

## Synthesis, Characterization and Studies on Metal (II) Complexes of 4-(((1H-Tetrazol-5-YL)Imino)Methyl)-2-Methoxy-6-Nitrophenol

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### ABSTRACT

A new ligand was synthesized from 5-amino tetrazole and 5-nitro vanillin. The metal(II) complexes of the ligand was synthesized and characterized. Spectroscopic and analytical studies assisted to arrive at the geometry of the newly synthesized compounds. The compounds were subjected to anti-microbial, anti-oxidant, fluorescence, NLO and power XRD studies.

**Keywords:** 5-amino tetrazole and 5-nitro vanillin, anti-oxidant, fluorescence, NLO and power XRD studies.

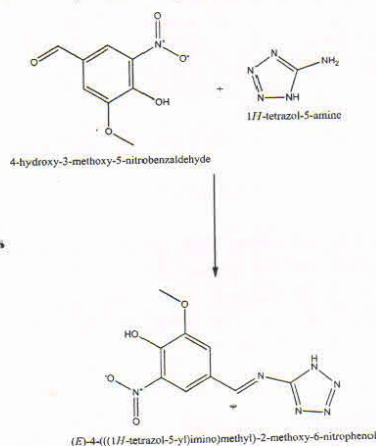
### INTRODUCTION

Due to biological activities of Tetrazole, it is present in new drugs & biologically active compounds<sup>1-7</sup>. Diverse biological activity exhibited by Tetrazole derivatives are known due to the active pharmaceutical ingredients present in highly effective drugs. They are used as components of materials for medical purpose & components of diagnostic complexes. It is an important descriptor in the methodology of the design of new drugs<sup>8-12</sup>. A substantial increase in the metabolic stability of the modified substrate tetrazole ring, upon replacement of amide group in peptide sequence. Lots of transition metal complexes with 5-substituted tetrazolate derivatives are known with good photoluminescence properties. Instead of 1,3-diketones and its analogues, tetrazolate lanthanide complexes are used as prospective photonic material because of their high photoluminescence efficiencies and high thermal stability<sup>13-16</sup>.

**EXPERIMENTAL**

**Synthesis of 4-(((1H-tetrazol-5-yl)imino)methyl)-2-methoxy-6-nitrophenol (AN)**

The ligand (AN) was prepared by mixing methanolic solution (20 mL) of 5-amino tetrazole (20mmol) and methanolic solution (20 mL) of 5-nitro vanillin (20mmol) 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 over calcium chloride in vacuum desiccators. Scheme.1 gives the synthetic step involved in the synthesis of Ligand (L<sup>d</sup>).



**Scheme.1. Synthesis of ligand 4-(((1H-tetrazol-5-yl)imino)methyl)-2-methoxy-6-nitrophenol,**

**Synthesis of metal(II) complexes of 4-(((1H-tetrazol-5-yl)imino)methyl)-2-methoxy-6-nitrophenol (AN)**

**Table.1.a. Physical characteristics and molar conductance data of ligand (AN) & its metal(II) complexes**

COMPOUND	COLOUR	% YIELD	MELTING POINT °C	CONDUCTANCE Scm <sup>2</sup> mol <sup>-1</sup>
L <sup>d</sup>	Turmeric yellow	60	91	-
Cu(L <sup>d</sup> ) <sub>2</sub> Cl <sub>2</sub>	Dark green	46	>300	7.3
Co(L <sup>d</sup> ) <sub>2</sub> Cl <sub>2</sub>	Pale yellow	51	>300	7.9
Ni(L <sup>d</sup> ) <sub>2</sub> Cl <sub>2</sub>	Green	47	>300	6.2
Zn(L <sup>d</sup> ) <sub>2</sub> Cl <sub>2</sub>	Greyish green	40	>300	5.9

A solution containing the metal salt (2m mol) {CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, or ZnCl<sub>2</sub>} in ethanol (20 ml) was added to a solution containing Ligand L<sup>d</sup> (0.56 g, 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.

## RESULTS AND DISCUSSION

**Table.1.b. Elemental Analysis of ligand (AN) & its metal(II) complexes**

COMPOUND	MOLECULAR FORMULA	MOLECULAR WEIGHT	CALCULATED % (FOUND %)			
			C	H	N	M
AN	C <sub>9</sub> H <sub>8</sub> N <sub>6</sub> O <sub>4</sub>	264	40.91 (40.89)	3.05 (3.02)	31.81 (31.76)	-
Cu(AN) <sub>2</sub> Cl <sub>2</sub>	C <sub>18</sub> H <sub>16</sub> C <sub>12</sub> N <sub>12</sub> O <sub>8</sub> Cu	661	32.62 (32.58)	2.43 (2.42)	25.36 (25.33)	9.59 (9.55)
Co(AN) <sub>2</sub> Cl <sub>2</sub>	C <sub>18</sub> H <sub>16</sub> C <sub>12</sub> N <sub>12</sub> O <sub>8</sub> Co	657	32.84 (32.80)	2.45 (2.42)	25.54 (25.51)	8.95 (8.94)
Ni(AN) <sub>2</sub> Cl <sub>2</sub>	C <sub>18</sub> H <sub>16</sub> C <sub>12</sub> N <sub>12</sub> O <sub>8</sub> Ni	656	32.86 (32.84)	2.45 (2.43)	25.54 (25.52)	8.92 (8.91)
Zn(AN) <sub>2</sub> Cl <sub>2</sub>	C <sub>18</sub> H <sub>16</sub> C <sub>12</sub> N <sub>12</sub> O <sub>8</sub> Zn	662	32.53 (32.49)	2.43 (2.42)	25.29 (25.24)	9.84 (9.81)

Table.1.a. presents the physical characteristics and molar conductance data of ligand (AN) & its metal(II) complexes. The ligand (AN) & its metal(II) complexes are colored. The ligand (AN) is turmeric yellow in colour, it is amorphous in nature and melts at 91 °C. The Cu(II) complex of ligand (AN) has dark green, Co(II) complex of ligand (AN) has pale yellow, Ni(II) complex of ligand (AN) has green and Zn(II) complexes of ligand (AN) has greyish green colour with melting point greater than 300 °C and 40-60% yield respectively. As the complexes are fairly soluble in DMSO, the conductivity measurements were done using 1 x 10<sup>-3</sup> M DMSO. The measured molar conductance values for the DMSO solutions of all the metal (II) complexes fall in the range of 5.9-7.9 Scm<sup>2</sup>mol<sup>-1</sup>; indicate that the complexes were nonelectrolyte<sup>17, 18</sup>. Hence the chloride ion present in the metal complexes must be inside the coordinating sphere. The Elemental Analysis data of ligand (AN) & its metal(II) complexes values are given in Table.1.b.

### Mass spectral studies

The mass spectrum of the ligand (AN) showed molecular ion peak at 264 m/z, whereas the complexes [Cu(II), Co(II), Ni(II), Zn(II)] gave molecular ion peaks at 661, 657, 656 and 662 m/z respectively. The presence of two chloride ions in the coordination sphere exhibit M+2 and M+4 isotopic peaks for the complex. The intensity of the peak in the ratio 9:6:1 also confirm the existence of two chloride atoms in the co-ordination sphere with molecular formula M<sub>2</sub>ANCl<sub>2</sub>. The ligand (AN) shows daughter peaks at 31, 233, 17, 247, 218, 46, 96, 168, 83, 181, 69, 195 m/z where as the complex shows additional daughter peaks corresponding to M-35 and M-70 m/z due to the loss of chlorine attached to the metal ion<sup>19, 20</sup>.

### IR spectral studies

The IR spectral data of ligand(AN) and its metal(II) complexes are listed in Table.2. The IR spectra of the Schiff base ligand(AN) and its complexes were carried out in the range 4000–200  $\text{cm}^{-1}$  are listed in Table.6.2. In order to determine the coordination sites that may be involved in chelation, the IR spectra of the complexes are compared with those of the free ligand. Some of the peaks in the spectra of the ligand are of more useful which upon chelation, the position and/or the intensities of these peaks are expected to be changed. While comparing it is found that: A broad peak at 3351  $\text{cm}^{-1}$ , in the IR spectrum of the ligand shows the presence of phenolic -OH group<sup>21,22</sup>. This  $\nu_{\text{O-H}}$  of the ligand appears at 3321-3329  $\text{cm}^{-1}$  in all complexes can be attributed to the involvement of phenolic OH in coordination, without the deprotonation of phenolic -OH in complexes<sup>23</sup>. The shift of  $\nu(\text{C-O})$  stretching peak observed at 1335  $\text{cm}^{-1}$  in the free ligand to a lower frequency to the extent of 10 to 21  $\text{cm}^{-1}$ . The shift of  $\nu(\text{C-O})$  peak to a lower frequency 1214  $\text{cm}^{-1}$  - 1225  $\text{cm}^{-1}$  suggests the weakening of methoxy  $\nu(\text{C-O})$  and formation of stronger Metal oxygen bond<sup>24</sup>. The medium peaks observed in the 1641–1612  $\text{cm}^{-1}$  frequency ranges in complexes were assigned to  $\nu(\text{C=N})$  mode<sup>25, 26</sup>. The  $\nu(\text{C=N})$  vibration is not shifted to a lower frequency in all the complexes suggests that the nitrogen atom of the ring is not involved in the complexation<sup>27</sup>. New peaks appeared between 621-629  $\text{cm}^{-1}$  and 501-519  $\text{cm}^{-1}$ , i.e., the stretching vibrations  $\nu(\text{M-O})$  which are assigned to the interaction of phenolic and methoxy oxygen to the metal atom<sup>28,29</sup>. In the IR spectra of the complexes, peaks are observed at 320 – 328  $\text{cm}^{-1}$  that is attributed to the  $\nu(\text{M-Cl})$  stretching vibrations.

Table.2. IR spectral data ( $\text{cm}^{-1}$ ) of (AN) and its metal(II) complexes

Compounds	Frequency ( $\text{cm}^{-1}$ )									
	$\nu_{\text{O-H}}$	$\nu_{\text{O-C}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-N}}$	$\nu_{\text{N-H}}$	$\nu_{\text{NO}_2}$	$\nu_{\text{C=N (ring)}}$	$\nu_{\text{C-N (ring)}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-Cl}}$
AN	3351	1335	1681	1233	3200	1364	1609	1267	-	-
Cu(AN) <sub>2</sub> Cl <sub>2</sub>	3329	1314	1676	1233	3209	1368	1616	1270	501	626
Co(AN) <sub>2</sub> Cl <sub>2</sub>	3321	1324	1680	1235	3205	1365	1612	1271	510	625
Ni(AN) <sub>2</sub> Cl <sub>2</sub>	3325	1316	1675	1235	3204	1362	1615	1269	520	629
Zn(AN) <sub>2</sub> Cl <sub>2</sub>	3321	1325	1679	1235	3201	1360	1610	1267	519	621

### NMR spectral studies

In the <sup>1</sup>H NMR of AN, the methoxy protons(three) were obtained at 3.7 ppm ( $\delta$ ) singlet<sup>30</sup>. The -OH proton was observed at 11.2 ppm ( $\delta$ ) as singlet<sup>31</sup>. The aromatic ring protons were obtained between 6.5 and 6.9 ppm ( $\delta$ )<sup>32,33</sup>. The azomethine proton was obtained at 8.0 ppm ( $\delta$ )<sup>34,35</sup>. The -NH proton was obtained at 9.1 ppm ( $\delta$ )<sup>36</sup>. The ZnANCl<sub>2</sub> 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.

### Electronic absorption spectral studies

The electronic absorption spectra of the ligand (AN) and its metal(II) complexes were recorded in DMSO at 300 K. The ligand (AN) shows a broad peak at 38168 and 36101  $\text{cm}^{-1}$

(262 and 277 nm) due to  $\pi \rightarrow \pi^*$  transition. The electronic spectral peak occurs at  $15674 \text{ cm}^{-1}$  (638 nm) corresponds to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition in Cu(II) complex. This suggests a distorted octahedral geometry for Cu(II) complex  $[\text{CuANCl}_2]$ <sup>37-39</sup>. The electronic spectra of the Co(II) complex  $[\text{CoANCl}_2]$  exhibits three peaks in the range of  $11001 \text{ cm}^{-1}$  (909 nm),  $14663 \text{ cm}^{-1}$  (682 nm) and  $19157 \text{ cm}^{-1}$  (522) assigned to  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ ,  ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$  and  ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$  transitions respectively. This suggests a distorted octahedral environment around Co(II) complex<sup>40-42</sup>. The nickel complex  $[\text{NiANCl}_2]$  exhibits three peaks at  $9728 \text{ cm}^{-1}$  (1028 nm),  $15060 \text{ cm}^{-1}$  (664 nm) and  $21645 \text{ cm}^{-1}$  (462 nm) corresponding to  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ ,  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$  and  ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$  transitions respectively indicates the presence of Ni(II) complex in a distorted octahedral environment<sup>43,44</sup>. The above predicated geometry for all the metal(II) complexes were further confirmed by magnetic moment studies. The Cu(II) complex of the ligand(L<sup>c</sup>) was found to possess 1.98 BM which suggest octahedral geometry<sup>45</sup>.  $\text{Co}(\text{L}^c)_2\text{Cl}_2$  had 5.09 BM, which also confirms the octahedral geometry around the Cobalt(II) ion<sup>46</sup>.  $\text{Ni}(\text{L}^c)_2\text{Cl}_2$  was found to have 3.27 BM, hence the Nickel (II) ion was confirmed to possess octahedral geometry<sup>47</sup>.

**Electrochemical behavior**

**Table.3. Redox potential of  $[\text{CuANCl}_2]$  at various scan rates**

Scan rate (mV/s)	-E <sub>pc</sub> (V)	E <sub>pa</sub> (V)
60	0.625	0.795
80	0.628	0.807
100	0.618	0.794
120	0.619	0.798

TBAP is used as the supporting electrolyte for recording the cyclic voltammograms of the copper(II) complex of ligand(AN) in DMSO at room temperature. The experiment was carried at different scan rates. As E<sub>pa</sub> varies with varying scan rate the reaction 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 and reduction steps. The E<sub>pa</sub>-E<sub>pc</sub> values are greater than 200 mV indicates that the reduction processes are irreversible in nature<sup>48</sup>. The ratio of anodic to cathodic peak currents corresponds to the following chemical change  $\text{Cu(II)} \rightarrow \text{Cu(I)} \rightarrow \text{Cu(II)}$ . Redox potential of  $[\text{CuANCl}_2]$  at various scan rates is given in Table.3.

**EPR spectral studies**

**Table.4. EPR spectral parameters of  $[\text{CuANCl}_2]$  at 300 K**

Compound	g <sub>  </sub>	g <sub>⊥</sub>	g <sub>av</sub>	a <sup>2</sup>	β <sup>2</sup>	A <sub>  </sub>	A <sub>⊥</sub>	A <sub>iso</sub>	g <sub>iso</sub>	g <sub>  </sub> / A <sub>  </sub>	μ <sub>eff</sub> BM
$[\text{CuANCl}_2]$	2.247	2.197	2.213	0.71	0.80	127	73	0.251	116	177	1.917

The EPR spectrum of  $[\text{CuANCl}_2]$  is shown in Figure.4. The EPR spectrum of copper(II) complex of ligand (AN) was recorded at 300 K (RT). The spin Hamiltonian parameters of the copper(II) complex of ligand (AN) is listed in Table.6.5 and it gives the various data obtained from EPR of Cu(II) complex of ligand (AN). g<sub>||</sub> (2.247) is greater than

$g_{\perp}$  and  $g_{\parallel}$  (2.197) is greater than  $g_e$ . Based on the above results the following conclusions were drawn: there is axial elongation in the octahedral geometry, the  $d_{x^2-y^2}$  is the ground state orbital and the odd electron may be located in the  $B_{1g}$  anti-bonding orbital<sup>49</sup>. The  $\beta^2$  (0.80) value supports the covalent nature of the metal(II) complex<sup>50</sup>. The covalency in the metal ligand bonds is indicated by value of  $g_{\parallel}$ , which is less than 2.3<sup>51</sup>. The Cu(II) complex of ligand (AN) is covalent in nature as: (i)  $\alpha^2$  (0.71) value is less than unity (ii) the value of  $g_{iso}$  is 1.16<sup>52, 53</sup>. The covalency in the in-plane  $\pi$  bonding than the in-plane  $\sigma$  bonding is expected as the  $\alpha^2$  value is less than  $\beta^2$ . Cu(II) complex of ligand (AN) is suggested to have highly distorted structure as the value of  $g_{\parallel}/A_{\parallel}$  is 177<sup>54-56</sup>.

Figure. 1. represents the proposed structure of the metal(II) complexes of ligand (AN). The conductivity studies and mass spectra gave the conclusion that the chlorine atoms(two) where present inside the coordinating sphere and the complex is neutral in nature, with the central metal ion have +2 oxidation state. There were two coordinate covalent bonds present formed by each ligand with the central metal ion. Totally two ligands, each one bidentate in nature are coordinated. All these gave a highly distorted structure for the metal(II) complex.

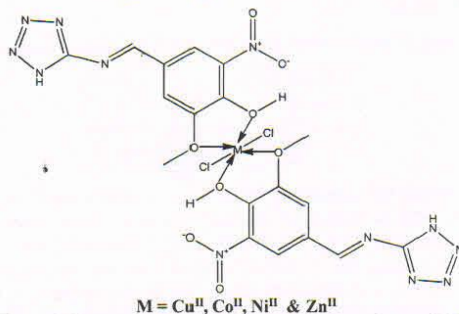


Figure.1. Proposed structure of the metal(II) complexes of (AN)

#### Antimicrobial activity

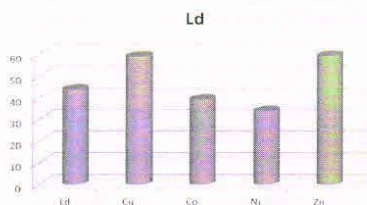
Table.5. The *in vitro* antimicrobial activity of (AN) and its metal(II) complexes\*

Type	Organism	Compound					AN	S
		[CuANCl <sub>2</sub> ]	[CoANCl <sub>2</sub> ]	[NiANCl <sub>2</sub> ]	[ZnANCl <sub>2</sub> ]			
Fungi	<i>Candida albicans</i>	4	5	15	2	20	18	
	<i>Aspergillus niger</i>	5	5	7	13	15	16	
Gram negative bacteria	<i>Pseudomonas aeruginosa</i>	6	3	3	15	13	15	
	<i>Klebsiella pneumonia</i>	3	4	7	15	17	21	
	<i>Escherichia coli</i>	-	-	13	14	-	15	
Gram positive bacteria	<i>Enterococcus faecalis</i>	-	15	15	15	19	20	
	<i>Staphylococcus aureus</i>	-	2	3	2	-	19	
	<i>Bacillus subtilis</i>	3	3	5	16	20	16	

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

*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 and the ligand(AN) 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.5. Anti bacterial activity of ligand(AN) is more or less the same as that of the standard against *Candida Albicans*, *Aspergillus Niger* & *Enterococcus faecelis*. Activity of Ni(II) was slightly lower than Ligand(AN). Cu(II) & Co(II) complexes of ligand(AN) are resistant to *Escheriachia Coli*, Ligand(AN) & Cu(II) of ligand(AN) is resistant to *Enterococcus faecelis* & *Staphylococcus faecalis*. Cu(II), Ni(II) & Zn(II) complexes of ligand(AN) are about to have the same activity but lesser than the ligand (AN) & standard. Activity of Zn(II) of ligand(AN) is almost the same as that of the standard against *Bacillus subitillis* but lesser than the ligand(AN)<sup>(57,60)</sup>.

**FRAP reducing assay**



**Figure.2. Iron chelating activity of (AN) and and its metal(II) complexes**

Iron chelating activity of (AN) and and its metal(II) complexes is given in Figure.2. The Zn(II) complex of ligand (AN) is more or less equally active as Cu(II) of ligand (AN). These are followed by ligand (AN), Co(II) and Ni(II) ligand (AN).

**Fluorescence studies**

The emission peaks for the ligand (AN) and that of metal(II) complexes are obtained at 277 nm and between 525-675 nm respectively. Due to charge transfer nature, all the complexes show broad emission peaks<sup>61-63</sup>. There is shift between peaks of ligand and metal(II) complex due to quenching of fluorescence (due to complex formation and the electron density is drained toward the electropositive metal ion)<sup>64</sup>. The emission maximum values of the ligand and metal(II) complexes are tabulated in Table.6.

**Table.6. Fluorescence parameters of (AN) and its metal(II) complexes**

Compound	Excitation maximum (nm)	Emission maximum (nm)	Quantum yield
AN	277	281	0.189
[CuANCl <sub>2</sub> ]	638	641	0.233
[CoANCl <sub>2</sub> ]	507	525	13.201
[NiANCl <sub>2</sub> ]	673	675	17.257

### SHG and XRD results

The ligand (AN) is found to be 10.3 times more NLO active than KDP and 0.596 times that of urea. The metal(II) complexes do not show any response in SHG measurement. The activity is not as that of the existing standards and this may be attributed to the imbalance in the flow of electron from donor end to the acceptor end<sup>65-68</sup>. The particle size of the ligand (L<sup>a</sup>) is 32.32 nm<sup>69</sup>.

### CONCLUSIONS

Spectroscopic and analytical techniques facilitated to arrive at the structure of the compounds synthesized. The metal(II) complexes were found to possess highly distorted octahedral geometry. Among the metal(II) complexes Zn(II) showed better anti-microbial activity. Similarly in anti-oxidant studies the activity of Zn(II) was more or less similar to that of Cu(II). The cyclic voltammetry studies showed one electron transfer for Cu(II) complex. These compounds possessed good fluorescence and NLO activity.

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