Synthesis and Characterisation of Novel Polydentate Ligand Type N₂O₆ Derived from Hypophosphinic Acid and Their Metal Complexes

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Abstract :

The synthesis of ligand $[H_3N_2O_6]$ including the preparation of the compound *bis-*(2Hydroxybenzamide) propane. Then the reaction of this compound with one mole of paraformaldehyde obtained the ligand. The complexes of the ligand with Ni^{+2} and Cu^{+2} ions were prepared by reacted the metal salts with ligand in 1:1 ratio. The prepared compounds were characterised by [IR, UV-Vis, ^1H, ^{13}C, ^{31}P NMR spectroscopy] and the physical method. The spectral studies showed the geometry around Ni ion is octahedral, while the geometry around the Cu ion is square planar.

الخلاصة :

تم حضير الليكاند متعدد السن نوع N_2O_6 من خلال تحضير المركب *bis-*(2Hydroxybenzamide) butane. ومن ثم تمت مفاعلة هذا المركب مع بارافورمالدهايد بنسبة ١:١ لتنتج الليكاند $[H_3N_2O_6]$ ، حضرت معقدات هذا الليكاند مع الايونـات الفلزيـة للخارصـي والزئبقو النيكل والنحـاس الثنائيـة مـن خـلال مفاعلـة امـلاح هـذة الايونـات مـع الليكنـد. شخصـت المركبات النـاتجة باستخدام تقنية مطيافية الاشعة تحت الحمراء وفوق البنفسجية- المرئية و اطياف الرنيين النووي المغناطيسـي البروتون والكاربون ١٣ والفسفور ٣١، كمـا تـم استخدام بعـض الطـرق الفيزيائيـة للتشـخيص. ومـن خـلال ماتقدم تـم اقتـراح الاشكال الفراغية للمركبات المحضرة حيث بينت النتـائج ان الشـكل الفراغـي لايـون النيكل ثمـاني السطوح بينمـا اعطـى ايـون النحاس الشكل المربع المستوي.

Introduction:

The reaction of compounds contain acidic hydrogen as in (ketons, acetylenes, phenols, aliphatic nitro compounds, indols, etc) with formaldehyde and secondary or primary amines or some times ammonium is called Mannich reaction[1,2,3], and the product is aminomethyl derivatives called as Mannich bases. The previous studies were focused on chemistry of Mannich bases, that were considered as active intermediate which can Easley converted into other compounds of important application in different fields[4,5]. Mannich bases are used as pigments for industrial fiber[6], especially which contains amino aryl[7], whereas ketonic Mannich bases are used for preparation of amino alcohols which have useful pharmaceutical properties[8,9].

In (1991) Ishikawa and co-workers[10], were reported the synthesis of phosphinic acid derivatives **Fig.(1)**, where : R_1= alkyl, cycloalkyl or aralkyl group, R_2, R_3= H or ester residue, A=C=CH-CH₃]. The compounds were prepared according to the general route, shown in **Scheme (1).**
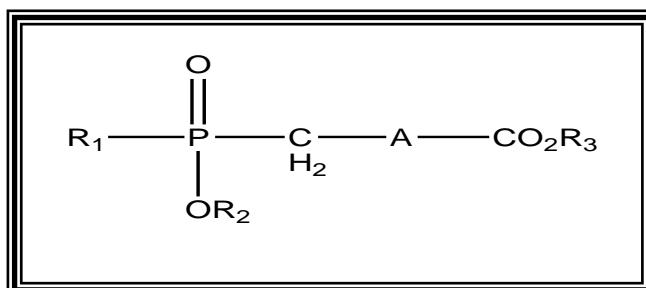

Fig.(1) The structure of

the phosphinic acid derivative

Hypo phosphorous acid is used in the formation of pharmaceuticals, discolouration of polymers, water treatment and reduction of arenediazonium salts, converting ArN^{2+} to Ar-H. and can be use the hypo phosphorus acid and it's salts in commercial laboratory field as a Trade, chemical plating , food preparation , water treatment , polymers (as a catalyst), and analytical chemistry[11] .

Devay and co-workers[12] used the macrocyclic organic- phosphanate compound in oil industry as barium sulfate inhibitors. The studies showed. These compounds are very useful for using as specific interaction with crystalline.

Coveney and co-workers[13] used the two amino methylene phosphinic acid groups operated by an ethylene linkage from the face of the fastest growing face in the crystal it could be seen that six sulphate groups are situated in a hexagonal array around the octahedral unit. The studies showed these compounds are very useful for using as specific interaction with crystalline and demonstration of a viable mechanism for the setting of cement. The 1-amino alkale phosphonic acid found a bioliogical activity as a enzmymological studies and opitaclly active isomers with α-amino acides such alnine and phenyl alnine. The activity of this compound due to the found of chiral center in this compound. Cristau[14] preparation of phosphinodipeptides at α or β position substituents to phosphorous atoms to be used as building blocks for combinatorial or parallel peptides of new enzyme inhibitors
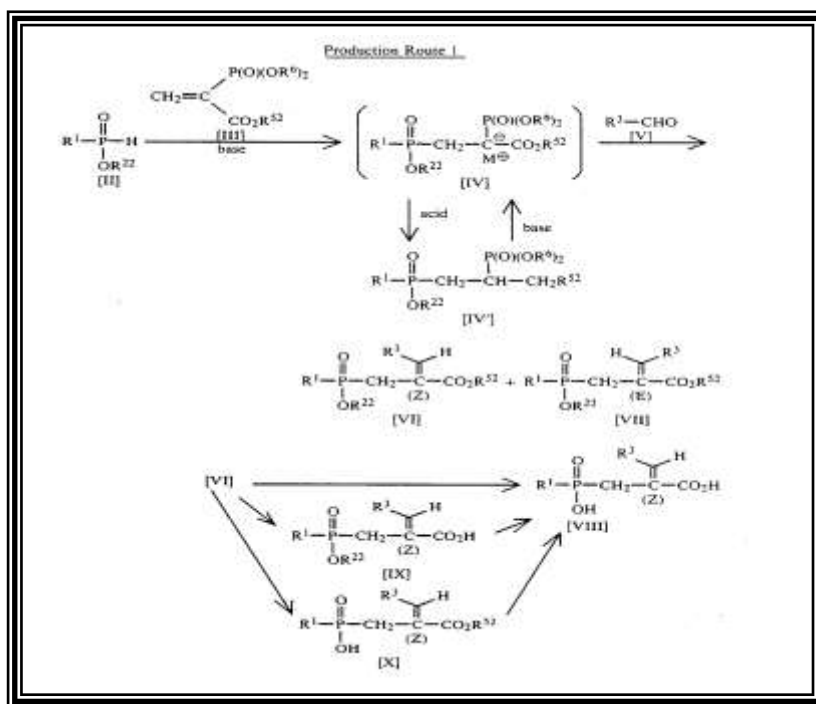
Scheme (1) The synthesis route of phosphinic compounds

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. ^{1}H, ^{13}C- ^{31}P 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 compound *bis*(2-hydroxybenamide) propane

(20.52, 134.91 mmole) of methylsalicylate was added drop wise with stirring to (5.00g, 67.45 mmole) of 1,3-proylenediamine, and a viscous mixture was obtained. Unreacted starting materials and methanol were removed by distillation under reduced pressure. A white solid was collected, washed with (5 ml) diethylether, and dried, yielded 15.20 (75%) of the title compound, m.p (67-69) °C.

2- Preparation of Ligand

The ligand was prepared in two different procedure can be describe in the following.

A. First procedure

A solution of paraformaldehyde (1.33g, 44.49 mmole), hypohpsphinic acid (50%) (1.47 g, 22.24 mmole) in (10mL) ethanol, was added slowly to a solution of [compound *bis*(2-hydroxybenamide) propane (7.00g, 22.24 mmole), and (0.50 mL) HCl (37%) in (10 mL) ethanol]. The resulting cloudy mixture was stirred and heated at reflux under nitrogen atmosphere for (2.5 hrs), during which time the mixture became clear in colour. The mixture allowed to cool at room temperature and then (2 mL) of acetone was added. The solution was concentrated under vacuum to give a white solid, washed with (5 mL) diethyiether and dried to yield 6.20g (68%), m.p (73-75) °C.

B. Second procedure

A mixture of [hyposphosphorous acid (50%) (0.73g. 11.12 mmole), and compound (2) (3.5g, 11.12 mmole) in 6M HCl (40 mL)] was heated at reflux, and formaldehyde (37%) (3.34g, 111.0 mmole) was added dropwise over (20) min. The mixture was allowed to reflux under nitrogen atmosphere about (4-5 hrs), and then cool to room temperature. The solution was concentrated under vacuum, and a pale-yellow precipitate was formed which was recrystallised from (methanol /ethanol). A white precipitate was obtained, collected by filtration, washed with (5 mL) diethylether, and dried. Yielded, .55g (59%), m.p (73-75) °C.

3- Preparation of complexes

A- Preparation of nickel complex

A solution of nickel(II) hexahydrate (0.117g, 0.495 mmole) in (10 mL) methanol was added slowly to a stirred solution of (H_2L) (0.20g, 0.495 mmole) in (10 mL) methanol and the PH of solution was adjusted to *Ca* 9 by using the alcoholic potassium hydroxide. The resulting mixture was heated at reflux and under N_2 atmosphere for (2 hrs), the mixture became brown in colour. The after one hour the mixture change in colour and became green solid, it was collected by filtration, washed with diethylether (5 mL) and dried to give 0.192g (74%), of the title compound, m.p (215-217) °C. The conductance of the complex is (126) S.cm^2.mole^{-1}, indicating (2:1) ratio electrolyte nature.

B- Preparation of copper complex

A solution of copper(II) hexahydrate (0.084g, 0.495 mmole) in (10 mL) methanol was added slowly to a stirred solution of (H_2L) (0.20g, 0.495 mmole) in (10 mL) methanol and the PH of solution was adjusted to *Ca* 9 by using the alcoholic potassium hydroxide. The resulting mixture was heated at reflux and under N_2 atmosphere for (2 hrs), the mixture became yellow in colour. The after one hour the mixture change in colour and became green solid, it was collected by filtration, washed with diethylether (5 mL) and dried to give 0.165g (71%), of the title compound, m.p (200-202) °C. The conductance of the complex is (33) S.cm^2.mole^{-1}, indicating nonelectrolyte nature.

Results and Discussions

1- The synthesis and characterisation of compounds

A- The synthesis and characterisation of *bis*(2-hydroxybenamide) propane

The *bis*(2-hydroxybenamide) propane was prepared was prepared from the addition of propylenediamine to methylsalicylate the method was summarised in **Scheme (2)**. The prepared compound was obtained in (75%) yield. The compound was characterised by IR, UV-Vis, ^{1}H, ^{13}C, NMR, and elemental analysis, this procedure is straightforward formed and required short time to obtain the compound. The compound was characterised by elemental analysis, **Table (1)**, IR **Table (2)**, (UV-Vis) **Table (3)**, 1H and ^{13}C NMR spectra **Table (4)**.

B- The synthesis and characterisation of the ligand [H$_3$L] and complexes

The condensation reaction of *bis*(2-hydroxybenamide) propane with two equivalent of paraformaldehyde and one equivalent of hypophosphinic acid, resulted in the preparation of the ligand [H$_3$L] according to the general method shown in **Scheme (3)**. The reaction of the ligand and the metal salts were obtained the complexes **Scheme (4).** The ligand and their complexes were characterised by elemental analysis, **Table (1)**, IR **Table (2)**, (UV-Vis) **Table (3)**, ^{1}H and ^{13}C NMR spectra **Table (4)**.

IR Spectra

The IR spectrum of the compound *bis*(2-hydroxybenamide) propane **Fig. (2).** Shows the broad band at (3342 cm^{-1}) assigned to ν(O-H) stretching, the band at (3290 cm^{-1}) assigned to ν(N-H) stretching. The strong bands at (1594 cm^{-1}) attributed to carbonyl ν(C=O) stretching of the amide group. IR spectrum of the ligand, **Fig. (3)**, displays no band at (3290 cm^{-1}) due to ν(N-H) stretching. The band at (3411 cm^{-1}) assigned to ν(O-H) stretching. The band at (1594 cm^{-1}) assigned to ν(C=O) stretching in the derivative compound was shifted to (1589 cm^{-1}) in the ligand.   A new bands at ($2731, 1245, 865 \text{ cm}^{-1}$) due to ν(P-OH), ν(P=O) and ν (P-O) stretching respectively. The disappearance of amine group and appearance the new bands of phosphinic acid group indicated of the ligand was obtained. The IR spectrum of the [Ni (HL)] complex **Fig. (4).** Showed no band at 1411 cm^{-1}) assigned to ν(O-H) stretching, the band at (1589 cm^{-1}) which is due to ν(C=O) stretching in the free ligand is shifted to higher frequency and appears at (1652 cm^{-1}). This shifting of the bands to higher wave number indicating the coordination of the ligand with metal ion is weak. While the bands at ($1256, 2651$ and 1598 cm^{-1}) can be attributed to ν(P=O), ν(P-OH), ν(C=C) stretching vibration respectively. The new bands at (545 and 451 cm^{-1}) can be attributed to ν(M-N) and ν(M-O) stretching respectively. While the IR spectrum of [Cu (HL)] complex **Fig. (5).** Showed the band at ν(1589 cm^{-1}) which is due to ν(C=O) stretching of the amide group in the free ligand is shifted to lower frequency and appears at (1562 cm^{-1}) indicating the deprotonation of the (O-H) of the phenol group. This shifting can be attributed to the delocalisation of the electron density of the metal ion in the system of the ligand   (HOMO$\rightarrow$ LUMO), while the bands at ($1250, 2655$ and 1495 cm^{-1}) can be attributed to ν(P=O), ν(P-OH), ν(C=C) stretching. New bands at (500 and 476 cm^{-1}) attributed to ν(M-N) and ν(M-O) stretching respectively[15,16].

UV-Vis Spectra

The (UV-Vis) spectrum of *bis*(2-hydroxybenamide) propane **Fig.(6)** exhibits a high intense absorption peak at ($280nm$)(35335cm^{-1})($\varepsilon_{max}=3763 \text{ molar}^{-1}\text{cm}^{-1}$) which is assigned to overlap of ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions[84], the (UV-Vis) spectrum of the ligand, **Fig.(7)** showed two absorption peaks at exhibits ($269nm$) (37174cm^{-1})($\varepsilon_{max}=962 \text{ molar}^{-1}\text{cm}^{-1}$) which is assigned to ($\pi\rightarrow\pi^*$) transition. Another peak at ($319nm$) (31347cm^{-1}) ($\varepsilon_{max}=365 \text{molar}^{-1}\text{cm}^{-1}$) assigned to ($n\rightarrow\pi^*$) transition. While the spectrum of Ni^{II} complex, **Fig.(8)** showed the absorption peaks at ($260nm$) (38461cm^{-1}) ($\varepsilon_{max}=1503$) due to ligand field and peak at ($755nm$)(13245cm^{-1})($\varepsilon_{max}=55 \text{molar}^{-1}\text{cm}^{-1}$) due to d-d transition type $^{3}B_{2g}\rightarrow^{3}B_{1g}$, the Cu^{II} complex, **Fig.(9)** showed the intense peaks at ($262nm$) (38168cm^{-1}) ($\varepsilon_{max}=2750 \text{molar}^{-1}\text{ cm}^{-1}$) assigned to charge transfer while

the peak at (530nm) (18868cm^{-1}) (ε_{max}=50molar^{-1}cm^{-1}) was assigned to ($^2A_{1g}\rightarrow{}^2B_{1g}$) (d–d) transitions, suggesting a square planer structure around Cu^{II} ion[17].

Empirical Formula	M. Wt	Yield %	m. p (°C)	Colour	Microanalysis found (calc) %				
					C	H	N	Cl	Metal

NMR Spectra

^{1}H NMR spectrum of the *bis*-(2-hydroxybenamide) propane in DMSO-d$_6$ displays in **Fig. (10).** Shows the broad signal at (δ= 12.57 ppm, b, 2H) assigned to (O-*H*) protons of two equivalent

hydroxyl groups. The signal at (δ= 9.36 ppm, s, 2H) is due to (N-*H*) protons. The resonance at (δ= 7.93, 7.40, 6.90 ppm, m, 8H) are attributed to the aromatic ring protons (C$_{9,9}$$^-$, C$_{8,8}$$^-$,$_{6,6}$$^-$, C$_{7,7}$$^-$) respectively. The chemical shift at (δ= 4.5 ppm, m, 4H) can be assigned to to methylene groups (C$_{2,2}$$^-$), while the resonance at δ= 3.37 ppm, m, 2H) assigned to methyl grope (C$_1$). The ^{13}C NMR spectrum shown in **Fig.(11).** The spectrum reveals two sharp resonances at (δ=171.89 ppm) and (δ=159.63 ppm) refer to the carbonyl (C=O) and (C-O), C$_3$ and C$_9$ carbons respectively. The five resonances at (δ=133.13, δ= 128.33, δ= 118.73, δ= 117.71, δ= 115.51, ppm) assigned to carbon atoms of aromatic ring (C$_{7,7}$$^-$, C$_{5,5}$$^-$, C$_{8,8}$$^-$, C$_{4,4}$$^-$, C$_{6,6}$$^-$) respectively. The chemical shifts at (δ=38.89 ppm) and (δ=37.63 ppm) refer to the methylene groups (C$_{2,2}$$^-$) and (C$_1$) respectively. The ^{31}P{^{1}H} NMR spectrum of the ligand in DMSO-d$_6$, **Fig. (12)**, displayed signal at (δ_p= 6.16ppm), in comparison with that in the ^{31}P{^{1}H} of hypohpsphinic acid spectrum of (δ_p= 9.57 ppm). **Fig. (13)**, the ^{1}H NMR spectrum of the ligand **Fig. (14)** appears the chemical shifts at (δ= 9.06 ppm, b, 2H) assigned to (O-*H*) protons of two equivalent hydroxyl groups in the aromatic rings, the signals at (δ= 8.18, 8.09, 7.39, 6.86 ppm, m, 8H) assigned to the aromatic protons of rings, the broad signal at chemical shift (δ= 4.96 ppm) attributed to (O-*H*) proton of hypophosphorous acid, the signals at (δ= 3.37, 2.85, 1.84 ppm) are attributed to (C$_{2,2}$$^-$, C$_{10,10}$$^-$, C$_1$) respectively. While the ^{13}C NMR spectrum of the ligand **Fig. (15)** showed the resonance at (δ= 169.73, 160.67 ppm) assigned to carbonyl (C=O) and (C-O) (C$_{3,3}$$^-$ and C$_{9,9}$$^-$) respectively, the chemical shifts at (δ= 134.52, 128.34, 119,06, 117.92,115.73 ppm) assigned to aromatic ring carbon atoms (C$_{7,7}$$^-$, C$_{5,5}$$^-$, C$_{6,6}$$^-$, C$_{4,4}$$^-$, C$_{8,8}$$^-$) respectively, while the methylene groups (C$_{2,2}$$^-$, C$_{10,10}$$^-$, C$_1$) appears the signals at (δ= 39.35, 29.30, 27.54 ppm) respectively[18].

Table (1) Results of elemental analysis and physical properties of [H$_3$L] and its metal complexes

$C_{17}H_{18}N_2O_4$	314.34	75%	67-69	White	(64.96)	(5.77)	(8.91)	-	-
					64.22	5.54	9.09	-	-
$C_{19}H_{21}N_2O_6P$	404.35	68	73-75	White	55.98	5.01	6.99	-	-
					(56.44)	(5.23)	(6.93)	-	-
$K_2Ni\ C_{19}H_{19}Cl_2N_2O_6P$	531.94	75	215-217	Green	42.62	3.57	5.29	13.21	10.55
					(42.90)	(3.60)	(5.27)	(13.33)	(11.03)
$CuC_{19}H_{19}N_2O_6P$	465.88	93	299-301	Green	48.77	4.05	6.11	-	13.61
					(48.98)	(4.11)	(6.01)	-	(13.64)

(calc): calculated ; (dec): decomposed,

Table (2) Infrared spectral data (wave number) cm^{-1} of the ligand [H$_3$L] and its complexes

Compound	$\upsilon(N–H)$	$\upsilon(O-H)$	$\upsilon(C=O)$	$\upsilon(P-OH)$	$\upsilon(P=O)$	$\upsilon(M-O)$	$\upsilon(M–N)$	$\upsilon(C=C)$	Additional bands
Derivative	3290 m	3342 br	1594s	-	-	-	-	1458s	3016m υ(C–H) arom. 2963m υ(C–H) aliph
Ligand	-	3411 br	1589s	1245m	2731m	-	-	1550	3010m υ(C–H) arom. 2953vw υ(C–H) aliph
Ni(II) Complex	-	-	1652s	1256m	2651m	545w	451w	1598w	3024m υ(C–H) arom. 2950vw υ(C–H) aliph
Cu(II) Complex	-	-	1562s	1250m	2655m	500m	476w	1598m	3050m υ(C–H) arom. 2900vw υ(C–H) aliph

(s) Strong,   (br) broad, (m) medium, (w) weak,

Table (3) Electronic spectral data of [H$_3$L] and its metal complexes

Compound	λnm	υcm^{-1}	ε_{max}molar^{-1} cm^{-1}	Assignment
Derivative	280	35335	3763	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$
Ligand	269	37174	962	$\pi\rightarrow\pi^*$
	316	31347	365	$n\rightarrow\pi^*$
Ni Complex	260	38461	1503	Ligand field
	755	13245	55	$^3B_{2g}\rightarrow{}^3B_{1g}$

|	262	38168	2750	Ligand field
Cu Complex	530	18868	50	$^2A_{1g} \rightarrow ^2B_{1g}$

Recorded in DMF

Table (4) ^1H, ^{13}C, ^{31}P NMR data for the ligands and precursors measured in DMSO–d$_6$ and chemical shift in ppm(δ)

Compound	Funct. Group	$\delta_H(ppm)^b$
Derivative **^1H**	O-H; N-H; Ar. C-H ($C_{9,9'}$, $C_{8,8'}$,$_{6,6'}$, $C_{7,7'}$) Aliph. (C-H) ($C_{2,2'}$) , (C_1)	12.57, (2H,br); 9.36, (2H, S); 7.93,7.40,6.90, (8H, m) 4.54, (4H, m), 3.37, , (2H, m)
^{13}C	C=O ($C_{3,3'}$,); Ar. C-OH($C_{9,9'}$) Ar. ($C_{7,7'}$, $C_{5,5'}$, $C_{8,8'}$, $C_{4,4'}$, $C_{6,6'}$) Aliph. ($C_{2,2'}$) , (C_1)	171.89; 159.63 133.13; 128.33; 118.73; 117.71; 115.51 38.89; 37.63
[H₃L] **$^{31}p\{^1H\}$**	^{31}p	6.16
^1H **^{13}C**	O-H Ar. C-H ($C_{7,7'}$, $C_{5,5'}$,$C_{6,6'}$, $C_{4,4'}$ $C_{8,8'}$) Aliph. (C-H) ($C_{2,2'}$) , ($C_{10,10'}$) , (C_1)	9.06, (2H, br); 8.18; 8.09; 7.39; 6.86, (8H, m) 3.37,2.85, 1.84
	C=O ($C_{3,3'}$,); Ar. C-OH($C_{9,9'}$) Ar. C-H ($C_{7,7'}$, $C_{5,5'}$,$C_{6,6'}$, $C_{4,4'}$ $C_{8,8'}$) Aliph. (C-H) ($C_{2,2'}$) , ($C_{10,10'}$) , (C_1)	169.73; 160.67 134.52; 128.34; 119.06; 117.92; 115.73 39.35; 29.30; 27.54

δ^b chemical shift from TMS; S = Singlet   br= broad
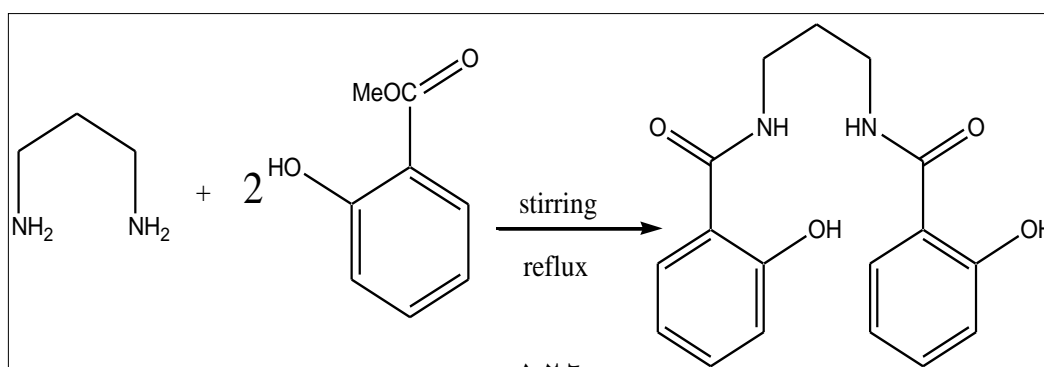
Scheme (2) synthesis rout of derivative

Ni Cl₂ or CuCl₂

stirring reflux
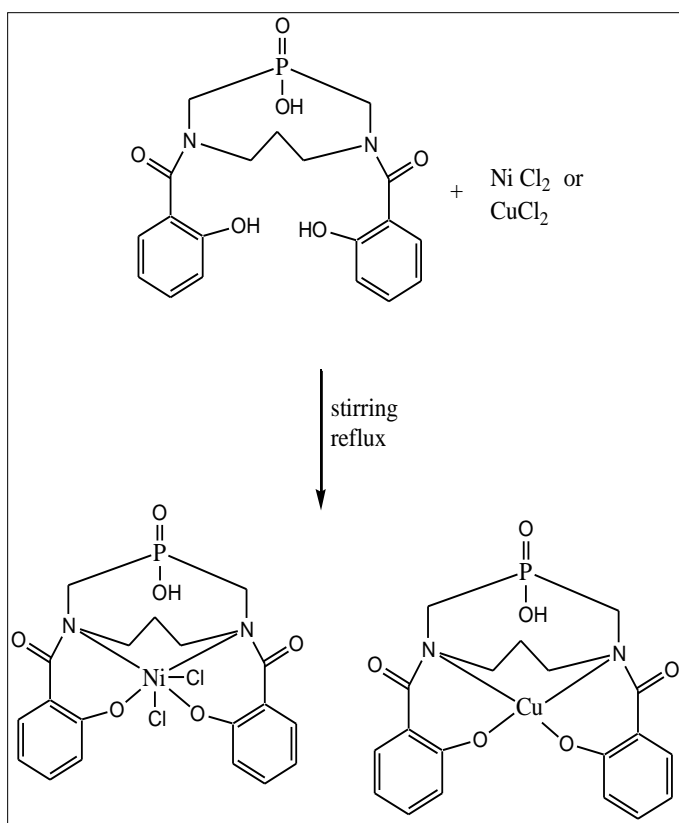
Scheme (4) synthesis rout of complexes

stirring reflux
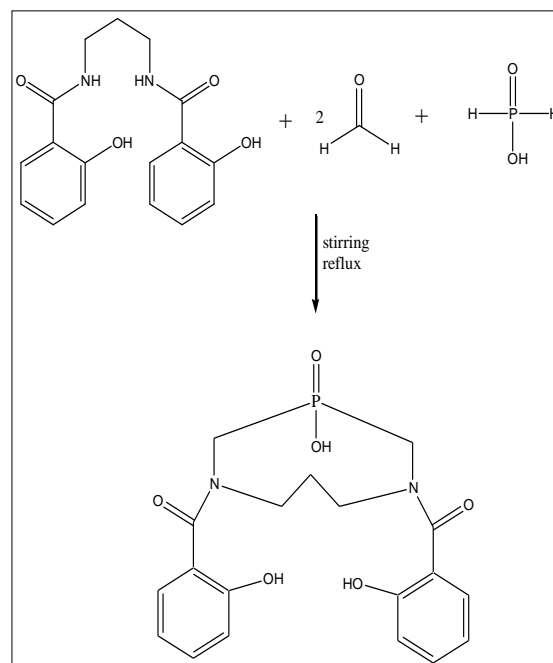
Scheme (3) synthesis rout of Ligand
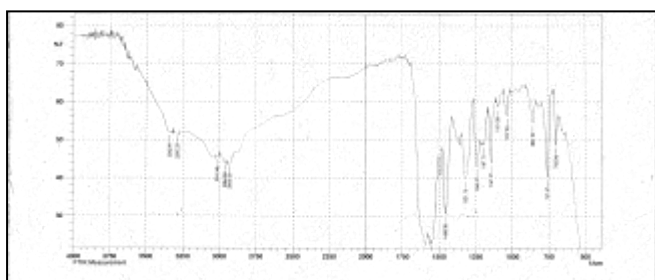
Fig.(2) IR spectrum of derivative
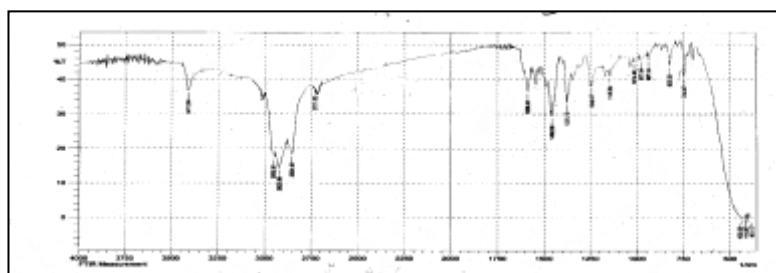
Fig.(3) IR spectrum of ligand
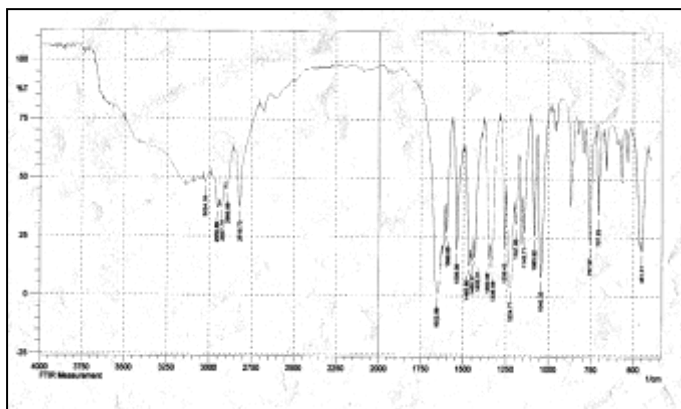
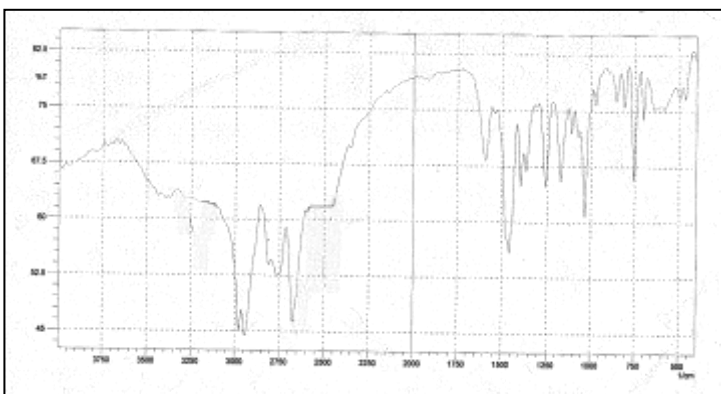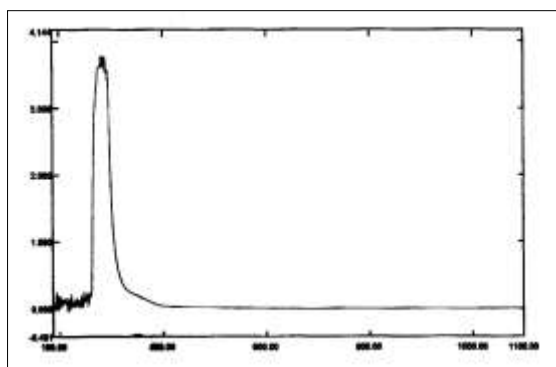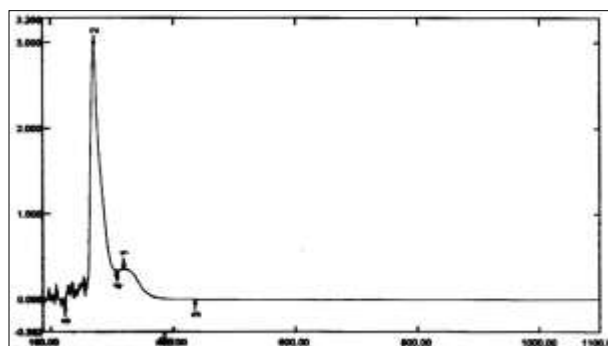**Fig.(4) IR spectrum of Ni complex**

Fig.(5) IR spectrum of Cu complex

Fig.(6) UV-Vis spectrum of derivative

Fig.(7) UV-Vis spectrum of ligand
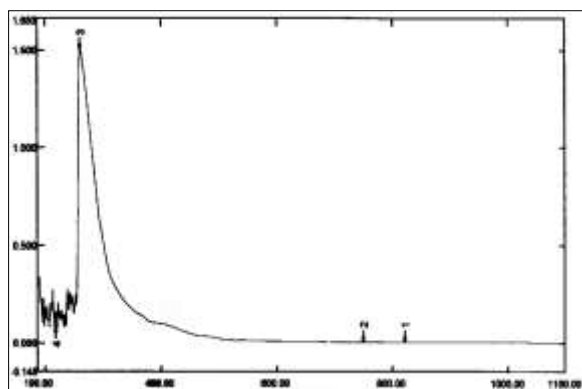
Fig.(8) UV-Vis spectrum of Ni complex
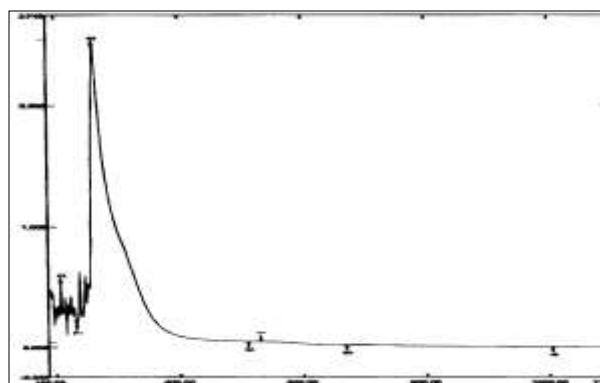
Fig.(9) UV-Vis spectrum of Cu complex
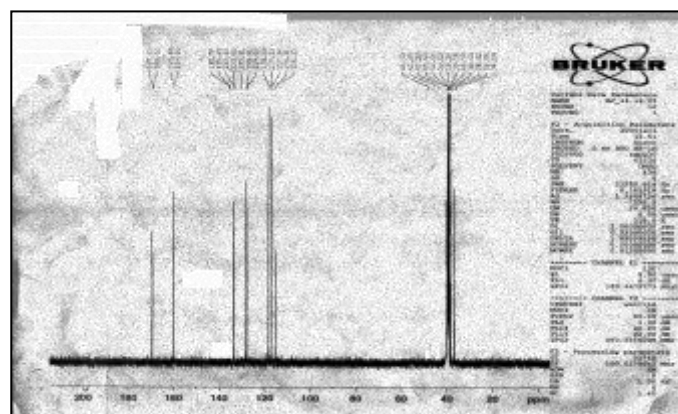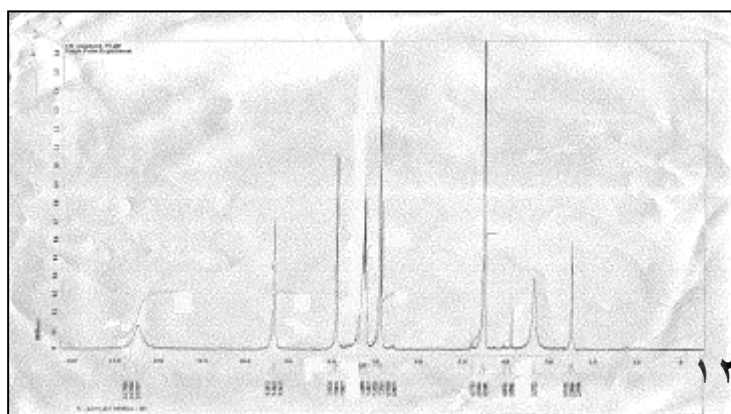
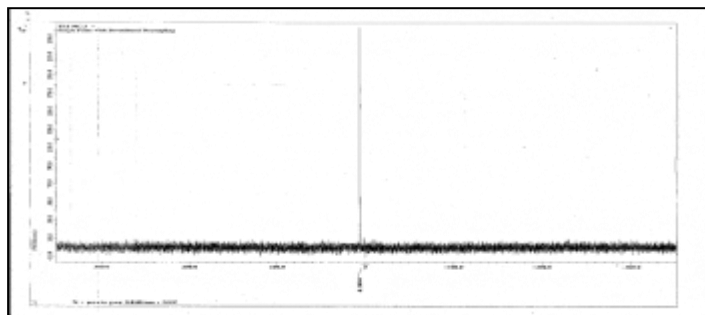**Fig.(10) ^{1}H NMR spectrum of derivative**   **Fig.(11) ^{13}C NMR spectrum of derivative**
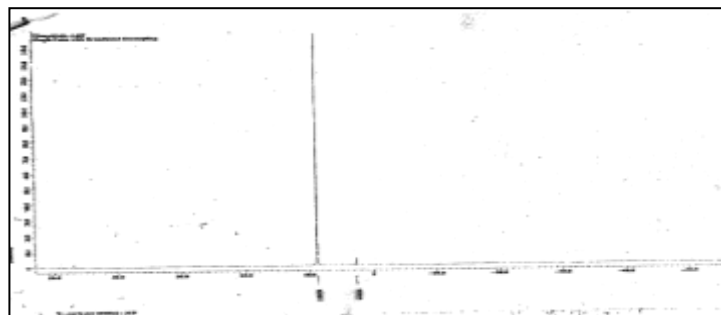

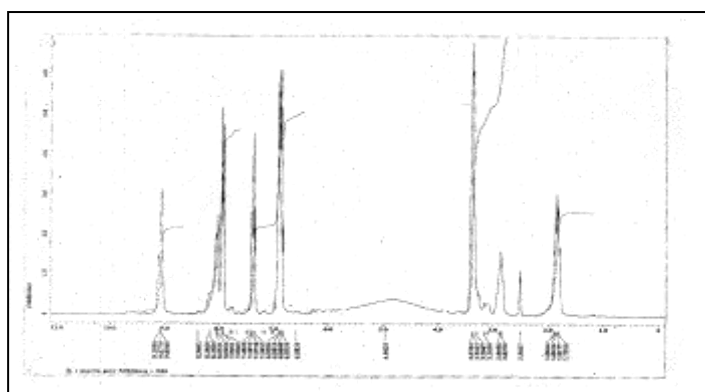**Fig.(12) ^{31}P NMR spectrum of ligand**   **Fig.(13) ^{31}P NMR spectrum of hypohpsphinic**
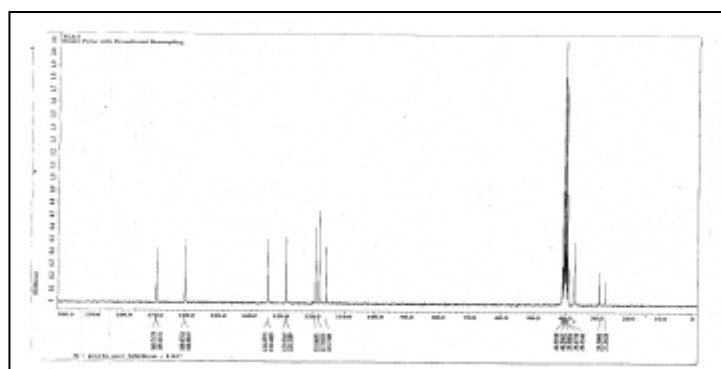

Fig.(14) ^{1}H NMR spectrum of ligand   **Fig.(15) ^{13}C NMR spectrum of ligand**

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