Synthesis and Spectroscopic Characterization of Some Novel Polypyridine and Phenanthroline Complexes of Mn(II), Fe(II), Co(II) and Zn(II) Incorporating a Bidentate Benzothiazolyl Hydrazine Ligand

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Abstract: Eight novel polypyridine and phenanthroline complexes of Mn(II), Fe(II), Co(II) and Zn(II) (1–8) of the type \([M(N–N)_2(L)]\text{Cl}_2\) where N–N is 2,2’-bipyridine (bpy)\textsubscript{2} and 1,10-phenanthroline (phen)\textsubscript{2} with three benzothiazolyl hydrazine ligands \textit{L}_1–\textit{L}_3 were synthesized and characterized by elemental analysis, thermal conductance, UV–Vis, IR, \textit{\textsuperscript{1}H} NMR, electronic absorption and emission spectral methods. The IR, \textit{\textsuperscript{1}H} NMR, electronic absorption and emission spectral data revealed that the ligands coordinate with the metal ions in a bidentate fashion through azomethine nitrogen and phenolic oxygen to form complexes. The analytical and thermogravimetrical data correlated with the observations from IR, \textit{\textsuperscript{1}H} NMR, electronic absorption and emission spectra permitted to attribute that the metal ions are six coordinated in all the complexes.

Keywords: Benzothiazolyl hydrazine, Polypyridine, Phenanthroline complexes

Introduction

The polypyridine complexes of transition metals have been studied extensively with the point of interest being their rich and well characterized photophysics\textsuperscript{1-3}. The therapeutic and diagnostic properties of transition metal polypyridine complexes have attracted considerable attention leading to their application in many areas of modern medicine\textsuperscript{4}. Also in recent years, transition metal complexes have been used extensively in the forefront of fields such as probes of DNA structure, DNA-dependent electron transfer and DNA site specific cleavage\textsuperscript{5-7}.

The area of metal complexes with hydrazones has been investigated intensively during the last years regarding their pharmacological applications such as tuberculostatic, antitumor, antibacterial and antifungal agents\textsuperscript{8-10}. The thiazole and benzothiazole hydrazine represent a very interesting class of ligands, due to additional donor sites; nitrogen, sulphur or oxygen atom which introduce a wide range in their coordinative and pharmaceutical properties\textsuperscript{8,11-13}. 
In this context, we investigated the synthesis and characterization of three ligands $L_1$–$L_3$: 2–(2-hydroxy, 5–chloro acetophenyl)benzothiazolyl hydrazone ($L_1$), 2–(2-hydroxy, 3–iodo, 4–methyl, 5–chloro acetophenyl)benzothiazolyl hydrazone ($L_2$), 2–(2-hydroxy, 3–iodo, 5–chloro acetophenyl)benzothiazolyl hydrazone ($L_3$) shown in Scheme 1 and their eight novel polypyridine [$M(bpy)_2L$]Cl$_2$ (1–4) and phenanthroline [$M(phen)_2L$]Cl$_2$ (5–8) complexes with Mn(II), Fe(II), Co(II) and Zn(II) shown in Scheme 2 and 3.

Scheme 1. Synthetic route of ligands $L_1$–$L_3$

Scheme 2. Synthesis of complexes 1–4
Experimental

All reagents and solvents were purchased commercially and were used as received. 2-mercapto benzothiazole, hydrazine hydrate, acetophenone, metal(II) chlorides were obtained from SD Fine chemicals (India). The compounds 2-hyrazinobenzothiazole, 2-(2-hydroxy, 5-chloro acetophenyl)benzothiazolyl hydrazone (L₃), 2-(2-hydroxy, 3-iodo, 4-methyl, 5-chloro acetophenyl)benzothiazolyl hydrazone (L₄), 2-(2-hydroxy, 3-iodo, 5-chloro acetophenyl) benzothiazolyl hydrazone (L₅)[11], [M(bpy)₂Cl₂].nH₂O and [M(phen)₂Cl₂].nH₂O[14] were synthesized according to the literature methods. Elemental analysis was carried out on a Perkin-Elmer 240Q elemental analyzer. The infrared spectra were recorded on a Shimadzu FTIR–8400 spectrometer in KBr pellets. ¹H NMR spectra were recorded on a 500 MHz Bruker FT-NMR spectrometer using CDCl₃ and all chemical shifts are given relative to TMS. UV-Vis spectra were recorded on a Shimadzu UV-1601 spectrophotometer and the emission spectra were recorded on a shimadzu RF-5000 luminescence spectrophotometer at room temperature. Thermogravimetric analysis was performed on a computer controlled TA Instrument 2050 TGA analyzer into alumina pans at a heating rate of 10 ºC/ min.

Preparation of ligands

The ligands utilized in the present investigation were synthesized by the condensation reaction between 2-hyrazinobenzothiazole and substituted acetophenones.

Synthesis of 2-hyrazinobenzothiazole

To a warm solution of 2-mercapto benzothiazole (1 mmol) in absolute ethyl alcohol (10 mL), hydrazine hydrate (1 mmol) was added and the mixture was refluxed on a water bath for 4 h or until H₂S gas ceased to evolve. The reaction mixture was concentrated and cooled. The white needle like crystals separated, was filtered and recrystallized from ethanol.

Synthesis of ligands

To a warm ethanolic solution of 2-hyrazinobenzothiazole (1 mmol, in 10 mL) was added an ethanolic solution of respective acetophenones (1 mmol, in 10 mL) and the mixture was refluxed for about 4 hours on a water bath, the precipitate was obtained, it was filtered, washed and recrystallized from ethanol.
2–(2–Hydroxy,5–chloro acetophenyl)benzothiazolyl hydrazone (L₁)

Yield 90%; Colour dirty yellow; M.P. 220 °C; IR (KBr, cm⁻¹): ν 3400 (OH), 3204 (N–H), 1595 (C=N), 1585 (C=N, cyclic), 1500 (N–N), 1465 (C–O), 1280 (C–N), 860 (C–S); ¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.45 (s, 3H, CH₃), 7.00 (s, 1H, NH), 7.19 (m, 3H, ArH), 7.37 (s, 4H, ArH), 12.60 (s, 1H, br, OH); UV–vis (CDCl₃, nm): λmax 305, 326, 334, 363, 391. Anal. Calcd for C₁₅H₁₂N₃OSCl: C, 56.78; H, 3.78; N, 13.24. Found: C, 56.72; H, 3.75; N, 13.19.

2–(2–Hydroxy,3–iodo,4–methyl,5–chloro acetophenyl)benzothiazolyl hydrazone (L₂)

Yield 90%; Colour brown; M.P. 208 °C; IR (KBr, cm⁻¹): ν 3400 (OH), 3198 (N–H), 1598 (C=N), 1510 (N–N), 1468 (C–O), 1287 (C–N), 862 (C–S); ¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.50 (s, 3H, CH₃), 7.08 (s, 1H, NH), 7.14 (m, 1H, ArH), 7.24 (m, 1H, ArH), 7.99 (s, 1H, br. OH); UV–Vis (CDCl₃, nm): λmax 323, 345, 359, 376; Anal. Calcd for C₁₆H₁₃N₃OSClI: C, 42.01; H, 2.84; N, 9.19. Found: C, 41.09; H, 2.80; N, 9.14.

Synthesis of complexes

Preparation of the complexes

A hot ethanolic solution of the respective ligands L₁-L₃ (1 mmol in 10 mL) was mixed with an ethanolic solution of respective hydrated metal(II) 2,2- bipridyl chloride or metal(II) 1,10 phenanthroline chloride (1 mmol in 10 mL) and the mixture was refluxed on a water bath for 3–4 h and then cooled to room temperature. On cooling, a colored solid product was formed. The solid was filtered, washed with ethanol, then ether and dried. Crystallization from ethanol gave the desired metal complexes.

[Co(bpy)₂(L₁)]Cl₂ (1)

Yield 90%; Colour pale yellow; M.P. 224 °C; IR (KBr, cm⁻¹): ν 3200 (N–H), 1602 (C=N, cyclic), 1564 (C=N), 1498 (N–N), 1422 (C–O), 1285 (C–N), 866 (C–S), 770 (bpy ring), 547 (M–N), 424 (M–O); ¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.35 (s, 3H, CH₃), 6.76 (s, 1H, NH), 7.10 (m, 3H, ArH), 7.28 (m, 4H, ArH), 7.58 (m, 8H, bpy protons), 7.81 (m, 8H, bpy protons); UV–vis (CDCl₃, nm): λmax 305, 326, 334, 363, 391; Anal. Calcd for CoC₃₅H₂₇N₇OCl₃S: C, 55.40; H, 3.56; N, 12.92; Co, 7.78. Found: C, 55.34; H, 3.50; N, 12.87; Co, 7.75.

[Zn(bpy)₂(L₁)]Cl₂ (2)

Yield 90%; Colour pale brown; M.P. >230 °C; IR(KBr, cm⁻¹): ν 3200 (N–H), 1602 (C=N, cyclic), 1567 (C=N), 1498 (C–O), 1285 (C–N), 866 (C–S), 770 (bpy ring), 547 (M–N), 424 (M–O); ¹H NMR (CDCl₃, 500 MHz, ppm): δ 2.40 (s, 3H, CH₃), 6.87 (s, 1H, NH), 7.09 (m, 3H, ArH), 7.26 (m, 4H, ArH), 7.58 (m, 8H, bpy protons), 7.81 (m, 8H, bpy protons); UV–vis (CDCl₃, nm): λmax 305, 322, 330, 360, 385; Anal. Calcd for ZnC₃₅H₂₇N₇OCl₃S: C, 54.40; H, 3.56; N, 12.92; Co, 7.78. Found: C, 55.34; H, 3.50; N, 12.87; Co, 7.75.
[Fe(bpy)$_2$(L$_2$)]Cl$_2$ (3)

Yield 85%; Colour dark brown; M. P. 205 °C; IR (KBr, cm$^{-1}$) ν: 3196 (N–H), 1592 (C=N, cyclic), 1586 (C=N), 1508 (N–N), 1459 (C–O), 1284 (C–N), 860 (C–S), 748 (bpy ring), 584 (M–N), 428 (M–O); $^1$H NMR (CDCl$_3$, 500 MHz): δ 2.45 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$), 6.81 (s, 1H, NH), 7.09 (m, 1H, ArH), 7.20 (m, 4H, ArH), 7.58 (m, 8H, bpy protons), 7.81 (m, 8H, bpy protons); Anal. Calcd for FeC$_{36}$H$_{28}$N$_7$OCl$_3$: C, 48.26; H, 3.12; N, 10.94; Fe, 6.25. Found: C, 48.21; H, 3.08; N, 10.90; Fe, 6.21.

[Mn(bpy)$_2$(L$_3$)]Cl$_2$ (4)

Yield 90%; Colour dirty green; M. p. 230 °C; IR (KBr, cm$^{-1}$) ν: 3198 (N–H), 1598 (C=N, cyclic), 1590 (C=N), 1502 (N–N), 1428 (C–O), 1282 (C–N), 858 (C–S), 745 (bpy ring), 514 (M–N), 426 (M–O); $^1$H NMR (CDCl$_3$, 500 MHz): δ 2.40 (s, 3H, CH$_3$), 6.85 (s, 1H, NH), 7.18 (s, 2H, ArH), 7.40 (m, 4H, ArH), 7.58 (m, 8H, bpy protons), 8.31 (m, 8H, bpy protons); Anal. Calcd for MnC$_{35}$H$_{26}$N$_7$OCl$_3$: C, 47.72; H, 2.95; N, 11.13; Mn, 6.25. Found: C, 47.69; H, 2.92; N, 11.10; Mn, 6.21.

[Co(phen)$_2$(L$_1$)]Cl$_2$ (5)

Yield 85%; Colour pale yellow; M. P. 218 °C; IR(KBr, cm$^{-1}$) ν: 3208 (N–H), 1604 (C=N, cyclic), 1568 (C=N), 1500 (N–N), 1423 (C–O), 1282 (C–N), 1058 (phen ring), 1058 (C–S), 589 (M–N), 428 (M–O); $^1$H NMR (CDCl$_3$, 500 MHz): δ 2.42 (s, 3H, CH$_3$), 6.98 (s, 1H, NH), 7.10 (m, 3H, ArH), 7.22 (m, 4H, ArH), 7.55 (m, 8H, phen protons), 7.81 (m, 8H, phen protons); UV-Vis(CDCl$_3$): $\lambda_{max}$ 298, 324, 355, 375; Anal. Calcd for CoC$_{39}$H$_{27}$N$_7$OSCl$_3$: C, 58.06; H, 3.34; N, 12.15; Co, 7.32. Found: C, 58.01; H, 3.30; N, 12.11; Co, 7.28.

[Zn(phen)$_2$(L$_1$)]Cl$_2$ (6)

Yield 90%; Colour pale brown; M. P. 225 °C; IR(KBr, cm$^{-1}$) ν: 3205 (N–H), 1598 (C=N, cyclic), 1564 (C=N), 1503 (N–N), 1423 (C–O), 1282 (C–N), 1056 (phen ring), 860 (C–S), 586 (M–N), 428 (M–O); $^1$H NMR (CDCl$_3$, 500 MHz): δ 2.40 (s, 3H, CH$_3$), 7.00 (s, 1H, NH), 7.15 (m, 3H, ArH), 7.26 (m, 4H, ArH), 7.55 (m, 8H, phen protons), 7.80 (m, 8H, phen protons); Anal. Calcd for ZnC$_{39}$H$_{27}$N$_7$OSCl$_3$: C, 57.63; H, 3.32; N, 12.06; Zn, 8.00. Found: C, 57.59; H, 3.28; N, 12.02; Zn, 7.97.

[Fe(phen)$_2$(L$_2$)]Cl$_2$ (7)

Yield 90%; Colour brown; M. P. 272 °C; IR(KBr, cm$^{-1}$) ν: 3195 (N–H), 1590 (C=N, cyclic), 1585 (C=N), 1505 (N–N), 1460 (C–O), 1285 (C–N), 1105 (phen ring), 858 (C–S), 515 (M–N), 428 (M–O); $^1$H NMR (CDCl$_3$, 500 MHz): δ 2.43 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$), 6.80 (s, 1H, NH), 7.08 (m, 1H, ArH), 7.21 (m, 4H, ArH), 7.56 (m, 8H, phen protons), 7.81 (m, 8H, phen protons); Anal. Calcd for FeC$_{40}$H$_{28}$N$_7$OCl$_3$: I: C, 50.90; H, 2.96; N, 10.39; Fe, 5.93. Found : C, 50.86; H, 2.92; N, 10.35; Fe, 5.89.

[Mn(phen)$_2$(L$_3$)]Cl$_2$ (8)

Yield 85%; Colour brown; M. p. 260 °C; IR (KBr, cm$^{-1}$) ν: 3196 (N–H), 1598 (C=N, cyclic), 1590 (C=N), 1502 (N–N), 1426 (C–O), 1282 (C–N), 1056 (phen ring), 862 (C–S), 586 (M–N), 426 (M–O); $^1$H NMR (CDCl$_3$, 500 MHz): δ 2.41 (s, 3H, CH$_3$), 6.85 (s, 1H, NH), 7.18 (m, 2H, ArH), 7.42 (m, 4H, ArH) 7.58 (m, 8H, phen protons), 7.80 (m, 8H, phen protons); UV-Vis(CDCl$_3$): $\lambda_{max}$ 300, 320, 335, 363, 369, 385; Anal. Calcd for MnC$_{39}$H$_{28}$N$_7$OCl$_3$: I: C, 50.43; H, 2.80; N, 10.56; Mn, 5.92. Found: C, 50.40; H, 2.75; N, 10.52; Mn, 5.89.
Results and Discussion

IR spectra

A broad strong absorption band observed at 3400-3350 cm\(^{-1}\) in the IR spectra of the ligands \(L_1\)–\(L_3\) is due to the stretching vibration of OH group which disappears in the spectra of the complexes, indicating the deprotonation of the phenolic group and the coordination of these ligands through the phenolic oxygen\(^{10,11,13}\). It is also supported by the shift to lower wave numbers of the band from 1450-1468 cm\(^{-1}\) to 1420-1460 cm\(^{-1}\) due to the stretching vibration of C–O phenolic when compared to the uncomplexed ligands\(^{12,13,15,16}\). In all the four ligands a strong band, with two maxima at 1600-1590 cm\(^{-1}\), 1590 cm\(^{-1}\) is observed due to the stretching vibration of the hydrazone function, \(\nu\)C=N exocyclic and benzothiazole group, \(\nu\)C=N endocyclic respectively\(^{11,13}\). The lowering of position of only one band in the corresponding metal complexes is observed at 1600-1590 cm\(^{-1}\), due to \(\nu\)C=N exocyclic in the region 1500–1590 cm\(^{-1}\) suggest that the azomethine nitrogen atom of ligands is involved in co-ordination. Literature data\(^{11,13,17}\) have revealed that the lowering of \(\nu\)C=N stretching vibration when azomethine nitrogen is coordinated with metal ion.

A new strong band, appeared in the IR spectra of the ligands at ~1512 cm\(^{-1}\), which may be assigned to the skeleton >C–HN–N=C< vibration. The downward shift of the band due to \(\nu\)N–N in the IR spectra of all the complexes is another proof for the coordination of azomethine nitrogen atom to the metal ion\(^{13}\). A multiple band system observed at ~1590 cm\(^{-1}\), ~1282 cm\(^{-1}\) and ~860 cm\(^{-1}\) attributed to \(\nu\)C=N(cyclic), \(\nu\)C–N (cyclic) and \(\nu\)C–S–C of benzothiazole group respectively. In the IR spectra of all the metal complexes, the position of these bands remain unchanged indicate that nonparticipation of the ring nitrogen atom in coordination. \(\nu\)N–H absorption band around 3200 cm\(^{-1}\), in these ligands unchanged in the IR spectrum of the complex also indicate non-participation of the ring nitrogen atom in coordination\(^{12,15,18}\). All the complexes showed bands in the regions 1050-1105 cm\(^{-1}\) and 745-770 cm\(^{-1}\) due to phen/bpy ring –C–H and –C=N stretching vibrations, respectively\(^{19,20}\).

The most notable change in the IR spectra as reported by literature is the involvement of azomethine nitrogen and phenolic oxygen atom of the ligand in the complexation which is confirmed by appearance of new additional bands due to \(\nu\)M–N and \(\nu\)M-O stretching vibrations in the range of 590-514 cm\(^{-1}\) and 428-424 cm\(^{-1}\) respectively\(^{15,21-24}\). On the basis of the Infra red spectral studies of the ligands \(L_1\)–\(L_3\) and their complexes, we can conclude that the ligands \(L_1\)–\(L_3\) act as bidentate NO donor in all the complexes.

\(^1\)H NMR spectra

In the \(^1\)H NMR spectrum of the ligands \(L_1\)–\(L_3\) a singlet observed at \(\delta\) 12–14 ppm for one proton correspond to the phenolic of the hydrazone ring. The metal complexes of these ligands did not show any proton signal to the phenolic OH range suggest that the phenolic oxygen participated in the coordination, after complete deprotonation. The assignment to the aromatic proton and the phenolic proton are supported by the literature\(^{3,12,25}\). The singlet observed at \(\delta\) 7 ppm for one proton in \(L_1\)–\(L_3\) is assigned to the NH proton of benzothiazolyl hydrazone. Two multiplet signals observed around \(\delta\) 7-8 ppm for four protons and three protons of \(L_1\) and for four protons and one proton of \(L_2\) and for four protons and two protons \(L_3\) are assigned to aromatic protons\(^{3,10,26}\).

In addition to these, one singlet peak observed at \(\delta\) 2.45 ppm for three protons in \(L_1\)–\(L_3\) is assigned to methyl group attached to the hydrazone ring. A singlet peak observed at \(\delta\) 2.30 ppm
for three protons in L₂ is assigned to methyl group attached to the phenyl ring. In the 1H NMR spectra of the all complexes, these protons of ligands are shifted downfield due to coordination to the metal ions, it further suggests complexation. Two multiplet signals of eight protons observed in the spectrum of the complexes 1-4 at δ 7.58 ppm and δ 8.31 ppm were assigned to bpy protons and the signals at δ 7.55-7.58 ppm and δ 7.81 ppm in the spectrum of complexes 5-8 were assigned to phen protons. Thus all the protons were found to be in their expected region. The conclusions drawn from these studies further support to the mode of bonding discussed in their IR spectra.

**UV–Vis absorption spectra and emission spectra**

The UV-Vis absorption spectra of ligand L₁ and its metal complex 1 in chloroform at room temperature are shown in Figure 1 and Figure 2 and the spectral data of various ligands and their complexes are listed in Table 1.

**Figure 1.** UV-Vis absorption spectrum of ligand L₁  
**Figure 2.** UV-Vis absorption spectrum of complex 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Absorption λ nm</th>
<th>Emission λ nm</th>
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<tbody>
<tr>
<td>L₁</td>
<td>305, 322, 330, 360, 385</td>
<td>545</td>
</tr>
<tr>
<td>L₂</td>
<td>323, 345, 359, 376</td>
<td>532</td>
</tr>
<tr>
<td>L₃</td>
<td>330, 365, 372, 385</td>
<td>542</td>
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<tr>
<td>8</td>
<td>300, 320, 335, 363, 369, 385</td>
<td>655</td>
</tr>
</tbody>
</table>

The absorption around 325 nm is attributed to π-π* transitions involving the benzothiazolyl hydrazone. In the UV–Vis absorption spectra of complexes the bands at 326, 323, 330 nm should receive a dominant contribution from transition involving the ligands L₁, L₂ and L₃ respectively. In particular, the bands with 290-300 nm range should receive a dominant contribution from π-π* transition involving bpy and phen moieties.

The other weak absorption bands of the complexes in the UV region are expected to include contributions from spin allowed metal to ligand charge transfer, MLCT. The Emission spectra of ligand L₁ and its metal complex L₃ in chloroform at room temperature is shown in Figure 3 and Figure 4 and the relevant data are collected in Table 1.
Figure 3. Emission spectrum of ligand $L_1$

Figure 4. Emission spectrum of complex 1

The luminescence of the ligands $L_1$, $L_2$ and $L_3$ are assigned to the benzothiazolyl hydrazone centered $\pi$-$\pi^*$ level\textsuperscript{34-37}. The ligands $L_1$, $L_2$ and $L_3$ showed the emission bands at 532 nm, 545 nm and 542 nm respectively. The metal complexes $2, 7, 9, 10$ showed the emission bands at 630 nm, 645 nm and 655 nm respectively. The complexes of Ru(II) are probably the most investigated inorganic luminophores\textsuperscript{29,38}. The metal complexes studied here exhibit relatively intense luminescence. In particular, emissions of complexes should originate from M–bpy and M–phen CT state\textsuperscript{28,33,38,39}. The metal complexes exhibited the usual MLCT emission\textsuperscript{3,38}.

**Thermogravimetric analysis**

The TG curves of the complexes showed an endothermic peak at 160-200 °C, due to the loss of coordinated water\textsuperscript{40}, which is in agreement with the results obtained from the IR spectra. The endothermic peaks observed at 340 °C correspond to the removal of the anionic chloride\textsuperscript{41}. All the complexes lose the organic ligand in a large exothermic process, in the range of 400-800 °C. On the basis of analytical and thermogravimetical data, IR, $^1$H NMR, electronic absorption and emission spectra it is concluded that that the ligands $L_1$–$L_3$ act as bidentate NO donor in all the complexes.

**Conclusion**

We have prepared eight novel polypyridine and phenanthroline complexes of Mn(II), Fe(II), Co(II) and Zn(II) with three benzothiazolyl hydrazone ligands. The analytical, thermogravimetical, IR, $^1$H NMR, electronic absorption and emission spectral data revealed that the ligands $L_1$–$L_3$ coordinate with the metal ions in a bidentate fashion through azomethine nitrogen and phenolic oxygen to form complexes 1–8.

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