Synthesis OF Ligands OF BIS-Oxadiazole, Triazole With Open OR Close Sides and Their Complxes With (Cu^{II}, Pd^{II})

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Abstract

A number of new ligands of open sides of Bis-Oxadiazole and Bis-triazole derived from dichloroethane and [Bis (2-chloro ethy) ether)] (BCEE) were synthesized. These include: $\overset{=}{1},\overset{=}{4}$- bis [-3{thio-$\overset{=}{2}$-(Chloroethyl)} 1,3,4 – oxadiazole –5yl] butane (L_1), $\overset{=}{1},\overset{=}{4}$-Bis [phenyl–3{thio – $\bar{2}$($\bar{2}$-chloroethoxy) ethyl} 1,3,4- oxadiazole-5yl] butane (L_2), Bis [4-phenyl –3{thio(chloroethyl)}1,2,4 – triazole-5yl] methane (L_3), Bis[4-phenyl-3{thio- $\bar{2}$($\bar{2}$-chloroethoxy) ethyl} 1,2,4 – triazole – 5yl] methane (L_4), $\overset{=}{1},\overset{=}{2}$- bis [4- phenyl –3 {thio-$\bar{2}$ (chloroethyl)} 1,2,4 – triazole – 5yl]ethane; monodimethyl sulphoxide (L_5), $\overset{=}{1},\overset{=}{2}$- Bis [4-phenyl –3 {thio- $\bar{2}$($\bar{2}$- chloroethoxy) ethyl} 1,2,4 – triazole – 5yl] ethane (L_6) and $\overset{=}{1},\overset{=}{4}$ – Bis [4-phenyl –3 {thio-2 (chloroethyl)} 1,2,4-triazole – 5yl] butane; mono dimethylsulphoxide (L_7) respectively. This was prepared from the reaction of one mole of the following compounds: $\bar{1},\bar{4}$- Bis [2-thio – 1,3,4 –oxadiazole –5yl] butane (M_1), Bis (4-phenyl-3-thiol-1,2,4 –triazole –5yl) methane (M_2), $\bar{1},\bar{2}$– Bis (4-phenyl –3- thiol – 1,2,4- triazole – 5yl) ethane (M_3) and $\bar{1},\bar{4}$– Bis [4-phenyl –3 – thiol – 1, 2, 4 – triazole – 5 yl] butane (M_4) respectively with two moles of dichloroethane and (BCEE) and two moles of sodium hydroxide. In addition, new close ligands of Bis-oxadiazole and Bis-triazole derivatives with some of their complexes of copper and palladium were synthesized. The ligands were

$\overline{2},\overline{2}$ – di [2 – thio { $\overset{=}{1},\overset{=}{\overline{4}}$ Bis(1,3,4–oxadiazole–5yl)butane] diethylether(L_1C)andDi–1,2–di [$\overline{3}$ – thio – Bis {4 – Phenyl – $\overline{1},\overline{2},\overline{4}$ – triazole – $\overline{5}$yl}methane] ethane. trihydrate **(L_3C)** were reacted with metal chloride.

(M^{+2} = Cu and Pd) and gave new complexes of general formula $(C_{12}H_{16}N_4O_3S_2)_2MCL_2and(C_{38}H_{32}N_{12}S_4)_2MCL_2$,respectively. The synthesis of ligands Di–1,2–di $\overline{3}$ – thio – $\overset{=}{1},\overset{=}{2}$ – Bis {$\overline{4}$ – Phenyl - $\overline{1},\overline{2},\overline{4}$ – triazole– $\overline{5}$yl} ethane] ethane.mono dimethylsulphoxide (L_5C)and Di–1,2–di[$\overline{3}$ – thio – $\overset{=}{1},\overset{=}{\overline{4}}$ – Bis{$\overline{4}$ – phenyl– $\overline{1},\overline{2},\overline{4}$ - *triazole* – $\overline{5}$*yl*} butane] ethane. Bis dimethylsulphoxide. **(L_7C)** All these ligands and complexes were characterized by appropriate physical measurements: CHN analysis, (IR), (Ft-IR), (U.V-Vis) and molar conductivity. In addition ,molar ratio method was used for ligand **(L_1C)** complex. The suggested structure of ligand **(L_1C)**, **(L_3C)** complexes were octahedral.

Introduction

Our current interest is in heterocyclic Bis-oxadiazole and triazole derivatives and their complexes with the fact that these compounds are reported to possess pesticidal(1), insecticidal(2), fungicidal(3,4) and bactericidal activities(5). Furthermore, the substituted oxadiazole were as antimitotic (6), muscle relaxants and tranquilizing agents(7). Each of these opens and closes ligands contains a thioether sulphur and heterocyclic nitrogen as donor atoms. However, particularly no work has been done in this field with complexes of these close macrocyclic ligands. These new complexes illustrate the relationships among macrocyclic ring size, donor atom type, and mode of chelation. Thus, this study reports the investigation and preparation of number of Cu^{II} and Pd^{II} complexes of Bis-macrocyclic Oxadiazole and Traizole derivatives ligands by elemental analysis, IR, Ft-IR, U. V-visible, molar conductivity and molar ratio.

Experimental

(a) Chemicals

All reagents used were analar or chemically pure grade.

(b) Instruments

-Melting points were determined by Gallen Kamp apparatus.

- Microanalysis for carbon, hydrogen and nitrogen were carried out by the International Petrolium Iraq / Baghdad and AL-Nahrain University Carlo Erba Instrument.
- IR spectra were recorded as KBr disks in the range of (4000-400 cm^{-1}) using Perkin – elemer 390 spectro photometer.
- (Ft-IR) spectra were recorded as CsI disks in the range of (4000-200 cm^{-1}) and far-IR at the range of (500-200 cm^{-1}) using Perkin –Elemer (1720 X) spectro photometer.
- U.V-vis spectra were recorded on Pye-Unicam-8700 spectrophotometer at 25° c using 1 cm quartz cell, and examined at the range of (200-800 nm).
- Molar conductance of the complexes at the range of (10^{-3}-0.25×10^{-3} M) in DMSO.

Preparation

Synthesis of Bis-Oxadiazole, Bis-Triazole derivatives ligands with open or close sides.

The ligands (**L_1, L_1C, L_2, L_3, L_3C, L_4, L_5, L_5C, L_7 and L_7C**). were prepared as follows:-

- preparation of $\overline{\overline{1}}$,$\overline{\overline{4}}$-Bis [3{thio-2-(chloroethyl)}-1, 3, 4-oxadiazole-5yl] butane (L_1).

0.13 gm (3.87 m mole) of sodium hydroxide with 15 ml of absolute ethanol was added to a 1 gm (3.87 m mole) of the compound 1,4-Bis [2-thio-1, 3, 4-oxadiazole-5yl] butane (M_1)(8) which was dissolved in absolute ethanol. The mixture was refluxed for 30 min and left for cooling. Then ,a dropwise of 0.7 ml of Dichloroethane was added. This was left overnight on stirrer and then acidified by hydrochloric acid under cooling conditions, then the product was filtered ,dried and crystallized by absolute ethanol to give a white precipitate. The physical data of all the ligands are given in (table -1-).

Synthesis of Close Oxadiazole Ligand

- Preparation of, $\overline{2}$, $\overline{2}$-di [2-thio { $\overline{\overline{1}}$, $\overline{\overline{4}}$ Bis(1, 3, 4-Oxadiazole-5yl) butane}] diethylether (L_1c).

By using the above method

0.32 gm (4 m mole) of sodium hydroxide was added to 1.04 gm (4.03 m mole) of the compound (M_1)(8). Then, 0.5 ml of Bis(2-

chloroethyl) ether (BCEE) was added drop wise to the mixture. The mixture was refluxed for 6 hrs. The product was filtered and dried using rotary evaporator to form an oil purple product which was purified by column chromotography(9) using silica gel (mash 40%) as a stationary phase and Benzene as mobile phase. Then, the mixture was mixed with silica gel and applied the column. The product was drawn down by adding a mixture of (benezene + methanol) sequentially in a series of (00 + 25 ml), (1.5 + 23.5 ml), (5 + 20 ml), (10 + 15 ml), (12 + 13 ml). Then, each fraction was monitored by Thin – Layer Chromatography (TLC) to give one spot with Rf different from the starting material. The product was purple oil, (table –1-).

- **preparation of $\overline{\overline{\overline{1}}}$, $\overline{\overline{4}}$ Bis [phenyl-3 {thio- $\overline{2}$ ($\overline{2}$ -chloroethoxy) ethyl} 1, 3, 4-Oxadiazole – 5yl] butane (L_2).**

(1.4 ml) of Bis-(2-chloroethyl) ether was added as dropwise to the mixture. Then, it was refluxed for 6 hrs and purified by column chromatography(9). Using a mixture of (benzene: methanol) which was added sequentially in a series of (00 + 25 ml), (3 + 22 ml), (5 + 20 ml), (7 + 18 ml), (10 + 15 ml). The product was monitored by (TLC) and gave oil yellow product, (table –1-).

- **Preparation of Bis [4-phenyl 3-{thio (chloroethoxy) ethyl} 1, 2, 4- traizole – 5yl] methane (L_4).**

0.16 gm (2 m mole) of sodium hydroxide was added to a 0.732 gm (2 m mole) of the compound bis (4-phenyl-3-thiol-1, 2, 4-triazole) (M_4)(10) which was dissolved in (20 ml) absolute ethanol. The mixture was refluxed for 30 min, then stirred until cooled, after that (0.23 ml) of (BCEE) was added as drop wise. Then, the mixture was refluxed for 10 hrs, filtered, dried and recrystallized by chloroform to form yellow crystals (table -1-).

Synthesis of Close and Open Triazole Ligands

- **preparation of Di-1, 2- di [3-thio-Bis {4-phenyl- $\overline{1}$, $\overline{2}$, $\overline{4}$ -triazole- $\overline{5}$ yl} methane] ethane. Trihydrate (L_3c).**

This ligand was prepared by two steps.

Step-1-

preparation of Bis [4-phenyl-3 {thio(chloroethyl)} 1, 2, 4-traizole-5yl] methane (L_3).

0.44 gm (5.5 m mole) of sodium hydroxide which was dissolved in 20 ml absolute ethanol and added to a 2.03 gm (4.54 m mole) of the compound bis(4-phenyl-3-thiol-1, 2, 4- traizole-5yl) methane (M_2). The mixture was refluxed for 30 min and stirred until cooling, (1 ml) of dichloroethane was added to the mixture and left stirring overnight, then acidified in ice water by drop wise of hydrochloric acid (conc). The product was crystallized by absolute ethanol to form white crystals. (table -1-).

Step -2-:- (Closing Ring)

0.08 gm (1 m mole) of sodium hydroxide which was dissolved in (20 ml) absolute ethanol was added to a 0.4 gm (1.09 m mole) of compound (M_2). The mixture was refluxed for 30 min , stirred until cooled. 0.46 gm (1 m mole) of the ligand (L_3) which was prepared in step-1- was added to the mixture. The mixture was refluxed for 2 hrs and left for stirring and cooling. Then, acidified by cooled hydrochloric acid was added. The product was recrystallized by absolute ethanol to form white crystals (table -1-).

- preparation of di-1, 2,-di [$\overline{3}$-thio-$\overline{1}$, $\overline{2}$-Bis {$\overline{4}$-phenyl-$\overline{1}$, $\overline{2}$, $\overline{4}$-triazole- $\overline{5}$yl ethane] monodimethyl sulphoxide (L_5c).
the ligand was prepared by two steps:-

Step -1- IS

preparation of $\overline{\overline{1}}$, $\overline{\overline{2}}$-Bis [4-phenyl-3 {thio-$\overline{2}$-chloroethyl}-1, 2, 4 triazole -5yl] ethane monodimethyl sluphoxide (L_5) by using the above method in ligand (L_4) except the change of ester to diethyl succinate 0.8 gm (5.25 m mole) of sodium hydroxide which was dissolved in absolute ethanol was added to 2 gm (2.56 m mole) of compound 1, 2-bis (4-phenyl-3- thiol-1, 2, 4-triazole-5yl) ethane (M_3). The mixture was refluxed for 30 min, stirred and added to the mixture drop wise of (1.6 ml) dichloroethane, and left stirring overnight then the mixture acidified in ice water by drop wise of hydrochloric acid (conc). The product was crystallized by dimethyl sulphoxide to form white precipitate (table -1-).

Step -2- (Closing Ring)

0.14 gm (1.75 m mole) of sodium hydroxide which was dissolved in absolute ethanol was added to 0.7 gm (1.82 m mole) of the compound (M_3), by using the same steps above in (L_3C) to form white crystals (table -1-).

- **preparation of $\overline{\overline{1}}$, $\overline{\overline{2}}$ -bis [4-phenyl-3 {thio-$\overline{2}$ ($\overline{2}$ chloroethoxy) ethyl} 1, 2, 4-triazole-5yl] ethane (L_6).**

By using the same method above, except the change of ester in compound (M_2) to diethyl succinate, 0.16 gm (2 m mole) of sodium hydroxide which was dissolved in (4 ml) absolute ethanol was added to 0.8 gm (2.1 m mole) of compound (M_3). The mixture was refluxed for 30 min, and left until cooled. Then ,(0.24 ml) (BCEE) was added drop wise and refluxed the mixture for 24 hrs. The product was filtered, dried by rotary evaporator, and recrystallized by chloroform to form white precipitate (table -1-).

- **preparation of di-1, 2-di [$\overline{3}$ -thio- $\overline{\overline{1}}$, $\overline{\overline{4}}$ -bis {$\overline{4}$ -phenyl-$\overline{1}$, $\overline{2}$, $\overline{4}$ -triazole-5yl} butane] ethane. didimethyl sulphoxide (L_7c).**

This ligand was prepared by two steps.

Step-1-:

- **preparation of 1, 4- bis [4-phenyl-3{thio-2(chloroethyl)}-1, 2, 4-triazole-5yl] butane. Monodimethyl sulphoxide (L_7).**

By using the above method of preparation of L_5, except the change of ester to diethyl adipate, 0.4 gm (5 m mole) of sodium hydroxide was added to 2 gm (4.9 m mole) of compound (M_4) to

- form a white precipitate which was recristallized by dimethyl sulphoxide (table-1-).

Step -2- : (Closing Ring)

0.17 gm (2.12 m mole) of sodium hydroxide which was dissolved in (40 ml) of absolute ethanol then added to 0.85 gm (2.08 m mole) of compound (M_4). The mixture was refluxed for 30 min and left stirring until cooled, and then added to the mixture 1.24 gm (2.08 m mole) of (L_7). The mixture was refluxed for 2 hrs to form white yellow, which was acidified by cooled hydrochloric acid (conc) and recrystallized by dimethyl sulphoxide to give the white yellow precipitate (table -1-).

Synthesis of Complexes

a- Metal complex of the ligand (L_1c) with a-Cu^{II}

An ethanolic solution of $CuCL_2$ 0.04 gm (0.29 m mole) was added to 0.1 gm (0.30 m mole) solution of ligand (L_1C) which was dissolved in the same solvent, the mixture was refluxed for 2 hrs. Then, it was filtered and washed in hot ethanol, and dried to give green copper precipitate complex. Complex formula and physical properties are shown in (table –1-).

b- Metal complex of the ligand (L_3C) with Pd^{II}

An ethanolic solution of $PdCl_2$ 0.04 (0.22 m mole) was added to 0.2 gm (0.24 m mole) of the ligand (L_3C) which was dissolved in the same solution. The mixture was refluxed for 2 hrs. then filtered

and washed with hot absolute ethanol to give red-brown precipitate (table -1-).

Results and Discussion

Synthesis and characterization of ligands L_1, L_2 and L_1C. The ligands L_1, L_2 and L_1C were synthesized according to the scheme -1-
The ligand (L_1C) is crown ether which contained three oxygen atoms, two sulpher atoms and four nitrogen atoms. This ligand was

characterized as purple oil in color. The ligand L_2 was yellow oil color and this ligand was dissolved in most organic solvents while the ligand (L_1C) is white precipitate and very stable in a wide range of temperature and dissolves in all organic solvents.

Studying IR-spectra (table -2-) of the ligand L_1, L_2 showed two weak absorption bands at the range of (2860-3000) cm^{-1} due to asym $\upsilon(C-H)$ and sym $\upsilon(C-H)$ alphatic(11) and $\upsilon(O-CH_2)$. The absence of $\upsilon(S-H)$ and $\upsilon(N-H)$ streching vibration at 2550 cm^{-1} ,respectively. This indicates the displacement of hydrogen SH by mean of CH_2CH_2-Cl group in dichloroethane to form the ligand L_1 the displacement of hydrogen SH by means of ether $\upsilon(C-O)$ at 1150 cm^{-1}. This is due to the bonding CH_2-CH_2-O-CH_2-CH_2-Cl of ether group to form the ether ligand L_2(12).

Also, IR spectra of the two ligands L_1, L_2 exhibited multi bands with some shifting to the lower frequency at the range of (1620-1580) cm^{-1}, (1285-1360) cm^{-1} , (940-955) cm^{-1} and (685-1045) cm^{-1} ,respectively. These were due to ν(C=C + C=N), ν(C=C + C- S) , ν(N-C-S) and ν(C-S), respectively.(13, 14). IR spectra of L_1, L_2 showed strong bands at (1455, 1480) cm^{-1} , (1240-1300) cm^{-1} and (505-760) cm^{-1} respectively is assigned to δ(S-CH_2) , ν(CH_2-Cl) and ν(C-Cl), respectively.

A comparison of IR spectra of the crown ether ligand L_1C with the ligand L_1 gave some information about the shifting of bands of crown ether ligand to the higher frequency. The ligand L_1C exhibited two absorption bands at 2925, 2860 cm^{-1} due to the streching vibration asym ν(C-H), sym ν(C-H) in (O-CH_2) group(12) gave another evidence to indicate ν(C-O) of crown ether by the observation of band at 1160 cm^{-1} which is assigned to the streching vibration of ν(C-O) and also IR spectra showed a strong band at 1485 cm^{-1} due to δ(CH_2) in (S-CH_2)(15) group with shifting in some bands as followed (1625,1585)cm^{-1},(1300,1385), 980 cm^{-1} and 850 cm^{-1}, respectively due to ν(C=C + C=N), ν(C=N + C-S), ν(N-C-S) and ν(C-S), respectively. The very important observation was the absence of band at 745 cm^{-1} in the spectra of L_1C which is due to the streching vibration of ν(C-Cl)(15, 16).

The CHN analysis of the ligand L_1, L_2 and L_1C may be taken as another evidence to give fit formula which were listed in (table-1-)

(U.V- visible) spectra of ligands L_1, L_2 and L_1C in DMSO solutions at the concentration 10^{-3} M. The ligands L_1, L_2 exhibited one strong absorption band at (262 nm) , (264 nm). The comparison of spectra of the ligand L_1 with the spectra of L_1C ligand gave an evidence for the formation of the crown ether which exhibited two absorption bands at (243, 266) nm. The band at (243 nm) was absent in the spectra of ligands L_1 and L_2. This gave another evidence for the formation of crown ether (L_1C). ,Furthermore these bands may be attributed to the $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$. transition(17). (table-1-).

Synthesis and characterization of L_1C complex of Cu^{II}. The new green complex of Cu^{II} for the ligand L_1C was obtained by the reaction of 2 moles of ligand L_1C with 1 mole of copper chloride by using absolute ethanol as a solvent.

A comparison of the IR spectra of the copper complex with free ligand L_1C gave some information about the functional groups involved in coordination (table -3-). IR spectra of copper complex showed no change in the absorption bands of L_1C at (2860, 2925) cm^{-1} which can be assigned to ν(C-H) asym and ν(C-H) sym Alpha(12). The L_1C complex showed shifting band of ν(C=C + C=N) to the lowered frequency at (1500, 1590) cm^{-1} with change in the intensity of these bands. This indicated the bonding of nitrogen with metal ion. Furthermore ,IR spectra of copper complex showed an absorption band at 1580 cm^{-1}. This may be due to coordination of CN vibration with metal ion(8). The spectra showed sharp band at 1485 which can be assigned to ($S-CH_2$) band in free ligand. This appeared at lowered frequency in metal complex about (5 cm^{-1}) and appeared strong and sharp bands at 1000 cm^{-1} and 940 due to (N-C-S) bond. This indicated that sulfur and nitrogen bonded with metal ion(18, 19). The IR spectra showed no change in the absorption bands at 1160 which may be due to the streching vibration of ν(C-O). In addition IR spectra showed two splitted absorption bands at(700,685) cm^{-1} , this indicates sulfur bonded, (Ft – Far – IR) spectrum fig (4) of L_1C complex brought out.

The following facts to light (table –3–). Far –IR showed two splitted and weak absorption bands approximately at (400-500 cm^{-1}) due to the streching vibration of ν(M-N), ν(M-S) ,respectivily.Copper complex was observed at 397 cm^{-1} due to ν(Cu-S)and another band at 500cm^{-1} due to ν(Cu-N). In order to prove the formation of (M-Cl) bonded (Fit – Far – IR) for copper complex exhibited band at 354 cm^{-1} due to ν (Cu-Cl).(20) The U.V- visible spectra data of L_1C and their complex are listed in (table –1-). The green copper compley; acoordingly the observed color of the copper complex showed broad band at 14286 cm^{-1} expected for the transition $^{2}Eg \rightarrow {}^{2}T_{2}g$. Our investigation suggested that L_1C complex with copper ion was octahedral fig (1). Conductivity of the copper complex were estimated by their molar conductivities (table-1-) in dimethyl sulphoxide at range of($10^{-1} - 0.25 \times 10^{-3}$ molar) which indicated non conductance.(21,22) The elemental analysis (CHN) (table-1-) suggested that the complex gave the formula $(C_{12}H_{16}N_4O_3S_2)_2 CuCl_2$. In order to prove the accurcy of (C.H.N) elemental analysis we decided to use the molar ratio method of metal: ligand by preparation servies of concentration having the same ratio by using a fix concentration fig (3). After a24 hour of preparation. the ratio of (L:M) was (1:1.7) to (1:1.8) this is approximatly was in agreement with ratio (1:2).

Synthesis and characterization of ligands L_4, L_3 and L3C were synthesized according to the scheme-2-.

IR spectra (table-2-) of the two ligands L_3, L4 exhibited multi weak bands at the range of (2920 - 3045) cm^{-1} due to the streching vibration of ν(C-H) alphat and ν (C-H) aromatic (23'10'12,24) , IR spectra showed the absence of ν (S-H) and ν (N-H) streching vibration at (2550 cm^{-1}) and (3100 cm^{-1}) respectively. This was observed in the spectrum of starting material (M_2) this indicates that the displacement of hydrogen SH by means of CH_2CH_2Cl, CH_2CH_2-O-CH_2CH_2Cl respectively to from the ligands L_3,L_4. Furthermore the specra of the ligand L_4 showed new band at 1100 cm^{-1} due to the streching vibration of ν (C-O). Also IR spectra of the ligands L_3,L_4 exhibited multi bands with some shifting to the lower frequency at the range of (1560-1630) cm^{-1}, (1270-1330) cm^{-1}. (910-920) cm^{-1} and (750-755) cm^{-1} respectivily. These bands were due to ν (C=C+C=N), ν (C=C+C-S), ν (N-C-S) and ν (C-S) respectively. IR spectra of L_3, L_4 showed strong bands at the range (1300 1240) cm^{-1} due to ν(CH_2-Cl) streching vibration of and also another strong bands at the range of (505-760) cm^{-1}due to ν(C-Cl).(12,16,15). IR spectra showed strong bands at the range (685-700) cm^{-1} is assigned to mono substituted benzene.

Fig. (4)of palladium showed one band at 354 cm^{-1} due to v(Pd-cl).(30,31) the elemental analysis (CHN) (table-l-) suggested that the complex gave the formula $(C_{28}H_{32}N_{12}S_4)_2PdC_{12}$. The U.V - visible spectra data of L_3C and their complex with palladium are listed (table-l-). The metal complex was brown palladium shoulder with lowered frequency at 31230 cm^{-1} and new band at 24654 cm^{-1}due to the transition $A_2g \rightarrow T_2g$.Our investigation suggested that L_3C ligand compley with palladium metal ion was octahedral the structure of palladium complex with L_3C is shown in fig (2). Conductivity of the palladium complex was estimated by their molar conductivitiy (table-l-) in dimethyl sulphoxide at the range of (10^{-3} - 0.25×10^{-3} molar) which indicated non conductance (32).

Synthesis and characterization of ligands L_6, L5 and L_5C were synthesized according to the scheme-3-.

IR spectra (table-l-) of the ligands L_5 and L6 exhibited two weak absorption band at the range of (2860-3045) cm^{-1} due to stretching vibration of v(C-H) alpha and v(C-H) arom(12) and also IR spectra showed the absence of v(S-H) and v(N-H)of the streching vibration at2550cm^{-1}and3100cm^{-1}respectivily.

This was observed in the spectrum of the starting material (M_3). This indicates that the displacement of hydrogen SH by means of CH_2 CH_2Cl, and CH_2 CH_2-O CH_2 CH_2-Cl respectivily to form the ligands L_5 and L_6 furthermore the IR spectra of the ligand L_6 showed new band at 1105 cm^{-1} due to the stretching vibration of v(C-O) band, another multi bands of the ligands L_5 and L_6 were showed in this spectra with shifting to higher frequency and changed of intensity of these bands at following range of (1565^{-1}-1600)cm^{-1}, (1245-1350)cm^{-1} (780-920)cm^{-1}, (770-780)cm^{-1}. These bands were due to v(C=C + C=N), (C=C + C=S) v(N-C-S) and v (C-S) respectivly(19,10).

IR spectra of L_5 L_6 showed strong bands at the range of (1410, 143 5) cm^{-1} due to the deformation bending vibration of v(S-CH2)(27) and strong bands at range of (1240-1300) cm^{-1} and (505-760) cm^{-1} due to v(CH_2-Cl) and v(C-C1). The ligand L_5 showed strong band at 1100 cm^{-1} due streching vibration of v(S=O) of the solvent (DMSO)(33). This refered to the formation of DMSO molecule bonded with L_5 ligand, Acomparison of I R spectra of the crown ligand (L_5C) with the ligand L_5 showed two weak absorption bands at (2920, 3040) cm^{-1} due to the

A comparison of IR spectra of the crown ligand L_3C with the ligand L_3 showed two weak absorption bands at 3060 cm^{-1}. 2925 cm^{-1} due to the streching vibration of ν (C-H) aromatic and ν (C-H) Alphat,(10,23) and also I R showed shifting to higher frequency at (1600, 1565) cm^{-1} about (10-20) cm^{-1} due to the streching vibration of ν (C=C + C-N) and shift at (1295, 1335) cm^{-1} about (5-10) cm^{-1} and 955 about 45 cm^{-1} due to the streching vibration of ν(C-S) at 775 cm^{-1} about 25 cm.(10).

The spectra showed another shifting to higher freqeny at 1415 cm^{-1} about 5 cm^{-1} due to the bending vibration of S(S-CH_2)(25,10) This fact was confirmed by the apperance of a strong band at (1015cm^{-1}) due the streching vibration of ν(C-S) (26), and another sharp strong band at 730 cm^{-1} due to mono substituted benzene.(11 , 27).

The elemental analysis (CHN, (table-1-) of the ligands. L_3, L_4 and L_3C may be taken as another evidence to give fit formula. (U.V - Visble) spectra of the ligands L_3, L_4 exhibited one strong band with lowered intensity at (264 nm), (262 nm) respectivily due to the transtions $\Pi \rightarrow \Pi^*$ and $n \rightarrow \Pi^*$ The ligands L_3c exhibited a strong band with shoulder at (296.5 nm) this indeciated the formation of the crown ligand (L_3c).(17).

Synthesis and characterization of L_3c complex of Pd∏ the new brown complex of palladium for the ligand L_3C was obtained through the reaction of 2 moles of ligand L_3C with mole of palladium chloried by using absolute ethanol as solvent. A comparision of the IR spectra of the palladium complex with free ligand L_3C(table-3-) two weak absorption bands at (2920,3040) cm^{-1} due to the streching vibration of ν (C-H) alpha. The IR spectra also showed shifting of bands to the lowered frequency at (1600,540 cm^{-1}) about 25 cm^{-1} due to (C=C + C=N) indicated. The coordination of nitrogen atom with palladium metal ion(10) , the band at 880 cm^{-1}, with shifting about 75 cm^{-1},(28) due to the streching vibration of ν (N-C-S) and another strong and sharp band at 1000 cm^{-1} due to ν (C-S). this fact was confirmed by the apperance of strong and sharp band with shifting to the lowered frequency at 690 cm^{-1}. This indicated the coordination of sulpher atom with palladium ion (17,19) Furthermore IR showed two new and weak absorption bands at 400 cm^{-1} and 500 cm^{-1} due to ν(M-S), ν(M-N)(29) at 398 cm^{-1}, 520 cm^{-1} due to the streching vibration of ν(Pd-S), ν(Pd-N) respectivily, the far - Ft - I R streching vibration of v(C-H) alpha, v(C-H) aromatic and shifting to the lowered frequency at (1560, 1590) cm^{-1} about (5-10) cm^{-1} due to the streching vibration of v(C=C+C=N)and shifting to the higher frequency at { 1285,1330} cm^{-1} about (30-40) cm^{-1} due to streching vibration v{C=N+C-S}. The spectra showed another shifting to higher frequency at 945 about 45 cm^{-1} due to the streching vibration of v(N-C-S) and at 765 cm^{-1} about 15 cm^{-1} due to streching vibration of v(C-S).(10,19) furthermore I R spectra exhibited a strong band at 1410 cm^{-1} due to the deformation bending vibration of S(S-CH_2)(27). The spectra showed a strong absorption band at 1100 cm^{-1} due to the streching vibration of v(S=0) of DMSO molecule (33) . This factconfirmed the formation of DMSO molecule in structure of the crown ligand (L_5C). Also the spectra showed a sharp and strong band at 720 cm^1 due to the mono substituted benzene ring (11,34). The CHN analysis of the ligand L_5, L_6 and L_5C may be taken as another evidence to give fit formula (table- I-). (U.V -- Visible) spectra of the ligands L_6, L_5 and L_5C respectivily in DMSO solutions exhibited strong absorption bands at (264 nm), (262 nm) and (292 nm) with shoulder at (275 nm) respectivily. This may be attributed to the $\pi \rightarrow \Pi^*$, $\Pi \rightarrow \Pi^*$ (11)transitions which indicate the forming of the crown ligand (table-I-).

Synthesis and characterization of ligands L_7 and L_7C were synthesized according to the **scheme –4–** .

IR spectra of the ligand L_7 comparison with the starting material (**M_4**) showed two weak absorption bands at (2920, 3040) cm^{-1} due to the streching vibration ν (C-H) alpha and ν (C-H) arom(23,35,27) I R spectra showed the absence of ν(S-H) and ν(N-H) streching vibration at 2550 cm^{-1}, 3100 cm^{-1}, respectivily. This was observed in the spectra of starting material (**M_4**). This indicates that the displacement of hydrogen SH by means of CH_2CH_2 Cl to form the ligand(10)(L_7). Furthermore the spectra showed the shifting to lowered frequency at (1565, 1595) cm^{-1} about (5-10) cm^{-1} due to the streching vibration of ν (C=C + C=N) and another band at (1315, 1240) cm^{-1}about 5 cm^{-1} due to the streching vibration of ν (C=N + C-S), and also a band at 985 cm^{-1} about 5 cm^{-1} due to the streching vibration of ν (N-C-S), a band at 780 cm^{-1} which shifted about 5 cm^{-1} due to the streching vibration of ν(C-S)(11,19). The ligand **(L_7)** showed a strong band at 1085 cm^{-1} due to the streching vibration of ν(S=O). This indicated the formation of DMSO molecular in structure of the ligand **(L_7)**. The spectra showed strong band at the range of(1240 – 1300) cm^{-1} due to the ν(CH_2-Cl) and another strong band at the range of (505 – 760) cm^{-1} due to the streching vibration of ν(C-Cl). The I R spectra showed two strong absorption bands at (690, 725) due to the streching vibration of ν(C-S) and mono substituted benzene ring.(11,34,36)

A comparsion of IR spectra of the crown ligand **L_7C** with the ligand L_7 showed two weak absorption bands at 2920 cm^{-1} and 3040 cm^{-1} due to the streching vibration of ν(C-H) alphatic and ν(C-H) aromatic,(23,35,27) and also I R spectra showed shifting to the higher frequency at (1600, 1570) cm^{-1} about 5 cm^{-1} due to the streching vibration of ν(C=C + C=N) and another band at (1245, 1315) cm^{-1} due to the streching vibration of ν(C=N + C-S) and 990 cm^{-1} about 5 cm^{-1} due to the streching vibration of ν(N-C-S) and band at 785 about 5 cm^{-1} due to the streching vibration of ν(C-S). the IR spectra showed another shifting to the higher frequency at 1415cm^{-1} about 5 cm^{-1} due to the deformation bending vibration of δ(CH_2-S)(27) and a medium band at 1085 cm^{-1} due to the streching vibration of ν(S=O). This indicated the forming of two molecule of DMSO in the structure of **L_7C** ligand(33).

The spectra showed a shifting to 685 cm^{-1} about 5 cm^{-1} due to the streching vibration of ν(C-S)(36) and another absorption band at 725 cm^{-1} due the mono substituted of benzene ring.(11,34)

The elemental analysis (CHN), (table-1-) of the ligands L_7 and L_7C may be taken as another evidence to give fit formula.

(U.V – Visible) spectra of the ligands L_7 and L_7C in DMSO solutions **(table**-1-), exhibited one absorption band at (263 nm) of **L_7** ligand and another absorption band and also shoulder at (278 nm).

This may be attributed to the $n \rightarrow \Pi^{*}$. $n \rightarrow \prod^{*}$ transtions**(11)** which indicated the formation of the ligands **L_7** and **L_7C**.

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(Table -1-) Physical Properties and spectra data for the ligands L_1, L_1C, L_2, L_3, L_3C, L_4, L_5, L_5C, L_7, L_7C and L_1C, L_7C Metal Complexes

No.	Compound	Color or state	Mp or (Dc)	% yield	Calcu % Foud ( )%			U.V. visible cm⁻¹ (nm) in DMSO	transition	Molar conductivity ohm⁻¹ cm² mole⁻¹ in DMSO		
					%C	%H	%N			10⁻³M	0.5M	0.25M
1	$C_{12}H_{16}N_4O_2S_3$ (L_1C)	Oil Purple	-	95	43.87 (43.42)	4.87 (5.85)	17.07 (17.07)	37594 (266) 41152 (243)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-
2	$C_{10}H_{14}N_4O_2S_2$ (L_2)	Oil Yellow	-	95	40.76 (41.65)	5.09 (4.40)	11.88 (13.90)	37879 (264)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-
3	$C_{12}H_{16}N_4O_2S_3$ (L_3)	White	206-208C°	80	37.59 (37.36)	4.17 (4.41)	14.62 (20.90)	38168 (262)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-
4	$C_{12}H_{16}N_4O_2S_3CuCl_2$ ($L_3C.CuCl_2$)	Green	234-236 C°	60	36.13 (36.45)	4.04 (3.35)	14.16 (8.89)	14286	$^2E_g \rightarrow {}^2T_{2g}$	39	23	15
5	$C_{24}H_{28}N_8O_2Cl_2S$ [illegible]	Yellow [illegible]	156-158 C°	90	49.56 (48.45)	4.92 (4.73)	13.24 (16.19)	38168 (262)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-
6	$C_{21}H_{20}N_8O_2Cl$ (L_5)	White	306-308 C°	75	51.32 (53.93)	4.07 (4.20)	17.10 (19.20)	38314 (264)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-
7	$C_{18}H_{22}N$ [illegible] (L_5C)	White	309-312 C°	75	54.41 (54.2)	4.53 (4.12)	20.04 (23.71)	30722 (325.5) 33727 (296.5)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-
8	$(C_{18}H_{22}N_{12}S_3)PdCl_2$ $(L_7C)_2$ $PdCl_2$	Brown	337-340 C°	80	52.25 (51.22)	3.06 (2.05)	19.25 (13.04)	36232 Sh (276) 24654	$^1A_{2g} \rightarrow {}^1T_{2g}$	39	23	15
9	$C_{20}H_{17}N_4O_2S_2Cl$ [illegible]	White	205-207 C°	90	52.61 (53.94)	5.05 (5.29)	14.16 (16.84)	37879 (263)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-
10	$C_{24}H_{16}N_8S_3ClO$ (L_7)	White	341-343 C°	95	44.45 (46.59)	4.04 (4.40)	14.14 (14.80)	38879 (262)	$n \rightarrow \Pi^*$ $\Pi \rightarrow \Pi^*$	-	-	-

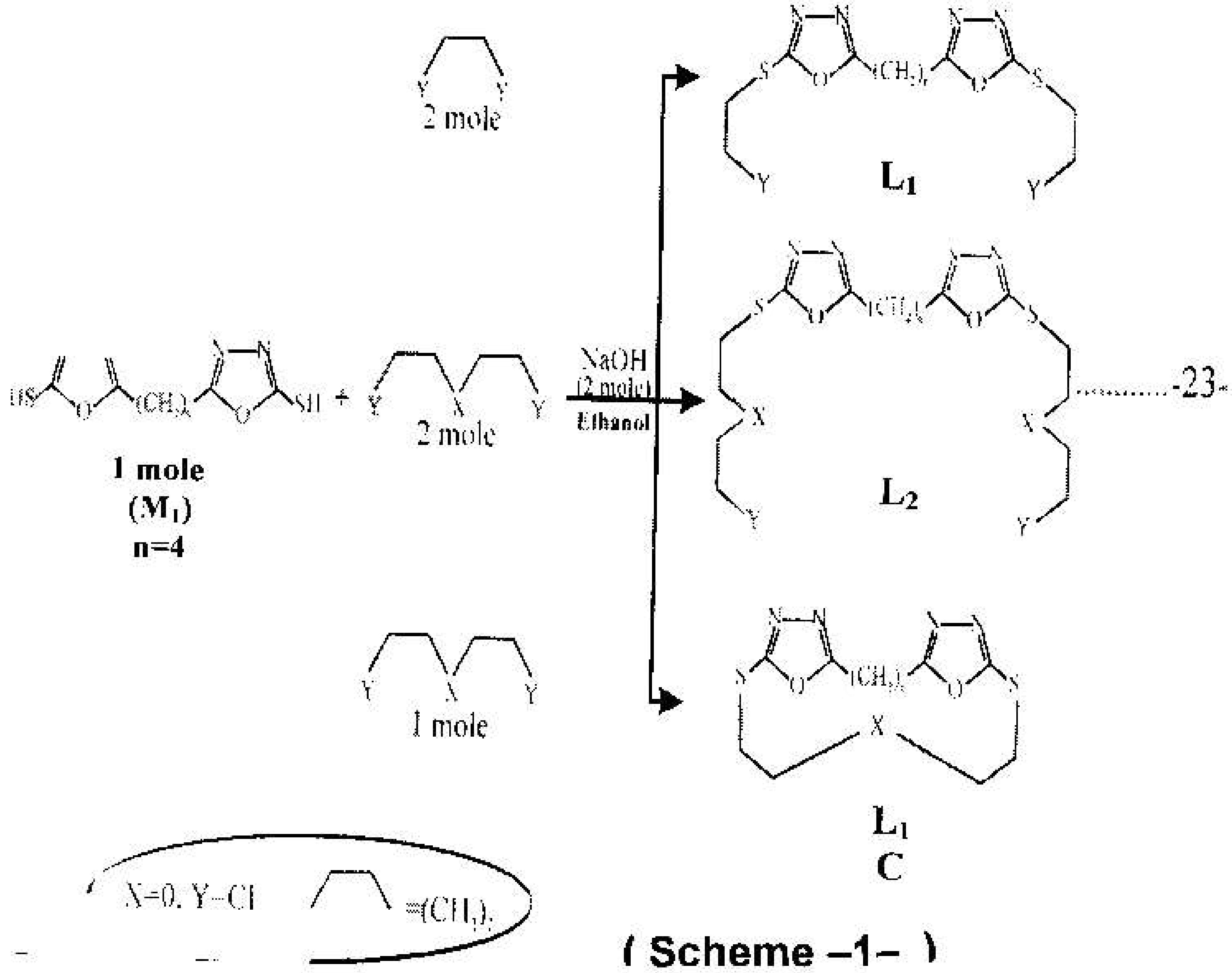
Table -2- The I R spectra data of the Ligands L_1, L_2, L_3, L_4, L_5, L_6, L_7, and L_7C

No.	Compound	V(C-H) alpha V(C-H) Arom.	V(C-H) [illegible] (C-H) alpha	V(N-H) V(S-H)	V(C=O)	V(C=C/C=N)	V(C-N-C-S)	V(C-N-S)	V(C-S)	δ(SCH₃)	V(CH₂-Cl)	V(C-Cl)	V(S=O)	Mono substituted benzene ring
1	L_1	2920(w)			-	1605 (Sh)	1350 (S) 1245 (S)	940 (Sh)	805 (S) 1045 (Sh) 685 (Sh)	1455 (M)	1285 (S)	760 (S) 505 (S)		-
2	L_2	-	2940 asym (S) 2860 sym (W)		1150(Sh)	1620 (S) 1580 (Sh)	1360 (W) 1200 (M)	955 (Sh)	870 (W) 840 (W)	1400 (Sh)	1300-1240 (S)	745 (S) 660 (S)		-
3	L_3	2870(m) 2900(w)				1590 (S) 1545 (W)	1330 (S) 1255 (S) split	910 (W)	758 (Sh) 685 (S) 1055 (S) split	1410 (Sh)	1300-1240 (S)	760-505 (S)	-	685-700 (S)
4	L_4	3045 (w)	asym 2920(W) sym 2860(W)		1100(Sh)	1650 (W) 1555 (S)	1290 (M)	920 (W)	755 (S) 690 (S)	1410 (M, b)	1300-1240 (S)	760-505 (S)	-	690-700 (S)
5	L_5	2960(w) 2980(W)			-	1600 (S) 1565 (Sh)	1300 (S) 1245 (Sh)	950 (W)	780 (Sh) 695 (S)	1410 (Sh)	1300-1240 (S)	505-760 (S)	1100 (S)	730 (S)

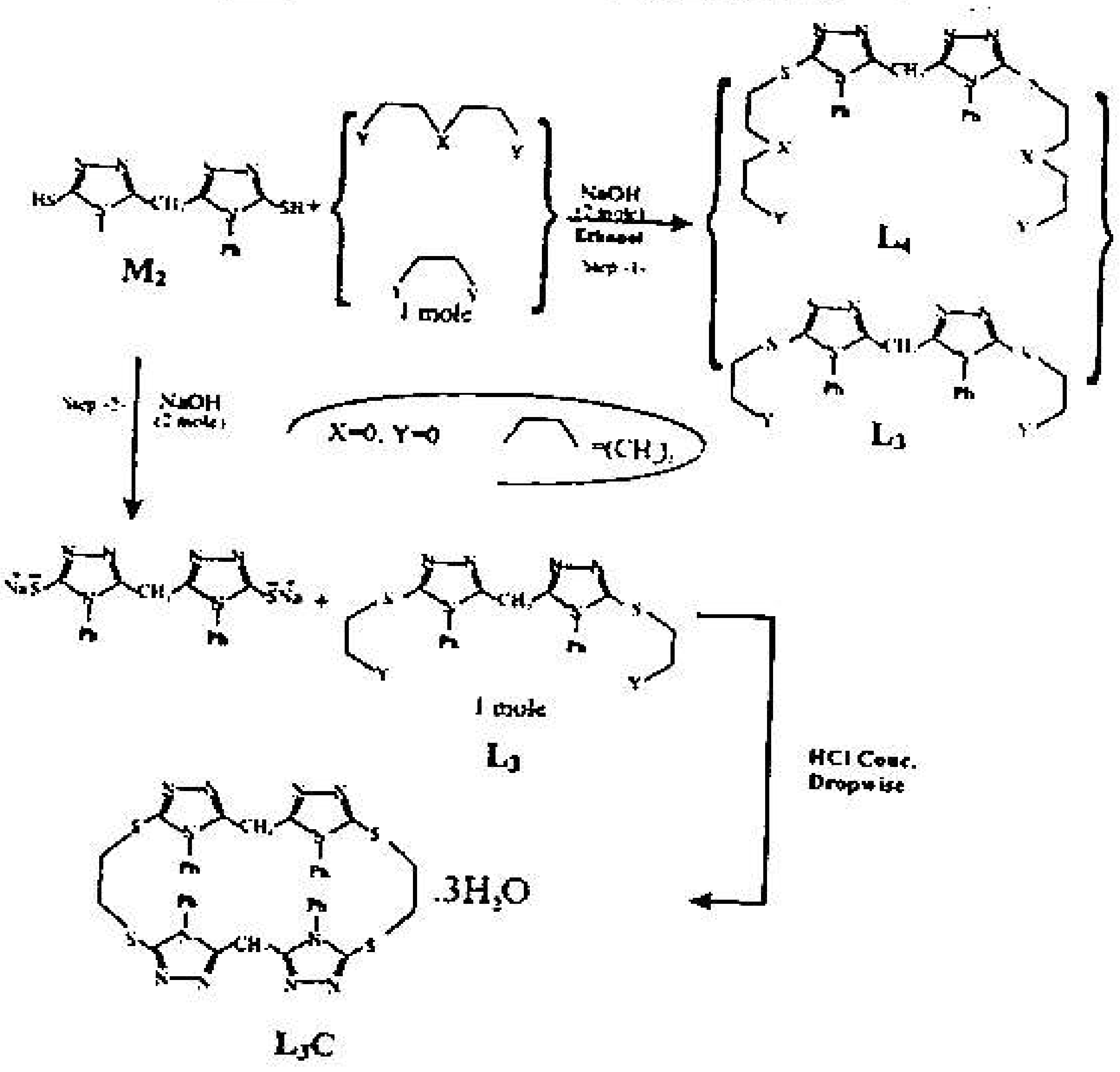
Table -3- The I R spectra data of the Ligands L_1C, L_5C and Ft – I R of their metal complexes with Cu^{II}, Pd^{II}

No	Compound	ν(C-H) Alpha cm^{-1}	ν(C=C+C=N) cm^{-1}	ν($S-CH_2$) cm^{-1}	ν(C-O) cm^{-1}	ν(C-N-S) cm^{-1}	ν(C-S) cm^{-1}	ν(M-N) cm^{-1}	ν(M-S) cm^{-1}	ν(M-Cl) cm^{-1}
1	L_1C	2925 (M) 2860 (W)	1625 (Sh) 1585 (Sh)	1485 (Sh)	1160 (Sh)	980 (Sh)	680 (N)	-	-	-
2	$(L_1C)_2$-$CuCl_2$	2925 (M) 2860 (W)	1590 (S) 1500 (Sh)	1480 (Sh)	1160 (Sh)	1000 (Sh) 940 (S)	685 (S) 700 (S)	500 (M)	397 (W)	354 (W)
3	L_5C	2925 (W) 3060 (W) Arom	1600 (S) 1565 (Sh)	1415 (Sh)	-	955 (S)	1000, 1015 (S,S) 775 (S)	-	-	-
4	$(L_5C)_2$ $PdCl_2$	2920 (W,M) 3040 (W) Arom	1600 (S) 1540 (S)	1400-1440 (W,S)	880 (S)	880 (S)	1000 (Sh) 720 (S)	520 (S)	398 (W)	354 (W)

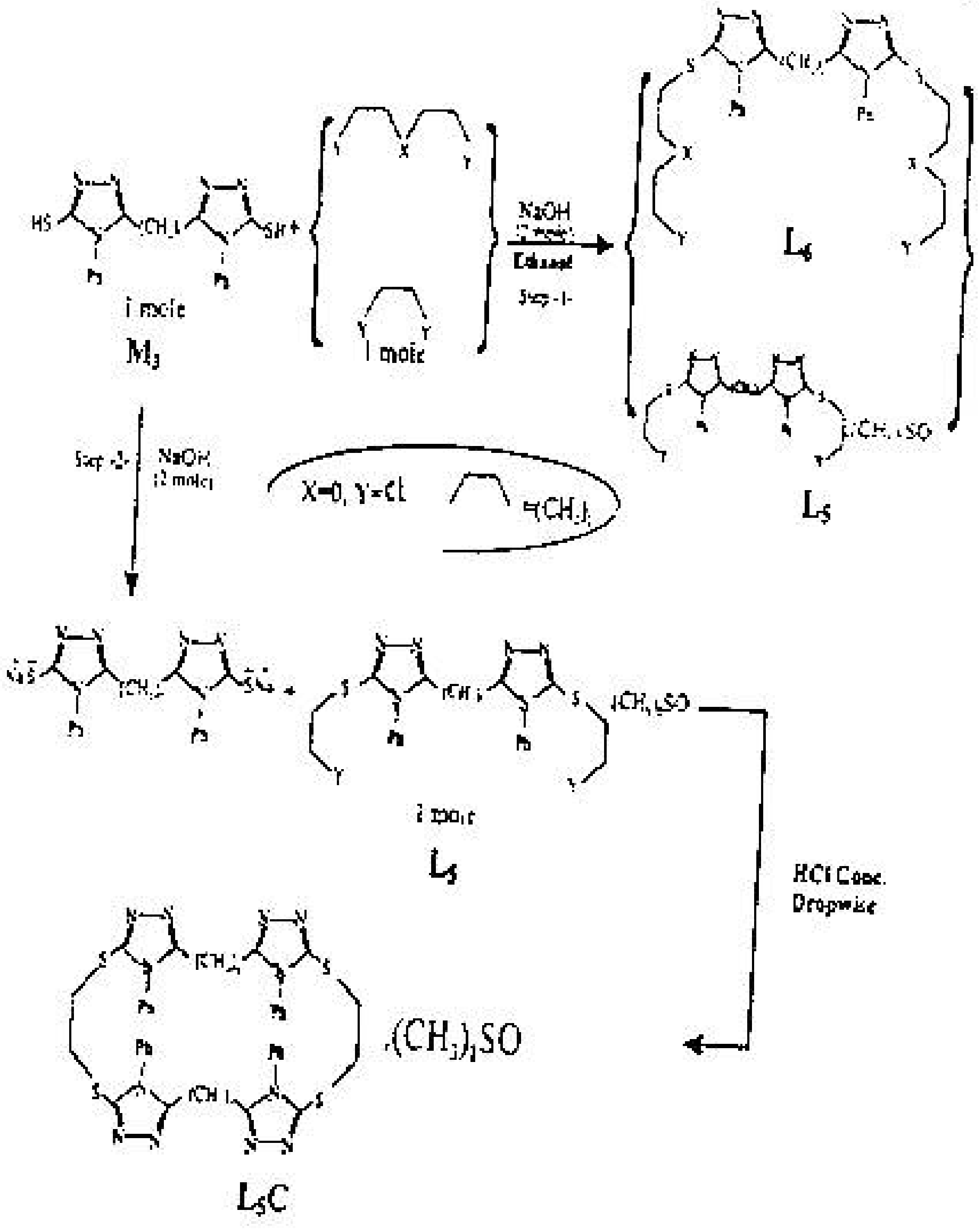
Sh= sharp, S= strong, M= medium, W= weak, b= broad



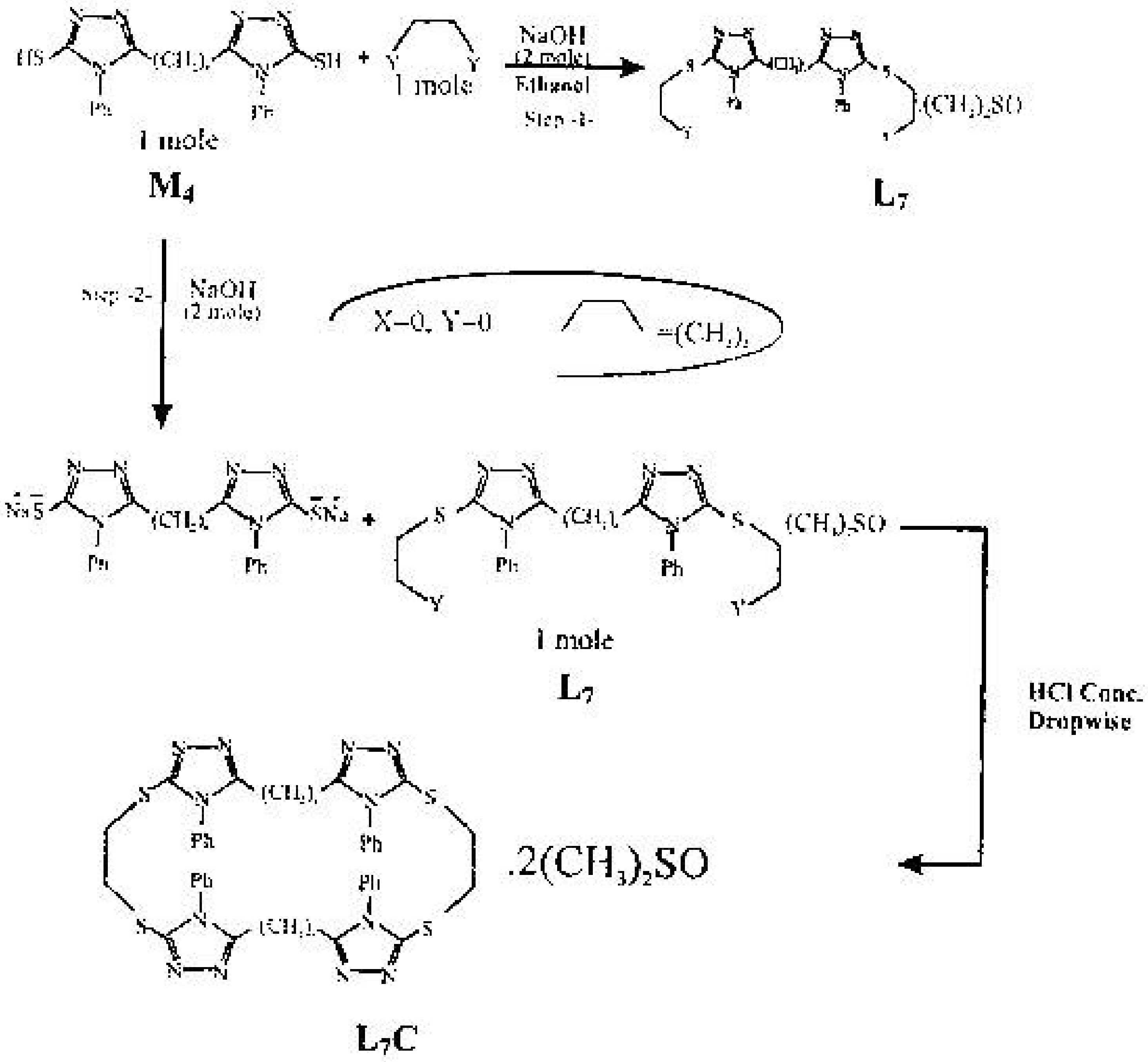
(Scheme –1–)



(Scheme –2–)



(Scheme -3-)



(Scheme -4-)

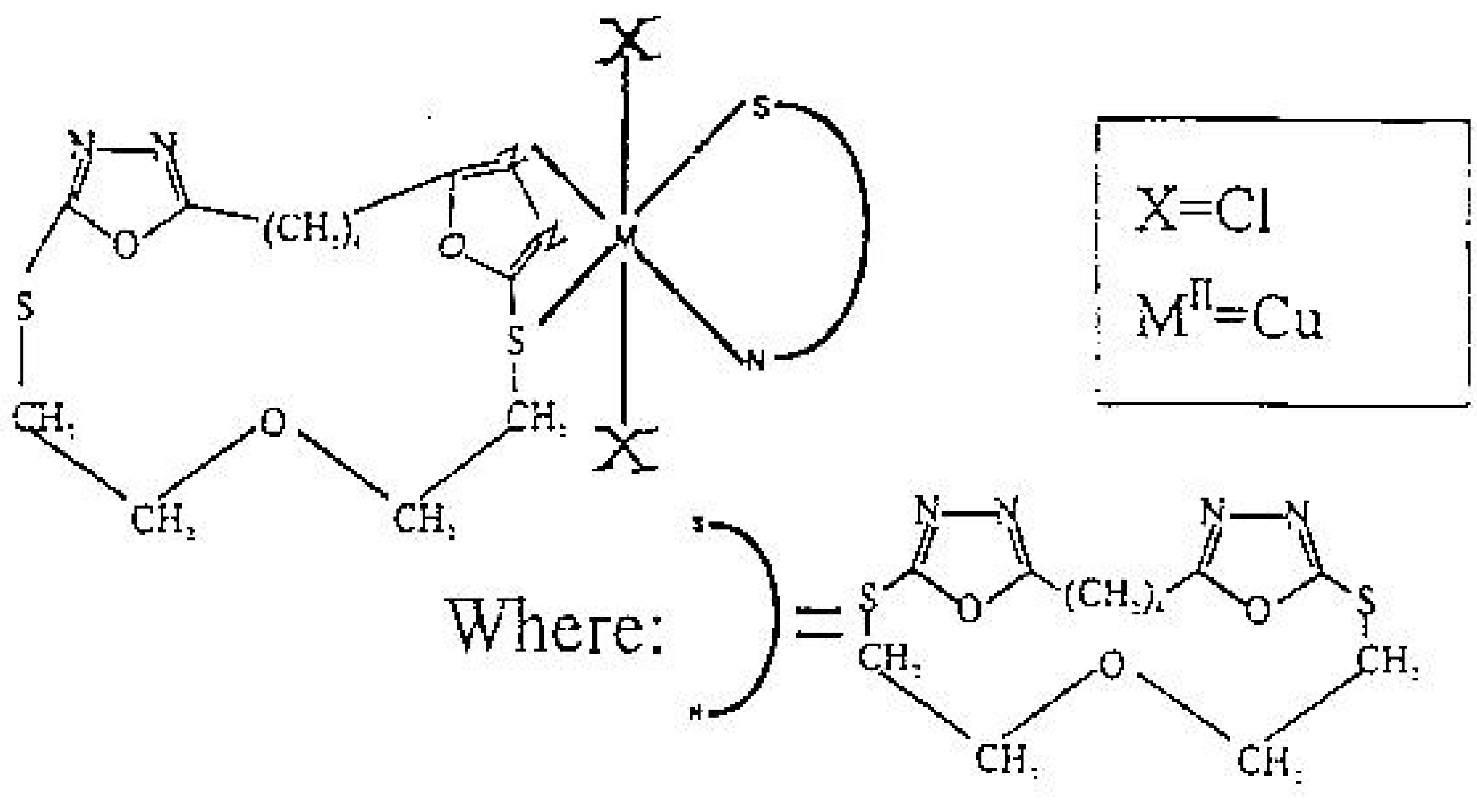


Fig –1– Copper Complex

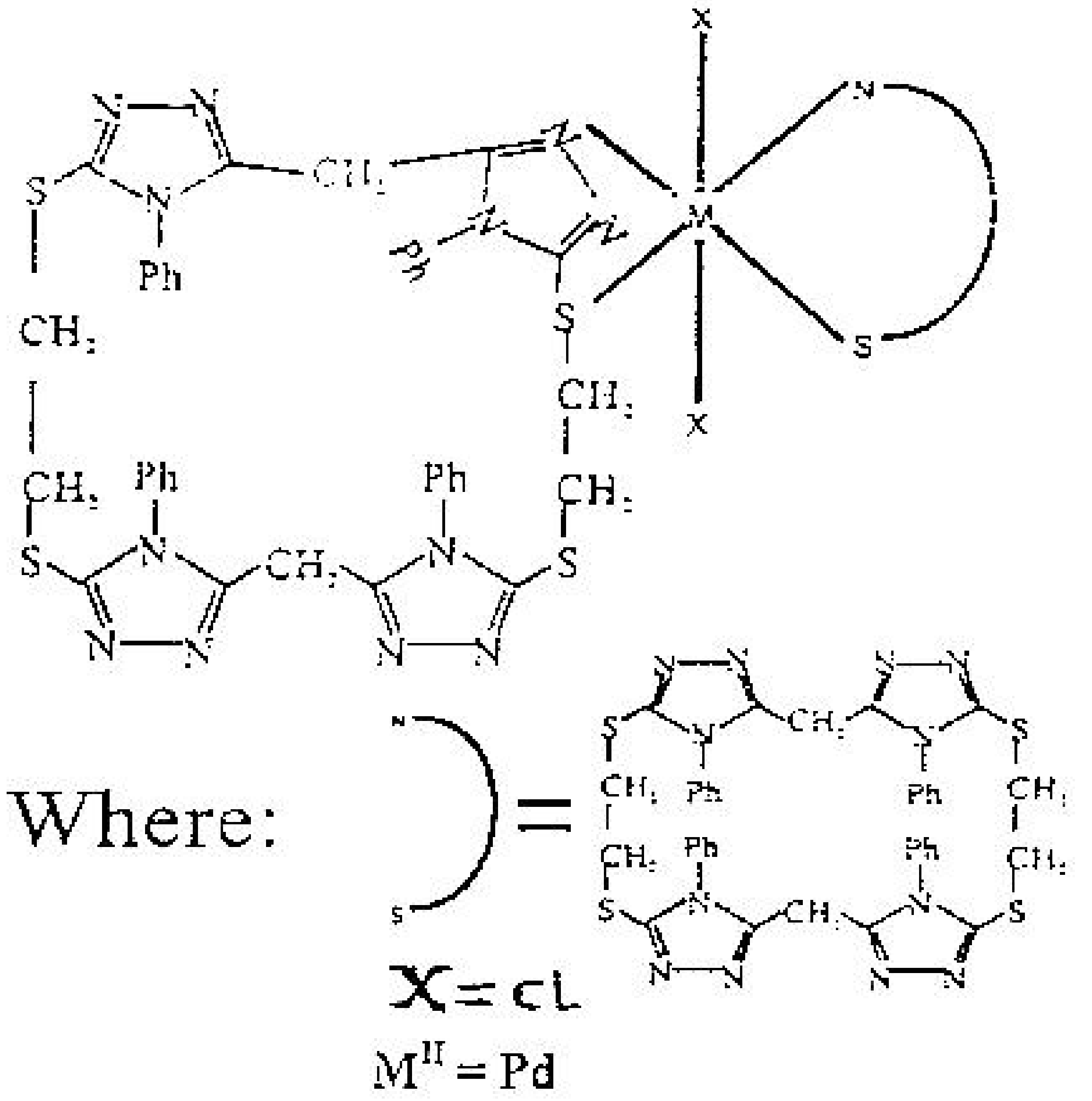


Fig –2– Palladium Complex

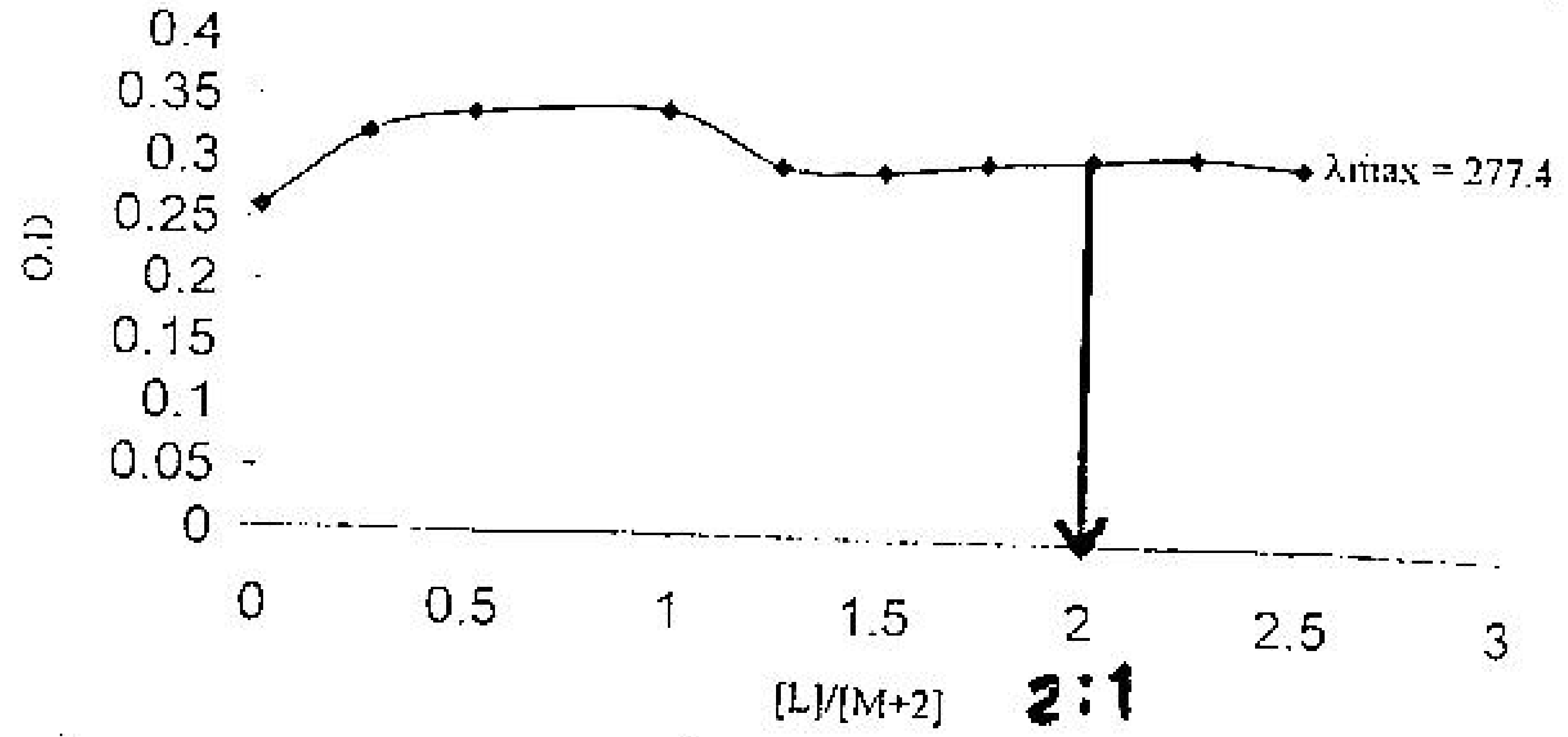


Fig -3- Molar ratio plot for copper complex

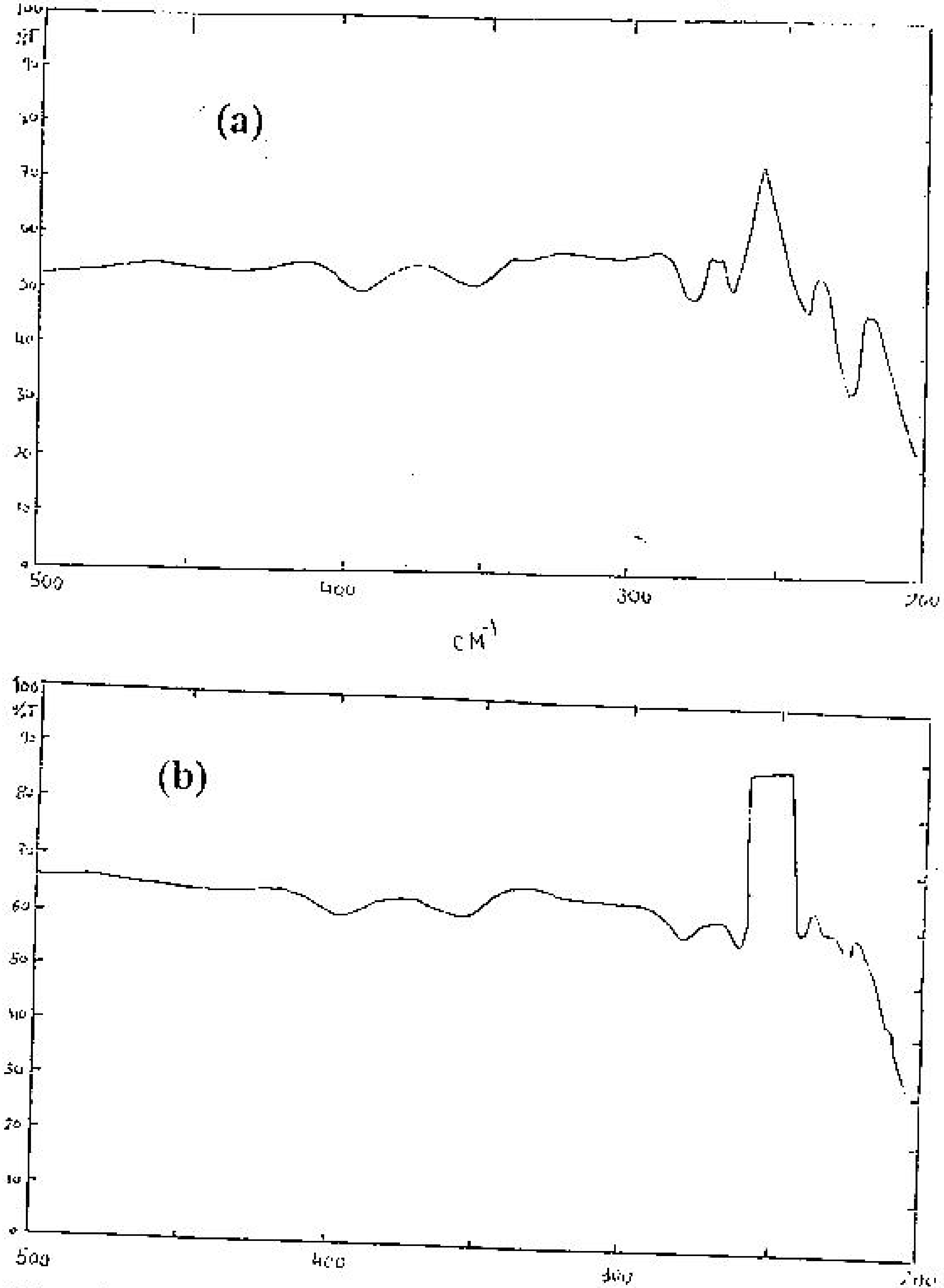


Fig -4- Far - Ft – I R of
a- Copper complex b- Palladium complex

تحضير ليكاندات ثنائية — الاوكسادايزول ، ترايزول المفتوحة الطرفين والمغلقة ومعقداتهمامع (Pd^{II} , Cu^{II})

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الخلاصة

حضرت عدداً من الليكاندات المفتوحة الجانبين لمشتقات ثنائية — الاوكسادايزول وثنائية الترايزول والمشتقة من ثنائي كلورو ايثان و [ثنائي (٢— كلورو ثنائي اثيل) ايثر (**BCEE**)]وهي كالاتي : ١، ٤— ثنائي [—٣{ثايو — ٢— (كلورو اثيل) } ١، ٣ ، ٤— أوكسادايزول—٥ يل] بيوتان (L_1) ، ١، ٤— ثنائي [—٣{ثايو — ٢— (كلورو أيثوكسي) أثيل) } ١، ٣ ، ٤— أوكسادايزول—٥ يل] بيوتان (L_2) ، ثنائي [٤— فنيل —٣{ثايو — ٢— (كلورو اثيل) }١،٢، ٤— ترايزول —٥ يل] ميثان (L_3) ، ثنائي [٤—[—٣{ثايو—٢(٢— كلورو أيثوكسي)أثيل) } ١،٢، ٤— ترايزول —٥ يل] ميثان (L_4) ١،٢— ثنائي [٤— فنيل —٣{ثايو— ٢—(كلورو اثيل) }١،٢، ٤— ترايزول —٥ يل] ايثان . احادى . ثنائي مثيل اوكسيد الكبريت(L_5) ، ١،٢— ثنائي [٤— فنيل —٣{ثايو—(٢— كلورو أيثوكسي) أثيل) } ١،٢، ٤— ترايزول —٥ يل] ايثان (L_6) و ١، ٤— ثنائي[٤— فنيل —٣{ثايو — ٢— (كلورو اثيل) }١،٢، ٤— ترايزول —٥ يل] بيوتان . احادى . ثنائي مثيل اوكسيد الكبريت (L_7) على التوالىمن مفاعلة مول واحد من المركبات الأتية : ١، ٤— ثنائي [٢— ثايو— ١، ٣ ، ٤— اوكسادايزول—٥— يل] بيوتان (M_1) ثنائي] (٤— فنيل—٣—ثايو)— ١،٢، ٤— ترايزول —٥ يل] ميثان(M_2) ١،٢— ثنائي[(٤— فنيل —٣—ثايو) ١،٢، ٤— ترايزول —٥ يل] ايثان (M_3) ١، ٤— ثنائي[(٤—فنيل—٣—ثايو) ١،٢، ٤— ترايزول —٥ يل] بيوتان على التوالى مع مولين من ثنائي كلورو ايثان و (وبوجود مولين من هيدروكسيد الصوديوم كما حضرت الليكاندات الجديدة والمغلقة لمشتقات ثنائية — الاوكسادايزول ، الترايزول

مع بعض معقداتهامع النحاس والبلاديوم منها الليكاند ٢، ٢- ثنائي[٢ ثايو{١، ٤- ثنائي(١، ٣ ، ٤-أوكسادايزول-٥ يل) بيوتان}ثنائي اثيل ايثر] (L_1C) وثنائي-١،٢- ثنائي[٣-ثايو-ثنائي{ ٤-فنيل-١،٢، ٤- ترايزول -٥ يل}ميثان] ايثان المائي (L_3C) اذ أعطى تفاعلهما مع كلوريدات الفلزات (M^{+2} = Cu , Pd) معقدين جديدين ، الصيغة العامةلهما هي $(C_{12}H_{16}N_4O_3S_2)_2MCl_2$ و $(C_{38}H_{32}N_{12}S_4)_2MCl_2$ على التوالي .

حضرت الليكاندات ثنائي -١،٢-ثنائي[٣-ثايو-١،٢- ثنائي{٤-فنيل -١،٢، ٤- -٥ يل}ايثان] ايثان . احادى . ثنائى مثيل اوكسيد الكبريت (L_5C) وثنائي-١،٢- ثنائي[٣-ثايو-١، ٤- ثنائي{٤- فنيل- ١،٢، ٤- ترايزول -٥ يل}بيوتان] ايثان . ثنائي . ثنائي مثيل اوكسيد الكبريت (L_7C) شخصت جميع الليكاندات ومعقداتها بالقياسات الفيزيائية المناسبة لها مثل : التحليل العنصري الدقيق (C.H.N) ، طيف الاشعة تحت الحمراء (IR) ، (Ft -IR) ، طيف الاشعة المرئية وفوق البنفسجية والتوصيلية المولارية وكذلك استخدمت طريقة النسب المولية لمعقد الليكاند (L_1C) ، ومنها اقترحت تركيب معقدي الليكاندين (L_1C) ، (L_3C) وهي ثمانية السطوح .