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Synthesis, Characterization and Thermal Studies of a New Imine-oxime Ligand and its Cu^{2+}, Ni^{2+}, Co^{3+} and Zn^{2+} Complexes

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(2E)-3-Aza-1-(hydroxyimino)-2,4-diphenylpent-2-ene (HL) was synthesized by the reaction of isonitrosoacetophenone with 1-phenyl-1-aminoethane in 1:1 molar ratio. The ligand was characterized by using IR, ^{1}H NMR, ^{13}C NMR, UV-vis spectra, elemental analysis, thermal analysis and mass spectroscopy. Ni(II), Cu(II), Co(III) and Zn(II) complexes of this ligand were synthesized and their structures were identified using AAS, IR, electronic spectra, thermal analysis, mass spectroscopy, elemental analyses, conductance and magnetic moment measurements. In the process of obtaining Co(III) complex, when the cobalt(II) chloride solution was added into the alcoholic solution of the ligand gave orange colored complex by air oxidation and this complex was seen polymeric and diamagnetic in nature.

Key Words: Imine-oxime, Schiff bases, Diamagnetic Co(III) complex.

INTRODUCTION

Schiff base ligands have been in the chemistry catalogue for over 150 years[1]. Their instant and enduring popularity undoubtedly stem from the ease with which they can be synthesized, their bewildering versatility and their wide ranging complexing ability once formed. The literature clearly shows that the study of this diverse ligand system is linked with many of the key advances made in inorganic chemistry. Not only they have played a seminal role in the development of modern coordination chemistry[2], but they can also be found at key points in the development of inorganic biochemistry[3], catalysis[4,5] and optical materials[6]. Although the magnetic, spectroscopic and catalytic properties of these Schiff base complexes are well documented[7], it still seems there could be new and specific applications for such a unique class of compounds.

Chiral Schiff bases are interesting ligands, because the π-system in a Schiff base imposes a geometrical constrant and also affects the electronic structure. This situation has given rise catalytic properties to the transition metal Schiff base complexes in oxidizing hydrocarbons[8] or reducing organic halides[9].

Considerable number of Schiff base complexes have potential biological interest, being used as more or less successful models of biological compounds[10]. Detection of essential transition metal ions, especially zinc, is of relevance in biochemistry, clinical diagnostics as well as in environmental pollution[11-15].

In this study, a new imine-oxime ligand (HL) and its mononuclear complexes with Co(III), Ni(II), Cu(II) and Zn(II) ions were synthesized and characterized by elemental analysis, thermal analysis, IR, ^{1}H NMR, electronic spectra, mass spectra, conductivity and magnetic susceptibility measurements at room temperature.

EXPERIMENTAL

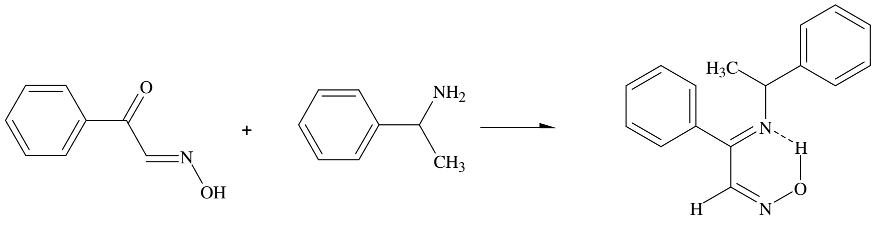
All the solvents, acetophenone, 1-phenyl-1-aminoethane, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ were reagent grade and used without further purification. Acetophenoneoxime and isonitrosoacetophenone were synthesized according to literature procedures[16,17].

IR spectra (4000-400 cm^{-1}) were recorded on a Thermo Nicolet 6700 FT-IR spectrometer using the KBr pellet technique. ^{1}H NMR spectra of the ligand and its Co(III) and Zn(II) complexes in DMSO-d_6 were recorded on a Varian mercury plus 400 MHz spectrometer at room temperature using TMS as internal standard. The TG-DTA measurements were obtained using a TA instruments SDT Q600 thermal analyzer in dry nitrogen atmosphere within the temparature range of 25-1000 °C. The heating rate was 10 ºC/min and sample weights ranged from 5 to 10 mg. Electronic spectra were obtained on a Shimadzu UV 2100 spectrophotometer. Mass spectrum and elemental analyses of the ligand and its metal complexes were obtained at the laboratories of scientific and technological research council of Turkey (TUBITAK). Metal contents in complexes were measured on a Ati-unicam 929 AAS spectrometer. Magnetic properties were determined by a Sherwood scientific MK1 model gouy magnetic susceptibility balance. Molar conductivity of 10^{-3} M solutions of the complexes in methanol were measured on the WTW model inoLab 730 conductivity meter. Melting points were measured on a Buchi melting point B-540 digital melting point apparatus without being corrected.

Preparation of the imine-oxime ligand (HL): A solution of 1-phenyl-1-aminoethane (10 mmol amine in 20 mL ethanol) was added dropwise to a solution of 10 mmol isonitrosoacetophenone in 20 mL ethanol for 20 min at room temperature. After the reaction mixture had been stirred for 3 h at the same temperature, the solution was left overnight at 0 °C. The crystallized product (2E)-3-aza-1-(hydroxyimino)-2,4-diphenylpent-2-ene (HL) was filtred, washed with diethyl ether and dried in air. Yield: 1.53 g, (60.7 %). MS: (ESI) m/z = 252 (100), 148 (60), 104 (10).

(2E)-3-Aza-1-(hydroxyimino)-2,4-diphenylpent-2-ene (HL) is soluble in acetone, THF, DMSO, DMF, dioxane and pyridine and is slightly soluble in $CHCl_3$, EtOH and MeOH. The synthesis scheme is given in Fig. 1. The chemical analysis of the ligand and its melting point are shown in Table-1.

Preparation of the metal complexes: Solutions of $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ (1 mmol) in 20 mL ethanol were added to a solution of the ligand (1, 1, 2, 1 mmol, respectively) in 30 mL ethanol and the solutions were continuously stirred for 3 h, during which the metal complexes precipitated. The resulting precipitates were filtered, washed with cold ethanol then diethyl ether and



(HL)

Fig. 1. Preparation of the imine-oxime ligand

TABLE-1
ANALYTICAL AND PHYSICAL DATA FOR THE LIGAND AND ITS METAL COMPLEXES

Compound	Color	m.p. (°C)	Yield (%)	Formula weight (g mol^{-1})	Elemental analyses (%): Found (calcd.)			
					C	H	N	M
HL	White	136	60.7	252	75.88 (76.19)	6.13 (6.35)	11.06 (11.11)	–
$Ni(HL)Cl_2.2H_2O$	Light brown	> 300*	84.7	418	46.07 (45.93)	4.52 (4.78)	6.71 (6.70)	13.88 (14.11)
$[Co(L)_2Cl\ 0.5H_2O]_n$	Orange	193*	79.8	606	63.70 (63.37)	4.95 (5.11)	9.32 (9.24)	8.98 (9.74)
$CuLClH_2O$	Green	120.7*	61.7	368	52.14 (52.17)	4.49 (4.62)	7.54 (7.61)	18.12 (17.26)
$Zn(HL)Cl_2$	Pale yellow	135*	72.7	389	49.65 (49.42)	4.06 (4.12)	7.08 (7.21)	16.49 (16.86)

*Decomposition point.

dried in air. MS: (ESI) m/z = for Ni(II) complex: 417 (35), 356 (25), 341 (20), 122 (100), 104 (70); for Co(III) complex: 606 (20), 436 (45), 311 (75), 284 (100); for Cu(II) complex: 366 (15), 338 (65), 284 (100); for Zn(II) complex: 391 (25), 372 (10), 348 (20), 319 (100).

The complexes are air stable in the solid state and soluble in EtOH, MeOH, DMF and DMSO and insoluble in H_2O, CCl_4 and diethyl ether.

RESULTS AND DISCUSSION

The reactions of the HL ligand with different metal ions produced a new series of metal complexes, M = Co(III), Ni(II), Cu(II) and Zn(II). In the process of obtaining Co(III) complex, the addition of cobalt(II) chloride solution prepared in ethanol to an alcoholic solution of the ligand gave orange colored complex by air oxidation[18]. The analytical and physical data of the metal complexes are given in Table-1.

Characterization of the ligand, HL: The mass (ESI) of ligand exhibited the molecular ion at m/z 252 $[M]^+$, which indicates formation of the HL ligand (Fig. 1).

IR spectrum of the ligand showed a medium band at 3244 cm^{-1} due to the stretching vibrations of oxime's hydroxyl group. This band proves that the HL ligand has intramoleculer hydrogen bonding (Fig. 1). The strong bands observed at 1612 and 1597 cm^{-1} were assigned to the stretching vibrations of the azomethine groups (Table-2). The band observed at 988 cm^{-1} was attributed to the oxime ν(N-O) stretching vibration[19].

TABLE-2
CHARACTERIZATION BANDS (cm^{-1}) OF THE INFRARED SPECTRA OF LIGAND (HL) AND ITS METAL COMPLEXES

Compounds	ν(NH_2)	ν(OH)	ν(OH_2)	ν$(CH)_{arom.}$	ν$(CH)_{aliph.}$	ν(C=O)	ν(C=N)	ν(NO)
Isonitroso-acetophenone	–	3272 br	–	3011 m	2894 m	1678s	1599 s	985 s
1-Phenyl-1-aminoethane	3365s, 3289m	–	–	3027 w	2925 w	–	–	–
HL	–	3244 s, br	–	3026 w	2973 w	–	1612 s 1597 s	998 s
$NiHLCl_2.2H_2O$	–	3542 br	3401 br	3056 w	2917 w	–	1597 s 1565 m	1000 m
$[Co(L)_2Cl.0.5H_2O]_n$	–	–	3452 br	3048 w	2921 w	–	1598 m 1542 m	1063 m
$CuLCl.H_2O$	–	–	3411 br	3059 m	2933 w	–	1594 s 1565 s	1049 w
$ZnHLCl_2$	–	3539 br	–	3055 w	2925 w	–	1611 m 1597 s	999 m

^1H NMR spectra of the imine-oximes exhibit a singlet peak for the OH proton of the oxime groups at 9.84-13.3 ppm[20,21]. But surprisingly, this proton wasn't observed in HL ligand in this study. The aromatic C-H protons of ligand were observed at 7.08-7.62 ppm, aliphatic C-H proton 4.59 ppm, aldehyde proton 8.03 ppm and CH_3 protons at 1.44 ppm. These values are in good agreement with those of known oximes[20,21] (Table-3).

TABLE-3
^1H NMR DATA OF AMINE, HL AND ITS Co(III) AND Zn(II) COMPLEXES

Compounds	O-H	$C-H_{alde.}$	$C-H_{arom.}$	$C-H_{aliph.}$	CH_3	N-H
1-phenyl-1-aminoethane	–	–	7.08-7.12 (m, 5H)	4.08 (m, 1H)	1.38 (d,3H)	2.00 (s, 2H)
HL	Not observed	8.03 (s, 1H)	7.08-7.62 (m, 10H)	4.59 (m, 1H)	1.44 (d,3H)	–
$[Co(L)_2Cl0.5H_2O]_n$	–	8.39 (s, 2H)	7.10-7.79 (m, 20H)	5.05 (m, 2H)	1.90 (d,6H)	–
$ZnHLCl_2$	11.78 (s, 1H)	8.03 (s, 1H)	7.10-7.66 (m, 10H)	4.69 (m, 1H)	1.34 (d,3H)	–

^{13}C NMR spectra of the HL ligand and 1-phenyl-1-aminoethane are presented in Table-4. In the ^{13}C NMR spectrum of ligand, the signals of the carbon atoms of azomethine groups appear at 162.8 and 149.0 ppm[22]. The peak which wasn't observed in isonitrosoacetophenone was seen to have resulted from the carbon atom of azomethine group at 162.8 ppm. The signals of the $C_{aromatic}$ carbon were observed at 140.7, 139.8, 131.1, 129.2, 128.9, 128.7, 127.8 and 126.0 ppm for HL, as 8 peaks[23]. The signals of C-H and CH_3 were seen at 57.1 and 24.6 ppm, respectively[24].

TABLE-4
^{13}C NMR SPECTRA OF AMINE AND LIGAND (HL) IN DMSO-d_6

Groups	^{13}C NMR spectra of amine and ligand	
	HL	1-Phenyl-1-aminoethane
R$\underline{C}$=NR'	162.8	–
H-$\underline{C}$=NOH	149.0	–
Ph($\underline{C}$-H)	126.0-140.7	126.8-143.5
$\underline{C}$-H	57.1	51.3
$\underline{C}H_3$	24.6	24.3

As a result, on the basis of IR, ^{1}H NMR, ^{13}C NMR, elemental analysis and mass spectroscopy, the structure of HL ligand was confirmed as shown in Fig. 1.

Characterization of the complexes

Infrared spectroscopy: The characteristic bands of the infrared spectra of HL and the transition metal complexes are listed in Table-2. The structure of HL and its metal complexes are shown in Figs. 2-5. The IR spectra of Co(III), Ni(II) and Cu(II) complexes exhibited a broad band ranging from 3455 to 3200 cm^{-1} assigned to ν(OH) of water molecules associated with the complex, which was also confirmed by elemental analyses. The IR spectra of the complexes showed a shift of the ν(C=N) band towards lower wave numbers of 1598-1542 cm^{-1} compared with the free ligand band at 1612-1597 cm^{-1}, except the Zn(II) complex, which showed bands at the same wave numbers as those of the HL ligand. This shift indicates coordination of the two azomethine groups to the metal ions[25]. The OH stretching vibration of the oxime was observed at 3542 and 3539 cm^{-1} in the Ni(II) and Zn(II) complexes, respectively (Figs. 2 and 4). This indicates that Ni(II) and Zn(II) complexes have a free OH group, while the ligand has intramoleculer hydrogen bonding. In the IR spectra, bands 3026-3059 and 2917-2973 cm^{-1} region belong to $CH_{(arom.)}$ and $CH_{(aliph.)}$ stretching vibration, respectively. The band observed at 998 cm^{-1} in the ligand is associated to the ν(N-O) stretching band. All complexes show a weak and sharp ν(N-O) stretching band centered in the 1063-999 cm^{-1} range. In the Cu(II) and Co(III) complexes (Figs. 3 and 5), N-O$^-$ bond is formed, which is clearly confirmed by the fact that ν(N-O) band is shifted to higher frequencies after the complex be formed (the negative charge is balanced by the positive charge on the copper and cobalt ions). The IR data of complexes are in good aggrement with those of similar compounds[19,26-28].

^{1}H NMR Spectra data of Zn(II) and Co(III) complexes: ^{1}H NMR spectra of the Zn(II) complex exhibited a singlet peak of the OH proton of the oxime group at

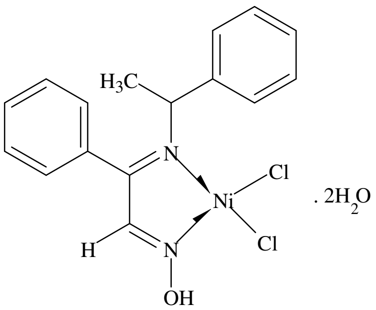


Fig. 2. Proposed structure of the Ni(II) complex

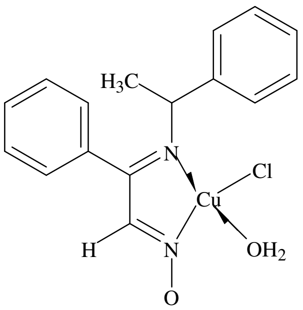


Fig. 3. Proposed structure of the Cu(II) complex

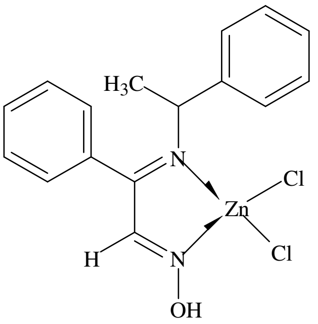


Fig. 4. Proposed structure of the Zn(II) complex

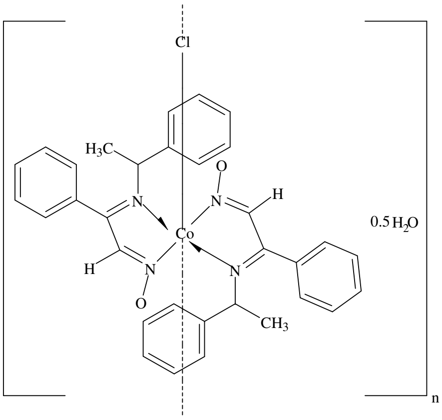


Fig. 5. Proposed structure of the Co(III) complex

11.78 ppm. This indicates that Zn(II) complex has a free OH group. The proton signal of -NOH group was absent in the Co(III) complex and thus provides solid evidence for the deprotonation of oxime group. Aromatic C-H protons of the complexes at 7.08-7.62 and 7.10-7.79 ppm, aliphatic C-H protons at 4.69 and 5.05 ppm, aldehyde protons at 8.03 and 8.39 ppm and CH_3 protons at 1.34 and 1.90 ppm were observed in Zn(II) and Co(III) complexes, respectively[21].

Electronic spectra: The electronic spectra of HL ligand and its transition metal complexes were measured in methanol at room temperature (Table-5). The UV-visible peak corres-ponding to the π–π* transition in the phenyl group of HL ligand were observed at 207 and 231 nm[29]. All the complexes demonstrated intense bands between 200 and 204 nm and between 223 and 255 nm assigned to the π–π* transitions associated with phenyl group[30]. Complexes of Ni(II), Co(III) and Cu(II) revealed less intense shoulder at 590, 472 and 667 nm assigned to *d-d* transitions of the metal ions, respectively. The spectra of all the complexes showed intense band between 335 and 350 nm, which could be associated with metal to ligand charge transfer transitions.

TABLE-5
MAGNETIC MOMENT, MOLAR CONDUCTANCE AND ELECTRONIC SPECTRAL DATA OF LIGAND AND ITS METAL COMPLEXES

Compounds	μ_{eff}	Λ_M (Ω^{-1} cm^2 mol^{-1})	λ_{max}, nm (ε, 10^4 L mol^{-1} cm^{-1})		
			C-T	*d-d*	$\pi \rightarrow \pi^*$ Phenyl group
HL	–	–	–	–	207(1.54), 231(1.27)
$NiHLCl_2.2H_2O$	2.73	6.5	334 (1.55)	590 (0.01)	201(2.39), 225(1.17)
$[Co(L)_2Cl.0.5H_2O]_n$	Dia	7.5	345 (1.84)	472 (0.014)	204(5.55), 255(2.70)
$CuLCl.H_2O$	1.68	5.9	337 (2.00)	667 (0.036)	201(1.64), 224(1.27)
$ZnHLCl_2$	Dia	0.4	–	–	203(0.73), 241(0.48)

Elemental analyses, mass spectra, magnetic moment studies, molar conductivity, thermal analyses and test of silver chloride: When the elemental analyses of the complexes were investigated, metal-ligand ratios were found to be 1:1 in the Ni(II), Cu(II) and Zn(II) complexes and 1:2 in the Co(III) complex of HL ligand.

The molecular ion peak in mass spectra appeared at (m/z, ESI) 417 $[M-1]^+$ for the Ni(II) complex, at 606 $[M]^+$ for the Co(III) complex, at 366 $[M-2]^+$ for the Cu(II) complex and at 391 $[M+2]^+$ for the Zn(II) complex, indicating the formation of the complexes.

In addition, the analyses of chlorine by the Mohr method were performed for the complexes. There are two chlorine ions bonded to the Ni(II) and Zn(II) complexes, on the other hand there is only one chlorine ion bonded with the coordination sphere of the Cu(II) and Co(III) complexes[31]. This has been supported by the elemental analyses data given in Table-1.

The magnetic moment of the Cu(II) complex was measured 1.68 BM, which fits the spin-only value, 1.73 BM in Cu(II) complex and the magnetic moment of the Ni(II) complex was observed 2.73, which indicates the presence of two unpaired electrons per the Ni(II) ion. On the other hand the magnetic moment of Co(III) complex was measured to be 0.29 BM, but that observed moment is regarded to be low enough to enable us to assume that the complex is diamagnetic, low-spin cobalt(III) complex[32]. The Zn(II) complex is diamagnetic.

The observed molar conductances of the complexes in 10^{-3} molar solutions in methanol were seen to be in the range 0.4-7.5 Ohm^{-1} cm^2 mol^{-1}. This is consistent with the non electrolytic nature of these complexes.

The thermal behaviour of the ligand and all the metal complexes was investigated using thermogravimetric techniques. The thermal analysis curves of the metal complexes were recorded in the temperature range of 20-1000 °C. The thermal behaviour of HL and the metal complexes are listed in Table-6. The Ni(II) complex showed two inflections, due to the presence of two hydrated water molecules, in the DTG curve at 71-151 °C and 1.52 % mass lost was seen in the Co(III) complex due to the half hydrate water molecule. The Cu(II) complex revealed a inflection, due to the presence of one coordinate water molecule in the DTG curve at 88 and 158 °C[33-35]. The Ni(II), Co(III) and Zn(II) complexes undergo complete decomposition

TABLE-6
TGA DATA OF THE LIGAND AND ITS METAL COMPLEXES

Compounds	Stage	Temp. range (°C)	DTG_{max} ^{a} (°C)	Rem. group	Mass loss (%) Found	Calcd.	Total mass loss (%) found	Calcd.	Solid decomp. product
HL	1	108-195	136 (–)	–	–	–	98.16	100	–
	2	196-590	325 (–)	–	–	–			
$NiHLCl_2.2H_2O$	1	67-176	151 (+)	$2H_2O$	8.13	8.61	82.98	83.09	NiO
	2	177-286	260 (+)	–	–	–			
	3	287-344	310 (+)	–	–	–			
	4	345-921	391 (–)	–	–	–			
$[Co(L)_2Cl0.5H_2O]_n$	1	68-163	147 (+)	$0.5H_2O$	1.52	1.49	88.15	87.63	CoO
	2	164-320	193 (–)	–	–	–			
	3	321-827	394 (–)	–	–	–			
$CuLCl.H_2O$	1	88-158	132 (+)	H_2O	4.52	4.89	83.10	82.75	Cu
	2	159-261	233 (–)	–	–	–			
	3	262-958	321 (–)	–	–	–			
$ZnHLCl_2$	1	87-321	168 (–)	–	–	–	80.10	79.15	ZnO
	2	322-931	413 (–)	–	–	–			

^{a}(+) Endothermic, (–) Exothermic.

to the corresponding metal oxides, NiO, CoO[36] and ZnO but the Cu(II) complex's final product is Cu^0 [37].

The 1-phenyl-1-aminoethane, used synthesis of the ligand, has a chiral carbon atom. But synthesized ligand isn't optical active. So the ligand was seen as a racemic compound. The chirality studies of complexes were done wheather the metal salt was enantioselective about HL ligand. But as well this studies were negative.

In an attempt to obtain a crystalline product suitable for X-ray diffraction studies, a range of solid metal complexes have not been isolated until now. Therefore, the structural studies of the ligand and its metal complexes were done by spectroscopic methods.

Conclusion

As a result, elemental analyses (Table-1), molar conductance, mass spectra, UV-vis spectra (Table-5), IR (Table-2) and magnetic moment measurements indicate that Ni(II) and Cu(II) complexes are tetrahedral structure[38] and Zn(II) complex is tetracoordinate and may be tetrahedral structure as is the Ni(II) complex. Also in the Co(III) complex, polymeric structure was suggested as far as result of mass and NMR spectra, elemental analyses, AgCl test and this complex is octahedral. The tetrahedral geometries are completed through chloride ions in Ni(II) complex (Fig. 2) and through chloride ion and a water molecule in Cu(II) complex (Fig. 3). The tetracoordinate structure is complete through chloride ions in Zn(II) complex (Fig. 4). The octahedral geometry is completed through chloride ions in Co(III) complex (Fig. 5).

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