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Coordination Compounds of Cobalt, Nickel, Copper, and Zinc with 2-Bromo-3-Phenylpropenal Benzoylhydrazone and Thiosemicarbazone

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Abstract—By X-ray structural analysis the crystal structure of 2-bromo-3-phenylpropenal benzoylhydrazone (HL) was determined. The molecule is not flat. In the crystal the HL molecules form infinite chains with reciprocal van der Waals interaction. 2-Bromo-3-phenylpropenal hydrazone (HL) and thiosemicarbazone (HL') react with cobalt, nickel, copper and zinc chlorides, nitrates and acetates to form coordination compounds of the composition $Cu(HL)(L)_2$ [HL = C_6H_5–CH=CBr–CH=N–NH–C(O)–C_6H_5], $MX_2 \cdot 2$ HL'·nH_2O [M = Co, Ni, Cu, Zn; X = Cl, NO_3, HL' = C_6H_5–CH=CBr–CH=N–NH–C(S)–NH_2; n = 0–3], $MX_2 \cdot HL \cdot n H_2O$ [M = Ni, Cu; n = 0, 1], and $ML'_2 \cdot nH_2O$ [M = Co, Ni, Zn; n = 0–3]. The same reactions in the presence of amines (A = C_5H_5N, 2-$CH_3C_5H_4N$, 3-$CH_3C_5H_4N$, 4-$CH_3C_5H_4N$) afford complexes of the composition CuALCl and $MALX \cdot n H_2O$ [M = Cu, Ni; X = Cl, NO_3; n = 0–2]. Structure of the coordination node in the amine-containing copper derivatives is polynuclear, in complexes $Cu(HL)(L)_2$ is octahedral, in other compounds it is tetrahedral. The azomethines (HL and HL') in these complexes behave as bidentate N,O and N,S ligands. Thermolysis of the complexes includes a step of dehydration (60–90°C) and complete thermal decomposition (430–590°C).

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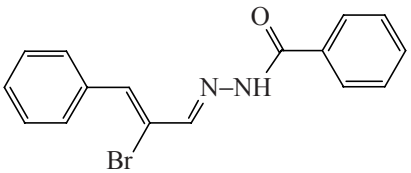
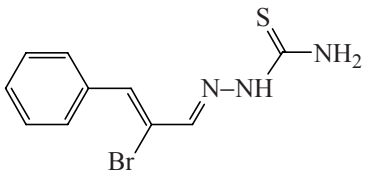
The azomethines based on 3-phenylpropenal react with transition metal ions affording coordination compounds with varied composition and structure [1–3]. It has been established that depending on the conditions of the synthesis and the nature of initial compounds either monomeric or polynuclear complexes can form. However, as far as only 3-phenylpropenal has been used as a parent compound, it seems interesting to elucidate the effect on the composition, structure and properties of introduction into the composition of this unsaturated aldehyde of such substituent as bromine.

The aim of this work is developing optimal conditions of the synthesis and study of the properties of cobalt, nickel, copper and zinc coordination compounds with 2-bromo-3-phenylpropenal benzoylhydrazone (HL) and thiosemicarbazone (HL').



HL



HL'

An experiment showed that in the reaction of hot (50–55°C) ethanol solutions of cobalt, nickel, copper and zinc chlorides, nitrates and acetates with these Schiff bases in a molar ratio 1:2 fine crystalline compounds **I, VI–XIV** were formed whose composition based of the data of elemental analysis (Table 1) was assumed as $Cu(HL)(L)_2$ (**I**), $MX_2{\cdot}2$ HL' (**VI–IX**) [M = Co (**VI**), Ni (**VII**), Cu (**VIII**), Zn (**IX**); X = NO_3 (**VI–VIII**), Cl (**IX**); n = 0 (**VII–IX**), 3 (**VI**)]; $MCl_2{\cdot}HL'{\cdot}n\ H_2O$ (**X, XI**) [M = Cu (**X**), Ni (**XI**); n = 0 (**XI**), 1 (**X**)], and $ML'_2{\cdot}n\ H_2O$ (**XII–XIV**) [M = Co (**XII**), Ni (**XIII**), Zn (**XIV**); n = 0 (**XIV**), 2 (**XII**), 3 (**XIII**)]. The reaction of the metal chlorides and nitrates with these azomethines (HL and HL') in the presence of pyridine or 2-, 3- or 4-picoline in a molar ratio 1:1:1 leads to isolation from the solution of the complexes Cu(A)(L)Cl (**II–V**) and Cu(A)(L')X·n H_2O (**XV–XX**) [A = C_5H_5N (**II, XV, XIX**), 2-$CH_3C_5H_4N$ (**III, XVI**), 3-$CH_3C_5H_4N$ (**IV, XVII, XX**), 4-$CH_3C_5H_4N$ (**V, XVIII**); X = Cl (**XV–XVIII**), NO_3 (**XIX, XX**); n = 0 (**XVI, XVII**), 1 (**XVIII**), 2 (**XV**)].

The synthesized coordination compounds **I–XX** are insoluble in diethyl ether, poorly soluble in water, better soluble in alcohols and well soluble in DMF, DMSO and acetonitrile. Yields and some physicochemical characteristics are listed in Table 1.

Table 1. Physicochemical characteristics of coordination compounds of cobalt, nickel, copper and zinc with 2-bromo-3-phenylpropenal benzoylhydrazone and thiosemicarbazone

Comp. no.	Yield, %	μ_{ef},[a] BM	Found, %				Formula	Calculated, %				t[c], °C
			Br	Cl	M[b]	N		Br	Cl	M[b]	N	
I	51	1.76	22.60	–	5.88	7.76	$C_{48}H_{37}Br_3CuN_6O_3$	22.88	–	6.10	8.01	470
II	55	1.55	15.48	6.71	12.40	8.01	$C_{21}H_{17}BrClCuN_3O$	15.76	7.00	12.61	8.28	445
III	68	1.40	15.12	6.55	12.12	7.80	$C_{22}H_{19}BrClCuN_3O$	15.37	6.82	12.30	8.07	430
IV	73	1.27	15.20	6.60	12.04	7.85	$C_{22}H_{19}BrClCuN_3O$	15.37	6.82	12.30	8.07	460
V	75	1.28	15.16	6.58	12.18	7.79	$C_{22}H_{19}BrClCuN_3O$	15.37	6.82	12.30	8.07	460
VI	70	4.19	19.69	–	7.49	14.13	$C_{20}H_{26}Br_2CoN_8O_9S_2$	19.85	–	7.33	13.91	540
VII	80	3.63	21.26	–	8.00	14.70	$C_{20}H_{20}Br_2N_8NiO_6S_2$	21.26	–	7.85	14.92	520
VIII	77	1.77	20.35	–	8.25	15.10	$C_{20}H_{20}Br_2CuN_8O_6S_2$	20.95	–	8.40	14.84	500
IX	70	–	22.46	9.88	9.00	11.62	$C_{20}H_{20}Br_2Cl_2N_6S_2Zn$	22.70	10.08	9.23	11.92	540
X	61	1.83	18.23	16.12	14.37	9.57	$C_{10}H_{12}BrCl_2CuN_3OS$	18.45	16.37	14.58	9.63	540
XI	63	3.80	19.48	8.39	14.06	10.32	$C_{10}H_{10}BrCl_2N_3NiS$	19.30	8.56	14.25	10.14	560
XII	67	3.92	24.05	–	9.12	12.55	$C_{20}H_{22}Br_2CoN_6O_2S$	24.18	–	8.90	12.70	590
XIII	58	3.54	23.39	–	8.50	12.13	$C_{20}H_{24}Br_2N_6NiO_3S$	23.54	–	8.68	12.37	570
XIV	52	–	12.44	–	10.11	13.01	$C_{20}H_{18}Br_2N_6S_2Zn$	12.66	–	10.30	13.31	590
XV	62	1.45	16.16	7.01	12.89	10.97	$C_{15}H_{18}BrClCuN_4O_2S$	16.08	7.13	12.78	11.26	580
XVI	75	1.31	16.68	7.17	13.15	11.53	$C_{16}H_{16}BrClCuN_4O_2S$	16.83	7.47	13.36	11.79	550
XVII	85	1.45	16.64	7.32	13.11	11.57	$C_{16}H_{16}BrClCuN_4S$	16.83	7.47	13.36	11.79	590
XVIII	83	1.62	16.39	7.15	13.08	11.08	$C_{16}H_{18}BrClCuN_4OS$	16.21	7.20	12.88	11.36	585
XIX	82	1.39	17.24	–	13.00	14.20	$C_{15}H_{14}BrCuN_5O_3S$	17.47	–	13.03	14.36	500
XX	70		15.81	–	12.43	13.70	$C_{16}H_{16}BrCuN_5O_3S$	15.93	–	12.67	13.96	510

[a] At 294 K. [b] M means a metal. [c] t is the temperature of complete decomposition of the complex.

Table 2. Crystallographic data, characteristics of the experiment and refinements of the structure of 2-bromo-3-phenylpropenal benzoylhydrazone (HL)

Compound	HL
Empirical formula	$C_{16}H_{13}BrN_2O$
M	329.19
Temperature, K	293(2)
Crystal system	Rhombic
Space group	*Pbca*
a, Å	18.334(3)
b, Å	8.150(2)
c, Å	19.051(3)
V, Å^3	2846.6(9)
Z	8
$\rho_{calc.}$, g cm^{-3}	1.536
μ_{Mo}, mm^{-1}	2.885
Crystal size, mm	0.35×0.30×0.08
Range of θ, deg	2.14 to 29.28
Range of intensity measurments	$-24 \le h \le 24$, $-11 \le k \le 11$, $-25 \le l \le 25$
Number of measured reflexes	26901
Number of independent reflexes	3559 (R_{int} 0.0462)
Number of the reflexes with $I > 2\sigma(I)$	1910
Number of refined parameters	181
GOOF over F^2	0.978
Final *R*-factor [$I > 2\sigma(I)$]	*R*1 0. 0.0392, *wR*2 0.1013
R-factor over the whole array	*R*1 0.1133, *wR*2 0.1240
$\Delta\rho_{max}$, $\Delta\rho_{min}$, *e* A^{-3}	0.68, –0.72

We succeeded to grow benzoylhydrazone HL single-crystals by crystallization from methanol, and its structure was established by the X-ray structural analysis. The crystals HL are rhombic, a = 18.334(3), b = 8.150(2), c = 19.051(3) Å; space group *Pbca*, Z = 8, R = 0.0392. It is found (Tables 2, 3 and Fig. 1) that the molecule of this azomethine is as a whole no-planar. The angle between the mean-square planes of phenyl rings C^5C^{10} and $C^{11}C^{16}$ is 15.0°, and the angles between the mean square plane formed by the atoms of the chain $N^1N^2C^1C^2C^3C^4$ with these rings is 27.7° and 21.3°, respectively. Deviations of the atoms of this chain from the plane composed by these atoms fall in the range from –0.038 to 0.117 Å. In crystal the benzoylhydrazone HL molecules form infinite chains because of sliding plane *b* owing to hydrogen bonds N^1–$H^3\cdots O^1$ ($H^3\cdots O^1$ 2.22 Å, $N^3\cdots O^1$ 3.064 Å, angle $N^1H^3O^1$ 166°) (Fig. 2). Between the chains there is van der Waals interaction, the shortest intermolecular contact of nonhydrogen atoms ($C^2\cdots C^{14'}$ 3.393 Å) was observed for the molecules with common symmetry center.

Visual microscopic investigation of complexes **I–XX** showed that they are powders of uniform phase and consist of crystallites differing by form. Due to the small size and the absence of single crystals of these compounds we used for elucidation of their individuality, composition and structure the methods of elemental and thermal analysis, molecular conductivity, IR spectroscopy and magnetochemistry. From the data obtained by measuring the molar electroconductivity of the synthesized compounds in DMF we found that complexes **VI–IX** are triionic electrolytes (æ 132–149 Ω^{-1} cm^2 mol^{-1}) while other are non-electrolytes (æ 2–4 Ω^{-1} cm^2 mol^{-1}).

From the data of magnetochemical investigation (Table 1) we established that all cobalt and nickel derivatives are paramagnetic substances and, judging from the values of effective magnetic moments, their central atoms coordination node is tetrahedral. Similar conclusion was made earlier [1–3] on the nickel compounds with 3-phenylpropenal thiosemicarbazone that was confirmed by X-ray structural analysis. The magnetochemical characteristics of copper complexes (**I, VIII**, and **X**) correspond to spin of one unpaired electron and point to monomer structure of these compounds. As to amine-containing copper complexes (**II–V** and **XV–XX**), they are polynuclear as follows from the values of effective magnetic moments that are below the value for the spin of one unpaired electron.

Thermal analysis of compounds **I–XX** (Table 1) showed that theromlysis includes a step of dehydration (60–90°C) and of a complete thermooxidative decomposition of the complexes (430–590°C). As seen from Table 1, the temperature (t) of complete decomposition of a substance depends on the nature of the central atom and for the series of coordination

Table 3. Selected interatomic distances and bond angles in 2-bromo-3-phenylpropenal benzoylhydrazone molecule

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
$Br^1–C^1$	1.874(4)	$N^1–C^4$	1.363(4)	$C^9–C^{10}$	1.376(6)
$O^1–C^4$	1.223(4)	$C^4–C^5$	1.495(5)	$C^{11}–C^{12}$	1.391(5)
$C^3–C^1$	1.330(4)	$C^5–C^6$	1.392(6)	$C^{11}–C^{16}$	1.395(6)
$C^3–C^{11}$	1.465(4)	$C^5–C^{10}$	1.395(5)	$C^{12}–C^{13}$	1.384(5)
$N^2–C^2$	1.259(4)	$C^6–C^7$	1.376(6)	$C^{13}–C^{14}$	1.366(6)
$N^1–N^2$	1.369(4)	$C^7–C^8$	1.357(6)	$C^{14}–C^{15}$	1.378(7)
$C^1–C^2$	1.442(5)	$C^8–C^9$	1.362(7)	$C^{15}–C^{16}$	1.379(6)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$C^1C^3C^{11}$	134.3(3)	$C^3C^4C^5$	114.4(3)	$C^{12}C^{11}C^{16}$	118.1(4)
$C^2N^2C^3$	116.4(3)	$C^6C^5C^{10}$	118.8(4)	$C^{12}C^{11}N^1$	124.8(4)
$N^1C^1C^2$	121.7(3)	$C^6C^5C^4$	123.0(4)	$C^{16}C^{11}N^1$	117.0(4)
$N^1C^1Br^1$	123.4(3)	$C^{10}C^5C^4$	118.2(4)	$C^{13}C^{12}C^{11}$	120.2(4)
$C^2C^1Br^1$	114.9(3)	$C^7C^6C^5$	120.0(4)	$C^{14}C^{13}C^{12}$	121.6(4)
$N^2C^2C^1$	122.1(4)	$C^8C^7C^6$	120.4(4)	$C^{13}C^{14}C^{15}$	118.5(4)
$C^4N^1N^2$	117.9(2)	$C^7C^8C^9$	120.6(4)	$C^{16}C^{15}C^{14}$	121.2(4)
$O^1C^4C^3$	123.3(3)	$C^8C^9C^{10}$	120.5(4)	$C^{15}C^{16}C^{11}$	120.4(4)
$O^1C^4C^5$	122.3(4)	$C^9C^{10}C^5$	119.6(4)		

compounds with the same intraspheric composition varies as follows: t(Zn) ≈ t(Co) > t(Ni) > t(Cu). The temperature of decomposition of a substance is affected also by the nature of innersphere ligands: it grows at the chloride ion substitution for nitrate and at the introduction of amine to the complex composition. In the case of the complexes containing amine **II–V** and **XV–XX**: t(3-$CH_3C_5H_4N$) ≥ t(4-$CH_3C_5H_4N$) ≥ t(C_5H_5N) > t(2-$CH_3C_5H_4N$).

For elucidating the mode of ligand coordination with the central ion we carried out comparative analysis of IR spectra of complexes **I–XX**, parent azomethines (HL and HL'), and of described in literature [1–3] coordination compounds of transition metals with similar Schiff bases. We found that the condensation products HL and HL' in the studied compounds behave as bidentate electroneutral or monodeprotonated N,S or N,O ligands attached to the

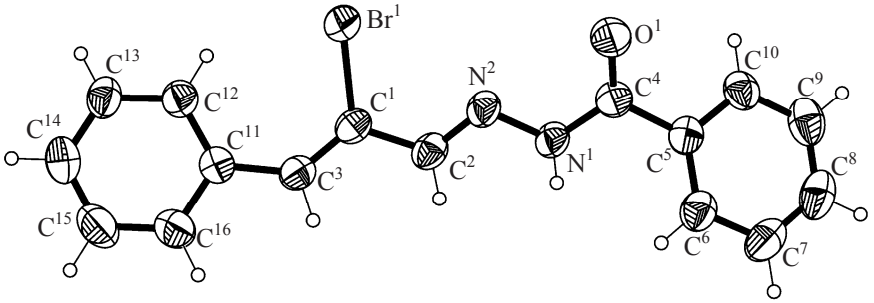


Fig. 1. Structure of 2-bromo-3-phenylpropenal benzoylhydrazone molecule (HL).

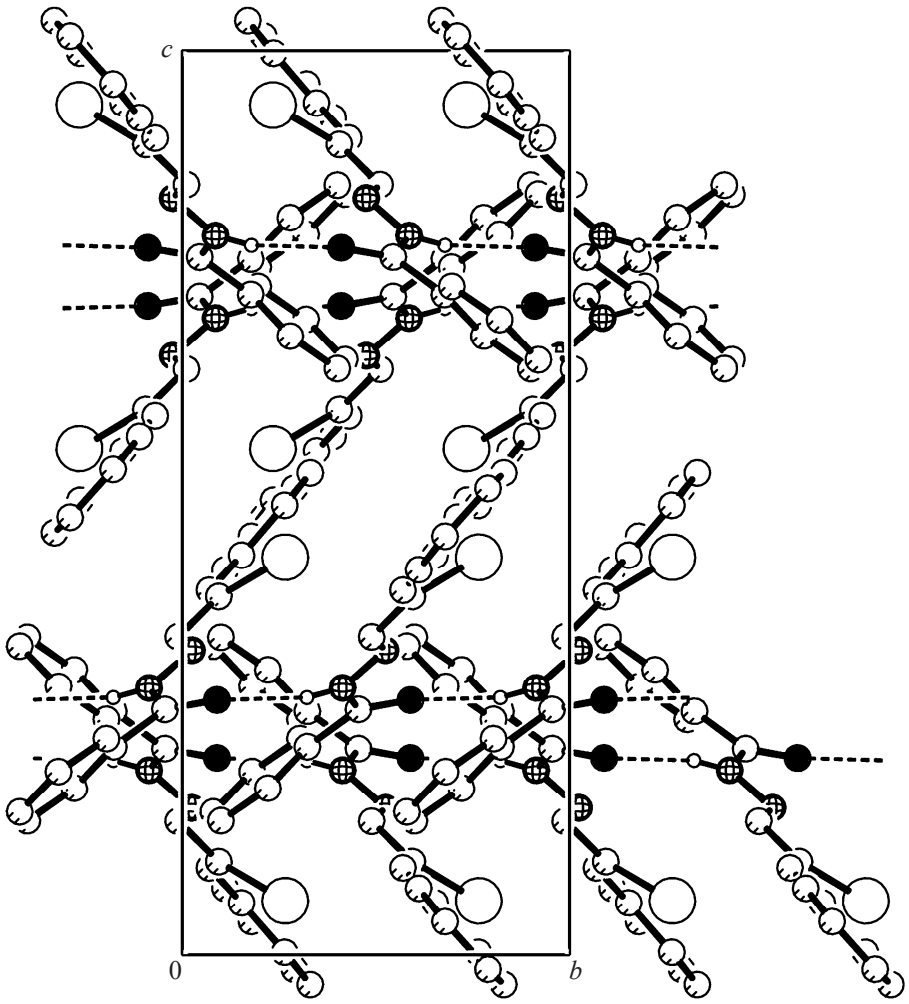
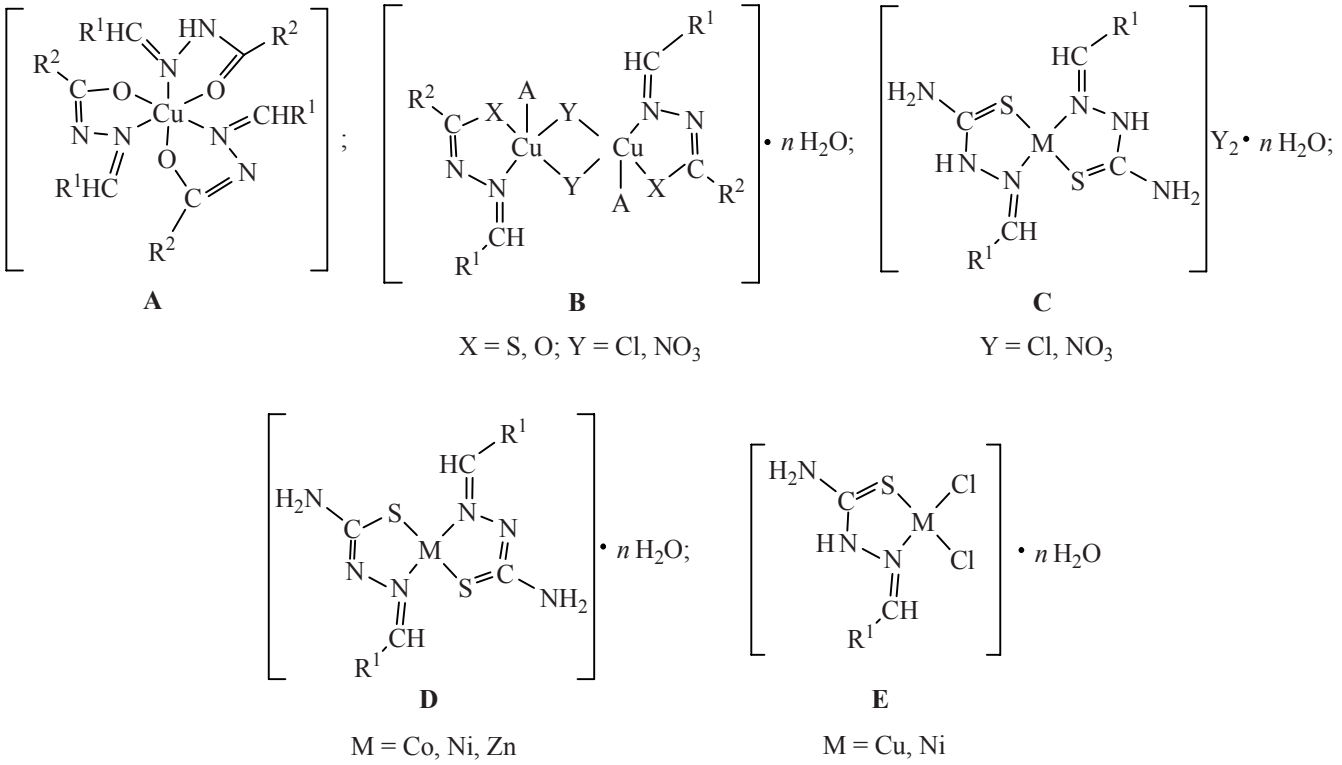


Fig. 2. A fragment of packaging of 2-bromo-3-phenylpropenal benzoylhydrazone (HL) molecules in crystal.

complex-forming ion via the atoms of azomethine nitrogen and sulfur or the carbamide fragment oxygen with formation of a five-membered metallocycle. This statement is confirmed by the low-frequency shift by 25–15 cm^{-1} of the absorption bands ν(C=O), ν(C=N) and ν(C=S) as compared with the analogous absorption bands of the parent azomethines HL and HL' that are located at 1660–1590 and 770–760 cm^{-1} respectively. The involvement of oxygen and sulfur atoms of the deprotonated enol and thioenol forms of the ligands HL and HL' to the coordination with the central atom is confirmed by the disappearance of the bands ν(C=S) at 770 cm^{-1}, ν(C=O) at 1660 cm^{-1} and ν(NH) at 3250–3200 and 3170–3150 cm^{-1} in the IR spectra of the complexes **I–V** and X**I–XX**, and by the appearance of new absorption bands at 605–585 cm^{-1} that according to the published data [4] are identified as ν(C–S), ν(C–O), and by splitting of the band ν(C=N) at 1595–1590 cm^{-1} into two components. The above-pointed coordination of the ligands HL and HL' follows also from the fact that in the IR spectra of all complexes appears a series of new absorption bands in the region of 530–400 cm^{-1} [ν(M–N) at 525–510 and 430–405 cm^{-1}, ν(M–O) at 490–470 cm^{-1}, and ν(M–S) at 460–445 cm^{-1}]. The involvement of the other groups of the Schiff bases HL and HL' in the coordination with the metal ions is excluded since their characteristic absorption bands are located in the same regions as those found for the parent azomethines. The presence in the studied complexes of coordinated amine molecules is confirmed by the presence in their IR spectra of the respective absorption bands: [ν(CC) + ν(CN) + δ(CCH) 1640–1635, 1530–1525, ν(CN) 1310–1305, δ(CCH) 1230–1225, δ(CCH) + ν(CC) + δ(CNC) 1060–1055,



A **B** **C**

X = S, O; Y = Cl, NO_3 Y = Cl, NO_3

D **E**

M = Co, Ni, Zn M = Cu, Ni

$R^1 = C_6H_5CH{=}CH$, $R^2 = C_6H_5$, NH_2, n = 0–3.

1030–1025, γ(CCC) + γ(CNC) 730–725, ρ(CH) 830–825 cm^{-1}].

The obtained physicochemical data make it possible to describe the chemical bonds in the complexes (**I–XX**) by the schemes **A–E**.

EXPERIMENTAL

The X-ray structural analysis of benzoylhydrazone (HL) was carried out on a Bruker Smart diffractometer with a CCD detector (MoK_α radiation, λ 0.71073). The correction on extintion was introduced using SHELXTL-NT V5.1 programs [5]. The structure was solved by the direct method with SHELX-97 programs [6] and refined by the least-squares method in an anisotropic approximation for the non-hydrogen atoms [6]. The hydrogen atoms were included into the HL structure at the refinement in geometrically calculated positions, their temperature factors U_H were taken as 1.5-fold larger than those of the respective linked carbon and nitrogen atoms. The principal experimental parameters are listed in Table 1, selected interatomic distances and bond angles, in Table 2. The coordinates of basic atoms of the studied structures are deposited in Camdridge Crystal Data Center (CCDC 649139). Calculations of geometry and images were prepared with PLATON program [7], for the representation of packaging of the structures were left only the hydrogen atoms involved in the hydrogen bonding.

Electric resistance of solutions of the complexes **I–XX** in DMF (20°C, c 0.001 mol l^{-1}) was measured with a rheostat-controlled bridge circuit R-38. The IR spectra of the substances that were preliminary kept in a drier at 105°C to constant weight were registered on a Specord M-80 spectrophotometer (from the suspensions in mineral oil). The effective magnetic moments of compounds **I–XX** were measured by the Gouy method. Calculation of molar magnetic susceptibility with a correction for diamagnetism was carried out proceeding from the theoretical values of magnetic susceptibility of organic compounds. The derivatograms of the complexes **I–XX** were taken on a Paulik–Paulik–Erdey derivatograph in the range of 20–1000°C under dry air atmosphere (Al_2O_3 as a reference, the corundum crucible).

2-Bromo-3-phenylpropenal benzoylhydrazone (HL). A hot solution (55–60°C) of 10 mmol of 2-

bromo-3-phenylpropenal in 15 ml of methanol was mixed with a solution of 10 mmol of benzoylhydrazine in 35 ml of CH_3OH. Upon cooling, from the reaction mixture settled a light-yellow precipitate that was filtered off on a glass filter, washed with little alcohol, and dried in air. Yield 58%, mp 187–189°C. Similarly from 2-bromo-3-phenylpropenal and thiosemicarbazide in 1:1 mole ratio was synthesized carbazone HL', yield 64%, mp 176–178°C. Compounds HL and HL' are well soluble in DMF and DMSO and in alcohols at heating.

Bis(2-bromo-3-phenylpropenylidenehydrazino)-2-bromo-3-phenylpropenylidenebenzoylhydrazino-copper (complex I). To a hot solution (50–55°C) of 10 mmol of copper(2+) dichloride dihydrate in 20 ml of ethanol was added 30 ml of a solution in alcohol of 30 mmol of 2-bromo-3-phenylpropenal benzoylhydrazone. The obtained reaction mixture was heated at continuous stirring for 30–40 min. Upon cooling, from the mixture precipitated a dark-green substance that was filtered off on a glass filter, washed with a little of alcohol and ether and dried in air to constant weight.

Similarly using as the parent ligands the azomethines HL and HL' and cobalt, nickel, copper and zinc chlorides and nitrates (mole ratio 1:1 or 2:1) were synthesized compounds **II–XIV**. The complexes **II–V** and **XV–XX** were prepared by the same procedure from copper(2+) chloride or nitrate and azomethines HL or HL' in the mole ratio 1:1 in the presence of either pyridine, or 2-, 3- or 4-picoline (pH 8). Yields of compounds **I–XX** and their physicochemical characteristics are listed in Table 1.

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