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SYNTHESIS AND CRYSTAL STRUCTURE OF THE NICKEL(II) COMPLEX WITH AROYL HYDRAZONE OF ETHYL ETHER OF 5,5-DIMETHYL-2,4-DIOXOHEXANE ACID

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Coordination complexes of nickel(II) with aroyl hydrazones of ethyl ether of 5,5-dimethyl-2,4-dioxohexane acid (H_2L^1–H_2L^6) are prepared and studied. The composition and structure of complexes obtained on the basis of these ligands are established by elemental analysis, IR, ^{1}H NMR spectroscopy, and XRD methods. IR and ^{1}H NMR parameters correlate with each other under the variation of the substituents in the *p*-position of the benzene ring located in the hydrazide part of ligand molecules. The ring-chain equilibrium in the complexes is established.

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INTRODUCTION

Recent studies in the field of coordination chemistry demonstrate a steadily increasing interest to more complex systems as opposed to simple mononuclear compounds, primarily due to the search of novel molecular materials and catalytic systems [1-3]. Besides considering geometric and electronic structures, these works allow making valid conclusions and predicting the paths for directed synthesis of coordination complexes with desired properties [4-6]. We synthesized coordination complexes $Ni(L^n)\cdot NH_3$ (n = 1-6) and $Ni(L^6)\cdot 3Py$ with H_2L^1–H_2L^6 ligands (aroyl hydrazones of ethyl ether of 5,5-dimethyl-2,4-dioxohexane acid) [7-9]. The red color of obtained complexes indicates their diamagnetism; they are soluble in chloroform, benzene, pyridine, and are virtually insoluble in water. The complexes have a square-planar structure, as is testified by their diamagnetic nature and obtained ^{1}H NMR data.

EXPERIMENTAL

In this work we used H_2L^1–H_2L^6 ligands synthesized according to [8, 9], nickel(II) acetate, ammonia (all reagent grade), pyridine (analytical grade), and EtOH and diethyl ether solvents (reagent grade, distilled).

Synthesis of complex $NiL^4\cdot NH_3$. A hot solution (1.25 g, 0.005 mol) of Ni(II) acetate in 15 mL of concentrated ammonia was gradually added to the solution (1.59 g, 0.005 mol) of aroyl hydrazone of ethyl ether of 5,5-dimethyl-2,4-dioxohexane acid (H_2L^4) in 25 mL of ethanol and stirred for 30 min at 60 °C. As a result, a red solution was obtained from

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TABLE 1. Yield, Melting Temperature, and Elemental Analysis Data for Ni(II) Coordination Complexes Based on Aroyl Hydrazones of Ethyl Ether of 2,4-Dioxocarbone Acids

Compound	Empirical formula	Yield,%	T_m, °C	Found / calculated,%			
				M	C	H	N
$NiL^1 \cdot NH_3$	$NiC_{19}H_{28}N_4O_4$	63	297	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	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	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	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	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	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	8.88 / 8.93	58.43 / 58.47	5.17 / 5.21	8.96 / 8.93

which red crystals precipitated in 5-10 min. The crystals were filtered, washed with water, 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 Ni(II) ammonium complexes with the corresponding ligands H_2L^1–H_2L^3 and H_2L^5–H_2L^6 (Table 1)were synthesized similarly.

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

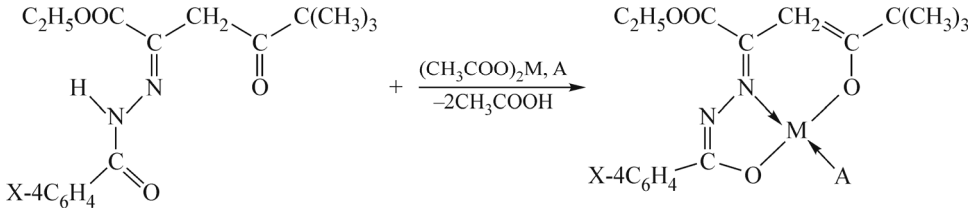
The ^1H NMR spectra of five to ten percent solutions of coordination complexes in d^6-DMSO were recorded on a Bruker DPX-300 spectrometer with an operating frequency of 300.13 MHz. The signals were calibrated with respect to the tetramethylsilane standard with $\delta = 0.00$ ppm.

Monoclinic crystals $NiC_{17}H_{23}N_3O_4$ were prepared by the recrystallization of $NiL^4 \cdot NH_3$ from an ethanol-chloroform mixture, and $NiL^6 \cdot 3Py$ [$2(NiC_{32}H_{34}N_6O_6)$] single crystals suitable for XRD were isolated from a solution of $NiL^6 \cdot NH_3$ in a large volume of pyridine.

The XRD study of $NiL^4 \cdot NH_3$ and $NiL^6 \cdot 3Py$ crystals was conducted on an Xcalibur (Oxford Diffraction) automated diffractometer ($\lambda Cu K_\alpha$ radiation, graphite monochromator, ω scanning, $2\theta_{max} = 50°$). The structures were solved and refined by full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were localized from the electron density maps of the difference Fourier synthesis and refined isotropically [10-12].

RESULTS AND DISCUSSION

This work presents a study of the composition and structure of nickel(II) coordination complexes obtained from the condensation product of ethyl ether of 5,5-dimethyl-2,4-dioxohexane acid with hydrazides of *p*-substituted benzoic acids. The composition and structure of the complexes were determined using elemental analysis, IR, and ^1H NMR methods (Scheme 1):



Scheme 1. 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($NiL^6 \cdot NH_3$); A = Py, X = NO_2($NiL^6 \cdot 3Py$).

The IR spectrum of the $NiL^3 \cdot NH_3$ coordination complex differs from that of the H_2L^3 ligand in that it contains no absorption bands in the region of 1660-1700 cm^{-1} and at 3400 cm^{-1} (Table 2, Fig. 1). This fact indicates that the ligand is deprotonated upon the complexation. The IR spectrum of the $NiL^3 \cdot NH_3$ complex is largely identical to the IR spectra of previously studied nickel(II) coordination complexes (Fig. 1) [6, 13, 14]. The IR spectrum of the $NiL^3 \cdot NH_3$ complex contains also absorption bands at 3345 cm^{-1}, 3337 cm^{-1}, 3280 cm^{-1}, and 3170 cm^{-1} which should be assigned to ν_s and ν_{as} vibrations of the coordinated ammonia molecule. Note also that the spectrum of this compound contains an intense band at 1730 cm^{-1} corresponding to the ν(C=O) frequency of the substituent ether and a no less intense band corresponding to the frequency ν(C=N) = 1595 cm^{-1}. The IR spectrum of the initial ligand (existing in a free state in the hydrazone form A) contains this band at 1740-1750 cm^{-1}. The low-frequency shift of ν(C=O) in the complexes as compared to its value in the ligands is due to the fact that the electron-accepting group $–COOC_2H_5$ is included in the six-membered conjugation system of the complex. In the IR spectrum of the complex, several bands of moderately and highly intense bands in the region of 1400-1620 cm^{-1} are to be assigned predominantly to stretching and bending vibrations of the conjugation system of bonds of order 1.5 in five- and six-membered metallacycles [15-17].

The analysis of ^1H NMR spectra of studied complexes suggests the following conclusions. The ^1H NMR spectrum of compound $NiL^4 \cdot NH_3$ in the CCl_4 + d_6-DMSO solution with substituted aroyl hydrazone of β-ketoether is very similar to the spectra of nickel complexes with different acyl- and aroyl hydrazones of β-diketones, β-ketoaldehydes, and β-ketoethers (Fig. 2) [9, 10]. The signals from the protons occurring in the ethyl radical of the ether C_2H_5OOC group, as well as the signals of other terminal protons, are clearly manifested. Triplet signals from three protons of the $–CH_3$ group were observed at

TABLE 2. Parameters of IR Spectra of Ni(II) Coordination Complexes Based on Aroyl Hydrazones of Ethyl Ether of 2,4-Dioxocarbone Acids

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

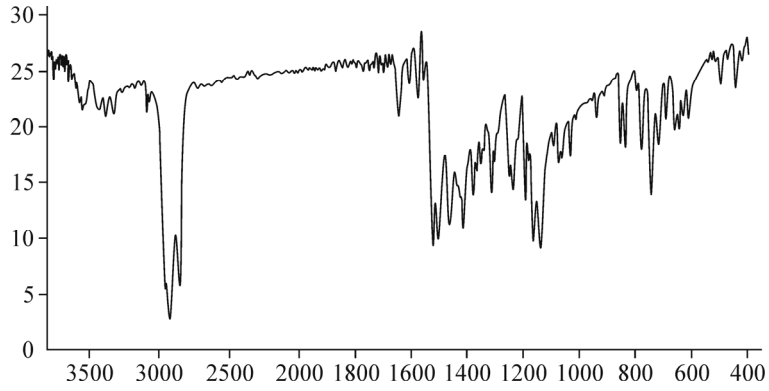


Fig. 1. IR spectrum of the nickel(II) coordination complex $NiL^3 \cdot NH_3$.

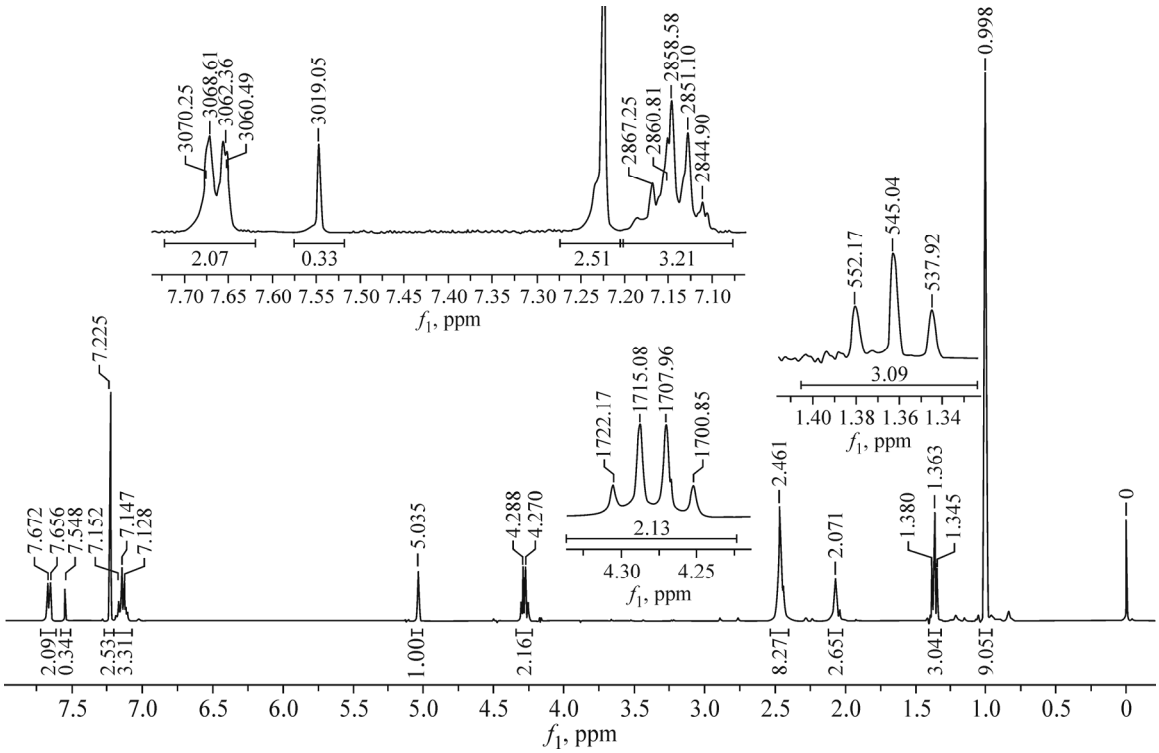


Fig. 2. ^{1}H NMR spectrum of the $NiL^4 \cdot NH_3$ coordination complex in the CCl_4 + d_6-DMSO solution.

δ = 1.36 ppm, and the protons of the $–CH_2$ group resonate in the form of a quartet at δ = 4.27 ppm with the integrated intensity ratio 3:2 and the spin-spin coupling constant J_{AB} = 7 Hz. The signals from a single vinyl proton occur at δ = 5.03 ppm, and nine protons of the *tert*-C_4H_9 group are manifested as a clear singlet at δ = 0.996 ppm. The multiplet signals of the protons from aromatic rings of the hydrazone fragment resonate in weak fields with peaks at 7.14 ppm, 7.25 ppm, and 7.67 ppm. The signals have somewhat complicated forms due to overlapping. The signal from the protons of the coordinated ammonia molecule occurs at δ = 2.07 ppm in the form of a singlet with intensity of 3H (Fig. 2).

The ^{1}H NMR spectra of $NiL^1 \cdot NH_3$–$NiL^3 \cdot NH_3$ and $NiL^5 \cdot NH_3$–$NiL^6 \cdot 3Py$ coordination complexes differ from the $NiL^4 \cdot NH_3$ spectrum by the presence of doublet-doublet signals from four protons. Two substituents with different electronegativities of *p*-phenylene of the organic ligand split the signals into two different δ values in the weak field region of 7.35-7.78 ppm (Table 3) [2, 4, 18].

The conclusions concerning the planar structure of the complex with a tridentate coordination of the dianionic ligand residue inferred above from spectral data were verified by the XRD method using a grown single crystal of the $NiL^4 \cdot NH_3$ complex [11, 19-21]. Single crystals $NiC_{17}H_{23}N_3O_4$ were isolated by the recrystallization of $NiL^4 \cdot NH_3$ from a solution of

TABLE 3. Parameters of ^{1}H NMR Spectra Of Nickel(II) Complexes in the CCl_4 + d_6-DMSO Solution (δ, ppm)

Compound	*X*	$C(CH_3)_3$	–CH=	$COOC_2H_5$	NH_3	C_6H_4X
$NiL^1 \cdot NH_3$	2.88	1.04	5.08	1.34; 4.26	2.05	7.35; 7.63
$NiL^2 \cdot NH_3$	2.92	1.06	5.12	1.33; 4.26	2.06	7.37; 7.65
$NiL^3 \cdot NH_3$	2.24	1.05	5.10	1.35; 4.28	2.08	7.40; 7.68
$NiL^4 \cdot NH_3$	–	0.99	5.18	1.36; 4.27	2.07	7.14; 7.25; 7.67
$NiL^5 \cdot NH_3$	–	1.03	5.13	1.37; 4.28	2.06	7.36; 7.63
$NiL^6 \cdot NH_3$	–	0.97	5.32	1.38; 4.28	2.08	7.50; 7.74
$NiL^6 \cdot 3Py$	–	1.02	5.34	1.39; 4.30	–	7.56; 7.78

a 1:1 methanol-chloroform mixture. The X-ray diffraction study was carried out on an Xcalibur (Oxford Diffraction) automated diffractometer (λCuK_α radiation, graphite monochromator, ω scanning, $2\theta_{max} = 50°$). The crystals are characterized by the composition $NiC_{17}H_{23}N_3O_4$, monoclinic system, unit cell parameters $a = 12.0019(5)$ Å, $b = 8.5823(4)$ Å, $c = 18.1664(6)$ Å, $\beta = 92.161(4)°$, $V = 1869.87(13)$ Å^3, $\rho_{calc} = 1.659$ g/cm^3, $Z = 2$, space group $P\bar{1}$. As expected, the molecule of the complex contains almost planar joined five- and six-membered metallacycles. A double deprotonated residue of the H_2L^4 ligand is coordinated to the nickel atom via two oxygen atoms and the nitrogen atom of the hydrazone fragment. The fourth position in the flat square of the *trans*-N_2O_2 coordination site is occupied by the ammonia molecule (Fig. 3).

The lengths of Ni–O(1) and Ni–O(2) bonds (1.851(2) Å and 1.834(2) Å, respectively) in the crystal of the complex are close to those found in the coordination polyhedron formed by the atoms of isostructural nickel complexes with aroyl hydrazone of methyl ether of 5,5-dimethyl-2,4-dioxohexane acid (Table 4) [6, 16]. The Ni–N(1) distance (1.819(2) Å) is significantly shorter than the Ni–N(1) distance (1.852(6) Å) [13, 14] and (1.90-1.99 Å) [18] in similar compounds, and the length of the Ni–N(3) bond (1.934(3) Å) is in good agreement with reported data (Table 4) [6, 14, 20]. The central nickel atom insignificantly deviates from the "average" plane of coordinated atoms O(1), O(2), N(1), N(3).

A large difference between bond angles O(1)NiN(1) (83.86°) and N(1)NiO(2) (95.84°) of the metallacycle is explained, in our opinion, by the presence and the size of conjugated five- and six-membered metallacycles around the central ion (Table 4). All these data agree well with those reported in [14, 20]. The atoms of the coordination polyhedron NiO(1)O(2)N(1)N(2) lie in the same plane with an accuracy of ±0.2 Å. Five-membered (NiO(1)N(1)N(2)C(4)) and six-membered (NiO(2)N(1)C(1)C(2)–C(3)) metallacycles are virtually planar with an accuracy of ±0.001-0.06 Å (Table 5). They are almost coplanar, but dihedral angles between them are somewhat different from those in other complexes; this distortion in the coplanarity of two metallacycles is apparently explained by the presence of two large (C_2H_5COOC– and $(CH_3)_3C$–) groups in the β-diketone fragment of the coordination complex. The conjugation of double and single bonds C(1)=N(1), C(1)–C(2), C(2)=C(3), C(3)–O(2) in the six-membered metallacycles, and N(1)–N(2), N(2)=C(4), C(4)–O(1) bonds in the five-membered metallacycle (Table 5) as well as the formation of the *d*–π-dative bond between *d* electrons of the central complexing ion and π orbitals of these cycles lead to the formation of a partially pseudoaromatic system and contribute towards the coplanarity of two metallacycles in space. The lengths of the C(1)–C(12) bond (1.507 Å) and the C(4)–C(5) bond (1.483 Å) are somewhat different from usual single bonds to indicate the formation of a conjugated system between the benzene ring and the five-membered pseudoaromatic metallochelate. The single π orbital of the aromatic core of the benzoyl fragment of the ligand molecule is conjugated with π electrons of the N(2) = C(4) double bond (1.302 Å) and with lone electron pairs of nitrogen atoms and the oxygen of the five-membered pseudoaromatic metallacycle. These conclusions are definitely confirmed by the values of bond angles O(1)–C(4)–C(5) (118.3(3)°), N(2)–C(4)–C(5) (118.7(3)°), C(6)–C(5)–C(4) (120.3(3)°), and C(10)–C(5)–C(6) (120.7(3)°), which also testify a presence of a single π–*p*–π conjugated system.

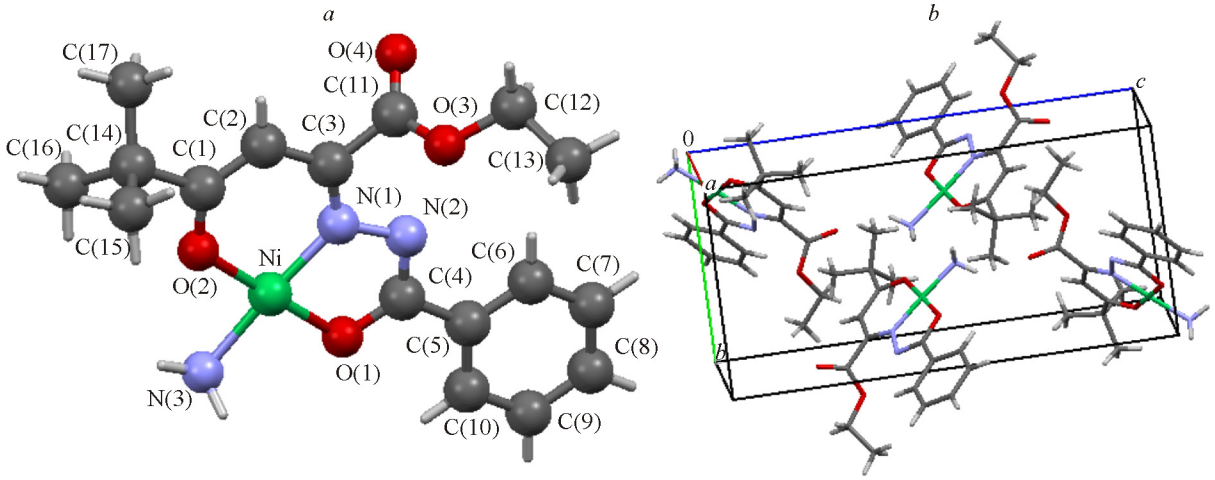


Fig. 3. Molecular structure (*a*) and the packing (*b*) of $NiL^4 \cdot NH_3$ molecules.

TABLE 4. Main Bond Lengths and of Bond Angles in $NiL^4 \cdot NH_3$

Bond	*d*, Å	Bond	*d*, Å
O(1)–Ni	1.851(2)	C(2)–C(3)	1.412(4)
O(2)–Ni	1.834(2)	C(3)–C(11)	1.508(4)
N(1)–Ni	1.819(2)	C(4)–C(5)	1.482(4)
N(3)–Ni	1.934(3)	C(5)–C(6)	1.390(4)
N(1)–N(2)	1.395(5)	C(6)–C(7)	1.386(5)
C(1)–O(2)	1.288(4)	C(7)–C(8)	1.372(6)
C(4)–O(1)	1.317(4)	C(8)–C(9)	1.375(6)
C(11)–O(3)	1.309(4)	C(9)–C(10)	1.395(5)
C(11)–O(4)	1.187(4)	C(11)–C(14)	1.541(5)
C(12)–O(3)	1.455(2)	C(12)–C(13)	1.477(6)
C(3)–N(1)	1.310(4)	C(14)–C(15)	1.523(7)
C(4)–N(2)	1.301(4)	C(14)–C(16)	1.531(6)
C(1)–C(2)	1.370(5)	C(14)–C(17)	1.520(6)
Angle	ω, deg	Angle	ω, deg
O(2)–C(1)–C(2)	124.4(3)	O(3)–C(12)–C(13)	107.9(4)
O(2)–C(1)–C(14)	114.0(3)	C(17)–C(14)–C(15)	109.9(5)
C(2)–C(1)–C(14)	121.5(3)	C(17)–C(14)–C(16)	107.6(4)
C(1)–C(2)–C(3)	124.1(3)	C(15)–C(14)–C(16)	110.1(4)
N(1)–C(3)–C(2)	122.7(3)	C(17)–C(14)–C(1)	112.4(3)
N(1)–C(3)–C(11)	119.2(3)	C(15)–C(14)–C(1)	107.5(3)
C(2)–C(3)–C(11)	118.1(3)	C(16)–C(14)–C(1)	109.3(3)
N(2)–C(4)–O(1)	123.0(3)	C(11)–O(3)–C(12)	117.3(3)
N(2)–C(4)–C(5)	118.7(3)	C(3)–N(1)–N(2)	117.8(3)
O(1)–C(4)–C(5)	118.3(3)	C(3)–N(1)–Ni	126.6(2)
C(10)–C(5)–C(6)	120.7(3)	N(2)–N(1)–Ni	115.68(18)
C(10)–C(5)–C(4)	119.0(3)	C(4)–N(2)–N(1)	107.7(3)
C(6)–C(5)–C(4)	120.3(3)	C(4)–O(1)–Ni	109.74(18)
C(7)–C(6)–C(5)	120.6(4)	C(1)–O(2)–Ni	126.3(2)
C(8)–C(7)–C(6)	120.0(4)	N(1)–Ni–O(2)	95.84(10)
C(7)–C(8)–C(9)	120.2(3)	N(1)–Ni–O(1)	83.86(10)
C(8)–C(9)–C(10)	120.2(4)	O(2)–Ni–O(1)	179.46(11)
C(5)–C(10)–C(9)	119.9(4)	N(1)–Ni–N(3)	175.83(12)
O(4)–C(11)–O(3)	125.7(4)	O(2)–Ni–N(3)	88.33(11)
O(4)–C(11)–C(3)	122.8(4)	O(1)–Ni–N(3)	91.98(11)
O(3)–C(11)–C(3)	111.4(3)		

TABLE 5. Atomic Deviations from "Average" Planes in the $NiL^4 \cdot NH_3$ Structure (Å)

Ni 0.0033	O(1) –0.0039	O(2) –0.0038	N(1) 0.0023	N(3) 0.0021	N(2)* 0.0354	C(4)* 0.0377	C(1)* –0.0609	C(3)* –0.0009
Ni 0.0117	N(1) –0.0113	N(2) 0.0037	C(4) 0.0097	O(1) –0.0138	C(1)* –0.0384	C(5)* 0.0257	O(2)* 0.0227	N(3)* 0.0327
Ni –0.0131	N(1) –0.0050	C(1) –0.0091	C(2) –0.0162	C(3) 0.0209	O(2) 0.0225	O(1)* –0.0633	C(12)* 1.4278	N(2)* 0.0011
C(5) –0.0036	C(6) 0.0011	C(7) 0.0020	C(8) –0.0027	C(9) 0.0002	C(10) 0.0030	C(4)* –0.0207		

* Atoms that were not included in the calculation of the plane.

Fig. 3*b* shows the packing of structural units in the $NiL^4 \cdot NH_3$ crystal. The coordinated ammonia molecule participates in intermolecular hydrogen bonds N(3)–H(1)···O(1) (–*x*, –*y*+1, –*z*+1) and N(3)–H(2)···N(2) (–*x*, –*y*+1, –*z*+1) which lead to the formation of a centrosymmetric dimer. The molecules are arranged within the centered motive the way that five- and six-membered metallacycles form pseudo-stacks along the *x* axis.

The effect of such a strong donor solvent as pyridine under the recrystallization in a large excess of this substance was studied for another ammonia coordination complex, namely, Ni(II) $NiL^6 \cdot NH_3$ with a ligand of *p*-nitrobenzoylhydrazone of ethyl ether of 5,5-dimethyl-2,4-dioxohexane acid (H_2L^6). The recrystallization of the ammonia solution of the complex in an excess of the solvent was used to isolate single crystals with a composition and a structure differing from those of the $NiL^4 \cdot NH_3$ single crystal. In was found that the dissolution of the $NiL^6 \cdot NH_3$ complex in a large excess of polar solvent pyridine did not led to square-planar crystals with a set of *trans*-(N_2O_2) donor atoms consisting of a double deprotonated residue of the tridentate organic ligand and the pyridine donor base; instead, the procedure resulted in an octahedral complex with a composition $(NiC_{32}H_{34}N_6O_6)_2$ having three additional coordinated pyridine molecules $NiL^6 \cdot 3Py$ which completes the environment of the Ni(II) ion to the octahedral with a set of Ni(*trans*-N_4O_2) donor atoms. Such changes in the coordination sphere from a flat-square structure via a square-pyramidal structure to a hexacoordinated octahedral structure were reported in our previous work in the case of mononuclear copper(II) complexes and heterobinuclear nickel(II) and copper(II) complexes [5, 13].

The isolated single crystals $(NiC_{32}H_{34}N_6O_6)_2$ were studied on an Xcalibur (Oxford Diffraction) automated diffractometer ($\lambda Cu K_\alpha$ radiation, graphite monochromator, ω scanning, $2\theta_{max} = 50°$). It was determined that the crystals have a composition $(NiC_{32}H_{34}N_6O_6)_2$, triclinic system, the unit cell parameters are $a = 9.5826(5)$ Å, $b = 14.1432(6)$ Å, $c = 26.1557(13)$ Å, $\alpha = 76.300(4)°$, $\beta = 89.447(4)°$, $\gamma = 73.234(4)°$, $V = 3291.0(3)$ Å^3, $\rho_{calc} = 1.659$ g/cm^3, $Z = 2$, space group $P\bar{1}$ (Table 6).

TABLE 6. Main Crystallographic Data and Refinement Parameters of $NiL^4 \cdot NH_3$ and $NiL^6 \cdot 3Py$ Structures

Parameter	$NiL^4 \cdot NH_3$ value	$NiL^6 \cdot 3Py$ value
M	392.09	1314.72
Temperature, K	293	298
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, b, c, Å	11.9969(8), 8.5818(4), 18.1740(13)	9.5826(5), 14.1432(6), 26.1557(13)
α, β, γ, deg	90.000, 89.447(4), 90.000	76.300(4), 89.447(4), 73.234(4)
V, Å^3	1869.7(2)	3291.0(3)
Z	4	2
ρ_{calc}, g/cm^3	1.206	1.327
μ, mm^{-1}	1.72	1.28
Crystal sizes, mm	0.2×0.3×0.7	0.2×0.3×0.3
θ range for data collection, deg	3.4-76.2	3.4-74.5
Index ranges	$-4 \le h \le 10$, $-10 \le k \le 9$, $-22 \le l \le 21$	$-11 \le h \le 11$, $-17 \le k \le 14$, $-32 \le l \le 32$
Reflections collected	6954	24252
Reflections unique (R_{int})	3768 (0.054)	13251 (0.042)
Reflections with $I > 2\sigma(I)$	2568	8945
Parameters	243	820
Goodness-of-fit on F^2	1.00	1.021
R_1, wR_2 ($I > 2\sigma(I)$)	0.048, 0.120	0.0513, 0.1457
R_1, wR_2 (all data)	0.047, 0.118	0.051, 0.146
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e/Å^3	0.29, –0.27	0.46, –0.48

The molecule of the $NiL^6 \cdot 3Py$ coordination complex has an octahedral structure, and the double deprotonated tridentate ligand residue forms joint five- and six-membered metallacycles around the central ion (Fig. 4; Table 7). The residue of the ligand molecule is coordinated by two oxygen atoms and by a nitrogen atom of the hydrazone fragment. The fourth position in the flat square *trans*-N_2O_2 coordination site and two axial positions are occupied by pyridine molecules to complete the central ion environment up to the octahedral. The lengths of Ni–O(1) and Ni–O(2) bonds (2.0665 Å and

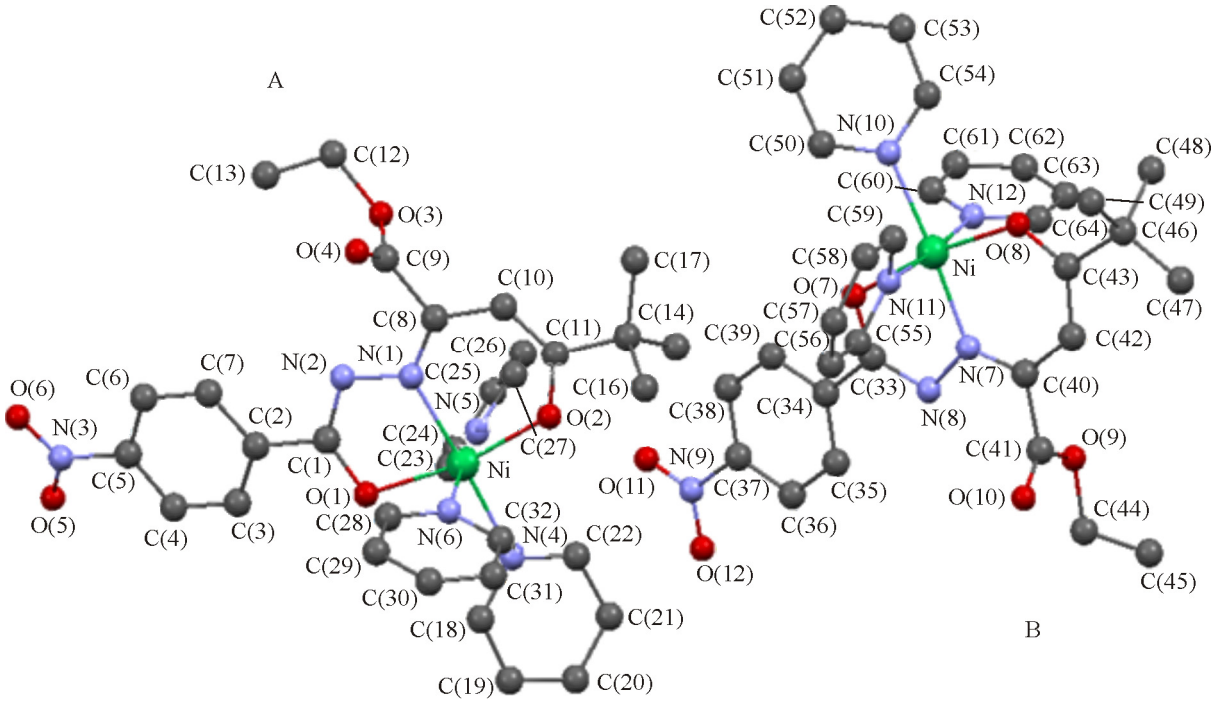


Fig. 4. Molecular structure of the coordination complex $NiL^6 \cdot 3Py$.

TABLE 7. Bond Lengths and Bond Angles in the Structure of the $NiL^6 \cdot 3Py$ Complex

Bond	*d*, Å	Bond	*d*, Å
1	2	3	4
	Molecule A		
O(1)–Ni(1)	2.0665(19)	C(2)–C(3)	1.373(5)
O(2)–Ni(1)	2.025(2)	C(2)–C(7)	1.388(4)
N(1)–Ni(1)	1.981(2)	C(4)–C(5)	1.372(5)
N1(2)–Ni(2)	2.141(2)	C(5)–C(6)	1.355(6)
N(4)–Ni(1)	2.092(2)	C(6)–C(7)	1.395(5)
N(5)–Ni(1)	2.164(2)	C(8)–C(9)	1.519(4)
N(3)–O(5)	1.229(5)	C(8)–C(10)	1.423(4)
N(3)–O(6)	1.217(5)	C(12)–C(13)	1.460(5)
N(1)–N(2)	1.400(3)	C(14)–C(15)	1.523(5)
C(1)–O(1)	1.296(3)	C(14)–C(16)	1.528(5)
C(9)–O(3)	1.321(4)	C(14)–C(17)	1.543(5)
C(9)–O(4)	1.191(4)	C(18)–C(19)	1.355(5)
C(12)–O(3)	1.490(4)	C(19)–C(20)	1.377(6)
C(1)–N(2)	1.309(4)	C(20)–C(21)	1.364(6)
C(5)–N(3)	1.472(4)	C(24)–C(25)	1.365(5)
C(8)–N(1)	1.297(4)	C(25)–C(26)	1.373(5)

TABLE 7. (Cont.)

1	2	3	4
C(18)–N(4)	1.327(4)	C(26)–C(27)	1.370(5)
C(22)–N(4)	1.334(4)	C(28)–C(29)	1.372(4)
C(23)–N(5)	1.322(4)	C(29)–C(30)	1.361(5)
C(27)–N(5)	1.329(4)	C(30)–C(31)	1.386(5)
C(1)–C(2)	1.499(4)	C(31)–C(32)	1.381(5)
	Molecule B		
O(7)–Ni(2)	2.0426(19)	C(36)–C(37)	1.363(5)
O(8)–Ni(2)	2.0147(19)	C(38)–C(39)	1.370(5)
N(6)–Ni(1)	2.154(2)	C(40)–C(41)	1.511(4)
N(7)–Ni(2)	1.979(2)	C(40)–C(42)	1.421(4)
N(10)–Ni(2)	2.078(2)	C(44)–C(45)	1.353(7)
N(11)–Ni(2)	2.157(2)	C(46)–C(47)	1.516(5)
N(9)–O(12)	1.196(5)	C(46)–C(48)	1.517(5)
N(9)–O(11)	1.137(6)	C(46)–C(49)	1.520(5)
N(7)–N(8)	1.400(3)	C(50)–C(51)	1.378(5)
C(33)–O(7)	1.296(3)	C(51)–C(52)	1.372(6)
C(41)–O(9)	1.323(4)	C(52)–C(53)	1.373(5)
C(41)–O(10)	1.191(4)	C(53)–C(54)	1.356(4)
C(44)–O(9)	1.462(4)	C(55)–C(56)	1.368(5)
C(55)–N(11)	1.327(4)	C(56)–C(57)	1.344(6)
C(59)–N(11)	1.327(4)	C(57)–C(58)	1.377(6)
C(64)–N(12)	1.337(3)	C(58)–C(59)	1.383(5)
C(33)–C(34)	1.490(4)	C(60)–C(61)	1.371(4)
C(34)–C(35)	1.385(4)	C(61)–C(62)	1.379(5)
C(34)–C(39)	1.383(4)		
Angle	ω, deg	Angle	ω, deg
	Molecule A		
O(2)–Ni(1)–O(1)	169.29(8)	O(11)–N(9)–C(37)	120.2(5)
O(1)–Ni(1)–N(4)	97.33(9)	O(12)–N(9)–C(37)	119.9(5)
O(1)–Ni(1)–N(6)	90.21(8)	O(1)–C(1)–C(2)	117.7(3)
O(1)–Ni(1)–N(5)	87.38(9)	O(3)–C(9)–C(8)	111.9(3)
O(2)–Ni(1)–N(4)	93.37(9)	O(4)–C(9)–C(8)	122.9(3)
O(2)–Ni(1)–N(6)	90.85(9)	O(2)–C(11)–C(10)	125.3(3)
O(2)–Ni(1)–N(5)	92.89(9)	O(2)–C(11)–C(14)	114.0(3)
N(1)–Ni(1)–O(1)	79.10(9)	C(9)–O(3)–C(12)	115.0(3)
N(1)–Ni(1)–O(2)	90.19(9)	C(13)–C(12)–O(3)	108.9(3)
N(1)–Ni(1)–N(4)	175.45(10)	C(4)–C(5)–N(3)	118.4(4)
N(1)–Ni(1)–N(5)	91.23(9)	C(6)–C(5)–N(3)	119.3(4)
N(1)–Ni(1)–N(6)	95.57(9)	C(18)–N(4)–C(22)	117.4(3)
N(4)–Ni(1)–N(6)	87.23(9)	C(28)–N(6)–C(32)	116.8(3)
N(4)–Ni(1)–N(5)	85.76(9)	C(2)–C(3)–C(4)	121.4(3)
N(6)–Ni(1)–N(5)	172.23(10)	C(5)–C(4)–C(3)	118.1(4)
C(1)–O(1)–Ni(1)	107.86(18)	C(6)–C(5)–C(4)	122.3(3)
C(18)–N(4)–Ni(1)	121.4(2)	C(5)–C(6)–C(7)	119.3(4)
C(22)–N(4)–Ni(1)	121.2(2)	C(2)–C(7)–C(6)	119.8(4)
C(23)–N(5)–Ni(1)	120.2(2)	C(3)–C(2)–C(1)	120.2(3)

TABLE 7. (Cont.)

1	2	3	4
C(27)–N(5)–Ni(1)	123.3(2)	C(3)–C(2)–C(7)	119.1(3)
C(28)–N(6)–Ni(1)	121.9(2)	C(7)–C(2)–C(1)	120.6(3)
C(32)–N(6)–Ni(1)	121.2(2)	C(10)–C(8)–C(9)	116.6(3)
C(1)–N(2)–N(1)	109.4(2)	C(11)–C(10)–C(8)	125.8(3)
C(23)–N(5)–C(27)	116.4(3)	C(10)–C(11)–C(14)	120.7(3)
N(1)–C(8)–C(9)	118.9(3)	C(15)–C(14)–C(11)	108.1(3)
N(1)–C(8)–C(10)	124.3(3)	C(15)–C(14)–C(16)	109.6(3)
N(2)–C(1)–C(2)	114.8(3)	C(15)–C(14)–C(17)	108.0(3)
N(4)–C(18)–C(19)	123.6(4)	C(16)–C(14)–C(11)	107.3(3)
N(4)–C(22)–C(21)	122.5(4)	C(16)–C(14)–C(17)	109.9(3)
N(5)–C(23)–C(24)	123.7(4)	C(17)–C(14)–C(11)	113.7(3)
N(5)–C(27)–C(26)	123.8(3)	C(18)–C(19)–C(20)	119.0(4)
N(6)–C(28)–C(29)	123.9(3)	C(21)–C(20)–C(19)	118.6(4)
N(6)–C(32)–C(31)	123.2(3)	C(20)–C(21)–C(22)	118.9(4)
O(4)–C(9)–O(3)	125.2(3)	C(25)–C(24)–C(23)	119.0(4)
O(6)–N(3)–O(5)	124.1(4)	C(24)–C(25)–C(26)	118.1(3)
O(11)–N(9)–O(12)	119.8(5)	C(27)–C(26)–C(25)	118.9(4)
O(1)–C(1)–N(2)	127.4(3)	C(30)–C(29)–C(28)	119.1(3)
O(5)–N(3)–C(5)	118.2(4)	C(29)–C(30)–C(31)	118.4(3)
O(6)–N(3)–C(5)	117.5(5)	C(32)–C(31)–C(30)	118.6(3)
O(7)–C(33)–N(8)	126.4(3)	N(11)–C(59)–C(58)	122.4(4)
O(8)–Ni(2)–O(7)	170.36(8)	N(12)–C(60)–C(61)	123.0(3)
O(7)–Ni(2)–N(10)	95.52(8)	N(12)–C(64)–C(63)	122.7(3)
O(7)–Ni(2)–N(11)	92.09(9)	N(7)–C(40)–C(42)	124.0(2)
O(7)–Ni(2)–N(12)	87.86(9)	N(10)–C(50)–C(51)	121.8(3)
O(8)–Ni(2)–N(10)	94.10(9)	C(54)–N(10)–C(50)	117.9(3)
O(8)–Ni(2)–N(11)	88.67(9)	C(55)–N(11)–C(59)	117.0(3)
O(8)–Ni(2)–N(12)	92.06(8)	C(36)–C(37)–N(9)	119.2(4)
N(7)–Ni(2)–O(7)	79.27(8)	C(38)–C(37)–N(9)	118.6(4)
N(7)–Ni(2)–O(8)	91.10(8)	C(64)–N(12)–C(60)	116.9(3)
N(7)–Ni(2)–N(10)	174.37(9)	C(35)–C(34)–C(33)	122.0(3)
N(7)–Ni(2)–N(11)	93.19(9)	C(34)–C(35)–C(36)	120.5(3)
N(7)–Ni(2)–N(12)	90.83(9)	C(39)–C(34)–C(33)	119.1(3)
N(10)–Ni(2)–N(11)	89.09(9)	C(39)–C(34)–C(35)	118.9(3)
N(10)–Ni(2)–N(12)	86.84(9)	C(37)–C(36)–C(35)	118.6(3)
N(12)–Ni(2)–N(11)	175.90(9)	C(38)–C(37)–C(36)	122.2(3)
C(11)–O(2)–Ni(1)	126.80(18)	C(37)–C(38)–C(39)	119.1(4)
C(33)–O(7)–Ni(2)	108.71(17)	C(38)–C(39)–C(34)	120.8(3)
C(43)–O(8)–Ni(2)	125.99(18)	C(42)–C(40)–C(41)	117.8(2)
		Molecule B	
C(50)–N(10)–Ni(2)	121.4(2)	N(11)–C(55)–C(56)	123.9(4)
C(54)–N(10)–Ni(2)	120.35(19)	C(43)–C(42)–C(40)	126.0(3)
C(55)–N(11)–Ni(2)	121.4(2)	C(42)–C(43)–C(46)	120.6(3)
C(59)–N(11)–Ni(2)	121.6(2)	C(47)–C(46)–C(43)	114.2(3)
C(60)–N(12)–Ni(2)	121.6(2)	C(47)–C(46)–C(48)	108.9(4)
C(64)–N(12)–Ni(2)	121.49(19)	C(47)–C(46)–C(49)	109.0(4)

TABLE 7. (Cont.)

1	2	3	4
O(7)–C(33)–C(34)	117.1(2)	C(48)–C(46)–C(43)	107.9(3)
O(8)–C(43)–C(42)	125.4(3)	C(48)–C(46)–C(49)	108.4(4)
O(8)–C(43)–C(46)	114.0(2)	C(49)–C(46)–C(43)	108.3(3)
O(10)–C(41)–O(9)	124.6(3)	C(52)–C(51)–C(50)	119.0(4)
O(9)–C(41)–C(40)	111.8(2)	C(51)–C(52)–C(53)	119.1(3)
O(10)–C(41)–C(40)	123.6(3)	C(54)–C(53)–C(52)	118.5(4)
C(41)–O(9)–C(44)	116.4(3)	C(57)–C(56)–C(55)	119.0(4)
C(45)–C(44)–O(9)	114.6(5)	C(56)–C(57)–C(58)	118.8(4)
C(33)–N(8)–N(7)	109.4(2)	C(57)–C(58)–C(59)	118.8(4)
N(8)–C(33)–C(34)	116.4(2)	C(60)–C(61)–C(62)	119.0(3)
N(7)–C(40)–C(41)	118.1(2)	C(63)–C(62)–C(61)	118.2(3)
N(10)–C(54)–C(53)	123.7(3)	C(62)–C(63)–C(64)	120.1(3)

2.025 Å, respectively) are close to their values in previously studied coordination complexes of nickel with the *trans*-N_2O_2 coordination sphere (Table 7) [5, 6, 19, 21]. The Ni–N(1) distance (1.981(2) Å) of the metallochelate is substantially shorter than three bonds Ni–N(4) (2.092 Å), Ni–N(5) (2.164(2) Å), Ni–N(6) (2.154(2) Å) of the donor base. The difference between the lengths of these bonds is due to their positions around the central complexing ion (Table 7) [5, 20].

TABLE 8. Atomic Deviations from "Average" Planes in the $NiL^6 \cdot 3Py$ Structure (Å)

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

* Atoms that were not included in the calculation of the plane.

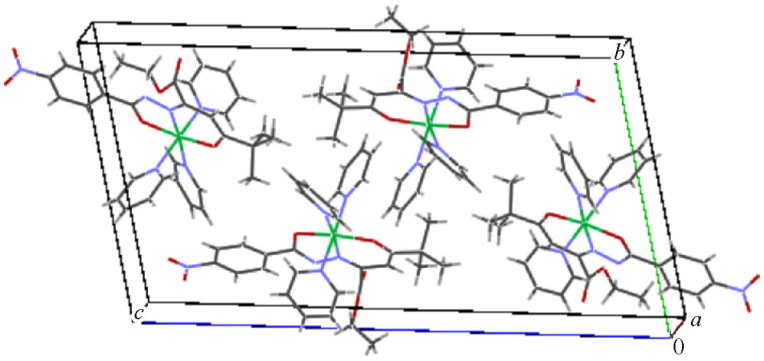


Fig. 5. Projections of the crystal packing of $NiL^6 \cdot 3Py$ molecules on the *ac* plane.

The central nickel atom deviates by 0.0272 Å from the "average" plane of the five-membered metallacycle NiN(1)N(2)C(1)O(2) as compared to the deviation by 0.0081 Å from the six-membered plane NiN(1)C(8)–C(10)O(2)C(11). This is due to the fact that the bonds are more strained in the five-membered ring than in the six-membered ring [5, 6, 20]. Virtually planar five- and six-membered conjugated metallacycles are nearly coplanar, which was discussed in our previous works [5, 6]. Comparing the structure of donor pyridine molecules coordinated around the Ni(II) ion in the complex, the Py c molecule with a set of atoms N(4)C(18)C(19)C(20)C(21)C(22) is more planar than other molecules coordinated to axial positions (Table 8, Fig. 5). In our opinion, this is due to the formation of a *d*–π dative bond between *d* electrons of the Ni(II) and the π orbital of the pyridine molecule (Table 8) [5, 6, 20].

CONCLUSIONS

1. It was established by IR and ^{1}H NMR methods that the 5-hydroxypyrazoline ring opens during the complexation process independently on the geometric structure of initial ligands.

2. It was shown by the XRD method that the double deprotonated residue of the H_2L^4 ligand (1-benzoyl-3-aryl-5-hydroxy-2-pyrazoline) in the linear enhydrazine-α-oxyazine form is coordinated to the central ion by three donor atoms (N,O_2) to form conjugated five- and six-membered pseudoaromatic metallacycles [NiN_2,O_2], their fourth positions being occupied by the ammonia molecule.

3. The recrystallization of the $NiL^6 \cdot NH_3$ coordination complex based on *n*-nitroaroyl hydrazone ethyl ether of 5,5-dimethyl-2,4-dioxohexane acid (H_2L^6) in the excess of pyridine leads to the isolation of $(NiC_{32}H_{34}N_6O_6)_2$ crystals of the $NiL^6 \cdot 3Py$ molecule with an octahedral environment of the central complexing ion

CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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