

# Coordination Compounds of Cobalt, Nickel, and Copper with Isonitrosoacetone Benzoylhydrazone

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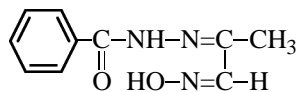
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Received March 6, 2000

**Abstract**—Benzoylhydrazine and isonitrosoacetone react in ethanol with cobalt, nickel, and copper halides and acetates to give the coordination compounds  $\text{MX}_2(\text{HL}) \cdot n\text{H}_2\text{O}$ ,  $\text{MX}_2(\text{HL})_2 \cdot n\text{H}_2\text{O}$ , and  $\text{ML}_2 \cdot n\text{H}_2\text{O}$  [ $\text{M} = \text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ;  $\text{HL} = \text{C}_6\text{H}_5\text{C}(\text{O})\text{NHNC}(\text{CH}_3)\text{CHNOH}$ ;  $n = 1-4$ ]. The same reactions performed in the presence of sodium acetate and pyridine (pH 7–8) yield the complexes  $\text{MLCl} \cdot n\text{H}_2\text{O}$  and  $\text{MPy}_2\text{LCl} \cdot n\text{H}_2\text{O}$  ( $n = 1-4$ ). All the complexes have a pseudooctahedral coordination geometry. The hydrazone HL behaves as a tridentate *O,N,N*-donor ligand. Thermolysis of the substances involves dehydration (70–90°C), deaquation (155–170°C) or deamination (175–195°C), and complete thermal decomposition (285–360°C).

Benzoylhydrazones of aliphatic and aromatic aldehydes or ketones contain a set of different donor atoms and form with transition metal ions various coordination compounds differing in the composition, structure, and properties [1–4]. Many of these substances exhibit biological activity [5, 6], which makes them promising as biochemical agents and pharmaceuticals. In this connection, synthesis and study of new coordination compounds of biometals with benzoylhydrazones is of both scientific and practical interest.

The goal of this work was to find optimal synthesis conditions, determine the composition and probable structure, and study physicochemical properties of cobalt, nickel, and copper complexes with isonitrosoacetone benzoylhydrazone HL.



HL

Experiment showed that reactions of ethanolic solutions of benzoylhydrazine and isonitrosoacetone with Co, Ni, and Cu chlorides or bromides (molar ratio 1 : 1 : 1 and 2 : 2 : 1) yield finely crystalline substances identified by elemental analysis (Table 1) as  $\text{MX}_2(\text{HL}) \cdot n\text{H}_2\text{O}$  (**I–V**) and  $\text{MCl}_2(\text{HL})_2 \cdot n\text{H}_2\text{O}$  (**VI**, **VII**), where  $\text{M}^{2+} = \text{Co}$  (**I**, **II**, **VI**),  $\text{Ni}$  (**III**, **VII**),  $\text{Cu}$  (**IV**, **V**);  $\text{X}^- = \text{Cl}$  (**I**, **III**, **IV**),  $\text{Br}$  (**II**, **V**);  $n = 1$  (**VII**), 2 (**II**, **VI**), 3 (**I**, **III**, **V**), 4 (**IV**).

When the reaction is performed in the presence of sodium acetate or pyridine (pH 7–8), the complexes  $\text{MLCl} \cdot n\text{H}_2\text{O}$  (**VIII–X**) and  $\text{MPy}_2\text{LCl} \cdot n\text{H}_2\text{O}$  (**XI–**

**XIII**) are formed, where  $\text{M}^{2+} = \text{Co}$  (**VIII**, **XI**),  $\text{Ni}$  (**IX**, **XII**),  $\text{Cu}$  (**X**, **XIII**);  $n = 0$  (**XIII**), 1 (**XI**, **XII**), 3 (**X**), 4 (**VIII**, **IX**).

Cobalt and nickel acetates react in ethanol with benzoylhydrazine and isonitrosoacetone (molar ratio 1 : 2 : 2) to form coordination compounds **XIV** and **XV** of the composition  $\text{ML}_2 \cdot n\text{H}_2\text{O}$  (**XIV**, **XV**), where  $\text{M}^{2+} = \text{Co}$  (**XIV**),  $\text{Ni}$  (**XV**);  $n = 2$  (**XV**), 3 (**XIV**).

Compounds **I–XV** are insoluble in ether, sparingly soluble in water and alcohols, and readily soluble in dimethylformamide and dimethyl sulfoxide. Their yields and physicochemical characteristics are listed in Table 1.

The analytical data for **I–XV** (Table 1) suggest that, similar to the reactions described in [7–9], template condensation of benzoylhydrazine with isonitrosoacetone occurs on the  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , or  $\text{Cu}^{2+}$  matrix with formation of the Schiff base HL forming with the metal ions coordination compounds **I–XV**.

Determination of the molar electrolytic conductivity of the complexes in DMF showed that compounds **I–V** and **VIII–XV** are nonelectrolytes, whereas compounds **VI** and **VII** are 1–2 electrolytes [ $\kappa(\text{VI})$  149,  $\kappa(\text{VII})$  160  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , 20°C,  $10^{-3}$  M].

Magnetochemical study showed (Table 1) that the cobalt ion in **I**, **II**, **VI**, **VII**, **XI**, and **XIV** occurs in the oxidation state 2+ (electronic state  $t_{2g}^5 e_g^2$ ). The nickel compounds **III**, **VII**, **IX**, **XI**, and **XV** are paramagnetic and, as judged from the effective magnetic moments, have the pseudooctahedral structure of the coordination core (electronic state of the central atom  $t_{2g}^6 e_g^2$ ). All the copper complexes are monomeric, as

**Table 1.** Physicochemical characteristics of cobalt, nickel, and copper coordination compounds with isonitrosoacetone benzoylhydrazone

Comp. no.	Yield, %	$\mu_{\text{eff}}$ , BM (294 K)	Found, %			Formula	Calculated, %		
			Cl (Br)	M	N		Cl (Br)	M	N
<b>I</b>	78	4.89	18.01	14.96	10.57	$\text{C}_{10}\text{H}_{17}\text{Cl}_2\text{CoN}_3\text{O}_5$	18.25	15.17	10.80
<b>II</b>	86	5.02	(34.47)	12.64	8.90	$\text{C}_{10}\text{H}_{15}\text{Br}_2\text{CoN}_3\text{O}_4$	(34.78)	12.83	9.13
<b>III</b>	81	2.87	18.14	15.25	10.61	$\text{C}_{10}\text{H}_{17}\text{Cl}_2\text{N}_3\text{NiO}_5$	18.25	15.17	10.80
<b>IV</b>	72	1.79	16.94	15.41	9.88	$\text{C}_{10}\text{H}_{19}\text{Cl}_2\text{CuN}_3\text{O}_6$	17.23	15.53	10.19
<b>V</b>	83	1.76	(32.87)	12.96	8.54	$\text{C}_{10}\text{H}_{17}\text{Br}_2\text{CuN}_3\text{O}_5$	(33.13)	13.25	8.70
<b>VI</b>	69	5.01	12.09	11.96	14.31	$\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{CoN}_6\text{O}_6$	12.33	10.24	14.58
<b>VII</b>	65	2.91	12.48	10.30	14.76	$\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{N}_6\text{NiO}_5$	12.72	10.57	15.05
<b>VIII</b>	79	5.11	9.29	15.69	11.06	$\text{C}_{10}\text{H}_{18}\text{ClCoN}_3\text{O}_6$	9.58	15.92	11.34
<b>IX</b>	76	2.94	9.37	15.74	11.20	$\text{C}_{10}\text{H}_{18}\text{ClN}_3\text{NiO}_6$	9.58	15.92	11.34
<b>X</b>	75	1.78	9.64	17.71	11.62	$\text{C}_{10}\text{H}_{16}\text{ClCuN}_3\text{O}_5$	9.93	17.90	11.75
<b>XI</b>	86	4.93	7.24	12.26	14.60	$\text{C}_{20}\text{H}_{22}\text{ClCoN}_5\text{O}_3$	7.48	12.43	14.75
<b>XII</b>	82	3.09	7.30	12.20	14.53	$\text{C}_{20}\text{H}_{22}\text{ClN}_5\text{NiO}_3$	7.48	12.43	14.75
<b>XIII</b>	83	1.87	7.45	13.81	14.86	$\text{C}_{20}\text{H}_{20}\text{ClCuN}_5\text{O}_2$	7.69	13.87	15.17
<b>XIV</b>	78	4.94	—	11.09	15.87	$\text{C}_{20}\text{H}_{26}\text{CoN}_6\text{O}_7$	—	11.32	16.12
<b>XV</b>	79	2.99	—	11.49	16.53	$\text{C}_{20}\text{H}_{24}\text{N}_6\text{NiO}_6$	—	11.73	16.70

**Table 2.** Results of thermal analysis of Co, Ni, and Cu coordination compounds with isonitrosoacetone benzoylhydrazone

Comp. no.	Number of endoeffect in the DTA curve	T, °C	Weight loss			Kinetic parameters of the processes		Temperature of complete decomposition, °C
			found, %	calculated, %	corresponds to loss of	$E_a$ , kJ mol <sup>-1</sup>	log Z	
<b>I</b>	1	75	9.0	9.2	2H <sub>2</sub> O	38.9	7.8	390
	2	175	4.5	4.6	H <sub>2</sub> O	56.4	9.6	
<b>II</b>	1	80	4.0	3.9	H <sub>2</sub> O	33.2	7.3	370
	2	165	4.3	3.9	H <sub>2</sub> O	52.1	8.9	
<b>III</b>	1	70	9.5	9.2	2H <sub>2</sub> O	36.6	7.6	390
	2	170	4.3	4.6	H <sub>2</sub> O	54.9	9.2	
<b>IV</b>	1	75	13.0	13.2	3H <sub>2</sub> O	31.6	6.8	355
	2	160	4.5	4.4	H <sub>2</sub> O	49.9	8.7	
<b>V</b>	1	70	7.5	7.4	2H <sub>2</sub> O	34.1	7.1	340
	2	150	4.0	3.7	H <sub>2</sub> O	47.8	8.7	
<b>VI</b>	1	90	6.5	6.3	2H <sub>2</sub> O	39.2	8.6	435
<b>VII</b>	1	85	3.0	3.2	H <sub>2</sub> O	34.5	7.5	430
<b>VIII</b>	1	85	9.5	9.7	2H <sub>2</sub> O	41.1	8.2	420
	2	180	9.5	9.7	2H <sub>2</sub> O	75.2	10.4	
<b>IX</b>	1	70	10.0	9.7	2H <sub>2</sub> O	42.9	8.6	410
	2	160	9.5	9.7	2H <sub>2</sub> O	74.1	10.3	
<b>X</b>	1	75	5.2	5.0	H <sub>2</sub> O	35.8	7.5	375
	2	145	9.6	10.0	2H <sub>2</sub> O	65.6	9.6	
<b>XI</b>	1	65	4.0	3.8	H <sub>2</sub> O	40.1	8.8	450
	2	195	33.0	33.3	2C <sub>5</sub> H <sub>5</sub> N	96.3	12.0	
<b>XII</b>	1	80	3.5	3.1	H <sub>2</sub> O	35.3	7.5	445
	2	180	33.1	33.3	2C <sub>5</sub> H <sub>5</sub> N	95.0	11.8	
<b>XIII</b>	1	165	35.5	34.2	2C <sub>5</sub> H <sub>5</sub> N	82.4	11.2	410
<b>XIV</b>	1	70	10.5	10.4	3H <sub>2</sub> O	38.7	8.5	485
<b>XV</b>	1	80	7.0	7.2	2H <sub>2</sub> O	40.4	8.7	480

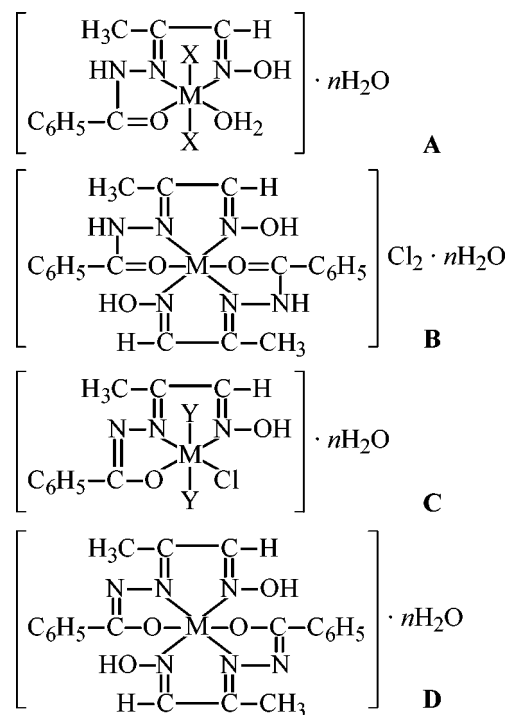
their effective magnetic moments at room temperature correspond to the spin value for one unpaired electron.

To determine the mode of the ligand coordination with the central ions, we compared the IR spectra of the initial substances and complexes **I–XV**. The spectra of the complexes contain no bands belonging to  $\nu(\text{C}=\text{O})$  of isonitrosoacetone and  $\nu(\text{NH})$  of the amino group in benzoylhydrazine, which proves formation of hydrazone HL. In **I–XV** it acts as a tridentate ligand coordinating with the central atom via amide oxygen, hydrazone nitrogen, and oxime nitrogen to form two five-membered chelate rings. This assumption is supported by the fact that in the IR spectra of the complexes the bands  $\nu(\text{C}=\text{O})$  at  $1650\text{--}1640\text{ cm}^{-1}$  and  $\nu(\text{C}=\text{N})$  at  $1605\text{--}1595\text{ cm}^{-1}$  are shifted by  $25\text{--}30\text{ cm}^{-1}$  toward lower frequencies as compared to the corresponding bands in the spectra of benzoylhydrazine, isonitrosoacetone, and related Schiff bases described in the literature [10–12]. Furthermore, it should be noted that in **VIII–XV** hydrazone occurs in the deprotonated (L) imidoalcoholic tautomeric form. This is indicated by the disappearance of the  $\nu(\text{C}=\text{O})$  band at  $1650\text{--}1640\text{ cm}^{-1}$  from the IR spectra of these compounds, splitting of the  $\nu(\text{C}=\text{O})$  band in two ( $1295\text{--}1285$  and  $1280\text{--}1275\text{ cm}^{-1}$ ), and also appearance of the  $\nu(>\text{C}=\text{N}-\text{N}=\text{C}<)$  band at  $1585\text{--}1575\text{ cm}^{-1}$ . Participation of the other functional groups of L in coordination with the metal ions can be ruled out, because their characteristic absorption bands are observed in the same regions as in the spectra of the initial benzoylhydrazine and isonitrosoacetone. The presence in **VIII–XIII** of coordinated water and pyridine molecules is confirmed by the presence in their IR spectra of the corresponding absorption bands: in the case of aqua complexes **VIII–X**,  $\nu(\text{H}_2\text{O})$   $3590\text{--}3580$ ,  $\delta(\text{H}_2\text{O})$   $1595\text{--}1590$ , and  $\gamma(\text{H}_2\text{O})$   $925\text{--}920\text{ cm}^{-1}$ ; in the case of pyridine complexes **XI–XIII**,  $\nu(\text{CC}) + \nu(\text{CN}) + \delta(\text{CCH})$   $1640\text{--}1635$ ,  $1530\text{--}1525$ ,  $\nu(\text{CN})$   $1310\text{--}1305$ ,  $\delta(\text{CCH})$   $1230\text{--}1225$ ,  $\delta(\text{CCH}) + \nu(\text{CC}) + \delta(\text{CNC})$   $1060\text{--}1055$ ,  $1030\text{--}1025$ ,  $\gamma(\text{CCC}) + \gamma(\text{CNC})$   $730\text{--}725$ ,  $\rho(\text{CH})$   $830\text{--}825\text{ cm}^{-1}$ .

Then, it was interesting to study the thermal behavior of **I–XV** and to examine the effect of the central atom and ligand surrounding on the temperature of possible phase transitions, and also to study the kinetics of these processes. Experiment showed (Table 2) that thermolysis of **I–XV** involves a sequence of stages. The endothermic effect observed in the DTA curves at  $70\text{--}90^\circ\text{C}$ , i.e., at a relatively low temperature, apparently corresponds to dehydration. The second endothermic effect is observed at higher temperatures:  $145\text{--}175^\circ\text{C}$  for **I–V** and **VIII–X** and  $165\text{--}195^\circ\text{C}$  for **XI–XIII**. As judged from the weight loss, this effect corresponds to deaquation or deamination.

The third endothermic effect in the DTA curves at  $340\text{--}485^\circ\text{C}$  corresponds to thermal oxidative degradation of the coordinated hydrazone L. The temperature of the maximum of this effect depends on the central atom and for compounds of similar composition decreases in the order  $\text{Co} > \text{Ni} > \text{Cu}$ . The temperature of complete decomposition is also influenced by the inner-sphere ligands: it increases on deprotonation of hydrazone L and replacement of  $\text{Br}^-$  by  $\text{Cl}^-$ . Using the Horowitz–Metzger method [13] supplemented by Topor [14], we estimated the kinetic parameters of dehydration, deaquation, and deamination of **I–XV**. The results are listed in Table 2. It is seen that the evaluated activation energies  $E_a$  and preexponential terms  $Z$  are close to those reported in the literature for similar topochemical processes [15–17]. Experiment showed (Table 2) that the kinetic parameters of elimination of inner-sphere water and pyridine molecules are affected by the nature of the central atom and acido ligand; for the compounds of similar composition, these parameters decrease in the order  $\text{Co} > \text{Ni} > \text{Cu}$  and  $\text{Cl} > \text{Br}$ . The nature of the leaving group also affects the kinetic parameters: In going from aqua to pyridine complexes  $E_a$  and  $\log Z$  increase, which is consistent with the increase in both  $\sigma$ -donor and  $\pi$ -acceptor power of the ligand.

The physicochemical data obtained suggest for **I–XV** structures **A (I–V)**, **B (VI, VII)**, **C (VIII–XIII)**, and **D (XIV, XV)**.



$\text{M} = \text{Co}, \text{Ni}, \text{Cu}; \text{X} = \text{Cl}, \text{Br}; \text{Y} = \text{H}_2\text{O}, \text{C}_5\text{H}_5\text{N}; n = 0\text{--}3$ .

## EXPERIMENTAL

The resistance of solutions of **I–XV** in DMF (20°C, 0.001 M) was measured with an R-38 rheochord bridge. The IR spectra of the substance samples were measured with a Specord M-80 spectrophotometer (mulls in mineral oil) after drying in an oven at 105°C to constant weight. The effective magnetic moments of **I–XV** were determined by the Gouy method. The molar magnetic susceptibility, corrected for diamagnetism, was calculated using theoretical susceptibilities of organic compounds. Thermal analysis of **I–XV** was performed with a Paulik–Paulik–Erdey derivatograph in air in the range 20–500°C (reference Al<sub>2</sub>O<sub>3</sub>, corundum crucible).

**Dichloro(2-hydroxyimino-1-methylethylidene)-benzhydrazideaquacobalt dihydrate I.** Hot (50–55°C) ethanolic solutions of 10 mmol of benzoylhydrazine and 10 mmol of isonitrosoacetone were mixed with an alcoholic solution of 10 mmol of cobalt(II) chloride hexahydrate. The mixture was continuously stirred with a magnetic stirrer at 50–55°C for 60 min. After cooling, a dark brown product precipitated, which was filtered off on a glass frit, washed with a small amount of alcohol and with ether, and air-dried.

Compounds **II–VII**, **XIV**, and **XV** were prepared similarly starting from benzoylhydrazine, isonitrosoacetone, and hydrate of Co, Ni, or Cu chloride, bromide, or acetate in the molar ratio of 1 : 1 : 1 or 2 : 2 : 1. Complexes **VIII–XIII** were prepared by the reaction of the above-mentioned compounds (molar ratio 1 : 1 : 1) in the presence of sodium acetate or pyridine (pH 8). The yields and some physicochemical characteristics of the substances are listed in Tables 1 and 2.

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