Studies on mononuclear chelates derived from substituted Schiff-base ligands (part 2): synthesis and characterization of a new 5-bromosalicyliden-*p*-aminoacetophenoneoxime and its complexes with Co(II), Ni(II), Cu(II) and Zn(II)

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STUDIES ON MONONUCLEAR CHELATES DERIVED FROM SUBSTITUTED SCHIFF-BASE LIGANDS (PART 2): SYNTHESIS AND CHARACTERIZATION OF A NEW 5-BROMOSALICYLIDEN-*p*-AMINOACETOPHENO- NEOXIME AND ITS COMPLEXES WITH Co(II), Ni(II), Cu(II) AND Zn(II)

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In this study, 5-bromosalicyliden-*p*-aminoacetophenoneoxime (LH) was synthesized starting from *p*-amino-acetophenoneoxime and 5-bromosalicylaldehyde. Complexes of this ligand with Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2} were prepared with a metal : ligand ratio of 1 : 2. Their structures have been elucidated on the basis of elemental analyses, IR, ^1H and ^{13}C NMR spectra, electronic spectra, magnetic susceptibility measurements, molar conductivity and thermogravimetric analyses (TGA).

INTRODUCTION

Numerous Schiff bases [1–3] and their transition metal complexes [4–6] have been investigated by various techniques for different purposes [7]. Schiff-base metal complexes have been widely studied because they have industrial, antifungal and biological applications [8,9]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions [10]. The presence of transition metals in human blood plasma indicates their importance in the mechanism for accumulation, storage and transport of transition metals in living organisms. Transition metals play a key role in biological systems such as cell division, respiration,

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nitrogen fixation and photosynthesis [11]. Also Schiff bases and their complexes in aqueous solutions have been studied because of their interesting and important properties. In this article, 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). As far as we know, this is the first report of this ligand.

EXPERIMENTAL

Measurements

Elemental analyses (C, H, N) were carried out using a CO-932 CHNSO instrument by the Technical and Scientific Research Council of Turkey, TUBITAK. IR spectra were recorded on a Mattson 1000 FT-IR spectrophotometer from 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 calibrant; diamagnetic corrections were calculated from Pascal's constants. The melting points were determined on a Gallenkamp melting point apparatus. Molar conductance 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. Physical characteristics of the complexes are listed in Table I.

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

To a solution of *p*-aminoacetophenoneoxime (1.502 g, 10 mmol) [12] in absolute ethanol (15 cm^3), 5-bromosalicylaldehyde (2.010 g, 10 mmol) and *p*-toluene sulfonic acid (0.01 mg) dissolved in absolute ethanol 35 cm^3 were added dropwise at 60°C with continuous stirring and monitoring of the course of the reaction with IR. The precipitate was filtered, washed with cold ethanol and diethyl ether several times, crystallized from acetone–water and dried at 60°C to constant weight.

TABLE I 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	$C_{15}H_{13}BrN_2O_2$ (333.18)	light yellow	231	82	54.07 (53.69)	3.93 (4.28)	8.41 (8.79)
Co(L)$_2$	$CoC_{30}H_{24}Br_2N_4O_4$ (723.28)	tile red	273[a]	66	49.82 (50.00)	3.34 (2.99)	7.75 (8.14)
Ni(L)$_2$	$NiC_{30}H_{24}Br_2N_4O_4$ (723.04)	dark green	> 300	70	49.83 (49.91)	3.35 (3.7)	7.75 (7.56)
Cu(L)$_2$	$CuC_{30}H_{24}Br_2N_4O_4$ (727.89)	mustard yellow	> 300	71	49.5 (49.22)	3.32 (3.69)	7.7 (8.06)
Zn(L)$_2$	$ZnC_{30}H_{24}Br_2N_4O_4$ (729.73)	cream	207	68	49.38 (48.99)	3.31 (2.98)	7.68 (7.83)

[a]Dec.

Bis(*p*-aminoacetophenoneoxime-5-bromosalicylaldiminato)cobalt(II) Co(L)₂

A solution of Co(AcO)₂ · 4H₂O (0.125 g, 0.50 mmol) in absolute ethanol (15 cm³) was added to a hot (50°C) solution of LH (0.333 g, 1.00 mmol) in absolute ethanol (30 cm³) under an argon atmosphere. The complex was obtained immediately upon addition of the metal salt solution. The precipitated complex was filtered off, washed with water, cold ethanol and cold diethyl ether several times and dried *in vacuo*.

Bis(*p*-aminoacetophenoneoxime-5-bromosalicylaldiminato)nickel(II) Ni(L)₂

Ni(L)₂ was prepared following the same procedure as described for Co(L)₂, starting from LH (0.333 g, 1.00 mmol) and Ni(AcO)₂ · 4H₂O (0.124 g, 0.50 mmol).

Bis(*p*-aminoacetophenoneoxime-5-bromosalicylaldiminato)copper(II) Cu(L)₂

Cu(L)₂ was prepared following the same procedure as described for Co(L)₂, starting from LH (0.333 g, 1.00 mmol) and Cu(AcO)₂ · H₂O (0.100 g, 0.50 mmol).

Bis(*p*-aminoacetophenoneoxime-5-bromosalicylaldiminato)zinc(II) Zn(L)₂

Zn(L)₂ was prepared following the same procedure as described for Co(L)₂, starting from LH (0.333 g, 1.00 mmol) and Zn(AcO)₂ · 2H₂O (0.110 g, 0.50 mmol).

RESULTS AND DISCUSSION

The new ligand, 5-bromosalicyliden-*p*-aminoacetophenoneoxime was synthesized starting from *p*-aminoacetophenoneoxime and 5-bromosalicylaldehyde in absolute ethanol (Scheme 1). The structure of the ligand and the complexes were determined by a combination of elemental analysis, IR, ¹H and ¹³C NMR spectra, electronic spectra, magnetic susceptibility measurements, molar conductivity and thermogravimetric analyses (TGA).

Table II lists the characteristic IR bands of the ligand and its complexes as KBr pellets. The ligand contains four potential donor sites: (1) the phenolic oxygen, (2) the azomethine nitrogen, (3) the oxime oxygen, (4) the oxime nitrogen. In the IR spectrum of the ligand (LH), the O–H (oxime) [13–15], O–H (phenolic), C=N (azomethine), C=N (oxime) [16–18], C–O and N–O stretching vibrations were observed at 3296, 3247, 1617, 1559, 1280 and 1007 cm⁻¹, respectively. These values are in agreement with those reported for similar compounds [19,20]. The azomethine vibration of the
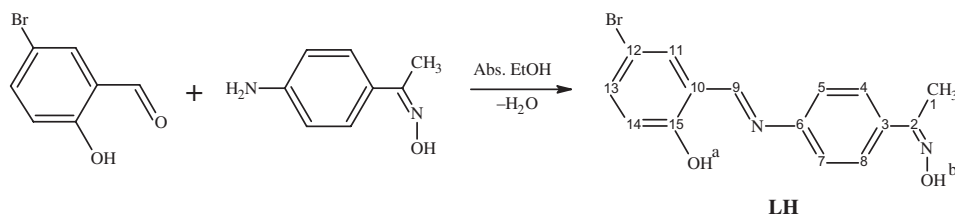
SCHEME 1.

TABLE II   Characteristic IR bands (cm^{-1}) of the ligand and the complexes

Compounds	(O–H) oxime	(O–H) phenolic	(C=N) azomethine	(C=N) oxime	(C–O)	(N–O)
LH	3300–3450	3247	1617	1559	1280	1007
Co(L)$_2$	3300–3450	–	1606	1555	1310	1007
Ni(L)$_2$	3300–3450	–	1610	1558	1323	1007
Cu(L)$_2$	3300–3450	–	1600	1557	1314	1011
Zn(L)$_2$	3300–3450	–	1613	1559	1290	1007

TABLE III ^{1}H and ^{13}C NMR spectral data (ppm) of the ligand and the zinc(II) complex

Compound	^{1}H NMR	^{13}C NMR
LH	2.18 (s, 3H, H$_1$), 6.84 (d, 1H, H$_{11}$), 7.24 (d, 2H, H$_4$ and H$_8$), 7.38 (d, 1H, H$_{13}$), 7.55 (d, 1H, H$_{14}$), 7.67 (d, 2H, H$_5$ and H$_7$), 8.63 (s, 1H, H$_9$), 10.80 (s, 1H, H^b), 13.16 (s, 1H, H^a)	11.33 (C$_1$), 110.02 (C$_{12}$), 114.94 (C$_{14}$), 118.78 (C$_{10}$), 120.36 (C$_5$ and C$_7$), 126.49 (C$_4$ and C$_8$), 134.05 (C$_{11}$), 135.29 (C$_3$), 136.11 (C$_{13}$), 147.37 (C$_2$), 152.58 (C$_6$), 159.74 (C$_9$), 160.95 (C$_{15}$)
Zn(L)$_2$	2.15 (s, 6H, H$_1$), 6.90-7.70 (m, 14H, arom-H), 8.60 (s, 2H, H$_9$), 10.79 (s, 2H, H^b)	11.47 (C$_1$), 109.97 (C$_{12}$), 114.52 (C$_{14}$), 118.57 (C$_{10}$), 120.14 (C$_5$ and C$_7$), 126.37 (C$_4$ and C$_8$), 133.95 (C$_{11}$), 135.13 (C$_3$), 136.00 (C$_{13}$), 147.90 (C$_2$), 154.09 (C$_6$), 161.42 (C$_9$), 164.29 (C$_{15}$)

s: singlet; d: doublet; t = triplet; m: multiplet.

ligand at 1617 cm^{-1} was shifted to lower frequencies after complexation, appearing at 1600, 1610, 1600 and 1613 cm^{-1} for cobalt(II), nickel(II), copper(II) and zinc(II) complexes, respectively. On the other hand, the C–O (phenolic) band at 1280 cm^{-1} in the free ligand was moved to a higher frequency by 10–43 cm^{-1} after complexation, which means that the shifts are due to ligand-to-metal coordination by the azomethine nitrogen and phenolic oxygen [21–23]. The practically unchanged O–H around 3300–3450 and C=N at 1559 cm^{-1} indicate that the oxime group itself does not coordinate to metal atoms through either oxygen or nitrogen.

^{1}H and ^{13}C NMR spectra of the ligand (LH) and the zinc(II) complex were recorded in CDCl$_3$/DMSO-d_6. ^{1}H and ^{13}C NMR assignments are detailed in Table III. Characteristic ^{1}H NMR peaks are at 13.16 (H^a), 10.80 (H^b) [24–26], 8.63 (H$_9$), 7.67–6.84 (arom-H) and 2.18 ppm (H$_1$). The H^a signal at 13.16 ppm disappeared upon addition of D$_2$O 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. C$_{15}$, C$_9$ and C$_6$ carbon atoms are observed at 160.95, 159.74 and 152.58 ppm respectively for LH. The detailed ^{13}C NMR spectral data are given in Table III. No OH peaks are expected in the ^{1}H-NMR spectra of the zinc(II) complex. The absence of the phenolic OH (H^a) proton signal (at 13.16 ppm in the ligand LH) in the zinc(II)

TABLE IV Magnetic moment, molar conductance and electronic spectral data of the ligand and the complexes

Compound	μ_{eff} (BM)	Λ_M $(\Omega^{-1} cm^2 mol^{-1})$	$\lambda_{max} \, \varepsilon (dm^3 mol^{-1} cm^{-1})$		
			d–d	C–T	$n \rightarrow \pi^*$ azomethine
LH	–	3.9	–	–	391 $[2.51 \times 10^3]$
Co(L)$_2$	3.91	5.2	667 (180)	437 $[2.81 \times 10^3]$	380 $[5.21 \times 10^3]$
Ni(L)$_2$	2.87	4.4	632 (160)	426 $[3.30 \times 10^3]$	385 $[2.43 \times 10^3]$
Cu(L)$_2$	1.79	6.3	560 (153)	420 $[1.22 \times 10^3]$	380 $[3.90 \times 10^3]$
Zn(L)$_2$	Dia	8.0	–	418 $[4.51 \times 10^3]$	376 $[2.39 \times 10^3]$

complex indicates coordination by phenolic oxygen to the metal ion after deprotonation [27,28]. Coordination of the azomethine nitrogen (H$_9$) is inferred from an upfield shift of the H$_9$ proton signal from 8.63 ppm in the ligand to 8.60 ppm in the complex [29]. In the ^{13}CNMR spectrum of the zinc(II) complex, C$_{15}$, C$_9$ and C$_6$ carbon atoms are observed at 164.29, 161.42 and 154.09 ppm, respectively. The remaining carbon atoms (Table III) are similar to the free ligand as expected. The signals corresponding to the H^b proton and C$_2$ carbon (both in oxime) groups are unchanged in the ^{1}H and ^{13}C NMR spectra of the complexes, indicating that these oxime groups do not take part in complexation.

The observed molar conductance of the complexes in 10^{-4} M solutions in DMSO lies in the range 4.4–8.0 Ω^{-1} cm^2 mol^{-1} (Table IV), consistent with non-electrolytes [30].

The metal-to-ligand ratio of all the complexes was found to be 1 : 2. While the zinc(II) complex is diamagnetic, the cobalt(II), nickel(II) and copper(II) complexes are paramagnetic, with magnetic susceptibility values 3.91, 2.87 and 1.79 BM, respectively [31,32].

The electronic spectra of the ligand and all the complexes were recorded in DMF at room temperature. The UV spectral data of the Schiff base LH and its complexes are given in Table IV. The aromatic band of the ligand at 255 nm is attributed to benzene $\pi \rightarrow \pi^*$ transition. The band around 391 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 cobalt(II), nickel(II) and copper(II) show less intense shoulders at ca. 560–667 nm ($\varepsilon = 153$–180 dm^3 mol^{-1} cm^{-1}), assigned as d–d transitions 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)$_2$ transitions for tetrahedral geometry. All the complexes show an intense band near 380 nm which is assigned to an n $\rightarrow \pi^*$ transition associated with the azomethine linkage [33]. The spectra of all the complexes show an intense band at ca. 418–437 nm ($\varepsilon = 1.22$– 4.51×10^3 dm^3 mol^{-1} cm^{-1}), which can be assigned to a charge-transfer transition for tetrahedral geometry [34–37].

Thermal behaviors of the ligand and complexes have been investigated using thermogravimetric techniques. Thermal stability data are listed in Table V. The decomposition temperature and weight losses of the complexes were calculated from TGA data. The

TABLE V   TGA data of the ligand and the complexes

Compound	Decomposition temperature (°C) loss (%) calculated (found)		Weight loss (%) calculated (found)	Residue (%) calculated (found)
	First step	Second step		
LH	228–294	294–729		
	24.02 (23.87)	75.98 (75.66)	(99.53)	(0.47)
Co(L)$_2$	257–270	270–718		
	10.79 (11.34)	78.85 (78.69)	89.64 (90.03)	10.36 (9.97)
Ni(L)$_2$	173–292	292–577		
	18.25 (19.30)	71.42 (69.11)	89.67 (88.41)	10.33 (11.59)
Cu(L)$_2$	216–288	288–353		
	18.16 (19.09)	70.91 (69.12)	89.07 (88.21)	10.93 (11.79)
Zn(L)$_2$	135–190	190–577		
	40.08 (39.56)	48.77 (49.04)	88.85 (88.60)	11.15 (11.40)

M(L)$_2$

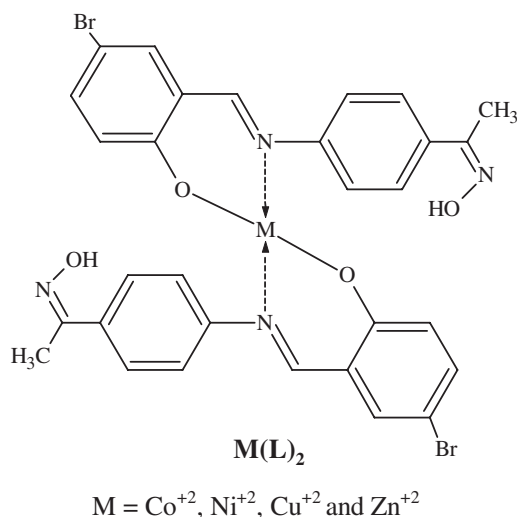M = Co^{+2}, Ni^{+2}, Cu^{+2} and Zn^{+2}

FIGURE I   Suggested structural formula of the tetrahedral complexes of the ligand

ligand is stable up to 228°C where its decomposition starts and is completed at 729°C. As can be seen in the TGA data (Table V) all the complexes and the ligand decompose in two steps at different temperature ranges. All complexes undergo complete decomposition to the corresponding metal oxides, CoO, NiO, CuO and ZnO [38,39].

Our group has been heavily engaged in 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 effects of functional groups, such as oxime, on the complexes have no effect. These functional groups are very far from the pendants taking part in the complexation. For these complexes, additional analytical data are given in Tables I–V. According to results obtained the geometries of all the complexes are tetrahedral. The suggested structures of the complexes are shown in Figure I.

Acknowledgments

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