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Chromium, Cobalt, and Iron based Schiff Base Metal Complexes with their Antimicrobial Activities

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Abstract

Metal complexes of cobalt (II), chromium (III), and iron (II) were produced using a Schiff base derived from the combination of dihydroxyacetone (DHA) and sulphanilamide. The structural analysis was conducted and corroborated using numerous spectroscopic techniques, comprising infrared (IR), UV-Visible spectrophotometry nuclear magnetic resonance (NMR) and mass spectrometry and. It was discovered that the structure of the cobalt complex is a square pyramidal, in contrast to the tetrahedral structure of the other complexes. Because of its greater capability for binding, chromium's complexes with metal ions were shown to have higher stability constants than those of the other two metal ions. The observed antimicrobial activity of the metal complex indicates that it exhibits effective antibacterial properties against both gram-positive in addition to gram-negative bacteria, through the exclusion of *E.coli*. Furthermore, it is evident that metal complexes display greater antibacterial activity compared to their respective Schiff ligand when targeting gram negative bacteria.

Keywords: DHA, Schiff base, geometry, sulphanilamide, antimicrobial activity

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1. Introduction

In the domain of Inorganic chemistry, the exploration of Schiff base and its metal complexes has emerged as a highly intriguing and captivating area of research. The formation of these complexes occurs via the bringing together of metal ions with Schiff base ligands, which are organic compounds that arise from the condensational reaction between an aldehydic group or ketonic group and an amine [1]. In latest years, there has been a substantial amount of research dedicated to the investigation of the diverse and intriguing properties exhibited by the resulting structures [2]. The widespread solicitations of Schiff base metal complexes in a diversity of domains, such as catalysis, medicinal chemistry, and materials research, make them particularly remarkable [3, 4, 5]. These complexes' one-of-a-kind electronic and structural features contribute to their wide range of applications and high level of reactivity. Understanding the fundamental principles governing their formation and behavior is crucial for harnessing their potential in practical applications [6, 7].

This study work emphases on the synthesis, characterization, and examination of the characteristics of Schiff base metal complexes by utilization of DHA (Dehydroacetic acid) and sulphanilamide, as well as their interactions with the metals Co, Cr, and Fe [8, 9]. By means of a methodical inquiry, our objective is to elucidate the complex intricacies of their molecular architectures and provide insights into the variables that impact their reactivity. Through this endeavor, our intention is to provide significant contributions and useful perspectives to the wider scientific community. This will facilitate the advancement of innovative materials and catalysts, leading to improved performance and greater applicability [10].

2. Experimental Procedure

The production of Schiff base ligands coordinated with metal complexes was successfully carried out following established protocols and standard operating procedures. All the chemicals were acquired from the pharmaceutical company Merck [11].

2.1. Making of described Schiff Base

The synthesis of below said Schiff base involves reflux of a combination comprising of DHA with sulphanilamide in an ethanol solvent. A solution containing 1 millimole of both DHA and sulphanilamide was prepared by dissolving them in 15 cm^3 of ethanol within a round bottom flask (RBF). The reflux process was conducted for a duration of three hours. Following the reflux process, the contents are next subjected to a cooling procedure. The Schiff bases is obtained in the solid form, subjected to washing, recrystallization using ethanol as the solvent, and subsequently parched in desiccator. The stability of this ligand is maintained even under ambient conditions. The substance exhibits solubility in alcohol, chloroform at elevated temperatures, as well as in DMSO and DMF. [12, 13]. The reaction scheme is shown in figure 1.

2.2. Synthesis of Metal Complex

The metal complexes are synthesized through refluxing the ligand, previously prepared, in an ethanol solution with a 2:1 mole ratio of metal chloride. In this study, ethanol was employed as a solvent for the dissolution of chromium (Cr) and iron (Fe), while dimethyl sulfoxide (DMSO) was utilized for cobalt (Co). In order to synthesize the metal complex, a quantity of 2 millimoles of the previously primed ligand was utilized, ensuring a slight excess, within a round-bottom flask (RBF) containing 15 cm^3 of solvent. The substance exhibits the capacity to dissolve Schiff bases. A solution was set by adding one millimole of metal chloride to a volume of 5 cm3 of solvent, followed by stirring. Subsequently, the metal chloride solution was introduced in a controlled and gradual manner into the ligand that was being subjected to heat. The pH is carefully controlled to remain within the slight range of 7.5 to 8.0 through the adding of a minor quantity of dil. Ammonia solution. The contents were subjected to a reflux process lasting three hours. Following the filtration process, the resultant precipitate of the compound was subjected to a thorough washing procedure employing alcohol. Subsequently, the precipitate was subjected to desiccation within a desiccator to facilitate the removal of any residual moisture [14, 15, 16].

3. Results and Discussion

3.1. Properties of synthesized Schiff Bases

The determination of the molecular formula of the formed ligand has been successfully accomplished and found to be $C_{14}H_{14}N_2O_5S$. Additionally, it exhibits a yellow coloration and possesses a melting point exceeding 350 ^oC. The compound exhibits a molecular weight of 253.26, while demonstrating a practical yield of 92.25 percent. The elemental composition of the sample was determined using analytical techniques, revealing the presence of carbon (C) at a relative abundance of 52.7%, hydrogen (H) at 4.3%, nitrogen (N) at 8.6%, oxygen (O) at 24.81%, and sulphur (S) at 9.9%. The synthesized Schiff Base exhibits an infrared spectrum that reveals a distinct -C=N- (azomethine) stretch band at a wavenumber of 1685.69 cm^{-1}.

This band is ascribed to the occurrence of the azomethine -C=N- functional group, providing evidence for the condensation reaction among the primary amino (-NH2) cluster of sulphanilamide and the ketonic group of the Schiff base derived from DHA. The identification of an infrared band at approximately 1699.56 cm^{-1} within the infrared bands obtained of the Schiff base Cobalt compound provides compelling indication for the involvement of azomethine in the electron donation process to Co^{2+}, thereby facilitating the founding of a coordination compound involving a metal. The infrared (IR) spectra analysis of Schiff Base compound reveals a notable shift in the IR band associated with the azomethine group, from approximately 1685.69 cm^{-1} to 1726.77 cm^{-1}. This shift provides compelling evidence that the azomethine moiety undergoes electron transfer to the Cr^{3+} ion, causing the founding of a metal complex. The infrared spectra obtained of the Fe complex containing a Schiff base ligand exhibit a prominent absorption band at approximately 1719.28 cm^{-1}. This observation suggests that the azomethine moiety contributes its electrons to facilitate the formation of the Fe^{2+} metal complex within the Schiff base framework. [17]. The IR values are given in table 1.

3.2. NMR Spectral data analysis

The proton nuclear magnetic resonance (NMR) studies reveal the presence of a peak at a chemical shift of around δ 2.0 ppm, which corresponds to the $–NH_2$ group that is involved to the $–SO_2$ cluster. The multiplet ranging from δ 6.71 to 7.71 is observed in the NMR spectrum, indicating the occurrence of a benzene ring. The observed peak at a chemical shift around 3.3 ppm δ corresponds to the occurrence of methine group (-CH-) fused to a nitrogen atom (-N=CH-). The N-H group exhibits a chemical shift around 2.0 (ppm) δ. These chemical shifts provide valuable insights into the molecular structure and bonding environment of the ring. The desired product formation is not indicated by the absence of a peak at approximately 3.5 ppm, which corresponds to the presence of one additional $–NH_2$ group [18, 19].

3.3. Mass Spectral Analysis

Based on the findings of the mass spectral investigation, the preparation of the Schiff base is evidenced by presence of a molecular ion exhibiting a highest at 323.3 m/e. Consequently, this molecular ion undergoes fragmentation, leading to the generation of smaller peaks.

3.4. Electronic absorption Spectra, Conductance and Magnetic Properties

The developments acquired remained examined in an ethanolic solution to ascertain the M/L proportion within the compound using Job's Method. A set of solutions was arranged, maintaining a consistent concentration of 10^{-3} M for both the metallic ion and the Schiff base, denoted as HL. The determination of the M/L ratio was based on the correlation observed amongst the absorption of the incident ray and mole fraction of M/L. The investigation revealed that the ratio of metal to ligand, denoted as HL, was determined to be 1/2 for complexes. Notably, this finding was observed to be consistent with the corresponding ratio observed in the solid state. Established on the results of the spectral analysis study, it was observed that complex 1 displayed a square pyramidal structure, while complex 2 and 3 exhibited a tetrahedral geometry [20]. The values are indicated in table 2.

3.5. Stability constant of complexes

With the use of spectrophotometric analysis, the equilibrium constants of the substances were calculated, in which the absorbance of five separate solutions containing complexes at known quantities was determined. The concentrations that were measured in this study were 0.001, 0.002, 0.003, 0.004, and 0.005 $moldm^{-3}$, respectively. Beer's Lambert law was used to get the stability constants. The molar absorption coefficient of the complex was determined based on the Beer's law plot. The equilibrium concentration of each complex compound was determined by employing the dilution formula and Beer's law, retaining the molar absorptivity [21, 22]. Values are shown in table 3.

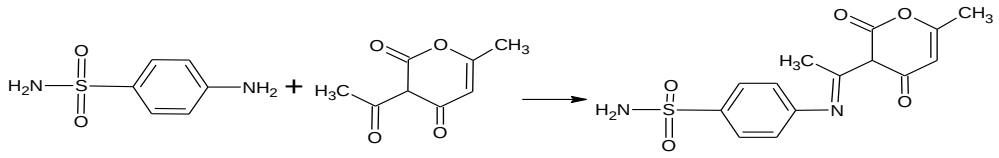

Figure 1. Schiff base ligand synthesized from sulphanilamide and DHA.

Table 1. Infrared spectral data of compounds.

Complex	**Wavelength (cm^{-1})**			
	v (M-O)	**v (C-0)**	**V (M-N)**	**v (C=N)**
Schiff base Ligand	---------	1650.77	---------	1685.69
Cr-L	602.52	1648.59	643.09	1726.77
Co-L	557.91	1632.41	635.98	1699.56
Fe-L	534.34	1647.91	580.65	1719.28

Table 2. Electronic absorption Spectra, Conductance and Magnetic Properties of the complexes.

Sr. no.	**Complex**	**Conductance $\Omega^{-1}cm^2mol^1$**	**Magnetic moments (B.M.)**	**Raccah Parameter (cm-1) (E/B)**	**Absorption Maxima cm^{-1} (nm)**	**Transition.**
1.	Co-L	35.2	1.732	0.0333	322, 354, 357	$T_{1g} \rightarrow T_{2g}$ $T_{1g} \rightarrow T_{1g(P)}$ $T_{1g} \rightarrow A_{1g}$
2.	Cr-L	33.1	3.872	0.03647	210, 352	$T_{2g} \rightarrow E_g(td)$ $E_g \rightarrow T_{2g}$
3.	Fe-L	26.3	diamagnetic	0.0509	210,405, 412, 470	$T_{2g} \rightarrow E_g(Td)$ $E_g \rightarrow T_{2g}$ $T_{2g} \rightarrow A_{2g}$ $T2g \rightarrow A1g$

Table 3. Stability constants of the complexes

Complexes	**Stability constant K in 10^{-3}**	**ΔG Joule/mole**
Co-L	0.75	-76009.02
Cr-L	0.8	-71308.98
Fe-L	0.5	-15040.77

Table 4. Antimicrobial activities of Schiff base ligand and its metal complexes.

Sr. No	Test organisms	Zone of inhibition of respective nanoparticles in mm			
		Ligand	Co-L	Cr-L	Fe-L
1	***B.cerus***	12	20	18	16
2	***S.aureus***	00	20	15	16
3	***B.subtilis***	19	17	23	18
4	***E. coli***	00	00	00	00
5	***P.aeruginosa***	00	20	19	20
6	***P. vulgaris***	00	19	12	13

To outline the equilibrium constant of the metallic ion and the Schiff base, the following expression was utilized.

$$[L]_{eqm} = [L]_0 - x\ [Complex]$$

$$[M^{2+}]_{eqm} = [M^{2+}]_0 - [Complex]$$

In light of the aforementioned circumstances, the determination of the equilibrium constant, denoted as K_f, was carried out utilizing the established mathematical relationship;

$$[complex] / [M^{2+}]_{eqm} [L]^x_{eqm.}$$

The Gibbs free energy can also be determined through the utilization of a specific mathematical relationship,

$$\Delta G = RT \ln K.$$

3.6. Antimicrobial activities

Standard solutions of the produced complex were meticulously ready at a concentration of 1 mg/ml in ethanol, sourced from Sigma Aldrich, a reputable supplier of laboratory chemicals and reagents. Subsequently, the antimicrobial activity of various samples was evaluated at concentrations of 100 µg/mL [23, 24].

3.7. Test organisms

In this study, a total of six bacterial strains were selected as the test organisms to represent disease-causing microorganisms. Among these, three strains were Gram-positive bacteria, namely *Bacillus cereus* [NCIM 2703], *Staphylococcus aureus* [NCIM 2654] and *Bacillus subtilis* [NCIM 2635], and. The remaining three strains were Gram-negative bacteria, namely, *Escherichia coli* [NCIM 2832], *Pseudomonas aeruginosa* [NCIM 5032] and *Proteus vulgaris* [NCIM 2813]. These bacterial strains were specifically chosen as bacterial test pathogens for the resolution of this research. The current study meant to assess the antibacterial effectiveness of different crude extracts and wine against a range of Gram-positive (*Bacillus cereus* [NCIM 2703], *Bacillus subtilis* [NCIM 2635], *Staphylococcus aureus* [NCIM 2654]) and Gram-negative (*Proteus vulgaris* [NCIM 2813], *Escherichia coli* [NCIM 2832], *Pseudomonas aeruginosa* [NCIM 5032]) bacterial strains. The modified agar well diffusion method was employed for this purpose. The suspension of the respective test pathogens was prepared using sterile saline solution and subsequently utilized for further investigation. In order to assess the antimicrobial activity, a series of pathogens were introduced onto the surface of sterile Muller and Hinton agar. The pathogens were then evenly distributed across the agar plates using a sterile spreader. Following aseptic techniques, the agar well was meticulously prepared using a sterilized cork borer, which possessed a diameter of 0.7 cm. Subsequently, a 100 µl aliquot of the corresponding test sample was introduced into the wells containing the designated test pathogens. The plates were initially exposed to a high temperature of up to 4 °C for a period of 20 minutes in direction to enhance the dispersion of the samples within the culture medium. Subsequently, the plates were transferred to an incubator set at a high temperature of up to 37 °C and allowed to incubate for a period of 24 hours.

The synthesized ligand demonstrates significant antimicrobial effectiveness against gram-positive bacterial strains, specifically *Bacillus cereus* and *Bacillus subtilis*, while demonstrating complete inactivity against gram-negative bacteria. The synthesized metal complex demonstrates significant antibacterial effectiveness against a diverse spectrum of gram-positive and gram-negative bacteria, excluding *Escherichia coli (E. coli)*. Furthermore, it is evident that metal complexes exhibit superior antibacterial activity compared to their corresponding ligands with exception of *B.subtilis.* Zones of inhibition values are given in table 4.

4. Conclusions

It is found that all the metal complex prepared have unique properties. They are comparatively stable have certain electrical conductivity. The Cobalt complex has square pyramidal geometry and Chromium and Iron complex have tetrahedral geometries confirmed from above experimental data. The synthesized metal complex demonstrates significant antibacterial efficacy against a diverse spectrum of gram-positive and negative bacteria, excluding *Escherichia coli (E. coli)*. Furthermore, it is evident that metal complexes display superior antibacterial activity compared to their conforming ligands.

Conflict of interest

None

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