Journal of Kerbala University , Vol. 7 No.1 Scientific. 2009

Synthesis and spectral studies of 2,6-diformyl-4-methylphenolsemicarbazone ligand and their binuclear metal complexes

Mohamad J. Al-Jeboori[A], Ashour Hamoad Dawood[*B]
A- Department of chemistry / College of Education-Ibn Al-Haitham / University of Baghdad
E-mail: mohamadaljeboori@yahoo.com
B- Department of chemistry / Science College / University of Karbala
E-mail: ashourdawood@yahoo.com

Abstract :

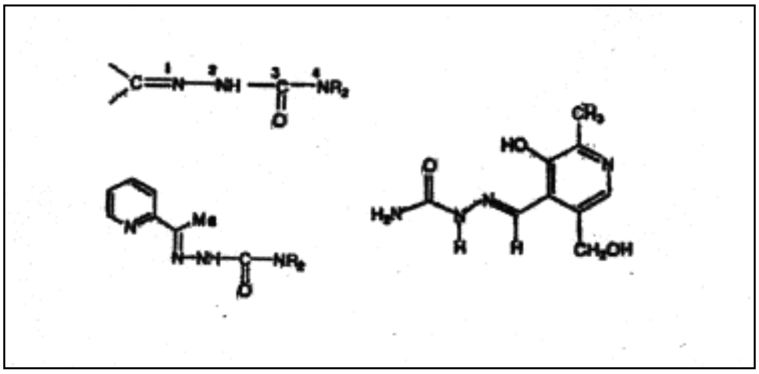
A new binuclear complexes of Ni^{+2}, Pd^{+2}, Zn^{+2}, Cd^{+2} and Hg^{+2} ions with [H_3L] {where H_3L= 4-Methyl-2,6-*bis*(formyl semicarbazone) phenol} type (N_2O_3). The ligand was prepared from reaction two equivalent of semicarbazide hydrochloride with 2,6-diformyl-*p*-cresol and then reacted with metal ions to form the title complexes. The precursor, ligand and complexes were characterized by {IR, UV-Vis, ^1H, ^{13}C, ^1H-^{13}C NMR and mass spectroscopy}, molar conductivity, atomic absorption, the microanalysis of elements (C.H.N) and chlore contain. 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_2O_3) و معقداته ثنائية النواة مع أيونات النيكل و البلاديوم و الخارصين والكادميوم والزئبق. حضر الليكند باستخدام مكافئين من semicarbazide hydrochloride ومكافئ واحد من 2,6-diformyl-*p*-cresol ، أما المعقدات فقد حضرت بالتفاعل المباشر بين الليكند وايونات الفلزات بنسبة 2:1 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 اعلاه اقترحت الأشكال الفراغية لمعقدات Ni^{+2} و Pd^{+2} مربعة مستوية ولمعقدات Zn^{+2} و Cd^{+2} و Hg^{+2} رباعية السطوح.

Introduction

Coordination compounds containing pentadentate ligand with nitrogen and oxygen donor atoms (N_2O_3) have been the subject of remarkable synthetic efforts due to their versatility in many applications (1). In bioinorganic chemistry (2) these compounds have a great application as mimic models of biomolecules. (3, 4) semicarbazone complexes have been the subject of much interest in recent years due to the biological activity of semicarbazones, in particular, and of a number of their complexes[1]. semicarbazones moiety, without substituents attached to the keton oxygen coordinates as a bidentate ligand (NO) (neutral or anionic) depending on the complex method preparation(5), 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) (6,7). 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, and the sulfur atom is considered not to be coordinated, weakly coordinated to the same metal centre, or coordinated to an adjacent metal centre.



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-4- methylphenol

The dialdehyde was prepared by a completely different method(8)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*(formylsemicarbazonyl) phenol] [H_3L]

A solution of semicarbazide hydrochloride (2.70g, 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 1.96g (58%) m.p. (274-276°C).

3. preparation of complexes

A solution of **[H_3L]** (0.10g, 0.035 mmole) in methanol (15 mL) was placed in a round-bottomed flask. A solution of nickel(II) chloride hexahydrate (0.17g, 0.071 mmole) in (15 mL) methanol was added drop-wise with stirring. The pH of the reaction mixture was adjusted to ≈ (9) by adding ethanolic solution of KOH. The resulting mixture was heated under reflux for two hrs, during which time the solution became red in colour. The solution was concentrated by evaporating methanol at room temperature. A purple solid was formed, which collected by filtration, washed with diethylether (5 mL) and dried under vacuum to give 0.12g (88%) yield, m.p. (322-324°C).

Table(1) stated the quantities, reaction condition and some physical properties of the prepared complexes.

Table (1) Some physical properties of the prepared complexes

Empirical formula	m.p. °C	Colour	Wt .of metal ion = 0.064 mmole	Wt. of product	Yield%
$[Zn_2Cl_2(L)]^-$	240-242	White-yellow	0.090g	0.132g	90
$[Cd_2Cl_2(L)]^-$	280-282	Yellow	0.131g	0.162g	90
$[Hg_2Cl_2(L)]^-$	196-198	Orange	0.195g	0.212g	87
$[Pd_2Cl_2(L)]^-$	289-291	Deep green	0.120g	0.145g	81

4- 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, ^{1}H and ^{13}C NMR spectra **Table (5)**. IR spectrum of the ligand, **Fig.(1)**, displays three bands at (3474, 3437, 3262 cm^{-1}) assigned to ν(O-H), ν($N_{(4)}$-H), and ν($N_{(2)}$-H) stretching respectively. The band at (1699cm^{-1}) is due to ν(C=O), which is shifted to lower wave number, in comparison with ν(C=O) at (1712 cm^{-1}) in the semicarbazide due to the synthesis of the ligand . In the spectrum the disappearance of the band at (1712 cm^{-1}) and the appearance of a new band at (1658 cm^{-1}) due to ν(C=N) stretching , supporting occurrence of the condensation reaction and the formation of the iminic group. (UV-Vis) spectrum **Fig.(2)** shows two absorption peaks at (251 nm) (39840 cm^{-1}) (ε_{max}= 1090 $mole^{-1}cm^{-1}$) and (298 nm) (33557 cm^{-1}) (ε_{max}= 990 $mole^{-1}cm^{-1}$) assigned to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions respectively(112). ^{1}H NMR spectrum of the ligand [H_3L] in DMSO-d_6 displays in **Fig.(3).** The broad signal at (δ= 10.70 ppm, 1H) is assigned to (O-*H*) proton .The singlet resonance at (δ= 10.35 ppm, 2H) is due to the proton resonance of two equivalent ($N_{(2,\,^{-}2)}$-*H*) groups, the signal at (δ= 8.13 ppm, 2H) assigned to (N= C-*H*) protons, the chemical shift at (δ= 7.48 ppm, 2H) is attributed to the protons of carbon atoms of aromatic ring (C_3, C_5- *H*) indicating these protons are in same environment, the broad signal at resonance (δ= 6.48 ppm, 4H) assigned to the ($N_{(4,\,^{-}4)}$ –*H*) groups, while the protons of methyl group (C_9) appear as a singlet signal at (δ= 2.24 ppm, 3H). The above chemical shift assignments are supported by ^{1}H–^{1}H correlated NMR spectrum, **Fig. (4).** While the ^{13}C NMR spectrum shown in **Fig.(5)**. The spectrum reveals two singlet signals at (δ= 156.27 ppm, δ= 152.42 ppm) attributed to amido carbonyl and imino carbon ($C_{10,\,^{-}10}$, $C_{7,\,8}$) atoms respectively. The signal at (δ= 138.60 ppm) assigned to (C- O) (C_1) atom, while the chemical shifts at (δ= 128.85, δ= 128.14, δ= 120.53, δ= 19.90 ppm) can be attributed to aromatic ring carbon atoms ($C_{3,5}$, C_4, $C_{2,6}$) and methyl group (C_9) respectively. The above chemical shift results are supported by ^{1}H-^{13}C NMR correlated spectra, **Fig.(6).** The negative mode (-) mass spectrum of the ligand, **Fig (7)** shows the parent ion peak at shows the parent ion peak at (M/Z= 277), which corresponds to (M-H) , other fragments and their relative abundance and fragmentation sequence is shown in **Scheme (3)**(9).

5- 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 range (76–93) Scm^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.(8-12)** respectively, shows no bands around (3474 and 3262 cm^{-1}) could be assigned to ν(O-H) and $\nu(N_{(2)}\text{-}H)$ stretching respectively in comparison with that in free ligand, **Fig(1)**. The sharp bands in free ligand at (1699 and 1658 cm^{-1}) assigned to the ν(C=O) and ν(C=N) stretches respectively are shifted to lower frequencies and appear at (1660,1624 cm^{-1}) for Ni^{+2} , at (1663, 1626 cm^{-1}) for Pd^{+2}. 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 in the π-system of the ligand (HOMO → LUMO). The spectra show new bands at (511, 412 cm^{-1}) for $Zn^{+2,}$ at (500, 411 cm^{-1}) for Cd^{+2}, and at (455, 412 cm^{-1}) for Hg^{+2}. These bands were attributed to ν(M-O) and ν(M-N) respectively.. These results show the coordination of the ligand towards the metal ion(10,11).

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. (13,14)** respectively**,** the spectra showed an intense peaks in the UV region at (326 nm) (30674 cm^{-1}) (ε_{max} = 680 $mole^{-1}cm^{-1}$) and (280 nm)(35714 cm^{-1}) (ε_{max}= 1570 $mole^{-1}cm^{-1}$) in complexes (15) and (16) respectively due to charge transfer (12), other peaks at (640 nm) (21739 cm^{-1}) (ε_{max} = 110 $mole^{-1}cm^{-1}$) and (450 nm) (22222 cm^{-1}) (ε_{max}= 150 $mole^{-1}cm^{-1}$) are assigned to d-d transition type $^1A_{1g}\rightarrow{}^1B_{1g}$. While the electronic spectra of Zn^{+2}, Cd^{+2}, Hg^{+2} complexes **Figs.(15-17)** respectively are appeared intense peaks at (344 nm) (29069 cm^{-1}) (ε_{max}= 600 $mole^{-1}cm^{-1}$), (375 nm)(26666 cm^{-1}) (ε_{max}= 400 $mole^{-1}cm^{-1}$) for Zn^{+2} ion, at (284 nm) (35211 cm^{-1}) (ε_{max}= 839 $mole^{-1}cm^{-1}$) (365 nm) (27397 cm^{-1}) (ε_{max}= 500 $mole^{-1}cm^{-1}$) at (278 nm)(35971 cm^{-1})(ε_{max}= 1637 $mole^{-1}cm^{-1}$), (362 nm)(27624 cm^{-1}) (ε_{max}= 768 $mole^{-1}cm^{-1}$) for Cd^{+2} and Hg^{+2} ions respectively. Since the metal ion in these compounds belong to d^{10} system, these peaks assigned to charge transfer (13)

References

1. R. Contreras, B. Fontal, A. Bahsas and T. Suares. ***Transition Met. Chem***., **29**, 51 (2004).
2. H. Gray. S. Lippard and J. Valentine, “***Bioinorganic chemistry Mill Valley***” California (1994).
3. Y. Kim, S. Kim and S. Choi, ***Inorg. Chem***., **40**, 4481 (2001).
4. B. Sun, J. R. Chen, Y. Z. Li, X. J. Li, ***Chinese Chemical Letters***, **13**, 6, 513- 514 (2002).
5 . N. V. Gerbeleu, M. D. Revenko, and V. M. Leovac**,** ***Russ. J. Inorg. Chem***., **22**, 1009 (1977).
6. C. K. Bhaskare, P. P. Hankare and R. S. Ranpure, ***J.Indian chem. Soc.***, **65**, 121 (1988).
7. M. D. Timken, S. R. Wilson and D. N. Hendrikson, ***Inorg. Chem***., **24**, 3450 (1985).
8. C. N. Verani, L. Rentschler, W. Thomas, E. Bill, and P. Chaudhuri, ***J, Chem. Soc.,Dalton trans,*** 251-258 (2000).
9. D. X . west, and A .A. Nassar, ***Trans . Met. Chem***., **23**, 423-427 (1998).
10. A. K . El-Sawaf, and D . X . West, ***Trans . Met . Chem***., **23**, 417- 421,(1998).
11. T . M . G. Carneiro, and H . Beradlo, ***J .Bras. Chem . Soc***., **10**, 3, 184- 188 (1999).
12. J. V. Babar, V. D. Khasvis, and M. V. Shinde, ***J. Indian Chem. Soc***., LVIII, 970 (1981).
13. N. N. GreenWood and A. Earnshow ***“Chemistry of the Elements”*** Jhon Wiley and Sons Inc. New York (1998).

Table (2) Elemental analysis data and some physical properties of [H_3L] and its metal complexes

Empirical Formula	M. Wt	Yield%	m.p (C)	Colour	Micro analysis found (calc) %				
					C	H	N	Cl	Metal
$C_{11}H_{14}N_6O_3$	278	58	274-276	Yellow	47.41	5.01	30.24	-	-
					(47.48)	(5.07)	(30.20)	-	-
K $Ni_2C_{11}H_{11}Cl_2N_6O_3$	502	88	301-303	Purple	25.21	2.09	16.69	13.06	22.30
					(26.29)	(2.21)	(16.72)	(14.11)	(23.35)
K $Pd_2C_{11}H_{11}Cl_2N_6 O_3$	598	81	299-301	Brown	21.31	1.68	14.09	10.81	34.55
					(22.09)	(1.85)	(14.05)	(11.86)	(35.59)
K $Zn_2C_{11}H_{11}Cl_2N_6 O_3$	516	90	317-319 dec	Yellow	24.57	2.13	16.34	12.84	23.33
					(25.60)	(2.15)	(16.29)	(13.74)	(25.34)
K $Cd_2C_{11}H_{11}Cl_2N_6 O_3$	610	90	260-262	Orange	20.52	1.78	13.81	10.78	35.81
					(21.66)	(1.82)	(13.78)	(11.62)	(36.85)
$KHg_2C_{11}H_{11}Cl_2N_6 O_3$	786	81	256-258 dec	Yellow	15.76	1.38	10.73	8.55	49.98
					(16.80)	(1.41)	(10.69)	(9.02)	(51.01)

(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=O)	υ(N–N)	υ(C-O)	υ(M-O)	υ(M–N)	υ(C=C)	Additional bands
[H_3L]	3262 m 3176 s	1658	1699 s	947 s	1347	-	-	1533	3053m υ(C–H) arom. 2956w υ(C–H) aliph 1581m δ(N-H)
K[Ni_2^{II}(L)Cl_2]	3331m	1623m	1660 m	1037m	1231s	498 m	413 w	1550m	3100w υ(C–H) arom. 2900vw υ(C–H) aliph 1418m δ(C-N)
K[Pd_2^{II}(L)Cl_2]	3300-3450b	1626s	1663 s	1035m	1420m	495 m	412 w	1550m	3090w υ(C–H) arom. 2930m υ(C–H) aliph 1510m δ(C-N)
K[Zn_2^{II}(L)Cl_2]	3200-3500b	1628m	1664 s	1043m	1348s	511 m	412 w	1542s	3000vwυ(C–H) arom. 2973vw υ(C–H) aliph 1448w δ(C-N)
K[Cd_2^{II}(L^1)Cl_2]	3220-3400b	1622s	1677 m	10054 m	1224m	500 w	411 w	1537m	3010vw υ(C–H) arom. 2920vw υ(C–H) aliph 1444m δ(C-N)
K[Hg_2^{II}(L)Cl_2]	3250-3400b	1611m	1652 m	1041m	1253	455 m	412 w	1558m	3029w υ(C–H) arom. 2900w υ(C–H) aliph 1436m δ(C-N)

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

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

Compound	**λnm**	**υcm^{-1}**	**ε$_{max}$mole^{-1} cm^{-1}**	**Assignment**
[H_3L]	251	39840	1090	$\pi\rightarrow\pi^*$
	298	33557	990	$n\rightarrow\pi^*$
[K [$Ni_2^{II}(L)Cl_2$]]	326	30674	680	Charge transfer
	460	21739	110	$^1A_{1g}\rightarrow{}^1B_{1g}$
K [$Pd_2^{II}(L)Cl_2$]]	280	35714	1570	Charge transfer
	450	22222	150	$^1A_{1g}\rightarrow{}^1B_{1g}$
K $Zn_2^{II}(L)Cl_2$]	344	29069	600	Charge transfer
	375	26666	400	Charge transfer
K [$Cd_2^{II}(L)Cl_2$]]	284	35211	839	Charge transfer
	365	27397	500	Charge transfer
K [$Hg_2^{II}(L)Cl_2$]]	278	35971	1637	Charge transfer
	362	27624	768	Charge transfer

Recorded in DMSO

Table (5) ^1H, ^{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 **^1H**	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] **^1H**	O-H; H-C=N ($C_{7,8}$); Ar. C-H ($C_{3,5}$); CH_3 (C_9); $N_{(2)}$-H; $N_{(4)}$-H	10.70,(1H, S); 8.31,(2H, S); 7.48, (2H, S); 2.24, (3H, S); 20.35, (2H, S); 6.48, (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, ($C_{10,\,^{-}10}$)	156; 39; 129; 129; 121 21; 153

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

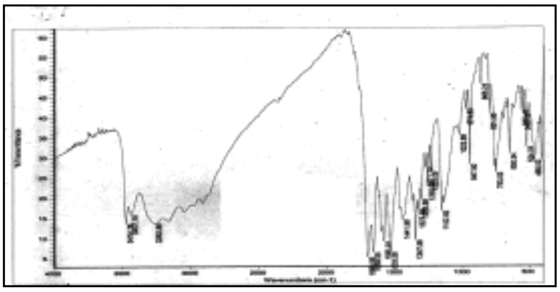


Fig.(1)

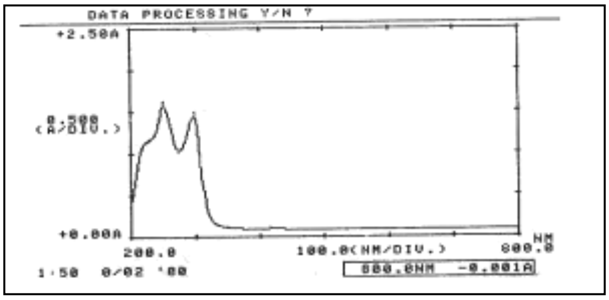


Fig.(2)

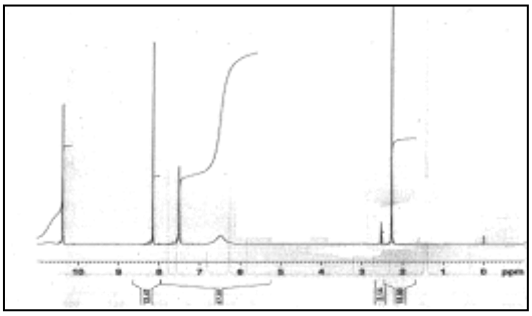


Fig.(3)

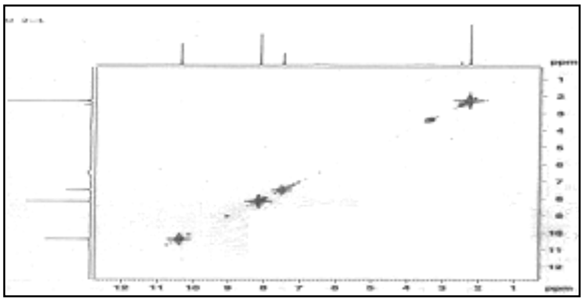


Fig.(4)

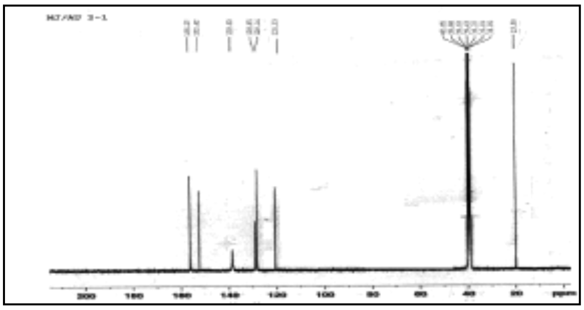


Fig.(5)

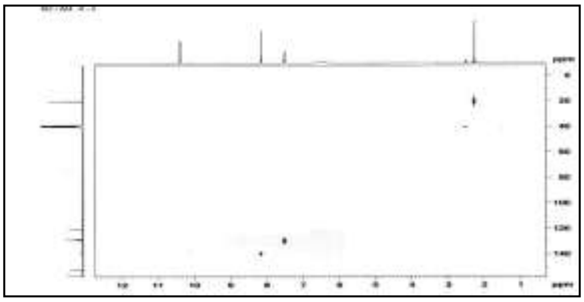


Fig.(6)

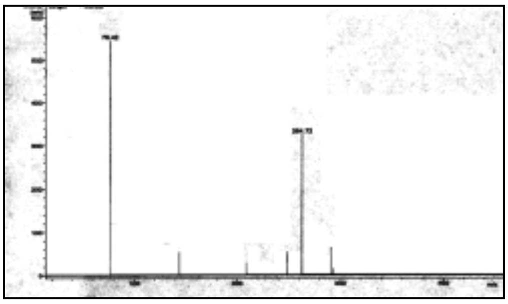


Fig.(7)

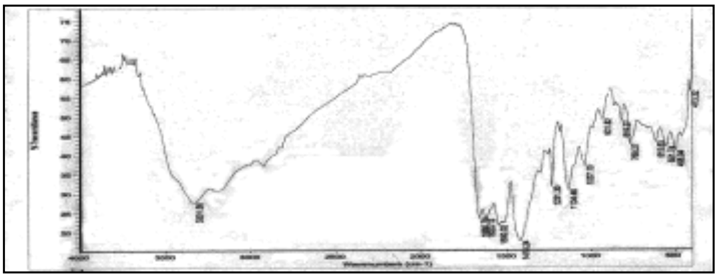


Fig.(8)

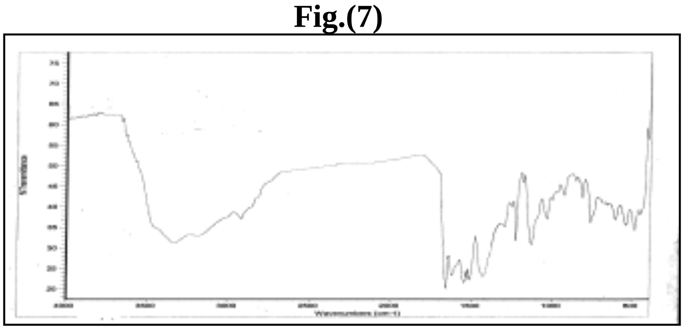


Fig.(9)

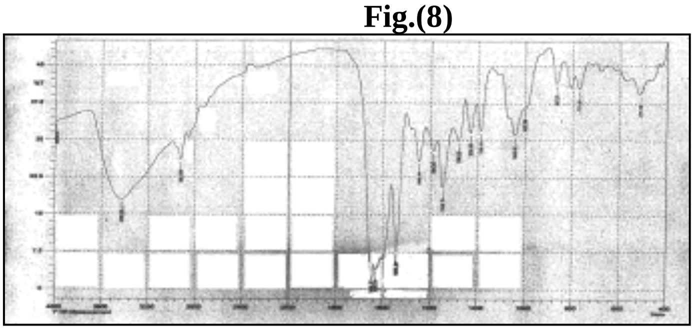


Fig.(10)

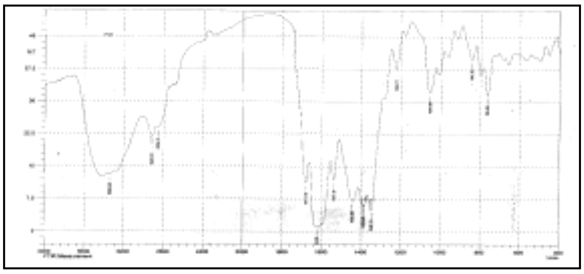


Fig.(11)

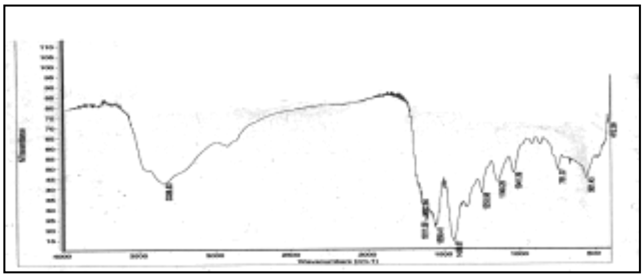


Fig.(12)

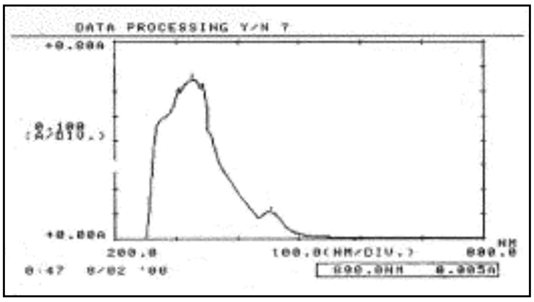


Fig.(13)

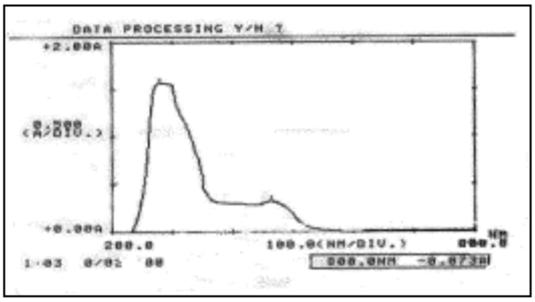


Fig.(14)

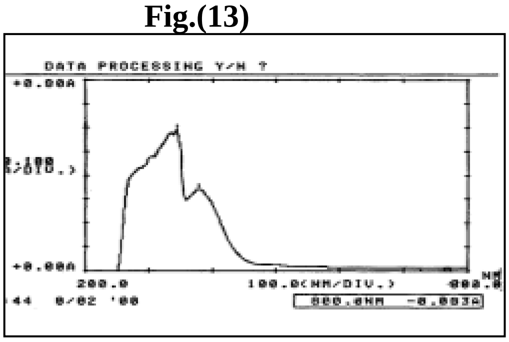


Fig.(15)

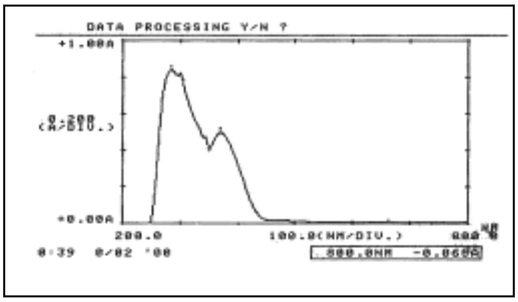


Fig.(16)

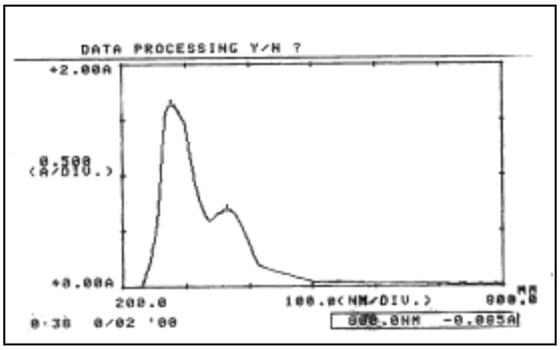
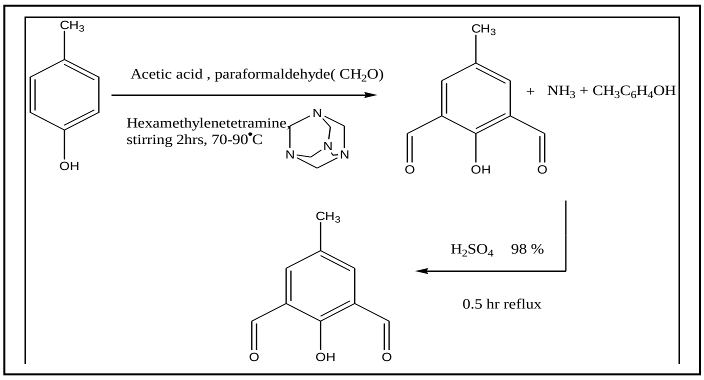
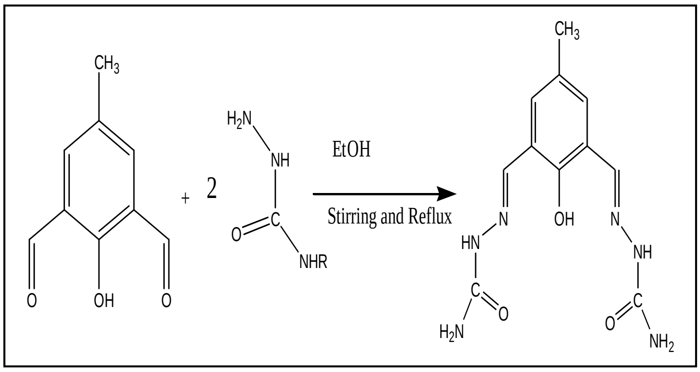


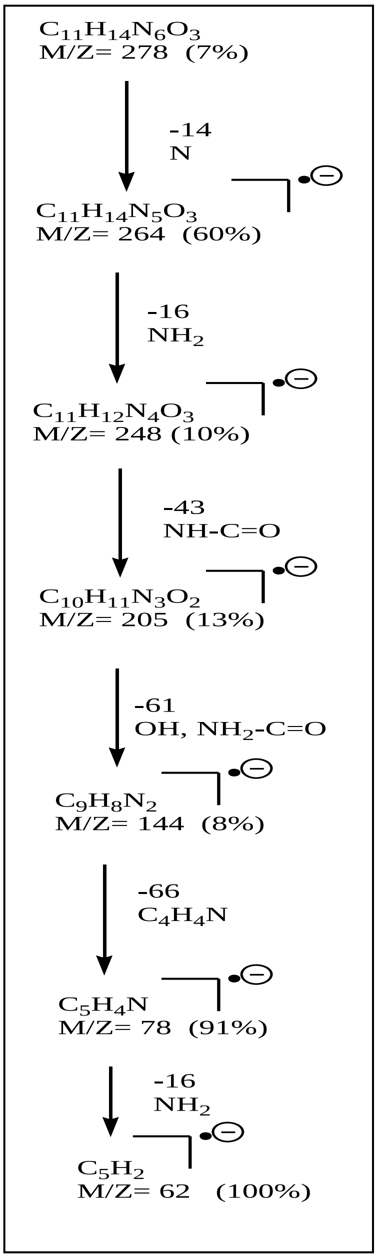
Fig.(17)



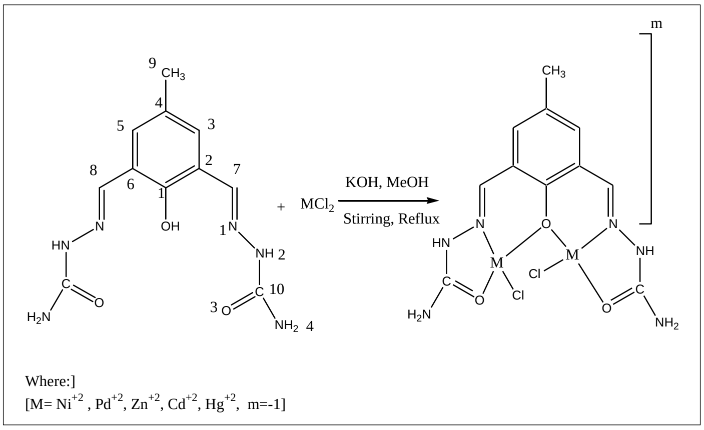
Scheme (1)



Scheme(2)



Scheme (3)



Scheme (4)