SYNTHESES, CHARACTERIZATION AND CHELATING PROPERTIES OF GUANIDO BENZIMIDAZOLE AND GUANIDOPHOSPHONATEBENZIMIDAZOLE

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The synthesis of guanidine derivatives of benzimidazole namely, guanidinobenzimidazole, (GBM), guanidinophosphonatebenzimidazole, (GPBM), and their chelating properties are reported in this work. The guanidine and phosphonate derivatives were synthesized along with their metal complexes, Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). The ligands were characterized by $^1$H NMR, $^{13}$C NMR spectroscopy while both the ligands and the metal complexes were characterized by C.H.N analysis, Percentage Metal Composition, FT-Infrared spectra Analysis, UV–Visible Electronic Spectroscopy and Magnetic susceptibility measurements. The results from the percentage composition of the metals in the complexes suggest that ratio of the metal to ligand is 1:2 (M:L) where M = Co(II), Ni(II), Cu(II), Fe(II), Zn(II). Thus, the prepared complexes have the general formulae [ML]. Electronic Spectral analyses indicated the participation of the imidazolic nitrogen atom and the nitrogen in position 12 of the guanidinobenzimidazole ligand in the coordination of the ligand to the metal ions while, the shifts in the position of the $\nu(P=O)$ absorption band of the phosphonate moiety in the guanidinophosphonatebenzimidazole, (GPBM) ligand from 1265 cm$^{-1}$ in the free ligand to 1141-1200 cm$^{-1}$ in the metal complexes suggested that the P=O is most likely involved together with the nitrogen atom in position 12 in the coordination of the metal ions to the guanidinophosphonatebenzimidazole, (GPBM) ligand. The electronic spectral data and the values of the magnetic susceptibility values suggest six coordinate octahedral/distorted octahedral geometry for all the complexes.

Keywords: Characterization, Chelating properties, Guanidine derivatives, Metal Complexes, Synthesis.

INTRODUCTION

Coordination compounds containing benzimidazole derivatives and transition metal ions continue to attract the interest of research groups, partly due to their very interesting chemistry as well as their possible applications including biological properties, (Malek et al., 2006).

Similarly, transition metal complexes of guanidine and phosphonates have been found to have good chelating capability, structural flexibility, interesting electrical as well as magnetic properties (Anitha, 2011). They are also known to possess antimicrobial potentials (Gupta et al., 2009; Rajeeva et al., 2009). Thus, guanidines, phosphonates and their complexes continue to receive attention both in academic research and industrial development as compounds with unique properties. Phosphonates are increasingly used in medicine to treat disorders associated with bone formation and calcium metabolism. They also serve as carriers for radionuclides in bone cancer treatments (Malek et al., 2006).

The coordination of 2-benzimidazole derivatives to metal ions has been shown to occur through a variety of sites, with groups bearing nitrogen, oxygen, sulphur and other donor atoms. The coordination occurs through the imidazolic nitrogen atom and also through N, S or O atoms present in the molecule, giving place to a variety of metal-ligand coordination modes, (Fabiola T., et al., 2008).

In spite of this great chelating properties, biochemical and pharmaceutical importance of benzimidazoles and guanidines, phosphorylation of guanidinobenzimidazole, its structural activities as well as the chelating properties of Guanidinophosphonatebenzimidazole, (GPBM) have not been reported. Thus, this work focused on the synthesis of Guanidinobenzimidazole, (GBM) and Guanidinophosphonate benzimidazole, (GPBM) ligands; investigated their chelating properties/differences and characterized these ligands as well as their metal complexes.
MATERIALS AND METHODS

Materials
High grade analytical chemicals and reagents were used and these included: 2-amino benzimidazole, silica gel, copper(II) sulphate, tetrahydrofuran, triethylamine, dimethylphosphite, perchloric acid, disodium ethylene diamine tetra acetic acid (EDTA), zinc(II) sulphate, ammonia solution, ammonium chloride, erichrome black T indicator, sodium hydroxide, methyl thymol blue indicator, Iron(II) chloride, cobalt(II) nitrate, nickel (II) nitrate, copper (II) nitrate, zinc(II) nitrate. These were all purchased from Sigma Aldrich.

Instrumentation
The NMR spectra were recorded on Agilent-NMR-400 MHz Spectrometer; TMS was used as the internal standard. IR spectra (4000–400 cm\(^{-1}\)) were recorded on Shimadzu FTIR- 8700 Spectrophotometer. The C.H.N elemental analyses were carried out on Perkin Elmer 240 C elemental analyzer and the electronic transitions using the T92-UVW in UV Visible Spectrophotometer.

Melting points of the samples were determined by using the Electro thermal Digital Melting Point Apparatus. The magnetic susceptibility measurements of the metal complexes were made at room temperature using MSB-MK1 Sherwood Susceptibility Balance.

Synthetic Methods

Guanidination and Phosphorylation of Benzimidazole.
Thiourea is converted into guanidines in a suitable solvent such as tetrahydrofuran and chloroform containing copper sulphate – silica gel in presence of tertiary amines, (Alan and Boris, 2005).

\[
\begin{align*}
\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4 = & H \\
\text{The synthesis of guanidinobenzimidazole and guanidinophosphonatebenzimidazole were carried out according to the methods of Alan, 2005 and Krishnamurthy, 1995.}
\end{align*}
\]

Synthesis of Guanidinobenzimidazole, (GBM).
Copper(II) sulphate and silica gel (1 g each) were added to 25 ml of tetrahydrofuran in a 250 ml round bottomed flask in the presence of 2 ml triethylamine in a 250 ml round bottom flask.

\[
\begin{align*}
\text{CuSO}_4, \text{SiO}_2 + \text{TEA, THF, rt} & \rightarrow \text{R}^1, \text{N} = \text{C} = \text{N} - \text{R}^2 \\
\text{R}^3, \text{R}^4 \text{NH} & \rightarrow \text{R}^1, \text{N} = \text{C} = \text{N} - \text{R}^2
\end{align*}
\]

Thiourea (1), 3.81 g (50 mM) was added and the solution was stirred at room temperature for 6 hr. to produce carbondiamide (2) intermediate. The intermediate was reacted with 50 mM of 2-aminobenzimidazole (3) by stirring again for 6 hr at room temperature. Crystals of guanidinobenzimidazole (4) produced were filtered and the filtrate was concentrated by using rotary evaporator. The crystals were washed with few mls of tetrahydrofuran and dried over activated silica gel in a desiccator, (Alan and Boris, 2005).
Synthesis of Guanidinophosphonate benzimidazole, (GPBM)

Excess paraformaldehyde (6) was reacted with guanidinobenzimidazole (5) (5 mM, 0.96 g) and 60 mg of silica-supported perchloric acid was stirred for 8 hr in 25 ml of ethanol. Dimethylphosphite (7) (50 mM, 4.50 ml) was then added and the stirring continued for 1 hr at room temperature in an oil bath and then refluxed at 80 °C with stirring for another 8 hr.

The cooled solution was filtered and washed with 5 to 10 ml of ethanol (Malek et al., 2011). The crude guanidinophosphonatebenzimidazole (8) was purified using column chromatography and n-hexane as the solvent. The yield, melting point and other analytical data are presented in Table 1.

Synthesis of Metal Complexes of Guanidinobenzimidazole and Guanidinophosphonatebenzimidazole.
The syntheses were carried out according to the method of Anitha et al., (2011) and Bakir et al., (2013).

Equimolar quantities, (0.5 mM) of the ligand and metal salt, (Co(NO3)2, Ni(NO3)2, Cu(NO3)2, Zn(NO3)2 and FeCl2) were reacted in 25 ml of ethanol in a 250 ml round bottom flask. The solution was stirred at room temperature for 18 hr. It was immediately followed by 4 hr reflux at 80 °C in an oil bath. The solution was cooled, filtered and concentrated by using rotary evaporator. The crystal was washed with ethanol and dried in a desiccator over activated silica gel. The ligands and their complexes were characterized 1H-NMR and 13C-NMR, Infra-red spectroscopy, Magnetic susceptibility, UV–Visible spectroscopy and C, H, and N elemental analysis.

Complexometric Titration of complexes

0.05mM of the metal- guanidinobenzimidazole complex (GBM)/ guanidinophosphonate benzimidazole, (GPBM), was mixed with 5 ml of concentrated nitric acid. The mixture was heated and evaporated to almost dryness on a hot plate. It was allowed to cool. Addition of little quantity of

deionized distilled water was carried out three times and heated to almost dryness. It was allowed to cool and 10 ml of deionized distilled water was added. The solution was transferred into a 50 ml standard volumetric flask and made up to mark. 10 ml of the complex solution was pipetted into a 250 ml conical flask followed by addition of 4 ml of 1M sodium hydroxide solution. Methyl thymol blue indicator was added and the solution was titrated with standardized EDTA in three replicates and average titre was calculated. At the end point, the colour changed from blue to grey. The molarity of the EDTA obtained when standardized with 0.01 M (1.61 g) of Zinc salt. This procedure was repeated for all the complexes. Percentage metal composition in each of the complexes was therefore determined.

RESULTS AND DISCUSSION

Analytical data of Guanidinobenzimidazole, (GBM) and guanidinophosphonate benzimidazole, (GPBM) and the metal complexes.
The analytical data such as colours, percentage yields, the melting points and other characterization data of the ligands guanidinobenzimidazole, (GBM), guanidinophosphonatebenzimidazole, (GPBM) and their complexes are given in (Tables 1 and 2).
The C, H, N Analysis of GBM and GPBM are presented in Table: 2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Empirical formula</th>
<th>Molecular weight</th>
<th>Yield (%)</th>
<th>Melting point (°C)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>GBM</td>
<td>C₆H₉N₃</td>
<td>175.19</td>
<td>88</td>
<td>92-94</td>
<td>Yellow</td>
</tr>
<tr>
<td>Fe- GBM</td>
<td>[Fe(C₆H₉N₃)₂]</td>
<td>406.22</td>
<td>84</td>
<td>127-129</td>
<td>Brown</td>
</tr>
<tr>
<td>Co- GBM</td>
<td>[Co(C₆H₉N₃)₂]</td>
<td>409.31</td>
<td>76</td>
<td>190-192</td>
<td>Brown</td>
</tr>
<tr>
<td>Ni- GBM</td>
<td>[Ni(C₆H₉N₃)₂]</td>
<td>409.07</td>
<td>78</td>
<td>147 – 149</td>
<td>Brown</td>
</tr>
<tr>
<td>Cu- GBM</td>
<td>[Cu(C₆H₉N₃)₂]</td>
<td>413.93</td>
<td>89</td>
<td>140 – 142</td>
<td>Green</td>
</tr>
<tr>
<td>Zn- GBM</td>
<td>[Zn(C₆H₉N₃)₂]</td>
<td>415.79</td>
<td>84</td>
<td>144 – 146</td>
<td>Orange</td>
</tr>
<tr>
<td>GPBM</td>
<td>C₁₀H₁₆N₅PO₃</td>
<td>297.25</td>
<td>89</td>
<td>139 – 141</td>
<td>Yellow</td>
</tr>
<tr>
<td>Fe- GPBM</td>
<td>[Fe(C₁₀H₁₆N₅PO₃)₂]</td>
<td>650.35</td>
<td>86</td>
<td>191 – 193</td>
<td>Brown</td>
</tr>
<tr>
<td>Co- GPBM</td>
<td>[Co(C₁₀H₁₆N₅PO₃)₂]</td>
<td>653.43</td>
<td>78</td>
<td>196 – 198</td>
<td>Brown</td>
</tr>
<tr>
<td>Ni- GPBM</td>
<td>[Ni(C₁₀H₁₆N₅PO₃)₂]</td>
<td>653.19</td>
<td>68</td>
<td>194 – 196</td>
<td>Brown</td>
</tr>
<tr>
<td>Cu- GPBM</td>
<td>[Cu(C₁₀H₁₆N₅PO₃)₂]</td>
<td>658.05</td>
<td>75</td>
<td>192 – 194</td>
<td>Brown</td>
</tr>
<tr>
<td>Zn- GPBM</td>
<td>[Zn(C₁₀H₁₆N₅PO₃)₂]</td>
<td>659.91</td>
<td>82</td>
<td>194-196</td>
<td>Pink</td>
</tr>
</tbody>
</table>

**C, H, N Analysis**

The CHN elemental Analysis of GBM and GPBM are presented in Table: 2

<table>
<thead>
<tr>
<th>LIGANDS</th>
<th>Analysis Calculated (Found)</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
</tr>
</thead>
<tbody>
<tr>
<td>GBM (C₆H₉N₃)</td>
<td></td>
<td>54.84</td>
<td>5.17</td>
<td>39.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(54.48)</td>
<td>(5.15)</td>
<td>(39.50)</td>
</tr>
<tr>
<td>GBPM (C₁₀H₁₆N₅PO₃)</td>
<td></td>
<td>46.10</td>
<td>6.43</td>
<td>22.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(46.08)</td>
<td>(6.01)</td>
<td>(22.30)</td>
</tr>
</tbody>
</table>

**Percentage composition of the metals in the complexes**

The results from calculations and the inferences from the percentage composition of the metals in the complexes suggest that ratio of the metal to ligands is 1:2 (M : L) where M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) and L for guanidinobenzimidazole and guanidinophosphonatebenzimidazole. The prepared complexes were therefore found to have the general formulae [ML₂].

**Table 3: Percentage composition of metals in the complexes, the stoichiometry and the Probable Formulæ.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>% Metal Found (Calculated)</th>
<th>Stoichiometry</th>
<th>Probable Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>M- GBM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe(C₆H₉N₃)₂]²⁺</td>
<td>13.32 (13.74)</td>
<td>1:2</td>
<td>Fe(L₂)</td>
</tr>
<tr>
<td>[Co(C₆H₉N₃)₂]²⁺</td>
<td>14.54 (14.40)</td>
<td>1:2</td>
<td>Co(L₂)</td>
</tr>
<tr>
<td>[Ni(C₆H₉N₃)₂]²⁺</td>
<td>14.48 (14.35)</td>
<td>1:2</td>
<td>Ni(L₂)</td>
</tr>
<tr>
<td>[Cu(C₆H₉N₃)₂]²⁺</td>
<td>15.41 (15.35)</td>
<td>1:2</td>
<td>Cu(L₂)</td>
</tr>
<tr>
<td>[Zn(C₆H₉N₃)₂]²⁺</td>
<td>15.91 (15.72)</td>
<td>1:2</td>
<td>Zn(L₂)</td>
</tr>
<tr>
<td><strong>M-GPBM</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe(C₁₀H₁₆N₅PO₃)₂]²⁺</td>
<td>8.58 (8.59)</td>
<td>1:2</td>
<td>Fe(L₂)</td>
</tr>
<tr>
<td>[Co(C₁₀H₁₆N₅PO₃)₂]²⁺</td>
<td>9.16 (9.02)</td>
<td>1:2</td>
<td>Co(L₂)</td>
</tr>
<tr>
<td>[Ni(C₁₀H₁₆N₅PO₃)₂]²⁺</td>
<td>8.98 (8.99)</td>
<td>1:2</td>
<td>Ni(L₂)</td>
</tr>
<tr>
<td>[Cu(C₁₀H₁₆N₅PO₃)₂]²⁺</td>
<td>9.65 (9.66)</td>
<td>1:2</td>
<td>Cu(L₂)</td>
</tr>
<tr>
<td>[Zn(C₁₀H₁₆N₅PO₃)₂]²⁺</td>
<td>10.00 (9.91)</td>
<td>1:2</td>
<td>Zn(L₂)</td>
</tr>
</tbody>
</table>
A high yield of 88% of a yellow solid of GBM was obtained. It had a melting point range of 92 - 94 °C. The results from the elemental analysis were close to the expected values with % C, H, N calculated being 54.84, 5.17, and 39.90 respectively while % C, H, N of the product were 54.48, 5.15 and 39.50 respectively. In the UV-Visible spectrum of guanidinobenzimidazole, (Figure 19), the band observed at 229 nm has been attributed to the absorption arising from the π* ← π electronic transitions while the transition around 275 nm characterizes the π* ← n resulting from the lone pair of electrons (Khatiwora et al., 2012, Rao et al., 1964, Anderson et al., 2004). The band at 3255 cm⁻¹ in the IR spectrum of GBM (Figure 7) is assigned to the ν(N-H) stretching frequency vibration. The vibration stretching frequencies of aromatic ν(C-H) and ν(C=C) were observed at 3055 cm⁻¹ and about 1700 cm⁻¹ respectively in the IR spectrum of GBM. The peaks at 1558 cm⁻¹ and 1272 cm⁻¹ in the spectrum of guanidinobenzimidazole are ascribed to ν(C=N) imidazolic and ν(C-N) vibration frequencies, respectively (Strivastava and Sen, 2008).

In the ¹H-NMR spectra of the free guanidinobenzimidazole ligand (Figure 1), the chemical shift about 7.00 - 7.30 ppm resonance is assigned to the benzene aromatic ring protons in the ligand (Sonmez, 2001). The resonance due to the imidazolic and exocyclic NH proton was observed at 6.80 - 6.90 ppm while the terminal exocyclic C=NH protons were observed upfield around 6.15 - 6.40 ppm (Lopez et al., 1997; Sonmez, 2001). The resonance due to the NH₂ proton signal also appeared almost around the 6.15 - 6.40 ppm. From the ¹³C-NMR spectra, (Figure 3) recorded in DCOD shift the chemical shift at 185 ppm is assigned to the resonance due to terminal carbon at position 11 (Scheme 1) of the guanidinobenzimidazole ligand (Padmaja et al., 2011). The signal at 155 ppm indicates resonance peak for the imidazolic position C-2 while the signal chemical shift around 138 ppm is ascribed to the resonance due to carbons at positions C-8 and C-9 of the aromatic ring system. It has been stated in the literature that slight asymmetric
coupling pattern occurs in aromatic ring (Andrade et al., 1997). However, the presence of protons contributed to the high intensities observed for the chemical shift values ascribed to the resonances due to carbons at positions 5 and 6 at 120 ppm and carbons at positions 4 and 7 at 112 ppm (Andrade et al., 1997)

Figure 5: Structure of Guanidino benzimidazole (GBM)

Guanidinophosphonatebenzimidazole (GPBM)
The synthesis of GPBM gave a yellow solid with a yield of 89%. It had a melting point range of 139 – 141 °C. The obtained results from the % C, H, N elemental analysis, 46.08, 6.01, 22.30 respectively, were close to the calculated values, 46.10, 6.43 and 22.35.

In the UV visible spectrum of GPBM ligand, (Figure 20), the band at 260 nm has been attributed to the absorption arising from the π*→π electronic transitions while the transition around 281 nm characterizes the π*→n resulting from the lone pair of electrons (Khatiworat et al., 2012, Rao et al., 1964, Anderson et al., 2004). The very strong band at 3379 cm⁻¹ in the IR spectrum of GPBM (Figure 8) is assigned to the ν(N-H) stretching frequency vibration. The vibration stretching frequencies of aromatic ν(C-H) and ν(C=C) were observed at 3163 cm⁻¹ and about 1651 cm⁻¹ respectively in the spectrum of GPBM. The peaks at 1566 cm⁻¹ and 1110 cm⁻¹ in the spectrum of guanidinophosphonate benzimidazole are ascribed to ν(C=N) imidazolic and ν(C-N) vibration frequencies, respectively (Strivastava and Sen, 2008), while the ν(P=O) gave the band at 1265 cm⁻¹

For the ¹³C-NMR spectrum, GPBM shows a chemical shift at 172 ppm which is assigned to the resonance due to the carbon at position 11 (Table 5, Figure 4). This reflects the phosphorus coupling effect compared to the chemical shift at about 150 ppm assigned to the resonance due to the imidazolic carbon at position 2 of the GPBM ligand (Andrade et al., 1997, Reddy et al., 2007). The signal at 129 ppm is attributed to the resonance due to the equivalent carbons at positions 8 and 9 of the aromatic ring system (Andrade et al., 1997). The signals at 131 and 111 ppm are due to the resonance attributed to the equivalent C₆₋C₆ and C₆₋C₆, respectively (Padmaja et al., 2011). The chemical shift of the resonance due to the PO(OCH)₃ is observed around 60 ppm while the methyl carbon with doublet character due to the coupling effect of the phosphorus are observed at the chemical shift of 49 ppm (Reddy et al., 2007).
CHARACTERIZATION OF THE METAL COMPLEXES

In order to study the binding mode of the guanidinobenzimidazole, (GBM) and guanidinophosphonatebenzimidazole, (GPBM) with the metal ions, comparisons of the IR spectra of the free ligands (Figures 7 and 8) and those of their metal complexes, (Figures 9-13) were made. The major characteristic bands in the IR spectra of the ligands and the ten metal complexes are listed in Table 6.

Analyses and comparisons of the electronic spectral data of the ligands, GBM, GPBM and their metal complexes indicated the participation of the nitrogen atoms of the guanidino benzimidazole ligand in the coordination of the ligands to the metal ions.

The vibration stretching frequencies of aromatic ν(C-H) and ν(C=C) observed at 3055 cm⁻¹ and about 1700 cm⁻¹ respectively in the spectrum of GBM, remain almost constant in the spectra of the metal complexes. This suggests the non-involvement of the proton ν(C-H) and the ν(C=C) in the complex formation. This is not unexpected.

The shifts in the position of the ν(P=O) absorption band of the phosphonate moiety in the guanidinophosphonatebenzimidazole, (GPBM) ligand from 1265 cm⁻¹ in the free ligand to 1141 cm⁻¹ - 1200 cm⁻¹ in the metal complexes suggested the involvement of the P=O together with the nitrogen atoms in the coordination of the metal ions to the guanidinophosphonate benzimidazole, (GPBM) ligand. The lowest shift occurred for the cobalt complex, Co(II)-GPBM.

The broadness of the bands in the region 3600 - 3200 cm⁻¹ in the spectra of the metal complexes as compared to that of the ligand suggest the presence of coordinated water molecule(s), (Singh, et al, 2002).

Fe(II)-GBM and Fe(II)-GPBM

Both Fe(II)-GBM and Fe(II)-GPBM complexes are brownish in colour with melting points of 127-129 °C and 191-193 °C and % yield of 84 and 86% respectively. The % metal found and the values calculated respectively were 13.32 % and 13.75% for Fe(II)-GBM and 8.58 and 8.59% for Fe(II)-GPBM.

FTIR Spectra.

The shift from 3255 cm⁻¹ band to 3332 cm⁻¹ in Fe(II)-GBM, (Figure 9) indicated the involvement of the amine nitrogen in the coordination with the metal ion, (Bakir et al, 2013, Anitha et al, 2011, Andrade et al, 1997). The shifts of the 1558 cm⁻¹ and 1272 cm⁻¹ in the spectrum of guanidinobenzimidazole ascribed to ν(C=N) imidazolic and ν(C=N) vibration frequencies, respectively to 1481 cm⁻¹ and 1211 cm⁻¹ in Fe(II)-GBM further indicated the participation of the imidazolic nitrogen atom and one of the guanidine nitrogen in the coordination of GBM to the metal ion, (Strivastava and Sen, 2008).

The appearance of new weak band at 532 cm⁻¹ due to M-N bond is suggestive of the coordination of the metal ion to the GBM.

For, (Fe-GPBM), (Figure 14), the strong band at 3379 cm⁻¹ in the GPBM ligand due to the ν(N-H) stretching frequency vibration of the amine moiety (Reddy et al, 2007) shifted to 3186 cm⁻¹ in Fe(II)-GPBM.

The strong absorption band at 1566 cm⁻¹ characteristic of the ν(C=N) stretching vibration shifted to 1527 cm⁻¹ in Fe(II)-GPBM while the peak at 1110 cm⁻¹ in GPBM due to ν(C-N), shifted to 1041 cm⁻¹ in Fe(II)-GPBM. These further confirmed the involvement of the nitrogen atom in coordination of the metal ion to the ligand, (Yadav et al, 2011 and Bakir et al, 2013).

The new band at 532 cm⁻¹ in the spectrum of the metal complex is indicative of ν(M-N) vibration frequency, (Padmaja et al, 2011).

The shift in the position of the ν(P=O) absorption band from 1265 cm⁻¹ in the free ligand to 1188 cm⁻¹
in Fe(II)-GPBM suggests that the P=O is probably involved in the coordination of the metal ion to the GPBM ligand. This is supported by the appearance of M-O band at 650 cm\(^{-1}\), (Ferrero, 1971).

**UV-Visible and Magnetic susceptibility data**

The electronic spectrum of the Fe(II)-GBM complex gave absorption peak of high intensities at 287 nm (Figure 21). This is related to ligand metal charge transfer (Bakir et al, 2013). The absence of peak in the visible region indicated that there was probably no (d-d) transition. However, the magnetic moment value of 2.06 B.M for the Fe(II) complex falls within the range for distorted octahedral geometry (Padmaja et al, 2011).

The electronic spectrum of the Fe(II)-GPBM showed absorption band around 560 nm (Figure 26) which could be attributed to \(T_{2g} \rightarrow E_g\) presumably arising from the octahedral geometry orientation, (Konig, E, et al, 1985), in agreement with the magnetic moment of 2.02 B.M for this complex, (Anitha et al., 2011).

Co(II)-GBM and Co(II)-GPBM

Co(II)-GBM and Co(II)-GPBM complexes are brownish in colour with melting points of 190-192 °C and 196-198 °C and % yield of 76 and 78% respectively. The % metal found and the values calculated respectively were 14.40 % and 14.54% for Co(II)-GBM and 9.02 and 9.16 % for Co(II)-GPBM.

**FTIR Spectra.**

The shift from 3255 cm\(^{-1}\) band to very broad band from 3400-3209 cm\(^{-1}\) in Co(II)-GBM, (Figure 10) indicated the involvement of the amine nitrogen in the coordination with the metal ion, (Bakir et al, 2013, Anitha et al., 2011, Andrade et al.,1997) as well as the incorporation of water molecules in the coordination sphere, (Singh, et al, 2002).The shifts of the 1558 cm\(^{-1}\) and 1272 cm\(^{-1}\) in the spectrum of guanidinobenzimidazole ascribed to \(\nu(C=N)\) imidazolic and \(\nu(C-N)\) vibration frequencies, respectively to 1481 cm\(^{-1}\) and 1211cm\(^{-1}\) in Co(II)-GBM further indicated the participation of the nitrogen atoms in the coordination of GBM to the metal ion, (Strivastava and Šen, 2008).

The position of the \(\nu(P=O)\) absorption band shifted from 1265 cm\(^{-1}\) in the free ligand to 1141 cm\(^{-1}\) in Co(II)-GPBM. This also suggests the involvement of P=O in the coordination of the metal ion to the GPBM ligand. This is supported by the appearance of M-O band at 624 cm\(^{-1}\).

UV-Visible and Magnetic susceptibility data

The electronic spectrum of the Co(II)-GBM complex, (Figure 22) gave an absorption peak at 530 nm. This must have resulted from the d-d transition of the type \(^{4}T_{2g}(F) \rightarrow ^{4}T_{2g}(F)\). The Co(II)-GBM also has magnetic susceptibility value of 1.78 B.M which lies within the range expected for octahedral geometry (Anderson et al., 2004).

The strong absorption band at 1566 cm\(^{-1}\) due to \(\nu(C=N)\) stretching vibration shifted to 1527 cm\(^{-1}\) while the peak at 1110 cm\(^{-1}\) in GPBM due to \(\nu(C-N)\), shifted to 1072 cm\(^{-1}\). The new band at 555 cm\(^{-1}\) in the spectrum of the metal complex is indicative of \(\nu(M-N)\) vibration frequency, (Padmaj et al, 2011).

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The strong absorption band at 578 cm\(^{-1}\) suggests the presence of an M-N bond. For, (Co-GPBM), (Figure 15), the strong band at 3379 cm\(^{-1}\) in the GPBM ligand due to the \(\nu(N-H)\) stretching frequency vibration of the amine moiety (Reddy et al, 2007) shifted into a very broad in the region 3500-3300 cm\(^{-1}\) in Co(II)-GPBM.

The lowering of the vibration frequencies also suggests complexation of the guanidinophosphonatebenzimidazole to the metal ion through the nitrogen atom, (Yadav et al., 2011 and Bakir et al, 2013).

The position of the \(\nu(P=O)\) absorption band shifted from 1265 cm\(^{-1}\) in the free ligand to 1141 cm\(^{-1}\) in Co(II)-GPBM. This also suggests the involvement of P=O in the coordination of the metal ion to the GPBM ligand. This is supported by the appearance of M-O band at 624 cm\(^{-1}\).

UV-Visible and Magnetic susceptibility data

The electronic spectrum of the Co(II)-GBM complex, (Figure 22) gave an absorption peak at 530 nm. This must have resulted from the d-d transition of the type \(^{4}T_{2g}(F) \rightarrow ^{4}T_{2g}(F)\). The Co(II)-GBM also has magnetic susceptibility value of 1.78 B.M which lies within the range expected for octahedral geometry (Anderson et al., 2004).

The electronic absorption spectrum of the Co(II)-guanidinophosphonatebenzimidazole complex shows a 560 nm signal (Figure 27). This also corresponds to \(^{4}T_{2g}(F) \rightarrow ^{2}T_{2g}(F)\) transition.

Ni(II)-GBM and Ni(II)-GPBM

Both Ni(II)-GBM and Ni(II)-GPBM complexes are brownish in colour with melting points of 147-148 °C and 194-196 °C and % yield of 78 and 68% respectively. The % metal found and the values calculated respectively were 14.35 % and
14.48% for Ni(II)-GBM and 8.98 and 8.99% for Ni(II)-GPBM.

**FTIR Spectra.**
The shift from 3255 cm\(^{-1}\) band to a broad from 3200 to 3340 cm\(^{-1}\) in Ni(II)-GBM, (Figure 11) indicated the involvement of the amine nitrogen and water molecules in the coordination with the metal ion, (Bakir et al., 2013, Anitha et al., 2011, Andrade et al., 1997). The shifts of the 1558 cm\(^{-1}\) and 1272 cm\(^{-1}\) in the spectrum of guanidinobenzimidazole ascribed to \(\nu(C=\text{N})\) imidazolic and \(\nu(C-\text{N})\) vibration frequencies, respectively to 1481 cm\(^{-1}\) and 1211cm\(^{-1}\) in Ni(II)-GBM further indicated the participation of these nitrogen atoms in the coordination of GBM to the metal ion, (Strivastava and Sen, 2008).

The appearance of new weak band at 540 cm\(^{-1}\) \(\nu(M-N)\) for confirms the coordination of the metal ion to the nitrogen atom.

For, (Ni-GPBM), (Figure16 ) , the strong band at 3379 cm\(^{-1}\) in the GPBM ligand due to the \(\nu(N-H)\) stretching frequency vibration of the amine moiety (Reddy et al., 2007) has been replaced by a very broad band 3000-3400cm\(^{-1}\).

The strong absorption band at 1566 cm\(^{-1}\) in the ligand has shifted to 1519 cm\(^{-1}\). While the peak at 1110 cm\(^{-1}\) in GPBM due to \(\nu(C-\text{N})\), shifted to 1056cm\(^{-1}\) in Ni(II)-GPBM. These further confirmed the involvement of the nitrogen atom in the coordination, (Osowole, 2012).

The new band at 547 cm\(^{-1}\) in Ni(II)-GPBM spectrum can be attributed to the \(\nu(M-N)\) vibration frequency, (Padmaja et al., 2011).

The shift in the position of the \(\nu(P=\text{O})\) absorption band from 1265 cm\(^{-1}\) in the free ligand to 1164 cm\(^{-1}\) in Ni(II)-GPBM suggests the coordination of the P=O to the metal ion. This is supported by the appearance of M-O band at 600 cm\(^{-1}\).

**UV-Visible and Magnetic susceptibility data**
The electronic spectral band of Ni(II)-GBM complex (Figure 23) gave a band with the peak at 650 nm and it is attributable to the electronic transition to \(3\text{A}_2(F) \rightarrow 3\text{T}_1(F)\). The magnetic moment was found to be 3.10 B.M, a value within the range of 2.9-3.3 B.M for octahedral complexes of Ni(II), thus suggesting octahedral geometry (Bakir et al., 2013).

The Ni(II)-GPBM complex exhibits a spectral band at 321nm which may likely be due to ligand metal charge transfer. The value of magnetic moment for Ni(II)-GPBM is 3.02 B.M which is within the predictable range for an octahedral geometry (Khatiwora et al., 2012).

**Cu(II)-GBM and Cu(II)-GPBM**
Cu(II)-GBM is greenish while Co(II)-GPBM is brownish in colour. Melting points are 140-142 °C and 192-194 °C respectively. The % yields are 89 and 75% respectively. The % metal found and the values calculated respectively were 15.35 % and 15.41% for Cu(II)-GBM and 9.65 and 8.66% for Cu(II)-GPBM.

**FTIR Spectra.** The shift from 3255 cm-1 band to a broad band from 3200 to 3340 cm-1 in Ni(II)-GBM, (Figure 12). This also suggests the involvement of the amine nitrogen and water molecules in the coordination with the metal ion, (Bakir et al., 2013, Anitha et al., 2011, Andrade et al., 1997). The shifts of the 1558 cm\(^{-1}\) and 1272 cm\(^{-1}\) bands in the spectrum of guanidinobenzimidazole ascribed to \(\nu(C=\text{N})\) imidazolic and \(\nu(C-\text{N})\) vibration frequencies, respectively to 1481 cm\(^{-1}\) and 1211cm\(^{-1}\) in Cu(II)-GBM further indicated the participation of the nitrogen atoms in the coordination of GBM to the metal ion, (Strivastava and Sen, 2008).

The appearance of new weak band at 524 cm\(^{-1}\) is indicative of (M-N) bond and confirms the coordination of the metal ion to through the nitrogen atom in the GBM.

For, (Cu(II)-GPBM), (Figure 17 ) , the strong band at 3379 cm\(^{-1}\) in the GPBM ligand due to the \(\nu(N-H)\) stretching frequency vibration of the amine moiety (Reddy et al., 2007) gave a very broad band 3000-3500cm\(^{-1}\) in Cu(II)-GPBM. This suggests complexation of the guanidinophosphonatebenzimidazole to the metal ion through the nitrogen atom, (Yadav et al.,...
The strong absorption band at 1566 cm\(^{-1}\) characteristic of the ν(C=N) stretching vibration is also shifted to 1527 cm\(^{-1}\) in Cu(II)-GPBM while the peak at 1110 cm\(^{-1}\) in GPBM due to ν(C-N), shifted to 1056 cm\(^{-1}\). These further confirmed the involvement of the nitrogen atom in coordination of the metal ion to the ligand, (Osowole, 2012).

The new band at 501 cm\(^{-1}\) in the spectrum of the metal complex is indicative of ν(M-N) vibration frequency, (Padmaja et al, 2011).

The shift in the position of the ν(P=O) absorption band from 1265 cm\(^{-1}\) in the free ligand to 1200 cm\(^{-1}\) in Cu(II)-GPBM suggests that the P=O is also involved in the coordination to the metal ion. The appearance of a band at about 620 cm\(^{-1}\) is likely due to an M-O band.

**FTIR Spectra.**

There was a shift from the slightly broad band at about 3200-3400 cm\(^{-1}\) in the GBM ligand to a broad band in the region 3200-3332 cm\(^{-1}\) in Zn(II)-GBM, (Figure 13). This as explained for the other complexes are due to the involvement of the amine nitrogen and water molecules from the solvent coordinating to the metal ion, (Bakir et al., 2013, Anitha et al., 2011, Andrade et al., 1997). The 1558 cm\(^{-1}\) and 1272 cm\(^{-1}\) bands in the spectrum of guanidinobenzimidazole ligand also shifted to 1448 cm\(^{-1}\) and 1118 cm\(^{-1}\). These further indicated the participation of the nitrogen atoms in the coordination, (Strivastava and Sen, 2008).

The appearance of new band at 532 cm\(^{-1}\) is suggestive of an ν(M-N) bond. For, (Zn-GPBM), (Figure 18), the strong band at 3379 cm\(^{-1}\) in the GPBM ligand due to the ν(N-H) stretching frequency vibration of the amine moiety (Reddy et al., 2007) shifted to a very broad band, 3000-3200 cm\(^{-1}\) in Zn(II)-GPBM.

The change in the stretching frequencies suggests complexation of the guanidinophosphonate benzimidazole to the metal ion through the nitrogen atom, (Yadav et al., 2011 and Bakir et al. 2013) and involvement of the water molecules.

Absorption band at 1566 cm\(^{-1}\) characteristic of the ν(C=N) stretching vibration shifted to 1519 cm\(^{-1}\) while the peak at 1110 cm\(^{-1}\) in GPBM due to ν(C-N), shifted to 1056 cm\(^{-1}\). These further confirmed the involvement of the nitrogen atom, (Osowole, 2012).

The new band at 447 cm\(^{-1}\) in the spectrum of the metal complex is indicative of ν(M-N) vibration frequency, (Padmaja et al, 2011).

The shift in the position of the ν(P=O) absorption band from 1265 cm\(^{-1}\) in the free ligand to 1200 cm\(^{-1}\) suggests that the P=O is most likely to be involved in the coordination of the metal ion to the GPBM ligand. This is supported by the appearance of M-O band at about 650 cm\(^{-1}\).
UV-Visible and Magnetic susceptibility data
The electronic absorption spectrum for the Zn(II)-GBM complex (Figure 25) presented a diamagnetic behaviour as a consequence of its $d^{10}$ electronic configuration. This is supported by the zero value for the magnetic moment. This is not unexpected.

For the Zn(II)-GPBM complex, the transition at 330nm in the electronic absorption spectrum (Figure 30) is most likely due to ligand metal charge transfer.

Table 6: Selected IR bands (cm$^{-1}$) of GBM, GPBM and their metal complexes

<table>
<thead>
<tr>
<th>S/N</th>
<th>L/M-L</th>
<th>ν(C-H)</th>
<th>ν(C=C)</th>
<th>ν(C=N)</th>
<th>ν(C=N)</th>
<th>ν(P=O)</th>
<th>ν(M-N)</th>
<th>ν(M=0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GBM</td>
<td>3255</td>
<td>3055</td>
<td>1700</td>
<td>1558</td>
<td>1272</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>Fe–GBM</td>
<td>3500-3332 br</td>
<td>3054</td>
<td>1697</td>
<td>1481</td>
<td>1211</td>
<td>--</td>
<td>532</td>
</tr>
<tr>
<td>3</td>
<td>Co–GBM</td>
<td>3400-3209</td>
<td>3065</td>
<td>1697</td>
<td>1481</td>
<td>1211</td>
<td>--</td>
<td>578</td>
</tr>
<tr>
<td>4</td>
<td>Ni–GBM</td>
<td>3400-3340</td>
<td>3055</td>
<td>1697</td>
<td>1481</td>
<td>1211</td>
<td>--</td>
<td>540</td>
</tr>
<tr>
<td>5</td>
<td>Cu–GBM</td>
<td>3500-3379</td>
<td>3200</td>
<td>1689</td>
<td>1490</td>
<td>1211</td>
<td>--</td>
<td>524</td>
</tr>
<tr>
<td>6</td>
<td>Zn–GBM</td>
<td>3400-3332 br</td>
<td>3209</td>
<td>1681</td>
<td>1448</td>
<td>1118</td>
<td>--</td>
<td>532</td>
</tr>
<tr>
<td>7</td>
<td>GPBM</td>
<td>3379 v.s</td>
<td>3163</td>
<td>1651</td>
<td>1566</td>
<td>1110</td>
<td>1265</td>
<td>--</td>
</tr>
<tr>
<td>8</td>
<td>Fe–GPBM</td>
<td>3400-3186 br</td>
<td>3093</td>
<td>1658</td>
<td>1527</td>
<td>1041</td>
<td>1188</td>
<td>532</td>
</tr>
<tr>
<td>9</td>
<td>Co–GPBM</td>
<td>3500-3000 br</td>
<td>3093</td>
<td>1658</td>
<td>1527</td>
<td>1072</td>
<td>1141</td>
<td>555</td>
</tr>
<tr>
<td>10</td>
<td>Ni–GPBM</td>
<td>3400-3000 br</td>
<td>3039</td>
<td>1658</td>
<td>1519</td>
<td>1056</td>
<td>1164</td>
<td>547</td>
</tr>
<tr>
<td>11</td>
<td>Cu–GPBM</td>
<td>3500-3000 br</td>
<td>2939</td>
<td>1658</td>
<td>1527</td>
<td>1050</td>
<td>1200</td>
<td>501</td>
</tr>
<tr>
<td>12</td>
<td>Zn–GPBM</td>
<td>3260-3000 br</td>
<td>2962</td>
<td>1705</td>
<td>1519</td>
<td>1056</td>
<td>1200</td>
<td>447</td>
</tr>
</tbody>
</table>
PROPOSED STRUCTURES FOR THE METAL –GBM AND THE METAL-GPBM COMPLEXES

Analyses and comparisons of the electronic spectral data of the ligands, GBM, GPBM, and their metal complexes indicated the participation of the nitrogen atoms of the guanidinobenzimidazole ligand in the coordination of the ligand to the metal ions.

The shifts in the position of the \( \nu(P=O) \) absorption band of the phosphonate moiety in the guanidinophosphonatebenzimidazole, (GPBM) ligand from 1265 cm\(^{-1}\) in the free ligand to 1141 cm\(^{-1}\) - 1200 cm\(^{-1}\) in the metal complexes suggested the involvement of the P=O in the coordination of the metal ions to the guanidinophosphonatebenzimidazole, (GPBM) ligand.

Thus, the following structures, Figures 31 and 32 can be proposed for the metal(II) complexes of guanidinobenzimidazole, (GBM) and guanidinophosphonatebenzimidazole, (GPBM), respectively from the Infra-red, UV-Visible spectroscopic data, and magnetic susceptibility measurements.

![Figure 31: Proposed Structure for Metal(II) - guanidinobenzimidazole complex. (Where M = Fe, Co, Ni, Cu and Zn)](image-url)
CONCLUSION

Guanidination of benzimidazole and phosphorylation of guanidinobenzimidazole were successfully carried out and the chelating properties investigated. The ligands and the metal complexes were characterized by elemental analysis, Infra-red, UV-Visible spectroscopic data, and magnetic susceptibility measurements.

The two ligands are bonded to the metal ions in different chelating modes. The metal ions coordinate to the guanidinobenzimidazole, (GBM) ligand through the imidazolic nitrogen and one of the guanidine nitrogen in position 12 to form six-membered rings.

The shifts in the position of the $\nu$(P=O) absorption band of the phosphonate moiety in the guanidinophosphonatebenzimidazole, (GPBM) ligand in the free ligand suggests the involvement of the P=O bond in the coordination to the metal ions by the guanidinophosphonatebenzimidazole, (GPBM) ligand leading to the formation of five membered rings.

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Figure 1: $^1$H-NMR Spectrum of Guanidinobenzimidazole

Figure 2: $^1$H-NMR Spectrum of guanidinophosphonatebenzimidazole
Figure 3: $^{13}$C-NMR Spectrum of Guanidinobenzimidazole

Figure 4: $^{13}$C-NMR Spectrum of Guanidinophosphonatebenzimidazole
Figure 7: FT IR spectrum of guanidinobenzimidazole

Figure 8: FT IR spectrum of guanidinophosphonatebenzimidazole
Figure 9: FT IR spectrum of Fe - guanidinobenzimidazole complex

Figure 10 FT IR spectrum of Co - guanidinobenzimidazole complex
Figure 11: FT IR Spectrum of Ni - guanidinobenzimidazole complex

Figure 12: FT IR spectrum of Cu - guanidinobenzimidazole complex
Figure 13: FT IR spectrum of Zn - guanidinobenzimidazole complex

Figure 14: FT IR spectrum of Fe - guanidinophosphonatebenzimidazole complex
Figure 15: FT IR spectrum of Co - guanidinophosphonatebenzimidazole complex

Figure 16: FT IR spectrum of Ni - guanidinophosphonatebenzimidazole complex
Figure 17: FT IR spectrum of Cu - guanidinophosphonatebenzimidazole complex

Figure 18: FT IR spectrum of Zn - guanidinophosphonatebenzimidazole complex
Figure 19: UV-Visible spectrum of guanidinobenzimidazole

Figure 20: UV-Visible spectrum of guanidinophosphonatebenzimidazole

Figure 21: UV-Visible spectrum of Fe - guanidinobenzimidazole complex
Figure 22: UV-Visible spectrum of Co - guanidinobenzimidazole complex

Figure 23: UV-Visible spectrum of Ni - guanidinobenzimidazole complex

Figure 24: UV-Visible spectrum of Cu - guanidinobenzimidazole complex
Figure 25: UV-Visible spectrum of Zn - guanidinobenzimidazole complex

Figure 26: UV-Visible spectrum of Fe - guanidinophosphonatebenzimidazole complex

Figure 27: UV-Visible spectrum of Co - guanidinophosphonatebenzimidazole complex
Figure 28: UV-Visible spectrum of Ni - guanidinophosphonatebenzimidazole complex

Figure 29: UV-Visible spectrum of Cu - guanidinophosphonatebenzimidazole complex

Figure 30: UV-Visible spectrum of Zn - guanidinophosphonatebenzimidazole complex