Russian Journal of General Chemistry, Vol. 73, No. 10, 2003, pp. 1611–1615. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 10, 2003, pp. 1704–1708.

Coordination Compounds of Copper(II) with Benzoylhydrazones of Substituted Salicylaldehydes

N. M. Samus', V. I. Tsapkov, and A. V. Kerner

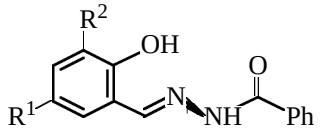
Moldova State University, Kishinev, Moldova

Received January 28, 2002

Abstract — Benzoylhydrazones of 5-nitro- (H_2L^1), 3-nitro- (H_2L^2), 5-chloro- (H_2L^3), 5-bromo- (H_2L^4), and 3,5-dibromosalicylaldehydes (H_2L^5) react in ethanol with copper acetate to form complexes $CuL^{1–5}$. In the presence of amines (A = C_5H_5N, 3-$CH_3C_5H_4N$), the above reactions give complexes $CuL^{1–5}A \cdot nH_2O$ (n = 0, 1). When cuprous bromide or nitrate and benzoylhydrazone H_2L^3 were used as starting materials, complexes $Cu(HL^3)X$ (X = Br^-, NO_3^-) were isolated. The resulting complexes all are polynuclear structures in which azomethines $H_2L^{1–5}$ behave as tridentate *O,N,O*-ligands. Thermolysis of the complexes involves the stages of dehydration (70–90°C), deaquation (120–150°C) or deamination (150–180°C), and complete thermal decomposition (350–500°C).

Hydrazine derivatives occupy a special place among organic ligands because of the diversity of their donor atoms and the ability to change dentacity depending on given reaction conditions [1]. Many hydrazine derivatives are known to be biologically active [2], and their activity is enhanced many times by coordination with biometals [3–5]. It is also known [6–8] that the physiological activity of coordination compounds is controlled by the properties both of the biologically active ligand and of the complexing metal. In this connection, accumulation of experimental data on the synthesis of coordination compounds of biometals with hydrazones is both of scientific and of practical interest.

The aim of the present study was to find the best conditions of synthesis, to determine the structure, and to study the physicochemical properties of copper (II) complexes with benzoylhydrazones $H_2L^{1–5}$ of 5-nitro- (H_2L^1), 3-nitro- (H_2L^2), 5-chloro- (H_2L^3), 5-bromo- (H_2L^4), and 3,5-dibromosalicylaldehydes (H_2L^5) .



$H_2L^{1–5}$

R^1 = NO_2 (H_2L^1), H (H_2L^2), Cl (H_2L^3), Br (H_2L^4, H_2L^5); R^2 = H (H_2L^1, H_2L^3, H_2L^4), NO_2 (H_2L^2), Br (H_2L^5).

It was experimentally shown that the reaction of equimolar amounts of copper acetate and benzoylhydrazones $H_2L^{1–5}$ in ethanol gives rise to compounds **I**–**V** as fine crystals. According to the elemental analyses (Table 1), the products have the composition $CuL^{1–5}$ [$H_L{}^{1–5}$ = H_2L^1 (**I**), H_2L^2 (**II**), H_2L^3 (**III**), H_2L^4 (**IV**), and H_2L^5 (**V**)]. Cupric bromide and nitrate under the same conditions give with the azomethine H_2L^3 complexes Cu(HL)X [X = Br (**VI**), NO_3 (**VII**)]. The reactions between copper acetate and hydrazones ($H_2L^{1–5}$), performed in the presence of pyridine or 3-picoline, yields complexes $CuAL^{1–5} \cdot nH_2O$ [A = C_5H_5N (**VIII**–**X**, **XII**, **XIII**), 3-$CH_3C_5H_4N$ (**XI**); $H_2L^{1–5}$ = H_2L^1 (**VIII**), H_2L^2 (**IX**), H_2L^3 (**X**, **XI**), H_2L^4 (**XII**), H_2L^5 (**XIII**); n = 0 (**VIII, IX, XI**–**XIII**), n = 1 (**X**)].

Complexes **I**–**XIII** are insoluble in water, alcohols, and ether and readily soluble in DMF and DMSO. Their yields and physicochemical properties are given in Table 1.

Magnetochemical investigation of complexes **I**–**XIII** at room temperature showed (Table 1) that their effective magnetic moments are lower than those expected for the spin value for one unpaired electron. As follows from these data, complexes **I**–**XIII** have a polynuclear structure in which there is spin–spin coupling between the paramagnetic copper ions.

Thermal analysis of compounds **I**–**XIII** (Table 2) showed that their thermolysis involves three stages. In the DTA curve of complex **X** in the range 70–90°C, there is an endothermic peak which, as judged from the relatively low temperature, corresponds to dehydration of the complex. At higher temperatures, one more endothermic peak appears in the DTA curves of compounds **I**–**V** and **VIII**–**XIII** (at 120–150°C for

1070-3632/03/7310-1611 $25.00 © 2003 MAIK "Nauka/Interperiodica"

Table 1. Physicochemical characteristics of coordination compounds of copper(II) with benzoylhydrazones of substituted salicylaldehydes

Comp. no.	Yield, %	μ_{app},[a] BM	Found, %			Formula	Calculated, %		
			Cl (Br)	M[b]	N		Cl (Br)	M[b]	N
I	82	1.41	–	17.05	11.68	$C_{14}H_{11}CuN_3O_5$	–	17.43	11.43
II	89	1.49	–	17.21	11.79	$C_{14}H_{11}CuN_3O_5$	–	17.43	11.43
III	65	1.59	10.25	17.65	6.67	$C_{14}H_{11}ClCuN_2O_3$	10.00	17.95	7.91
IV	62	1.58	19.84	16.24	7.25	$C_{14}H_{11}BrCuN_2O_3$	20.05	15.95	7.03
V	76	1.65	33.26	13.09	5.64	$C_{14}H_{10}Br_2CuN_2O_3$	33.48	13.31	5.87
VI	73	1.52	27.56	14.94	6.95	$C_{14}H_{10}BrClCuN_2O_2$	27.68	15.24	6.72
VII	72	1.64	8.62	15.74	10.81	$C_{14}H_{10}ClCuN_3O_5$	8.90	15.92	10.53
VIII	75	1.57	–	14.57	13.46	$C_{19}H_{14}CuN_4O_4$	–	14.93	13.16
IX	67	1.58	–	14.66	13.18	$C_{19}H_{14}CuN_4O_4$	–	14.93	13.16
X	86	1.54	7.98	14.52	9.99	$C_{19}H_{16}ClCuN_3O_3$	8.20	14.67	9.70
XI	79	1.61	8.42	14.66	7.89	$C_{20}H_{16}ClCuN_3O_2$	8.27	14.81	9.79
XII	89	1.52	17.12	13.77	9.42	$C_{19}H_{14}BrCuN_3O_2$	17.39	13.83	9.14
XIII	81	1.60	29.45	11.62	8.09	$C_{19}H_{13}Br_2CuN_3O_2$	29.68	11.80	7.80

[a] At 293 H. [b] Metal.

Table 2. Results of thermal analysis of coordination compounds of copper (II) with benzoylhydrazones of substituted salicylaldehydes

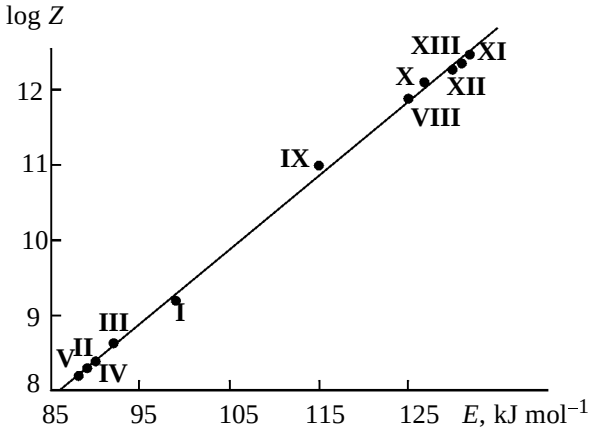
Comp. no.	Number of endothermic peak in the DTA curve	*t*, °C	Weight loss			Kinetic parameters		Temperature of complete decomposition, °C
			found, %	calculated, %	species lost	E^*, kJ mol^{-1}	log *Z*	
I	1	140	4.9	4.9	H_2O	99	9.2	360
II	1	130	5.0	4.9	H_2O	90	8.4	350
III	1	120	5.0	5.1	H_2O	92	8.6	440
IV	1	135	4.8	4.5	H_2O	89	8.3	440
V	1	150	4.0	3.8	H_2O	88	8.2	435
VI	–	–	–	–	–	–	–	450
VII	–	–	–	–	–	–	–	395
VIII	1	170	18.8	18.5	C_5H_5N	125	11.9	375
IX	1	150	18.6	18.5	C_5H_5N	115	11.0	365
X	1	80	4.0	4.2	H_2O	46	3.9	480
	2	155	18.0	18.2	C_5H_5N	127	12.1	
XI	1	185	21.5	21.7	C_6H_7N	132	12.5	500
XII	1	160	17.0	17.2	C_5H_5N	130	12.3	460
XIII	1	180	15.0	14.7	C_5H_5N	131	12.4	440

I–**V** and at 150–180°C for **VIII**–**XIII**). Judging from the weight loss, it corresponds to deaquation or deamination of these complexes. The ensuing heat effect in the DTA curves of the compounds under study observed in the range 350–500°C is exothermic and corresponds is thermooxidative decomposition of the coordinated hydrazones H_2L[1–5]. It was found that this peak maximum temperature depends on the nature of the substituent in the benzene ring of the salicylaldehyde moiety of the azomethine, and at the same composition of the complex varies in the following order: Br ≥ 5-Cl ≥ 5-NO_2 ≥ 3-NO_2. The temperature of complete decomposition is also dependent on the nature of the other inner-sphere ligands: It increases

on replacement of water by amines or of the nitrate ion by chloride.

Using the Horowits–Metzger method [9] with supplements made by Topor [10], we estimated the kinetic parameters of dehydration, deaquation, and deamination of compounds **I**–**V** and **VIII**–**XIII** (Table 2). As follows from Table 2, the resulting activation energies E^* and preexponential factors Z are close to the E^* and Z values for the similar topochemical processes described in [11–13]. As shown experimentally (Table 2), the kinetic parameters are primarily controlled by the nature of the leaving ligand: In going from aqua- to pyridine- or picoline-containing complexes the E^* and log Z values increase, in parallel with the increasing σ-donor and π-acceptor power of these ligands. The calculated kinetic parameters fit well with the compensation effect (see figure). According to [13, 14], its presence indicates that, regardless of the nature of the substituent in the benzene ring of the salicylaldehyde moiety of the hydrazone and the leaving ligand (water or amine), the coordination compounds studied undergo the same thermolysis reactions.

To determine the mode of coordination of the ligands with the central ions, we performed a comparative analysis of the IR spectra of complexes **I**–**XIII**, starting hydrazones H_2L^{1-5}, and the coordination compounds of transition metals with similar Schiff bases, described in [15–17]. It was found (Table 3) that azomethines H_2L^{1-5} in the compounds studied behave as tridentate *O,N,O*-ligands and add to the complexing ion via the phenol and amide oxygen atoms, as well as via the azomethine nitrogen to form five- and six-membered metal rings. This suggestion is supported by the presence in the IR spectra of complexes **I**–**XIII** of ν(C=O), ν(C=N), and ν(C–O) bands shifted by 50–15 cm^{-1} to the long-wave region relative to the corresponding absorption bands of the starting hydrazones and similar Schiff bases, as well as by the appearance of a series of new bands in the range 530–340 cm^{-1} due to absorption of metal–nitrogen and metal–oxygen bonds. It should be noted that in all the complexes, except for **VI** and **VII**, the amide oxygen atom of hydrazones H_2L^{1-5} is present in the deprotonated enol form. It follows from the lack in the IR spectra of these compounds of the ν(C=H) band at 1650–1645 cm^{-1}, as well as the appearance of a new band ν(>C=N–N=C<) in the region of 1570–1565 cm^{-1}. Furthermore, the spectra of all the complexes, a new band appears at 703–725 cm^{-1}, which, according to [3, 18], is indicative of bridging bonds. The other functional groups of ligands H_2L^{1-5} are definitely not involved in coordination with the copper(II) ion, since their characteristic absorption bands appear in the same regions as in the free benzoylhydrazones. The presence in the obtained compounds of coordinated molecules of water or amines (pyridine or 3-picoline) is confirmed by the observation in their IR spectra of the corresponding absorption bands [**I**–**V**: ν(H_2O) 3600–3585, δ(H_2O) 1595–1585, and γ(H_2O) 925–920; **VIII**–**XIII**: ν(CC) + ν(CN) + δ(CCH) 1640–1635 and 1530–1525, ν(CN) 1310–1305, δ(CCH) 1230–1225, δ(CCH) + ν(CC) + δ(CNC) 1065–1055 and 1030–1025, γ(CCC) + γ(CNC) 740–735, and ρ(CH) 830–825 cm^{-1}]. The IR spectrum of complex **VII** contains all bands characteristic inner-sphere monodentate nitrate ions [$\nu_1(A_1)$ 1290, $\nu_2(A_2)$ 1025, $\nu_3(A_3)$ 720, $\nu_4(B_1)$ 1480, $\nu_5(B_1)$ 710, and $\nu_6(B_2)$ 800 cm^{-1}].



Compensation effect for the deaquation and deamination reactions of complexes **I**–**V** and **VIII**–**XIII**.

EXPERIMENTAL

The IR spectra were registered on a Perkin–Elmer-337 spectrophotometer (suspensions in Vaseline and fluorinated oils). The effective magnetic moments of compounds **I**–**XIII** were determined by the Gouy method. The calculation of the molar magnetic susceptibility corrected for diamagnetism was carried out basing on the theoretical magnetic susceptibilities of organic compounds. The thermoanalytical curves of complexes **I**–**XIII** were obtained on a Paulik–Paulik–Erdey derivatograph at 20–1000°C in air (reference Al_2O_3, corundum crucible). The starting benzoylhydrazones [H_2L^{1-5}, mp, °C: H_2L^1, 97; H_2L^2, 95; H_2L^3, 130; H_2L^4, 135; H_2L^5, 141] were obtained by the procedures described in [19].

Di(μ-*O*)di[[*N*-(5-nitro-2-oxy-1-benzylidene)-*N*′-α-oxybenzylidenehydrazine]aquacopper] (I). A solution of 10 mmol of 5-nitrosalicylaldehyde benzoylhydrazone in 50 ml of ethanol was mixed with

Table 3. IR spectra (ν, cm^{-1}) of coordination compounds of copper with benzoylhydrazones of substituted salicylaldehydes

Comp. no.[a]	ν_{as}(NH)	ν_s(NH)	ν(C=O)	ν(C=N)	ν(>C=N–N=C<)	ν(C–O)	ν(N–N)	ν(M<O,O>M)[b]	ν(M–O),[b] phenol	ν(M–O),[b] ketone/enol	ν(M–N)[b]
H_2L^1	3275	3210	1648	1630	–	1520, 1276	970	–	–	–	–
H_2L^2	3272	3212	1645	1630	–	1518, 1280	972	–	–	–	–
H_2L^3	3270	3210	1646	1630	–	1520, 1280	970	–	–	–	–
H_2L^4	3276	3208	1646	1628	–	1520, 1276	970	–	–	–	–
H_2L^5	3278	3208	1645	1628	–	1520, 1276	970	–	–	–	–
I	–	–	–	1586	1570	1510, 1295	982	725	448	340	510, 420
II	–	–	–	1588	1568	1506, 1290	980	727	445	340	512, 425
III	–	–	–	1585	1568	1508, 1297	980	725	445	342	515, 415
IV	–	–	–	1586	1565	1509, 1295	980	725	447	340	514, 417
V	–	–	–	1587	1567	1506, 1295	981	730	446	343	520, 420
VI	3278	3216	1608	1585	–	1506, 1295	983	728	445	343	517, 415
VII	3276	3215	1610	1590	–	1505, 1280	985	730	440	345	525, 420
VIII	–	–	–	1587	1565	1506, 1285	985	730	440	345	530, 422
IX	–	–	–	1588	1565	1510, 1295	984	727	442	340	515, 425
X	–	–	–	1586	1566	1508, 1295	980	725	447	340	520, 415
XI	–	–	–	1586	1565	1506, 1290	980	728	445	342	520, 425
XII	–	–	–	1585	1570	1505, 1292	983	727	448	344	525, 418
XIII	–	–	–	1585	1568	1505, 1291	982	727	448	345	520, 430

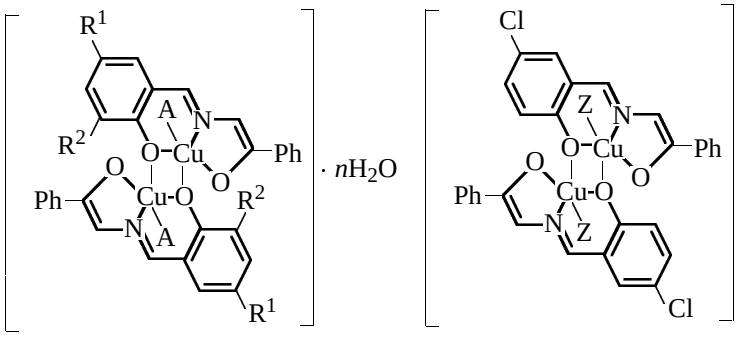
[a] The complexes were heated at 105°C to constant weight. [b] M is metal.

10 mmol of $Cu_2(CH_3COO)_4 \cdot 2H_2O$. The reaction mixture was heated at 45–50°C with stirring for 30–40 min. After cooling, a dark green precipitate formed and was filtered off on a glass filter, washed with small amounts of ethanol and ether, and dried in air.

Complexes **II**–**VII** were obtained in a similar way from benzoylhydrazones of H_2L^{1-5} and copper acetate, chloride, or nitrate hydrates.

Complexes **VIII**–**XIII** were obtained from the above starting compounds in the presence of pyridine or 3-picoline (pH 8). The yields and some physicochemical constants of the resulting compounds are given in Tables 1–3.

The above physicochemical data allow the bond distribution in complexes I–XIII to be presented by schemes **B** (**I**–**V, VIII**–**XIII**) and **C** (**VI**, **VII**).



B **C**

A = H_2O (**I**–**V**), C_5H_5N (**VIII**–**X, XII, XIII**), 3-$CH_3C_5H_4N$ (**XI**); R^1 = H (**II, IX**), Cl (**III, X, XI**), Br (**IV, V, XII, XIII**); R^2 = H (**I, III**–**V, VIII, X**–**XIII**), Br (**V, XIII**); n = 0 (**I**–**V, VIII, IX, XI**–**XIII**), 1 (**X**); Z = Br (**VI**), NO_3 (**VII**).

REFERENCES

1. Kogan, V.A., Zelentsov, V.V., Larin, G.H., and Lukov, V.V., *Kompleksy perekhodnykh metallov s gidrazonami. Fiziko-khimicheskiye svoistva i stroeniye* (Complexes of Transition Metals with Hydrazones. Physicochemical Properties and Structure), Moscow: Nauka, 1990, p. 109.
2. Mashkovskii, H.D., *Lekarstvenny'ye sredstva* (Medicinals), Minsk: Belarus', 1987, vol. 2, p.528.
3. Mohan, M., Kumar, A., and Kumar, M., *Inorg. Chim. Acta*, 1987, vol. 136, no. 1, p. 65.
4. Samus', N.H., Tsapkov, V.I., Burdenko, T.A., Tongai, H.H., Hianperem, T., and Vakarash, N.A., *Khim.-Farm. Zh.*, 1993, vol. 27, no. 7, p. 39.
5. Samus', N.H., Tsapkov, V.I., Burdenko, T.A., Buracheva, S.A., Tongai, H.H., and Sokhan, Sh.Ch., *Khim.-Farm. Zh.*, 1994, vol. 28, no. 7, p. 41.
6. Krymova, N.H., Ivanov, V.H., and Ostapkevich, N.A., *Khim.-Farm. Zh.*, 1985, vol. 19, no. 4, p. 430.
7. Johari, R.B. and Sharma, R.C., *J. Indian Chem. Soc.*, 1988, vol. 65, no. 11, p. 793.
8. Samus', N.H., Toleva, A.D., Petets, D., Tsapkov, V.I., Buracheva, S.A., and Burdenko, T.A., *Khim.-Farm. Zh.*, 1994, vol. 28, no. 10, p. 50.
9. Horowitz, H.H. and Metzger, G.A., *Anal. Chem.*, 1963, vol. 35, no. 10, p. 1398.
10. Topor, N.D., *Vestn. Mosk. Gos. Univ., Ser. Geol.*, 1967, no. 1, p. 84.
11. Kukushkin, Yu.N., Budanova, V.F., and Sedova, G.N., *Termicheskiye prevrashcheniya koordinatsionnykh soedinenii v tverdoi faze* (Thermal Transformations of Coordination Compounds in Solid Phase), Leningrad: Leningr. Gos. Univ., 1981, p. 178.
12. Kukushkin, Yu.N., Khodzhaev, H.F., Budanova, V.F., and Parpiev, N.A., *Termoliz koordinatsionnykh soedinenii* (Thermolysis of Coordination Compounds), Tashkent: Fan, 1986, p. 198.
13. Logvinenko, V.A., *Termicheskii analiz koordinatsionykh soedinenii i klatratov* (Thermal Analysis of Coordination Compounds and Clathrates), Novosibirsk: Nauka, 1982, p. 128.
14. Nikolaev, A.V., Logvinenko, V.A., Shestak, Ya., and Shkvara, V., *Dokl. Akad. Nauk SSSR*, 1976, vol. 231, no. 1, p. 146.
15. Garnovskii, A.D., *Koord. Khim.*, 1993, vol. 19, no. 5, p. 394.
16. Kogan, V.A. and Lukov, V.V., *Koord. Khim.*, 1993, vol. 19, no. 6, p. 476.
17. Ramachandran, R., Singh, B., Gupta, P.K., and Kapoor, P.N., *Main Group Metal. Chem.*, 1989, vol. 12, no. 3–4, p. 259.
18. Hewkin, D.J. and Griffith, W.P., *J. Chem. Soc. A*, 1966, no. 2, p. 472.
19. Mohan, M., Gupta, N.S., Kumar, A., and Kumar, M., *Inorg. Chim. Acta*, 1987, vol. 136, no, 2, p. 167.