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SYNTHESIS AND CHARACTERIZATION OF Mn(II), Ni(II), Fe(III), Co(III), Cu(II), Zn(II) AND Cd(II) COMPLEXES OF o-HYDROXYBENZOIC ACID HYDRAZIDE

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ABSTRACT

A series of complexes of o-Hydroxybenzoic acid hydrazide (HBH) with Mn(II), Ni(II), Fe(III), Co(III), Cu(II), Zn(II) and Cd(II) were synthesized. The stoichiometry and structures for the complexes have been established by elemental analysis, electrical conductivity measurements, magnetic moment measurements and spectral (UV-Vis, IR and NMR) studies.

KEYWORDS

Metal Complexes, Hydroxybenzoic acid hydrazide Ligand, Characterization, Stoichiometry and Geometry

RESUMO

Uma série de complexos da hidrazida do ácido o-hidroxibenzóico (HBH) com Mn(II), Ni(II), Fe(III), Co(III), Cu(II), Zn(II) e Cd(II) foram sintetizados. A estequiometria e a estrutura dos complexos foram estabelecidas usando análise elementar, medidas de condutância elétrica, momento magnético e estudos espectroscópicos de uv-visível, infravermelho e ressonância magnética nuclear.

PALAVRAS-CHAVE

Complexos metálicos, Hidrazida do ácido hidroxibenzóico com ligante, Caracterização, Estequiometria e Geometria

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INTRODUCTION

In the recent past, there has been a growing interest in the synthesis and characterization of metal complexes of hydrazides. The obvious reason being the metal coordinated complexes of hydrazides act as effective antimicrobial agents[1,2]. Various research articles have described the fungicide and bactericide properties of metal complexes of hydrazides and hydrazones[3-8]. They have indicated that, hydrazides have remarkable antimicrobial, anticonvulsant, analgesic, anti inflammatory and antitumorial activities[9-15]. The biological activity is due to the existence of potential sites for metal ions[16-18] namely $-\overset{|}{C}=O$, N-H and $-NH_2$ that can be engaged in complexation with the transition metal ions[19,20]. Isonicotinic acid hydrazide is a drug of proven therapeutic importance and is used against a wide spectrum of bacterial ailments e.g., tuberculosys[21]. Agarwal et al have investigated the coordinating ability of hydrazide derivatives with metal ions[22]. Many such articles reported in the literature serve as the testimony for the versatility of these compounds to their potential chelating and antimicrobial abilities. In view of the versatile importance of hydrazides, the authors made an attempt to synthesize and characterize certain metal complexes of HBH.

EXPERIMENTAL

All chemical and reagents used were analytical grade obtained from Merck, India.

The stock solutions Mn(II), Ni(II), Fe(III), Co(III), Cu(II), Zn(II) and Cd(II) were prepared by dissolving appropriate amounts manganous sulphate, nickel(II) sulphate, ferric chloride, cobalt(II) nitrate [Cobalt(II) solution by aerial oxidation is converted to cobalt(III)], copper(II) sulphate, zinc(II) sulphate and cadmium(II) sulphate in required amount of double distilled water.

An Elico pH meter supplied by ELICO Private Limited, Hyderabad, India used for pH measurements.

Synthesis of o-Hydroxybenzoic acid hydrazide (HBH)

Required amounts of methyl salicylate, hydrazine hydrate and 100 mL of methanol were taken in a 250 mL round bottom flask. The contents of the flask were refluxed for about 2 hours at 35-40°C. A white crystalline solid separated out after cooling was filtered and washed with aqueous methanol. The crude sample was recrystallysed from aqueous methanol. (Melting point: 147°C)

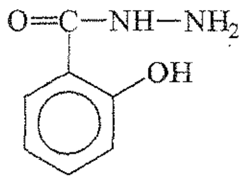


Figure 1. Structure of o-Hydroxybenzoic acid hydrazide

Synthesis of Metal-HBH complex

A methanolic solution containing the metallic salt and HBH in required concentrations was refluxed for about one hour in a 250 mL round bottomed flask. The crystalline sample (pale pink-Mn(II)-HBH; light green-Ni(II)-HBH; dark brown-Fe(III)-BAH; dark pink- Co(III)-HBH;

bluish green-Cu(II)-HBH; light yellow-Zn(II)-HBH and yellow-Cd(II)-BAH) obtained on cooling was filtered, washed with distilled water and finally dried in vacuo.

RESULTS AND DISCUSSION

Elemental analysis

The elemental analysis and magnetic moment data of HBH and its metal complexes under investigation are presented in Table 1.

Table 1. Analytical data of complexes under investigation.

S.No.	Complex	Colour	Melting point °C	Molecular weight	Found (Cal)%				μ_{eff} BM	Molar Conductivity ohm^{-1} cm^{2} mole^{-1}
					C	H	N	M		
1.	HBH	Yellow	220	152	55.20 (55.26)	5.19 (5.26)	18.39 (18.42)	-	-	-
2.	Mn(II)-HBH	Pale yellow	194	428	39.21 (39.28)	3.20 (3.30)	13.01 (13.09)	12.63 (12.83)	5.20	12.6
3.	Fe(III)-HBH	Dark brown	206	509	49.45 (49.53)	4.05 (4.15)	16.43 (16.50)	10.89 (10.97)	1.96	14.8
4.	Co(III)-HBH	Dark pink	117	512	49.12 (49.23)	4.03 (4.13)	16.33 (16.40)	11.30 (11.50)	Diamagnetic	-
5.	Ni(II)-HBH	Light green	110	432	38.83 (38.93)	3.17 (3.27)	12.90 (12.97)	13.41 (13.59)	3.20	28.4
6.	Cu(II)-HBH	Bluish green	121	366	45.88 (45.96)	3.76 (3.86)	15.24 (15.32)	17.18 (17.37)	2.05	22.5
7.	Zn(II)-HBH	Light yellow	181	368	45.66 (45.74)	3.74 (3.84)	15.18 (15.24)	17.59 (17.78)	Diamagnetic	-
8.	Cd(II)-HBH	Yellow	283	415	40.50 (40.55)	3.30 (3.40)	13.45 (13.51)	26.94 (27.10)	Diamagnetic	-

The elemental analysis data of the complexing agent and its complexes were in agreement with the theoretically calculated values shown in the parenthesis. The stoichiometry of the complexes have been deduced from the data and was found to be 1:2 (Metal : Ligand) for the

Mn(II), Ni(II), Zn(II), Cu(III) and Cd(II)-HBH complexes and 1:3 (Metal : Ligand) for Co(III) and Fe(III)-HBH complex.

Molar conductivity data

The molar conductivity values of the metal complexes determined in dimethylformamide solutions of concentration 1 × 10^{-3} M are presented in Table 1. The molar conductivity values were in the range 12.6 – 28.4 ohm^{-1} cm^{2} $mole^{-1}$. This suggests the non-electrolytic behavior[23] of the metal complexes under investigation.

Electronic spectral details

UV-Vis spectra of the complexes were recorded in the solid phase and are presented in Table 2 and in Figure 2 – Figure 6.

Table 2. Electronic spectral data

Complex	Frequency			ν_2/ν_1	B	β
	ν_1	ν_2	ν_3			
Mn(II)-HBH	15506	17730	22701	1.143	860	1.1631
Fe(III)-HBH	9852	11383	18215	1.155	1015	0.6241
Co(III)-HBH	-	19724	27435	-	1065	-
Ni(II)-HBH	11167	18832	24845	1.686	1030	0.6586
Cu(II)-HBH	17778	27100	-	1.524	-	-
Zn(II)-HBH	-	-	-	-	-	-
Cd(II)-HBH	-	-	-	-	-	-

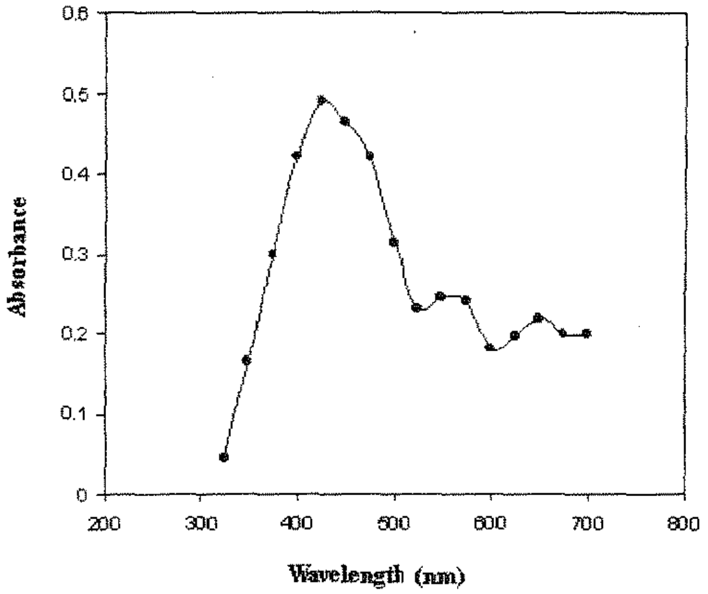


Figure 2. UV-Vis spectrum of Mn(II)-HBH complex

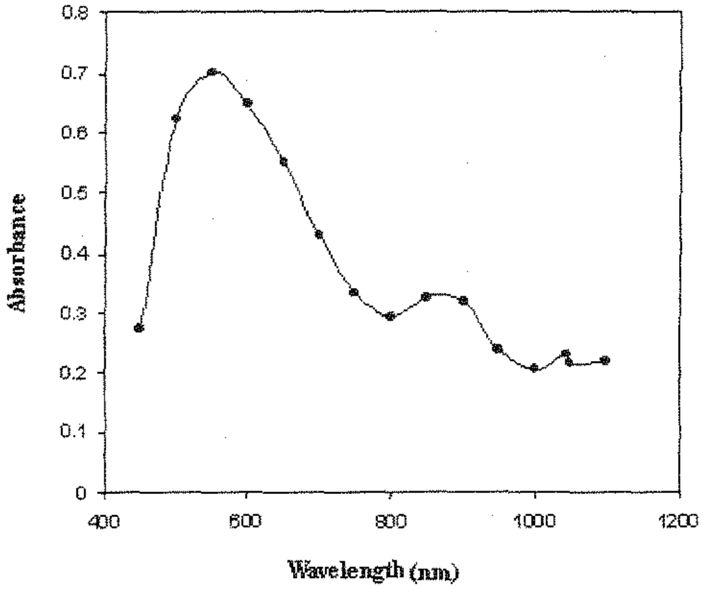


Figure 3. UV-Vis spectrum of Fe(III)-HBH complex

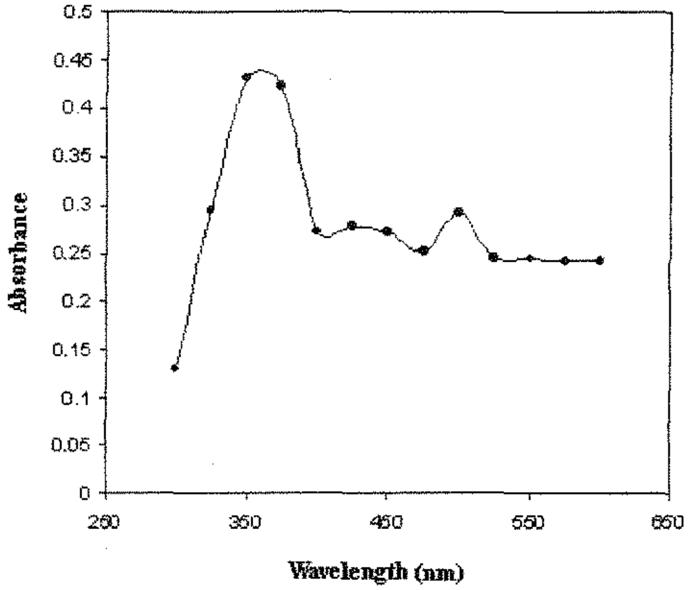


Figure 4. UV-Vis spectrum of Co(III)-HBH complex

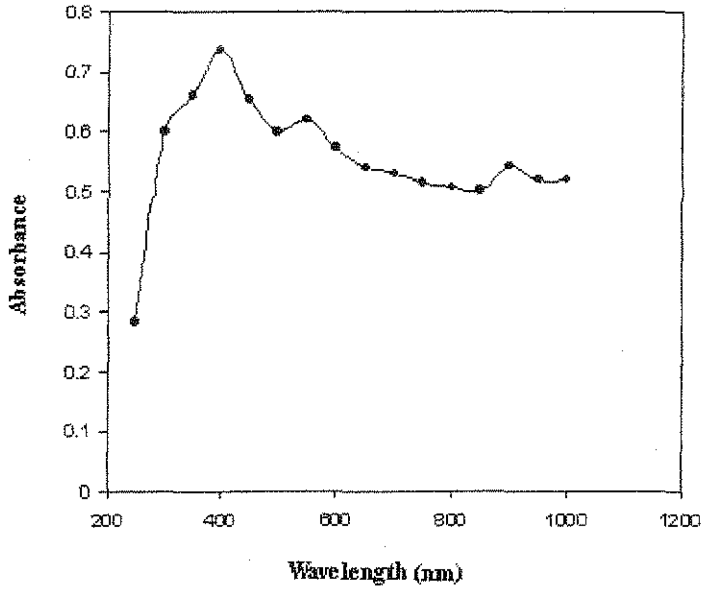


Figure 5. UV-Vis spectrum of Ni(II)-HBH complex

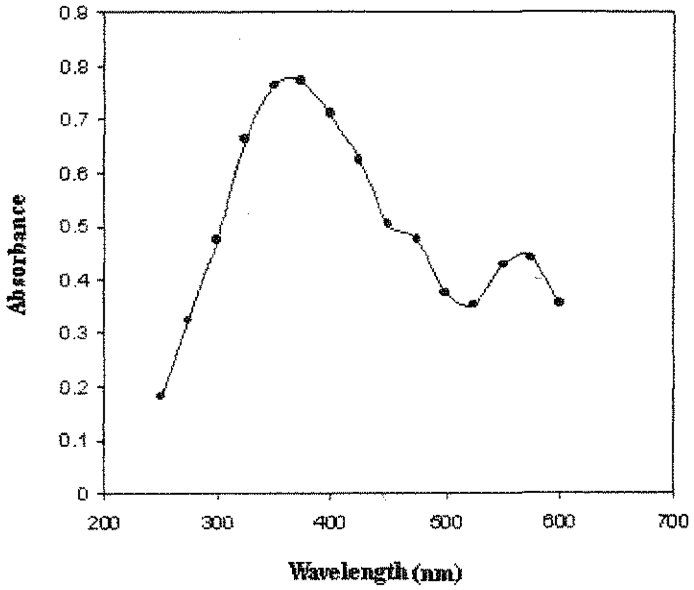


Figure 6. UV-Vis spectrum of Cu(II)-HBH complex

Majority of manganese (II) complexes are found in octahedral structure. The ground state of Mn(II) (d^5) in high spin octahedral coordination is $^6A_{1g}$. The alteration of the electron distribution in the octahedral coordination results in the pairing of electrons. Due to weak spin orbit interactions, weak absorption bands that might correspond to $^6A_{1g} \rightarrow {}^4T_{1g(G)}$, $^6A_{1g} \rightarrow {}^4T_{2g(G)}$ and $^6A_{1g} \rightarrow {}^4E_{g(G)}$[24-26] transitions may occur. The spectrum of Mn(II)–HBH complex contains three bands at 15516, 17730 and 22701 cm^{-1} and correspond to $^6A_{1g} \rightarrow {}^4T_{1g(G)}$, $^6A_{1g} \rightarrow {}^4T_{2g(G)}$ and $^6A_{1g} \rightarrow {}^4E_{g(G)}$ transitions respectively indicating the octahedral geometry. The magnetic moment value of 5.20 BM also supports the octahedral geometry for Mn(II)–HBH complex.[8]

Fe(III) ion is isoelectronic with Mn(II) ion. The spectral bands observed are 9852, 11383, 18215 cm^{-1}. Fe(III) is high spin in majority of its octahedral complexes. The ground state of Fe(III) is $^6A_{1g}$ and correspondingly four weak transitions are expected[27]. However low spin complexes with t_{2g}^5 configuration possess $^2T_{2g}$ ground state and as such in this case also four transitions are expected[28]. Further, in low spin complexes, a high degree of covalence and electron delocalization were observed. The magnetic moment value is 1.96 BM. The greatest loss of exchange energy occurs when the d^5 configuration is forced to pair up during the formation of low spin complexes. Further in low spin complexes, the ligands approach the empty e_g orbitals more closely. This is justified by the greater observed value of μ_{eff} 2.09 BM.

Based on the electronic spectral data and magnetic moment data, an octahedral geometry was suggested for Fe(III)-HBH complex.

In general, all known Co(III) complexes are octahedral. The energy level features of free Co(III) ion (d^6) is qualitatively same as that of Fe(II). All Co(III) complexes are expected to possess bands characteristic of transition from $^1A_{1g}$ ground state to other singlet states. The two absorption bands observed in the visible region at 19724 and 27435 cm^{-1} correspond to such transitions namely, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ respectively. The electronic spectral data and diamagnetic behavior of the complex suggest an octahedral structure for Co(III)–HBH complex.

The ground state of Ni(II) ion in octahedral coordination is $^3A_{2g}$ ($t_{2g}^6e_g^2$). In the present investigations, the spectrum of Ni(II)–HBH complex in dimethylformamide solution contains three peaks at 11167, 18832 and 24845 cm^{-1}. These absorption bands correspond to transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g(F)}$ and $^3A_{2g} \rightarrow {}^3T_{1g(P)}$ respectively [29]. The value of ν_2/ν_1 was found to be 1.686[30,31] which is lower than that of 1.800 observed for the regular octahedral nickel aquo complex. The lower value of ν_2/ν_1 is attributed to the asymmetric environment around Ni(II). The Racah parameter value and nephelauxetic factor (β) suggest the delocalization of d-orbitals and covalency of the metal-ligand bond in metal complexes. The ground state of regular octahedral complex is $^3A_{2g}$. In such a case, the μ_{eff} value should be equal to spin only value (2.8 BM) as the orbital angular momentum contribution to the magnetic moment is zero. The reason being the fact that the ground state $^3A_{2g}$ is usually be non degenerate. The slightly greater observed value of 3.2 BM observed for Ni(II)–HBH complex in the present investigation was due to the spin orbit coupling between the ground state $^3A_{2g}$ and the first excited state $^3T_{2g}$. The data supports octahedral geometry for the Ni(II) complex[32-34].

Cu(II) complexes usually have distorted octahedral with a limiting structure of either square planar or tetrahedral. The ground term in square planar geometry is $^3B_{1g}$ and the excited terms are $^2A_{1g}$, $^2B_{2g}$ and ^2E_g. Corresponding to these three transitions, the spectrum of square planar copper(II) complex is expected to contain three peaks. However these peaks usually overlap to give one or two broad peaks[35,36]. The d-d bands of square planar complexes[37,38] are observed in the range 14000 and 22000 cm^{-1}. In the present investigation two bands, one at 17778 cm^{-1} and the other at 27100 cm^{-1} are observed. The band at 17778 cm^{-1} may be attributed either to $^2B_{1g} \rightarrow {}^2B_{2g}$ or $^2B_{1g} \rightarrow {}^2E_g$ transition. The band at 27100 cm^{-1} may be attributed to the ligand to metal charge transfer transition. The absence of bands below 10000 cm^{-1} rules out the tetrahedral or pseudo tetrahedral environment for this complex[39]. Irrespective of stereochemistry, Cu(II) complexes possess one unpaired electron. Figgis and Lewis[40] have predicted a magnetic moment value less than 1.90 BM (spin only value) for square planar geometry. Usually the magnetic moment values for square planar complexes would be slightly greater than the spin only value of 1.90 BM. The magnetic moment value of 2.05 BM observed in the present studies could be due to spin-orbit coupling.

Based on elemental analysis data, the electronic spectral data and magnetic moment value, a square planar geometry is proposed for the complex.

Zn(II) and Cd(II) complexes possess d^{10} configuration and hence do not show spectral absorptions due to d-d transitions. The complexes are diamagnetic in nature. Based on the elemental analysis, conductance and infrared spectral data[41], tetrahedral geometry is suggested for the Zn(II) and Cd(II)–HBH complexes.

IR spectral studies

The IR spectra of the ligand and its metal complexes under investigation are presented in Figure 7–Figure 14. The important absorption assignments observed in the respective spectra are given in the Table 3.

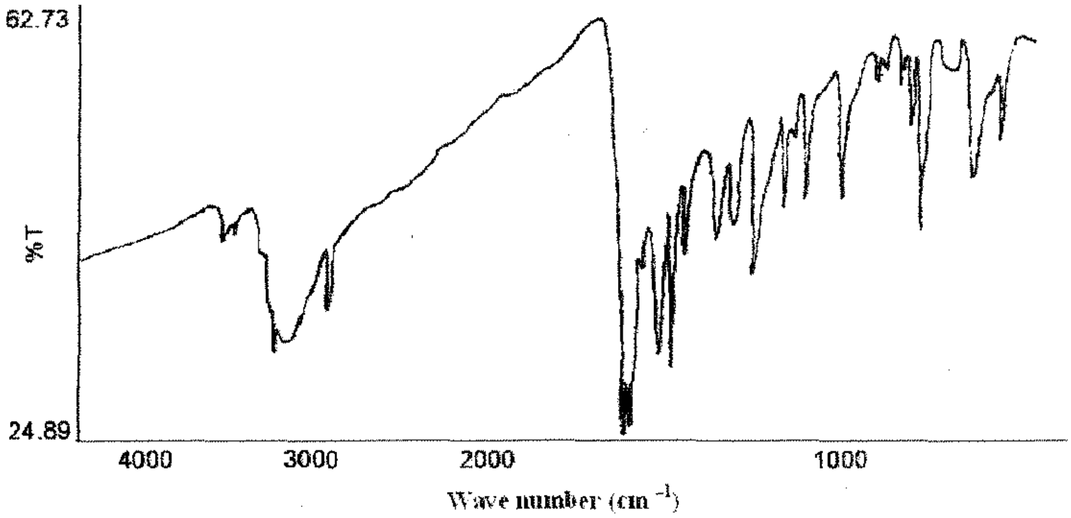


Figure 7. IR spectrum of HBH

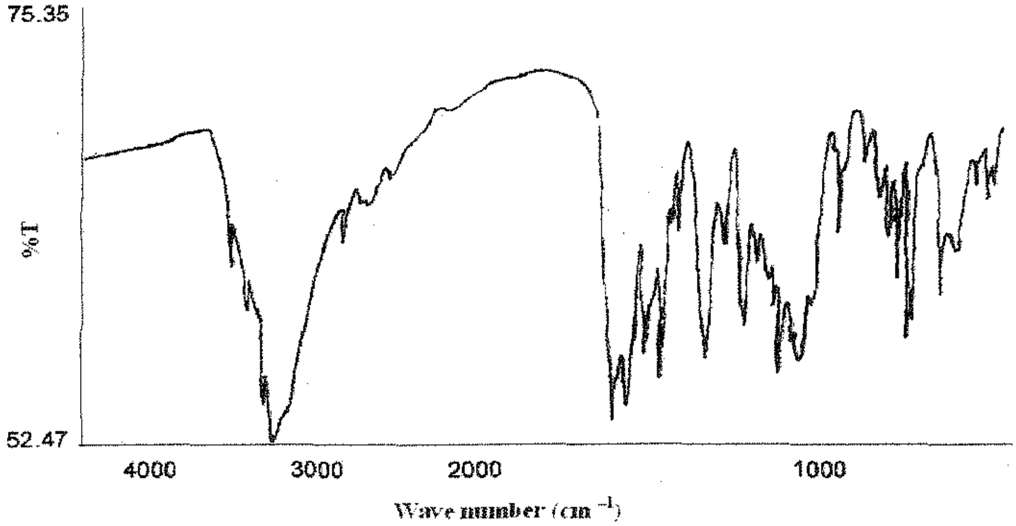


Figure 8. IR spectrum of Mn(II)-HBH complex

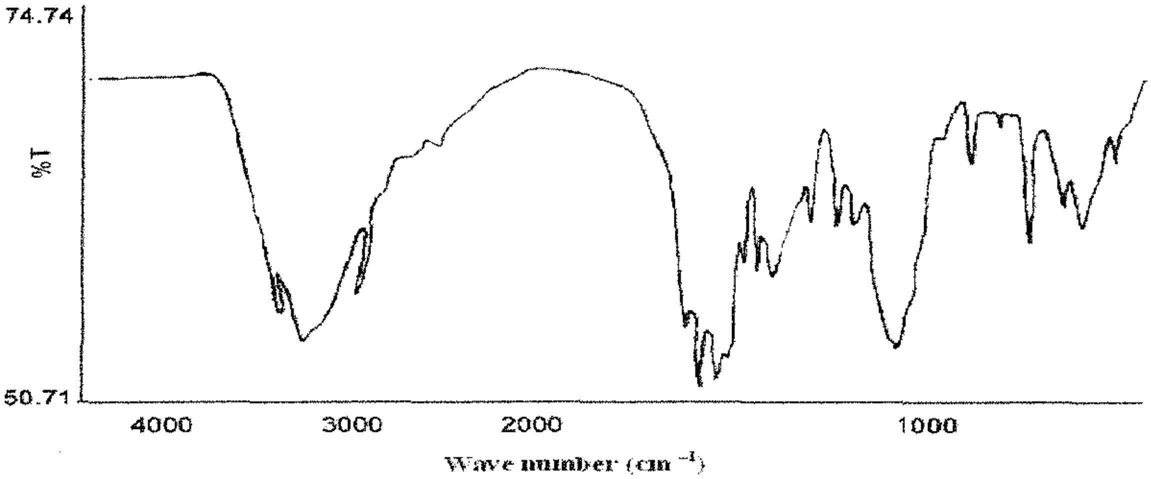


Figure 9. IR spectrum of Ni(III)-HBH complex

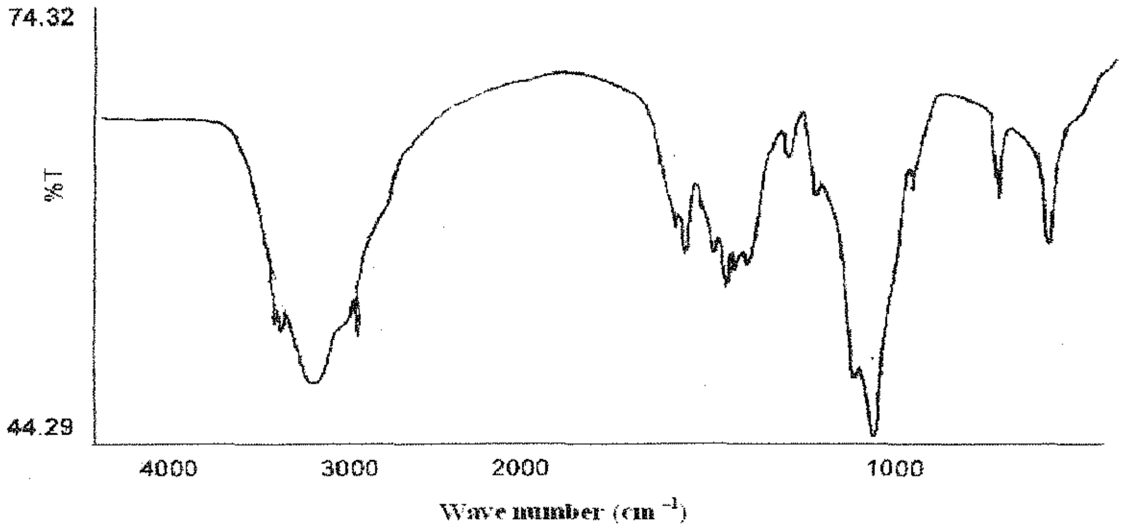


Figure 10. *IR spectrum of Fe(III)-HBH complex*

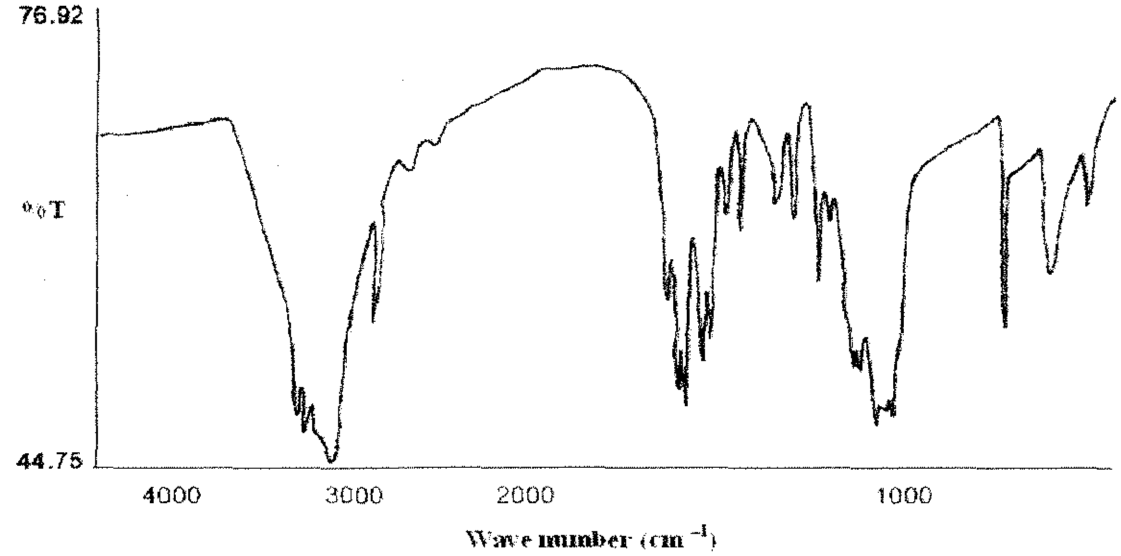


Figure 11. IR spectrum of Co(III)-HBH complex

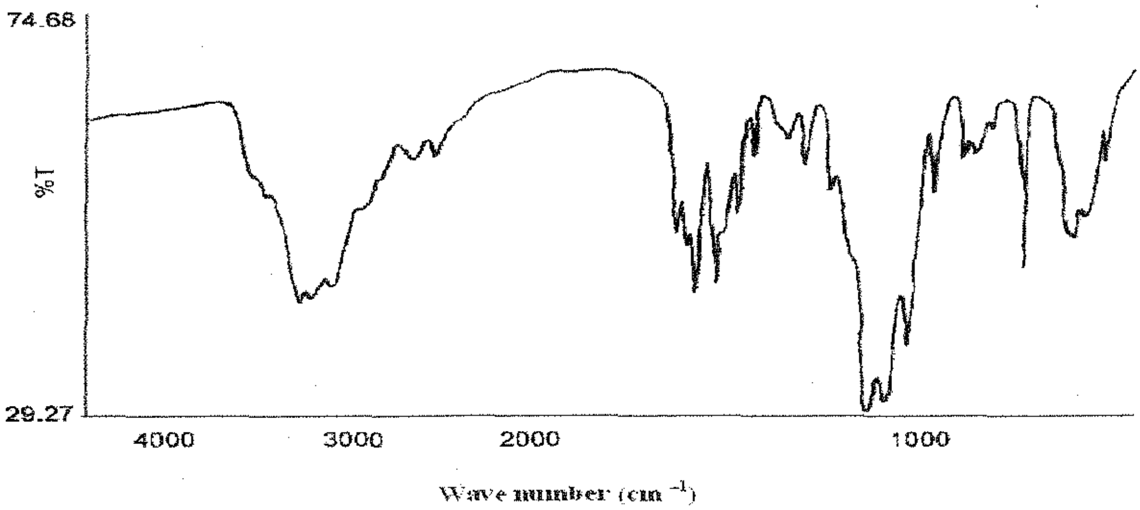


Figure 12. IR spectrum of Zn(II)-HBH complex

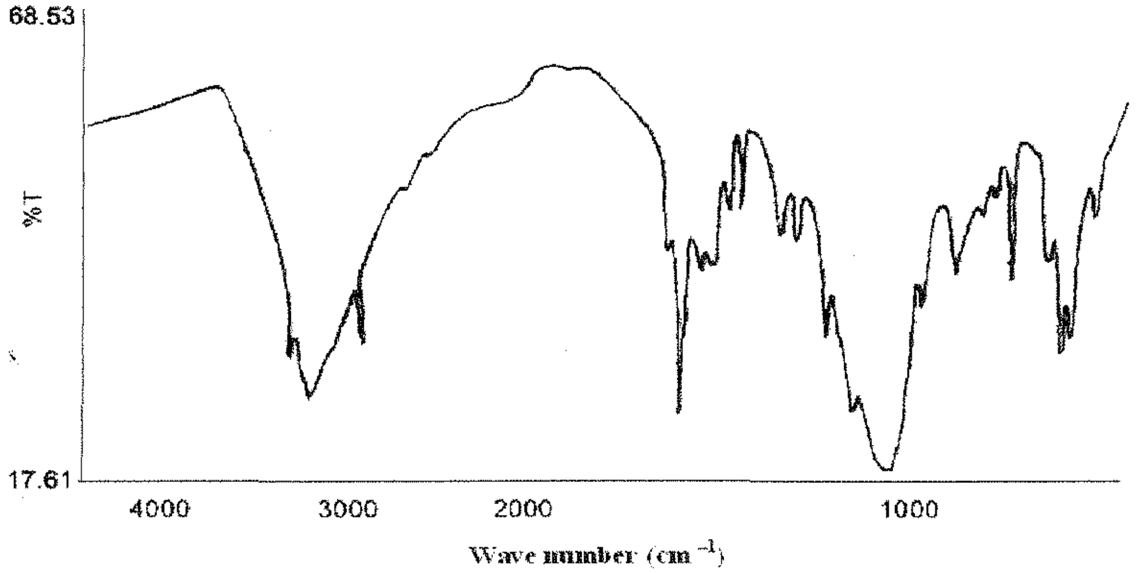


Figure 13. IR spectrum of Cd(II)-HBH complex

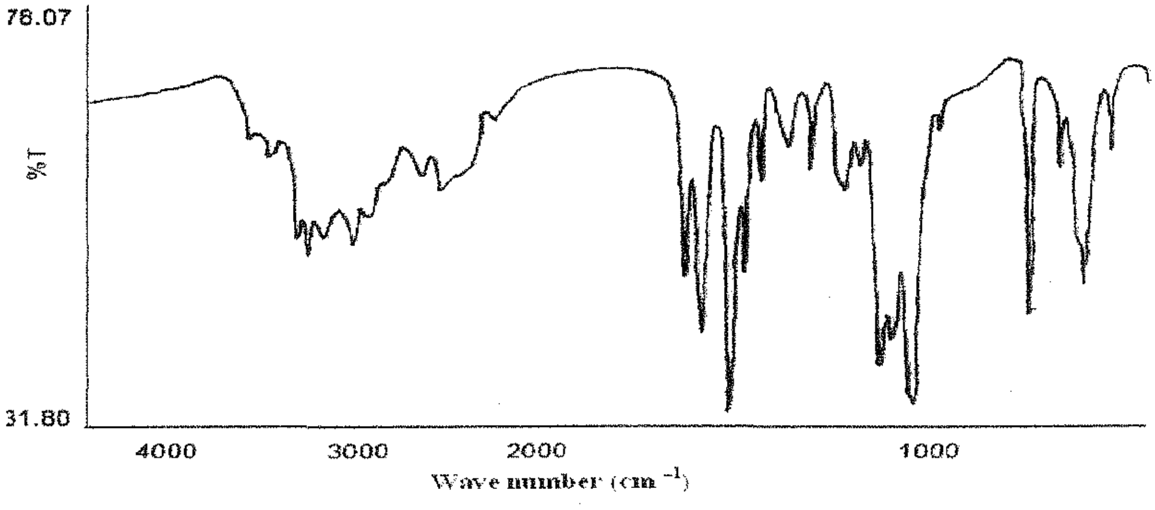
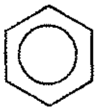
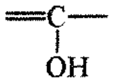


Figure 14. IR spectrum of Cu(II)-HBH complex

Table 3. Characteristic IR absorption frequencies (cm^{-1}) and their assignments

	Reagent (HBH)	**Mn(II)-HBH**	**Fe(III)-HBH**	**Co(III)-HBH**	**Ni(II)-HBH**	**Cu(II)-HBH**	**Zn(II)-HBH**	**Cd(II)-HBH**
ϕ-OH	3245	-	-	-	-	-	-	-
>C=O	1645	-	-	-	-	-	-	-
-NH	3290	-	-	-	-	-	-	-
$-NH_2$	3495 3395	3450 3321	3445 3325	3445 3330	3440 3320	3435 3312	3440 3320	3445 3328
	1450 1490 1540 1595	1440 1486 1534 1586	1442 1492 1532 1595	1459 1496 1544 1567	1456 1497 1530 1563	1457 1496 1537 1570	1457 1495 1554 1609	1460 1494 1531 1567
$-NH_2$ (amide II)	-	1590	1590	1590	1590	1590	1590	1590
 $=\underset{\substack{\vert \\ OH}}{C}-$	-	2850	2845	2860	2840	2870	2860	2845
>C=N	-	1608	1604	1609	1609	1608	1609	1606
N-N	980	979	980	978	980	981	981	980
M-O	-	529	565	516	529	530	530	522
M-N	-	748	752	748	752	746	747	748

A doublet noticed at 3495 cm^{-1} and 3395 cm^{-1} is attributed to the presence of $-NH_2$ group in the molecule. Another band at 3290 cm^{-1} is ascribed to the $-\overset{|}{N}H$ group attached to the carbonyl group. A band at 3245 cm^{-1} is due to the phenolic –OH (ϕ-OH). A band at 1645 cm^{-1} may be ascribed to the ν (C=O). The bands observed at 1450, 1490, 1540, 1595 cm^{-1} are ascribed to the benzene skeleton.

The important IR frequencies exhibited by Mn(II)-HBH and Ni(II)-HBH complexes and their assignments are shown in the Table 3 and in Figure 8 and Figure 9 respectively. The appearance of a new band at 2930 cm^{-1} in Mn(II)-HBH spectrum and 2933 cm^{-1} in Ni(II)-HBH spectrum may be attributed to the enolic –OH group. This suggests that the reagent in these complexes is in the enolic form but not in the keto form as is present in the free ligand. The bands at 3495 and 3395 cm^{-1} corresponding to $-NH_2$ group are shifted to lower wave numbers by about 75 cm^{-1} in the spectra of both these complexes. This shift is ascribed to the strong intra molecular hydrogen bonding between nitrogen of $-NH_2$ and hydrogen of enolic –OH. The appearance of a new band at 1590 cm^{-1} in both the complexes may be attributed to amide-II NH_2 group. The bands due to benzene skeleton present in the free ligand are not displaced in the spectra of complexes. A band at 1645 cm^{-1} due to the amide carbonyl group is absent in the spectra of complexes. This further suggests that the reagent in these complexes is in the enolic form. Similarly a band at 3290cm^{-1} due to $-\overset{|}{N}H$ stretching is absent in the spectra of complexes suggesting that not only the reagent is present in the enolic form but the nitrogen of the $-\overset{|}{N}H$ group is involved in coordination with the metal ion. The bands that are not observed in the spectrum of free ligand and observed at 1608 and 1609 cm^{-1} in the spectrum of the complex may be attributed to the presence of azomethine (>C=N-) group in the complexes. The bands at 748, 752 cm^{-1} may be due to ν_{M-N}[42,43] vibrations respectively in the complexes. A shift in ν_{N-N} to higher wave numbers is observed in the spectra of complexes and this may be explained by the fact that the ligand coordinates in a bidentate manner via azomethine nitrogen[44,45].

The elemental analysis data predicts 1:2 metal to ligand ratio for the complexes. Further, magnetic moment value[46], elemental analysis data and IR spectral data reaffirms the octahedral structure. Out of six coordination sites, two nitrogen atoms occupy two coordinate positions, two oxygen atoms occupy the other two coordinate positions and two solvent molecules occupy remaining two coordinate positions (Figure 15).

The IR spectral data of Fe(III) and Co(III)–HBH complexes are presented in Table 3 and the spectra are shown in Figure 10 and Figure 11. The behavior is almost same as described for Mn(II) and Ni(II)–HBH complexes. The elemental analysis data predicts a stoichiometry of 1:3 (M:L) for these complexes. Based on the IR spectral and elemental analysis data, an octahedral structure is proposed for these complexes (Figure 15).

The IR spectrum of Zn(II) and Cd(II)–HBH complexes are shown in Figure 12 and Figure 13 and the data is presented in Table 3. The same scenario of IR spectral bands was observed for these complexes also. The most preferred geometry for d^{10} systems is tetrahedral. Further keeping in view the experimental data, a tetrahedral geometry was suggested for Zn(II) and Cd(II) complexes (Figure 15). Based on the elemental analysis data, IR and electronic spectral data[47,48], a square planar geometry is suggested for Cu(II)–HBH complex (Cu(II) has d^9 configuration). The stoichiometry of the complexes determined from elemental analysis data is found to be 1:2 (Figure 15).

NMR spectral studies

The ^1H NMR spectral data of the ligand and its metal complexes studied in DMSO d^6 using TMS as an internal standard is given in the Table 4.

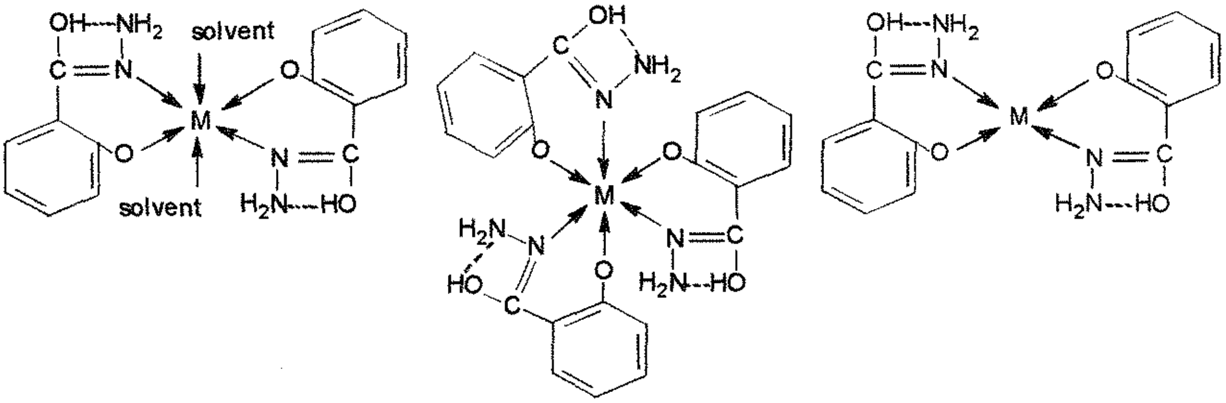
The ^{1}H NMR signal at 4.80 ppm was assigned to phenolic –OH. Broad peaks observed at 6.10 ppm and 11.20 ppm were attributed to amino (-NH_2) and imino (-$\overset{|}{N}H$) groups respectively.

Table 4. ^{1}H NMR spectral data (δ ppm) and their assignments

S.No.	Compound	H_a	H_b	H_c	-$\overset{|}{N}H$	-NH_2	-OH (phenolic)	-OH (enolic)
1.	HBH	7.50	7.10	6.80	11.20	6.10	4.80	-
2.	Mn(II)-HBH	7.95	7.50	7.10	-	5.90	-	5.60
3.	Fe(III)-HBH	8.20	8.00	7.70	-	5.80	-	5.62
19.	Co(III)-HBH	8.19	7.99	7.69	-	5.70	-	5.73
5.	Ni(II)-HBH	8.18	7.98	7.68	-	5.75	-	5.78
6.	Cu(II)-HBH	8.40	8.20	7.90	-	5.85	-	5.65
7.	Zn(II)-HBH	7.70	7.50	7.20	-	5.90	-	5.68
8.	Cd(II)-HBH	8.00	7.80	7.50	-	5.80	-	5.70

The complex multiplet noticed in the ^{1}H NMR spectra of the complexes in the range 7.10 – 8.40 ppm were attributed to the aromatic protons H_a, H_b and H_c[49]. The signal corresponding to the phenolic –OH (4.80 ppm) were absent in the spectra of complexes, thereby indicating the coordination of phenolic oxygen atom to the metal[50]. The spectra of all metal complexes studied contain signal in the range of 5.60 – 5.78 ppm and this was absent in the spectrum of free ligand. This may be attributed to the presence of an enolic –OH in the complexes. The signals observed for the amino protons in the ligand were unaffected in the spectra of complexes. However, the signal for imino proton found in the spectrum of free ligand was absent in the spectra of metal complexes. This fact further confirms the presence of enolic –OH in the metal complexes.

Based on the above studies following structures have been assigned for the complexes under investigation.



(a)M = Mn^{2+} and Ni^{2+} (b) M = Fe^{3+} and Co^{3+} (c) M = Zn^{2+}, Cd^{2+} and Cu^{2+}

Figure 15. Structure of Metal-HBH complexes under investigation

CONCLUSION

Mn(II), Ni(II), Fe(III), Co(III), Cu(II), Zn(II) and Cd(II) complexes of o-Hydroxybenzoic acid hydrazide were synthesized and characterized. The metal complexes were characterized by elemental analysis, molar conductivity, UV-Vis spectral, IR spectral and NMR spectral studies and stoichiometry was established in each case. In all the cases, the ligand acts a neutral bidentate ligand and coordinates to the metal via N and O.

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