

International Journal for Pharmaceutical Research Scholars (IJPRS)



ISSN No: 2277 - 7873

## **RESEARCH ARTICLE**

## Synthesis, Characterization and Studies on Metal (II) Complexes of 4-(((1h-1, 2, 4-Triazol-3-Yl) Imino) Methyl)-2-Methoxy-6-Nitrophenol

Southamani K\*<sup>1</sup>, Ebenezer R<sup>2</sup>, Anitha R<sup>1</sup>, Kalaimathi M<sup>1</sup>, Yesu Thangam Y<sup>1</sup>

<sup>1</sup>PG & Research Center of Chemistry, Jayaraj Annapackiam College for Women (Autonomous), Periyakulam, 625-601, affiliated to Mother Teresa Women's University Kodaikanal, Tamilnadu, India.

<sup>2</sup>PG & Research Department of Chemistry, The American College (Autonomous), Madurai-625 002, affiliated to Madurai Kamaraj University, Madurai, Tamilnadu, India.

Manuscript No: IJPRS/V5/I4/00155, Received On: 19/11/2016, Accepted On: 22/11/2016

#### ABSTRACT

The 3-Amino - 1,2,4-triazole and 5-nitro vanillin were used as precursors to synthesis the metal(II) complexes. Confirming the formation of the ligand and the geometry of the metal (II) complexes were done using various spectroscopic and analytical techniques. The prepared compounds where screened for anti-bacterial and anti-oxidant properties. Fluorescence, NLO and powder XRD studies were also performed on the newly synthesized compounds.

#### **KEYWORDS**

5-Nitro Vanillin, 3-Amino - 1,2,4-Triazole, Metal Complex, Biological Activity, Fluorescent Studies, NLO Property, Anti-Oxidant Studies, Cyclic Voltammetry

### **INTRODUCTION**

Azoles are found in innumerable molecules of biological origin<sup>1-3</sup> having a number of pharmaceutical properties. Azoles are fivemembered heterocycles with two or more heteroatoms, one of which is nitrogen having wider application in medicines. 1,2,4-Triazoles<sup>4,5</sup> are the heterocycles, with versatile biological activities. Triazoles are nitrogen containing organic compounds and their metal complexes act as antitumor, antibacterial, antifungal and antiviral agents<sup>6,7</sup> and find application in photographic process, corrosion control. agriculture<sup>8-13</sup> and industry. Derivatives of 4amino-3-substituted-5-mercapto-1,2,4-triazoles possess broad spectrum of biological activities<sup>14</sup>. O. N and S donor atoms of the triazole Schiff

\*Address for Correspondence:

PG & Research Center of Chemistry, Jayaraj Annapackiam College for Women (Autonomous), Periyakulam, 625-601, affiliated to Mother Teresa Women's University Kodaikanal, Tamilnadu, India. **E-Mail Id**: <u>mary.christella@gmail.com</u> bases<sup>15</sup> are important biologically and are used as versatile ligands forming mono to polynuclear complexes<sup>16,17</sup> which are more stable than complexes derived from monodentate ligands in coordination chemistry. Metal chelates containing heterocyclic rings have the biological effect, due to the presence of exocyclic nitrogen and sulphur atoms as the coordination sites to link directly with the transition metal ions. Several such metal chelates have been synthesized because of their importance in antimicrobial, anti-inflammatory, and anti-HIV applications<sup>18</sup>.

### MATERIALS AND METHODS

### Synthesis of 4-(((1H-1,2,4-triazol-3-yl) imino)methyl)-2-methoxy-6-nitrophenol

Schiff base ligand(TIMNP) was synthesized by condensing (refluxing) 3-Amino - 1,2,4-triazole (20 mmol) in Methanol (20ml) with 5-nitro vanillin (20 mmol) in methanol (20 ml) with

Southamani K.,

constant stirring in the presence of few drops of 4 % NaOH.



Scheme 1: Synthesis of ligand 4-(((1H-1,2,4triazol-3-yl)imino)methyl)-2-methoxy-6nitrophenol, [PM, (TIMNP)]

#### Synthesis of metal (II) complexes of 4-(((1H-1,2,4-triazol-3-yl)imino)methyl)-2-methoxy-6nitrophenol

A solution containing the metal salt (2 mmol) {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 (TIMNP) (2 mmol) 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 dry calcium chloride in vacuum desiccators.

### **RESULTS AND DISCUSSION**

Table 1.a. presents the physical characteristics and molar conductance data of ligand (TIMNP) & its metal(II) complexes. The ligand & its metal(II) complexes are colored. The ligand (TIMNP) is chilly red in colour, it is amorphous in nature and melts at 145°C.

The Cu(II) complex of ligand (TIMNP) has plae

		-		
Compound	Colour	% Yield	Melting Point °C	Conductance Scm <sup>2</sup> mol <sup>-1</sup>
(TIMNP)	Chillyred	75	145	-
Cu(TIMNP) <sub>2</sub> Cl <sub>2</sub>	Pale green	70	>300	6.1
Co(TIMNP) <sub>2</sub> Cl <sub>2</sub>	Greyish brown	72	>300	7.0
Ni(TIMNP)2Cl2	Dark green	70	>300	6.4
Zn(TIMNP) <sub>2</sub> Cl <sub>2</sub>	Pale yellow	65	>300	9

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

(TIMNP) = 4 - (((1H-1,2,4-triazol-3-yl)imino)methyl) - 2-methoxy-6-nitrophenol

This mixture was refluxed for 36 h & then allowed to cool overnight. The crude product was separated by filtration and washed several times with pet ether. The dark red colored product was recrystallized from hot ethanol and dried under vacuum over anhydrous CaCl<sub>2</sub>. Scheme.1 gives the synthetic step involved in the synthesis of ligand (TIMNP).

green, Co(II) complex of ligand (TIMNP) has grayish brown, Ni(II) complex of ligand (TIMNP) has dark green and Zn(II) complexes of ligand (TIMNP) has very plae yellow colour with 65-75 % yield and greater than 300°C respectively. As the complexes are fairly soluble in DMSO, the conductivity measurements were done using 1 x 10<sup>-3</sup> M DMSO.

Compound	Molecular Formula	Molecular Weight	CA(TIMNP)ULATED % (FOUND %)					
		,, eight	С	Н	Ν	Μ		
(TIMNP)	$C_{10}H_9N_5O_4$	263	463 (458)	3.45 (3.44)	26.61 (26.51)	-		
Cu(TIMNP)2Cl2	$C_{20}H_{18}C_{12}N_{10}O_8Cu$	659	36.35 (36.32)	2.75 (2.74)	21.19 (21.11)	9.62 (9.60)		
Co(TIMNP)2Cl2	$C_{20}H_{18}C_{12}N_{10}O_8Co$	655	36.60 (36.51)	2.76 (2.74)	21.34 (21.33)	8.98 (8.96)		
Ni(TIMNP) <sub>2</sub> Cl <sub>2</sub>	$C_{20}H_{18}C_{12}N_{10}O_8Ni$	654	36.62 (36.58)	2.77 (2.71)	21.35 (21.30)	8.95 (8.94)		
Zn(TIMNP) <sub>2</sub> Cl <sub>2</sub>	$C_{20}H_{18}C_{12}N_{10}O_8Zn$	660	36.25 (36.20)	2.74 (2.73)	21.14 (21.12)	9.87 (9.81)		

Table 1b: Elemental Analysis of ligand (TIMNP) & its metal (II) complexes

(**TIMNP**) = 4-(((1H-1,2,4-triazol-3-yl)imino)methyl)-2-methoxy-6-nitrophenol

Table 2: IR spectral data (cm<sup>-1</sup>) of (TIMNP) and its metal (II) complexes.

	Frequency (cm <sup>-1</sup> )									
Compounds	v О-Н	v O-C	v C=N	v C-N	v N-H	v NO <sub>2</sub>	v C=N (ring)	v C-N (ring)	v M–O	v M–O
(TIMNP)	3368	1144	1659	1248	3123	1364	1608	1206	-	-
Cu(TIMNP)2Cl2	3328	1125	1651	1246	3127	1362	1611	1206	520	629
Co(TIMNP) <sub>2</sub> Cl <sub>2</sub>	3345	1103	1653	1251	3124	1370	1612	1215	501	624
Ni(TIMNP) <sub>2</sub> Cl <sub>2</sub>	3325	1119	1652	1250	3125	1359	1608	1215	516	624
Zn(TIMNP)2Cl2	3329	1107	1653	1254	3124	1361	1611	1205	505	627

Digisun Electonics Digital conductivity meter – model: D1-909; cell constant-1.007. The measured molar conductance values ranging from 9-7.0 Scm<sup>2</sup>mol<sup>-1</sup> for the DMSO solutions of all the metal (II) complexes are very negligible as given in Table 1.a. This suggests a nonelectrolytic nature for these complexes. Hence the chloride ion present in the metal complexes must be inside the coordinating sphere<sup>19,20</sup>. The Elemental Analysis data of ligand (TIMNP) & its metal(II) complexes values are given in Table 1.b.

## **Mass Spectral Studies**

The mass spectrum of the ligand (TIMNP) gives a molecular ion peak at 263 m/z, which coincide with its formula weight. The molecular ion peaks at 659, 655, 654 and 660 m/z were given for Cu(II), Co(II), Ni(II) and Zn(II) complexes respectively. Two chloride atoms in the coordination sphere with molecular formula  $M(TIMNP)Cl_2$  exist as the intensity of the peak in the ratio 9:6:1.  $M^{+2}$  and  $M^{+4}$  isotopic peaks exhibited for the complex also confirm the presence of two chloride ions in the coordination sphere. Due to the loss of chlorine attached to the metal ion the ligand (TIMNP) shows daughter peaks at 17,31, 46, 217, 246, 232, 168, 95, 181, 82, 195, 68, and the complex shows additional daughter peaks corresponding to M-35 and M-70 m/ $z^{21,22}$ .

## **IR Spectral Studies**

The IR spectral data of the Schiff base ligands (TIMNP) and its metal(II) complexes are listed in Table.2. The absence of characteristic peaks appearing at 1670 & 3315 cm<sup>-1</sup> in the IR spectra of the ligand assigned to formyl ( $v_{C=O}$ ) & amino (v<sub>NH2</sub>) moieties respectively indicated the formation of schiff base from 5-nitrovanillin & 3amino 1,2,4-triazole<sup>23</sup>. The IR spectra of the complexes have been compared with those of the free ligand in order to determine the coordination sites that may get involved in chelation. By comparing, it was found that azomethine group frequency v(N=CH) is present in the free ligand. In the IR spectra of the ligand  $v_{C=N}$  of the free ligand at 1659 cm<sup>-1</sup> has not been shifted to lower frequency(lower wave numbers) i.e appeared at 1651-1653 cm<sup>-1</sup> in the complexes indicating the non-coordination of azomethine nitrogen with metal<sup>24,25</sup>. The peak at 3348 cm<sup>-1</sup>attributed to  $v_{O-H}$ of the ligand is shifted to 3325-3331cm<sup>-1</sup> in its metal complexes indicating coordination of to metal(II) ion oxygen atom without deprotonation<sup>26</sup>.  $v_{C=N}$  &  $v_{C-N}$  cyclic of triazole ring at 1608-1612 &1205-1215 cm<sup>-1</sup> in Schiff base ligand does not alter in the spectra of the complexes rule out the participation of cyclic group in coordination by nitrogen<sup>27,28</sup>. No remarkable shift in the stretching vibrations of  $v_{C-}$ N, VN-H & VNO2 at 1246-1254, 3123-3127 & 1359-1368 cm<sup>-1</sup> suggested the non-coordination of nitrogen & NO<sub>2</sub> group with metal(II) ion<sup>29</sup>. New peaks appearing at 501-520 & 624-629 cm<sup>-1</sup> in the complexes assignable to  $v_{M-O}$  vibrations of phenolic and methoxy groups respectively<sup>30,31</sup>.

## **NMR** Spectral Studies

In the <sup>1</sup>H NMR of (TIMNP), the methoxy protons (three) were obtained at 3.3 ppm ( $\delta$ ) singlet<sup>32</sup>. The –OH proton was obtained at 11.8 ppm ( $\delta$ ) as singlet<sup>33</sup>. The aromatic and the hetero ring protons were obtained between 6.9 and 7.9 ppm ( $\delta$ )<sup>34,35</sup>. The azomethine proton was obtained at 8.1 ppm ( $\delta$ )<sup>36-37</sup>. The –NH proton was obtained at 9.3 ppm ( $\delta$ )<sup>38</sup>. The Zn(TIMNP)Cl<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 (TIMNP) and its metal(II) complexes were recorded in DMSO at 300 K. The ligand (TIMNP) shows a broad peak at 35842 and 43290 cm<sup>-1</sup> (231 and 279 nm) due to  $\pi \rightarrow \pi^*$  transition. The electronic spectra of Cu(II) complex shows a single broad band at 15625 cm<sup>-1</sup> (640 nm) corresponding to  ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$  transition. A distorted octahedral geometry has been suggested for Cu(II) complex [Cu(TIMNP)Cl<sub>2</sub>]<sup>39-41</sup>. For the Co(II) complex [Co(TIMNP)Cl<sub>2</sub>] three transitions were obtained at 10417 cm<sup>-1</sup> (960 nm), 14903 cm<sup>-1</sup> (671 nm) and 18116 cm<sup>-1</sup> (552nm) assigned to  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P), {}^{4}T_{1g}(F) \rightarrow$ 

 ${}^{4}A_{2g}(F)$ and  ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$  transitions respectively. This suggests a distorted octahedral environment around Co(II) complex<sup>42-44</sup>. The nickel complex [Ni(TIMNP)Cl<sub>2</sub>] exhibits three bands at 9823 cm<sup>-1</sup> (1018 nm), 14728 cm<sup>-1</sup> (679 nm) and 22422 cm<sup>-1</sup> (446 nm) corresponding to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P), {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$  and  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$  transitions respectively. The above observed transitions reveals that Ni(II) complex distorted octahedral has а environment<sup>45,46</sup>.

### **Magnetic Moment Studies**

The above predicated geometry for all the metal(II) complexes were further confirmed by magnetic moment studies. The Cu(II) complex of the ligand(TIMNP) was found to possess 1.90 BM which suggest octahedral geometry<sup>47</sup>. Co(TIMNP)<sub>2</sub>Cl<sub>2</sub> had 4.91 BM, which also confirms the octahedral geometry around the Cobalt(II) ion<sup>48</sup>. Ni(TIMNP)<sub>2</sub>Cl<sub>2</sub> was found to have 3.15 BM, hence the Nickel (II) ion was confirmed to possess octahedral geometry<sup>49</sup>.

#### **Electrochemical Behavior**

# Table 3: Redox potential of [Cu(TIMNP)Cl<sub>2</sub>] at various scan rates

Scan rate (mV/s)	-E <sub>pc</sub> (V)	E <sub>pa</sub> (V)
60	0.605	0.800
80	0.601	0.804
100	0.592	0.702
120	0.597	0.797

TBAP is used as the supporting electrolyte for recording the cyclic voltammograms of the copper(II) complex of ligand(TIMNP) in DMSO at room temperature. The experiment was carried at different scan rates. As  $E_{pa}$  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  $E_{pa}$ -

 $E_{pc}$  values are greater than 200 mV indicates that the reduction processes are irreversible in nature<sup>50</sup>. The ratio of anodic to cathodic peak currents corresponds to the following chemical change Cu(II)  $\rightarrow$  Cu(I)  $\rightarrow$  Cu(II). Redox potential of [Cu(TIMNP)Cl<sub>2</sub>] at various scan rates is given in Table 3. Typical cyclic voltammogram of Cu(II) complex at the scan rate of 100 mV/s is shown in Figure 1.



# Figure 1: Cyclic voltammogram of [Cu(TIMNP)Cl<sub>2</sub>] at 50 mV/s scan rate

### **EPR** spectral studies

The EPR spectrum of copper(II) complex of ligand (TIMNP) was recorded at 300 K (RT). The spin Hamiltonian parameters of the copper(II) complex of ligand (TIMNP) is listed Table 4. And it gives the various data in obtained from EPR of Cu(II) complex of ligand (TIMNP). The EPR spectrum of copper(II) complex of ligand (TIMNP) was recorded at 300 K (RT). The spin Hamiltonian parameters of the copper(II) complex of ligand (TIMNP) is listed Table.4.5 and it gives the various data in obtained from EPR of Cu(II) complex of ligand (TIMNP).  $g\perp$  (2.209) is greater than  $g_e$  and  $g_{\parallel}$ (2.244) is also greater than g<sub> $\perp$ </sub>. On the basis of above observation the following inferences were made: the  $d_{x^2-y^2}$  is the ground state orbital, there is axial elongation in the octahedral geometry and the odd electron may be located in the  $B_{1g}$ 

anti-bonding orbital<sup>51</sup>. The  $\beta^2$  (0.78) value supports the covalent nature of the complex. There is covalency in the metal ligand bonds as the value of  $g_{\parallel}$  is less than 2.3<sup>52</sup>. The complex has covalent character as  $\alpha^2$  (0.74) is less than unity, moreover the value of  $g_{iso}$  (107) suggest the same<sup>53-54</sup>. There is presence of covalency in the in-plane  $\pi$  bonding than the in-plane  $\sigma$ bonding as the  $\alpha^2$  value is less than  $\beta^{55}$ . Cu(II) complex is suggested to have highly distorted structure as the  $g_{\parallel}/A_{\parallel}$  is 170<sup>56-58</sup>.

Figure 2 represents the proposed structure of the metal(II) complexes of ligand (TIMNP). The mass spectral data and conductivity studies suggested that the chlorine atom is present with in the coordinating sphere. Both the oxygens of the ligand must be bonded through coordinate covalent bond. Two such ligands must be present. Thus a highly distorted octahedral geometry is suggested on the basis of electronic spectal data, magnetic moment studies and EPR spectra of Cu(II) complex.

Compound	a.	a	a	cr <sup>2</sup>	$a^2$ $b^2$	A	A⊥	Aiso	~	g∥ /	μ <sub>eff</sub>
Compound	g∥	g⊥	gav	u	μ	10 <sup>-4</sup> cm <sup>-1</sup>		giso	Ä∥	BM	
[Cu(TIMNP)Cl <sub>2</sub> ]	2.244	2.209	2.221	0.74	0.78	131	76	0.261	107	171	1.924

Table 5: The in vitro antimicrobial activity of (TI	IMNP) and its metal (II) complexes*
---	-------------------------------------

		Compound tri								
Туре	Organism	[Cu TIMNP Cl2]	[Co TIMNP Cl2]	[Ni TIMNP Cl2]	[Zn TIMNP Cl2]	ANMIL	Standard			
Fungi	Candida albicans	-	<u>- / j p f</u>	11	6	13	18			
	Aspergillus niger	-	-	4	2	-	16			
Gram negative	Pseudomonas aeruginosa	-	5	13	3	5	15			
bacteria	Klebsiella pneumonia	-	-	2	8	4	21			
	Escherichia coli	-	11	7	-	-	15			
Gram	Enterococcus faecalis	-	14	15	16	20	20			
positive bacteria	Staphylococcus aureus	-	-	2	-	-	19			
	Bacillus subtilis	-	8	9	7	16	16			

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



 $M = Cu^{II}, Co^{II}, Ni^{II} \& Zn^{II}$ 



### **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 and the ligand (TIMNP) against the bacteria (Enterococcus faecalis, Staphylococcus Bacillus subtilis, **P**seudomonas aureus, pneumonia aeruginosa, Klebsiella and Escherichia coli) and fungi (Candida albicans and Aspergillus niger) are given in the Table 5. Anti-bacterial activity of ligand (TIMNP) showed slightly higher activity than Ni(II) complex of ligand (TIMNP) but lesser than the standard. Cu(II) & Co(II) complexes of are resistant to Candida ligand(TIMNP) Albicans, Ni(II) & Zn(II) complexes of ligand(TIMNP) are active but lesser than the standard. Ligand, Cu(II) & Co(II) complexes of ligand(TIMNP) are resistant to Aspergillus Niger, mild activity was shown by Ni(II) & Zn(II) complexes of ligand(TIMNP). Ni(II) complex of ligand(TIMNP) has more or less the same activity as that of the standard against Ligand(TIMNP), Pseudomonas aeruginosa. Co(II) & Zn(II) complexes are lower in activity except Cu(II) complex of ligand(TIMNP) which is resistant to Pseudomonas aeruginosa. Mild activity was shown by ligand, Ni(II) & Zn(II) complexes of ligand(TIMNP) and not Cu(II) &

Co(II) complexes of ligand(TIMNP) which are resistant to *Klebsiella pneumonia*. Co(II) complex of ligand(TIMNP) is slightly active against *Staphylococcus faecalis*, Cu(II), Ni(II) & Zn(II) complexes of ligand(TIMNP) are resistant to it. Cu(II), Co(II) & Zn(II) complexes of ligand(TIMNP) are active lesser than the standard against *Staphylococcus faecalis*. Ligand(TIMNP) is equally active as that of standard against *Bacillus subtillis* & others are resistant to it<sup>59-62</sup>.

#### **FRAP Reducing Assay**



Figure 3: Iron chelating activity of (**TIMNP**) and and its metal(II) complexes

Iron chelating activity of (**TIMNP**) and and its metal(II) complexes is given in Figure 3. The Cu(II) complex of ligand (TIMNP) is more active than, Zn(II), Ni(II), ligand (TIMNP) and Co(II) complex of ligand (TIMNP).

### **Fluorescence Studies**

The ligand (TIMNP) and that of metal(II) complexes show emission bands at 271 nm and between 643-681 nm respectively. Due to charge transfer nature, all the complexes show broad emission bands<sup>63-65</sup>. Quenching of fluorescence (due to complex formation and the electron density is drained toward the electropositive metal ion) is suggested as there is shift between bands of ligand and metal(II) complex<sup>66</sup>. The emission maximum values of the ligand and metal(II) complexes are tabulated in Table 6.

Compound	Excitat ion maxim um (nm)	Emission maximum (nm)	Quant um yield
(TIMNP)	271	273	0.117
[Cu(TIMNP)Cl <sub>2</sub> ]	640	643	0.549
[Co(TIMNP)Cl <sub>2</sub> ]	678	678	0.433
[Ni(TIMNP)Cl <sub>2</sub> ]	680	681	0.108

Table 6: Fluorescence parameters of (TIMNP) and its metal(II) complexes

### SHG XRD Results

The ligand (TIMNP) is found to be 0.923 times the NLO activity of KDP and 0.211times 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<sup>67-70</sup>. The particle size of the ligand (TIMNP) is 16 nm<sup>71</sup>.

### CONCLUSION

The ligand and metal(II) complexes were successfully synthesized and characterized using various spectroscopic and analytical methods. The metal(II) complex was suggested to have distorted octahedral geometry. The cyclic voltammetry studies showed one electron transfer in the case of Cu(II) complex. The Ni(II) complex had better anti-microbial activity when compared with the rest of the metal(II) complexes. Cu(II) complex showed good antioxidant property. The fluorescence and NLO property were not as expected.

### REFERENCES

- Banday, A. H., Shameem, S. A., and Ganai, B. A. (2012). Antimicrobial studies of unsymmetrical bis-1, 2, 3-triazoles, *Organic* and Medicinal Chemistry Letters, 2, 1.
- Cacic, M., Trkovnik, M., Cacic, F., and Has-Schon, E. (2006). Synthesis and Antimicrobial Activity of Some Derivatives on the Basis (7-hydroxy-2-oxo-2H-chromen-

4-yl)-acetic Acid Hydrazide, *Molecules*, 11, 134-147.

- 3. Yadav, R., Srivastava, S., and Srivastava, S. (2005) Synthesis, antimicrobial and antiinflammatory activities of 4-oxothiazolidines and their 5-arylidenes, *Indian Journal of Chemistry- B* 44, 1262-1266.
- Kharitonov, Y. V., Shul'ts, E., Shakirov, M., 4. Pokrovskii, М., Pokrovskii, A., and Tolstikov. G. (2013)Synthetic transformation of higher terpenoids 31. Synthesis of 1, 2, 3-triazolyl-containing furan labdanoids and studies of their cytotoxic activity, Russian Chemical Bulletin. 62, 2046-2055.
- Rammah, M. M., Gati, W., Mtiraoui, H., Rammah, M. E. B., Ciamala, K., Knorr, M., Rousselin, Y., and Kubicki, M. M. (2016) Synthesis of Isoxazole and 1, 2, 3-Triazole Isoindole Derivatives via Silver-and Copper-Catalyzed 1, 3-Dipolar Cycloaddition Reaction, *Molecules*, 21, 307.
- 6. Saravanan, N. (1996) Studies On Some New 3d-Transition Metal Complexes Of Llgands Derived From Benzimidazole And Triazole, University of Science And Technology.
- 7. Zaidi, R., and Rawat, P. R. (2012) Evaluation of Cytotoxicity of Food in Human Hepatoma HepG2 Cells: Comet Assay Coupled to the MTT Assay, *Journal of Nutrition & Food Sciences 2012.*
- 8. Chohan, Z. H., Sumrra, S. H., Youssoufi, M. H., and Hadda, T. B. (2010) Design and synthesis of triazole Schiff bases and their oxovanadium (IV) complexes as antimicrobial agents, *Journal of Coordination Chemistry*, 63, 3981-3998.
- Diggs, D. L., Huderson, A. C., Harris, K. L., Myers, J. N., Banks, L. D., Rekhadevi, P. V., Niaz, M. S., and Ramesh, A. (2011) Polycyclic aromatic hydrocarbons and digestive tract cancers: a perspective, *Journal of Environmental Science and Health, Part C 29*, 324-357.

- Kajdan, T. W., Squattrito, P. J., and Dubey, S. N. (2000). Coordination geometries of bis (4-amino-3-ethyl-1, 2, 4-triazole-5-thione) complexes of Mn, Fe, Co, Ni, Cu and Zn: relationship to the 3-methyl analogs, *Inorganica Chimica Acta*, 300, 1082-1089.
- 11. Kumar, R., Roy, I., Ohulchanskky, T. Y., Vathy, L. A., Bergey, E. J., Sajjad, M., and Prasad, P. N. (2010). In vivo biodistribution and clearance studies using multimodal organically modified silica nanoparticles, *ACS nano*, *4*, 699-708.
- 12. Matesanz, A. I., Pastor, C., and Souza, P. (2007). Synthesis and structural characterization of a disulphide-bridged tetranuclear palladium (II) complex derived from 3, 5-diacetyl 1, 2, 4-triazole bis (4-ethylthiosemicarbazone), Inorganic Chemistry Communications, 10, 97-100.
- 13. Mishra, L., and Jha, A. (1995). Synthesis and Spectroscopic Studies of Nickel (II) and Copper (II) Polynuclear Complexes with Azolo-2, 4-Pentanediones, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 25, 601-613.
- Pattan, S., Dighe, N., Nirmal, S., Merekar, A., Laware, R., Shinde, H., and Musmade, D. (2009). Synthesis and biological evaluation of some substituted amino thiazole derivatives, *Asian Journal of Research in Chemistry*, 2, 196-201.
- 15. Joshi, K., Pancholi, A., Pandya, K., and Thakar, A. (2011). Synthesis, characterization and antimicrobial activity of novel schiff base and its transition metal complexes derived from 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one with 2-amino-4phenyl thiazole, *Journal of Chemical and Pharmaceutical Research 3*, 741-749.
- 16. Al-Jibouri, M. N., Hafith, F. R., and Rasheed, A. M. (2014). Synthesis and characterization of new metal complexes with n3 donor schiff base derived from 2aminothiazol, *European Chemical Bulletin 3*, 559-562.

- Kumar, U., and Chandra, S. (2010). Biological Active Cobalt (II) and Nickel (II) Complexes of 12-Membered Hexaaza [N 6] Macrocyclic Ligand Synthetic and Spectroscopic Aspects, *Journal of Chemistry*, 7, 1238-1245.
- Kelode, S. (2012). Synthesis, Characterization, And Thermal Studies Of Co (Ii), Ni (Ii), Cu (Ii), Cr (Iii), Mn (Iii), Fe (Iii), Vo (Iv), Zr (Iv) And Uo2 (Vi) Complexes Derived From Thiazole Schiff Base, Synthesis, 4, 1442-1446.
- 19. Refat, M. S. (2007). Complexes of uranyl (II), vanadyl (II) and zirconyl (II) with orotic acid "vitamin B13": synthesis, spectroscopic, thermal studies and antibacterial activity, *Journal of Molecular Structure*, 842, 24-37.
- 20. Refat, M. S., El-Deen, I. M., Zein, M. A., Adam, A. M. A., and Kobeasy, M. I. (2013). Spectroscopic, structural and electrical conductivity studies of Co (II), Ni (II) and Cu (II) complexes derived from 4acetylpyridine with thiosemicarbazide, *International Journal of Electrochemical Science*, *8*, 9894-9917.
- 21. Behan, A. (2005). Mass Spectrometry: A Textbook. By Jürgen H. Gross, *Proteomics*, 5, 4638-4638.
- 22. Silverstein, R. M., Webster, F. X., Kiemle, D. J., and Bryce, D. L. (2014). *Spectrometric identification of organic compounds*, John Wiley & Sons.
- 23. Nag, J., Das, D., Sinha, C., and De, B. (1998). Synthesis and characterization of copper (II), nickel (II), zinc (II), palladium (II) and dioxouranium (VI) complexes with a tridentate ONS donor Schiff base, *Journal of the Indian Chemical Society* 75, 496-498.
- Bottino, F., Finocchiaro, P., and Libertini, E. (1988). Synthesis and characterization of schiff base complexes with zinc halides, *Journal of Coordination Chemistry*, 16, 341-345.

- Gluvchinsky, P., Mockler, G. M., and Sinn, E. (1977). Nickel (II) complexes of some quadridentate Schiff-base ligands—II. Infrared spectra, *Spectrochimica Acta Part* A: Molecular Spectroscopy, 33, 1073-1077.
- 26. Beck, W. (1988). K. Nakamoto: Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4. Auflage, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore 1986. 484 Preis: \$55.-. **Berichte** Seiten. der Bunsengesellschaft für physikalische Chemie 92, 561-561.
- 27. Percy, G., and Stenton, H. (1976). Infrared and electronic spectra of Nsalicylideneglycinate complexes of cobalt and nickel, *Spectrochimica Acta Part A: Molecular Spectroscopy*, 32, 1615-1621.
- 28. Soliman, A., and Linert, W. (1999). Investigations on new transition metal chelates of the 3-methoxy-salicylidene-2aminothiophenol Schiff base, *Thermochimica acta, 338*, 67-75.
- 29. Elzahany, E. A., Hegab, K. H., Khalil, S. K., and Youssef, N. S. (2008). Synthesis, characterization and biological activity of some transition metal complexes with schiff bases derived from 2-formylindole, salicyladehyde and N-amino rhodanine, *Australian Journal of Basic and Applied Sciences*, 2, 210-220.
- Belaid, S., Landreau, A., Djebbar, S., Benali-Baitich, O., Bouet, G., and Bouchara, J.-P. (2008). Synthesis, characterization and antifungal activity of a series of manganese (II) and copper (II) complexes with ligands derived from reduced N, N'-O-phenylenebis (salicylideneimine), *Journal of Inorganic Biochemistry*, 102, 63-69.
- Cramer, R. E., Ho, D. M., Van Doorne, W., Ibers, J. A., Norton, T., and Kashiwagi, M. (1981). Triphenylmethylphosphonium trichloro (caffeine) platinum (II)[P (C6H5) 3 (CH3)][PtCl3 (caffeine)], structure and anticancer activity, *Inorganic Chemistry*, 20, 2457-2461.

- Potts, R. A., Gaj, D. L., Schneider, W. F., Dean, N. S., Kampf, J. W., and Oliver, J. P. (1991). Alcoholysis of nitriles in gold (III) complexes: The structure of [EtC (OEt) NH 2]+[AuCl 4]-, *Polyhedron 10*, 1631-1637.
- Kriza, A., Reiss, A., Florea, S., and Caproiu, T. (2000). Studies on complexes of cobalt-, nickel-, copper-, zinc-and cadmium (II) with Schiff base derived from 3aminodibenzofuran and salicylaldehyde, *Journal of the Indian Chemical Society*, 77, 207-208.
- 34. Mishra, A. (1999). Physicochemical and antimicrobial studies on nickel (II) and copper (II) Schiff base complexes derived from 2-furfuraldehyde, *Journal of the Indian Chemical Society*, *76*, 35-37.
- 35. Srivastava, T., and Singh, J. (1986) SOME Molecular adducts of diphenyltellurium (iv)bis-(trifluoroacetate) and bis-(trichloroacetate), *Journal of the Indian Chemical Society*, 63, 1015-1017.
- 36. El-Shahawi, M., and Shoair, A. (2004). Synthesis, spectroscopic characterization, redox properties and catalytic activity of some ruthenium (II) complexes containing aromatic aldehyde and triphenylphosphine or triphenylarsine, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 60, 121-127.
- Mohamed, G. G., Omar, M., and Ibrahim, A. A. (2009) Biological activity studies on metal complexes of novel tridentate Schiff base ligand. Spectroscopic and thermal characterization, *European Journal of Medicinal Chemistry*, 44, 4801-4812.
- Modarresi-Alam, A. R., and Nasrollahzadeh, M. (2009). Synthesis of 5-arylamino-1H (2H)-tetrazoles and 5-amino-1-aryl-1Htetrazoles from secondary arylcyanamides in glacial acetic acid: a simple and efficient method, *Turkish Journal of Chemistry 33*, 267-280.
- Babu, M. S., Reddy, K. H., and Krishna, P. G. (2007). Synthesis, characterization, DNA interaction and cleavage activity of new

mixed ligand copper (II) complexes with heterocyclic bases, *Polyhedron 26*, 572-580.

- 40. Cotton, F. A., and Wilkinson, G. (1988). Advanced Inorganic Chemistry, Vol. 594, Wiley New York.
- Sharaby, C. M. (2007). Synthesis, spectroscopic, thermal and antimicrobial studies of some novel metal complexes of Schiff base derived from [N 1-(4-methoxy-1, 2, 5-thiadiazol-3-yl) sulfanilamide] and 2thiophene carboxaldehyde, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 66, 1271-1278.
- 42. Dholakiya, P. P., and Patel, M. (2002). Preparation, magnetic, spectral, and biocidal studies of some transition metal complexes with 3, 5-dibromosalicylideneaniline and neutral bidentate ligands, *Synthesis and reactivity in inorganic and metal-organic chemistry*, 32, 819-829.
- 43. Rao, Y. S., Prathima, B., Reddy, S. A., Madhavi, K., and Reddy, A. V. (2010). Complexes of Cu (II) and Ni (II) with Bis (Phenylthiosemicarbazone): Synthesis, Spectral, EPR and in Vitro-Antibacterial and Antioxidant Activity, *Journal of the Chinese Chemical Society*, 57, 677-682.
- 44. Sharaby, C. M. (2005). Preparation, characterization and biological activity of Fe (III), Fe (II), Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and UO 2 (II) complexes of new cyclodiphosph (V) azane of sulfaguanidine, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 62, 326-334.
- 45. Chandra, S., Jain, D., Sharma, A. K., and Sharma, P. (2009). Coordination modes of a Schiff base pentadentate derivative of 4aminoantipyrine with cobalt (II), nickel (II) and copper (II) metal ions: synthesis, spectroscopic and antimicrobial studies, *molecules*, 14, 174-190.
- 46. Omar, M., and Mohamed, G. G. (2005). Potentiometric, spectroscopic and thermal studies on the metal chelates of 1-(2thiazolylazo)-2-naphthalenol,

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 61, 929-936.

- 47. Patroniak-Krzyminiewska, V., Litkowska, H., and Radecka-Paryzek, W. (1999). Metaltemplate synthesis and characterization of a nitrogen-oxygen donor schiff base macrocyclic system, *Monatshefte für Chemie/Chemical Monthly, 130*, 243-247.
- 48. Kumar, N., Nethaji, M., and Patil, K. (1991). Preparation, characterization, spectral and thermal analyses of (N 2 H 5) 2 MCl 4· 2H 2 O (M= Fe, Co, Ni and Cu); crystal structure of the iron complex, *Polyhedron*, *10*, 365-371.
- 49. Prasad, R., Thankachan, P., Thomas, M., and Pathak, R. (2001). Synthesis of aryl substituted azomethine complexes of iron-, cobalt-and copper (II), *Journal of the Indian Chemical Society*, *78*, 28-31.
- 50. Kannappan, R., Mahalakshmy, R., Rajendiran, T., Venkatesan, R., and Rao, P. S. (2003). Magnetic, catalytic, EPR and electrochemical studies on binuclear copper (II) complexes derived from 3, 4disubstituted phenol, *Journal of Chemical Sciences, 115*, 1-14.
- 51. Raman, N., Kulandaisamy, A., and Jeyasubramanian, K. (2001). Synthesis, spectroscopic characterization, redox, and biological screening studies of some Schiff base transition metal (II) complexes derived from salicylidene-4-aminoantipyrine and 2-aminophenol/2-aminothiophenol, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 31, 1249-1270.
- 52. Ray, R., and Kauffmann, G. B. (1990). An EPR study of copper (II)-substituted biguanide complexes. Part III, *Inorganica Chimica Acta*, 174, 237-244.
- 53. Anitha, C., Sumathi, S., Tharmaraj, P., and Sheela, C. (2012). Synthesis, characterization, and biological activity of some transition metal complexes derived from novel hydrazone azo schiff base ligand, *International Journal of Inorganic Chemistry*, 2011.

- 54. Sumathi, S., Anitha, C., Tharmaraj, P., and Sheela, C. (2012). Spectral, NLO. Fluorescence, and Biological Activity of Condensate of-Diketone Knoevenagel Ligands and Their Metal (II) Complexes, International Journal Inorganic of Chemistry, 2011.
- 55. Ray, R., and Kauffman, G. B. (1990). An EPR Study of some copper (II) coordination compounds of substituted biguanides. Part IV, *Inorganica Chimica Acta 174*, 257-262.
- Ainscough, E. W., Brodie, A. M., Depree, C. V., Moubaraki, B., Murray, K. S., and Otter, C. A. (2005). Copper (II) chloride complexes with multimodal ligands based on the cyclotriphosphazene platform, *Dalton Transactions*, 3337-3343.
- 57. Chandrasekhar, V., Pandian, B. M., and Azhakar, R. (2006). Di-and Trinuclear Complexes Derived from Hexakis (2-pyridyloxy) cyclotriphosphazene. Unusual PO Bond Cleavage in the Formation of [{(L'CuCl) 2 (Co (NO3)} Cl](L'= N3P3 (OC5H4N) 5 (O)), *Inorganic Chemistry*, 45, 3510-3518.
- 58. Shimono, S., Takahashi, H., Sakai, N., Tamura, R., Ikuma, N., and Yamauchi, J. (2005). Use of cyclotriphosphazene as a molecular scaffold for building chiral multispin systems, *Molecular Crystals and Liquid Crystals 440*, 37-52.
- 59. Chohan, Z. H., Scozzafava, A., and Supuran, C. T. (2003). Zinc complexes of benzothiazole-derived Schiff bases with antibacterial activity, *Journal of Enzyme Inhibition and Medicinal Chemistry*, 18, 259-263.
- 60. Chohan, Z. H., Supuran, C. T., and Scozzafava, A. (2005). Metal binding and antibacterial activity of ciprofloxacin complexes, *Journal of Enzyme Inhibition and Medicinal Chemistry*, 20, 303-307.
- 61. Daniel, V. P., Murukan, B., Kumari, B. S., and Mohanan, K. (2008). Synthesis, spectroscopic characterization, electrochemical behaviour, reactivity and

antibacterial activity of some transition metal complexes with 2-(Nsalicylideneamino)-3-carboxyethyl-4, 5dimethylthiophene, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 70, 403-410.

- 62. Murukan, B., and Mohanan, K. (2006). Synthesis, characterization, electrochemical properties and antibacterial activity of some transiton metal complexes with [(2-hydroxy-1-naphthaldehyde)-3-isatin]-bishydrazone, *Transition Metal Chemistry 31*, 441-446.
- 63. Hou, L., and Li, D. (2005). A novel photoluminescent Ag–terpyridyl complex: one-dimensional linear metal string with double-helical structure, *Inorganic Chemistry Communications 8*, 128-130.
- 64. Ma, D.-L., Shum, T. Y.-T., Zhang, F., Che, C.-M., and Yang, M. (2005). Water soluble luminescent platinum terpyridine complexes with glycosylated acetylide and arylacetylide ligands: photoluminescent properties and cytotoxicities, *Chemical Communications*, 4675-4677.
- 65. Wang, P., Leung, C. H., Ma, D. L., Yan, S. C., and Che, C. M. (2010). Structure-Based Design of Platinum (II) Complexes as c-myc Oncogene Down-Regulators and Luminescent Probes for G-Quadruplex DNA, *Chemistry–A European Journal 16*, 6900-6911.
- 66. Yu, T., Zhang, K., Zhao, Y., Yang, C., Zhang, H., Qian, L., Fan, D., Dong, W., Chen, L., and Qiu, Y. (2008). Synthesis, crystal structure and photoluminescent properties of an aromatic bridged Schiff base ligand and its zinc complex, *Inorganica Chimica Acta 361*, 233-240.
- 67. Allcock, H. R., Laredo, W. R., Kellam, E. C., and Morford, R. V. (2001). Polynorbornenes bearing pendent cyclotriphosphazenes with oligoethyleneoxy side groups: behavior as solid polymer electrolytes, *Macromolecules 34*, 787-794.
- 68. Chen, C., Wu, Y., Jiang, A., Wu, B., You, G., Li, R., and Lin, S. (1989). New

nonlinear-optical crystal: LiB 3 O 5, *JOSA B* 6, 616-621.

- 69. Choy, M. M., and Byer, R. L. (1976). Accurate second-order susceptibility measurements of visible and infrared nonlinear crystals, *Physical Review B* 14, 1693.
- 70. Umemura, Y., Yamagishi, A., Schoonheydt,

R., Persoons, A., and De Schryver, F. (2002). Langmuir-Blodgett films of a clay mineral and ruthenium (II) complexes with a noncentrosymmetric structure, *Journal of the American Chemical Society* 124, 992-997.

71. Patterson, A. (1939). The Scherrer formula for X-ray particle size determination, *Physical review 56*, 978.

