Studies on Mononuclear Chelates Derived from Substituted Schiff Bases Ligands (Part 3). Synthesis and Characterization of a New 5-Nitrosalicylidene-*p*-aminoacetophenoneoxime and Its Complexes with Co(II), Ni(II), Cu(II), and Zn(II)¹

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Abstract—A new ligand, 5-nitrosalicylidene-*p*-aminoacetophenoneoxime (HL), was synthesized from *p*-aminoacetophenoneoxime and 5-nitrosalicylaldehyde under reflux in absolute EtOH at 60°C for 3 h. Mononuclear complexes with a metal : ligand ratio of 1 : 2 were prepared with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} salts. Their structures were determined on the basis of elemental analyses, IR, ¹H and ¹³C NMR, electronic spectra, magnetic susceptibility measurements, molar conductivity, and thermogravimetric analyses. According to the results, two ligands were suggested to be coordinated to each metal atom by phenolic oxygen and imino nitrogen to form high-spin tetrahedral complexes with cobalt(II), nickel(II), and copper(II) while forming a diamagnetic complex with zinc(II).

In modern coordination chemistry, many different inorganic and organic compounds are used as ligands. In spite of the tremendous variety of these ligand systems, typical structures are defined as a basis for the study of their coordination chemistry [1-5].

Due to recent increasing use of coordination compounds in various fields of chemistry, biochemistry, analytical, pigment, and medicinal chemistries, many investigators have studied these topics [6]. One of the important subjects of this topic is Schiff bases, particularly, Schiff bases derived from substituted salicylaldehydes are well-known polydentate ligands coordinating in deprotonated or neutral forms [7].

In order to emulate the biological activity of proteins and enzymes, various model complexes were prepared. A lot of investigations on the synthesis and biological activity of metal complexes have been done recently. These investigations have shown that these compounds are active against bacteria, viruses, and cancers [8].

In the present paper, we report the synthesis and characterization of a new Schiff base ligand and its complexes with cobalt(II), nickel(II), copper(II), and zinc(II) ions. As far as we know, this is the first report on this ligand.

EXPERIMENTAL

Elemental analyses (C, H, N) were carried out using LECO-932 CHNSO by Technical and Scientific Research Council of Turkey (TUBITAK). IR spectra were recorded on a Mattson 1000 FT-IR spectrometer with KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz high-performance digital FT-NMR spectrometer at TUBITAK. Electronic spectra were obtained on a Shimadzu 1240 UV spectrometer. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using Hg[Co(SCN)₄] as a calibrant; diamagnetic corrections were calculated from Pascal's constants. Melting points were determined on a Gallenkamp melting point apparatus. Molar conductances of the Schiff base ligand and its transition-metal complexes were determined at room temperature using a CMD 750 WPA conductivity meter. Thermogravimetric analyses (TGA) were carried out using Shimadzu TG-50 thermobalance.

5-Nitrosalicylidene-*p*-aminoacetophenoneoxime (HL). To a solution of *p*-aminoacetophenoneoxime (1.502 g, 10 mmol) in absolute EtOH (10 ml), 5-nitrosalicylaldehyde (1.671 g, 10 mmol) and *p*-toluene sulfonic acid (0.01 mg) dissolved in absolute EtOH (40 ml) were added dropwise at 60°C with continuous stirring and IR monitoring of the course of the reaction. The precipitate was filtered off, washed with cold EtOH and Et₂O several times, and crystallized from an acetone–water mixture and dried at 60°C to a constant weight.

Bis(p-aminoacetophenoneoxime-5-nitrosalicylaldiminato)cobalt(II) CoL₂. A solution of $Co(AcO)_2 \cdot 4H_2O$ (0.125 g, 0.50 mmol) in absolute EtOH (20 ml) was added to a hot (50°C) solution of HL (0.299 g, 1.00 mmol) in absolute EtOH (25 ml) under an argon atmosphere. The complex formed immediately upon

¹ This article was submitted by the authors in English.

Compounds	Empirical formula	EW a/mol	Color	M n °C	Vield %	Content (calcd/found), %		
Compounds		1 [°] . w ., g/1101	Color	M. p., C	1 iciu, 70	С	Н	Ν
HL	C ₁₅ H ₁₃ N ₃ O ₄	299.28	Yellow	263	79	60.20/59.86	4.38/3.99	14.04/13.75
CoL ₂	$CoC_{30}H_{24}N_6O_8$	655.48	Dark yellow	249	70	54.97/55.28	3.69/4.01	12.82/13.19
NiL ₂	NiC ₃₀ H ₂₄ N ₆ O ₈	655.24	Green	274	64	54.99/55.30	3.69/3.57	12.83/13.11
CuL ₂	CuC ₃₀ H ₂₄ N ₆ O ₈	660.09	Mustard yellow	295	67	54.59/54.23	3.66/3.60	12.73/13.04
ZnL ₂	ZnC ₃₀ H ₂₄ N ₆ O ₈	661.94	Yellow	299	66	54.43/54.39	3.65/3.51	12.70/13.07

 Table 1. Analytical and physical data of the ligand and the complexes

Table 2. Characteristic IR bands of the ligand and the complexes (cm⁻¹)

Compounds	v(O–H) oxime	v(O–H) phenolic	v(C=N) azomethine	v(C=N) oxime	v(C-O)	v(N-O)
HL	3286	3260	1644	1617	1303	1007
CoL ₂	3290		1635	1621	1315	1011
NiL ₂	3289		1621	1615	1320	1007
CuL ₂	3285		1617	1616	1322	1011
ZnL_2	3285		1620	1615	1317	1007

addition of the metal salt solution. The precipitated complex was filtered off, washed with H_2O , cold EtOH, and cold Et_2O several times, and dried *in vacuo*.

Bis(*p*-aminoacetophenoneoxime-5-nitrosalicylaldiminato)nickel(II) NiL₂. NiL₂ was prepared following the same procedure as described for CoL₂, starting from HL (0.299 g, 1.00 mmol) and Ni(AcO)₂ · 4H₂O (0.124 g, 0.50 mmol).

Bis(p-aminoacetophenoneoxime-5-nitrosalicylaldiminato)copper(II) CuL₂. CuL₂ was prepared following the same procedure as described for CoL₂, starting from HL (0.299 g, 1.00 mmol) and Cu(AcO)₂ · H₂O (0.100 g, 0.50 mmol). **Bis**(*p*-aminoacetophenoneoxime-5-nitrosalicylaldiminato)zinc(II) ZnL₂. ZnL₂ was prepared following the same procedure as described for CoL₂, starting from HL (0.299 g, 1.00 mmol) and Zn(AcO)₂ \cdot 2H₂O (0.110 g, 0.50 mmol).

Analytical and physical data of ligand and its complexes are given in Table 1.

RESULTS AND DISCUSSION

The reaction steps for the synthesis of ligand HL are given below:



This ligand was synthesized starting from *p*-aminoacetophenoneoxime (**A**) and 5-nitrosalicylaldehyde (**B**) in absolute EtOH. For the structural characterization of the ligand and its complexes, a combination of elemental analysis, IR, ¹H and ¹³C NMR, electronic spectra, magnetic susceptibility measurements, molar conductivity, and *TGA* were used.

Table 2 lists the characteristic IR bands of the ligand and its complexes. The ligand contains four potential donor sites: phenolic oxygen; azomethine nitrogen;

Compound	¹ H NMR	¹³ C NMR
HL	$\begin{array}{c} 2.20 \ ({\rm s., 3H, H^1}), \ 6.80 \ ({\rm d., 1H, H^{11}}), \ 6.94 \ ({\rm d., 1H, H^{13}}), \\ 7.16 \ ({\rm d., 1H, H^{14}}), \ 7.30 \ ({\rm d., 2H, H^4 \ and H^8}), \ 7.61 \ ({\rm d., 2H, H^5 \ and H^7}), \ 9.20 \ ({\rm s., 1H, H^9}), \ 10.99 \ ({\rm s., 1H, H^b}), \\ 13.68 \ ({\rm s., 1H, H^a}) \end{array}$	11.24 (C ¹), 121.32 (C ¹⁰), 122.44 (C ¹⁴), 124.09 (C ⁵ and C ⁷), 127.55 (C ¹¹), 130.19 (C ⁴ and C ⁸), 132.38 (C ¹³), 135.64 (C ³), 137.07 (C ¹²), 147.50 (C ²), 153.75 (C ⁶), 161.54 (C ⁹), 163.09 (C ¹⁵)

Table 3. ¹H and ¹³C NMR spectral data of the ligand, ppm

Table 4. Magnetic moment, molar conductance, and electronic spectral data of the ligand and the complexes

Compounds	μ_{eff}, μ_{B}	$\Lambda_{\rm M},$ cm ² /(Ω mol)	$λ_{max}$, nm (ε, l/(mol cm))			
			d–d	C–T	$n \longrightarrow \pi^*$ azomethine	
HL		2.7			$390 (2.80 \times 10^3)$	
CoL ₂	4.10	3.6	676 (185)	$442 (3.00 \times 10^3)$	$381 (5.95 \times 10^3)$	
NiL ₂	3.00	5.2	635 (169)	$430 (4.00 \times 10^3)$	$386 (2.85 \times 10^3)$	
CuL ₂	1.88	5.0	571 (177)	$425 (1.30 \times 10^3)$	$385 (4.01 \times 10^3)$	
ZnL_2	Dia	6.1		$428 (5.00 \times 10^3)$	$380 (3.04 \times 10^3)$	

oxime oxygen, and oxime nitrogen. In the IR spectrum of HL, the most characteristic absorptions are at 3286 cm⁻¹ v(O–H_{oxime}) [9–12], 3260 cm⁻¹ v(O–H_{phenolic}), 1644 cm⁻¹ v(C=N_{azomethine}), 1617 cm⁻¹ v(C=N_{oxime}) [13–16], 1303 cm⁻¹ v(C–O), and 1007 cm⁻¹ v(N–O). These values are in agreement with similar compounds [17, 18]. The azomethine vibration of the ligand at 1644 cm⁻¹ was at ~1617–1635 cm⁻¹ for the complexes. At the same time, the v(C–O_{phenolic}) band at 1303 cm⁻¹ in the free ligand shifted to higher frequency by 12–19 cm⁻¹ after complexation, which means that the shifts are due to the coordination of the ligand to the metal atom by the azomethine nitrogen and phenolic oxygen [19, 20]. The practically unchanged positions of O–H at 3296 and C=N at 1559 cm⁻¹ of the oxime group confirm that the oxime group itself does not coordinate to metal atoms by either oxygen or nitrogen atoms.

¹H and ¹³C NMR spectra of ligand HL were recorded in CDCl₃/DMSO-D₆. The ¹H and ¹³C NMR data of the ligand and their assignments are shown in Table 3. The results confirm the proposed structure of the ligand. The characteristic ¹H NMR peaks are at 13.68 (H^a), 10.99 (H^b) [21–24], 9.20 (H₉), 6.80–7.61 (H_{Ar}), and 2.20 ppm (H¹). The H^a and H^b signals at 13.68 ppm disappeared upon the addition of D₂O to the solution, indicating that it is an acidic proton. More detailed information about the structure of the ligand was provided by the ¹³C NMR spectral data. Carbon atoms are observed at 11.24 (C¹), 121.32 (C¹⁰), 122.44 (C¹⁴), 124.09 (C⁵ and C⁷), 127.55 (C¹¹), 130.19 (C⁴ and C⁸), 132.38 (C¹³), 135.64 (C³), 137.07 (C¹²), 147.50 (C²), 153.75 (C⁶), 161.54 (C⁹), and 163.09 (C¹⁵) ppm, respectively, for HL.

The metal-to-ligand ratio of all complexes was found to be 1 : 2 according to the elemental analyses results. As known, magnetic susceptibility measurements provide information regarding the structure of the complexes. The magnetic moments of the complexes were measured at room temperature and are listed in Table 4. The cobalt(II), nickel(II), and copper(II) complexes are paramagnetic, while the zinc(II) complex is diamagnetic. The magnetic moments of the cobalt(II), nickel(II), and copper(II) complexes of the ligand at room temperature fall in a range of 4.10, 300, and 1.88 μ_B , respectively, which is characteristic of mononuclear tetrahedral complexes [25, 26].

The electronic spectra of the ligand and all the complexes were recorded in DMF at room temperature. The UV spectral data of the ligand and its complexes are given in Table 4. The aromatic band of the ligand at 260 nm is attributed to the benzene $\pi \longrightarrow \pi^*$ transition. The band around 390 nm is due to the $n \longrightarrow \pi^*$ transition of the nonbonding electrons present on the nitrogen of the azomethine group in the Schiff base. The complexes of cobalt(II), nickel(II), and copper(II) show less intense shoulders at ~571–676 nm ($\epsilon = 169-185 \text{ l/(mol cm)}$), which are assigned to the *d*-*d* transition of the metal ions. The former band is probably due to the ${}^{4}A_{2} \longrightarrow {}^{4}T_{1}(P)$ for CoL₂, ${}^{3}A_{2} \longrightarrow {}^{3}T_{2}(F)$ for NiL₂, and ${}^{2}T_{2} \longrightarrow {}^{2}E(G)$ for CuL₂ transition of tetrahedral geometry. All the complexes show an intense band at ~380-386 nm which is assigned to the $n \longrightarrow \pi^*$ transition associated with the azomethine linkage [27]. The spectra of all the complexes show intense band at ~425-442 nm (ϵ = $(1.30-5.00) \times 10^3$ l/(mol cm)), which can be assigned to a charge-transfer transition of tetrahedral geometry [28-31].

The observed molar conductance of the complexes in 10^{-4} M solutions in DMSO lies in a range of 3.6–6.1 cm²/(Ω mol) (Table 4). This is consistent with the nonelectrolytic nature of these complexes [32].

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Compounds	Decomposition temperature (weight loss (calcd/found), %)	Total weight loss	Residue (calcd/found), %	
	first step	second step	(calcd/found), %		
HL	234–272 (25.75/26.23)	272–598 (74.25/72.97)	/99.20	/0.80	
CoL ₂	221–267 (20.15/19.64)	267–557 (68.42/67.74)	88.57/87.38	11.43/12.62	
NiL ₂	186–233 (20.16/19.69)	233-542 (68.44/68.82)	88.60/88.51	11.40/11.49	
CuL_2	197–326 (20.00/19.05)	326-358 (67.95/68.60)	87.95/87.65	12.05/12.35	
ZnL_2	208–375 (25.72/26.31)	375–511 (61.99/62.17)	87.71/88.48	12.29/11.52	

 Table 5. TGA data of the ligand and the complexes

The thermal behavior of the ligand and all the complexes was investigated using thermogravimetric techniques. The thermal stability data are listed in Table 5. The decomposition temperature and weight losses of the complexes were calculated from the *TGA* data. The ligand is stable up to 234°C, and its decomposition starts at 234°C and is completed at 598°C. As can be seen from the TGA data in Table 5, all the complexes and the ligand decompose in two steps in different temperature ranges. All these complexes undergo complete decomposition to the corresponding metal oxides, CoO, NiO, CuO, and ZnO [33, 34].

As mentioned in Introduction, our research group has been heavily engaged in the synthesis of novel substituted oximes and their Schiff base derivatives. Many other Schiff base derivatives containing substituted oxime were synthesized, characterized in detail, and used for complexation with some transition-metal salts. Functional groups, such as oxime, have no effect on the complexes. These functional groups are very far from the pendants taking part in the complexation. For these complexes, additional analytical data are given in Tables 1–5. According to the results obtained, the geometries of all the complexes are tetrahedral. The suggested structures of the complexes are shown below:



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