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Vol. 10(35), pp. 728-736, 22 September, 2016
DOI: 10.5897/AJPP2016.4644
Article Number: C55554260691
ISSN 1996-0816

http://www.academicjournals.org/AJPP

African Journal of Pharmacy and Pharmacology

Full Length Research Paper

Synthesis and characterization of Cu(II) and Fe(II) metal complexes of oxazepine derivative via Schiff base [Fe(HPOHBOT)Cl_2] and [Cu(HPOHBOT)Cl_2]

Najim abbas Jabir Al awwadi[1] Bassam Abdulhussein Hasan Alsafee[1], and Maitham Mohamed Abdulridha[2]

[1]Thi-qar University-College of Pharmacy, Iraq.
[2]Technical institute of Shatra, Iraq.

Received 4 August 2016: Accepted 24 August 2016

A Schiff base and its derivative (oxazepine) have been synthesized by the reaction between thio-semicarbazide and aromatic aldehyde 4-hydroxybenzaldehyde in ethanol in the presence of acetic acids to yield the Schiff base. This Schiff base on treatment with phthalic anhydride to give seven-member heterocyclic ring called oxazepine. Oxazepineas di-dentate ligand treated with hydrated metal chlorides $CuCl_2$ and $FeCl_2$ in the presence of ethanol as solvent to yield tetrahedral complexes. The structures of synthesized ligand and complexes have been established on the basis of their spectral Fourier transform infrared (FTIR), mass, 1H-NMR, elemental analysis C, H, N as well as molar conductance. The purity of the compounds was confirmed by thin layer chromatography (TLC).

Key words: Characterization, complexes, oxazepine, Schiff bases.

INTRODUCTION

1,3-Oxazepine is unsaturated seven-member heterocyclic ring containing oxygen atom in position1 and nitrogen atom in position 3 in addition to the five carbon atoms (Zeid, 2013).

It is synthesized by (2+5) → 7 cycloaddition reaction of imine group (Schiff bases) as two-member component to five-member component such as maleic or phthalic, nitrophthalic and succinic anhydrides to give a seven-membered heterocyclic ring (Rahman, 2011).

Oxazepine derivatives showed a vast variety of biological activities like cancer diseases, psychotic depression (Khalid et al., 2014), mental depression associated with schizophrenia, affecting the nervous centre (CNS) (Khuluod and Hamid, 2013) used for the control of anxiety and tension states, the relief of muscle spasm and for the management of acute agitation during with drawls from alcohol (Saoud, 2011). Oxazepine derivatives showed biological activities against different types of bacteria (Abood, 2009).

The aim of this study was to synthesize new metals complexes of oxazepine derivative via Schiff base which are expected to have enhanced biological activity

*Corresponding author. E-mail: najimabbas@yahoo.fr.

Table 1. The experimental result and physical data of ligand and its complexes.

Code No.	Compounds M.F.	M. W. (g/mole)	Colour	M.P. (°C)	Yield (%)	Elemental analysis of ligand		
						C	H	N
Ligand	$C_{16}H_{13}N_3O_4S$	343	Yellow	153	94	-	-	-
						% Theoretical data		
Ligand +Fe	$C_{32}H_{26}Cl_3CoN_6O_8S_2$	470	Green Brownish	266	62	55.97	3.82	12.24
						% Practical data		
Ligand +Cu	$C_{16}H_{13}Cl_2CuN_3O_4S$	477	Deep Green	272	64	56.12	3.71	12.15

compared to free oxazepine (Nagham et al., 2014).

EXPERIMENTAL

Melting points of ligand and metal complexes were taken in melting points apparatus U.k. 1H NMR spectra was recorded on a Bruker avance Mercury-300BB NMR 300 spectrometer. FT-IR spectra was obtained in KBr pallet in the 4000 to 200 cm^{-1} region on a Fourier transform infrared spectrophotometer Shimandzu. Mass spectra were recorded in the range of 0 to 900 m/z on a 5973 network mass selective detector. Elemental analysis C, H, and N were carried out on a Thermo finigan flash analyser, molar conductance, and molar conductance measurements were made in anhydrous DMSO at 25°C using Inolabcond 720 professional bench top meter.

Step I: Synthesis of 2-(4-hydroxybenzylidene) hydrazine carbothioamide (Schiff bases)

An equimolar amount of thiosemicarbazide (0.01 mole) and 4-hydroxybenzaldehyde (0.01 mole) was dissolved in 60 ml ethanol. The resulting mixture was refluxed for 6 h in the presence of few drops of catalytic amount of glacial acetic acid. After completion of the reaction, the mixture was poured into crushed ice; thereafter, the separated product was filtered and dried at room temperature. The product was purified by re-crystallization from ethanol, and was followed by TLC giving a yellow colour, yield percent of 81 and a melting point (m.p) of between 141 to 143°C (Rakesh et al., 2011).

Step II: Synthesis of 1-[3-(4-hydroxyphenyl)-1,5-dioxo-1,5-dihydro-2,4-benzoxazepin-4(3*H*)-yl]thiourea (Ligand) (HPOHBOT) .

The resulting mixture of an equimolar amount (0.02 mole) of Schiff's bases and 0.02 mole phthalic anhydride in 25 ml of dry toluene was refluxed for 7 h. After completion of the mixture, it was allowed to cool down at room temperature. The separated product was filtered and dried at room temperature. The product was purified by re-crystallization from dioxin. The purity of the compound was followed by TLC. The physical appearance yield and melting point are shown in Table 1 (Zainab and Hasan, 2011).

Step III: Synthesis of Cu(II) and Fe (II) metal complexes of oxazepine derivative

Ligand HPOHBOT was obtained by refluxing the mixture of hydrated metal chlorides $CuCl_2$ and $FeCl_2$ (0.001) and (0.001) of the ligand (HPOHBOT) in 70 ml ethanol until the complexes precipitated out. The colours of the complexes were filtered, washed with water, ethanol and dried under vacuum. The purity of the compound was followed by TLC. The physical appearance yield and melting point are shown in Table 1 (Matheel et al., 2009).

RESULTS AND DISCUSSION

The HPOHBOT ligand and their metal complexes were subjected to elemental analyses. The results of elemental analyses (C, H, N) with molecular formula and melting points are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula. The structures of the ligand and metal complexes are also confirmed by IR, MASS, 1H NMR spectra and molar electrical conductivity which are discussed subsequently.

Infra-red spectroscopy

FTIR (KBr, cm^{-1}) of ligand HPOHBOT showed 3483(O-H), 3409 (N-H), 3062(C-H)A, 2940(C-H)Ali, and 1639 (C=O)1482 (Abood, 2009). The band (N-H) of the complexes was shifted to a lower frequency, indicating its involvement in coordination with metal ion. These findings were further supported by the appearance of new bands at 694 to 696 and 700 to 703 cm^{-1} which belong to both v(M–N) vibrations, respectively. All data tabulated in Table 1 are as shown in Figures 1 and 2 (Nagham, 2013).

^{1}H NMR spectra data of ligand

The 1H NMR spectra of the HPOHBOT (L) in DMSO solutions with assignments are collected in Table 2 and 3. The 1H NMR spectra of the free ligand (Figure 3) showed the aromatic proton signals appearing at 7 to 8 ppm and also showed C-H proton at 8.2 ppm, secondary amine proton at 9.8 and 9.2 ppm of primary amine proton. The phenol OH proton has a signal at 10.5 ppm (Dhanya et al., 2014).

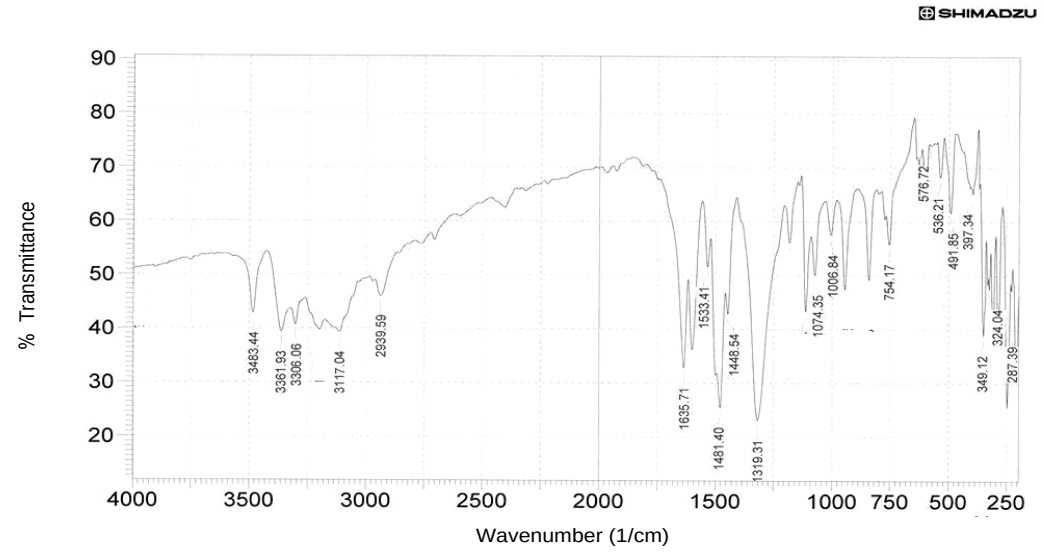


Figure 1. IR spectra of ligand.

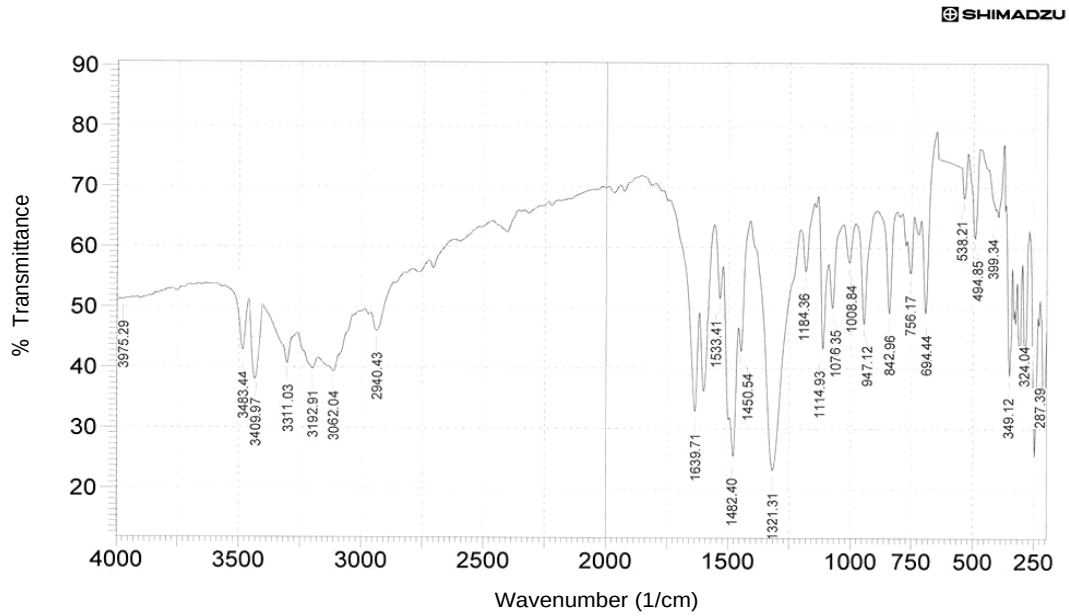


Figure 2. IR spectra of Cu(II) complexes.

Table 2. IR spectral data (cm-1) of the ligand and their metal complex in KBr pellets.

Vibration mode	Ligand	Ligand+Fe	Ligand+Cu
ν(O-H)	3483	3483	3488
νN-H)	3361	3409	3416
ν(C-H)Aro	3061	3062	3067
ν(C-H)Ali	2939	2940	2945
ν(C=O)	1635	1639	1644
ν(C=S)	1481	1482	1487
ν(M-N)	576	669	694

Table 3. 1H NMR spectra data of ligand.

Signal No.	Signal position (ppm)	Relative No. of Protons	Inference
1	7-8	2H	Ar-H
2	7-8	2H	Ar-H
3	7-8	2H	Ar-H
4	7-8	1H	Ar-H
5	7-8	1H	Ar-H
6	8.2	1H	-CH
7	9.2	2H	-NH
8	9.8	1H	-NH
9	10.5	1H	-OH

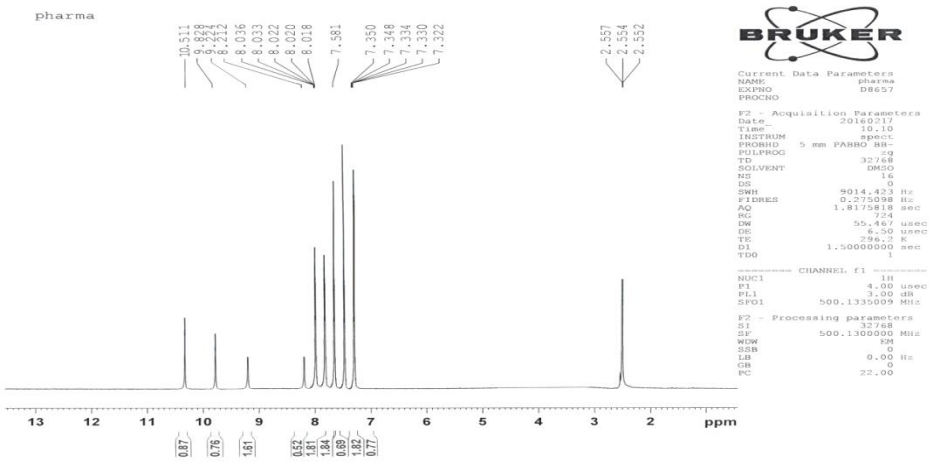
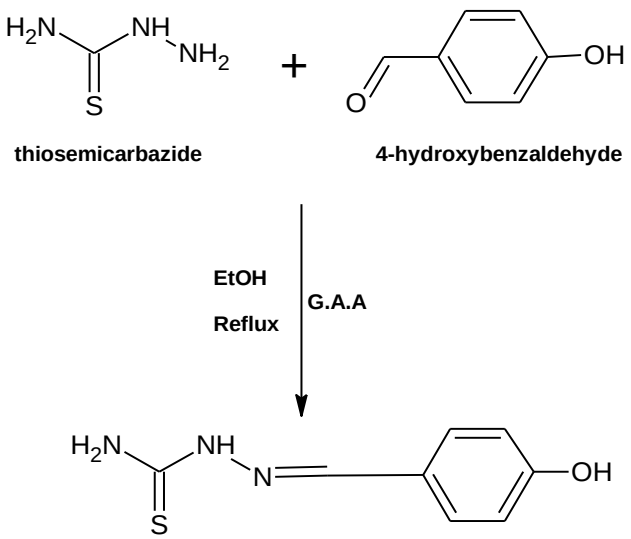
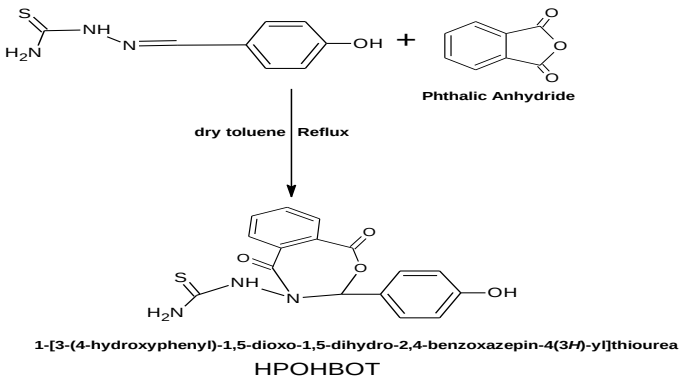


Figure 3. 1H NMR spectra of ligand.



Scheme 1. Step I: Synthesis of 2-(4-hydroxybenzylidene) hydrazinecarbothioamide.

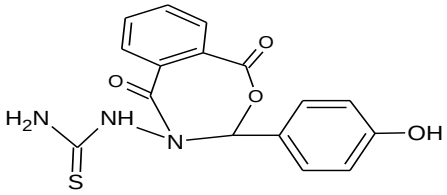
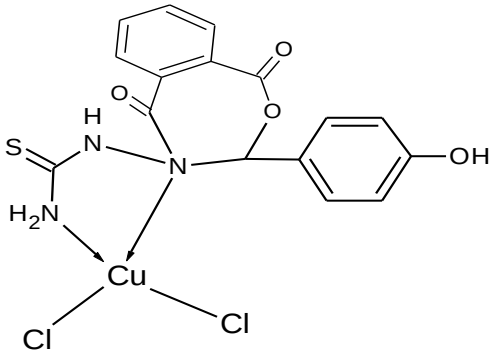
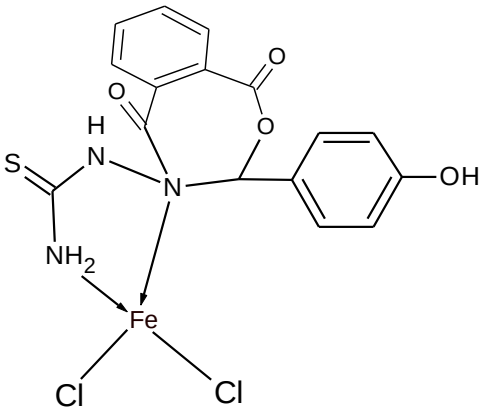


Scheme 2. Step II: Synthesis of 1-[3-(4-hydroxyphenyl)-1,5-dioxo-1,5-dihydro-2,4-benzoxazepin-4(3*H*)-yl]thiourea.

Mass spectra

Mass spectral data confirm the structure of the ligand and their Cu(II) and Fe (II) complexes as indicated by the molecular ion peaks corresponding to their molecular weight. All data are as shown in Scheme 1 and 2,

Table 4. Mass spectral data of the ligand and their Cu (II) and Fe (II) complexes.

Ion	The structure	Molecular ion
Ligand		343
$C_{15}H_{13}N_3O_3S$	-	315
$C_{10}H_7N_2O_3S$	-	250
$C_{10}H_6N_2O_3S$	-	234
$C_9H_7N_2O_3$	-	191
$C_9H_6NO_3$	-	176
C_5H_5	-	65
$[Cu(L)Cl_2]^{+\cdot}$		477
$[Cu\ (L)Cl]^{+\cdot}$	-	442
$[Cu\ (L)]^{+\cdot}$	-	406
$[Fe\ (L)Cl_2]^{+\cdot}$		470
$[Fe\ (L)Cl]^{+\cdot}$	-	435
$[Fe\ (L)]^{+\cdot}$	-	399

tabulated in Table 4 (Figures 4, 5 and 6) (Mukhlus et al., 2012).

Molar conductance measurements

The molar conductance data of the prepared complexes solution tabulated in the Table 6 were measured at room temperature in 10^{-3} M DMSO solvent. All exhibited low value of molar conductivity (0 to 20) which indicates that complexes under study is non-electrolyte Table 5. The obtained value suggested that no anions (Counter Ions) present outside the coordination sphere and showed

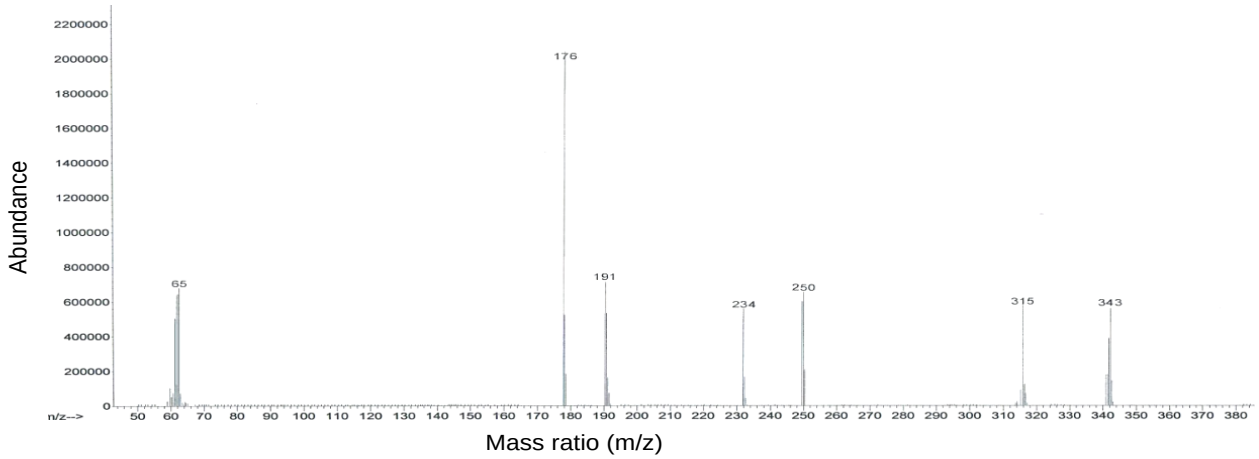


Figure 4. Mass spectral data of the ligand.

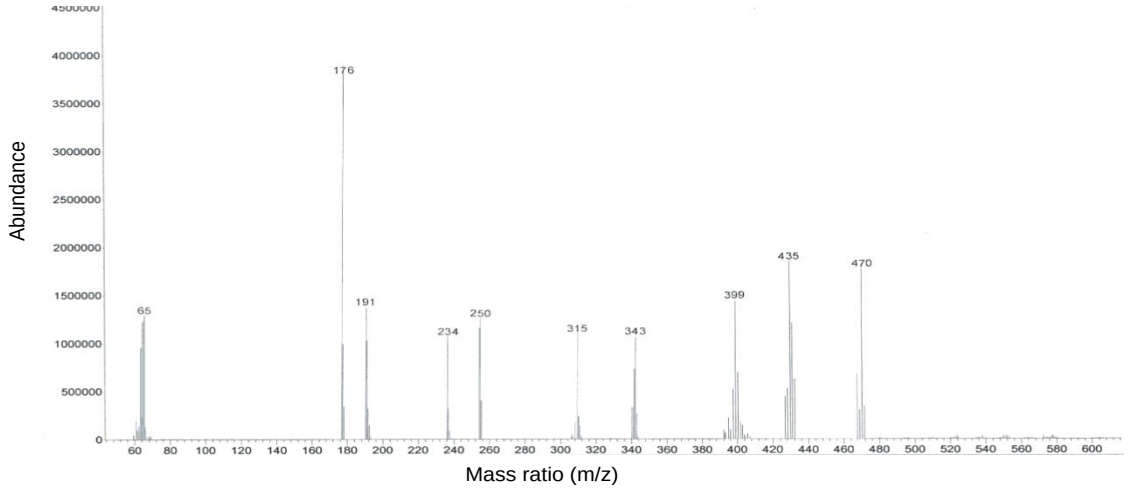


Figure 5. Mass spectral data of the Fe(II) complexes.

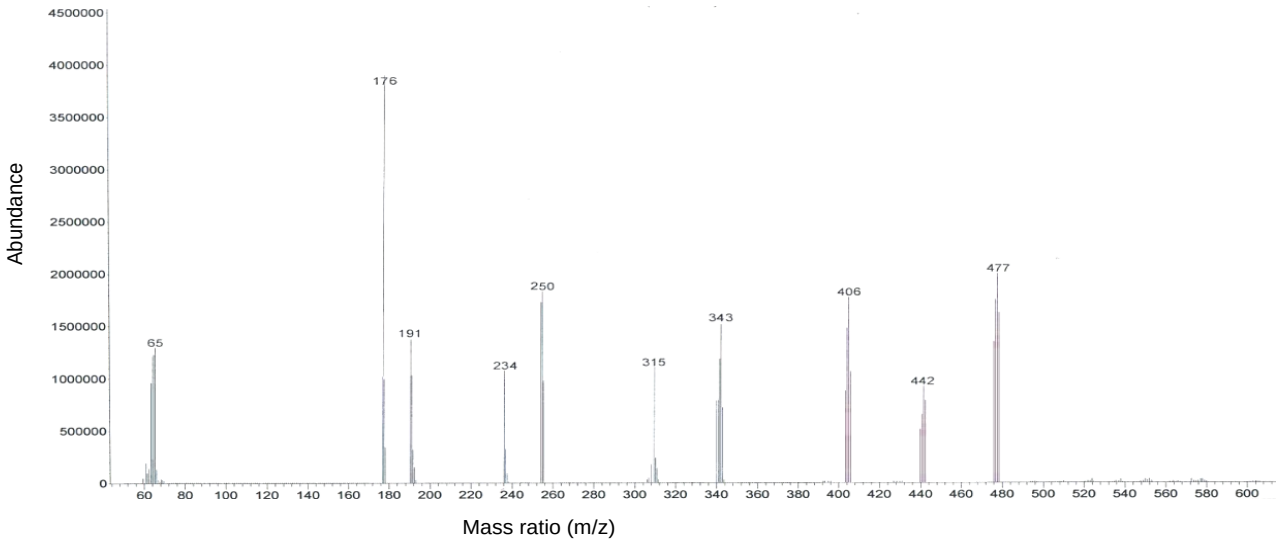


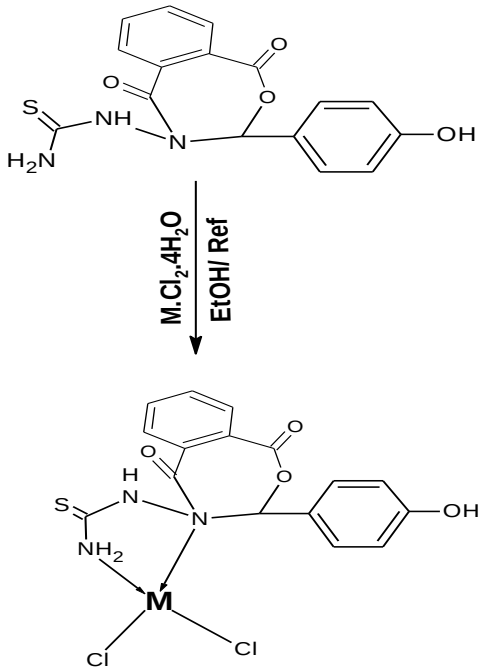
Figure 6. Mass spectral data of the Cu(II) complexes.

Table 5. Standard value of molar conductance data.

Solvent	Electrolyte type Λ_M(S .cm^2 .mole^{-1})		
	Non electrolyte	1:1	1:2
Dimethyl sulfoxide	0-20	30-40	70-80

Table 6. Molar conductance data of all complexes measurements were made in anhydrous DMSO at 25°C, concentration 10^{-3} at 298 K.

N	Formula	Solvent	Standard ΛM	Practical ΛM (S.cm^2.mol^{-1})	Electrolyte type
1	[Fe(L) Cl_2]	Dimethyl sulfoxide	0-20	13.3	Non electrolyte
2	[Cu(L)Cl_2]	Dimethyl sulfoxide	0-20	12.6	Non electrolyte



M= Cu,Fe

Scheme 3. Step III: Synthesis of Fe (II) and Cu (II) metal complexes of Oxazepine derivative. [Fe(HPOHBOT)Cl_2] and [Cu(HPOHBOT)Cl_2].

good agreement with that reported in the literature (Alya, 2015).

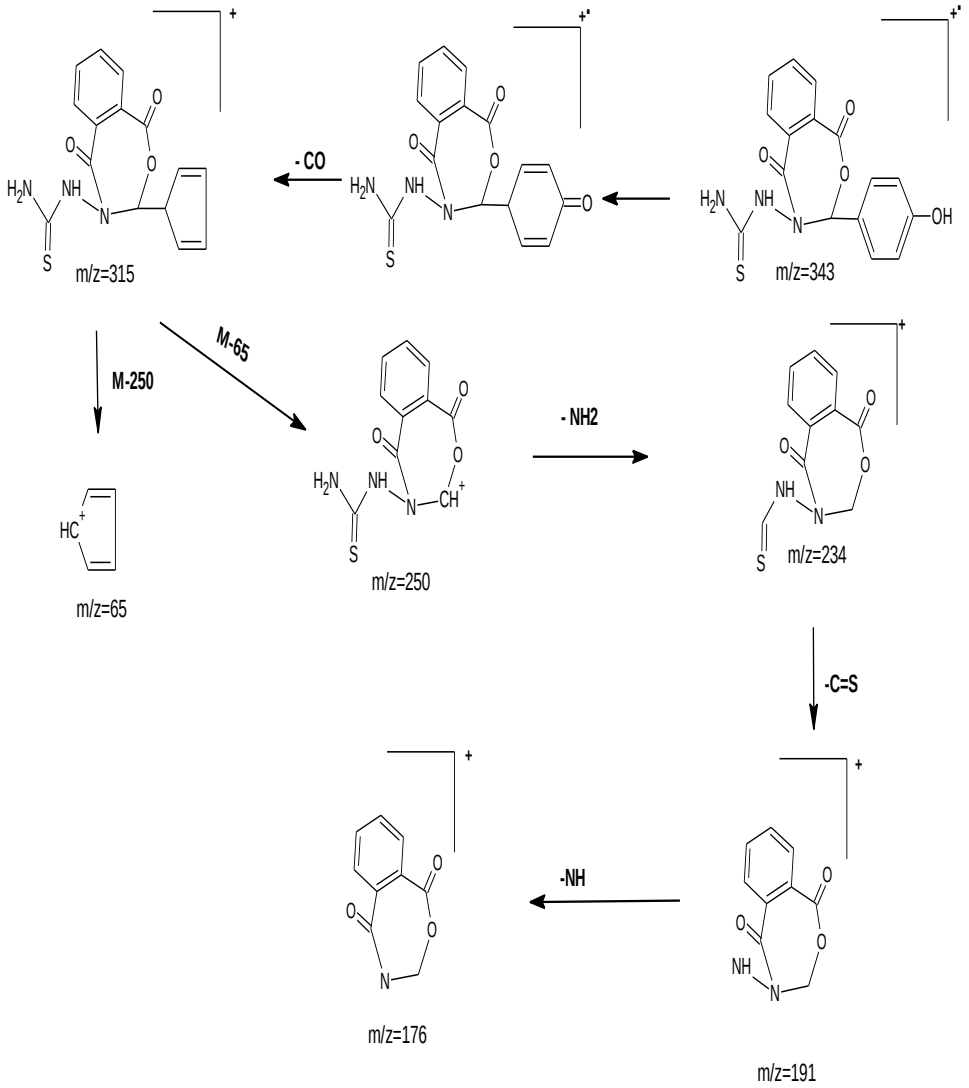
Conclusion

In the present study, Fe(II) and Cu(II) complexes with ligand HPOHBOT (L) have been synthesized and identified by IR, ^{1}HNMR, mass spectra, elemental analyses C, H, N, and molar conductance. v(M-N) band of ligand appeared in the prepared complexes at 694 cm^{-1} in Cu complex and 669 cm^{-1} in Fe complex and also (N-H) band of NH_2 for the synthesized ligand shifted from 3361 to 3416 cm^{-1} in Cu complex and 3409 cm^{-1} in Fe complex due to the coordination with the matal. This view further support that the coordinate appeared through the nitrogen of (C-N) and N of NH_2.

In all the physical and chemical measurements, it was suggested that the chemical configuration of the prepared complexes as tetrahedral geometry complexes is as shown in Scheme 3 and 4 (Selvana, 2012).

Conflict of Interests

The authors have not declared any conflict of interest.



Scheme 4. fragmentation mass spectral of the prepared ligand.

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