Research on Nickel(II) Complexes with Aroyl Hydrazones of 5,5-Dimethyl-2,4-Dioxohexanoic Acid Ethyl Ester

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Abstract—Complex compounds of nickel(II) with aroyl hydrazones of 5,5-dimethyl-2,4-dioxohexanoic acid ethyl ester (H_2L^1–H_2L^6) are synthesized and studied. The composition and structure of the obtained complex compounds based on these ligands are established by elemental analysis, infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and X-ray diffraction analysis. The full set of the X-ray diffraction data of the $NiL^6 \cdot 3Py$ complex is deposited in the Cambridge Structural Database (CCDC deposit no. 1911468), and it is available on request from the following site: www.ccdc.cam.ac.uk/data_request/cif

In recent years, the studies in the field of coordination chemistry are distinguished by a consistent trend to transfer the center of gravity from simple mononuclear compounds to more complex systems, which is determined by the search for new molecular materials and catalyst systems in the first place [1–3]. These works, together with the consideration of the geometric and electron structure, make it possible to draw justified conclusions and predict the routes for the directed synthesis of complex compounds with predetermined properties [3–5].

We synthesized [$NiL^n \cdot NH_3$ ($n = 1$–6) and $NiL^6 \cdot 3Py$] complex compounds based on H_2L^1–H_2L^6 (aroyl hydrazones of 5,5-dimethyl-2,4-dioxohexanoic acid ethyl ester) [6–8]. The obtained compounds are diamagnetic; soluble in chloroform, benzene, and pyridine; and practically insoluble in water. The data of the infrared (IR) and proton nuclear magnetic resonance (^1H NMR) spectra indicate the square–planar structure of these complexes.

EXPERIMENTAL

In this study, we used ligands H_2L^1–H_2L^6 synthesized according to [4, 5], nickel(II) acetate, and ammonia (all reagent grade); pyridine (analytical grade); and solvents C_2H_5OH and diethyl ether (reagent grade, distilled).

The synthesis of the $NiL^4 \cdot NH_3$ complex. A hot solution of 1.25 g (0.005 mol) of Ni(II) acetate in 15 mL of concentrated ammonia was gradually added to a solution of 1.59 g (0.005 mol) of benzoyl hydrazone of 5,5-dimethyl-2,4-dioxohexanoic acid ethyl ester (H_2L^4) in 25 mL of ethanol and stirred for 30 min at 60°C. A polycrystalline red precipitate sedimented from the obtained red solution after 5–10 min. The complex was filtered off, rinsed with water and ethanol, and dried in a vacuum desiccator over P_2O_5. The yield of $NiL^4 \cdot NH_3$ was 1.35 g (69%).

Other ammonium complexes of Ni(II) with the corresponding ligands H_2L^1–H_2L^3 and H_2L^5–H_2L^6 were synthesized in a similar manner (Table 1).

The IR absorption spectra were recorded on a Specord 75IR spectrometer in the range 400–4000 cm^{-1} in KBr pellets.

The ^1H NMR spectra of 5 to 10% solutions of the complex compounds were recorded on a Bruker DPX-300 spectrometer (300.13 MHz).

Upon dissolving $NiL^6 \cdot NH_3$ in a large volume of pyridine, single crystals ($NiC_{32}H_{34}N_6O_6$)$_2$ corresponding to the formula $NiL^6 \cdot 3Py$ sedimented. The X-ray diffraction analysis (XRD) of the $NiL^6 \cdot 3Py$ compound was performed on an Xcalibur automated diffractometer (Oxford Diffraction) (λCuK_α radiation,

Table 1. Yields, melting points, and results of the elemental analysis of the complex compounds of Ni(II) based on aroyl hydrazones of 2,4-dioxocarboxylic acid ethyl ester

Compound	Empirical formula	Yield, %	T_m, °C	Found/calculated, %			
				Ni	C	H	N
$NiL^1 \cdot NH_3$	$NiC_{19}H_{28}N_4O_4$	63	297−298	13.43/13.49	52.37/52.44	6.42/6.49	12.94/12.88
$NiL^2 \cdot NH_3$	$NiC_{18}H_{25}N_3O_5$	58	278−280	13.86/13.91	51.15/51.22	5.94/5.97	9.98/9.95
$NiL^3 \cdot NH_3$	$NiC_{18}H_{25}N_3O_4$	66	265−267	14.39/14.45	53.19/53.24	6.17/6.20	10.41/10.35
$NiL^4 \cdot NH_3$	$NiC_{17}H_{23}N_3O_4$	69	258−260	14.91/14.97	52.02/52.08	5.87/5.91	10.78/10.72
$NiL^5 \cdot NH_3$	$NiC_{17}H_{22}N_3O_4Br$	73	304−306	12.42/12.46	43.32/43.35	4.68/4.71	8.95/8.92
$NiL^6 \cdot NH_3$	$NiC_{17}H_{22}N_4O_6$	74	274−276	13.43/13.46	46.69/46.72	5.04/5.07	12.87/12.82
$NiL^6 \cdot 3Py$	$NiC_{32}H_{34}N_6O_6$	78	282−284	8.88/8.93	58.43/58.47	5.17/5.21	8.96/8.93

graphite monochromator, ω scanning, $2\theta_{max} = 50°$). The structure was interpreted and refined by the least squares method on an anisotropic approximation for nonhydrogen atoms. The hydrogen atoms were localized from the electron density maps of the difference Fourier synthesis and refined on the isotropic approximation [9−11].

RESULTS AND DISCUSSION

The investigation of the composition and structure of the complex compounds of nickel(II) obtained based on the condensation products of 5,5-dimethyl-2,4-dioxohexanoic acid ethyl ester with *para*-substituted benzoic acid hydrazides (Scheme 1, I) is discussed in this communication. The results of the elemental analysis and spectroscopic studies made it possible to determine the structure of the obtained compounds (Scheme 1, II).

The composition and structure of the obtained complexes have been determined by elemental analy-

sis and IR and ^{1}H NMR spectroscopy. The IR spectrum of the $NiL^1 \cdot NH_3$ complex compound differs from the spectrum of the ligand H_2L^1 by the fact that it has no absorption bands in the region of 1660 to 1700 and 3400 cm^{-1} (Fig. 1). This indicates the deprotonation of the ligand in the process of complex formation.

The IR spectrum of the $NiL^1 \cdot NH_3$ complex is to a great extent similar to the IR spectra of the earlier studied complex compounds of nickel(II) (Fig. 1, Table 2) [4, 12−14]. The presence of an intensive band in the region of 1730 cm^{-1} which is determined by the stretching vibrations of the C=O bond of the ester substituent in the spectrum of the $NiL^1 \cdot NH_3$ complex compound should be noted. This band manifests itself in the region of 1740 to 1750 cm^{-1} in the IR spectrum of the initial ligand that exists in the free state in the hydrazone form. Such a low-frequency shift of $\nu_{(C=O)}$ upon the transition from the ligands to the complexes is determined by the inclusion of the electron-withdrawing −COOC$_2$H$_5$ group into the conjugation sys-
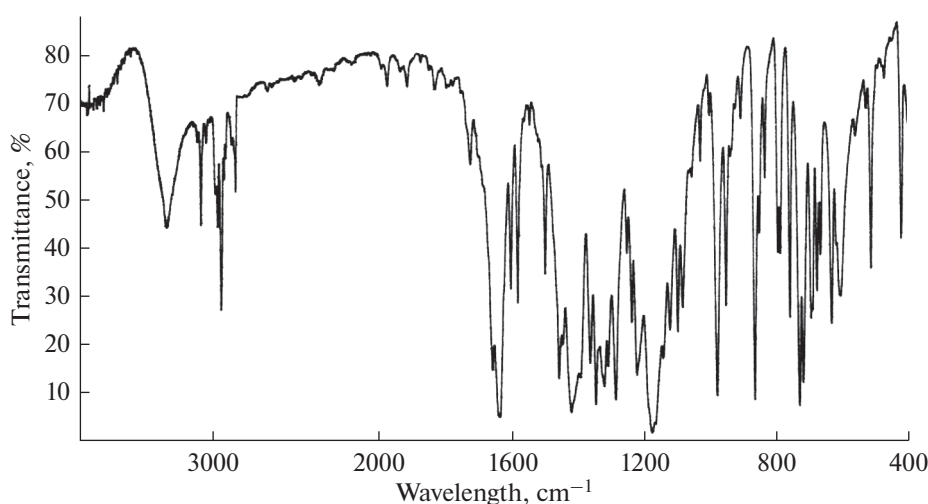

Fig. 1. IR spectrum of the complex compound $NiL^1 \cdot NH_3$.

Table 2. Parameters of the IR spectra of the complex compounds of Ni(II) based on aroyl hydrazones of 2,4-dioxocarboxylic acid ethyl ester

Compound	NH_3	C–H	C=N	N=C–C=N	N=C–O⁻	N–N	Ni–O
$NiL^1 \cdot NH_3$	3354	2975	1600	1525	1494	1068	483
$NiL^2 \cdot NH_3$	3360	2972	1608	1532	1507	1071	490
$NiL^3 \cdot NH_3$	3345	2973	1595	1523	1464	1075	475
$NiL^4 \cdot NH_3$	3355	2984	1600	1527	1488	1073	490
$NiL^5 \cdot NH_3$	3358	2976	1605	1531	1489	1075	487
$NiL^6 \cdot NH_3$	3357	2977	1599	1528	1484	1070	488
$NiL^6 \cdot 3Py$	–	2976	1595	1530	1486	1070	485

tem with its six-membered metal cycle. Some medium- and strong-intensity bands in the region of 1400 to 1620 cm⁻¹ in the IR spectrum of the complex should be related to the predominantly stretching and deformation vibrations of the sesquialteral bonds in the five- and six-membered metal cycles [4, 5, 7, 12]. Absorption bands in the region of 3375, 3337, 3280,

and 3170 cm⁻¹ are also observed in the IR spectrum of the $NiL^1 \cdot NH_3$ complex, which should be assigned to the symmetric and antisymmetric stretching vibrations of an ammonia molecule. As expected, there are no absorption bands in this region in the IR spectrum of $NiL^6 \cdot 3Py$, and a band near 1600 cm⁻¹, which has been assigned to $\nu_{(C=N)}$ of pyridine [3–7, 12, 17], appears.
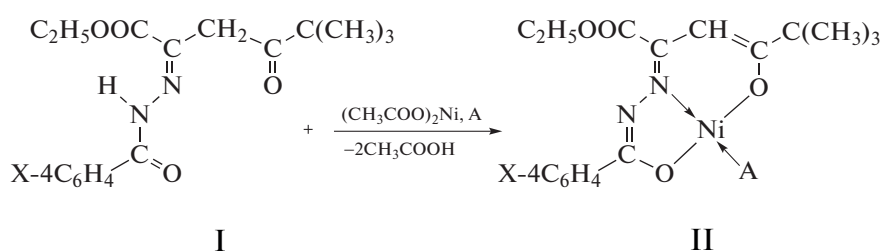
$A = NH_3$: $X = N(CH_3)_2(NiL^1 \cdot NH_3)$; $OCH_3(NiL^2 \cdot NH_3)$; $CH_3(NiL^3 \cdot NH_3)$;

$H (NiL^4 \cdot NH_3)$, $Br (NiL^5 \cdot NH_3)$, $NO_2 (NiL^6 \cdot NH_3)$; $X = NO_2$, $A = Py(NiL^6 \cdot 3Py)$;

Scheme 1.

The ¹H NMR spectra of the complexes under study make it possible to acquire the following information. The ¹H NMR spectrum of the $NiL^4 \cdot NH_3$ compound in a solution in $CCl_4 + d_6$-DMSO with benzoyl hydrazone of β-ketoester is very similar to the spectra of the complexes of nickel with various acyl and aroyl hydrazones of β-diketones, β-ketoaldehydes, and β-ketoesters (Fig. 2) [3–8, 12, 17]. It should be noted that the signals from the protons of the ethyl radical of the C_2H_5OOC ester group (as well as other terminal products) clearly manifest themselves. The signals in the form of a triplet from the three protons of the $-CH_3$ group have been recorded at δ of 1.36 ppm, and the protons of the $-CH_2$ group resonate in the form of a quadruplet at δ of 4.28 ppm, integral intensity ratio of 3 : 2, and spin-spin coupling constant (SSCC) $J_{AB} = 7$ Hz. The signals from the single vinyl proton have been recorded

at δ of 5.03 ppm, and the nine protons of the *tert*-C_4H_9 substituent resonate in the form of a singlet at δ of 0.99 ppm. The multiplet signals from the protons of the phenyl radical of the hydrazone fragment of the molecule resonate in the region of weak fields with the centers at δ of 7.14 and 7.67 ppm. The shape of the signals is somewhat complicated in terms of their overlapping. The signal from the protons of the coordinated NH_3 molecule in the form of a singlet with the intensity of 3H has been recorded at δ of 2.07 ppm (Fig. 2, Table 3).

Upon dissolving the ammonium complex $NiL^6 \cdot NH_3$ based on *para*-nitrobenzoyl hydrazone of 5,5-dimethyl-2,4-dioxohexanoic acid ethyl ester (H_2L^6) in an excess of pyridine, crystals that sharply differ from their analogues with respect to the molecular structure have been isolated as opposed to the earlier grown single crystals with the square–planar structure of the $NiL \cdot NH_3$ type
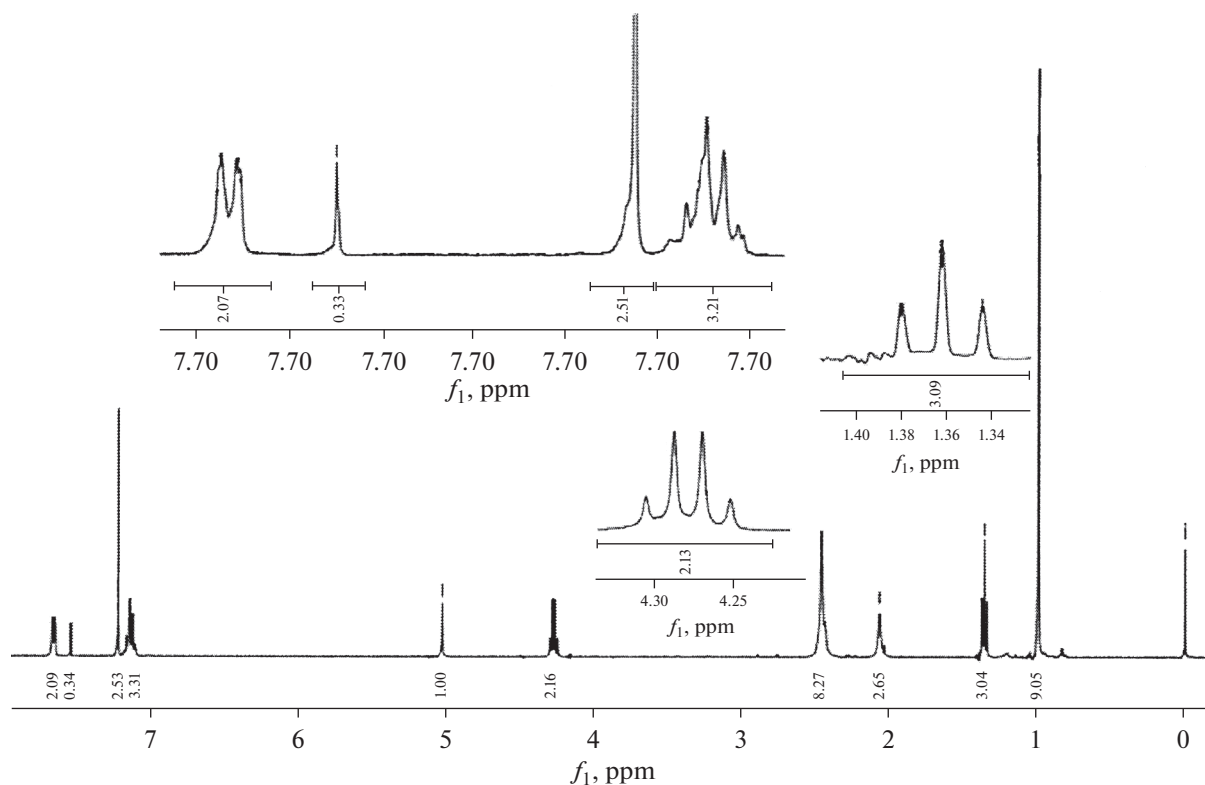
Fig. 2. ^{1}H NMR spectrum of the complex compound NiL^4 · NH$_3$ in a solution in CCl$_4$ + d$_6$-DMSO (δ, ppm).

[4–8, 12]. The coordination sphere of the Ni(II) ion in the crystal has an octahedral structure with a set of donor atoms Ni(*trans*-N$_4$O$_2$) due to the replacement of ammonia by pyridine and additional coordination of two pyridine molecules to the axial positions (Fig. 3, Table 4).

The structure of (NiC$_{32}$H$_{34}$N$_6$O$_6$)$_2$ was subjected to an XRD study on an Xcalibur automated diffractometer (Oxford Diffraction) (CuK_α radiation, graphite monochromator, ω scanning, 2θ$_{max}$ = 50°). The crystals with the composition (NiC$_{32}$H$_{34}$N$_6$O$_6$)$_2$ are triclinic with the following unit cell parameters: a = 9.5826 (5), b = 14.1432 (6), and c = 26.1557 (13) Å; α = 76.300 (4)°; β = 89.447 (4)°; γ = 73.234 (4)°; V =

3291.0 (3) Å^3; ρ$_{calc}$ = 1.659 g/cm^3; Z = 2; and sp. gr. P-1. Such changes in the coordination sphere from square–planar (through square–pyramidal) to an octahedral polyhedron were earlier studied by us by way of example of both mononuclear complexes of copper(II) and heterobinuclear complexes of nickel(II) and copper(II) [8, 12].

A NiL^6 · 3Py molecule has an octahedral structure, and the doubly protonated tridentate ligand residue forms fused five- and six-membered metal cycles around the nickel(II) ion (Fig. 3). The Ni−N (1) distance (1.981(2) Å) of the metal chelate is significantly shorter than the lengths of the three Ni−N (4) (2.092 Å), Ni−N (5) (2.164 (2) Å), and Ni−N (6) (2.154 (2) Å)

Table 3. Parameters of the ^{1}H NMR spectra of the complexes of nickel(II) in a solution in CCl$_4$ + d$_6$-DMSO (δ, ppm)

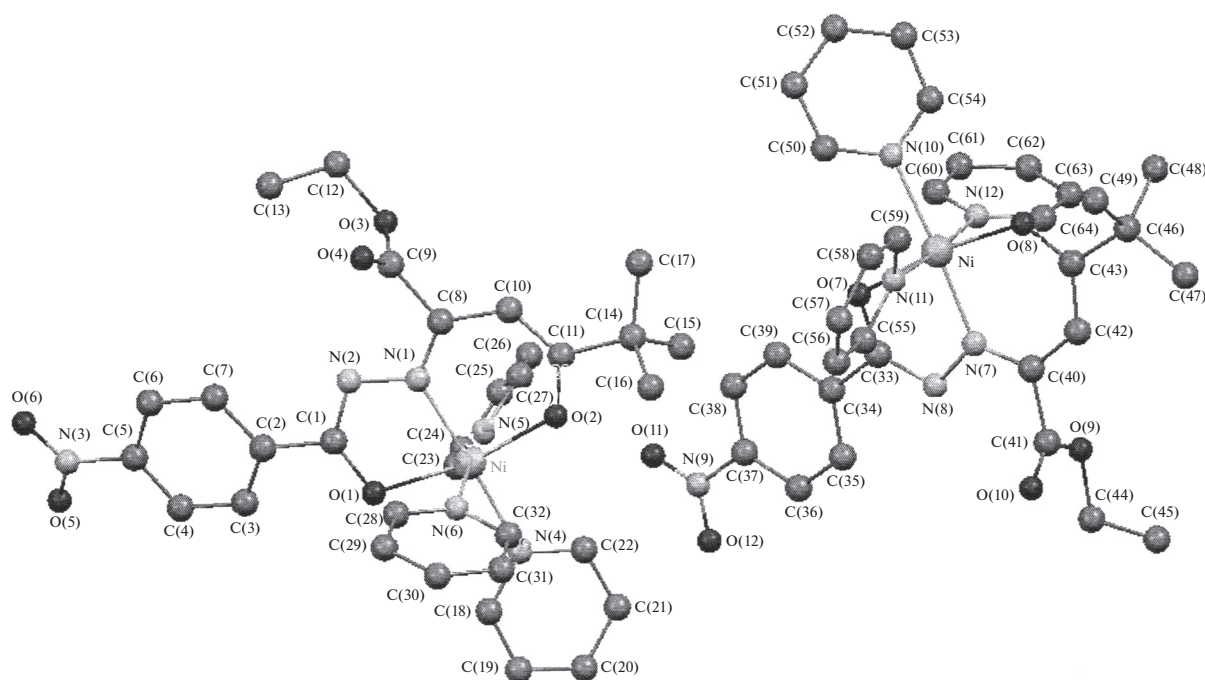| Compound	X	C(CH$_3$)$_3$	−CH=	COOC$_2$H$_5$	NH$_3$	C$_6$H$_4$X
NiL^1 · NH$_3$	2.88	1.04	5.08	1.34; 4.26	2.05	7.35; 7.63
NiL^2 · NH$_3$	2.92	1.06	5.12	1.33; 4.26	2.06	7.37; 7.65
NiL^3 · NH$_3$	2.24	1.05	5.10	1.35; 4.28	2.08	7.40; 7.68
NiL^4 · NH$_3$	−	0.99	5.18	1.36; 4.27	2.07	7.14; 7.25; 7.67
NiL^5 · NH$_3$	−	1.03	5.13	1.37; 4.28	2.06	7.36; 7.63
NiL^6 · NH$_3$	−	0.97	5.32	1.38; 4.28	2.08	7.50; 7.74
NiL^6 · 3Py	−	1.02	5.34	1.39; 4.30	−	7.56; 7.78

Fig. 3. Molecular structure of the complex compound NiL^6 · 3Py with *para*-nitrobenzoyl hydrazone of 5,5-dimethyl-2,4-dioxo-hexanoic acid ethyl ester.

bonds of the donor base. The difference between the lengths of these bonds is determined by their position around the central complex forming ion. The residue of the ligand molecule is coordinated by two oxygen atoms and the nitrogen atom of the hydrazone fragment. Three pyridine molecules occupy the fourth place in the plane square of the *trans*-N$_2$O$_2$ coordination site and two axial positions, thus bringing the environment of the central ion to an octahedral polyhedron. The lengths of the Ni−O (1) 2.0665 Å and Ni−O (2) 2.025 Å bonds are close to the similar values of the bond lengths in the complex compounds of nickel with *trans*-[N$_2$, O$_2$] of the coordination sphere [4, 6, 12−15] studied earlier. The central nickel atom deviates from the NiN(1)N(2)C(1)O(2) average plane of the five-membered metal cycle by 0.0272 Å in comparison with the NiN(1)C(8)-C(10)O(2)C(11) six-membered plane (0.0081 Å). This is explained by the high internal stress of the bonds of the five-membered cycle in comparison with the six-membered cycle. The almost flat five- and six-membered conjugated metal cycles are coplanar between each other, which was discussed earlier in [4, 16, 17]. Upon comparing the structure of the donor pyridine molecules coordinated around the nickel(II) atom in the complex compound, the pyridine molecule with the N(4)C(18)C(19)C(20)C(21)C(22) set of atoms is the most planar in comparison with the two other pyridine molecules coordinated in the axial positions (Table 5). In our point of view, this is explained by the formation of an inverse dative *d*−π bond between the *d* electrons

Table 4. Main crystallographic data and refinement parameters of the structure of NiL^6 · 3Py

Parameter	Value
M	1314.72
Temperature, K	298
Syngony	Triclinic
Sp. gr.	$P\bar{1}$
a, Å	9.5826 (5)
b, Å	14.1432 (6)
c, Å	26.1557 (13)
α, deg	76.300 (4)
β, deg	89.447 (4)
γ, deg	73.234 (4)
V, A^3	3291.0 (3)
Z	2
ρcalc, g/cm^3	1.327
μ, mm^{-1}	1.28
Crystal sizes, mm	0.2 × 0.3 × 0.3
Scanning region by θ, deg	3.4−76.2
Index area h, k, l	−11 ≤ h ≤ 11, −17 ≤ k ≤ 14, −32 ≤ l ≤ 32
Reflections collected	24252
Independent reflections (R_{int})	13251 (0.042)
Reflections with $I > 2\sigma(I)$	8945
Number of refine parameters	820
GOOF (F^2)	1.021
R_1, wR_2 ($I > 2\sigma(I)$)	0.0513; 0.1457
R_1, wR_2 (all reflections)	0.051; 0.146
Δρ$_{max}$, Δρ$_{min}$(e Å^{-3})	0.46−0.48

Table 5. Deviation of the atoms from the average planes in the structure of NiL^6 · 3Py

Atom and its deviation, Å							
C (1)	C (2)	C (3)	C (4)	C (5)	C (6)	C (7)	
−0.0392	0.0263	0.0275	−0.0074	−0.0265	−0.0022	0.0215	
Ni (1)	C (1)	N (1)	N (2)	O (1)			
−0.0272	−0.0261	0.0291	−0.0106	0.0347			
Ni (1)	N (1)	C (8)	C (10)	O (2)	C (11)		
0.0081	0.0064	−0.0153	0.0059	−0.0206	0.0155		
C (8)	C (9)	O (3)	O (4)	C(12)* −	C(13)*		
0.0038	−0.0138	0.0045	0.0055	0.0226	−1.4119		
N (4)	C (18)	C (19)	C (20)	C (21)	C (22)	Ni (1)*	
−0.0010	0.0003	0.0009	−0.0015	0.0008	0.0004	−0.0939	
N (6)	C (23)	C (24)	C (25)	C (26)	C (27)	Ni (1)*	
0.0126	−0.0229	0.0049	0.0196	0.0113	−0.0256	−0.1018	
N (5)	C (28)	C (29)	C (30)	C (31)	C (32)	Ni (1)*	
0.0549	−0.1011	0.0263	0.0966	0.0278	−0.1045	−0.1948	
C (33) −	C (34) −	C (35) 0.0031	C (36) 0.0092	C (37) −	C (38)	C (39)	N (9)*
0.0050	0.0052			0.0147	0.0019	0.0107	−0.0174
C (33)	N (8)	N (7)	N (12)	O (7)			
0.3328	0.3952	−0.5105	0.2425	−0.4601			
Ni (2)	C (42)	C (43)	C (40)	N (7)	C (8)	C (46)*	C (47)*
−0.0433	−0.0376	−0.0070	0.0159	0.0260	0.0460	−0.0230	−0.1030
C (40)	C (41)	C (44)	O (9) 0.0580	O (10)			
−0.0346	0.0112	−0.0451		0.0104			
N (10)	C (50)	C (51)	C (52)	C (53)	C (54)	Ni (2)*	
−0.0073	−0.0010	0.0109	−0.0128	0.0047	0.0055	−0.2420	
N (11)	C (55)	C (56)	C (57)	C (58)	C (59)	Ni (2)*	
−0.0060	−0.0042	0.0078	−0.0018	−0.0081	0.0122	0.0286	
N (12)	C (60)	C (61)	C (62)	C (63)	C (64)	Ni (2)*	
−0.0125	0.0131	−0.0030	−0.0076	−0.0081	0.0018	−0.0595	

* Atoms not included in the calculation of this plane.

of the Ni(II) ion and π orbital of the pyridine molecule (Table 5). The packing of the structural units in the crystal of a NiL^6 · 3Py molecule is shown in Fig. 4.

It has been found as a result of the studies by IR and ^{1}H NMR spectroscopy that, in the process of complex formation, the initial ligands with the 5-hydroxy-2-pyrazoline structure transform into a linear enehydrazine−oxyazine form and coordinate with the central ion by the three donor (N, O$_2$) atoms. It has been shown by XRD that, in the process of complex forma-
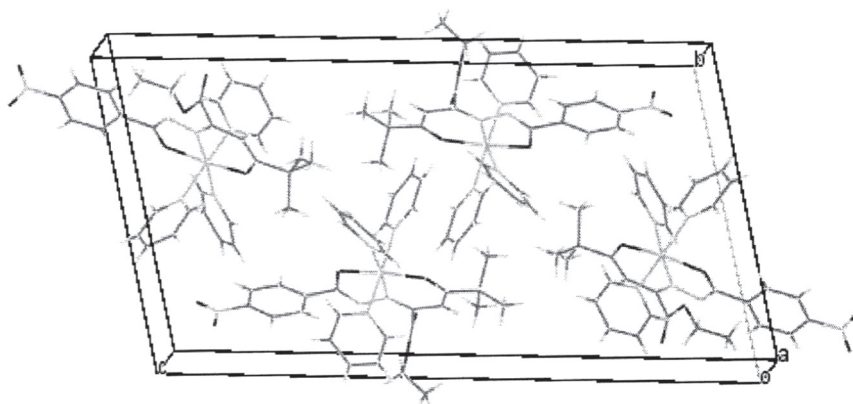

Fig. 4. Projections of the crystal packing of NiL$_6$ · 3Py molecules on the *ac* plane.

tion, the cycle-shaped doubly deprotonated 5-hydroxy-2-pyrazoline residue of the ligand H_2L^4 transforms into a linear enehydrazine−oxyazine form and coordinates with the central ion to form coupled five- and six-membered pseudoaromatic metal cycles $[N_2, O_2]$ where the fourth place is occupied by an ammonia molecule. In the case of recrystallization of the molecules of the complex compound $NiL^6 \cdot NH_3$ based on *para*-nitrobenzoyl hydrazone of 5,5-dimethyl-2,4-dioxohexanoic acid ethyl ester (H_2L_6) in an excess of pyridine, crystals $(NiC_{32}H_{34}N_6O_6)_2$ of two $NiL^6 \cdot 3Py$ molecules with the octahedral environment of the central atom sediment.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Agrawal, A., Sharma, K.M., and Prasad, R.N., *Pol. J. Chem.*, 2007, vol. 81, no. 12, p. 2081.
2. Pakal'nis, V.A., Zerova, I.V., Yakimovich, S.I., Ershov, A.Yu., and Lagoda, I.V., *Russ. J. Org. Chem.*, 2009, vol. 45, no. 2, p. 285.
3. Tursunov, M.A. and Umarov, B.B., *Universum: Khim. Biol.*, 2018, no. 3 (45), p. 45.
4. Umarov, B.B., Tursunov, M.A., and Minin, V.V., *Kompleksy s proizvodnymi ketoal'degidov i ketoefirov* (Complexes with the Ketoaldehydes and Ketoesters Derivatives), Tashkent: Nishon Noshir, 2016.
5. Avezov, K.G. and Umarov, B.B., *Universum: Khim. Biol.*, 2017, no. 2 (32), p. 39.
6. Tursunov, M.A. and Umarov, B.B., *Universum: Khim. Biol.*, 2018, no. 12 (54), p. 50.
7. Tursunov, M.A., Avezov, K.G., Umarov, B.B., and Parpiev, N.A., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 4, p. 93.
8. Tursunov, M.A., Umarov, B.B., and Avezov, K.G., *Razvit. Nauki Tekhnol. Nauchno-Tekh. Zh.*, 2018, no. 2, p. 71.
9. CrysAlisPro, version 1.171.33.40, Oxford Diffraction, 2007.
10. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
11. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
12. Umarov, B.B., Complex compounds of some transition metals with bis-5-hydroxypyrazolines, *Extended Abstract of Doctoral (Chem.) Dissertation*, Tashkent, 1996.
13. Kawamoto, T. and Kushi, Y., *Bull. Chem. Soc. Jpn.*, 2004, vol. 77, no. 2, p. 289.
14. Toshev, M.T., Yusupov, V.G., Dustov, Kh.B., and Parpiev, N.A., *Kristallokhimiya kompleksov metallov s gidrazidami i gidrazonami* (Crystal Chemistry of Metal Complexes with Hydrazides and Hydrazones), Tashkent: Fan, 1994.
15. Kogan, V.A., Zelentsov, V.V., Larin, G.M., and Lukov, V.V., *Kompleksy perekhodnykh metallov s gidrazonami. Fiziko-khimicheskie svoistva i stroenie* (Complexes of Transition Metals with Hydrazones: Physical and Chemical Properties and Structure), Moscow: Nauka, 1990.
16. Umarov, B.B., Toshev, M.T., Saidov, S.O., et al., *Koord. Khim.*, 1992, vol. 18, no. 9, p. 980.
17. Tursunov, M.A., Avezov, K.G., and Umarov, B.B., *Moscow Univ. Chem. Bull. (Engl. Transl.)*, 2019, vol. 74, no. 3, p. 138.

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