Russian Journal of General Chemistry, Vol. 72, No. 8, 2002, pp. 1266–1270. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 8, 2002, pp. 1349–1353.
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Synthesis and Characterization of 1,2-Benzylidenedioxy-7-(2-hydroxybenzylideneamino)-4-azaheptane and Its Complexes with Transition Metals[1]

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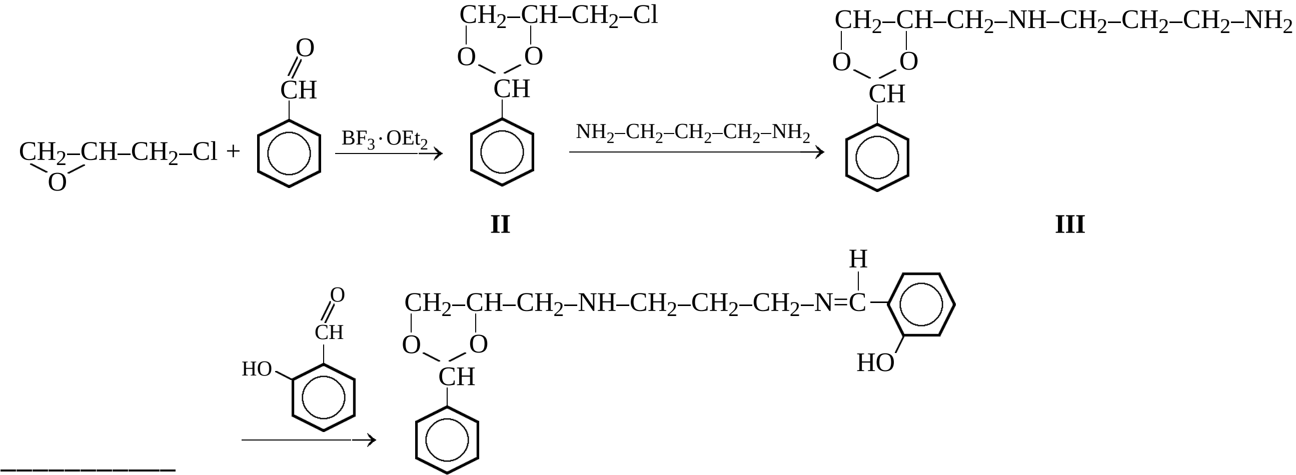
Received December 22, 2000

Abstract — 1,2-Benzylidenedioxy-7-(2-hydroxybenzylideneamino)-4-azaheptane was synthesized by reaction of 1,2-benzylidenedioxy-3-chloropropane with 1,3-diaminopropane and subsequent condensation of 1,2-benzylidenedioxy-7-amino-4-azaheptane with salicylaldehyde. Complexes of 1,2-benzylidenedioxy-7-(2-hydroxybenzylideneamino)-4-azaheptane with cobalt(II), nickel(II), and copper(II) salts were obtained. The structure of the ligand and its complexes was established on the basis of their elemental compositions, IR, UV, and ^{1}H NMR spectra, magnetic susceptibilities, and thermogravimetric data.

Schiff bases possessing at least two donor centers are important as ligands capable of forming fairly stable chelate complexes with transition metals. Some Schiff bases and their complexes exhibit a considerable biological activity (e.g., antifungal) [1]. Metal complexes of Schiff bases occupy a central place in the development of inorganic chemistry of chelate systems [2–4]. A number of Schiff bases and their comlexes with Cu(II), Ni(II), and Zn(II) were reported in [5]. Complexes of Schiff bases are used in many areas such as medicine and industry [6, 7]. The goal of the present study was to synthesize a new Schiff base ligand and its complexes and to investigate their structures. We also planned to test the compounds obtained for antifungal and antibacterial activity.

Here, we describe the synthesis and spectral and magnetic properties of cobalt(II), nickel(II), and copper(II) complexes of 1,2-benzylidenedioxy-7-(2-hydroxybezylideneamino)-4-azaheptane (**I**) which was prepared in three steps as shown in the scheme below. The first step is the synthesis of 1,2-benzylidenedioxy-3-chloropropane (**II**) by reaction of benzaldehyde with epichlorohydrin in the presence of boron trifluoride–ether complex as catalyst. In the second step, compound **II** was brought into reaction with 1,3-diaminopropane to obtain 7-amino-1,2-benzylidenedioxy-4-azaheptane (**III**). Finally, condensation of amine **III** with salicylaldehyde gave Schiff base **I**. Its structure was proved by a combination of data of elemental analysis and IR, UV, and ^{1}H NMR spec-



I

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[1] The original article was submitted in English.

Table 1. Yields, melting points, elemental analyses, and magnetic susceptibilities (χ) of ligand **I** and complexes **IV**–**VI**

Comp. no.	Yield, %	mp, °C (color)	θ, BM	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
I	68	89 (red)	–	70.10	7.11	8.20	$C_{20}H_{24}N_2O_3$	70.59	7.06	8.24
IV	75	122 (green)	1.46	51.35	5.95	7.18	$C_{20}H_{27}N_2O_5ClCu$	50.63	5.70	5.90
V	62	143 (dirty yellow)	2.54	30.11	5.18	5.35	$C_{20}H_{45}N_2O_{14}Cl_3Ni_2$	31.54	5.91	3.68
VI	79	103 (brown)	4.17	58.19	7.45	7.04	$C_{40}H_{56}N_4O_{11}Co$	58.04	6.77	6.77

Table 2. IR and UV spectra of ligand **I** and complexes **IV**–**VI**

Comp. no.	IR spectrum (KBr), ν, cm^{-1}	UV spectrum ($CHCl_3$), λ_{max}, nm
I	3446 (OH_{phenol}); 3365 (N–H); 3062 ($C-H_{arom}$); 2950, 2853 ($C-H_{aliph}$); 2000–1600 [$\delta(C-H_{arom})$]; 1666 [δ(N–H)]; 1633 (C=N); 1581 (C=C); 1175 (C–O)	240.0, 250.0, 260.0, 333.3
IV	3562 (H_2O_{coord}); 3235 (N–H); 3052 ($C-H_{arom}$); 2953, 2951 ($C-H_{aliph}$); 1651 [δ(N–H)]; 1600 (C=N); 1548 (C=C); 1114 (C–O); 859 [$\delta(H_2O_{coord})$]; 576, 450 (M–N, M–O)	308.0, 380.0, 666.6
V	3565, 3520 (H_2O_{coord}); 3438 (H_2O_{cryst}); 3240 (N–H); 3042 ($C-H_{arom}$); 2953, 2876 ($C-H_{aliph}$); 1651 [δ(N–H)]; 1600 (C=N); 1548 (C=C); 1114 (C–O); 855 [$\delta(H_2O_{coord})$]; 578, 455 (M–N, M–O)	306.0, 380.0, 470.0, 630.0, 795.0
VI	3438 (H_2O_{cryst}); 3230 (N–H); 3050 ($C-H_{arom}$); 2953, 2876 ($C-H_{aliph}$); 1651 [δ(N–H)]; 1610 (C=N); 1548 (C=C); 1114 (C–O); 578, 455 (M–N, M–O)	270.0, 360.0, 400.0, 730.0, 810.0

troscopy (see Experimental). The most characteristic bands in the IR spectrum of **I** are the following: 3446 (OH), 1633 (C=N), and 1175 cm^{-1} (C–O) [8]. The ^1H NMR spectrum of **I** contains singlets at δ 9.86 (OH) and 8.23 ppm (N=CH) [8].

The reactions of ligand **I** with Cu(II), Ni(II), and Co(II) salts in anhydrous ethanol gave complexes corresponding to the formulas $[CuL(H_2O)_2]\cdot Cl$ (**IV**), $[NiCl_3(H_2O)_6]\cdot 5H_2O$ (**V**), and $[CoL_2]\cdot 5H_2O$ (**VI**), respectively.

$$\mathbf{I} + CuCl_2\cdot 2H_2O \xrightarrow[EtOH]{} \underset{\mathbf{IV}}{[CuL(H_2O)_2]\cdot Cl} + HCl,$$

$$\mathbf{I} + 2NiCl_2\cdot 6H_2O \xrightarrow[EtOH]{} \underset{\mathbf{V}}{[Ni_2LCl_3(H_2O)_6]\cdot 5H_2O} + HCl,$$

$$2\mathbf{I} + CoCl_2\cdot 6H_2O \xrightarrow[EtOH]{} \underset{\mathbf{VI}}{[CoL_2]\cdot 5H_2O} + 2HCl + H_2O.$$

The analytical and spectral data and other parameters of complexes **IV**–**VI** are given in Tables 1–3. The metal-to-ligand ratio in copper complex **IV** is 1 : 1; in addition, there are two molecules of coordination water and one chloride ion. In nickel complex **V**, the metal-to-ligand ratio is 2 : 1. Its inner coordination sphere also contains three chloride ions and six water molecules. Complex **V** includes five molecules of crystallization water. Cobalt complex **VI** is characterized by a metal-to-ligand ratio of 1 : 2; it contains five molecules of crystallization water [9]. Complexes **IV**–**VI** show in the IR spectra a broad band in the region of 3450 cm^{-1}, which belongs to stretching vibrations of water molecules [9]. The ν(C=N) band in the spectra of the complexes is displaced by 30 cm^{-1} toward lower frequencies relative to the corresponding band of the free ligand. Analogous shift of the ν(C–O) band is 61 cm^{-1}. These data show that the phenolic hydroxy group and the CH=N bond are involved in complex formation. Ligand **I** in the complexes is deprotonated; therefore, no ν(OH) band is observed in the IR spectra of **IV**–**VI**. Some new absorption bands appearing in the low-frequency region were attributed to stretching vibrations of the M–O and M–N bonds [9].

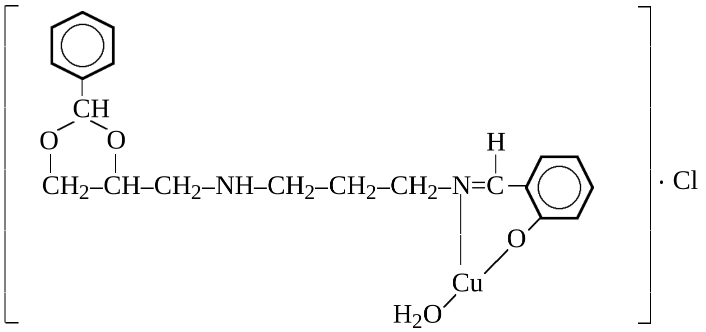
The cobalt(II), nickel(II), and copper(II) complexes are paramagnetic; the magnetic susceptibilities of complexes **IV**–**VI** are 1.46, 2.54, and 4.17 BM, respectively. These data led us to presume that the copper(II) and cobalt(II) complexes are tetrahedral [2, 10], while the nickel(II) complex is characterized

Table 3. Data of thermogravimetric analysis of complexes **IV**–**VI**

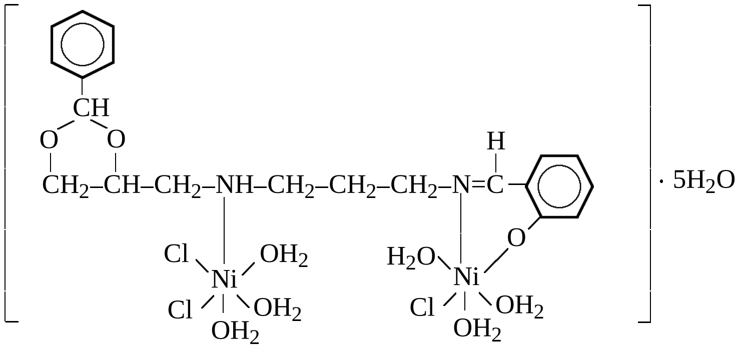
Comp. no.	Temperature range, °C			Weight loss,[a] %			Residue (MO), %	
	1st stage	2nd stage	3rd stage	1st stage	2nd stage	3rd stage	found	calculated
IV	115–165	165–490	490–720	6.85 (7.49)	36.75 (37.54)	39.25 (38.20)	17.15	16.77
V	58–230	230–350	350–645	11.21 (11.84)	26.02 (25.22)	43.77 (43.78)	19.00	19.16
VI	45–220	220–580	580–715	9.15 (10.88)	43.02 (43.05)	38.98 (37.02)	8.85	9.05

[a] The calculated values are given in parentheses.

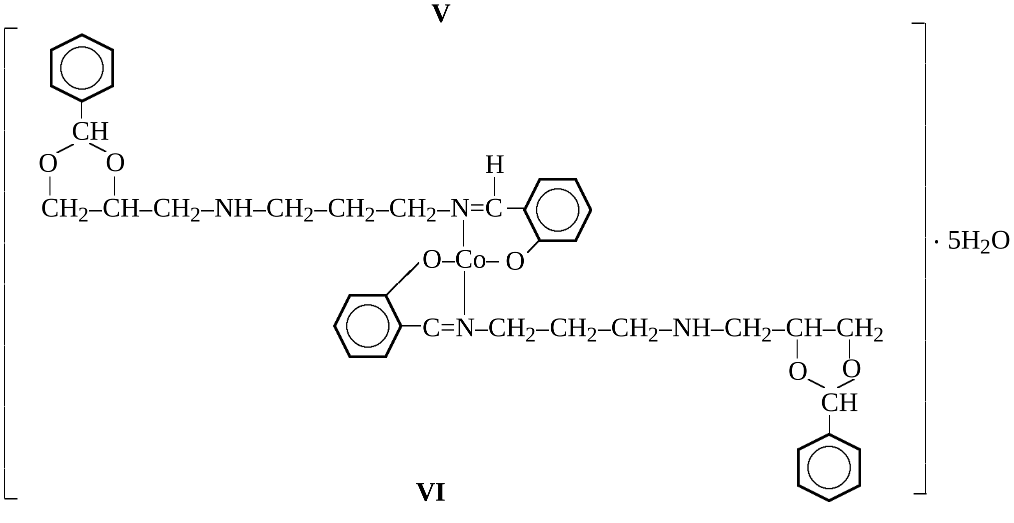
by a high-spin distorted octahedral geometry [11]. The proposed structures of **IV**–**VI** are shown below. Insofar as all the complexes are paramagnetic, their ^1H NMR spectra could not be obtained.



IV



V



VI

The electronic spectra of complexes **IV**–**VI** contain strong absorption bands at λ 270.0–306.0 and 360.0–380.0 nm due to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions in the ligand and also weak $d\rightarrow d$ bands at 666.6 nm; 470.0, 630.0, 795.0 nm; and 400.0, 730.0, 810.0 nm for the Co(II), Ni(II), and Cu(II) complexes, respectively. The molar conductivity value for a 10^{-3} M solution of the copper(II) complex in anhydrous ethanol is 47 Ω^{-1} cm^2 mol^{-1}; this indicates that complex **IV** is a 1 : 1 electrolyte [12]. The nickel(II) and cobalt(II) complexes are nonelectrolytes, as follows from their molar conductivities in anhydrous ethanol: 3 and 8 Ω^{-1} cm^2 mol^{-1}, respectively [12].

The thermal stability of the complexes was studied by thermogravimetric analysis (Table 3). Nickel complex **V** is stable up to 58°C, where dehydration begins, and the decomposition is complete at 650°C with formation of NiO (19%). The process includes three stages corresponding to the temperature ranges 58–230°C (loss of five molecules of crystallization water), 230–350°C (loss of six water molecules and two chloride ligands from the inner coordination sphere) and 350–645°C (decomposition of the organic fragment). All three stages are irreversible.

Copper(II) complex **IV** begins to decompose at 115°C, and the temperature of complete decomposition is 720°C (CuO, 17.15%). The process also consists of three stages in the temperature ranges 115–165°C (loss of chlorine), 165–490°C (elimination of the 2,3-benzylidenedioxypropylamino group), and 490–720°C (loss of two molecules of coordination water and decomposition of the remaining organic moiety. All decomposition stages are irreversible.

The decomposition of cobalt(II) complex **VI** starts at 45°C with loss of crystallization water. The process is complete at 715°C to give CoO (8.85%). As with complexes **IV** and **V**, three decomposition stages are observed, which are accompanied by weight losses corresponding to five molecules of crystallization water (45–220°C), 2,3-benzylidenedioxypropylamino group (220–580°C), and the remaining organic fragment (580–715°C). All stages are irreversible.

Thus, the copper(II) complex is the most stable. The nickel(II) and cobalt(II) complexes, which contain crystallization water, begin to decompose at considerably lower temperatures (58 and 45°C, respectively). The weight loss corresponds to five water molecules per complex molecule: 11.21% for complex **V** (230°C) and 9.15% for **VI** (220°C). The presence of crystallization water in these compounds is also confirmed by the appearance of a broad band in the IR spectra at 3200–3600 cm^{-1} [ν(OH)] [13]. The complete decomposition of all complexes **IV**–**VI** gives the corresponding metal oxides CuO, NiO, and CoO [10, 11, 13].

EXPERIMENTAL

The elemental compositions of ligand **I** and complexes **IV**–**VI** were determined at the TUBITAK Laboratory (Scientific and Technical Research Council of Turkey). The IR spectra were recorded in KBr on a Mattson IR-1000FT spectrometer. The ^{1}H NMR spectra were obtained on Bruker DPX-400 (400 MHz) or Jeol FX-90Q instruments. The magnetic susceptibilities were determined on a Sherwood Scientific magnetic susceptibility balance (Model MK-1) at room temperature (20°C) using $Hg[Co(SCN)_2]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants [14]. The refractive indices were measured on a Bellingam–Stanley 60/70 Abbe instrument using a calibration oil with n^{20} = 1.47577. Thermogravimetric curves were recorded on a Shimadzu TG-50 thermobalance at a heating rate of 10 deg/min over the temperature range from 23.0 to 949.9°C under nitrogen. The electronic spectra were recorded on a Secoman S-1000 spectrophotometer. The molar conductivities were measured on a CMD-750WPA conductometer from 0.001 M solutions in anhydrous ethanol.

Reagent grade chemicals were used. Benzaldehyde, 1,3-diaminopropane, salicylaldehyde, and epichlorohydrin of pure grade were purchased from Merck and were used without additional purification. 1,2-Benzylidenedioxy-3-chloropropane (**II**) and 7-amino-1,2-benzylidenedioxy-4-azaheptane (**III**) were synthesized as described in [15].

1,2-Benzylidenedioxy-7-(2-hydroxybenzylideneamino)-4-azaheptane (I). A solution of 2–3 ml of glacial acetic acid 50 ml of anhydrous ethanol was added dropwise to 1.416 g of 7-amino-1,2-benzylidenedioxy-4-azaheptane (**III**). The mixture was heated to the boiling point, and 0.53 g of salicylaldehyde was added dropwise under continuous stirring. The mixture was refluxed under stirring for 24 h, and the precipitate was filtered off, washed with cold ethanol, diethyl ether, and acetone, and dried at room temperature. Yield 1.16 g (68%). The product is soluble in common organic solvents, such as chloroform, DMSO, DMF, and ethanol. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.20–1.80 m (3H, CH_2, NH), 2.59–2.72 m (4H, NCH_2), 2.83–3.60 m (2H, N=CH), 3.60–3.80 m (2H, CH_2O), 3.83–4.16 m (1H, CHO), 4.16–4.56 s (1H, OCHO), 6.63–7.63 m (9H, C_6H_5, C_6H_4), 8.23 s (1H, N=CH), 9.86 s (1H, OH).

Complexes of 1,2-benzylidenedioxy-7-(2-hydroxybenzylideneamino)-4-azaheptane (I) with

Cu(II), Ni(II), and Co(II). A 50-ml round-bottomed flask was charged with a solution of 0.34 g [0.68 g in the synthesis of the cobalt(II) complex] of ligand **I** in 10 ml of anhydrous ethanol. The solution was heated to the boiling point, and a solution of 0.4574 g of $NiCl_2 \cdot 6H_2O$ or 0.1705 g $CuCl_2 \cdot 2H_2O$ in 10 ml of anhydrous ethanol or of 0.2379 g of $CoCl_2 \cdot H_2O$ in 5 ml of anhydrous ethanol was added dropwise over a period of 30 min under continuous stirring. The mixture was refluxed for 24 h and then stirred for 2 h at room temperature. The precipitate was filtered off, washed with cold ethanol, diethyl ether, and acetone, and dried at room temperature. The yields of complexes **IV**–**VI** were, respectively, 0.36 (75%), 0.47 (62%), and 0.65 g (79%). Complexes **IV**–**VI** are soluble in chloroform, DMSO, DMF, methylene chloride, ethanol, and water. Their melting points, elemental analyses, magnetic susceptibilities, and IR and UV spectra are given in Tables 1 and 2.

ACKNOWLEDGMENTS

The authors thank the FUNAF (Firat Universitesi Araștima Fonu) for financial support.

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