SYNTHESIS AND CHARACERISATION OF NOVEL PENTADENTATE LIGAND TYPE N_2S_2O 4-METHYL-2,6- *BIS*[4-METHYL THIOSEMICARBAZONYLIDEN]- PHENOL AND THEIR COMPLEXES WITH Ni^{+2}, Pd^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2}

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Abstract

Two equivalent of 4-methyl thiosemicarbazide was reacted with 2,6-diformyl-4-methyl phenol to give the new pentadentate ligand H_3L type N_2S_2O {where H_3L= 4-methyl-2,6- *Bis*[4-methyl thiosemicarbazonyliden]-phenol. Also complexes of the ligand of H_3L in general formula $[M\ H_nLX]^y$ where M=Ni^{+2}, Cu^{+2}, n=2, X=Cl, y=0; M=, pd^{+2} , Zn^{+2}, Cd^{+2} and Hg^{+2} ions , n=3, X=0, y=+2 were prepared. All complexes and ligand have been characterised by spectroscopy methods {IR, UV-Vis, ^1H, ^{13}C, ^1H-^{13}C NMR spectroscopy}, atomic absorption, microanalysis of elements (C.H.N), along with conductivity measurement. From the above data, the proposed molecular structure for Ni^{+2} and Cu^2 ions are octahedral, pd^{+2} complexes is square planner, while Zn^{+2} ,Cd^{+2}, Hg^{+2} complexes are forming distorted tetrahedral.

Introduction

Various transition and inner-transition metal complexes with bi-, tri-, and tertradentate Shiff bases containing nitrogen and oxygen donor atoms play important role in biological systems and represent interesting models for metalloenzymes, which efficiently catalyst the reduction of dinitrogen and dioxgen (1,2).

Schiff base derived from condensation of thiosemicarbazide with carbonyl compounds have been reported as complexing agents for various transition metal ions. Thiosemicarbazone moiety without substitute attachted to the thiol sulfur coordinates as either neutral or anionic (N, S) bidentate Ligand depending on the method of complex preparation (3), when an additional coordinating functionality is presented in the proximity of the donating centers, the ligands bind in atridentate manner N N S, O N S. This occurs with either the neutral molecul or the monobasic anion upon loss of a hydrogen from N. If the additional functionality can also lose a proton phenol group, anions of greater negative charge are formed. There are instances reported. However, where the hetrocyclic atom and the azomethine nitrogen are involved in bidentite coordination, and the sulfur atom is considered not be coordinated, weakly coordinated to the same metal center or coordinated to an adjacent metal center(4). In (2005) Chandra and co-worker(5) reported the synthesis and charactrisation of 2- methyl cyclohexanon thiosemicarbazone [MCHTSCL] 2-methylcyclohexannon N(4) methyl-3-thiosemicarbazone [$MCHTSCL_2$] ligands, and their complexes with Mn (II), Co(II) and Ni(II) ions. This paper reports the synthesis and characterissation of anew ligand type N_2S_2O derived from the reaction of two equivalent of 4-methyl thiosemicarbazide with 2,6 diformyl -4-methyl phenol and it 's complexes with Ni^{+2}, Cu^{+2}, Pd^{+2}, Zn^{+2}, Cd^{+2}, and Hg^{+}.

Experimental

Reagents were purchased from Fluka and BDH and Redial-Dehenge Chemical company. IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in range (4000-400) cm^{-1}. Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for 10^{-3} M solution in DMF at 25 °C using Shimadzu 160 spectrophotometer, with 1.000 ± 0.001cm matched quartz cell. ^1H, ^{13}C- NMR were acquired with BRUKER-400 spectrometer in DMSO-d_6. The NMR spectra were recorded at Queen Mary, University of London/ United Kingdom. Elemental microanalysis were performed on a (C.H.N) analyser from heraeus (Vario EL) at the university of free Belin/Germany The chloride contents for complexes were determined by using potentiometic titration method on (686-Swiss). Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3} M solution of the sample in DMF using a PW9526 digital conductivity meter.

1. Preparation of precursor 2,6-diformyl-4-methylphenol [R]

To a solution of 4-methylphenol(10.8g, 10 mmole) in (50mL) acetic acid, hexamethylenetetraamine (28.2g, 20 mmole) and (30g, 100mmole) of paraformaldehyde were added. The mixture was allowed to stirred continuously until the light brown viscous solution was obtained then heated to (70-90°C.) for two hrs. The solution was cooled to room temperature and concentration H_2SO_4 (10mL) carefully added. The resulting solution was refluxed for half-hr, and then on treatment with distilled water (400mL) a light yellow precipitate was formed, which was stored overnight at (4 °C). The yellow product was isolated by filtration and washed in small amount of cold methanol. More pure product with light yellow colour was obtained by means of recrystallisation from toluene, yield 5.7g (35%) m.p. (134°C) (6) Table (1).

2. Preparation of 4-methyl-2,6- *Bis*[4-methyl thiosemicarbazonyliden]- phenol [H_3L]

A solution of 4-methyl thiosemicarbazide (2.22g, 21mmole) in ethanol (20 mL) was added slowly to a mixture of 2,6 diformyl-4-methyl phenol (1.96g, 10.5mmole) dissolved in ethanol (15 mL). The mixture was allowed to reflux for two hrs under nitrogen blanket, then cooled to room temperature. A yellow solid was collected by filtration, recrystallised from methanol/ H_2O, dried under vacuum to give [H_3L] as a pale orange solid. Yield 2.48g (61%) m.p. (288-290°C) (Table -1).

3. Preparation of complexes

A solution of **[H_3L]** (0.20g, 0.59 mmole) in methanol (15 mL) was placed in a round bottomed flask. A solution of nickel(II) chloride hexahydrate (0.15g, 0.59 mmole) in (15mL) methanol was added drop-wise with stirring. The pH of the reaction mixture was adjusted to ≈ (9) by adding ethanolic solution of KOH. The resulted mixture was heated at reflux and under nitrogen atmosphere for two hrs, during which time the solution colour became a purple. The solvent was evaporated under reduced pressure. A purple solid was obtained, collected by filtration, washed with dry diethylether (5 mL) and dried under vacuum to give 0.17g (68%) yield of the title complex, m.p. (300°C). A similar method to that mentioned in preparation the complex of [H_3L] with Ni(II) was used to prepare the complexes of [H_3L] with [Pd^{II}, Cu^{II},Zn^{II}, $Cd^{II}$and Hg^{II}] ions by using metal chloride salt . (Table-1) stated the quantities reaction condition and some physical properties of the prepared complexes.

Result and Discussion

A- Synthesis of precursor of 2,6-diformyl-4 methylphenol [R]

The precursor 2,6-diformyl-4-methyl phenol was prepared according to the general method shown in, Scheme (1). This procedure was characterized by elemental analysis, Table (2), ^{1}H, ^{13}C NMR spectra Table (5) and IR spectra Table (3), which displayed band at (3100|)cm^{-1} referred to aromatic C-H stretching while two bands at (2870, 2660)cm-^{1} can be referred to aldehydic (C-H) stretching (7) . The bands at (1682 and 1667)cm^{-1} can be assigned to stretching of two (C=O) carbonyl groups which are non equivalent because of intramolecular hydrogen bonding with phenolic OH (8).

B- Synthesis of the ligand [H_3L]

The condensation reaction of 2,6-diformyl-4-methyl phenol [R] with thiosemicarbazide, resulted in the preparation of the ligand [H_3L] according to the general method shown in (Scheme-2). The ligand was characterised by elemental analysis, (Table-2), IR spectra (Table-3), (UV-Vis) spectra (Table -4), ^{1}H and ^{13}C NMR spectra (Table 5**)**. IR spectrum of the ligand, (Fig. 1), displays a band at (1652, 1645 cm^{-1}) due to ν(C=N) stretching of the imine groups. These two groups are in different environment due to intramolecular hydrogen bonding while the band at 3326 cm^{-1} attributed to OH stretching. The bands at (1348 and 933 cm^{-1}) assigned to ν(C=S) stretching. The appearance of the imine band and the disappearance of carbonyl group band in 2,6-diformyl-4-methyl phenol compound indicated the formation of [H_3L]. Finally the spectrum displayed band at 1267cm^{-1} which may related to phenolic (C-O) stretching frequency. (UV-Vis) spectrum Fig.(2) exhibits two absorption peaks at (304 nm) (32894 cm^{-1}) (ε_{max}= 2300 $molar^{-1}cm^{-1}$) and (373 nm) (26809 cm^{-1}) (ε_{max}= 1370 $molar^{-1}cm^{-1}$) assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) electronic transitions respectively(9). ^{1}H NMR spectrum of the ligand [H_3L] in DMSO-d_6 displays in Fig.(3**).** The signal at (δ= 11.50 ppm, 2H) assigned to ($N_{(2,\,^{-}2)}$-*H*) protons. The broad signal at (δ= 9.60 ppm,1H) is due to (O-*H*) proton. The resonance at (δ= 8.38 ppm, 2H) is attributed to (N=C-*H*) protons. These protons are equivalent and appears as a singlet, ($N_{(4',4)}$-*H*-CH_3) protons appear as a doublet at chemical shift (δ= 8.15, 8.20 ppm, 4H). These NH_2 groups are not equivalent and each resonance is equivalent to two protons(10). The signal at (δ= 7.60 ppm, 2H) appears as a singlet which is equivalent to two protons assigned to (C_3, C_5-*H*) aromatic protons. The broadness of the signal may be related to the mutual phenomena(11). While the ^{13}C NMR spectrum shown in Fig.(4**)**. The spectrum reveals two sharp resonances at (δ=177.54 ppm) and (δ=152.63 ppm) refer to the thioamide and imino carbons respectively. The four resonance at (δ=141.13, δ= 130.33, δ= 128.73, δ= 120.71 ppm) assigned to carbon atoms of aromatic ring (C_1, C_2, C_4, C_3) respectively. The assignment of the chemical shift are supported by ^{1}H- ^{13}C correlated NMR spectrum Figs.(5), (5a**)**(12).

C- Synthesis of complexes

All complexes were prepared by a similar method, shown in Scheme-(3). The complexes were prepared from the reaction of the ligand with metal chloride salt at reflux in ethanol, Potassium hydroxide was used as a base, and pure complexes formed only at pH =(9). The complexes are stable in solution and in solid state. The molar conductance of the prepared complexes Ni(II), Cu(II) in (DMF) lies in the (20-30) S cm^2mole^{-1} range, indicating non electrolyte nature, while the conductance of the complexes Pd(II), Zn(II),Cd(II)and Hg(II) were in range (80- 120) indicated electrolyic nature with (1- 2) ratio. (. The analytical and physical data Table -(2**),** and spectral data Tables (3, 4 and 5) are compatible with the suggested structure (Scheme-3).

IR- spectra

The IR spectra data for all complexes were presented in (Table -3). In general the I-R spectra of all complexes showed bands at range (1618-1603)cm^{-1} due to ν(C=N) which were shifted to lower frequency when it comparison with that of free ligand [H_3L], also two bands of ν(C=S) which appeared at range (1331-1314)$cm^{-1}$and (867-814)cm-1 in spectra of all complexes were shifted to lower frequency. The shift in ν(C=N) and ν(C=S) can be related to the delocalization of the metal electronic density in to the ligand (π-system) (HOMO → LUMO) and these shifting indicated the coordination between the ligand [H_3L] and metal ions was happened *via* N and S atoms(13). The spectra of all complexes show a very broad band at range (3380-3500)cm^{-1}, this band may be due to overlap of two bands, band of ν(O-H) and band of ν(N-H). On the other hand the band at 1267cm^{-1} due to phenolic ν(C-O) in the free ligand was shifted to lower frequency and papered at range(1256- 1252)cm^{-1} in IR spectra of Ni(II) and Cu(II) complexes only respectively , these shifting in ν(C-O) was confirmed by formation of new band at (462) cm^{-1} and (450) cm^{-1}in IR spectra of Ni(II) and Cu(II) complexes only, which due to ν(Ni-O) and ν (Cu-O) respectively . All complexes showed two bands the first at range (480-516)cm^{-1} and the second at (418)cm^{-1} due to vibration frequencies ν(M-N) and (ν(M-S) respectively(14). These results show the coordination of ligand *via* N, O, S donor atom with metal ions.

UV-Vis spectra

The electronic spectral data of all complexes are summarized in Table -4. The UV-Vis spectra of complexes displayed absorption at (279-344)nm assigned to ligand field which were shifted to lower frequency when it comparison with the spectrum of free ligand [H_3L]. The electronic spectra of all complexes exhibited anew absorption peak at range (351-377)nm which are attributed to charge transfer M→L(15). The UV-Vis spectrum of [Ni (H_2L)Cl] shows anew absorption peak at (390)nm due to (d-d) electronic transition type ($^3A_2g \rightarrow {}^3T_1g_{(p)}$ suggesting octahedral geometry about Ni(II)(16,17). The new absorption peak at

(734)nm in electronic spectrum of [Cu $(H_2L)Cl$] complex is assigned to (d-d) electronic transition type($^2B_2g \rightarrow ^2B_1g$), in fact this result is a good agreement with the previous work of cu(II) complexes of distorted octahedral geometry because of Jahn-Teller effect(18,19,20). While [Pd$(H_2L)Cl_2$] electronic spectrum appeared anew peak at (450)nm assign to (d-d) electronic transition type ($^1A_2g \rightarrow ^1B_1g$) which is a good evidence for square planner geometry about Pd(II) (21). The UV-Vis spectra of Zn(II), Cd(II)and Hg(II) complexes show no absorption peak at range (380-1000)nm that is indicates no(d-d) electronic transition happened (d^{10} -system) in visible region, that is a good result for Zn(II), Cd(II) and Hg(II) tetrahedral complexes(22, 23).

Table (1)

Physical properties compound and weight of the prepared of metal chloride salt.

Product compounds	colour	m.p. °C	Metal chloride	Wt .of metal chloride(g) salt = 0.59 mmole	Wt. of product compounds (g)	Yield %
[R]*	Light yellow	134	-	-	5.7	35
[H_3L]**	Pale orang	288-290	-	-	2.48	61
[Ni(H_2L)Cl] ***	Purple	300	$NiCl_2.6H_2O$	0.14	0.17	68
[Pd (H_3L)]Cl_2	Brown	299-301	$PdCl_2$	0.104	0.16	61
[Cu(H_2L)Cl]	Brown	290	$CuCl_2.2H_2O$	0.10	0.15	60
[Zn (H_3L)] Cl_2	Yellow	317-319 dec	$ZnCl_2$	0.080	0.15	65
[Cd (H_3L)]Cl_2	Yellow	260-262 dec	$CdCl_2.H_2O$	0.118	0. 17	65
[Hg (H_3L)]Cl_2	Yellow	256-258 dec.	Hg Cl_2	0.159	0.20	64

dec. = decompose

**** [R] = $C_9H_8O_3$***
***** [H_3L] =$C_{13}H_{18}N_6OS_2$***
******[H_2L] =$C_{13}H_{17}N_6OS_2$***

Table (2)
Results of elemental analysis of [H_3L] and its metal complexes) Results of elemental analysis for prepared compounds..

Product compound	**M. Wt**	**Microanalysis found (calc) %**				
		C	**H**	**N**	**Cl**	**Metal**
$C_9H_8O_3$	164	(62.07)	(4.07)	-	-	-
		62.02	4.05	-	-	-
$C_{13}H_{18}N_6OS_2$	338	42.49	4.52	27.17	-	-
		(46.13)	(5.36)	(24.83)	-	-
[Ni($C_{13}H_{17}N_6OS_2$)Cl]	431.5	34.62	2.01	21..27	7.21	11.55
		(36.18)	(3.97)	(19.47)	(8.21)	(13.60)
[Cu($C_{13}H_{17}N_6OS_2$)Cl]	436	33.11	2.70	20.01	11.71	12.11
		(35.78)	(3.93)	(19.26)	(8.12)	(14.56)
[Pd($C_{13}H_{18}N_6OS_2$)]Cl_2	515	30.78	3.68	19.43	-	33.61
		(35.10)	(4.08)	(18.89)	-	(23.92)
Zn($C_{13}H_{18}N_6OS_2$)]Cl_2	474	34.00	3.99	22.48	-	14.71
		(38.66)	(4.49)	(20.81)	-	(16.19)
[Cd($C_{13}H_{18}N_6OS_2$)]Cl_2	521	30.52	3.70	20.10	-	22.95
		(34.63)	(4.02)	(18.64)	-	(24.93)
[Hg($C_{13}H_{18}N_6OS_2$)]Cl_2	609	26.11	2.31	16.21	-	33.98
		(28.97)	(3.37)	(15.59)	-	(37.21)

Table (3)
Infrared spectral data (wave number)cm^{-1} of the ligand [H_3L] and its complexes.

products	**υ(N–H), υ (OH)**	**υ(C=N)**	**υ (C=C**	**υ(C=S)**	**υ(N–N)**	**υ(C-O)**	**υ(M-O)**	**υ(M–N)**	**Additional bands**
[H_3L]	3326 m	1652 1645 m	1530	933 1348	999s	1267			3003m υ(C–H) arom. 2900w υ(C–H) aliph
[(NiH_2L)Cl	3400br	1616s	1557 m	867m 1331m	1082 m	1256	462m	516w	3000m υ(C–H) arom. 2970vw υ(C–H) aliph 1457w δ(C-N)
[Pd(H_3L)]Cl_2	3414	1618s	1505w	840 1318m	1016m	1254	-	488	3090m υ(C–H) arom. 2930vw υ(C–H) aliph 1490w δ(C-N)
[Cu(H_2L)Cl	3500br	1607m	1529w	830w 1319w	1050w	1252	550w	506	3000m υ(C–H) arom. 2970vw υ(C–H) aliph 1440w δ(C-N)
[Zn(H_3L)]Cl_2	3420w	1616s	1551m	824m 1318m	1015 m	1256		504	3050m υ(C–H) arom. 2900vw υ(C–H) aliph 1446w δ(C-N)
[Cd (H_3L]Cl_2	3400b	1613m	1540m	814m 1314m	1117s	1252m	-	482w	3010m υ(C–H) arom. 2940vw υ(C–H) aliph 1488w δ(C-N)
[Hg (H_3L]Cl_2	3380	1603s	1558w	814m 1316m	1122s	1252w	-	480w	300m υ(C–H) arom. 2900vw υ(C–H) aliph 1458w δ(C-N)

(s) strong, (br) broad, (m) medium, (w) weak, (vw) very weak

Table (4)
Electronic spectral data of [H_3L] and its metal complexes.

Compound	l nm	u cm^{-1}	ε_{max}(mol^{-1} .lit.cm^{-1})	Assignment
[H_3L]	304	32894	2300	$\pi\rightarrow\pi^*$
	373	26809	1370	$n\rightarrow\pi^*$
[[Ni^{II}(L)Cl]	282	35460	2479	Ligand field
	351	28490	1705	Charge transfer
	390	25641	1107	$^4A_{2g}\rightarrow{}^4T_{1g\,(p)}$
[Pd^{II}(L)Cl_2]	280	35714	1570	Ligand field
	450	22222	150	$^1A_{1g}\rightarrow{}^1B_{1g\,(p)}$
[Cu^{II}(L)Cl]	295	33898	2502	Ligand field
	387	25839	1650	Charge transfer
	734	13623	700	$^2B_{2g}\rightarrow{}^2B_{1g}$
[Zn^{II}(L)Cl_2]	344	29069	1175	Ligand field
	359	27855	849	Charge transfer
[Cd^{II}(L)Cl_2]	279	35842	1591	Ligand field
	359	27855	500	Charge transfer
[Hg^{II}(L)Cl_2]	301	33222	1331	Ligand field
	377	26525	668	Charge transfer

Recorded in DMSO

Table (5)
^{1}H, ^{13}C NMR data for the ligands and precursors measured in DMSO–d_6 and chemical shift in ppm(δ).

Compound	Funct. Group	δ_H(ppm)^b
2,6-diformyl-4-methyl phenol **^{1}H**	O-H; H-C=O ($C_{7,8}$); Ar. C-H ($C_{3,5}$); CH_3 (C_9)	11.40, (1H,S); 10.50, (2H, S); 7.8, (2H, S); 2.4, (3H, S)
^{13}C	H-C=O ($C_{7,8}$); Ar. C-OH(C_1) C-H , ($C_{3,5}$); C=C,($C_{2,6}$) ; C-C(C_4); Aliphatic CH_3, (C_9)	192.80; 162.92 137.89; 129.81; 123.83; 20.10
[H_3L] **^{1}H**	O-H; H-C=N ($C_{7,8}$); Ar. C-H ($C_{3,5}$); CH_3 (C_9); $N_{(2)}$-H; $N_{(4)}$-H	9.60, (1H, S); 8.38, (2H,S); 7.60, (2H, S); 2.20, (3H, S); 11.50, (2H, S); 7.90, 8.10, (4H, S)
^{13}C	H-C=N ($C_{7,8}$); Ar. C-OH(C_1) C-H , ($C_{3,5}$); C=C,($C_{2,6}$) ; C-C(C_4); Aliphatic CH_3, (C_9); C=S, ($C_{10,\ ^{-}10}$)	155.15; 142.11 121.23; 131.87; 129.34 20.20; 178.11

δ^b chemical shift from TMS; S = Singlet   br= broad

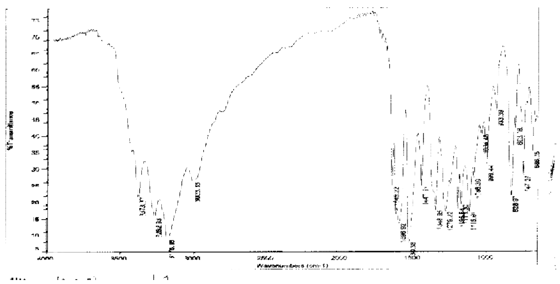


Fig.(1): IR spectrum of $[H_3L]$.

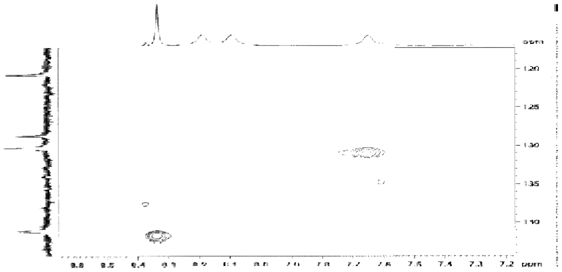


Fig.(5a):^1H –^{13}C NMR correlation of$[H_3L]$.

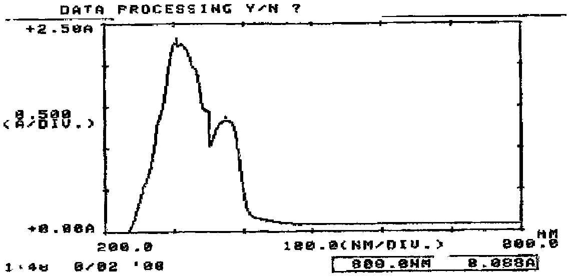


Fig.(2) : UV-Vis spectrum of $[H_3L]$.

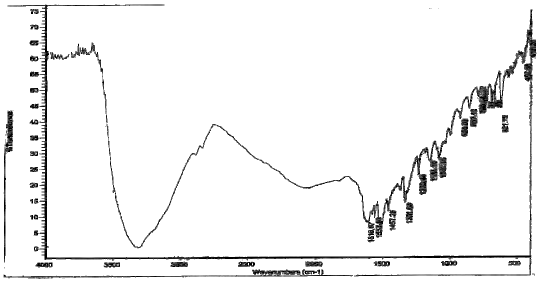


Fig.(6) : IR spectrum of $[Ni^{II}(H_2L)Cl]$.

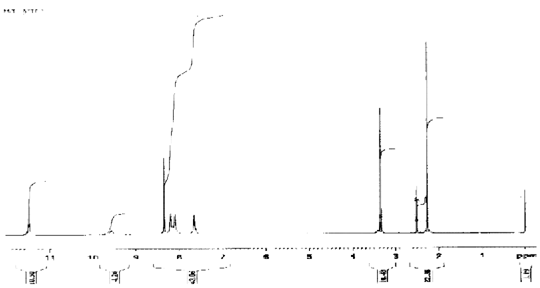


Fig.(3):^1H-NMR of $[H_3L]$.

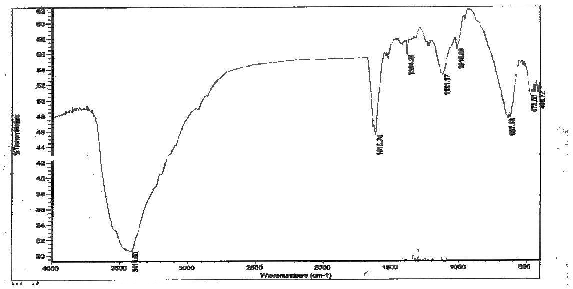


Fig.(7): IR spectrum of $[Pd^{II}(H_3L)]Cl_2$.

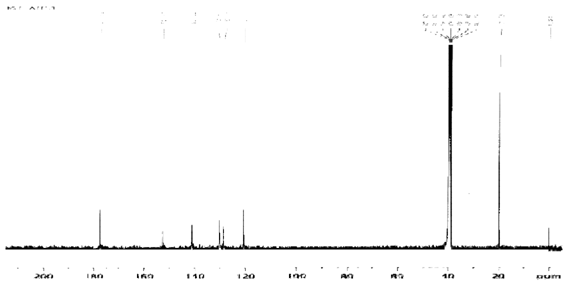


Fig.(4):^{13}C-NMR spectrum $[H_3L]$.

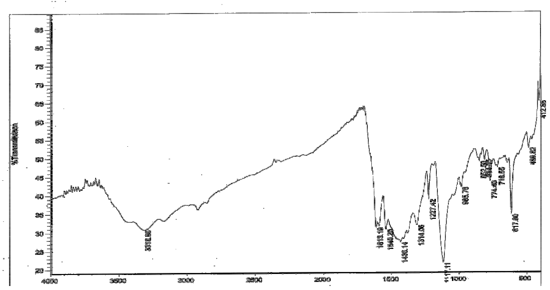


Fig.(8) : IR spectrum of $(Cd(H_3L)Cl_2$.

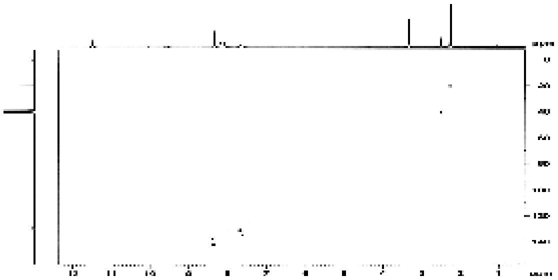


Fig.(5): ^1H –^{13}C NMR correlation of $[H_3L]$.

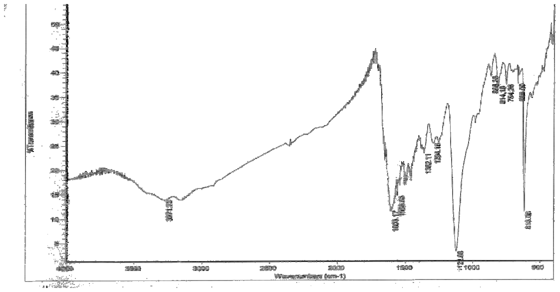


Fig.(9):IR spectrum of $(Hg(H_3L)Cl_2$.

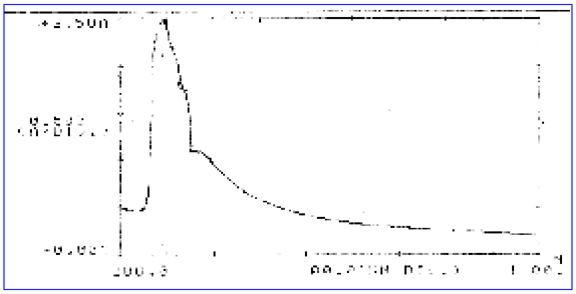


Fig.(10) : Uv-Vis spectrum of[Ni(H_2L)Cl].

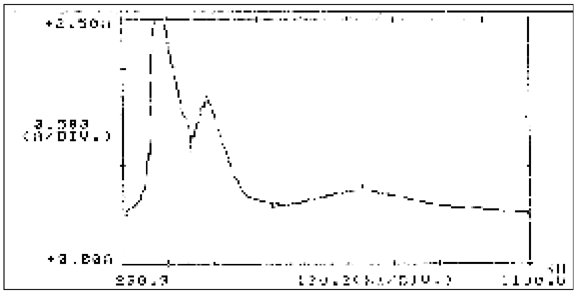


Fig.(12):UV-Vis spectrum of (Cu(H_2L)Cl.

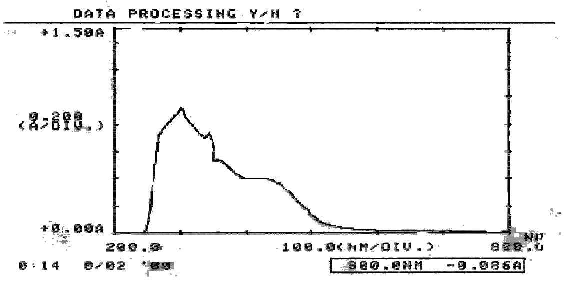


Fig.(11) : Uv-Vis spectrum of(pd(H_3L)Cl_2.

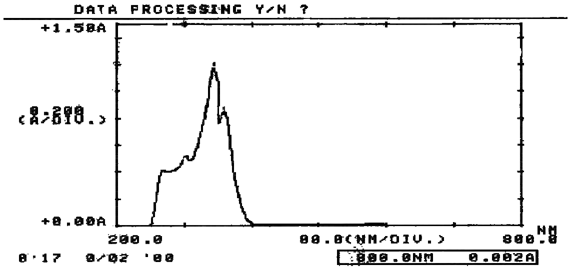
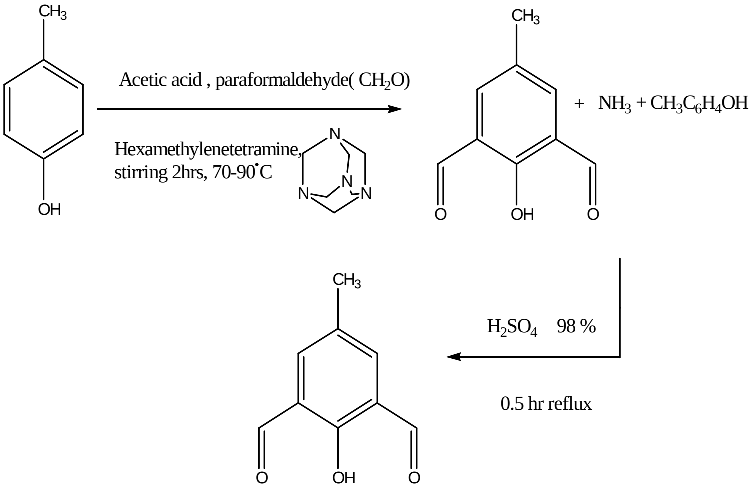
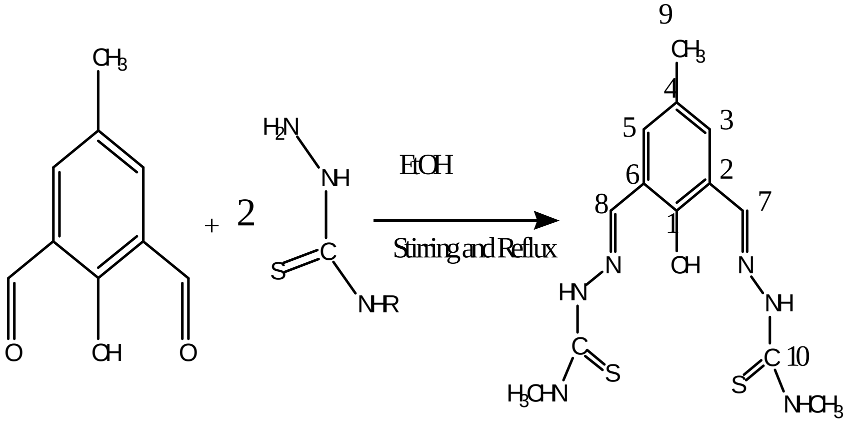


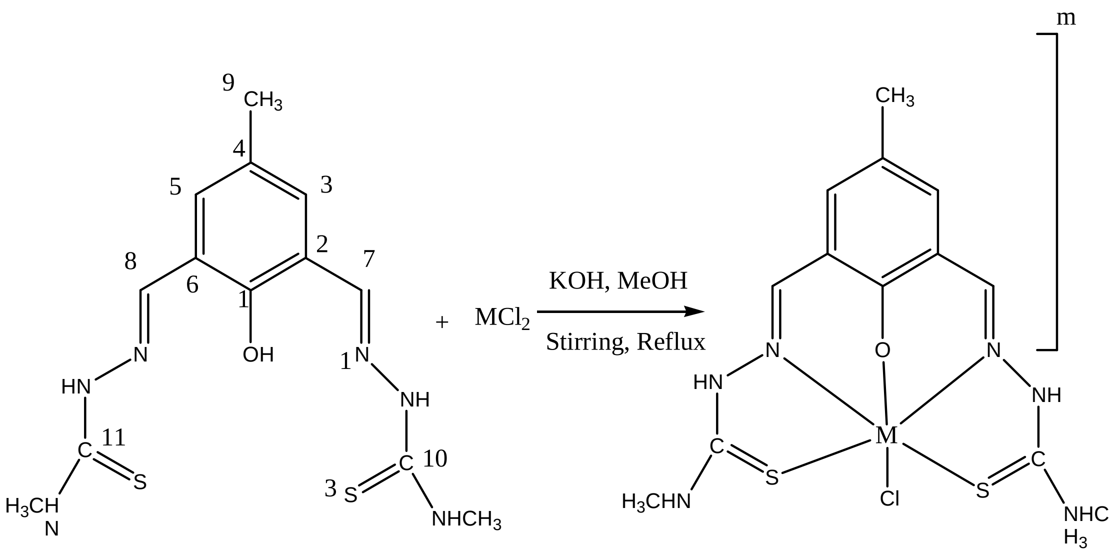
Fig.(13):UV-Vis spectrum of(Zn(H_3L)Cl_2.



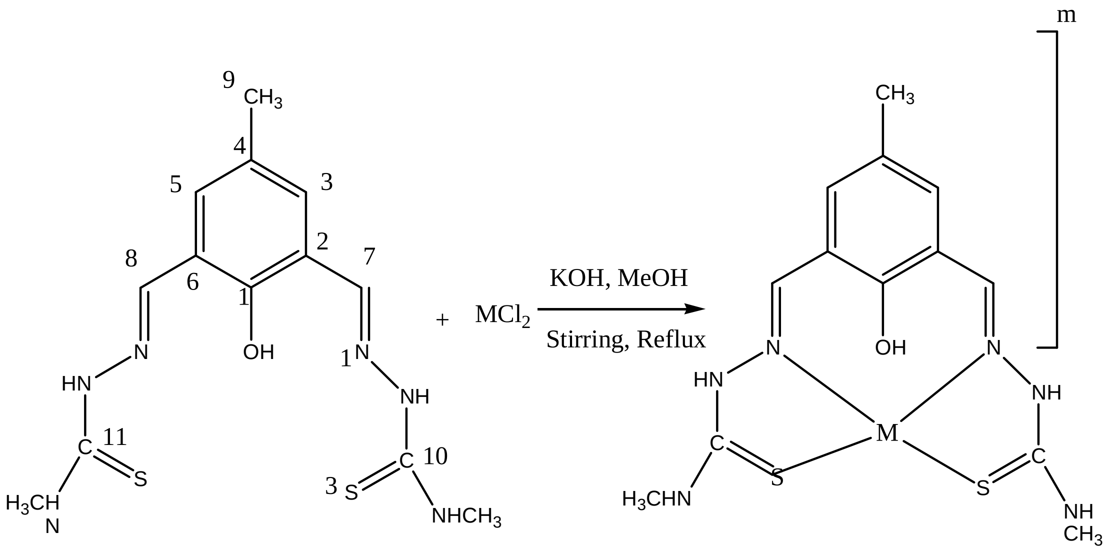
Scheme (1) Synthesis route of precursor[R].



Scheme(2) Synthesis route of [H_3L].



Where:]
[M= Ni^{+2} , Cu^{+2}, m=0,]



Where:]
[,pd^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2}, m=-2]

Scheme (3) Synthesis route of Complexes.

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الخلاصة

تضمن البحث تحضير الليكند خماسي السن الجديد من نوع (N_2S_2O) و معقداته مع أيونات النيكل(II) والنحاس(II) والبلاديوم(II) و الخارصين(II) والكادميوم(II) والزئبق(II). حضر الليكاند باستخدام مكافئين من 4-methyl thiosemicarbazide ومكافئ واحد من 2,6-diformyl-4-methyl phenol، كذللك تم تحضير معقدات الليكاند [H_3L] ذات الصيغه العامه $[MH_nLX]^y$ حيث تمثل: M= Ni^{+2}, Cu^{+2} وان ; n=2, X=Cl, y=0 وتمثل: Pd^{+2}, Zn^{+2}, Cd^{+2}, Hg^{+2} , وان= M, n=3, y= +2 , X=0 .

أما المعقدات فقد حضرت بالتفاعل المباشر بين الليكاند وايونات الفلزات بنسبة1:1 وبطريقة التصعيد العكسي باستخدام الميثانول كوسط للتفاعل جميع المركبات المحضرة شخصت بوساطة التحليل الكمي الدقيق للعناصر والتوصيلية المولارية والامتصاص الذري وقياس محتوى الكلور إضافة إلى الطرائق الطيفية مثل :- {IR, UV-Vis, ^{1}H, ^{13}C, ^{1}H-^{13}C NMR spectroscopy} واغتمادا المعطيات أعلاه اقترح الشكل ثماني السطوح لمعقدات Ni^{+2} و Cu^{+2} ولمعقد pd^{+2} المربع المستوي بينما اتخذت معقدات Zn^{+}, Cd^{+2}, Hg^{+2}شكل رباعي السطوح المشوه.