Synthesis and Characterization of New Schiff Base Ligand Type $[N_4O_4]$ from 3-(Ethoxymethylene) Pentane-2.4-dione and its Ni^{II} Complex

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Abstract*–The Schiff base reaction plays an important role in the condensation reaction between 3-(ethoxymethylene) pentane-2.4-dione and 3,3'-diaminobenzidine in the presence of calculated amounts of KOH as a catalyst. This reaction has been carried out in the ethanol under reflux and overnight stirring condition. All syntheses were carried out under an atmosphere of hydrogen forming a new ligand [3,3',3",3'"-(1E,1'E,1"E,1'"E)-(biphenyl-3,3',4,4'-tetrayltetrakis (azan-1-yl-1-ylidene)) tetrakis (methan-1-yl-1-ylidene) tetrakis (4-methoxybut-3-en-2-one)] type $[N_4O_4]$. The ligand and its Ni^{II} complex of the general formula $[Ni_2(L)]$ have been characterized by spectroscopic methods (Fourier transform infrared and ultraviolet-visible), elemental analysis (C.H.N), metal content, magnetic susceptibility measurement, thin-layer chromatography, mass spectrometry, X-ray powder diffraction powder diffraction, ^{1}H-nuclear magnetic resonance, molar conductance, and biological activity. The ligand and its Ni complex were exposed to two types of bacteria (Staphylococcus aureus and Bacillus subtilis), using the agar disc diffusion method, and the ligand and its Niᴨ complex exhibited significant activities against these two types of bacteria. Our study revealed the formation of a new ligand type $[N_4O_4]$ and four-coordinate tetrahedral structure around Ni^{II} metal ion with the ratio of 1:2 (ligand:metal) stable compounds which can be used in many fields, such as medicine and industry.

***Index Terms*—3-(Ethoxymethylene) pentane-2.4-dione, Four-coordinate tetrahedral complex, Nickel(II) acetate hydrate-99+%, Structural study, Schiff bases.**

I. Introduction

3-(Ethoxymethylene) $C_8H_{12}O_3$ Average mass 156.179 Da Boiling Point 140–142°/15 mm is a chemical that can be prepared by triethoxymethane and pentane-2,4-dione. This reaction is a kind of substitution. 3-(ethoxymethylene) can be used to produce (2-acetyl-3-oxo-but-1-enyl)-phosphonic acid diethyl ester with phosphonic acid diethyl ester, sodium salt (Anne-Louise et al., 2005). Nickel(II) acetate hydrate-99+% with the formula $Ni(CH_3COO)_2{\bullet}H_2O$ and formula weight 176.97 (hydrate), soluble in water, alcohol ambient temperatures is used in synthesis of polynuclear-nickel polyoxotungstate cluster compounds that are ideal for the design of molecular magnets. 3,3'-Diaminobenzidine (DAB) (Yang et al., 2016) is an organic compound with the formula $(C_6H_3(NH_2)_2)_2$. This derivative of benzidine is a precursor to polybenzimidazole, which forms fibers that are renowned for their chemical and thermal stability (Hans and Dieter, 2005). DAB is symmetric about the central carbon bond between both ring structures. In the crystal, the rings of each molecule are co-planar, and the amine units connect molecules to form an intermolecular 3-dimensional hydrogen bond network (Qian and Huang, 2010). Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. The chemistry of Schiff base ligands species has been gaining considerable interest primarily due to their fascinating structural diversities (Asadi et al., 2011; Monfared et al., 2011; Chamayou et al., 2011). The electrophilic carbon atoms of aldehydes and ketones can be targets of nucleophilic attack by amines. The end result of this reaction is a compound in which the C=O double bond is replaced by a C=N double bond. This type of compound is known as an imine, or Schiff base with the general formula $R_1R_2C{=}NR_3$, where R is an organic side chain. In this definition, the Schiff base is synonymous with Azomethine. Many Schiff base complexes show excellent catalytic activity in various reactions and the presence of moisture (Abu-Dief and Mohamed, 2015). The Schiff bases are widely used for industrial purposes and also exhibit a broad range of biological activities. This short review compiles examples of the most promising antimalarial, antibacterial, antifungal, and antiviral Schiff bases. An overview of synthetic methodologies used for the preparation of Schiff bases is also described (Da Silva et al., 2011). In this manuscript, we describe the synthesis and physical characterization of 3,3',3",3'"-(1E,1'E,1"E,1'"E)-(biphenyl-3,3',4,4'-tetrayltetrakis(azan-1-yl-1-ylidene))tetrakis(methan-1-yl-1-ylidene) tetrakis(4-methoxybut-3-en-2-one) type $[N_4O_4]$ ligand in the ratio of 1:4 (DAB) and 3-(Ethoxymethylene),

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and its new monomeric metal complex with a range of divalent transition metal ion Ni^{II}, in the ratio of 2:1 metal ligands, forming new compound of M-N and M-O new bands by condensation reaction, and it has been supported by the most important techniques.

II. Materials and Technique

A. Materials

The chemical reagents (3-(Ethoxymethylene), DAB, KOH, methanol, ethanol, and nickel acetate hydrate) were commercially available and used without purification. Solvents were distilled from appropriate drying agents immediately before use.

B. Physical Measurements

Reagents were purchased from Fluka and Redial–Dehenge Chemical Co. Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Fourier transform infrared (FT-IR) spectra were recorded as FT-IR spectrophotometer in the range 4000–400 cm−0. Electronic spectra of the prepared compounds were measured in the region 200–900 nm for 10−0 M solutions in dimethyl sulfoxide (DMSO) and distilled water at 25°C using a Shimadzu160 spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. Elemental microanalyses were performed on a C.H.N. analyzer, whereas metal contents of the complexes were determined by atomic absorption (A.A.) technique using a Shimadzu A.A. 680G A.A. spectrophotometer. Electrical conductivity measurements of the complexes were recorded at room temperature for 10−f M solutions of the samples in DMSO and distilled water using a PW 9526 digital conductivity meter. Magnetic measurements were recorded on a Bruker BM6 instrument at room temperature following the Faraday's method. The mass spectrum for the ligand was obtained by electron-impact on (Shimadzu GCMSQPA 1000), and proton one-nuclear magnetic resonance (1H-NMR) spectrum were acquired in (DMSO-d6) solutions using (Jeol Lambda 400 MHz) spectrometer with tetramethylsilane.

III. Synthesis of [N_4O_4] Ligand

A. Preparation of [3,3',3",3"'-(1E,1'E,1"E,1"'E)-(biphenyl-3,3',4,4'-tetrayltetrakis(azan-1-yl-1-ylidene))tetrakis(methan-1-yl-1-ylidene)tetrakis(4-methoxybut-3-en-2-one)] Type [N_4O_4] Ligand. Scheme 1

All syntheses were carried out under an atmosphere of hydrogen. To a solution of DAB (2 g, 9.33 mmol) in ethanol (20 mL) was added 3-(ethoxymethylene) (3.4 mL) in ethanol (1.5 mL) in one portion in the ratio of 1:4, respectively. The solution was stirred for (24 h) overnight reaction at room temperature. After this time the mustard precipitate was filtered off, recrystallized with some drops of methanol, and dried in vacuum Yield: (1.2 g, 72%) m.p. (120°C).

B. Synthesis of the Ni^{II} Complex [$Ni_2(L)$]

[N_4O_4] ligand complex was prepared by the general methods Scheme 2, and as follows:

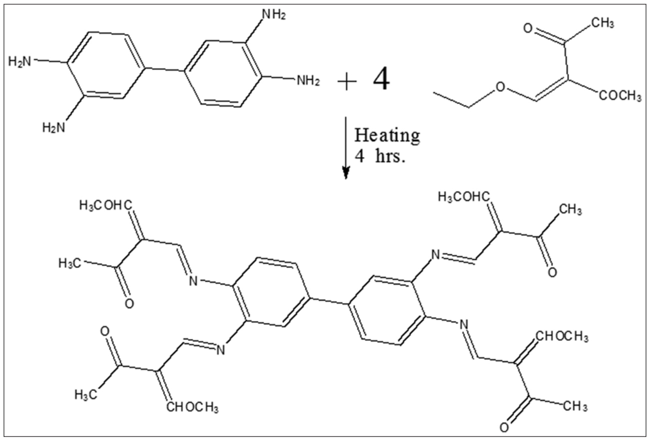
A suspension of nickel (II) acetate hydrate (0.44 g, 2.49 mmol) and [N_4O_4] (0.8 g, 1.52 mmol) in methanol (20 mL) with calculated amount of KOH was heated at reflux for (2 h). After cooling, a pale mustard precipitate was obtained that was collected, washed with methanol (5 mL) and dried in vacuum Yield: (0.52 g, 65%) m.p. (175°C). The [Ni2(L)] metal ion complex has been prepared in the ratio of 2:1 metal-ligand. Elemental analysis data, colors, and yields for the complexes are given in Table I.

IV. Results and Discussion

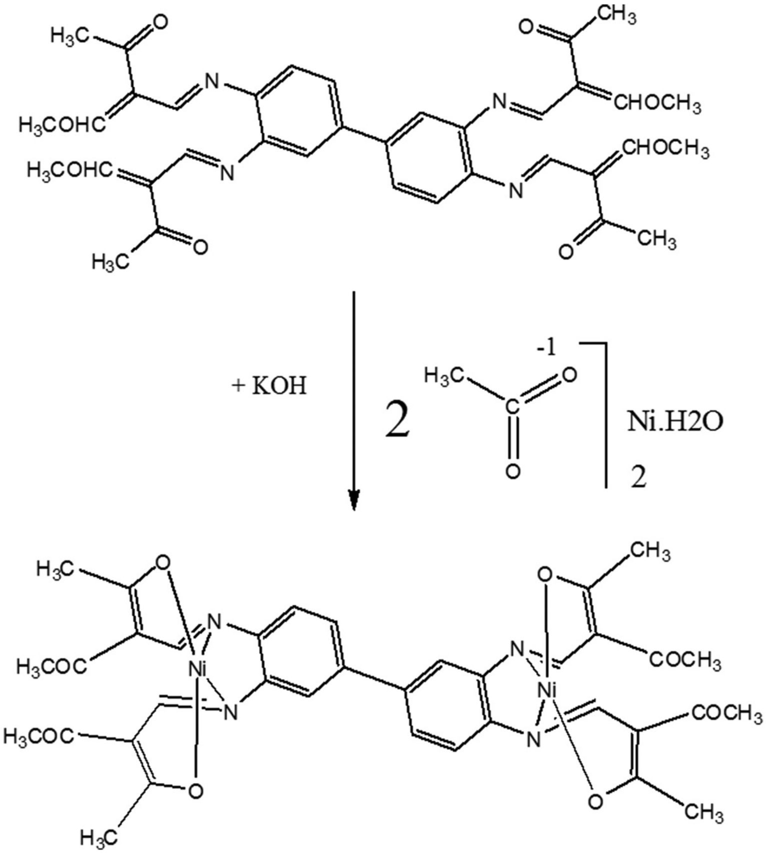
The [N_4O_4] ligand was achieved from the reaction of DAB and 3-(ethoxymethylene) in the ratio of 1:4 in alkaline medium. The general synthetic method for the preparation of the ligand and its Ni^{II} complex is according to Scheme 2. The ligand was obtained in almost a quantitative yield, and the metal complex of the ligand with Ni^{II}, metal ion was obtained in moderate yields. The compounds were characterized by elemental analysis, I.R, ultraviolet-visible (U.V-Vis.), magnetic susceptibility, melting point, thin-layer chromatography (T.L.C.), X-ray powder diffraction (X-RD), mass spectrophotometer,1H-NMR, and conductivity measurements.

A. The IR Spectrum of the Ligand

The bands are at 3400 and 3200 cm^{-1} due to the υ(NH_2) primary amine group (Anto et al., 2009 and Varghese et al., 2006) of DAB Fig. 1-b. The strong band is at 1200–1250 cm^{-1} due to the υ(C-O-C) group (Devi and Mohamed, 2012) of 3-(Ethoxymethylene) Fig. 1-a. These two bands disappeared in the spectrum of the [N_4O_4] ligand (Fig. 1-c), as a result of the replacement of the hydrogen atoms of the imine group by 3-(ethoxymethylene) and the formation of a new [N_4O_4] ligand. This causes the appearance of new band at 1579.6 cm^{-1} due to the υ(C=N) group, which indicates Schiff base reaction. In the spectrum of 3,3'-Diaminobenzidine (Fig. 1-b), the band is at 3000 cm^{-1},which, due to the υ(C-H ring) (Shayma et al.,



Scheme 1: Synthetic route for ligand [N_4O_4].



Scheme 2: The general structure for suggested [Ni_2(L)] metal ion complex.

TABLE I
The Physical Properties of the Ligand and its [Ni_2(L)] Metal Ion Complex

Molecular formula	M.Wt	Yield%	Color	m.pc°	Found, (calc%)					ƐM(Ω^{-1} cm^2 mol^{-1})
					Ni	C	H	H	O	
[N_4O_4] $C_{36}H_{38}N_4O_8$	654.71	72	Musterd	120	-	66.04	5.85	5.85	19.55	-
					-	50.54	4.21	4.21	17	-
$C_{36}H_{35}N_4Ni_2O_8$	769.07	65	Pale musterd	175	15.26	56.22	4.59	4.59	16.6414.71	19
					13.33	48.31	3.06	3.06		

TABLE II
FT-IR Spectra for the Ligand and its Precursors with its [Ni_2(L)] Metal Ion Complex

Χομπουνδ	ν(−NH_2)	ν(X−H) Ρινγ	ν(X=O)	ν(−NH)	CH3	ν(X−O−X)	ν(X=N)	ν(M−N)	ν(M−O)
3-(ethoxymethylene)	-	-	1650	-	1390	1200-1250	-	-	-
3,3'-Diaminobenzidine	3400-3200	3000	-	-	-	-	-	-	-
[N_4O_4] $C_{36}H_{38}N_4O_8$	-	2900	1600	-	1273	-	1579.6	-	-
$C_{36}H_{35}N_4Ni_2O_8$	-	2951	1773	-	1371	-	1598	598.6	600

2016) has been shifted to higher frequency for the ligand at (2900 cm^{-1}), whereas the υ(C=O) band at 1650 cm^{-1} (Baran et al., 2007 and Roeges, 1994) of 3-(Ethoxymethylene) Fig. 1-a is shifted to the lower frequency at (1600 cm^{-1}) in comparison with that of the spectrum of the free ligand (Fig. 1-c), as a result of the coordination between DAB and 3-(Ethoxymethylene) starting materials Table II.

B. The UV-Vis Spectrum of the Ligand

The UV-Vis spectrum of the ligand exhibits a high intense absorption peak at (210 nm) (47619 cm^{-a}) (ϵ_{max}=1421 $molar^{-1}$. cm^{-}), assigned for (π→ π*) transition (Anuradha and Rajarel, 2011) Table III.

C. The IR Spectrum of the [Ni_2(L)] Metal Ion Complex

In the spectrum of the free ligand Fig. 1-c, there are important bands at 1579.7 cm^{-1}, 1600 cm^{-1}, and 2900 cm^{-1} due to the υ(C=N), υ(C-O), and υ(C-H) ring, respectively. All these bands have been shifted to higher frequencies in comparison with that of the spectrum of Ni^{II} complex Fig. 1-d, as a consequence of the coordination of the ligand with the metal ion, whereas the characteristic new formed

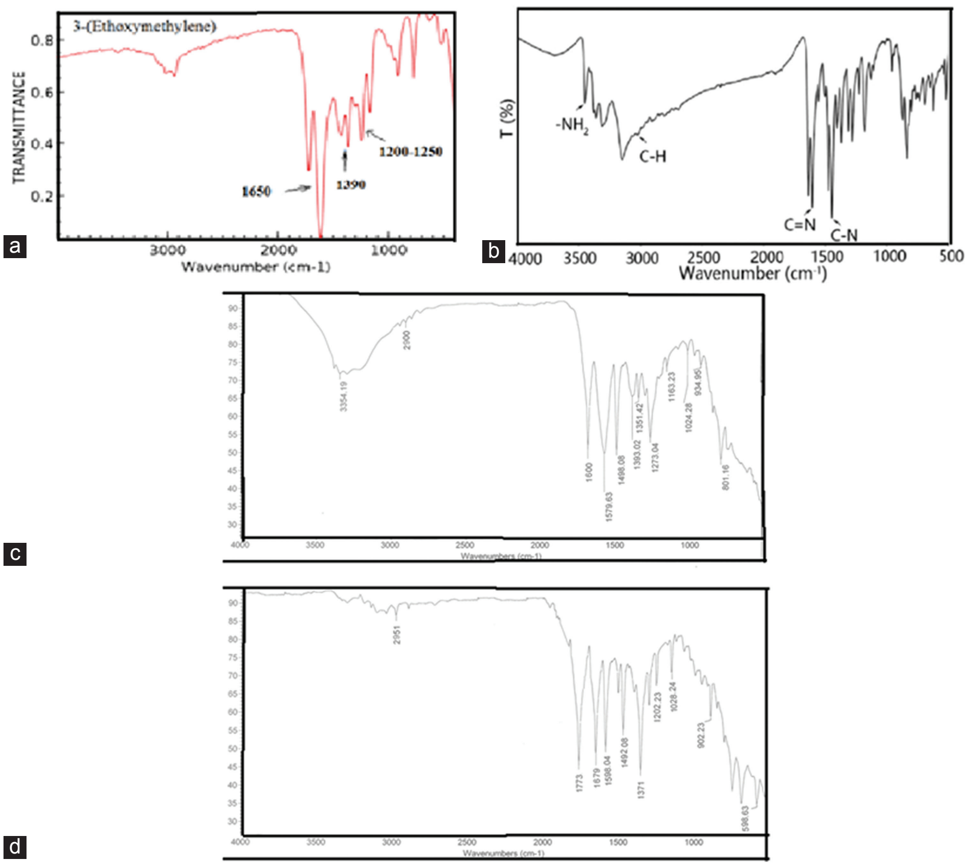


Fig. 1. (a-d) The Fourier transform infraredspectrum for the [N_4O_4] ligand and its starting materials with its [$Ni_2(L)$] metal ion complex.

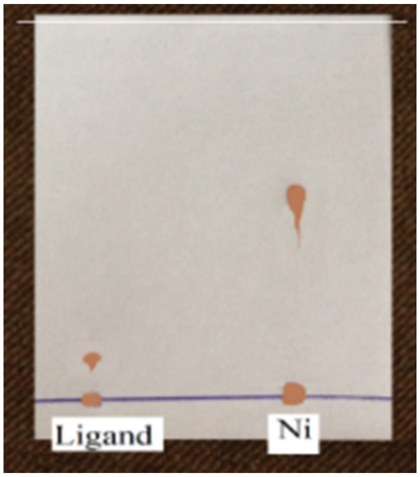


Fig. 2. The thin-layer chromatography measurements for the [N_4O_4] ligand and its [$Ni_2(L)$] metal ion complex.

bands at 598.6 cm^{-1} and 600 cm^{-1} range are assigned to the υ(Ni-N) and υ(Ni-O) (Ali et al., 2001), respectively, for all the formed complex Table II.

D. The UV-Vis Spectrum of the Ni^{II} Complex

The UV-Vis spectra of Ni^{II} complex showed two intense absorption peaks in the range at 285 nm (35087 cm^{-1}) (ϵ_{max}=1560 $molar^{-1}$. cm^{-1}) and (300 nm) (33333 cm^{-1}) (ϵ_{max}=90 $molar^{-1}$. cm^{-1}), range assigned to the ligand field and C.T., respectively (Griffith et al., 2011). The third peak detected in the visible region at 610 nm (16666 cm^{-1}) (ϵ_{max}=1235 $molar^{-1}$. cm^{-1}), range attributed to the electronic transition ($^3T_1 \rightarrow {}^3T_{1P}$) (Dhanaraj and Nair, 2014).

Thus, the magnetic moment value is 3.7 B. M (Uppadin et al., 2001, and Al-Jeboori et al., 2010), which demonstrates that the Ni^{II} complex is paramagnetic and has high spin tetrahedral geometry Table III.

E. Molar Conductance

The prepared complex found to be solids. It is soluble in some organic solvents such as dimethylformamide and dimethyl sulfoxide. The lower value observed of molar conductivities in DMSO in the range of 19 indicates the non-electrolyte behavior of the Ni^{II} metal ion complex (Kai et al., 2009 and Kettle, 1975).

F. Elemental Analysis (C.H.N) and Metal Determination

Elemental analysis (C.H.N) and metal determination were in good agreement with the general formula given for the Ni^{II} metal ion complex. Table I gives, in details, the physical properties of the complexes.

T.L.C. measurement for the derivative ligands [N_4O_4] and its Ni^{II} complexare shown in Fig. 2. The appearance of new spots with different Rf. compared with the Rf. of the ligand Table IV for Ni^{II} indicated the formation of the complex. Since the spots positions belong to Ni^{II} ion complex, they differ from the position of the ligands spot.

The biological activity of the [N_4O_4] ligand and its Ni^{II} complex was tested on two types of pathogenic bacteria using inhibition method (Anacona, 2006, Tauber and Nau, 2008, Petra et al., 2005, and Sultana and Arayne, 2007). The two types of bacteria were Gram-positive *Staphylococcus aureus* and *Bacillus subtilis*. The ligand [N_4O_4] was not affected by any of the two types of bacteria, whereas its [Ni_2(L)] complex showed inhibition diameter against the two types of bacterial after 24 h, and this inhibition diameter was increased after 48 h Fig. 3.

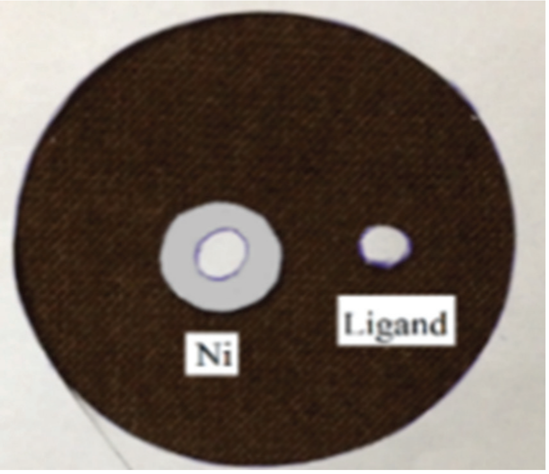


Fig. 3. The biological activity of the [N_4O_4] ligand and its [Ni_2(L)] metal ion complex after 48 h.

The mass spectrum shows the base peak at 654.72 related to the molecular weight of the ligand. Moreover, all the other fragmentations are compatible with the value of the fragments of the ligand as shown in Fig. 4.

The X-RD pattern of [Ni_2(L)] complex shows well-defined crystalline peaks indicating that the sample is 53% crystalline in nature (Dokken et al., 2009 and Khalaj and Das, 2014). An X-RD powder diffraction pattern of [Ni_2(L)] metal ion complex has been given in Fig. 5. The sample has been dried and then scanned in the 2θ range of 10–80°, confirming tetrahedral geometry around [Ni_2(L)] ion complex (Kavitha and Lakshm, 2017 and Zheng et al., 2017).

The ^{1}H-NMR spectrum for [N_4O_4] ligand in DMSO-d6 solvent Fig. 6 showed a single signal peak which appears at 2.1 ppm –CH(3H) attributed to a methyl group. Table V summarized the details of the other chemical shifts.

V. Conclusion

The reaction of 3-(ethoxymethylene) with DAB gives the required [N_4O_4] ligand. The reaction of this ligand with metal (II) acetates resulted in the formation of the required

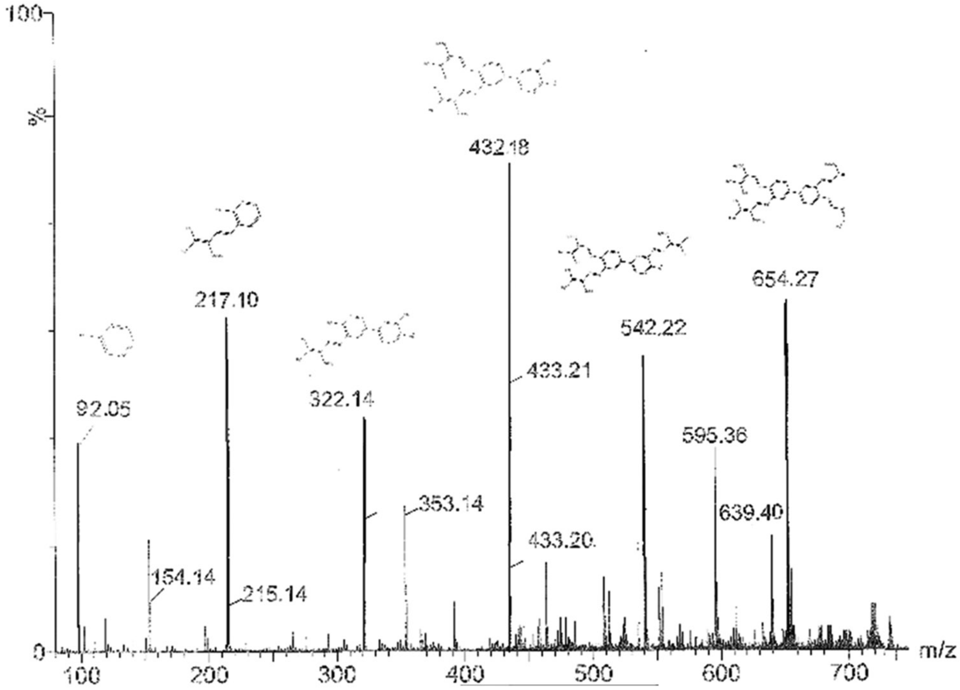


Fig. 4. The mass spectrum for the [N_4O_4] ligand.

TABLE III
The Electronic Spectral Data for the Ligand and its [Ni_2(L)] Metal Ion Complex

Compound	Band position λ_{nm}	Wave number (cm^{-1})	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	Assignment	Magnetic moment (B.M)	Suggested configuration
[N_4O_4] $C_{36}H_{38}N_4O_8$	210	47619	1421	$\pi \rightarrow \pi^*$	-	-
$C_{36}H_{35}N_4Ni_2O_8$	285	35087	1560	$\pi \rightarrow \pi^*$	3.4	Tetrahedral
	300	33333	90	Ch.T	paramagnetic	
	610	16666	1235	$^3T_1$–$^3T_{1P}$		

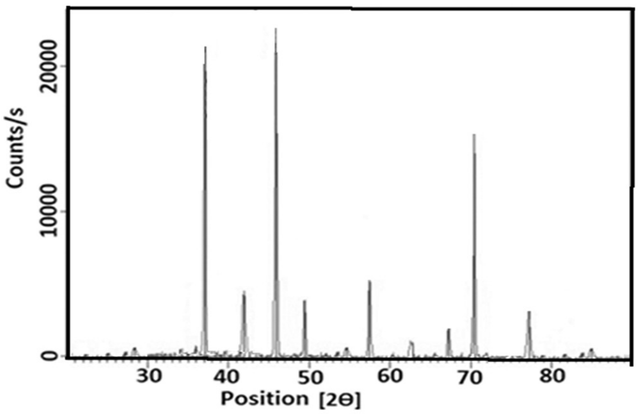


Fig. 5. The X-ray powder diffraction powder diffraction pattern for $[Ni_2(L)]$ complex.

TABLE IV
THE T.L.C. MEASUREMENTS FOR $[N_4O_4]$ LIGAND AND ITS $[Ni_2(L)]$ METAL ION COMPLEX

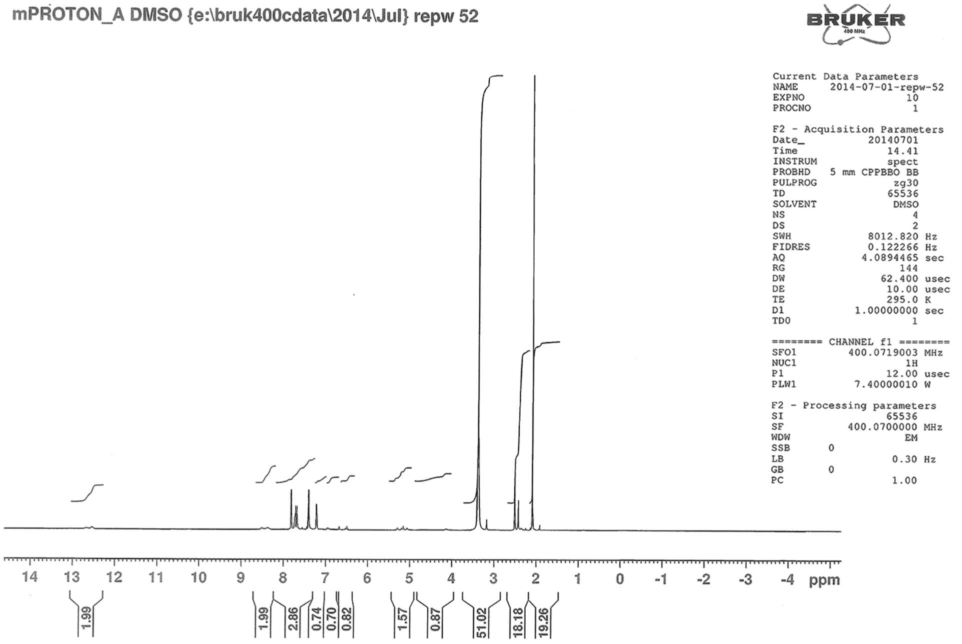
Compound	Range of R_f (mm)
$[N_4O_4]$ $C_{36}H_{38}N_4O_8$	4.1
$C_{36}H_{35}N_4Ni_2O_8$	1.2

T.L.C.: Thin-layer chromatography

TABLE V
THE CHEMICAL SHIFTS IN ^{1}H-NMR SPECTRA OF $[N_4O_4]$ LIGAND

Proton environment	H	Δ (ppm)
CH_3 methyl	8(C-H)	2.1
C-H benzene	6(C-H)	7.7
H ethylene	4(C-H)	7.7
C-H aldimine	4(C-H)	7.9
DMSO solvent	-	3.4

^{1}H-NMR: ^{1}H-nuclear magnetic resonance, DMSO: Dimethyl sulfoxide



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Current Data Parameters
NAME      2014-07-01-repw-52
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140701
Time                 14.41
INSTRUM              spect
PROBHD   5 mm CPPBBO BB
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                       4
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894465 sec
RG                     144
DW                  62.400 usec
DE                   10.00 usec
TE                   295.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           400.0719003 MHz
NUC1                    1H
P1                   12.00 usec
PLW1            7.40000010 W

F2 - Processing parameters
SI                   65536
SF             400.0700000 MHz
WDW                     EM
SSB        0
LB                    0.30 Hz
GB         0
PC                    1.00
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Fig. 6. The ^{1}H-nuclear magnetic resonance spectrum for the $[N_4O_4]$ ligand.

complex with tetrahedral geometry around $[Ni_2(L)]$ ion complex. Physical, chemical, and spectroscopic methods were used to investigate the mode of bonding and overall structure of the Ni^{II} complex of $[N_4O_4]$ ligand which has been synthesized and characterized by elemental analyses and spectroscopic techniques. The X-RD of the Ni^{II} ion complex revealed that the complexes are 53% crystalline. The F.T-I.R. measurements, U.V-Vis., and mass spectrum for the ligand and its complexes reveal the exact peak for each of the compounds functional groups. Moreover, the aims of this study are as follows:

1. The formation of a new complex by the reaction between DAB and 3-(ethoxymethylene) with Ni^{II} metal ion.
2. Determine some of the best metal complexes for activating the multiple bonds in M-N and M-O.
3. Syntheses of the new ligand with 3-(ethoxymethylene)
4. Studying the characteristic properties of the (3Z,3'Z,3''Z)-3,3',3''-((1E,1'E,1''E)-(4'-((E)-((E)-2-acetyl-3-hydroxybut-2-enylidene)amino)biphenyl-3,3',4-triyl)tris(azan-1-yl-1-ylidene)tris(methan-1-yl-1-ylidene))tris(4-hydroxypent-3-en-2-one) type $[N_4O_4]$ ligand.

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