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Microwave assisted synthesis and identification of new Azo-Schiff bases with N,O Donor atoms and their Ni(II) and Cu(II) complexes

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***Abstract*---**The present paper describes the synthesis of two Azo-Schiff base named (2-(((2-aminophenyl)imino)methyl)-6-ethoxy-4-((Z)-phenyldiazenyl) phenol, 2-((Z)-((4-aminobutyl)imino)methyl)-6-ethoxy-4-((Z)-phenyldiazenyl)phenol) by diazotization reaction of the synthesized (3-Ethoxy-2-hydroxy benzaldehyde) with aniline compound to gave Al- Azo – aldehyde and reacted with (O-phenylenediamine or1,4-butanediamine) to gave Azo-Schiff bases compounds. All new synthesized derivatives (ligands and complexes with Ni(II) and Cu(II)) were identified by melting points, FT-IR, ^{1}H-NMR, Mass, molar conductivity and magnetic susceptibility. The ligands are coordinate to metal ion by nitrogen atom of azomethine and oxygen atom of hydroxyl group to form Ni(II) complex with square planer geometry and Cu(II) complex with octahedral geometry.

***Keywords*---**synthesis, nitrogen atom, octahedral geometry.

Instrumentation

The FT-infrared measurements were recorded by using FT-IR affinity Spectrophotometer (Shimadzu) Japan; Mass spectra are recorded of compounds using Agilent Technology (HP)/MS Model 5973 Network Mass Selective Detector and the University of Tehran, Iran. The ^{1}H-NMR with using DMSO as solvent in Tehran, Iran. magnetic susceptibility (μeff. B.M)

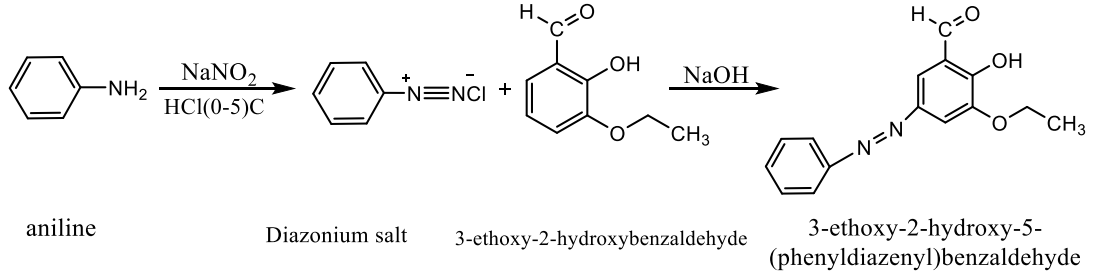
Synthesis

Preparation of the ligand (L_1H) and (L_2H)

A: Preparation azo-aldehyde

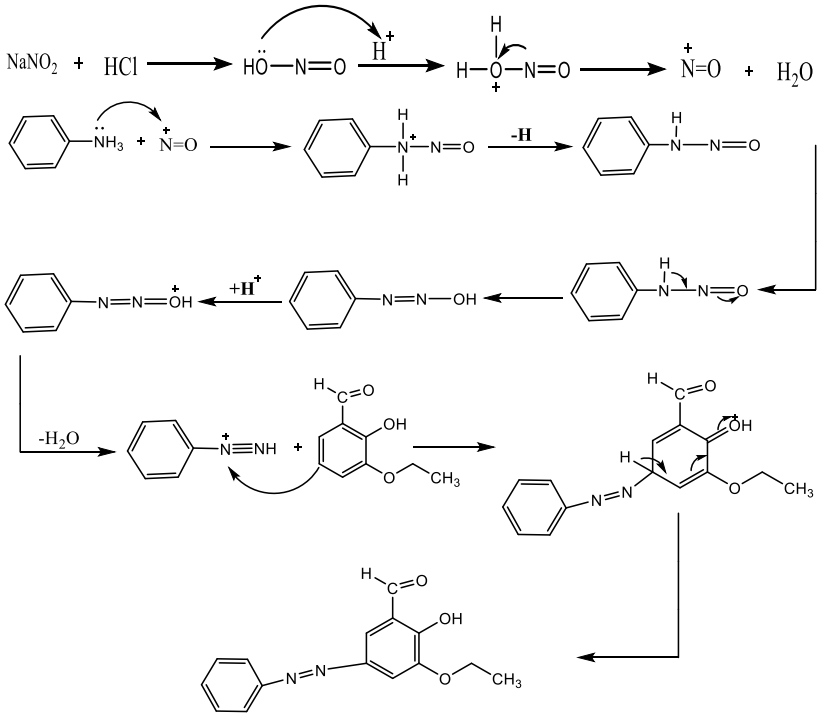
The preparation included dissolving (0.95 ml, 0.01 mol) of aniline in a mixture of (5 ml, 37%) of concentrated hydrochloric acid and (30 ml) of distilled water in a (250 ml) beaker with continuous stirring and cooling the solution between (0-5).

°C) using an ice bath and treated with a solution of sodium nitrite (0.75gm, 0.01 mol) in (20ml) of distilled water in the form of drops with continuous shaking for (30 min) while maintaining the mixture at a degree (0-5 oC). Then, the diazonium chloride solution was added to 3-ethoxysalisaldehyde (1.66 gm, 0.01 mol) solution dissolved in (50 ml ethanol + 70 ml 10% NaOH) in batches and left to settle for 24 hrs) with acidification with dilute hydrochloric acid and maintained. The value of (pH=6). The precipitate was filtered through a filter paper, washed several times with distilled water, then left to air dry, and recrystallized twice using ethanol, then dried using a thermal oven at a temperature of (6 °C) for a period of (2 hrs).



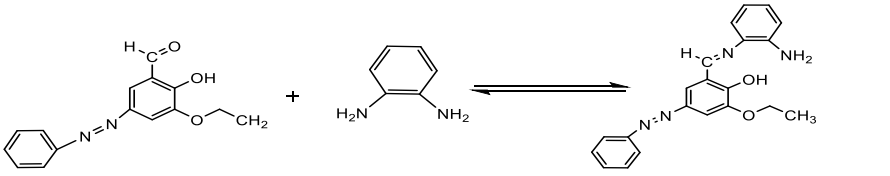
Scheme-1: Structure of the Azo-aldehyde.

Mechanism of preparing azo – aldehyde



B- Azo Schiff (L_1H)

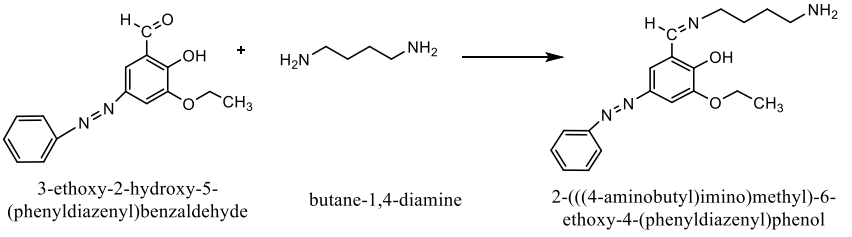
The compound (Azo Schiff L_1H) was prepared by mixing azo-aldehyde (2.7 gm, 0.01 mol) in (20 ml) of absolute ethanol with O-phenylenediamine (1.08 gm, 0.01 mol) in (20ml) of absolute ethanol in a molar ratio (1:1) With the addition of drops of glacial acetic acid to the reaction mixture. After that, it was irradiated in the microwave for 15 minutes, with follow-up of the reaction every 3 minutes, using thin layer chromatography (TLC). The precipitate was separated through a filter paper and recrystallized using absolute ethanol.



Scheme-2: Structure of the Azo-L_1H.

C- Azo Schiff (L_2H)

Azo-Schiff (L_2H) was prepared by mixing azo-aldehyde (2.7 gm, 0.01 mol) in (20 ml) of absolute ethanol with 1-4 butanediamine (0.88 gm, 0.01 mol) in (20ml) of absolute ethanol at a ratio of molarity (1:1) with the addition of drops of glacial acetic acid to the reaction mixture. After that, it was irradiated in the microwave for 15 minutes, with follow-up of the reaction every 3 minutes, using thin layer chromatography (TLC). The precipitate was separated through a filter paper and recrystallized using absolute ethanol.



Scheme-2: Structure of the Azo-L_2H.

Table (1): Chemical compositions and physical properties of the prepared azo compounds

Symbol	M.Wt	Color	°cm.p	Yield%
Azo-aldehyde	270	Yellow	205-208	77
Azo Schiff base L_1H	360	Yellow	>300	74
Azo Schiff base L_2H	340	Orange	>300	73

Preparation of transition metals complexes:

(0.001mol)) of each of the ligands prepared in paragraphs (B) and (C) dissolved in 15 ml of hot methanol was mixed with 0.001) of the salts of the elements ($CuCl_2.2H_2O$ and $NiCl_2.6H_2O$) and dissolved in 10 ml of hot methanol in a rawndbootem (100 ml) equipped with a condenser, where metal salts were gradually added and irradiated in the microwave for (5-10 min) The reaction was followed up using thin layer chromatography (TLC), and after the end of the reaction, the mixture was left to cool, then the formed product was filtered through a filter paper and washed several times with water, then with absolute ethanol and left to dry.

Table (2): Molecular formula and some physical properties of complexes of the prepared compounds

No	Formula	M.wt	Color	m.p. °c	Yield%
Azo schiff Cu-L_1H	$[Cu(L_1)(Cl)_2(H_2O)_2]$	494	Green	233-235	67
Azo schiff Ni-L_2H	$[Ni(L_2)(Cl_2]$	469	Deep yellow	213-215	65

Table- 3: Spectroscopic data for Azo-Schiff bases and its complexes

Compound	IR C=N $(cm)^{-1}$ N=N $(cm)^{-1}$	H^1-NMR &(ppm)	Mass spectra
Azo-aldehyde	------ 1584	H-C=O (10.2) -OH (10.4) $-CH_2$ (4.2) -OCH (1,7) -Ar-H (6.9 – 7.2)	-------
L_1H	1612 1585	-N=CH- (7.8) -OH (13.3) $-CH_3$ (1.48) -Ar-H (7 - 7.8) -NH2 (1.4)	m/s; 360 M^+
a	1624 1593	----------	m/s; 494 M^+
L_2H	1623 1572	-N=CH- (8.5) -OH (13.9) $-CH_3$ (1.4) -Ar-H (6.8 - 7.1) -NH2 (6.9)	m/s; 340 M^+
b	1639 1546	----------	m/s; 469 M^+

a- $(Cu(L_1H)(H_2O)_2(CL)_2)$ b- $[Ni(L_2H)CL_2]$

Result and Discussion

The formation of the complexes may be represented as follow.
$Cu(Cl)2.2H2O+L_1H \rightarrow [Cu(L_1H)(Cl)_2(H_2O)_2].nH2O+CH3COOH$
n=0
$Ni(Cl)2.6H2O+L_2H \rightarrow [Ni(L_2H)(Cl)_2(H_2O)_2].nH2O+CH3COOH$
n=4

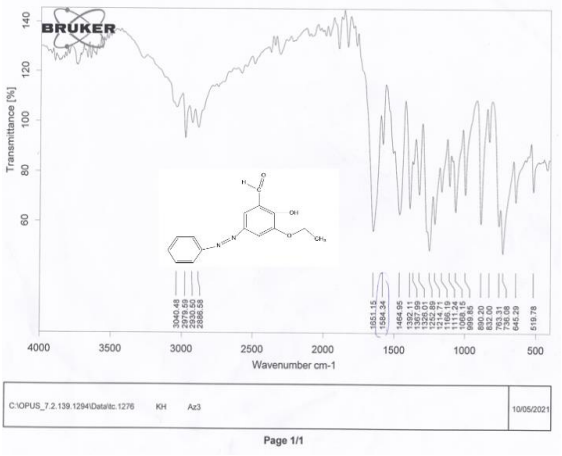


Fig. 1 Azo- aldehyde

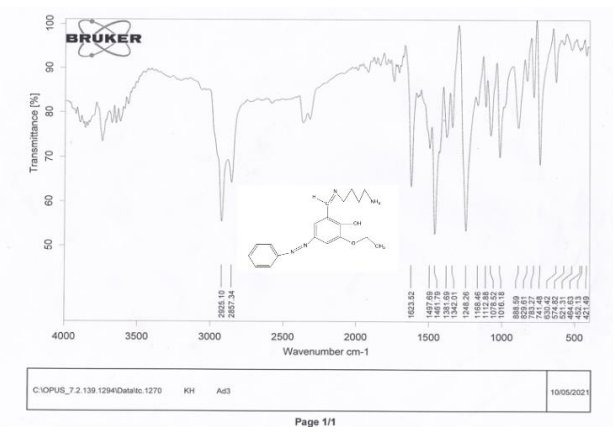


Fig 2 Azo – L2H

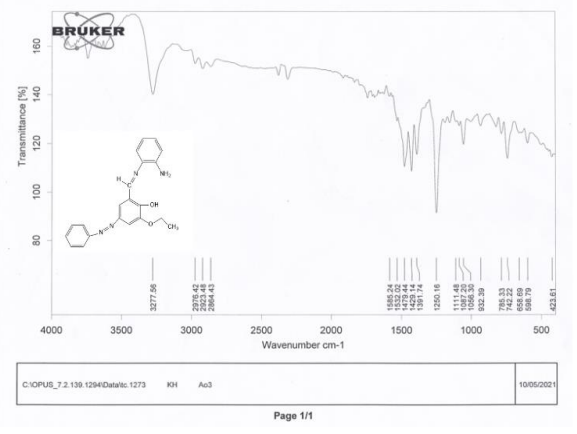


Fig. 3 Azo – L_1H

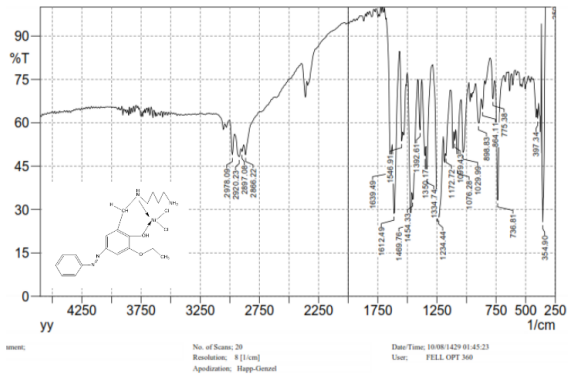


Fig.4 Azo- L_2 –Ni

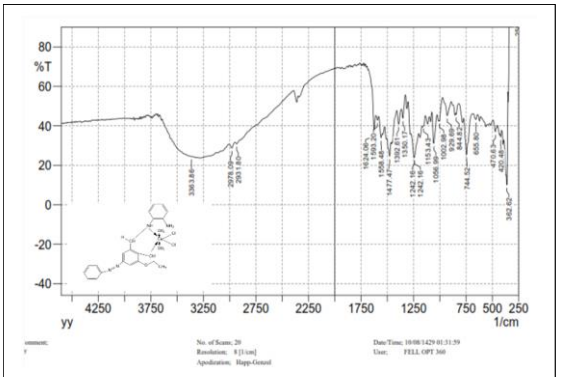


Fig. 5 Azo- L_1 –Cu

: IR spectrum of ligand and complexes.

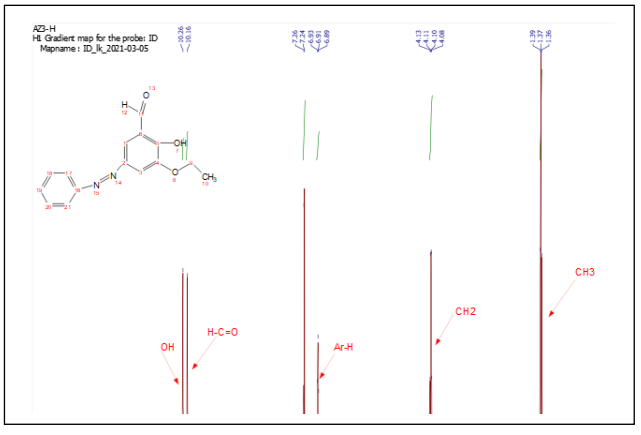


Fig. 6 Azo- aldehyde

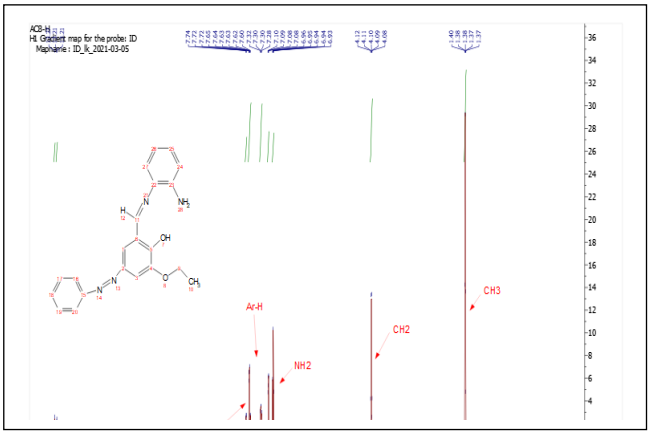


Fig :7 Azo- L_1H

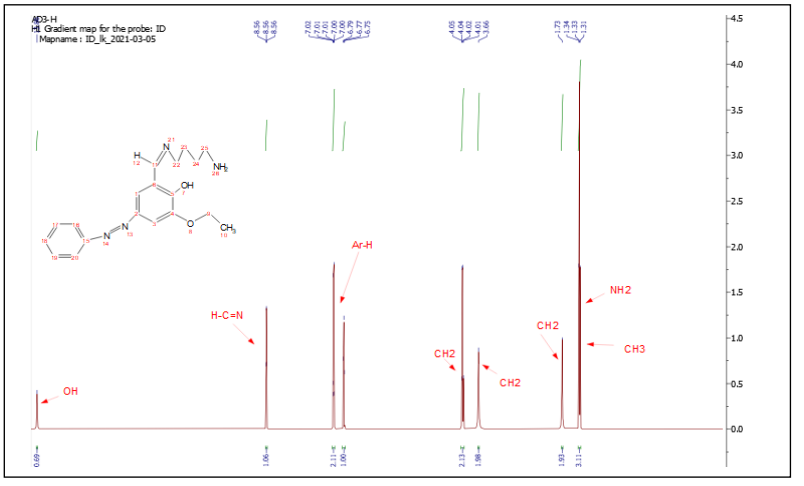


Fig :8 Azo- L_2H ^1H-NMR spectrum ligand

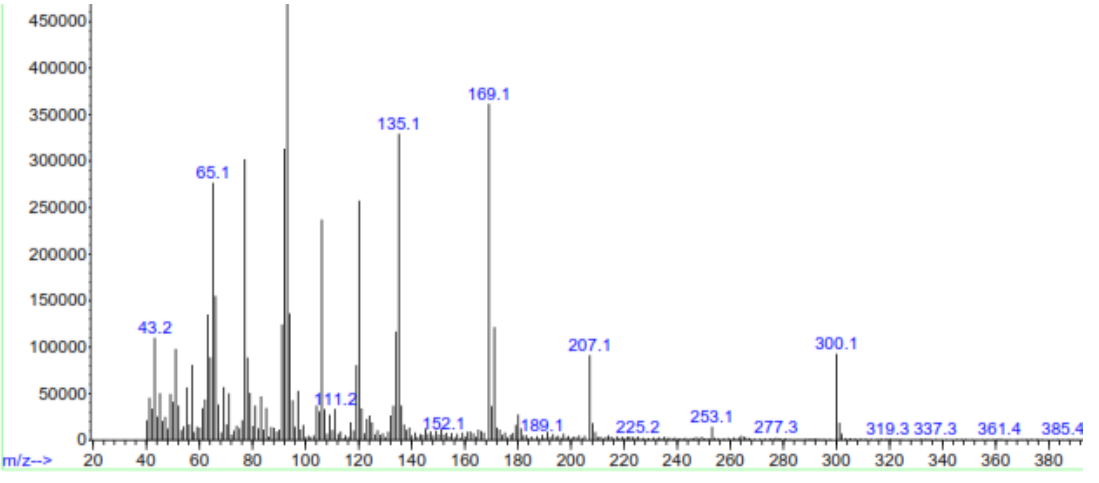


Fig 9 Azo-L1H

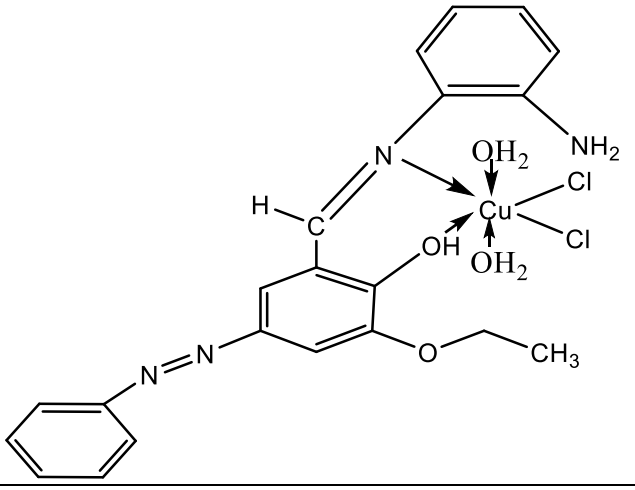
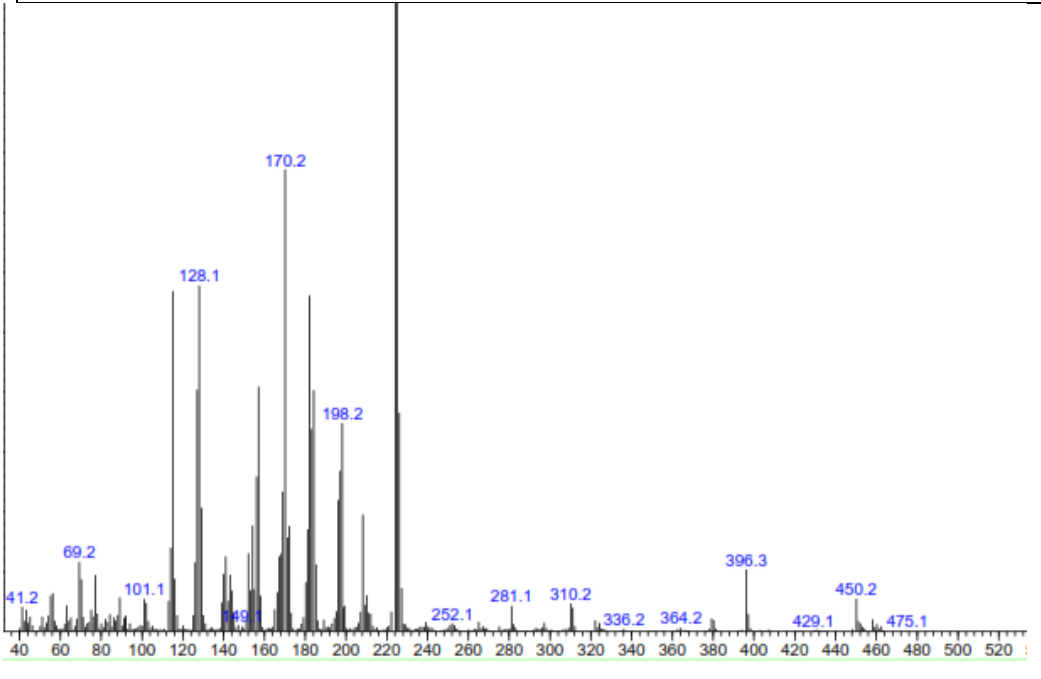
	m/z
	
[Cu(Azo Schiff L_1)$CL_2(H_2O)_2$]	494
[Cu(Azo Schiff L_1)$CL(H_2O)_2$]	459
Azo Schiff L_1	360
	

Fig 10 Azo-L1H -Cu

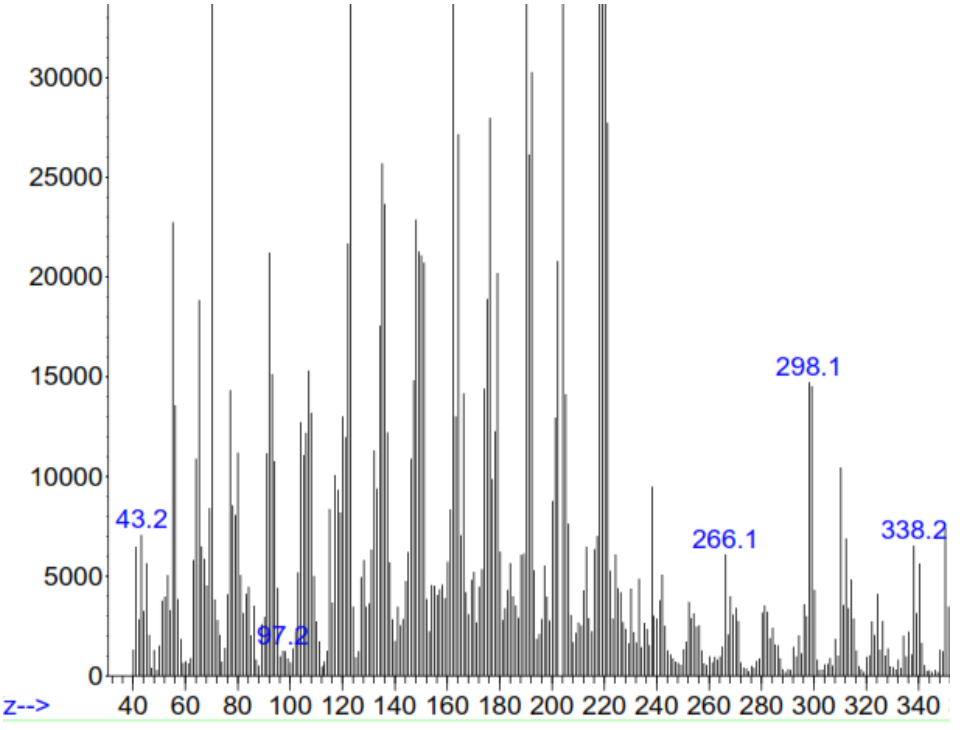
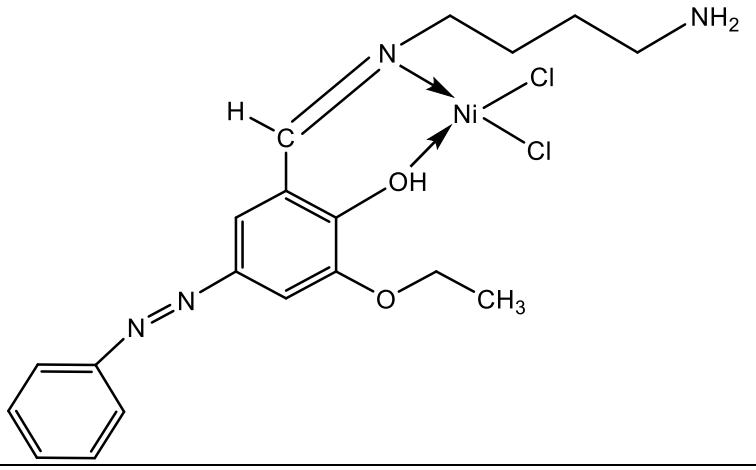


Fig 11 Azo-L2H

	m/z
[Ni(Azo Schiff L_2)CL_2]	469
[Ni(Azo Schiff L_2)CL]	434
Azo Schiff L_2	340

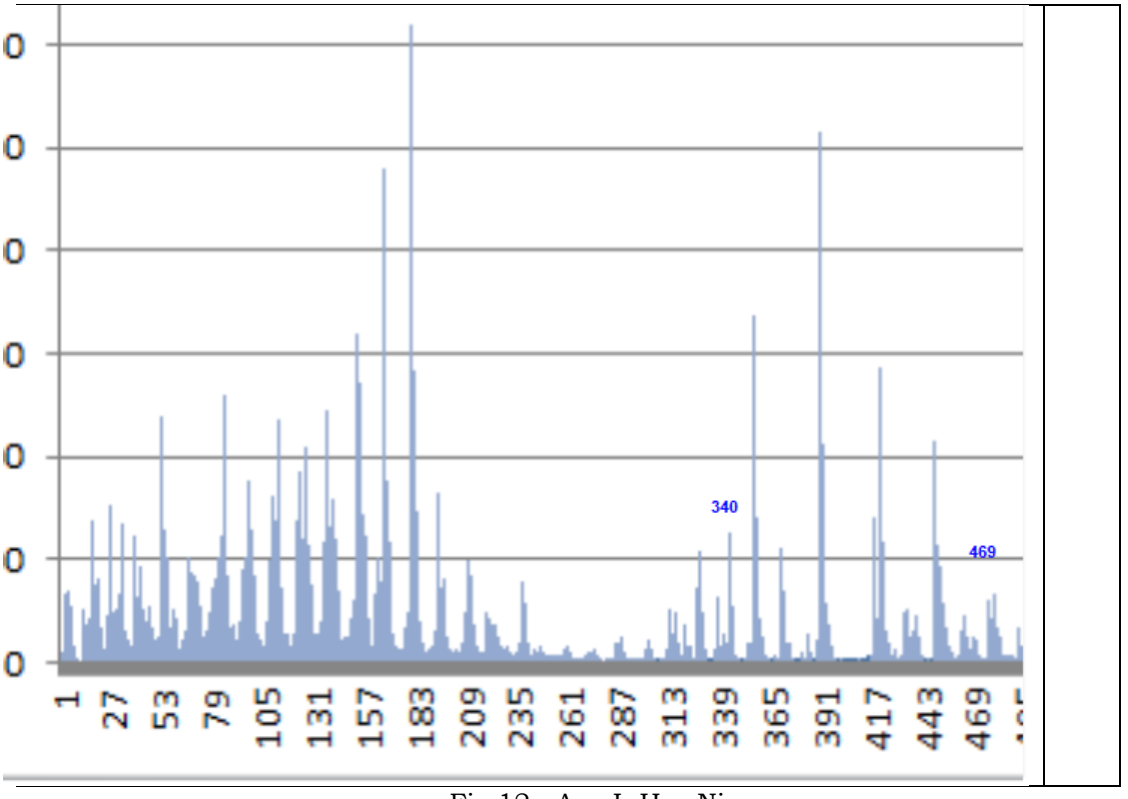


Fig 12 Azo-L_2H - Ni
mass spectrum ligand

^{1}H-NMR spectroscopy

The ^{1}H-NMR of L_1H and L_2H were recorded. The significants of ligand are shown in Figs (2) and (3), respectively . in the spectrum of shown a signal at (13.3 , 13.9) ppm appointed to the phenolic -OH protons [13]. the presence of this singlet , may be due to the H- bonded OH group . A characteristic singlet at (7.8 , 8.5) ppm assigned to the protons of azomethine groups (-CH=N) [14].

FT- IR spectroscopy

The characteristic IR data of L_1H and L_2H and its metal complexes listed in table (3), the IR spectra of the ligands exhibit bands at (3277 , 3700)and (3020 , 3025)cm^{-1} that are assignable to (OH) and (Ar – H)[15], and the appearance of absorptions bands at (1612 , 1623) cm^{-1} due to azomethine (C=N) bond stretching vibrations , and bands at (1585 , 1572)cm^{-1} appointed to stretching of azo group (N=N). both complexes indicating that the stretching frequency of the (C=N) bond shifted to higher wave numbers comparison with the free ligands after coordination because the coordination of nitrogen to the metal center and its agreement with results from the similar complexes prepared previously [16]. On the other hand , the appearance of the OH band of the free ligands in the spectra of metals of

ligands indicates that the OH group has been coodinates to the metal ion [17].

Mass spectra

The mass spectrum of the prepared Schiff bases shows a peak for the molecular ion which agrees with the proposed molecular formula for these bases. The mass spectra of (azo-L_1H) appeared molecular ion peak at 362 m/z which is in conformity with the molecular formula. for $C_{21}H_{22}N_4O2$; 362; found: 362, (M/S) $Cu(L_1H)(Cl)_2(H_2O)_2$ =496 M+ ; found: 496
The mass spectra of (azo-L_2H) appeared molecular ion peak at 342 m/z which is in conformity with the molecular formula. for $C_{19}H_{20}N_4O2$; 342; found: 342 and $Ni(LH)(Cl)_2$= 471 [M+H]; found: 471.[18,19].

Table 4: Measurement of the atomic absorption and magnetic of complexes

Sample	Formula	M.Wt	Atomic Absorption		M:L Ratio	Ueff(B.M)
			Partical	Theortical		
Azo schiff Cu-L_1	$C_{31}H_{30}N_2O_4NiCL_2$	494	6.1ppm	6.3ppm	1:1	0.61
Azo schiff Ni-L_2	$C_{31}H_{30}N_2O_4CuCL_2$	469	5.5ppm	5.8ppm	1:1	0.43

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