

**SYNTHESIS, STRUCTURAL AND PHOTO-PHYSICAL STUDIES OF
TRANSITION METAL COMPLEXES WITH MANNICH BASES
DERIVED FROM 2-MERCAPTOBENZIMIDAZOLE**

Amna Farooq¹, Muhammad Imran^{1*}, Zafar Iqbal², Tanveer Hussain Bokhari³,
Shoomaila Latif⁴, Ayesha Farooq¹, Muhammad Liaqat¹ and Liviu Mitu^{5*}

¹Institute of Chemistry, University of the Punjab, Lahore, Pakistan

²Department of Chemistry, Syed Babar Ali School of Science and Engineering,
Lahore University of Management Sciences (LUMS), DHA,
Lahore Cantt-54792, Lahore, Pakistan

³Department of Chemistry, Government College University, Faisalabad, Pakistan

⁴Department of Chemistry, University of Lahore, Lahore, Pakistan

⁵Department of Nature Sciences, University of Pitesti, Pitesti, 110040, Romania

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ABSTRACT. Two Mannich base ligands, [1-(di-*n*-butylamine-*N*-methyl)mercapto-1*H*-benzimidazole] (**L**¹) and [1-(diphenylamine-*N*-methyl)mercapto-1*H*-benzimidazole] (**L**²) have been synthesized and further reacted with Co(II), Ni(II), Cu(II) and Zn(II) ions to afford their respective complexes. The progress of the reaction was monitored by thin layer chromatography. The structural elucidation of Mannich base ligands and their metal complexes was done by Fourier Transform Infrared (FTIR), UV-Visible, Nuclear Magnetic Resonance spectroscopy (¹H NMR & ¹³C NMR) and Atomic absorption spectroscopy (AAS) / Inductively coupled plasma emission spectroscopy (ICPES). FTIR and NMR studies supported the monoanionic bidentate coordination mode of **L**¹ and **L**² while tetrahedral geometries of metal complexes were proposed on the basis of AAS/ICP, magnetic moment and electronic spectroscopic data. The synthesized compounds were also investigated for their luminescent behavior which exhibited broad emission bands indicating charge transfer nature of the involved transitions.

KEY WORDS: Metal complexes, Mannich bases, 2-Mercaptobenzimidazole, Luminescence

INTRODUCTION

Mannich in 1912 reported first “Mannich base”, in which two different chemical moieties formed linkage by means of methylene bridge (–CH₂–) [1]. The Mannich bases have played a vital role in the development of synthetic organic chemistry due to the versatile reactivity of these compounds. They are very reactive, useful intermediates of synthetic chemistry and can easily be transformed into variety of new compounds [2, 3]. The “Mannich reaction” is the nucleophilic addition reaction of *non enolizable aldehyde* (mostly formaldehyde) and an *amine* (primary, secondary or ammonia) to form resonance stabilized imine (iminium ion or imine salt) and then allowed to react with the *substrate* involving active hydrogen containing (any enolizable carbonyl compound, nitriles, amide, carbamate, electron-rich heterocycles such as furan, pyrrole, and thiophene, or urea) [4-6]. Benzimidazole is an interesting precursor in this direction. A literature survey reveals that benzimidazole derivatives exhibit several biological and pharmaceutical properties such as anti-inflammatory, anti-HIV, anticancer, antiviral, antihelminthic, antitubercular, antipsychotic etc [7-19]. It is well established that combining two or more active moieties may possibly augment the activity and more particularly prevent the development of resistance by the infectious micro-organisms [8].

*Corresponding author. E-mail: imran_inorganic@yahoo.com, ktm7ro@yahoo.com

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Keeping in view structural diversity and enormous applications of Mannich bases, in the present work, synthetic strategies for the previously synthesized [20-21] two Mannich bases [1-(di-*n*-butylamine-*N*-methyl)mercapto-1*H*-benzimidazole] (**L**¹) and [1-(diphenylamine-*N*-methyl)mercapto-1*H*-benzimidazole] (**L**²) derived from 2-mercaptobenzimidazole and their eight transition metal complexes have been developed. The structural and bonding aspects of the synthesized compounds and their luminescent behavior are part of this manuscript.

EXPERIMENTAL

Materials

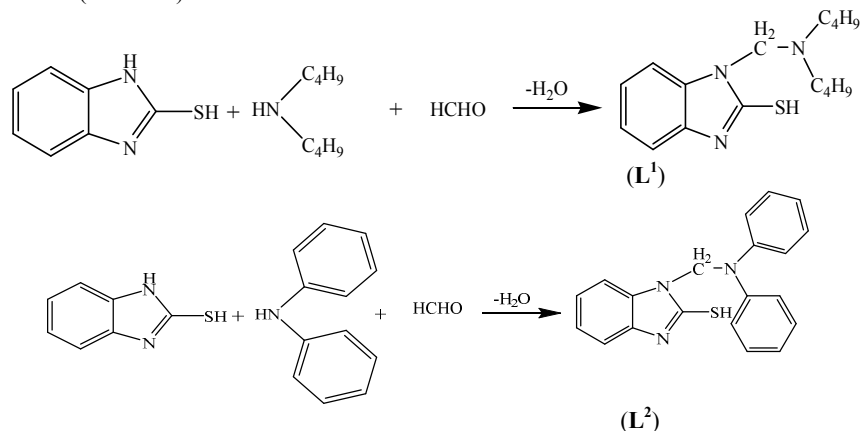
All reagents, 2-mercaptobenzimidazole (M.p: 300–304 °C), methanol (B.p: 64.7 °C), THF (B.p: 66 °C), diphenylamine, di-*n*-butylamine, CoCl₂, NiCl₂, CuCl₂, ZnCl₂ were procured from Sigma Aldrich and used without further purification.

Analytical methods

UV/Visible spectrophotometer (model T90+), FT-IR spectrophotometer (Cary 630 FT-IR), Atomic absorption spectrophotometer (Perkin Elmer AA Analyst 100), Conductivitymeter (Cyber scan 500 con), PerkinElmer multimode plate reader for photoluminescence and Avance 500 Nuclear magnetic spectrometer for ¹H and ¹³C NMR were used to characterize the synthesized compounds. The melting points were determined by Gallen Kemp apparatus.

Synthesis of ligands

Mannich base (L¹). Ligand [1-(di-*n*-butylamine-*N*-methyl)mercapto-1*H*-benzimidazole], (**L**¹) was synthesized according to a reported procedure [20] with the slight modifications particularly with reference to solvents used and reflux time. Briefly, equimolar solutions of di-*n*-butylamine (0.01 mol, 1.7 mL) and paraformaldehyde (0.01 mol, 0.30 g) in methanol, 2-mercaptobenzimidazole (0.01 mol, 1.5 g) in tetrahydrofuran were mixed. The resulting mixture was stirred in an ice cold condition for about 30 minutes and then gradually heated to reflux for 5 h. The resulting solid obtained was filtered, washed with *n*-hexane, dried and kept in dessicator (scheme 1).

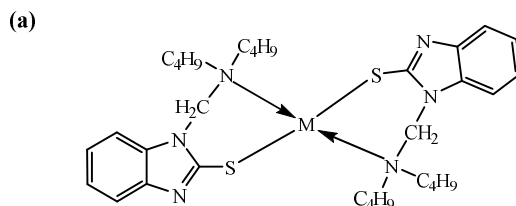


Scheme 1. Synthesis route of ligands.

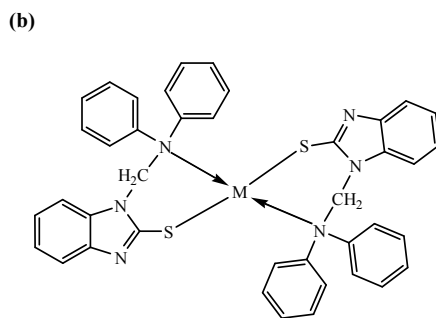
Mannich base (L²). Ligand [1-(diphenylamine-*N*-methyl)mercapto-1*H*-benzimidazole] (L²) was synthesized according to reported procedure [21] as by taking equimolar quantities of 2-mercaptobenzimidazole (0.01 mol, 1.5 g), diphenylamine (0.01 mol, 1.69 g) and Paraformaldehyde (0.01 mol, 0.30 g) in 20 mL of methanol. (Scheme 1).

General method for the synthesis of metal complexes

Metal complexes of L¹[1-(di-*n*-butylamine-*N*-methyl)mercapto-1*H*-benzimidazole] and L²[1-(diphenylamine-*N*-methyl)mercapto-1*H*-benzimidazole] were synthesized by adding methanolic solution of ligands (L¹) (0.58 g, 0.002 mol) and (L²) (0.66 g, 0.002 mol) dropwise with continuous stirring to methanolic solution of respective metal salts CoCl₂ (0.129 g, 0.001 mol), NiCl₂ (0.129 g, 0.001 mol), CuCl₂ (0.134 g, 0.001 mol), ZnCl₂ (0.136 g, 0.001 mol). The resulting solutions were stirred at room temperature for about 1 h. Subsequently, the mixture were refluxed for 2 h and then cooled to room temperature. The resulting solids were filtered, washed with methanol thrice, dried and then stored in desiccator for further use (Scheme 2 and 3).

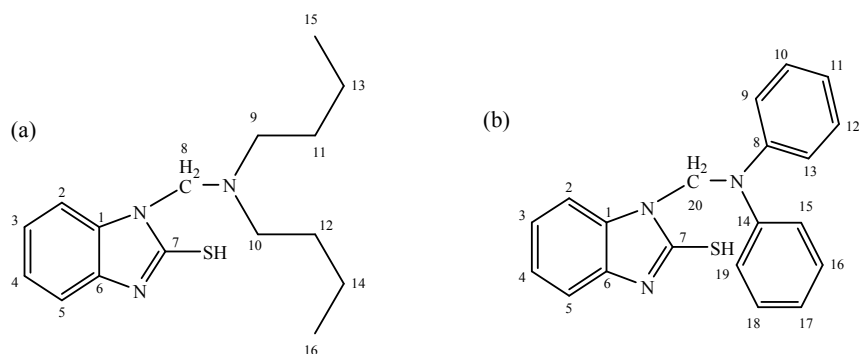


where, M = Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺



where, M = Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺

Scheme 2. Proposed structures of metal complexes (a) L¹-M (II) complexes and (b) L²-M (II) complexes.



Scheme 3. Labeling of L^1 and L^2 for $^1\text{H}/^{13}\text{C}$ NMR spectral interpretation (a) L^1 and (b) L^2 .

RESULTS AND DISCUSSION

Both the ligands L^1 [1-(di-*n*-butylamine-*N*-methyl)mercapto-1*H*-benzimidazole] and L^2 [1-(diphenylamine-*N*-methyl)mercapto-1*H*-benzimidazole] and their respective complexes were prepared by the general outlines given above in experimental section (Schemes 1 and 2). At room temperature each complex is stable solid towards air and moisture. All the complexes are colored except zinc complexes. Generally, these ligands and metal complexes are insoluble in most of the organic solvents, except DMSO and DMF. Moreover, the solubility of L^2 -metal complexes is quite low compared to fair solubility of L^1 -metal complexes. Physical properties of ligands and their respective metal complexes are shown in Table 1.S

Table1. Analytical data of the ligands and their complexes

S. No.	Compound	Decomposition point/ $^{\circ}\text{C}$	Color	% Yield	% of metal ML_2 1:2	
					Found (%)	Calculated (%)
1	Ligand L^1	131 – 135	White	72	---	---
2	Ligand L^2	165 –170	White	70	---	---
3	L^1 -Co(II) complex	> 210	Dark blue	68	9.7	10.1
4	L^1 -Ni(II) complex	> 190	Bright green	71	9.8	10.0
5	L^1 -Cu(II) complex	> 250	Bright blue	78	10.0	10.9
6	L^1 -Zn(II) complex	>180	White	60	10.9	11.2
7	L^2 -Co(II) complex	>220	Bright blue	75	8.26	8.87
8	L^2 -Ni(II) complex	> 200	Dark green	72	8.44	8.84
9	L^2 -Cu(II) complex	> 250	Blue	76	9.25	9.57
10	L^2 -Zn(II) complex	>170	White	65	9.11	9.98

FT-IR spectra

The well-defined peaks of [1-(di-*n*-butylamine-*N*-methyl)mercapto-1*H*-benzimidazole] (L^1), [1-(diphenylamine-*N*-methyl)mercapto-1*H*-benzimidazole] (L^2) and their complexes were recorded in IR spectra ranging 4000–400 cm^{-1} and compared (Table 2). The peaks at 1619 and 1591 cm^{-1} can be assigned to $\nu\text{C}=\text{N}$ functional group present in the ring L^1 and L^2 , respectively [21]. The presence of C=N functional groups in L^1 and L^2 and absence of stretching frequencies for C=S suggest that both the ligands exhibit *enol* tautomer (C-SH) instead of keto form (C=S). These

proposed structures are well supported by ^{13}C NMR, where chemical shift of C–S was observed at 167 ppm clarifying thiol (C–SH) moiety instead of C=S. ^{13}C NMR is a best tool to distinguish between C–SH and C=S, for C=S, chemical shift appears above 190 ppm [22]. The comparison of IR spectral data of ligands and metal complexes also revealed the coordination through nitrogen (N) and sulfur (S). The results are in agreement with [23-25].

Table2. IR assignments ($4000 - 700\text{ cm}^{-1}$) of ligands L^1 , L^2 and their metal complexes

Compound	$\nu(\text{C}=\text{N})\text{ cm}^{-1}$ (Aromatic)	$\nu(\text{CH}_2)\text{ cm}^{-1}$	$\nu(\text{C}-\text{N}-\text{C})\text{ cm}^{-1}$
Ligand L^1	1619	1466	1358
Ligand L^2	1591	1460	1335
L^1 -Co(II) complex	1655	1459	1230
L^1 -Ni(II) complex	1625	1454	1239
L^1 -Cu(II) complex	1619	1421	1346
L^1 -Zn(II) complex	1621	1456	1346
L^2 -Co(II) complex	1619	1460	1334
L^2 -Ni(II) complex	1619	1415	1350
L^2 -Cu(II) complex	1620	1456	1346
L^2 -Zn(II) complex	1578	1493	1338

^1H NMR spectra

The ^1H NMR spectra of the Mannich bases L^1 and L^2 and their complexes were recorded in DMSO- d_6 (Table 3). For assigning chemical shifts to the various protons, the structures of both these ligands have been labeled (Scheme 3). The ^1H NMR spectra of L^1 and L^2 exhibit a multiplets in the range δ 6.67–7.49 and δ 6.78–7.50 ppm respectively, which can be attributed to aromatic protons. Both the ligands L^1 and L^2 show a singlet at δ 5.67 and δ 5.69 ppm respectively, which can be assigned to methylene linkage (2H, $-\text{CH}_2$) formed between the benzimidazole moiety and amino compound (Table 3). In the metal complexes, the very fine information was not observed because of the broadness of signals except zinc complexes (Table 3) making the interpretation complicated. However, shifting of chemical shift values of protons in the down field region may be attributed to the involvement of ligand with metal ions [24, 25] as elucidated on the basis of FT-IR.

Table 3. ^1H NMR data of Mannich bases and their Zinc complexes

Compound	δ/ppm
L^1	(DMSO- d_6 , 500 MHz, δ) 6.67–7.49 (m, 4H, ArH), 5.67 (s, 2H, CH_2), 1.25–2.49 (m, 12H, CH_2), 0.89 (m, 6H, CH_3).
L^2	(DMSO- d_6 , 400 MHz) (DMSO- d_6 , 400 MHz, δ): 6.78–7.50 (m, 14H, ArH); 5.69 (s, 2H, CH_2).
L^1 -Zn(II) complex	(DMSO- d_6 , 400 MHz) 6.65–7.85 (m, 8H, ArH); 5.56 (s, 4H, CH_2); 1.30–2.49 (m, 24H, CH_2); 0.84 (m, 12H, CH_3)
L^2 -Zn(II) complex	(DMSO- d_6 , 400 MHz) 6.07–7.12 (m, 28H, ArH); 4.15 (s, 4H, CH_2).

¹³C NMR spectra

The ¹³C NMR spectra of the Mannich bases **L**¹, **L**² and their metal complexes were recorded in DMSO-*d*₆ and the chemical shifts of various carbons have been given in Table 4. The prominent chemical shifts at δ 168.9 ppm can be assigned to the thiol carbon (C7). Similarly chemical shifts at δ 67.05 and 67.07 ppm in **L**¹ and **L**² can be assigned to the methylene carbon C8 and C20 (a linkage between benzimidazole moiety and amino compounds), respectively (Table 4). In respective zinc complexes, the chemical shift of C7 carbon has been observed at 189.7 and 189.9 ppm suggesting coordination through thiol moiety. Moreover, there is also change in chemical shift values C8 and C20 (surrounding nitrogen atoms of amine moiety) in these complexes revealing involvement of these nitrogen atoms in coordination with zinc ions (Table 4).

Table 4. ¹³C NMR data of Mannich bases and their Zinc complexes

Compound	δ/ppm
L ¹	(DMSO- <i>d</i> ₆ , 500 MHz, δ) 67.07 (C8); 110.15, 123.05, 131.11(C1-C6); 168.99 (C7); 23.20–39.91 (C9-C12); 10.75 (C15, C16)
L ²	(DMSO- <i>d</i> ₆ , 400 MHz, δ) 67.05 (C20); 116.70–143.40 (C1-C6, C8-C19); 168.97 (C7).
L ¹ -Zn(II) complex	(DMSO- <i>d</i> ₆ , 400 MHz, δ) 67.40 (C8); 109.42–141.31 (C1-C6); 189.70 (C7); 23.20–39.91 (C9-C12); 10.75 (C15, C16).
L ² -Zn(II) complex	(DMSO- <i>d</i> ₆ , 400 MHz, δ) 66.05 (C20); 109.21–131.97 (C1-C6, C8-C19); 188.97 (C7).

UV/Vis data and Magnetic moment

Electronic spectrum of the Co(II)-complexes illustrated two allowed transitions assignable to ⁴A₂(F) → ⁴T₁(F) (11708–11721 cm⁻¹) and ⁴A₂(F) → ⁴T₁(P) (17413–17456 cm⁻¹) which were in good agreement with tetrahedral geometry for Co(II) ions. The magnetic moment values of Co (II) complexes were 4.31 B.M., 4.36 B.M., revealing that both Co (II) complexes have typical tetrahedral geometry [26]. Ni (II) complexes depicted two absorption bands in their electronic spectrum at 11646–11676 cm⁻¹ and 15456–15470 cm⁻¹ assignable to ³T₁(F) → ³A₂(F), ³T₁(F) → ³T₁(P) transitions which revealed the tetrahedral environment around Ni(II) ion. Similarly, the magnetic moment values (3.31 B.M., 3.20 B.M.) also support this environment around Ni (II) ions [27]. Cu (II) complexes in their electronic spectra show an absorption band at 13146 and 13233 cm⁻¹ that can be assigned to ²T₂ → ²E transition of tetrahedral geometry. The magnetic moment values (2.21 B.M., 2.13 B.M.) of these complexes also support 4-coordinate tetrahedral geometry and presence of one unpaired electron in d⁹ [28]. Zn (II) complexes have d¹⁰ configuration and were found to be diamagnetic. The diamagnetic nature of this complex supports only presence of charge transfer band and absence of d-d transition proposing its tetrahedral geometry [28, 29].

Photo-physical studies

The fluorescence emission spectra of the Mannich bases **L**¹, **L**² and their transition metal complexes were recorded at excitation wavelength 320 and 520 nm at room temperature. The fluorescence emission spectrum of **L**¹, **L**² and their transition metal complexes are depicted in

Figures 1 and 2. Both the ligands and their metal complexes showed broad emission bands indicating charge transfer nature of the transitions. Significant differences in positions of emission maximum from those of the ligand and metal complexes establish the complexation process [28]. At excitation wavelength 320 nm, **L**¹ and **L**² showed the emission at 426 and 359 nm, and their complexes showed the emission at 370, 416, 430, 425, 427, 359, 386 and 368 nm for **L**¹-Co(II), **L**¹-Ni(II), **L**¹-Cu(II), **L**¹-Zn(II), **L**²-Co(II), **L**²-Ni(II), **L**²-Cu(II) and **L**²-Zn(II), respectively. **L**², **L**²-Zn(II) and **L**¹-Co(II) showed strong fluorescence emission with high intensity as compared to others due to different electronic configurations of metal ions and metal-charge transfer transition. At excitation wavelength 520 nm, **L**¹ and **L**² showed the strong fluorescence emission at 520 and 523 nm. Their complexes showed the emission at 525, 522, 520, 519, 518, 519, 521 and 520 nm for **L**¹-Co(II), **L**¹-Ni(II), **L**¹-Cu(II), **L**¹-Zn(II), **L**²-Co(II), **L**²-Ni(II), **L**²-Cu(II) and **L**²-Zn(II), respectively. Among other metal complexes, the **L**¹-Zn(II) and **L**²-Zn(II) complexes exhibited, the enhanced fluorescence intensity, was attributed to ligand to metal charge transfer (LMCT) transitions and diamagnetic nature (d^{10} configuration) of Zn(II) ions, which significantly increase the emission lifetime. The factors, which are assigned to be responsible for increase in the photoluminescence, are the simple binding of ligand to the d^{10} metal ions, an increased rigidity in structure of the complexes and a restriction in the photo induced electron transfer, etc [29, 30]. It is evident from the fluorescence spectra that fluorescence emission intensity of Mannich bases changed dramatically on complex formation with transition metal ions. The change in fluorescence intensity with formation of metal complexes is due to change in electron density on Mannich bases [31].

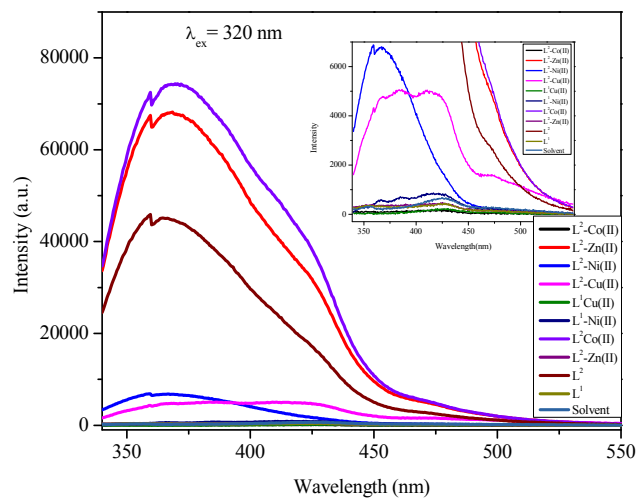


Figure 1. Fluorescence spectra at excitation wavelength 320 nm.

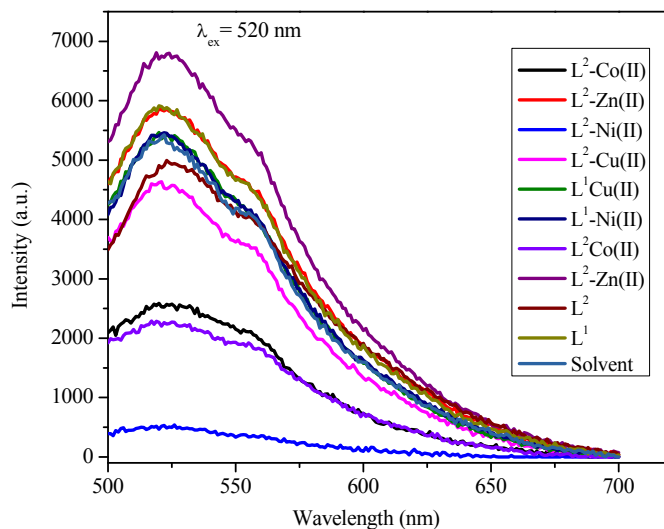


Figure 2. Fluorescence spectra at excitation wavelength 520 nm.

CONCLUSION

In this study, we have explored the synthesis and coordination chemistry of two previously synthesized Mannich base ligands and their eight transition metal complexes. The structural elucidation revealed that both the ligands behave in a monoanionic bidentate fashion. The geometries of all the resulting complexes were found to be tetrahedral. The metal complexes of both sulfur based Mannich bases were found to possess appreciable luminescence activity. It is evident from the fluorescence spectra that fluorescence emission intensity of L^1 and L^2 changed dramatically on complex formation and maximum fluorescence emission was showed by L^1 -Zn(II) and L^2 -Zn(II) complexes.

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