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Synthesis, Chracterization and Antibacterial Activity of Cd(II) and Zr(IV) Peroxo-complexes

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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 and wrote the protocol. 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 Cd(II) and Zr(IV) ion containing Schiff base (SB) were synthesized and characterized by Thin Layer Chromatography (TLC), Elemental analyses, conductivity, magnetic moment measurements, UV-Vis. and FT-IR spectral studies. The Schiff base ligand derived from cinnamaldehyde and *o*-aminophenol participated in complexation through a single pot reaction. FT-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). The molar conductance values indicated the non-electrolytic nature of both 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 standard *Kanamycin*-30. The result showed that Cd(II) complex exhibited more potential antibacterial activity than the Zr(IV) complex against all the tested pathogens.

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1. INTRODUCTION

Peroxo metal complexes has drawn special attention to the chemists because of their fascinating and comprehensible area of investigation in chemistry [1]. Consequently, studies on the synthesis of well-defined peroxo metal complexes have received significant attention due to their application in synthetic and coordination chemistry [2-4]. Many peroxo complexes of transition metals are excellent sources of active oxygen atoms [5,6]. Peroxo complexes undergo oxygen transfer reactions in presence of monodentate and bidentate auxiliary ligands and remain inert in presence of tridentate and quadridentate ligands [7,8]. Many of these complexes possess to have potential antimicrobial activity. Md. Kudrat-E-Zahan et al. have studied the *in vitro* antimicrobial and *in vivo* cytotoxic properties of peroxo coordination complexes of Mg(II), Fe(II) & Ni(II) ion [9]. Also, M. Ashraful Alam et al. have carried out the studies on the antimicrobial and cytotoxic activity of three cobalt peroxo complexes and two zirconium peroxo-complexes [10].

Keeping these facts in consideration, the present study deals with the investigation of direct synthesis, characterization and antibacterial properties of Cd(II) and Zr(IV) peroxo complexes containing Schiff base ligand derived from the condensation of cinnamaldehyde and *o*-aminophenol during the single pot reaction.

2. MATERIALS AND METHODS

2.1 Reagents and Chemicals

All the reagents and chemicals were reagent grade and used as supplied. Cadmium nitrate and Zirconium oxy-nitrate were purchased from Loba Chemie pvt. Ltd. (India). Cinnamaldehyde and *o*-aminophenol were purchased from BDH Chemicals Ltd. (England). Silica gel used as the stationary phase of Thin Layer Chromatography (TLC) was purchased from Thomas Baker (India).

2.2 Physical Measurements

All the weighing operations were carried out by a Mettler PM-200 electronic balance. Melting point of the complexes was obtained with an electro thermal melting point apparatus (model AZ 6512). Molar conductance of the complexes in DMSO (l.0 x 10^{-3} mol/dm^3) 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 used to measure the magnetic susceptibility. 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). Analyses 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 Cd(II) and Zr(IV) Complexes

For Cd(II) complex (0.6169 g, 2 mmol) of $Cd(NO_3)_2.4H_2O$ and for Zr(IV) complex (0.6426 g, 2 mmol) of $ZrO(NO_3)_2.5H_2O$ 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 (0.4360 g, 4 mmol) of *o*-aminophenol was made in 5 mL ethanol in another 50 mL beaker. Then a solution of ammonium thiocyanide (0.3044 g, 4 mmol) was prepared in 5 mL ethanol in another 50 mL beaker. The four solutions were mixed in a round bottom flask and stirred for half an hour at room temperature and allowed to stand for several minutes. Then about (8 mmol) of 30% H_2O_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). Then a solid precipitate was formed. The resulting precipitate was filtered and dried in vacuum desiccator over anhydrous $CaCl_2$.

$$Cd(NO_3)_2.4H_2O + X + Y + NH_4SCN + H_2O_2 \rightarrow [Cd(O_2)(SB)_2]$$

$$ZrO(NO_3)_2 .5H_2O + X + Y + NH_4SCN + H_2O_2 \rightarrow [ZrO(O_2)(SB)_2]$$

Where,

X = Cinnamaldehyde
Y = *o*-Aminophenol
SB = Schiff base derived from X and Y during reaction.

2.3.1 Cd(II) complex, $[Cd(O_2)(SB)_2]$

Color: Yellow, Melting point: 250^{0}C, Yield: 73%, Molar conductance (Ohm^{-1}cm^{2}mol^{-1}): 5.5, Magnetic moment (μ_{eff}/B.M.): 0.43, FT-IR (cm^{-1}): 3436br, ν(O-H); 3058w, ν(C-H); 1621s, ν(C=N); 808s, ν_1(O-O); 641w, ν_2($\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$); 688m, ν_3($\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$), 453m, ν(M-O); 746s, ν(M-N); UV-Vis. (λ_{max}/nm): 330. Elemental analysis for $[CdC_{30}H_{24}N_2O_4]$, (M.W.= 588.93): Calculated: C, 61.18; H, 4.11; N, 4.76%. Found: C, 59.97; H, 4.27; N, 4.79%.

2.3.2 Zr(IV) complex, $[ZrO(O_2)(SB)_2]$

Color: Gray, Melting point: 270^{0}C, Yield: 71%, Molar conductance (Ohm^{-1}cm^{2}mol^{-1}): 5.5, Magnetic moment (μ_{eff}/B.M.): 0.47, FT-IR (cm^{-1}): 3401br, ν(O-H); 1615s, ν(C=N); 987, ν(M=O); 832w, ν_1(O-O); 641w, ν_2($\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$); 701m, ν_3($\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$), 472w, ν(M-O); 754m, ν(M-N); UV-Vis. (λ_{max}/nm): 450. Elemental analysis for $[ZrC_{30}H_{24}N_2O_5]$, (M.W.= 583.75): Calculated: C, 61.73; H, 4.14; N, 4.80%. Found: C, 60.27; H, 4.35; N, 4.73%.

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

3. RESULTS AND DISCUSSION

3.1 Elemental Analysis and Conductivity Measurement

The molar conductance of 10^{-3} M solution of both the complexes in DMSO was measured at 30°C. The molar conductance value (5.5 Ω^{-1}cm^{2}mol^{-1}) indicate that both the complexes are non-electrolytic in nature [11]. The elemental analysis data are in good agreement with the proposed structure (Fig. 1) of the complexes.

3.2 Magnetic Moment and Electronic Spectra

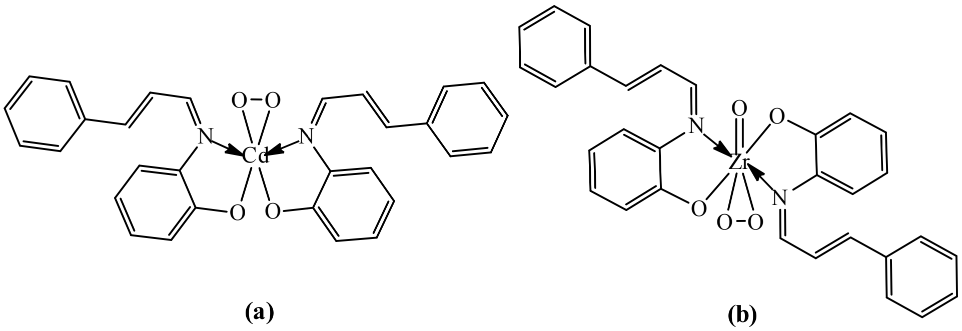
The observed values of effective magnetic moment (μ_{eff} = 0.43 to 0.47 B.M.) at room temperature suggested that both the complexes possess to have no unpaired electron i.e. they are diamagnetic in nature indicating no changes in the oxidation state of the metal ions upon complexation. The UV-Vis. spectral data of the complexes exhibited bands between 330 to 450 nm region due to the charge transfer band only [12,13].

3.3 FT-IR Spectral Studies

IR spectral data of the complexes showed ν(C=N) stretching frequency in between 1615-1621 cm^{-1} indicate the presence of azomethine linkage in the complexes. The presence of ν(M-O) stretching frequency in the region 453-472 cm^{-1} and ν(M-N) stretching frequency in between 746-754 cm^{-1} in the spectra of the complexes indicating the coordination through O and N atom [14-21].

Three FT-IR active vibrational modes are observed due to the presence of metal peroxo group in the complexes. These are predominantly O-O stretching ν_1, the symmetric $\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$ stretch ν_2 and the antisymmetric $\mathrm{M}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$ stretch ν_3. The characteristics ν_1(O-O) modes of the complexes appear in between 808-832 cm^{-1} whereas the ν_2 and ν_3 modes appear at 641 cm^{-1} and 688-701 cm^{-1} respectively. In case of Zr(IV) complex a band at 987 cm^{-1} is appeared indicates the presence ν(M=O) streching.

Based on the above analyses the proposed structure of the synthesized peroxo-complexes (Fig. 1) of Cd(II) and Zr(IV) with HOMO, LUMO orbitals of Cd(II) complex (Fig. 2) are presented as below.



(a) (b)

Fig. 1. Proposed structure of the (a) Cd(II) complex and (b) Zr(IV) complex

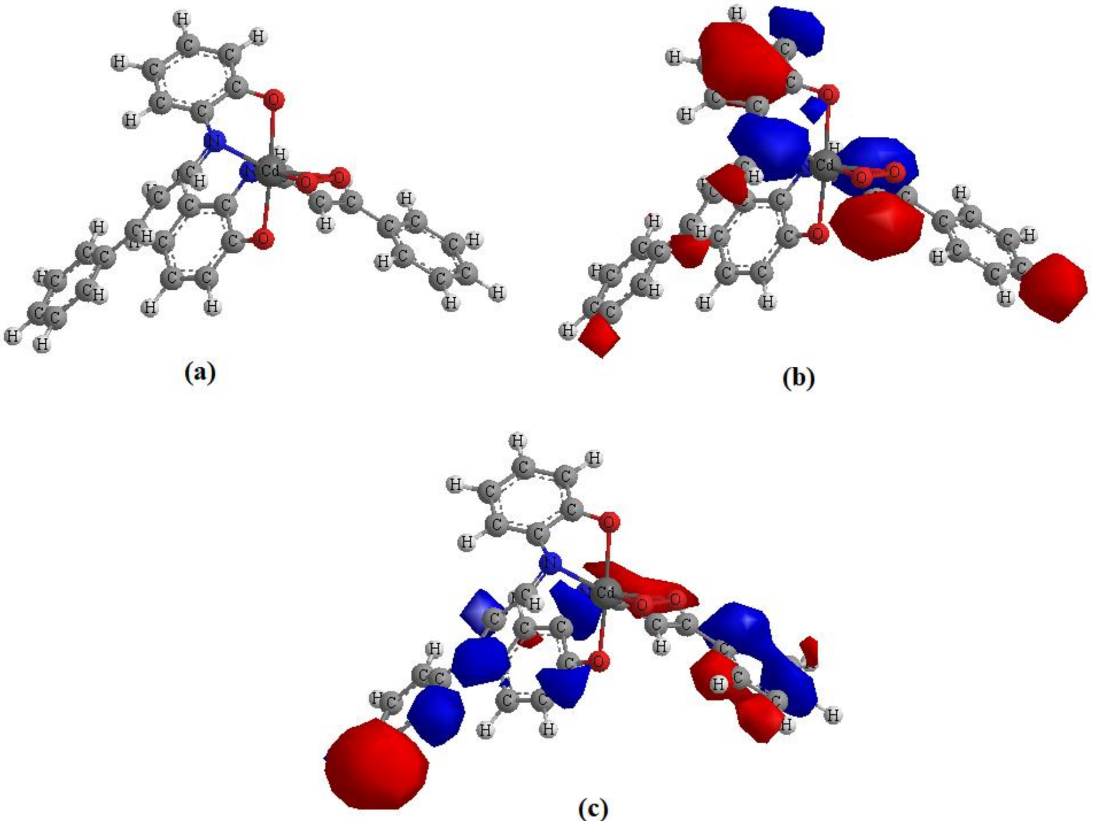


Fig. 2. (a) 3D structure; (b) Highest Occupied Molecular Orbital (HOMO); (c) Lowest Unoccupied Molecular Orbital (LUMO) of the Cd(II) Complex, $[Cd(O_2)(SB)_2]$

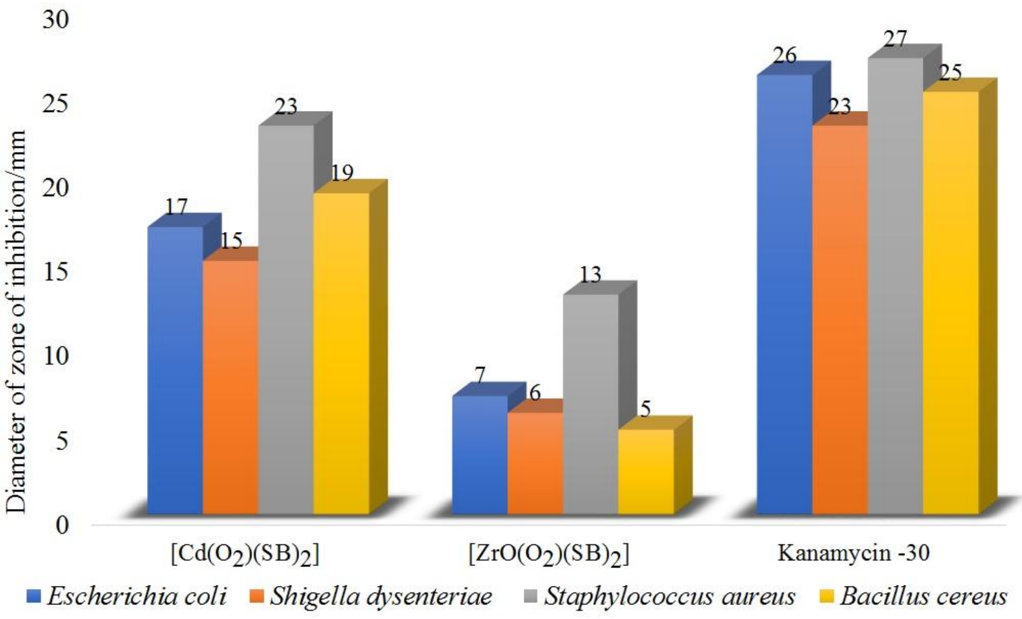


Fig. 3. Graphical representation of antibacterial activity of the complexes against *E. coli, S. dysenteriae, S. aureus* and *B. cereus*

Table 1. Antibacterial activity of the Cd(II) and Zr(IV) complexes with standard *Kanamycin*

Compounds	**Diameter of zone of inhibition (mm) for 50 μg/disc of the samples**			
	Gram negative		**Gram positive**	
	Escherichia coli	***Shigella dysenteriae***	***Staphylococcus aureus***	***Bacillus cereus***
$[Cd(O_2)(SB)_2]$	17	15	23	19
$[ZrO(O_2)(SB)_2]$	07	06	13	05
Kanamycin -30	26	23	27	25

3.4 Antibacterial Activity of the Complexes

Aantibacterial screening was carried out to determine the susceptibility of the pathogenic microorganism to the synthesized compounds. Among different methods the disc diffusion method is largely admissible for performing the antibacterial screening of compounds [22-24]. 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 were tested against four pathogenic bacteria namely *Staphylococcus aureus*, *Bacillus cereus*, *Escherichia coli* & *Shigella dysenteriae* with *Kanamycin (K-30)* standard. The result shows that Cd(II) complex exhibited more potential antibacterial activity than the Zr(IV) complex against all the tested pathogens. The results are graphically represented in Fig. 3.

4. CONCLUSION

The synthesis and characterization of the peroxo-complexes of Cd(II) and Zr(IV) ion containing Schiff base (SB) derived from cinnamaldehyde and *o*-aminophenol was carried out in this study. IR spectral data indicated that the ligand coordinated to the central metal ion through N and O atoms. Elemental analyses, conductivity measurements, magnetic moment measurements, electronic spectral data and infrared spectral data confirmed the proposed structure of metal complexes. Antibacterial activity revealed that Cd(II) complex is more potent than the Zr(IV) complex against all the tested organisms.

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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