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Journal of Chemical and Pharmaceutical Research, 2016, 8(12):22-33

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis, Characterization and Thermal Studies of Schiff Bases derived from 2-Pyridinecarboxaldehyde and Benzaldehyde and their Complexes with Cupper (II) and Cobalt (II)

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ABSTRACT

Two new Schiff base ligands (L1, L2) derived from 2-pyridinecarboxaldehyde, benzaldehyde and 5-amino-1,3,4-thiadiazol-2-thiol have been synthesized. These ligands were treated with Cu (II) and Co (II) chloride with a metal : ligand ratio of 1:1 to afford the four new complexes $[CuL1(H_2O)_2]Cl_2$, $[CoL1Cl_2]$, $[CuL2(H_2O)_2]Cl_2$ and $[CoL2(H_2O)_2]Cl_2$.These ligands and complexes have been characterized by IR, UV-visible absorption, molar conductance, magnetic measurements and atomic absorption . The data shows that the ligands are coordinate to metal atom by nitrogen to form square planer or tetrahedral complexes with Cu (II) and Co (II). The thermal properties were studied by TGA and DTG to discover the thermal stability of the complexes. The thermal behaviours of all the metal complexes were studied from room temperature to 700 ^oC in nitrogen atmosphere. The TGA and DTG studies of complexes expose that the decomposition continues in three steps.

Keywords: Schiff bases; Transition metal complexes; Spectrophotometric; Conductivity; Thermal analysis

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INTRODUCTION

Schiff bases are first known by Hugo Schiff [1] since 1864 and they are produced by condensation of a primary amine with carbonyl compounds [2]. The azomethine group is common structural feature of these compounds with a general formula RHC=N-R1, where R and R1 are alkyl, aryl, or heterocyclic groups which might be variously substituted [3, 4]. These compounds are also significant class of ligands in coordination chemistry [5]. Schiff base ligands have been used to synthesis a large number of the metal complexes with different electronic structures [6]. In recent years, metal complexes of Schiff bases have been presented to exhibit a broad range of biological and pharmaceutical activities, counting antibacterial, antioxidative and antitumor activities [7]. The metal complexes of Schiff bases resulted from 4- hydroxy salicylaldehyde and amines have strong anticancer activities. The Schiff base Ligand, Tetradentate N_2S_2, achieved by the condensation of thiophene-2- carboxaldehyde and 1,8-diaminonaphthalene, has been used to synthesize a complex of the type, [CuL] $(NO_3)_2$ [6]. A series of new 2,5-disubstituted-1,3,4-thiadiazole hitched 1,2,4-triazole, 1,3,4-thiadiazole, 1,3,4-oxadiazole and Schiff base derivatives were manufactured. All these compounds were separated for their antibacterial, antifungal and antiproliferative activity [8]. The thermal behaviours of metal complexes of Schiff bases were explored [9, 10]. The thermal analysis techniques, such as (DTG, TGA, and DTA) show a significant role in studying the thermal behaviour and the structure of metal complexes [11]. In the present work, we report the synthesis and structural studies of the complexes isolated from the reactions of copper (II) and cobalt (II) chloride with (L1), (L2).

MATERIALS AND METHODS

Physical measurements

FT-IR spectra were obtained on a Shimadzu FT-IR84005 spectrometer at College of Education Pure Science. The UV-Vis spectra were recorded in the range (200-700) nm on a PG Instruments Ltd spectrophotometer, in freshly prepared 10^{-3} M solutions in DMF at room temperature using quartz cell (1.000) cm. The molar conductivity of the complexes was measured at a concentration of 1.0×10^{-3} M in DMF at room temperature using HI 2315 Digital conductivity meter. Measurements of the magnetic susceptibility were comprehended at room temperature by the Guoy method using Hg

[Co(NCS)4] as calibrant. The molar ratio of metals - ligands was determined by atomic absorption apparatus (A Analyst 200 Atomic Absorption Spectrometer). The thermal experiments were performed from room temperature to 700 ^{o}C in N_2 atmosphere at a heating rate of 10 ^{o}C min^{-1}using AL_2O_3 crucibles. A concurrent TGA and DTG have been achieved by a model TGA Q50V20.13 Build 39 thermal analyser at College of Science.

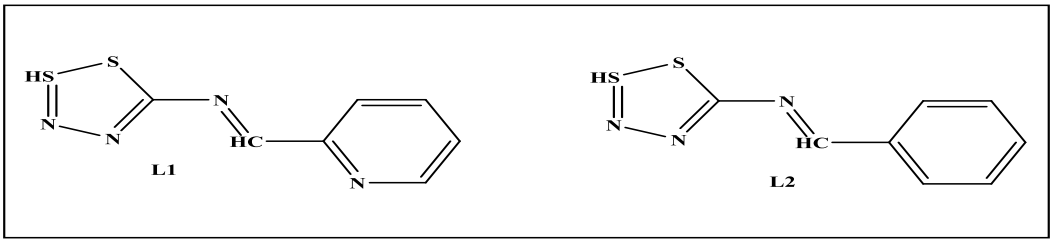


Figure 1: Chemical structure of the prepared Schiff base ligands

Synthesis of 5-amino-1, 3, 4-thiadiazole-2-thiol

To thiosemicarbazide (4.5 gm, 49.37 mmol) suspended in ethanol (20 ml) were added anhydrous sodium carbonate (5.23 gm, 49.37 mmol) and carbon disulphide (3 ml, 49.37 mmol). The reaction mixture was heated with stirring under reflux for1 hr, and then heated on steam bath for 4 hrs. The solvent was removed and the residue was dissolved in ice-water and acidified with concentrated hydrochloric acid. The product was recrystallized from ethanol to give yellow precipitate, m.p.233 °C.

Synthesis of the Schiff base (L1)

5-amino-1,3,4-thiadiazol-2-thiol (0.5 gm, 3.75 mmol) in 20 ml hot ethanolic solution was added drop wise into a solution of 2-pyridinecarboxaldehyde (0.35 ml, 3.75 mmol), the mixture refluxed for 5 hours. The resulting deep orange colored precipitate was filtered and washed with ethanol followed by petroleum ether, then dried at room temperature, the purity of L1was tested by TLC.

Synthesis of the Schiff base (L2)

5-amino-1,3,4-thiadiazol-2-thiol (0.5 gm, 3.75 mmol) in 20 ml hot ethanolic solution was added drop wise into a solution of benzaldehyde (0.38 ml, 3.75 mmol), the mixture refluxed for 5 hours. After cooling the achieved precipitate was filtered and recrystallized from ethanol. The resulting solid washed with petroleum ether, then dried to obtain yellow precipitate, the purity of L2 was tested by TLC.

Synthesis of Cu (II) and Co (II) complexes of Schiff base (L1)

The preparation of the complexes were performed by adding a hot solution of each of (0.16 g, 0.951 mmole) copper chloride $CuCl_2.2H_2O$ and (0.23g, 0.951 mmole) cobalt chloride $CoCl_2.6H_2O$ in absolute ethanol (5 ml) to (0.20g, 0.951 mmole) of L1 in absolute ethanol (10 ml). The mixtures were refluxed with stirring for four hours, the resulting precipitates were filtered and washed with diethyl ether and recrystallized from hot ethanol, and it was then dried at room temperature. Table (1) shows the physical properties of the ligand and metal complexes.

Synthesis of Cu (II) and Co (II) complexes of Schiff base (L2)

These complexes were prepared by adding a hot solution of each of (0.16 g, 0.955 mmole) copper chloride $CuCl_2.2H_2O$ and (0.23g, 0.955 mmole) cobalt chloride $CoCl_2.6H_2O$ in absolute ethanol (5 ml) to (0.20g, 0.955 mmole) of L2 in absolute ethanol (10 ml). The mixtures were refluxed with stirring for four hours, the resulting precipitates were filtered and washed with diethyl ether and recrystallized from hot ethanol, and it was then dried at room temperature. Table (1) shows the physical properties of the ligand and metal complexes.

Table 1: Physical properties of the (L1, L2) ligands and their metal complexes

Symbols	Formula	Color	M.P ^{o}C	Yield %
L1	$C_7H_6N_4S_2$	Deep orange	192-194	85
Cu L1	$CuC_7H_6N_4S_2$	Dark green	284-286	65
Co L1	$CoC_7H_6N_4S_2$	Reddish brown	335-337	74
L2	$C_8H_7N_3S_2$	yellow	173-175	78
Cu L2	$CuC_8H_7N_3S_2$	Green	272-274	73
Co L2	$CoC_8H_7N_3S_2$	Dark brown	341-343	79

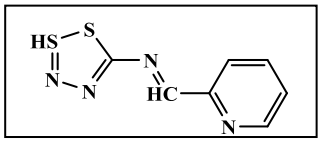
RESULTS AND DISCUSSION

The synthesized ligands and their complexes were characterized based on IR, UV-Vis spectra, magnetic susceptibility and conductivity measurements and thermal studies.

Infrared spectra

The FT-IR spectra of the Schiff base ligands L1, L2 and their complexes are given in Table 2 and figures (2-7). The azomethine vibration of the ligand (L1) at 1606 cm-1 was shifted to a higher frequencies in thecomplexes (CuL1 and CoL1) because of back bonding and decreasing the planar property after complexation [12, 13] .

The most signification differences in the IR spectra of the ligand (L2) and their complexes (CuL2 and CoL2) was the shift of C=N stretching frequencies to lower frequencies due to metal-ligand coordination [14,15].



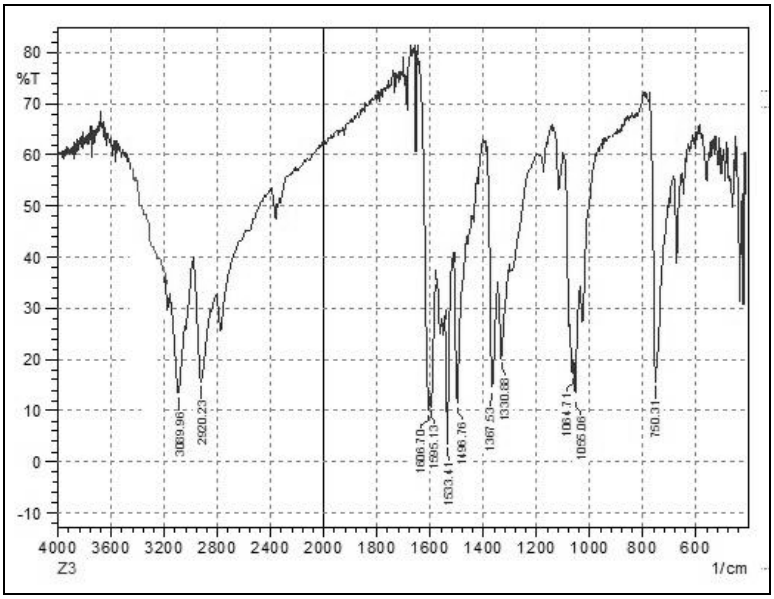
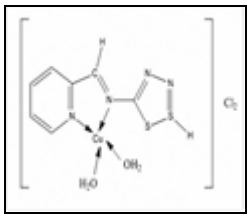


Table 2: Characteristic IR bands (cm^{-1}) of the ligands (L1) and (L2) and their complexes

Symbols	Formula	νC-H Alph cm^{-1}	νC-H Arom cm^{-1}	C=N str.cm^{-1}	C=C str.cm^{-1}	C-N str.cm^{-1}
L1	C7H6N4S2	2920m	3089m	1606s	1533m	1367m
Cu L1	CuC7H6N4S2	2929w	3032w	1687s	1560m	1369m
Co L1	CoC7H6N4S2	3026w	3099w	1647m	1481m	1319m
L2	C8H7N3S2	2895w	3072w	1687s	1556m	1327m
Cu L2	CuC8H7N3S2	2987w	3001w	1606s	1523m	1356m
CoL2	CoC8H7N3S2	2924m	3095m	1606s	1564m	1363m

S: strong; w: weak str: stretching; m: medium

Figure 2: I.R Spectrum of the ligand (L1)



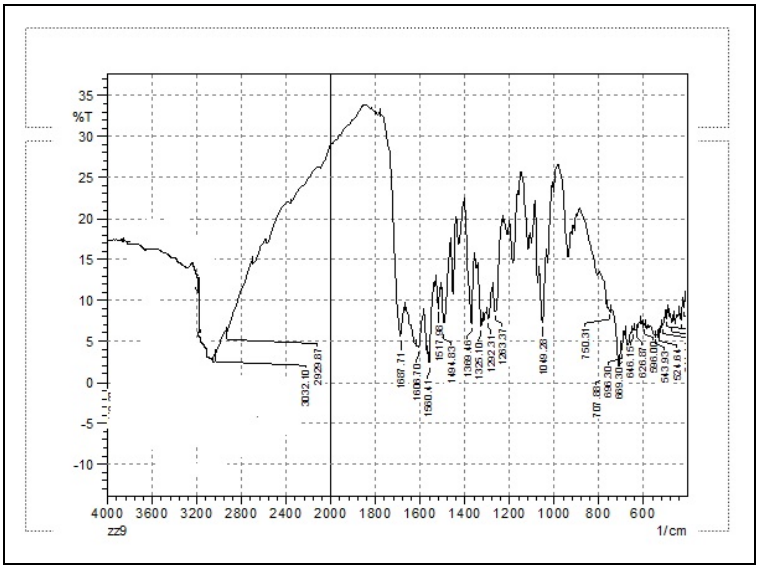
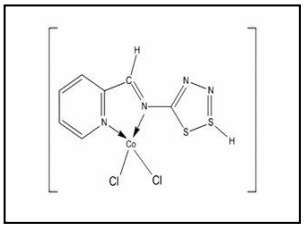


Figure 3: I.R Spectrum of the complex (CuL1)



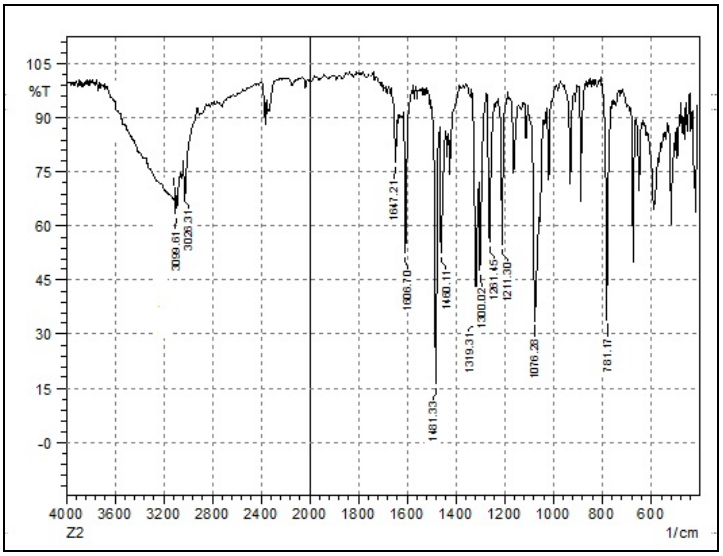
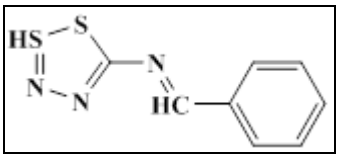


Figure 4: I.R Spectrum of the complex (CoL1)



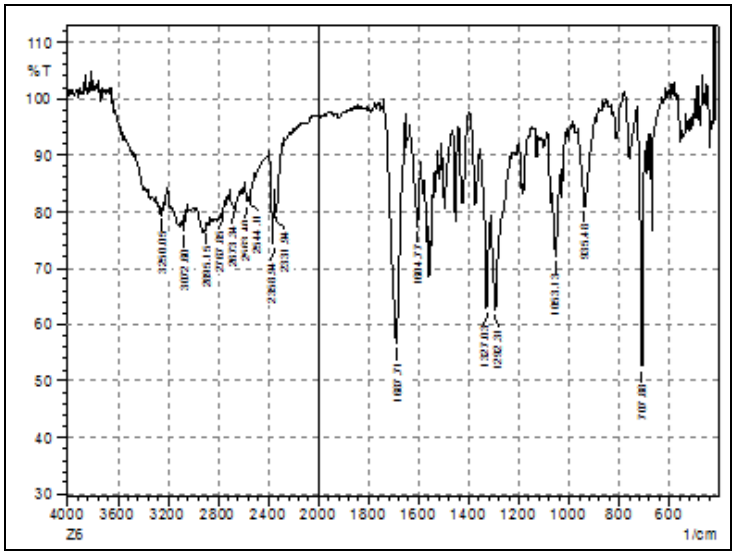
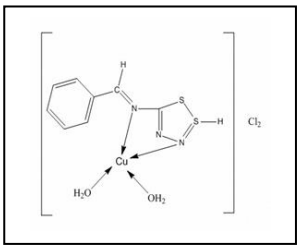


Figure 5: I.R Spectrum of the ligand (L2).



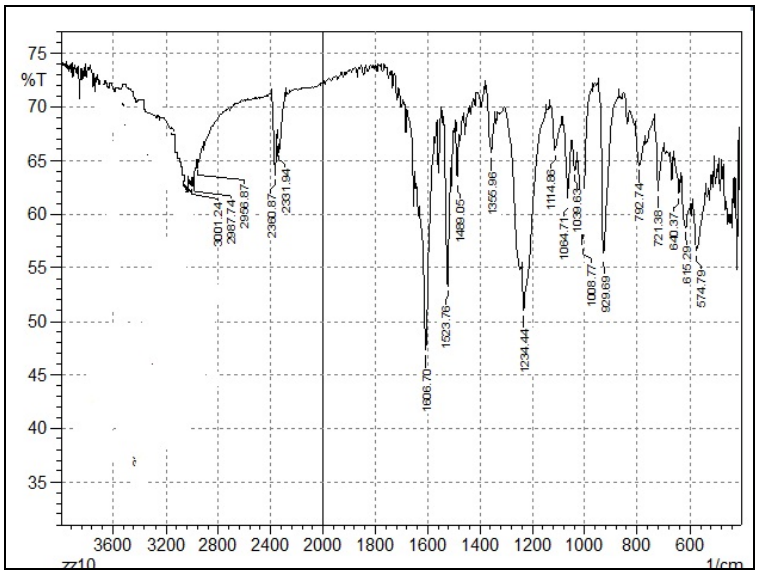
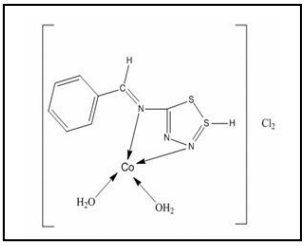


Figure 6: I.R Spectrum of the complex (CuL2).



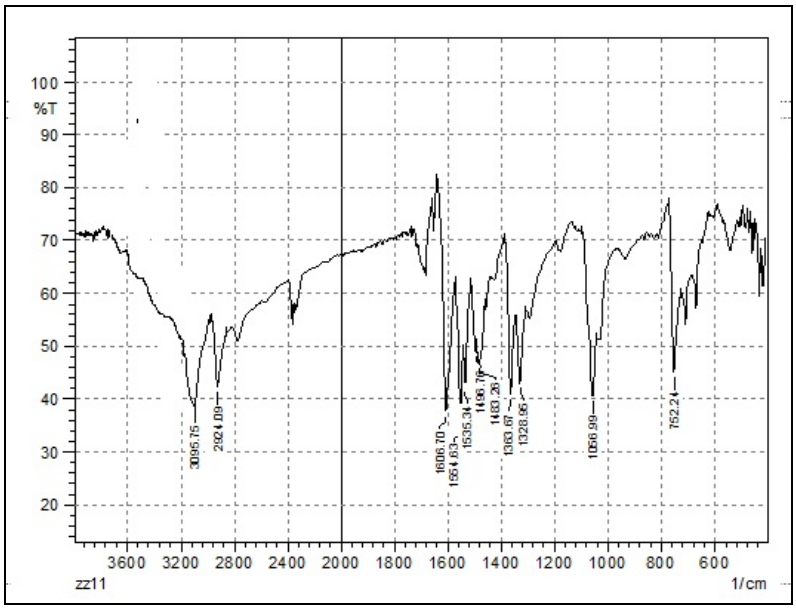


Figure 7: I.R Spectrum of the complex (CoL2).

Electronic Spectra

The electronic spectral data for the ligands and their complexes are presented in Table 3 and figures (8-13).The aromatic band of the ligand L1 at 242 nm is attributed to pyridine ring n → π* transition, while the band at 312 nm is ascribed to the n–π* transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base [16, 17]. The ligand L2 showed aromatic band at 226 nm is attributed to benzene ring π–π* transition, while the band at 343 nm is ascribed to the n–π* transition of the non-bonding electrons present on the nitrogen of the azomethine group in the Schiff base [16, 17]. For ML1 complexes, the spectra of the complexes, showed that the azomethine chromophore n–π* transitions shifted to 322 and 330 nm for CuL1 and CoL1 complexes. The [CuL1] complex showed a broad band with maximum at 412 nm due to metal to ligand charge transfer [18, 19].

Table 3: U.V-Visible spectra of the ligands (L1) and (L2) and their complexes in DMF

		λMax nm			
Symbols	**Formula**	**Band I**	**Band II**	**Band III**	**Solvent**
L1	$C_7H_6N_4S_2$	242	312	-	Dimethyl formamide
Cu L1	$CuC_7H_6N_4S_2$	240	322	412	Dimethyl formamide
Co L1	$CoC_7H_6N_4S_2$	254	330	420	Dimethyl formamide
L2	$C_8H_7N_3S_2$	226	343	-	Dimethyl formamide
Cu L2	$CuC_8H_7N_3S_2$	241	365	421	Dimethyl formamide
CoL2	$CoC_8H_7N_3S_2$	242	354	416	Dimethyl formamide

The [CoL1] complex displayed band at 420 nm due to metal to ligand charge transfer. On the other hand, the spectra of the complexes of ML2 showed that the azomethine chromophore n–π* transitions shifted to 365 and 354 nm for CuL1 and CoL1 complexes. Similarly, the [CuL1] complex showed a broad band with maximum at 421 nm due to metal to ligand charge transfer. The [CoL1] complex exposed band at 416 nm due to metal to ligand charge transfer (MLCT) transirions [18, 19].

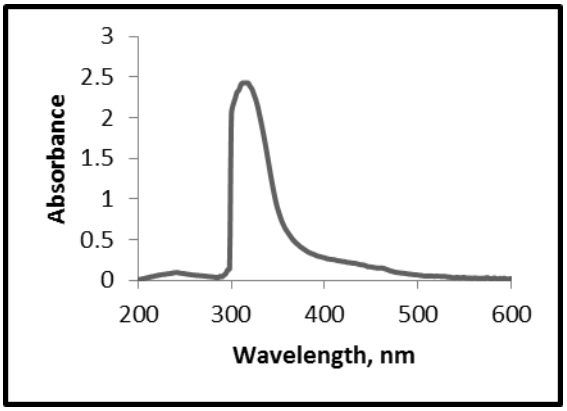


Figure 8: Uv-visible spectrum of ligand

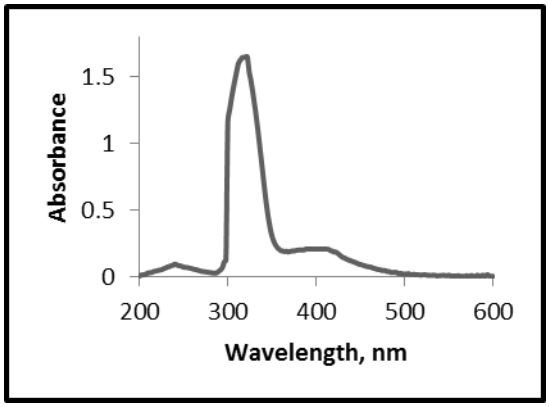


Figure 9: Uv-visible spectrum of complex

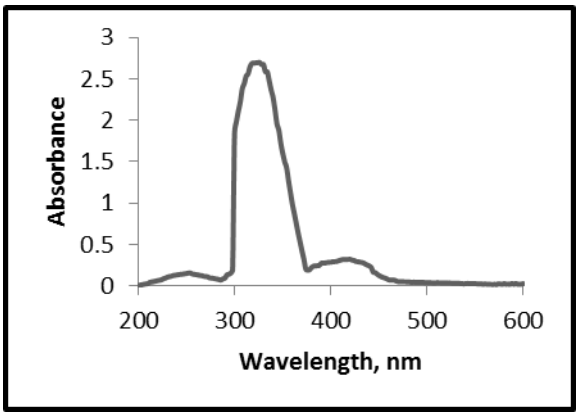


Figure 10: Uv-visible spectrum of complex

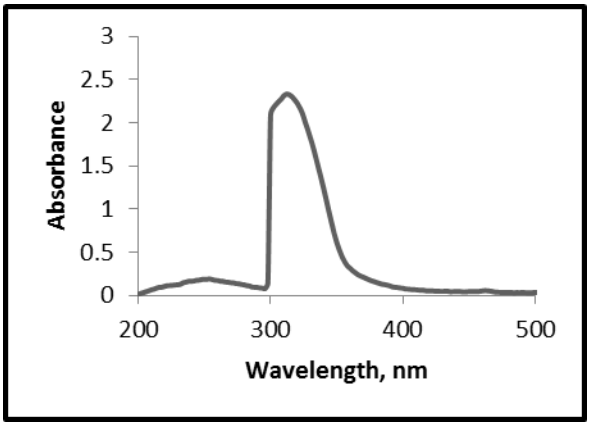


Figure 11: Uv-visible spectrum of ligand (L2)

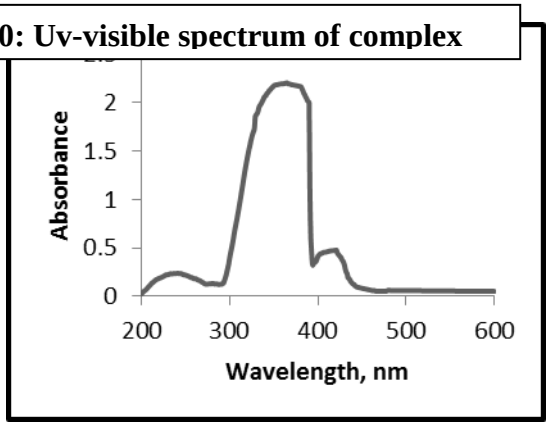


Figure 12: UV-visible spectrum of complex

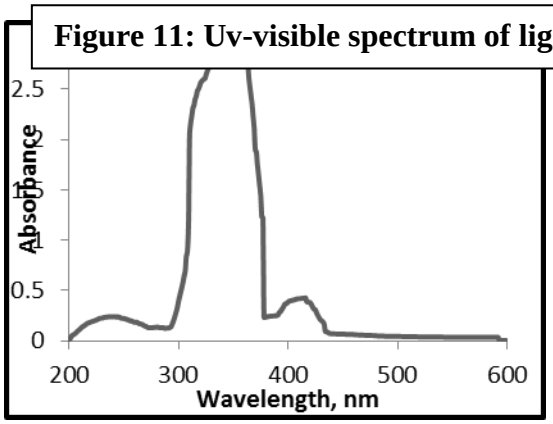


Figure 13: UV-visible spectrum of complex

Magnetic Susceptibility and Molar Conductivity Analysis

The magnetic susceptibilities and molar conductivities are listed in Tables 4. The magnetic moment μeff of the ligand complexes was measured by Faraday method [20] at room temperature. The μeff values for the complexes CuL1 and CoL1 were 1.663 and 1.721 BM respectively indicating these complexes are square planar geometry [21, 22]. While the magnetic

moment values for the complexes CuL2 and CoL2 were 1.862 and 2.731 BM respectively indicating these complexes are tetrahedral [23, 24, 25]. The molar conductivities of the complexes were measured using Johns and Brad Method [26, 27] at room temperature ($1x10^{-3}$ M) in DMF. The molar conductance values of the complexes were high indicating their electrolytic nature (Table 4).

Table 4: Magnetic measurements and molar conductance data of the complexes

Symbol of complexes	Formula of complexes	Mass magnetic susceptiblity $Xg.10^{-6}$	Molar magnetic susceptiblity $Xm.10^{-6}$	Correc. factor $D.10^{-6}$	Atomic magnetic susceptiblity $X_A.10^{-6}$	Effactive magnetic moment µeff (B.M.)	Molar conductivity Ω^{-1} cm^2 mol^{-1}
CuL1	$[CuL1(H_2O)_2]Cl_2$	1.547	891.01	269-	1160.01	1.663	120
CoL1	$[CoL1Cl_2]$	1.811	913.13	327-	1240.12	1.721	31
CuL2	$[CuL2(H_2O)_2]Cl_2$	1.146	622.1	273.5-	895.6	1.862	91
CoL2	$[CoL2(H_2O)_2]Cl_2$	5.301	2853.15	274.5-	3127.15	2.731	73

Atomic absorption

The molar ratio of the metals in the complexes (CuL1, CoL1, CuL2 and CoL2) was calculated by (Rast's Camphor Method) [28] indicating that practical data were in good agreement with the suggested general formula of complexes with 1:1 molar ratio (metal : ligand).

Table 5: Atomic absorption data of the complexes

Complex	M.wt	Concentration from AAS ppm	Metal %		M:L ratio
			calculated	found	
$[CuL1(H_2O)_2]Cl_2$	380.75	0.026	12.02	11.9	1:1
$[CoL1Cl_2]$	340.11	0.028	11.69	11.57	1:1
$[CuL2(H_2O)_2]Cl_2$	379.76	0.051	9.28	9.14	1:1
$[CoL2(H_2O)_2]Cl_2$	375.15	0.035	10.54	10.31	1:1

Thermal analysis of the complexes

In order to give more acumen into the structure of the complexes, the thermal behaviour of the prepared complexes has been studied to establish different decomposition process and to approve the suggested stoichiometry. The thermal behaviour of synthesised complexes was characterized on the basis of TGA and DTG method. Thermal analysis shows a significant role in studying the stability, melting point, structure and decomposition properties of the metal complexes. TGA of complexes were recorded in the temperature range between 25 to 700 ^oC in N_2 atmosphere.

$[CuL1(H_2O)_2]Cl_2$ complex

TGA and DTG curves of the $[CuL1(H_2O)_2]Cl_2$ complex were represented, and the thermal decomposition takes place in three stages. In the first stage of thermal dehydration of the complex takes place in a single step that is between 120-220 ^oC with mass loss 8.95% (calculated 9.1%). The two coordinated water molecules were removed in this step, and the maximum rate of mass loss indicated by DTG peak at 134.76 ^oC and 171.28 ^oC [29]. The second stage which accounts in the temperature range 220-378 ^oC with DTG peak observed at 315.41 ^oC, and the observed mass loss was recorded as 9.6% (calculated 9.8%), corresponded to the elimination of Cl atom of HCl [30, 31]. The final stage, which correspond to removal of Cl atom with a part of ligand L1 of $CH_3N_3S_2Cl$ [32, 33] in the temperature range 378-700 ^oC with the DTG peak observed at 502.89 ^oC, and the observed mass loss was recorded as 39.3% (calculated 41.34%) (Figure14).

$[CoL1Cl_2]$ complex

The $[CoL1Cl_2]$ complex showed almost the same two stage decomposition process. The first stage occurred in the temperature range 162-370 ^oC, with a mass loss of18.2% (calcd. 18.8%) due to the removal of 2 Cl atoms, and the maximum rate of mass loss was indicated by DTG peak at 267.36 and 323.10 ^oC. In the next stage, ligand L1 was decomposition in the temperature range 370-700 ^oC with the DTG peak observed at 398.04 ^oC (Figure 15).

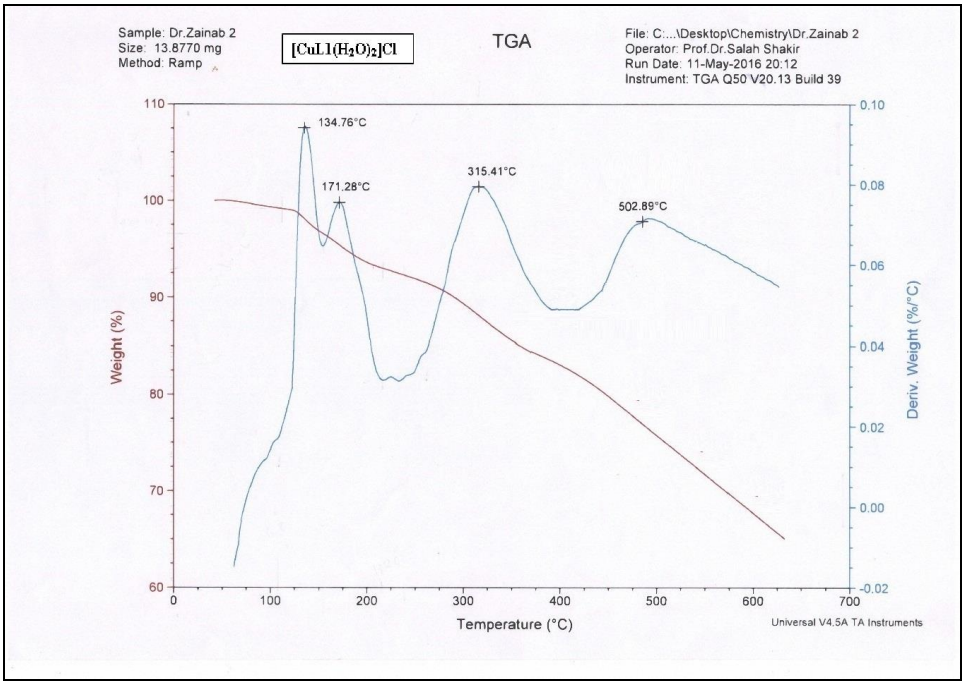


Figure 14: TGA and DTG curves of $[CuL1(H_2O)_2]Cl_2$ complex

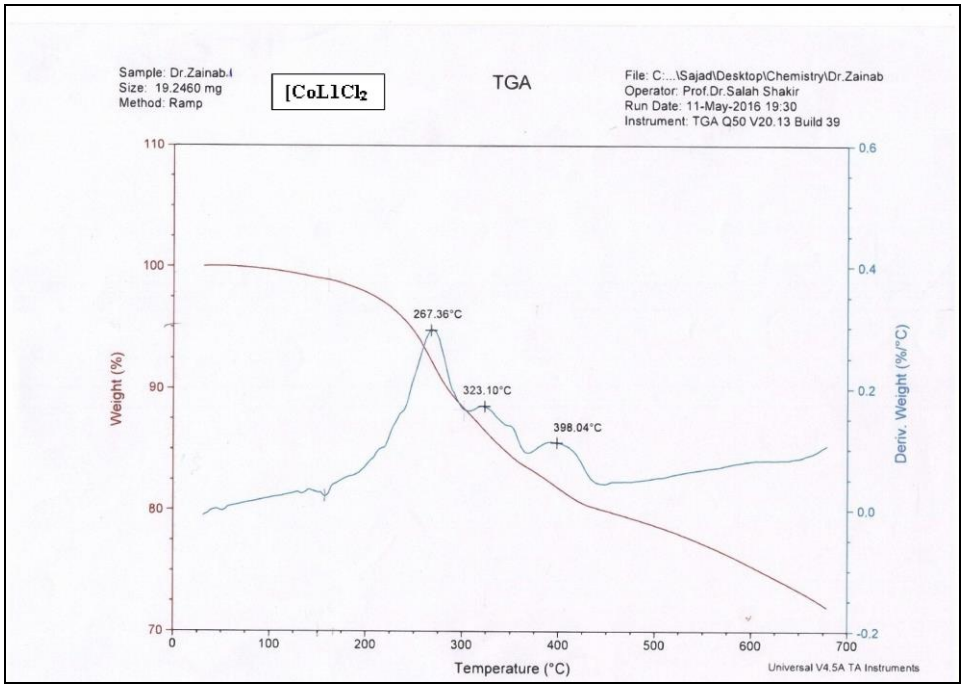


Figure 15: TGA and DTG curves of $[CoL1Cl_2]$ complex

$[CuL2\ (H_2O)_2]Cl_2$ complex

The thermal analysis of this complex was represented in three stages. In the first stage of thermal dehydration of the complex takes place in the temperature range 112-200 ^oC with mass loss 9.23% (calculated 9.1%). The two coordinated water molecules were removed in this step, and the maximum rate of mass loss indicated by DTG peak at 126.15 ^oC [29]. The second stage occurred in the temperature range 200-360℃ with DTG peak observed at 205.07℃ and the observed mass loss was recorded as18.9% (calculated 19.8%), this range correspond to the decomposition of 2Cl atoms of 2HCl [30, 31]. In the third stage, ligand L2 was decomposition in temperature range of 360-700 ^oC with the DTG peak observed at 613.28℃, and the observed mass loss was recorded as 37.3% (calculated 39.34%) (Figure16).

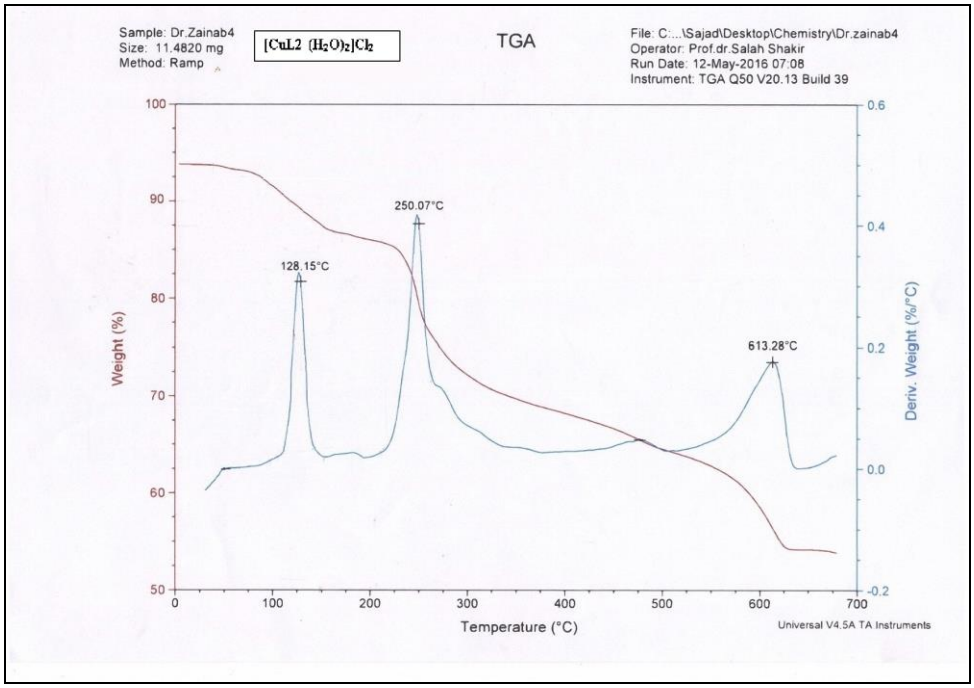


Figure 16: TGA and DTG curves of [CuL2 $(H_2O)_2$]Cl_2 complex.

[CoL2$(H_2O)_2$]Cl_2 complex

The thermal behaviour of this complex has been studied in three stages. In the first stage occurred in the temperature range 100-210 ^oC with mass loss 9.31% (calculated 9.23%). The two coordinated water molecules were removed in this step, and the maximum rate of mass loss indicated by DTG peak at 195.45 ^oC [29]. The second stage occurred in the temperature range 210-380 ^oC with mass loss 8.89 % (calculated 9.02 %), and the DTG peak was observed at 337.48 ^oC, this range correspond to the decomposition of Cl atom of HCl [30, 31]. The third stage was decomposition of ligand L2 in temperature range of 380-700 ^oC with mass loss 41.3% (calculated 42.34%) indicated to loss $CH_3N_3S_2Cl$ [32, 33] with the DTG peak was observed at 589.77 ^oC (Figure 17).

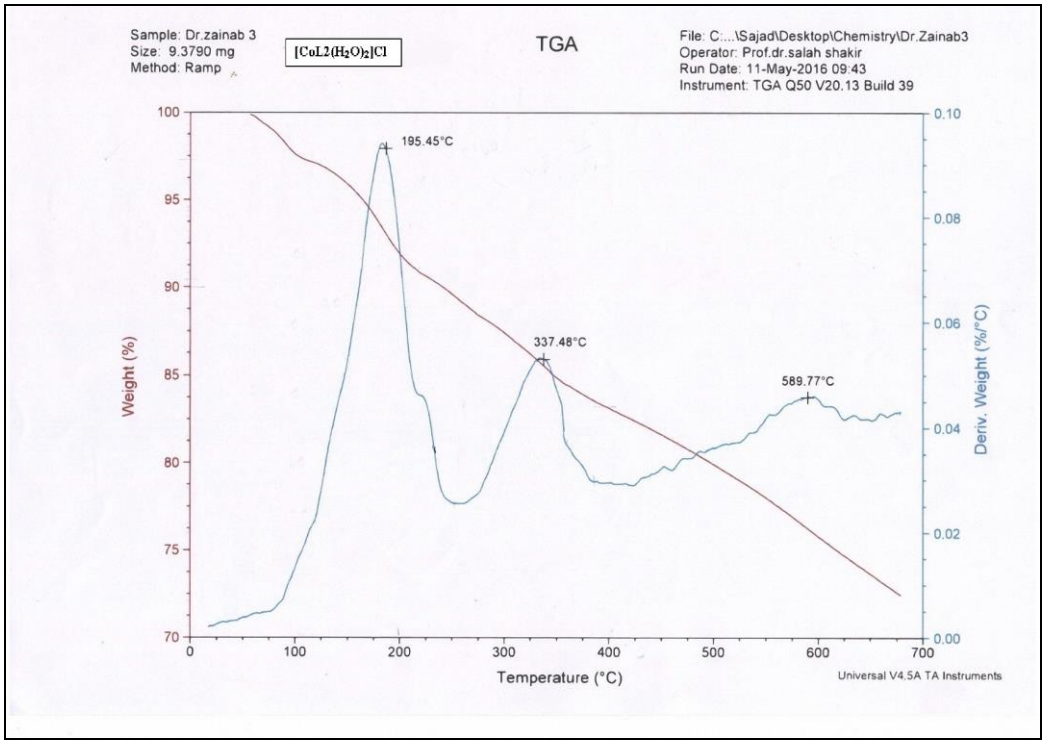


Figure 17: TGA and DTG curves of [CoL2$(H_2O)_2$]Cl_2 complex

Based on the above analytical, spectral and magnetic data together with the thermal decomposition studies, the structural formulas are proposed.

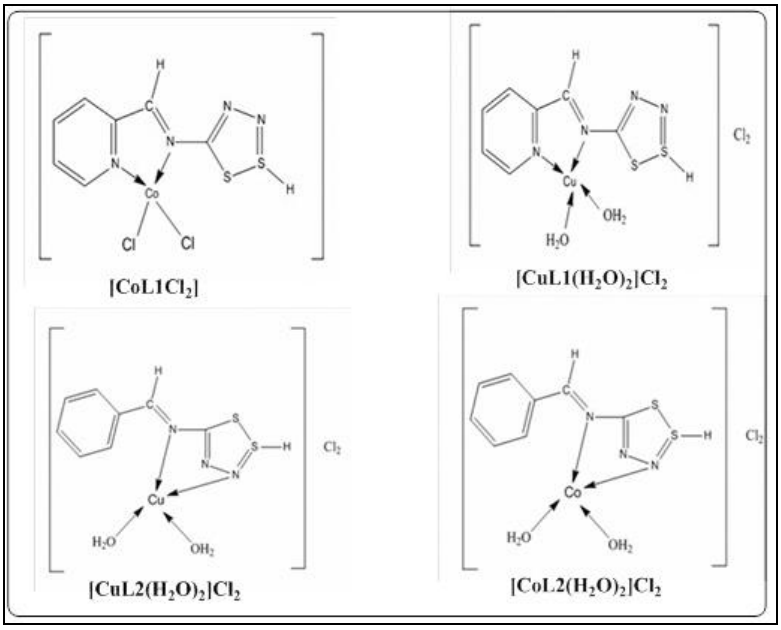


Figure 18: the expected structures of the synthesis complexes

CONCLUSION

In this paper reported the preparation and characterization of a new bidentate Schiff bases namely: (*E*)-*N*-(1,2λ4,3,4-dithiadiazol-5-yl)-1-(pyridin-2-yl) methanimine (L1) and (*E*)-*N*-(1,2 λ4,3,4-dithiadiazol-5-yl)-1-phenyl methanimine (L2) and their complexes. All the complexes are coloured, stable in air and insoluble in water and common solvents but soluble in polar solvent like DMF and DMSO. The analytical data obtained suggested 1:1(M: L) stoichiometry for all complexes. The prepared complexes have electrolytic nature. Based on the above observations of FTIR, electronic spectral data, magnetic, conductance measurements, thermal behaviours and high melting points, proposed the square planar structure for CuL1 and CoL1 complexes and tetrahedral structure for CuL2 and CoL2 complexes.

ACKNOWLEDGEMENTS

The authors are thankful to Prof. Dr. S. Shakir, Science College, Hesham for encouragement during the process of carrying out this work.

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