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# Synthesis, Characterization and Structural Studies of Co(II), Ni(II), Cu(II) and Cd(II) Complexes of Hydrazone Schiff Base Ligands Pyrimidine Derivative

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**Abstract:** The tridentate Schiff base ligands containing donor ONO were prepared by the reaction of 2-Furaldehyde and urea or thiourea with ethyl acetoacetate to product pyrimidine derivatives (1a, 1b) which upon treatment with hydrazine afforded the hydrazide derivatives (2a, 2b) the reaction of (2a, ab) with 3-acetyl coumarin obtained novel Schiff base Ligands ($L_1$, $L_2$) in good yield. The Ligands ($L_1$, $L_2$) were characterized by elemental analysis (C.H.N.S), FT-IR, Uv spectroscopy, HNMR and mass spectral analysis. Complexes of Co(II), Ni(II), Cu(II) and Cd(II) with the novel Schiff base ligands have been prepared. The prepared complexes were identified and their structural geometries were suggested by using elemental analysis (C.H.N.S), FT-IR, UV-Vis spectroscopy and flame atomic absorption technique in additionmagnetic susceptibility, conductivity measurements and thermal analysis TG-DSC. The results suggest that the Schiff base Ligands ($L_1$, $L_2$) coordinate with their tridentate O, N, O donors derived from carbonylamide and azomethine nitrogen and carbonyl oxygen atom on the coumarin ring.

**Key words:** Pyrimidine derivative, coumarine derivative, Schiff base, transition metal complexes, spectral studies, susceptibility

## INTRODUCTION

Pyrimidine derivatives represent very important heterocyclic compounds for their antimicrobial activity (Gulcan *et al*., 2012) and photoluminescence properties (Onal *et al*., 2011). The coordination chemistry of hydrazones system has received an increasing interest because of its play an important role in inorganic chemistry (Pouralimardan *et al*., 2007; Fouda *et al*., 2008) as they easily from stable complexes with most transition metal ions (Yaul *et al*., 2009; Kriza *et al*., 2010). Many of derivatives of this system showed biological significance (Dhande *et al*., 2007). The derivatives of coumarine nucleus have occupied a unique place in field of medicinal chemistry due to wide range of biological activities like antimicrobial (Lamani *et al*., 2009; Farshori *et al*., 2011), anticancer (Bhattacharyya *et al*., 2009), antibacterial activity and antifungal activity of coumarin (Darla *et al*., 2015). Schiff bases and their transition metal complexes have also been widely reported to be biologically versatile compounds having antimicrobial (Kulkarni *et al*., 2009) and antifungal (Mishra and Soni, 2008; Srivastava *et al*., 2014). The present paper describes the preparation of new Schiff's base derivatives produced from the reaction of hydrazide derivatives and 3-acetyl coumarin to be used Ligands ($L_1$, $L_2$) that provide three potential donor sites to from complexes with some transition metal ions. The Ligands ($L_1$, $L_2$) and it's complexes have been fully characterized and their structures were determined as out lined (Fig. 1).

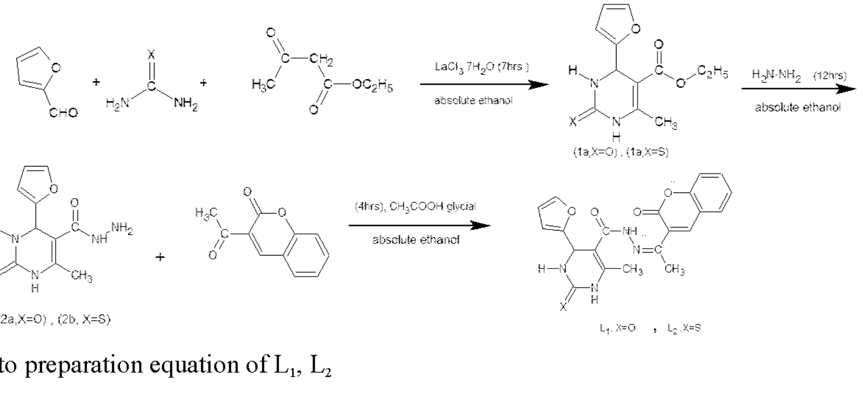

Fig. 1: Referred to preparation equation of $L_1$, $L_2$

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## MATERIALS AND METHODS

All the chemicals used were analytical annular and of highest purity available. Melting points were measured on a Gallan Kamp MFB-600 melting points apparatus. Fourier Transform Infrared (FT-IR) spectra were recorded on a Shimadzu spectrophotometer. Electronic spectra using varian UV-visible spectrophotometer. Elemental analysis for ligand and metal complexes were carried out using CHNS elemental analyzer and atomic absorption using Shimadzu Model 6809. Mass spectra were recorded by Electron Impact Mass Spectrometry (EIMS) using a Direct injection probe on a Shimadzu GCMS-QP5050 A spectrometer. Molar conductivity of the complexes were measured in DMF as solvent in 0.001M solution using a CON 510 bench conductivity meter with 2-ring stainless steel conductivity electrode (Cell constant, K = 1.0) 1HNMR spectra were recorded on Burker DMX-5000 NMR (300-600 MHz) spectrophotometer with using $CDCl_3$ as a solvent in Jordan University. TG and DSC (differential scanning Colorimetry) thermos grams indifferent ranges were carried out at (RT) heating rate = 10°C/min. (Linseis STA university Abn Al-Hitham College.

**Synthesis:** The two ligands were prepared in a similar manner and here the synthesis of ($L_1$, $L_2$) are given:

**Synthesis of pyrimidine derivative (1a), (1b):** Ethyl-4-(furan-2-yl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (1a). Ethyl-4-(furan-2-yl)-6-methyl-2-thioxo-1, 2, 3, 4-tetrahydropyrimidine-5-carboxylate (1b).

Ethyl acetoacetate (1.30 g, 0.01 mole) was addedtothe mixture of 2-furaldehyde (0.96 g, 0.01 mole) and urea (1.80 g, 0.03 mole) or thiourea (2.28 g, 0.01 mole), respectively was dissolved in absolute ethanol (30 mL). To this solution added (0.9 g) from Lanthanum Chloride heptahydrate and the mixture was refluxed for 7 h then cooled at room temperature. The reaction mixture was poured to crushed ice (30 g) with stirring for 10 min. The precipitates (1a, 1b) were filtered and washed with cold water then recrystallized from ethanol.

**Synthesis of hydrazide derivative (2a), (2b):** 4-(furan-2-yl)-6-methyl-2-oxo-1, 2, 3, 4-tetrahydropyrimidine-5-Carbohydrazide.(2a). 4-(furan-2-yl)-6-methyl-2-thioxo-1, 2, 3, 4-tatrahydropyrimidine-5-carbohydazide (2b).

To a solution of compound (1a) (2.5 g, 0.01 mole) or compound (1b) (2.66 g, 0.01 mole), respectively in absolute ethanol (20 mL), hydrazide hydrate (2.5 g, 0.05 mole) was added. The mixture was refluxed for 12 h. The solvent was removed and the solid products (2a, 2b) were collected and crystallized from ethanol.

**Synthesis of Coumarin derivative (C):** A mixture of sailcyldehyde (1.06 g, 0.01 mole) and ethyl aceto acetate (1.3 g, 0.01 mole) in absolute ethanol (20 mL) with drops of tripropyl amine was added. The mixture was refluxed for 5 h. After cooling, the product was filtrated and recrystallized from ethanol.

**Synthesis of hydrazone Schiff base Ligands ($L_1$, $L_2$):** 4-(furan-2-yl)-6-methyl-2-oxo-N-[1-(2-oxo-2H-Chromen-3-yl) ethylidene] -1, 2, 3, 4-tatrahydropyimidene-5-carbohydrazide ($L_1$). 4-(furan-2-yl)-6-methyl-N-[1-(2-oxo-2H-chromen-3-ethylidene]-2-thioxo-1, 2, 3, 4-tetrahydropyrimidine-5- carbohydrazide ($L_2$). A mixture of compound (2a) (2.36 g, 0.01 mole) or compound (2b) (2.52 g, 0.01 mole), respectively and (1.88 g, 0.0 mole) of acetyl coumarin in absolute ethanol (25 mL) with three drops of glacial acetic acid was added. The mixture was refluxed for 4 h and cooled at room temperature. The solid products were collected by filtration and then recrystallized from ethanol. The physical properties of the prepared ligands are given in Table 1.

Table 1: Physical data for (1a, 1b, 2a, 2b, $L_1$, $L_2$) and their complexes

| | | | | Elementa analysis found (Calc.) (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Comp. No. | Colors | M.P.°C | M.wt g/mol | C% | H% | N% | S% | M% | M:L (EtOH) | Suggest formula |
| 1a | Pale yellow | 147 | 250 | --- | --- | --- | --- | --- | ---- | $C_{12}H_{14}N_2O_4$ |
| 2a | Light yellow | 196 | 236 | --- | --- | --- | --- | --- | ---- | $C_{10}H_{12}N_4O_3$ |
| $L_1$ | Yellow | 109 | 406 | 62.32 (62.06) | 4.65 (13.79) | 13.47 | --- | --- | ---- | $C_{21}H_{18}N_4O_5S$ |
| 1b | Light brown | 160 | 266 | --- | --- | --- | --- | --- | ---- | $C_{12}H_{14}N_2O_3S$ |
| 2b | Light grey | 202 | 252 | --- | --- | --- | --- | ---- | ---- | $C_{10}H_{12}N_4O_2S$ |
| L2 | Dark green | 212 | 422 | 59.93 (59.71) | 4.09 (4.26) | 13.52 (13.27) | 7.75 (7.58) | ---- | ---- | $C_{21}H_{18}N_4O_4S(L_2)$ |
| C | Yellowish white | 119 | 188 | --- | --- | --- | --- | --- | ---- | $C_{11}H_8O_3$ |
| $CoL_1$ | Brown | 175 | 535.9 | 47.27 (47.02) | 3.60 (3.35) | 10.21 (10.44) | --- | 10.65 (10.99) | 1:1 | $[Co(L_1)Cl]Cl$ |
| $NiL_1$ | Light brown | 155 | 941.7 | 53.401 | 3.95 | 11.99 | --- | 6.49 | 1:2 | $[Ni(L_1)_2]Cl_2$ |
| $CuL_1$ | Green | 190 | 946.5 | 53.61 (53.24) | 3.63 (3.80) | 11.55 (11.83) | --- | 6.47 (6.70) | 1:2 | $[Cu(L_1)_2]Cl_2$ |
| $CdL_1$ | Light yellow | 180 | 589.4 | 42.51 | 3.30 | 9.40 | --- | 19.32 | 1:1 | $[Cd(L_1)Cl]Cl$ |
| $CoL_2$ | Dark brown | 245d* | 551.9 | 45.48 (45.66) | 3.55 (3.26) | 10.36 (10.14) | 5.42 (5.79) | 10.39 | 1:1 | $[Co(L_2)Cl]Cl$ |
| $CuL_2$ | Brown | 235d* | 978.5 | 51.39 (51.50) | 3.552 (3.67) | 11.41 (11.44) | 6.23 (6.48) | 6.29 | 1:2 | $[Cu(L_2)_2]Cl_2$ |

d* = decompose

**Synthesis of metal complexes:** A hot ethanolic solution of each of metal ion salts (1 m mole) [(0.238 g, of $CoCl_2.6H_2O$), (0.237 of $NiCl_2.6H_2O$), (0.17g of $CuCl_2.2H_2O$) and (0.219 g of $CdCl_2.2H_2O$)], respectively was added to a hot ethanolic solution of Ligand ($L_1$) (0.406 g, 1 m mole) or of Ligand ($L_2$) (0.422 g, 1 m mole), respectively with stirring. The mixture was heated under reflux 2 h during this time the color solid was formed. The products were collected by filtration and then recrystallized from absolute ethanol. The physical data of the prepared complexes are shown in Table 1.

**Study of complexes formation in solution:** Complexes of Schiff base Ligands ($L_1$, $L_2$) with metal ions have been studies in solution using ethanol as a solvent in order to evaluate the ratio of metal to ligand in complex using molar ratio method (Douglas *et al*., 2011). A series of solution have been prepared having a constant concentration $10^{-3}$ M for each metal ion and ligand. The ratio have been determined from the relationship between the absorption of the absorbed light and molar ratio of [M: L] at $\lambda_{m-ax}$ of maximum absorption.

## RESULTS AND DISCUSSION

Reaction between 2-Furaldehyde, (Urea or thiourea) and ethylacetoacetate in absolute ethanol with lanthanum chloride heptahydrate afforded the pyrimidine derivative (1a, 1b) which were treated with hydrazine afforded the hydrazide derivative (2a, 2b). These compounds were treated with coumarin derivative to obtain Ligands ($L_1$, $L_2$) in good yield. Compounds were formed through the following suggest mechanism (Fig. 2):

**Elemental analysis:** The analytical data of Ligands ($L_1$, $L_2$) and it's metal complexes are given in Table 1 and are in a satisfactory agreement with the calculated values. The suggested molecular is formulated and characterized by subsequent spectral and molar ratio as well as magnetic moment.

**$^1$HNMR spectra:** The $^1$HNMR spectrum of the Ligand ($L_1$) in (300 MHz, $CDCl_3$) exhibited (Batterham, 1973) peaks at 1.2 ppm (1H, CH) and 2.3-2.5 ppm (2H, $CH_2$) due to $CH_3$ pyrimidine ring, 3.5 ppm (3H, methyl) (Yaul *et al*., 2009),

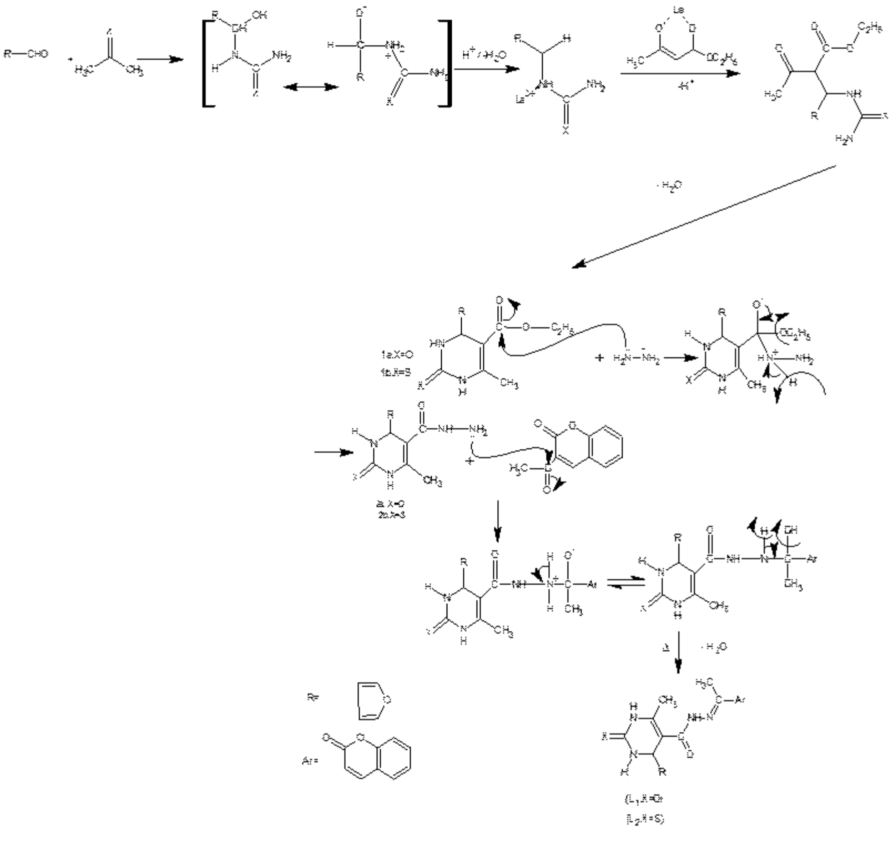

Fig. 2: Referred to preparation steps of $L_1$, $L_2$

4-4.2 ppm (2H, furanyl), 5.3 ppm (1H, furanyl) (Chohan and Kausar, 2000), 9.3 ppm (1H, iminol) (Yaul *et al*., 2009), 6.3-7.9 ppm (6H, Ar-H), 8.6 ppm (2H, NH pyrimidine ring) (Yaul *et al*., 2009; Silverstein *et al*., 1981) (Fig. 1).

**Mass spectra:** The formation of compounds (1a,1b) and Ligand ($L_2$) were studies through their GC-Mass spectrometer. The proposed molecular formula of compounds was confirmed by comparing their molecular formula weight with the m/z values. In the mass spectra of the compounds, peaks were attributed to the molecular ions, m/z:249 for the compound (1a) $C_{12}H_{14}N_2O_4$; 266 for the compound (1b) $C_{12}H_{14}N_2O_3S$; 252 for the compound (2b) $C_{10}H_{12}N_4O_2S$; 188 for the compound (C) $C_{11}H_8O_3$ and m/z: 422 for the Ligand ($L_2$) which data excellent agreement with theoretical values (Srivastava *et al*., 2014; Parikh, 1974; Porter, 1985). These results showed in Fig. 2-5.

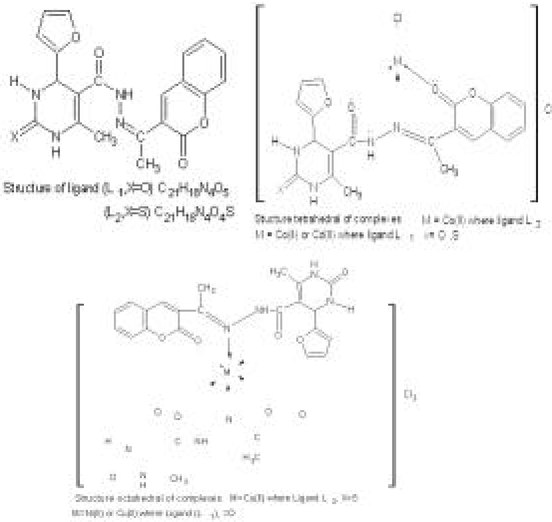

Fig. 3: Referred to preparation steps of $L_1$, $L_2$

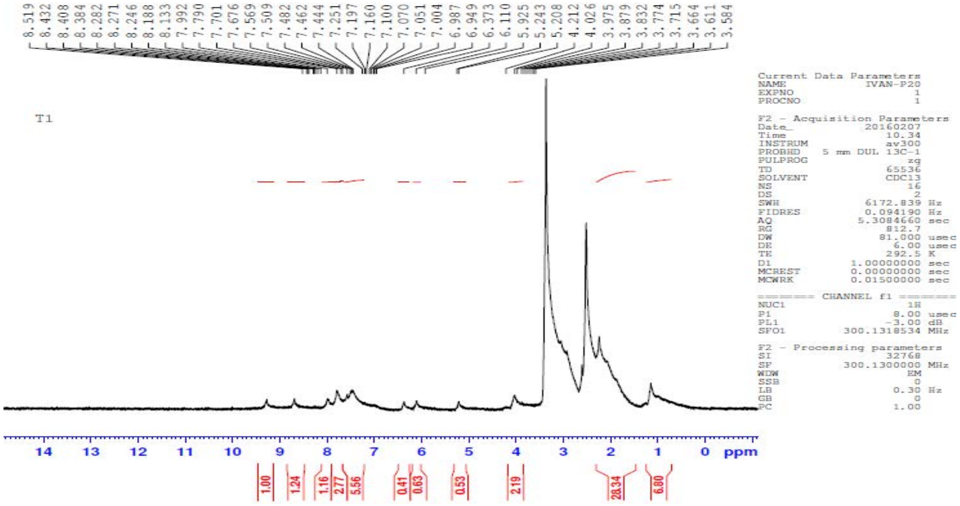

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Fig. 4: $^1$HNMR spectra of free Ligand ($L_1$)

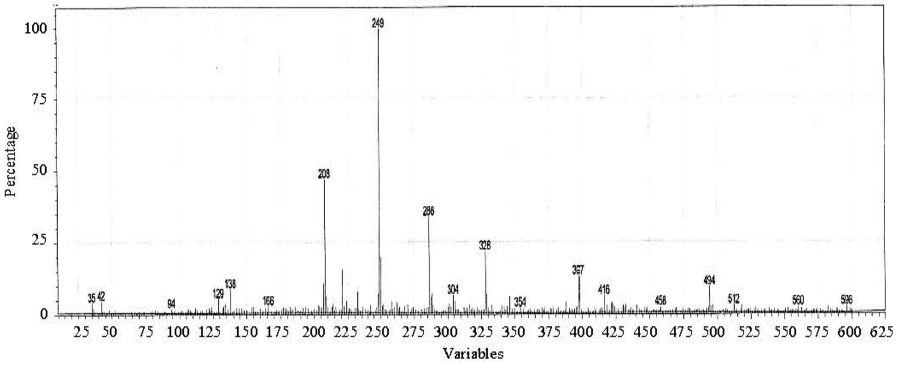

Fig. 5: GC-Mass spectrum of compound (1a)

Table 2: Characteristic infrared absorption frequencies in (cm$^{-1}$) of Ligands ($L_1$, $L_2$) and their metal complexes

| Comp.No. | $\nu C = O_{amide}$ | $VC = N_{azomethine}$ | $VC = O_{coumarine\ ring}$ | M-N | M-O | M-Cl |
|---|---|---|---|---|---|---|
| $L_1$ | 1645 | 1610 | 1699 | ---- | ---- | ---- |
| $CoL_1$ | 1629 | 1589 | 1660 | 570 | 460 | 395 |
| $NiL_1$ | 1625 | 1540 | 1678 | 560 | 455 | ---- |
| $CuL_1$ | 1620 | 1589 | 1687 | 565 | 450 | ---- |
| $CdL_1$ | 1637 | 1558 | 1689 | 555 | 435 | 385 |
| $L_2$ | 1647 | 1600 | 1726 | ---- | ---- | ---- |
| $CoL_2$ | 1639 | 1585 | 1687 | 550 | 445 | 390 |
| $CuL_2$ | 1641 | 1527 | 1697 | 565 | 430 | ---- |

Table 3: Electronic spectra, conductance in (DMF) and Magnetic moment (B.M) for ($L_1$, $L_2$) and their metal complexes

| Comp. NO. | Bands (cm$^{-1}$) | Assignment | Molar Cond. (µs.cm$^{-1}$) | µB.M | Suggested structure |
|---|---|---|---|---|---|
| $L_1$ | 38461 | $\pi\rightarrow\pi^*$ | ----- | ---- | --- |
| | 28490 | $n\rightarrow\pi^*$ | | | |
| $CoL_1$ | 15384 | ${}^4A_2\rightarrow{}^4T_{1(F)}$ | 71 | 4.49 | T.h |
| | 16949 | ${}^4A_2\rightarrow{}^4T_{1(P)}$ | | | |
| | 25974 | C.T | | | |
| $NiL_1$ | 12820 | ${}^3A_2\xrightarrow[\nu_2]{\nu_{13}}t_2g(F)$ | 135 | 2.92 | O.h |
| | 18348 | ${}^3A_2g\xrightarrow[\nu_3]{}t_2 3T1(F)$ | | | |
| | 29069 | ${}^3A_2g\rightarrow{}^3T_1g(P)$ | | | |
| $CuL_1$ | 15267 | ${}^2Eg\rightarrow{}^2T_2g$ | 168 | 1.79 | O.h |
| $CdL_1$ | 47619 | $\pi\rightarrow\pi^*$ | 78 | 0.00 | T.h |
| | 32258 | $n\rightarrow\pi^*$ | | | |
| | 12987 | L→M(C.T) | | | |
| $L_2$ | 35087 | $\pi\rightarrow\pi^*$ | ----- | ----- | ---- |
| | 29154 | $n\rightarrow\pi^*$ | | | |
| $CoL_2$ | 15037 | ${}^4A_2\rightarrow{}^4T_1(F)$ | 66 | 4.52 | T.h |
| | 17921 | ${}^4A_2\rightarrow{}^4T_1(P)$ | | | |
| | 25641 | C.T | | | |
| $CuL_2$ | 14925 | ${}^2Eg\rightarrow{}^2T_2g$ | 159 | 1.83 | O.h |

**Infrared spectroscopic study:** The main stretching frequencies of the IR spectra of the Ligands ($L_1$, $L_2$) and their metal complexes are given in Table 2. The structure of compounds (1a, 1b) were confirmed by the presence of νC = O ester stretching vibration at (1734, 1716) cm$^{-1}$ in addition to the bands at (1215, 1203), (2920, 2990) and (3170-3275) cm$^{-1}$ due to νC = O ester, νC-H and νN-H for pyrimidine ring (Nakamoto, 2009). The reaction of compounds (1a, 1b) with hydrazine hydrate afforded the compounds (2a, 2b), the appearance of IR new absorption bands at (3215-3344) cm$^{-1}$ due to $\nu NH_2$ (Nakamoto, 2009). The structure of compound 3-acetyl Coumarine (C) was confirmed by the appearance of ν(C = O, C-O) coumarin ring stretching frequency at (1735, 1047) cm$^{-1}$ and νC = O ester coumarin stretching frequency at (1674) cm$^{-1}$ (Sonmez and Sekerci, 2002). Moreover, treatment of $NH_2$ in hydrazide derivatives (2a, 2b) with 3-acetyl coumarin to give Schiff base Ligands ($L_1$, $L_2$). These reaction were followed by disappearance absorption bands due to $\nu(NH_2)$ and characteristic bands at (1610,1600) cm$^{-1}$ for azomethine group ν(C = N) are utilized confirm the structures of ($L_1$, $L_2$) (Abon-Melha and Faruk, 2008). The all metal complexes of the Ligands ($L_1$, $L_2$) behave as tridentate coordinating to the metal throw the oxygen of carbonyl (amide and coumarin ring) and nitrogen of the azomethine groups, therefore, the bands due to νC = O and νC = N) were shifted to lower frequencies (Tharmaraj *et al*., 2009), Table 2. These observation were further indicated by the appearance of (νM-O, νM-N and νM-Cl), respectively (Tharmaraj *et al*., 2009) (Table 2).

**Electronic spectra, magnetic moment and conductance studies:** The Uv spectrum of the Ligand ($L_1$) mostly showed two intense maxima bands at 260 nm and 351 nm which belong to π→π* and π→π*, respectively (Silverstein *et al*., 1981), (Fig. 6) while the Uv spectrum of the Ligand ($L_2$) showed intense bands at 285 and 343 nm which belong to π→π* and π→π*, respectively (Silverstein *et al*., 1981) (Fig, 7 and Table 3). The solution spectra of the Cobalt (II) complex for the Ligand ($L_1$) showed three band at (15384,16949) cm$^{-1}$ due to ${}^4A_2\rightarrow{}^4T_{1(F)}$, ${}^4A_2\rightarrow{}^4T_{1(P)}$ with charge transfer band at 25974 cm$^{-1}$ (Fig. 8), these bands correspond to those of tetrahedral geometry (Mohamed *et al*., 2006), magnetic moment of the solid complex (4.49B.M) showed a high spin Co(II) complex (Nicholls, 1973). Conductivity measurement in DMF showed that the complex was conductive behavior (Table 3). The solution spectra of the Ni(II) complex exhibited a well-discernable band with a shoulder on the low energy side the bands genera -lly observed in the region at (12820, 18348, 29069) cm$^{-1}$ are assigned to ${}^3A_2g_{(F)}\rightarrow{}^3T_2g_{(F)}$, ${}^3A_2g_{(F)}\rightarrow{}^3T_1g_{(F)}$ and ${}^3A_2g_{(F)}\rightarrow{}^3T_1g_{(P)}$ transition, respectively (Singh *et al*., 2010) (Fig. 9). The magnetic

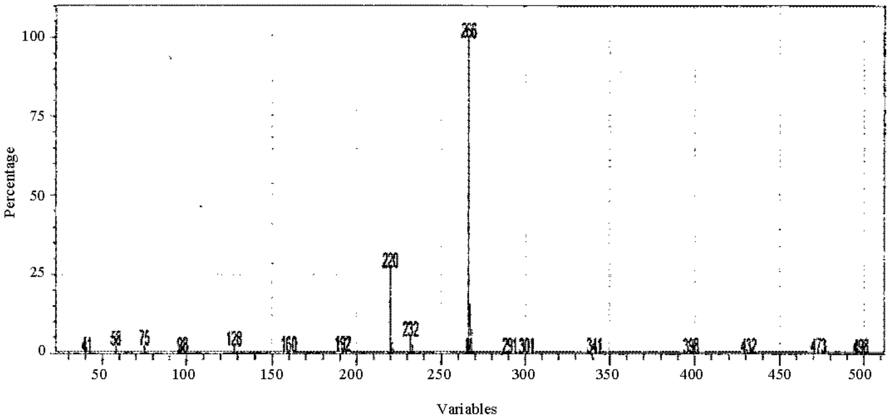

Fig. 6: GC-Mass spectrum of compound (1b)

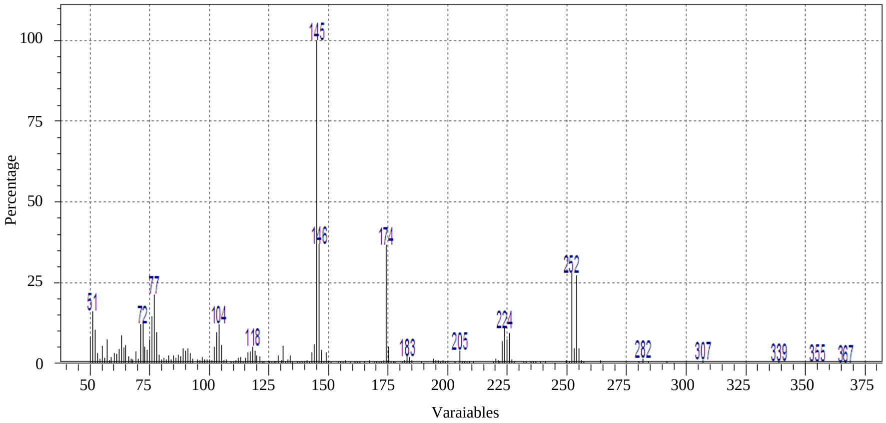

Fig. 7: GC-Mass spectra of compound (2b)

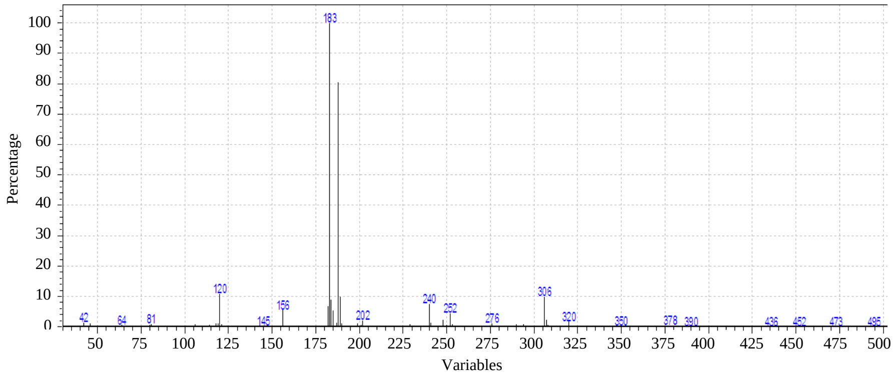

Fig. 8: GC-Mass spectrum of compound (C)

moment of the Nickel complex at room temperature was (2.92 B.M) showing an octahedral environment around the Ni(II) ion in the complex (Kriza *et al*., 2010), table. Conductivity measurement in DMF showed an electrolyte behavior of the complex. The electronic absorption spectrum of Cu(II) complex for the Ligand ($L_2$) exhibits a band at15267 cm$^{-1}$ that was assigned to the $^2Eg \rightarrow ^2T_2g$ transition, suggesting octahedral geometry around the Cu(II) ion. The magnetic moment value of this complex was (1.79 B.M) which indicates the presence of one unpaired electron per Cu(II) ion (Lever, 1984). The conductivity measurement showed that the complex was

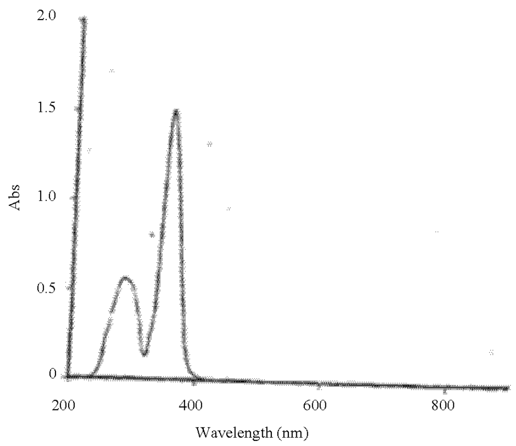

Fig. 9: UV-visible spectrum of $(L_1)$

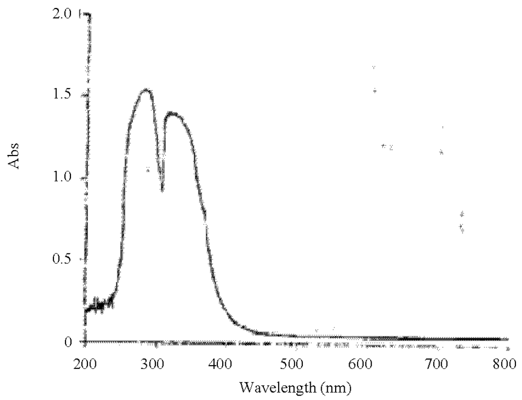

Fig. 10: UV-visible spectrum of Ligand $(L_2)$

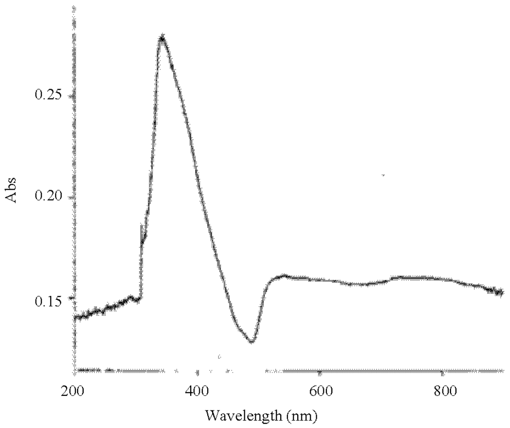

Fig. 11: UV-visible spectrum of $NiL_1$ complex

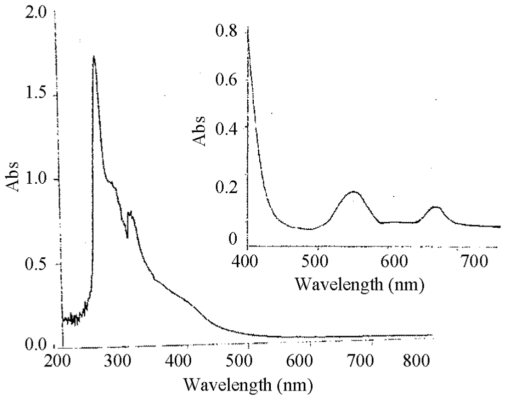

Fig. 12: UV-visible spectrum of $CoL_2$ complex

to be ionic, Table 3, Cd (II) complex show no absorption peak at range (380-1000) nm that indicates no d-d electronic transition happened ($d^{10}$-system) invisible region that is a good result for Cd (II) tetrahedral complex (Abid *et al*., 2016). Conductivity measurement in DMF showed that the complex was to be ionic (Table 3). The solution spectrum of the prepared Co(II) complex for the Ligand $(L_2)$ showed three bands at (15037, 17921) $cm^{-1}$ due to $^4A_2 \rightarrow {}^4T_{1(F)}$, $^4A_2 \rightarrow {}^4T_{1(P)}$ with charge transfer band at (25641) $cm^{-1}$ (Fig. 10) these bands correspond to those of tetrahedral geometry (Al-Hasani *et al*., 2011). The value of the magnetic measurement (4.52 B.M) showed a high spin Co(II) complex (Earnshaw, 1968). Conductivity measurement in DMF showed that complex was due to be ionic (Table 3). The electronic spectrum of Cu(II) complex for Ligand $(L_2)$ gave broad band at (14925) $cm^{-1}$ which assigned to $^2Eg \rightarrow {}^2T_2g$ transition of the octahedral geometry (Al-Jibori *et al*., 2013). The magnetic moment value was (1.83 BM) corresponding to one unpaired electron (Rasheed *et al*., 2014). Conductivity measurement in DMF showed a conductive behavior of this complex (Table 3).

**Thermal degradation of ligand and complexes:** The TG data a suggest a mechanism for degradation of the complexes of $[Cu\,(L_1)_2]Cl_2[Co(L_2)Cl]Cl$, to 351°C. while the $[L_2]$ and Complex of $[Cu\,(L_2)_2]Cl_2$ to 600°C. The thermal degradation of $[L_2]$ display in Fig. 11. The thermo gram curve show three decomposition steps. The TGA peak observed at 259.59°C assigned to the loss of (C-O) furfural group fragment, (det.1.43 mg, 6.63%; calcu. = 1.40 mg). The other steps occurred at 437.5°C revealed the loss of (COO) of coumarin ring, (obs.2.31 mg, 11.20%; calcu. = 2.34 mg). The third step of decomposition of compound 592.9 is related to the loss (CH = CHO) furfural ring, (obs.2.46 mg, 11.74%; calcu. = 2.30 mg). The differences in the weight may be related to a sublimation process occurred at high temperature. The DSC curve recorded peaks at 84.3, 269.6 which refer to an exo thermic

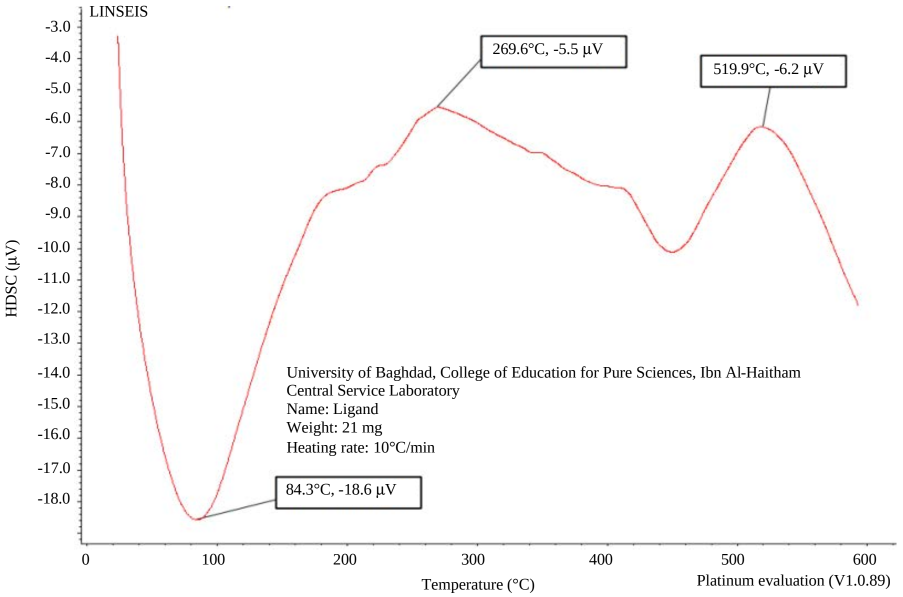

Fig. 13: DSC thermogram of an argon atmosphere [$L_2$]

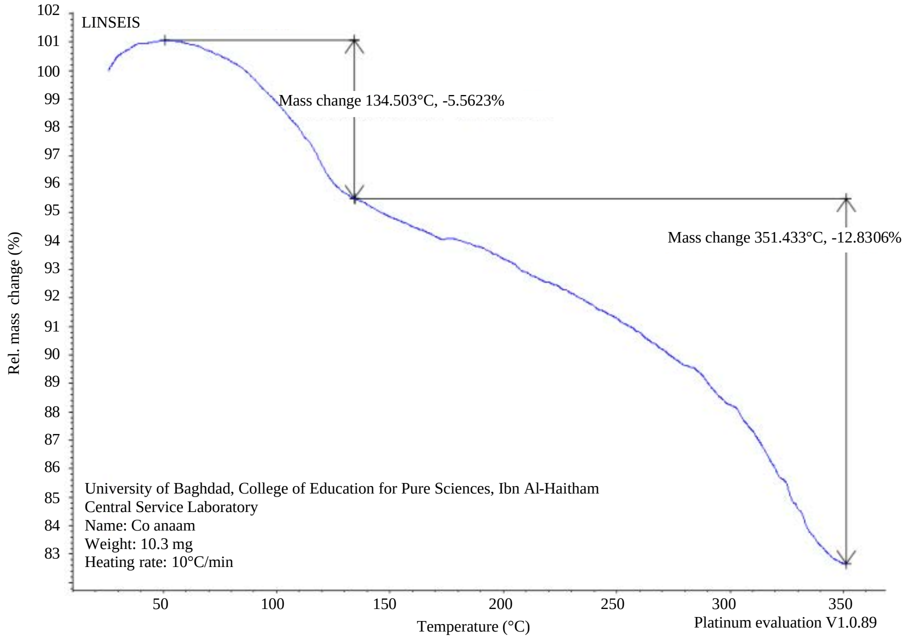

Fig. 14: TG thermogram of an argon atmosphere [$Co(L_2)$]$Cl_2$

decomposition process (Abid *et al*., 2016) (Fig. 12). The thermal analysis clearly indicated that the decomposition of the complexes of [$Co(L_2)Cl$] is shown in Fig. 13-16 which indicated the complex is stable up in 134°C. The TGA peak observed at 134°C assigned to the loss of Cl coordination outer sphere (counter ions), (det = 0.51 mg, 5.56%; calcu. = 0.5749 mg. Figure 13 and 14 TG thermo gram of an argon atmosphere of [$Cu(L_2)_2$]$Cl_2$, [$Cu(L_1)_2$]$Cl_2$, respectively (Al-Bayati *et al*., 2018). The molecular model using Hyperchem. Program for $L_1$, $Cd(L_1)$ complex, $L_2$ and $CoL_2$ complex were indepicted, respectively in Fig. 18 and 19. According to these results the structure configuration of ligands and these metal complexes may be proposed in Fig. 16-21.

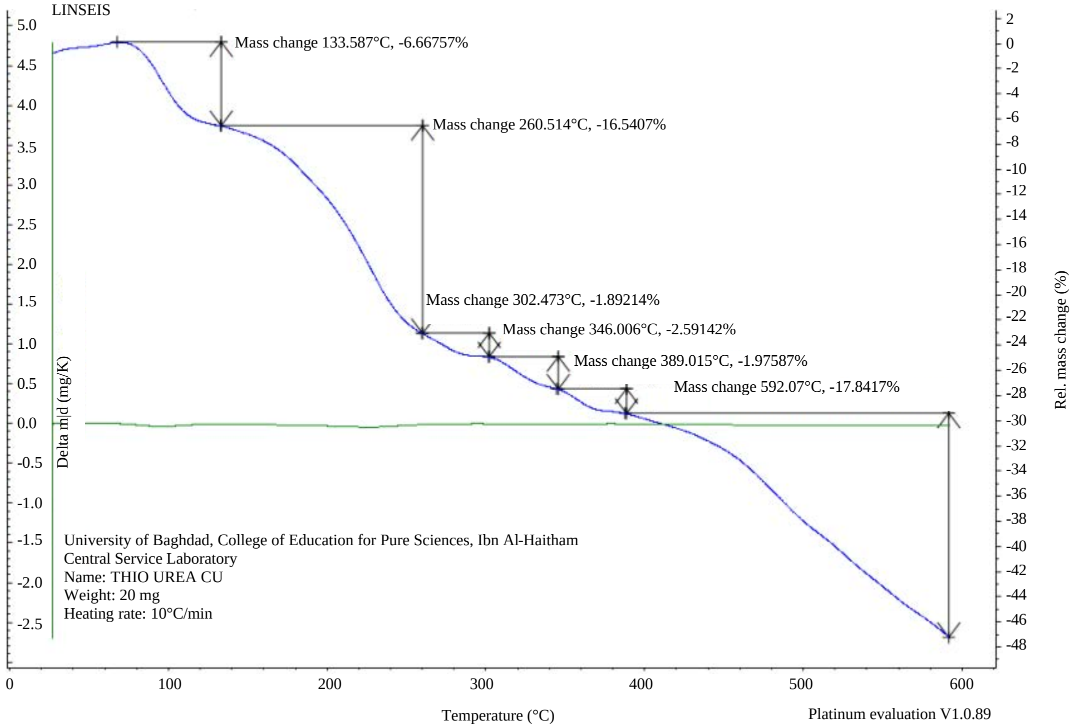

Fig. 15: TG thermogram of an argon atmosphere [Cu($L_2$)2]$Cl_2$

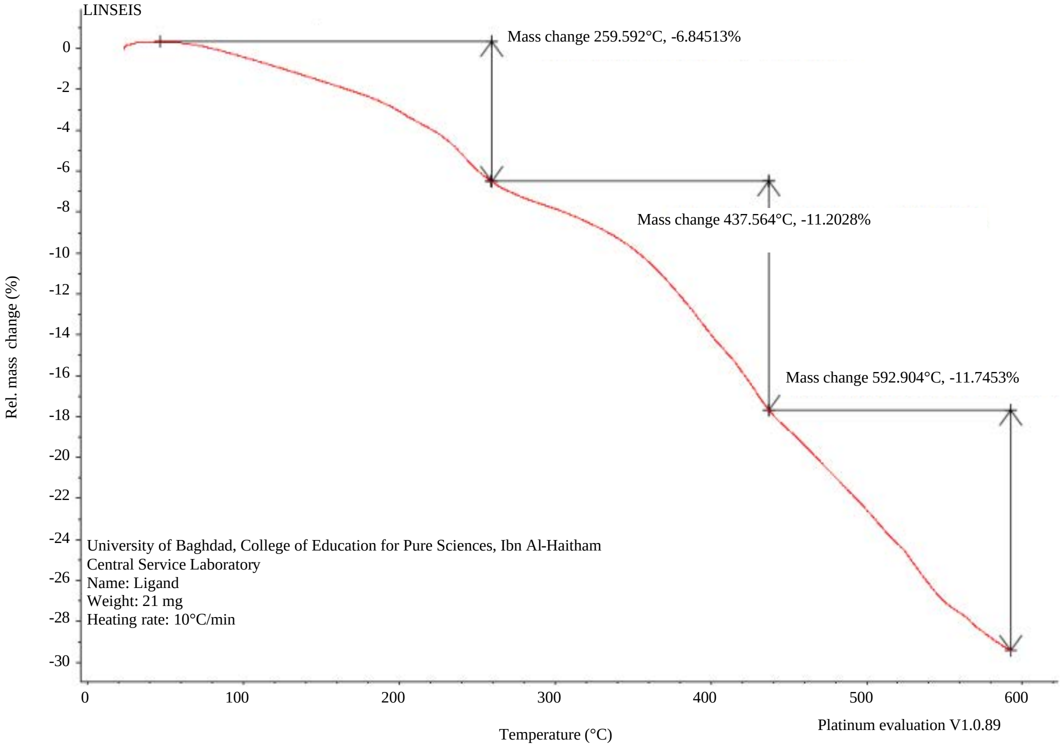

Fig. 16: TG thermogram of an argon atmosphere [$L_2$]

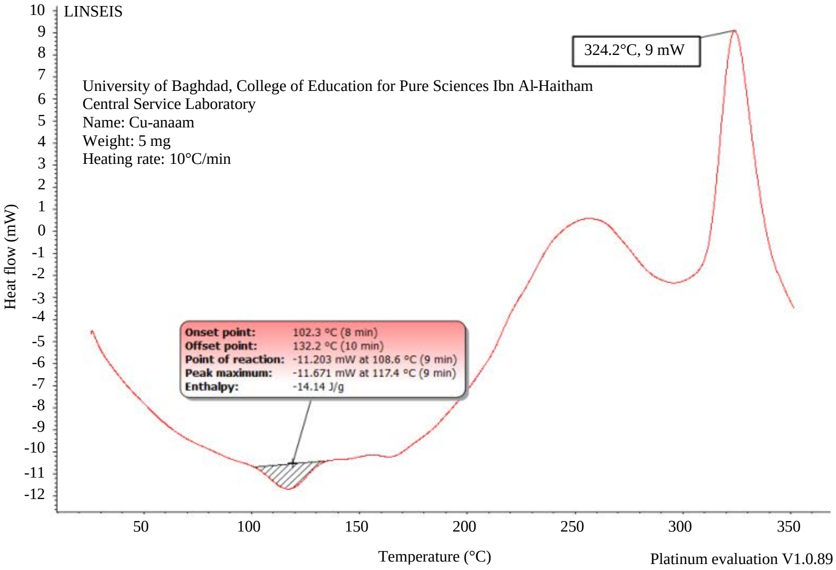

Fig. 17: DSC thermogram of [Cu $(L_1)2]Cl_2$ an argon atmosphere

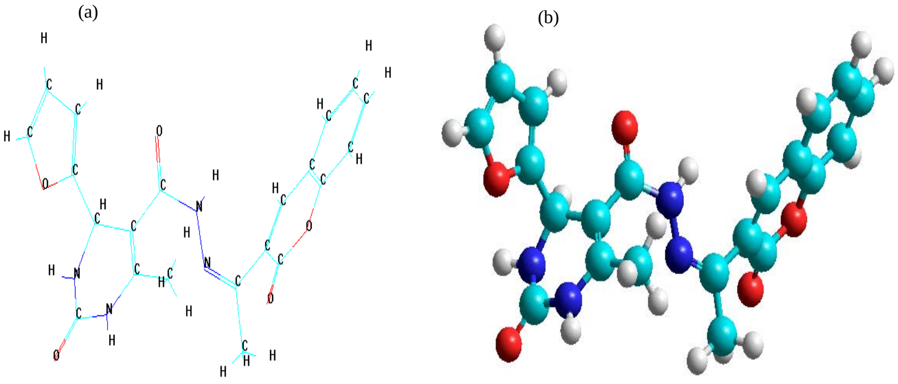

Fig. 18: a, b) The proposed molecular structure of Ligand [$L_1$]

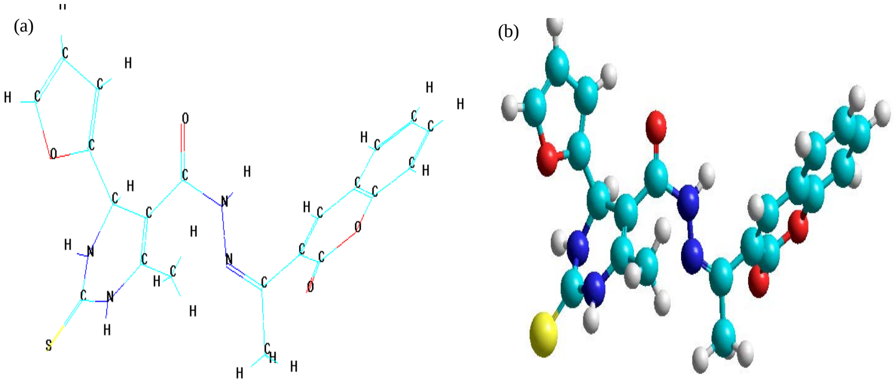

Fig. 19: a, b) The proposed molecular structure of Ligand [$L_2$]

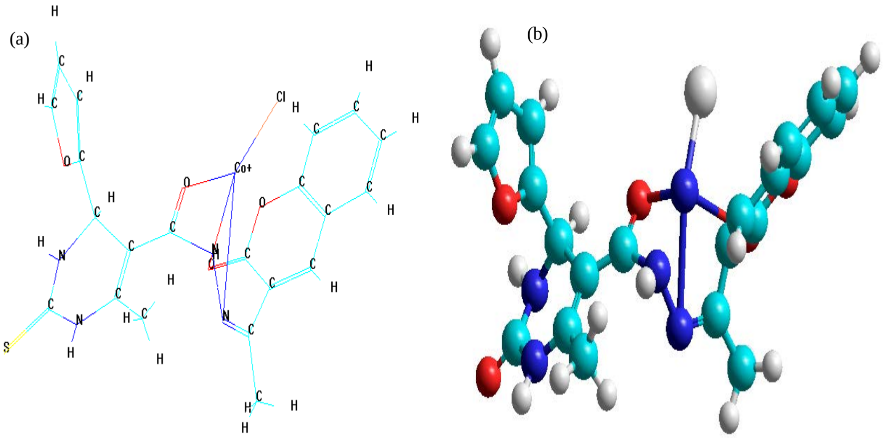

Fig. 20: a, b) The proposed molecular structure of $[Co(L_2)Cl]C_1$

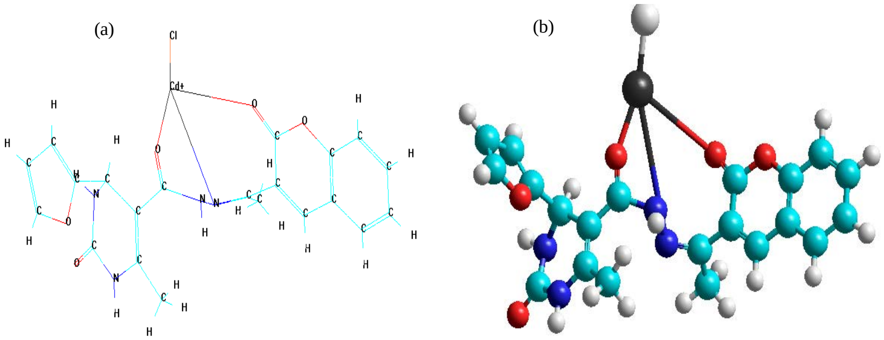

Fig. 21: a, b) The proposed molecular structure of $[Cd(L_1)Cl]C_1$

## CONCLUSION

We have prepared two Schiff base Ligands ($L_1$, $L_2$) the ligands behave as tridentate ligand through (O, N, O) atoms. According to the results obtained from GC-Mas spectra and elemental analysis (C.H.N.) gave formula $C_{21}H_{18}N_4O_5$) ($L_1$) and $C_{21}H_{18}N_4O_4S$($L_2$). Spectroscopic (FT-IR, HNMR) data showed the structure of the ligand contain azomethine and carbonyl groups. From conductivity measurements showed that all prepared complexes are ionic as well as magnetic moment, Uv-visible study and the molecular model using Hyper Chem for [$CoL_1$,$CdL_1$ and $CoL_2$] complexes have tetrahedral geometry and [$NiL_1$, $CuL_1$ and $CuL_2$] complexes have octahedral geometry.

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