

Synthesis of Schiff Base Metal Complexes of 1-(2-hydroxy-5-methylphenyl) Ethan-1-One and Benzohydrazide, Their Characterization and Biological Studies

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Abstract: Schiff base ligand was prepared by the condensation of 1-(2-hydroxy-5-methylphenyl) ethan-1-one and benzohydrazide, and then metal complexes of Co (II), Cu (II), Fe (III), Mn (III) and VO (IV) were synthesized. The metal complexes were characterized and investigated by physical and spectral techniques, namely, elemental analysis, melting point, conductivity, ¹H NMR, IR, UV-Vis spectra. The antibacterial activity of all the compounds was screened against four bacterial pathogens, namely, *E. coli*, *S. aureus*, *S. typhi* and *P. vulgaris*. It has been found that the Schiff base and its metal complexes showed significant antimicrobial activity.

Keywords: Benzohydrazide, Schiff base, Metal complexes, Antibacterial activity

1. Introduction

The coordination chemistry of transition metal with ligand from the hydrazide family has been of interest due to different bonding modes shown by these ligands with both electron rich electron poor metals. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased interest in Schiff base complexes, since it has been recognized that many complexes may serve as models for biologically important species [1].

Hydrazide compounds were considered to act against a wide range of bacteria and were used in oral medication to cure genetic disorders such as thalassemia [2-3]. Interest in the study of Schiff base hydrazones have been growing because of their antimicrobial, anti-tuberculosis and anti-tumour activity [4-6].

The coordination compound of hydrazide has been fascinating many researchers, but comparatively less study is carried out. In view of the above facts the present investigation is focused on synthesizing Schiff base ligands and their complexes, finding out binding mode of ligands towards different metal ions and also studying the stereochemistry of complexes.

2. Experimental

Reagents and materials-

All the metal salts and solvents used were analytical reagent grade supplied by SD Fine and Merck. Solvents were

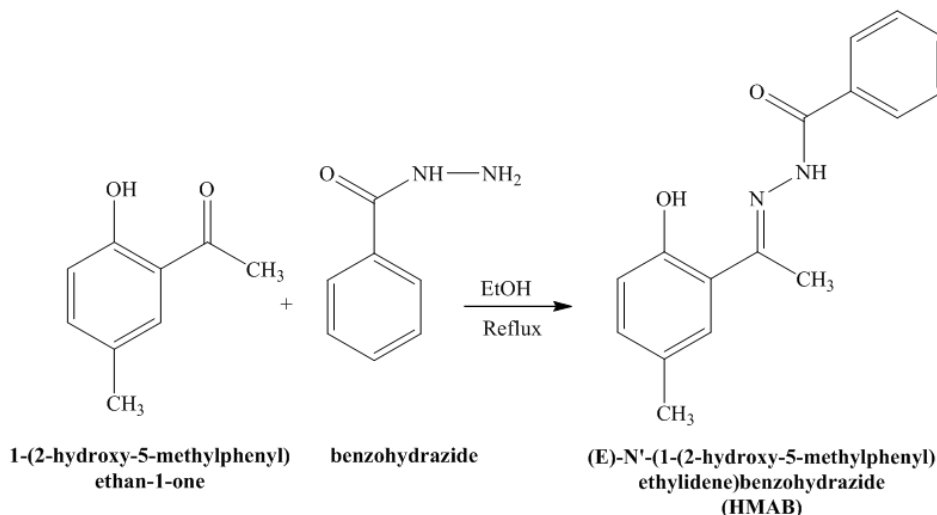
purified and dried before use by literature method [5]. Manganese acetate dihydrate was prepared by the oxidation of Mn (OAc)₂·4H₂O using Christensen's method [6] while all other metal salts are commercially available and used as received. The pure product was characterized by its melting point.

Physical measurements-

The amounts of metal present in the complexes were estimated by metal oxide method [7]. The molar conductance of the complexes in dimethyl formamide (DMF) solution (10⁻³ M), was measured using Equiptronic digital conductivity meter EQ-660 with a cell constant of 1.00cm⁻¹ at room temperature. The magnetic susceptibility values were recorded at room temperature by Gouy method using Hg [Co (NCS)₄] as a calibrant type magnetic balance. ¹H-NMR spectra of the ligand were recorded in DMSO-d₆ solution on EM-360, 60 MHz NMR Spectrometer. The infrared Fourier-transform infrared (IR) spectra of ligand and complexes were recorded as KBr pellets using Shimadzu spectrometer (IRAffinity-1S).

Synthesis of the ligand HMAB:

Equimolar (0.004m) solutions of 1-(2-hydroxy-5-methylphenyl) ethan-1-one and benzohydrazide were separately dissolved in ethanol and refluxed for four hours. The volume of reaction mixture was reduced to one third and cooled at 0°C. The solid residue was filtered off and recrystallized by ethanol. The purity of the compounds were checked by thin layer chromatography (TLC).
% yield: 80%



Synthesis of complexes

The complexes were synthesized by adding equimolar ethanolic solution of the ligand and respective metal salt, i. e., Co (OAc)₂·4H₂O, Cu (OAc)₂·H₂O, FeCl₃·6H₂O, Mn (OAc)₃·2H₂O and VOSO₄·5H₂O. The reaction mixture was refluxed in water bath for about 5-6 h. The colored solids obtained were filtered off, washed several times with ethanol followed by petroleum ether and finally dried over fused calcium chloride.

3. Result and Discussion

In the present study, all the complexes are found to be colored solids, air stable and non-hygroscopic. The analytical data indicate 1: 1 metal ligand stoichiometry. The complexes are insoluble in water and common organic solvents but soluble in coordinating solvents like DMF and DMSO. Lower values of molar conductance indicate that complexes are nonelectrolytes. The analytical and physical data of ligand and its complexes are given in Table 1.

Table 1: Elemental analysis, colour and formula weight of the compound

Compound	Formula wt.	Colour	Found (Calc.) %			
			C	H	N	M
HMAB	268.31	Yellow	71.62 (70.66)	5.98 (5.79)	7.33 (7.26)	-
HMAB-Co (II)	593.55	Green	64.75 (63.51)	5.09 (5.03)	9.44 (9.37)	9.93 (9.15)
HMAB-Cu (II)	598.16	Dark blue	64.26 (63.52)	5.06 (5.08)	9.37 (9.13)	10.62 (10.12)
HMAB-Fe (III)	661.36	Brown	58.12 (57.13)	4.57 (4.60)	8.47 (8.24)	8.44 (8.88)
HMAB-Mn (III)	708.55	Red	61.03 (60.24)	5.12 (5.28)	7.91 (7.22)	7.88 (7.42)
HMAB-VO (IV)	601.56	Black	63.89 (62.51)	5.03 (4.89)	9.31 (8.84)	8.47 (8.10)

¹H NMR spectra:

DMSO-d₆ spectrophotometer was used to record ¹H NMR spectra of complexes. Azomethine (-CH=N-) group was confirmed by the peak at δ8.5 ppm. This peak on complexation with metal gets upfield. The peaks at δ 6.53-8.49 ppm confirms the presence of phenolic hydrogen.

Infrared spectra:

There are certain changes in the properties of the ligand due to the formation of the new metal ligand bands and these can be usefully studied for the elucidation of the structure of complex, also the coordination of the ligand molecule with the metal ion changes the symmetry of the molecule. It is normally reduced and hence a band which is IR inactive in the free molecule or ion may become IR active on its coordination with metal or a single band corresponding to degenerate vibrations may split up in the complex due to lowering of symmetry.

In present investigation, IR Spectra of all the synthesized compounds were recorded in the range 4000-400 cm⁻¹, with

objective of obtaining information about the coordination sites in the ligand which would help in arriving at the stereochemistry of the complexes.

The free ligand medium broad band at 2968 cm⁻¹ due to intramolecular hydrogen bonded OH group is found to be lacking in the spectra of all complexes indicating the deprotonation of the replaceable hydrogen atom [9-10]. The absorption peak for ν (C=N) at 1660 cm⁻¹ in the ligand is shifted to a lower frequency by 30-40 cm⁻¹ in all complexes due to coordination of azomethine nitrogen [11-12]. Further conclusive evidence of the coordination of the ligand with the metal ions was shown by the appearance of new bands at 512-574 cm⁻¹ and 430-499 cm⁻¹ assigned to the metal-nitrogen (M-N) and metal-oxygen (M-O) stretching vibrations, respectively [13]. These bands were absent in the spectra of the free ligands, thus confirming participation of the O and N in the coordination. The data of the IR spectra of Schiff base ligand and their metal complexes are listed in Table 2.

Table 2: IR frequencies of ligand and its metal complexes (cm⁻¹)

Compound	ν (OH)	ν (C-O)	ν (C=N)	ν (C=O)	ν (M-O)	ν (M-N)
HMAB	2968	1480	1660	1669	-	-
HMAB-Co (II)	-	1498	1620	1630	430	574
HMAB-Cu (II)	-	1484	1630	1650	499	572
HMAB-Fe (III)	-	1485	1630	1640	439	514
HMAB-Mn (III)	-	1490	1624	1660	447	516
HMAB-VO (IV)	-	1482	1650	1668	435	512

Antibacterial activity

In present work, the antibacterial activity of the ligand and its metal complexes have been screened against the four bacteria *E. coli*, *S. aureus*, *S. typhi* and *P. vulgaris* strains by the cup plate method. The results revealed that the ligand and its complexes show weak to good activity. The ligand and Cu (II) complex are strongly active against all bacterial strain with the zone of inhibition 10-14 mm. The Fe (III), Mn (III) and VO (IV) complex show moderate activity as compared with its ligand with zone of inhibition 15-18 mm. The Cu (II) complex with the zone of inhibition 18-23 mm.

Table 3: Antibacterial activity of ligand and its complexes

Ligand and its complexes	<i>E. coli</i> (mm)	<i>S. aureus</i> (mm)	<i>S. typhi</i> (mm)	<i>P. vulgaris</i> (mm)
HMAB	10	11	11	12
HMAB-Co (II)	23	19	18	19
HMAB-Cu (II)	12	13	13	14
HMAB-Fe (III)	17	16	16	15
HMAB-Mn (III)	18	18	15	16
HMAB-VO (IV)	15	13	14	18

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