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SYNTHESES, CHARACTERIZATION AND CHELATING PROPERTIES OF GUANIDOBENZIMIDAZOLE AND GUANIDOPHOSPHONATEBENZIMIDAZOLE

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ABSTRACT

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_2]. 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 theν(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

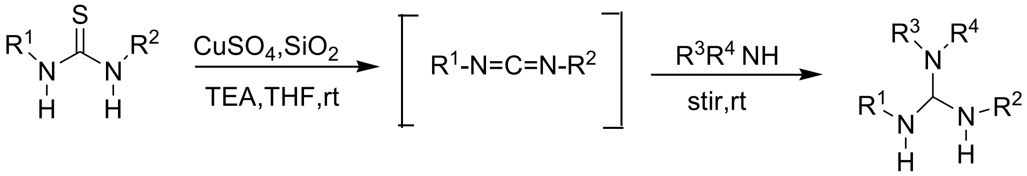
The NMR spectra were recorded on Agilent-NMR-400 MHz Spectrometer; TMS was used as the internal standard. IR spectra (4000–400 cm^{-1}) were recorded on Shimadzu FTIR- 8700 Spectrophotometer. The C.H.N elemental analyses were carried out on Perkin Elmer 240 C elemental analyzer and the electronic transitions using the T92-UVWin 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 guanidinesin a suitable solvent such as tetrahydrofuran and chloroform containing copper sulphate – silica gel in presence of tertiary amines, (Alan and Boris, 2005).

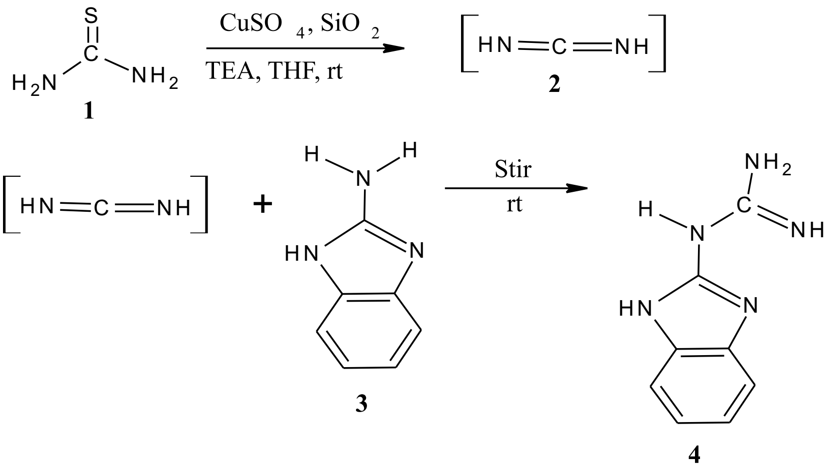


R^1, R^2, R^3, R^4 =H.

The synthesis of guanidinobenzimidazole and guanidinophosphonatebenzimidazole were carried out according to the methods of Alan, 2005 and Krishnamurthy, 1995.

Synthesis of Guanidinobenzimidazole, (GBM).

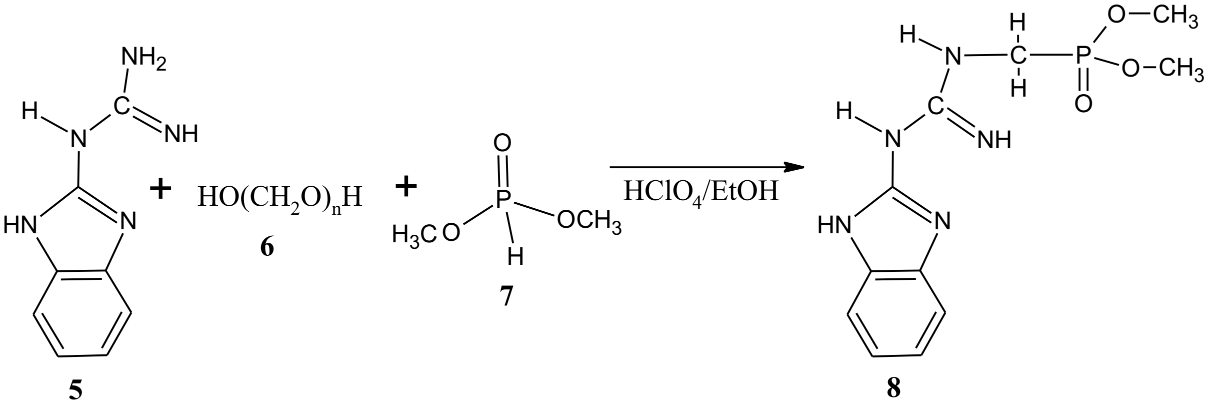
Copper(II) sulphate and silica gel (1 g each) were added to 25 ml of tetrahydrofuran in a 250 ml round bottomed flask in the presence of 2 ml triethylamine in a 250 ml round bottom flask. Thiourea (**1**), 3.81 g (50 mM) was added and the solution was stirred at room temperature for 6 hr. to produce 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 Guanidinophosponate 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 **y**ield**,** melting point and other analytical dataare presented in Table 1.



Synthesis of Metal Complexes of Guanidinobenzimidazole and Guanidinophosponatebenzimidazole.

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 metalsalt, ($Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $FeCl_2$) 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 ^{1}H-NMR and ^{13}C-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).

Table 1: Analytical data of the ligands and the Complexes

Compounds	Empirical formula	Molecular weight	Yield (%)	Melting point (°C)	Colour
GBM	$C_8H_9N_5$	175.19	88	92-94	Yellow
Fe- GBM	$[Fe(C_8H_9N_5)_2]$	406.225	84	127-129	Brown
Co- GBM	$[Co(C_8H_9N_5)_2]$	409.31	76	190-192	Brown
Ni- GBM	$[Ni(C_8H_9N_5)_2]$	409.07	78	147 – 149	Brown
Cu- GBM	$[Cu(C_8H_9N_5)_2]$	413.93	89	140 – 142	Green
Zn- GBM	$[Cu(C_8H_9N_5)_2]$	415.79	84	144 –146	Orange
GPBM	$C_{11}H_{16}N_5PO_3$	297.25	89	139 – 141	Yellow
Fe- GPBM	$[Fe(C_{11}H_{16}N_5PO_3)_2]$	650.35	86	191 –193	Brown
Co- GPBM	$[Co(C_{11}H_{16}N_5PO_3)_2]$	653.43	78	196 –198	Brown
Ni- GPBM	$[Ni(C_{11}H_{16}N_5PO_3)_2]$	653.19	68	194 – 196	Brown
Cu- GPBM	$[Cu(C_{11}H_{16}N_5PO_3)_2]$	658.05	75	192 – 194	Brown
Zn- GPBM	$[Zn(C_{11}H_{16}N_5PO_3)_2]$	659.91	82	194 -196	Pink

C,H, N Analysis

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

Table 2: C, H, N elemental Analysis of GBM and GPBM

LIGANDS	Analysis Calculated (Found)		
	% C	% H	% N
GBM ($C_8H_9N_5$)	54.84 (54.48)	5.17 (5.15)	39.90 (39.50)
GBPM ($C_{11}H_{16}N_5PO_3$)	46.10 (46.08)	6.43 (6.01)	22.35 (22.30)

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 $[ML_2]$.

Table 3: Percentage compositionof metals in the complexes, the stoichiometry and the Probable Formulae.

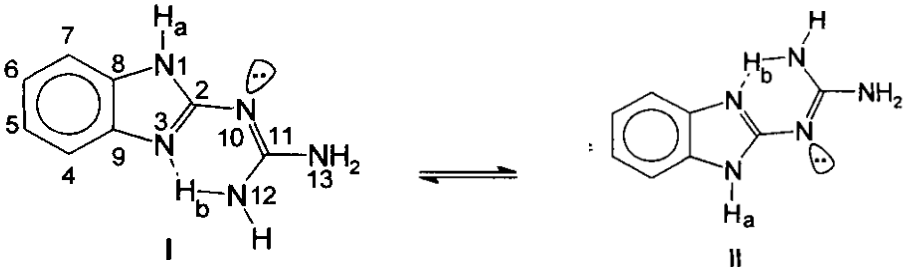
Compounds	% Metal Found (Calculated)	Stoichiometry	Probable Formula
M- GBM			
$[Fe(C_8H_9N_5)_2]^{2+}$	13.32 (13.74)	1:2	$Fe(L)_2$
$[Co(C_8H_9N_5)_2]^{2+}$	14.54 (14.40)	1:2	$Co(L)_2$
$[Ni(C_8H_9N_5)_2]^{2+}$	14.48 (14.35)	1:2	$Ni(L)_2$
$[Cu(C_8H_9N_5)_2]^{2+}$	15.41 (15.35)	1:2	$Cu(L)_2$
$[Zn(C_8H_9N_5)_2]^{2+}$	15.91 (15.72)	1:2	$Zn(L)_2$
M-GPBM			
$[Fe(C_{11}H_{16}N_5PO_3)_2]^{2+}$	8.58 (8.59)	1:2	$Fe(L)_2$
$[Co(C_{11}H_{16}N_5PO_3)_2]^{2+}$	9.16 (9.02)	1:2	$Co(L)_2$
$[Ni(C_{11}H_{16}N_5PO_3)_2]^{2+}$	8.98 (8.99)	1:2	$Ni(L)_2$
$[Cu(C_{11}H_{16}N_5PO_3)_2]^{2+}$	9.65 (9.66)	1:2	$Cu(L)_2$
$[Zn(C_{11}H_{16}N_5PO_3)_2]^{2+}$	10.00 (9.91)	1:2	$Zn(L)_2$

Table 4: ^{1}H-NMR chemical shift (δ) of GBM and GPBM.

S/N	Ligands	CH aromatic protons (ppm)	NH protons imidazol (ppm)	N-H protons Exo (ppm)	NH_2, C=NH protons Exo (ppm)	NH, C=NH protons Exo (ppm)	P-C-H proton (ppm)	$PO(OCH_3)_2$ (ppm)
1.	GBM	7.00-7.30	6.80-6.90	6.80-6.90	6.15-6.40		---	---
2.	GPBM	7.00-7.90	6.00-6.30	4.20-5.40	--	1.1-1.3	2.50-2.80	3.20-4.20

Table 5: ^{13}C-NMR chemical shift (δ) of GBM, GPBM

Compounds	C_2 (ppm)	C_4-C_7 (ppm)	C_5-C_6 (ppm)	C_8-C_9 (ppm)	C_{11} (ppm)	C_{14}	C_{16}-C_{17}
GBM($C_8H_9N_5$)	155.35	112.00	119.62	138.22	185.28		
GPBM ($C_{11}H_{16}N_5PO_3$)	150.83	111.75	131.61,	129.42	172.63	49.03	60.95



Scheme 1: The guanidine- benzimidazole structure.

Guanidinobenzimidazole (GBM)

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 $\pi^{*}\leftarrow\pi$electronic transitions while the transition around 275 nm characterizes the $\pi^{*}\leftarrow n$ resulting from the lone pair of electrons (Khatiwora*et al.*, 2012, Raoet *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 ^{1}H-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 NH_2 proton signal also appeared almost around the 6.15 - 6.40 ppm. From the ^{13}C-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)

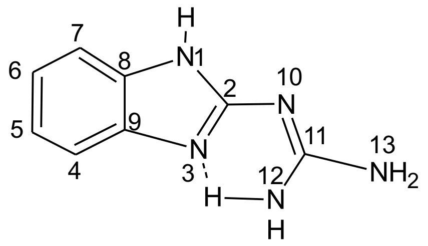


Figure 5: Structure of Guanidino benzimidazole (GBM)

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.

^{1}H-NMR spectra of guanidinophosphonatebenzimidazole ligand (Figure 2), the aromatic protons of the benzene ring of the guanidinophosphonatebenzimidazole (Figure 6) showed a multiplet at chemical shift of 7.00-7.90 ppm (Reddy *et al.*, 2007). The imidazolic N-H proton resonated at a chemical shift of 6.00-6.30 ppm. The N-H next to the imidazolic ring of the guanidinophosphonatebenzimidazole ligand resonated at 4.20-5.40 ppm. Both the C=NH and the methylene N-H amine moiety of GPBM gave a signal around 1.1-1.3 ppm as multiplet due to electron delocalization and coupling effect with the methoxyl groups. The resonance due to the P-C-H proton appeared as doublet at 2.50-2.80 ppm while the chemical shift around 3.20-4.20 ppm is assigned to the resonance due to the two methoxyl groups of the GPBM ligand. The high intensities result from their positions in the same chemical environment (Reddy *et al.*, 2007).

For the ^{13}C-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 111ppm are due to the resonance attributed to the equivalent C_5-C_6 and C_4-C_7 respectively (Padmaja *et al.,* 2011). The chemical shift of the resonance due to the $PO(OCH_3)_2$ 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).

In the UV visible spectrum of GPBM ligand, (Figure 20), the band at 260 nm has been attributed to the absorption arising from the $\pi^*\leftarrow\pi$electronic transitions while the transition around 281 nm characterizes the $\pi^*\leftarrow n$ resulting from the lone pair of electrons (Khatiwora*et al.*, 2012, Raoet *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}

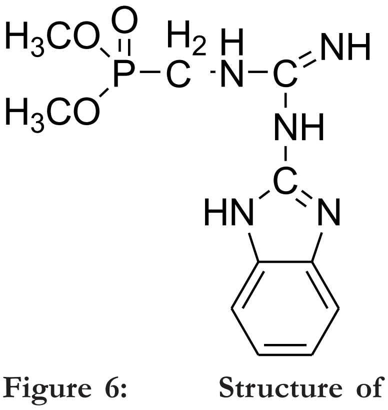


Figure 6: Structure of Guanidinophos phonatebenzimidazole (GPBM)

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 about1700 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 1211cm^{-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 lowering of the vibration frequenciessuggests complexation of the guanidinophos phonatebenzimidazole to the metal ion through the nitrogen atom, (Yadav *et al.*, 2011and Bakir *et al,* 2013).

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 1041cm^{-1} in Fe(II)-GPBM. These further confirmed the involvement of the nitrogenatom in coordination of the metal ion to the ligand, (Osowole, 2012).

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 theν(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^3T_2g → Eg 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 ν(C=N) imidazolic and ν(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 Sen, 2008). The appearance of new weak 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 ν(N-H) stretching frequency vibration of the amine moiety (Reddy *et al.*, 2007**)** shifted into a very broad in the region 3500-3300cm^{-1} in Co(II)-GPBM.

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

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

The position of theν(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 peakat 530 nm. This must have resulted from the d-d transition of the type $^{4T1g}(F) \rightarrow {}^4T_{2g}(F)$. 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 $^4T_1g(F) \rightarrow {}^4T_{2g}(F)$ 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 ν(C=N) imidazolic and ν(C-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} ν(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 ν(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 ν(C-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 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 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 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$. 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 ν(C=N) imidazolic and ν(C-N) vibration frequencies, respectively to 1490 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 ν(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. Thissuggests complexation of the guanidinophosphonatebenzimidazole to the metal ion through the nitrogen atom, (Yadav *et al.*, 2011and Bakir *et al,* 2013) and involvement of the water molecules.

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 1050cm^{-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 501cm^{-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 theν(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.

UV-Visible and Magnetic susceptibility data

The guanidinobenzimidazole-Cu(II)-GBM complex has a peak at 350 nm (Figure24 **.).** This is likely due to ligand metal charge transfer. However the observed magnetic susceptibility of 2.08 B.M (Table 7) is within the range expected for distorted octahedral geometry (Padmaja *et al.*, 2011).

The electronic absorption spectral band at 680nm for the Cu(II)-GPBM complex (Figure 29) is assigned to ^{2}Eg - ^{2}T$_{2}$g transition. The transition is in agreement with the magnetic susceptibility result of 2.01B.M suggesting distorted octahedral geometry for the Cu(II)-GPBM complex.

The electronic absorption spectral band at 680nm for the Cu(II)-GPBM complex (Figure 29**)** is assigned to ^{2}Eg $\rightarrow$ ^{2}T$_{2}$g transition. The transition is in agreement with the magnetic susceptibility result of 2.01B.M suggesting distorted octahedral geometry for the Cu(II)-GPBM complex.

Zn(II)-GBM and Zn(II)-GBM

Zn(II)-GBM is orange in colour while Zn(II)-GPBM complex is pink. The melting points are 144-146 °C and 194-196 °C and % yields were 84 and 82% respectively. The % metal found and the values calculated respectively were 15.91 % and 15.72% for Zn(II)-GBM and 10.00 % and 9.91% for Zn(II)-GPBM.

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 1118cm^{-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), (Figure18 **)** , 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 frequenciessuggests complexation of the guanidinophosphonate benzimidazole to the metal ion through the nitrogen atom, (Yadav *et al.*, 2011and 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 1056cm$^{-1.}$ These further confirmed the involvement of the nitrogenatom, (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 theν(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

S/N	L/M-L	ν(NH)	ν(C-H)	ν(C=C)	ν(C=N)	ν (C-N)	ν(P=O)	ν(M-N)	ν(M-0)
1	GBM	3255	3055	1700	1558	1272	---	----	----
2	Fe–GBM	3500-3332 br	3054	1697	1481	1211	---	532	-----
3	Co–GBM	3400-3209	3065	1697	1481	1211	----	578	-----
4	Ni–GBM	3400-3340	3055	1697	1481	1211	---	540	-----
5	Cu-GBM	3500-3379	3200	1689	1490	1211	---	524	------
6	Zn–GBM	3400-3332 br	3209	1681	1448	1118	----	532	------
7	GPBM	3379 v.s	3163	1651	1566	1110	1265	-----	------
8	Fe-GPBM	3400-3186 br	3093	1658	1527	1041	1188	532	650
9	Co–GPBM	3500-3000 br	3093	1658	1527	1072	1141	555	624
10	Ni–GPBM	3400-3000 br	3039	1658	1519	1056	1164	547	600
11	Cu-GPBM	3500-3000 br	2939	1658	1527	1050	1200	501	620
12	Zn–GPBM	3260-3000 br.	2962	1705	1519	1056	1200	447	650

Table 7: UV-Visible electronic spectra data and magnetic susceptibility values of GBM, GPBM and their metal complexes.

Compounds	UV-Visible Spectra		Magnetic Moment μeff(B.M)	Proposed geometry
	Absorption (nm)	Transition		
$C_8H_9N_5$	229, 275	π → π*, n → π*	-	
$[Fe(C_8H_9N_5)_2]$	287	LMCT	2.06	Octahedral
$[Co(C_8H_9N_5)_2]$	530	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	1.78	Octahedral/ distorted Octahedral
$[Ni(C_8H_9N_5)_2]$	650	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	3.10	Octahedral/ distorted Octahedral
$[Cu(C_8H_9N_5)_2]$	350	LM CT	2.08	Distorted Octahedral
$[Zn(C_8H_9N_5)_2]$	274	LMCT	0	Octahedral/ distorted Octahedral
$C_{11}H_{16}N_5PO_3$	260, 281	π → π*, n → π*	-	
$[Fe(C_{11}H_{16}N_5PO_3)_2]$	560	$^3T_2g \rightarrow Eg$	2.02	Octahedral/distorted Octahedral
$[Co(C_{11}H_{16}N_5PO_3)_2]$	560	$^4T_1g(F) \rightarrow {}^4T_2g(F)$,	1.79	Octahedral/ distorted Octahedral
$[Ni(C_{11}H_{16}N_5PO_3)_2]$	321	LM CT	3.02	Octahedral/ distorted Octahedral
$[Cu(C_{11}H_{16}N_5PO_3)_2]$	680	$^2Eg \rightarrow {}^2T_2g$	2.01	Distorted Octahedral
$[Zn(C_{11}H_{16}N_5PO_3)_2]$	330	LMCT	0	Octahedral/ distorted Octahedral

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 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 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.

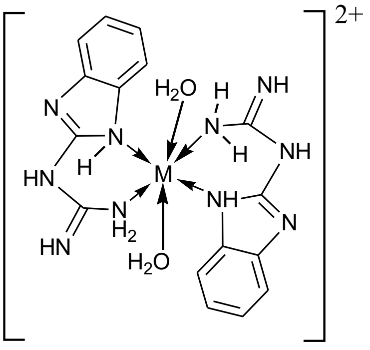


Figure 31: Proposed Structure for Metal(II) - guanidinobenzimidazole complex. (Where M = Fe, Co, Ni, Cu and Zn)

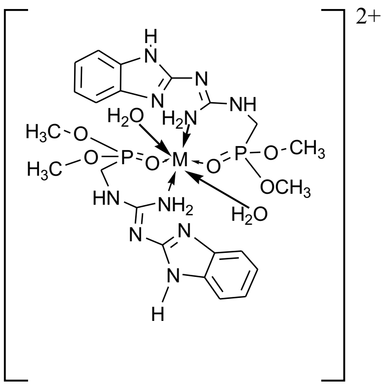


Figure 32: Proposed Structure for Metal(II)-guanidinophosphonatebenzimidazole Where M = Fe, Co, Ni, Cu and Zn

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 ν(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.

REFERENCES

Anderson, R. J., Bendell, D. J., and Groundwater, P. W. (2004).Ultraviolet-visible (UV-Vis) Spectroscopy. In: Organic Spectroscopic Analysis; Royal Society of Chemistry, Vol 22, pp 7– 23

Andrade, N Ariza-Castolo, A. and Contreas, R;(1997); Versatile Behaviour of Guanidinobenzimidazole Nitrogen atoms toward protonation, Coordination and Methylation; *Heteroatom Chemistry*, 8, pp.397-410.

Anitha, C., Sumathi, 1. S., Tharmaraj, 1.P. and Sheela, C. D. (2011). Synthesis, Characterization, and Biological Activity of Some Transition Metal Complexes Derived from Novel HydrazoneAzo Schiff Base Ligand; *International Journal of Inorganic Chemistry*, pp201, 1-8.

Bakir, S. R, Al-hamdani, A.A and Jarad. A. J.; (2013). Synthesis and Characterization of Mixed Ligands of Dithizone and Schiff Base Complexes with Selected Metal ions; *Journal for Pure Sciences*, 9, pp 82-94.

Daniel, H. O. D. and Isabel, R. I. A. (2011); Concise Synthesis of Asymmetrical N,N'Disubstituted Guanidines.; *Tetrahedron Letters*, 5, pp 132.

FabiolaTéllez, HoracioLópez-Sandoval, Silvia E. Castillo-Blum, and

NoráhBarba-Behrens; (2008); Coordination Behavior of Benzimidazole, 2-Substituted Benzimidazoles and Benzothiazoles, Towards Transition Metal ions; *ARKIVOC* (V) pp. 245-275.

Ferrero, J.R, (1971); Low frequency Vibrations of Inorganic and coordination Compounds, Wiley-Interscience, New York.

Katritzky, A. R. and Rogovoy, B. V. (2005).Recent Developments in Guanylating Agents.*ARKIVOC* (IV), pp.49 - 87.

Khatiwora, E., Mundhe, K., Deshpande, N.R. and Kashalkar. R.V;. (2012). Anthelmintic activity of transition metal complexes of somebenzamides;. *Der PharmaChemica*, 4, pp 1264-1269.

Kong, E, Ritter, G and Kulsheshtha, S.K; (1985); The Nature of Spin State Transitions in Solid Complexes of Iron (II) and the Interpretation of Some Associated Phenomena, *Chemical Reviews*, 85, (3), pp 219-234.

Krishnamurthy Ramadas and NatarajanSrinivasan (1995).;An expedient synthesis of substituted guanidines.; *Tetrahedron Letters, Elsevier Science*. 36, pp 2841-2844.

Lopez, N. A., Castolo, A. A, Contreras, R. (1997) Versatile Behavior of 2-Guani dinobenzimidazole Nitrogen Atoms toward Protonation Coordination and Methylation *Heteroatom Chemistry*, 8, pp

397-410.

Magsoodloua, M.T, Nourollah, Hazeria, S.M.Habibi-Khorassania, L.S, Mohammad,K.R; and Mojtaba, R.(2006); Diastereoselective synthesis of phosphonate esters by reaction between triphenylphosphite and acetylenic esters in the presence of NH-acid compoumds, *ARKIVOC*, 13, pp.117-123.

Malek, Sedlavora, E; Andriamanity, F; Sollei, C, (2006); Activity of Transition Metal Complexes of some Benzamides; *Journal of Pharmaceutical Sciences*, 75, pp 3-9.

Malek, T. M.;Sayyed, M. H.;Reza, H.; Nourallah, H.;Seyed, S. S. and Mohsen, R. (2011).; An efficient and simple synthesis of α-amino phosphonates as drug like molecules catalyzed by silica supported per chloric acid ($HClO_4$–SiO_2); *Arabian Journal of Chemistry*. 4, pp 481–485.

Osowole, A.A (2012). Synthesis, Spectroscopic Characterization, In-vitro Antibacterial and Antiproliferative Activities of Some Metal(II) Complexes of 3,4 - dihydronaphthalen-1 (2H) one Schiff Base. *EXCLI Journal,* (11), pp 338-345

Padmaja, M., Pragathi, J. and Kumari, C.G (2011).Synthesis, Spectral Characterization, Molecular Modeling and Biological Activity of First Row Transition Metal Complexes with Schiff Base Ligand Derived from Chromone-3-Carbaldehyde and o-Amino Benzoic Acid.*Journal of Chemical and Pharmaceutical Research*, 3, pp 602-613

Rao, C.N.R, Exkataraghavax, R; and Kasturi, T.R, (1964); Contribution to the Infrared Spectra of Organosulphur Compounds; *Canadian Journal of Chemistry*, 42, pp 36-42

Reddy, M. V. N., Kumar, B. S.,Balakrishna, A.. Reddy, C. S., Nayak, S. K.and Reddy, C. D. (2007). One-pot Synthesis of Novel α-AminoPhosphonates using Tetramethyl guanidine as a Catalyst, *ARKIVOC*, 15, pp 246-254

Singh, G, Singh, P A, Singh, K. (2002); Synthesis and structural studies of some bivalent metal complexes with bidentate Schiff base ligands; *Proceedings of the National Academic Sciences, India,* 72, pp 87-94.

Sonmez, M. (2001). Synthesis and Characterization of Copper(II), Nickel(II), Cadmium(II), Cobalt(II) and Zinc(II) Complexes with 2-Benzoyl-3-Hydroxy-1-Naphthylamino-3-Phenyl-2 Propen-1-on.*Turkish Journal of Chemistry*, 25, pp 181-185.

Strivastava, S. D. and Sen, J. P; (2008). Synthesis and Biological Evaluation of 2-Aminobenzothiazole Derivatives, *Indian Journal of Chemistry*, 47 (B), pp 1583-1586.

Yadav, P. S. and Devprakash, S. G. P; (2011); Benzothiazole: Different Methods of Synthesis and Diverse Biological Activities, *International Journal of Pharmaceutical Sciences and Drug Research*, 3, pp 1-71

APPENDICES

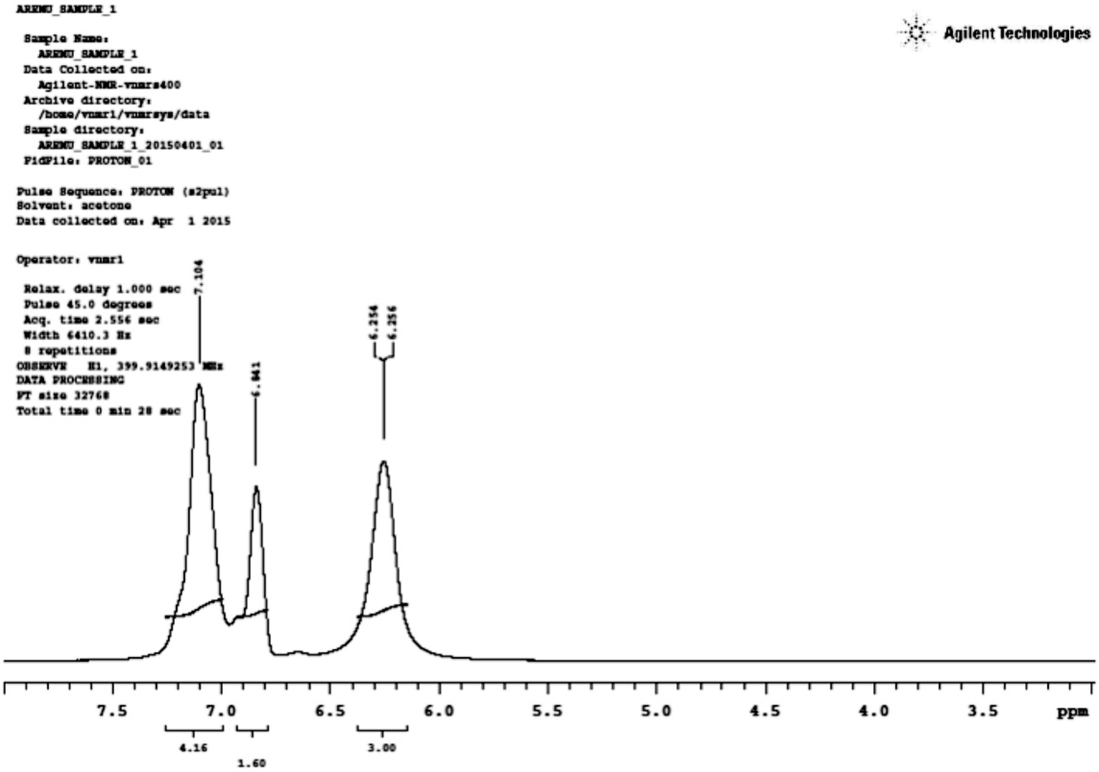


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Figure 1:^{1}H-NMR Spectrum of Guanidinobenzimidazole

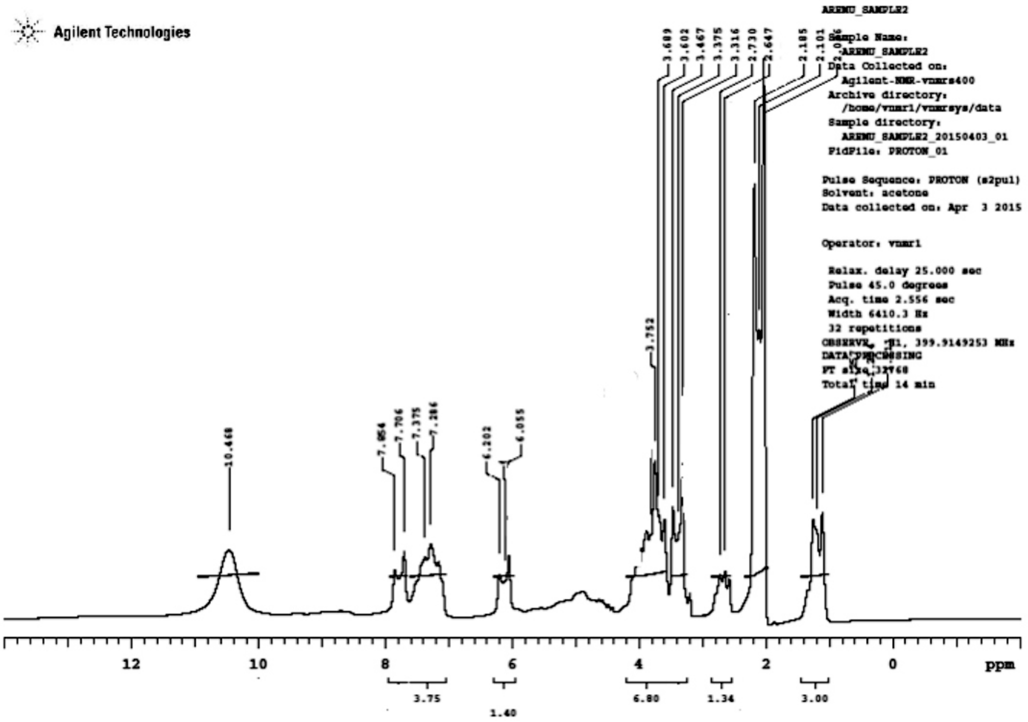

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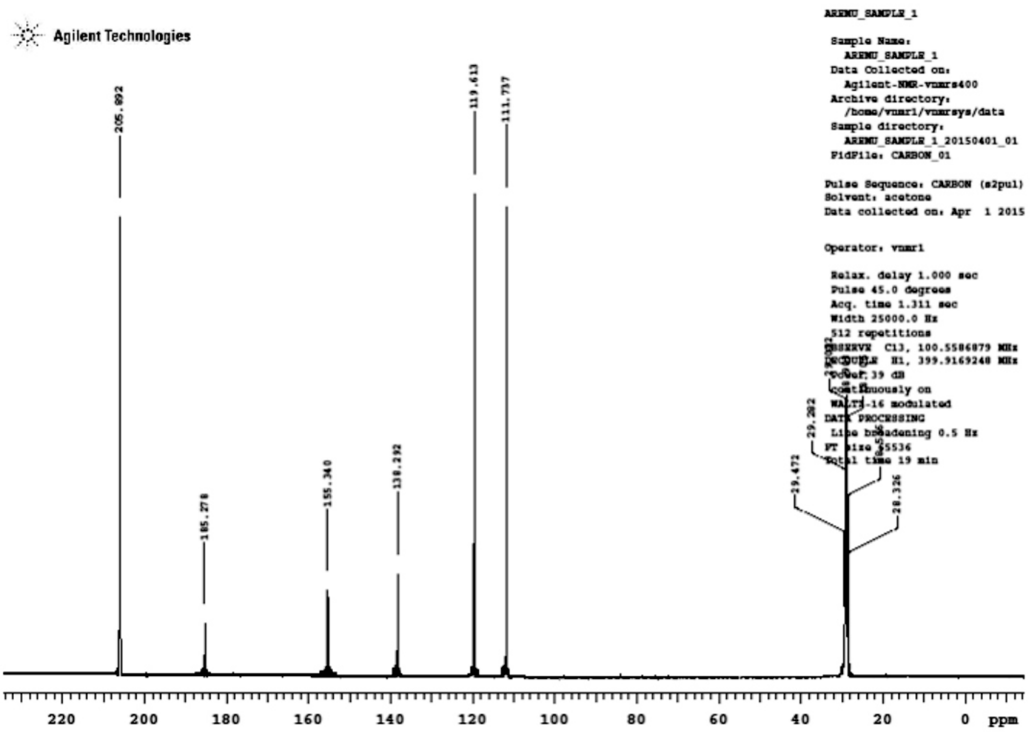
Figure 2:^{1}H-NMR Spectrum of guanidinophosphonatebenzimidazole



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DATA PROCESSING
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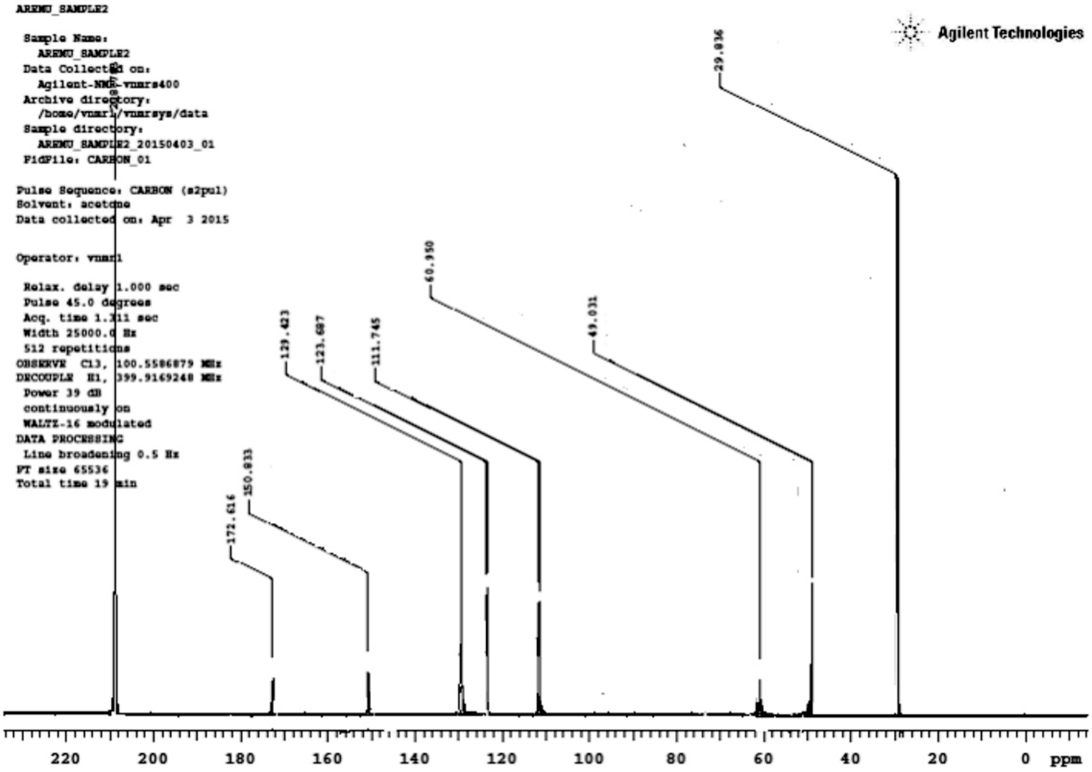
Figure 3:^{13}C-NMR Spectrum of Guanidinobenzimidazole



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Pulse Sequence: CARBON (s2pul)
Solvent: acetone
Data collected on: Apr  3 2015

Operator: vnmr1

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 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 512 repetitions
OBSERVE  C13, 100.5586879 MHz
DECOUPLE  H1, 399.9169248 MHz
 Power 39 dB
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FT size 65536
Total time 19 min
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Figure 4:^{13}C-NMR Spectrum of Guanidinophosphonatebenzimidazole

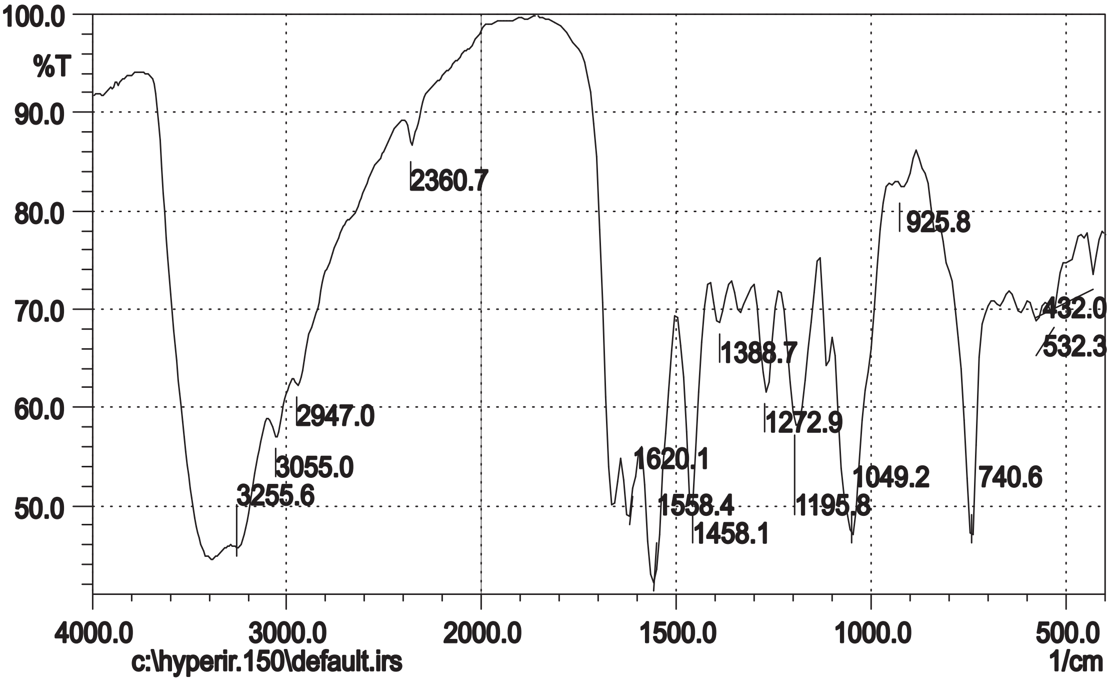

Figure 7: FT IR spectrum of guanidinobenzimidazole

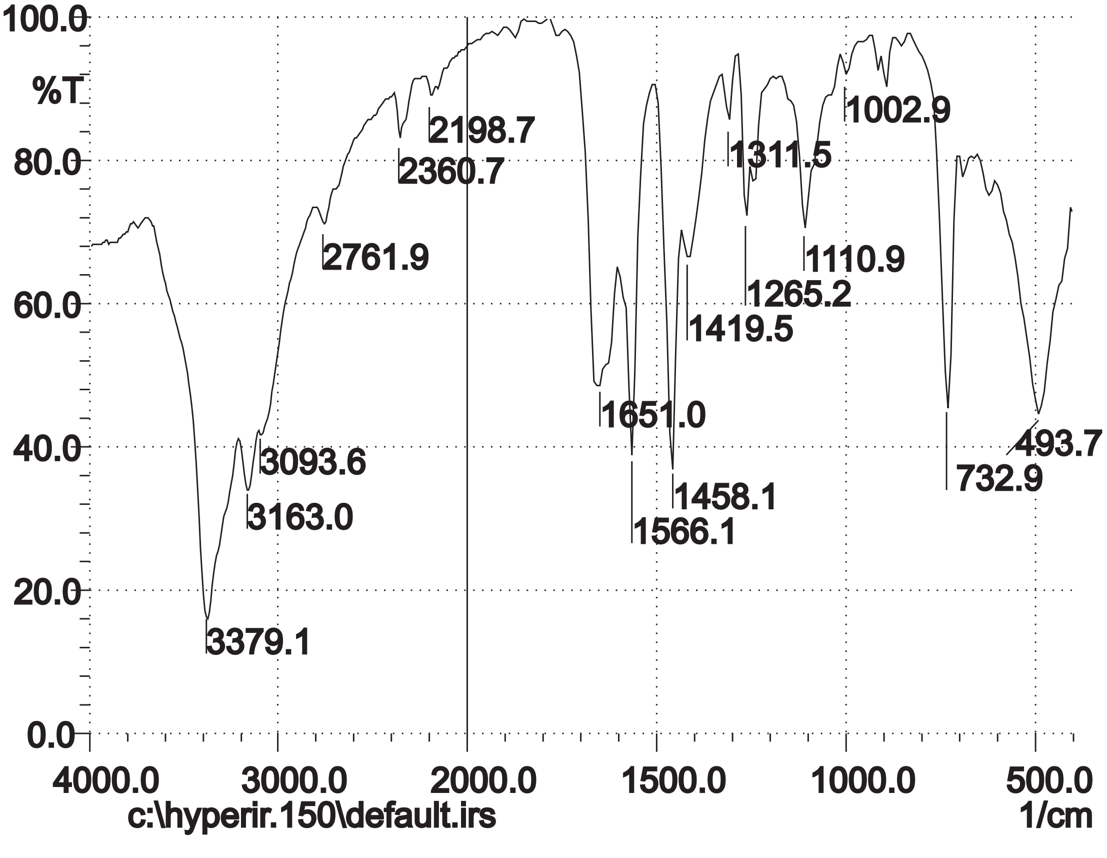

Figure 8: FT IR spectrum of guanidinophosphonatebenzimidazole

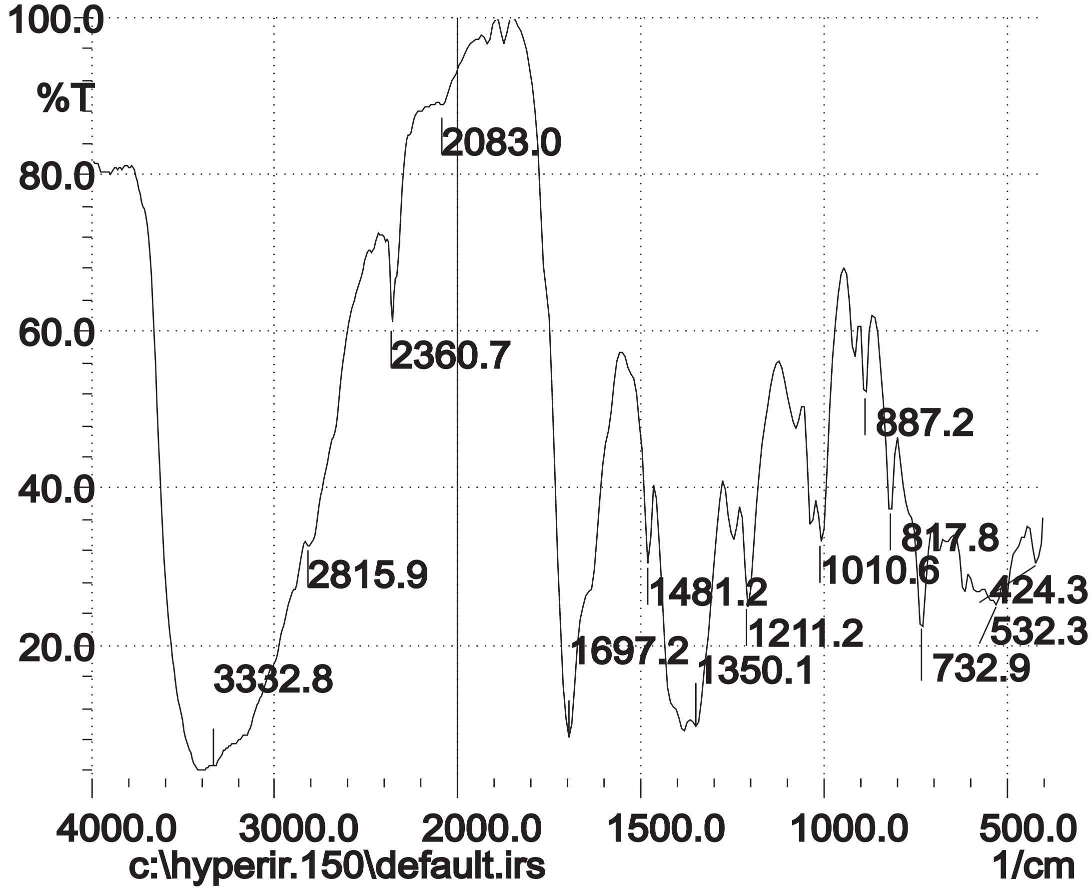

Figure 9: **FT IR spectrum of Fe - guanidinobenzimidazole complex**

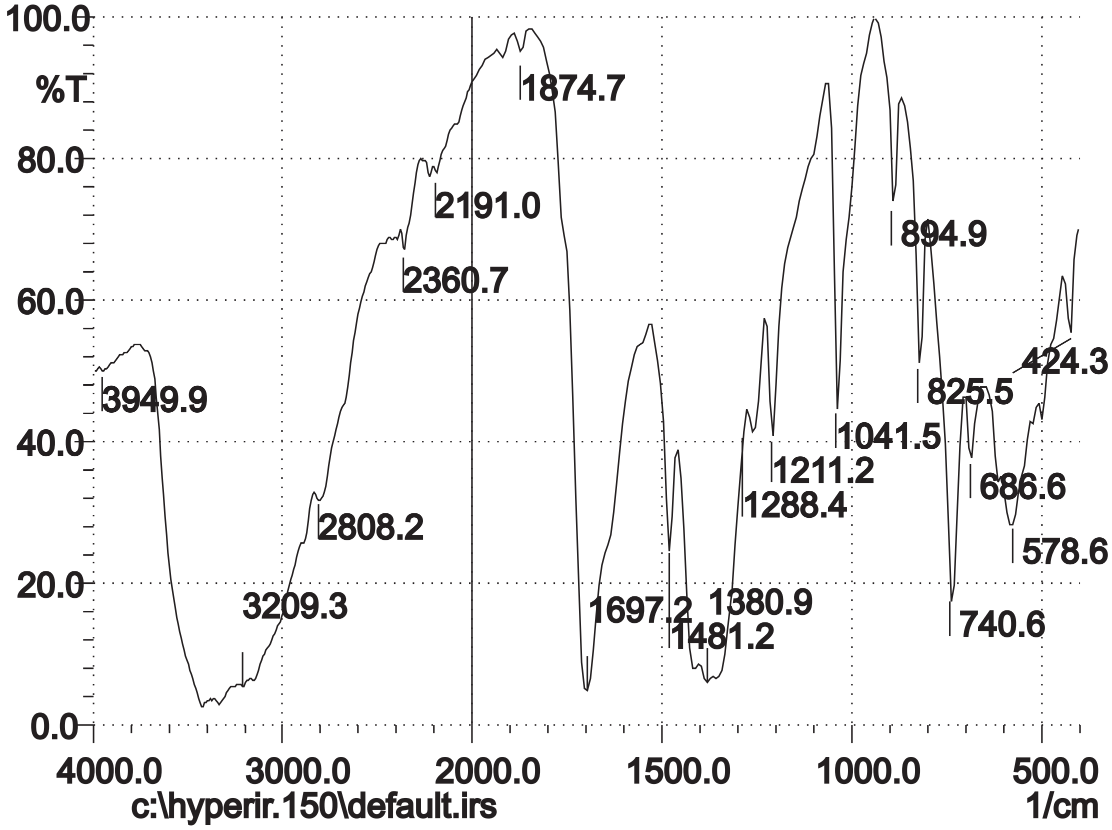

Figure 10 FT IR spectrum of Co - guanidinobenzimidazole complex

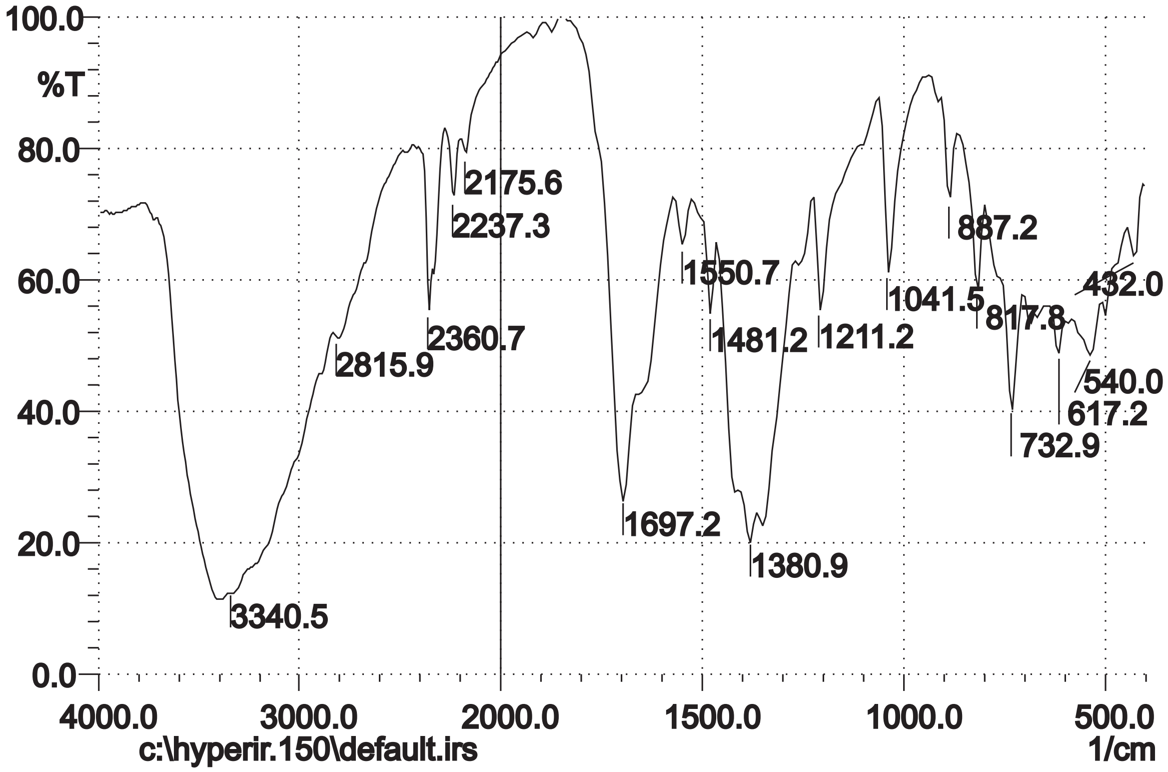

Figure 11: FT IR Spectrum of Ni - guanidinobenzimidazole complex

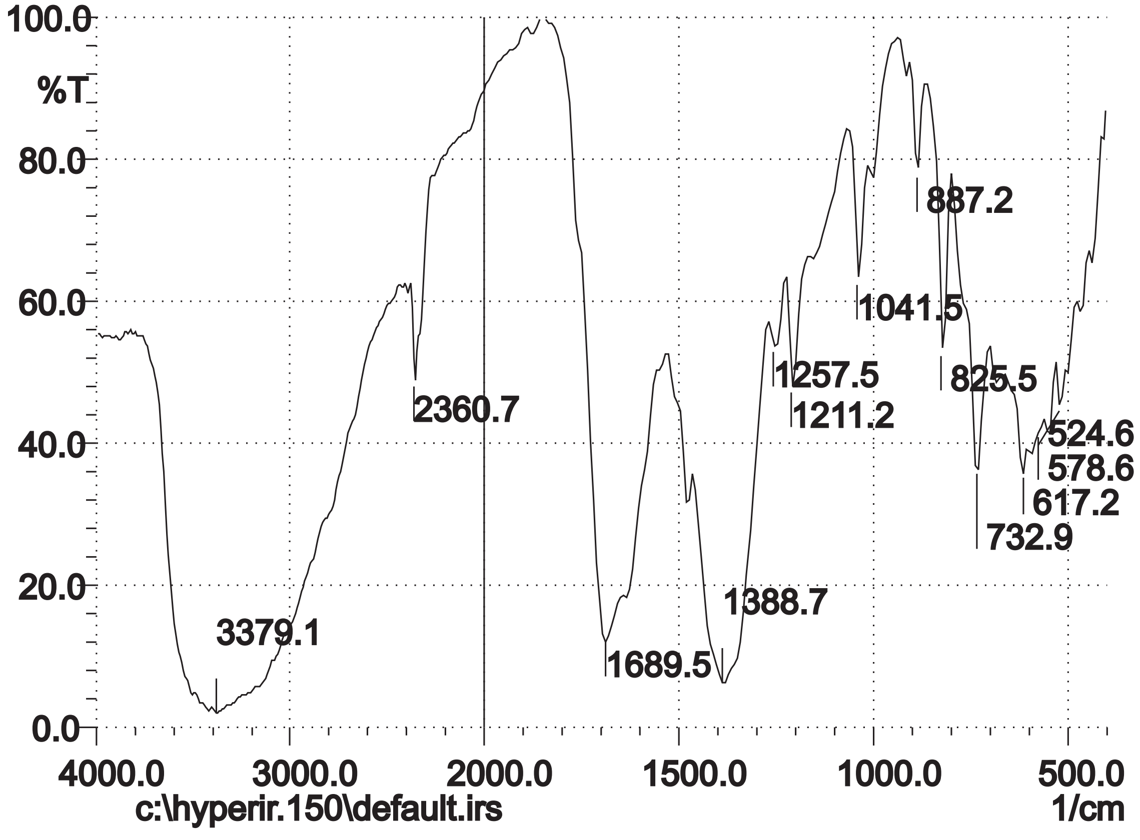

Figure 12: FT IR spectrum of Cu - guanidinobenzimidazole complex

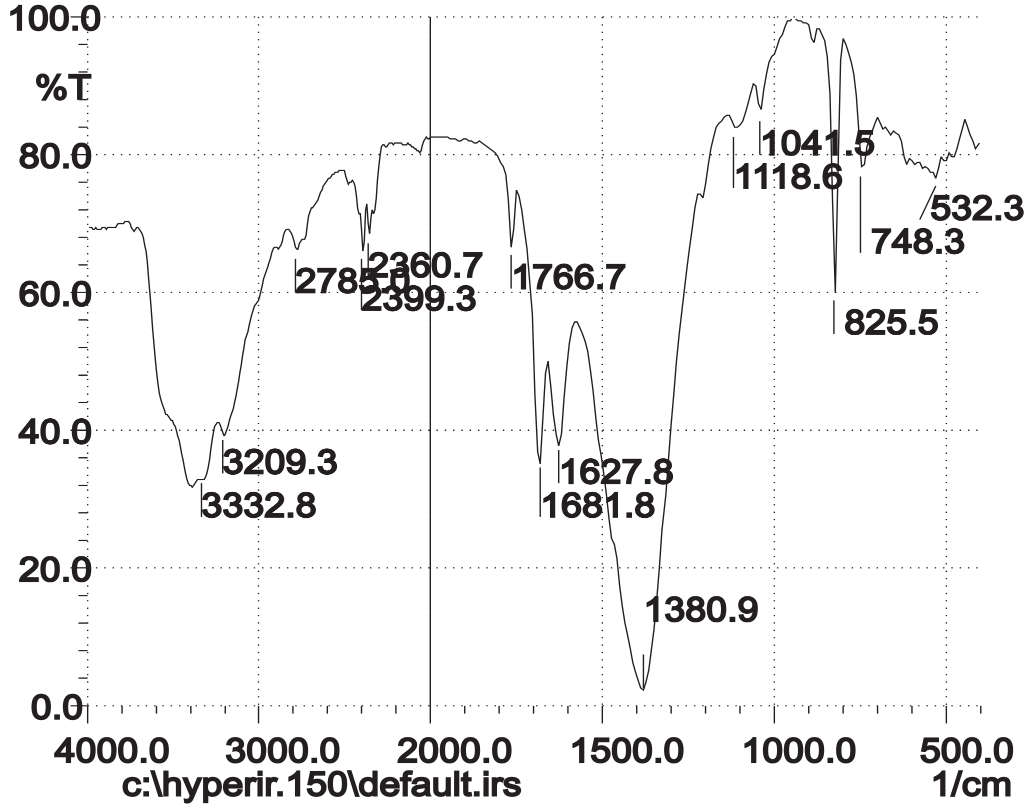

Figure 13: FT IR spectrum of Zn - guanidinobenzimidazole complex

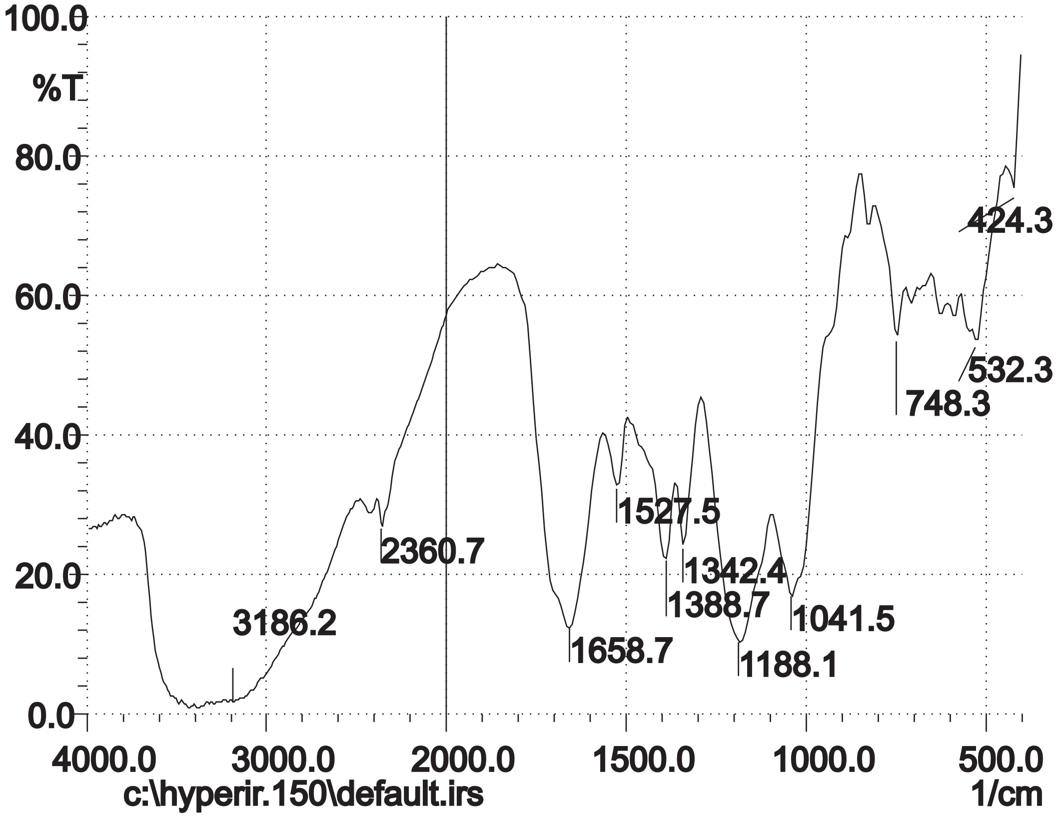

Figure 14: FT IR spectrum of Fe - guanidinophosphonatebenzimidazole complex

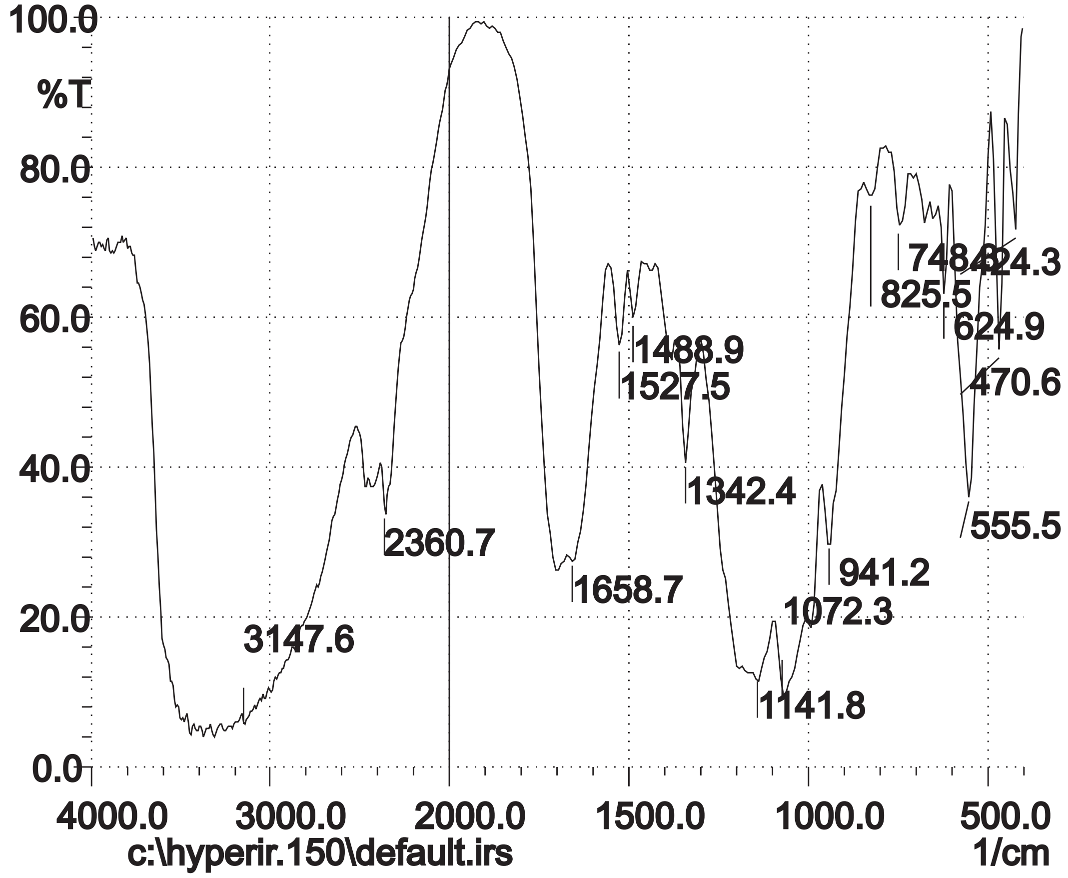

Figure 15: FT IR spectrum of Co - guanidinophosphonatebenzimidazole complex

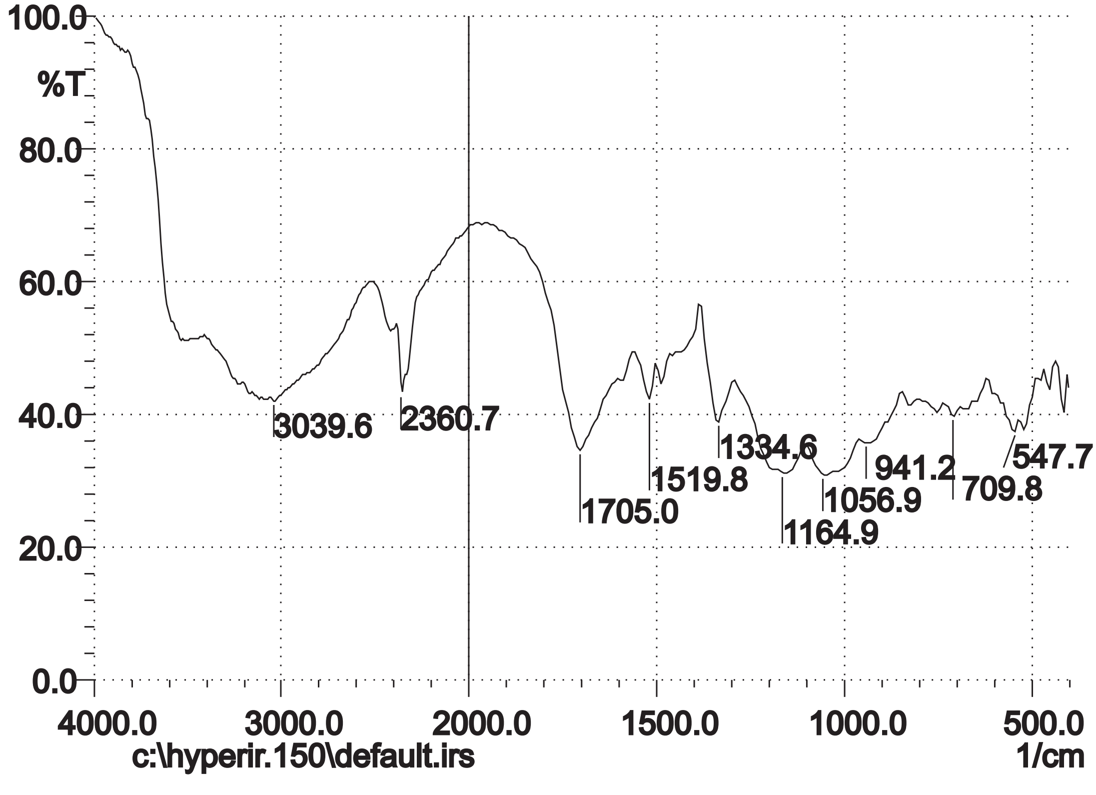

Figure 16: FT IR spectrum of Ni - guanidinophosphonatebenzimidazole complex

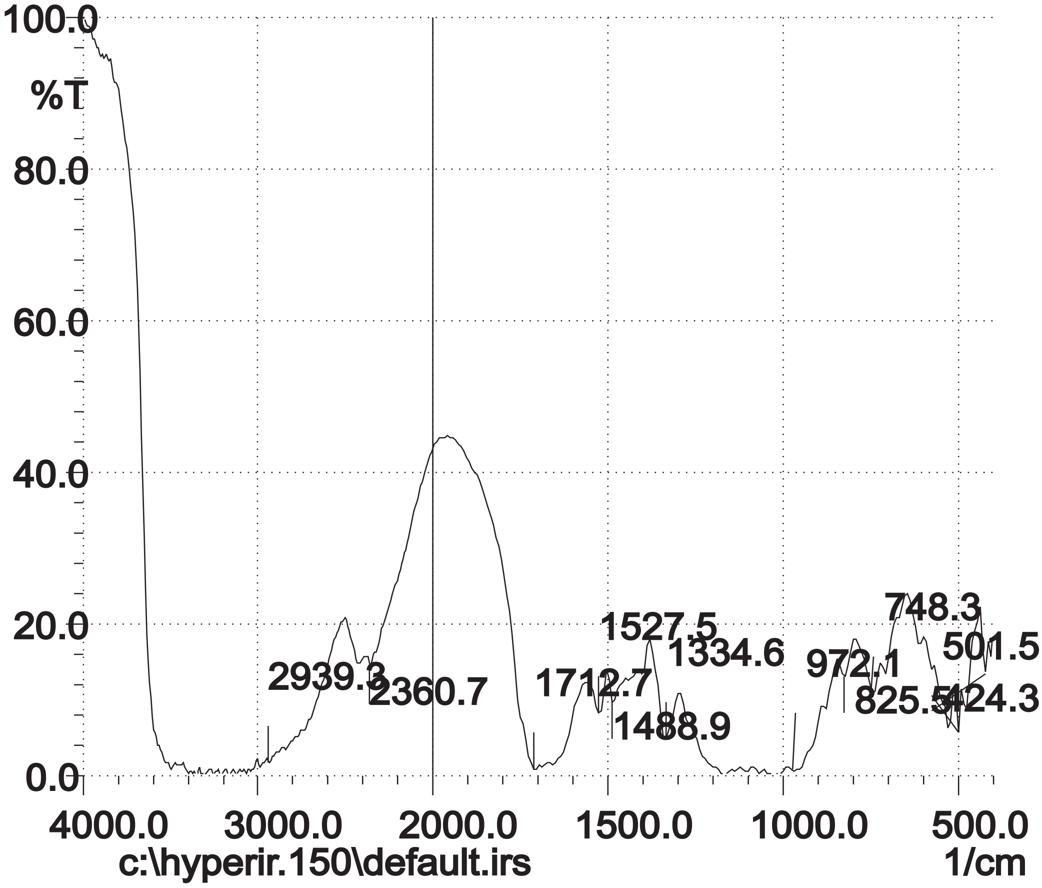

Figure 17: FT IR spectrum of Cu - guanidinophosphonatebenzimidazole complex

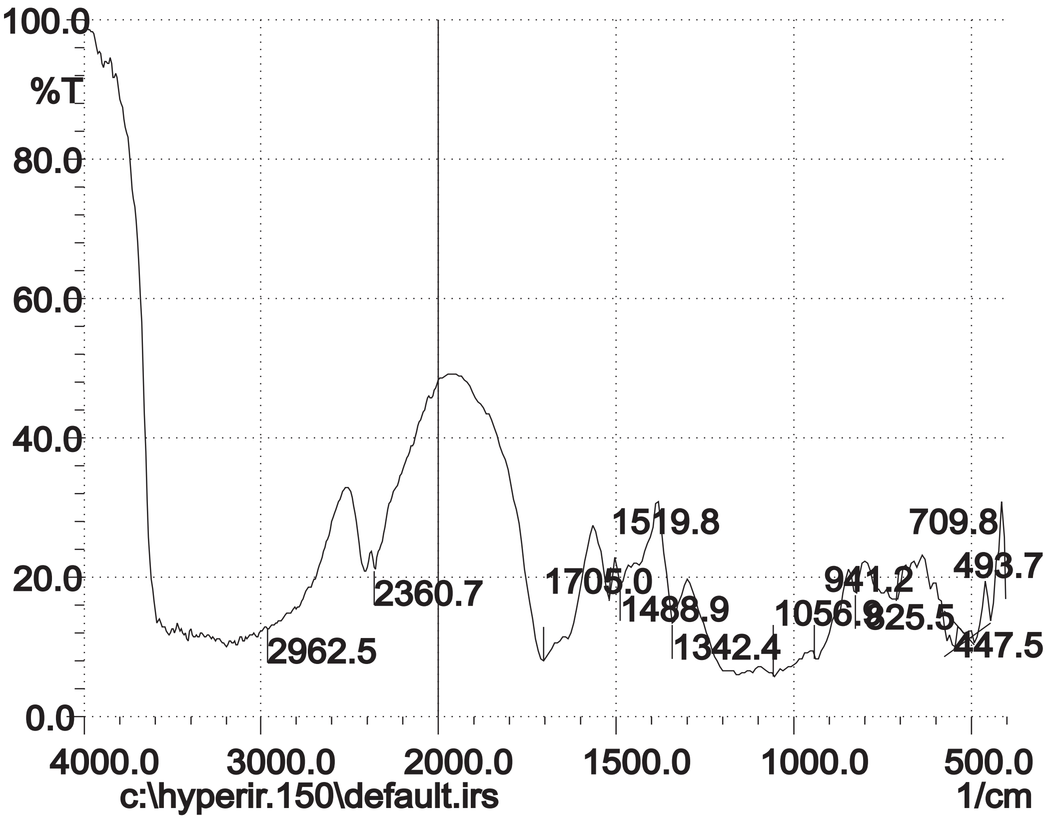

Figure 18: FT IR spectrum of Zn - guanidinophosphonatebenzimidazole complex

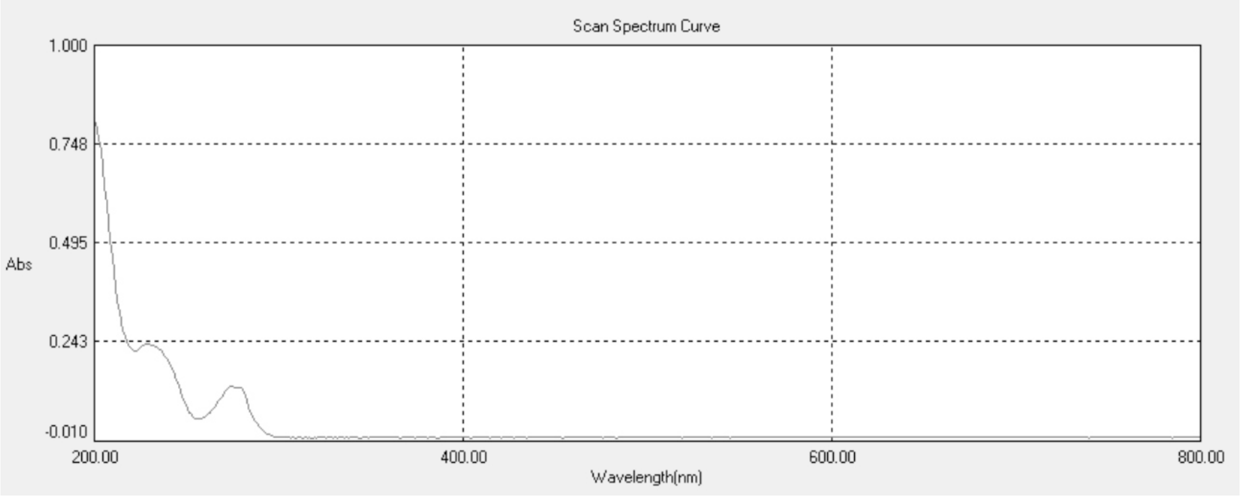

Figure 19: UV-Visible spectrum of guanidinobenzimidazole

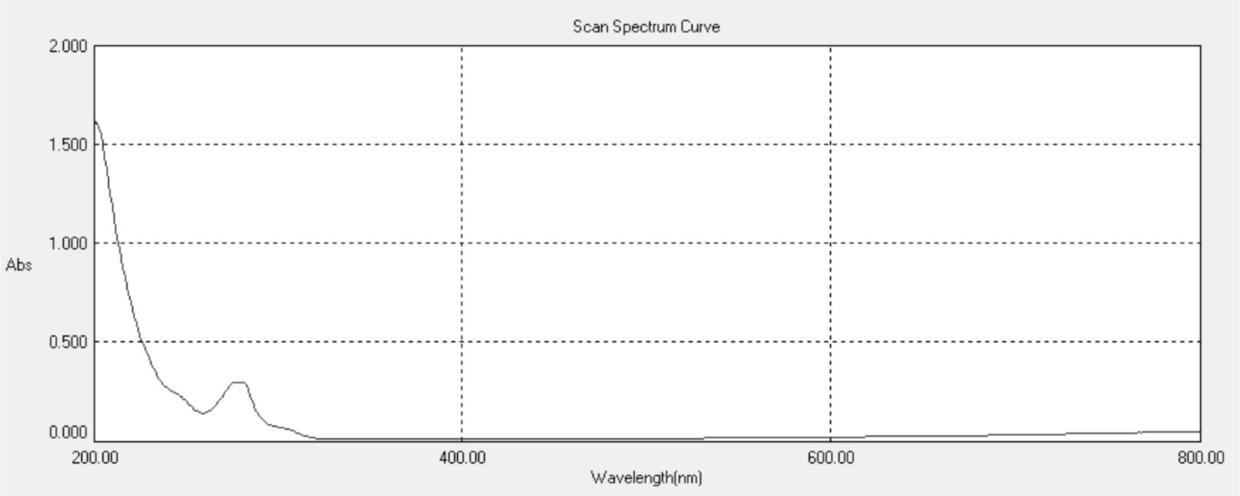

Figure 20: UV-Visible spectrum of guanidinophosphonatebenzimidazole

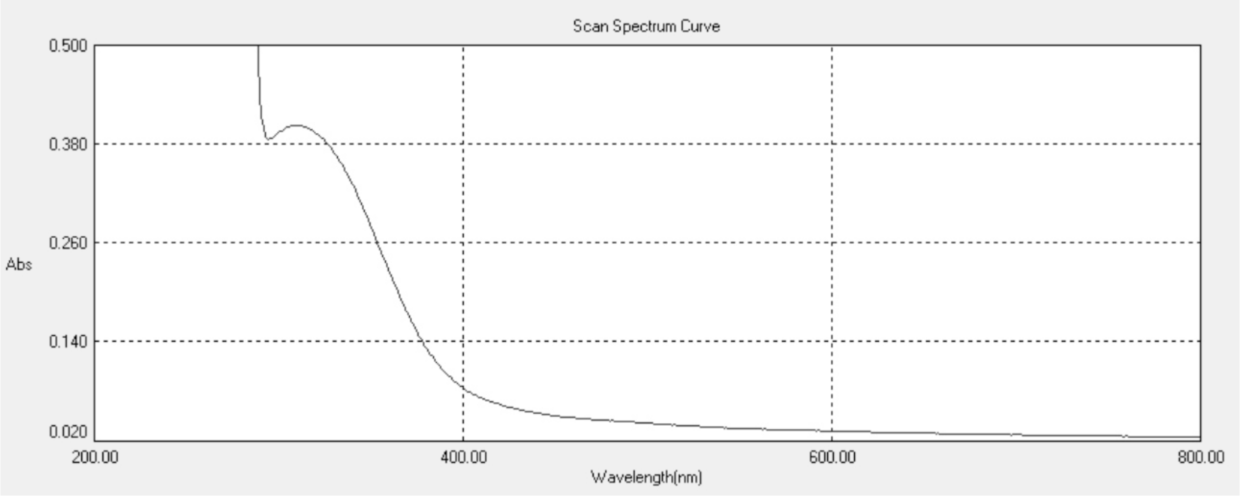

Figure 21: UV-Visible spectrum of Fe - guanidinobenzimidazole complex

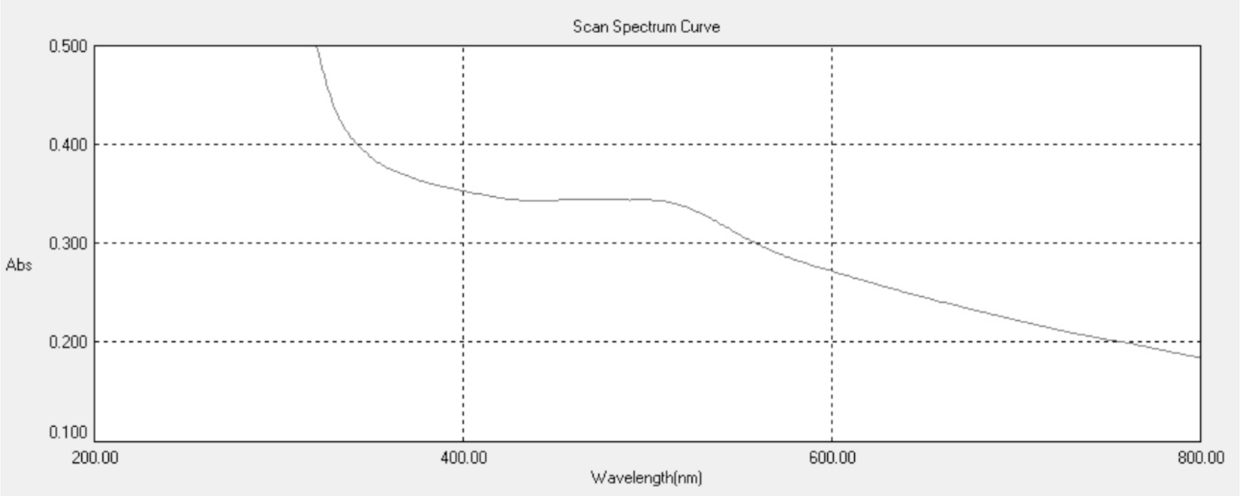

Figure 22: UV-Visible spectrum of Co - guanidinobenzimidazole complex

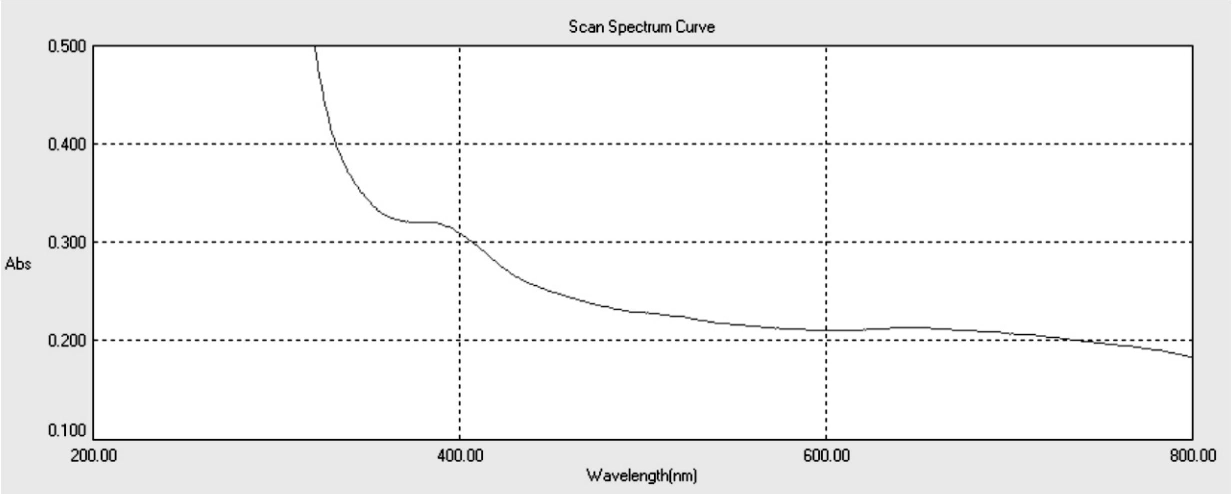

Figure 23: UV-Visible spectrum of Ni - guanidinobenzimidazole complex

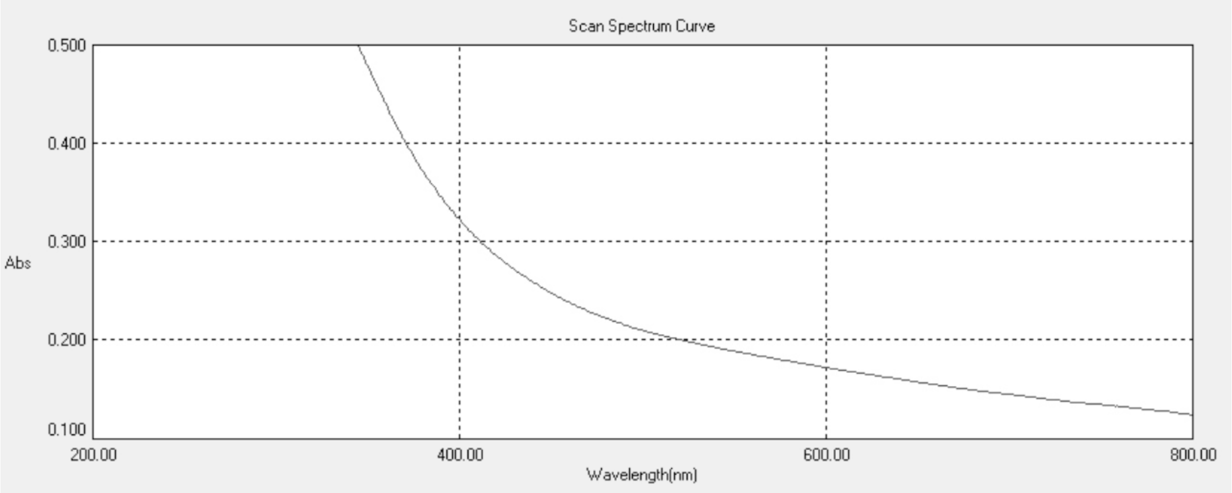

Figure 24: UV-Visible spectrum of Cu - guanidinobenzimidazole complex

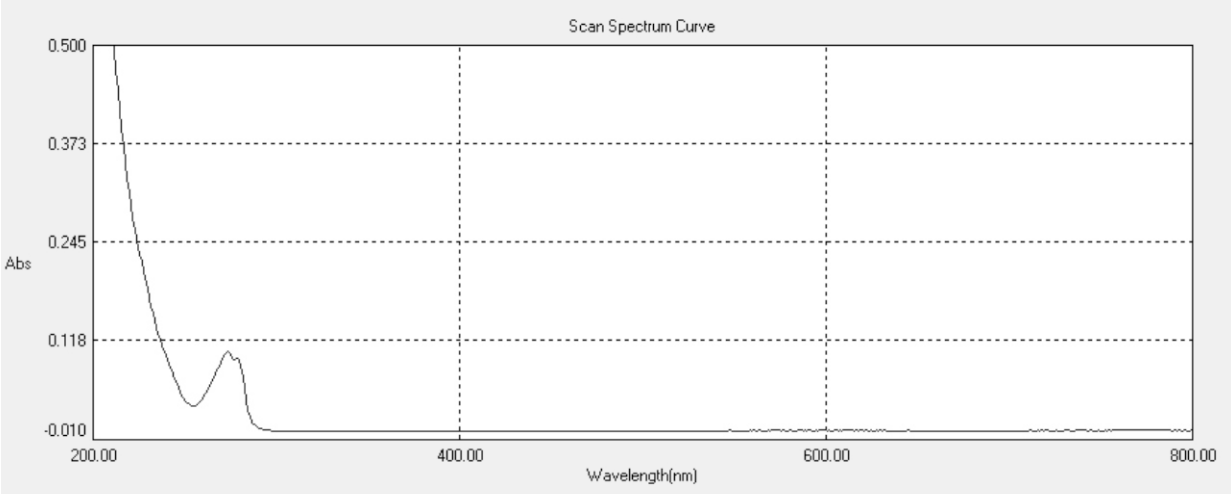

Figure 25: UV-Visible spectrum of Zn - guanidinobenzimidazole complex

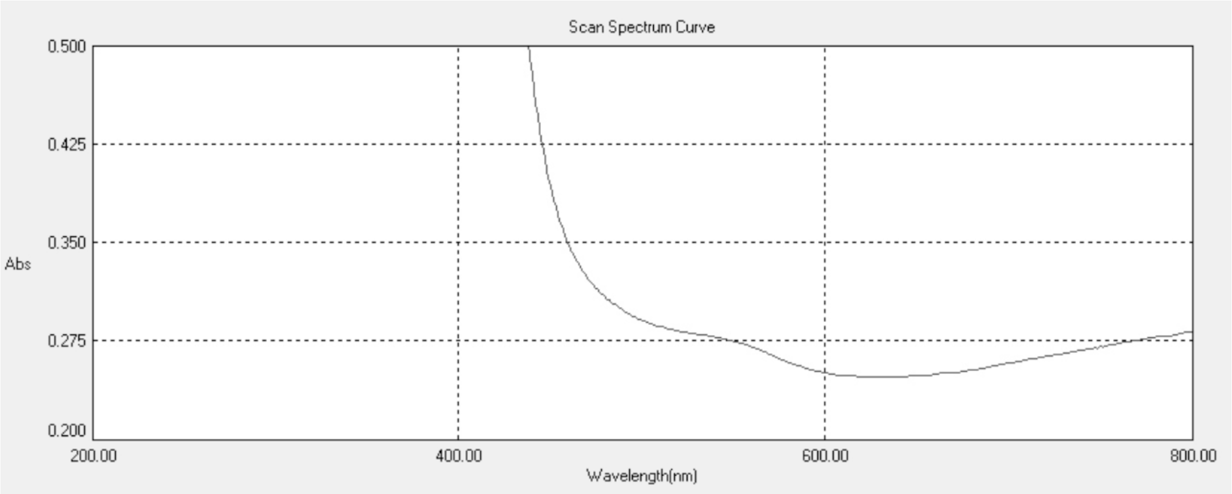

Figure 26: UV-Visible spectrum of Fe - guanidinophosphonatebenzimidazole complex

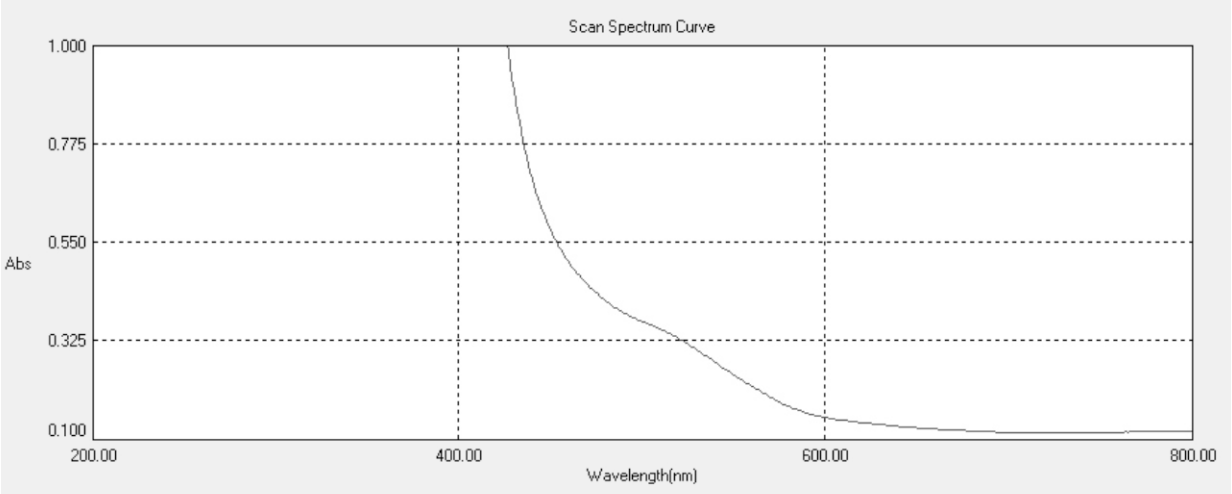

Figure 27: UV-Visible spectrum of Co - guanidinophosphonatebenzimidazole complex

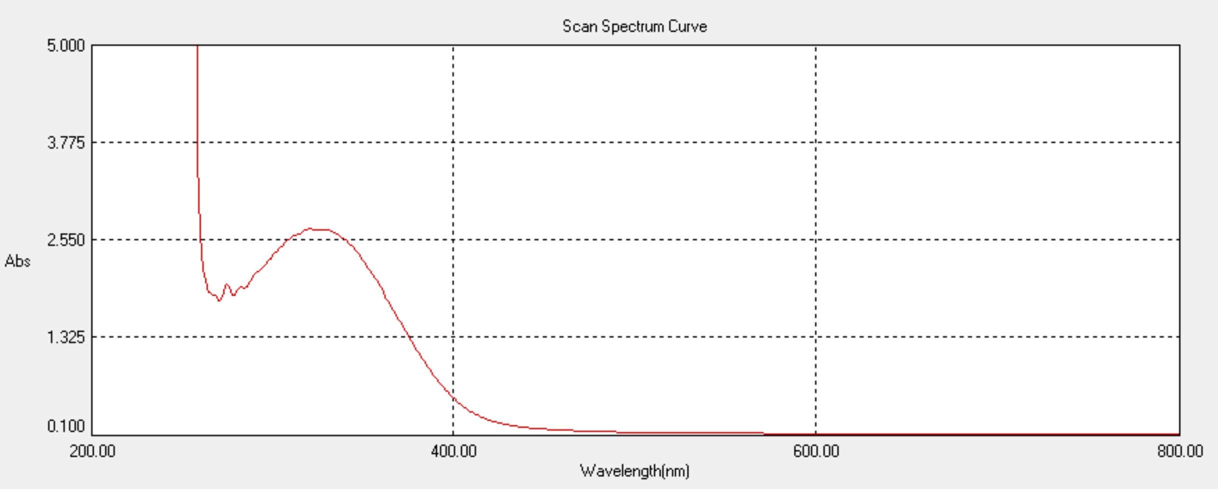

Figure 28: UV-Visible spectrum of Ni - guanidinophosphonatebenzimidazole complex

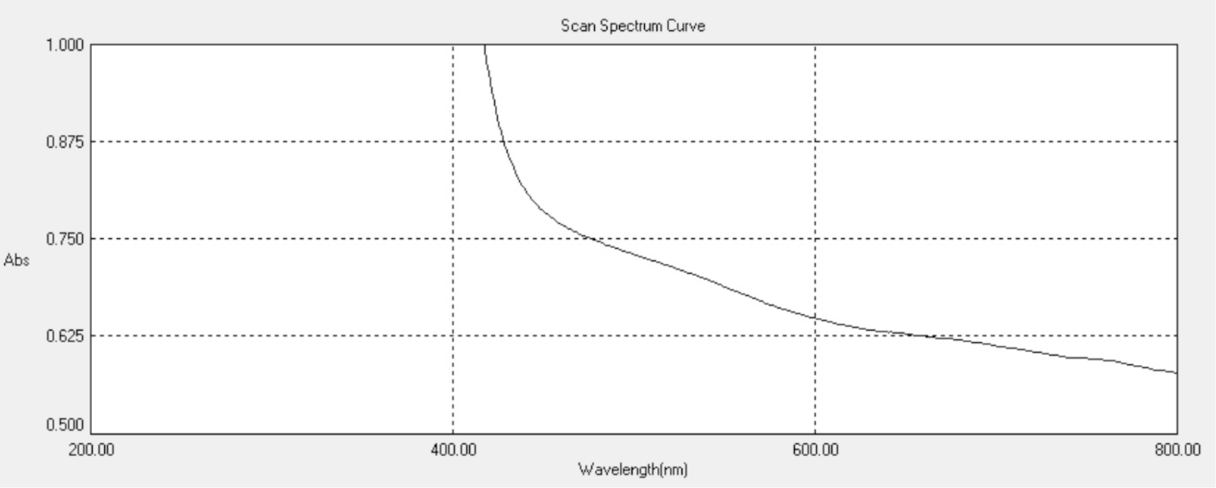

Figure **29: UV-Visible spectrum of Cu - guanidinophosphonatebenzimidazole complex**

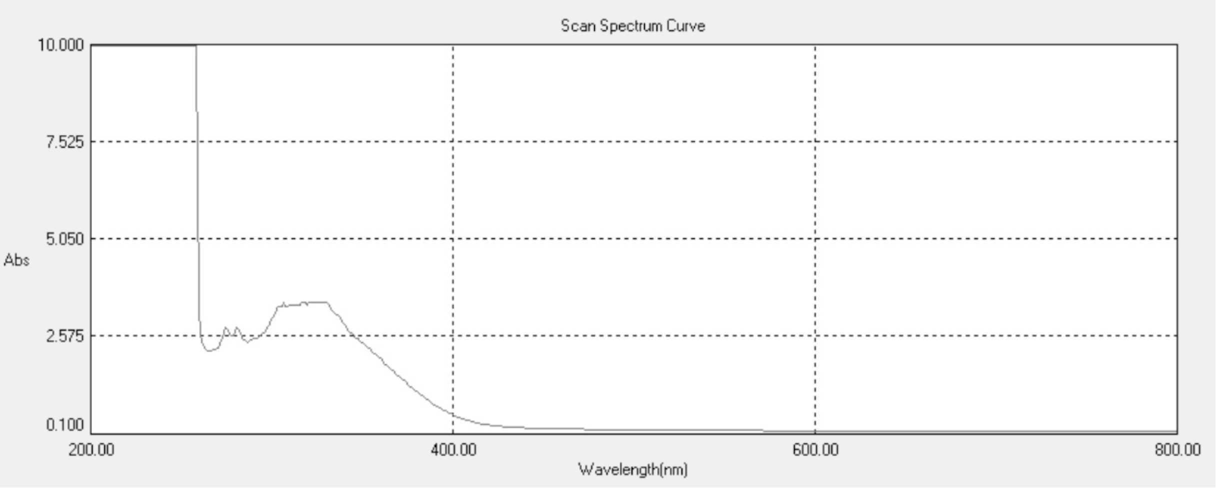

Figure 30**: UV-Visible spectrum of Zn - guanidinophosphonatebenzimidazole complex**