



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

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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 were 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 origin¹⁻³ having a number of pharmaceutical properties. Azoles are five-membered heterocycles with two or more heteroatoms, one of which is nitrogen having wider application in medicines. 1,2,4-Triazoles^{4,5} 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^{6,7} and find application in photographic process, corrosion control, agriculture⁸⁻¹³ and industry. Derivatives of 4-amino-3-substituted-5-mercapto-1,2,4-triazoles possess broad spectrum of biological activities¹⁴. O, N and S donor atoms of the triazole Schiff

bases¹⁵ are important biologically and are used as versatile ligands forming mono to polynuclear complexes^{16,17} 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 applications¹⁸.

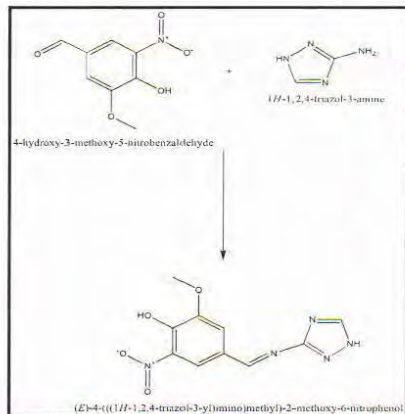
MATERIALS AND METHODS

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

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



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

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

A solution containing the metal salt (2 mmol) {CoCl₂.6H₂O, NiCl₂.6H₂O, CuCl₂.2H₂O or ZnCl₂}, 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

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

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

(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 CaCl₂. 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 10⁻³ M DMSO.

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

Compound	Molecular Formula	Molecular Weight	CA(TIMNP)ULATED % (FOUND %)			
			C	H	N	M
(TIMNP)	C ₁₀ H ₉ N ₃ O ₄	263	463 (458)	3.45 (3.44)	26.61 (26.51)	-
Cu(TIMNP) ₂ Cl ₂	C ₂₀ H ₁₈ C ₁₂ N ₁₀ O ₈ Cu	659	36.35 (36.32)	2.75 (2.74)	21.19 (21.11)	9.62 (9.60)
Co(TIMNP) ₂ Cl ₂	C ₂₀ H ₁₈ C ₁₂ N ₁₀ O ₈ Co	655	36.60 (36.51)	2.76 (2.74)	21.34 (21.33)	8.98 (8.96)
Ni(TIMNP) ₂ Cl ₂	C ₂₀ H ₁₈ C ₁₂ N ₁₀ O ₈ Ni	654	36.62 (36.58)	2.77 (2.71)	21.35 (21.30)	8.95 (8.94)
Zn(TIMNP) ₂ Cl ₂	C ₂₀ H ₁₈ C ₁₂ N ₁₀ O ₈ Zn	660	36.25 (36.20)	2.74 (2.73)	21.14 (21.12)	9.87 (9.81)

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

Table 2: IR spectral data (cm⁻¹) of (TIMNP) and its metal (II) complexes.

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

Digisun Electronics Digital conductivity meter – model: D1-909; cell constant-1.007. The measured molar conductance values ranging from 9-7.0 $\text{Scm}^2\text{mol}^{-1}$ for the DMSO solutions of all the metal (II) complexes are very negligible as given in Table 1.a. This suggests a non-electrolytic nature for these complexes. Hence the chloride ion present in the metal complexes must be inside the coordinating sphere^{19,20}. 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 $\text{M}(\text{TIMNP})\text{Cl}_2$ 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^{-1} in the IR spectra of the ligand assigned to formyl ($\nu_{\text{C=O}}$) & amino (ν_{NH_2}) moieties respectively indicated the formation of schiff base from 5-nitrovanillin & 3-amino 1,2,4-triazole²³. 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 $\nu(\text{N}=\text{CH})$ is present in the free ligand. In the IR spectra of the ligand $\nu_{\text{C=N}}$ of the free ligand at 1659 cm^{-1} has not been shifted to lower frequency(lower wave numbers) i.e appeared at

1651-1653 cm^{-1} in the complexes indicating the non-coordination of azomethine nitrogen with metal^{24,25}. The peak at 3348 cm^{-1} attributed to $\nu_{\text{O-H}}$ of the ligand is shifted to 3325-3331 cm^{-1} in its metal complexes indicating coordination of oxygen atom to metal(II) ion without deprotonation²⁶. $\nu_{\text{C=N}}$ & $\nu_{\text{C-N}}$ cyclic of triazole ring at 1608-1612 & 1205-1215 cm^{-1} in Schiff base ligand does not alter in the spectra of the complexes rule out the participation of cyclic group in coordination by nitrogen^{27,28}. No remarkable shift in the stretching vibrations of $\nu_{\text{C-N}}$, $\nu_{\text{N-H}}$ & ν_{NO_2} at 1246-1254, 3123-3127 & 1359-1368 cm^{-1} suggested the non-coordination of nitrogen & NO_2 group with metal(II) ion²⁹. New peaks appearing at 501-520 & 624-629 cm^{-1} in the complexes assignable to $\nu_{\text{M-O}}$ vibrations of phenolic and methoxy groups respectively^{30,31}.

NMR Spectral Studies

In the ¹H NMR of (TIMNP), the methoxy protons (three) were obtained at 3.3 ppm (δ) singlet³². The -OH proton was obtained at 11.8 ppm (δ) as singlet³³. The aromatic and the hetero ring protons were obtained between 6.9 and 7.9 ppm (δ)^{34,35}. The azomethine proton was obtained at 8.1 ppm (δ)³⁶⁻³⁷. The -NH proton was obtained at 9.3 ppm (δ)³⁸. The Zn(TIMNP)Cl₂ 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^{-1} (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^{-1} (640 nm) corresponding to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition. A distorted octahedral geometry has been suggested for Cu(II) complex $[\text{Cu}(\text{TIMNP})\text{Cl}_2]$ ³⁹⁻⁴¹. For the Co(II) complex $[\text{Co}(\text{TIMNP})\text{Cl}_2]$ three transitions were obtained at 10417 cm^{-1} (960 nm), 14903 cm^{-1} (671 nm) and 18116 cm^{-1} (552nm) assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow$

${}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transitions respectively. This suggests a distorted octahedral environment around Co(II) complex⁴²⁻⁴⁴. The nickel complex $[Ni(TIMNP)Cl_2]$ exhibits three bands at 9823 cm^{-1} (1018 nm), 14728 cm^{-1} (679 nm) and 22422 cm^{-1} (446 nm) corresponding to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions respectively. The above observed transitions reveals that Ni(II) complex has a distorted octahedral environment^{45,46}.

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 geometry⁴⁷. $Co(TIMNP)_2Cl_2$ had 4.91 BM, which also confirms the octahedral geometry around the Cobalt(II) ion⁴⁸. $Ni(TIMNP)_2Cl_2$ was found to have 3.15 BM, hence the Nickel (II) ion was confirmed to possess octahedral geometry⁴⁹.

Electrochemical Behavior

Table 3: Redox potential of $[Cu(TIMNP)Cl_2]$ at various scan rates

Scan rate (mV/s)	$-E_{pc}$ (V)	E_{pa} (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 nature⁵⁰. 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 $[Cu(TIMNP)Cl_2]$ 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.

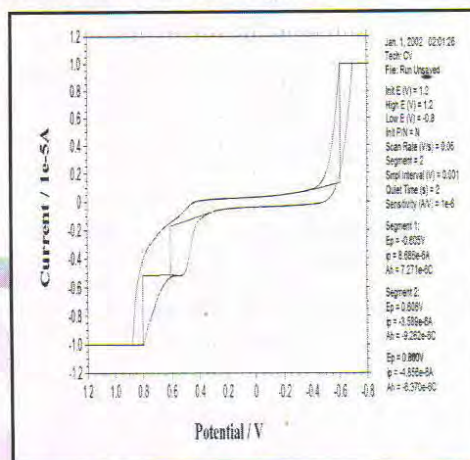


Figure 1: Cyclic voltammogram of $[Cu(TIMNP)Cl_2]$ at 50 mV/s scan rate-

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 in Table 4. And it gives the various data 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 in Table.4.5 and it gives the various data 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_{\perp} . 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 orbital⁵¹. The β^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 2.3⁵². The complex has covalent character as α^2 (0.74) is less than unity, moreover the value of g_{iso} (107) suggest the same⁵³⁻⁵⁴. There is presence of covalency in the in-plane π bonding than the in-plane σ bonding as the α^2 value is less than β^2 ⁵⁵. Cu(II) complex is suggested to have highly distorted structure as the $g_{\parallel}/A_{\parallel}$ is 170⁵⁶⁻⁵⁸.

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 spectral data, magnetic moment studies and EPR spectra of Cu(II) complex.

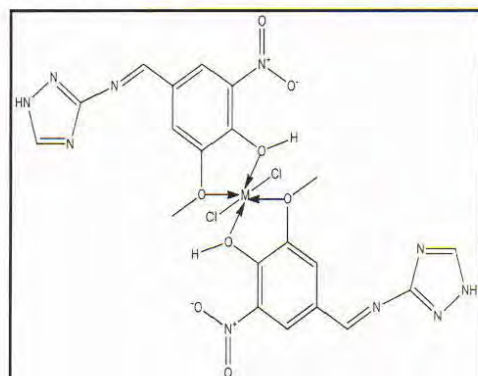
Table 4: EPR spectral parameters of [Cu(TIMNP)Cl₂] at 300 K

Compound	g_{\parallel}	g_{\perp}	g_{av}	α^2	β^2	A_{\parallel}	A_{\perp}	A_{iso}	g_{iso}	$g_{\parallel} / A_{\parallel}$	μ^{eff} BM
						$10^{-4}cm^{-1}$					
[Cu(TIMNP)Cl ₂]	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 (TIMNP) and its metal (II) complexes*

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

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



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

Figure 2: Proposed structure of the metal (II) complexes of (TIMNP)

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 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 (TIMNP) showed slightly higher activity than Ni(II) complex of ligand (TIMNP) but lesser than the standard. Cu(II) & Co(II) complexes of ligand(TIMNP) are resistant to *Candida 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 *Pseudomonas aeruginosa*. Ligand(TIMNP), 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 subtilis* & others are resistant to it⁵⁹⁻⁶².

FRAP Reducing Assay

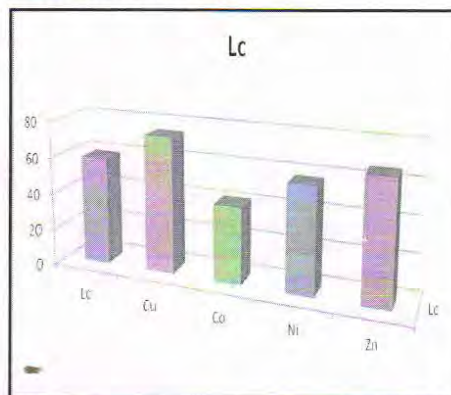


Figure 3: Iron chelating activity of (TIMNP) and its metal(II) complexes

Iron chelating activity of (TIMNP) 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 bands⁶³⁻⁶⁵. 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) complex⁶⁶. The emission maximum values of the ligand and metal(II) complexes are tabulated in Table 6.

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

Compound	Excitation maximum (nm)	Emission maximum (nm)	Quantum yield
(TIMNP)	271	273	0.117
[Cu(TIMNP)Cl ₂]	640	643	0.549
[Co(TIMNP)Cl ₂]	678	678	0.433
[Ni(TIMNP)Cl ₂]	680	681	0.108

SHG XRD Results

The ligand (TIMNP) is found to be 0.923 times the NLO activity of KDP and 0.211 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 molecule⁶⁷⁻⁷⁰. The particle size of the ligand (TIMNP) is 16 nm⁷¹.

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 anti-oxidant property. The fluorescence and NLO property were not as expected.

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