



Synthesis, Characterization and Biological Studies of Nano Sized Metal Complexes of Fe(II), Co(II) and Cr(II) with N,N' –bis(benzoin)-1,4 butane diimine

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ABSTRACT

The objective of the present study is to synthesize Schiff base ligand, N,N'–bis(benzoin) 1,4 butane diimine and its Fe(II), Co(II) and Cr(II) complexes. The synthesized complexes were characterized by IR and SEM. The synthesized Schiff base ligand and its Fe(II), Co(II) and Cr(II) complexes were screened for antibacterial and antifungal activity. IR data shows that the complexes are four coordinate. The SEM shows that all the complexes are nano crystalline. The synthesized complexes were tested against the bacterial and fungal species. The synthesized complexes were showed remarkable zone of inhibition with standards and have good antibacterial and antifungal activities.

Keywords: Schiff base, N,N'–bis(benzoin) 1,4 butane diimine, Metal Complex, Antimicrobial

INTRODUCTION

A Schiff base (or azomethine), named after Hugo Schiff, is a functional group that contains a carbon–nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. Schiff bases are of the general formula $R_1R_2C=N-R_3$, where R_3 is an aryl or alkyl group that makes the Schiff base a stable imine¹. A Schiff base is a chemical compound containing of a $C=N$ group²⁻⁴. Transition metal Schiff base complexes have been generally prepared by refluxing the solutions of a metal salt, a diamine and a compound containing a carbonyl group and a primary amine. Holm (1966) reported the synthesis and characterization of some divalent copper complex compounds by refluxing the solutions of copper (II) salt, salicylaldehyde but different diamines. Thakur⁵ reported the synthesis and characterization of Ni (II), Co (II) and Fe (II) Schiff base complex compounds. The compounds were prepared by refluxing mixture of the solutions of a divalent metal chloride, acetylacetone and hydrazine hydrate.

However, recent reports indicated synthetic modification in which the ligand is separately prepared before its interaction with a metal salt. Xishi (2003)⁶ showed the synthesis and spectroscopic properties of Mn (II), Co (II) and Cu (II) complexes with novel Schiff base ligand derived from 2, 2'bis(p-methoxyphenylamine) and salicylic aldehyde. Schiff base complexes of transition metals are of great importance in medicine, biochemistry and industries among others⁷⁻⁹.

For example, the field of medicine has witnessed an increase in the number of complexes with therapeutic value. Cobalt (II) Schiff base complexes are potential antiviral agents, cis-dichlorodiamineplatinum (II) complex is an anti cancer agent while copper (II) Schiff base is an anti-tubercular agent^{10,11}.

This paper reports the synthesis and characterization of N, N'–Bis(Benzoin) 1,4 butane diimine metal(II) complex compounds due to paucity of information.

MATERIALS AND METHODS

The chemicals and solvents used in this work were of Analar grade. All the glass wares used were washed thoroughly with distilled water and dried in an oven. Infrared spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wave number region $200-4000\text{ cm}^{-1}$. SEM images were recorded in VEGA3 TESCAN SEM analyzer.

Preparation of N, N'–Bis(Benzoin)-1,4 butane diimine

To a methanolic solution of 2.12g (0.01mol) benzoin and 1.09g (0.005mol) 1,4 butane diimine was added anhydrous sodium acetate (4g) and the mixture refluxed for an hour.

The hot solution was poured into ice-cold water where upon yellow precipitate of the schiff's base separated, it was filtered. Washed with water, dried and recrystallised from ethanol¹².

Preparation of N, N'–Bis(benzoin)-1,4 butane diimine Metal (II) Complexes

The ethanolic mixture of each (0.01 mol) Iron (II) chloride, (0.01mol) Cobalt (II) chloride, (0.01mol) Chromium(II) chloride and N, N'–bis(benzoin) 1,4 butane diimine schiff base (0.01mol) was refluxed separately, followed by drop wise addition of ammonia. The metal chelate separated out was filtered, washed with ethanol followed by ether and dried in an oven at 50°C .¹²

Determination of Antimicrobial Activity

The antimicrobial activity was performed by agar cup plate method.



Microorganisms

Escherichia coli (Gram negative) and fungi as *Candida albicans* were the microorganisms used and they were obtained from the Microbiology Laboratory of the Thanjavur Medical College Hospital, Thanjavur. These microorganisms were identified and confirmed by Microbiologists, Department of Microbiology, Thanjavur Medical College, Thanjavur.

Preparation of 24 hours Pure Culture

A loop full of each of the microorganisms was suspended in about 10ml of physiological saline in a Roux bottle. Each of these was streaked on to the appropriate culture slants and was incubated at 37°C for 24 hours except for *Candida albicans* which was incubated at 25°C for 24-48 hours. After completion of incubation period, when growth was observed the tubes were kept into 2-8°C until use.

Sample Solutions for the Experiment

The sample solutions as 50µl, 100µl and 150µl were used for the experiment. Standard antibiotic solution as Chloromphenicol for bacteria and Nystatin (25mg/ml distilled water-30µl) for fungi used to compare the test solution.

Preparation of Dried Filter Paper Discs

Whatman filter paper (No: 1) was used to prepare discs approximately 6 mm in diameter, which are placed in hot air for sterilization. After sterilization, the discs were loaded with different concentrations of prepared sample solutions again kept under refrigeration for 24 hrs.

Application of Discs to Inoculated Agar Plates

Previously prepared paper discs were dispensed onto the surface of the inoculated agar plate. Each disc was pressed down firmly to ensure complete contact with the agar surface. The discs were placed on the medium suitably apart and the plates were incubated at 5°C for 1 hr to permit good diffusion and then transferred to incubator at 37°C for 24 hrs. After completion of 24hrs, the plates were inverted and placed in an incubator set to respective temperature for 24 hrs.

Antimicrobial Assay

Antibiogram was done by disc diffusion method^{13,14}. Petri plates were prepared by pouring 30 ml of NA/PDA medium for bacteria/fungi. The test organism was inoculated on solidified agar plate with the help of micropipette and spread and allowed to dry for 10 minutes. The surfaces of media were inoculated with bacteria/fungi from a broth culture. A sterile cotton swab is dipped into a bacterial/fungi test suspension and used to evenly inoculate the entire surface of the Nutrient agar/PDA plate. Briefly, inoculums containing *Escherichia coli* was spread on Nutrient agar plates for bacteria and *Candida albicans* was spread on potato dextrose agar for fungus strains. Using sterile forceps, the sterile filter

papers (6 mm diameter) containing the sample (50µl, 100 µl, 150µl and 30µl for respective standard) were laid down on the surface of inoculated agar plate. The plates were incubated at 37°C for 24 h for the bacteria and at room temperature (30 ± 1) °C for 24-48 h for yeasts strains. Each sample was tested in triplicate.

Measurement of Zone of Inhibition

The antimicrobial potential of test compounds was determined on the basis of mean diameter of zone of inhibition around the disc in millimeters. The zones of inhibition of the tested microorganisms by the extracts were measured using a millimeter scale.

RESULTS AND DISCUSSION

The interaction between metal (II) ions and N, N'-Bis(Benzoin)-1,4 butane diimine, yielded the desired crystalline, yellow metal (II) complexes compound. These compounds are insoluble in water and common organic solvents, but are readily soluble in acetone.

The IR spectra [Table 1] of the metal (II) complex compounds show bands in the region 1530-1570cm⁻¹ which are assigned to ν(C=N) stretching vibration, a fundamental feature of azomethine group¹⁵.

The band in the region 1600-1660cm⁻¹ corresponds to ν(C=C) stretching vibration due to phenyl group, indicating the coordination of bis(benzoin)-1,4 butane diimine Schiff base to the metal (II) ions. The bands within 550-590 cm⁻¹ and 430-480 cm⁻¹ are assigned to ν(M—O) and ν(M—N) stretching vibrations, respectively^{16,17}. These bands confirmed the coordination of the Schiff base to the metal (II) ions. The metal (II) complex compounds revealed 1:1 metal to ligand ratio, resulting in a four coordinate complex compounds of which the following molecular structure below is proposed.

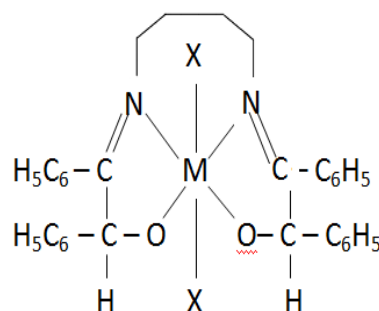


Figure1: Shows the molecular structure of bis(benzoin)-1,4 butane diimine complex compounds

Table 1: The Infrared Spectral Data of the Complex Compounds.

Compound	ν(C-H) (cm ⁻¹)	ν(C=C) (cm ⁻¹)	ν(C=N) (cm ⁻¹)	ν(M-O) (cm ⁻¹)	ν(M-N) (cm ⁻¹)
[Fe L']	2822	1610	1569	580	465
[Fe L']	2942	1612	1567	586	458
[Cr L']	2892	1614	1560	581	460

The antimicrobial activities of the Schiff base ligand and its Fe (II), Co (II) and Cr (II) complexes are shown in **Table 2** to **Table 5**.

Table 2: Antimicrobial activity of Ligand

Ligand	<i>Escherchia Coli</i> (mm)	<i>Candida albicans</i> (mm)
50 μ l	-----	2 \pm 0.14
100 μ l	8 \pm 0.56	4 \pm 0.28
150 μ l	13 \pm 0.91	5 \pm 0.35
Standard (30 μ l) (Chloromphenicol)	13 \pm 0.91	-----
Standard (30 μ l) (Nystatin)	-----	13 \pm 0.91

Table 3: Antimicrobial activity of Iron complex

Fe complex	<i>Escherchia Coli</i> (mm)	<i>Candida albicans</i> (mm)
50 μ l	-----	-----
100 μ l	2 \pm 0.14	4 \pm 0.28
150 μ l	7 \pm 0.49	5 \pm 0.35
Standard (30 μ l) (Chloromphenicol)	12 \pm 0.84	-----
Standard (30 μ l) (Nystatin)	-----	14 \pm 0.98

Table 4: Antimicrobial activity of Cobalt complex

Co complex	<i>Escherchia Coli</i> (mm)	<i>Candida albicans</i> (mm)
50 μ l	-----	-----
100 μ l	-----	-----
150 μ l	12 \pm 0.84	10 \pm 0.7
Standard (30 μ l) (Chloromphenicol)	12 \pm 0.84	-----
Standard (30 μ l) (Nystatin)	-----	14 \pm 0.98

Table 5: Antimicrobial activity of Chromium complex

Cr complex	<i>Escherchia Coli</i> (mm)	<i>Candida albicans</i> (mm)
50 μ l	-----	-----
100 μ l	-----	-----
150 μ l	10 \pm 0.84	-----
Standard (30 μ l) (Chloromphenicol)	12 \pm 0.84	-----
Standard (30 μ l) (Nystatin)	-----	14 \pm 0.98

Scanning Electron Microscope

The SEM micrographs of Fe(II), Co(II) and Cr(II) complexes are shown in Figures 2a, 2b and 2c. It is seen from the figure that Fe(II), Co(II) and Cr(II) complexes shows cauliflower like structures. The particle sizes of Fe(II), Co(II) and Cr(II) complexes were in the diameter range of few microns. However, particles with size less than 100 nm were also observed which groups agglomerates of larger size. The average crystalline size shows that the

particles were agglomerated that these complexes were polycrystalline with nanosized grains.

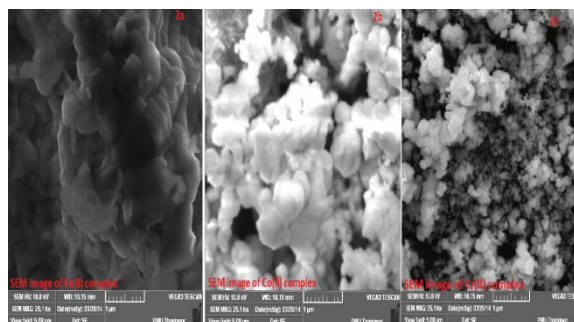


Figure 2: SEM images of Fe(II), Co(II) and Cr(II) Complexes

CONCLUSION

The Schiff base ligand and its Fe(II), Co(II) and Cr(II) complexes were prepared. Fe(II), Co(II) and Cr(II) complexes were characterized by IR spectra and SEM. The proposed structure of metal complexes has been illustrated in Figure 1. The surface morphology using SEM showed that the particles were polycrystalline with nano sized grains. The antimicrobial activity of ligand and its complexes indicate that both ligand and metal complexes are potentially active against both fungi and bacteria.

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