

Synthesis, characterization and studies on metal (II) complexes of 2-methoxy-6-nitro-4-((thiazol-2-ylimino)methyl)phenol

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ABSTRACT

A new set of metal(II) complex was prepared from the ligand formed by reacting 2-aminothiazole with 5-nitro vanillin. The compounds were characterized using various spectroscopic and analytical techniques. The anti bacterial and antifungal studies were done using well cut method, apart from that anti-oxidant studies, powder XRD studies were performed on the compounds.

Keywords: Metal(II) complex, 2-aminothiazole, 5-nitro vanillin, 2-methoxy-6-nitro-4-((thiazol-2-ylimino)methyl)phenol and biological studies.

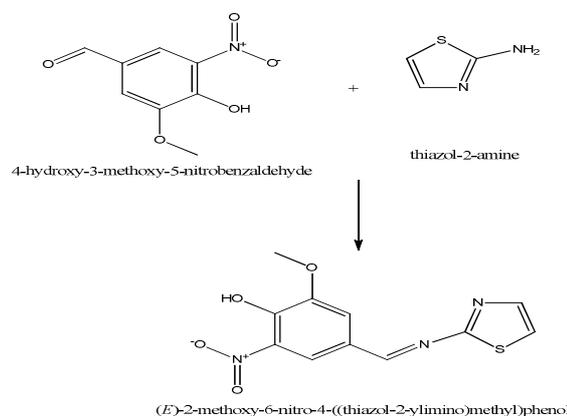
1. INTRODUCTION

Schiff bases are formed by condensation of a primary amine and aldehydes or ketones easily due to their availability, electronic properties and good solubility in common solvents. Because of wider applications as antimicrobial, anti-inflammatory, anti-degenerative and anti-HIV agents, drugs [1-5]. Various bioactive heterocyclic compounds are synthesized in which Thiazole containing Schiff bases are important because of the coordination ability of exocyclic nitrogen, cyclic sulphur and nitrogen and π electrons present in the ring. Derivatives of Thiazoles are used as starting material for the synthesis of bioactive materials in the design of molecular models and material chemistry form a part of vitamin B1 and coenzyme carboxylase [6-8]. The facile syntheses, easily availability, electronic properties and good solubility in common solvents of 2-aminothiazole containing nitrogen and sulphur as the donor atoms in the ring exhibit a wide spectrum of biological activities. Due to the strong aromaticity of the ring system, thiazole and substituted thiazoles possess very interesting biological activity. So 2-aminothiazoles are used to synthesize sulphur drugs, biocides, fungicides, dyes and chemical reaction accelerators. They provide many potential binding sites for

complexation with metal ions [9]. Schiff bases of them have very good antibacterial, antiviral and anti fungal property which increases upon complexation. Transition metal complexes of amino thiazoles Schiff-bases play a significant role in pharmaceuticals chemistry along with coordination chemistry [10-14].

2. MATERIALS AND METHODS

2.1. Synthesis of (E)-2-methoxy-6-nitro-4-((thiazol-2-ylimino)methyl)phenol



Scheme - 1: Synthesis of (E)-2-methoxy-6-nitro-4-((thiazol-2-ylimino)methyl)phenol

The ligand was prepared by mixing methanolic solution (20 ml) of 2-aminothiazole (20 mmol) and methanolic solution (20 ml) of 5-

Table - 1: Physical characteristics and molar conductance data of ligand & its metal(II) complexes

Compound	Colour	Yield (%)	Melting point (°C)	Conductance Scm ² mol ⁻¹
Ligand	Dark brown	65	198	-
Cu(L) ₂ Cl ₂	Dark green	50	>300	7.2
Co(L) ₂ Cl ₂	brown	51	>300	8.1
Ni(L) ₂ Cl ₂	Brownish green	58	>300	7.9
Zn(L) ₂ Cl ₂	Pale brown	62	>300	3.5

L = (E)-2-methoxy-6-nitro-4-((thiazol-2-ylimino)methyl)phenol

nitro vanillin (20 mmol) with constant stirring in the presence of few drops of 4 % NaOH. This mixture was refluxed for 36 h & then allowed to cool overnight at room temperature. The dark brown colored precipitate was isolated, filtered off, washed with pet ether and dried under vacuum over anhydrous CaCl₂. Scheme.4.1 gives the synthetic step involved in the synthesis of Ligand.

2.2. Synthesis of metal(II) complexes of (E)-2-methoxy-6-nitro-4-((thiazol-2-ylimino)methyl)phenol

A solution containing the metal salt (2m mol) {CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O, or ZnCl₂} in ethanol (20 ml) was added to a solution containing Ligand (2mmol) in ethanol (20 ml). The mixture was stirred and refluxed for about 12 h. The precipitated solid metal complexes were filtered off and washed with pet ether and dried over calcium chloride in vacuum desiccators.

3. RESULTS AND DISCUSSION

Table 1 presents the physical characteristics and molar conductance data of ligand & its metal(II) complexes. The ligand & its metal(II) complexes are colored. The ligand is dark brown in colour, it is amorphous in nature and melts at 198 °C. The Cu(II) complex of ligand has dark brown, Co(II) complex of ligand has brown, Ni(II) complex of ligand has brownish green and Zn(II) complexes of ligand has very pale brown colour with 50-65 as the % yield and melts greater than 300 °C respectively. As the complexes are fairly soluble in DMSO, the conductivity measurements were done using 1 x 10⁻³ M DMSO Digisun Electronics Digital conductivity meter –model: D1-909; cell constant-1.007. The measured molar conductance values for the DMSO solutions of all the metal (II) complexes are very negligible i.e 3.5-8.1 as given in Table 1. This suggests a non-electrolytic nature for these complexes^[15, 16]. Hence the chloride ion present in the metal complexes must be inside the coordinating sphere. The Elemental Analysis data of ligand & its metal(II) complexes values are given in Table 2.

3.1. Mass spectral studies

The mass spectral data of Schiff base ligand and its metal complexes are given in table. Mass spectra of the ligand and its metal complexes showed molecular ion peaks at 279 m/z and at 691, 687, 686 and 692 m/z for Cu(II), Co(II), Ni(II) and Zn(II) respectively which were in good agreement with the expected values. M+2 and M+4 isotopic peaks showed for the presence of two chloride ions in the coordination sphere of the complex. The existence of two chloride atoms in the co-ordination sphere with molecular formula MLCl₂ was confirmed by the intensity of the peak in the ratio 9:6:1. The daughter peaks 46, 233, 17, 262, 31, 248, 111, 168, 181, 98, 195, 84 m/z for the ligand and an additional daughter peaks for the complexes corresponding to M-35 and M-70 m/z due to the loss of chlorine attached to the metal ion were shown^[17, 18].

3.2. IR spectral studies

The IR spectral data of L and its metal(II) complexes are listed in Table 3. In order to study the bonding mode of the ligand in the metal complexes, the IR spectrum of the free ligand was compared with those of the corresponding metal complexes. The absence of C=O & NH₂ peaks in the ligand indicated the formation of schiff base from 5-nitrovanillin & 2-aminothiazole & the peak appeared in the region $\nu_{C=N}$ 1684 cm⁻¹ due to azomethine group of the Schiff base^[19]. After complexation the peaks appeared almost in the same region 1681-1689 cm⁻¹ shows that the electrons from the nitrogen of the azomethine are not donated for bonding with metal ion^[20, 21]. The new peak appeared at ν_{C-O} 1141 cm⁻¹ for the methoxy C-O stretching vibrations in Schiff base has been shifted to lower frequencies (10-21 cm⁻¹) in the complexes confirms the coordination of oxygen with metal i.e C-O-M bond^[22]. The appearance of peaks $\nu_{C=N}$ at 1684 cm⁻¹, ν_{C-N} at 1388 cm⁻¹ & ν_{C-S-C} at 766 cm⁻¹ of the thiazole ring remain unchanged suggested that thiazole group does not participate in coordination with metal through neither nitrogen nor sulphur atom^[23, 24]. ν_{NO_2} between 1351-1357 cm⁻¹ also remains unaltered both in ligand & complexes revealed the non coordination of -NO₂ group with M atom. The stretching vibrations of the free ligand ν_{O-H} at 3404

Table - 2: Elemental Analysis of ligand & its metal(II) complexes

Compound	Molecular formula	Molecular weight	Amount Found (%)			
			C	H	N	M
Ligand	C ₁₁ H ₉ N ₃ O ₄ S	279	47.31 (47.28)	3.25 (3.24)	15.05 (15.00)	-
Cu(L) ₂ Cl ₂	C ₂₂ H ₁₈ Cl ₂ N ₆ O ₈ S ₂ Cu	691	38.13 (38.10)	2.62 (2.58)	12.13 (12.11)	9.17 (9.16)
Co(L) ₂ Cl ₂	C ₂₂ H ₁₈ Cl ₂ N ₆ O ₈ S ₂ Co	687	38.38 (38.35)	2.64 (2.62)	12.21 (12.16)	8.56 (8.55)
Ni(L) ₂ Cl ₂	C ₂₂ H ₁₈ Cl ₂ N ₆ O ₈ S ₂ Ni	686	38.40 (38.33)	2.64 (2.61)	12.21 (12.17)	8.53 (8.49)
Zn(L) ₂ Cl ₂	C ₂₂ H ₁₈ Cl ₂ N ₆ O ₈ S ₂ Zn	692	38.03 (38.02)	2.61 (2.55)	12.10 (12.08)	9.41 (9.40)

Table - 3: IR spectral data (cm⁻¹) of and its metal(II) complexes

Compounds	Frequency (cm ⁻¹)									
	ν_{O-H}	ν_{O-C}	$\nu_{C=N}$	ν_{C-N}	ν_{NO_2}	$\nu_{C=N}$ (ring)	ν_{C-N} (ring)	ν_{S-C} (ring)	ν_{M-O}	ν_{M-O}
L	3404	1141	1684	1256	1351	1604	1388	766	-	-
Cu(L) ₂ Cl ₂	3344	1131	1681	1254	1352	1609	1383	767	517	625
Co(L) ₂ Cl ₂	3349	1123	1684	1253	1358	1602	1387	766	558	642
Ni(L) ₂ Cl ₂	3341	1120	1689	1251	1351	1605	1388	761	529	625
Zn(L) ₂ Cl ₂	3320	1126	1685	1259	1357	1605	1387	767	543	621

cm⁻¹ is observed in the range 3320-3349 cm⁻¹ in the IR spectra of the complexes indicated the formation of metal-oxygen bonds with non deprotonation of the-OH phenolic group. The new peaks appeared in the low frequency region 517-558 cm⁻¹ & 621-642 cm⁻¹ is attributed to $\nu(M-O)$ of phenolic and methoxy groups respectively [25, 26]. The medium and low intensity peaks due to $\nu(C-N)$, $\nu(C-S)$ and $\nu(C=N)$ modes of thiazole ring in the frequency ranges 1383-1388 cm⁻¹, 761-767 cm⁻¹ and 1602-1609 cm⁻¹ are not shifted to the lower frequency region which suggests the presence of C-S and C=N bonds and formation of metal-sulphur and metal-nitrogen bonds are not observed [27]. However ν_{M-Cl} could not be ascertained due to non availability of far IR data.

3.3. NMR spectral studies

In the ¹H NMR of L, the methoxy protons(three) were obtained at 3.8 ppm (δ) singlet[28]. The -OH proton was obtained at 10.7 ppm (δ) as singlet [29]. The aromatic ring protons were obtained between 6.5 and 6.9 ppm (δ)[30, 31]. The azomethine proton was obtained at 7.9 ppm (δ)[32, 33]. The ZnL₂Cl₂ showed no loss of peak there by confirming the non- de-protonation of any of the hydrogen. The hydroxyl proton and methoxy protons showed some de-shielding effect, there by confirming their participation in complex formation.

3.4. Electronic absorption spectral studies

The ligand exhibited a maxima at 26667 and 33223 cm⁻¹ (375 and 301 nm) due to $\pi \rightarrow \pi^*$ transition. The electronic spectral band observed at 15576 cm⁻¹ (642 nm) corresponds to ²E_g → ²T_{2g}

transition in Cu(II) complex. This suggests a distorted octahedral geometry for Cu(II) complex [CuL₂Cl₂] [34-36]. The Co(II) complex [CoL₂Cl₂] revealed three bands at 10661 cm⁻¹ (938 nm), 12953 cm⁻¹ (772 nm) and 17065 cm⁻¹ (586nm) assigned to ⁴T_{1g}(F) → ⁴T_{1g}(P), ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{2g}(F) transitions respectively which is indicative of a distorted octahedral environment around Co(II) complex [37-39]. The nickel complex [NiL₂Cl₂] exhibits three bands at 9911 cm⁻¹ (1009 nm), 15898 cm⁻¹ (629 nm) and 21930 cm⁻¹ (456 nm) corresponding to ³A_{2g}(F) → ³T_{1g}(P), ³A_{2g}(F) → ³T_{1g}(F) and ³A_{2g}(F) → ³T_{2g}(F) transitions respectively. The above observed transitions shows that Ni(II) complex is present in a distorted octahedral environment[40,41]. The magnetic moment studies for Cu(II) [42], Co(II)[43] and Ni(II)[44] complexes of ligand gave values at 1.91, 5.03 and 3.28 BM respectively. These values confirm that all the metal(II) ions were present in octahedral geometry.

3.5. Electrochemical behavior

Table - 4: Redox potential of [CuL₂Cl₂] at various scan rates

Scan rate (mV/s)	-E _{pc} (V)	E _{pa} (V)
60	0.582	0.821
80	0.569	0.788
100	0.553	0.601
120	0.558	0.723

TBAP is used as the supporting electrolyte for recording the cyclic voltammograms of the copper(II) complex of

ligandin DMSO at room temperature. The experiment was carried at different scan rates.

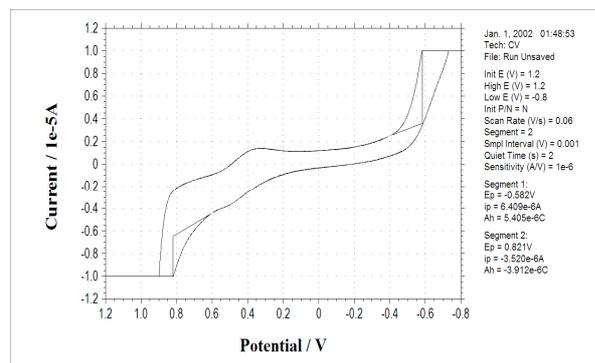


Figure - 1: Cyclic voltammogram of $[\text{CuL}_2\text{Cl}_2]$ at 50 mV/s scan rate.

As E_{pa} varies with varying scan rate the electron transfer process is not reversible. More over the ratio of i_{pa}/i_{pc} (peak currents) shows the electron transfer process to involve one electron each in oxidation process and reduction steps. The obtained $E_{pa}-E_{pc}$ values are greater than 200 mV, thereby suggesting the reduction processes to be irreversible in nature^[45]. On the basis of the ratio anodic to cathodic peak currents ratio the following chemical change $\text{Cu(II)} \rightarrow \text{Cu(I)} \rightarrow \text{Cu(II)}$ is suggested. Redox potential of $[\text{CuL}_2\text{Cl}_2]$ at various scan rates is given in Table 4. Typical cyclic voltammogram of Cu(II) complex at the scan rate of 100 mV/s is shown in Figure 1.

3.6. EPR spectral studies

Table - 5: EPR spectral parameters of $[\text{CuL}_2\text{Cl}_2]$ at 300 K

Compound	$[\text{CuL}_2\text{Cl}_2]$
g_{\parallel}	2.261
g_{\perp}	2.207
g_{av}	2.225
α^2	0.75
β^2	0.81
A_{\parallel}	133
A_{\perp}	10^{-4}cm^{-1}
A_{iso}	0.262
g_{iso}	86
$g_{\parallel} / A_{\parallel}$	170
$\mu_{eff} \text{ BM}$	1.927

The EPR spectrum of copper(II) complex of ligand was recorded at 300 K (RT). The spin Hamiltonian parameters of the copper(II) complex of ligand is listed in table 5 and it gives the various data obtained from EPR of Cu(II) complex of ligand (L). g_{\perp} (2.207) is greater than g_e more over g_{\parallel} (2.261) is also greater than g_{\perp} , these

observations suggest that $d_{x^2-y^2}$ orbital to be the ground state orbital and there is axial elongation in the octahedral geometry^[46]. Therefore the odd electron may be located in the B_{1g} anti-bonding orbital. The observed value of β^2 (0.81) shows the covalent nature of the complex^[47]. The value of g_{\parallel} is less than 2.3, hence there will be covalency in the metal ligand bonds. α^2 (0.75) is less than unity, so the complex has covalent character^[48]. The low value of g_{iso} (86) suggest the same^[49, 50]. The α^2 is less than β^2 inferring the presence of covalency in the in-plane π bonding than the in-plane σ bonding. The $g_{\parallel}/A_{\parallel}$ (170) value suggest highly distorted structure for the Cu(II) complex is suggested^[51-53].

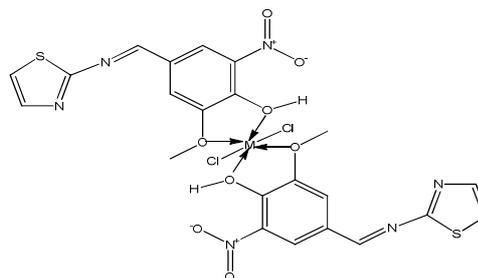


Figure - 2: Proposed structure of the metal(II) complexes of (L) (M = Cu^{II}, Co^{II}, Ni^{II} & Zn^{II})

Figure 2 represents the proposed structure of the metal(II) complexes of ligand (L). The two oxygen atom of each ligand is bonded via coordinate covalent bond with the metal(II) ion. Two such ligands along with two chlorine atom are bonded to give a highly distorted octahedral geometry. The complex is neutral in nature.

3.7. Antimicrobial activity

Streptomycin and *Nystatin* were used as standard reference compounds for antibacterial and antifungal activities respectively. The detailed summary of zone of inhibition of the metal(II) complexes of ligand and the ligand against the bacteria (*Enterococcus faecalis*, *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Klebsiella pneumonia* and *Escherichia coli*) and fungi (*Candida albicans* and *Aspergillus niger*) are given in the table 6. Cu(II) complexes of ligand are more active against *Candida Albicans* and the standard whereas Zn(II) complexes of ligand are less active but are more active than Ni(II) whence ligand and Co(II) are resistant to them. Ligand, Cu(II), Co(II) and Zn(II) are resistant to *Aspergillus Niger*, Ni(II) shows mild activity. Cu(II) complexes of ligand are more active against *Enterococcus faecalis* as well as the standard. Ligand exhibits somewhat slightly higher activity than Zn(II) and Ni(II) complexes of ligand but lesser than the standard. Ligand(L), Cu(II) & Co(II) complexes of ligand are resistant

Table - 6: The *in vitro* antimicrobial activity of L and its metal(II) complexes*

Organism	Compound				
	[Cu(L) ₂ Cl ₂]	[Co(L) ₂ Cl ₂]	[Ni(L) ₂ Cl ₂]	[Zn(L) ₂ Cl ₂]	L S
<i>Candida albicans</i>	21	-	2	13	- 18
<i>Aspergillus niger</i>	-	-	3	-	- 16
<i>Pseudomonas aeruginosa</i>	-	-	2	-	- 15
<i>Klebsiella pneumonia</i>	-	-	2	-	- 21
<i>Escherichia coli</i>	-	-	4	4	- 15
<i>Enterococcus faecalis</i>	21	-	11	16	18 20
<i>Staphylococcus aureus</i>	-	-	1	-	- 19
<i>Bacillus subtilis</i>	-	-	3	2	- 16
<i>Candida albicans</i>	21	-	2	13	- 18

*Zone of inhibition in mm. Error limit of ± 2 , R= Resistant, S= Standard.

to *Staphylococcus faecalis* and *Bacillus subtilis* whereas Ni shows mild activity. Zn(II) complex of ligand is resistant to *Staphylococcus faecalis* & mild against *Bacillus subtilis*. Ligand(L), Cu(II) & Co(II) complexes of ligand are resistant to *Pseudomonas aeruginosa*, *Klebsiella pneumonia* & *Escherichia coli*, Ni(II) shows mild activity. Zn(II) complex of ligand is resistant to *Pseudomonas aeruginosa* & *Klebsiella pneumonia* except *Escherichia coli* [2, 54-56].

3.8. FRAP reducing assay

Iron chelating activity of L and its metal(II) complexes of ligand is given in Figure 3. Zn(II) complex of ligand showed more activity followed by Cu(II), Ni(II), ligand and Ni(II).

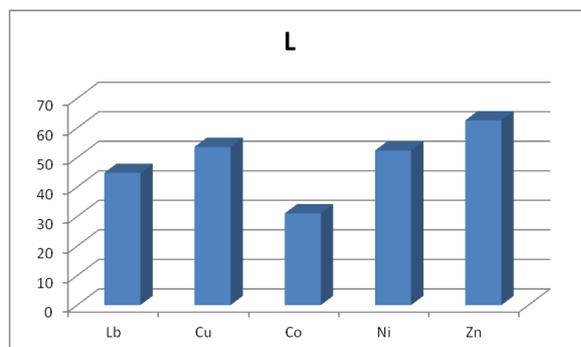


Figure - 3: Iron chelating activity of L and its metal(II) complexes.

3.9. Fluorescence studies

The emission bands for the ligand and that of metal(II) complexes are obtained at 375 nm and between 628-773 nm respectively. Due to charge transfer nature, all the complexes show broad emission bands [57-59]. The bands of ligand and metal(II) complex are shifted due to quenching of fluorescence (upon complex formation, the electron density is drained toward the electropositive metal ion) [60]. The emission

maximum values of the ligand and metal(II) complexes are tabulated in table 7.

Table - 7: Fluorescence parameters of L and its metal(II) complexes.

Compound	Excitation maximum (nm)	Emission maximum (nm)	Quantum yield
L	375	380	0.849
[Cu(L) ₂ Cl ₂]	640	644	12.297
[Co(L) ₂ Cl ₂]	768	773	4.764
[Ni(L) ₂ Cl ₂]	632	628	0.101

3.10. SHG Studies and XRD results

The ligand is found to be 0.538 times the NLO activity of KDP and 0.122 times that of urea. The metal(II) complexes do not show any response in SHG measurement. The imbalance in electron flow from donor end to the acceptor may be the reason for poor activity. The imbalance is actually due to the presence of central metal atom at one corner of the whole molecule [61-64]. The particle size of the ligand is 34.7 nm [65].

4. CONCLUSIONS

The ligand and its metal(II) complexes were synthesized and characterized as given above. The metal(II) complexes were found to form highly distorted octahedral geometry. Only the Ni(II) complex showed some activity that too very poor.

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