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Preparation, Spectral Characterization, Structural study, and Evaluation of antibacterial activity of Metal Complexes with Schiff base derived from (N, N'-Bis (1,5-dimethyl-2-phenyl-1,2-dihydro- pyrazolidine-3-one)-1,2-diamino ethane).

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ABSTRACT

Herein, we show the preparation and the characterization of new metal complexes by using a Schiff base ligand (N,N'-Bis(1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazolidine-3-one)-1,2-diamino ethane) (L) with the metals Co(II), Cr(III), Cu (II), Mn(II), and VO(II). This Schiff base ligand was synthesized via condensing [4-antipyrincarboxaldehyde] with [Ethylene di-amine] in ethanol. For preparing complexes tetradentate Schiff bases ligand were employed with metal ions of Co(II), Cr(III), Cu (II), Mn(II), and VO(II) as nuclear formula ML. The synthesized ligand and its metal complexes were well characterized using FTIR, UV-Vis absorption, elemental analysis, $^1\text{H-NMR}$, and mass spectroscopy. Based on these characterizations, the chemical structures of the ligand and the metal complexes were confirmed. Furthermore, the electronic and magnetic properties of the prepared metal complexes were clearly understood.

Keywords: 4-antipyrincarboxaldehyde, Schiff base, Ultrasonic bath, Complexes.

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INTRODUCTION

There have been a great implementation of Schiff bases derived from aromatic amines and aromatic aldehydes in various scientific domains, e.g. biological, inorganic and analytical chemistry [1-3]. Over the last century, there have been a high demand for synthesizing Schiff bases based ligands due to their significant importance especially in clinical applications. This importance stems from the fact that these ligands possess electron rich atoms such as nitrogen and oxygen as anchors which increasing physiological importance of nitrogen and oxygen donor organic compounds and active role played by coordination certain act as coordination sites if reacted with metals [4-6].

The plethora of reports have showed that various isomers particularly Schiff bases resulted from aromatic aldehydes and aromatic amines have shown many of applications in many fields including pharmaceutical, life sciences and chemical science including inorganic and analytical chemistry [7]. Schiff bases metal complexes play important role in coordination chemistry as ligands because of their excellent donor abilities [8], and Schiff bases are organic compound have been high polarity due to the imine group and double bond (C=O) which can form coordination complexes with metal ions [9], due to a perfect selectivity, sensitivity and stability of for specific metal ions such as Ag(II), Al(III), Co(II), Cu(II), Gd(III), Hg(II), Ni(II), Pb(II), Y(III) and Zn(II), so Schiff base ligands act as cation carriers in potentiometric sensors [10].

In the present paper, Co(II), Cr(III), Cu(II), Mn(II), and VO(II) complexes with Schiff bases ligands are reported. These compounds have been characterized in the basis of analysis of the Schiff bases liquid and solid complexes. ¹H NMR, elemental microanalysis (C, H, N, S, and M), magnetic measurements, UV-Visible, LC-Mass, FT-IR spectra, conductivity measurement.

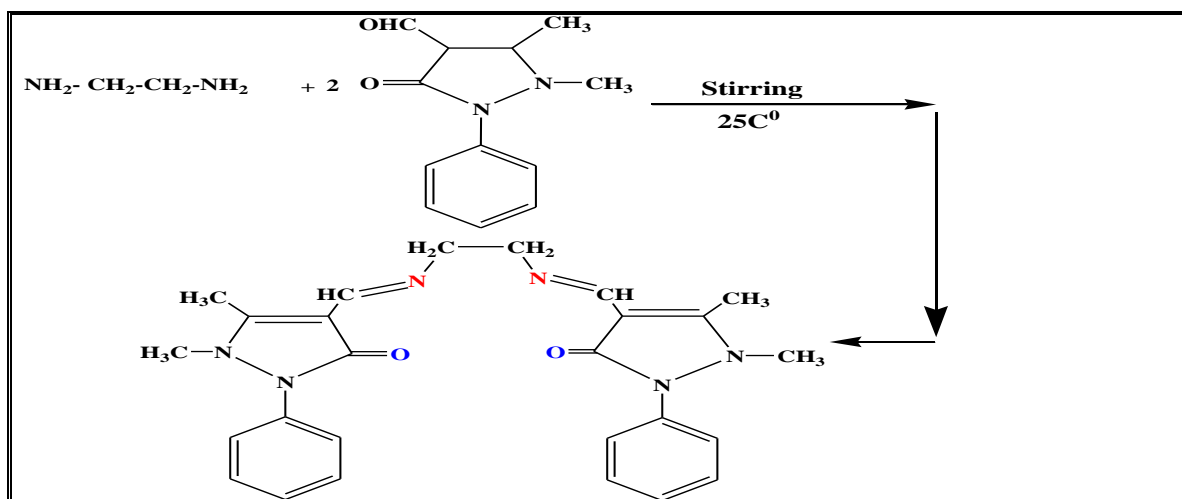
MATERIALS AND METHODS

All chemicals were obtained from commercial sources and all the chemicals used for the synthesis of Schiff bases and their metal complexes were of analytical grade and used directly. [CoCl₂.6H₂O, Cr(NO₃)₃.9H₂O, VOSO₄.xH₂O, CuCl₂.6H₂O, MnCl₂.3H₂O] and ethanol were obtained from Sigma Aldrich and B.D.H. The main instruments employed in this work are a Shimadzu double-beam UV-Vis Spectrophotometer model UV-1800 (Kyoto, Japan), Shimadzu Fourier Transform Infrared Spectrophotometer model IR- Shimadzu 3800 (Japan). Elemental microanalysis was carried out using Elemental Analyzer Model 5500 Carlo Erba Instruments (Italy). Magnetic susceptibility measurements for complexes were obtained at room temperature using (Magnetic Susceptibility Balance) Johnson Matthey Catalytic Systems Division.

Synthesis

Synthesis of ligand

A stirred solution of 4-Antipyrinecarboxaldehyde (1 gm, 4.63 mmol) in ethanol (20 ml), ethylene diamine (0.139 gm, 2.313 mmol) in ethanol was slowly added by a separation funnel with stirring at room temperature. Stirring continued for a further 6 hours and the white precipitate that had formed was filtered off with a Buchner funnel and washed with ethanol (5 ml) and diethyl ether (5 ml) before drying in vacuo affording a white crystalline powder in 81% yield and melting point 207-209°C. The reaction is illustrated schematically in scheme (1).



Scheme (1) Synthesis of Schiff base ligand

Preparation of Metal Complexes

Method(1) : An ethanol solution of the metal ions [$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{VOSO}_4 \cdot \text{XH}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 3\text{H}_2\text{O}$]:(0.13 mmol, 5mL) was added to ethanol solution of ligand (L) (0.13 mmol, 5mL) 1:1 (metal : ligand) molar ratios with continuous stirring for (2-4) hours and colored precipitates were obtained, at room temperature. washed with distilled water, dried and recrystallized from ethanol and dried at 50°C . yield, microanalysis are shown in Table (1).

Method(2) : An ethanol solution of the metal ions [$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{VOSO}_4 \cdot \text{XH}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 3\text{H}_2\text{O}$]:(0.13 mmol, 5mL) was added to ethanol solution of ligand (L) (0.13 mmol, 5mL) 1:1 (metal : ligand) molar ratios. And put in ultrasonic bath 30°C . After 50 mints crystalline colored precipitates formed after cooling at room temperature, the resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50°C . yield, microanalysis are shown in Table (1).

Stoichiometric Determination of Complexes:

The colors were change immediately when added the ligand to metal ions in different concentration, which appear the bands of complexes in visible region at maximum wavelengths. For this used Mole ratio and Continuous variation (JOB) method to make sure from the correlation ratio between ions and ligand in equilibrium media.

Mole Ratio Method:

In series of clean volumetric flask (10ml) containing $5 \times 10^{-4} \text{molL}^{-1} \text{Co}(\text{II})$, $3 \times 10^{-4} \text{molL}^{-1} \text{Cu}(\text{II})$, $3.8 \times 10^{-4} \text{molL}^{-1} \text{Cr}(\text{III})$, $2 \times 10^{-4} \text{molL}^{-1} \text{V}(\text{II})$ and $5.5 \times 10^{-4} \text{molL}^{-1} \text{Mn}(\text{II})$, added different concentration range from ligand ($5 \times 10^{-5} - 7.5 \times 10^{-4} \text{molL}^{-1}$), and diluting to the mark. The absorbances of the solutions were measured by UV-Vis spectrophotometer at λ_{max} for each complex. Then the absorbance's draw against (C_L/C_M) and estimated the molar correlation ratio from the obtaining structure.

Continuous variation (JOB) method:

In this method we depended on the same concentration for ligand and metal ions by taking a series of 1, 2, 3, 4, 5, 6, 7, 8, 9 ml of $3 \times 10^{-4} \text{molL}^{-1} \text{Co}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Cr}(\text{III})$, $\text{V}(\text{II})$, and $\text{Mn}(\text{II})$, was pipetted into each of 10 ml volumetric flask, then 9,8,7,6,5,4,3,2,1 ml of $3 \times 10^{-4} \text{molL}^{-1}$ ligand added into each volumetric flasks, after that diluting to the mark ,the solutions transferred to the cell and measurement the absorbance sequentially at λ_{max} for each complex. Then the absorbances draw against the ($\text{VM}/\text{VM}+\text{VL}$) and estimated the molar correlation ratio from the obtaining structure.

Biological Activity Studies

Bactericidal activity of the ligands and its complexes were evaluated against representative *Staphylococcus aureus* (gram-positive) and *E. coli* (gram-negative) bacteria by agar-plate method. All the compounds were prepared freshly by dissolving them in ethanol to obtain a final concentration of 5 mM. All bacteria were cultivated in nutrient agar.

RESULT AND DISCUSSION

Schiff bases were readily soluble in most of the organic solvents but their metal complexes were insoluble. The metal complexes were found soluble in DMSO. All metal complexes solids, and stable in air at room temperature but decomposed at higher temperature. The analytical data of Schiff base ligand (L) and its metal complexes are given at table (1), in a satisfactory agreement with the calculated values.

Table 1: Characterization and physical data of the prepared compounds / Found (calcd) for ligand and complexes

Compounds	Physical appearance	Melting point (C)	Elemental Analysis found%, Calc.				
			Yield %	C	H	N	O
L $C_{26}H_{28}N_6O_2$	White	207-209	81%	68.75 (68.40)	5.90 (6.18)	18.64 (18.41)	6.71 (7.01)
[VO(L)] SO ₄	Brown	>300	76%	50.86 (50.40)	4.38 (4.56)	13.62 (13.56)	17.85 (18.08)
[Cr (L) (H ₂ O) ₂](NO) ₃	Blue	294-296	69%	51.17 (51.48)	5.13 (5.32)	16.31 (16.16)	17.77 (18.46)
[Mn (L)(H ₂ O) ₂] Cl ₂	Pale - White	>300	71%	50.86 (50.50)	5.13 (5.22)	13.48 (13.59)	10.15 (10.35)
[Co (L) (H ₂ O) ₂] Cl ₂	Violet	271-273	68%	50.62 (50.17)	5.03 (5.18)	13.60 (13.50)	9.94 (10.28)
[Cu (L) (H ₂ O) ₂] Cl ₂	Green	253-255	70%	49.41 (49.80)	5.05 (5.14)	13.51 (13.40)	10.35 (10.21)

Mass spectra of the ligand

The mass spectral data of Schiff base ligand showed molecular ion peaks, which were in good agreement with the expected values. The mass spectrum of ligand L gives a peak at 456 m/z.

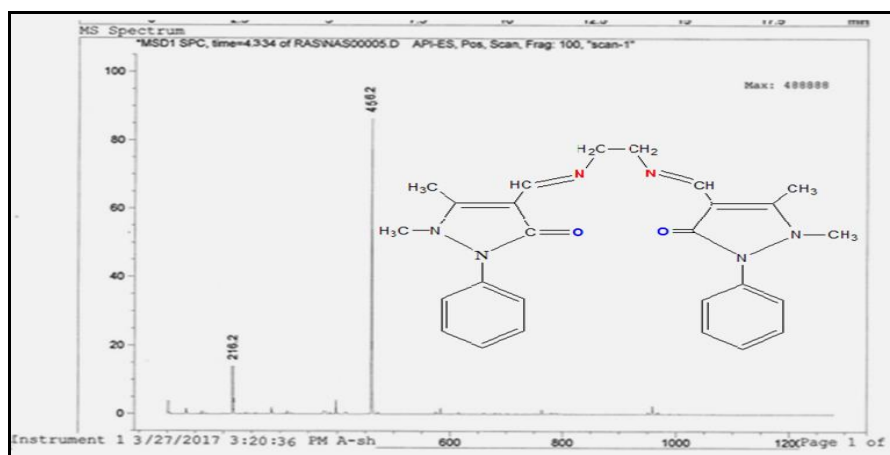


Fig 1: LC-Mass spectrum of ligand

¹H NMR Spectra

The ¹H NMR spectra of Schiff base ligand (L) is recorded in d₆-dimethylsulfoxide (CDCl₃) solution using tetramethylsilane Me₄Si (TMS) as internal standard. The singlet signal observed at ca. δ=8.431 ppm due to spectrum of free Schiff base [L] was assigned to the imine group (N=CH, H), four singlets at ca.δ=2.787-3.555ppm (s, 12H,CH₃) due to the twelve protons of four methyl groups, at ca. δ=7.291-7.549 ppm (m,10H, aromatic) due to the protons of two phenyl rings, at ca. δ=7.993 ppm (s, 4H, CH₂) due to the four protons of two methyl group, at ca. δ=1.7785ppm can be assigned to the solvent (CDCl₃). NMR data of ligand [L] are given in Table(2) & (Fig 2).

Table 2: ¹H-NMR spectral data for ligands [L] and chemical shift in ppm.

Ligand	Functional. Group	δ (ppm)
	(s, H, CH=N)	8.431
	(s, 4H, 2CH ₂)	7.993
	(m,10 H, Ar-H)	7.291 -7.549
	(s, 12H, CH ₃)	2.787,3.555
	(solvent)	1.7785

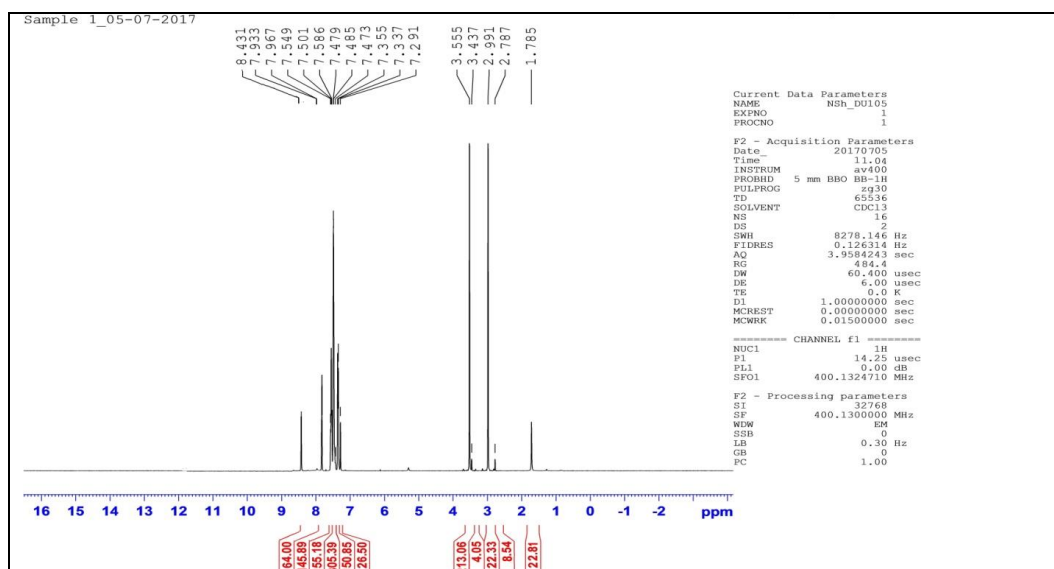


Fig 2: ¹H NMR spectrum of the ligand [L]

The FTIR Spectrum of Ligand [L] and Complexes:

The ligand [L] exhibited a strong high intensity bands appeared at 1651 and 1593 (s) cm⁻¹ which were ascribed to the stretching mode of ν(C=O) (ring pyrozol) and ν(C=N) group. The weak absorption bands appeared at 3043-3008 cm⁻¹ assigned to ν(C-H) aromatic and 2904-2935 ν(C-H) aliphatic, Table (3) and Figure (3) respectively show the FTIR of ligand. Schiff base behaved as a tetra- dentate ligand, which was been coordinating with the metal via oxygen of the carbonyl group and nitrogen of azomethane group. FTIR spectra of the complexes abroad bands were observed a round (3263, 3437, 3429, 3437) cm⁻¹ in each of Cr(III), Mn(II), Co(II) and Cu(II) complexes spectra, which are assigned to the ν(O-H) (H₂O), results led to a suggestion for the presence of coordinated water molecules[11]. New bands at (439, 439, 424, 416, 432) cm⁻¹ for metal complexes VO(II), Cr(III), Mn(II), Co(II) and Cu(II), respectively. Refer to the coordination of the ligand to the central metal ion through nitrogen atom of imine group (M-N), and (545, 536, 515, 534, 547) cm⁻¹ can be referred to ν(M-O) for the complexes with metals ions VO(II), Cr(III), Mn(II), Co(II) and Cu(II), respectively[12].

Table 3: Infrared data of Ligand and metal complexes (cm⁻¹)

Symbol	v(C=N)	v(C=O)	v(C-H) Ar	v (C-H) Al	v (O-H) H2O	v(M-O)	v(M-N)
L C26H28N6O2	1593	1651	3043-3008	2904-2935	-	-	-
[VO(L)] SO4	1599	1645	3056-3016	2885	--	545	439
[Cr (L) (H2O)2] (NO)3	1587	1643	3055	2970	3263	536	439
[Mn (L) (H2O)2] Cl2	1600	1642	3051	2943	3437	515	424
[Co (L) (H2O)2] Cl2	1600	1643	3055-3012	2931	3429	534	416
[Cu (L) (H2O)2] Cl2	1604	1642	3051-3016	2951-2900	3437	547	432

Electronic Spectra

The ultraviolet visible electronic spectrum of the ligand and complexes are given in Table(4). Electronic spectra of the all compounds were recorded in the range 190-1100 nm. The absorption spectrum of the one ligand observes absorption at 285 nm, which can be attributed to $\pi \rightarrow \pi^*$ transitions of the Schiff base ligand[9]. The UV-Vis spectrum of the vanadyl(II) complex exhibits two d-d bands observed at 582 and 427 nm assignable to ${}^2B_2 \rightarrow {}^2E$, and ${}^2B_2 \rightarrow {}^2A_1$ transitions which are characteristic of square-pyramidal geometry. The electronic spectra of Cr(III) complexes show bands at around 576, 413, and 288 nm, which may be attributed to ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$, transitions, respectively, transitions, respectively, indicating an octahedral geometry around Cr(III) ions[13]. The electronic spectrum of the Mn(II) complex shows two absorption bands at 418 and 578nm. which ascribed to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}(P)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ respectively. [14], The electronic spectra of Co(II)ion complexes showed d-d transition at 907,483.5,315, 239.5 nm, which may be attributed to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(p)$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, indicating an octahedral geometry around Co(II) ions[15,16]. electronic spectra of Cu(II) reveals bands at 902,651,330,307,235nm which are attributed to the electronic transition of ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ which refer as (${}^2E_g \rightarrow {}^2T_{2g}$) because the distorted in octahedral geometry, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ [17,18].

Table 4: Electronic spectral data of L and complexes

Compounds	Absorption bands (cm-1)	Assigned transition
L	35,088	$\pi \rightarrow \pi^*$
VO(II)	23,419 17,307	${}^2B_2 \rightarrow {}^2A_1$ ${}^2B_2 \rightarrow {}^2E$
Cr(III)	17,361 24,213 34,722	${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ $\pi \rightarrow \pi^*$
Mn(II)	23,923 17,301	${}^6A_{1g} \rightarrow {}^4T_{1g}(P)$ ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$
Co(II)	20,667 31,746 41,754	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(p)$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
Cu(II)	11,087 , 15,361 30,303 32,573 42,553	${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ${}^2B_{1g} \rightarrow {}^2E_g$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ $\pi \rightarrow \pi^*$

Molar Conductivity Measurements

Measurements of molar conductivity of complexes were dissolved in DMSO (1×10^{-3} M) and solutions of ligand and complexes were measured at room temperature (25°C), the conductance listed in Table(4).

Magnetic susceptibility measurement

Magnetic susceptibility values of the metal complexes are listed in table (5). Magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbital in the outer shell of these elements, these magnetic measurements give an outline about the electronic state of the metal ion in the complexes. VO(II) complex was approximately 1.72 B.M. and referred as paramagnetic and the geometry of Vanadyl(II) metal center was square pyramidal [19]. Co(II) complexes have magnetic moment values 4.8 B.M. which agrees well with the expected value for a high-spin Co(II) ion in an octahedral [20], Cr(III) complexes are the 3.9 B.M. being consistent with mononuclear complexes and free from antiferromagnetism. The complexes may exist in octahedral geometries [21], also or Cu(II) metal complexes magnetic moment was found in the range 1.80 B.M. These values suggested the octahedral geometry around Cu(II) ion and magnetic moment for Mn^{2+} is 5.9 B.M. tetrahedral.

Table 5: Magnetic moment and Conductivity measurements of complexes

Compounds	Conductivity ($\mu S/cm$) in DMSO	Magnetic moment (B.M.)	Proposed structure
VO(II)	32	1.72	square pyramidal
Cr(III)	155	3.9	octahedral
Mn(II)	71	5.9	octahedral
Co(II)	77	4.8	octahedral
Cu(II)	81	1.8	octahedral

Stoichiometric Determination of Complexes:

Mole Ratio Method:

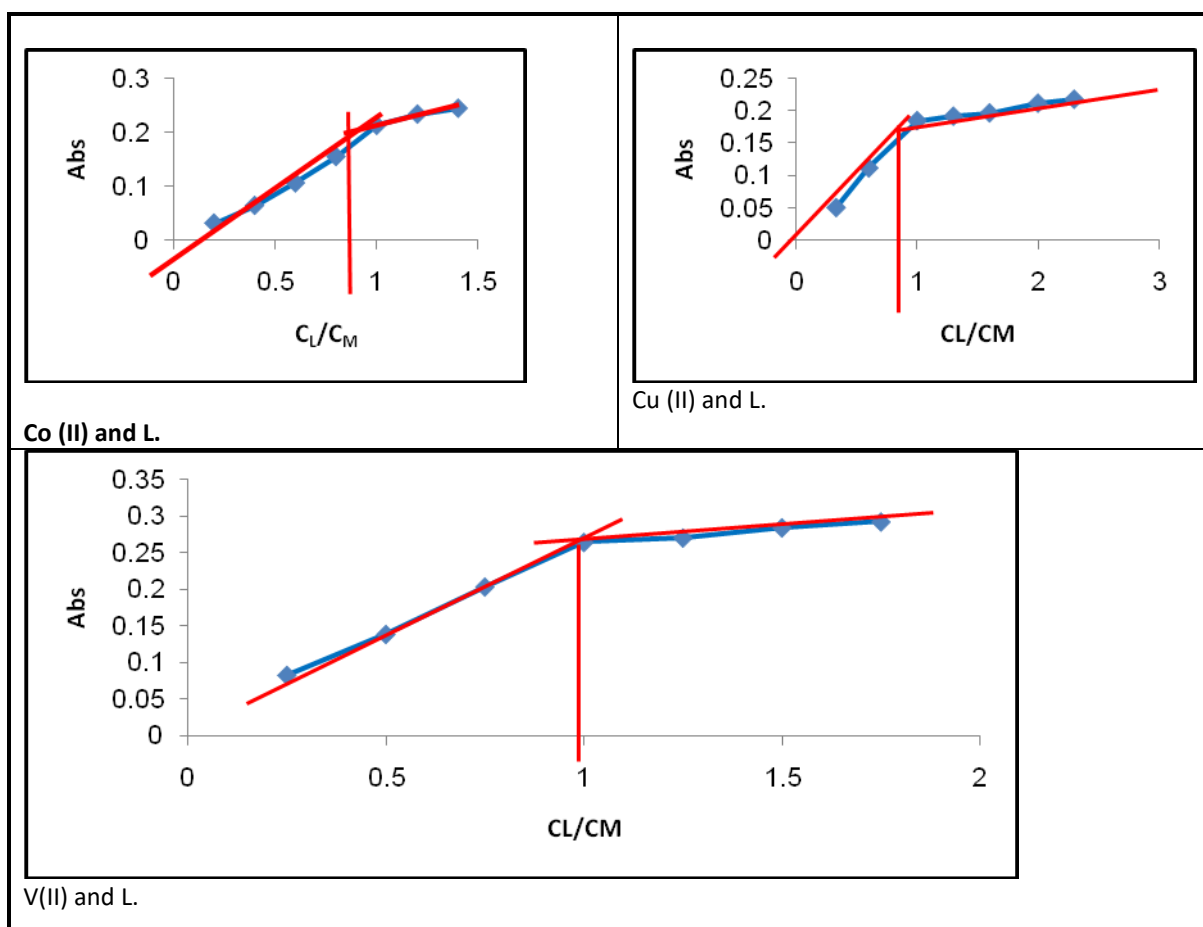


Fig 3: Mole ratio plot of complex between metal and L Continuous variation (JOB) method:

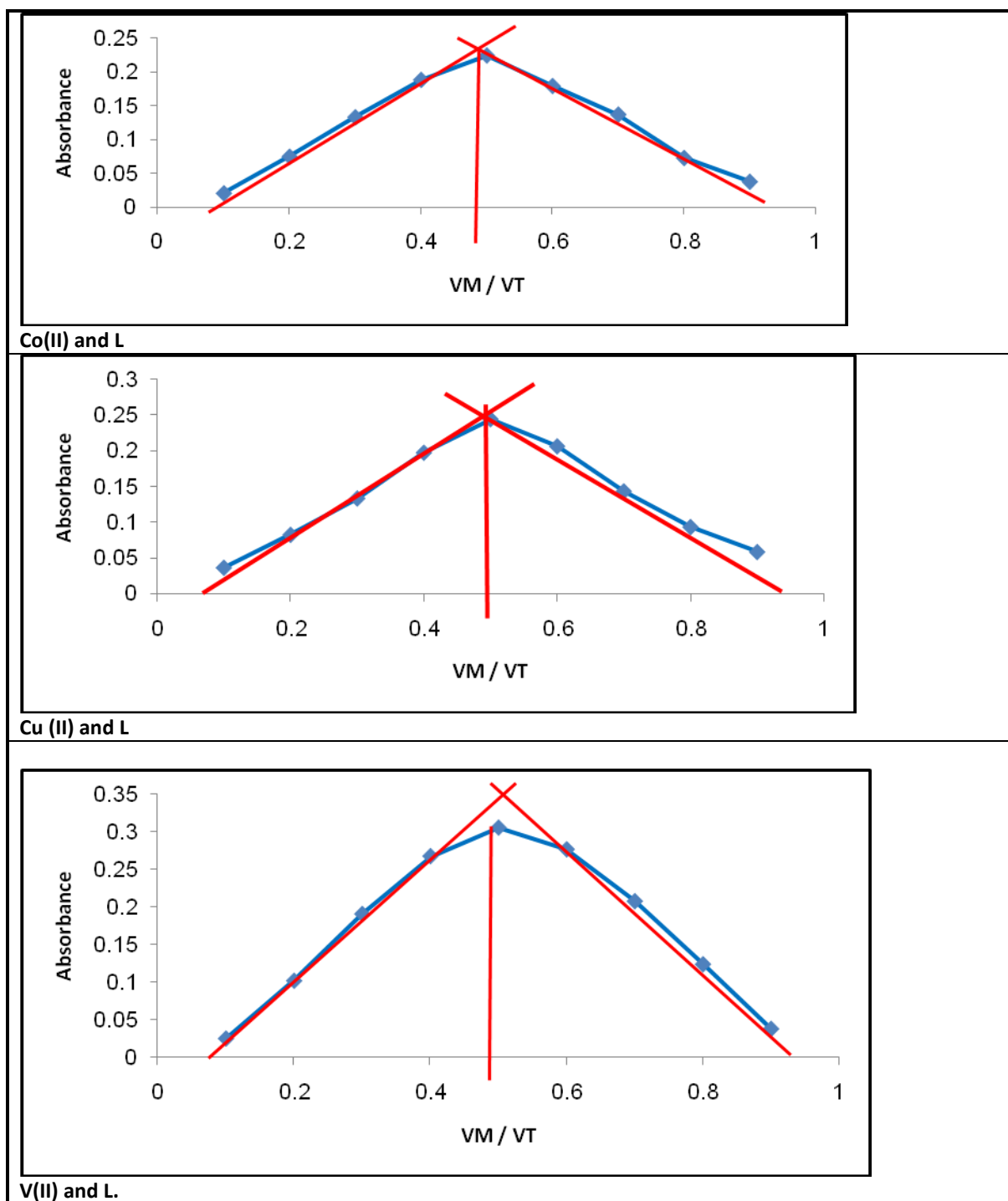


Fig 4: Continuous variation method plot of complex between metal and L

Biological Activity Studies

The bacteriological activity of the ligand [L] and its metal complexes was studied by using inhibition method for two types of pathogenic bacteria. One type of bacteria was gram positive, which is *Staphylococcus aureus*. The second one was gram negative, which is *Escherichia coli*. The biological effect of the chemical complexes was studied for the (2) types of bacteria as shown in Table (6).

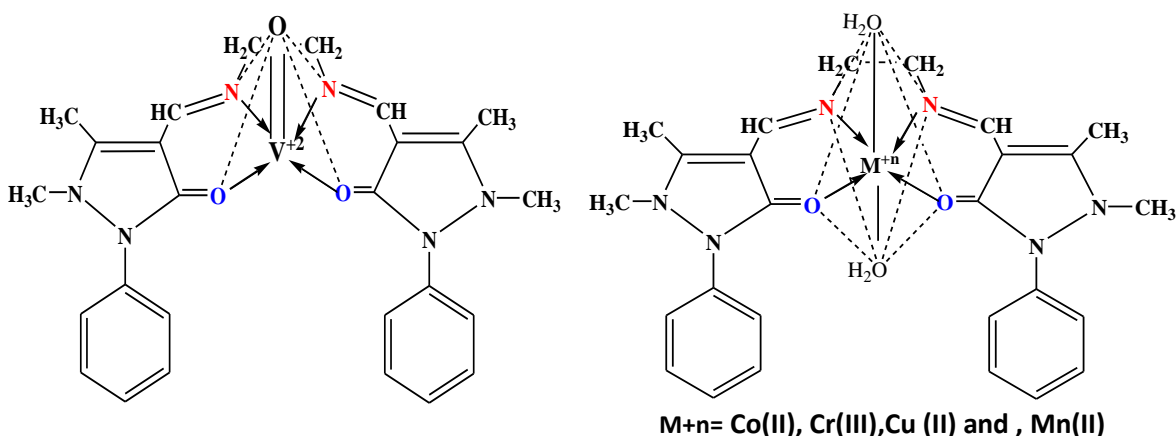
Table 6: Biological activity of the ligands and their mixed ligand metal complexes

Compounds	Staphylococcus aureus (5mm)	Escherichia coli(5mm)
L	++	+
VO(II)	+	++
Cr(III)	+++	++
Mn(II)	++	++
Co(II)	++	+++
Cu(II)	++	++

Effectiveness was classified into three zones on the bases of their diameter of zone of inhibition: / :+++Most effective, /++: Moderate effective., / +: Slightly effective.

CONCLUSION

This paper describes the synthesis and characterization of a Schiff base derived from 4-antipyrincarboxaldehyde] with [Ethylene di-amine] and its five complexes. [L] was coordinated to five different metal ions via oxygen and nitrogen atoms to afford the corresponding complexes.. General structures of the complexes are shown in Fig (5). The Co(II), Cr(III),Cu (II) and , Mn(II) complexes probability show octahedral geometry, while VO(II) complex probability shows square pyramidal geometry.


Fig (3) complexes

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