

# Cobalt, Nickel, and Copper Coordination Compounds with 3-Phenylpropenal Benzoylhydrazone

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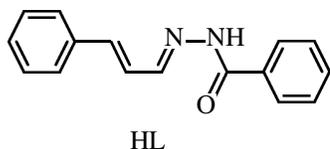
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**Abstract**—3-Phenylpropenal benzoylhydrazone (HL) reacts with cobalt, nickel, and copper chlorides, nitrates, and acetates to give coordination compounds  $\text{MX}_2 \cdot 2\text{HL} \cdot n\text{H}_2\text{O}$  [ $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ ;  $\text{X} = \text{Cl}, \text{NO}_3$ ,  $\text{HL} = \text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{NNHC}(\text{O})\text{C}_6\text{H}_5$ ;  $n = 0, 2$ ] and  $\text{ML}_2 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ ;  $n = 1-3$ ). Complexes  $\text{MALCl}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ ) were obtained by these reactions in the presence of amines ( $\text{A} = \text{C}_5\text{H}_5\text{N}, 2\text{-CH}_3\text{C}_5\text{H}_4\text{N}, 3\text{-CH}_3\text{C}_5\text{H}_4\text{N}, 4\text{-CH}_3\text{C}_5\text{H}_4\text{N}$ ). All the compounds have a monomeric structure. Azomethine (HL) in them behaves as a bidentate *N,O*-ligand. Thermolysis of the complexes involves the stages of dehydration (70–90°C), deaquation (145–155°C) or deamination (145–185°C), and complete thermal decomposition (330–490°C).

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Benzoylhydrazones of aromatic aldehydes and ketones contain a broad range of donor atoms in their composition and form with transition metal ions coordination compounds with various composition, structure, and properties [1–5]. Many of these substances are biologically active [6–8], which allows them to be used as a basis for creation of selective microbiological nutrient media, as well as potential disinfectants and antiseptics. In this connection synthesis and study of new coordination compounds of biometals with benzoylhydrazones are of both scientific and practical interest.

The aim of the present work was to find optimal conditions for synthesis of cobalt, nickel, and copper complexes with 3-phenylpropenal benzoylhydrazone HL, to determine their composition and structure, and to study their physicochemical properties.



It was shown that the reactions of hot (50–55°C) ethanol solutions of cobalt, nickel, and copper chlorides, nitrates, and acetates with hydrazone (HL) in a 1:2 molar ratio yield compounds **I–VIII** as fine crystals. On the basis of the elemental analysis (Table 1) we proposed the compositions  $\text{MX}_2 \cdot 2\text{HL} \cdot n\text{H}_2\text{O}$  [ $\text{M} = \text{Co}$  (**I**, **II**),  $\text{Ni}$  (**III**, **IV**),  $\text{Cu}$  (**V**);  $\text{X} = \text{Cl}$  (**I**, **III**, **V**),  $\text{NO}_3$  (**II**, **IV**);  $n = 0$  (**I**, **III**, **V**), 2 (**II**, **IV**)] and  $\text{ML}_2 \cdot n\text{H}_2\text{O}$  [ $\text{M} = \text{Co}$  (**VI**),  $\text{Ni}$  (**VII**),  $\text{Cu}$  (**VIII**);  $n = 1$

(**VIII**), 2 (**VI**), 3 (**VII**)]. The above reactions in the presence of sodium acetate, pyridine, or 2-, 3-, or 4-picoline (pH 7.0–7.5) result in the isolation of complexes  $\text{MALCl} \cdot n\text{H}_2\text{O}$  (**IX–XV**) [ $\text{M} = \text{Co}$  (**IX**),  $\text{Ni}$  (**X**),  $\text{Cu}$  (**XI–XV**);  $\text{A} = \text{H}_2\text{O}$  (**XI**),  $\text{C}_5\text{H}_5\text{N}$  (**IX**, **X**, **XII**), 2- $\text{CH}_3\text{C}_5\text{H}_4\text{N}$  (**XIII**), 3- $\text{CH}_3\text{C}_5\text{H}_4\text{N}$  (**XIV**), 4- $\text{CH}_3\text{C}_5\text{H}_4\text{N}$  (**XV**);  $n = 0$  (**IX**, **X**, **XII–XV**), 1 (**XI**)].

Complexes **I–XV** are insoluble in diethyl ether, sparingly soluble in water, better soluble in alcohols, and readily soluble in DMF, DMSO, and acetonitrile. Their yields and certain physicochemical properties are given in Table 1.

The molecular conductivities of the synthesized complexes in DMF show that compounds **I**, **III**, and **V–XV** are nonelectrolytes, and compounds **II** and **IV**, ternary electrolytes. Magnetochemical study showed that all the cobalt and nickel compounds are paramagnetic, and, judging from the effective magnetic moments, the central atoms in adducts **I–IV** have a pseudo-octahedral structure, and in complexes **VI**, **VII**, **IX**, and **X**, a tetrahedral structure. Similar structures were observed earlier [9] in nickel complexes with 3-phenylpropenal azomethines and were confirmed by X-ray diffraction analysis. The magnetochemical characteristics of copper complexes **V**, **VIII**, and **XI–XV** correspond to the spin value for one unpaired electron and point to their monomeric structure.

Thermal analysis of compounds **I–XV** (Table 2) showed their thermolysis involves the stages of dehydration (60–90°C), deaquation (160–190°C) or deamination (170–210°C) up to complete thermo-

**Table 1.** Physicochemical characteristics of cobalt, nickel, and copper coordination compounds **I–XV** with 3-phenylpropenal benzoylhydrazone

Comp. no.	Yield, %	$\mu_{\text{eff}}^a$ , BM	$\alpha^a$ , $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$	Found, %			Formula	Calculated, %		
				Cl	M <sup>b</sup>	N		Cl	M <sup>b</sup>	N
<b>I</b>	69	4.98	3	11.07	9.16	8.60	$\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{CoN}_4\text{O}_2$	11.30	9.37	8.89
<b>II</b>	74	5.06	136	–	7.95	11.51	$\text{C}_{32}\text{H}_{32}\text{CoN}_6\text{O}_{10}$	–	8.21	11.68
<b>III</b>	75	3.06	5	11.16	9.49	8.99	$\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{N}_4\text{NiO}_2$	11.30	9.37	8.89
<b>IV</b>	66	2.98	144	–	8.05	11.46	$\text{C}_{32}\text{H}_{32}\text{N}_6\text{NiO}_{10}$	–	8.21	11.68
<b>V</b>	87	1.78	2	11.29	9.90	8.59	$\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{CuN}_4\text{O}_2$	11.18	10.08	8.82
<b>VI</b>	56	4.12	2	–	10.11	9.28	$\text{C}_{32}\text{H}_{30}\text{CoN}_4\text{O}_4$	–	9.95	9.44
<b>VII</b>	57	4.55	4	–	9.37	8.98	$\text{C}_{32}\text{H}_{32}\text{N}_4\text{NiO}_5$	–	9.66	9.17
<b>VIII</b>	65	1.83	3	–	10.77	9.39	$\text{C}_{32}\text{H}_{28}\text{CuN}_4\text{O}_3$	–	11.03	9.66
<b>IX</b>	74	4.02	6	8.26	14.16	10.05	$\text{C}_{21}\text{H}_{18}\text{ClCoN}_3\text{O}$	8.40	13.96	9.94
<b>X</b>	64	4.64	3	8.19	13.71	9.80	$\text{C}_{21}\text{H}_{18}\text{ClN}_3\text{NiO}$	8.40	13.96	9.94
<b>XI</b>	84	1.75	2	8.98	16.45	6.99	$\text{C}_{16}\text{H}_{17}\text{ClCuN}_2\text{O}_3$	9.23	16.64	7.28
<b>XII</b>	59	1.89	3	8.03	15.7	9.65	$\text{C}_{21}\text{H}_{18}\text{ClCuN}_3\text{O}$	8.30	14.97	9.82
<b>XIII</b>	91	1.80	3	7.81	14.70	9.25	$\text{C}_{22}\text{H}_{20}\text{ClCuN}_3\text{O}$	8.04	14.97	9.51
<b>XIV</b>	90	1.94	4	8.16	14.79	9.64	$\text{C}_{22}\text{H}_{20}\text{ClCuN}_3\text{O}$	8.04	14.97	9.51
<b>XV</b>	93	1.79	3	7.93	14.90	9.30	$\text{C}_{22}\text{H}_{20}\text{ClCuN}_3\text{O}$	8.04	14.97	9.51

<sup>a</sup> At 293 K. <sup>b</sup> M is metal.

**Table 2.** Thermal analysis of cobalt, nickel, and copper coordination compounds **I–XV** with 3-phenylpropenal benzoylhydrazone

Comp. no.	Number of the endo effects in DTA curve	Temperature of maximum effect, °C	Weight loss			Kinetic parameters		Temperature of complete decomposition, °C
			found, %	calculated, %	corresponds to detachment of	$E_a$ , $\text{kJ mol}^{-1}$	$\log Z$	
<b>I</b>	–	–	–	–	–	–	–	460
<b>II</b>	1	155	5.3	5.0	$2\text{H}_2\text{O}$	55.2	6.6	410
<b>III</b>	–	–	–	–	–	–	–	440
<b>IV</b>	1	145	4.9	5.0	$2\text{H}_2\text{O}$	49.7	5.8	400
<b>V</b>	–	–	–	–	–	–	–	400
<b>VI</b>	1	85	6.0	6.1	$2\text{H}_2\text{O}$	38.2	4.6	360
<b>VII</b>	1	75	9.0	8.8	$3\text{H}_2\text{O}$	35.9	4.5	360
<b>VIII</b>	1	70	3.4	3.1	$\text{H}_2\text{O}$	32.7	4.4	330
<b>IX</b>	1	185	18.5	18.7	$\text{C}_5\text{H}_5\text{N}$	89.2	9.4	490
<b>X</b>	1	170	18.6	18.7	$\text{C}_5\text{H}_5\text{N}$	75.4	8.6	480
<b>XI</b>	1	90	4.5	4.7	$\text{H}_2\text{O}$	34.1	4.5	440
	2	155	5.0	4.7	$\text{H}_2\text{O}$	48.6	5.7	
<b>XII</b>	1	160	18.8	18.5	$\text{C}_5\text{H}_5\text{N}$	68.9	7.8	460
<b>XIII</b>	1	145	21.5	21.1	$\text{C}_6\text{H}_7\text{N}$	67.2	7.7	445
<b>XIV</b>	1	175	21.3	21.1	$\text{C}_6\text{H}_7\text{N}$	75.1	8.5	475
<b>XV</b>	1	160	21.2	21.1	$\text{C}_6\text{H}_7\text{N}$	72.5	8.4	465

oxidative decomposition (360–530°C). The complete decomposition temperature ( $t$ ) depends on the central atom and changes in the following order at the same inner-sphere composition of the coordination com-

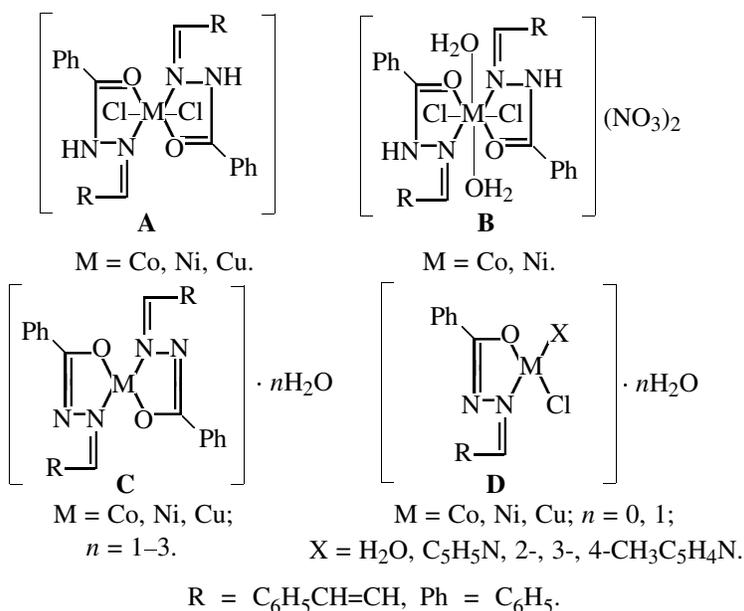
pound:  $t(\text{Co}) > t(\text{Ni}) > t(\text{Cu})$ . The decomposition temperature is also affected by the nature of inner-sphere ligands. It increases when nitrate ion is replaced by chloride ion and the inner-sphere water is

replaced by amines, and for amine complexes **IX**, **X**, and **XII–XV** with the same central atom the following order is observed:  $t(3\text{-CH}_3\text{C}_5\text{H}_4\text{N}) \geq t(4\text{-CH}_3\text{C}_5\text{H}_4\text{N}) \geq t(\text{C}_5\text{H}_5\text{N}) > t(2\text{-CH}_3\text{C}_5\text{H}_4\text{N})$ . Using the Horowitz–Metzger method [10] with the Topor additions [11], we estimated kinetic parameters for deaquation and deamination of the complexes under study. The resulting data (Table 2) show that the activation energies ( $E_a$ ) and preexponential factors ( $Z$ ) are close to those for similar reactions described in the literature [12–14]. We found that the nature of the central atom and inner-sphere ligands affect  $E_a$  and  $\log Z$  of the processes under study, and for complexes with the same composition they vary as follows:  $\text{Zn} > \text{Co} > \text{Ni}$ ,  $3\text{-H}_3\text{C}_5\text{H}_4\text{N} > 4\text{-H}_3\text{C}_5\text{H}_4\text{N} > \text{C}_5\text{H}_5\text{N} > 2\text{-H}_3\text{C}_5\text{H}_4\text{N}$ . The revealed order parallels the above sequence of complete decomposition temperatures and the order of amine basicities. The only outlier in the latter order is  $2\text{-H}_3\text{C}_5\text{H}_4\text{N}$ , probably, by steric reasons.

To determine the mode of ligand coordination with central ions, we compared the IR spectra of complexes **I–XV**, starting hydrazone HL, and coordination compounds of transition metals with similar Schiff bases described in the literature [1–9]. Azomethine HL in the complexes under study behaves as a bidentate electroneutral or monodeprotonated *N,O*-ligand attached to the complex-forming ion through the azomethine nitrogen atom and the oxygen atom of the carbamide fragment to form a five-membered metal cycle. Evidence for this conclusion is provided by a  $30\text{--}25\text{ cm}^{-1}$  low-frequency shift of the  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{O})$  absorption bands compared to analogous absorption bands in the spectrum of the starting hydrazone, where they are observed at  $1600$  and  $1630\text{ cm}^{-1}$ ,

respectively. The fact that the oxygen atom of the ligand in the deprotonated thiocarbamide form coordinates with the central atoms is confirmed by the disappearance of the  $\nu(\text{C}=\text{O})$  band at  $1630\text{ cm}^{-1}$  and the  $\nu(\text{NH})$  bands at  $3230\text{--}3200$  and  $3170\text{--}3150\text{ cm}^{-1}$  from the IR spectra of complexes **VI–XV** and also by the appearance of a new absorption band at  $600\text{--}580\text{ cm}^{-1}$ , assignable to  $\nu(\text{C}=\text{O})$  [15], and by the splitting the  $\nu(\text{C}=\text{N})$  band at  $1595\text{--}1590\text{ cm}^{-1}$  into two components. Further evidence for the above coordination of hydrazone HL comes from the appearance of a number of new absorption bands in the region of  $550\text{--}400\text{ cm}^{-1}$  [ $\nu(\text{M}\text{--}\text{N})$  at  $530\text{--}510$  and  $425\text{--}405\text{ cm}^{-1}$  and  $\nu(\text{M}\text{--}\text{O})$  at  $490\text{--}470\text{ cm}^{-1}$ ] in the IR spectra of all the complexes. Participation of the other functional groups of the Schiff base in the coordination with metal ions is excluded, since their characteristic absorption bands appear in the same regions as in the spectrum of the starting hydrazone. The presence of coordinated molecules of water and amines in the complexes is confirmed by the presence of the corresponding absorption bands in their IR spectra [ $\nu(\text{H}_2\text{O})$   $3595\text{--}3580$ ,  $\delta(\text{H}_2\text{O})$   $1580\text{--}1575$ , and  $\gamma(\text{H}_2\text{O})$   $920\text{--}915\text{ cm}^{-1}$  in the case of aqua complexes **II**, **IV**, and **XI** and  $\gamma(\text{CC}) + \nu(\text{CN}) + \delta(\text{CCH})$   $1640\text{--}1635$ ,  $1530\text{--}1525$ ,  $\nu(\text{CN})$   $1310\text{--}1305$ ,  $\delta(\text{CCN})$   $1230\text{--}1225$ ,  $\delta(\text{CCN})$   $1230\text{--}1225$ ,  $\delta(\text{CCH}) + \nu(\text{CC}) + \delta(\text{CNC})$   $1060\text{--}1055$ ,  $1030\text{--}1025$ ,  $\gamma(\text{CCC}) + \gamma(\text{CNC})$   $730\text{--}725$ , and  $\rho(\text{CH})$   $830\text{--}825\text{ cm}^{-1}$  in the case of amine complexes **IX**, **X**, and **XII–XV**].

The obtained physicochemical data allow us to present the distribution of chemical bonds in complexes **I–XV** by schemes **A–D**.



## EXPERIMENTAL

The resistance of solutions of complexes **I–XV** in DMF (20°C, *c* 0.001 M) was measured by a P-38 slide-wire bridge. The IR spectra of Nujol suspensions of samples preliminarily dried at 105°C to constant weight were recorded on a Specord M-80 spectrophotometer. The effective magnetic moments of compounds **I–XV** were determined by the Gouy method. The molar magnetic susceptibility corrected for diamagnetism was calculated on the basis of theoretical magnetic susceptibilities of organic compounds. The thermoanalytical curves of complexes **I–XV** were taken on a Paulik–Paulik–Erdey derivatograph in the range 20–1000°C in air (standard Al<sub>2</sub>O<sub>3</sub>, corundum crucible).

The starting 3-phenylpropenal benzoylhydrazone was prepared by the published procedure [16.]

**Dichlorobis[N-(3-phenylprop-2-enylidene)-N'-benzoylhydrazine]cobalt.** To a hot (50–55°C) solution of 10 mmol of cobalt dichloride hexahydrate in 25 ml of ethanol, 25 ml of a solution of 20 mmol of 3-phenylpropenal benzoylhydrazone in ethanol. The reaction mixture was heated for 30–40 min with continuous stirring. A dark brown substance was precipitated from it on cooling and was filtered off on a glass filter, washed with small amounts of alcohol and ether, and dried in air to constant weight.

Complexes **II–VIII** were synthesized in a similar way starting from benzoylhydrazone HL and hydrates of cobalt, nickel, or copper chlorides, nitrates, or acetates. Complexes **IX, X, and XII–XV** were obtained by the above-described procedure by the reactions of the salts and azomethine HL in a 1:1 molar ratio in the presence of pyridine or 2-, 3-, or 4-picoline (pH 8). Compound **XI** was synthesized similarly, using ethanolic sodium acetate (pH 7.5) as proton acceptor.

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