



**SYNTHESIS, SPECTROSCOPIC ELUCIDATION AND BIOLOGICAL ACTIVITY OF TRANSITION METAL (II) COMPLEXES OF AZOMETHINE DERIVED FROM 4-MORPHOLINOANILINE AND ORTHO - VANILLIN**

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**ABSTRACT**

**Key Words**

4-Morpholinoaniline,  
O-Vanillin,  
Methanol,  
Ether and Lemon juice



The transition Metal complexes of Mn (II) and Ni (II) with a new Azomethine derived from 4-Morpholinoaniline and O-vanillin (OVMA) are discussed and characterized based on elemental analysis, IR, <sup>1</sup>HNMR, UV-Vis, Molar conductance, XRD, TG/DTA, Scanning electron microscopy (SEM). The molar conductivity of metal complexes indicate that the complexes are non-electrolytes. According to these data, we propose octahedral geometry for transition metal (II) complexes. The complex was colour and stable in air. The *in vitro* antibacterial activities of the investigated azomethine metal complexes were determined by using diffusion technique. It was found that the metal complexes have higher activity than the azomethine.

**INTRODUCTION:**

Azomethine compounds derived from aromatic amine and aromatic aldehydes and azomethine metal complexes have a huge range of applications in many fields like inorganic, biological, Medicinal, Pharmaceutical, Agriculture, Industry and analytical chemistry [1-6]. Azomethine are an important class of compounds due to their flexibility and the presence of imine moiety (-N=CH-) with natural biological substances. Azomethine can be prepared by using different methods from primary amine and carbonyl compounds. The original reaction of Azomethine preparation was first

reported by Hugo Schiff in 1864, by the condensation of primary amine and carbonyl compounds [7-9]. This reaction can be facilitated by acid catalysis and is generally carried out by refluxing a mixture of a primary amine and carbonyl compounds. The other method is the green method; it is an eco-friendly method. The most of the solvents are either toxic or flammable and considerably to the cost of an overall synthesis, so in recent years solvent-free conditions organic reactions having popularity [10-11]. The solvent-free reactions usually more efficiently work,

shorter reaction time, in expensive, non toxic, safer, more improved selectivity's and simplifies separation and purification of products than the traditional method [12]. Fruit juices are powerful and selective natural acid catalyst for the condensation reaction [13-16]. So in present work lemon juice was used as a catalyst for the synthesis of azomethine from 4-Morpholinoaniline and O- Vanillin.

**2. MATERIALS AND METHODS:** O-Vanillin, 4- Morpholino aniline purchased from Sigma –Aldrich. Limon, Methanol, Ruthenium chloride and Lanthanum chloride materials are used.

**2.1. Preparation of lemon juice:** Lemon is originating in the north –west region of India. In India it is also cultivated in the home gardens. While lime fruits was peeled off with knife and fruit slices were pressed into fruit juice to get semisolid mass. It was

then filtered with muslin cloth to get liquid juice. Lemon juice is sour in taste. The juice contains 1% citric acid and 0.5% ascorbic acid along with some organic acids, moisture, carbohydrates, protein, fat, minerals and fibers. It is a powerful and selective natural acid catalyst for condensation of 4-Morpholinoaniline and O- Vanillin.

## 2.2. Preparation of Azomethine:

The equimolar amount of 4-Morpholinoaniline with O-Vanillin was taken to the beaker. To this mixture natural acid catalyst Lemon juice were added and then starring for 5-10 minutes at room temperature. The yellow solid product was appeared. The product was washed with distilled water and recrystallization with ether. The percentage of yield is 96 and melting point is 158-161<sup>o</sup>C. The equation was represented in Fig: 1

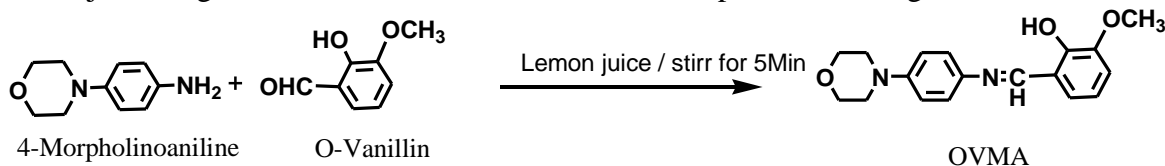


Fig:1

## 2.3. Preparation metal complex:

2:1 ratio of azomethine (OVMA) ligand and Mn (II) and Ni (II) metal salts were dissolved separately in 50 ml methanol in 250 ml clean round bottom flask and refluxed the mixture for half an hour on a water bath. Then few drops of hydrochloric acid were added and refluxing was continued for 6 hours. The reaction mixtures were poured in ice gives a colored precipitates. It was separated by filtration and washed with water. The compounds were re-crystallized with ether and dried in vacuum desiccators. The percentage of complexes and physical properties are represented in Table: 1

**3. RESULTS AND DISCUSSION:** The analytical data of azomethine and metal complexes are given in Table- 1. The

azomethine ligand and complexes were characterized by elemental analysis to determine percentage of C, N, O and H. The calculated and observed percentages of the elements are in good agreement and support two azomethines ligand to a metal ion. The molar conductivity data of the complexes are consistent with the non-electrolytic nature of the complexes.

**FTIR Spectral Analysis:** Infrared spectra of Azomethine and metal complexes were recorded with FTIR Affinity -I techniques on a shimadzu spectrometer in wave number region 4000-400 cm<sup>-1</sup> using KBr pellets. By using FTIR spectroscopy, the important functional groups present in the compound can be identified. The analyzed FT IR spectra of azomethine and metal complexes are represented Table-2. The typical FTIR

spectra are presented in the Fig.2-3. Infrared spectra of the Azomethine (OVMA) absorption band is exhibited in the region  $1648\text{cm}^{-1}$ , which indicates Stretching vibration of the (-C=N-) imines group [17]. In the complexation, the imines absorption peak appeared at  $1612\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$  for Mn (II) and Ni (II) complexes respectively. On complex formation, this band is shifted to lower frequency indicates that the ligand is coordinated to metal ion via azomethine nitrogen in all complexes. This change in shift is due to the decrease of the lone pair density of azomethine nitrogen towards metal atom. In the far IR spectral region, additional medium bands at  $648\text{ cm}^{-1}$  assigned to  $\nu$  M-N and other medium bands at  $516$  and  $586\text{ cm}^{-1}$  assigned to  $\nu$  M-O for OVMA-Mn and OVMA-Ni complexes [18-19] respectively.

**$^1\text{H}$  - NMR spectroscopic analysis:** The NMR spectra of the ligand and metal complex were recorded on AV-400 M-HZ NMR spectrometer in IICT, Hyderabad in  $\text{CDCl}_3$  solvents at room temperature. The  $^1\text{H}$ -NMR spectra values of the Azomethine ligand and metal complex are represented in the Table: 3. Fig: 5, 6 and 7 are shows the NMR specters of Azomethine and metal complexes. The Multiplets are observed around 6.84-7.45 ppm in azomethine have been assigned to aromatic protons. A Singlet is obtained at 8.74 ppm, which is shifted to 8.52 and 8.56 ppm in the complexes.

**Electronic spectra:** The electronic spectra of the methanolic solutions of azomethine ligand and its complexes are recorded in at IIT Edupula paya Kadapa district. The methanolic solution of azomethine ligand transition shows the band at 288 nm. But in methanolic solution of OVMA azomethine of Manganese and Nickel metal complexes new bands appeared at 364 and 372 nm respectively. Bands occurred in the region of 364-372 nm for complexes are assigned to charge transfer transition. The d-d transition

was observed in visible region in the metal complexes. Based on the results octahedral structure was proposed for metal complexes [19]. The electronic spectra of azomethine and metal complexes are represented in Fig: 16-18.

**Conductivity measurements:** The molar conductance of metal complexes in methanol was determined at  $27\pm 2^\circ\text{C}$  using Systronic 303 direct reading conductivity bridge. A known amount of solid metal complexes is transferred into 25ml standard flask and dissolved in methanol. The contents are made up to the mark with methanol. The metal complex solution is transferred into a clean and dry 100ml beaker. The molar conductance of the complexes was less than  $20\text{ Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$  indicating that Non-electrolytic nature. The molar conductance values of OVMA-Mn and OVMA-Ni are 13 and  $15\text{ Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$  respectively. These values suggest non electrolytic nature of the synthesized metal complexes.

**Magnetic susceptibility:** The magnetic moment value of OVMA-Mn and OVMA-Ni are 6.12 and 3.25 BM respectively. These values are higher than the magnetic momentum indicates that the complexes are monomeric in nature and there is no metal-metal interaction along the axial position in the complex and have octahedral structure. In metal complex, metal ion contains unpaired electrons paramagnetism.

**TG/DTA studies:** Mn(II) and Ni(II) complexes of the Azomethine ligand TG/ are shown in Fig.8-9. All the metal complexes were decomposed in three steps. The both metal complexes are thermally stable up to  $60^\circ\text{C}$ . The first stage of decomposition corresponding to endothermic dehydration of complexes by the loss of two water molecules occur [21] in the temperature range  $60\text{-}152^\circ\text{C}$  and  $75\text{-}$

140°C OVMA-Mn and OVMA-Ni complexes respectively. The second decomposition with exothermic peak by the loss of ligand moiety occurs in the temperature range 152- 462 and 142-475°C. The solid residues (MnO and NiO) are identified above 462 and 475°C respectively. The complexes, the final products are metal oxides. The thermal analysis data of the metal complexes are represented in Table -4.

**POWDER XRD:** The XRD patterns are used to explain qualitatively the degree of crystallinity. The diffractogram reflects is given in the Fig: 10 & 11. All the peaks have been indexed 2θ values compared in graph. Calculated 'd' values and '2θ' values by using Bragg's equation:  $n\lambda=2d\sin\theta$ . Comparison values reveals that there is good agreement between values of 2θ and d-values. The OVMA-Mn and OVMA-Ni complex do not form well define crystalline peaks due to their very poor crystallinity [22].

**SEM:** The SEM image of the azomethine and metal complexes were taken to analyze their surface design [23]. The OVMA Azomethine ligand and its Mn(II) and Ni(II) complexes were shown in Fig: 12-14. The SEM image of azomethine ligand has shown

a un uniform surface with different size pallets. OVMA –Mn SEM look like large voids irregular agglomerated particles, OVMA – Ni SEM image look like as a rain drops. The SEM surfaces Morphology are different in the case of Azomethine ligand and metal complexes.

**Anti biological activity:** The zone of inhibition of the azomethine ligand and its metal complexes against gram positive and gram negative bacterial strains was determined by using disc diffusion method. The inhibition values are tabulated in the below Table.5. Azomethine and its Mn(II) and Ni(II) complexes showed moderate activity against tested bacterium, and they were compared with the standard drugs (Streptomycin). It is observed that the metal complex have shown greater activity than free azomethine ligand. The metal complexes have shown better activity against the Bacillus subtilis, Streptococcus aureus and Escherichia coli than azomethine ligands. Streptomycin is used as standard drugs for gram positive and gram negative strains. Antibacterial activity of the Azomethine ligands and their complexes Bacillus subtilis, Streptococcus aureus and Escherichia coli have shown in Fig.15

**Table: 1 Analytical data of Azomethine ligand and its complex**

Ligand /complex	Molecular weight(grams)	Percentage of elements analyzed (calculated)					% of yield (colour)	Melting point (°c)
		C	H	N	O	M(Metal)		
Azomethine OVMA	312.38	69.11 (69.20)	6.39 (6.40)	8.94 (8.97)	15.38 (15.38)	-	96 (Yellow)	158-161
OVMA -Mn	713.67	60.53 (60.59)	5.88 (5.92)	7.84 (7.85)	17.94 (17.93)	7.69 (7.70)	88 (Light yellow)	282-284
OVMA -Ni	717.45	60.21 (60.26)	5.85 (5.89)	7.80 (7.81)	17.84 (17.86)	8.18 (8.19)	83 ( Black)	278-279

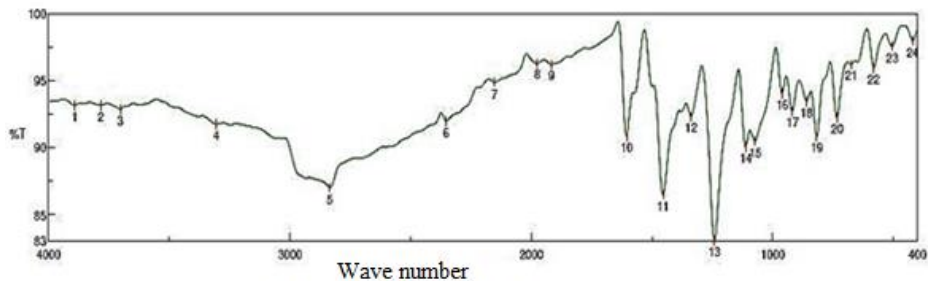


Fig.2. FTIR Spectra of Azomethine

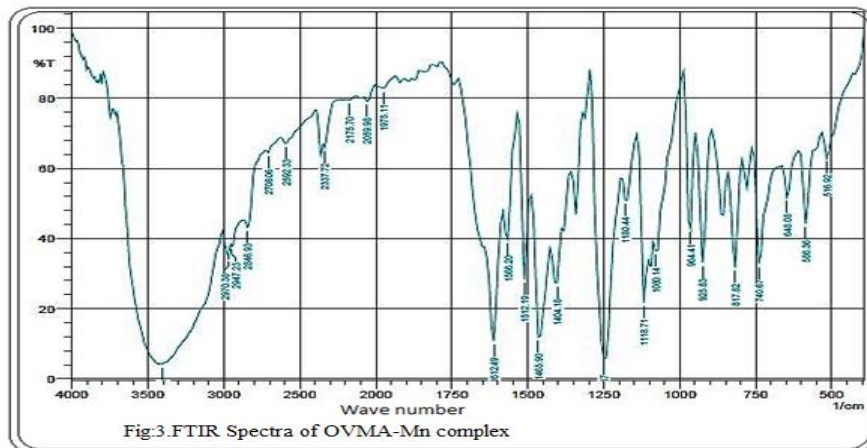


Fig.3. FTIR Spectra of OVMA-Mn complex

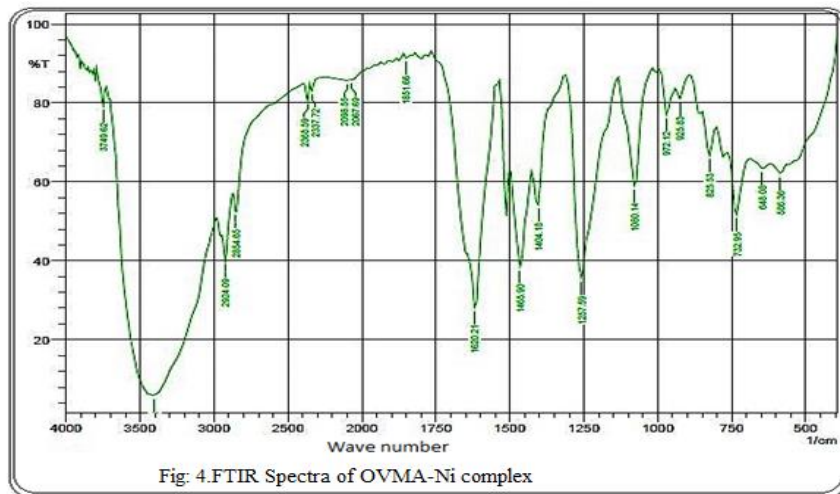


Fig. 4. FTIR Spectra of OVMA-Ni complex

Table:2. FTIR Spectral bands of OVMA ligand and its complexes

S.No.	Compound	$\nu$ OH Water	$\nu$ OH Phenolic	$\nu$ C=N	$\nu$ M-O	$\nu$ M-N
1	Azomethine(OVMA)	-	3194	1648	-	-
2	OVMA -Mn	3402	3232	1612	516	648
3	OVMA -Ni	3402	3232	1620	586	648

Table 3. <sup>1</sup>H – NMR Spectral data of Azomethine and complexes.

Compound	<sup>1</sup> H –NMR (Ppm)
Azomethine (OVMA)	8.74 (S, -N=CH-), 6.84-7.45( m, Aromatic ), 3.95(S, -OCH <sub>3</sub> ), 14.12(S, -OH), 3.15-3.85( m, -CH <sub>2</sub> - in cyclic group)
OVMA -Mn	8.52 (S, -N=CH-), 6.50-7.26( m, Aromatic ), 3.42(S, -OCH <sub>3</sub> ), 4.12(S, H <sub>2</sub> O-OH), 2.08-0.75( m, -CH <sub>2</sub> - in cyclic group)
OVMA -Ni	8.56 (S, -N=CH-), 6.25-7.62( m, Aromatic ), 3.92(S, -OCH <sub>3</sub> ), 4.25(S, H <sub>2</sub> O-OH), 3.42-1.02( m, -CH <sub>2</sub> - in cyclic group)

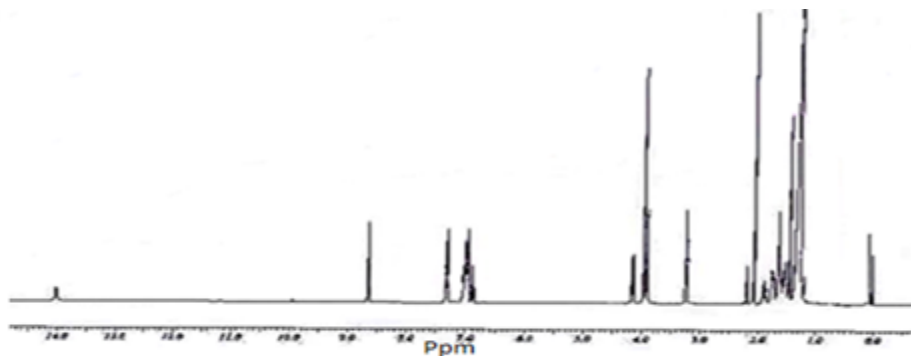


Fig. 5. NMR Spectra of Azomethine

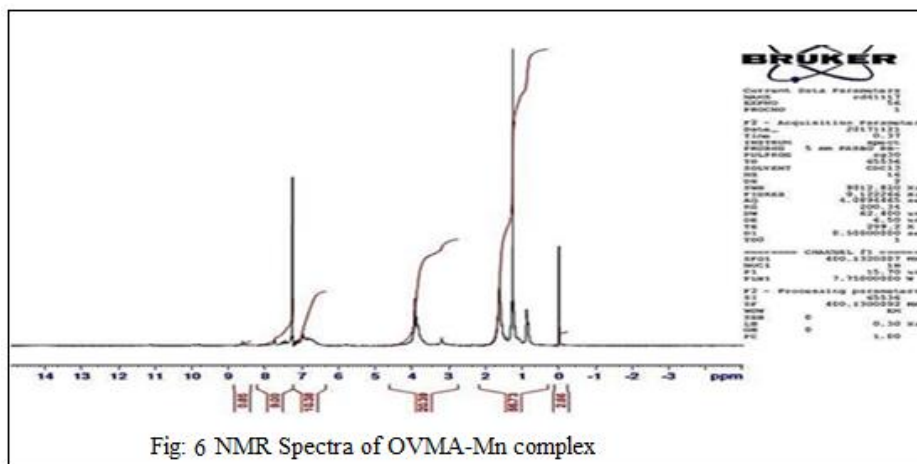


Fig. 6 NMR Spectra of OVMA-Mn complex

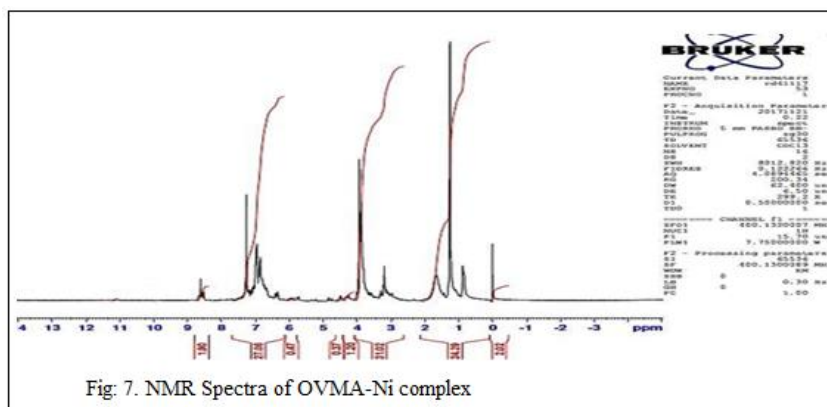
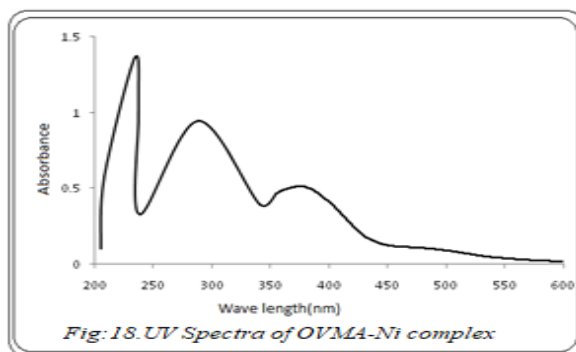
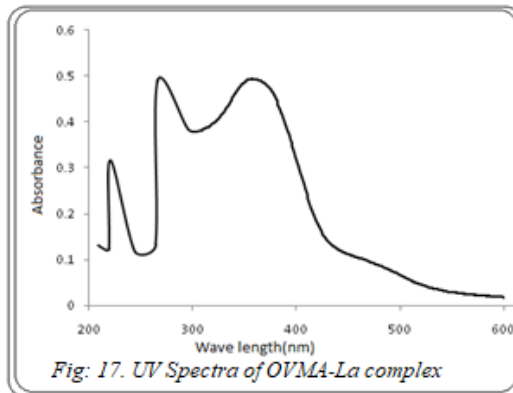
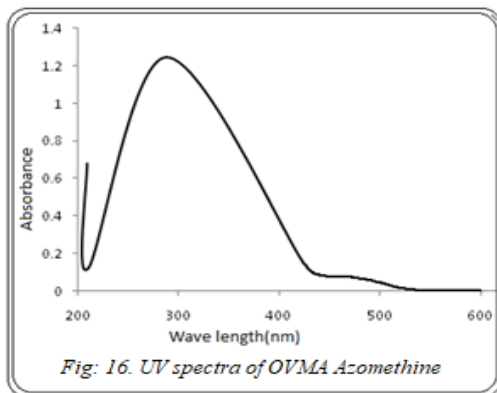
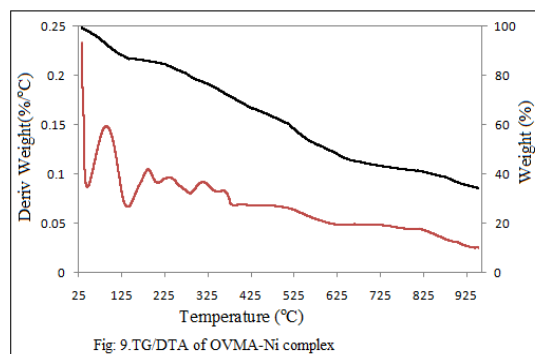
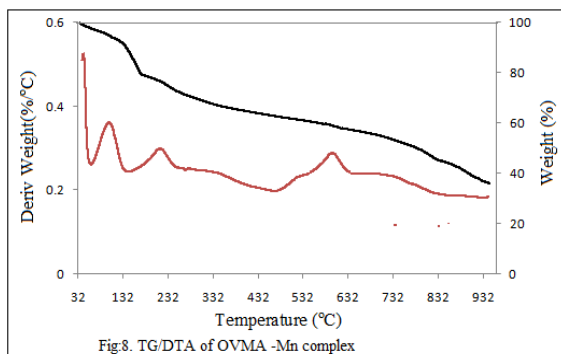


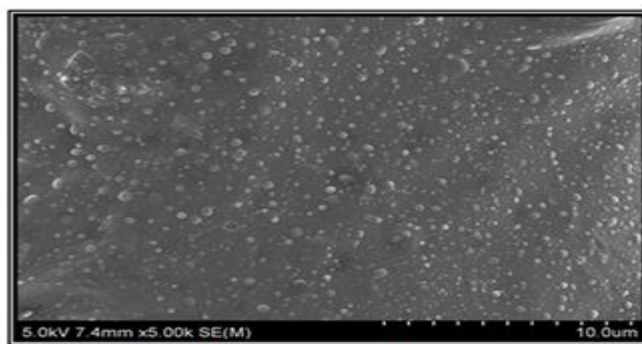
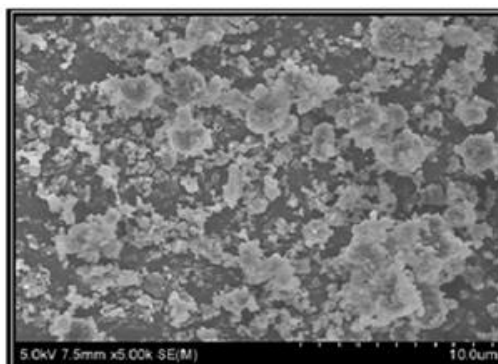
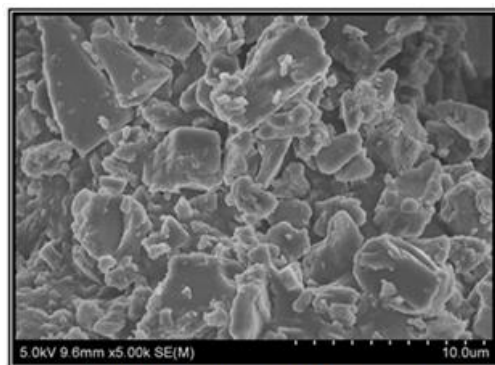
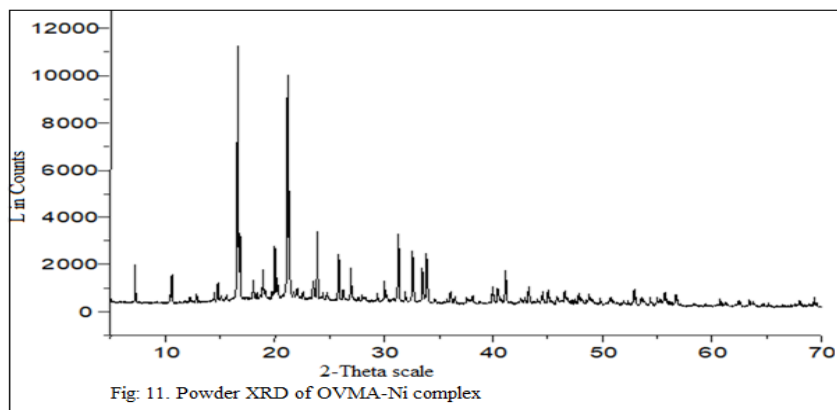
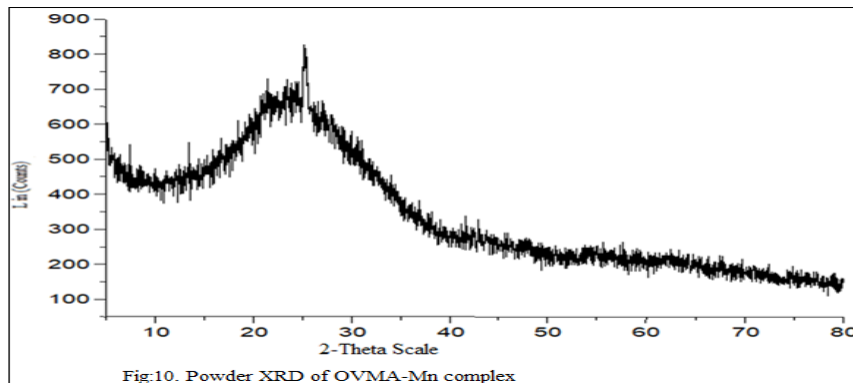
Fig. 7. NMR Spectra of OVMA-Ni complex



**Table-4: The thermal analysis data of the azomethine metal complexes**

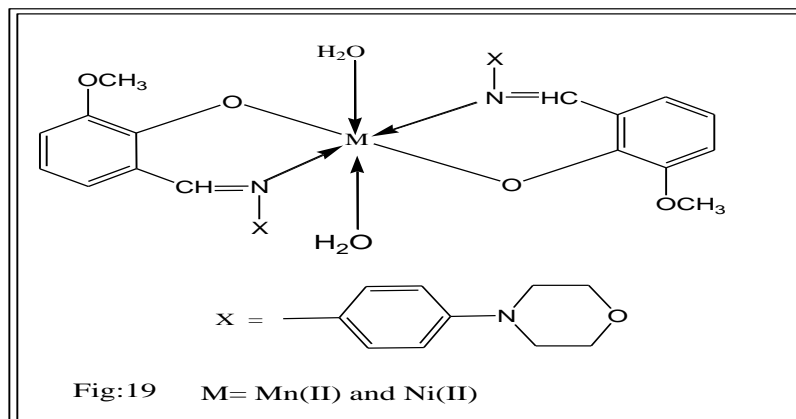
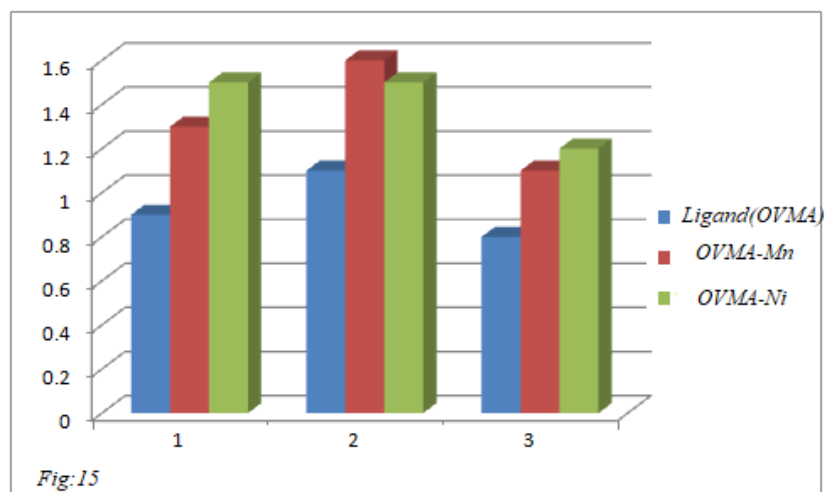
Compound	Molecular weight	Temperature range in °C	Probable assignment
[Mn L <sub>2.2</sub> H <sub>2</sub> O] L=C <sub>21</sub> H <sub>18</sub> O <sub>2</sub> N <sub>2</sub>	713.69	60-152 152-462 Above 462	Loss of 2H <sub>2</sub> O molecules Loss of 2L molecules Corresponds to MnO
[NiL <sub>2.2</sub> H <sub>2</sub> O] L=C <sub>21</sub> H <sub>18</sub> O <sub>2</sub> N <sub>2</sub>	717.45	75-140 142-475 Above 475	Loss of 2H <sub>2</sub> O molecules Loss of 2L molecules Corresponds to NiO







SNo	Compound	Bacillus subtilis(1)	Streptococcus aureus (2)	E.coli (3)
1.	Ligand	0.9	1.1	0.8
2.	DHBPMA-La	1.3	1.6	1.1
3.	DHBPMA-Ru	1.5	1.5	1.2
S	Streptomycin	2.5	3.5	2.9



### CONCLUSION:

Mn(II) and Ni(II) complexes of the azomethine derived from 4-Morpholinoaniline and O-Vanillin were prepared and characterized. The structural characterizations of synthesized compound were made by using the elemental analysis,

spectroscopic methods, magnetic and conductance etc. The study reveals that complexes are non-electrolytes and azomethine behaves as a neutral Bidentate ligand. The metal (II) complexes have octahedral geometry it was represented in Fig19. The biological activity of all the

complexes is higher than that of the free azomethine ligand which indicates that activity increases with the chelation.

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