



## Synthesis, Spectroscopic, Characterization, and Antimicrobial Studies of New Schiff Bases and Their Metal Complexes

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### Abstract

Schiff's foundations complexes produced from the condensation of 4-aminoantipyrine with 4-(dimethylamino)benzaldehyde and the resultant condensation with the valine salt amino acid ligand (4-ANdmV) coordinated through NNO donor sites. Spectroscopic (IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV-vis), for all Co(II), Ni(II), Cu(II), and Zn, magnetic and other research imply octahedral geometry (II). The metal complexes and ligands were also tested against bacterial strains it was discovered that these chemicals had varied inhibitory activity on the growth of bacterium, such as three gram negative bacterium (*Salmonella coli*, *Pseudomonas aeruginosa*) and one pathogenic bacteria (*Staphylococcus aureuginosa*, and *Klebsiella pneumoniae*).

**Key Words:** Valine amino acid, 4-Amino antipyrine, Schiff base complexes.

### 1. Introduction

The heterocyclic compound 4-Aminoantipyrine (4-AAP) has two nitrogen atoms in its ring, a highly reactive amine and a carbonyl functional group. The presence of hetero atoms modifies the redistribution of electrons, resulting in aromatic character, and thus produces the heteroatom effect [1], which adds reactivity, chelating action, and other properties. It is used in a variety of academic subjects as a result [2,3]. In this regard, Schneider *et al.* and Takatori *et al.* [4,5] employed 4-AAP to research antibody-mediated drug allergy in guinea pigs, researchers looked on antibody-mediated drug allergy in rats using 4-AAP. Using a radioimmunoassay the metabolic activities of 4-AAP in biomaterials were determined. The use of these molecules in biological processes inspires scientists to create novel compounds and study their biological effects. Along with in vitro the condensation reaction between the amine group contained in 4-AAP and carbonyl group attached to various aliphatic/aromatic aldehyde and ketone results in the creation of imine (>C=N-) (or) azomethine (-CH=N-) group [6,7]. Applications like catalysis are among them, dye synthesis, pigments, chemosensor, food industry, analytical reagent, and medicinal agents [8-14]. Furthermore, the 4-AAP derivatives have chelating properties and the ability to form metal complexes with nearly all transition metal ions and lanthanides, both of which have crucial applications. Development of sensors, mechano history indicators, security papers, cell imaging, light emitting diodes, electrochemical thin film, dye sensitized solar cell, antipyretic, antimicrobial, anticancer, anti-inflammatory, antioxidant, analgesic, antipyretic [15-28] until now, the few reports available on 4-AAP and its derivatives focused primarily on the numerous dent cities and chelation capacity. The physicochemical

properties, stability, and selectivity of metal complexes were discussed by certain researchers [29]. This review compiles the uses of several metal complexes produced from 4-AAP derivatives, which are widely used in materials science, biology, and catalysis. The synthesis, characterization, and antibacterial investigations of Schiff base made from 4-(dimethylamino) benzaldehyde, -4-aminoantipyrine, and valine amino acid in transition metal complexes are described here. The ligation behavior of the NNO donor compounds with various metal ions was examined after they were produced. Using the paper disc diffusion method and serial dilutions in liquid broth method, complexes and ligand were examined for in vitro antibacterial activity against *K. pneumoniae*, *S. aureus*, *P. aeruginosa*, and *E. coli pathogens*.

### 2. Materials and methods

#### 2.1. Chemicals and measuring devices :

(BHD and Fluke) provided all of the compounds, that were employed without additional purification. The electro thermal melting point was used to determine the ligand's and its complexes' melting point contemporary 9300 molecular. Measurements of conductivity of electrical in a DMF(10<sup>-3</sup> M) was done by meter fur conductivity (model 4510-jenway). Electronic spectra in DMF(10<sup>-3</sup>M) were captured using a Shimadzu spectrophotometer double beam model 1700 UV-vis spectrophotometer, and FTIR spectra recorded reflective on spectrophotometer (ATR platinum Germany) in wave number (400-4000cm<sup>-1</sup>), the solvent DMSO-d<sup>6</sup> was employed in <sup>1</sup>H-NMR spectroscopy. The Gouy method was used to assess magnetic susceptibility on a magnetic equilibrium MSB-MK (at ambient temperature). A spectrometer using Pascal's average absorb flame and

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graphite were used to rectify molar susceptibilities study.

## 2.2. Prepare of 4-(4-dimethylamino)benzylidene - 4-aminoantipyrine (4-ANdM)

A solution component of (0.152 g, 1 mmol) of 4-(dimethylamino) benzaldehyde in (10 ml) ethanol mixed with solution of (0.203 g, 1mmol) 4-Aminoantipyrine in (10 ml) ethanol as shown (scheme 1). The reaction had been mixed at room temperature in two hours [4,21], then it was heated to reflux for two hours and maintained at 40 degrees Celsius for three days. A filtered and recrystallized yellow precipitate is left resulting in yellow crystals of outstanding quality.

## 2.3. Formulation of newfangled ligand (K4-ANdMV)

The K salt of the valine was prepared as stated [4,21] in the literature, in an equal ratio 1:1 water-ethanol (40 ml) solution, the valine (0.01 mol) was dissolved before being KOH (0.01 mol) was added to a hot ethanolic solution (30 ml) and agitated to obtain a homogenous solution. Following that gradual addition ethanolic solution is applied is added of 4-(4-dimethylamino)benzylidene-4-aminoantipyrine (0.01 mol) was added to this solution, and the combination was refluxed for approximately 6 hours as shown (scheme 2). The Schiff base was filtered and recrystallized to obtain a plate-like crystalline material [22].

## 2.4. Complexes' synthesis

An alcohol solution of ligand (2 mmol) was mixed to an aq. alcoholic solution (15 ml) contained 1 mmol of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  /  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  /  $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$  /  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$  and refluxed on a boiling water bath 2 hour. After that, 2mmol sodium acetate was added to the reaction mixture, and reflux was maintained for 3 hours[4,21]as shown (scheme 3). The isolated complex was filtered before being vacuum dried on fused  $\text{CaCl}_2$  after being washed extensively with water, ethanol, and ether.

## 3. Result as well as debate:

### 3.1. General

The Schiff base is a dark yellow crystal that is insolubleattractiveness, significantly supporting the in water but almost dissolves in a variety of organicdistribution of the proposed coordination sites were solvents, such as dimethyl sulfoxide, dimethylformamidemedium bands about 432- 448  $\text{cm}^{-1}$  and 534-558  $\text{cm}^{-1}$ , and chloroform. Various colored crystals form when theywhich may be attributed to the (M-N) and (M-O) react with metal ions and are stable in air.

### 3.2. Elemental investigation and physical characteristics

Summarizes the physical properties and outcomes of the organized complexes based on C.H. and N. (Table1) research as well as metals and the molar conductivities [ $10^{-3}\text{M}$ ] of the metal(II)

complex solution at room temperature were tested after they were dissolved in dimethyl sulphoxid. The reduced conductivity values (10.6-19.6  $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ ) for the resulting complexes are indicative of the non-electrolytic nature of the resulting complexes, with planned magnitudes, the investigational data was acceptable. These results, together with those obtained from spectrum, magnetic susceptibility, and molar conductivities, were used to propose a molecular structure for the ligand and its metal complexes. Every solid compound (1:2) of metal to ligand has been isolated. , as well as demonstrating the complexes have a [1:2] ratio stoichiometry of metal–ligand.

### 3.3. Infrared spectra

The Infrared spectrum reveal the ligand's coordinating sites (Table 2), which is useful information. To determine the alterations that may have occurred during complexation, the compound's infrared spectrum was compared to that of the free ligand in Figure1-3. Because specific peaks in the Infrared spectrum of the ligand and its element complexes are shared, only the most significant peaks that have been relocated or those that have recently appeared are discussed.

The spectrum of the free Schiff base ligand (K4-ANdMV) showed a band of the  $-\text{C}=\text{N}-$  group of 1579 $\text{cm}^{-1}$  and 1566 $\text{cm}^{-1}$  of the ligand (4-ANdM), that was transmitted to lower frequencies in the spectra of at 1545-1567 $\text{cm}^{-1}$ , showing that the  $-\text{C}=\text{N}-$  nitrogen was involved in metal ion coordination [10]. The (C=N) vibration should be reduced and in the azomethine link's electron density should be reduced as the Schiff base is coordinated to the metal via the nitrogen atom, the assym ( $\text{COO}^-$ ) band of free ligand appears in the spectra of 1516, in metal complexes which was displaced to a lower number of waves 1501-1515  $\text{cm}^{-1}$ .

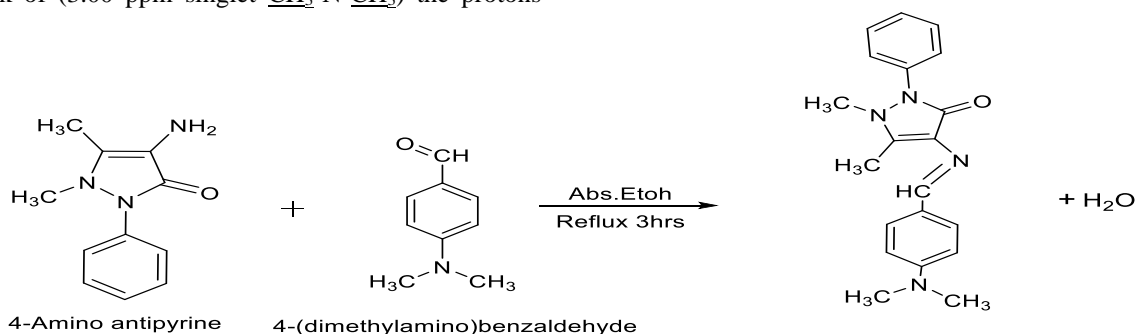
In the spectra of metal complexes the sym ( $\text{COO}^-$ ) band of free ligand, which was seen at 1443  $\text{cm}^{-1}$ , was moved to a higher wave number, 1452-1463  $\text{cm}^{-1}$ , representing coordination of through the oxygen atom, the carboxylic acid group interacts with the element ion [17]. The allocation of the planned coordination sites was enhanced by their [10,17] oscillations, respectively. found in (Table 2).

### 3.4. Spectra of $^1\text{H-NMR}$

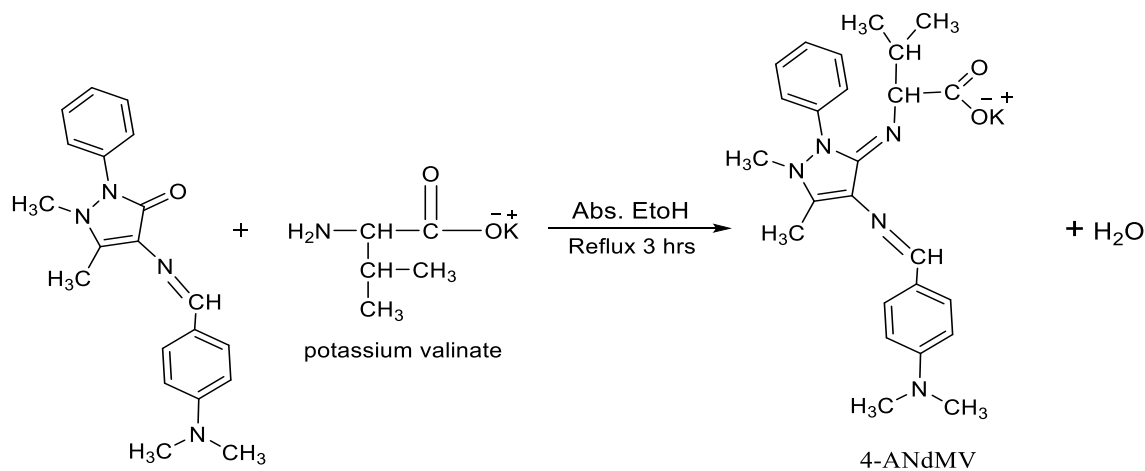
The ligand's  $^1\text{H-NMR}$  spectra was obtained in ( $\text{DMSO-d}^6$ ), and the spectrum is depicted in Figure 4. The Schiff base ligand's  $^1\text{H-NMR}$  spectra exhibits an aromatic peak at (6.68-7.60 ppm, multiplet 9H)[21]. The azomethine group peaks at (8.14 ppm singlet H-

C=N-) [29]. The ligand also exhibits the following characteristics: (2.27ppm singlet -CH<sub>3</sub>), (3.04 ppm singlet -N-CH<sub>3</sub>)[22], (4.59-4.61 ppm triplet 1H CH-COO-) respectively, The peaks at (2.17-2.23 ppm septet CH<sub>3</sub>-CH-CH<sub>3</sub>) for amino acid valine, and the peak of (3.00 ppm singlet CH<sub>3</sub>-N-CH<sub>3</sub>) the protons

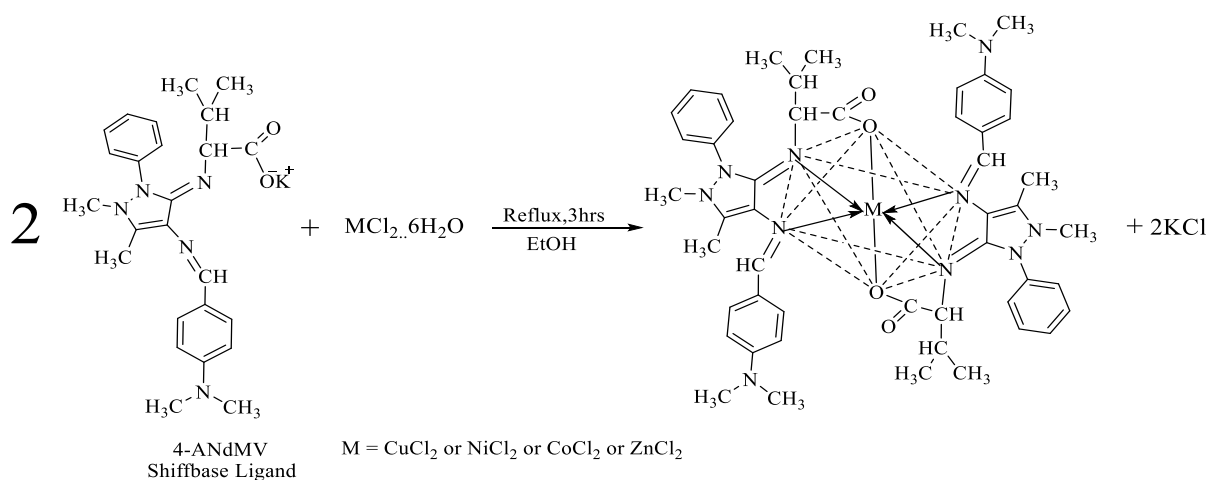
had been discovered to be accurate positions. These are the results support the bonding mode described in their infrared spectra the amount of protons in the universe.



**Scheme 1:** part of ligand 4-(4-(dimethylamino)benzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one.



**Scheme 2:** Schiff base ligand potassium 2-(4-(4-(dimethylamino)benzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-ylidene)amino)-3-methylbutanoate



**Scheme3:** Synthetic pathway of metal complexes.

### 3.5. <sup>13</sup>C-NMR spectra

In (DMSO-d<sub>6</sub>), the <sup>13</sup>C-NMR spectrum of the ligand was acquired, and the spectrum is presented in Figure 5. The Schiff base ligand's <sup>13</sup>C-NMR spectra exhibits an aromatic peak at (111.79-151.98ppm)[4]. The azomethine group peaks at (149.20 ppm H-C=N-) [29]. The ligand also exhibits the following properties (13.72 ppm -C<sub>H</sub>₃), (36.47 ppm -N-C<sub>H</sub>₃) of methyl of pyrrolene group [21]. (71.70 ppm C<sub>H</sub>-COO-) (176.86 ppm C<sub>H</sub>-COO-) respectively. The peaks at (31.81 ppm CH₃-C<sub>H</sub>-CH₃) (18.54 ppm C<sub>H</sub>-CH-CH₃) for amino acid valine, and the peak of (40.37 ppm C<sub>H</sub>-N-C<sub>H</sub>₃) the carbons were all found to be in the right place Figure 5. These findings support the bonding mode described C.H.N.

### 3.6. Measurements of magnetic fields and electronic spectra

The cobalt(II) compound possesses a magnetic field of 5.13 B.M. (Table 3), which is comparable with prior findings for octahedral Co<sup>+2</sup> complex [12]. The current Ni<sup>+2</sup> complex has a magnetic moment of 2.98 which falls within the 2.9–3.3 B.M. range [21]. An octahedral habitat is suggested the magnetic moment of the Cu<sup>+2</sup> complex is 1.92 B.M. which is larger than the 1.73 B.M. expected for a single unpaired electron in a monomeric system deformed octahedral shape [4].

According to empirical evidence, the Zn<sup>+2</sup> complex was diamagnetic and had an octahedral shape formulas for these complexes, and the spectrum features of ligand and its complexes in DMF have been investigated, and they are represented in (Table 3).

The observed absorption bands of the ligand (K4-ANdMV) free donor at 32258 and 26954 cm<sup>-1</sup> were attributed to the π → π\* and n → π\* transformations, accordingly. Complexation behavior is what caused the absorption bands of Co(II), Ni(II), and Cu(II) compounds to shift to higher values and the formation of new bands. Complexes with novel bands that might be attributed

to ligand-metal charge transfer [29], the spectral details have been depicted in (Table 3) and Figure 6.

### 4. Properties that fight bacteria

The examined the disc diffusion method was used to assess compounds' in-vitro biological screening effects against bacteria using nutrients agar as the medium, and three separate runs of the experiment under similar conditions data is collected using DMF as a negative control and amoxicillin as a positive standard were summarized in (Table 4).

From the start metal chelates have a significantly broader zone of inhibition than ligands, which is obvious. Chelation theory can explain metal chelates' activity is boosted in this manner because the ligand orbitals overlap, the during chelation, the polarity of the element ion will reduced to a bigger extent. In addition, it increases the electrons' delocalization across the chelate ring as a whole, which improves the lipophilicity of the complexes [30]. The permeability barrier of the cell is broken as a result of the increased lipophilicity, typical cell operations are slowed in Figure 7.

### 5. Conclusions

Five novel biologically active the ligands generated from 4-aminoantipyrine, as well as spectral and analytical data were used to produce and analyze their Co(II), Cu(II), Ni(II), and Zn(II) complexes.

The architecture of recently discovered complicated combinations the azomethine nitrogen and the carboxylic oxygen atoms were discovered to be responsible for the Schiff base's coordination to the metal atom, the geometry of the complexes is described as octahedral. Finally combining 4-amino antipyrine compounds having pharmacologically significant properties intriguing metals including cobalt, copper, nickel, and zinc could be a promising technique for producing novel therapeutic instruments for medical therapy, according to the research.

Table1: Some physical properties and an examination of the elements for (K4-ANdMV) and its chelate.

Compounds	Color	M.p (°C)	Yield %	Mol. formula (mol. Wt)	Found (calc)%			
					C	H	N	O
L=K4-ANdMV	Dark yellow	246	77	C <sub>25</sub> H <sub>30</sub> KN <sub>5</sub> O <sub>2</sub> (471.65)	65.02 (65.10)	6.41 (6.44)	14.85 (14.90)	----
L= 4-ANdM	yellow	234	69	C <sub>2</sub> .H <sub>22</sub> N <sub>4</sub> O (334.42)	71.83 (71.98)	6.630 (6.58)	16.75 (16.67)	----
[Co (4-ANdMV) <sub>2</sub> ]	Dark green	274	71	[C <sub>50</sub> H <sub>60</sub> CoN <sub>10</sub> O <sub>4</sub> ] (924.42)	64.99 (64.11)	6.55 (65.58)	15.16 (15.18)	6.38 (6.40)
[Ni (4-ANdMV) <sub>2</sub> ]	Light green	268	68	[C <sub>50</sub> H <sub>60</sub> N <sub>10</sub> NiO <sub>4</sub> ] (923.42)	65.01 (65.04)	6.55 (65.57)	15.16 (65.19)	6.35 (6.37)
[Cu (4-ANdMV) <sub>2</sub> ]	Dark brown	282	72	[C <sub>50</sub> H <sub>60</sub> CuN <sub>10</sub> O <sub>4</sub> ] (928.42)	64.67 (65.69)	6.51 (6.53)	15.08 (15.10)	6.84 (6.86)
[Zn (4-ANdMV) <sub>2</sub> ]	Lemon yellow	269	69	[C <sub>50</sub> H <sub>60</sub> N <sub>10</sub> O <sub>4</sub> Zn] (931.42)	64.54 (65.56)	6.50 (6.54)	15.05 (15.07)	7.03 (7.07)

**Table2: Infrared frequencies that are vital to know in (cm<sup>-1</sup>) of (K4-ANdMV) and their metal.**

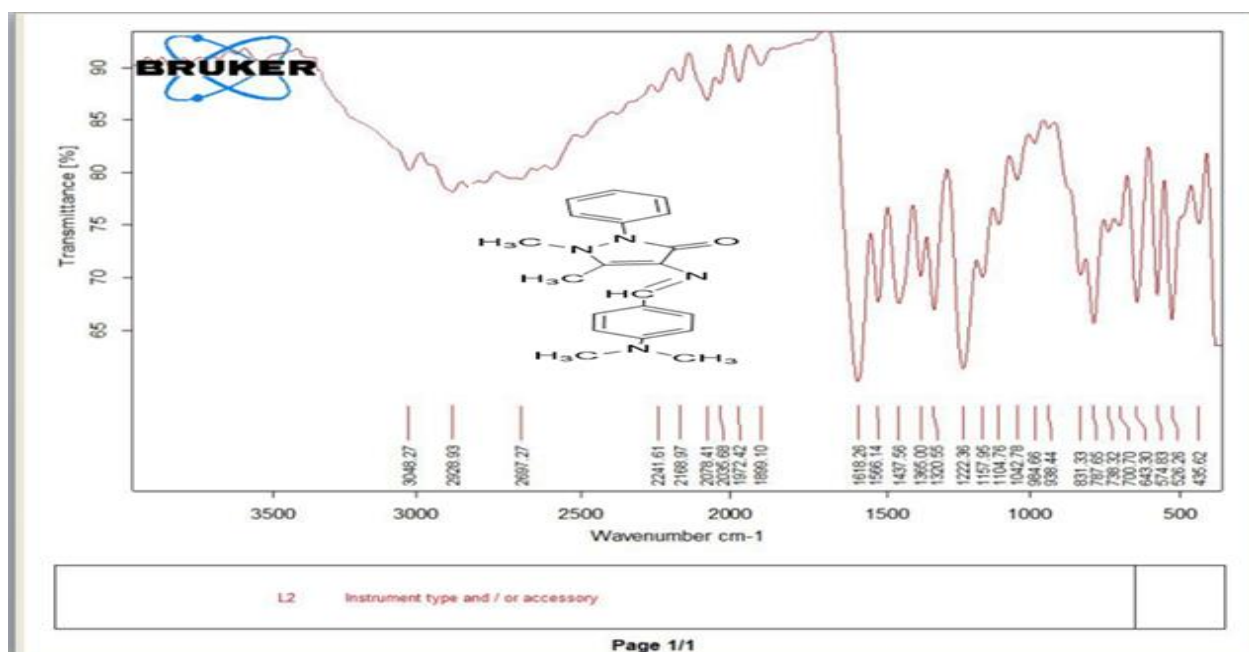
Compounds	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu_{\text{asym}}(\text{COO}^-)$	$\nu_{\text{sym}}(\text{COO}^-)$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
L=K4-ANdMV	1579	1158	1516	1443	----	----
L= 4-ANdM	1566	1157	1510	1437	----	----
[Co (4-ANdMV) <sub>2</sub> ]	1567	1154	1501	1463	438	534
[Ni (4-ANdMV) <sub>2</sub> ]	1566	1152	1515	1452	432	550
[Cu (4-ANdMV) <sub>2</sub> ]	1545	1157	1504	1456	440	552
[Zn (4-ANdMV) <sub>2</sub> ]	1548	1156	1510	1453	448	558

**Table 3: The electronic spectrum of the L=K4-ANdMV and its complexes, as well as their magnetic susceptibility.**

Compounds	Band position, cm <sup>-1</sup>	Transition	$\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	Suggested Geometry	$\mu_{\text{eff}}$ (BM)
L=K4-ANdMV	32258	$\pi \rightarrow \pi^*$	----	----	----
	26954	$n \rightarrow \pi^*$	----	----	----
L= 4-ANdM	44843	$\pi \rightarrow \pi^*$	----	----	----
	35460	$n \rightarrow \pi^*$	----	----	----
[Co (4-ANdMV) <sub>2</sub> ]	39063	Center ligand			
	33670	Center ligand			
	19802	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$	19.6	octahedral	5.13
	10309	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$			
[Ni (4-ANdMV) <sub>2</sub> ]	21053	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$			
	15748	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	13.2	octahedral	2.98
	10256	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$			
[Cu (4-ANdMV) <sub>2</sub> ]	15038	${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$	10.6	octahedral	1.78
[Zn (4-ANdMV) <sub>2</sub> ]	21008	$d \pi(\text{Zn})^{+2} \rightarrow \pi^*(\text{L})$	17.4	octahedral	Dimg

**Table 4: MIC values for the produced compounds in the face of the proliferation of 4 bacteria in (  $\mu\text{g/ml}$ ).**

Compound	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>	<i>Staphylococcus aureus</i>	<i>Klebsiella pneumonia</i>
L=K4-ANdMV	75	70	60	64
[Co (4-ANdMV) <sub>2</sub> ]	65	64	66	66
[Ni (4-ANdMV) <sub>2</sub> ]	70	76	68	72
[Cu (4-ANdMV) <sub>2</sub> ]	68	68	52	62
[Zn (4-ANdMV) <sub>2</sub> ]	52	52	50	50
Amoxicillin	8.8	6.6	12	10

**Fig. 1. IR spectrum of part of ligand 4-(4-(dimethylamino)benzylidene)amino)-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one**

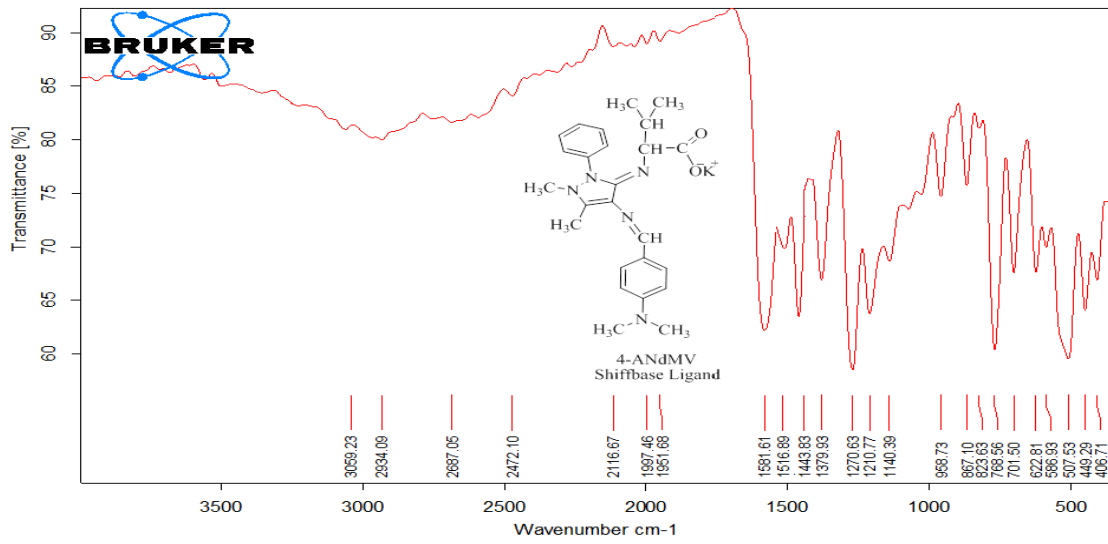


Fig. 2. IR spectrum of ligand

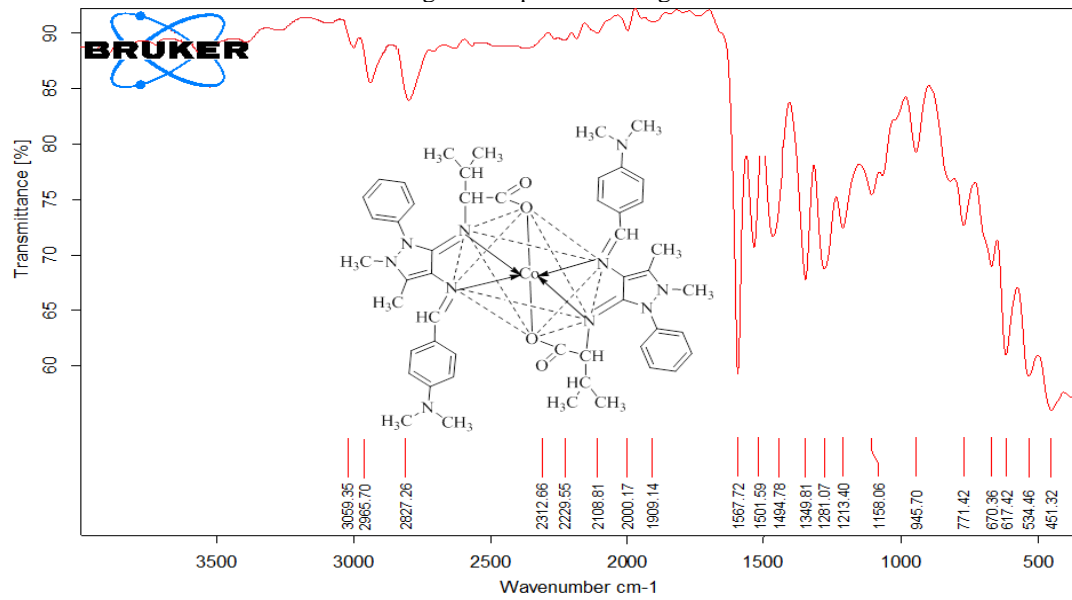


Fig. 3. IR spectrum of Co(II) complex .

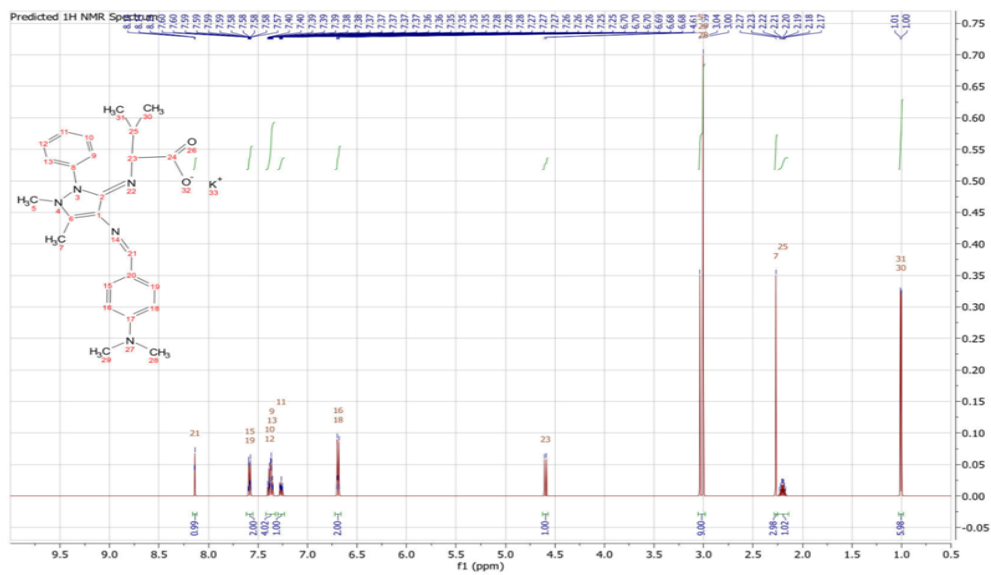


Fig. 4. <sup>1</sup>H-NMR of K4-ANdMV ligand



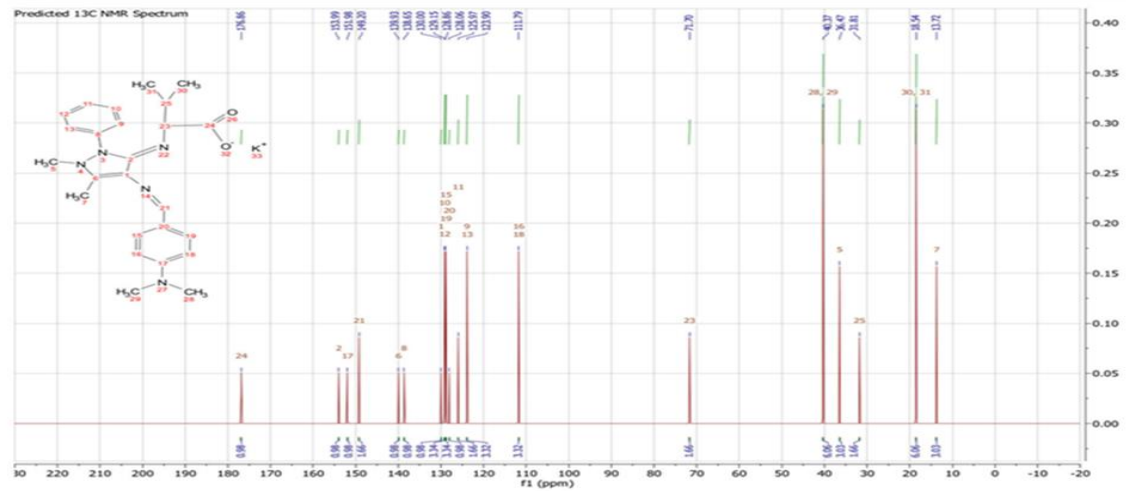


Fig. 5.  $^{13}\text{C}$ -NMR of K4-ANdMV ligand

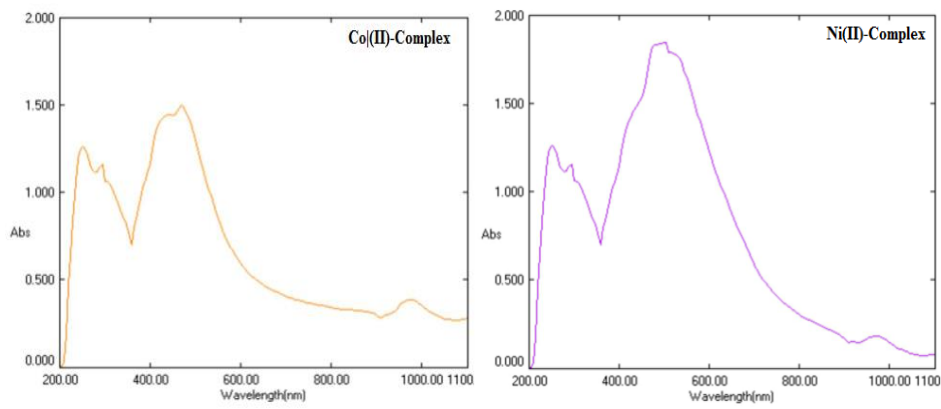


Fig. 6 . U.V – Vis of complexes

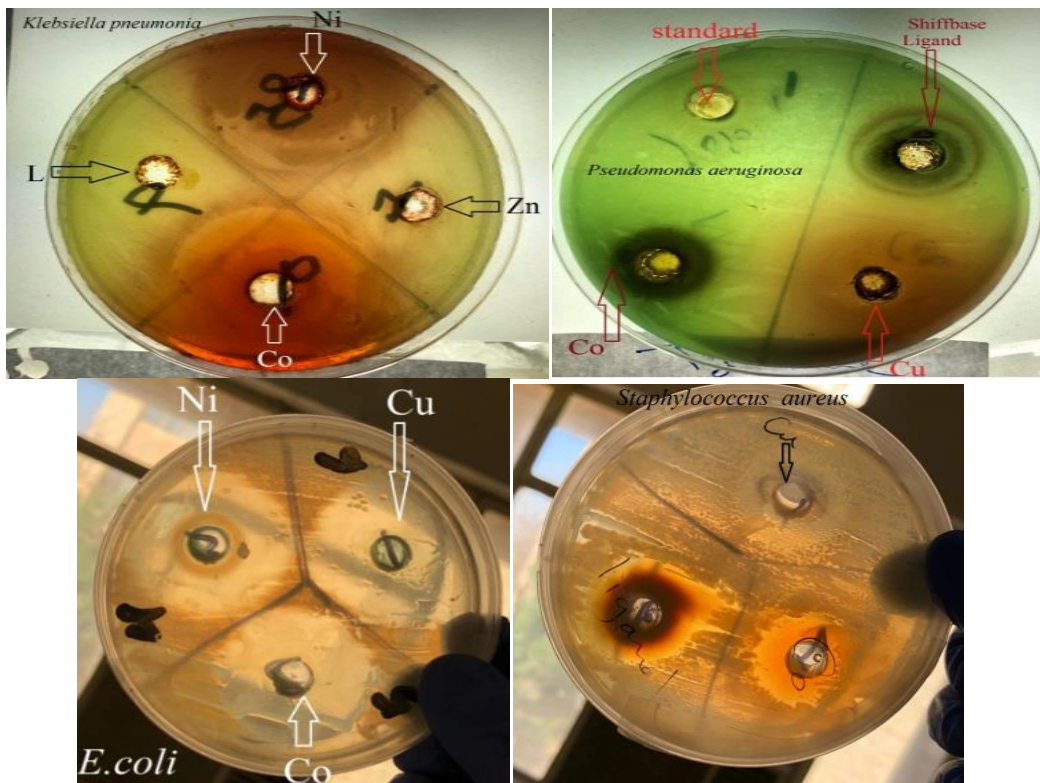


Fig.7. Zone of Inhibition of bacterial growth (mm) – bacteria image of K4-ANdMV ligand and its complexes.

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