Synthesis and Spectroscopic Studies of Copper(II) and Cobalt(II) Complexes with Tetradentate Ligand Derived from Thiophene-2-carbaldehyde

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Abstract

The Synthesis of two Tetradentate Schiff base Ligands N2S2 were carried out by the condensation of aldehyde with primary amine. New tetradentate ligands N,N`bis (2-MethylenThiophene)-1,4 phenylene diamine (MTPA) and N,N`bis (2- Methylen Thiophene) ethylenediamine (MTEA) were synthesized from the reaction of thiophene- 2-carbaldehyde with phenylene 1,4 diamine and ethylene diamine, respectively.The ligands were reacted with Co(II) and Cu(II) metal salts, where the molar ratio of reaction was (1:2) (MTPA:Metal) and (1:1) (MTEA:Metal) molar ratio to form four new coordinated complexes. The mode of bonding and overall geometry of the complexes were determined through elemental analyses, FT-IR, ^{1}H,^{13}C NMR and electronic spectral studies. These studies revealed octahedral geometries for the Co(II) and tetrahedral for Cu(II) complexes with MTPA ligand. While for MTPA complexes with Co(II) and Cu(II) were monomeric octahedral complexes.The structure of the ligands and its metal complexes were elucidated by elemental analyses, IR, ^{1}H,^{13}C NMR, electronic spectra.

Keywords: Tetradentate Ligand , Schiff base, Copper(II) and Cobalt(II) Complexes.

1. Introduction

A special interest for the coordinative chemistry is represented by heterocyclic ligands, which contain sulphur atoms, because of the coordination potential and their implications in biological activity [1]. A Schiff base is a neutral molecule with an electron pair and contains a carbon-nitrogen double bond. This class of compound was discovered in 1864 by Hugo Schiff, when he reacted an aldehyde and amine, leading to a Schiff base. The Schiff bases are also called as imines [2], anilis and azomithines. The kinetic studies of Schiff base formation as well as other carbonyl addition reaction have been interested chemists for some time. Schiff bases derived from Thiophene-2-carbaldehyde have a wide variety of applications in biological [3]and analytical chemistry [4].Schiff bases are known to be neoplasm inhibitors [5], antiviral [6],antimicrobial [7],Transition metal complexes containing N and S donors are of special interest due to their applications in biomedical [8,9], biological [10], and asymmetric catalysis [11,12]. Compounds with N and S donor atoms such as N2S2 are considered to be good coordinating ligands because they involve both hard nitrogen atoms and soft sulfur atoms. The importance of complexes with N2S2 ligands arise from use in the medical fields for therapeutic and diagnostic purposes [13,1].

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In the present work, Schiff bases derived from Thiophene -2- carboxaldehyde were prepared. The obtained Schiff bases ligand are reacted in (1:2), (1:1) mole ratio with the appropriate metal salt using ethanol solvent. The work is dedicated to the synthesis, structural characterization of a new Cu(II), Co(II) complexes by using Schiff Bases ligand.

2. Experimental:

2.1. Apparatus and chemicals:

(Thiophene-2-carbaldehyde for synthesis by MERK), cobalt chlorid 6-hydrate 97% (bySCP), cuper(II)-chloride 97% (by BDH),absolute etanole(byCHEMLAB),ethylene diamine 99.5%(by ROTH) ,1,4phenylendiamine 98% (byMERK) ,triethylamine 99.5%(by PS).

UV/Vis spectroscopy (model: Optizen 2120 UV), spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company, optical absorption spectrum infrared device model FT-IR-4100 from the Japanese company Jasco, rotar evaporator 4.91 model from the German company Normschiff, thin layer chromatographic of aluminum coated by Silica Gel 60F254 measuring 20 X 20 from the German company Merck.

2.2. Experimental Procedure:

2.2.1. Synthesis of the ligand (MTPA):

The Schiff base, MTPA was prepared by mixing hot solution (~70°C) of 1,4- phenyldiamine (0.108gr ,0.001mol) with thiophene-2-carboxaldehyde (0.2243gr, 0.002mol) in alcoholic solution, at reflux. The mixture was refluxed for 3h. The formed solid product was separated by filtration, purified by crystallization from ethanol. Then washed several times with diethyl ether and dried in vacuum over anhydrous calcium chloride. Ligand as yellow crystals was obtained with a yield of (70.6%).

2.2.2. Synthesis of the ligand (MTEA):

A absolute ethanol mixture of thiophene-2-carboxaldehyde (0.2243gr, 0.002mol) and ethyldiamine (0.060gr, 0.001mol) was heated under reflux with stirring for one day and then cooled to about 0°C to obtain yellow crystals, the crystals were separated by filtration. purified by crystallization from ethanol, washed several times with diethyl ether. Ligand as yellow crystals was obtained with a yield of (61.6%).

2.2.3. Synthesis of metal complexes:

The hot ethanolic solution (20mL) of corresponding metal salts Metal:MTPA = (2:1) for Co(II) and Cu(II), and Metal:MTEA = (1:1) for Co(II) and Cu(II)) was mixed with hot ethanolic solution of the respective ligands and refluxed for 2h by using a water bath. By cooling the contents, the colored complex separated out in each case. The same was filtered, then washed with ethanol and washed several times with diethyl ether .

3. Results and Discussion:

3.1. Elemental analysis and characterization for ligands and their complexes:

The tridentate Schiff base (MTPA) was prepared by the condensation of thiophene-2-carboxaldehyde and 1,4 phenyldiamine in their 2:1 molar ratio. Another tetradentate Schiff base (MTEA) was prepared by the condensation of thiophene-2-carboxaldehyde with ethyldiamine in their 1:1 molar ratio. Both ligands were obtained after reflux and then on cooling as yellow precipitates. The Schiff bases were subjected to elemental analyses. The results of elemental analyses (C, H, N) colors,yield and the melting points are presented in Table 1.

Table 1. Elemental analysis, molecular weight and melting point of the ligands.

Compounds	**Mol. Weight**	**Color**	**Yield (%)**	**M.P. (°C)**	**Elemental Analysis % Found (% Calc.)**			
					C	***H***	***N***	***S***
MTEA	**248.36**	**yellow**	**61.6**	**90-91**	**57.60 (58.0)**	**3.20 (2.5)**	**11.60 (11.3)**	**25.01 (25.80)**
MTPA	**296.40**	**yellow**	**70.6**	**171-172**	**64.60 (64.46)**	**4.3 (4.05)**	**9.21 (10.44)**	**20.77 (21.62)**

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Table 2. Molecular weight and melting point of the different complexes.

Complexes	Mol. Weight	Color	Yield (%)	M.P. (°C)
[Co_2MTPA]Cl_2		black	84	305
[Cu_2MTPA]Cl_2		brown	62	320
[CoMTEA]Cl_2		green and dark	45	295
[CuMTEA]Cl_2		bottle green	70	200

3.2. Infrared Spectra

The infrared spectra for the present compounds taken in the range 400-4000 cm-1 help to indicate regions of absorption vibrations. The main stretching modes are for ν(C=N), ν(C=C) and ν(C-S). The IR data of the spectra of Schiff base ligands (MTPA and MTEA) and their complexes are presented in Table 3. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation.

Spectrum of the MTPA ligand shows a sharp band at (1607cm-1) du to ν(C=N) azomethine group which has shifted to lower frequency by (10cm-1) in the complexes indicating its participation in chelation through azomethine nitrogen. The lowering of band is du to the reduction of electron density in the azomethine link. Thiophene ring ν(C-S) shows absorption band at (727cm^{-1}) in the Schiff base spectrum. These band rises shift by (735cm^{-1}) in the complex. Azomethine group in the Schiff base MTPA ahanged after complexation with Cu(II) from (1607cm^{-1}) to (1578cm^{-1}) this indicate that involvement of Azomethine group in complexation.

IR spectrum of MTEA ligand shows a band at (1629cm-1) du to ν(C=N) Azomethine group, wich shifts down by (1617cm^{-1}) in Co(II) complex this suggests coordination through azomethine group. Thiophene ring shows absorption band at (714cm-1) in Schiff base MTEA spectrum, this band shows higher shift by (720cm^{-1}) in Co(II) complex and (750cm$^{-1)}$ in Cu(II) complex. The band in the Schiff base MTEA changed after complexation with Cu(II) from (1629cm-1) to (1616cm^{-1}) this indicate that involvement of Azomethine group in complexation.

Table 3. Characteristic infrared absorption frequencies (cm^{-1}) of the ligand and complexes.

Compounds	ν(C=N) cm^{-1}	ν(C-S) cm^{-1}
MTPA	1607	727
[Co_2MTPA]Cl_2	1587	735
[Cu_2MTPA]Cl_2	1578	701
MTEA	1629	714
[CoMTEA]Cl_2	1617	720
[CuMTEA]Cl_2	1616	750

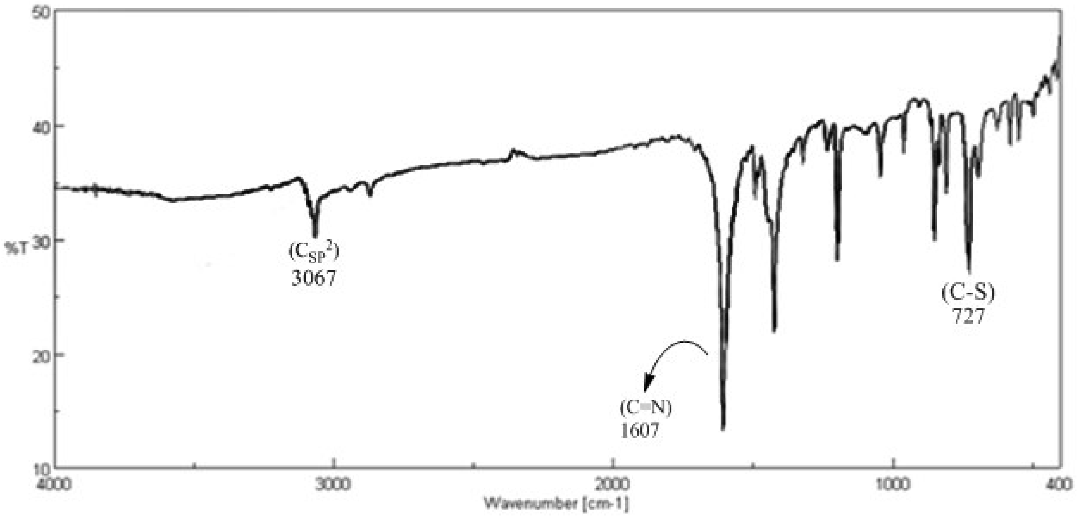

Figure 1. IR absorption spectra of ligand (MTPA)

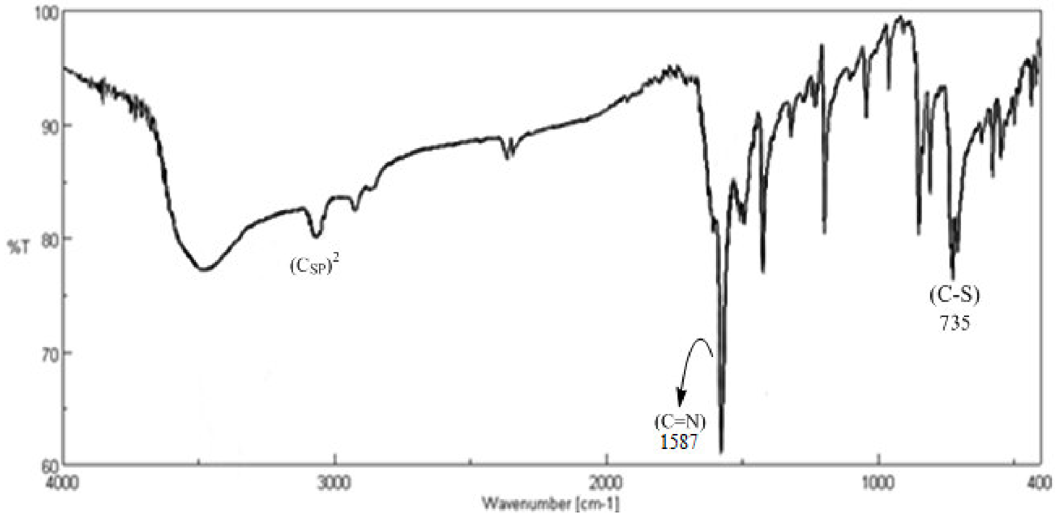

Figure 2. IR absorption spectra of $[Co2MTPA]Cl_2$

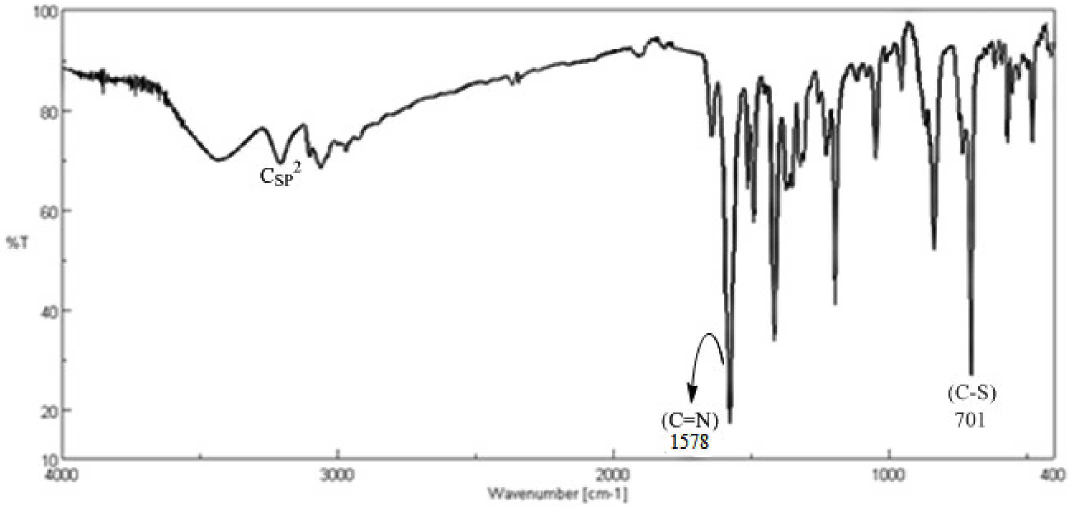

Figure 3. IR absorption spectra of $[CuMTPA]Cl_2$

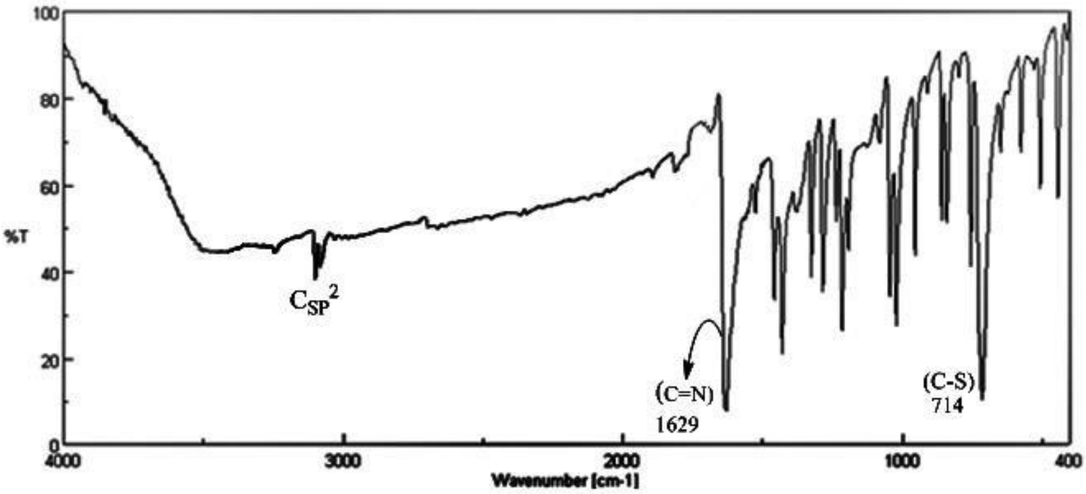

Figure 4. IR absorption spectra of MTEA.

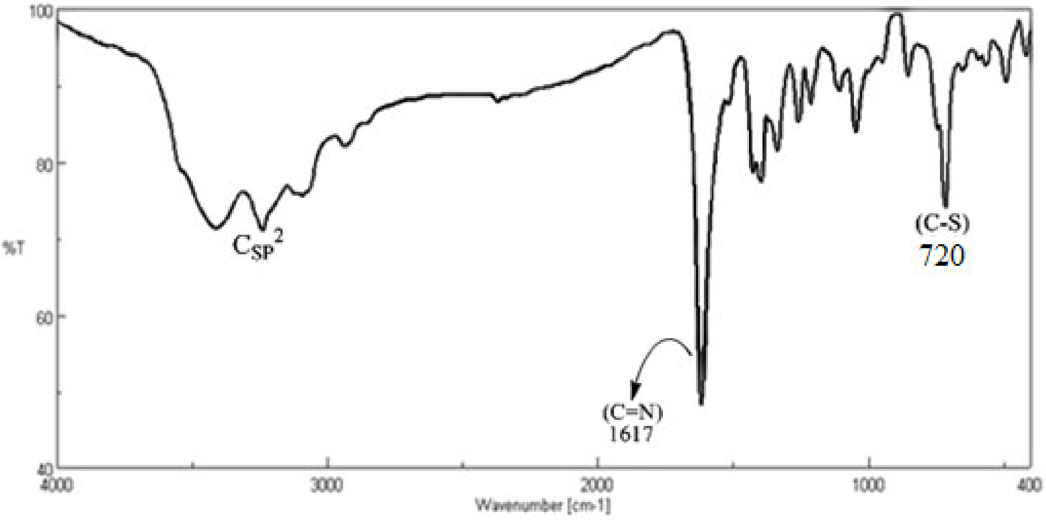

Figure 5. IR absorption spectra of [CoMTEA]Cl_2

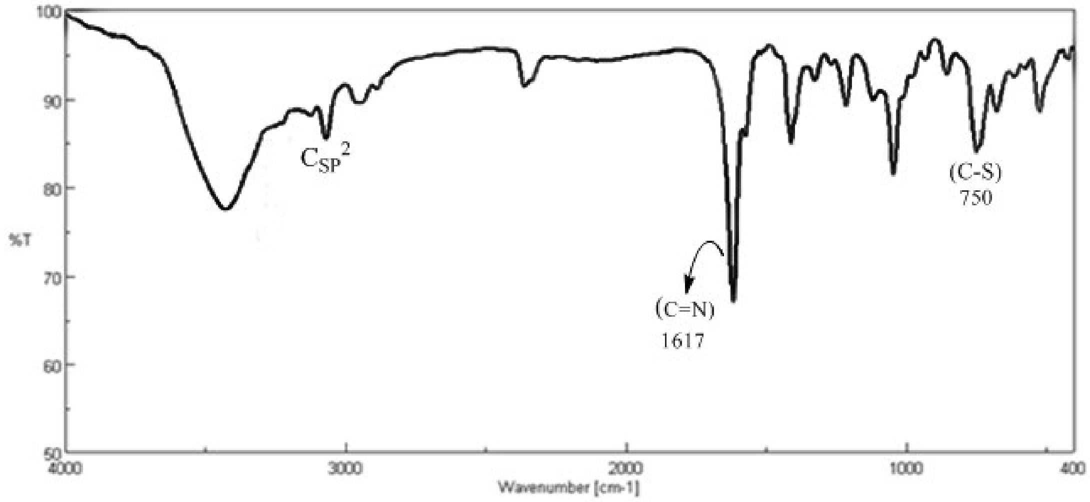

Figure 6. IR absorption spectra of [CuMTEA]Cl2

3.3. Electronic spectral data:

The data of the electronic spectra of the ligand and its complexes are given in Table 3. The spectrum of Schiff base (MTPA) presented two bands in the UV interval at 210nm and 365nm , assigned to (π → π*) and (n → π*) transitions respectively.

The electronic spectra of the [Co2MTPA]Cl_2 in ethanol solution has three bands at (580,640,690) nm These bands may be assigned to the transitions (d-d),The position of these bands suggests an octahedral environment[1] (Fig 7.):

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[1] T. Chandrasekaran, M. Suresh, F. M. MashoodAhamed and M. Syed Ali Padusha, (2014)-Synthesis, characterization and antimicrobial studies of novel compound and its metal complexes derived from nicotinic acid, Der ChemicaSinica, PP. 581-90.

Table 4. Electronic spectral data and geometries of ligand and complexes.

Compounds	**Electronic Spectra (nm)**	**Assignments**	**Geometry**
MTPA	210 365	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	
$[Co_2\,MTPA]Cl_2$	580 640 690	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	**octahedral**
$[Cu_2\,MTPA]Cl_2$	640	$^2T_2 \rightarrow {}^2E_2$	**tetrahedral**
MTEA	205, 265, 285	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	
$[Co\,MTEA]Cl_2$	575, 630, 675	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	**octahedral**
$[Cu\,MTEA]Cl_2$	510, 435	$^2B_{1g} \rightarrow {}^2B_{2g}$ $^2B_{1g} \rightarrow {}^2A_{1g}$	**octahedral**

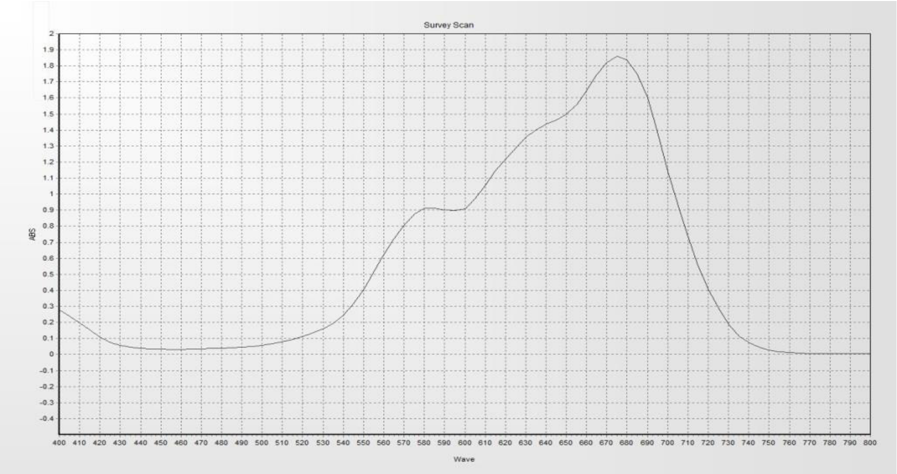

Figure 7. UV absorption spectra of $[Co_2MTPA]Cl2$

The electronic spectra of the $[CuMTPA]Cl_2$ in ethanol solution has one band at (640nm) These band may be assigned to the transitions (d-d),The position of these band suggests an tetrahedral environment[1] (**Fig 8.**):

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[1] B.G.Hthaway, G. Wilkinson, R.D.Gillard & J.A. McCleverty (1987)- Compehesinsve Coordnation Chemistry, V5, pergamon press, Oxford, pp.674-680

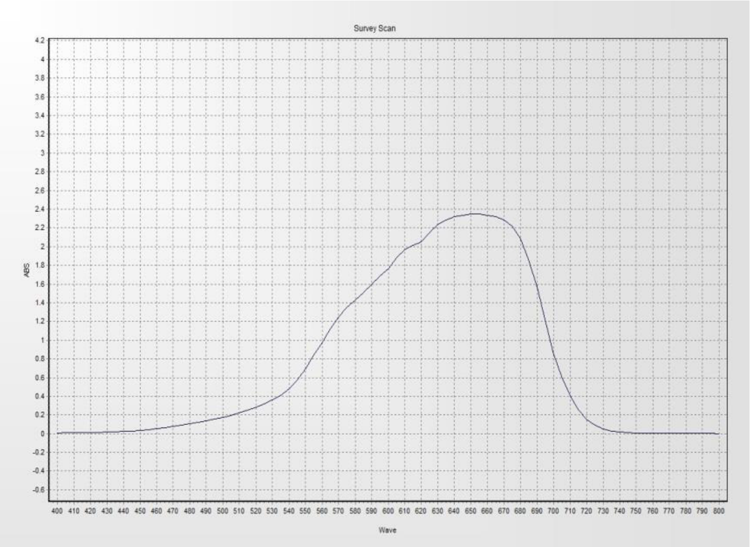

Figure 8. UV absorption spectra of[Cu2MTPA]Cl_2

The spectrum of Schiff base MTEA presented three bands in the UV interval at (205nm), (260nm) and (285nm), assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transition.

The electronic spectra of the [CoMTEA]Cl_2 in ethanol solution has three bands at (575nm), (630nm) and (675nm), These bands may be assigned to the transitions (d-d),The position of these bands suggests an octahedral environment[1] (Fig 9.):

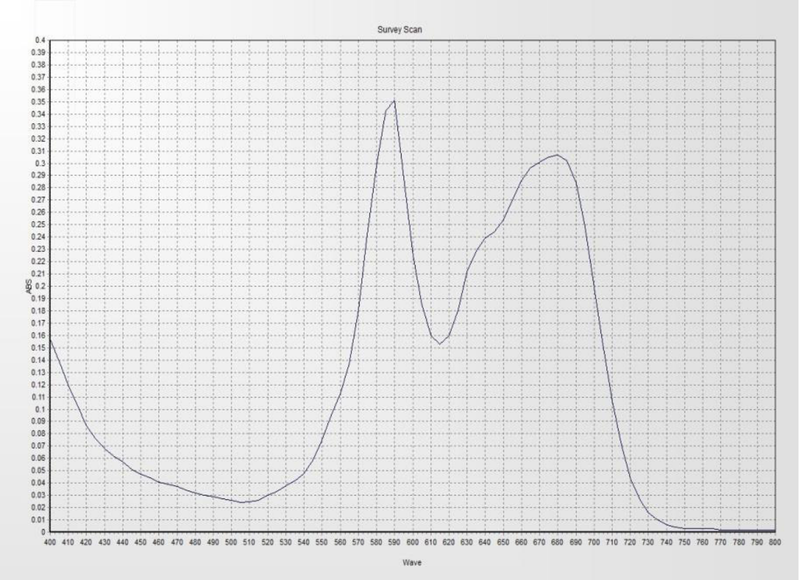

Figure 9. UV absorption spectra of [CoMTEA]Cl_2

The *electronic spectra* of the [*CuMTEA*]*Cl_2* in ethanol solution has two bands at (435nm), (510nm) These bands may be assigned to the transitions (d-d),The position of these bands suggests an octahedral environment[2] (**Fig 10.**):

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[1] .Spino,M.Pleniseanu,M.Isvoranu and L.Spinut, (2005)-Studies on N-(2-Thienylmethylidene)-2—aminothiophenol Complexes of Co(II), Ni(II), andCu(II),Asianjournal of chemistry,V4,PP. 2122-2128.

[2] .Spino,M.Pleniseanu,M.Isvoranu and L.Spinut, (2005)-Studies on N-(2-Thienylmethylidene)-2—aminothiophenol Complexes of Co(II), Ni(II), andCu(II),Asianjournal of chemistry,V4,PP. 2122-2128.

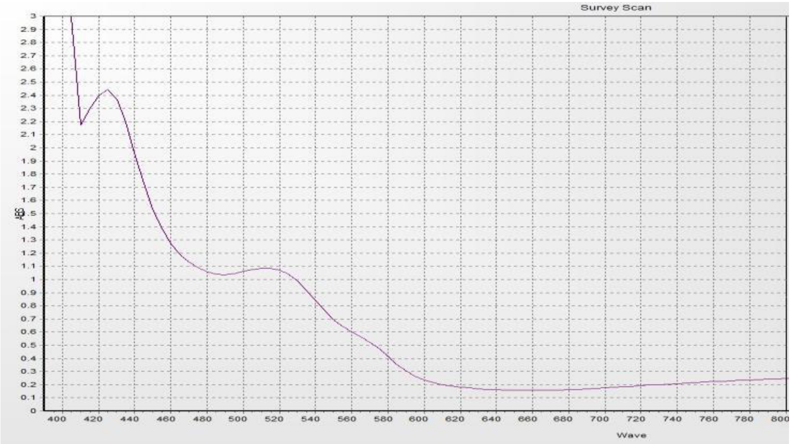
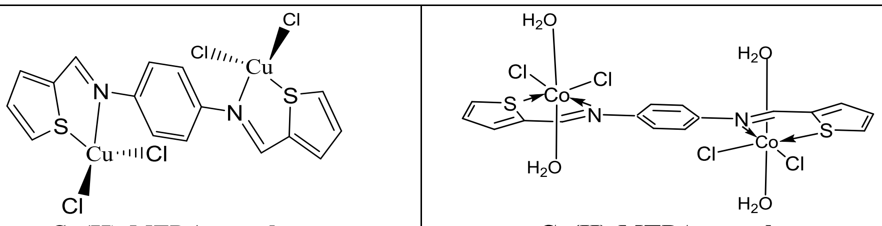
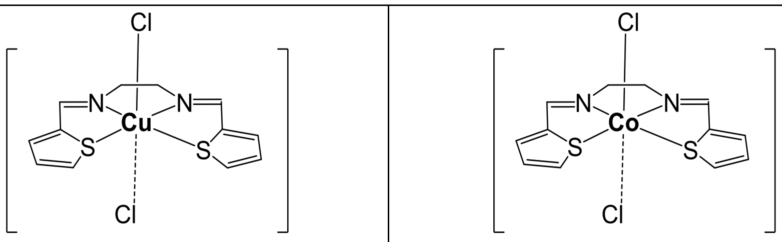


Figure 10. UV absorption spectra of $[CuMTEA]Cl_2$



***Cu(II)-MTPA* complex** **Co(II)-MTPA complex**

Figure 11. Suggested structures for the MTPA complexes



***Cu(II)-MTEA* complex** **Co(II)-MTEA complex**

Figure 12. Suggested structures for the MTEA complexes

3.4. ***^{13}C and ^{1}HNMR spectroscopic measurements*:**

(*^{1}H-NMR) spectra* of the Schiff base ligand *MTPA* revealed its formation by the presence of *(-CH=N*) proton signal at (δ=8.36ppm). the (*^{13}CNMR*) of the *MTPA* ligand exhibits signals at (δ=152.08ppm) These signal assigned to carbon azomethine group.

The *(^{13}C and ^{1}HNMR) spectroscopic measurements* of *MTPA*, *MTEA* Schiff bases are given in **Table 5.**

Table 5. The (^{13}C and ^{1}HNMR) spectroscopic measurements of MTPA and MTEA Schiff bases.

Compounds	**^{1}H-NMR(δ ppm)**	**^{13}C-NMR(δ ppm)**
MTPA	1-7.6(d, 2H) 2-7.1 (t, 2H) 3-7.5(d, 2H) 5-8.68 (S, 2H) 7,8- (S,4H)	-CH (Ar) 148-121 -CH=N 152.08
MTEA	1-7.39(dt, 2H) 2-7.25 (dd, 2H) 3-7.05(dd, 2H) 5-8.36 (S, 2H) 6-4 (S,4H)	$-CH_2$ 59.97 -CH (Ar) 141-126 -CH=N 155.02

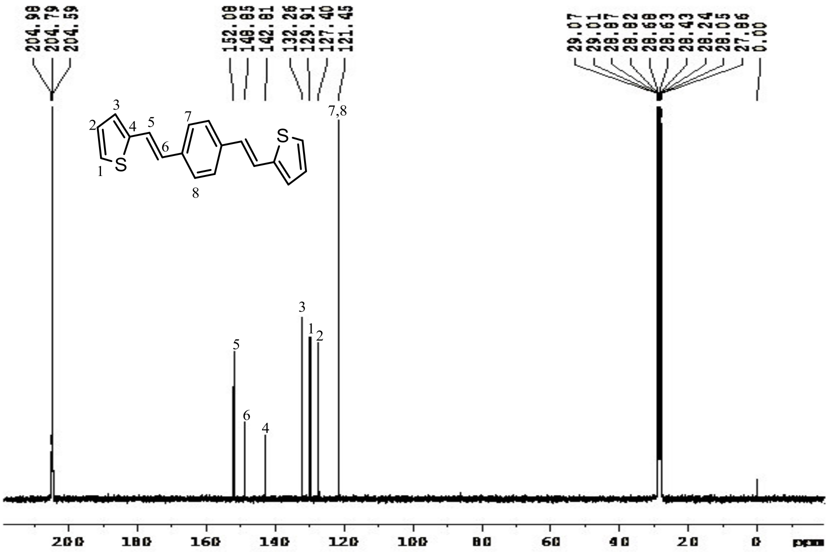


Figure 13. ^{13}CNMR spectrum of MTPA.

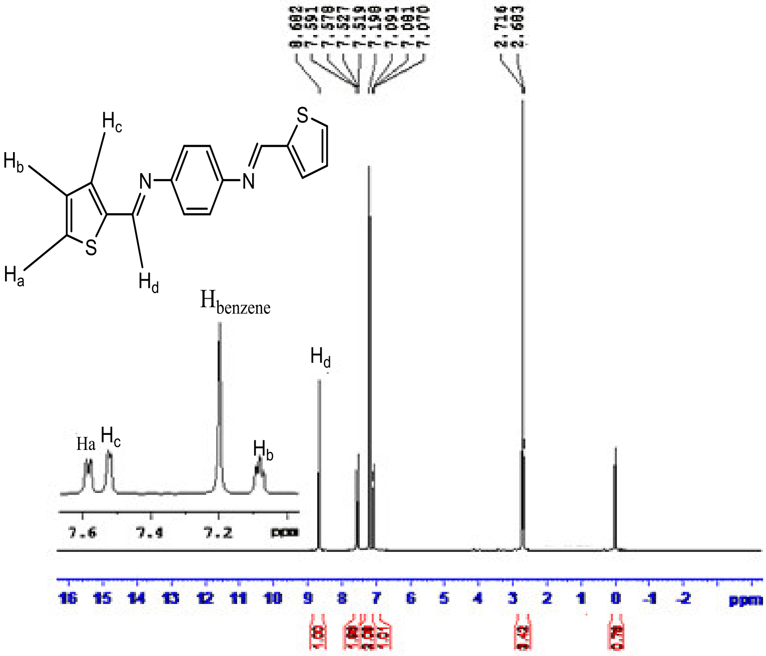


Figure 14. ^{1}HNMR spectrum of MTPA.

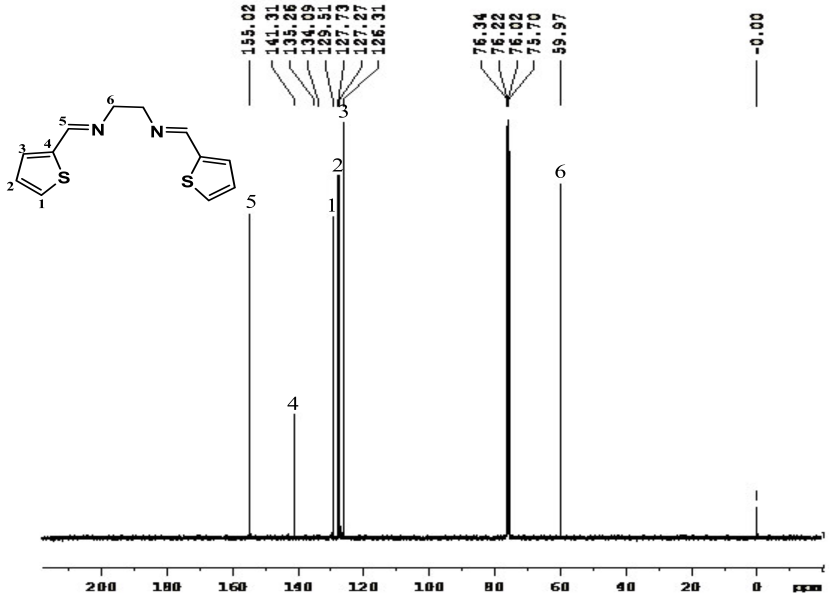


Figure 15. ^{13}CNMR spectrum of MTEA.

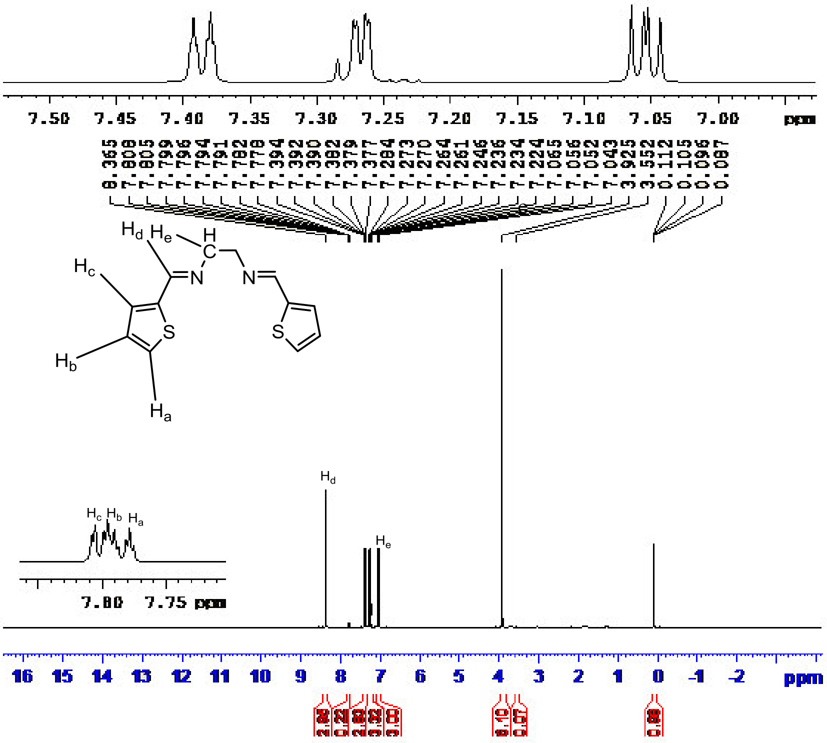


Figure 16. ^{1}HNMR spectrum of MTEA.

Conclusions

In this paper we reported the preparation, isolation, and characterization of a new tetradentate Schiff base derived from thiophene-2-carboxaldehyde, and its complexes with Co(II) and Cu(II). It is tentatively proposed that the Schiff base ligand coordinates through the nitrogen of the azomethine group and the sulfur of the thiophene ring, forming a stable chelate ring structure.

In the light of the above discussion, octahedral structures for Co(II), and Cu(II) complexes for MTEA, and tetrahedral structure for MTPA with Cu(II) and octahedral structure for Co(II), compounds are proposed (Figure 11, Figure 12).