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Studies on Mononuclear Chelates Derived from Substituted Schiff Base Ligands (Part 4): Synthesis and Characterization of a New 5-Hydroxysalicyliden-*P*-Aminoacetophenoneoxime and Its Complexes with Co(II), Ni(II), Cu(II) and Zn(II)

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5-Hydroxysalicyliden-*p*-aminoacetophenoneoxime (LH) was synthesized starting from *p*-aminoacetophenoneoxime and 5-hydroxysalicylaldehyde. Complexes of this ligand with Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} salts were prepared. With this ligand, complexes were synthesized using Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} salt with a metal:ligand ratio of 1:2. Their structures were elucidated on the basis of elemental analyses, IR, ^{1}H- and ^{13}C-NMR, electronic spectra, magnetic susceptibility measurements, molar conductivity and thermogravimetric analyses.

Key Words: Schiff bases, transition metal complexes, oxime.

Introduction

Schiff bases derived from an amine and an aldehyde are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively[1−3]. Schiff base complexes are important for designing metal complexes related to synthetic and natural oxygen carriers[4]. The complexes make these compounds effective and stereospecific catalysts for oxidation, reduction and hydrolysis and they show biological activity, and other transformations of organic and inorganic chemistry[5]. It is well known that some drugs have higher activity when administered as metal complexes than as free ligands[5]. In this article we describe the synthesis and characterization of a Schiff base ligand and its mononuclear complexes with Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} ions. As far as we know, this is the first report on this ligand.

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Experimental

Elemental analyses (C, H, N) were carried out using LECO-932 CHNSO by the Scientific and Technical Research Council of Turkey (TÜBİTAK). IR spectra were recorded on a Mattson 1000 FT-IR Spectrometer as KBr pellets. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker GmbH Dpx-400 MHz High Performance Digital FT-NMR Spectrometer. Electronic spectra were obtained on a Shimadzu 1240 UV Spectrometer at Hacettepe University. Magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $Hg[Co(SCN)_4]$ as a calibrate; diamagnetic corrections were calculated from Pascal's constants. The 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. TGA curves were recorded on a Shimadzu TG-50 thermo balance.

5-Hydroxysalicyliden-*p*-aminoacetophenoneoxime (LH)

To a solution of (1.502 g, 10 mmol) *p*-aminoacetophenoneoxime[6] in 15 mL of absolute EtOH were added dropwise 5-hydroxysalicylaldehyde (1.381 g, 10 mmol) and (0.01 mg) *p*-toluene sulfonic acid dissolved in 35 mL of absolute EtOH at 60 °C with continuous stirring and monitoring of the course of the reaction with IR (Scheme). The precipitate was filtered, washed with cold EtOH and Et_2O several times and crystallized from acetone-water and dried at 60 °C to a constant weight.

Bis(*p*-aminoacetophenoneoxime-5-hydroxysalicylaldiminato)cobalt(II) $Co(L)_2$

A solution of $Co(AcO)_2 \cdot 4H_2O$ (0.125 g, 0.50 mmol) in absolute EtOH (15 mL) was added to a hot (50 °C) solution of the LH (0.270 g, 1.00 mmol) in absolute EtOH (30 mL) under an argon atmosphere. The complex was obtained immediately upon 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-hydroxysalicylaldiminato)nickel(II) $Ni(L)_2$

$Ni(L)_2$ was prepared following the same procedure as described for $Co(L)_2$, starting from LH (0.270 g, 1.00 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (0.124 g, 0.50 mmol).

Bis(*p*-aminoacetophenoneoxime-5-hydroxysalicylaldiminato)copper(II) $Cu(L)_2$

$Cu(L)_2$ was prepared following the same procedure as described for $Co(L)_2$, starting from LH (0.270 g, 1.00 mmol) and $Cu(AcO)_2 \cdot H_2O$ (0.100 g, 0.50 mmol).

Bis(*p*-aminoacetophenoneoxime-5-hydroxysalicylaldiminato)zinc(II) $Zn(L)_2$

$Zn(L)_2$ was prepared following the same procedure as described for $Co(L)_2$, starting from LH (0.270 g, 1.00 mmol) and $Zn(AcO)_2 \cdot 2H_2O$ (0.110 g, 0.50 mmol).

Results and Discussion

A new 5-hydroxysalicyliden-*p*-aminoacetophenoneoxime, the Schiff base ligand (LH), was synthesized from the reaction of *p*-aminoacetophenoneoxime and 5-hydroxysalicylaldehyde in absolute ethanol (Scheme). The structure of the ligand and the complexes were determined by a combination of elemental analysis, IR, ^{1}H- and ^{13}C-NMR spectra, electronic spectra, magnetic susceptibility measurements, molar conductivity and thermogravimetric analyses (TGA). The compounds are soluble in polar organic solvents, such as DMSO, THF, DMF, CH_2Cl_2 and MeOH, and in nonpolar organic solvents, such as $n-$hexane, benzene and petroleum ether.

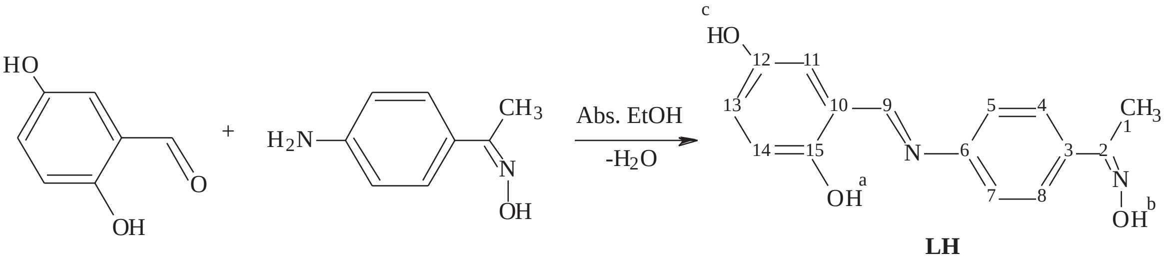
The important infrared spectral bands for the synthesized complexes and ligand are given in Table 2. The ligand contains 4 potential donor sites: 1) the phenolic oxygen, 2) the azomethine nitrogen, 3) the oxime oxygen, 4) the oxime nitrogen. The absorption bands at 3277, 3248, 1623, 1600, 1276 and 1005 cm^{-1} in the spectrum of LH were attributed to υ(O-H$_{oxime}$)$^{7-9}$, υ(O-H$_{phenolic}$), υ(C=N$_{azomethine}$), υ(C=N$_{oxime}$)$^{10-12}$, υ(C-O) and υ(N-O), respectively. These values are in agreement with those of similar compounds[13,14]. The azomethine vibration of the ligand at 1623 cm^{-1} was shifted to lower frequencies after complexation, i.e. 1615, 1618, 1617 and 1609 cm^{-1} for Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} complexes, respectively. On the other hand, the υ(C-O$_{phenolic}$) band at 1276 cm^{-1} in the free ligand was moved to a higher frequency by 19-47 cm^{-1} after complexation, which means that the shifts are due to coordination of ligand to metal atom by the azomethine nitrogen and phenolic oxygen[15,16]. The practically unchanged O-H at 3277 and C=N at 1600 cm^{-1} of the oxime group confirm that the oxime group itself does not coordinate to metal atoms by oxygen or nitrogen atoms[17].

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

Compounds	Formula (F.W) g/mol	Color	M.p. (°C)	Yield (%)	Calculated (Found) (%) C	H	N
LH	$C_{15}H_{14}N_2O_3$ (270.28)	mustard yellow	231	68	66.66 (66.30)	5.22 (4.84)	10.36 (9.98)
$Co(L)_2$	$CoC_{30}H_{26}N_4O_6$ (597.48)	black	> 300	64	60.31 (60.70)	4.39 (4.00)	9.38 (8.99)
$Ni(L)_2$	$NiC_{30}H_{26}N_4O_6$ (597.24)	dark brown	> 300	61	60.33 (60.61)	4.39 (4.35)	9.38 (9.71)
$Cu(L)_2$	$CuC_{30}H_{26}N_4O_6$ (602.10)	black	> 300	61	59.84 (60.19)	4.35 (3.97)	9.31 (8.95)
$Zn(L)_2$	$ZnC_{30}H_{26}N_4O_6$ (603.94)	dark brown	210	60	59.66 (60.01)	4.34 (3.98)	9.28 (8.88)

Table 2. Characteristic IR bands of the ligand and the complexes (in cm^{-1}).

Compounds	υ (O-H) oxime	υ (O-H) phenolic	υ (C=N) azomethine	υ (C=N) oxime	υ (C-O)	υ (N-O)
LH	3277	3248	1623	1600	1276	1005
$Co(L)_2$	3278	—	1615	1600	1295	1000
$Ni(L)_2$	3277	—	1618	1604	1323	1000
$Cu(L)_2$	3278	—	1617	1605	1300	1000
$Zn(L)_2$	3277	—	1609	1600	1305	1005



Scheme. Structure of the ligand.

The ^1H- and ^{13}C-NMR spectra of the ligand (LH) were recorded in $CDCl_3$/DMSO-d_6. ^1H- and ^{13}C-NMR data of ligand and their assignments are given in Table 3. The results confirm the proposed structure of the ligand (Scheme). Characteristic ^1H-NMR peaks are observed at 12.42 (H^a), 10.70 (H^b)$^{18-20}$ and 8.57 ppm (H_9). The H^a, H^b and H^c signals at 12.42, 10.70 and 8.49 ppm respectively, disappeared upon addition of D_2O to the solution, indicating that it is an acidic proton. More detailed information about the structure of the ligand was provided by ^{13}C-NMR spectral data. Characteristic carbon atoms are observed at 156.04 (C_6), 157.61 (C_{15}) and 162.88 (C_9) ppm for LH.

Table 3. ^1H- and ^{13}C-NMR spectral data of the ligand (in ppm).

Compounds	^1H-NMR	^{13}C-NMR
LH	2.15 (s, 3H, H_1), 6.77 (d, 1H, H_{13}), 6.85 (s, 1H, H_{11}), 6.92 (d, 1H, H_{14}), 7.19 (d, 2H, H_4 and H_8), 7.61 (d, 2H, H_5 and H_7), 8.49 (s, 1H, H^c), 8.57 (s, 1H, H_9), 10.70 (s, 1H, H^b), 12.42 (s, 1H, H^a)	11.95 (C_1), 117.43 (C_{11}), 118.04 (C_{14}), 119.91 (C_{10}), 121.35 (C_5 and C_7), 122.70 (C_{13}), 128.44 (C_4 and C_8), 136.15 (C_3), 149.66 (C_{12}), 150.24 (C_2), 156.04 (C_6), 157.61 (C_{15}), 162.88 (C_9)

s: singlet, d: doublet, t: triplet, m: multiplet

The metal to ligand ratio of all the complexes was 1:2 according to the elemental analyses results. While the Zn^{+2} complex is diamagnetic, the Co^{+2}, Ni^{+2} and Cu^{+2} complexes are paramagnetic, and their magnetic susceptibility values are 3.85, 2.71 and 2.02 B.M., respectively[21] (Table 4). Since the Co^{+2}, Ni^{+2} and Cu^{+2} complexes are paramagnetic their ^1H and ^{13}C-NMR spectra could not be obtained.

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

Compounds	μ_{eff} (B.M.)	Λ_M (Ω^{-1} cm^2 mol^{-1})	λ_{max} [ε, L mol^{-1} cm^{-1}]		
			d-d	C-T	$n \rightarrow \pi^*$ azomethine
LH	—	2.2	—	—	372 [1.55 x 10^3]
Co(L)$_2$	3.85	1.9	682 [166]	430 [1.90 x 10^3]	380 [4.22 x 10^3]
Ni(L)$_2$	2.71	3.7	651 [175]	420 [2.98 x 10^3]	387 [1.99 x 10^3]
Cu(L)$_2$	2.02	6.0	584 [130]	440 [1.00 x 10^3]	379 [3.01 x 10^3]
Zn(L)$_2$	dia	5.4	—	445 [3.04 x 10^3]	375 [1.52 x 10^3]

The electronic spectra of the ligand and the Co^{+2}, Ni^{+2} and Cu^{+2} 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 275 nm is attributed to benzene $\pi \rightarrow \pi^*$ transition. The band around 372 nm is due to the $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base. The complexes of the Co^{+2}, Ni^{+2} and Cu^{+2} show less intense shoulders at ca. 584-682 nm (ε = 130-175 L mol^{-1} cm^{-1}), which are assigned as $d-d$ transition of the metal ions. The former band is probably due to the $^4A_2 \rightarrow ^4T_1$ (P) for $Co(L)_2$, $^3A_2 \rightarrow ^3T_2$ (F) for $Ni(L)_2$ and $^2T_2 \rightarrow ^2E$ (G) for $Cu(L)_2$ transition of tetrahedral geometry[22]. All the complexes show an intense band at ca. 375-387 nm, which is assigned to $n \rightarrow \pi^*$ transition associated with azomethine linkage[23]. The spectra of the Co^{+2}, Ni^{+2} and Cu^{+2} complexes show an intense band at ca. 420-440 nm (ε = 1.00-2.98 x 10^3 L mol^{-1} cm^{-1}), which can be assigned to charge transfer transition of tetrahedral geometry[24−26] in Table 4.

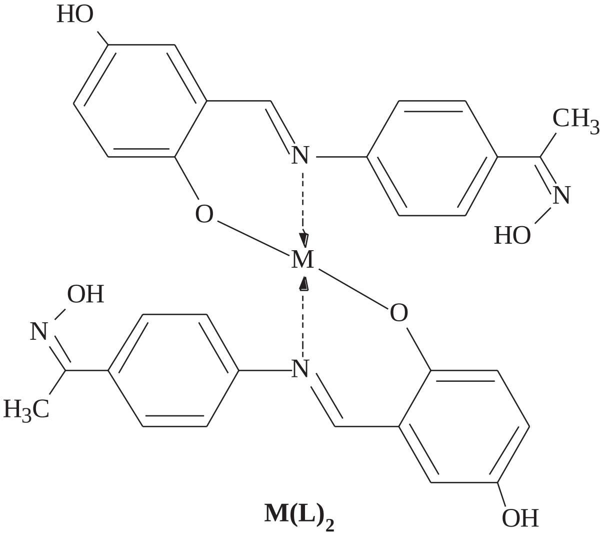
The observed molar conductances of the complexes in 10^{-4} molar solutions in DMSO are in the range 1.9-6.0 Ω^{-1} cm^2 mol^{-1} (Table 4). This is consistent with the no electrolytic nature of these complexes[27].

The thermal behavior of the ligand and all the complexes was investigated using thermogravimetric techniques. Thermal stability data are listed in Table 5. The decomposition temperature and the weight losses of the complexes were calculated from TGA data. The ligand is stable up to 218 °C and its decomposition starts at 218 °C and is completed at 678 °C. As can be seen in the TGA data (Table 5), all the complexes and the ligand decompose in 2 steps at different temperature ranges. All these complexes undergo complete decomposition to the corresponding metal oxides, CoO, NiO, CuO and ZnO. When the complexes are heated to higher temperatures, they decompose to give oxides of the MO type[28,29].

Table 5. TGA data of the ligand and the complexes.

Compounds	Decomposition temperature (%) calculated (found)		Weight loss (%) calculated (found)	Residue (%) calculated (found)
	first step	second step		
LH	218-232	232-678		
	21.48 (22.05)	78.52 (76.55)	(98.60)	(1.40)
$Co(L)_2$	196-317	317-411		
	22.11 (21.64)	65.35 (64.91)	87.46 (86.55)	12.54 (13.45)
$Ni(L)_2$	193-232	232-408		
	27.81 (28.59)	59.68 (59.13)	87.49 (87.72)	12.51 (12.28)
$Cu(L)_2$	205-236	236-357		
	21.93 (22.76)	64.86 (63.87)	86.79 (86.63)	13.21 (13.37)
$Zn(L)_2$	200-221	221-593		
	12.94 (13.88)	73.59 (73.06)	86.53 (86.94)	13.47 (13.06)

Our group has been heavily engaged in the synthesis of novel substituted oximes and their Schiff base derivatives. Many more Schiff base derivatives, containing substituted oximes, were synthesized, characterized in detail and used for complexation with some transition metal salts. The 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 in Figure.



$M(L)_2$

$M = Co^{+2}, Ni^{+2}, Cu^{+2}$ and Zn^{+2}

Figure. Suggested structural formula of the tetrahedral complexes of the ligand.

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