ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 4, pp. 641–644. © Pleiades Publishing, Inc., 2006.
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Synthesis and Study of Copper(II), Nickel(II), and Cobalt(II) Complex Compounds with Dihydrobenzoxazine Derivatives

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Received December 21, 2004

Abstract—Complex compounds ML_2 of copper(II), nickel(II), and cobalt(II) with 2-(2-hydroxy-5-nitrophenyl)-4,4-diphenyl-1,4-dihydro-2*H*-3,1-benzoxazine and 2-(2-hydroxyphenyl)-4,4-diphenyl-1,4-dihydro-2*H*-3,1-benzoxazine (HL) were prepared by electrochemical and chemical syntheses. The complex formation involves the azomethine form of the ligand and gives a six-membered chelate cycle comprising deprotonated phenol and azomethine groups. The coordination entity has a planar structure with trans arrangement of the nitrogen and oxygen atoms.

DOI: 10.1134/S1070363206040244

1,4-Dihydro-2*H*-3,1-benzoxazines are original chemical systems whose peculiar reactivity and structure result from the annelation of the 1,3-oxazine and benzene rings [1]. Dihydrobenzoxazines bearing no substituents in the 4 position can undergo tautomeric transformation into a linear azomethine form (Schiff bases) [2–4]. This tendency is the most clearly pronounced in compounds with the alternative unsaturated structure stabilized by an intramolecular hydrogen bond [5].

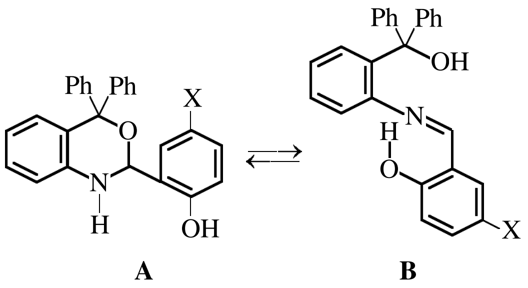
2*H*-3,1-Benzoxazines and their 1,2-dihydro derivatives in the form of free bases and salts have been offered as herbicides and plant growth regulators [6, 7]. These compounds combine low toxicity with pharmacologic activity [8]. They can be used as tranquilizers, analgetics, antispasmodics and exhibit sedative, hypnosedative, and anticonvulsant effects [9].

It is known [10] that complexes of transition metals with biologically active ligands possess a higher biological activity and lower toxicity that the starting ligands. Therefore, synthesis and isolation of complexes of 3*d* elements with benzoxazine derivatives is a perspective area of coordination chemistry. 1,4-Dihydro-2*H*-3,1-benzoxazines with a 2-hydroxyphenyl substituent are potentially tridentate ligands capable of complex formation with transition metals. Complexes of such ligands with *d* elements have not been studied before.

The purpose of the present work was to prepare solid Co(II), Ni(II), and Cu(II) complexes with 1,4-dihydro-2*H*-3,1-benzoxazines and to study their composition and structure. As ligands we used 2-(2-hydroxy-5-nitrophenyl)-4,4-diphenyl-1,4-dihydro-2*H*-3,1-benzoxazine (HL^1) and 2-(2-hydroxyphenyl)-4,4-diphenyl-1,4-dihydro-2*H*-3,1-benzoxazine (HL^2), which we synthesized previously [1].

According to the elemental analysis, the complex formation yields compounds **I**–**VI** of the ML^1_2 and ML^2_2 types. Their physicochemical characteristics are given in Table 1. The solvent and acetic acid formed in the reaction do not enter into the compounds, which is also proved by the IR spectra and points to the fact that all possible coordination sites of the metal ion are occupied by donor groups of the ligand.

The dihydrobenzoxazines HL^1 and HL^2 can exist in two tautomeric forms **A** and **B** [2, 3].



X = NO_2 (HL^1), H (HL^2).

Table 1. Yields, decomposition temperatures, and elemental analyses of complexes **I**–**VI**

Comp. no.	M	L	Yield, %	T_d, °C	Color	Found, %				Formula	Calculated, %			
						C	H	N	M		C	H	N	M
I	Cu	L^1	53	182[a]	Dark green	68.52	4.19	6.17	6.75	$C_{52}H_{38}CuN_4O_8$	68.60	4.21	6.15	6.98
II	Ni	L^1	58	>230	Orange	68.88	4.21	6.21	6.05	$C_{52}H_{38}N_4NiO_8$	68.97	4.23	6.19	6.48
III	Co	L^1	63	>220	Dark red	68.90	4.21	6.20	6.28	$C_{52}H_{38}CoN_4O_8$	68.95	4.23	6.19	6.51
IV	Cu	L^2	45	195[a]	Dark green	76.11	4.89	3.43	7.48	$C_{52}H_{40}CuN_2O_4$	76.09	4.91	3.41	7.75
V	Ni	L^2	51	>240	Light green	76.49	4.92	3.46	7.03	$C_{52}H_{40}N_2NiO_4$	76.58	4.94	3.43	7.20
VI	Co	L^2	48	>230	Dark red	76.58	4.92	3.46	7.09	$C_{52}H_{40}CoN_2O_4$	76.56	4.94	3.43	7.22

[a] Melting point.

Table 2. IR spectra of ligands HL^1 and HL^2 and their complexes **I**–**VI**

Compound	IR spectrum, cm^{-1}
HL^1	3314 [ν(NH)], 3330 w [ν(OH)], 1616 [ν(C=N)], 1522 [$\nu_{as}(NO_2)$], 1336 [$\nu_s((NO_2)$], 1285 [$\nu(CO_{phenol})$], 1071 [$\nu(CO_{cycl})$]
HL^2	3329 [ν(NH)], 3350 w [ν(OH)], 1624 [ν(C=N)], 1250 [$\nu(CO_{phenol})$], 1065 [$\nu(CO_{cycl})$]
I	3530 w [ν(OH)], 1543 [ν(C=N)], 1540 [$\nu_{as}(NO_2)$], 1329–1280 [$\nu_s((NO_2)$], 1329–1280 [$\nu(CO_{phenol})$], 1035 [$\nu(CO_{alcohol})$], 569 m [ν(M–O)], 459 m [ν(M–N)]
II	3500 w [ν(OH)], 1547 [ν(C=N)], 1541 [$\nu_{as}(NO_2)$], 1326–1279 [$\nu_s((NO_2)$], 1326–1279 [$\nu(CO_{phenol})$], 1045 [$\nu(CO_{alcohol})$], 568 m [ν(M–O)], 461 m [ν(M–N)]
III	3480 w [ν(OH)], 1548 [ν(C=N)], 1540 [$\nu_{as}(NO_2)$], 1333–1277 [$\nu_s((NO_2)$], 1333–1277 [$\nu(CO_{phenol})$], 1045 [$\nu(CO_{alcohol})$], 567 m [ν(M–O)], 461 m [ν(M–N)]
IV	3500 w [ν(OH)], 1534 [ν(C=N)], 1310 [$\nu(CO_{phenol})$], 1015 [$\nu(CO_{alcohol})$], 594 m [ν(M–O)], 456 m [ν(M–N)]
V	3480 w [ν(OH)], 1544 [ν(C=N)], 1297 [$\nu(CO_{phenol})$], 1009 [$\nu(CO_{alcohol})$], 597 m [ν(M–O)], 453 m [ν(M–N)]
VI	3455 w [ν(OH)], 1528 [ν(C=N)], 1310 [$\nu(CO_{phenol})$], 1005 [$\nu(CO_{alcohol})$], 601 m [ν(M–O)], 453 m [ν(M–N)]

The IR spectra of solid HL^1 and HL^2 show N–H stretching vibration bands at 3314 (HL^1) and 3329 cm^{-1} (HL^2) (Table 2). Its presence provides evidence to show that the ligands exist in the solid state in the form of structure **A**.

The N–H stretching vibration band is absent from the IR spectra of the complexes (Table 2). The O–H stretching vibration frequency increases to 3530–3450 cm^{-1}, which is attributable to the appearance of the triphenylcarbinol OH bond and the absence of the phenol O-H bond. The reason for this phenomenon is that the complex formation involves the azomethine form of the ligand (structure B), which is confirmed by the appearance of a strong C=N stretching vibration band in the region of 1620–1590 cm^{-1} in the spectra of the complexes.

Stretching vibrations of the $C–O_{phenol}$ bond in the complexes have a higher frequency than in the starting ligands and superimpose on symmetrical stretching vibrations of the nitro group [11], implying binding of the phenol oxygen atom with the metal ion. The increase of the NO_2 antisymmetric stretching vibration frequency is also connected with the formation of the coordination entity and with attenuation of the conjugation of the nitro group with the benzene ring.

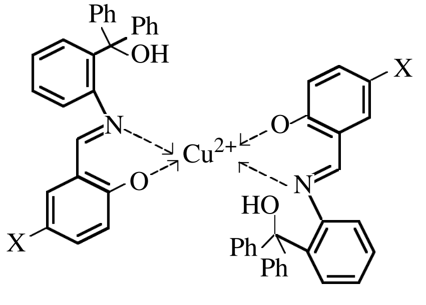
The change in the stretching vibration frequency of the C–O bond in the C–O–C fragment of the benzoxazine ring is caused by ring opening and appearance of the triphenylcarbinol group. The IR spectrum gives no evidence to show whether this group takes part in coordination. The involvement of the phenol oxygen atom in coordination is proved by the presence of an absorption band in the region of 600–560 cm^{-1} in the IR spectra of compounds **I**–**VI**. According to [11], we assigned this band to M–O stretching vibrations.

The absorption band in the region of 470–450 cm^{-1}, which is absent from the spectra of the ligands, is assignable to stretching vibrations of the M–N bond. Thus, we can suggest that the nitrogen atom takes part in binding with the metal ion.

The ESR spectra of powdered compounds **I** and **IV** (Fig. 1a), measured at room temperature, point to an axial symmetry of the nearest surrounding of the metal ion with the unpaired electron localized on the $d_{x^2-y^2}$ orbital. According to [12, 13], the spin-Hamiltonian parameters [compound **I**: $g_\perp$ 2.0835 ± 0.0002 and $g_\parallel$ 2.223 ± 0.002; compound **IV**: $g_\perp$ 2.0811 ± 0.0002 and $g_\parallel$ 2.221 ± 0.002] point to the presence of two nitrogen and two oxygen atoms in the equatorial plane of the complex. The $g_\parallel$ value of ~2.22 is characteristic of *trans*-N_2O_2 surrounding of the copper(II) ion [12] and points to *trans* arrangement of the phenol and azomethine groups.

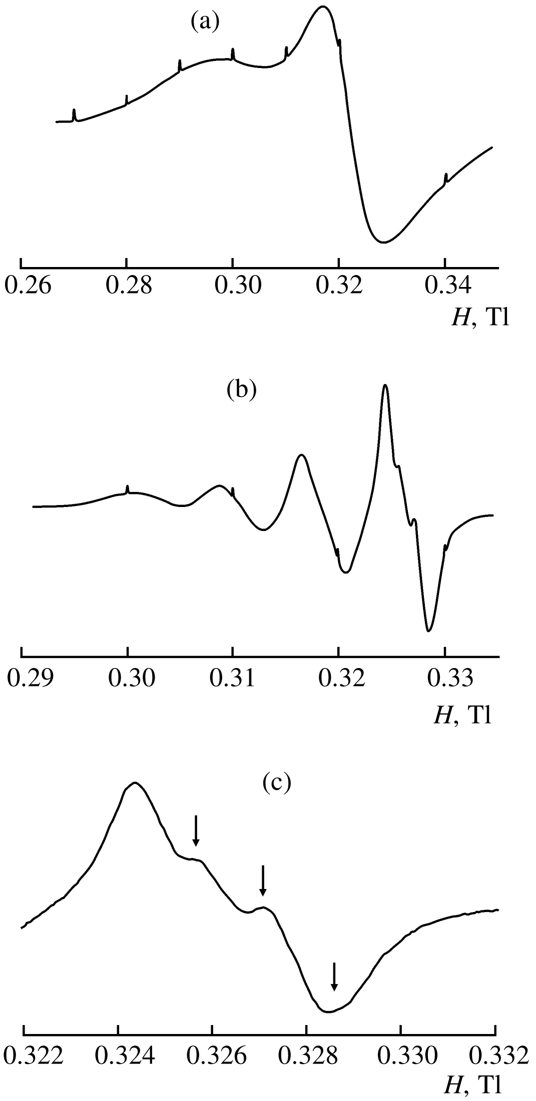
The ESR spectrum of compound **IV** in chloroform (Fig. 1b) shows a copper hyperfine structure and, on the upfield component of this hyperfine structure, an additional hyperfine structure from ^{14}N nuclei (I 1) (Fig. 1c). The fact that the three well-defined components of the additional hyperfine structure (A 1.44×10^{-3} cm^{-1}) have different intensities suggests that the unpaired electron of copper(II) is coupled with two paramagnetic nuclei of the ligands [14, 15]. In this case, the intensity ratio of all the five components is 1 : 2 : 3 : 2 : 1, the extreme components being weak. Were a single nitrogen atom present, the bands would have equal intensities. The absence of the additional nitrogen hyperfine splitting from the ESR spectrum of compound **I** cannot be considered evidence for the absence of Cu–N coupling [16], and the closeness of the g-factors and hyperfine coupling constants for compounds **I** and **IV** [**I**: g_{iso} 2.1294, A 7.19×10^{-3} cm^{-1}; and **IV**: g_{iso} 2.1264, A 7.19×10^{-3} cm^{-1}] suggests analogous coordination modes in these two compounds. The isotropic factors (g_{iso}) satisfy the rule $g_{iso} = (g_\parallel + 2g_\perp)/3$, implying that the structure of the coordination entity is preserved on solution. Whether alcohol groups coordinate with the copper(II) ion in the axial position cannot be either confirmed or denied on the basis of the ESR spectra.

Thus, in our opinion, the following structure is the most probable for the copper(II) complexes.



X = NO_2 (**I**), H (**IV**).

According to the IR spectra, the phenol and azomethine groups are also involved in coordination in the nickel(II) and cobalt(II) compounds.



ESR soectra (298 K) of compound **IV** in (a) powder and (b) chloroform, and (c) the upfield component of the hyperfine structure in the latter spectrum.

In the electrochemical synthesis, anodic dissolution at specified electrode potentials results in the following electrode processes.

Cathode: $2H^+ + 2\bar{e} \longrightarrow H_2$ (HL + $n\bar{e} \longrightarrow L^- + n/2H_2$),
Anode: $2L^- + M - 2\bar{e} \longrightarrow ML_2$,
HL = HL^1, HL^2; M = Cu, Ni.

According to the IR and ESR spectra, the complexes obtained by the electrochemical method are completely identical to compounds **I**, **II**, and **IV** described above. The advantages of this method are high yields (80–90%) of the reaction products and the possibility of controlling kinetic parameters of the process. Unlike the chemical synthesis, this method does not involve the stage of crystal "maturing."

EXPERIMENTAL

The IR spectra were measured in KBr on an Infralyum FT-02 Fourier spectrometer over the range 4000–350 cm^{-1} with a resolution of 1 cm^{-1}.

The ESR spectra of solid samples and chloroform solutions were recorded at room temperature on a Radiopan SE/X-2543 spectrometer. The magnetic field was measured with a built-in JTM NMR magnetometer (accuracy in measuring magnetic induction 2×10^{-5} T). The frequency was calibrated by the spectrum of diphenylpicrylhydrazyl (*g* 2.0027).

Chloroform of chemical grade, 96% rectified alcohol, a 0.1 N solution of ethylenediamine tetraacetate prepared from a volumetric standard solution, a 0.1% alcohol solution of xylene orange, concentrated nitric acid of special purity grade, a 25% solution of urotropin, and nickel(II), cobalt(II), and copper(II) acetates of chemical grade were used.

The metal contents of the complexes were determined by complexometric titration [17]. The elemental analysis was carried out on a Carlo Erba C, H, N analyzer.

Complexes **I**–**VI** were synthesized according to the procedure [18]. A preliminarily prepared solution containing 10^{-4} mol of metal acetate in ethanol was added with stirring to a solution containing 2×10^{-4} mol of compound (HL^1) or (HL^2) in ethanol. The solution was heated for 30 min at 50–60°C. Therewith, the solvent evaporated and partial precipitation occurred. After 1 h, the precipitate was filtered off, washed on the filter with cold ethanol, recrystallized from ethanol, and dried in air.

The electrochemical synthesis was carried out at a permanently controlled anode potential in a glass three-electrode cell equipped with a magnetic stirrer. The working and auxiliary electrodes were made of a dissolving metal according to the procedure in [19]. The synthesis was carried out at 25°C and a potential of 1.0–1.5 V, which was set by a PR-8 programmer and measured accurate to ±0.001 V by a PI-50-1.1 potentiostat. A standard silver chloride electrode was applied as a reference electrode. The anode and cathode compartments were separated with a glass separator that allowed fine metal powder and other reaction products to be retained in the cathode compartment, thus preventing contamination of the anodic synthesis products.

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