Synthesis and Structural Studies of Novel 2,6-Diformyl-*p*-Cresol *Bis*-(thiosemicarbazone) Ligand and Their Binuclear Complexes with Ni^{+2}, Pd^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2} Metal Ions

تحضير ودراسة تركيبية لليكاند الجديد 2,6-diformyl-*p*-cresol *bis*-(thiosemicarbazone) ومعقداتة مع بعض الايونات الفلزية

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Abstract :

A new binuclear complexes of Ni^{+2}, Pd^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2} ions with $[H_3L]$ {where H_3L= 4-Methyl-2,6-*bis*(formylthiosemicarbazonyl) phenol}. The ligand was prepared from reaction two equivalent of thiosemicarbazide with 2,6-diformyl-*p*-cresol and then reacted with metal ions to form the title complexes. The ligand and complexes were characterized by {IR, UV-Vis, ^1H, ^{13}C, ^1H-^{13}C NMR and mass spectroscopy}, molar conductivity, atomic absorption and the microanalysis of elements (C.H.N). The spectral studies showed the geometry around the Ni^{+2} and Pd^{+2} ions are square planar and the Zn^{+2}, Cd^{+2} and Hg^{+2} ions are distorted tetrahedral.

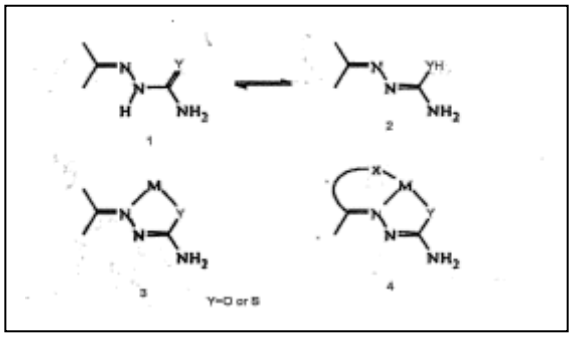
الخلاصة :

تضمن البحث تحضير الليكند خماسي السن من نوع (N_2S_2O) و معقداته ثنائية النواة مع أيونات النيكل و البلاديوم و الخارصين والكادميوم والزئبق. حضر الليكند باستخدام مكافئين من thiosemicarbazide ومكافئ واحد من 2,6-diformyl-*p*-cresol ، أما المعقدات فقد حضرت بالتفاعل المباشر بين الليكند وايونات الفلزات بنسبة ٢:١ وبطريقة التصعيد العكسي باستخدام الميثانول كوسط للتفاعل . المشتق الليكند والمعقدات المحضرة شخصت بواسطة التحليل الكمي الدقيق للعناصر والتوصيلية المولارية والامتصاص الذري وقياس محتوى الكلور إضافة إلى الطرق الطيفية مثل {IR, UV-Vis, ^1H, ^{13}C, ^1H-^{13}C NMR and mass spectroscopy} . ومن خلال الدراسات أعلاه اقترحت الأشكال الفراغية لمعقدات Ni^{+2} و Pd^{+2} مربعة مستوية ولمعقدات Zn^{+2} و Cd^{+2} Hg^{+2} رباعية السطوح.

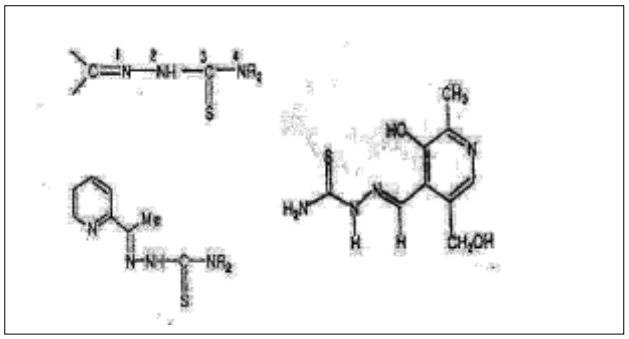
Introduction :

The chemistry of thiosemicarbazones binuclear complexes with many transition elements is well explored[1,2] and some of the compound show interesting biological properties, which make them capable for medical applications[3]. In the solid state the majority of thiosemicarbazones exist in thion form (1), while in the solution they are known to toutomrise into the thiol form (2). Complexation usually take place via dissociation of the acidic proton, resulting in the formation of a five membered ring (3). When an additional donor site (X) incorporated in such ligands, linked to the carboxylic carbon via one or two intervening atoms X, O, or S tri coordination usually take place,**(1)**. In particular binuclear thiosemicarbazones have remarkable *antibacterial, antimalarial, antiviral, and antitumor* properties[4-6], and the activity of the uncomplexed thiosemicarbazones can be increased significantaly by the formation of metal complexes as has been demonstrated for Ni^{+2}, Pd^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2} chelates[7-9]. Thiosemicarbazone moiety **(2)** without substituents attached to the thion sulfur coordinates as a bidentate ligand (NS) (neutral or anionic) depending on the complex method preparation[6], a third coordinating atom often gives (NNS) (e.g.2-acetylpyridine thiosemicarbazone) tridentate ligand[7], when an additional coordinating functionality is present in the nearest of the donating centre, the ligands bind in tridentate manner. This occurs with either the neutral molecule or the monobasic anion upon loss of a hydrogen from N(2). If the additional functionality can also lose a proton (e.g. phenol group), anions of greater negative charge are

formed. There are instances reported, however, where heterocyclic atom and the azomethine nitrogen are involved in bidentate[9], and the sulfur atom is considered not to be coordinated, weakly coordinated to the same metal centre, or coordinated to an adjacent metal centre.



(2)



(1)

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 (200-800) nm for 10^{-3} M solution in DMF at 25 °C using Shimadzu 160 spectrophotometer, with 1.000 ± 0.001 cm matched quartz cell. Mass spectrum for the ligand was obtained by Laser absorption technique using BRUKER DALTONICS -400 MHz. ^{1}H, ^{13}C- NMR were acquired with BRUKER-400 spectrometer in DMSO-d_6. The 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 potentiometer 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 2,6-diformyl-*p*-cresol

The dialdehyde was prepared by a completely different method[10]as follow. To a solution of *p*-cresol (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 was obtained by means of recrystallisation from toluene, yield 5.7g (35%) m.p. (132-134°C.).

2. Preparation of 4-Methyl-2,6-*bis*(formyl thiosemicarbazonyl) phenol [H_3L]

A solution of thiosemicarbazide (2.22g, 24mmole) in ethanol (20 mL) was added slowly to a mixture of 2,6 diformyl-*p*-cresol (2.00g, 12mmole) 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 1.89g (50%) m.p. (286-288°C.)

3. Preparation of complexes

A solution of **[H_3L]** (0.10g, 0.032 mmole) in methanol (15 mL) was placed in a round-bottomed flask. A solution of nickel(II) chloride hexahydrate (0.15g, 0.064 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 became a purple in colour. The solvent was evaporated under reduced pressure. A deep green solid was obtained, collected by filtration, washed with dry diethylether (5 mL) and dried under vacuum to give 0.11g (81%) yield of the title

complex, m.p. (301-303°C). molar conductivity in DMF = 81 equivalent to 1:1 ratio. A similar method to that mentioned in preparation of Ni(II) complex was used to prepare the complexes of **[H_3L]** with [Zn^{II}, Cd^{II}, Hg^{II}, Pd^{II}] ions. The pH of the reaction mixture was adjusted to ≈ (9) by adding ethanolic solution of KOH. All complexes were soluble in Ethanol and DMF solvents. **Table (1)** stated the quantities, reaction condition and some physical properties of the prepared complexes.

Table (1) some physical properties of the prepared complexes
dec. = decompose

Empirical formula	m.p. °C	Colour	Wt .of metal ion = 0.064 mmole	Wt. of product	Yield %	Molar conductivity in DMF Scm^2mol^{-1}
$[Zn_2\ Cl_2\ (L^1)]^-$	317-319 dec.	Yellow	0.08g	0.125g	88	77 = 1:1
$[Cd_2\ Cl_2\ (L^1)]^-$	260-262	Orange	0.118g	0.144g	84	81=1:1
$[Hg_2\ Cl_2(L^1)]^-$	256-258 dec.	Yellow	0.174g	0.18g	81	94=1:1
$[Pd_2Cl_2\ (L^1)]^-$	299-301	Brown	0.114g	0.15g	93	76=1:1

Results and Discussions :

1- The synthesis and characterisation of compounds

A- The synthesis and characterisation of 2,6-diformyl-*p*-cresol

The 2,6-diformyl-*p*-cresol was prepared by one pot reaction. *p*-Cresol, paraformaldehyde, acetic acid and hexamethylenetetramine were mixed in MeOH at reflux to obtain the title compound. Sulfuric acid (98%) was used to neutralised the ammonia and to dissolve the unreacted phenol, **Scheme (1)**. This procedure is straightforward formed and required short time to obtain the compound. The compound was characterized by elemental analysis, **Table (2)**, IR **Table (3)**, ^1H and ^{13}C NMR spectra **Table (5)**.

B- The synthesis and characterisation of the ligands [H_3L]

The condensation reaction of 2,6-diformyl-*p*-cresol with thiosemicarbazide, resulted in the preparation of the ligand [H_3L] according to the general method shown in **Scheme (2)**. The ligand was characterized by elemental analysis, **Table (2)**, IR **Table (3)**, (UV-Vis) **Table (4)**, mass spectroscopy, ^1H 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. 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-*p*-cresol compound indicated the formation of [H_3L]. (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 ($n\rightarrow\pi^*$) transitions respectively[11]. ^1H 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*) 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[15]. 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[12]. 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)**[16]. The negative mode (-) mass spectrum of the ligand, **Fig (6)** shows the parent ion peak at (M/Z= 309), which corresponds to (M-H), other fragments and their relative abundance and fragmentation sequence is shown in **Scheme (3)**[13].

C- The synthesis and characterisation of the complexes

All complexes were prepared by a similar method, shown in **Scheme(4)**. 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 *ca*.(9). The complexes are stable in solution and in solid state. The molar conductance of the prepared complexes in (DMF) lies in the (74–94) S cm^2mole^{-1} range, indicating their electrolyte nature with (1:1) ratio. The analytical and physical data **Table (2),** and spectral data **Tables (3, 4** and **5)**

IR Spectra :

The IR spectra for $[Ni_2Cl_2(L)]^-$, $[Pd_2Cl_2(L)]^-$, $[Zn_2Cl_2(L)]^-$, $[Cd_2Cl_2(L)]^-$ and $[Hg_2Cl_2(L)]^-$ complexes, **Figs.(7-11)** respectively, shows no bands around (3176 and 3373 cm^{-1}) could be assigned to $\nu(N_{(2)}\text{-H})$ and ν(O-H) stretching respectively in comparison with that in free ligand, **Fig(1)**. The broad band in the range (3250-3400 cm^{-1}) may be attributed to $\nu_{asym.,\ sym.}$ $(N_{(4)}\text{-H})$ stretching. The bands at (1616,1645 cm^{-1}) which is due to ν(C=N) stretching in the free ligand is shifted to lower frequency and appears at the range (1603-1616 cm^{-1}). This shifting can be attributed to the delocalisation of the electron density of the metal ion in the π-system of the ligand (HOMO → LUMO) [where HOMO= Highest Occupied Molecular Orbital; LUMO= Lowest Unoccupied Molecular Orbital]. A new bands at the range (489-550 cm^{-1}) attributed to ν(M-O) and the range (412-418 cm^{-1}) attributed to ν(M-N) stretching respectively. These results show the coordination of the ligand towards the metal ion[14,15].

UV-Vis Spectra :

The UV-Vis spectra of K $[Ni_2^{II}(L)Cl_2]$ and K $[Pd_2^{II}(L)Cl_2]$ complexes **Figs.(12,13),** displayed absorption peaks at (343, 300 nm) (29154, 33333 cm^{-1}) (ε_{max}=1450, 916 $molar^{-1}$ cm^{-1}), (367, 345 nm) (27247, 28985 cm^{-1}) (ε_{max}=937, 780 $molar^{-1}$ cm^{-1}), assigned to ligand field and charge transfer, the peaks at (457. 480 nm) (21881, 20833 cm^{-1}) (ε_{max}=300, 200 $molar^{-1}$ cm^{-1}) assigned to (d-d) transition type $^{1}A_{1g}\rightarrow{}^{1}B_{1g}$. While the electronic spectra of Zn^{+2} , Cd^{+2}, Hg^{+2} complexes **Figs.(14-16)**, are appeared intense peaks at (344 nm) (29069 cm^{-1}) (ε_{max}= 1175 $molar^{-1}cm^{-1}$), (359 nm)(27855cm^{-1}) (ε_{max}= 849 $molar^{-1}cm^{-1}$), (279 nm) (35842 cm^{-1}) (ε_{max}= 1591 $molar^{-1}cm^{-1}$), (359 nm) (27855 cm^{-1}) (ε_{max}= 500 $molar^{-1}cm^{-1}$) and (301 nm)(33222 cm^{-1}) (ε_{max}= 1331 $molar^{-1}cm^{-1}$) and (377 nm) (26525 cm^{-1}) (ε_{max}= 668 $molar^{-1}cm^{-1}$) respectively. These peaks are assigned to charge transfer.

^{1}H and ^{13}C NMR spectra :

The ^{1}H NMR spectrum of the complex $K[Zn_2(L)Cl_2]$, **Fig.(17)**, show no resonance in the range (δ= 9–12ppm), could be attributed to $(N_{(2)}H$ and O-*H*) indicated the losing of these protons upon complexation. The signal at (δ= 8.26 ppm, 2H) refers to the (N=C-*H*), which shifted to downfield in comparison to that in the free ligand. The signal at (δ=7.01ppm, 2H) refers to the ($C_{3,}C_5$-*H*) which is shifted to downfield in comparison with that in the free ligand, The broad signal at (δ= 6.13 ppm, 4H) refers to the ($N_{(4,4^{-})}H$). This resonance disappeared upon addition of D_2O to the solution[20], **Fig.(18)**. The chemical shift at (δ= 2.20 ppm, 3H) is assigned to methyl group protons.

The ^{13}C NMR spectrum of the complex $K[Zn_2(L)Cl_2]$, **Fig.(19)** shows the signals at (δ= 173.59, 152.66, 136.30, 125.18, 122.20, 118.18 ppm) assigned to (C_1, C_2, C_4, $C_{3,5}$) respectively, these signals have been shifted to low field compared with that in the free ligand. The methyl group carbon atom appear at (δ= 20.00 ppm, 3H). The ^{1}H NMR spectrum of the complex $K[Hg_2(L)Cl_2]$, **Fig.(20)**, shows no resonance in the range (δ= 9.5–12ppm), can be attributed to $(N_{(2)}H$ and O-*H*) indicates the losing of these protons upon complexation. The signal at (δ= 8.90 ppm, 2H) refers

with the of (N=C-*H*), which shifted to upper field in comparison to that in the free ligand. The signal at (δ=8.59ppm, 2H) refers to the (C_3,C_5-*H*) which is shifted to upper field in comparison with that in the free ligand, The broad signal at (δ= 7.73 ppm, 4H) refers to the (($N_{(4,4')}$-*H*). This resonance disappears upon addition of D_2O to the solution[16], **Fig.(21)**. The chemical shift at (δ= 2.20 ppm, 3H) is assigned to methyl group. From the above results the suggested geometry around Ni, Pd ions are square planar and the geometry of other ions are distorted tetrahedral.

Table (2) Results of elemental analysis and physical properties of [H_3L] and its metal complexes

Empirical Formula	M.Wt	Yield %	m.p (°C)	Colour	Microanalysis found (calc) %				
					C	H	N	Cl	Metal
$C_9H_8O_3$	164	35%	134	Light yellow	(62.07)	(4.07)	-	-	-
					62.02	4.05	-	-	-
$C_{11}H_{14}N_6OS_2$	310	50	286-288	Pale orange	42.49	4.52	27.17	-	-
					(42.56)	(4.55)	(27.07)	-	-
K $Ni_2C_{11}H_{11}Cl_2N_6OS_2$	534	81	301-303	Purple	24.62	2.01	15.27	13.21	21.55
					(24.71)	(2.07)	(15.72)	(13.26)	(21.95)
K $Pd_2C_{11}H_{11}Cl_2N_6OS_2$	630	93	299-301	Brown	20.78	1.68	13.43	11.11	33.61
					(20.96)	(1.76)	(13.34)	(11.25)	(33.77)
K $Zn_2C_{11}H_{11}Cl_2N_6OS_2$	548	88	317-319 dec	Yellow	24.00	1.99	15.48	12.88	23.71
					(24.10)	(2.02)	(15.33)	(12.94)	(23.86)
K $Cd_2C_{11}H_{11}Cl_2N_6OS_2$	642	84	260-262	Orange	20.52	1.70	13.10	-	29.95
					(20.57)	(1.73)	(13.09)	-	(35.01)
$KHg_2C_{11}H_{11}Cl_2N_6OS_2$	818	81	256-258 dec	Yellow	16.11	1.31	10.21	-	48.98
					(16.14)	(1.35)	(10.27)	-	(49.01)

(calc): calculated ; (dec): decomposed

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

Compound	υ(N–H)	υ(C=N)	υ(C=S)	υ(N–N)	υ(C-O)	υ(M-O)	υ(M–N)	υ(C=C)	Additional bands
[H_3L]	3262 m 3176 s	1645 m	933 1348	999s				1530	3003m υ(C–H) arom. 2900w υ(C–H) aliph
K [Ni_2^{II}(L)Cl_2]	3200-3400br	1616s	867m 1331m	1082m	1233m	498m	418w	1557m	3000m υ(C–H) arom. 2970vw υ(C–H) aliph 1457w δ(C-N)
K [Pd_2^{II}(L)Cl_2]	3200-3500br	1607m	830w 1319w	1050w	1229m	550w	412w	1529w	3000m υ(C–H) arom. 2970vw υ(C–H) aliph 1440w δ(C-N)
K [Zn_2^{II}(L)Cl_2]	3390w 3420w	1616s	824m 1318m	1015m	1386w	497m	418w	1551m	3050m υ(C–H) arom. 2900vw υ(C–H) aliph 1446w δ(C-N)
K [Cd_2^{II}(L)Cl_2]	3250-3400b	1613m	814m 1314m	1117s	1227m	489w	412w	1540m	3010m υ(C–H) arom. 2940vw υ(C–H) aliph 1488w δ(C-N)
K [Hg_2^{II}(L)Cl_2]	3190br 3271br	1603s	814m 1362m	1122s	1294w	500w	412w	1558w	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^1] and its metal complexes

Compound	λnm	υcm^{-1}	ε_{max}molar^{-1} cm^{-1}	Assignment
[H_3L]	304	32894	2300	$\pi\rightarrow\pi^*$
	373	26809	1370	$n\rightarrow\pi^*$
[K [$Ni_2^{II}(L)Cl_2$]	343	29154	1450	Charge transfer
	367	27247	937	Charge transfer
	457	21881	300	$^1A_{1g}\rightarrow{}^1B_{1g}$
K [$Pd_2^{II}(L)Cl_2$]	300	33333	916	Charge transfer
	345	28985	780	Charge transfer
	480	20833	200	$^1A_{1g}\rightarrow{}^1B_{1g}$
K $Zn_2^{II}(L)Cl_2$]	344	29069	1175	Charge transfer
	359	27855	849	Charge transfer
K [$Cd_2^{II}(L)Cl_2$]	279	35842	1591	Charge transfer
	359	27855	500	Charge transfer
K [$Hg_2^{II}(L)Cl_2$]	301	33222	1331	Charge transfer
	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-*p*-cresol **^{1}H** **^{13}C**	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)
	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** **^{13}C**	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)
	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
K[$Zn_2(L)Cl_2$] **^{1}H**	H-C=N ($C_{7,8}$); Ar. C-H ($C_{3,5}$); CH_3 (C_9); $N_{(4)}$-H	8.26, (2H,S); 7.01, (2H,S); 2.20, 3H; 6.13, (4H)
^{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)	152.66; 173.59 118.18; 136.30; 122.20 20.12
K[$Hg_2(L)Cl_2$] **^{1}H**	H-C=N ($C_{7,8}$); Ar. C-H ($C_{3,5}$); CH_3 (C_9); $N_{(4)}$-H	8.90, (2H); 8.59, (2H) 2.20, (3H); 7.73, (4H)

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

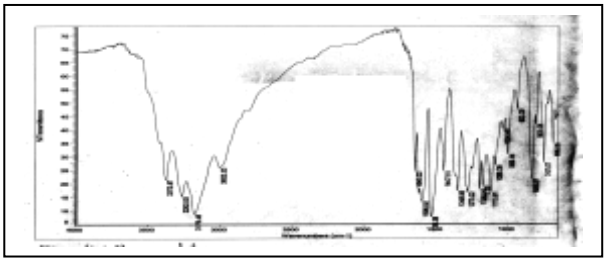


Fig.(1) IR spectrum of [H_3L]

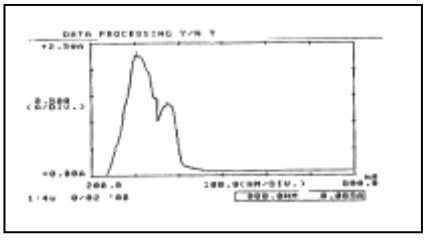


Fig.(2) UV-Vis spectrum of [H_3L]

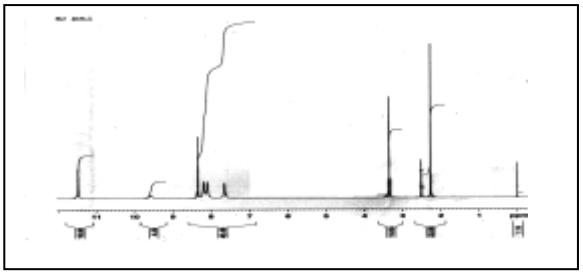


Fig.(3) ^{1}H-NMR of [H_3L]

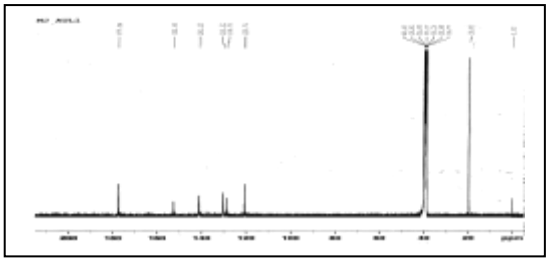


Fig.(4) ^{13}C-NMR spectrum of [H_3L]

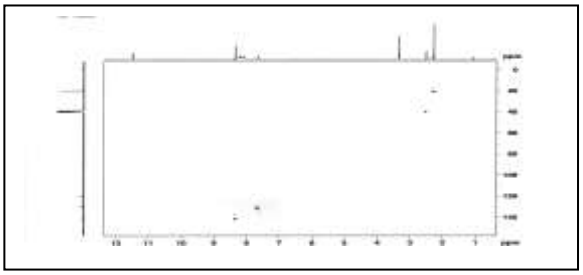


Fig.(5) ^{1}H –^{13}C NMR correlation of [H_3L]

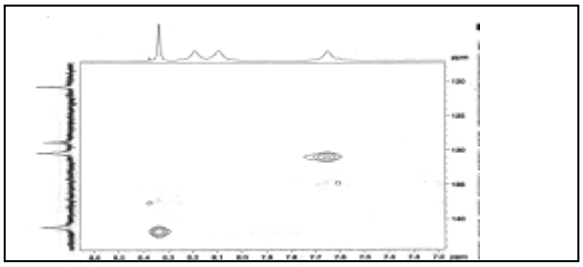


Fig.(5a) ^{1}H –^{13}C NMR correlation of [H_3L]

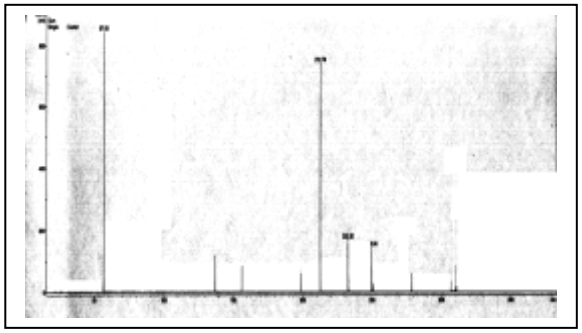


Fig.(6) mass spectrum of [H_3L]

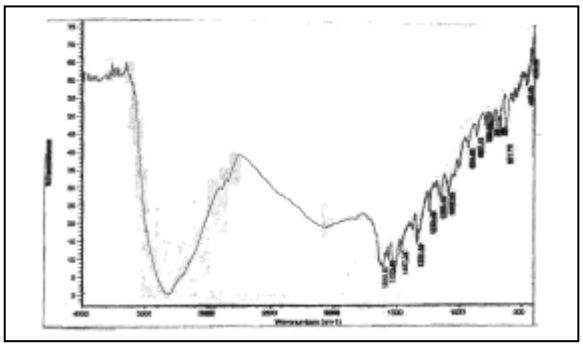


Fig.(7) IR spectrum of K [$Ni_2^{II}(L)Cl_2$]

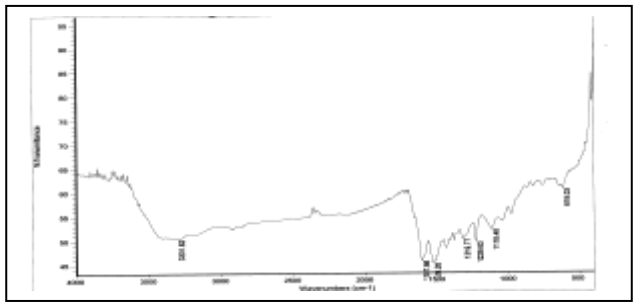


Fig.(8) IR spectrum of K [$Pd_2^{II}(L)Cl_2$]

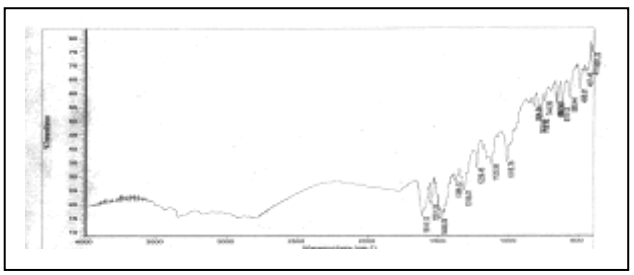


Fig.(9) IR spectrum of K [$Zn_2^{II}(L)Cl_2$]

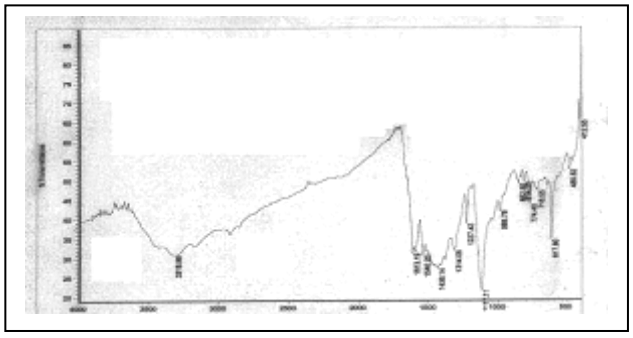


Fig.(10) IR spectrum of K [$Cd_2^{II}(L)Cl_2$]

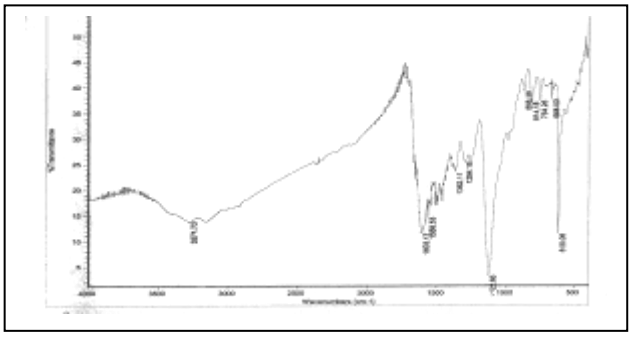


Fig.(11) IR spectrum of K [$Hg_2^{II}(L)Cl_2$]

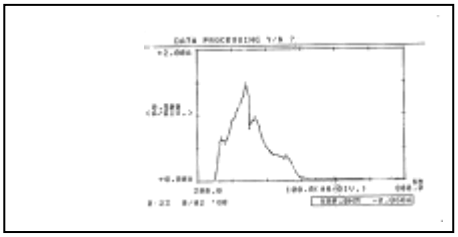


Fig.(12) UV-Vis spectrum of K $[Ni_2^{II}(L)Cl_2]$

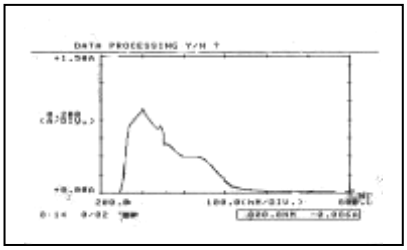


Fig.(13) UV-Vis spectrum of K $[Pd_2^{II}(L)Cl_2]$

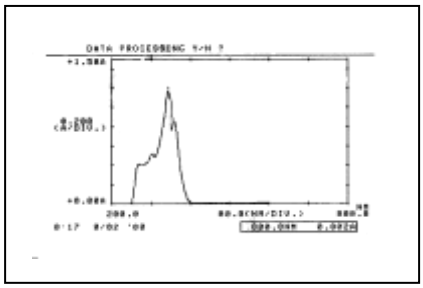


Fig.(14) UV-Vis spectrum of K $[Zn_2^{II}(L)Cl_2]$ $[Cd_2^{II}(L)Cl_2$

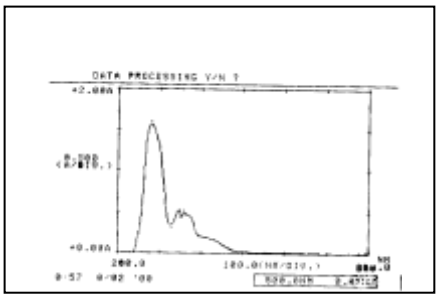


Fig.(15) UV-Vis spectrum of K

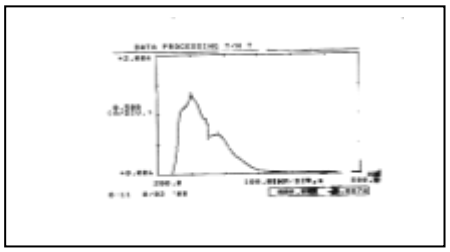


Fig.(16) UV-Vis spectrum of K $[Hg_2^{II}(L)Cl_2]$ $[Zn_2^{II}(L)Cl_2]$

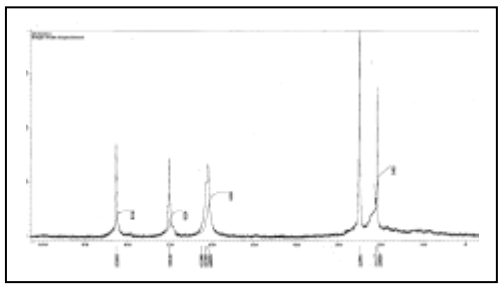


Fig.(17) ^{1}H-NMR spectrum of K

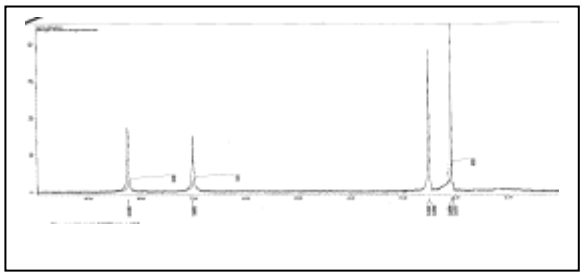


Fig.(18) ^{1}H-NMR spectrum of K $[Zn_2^{II}(L)Cl_2]$ inD_2O

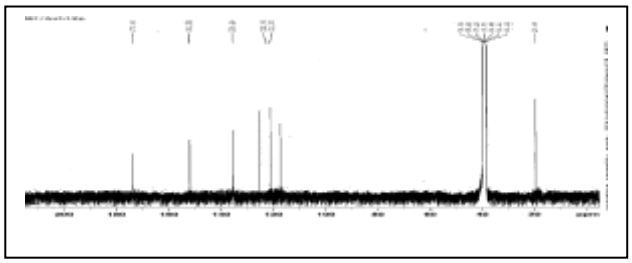
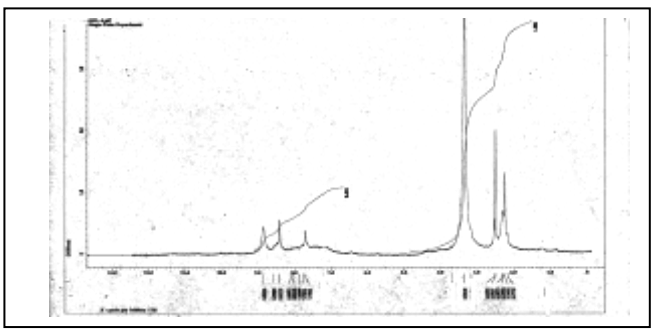


Fig.(19) ^{13}C-NMR spectrum of K $[Zn_2^{II}(L)Cl_2]$



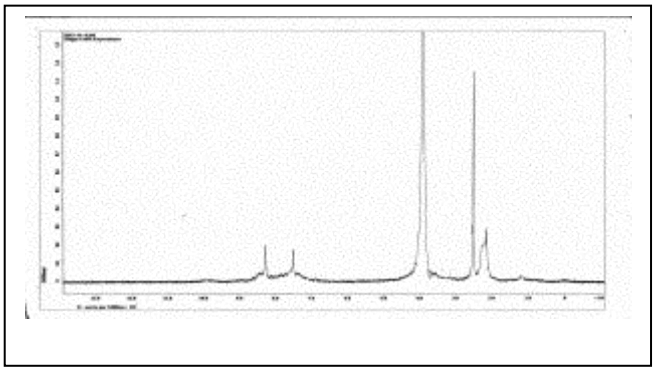
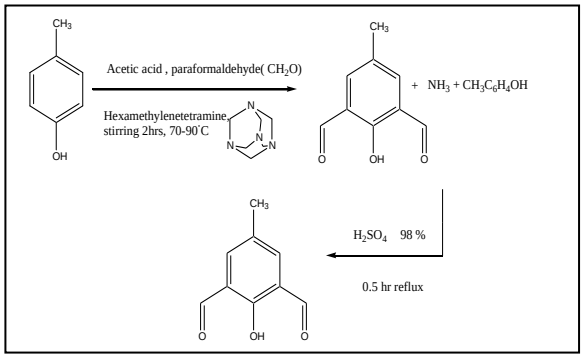
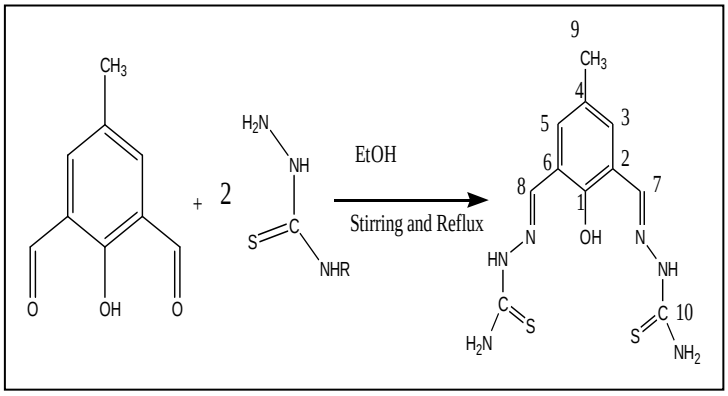


Fig. (20) ^{1}H-NMR spectrum of K $[Hg_2^{II}(L)Cl_2]$ in D_2O

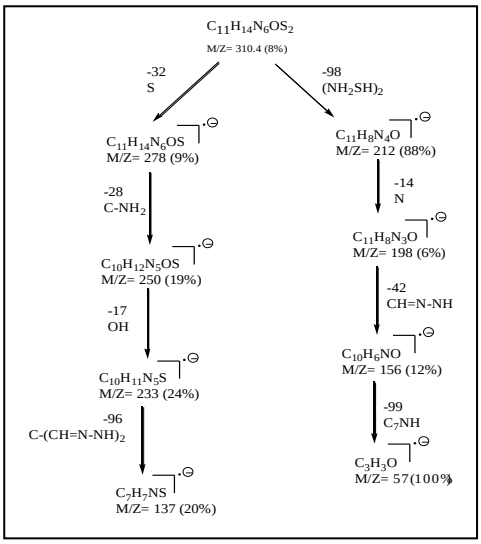
Fig.(21) ^{1}H-NMR spectrum of K $[Hg_2^{II}(L)Cl_2]$



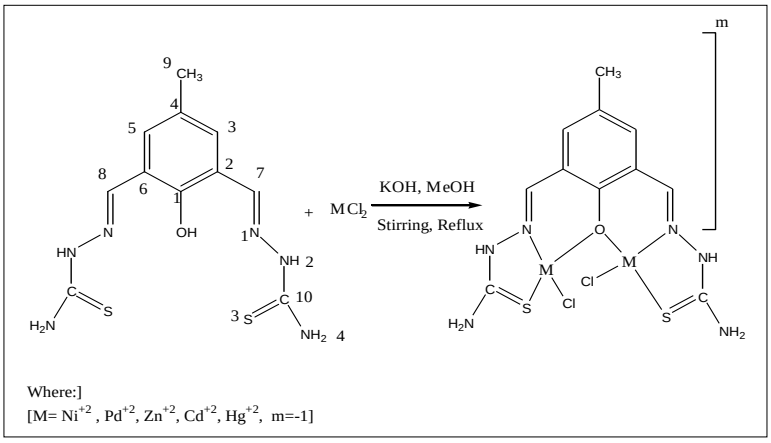
Scheme (1) Synthesis route of precursor



Scheme(2) Synthesis route of $[H_3L]$



Scheme (3) Mass fragmentation



Scheme (1) Synthesis route of complexes

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