

## Synthesis and characterization Studies of Mixed Ligand (1,3,4-oxadiazole derivative and ethylenediamine or acetylacetone) complexes with Ni(II)

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### الخلاصة

يتضمن البحث تحضير ليكنادات (POTL) = 5- فنيل- 1،3، 4- أوكسادايوزول- 2- ثايول ، (NPOTL) = 5- (3- نايترو- فنيل)- 1،3، 4- أوكسادايوزول- 2- ثايول ، (NPOTE) = 5- (3- نايترو- فنيل) -H3 ، 1،3، 4- أوكسادايوزول- 2- ثايون. تم تشخيص جميع الليكنادات المحضرة باستخدام طيف (IR)، و تم تشخيص بعضها باستخدام أطياف ( $^1\text{H-NMR}$ ) و ( $^{13}\text{C-NMR}$ ) و (NMR) و (UV-visible) و التوصيلية الكهربائية. تم تحضير معقدات النيكل (II) مع ليكناد (NPOTE) و كذلك أثيلين ثنائي أمين (en) و أسيتايل أسيتون (acac) يتفاعل مع ( $\text{Ni(OAC)}_2 \cdot 4\text{H}_2\text{O}$ ) مع (NPOTE) بوجود (en) و (acac) حيث يعطي معقدين ذي صيغتين  $[\text{Ni(NPOTE)}_2(\text{en})_2]$  و  $[\text{Ni(NPOTE)}_2(\text{acac})_2]$  على التوالي. في كلتا المعقدين، يتناسق ليكنادات الحلقة الغير متجانسة من خلال ذرة النايتروجين في حلقة أوكزادايوزول و مع أبقاء ليكند على شكل (thione). تم تشخيص المعقدين باستخدام أطياف (IR) و (UV-visible) و الأمتصاص الذري و التوصيلية المولارية و الحساسية المغناطيسية و أظهرت النتائج بأن المعقدين لهما شكل ثماني السطوح حول ايون نيكل (II).

### ABSTRACT

This work includes the synthesis of the ligands (POTL = 5-Phenyl-1,3,4-oxadiazole-2-thiol , NPOTL = 5-(3-Nitro-phenyl)-1,3,4-oxadiazole-2-thiol , and NPOTE = 5-(3-Nitro-phenyl)-3H-1,3,4-oxadiazole-2-thione . All synthesized ligands were characterized by IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , UV-visible spectra and molar conductivity.

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Two nickel(II) complexes of mixed ligands (NPOTE) and en/acac were obtained by the reaction of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  with (NPOTE), on treatment with ethylenediamine (en) or acetylacetonate (acac), gave the complexes of the type  $[\text{Ni}(\text{NPOTE})_2(\text{en})_2]$ , and  $[\text{Ni}(\text{NPOTE})_2(\text{acac})_2]$  respectively. In both complexes, the heterocyclic ligand coordinate through oxadiazole nitrogen, and the ligand exist as a thione form. The characterization data of IR-spectra, UV-visible spectra, conductivity measurement, magnetic susceptibility and atomic absorption, exhibited that both complexes have octahedral geometries around the Ni(II) center.

**Keyword: oxadiazole derivative, mixed ligands, nickel (II) complexes .**

## INTRODUCTION

The 1, 3, 4-oxadiazole-2-thiones represent an important type of compounds in the field of coordination chemistry due to of their potential multifunctional donor sites, viz either exocyclic sulfur or endocyclic nitrogen <sup>[1]</sup>.

Since 1,3,4-oxadiazole-2-thiones are biologically active compounds, information about their 3-dimensional structures may be of great interest for rational drug design. 1, 3, 4-oxadiazole-2-thione consist of an equilibrium mixture of its thione and thiol forms, therefore it will be of interest to investigate the bonding mode of oxadiazole in their complexes <sup>[2]</sup>.

In 2008, Singh M. and coworkers <sup>[3]</sup> prepared the mononuclear complex  $[\text{Cu}(\text{bzsm})_2\text{Cl}_2]$  where { bzsm = 2-benzylsulfanyl-5-(2-methoxy-phenyl)-1, 3, 4-oxadiazole} . The complex had been characterized by analytical spectroscopic and X-ray data. The organic ligand (bzsm) acts as neutral bidentate ligand to form six membered chelate ring.

Two novel mononuclear mixed-ligand complexes  $[\text{Ni}(\text{en})_2(3\text{-pyt})_2]$ , and  $[\text{Cu}(\text{en})_2](3\text{-pyt})_2$  where 3-pyt = 5-(3-pyridyl)-1,3,4-oxadiazole-2-thione synthesized by Singh M. and coworkers in 2008 <sup>[1]</sup>. The single crystal X-ray diffraction studies of both complexes indicate that (3-pyt)<sup>-</sup> adopts a thione form in  $[\text{Ni}(\text{en})_2(3\text{-pyt})_2]$ , and a thiolato form in  $[\text{Cu}(\text{en})_2](3\text{-pyt})_2$ .

Singh N.K. *et al.* in 2009 <sup>[4]</sup> prepared two complexes by the reaction of  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  with Hpot (Hpot=5-phenyl-1,3,4-oxadiazole-2-thione), and  $[\text{K}(\text{H}_2\text{fchc})]$  [potassium N<sup>1</sup>-(furan-2-carbonyl) hydrazine carbodithioate], oxadiazole-2-thione). Both complexes had been characterized by their .The complexes have distorted octahedral

geometries around Ni (II) center. In both complexes, the heterocyclic ligand coordinates through oxadiazole nitrogen, and the ligand exists in thione form.

The same group, Singh N.K. and coworkers in 2010 <sup>[5]</sup> prepared three new mixed ligand complexes  $[\text{Mn}(4\text{-pytone})_2(\text{bipy})_2]\text{bipy}$ ,  $[\text{Mn}(\text{pot})_2(\text{en})_2]$ , and  $[\text{Mn}(4\text{-mot})_2(\text{en})_2]$  where (4-pytone=5-(4-pyridyl)-1,3,4-oxadiazole-2-thione), (pot= 5-phenyl-1,3,4-oxadiazole-2-thione), (4-mot=5-(4-methoxy-phenyl)-1,3,4-oxadiazole-2-thione). In all cases, the manganese has a six coordinate octahedral arrangement coordinated by 4N atoms of two bipy/en and two covalently bonded N atoms of the oxadiazole-2-thione anions.

Gallego B., and coworkers in 2010 <sup>[6]</sup> synthesized some complexes. One of the complexes was obtained by reaction of the heterocyclic 5-phenyl-1, 3, 4-oxadiazole-2-thiol (SH-oxa), with trimethylgallium (1:1) afforded a tetrameric complex  $[\text{Me}_2\text{Ga}(\text{S-oxa})_4]$ . The complex showed a dose dependent anti proliferative effect toward some cancer cells. The present work deals with preparation of some new heterocyclic ligands containing 1, 3, 4-oxadiazole moiety and their transformation to stable macro-ligands because their stability. In other hand, the work aims to prepare some complexes by reacting macro-ligands with some transition metals  $[\text{M}(\text{II}) = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}]$  ion.

## Experimental

### Chemical Compounds:

All chemical compounds that are used in this work were of reagent grade.

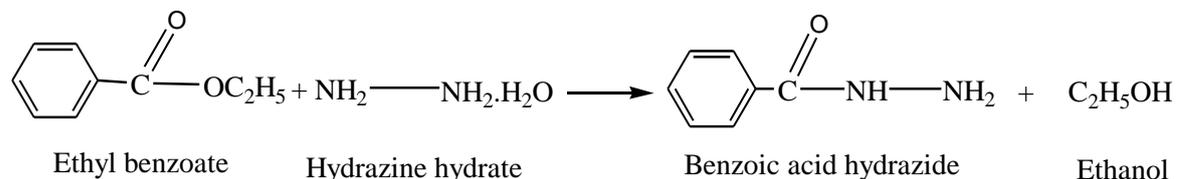
### Instrumentation:

- I. Melting point and decomposition point of the ligands and complexes were determined on a BÜCHI melting point B-545.
- II. IR spectra were recorded in the  $400\text{-}4000\text{ cm}^{-1}$  range as KBr disc on Thermo Mattson 300 FT-IR spectrophotometer.
- III.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were taken on Bruker ultra shield 300 MHz with TMS as internal reference, in Al-al-Bayt University Central Labs (Jordon), in DMSO as a solvent.
- IV. The conductivity of the ligands and their complexes were determined on a EUTECH con 510.
- V. The maximum absorbance ( $\lambda$  max) of the synthesized compounds was determined on a Datastream-CE3000 in DMSO as a solvent.

VI. Magnetic susceptibilities of the synthesized complexes were determined on a Bruker Magnet NM6.

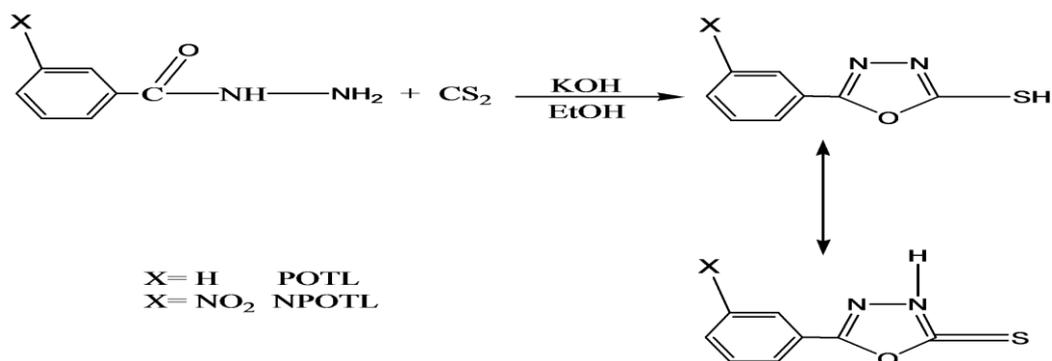
### Preparation of (BAHZ):

Refluxing an ethanolic solution of ethyl benzoate with hydrazine hydrate, in the molar ratio 1:1 for three hrs, gave benzoic acid hydrazide [7-11], as illustrated in the following reaction:



### Preparation of (POTL) and (NPOTL):

Refluxing ethanolic solution of benzoic acid hydrazide or m-nitrobenz hydrazide with CS<sub>2</sub> in a molar ratio 1:1 for five hrs in the presence of one mole potassium hydroxide as a deprotonating reagent in ethanol gave POTL and NPOTL ligands respectively [14,15] as in the following reaction:



### Preparation of (NPOTE):

CS<sub>2</sub> was added to a solution of m-nitrobenzhydrazide in (EtOH-CHCl<sub>3</sub>) with a molar ratio 1:1 in the presence of Et<sub>3</sub>N as a deprotonate reagent and refluxed for six hrs to give NPOTE [4], as declared in the following reaction:

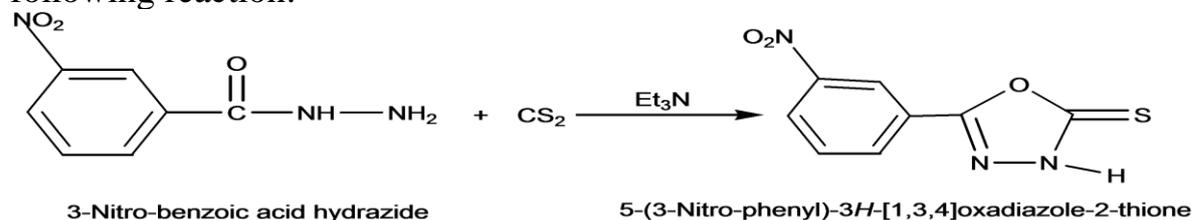
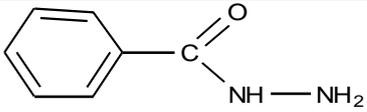
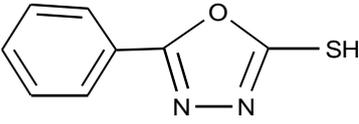
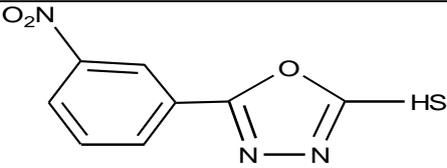
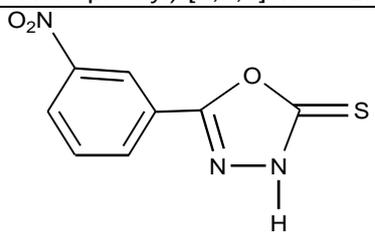


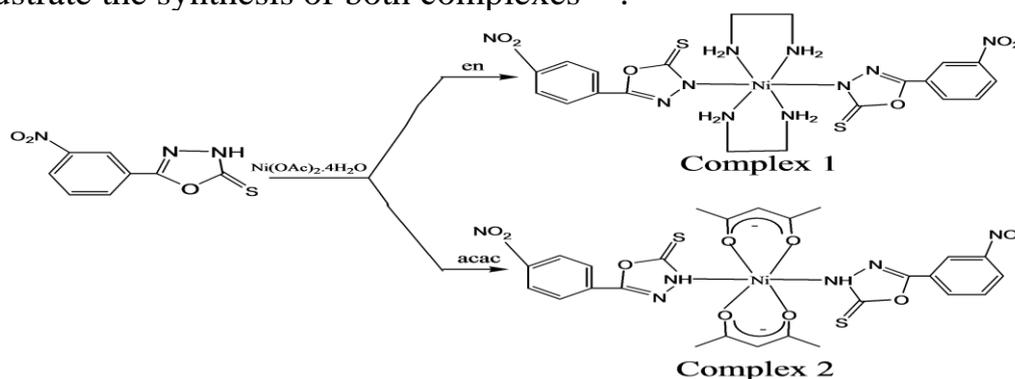
Table (1), summarizes the formula, chemical structure, Abbreviation and name of synthesized compound

**Table (1): Formula, chemical structure, name, and abbreviation of synthesized compounds**

Formula	Structure and Name	Abbreviation
$C_7H_8N_2O$	 Benzoic acid hydrazide	BAHZ
$C_8H_6N_2OS$	 5-Phenyl-[1,3,4]oxadiazole-2-thiol	POTL
$C_8H_5N_3O_3S$	 5-(3-Nitro-phenyl)-[1,3,4]oxadiazole-2-thiol	NPOTL
$C_8H_5N_3O_3S$	 5-(3-Nitro-phenyl)-3H-[1,3,4]oxadiazole-2-thione	NPOTE

### Preparation of $[Ni(NPOTE)_2(en)_2]$ (1) and $[Ni(NPOTE)_2(acac)_2]$ (2) Complexes :

A 2:1 ratio of NPOTE: $Ni(OAc)_2 \cdot 4H_2O$  were dissolved separately in methanol, then two solutions were mixed together and stirred, a brown solid precipitated, then separated and filtered off <sup>[4]</sup>. Complex(1) and complex(2) were obtained by shaking a methanol suspension of the brown precipitate with a methanol solution of ethylenediamine or acetylacetonate in 1:4 molar ratios respectively. The following reactions illustrate the synthesis of both complexes <sup>[4]</sup>:



## RESULTS AND DISCUSSION

### Identification of (BAHZ):

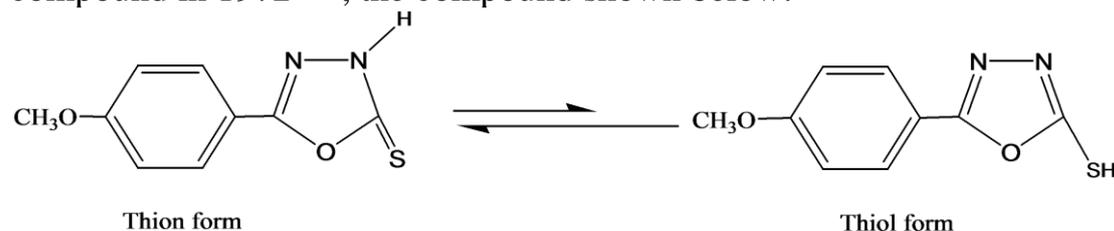
The IR spectrum of this ligand showed strong absorption band at  $1661\text{ cm}^{-1}$  which was assigned to C=O stretching <sup>[10,12]</sup>. Bands  $3198\text{ cm}^{-1}$  and  $3299\text{ cm}^{-1}$  were assigned to stretching vibration mode of N-H <sup>[7,10,12]</sup>. Absorption bands observed at  $3016\text{ cm}^{-1}$  and  $3020\text{ cm}^{-1}$  indicate the aromatic C-H stretching <sup>[10,13]</sup>, as explained in the Figure(1)and Table (2).

### Identification of (POTL) and (NPOTL):

The IR spectrum of (POTL) and (NPOTL) ligands, showed two new bands at  $1060\text{ cm}^{-1}$  and  $1068\text{ cm}^{-1}$  assigned to C-O-C stretching vibration of oxadiazole ring in both ligands respectively <sup>[12-20]</sup>. The disappearance of C=O stretching band, absence of two N-H bands of the hydrazide, and detection of strong C=N stretching band at  $1610\text{ cm}^{-1}$  and  $1623\text{ cm}^{-1}$  are evidences on 1,3,4-oxadiazole closed ring in POTL and NPOTL respectively <sup>[8,9,21,22]</sup>. New bands observed at  $2774\text{ cm}^{-1}$  and  $2775\text{ cm}^{-1}$  in both ligands respectively due to stretching vibration of S-H <sup>[23]</sup>, as showed in the Figure (2), and Figure (3) and Table (2).

### Identification of (NPOTE):

The comparison between IR spectrum of prepared ligand (NPOTE) and IR spectrum of corresponding hydrazide showed some differences. The stretching vibration C-O-C ring of 1,3,4-oxadiazole molecule was confirmed by the presence of a band at  $1080\text{ cm}^{-1}$  <sup>[24,12,17,25]</sup>. A new band observed at  $1646\text{ cm}^{-1}$  due to C=N stretching, and that is another support for ring atoms closure of 1,3,4-oxadiazole <sup>[49,8,9,21,22]</sup>. The absence of S-H stretching band and detection of C=S stretching band at  $1170\text{ cm}^{-1}$  with N-H stretching vibration band at  $3496\text{ cm}^{-1}$  are evidences of being in thion form instead of being in thiol form <sup>[4,21,27]</sup>. Horning D.E., and Muchowski J.M., noticed tautomeric equilibrium in their synthesized compound in 1972 <sup>[28]</sup>, the compound shown below:

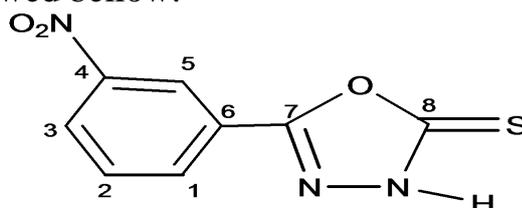


On the basis of IR and <sup>1</sup>HNMR data, 5-(4-methoxyphenyl)-1,3,4-oxadiazole-2-thione is exist in thion form in solution rather than thiol form. The same phenomina noticed by Tomi I.H.R. in 2010 <sup>[24]</sup>.

The band observed around  $3202\text{ cm}^{-1}$  due to overtone of N-H deformation band around  $1619\text{ cm}^{-1}$  <sup>[29,30]</sup>. Two new strong bands at  $1350$

$\text{cm}^{-1}$ , and  $1532 \text{ cm}^{-1}$  were assigned to symmetric and asymmetric stretching vibration of  $\text{NO}_2$  group <sup>[31]</sup>, as shown in Figure (4) and Table (2).

The  $^1\text{H-NMR}$  spectra of the (NPOTE) in DMSO are shown in Figure (5). All protons were seen according to the expected chemical shift. The  $^1\text{H-NMR}$  for aromatic ring protons was appeared at 7.85, 8.35, 8.38, and 8.76 ppm <sup>[16,32]</sup>. The N-H protons of 1,3,4-oxadiazole ring were seen at 11.08 ppm <sup>[16,27,33]</sup>.  $^{13}\text{C-NMR}$  data in DMSO exhibit signal at 141.24 due to  $\text{C}_7, \text{C}_8$  of oxadiazole ring <sup>[22,34]</sup>, also at 130.27, 129.92, 127.38, 136.27, 127.20, 130.33 which were assigned to the aromatic ring  $\text{C}_1, \text{C}_2, \text{C}_3, \text{C}_4, \text{C}_5, \text{C}_6$  respectively <sup>[35]</sup> as shown in Figure (6). The carbon numbering showed bellow:



Carbon numbering of the NPOTE

The electronic spectra and molar conductivity of NPOTE ligand were recorded at  $10^{-3} \text{ M}$  concentration in DMSO as a solvent, were carried out by equipment in the range 200-400 nm. The electronic spectra showed absorption bands at  $38167 \text{ cm}^{-1}$  this band has been assigned to the  $\pi \rightarrow \pi^*$ . The molar conductivity value was  $2.35 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{Mol}^{-1}$  which indicated non electrolyte ligand.

### Identification of $[\text{Ni}(\text{NPOTE})_2(\text{en})_2]$ (1) and $[\text{Ni}(\text{NPOTE})_2(\text{acac})_2]$ (2) Complexes :

The complexes were characterized with the IR, UV-visible spectroscopy, magnetic susceptibility, conductivity measurement, and atomic absorption as explained in the following subsections:

#### IR spectra:

Figure (7) show the IR spectrum of complex(1). Two Bands at  $3307 \text{ cm}^{-1}$  and  $3190 \text{ cm}^{-1}$  due to N-H stretching vibration of ethylenediamine which are shift to lower frequencies than those encountered in free ethylenediamine, a negative shift in N-H of ethylenediamine and the presence of a new band at  $525 \text{ cm}^{-1}$  attributed to M-N suggest formation of a complex <sup>[25,36-40]</sup>. The negative shift in stretching vibration of  $\text{C}=\text{S}$  appear at  $1161 \text{ cm}^{-1}$  in complex(1) showing that exocyclic sulfur is not participating in bonding, rather, this small shift can be attributed to the involvement of sulfur in hydrogen bonding with the  $\text{NH}_2$  hydrogens of ethylenediamine <sup>[4,36]</sup>.

The IR spectrum of complex(2) showed in the Table (4-1). It shows a new band at  $1600\text{ cm}^{-1}$  due to stretching vibration of C=O [41]. A band appear at  $3300\text{ cm}^{-1}$  due to N-H stretching vibration .Two new bands appear at  $490\text{ cm}^{-1}$ ,  $413\text{ cm}^{-1}$  attributed to stretching vibration of M-N and M-O respectively suggest formation of a Complex(2) [3,4,36,38].

Upon complexation IR spectrum of both complexes show stretching bands of C=N and C-O-C shift to lower energy [24], also the presence of weak peaks in the range  $2810\text{-}2927\text{ cm}^{-1}$  due to C-H aliphatic stretching vibration of ethylenediamine and acetyl acetate in both complexes [42,43]

### UV-visible spectra:

Within inorganic chemistry the field of study most often associated with UV- visible spectroscopy is that of the colored transition metal complexes [44]. Colors most often associated with metal complexes arise from transitions between different energy levels corresponding to a redistribution of electrons in the partially field d-orbitals. These are referred to as metal-metal or d-d transitions. Also, the colored transition metal complexes arise from electronic transitions between the metal and ligand, these are called charge transfer (CT) bands [44].

UV-visible spectrum of Ni(II) in both complexes exhibit two absorption bands in the range  $27548\text{-}27855\text{ cm}^{-1}$  ( $\nu_3$ ) assigned to  ${}^3A_2g$  (F)  ${}^3T_1g$  (P) transition [4] and in the range  $26246\text{-}26666\text{ cm}^{-1}$  ( $\nu_2$ ) assigned to  ${}^3A_2g$  (F)  ${}^3T_1g$  (F) transition respectively [4]. These are characteristic bands of high spin octahedral Ni(II) complexes. The absence of transition ( $\nu_1$ ) which is equal to  $(10Dq)$  was calculated by fitting the ratio ( $\nu_3/\nu_2$ ) to the Tanabe-Sugans diagram for octahedral  $d^8$  ion , the ratio ( $\nu_3/\nu_2$ )=1.049, 1.044 for both complexes respectively, fitted the diagram at 9.021, 9.010 then the value of  $\nu_1 = (9.021, 9.010) \times 1030 = 9291, 9280\text{ cm}^{-1}$  which attributed to  ${}^3A_2g$  (F)  ${}^3T_2g$  (F) [45]. Other high energy bands observed in the range  $29850\text{-}31250\text{ cm}^{-1}$  may assign to MLCT transfer transition [46], as shown in Figure (8), and Table (3).

### Magnetic Susceptibility:

The magnetic susceptibility measurement provided good information regarding the arrangement of ligands around metal ions. Ni(II) complexes show magnetic susceptibility 2.5, 2.7 B.M. as shown in Table (3), which corresponds to octahedral environment around the central metal ion [4,36].

### Conductivity Measurement:

The molar conductivities of both complexes were measured for  $10^{-3}$  M solution in dimethylsulphoxide (DMSO) at 25 °C. Values of the molar conductance ( $\text{cm}^2.\text{ohm}^{-1}.\text{mol}^{-1}$ ) and  $\text{AgNO}_3$  test are given in Table (4). The observed values in DMSO for all complexes were compared with data in Table (5) as a standard <sup>[47]</sup>. Both complexes correspond to non-electrolytic nature; this is also confirmed with negative  $\text{AgNO}_3$  test for chloride containing complexes, as shown in the Table (4)

### Atomic Absorption

The atomic absorption analysis were used to determine the ratio of M:L for  $[\text{Ni}(\text{NPOTE})_2(\text{en})_2]$  complex curve fitting least square equation to get a line equation  $\{y = -3.5 + 27.9 x\}$ . Replacing absorbance 125 instead of y to get concentration  $x=4.6 \mu\text{g}$ .

From 10  $\mu\text{g}$  of complex the weight of ligand NPOTE= $10-4.6=5.4 \mu\text{g}$ . The ratio of mixed-ligand/ metal = 1.17 ~ 1. This indicates the mixed-ligand to metal ratio is 1:1 <sup>[47]</sup>. The data shown in the Table (6)

Selected IR spectra of synthesized compounds ( $\text{cm}^{-1}$ ) Table (2) :

No.	Compound	N-H	(C-H) A.rom	S-H	C=N Ring	C=O	C=S	C-O-C	NO <sub>2</sub>
1	BAHZ	3299 (m) 3198 (m)	3016 (m) 3020 (w)	----- -	-----	1661 (s)	-----	-----	-----
2	POTL	-----	3000 sy(w) 3067 asy(m)	2774 (m)	1610 (s)	----- -	-----	1060 (s)	-----
3	NPOTL	----- -	3085 sy(m) 3100 asy(w)	2775 (m)	1623 (m)	----- --	-----	1068 (m)	1340 sy(s) 1526 asy(s)
4	NPOTE	3496 (m)	3030 sy(w) 3080 asy(w)	----- --	1646 (s)	-----	1170 (w)	1080 (m)	1350 sy(s) 1532 asy(s)
5	Ni(NPOTE) <sub>2</sub> (en) <sub>2</sub>	3190 3307 (m)	-----	----- ---	1580(m)	----- -	1161(s)	1031	1331 sy(s)
6	Ni(NPOTE) <sub>2</sub> (acac) <sub>2</sub>	3300	-----	----- --	-----	1600	-----	-----	-----

**Table (3): Electronic spectra and molar conductivity of some synthesized complexes**

No.	Magnetic Suscep. (B.M)	$\epsilon \times 10^3$ l.mol <sup>-1</sup> .cm <sup>-1</sup>	Transition Assignment	Absorption Band cm <sup>-1</sup> (nm)	Complex Structure
1	2.5	0.28	MLCT	29850 (335)	[Ni(NPOTE) <sub>2</sub> (en) <sub>2</sub> ]
		0.23	<sup>3</sup> A <sub>2g</sub> (F) <sup>3</sup> T <sub>1g</sub> (P)	27548 (363)	
		0.18	<sup>3</sup> A <sub>2g</sub> (F) <sup>3</sup> T <sub>1g</sub> (F)	26246 (381)	
		0.28	MLCT	31250 (320)	
2	2.7	0.25	<sup>3</sup> A <sub>2g</sub> (F) <sup>3</sup> T <sub>1g</sub> (P)	27855 (359)	[Ni(NPOTE) <sub>2</sub> (acac) <sub>2</sub> ]
		0.15	<sup>3</sup> A <sub>2g</sub> (F) <sup>3</sup> T <sub>1g</sub> (F)	26666 (375)	

**Table (4): Molar conductivity (cm<sup>2</sup>.ohm<sup>-1</sup>.mol<sup>-1</sup>) at 25 °C and AgNO<sub>3</sub> test of (10<sup>-3</sup> M) solution of prepared complexes:**

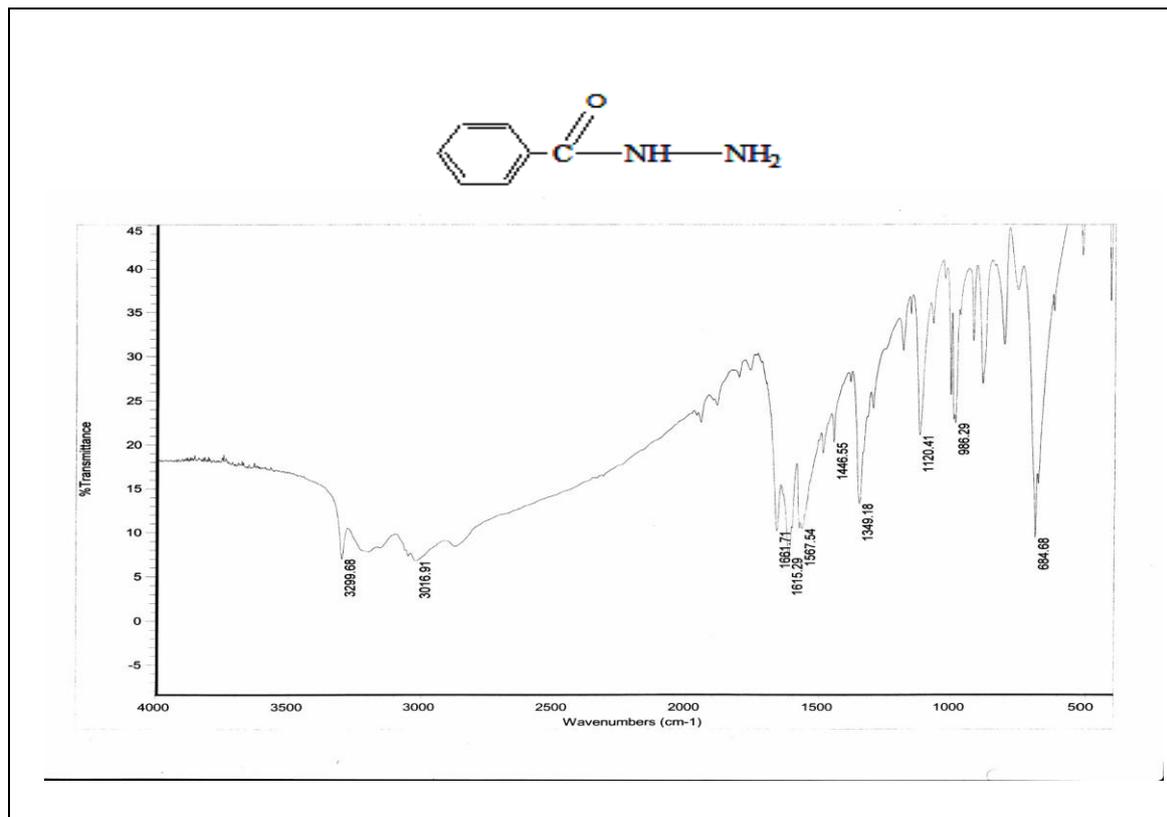
No.	AgNO <sub>3</sub>	DMSO	Complex
1	-	4.4	[Ni(NPOTE) <sub>2</sub> (en) <sub>2</sub> ]
2	-	3.8	[Ni(NPOTE) <sub>2</sub> (acac) <sub>2</sub> ]

**Table (5): Molar conductivity (cm<sup>2</sup>.ohm<sup>-1</sup>.mol<sup>-1</sup>) (10<sup>-3</sup> M) observed for various electricity types in different solvents <sup>[78]</sup> :**

Electrolyte type				Non-electrolyte	Solvent
1:4	1:3	1:2	1:1		
480	360	240	120	0	Water
~500	340-420	220-300	120-160	10-30	Methyl cyanide
290-330	220-260	150-180	75-95	0-20	Nitro methane
~300	200-240	150-170	65-90	0-30	Dimethylformamide
~160	~120	70-90	35-45	0-20	Ethanol
----	----	70-80	30-40	0-20	Dimethylsulphoxide
~400	270-350	160-220	80-115	0-50	Methanol

**Table (6): The atomic absorption data for [Ni(NPOTE)<sub>2</sub>(en)<sub>2</sub>] complex**

Standard Curve Ni(II) ion	
Conc. (ppm)	Abs.
2	51
4	111
6	162
8	220
*[Ni(NPOTE) <sub>2</sub> (en) <sub>2</sub> ]	125
Line equation : $y = a + b x$ $y = -3.5 + 27.9 x$ where a is intercept, b is a slope, x is concentration, and y is absorbance	
a = -3.5	
b = 27.9	
r = 0.998	
*Conc. = 4.6	



**Figure (1): Infrared spectrum of (BAHZ)**

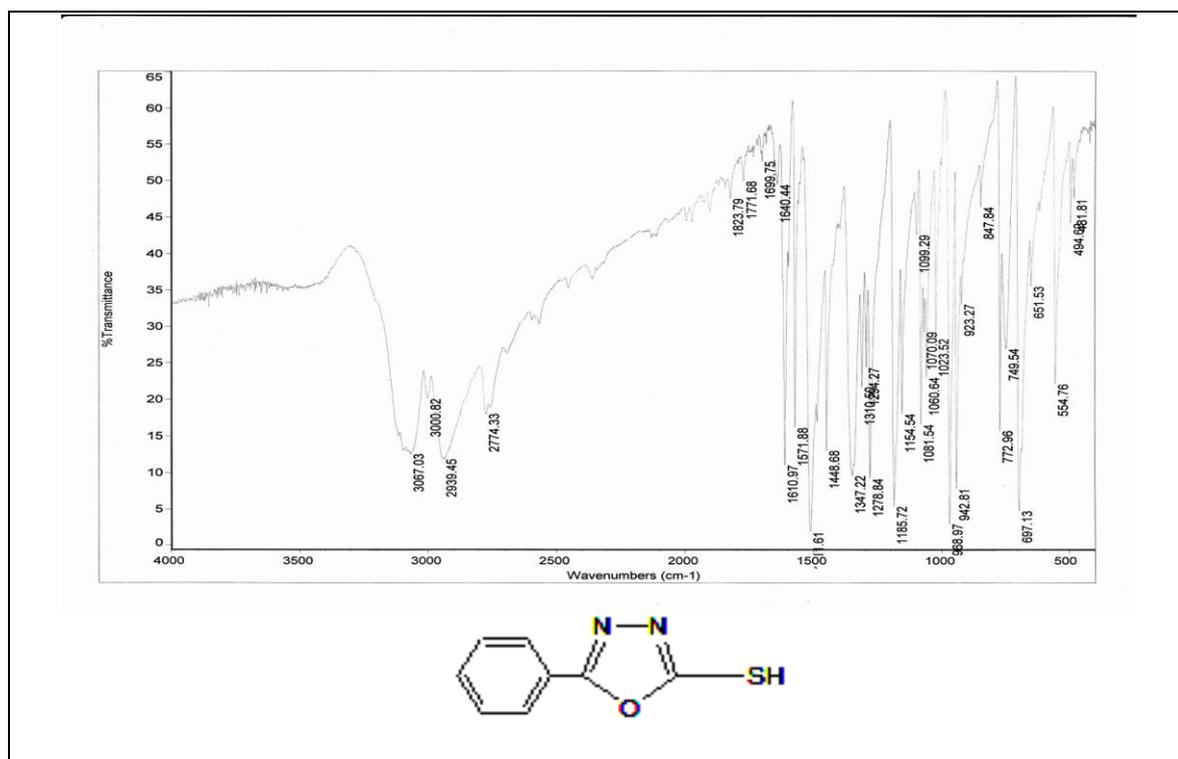


Figure (2): Infrared spectrum of (POTL)

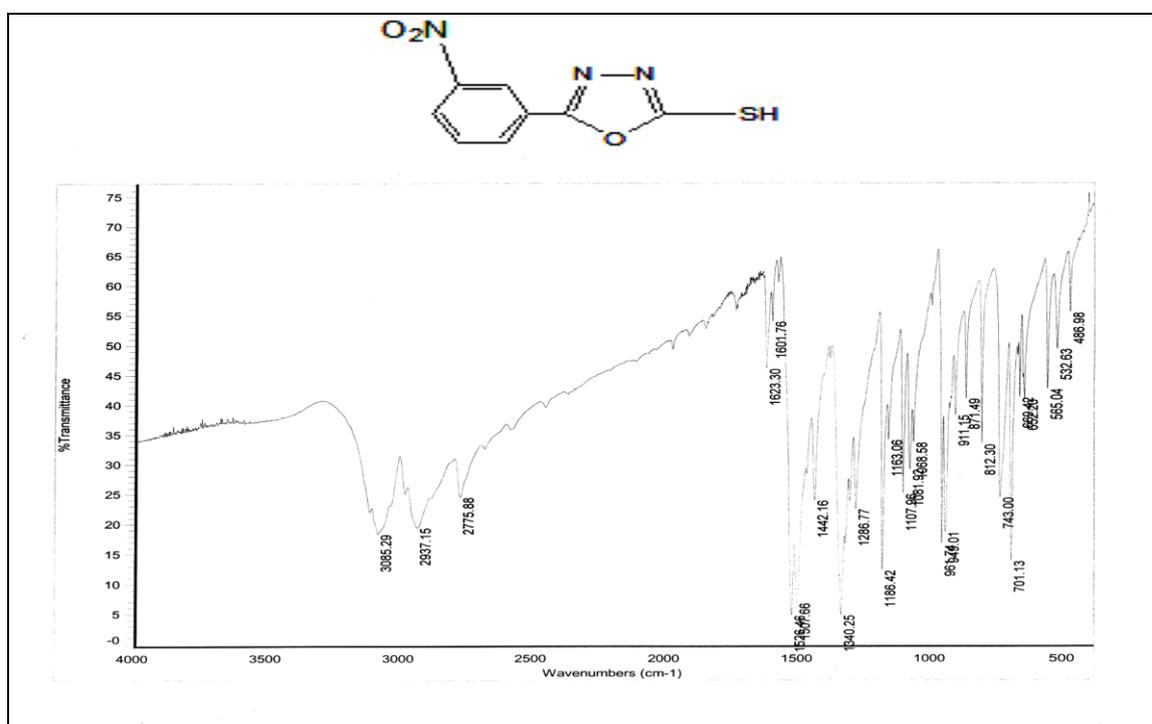


Figure (3): Infrared spectrum of (NPOTL)

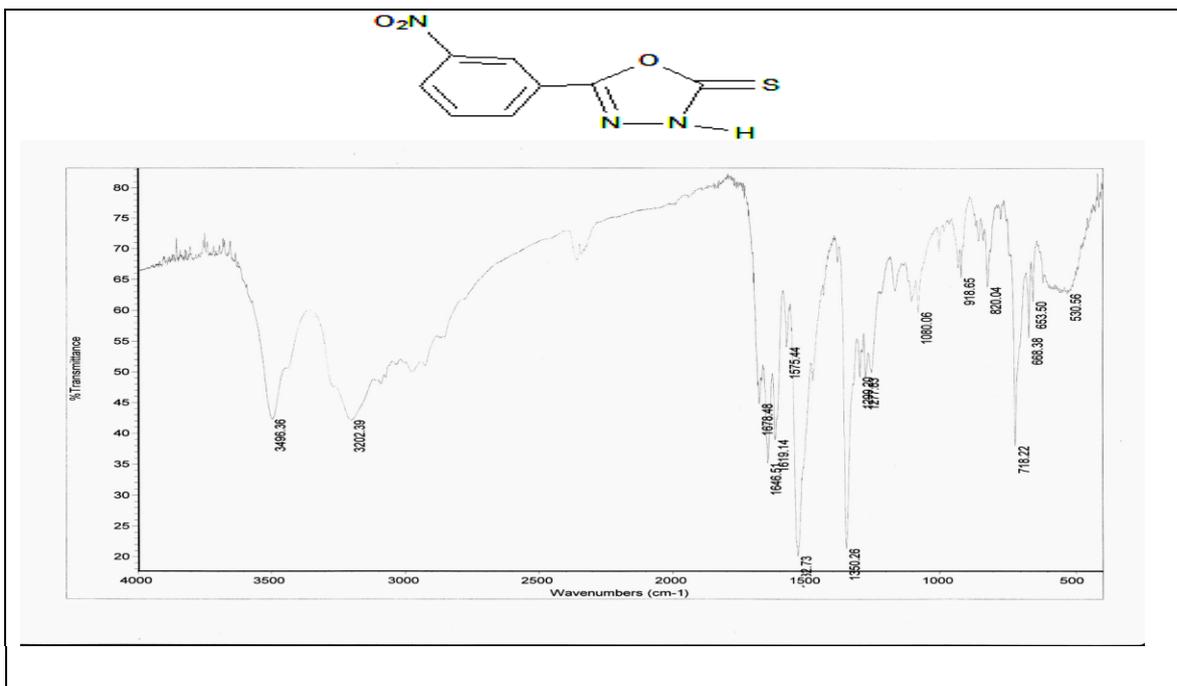


Figure (4): Infrared spectrum of (NPOTE)

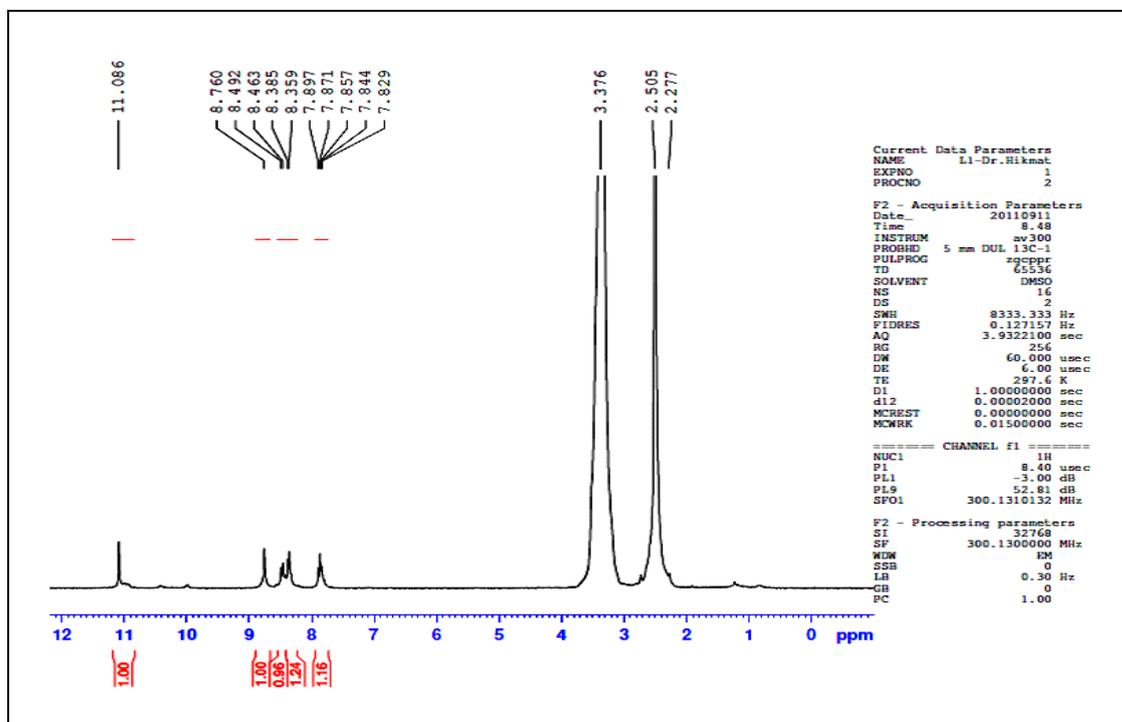


Figure (5): <sup>1</sup>H-NMR of NPOTE

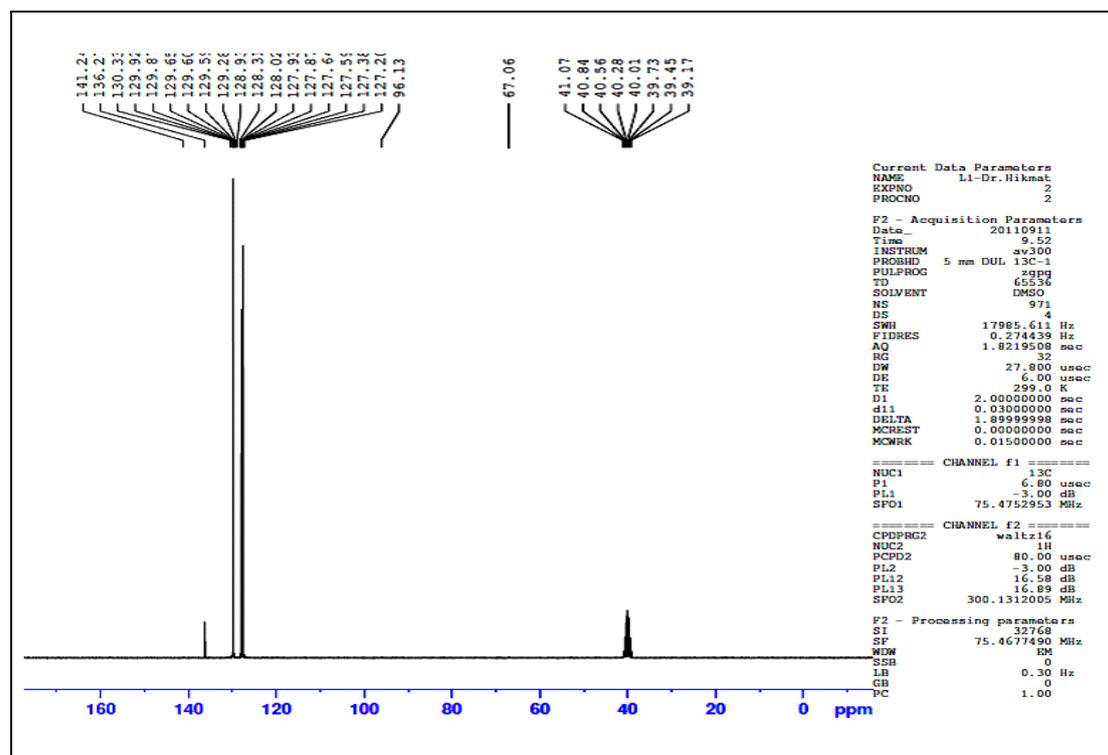


Figure (6):  $^{13}\text{C}$ -NMR of NPOTE

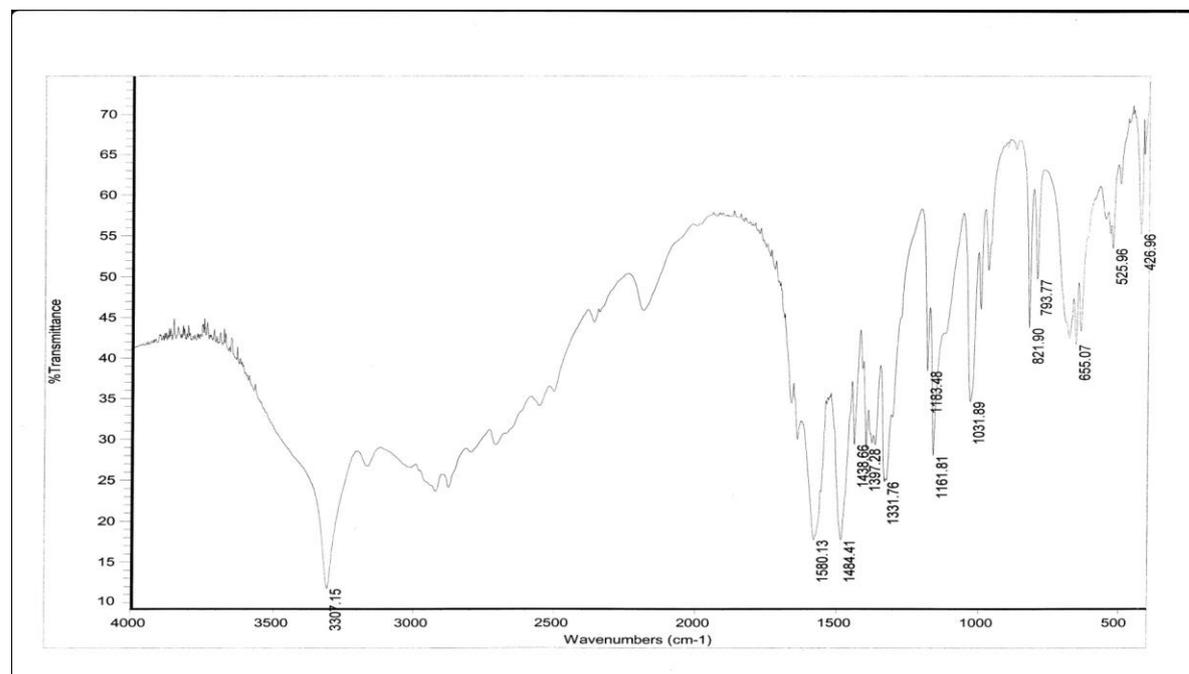


Figure (7): Infrared spectrum of  $[\text{Ni}(\text{NPOTE})_2(\text{en})_2]$

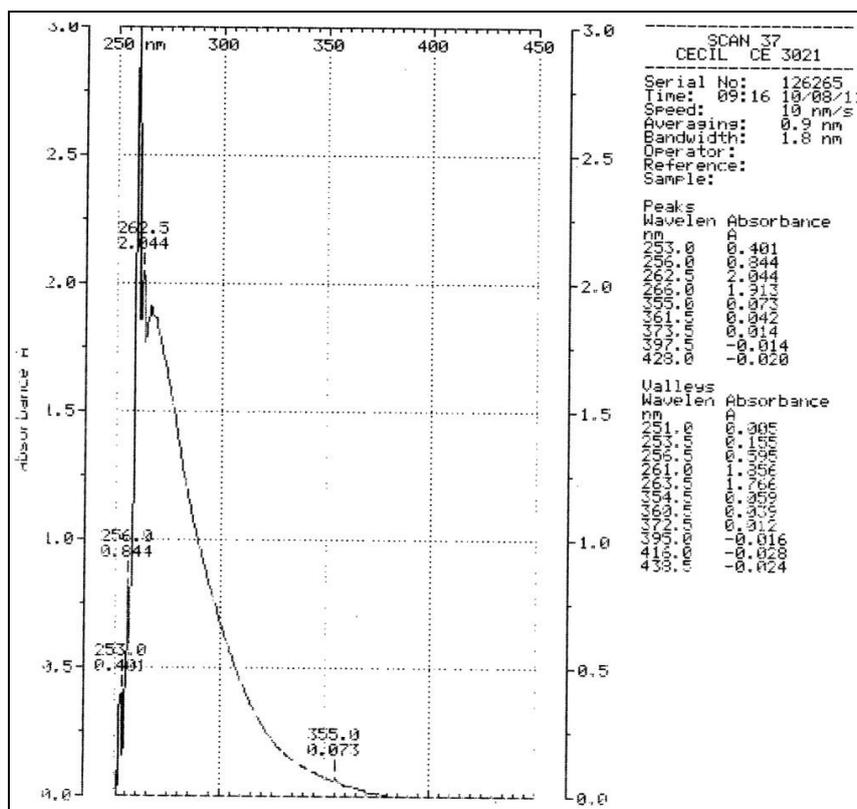


Figure (8): Electronic spectrum of NPOTE

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