



SYNTHESIS, CHARACTERIZATION OF SODIUM (2-([1,1'-BIPHENYL]-4-YL)-1-(HYDROXYIMINO)-2-OXOETHYL)TYROSINATE AND ITS MONONUCLEAR Fe(II) AND Cu(II) COMPLEXES

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ABSTRACT

A new aminoketooxime ligand (HL) was synthesized starting from biphenyl. Then, its Fe(II) and Cu(II) complexes were synthesized by reaction of the ligand and appropriate metal salts. The ligand and its metal complexes were characterized by elemental analysis, magnetic susceptibility, molar conductivity, ¹H- and ¹³C-NMR, FT-IR, ICP-OES and Uv-vis studies. Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicated that the metal:ligand ratio of Fe(II) complex was found to be 1:2 while this ratio was 1:1 in Cu(II) complex and the metal complexes indicated that the metal ions are coordinated to the oxygen atoms of oxime and carboxylate groups and nitrogen atom of amino acid group.

Keywords: Oxime, tyrosine, complex, characterization, spectroscopy

INTRODUCTION

Coordination compounds play a vital role in life and in the chemical industry. Coordination compounds are often used in qualitative analyzes as a way to distinguish certain metal ions and also to identify some unknown ions [1]. The oximes forming an important group of

ligands in the coordination chemistry are compounds containing the group $-C=N-OH$ in structure. The oxime term is a generic term and can be simply defined as the condensation product of aldehydes and ketones with hydroxylamine. Mono oximes and *vic*-dioximes are most commonly used as ligands in coordination chemistry. Oximes are also commonly referred to as versatile ligands capable of binding to the central atom via O and N atoms [2].

Oximes are used for various purposes in many fields of organic, analytical, inorganic, industrial and biochemical. Some oximes and their various derivatives have physiological and biologically active properties and they are also used as an additive to improve certain properties of engine oils, dyes, resins, tires etc. Many polymer materials used in the industry are not resistant to high temperature, light, impact, tensile and so on. Various active additives, such as oximes, are used to improve these deficient properties of polymeric materials [3-5].

Herein we have reported the synthesis and characterization of a novel oxime ligand group and its mononuclear Fe(II) and Cu(II) complexes.

EXPERIMENTAL

Materials and Methods

All reagents were purchased commercially and used as received. 1H - and ^{13}C -NMR spectra were recorded using a model Varian Unity (400 MHz) spectrometer from $CDCl_3$ solutions with TMS as internal standard. FT-IR spectra were recorded on a Shimadzu IRPrestige-21 FT-IR Spectrophotometer on KBr discs in the wavenumber range of $4000-400\text{ cm}^{-1}$. Electronic spectral studies were performed on a PG T80+ Spectrophotometer. The elemental analyses of the compounds were carried out using LECO 932 CHNS analyzer. Metal content of the complexes were measured on a Perkin Elmer Optima 5300 DV ICP-OES Spectrometer. Magnetic susceptibility measurements were performed at room temperature on a Sherwood Scientific Magnetic Susceptibility Balance (Model MX1) in powder form. The conductance measurements were carried out using an Optic Ivymen System conductivity meter. Melting points were determined on a digital melting point instrument from Electrothermal model IA 9100.

Synthesis of Aminoketooxime Ligand (HL)

1-(4-Phenylphenyl)-2-chloro-2-hydroxyimino-1-ethanone was synthesized according to the literatures [6,7].

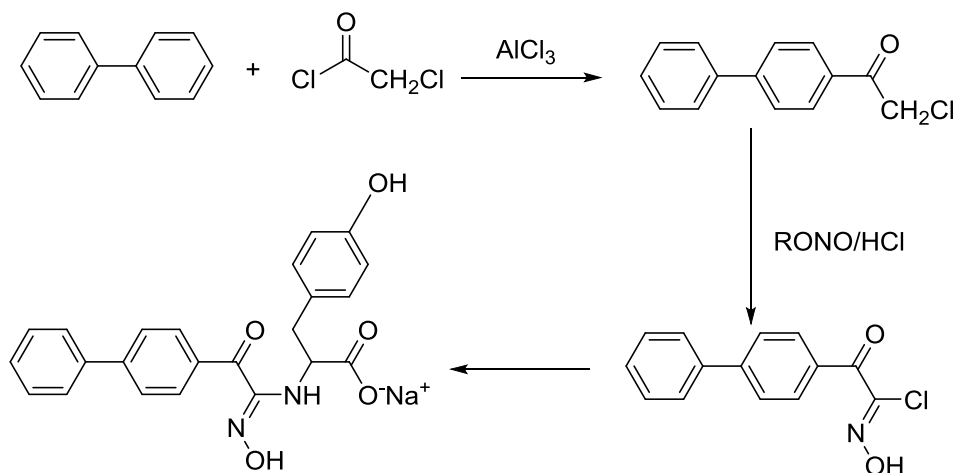
15 mmol (3.89 g) of 1-(4-phenylphenyl)-2-chloro-2-hydroxyimino-1-ethanone (chloroketooxime) was dissolved in 50 mL of methyl alcohol and cooled to below 0 °C in a salt-water bath. 30 mmol of tyrosine was then weighed and a sufficient amount of NaOH solution was added to prepare a methanol solution. The amino acid solution was then added dropwise to the chloroketooxime solution, ensuring that the temperature did not rise above 0 °C. The mixture was stirred in cold for 2 hours, at room temperature for 1 hour, and the filtrate was washed successively with 1% NaHCO₃ and methanol and dried over P₂O₅.

Synthesis of Complexes

2 or 1 mmol of ligand were dissolved in 10-15 mL of methanol and 1 mmol of FeCl₂.4H₂O or Cu(CH₃COO)₂.4H₂O dissolved in 10 mL of methanol was added and the pH of the solution was adjusted to 5.5-6. The resulting mixture was stirred at reflux for 2 hours. The resulting product was filtered, washed with water, cold ethanol and diethylether, and dried over P₂O₅.

RESULTS and DISCUSSION

Initially, 4-(chloroacetyl) biphenyl was obtained in the presence of AlCl₃ catalyst by the reaction of biphenyl and chloroacetylchloride according to the Friedel Crafts reaction. From the reaction of this compound with the alkylnitride in the acidic medium, 1-(4-phenylphenyl)-2-chloro-2-hydroxyimino-1-ethanone (chloroketooxime), which was present in the literature, was synthesized. Melting points of these synthesized compounds were found to be 114 and 169 °C, respectively, as indicated in the literature. The sodium salt of the new ligand was obtained as a result of the condensation reaction of 1-(4-phenylphenyl)-2-chloro-2-hydroxyimino-1-ethanone with tyrosine (Scheme 1). The mononuclear Fe(II) and Cu(II) metal complexes of the ligand were synthesized by reacting of oxime ligand with the appropriate metal salts.



Scheme 1. Synthetic route for the synthesis of the ligand (HL)

Some physical properties of all synthesized compounds and the results of elemental analysis are given in Table 1.

Table 1. Some physical properties and elemental analysis results of ligand and its metal complexes

Comp.	μ_{eff} (B.M.)	Conduc. ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	Colour	m.p. ($^{\circ}\text{C}$)	Yield (%)	Calculated(Found) %				
						C	H	N	Fe	Cu
HL	-	-	cream	185	72	64.79 (64.53)	4.49 (4.36)	6.57 (6.78)	-	-
(HL) ₂ Fe	4.85	10.6	brown	247	63	64.05 (64.36)	4.44 (4.65)	6.49 (6.20)	6.47 (6.28)	-
LCu(H ₂ O)	1.68	14.2	blue	225	51	57.08 (57.27)	4.17 (4.32)	5.79 (5.52)	-	13.13 (13.41)

¹H- and ¹³C-NMR Spectra

The ¹H- and ¹³C-NMR spectra of the ligand synthesized were recorded in CDCl₃ solvent and the chemical shifts obtained from these spectra are given in Table 2 and Table 3, respectively.

When the ^1H -NMR spectrum of the ligand was examined, it was observed that the oxime proton appeared as a singlet peak corresponding to a single proton at 8.62 ppm. The phenolic proton in the ligand was observed as a singlet peak at 6.98 ppm. Peaks belonging to the aromatic groups in the structure of the synthesized ligand appeared as multiplet peaks in the range of 7.41-8.30 ppm. The proton belonging to the N-H group in the structure appeared as a singlet peak corresponding to a single proton at 4.73 ppm.

Table 2. The chemical shifts observed in the ^1H -NMR spectra of the ligand $\delta(\text{ppm})$

Comp.	O-H _(oxime)	O-H _(phenol)	C-H _(aromatic)	N-H	C-H _(aliphatic)
HL	8.62 (s,1H)	6.98 (s,1H)	7.41-8.30 (m,13H)	4.73 (s,1H)	4.18 (-CH) (q,1H) 1.54 (-CH ₂ -) (d,2H)

When the ^{13}C -NMR spectrum of the ligand was examined, it was found that the carbonyl carbon adjacent to the biphenyl structure appeared in the lowest area (184.25 ppm). The peak of the ligands oxime carbon was found at 156.44 ppm while the aromatic carbons were observed at the range of 126.61 to 144.73 ppm. The data obtained from the ^1H - and ^{13}C -NMR spectra of the ligand were found to be consistent with those of the compounds obtained in similar studies in the literature [8-10].

Table 3. The chemical shifts observed in the ^{13}C -NMR spectra of the ligand $\delta(\text{ppm})$

Comp.	C _(ketone)	C _(aminoacid)	C _(oxime)	C _(aromatic)	C _(aliphatic)
HL	184.25	176.27	156.44	126.61-144.73	57.61 (-CH-) 29.79 (-CH ₂ -)

FT-IR Spectra

The FT-IR spectra of the resulting new ligand and its mononuclear Fe(II) and Cu(II) complexes were recorded and some characteristic vibrational frequencies seen in these spectra are given in Table 4.

Table 4. The characteristic band values (cm^{-1}) observed in the FT-IR spectra of the ligand and its metal complexes

Comp.	O-H _(water)	O-H _(ox)	N-H	C=N _(ox)	COO ⁻	C-N	N-O	M-O	M-N
HL	-	3137w	3199s	1608s	1415w, 1639w	1512s	1327s	-	-
(HL) ₂ Fe	-	3132w	3232m	1604s	1378m, 1631w	1519s	1335s	517m	456w
LCu(H ₂ O)	3326s	-	3226w	1595s	1397m, 1618w	1517s	1336m	545m	460w

b: broad, s: sharp, m: medium, w: weak

The stretching vibration of the OH group of the oxime moiety in the synthesized ligand was found at 3137 cm^{-1} . When the FT-IR spectra of the complexes were examined, OH bands belonging to the oxime group shifted to 3132 cm^{-1} in Fe(II) complex. In the Cu(II) complex, this band disappeared and a new band of 3326 cm^{-1} was observed, belonging to the coordination water.

The stretching vibration of the N-H group was observed at 3199 cm^{-1} in the ligand. In complexes, this band was clearly shifted to higher frequencies. The observation of this shift in the vibrational frequencies of the N-H group showed that the metal atoms were ligated from the N-H nitrogen in the amino acid structure of the ligand. The vibration of the carboxylate group observed at 1415 cm^{-1} in the spectrum of the ligand shifted to a lower frequency as a result of the complex formation. Significant low-frequency shifts in the $\nu_s(\text{COO}^-)$ and $\nu_{as}(\text{COO}^-)$ structures of the ligand indicated that the ligand was bound to the metal by the anionic oxygen atom of the COO⁻ functional group. The bands at 517 and 545 cm^{-1} observed in the spectra of the complexes, which were not observed in the FT-IR spectra of the ligand, were due to the stretching vibrations of the M-O bond. Similarly, the bands at 456 and 460 cm^{-1} observed only in the spectra of the complexes were due to the stretching vibrations of the M-N bond [11-12].

UV-Vis Spectra

The UV-vis spectra of the synthesized ligand and its mononuclear Fe(II) and Cu(II) complexes were obtained by preparing $1 \times 10^{-5} \text{ M}$ solutions in DMF. The maximum

absorbance wavelength and electronic transitions observed in these spectra are given in Table 5.

Table 5. UV-vis absorption band values of the ligand and its metal complexes (nm)

Comp.	$\pi \rightarrow \pi^*$ (benzene)	$\pi \rightarrow \pi^*$ (imine)	$n \rightarrow \pi^*$	Charge Transfer C-T	$d \rightarrow d$
HL	269	289	313	-	-
(HL) ₂ Fe	270	282	283	382	687
LCu(H ₂ O)	270	278	278	395	597

The band observed at 289 nm in the UV-vis spectrum of the ligand and originating from the $\pi \rightarrow \pi^*$ transitions of the imine group in the structure, shifted to a lower wavelength with complex formation. The band at 313 nm corresponding to the $n \rightarrow \pi^*$ transition observed in the spectrum of HL appeared at 283 and 278 nm in the (HL)₂Fe and LCu(H₂O), respectively. These low wavelength shifts indicated that the ligand was coordinated via oxime oxygen. The bands observed at 382 and 395 nm in the spectrum of the complexes were due to the charge transfer transitions in the complexes. Finally, the weak bands at 687 and 597 nm, which were not observed in the spectrum of the ligand but only in the spectra of the complexes, were due to $d \rightarrow d$ transitions in the metals.

Magnetic Susceptibility

The magnetic susceptibility values of the synthesized complexes were measured at room temperature using Gouy balance. As seen in Table 1, it was found that both complexes showed paramagnetic properties. It was determined that 4.85 BM value calculated for the (HL)₂Fe were compatible with 4.89 BM value of Fe(II) ion with high spin d^6 electron configuration. On the other hand the value of 1.68 BM calculated for the LCu(H₂O) was found to be in good agreement with the value of 1.73 BM corresponding to the single unpaired electron of the Cu(II) ion in quadrature coordination with the d^9 electron configuration.

Molar Conductivity

Molar conductivities of the synthesized complexes were measured in N,N-dimethylformamide solvent at 1×10^{-3} M solutions at room temperature. As can be seen from Table 1, molar conductivity values of the synthesized complexes were found to be 10.6 and $14.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for the $(\text{HL})_2\text{Fe}$ and $\text{LCu}(\text{H}_2\text{O})$, respectively. From these measured values, it was determined that the complexes were not electrolytes and that there was no ionic species in the structures [13].

As a result of spectroscopic and stoichiometric studies, the structures determined for the synthesized complexes are given in Figure 1 and Figure 2.

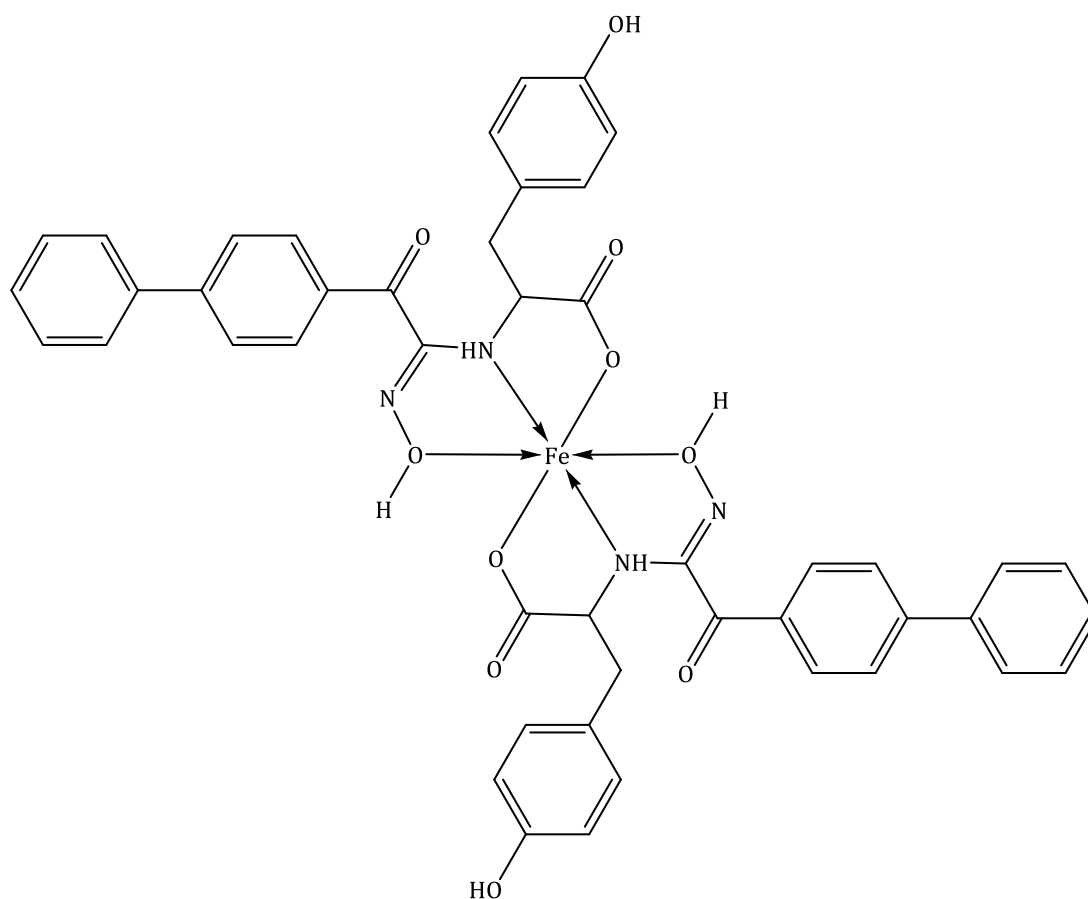


Figure 1. Structure of the mononuclear Fe(II) complex of HL $[(\text{HL})_2\text{Fe}]$

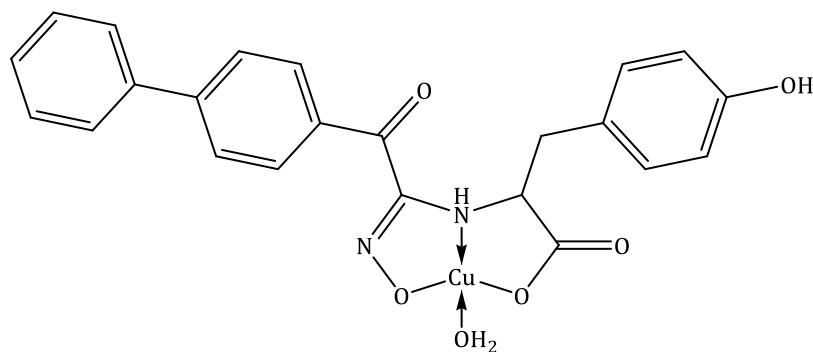


Figure 2. Structure of the mononuclear Cu(II) complex of HL [LCu(H₂O)]

CONCLUSION

As a result, new oxime ligand and mononuclear Fe(II) and Cu(II) metal complexes of this molecule were synthesized in this work. Elemental analysis and ICP-OES analyzes of the ligand and complexes were carried out and the values found were in agreement with the calculated values. Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicated that the metal:ligand ratio of Fe(II) complexes was found to be 1:2 while this ratio was 1:1 in Cu(II) complex. As a result of the studies, it was found that the metal atom was bound to the ligand via oxime oxygen atom, carboxylate oxygen atom and the nitrogen atom of the amino acid moiety.

ACKNOWLEDGEMENTS

This work was supported by the Research Fund of Süleyman Demirel University, Turkey (4625-YL1-16).

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