

Synthesis and Properties of *N'*-Hydroxy-2-(hydroxyimino)-*N*-(4-[(2-hydroxyphenyl)methylene]amino)-1-naphthyl)-ethanimidamide and Its Metal Complexes

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Abstract—A new vicinal dioxime, *N'*-hydroxy-2-(hydroxyimino)-*N*-(4-[(2-hydroxy-phenyl)methylene]amino)-1-naphthyl)ethanimidamide was synthesized. The initial compound for the synthesis of this dioxime was naphthalene. Complexes of this ligand were obtained with nickel, copper, and cobalt. The dioxime and its complexes were characterized by Fourier IR, UV, ¹H NMR spectroscopy, mass spectrometry, elemental analysis, differential thermal analysis, and conductometric measurements.

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Vicinal dioximes and their complexes are an important class compounds possessing versatile reactivity. The outstanding stability of the complexes of vicinal dioximes was reported [1]. These compounds were investigated as liquid crystals, gas sensors, and inhibitors of chemical agents of military application [2–4]. The research involved numerous representatives of oximes, Schiff's bases, and their metal complexes [5, 6]. The exclusive stability and unique electronic characteristics might originate from their planar structure [7]. In this study a new vicinal dioxime was synthesized: *N'*-hydroxy-2-(hydroxyimino)-*N*-(4-[(2-hydroxyphenyl)methylene]amino)-1-naphthyl)-ethanimidamide. As the starting material for the synthesis served naphthalene (Scheme 1). The intermediate 4-(nitro-1-naphthyl)amine (**I**) and also the noncommercial initial reagents were obtained by published procedures [8–13].

Complexes **V**–**VII** of ligand H₂L **IV** (Scheme 2) with transition metals Ni(II), Co(II), and Cu(II) were obtained by treating the alcoholic solutions of the ligand with water solutions of appropriate acetates.

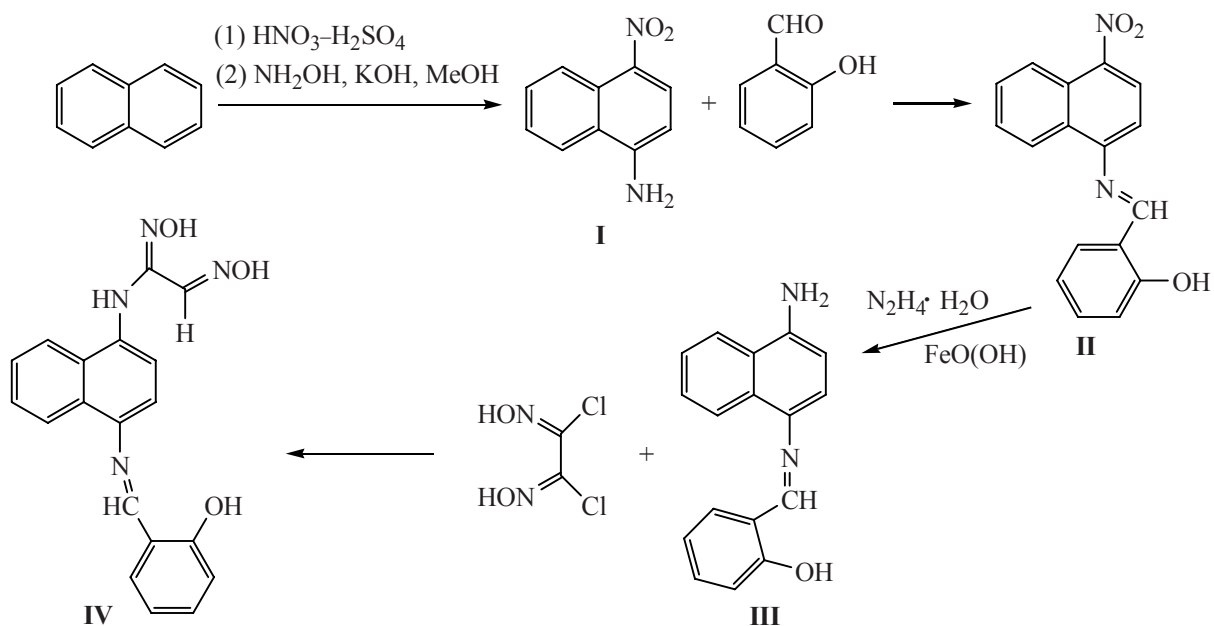
Ligand **IV**, Schiff's base, is soluble in common organic solvents. All the complexes are soluble in DMF and DMSO and insoluble in the other organic solvents. In the electronic spectra of ligand **IV** (see the table) the bands

at 231–267 nm were assigned to the π – π^* transitions in the aromatic rings [14–16]. The bands at 332–431 nm were attributed to the π – π^* transition of the imine. Compared to the free ligand the imine π – π^* transitions in complexes were somewhat shifted for the imine nitrogen was involved into the coordination with the metal ion. In the IR spectra bands of sterically hindered oxime groups of compound **III** and of oximinoligand H₂L **IV** were observed at 3400–3500 cm⁻¹ [17]. The comparison of the spectra of complexes with those of free ligand (Schiff's base) shows that the bands $\nu_{C=N}$ displaced to low frequencies [18, 19]. This means that the imine nitrogen coordinated with the metal ion. In the spectra of the complexes appear several expected absorption bands in the regions 525–560 and 400–420 cm⁻¹ attributed to vibrations $\nu_{M=N}$ [18] and $\nu_{M=O}$ [19].

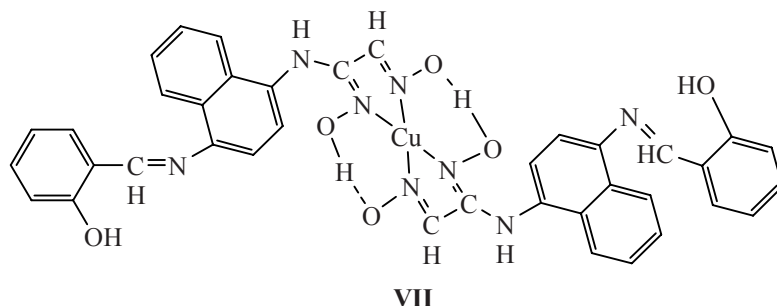
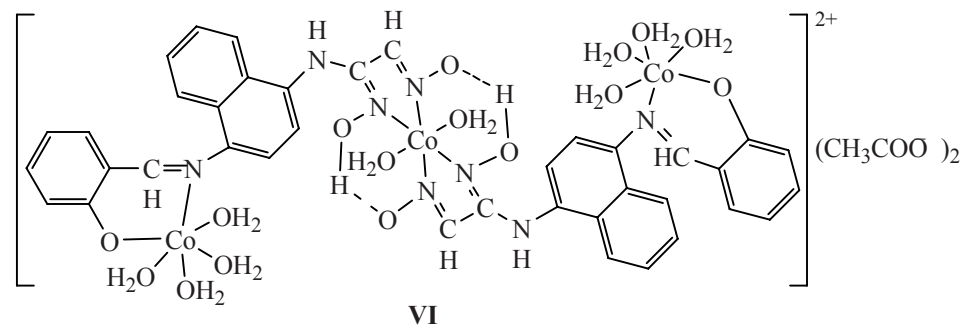
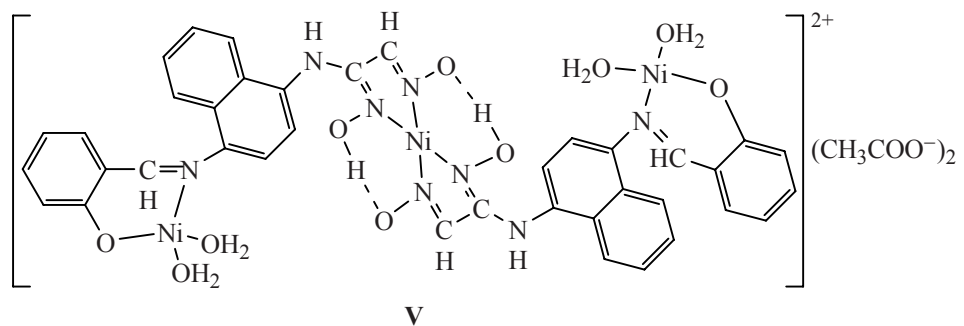
To elucidate the structures of new ligands in solution, oxime **IV** and free Schiff's base **III**, we registered ¹H NMR spectra. The singlet (2H) at 12.0 ppm was assigned to the proton of =NOH group in molecule **IV**. The singlets (1H) at 8.9 and 8.1 ppm were assigned to the CH protons of methyleneamine and aldoxime group respectively.

Multiplet (10H) at 6.7–8.4 ppm was assigned to the protons of the aromatic ring of molecule **IV**. Finally, the

Scheme 1.



Scheme 2.



Magnetic moments and electronic spectra of liganda H₂L **IV** and metal complexes

Compound	μ_{eff}	λ_{max} , nm
H ₂ L	–	430, 399, 359, 335, 322, 267, 211
Ni ₃ (H ₂ L) ₂ ²⁺ ·(AcO [–]) ₂ ·4H ₂ O	2.51	430, 332, 266, 251, 232
Co ₃ (H ₂ L) ₂ ²⁺ ·(AcO [–]) ₂ ·10H ₂ O	3.62	430, 335, 265, 251, 231
Cu[H ₂ L] ₂	1.69	651, 502, 431, 401, 321, 247

singlets at 15.1 and 3.8 ppm in the spectrum of ligand **IV** were assigned to the protons of phenol OH and NH groups respectively.

The values of molar electrical conduction of Ni(II), Co(II), and Cu(II) complexes lie in the range from 5 to 32 Ohm^{–1} cm² mol^{–1} in 0.001 M DMF solution showing the nonelectrolyte nature of these compounds [19].

It followed from the results of thermogravimetric (TG) analysis that Ni(II) complex of ligand H₂L lost 92.13% of initial mass between 198 and 650°C, and the residue (7.87%) was a black solid with a greenish tint. The sample decomposed in four stages. The first stage occurred between 198 and 250°C with the mass loss 11.21%, the second stage proceeded between 250 and 300°C with the mass loss 24.33%; the third stage corresponded to the interval between 300 and 450°C with the mass loss 54.08%, and the fourth, between 425 and 640°C with the mass loss 72.44%.

The theoretical mass of the residual NiO is 7.12%, and 7.87% obtained in the thermogravimetric analysis is consistent with their value. The calculated mass losses for the second, third, and fourth stages comprise 24.19%, 54.33, and 72.24% respectively and are well consistent with the TG data: 24.33%, 54.08, and 72.44% respectively. Similar results of the thermogravimetric analysis were obtained for cobalt and copper complexes. It follows from TG study that all complexes under investigation transformed into the corresponding oxides [20].

EXPERIMENTAL

Analyses for carbon, hydrogen, and nitrogen were carried out on an automatic elemental analyzer Carlo Erba 1106. Electronic spectra in the region 200–800 nm were recorded from solutions in DMF on a spectrophotometer Shimadzu UV-160A, IR spectra, on a spectrophotometer Jasco FT/IR-300 E. ¹H NMR spectra of liganda (H₂L) were registered on a spectrometer Bruker

Avance-500. The electrical conduction was measured in DMF at 24°C using a conductometer LF 330/SET. The magnetic moments were determined by Gouy method using Hg[Co(SCN)₄] for calibration. The DTA/TG curves of the complexes were recorded on a differential scanning calorimeter Setaram Setys Evolution TGA-DTA/DSC 1750 in the temperature range 0–1100°C. The samples were placed into platinum crucibles, α -Al₂O₃ was used as reference. The heating was performed under nitrogen atmosphere at the gas flow rate 60 ml/min. In all cases the sample weight was 2–8 mg, the heating rate 10 deg/min.

The reagents were purchased from Sigma-Aldrich and purified by published procedures [21].

2-[(4-Nitro-1-naphthyl)imino]methyl}phenol (II). A solution of 5.64 g (0.03 mol) of 4-(nitro-1-naphthyl)amine (**I**) in 50 ml of anhydrous ethanol was added at continuous stirring to a solution of 3.66 g (0.03 mol) of salicylaldehyde in anhydrous ethanol. The mixture was boiled at stirring for 24 h. On cooling the formed precipitate was filtered off, recrystallized from anhydrous ethanol, washed several times with ethyl ether, and dried over calcium chloride in a vacuum. Yield 61%, light-yellow crystals, mp 155°C. IR spectrum, ν , cm^{–1}: 3360 (OH), 3070 (CH_{arom}), 1642 (C=N), 1585 (C=C), 1155 (CN), 985 (NO). ¹H NMR spectrum, δ , ppm: 6.7–8.4 m (10H_{arom}), 8.9 s (1H, CH=N), 15.1 s (1H, ArOH). Mass spectrum, m/z : 291.8 [M]⁺. Found, %: C 69.48; H 4.03; N 9.93. C₁₇H₁₂N₂O₃. Calculated, %: C 69.86; H 4.11; N 9.59. *M* 292.3.

2-[(4-Amino-1-naphthyl)imino]methyl}phenol (III). In water was activated for 0.5 h 0.5 g of FeO(OH) as catalyst, then it was added to a solution of 5.35 g (18 mmol) of compound **II** in 130 ml of anhydrous ethanol. To the mixture was added dropwise within 5 min a solution of 1.37 g (27.4 mmol) of hydrazine hydrate in anhydrous ethanol, and the reaction mixture was boiled for 5 h. On cooling the content of the flask to room temperature the catalyst was filtered off, the excess ethanol was removed in a vacuum, and the yellow residue was recrystallized from anhydrous ethanol. Yield 92%, dark-yellow crystals, mp 120°C. IR spectrum, ν , cm^{–1}: 3350 (OH), 3330 (NH), 3065 (CH_{arom}), 1645 (C=N), 1585 (C=C), 1150 (CN). ¹H NMR spectrum, δ , ppm: 4.2 s (2H, NH₂), 6.7–8.4 m (10H_{arom}), 8.9 s (1H, CH=N), 15.1 s (1H, ArOH). Mass spectrum, m/z : 262.7 [M]⁺. Found, %: C 77.80; H 5.44; N 10.39. C₁₇H₁₄N₂O. Calculated, %: C 77.86; H 5.34; N 10.69. *M* 262.3.

***N*-Hydroxy-2-(hydroxyimino)-*N*-(4-[(2-hydroxyphenyl)methylene]amino)-1-naphthyl)ethanimidamide (IV).** A water solution of 0.84 g (10 mmol) of NaHCO₃ was added to a solution of 1.32 g (5 mmol) of compound III in 40 ml of anhydrous ethanol, then a solution of 0.613 g (5 mmol) of *anti*-chloroglyoxime in 30 ml of anhydrous ethanol was added dropwise to the mixture at room temperature within 2 h. The mixture was additionally stirred while heating at a water bath at 60–70°C for 5 h, then it was filtered, and excess ethanol was removed on a rotary evaporator. The reaction product was precipitated by adding ethyl ether, filtered off, washed several times with ethyl ether, and dried in a vacuum for 24 h. Yield 57%, yellow crystals, mp 160°C. IR spectrum, ν , cm⁻¹: 3400 (OH), 3320 (NH), 3070 (CH_{arom}), 1640 (C=N), 1590 (C=C), 1150 (CN), 970 (NO). ¹H NMR spectrum, δ , ppm: 3.8 s (1H, NH), 6.7–8.4 m (10H_{arom}), 8.1 c (1H, CH=N), 8.9 d (1H, CH=N), 12.0 s (2H, =NOH); 15.1 s (1H, ArOH). Mass spectrum, m/z : 347.9 [*M*]⁺. Found, %: C 65.18; H 4.25; N 15.95. C₁₉H₁₆N₄O₃. Calculated, %: C 65.52; H 4.60; N 16.09. *M* 348.3.

Synthesis of complexes V–VII. *General procedure.* A solution of 3 mmol of acetate of Ni, Co or 1 mmol of copper acetate in 20 ml of distilled water was added to a solution of 2 mmol of ligand (H₂L) in 20 ml of ethanol. The pH of the mixture was adjusted to 4.5–5.0 by adding 0.1 N solution of NaOH. For the completion of precipitation the mixture prior to filtration was kept on a water bath at 25°C for 2 h. The obtained complex was filtered off, washed with water, ethyl ether, and cold ethanol, and then it was dried in a vacuum at 70°C.

Complex Ni₃(H₂L)₂²⁺·(AcO⁻)₂·4H₂O (V). Yield 77%, yellow powder, mp 230°C (decomp.). IR spectrum, ν , cm⁻¹: 3300–3500 (OH, H₂O), 3060 (CH_{arom}), 1650 (C=N), 1590 (C=C), 1165 (CN), 950 (NO), 525 (M–N), 400 (M–O). Mass spectrum, m/z : 1058.1 [*M*]⁺. Found, %: C 47.58; H 3.07; N 10.54. C₄₂H₄₂N₈Ni₃O₁₄. Calculated, %: C 47.64; H 4.00; N 10.58. *M* 1058.9.

Complex Co₃(H₂L)₂²⁺·(AcO⁻)₂·10H₂O (VI). Yield 71%, green powder, mp >300°C. IR spectrum, ν , cm⁻¹: 3300–3500 (OH, H₂O), 3065 (CH_{arom}), 1645 (C=N), 1585 (C=C), 1160 (CN), 960 (NO), 560 (M–N), 410 (M–O). Mass spectrum, m/z : 1167.2 [*M*]⁺. Found, %: C 43.14; H 4.62; N 9.55. C₄₂H₅₄CoN₈O₂₀. Calculated, %: C 43.20; H 4.66; N 9.60. *M* 1167.7.

Complex Cu(H₂L)₂ (VII). Yield 55%, orange powder, mp 195°C. IR spectrum, ν , cm⁻¹: 3350 (OH), 3060 (CH_{arom}), 1645 (C=N), 1585 (C=C), 1150 (CN), 960

(NO), 550 (M–N), 420 (M–O). Mass spectrum, m/z : 757.2 [*M*]⁺. Found, %: C 60.07; H 3.96; N 14.72. C₃₈H₁₀CuN₈O₆. Calculated, %: C 60.19; H 3.99; N 14.78. *M* 758.2.

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