Synthesis, Characterization and Biological Activity of a Bidentate NS Schiff Base Containing S-Benzyl Dithiocarbazate and Its Zr(IV), Sn(II) Complexes

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ABSTRACT

Zr (IV) and Sn (II) complexes were prepared with bidentate ligand, benzyl 2-(3-phenylallylidene) hydrazinecarbodithioate, derived from the condensation of S-benzyldithiocarbazate (SBDTC) with cinnamaldehyde and characterized by microanalysis, molar conductance and magnetic measurements, IR, electronic and ESI-MS studies. It was found that the ligand coordinated to the metal center through azomethine nitrogen and thiol sulfur atoms to form octahedral complexes with both the metal ions. The antimicrobial activities of the ligand and its complexes were investigated against the gram-positive and gram-negative bacteria and the fungus strain. The metal complexes showed strong activity than the free ligand.

Keywords: Schiff base; metal complex; antibacterial activity; antifungal activity.
1. INTRODUCTION

The chemistry of transition metal ions when interact with biological molecules offers one of the most captivating areas of coordination chemistry. Coordination chemistry, the science related with the interaction of inorganic / organic ligands with metal ions has remained one of the most dynamic research areas in inorganic chemistry. Coordination compounds act as bridge between organic and inorganic molecules. Organic molecules coordinated with transition metal ions exhibit several biological functions such as changing the bioavailability of metal ions by using metal chelating agents that modify metal hemostasis and metalloprotein inhibition which then increase Magnetic Resonance Imaging (MRI) signals or release bioactive molecule through ligand exchange, for electrical conduction in nervous systems through charge balance etc. [1]. MRI is a spectroscopic technique based on NMR and utilized as a diagnostic tool in medical treatment to identify injuries in human body or the presence or absence of water in soft tissues to distinguish the live or dead cells by investigating an image produced by MRI technique. S-alkyl or aryl dithiocarbazate and its Schiff bases as NS donor ligands in coordination with numerous transition metal ions has gained substantial attention by researchers due to their noteworthy biological applications in anticancer, antitumor, analgesic and anti-inflammatory, anti-hiv, anti-trypanosoma cruizi, antibacterial and antifungal activity [2-10]. Zr (IV) and Sn(II) complexes exposed the applicability in various fields of chemistry [11-14]. Complexes of Zr (IV) and Sn(II) with the Schiff base of S-benzyl dithiocarbazate could present interesting metallo-organic compounds with significant biological activity. As a continuation of research in this area, we report here the syntheses of Zr (IV) and Sn(II) complexes of S-benzyl dithiocarbazate Schiff base containing cinnamaldehyde and study of their antimicrobial activity against some pathogenic bacteria and fungi.

2. EXPERIMENTAL SECTION

2.1 Chemical and Reagents

Zr(NO₃)₄·6H₂O, SnCl₂·2H₂O, KOH, CS₂, hydrazine hydrate, cinnamaldehyde, benzyl chloride, DMF, DMSO, CH₃OH, and C₂H₅OH used in this research works were purchased from Sigma-Aldrich and Merck and used without further purification.

2.2 Instrumentation

Elemental analysis (C, H, and N) for the ligand and complexes were carried out on a Perkin-Elmer automatic equipment model 240B. The melting points of synthesized compounds were obtained on a digital melting point apparatus (METTLER TOLEDO). Conductivity measurements were measured of freshly prepared 1.0×10⁻³ mol/dm⁻³ DMSO solutions of the synthesized compounds using a Jenway 4071 digital conductivity meter at room temperature. FT-IR spectra of the ligand and its complexes were recorded using KBr disc technique on a Nicolet 170 SX FT-IR spectrometer. UV-vis spectra were measured for 10⁻³ M solutions in DMSO at 25°C using a Shimadzu 160 spectrophotometer. ESI-MS spectra were recorded with an Agilent Technologies MSD SL Trap mass spectrometer with ESI source coupled with an 1100 Series HPLC system for the confirmation of molecular formulas of compounds. Magnetic susceptibilities were measured in a Variable-Temperature Gouy Balance manufactured by the Newport Instruments Company, Ltd. Field strengths were calibrated using [HgCo(NCS)₄] as the standard. Diamagnetic corrections for the constituent elements were obtained using Pascal's law and employing tabulated constants [15].

2.3 Preparation of S-benzyl dithiocarbazate (SBDTC)

SBDTC was synthesized following the reported procedure [3]. Potassium hydroxide (0.05 mol) was dissolved in ethanol 90% (50 mL). To this solution, hydrazine hydrate (0.05 mol) was added and the mixture was cooled in an ice-salt bath to 0°C. Carbon disulfide (0.05 mol) was added drop wise with constant stirring over a period of one hour. During this time, two layers were formed. The light-brown lower layer was separated and dissolved in 40% ethanol (50 mL), maintained at 5°C. The mixture was kept in ice-bath and to this benzyl chloride (0.05 mol) was added drop wise with vigorous stirring. The white product (SBDTC) formed was filtered and washed with ethanol. It was recrystallized from absolute ethanol after drying. The recrystallized SBDTC was dried and kept in a desiccator.
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\[
\text{NH}_2\text{NH}_2\text{H}_2\text{O} + \text{CS}_2 + \text{KOH} \rightarrow \text{H}_2\text{N}^+\text{C}^-\text{S}^{2-} \rightarrow \text{H}_2\text{N}^+\text{C}^-\text{S}^{2-}\text{K}^+
\]

**Potassium Dithiocarbazate (KDC)**

\[
\text{H}_2\text{N}^+\text{C}^-\text{S}^{2-} + \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \rightarrow \text{H}_2\text{N}^+\text{C}^-\text{S}^{2-}\text{C}_6\text{H}_5\text{CH}_2\text{H}_5
\]

**S-benzyldithiocarbazate (SBDTC)**

Scheme 1. Synthesis of SBDTC

\[
\text{H}_2\text{N}^+\text{C}^-\text{S}^{2-} + 2\text{C}_6\text{H}_5\text{CH}==\text{CHCHO} \rightarrow \text{H}_2\text{N}^+\text{C}^-\text{S}^{2-}\text{C}_6\text{H}_5\text{CH}==\text{CHNNHC}^-\text{S}^{2-}\text{C}_6\text{H}_5\text{CH}==\text{CH}_2
\]

**Scheme 2. Synthesis cinnamaldehyde Schiff base of SBDTC**

2.4 Synthesis of the Cinnamaldehyde Schiff Base of SBDTC, Benzyl 2-(3-Phenylallylidene) Hydrazinecarbodithioate

Ethanolic solution (50 mL) of SBDTC (10 mmol) was mixed with equimolar ethanol solution (20 mL) of cinnamaldehyde. The mixture was refluxed for 40 mins. The yellow precipitate which formed was separated and dried in vacuo over anhydrous CaCl\(_2\).

\[
\text{Zr(NO}_3\text{)}_4\cdot 6\text{H}_2\text{O} + \text{NS} \rightarrow [\text{Zr(IV)}(\text{NS})_2(\text{NO}_3)_2]
\]

\[
\text{SnCl}_2\cdot 2\text{H}_2\text{O} + \text{NS} \rightarrow [\text{Sn(II)}(\text{NS})_2(\text{H}_2\text{O})_2]
\]

NS = Cinnamaldehyde Schiff base of SBDTC, benzyl 2-(3-phenylallylidene) hydrazinecarbodithioate.

2.5 General Method for the Synthesis of Complexes with the Schiff Base, Benzyl 2-(3-Phenylallylidene) Hydrazinecarbodithioate

Metal salt (0.5 mmol) was dissolved in absolute ethanol (20 mL) and to this, Schiff base ligand (1 mmol) dissolved in hot absolute ethanol (70 mL) was added. The mixture was then refluxed for 30 mins and then cooled. The precipitate formed was filtered off and washed with ethanol and dried in vacuo over anhydrous CaCl\(_2\).

2.6 Metal Weight Estimation

A known quantity of metal complex was put into a conical flask whose weight was known. Then, concentrated H\(_2\)SO\(_4\) (500 \(\mu\)L) was added. It was fumed until dry and the process was repeated three times. Concentrated HNO\(_3\) (500 \(\mu\)L) and HClO\(_4\) (500 \(\mu\)L) were then added and the mixture was further fumed until dry. The process of
adding acids and fuming to dry was continued until there was no black materials. 100 mL distilled water was added to dissolve the residue. Finally, the weight of the metal was estimated complexometrically and gravimetrically using EDTA (Ethylenediamine tetraacetic acid) and DMG (Dimethyl glyoxime) [16].

2.7 Biological Activity

Disc-agar diffusion method was used to check the antimicrobial activity of the Schiff base ligand and its metal complexes in DMF against two Gram positive bacteria, Staphylococcus aureus and Bacillus subtilis, two Gram negative bacteria, Salmonella typhimurium and Escherichia coli and two fungus strains Candida albicans and Aspergillus fumigates. The antibiotic chloramphenicol was used as reference in the case of Gram-positive bacteria, cephalothin in the case of Gram-negative bacteria and cycloheximide in the case of fungi.

3. RESULTS AND DISCUSSION

3.1 Syntheses and Characterization

The Schiff base ligand was synthesized by 1:1 condensation of S-benzylthiocarbazate (SBDTC) and cinnamaldehyde in ethanol under reflux, which on following reaction with metal salts in 2:1 molar ratio, generated the metal complexes. All the synthesized compounds are air stable and non-hygrosopic.

3.2 Microanalysis

The microanalysis data (Table 2) indicates that the complexes are mononuclear. These data also exposed that the metal-to-ligand ratio for the synthesized complexes were 1:2. The proposed structure of the ligand and complexes were consistent with elemental analysis data.

3.3 Molar Conductivity Measurements

The molar conductivity of the synthesized compounds were determined at room temperature at a concentration of 10^{-3} M in DMSO. The conductance value exposed that the complexes are non-electrolyte in nature (Table 1) [17].

3.4 FT-IR Spectral Studies

In a neutral medium, condensation of SBDTC with cinnamaldehyde provided the isomeric Schiff base (Scheme 2) with high yield. The Schiff base exist in tautomeric forms through the loss of thiol protons as shown in Fig. 1. Schiff base behaved as uninegatively charged bidented ligand by coordinating through the thiol sulfur and the azomethine nitrogen. The IR spectra of the Schiff base showed strong band at 3106 cm^{-1} due to the vibration of secondary amine group [\nu(N-H)] of the free ligand. The thione form is relatively unstable in the monomeric form and tend to turn to the more stable thiol form by enethiolization in solution (Fig. 1). The absence of \nu(S-H) absorbance at approximately 2575 cm^{-1} indicated that in the solid state, the Schiff base exists primarily in the thione form. The disappearance of \nu(N-H) band in the FT-IR spectra of the metal complexes suggested deprotonation and consequent coordination through the thiolate anions. The Schiff base also showed strong band at 1623 cm^{-1} assigned to the \nu(C=N) stretching. In the metal complexes, this band shifted to lower frequencies due to the lowering of the C=N bond order as a result of the metal–nitrogen bond formation. The Schiff base also displayed \nu(C=S) stretching at 1031 cm^{-1}. The \nu(C=S) mode observed in the free ligand disappeared in the complexes, thus supporting the above argument of thiolate bonding with metal ions. Consequently, the \nu(C=S) mode was observed in the spectra of the complexes supporting thiolate coordination.

The Schiff base coordinated to the metal through the thiolate sulphur and the azomethine nitrogen atoms as evident from the FT-IR spectrum showing bands at 389 and 409 cm^{-1} due to M-S bond stretching and bands at 481 and 485 cm^{-1} due to M-N bond stretching.

In the Zr(IV) complex, the nitrate ion is O-coordinated in monodentate fashion [18,19].The three IR-active stretching modes expected for nitrate group coordinated metal complex and would be a low-frequency \nu(O=N) band for the coordinated oxygen and two (symmetric and asymmetric) modes for the uncoordinated NO_{2} fragment. Three bands at 1475, 1384, and 1157 cm^{-1} were found in the IR spectrum of the antimony complex [18].

The broad band appeared at 3435 cm^{-1} together with new band at 685 cm^{-1} in the spectra of the Sn(II) complex confirmed the presence of coordinated water molecules [20].
Table 1. Analytical data and physical properties of the compounds

| Compounds                        | Color | Melting point or decomposition temperature (± 5°C) | Molar conductance (ohm⁻¹ cm² mol⁻¹) |
|----------------------------------|-------|--------------------------------------------------|-----------------------------------|
| NS                               | White | 181                                              | 2.50                              |
| [Zr(IV) (NS)₂(NO₃)₂]             | Yellow| 198                                              | 2.45                              |
| [Sn(II)(NS)₂(H₂O)₂]              | Yellow| 211                                              | 2.34                              |

Table 2. Microanalysis data of the ligand and its complexes

| Compound                        | Found (Calculated) (%) | Metal | C    | H    | N    |
|---------------------------------|------------------------|-------|------|------|------|
|                                 |                        |       |      |      |      |
| NS                              |                        |       | 65.21| 5.09 | 8.88 |
| [Zr(IV) (NS)₂(NO₃)₂]            | 10.62 (10.88)          | 48.56 | 3.45 | 9.98 |
| [Sn(II)(NS)₂(H₂O)₂]             | 15.14 (15.27)          | 52.32 | 4.19 | 7.11 |

Table 3. Important infrared spectral bands of the ligand and the metal complexes (cm⁻¹)

| Compound                        | ν(N-H) | ν(C=S) | ν(C=N) | ν(C-S) | ν(M-S) | ν(M-N)  | ν(NO₃) | ν(OH) |
|---------------------------------|--------|--------|--------|--------|--------|---------|--------|-------|
|                                 |        |        |        |        |        |         |        |       |
| NS                              | 3106   | 1031   | 1623   | -      | -      | -       | -      | -     |
| [Zr(IV) (NS)₂(NO₃)₂]            | -      | 1532   | 768    | 389    | 481    | 1475, 1384, 1157 | -     |
| [Sn(II)(NS)₂(H₂O)₂]             | -      | 1530   | 760    | 409    | 485    | -       | 3435   |

Fig. 1. Tautomeric forms (a) Thione form (b) Thiol form

Fig. 2. FTIR spectrum of cinnamaldehyde Schiff base of SBDTC (NS)
3.5 Magnetic Moment and Electronic Spectra

In order to obtain further structural information on the metal complexes, the magnetic moments and electronic spectra were measured and the results tabulated in Table 4. Gouy’s method have been used to find out the magnetic nature of the metal complexes. The electronic spectra of the ligand, L and all the complexes were recorded in DMSO at ambient temperature (Fig. 5). The absorption band at 266 nm of the Schiff base ligand is due
to benzene $\pi \rightarrow \pi^*$ transition [21]. Another band at 334 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the non-bonding electron located on azomethine nitrogen atom of the ligand.

The octahedral Zr(IV) complex was diamagnetic and showed bands at 270 and 373 nm are due to the $\pi \rightarrow \pi^*$ transitions within the aromatic ring and another band at 476 nm is due to the $\pi \rightarrow \pi^*$ transitions within the $>\text{C}=\text{N}<$ chromophore in UV-visible spectrum [22].

The complex $[\text{Sn(II)}(\text{NS})_2(\text{H}_2\text{O})_2]$ was diamagnetic and its UV-visible spectrum showed bands at 269 and 312 nm are due to $\pi \rightarrow \pi^*$ transitions and one broad bands in the region 433 nm which may be assigned as charge transfer (CT). It was reported that the metal is able to form $\text{d}^2\pi-\text{p}^*\pi$ bonds with ligands containing nitrogen as the donor atom. The d orbital of Sn atom has 5d completely vacant, so the nitrogen-metal coordination bond can formed by the acceptance of the nitrogen lone pair of electrons [23, 24].

### 3.6 ESI-MS Studies

ES-MS has been increasingly used as a dominant structural characterization method in coordination chemistry. The spectra of the ligand and Zr(IV) and Sn(II) complexes show molecular ion peaks at $m/z = 312.45$, 838.08 and 777.85 amu respectively, which are equivalent to their molecular mass respectively. The molecular ion peaks are in good agreement with the proposed molecular formulae indicated from microanalysis.

### 3.7 Structures

On the basis of the different physicochemical and spectral data presented and conferred above, the structures of the Zr(II) and Sn(II) complexes are shown in Figs. 7 and 8.

#### Table 4. Electronic spectral data of the complexes

| Compound | $\mu_{\text{eff}}$(BM) at 303 K | Band position ($\lambda$ nm) | Assignments | Geometrical structure |
|----------|-------------------------------|-----------------------------|--------------|----------------------|
| NS       | -                             | 266, 334                    | $\pi \rightarrow \pi$, $\pi \rightarrow \pi^*$ | -                     |
| $[\text{Zr(IV)}(\text{NS})_2(\text{NO}_3)_2]$ Dia | 270, 373, 476 | $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ | Octahedral |
| $[\text{Sn(II)}(\text{NS})_2(\text{H}_2\text{O})_2]$ Dia | 269, 312, 433 | $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ | Octahedral |

#### Fig. 5. UV visible spectrum of the synthesized compounds

#### 3.6 ESI-MS Studies
Fig. 6. ESI-MS spectra of (a) ligand (NS); (b) [Zr(IV)(NS)₂(NO₃)₂] and (c) [Sn(II)(NS)₂(H₂O)₂]

Fig. 7. Octahedral structure of the complex, [Zr(IV)(NS)₂(NO₃)₂]

Fig. 8. Octahedral structure of the complex [Sn(II)(NS)₂(H₂O)₂]
Table 5. Biological activity of the ligand and complexes expressed in mean of inhibition zone diameter (mm)

| Compound              | Gram-positive bacteria | Gram-negative bacteria | Fungi                |
|-----------------------|------------------------|------------------------|----------------------|
|                       | Staphylococcus aureus  | Salmonella typhimurium | Escherichia coli     | Candida albicans     | Aspergillus fumigatus |
| NS                    | 6                      | 5                      | 2                    | 4                    | 4                      | 5                      |
| [Zr(IV)(NS)(NO3)2]    | 20                     | 21                     | 19                   | 22                   | 17                     | 22                     |
| [Sn(II)(NS)(H2O)2]    | 21                     | 23                     | 20                   | 24                   | 19                     | 25                     |
| Reference             | 34                     | 36                     | 27                   | 24                   | 31                     | 29                     |

3.8 Antimicrobial Studies

The biological activity of the Schiff base ligand and its metal complexes were investigated against the sensitive organisms *Staphylococcus aureus* and *Bacillus subtilis* as Gram-positive bacteria, *Salmonella typhimurium* and *Escherichia coli* as Gram-negative bacteria, *Candida albicans* and *Aspergillus fumigatus* as fungus strains. It was observed that the biological activity of all the synthesized compounds improved on coordination. Improved activity on coordination can be explained on the basis of chelation theory along with considering the nature of the ligand and metal ions, stereochemistry of the complexes etc. [7,20,25]. The metal complexes showed higher activities than the Schiff base ligand.

4. CONCLUSION

The Schiff base ligand and its Zr (IV) and Sn (II) complexes have been successfully prepared. Micro analysis data attained are in good agreement with the proposed formula. Octahedral geometries have been proposed for both the complexes with the help of several physicochemical studies. The synthesized metal complexes, in comparison to the uncomplexed Schiff base ligand, were screened for their biological activity against pathogenic bacterial species. The activity of the Schiff base complexes became more pronounced when coordinated with metal ions.

ETHICAL APPROVAL

Authors have ethical approval to draw their own conclusions about the results presented in the paper.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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