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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Online publication date: 04 January 2011

To cite this Article Singh, Vinod P. and Katiyar, Anshu(2008) 'Synthesis, Spectral Studies and Bio-activity of Some Ligand Bridged Polymeric Transition Metal Complexes of Acetone *p*-Amino Acetophenone Isonicotinoyl Hydrazone', Journal of Macromolecular Science, Part A, 45: 6, 470 – 478

To link to this Article: DOI: 10.1080/10601320801977764

URL: <http://dx.doi.org/10.1080/10601320801977764>

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Synthesis, Spectral Studies and Bio-activity of Some Ligand Bridged Polymeric Transition Metal Complexes of Acetone *p*-Amino Acetophenone Isonicotinoyl Hydrazone

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Received and accepted November, 2007

Ligand bridged polymeric complexes of the type $[M(\text{apainh})(\text{H}_2\text{O})\text{X}]$ where, M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II); X = Cl₂ or SO₄; apainh = acetone *p*-amino acetophenone isonicotinoyl hydrazone have been synthesized and characterized. The complexes are stable solids, insoluble in common organic solvents and are non-electrolytes. Magnetic moments and electronic spectral studies suggest a spin-free octahedral geometry for all Mn(II), Co(II), Ni(II), and Cu(II) complexes. IR spectra show tridentate nature of the ligand bonding through two >C=N and a >C=O groups. X-ray powder diffraction parameters for some of the complexes correspond to orthorhombic and tetragonal crystal lattices. Thermal studies (TGA and DTA) of $[\text{Mn}(\text{apainh})(\text{H}_2\text{O})\text{SO}_4]$ complex show multi-step decomposition pattern of both an endothermic and exothermic nature. ESR data of Cu(II) chloride complex in solid state show an axial spectra, whereas, Cu(II) sulfate complex is isotropic in nature. The complexes show a significant antifungal activity against a number of pathogenic fungal species and antibacterial activity against *Pseudomonas sp.* and *Clostridium sp.* The metal complexes are more active than the ligand.

Keywords: transition metal(II) polymeric complexes; isonicotinoyl hydrazone; spectral studies; thermal studies; bio-activity

1 Introduction

Considerable interest is being evinced in the phenomenon of metal chelation in biological systems. The role of several drugs in relation to their metal binding has been established. The discovery of anti-tumor activity of certain platinum coordination compounds opened up a new class of anti-tumor agents, namely inorganic coordination complexes. It is accepted that the anti-tumor activity is due to inhibition of DNA synthesis in the cancer cells (1). The anti-tumor activity of platinum(II) complexes with nucleosides and their bases have been investigated extensively (2, 3). Several bivalent (4–6) and trivalent (7–10) transition metal complexes of uracil, substituted uracils and their mixed ligand complexes have been reported to show appreciable antitumour activity.

Since acylhydrazones are strong biologically active compounds (11–13), their complexes may have potential use as fungicides and bactericides. Expecting some new compounds of biological interest, we have synthesized and characterized a number of bivalent transition metal complexes with acetone

p-amino acetophenone isonicotinoyl hydrazone (apainh) and studied their antifungal and antibacterial properties.

2 Experimental

2.1 Materials

All the chemicals used were of BDH 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 Isonicotinoyl Hydrazone

p-Amino acetophenone isonicotinoylhydrazone (painh), H₂-NC₆H₄C(CH₃)=NNHCOC₅H₄N 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 in a RB 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 CaCl₂ in a desiccator.

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2.3 Preparation of Acetone *p*-Amino Acetophenone Isonicotinoyl Hydrazone

Acetone *p*-amino acetophenone isonicotinoyl hydrozone (apainh), $(\text{CH}_3)_2\text{C}=\text{NC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NNHCOC}_5\text{H}_4\text{N}$ was prepared by reacting Hpainh (5 mmol, 12.70 g) with an excess of acetone (100 mL). The reaction mixture was refluxed for 2 h at 40°C in a RB flask and then it was transferred in a beaker. The excess acetone was allowed to evaporate and the residue was recrystallized from hot ethanol.

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

2.4 Synthesis of the Metal Complexes

The metal complexes were synthesized by reacting a 10 mmol solution of each metal salts dissolved in 50 mL ethanol (50% v/v) separately with a 10 mmol solution of the ligand apainh (2.94 g) dissolved in 50 mL hot ethanol in a beaker in 1:1 (M:L) molar ratio. The reactants were stirred with a glass rod at room temperature for 5–10 min. The colored complexes were formed immediately as precipitates and filtered in a glass crucible. The complexes were purified by washing the products several times with water followed by ethanol and finally with diethyl ether and were dried in a desiccator over anhydrous calcium chloride.

2.5 Analyses of the Complexes

2.5.1 Elemental Analyses

The complexes were analyzed for metal content gravimetrically by literature procedures (14) 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.

2.5.2 Physico-chemical Measurements

The molar conductance of the complexes was determined by preparing 10^{-3} M solutions of the complexes 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 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 (15). The electronic spectra of the complexes were recorded in DMSO solution on a Perkin-Elmer Lambda-2 spectrophotometer in the 1100–200 nm range. Infrared spectra of the complexes and parent ligand were recorded on Vector-22 spectrophotometer in

the range 4000–500 cm^{-1} in KBr medium. 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 1–5.

2.6 Biological Activity

2.6.1 Antifungal Activity

The ligand, as well as its complexes, were screened for their antifungal activity against various fungi viz. *Rizoctonia sp.*, *Aspergillus 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 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 (approx. 200) lifted with the help of an inoculating needle, were mixed in every drop of each compound separately. Each treatment was replicated three times and a parallel DMSO solvent control set was run concurrently on separate glass slides. All the slides were incubated in humid chambers at $25 \pm 2^\circ\text{C}$ 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.

2.6.2 Antibacterial Activity

The antibacterial activity of the ligand and its complexes were studied against *Clostridium sp.* and *Pseudomonas sp.* bacteria. Each of the compounds was dissolved in DMSO 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 Petri dishes containing nutrient agar media (agar 20 g + beef extract 3 g + peptone 5 g) seeded with *Clostridium sp.* and *Pseudomonas sp.* 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 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

Table 1. Analytical data of the ligand and its complexes

Compounds (colour)	Empirical formula (formula wt.)	Melting point (°C)	Found (calculated) %					Yield (%)	Λ_M ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
			Metal	Cl ⁻ /SO ₄ ²⁻	C	H	N		
apainh	C ₁₇ H ₁₈ N ₄ O (294)	164							
[Mn(apainh)(H ₂ O)Cl ₂] (Light yellow)	C ₁₇ H ₂₀ N ₄ O ₂ Cl ₂ Mn (438)	198	12.50 (12.56)	16.16 (16.21)	46.36 (46.57)	4.59 (4.57)	12.66 (12.78)	82	3.82
[Co(apainh)(H ₂ O)Cl ₂] (Pinkish brown)	C ₁₇ H ₂₀ N ₄ O ₂ Cl ₂ Co (442)	203	13.45 (13.35)	16.00 (16.06)	46.23 (46.15)	4.56 (4.52)	12.49 (12.67)	84	7.51
[Ni(apainh)(H ₂ O)Cl ₂] (Green)	C ₁₇ H ₂₀ N ₄ O ₂ Cl ₂ Ni (442)	216	13.30 (13.35)	16.21 (16.06)	45.97 (46.15)	4.42 (4.52)	12.55 (12.67)	80	10.12
[Cu(apainh)(H ₂ O)Cl ₂] (Dark green)	C ₁₇ H ₂₀ N ₄ O ₂ Cl ₂ Cu (446.5)	228	14.25 (14.22)	15.78 (15.90)	45.54 (45.69)	4.56 (4.48)	12.41 (12.54)	85	6.35
[Zn(apainh)(H ₂ O)Cl ₂] (Yellow)	C ₁₇ H ₂₀ N ₄ O ₂ Cl ₂ Zn (448)	207	14.60 (14.51)	15.80 (15.85)	45.45 (45.53)	4.57 (4.46)	12.58 (12.50)	80	4.42
[Mn(apainh)(H ₂ O)SO ₄] (Light yellow)	C ₁₇ H ₂₀ N ₄ O ₆ SMn (463)	255	12.00 (11.88)	20.56 (20.73)	43.89 (44.06)	4.33 (4.33)	11.93 (12.09)	78	5.09
[Co(apainh)(H ₂ O)SO ₄] (Pink)	C ₁₇ H ₂₀ N ₄ O ₆ SCo (467)	267	12.55 (12.63)	20.64 (20.55)	43.76 (43.68)	4.19 (4.28)	11.82 (11.99)	82	3.22
[Ni(apainh)(H ₂ O)SO ₄] (Yellowish green)	C ₁₇ H ₂₀ N ₄ O ₆ SNi (467)	260	12.70 (12.63)	20.47 (20.55)	43.57 (43.68)	4.30 (4.28)	11.85 (11.99)	85	4.25
[Cu(apainh)(H ₂ O)SO ₄] (Brownish green)	C ₁₇ H ₂₀ N ₄ O ₆ SCu (471.5)	248	13.50 (13.47)	20.29 (20.36)	43.18 (43.27)	4.34 (4.28)	11.93 (11.88)	85	3.30
[Zn(apainh)(H ₂ O)SO ₄] (Dirty yellow)	C ₁₇ H ₂₀ N ₄ O ₆ SZn (473)	214	13.62 (13.74)	20.18 (20.29)	42.96 (43.13)	4.16 (4.23)	11.69 (11.84)	78	2.61

formula as under:

%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 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 6B.

3 Results and Discussion

The analytical data of the complexes (Table 1) show that the ligand, acetone *p*-amino acetophenone isonicotinoyl hydrazone (apainh) reacts with metal salts in 1:1 (M:L) molar ratio to give complexes of general composition, [M(apainh)(H₂O)X]. The reaction may occur in the following manner:



where, M = Mn(II), Co(II), Ni(II), Cu(II), and Zn(II); X = Cl₂ or SO₄.

The complexes are light yellow, yellow, green, dark green to pink in color. They are insoluble in water and common organic solvents viz. ethanol, methanol, benzene, chloroform, carbon tetrachloride and diethyl ether but are fairly soluble in DMF and DMSO. They melt with decomposition between 198–267°C. The high decomposition point, together with the low solubilities suggests that the complexes are polymeric. The complexes were finely divided powders which could not be recrystallized because of insolubility in water and common organic solvents.

The low molar conductance values (2.61–10.12 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ of 10^{-3} M solutions of the complexes in DMSO at room temperature suggest that all the complexes are non electrolytes (16).

3.1 Magnetic moments

In Cu(II) complexes, the μ_{eff} values are generally observed between 1.75–2.20 B.M. The μ_{eff} values for the complexes in this study have been observed between 1.75–1.78 B.M. These values indicate a distorted octahedral geometry around Cu(II).

For high spin octahedral complexes of nickel(II), the μ_{eff} values are in the range 2.9–3.4 B.M., while for tetrahedral

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

Complexes	μ_{eff} (B.M.)	Band maxima (cm^{-1})			10 Dq	B (cm^{-1})	β	β° (%)	LFSE (kcal/mol)
		ν_1	ν_2	ν_3					
[Mn(apainh)(H ₂ O)Cl ₂]	5.91	19800	25000	—	—	—	—	—	—
[Co(apainh)(H ₂ O)Cl ₂]	4.82	9295	—	20350	10500	817	0.841	15.90	23.93
[Ni(apainh)(H ₂ O)Cl ₂]	3.03	10380	16555	27790	10380	880	0.845	15.50	35.49
[Cu(apainh)(H ₂ O)Cl ₂]	1.75	11300	14285	—	—	—	—	—	—
[Mn(apainh)(H ₂ O)SO ₄]	5.89	19880	25310	—	—	—	—	—	—
[Co(apainh)(H ₂ O)SO ₄]	4.76	9410	—	20490	10630	820	0.844	15.60	24.23
[Ni(apainh)(H ₂ O)SO ₄]	2.99	10360	16925	27360	10360	880	0.845	15.50	35.42
[Cu(apainh)(H ₂ O)SO ₄]	1.78	11360	14815	—	—	—	—	—	—

complexes, the values range from 3.5–4.0 B.M. (17). Ni(II) complexes, in this study show μ_{eff} values between 2.99–3.03 B.M., corresponding to two unpaired electrons in octahedral environment.

For octahedral cobalt(II) complexes the spin only magnetic moment is 3.87 B.M., but because of the orbital contribution they usually show μ_{eff} values between 4.8–5.2 B.M. (15). The μ_{eff} values observed for the present complexes (4.76, 4.82 B.M.) are reasonably close to that reported for three unpaired electrons in octahedral Co(II). Both Mn(II) complexes show their μ_{eff} values 5.91 and 5.89 B.M. corresponding to five unpaired electrons (Table 2).

3.2 Electronic Spectra

The copper(II) complexes in this study, show two bands in the ranges 11300–11360 cm^{-1} and 14285–14815 cm^{-1} , which

may be assigned to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and $\rightarrow {}^2A_{1g}$ transitions, suggesting a tetragonally distorted octahedral geometry (18) for the complexes (Table 2). Octahedral nickel(II) complexes generally show three bands corresponding to the transitions ${}^3A_{2g} (F) \rightarrow {}^3T_{2g} (F) (\nu_1)$, $\rightarrow {}^3T_{1g} (F) (\nu_2)$ and $\rightarrow {}^3T_{1g} (P) (\nu_3)$ (14). The present complexes also show above three transitions in the region 10380–10360 cm^{-1} (ν_1), 16555–19925 cm^{-1} (ν_2) and 27790–27360 cm^{-1} (ν_3) suggesting octahedral geometry for both complexes. Ligand field parameters (10 Dq, B, β , β° and LFSE) have also been calculated by the procedure laid down by Lever (18). Energy of the first absorption band is taken to be equal to 10 Dq. The low value of Racah parameter, B (880 cm^{-1}), compared to the free ion value of 1041 cm^{-1} indicates significant covalent character in the complexes. The nephelauxetic ratio β (0.845) and other parameters also support some covalent character in the metal-ligand bond.

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

Complex	g_{\parallel} (G)	g_{\perp} (G)	g_{av} (G)	A_{\parallel} (G)	A_{\perp} (G)	A_{av} (G)
[Cu(apainh)Cl]	2.2978	2.0662	2.1434	146	70	95
[Cu(apainh)(H ₂ O)SO ₄]	—	—	$g_{\text{iso}} = 2.1306$	—	—	$A_{\text{iso}} = 70$

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

Compounds	$\nu(\text{OH/NH})$	Amide I $\nu(\text{C=O})$	$\nu(\text{C=N})$	Amide II	Amide III	$\nu(\text{N-N})$	$\nu(\text{M-O})$	Water bands
apainh	3308b	1673s	1657s	1560m	1346s	982m	—	—
[Mn(apainh)Cl ₂]	3420b, 3306s	1655s	1600m	1542m	1361s	998m	568w	908s, 740w, 640w
[Co(apainh)Cl ₂]	3418b, 3311s	1660s	1607s	1545m	1365s	995m	570w	902s, 745w, 656w
[Ni(apainh)Cl ₂]	3426b, 3308s	1652s	1595s	1548m	1358s	1002s	566w	915m, 751w, 660w
[Cu(apainh)Cl ₂]	3430b, 3312s	1657s	1594s	1538m	1355s	1000w	565w	920m, 755w, 662w
[Zn(apainh)Cl ₂]	3422b, 3316s	1651s	1592s	1541m	1360s	997w	580w	905w, 758w, 645w
[Mn(apainh)(H ₂ O)SO ₄]	3440b, 3305s	1657s	1602s	1543m	1358s	1005w	558w	911w, 760w, 642w
[Co(apainh)(H ₂ O)SO ₄]	3419b, 3309s	1658s	1595s	1547s	1362s	1008w	591w	903m, 763w, 636w
[Ni(apainh)(H ₂ O)SO ₄]	3422b, 3325s	1644s	1599s	1550s	1356s	1001w	560w	911w, 742w, 650w
[Cu(apainh)(H ₂ O)SO ₄]	3422b, 3310s	1656s	1598s	1537m	1365s	1010w	562w	908w, 756w, 640w
[Zn(apainh)(H ₂ O)SO ₄]	3425b, 3311s	1650s	1402s	1538m	1366s	1008w	565w	910w, 752w, 647w

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

Table 5. Observed and calculated Q and hkl values

Powder pattern	Angle ^o	Intensity	D(Å)	Qobs(1/d ²)	Qcalc	hkl
[Mn(apainh)(H₂O)Cl₂]						
1	15.68	77.26	5.6519	0.0313	0.0313	100
2	16.72	66.29	5.3036	0.0355	0.0355	010
3	17.80	73.86	4.9823	0.0403	0.0403	001
4	23.19	68.92	3.8363	0.0679	0.0668	110
5	24.27	72.31	3.6670	0.0744	0.0758	011
6	29.16	66.16	3.0624	0.1066	0.1071	111
7	31.53	50.58	2.8374	0.1242	0.1252	200
8	34.15	46.37	2.6257	0.1450	0.1420	020
9	23.78	44.33	2.5097	0.1588	0.1607	210
10	36.96	36.23	2.4319	0.1691	0.1655	201
11	38.20	39.68	2.3561	0.1801	0.1823	021
12	39.33	51.57	2.2907	0.1606	0.1925	102
13	40.32	50.73	2.2368	0.1999	0.1967	012
14	40.81	42.44	2.2109	0.2046	0.2010	211
15	42.05	39.26	2.1488	0.2166	0.2136	121
16	46.99	28.33	1.9338	0.2674	0.2672	220
17	48.47	26.85	1.8781	0.2835	0.2817	300
18	49.65	25.35	1.8360	0.2966	0.3032	022
19	50.44	33.73	1.8091	0.3055	0.3075	221
20	52.91	22.05	1.7304	0.3340	0.3345	122
21	54.99	28.90	1.6699	0.3586	0.3575	311
22	55.93	23.10	1.6441	0.3699	0.3627	033
23	60.62	20.68	1.5276	0.4285	0.4284	222
24	61.60	21.31	1.5055	0.4412	0.4429	302
[Cu(apainh)(H₂O)SO₄]						
1	14.70	80.29	6.0258	0.0275	0.0275	100
2	22.83	93.90	3.8953	0.0659	0.0659	101
3	26.94	94.89	3.3093	0.0913	0.0934	111
4	27.97	88.82	3.1899	0.0982	0.0951	101
5	30.22	88.01	2.9571	0.1143	0.1100	200
6	33.06	83.54	2.7093	0.1362	0.1375	210
7	38.30	83.10	2.3499	0.1811	0.1811	102
8	41.05	88.14	2.1990	0.2068	0.2086	112
9	42.95	82.02	2.1056	0.2265	0.2200	220
10	44.91	80.08	2.0182	0.2455	0.2475	300
11	46.73	87.68	1.9441	0.2646	0.2636	202
12	47.41	93.13	1.9175	0.2720	0.2750	310
13	48.19	92.09	1.8882	0.2805	0.2859	301
14	48.98	92.69	1.8598	0.2891	0.2911	212
15	50.79	84.51	1.7976	0.3094	0.3134	311
16	52.99	84.23	1.7279	0.3349	0.3456	003
17	58.33	80.39	1.5819	0.3996	0.4006	113
[Zn(apainh)(H₂O)SO₄]						
1	15.70	95.43	5.6451	0.0314	0.0314	100
2	16.98	83.85	5.2231	0.0366	0.0366	010
3	17.22	84.28	5.1492	0.0377	0.0377	001
4	23.16	74.25	3.8397	0.0678	0.0680	110
5	23.41	74.40	3.7999	0.0692	0.0691	101
6	25.72	57.25	3.4638	0.0833	0.0743	011
7	28.76	68.97	3.1036	0.1038	0.1057	111
8	31.71	67.62	2.8216	0.1256	0.1256	200
9	36.18	44.89	2.4826	0.1622	0.1633	201
10	41.44	44.85	2.1790	0.2106	0.2155	121
11	47.78	50.36	1.9037	0.2759	0.2764	202

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 ground state ${}^4T_{1g}$ (F) to the excited state ${}^4T_{2g}$ (F), ${}^4A_{2g}$ (F), and ${}^4T_{1g}$ (P). In the present study, only two bands are observed between $9295\text{--}9410\text{ cm}^{-1}$ (ν_1) and $20350\text{--}20490\text{ cm}^{-1}$ (ν_3) suggesting octahedral geometry for the complexes. The ν_2 transition was not observed due to very weak intensity (18). The various ligand field parameters were also calculated and indicate a considerable covalent character of the M-L bonds.

3.3 ESR Spectra

ESR spectra of $[\text{Cu}(\text{apainh})(\text{H}_2\text{O})\text{Cl}_2]$ in solid state show an axial signal with two g values at 298 K (Figure 1). The axial signals were analyzed by using the procedure given by Hathaway and Billing (19). The both g values ($g_{\parallel} = 2.2978$ and $g_{\perp} = 2.0662$) are >2.04 (Table 3). These values indicate an elongated tetragonally distorted octahedral stereochemistry. The g_{av} and A_{av} values were calculated using the equations $g_{\text{av}} = (g_{\parallel} + 2g_{\perp})/3$; $A_{\text{av}} = (A_{\parallel} + 2A_{\perp})/3$. The trend $g_{\parallel} > g_{\perp} > g_e$ suggest that the unpaired electron is in the $d_{x^2-y^2}$ orbital of the copper (II) ion (20, 21).

$[\text{Cu}(\text{apainh})(\text{H}_2\text{O})\text{SO}_4]$ shows isotropic spectra with intense broad signals having no hyperfine structure. This may be due to dipolar exchange and unresolved hyperfine interactions in solid state (22). The g_{iso} value of 2.1306 suggests a geometry involving grossly misaligned axes (19).

3.4 IR Spectra

The bonding of the ligand to metal has been judged by a careful comparison of the infrared spectra of the complex

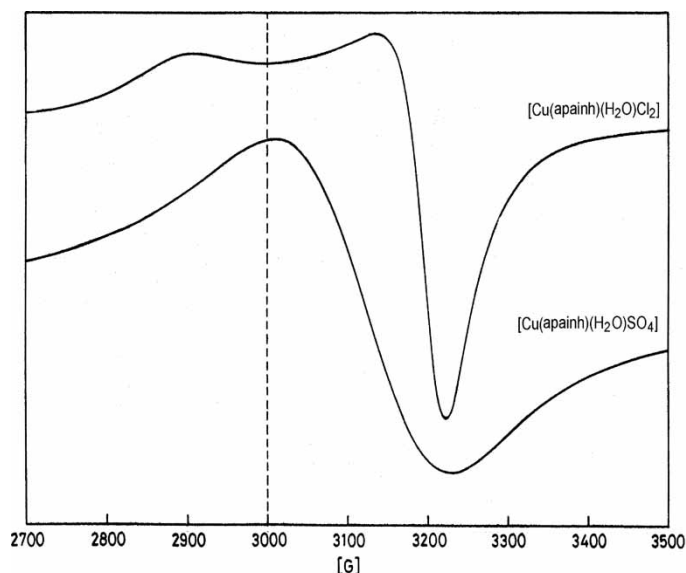


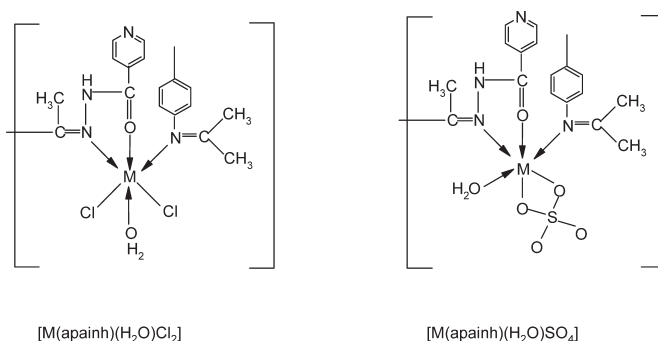
Fig. 1. ESR spectra of copper (II) complexes at 298 K in the solid state.

with that of the free ligand. A few significant bands have been selected to observe the effect on ligand vibration in the complexes. In the ligand apainh, the $\nu(\text{N-H})$ band is broad and is observed at 3308 cm^{-1} . In the metal complexes $\nu(\text{N-H})$ occur either at the same wave number as in ligand or slightly shifted to higher wave numbers, indicating non-involvement of $>\text{N-H}$ group in bonding. A broad band in the same region assigned as $\nu(\text{OH})$ indicates the presence of water molecule in the complexes.

The amide I band, $\nu(\text{C}=\text{O})$ is shifted to lower frequency by $13\text{--}29\text{ cm}^{-1}$ compared to the parent ligand (Table 4), indicating coordination of $>\text{C}=\text{O}$ group to metal (23). The amide II band appear to have shifted considerably to lower frequency ($10\text{--}23\text{ cm}^{-1}$) upon complex formation. Compared to the ligand bands, a shift to higher frequency ($9\text{--}20\text{ cm}^{-1}$) is observed in the amide III bands in all the complexes supporting coordination through the $>\text{C}=\text{O}$ group. The $\nu(\text{C}=\text{N})$ band observed at 1617 cm^{-1} in the spectra of the ligand shifted to lower frequency by $10\text{--}25\text{ cm}^{-1}$ in the metal complexes suggesting coordination through the azomethine group (24).

$\nu(\text{N-N})$ observed at 982 cm^{-1} in the ligand shifts to higher frequency by $13\text{--}28\text{ cm}^{-1}$ in the complexes, indicating the coordination of one of the nitrogen atom of the N-N group (25). All the metal complexes also show weak bands in the region $902\text{--}920\text{ cm}^{-1}$, $740\text{--}763\text{ cm}^{-1}$, and $636\text{--}660\text{ cm}^{-1}$ due to coordinated water (26). The bands observed near $1208\text{--}1230$, $1165\text{--}1178$, and $1045\text{--}1056\text{ cm}^{-1}$ suggest a bidentate chelating nature of the sulfate group in all the metal(II) sulfate complexes (22). A non-ligand band observed between $558\text{--}591\text{ cm}^{-1}$ has been assigned to $\nu(\text{M-O})$.

Since the para-substituted $-\text{NH}_2$ group of the benzene ring in the ligand is highly involved in coordination with metal ion, the polymeric ligand bridged structures for the metal complexes have been suggested (Figure 2). The high decomposition points and low solubilities in common solvents favor their polymeric nature.



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

Fig. 2. Representative structures of the complexes.

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

Compounds	% Inhibition of spore germination								
	<i>Rizoctonia sp.</i> (mg/mL)			<i>Aspergillus 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
apainh	42	47	52	40	46	50	35	39	45
[Co(apainh)(H ₂ O)Cl ₂]	83	90	96	53	67	82	58	75	88
[Ni(apainh)(H ₂ O)Cl ₂]	82	87	98	55	68	89	65	72	89
[Cu(apainh)(H ₂ O)Cl ₂]	90	95	99	56	76	88	68	75	92
[Zn(apainh)(H ₂ O)Cl ₂]	72	88	93	50	69	82	60	71	85
[Co(apainh)(H ₂ O)SO ₄]	80	88	95	68	73	90	60	73	89
[Ni(apainh)(H ₂ O)SO ₄]	73	86	97	55	81	91	62	78	86
[Cu(apainh)(H ₂ O)SO ₄]	86	92	100	60	71	95	45	73	89
[Zn(apainh)(H ₂ O)SO ₄]	85	90	100	62	74	89	52	74	84
Miconazole (standard)	50	72	96	62	80	90	60	78	85

3.5 Thermal Analyses (TGA and DTA)

Thermal analyses of [Mn(apainh)(H₂O)SO₄] indicate that the complex is stable and shows no weight loss up to 155°C. At 155°C, it loses its water molecule indicating that the water molecule is involved in coordination. The decomposition of organic ligand in the complex takes place gradually in various steps at different temperatures by exothermic process. The DTA curve shows significant heat liberation as a result of ligand decomposition (27). The decomposition of organic ligand from the complex starts at 250°C and does not complete up to 450°C.

3.6 X-ray Diffraction Studies

Since the complexes are insoluble in common inert organic solvent for single crystal growth for X-ray analysis, X-ray

powder diffraction patterns for three of the complexes were recorded and successfully indexed by using Ito's method (13) (Table 5). The following lattice constants were calculated:

$$[\text{Mn}(\text{apainh})(\text{H}_2\text{O})\text{Cl}_2] \quad a = 5.65, b = 5.30 \text{ and } c = 4.98 \text{ \AA}$$

$$[\text{Cu}(\text{apainh})(\text{H}_2\text{O})\text{SO}_4] \quad a = 6.03, b = 6.03 \text{ and } c = 5.10 \text{ \AA}$$

$$[\text{Zn}(\text{apainh})(\text{H}_2\text{O})\text{SO}_4] \quad a = 5.64, b = 5.22 \text{ and } c = 5.15 \text{ \AA}$$

The above values of lattice parameters indicate an orthorhombic crystal lattice for [Mn(apainh)(H₂O)Cl₂] and [Zn(apainh)(H₂O)SO₄] complexes and a tetragonal crystal lattice for [Cu(apainh)(H₂O)SO₄]. The presence of very few lines in X-ray powder diffraction patterns of all the three complexes may be due to the polymeric nature of the complexes.

Table 6B. Antibacterial activity of the ligand and its 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
apainh	0.8	2	4	11	22	0.8	2	3	14	19
[Co(apainh)(H ₂ O)Cl ₂]	0.3	14	15	78	83	0.5	9	13	64	81
[Ni(apainh)(H ₂ O)Cl ₂]	0.5	12	16	67	89	0.5	10	14	71	88
[Cu(apainh)(H ₂ O)Cl ₂]	0.4	13	16	72	89	0.3	12	15	86	94
[Zn(apainh)(H ₂ O)Cl ₂]	0.5	12	13	67	72	0.5	11	14	79	88
[Co(apainh)(H ₂ O)SO ₄]	0.3	14	16	78	89	0.5	10	15	71	94
[Ni(apainh)(H ₂ O)SO ₄]	0.2	18	18	100	100	0.3	12	14	86	88
[Cu(apainh)(H ₂ O)SO ₄]	0.2	17	18	94	100	0.2	13	15	93	94
[Zn(apainh)(H ₂ O)SO ₄]	0.4	13	14	72	78	0.5	10	12	71	75
Ampicillin (standard)	0.2	18	18	100	100	0.2	14	16	100	100

3.6 Antifungal Activity

The experimental antifungal data (Table 6A) indicate that the complexes show a significant activity against *Rizoctonia sp.*, *Aspergillus sp.* and *Penicillium sp.* at the concentration of 0.5, 1.0, and 1.5 mg/mL. However, they are more effective against *Rizoctonia sp.* as compare to *Aspergillus sp.* and *Penicillium sp.* Their activity is enhanced at higher concentration of the compounds. DMSO control has shown a negligible activity as compare to the metal complexes and ligands. The antifungal results of the compounds were compared against DMSO as the control and are expressed as percentage inhibition versus control. The ligand shows lower activity than its complexes (28). [Cu(apainh)(H₂O)SO₄] and [Zn(apainh)(H₂O)SO₄] show the highest activity (100%) against *Rizoctonia sp.* at 1.5 mg/mL concentration among all the complexes. [Cu(apainh)(H₂O)Cl₂] shows the best activity (92%) against *Penicillium sp.*, whereas, [Cu(apainh)(H₂O)SO₄] shows highest activity (95%) against *Aspergillus sp.* at the dose of 1.5 mg/mL.

The effectiveness of the complexes generally vary in the following order of fungal species.

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

Most of the metal complexes exhibited better activity against *Rizoctonia sp.* and *Penicillium sp.* as compared to the standard drug Miconazole. However, Ni(II) sulfate and Cu(II) sulfate complexes show greater activity than the standard against *Aspergillus sp.*

3.7 Antibacterial Activity

The metal complexes, ligands, standard drug Ampicillin and DMSO solvent control were screened separately for their antibacterial activity against *Pseudomonas sp.* (Gram -ve) and *Clostridium sp.* (Gram +ve) at the concentration of 1.0 and 2.0 mg/mL. The metal complexes show higher activity than the ligand. The activity increases with increasing concentration of the complexes (29). The activity has been compared with the activity of a common standard antibiotic Ampicillin and % Activity Index was calculated for all the complexes. The antibacterial results suggest that the ligands and their complexes (Table 6B) show a moderate activity against both the bacteria (30, 31) as compared to the standard drug (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 indicate that [Ni(apainh)(H₂O)SO₄] and [Cu(apainh)(H₂O)SO₄] show 100% activity against *Pseudomonas sp.* at 2.0 mg/mL concentration. However, most of the complexes show fair activity against *Clostridium sp.*

4 Conclusions

The above studies suggest a polymeric ligand bridged 6-coordinate high-spin octahedral structure for all the complexes. The ESR spectra of copper(II) complexes are axial type and suggest that the unpaired electron is in the d_{x₂-y₂} orbital of

the copper (II) ion. The complexes show exothermic ligand decomposition above 250°C. Most of the metal complexes exhibit significant and better antifungal and antibacterial activity than the parent ligands.

5 Acknowledgements

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

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