

Synthesis, Spectral Characterization And Pharmacological Significance of Fe(III) Complex With Schiff Base and Thiocyanate ION as Ligands

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Abstract- A novel Fe(III) complex of Schiff's base derived from phenylacetylurea condensed with salicylaldehyde (SBPS) and thiocyanate(SCN⁻) ion was synthesized by using microwave irradiation. Microwave synthesis gives high yield of the complex within a short time. The molecular formula and the probable geometry of the complex have been deduced from elemental analysis, molar conductance, UV, FT-IR, and Far IR spectra. The molar conductance indicates that the Fe(III) complex is a non-electrolyte. FT-IR spectra show that Schiff's base and thiocyanate ion are coordinated to the metal ion in a monodentate manner. The electronic spectrum and the magnetic moment indicate the geometry of the complex is found to be distorted octahedral. The antimicrobial activities of ligands and their Fe(III) complex were studied against the few microorganisms by agar - well diffusion method. The complex shows moderate activity against the bacteria and enhanced activity against the fungi as compared to the SBPS ligand.

Keywords: Fe(III) complex, SBPS, thiocyanate ion, antimicrobial

I. INTRODUCTION

The class of compounds, so-called imines, are often referred to as Schiff bases, named after the German chemist Hugo Schiff. Schiff bases contain the azomethine group (—RC=N—) and are typically formed by the condensation of a primary amine with an active carbonyl compound. They have drawn considerable research attention of scientists owing to the ease of synthesis and metal complexation [1,2]. The schiff bases are interesting and substantial ligands find extensive applications in the field of coordination chemistry. Schiff bases also called as privileged ligands act as chelating ligands for many metal ions [3,4]. In modern years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance as catalysts in many reactions. Also Schiff base complexes derived from heterocyclic compounds have acquired more attention in the field of bioinorganic chemistry because of their biological activities [5-16].

However, the schiff base has several applications in biological, clinical and analytical fields [17] due to their enhanced biological and pharmaceutical activities and the Schiff base have attracted many workers [18]. Schiff base ligand complexes are very important in many catalytic reactions [19]. It is also used in the di-oxygen uptake and oxidative catalyst [20,21]. Microwave-assisted synthesis is eco-friendly. This technique is certainly going to be the technology of tomorrow. The advantages of microwave reactions over conventional techniques are fast, clean, economic, pollution free, shorter time high yield [22,23].

In the present paper, the Schiff base is derived from phenylacetylurea and salicylaldehyde by condensation which is used in primary ligand for the preparation of Fe(III) complexes. The prepared complexes were characterized by the physico-chemical and spectral studies.

II. EXPERIMENTAL

2.1. MATERIALS AND METHODS:

Phenylacetylurea, potassium thiocyanate and iron nitrate were purchased from Alfa Aaser Company and used as such. The organic solvents used, *viz.*, DMSO, DMF, methanol, ethanol which were of AnalaR grade, and used as such without further purification.

2.2. Preparation of Schiff's base

The Schiff's base (primary ligand) was prepared by refluxing an ethanolic solution of required mole ratios of phenylacetylurea with salicylaldehyde in the presence of NaOH, for about an hour.

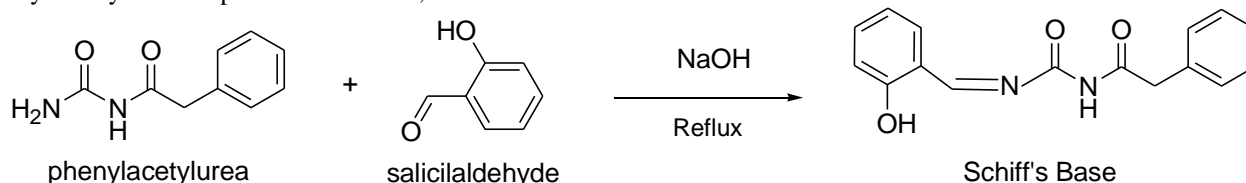


Fig. 1 Schiff's Base of Phenylacetylurea with Salicylaldehyde (SBPS)

2.3. INSTRUMENTATIONS

CHN elemental analyses were performed using Thermo Finnegan make, Flash EA1112 Series CHNS(O) analyzer. The electrical conductivity measurements were conducted using 10^{-3} M solutions of the metal complex in acetonitrile with Systronic Conductivity Bridge (model number-304) at 30°C. The UV-Visible spectrum of the Fe(III) complex was recorded on Varian, Cary 5000 model UV Spectrophotometer. Infra red spectra for the complex and the ligands were recorded on a Perkin Elmer, Spectrum RX-I, FT IR spectrometer in KBr discs at room temperature. The Far-IR Spectrum of the complex was recorded by Bruker 3000, FT IR Spectrometer. The antibacterial and antifungal activities of the ligand SBPS and the Fe(III) complex were determined by agar- well diffusion method.

2.4. SYNTHESIS OF METAL COMPLEX

2.41g (8.77mmol) of SBPS in ethanol and 0.93g (7.36mmol) of potassium thiocyanate in ethanol were added to the iron nitrate 1.00g (2.92mmol) in methanol followed by microwave irradiation for a few seconds after each addition by using IFB 25 BG-1S model microwave oven. The resulting precipitate was filtered off, washed with 1:1 ethanol: water mixture and dried under vacuum. A pale brown colored complex was obtained with the yield of 76.1 %.

III. PHARMACOLOGY

3.1. Antimicrobial activity:

The Fe(III) complex and the ligands were tested for *in vitro* antimicrobial activity by the well diffusion method [24] using agar nutrient as the medium. The antibacterial and the antifungal activities of the ligands and the Fe(III) complex were evaluated by well diffusion method against the strains, cultured on potato dextrose agar as medium. The stock solution (10^{-2} M) was prepared by dissolving the compounds in DMSO and the solutions were serially diluted to find Minimum Inhibitory Concentration values. According to the typical procedure [25] a well was made on the agar medium inoculated with the microorganisms. The well was filled with the test solution using a micropipette and the plate was incubated for 24 hours for bacteria and 72 hours for fungi at 35°C. At the end of the period, inhibition zones formed on the medium were evaluated in millimeters (mm) and diameter.

IV. . RESULTS AND DISCUSSION

4.1. Elemental analysis and metal estimation

The elemental analysis and metal estimation of the complex lead to the formula $[M(\text{SBPS})_3(\text{SCN})_3]$. The percentages of carbon, hydrogen, nitrogen and iron in the complex were found to be 56.87(56.83), 3.93(3.90), 11.70(11.73) and 5.18(5.13) respectively. The experimental data are in good agreement with the theoretical values (given in the parentheses).

4.2. Molar conductance

The molar conductance of 10^{-3} M solution of $[\text{Fe}(\text{SBPS})_3(\text{SCN})_3]$ in acetonitrile was found to be $77.56 \text{ } \Lambda_{\text{m}}(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$ indicating its non electrolyte [26] nature.

4.3. Electronic Spectra:

The electronic spectrum of Fe(III) complex gave three wavelength maximum at 680 nm ($14,705\text{cm}^{-1}$), 385 nm ($25,974 \text{ cm}^{-1}$), 260 nm ($38,461 \text{ cm}^{-1}$) which corresponding transitions are ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$, ${}^5\text{B}_{1g} \rightarrow {}^5\text{B}_{2g}$ and CT-band respectively [27]. The magnetic moment of Fe(III) complex is 5.8BM. These facts confirmed the six coordinated distorted octahedral geometry of the complex.

4.4. FT-IR spectra

The IR spectrum of the pure ligand shows the characteristic frequencies as follows: the band at 3388cm^{-1} indicates the $\nu(\text{N-H})$ stretching frequency of primary amine, at 1668 cm^{-1} indicates symmetric stretching frequency and at 1622 cm^{-1} the asymmetric stretching frequency of $\nu(\text{N-H})$ in secondary amine. The $\nu(\text{C=O})$ stretching frequency of the ligand is observed at 1475cm^{-1} . In the Fe(III) complex, $\nu(\text{N-H})$ is shifted to 1685cm^{-1} and the symmetric stretching frequency at (1619 cm^{-1}) is shifted to 1605cm^{-1} which confirms the entry of ligands into the coordination sphere. In addition to that, the value at 2068 cm^{-1} indicates the presence of SCN^- in the coordination sphere of the complex [28-31].

4.5. Far-IR Spectra

In the Far-IR spectrum of the complex, the frequency at 448.5 cm^{-1} corresponds to HC=N bond and at 342.2 cm^{-1} indicates the Fe-N (from thiocyanate) bond [32] thus, it is confirmed.

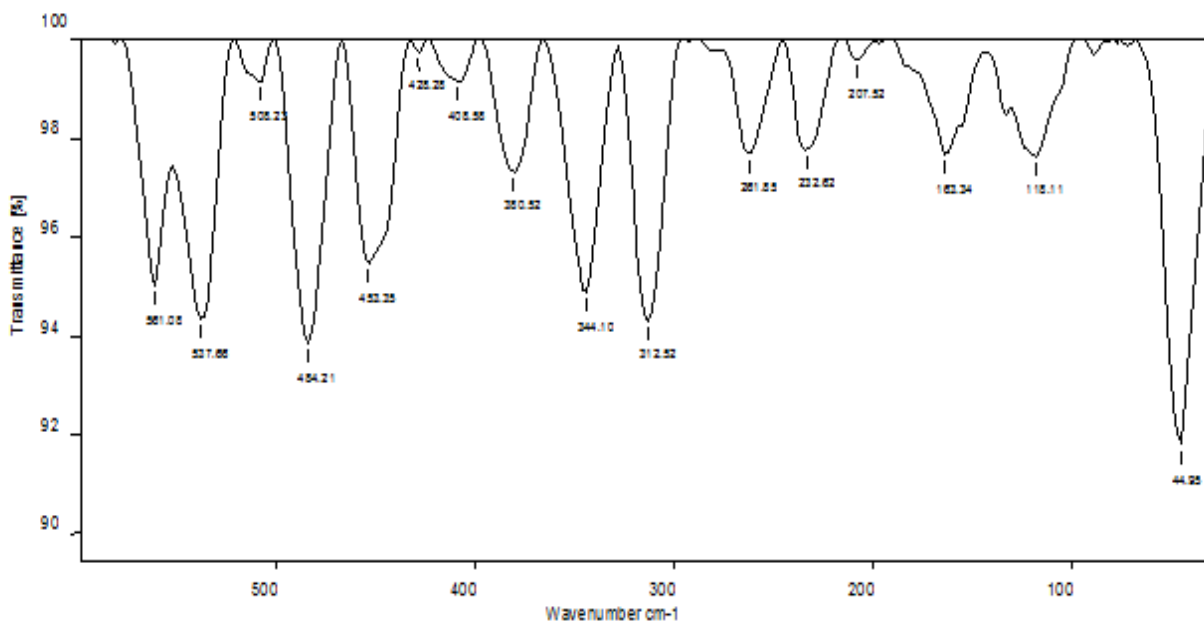


Fig. 2 Far-IR-spectrum of Fe(III) complex

4.6. CYCLIC VOLTAMMOGRAM OF Fe(III) COMPLEX:

Cyclic voltammogram of Fe(III) complex was recorded in DMSO solution. This shows a well redox process corresponding to the formation of Fe(III)/Fe(II) couple at $E_{\text{pa}} = -0.900\text{V}$, $E_{\text{pc}} = -0.480\text{V}$ and the $\Delta E_{\text{p}} = 0.420\text{V}$. This also indicates the quasi-reversible [33] nature of one electron transfer reactions.

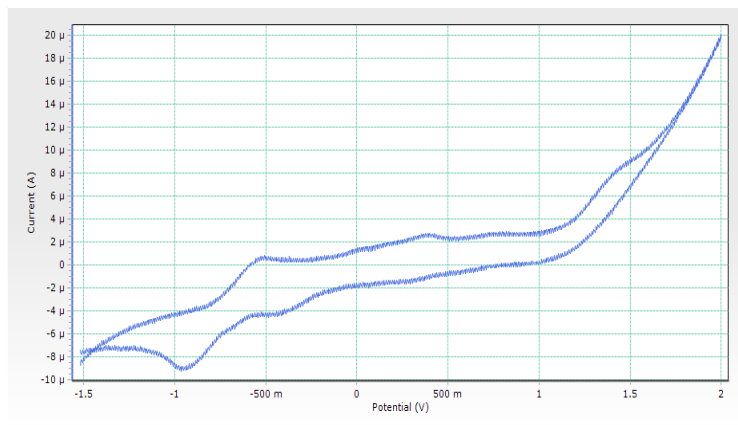


Fig.3 Cyclic voltammogram of Fe(III) complex

V. BIOLOGICAL ACTIVITY

5.1. Antibacterial activity

The synthesized Fe(III) complex and the free ligands were evaluated against the bacteria *E.coli*, *Klebsiella Pneumonia*, *P.aeurginosa*, *S. aureus*, *Bacillus cereus*. *Aspergillusflavus*, *Aspergillusniger*, *Aspergillusoryzae*, *Aspergillussojae* and *Candida albicans* at MIC concentration using agar-well diffusion method. The complex shows does not active against the tested microbes. The antibacterial activities of the free ligands and the complex are as shown in Table1.

Table 1. Antibacterial activity

S.No	Ligand /Complex	Zone of Inhibition(mm)				
		<i>S.aureus</i>	<i>Bacillus cereus</i>	<i>E.coli</i>	<i>P.aeruginosa</i>	<i>Klebsiella</i>
1	SBPS	6	10	10	6	5
2	[Fe(SBPS) ₃ (SCN) ₃]	5	6	5	5	6

5.2. Antifungal activity

The synthesized compounds and the free ligands were evaluated against the fungi, viz., *Aspergillus flavus*, *Aspergillus niger*, *Aspergillus oryzae*, *Aspergillus sojae* and *Candida albicans* at various concentration and compared to pure SBPS and KSCN. But, the antifungal activities of all the complexes are lower than those of Fluconazole (standard).The complex shows enhanced activity against the tested fungus. The antifungal activities of the free ligands and the complex are as shown in Table 2.

The complex shows high antifungal activity against *Aspergillus sojae* (30mm), moderate activities against *Aspergillus flavus* (23mm) and *Aspergillus niger* (24mm), and low activity against *Candida albicans* (21mm) . The results are given in Table2.

Table 2. Antifungal activity

S.No	Fungus	Concentration		
		100μgml ⁻¹	200 μgml ⁻¹	400 μgml ⁻¹
1	<i>Aspergillus flavus</i>	6	11	23
2	<i>Aspergillus niger</i>	9	14	24
3	<i>Aspergillus oryzae</i>	4	11	21
4	<i>Aspergillus sojae</i>	13	21	30
5	<i>Candida albicans</i>	5	12	21

However, the antimicrobial activity values indicate that the complexes possess higher growth of inhibition potential compared to those of their free ligands. The antibacterial activity of the metal complexes increase with the increase in the concentration of the complexes. It suggests that the complexes having antibacterial activities inhibit multiplication process of the microbes by blocking their active sites [34]. The increased activity of the metal complexes can be explained on the basis of chelation theory [35]. It is known that chelation tends to make the ligand act as powerful and potent bactericidal agents, killing more number of

bacteria than the ligand. It is observed that, in a complex, the positive charge of the metal is partially shared by the donor atoms present in the ligands, and there may be π -electron delocalization over the whole chelating space [36].

VI. CONCLUSION

In the present study, our efforts were to synthesize and characterize a new Fe(III) metal complex with SBPS and thiocyanate ion as ligands. The new complex was synthesized using microwave irradiation (Green synthesis). These synthesized compounds were characterized by various chemical and spectral analyses. Based on the analytical, electrical conductance, spectral and magnetic moments data, distorted octahedral geometry has been suggested for the Fe(III) complex. The antibacterial and the antifungal activities of the ligands were compared with the Fe(III) complex. The complex shows does not active against the bacteria and enhanced activity against the fungus.

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