

Synthesis and Spectral Studies of Some Zn(II) Complexes with Substituted N,N-Donor Ligands Derived from Pyridine-2-carbaldehyde

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A series of four neutral zinc complexes with substituted N,N-donor ligands *viz.* $L_n = (E)\text{-N}(\text{pyridin-2-ylmethylene})\text{anilines}$ of composition $[\text{Zn}(\text{NO}_3)_2(L_1)]$ (1), $[\text{Zn}(\text{NO}_3)_2L_2]$ (2), $[\text{Zn}(\text{NO}_3)_2L_3]$ (3), $[\text{Zn}(\text{NO}_3)_2L_4]$ (4) were synthesized and characterized. The spectroscopic properties of the Zn(II) complexes were studied by UV-visible, fluorescence, IR and ^1H NMR spectral analysis. All the zinc(II) complexes are water soluble and non-electrolyte in solution. Efforts for getting single crystals suitable for X-ray crystal structure could not be achieved. However, on the basis of spectral studies, compounds 1-4 are proposed to have octahedral geometry. The emission spectra of all the complexes show $\pi\text{-}\pi^*$ (intra-ligand) transition.

Keywords: Water soluble, Zinc(II) nitrate complexes, (E)-N-(pyridin-2-ylmethylene)aniline.

INTRODUCTION

Heterocyclic compounds have been very important compounds for organic synthesis and they are also essential for biological processes [1]. Many effective antibacterial and antifungal Schiff base compounds of heterocyclic compounds were synthesized [1-4]. Several research groups studied heterocyclic ligands and their metal complexes due to their prominent antibacterial, antimalarial, antitumor and antileukaemic activity [5-13]. Further, a large number of metal complexes with the heterocyclic ligands have been studied and biological activities of some of them have been explored [13]. Among the heterocyclic compounds, pyridine derivatives ligands are of high interest in several areas of biochemistry particularly aminopyridinyl and aminopyridinamines [14]. These compounds have been considered as pain killer as well as anti-inflammatory agents for treating Alzheimer's disease [15]. Furthermore, the heterocyclic compounds containing pyridine ring namely niflumic acid and flunixin [16] are the two standard drugs belonging to the class of fenamates drugs. Flunixin meglumine [17,18] is a substituted derivative of nicotinic acid which is structurally unique when compared to other standard drugs.

Recently, coordination chemistry of Schiff bases resulting from pyridine 2-carboxaldehyde has received much interest

[19-23]. In recent years, a series of transition metal complexes with such ligands system have been synthesized and spectroscopically characterized [24-26]. Heterocyclic compounds of 4-pyridine carboxaldehyde and 3-amino pyridine form a stable complex with different transition metal ions [27]. Furthermore, Das *et al.* [28] reported the antiproliferative activity of zinc(II) complexes of 2-acetylpyridine-1-(4-fluorophenyl)piperazinylthiosemicarbazone. Moreover, Claffey *et al.* [29] also investigated Co(II) complexes of 2-acetylpyridine. In addition, a group of different metal complexes with 3-(pyridin-2-yl)imidazo[1,5-a]pyridines used as ligands were explored [30-36]. Consequently, some related derivatives of above ligands have been used *in situ* to regulate metal induced amyloid- β aggregation [37]. In addition, Kundu *et al.* [38] investigated the cytotoxic properties of water soluble zinc(II) compounds with (E)-N-(pyridin-2-ylmethylene)arylamines and the complexes increased the HeLa cell death in a concentration-dependent manner. Thus, study of the derivatives possessing pyridine moiety may provide interesting results and also help to develop an understanding of the biological activity of this class of compounds. In view of the above all facts, we reported herein the synthesis and spectroscopic characterization of water soluble zinc complexes with (E)-N-(pyridin-2-ylmethylene)anilines.

EXPERIMENTAL

Pyridine-2-carboxaldehyde (Avra Synthesis Pvt. Ltd.), 2,4-methoxyaniline (Sigma-Aldrich), 3-hydroxyaniline (Merck), *p*-nitroaniline (Sigma-Aldrich), *p*-chloroaniline and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) were used without further purification. Solvents were purified by standard procedures and were freshly distilled prior to use. Melting points were recorded in capillary tubes on a Scanca apparatus and are uncorrected. IR spectra in the range 4000-400 cm^{-1} were obtained using KBr pellets on a Shimadzu FT-IR-8400S spectrophotometer and UV-visible spectra of the complexes were observed in UV-1800 Shimadzu spectrophotometer in ACN at 200-800 nm range. Fluorescence spectra were obtained on a Perkin-Elmer spectrofluorimeter model LS55 (excitation and emission slits fixed at 10 and 15 nm, respectively) and corrected for the instrument response function. Quartz cuvettes of 10 mm optical path length received from PerkinElmer, USA (part no. B0831009) and Hellma, Germany (type 111-QS) were used for measuring absorption and fluorescence spectra, respectively. Fluorescence quantum yields (ϕ_F) spectroscopic range with that of a standard using the method described elsewhere [39]. The relative experimental error of the measured ϕ_F was estimated to be within $\pm 10\%$. Solution electrical conductivity measurements were made using a Eutech Instruments automatic precision bridge Con510. The ^1H NMR spectra were recorded on a Bruker Avance II spectrometer and measured at 400.13 MHz. The ^1H chemical shifts were referenced to Me_4Si set at 0.00 ppm.

Synthesis of zinc(II) complexes

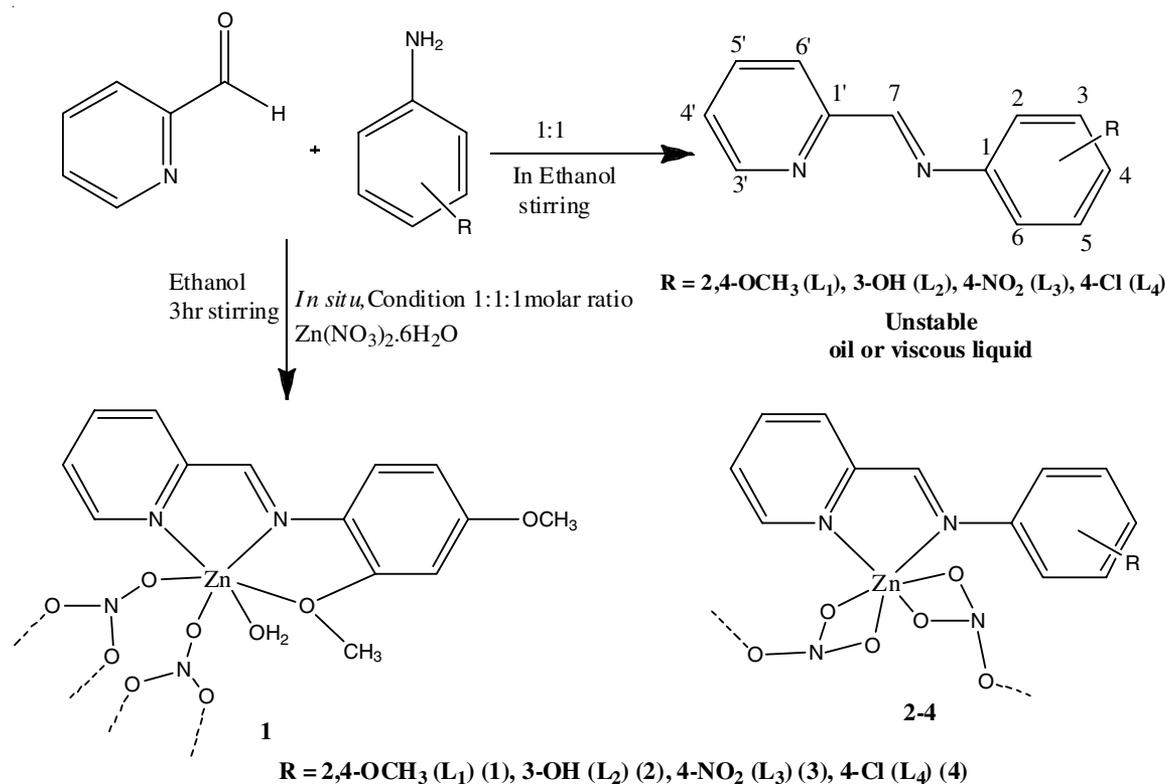
$[\text{Zn}(\text{NO}_3)_2(\text{L}_1)]$ (**1**): To a solution of 2,4-dimethoxyaniline (1 g, 6.52 mmol) in ethanol (5 mL) was added a solution of pyridine-2-carboxaldehyde (0.85 g, 6.51 mmol) in ethanol (5

mL). The mixture was stirred at ambient temperature for 30 min. To this reaction mixture, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.942 g, 6.52 mmol) in ethanol (20 mL) was added dropwise under stirring conditions which resulted in the immediate formation of a yellow precipitate. The stirring was continued for 3 h and then the mixture was filtered. The residue was collected and dried under vacuum (**Scheme-I**). Yield: 70%. m.p.: 137-141 °C. Anal. calcd. (found) % for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_8\text{Zn}$: C, 37.39 (38.00); H, 3.59 (3.90); N, 12.46 (13.00). Λ_m (CH_3CN): $4 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): 1596 $\nu_{\text{asym}}(\text{C}(\text{H})=\text{N})$; 1553, 1513, 1395 $\nu(\text{C}=\text{N})_{\text{py}}$; 1395 vs, 1446 s, 1336 vs, 1300 s, 1210 w: $\nu(\text{NO}_3)$. ^1H NMR ($\text{DMSO}-d_6$): δ 8.99 (s, 1H, H-7), 8.70 (d, 1H, H-3'), 8.27 (t, 1H, H-4'), 8.10 (d, 1H, H-6'), 7.77 (t, 1H, H-5'), 7.46 (d, 1H, H-2), 6.69 (s, 1H, H-5), 6.63 (d, 1H, H-3), 3.85 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3) ppm.

Complexes **2-4** were prepared as yellow crystals in a similar manner to that described for the preparation of complex **1**, using appropriate anilines and metal salts as starting materials.

$[\text{Zn}(\text{NO}_3)_2(\text{L}_2)]$ (**2**): Yield: 39%. m.p.: 171-175 °C. Anal. calcd. (found) % for $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_7\text{Zn}$: C, 37.18 (37.90); H, 2.60 (2.80); N, 14.45 (14.96). Λ_m (CH_3CN): $6 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): 1620 $\nu_{\text{asym}}(\text{C}(\text{H})=\text{N})$; 1588, 1556, 1421 $\nu(\text{C}=\text{N})_{\text{py}}$; 1384 vs, 1521 s, 1314 w: $\nu(\text{NO}_3)$. ^1H NMR ($\text{DMSO}-d_6$): δ 8.70 (s, 1H, H-7), 8.52 (d, 1H, H-3'), 8.14 (t, 1H, H-5'), 7.96 (d, 1H, 6'), 7.54 (t, 1H, 4'), 7.22 (s, 1H, H-2), 6.44 (t, 1H, 5), 5.91 (d, 1H, 4), 5.66 (d, 1H, 6) ppm.

$[\text{Zn}(\text{NO}_3)_2(\text{L}_3)]$ (**3**): Yield: 64%, m.p.: 200-204 °C. Anal. calcd. (found) % for $\text{C}_{12}\text{H}_9\text{N}_5\text{O}_8\text{Zn}$: C, 34.60 (35.00); H, 2.18 (2.96); N, 16.81 (17.06). Λ_m (CH_3CN): $8 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (cm^{-1}): 1624 $\nu_{\text{asym}}(\text{C}(\text{H})=\text{N})$; 1577, 1556, 1401 $\nu(\text{C}=\text{N})_{\text{py}}$; 1384 vs, 1527 s, 1297 w: $\nu(\text{NO}_3)$. ^1H NMR ($\text{DMSO}-d_6$): δ 8.82 (d, 1H, H-3'), 8.76 (s, 1H, H-7), 8.28 (d, 1H, H-6'), 8.10 (t,



Scheme-I: Reaction scheme for the synthesis of $[\text{Zn}(\text{NO}_3)_2\text{L}_n]$ complexes

1H, H-5'), 7.86 (t, 1H, 4'), 7.15 (b, 2H, H-3,5), 6.79 (dd, 2H, H-2,6) ppm.

[Zn(NO₃)₂(L₄)] (4): Yield; 69 %, m.p.: 105-108 °C. Anal. calcd. (found) % for C₁₂H₉N₄O₆ClZn: C, 35.49 (35.90); H, 2.23 (2.80); N, 13.80 (14.00). Λ_m (CH₃CN): 6 Ω^{-1} cm² mol⁻¹. IR (cm⁻¹): 1625 ν_{asym} (C(H)=N); 1573, 1510, 1428 ν (C=N)py; 1381 vs, 1534 s, 1410, 1274 w: ν (NO₃). ¹H NMR (DMSO-*d*₆): δ 8.81 (d, 1H, H-3'), 8.75 (s, 1H, H-7), 8.21 (t, 1H, H-4'), 8.04 (d, 1H, H-6'), 7.75 (t, 1H, H-5'), 7.29 (dd, 2H, H-2,6), 6.77(dd, 2H, H-3,5) ppm.

RESULTS AND DISCUSSION

Light yellow Schiff base metal complexes (**1-4**) were synthesized by the reaction of an equimolar amount of Zn(NO₃)₂·6H₂O with ligand (generated *in situ* from pyridine-2-carboxaldehyde and a substituted aniline) *in situ* following analogues procedure reported earlier [38]. The general stoichiometry of the complexes [Zn(NO₃)₂ (L^{*n*})] have been compared by their micro-analytical results which clearly evidence the formation of 1:1 adducts between the bidentate N,N-donors (L²⁻³) or tridentate N,N,O (L¹) with Zn(NO₃)₂. In all cases, air stable light yellow solid was obtained in moderate to good yield and these compounds behave as non-electrolytes in acetonitrile solution. Complexes (**1-4**) are soluble in water, alcohol, acetonitrile, DMSO and DMF. The ligand skeleton used in the synthesis of zinc(II) complexes and the structural motifs of zinc(II) nitrate complexes with (*E*)-N-(pyridin-2-ylmethylene)aniline (L¹⁻⁴) are shown in Fig. 1.

IR analysis: The infrared spectra of complexes **1-4** are very similar and the IR assignments of selected diagnostic bands are given in the experimental section. The entire complex spectra were compared with literature value. The complexes display a moderately intense IR band in the region 1620-1590 cm⁻¹ which is assigned to be ν_{asym} (C(H)=N) stretch of the coordinated schiff base ligands [40-42]. In addition, well resolved sharp bands of variable intensity observed in the regions 1600-1580, 1490-1475 and 1450-1435 cm⁻¹ are assigned to the coordinated pyridine ring [42-44]. The cited nitrate frequencies in the complexes showed a very strong band at approximately around 1381 cm⁻¹ indicating the presence of coordinated nitrates [43,45]. In addition, the solid-state spectrum of complexes **2-4** displayed bands at around 1527 and 1321 cm⁻¹, which are indicative of bidentate chelating nitrate groups [40,43,46-49]. The bidentate coordination mode of nitrate groups was subsequently confirmed

by the X-ray crystal structure determination of similar system reported earlier [40]. Compound **1** displays IR bands around 1416 s, 1336 vs, 1300 s, 1412 s, 1306 w suggesting the presence of monodentate nitrate anions [43,47-49].

¹H NMR analysis: The ¹H NMR spectra of the complexes (**1-4**) were recorded in DMSO-*d*₆ and the spectra displayed the expected signals which correlate well with the hydrogen atoms present in the molecules and therefore, revealed the presence of the ligand skeleton in the respective complexes [50]. The NMR assignments for the compounds presented in the experimental section are based on the splitting patterns of the signals by comparing the data with those in previous reports [41,49]. The effect of coordination to zinc(II) upon the ¹H NMR chemical shifts could not be judged in the absence of NMR data for the ligands which could only be prepared *in situ*. In all the complexes, a singlet peak was observed at around 9.21-8.70 ppm which can be assigned for Schiff base (C(H)=N) protons [41,49]. The doublet and triplet signals were observed at around 8.26-6.52 ppm, which can be assigned to pyridine rings [40]. The ¹H NMR spectra of complex **1** shows a two singlet peak at around 3.85 and 3.72 ppm due to methoxy protons at *ortho*- and *para*-position, respectively. Aromatic protons were observed as singlet, doublet and triplet in the complexes in the range 6.03 to 8.20 ppm.

UV and fluorescence analyses: The electronic properties of complexes **1-4** are given in Table-1. The absorption spectra of zinc(II) nitrate complexes were recorded in the range 250-600 nm in acetonitrile solutions at concentration of ~10⁻⁵ M and the complexes generally showed one intense bands (Fig. 2a). The electronic spectra exhibited an absorption in the range of 300 to 400 nm. The origin of the band could not be assigned unambiguously due to the non-availability of data for the free ligands which could only be prepared *in situ*. The complexes showed a broad fluorescence emission band at around λ_{em} = 375-475 nm (Fig. 2b) at room temperature. However, these emissions could not be assigned to be metal-to-ligand charge transfer (M→L) or ligand-to-metal charge transfer (M←L) as zinc(II) ion with a *d*¹⁰ configuration, is not easily oxidized or reduced [51]. The emissions are attributed to the intra-ligand (IL) (π - π^*) emission. Consequently, Zn compounds show very low fluorescence quantum yields [52,53] indicating that they are weak emission at room temperature (Table-1).

Proposed structure of complexes: A considerable amount of work has been reported with similar ligands arrangement,

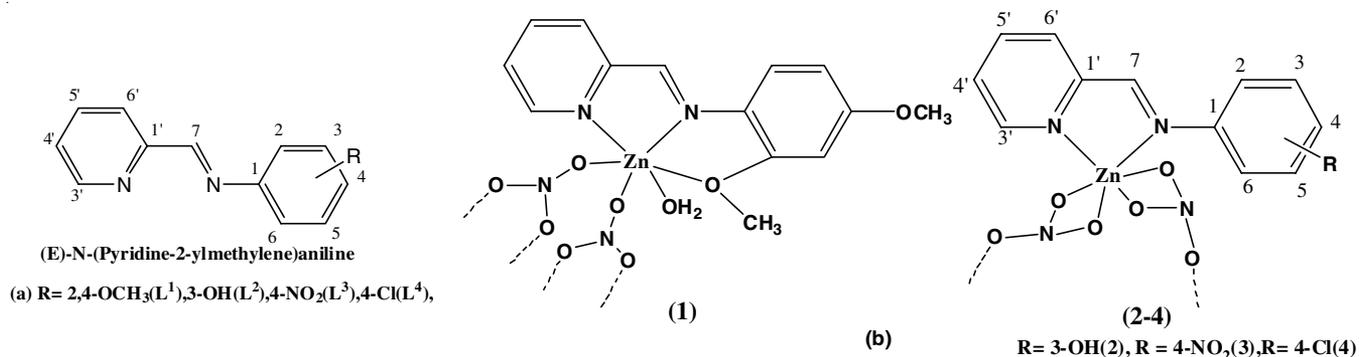


Fig. 1. Generic structure of ligands abbreviations: (a) L^{*n*} (*n* = 1-4) with the numbering protocol and (b) Structural motifs of [Zn(NO₃)₂(L^{*n*})] complexes

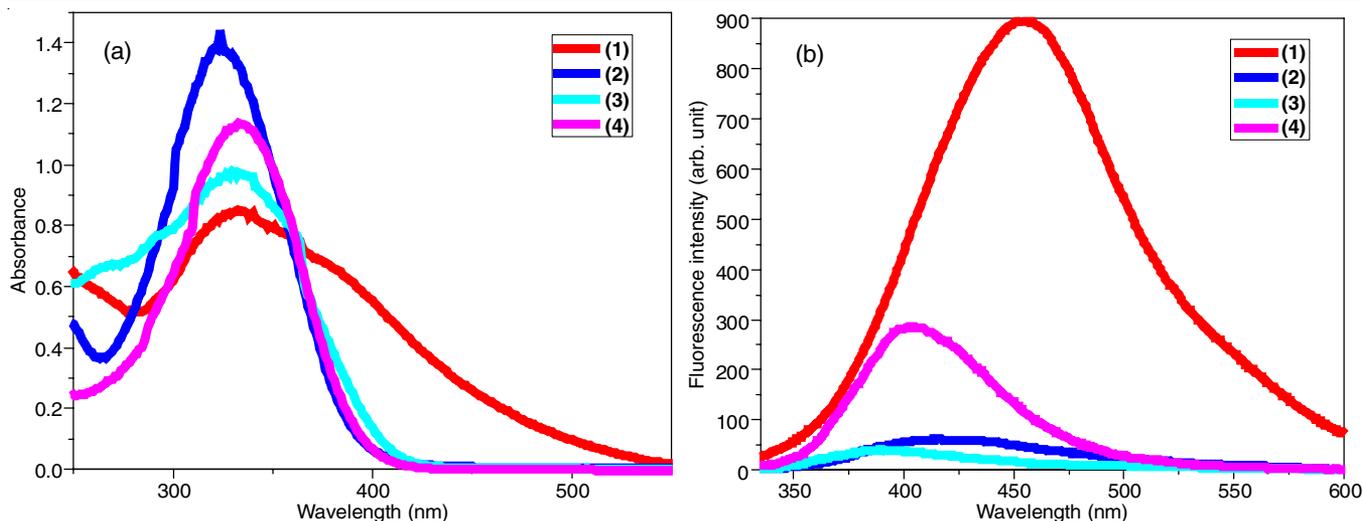


Fig. 2. (a) UV-visible spectra of compounds (1-4) in acetonitrile (concentration $\sim 10^{-5}$ M), (b) Fluorescence spectra of compounds (1-4) in acetonitrile (concentration $\sim 10^{-5}$ M) obtained by excitation at the respective absorption maxima

TABLE-1
PHOTOPHYSICAL DATA FOR COMPLEXES 1-4
IN ACETONITRILE SOLUTION

Complexes	Electronic spectroscopic data λ_{\max} (nm)	Photoluminescence data	
		λ_{em} (nm)	Φ_F
1	328	451	0.16
2	321	425	0.21
3	330	400	0.11
4	332	403	0.31

however to the best of our information the existing literature contains no crystallographic characterization of the ligands except for the aniline derivatives as described by Wiebcke and Mootz [54]. To examine infrared bands of the ligands generated during the reaction, quantum chemical calculations were carried out on some of the similar ligands system reported earlier [40]. Crystal structures of few zinc(II) nitrate complexes were also reported with similar ligands [40,48,49] and found to be in consistent with the spectroscopic properties of zinc complexes (1-4). However, from the structure of complexes of the similar ligands system, it is clear that zinc atom prefers an octahedral environment; depending on the bulkiness of ligands. The IR stretching vibration of imino nitrogen and pyridine nitrogen of the complexes indicated that ligands coordinated to the metal ions [40,48-50]. It is also worth mentioning that very strong band at around 1384 cm^{-1} are due to stretching frequency of $\nu_{\text{asym}}(\text{NO}_3)$ [43,46,48,49]. From the molar conductance data, Zn(II) chelate may be considered as non-electrolytes in solution [40]. The $^1\text{H NMR}$ spectra of the complexes are in good agreement with the formation of the expected compounds [40,48]. On the basis of above observations and crystal structures of the complexes with similar ligand systems reported earlier [38,46], complexes thought to have six-coordinated geometry around zinc atom. It can be assumed that in compound 1, ligand anions act as N,N,O tridentate chelators, two $(-\text{ONO}_2)$ anions function as monodentate ions and in addition, water molecule also coordinated to Zn(II) unit, as reported in crystal structures of related complexes [40,48]. Therefore, complex 1 is proposed to have octahedral structure and it is also assumed that the

nitrate is coordinated to the metal ion as non-bridging terminal fashion which is reflected in broad unresolved IR absorption band at around 1384 s , 1300 s , 1412 m , 1306 w [38,43,48,49]. Moreover, in complexes 2-4, L anions act as N,N-bidentate chelators, $(\text{ONO}_2)_2$ function as two bridged bidentate ions [40, 43,49] and also reflected in doublet unresolved IR absorption bands at around 1527 , 1384 , 1314 cm^{-1} [40,43,49,50]. Therefore, the structures of complexes are proposed to be octahedral geometry.

Conclusion

The syntheses of four neutral water soluble zinc(II) nitrate complexes with substituted ligands *viz.* (*E*)-N-(pyridine-2-ylmethylene)aniline were successfully accomplished. These compounds have been characterized by IR, $^1\text{H NMR}$, UV-visible and fluorescence spectroscopies. In all the cases, the complexes behave as non-electrolyte in acetonitrile solution. UV-visible, fluorescence, $^1\text{H NMR}$ and IR spectral studies indicate that ligands (L^{1-4}) are coordinated to the metal complexes. The study of the complexes suggested to be six coordinated octahedral geometry around zinc atom with monodentate or bidentate coordination of nitrate ion. The emission spectra of all the complexes shows $\pi-\pi^*$ (intra-ligand) transition and Zn compounds show very low fluorescence quantum yields indicating that weak emitters at room temperature.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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