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PMR AND X-RAY STRUCTURAL STUDY OF Ni(II) COMPLEXES BASED ON BENZOYLACETALDEHYDE DERIVATIVES

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Abstract: Tridentate organic ligands H_2L (H_2L^1-H_2L^3) were obtained by condensation of aromatic acid hydrazides with benzoylacetaldehyde in alcoholic solutions in equimolar proportions. Square-planar NiL·A (A=NH_3, Py) complexes were synthesized by reacting their alcoholic solutions with aqueous ammonia solutions of nickel(II) acetate in a 1:1 ratio. The composition and structure of the resulting complexes were studied by elemental analysis, ^{1}H NMR spectroscopy and X-ray structural analysis.

Keywords: benzoylacetaldehyde, aroylhydrazone, hydrazone, enehydrazine, pyrazoline, X-ray structural analysis (XSA), pseudoaromatic.

Abstract: Tridentate organic ligands H_2L (H_2L^1-H_2L^3) were obtained by cross-condensation of aromatic acid hydrazides with alcoholic solutions of benzoylacetaldehydes in equimolar proportions. Square-planar NiL·A (A=NH_3, Py) complexes were synthesized by reacting aqueous ammonia solutions of nickel(II) acetate with alcoholic ligand solutions in a 1:1 ratio. The composition and structure of the resulting complexes were studied by elemental analysis, ^{1}H NMR spectroscopy and X-ray structural analysis.

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Abstract: H_2L tridentate organic ligands (H_2L^1-H_2L^3) were obtained from mutual condensation of aromatic acid hydrazides in alcohol solutions of formilpinacoline and benzoylacetic aldehydes in equivalent proportions. With their solutions in alcohol, compounds of NiL·A (A=NH_3, Py) with a flat-square structure were synthesized from the interaction of water-ammonia solutions of nickel(II)-

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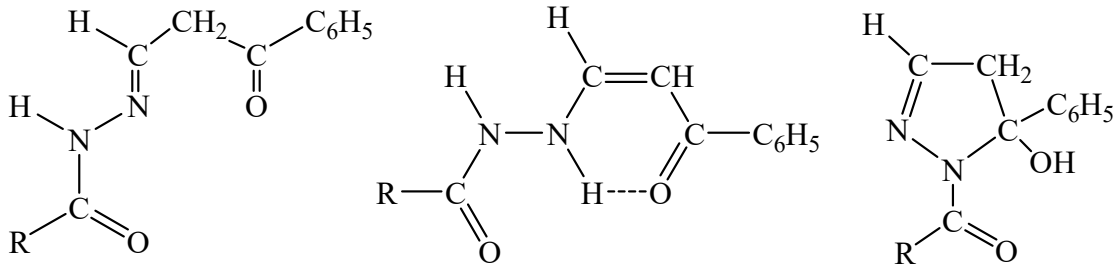
acetate in a 1:1 ratio. The composition and structure of the obtained complex compounds were studied by element analysis, NMR-^{1}H spectroscopy and RSA methods.

Key words: benzoyl acetic aldehydes, aroilhydrazone, hydrazone, engidrazine, pyrazoline, X-ray diffraction analysis (RSA), polyhedrine, metal ring.

INTRODUCTION

According to the ^{1}H NMR spectroscopic parameters obtained in polar and nonpolar solvents, the condensation products H_2L^1-H_2L^3 of benzoylacetaldehyde with nitrogen-containing nucleophilic reagents exist in hydrazone (A), open-chain enehydrazine (B) and cyclic pyrazoline (V) tautomeric forms [1-7].

Such tautomeric transformations are not observed in β-ketoaldehyde aroylhydrazone derivatives in the solid state. The synthesis of complexes of tridentate organic ligands with 3d metals provides an opportunity to obtain interesting information by identifying their tautomeric forms under the influence of metal ions [1-7, 13].



A B V

R=C_6H_5(H_2L^1), *p*-$CH_3C_6H_4$(H_2L^2), *o*-OHC_6H_5 (H_2L^3).

LITERATURE REVIEW

Studies cited in this article show a consistent research line from 1,3-diketone chemistry and acyl-/aroylhydrazone tautomerism to transition-metal coordination. Shokova et al. [1] summarized the synthesis and properties of 1,3-diketones, while Umarov, Tursunov, Avezov and co-authors examined the structure and tautomerism of acyl- and aroylhydrazones derived from formylpinacolone and benzoylacetaldehyde [2-7]. These works provide the literature basis for considering hydrazone, enehydrazine and cyclic pyrazoline forms when analyzing the behavior of the ligands used in the present study.

The coordination-chemical direction of this research is represented by studies of transition-metal complexes based on acyl-, thioacyl- and aroylhydrazone systems [8-13]. The cited dissertations, monograph and experimental papers address the synthesis, coordination behavior and crystal chemistry of such ligands, including Ni(II)-containing systems. Later publications on nickel(II) and zinc(II) complexes with benzoylacetaldehyde derivatives and related aroylhydrazones further develop this structural approach [18-20]. Together, these sources support examining ligand tautomerism in direct connection with chelate formation and the geometry of the coordination polyhedron.

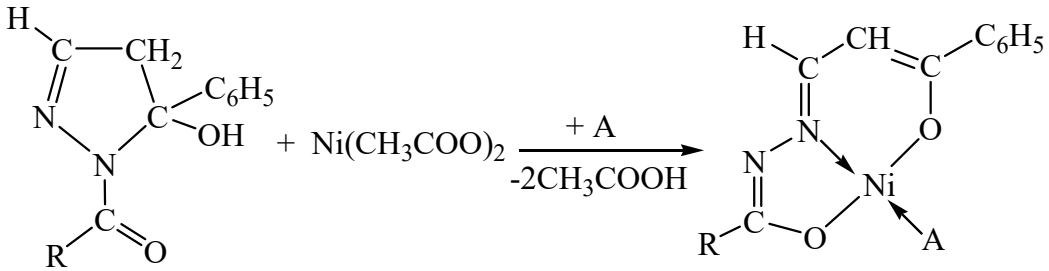
The cited literature also demonstrates the complementary role of spectroscopic and diffraction methods. PMR/1H NMR investigations are used to characterize ligand and complex structures in solution [7], whereas single-crystal X-ray studies provide direct information on coordination geometry

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and molecular packing [10,12,18-20]. The crystallographic software and structure-solution approaches referenced in the article - CrysAlisPro, SHELXS/SHELXL and OLEX2 - constitute the methodological basis for refinement and analysis of the crystal structures [14-17]. Thus, the available literature substantiates the combined use of 1H NMR spectroscopy and X-ray structural analysis for studying Ni(II) complexes based on benzoylacetaldehyde derivatives.

MATERIALS AND METHODS

Metal complexes of composition NiL·A (A=NH_3, Py), where L is the doubly deprotonated ligand residue, were synthesized by reacting aqueous ammonia solutions of Ni(II) acetate with equimolar amounts of H_2L^1-H_2L^3 in alcohol. The elemental analysis results and ^1H NMR spectroscopic parameters allow a square-planar coordination polyhedron to be assigned [8-10]:



R=C_6H_5, ($NiL^1{\cdot}NH_3$), ($NiL^1{\cdot}Py$), *p*-$CH_3C_6H_4$, ($NiL^2{\cdot}Py$), *o*-OHC_6H_5, ($NiL^3{\cdot}NH_3$).

RESULTS AND DISCUSSION

The reaction yields and elemental analysis results for the Ni(II) complexes obtained are given in Table 1.

Table 1

Reaction yields and elemental analysis results for the synthesized Ni(II) complexes

Com-pounds	Yield, %	Molecular formula	Found/Calculated, %			
			M	C	H	N
$NiL^1{\cdot}NH_3$	86	$NiC_{16}H_{15}N_3O_2$	17,13/17,27	56,42/56,51	4,23/4,45	12,75/12,36
$NiL^1{\cdot}Py$	82	$NiC_{21}H_{17}N_3O_2$	14,55/14,60	62,43/62,72	4,25/4,26	10,63/10,45
$NiL^2{\cdot}Py$	69	$NiC_{22}H_{19}N_3O_2$	14,01/14,10	63,28/63,49	4,43/4,60	10,47/10,12
$NiL^3{\cdot}NH_3$	82	$NiC_{17}H_{17}N_3O_4$	15,11/15,20	52,76/52,89	4,32/4,44	11,00/10,89

The ammine complexes dissolve readily in organic solvents but are insoluble in water. Dissolving the nickel(II) ammine complexes $NiL^1{\cdot}NH_3$ and $NiL^2{\cdot}NH_3$ in a minimum amount of pyridine afforded complexes of composition $NiL^1{\cdot}Py$ and $NiL^2{\cdot}Py$ [10-13].

Since the isolated nickel(II) complexes are diamagnetic, their ^1H NMR spectral parameters in polar and nonpolar solvents were examined to study their solution structures. The ^1H NMR spectral parameters of the nickel(II) complexes in deuterated DMSO-d_6 are given in Table 2.

Table 2.

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^{1}H NMR spectra (δ, ppm) of nickel(II) complexes based on benzoylacetaldehyde derivatives in DMSO-d_6

Com-pounds	$C_6\mathbf{H}_5$-	**H**–C=N	–C**H**=	R proton signals	A proton signals
$NiL^1 \cdot NH_3$	7,29m; 7,66m	5,95	5,86	7,29m; 7,66m	–
$NiL^1 \cdot Py$	7,34m; 7,66m	6,04	5,98	7,34m; 7,66m	7,74m; 8,08m; 8,95m
$NiL^2 \cdot Py$	7,32m; 7,64m	6,08	6,02	7,36m; 7,69m	7,76m; 8,09m; 9,07m
$NiL^3 \cdot NH_3$	7,25m;7,48m	6,34	5,28	7,25m;7,48m	1,86

Compared with $NiL^1 \cdot NH_3$, the ^{1}H NMR spectrum of $NiL^1 \cdot Py$ shows a downfield shift of the signals of the peripheral ligand protons. This indicates the formation of a d–π-type Ni→Py dative bond between the d orbitals of the central ion and the π orbitals of the pyridine molecule (Table 2) [9,13].

To confirm the conclusions regarding the square-planar structure, single crystals of $NiL^2 \cdot Py$ and $NiL^3 \cdot NH_3$ were grown by recrystallization from methanol. X-ray structural studies were performed on an automated Xcalibur, Oxford Diffraction diffractometer (λ=1,5418 Å, CuKα radiation, graphite monochromator, ω scans). The structure was solved by direct methods using SHELXS-97 [14-15] and refined by least squares using SHELXL-97 [16-17].

The $NiC_{22}H_{19}N_3O_2$ crystals of the $NiL^2 \cdot Py$ complex are triclinic, with the following unit-cell parameters: a=9,3151(9), b=10,5675(11), c=11,9266(7), α=112,030(7), β=92,227(6), γ=115,341(10)°, V=955,33(17) Å^3, Z=2, space group P-1.

The $NiC_{17}H_{17}N_3O_4$ crystals of the $NiL^3 \cdot NH_3$ complex are monoclinic, with the following unit-cell parameters: a=10,3837(9), b=8,2507(6), c=19,630(2), α=90, β=98,658(11), γ=90°, V=1662,5(3) Å^3, Z=3, space group P_{21}/s.

Figures 1 and 2 show the molecular structures of these complexes. In both molecules, the doubly deprotonated ligand residues perform the same tridentate chelating function. Each nickel atom is bonded to the phenoxide oxygen atom, the azomethine nitrogen atom and the oxygen atom of the ligand in its α-oxyazine tautomeric form. The fourth coordination site of nickel is occupied by pyridine in $NiL^2 \cdot Py$ and by ammonia in $NiL^3 \cdot NH_3$ [18-20].

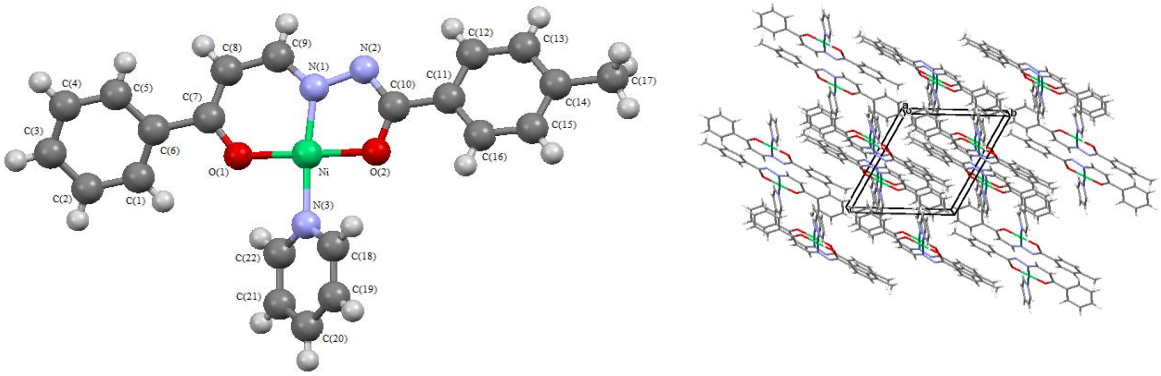


Figure 1. Molecular structure of the $NiL^2 \cdot Py$ complex and its packing projection onto the ab plane

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The Ni–O(1), Ni–O(2), Ni–N(1) and Ni–N(3) bond lengths in the complex crystal, 1,826(2), 1,835(2), 1,823(3) and 1,926(3) Å, respectively, are close to those in nickel complexes with the benzoylhydrazones of ethyl 5,5-dimethyl-2,4-dioxohexanoate [18-20], methyl 5,5-dimethyl-2,4-dioxohexanoate [9,13] and trifluoroacetylacetone [8]. In $NiL^2 \cdot Py$, the central nickel atom shows virtually no displacement from the mean plane of the coordinated O(1), O(2), N(1) and N(3) atoms. The large difference between the O(1)NiN(1) (95,76(12)°) and N(1)NiO(2) (83,76(13)°) bond angles is explained by the presence and sizes of the five- and six-membered metallacycles around the complex-forming ion. The NiO(1)O(2)N(1)N(3) atoms of the coordination polyhedron lie in one plane within 0,2 Å. The 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 fused.

Figure 1 shows the packing of the structural units in the $NiL^2 \cdot Py$ crystal. One hydrogen atom of the coordinated pyridine molecule participates in an intramolecular C(18)–H(18)...O(2) hydrogen bond of 2,937(4) Å and an intermolecular C(18)–N(18)...N(2) hydrogen bond of 3,437(4) Å, resulting in a centrosymmetric dimer. The molecules are arranged so that the five- and six-membered metallacycles form a pseudoring with one another. The molecule contains another intramolecular hydrogen bond, C(18)–H(18)...O(1), of 2,861(3) Å, with a bond angle of 104,3°. In this fragment, the C(22)–H(22) and H(22)...O(1) distances are 0,93 and 2,48 Å, respectively.

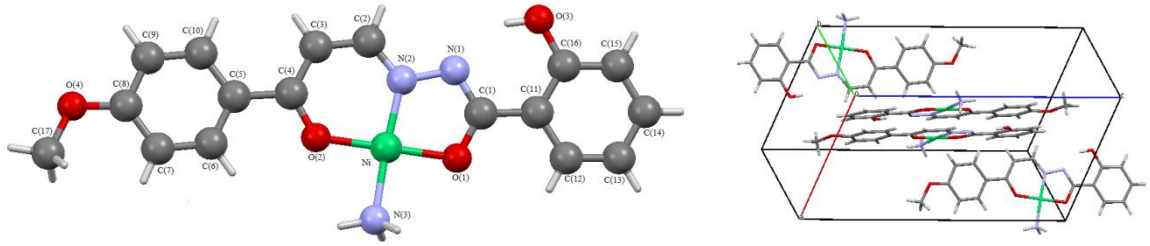


Figure 2. Molecular structure of the $NiL^3 \cdot NH_3$ complex and its packing projection onto the ab plane.

In the NiL^3NH_3 complex crystal, the Ni–O(1), Ni–O(2), Ni–N(1) and Ni–N(3) bond lengths are 1,853(3), 1,821(3), 1,818(3) and 1,934(3) Å, respectively (Figure 2).

The NiO(1)O(2)N(1)N(3) atoms of the coordination polyhedron lie in one plane within 0,045 Å. In $NiL^3 \cdot NH_3$, the central nickel(II) atom shows virtually no displacement from the mean plane of the coordinated O(1), O(2), N(2) and N(3) atoms. The large difference between the O(1)NiN(2) (84,11(14)°) and N(3)NiO(1) (92,57(16)°) bond angles is explained by the sizes of the fused five- and six-membered metallacycles around the complex-forming ion. The bond angles involving O(2) range from 87,90 to 95,5°, while the O(1)NiO(2) and N(2)NiN(3) angles are 177,17(12) and 175,17(12)°, respectively.

CONCLUSION

The aroylhydrazones of benzoylacetaldehyde were found to exhibit ring–chain tautomeric equilibrium in solvents of different nature. Increasing the steric bulk of the substituent in the acyl moiety of the molecule (a tert-butyl or phenyl group) decreases the proportion of the cyclic pyrazoline form.

During complex formation, the ligands undergo ring–chain tautomerism, changing the electron density distribution in the fused five- and six-membered metallacycles. In chelate complexes of 3d

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metals, the central ion and the doubly deprotonated ligand were found to form five- and six-membered pseudoaromatic metallacycles. Dissolving square-planar Ni(II) ammine complexes in pyridine was shown to produce a d–π back-dative bond between the metal d electrons and the pyridine π orbital.

^{1}H NMR spectroscopy and X-ray structural analysis established that the Ni(II) complexes have a square-planar structure with a trans-[N_2O_2] donor-atom arrangement.

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