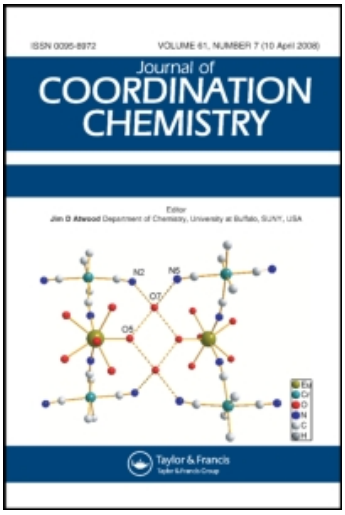

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, physico-chemical investigations and biological studies on Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with p-amino acetophenone isonicotinoyl hydrazone

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First published on: 29 July 2010

To cite this Article Singh, Vinod P. , Katiyar, Anshu and Singh, Shweta(2009) 'Synthesis, physico-chemical investigations and biological studies on Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with **p**-amino acetophenone isonicotinoyl hydrazone', Journal of Coordination Chemistry, 62: 8, 1336 — 1346, First published on: 29 July 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958970802546016
URL: http://dx.doi.org/10.1080/00958970802546016

Journal of Coordination Chemistry
Vol. 62, No. 8, 20 April 2009, 1336–1346

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Synthesis, physico-chemical investigations and biological studies on Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with *p*-amino acetophenone isonicotinoyl hydrazone

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(*Received 29 February 2008; in final form 1 August 2008*)

Complexes of the type $[M(painh)(H_2O)_2X]$, where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X = Cl_2 or SO_4; painh = *p*-amino acetophenone isonicotinoyl hydrazone, have been synthesized and characterized by spectral and other physico-chemical techniques. The synthesized complexes are stable powders, insoluble in common organic solvents such as ethanol, benzene, carbon tetrachloride, chloroform and diethyl ether, and are non-electrolytes. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) studies show that the organic ligand decomposes exothermically through various steps. TGA and Infrared (IR) spectral studies indicate the presence of coordinated water in the metal complexes. Magnetic susceptibility measurements and electronic spectra suggest that Mn(II), Co(II), and Ni(II) complexes are paramagnetic with octahedral geometry, whereas Cu(II) complexes have distorted octahedral geometry. The neutral bidentate ligand bonds through >C=O and >C=N– groups in all the complexes. Electron Spin Resonance (ESR) spectra in the solid state show axial symmetry for $[Cu(painh)(H_2O)_2(SO_4)]$ and elongated rhombic symmetry for $[Cu(painh)(H_2O)_2Cl_2]$, suggesting an elongated tetragonally-distorted octahedral structure for both complexes. X-ray powder diffraction parameters for two complexes correspond to tetragonal and orthorhombic crystal lattices. The metal complexes show fair antifungal activity against *Rizoctonia* sp., *Aspergillus* sp., *Stemphylium* sp., and *Penicillium* sp. and appreciable antibacterial activity against *Pseudomonas* sp. and *Escherichia coli*.

Keywords: Metal(II) complexes; *p*-Amino acetophenone isonicotinoyl hydrazone; Electronic and IR spectral studies; ESR spectra; Antifungal and antibacterial

1. Introduction

Transition metal ions with different oxidation states have a strong role in bio-inorganic chemistry and redox enzyme systems [1, 2] and may provide models for active sites of biological systems [3, 4] or act as catalysts [5–7]. Metal complexes of multidentate acylhydrazone Schiff bases have been extensively studied [8–10] because such ligands can bind with one, two or more metal centers involving various coordination modes and allow synthesis of homo and hetero nuclear metal complexes with interesting stereochemistry [11–13]. A number of papers [14–18] highlight the flexible nature of acylhydrazone ligands, their analytical and biological properties.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802546016

Since acylhydrazones are biologically active compounds [19–21], the metal complexes formed should be more biologically active than the metal salts or the ligand, individually [22]. Here we report the synthesis, structural investigations, and biological studies on Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes with *p*-amino acetophenone isonicotinoyl hydrazone.

2. Experimental

2.1. *Materials*

All the chemicals used were of BDH Chemicals Limited or equivalent grade. Isonicotinic acid hydrazide (inh) was obtained from CDH Chemicals, New Delhi, and used after recrystallization in ethanol.

2.2. *Preparation of* p-*amino acetophenone isonicotinoylhydrazone*

p-Amino acetophenone isonicotinoylhydrazone (painh), $H_2NC_6H_4C(CH_3)=NNHCOC_5H_4N$ was prepared by reacting *p*-amino acetophenone (10 mmol, 13.5 g) with inh (10 mmol, 13.7 g) dissolved in 50 mL ethanol. The reaction mixture was taken into a round bottom flask and refluxed for 5 h and then transferred into a beaker. The product was filtered on a suction pump, washed several times with aqueous ethanol (50%, v/v) and recrystallized from hot ethanol. The pure products were dried over anhydrous $CaCl_2$ in a desiccator. The ligand was characterized by elemental analyses (C, H, N), melting point, and Infrared (IR) spectra.

2.3. *Synthesis of the metal complexes*

The metal complexes were synthesized by reacting 10 mmol solutions of each metal salt $MnCl_2 \cdot 4H_2O$ (1.98 g), $MnSO_4 \cdot H_2O$ (1.69 g), $CoCl_2 \cdot 6H_2O$ (2.38 g), $CoSO_4 \cdot xH_2O$ (1.55 g), $NiCl_2 \cdot 6H_2O$ (2.38 g), $NiSO_4 \cdot 7H_2O$ (2.81 g), $CuCl_2 \cdot 2H_2O$ (1.70 g), $CuSO_4 \cdot 5H_2O$ (2.50 g), $ZnCl_2$ (1.36 g), and $ZnSO_4 \cdot 7H_2O$ (2.88 g) in 50 mL aqueous ethanol (50%, v/v) at room temperature with 50 mL hot ethanolic solution of painh (l0 mmol, 2.54 g) separately in a beaker (1 : 1, M : L molar ratio). The reactants were stirred with a glass rod at room temperature for 5 min. The complexes precipitated immediately, were filtered in a glass crucible and purified by washing several times with water, ethanol and finally with diethyl ether. The complexes were dried in a desiccator over anhydrous calcium chloride. The complexes were finely divided powders which could not be recrystallized.

2.4. *Analyses of the complexes*

2.4.1. Elemental analyses. The complexes were analyzed for metal content gravimetrically by literature procedures [23] after decomposing the organic matter with HNO_3/HCl and evaporating the residue to dryness with conc. H_2SO_4. The chloride

content 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.

2.4.2. Physico-chemical measurements. The molar conductance of the complexes was determined by preparing 10^{-3} M solutions in Dimethyl Sulfoxide (DMSO) at room temperature and measured on a Systronic conductivity meter model-306. Thermal studies (Thermogravimetric Analysis, TGA and Differential Thermal Analysis, DTA) of one complex were carried out on a Perkin–Elmer thermal analyzer from room temperature to 600°C at a heating rate of 10°C min^{-1} under N_2. Room temperature magnetic susceptibility measurements were carried out on a Faraday balance using $Hg[Co(SCN)_4]$ as calibrant and corrected for diamagnetism [24]. Electronic spectra of the complexes were recorded in DMSO on a Perkin–Elmer Lambda-2 spectrophotometer in the range of 9100–50,000 cm^{-1}. IR spectra of the complexes and parent ligand were recorded on a Vector-22 spectrophotometer in the range of 400–4000 cm^{-1} in KBr. X-band Electron Spin Resonance (ESR) spectra of copper(II) complexes were recorded on a Bruker EMX 1444 Electron Paramagnetic Resonance (EPR) spectrometer (Germany) at room temperature (298 K) in solid state using Diphenyl Picrylhydrazyl (DPPH) as g marker ($g = 2.0023$). X-ray diffraction patterns of a few complexes were recorded on an Iso Debye Flex X-ray diffractometer model-2002 of Rich and Seifert Co., Germany, using Cu-Kα radiation. The analytical and physicochemical data are given in tables 1–4.

3. Results and discussion

Analytical data of the complexes (table 1) show that *p*-amino acetophenone isonicotinoyl hydrazone (painh) reacts with metal salts in 1:1 molar ratio to give complexes of general composition $[M(painh)(H_2O)_2X]$. The reaction proceeds in the following manner:

$$MX \cdot nH_2O + painh \rightarrow [M(painh)(H_2O)_2X] + (n-2)H_2O$$

where M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X = $2Cl^-$ or SO_4^{2-}.

The complexes are insoluble in water, cold ethanol, benzene, carbon tetrachloride, chloroform and diethyl ether but are fairly soluble in hot ethanol, Dimethylformamide (DMF), and DMSO. All the complexes decompose between 184 and 290°C. Very low values of molar conductance (2.51–7.32 Ω^{-1} cm^2 mol^{-1}) of 10^{-3} M solutions of the complexes in DMSO at room temperature indicate that they are non-electrolytes [25].

3.1. *Magnetic moments and electronic spectra*

The magnetic moments of the two Cu(II) complexes (1.85 and 1.76 B.M.) correspond to μ_{eff} values for one unpaired electron [26]. Two transitions for $[Cu(painh)(H_2O)_2Cl_2]$ at 10640 and 13790 cm^{-1} and for $[Cu(painh)(H_2O)_2(SO_4)]$ at 9750 and 13330 cm^{-1} suggest distorted octahedral geometry for both complexes. Cu(II) complexes generally show three transitions, $^2B_{1g} \rightarrow {}^2A_{1g}(\nu_1)$, $\rightarrow {}^2B_{2g}(\nu_2)$, and $\rightarrow {}^2E_g(\nu_3)$ in distorted octahedral

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

Compounds (Color)	Empirical formula (Formula wt.)	Yield (%)	Decomp. point (°C)	Found (calculated) %					Λ_M ($^{-1}cm^2mol^{-1}$)
				Metal	Cl^-/SO_4^{2-}	C	H	N	
Painh	$C_{14}H_{14}N_4O$	75	152	–	–	65.86	5.41	21.79	–
(Cream yellow)	(254)					(66.14)	(5.51)	(22.04)	
[Mn(painh)$(H_2O)_2Cl_2$]	$C_{14}H_{18}N_4O_3Cl_2Mn$	78	192	13.10	17.00	40.12	4.35	13.35	3.67
(Light yellow)	(416)			(13.22)	(17.07)	(40.38)	(4.33)	(13.46)	
[Co(painh)$(H_2O)_2Cl_2$]	$C_{14}H_{18}N_4O_3Cl_2Co$	82	242	14.16	16.75	39.82	4.25	13.26	7.32
(Pink)	(420)			(14.05)	(16.90)	(40.00)	(4.28)	(13.33)	
[Ni(painh)$(H_2O)_2Cl_2$]	$C_{14}H_{18}N_4O_2Cl_3Ni$	85	250	13.92	16.80	39.85	4.22	13.21	3.56
(Light green)	(420)			(14.05)	(16.90)	(40.00)	(4.28)	(13.33)	
[Cu(painh)$(H_2O)_2Cl_2$]	$C_{14}H_{18}N_4O_3Cl_2Cu$	85	285	14.82	16.60	39.42	4.20	13.11	8.20
(Green)	(424.5)			(14.96)	(16.72)	(39.58)	(4.24)	(13.19)	
[Zn(painh)$(H_2O)_2Cl_2$]	$C_{14}H_{18}N_4O_3Cl_2Zn$	80	184	15.15	16.50	39.28	4.19	13.20	2.51
(Dark yellow)	(426)			(15.26)	(16.67)	(39.44)	(4.22)	(13.15)	
[Mn(painh)$(H_2O)_2(SO_4)$	$C_{14}H_{18}N_4O_7SMn$	80	251	12.35	21.65	37.92	4.02	12.61	4.44
(Light yellow)	(441)			(12.47)	(21.77)	(38.09)	(4.08)	(12.70)	
[Co(painh)$(H_2O)_2(SO_4)$]	$C_{14}H_{18}N_4O_7SCo$	82	248	13.10	21.42	37.56	3.98	12.46	6.26
(Pink)	(445)			(13.26)	(21.57)	(37.75)	(4.04)	(12.58)	
[Ni(painh)$(H_2O)_2(SO_4)$]	$C_{14}H_{18}N_4O_7SNi$	86	256	13.14	21.50	37.61	3.96	12.49	5.14
(Greenish yellow)	(445)			(13.26)	(21.57)	(37.75)	(4.04)	(12.58)	
[Cu(painh)$(H_2O)_2(SO_4)$]	$C_{14}H_{18}N_4O_7SCu$	88	290	14.15	21.18	37.25	3.92	12.57	3.71
(Light green)	(449.5)			(14.13)	(21.36)	(37.37)	(4.00)	(12.46)	
[Zn(painh)$(H_2O)_2(SO_4)$]	$C_{14}H_{18}N_4O_7SZn$	78	265	14.30	21.20	37.12	3.94	12.31	5.52
(Yellow)	(451)			(14.41)	(21.28)	(37.25)	(3.99)	(12.42)	

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 D_q	B (cm^{-1})	β	β° (%)	LFSE (kcal mol^{-1})
$[Mn(painh)(H_2O)_2Cl_2]$	5.92	20,620	24,100	–	–	–	–	–	–
$[Co(painh)(H_2O)_2Cl_2]$	4.83	9190	–	20,425	10,385	828	0.853	14.70	23.67
$[Ni(painh)(H_2O)_2Cl_2]$	2.98	10,205	15,625	28,570	10,205	905	0.869	13.10	34.89
$[Cu(painh)(H_2O)_2Cl_2]$	1.85	10,640	13,790	–	–	–	–	–	–
$[Mn(painh)(H_2O)_2(SO_4)]$	5.90	20,000	23,920	–	–	–	–	–	–
$[Co(painh)(H_2O)_2(SO_4)]$	4.87	9340	–	20,120	10,555	799	0.823	17.70	24.06
$[Ni(painh)(H_2O)_2(SO_4)]$	2.96	10,275	15,885	26,840	10,275	793	0.762	23.80	35.13
$[Cu(painh)(H_2O)_2(SO_4)]$	1.76	9750	13,330	–	–	–	–	–	–

Table 3. Thermal decomposition scheme of $[Ni(painh)(H_2O)_2(SO_4)]$.

S. No.	Temp.	Proposed decomposition pattern	% Loss of wt. Obs.	Calcd	Energy change	Remarks
1.	155	$[Ni(painh)(H_2O)_2(SO_4)]$ minus two water molecules	8.00	8.09	Endothermic	Removal of water molecule
2.	256	Above product minus pyridyl and phenylamine groups	49.50	49.66	Exothermic	Partial decomposition of organic ligand
3.	375	$NiSO_4$	65.00	65.17	Exothermic	Complete removal of organic ligand

Table 4. Important IR spectral bands (cm^{-1}) and their assignments.

Compounds	(OH/NH)	Amide I ν(C=O)	ν(C=N)	Amide II	Amide III	ν(N–N)	ν(M–O)
Painh	3240m, 3200b	1662s	1617s	1564s	1316s	996s	–
$[Mn(painh)(H_2O)_2Cl_2]$	3420b, 3245b, 3200b	1640s	1600s	1549s	1330s	1020s	490w
$[Co(painh)(H_2O)_2Cl_2]$	3440b, 3240w, 3205b	1649s	1597s	1547s	1332s	1020s	474w
$[Ni(painh)(H_2O)_2Cl_2]$	3425b, 3240m, 3210b	1650s	1599s	1547s	1333s	1029s	488w
$[Cu(painh)(H_2O)_2Cl_2]$	3436b, 3245m, 3200b	1647s	1592s	1540s	1325s	1027m	480w
$[Zn(painh)(H_2O)_2Cl_2]$	3440b, 3240w, 3200b	1642s	1595s	1545s	1325s	1024s	475w
$[Mn(painh)(H_2O)_2(SO_4)]$	3400b, 3245w, 3195b	1640s	1600s	1542m	1328s	1022s	472w
$[Co(painh)(H_2O)_2(SO_4)]$	3465b, 3245m, 3200b	1644s	1602s	1546s	1332s	1018m	486w
$[Ni(painh)(H_2O)_2(SO_4)]$	3398b, 3243w, 3200b	1648s	1593s	1548s	1328s	1025m	480w
$[Cu(painh)(H_2O)_2(SO_4)]$	3416b, 3240m, 3196b	1643s	1597s	1545s	1329s	1026w	482m
$[Zn(painh)(H_2O)_2(SO_4)]$	3477b, 3243w, 3205b	1642s	1604s	1548m	1330s	1022m	476w

Note: b = broad, s = strong, m = medium and w = weak.

environment [27]. The third band is probably mixed with a ligand–metal charge transfer transition. Ni(II) complexes (2.98 and 2.96 B.M.) correspond to μ_{eff} values for two unpaired electrons suggesting octahedral geometry. Bands at 10205, 15625, and 28570 cm^{-1} for $[Ni(painh)(H_2O)_2Cl_2]$ and at 10275, 15885, and 26840 cm^{-1} for $[Ni(painh)(H_2O)_2(SO_4)]$ may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $\rightarrow {}^3T_{1g}(F)$

(ν_2), and $\rightarrow {}^3T_{1g}$(P) (ν_3) transitions, respectively, assuming octahedral geometry around Ni(II) [26]. The μ_{eff} value observed for Co(II) complexes (4.83 and 4.87 B.M.) is fairly close to that for three unpaired electrons in octahedral environment [24]. The position of the bands at 9190 and 20425 cm^{-1} for [Co(painh)$(H_2O)_2Cl_2$] and 9340 and 20120 cm^{-1} for [Co(painh)$(H_2O)_2(SO_4)$] also suggests octahedral geometry, where three transitions ${}^4T_{1g}$(F) $\rightarrow$ ${}^4T_{2g}$(F), (ν_1) $\rightarrow$ ${}^4A_{2g}$(F) (ν_2), and $\rightarrow$ ${}^4T_{1g}$(P) (ν_3) are possible. The ν_2 transition is not observed due to very weak intensity [27]. The ligand-field parameters 10 D_q, B, β, β°, and LFSE were also calculated for Ni(II) and Co(II) complexes and indicate considerable covalent character of the M–L bonds. Both Mn(II) complexes show μ_{eff} values of 5.92 and 5.90 B.M. corresponding to five unpaired electrons. Two weak bands for [Mn(painh)$(H_2O)_2Cl_2$] at 20620 and 24100 cm^{-1} and for [Mn(painh)$(H_2O)_2(SO_4)$] at 20,000 and 23,920 cm^{-1} are assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$(G) and $\rightarrow {}^4T_{2g}$(G), in an octahedral environment [27].

3.2. *ESR spectra*

As powder at room temperature [Cu(painh)$(H_2O)_2(SO_4)$] gives two anisotropic signals with $g_\parallel$ at 2.2663 and $g_\perp$ at 2.0657, suggesting an axial symmetry with all principal axes aligned parallel; the geometry is proposed to be an elongated tetragonally-distorted octahedron [28]. $G = 4.0533$ suggests that the local tetragonal axes are only slightly misaligned. Powder spectra of [Cu(painh)$(H_2O)_2Cl_2$] show a rhombic signal (Supplemental Material) with $g_1 = 2.2450$, $g_2 = 2.1034$, and $g_3 = 2.0453$ typical for (lowest $g > 2.04$) copper(II) ion in an elongated rhombic symmetry with all the axes aligned parallel, consistent with distorted octahedral stereochemistry [28]. The large rhombicity of the g-tensor can be explained as a highly distorted coordination geometry around copper(II) and suggests that the ground state wave functions have considerable admixture of the excited state. This is further supported by the calculated R factor [$R = (g_2 - g_1)/(g_3 - g_2)$] which is less than unity ($R = 0.41$), suggesting an essentially $d_{x^2-y^2}$ ground state [29, 30].

3.3. *Thermal analyses (TGA & DTA)*

[Ni(painh)$(H_2O)_2(SO_4)$] is stable to 154°C showing no significant weight loss. Thereafter, it shows weight loss corresponding to two coordinated water molecules at 155°C by an endothermic process. The DTA curve (Supplemental Material) shows significant heat liberation as a result of ligand decomposition between 256°C and 375°C. The final weight of the residue at 375°C corresponds to $NiSO_4$. The proposed decomposition scheme for the complex is given in table 3.

3.4. *IR spectra*

The ligand painh shows broad ν(N–H) bands at 3240 cm^{-1} and 3200 cm^{-1} due to >NH/–NH_2 groups. In all the metal complexes, these bands only slightly shift to lower/higher wavenumbers, indicating non-involvement of >NH or –NH_2 groups in bonding (table 4). The amide I band, ν(C=O) in the ligand at 1662 cm^{-1} is shifted to lower frequency by 12–22 cm^{-1} in the metal complexes suggesting coordination of the >C=O

to the metal [31]. The amide II bands shift to lower frequency (5–24 cm^{-1}) upon complex formation. A shift to higher frequency (9–17 cm^{-1}) is observed in amide III bands in all the complexes supporting coordination. The ν(C=N) at 1617 cm^{-1} in the ligand shift to lower frequency by 13–25 cm^{-1} in the metal complexes suggesting coordination through azomethine [32]. A shift to higher wavenumber for ν(N-N) from the free ligand to the complex by 22–33 cm^{-1} suggests involvement of only one nitrogen of the hydrazone (–NHN=C<) [33].

The metal complexes show a broad band centered between 3400–3477 cm^{-1} due to presence of water [34]. All the metal(II) sulfate complexes also show weak bands near 1210–1228, 1155–1180 and 1055–1070 cm^{-1} indicating the presence of a bidentate chelating sulfate [35]. A non-ligand band in the region 472–490 cm^{-1} in all the complexes has been tentatively assigned to ν(M–O). On the basis of above discussion, general structures for the metal complexes have been proposed in figure 1.

3.5. *X-ray diffraction studies*

The diffraction patterns for the complexes were recorded and indexed by Ito's method [36]. The following lattice constants were obtained.

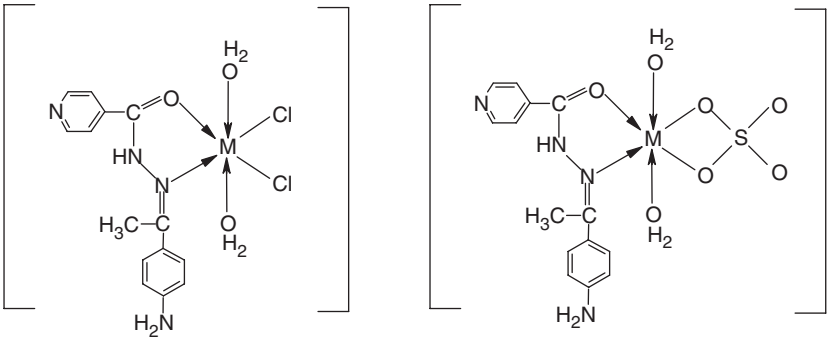
$$[Ni(painh)(H_2O)_2Cl_2] \quad a = 5.86,\ b = 5.86, \text{ and } c = 15.62A^\circ$$

$$[Co(painh)(H_2O)_2SO_4] \quad a = 5.77,\ b = 5.52, \text{ and } c = 5.20A^\circ$$

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

3.6. *Biological activity*

3.6.1. Antifungal activity. The free ligand painh, its metal complexes, metal salts, control (DMSO solvent) and the standard drug Miconazole were screened for



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

Figure 1. Proposed structures of the complexes.

antifungal activity against various fungi viz. *Rizoctonia* sp., *Aspergillus* sp., *Penicillium* sp. and *Stemphylium* sp. These species were isolated from 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. Different concentrations 0.5, 1, and 1.5 mg/mL of each compound in DMSO were prepared for testing against spore germination. A drop of the solution of each concentration was kept separately on glass slides. The conidia, fungal reproducing spores (~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 $25 \pm 2^{\circ}C$ 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.

From the experimental data (table 5), the ligand painh, metal salts and the metal complexes exhibit varying inhibitory effects on the growth of *Rizoctonia* sp., *Aspergillus* sp., *Stemphylium* sp., and *Penicillium* sp. at 0.5, 1.0, and 1.5 mg/mL concentrations. The activity is susceptible to the concentration of the compound used for inhibition and greatly enhanced at higher concentration. The metal complexes show better activity than the corresponding metal salts or the free ligand [36, 37]. DMSO control has negligible activity compared to the metal complexes and ligand. Antifungal activity is more pronounced against *Aspergillus* sp., where $[Cu(painh)(H_2O)_2Cl_2]$ and

Table 5. Antifungal activity of the ligand and its complexes.

	% Inhibition of spore germination											
	Rizoctonia sp. ($mg\,mL^{-1}$)			*Aspergillus* sp. ($mg\,mL^{-1}$)			*Stemphylium* sp. ($mg\,mL^{-1}$)			*Penicillium* sp. ($mg\,mL^{-1}$)		
Compounds	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
Painh	38	57	77	42	53	72	48	64	82	43	59	74
$MnCl_2 \cdot 4H_2O$	42	65	84	47	59	81	52	67	86	48	67	83
$CoCl_2 \cdot 6H_2O$	43	69	87	45	58	78	50	67	88	49	68	82
$NiCl_2 \cdot 6H_2O$	39	64	83	49	69	83	53	70	89	53	74	87
$CuCl_2 \cdot 2H_2O$	40	63	83	51	67	86	51	72	89	53	74	87
$ZnCl_2$	41	59	82	48	60	81	54	69	87	48	66	80
$[Mn(painh)(H_2O)_2Cl_2]$	45	72	90	52	64	89	55	69	90	52	74	92
$[Co(painh)(H_2O)_2Cl_2]$	47	81	96	48	62	83	52	70	93	55	77	90
$[Ni(painh)(H_2O)_2Cl_2]$	40	71	88	55	85	93	58	75	96	62	88	99
$[Cu(painh)(H_2O)_2Cl_2]$	42	69	88	59	81	100	54	79	95	62	89	99
$[Zn(painh)(H_2O)_2Cl_2]$	43	61	86	53	67	90	60	73	91	53	72	85
$MnSO_4 \cdot H_2O$	43	60	79	50	58	79	49	64	84	51	68	83
$CoSO_4 \cdot xH_2O$	44	63	81	50	67	86	53	66	87	58	71	85
$NiSO_4 \cdot 7H_2O$	43	62	82	45	65	82	51	71	87	56	70	86
$CuSO_4 \cdot 5H_2O$	41	61	83	47	59	80	53	68	88	53	71	84
$ZnSO_4 \cdot 7H_2O$	42	64	83	46	59	79	52	66	85	50	70	82
$[Mn(painh)(H_2O)_2(SO_4)]$	48	63	81	58	62	85	50	65	85	58	75	91
$[Co(painh)(H_2O)_2(SO_4)]$	50	68	84	59	81	100	57	68	92	72	83	95
$[Ni(painh)(H_2O)_2(SO_4)]$	48	67	87	48	76	92	54	77	92	68	80	98
$[Cu(painh)(H_2O)_2(SO_4)]$	43	64	89	51	64	88	57	72	93	63	82	93
$[Zn(painh)(H_2O)_2(SO_4)]$	46	70	88	50	65	86	55	67	88	56	80	91
Miconazole	50	72	96	62	80	90	52	70	90	60	78	89

$[Cu(painh)(H_2O)_2(SO_4)]$ show 100% activity at the concentration of 1.5 mg/mL. All the complexes are effective against *Penicillium* sp. showing activity above 90%. The complexes generally vary in their antifungal activity in the following order of fungal species:

Penicillium sp. > *Stemphylium* sp. > *Aspergillus* sp. > *Rizoctonia* sp.

The antifungal experimental results of the compounds were compared with the standard antifungal drug Miconazole at the same concentration. Most of the metal complexes exhibited better activity against *Stemphylium* sp. and *Penicillium* sp. but slightly less activity against *Rizoctonia* sp. compared to the standard drug Miconazole.

3.6.2. Antibacterial activity. The antibacterial activity of the free ligand painh, its complexes and the control (DMSO solvent) were studied against *Pseudomonas* sp. and *Escherichia coli* bacteria. Each compound was dissolved in DMSO and solutions of concentration 1 mg/mL and 2 mg mL^{-1} were prepared separately. Paper discs of Whatman filter paper (No. 42) of uniform diameter (2 cm) were cut and sterilized in an autoclave. Paper discs soaked in the desired concentration of the complex solutions were placed aseptically in the petri dishes containing nutrient agar media (agar 20 g + beef extract 3 g + peptone 5 g) seeded with *Pseudomonas* sp. and *E. coli* bacteria separately. The petri dishes were incubated at 37°C and the inhibition zones were recorded after 24 h of incubation. Each treatment was replicated nine times.

The antibacterial activity of a common standard antibiotic "Ampicillin" was also recorded maintaining the same protocol at the same concentrations and solvent. The antibacterial results of the compounds were compared with the standard and % Activity Index for the complexes was calculated by the formula:

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

Determination of minimum inhibitory concentration (MIC) value: The MIC was determined using the disc diffusion technique by preparing discs containing 0.1–1.0 mg mL^{-1} of each compound against both the bacteria. 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 the bacteria. The results of MIC values (mg/mL) are given in table 6.

The metal complexes show higher antibacterial activity than the ligands. The DMSO control showed no activity against either bacterial strain. The activity increases with increasing concentration of the compounds [38]. The antibacterial activity of the complexes has been compared with the activity of Ampicillin and % Activity Index for the complexes has been calculated. The antibacterial results suggest that the ligands and their complexes (table 6) show moderate activity against both the bacteria [39, 40] as compared to Ampicillin. The % Activity Index data show the highest activity (94%) for $[Co(painh)(H_2O)_2(SO_4)]$ against *E. Coli* at 2.0 mg mL^{-1}. The complexes are more effective against *E. Coli* than *Pseudomonas* sp. The highest activity (89%) has been observed against *Pseudomonas* sp. by $[Cu(painh)(H_2O)_2Cl_2]$ at 2.0 mg mL^{-1}.

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

Compounds	*Pseudomonas* sp. ($mg\,mL^{-1}$)					*E. coli.* ($mg\,mL^{-1}$)				
	MIC ($mg\,mL^{-1}$)	Diameter of inhibition zone (in mm)		% Activity index		MIC ($mg\,mL^{-1}$)	Diameter of inhibition zone (in mm)		% Activity index	
		1.0	2.0	1.0	2.0		1.0	2.0	1.0	2.0
Painh	0.7	3	5	20	28	0.7	4	6	25	38
$[Mn(painh)(H_2O)_2Cl_2]$	0.5	8	10	53	56	0.5	9	12	56	75
$[Co(painh)(H_2O)_2Cl_2]$	0.5	8	12	53	67	0.5	8	12	50	75
$[Ni(painh)(H_2O)_2Cl_2]$	0.5	8	10	53	56	0.5	9	13	56	81
$[Cu(painh)(H_2O)_2Cl_2]$	0.5	10	16	67	89	0.5	10	14	63	88
$[Zn(painh)(H_2O)_2Cl_2]$	0.5	9	14	60	78	0.5	9	11	56	69
$[Mn(painh)(H_2O)_2(SO_4)]$	0.5	10	12	67	67	0.5	9	11	56	69
$[Co(painh)(H_2O)_2(SO_4)]$	0.5	10	12	67	67	0.3	14	15	88	94
$[Ni(painh)(H_2O)_2(SO_4)]$	0.3	13	14	87	78	0.3	13	14	81	88
$[Cu(painh)(H_2O)_2(SO_4)]$	0.4	12	13	80	72	0.4	11	12	69	75
$[Zn(painh)(H_2O)_2(SO_4)]$	0.4	11	13	73	72	0.5	10	13	63	81
Ampicillin (standard)	0.2	15	18	100	100	0.2	16	16	100	100

Acknowledgements

The authors thank the Head, Department of Chemistry, Indian Institute of Technology, Kanpur, for recording UV–Vis, IR, and ESR spectra and Dr Nand Lal, Department of Life Sciences, C.S.J.M. University, Kanpur, for his help in biological screening.

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