



Synthesis, spectral characterization and antimicrobial activity of some transition metal(II) complexes with acetone *p*-amino acetophenone benzoylhydrazone

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ABSTRACT

Complexes of the type $[M(\text{apabh})\text{Cl}]$ and $[M(\text{Hapabh})(\text{H}_2\text{O})\text{SO}_4]$, where $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) ; Hapabh = acetone *p*-amino acetophenone benzoylhydrazone have been synthesized and characterized. Electronic spectra and μ_{eff} values suggest a square planar geometry for Co(II), Ni(II) and Cu(II) chloride complexes, whereas, octahedral geometry for the sulfato complexes. ESR data show isotropic spectra for $[\text{Cu}(\text{apabh})\text{Cl}]$ and axial spectra for $[\text{Cu}(\text{Hapabh})(\text{H}_2\text{O})\text{SO}_4]$ and $d_{x^2-y^2}$ as the ground state for both Cu(II) complexes. The ligand acts as tridentate monobasic in all chloro complexes bonding through two $>\text{C}=\text{N}-$ and a deprotonated enolate groups, whereas tridentate neutral in all sulfato complexes coordinating through two $>\text{C}=\text{N}-$ and a $>\text{C}=\text{O}$ groups. Thermal analysis (TGA & DTA) of $[\text{Ni}(\text{apabh})\text{Cl}]$ complex shows a multi-step exothermic decomposition pattern. The complexes show a significant antifungal activity against *Rizoctonia* sp., *Aspergillus* sp. and *Penicillium* sp. and a considerably fair antibacterial activity against *Pseudomonas* sp. and *Clostridium* sp. The activity increases at higher concentration of the compound.

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1. Introduction

Mono acylhydrazones of salicylaldehyde and many other similar ligands have been recognized as potential tridentate ligands where maintenance of π -conjugation markedly favors planarity [1]. Metal complexes of such acylhydrazones, particularly the copper(II) complexes of 2-pyridine carboxaldehyde-2-pyridyl-hydrazone [2] and salicylaldehyde benzoylhydrazone [3] show antitumour activity. Similarly, metal complexes of 3- and 5-substituted salicylaldehyde *o*-hydroxy benzoylhydrazones [4], salicylaldehyde benzene sulphonyl hydrazone [5], furfurylidene and 5-nitrofurfurylidene benzoylhydrazones [5], have been found to be bioactive.

Since acylhydrazones constitute an interesting class of chelating agents, their metal complexes may have potential use in the biological fields. Very recently, several papers based on antifungal and antibacterial evaluation of transition metal complexes with similar ligands have been appeared [6–11]. Accordingly, a number of bivalent transition metal complexes with acetone *p*-amino acetophenone benzoyl hydrazone (Hapabh) have been synthesized, characterized and studied for their bio-activity.

2. Materials and methods

2.1. Chemicals

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 [12] 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. bh, mp 111 °C (lit. 112 °C).

2.2. Preparation of *p*-amino acetophenone benzoylhydrazone

p-Amino acetophenone benzoylhydrazone (Hapbh), $\text{H}_2\text{NC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NNHCOC}_6\text{H}_5$ was prepared by reacting *p*-amino acetophenone (10 mmol, 13.5 g) with bh (10 mmol, 13.6 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 then recrystallized from hot benzene. The pure product was dried over anhydrous CaCl_2 in a desiccator.

2.3. Preparation of acetone *p*-amino acetophenone benzoylhydrazone

Acetone *p*-amino acetophenone benzoylhydrazone (Hapabh), $(\text{CH}_3)_2\text{C}=\text{NC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NNHCOC}_6\text{H}_5$ was prepared by reacting

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Hapbh (5 mmol, 12.65 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 of acetone was allowed to evaporate and the residue was recrystallized from hot ethanol. The ligand was characterized by elemental analyses (C, H, N), melting points and infrared spectra.

2.4. Synthesis of the metal complexes

The metal(II) chloride complexes were synthesized by reacting 10 mmol ethanolic solutions of each metal(II) chloride (50 mL) separately with 50 mL ligand solution of Hapabh (10 mmol, 2.93 g) in hot ethanol in 1:1 (M:L) molar ratio and were refluxed for 2–3 h. The complexes were precipitated after cooling the reaction mixture at room temperature and were filtered in a glass crucible. The pure products were obtained by washing the compound several times with ethanol and finally with diethyl ether. The complexes were dried in a desiccator over anhydrous CaCl₂ at room temperature.

The metal(II) sulfate complexes were prepared by reacting 10 mmol solutions of each metal(II) sulfate in 50 mL aqueous ethanol (50%, v/v) with 50 mL hot ethanolic solution of the ligand Hapabh (10 mmol, 2.93 g) in a beaker. 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.

2.5. Analyses of the complexes

The complexes were analyzed for metal content gravimetrically by literature procedures [13] after decomposing the organic matter with a mixture of HNO₃ and HCl and evaporating the residue to dryness with conc. H₂SO₄. The chloride content in the complex was determined gravimetrically as AgCl and sulfate as BaSO₄. Carbon, hydrogen and nitrogen were determined microanalytically on a Elementar Vario EL III Carlo Erba 1108 model, microanalyzer.

2.6. 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 at a heating rate of 10 °C/min in a N₂ atmosphere. Room temperature magnetic susceptibility measurements were carried out on a Faraday balance using Hg[Co(SCN)₄] as calibrant and corrected for diamagnetism [14]. The electronic spectra of the complexes were recorded in DMSO solution on a Perkin-Elmer Lambda-2 spectrophotometer in the range 1100–200 nm. 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 CuK α radiation. The analytical and physico-chemical data are given in Tables 1–5.

2.7. Biological activity

2.7.1. Antifungal activity

The free ligand Hapabh, its metal complexes, blank (DMSO solvent) and the standard drug Miconazole were screened for their antifungal activity against various fungi viz. *Rizoctonia* sp., *Aspergillus* sp. and *Penicillium* sp. These species were isolated from the in-

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		
Hapabh (light yellow)	C ₁₈ H ₁₉ N ₃ O(293)	182				85	
[Mn(apabh)Cl] (yellow)	C ₁₈ H ₁₈ N ₃ OClMn(382.5)	208	14.45(14.38)	9.36(9.28)	73.51(73.72)	85	2.86
[Co(apabh)Cl] (green)	C ₁₈ H ₁₈ N ₃ OClCo(386.5)	276	15.30(15.26)	9.25(9.18)	46.26(46.47)	82	4.95
[Ni(apabh)Cl] (light pink)	C ₁₈ H ₁₈ N ₃ OClNi(386.5)	281	15.33(15.26)	9.06(9.18)	55.73(55.89)	90	6.67
[Cu(apabh)Cl] (dark brown)	C ₁₈ H ₁₈ N ₃ OClCu(391)	267	16.10(16.24)	9.20(9.08)	55.66(55.89)	88	3.42
[Zn(apabh)Cl] (light yellow)	C ₁₈ H ₁₈ N ₃ OClZn(392.5)	202	16.60(16.50)	9.00(9.04)	55.13(55.24)	76	7.32
[Mn(Hapabh)(H ₂ O)SO ₄] (yellow)	C ₁₈ H ₂₁ N ₃ O ₆ SMin(462)	265	12.04(11.90)	20.62(20.78)	46.59(46.75)	75	5.15
[Co(Hapabh)(H ₂ O)SO ₄] (pink)	C ₁₈ H ₂₁ N ₃ O ₆ SCo(466)	270	12.70(12.66)	20.50(20.60)	46.22(46.35)	80	9.22
[Ni(Hapabh)(H ₂ O)SO ₄] (green)	C ₁₈ H ₂₁ N ₃ O ₆ SNi(466)	286	12.56(12.66)	20.68(20.60)	46.44(46.35)	85	3.46
[Cu(Hapabh)(H ₂ O)SO ₄] (greenish brown)	C ₁₈ H ₂₁ N ₃ O ₆ SCu(470.5)	222	13.50(13.50)	20.28(20.40)	46.11(45.91)	90	2.76
[Zn(Hapabh)(H ₂ O)SO ₄] (light yellow)	C ₁₈ H ₂₁ N ₃ O ₆ SZn(472)	279	13.65(13.77)	20.42(20.34)	45.58(45.76)	80	6.48

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