



One Pot Synthesis of Cu(II) and Ni(II) Peroxo Complexes Containing Schiff Base: Physicochemical, Spectral and Antibacterial Investigations

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Authors' contributions

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

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ABSTRACT

Two new peroxo complexes of Cu(II) and Ni(II) ion containing Schiff base (SB) were synthesized and characterized by TLC, Elemental analyses, conductivity, magnetic moment measurements, UV-Vis. and IR and ESI-MS spectral studies. The Schiff base ligand derived from cinnamaldehyde and *o*-aminophenol participated in complexation through a single pot reaction. IR spectra showed that the Schiff base ligand coordinated to the metal ion through nitrogen of azomethine group and oxygen of hydroxyl group & peroxo group (O-O). Magnetic moment value coupled with electronic spectral data suggested a square planar geometry for both the complexes. The molar conductance

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values indicated the non-electrolytic nature of the complexes. Antibacterial activity of the complexes was tested against four pathogenic bacteria, two Gram-positive *Staphylococcus aureus* & *Bacillus cereus* and two Gram-negative *Escherichia coli* & *Shigella dysenteriae* with *Kanamycin (K-30)* standard. The result shows that Cu(II) complex exhibited more potential antibacterial activity than the Ni(II) complex against all the tested organisms.

Keywords: Peroxo complexes; schiff base; cinnamaldehyde; o-aminophenol; antibacterial activity.

1. INTRODUCTION

Chemists have greater attention to the chemistry of peroxo metal complexes because of their fascinating and comprehensible area of investigation. The synthesis of well-defined peroxo-metal complexes therefore is an important prerequisite for a heuristic approach in the field of coordination chemistry [1]. Studies on the peroxo metal complexes have received significant attraction due to their application in synthetic and coordination chemistry [2-6]. Many peroxo complexes of transition metals are used as catalytic oxidants for organic and inorganic substrate. Also, they are excellent sources of active oxygen atoms [7,8]. It has been observed that peroxo complexes undergo oxygen transfer reactions in presence of monodentate and bidentate auxiliary ligands [9,10]. In case of tridentate and quadridentate ligands the complexes remain inert towards oxidation reaction. Many of these complexes possess to have potential antimicrobial activity.

Keeping these facts in mind, the present study deals with the direct synthesis, characterization and investigation of antibacterial activity of Cu(II) and Ni(II) peroxo complexes containing Schiff base ligand derived from the condensation of cinnamaldehyde and o-aminophenol during the one pot reaction.

2. MATERIALS AND METHODS

2.1 Reagents and Chemicals

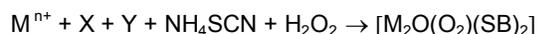
All the reagents and chemicals used were reagent grade and used as received. Nickel nitrate salt was purchased from Loba Chemie pvt. Ltd. (India). Cinnamaldehyde, o-aminophenol and Copper nitrate were purchased from BDH chemicals Ltd. (England).

2.2 Physical Measurements

A Mettler PM-200 electronic balance was used to perform all the weighing operations. Melting point of the complexes were obtained with an electro-

thermal melting point apparatus (model AZ 6512). Molar conductance of the complexes in DMSO (1.0×10^{-3} mol/dm³) 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. Magnetic susceptibility measurement was performed by A SHERWOOD SCIENTIFIC magnetic susceptibility balance. 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). ESI-MS was recorded in acetonitrile on a JEOL JST-T100LP. Elemental analysis for carbon, hydrogen and nitrogen were performed by PerkinElmer 2400 organic elemental analyzer-II at Okayama University, Japan.

2.3 General Method for the Preparation of the Complexes of Type [M₂O(O₂)(SB)₂]:



Where,

Mⁿ⁺ = Cu(II) and Ni(II) ions.

X = Cinnamaldehyde

Y = o-aminophenol

-SB = Schiff base derived from X and Y during reaction.

For Cu(II) complex (0.4830 g, 2 mmol) of Cu(NO₃)₂·3H₂O and for Ni(II) complex (0.5815 g, 2 mmol) of Ni(NO₃)₂·6H₂O was dissolved in 5 mL ethanol in a 50 mL beaker. A solution of (0.26524 g, 2 mmol) of cinnamaldehyde was made in 5 mL ethanol in a 50 mL beaker. A solution of (0.2180 g, 2 mmol) of o-aminophenol was made in 5 mL ethanol in another 50 mL beaker. Then a solution of ammonium thiocyanide (0.1522 g, 2 mmol) was prepared in 5 mL ethanol in another 50 mL beaker. The four solutions were mixed in a single pot (250 mL round bottom flask), stirred for half an hour at room temperature and allowed to stand for several minutes. Then about (8 mmol)

of 30% H₂O₂ 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 chromatographic method (TLC). Then a solid precipitate was formed. The resulting precipitate was filtered and dried in vacuum desiccators over anhydrous CaCl₂.

2.3.1 Cu(II) complex, [Cu₂O(O₂)(SB)₂]

Color: Gray, Melting point: 280°C, Yield: 75%, Molar conductance (Ohm⁻¹cm²mol⁻¹): **7.0**, Magnetic moment (μ_{eff}/B.M.): 1.63, FT-IR (cm⁻¹): 3436br, ν(O-H); 3059m, ν(C-H); 1614vs, ν(C=N); 823m, ν₁(O-O); 659w, ν₂(^MO₂); 685m, ν₃(^MO₂), 585m, ν(M-O); 749s, ν(M-N); UV-Vis. (λ_{max}/nm): 345. ESI-MS (CH₃CN, *m/z*): 619.6138 ([Cu₂O(O₂)(SB)₂]⁺), 301.1062 ([Cu(SB)O]⁺), 586.0732 ([Cu₂(SB)₂O]⁺). Elemental analysis for [Cu₂O(O₂)(SB)₂], (Mol. Wt: 619.61): Calculated: C, 58.15; H, 3.90; N, 4.52%. Found: C, 55.97; H, 3.77; N, 4.49%.

2.3.2 Ni(II) complex, [Ni₂O(O₂)(SB)₂]

Color: Yellow, Melting point: >300°C, Yield: 72%, Molar conductance (Ohm⁻¹cm²mol⁻¹): **4.5**, Magnetic moment (μ_{eff}/B.M.): 0.45, FT-IR (cm⁻¹): 3436br, ν(O-H); 3062w, ν(C-H); 1623s, ν(C=N); 812m, ν₁(O-O); 646w, ν₂(^MO₂); 687m, ν₃(^MO₂), 580w, ν(M-O); 740s, ν(M-N); UV-Vis. (λ_{max}/nm): 340. ESI-MS (CH₃CN, *m/z*): 609.9182 ([Ni₂O(O₂)(SB)₂]⁺), 296.691 ([Ni(SB)O]⁺), 577.3855 ([Ni₂(SB)₂O]⁺). Elemental analysis for [Ni₂O(O₂)(SB)₂], (Mol. Wt: 609.19): Calculated: C, 59.08; H, 3.97; N, 4.59%. Found: C, 57.38; H, 3.92; N, 4.45%.

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

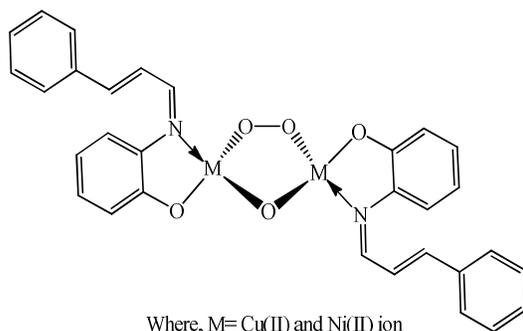


Fig. 1. Proposed structure of the complexes

The proposed structure of the synthesized peroxy complexes of Cu(II) and Ni(II) is given in Fig. 1.

3. RESULTS AND DISCUSSION

3.1 Elemental Analysis and Conductivity Measurement

The molar conductance of 10⁻³ M solution of the complexes in DMSO were measured at 30°C. The molar conductance values (4.5-7.0 Ω⁻¹cm²mol⁻¹) indicate that both the complexes are non-electrolytic in nature. The elemental analysis data are in good agreement with the proposed structure (Fig. 1) of the complexes.

3.2 Magnetic Moment and Electronic Spectra

The observed values of effective magnetic moment (μ_{eff}) 1.63 B.M. at room temperature suggested that the Cu(II) complex is paramagnetic in nature and possess to have one unpaired electron. The Ni(II) complex (μ_{eff}= 0.43 B.M.) is diamagnetic in nature indicating no changes in the oxidation state of the metal ions upon complexation. The UV-Vis. spectral data of the complexes exhibited bands between 340 to 345 nm region due to the charge transfer band only [11,12]. The magnetic moment value coupled with electronic spectral data suggested that the complexes are assumed to have square planar geometry.

3.3 IR Spectral Studies

IR spectral data of the complexes showed ν(C=N) stretching frequency in between 1614-1623 cm⁻¹ indicate the presence of azomethine linkage in the complexes. The presences of ν(M-O) stretching frequency in the region 580-585 cm⁻¹ and ν(M-N) stretching frequency in between 740-749 cm⁻¹ in the spectra of the complexes indicating the coordination through O and N atom [13-20].

Three IR active vibrational modes are observed due to the presence of metal peroxo group in the complexes. These are predominantly O-O stretching ν₁, the symmetric M-O-O stretch ν₂ and the antisymmetric M-O-O stretch ν₃. The characteristics ν₁(O-O) modes of the complexes appear in between 822-823 cm⁻¹ whereas the ν₂ and ν₃ modes appear in the range 646-659 and 685-687 cm⁻¹ respectively.

3.4 ESI-MS Spectral Study

ESI-MS spectrum of the Cu (II) complex was recorded in positive ion mode in acetonitrile and shows a molecular ion peak at 619.6138 amu for the $[\text{Cu}_2\text{O}(\text{O}_2)(\text{SB})_2]^+$. Another fragment ion is observed at 301.1062 amu which has been

tentatively assigned to $[\text{Cu}(\text{SB})\text{O}]^+$. Moreover, an ion at 586.0732 amu ($[\text{Cu}_2(\text{SB})_2\text{O}]^+$) presumably arise from O_2 dissociation of the di-nuclear copper core (Fig. 2). Similar results were observed for the Ni(II) complex. Thus, ESI-MS spectra of the peroxo complexes clearly supports the proposed din-nuclear structure.

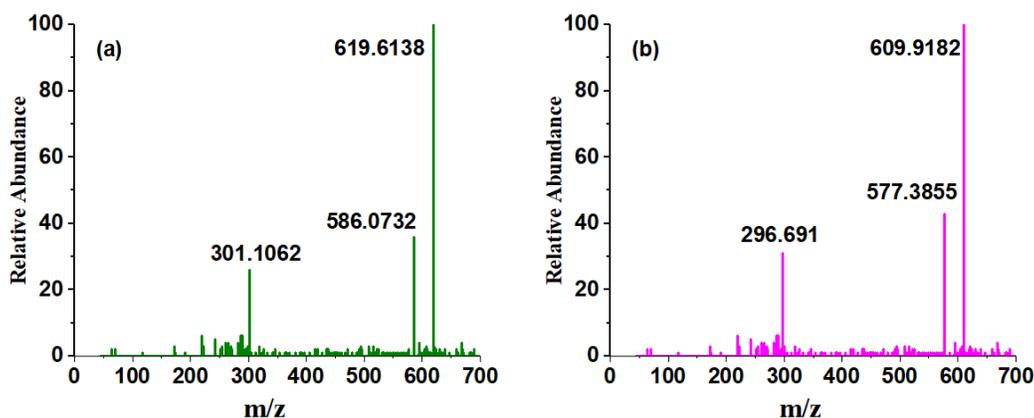


Fig. 2. ESI-MS spectra of (a) $[\text{Cu}_2\text{O}(\text{O}_2)(\text{SB})_2]$ and (b) $[\text{Ni}_2\text{O}(\text{O}_2)(\text{SB})_2]$

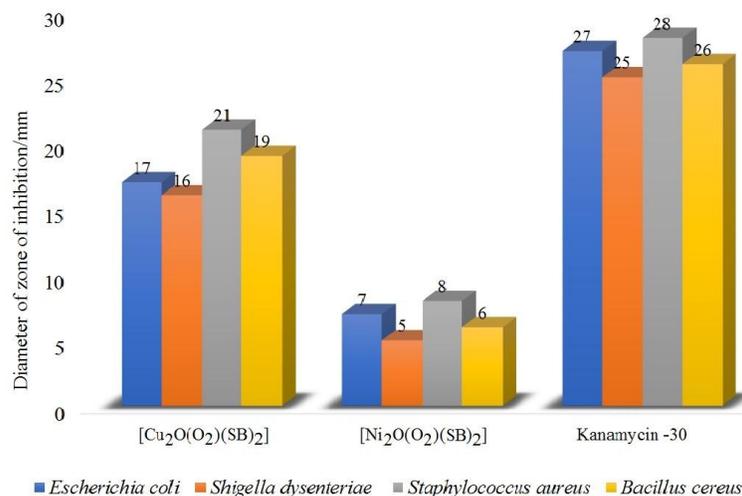


Fig. 3. Graphical representation of antibacterial activity of the complexes against *E. coli*, *S. dysenteriae*, *S. aureus* and *B. cereus*

Table 1. Antibacterial activity of the Cu(II) and Ni(II) complexes with Kanamycin (K-30) standard

Complexes	Diameter of zone of inhibition (mm) for 50 $\mu\text{g}/\text{disc}$ of the samples			
	Gram negative		Gram positive	
	<i>Escherichia coli</i>	<i>Shigella dysenteriae</i>	<i>Staphylococcus aureus</i>	<i>Bacillus cereus</i>
$[\text{Cu}_2\text{O}(\text{O}_2)(\text{SB})_2]$	17	16	21	19
$[\text{Ni}_2\text{O}(\text{O}_2)(\text{SB})_2]$	07	05	08	06
Kanamycin -30	27	25	28	26

3.5 Antibacterial Activity of the Metal Complexes

To determine the susceptibility of the pathogenic microorganism to the synthesized compounds antibacterial screening was carried out. Among different methods the disc diffusion method is broadly admissible for performing the antibacterial screening of compounds [21-25]. The measured diameter of zone of inhibition for the activity of complexes are tabulated in Table 1. Antibacterial activity of the compounds at a concentration of 50 µg/0.01 mL in DMSO solution [25] were tested against four pathogenic bacteria, two Gram-positive *Staphylococcus aureus* & *Bacillus cereus* and two Gram-negative *Escherichia coli* & *Shigella dysenteriae* with *Kanamycin (K-30)* standard. The result shows that Cu(II) complex exhibited more potential antibacterial activity than the Ni(II) complex against all the tested organisms. The results are graphically represented in Fig. 3.

4. CONCLUSION

In this study we carried out the synthesis and characterization of the peroxo complexes of Cu(II) and Ni(II) ion containing Schiff base (SB) derived from cinnamaldehyde and *o*-aminophenol in one pot reaction. IR spectral data indicated the coordination of ligands to the central metal atom through N and O atoms. Elemental analyses, conductivity measurements, magnetic moment measurements, electronic spectral data and infrared and ESI-MS spectral data confirmed the proposed structure of metal complexes. Antibacterial activity exhibited that Cu(II) complex exhibited more potential antibacterial activity than the Ni(II) complex against all the tested pathogens.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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