

Luminescent Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Bi(III) with 2-Aminothiazole based Ligand and their Biological Studies

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3-(thiazol-2-yl carbamoyl) propanoic acid was synthesized by the reaction of 2-aminothiazole and succinic anhydride, which was employed as ligand (LH) for further reaction with Co(II), Ni(II), Cu(II), Zn(II) and Bi(III) chlorides at ambient conditions to afford respective metal complexes, denoted as Co-L₂, Ni-L₂, Cu-L₂, Zn-L₂ and Bi-L₃. Both the ligand LH and metal complexes were characterized by techniques FT-IR, ¹H-NMR, ¹³C-NMR, powder XRD, TGA and conductometry. FT-IR and NMR studies revealed that ligand (LH) behaved in anisobidentate fashion via carboxylate moiety. The ligand and metal complexes are also screened for their antibacterial and antifungal potential and found non-significant activities by most of the complexes, luminescent studies were also made and found Bi-L₃ appreciably luminescent.

Keywords: 2-aminothiazole; metal complexes; anti-fungal; anti-bacterial; luminescence

Thiazole, an organic compound from azole class with aromatic behavior due to presence of delocalized π -electrons of sulfur, is very vital in many different reactions of biological importance such as thiamine. Among the various derivatives of thiazole, 2-aminothiazole is an important member from thiazole class and is well reported for the synthesis of many different compounds [1]. The thiazole core is reportedly active pharmacophore and very popular among drug researchers [2-6]. Several drugs with 2-aminothiazole derivatives are available in the market such as Famotidine, Cefdinir, Meloxicam etc. Apart from the medicinal applications, thiazole derivatives such as 4-hydroxythiazole [7], 4-ethoxy-1,3-thiazole [8] and various other derivatives such as coumarin thiazole hybrid [9, 10], have been extensively studied for their luminescence properties [8, 11]. Study of luminescence properties has been ever growing due to the immense applications of materials possessing this particular property [12]. This property is applicable for the production of Solid-state lighting, light-emitting diodes, instrument display, night-vision devices, tunable solid state lasers, and biological imaging for the detection of protein [10, 11]. Moreover, it has been reported that the luminescence properties of material could be enhanced upon complexation with metal salts and non-metals [13-17].

A number of metal complexes are in practice when it comes to bio-sensing and cell imaging. These applications are mainly supported by some unique properties i.e sensitivity towards change in local environment and also their easy emission and resolution of light [18-21]. Such metal complexes show high spin-orbit coupling in between singlet and triplet states to assist the intersystem crossing which leads to notable luminescent activity [22]. Recently bismuth has achieved much attention, in this direction because of its remarkably less toxicity compared to its neighboring elements i.e. Lead and Thallium, large ionic radius, flexible coordination and more particularly strong spin orbit coupling constant, a prerequisite for the development of OLED materials [23, 24].

Keeping in view structural/luminescence/biological importance of 2-aminothiazole, in this study, we report the coupling of 2-aminothiazole with succinic anhydride to yield the carboxylate bearing ligand LH, which was further complexed with various metal ions such as Co(II), Ni(II), Cu(II), Zn(II) and Bi(III) to afford ligand-metal complexes. The antifungal, antibacterial and luminescent behaviors of these metal complexes were investigated and are part of this manuscript.

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Experimental part

Materials

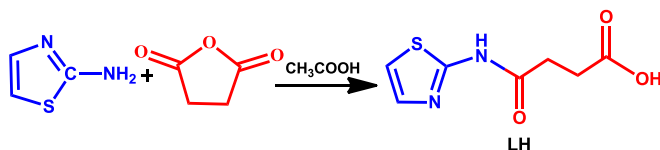
Aminothiazole (Sigma aldrich; m.p: 91-93°C), Acetic Acid (b.p:118.1°C), Succinic anhydride (M & B Chem; m.p 117-119 °C), Methanol (b.p: 78 °C), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Uni chem; m.p: 86°C), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (United Lab; m.p: 140 °C), CuCl_2 (Fluka Chemika; m.p: 498 °C), ZnCl_2 (Riedel-de-Haen; m.p: 290 °C), BiCl_3 (Beijing chem.; m.p: 227°C), KOH were used without purification. Pyrex made oven dried glassware was utilized for synthesis and subsequent workup process. Gallon Kamp apparatus was used to measure melting point. FTIR spectra were recorded using Cary 630 FT-IR Agilent Technologies. UV-visible spectra were recorded by Perkin Elmer multimode T90+ model double beam spectrophotometer. Metal contents were determined by Atomic absorption spectrophotometer GBC model 400 XplorAA Dual and Conductivity Meter Cond 720. Thermal analysis was carried out on a TGA/DSC1 (Mettler Toledo AG, Analytical, Schwerzenbach, Switzerland). The TGA measurements were performed under nitrogen at a heating rate of 10 °C/min. XRD measurements were performed on a D2 Phaser X-ray diffractometer (Bruker, Karlsruhe, Germany) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Synthesis

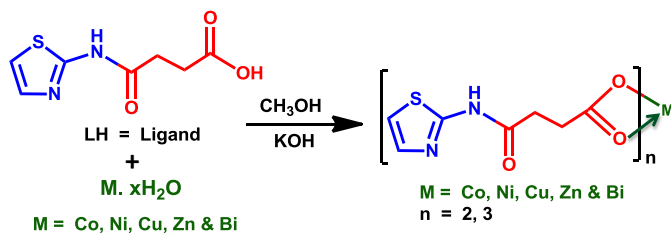
LH was synthesized using previous protocol with slight modifications [25, 26]. Drop wise addition of succinic anhydride solution in acetic acid (1 mmol, 0.1001g) was added dropwise into the acetic acidic solution of 2-aminothiazole (1 mmol, 0.10 g). The solution was stirred over night at room temperature. The resulting solution was concentrated at 40 °C for few hours and straw colored precipitates were obtained. These precipitates were washed with small amount of methanol and n-hexane, recrystallized from hot methanol, dried and stored in desiccator for further use.

General method for preparation of metal complexes

Equimolar solutions of the prepared ligand (LH) (0.1 mmol, 10 mL) and corresponding metal salt (0.1 mmol, 5 mL) was prepared in methanol (0.1 mmol, 10 mL). In first step, deprotonation of LH was done by the addition of small volume of KOH solution gradually and pH was maintained at 7. Then respective metal salt solution was added along with continuous stirring. The resulting mixture was stirred at room temperature for 1 hour and then concentrated up to half. This concentration resulted precipitates, which were washed with small amount of methanol and n-hexane and then dried. For further analysis, these were stored in desiccator.



Scheme 1. Synthesis of ligand LH



Scheme 1. Synthesis of L-metal complexes

Results and discussions

The ligand **LH** was obtained in appreciable yield (42%) by reacting succinic anhydride and 2-aminothiazole at room temperature (Scheme 1). LH was subsequently deprotonated and reacted with respective metal salts to afford metal complexes in appreciable to good yields (45-82%). All the metal complexes as well as ligand L are quite stable towards air. Both the ligand L and metal complexes have good solubility in common organic solvents but remarkable solubility in DMSO and DMF. Conductometric studies of metal complexes (0.1 - 0.5 μS) revealed their non-electrolytic nature (Table 1.) [27, 28]. The metal contents were determined on the basis of AAS/ICP-MS that showed Co-L₂, Ni-L₂, Cu-L₂ & Zn-L₂ and Bi-L₃ type complexes. The prepared ligand LH is amine-bidentate in behavior, explicated by FT-IR (detail below in FT-IR section).

UV-visible spectral analysis and Magnetic moment

UV-visible spectra of ligand LH and the complexes were obtained in DMF as solvent using 10^{-3} concentration solutions. The electronic spectrum of Cu-L₂ complex shows an absorption band at 1323.3 cm⁻¹ that can be assigned to $^2T_2 \rightarrow ^2E$ transition of a 4-coordinate tetrahedral geometry while that of Ni-L₂ complex exhibits two absorption bands at 1166.6 cm⁻¹, 1541.2 cm⁻¹ assigned to $^3T_1(F) \rightarrow ^3A_2(F)$, $^3T_1(F) \rightarrow ^3T_1(P)$ transitions suggesting tetrahedral environment around it. Similarly, electronic spectrum of the Co-L₂ complex depicts two allowed transitions at 1169.8 cm⁻¹, 1740.5 cm⁻¹ assignable to $^4A_2(F) \rightarrow ^4T_1(F)$ and $^4A_2(F) \rightarrow ^4T_1(P)$ transitions respectively. These three transitions are in good agreement with tetrahedral stereochemistry [27, 28].

The magnetic moment values for Cu-L₂, Ni-L₂, and Co-L₂ complexes are 1.89 B.M., 3.31 B.M., 4.24 B.M respectively. These values also support 4-coordinate tetrahedral geometry around each ion as proposed by electronic spectroscopy [29, 30]. Also, Zn-L₂ complex has d¹⁰ configuration and was found to be diamagnetic. The diamagnetic nature of this complex supports its tetrahedral geometry. Bi-L₃ complex exhibited octahedral geometry as proposed on the basis of M-L ratio obtained from ICP-MS/AAS and corroborative with CHN analysis.

Table 1
PHYSIO ANALYTICAL DATA OF LIGAND LH AND ITS COMPLEXES

Compo und	M .P [†]	Col or	Conduct ance ^{††}	Solubility	Elemental Analysis (%)		
					C	H	N
LH	62 -67	Bro wn	-	Methanol, ethanol, DMSO, DMF, acetone, acetonitrile	44.85 (44.53)	4.70 (4.22)	13.08 (12.56)
Co-L ₂	75	Blue	0.578	Methanol, ethanol, DMSO, DMF, acetone, acetonitrile	39.59 (39.07)	3.74 (3.39)	12.14 (11.89)
Ni-L ₂	11 5	Dar k green	0.557	Methanol, ethanol, DMSO, DMF, acetonitrile	39.61 (38.98)	3.74 (3.19)	11.55 (11.17)
Cu-L ₂	50	Gree n	0.282	Methanol, ethanol, DMSO, DMF, acetonitrile	39.22 (38.77)	3.70 (3.24)	12.97 (12.08)
Zn-L ₂	10 5	Stra w color	0.569	Methanol, ethanol, DMSO, DMF, acetonitrile	39.07 (38.27)	3.69 (3.29)	11.39 (10.70)
Bi-L ₃	11 0	Off white	0.838	Methanol, ethanol, DMSO, DMF, acetonitrile	33.97 (33.06)	3.21 (2.86)	9.90 (9.11)

[†]°C; ^{††}Λ_m μOhm⁻¹cm⁻² mol⁻¹

FT-IR Spectral analysis

FT-IR spectra were recorded for the ligand LH as well as metal complexes in the range 4000 – 700 cm⁻¹ and are shown in Figure 1. The FTIR spectrum of LH showed characteristic peak at 3105 cm⁻¹ attributed to NH group. Also a clear peak at 1300 cm⁻¹ is labeled as C-N. The presence of carboxylate moieties in LH, was confirmed by peaks at 1699 and 1364 cm⁻¹ attributed to symmetric and asymmetric vibrations respectively. Both types of these peaks in LH support its proposed structure. The comparison between the frequencies of LH and its metal complexes showed a shift that indicates the contribution of COO⁻ moiety in the formation of complexes [27]. The difference, (Δν), between ν(COO)_{asym} and ν(COO)_{sym} lies between <350 and 200> , that directs an intermediate state between bi and mono-dentate named as anisobidentate [31]. Hence it is concluded from FTIR studies that ligand LH behave in a monodentate as well as bidentate fashion.

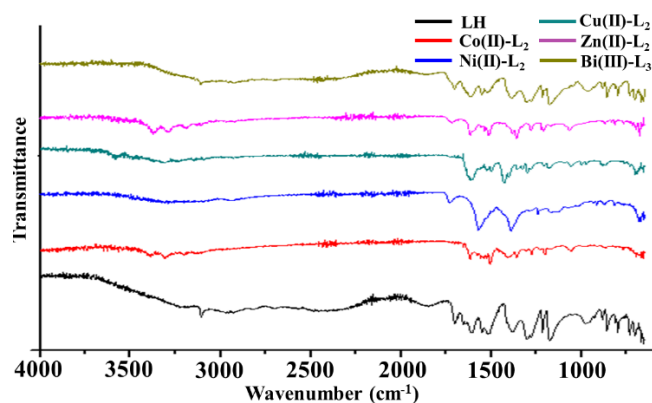


Fig.1. IR spectra of LH and its metal complexes

NMR Studies

Keeping in view paramagnetic nature of complexes as determined from magnetic moment data, ^1H -NMR spectra of LH, Zn-L₂ and Bi-L₃ complexes were recorded in DMSO-d₆. The ^1H -NMR spectrum of ligand LH displays a doublet in at 6.73–6.74 ppm and 7.05–7.06 ppm which can be assigned to protons H_a and H_b respectively. Chemical shift value at 2.58 ppm indicates the presence of methylene protons (CH₂-CH₂). Chemical shifts of various protons observed in ^1H -NMR of spectra of Zn-L₂ and Bi-L₃ complexes are also in agreement with the proposed positions. The most notable change is the disappearance of signal for –OH moiety (11.0 ppm in LH) thereby indicating its deprotonation and subsequent involvement with metal ions through this moiety. Similar information has been obtained from ^{13}C -NMR spectra. The slight chemical shift was observed for the carbon of carboxylate moiety indicating coordination of metal ion via this moiety [–C=O: – LH=173.6 ppm; Zn-L₂ = 170.6 ppm; Bi-L₃ = 169.9 ppm].

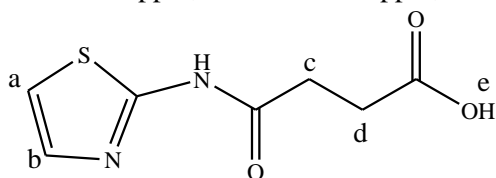


Fig. 2. Labeling of atoms for NMR values

Powder X-ray Diffraction Studies

In the XRD spectral analysis of the ligand (LH) and the complexes, it is found that the ligand and the prepared complexes yield well-defined peaks indicating the crystalline nature of the complexes and the ligand (Figure 3). The appearance of crystallinity in the complexes can be attributed to the inherent crystalline nature of the metallic compounds. The calculation of the grain size of the complexes was carried out using Debye-Scherrer's formula employing the full width at half maximum of the XRD peaks.

$$d = \frac{0.9\lambda}{\beta \cos \theta}$$

where 'λ' is the wavelength, 'β' is the full width at half maximum and 'θ' is the peak angle. The prepared complexes are found to possess the average crystallite size in the range of 11–68 nm. The obtained average crystallite size was found to be 68, 39.9, 11.3, 14.1, 21.3 nm for Co-L₂, Ni-L₂, Cu-L₂, Zn-L₂ and Bi-L₃ respectively suggesting that the complexes are nano-crystalline in nature.

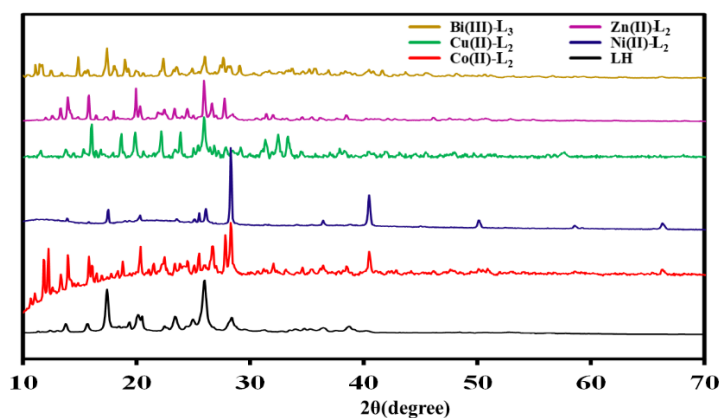


Fig. 3. XRD pattern of the ligand LH and complexes

TGA analysis

The thermal stability of the prepared complexes is studied by subjecting it to thermogravimetric analysis (Figure 4). For instance; it is revealed that decomposition results of Cu-L₂ complex takes place in three stages. The first stage of decomposition is noticed in the temperature range 120–135°C (Figure 4). It is due to the elimination of coordinated water molecule [32]. The mass loss observed in this step is 4.45% against the calculated loss of 4.37%. The second stage of decomposition occurs in the temperature range of 210–235°C, due to melting and partial decomposition of the ligand, this step bringing the weight loss of 17% (calc. 17.76%). The decomposition range (310–335°C) of weight loss in third stage gives 70% (calc. 70.21%). This is due to the decomposition of the ligand molecule. The complex (residual product) is present in the form of its metal oxide above 400°C.

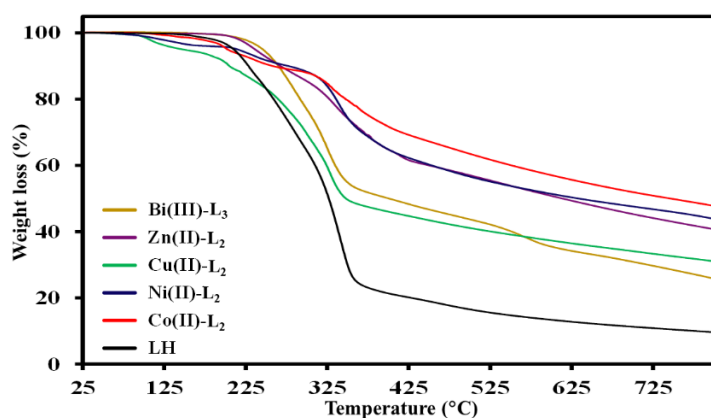


Fig. 4. Thermogravimetric analysis of LH and its metal complexes

SEM Analysis

Scanning electron microscopy has been widely used to elucidate the morphological features of metal complexes. It has been observed that coordination of metal ion with ligand significantly changes the surface morphology of resulting metal complexes, the same was investigated by SEM analysis [33]. The SEM images of LH and its respective metal complexes are shown in Figure 5. The differences are seen in surface morphology of the ligand and metal complexes which can be used as corroborative evidence to support the formation of metal complexes. For instance; the ligand LH showed irregular sponge shaped morphology with porous nature, while Co-L₂ showed shiny particles as an irregular aggregation. Similarly, the SEM micrograph of Ni-L₂ showed small irregular shaped particles, entrapped in bigger one to constitute a cotton shape structure. Cu-L₂ showed distribution of particles as clusters of irregular shape having some crystalline type particles. The SEM image of the Zn-L₂ exhibited a polyhedral appearance with only a few particles that are aggregated. Bi-L₃ showed distribution of particles arranged as rod shape.

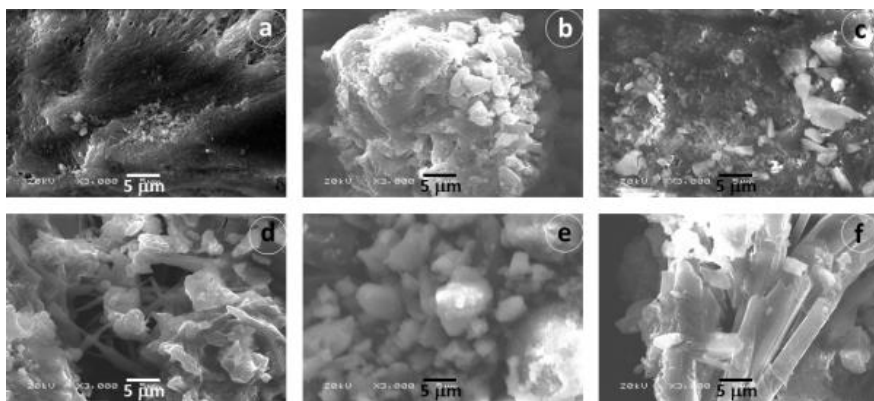


Fig. 5. SEM images of (a) LH
(b) Co-L₂ (c) Ni-L₂ (d) Cu-L₂
(e) Zn-L₂ (f) Bi-L₃

Biological studies

Antibacterial studies: Antibacterial activity of LH and metal complexes was investigated against various gram positive and gram negative bacterial stains *i.e.* gram positive bacterial stains *Bacillus subtilis*, *Staphylococcus aureus* and gram negative bacterial stains *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhi* by disc diffusion method using 200 µg/mL as minimum inhibitory concentration (MIC) [34]. The results presented in the table 2 depict that the ligand LH and most of the prepared metal complexes displayed non-significant activity, however the Co-L₂ and Bi-L₃ exhibited relatively significant activity (58.6% & 57.6%, respectively) only against *E. coli*. This enhanced antibacterial activity of metal complexes compared to LH can be explained on the basis of chelation theory, which says that upon chelation polarity of the complex decreases compared to ligand and also the π electron become more polarized. All this phenomenon facilitates the penetration of complexes into the bacterial cell that ultimately disturbs the internal system of cells and control their growth [35, 36]. Overall this activity was much less than that of standard drug *i.e.* Arythromycin (89.6%) (Table 2).

Antifungal studies: Antifungal activity of LH and metal complexes against six fungal stains, (*Candida albicans*, *Trichyton rubrum*, *Aspergillus niger*, *Microsporum canis*, *Fusarium lini* and *Candida glabrata*) was investigated by agar tube dilution protocol [37]. MIC (minimum inhibition concentration) of samples was 400 µg/mL. Overall the complexes exhibited non-significant activity against various strains except cobalt complex which showed appreciable inhibition (85%) that is comparable to that of standard drug miconazole (97.8%), against *C. albicans* (Table 3). This inhibition value can be justified on the basis of partial sharing and delocalized electron on metal and ligand in the complex that enhances the lipophilic property of complex and helps in lipid layer penetration that ultimately destroys the internal system of fungal stain [36, 37].

Table 2
ANTIBACTERIAL ACTIVITY OF LIGAND LH AND ITS METAL COMPLEXES

Name of bacteria	% inhibition of drug	Percentage inhibition of compound	
		Co-L ₂	Bi-L ₃
<i>Bacillus subtilis</i>	90	–	–
<i>Staphylococcus aureus</i>	96	33	–
<i>Escherichia coli</i>	89.6	58.6	57.6
<i>Pseudomonas aeruginosa</i>	90	–	–
<i>Salmonella typhi</i>	89	–	–

Table 3
ANTIFUNGAL ACTIVITY OF LIGAND LH AND ITS METAL COMPLEXES

Fungal Strains	Standard drug	% inhibition of drug	Ligand LH	Co-L ₂
<i>Trichophyton rubrum</i>	Miconazole	113.5	–	32.5
<i>Candida albicans</i>	Miconazole	97.8	–	85
<i>Aspergillus niger</i>	Amphotericin B	20.70	5	–
<i>Microsporum canis</i>	Miconazole	98.1	–	–
<i>Fusarium lini</i>	Miconazole	73.5	10	37.5
<i>Candida glabrata</i>	Miconazole	49.58	–	15

Luminescence Studies

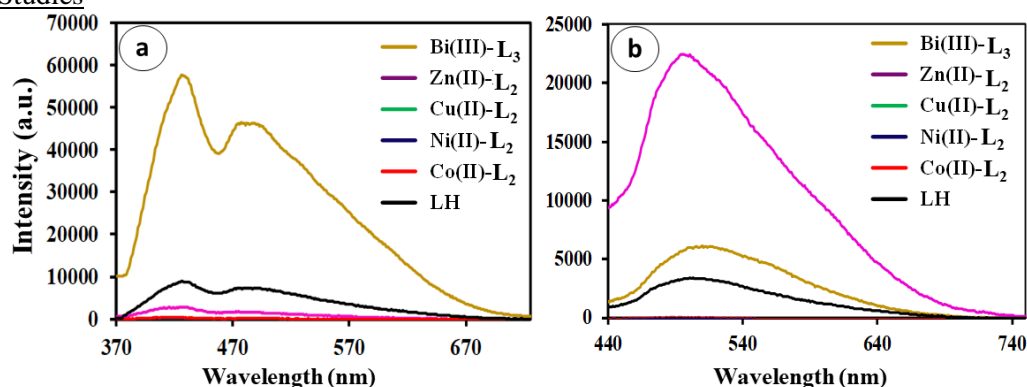


Fig. 6. Fluorescent spectra of LH and its complexes at wavelengths (a) 350 nm and (b) 420 nm

The photoluminescence measurements of ligand LH and its complexes were carried out. The micromolar solution in methanol was sonicated for 2 min to form a homogeneous solution. The samples were excited at 350 and 420 nm to observe the photoluminescence phenomena. It has been observed that metal complex (Bi-L₃, Zn-L₂) shows enhanced PL intensity as compared to ligand (Figure 6) that can be attributed to the $\pi-\pi^*$ transitions present in the complexes [38, 39]. The Zn-L₂ complex too displayed mild fluorescence, however it was observed to be less than the ligand LH, itself. These shows quite different emission pattern when the PL data was measured at 420 nm. Comparative to ligand LH and other complexes, bismuth complex showed highest emission intensity which is actually a function of high SOC [40]. The emission peaks of ligand L and metal complexes were found in the range 410- 425 nm, which can be attributed to the $\pi-\pi^*$ transitions. The increase in emission intensity indicates an exciting opportunity of employing the complexes Bi-L₃ and Zn-L₂ for various photochemical applications.

Conclusions

A carboxylate containing ligand LH and its five metal complexes have been synthesized and structurally characterized. Ligand LH behaved in anisobidentate fashion via carboxylate moiety thus resulting four tetrahedral and one octahedral complex. All the metal complexes are nano-crystalline in nature as evident from PXRD studies. All of these complexes exhibited appreciable luminescence activity. Keeping in view their straightforward synthesis, these can be used as inexpensive precursors for their possible applications in the development of OLED materials, specifically the bismuth complex which is relatively less toxic compared to its neighboring atoms and high spin orbit coupling constant, a pre-requisite for triplet harvesting.

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