Synthesis, Spectral, Biological, Studies of Schiff base complex of Cu(II), Co(II), Ru(III) and V(II) of Thiophene-2- Carboxaldehyde and 4-aminoantipyrine

[1]Mrs.N.SRIVIDHYA,
ASSISTANT PROFESSOR, DEPARTMENT OF CHEMISTRY,
PSNA COLLEGE OF ENGINEERING AND TECHNOLOGY, DINIDIGUL.

Abstract

New coordinated ruthenium (III) complex, copper, cobalt and vanadium complexes of the type [M(L)] (L = monobasic bidentate Schiff base derived from the condensation of 4- aminoantipyrine with Thiophene -2-carboxaldehyde) have been synthesized. The new complexes have been characterized by analytical, spectral (^{1}H-NMR, IR, UV-Vis and EPR), antibacterial, antifungal and antioxidant studies. The results indicate that the some metal complexes are having significant activity than its ligands against the some microorganisms under identical experimental conditions. Some metal complexes show good Anti-oxidant properties.

Key words: 4 –Aminoantipyrine, Antimicrobial studies, Cytotoxic Studies

1. Introduction

Schiff bases are significant class of compounds which can be used in a variety of studies, such as organic synthesis, catalyst and drug design [1–3] and models for active sites of metalloenzymes [4]. They are the most versatile group of chelators for facile preparation of metal–organic hybrid materials [5–10], single molecule based magnets [11–16], highly porous materials [17,18], optoelectronic devices [19–21], and sensors [22–24]. The syntheses of 4-aminoantipyrine derivatives have attracted the attention of several research groups due to their potential biological activities [25]. In this context, broad spectra of bioactive 4-aminoantipyrine derivatives and their metal complexes have been investigated and diversities of bioactivities such as analgesic[26-27],anti-inflammatory,anti-microbial[28-29],anti-cancer activity[30] have been reported. The increasing microbial resistance to antibiotics is a very important necessity which inculcates the search for new compounds with potential effects against pathogenic bacteria and fungi [31,32]. The most spectacular advances in medicinal

chemistry have been made when heterocyclic compounds played an important role in regulating biological activities. Heterocyclic moieties can be found in a large number of compounds which display biological activity

[33]. Anti-pyrine (N-heterocyclic compound) and its derivatives exhibit a wide range of biological activities and applications. Because of their interesting structural features as well as the biological activity, a wide range of metal complexes derived from anti-pyrine derivatives have been reported [34,35]. Pyrazolone-based ligands display variable complexing behaviour and a variety of co-ordination possibilities to metal centre.

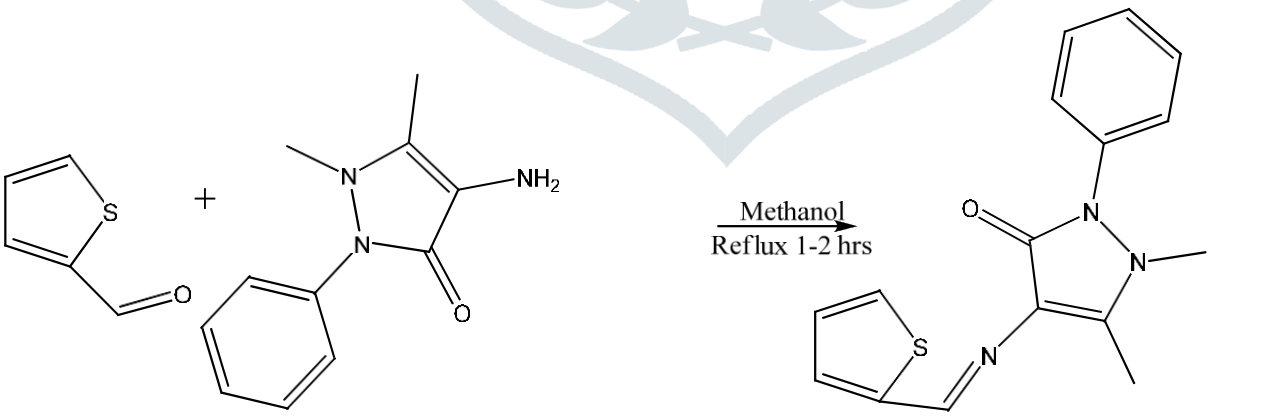
In view of biological importance of Schiff base derived from the condensation of 4-aminoantipyrine with derived thiophene-2-aldehyde, its applications in various fields, in the present investigation it is thought to synthesize the metal complexes with transition metal ions such as Co(II), Cu(II), Ru(III) and V(II). It is therefore of interest to carryout investigations to understand how a ligand environment and its metal complexes show the activity in bacterial and fungal activity and the spectral properties show the interest in cytotoxic studies of the inorganic complex.

2. Experimental

The instruments used for various physical measurements are (**FT- IR, ^{1}H-NMR, UV-Vis, EPR**).

2.1 Synthesis of Schiff base ligand

A solution of 1-phenyl-2,3-dimethyl-4-amino-3-pyrazolin-5-one (0.4065g,1 mmol) in ethanol (5 ml) was added to a solution of thiophene-2-Carboxaldehyde (1.869 ml, 1 m mol) in methanol (5 ml). The reaction mixture was stirred for 2 hrs at room temperature then heated to reflux for 2 hrs and kept at 273 K for 4hrs. The characteristic pale-green precipitate obtained was filtered and recrystallized by dissolving in methanol (m.p. 175ºC). Yield: 86%.

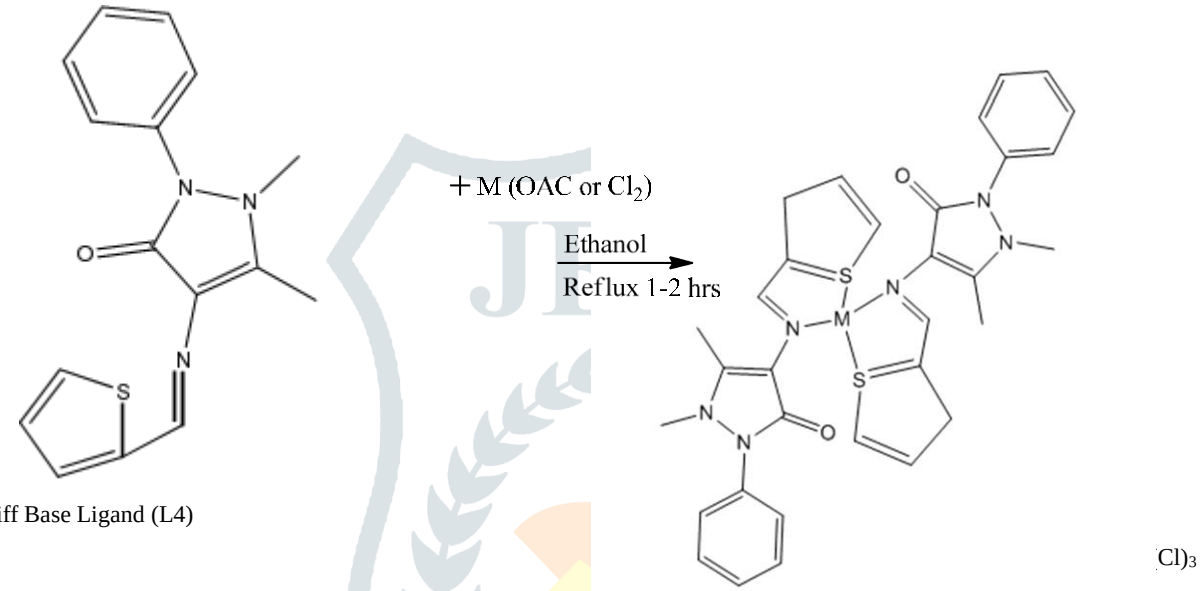


Thiophene-2- carboxaldehyde 4-Aminoantipyrine (E)-1,5dimethyl-2-pheyl-4-(thiophene-2-ylmethyleneamnio)-1H-pyrazole-3(2H)-one

Figure .1 Synthesis of Schiff base Ligand (L4)

2.2 Synthesis of metal complexes

An ethanol solution of Metal (II) acetate and Chloride (1 m mol, 15 ml aqueous ethanol) was added drop wise to a stirred ethanol solution of the Schiff base ligand. The resulting solution was gently heated for 5 hrs with constant stirring. The precipitate solid was filtered, washed with hot water, and then ethanol followed by ether and dried in Vacuum. Yield: 70%; M.p. 210ºC. The complex is soluble in DMF and DMSO.



Schiff Base Ligand (L4)

Figure.2 Synthesis of Schiff base metal complexes

3. Results andDiscussion

Analytical, colour and magnetic susceptibility data of all metal complexes are given in Table.1 and are in good agreement with proposed composition.

Table.1 Colour, Analytical data and Magnetic Moment of complexes.

Compound	Empirical formula	Color	Elemental Analysis Cal. % (Found) C	H	N	Magnetic moment (μ_B)
Ligand (L4)	$C_{16}H_{15}N_3OS$	Pale brown	72.32 (69.75)	6.43 (6.82)	9.92 (9.54)	-
Cu(L4)	$C_{32}H_{30}CuN_6O_2S_2$	Brown	65.21 (65.55)	5.47 (5.65)	8.95 (8.72)	1.89
Co(L4)	$C_{32}H_{30}CoN_6O_2S_2$	Red	65.70 (65.43)	5.51 (5.89)	9.01 (8.85)	4.62
			64.86 (64.55)	5.44 (5.75)	8.90 (8.61)	1.92
			65.02	5.46	8.92	-

Ru(L4)	$C_{32}H_{30}RuN_6O_2S_2$	Green
V(L4)	$C_{32}H_{30}VN_6O_2S_2$	Pale yellow

3.1. ^{1}H-NMRSpectra

The ^{1}H-NMR spectrum of the ligand were recorded at room temperature in $CDCl_3$.The ^{1}H-NMR spectrum shows the peaks at 6.2-7.2 δ (m) shows the phenyl multiplet of Schiff base ligand (Fig.3.1a) The ligand also shows the following signals:=C-CH_3 2.1–2.8(S); -CH=N 9.3 δ (s) and 7.72, 7.94 and 7.983.

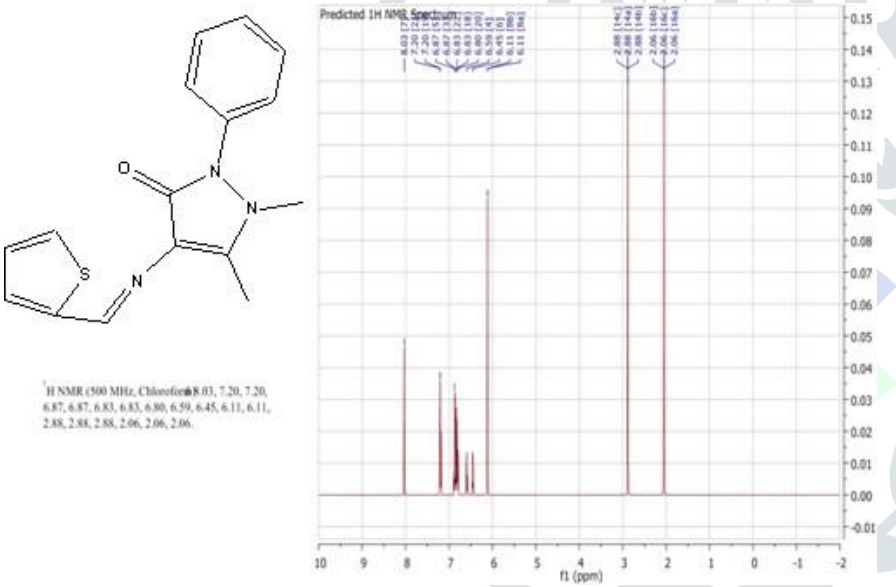


Figure . 3.1 a ^{1}H-NMR Spectra for Schiff base Ligand

3.2. Infrared spectra of the ligands and their metal complexes

The coordination sites of the ligand to the metal ions were investigated by comparing the infrared spectra of the free ligand with their metal complexes. The IR spectra of the Schiff base ligand (L_4) show a band at 1630 cm^{-1} which is assigned to azomethine ν (CH=N) linkage. These bands are shifted towards lower frequencies in the spectra of their metal complexes (1608–1606 cm^{-1}). The comparison of the IR spectra of the complexes with the above Schiff bases indicates the involvement of the azomethine nitrogen in chelation with the metal ion. The coordination of nitrogen to the metal ion could be expected to reduce the electron density of the azomethine link and thus causes a shift in the ν(CH=N) group Conclusive evidence of the bonding is also shown by the

observation that new bands in the spectra of all metal complexes appearing in the low frequency regions at 768-763 cm^{-1} and 681-603 cm^{-1} characteristic to ν(M-S) and ν(M-N) stretching vibrations respectively, that are not observed in the spectra of free ligands [36-40].

Table . 2 FT-IR Spectrum of ligand and its metal complexes (in cm^{-1})

Compound	**υ*(CH=N)***	**υ*(C-N)***	**υ*(M-N)***
L4	1645	1325	-
Cu(L4)	1631	1246	778
Co(L4)	1619	1252	766
Ru(L4)	1610	1277	763
V(L4)	1604	1303	767

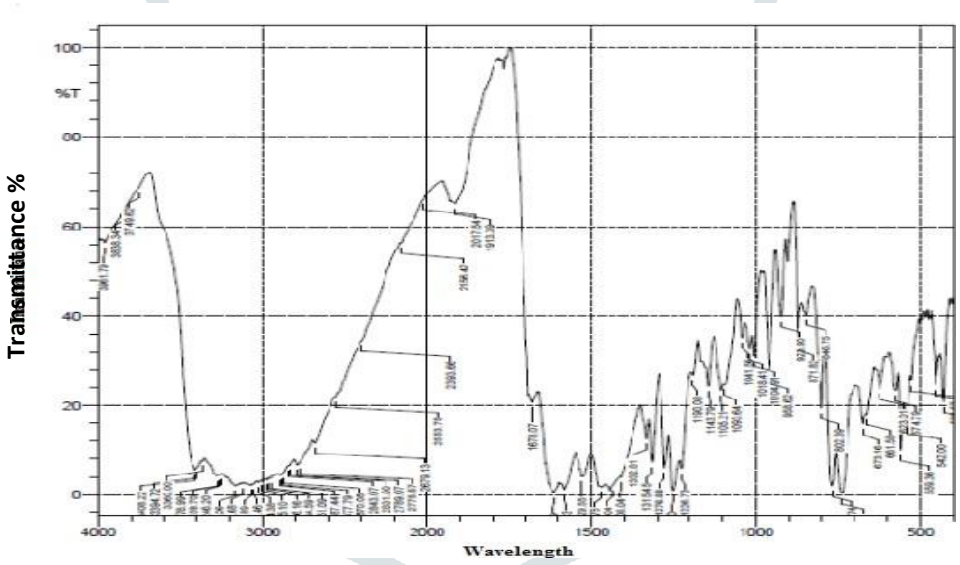


Figure.3.2a FT-IR spectrum of ligand (L)

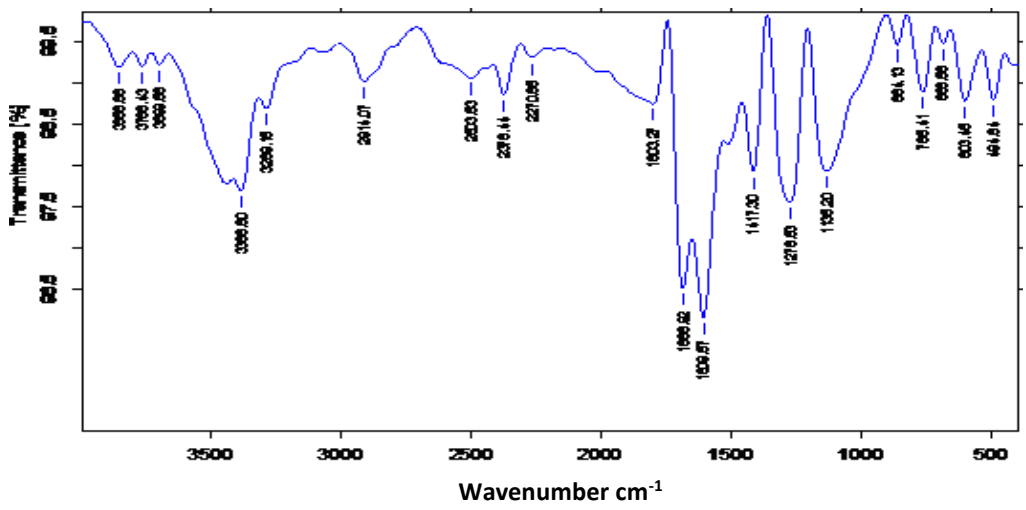


Figure .3.2b FT-IR spectrum of Copper (II) complex

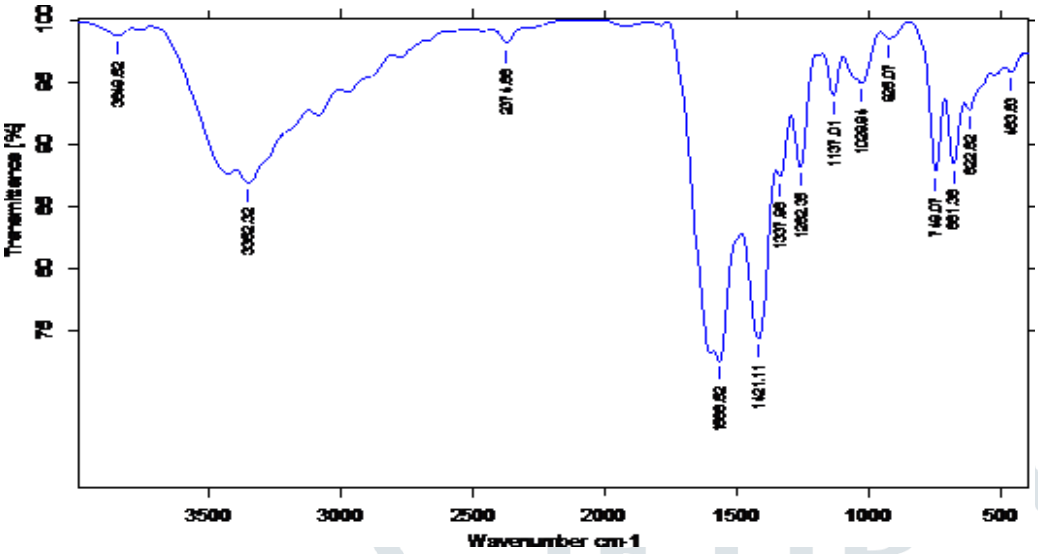


Figure.3.2c FT-IR spectrum of Cobalt (II) complex

3.3 Electronic spectra of ligand and its metal complexes

The UV-Visible spectra are recorded in $CHCl_3$ in the range of 726 nm of the Schiff base. The UV–Vis. spectrum of the ligand exhibits an absorption band at 355 nm, which can be attributed to the n-π* transition of azomethine chromophore. The molar absorptivity ligand at 355nm may be assigned to a transition between the lone- pair electrons of the p orbitals of the N atoms in the azomethine (HC=N) groups and the π bonds of the aromatic rings [41, 42]. The peaks at 276 nm are assigned to the π-π* transitions of the Schiff base. In the present case, the absorption band in the

420 nm range, which is assigned to a metal ligand charge transfer band. The electronic spectrum of the Cu(II) complex shows a broad band at 515 nm assignable to transition [43] which is characteristic of square planar environment.

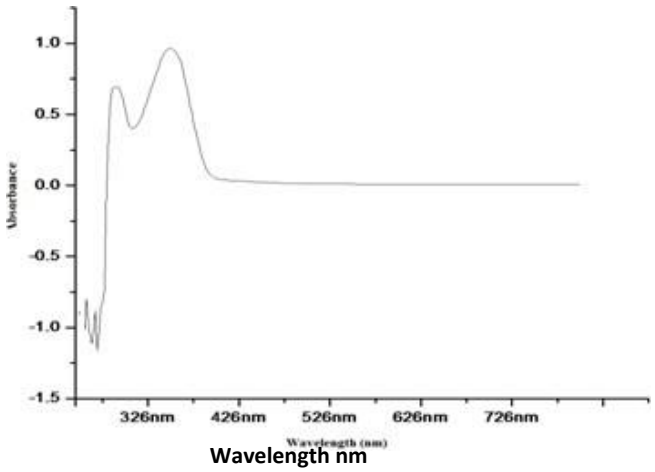


Figure.3.3 a UV-visible Spectrum of Ligand

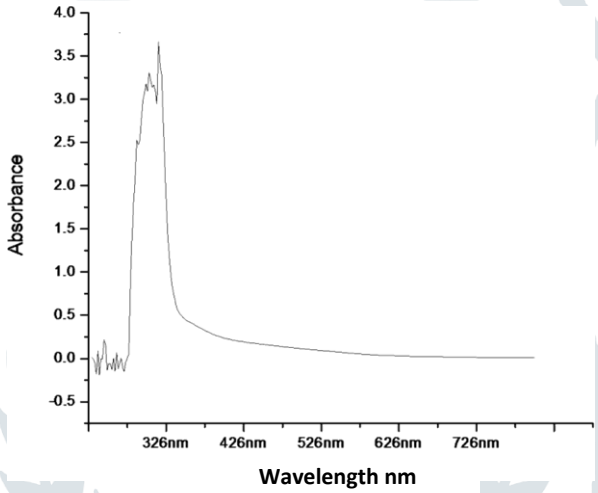


Figure.3.3 b UV-visible Spectrum of Copper (II) Complex

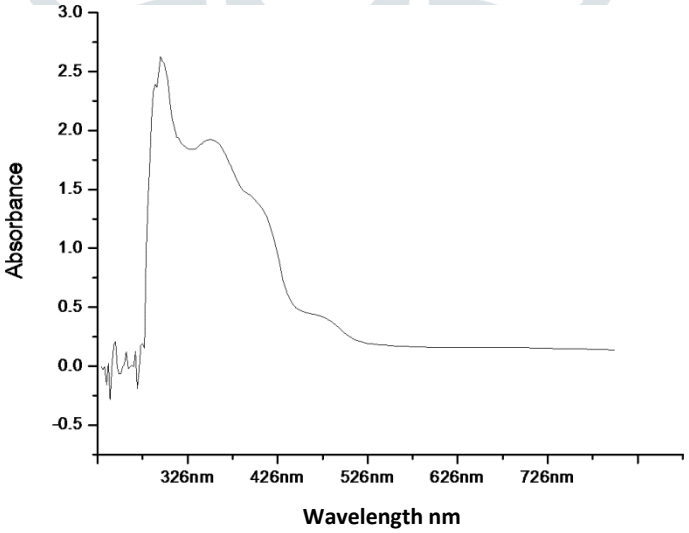


Figure.3.3 c UV-Visible Spectrum of Vanadium (II) Complex

3.4 Anti-bacterial activity

The results of the anti-bacterial and anti-fungal activity are tabulated in Table.3

DMSO was used as a negative control and Amikacin was used as positive standards for anti-bacterial studies. The ligand and metal complexes show greater anti-microbial activity than those of the control drug; this indicates that the complexation with metal enhances the activity of the ligand. This is explained on the basis of Overtone's concept and chelation theory [45]. Chelation tends to make the ligand a more powerful and potent bacterial agent. A possible explanation for this increase in the activity upon chelation is that, in a chelated complex, the positive charge of the metal is partially shared with donor atoms present in the ligands and there is an electron delocalization over the whole chelated ring. This, in turn, increases the lipid layers of the bacterial membranes. Generally, it is suggested that the chelated complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these micro-organisms [46 47]. The synthesized compounds exhibit moderate to strong anti-microbial activity. The Co(II) complex exhibits a higher activity than the other metal complexes towards bacterial species. The Cu(II) shows equal activity against *S.Typhi*, *K.Pneumonia*, *S.Aureus* bacteria compared to the standard and moderate activity was found against other bacterial species. Co(II) and V(II) complexes are having low activity compared to the standard. Ru(III) complex displays moderate activity against the bacteria. Other complexes are having moderate to low activity compared to the standard.

Table.3 Minimum inhibition Concentration (MIC) μg/ml data of the synthesized ligand and metal complexes against growth of bacteria

Minimum inhibition Concentration

Compound	**Salmonellatyphi**	**Klebsiella Niger**	**Staphylococci aureus**
Standard(Amikacin)	**17**	**18**	**16**
L4	**14**	**10**	**12**
[Cu(L4)	**11**	**11**	**14**
[Co(L4)	**8**	**10**	**9**
[Ru(L4)	**10**	**12**	**13**
[V(L4)	**12**	**11**	**6**

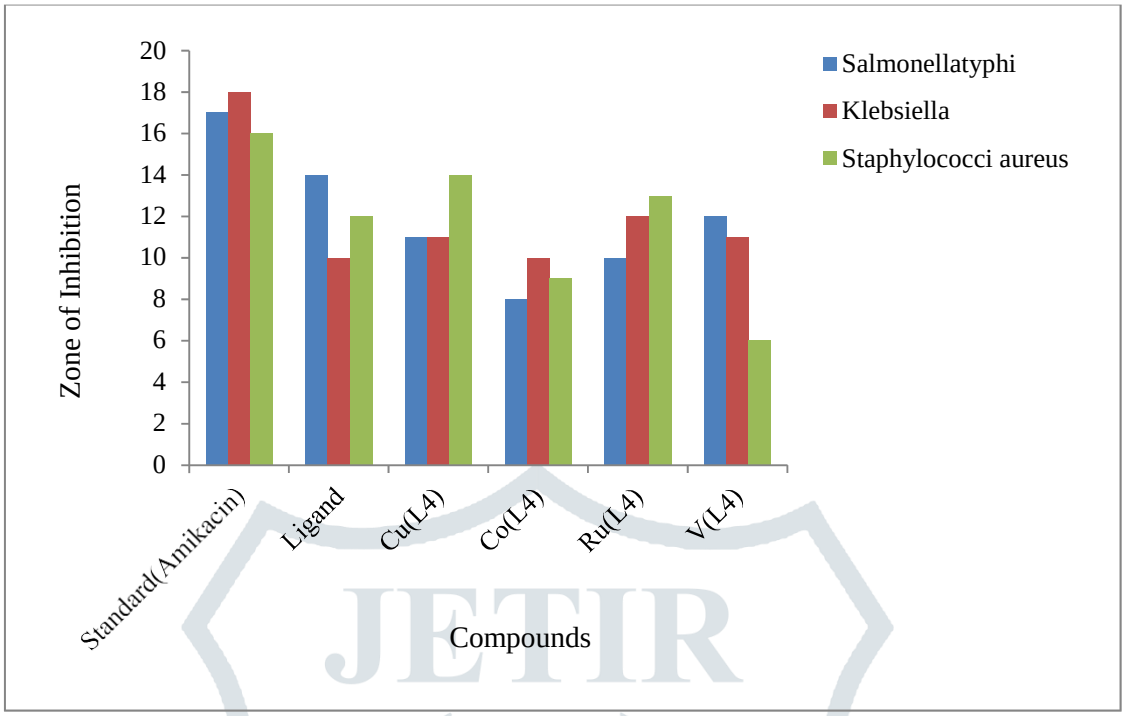
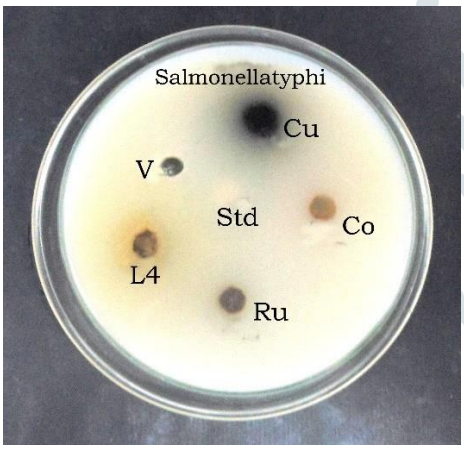
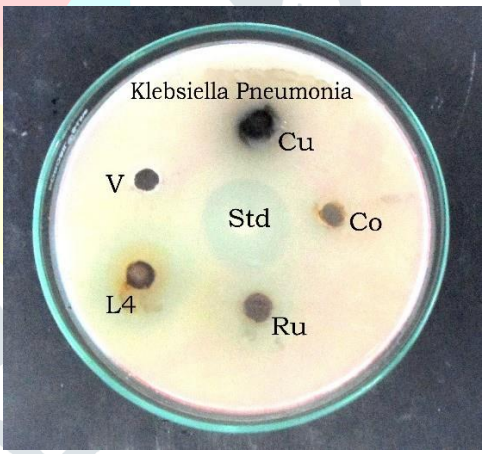


Figure .3.4a Zone of Inhibition for Synthesized compounds against various pathogenicbacteria





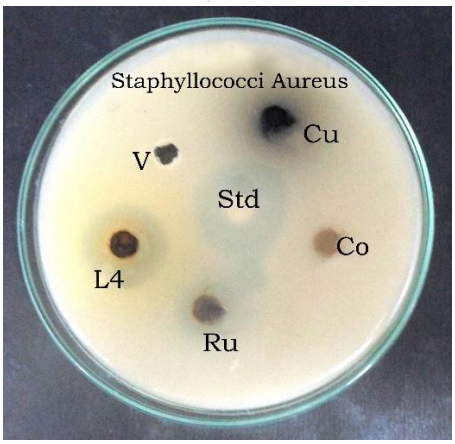


Figure.3.4b Image Zone of Inhibition of Synthesized compounds against various pathogenic bacteria

3.5 Anti-fungal activity

To provide a medicinal scope in the field of bio-inorganic chemistry, consequently, the metal complexes synthesized have been evaluated for their anti- fungal actions. The anti-fungal tests were carried out using the disc diffusion method. The Schiff base ligands and their metal complexes were screened in vitro in order to find out the anti-fungal activity against Aspergillus Niger, Candidatrophical and Candida albicans. The results of the anti-fungal studies are presented in Table 4. which reveal that the metal complexes are toxic than the free ligands against the same organisms. As the number of alkyl group in the ligand increases, it will decrease anti-fungicidal activity of the complexes. The increase in the anti-fungal activity of the metal complexes inhibits multiplication process of the microbes by blocking their active sites. Such increased activity on metal chelation can be explained on the basis

of Tweedy's chelation theory [47]. The chelation also increases the lipophilic nature and the interaction between the metal ion and the lipid is favoured. This may lead to the breakdown of the permeability barrier of the cell resulting in interference with the normal cell processes. While chelation is not the only factor for antimicrobial activity, it is an intricate blend of several aspects such as nature of the metal ion and the ligand, the geometry of the metal complexes, the lipophilicity, the presence of co-ligands, the steric and pharmacokinetic factors [48]. The synthesized compounds having amino acid moieties also show good activity.

Table 4. Minimum Inhibition Concentration (MIC) µg/ml data of the synthesized ligand and metal complexes against growth of fungi

Minimum Inhibition Concentration Compound		**Salmonellatyphi**	**Klebsiella Niger**	**Staphylococci aureus**
Standard(Ketaconazole)	Zone of Inhibition	17	18	16
L(4)		16	16	17
[Cu(L4)		16	10	13
[Co(L4)		10	8	10
[Ru(L4)		12	11	13
[V(L4)		10	10	12

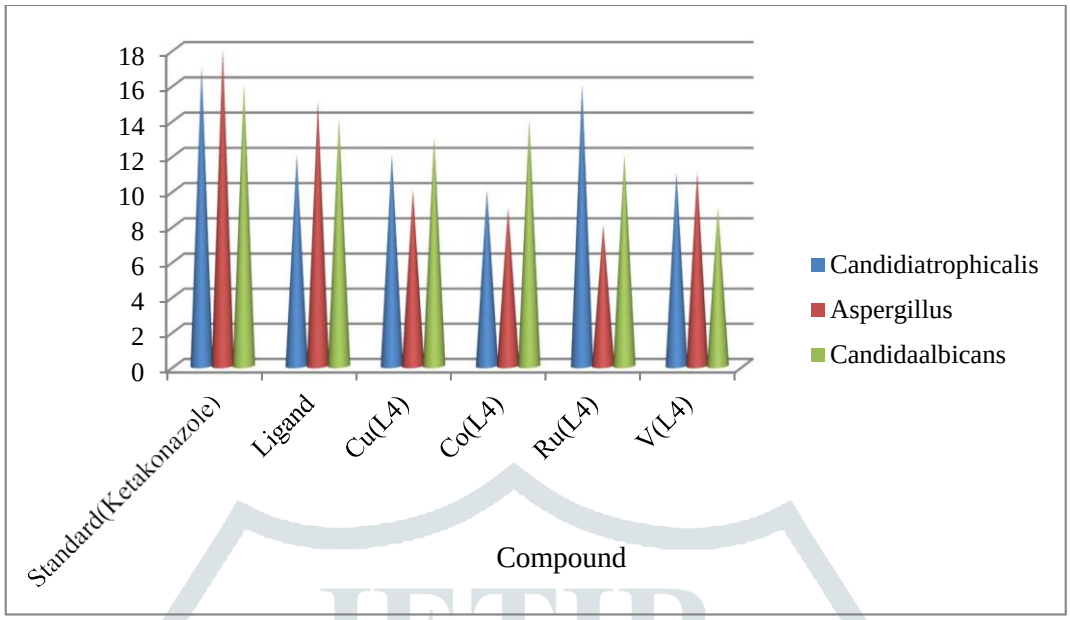


Figure.3.5 a Zone of Inhibition for synthesized compounds against various pathogenic fungi

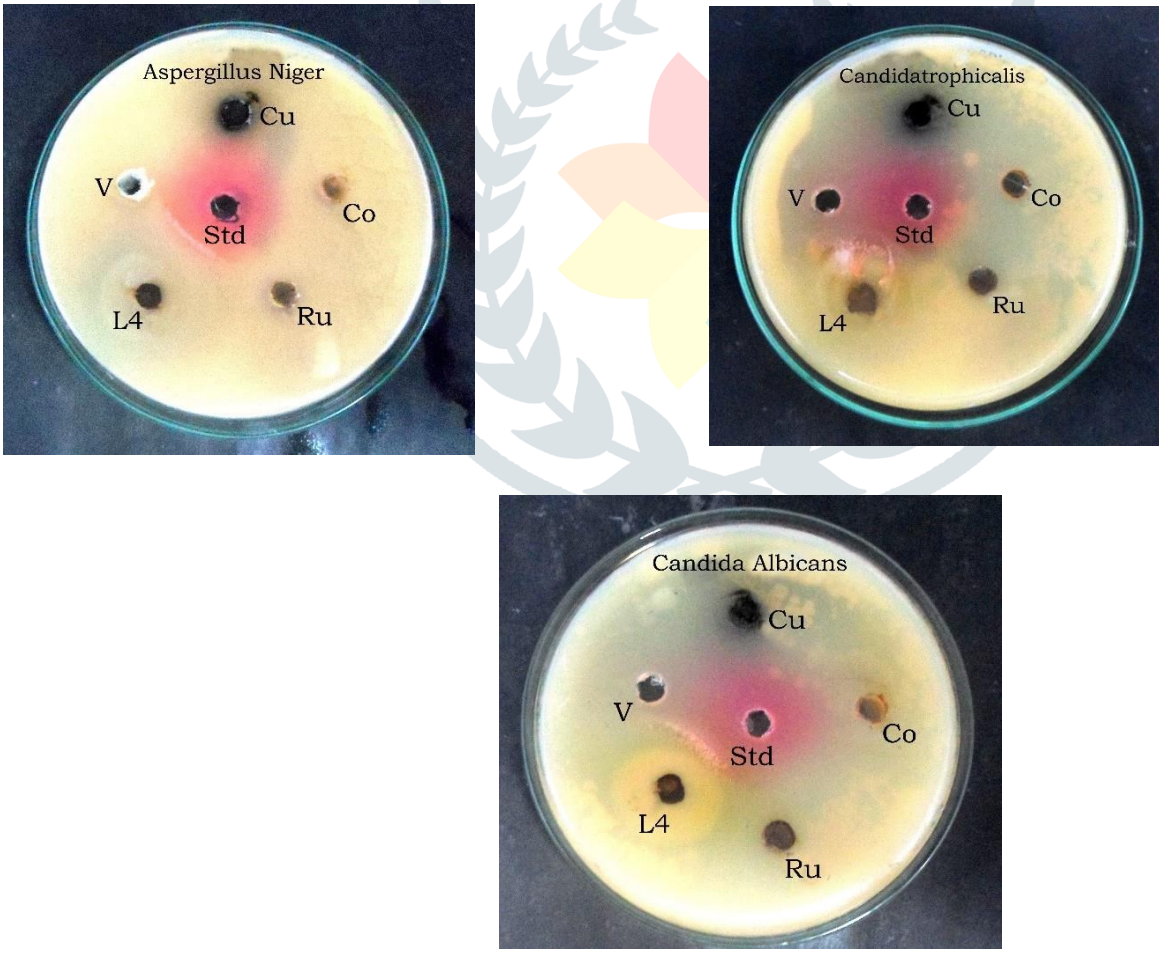


Figure 3.5b Images Zone of Inhibition of synthesized compounds against various pathogenic Fungi

3.6 Anti-oxidant assay (free radical scavenging activity)

It is well documented that the reactive oxygen species (ROS) are involved in the pathogenesis numerous chronic disease such as atherosclerosis, hypertension and coronary heart disease [49] These free radicals are produced under certain environmental conditions and during normal cellular functions in the body. Antioxidants thus play an important role to protect the human by reactive oxygen species. The ability of Schiff bases and their metal complexes to scavenge free radicals is an important property. Different modes of action such as being free radical terminators chelators of metal ions involved in catalyzing lipid oxidation or oxygen scavengers that react with oxygen closed system have been used in categorizing antioxidants [50]. In this study, we present the DPPH scavenging ability of the Schiff base and the corresponding Ru(II),V(II),Co(II),Cu(II)complexes.The anti-oxidant

assay was carried out using different concentration of the test samples, while ascorbic acid (Vitamic C) were used as standards.

3.7 DPPH Radical Scavenging ActivityAssay

The scavenging activity of a chemical/or compound on the DPPH radical as a fast and reliable parameter to measure the *in vitro* antioxidant activity of such sample have been used by diverse researchers [51]. This assay is based on the measurement of the decrease in molar absorptivity of DPPH at 517 nm after reaction with the test compound. The effect of antioxidants on DPPH radical scavenging is due to the hydrogen donating ability or radical scavenging activity of the samples [52].

The scavenging reaction between (DPPH) and an antioxidant (H-D) can be written as: (DPPH) + (H-D) →

DPPH-H + (D)

(Purple) (Yellow)

Anti-oxidants react with DPPH, a stable free radical that is thus reduced, and as a result the absorbance decreases due to the formation of the DPPH-H from the DPPH radical. The degree of decolouration indicates the scavenging potential of the anti-oxidant compounds or samples in terms of hydrogen donating ability. Figure 3.7a shows the dose-response curve of DPPH radical scavenging activity of the Schiff base $DPPH_2$ and its Cu(II), Co(II), Ru(III) and V(II) complexes, compared with ascorbic acid.

It was observed that metal (II) complexes had higher activity than that of the free Schiff Base ligand. At the lowest concentration (100 μg/mL) the antioxidant activity of the free ligand was found to be low but, upon

complexation, it increased significantly.

The Schiff base ligand and its metal complexes were screened for free radical scavenging activity by the DPPH method. The results of free radical scavenger activity of compounds at different concentration are presented in fig. Among the examined compounds Schiff base ligand and its metal complexes have exhibited a good free radical scavenging activity. Further the synthesized compounds scavenged the DPPH radical in a concentration (**100(µg/ml)** dependent manner.

Table.5 % Anti-oxidant of Ligands and Metal (II) Complexes

Concentration (µg/ml)	**Ligand (L)**	**Cu(L4)**	**Co(L4)**	**V(L4)**	**Ru(L4)**
100	19.5	12.1	12..3	13	14.2
200	25	28.2	24.6	28.2	21.2
300	31	30.1	31.2	33.1	27.6
400	37	34.5	38.4	37.2	39
500	42	39.5	47.3	43.2	45.3

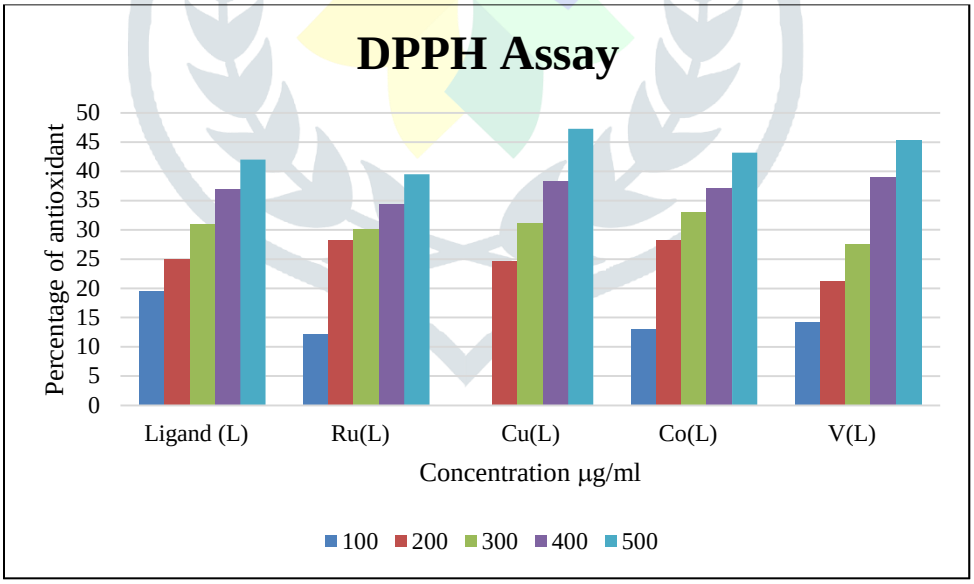


Figure .3.7a DPPH scavenging activity of Schiff bases and their metal (II) complexes

4. Conclusion

The Synthesis, isolation of solid products and spectroscopic characterization of a new bidentate Schiff base

derived from Thiophene-2-Carboxaldehyde with 4- Aminoantipyrine and its complexes with Cu(II), Co(II), Ru(III), V(II). It is tentatively proposed that the Schiff base ligand coordinates through the nitrogen of the 4-aminoantipyrine moiety and the sulfur of the thiophene ring, forming a stable chelate ring structures. Based on the above interpretations, proposed structure for all the complexes shows proposed structure. The synthesized metal complexes, in comparison to the free Schiff base ligand, were screened for their antibacterial activity.The anti-microbial activities of the complexes shows good activity for the copper complexes and for Co(II), Ru(III),V(II) shows the moderate activity. The Anti-fungal activities of the copper complexes shows good activity. Further, the anti-oxidant activity results obtained against free radicals confirmed that the complexes are effective at preventing the formation of the DPPH and the lower IC50 values observed in antioxidant assay showed that the synthesized complexes exhibited differential and selective effects to scavenge radicals and hence potential as chemotherapeutic drugs to eliminate pathological radical-related diseases from the system.

5. References

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