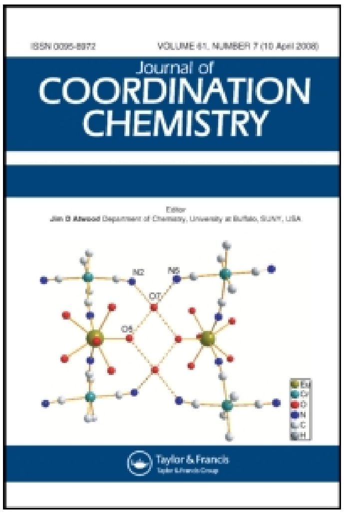

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Synthesis, structural studies and bio-activity of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with <i>p</i>-amino acetophenone salicyloyl hydrazone

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Synthesis, structural studies and bio-activity of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with *p*-amino acetophenone salicyloyl hydrazone

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Complexes of the type [M(pash)Cl] and [M(Hpash)(H_2O)SO_4] (M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); Hpash = *p*-amino acetophenone salicyloyl hydrazone) have been synthesized and characterized by elemental analyses, molar electrical conductance, magnetic moments, electronic, ESR and IR spectra, thermal studies and X-ray powder diffraction. All the complexes are insoluble in common organic solvents and are non-electrolytes. The magnetic moment values and electronic spectra indicate a square-planar geometry for Co(II), Ni(II) and Cu(II) chloride complexes and spin-free octahedral geometry for the sulfato complexes. The ligand coordinates through >C=N–, –NH_2 and a deprotonated enolate group in all the chloro complexes, and through >C=N–, >C=O and –NH_2 in the sulfato complexes. Thermal analyses (TGA and DTA) of [Cu(pash)Cl] show a multi-step exothermic decomposition pattern. ESR spectral parameters of Cu(II) complexes in solid state at room temperature suggest the presence of the unpaired electron in $d_{x^2-y^2}$. X-ray powder diffraction parameters for [Cu(pash)Cl] and [Ni(Hpash)(H_2O)SO_4] correspond to tetragonal and orthorhombic crystal lattices, respectively. The complexes show a fair degree of antifungal activity against *Aspergillus* sp., *Stemphylium* sp. and *Trichoderma* sp. and moderate antibacterial activity against *E. coli* and *Clostridium* sp.

Keywords: Synthesis; Structure; Bioactivity; Salicyloyl hydrazone; Metal(II) complexes

1. Introduction

Schiff-bases containing (–RC=N–) have gained importance because of physiological and pharmacological activities [1–3], constituting an interesting class of flexidentate chelating agents. Since *p*-amino acetophenone has an active carbonyl group, the resulting Schiff base derived from salicyloyl hydrazine and *p*-amino acetophenone and its complexes show different physico-chemical behavior; *p*-amino acetophenone salicyloyl hydrazone can bond to metal ions either in keto form (I) or in enolic

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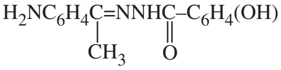
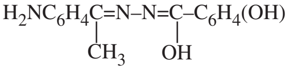
form (II) as a neutral or monobasic chelating ligand depending upon the metal or pH of the medium.



$H_2NC_6H_4\underset{\underset{CH_3}{|}}{C}{=}NNH\underset{\underset{O}{\|}}{C}{-}C_6H_4(OH)$

(I)



$H_2NC_6H_4\underset{\underset{CH_3}{|}}{C}{=}N{-}N{=}\underset{\underset{OH}{|}}{C}{-}C_6H_4(OH)$

(II)

A number of transition metal complexes with a variety of multidentate acylhydrazone Schiff bases have been reported [4–7]. In view of the analytical and biological properties of acylhydrazone ligands and their complexes, we have synthesized Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with *p*-amino acetophenone salicyloyl hydrazone and characterized them by magnetic moment, electronic, ESR, IR spectra and X-ray diffraction data. Biological activity of the complexes has also been studied.

2. Experimental

2.1. *Materials*

All the chemicals used were of BDH or equivalent grade. The precursor salicyloyl hydrazine, $C_6H_4(OH)CONHNH_2$ (sh) was prepared by the reported procedure [8] by refluxing methyl salicylate with hydrazine hydrate in 1 : 1 molar ratio in a flask containing 10 mL ethanol for 3–4 h. The pure product was characterized by its melting point. m.p. 146°C (lit. 147°C).

2.1.1. Preparation of p-amino acetophenone salicyloyl hydrazone. *p*-Amino acetophenone salicyloyl hydrazone (Hpash), $H_2NC_6H_4C(CH_3){=}NNHCO\ C_6H_4OH$ was prepared by reacting *p*-amino acetophenone (10 mmol, 13.5 g) with salicyloyl hydrazine (10 mmol, 15.2 g) dissolved in 50 mL ethanol. The reaction mixture was refluxed for 5–6 h and then transferred into a beaker. The product was filtered, washed several times with aqueous ethanol (50%, v/v) and recrystallized from hot ethanol. The pure product was dried over anhydrous $CaCl_2$ in a desiccator.

The ligand was characterized by elemental analyses (C, H, N), melting points and infrared spectra.

2.1.2. Synthesis of the metal complexes. The metal complexes were synthesized by reacting 10 mmol solutions of each metal salt in 50 mL aqueous ethanol (50%, v/v) with 50 mL solution, *p*-amino acetophenone salicyloyl hydrazone (Hpash) (10 mmol, 2.69 g) in hot ethanol separately, in 1 : 1 (M : L) molar ratio. The reactants were refluxed for 1–3 h and the complexes precipitated after cooling to room temperature and were filtered in a glass crucible. The products were purified by washing several times with water followed by ethanol and finally with diethyl ether and dried in a desiccator over anhydrous $CaCl_2$ at room temperature.

2.2. *Analyses of the complexes*

2.2.1. Elemental analyses. The complexes were analyzed for metal content gravimetrically by literature procedures [9] 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 an Elementar Vario EL III Carlo Erba 1108 model microanalyzer.

2.2.2. Physico-chemical measurements. The molar conductance of the complexes was determined by preparing 10^{-3} M solutions in DMSO 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 and 800°C. Room temperature magnetic susceptibility measurements were carried out on a Faraday balance using $Hg[Co(SCN)_4]$ as calibrant and corrected for diamagnetism [10]. Electronic spectra of the complexes were recorded in DMSO on a Perkin-Elmer Lambda-2 spectrophotometer in the range 1100–200 nm. Infrared spectra of the complexes and parent ligand were recorded on a Vector-22 spectrophotometer in the range 4000–500 cm^{-1} in KBr. 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 Cu-Kα radiation. The analytical and physico-chemical data are given in tables 1–5.

2.3. *Biological activity*

2.3.1. Antifungal activity. The ligand and its complexes were screened for antifungal activity against *Aspergillus* sp., *Trichoderma* sp. and *Stemphylium* 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.

Solutions of concentrations 0.5, 1 and 1.5 mg mL^{-1} of each compound in DMSO were prepared for testing against spore germination. A drop of solution of each concentration was kept separately 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 DMSO solvent control set was run concurrently on separate glass slides. All the slides were incubated in humid chambers at 25 ± 2°C for 24 h. Each slide was observed under the microscope for spore germination and percent germination was calculated. The results were compared with a standard antifungal drug Miconazole at the same concentrations.

2.3.2. Antibacterial activity. The antibacterial activity of the ligand and its complexes was studied against *Clostridium* sp., and *E. coli* bacteria. Each of the

Table 1. Analytical data of the ligand and its complexes.

Compounds (Color)	Empirical formula (Formula wt.)	Melting point (°C)	Found (Calculated)%					Yield (%)	Λ_M (Ω^{-1}cm^2 mol^{-1})
			Metal	Cl^-/SO_4^{2-}	C	H	N		
Hpash (Light yellow)	$C_{15}H_{15}N_3O_2$ (269)	192			66.73 (66.91)	5.64 (5.58)	15.49 (15.61)	82	6.43
[Mn(pash)Cl] (Yellow)	$C_{15}H_{14}N_3O_2ClMn$ (358.5)	222	15.3 (15.34)	9.75 (9.90)	50.04 (50.21)	3.76 (3.90)	11.62 (11.71)	75	5.28
[Co(pash)Cl] (Brown)	$C_{15}H_{14}N_3O_2ClCo$ (362.5)	260	16.15 (16.27)	9.68 (9.79)	49.51 (49.65)	3.77 (3.86)	11.47 (11.59)	80	7.62
[Ni(pash)Cl] (Light pink)	$C_{15}H_{14}N_3O_2ClNi$ (362.5)	251	16.33 (16.27)	9.83 (9.79)	49.46 (49.65)	3.93 (3.86)	11.51 (11.59)	85	4.15
[Cu(pash)Cl] (Brown)	$C_{15}H_{14}N_3O_2ClCu$ (367)	273	17.20 (17.30)	9.56 (9.67)	49.18 (49.05)	3.87 (3.81)	11.36 (11.44)	86	2.68
[Zn(pash)Cl] (Yellow)	$C_{15}H_{14}N_3O_2ClZn$ (368.5)	218	17.49 (17.64)	9.50 (9.63)	48.72 (48.85)	3.91 (3.80)	11.42 (11.40)	80	9.21
[Mn(Hpash)(H_2O)SO_4] (Light yellow)	$C_{15}H_{17}N_3O_7SMn$ (438)	225	12.45 (12.56)	21.76 (21.92)	40.93 (41.09)	3.82 (3.88)	9.66 (9.59)	78	2.25
[Co(Hpash)(H_2O)SO_4] (Pinkish brown)	$C_{15}H_{17}N_3O_7SCo$ (442)	256	13.17 (13.35)	21.57 (21.72)	40.56 (40.72)	3.75 (3.85)	9.38 (9.50)	80	5.36
[Ni(Hpash)(H_2O)SO_4] (Light green)	$C_{15}H_{17}N_3O_7SNi$ (442)	270	13.22 (13.35)	21.60 (21.72)	40.59 (40.72)	3.91 (3.85)	9.42 (9.50)	85	3.26
[Cu(Hpash)(H_2O)SO_4] (Green)	$C_{15}H_{17}N_3O_7SCu$ (446.5)	248	14.07 (14.22)	21.41 (21.50)	40.17 (40.31)	3.94 (3.81)	9.31 (9.41)	85	1.77
[Zn(Hpash)(H_2O)SO_4] (Yellow)	$C_{15}H_{17}N_3O_7SZn$ (448)	210	14.5 (14.51)	21.28 (21.43)	40.05 (40.18)	3.75 (3.79)	9.33 (9.37)	80	2.12

Table 2. Magnetic moments, electronic spectral data and ligand field parameters of the complexes.

Complexes	μ_{eff} (B.M.)	Band maxima (cm^{-1}) ν_1	ν_2	ν_3	10 Dq	B(cm^{-1})	β	$\beta°$ (%)	LFSE (kcal mol^{-1})
[Mn(pash)Cl]	5.95	19050	23810						
[Co(pash)Cl]	2.20	–	21740	28985					
[Ni(pash)Cl]	Diamagnetic	12345	19610	26315					
[Cu(pash)Cl]	1.72	–	16530	–					
[Mn(Hpash)(H_2O)SO_4]	5.91	20410	24390						
[Co(Hpash)(H_2O)SO_4]	4.79	9280	–	20180	10440	804	0.828	17.20	23.79
[Ni(Hpash)(H_2O)SO_4]	2.88	10570	16345	28285	10570	861	0.827	17.30	36.14
[Cu(Hpash)(H_2O)SO_4]	1.85	10640	13790						

Table 3. ESR spectral parameters of Cu(II) complexes in solid state at room temperature (298 K).

Complex	$A_{\parallel}(G)$	$A_{\perp}(G)$	$A_{av}(G)$	$g_{\parallel}$	$g_{\perp}$	g_{av}	G
[Cu(pash)Cl]	95	63	73.6	2.2398	2.0409	2.1072	5.8630
[Cu(Hpash)(H_2O)SO_4]	141	91	108.0	2.2649	2.0612	2.1291	4.3284

Table 4. Thermal decomposition of [Cu(pash)Cl] complex.

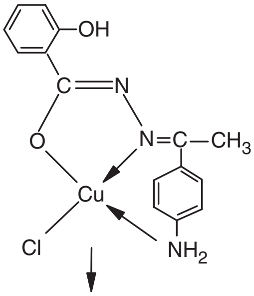
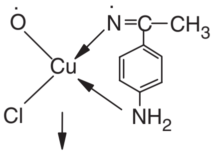
S. No	Temp. (°C)	Proposed decomposition pattern	% Loss of wt. Obs	Calcd	Energy change	Remarks
1	40–273		0.00	0.00	Endothermic	No decomposition
2	273		32.00	32.42	Exothermic	Partial decomposition of organic ligand
3	490	Cu–Cl	72.50	73.00	Exothermic	Complete decomposition of organic moiety

Table 5. Important IR spectral bands (cm^{-1}) and their assignments.

Compounds	ν(OH/NH)	Amide I ν(C=O)	ν(C=N)	Amide II	Amide III	ν(N=C–O)	ν(C–O)	ν(N–N)	ν(M–O)	Water bands
Hpash	3450b, 3295b	1669s	1632s	1560m	1370s	–	–	980w	–	–
[Mn(pash)Cl]	3440b, 3246s	–	1622s	–	–	1493s	1333s	1005w	572w	–
[Co(pash)Cl]	3442b, 3255s	–	1618s	–	–	1490s	1335w	998w	574w	–
[Ni(pash)Cl]	3435b, 3248s	–	1615s	–	–	1482m	1337w	1004w	580w	–
[Cu(pash)Cl]	3433b, 3260s	–	1612s	–	–	1485m	1341w	1008w	582w	–
[Zn(pash)Cl]	3442b, 3252s	–	1619s	–	–	1492w	1342w	1010w	585w	–
[Mn(Hpash)(H$_2$O)SO$_4$]	3429b, 3250b	1638s	1610s	1545m	1381s	–	–	1005w	570w	904w, 760w, 633m
[Co(Hpash)(H$_2$O)SO$_4$]	3425b, 3262b	1642s	1608s	1548s	1382s	–	–	995w	576w	902w, 758s, 632m
[Ni(Hpash)(H$_2$O)SO$_4$]	3433b, 3243b	1638s	1603s	1530m	1378s	–	–	1002w	572s	906w, 752s, 622w
[Cu(Hpash)(H$_2$O)SO$_4$]	3419b, 3264b	1647s	1609s	1537m	1382s	–	–	1009w	594m	910w, 749w, 618m
[Zn(Hpash)(H$_2$O)SO$_4$]	3440b, 3248b	1645s	1612s	1542m	1385s	–	–	1012w	582w	907w, 748w, 630w

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

Table 6A. Antifungal activity of the ligand and its complexes.

	% Inhibition of spore germination								
	Aspergillus sp. ($mg\,mL^{-1}$)			*Stemphylium* sp. ($mg\,mL^{-1}$)			*Trichoderma* sp. ($mg\,mL^{-1}$)		
Compounds	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
Hpash	44	56	62	49	57	65	31	37	48
[Co(pash)Cl]	56	77	92	78	86	98	44	72	85
[Ni(pash)Cl]	63	71	86	84	90	97	49	69	90
[Cu(pash)Cl]	65	77	90	87	92	100	42	65	86
[Co(Hpash)(H$_2$O)SO$_4$]	67	80	93	75	88	91	40	62	89
[Ni(Hpash)(H$_2$O)SO$_4$]	58	69	87	74	85	98	50	70	85
[Cu(Hpash)(H$_2$O)SO$_4$]	66	81	95	78	90	100	45	67	88
Miconazole (standard)	62	80	90	52	70	90	55	70	92

compounds was dissolved in DMSO and solutions of $1\,mg\,mL^{-1}$ and $2\,mg\,mL^{-1}$ were prepared separately. Article discs of Whatman filter article (No. 42) of uniform diameter (2 cm) were cut and sterilized in an autoclave. Article discs soaked in the desired concentration of the complex solutions were placed aseptically in petridishes containing nutrient agar media (agar 20 g + beef extract 3 g + peptone 5 g) seeded with *Clostridium* sp. and *E. coli* 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 at the same concentrations and solvent. The % Activity Index for the complex was calculated by the formula:

$$\%\ \text{Activity index} = \frac{\text{Zone of inhibition by test compound (diamter)}}{\text{Zone of inhibition by standard (diamter)}} \times 100$$

Table 6B. Antibacterial activity of the ligand and its complexes.

	E. coli (mg mL^{-1})					*Clostridium* sp. (mg mL^{-1})				
		Diameter of inhibition zone (in mm)		% Activity index			Diameter of inhibition zone (in mm)		% Activity index	
Compounds	MIC (mg mL^{-1})	1.0	2.0	1.0	2.0	MIC (mg mL^{-1})	1.0	2.0	1.0	2.0
Hpash	0.8	2	4	13	22	0.7	3	4	21	25
[Co(pash)Cl]	0.5	11	13	73	61	0.5	10	12	71	75
[Ni(pash)Cl]	0.3	13	15	87	83	0.5	11	14	79	88
[Cu(pash)Cl]	0.5	10	14	67	78	0.5	11	15	79	94
[Co(pash)(H_2O)SO_4]	0.3	13	15	87	87	0.4	12	13	86	81
[Ni(pash)(H_2O)SO_4]	0.3	14	16	93	89	0.3	13	14	93	88
[Cu(pash)(H_2O)SO_4]	0.4	12	17	80	94	0.3	13	15	93	94
Ampicillin (standard)	0.2	15	18	100	100	0.2	14	16	100	100

Determination of minimum inhibitory concentration (MIC) value: 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^{-1} 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^{-1} concentrations. Consequently all the compounds were screened at these concentrations against both bacteria. The results of MIC values (mg mL^{-1}) are given in table 6B.

3. Results and discussion

It appears from the analytical data that Hpash enolizes and deprotonates during complexation with metal(II) chlorides. However, such deprotonation does not occur during the reaction with metal(II) sulfate and the ligand reacts in the keto form. The analytical data (table 1) show that Hpash reacts with metal salts in 1 : 1 (M : L) molar ratio to give complexes of general compositions [M(pash)Cl] and [M(Hpash)(H_2O)SO_4]. The reactions may be written as:

$$\mathrm{MCl_2 \cdot \mathit{n}H_2O + Hpash \rightarrow [M(pash)Cl] + HCl + \mathit{n}H_2O}$$
$$\mathrm{MSO_4 \cdot \mathit{n}H_2O + Hpash \rightarrow [M(Hpash)(H_2O)SO_4] + (\mathit{n}-1)H_2O}$$

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

All the metal complexes are insoluble in water and common organic solvents, such as ethanol, methanol, benzene, chloroform, acetone and diethyl ether, but are soluble in polar solvents such as DMF and DMSO. Metal(II) chloride complexes are also soluble in hot ethanol. The complexes are yellow, green, brown to pink in color, melting with decomposition between 210–273°C. The low molar conductance values of 10^{-3} M solutions of the complexes in DMSO at room temperature show that they are all non electrolytes [11].

3.1. *Magnetic moments*

Where spin–spin coupling between unpaired electrons of 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 Cu(II) complexes correspond to μ_{eff} values for one unpaired electron (1.72 and 1.85 B.M.). Nickel(II) chloride complex is diamagnetic suggesting square-planar geometry for the complex, whereas nickel(II) sulfate complex shows μ_{eff} value 2.88 B.M. corresponding to two unpaired electrons in octahedral environment [12].

Cobalt(II) octahedral complexes generally show magnetic moments between 4.7–5.2 B.M. because of the orbital contribution. In the present study, cobalt(II) sulfate complex shows μ_{eff} of 4.79 B.M., fairly close to those reported for three unpaired electrons in an octahedral environment. Co(II) chloride complex shows μ_{eff} of 2.20 B.M. corresponding to one unpaired electron and suggests square-planar geometry [10]. Mn(II) complexes have μ_{eff} values 5.95 and 5.91 B.M. corresponding to five unpaired electrons (table 2).

3.2. *Electronic spectra*

[Cu(pash)Cl] shows a broad band near 16,530 cm^{-1} similar to $[\text{Cu(NH}_3)_4]^{2+}$ (16,600 cm^{-1}), suggesting square-planar geometry [13]. However, [Cu(Hpash)(H_2O)SO_4] shows two bands at 10,640 cm^{-1} and 13790 cm^{-1}, which may be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $\rightarrow {}^2A_{1g}$ indicating a distorted octahedral geometry. The electronic spectra of [Ni(pash)Cl] shows weak bands at 12,345, 19,610 and 26,315 cm^{-1} corresponding to $^1A_{1g} \rightarrow {}^1B_{1g}, \rightarrow {}^1B_{2g}$ and a charge transfer transition similar to that reported for Ni(II) acetylacetone *bis*-acylhydrazones [14] and many other nickel(II) complexes with a square-planar geometry [15]. Nickel(II) complexes generally show three bands in octahedral environment corresponding to the transitions $^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F) (ν_1), $\rightarrow$ $^3T_{1g}$ (F) (ν_2) and $\rightarrow$ $^3T_{1g}$ (P) (ν_3) [12]. [Ni(Hpash)(H_2O)SO_4] shows three transitions at 10,570 cm^{-1} (ν_1), 16,345 cm^{-1} (ν_2) and 28,285 cm^{-1} (ν_3) suggesting octahedral geometry.

The bands observed for [Co(pash)Cl] are in good agreement with bands reported for cobalt(II) square planar complexes [16]. [Co(Hpash)(H_2O)SO_4] shows two bands at 9,280 and 20,180 cm^{-1} indicating octahedral geometry. The above bands are assigned as $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F) (ν_1) and $\rightarrow$ $^4T_{1g}$ (P) (ν_3). The ν_2 transition was not observed due to very weak intensity [13]. Ligand field parameters (10 Dq, B, β, β° and LFSE) have been calculated for both Ni(II) and Co(II) sulfate complexes by the procedure of Lever [13]. The low value of Racah parameter (B) for the complexes compared to the free ion value indicates significant covalent character of the metal-ligand bonds. The nephelauxetic ratio β and other parameters (table 2) also support some covalent character. The weak intensity bands observed for [Mn(pash)Cl] and [Mn(Hpash)(H_2O)SO_4] suggest a tetrahedral and an octahedral geometry, respectively.

3.3. *ESR spectra*

ESR spectra of copper(II) complexes exhibit an axial signal (figure 1) with separate $g_{\parallel}$ and $g_{\perp}$ values in the solid state at 298 K. The $g_{\parallel}$ and $g_{\perp}$ values are >2.04 (table 3),

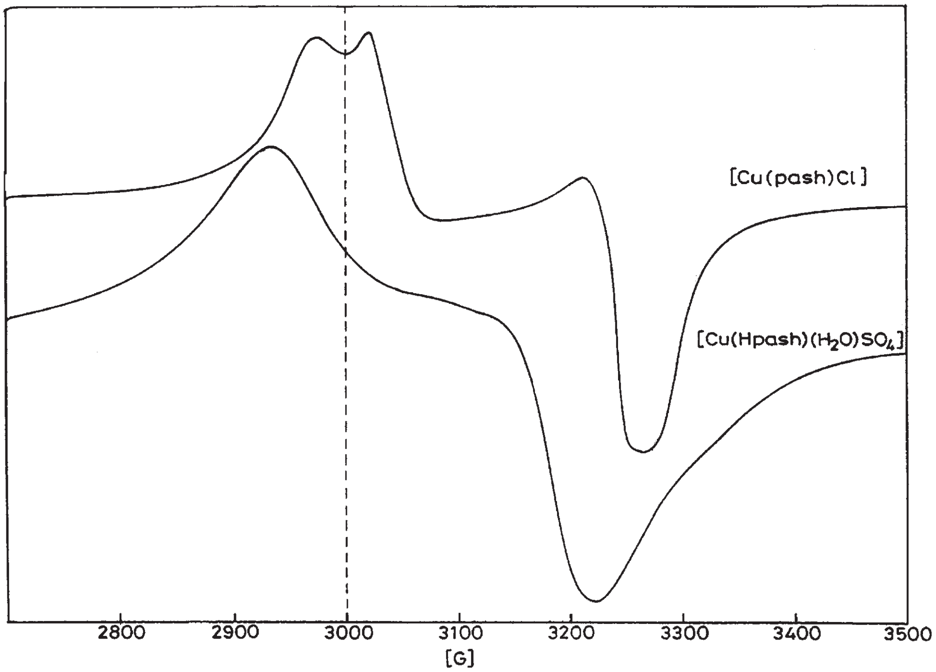


Figure 1. E.S.R spectra of copper(II) complexes at 298 K in the solid state.

indicating that Cu(II) has axial symmetry with all the principal axes aligned parallel [17]. This would be consistent with an elongated tetragonally distorted octahedral geometry for the complexes. The trend $g_{\parallel} > g_{\perp} > g_e$ suggests the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital of Cu(II) [18, 19]. The G factor [defined as $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, is 4.3284 and 5.8630, respectively, for [Cu(pash)Cl] and [Cu(Hpash)(H_2O)SO_4], suggesting that the local tetragonal axes are only slightly misaligned and the exchange interactions between copper(II) centers in the solid state negligible [17]. The g_{av} and A_{av} values were calculated using the equations $g_{av} = (g_{\parallel} + 2g_{\perp})/3$, $A_{av} = (A_{\parallel} + 2A_{\perp})$.

3.4. *Thermal analyses (TGA and DTA)*

Thermal studies on [Cu(pash)Cl] indicate that the complex is stable, showing no weight loss to 273°C (table 4). At 273°C, the complex loses weight appreciably due to the partial decomposition of organic ligand. The DTA curve (figure 2) shows significant heat liberation during ligand decomposition. Between 273–490°C, it further decomposes exothermically and the final residue obtained at 490°C corresponds to Cu–Cl.

3.5. *IR spectra*

The ligand Hpash shows broad bands centered at 3450 cm^{-1} and 3295 cm^{-1} due to ν(OH) and ν(NH), respectively. In all the complexes ν(NH) occurs at lower

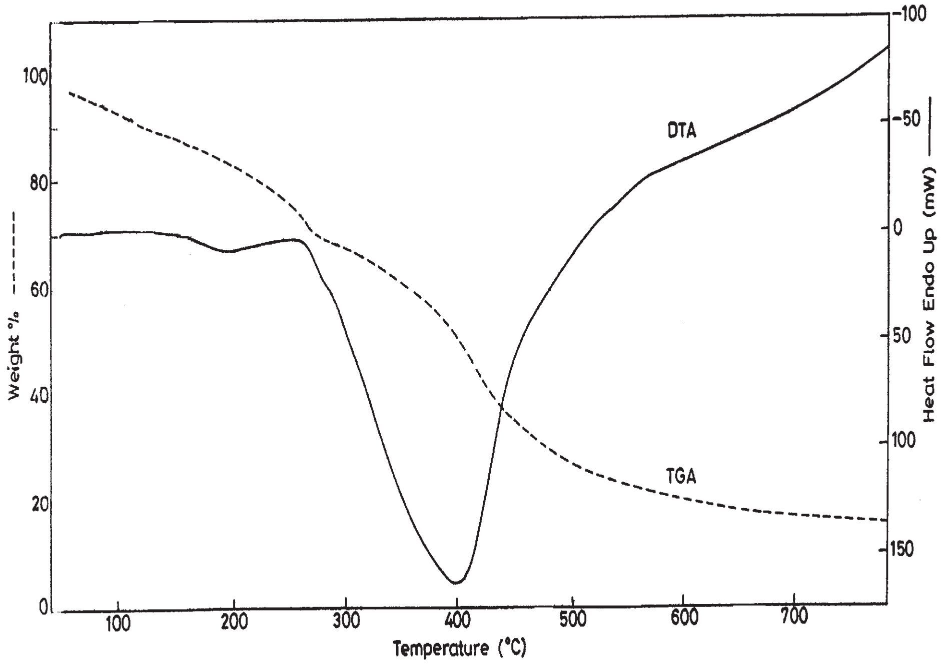
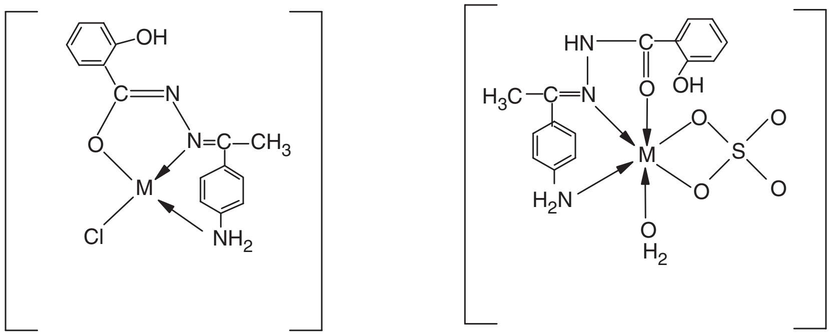


Figure 2. Thermograms (TGA & DTA) of [Cu(pash)Cl].



[M(pash)Cl] [M(Hpash)(H$_2$O)SO$_4$]

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

Figure 3. Representative structures of the complexes.

frequency (30–50 cm^{-1}) than the ligand, suggesting participation of –NH$_2$ group in bonding. The ν(C=O) band in the ligand at 1669 cm^{-1} is shifted to lower wavenumber by 22–31 cm^{-1} in the metal(II) sulfate complexes (table 5), indicating coordination of the >C=O to the metal ion [20]. In these complexes, amide II bands shift to lower frequency (12–30 cm^{-1}) compared to the ligand, and a shift to higher frequency (8–15 cm^{-1}) in the amide III bands in all the metal(II) complexes further supports coordination through the >C=O. However, disappearance of ν(C=O) and appearance of ν(N=C–O) and ν(C–O) in the region 1482–1493 cm^{-1} and 1333–1342 cm^{-1}, respectively, suggest bonding to the metal through deprotonated C–O group in all the metal(II) chloride complexes [21].

The ν(C=N) band at 1632 cm^{-1} in the ligand shifts to lower frequency by 10–29 cm^{-1} in all the metal complexes, suggesting coordination through the azomethine group [14]. ν(N–N) observed at 980 cm^{-1} in the ligand shifts to higher frequency by 15–32 cm^{-1} in the complexes, indicating coordination of nitrogen of the N–N group [22]. The metal(II) sulfate complexes also show weak bands between 902–910 cm^{-1}, 748–760 cm^{-1} and 618–633 cm^{-1} due to coordinated water [23]. The bands observed near 1215–1228 cm^{-1}, 1140–1170 cm^{-1} and 1042–1055 cm^{-1} in the metal(II) sulfate complexes indicate the bonding of a bidentate chelating sulfate. A non-ligand band observed in the region 570–594 cm^{-1} has been assigned to ν(M–O).

Structures are proposed for the metal complexes on the basis of the above discussion (figure 3).

3.6. *X-ray diffraction studies*

Since the complexes are insoluble in common inert organic solvents suitable for single crystal growth for X-ray analysis, X-ray powder diffraction patterns for two complexes were recorded and the prominent lines were indexed by Ito's method [24] (Supplementary Data). The following lattice constants were calculated:

[Cu(pash)Cl] $a = 5.73$, $b = 5.73$ and $c = 5.50$ Å

[Ni(Hpash)(H_2O)SO_4] $a = 7.24$, $b = 6.48$ and $c = 5.41$ Å

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

3.7. *Antifungal activity*

The antifungal experimental data (table 6A) indicate that the ligand and its complexes show a fair degree of activity against *Aspergillus* sp., *Stemphylium* sp. and *Trichoderma* sp. at 0.5, 1.0 and 1.5 $\mathrm{mg\,mL}^{-1}$ doses. The effect is susceptible to the concentration of the compound, enhanced at higher concentration. DMSO control shows negligible activity compared to the metal complexes and ligands. The experimental results of the compounds were compared against DMSO as the control and are expressed as percentage inhibition *versus* control. [Cu(pash)Cl] and [Cu(Hpash)(H_2O)SO_4] show 100% activity against *Stemphylium* sp. at 1.5 $\mathrm{mg\,mL}^{-1}$ dose. From the data it has been observed that the complexes show greater activity than the ligand [25]. The complexes are highly effective (91–100%) against *Stemphylium* sp. and least against *Trichoderma* sp. (85–90%).

All the metal complexes exhibited greater antifungal activity against *Stemphylium* sp. compared to the standard drug Miconazole, but less activity against *Trichoderma* sp.

The Co(II) and Cu(II) complexes are more effective against *Aspergillus* sp. than the standard.

3.8. *Antibacterial activity*

The metal complexes, ligands, standard drug Ampicillin and DMSO solvent control were screened separately for their antibacterial activity against *E. coli* and *Clostridium* sp. at 1.0 and 2.0 mg mL^{-1} doses. The activity increases with increasing concentration [26]. The activity of the complexes has been compared with the activity of a common standard antibiotic Ampicillin and % Activity Index has been calculated. The antibacterial results suggest that the ligands and their complexes (table 6B) show moderate activity against both the bacteria [27, 28] as compared to Ampicillin. The metal complexes show higher antibacterial activity than the ligands. The DMSO control showed no activity against any bacterial strain. The % Activity Index data show that [Cu(Hpash)(H_2O)SO_4] shows the highest activity (94%) against both bacteria at 2.0 mg mL^{-1} among all the metal complexes. [Cu(pash)Cl] also shows 94% activity against *Clostridium* sp. at the dose of 2.0 mg mL^{-1}. The activity data show that the complexes are more active than the parent ligand.

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