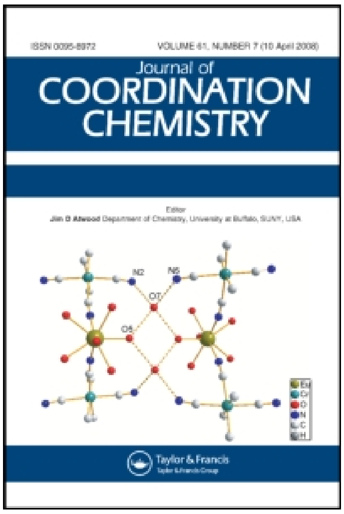

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Studies on mononuclear chelates derived from substituted Schiff-base ligands (part 6): synthesis and characterization of a new 3-ethoxysalicyliden-*p*-aminoacetophenoneoxime and its complexes with cobalt(II), nickel(II), copper(II) and zinc(II)

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Schiff-base complexes of cobalt(II), nickel(II), copper(II) and, zinc(II) with 3-ethoxysalicyliden-*p*-aminoacetophenoneoxime (HL) were prepared and characterized on the basis of elemental analyses, IR, ^{1}H- and ^{13}C-NMR, electronic spectra, magnetic susceptibility measurements, molar conductivity and thermogravimetric analyses (TGA). A tetrahedral geometry has been assigned to the complexes.

Keywords: Schiff bases; Cobalt(II); Nickel(II); Copper(II); Zinc(II) complexes

1. Introduction

Among the variety of ligand systems [1–5], Schiff bases are an important class having many applications [6] and many complexes of different Schiff bases have been reported by a number of authors [7, 8]. Schiff-base complexes have a wide variety of structures, coordinating to metal in either mono- or bidentate modes, depending upon the aldehyde and amines [9]. Unsymmetrical Schiff-base ligand complexes have been suggested as useful biological models in understanding irregular binding of peptides [10] and also as catalysts in some chemical processes [11]. 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 [12]. In the present 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) ions.

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2. Experimental

Elemental analyses (C, H, N) were carried out using LECO-932 CHNSO by the Technical and Scientific Research Council of Turkey, TUBITAK. 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 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. TGA curves were recorded on a Shimadzu TG-50 thermo balance.

2.1. *3-Ethoxysalicyliden-*p*-aminoacetophenoneoxime (LH)*

To a solution of (1.502 g, 10 mmol) *p*-aminoacetophenoneoxime [13] in 15 mL absolute EtOH, 3-ethoxysalicylaldehyde (1.662 g, 10 mmol) and (0.01 mg) *p*-toluene sulfonic acid dissolved in 20 mL absolute EtOH was 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 EtOH and Et_2O several times and crystallized from acetone–water and dried at 60°C to constant weight.

2.2. Bis*(*p*-aminoacetophenoneoxime-3-ethoxysalicylaldiminato)cobalt(II) CoL$_2$*

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 HL (0.298 g, 1.00 mmol) in absolute EtOH (20 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*.

2.3. Bis*(*p*-aminoacetophenoneoxime-3-ethoxysalicylaldiminato)nickel(II) NiL$_2$*

NiL_2 was prepared following the same procedure as described for $Co(L)_2$, starting from HL (0.298 g, 1.00 mmol) and $Ni(AcO)_2 \cdot 4H_2O$ (0.124 g, 0.50 mmol).

2.4. Bis*(*p*-aminoacetophenoneoxime-3-ethoxysalicylaldiminato)copper(II) CuL$_2$*

CuL_2 was prepared following the same procedure as described for $Co(L)_2$, starting from HL (0.298 g, 1.00 mmol) and $Cu(AcO)_2 \cdot H_2O$ (0.100 g, 0.50 mmol).

2.5. Bis*(*p*-aminoacetophenoneoxime-3-ethoxysalicylaldiminato)zinc(II) ZnL$_2$*

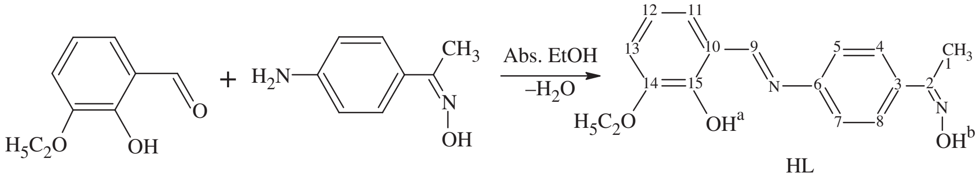
ZnL_2 was prepared following the same procedure as described for $Co(L)_2$, starting from HL (0.298 g, 1.00 mmol) and $Zn(AcO)_2 \cdot 2H_2O$ (0.110 g, 0.50 mmol).

3. Results and discussion

The ligand (LH) was prepared by reacting equimolar amounts of 3-ethoxysalicylaldehyde with *p*-aminoacetophenoneoxime in absolute ethanol (scheme 1). Structures of the ligand and complexes were established with the use of IR, ^{1}H- and ^{13}C-NMR spectra, elemental analyses, UV, magnetic susceptibility measurements and thermogravimetric analyses (tables 1–5).

Reactions of the Schiff-base ligand with the corresponding metal salt may be represented by the follows:

$$2HL + Co(CH_3COO)_2 \cdot 4H_2O \rightarrow CoL_2 + 2CH_3COOH + 4H_2O$$
$$2HL + Ni(CH_3COO)_2 \cdot 4H_2O \rightarrow NiL_2 + 2CH_3COOH + 4H_2O$$
$$2HL + Cu(CH_3COO)_2 \cdot H_2O \rightarrow CuL_2 + 2CH_3COOH + H_2O$$
$$2HL + Zn(CH_3COO)_2 \cdot 2H_2O \rightarrow ZnL_2 + 2CH_3COOH + 2H_2O$$



Scheme 1. Structure of the ligand.

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

Compounds	Formula (Fw) g mol^{-1}	Color	M.p. (°C)	Yield (%)	Elemental analysis Calculated (found) (%) C	H	N
HL	$C_{17}H_{18}N_2O_3$ (298.34)	Dark orange	152	77	68.44 (68.07)	6.08 (5.72)	9.39 (8.99)
CoL_2	$CoC_{34}H_{34}N_4O_6$ (653.59)	Light red	145	64	62.48 (62.81)	5.24 (4.87)	8.57 (8.90)
NiL_2	$NiC_{34}H_{34}N_4O_6$ (653.35)	Light green	247	61	62.50 (62.79)	5.25 (4.95)	8.58 (8.86)
CuL_2	$CuC_{34}H_{34}N_4O_6$ (658.20)	Dark green	>300	68	62.04 (61.72)	5.21 (5.60)	8.51 (8.32)
ZnL_2	$ZnC_{34}H_{34}N_4O_6$ (660.05)	Dark yellow	>300	62	61.87 (62.20)	5.19 (4.81)	8.49 (8.18)

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

Compounds	ν(O–H) oxime	ν(O–H) phenolic	ν(C=N) azomethine	ν(C=N) oxime	ν(C–O)	ν(N–O)
HL	3430s	3238s	1617vs	1594s	1257s	1004w
CoL_2	3427s	–	1610vs	1594s	1272m	1004w
NiL_2	3429s	–	1609vs	1594s	1275m	1007w
CuL_2	3430s	–	1610vs	1594s	1267m	1011w
ZnL_2	3430s	–	1605vs	1590s	1270m	1007w

Note: m, medium; s, strong; vs, very strong; w, weak.

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

Compounds		
HL	1.36(s, 3H, H_1), 2.15(t, 3H, H_{17}), 4.04(d, 2H, H_{16}), 6.79–7.65(m, 7H, Ar–H), 8.69(s, 1H, H_9), 10.88(s, 1H, H^b), 13.50(s, 1H, H^a)	10.85(–CH_3), 14.16 and 63.72(–OC_2H_5), 115.97–135.29(Ar–C), 118.42(*C–CH=N), 146.64(C=NOH), 147.03(C–O–C_2H_5), 150.75(C–OH), 152.04(CH=N–C*), 162.09(CH=N)
ZnL_2	1.38(s, 6H, H_1), 2.13(t, 6H, H_{17}), 4.06(d, 4H, H_{16}), 6.94–7.64(m, 14H, Ar–H), 8.55(s, 2H, H_9), 10.90(s, 2H, H^b)	11.02(–CH_3), 14.47 and 63.98(–OC_2H_5), 116.06–135.55(Ar–C), (*C–CH=N), 146.26(C=NOH), 147.03(C–O–C_2H_5), 152.13(C–OH), 153.21(CH=N–C*), 165.32(CH=N)

s: singlet, d: dublet, t = triplet, m: multiplet.

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

			λ_{max}, nm (ε, L mol^{-1} cm^{-1})		
Compounds	μ_{eff}, μ_B	Λ_M (Ω^{-1} cm^2 mol^{-1})	d–d	C–T	$n \rightarrow \pi^*$ azomethine
HL	–	1.9	–	–	378(2.06×10^3)
CoL_2	4.18	3.4	660(191)	431(2.07×10^3)	370(3.95×10^3)
NiL_2	2.99	2.7	620(162)	417(2.80×10^3)	362(1.50×10^3)
CuL_2	1.87	3.6	553(160)	425(2.27×10^3)	384($2.83 \times 10^{3)}$
ZnL_2	Dia	4.0	–	419(3.00×10^3)	387(2.50×10^3)

Table 5. TGA data of the complexes.

	Decomposition temperature (%) Calculated (found)			
Compounds	First step	Second step	Weight loss (%) Calculated (found)	Residue (%) Calculated (found)
CoL_2	155–258 20.20(21.79)	258–493 68.34(66.17)	88.54(87.96)	11.46(12.04)
NiL_2	211–282 20.21(19.24)	282–482 68.36(68.65)	88.57(87.89)	11.43(12.11)
CuL_2	197–261 11.85(12.39)	261–394 76.07(74.49)	87.92(86.88)	12.08(13.12)
ZnL_2	144–187 20.00(21.63)	187–463 67.67(66.58)	87.67(88.21)	12.33(11.79)

The analytical and physical data given in table 1 for the ligand and its complexes are in good agreement with the formulae proposed.

The characteristic infrared frequencies (as KBr pellets) for all the complexes and the ligand listed are given in table 2. The ligand contains four potential donor sites: (1) the phenolic oxygen, (2) the azomethine nitrogen, (3) the oxime oxygen, and (4) the oxime nitrogen. The O–H (phenolic) absorption observed at 3238 cm^{-1} in the free Schiff base is absent in the complexes, indicating deprotonation occurs prior to the coordination through the oxygen atom. A strong band was observed at 1617 cm^{-1} in the free ligand, characteristic of the C=N (azomethine) group. It is expected that coordination of the nitrogen to the metal would reduce the electron density in the azomethine link and thus, lower the C=N stretching frequency. In the complexes the frequency was observed in the region 1605–1610 cm^{-1}, indicating coordination of the Schiff base through the azomethine nitrogen [13–17]. The practically unchanged O–H (oxime) [18–20] at 3430 and C=N (oxime) [21–23] at 1594 cm^{-1} of the oxime group confirm that the oxime group itself does not coordinate to metal by oxygen or nitrogen [24].

The ^{1}H- and ^{13}C-NMR spectra of the ligand and its zinc(II) complex were recorded in a mixture of $CDCl_3$ and DMSO-d_6; data are given in table 3. The H^a signal at 13.50 ppm disappeared upon addition of D_2O to the solution, indicating that it is an acidic proton [25]. More detailed information about the structure of ligand was provided by ^{13}C-NMR spectral data. C_{15}, C_9 and C_6 carbon atoms are observed at 150.75, 162.09 and 152.04 ppm, respectively, for HL. The ^{1}H-NMR spectra of the zinc(II) complex shows no OH peaks, indicating coordination by phenolic oxygen to the metal ion after deprotonation [26]. The coordination of the azomethine nitrogen (H_9) is inferred by upfield shift of H_9 from 8.69 ppm in the ligand to 8.55 ppm in the complex [27]. In the ^{13}C-NMR spectrum of the zinc(II) complex C_{15}, C_9 and C_6 carbon atoms are observed at 152.13, 165.32 and 153.21 ppm, respectively. The rest of the carbon atoms showed similar features for the free ligand and complex. The signals of H^b and C_2 carbon (both in oxime) [28] 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.

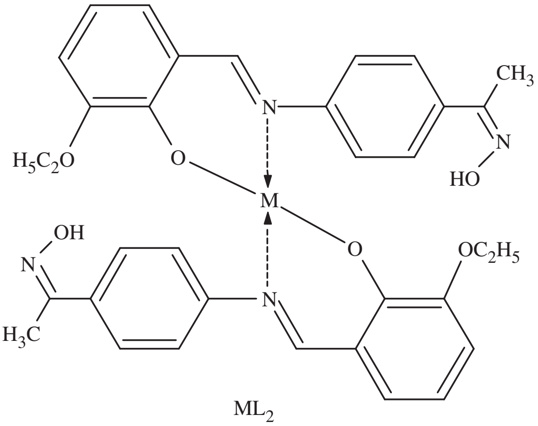
The characteristic properties of the complexes and the Schiff base are shown in table 1. The elemental analysis results agree with the calculated values showing 1 : 2 metal/ligand ratios.

The electronic spectra of the ligand and all 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 265 nm is attributed to benzene $\pi \rightarrow \pi^*$ transition. The band around 378 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. Complexes of cobalt(II), nickel(II) and copper(II) show less intense shoulders at ca 553–660 nm ($\varepsilon = 160$–$191\ \mathrm{L\,mol^{-1}\,cm^{-1}}$), assigned as d–d transitions of the metal ions, due to the $^4A_2 \rightarrow {}^4T_1$ (P) for CoL_2, $^3A_2 \rightarrow {}^3T_2$ (F) for NiL_2 and $^2T_2 \rightarrow {}^2E$ (G) for CuL_2 transitions of tetrahedral geometry. All the complexes show an intense band at ca 362–387 nm ($\varepsilon = 1.50$–$3.95 \times 10^3\ \mathrm{L\,mol^{-1}\,cm^{-1}}$) assigned to the $n \rightarrow \pi^*$ transition associated with azomethine [29, 30]. The spectra of all the complexes show an intense band at ca 417–431 nm ($\varepsilon = 2.07$–$3.00 \times 10^3\ \mathrm{L\,mol^{-1}\,cm^{-1}}$), which can be assigned to charge transfer (C–T) transition of tetrahedral geometry [31–33].

The magnetic moments for complexes have been measured at room temperature using a vibrating magnetometer with diamagnetic corrections applied. Effective magnetic moments of the complexes are shown in table 4. The cobalt(II), nickel(II) and copper(II) complexes are paramagnetic with magnetic moments of 4.18, 2.99 and 1.87 BM, respectively. The zinc(II) complex is diamagnetic [34].

The molar conductance of freshly prepared solutions of the complexes in 10^{-4} M DMSO solutions are observed in the range 2.7–4.0 ($\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$) (table 4) indicating non-electrolytes [35] in table 4.

The thermal behavior of the ligand and complexes has been investigated using thermogravimetric techniques. The thermogravimetric (TG), curves for the complexes were obtained at a heating rate of 10°C min^{-1} in 30 mL min^{-1} flowing nitrogen over a temperature range of 20–800°C. Approximately 10 mg samples of the complexes were



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

Figure 1. Suggested structure of the tetrahedral complexes.

used in each case. Thermal stability data are listed in table 5. The decomposition temperature and the weight losses were calculated from TGA data. The ligand is stable up to 185°C and its decomposition starts at 185°C and is completed at 597°C. All the complexes and the ligand decompose in two steps at different temperature ranges. Thermogravimetric studies of all the complexes showed no weight loss up to 144°C, indicating absence of water in the complexes. In all cases the final products are the metal oxides [36, 37]. In addition, the thermal stability of the complexes increases in the order: $Cu < Zn < Ni < Co$.

4. Conclusion

Our research group has been heavily engaged in the synthesis of novel substituted oximes and their Schiff-base derivatives; many Schiff-base derivatives containing substituted oxime, have been synthesized, characterized and used for complexation of transition metals. Functional groups, such as oxime are very far from the pendants taking part in complexation and have no effect on the complexes. TGA and elemental analyses indicate no lattice/coordinated water molecules in the complexes. For these complexes, analytical and physical data in tables 1–5 suggest the complexes are tetrahedral. The suggested modes of coordination are shown in figure 1. All complexes are soluble in DMSO and DMF.

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