.

Thermal Analysis (TG)

The thermal stability of the complex was performed in the temperature range 22 to 990 °C under an nitrogen atmosphere using the thermogravimetric analysis technique.The thermal decompositions of the thiosemicarbazone complexes have been studied by many researchers and show similar thermal decomposition behavior [1-3]. The observed trend is the formation of NiO or NiS as final residue. However, the synthesized nickel complex in this study showed unexpected behavior [33]. The thermogram of **1** complex shows five decomposition steps within the temperature range of 22-990 °C.The first step of decomposition water molecule, mass loss of 17.538%. The subsequent three steps (2nd, 3rd, and 4th) (255-990°C) correspond to the removal of the organic part of the ligand leaving metal oxide as a residue. The overall weight loss amounts to 61.85%. The residue of nickel oxide is 35.04%.

X-ray structural determination

Complex **1**

The molecular structure of complex **1**, with the atom numbering scheme, is shown in Fig. 1. The asymmetric unit of the complex **1** consists of one Ni(II) ion and one2-[2-(aminothioxomethyl)hydrazinyl]acetic acid (H_2TAA)ligand. The Ni(II) ion is located on a centre of symmetry and coordinated by two oxygen [Ni1-O1 = 2.052(3) Å], two nitrogen [Ni1-N3 = 2.110(4) Å] and two sulfur [Ni1-S1 = 2.4028(13) Å] atoms from two different 2-[2-(aminothioxomethyl)hydrazinyl]acetic acid (H_2TAA) ligands, thus showing a distorted octahedral coordination geometry. The molecules of **1** are connected by N-H···O hydrogen bonds (Table 3). In **1**, atom N3 in the molecule at (x, y, z) acts as the hydrogen-bond donor to O1^{iv} atom, so forming a centrosymmetricR_2^2(8) ring [(iv) x, y+1, z]. Similarly, atom N2 in the molecule at (x, y, z) acts as hydrogen-bond donor to O2^{ii} atom, so forming a centrosymmetricR_2^2(14) ring [(ii) -x+1/2, -y+3/2, -z+1]. The combination of R_2^2(8) and R_2^2(14) rings running parallel to the [010] direction (Fig. 2a). The combination of other N-H···O hydrogen bonds produces edge-fused R_2^1(6)R_2^2(12) rings which are running parallel to the *ac* plane (Fig. 2b).

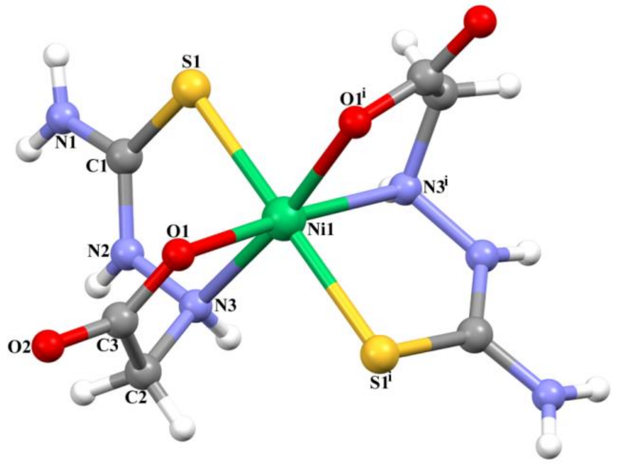


Fig. 1. The molecular structure of complex 1 showing the atom numbering scheme [(i) -x+1, y, -z+3/2]

Рис. 1. Молекулярная структура комплекса 1, показывающая схему нумерации атомов [(i) -x+1, y, -z+3/2]

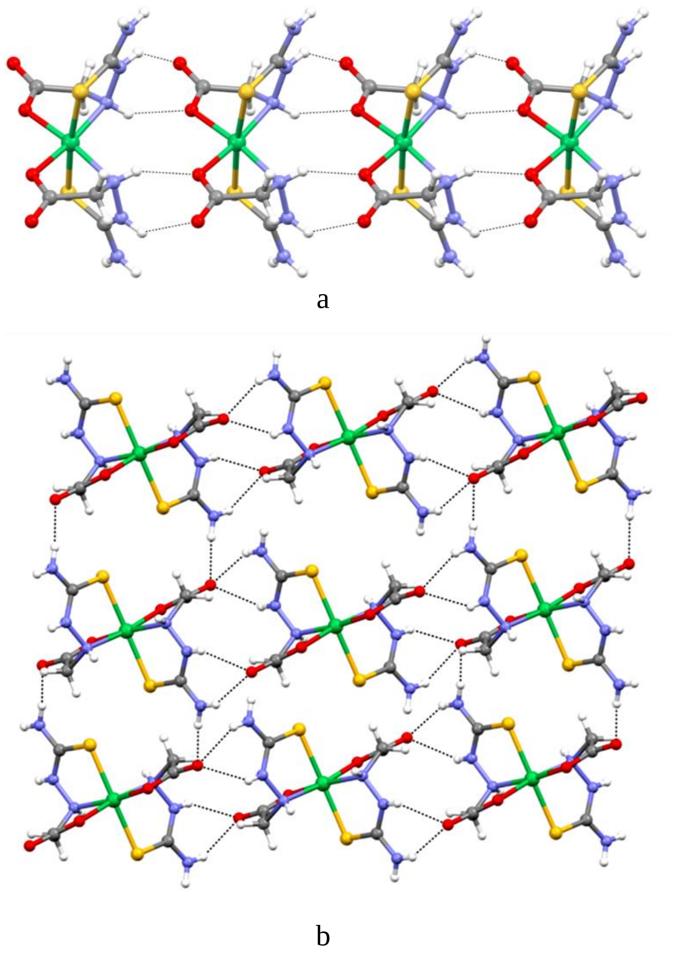


Fig. 2. a) An infinite 1D, b) 2D layer in 1

Рис. 2. а) Бесконечное 1D, в) 2D слой в 1

Table 1

Crystal data and structure refinement parameters for 1

Таблица 1. **Кристаллические данные и параметры уточнения структуры для 1**

Empirical formula	$C_6H_{12}N_6NiO_4S_2$
Formula weight	355.05
Crystal system	Monoclinic
Space group	C2/c
a (Å)	20.473 (3)
b (Å)	5.5012 (8)
c (Å)	14.022 (3)
β (º)	125.666 (11)
V (Å^3)	1283.0 (4)
Z	4
D_c (g cm^{-3})	1.838
θ range (º)	2.9-28.3
Measured refls.	14799
Independent refls.	1254
R_{int}	0.083
S	1.25
R1/wR2	0.056/0.127
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	1.37/-1.04

Table 2

Selected bond distances and angles for 1 (Å, º)

***Таблица 2*. Выбранные расстояния и углы скрепления для 1 (Å, º)**

Bond lengths			
Ni1-O1	2.052(3)	Ni1-N3	2.110(4)
Ni1-S1	2.4028(13)		
Bond angles			
O1-Ni1-O1^{i}	95.98(18)	O1-Ni1-N3^{i}	172.76(15)
N3-Ni1-N3^{i}	103.5(2)	O1-Ni1-N3^{i}	80.60(14)
O1-Ni1-S1	93.74(11)	O1-Ni1-S1^{i}	90.17(11)
N3-Ni1-S1^{i}	92.65(11)	N3-Ni1-S1	83.72(11)

Symmetry code: (i) -x+1, y, -z+3/2.

Код симметрии: (i) -x+1, y, -z+3/2.

Table 3

Hydrogen-bond parameters for 1 (Å, º)

***Таблица 3*. Параметры водородной связи для 1 (Å, º)**

D-H· · ·A	D-H	H···A	D···A	D-H···A
N1—H1A···O2^{ii}	0.85 (2)	2.22 (4)	2.970 (6)	148
N1—H1B···O2^{iii}	0.86 (2)	2.06 (3)	2.900 (6)	166
N2—H2···O2^{ii}	0.86 (6)	2.34 (6)	3.076 (5)	143
N3—H3···O1^{iv}	0.84 (6)	2.09 (6)	2.833 (5)	147

Symmetry codes: (ii) −x+1/2, −y+3/2, −z+1; (iii) x, −y+1, z+1/2; (iv) x, y+1, z.

Код симметрии: (ii) −x+1/2, −y+3/2, −z+1; (iii) x, −y+1, z+1/2; (iv) x, y+1, z.

CONCLUSION

Nickel complex seems to be influenced significantly by the nature of the metal saltand consequently, independent of the metal: ligand molar ratio and the reaction temperature. $Ni(C_3H_6N_3O_2S)_2$ have prepared based on H_2TAA and have been characterized by elemental analysis, FT-IR and UV-Vis. spectroscopies and X-ray diffraction. It was shown that the Ni(II) ion in aqueous solutions form an octahedral mononuclear complex with 2-[2-(aminothioxomethyl)hydrazinyl]acetic acid (H_2TAA). The metal ion is coordinated by two sulfur atoms, two nitrogen atoms and two oxygen atoms from two ligands, a ligand in this complex carry itself as a tridentate and monoanionic.

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