CHAPTER- 2
SYNTHESIS AND SPECTRAL/STRUCTURAL CHARACTERIZATION
CHAPTER- 2

Synthesis and spectral/structural characterization

In the present chapter the procedure for the synthesis of N-hydroxyamidines and their Co(II), Cr(II) and Zn(II) complexes using the previously reported procedures [1-9] have been discussed. All the compounds were then purified and structures were confirmed using various spectral and physical techniques. Geometry was confirmed using FTIR, NMR, MASS and UV-Vis spectral studies. Physical properties were observed using thermo gravimetric analysis (TGA), elemental analysis and magnetic moment.

EXPERIMENTAL

Synthesis of ligand and their metal ion complexes

We have synthesized five N-hydroxyamidine derivatives, 3-methyl-N-hydroxyamidine, 3-amino-N-hydroxybenzamidine, 2-amino-5-nitro-N-hydroxybenzamidine, N-hydroxy-4-[(hydroxyimino)methyl]benzamidine and N-4-(dihydroxy)benzamidine, which may be unknown or frequently not used. Their Co(II), Cr(II) and Zn(II) complexes were synthesized using the below mentioned procedure. We have the below mentioned methods for the synthesis of different ligands-

Synthesis of N-hydroxybenzamidine ligand (L)

N-hydroxybenzamidines were synthesized (scheme 1 & 2) by refluxing corresponding benzonitrile, 0.012 mole, NH₂OH.HCl, 0.2 mole and NaNO₃ 0.012 mole in a 250 ml conical
Where, M= Co(II) and Cr(II)

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<td>MHB</td>
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<td>AHB</td>
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<td>ANHB</td>
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<td>H</td>
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<td>NO₂</td>
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**Scheme 1.** Synthesis of N-hydroxyamidines and their metal ion complexes

flask and 80 mL water/ ethanol (2:1) was added to this mixture and stirred using magnetic stirrer. The solution was then refluxed at 80 °C in water bath for 2.5 hr. As the solution was cooled, crystals of N-hydroxybenzamidines separated out, solvent was removed under reduced pressure and crystals were recrystallized using ethanol and then by diethyl ether [17]. The completion of the reaction was confirmed by thin layer chromatography continuously. (Yield 79-95%) [18].

**Synthesis of N-hydroxybenzamidine metal(II) complexes**

Ligand, 0.01 mole was dissolved in 50 mL CH₃OH in a 250 mL conical flask. MCl₂.xH₂O metal
Where, M= Co(II) and Cr(II)

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<td>PHB</td>
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<td>HIMB</td>
<td>H</td>
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<td>H</td>
<td>CHNOH</td>
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Scheme 2. Synthesis of N-hydroxyamidines and their metal ion complexes

salt of Co(II), Cr(II) and Zn(II), (0.02 mole) was dissolved in 50 mL MeOH and mixed with the ligand solution drop wise using magnetic stirrer [19]. The final solution was then transferred into a 250 mL round bottom flask and refluxed for 2 hr in a water bath maintained at 70 °C. On cooling, crystals of metal complexes were separated out which were then filtered and recrystallized using ethanol and water mixture and dried under vacuum, scheme 1. (Yield; 79-91%). The purity was checked by thin layer chromatography and the compounds were characterized using various spectroscopic techniques, discussed in next chapter.
Spectral characterization of ligand and their metal ion complexes

Many organometallic compounds are used in biological systems, but their effects are based on purity. To check the purity there are various techniques available, among them spectroscopic characterization are widely used. Organic molecules exhibit their activities depends on various factors e.g. functional group attached, geometry and the presence of neighbor atoms. The chemical properties can be predicted according to their functional group but the geometry and neighbor atoms decide their physical properties.

Spectroscopic analyses are used to determine the geometry and structural properties e.g. NMR, IR, Mass and UV-Vis. While the thermal properties were evaluated using thermogrametric analysis (TGA) and elemental analysis are performed to determine the % composition. In this section we have discussed the characterization using above mentioned techniques.

\(^1\text{H NMR spectral studies}\)

Thorough investigation of transition metal NMR spectroscopy of organometallic compounds was difficult for a long time due to lack of sensitive detection techniques suitable for a wide range of resonance frequencies. During past few years, the availability of high-field spectrometers, for the use of large samples volumes added with broadband radiofrequency, electronics and programmable pulse generators have resulted a real break-through in organometallic chemistry and homogeneous catalysis. In this section we have discussed \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of N-hydroxybenzamidine and their metal ion complexes. The spectra we have
obtained using WATERS 400 MHz FTNMR spectrometer, are corresponding to their geometrical orientation confirming their structure [20].

Results and discussions

1. 2-amino-5-nitro-N-hydroxybenzamidine (ANHB) and their metal ion complexes

$^1$H NMR spectra of ligand displayed amino (Ar-NH$_2$) peak at $\delta$ 6.35 ppm and H-2, H-6 protons of benzene ring at 6.83 and 6.63 ppm respectively as singlet. H-3 protons appeared

![ANHB ligand](image1)

![Co(II) complex](image2)

Fig. 1. $^1$H NMR spectra of ANHB ligand and their Co(II) complex
Fig. 2. $^1$H NMR spectra of ANHB Zn(II) and Cr(II) complexes, dissolved in CDCl$_3$ at room temperature.

at 7.72-7.7 ppm as doublet. A singlet was observed at 6.86 ppm assigned for (C-NH$_2$) protons of hydroxyamidine moiety. Peak at 9.88 ppm was assigned for (=N-OH) proton (Fig.1). On the formation of metal complexes many changes were observed in the chemical shifts, which was confirmed by the disappearance of -OH proton. In all complexes of Zn(II), Co(II) and Cr(II), =C-NH$_2$ (amidinie moiety) protons retains its position at 1.50 ppm (Fig.1 and 2). A singlet of Ar-NH$_2$ proton was observed downfield at 6.34 ppm in Cr(II) and Co(II) complexes, which was observed at 5.74 ppm in Zn(II) complex. Phenyl proton H-14 and H-20 in Cr(II) and Co(II) complexes were observed as doublet at 7.08-7.11ppm. The same protons were observed at 6.75 ppm for Zn(II) complex. H-17, H-15, H-21 and H-23 exhibiting singlet between 7.08-8.35 ppm.
of aromatic ring in complexes. Furthermore, the number of the proton calculated from the integration curves and those obtained from the values of the expected CHN analysis agreed well with each other.

2. 3-methyl-N-hydroxybenzamidine (MHB) and their metal ion complexes

$^1$H NMR spectra of ligand and Cr(II), Zn(II) and Co(II) complexes displayed methyl (Ar-CH3) peak at δ 2.30 ppm as singlet. H-2 protons of phenyl ring at δ 6.28 ppm as singlet and H-4 proton as doublet at δ 7.25 ppm (Fig. 3). H-6 appeared as multiplet at δ 7.35 ppm. The H-8 (N=C-NH) proton was assigned at δ 7.38 ppm as singlet. H-5 proton appeared as triplet at δ 7.16 ppm. A singlet was observed at δ 2.36 ppm assigned for C=N-OH proton of hydroxyamidine moiety. On formation of metal complexes, many changes were observed in the chemical shifts, which was confirmed by the disappearance of C=N-OH proton. A singlet of N=C-NH2 proton in complexes were observed lower downfield at δ 1.50 ppm as compared to ligand. 1H spectrum of H-11, H-14, H-17 and H-20 in phenyl ring for Cr(II), Co(II) and Zn(II) complexes showed, as multiplet at δ 7.06 ppm. A doublet of triplet at H-13, H-19 and H-15, H-21 proton in Zn(II) complex were assigned at δ 7.28 ppm and δ 7.74 ppm complexes (Fig. 4).

Similarly a doublet of triplet was displayed for H-13, H-21 and H-15, H-23 protons at the same position in Co(II) and Cr(II) Furthermore, the number of the proton calculated from the integration curves and those obtained from the values of the expected CHN analysis agreed well with each other.
Fig. 3. $^1$H NMR spectra of MHB ligand and their Zn(II) and Co(II) complexes, dissolved in CDCl$_3$ at room temperature.
3. 3-amino-\textit{N}-hydroxybenzamidine (AHB) ligand and their metal ion complexes

$^1$H NMR spectra of Cr(II), Zn(II) and Co(II) complexes of AHB, displayed amino (Ar-NH$_2$) peak at $\delta$ 5.35 ppm as singlet. A singlet for Ar-NH$_2$ was observed more downfield at 5.48 ppm. Doublet of H-2 and H-4 protons of phenyl ring were observed at $\delta$ 6.63-6.65 and 6.79-6.81 ppm (Fig. 5), H-6 proton was observed as singlet at $\delta$ 6.18 ppm in ligand. The H-9 from N=C-NH proton (amidine moiety) at $\delta$ 5.99 ppm and H-3 protons (Ar-H) was assigned as triplet at $\delta$ 7.0-7.05 ppm in ligand. A singlet was observed at $\delta$ 9.88 ppm assigned for (C=N-OH) proton of hydroxyamidine moiety for ligand. On formation of metal complexes, many changes were observed in chemical shifts, which was confirmed by the disappearance of (C=N-OH) proton.

A singlet of (N=C-NH$_2$) and amino (Ar-NH$_2$) proton in complexes were observed less downfield at $\delta$ 1.50 and 5.35 ppm respectively. $^1$H spectrum of H-22 from phenyl ring was observed corresponds to Co(II) and Cr(II) complexes as triple at $\delta$ 7.12 ppm (Fig.6). This peak was observed shifted to 6.90 ppm in Zn(II) complexes. A doublet of phenyl H-15 and H-17 proton in Co(II) and Cr(II) complexes were assigned at $\delta$ 6.82 and $\delta$ 7.31 ppm, but in Zn(II) complexes, it was observed at 6.45 and 7.0 ppm. Similarly a doublet of triplet was displayed for
H-13 and H-19 protons at 5.95 ppm in Zn(II) complexes, while in Co(II) and Cr(II) complexes it was observed at 6.45 ppm. Furthermore, the number of the proton calculated from the integration curves and those obtained from the values of the expected CHN analysis agreed well with each others.

Fig. 5. $^1$H NMR spectra of AHB ligand and their Co(II) complexe, dissolved in CDCl$_3$ at room
Fig. 6. $^1$H NMR spectra of AHB ligand and their Co(II) complexe, dissolved in CDCl$_3$ at room

4. **N-4-[(hydroxyimino)methyl]benzamidine (HIMB) and their metal ion complexes**

$^1$H NMR spectra of ligand displayed distal hydroxyl proton H-14 peak at 10.93 ppm and H-2, H-6, H-5 and H-1 protons of benzene ring at 7.39-7.47 ppm as doublet of doublet. Distal H-12 (free hydrogen) proton appeared at 7.82 ppm as singlet, confirming the structure of ligand. A singlet was observed at 5.99 ppm assigned for C-NH$_2$ protons of hydroxyamidine moiety. Peak at 9.88 ppm was assigned for =N-OH proton corresponding to HIMB ligand. On formation of metal complexes, many changes were observed in the chemical shifts, which were confirmed by the disappearance of amidine hydroxyl -OH proton. In all complexes of Zn(II), Co(II) and Cr(II), a singlet of =C-NH$_2$ proton was observed lower downfield at 1.50 ppm than ligand. H-11, H-12, H-14 and H-15 exhibiting multiplate between 7.90-7.97 ppm of aromatic ring. Distal proton for Co(II) and Cr(II) were observed at 8.07 and 8.29 ppm, which differ from Zn(II) complex
Fig. 7. $^1$H NMR spectra of HIMB ligand and their Co(II) and Cr(II) complexes, dissolved in CDCl$_3$ at room
observed at 8.07 and 8.54 ppm, confirming different geometry of Zn(II) than Cr(II) and Co(II) complexes. A singlet was observed for distal hydroxyl group H-24 at 10.93 ppm for Co(II) and Cr(II) and at 9.58 ppm for Zn(II) complex. Furthermore, the number of the proton calculated from the integration curves and those obtained from the values of the expected CHN analysis agreed well with each other.

5. N-4-(dihydroxy)benzamidine (PHB) ligand and their metal ion complexes

\(^1\)H NMR spectra of ligand displayed hydroxyl Ar-OH peak at 9.95 ppm and H-2, H-3, H-5 and H-6 protons of benzene ring at 6.72-6.89 ppm as doublet. H-3 protons appeared at 7.72-7.7 ppm as doublet. A singlet was observed at 7.54 ppm assigned for C-NH protons of hydroxyamidine moiety. Peak at 2.18 ppm was assigned for =N-OH proton in ligand. On formation of metal complexes, many changes were observed in chemical shifts, it was confirmed by the disappearance of -OH proton. In Zn(II), Co(II) and Cr(II) complexes, a singlet of =C-NH proton was observed lower downfield at 1.50 ppm than ligand (Fig.5). H-13, H-14, H-16, H-17, H-20, H-21 and H-23 protons of aromatic ring in Co(II) and Cr(II) complexes were exhibited.

Fig. 8. \(^1\)H NMR spectra of HIMB Zn(II) complexe, dissolved in CDCl\(_3\) at room
Fig. 7. $^1$H NMR spectra of HIMB ligand and their Co(II) and Cr(II) complexe, dissolved in CDCl$_3$ at room
as doublet between 6.85-7.17 ppm corresponding to coupling with neighbor proton. The same protons were observed at between 7.98-8.3 ppm in Zn(II) complex. Furthermore, the number of the protons calculated from the integration curves and those obtained from the values of the expected CHN analysis agreed well with each other.
13C NMR of N-hydroxyamidines and their metal ion complexes

In this section results of the 13C NMR spectral studies of N-hydroxyamidines and their metal ion complexes have discussed. The spectra we have obtained are corresponding to their geometrical orientation confirming their structure [21].

Results and discussions

1. 2-amino-5-nitro-N-hydroxybenzamidine (ANHB) ligand and their metal ion complexes

13C NMR spectra of ligand displayed the entire characteristic peak at the expected position which further supported the results obtained from IR and 1H NMR spectra. Ligand containing aromatic ring of C2, C3, C5 and C6 carbons exhibits shift at 109.08, 126.95, 128.72 and 119.10 ppm respectively. The amino group attached to C1 carbon exhibits shifting peak downward at 149.91 ppm, due to the sharing of electron of nitrogen towards the benzene ring system. The nitro group (-NO2) attached to C4 carbon causes the shifting at position 146.59 ppm as compared to amino group due to higher electronegative oxygen atom pulling electron clouds from the benzene ring increasing the shielding effect hence the lower downward shifting, amidine moiety containing C9 were assigned at more downfield 147.91 ppm due to deshielding effect. On complex formation, many changes in chemical shifts were observed (Fig.1), amidine carbon C5 and C8 were shifted more downfield at 157.82 ppm in Cr(II) and Co(II) complexes, in Zn(II) complex it was observed at 152 ppm, due to increase in electron cloud and steric hindrance. Aromatic carbon C18 and C12 attached to amidine carbon, exhibited only a slight shifting at position 111.67 ppm in all complexes, due to delocalisation electron on complexation, refered to
Fig. 1. $^{13}$C NMR spectra of ANHB ligand and their Cr(II) and Co(II) complexes
ligand tom etal charge transfer. Aromatic carbon C\textsubscript{13}, C\textsubscript{19} attached to amino group, was observed at 152.52 ppm in Co(II) and Cr(II) complexes, which was exhibited for Zn(II) complex at 147. ppm. The carbon C\textsubscript{22}, C\textsubscript{16} attached to nitro group was seen at 139.93 ppm correspond to Zn(II), Co(II) and Cr(II) complexes (Fig.2). Other carbon in phenyl ring was observed between 127.45 ppm, correspond to C\textsubscript{15} of Co(II) and Cr(II) complexes, the value for this proton in Zn(II) complex was seen at 130.5 ppm, confirming tetrahedral geometry of Zn(II) complex. Furthermore, the number of carbons calculated from the integration curves agree well with those obtained from the values of the expected CHN analyses.

2. 3-methyl-N-hydroxybenzamidine (MHB) ligand and their metal ion complexes

\(^{13}\text{C}\) NMR spectra of ligand and metal complexes displayed methyl (Ar-CH\textsubscript{3}) peak at 21.14 and 21.20 ppm, which further supported the results obtained in IR and \(^{1}\text{H}\) NMR (Fig. 2). Ligand containing phenyl ring of C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3}, C\textsubscript{4}, C\textsubscript{5} and C\textsubscript{6} carbons showing shift at δ 130.16, 127.30, 138.60, 130.99, 130.20 and 123.91 ppm respectively. Amidine moiety containing C\textsubscript{7} were assigned at more downfield δ 152.59 ppm. On complex formation, changes in chemical shifts
Fig. 3. $^{13}$C NMR spectra of MHB ligand and their Zn(II) and Co(II) complexes.
were observed. Methyl (Ar-CH$_3$) peak shifted at position $\delta$ 21.20 ppm. Amidine carbon C$_5$ and C$_8$ were shifted to more downfield at $\delta$ 145.24 ppm. In Zn(II) complex this proton was observed at 147.5 ppm.cloud and hindrance (Fig.3). Aromatic carbon C$_{10}$ and C$_{18}$ attached to amidine carbon exhibited slight shifting at position $\delta$ 129.49 ppm. Aromatic carbon C$_{18}$, attached to methyl group was observed at $\delta$ 137.23 ppm [for Co(II) and Cr(II) complexes], 142.5 ppm [for Zn(II) complex], less shifting upon complexation (Fig. 4). C$_{14}$, C$_{22}$-phenyl displayed chemical shift at $\delta$ 128.38 ppm in all complexes. Similarly C$_{15}$, C$_{23}$-phenyl peak was observed at $\delta$ 126.58 ppm [for Co(II) and Cr(II) complexes], 117 ppm [for Zn(II) complex]. Other carbon C$_{13}$, C$_{21}$-phenyl and C$_{11}$, C$_{19}$-phenyl was observed at $\delta$ 130.76 and 127.37 ppm respectively, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex. Furthermore, the number of carbons calculated from the integration curves and those obtained from the values of the expected CHN analyses agree well with each other.

3. 3-amino-N-hydroxybenzamidine (AHB) ligand and their metal ion complexes

$^{13}$C NMR spectra of ligand displayed the entire characteristic peak at the expected position which further supported the results obtained in IR and $^1$H NMR.
Fig. 5. $^{13}$C NMR spectra of AHB ligand and their metal ion complexes
Fig. 6. $^{13}$C NMR spectra of AHB Zn(II) complexe

Ligand containing phenyl ring of C$_1$, C$_2$, C$_3$, C$_4$, C$_5$ and C$_6$ carbons showing shift at 148.75, 115.70, 128.00 and 124.15, 132.27 and 112.77 ppm respectively (Fig. 5). The amino group attached to C$_8$ carbon exhibits peak downfield at 152.59 ppm, due to deshielding effect. On complex formation many changes in chemical shifts were observed. Amidine carbon C$_4$ and C$_8$ for Co(II) and Cr(II) complexes, shifted more downfield, at 149.81 ppm and 155.8 ppm corresponding to Zn(II) complex caused by the increase in electron cloud and hence hindrance. Aromatic carbon C$_{18}$ and C$_{12}$, in Co(II) and Cr(II) complexes, attached to amidine carbon C$_5$ and C$_8$ exhibited only a slight shifts at position 130.97 ppm, due to ligand to metal to charge transfer (Fig. 6). The same carbon in Zn(II) complex 140 ppm. Aromatic carbon C$_{14}$, C$_{20}$ attached to amino was observed at 147.37 ppm corresponds to Co(II) and Cr(II) complexes, for Zn(II) complex it was exhibited at 150.5 ppm. Other carbon in phenyl ring was observed between 116.68-129.45 ppm, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex. Furthermore, the number of carbons calculated from the integration curves and those obtained from the values of the expected CHN analyses agree well with each other.
4. \textit{N-4-(dihydroxy)benzamidine (PHB) and their metal ion complexes}

$^{13}$C NMR spectra of N-4-(dihydroxy)benzamidine ligand and their Cr(II), Co(II) and Zn(II)

Fig. 7. $^{13}$C NMR spectra of PHB ligand and their Zn(II) and Cr(II) complexes
complexes displayed the entire characteristic peak at the expected position which further shift at 129.18 ppm. Similarly peaks at 125.64, 153.10 and 158.48 ppm were assigned to C₄, C₈ and C₁. As the complexes were formed many changes in chemical shifts were observed. Amidine carbon C₃ and C₈ shifted higher downfield at 152.99 ppm than ligand due to increase in electron cloud and hence hindrance, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex. Aromatic carbon C₁₈ and C₁₂ attached to amidine carbon C₅ and C₈ exhibited only a slight shifting at position 111.67 ppm, due to increase in electron cloud on complexation (Fig.7).

Aromatic carbon C₁₃, C₁₉ attached to free hydroxyl group was observed at 158.99 ppm, and the carbon C₁₀, C₁₆ attached to amidine carbon at 122.71 ppm. Other carbon in phenyl ring was observed at 128.27 and 115.95 ppm. Furthermore, the number of carbons calculated from the integration curves (Fig.8) and those obtained from the values of the expected CHN analyses agree well with each other.
5. *N*-hydroxy-4-[(hydroxyimino)methyl]benzamidine (HIMB) ligand and their metal ion complexes

$^{13}$C NMR spectra of ligand displayed the entire characteristic peak at the expected position which further supported the results obtained in IR and $^1$H NMR.

Fig. 9. $^{13}$C NMR spectra of HIMB ligand and their Co(II) and Cr(II) complexes
Ligand containing aromatic ring of C₂ and C₆ carbons exhibited shift at 130.24 ppm. The C₁ and C₅ carbon gives shifting peak downward at 128.78 ppm, due to the sharing of electron of nitrogen towards the benzene ring system. Amidine moiety containing C₇ were assigned more downfield at 153.10 ppm due to deshielding effect. Another characteristic peak of distal C₁₁ was observed at 149.34 ppm. On formation of complex, many changes in chemical shifting were observed. Amidine carbon C₃ and C₈ in Co(II) and Cr(II) complexes shifted to more downfield at 161.09 ppm and 151.5 ppm in Zn(II) complex, due to increase in electron cloud and hence hindrance.

Aromatic carbon C₁₈ and C₁₀ attached to amidine carbon exhibited only a slight shifting at position 129.45 ppm, due to ligand to metal charge transfer, in all complexes. Aromatic carbon C₁₃, C₁₄ and C₁₂ attached to iminomethyl group was observed at 130.49 ppm [Co(II) and Cr(II) complexes], 130.75 ppm for ZN(II) complex. The carbon C₂₇ of iminomethyl group at 149.34 ppm. Other carbon in amidine moiety was observed at 152.99 ppm, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex. Furthermore, the number of carbons calculated from the integration curves (Fig.9 and Fig.10) and those obtained from the values of the expected CHN analyses agree well with each other.
Thermogravimetric analysis of N-hydroxyamidine and their metal ion complexes

Thermogravimetry (TG) is the branch of thermal analysis which examines the mass change of a sample as a function of temperature in the scanning mode or as a function of time in the isothermal mode. Not all thermal events bring about a change in the mass of the sample (for example melting, crystallization or glass transition), but there are some very important exceptions which include desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition [22]. Thermogravimetry is used to characterize the thermal stability of materials in various conditions and to examine the kinetics of the physicochemical processes occurring in the sample. Thermogravimetric curves are characteristic for a given polymer or compound because of the unique sequence of the physiochemical reactions that occurs over specific temperature ranges and heating rates and are function of the molecular structure. The mass change characteristics of a material are strongly dependent on the experimental conditions employed [23]. Factors such as sample mass, volume physical form, the shape and nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber, and the scanning rate have significant influences on the characteristics of the recorded TG curve.

TG curves are normally plotted with the mass change (Δm) expressed as a percentage on the vertical axis and temperature (T) or time (t) on the horizontal axis. The reaction is characterized by two temperatures, \( Ti \) and \( Tf \), which are called the procedural decomposition temperature and the final temperature, respectively. TGA makes continuous weighing of a small sample in a controlled atmosphere (e.g., air or nitrogen) as the temperature is increased at a programmed linear rate. TGA is a very simple technique for quantitatively analyzing polymer
compound (e.g., carbon black decomposed in air but not nitrogen). While oil can be readily detected in the thermogram it almost always overlaps with the temperature range of hydrocarbon polymer degradation. The curves cannot be reliably deconvoluted since the actual decomposition range of a polymer in a polymer blend can be affected by the sample morphology. In this section we have discussed thermogrametric (TGA) analysis of N-hydroxyamiidnes and their Co(II), Cr(II) and Zn(II) complexes. The spectra we have obtained, corresponding to their geometrical orientation confirms their structure [24].

**Results and discussions**

1. **Thermogravimetric studies of 3-methyl-N-hydroxybenzamidine (MHB) ligand and their metal ion complexes**

   The thermal properties of the ligand and its metal complexes were investigated by thermal gravimetric analysis (TGA). The recorded curves of 3-methyl-N-hydroxybenzamidine and their Zn(II), Co(II) and Cr(II) complexes under nitrogen atmosphere with a heating rate of 10 °C/min at temperature range 20-1000 °C is exhibited in Fig.1. The thermal decomposition of all the compounds starts at different temperature, ligand at 130 °C, Zn(II) at 150 °C and Co(II) and Cr(II) complex at 210 °C. It was observed that all the compounds decompose in one step. The Cr(II) and Co(II) complex exhibits degradation above 200 °C which shows that coordinated water molecule is removed on increase of temperature, confirms octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex.
2. Thermogravimetric studies of 3-amino-N-hydroxybenzamidine (AHB) ligand and their metal ion complexes

The thermal properties of the metal(II) complexes were investigated by thermogravimetric analysis (TGA). Fig. 2 exhibit the recorded TGA curves of the 3-amino-N-hydroxybenzamidine and three metal(II) complexes under a nitrogen atmosphere. It is observed that the TGA curves of the Cr(II) and Co(II) complexes exhibit mass loss up at 150 °C, indicating the presence of coordinated water molecules in the coordination sphere. As the temperature is increased, the TGA curves exhibit a sharp mass loss at about 150-200 °C of about 25% and 38% in Co(II) and Cr(II) complexes respectively. In Co(II) complex ligand was decomposed above 200 °C and the mass loss of 55% in the range 200-650 °C.
It was observed that Cr(II) complex decomposed in the range 200-600 °C, 28% compound decomposed in this range. Zn(II) starts decomposing at 140 °C and 25% decomposition was completed. Second step starts in the range 140-330 °C in which almost 55% compound completely decomposed into metal ZnO, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex. Ligand was observed to be decomposed in the range 130-270 °C, 75% compounds decomposed at these range.

3. Thermogravimetric studies of 2-amino-5-nitro-N-hydroxybenzamidine (ANHB) ligand and their metal ion complexes

The thermal properties of the 2-amino-5-nitro-N-hydroxybenzamidine and their Zn(II), Co(II) and Cr(II) complexes ligand and its metal complexes were investigated. Fig. 3 exhibit
the recorded TGA curve in under nitrogen atmosphere with a heating rate of 10 °C/min at temperature range of 20-1000 °C.

![TGA curves](image)

Fig. 3. TGA curve of ANHB ligand and their metal ion complex

It was observed that ligand starts decomposing at 180 °C, 50% decomposition was observed in these range. Other 30% decomposition was observed between 180-700 °C. The Co(II) and Cr(II) complexes were decomposed at 230 and 240 °C respectively. Co(II) complex decomposed in the range 230-450 °C of 45% and 53% Cr(II) complex in the range 240-400 °C. TGA curve display 35% decomposition of Co(II) complex in the range 250-550 °C and Cr(II) complex in the range 250-670 of 25%. Zn(II) decomposed in two steps, 52% decomposition was observed at 180-530 °C, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral
geometry of Zn(II) complex. Second step involve the decomposition of 25% in the range 530-600 °C.

4. Thermogravimetric studies of N-hydroxy-4-[(hydroxyimino)methyl]benzamidine ligand and their metal ion complexes

The thermal properties of the ligand and its metal complexes were investigated by thermal gravimetric analysis (TGA). Fig. 4 and 5 exhibit the recorded TGA curve of N-hydroxy-4-[(hydroxyimino)methyl]benzamidine and their Zn(II), Co(II) and Cr(II) complexes under nitrogen atmosphere with a heating rate of 10 °C/min at temperature range 20-1000 °C. It was seen that ligand start decomposing at 93 °C, 50% decomposition was observed in these range.

Other 30% decomposition was observed between 93-600 °C. The Co(II) and Cr(II) complexes were decomposed at 210 and 240 °C respectively. TGA curve display 35% decomposition of Co(II) complex in the range 250-550 °C and Cr(II) complex in the range 250-670 of 25%. Zn(II) decomposed in two steps, 52% decomposition was observed at 180-530 °C, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex. Second step involve the decomposition of 25% in the range 530-600 °C.
5. Thermogravimetric studies of N-4-(dihydroxy)benzamidine (PHB) ligand and their metal ion complexes

The thermal properties of the ligand and its metal complexes were investigated. Fig. 6 shows the recorded TGA curve of N-4-(dihydroxyl)benzamidine and their Zn(II), Co(II) and Cr(II) complexes under nitrogen atmosphere with a heating rate of 10 °C/min at temperature range 20-1000 °C. It was seen that ligand starts decomposing at 100 °C, 50% decomposition was observed in this range. Other 30% decomposition was observed between 100-400 °C. The Co(II) and Cr(II) complexes were decomposed at 250 and 260 °C respectively. Co(II) complex decomposed in the range 250-450 °C of 70% and Cr(II) complex in the range 260-400 °C of 75%, confirming octahedral nature of Co(II) and Cr(II) complexes and tetrahedral geometry of Zn(II) complex. TGA curve displayed Zn(II) decomposed in single steps and observed in the range 129-530 °C of about 60%.
Fig. 6. TGA curve of PHB ligand and their metal ion complexes

- **PHB ligand**
- **Zn(II) complex**
- **Co(II) complex**
- **Cr(II) complex**
Ultraviolet and visible spectroscopic characterization of N-hydroxyamidines and their metal ion complexes

Ultraviolet visible spectroscopic is the most important tool for the characterization of organic molecules. It helps in determination of geometrical orientation of molecules with the description of possible electronic transition. Maximum wavelength we obtain exhibits the possible hybridization and their HOMO-LUMO interactions. In this chapter we have discussed the UV-vis spectral characterization of N-hydroxyamidines and their Cr(II), Co(II) and Zn(II) complexes, using VARIAN 50-BIO UV-Vis spectrophotometer.

Results and discussions

1. UV-Vis absorption spectral studies of 3-methyl-N-hydroxybenzamidine (MHB) ligand and their metal ion complexes

The UV absorption spectra of ligands and their complexes at very low concentrations (0.02–0.08 mM range) was recorded in the wavelength range 200–700 nm using a VARIAN 50-BIO, UV–Vis spectrophotometer. It was observed that ligand display prominent peaks at around 280 nm, corresponding to π- π* transition due to phenyl ring. Another characteristic peak at 370 nm was observed due to n-π* transition of C=N group. On the formation of complex, many changes were observed. In the Zn(II) complex, blue shift were observed, the higher energy spectra of the complex shown at 260 and 300 nm correspond to the ligand π- π*transition and ligand to metal charge transfer π- π*transition. A low energy spectra were observed at 450 nm and maximum wavelength due to the LMCT (ligand to metal charge transfer) in metal ion (Fig. 1), confirming tetrahedral geometry of Zn(II) complex. Electronic spectra of Cr(II) and Co(II) complexes were also studied and found many peaks corresponding to various transitions.
Fig: 1. UV-Vis spectra of 3-methyl-N-hydroxybenzamidine and their Zn(II), Co(II) and Cr(II) complexes

Absorption at 245 and 215 nm due to ligand $\pi-\pi^*$ transition in Co(II) and Cr(II) complexes respectively in the UV region. In the UV region at 275-280 nm correspond to C=N due to n-$\pi^*$ transition, which shifted towards the lower wavelength and higher energy as the coordination with metal ions. The ligand to metal charge transfer was observed at 380 nm in Co(II) complex and 410 nm in Cr(II) complex a low energy d-d transition was observed at 530 nm (high energy) and 590 nm (low energy) for Co(II) and Cr(II) complex respectively, confirming there octahedral geometry. Magnetic moment for Co(II) complex was observed 1.5
BM which is characteristic of low spin spin d⁷ ions in octahedral field. The magnetic moment observed for Cr(II) complex is quite low (2.7 BM) for d⁴ ions in octahedral field.

2. UV-Vis absorption spectral studies of 3-amino-N-hydroxybenzamidine (AHB) ligand and their metal ion complexes

The UV absorption spectra of ligands and their complexes at very low concentrations (0.02–0.08 mM range) in CHCl₃ are recorded in the wavelength range 200–700 nm using a

![UV-Vis spectra](image)

Fig: 2. UV-Vis spectra of 3-amino-N-hydroxybenzamidine and their Zn(II), Co(II) and Cr(II) complexes
VARIAN UV–Vis spectrophotometer. It was observed that ligand display high energy prominent peaks at around 220 nm, corresponding to π- π* transition due to phenyl ring. Another characteristic peak at 315 nm was observed due to n-π* transition of C=N group, the high energy peak as same as the former peak rise due to the presence of electron withdrawing amino group at meta position. On complex formation, many changes were observed (Fig.2). In Zn(II) complex, lower energy spectra was observed at 280-350 nm corresponding to the ligand π- π*transition and ligand to metal charge transfer n- π*transition.

Another high energy sharp spectrum was observed at 395 nm and maximum wavelength due to ligand to metal charge transfer spectra (Fig. 2), confirming tetrahedral geometry of Zn(II) complex. The electronic spectra of Cr(II) and Co(II) complexes were also studied and found 3-4 peaks corresponding to various transitions. The shift at 210 nm is due to ligand π- π*transition in Co(II) and Cr(II) complexes in the UV region. In the UV region at 300 nm correspond to C=N due to n-π*transition, which shifted towards the lower wavelength and higher energy on coordination with metal ions. The ligand to metal charge transfer was observed at 400 nm in Cr(II) complex. A low energy d-d transition was observed at 500 nm (high energy) and 530 nm (low energy) in Co(II) and Cr(II) complex respectively, confirming thier octahedral geometry. Magnetic moment for Co(II) complex was observed 1.8 BM which is characteristic of low spin spin d^7 ions in octahedral field. The magnetic moment observed for Cr(II) complex is quite low (2.9 BM) for d^4 ions in octahedral field.

3. UV-Vis absorption spectral studies of 2-amino-5-nitro-N-hydroxybenzamidine (ANHB) ligand and their metal ion complexes

The UV absorption spectra of ligands and their complexes at very low concentrations using CHCl₃ as solvent were recorded in the wavelength range 200–700 nm using a VARIAN
UV–Vis spectrophotometer. It is observed that ligand display prominent peaks at around 280 nm, corresponding to π- π* transition due to phenyl ring.

![Graph showing UV-Vis spectra](image)

Fig: 3. UV-Vis spectra of 2-amino-5-nitro-N-hydroxybenzamidine and their Zn(II), Co(II) and Cr(II) complexes

Another characteristic peak at 380 nm was observed due to n-π* transition of C=N group. On complex formation many changes were seen. In the Zn(II) complex blue shift were observed, the higher energy spectra of the complex was shown sharp and broad peak at 305 and small peak at 440 nm correspond to the ligand π- π*transition and ligand to metal charge transfer
\[ \pi-\pi^* \text{transition and as maximum wavelength also due to the LMCT (ligand to metal charge transfer) in metal ion, confirming tetrahedral geometry of Zn(II) complex (Fig. 3).} \]

The electronic spectra of Cr(II) and Co(II) complexes were also studied and found many peaks corresponding to various transitions. The shift at 210 and 215 nm due to ligand \( \pi-\pi^* \) transition in Co(II) and Cr(II) complexes respectively in the UV region. In the UV region at 270-285 nm correspond to \( n-\pi^* \) transition in C=N, which shifted lower wavelength and higher energy on coordination with metal ions.

The ligand to metal charge transfer was observed at 365 nm in Co(II) complex and 410 nm in Cr(II) complex. A low energy d-d transition was observed at 520 nm (high energy) and 590 nm (low energy) in Co(II) and Cr(II) complex respectively, confirming there octahedral geometry. Magnetic moment for Co(II) complex was observed 1.8 BM which is characteristic of low spin spin \( d^7 \) ions in octahedral field. The magnetic moment observed for Cr(II) complex is quite low (2.9 BM) for \( d^4 \) ions in octahedral field.

4. UV-Vis absorption spectral studies of N-hydroxy-4-[(hydroxyimino)methyl]benzamidine (HIMB) ligand and their metal ion complexes

The UV absorption spectra of ligands and their complexes at very low concentrations are recorded in the wavelength range 200–700 nm using a VARIAN UV–Vis spectrophotometer. It was observed that ligand displayed peaks at around 260 nm, corresponding to \( \pi-\pi^* \) transition due to phenyl ring. Another characteristic peak at 350 nm was observed due to \( n-\pi^* \) transition of C=N group. On complex formation many changes were observed. In the Zn(II) complex, higher energy spectra was exhibited at 245 and 310 nm corresponding to the ligand \( \pi-\pi^* \) transition and ligand to metal charge transfer \( \pi-\pi^* \) transition. A low energy spectra was observed at 420 nm and maximum wavelength due to the LMCT (ligand to metal charge transfer) in metal ion,
confirming tetrahedral geometry of Zn(II) complex. Electronic spectra of Cr(II) and Co(II) complexes were also studied and many peaks were observed corresponding to various transitions. Absorbance at 230 and 205 nm due to ligand π-π*transition in Co(II) and Cr(II) complexes respectively in the UV region (Fig 4 and 5).

Fig: 4. UV-Vis spectra of HIMB and their Zn(II) complex

Fig: 5. UV-Vis spectra of HIMB ligand and their metal ion complexes
In the UV region at 280-300 nm correspond to C=N due to n-\(\pi^*\)transition, which shifted towards the lower wavelength and higher energy on coordination with metal ions. The ligand to metal charge transfer was observed at 505 nm in Co(II) complex and 425 nm in Cr(II) complex. A low energy d-d transition was observed at 510 nm (low energy) and 580 nm (low energy) in Co(II) and Cr(II) complex respectively, confirming there octahedral geometry. Magnetic moment for Co(II) complex was observed 1.6 BM which is characteristic of low spin spin d\(^7\) ions in octahedral field. The magnetic moment observed for Cr(II) complex is quite low (2.6 BM) for d\(^4\) ions in octahedral field.

5. **UV-Vis absorption spectral studies of N-4-(dihydroxy)benzamidine (PHB) ligand and their metal ion complexes**

The UV absorption spectra of ligands and their complexes at very low concentrations in CHCl\(_3\) are recorded in the wavelength range 200–700 nm using a VARIAN UV–Vis spectrophotometer. It was observed that ligand display prominent peaks at around 240 nm, corresponding to \(\pi-\pi^*\) transition due to phenyl ring. Another characteristic peak at 360 nm was observed, due to n-\(\pi^*\) transition of C=N group. On complex formation, many changes were seen. In the Zn(II) complex, 200 nm correspond to the ligand \(\pi-\pi^*\) transition and the absorbance at 302 nm correspond to n-\(\pi^*\) transition.

Low energy spectra were observed at 400 and 440 nm and maximum wavelength due to the the LMCT (ligand to metal charge transfer) in metal ion, confirming tetrahedral geometry of Zn(II) complex (Fig. 6). The electronic spectra of Cr(II) and Co(II) complexes were also studied and found many peaks corresponding to various transitions. The shift at 200 nm due to ligand \(\pi-\pi^*\) transition both in Co(II) and Cr(II) complexes respectively in the UV region. In the UV region at 305 and 310 nm correspond to C=N due to n-\(\pi^*\) transition, which shifted towards the
lower wavelength and higher energy on coordination with metal ions. The ligand to metal charge transfer was observed at 510 nm in Co(II) complex and 600 nm in Cr(II) confirming there octahedral geometry. Magnetic moment for Co(II) complex was observed 1.7 BM which is characteristic of low spin spin d^7 ions in octahedral field. The magnetic moment observed for Cr(II) complex is quite low (2.8 BM) for d^4 ions in octahedral field.

Fig: 6. UV-Vis spectra of PHB ligand and their metal ion complex
Mass spectral analysis of N-hydroxyamidines and their metal ion complexes

Mass spectrometry (MS) is a tool that produces spectra (singular spectrum) according to the masses of molecules. The spectra are used for the determination of elemental or isotopic abundance. The masses of particles and molecules elucidate the chemical structures of molecules, such as peptides and other chemical compounds. Mass spectrometry starts by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios. In a typical MS procedure, a sample, which may be solid, liquid or gas is ionized by bombarding it with electrons [28-35].

This may cause some of molecules to break into charged fragments, which are separated according to their mass-to-charge ratio (m/z). Typically by accelerating in an electric or magnetic field, ions undergo deflection. Results are displayed as spectra of the relative abundance of ions as a function of the mass-to-charge ratio. The atoms or molecules in the sample can be identified by correlating known masses to the identified masses or through a characteristic fragmentation pattern. In this section we have discussed the mass spectral studies of N-hydroxyamidines and their Cr(II), Co(II) and Zn(II) complexes and their interpretation [36-41]. The spectra we have obtained correspond to their geometrical orientation confirming their structure.
Scheme 2: Mass fragmentation pattern of ANHB Co(II) complex
RESULTS AND DISCUSSION

1. Mass analysis of N-4-(dihydroxy)benzamidine (PHB) and their metal ion complexes

Mass spectral analysis of PHB ligand and their metal ion complexes were performed using ESI-MASS spectral analyzer. The molecular ion peak of N-4-(dihydroxy)benzamidine and Zn(II), Cr(II) and Co(II) was observed at m/z 152.15, 366.03, 390.31 and 397.05 respectively are correspond to their molecular formula as the parent ion peak with 100% intensity. The ligand loses hydroxyl (Ar-OH) shown at 136.15. Further fragmentation was observed at 120.15 for
amidine OH atom and phenyl group removed on further electronization shown value at 29.04. Tetrahedral geometry of Zn(II) complex was confirmed upon no loss of water molecule. The m/z value at 351.69, 335.59, 259.59, 183.50, 143.57, 103.62 correspond to OH, distal OH, phenyl ring, distal phenyl ring, C=N group and distal C=N group of Zn(II) complex. Similarly Cr(II) and Co(II) complexes were confirmed their octahedral geometry using mass fragmentation pattern. The coordinated water molecule was removed and observed at m/z 390.06 and 372.29. Other values were observed at their corresponding values, 354.28, 338.28, 246.18, 170.09, 153.09, 126.73 were measured due to fragmentation of OH, distal OH, phenyl ring, distal phenyl ring, C=N group of amidine moiety. Other m/z values were at their corresponding position (Fig.1), results have well correlation with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex.

2. N-hydroxy-4-[(hydroxyimino)methyl]benzamidine (HIMB) and their metal ion complexes

The mass spectral characterization of N-hydroxy-4-[(hydroxyimino)methyl]benzamidine and their Zn(II), Cr(II) and Co(II) complexes were performed to confirm their orientation. The molecular ion peak at m/z 179.10, 444.32, 451.29 and 421.74 corresponds to ligand, Cr(II), Co(II) and Zn(II) complexes related to their molecular weight (Fig.2). The peak at 163.17, 404.74, 398.26 and 391.33 corresponds to the isotopic abundance after removal of distal hydroxyl group. Phenyl ring was removed and the peak was observed at 253.12 and 177.02 in Zn(II) complex and 259.59, 246.8 and 170.09 in Cr(II) and Co(II) complexes.

The water molecule was removed and the corresponding peak was observed at 433.2 and 415.26 for Co(II) complex, 426.34 and 408.33 for Cr(II) complex. The removal of coordinated water molecule in both these complexes confirms their octahedral geometry. The C=N group was
removed as free radical and the peak was observed at m/z value at 151.01, 158.49, 120.15 and 144.08 corresponds to Co(II), Zn(II), ligand and Cr(II) complexes respectively. The ZnO remained as residue in Zn(II) complex NH$_2$ was remained as residue in Cr(II) and Co(II) complexes.

Fig: 2. FAB MASS spectra of HIMB ligand and their metal complexes

3. **2-amino-5-nitro-N-hydroxybenzamidine (ANHB) and their metal ion complexes**

The mass spectra observed as molecular ion peak at m/z, 196.16, 478.29, 485.27 and 455.71 corresponds ligand, Cr(II), Co(II) and Zn(II) complexes. The nitro group was removed and the peak was observed at m/z, 135.6, 404.24, 365.72 and 397.30 for ligand, Co(II), Cr(II) and Zn(II) complexes respectively. Fragmentation peak after removal of amino group (Ar-NH$_2$) was found
at 120.15, 337.29, 335.69 and 344.23 for ligand, Co(II), Cr(II) and Zn(II) complexes respectively. It was observed that m/z value after the removal of phenyl ring as free radical values were recorded at 44.05, 246.18, 253.12 and 259.59 for ligand, Co(II), Cr(II) and Zn(II) complexes respectively. Other spectra were observed at their corresponding position. The residue for Zn(II) complex was ZnO and NH$_2$ for others were observed (Fig: 3), results have well correlation with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex.

Fig: 3. FAB MASS spectra of ANHB ligand their metal complexes
4. 3-amino-N-hydroxybenzamidine (AHB) and their metal ion complexes

The molecular ion peak was observed at m/z, 151.16, 366.72, 388.74 and 395.27 corresponds to ligand, Zn(II), Co(II) and Cr(II) complexes according to their molecular weight. The amino group (Ar-NH₂) was removed as free radical and the residue gives the peak at 120.15, 335.69, 337.29 and 344.23 for ligand, Zn(II), Cr(II) and Co(II) complexes. The hydroxyl group amidine moiety from ligand and the residue was confirmed at m/z 135.16. The octahedral geometry of Co(II) and Cr(II) complexes were confirmed by the removal of coordinated water and the corresponding peak at 377.26 and 370.32 for Co(II) and Cr(II) complexes respectively. The m/z value observed at m/z, 29.04, 83.50, 246.8 and 177.02 for ligand, Zn(II), Cr(II) and Co(II) complexes respectively. Other peaks were observed at their corresponding position (Fig: 4),

Fig: 4. FAB-MASS spectra of AHB ligand and their Zn(II), Co(II) and Cr(II) complexes
results have well correlation with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex.

5. 3-methyl-N-hydroxybenzamidine (MHB) and their metal ion complexes

The molecular ion peak was observed at m/z, 150.17, 363.74, 386.36 and 393.30 corresponds to ligand, Zn(II), Cr(II) and Co(II) complexes according to their molecular weight. The amino group (Ar-CH₃) was removed as free radical and the residue gives the peak at 136.17, 349.72, moiety from ligand and the residue was confirmed at m/z 120.15. The octahedral geometry of 322.28 and 343.24 for ligand, Zn(II), Co(II) and Cr(II) complexes. The hydroxyl group amidine
Co(II) and Cr(II) complexes were confirmed by the removal of coordinated water and the corresponding peak at 350.33 and 357.27 for Cr(II) and Co(II) complexes respectively (Fig.7). The m/z value observed as the removal of phenyl ring at m/z, 29.04, 83.50, 246.8 and 177.02 for ligand, Zn(II), Cr(II) and Co(II) complexes respectively. Other peaks were observed at their corresponding position (Fig. 5), results correlates well with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex.

**Elemental analysis**

We have conducted elemental analysis of N-hydroxyamidine and their metal ion complexes using Perkin CHN analyser and the results were recorded. Results exhibited the expected values.

1. **Elemental composition of 2-amino-5-nitro-N-hydroxybenzamidine (ANHB) ligand and their metal ion complexes**

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<th>Compounds</th>
<th>Elemental composition (%)</th>
<th>M.p. (°C)</th>
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<td>M.wt.</td>
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<tr>
<td>C14H18N8O8Co</td>
<td>485.27</td>
<td>42.86</td>
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2. **Elemental composition of 3-methyl-N-hydroxybenzamidine (MHB) ligand and their metal ion complexes**

<table>
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<th>Elemental composition (%)</th>
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<td>C16H18N4O2Co</td>
<td>357.27</td>
<td>53.79</td>
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### 3. Elemental composition of 3-amino-N-hydroxybenzamidine (AHB) ligand and their metal ion complexes

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<th>H</th>
<th>N</th>
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### 4. Elemental composition of N-hydroxy-4[(hydroxyimino)methyl]benzamidine (HIMB) ligand and their metal ion complexes

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<th>Elemental composition (%)</th>
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<th>H</th>
<th>N</th>
<th>O</th>
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### 5. Elemental composition of N-4-(dihydroxy)benzamidine (PHB) ligand and their metal ion complexes

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<th>Elemental composition (%)</th>
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Infrared spectral characterization

Infrared (IR) radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions. Of greatest practical use to the organic chemist is the limited portion between 4000-400 cm\(^{-1}\). From the brief theoretical discussion that follows, it is clear that even a very simple molecule can give an extremely complex spectrum. The organic chemist takes advantage of this complexity when matching the spectrum of an authentic sample. A peak by peak correlation is excellent evidence for identity. Any two compounds except enantiomer, are unlikely to give exactly the same IR spectrum.

The infrared spectra of hydroxyamidines and their metal complexes have been examined and empirical assignments have been made for principal absorption bands associated with O-H, C=N, C-NH, N-O and Ar-H stretching vibrations.

In hydroxyamidines the vibrations due to -OH group should be observed in the range 2900-3000 cm\(^{-1}\), because the intramolecular hydrogen bonding involving the azomethyne nitrogen is not possible due to protonation. C=N and C-N band observed between 1600-1650 cm\(^{-1}\) and 2400-2550 cm\(^{-1}\). C-N should appear at lower frequency due to presumable loss of meromism which will result in an increase in the single bond character. N-O stretching vibration is assigned in the region 915-950 cm\(^{-1}\). C-H stretching frequencies associated with aromatic rings generally appear in the region 3030 cm\(^{-1}\) and 600-1000 cm\(^{-1}\). In this section we have discussed the infrared spectral analysis of Co(II), Cr(II) and Zn(II) complexes of N-hydroxyamidines, characterized using SCHIMADZU 8400S FTIR spectrometer.
Results and discussions

1. FTIR spectra of 2-amino-5-nitro-N-hydroxybenzamidine (ANHB) and their metal ion complexes

The IR spectra of the complexes have been examined in comparison with the spectra of the ANHB ligand.

Fig. 1. IR vibrations of ANHB ligand and their Co(II) complex

IR spectra of the ligand in particular show main characteristic absorptions in the range 1628, 930, 2850, 3310 and 3270 cm\(^{-1}\), which can be assigned to C=N, NO, NH\(_2\) and OH stretching
Fig. 2. IR vibrations of ANHB Co(II) and Zn(II) complexes

vibrations respectively. All the other functional group vibrations are appeared at their expected positions (Fig 1 and 2). The characteristic peak for NH$_2$ and NO$_2$ group in ligand was appeared at 3350 (as broad peak) and 1300 cm$^{-1}$, another N-H stretching vibrations was observed between
1530-1610 cm\(^{-1}\) on coordination. Another peak for nitro group (Ar-NO\(_2\)) was observed 1250-1300 cm\(^{-1}\) correspond to ligand. On coordination of Zn(II), Cr(II) and Co(II) metal ion with ligand, (OH) frequency disappeared and new M-O bond formed having stretching frequencies 400, 450 and 400 cm\(^{-1}\) respectively. Metal(II) ion also coordinates with (NH\(_2\)) gave M-N vibration at 540, 600 and 500 cm\(^{-1}\) corresponding to Zn(II), Cr(II) and Co(II) complexes respectively. The (C=\(N\)) bond also exhibited as strong stretching vibrations at 1680, 1640 and 1628 for Co(II), Cr(II) and Zn(II) respectively.

The (Ar-NH\(_2\)) amino group attached to benzene ring exhibited between 3100-3600 cm\(^{-1}\) as very broad band in Cr(II) and Co(II) complexes, similarly amino group was observed at 3600 cm\(^{-1}\). Nitro group (NO\(_2\)) was observed 1320-1350 cm\(^{-1}\) for all metal complexes. Aryl ring exhibited as the vibrations between 800-1200 cm\(^{-1}\). Results have well correlation with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex.

2. FTIR studies of 3-methyl-N-hydroxybenzamidine (MHB) and their metal ion complexes

The IR vibrational spectra of the complexes have been examined in comparison with the spectra of the MHB ligand. Ligand in particular exhibit main characteristic absorptions in the range 1690, 1072, 3259 and 3315 cm\(^{-1}\), which can be assigned to C=\(N\), NO, NH\(_2\) and OH stretching vibrations, respectively (Fig.3). A small band in IR vibration of methyl (Ar-CH\(_3\)) group was observed at 2972 cm\(^{-1}\). A combination of (C=\(N\)), (NOH) and (C-\(N\)) is observed very strong band in IR at 1662 cm\(^{-1}\). The C-N band appears at 1381 cm\(^{-1}\). The C-C stretching of benzene ring appeared between 1288-890 cm\(^{-1}\). All the other functional group vibrations are appeared at their expected positions. On coordination of Zn(II), Cr(II) and Co(II) metal ion with
ligand, (O-H) frequency disappeared and new M-O bond formed having stretching frequencies 440, 500 and 450 cm$^{-1}$ respectively (Fig.3). Metal ion also coordinate with (-NH$_2$) group, gave asymmetric stretching vibration between 594-634 cm$^{-1}$. Methyl group (Ar-CH$_3$) was assigned between 2850-2950 cm$^{-1}$ for all compounds. The N-O and C-N vibration was observed between 760-790 cm$^{-1}$ and 1400-1450 cm$^{-1}$. The (C=N) bond also exhibited stretching frequencies at 1680, 1652 and 1640 cm$^{-1}$ Zn(II), Cr(II) and Co(II) complexes as compared to other complexes.
The phenyl C-C and C-H vibration were observed between 800-1200 cm\(^{-1}\). The IR vibration of M-N was observed as strong peak at 600 cm\(^{-1}\) in Co(II) and Cr(II) complexes, at 580 cm\(^{-1}\) for Zn(II) complex. Results have well correlation with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex (Fig. 4).

Fig. 4. IR vibrations of MHB Co(II) and Zn(II) complexes
3. IR spectral studies of N-hydroxy-4-[(hydroxyimino)methyl]benzamidine (HIMB) and their metal ion complexes

The IR spectra of the complexes have been examined in comparison with the spectra of the HIMB ligand.

Fig. 5. IR vibrations of HIMB ligand and their Co(II) complex
The IR spectra of the complexes have been examined in comparison with the spectra of the N-hydroxy-4-[(hydroxyimino)methyl]benzamidine ligand (Fig.5). IR spectra of the ligand in particular show main characteristic absorptions in the range 1653, 972, 2914, 3495 and 3292 cm$^{-1}$, which can be assigned to C=N, NO, C-N, distal OH and amidine OH stretching vibrations,
respectively. All the other functional group vibrations are appeared at their expected positions. The characteristic peak for distal OH and C-NH vibrational peak in ligand was observed at 3100-3200 cm\(^{-1}\). On coordination of Zn(II), Cr(II) and Co(II) metal ion with ligand, (amidine OH) frequency disappeared and new M-O bond formed having stretching frequencies 440, 390 and 450 cm\(^{-1}\) respectively (Fig.6). Metal(II) ion also coordinates with (NH\(_2\)) gave transmittance between 511-580 cm\(^{-1}\). The C=N and C-N bond also exhibited stretching frequencies higher in Co(II) complex of value 1648 cm\(^{-1}\), as compared to ligand (1660 cm\(^{-1}\)) and other complexes. The Zn(II) and Cr(II) complexes showed vibrational peak at 1680 and 1700 cm\(^{-1}\) respectively. Distal OH and C=NH vibrational peak in metal complexes were observed at 3150-3600 cm\(^{-1}\). Other peaks were observed at their respective positions.

4. **FTIR spectra of N-4-(dihydroxy)benzamidine (PHB) and their metal ion complexes**

The IR spectra of the complexes have been examined in comparison with the spectra of the PHB ligand. IR spectra of the ligand in particular show main characteristic absorptions in the range 1600, 1000, 2850 and 3300 cm\(^{-1}\), which can be assigned to C=N, NO, C-NH and OH stretching vibrations, respectively. All the other functional group vibrations are appeared at their expected positions. The characteristic peak for OH group para position in ligand was appeared at 3500 cm\(^{-1}\) (Fig.7).

On coordination of Zn(II), Cr(II) and Co(II) metal ion with ligand, OH frequency disappeared and new M-O bond formed having stretching frequencies 440, 510 and 430 cm\(^{-1}\) respectively. Metal(II) ion also coordinates with =NH gave stretching vibrations 520, 610 and 500 cm\(^{-1}\). The C=N bond also showed stretching frequencies at 1650, 1610 and 1600 for Co(II) Zn(II) and Cr(II) complexes. The OH group attached at para position to benzene ring exhibited at 3580, 3300 and 3600 cm\(^{-1}\) for Zn(II), Cr(II) and Co(II) complexes respectively. The C-N
stretching was observed at 1400, 1500 and 1550 cm\(^{-1}\) for Zn(II), Cr(II) and Co(II) complexes respectively. The N-O bond exhibited vibration at 1300, 1400 and 1350 cm\(^{-1}\) respectively. Results have well correlation with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex (Fig.8).

Fig. 7. IR vibrations of PHB ligand and their Co(II) complex
5. FTIR spectra of 3-amino-N-hydroxybenzamidine (AHB) and their metal ion complexes

The IR spectra of the complexes have been examined in comparison with the spectra of the AHB ligand. IR spectra of the ligand in particular show main characteristic absorptions in the range 1590, 1410, 2850 and 3200 cm\(^{-1}\), which can be assigned to C=N, NO, NH and OH stretching vibrations, respectively. All the other functional group vibrations are appeared at their
Fig. 9. IR vibrations of AHB ligand and their Co(II) complex

expected positions (Fig.9). The characteristic peak for Ar-NH$_2$ group in ligand was appeared at 3500 cm$^{-1}$, which upon coordination shifted in the range 1530-1610 cm$^{-1}$. On coordination of Zn(II), Cr(II) and Co(II) metal ion with ligand, (OH) frequency disappeared and new M-O bond formed having stretching frequencies 450, 460 and 430 cm$^{-1}$ respectively. Metal(II) ion also
coordinate with (=NH) gave transmittance between 560, 590 and 510 cm\(^{-1}\). The C=N bond also exhibit stretching frequencies at 1600, 1610 and 1670 for Zn(II), Cr(II) and Co(II) complexes respectively. The C-N bond was observed at 1700, 1710 and 1600 cm\(^{-1}\). N-O and N-H vibrations
were exhibited at 1390, 1310 and 1350 corresponding to Zn(II), Cr(II) and Co(II) complexes respectively (Fig.10). Aryl ring exhibited as the vibrations between 800-1200 cm\(^{-1}\). The amino (Ar-NH\(_2\)) group attached to benzene ring at meta position exhibited stretching at 3200-3600 cm\(^{-1}\) for Zn(II), Cr(II) and Co(II) complexes. All the results have well correlation with expected values confirming the ligand structure and tetrahedral geometry of Zn(II) and octahedral geometry of Cr(II) and Co(II) complex.

### Conclusion

These sectioned was aimed to the spectral and structural characterization of N-hydroxyamidines and their metal ion complexes. The results exhibit well correlation with the structural properties using FTIR, UV-Vis, Mass, \(^1\)H NMR, \(^{13}\)C NMR spectral, Elemental analysis and TGA analysis. All the spectral and structural analysis of N-hydroxyamidine and their metal ion complexes. TGA and MASS analysis confirmed the coordinated water molecules and the their octahedral geometry. Similar analysis that Zn(II) complex exhibit its tetrahedral geometry. FTIR, NMR, magnetic moment and Elemenal analysis velas the hybridization and the behavior of surrounding molecules of hydroxyamidines and their metal complexes. We confirm the synthesis and geometrical orientation as well as thermal properties and elemental compostion of ligand and their metal.
Reference