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Original Research Article

Synthesis and Characterization of Cu^{+2}, Ni^{+2} Heteronuclear Complexes with Macrocyclic (N_2O_2, N_2S_2) Type Ligands

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The heteronuclear of divalent nickel and copper complexes were prepared through the template reaction with the prepared precursors, which were synthesised via the reaction of benzoyl acetone. With o-amino phenol and o-amino thiophenol respectively as Schiff base compounds, the prepared complexes and precursors were characterised by IR, UV, Mass and ^{1}H NMR, ^{13}C NMR spectroscopies, the elemental micro analysis C. H. N. S and Atomic absorption was carried out. The physical measurements were tailed m.p, solubility and magnetic susceptibility. The measurements show the suggested geometry of complexes is square planar (D_4h) geometry around the metal ions.

Keywords: Heteronuclear, Macrocyclic compounds.

INTRODUCTION

The complexes have two central atoms like homo- and hetero-binocular in nature. In this analogue the ligand can be reacted with two of transition metal ions. These complexes behave as biochemical models to the active sites for metal enzymes in human cells. The large success achieved by these kind of complexes, especially copper, palladium, and platinum in medical field like anti-cancer or anti-tumor gave the organ metallic chemistry great attention in scientific research.

Aromatic nitrogen heterocycles represent an important class of compounds which can act as ligands towards metal ions(1, 2). The interest in heteronuclear complexes containing two different metal ions is fundamental compared with the studies dealing with heteronuclear system comprising (d) transition metal ions(3, 4). These compounds have been paid considerable attention due to their wide applicability in medicine(4, 5) such as anti-tumour, anti-inflammatory, anti-pyretic, anti-viral, anti-cancer. In coordination chemistry, these derived ligands exhibit various coordination modes and have received considerable attention for the synthesis of transition metal complexes with various nuclearities(6, 7).

EXPERIMENT

A. Preparation of precursor 1(p^1) type (N_2O_2)

In 500ml two necked flask(8-10), equipped with a condenser, and a thermometer were placed of Benzoyl acetone (1g,6.16mmol) in EtOH (15ml) which was added slowly with stirring to a mixture (1.34g, 12.27mmol) of o-aminophenol in (15ml) EtOH, the reaction mixture was refluxed for (2)hrs in (80-70)C°. This was followed by filtration and drying under

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vacuum to give the precursor as a yellow solid, yield (1.52g, 47%), mp (142)C°. Scheme (1) shows this.

B. Preparation of precursor 4(P^4) Type (N_2S_2)

In 500ml two necked flask(8-10), equipped with a condenser, and a thermometer were placed of Benzoyl acetone (1g, 6.16mmol) in EtOH (15ml) was added slowly with stirring to a mixture (1.31g,10.47mmol) of o-mercaptoaniline in (15ml) EtOH, the reaction mixture was refluxed for (2) hrs in (80-70) C°. This was followed by filtration and drying under vacuum to give the precursor as a Deep Red semisolid, yield (1.97g, 85.28%)? Scheme (1) shows this.

C. Preparation of complexes

The metal ions complexes were prepared via template reaction. The precursors N_2O_2 was dissolved of methanol with stirring, the metal ion salt of copper acetate dissolve in methanol and the pentaerythretol tetrabromide as bridge added together to the precursor solution, then the nickel salt dissolved in methanol added to the mixture, the overall mixture was refluxed to three hrs. The procedure is In (500) ml two necked flask, equipped with a condenser and thermometer and by using the template method placed two mol solution of precursor 1 (0.88g, 2.55mmol) in (10ml) EtOH and added slowly with stirring of (0.5g,1.28mmol) of pentaerthretol tetra bromide, waiting (10) mins after this, added the mixture of $[Cu(acetate)_2]$ (0.23g,1.26mmol) and added of $[Ni(acetate)_2]$ (0.22g,1.24mmol).

Dissolved in EtOH, the reaction mixture was heated under reflux (2hr) in (80-70)C°. The collected complex was obtained by filtration and washed in excess EtOH and dried under vacuum. While the N_2S_2 complex was prepared as A similar method to that mentioned in the preparation of $[Cu, Ni (P^1)_2]$, the complex was used to prepare the complex of $[Cu, Ni (P^4)_2]$ (0.96g,2.55mmol) of P^4, (0.23g ,1.26mmol)of$[Cu (acetate)_2]$ and (0.22g, 1.24mmol) of $[Ni (acetate)_2]$.

Synthesis and Characterization of Homo- Precursors with Hetrometal Complexes

The template method and condensation(8-10) reaction between precursor type (N_2O_2) or precursor type (N_2S_2) and bridge compound (pentaerythretol tetra bromide) with hetro-[metals$(acetate)_2$] for ions such as (Cu^{+2}, Co^{+2}, Ni^{+2}) to give the complexes as shown in–Scheme (2) illustrates this. Table (1) Shows the physical properties of the complexes.

FTIR Spectrum of Homo Precursors with Hetrometals

The FTIR spectrum(11,12) for Homo precursors [any precursors from type (N_2O_2) or type (N_2S_2)] with two metals, copper and nickel complexes $[Cu\ Ni\ (P^1)_2]$ and $[Cu\ Ni\ (P^4)_2]$ Fig. (1), (2) respectively, appears to show a shift to a lower frequency for stretching the bands of υ (C=N) between (1490-1589)cm^{-1} compared to the free precursor.

Also, the absence of observed bands for υ(OH) and υ(SH) inductor coordinates between metal and ligand, and the appearance exhibits some bands at (694-756) cm^{-1}, (483-495) cm^{-1} and (580-609) cm^{-1} which are attributed to υ(M-N), υ(M-S) and υ (M-O) respectively.

These changes (13) in some bands can be attributed to the delocalization of electronic density towards the metal centre upon coordination (HOMO→LOMO) [HOMO=highest occupied molecular orbital, LUMO=lowest unoccupied molecular orbital]. The assignments of the characteristic bands are summarized in Table (2).

UV-Vis spectrum of [Cu, Ni, $(P^1)_2$] complex

The electronic(14, 15) spectrum of [Cu, Ni, $(P^1)_2$] complex Fig. (3) exhibits peak at (256) nm (39062) cm^{-1} (ε_{max} =1581$molar^{-1}$. cm^{-1}) and (340) nm (29411cm^{-1}) (ε_{max} =331 $molar^{-1}$. cm^{-1}) assigned to ligand field and charge transfer. The d-d transitions was mixed between the two d-d transitions of Cu^{+2} and Ni^{+2}, hence the complex displays additional peaks at (607) nm (16474) cm^{-1} (ε_{max} =76 $molar^{-1}$. cm^{-1}) and (648)nm (15432)cm^{-1} (ε_{max} = 38 $molar^{-1}$.cm^{-1}), which is attributed to (d-d) transitions type ($^4A_1g \rightarrow {}^4A_2g$) and ($^4A_1g \rightarrow {}^4B_1g$) respectively. This is an indication of the square planer structure of the hetrometal homo precursor complex. Table (3) shows these peaks.

This result is in agreement with that reported previously about the electronic spectra of four coordinate (square planer) for hetrometal complexes.

UV-Vis spectrum of [Cu, Ni, $(P^4)_2$] complex

The electronic spectrum(14, 15) of [Cu, Ni, $(P^4)_2$] complex Fig. (4) appears peak at (246) nm (40650) cm^{-1} (ε_{max} =2545 $molar^{-1}$.cm^{-1}) and (280) nm (35714) cm^{-1} (ε_{max} =403 $molar^{-1}$. cm^{-1}), assigned to ligand field and charge transfer. The d-d transitions were mixed between the two d-d transitions of Cu^{+2} and Ni^{+2}, hence the complex shows additional peaks at (557)nm (17953)cm-1 (ε_{max}=46 $molar^{-1}$.cm^{-}) and (639) nm (15649) cm^{-1} (ε_{max} =39 $molar^{-1}$. cm^{-1}), which attributed to (d-d) transition type ($^4A_1g \rightarrow {}^4A_2g$) and ($^4A_1g \rightarrow {}^4B_1g$) respectively. This is an indication of the square planer structure of the hetrometal homo precursor complex. Table (3) shows these peaks.

This result is in agreement with that reported previously about the electronic spectra of four coordinate (square planer) for heterometals complexes

^1H NMR spectrum of [Cu, Ni P^1] complex

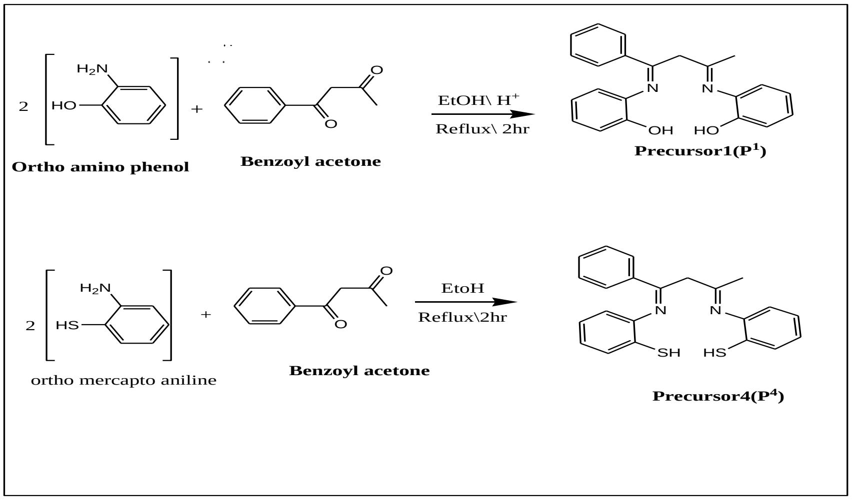
The ^1H NMR spectrum for [Cu, Ni P^1] complex(15) Fig. (5) in DMSO-d^6, shows the disappearing of proton of the hydroxyl group which that show in precursor 1(P^1) at (δ= 12.8 and 10. 3) ppm, refer to a good evidence for the binding between the bridge and the precursor, and the new chemical shift shows at (δ= 3.4 and 2.6 ppm) due to the CH_2 groups of pentaerythritolyl tetrabromide as a bridge and methyl groups respectively. Which the benzene rings appear as broad signals at the range (8.1- 6.2) ppm refer to the binding between the metal, precursors and bridge to obtain the complex. The chemical shifts were summarised in Table (4).

^1H NMR spectrum of [Cu, Ni P^4] complex

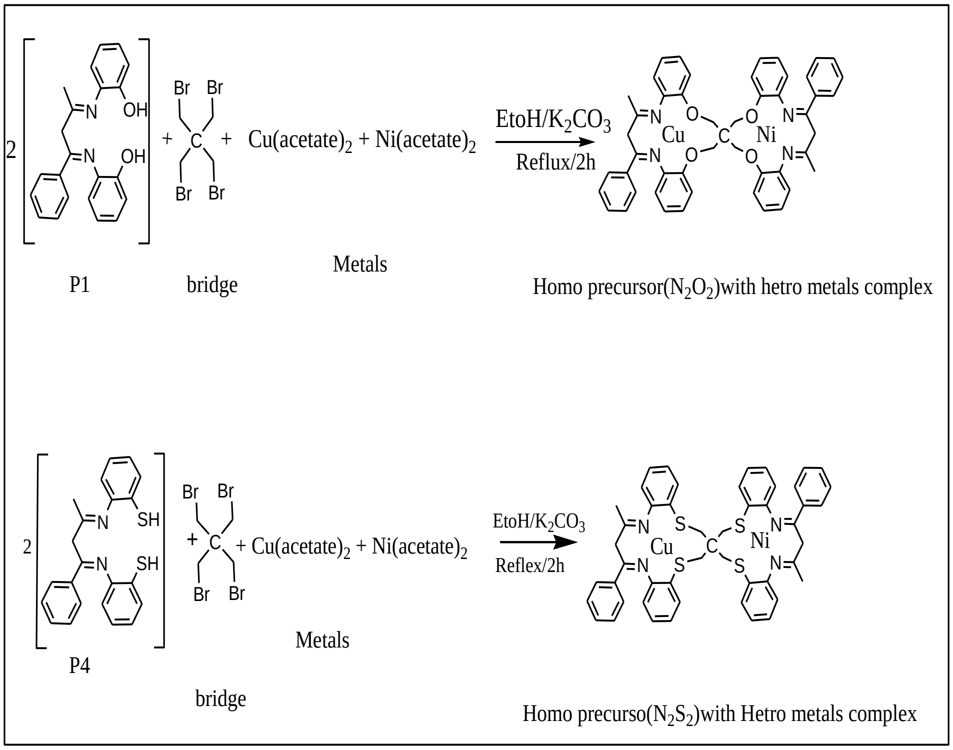
The ^1H NMR spectrum for [Cu, Ni P^4] complex(16) Fig. (6) in DMSO-d^6, shows disappearance of the sulphide group protons in precursor 4(P^4) at (δ= 9.8 and 9.4ppm) this indicates the binding between the bridge and precursor. The chemical shift between (δ= 8.2 – 6.3ppm) can be attributed to the six benzene ring existed at one situation, the signal at(δ=3.6ppm, 2H) and (δ=2.4ppm) due to the protons of methylene and methyl groups respectively. These signals are shifted compared with that in the free precursors. This shifting is caused by the lower electron density existing on these protons in the complex, the chemical shifts were summarised in Table (4).

Table (1): Some physical properties for prepared complexes of heterometal with homo precursor.

Compounds Complexes	M.p C°	Colour	Wt of product (gm)	Yield %	M.Wt g/mol	Macroanalysis(calc)%				
						M	C	H	N	S
[Cu, Ni(P^1)]	**229-234**	**Green-**	**0.51**	**57.95**	**874.14**	**13.98** **14.26**	**67.33** **67.41**	**5.03** **5.27**	**6.41** **6.72**	
[Cu, Ni(P^4)]	**>292dec**	**Gray**	**0.46**	**52.87**	**938.23**	**13.02** **13.38**	**62.67** **63.00**	**4.68** **4.89**	**5.96** **6.37**	13.64 14.02



Scheme (1): The rote of preparation of precursors (1,4) P^1, P^4.



Scheme (2): Homo precursor with Hetero metals complexes.

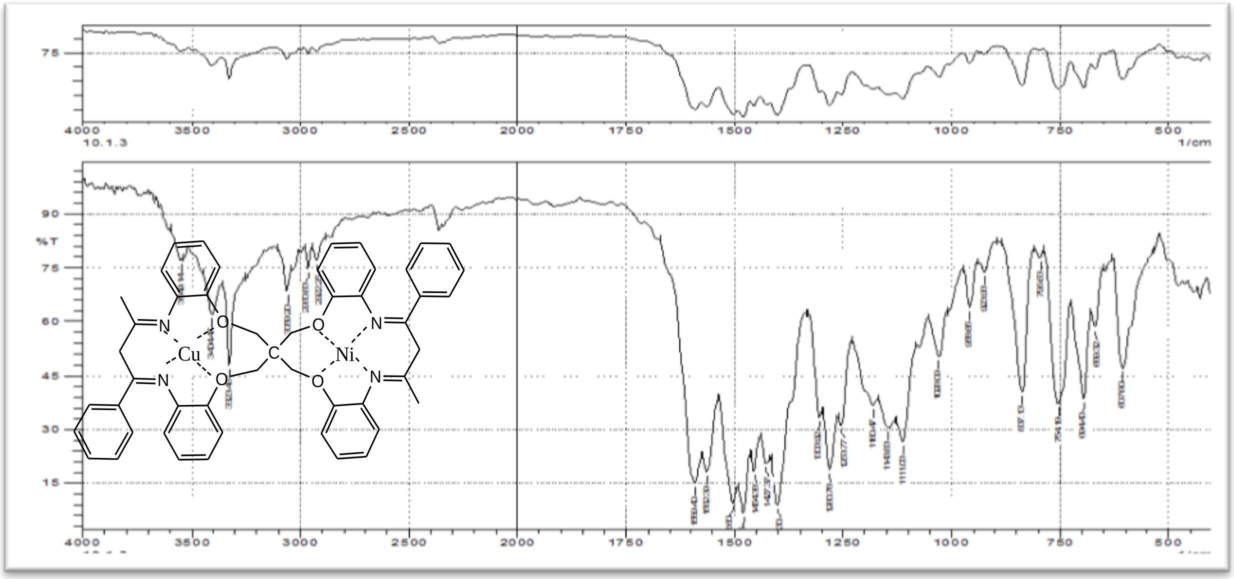


Fig. (1): FTIR spectrum of Hetrometals [Cu, Ni $(P^1)_2$].

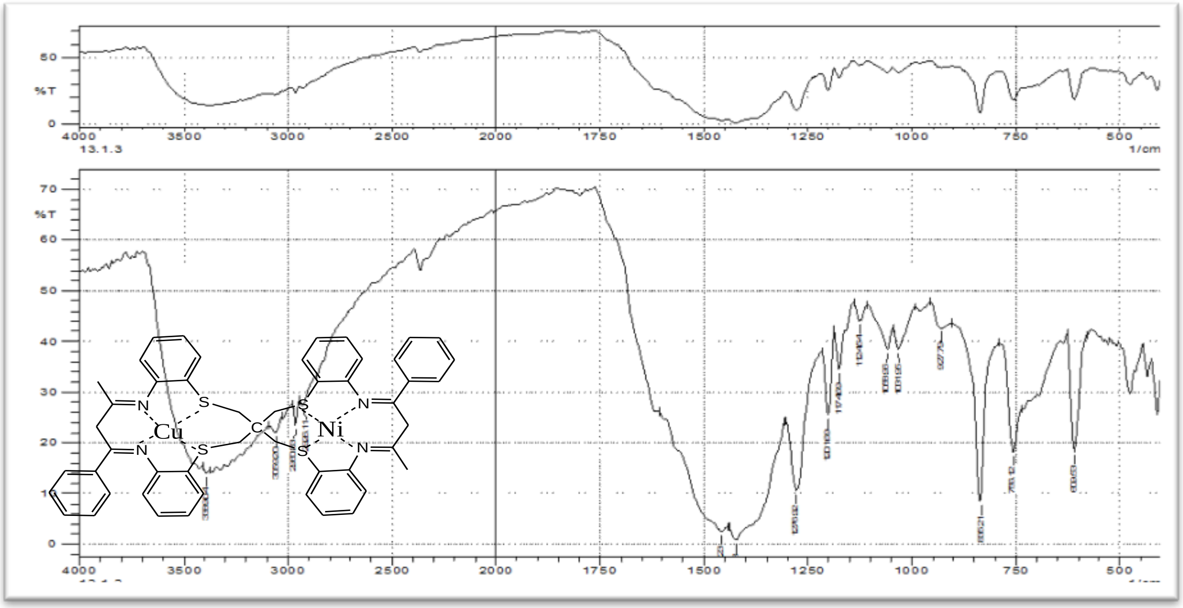


Fig. (2): FTIR spectrum of Hetrometals $[(P^4)_2$Cu,Ni].

Table (2): FTIR spectrum of Homo precursors with hetrometals.

Compounds	**ν_{ar}(C-H)**	**ν_{ali}(C-H)**	**ν(C=N)**	**ν(C-N)**	**ν(C-O)**	**ν(C-S)**	**ν(M-N)**	**ν(M-O)**	**ν(M- S)**
[Cu, Ni $(P^1)_2$]	**3323m**	**2921m**	**1589m**	**1280s**	**1028w**	**--------**	**644w**	**607m**	**--------**
[Cu, Ni $(P^4)_2$]	**3059w**	**2926w**	**1490s**	**1276s**	**1058m**	**927m**	**756w**	**609w**	**495w**

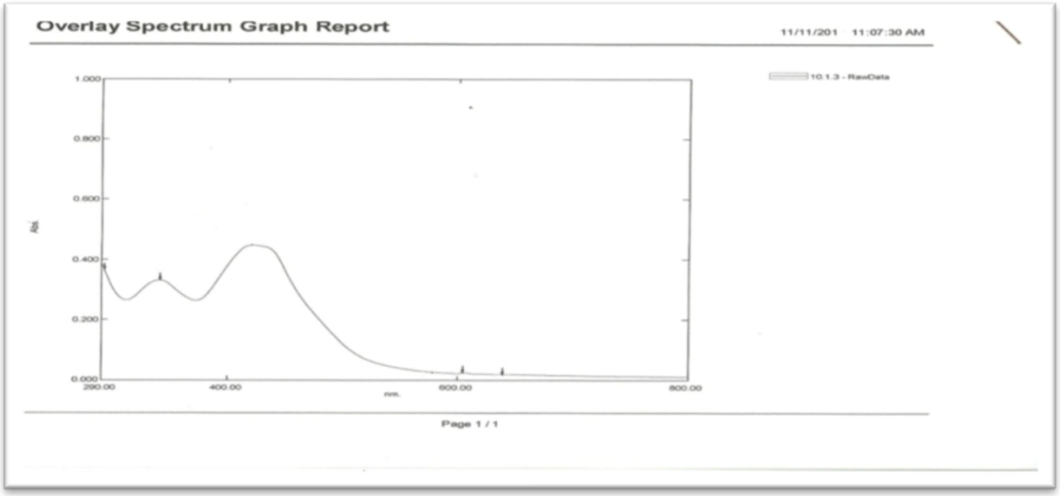


Fig. (3): Electronic spectrum of [Cu, Ni, $(P^1)_2$] complex.

Table (3): Uv-Visible spectral data for Hetro metals Homo precursors

Compound	**λ nm**	**v cm^{-1}**	**Ɛmax (molar^{-1}cm-1) Ɛmax (molar^{-1}cm-1**	**Assignments**	**Expected form**
[Cu, Ni P^1]	256 340 607 648	39062 29411 16474 15432	1581 331 76 38	Ligand filed and Charge transfer $^4A_1g \rightarrow {}^4A_2g$ $^4A_1g \rightarrow {}^4B_1g$	Square planer D_4h
[Cu, Ni P^4]	246 280 557 639	40650 35714 17953 15649	2545 403 46 39	Ligand filed and Charge transfer $^4A_1g \rightarrow {}^4A_2g$ $^4A_1g \rightarrow {}^4B_1g$	Square planer D_4h

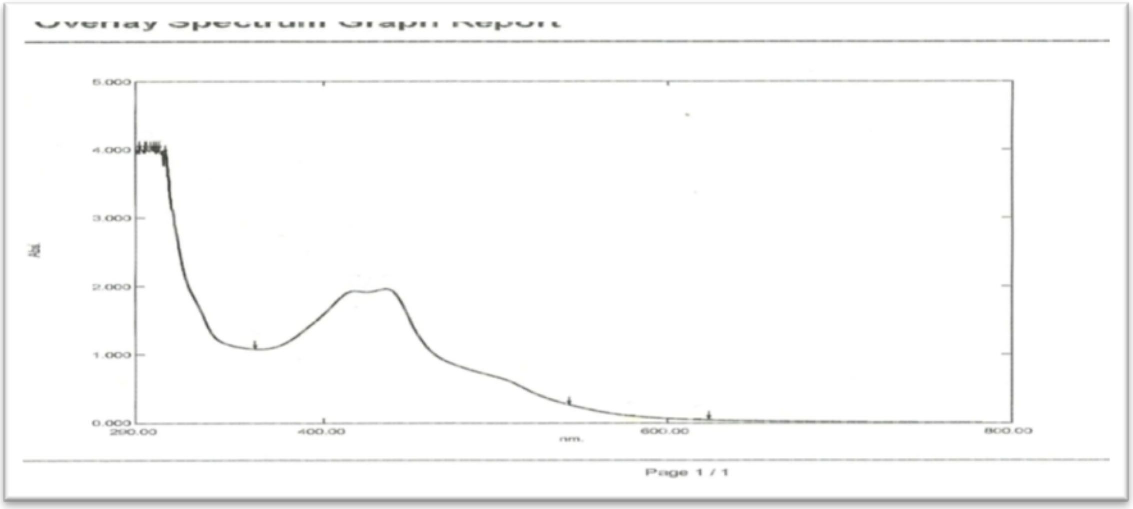


Fig. (4): Electronic spectrum of [Cu, Ni, $(P^4)_2$] complex.

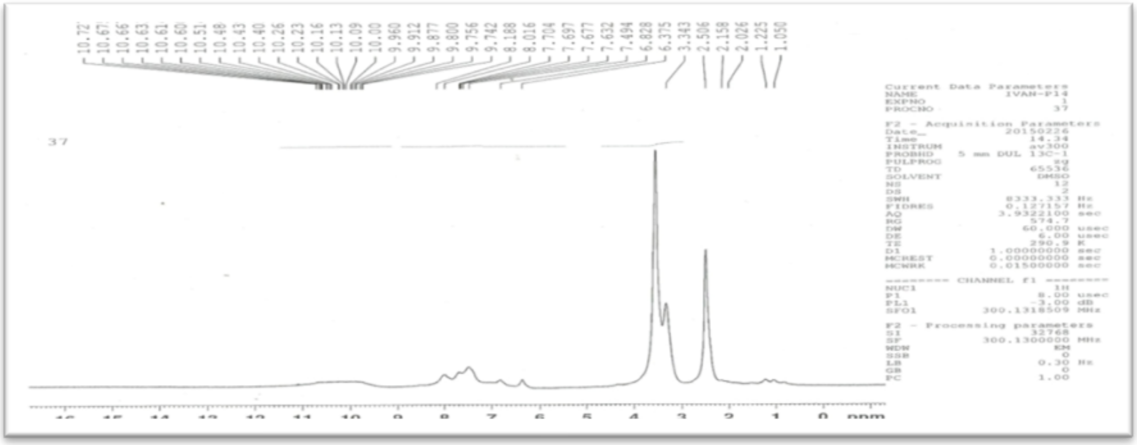


Fig. (5): ^{1}H NMR Spectrum of [Cu, Ni P^1] complex.

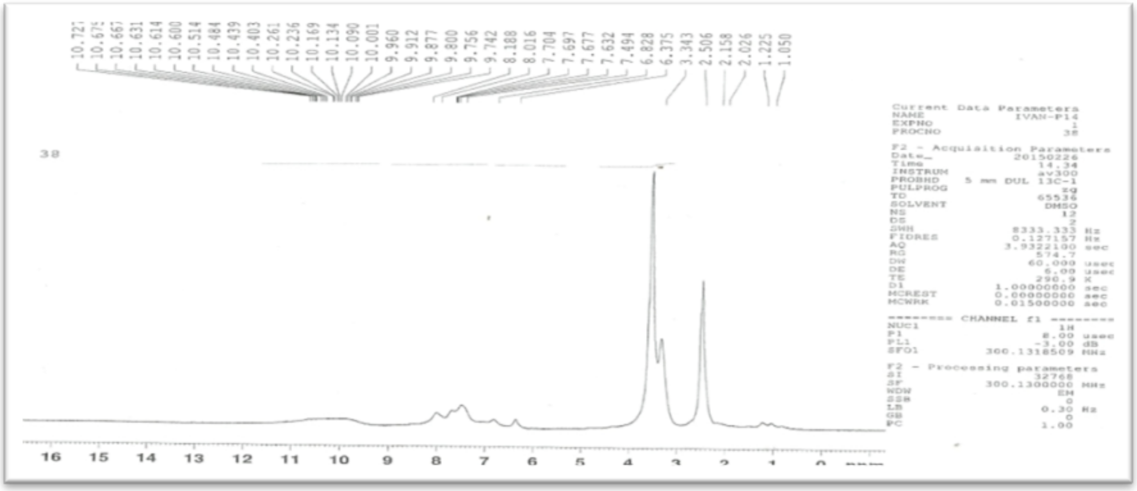


Fig. (6): ^{1}H NMR Spectrum of [Cu, Ni P^4] complex.

Table (4) ^{1}H NMR data for Hetro and Homo metal complexes.

Compounds	Functional groups	Chemicals shift δ ppm
[Cu, Ni P^1]	6(benzene-ring) (CH2, CH3) groups	(8.1 – 6.2 ppm (3.4 and 2.6) ppm
[Cu, Ni P^4]	6(benzene-ring) (CH2, CH3) groups	(8.2 – 6.3) ppm (3.6 and 2.4) ppm

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