

Synthesis, physico-chemical studies of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with some *p*-substituted acetophenone benzoylhydrazones and their antimicrobial activity

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Abstract

Complexes of the type $[M(\text{pabh})(\text{H}_2\text{O})\text{Cl}]$, $[M(\text{pcbh})(\text{H}_2\text{O})\text{Cl}]$ and $[M(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ where, $M = \text{Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)}$; Hpabh = *p*-amino acetophenone benzoyl hydrazone and Hpcbh = *p*-chloro acetophenone benzoyl hydrazone have been synthesized and characterized with the help of elemental analyses, electrical conductance, magnetic susceptibility measurements, electronic, ESR and IR spectra, thermal (TGA & DTA) and X-ray diffraction studies. Co(II), Ni(II) and Cu(II) chloride complexes are square planar, whereas their sulfate complexes have spin-free octahedral geometry. ESR spectra of Cu(II) complexes with Hpabh are axial and suggest $d_{x^2-y^2}$ as the ground state. The ligand is bidentate bonding through $>\text{C}=\text{N}-$ and deprotonated enolate group in all the chloro complexes, whereas, $>\text{C}=\text{N}$ and $>\text{C}=\text{O}$ groups in all the sulfato complexes. Thermal studies (TGA & DTA) on $[\text{Cu}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ indicate a multistep decomposition pattern, which are both exothermic and endothermic in nature. X-ray powder diffraction parameters for $[\text{Co}(\text{pabh})(\text{H}_2\text{O})\text{Cl}]$ and $[\text{Ni}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ correspond to tetragonal and orthorhombic crystal lattices, respectively. The ligands as well as their complexes show a significant antifungal and antibacterial activity. The metal complexes are more active than the ligand.

Keywords: Metal complexes, synthesis, physico-chemical studies, *p*-substituted acetophenone benzoylhydrazone, antimicrobial

Introduction

The chemistry of transition metal complexes with multidentate Schiff base ligands has attracted particular attention because these metal ions can exhibit several oxidation states [1]. Such complexes with different oxidation states have a strong role in bio-inorganic chemistry and redox enzyme systems [2,3] and may provide the basis of models for active sites of biological systems [4,5] or act as catalysts [6–8].

Metal complexes of multidentate acylhydrazone Schiff bases have been extensively studied [9–11] because such ligands can bind with one, two or more metal centers involving various coordination modes and allow successful synthesis of homo and hetero nuclear metal complexes with interesting stereo-chemistry [12–14]. Since the complexes of acylhydrazones involving bivalent transition metal ions may

have their potential use in the biological fields, it is worthwhile to undertake the present study. Accordingly, we have synthesized and characterized a number of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with *p*-substituted acetophenone benzoylhydrazone ligand and studied their bio-activity.

Experimental

Materials

All the chemicals used were of BDH or equivalent grade. The precursor benzoyl hydrazine, $\text{C}_6\text{H}_5\text{CONHNH}_2$ (bh) was prepared by the reported procedure [10] by refluxing methyl benzoate with hydrazine hydrate in 1:1 molar ratio in a RB flask containing 10 mL ethanol for 4 h. The pure product was characterized by its melting point, mp 111°C (lit. 112°C).

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Preparation of *p*-substituted acetophenone benzoylhydrazone

p-Amino acetophenone benzoylhydrazone (Hpabh), $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NNHCO C}_6\text{H}_5$ and *p*-chloro acetophenone benzoylhydrazone (Hpcbh), $\text{ClC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NNHCO C}_6\text{H}_5$ were prepared separately by reacting *p*-amino acetophenone (10 mmol, 13.5 g) or *p*-chloro acetophenone (10 mmol, 15.5 g) with bh (10 mmol, 13.6 g) dissolved in 50 mL ethanol. The reaction mixtures were taken in a RB flask and refluxed for 4-5 h and then transferred into a beaker. The products were filtered on a suction pump, washed several times with distilled water and a little ethanol and recrystallized from hot benzene. The pure compounds were dried over anhydrous CaCl_2 in a desiccator.

The ligands were characterized by elemental analyses (C, H, N), melting points (Table I), infrared spectra (Table IV) ^1H and ^{13}C NMR spectra.

Hpabh. ^1H NMR (ppm): $-\text{CH}_3$ protons (1.0), $-\text{NH}_2$ (4.2), $> \text{NH}$ (6.8), aromatic ring protons (7.0-7.9). *Hpabh*, ^{13}C NMR (ppm): $-\text{CH}_3$ (11.4), aromatic ring carbons (118.0-147.1), $> \text{C}=\text{N}$ - (156.3), $> \text{C}=\text{O}$ (171.4).

Hpcbh. ^1H NMR (ppm): $-\text{CH}_3$ protons (1.1), $> \text{NH}$ (6.6), aromatic ring protons (7.1-7.7). *Hpcbh*, ^{13}C NMR (ppm): $-\text{CH}_3$ (11.6), aromatic ring carbons (128.7-139.3), $> \text{C}=\text{N}$ - (158.2), $> \text{C}=\text{O}$ (171.0).

Synthesis of the metal complexes

The metal(II) chloride complexes were synthesized by reacting 50 mL of ethanolic solution containing 10 mmol each of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1.98 g), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.38 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.38 g), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.70 g), $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ (1.54 g) with 50 mL ligand solution of Hpabh (10 mmol, 2.53 g) or Hpcbh (10 mmol, 2.73 g) in hot ethanol in 1:1 (M:L) molar ratio and were refluxed in a RB flask for ~ 2 h. Adding 10 mL diethyl ether after cooling the reaction mixture at room temperature precipitated the complexes. The compounds were filtered in a glass crucible and were purified by washing several times with ethanol and finally with diethyl ether and dried in a desiccator over anhydrous CaCl_2 at room temperature.

The metal(II) sulfate complexes with Hpabh were prepared by reacting 50 mL of aqueous ethanolic solution (50%, v/v) containing 10 mmol each of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (2.23 g), $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (2.81 g), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (2.81 g), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2.50 g) and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (2.87 g) at room temperature with hot ethanolic solution of Hpabh (10 mmol, 2.53 g) separately in a beaker in 1:1 (M:L) molar ratio. The complexes

were precipitated immediately and were filtered in a glass crucible, washed with aqueous ethanol and finally with diethyl ether and dried in a desiccator.

Analyses of the complexes

Elemental analyses. The complexes were analyzed for metal content gravimetrically by literature procedures [15] after decomposing the organic matter with a mixture of HNO_3 and HCl and evaporating the residue to dryness with conc. H_2SO_4 . The chloride content in the complex was determined gravimetrically as AgCl and sulfate as BaSO_4 .

Carbon, hydrogen and nitrogen were determined microanalytically on a Elementar Vario EL III Carlo Erba 1108 model, microanalyzer.

Physico-chemical measurements. The molar conductance of the complexes was determined by preparing 10^{-3} M solutions of the complexes in distilled water at room temperature and measured on a Systronic Conductivity meter model-306. Thermal studies (TGA and DTA) of some of the complexes were carried out on a Perkin-Elmer Thermal Analyzer between room temperature to 800°C . Room temperature magnetic susceptibility measurements were carried out on a Faraday balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant and corrected for diamagnetism [16]. The electronic spectra of the complexes were recorded in nujol on a Perkin-Elmer Lambda-2 spectrophotometer in the range 1100-200 nm. Infrared spectra of the complexes and parent ligands were recorded on Vector-22 spectrophotometer in the range $4000\text{-}500\text{ cm}^{-1}$ in KBr medium. ^1H and ^{13}C NMR spectra of the ligands were recorded in DMSO on a JEOL AL 300 FT NMR Spectrometer. The X-band ESR spectra of copper(II) complexes were recorded on a EMX 1444 EPR spectrometer at room temperature (298 K) in solid state using DPPH as g marker ($g = 2.0023$). Powder X-ray diffraction patterns of a few complexes were recorded on Iso Debye Flex 2002 apparatus using $\text{CuK}\alpha$ radiation. The analytical and physico-chemical data are given in Tables I-VI.

Biological activity

Antifungal activity. The ligands as well as their complexes were screened for their antifungal activity against various fungi viz. *Alternaria sp.*, *Rizoctonia sp.*, *Stemphylium sp.* and *Penicillium sp.* These species were isolated from the infected organs of the host plants on potato dextrose agar (potato 250 g + dextrose 20 g + agar 20 g) medium. The cultures of the fungi were purified by single spore isolation technique.

The solution in different concentrations 0.5, 1 and 1.5 mg/mL of each compound in water were prepared for testing against spore germination. A drop of the solution of each concentration was kept separately

Table I. Analytical data of the ligands and their complexes.

Compound (Colour)	Empirical Formula (Formula wt.)	Melting point (°C)	Found (Calculated) %				Yield (%)	ΔM ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in water	
			Metal	$\text{Cl}^-/\text{SO}_4^{2-}$	C	H			N
Hpabh (White)	$\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$ (253)	179	–	–	70.82 (71.15)	5.78 (5.93)	16.46 (16.60)	80	–
Hpcbh (White)	$\text{C}_{15}\text{H}_{13}\text{N}_2\text{OCl}$ (272.5)	212	–	–	65.85 (66.06)	4.68 (4.77)	10.16 (10.28)	82	–
[Mn(pabh)(H ₂ O)Cl] (Yellow)	$\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2\text{ClMn}$ (360.5)	188	15.10 (15.26)	9.72 (9.85)	49.74 (49.93)	4.38 (4.44)	11.52 (11.65)	75	4.60
[Co(pabh)(H ₂ O)Cl] (Dark green)	$\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2\text{ClCo}$ (364.5)	210	16.20 (16.19)	9.65 (9.74)	49.16 (49.38)	4.37 (4.39)	11.44 (11.52)	78	7.46
[Ni(pabh)(H ₂ O)Cl] (Pink)	$\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2\text{ClNi}$ (364.5)	218	16.10 (16.19)	9.68 (9.74)	49.20 (49.38)	4.31 (4.39)	11.42 (11.52)	72	8.19
[Cu(pabh)(H ₂ O)Cl] (Brown)	$\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2\text{ClCu}$ (369)	190	17.12 (17.21)	9.54 (9.62)	48.58 (48.78)	4.35 (4.34)	11.30 (11.38)	75	2.08
[Zn(pabh)(H ₂ O)Cl] (Light yellow)	$\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_2\text{ClZn}$ (370.5)	198	17.50 (17.54)	9.50 (9.58)	48.42 (48.58)	4.28 (4.32)	11.21 (11.34)	70	3.56
[Mn(pcbh)(H ₂ O)Cl] (Yellow)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Mn}$ (380)	232	14.36 (14.47)	18.54 (18.68)	47.20 (47.37)	3.66 (3.68)	7.28 (7.37)	76	5.45
[Co(pcbh)(H ₂ O)Cl] (Green)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Co}$ (384)	246	15.22 (15.36)	18.50 (18.49)	46.64 (46.88)	3.61 (3.65)	7.35 (7.29)	80	6.37
[Ni(pcbh)(H ₂ O)Cl] (Light pink)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Ni}$ (384)	252	15.24 (15.36)	18.35 (18.49)	46.68 (46.88)	3.58 (3.65)	7.26 (7.29)	78	7.98
[Cu(pcbh)(H ₂ O)Cl] (Brown)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Cu}$ (388.5)	240	16.22 (16.34)	18.20 (18.28)	46.15 (46.33)	3.55 (3.60)	7.26 (7.21)	82	4.62
[Zn(pcbh)(H ₂ O)Cl] (Light yellow)	$\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Cl}_2\text{Zn}$ (390)	226	16.56 (16.67)	18.10 (18.21)	46.03 (46.15)	3.53 (3.59)	7.11 (7.18)	75	3.60
[Mn(Hpabh)(H ₂ O) ₂ (SO ₄)] (Yellow)	$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_7\text{SMn}$ (440)	258	12.40 (12.50)	21.72 (21.82)	40.72 (40.91)	4.32 (4.32)	9.45 (9.54)	80	7.70
[Co(Hpabh)(H ₂ O) ₂ (SO ₄)] (Pink)	$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_7\text{SCo}$ (444)	261	13.21 (13.29)	21.49 (21.62)	40.38 (40.54)	4.22 (4.28)	9.38 (9.46)	85	9.02
[Ni(Hpabh)(H ₂ O) ₂ (SO ₄)] (Green)	$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_7\text{SNi}$ (444)	270	13.20 (13.29)	21.51 (21.62)	40.36 (40.54)	4.24 (4.28)	9.40 (9.46)	82	6.41
[Cu(Hpabh)(H ₂ O) ₂ (SO ₄)] (Brownish green)	$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_7\text{SCu}$ (448.5)	250	14.12 (14.16)	21.31 (21.40)	39.96 (40.13)	4.20 (4.24)	9.28 (9.36)	90	5.35
[Zn(Hpabh)(H ₂ O) ₂ (SO ₄)] (Light yellow)	$\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_7\text{SZn}$ (450)	252	14.35 (14.44)	21.22 (21.33)	39.85 (40.00)	4.18 (4.22)	9.28 (9.33)	76	2.11

Table II. Magnetic moments and electronic spectral data of the complexes.

Complexes	μ_{eff} (B.M.)	Band maxima (cm^{-1})		
		ν_1	ν_2	ν_3
[Mn(pabh)(H ₂ O)Cl]	5.90	19415	23530	–
[Co(pabh)(H ₂ O)Cl]	2.10	–	21980	27930
[Ni(pabh)(H ₂ O)Cl]	diamagnetic	12345	19230	27025
[Cu(pabh)(H ₂ O)Cl]	1.70	–	16600	–
[Mn(pcbh)(H ₂ O)Cl]	5.92	19232	23185	–
[Co(pcbh)(H ₂ O)Cl]	2.21	–	21720	27685
[Ni(pcbh)(H ₂ O)Cl]	diamagnetic	12170	19100	27160
[Cu(pcbh)(H ₂ O)Cl]	1.80	–	16770	–
[Mn(Hpabh)(H ₂ O) ₂ (SO ₄)]	5.88	20530	24690	–
[Co(Hpabh)(H ₂ O) ₂ (SO ₄)]	4.71	9260	–	19880
[Ni(Hpabh)(H ₂ O) ₂ (SO ₄)]	2.91	10630	16520	26850
[Cu(Hpabh)(H ₂ O) ₂ (SO ₄)]	1.82	11235	14700	–

on glass slides. The conidia, fungal reproducing spores (approx. 200) lifted with the help of an inoculating needle, were mixed in every drop of each compound separately. Each treatment was replicated thrice and a parallel water solvent control set was run concurrently on separate glass slides. All the slides were incubated in humid chambers at $25 \pm 2^\circ\text{C}$ for 24 h. Each slide was observed under the microscope for spore germination and percent germination was finally calculated. The results were also compared with a standard antifungal drug miconazole at the same concentrations.

Antibacterial activity. The antibacterial activity of the ligands and their complexes was studied against *Clostridium sp.* and *Pseudomonas sp.* bacteria. Each of the compounds was dissolved in water and solutions of the concentration 1 mg/mL and 2 mg/mL were prepared separately. Paper discs of Whatman filter paper (No. 42) of uniform diameter (2 cm) were cut and sterilized in an autoclave. The paper discs soaked in the desired concentration of the complex solutions were placed aseptically in the petridishes containing nutrient agar media (agar 20 g + beef extract 3 g + peptone 5 g) seeded with *Clostridium sp.* and *Pseudomonas sp.* bacteria separately. The petridishes were incubated at 37°C and the inhibition zones were recorded after 24 h of incubation. Each treatment was replicated 9 times.

The antibacterial activity of a common standard antibiotic Ampicillin was also recorded using the same procedure as above at the same concentrations and solvent. The % Activity Index for the complex was calculated by the formula as under:

%Activity index

$$= \frac{\text{Zone of inhibition by test compound(diam)}}{\text{Zone of inhibition by standard(diam)}} \times 100$$

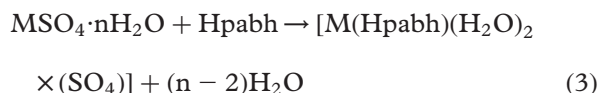
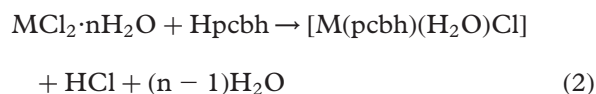
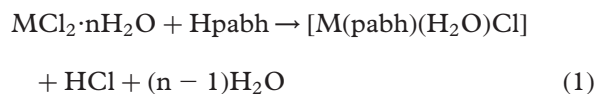
Determination of minimum inhibitory concentration (MIC) value. The antibacterial screening concentrations of the compounds to be used were estimated

from the minimum inhibitory concentration (MIC) value. The MIC was determined using the disc diffusion technique by preparing discs containing 0.1 to 1.0 mg/mL of each compound against both the bacteria and applying the protocol. All the compounds were more effective at 1.0 and 2.0 mg/mL concentrations. Consequently all the compounds were screened at these concentrations against both the bacteria. The results of MIC values (mg/mL) are given in Table VIIB.

Results and discussion

Analysis of complexes

The analytical data of the complexes (Table I) show that the ligands *p*-amino acetophenone benzoylhydrazone (Hpabh) and *p*-chloro acetophenone benzoyl hydrazone (Hpcb) react with metal(II) salts in 1:1 (M:L) molar ratio to give complexes of general compositions [M(pabh)(H₂O)Cl], [M(pcbh)(H₂O)Cl] and [M(Hpabh)(H₂O)₂(SO₄)]. It also appears from the analytical data that both the ligands Hpabh and Hpcb enolize and deprotonate during complexation with metal(II) chloride. The reactions may have proceeded as follows:



where, M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)

Table III. Important IR spectral bands (cm^{-1}) and their assignments.

Compounds	$\nu(\text{OH})/\nu(\text{NH})$	Amide I $\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	Amide II	Amide III	$\nu(\text{N}=\text{CO})$	$\nu(\text{CO})$	$\nu(\text{NN})$	$\nu(\text{MO})$	Water bands
Hpbh	3290b	1672s	1630m	1573m	1378s	—	—	990m	—	—
Hpcb	3282b	1678s	1632m	1568m	1375s	—	—	985m	—	—
[Mn(pabh)(H ₂ O)Cl]	3400b, 3292b	—	1609s	—	—	1470s	1320s	1020m	580w	912s, 760m, 642m
[Co(pabh)(H ₂ O)Cl]	3385b, 3288b	—	1605s	—	—	1490s	1328s	1016m	577m	905s, 758m, 645m
[Ni(pabh)(H ₂ O)Cl]	3390b, 3290b	—	1603s	—	—	1480s	1327m	1022w	585s	910s, 756m, 638m
[Cu(pabh)(H ₂ O)Cl]	3400b, 3291b	—	1600s	—	—	1486m	1326m	1025w	588s	913s, 752m, 645m
[Zn(pabh)(H ₂ O)Cl]	3392b, 3290b	—	1605s	—	—	1470m	1320m	1015w	570m	910s, 755m, 640m
[Mn(pcbh)(H ₂ O)Cl]	3394b, 3285b	—	1608s	—	—	1476s	1326s	1010m	582w	911s, 754m, 640m
[Co(pcbh)(H ₂ O)Cl]	3395b, 3280b	—	1606s	—	—	1480s	1322s	1012m	580m	908s, 760m, 640m
[Ni(pcbh)(H ₂ O)Cl]	3396b, 3282b	—	1605s	—	—	1470s	1330m	1016w	581w	912s, 758m, 635m
[Cu(pcbh)(H ₂ O)Cl]	3400b, 3284b	—	1602s	—	—	1482m	1327m	1020w	580s	915s, 750m, 642m
[Zn(pcbh)(H ₂ O)Cl]	3398b, 3280b	—	1609s	—	—	1478m	1323m	1012w	576m	910s, 752m, 645m
[Mn(Hpbh)(H ₂ O) ₂ (SO ₄)]	3390b, 3260b	1633s	1606s	1555m	1385s	—	—	1002m	580w	900s, 752m, 638m
[Co(Hpbh)(H ₂ O) ₂ (SO ₄)]	3410b, 3270b	1635s	1610s	1558s	1392s	—	—	1005w	590w	910s, 758m, 642m
[Ni(Hpbh)(H ₂ O) ₂ (SO ₄)]	3380b, 3260b	1638s	1606s	1552m	1390s	—	—	1008w	586s	908s, 760m, 649m
[Cu(Hpbh)(H ₂ O) ₂ (SO ₄)]	3400b, 3270b	1640s	1604s	1558s	1388s	—	—	1015w	582w	901s, 755m, 646m
[Zn(Hpbh)(H ₂ O) ₂ (SO ₄)]	3380b, 3265b	1635s	1612s	1560s	1383s	—	—	1010w	578w	905s, 758m, 640m

b = broad, s = strong, m = medium, w = weak

The complexes are insoluble in benzene, carbon tetrachloride, chloroform, diethyl ether and n-hexane but soluble in water, hot ethanol, DMF and DMSO. They are light yellow, pink and brown to dark green in color. The complexes melt with decomposition between 188–270°C and are non-electrolytes [17] as indicated by their low molar conductance values of 10^{-3} M solutions of the complexes in water at room temperature ($2.08\text{--}9.02 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$).

Magnetic moments

Where spin–spin coupling between unpaired electrons belonging to different copper ions is absent, μ_{eff} varies between 1.75 and 2.20 B.M., depending on the geometries of the complexes due to difference in orbital contribution. The magnetic moments of the three Cu(II) complexes correspond to μ_{eff} values of one unpaired electron (1.70, 1.80, 1.82 B.M.) suggesting a square planar or distorted octahedral geometry for the complexes. The effective magnetic moments reported for high spin octahedral Ni(II) complexes are in the range 2.9–3.4 B.M., while for the tetrahedral nickel(II) complexes, the values range from 3.5–4.0 B.M. [18]. Ni(II) sulfate complex in this study, shows μ_{eff} value 2.91 B.M. corresponding to two unpaired electrons in octahedral environment, whereas Ni(II) chloride complexes are diamagnetic suggesting square planar geometry for the complex (Table II).

Cobalt(II) tetrahedral complexes generally show magnetic moments between 4.0–4.6 B.M. while the octahedral complexes show between 4.7–5.2 B.M. because of the orbital contribution [16]. The μ_{eff} value 4.71 B.M. observed for Co(II) sulfate complex is fairly close to those reported for three unpaired electrons in an octahedral environment. However, Co(II) chloride complexes show a low μ_{eff} value (2.10, 2.21 B.M.) corresponding to one unpaired electron suggests square planar geometry for the complexes. The Mn(II) complexes have their μ_{eff} values 5.90, 5.92 and 5.88 B.M. corresponding to five unpaired electrons in tetrahedral or octahedral environment.

Electronic spectra (Table II)

[Cu(pabh)(H₂O)Cl] and [Cu(pcbh)(H₂O)Cl] show a broad band centered at 16,600 and 16,770 cm^{-1} , respectively, indicating a square planar geometry for both the complexes, similar to [Cu(NH₃)₄]²⁺ (16,660 cm^{-1}) [19]. The other complex in this study [Cu(Hpbh)(H₂O)₂(SO₄)] shows two bands at 11,235 cm^{-1} and 14,700 cm^{-1} , which may be assigned to ²B_{1g} → ²B_{2g} and → ²A_{1g} suggesting a tetragonally distorted octahedral geometry for the complex.

Nickel(II) complexes generally show three bands in octahedral environment corresponding to the

Table IV. ESR spectral parameters of Cu(II) complexes in solid state at room temperature (298 K).

Complexes	A (G)	A _⊥ (G)	A _{av} (G)	g (G)	g _⊥ (G)	g _{av} (G)	G
[Cu(pabh)(H ₂ O)Cl]	92.0	38.3	56.2	2.2403	2.0473	2.1116	5.0803
[Cu(Hpabh)(H ₂ O) ₂ (SO ₄)]	130.0	56.60	81.1	2.2611	2.0642	2.1298	4.0670

transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) (v_1)$, $\rightarrow {}^3T_{1g}(F) (v_2)$ and $\rightarrow {}^3T_{1g}(P) (v_3)$ [18]. In the spectra of $[\text{Ni}(\text{NH}_3)_6]^{2+}$, these bands have been reported at 10,700, 17,540 and 28,170 cm^{-1} , respectively. $[\text{Ni}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ complex also shows above three transitions at 10,630 cm^{-1} (v_1), 16,520 cm^{-1} (v_2) and 26850 cm^{-1} (v_3) suggesting an octahedral geometry for the complex. Ligand field parameters (10 Dq, B, β and β°) have also been calculated by the procedure laid down by Lever [19]. Energy of the first absorption band is taken to be equal to 10 Dq. The low value of Racah parameter, B (765 cm^{-1}) compared to the free ion value of 1041 cm^{-1} indicates significant covalent character in the complex. The nephelauxetic ratio β (0.735) and percent covalency β° (26.50) also support some covalent character in the metal-ligand bond. The electronic spectra of $[\text{Ni}(\text{pabh})(\text{H}_2\text{O})\text{Cl}]$ and $[\text{Ni}(\text{pcbh})(\text{H}_2\text{O})\text{Cl}]$ complexes suggest a square planar geometry similar to that reported for Ni(II) acetylacetonate bis-acylhydrazones [9] and many other nickel(II) complexes [20].

Cobalt(II) complexes give rise to three absorption bands in the visible region under the influence of the octahedral field by the excitation of the electron from the ground state ${}^4T_{1g}(F)$ to the excited states ${}^4T_{2g}(F)$, ${}^4A_{2g}(F)$ and ${}^4T_{1g}(P)$. In case of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, three transition are observed at 8,130, 17,540 and 21,980 cm^{-1} , respectively. In $[\text{Co}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ complex, only two bands are observed at 9,260 cm^{-1} (v_1) and 19,880 cm^{-1} (v_3) indicating octahedral geometry for the complex. The v_2 transition was not observed due to very weak intensity [19]. The various ligand field parameters 10 Dq (10,415 cm^{-1}), B (785 cm^{-1}), β (0.808) and β° (19.20) were also calculated for this complex. The two bands observed for $[\text{Co}(\text{pabh})(\text{H}_2\text{O})\text{Cl}]$ and $[\text{Co}(\text{pcbh})(\text{H}_2\text{O})\text{Cl}]$ complexes are in good agreement with the bands reported for cobalt(II) square planar complexes [21].

The intensities of octahedral manganese(II) complexes are extremely low as a consequence of their doubly forbidden nature. For both tetrahedral and octahedral fields the ground state of Mn(II) being unaffected by the crystal field will be the same [19]. It has already been proven that the octahedral field energy level sequence for a d^n configuration is the same as the tetrahedral field energy level sequence for the d^{10-n} configuration. It follows therefore that for a d^5 ion, which is its own hole equivalent, the same energy level diagram may be used for octahedral or tetrahedral fields. The weak bands observed for $[\text{Mn}(\text{pabh})(\text{H}_2\text{O})\text{Cl}]$ and $[\text{Mn}(\text{pcbh})(\text{H}_2\text{O})\text{Cl}]$

complexes suggest a tetrahedral geometry whereas, $[\text{Mn}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ shows an octahedral geometry.

IR spectra (Table III)

The ligands Hpabh and Hpcb show a broad band in the region 3290 and 3282 cm^{-1} respectively, due to $\nu(\text{NH}/\text{NH}_2)$. In the metal complexes, this band occurs either at the same wave number as in the parent ligands or at slightly shifted wave numbers, indicating non-involvement of $>\text{NH}$ or $-\text{NH}_2$ groups in bonding. A broad band in the same region (centered between 3380-3410 cm^{-1}) in all the metal complexes may also indicate $\nu(\text{OH})$ due to presence of H_2O molecule in these complexes.

A shift to lower wave numbers in amide I, $\nu(\text{C}=\text{O})$ (15-20 cm^{-1}) and amide(II) (13-21 cm^{-1}) and a shift to higher wave numbers in the amide(III) band (5-14 cm^{-1}) in spectra of all the metal(II) sulfate complexes (Table III) compared to that of the parent ligands indicates coordination through carbonyl oxygen [22]. The disappearance of $\nu(\text{C}=\text{O})$ band in all the metal(II) chloride complexes and appearance of $\nu(\text{N}=\text{C}-\text{O})$ and $\nu(\text{C}-\text{O})$ in the ranges 1470-1490 cm^{-1} and 1320-1330 cm^{-1} , respectively, suggest bonding to metal through deprotonated C-O group [23]. In all the complexes $\nu(\text{C}=\text{N})$ band appears at the lower frequency (18-30 cm^{-1}) than that observed in the ligands, indicating the coordination through nitrogen atom of the azomethine ($>\text{C}=\text{N}-$) group to the metal [9]. $\nu(\text{N}-\text{N})$ observed at 990 and 985 cm^{-1} in the ligands Hpabh and Hpcb respectively, shifts to higher frequency by 12-32 cm^{-1} in the complexes, indicating the coordination of one of the nitrogen atom of the N-N group [24].

All the metal complexes also show weak bands in the 901-910, 752-760 and 638-649 cm^{-1} ranges due to coordinated water [25]. The bands observed near 1200-1220, 1160-1175 and 1040-1060 cm^{-1} ranges suggest the presence of bidentate chelating sulfate groups in all the metal(II) sulfate complexes. A non-ligand band observed in the region 570-590 cm^{-1} has been assigned to $\nu(\text{M}-\text{O})$.

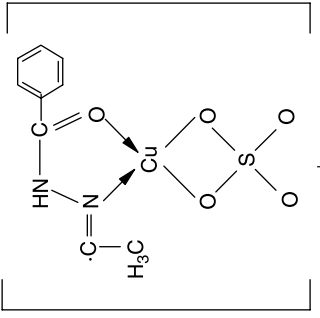
ESR spectra (Table IV)

ESR spectra of powdered samples of the Cu(II) complexes at room temperature exhibit an axial signal with two g values (Figure 1). The axial signals were analyzed by the procedure given by Hathaway and

Table V. Thermal decomposition of $[\text{Cu}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ complex.

S.No.	Temp.	Proposed decomposition pattern	% Loss of wt.		Energy Change	Remarks
			Obs.	Calc.		
1	2s-1s4		0.00	0.00	Endothermic	No decomposition
2	155		8.00	8.03	Exothermic	Decomposition of coordinated water

Table V – continued

S.No.	Temp.	Proposed decomposition pattern	% Loss of wt.		Energy Change	Remarks
			Obs.	Calc.		
3	250		28.70	28.54	Exothermic	C ₆ H ₄ NH ₂ decomposed
4	360	CuSO ₄	64.35	64.44	Endothermic	Loss of organic moiety

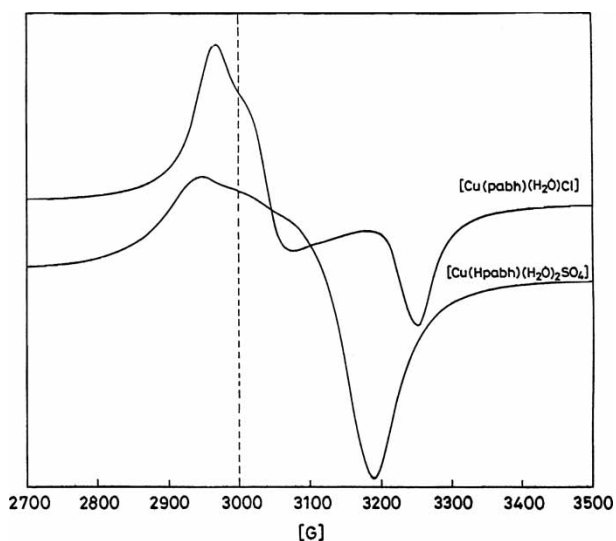


Figure 1. ESR spectra of copper (II) complexes at 298 K in the solid state.

Billing [26]. The g_{\parallel} and g_{\perp} values are >2.04 (Table IV), consistent with copper(II) in axial symmetry with an elongated tetragonally distorted octahedral stereochemistry for copper(II) sulfate complex and a square planar stereochemistry for copper(II) chloride complex. The G factor, defined as $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, is greater than 4.00, suggests that the local tetragonal axes are only slightly misaligned and that the exchange interactions between copper(II) centers in the solid state are negligible [26]. Moreover, the observation that $g_{\parallel} > g_{\perp} > g_e$ (2.0023), shows that the unpaired electron is in $d_{x^2-y^2}$ orbital of the copper(II) ion [27,28].

General structures are proposed for the metal complexes on the basis of above discussion (Figure 2).

Thermal analyses (TGA & DTA)

Thermal studies on $[\text{Cu}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ complex (Table V) indicate that the complex is highly stable and shows no weight loss upto 154°C . The complex loses weight at 155°C corresponding to the removal of two water molecules. This indicates that both the water molecules are coordinated to the metal. The complex further loses weight appreciably near 250°C due to partial decomposition of organic ligand. The DTA study shows significant heat liberation during ligand decomposition. The weight of the complex observed at 360°C corresponds to CuSO_4 as a result of complete decomposition of organic ligand.

X-ray diffraction studies

The X-ray powder diffraction patterns for $[\text{Co}(\text{pabh})(\text{H}_2\text{O})\text{Cl}]$ and $[\text{Ni}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$ complexes were recorded and successfully indexed

Table VI. Observed and calculated Q and hkl values.

Powder pattern	Angle	Intensity	d(Å)	Q _{obs.} (1/d ²)	Q _{calc.}	hkl
[Co(pabh)(H ₂ O)Cl]						
1	11.41	94.30	7.7572	0.0166	0.0166	100
2	12.71	88.88	6.9628	0.0206	0.0206	101
3	15.98	86.27	5.5462	0.0325	0.0326	102
4	17.09	70.94	5.1897	0.0371	0.0372	111
5	19.35	72.96	4.5880	0.0475	0.0492	112
6	20.10	85.21	4.4176	0.0512	0.0526	103
7	23.22	59.98	3.8313	0.0681	0.0664	200
8	24.07	69.02	3.6972	0.0731	0.0704	201
9	25.53	67.18	3.4894	0.0821	0.0824	202
10	26.48	48.34	3.3657	0.0883	0.0870	211
11	27.29	56.38	3.2683	0.0936	0.0972	11
12	28.04	49.53	3.1822	0.0987	0.0990	212
13	29.10	46.45	3.0691	0.1062	0.1024	203
14	30.75	49.89	2.9073	0.1183	0.1190	213
15	32.31	39.09	2.7706	0.1303	1.1304	204
16	33.02	42.98	2.7131	0.1358	0.1368	221
17	34.47	42.06	2.6017	0.1477	0.1470	214
18	36.28	34.04	2.4760	0.1631	0.1654	302
19	37.19	33.91	2.4179	0.1710	0.1700	311
20	38.59	30.13	2.3329	0.1837	0.1820	312
21	40.85	31.02	2.2088	0.2050	0.2020	313
22	42.06	32.22	2.1482	0.2167	0.2134	304
23	42.61	31.82	2.121	0.2222	0.2198	321
24	43.27	35.83	2.0911	0.2287	0.2300	314
25	43.72	35.98	2.0705	0.2333	0.2328	225
26	45.03	31.79	2.0134	0.2467	0.2494	305
27	45.53	30.46	1.9924	0.2519	0.2518	323
28	47.04	27.63	1.9320	0.2679	0.2696	401
29	48.54	28.54	1.8754	0.2843	0.2862	411
30	49.25	29.59	1.8503	0.2921	0.2982	412
31	50.00	29.49	1.8241	0.3005	0.3016	403
32	51.61	27.44	1.7710	0.3188	0.3182	413
33	51.96	27.07	1.7599	0.3229	0.3296	404
[Ni(Hpabh)(H ₂ O) ₂ (SO ₄)]						
1	16.25	33.97	5.4546	0.0336	0.0336	100
2	17.10	24.86	5.1854	0.0372	0.0372	010
3	18.35	100.00	4.8348	0.0428	0.0428	001
4	23.55	30.25	3.7777	0.0701	0.0708	110
5	24.30	34.21	3.6628	0.0745	0.0764	101
6	25.95	42.68	3.4335	0.0848	0.0800	011
7	29.70	35.71	3.0080	0.1105	0.1136	111
8	33.45	22.77	2.6789	0.1393	0.1344	200
9	37.10	17.94	2.4233	0.1703	0.1712	002
10	38.95	19.00	2.3123	0.1870	0.1824	120
11	39.55	19.20	2.2786	0.1926	0.1916	021
12	40.65	18.29	2.2195	0.2030	0.2048	102
13	42.05	30.64	2.1487	0.2166	0.2144	211
14	54.20	19.07	1.6923	0.3492	0.3452	301

(Table VI) by using Ito's method [29] and the lattice constants calculated as follows:

$$[\text{Co}(\text{pabh})(\text{H}_2\text{O})\text{Cl}]$$

$$a = 7.76, \quad b = 7.76 \text{ and } c = 15.81 \text{ \AA}$$

$$[\text{Ni}(\text{Hpabh})(\text{H}_2\text{O})_2(\text{SO}_4)]$$

$$a = 5.45, \quad b = 5.18 \text{ and } c = 4.83 \text{ \AA}$$

The above constants indicate a tetragonal crystal lattice for the former and an orthorhombic crystal lattice for the latter complex.

Antifungal activity

The antifungal experimental data (Table VIIA) indicate that the complexes show a fair degree of activity against *Alternaria sp.*, *Rizoctonia sp.*, *Stemphylium sp.* and *Penicillium sp.* at 0.5, 1.0 and 1.5 mg/mL concentration. Comparative analysis shows a higher antifungal activity for the metal complexes than the free ligands [30]. The activity is appreciably enhanced at the higher concentration of the compounds. Both the ligands Hpabh and Hpcb show better activity against *Stemphylium sp.* [Cu(pabh)(H₂O)Cl] shows

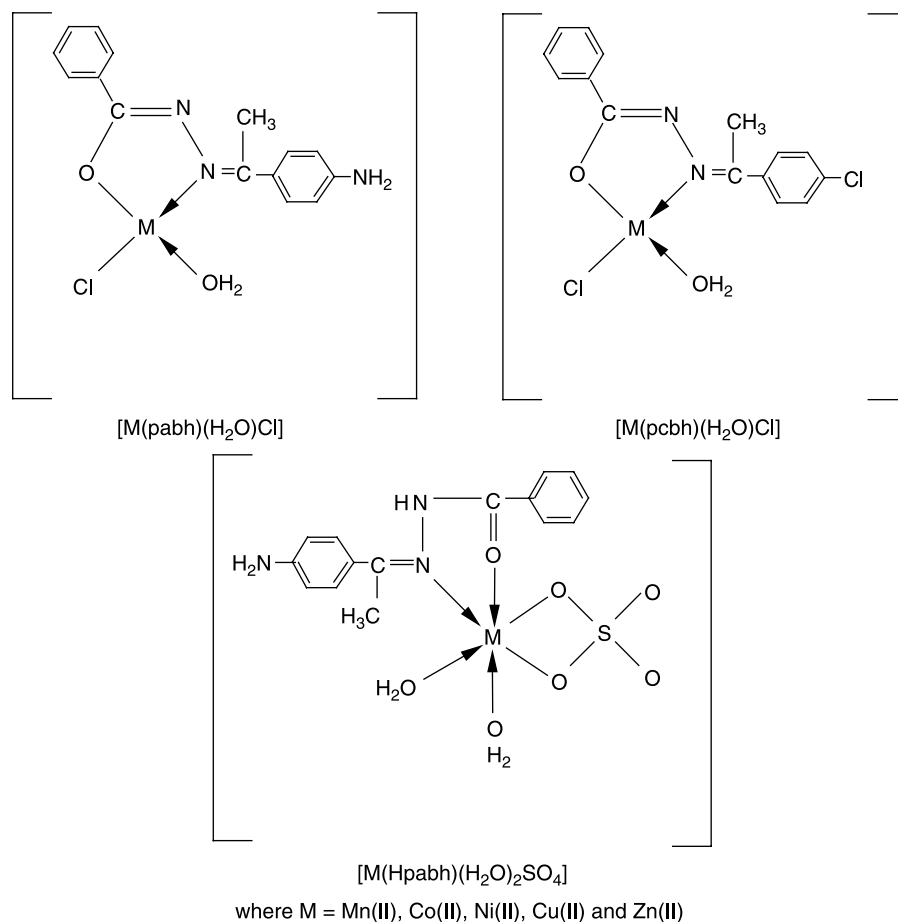


Figure 2. Representative structures of the complexes.

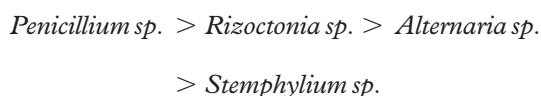
Table VIIA. Antifungal activity of the ligands and their complexes.

Compounds	% Inhibition of spore germination											
	<i>Alternaria sp.</i> (mg/mL)			<i>Rizoctonia sp.</i> (mg/mL)			<i>Stemphylium sp.</i> (mg/mL)			<i>Penicillium sp.</i> (mg/mL)		
	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
Hpabh	40	46	52	50	53	59	42	46	51	42	49	51
Hpcbh	36	40	45	48	52	56	40	43	47	41	45	49
[Mn(pabh)(H ₂ O)Cl]	55	62	87	56	65	86	47	61	88	59	81	92
[Co(pabh)(H ₂ O)Cl]	52	63	92	52	58	73	45	60	75	54	77	91
[Ni(pabh)(H ₂ O)Cl]	48	56	69	63	67	79	44	56	73	52	73	90
[Cu(pabh)(H ₂ O)Cl]	80	85	95	76	86	97	49	62	90	80	93	98
[Zn(pabh)(H ₂ O)Cl]	50	66	76	60	71	83	43	57	83	47	55	85
[Mn(pcbh)(H ₂ O)Cl]	51	60	82	52	62	85	42	58	86	55	78	90
[Co(pcbh)(H ₂ O)Cl]	48	62	91	50	56	70	42	57	72	52	76	89
[Ni(pcbh)(H ₂ O)Cl]	45	55	66	60	65	78	43	55	71	49	70	90
[Cu(pcbh)(H ₂ O)Cl]	68	78	92	70	82	95	48	60	88	78	91	95
[Zn(pcbh)(H ₂ O)Cl]	49	65	75	58	70	82	40	55	80	46	52	84
[Mn(Hpabh)(H ₂ O) ₂ (SO ₄)]	46	59	79	52	66	87	49	77	95	49	64	88
[Co(Hpabh)(H ₂ O) ₂ (SO ₄)]	44	77	96	68	80	92	47	62	85	63	80	95
[Ni(Hpabh)(H ₂ O) ₂ (SO ₄)]	56	69	77	67	76	94	60	70	92	54	80	97
[Cu(Hpabh)(H ₂ O) ₂ (SO ₄)]	50	62	92	76	87	94	52	67	87	51	68	89
[Zn(Hpabh)(H ₂ O) ₂ (SO ₄)]	43	66	76	55	66	78	48	62	91	47	55	86
Miconazole (standard)	42	56	80	50	70	90	45	58	85	50	70	82

Table VIII. Antibacterial activity of the ligands and their complexes.

Compounds	<i>Pseudomonas sp.</i> (mg/mL)					<i>Clostridium sp.</i> (mg/mL)				
	MIC (mg/mL)	Diameter of inhibition zone (in mm)		% Activity Index		MIC (mg/mL)	Diameter of inhibition zone (in mm)		% activity Index	
		1.0	2.0	1.0	2.0		1.0	2.0	1.0	2.0
Hpabh	0.7	3	4	20	22	0.8	2	4	14	25
Hpcbh	0.7	3	4	20	22	0.8	2	3	14	19
[Mn(pabh)(H ₂ O)Cl]	0.6	6	10	40	56	0.7	4	6	29	38
[Co(pabh)(H ₂ O)Cl]	0.5	8	12	53	67	0.5	8	12	57	75
[Ni(pabh)(H ₂ O)Cl]	0.5	8	10	53	56	0.6	6	10	43	63
[Cu(pabh)(H ₂ O)Cl]	0.4	10	16	67	89	0.4	10	14	71	88
[Zn(pabh)(H ₂ O)Cl]	0.6	7	11	47	61	0.6	7	10	50	63
[Mn(pcbh)(H ₂ O)Cl]	0.6	6	9	40	50	0.7	4	5	29	31
[Co(pcbh)(H ₂ O)Cl]	0.5	8	10	53	56	0.5	8	11	57	69
[Ni(pcbh)(H ₂ O)Cl]	0.5	8	9	53	50	0.6	6	9	43	56
[Cu(pcbh)(H ₂ O)Cl]	0.4	9	15	60	83	0.4	9	14	64	88
[Zn(pcbh)(H ₂ O)Cl]	0.6	7	10	47	56	0.6	7	9	50	56
[Mn(Hpabh)(H ₂ O) ₂ (SO ₄)]	0.3	12	14	80	78	0.4	10	12	71	75
[Co(Hpabh)(H ₂ O) ₂ (SO ₄)]	0.3	12	15	80	83	0.3	12	14	86	88
[Ni(Hpabh)(H ₂ O) ₂ (SO ₄)]	0.2	14	16	93	89	0.5	8	10	57	63
[Cu(Hpabh)(H ₂ O) ₂ (SO ₄)]	0.3	13	16	87	89	0.5	9	13	64	81
[Zn(Hpabh)(H ₂ O) ₂ (SO ₄)]	0.4	11	15	73	83	0.5	8	10	57	63
Ampicillin (standard)	0.2	15	18	100	100	0.2	14	16	100	100

the highest activity (95, 97, 90 and 98%) against *Alternaria sp.*, *Rizoctonia sp.*, *Stemphylium sp.* and *Penicillium sp.*, respectively, among all the complexes at the concentration of 1.5 mg/mL. The complexes generally vary in their antifungal activity in the following order of fungal species;



All the metal complexes exhibited better antifungal activities against *Penicillium sp.* as compared to the standard drug Miconazole. They are also more effective against *Alternaria sp.* than the standard except the Ni(II) and Zn(II) complexes. Cu(II), Co(II) and Ni(II) sulfate complexes exhibited greater activity against *Rizoctonia sp.* than the standard drug. The ligand Hpabh and its complexes are more effective as compared to ligand Hpcbh and its complexes.

The increase in antimicrobial activity of metal complexes may be explained on the basis of chelation theory. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups [31]. Further, the mode of action of the compounds may involve the formation of a hydrogen bond through the azomethine group with the active centre of cell constituents, resulting in interference with the normal cell process [32]. The toxicity of the complexes can be related to the strength of the metal-ligand bond, besides other

factors such as size of the cation [33] receptor sites, diffusion and a combined effect of the metal and ligands for inactivation of the biomolecules [34].

Antibacterial activity

The metal complexes, ligands, standard drug Ampicillin and control were screened separately for their antibacterial activity against *Pseudomonas sp.* (Gram – ve) and *Clostridium sp.* (Gram + ve). The activity generally increases with increasing the concentration of the complexes [35]. The metal complexes are more effective against *Pseudomonas sp.* than *Clostridium sp.* The activity of the complexes has been compared with the activity of a common standard antibiotic Ampicillin and % Activity Index has been calculated for the complexes. The antibacterial results suggest that the ligands and their complexes (Table VIII) show a moderate activity against both the bacteria [36,37] as compared to the standard drug (Ampicillin). The metal complexes show higher antibacterial activity than the parent ligands. The % Activity Index data indicate the highest activity (89 %) for [Cu(pabh)(H₂O)Cl], [Cu(Hpabh)(H₂O)₂(SO₄)] and [Ni(Hpabh)(H₂O)₂(-SO₄)] complexes against *Pseudomonas sp.* at the concentration of 2.0 mg/mL.

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