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Co(II), Ni(II), Cu(II) COMPLEXES WITH 1-NICOTINOYL-2-(2-HYDROXYBENZYL) HYDRAZINE

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By reduction of 1-nicotinoyl-(2-salicylidene)hydrazone with use NaBH_4 1-nicotinoyl-2-(2-hydroxybenzyl)hydrazine was obtained. Co(II), Ni(II), Cu(II) complexes with these ligands were synthesized and their structure was studied. It was shown that first ligand behaves as a dianionic tridentate, while second is monoanionic tridentate.

Keywords: hydrazides hydrazones, nicotinic acid, metal complexes Co(II), Ni(II), Cu(II).

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Introduction

Metal complexes with nicotinoylhydrazones-o-hydroxyaryl- aldehydes exhibit antioxidant, antimicrobial [1], antituberculosis activity [2], have catalytic activity in the alcohols oxidation [3], epoxidation of olefins [4] and catalyze the reaction of benzoyl chloride with arylboronic acid to form fluorenes [5].

Nicotinoilsalicylidenehydrazides are potentially dianionic tetradentate ligands, therefore they are capable to forming various mono-, bi- and polynuclear structures with metal ions.

In the present of time, mononuclear oxo- and dioxovanadium complexes [6, 7], mono-, binuclear dioxomolybdenum complexes [3, 7, 8], polynuclear zinc complexes [9], mononuclear complexes of V(IV), Mn(III), Ni(II), Cu(II) [1], Ag(I) [10], Fe(III) [11], Pb(II) [12] and Pd(II) are known [5].

Almost in all these complexes, 1-nicotinoyl-2-salicylidenehydrazone behaves as a tridentate and mono- or dianionic (depending on the nature of the metal ion) ligand. It is noteworthy, that in most cases the pyridine nitrogen atom does not participate in coordination, however, in some cases it enters into coordination with neighboring metal atoms, forming polymeric structures [9].

An analysis of the literature has shown, that so far there have been no publications in the literature on metal complexes with hydrazones, reduced on the azomethine bond. At the same time, such ligands can be of interest due to their flexible structure. In this work, we obtained 1-nicotinoyl-2-(2-hydroxybenzyl)hydrazine, Co(II), Ni(II), Cu(II) complexes with this ligand and studied their structure and properties.

Experimental part

Nicotinoylhydrazide bought from the firm "Sigma Aldrich"

1-nicotinoyl-(2-salicylidene)hydrazone (I).

10^{-3} mol (0.137 g) of nicotinoilhydrazide was dissolved in 15 ml of dioxane and there solution of 10^{-3} mol (0.122 g) of salicylic aldehyde in 10 ml methanole was added. The mixture was stirred in the magnetic stirrer at 40°C for 20 minutes. After cooling the solution bright yellow Schiff base I crystals precipitated, which were filtered and dried, m.p. = 222°C .

Cu(II) complex with ligand 1-nicotinoyl-(2-salicylidene)hydrazone (I). 10^{-3} mol (0.241 g) of the hydrazone (I) was dissolved in 10 ml of dioxane, and there a solution of 10^{-3} mol (0.199 g) of copper(II) acetate in 10 ml of water was added. The mixture was heated at 50°C for 20 min, then the solution was filtered. After cooling dark green crystals with a melting point $>250^\circ\text{C}$ dropped out.

The Co(II) and Ni(II) complexes were obtained similarly.

Reduction of 1-nicotinoyl-(2-salicylidene)hydrazone (I). 0.1 mol of 1-nicotinoyl-2-salicylidene) hydrazone was suspended in 40 ml of methanol and there added in small portions of 0.15 mol of sodium borohydride with at intensive stirring. After adding the whole amount of NaBH_4 , stirring was continued for 0.5 hour, then the colorless solution was diluted three times with water and acidified with a solution of HCl (~10%) to pH ~7.5. The dropped out substance was separated on a porous filter, washed by water, dried and recrystallized from mixture ethanol-water 1:1. After drying under vacuum, $T_{\text{melt}} > 250^\circ\text{C}$.

Cu(II) complex with 1-nicotinoyl-2-(2-hydroxybenzyl) hydrazine (II). 10^{-3} mol (0.243 g) 1-nicotinoyl-2-(2-hydroxybenzyl)hydrazine(II), dissolved in 30 ml of ethanol, mixed with a methanol solution of $1 \cdot 10^{-3}$ mol (0.199 g) of Cu $(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. After some time, dark blue small crystals dropped out, which was separated and dried. The melting point is $> 250^\circ\text{C}$.

Calculated% C 49.38, H 4.12, O 17.56, N 11.52, Cu 17.42. $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3\text{Cu}$.

Found, %: C 49.40, H 4.17, O 17.46, N 11.59, Cu 17.32.

The Co(II) and Ni(II) complexes were obtained similarly to the copper complex with using cobalt and nickel tetrahydrate acetate.

Calculated, % : C 50.09, H 4.17, O 17.78, N 11.67, Co 16.37($\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3\text{Co}$).

Found, % : C 50.08, H 4.19, O 17.83, N 11.71, Co 16.42.

Calculated,%: C 50.04, H 4.17, O 17.79, N 11.68, Ni 16.3. $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3\text{Ni}$.

Found, %: C 50.08, H 4.12, O 17.81, N 11.70, Ni 16.45.

A fine crystalline precipitate of brown and green color, respectively, precipitated from

the resulting solutions, which were separated and dried in vacuum.

Results and discussion

We have synthesized for the first time 1-nicotinoyl-2-(2-hydroxybenzyl)hydrazine (II) by reducing of 1-nicotinoyl-(2-salicylidene)hydrazine (I) with using sodium borohydride and its complexes with Co(II), Ni(II), Cu(II). For comparison the Co(II), Ni(II), Cu(II) complexes without reduced ligand I were received and studied.

The IR spectrum the reduced hydrazone(II) (Figure 1) contains an intense absorption band at 3360 cm^{-1} , related to stretching vibrations of N–H and also band of vibrations of amide carbonyl group at 1662 cm^{-1} . The absorption band at 1620 cm^{-1} , which is observed in the Schiff base I, is absent in the reduced ligand II. It should be noted the absence in the IR spectrum of the Schiff base of the absorption band of the carbonyl amide group at $\approx 1660\text{ cm}^{-1}$, which undoubtedly is result of strong shift of keto-enol equilibrium towards the formation of the enol form (compound Ib):

Fig.1. IR spectra 1-nicotinoyl-(2-salicylidene)hydrazine (I) and 1-nicotinoyl-2-(2-hydroxybenzyl) hydrazine (II) (dashed line).

Electronic absorption spectra of hydrazine I and reduced hydrazone II (Figure 2) confirm the predominant presence of the enol form in compound I. The long-wavelength absorption band at 360 nm in compound I can be attributed to the $C=N-N=C$ fragment, conjugated with aromatic rings and the band at 300 nm – to absorption due to aromatic rings. In the reduced compound II, the absorption band of the aromatic rings is shifted to the shortwave region and is observed at 280 nm.

Fig. 2. Electronic absorption spectra of compounds I and II in ethanol.

The IR spectra of metal complexes (Cu(II), Co(II) and Ni(II)) with hydrazine I contain the absorption band of the azomethine group at $1615\text{--}1630\text{ cm}^{-1}$ and do not contain the absorption band of amide carbonyl at $\approx 1660\text{ cm}^{-1}$. This confirms his participation in coordination with the metal ion in the enolic form. There is also an absorption peak at 3400 cm^{-1} related to coordinated water.

Thus, the data of elemental analysis and IR spectroscopy suggest the following structure for metal complexes with ligand I (structure III).

In the IR spectra of a nickel (II) complex with a reduced ligand II, the amide carbonyl band observed in the starting ligand at 1666 cm^{-1} shifts towards lower frequencies. The presence of this band and its shift during complexation indicate its participation in coordination in the keto-form. This, in turn, is evidence that the ligand in this case is monoanionic. In addition, the IR spectrum of this complex contains absorption bands of the carboxylate group at 1580 and 1420 cm^{-1} .

The obtained data allows us to accept the structure (IV) for these complexes.

III

IV

$M=\text{Co(II), Ni(II), Cu(II)}$

Thus, it has been shown that nicotinoyl-hydrazone of salicylic aldehyde can be reduced to the corresponding nicotinoyl 2-hydroxybenzyl hydrazide. Studies have also shown the different nature of coordination of 1-nicotinoyl-2-salicylidenehydrazone and its reduced analogue 1-nicotinoyl-2-(2-hydroxybenzyl)hydrazine. If in the first case the ligand behaves as dianionic tridentate, in the second case it is monoanionic tridentate.

A number of works are known in which it has been shown that carbohydrate hydrazides, hydrazones carboxylic acids possess bactericidal and fungicidal properties [1, 2].

However, hydrazones and their complexes reduced by the azomethine group have not been studied yet in this respect. We have shown the bactericidal and fungicidal properties of 1-nicotinoyl-2-(2-hydroxybenzyl)hydrazine (II) and its Co(II) complex (see table).

It can be seen from table, that 1-nicotinoyl-2-(2-hydroxybenzyl)hydrazine (II) showed the high fungicidal and bactericidal activity. The Co(II) complex showed only bactericidal activity.

Antimicrobial properties of 1-nicotinoyl-2-(2-hydroxybenzyl) hydrazine (II) and its Co(II) complex

Conc, at %	Chemical formula	The diameter of the zone of inhibition, cm	
		Bacterium in the environment of MPA (meat-peptide agar)	agar mushrooms
1		2.0–2.2	1.0–1.2
0.5		1.6–1.8	0.8–1.0
0.25		1.4–1.4	+ +
1.0		1.8–2.0	+ + +
0.5		1.6–1.6	+ + +
0.25		1.2–1.3	+ + +

+ – the absence of activity

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1-NİKOTİNOİL-2-(2-HİDROKSİBENZİL)HİDRAZİNİN Co(II), Ni(II), Cu(II) KOMPLEKSLƏRİ**P.A.Fatullayeva**

1-nikotinoil-2-(caliciliden)hidrazonun(I) NaBH_4 vasitəci ilə reduksiyası yolu ilə 1-nikotinoil-2-hidroksibenzil)hidrazin alınmışdır. Bu liqandla Co(II), Ni(II), Cu(II) kompleksləri sintez olunmuş və onların quruluşu öyrənilmişdir. Göstərilmişdir ki, 1-nikotinoil-2-(caliciliden) hidrazon (I) özünü dianion tridentat liqand kimi, 1-nikotinoil-2-(2-hidroksibenzil)hidrazin(II) özünü monoanion tridentat liqand kimi aparır.

Açar sözlər: nikotin turşusunun hidrazidləri, hidrazonların reduksiyası, metal kompleksləri.

КОМПЛЕКСЫ Co(II), Ni(II), Cu(II) С 1-НИКОТИНОИЛ-2-(2-ГИДРОКСИБЕНЗИЛ) ГИДРАЗИНА**П.А.Фатуллаева**

Восстановлением 1-никотиноил-(2-салицилиден)гидразона с помощью NaBH_4 получен 1-никотиноил-2-(2-гидроксибензил)гидразин. Синтезированы комплексы Co(II), Ni(II), Cu(II) с этими лигандами и изучено их строение. Показано, что первый ведет себя как дианионный тридентатный, в то время как второй – моноанионный тридентатный лиганд.

Ключевые слова: гидразиды никотиновой кислоты, восстановление гидразонов, комплексы металлов.