



Synthesis, Characterization and Antimicrobial Activity of Isomeric Pyridyl-Tetrazole Derivative Ligands and their Bivalent Metal Complexes

B. UMAMAHESWARA RAO¹, V. KRISHNA^{2,*} and G. NAGESWARA RAO¹

¹Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam-530 003, India

²Department of Chemistry, Malla Reddy Engineering College (Autonomous), Hyderabad-500 100, India

*Corresponding author: E-mail: krishnanitw2010@gmail.com; vaddadi_krishna@yahoo.com

Received: 2 March 2015;

Accepted: 21 April 2015;

Published online: 29 August 2015;

AJC-17481

Nickel(II) and zinc(II) complexes were synthesized from bidentate isomeric pyridyl tetrazole ligands such as 2-(1-vinyl-1H-tetrazol-5-yl)pyridine (L¹), N,N-dimethyl-3-(5-(pyridin-2-yl)-1H-tetrazol-1-yl)propan-1-amine (L²), 2-(2-vinyl-2H-tetrazol-5-yl)pyridine (L³), N,N-dimethyl-3-(5-(pyridin-2-yl)-2H-tetrazol-2-yl)propan-1-amine (L⁴). All the complexes were characterized in the light of elemental analysis, FTIR, UV-visible and magnetic studies. The spectroscopic data suggested that, the ligands act as neutral and monobasic bidentate ligands and form octahedral complexes with general formula [M(L¹⁻⁴)₂Cl₂] (M = Ni(II) and Zn(II)). The isomeric pyridyl-tetrazole derivative ligands and their Ni(II) and Zn(II) complexes have also been screened for their antibacterial (*Bacillus subtilis*, *Staphylococcus aureus*, *Proteus vulgaris*) and antifungal activities (*Aspergillus niger*, *Candida albicans*) by MIC method.

Keywords: Isomeric pyridyl-tetrazole derivatives, Nickel and Zinc complexes, Antimicrobial activity.

INTRODUCTION

Biologically active isomeric pyridyl tetrazole derivatives have been under investigations as part of inorganic chemistry. Polyazole rings are versatile ligands¹ for coordinating transition metals, therefore synthesis of transition metal complexes containing polyazole rings, particularly tetrazoles and their derivatives have given enormous significance, due to their practical applications²⁻⁴. There is an increasing interest of tetrazole derivatives for the development of “click” chemistry which was reported by Sharpless and co-workers⁵. Conversely, tetrazole-based compounds have made known special functionalities with interesting structures⁶. Tetrazole derivatives have found applications in therapeutics as anti-hypertensive agents⁷, antibiotics⁸ and drugs for AIDS treatment⁹.

Even though many tetrazole containing derivatives are available in the literature, there is always an increasing demand for the development of novel and effective tetrazole containing therapeutic agents. In continuation of our ongoing research on DNA binding and cleavage activities of transition metal complexes¹⁰, in this paper we presented the synthesis, antimicrobial activities of Ni(II) and Zn(II) complexes which are obtained by the reaction of pyridyl-tetrazole derivatives which contain pendant arms like vinyl or propyl-N(CH₃)₂ group.

EXPERIMENTAL

Chemicals were purchased from Sigma, Aldrich and metal salts used in the preparation of the complexes are of reagent grade. The solvents used in the synthesis of the ligands and metal complexes were distilled before use. All other chemicals were of AR grade and were used without further purification. The elemental analysis of carbon, hydrogen and nitrogen, contents was performed using Perkin Elmer CHNS analyzer. The electronic absorption spectra of the complexes were recorded on JASCO V-670 spectrophotometer in the wavelength region of 250-1400 nm in the solid state. The FTIR spectra of the complexes were recorded on Tensor 2 FTIR spectrophotometer in the region of 4000-400 cm⁻¹ using KBr disc. The magnetic susceptibilities of Ni(II) complexes were measured with a Sherwood scientific balance. Diamagnetic corrections were calculated from Pascal's constants. The magnetic moment values were calculated using the relation $\mu_{\text{eff}} = 2.83 (\chi_m T)^{1/2}$ B.M.

Synthesis of ligands: The preparation of L is carried as per literature¹¹ m.p. 221-223 °C. C, 48.98; H, 3.43; N, 47.60, ¹H NMR (CD₃OD): 8.56 (d, 1H, J = 7.9 Hz, pyr-H), 8.0 (d, 1H, J = 7.8 Hz, pyr-H), 7.79 (t, 1H, J = 7.8 Hz, pyr-H), 7.26 (t, 1H, J = 7.9 Hz, pyr-H), 7.1 (s, 1H, tetrazole-H) ppm.

N,N-Dimethyl-3-(5-(pyridin-2-yl)-1H-tetrazol-1-yl)propan-1-amine(L²-L⁴): To the compound L (1 g, 6.8

mmol) dissolved in acetonitrile (30 mL) was added potassium carbonate (4.6 g, 34 mmol). The resulting solution was refluxed for 0.5 h and to hot solution was added 3-chloro-N,N-dimethylpropan-1-amine (3.1 g, 22 mmol). The reaction mixture was then stirred at reflux temperature for a further 24 h. After cooling, the solvent was removed under reduced pressure to afford a white precipitate, which was purified by column chromatography on silica gel (ethyl acetate:hexane by the ratio of 20:80) to give isomers L^1 and L^3 .

L^2 : White brown solid (0.55 g, yield 26 %). m.p. 72-76 °C. Anal. calcd. for $C_{11}H_{16}N_6$ (232.28): C, 56.88; H, 6.94; N, 36.18; 1H NMR ($CDCl_3$, 300 MHz): δ 8.71 (d, 1H, $J = 4.5$ Hz, pyr-H), 8.37 (d, 1H, $J = 8.1$ Hz, pyr-H), 7.91 (dt, 1H, $J = 7.8, 1.8$ Hz, pyr-H), 7.45 (dd, 1H, $J = 7.5, 5.1$ Hz, pyr-H), 5.12 (t, 2H, $J = 6.9$ Hz, CH_2N), 2.88 (t, 2H, $J = 6.9$ Hz, CH_2), 2.42(p, 2H, $J = 6.9$ Hz, CH_2), 2.29 (s, 6H, $N(CH_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 60 MHz): δ 150.45 (CN_4), 148.53, 144.66, 137.16, 123.15, 122.24, 48.24 (CH_2N_4), 43.56 ($CH_2N-(CH_3)_2$), 26.82, ppm.

L^4 : White brown solid (0.55 g, yield 26 %). m.p. 66-68 °C. Anal. calcd. for $C_{11}H_{16}N_6$ (232.28): C, 56.88; H, 6.94; N, 36.18; 1H NMR ($CDCl_3$, 300 MHz): δ 8.65 (d, 1H, $J = 4.5$ Hz, pyr-H), 8.28 (d, 1H, $J = 8.1$ Hz, pyr-H), 7.87 (dt, 1H, $J = 7.8, 1.8$ Hz, pyr-H), 7.34 (t, 1H, $J = 7.5, 5.1$ Hz, pyr-H), 5.06 (t, 2H, $J = 6.9$ Hz, CH_2N), 2.82 (t, 2H, $J = 6.9$ Hz, CH_2), 2.42(p, 2H, $J = 6.9$ Hz, CH_2), 2.27 (s, 6H, $N(CH_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 60 MHz): δ 151.35 (CN_4), 149.44, 145.36, 138.08, 124.64, 122.12, 49.54 (CH_2N_4), 44.34 ($CH_2N-(CH_3)_2$), 26.82, ppm.

Synthesis of 2-(1-vinyl-1H-tetrazol-5-yl)pyridine: The above procedure is followed with 2-chlorovinyl (2.0 g, 24 mmol) to give L^1 and L^3 .

L^1 : White brown needles, (0.35 g, yield 27 %). m.p. 57-59 °C. Anal. calcd. for $C_8H_7N_5$ (173.17): C, 55.48; H, 4.07; N, 40.44; 1H NMR ($CDCl_3$, 300 MHz): δ = 8.70 (d, 1H, $J = 4.8$ Hz, pyr-H), 8.37 (d, 1H, $J = 7.8$ Hz, pyr-H), 7.86 (dt, 1H, $J = 7.8, 1.5$ Hz, pyr-H), 7.53 (dd, 1H, $J = 6.9, 5.1$ Hz, pyr-H), 5.32(t, 1H, $J = 6.9$, vinyl-H), 4.21-4.18 (d, 2H, $J = 6.9$, vinyl-2H). ^{13}C NMR ($CDCl_3$, 60 MHz): δ 152.15 (CN_4), 149.73, 144.39, 138.14, 125.79, 124.35, 127.3 (HC, vinyl), 102.9 ppm (2H, vinyl).

L^3 : White brown needles, (0.35 g, yield 27 %). m.p. 57-58 °C. Anal. calcd. for $C_8H_7N_5$ (173.17): C, 55.48; H, 4.07; N, 40.44; 1H NMR ($CDCl_3$, 300 MHz): δ = 8.70 (d, 1H, $J = 4.8$ Hz, pyr-H), 8.37 (d, 1H, $J = 7.8$ Hz, pyr-H), 7.86 (dt, 1H, $J = 7.8, 1.5$ Hz, pyr-H), 7.53 (dd, 1H, $J = 6.9, 5.1$ Hz, pyr-H), 5.31(t, 1H, $J = 6.9$, vinyl-H), 4.21-4.18 (d, 2H, $J = 6.9$, vinyl-2H). ^{13}C NMR ($CDCl_3$, 60 MHz): δ 151.15 (CN_4), 149.73, 144.39, 138.14, 125.79, 124.35, 127.3 (HC, vinyl), 102.9 ppm (2H, vinyl).

Synthesis of complexes: The appropriate ligand (L^1 - L^4) (1.36 mol) was dissolved in methanol (30 mol) and added to a methanolic solution (10 mol) of $MCl_2 \cdot H_2O$ (1.36 mol). The resulting pale green to green coloured solutions were then heated to reflux for 2-3 h. The solution was left over night at room temperature and filtered to collect respective precipitate.

$[Ni(L^1)_2]Cl_2$: Dark green solid (0.12 g, yield 28 %) Anal. calcd. for $C_{16}H_{14}N_{10}NiCl_2$ (475.95): C, 40.38; H, 2.96; N, 29.43; Found: C, 40.76; H, 2.98; N, 29.96 % IR (KBr, ν_{max} , cm^{-1}): 3245, 2945, 1648, 1594, 1496, 1196, 1147, 1023, 835, 785.

λ_{max} (MeOH) 376 nm, $\epsilon = 40 M^{-1}cm^{-1}$. Magnetic moment: 3.2 B.M.

$[Ni(L^3)_2]Cl_2$: Pale green crystals (0.14 g, yield 32 %) Anal. calcd. for $C_{16}H_{14}N_{10}NiCl_2$ (475.95): C, 40.38; H, 2.96; N, 29.43; Found: C, 40.76; H, 2.98; N, 29.96 % IR (KBr, ν_{max} , cm^{-1}): 3245, 2945, 1648, 1594, 1496, 1196, 1147, 1023, 835, 785. λ_{max} (MeOH) 388 nm, $\epsilon = 38 M^{-1}cm^{-1}$. Magnetic moment: 3.2 B.M.

$[Zn(L^1)_2]Cl_2$: Waxy cream solid (0.17 g, 56 %). $C_{16}H_{14}N_{10}ZnCl_2$ (482.64): Calc. C, 39.82; H, 2.92; N, 29.02; Found: C, 26.92; H, 2.63; N, 17.06 %. IR (KBr, ν_{max} , cm^{-1}): 2945, 2823, 1610, 1565, 1548, 1453, 1058, 1015, 850, 770. 1H NMR ($CDCl_3$): δ = 8.78 (m, 1H, pyr-H), 8.35 (m, 1H, pyr-H), 7.95 (m, 1H, pyr-H), 7.45 (m, 1H, pyr-H), 3.49 (d, 2H, $J = 6.2$ Hz, vinyl CH_2), 2.18 (t, 1H, $J = 6.2$ Hz vinyl CH) ppm. ^{13}C NMR ($CDCl_3$): δ 152.15 (CN_4), 149.73, 144.39, 138.14, 125.79, 124.35, 127.3 (HC, vinyl), 102.9 ppm (2H, vinyl).

$[Zn(L^3)_2]Cl_2$: Waxy orange solid (0.19 g, 58 %). $C_{16}H_{14}N_{10}ZnCl_2$ (482.64): Calc. C, 39.82; H, 2.92; N, 29.02; Found: C, 26.92; H, 2.63; N, 17.06 %. IR (KBr, ν_{max} , cm^{-1}): 2965, 2833, 1612, 1568, 1548, 1453, 1058, 1015, 850, 780. 1H NMR ($CDCl_3$): δ = 8.68 (m, 1H, pyr-H), 8.45 (m, 1H, pyr-H), 7.95 (m, 1H, pyr-H), 7.45 (m, 1H, pyr-H), 3.49 (d, 2H, $J = 6.2$ Hz, vinyl CH_2), 2.18 (t, 1H, $J = 6.2$ Hz vinyl CH) ppm. ^{13}C NMR ($CDCl_3$): δ 153.15 (CN_4), 149.73, 145.39, 138.14, 125.79, 124.35, 127.3 (HC, vinyl), 102.9 ppm (2H, vinyl).

$[Ni(L^2)_2]Cl_2$: Pale green precipitate (0.12 g, yield 32 %) Anal. calcd. for $C_{22}H_{32}N_{12}NiCl_2$ (594.17): C, 44.47; H, 5.43; N, 28.29; Found: C, 44.36; H, 5.33; N, 28.96 % IR (KBr, ν_{max} , cm^{-1}): 3245, 2945, 1648, 1594, 1496, 1196, 1147, 1023, 835, 785. λ_{max} (MeOH) 346 nm, $\epsilon = 86 M^{-1}cm^{-1}$. Magnetic moment: 3.2 B.M.

$[Ni(L^4)_2]Cl_2$: Pale green precipitate (0.13 g, yield 42 %) Anal. calcd. for $C_{22}H_{32}N_{12}NiCl_2$ (594.17): C, 44.47; H, 5.43; N, 28.29; Found: C, 44.34; H, 5.32; N, 28.86 % IR (KBr, ν_{max} , cm^{-1}): 3235, 2925, 1648, 1594, 1496, 1196, 1157, 1023, 835, 785. λ_{max} (MeOH) 366 nm, $\epsilon = 52 M^{-1}cm^{-1}$. Magnetic moment: 3.2 B.M.

$[Zn(L^2)_2]Cl_2$: Waxy cream solid (0.17 g, 56 %). $C_{22}H_{32}N_{12}ZnCl_2$ (600.86): calc. C, 43.98; H, 5.37; N, 27.97; Found: C, 43.92; H, 5.33; N, 28.36 %. IR (KBr, ν_{max} , cm^{-1}): 2955, 2823, 1610, 1545, 1548, 1453, 1058, 1015, 850, 770. 1H NMR ($CDCl_3$, 300 MHz): δ 8.71 (d, 1H, $J = 4.5$ Hz, pyr-H), 8.37 (d, 1H, $J = 8.1$ Hz, pyr-H), 7.91 (dt, 1H, $J = 7.8, 1.8$ Hz, pyr-H), 7.45 (dd, 1H, $J = 7.5, 5.1$ Hz, pyr-H), 5.12 (t, 2H, $J = 6.9$ Hz, CH_2N), 2.88 (t, 2H, $J = 6.9$ Hz, CH_2), 2.42(p, 2H, $J = 6.9$ Hz, CH_2), 2.29 (s, 6H, $N(CH_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 60 MHz): δ 150.45 (CN_4), 148.53, 144.66, 137.16, 123.15, 122.24, 48.24 (CH_2N_4), 43.56 ($CH_2N-(CH_3)_2$), 26.82, ppm.

$[Zn(L^4)_2]Cl_2$: Cream solid (0.18 g, 46 %). $C_{22}H_{32}N_{12}ZnCl_2$ (600.86): Calc. C, 43.98; H, 5.37; N, 27.97; Found: C, 43.92; H, 5.33; N, 28.36 %. IR (KBr, ν_{max} , cm^{-1}): 2965, 2833, 1610, 1545, 1548, 1453, 1058, 1015, 850, 770. 1H NMR ($CDCl_3$, 300 MHz): δ 8.61 (d, 1H, $J = 4.5$ Hz, pyr-H), 8.37 (d, 1H, $J = 8.1$ Hz, pyr-H), 7.91 (dt, 1H, $J = 7.8, 1.8$ Hz, pyr-H), 7.45 (dd, 1H, $J = 7.5, 5.1$ Hz, pyr-H), 5.12 (t, 2H, $J = 6.9$ Hz, CH_2N), 2.88 (t, 2H, $J = 6.9$ Hz, CH_2), 2.42 (p, 2H, $J = 6.9$ Hz, CH_2), 2.29 (s, 6H, $N(CH_3)_2$) ppm. ^{13}C NMR ($CDCl_3$, 60 MHz): δ

151.45 (CN₄), 148.53, 144.66, 137.16, 123.15, 122.24, 48.24 (CH₂N₄), 43.56 (CH₂N-(CH₃)₂), 26.82, ppm.

Antimicrobial activity: *in vitro* antimicrobial activity of the metal complexes towards the bacteria *Proteus vulgaris*, *Klebsiella pneumoniae*, *Staphylococcus aureus* and *Bacillus subtilis* and fungi *Candida albicans* was carried out using disc diffusion method. The antibiotics kanamycin and clotrimazole are the standards for antibacterial and antifungal activity studies. Standard inoculum, $1-2 \times 10^7$ cfu/mL 0.5 McFarland bacterial growth (no turbidity) in comparison to control was regarded as MIC.

RESULTS AND DISCUSSION

All the Ni(II) complexes were coloured, stable and non-hygroscopic in nature. The complexes are insoluble in common organic solvents but soluble in DMF and DMSO. The elemental analysis showed that the complexes have 1: 2 stoichiometry of the type $[M(L^{1-4})_2] \cdot Cl_2$, where L stands for singly deprotonated ligands¹².

Determination of metal content of the complexes:

Known amount (0.150 g) of complexes was decomposed with concentrated nitric acid. This process was repeated till the organic part of the complexes got completely lost. The excess nitric acid was expelled by evaporation with concentrated sulphuric acid. The Ni(II) and Zn(II) contents of the complexes were determined as per the procedure available in the literature¹³.

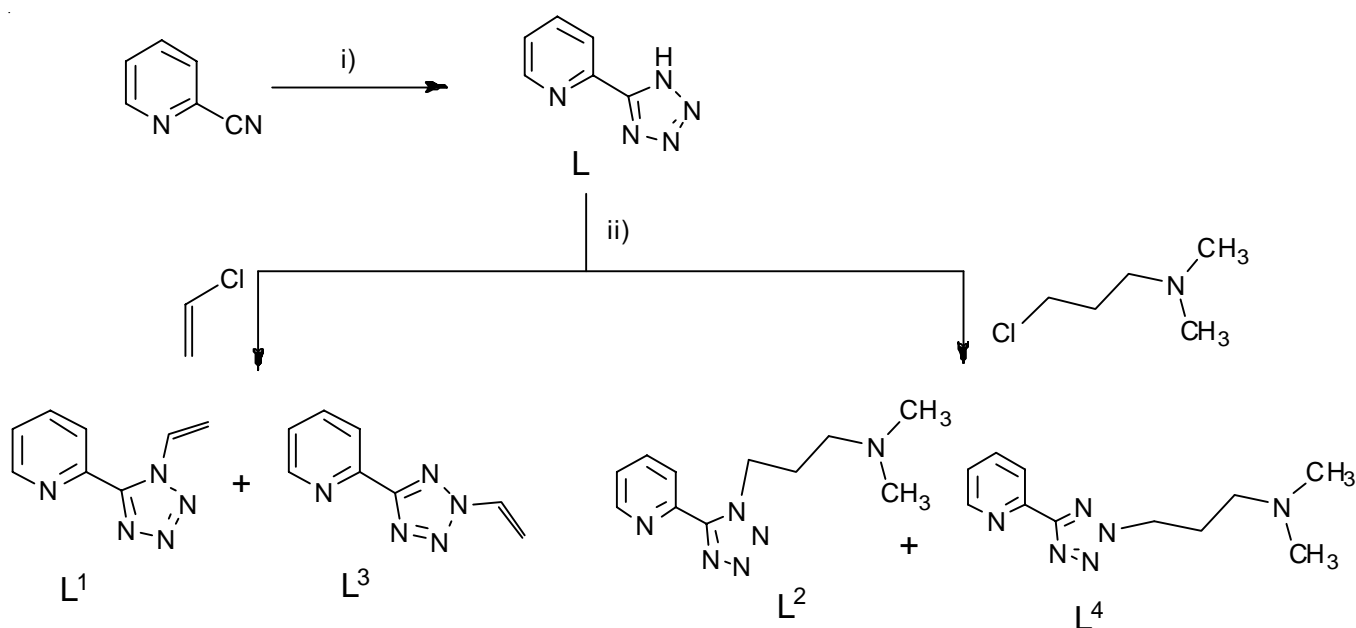
Spectral data

A signal at 154.9 ppm in the ¹³C NMR spectrum of compound **L** indicated the formation of a 1,5-disubstituted tetrazole and the presence of a signal at 2220 cm⁻¹ in the IR spectrum indicated an azide bond (N-N or N=N band)¹⁴. The ¹H NMR spectrum of **L**, showed the expected signals for the pyridine ring, while the NH proton on the tetrazole has appeared as a broad signal at 7.1 ppm. Ligand (**L**) on treatment with *N,N*-

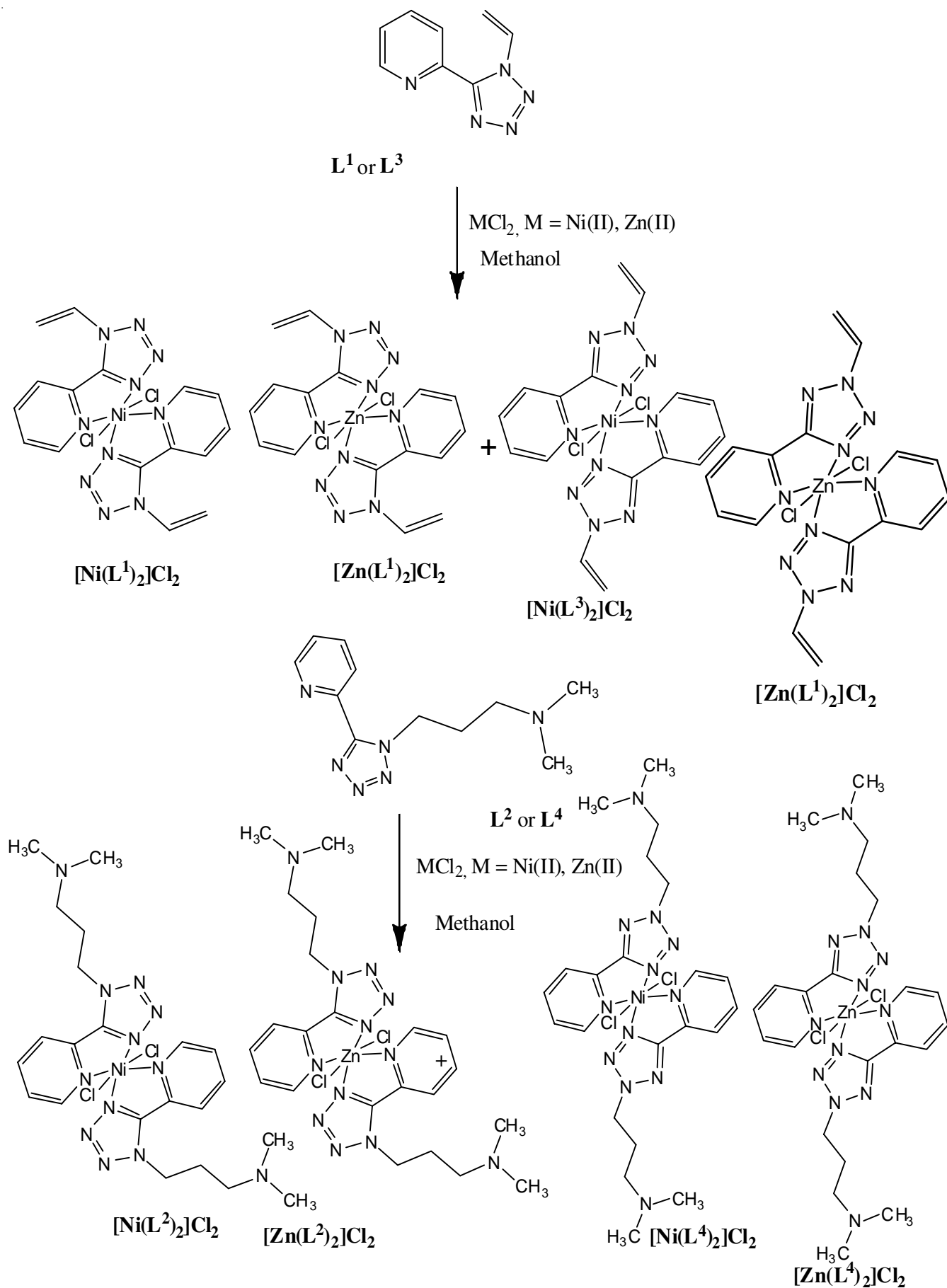
dimethyl-[2-(5-pyridin-2-yl-tetrazol-1-yl)-ethyl]amine-HCl and 2-chloroethanol in basic medium afford regio isomers **L**¹, **L**², **L**³ and **L**⁴ by alkylation at either the 1-N or 2-N positions in **Scheme-I**. The structures for the isomers are readily assigned by their ¹³C NMR and ¹H NMR spectra. The chemical shift values for the quaternary carbon of tetrazole ring appeared in range about 150.1-154.7 ppm in the 1-N- and 2-N-isomers respectively. The 1-N isomer gave the signal at 150.45 (**L**¹) and 152.15 (**L**²) ppm respectively; while the 2-N isomer gave the signal at 151.35 (**L**³) and 154.77(**L**⁴) ppm respectively. The ¹H NMR spectra of **L**¹-**L**⁴ showed separately four signals corresponding to pyridyl protons and two triplets for the methylene groups. A singlet is observed in the spectra of **L**¹ and **L**³ at 2.29 and 2.27 ppm which indicated the presence of six protons of -N(CH₃)₂ groups respectively. The methylene protons of **L**¹-**L**⁴ beside the tetrazole ring appeared at 5.12, 5.06, 5.08 and 4.87 ppm respectively. Presence of -N(CH₃)₂ in **L**² and **L**⁴ is confirmed by infrared spectra with broad peak at 1190-1058 cm⁻¹.

Infrared spectra of ligands (**L**² and **L**⁴) show a broad band in range 1190-1058 cm⁻¹ corresponding to -N(CH₃)₂ and peaks at 1650-1500 cm⁻¹. Two similar peaks around 1150-900 cm⁻¹ corresponds to tetrazole group¹⁵. The formation of coordination bonds between tetrazole ring and Ni(II), Zn(II) is confirmed by observing the IR frequencies of tetrazole ring. The ligands **L**¹-**L**⁴ showed characteristic infrared absorption bands at 1630-1570 cm⁻¹ which are shifted to lower frequencies in all Ni(II) and Zn(II) complexes. Additional peaks around 1340-1200 cm⁻¹ and 800-600 cm⁻¹ are appeared due to the coordination of pyridine ring with Ni(II) and Zn(II) atom.

The ligands (**L**¹-**L**⁴) are treated with NiCl₂·2H₂O and ZnCl₂·2H₂O salt, in methanol at reflux temperature under N₂ atmosphere for 2-3 h. All reactions were carried out using a 1:2 metal: ligand stoichiometry ratio to give corresponding complexes (**1-4**) in **Scheme-II**. Physical properties of nickel and zinc are shown in the synthesis. Elemental analysis of the



Scheme-I: Synthetic route for ligands **L**¹-**L**⁴, reaction conditions (i) NaN₃, LiCl, NH₄Cl, DMF, reflux 10 h; (ii) K₂CO₃, acetonitrile, reflux 24 h



Scheme-II: Synthesis of 1N and 2N-substituted nickel and zinc, pyridyl-tetrazole ligands tetrazole complexes (1-4)

metal complexes showed that these (**1-4**) are in 1:2 composition. All nickel complexes have magnetic moments value ranging 3.2 BM, slightly higher than the spin only values (2.82 μ_{eff}) expected for a d^8 system with one unpaired electron¹⁶ in Ni(II) complexes.

Electronic spectra and magnetic moments: The electronic absorption spectra of the isomeric pyridyl tetrazole metal complexes in solid state were recorded at room temperature and the band positions of the absorption maxima, band assignments, ligand field parameters and magnetic moment values are listed in Table-1. The electronic spectra of Ni(II) complexes displayed three absorption bands in the range 8000-9000, 14000-16000 and 20000-24000 cm^{-1} . Thus, these bands may be assigned to the three spin allowed transitions ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ (ν_1), ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ (ν_2) and ${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ (ν_3), respectively, characteristic of octahedral geometry. The values of transition ratio [ν_2/ν_1] and β lie in the range of 1.70-1.80 and 0.89-0.95, respectively, providing further evidence for octahedral geometry of Ni(II) complexes¹⁷. The B values for the complexes are lower than the free ion value, thereby indicating orbital overlap and delocalization of d -orbitals. The β -values obtained are less than unity suggesting the covalent character of the metal-ligand bonds. All Ni(II) complexes are paramagnetic and the magnetic moment values at room temperature are in the range of 3.2 B.M. which is well agreed with the reported octahedral Ni(II) complexes¹⁸. All Zn(II)

complexes showed two bands around 25000 and 30000 cm^{-1} and are attributed to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. Zinc(II) complexes are in d^{10} configuration and diamagnetic in nature and thus do not show any $d-d$ transitions.

Antimicrobial activity: The minimum inhibitory concentrations (MIC) of the complexes compared with the ligands and standard drugs are listed in Table-2. The results indicate that the metal complexes displayed more antibacterial activity compared to the parent ligands under similar experimental conditions. The results indicate that the metal complexes displayed more antibacterial activity compared to the parent ligands under similar experimental conditions on same microorganisms except L^1 and L^3 . However, while the remaining ligands did not show any activity. All Ni(II) and Zn(II) complexes showed antifungal activity. Among all the metal complexes complex showed good activity against all bacteria and fungi strains. Increase in the activity of the complexes compared to that of ligands can be explained on the basis of Overtone's concept and Tweedy's chelation theory. The theory states that the polarity of the metal ion is reduced on complexation due to the partial sharing of its positive charge with donor groups. Consequently, the positive charge is delocalized over the whole ring, which causes the improved lipophilicity of the compound through cell membrane of the pathogen¹⁹. The negative results can be attributed either to the inability of the complexes to diffuse into the bacteria cell membrane and

TABLE-1
ELECTRONIC, MAGNETIC AND LIGAND FIELD PARAMETERS OF THE PYRIDYL-TETRAZOLE Ni(II) COMPLEXES

Compound	Absorption maxima (cm^{-1})	Tentative assignments	Magnetic moment (B.M.)	ν_2/ν_1	10 Dq (cm^{-1})	B (cm^{-1})	β	LFSE (kJ mol^{-1})
[Ni(L^1) ₂]Cl ₂	8532	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ (ν_1)	3.12	1.78	8532	966	0.92	122.50
	15200	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ (ν_2)						
	24900	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ (ν_3)						
[Ni(L^2) ₂]Cl ₂	8787	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ (ν_1)	3.18	1.82	8787	935	0.89	126.19
	16000	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ (ν_2)						
	24390	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ (ν_3)						
[Ni(L^3) ₂]Cl ₂	8313	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ (ν_1)	3.25	1.76	8313	943	0.90	119.40
	14705	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ (ν_2)						
	24390	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ (ν_3)						
[Ni(L^4) ₂]Cl ₂	8628	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$ (ν_1)	2.91	1.89	8628	999	0.95	123.92
	16313	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$ (ν_2)						
	24570	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$ (ν_3)						

TABLE-2
MIC VALUES OF ANTIMICROBIAL ACTIVITY OF LIGANDS AND THEIR METAL COMPLEXES ($\mu\text{g/mL}$)

Compound	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Proteus vulgaris</i>	<i>Aspergillus niger</i>	<i>Candida albicans</i>
L^1	15	14	12	13	16
L^2	12	12	12	12	-
L^3	18	16	17	18	19
L^4	10	12	12	11	-
[Ni(L^1) ₂]Cl ₂	41	46	43	49	67
[Ni(L^2) ₂]Cl ₂	35	39	36	43	52
[Ni(L^3) ₂]Cl ₂	43	46	45	48	68
[Ni(L^4) ₂]Cl ₂	35	38	36	42	50
[Zn(L^1) ₂]Cl ₂	38	40	40	45	62
[Zn(L^2) ₂]Cl ₂	33	33	39	40	55
[Zn(L^3) ₂]Cl ₂	39	40	41	43	62
[Zn(L^4) ₂]Cl ₂	33	32	38	40	54
Kanamycin	3	-	-	2	-
Clotrimazole	5	11	7	10	-

hence they become unable to interfere with its biological activity or they can diffuse and become inactivated by unknown cellular mechanism, that is, bacterial enzymes²⁰.

Conclusion

Nickel(II) and zinc(II) complexes have been synthesized using isomeric pyridyl-tetrazole derivative ligands and characterized by various analytical and spectral data. Based on the electronic spectra, magnetic moment and elemental analysis data, octahedral geometry was proposed for Ni(II) and Zn(II) complexes. The antimicrobial activity data has shown that all complexes displayed higher activity among all other ligands.

ACKNOWLEDGEMENTS

This work was supported by GRIET (A) for financial assistance.

REFERENCES

- (a) P. Lin, W. Clegg, R.W. Harrington and R.A. Henderson, *Dalton Trans.*, 2388 (2005); (b) T. Hu, L. Liu, X. Lv, X. Chen, H. He, F. Dai, G. Zhang and D. Sun, *Polyhedron*, **29**, 296 (2010); (c) Y. Qiu, B. Liu, G. Peng, J. Cai, H. Deng and M. Zeller, *Inorg. Chem. Commun.*, **13**, 749 (2010).
- R.J. Herr, *Bioorg. Med. Chem.*, **10**, 3379 (2002).
- J. McGinley and A. Fleming, *J. Incl. Phenom. Macrocycl. Chem.*, **61**, 1 (2008).
- G. Aromi, L.A. Barrios, O. Roubeau and P. Gamez, *Coord. Chem. Rev.*, **255**, 485 (2011).
- (a) Z.P. Demko and K.B. Sharpless, *J. Org. Chem.*, **66**, 7945 (2001); (b) F. Himo, Z.P. Demko, L. Noodleman and K.B. Sharpless, *J. Am. Chem. Soc.*, **125**, 9983 (2003).
- (a) Y. Tao, J.R. Li, Z. Chang and X.H. Bu, *Cryst. Growth Des.*, **10**, 564 (2010); (b) M.F. Wu, M.S. Wang, S.P. Guo, F.K. Zheng, H.F. Chen, X.M. Jiang, G.N. Liu, G.C. Guo and J.S. Huang, *Cryst. Growth Des.*, **11**, 372 (2011).
- T. Mavromoustakos, A. Kolocouris, M. Zervou, P. Roumelioti, J. Matsoukas and R. Weisemann, *J. Med. Chem.*, **42**, 1714 (1999).
- (a) R.A. Powers and B.K. Shoichet, *J. Med. Chem.*, **45**, 3222 (2002); (b) S.Y. Kang, S.H. Lee, H.J. Seo, M.E. Jung, K. Ahn, J. Kim and J. Lee, *Bioorg. Med. Chem. Lett.*, **18**, 2385 (2008).
- (a) G.C.G. Pais, X. Zhang, C. Marchand, N. Neamati, K. Cowansage, E.S. Svarovskaia, V.K. Pathak, Y. Tang, M. Nicklaus, Y. Pommier and T.R. Burke Jr., *J. Med. Chem.*, **45**, 3184 (2002); (b) B.C.H. May and A.D. Abell, *J. Chem. Soc., Perkin Trans. 1*, 172 (2002).
- M.S. Surendrababu and K.H. Reddy, *J. Chil. Chem. Soc.*, **59**, 843 (2012).
- (a) A.D. Bond, A. Fleming, J. Gaire, F. Kelleher, J. McGinley, V. McKee and U. Sheridan, *Polyhedron*, **33**, 289 (2012); (b) A. Fleming, F. Kelleher, M.F. Mahon, J. McGinley and V. Prajapati, *Tetrahedron*, **61**, 7002 (2005).
- W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
- A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, Longman, edn 3 (1961).
- (a) H. Gallardo, R. Magnago and A.J. Bortoluzzi, *J. Liq. Cryst.*, **28**, 1343 (2001); (b) P.A. Bethel, M.S. Hill, M.F. Mahon and K.C. Molloy, *J. Chem. Soc., Perkin Trans. 1*, 3507 (1999).
- P.N. Gaponik, S.V. Voitekhovich and A.S. Lyakhov, *Chem. Heterocycl. Comp.*, **36**, 326 (2000).
- A.D. Kulkarni, S.A. Patil, V.H. Naik and P.S. Badami, *Med. Chem. Res.*, **20**, 346 (2011).
- S. Chandra and L.K. Gupta, *Spectrochim. Acta A*, **62**, 1089 (2005).
- P.K. Singh and D.N. Kumar, *Spectrochim. Acta A*, **64**, 853 (2006).
- A.K. Sharma and S. Chandra, *Spectrochim. Acta A*, **78**, 337 (2011).
- T.A. Yousef, G.M. Abu El-Reash, O.A. El-Gammal and R.A. Bedier, *J. Mol. Struct.*, **1029**, 149 (2012).