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# Synthesis and structural characterization of some transition metal complexes with cyclic $N_2OS_2$ ligand

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**ABSTRACT**

*The reaction of two equivalents of cystamine [2-mercaptoethyl ammonium chloride] with one equivalent of cis-dichloroethene in a methanolic solution of potassium hydroxide gave the diamine compound which reacted in suit with 2,6-diformyl -4- methyl phenol to give cyclic ligand with $N_2OS_2$ donor atoms is formed [$H_1L$]. Also neutral complexes of this ligand with different metal ions were prepared. Ligand and its complexes were characterized by microanalysis spectroscopic methods [FT-IR, U.V- Vis, NMR, Mass], a long with molar conductivity and magnetic moment measurements from the above data the proposed molecule structure was suggested.*

**Keywords**: Schiff base, dichloroethene, NOS donor, ligand, polydentate, complexes.

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## INTRODUCTION

Schiff bases constitute an important class of polydentate ligands. The direct approach of synthesizing a Schiff base containing azomethine group (>C=N) formed by condensation of primary amine and carbonyl compounds are known as imine. Schiff's base derivatives are the subject of renowned interest because they have been found to be useful intermediates for the synthesis of various heterocyclic compounds and have a wide variety of application in many fields. Schiff's bases have been posses antimicrobial activity, anti-malarial, anticancer, antioxidant, anti-tuberculosis, and anticonvulsant. The reaction of aromatic amine such as o-hydroxy, o- amine, or o- mercaptoamino- , with a carbonyl compound, some time gives undesirable side reaction involving ring closure with the formation of a heterocyclic compound[1].

There is a considerable interest in the design and synthesis of ligands consisting of both soft and hard donors to accommodate metal ions for fine- tuning their properties. According, unsymmetrical polydentate ligands with a nitrogen, oxygen and sulfur donor atoms [referred to as NSO ligands] have received much attention recently, due to the distinct trans effect of these donors[2]. Furthermore, hetero-tridentate NSO ligands resulted from the combination of NOS displaying unique feature in manipulating the catalytic activity on polymerization [3].

The great interest in synthetic macrocycles and their corresponding metal complexes is related to the fact they can mimic naturally- occurring macrocyclic molecules in their structural features. The formation of macrocyclic complexes depends significantly on the dimension of the internal cavity, on the rigidity of macrocycle, on the nature of its donor atoms and on the complexing properties of the counterion.The syntheses of the macrocyclic ligands are generally carried out in the presence of a suitable salt. [4].

## EXPERMENTAL SECTION

**Chemicals**: all common laboratory chemicals and reagents were from Aldrich and Fluka and have been used without further purifications.

**Measurements:**
An electrothermal apparatus Stuart melting point was used to measure the melting points. Infrared spectra were done with Shimadzu FTIR Shimadzu, Japan and Ultraviolet-Visible spectra with 1601PC, Shimadzu, Japan. Conductivity measurements were recorded at CDM 83 conductivity - meter (25ºC) for ($10^{-5}$-$10^{-3}$) M solutions of the samples in DMSO or DMF.

Mass spectra for ligands and some complexes were obtained by (+) Laser adsorption technique using BRUKER DALTONICS. All isotopes distribution was compared to a computer generated distribution pattern. The spectra were recorded at Queen Mary, London University / United Kingdom.

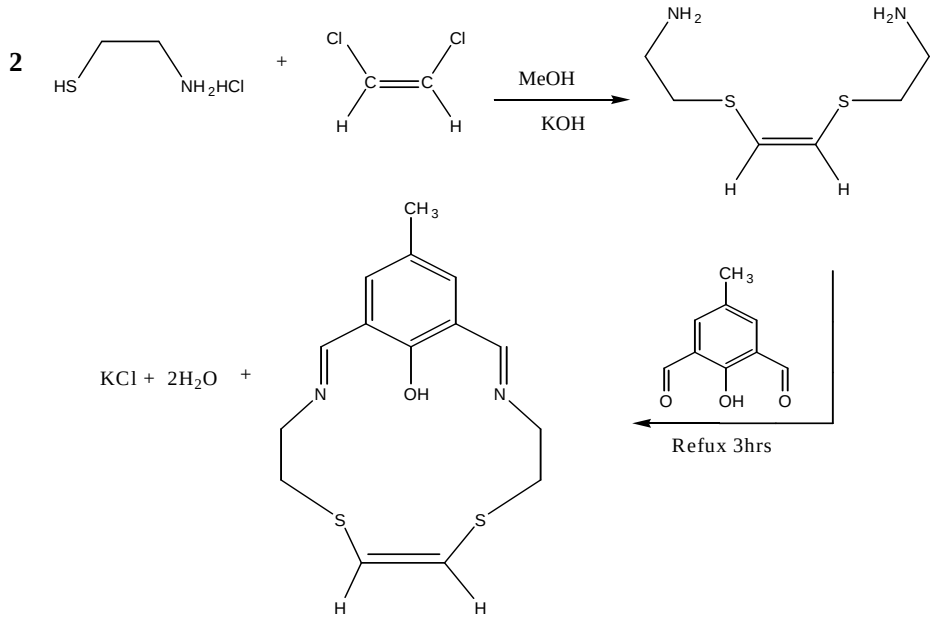
$^{1}$H-, $^{13}$C-, $^{1}$H - $^{1}$H, and $^{1}$H - $^{13}$C correlated NMR spectra for the ligands and some complexes were recorded in DMSO-d6 , $_{D2O}$ using a Brucker 400 MHZ , Ex 400 MHZ and a Jeol 270 $MH_Z$ instruments with a tetramethylsilane (TMS) as an internal standard . The samples were recorded at Queen Mary/ University of London/United Kingdom. Elemental microanalyses were performed on a (C.H.N) analyzer, from Herause (Vario EI) at Free Berlin University/ Germany.

**Synthesis of 2,6- diformyl -4 methyl phenol:**[5,6]
To a solution of p-cresol (10 mmole) in (50 ml) acetic acid, hexamethylene tetraamine (20 mmole) and (100 mmole) of paraformaldehyde were added. The mixture was allowed to stirred continuously until the light brown viscous solution was obtained then heated to (70- 90ºC) for 2 hrs. The solution was cooled to room temperature and concentration $H_2SO_4$ (10 ml) carefully added.

The resulting solution was refluxed for 30 min. and then on treatment with distilled water (400 ml) a light yellow precipitate was formed which was stored overnight at (40ºC). The yellow product was isolated by filtration and washed in small a mount of cold methanol more pure product was obtained by means a recrystallization from toluene, yielded (35%), m. p(132- 134ºC). Elemental microanalysis for this precursor was C% 65.85 (65.66), H% 4.91 (4.87).

**Synthesis of ligand [$H_1$L]**
To (0.113g, 0.08 ml, 0.67 mmole) of tetrachloroethene was added dropwise a solution to potassium hydroxide (0.08g, 1.3 mmole) in (15 ml) methanol. The reaction mixture was stirred vigorously and refluxed for 30 minutes. After cooling, potassium chloride was removed by filtration, then a solution of 2- mercapto ethyl ammonium chloride (0.159, 1.37 mmole) in methanol (15 ml) was added gradually.

The reaction mixture was stirred and refluxed for four hours. The reaction mixture (yellow solution) cooled to room temperature, then 2, 6 diformyl-4 methyl phenol (5.0g, 30 mmole) dissolved in (20 ml) of ethanol was added gradually; the reaction mixture was refluxed for three hours, and a yellow precipitate was observed after refluxing for one hour. The precipitate was filtered off and washed several time with (1,2- dichoromethane).



**Scheme (1): The Synthesis Route of [$H_1L$]**

**Table (1): Microelemental analysis results and some physical properties of the prepared [$HL^2$]**

| compound | Empirical Formula | Yield % | m.p (C°) | colour | Found (calc.) % | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | H | N |
| [$H_1L$] | $C_{15}H_{18}Cl_2N_2OS_2$ | 83 | 250-252 | Yellow orange | 48.00 | 4.30 | 7.46 |
| | | | | | (48.70) | (4.34) | (7.40) |

**[$H_1L$] – Metal ions complexes:**

(1.4 mmole) of metal ion salt dissolved in methanol (10ml) was added dropwise to a solution of [$H_1L$] (0.26 g, 0.7 mole) dissolved in (15 ml) methanol. The reaction mixture was stirred and PH was adjusted to Ca 9 by adding methanolic potassium hydroxide. The reaction mixture was filtered off, and allowed to reflux for two hours. The (Brown) precipitate was formed which filtered off, washed several time with absolute ethanol and dried.Somephysical properties of the prepared [$H_1L$] and its complexesshowed in table (2).

**Table (2): The Quantities Reaction Condition and some Physical Properties of The Prepared [$H_1L$] Complexes**

| Empirical Formula | colour | m.p ºC | Wt of metal ion = $1.4\times10^{-3}$ mole | Wt. of product (g) | Yield % |
|---|---|---|---|---|---|
| [$Mn_2$(L)] | Black brown | >250 dec | 0.28 g | 0.45 | 84 |
| [$Fe_2$(L)] | Red | 250 – 254 | 0.18 g | 0.35 | 85 |
| [$Co_2$(L)] | Deep brown | 255 – 258 | 0.34 g | 0.48 | 82 |
| [$Ni_2$(L)] | Light Brown | 256 – 258 | 0.33 g | 0.49 | 85 |
| [$Cu_2$(L)] | Light green | >250 dec | 0.24 g | 0.42 | 84 |
| [$Zn_2$(L)] | Deep yellow | 260 – 264 | 0.19 g | 0.33 | 80 |
| [$Cd_2$(L)] | Yellowish white | 260 – 264 | 0.32 g | 0.42 | 82 |
| [$Hg_2$(L)] | Pale yellow | >280 dec | 0.38 g | 0.52 | 85 |

## RESULTS AND DISCUSSION

In general, acyclic ligand was prepared to change the properties of the ligands from hydrophilic to lipophilic and to change reduction-oxidation behavior of the prepared complexes by imposing different substituents on the backbone. 2,6-Diformyl- 4-methyl phenol] was obtained in a moderate yield (35 %) as a yellow crystalline solid with m.p (132–134) ºC, andwas soluble in ethanol, methanol, and water. Also, this compound was characterized by using $^1$H-NMR and $^{13}$C-NMRspectra as previously published [6].The ligand showed a good solubility in $H_2O$, DMSO, DMF, EtOH, and MeOH but not $CH_2Cl_2$ or $CHCl_3$.

The (UV–Vis) spectrum for [$H_1L$] exhibits three high intense absorption bands at (276 nm) (36231 $cm^{-1}$) ( $\varepsilon_{max}$ = 4000 $molar^{-1}$ $cm^{-1}$) (343 nm) (29154 $cm^{-1}$) ($\varepsilon_{max}$ = 4000 molar $^{-1}$ $cm^{-1}$) and (440 nm) (27727 $cm^{-1}$) ($\varepsilon_{max}$ = 2121 molar $^{-1}$ $cm^{-1}$ ) which are assigned to ( $\pi \rightarrow \pi^*$), ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively.

The FTIR spectrum of the tetrachloroethene showed characteristic band at (1580) $cm^{-1}$ attributed to the ν(C=C) stretching. The two bands at (520 and 450) $cm^{-1}$ were assigned to the ν(C-Cl) symmetric and asymmetric stretching vibration bands respectively. Also the two bands at (360, 240) $cm^{-1}$ assigned to δ (C-Cl) out of plane and in plane bending vibration, these bands have been disappeared in the spectrum of the prepared ligand [$H_1L$], and new sharp double bands are observed at (1628 and 1600) $cm^{-1}$ due to asymmetric and symmetric stretching of the (C=N) groups[7,8,9], as a result of intramolecular hydrogen bonding (N----H—O).

The medium band at (1458) $cm^{-1}$ is assigned to ν(C=C) aromatic stretching vibration. These results are in agreement with several reported[9,10]. The broad bands observed at (1285 and 3403) $cm^{-1}$ assigned to ν(C–O) and ν(O–H) respectively[10,11].

While the bands at (1047 and 763) $cm^{-1}$ were assigned to ν(C–S) and ν(C–Cl) stretching vibration, which is in a good agreement with that reported by Shipman and co-workers[12]. Also, the medium bands observed at (990 and 850) $cm^{-1}$ were assigned to the macrocyclic framework[13].

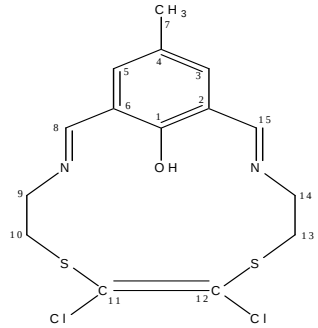


**Table (3): Infrared Spectral Data ($cm^{-1}$) of the Ligand and Starting Materials**

| Compounds | ν (C=N) | ν (C=C) | ν (C–S) | ν(CH) ali ν(CH) ar | ν(C–O) | ν($CH_2$) | ν(OH) | ν(C-Cl) |
|---|---|---|---|---|---|---|---|---|
| tetrachloroethene | | 1580m | | | | | | 450m 520m |
| Cystamine | | | 1100 w | | | 2900m | | $2525_{(w)}$ |
| $H_1L^2$ | $1628_{(s)}$ 1600 | 1458 | $1041_{(m)}$ | $2918_{(w)}$ 2845 | $1228_{(m)}$ | $1350_{(m)}$ | $3403_{(br)}$ | 763 |
| $H_3L^1$ | 1649 $1633_{(s)}$ | 1450 | $1066_{(m)}$ | $2925_{(w)}$ 2870 | 1215m | $1350_{m)}$ | $3390_{(br)}$ | $2525_{(w)}$ |

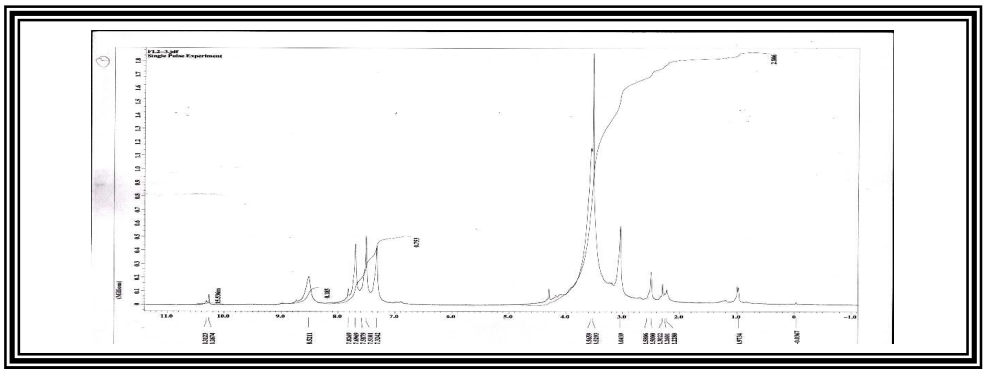
$^1$H-NMR spectrum for [$H_1L$] in DMSO-$d^6$ displayed, a singlet signal at chemical shifts ($\delta_H$=10.26 ppm, 1H, S) attributed to the proton of the (O–*H*) phenolic group [(11)]. The signals at chemical shift ($\delta_H$ = 8.45 and $\delta_H$ = 7.65 ppm, 2H, S), (N=$C_{8,15}$-*H*). Which is equivalent to two protons are assignable to protons of the azomethine groups[(11,14)].

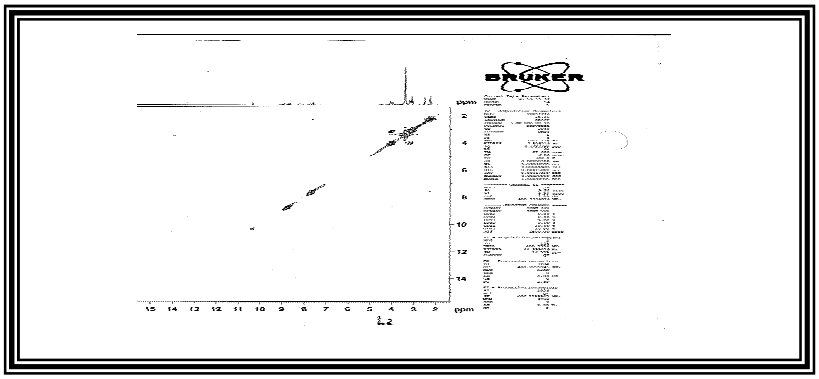
The appearances of azomethine protons in deferent chemical shift is due to hydrogen bonding ( N…..H—O ). The resonances at chemical shift ($\delta_H$ = 7.27 and ($\delta_H$= 7.46 ppm , 2H, d), (Ar–H) , ($J_{H-H}$= 13.5 Hz) are assignable to protons of aromatic ring[(15,16)] (Ar–$C_{3,5}$) . The appearances of these protons as a doublet is due to mutual coupling[(15,16)] .

The resonance for methylene (N–C$H_2$) groups[(11,17)] is located at ($\delta_H$ = 3.66 – 2.24 ppm) range (4H, S, N-C$H_2$ ), ad jacent to ($C_{9,14}$), as can be seen from the spectrum the resonance at chemical shift ($\delta_H$ = 3.04 ppm, 4H, S, –SC$H_2$), is assignable to protons of the (–SC$H_2$) methylene groups[(11,17)] ($C_{10,13}$).

The sharp singlet signal at ($\delta_H$ = 2.21 ppm) equivalent to three protons (3H,S) is attributed to the protons of methyl group[(11,14)]. ($C_7$).The above chemical shift assignments were supported by $^1$H–$^1$H, 2D, correlated NMR spectra.

**Figure (1): $^1$H-NMR Spectrum of [$HL^2$] in DMSO-$d^6$**





**Figure(2): $^{1}$H–$^{1}$H, 2D Correlated NMR Spectrum of [HL$^{2}$] in DMSO-d$^{6}$**

The $^{13}$C-NMR spectrum for [$H_1$L] showed in DMSO-d$^{6}$ solvent displayed, the two azomethine group are non equivalent and appeared at chemical shift ($\delta_c$ = 168.81 and 192.21 ppm). Also, the spectrum showed the two (C-N) groups are non equivalent and appeared at ($\delta_c$=65.51 ppm and $\delta_c$=35.61 ppm).

The differences in the chemical environment can be attributed to the hydrogen bonding between the hydrogen of the phenolic group and the nitrogen of an azomethine group. This result is in accordance with that observed in the $^{1}$HNMR spectrum in which the two azomethine groups are non equivalents due to the hydrogen bonding with the (OH) group.

Also, these results supported that observed in the IR spectrum in which the hydrogen bonding is occurred in the solid state and in solution[11]. The chemical shift of the aromatic carbon atoms are shown at ($\delta_c$= 118.53 ppm, Ar–$C_2$), ($\delta_c$=124.51 ppm, Ar–$C_{3,5}$), (δc=129.23ppm, Ar–$C_4$), ( δc=140.34ppm, Ar–$C_6$) and ($\delta_c$=149.43 ppm, Ar–$C_1$) [18,19,20].

The chemical shift at ($\delta_c$=63.51 ppm) assigned to ethylene carbon atoms ($C_{9,14}$-N) and ($C_{10,13}$-S) respectively[20], while the resonance at ($\delta_c$=73.53 ppm) is due to the halide carbon, $C_{11,12}$-Cl)[11]. The appearance of the chemical shift at down field is related to the halide moiety. The resonance at chemical shift $\delta_c$=21.50 ppm assigned to methyl group ($C_7$)[19]. The $^{1}$H–$^{13}$C, 2D correlated NMR spectrum supported these results, which are in a good agreement with the reported results [20].

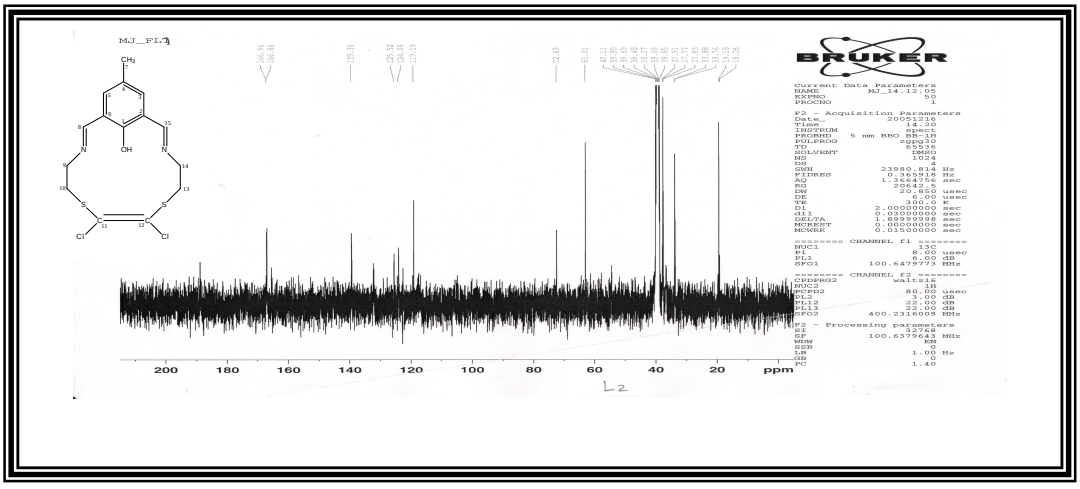


**Figure (3):$^{13}$C-NMR Spectrum of [HL$^{2}$] in DMSO-d$^{6}$**

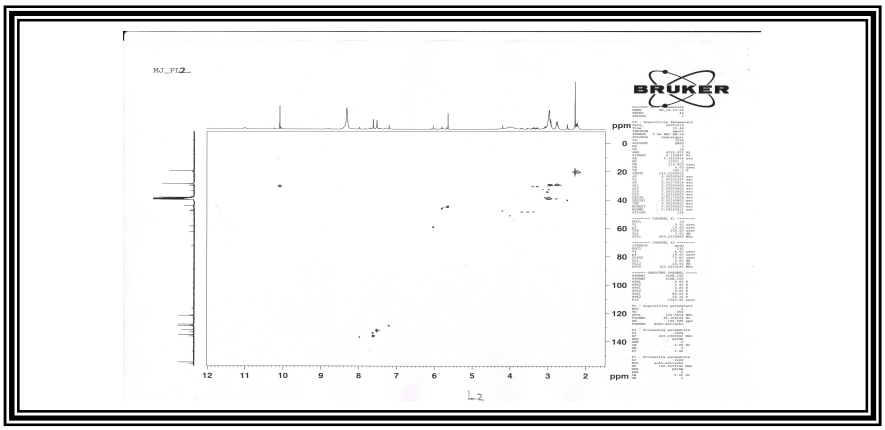



**Figure (4):$^{1}$H–$^{13}$C, 2D Correlated NMR Spectrum of [HL$^{2}$] in DMSO-d$^{6}$**

The laser adsorption (+) mass spectrum of the ligand [$H_1L$] showed the parent ion peak at ( M/Z ) = 374.53, which corresponds to [$M^+$], other fragments and their relative abundance and fragmentation sequence is shown below.

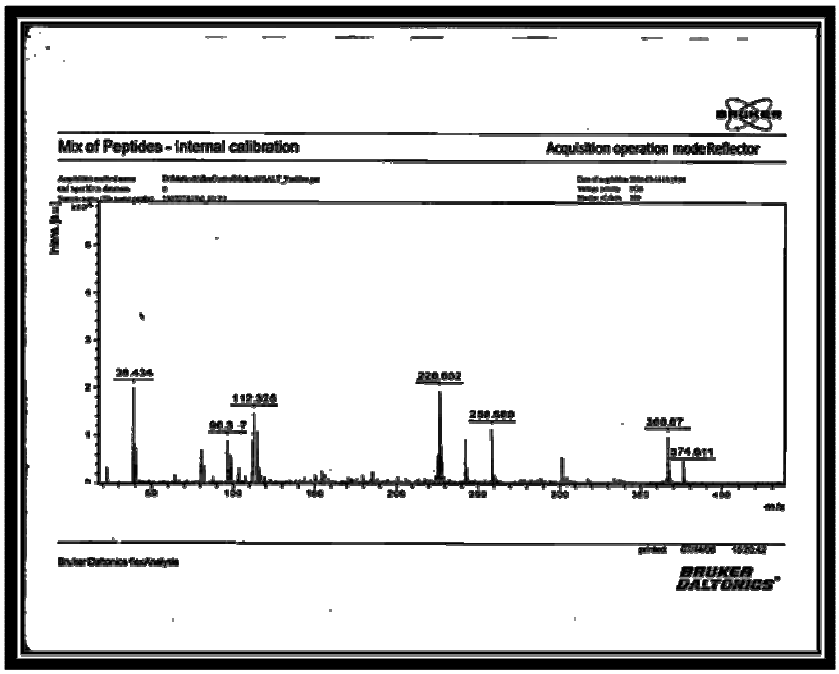
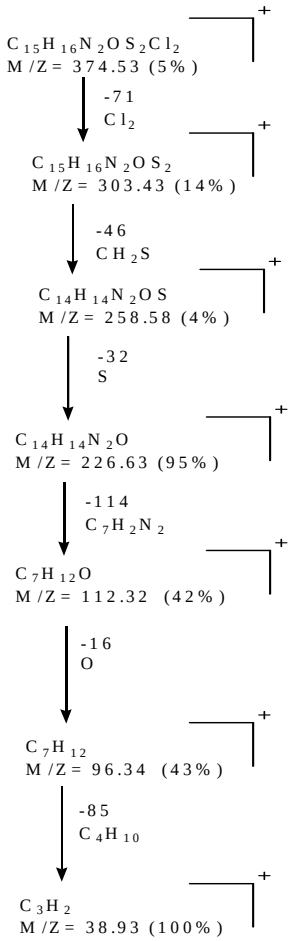
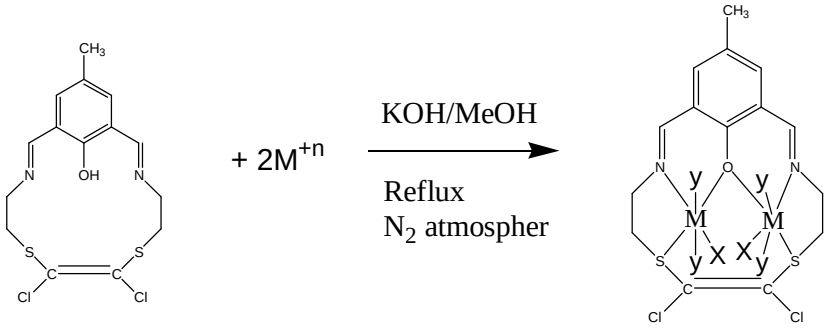



**Figure (5): The Laser Adsorption (+) Mass Spectrum of the Ligand[ HL$^{2}$]**




**Scheme (2): The Fragmentation Sequence of The Ligand [$H_1L$]**

The complexes were prepared by a similar method, form the reaction of the ligands with metal chloride salt, according to general method shown below.




**Where: M=$Cr^{+3}$,$Co^{+2}$ : X=Cl : Y=$H_2O$ : n= +3, +2 :m=+1,-1**
**M=Mn : X=$H_2O$ : Y=$H_2O$ : n= +2 :m=+1**
**M=Fe,Cu,Zn,Cd,Hg : X=$H_2O$ : Y=0 : n= +2 :m=+1**
**M=Ni : X=Cl : Y=0 : n= +2 :m=-1**

Solubility of the prepared complexes, microanalysis of the complexes with metal and chloride analyses, spectroscopic methods [IR, UV–Vis, Laser adsorption(+) mass spectroscopy, $^1$HNMR], molar conductivity measurements, and melting point were used to characterize these complexes.

The FTIR spectra of the complexes showed the double bands at (1628 and 1609) $cm^{-1}$ corresponding to asymmetric and symmetric stretching ν(C=N) in the free ligand [$H_1L$], are shifted to lower frequency and appear as a double bands at (1622, 1595) $cm^{-1}$ and (1633, 1598) $cm^{-1}$ for two complexes in which the two (C=N) are non equivalent.

**Table (4): Elemental Analysis Results of [$H_1L$]and Its Metal Complexes**

| Empirical Formula | M.wt. | Microanalysis found , (Calc. ) % | | | | |
|---|---|---|---|---|---|---|
| | | C | H | N | Metal | Cl |
| $C_{15}H_{16}Cl_2N_2OS_2$ | 374.01 | 48.00 | 4.30 | 7.46 | —— | 18.90 |
| | | 48.20 | 4.40 | 7.56 | | |
| $[Cr_2C_{15}H_{15}Cl_2N_2OS_2(H_2O)_2Cl_4]Cl$ | 691.48 | 26.52 | 2.81 | 4.13 | 14.98 | 36.03 |
| | | (26.03) | (2.74) | (4.05) | (15.03) | (35.93) |
| $[Mn_2{}_{15}H_{15}Cl_2N_2OS_2(H_2O)_4Cl_2]Cl$ | 662.36 | 27.35 | 3.01 | 3.94 | 16.60 | 27.02 |
| | | (27.19) | (2.87) | (4.22) | (16.61) | (26.81) |
| $[Fe_2C_{15}H_{15}Cl_2N_2OS_2Cl)_2]Cl$ | 592.18 | 30.91 | 2.72 | 5.11 | 20.31 | 30.51 |
| | | (30.40) | (2.53) | (4.72) | (18.41) | (24.98) |
| $K[Co_2C_{15}H_{15}Cl_2N_2OS_2(H_2O)_2Cl_4]$ | 708 | 26.02 | 2.86 | 3.49 | 17.02 | 31.21 |
| | | (25.42) | (2.68) | (3.95) | (16.66) | (30.08) |
| $[Ni_2C_{15}H_{15}Cl_2N_2OS_2Cl)_2]Cl$ | 597.92 | 31.21 | 2.69 | 4.86 | 20.63 | 30.10 |
| | | (30.10) | (2.50) | (4.68) | (19.63) | (29.68) |
| $[Cu_2C_{15}H_{15}Cl_2N_2OS_2Cl_2]Cl.H_2O$ | 625.58 | 24.02 | 2.71 | 4.95 | 20.91 | 28.97 |
| | | (28.77) | (2.71) | (4.47) | (20.30) | (28.37) |
| $[Zn_2C_{15}H_{15}N_2OS_2Cl_2Cl_2]Cl.H_2O$ | 628.24 | 29.32 | 2.77 | 4.22 | 21.53 | 29.02 |
| | | (29.07) | (2.74) | (4.52) | (21.12) | (28.67) |
| $[Cd_2C_{15}H_{15}Cl_2N_2OS_2Cl_2]Cl$ | 705.3 | 25.02 | 2.41 | 3.95 | 31.31 | 25.31 |
| | | (24.89) | (2.35) | (3.87) | (30.98) | (24.55) |
| $Hg_2C_{15}H_{15}Cl_2N_2OS_2Cl_2]Cl.H_2O$ | 898.62 | 20.91 | 1.92 | 3.15 | 44.92 | 20.02 |
| | | (20.03) | (1.84) | (3.11) | (44.64) | (19.75) |

*(Calc.) Calculated*

**Table (5): Infrared Spectral Data ($cm^{-1}$) of The Ligand [$HL^2$] Complexes**

| Compounds | ν (C=N) | ν (C=C) | ν(S-$CH_2$) | ν(C–S) | ν(C–H)Ali ν(C–H)Ar | ν(–$CH_2$) | ν(C–O) | ν(–OH) | ν (OH) | ν(C–Cl) | Additional peak ν (M-N), ν (M-O), ν (M-S) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $[Cr_2(L)(H_2O)_2Cl_4]Cl$ | $1622_{(s)}$ 1595 | 1460 1498 | ——— | $1058_{(m)}$ | $2929_{(w)}$ 2817 | 1352 | $1236_{(m)}$ | $3390_{(br)}$ | $838_{(w)}$ | 763 | 519, 499, 420 |
| $[Mn_2(L)(H_2O)_4Cl)_2]Cl$ | $1623_{(s)}$ 1598 | 1446 | 1120 | $1037_{(m)}$ | $2920_{(w)}$ 2862 | 1350 | $1230_{(m)}$ | $3404_{(br)}$ | $833_{(w)}$ | | 551, 524, 414 |
| $[Fe_2(L)Cl_2]Cl.H_2O)$ | $1620_{(s)}$ | 1446 1548 | 1184 | $1039_{(m)}$ | $2918_{(w)}$ 2858 | 1346 | $1232_{(m)}$ | $3415_{(br)}$ | $836_{(w)}$ | 763 | 524, 501, 450 |
| $K[Co_2(L)(H_2O)_2Cl]_4]$ | $1623_{(s)}$ 1600 | 1448 1544 | 1193 | $1054_{(m)}$ | $2920_{(w)}$ 2817 | 1350 | $1236_{(m)}$ | $3463_{(br)}$ | 804 | 761 | 561, 518, 450 |
| $[Ni_2(L)Cl_2]Cl$ | $1620_{(s)}$ | 1454 | 1137 | $1058_{(m)}$ | $2920_{(w)}$ 2873 | 1348 | $1234_{(m)}$ | $3388_{(br)}$ | ——— | | 450, 408 |
| $[Cu_2(L)Cl_2](Cl.H_2O$ | $1627_{(s)}$ | 1450 1552 | 1122 | $1047_{(m)}$ | $2921_{(w)}$ 2862 | 1348 | $1232_{(m)}$ | $3407_{(br)}$ | $825_{(w)}$ | 763 | 501, 474 |
| $[Zn_2(L)Cl_2]Cl.H_2O$ | $1629_{(s)}$ | 1448 1542 | 1186 | $1043_{(m)}$ | $2923_{(w)}$ 2858 | 1348 | $1236_{(m)}$ | $3429_{(br)}$ | 810 $867_{(w)}$ | 771 | 580, 511, 450 |
| $[Cd_2(L)Cl_2]Cl.H_2O$ | $1622_{(s)}$ | 1444 1517 | ——— | $1054_{(m)}$ | $2920_{(w)}$ 2858 | 1348 | $1224_{(m)}$ | $3409_{(br)}$ | 844 | 765 | 580, 550, 460 |
| $[Hg_2(L)Cl_2]Cl.H_2O$ | $1622_{(s)}$ 1595 | 1448 1531 | 1108 | $1043_{(m)}$ | $2923_{(w)}$ 2854 | 1350 | $1228_{(m)}$ | $3394_{(br)}$ | $833_{(w)}$ | 763 | 585, 550, 440 |

While with other complex, these bands appeared as a single band at (1620) $cm^{-1}$. These bands can be assigned to the ν(C=N) stretching of reduced bond order due to delocalization of metal electron density into the ligand π –system forming a π- back bonding [21,22]. The medium band at (1228) $cm^{-1}$ assigned to ν(C-O) stretching for the ligand is shifted by *Ca*. (8-2) $cm^{-1}$ to higher frequency and appeared at (1236, 1230 and 1232) $cm^{-1}$.

This is presumably due to the increase in bond order character of (C-O) upon complexization with metal ion. The medium ν (C-S) stretching band in the free ligand at (1041) $cm^{-1}$ is shifted and appeared at (1058, 1037 and 1039) $cm^{-1}$ confirming the coordination of the ligand through sulfur atoms to the metal ion [23].

The bonding of metal ions to the ligand through the nitrogen, oxygen and sulfur atoms is further supported by the presence of new bands at (572-535, 538-505)$cm^{-1}$ and (480-420) $cm^{-1}$, ranges due to ν(M-N) , ν(M-O) and ν(M-S) stretching vibration [19,24] . The medium band at 763 $cm^{-1}$is attributed to ν(C-Cl) stretching[12].

The (UV–Vis) spectra of the prepared complexes showed an intense peak in the (U.V) region assigned to ligand field and charge transfer transition while in the visible region assigned to (d-d) transition type ($^4A_2g^{(F)} \rightarrow {}^4T_2g^{(F)}$ ), ($^6A_2g^{(F)} \rightarrow {}^6T_2g$),($B_2 \rightarrow E$), ($^4T_1g^{(F)} \rightarrow {}^4T_1g^{(p)}$), ($A_1g \rightarrow B_1g$) and ($^2B_1g \rightarrow {}^2Eg$) which can be used to characterize the

transitions[25-27]. Metals that did not show(d-d) transitions made the stereochemistry of their complexes can not be derived from the electronic spectra.

**Table (6): Electronic Spectral Data of [$H_1L$] and Its Metal Complexes**

| Compound | wave length λ nm | wave number $\bar{\nu}$ $cm^{-1}$ | $\varepsilon_{max}$ $molar^{-1}$ $cm^{-1}$ | Assignment | Proposed structure |
|---|---|---|---|---|---|
| [$H_1L$] | 276 | 36231 | 4000 | $\pi \rightarrow \pi^*$ | |
| | 343 | 29154 | 4000 | $n \rightarrow \pi^*$ | |
| | 440 | 27727 | 2121 | $n \rightarrow \pi^*$ | |
| [$Cr_2(L)(H_2O)_2Cl_4$]Cl | 285 | 35087 | 415 | Ligand field | Octahedral |
| | 430 | 23809 | 90 | $^4A_2g^{(F)} \rightarrow {}^4T_2g^{(F)}$ | |
| [$Mn_2(L)(H_2O)_4Cl_2$]Cl | 270 | 37037 | 2499 | Ligand field | Octahedral |
| | 395 | 25316 | 1094 | $^6A_2g \rightarrow {}^6T_2g$ | |
| [$Fe_2(L)Cl_2$]Cl.$H_2O$ | 271 | 36900 | 556 | Ligand field | Tetrahedral |
| | 711 | 14064 | 40 | $B_2 \rightarrow E$ | |
| K[$Co_2(L)(H_2O)_2Cl_4$] | 270 | 37037 | 778 | Ligand field | Octahedral |
| | 430 | 27255 | 210 | Charge transfer | |
| | 664 | 15060 | 71 | $^4T_1g^{(F)} \rightarrow {}^4T_1g^{(P)}$ | |
| [$Ni_2(L)Cl_2$]Cl | 271 | 36900 | 450 | Ligand field | Tetrahedral |
| | 406 | 34578 | 150 | $A_1g \rightarrow B_1g$ | |
| [$Cu_2(L)Cl_2$]Cl.$H_2O$ | 270 | 37037 | 2970 | Ligand field | Square planar |
| | 343 | 29154 | 1219 | Charge transfer | |
| | 408 | 24509 | 50 | $^2B_1g \rightarrow {}^2Eg$ | |
| [$Zn_2(L)Cl_2$]Cl.$H_2O$ | 289 | 34602 | 3957 | Ligand field | Tetrahedral |
| | 403 | 24813 | 3436 | Charge transfer | |
| [$Cd_2(L)Cl_2$]Cl.$H_2O$ | 271 | 36900 | 3564 | Ligand field | Tetrahedral |
| | 401 | 24937 | 2157 | Charge transfer | |
| [$Hg_2(L)Cl_2$](.Cl.$H_2O$) | 279 | 35842 | 4000 | Ligand field | Tetrahedral |
| | 344 | 29069 | 1521 | Charge transfer | |
| | 427 | 23419 | 546 | Charge transfer | |
| Recorded in DMF | | | | | |

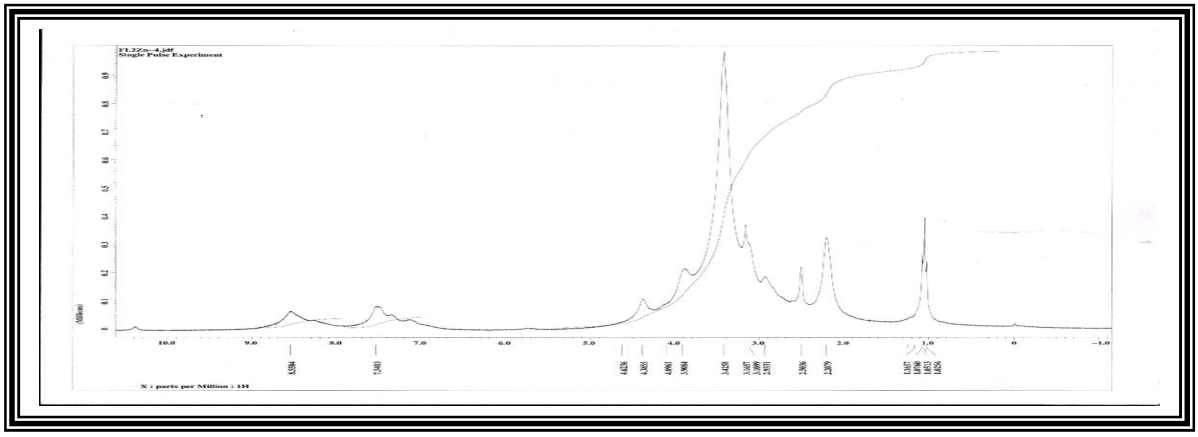


**Figure (7): $^1$H-NMR Spectrum of [$Zn_2(L^2)Cl_2$]Cl.$H_2O$**

The$^1$H NMR spectrum for the complex [$Zn_2(L)Cl_2$]Cl.$H_2O$, showed, no signals in the (δ=10.26 ppm), which indicated the losing of the (O-*H*) upon complexization. The signals at (δ= 8.55 and 7.54 ppm) assigned to (N=C-*H*) and (Ar-*H*) protons respectively which shifted to down field compared to that in the free ligand.

The appearance of the signal of azomethine (N= C-*H*) as a doublet may be related to the slightly difference in the chemical environment of the two groups. The methyl and methylene group protons have same positions as in the free ligand.

The$^1$H NMR spectrum for the complex [$Hg_2(L)Cl_2$]Cl.$H_2O$, showed, no signals in the (δ=10.26ppm), which indicated the losing of the(O-*H*) complexization. The doublet signal at (δ=8.62 and 8.54 ppm) and sharp signal at (δ=7.54 ppm) refer to (N= C-*H*) and (Ar–*H*) protons respectively which shifted to down field compared to that in the free ligand. The appearance of the signal of azomethine (N= C-*H*) as a doublet may be related to the slightly difference in the chemical environment of the two groups. The methyl and methylene group protons have same positions as in the free ligand.

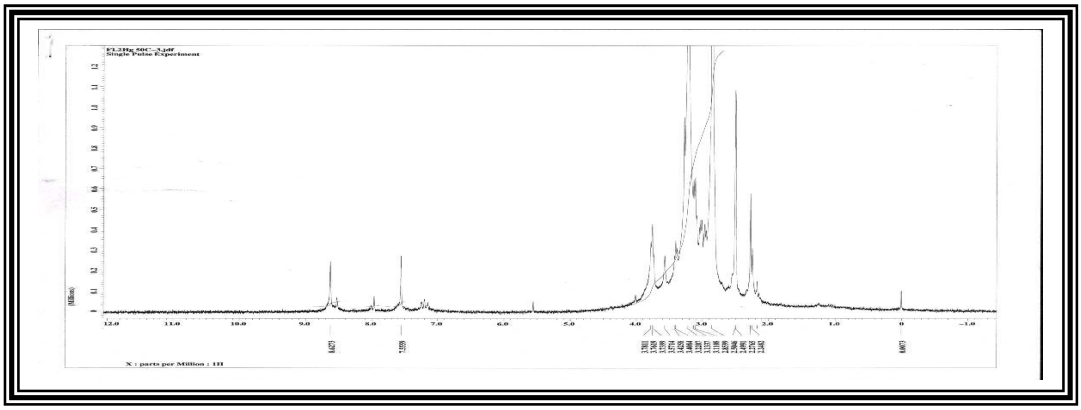


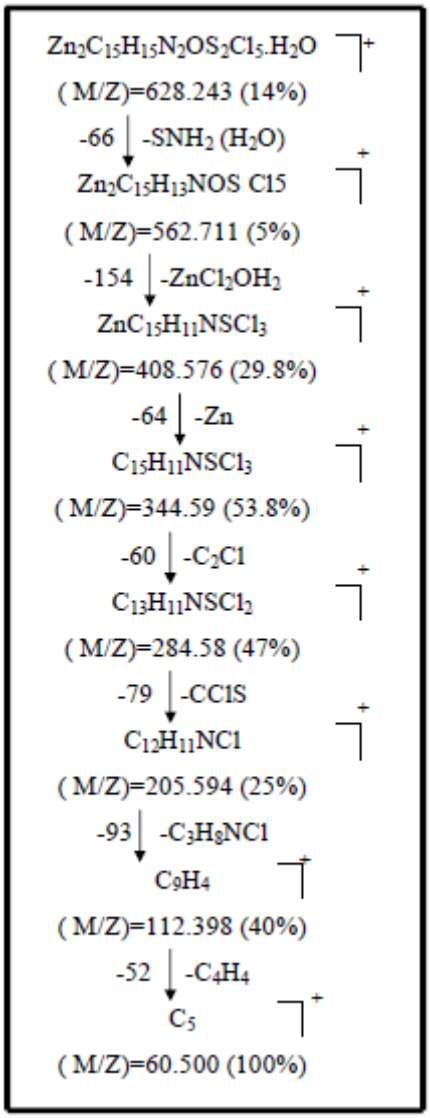
**Figure (8): $^1$H-NMR Spectrum of $[Hg_2(L^2)Cl_2]Cl.H_2O$**

**Table (7):$^1$HNMR Data For The Complexes Measured In DMSO-d6**

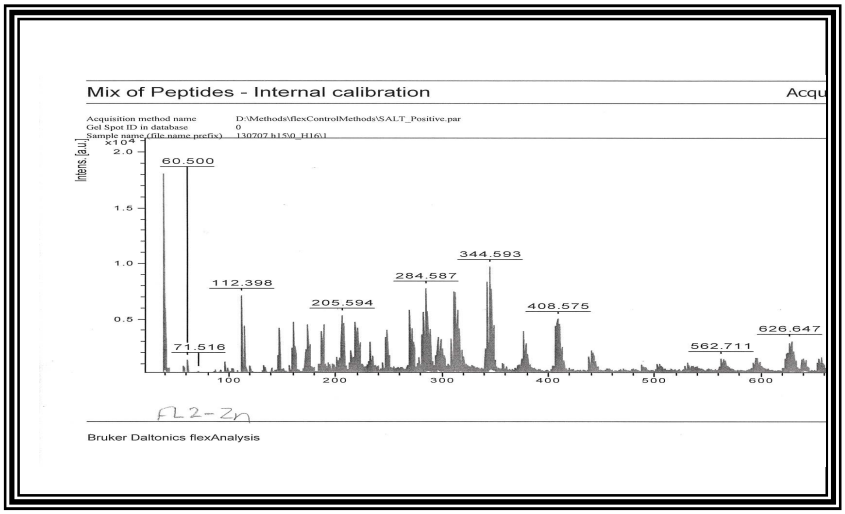
| Compound | Funct. Group | $\delta_s$ (ppm)[b] |
|---|---|---|
| **$[Zn_2(L)Cl_2]Cl.H_2O$** | N=C–*H* | 8.55 ( 2H, br ) |
| | Ar –C–*H* | 7.54 (2H, br) |
| | –NC*H*$_2$– | 3.66 -3.24 (4H, br) |
| | S–C*H*$_2$ | 3.o4 (4H, S) |
| | –C*H*$_3$ | 2.21 (3H, S) |
| **$[Hg_2(L)Cl_2]Cl.H_2O$** | N=C–*H* | 8.62, 8.54 (2H, d) |
| | Ar– C–*H* | 7.54 (2H , S) |
| | –NC*H*$_2$ | 3.66 – 3.24 (4H, br) |
| | S–C*H*$_2$ | 3.o4 (4H, S) |
| | –C*H*$_3$ | 2.21 (3H, S) |

*r = broad m= multiple d= doublet s = sharp*

The laser adsorption (+) mass spectrum of the $[Zn_2(L).(Cl)_2](Cl)(H_2O)$ shows the parent ion peak at M/Z ) = 628.243, which corresponds to $[M^+]$, other fragments and their relative abundance and fragmentation sequence is shown below.




**Scheme (3): The Fragmentation Sequence of $[Zn_2(L)Cl_2]Cl.H_2O$**



The laser adsorption (+) mass spectrum of the $[Cd_2(L)Cl_2]Cl.H_2O$ shows the parent ion peak at ( M/Z ) = 705.500, which corresponds to $[M^+]$, other fragments and their relative abundance and fragmentation sequence is shown below.

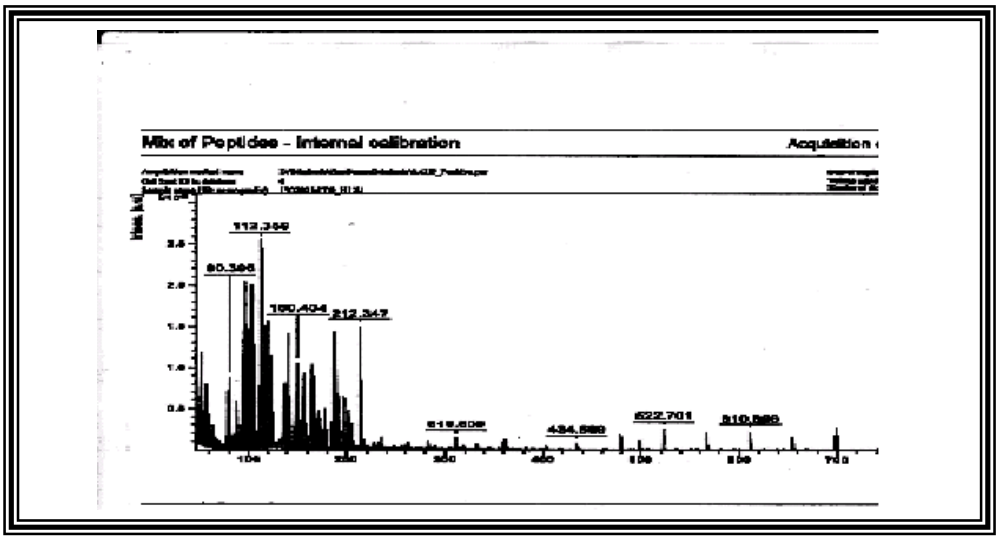
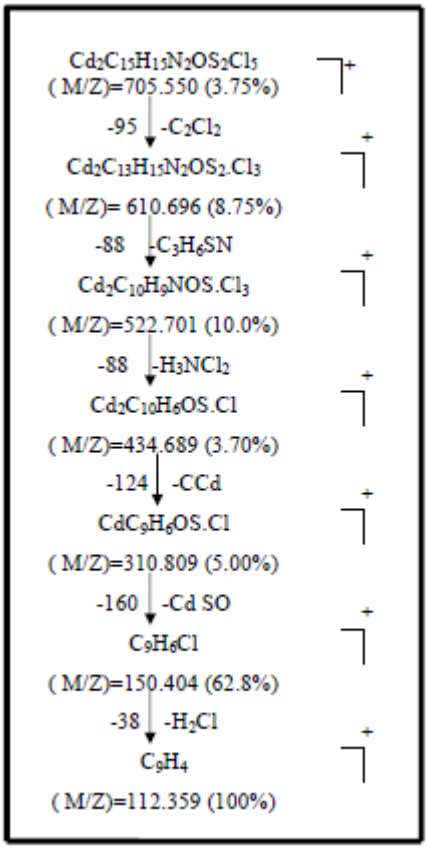



**Figure (10): The Laser Adsorption (+) Mass Spectrum of $[Cd_2(L)Cl_2]\ Cl.H_2O$**




**Scheme (4): The Fragmentation Sequence of $[Cd_2(L)Cl_2]\ Cl.H_2O$**

The molar conductivity of the complexes in (DMF) werein the range (70 – 86) $S.cm^2.\ mole^{-1}$ indicating the (1:1) electrolyte nature [28,29].

Magnetic moment has been determined in the solid state by faraday's method. The magnetic properties of these complexes should provide a testing ground for the oxidation state of the complexes, therefore provides a way of

counting the number of unpaired electrons. This should help in predicting the bonding model and electronic structure. The magnetic susceptibility for complexes was measured at room temperature and the effective magnetic moment $\mu_{eff}$ / B.M.) is given by:

$$\mu_{eff} = 2.828\sqrt{X_A\ T}$$

Where:[T= Absolute temperature (25+273=298)]
[$X_A$= Atomic susceptibility corrected from diamagnetic presence]

**Table (8): Data of magnetic moment ($\mu_{eff.}$=B.M.) of solid at 298K and suggested stereo chemical structure of complexes**

| Complexes | $X_g \times 10^{-6}$ Gram Susceptibility | $X_M \times 10^{-6}$ Molar Susceptibility | $X_A \times 10^{-6}$ Atom Susceptibility | $\mu_{eff.}$ B.M. expt. | $\mu_{eff.}$ B.M calc. | Suggested Structure |
|---|---|---|---|---|---|---|
| $K[Co_2^{II}(L)(H_2O)_4Cl_2]$ | 1.88675 | 5743.07 | 5775.27 | 3.71 | 3.88 | Octahedral |
| $K[Ni_2^{II}(L)\ Cl_2]$ | 0.00 | 0.00 | 0.00 | Dia | 0.00 | Square planar |

The $\mu_{eff}$ of the experimental magnetic moment are showed decrease in values due to the antiferromagnetism for the binuclear and polynuclear complexes.

The microanalyses (C.H.N) along with metal (AAS) results for the prepared complexes are in good agreement with the calculated values, which supported the proposed formula of the complexes.

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## REFERENCES

[1] Kenichi O; Yoshihisa Y; Toyonari O; Toru I; Yoshio I, *J. Med. Chem.* **1985**, 28, 568-576;Desai S; Desai P; Desai K, *Hetercycl. Commun*. **2001**, 7, 83-90; Al-Garsamy V; Muthukumar V; Pavalarani N; Vasanthanathan P; Revathi R, *Biol. Pharm. Bull.* **2003,** 26(4) 557—559; Li Y; Yang Z; Zhang H; Cao B; Wang F, *Bioorg. Med. Chem.* **2003**, 11, 4363-4367; Cozzi P, *Chem. Soc. Rev*. **2004**, *33*, 410-421; Verma M; Pandeya S; Singh K; Stables J, *Acta Pharm*. **2004**, 54, 49-56. ; Karali N; Gasoy A; Kandamirli F; Shvets N; Kaynak F; Ozbey S; Koalishyn U; Dimoglo, *Bioorg. Med. Chem*. **2007**, 15, 5888-5904; Panneerselvam P; Rather B; Reddy D; Kumar N, *Eur. J. Med. Chem.* **2009**, 44, 2328-2333; Wadher S; Puranik M; Karande N; Yeole P, *International J. Pharm. Tech. Res.* **2009**, 1, 22-23; Krishna S; Ganguly S; Veerasamy R; Jan B, *Eur. Rev. Med. Pharm. Sci.* **2011**, 15, 673-681; Kumar P; Rani B, *J. Chem. Tech. Res.* **2011**, 3, 155-160; Tiwari S; Mujalda V; Sharma V; Saxena P; Sharivastava M, *Asian J. Pharm. Clin. Res.* **2012**, 5(1), 98-100.
[2] Garnovskii A; Nivorozhkin, A.; Minkin V, *Coord. Chem. Rev*. **1993,***126*, 1-69.
[3] Gomez M; Muller G; Rocamora M, *Coord. Chem. Rev*. **1999**, *769*, 193-195.
[4] Shi P; Liu Y; Peng S, Organomet. Chem. **2002**, *21*, 3203-3209.
[5] Ghaudhuri V; Claudio, P; Thoma E, *J. Chem. Soc.*, Dalton Trans. **2000**, 569- 575.
[6] Al-Jeboori F; Al-Jeboori M; Hammud K; Ashour H.; Mohammad J,*J. Chem. Pharm. Res.* **2013**, 5(4),160-170.
[7] Sanmartim J; Bermejo M; Garcia Deibe A; Rivas I, *J. Chem. Soc.* Dalton Trans. **2000**, 4174-4181 .
[8] Nakamoto K;Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd Ed., John Wiley, New York 1978.
[9] Aime S; Bottaand M; Casellato U, *Inorg. Chem*.**1995**, 34, 5825.
[10] Tumer M; Koksal H; Serin S, *Transition Metal Chem.* **1999**, 24, 13.
[11] Koksal H; Tumer M; Serin S, *Synth. React. Inorg. Met. Org. Chem*.**1996**, 26, 1577.
[12] Shipman J, *Spectro. Chim. Acta***1962**,18, 1603.
[13] Santokh S; ThompsonL;. Bridson J, *Inorg. Chem*.**1993**,32, 32-39.
[14]Huang W; Gou S; Meing Q, *Inorg. Chem*.**2001**, 40, 1712-1715.
[15] Atkins A; Blake A; Scheoder M, *J. Chem. Soc. Chem. Commun*. **1993**, 353.
[16] Atkins A; Black D; Ruiz-Ramirez L, *J. Chem. Soc. , Chem. Commun*. **1996**,457.
[17] Guodong D; Arkady E; Kelth W, *Inorg. Chem.* **2003**, 42, 873-877.
[18]Okawa H; Bridson J, *Inorg. Chem*. **1993**, 32, 2949.
[19]Wang Z; Reibenspies J; Arthur E, *Inorg. Chem*. **1997** ,36, 629-636.
[20] Tumer M; Deligonul N; Dolaz M, *Transition Metal Chem*. **2006**, 31, 1-12.
[21] Smith P; Morris J; Ryan G, *J. Am. Chem. Soc*.**1989**, 111, 7437.

[22]Jeannin S;Jeannin Y; Lavigne G, *Trans. Metal Chem*.**1976**, 1, 192-195 .
[23] Dehand J; Jordanov ; Mosset A; Galy J, *Inorg. Chem*.**1979**, 18, 1543.
[24] Preti C; Tosi G, *Canadian J. Chem*.**1977**, 55, 1409.
[25] Oberhausen K; Richandon J; Buchanan R, *Inorg. Chem*.**1991**,30, 1357.
[26] El-Asmy A; Khalifa M; Mostafa M, *Synth. React. Inorg Met. Org.Chem*.**1986**, 16, 1305.
[27] Wilkins G; Gillared R;. Mecleverly J, Comprehensive Coordination Chemistry, Pergamon , Oxford, London 1987.
[28] Kette S, Coordination Compounds, Thomas Nelson and Sons, London 1975.
[29] Quaylian J; Usita J; Franz G, *J. Am. Chem. Soc*.**1965**, 81, 3770.