Comparative Studies on Synthesis, Characterization and Antibacterial Properties between Schiff Base Co(II) Complex and Peroxo Complex

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Authors’ contributions
This work was carried out in collaboration among all authors. Author MAF designed the study. Authors MNAB and MMA performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MSH, MFH, MAA, MMH and MKEZ managed the analyses of the study and managed the literature searches. All authors read and approved the final manuscript.

ABSTRACT
A new Schiff base Co(II) complex and - peroxy complex were synthesized and characterized by thin layer chromatography (TLC), elemental analyses, magnetic moment, conductivity measurements, UV-Vis., IR and ESI-MS spectral studies. The cobalt ion was participated in direct complexation with the Schiff base (SB) ligand derived from o-aminobenzoic acid and cinnamaldehyde during the single pot reaction. IR spectral data showed that the Schiff base ligand coordinated to the metal ion through nitrogen of azomethine group and oxygen of carboxyl group (COO). The molar
conductance values indicated that both the complexes are non-electrolytic in nature. Antibacterial activity of the complexes was tested against four pathogenic bacteria namely *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* & *Shigella dysenteriae* with standard Kanamycin-30. The results showed that both type of complexes have moderate to strong antibacterial activity and the peroxo complex is relatively more potential towards all the tested organisms.

**Keywords:** Schiff base; Peroxo complex; o-Aminobenzoic acid; Cinnamaldehyde; antibacterial activity.

### 1. INTRODUCTION

Antibiotic resistances are increasing at an alarming rate day by day. As a result, searching for new antibacterial agent is a crying need. Schiff bases are important type of ligands having versatile applications [1]. They are well known for their various biological applications [2,3]. Moreover, metal-amino acid [4] as well as peroxo-metal system has drawn special attention to the chemist due to their interesting applications in synthetic and coordination chemistry [5-7]. Many peroxo complexes of transition metals possess fantastic catalytic activity. Importantly peroxo complexes are excellent sources of active oxygen atoms and undergo oxygen transfer reactions [8,9]. Many of these complexes possess to have potential antimicrobial activity such as antibacterial activity, antifungal activity, cytotoxic activity and antioxidant Properties [10,11].

Keeping these facts in consideration, the present research deals with the comparative studies on the synthesis, characterization and potential antibacterial Properties between the Co(II) complex and peroxo complex containing Schiff base derived from o-aminobenzoic acid & cinnamaldehyde.

### 2. MATERIALS AND METHODS

#### 2.1 Reagents and Chemicals

All the reagents and chemicals were analar grade and used as supplied. Cobalt acetate salt was purchased from Loba Chemie Pvt. Ltd. (India). Cinnamaldehyde and o-aminobenzoic acid were purchased from BDH Chemicals Ltd. (England). Silica gel for the stationary phase of thin layer chromatography (TLC) was purchased from Thomas Baker (India).

#### 2.2 Physical Measurements

All the weighing operations were performed by using a Mettler PM-200 electronic balance. An electro thermal melting point apparatus (model AZ 6512) was used to obtain the melting point of the complexes. Molar conductance of the complexes of 1.0 x 10\(^{-3}\) mol/dm\(^3\) DMSO solutions were measured at room temperature using a type CG 857 No. 71798 SCHOTT-GERATE Gumbo, Germany, digital conductivity meter and a dip-cell with platinized electrodes. A SHERWOOD SCIENTIFIC magnetic susceptibility balance was employed to measure the magnetic susceptibility of the complexes. Infrared spectra were recorded as KBr disc with a NICOLET 310, FTIR spectrophotometer, Belgium, from 4000-400 cm\(^{-1}\). UV-visible spectra were recorded with a SHIMADZU DOUBLE BEAM spectrophotometer (model UV-1650pc). Elemental (C, H, N) analyses were performed by PerkinElmer 2400 organic elemental analyzer-II at Okayama University, Japan.

### 2.3 Preparation of the Schiff Base Co(II) Complex and Peroxo Complex

About (0.4980 g, 2 mmol) of Co(CH\(_3\)COO)\(_2\). 4H\(_2\)O was dissolved in 5 mL ethanol in a 50 mL beaker. A solution of (0.5304 g, 4 mmol) of cinnamaldehyde was made in 5 mL ethanol in a 50 mL beaker. A solution of (0.5485 g, 4 mmol) of o-aminobenzoic acid was also made in 5 mL ethanol in another 50 mL beaker. Then the three solutions were mixed, stirred for half an hour at room temperature and allowed to stand for several minutes to obtain the Schiff base complex. In addition, for - peroxo complex a solution of ammonium thiocyanide (0.3044 g, 4 mmol) was prepared in 5 mL ethanol in another 50 mL beaker. Then the four solutions were mixed in a round bottom flask, stirred for half an hour at room temperature and allowed to stand for several minutes. Then about (8 mmol) of 30% H\(_2\)O\(_2\) was poured into the beaker. The mixture was stirred for 22 hours at room temperature. The completion of the reactions was monitored by thin layer chromatography (TLC). After completion of reaction a solid precipitate was observed. The resulting precipitate was filtered and dried in vacuum desiccator over anhydrous CaCl\(_2\).
3. RESULTS

The molar conductance value \( \mu_{\text{m}} \) were measured at room temperature (30°C) in 10^{-3} M dimethyl sulfoxide (DMSO) solution. The molar conductance value (6.9 & 7.5 \( \Omega^{-1} \text{cm}^2\text{mol}^{-1} \)) indicate that both the complexes are non-electrolytic in nature [12]. The elemental analysis data support the proposed structure (Fig. 2) of the complexes.

2.3.1 Schiff base complex of Co(II) ion, \([\text{Co(SB)}]_{2}\)

Color: Light ash, Melting point: >300°C, Yield: 79%. Molar conductance (\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}): 6.9, Magnetic moment (\( \mu_{\text{eff}}/\text{B.M.} \)): 2.20, FT-IR (cm\(^{-1}\)): 1618m, \( \nu(\text{C}=\text{N}) \); 1540s, \( \nu_{\text{as}}(\text{COO}) \); 1408, \( \nu_{\text{s}}(\text{COO}) \); 472s, \( \nu(\text{Co-O}) \); 736m, \( \nu(\text{Co-N}) \); UV-Vis. (\( \lambda_{\text{max}}/\text{nm} \)): 385; ESI-MS (m/z): 559.34 \([\text{Co(SB)}]_{2}^{+}\), 250.27 \([\text{SB}]^{-}\); Elemental analysis for \([\text{CoC}_{32}\text{H}_{22}\text{N}_{2}\text{O}_{4}] \); (M.W.= 559.48 g/mol): Calculated: C, 65.79%; H, 4.67%; N, 4.96%.

2.3.2 Peroxo complex of Co(II) ion, \([\text{Co(O}_2\text{)}(\text{SB})]_{2}\)

Color: Deep ash, Melting point: >300°C, Yield: 72%. Molar conductance (\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}): 7.5, Magnetic moment (\( \mu_{\text{eff}}/\text{B.M.} \)): 2.02, FT-IR (cm\(^{-1}\)): 1615m, \( \nu(\text{C}=\text{N}) \); 1538s, \( \nu_{\text{as}}(\text{COO}) \); 1408, \( \nu_{\text{s}}(\text{COO}) \); 884w, \( \nu(\text{O-O}) \); 602w, \( \nu_{2}(\text{COO}) \); 726v, \( \nu_{3}(\text{COO}) \); 474s, \( \nu(\text{Co-O}) \); 737m, \( \nu(\text{Co-N}) \); UV-Vis. (\( \lambda_{\text{max}}/\text{nm} \)): 395; ESI-MS (m/z): 591.16 \([\text{Co(O}_2\text{)}(\text{SB})]_{2}^{+}\), 250.26 \([\text{SB}]^{-}\); Elemental analysis for \([\text{CoC}_{32}\text{H}_{22}\text{N}_{2}\text{O}_{4}] \); (M.W.= 591.48 g/mol): Calculated: C, 64.98%; H, 4.09%; N, 4.74%; Found: C, 63.77%; H, 4.43%; N, 4.67%

Here, the related band intensities for FT-IR are denoted by s, m, and w representing strong, medium, and weak band respectively.

3. RESULTS AND DISCUSSION

3.1 Elemental Analysis and Conductivity Measurement

The molar conductance of both the complexes were measured at room temperature (30°C) in \( 10^{-3} \) M dimethyl sulphoxide (DMSO) solution. The molar conductance value (6.9 & 7.5 \( \Omega^{-1} \text{cm}^2\text{mol}^{-1} \)) indicate that both the complexes are non-electrolytic in nature [12]. The elemental analysis data support the proposed structure (Fig. 2) of the complexes.

3.2 Magnetic Moment and Electronic Spectra

The observed effective magnetic moment values (\( \mu_{\text{eff}} = 2.02 \) to 2.20 B.M.) at room temperature suggested that both the complexes possess to have one unpaired electron i.e. they are paramagnetic in nature. The UV-Vis. spectral data of the complexes exhibited absorption bands between 385 to 395 nm region due to the charge transfer band only [13,14].

3.3 IR Spectral Studies

IR spectral data of the complexes showed \( \nu(\text{C}=\text{N}) \) stretching frequency in between 1615-1618 cm\(^{-1}\) indicate the presence of azomethine linkage in the complexes. The appearance of absorption band in the range (1538-1540 cm\(^{-1}\)) and at 1408 cm\(^{-1}\) indicates the asymmetric \( \nu_{\text{s}}(\text{COO}) \) and symmetric \( \nu_{\text{as}}(\text{COO}) \) stretching frequencies respectively. Furthermore, the presence of \( \nu(\text{Co-O}) \) stretching frequency in the range 472-474 cm\(^{-1}\) and \( \nu(\text{Co-N}) \) stretching frequency in between 736-737 cm\(^{-1}\) in the spectra of the complexes indicating the coordination through O and N atom [15-20].

In case of peroxo complex three IR active vibrational modes were observed due to the presence of metal peroxo group in the complex. These are predominantly O-O stretching \( \nu_{1} \), the symmetric \( \nu_{0} \) stretch \( \nu_{2} \) and the antisymmetric \( \nu_{0} \) stretch \( \nu_{3} \). The characteristics \( \nu_{1}(\text{O-O}) \) modes of the complex appear at 884 cm\(^{-1}\) whereas the \( \nu_{2} \) and \( \nu_{3} \) modes appear at 602 cm\(^{-1}\) and 726 cm\(^{-1}\) respectively [21,22].

3.4 ESI-MS Studies

The ESI mass spectra of the complexes are shown in Fig. 1. The observed peaks in the spectra confirm the elemental composition of the ions observed and supports the proposed structure of the synthesized complexes (Fig. 2).

Depending on the above analyses the structure of the Co(II) complexes (Fig. 2) are proposed as below.

3.5 Antimicrobial Activity of the Metal Complexes

3.5.1 Antibacterial activity

To determine the susceptibility of the pathogenic microorganism to the synthesized complexes, the largely acceptable disc diffusion method was
Fig. 1. ESI-MS spectra of the complex (a) [Co(SB)₂] and (b) [Co(O₂)(SB)₂]

Fig. 2. Proposed structure of (a) Schiff base complex and (b) Peroxo complex of Co(II) ion

Table 1. Antibacterial activity of the schiff base Co(II) complex and - peroxo complex with standard kanamycin

| Complex          | Diameter of zone of inhibition (mm) for 50 μg/disc of the sample |
|------------------|---------------------------------------------------------------|
|                  | Gram Negative                  | Gram Positive                  |
|                  | Escherichia coli | Shigella dysenteriae | Staphylococcus aureus | Bacillus cereus |
| [Co(SB)₂]        | 11                          | 09                           | 13                     | 10              |
| [Co(O₂)(SB)₂]    | 19                          | 14                           | 23                     | 17              |
| Kanamycin -30    | 25                          | 22                           | 27                     | 24              |

Where, SB = Schiff base derived from cinnamaldehyde and α-aminobenzoic acid

employed [23-25]. Antibacterial activity of the complexes expressed by measuring the diameter of zone of inhibition are tabulated in Table 1. The complexes (50 μg/0.01 mL in DMSO solution) were screen for their antibacterial activity against two Gram negative bacteria Escherichia coli & Shigella dysenteriae, and two Gram positive bacteria Staphylococcus aureus & Bacillus cereus with standard Kanamycin (K-30). The result showed that the peroxo complex possess to have more potential antibacterial activity than the normal Schiff base complex against all the tested bacteria. The results are graphically represented in Fig. 3.
Fig. 3. Graphical representation of antibacterial activity of the complexes

4. CONCLUSION

In this research we have carried out the comparative study on the synthesis, characterization and antibacterial activity of the Schiff base complex of Co(II) ion and its peroxo complex. Here, the Schiff base (SB) was derived from cinnamaldehyde and o-amino benzoic acid. IR spectral data indicated that the ligand coordinated to the cobalt ion through N and O atoms. Elemental analyses, magnetic moment, conductivity measurements, UV-Vis., IR and ESI-MS spectral data confirmed the proposed structure of metal complexes. The result of antibacterial activity showed that the peroxo complex possesses more potential antibacterial activity than the normal Schiff base complex against all the tested pathogenic bacteria.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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