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Synthesis, Spectral Characterization on Bioactive Complexes Containing Schiff base Ligand

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ABSTRACT

Synthesis of metal complexes has been made possible by the Schiff base ligand 2,2'-diphenylenebis(1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenyl. The ligand was synthesised by condensing 3-hydroxythiophene-2-carbaldehyde and benzene-1,2-diamine. UV-Visible, FT-IR, and certain physiochemical studies validated the structural and spectral features of the ligand and metals. For Schiff bases, it was found that the N and O atoms have been identified as ligand binding sites for metal ions. Evidence from molar conductance measurements suggests that the complexes are not electrolytic. TLC analysis was used to check the total responses. In addition to the tetrahedral geometry predicted by magnetic susceptibility data, electronic spectra for the $[ZnC_{16}H_{10}O_2N_2S_2]$, $[SnC_{16}H_{10}O_2N_2S_2]$, $[VOC_{16}H_{10}O_2N_2S]$, $[MgC_{16}H_{10}O_2N_2S]$ complexes indicated a square planar geometry, And their activity tested for using a disc diffusion technique.

Keywords: Spectral analysis, Metal complex, *In vitro* antibacterial activity.

INTRODUCTION

When primary amines combine with carbonyl compounds, Schiff bases are produced. Because of their potential as physiological, analytical, and antibacterial reagents, Schiff bases have attracted a lot of attention.[1] Schiff bases have been utilized, and they may be made from a wide variety of carbonyl compounds and amines[2-3]. Schiff base oxygen and nitrogen donor transition metal complexes have a unique configuration, structural liability, and sensitivity to their molecular environment[4-7]. The lanthanides, often known as lanthanos, constitute the longest series in the periodic table[8]. In 4f, there is a series of internal transitions[9]. Enormous lanthanide (III) ions are useful for stable complexes with high coordination numbers because of their large sizes[10]. Only a few studies have been done on Schiff base complexes containing lanthanides[11].

Drug-binding sites are provided by the complex's metal ions in the centre. Several compounds showed antibacterial, antitumor, anticancer, antifungal properties adding to the growing body of evidence that these compounds represent a significant class of molecules with important medical and pharmaceutical applications[12-17]. Schiff bases biological action derives from the azomethine bond. Only a few number of N, O donor Schiff bases and associated metals have been synthesised by our group recently[18].

Schiff base-ligand containing compounds generated from 3-hydroxythiophene-2-carbaldehyde and o-phenylenediamine are described here[19].

MATERIALS AND METHODS

They all have to be Analar or chemically pure. A wide variety of metal(II) nitrates and chlorides were utilised. Distillation was used to remove impurities from solvents such as petroleum ether, acetonitrile, chloroform, diethyl ether, DMSO, acetone, ethanol, methanol, and DMSO.

Synthesis of Schiff base Ligand $C_{16}H_{12}O_2N_2S_2$

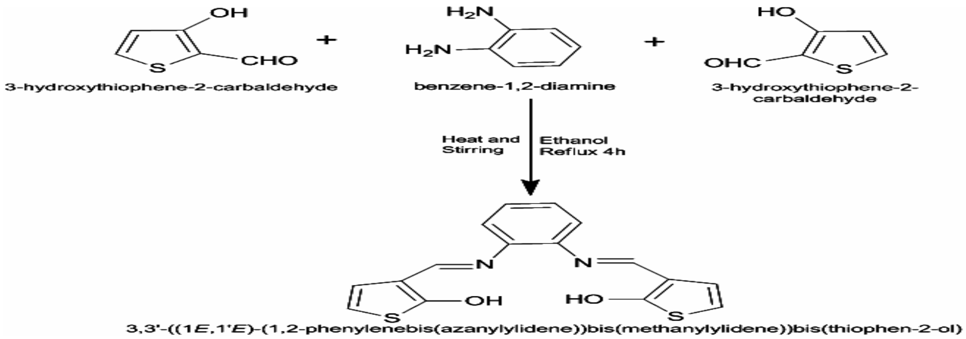
In a clean, round-bottomed flask, 20mmole of 3-hydroxythiophene-2-carbaldehyde (2.1 mL) was condensed with 10mmole (1.08 g) of o-phenylenediamine to make the ligand. We used hot ethanol to dissolve the o-phenylenediamine and 20 mL of ethanol to dissolve the 3-hydroxythiophene-2-carbaldehyde. The solutions were combined and allowed to reflux for around 3-4 hours. To extract moisture, the resultant yellowish substance was dried in vacuum autoclave over anhydrous $CaCl_2$ before being rinsed with alcohol, acetone, and diethyl ether. TLC was used using a variety of solvents to determine the ligand purity. In addition to methanol and chloroform, DMSO was also shown to be effective in dissolving the product. In fact, at 340^{0}C, it yielded 87%. (Scheme 1).

Synthesis of Metals with Schiff base ligand $C_{16}H_{12}O_2N_2S_2$.

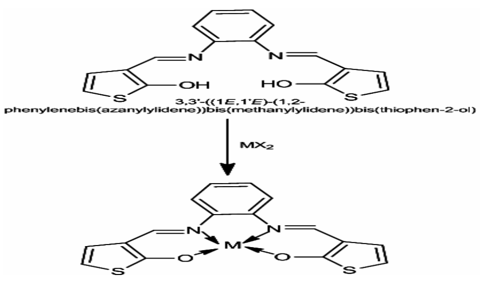
Synthetic complex are written as [M(SB),] where M is one of the metal ions Zn(II), VO(II), Sn(II), or Mg(II) and SB is the synthesised Schiff base ligand $C_{16}H_{12}O_2N_2S_2$. To accelerate the functionalization action, a 15 mL methanol extract sample solution Zn(II) nitrate hexahydrate (0.2975 g, 1mmol), Sn(II) chloride tetrahydrate (0.261 g, 1mmol), VO(II) sulphate tetrahydrate (0.235 g, 1mmol), and Mg(II) chloride hydrate (0.203 g, 1mmol) was stirred On cooling, a colourful solid was produced, then rinsed in methanol, acetone, as well as ether before drying in a vacuum over anhydrous $CaCl_2$. Different solvents were employed for TLC analysis. Target Schiff bases and metal complexes are presented in (Scheme 2).

RESULT

Thermal characteristics, colour, pH, conductivity, and activation energy of compounds are listed below. Above 300^{0}C, the complexes become a luminous powder. Low molecular conductance values (7-9 S/cm) in water and DMSO (10-3M) demonstrate the complexes are non-electrolytes (Table 2).



Scheme 1. Synthesis of Schiff base ligand $C_{16}H_{12}O_2N_2S_2$



Scheme 2. Synthetic route of metals, M=Zn(II), Sn(II), VO(II), and Mg(II) ion

Table 1: Physical and Analytical complex, ligand characteristics

Compound	Colour	Molecular Weight	Yield(%)	Melting Point	Activation Energy, Ekj/mol	Conductivity µS/cm
Ligand $C_{16}H_{12}O_2N_2S_2$	Yellow	328.70	80%	155⁰C-165⁰C	20.78	-
$[ZnC_{16}H_{10}O_2N_2S_2]$	Lemon	393.43	75%	210⁰C-215⁰C	25.20	2
$[SnC_{16}H_{10}O_2N_2S_2]$	Metallic gold	446.27	61%	above 300⁰C	16.74	5
$[VOC_{16}H_{10}O_2N_2S]$	Olive	394.02	82%	above 300⁰C	18.56	3
$[MgC_{16}H_{10}O_2N_2S]$	Lemon	352.02	78%	above 300⁰C	17.20	6

Table 2: FTIR spectral information of the ligand and metals

Ligand/Metals	IR/cm^{-1} υ(O-H)	υ(C=N)	υ(C-O)	υ(M-O)	υ(M-N)
$C_{16}H_{12}O_2N_2S_2$	3466	1614	1193	-	-
$[ZnC_{16}H_{10}O_2N_2S_2]$	3435	1607	1180	533	448
$[SnC_{16}H_{10}O_2N_2S_2]$	3434	1605	1188	538	490
$[VOC_{16}H_{10}O_2N_2S]$	3435	1606	1192	542	486
$[MgC_{16}H_{10}O_2N_2S]$	3434	1609	1181	538	466

Spectral data of Schiff Base ligand $[C_{16}H_{12}O_2N_2S_2]$

Condensation between the CHO moiety of 3-hydroxythiophene-2-carbaldehyde and the $–NH_2$ moiety of O-phenylenediamine was derived from the strong absorption band at 1614 cm^{-1} in ligand spectra. The hydroxyl group (O-H) was assigned to the 3466 cm^{-1}. A sharp band at 1193 cm^{-1} for (C-O) indicates the existence of a C-O bond in Schiff base ligand (Fig. 1). Data for FTIR spectra of Schiff base and metal complexes are shown in Table 2. The electronic absorption spectra and magnetic moments of ligands bound to transition metals are shown here (Table 3). It was revealed in the ^{1}H NMR spectrum of complexes 1-5 that the complexation process was confirmed. The complexes lacked the prominent peak, (OH) at 8.25ppm, in their ^{1}H NMR spectra that was present in the ligand HL spectra. That is, they were not present in any of the other spectra. 328.70 is the molecular weight of the Schiff base ligand.

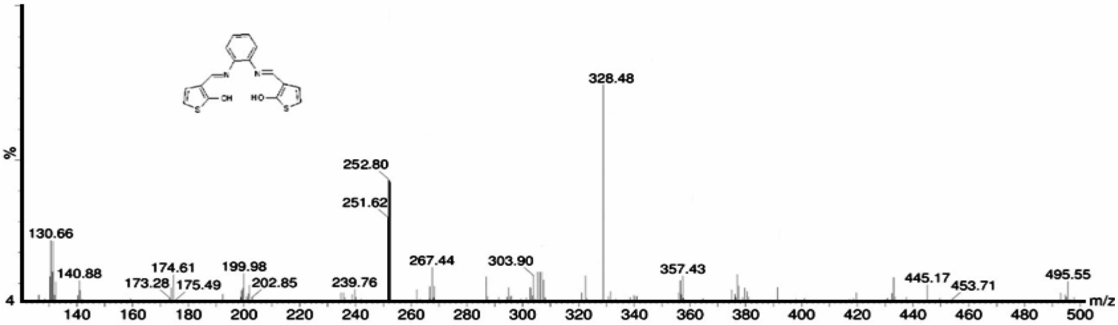


Fig. S1. Mass spectra of Schiff base ligand

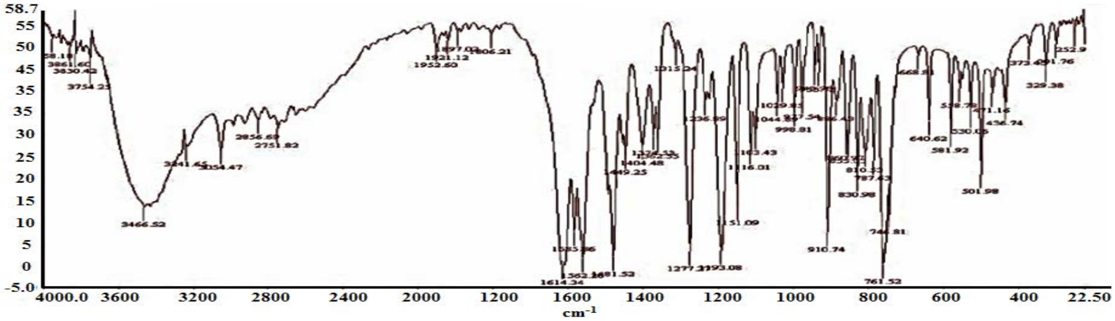


Fig. S2. IR spectra of Schiff base ligand

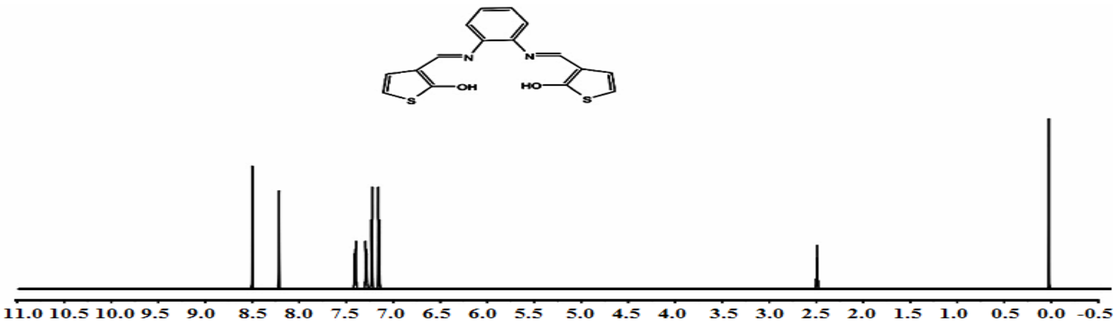


Fig. S3. Schiff base ligand ^{1}H NMR spectra

Table 3: ligands and metals electronic spectra and magnetic moments

Compound	λmax nm	Wave number cm^{-1}	µeff/B.M	Assignment
$C_{16}H_{12}O_2N_2S_2$	277	36101	-	$\pi \longrightarrow \pi^*$
	339	25062		$n \longrightarrow \pi^*$
[$VOC_{16}H_{10}O_2N_2S$]	265	37735	1.4	$\pi \longrightarrow \pi^*$
	323	30959		ngπ*
	400	24691		C.T (M⟶L)
[$MgC_{16}H_{10}O_2N_2S$]	269	29585	0.48	$n \longrightarrow \pi^*$
	297	37174		$\pi \longrightarrow \pi^*$
	338	33670		$\pi \longrightarrow \pi^*$
	395	24691		C.T (M⟶L)
[$ZnC_{16}H_{10}O_2N_2S_2$]	265	31152	0.86	$n \longrightarrow \pi^*$
	296	37735		$\pi \longrightarrow \pi^*$
	321	33783		$\pi \longrightarrow \pi^*$
	395	24691		C.T (M⟶L)
[$SnC_{16}H_{10}O_2N_2S_2$]	267	37453	0.6	$\pi \longrightarrow \pi^*$
	325	30769		$n \longrightarrow \pi^*$
	394	25380		C.T (M ⟶ L)

Spectral data of [Zn $C_{16}H_{10}O_2N_2S_2$] complex

Free ligand's azomethine υ(C=N) stretching frequency caused a significant absorption maxima at 1614 cm^{-1}. The Zn(II) UV–Vis spectra show three absorption peaks at 265, 296 and 321nm. When bound to Zn(II), the ligand UV-spectra at 277nm and 339nm are changed. The 265nm and 296nm peaks are $\pi \longrightarrow \pi^*$ transitions, whereas the 321nm peak is $n \longrightarrow \pi^*$. The ^{1}H NMR spectra of the –N=CH– is identified at 8.51 (s) and Aromatic is identified at 7.01–7.45 (m).

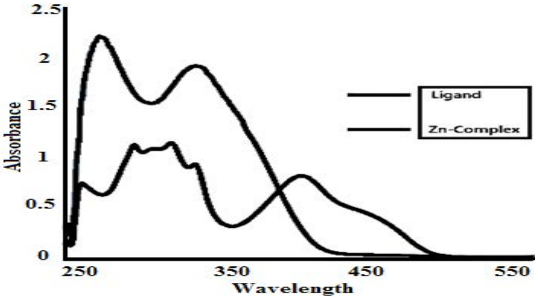


Fig. S4. Electronic spectra of Zn Complex

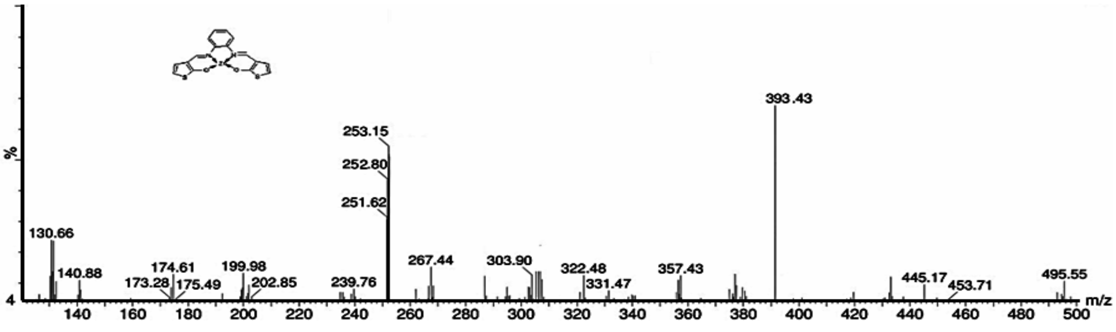


Fig. S5. Mass spectra of Zn Complex

Spectral data of [Sn $C_{16}H_{10}O_2N_2S_2$] complex

The stretching frequency of the azomethine υ(C=N) in Sn complexes decreases from 1614 cm^{-1} to 1605 cm^{-1} There is no (O-H)-induced 3466 cm^{-1} band. In the unbound ligand, the υ(C-O) stretching vibration has a frequency of 1193 cm^{-1}, although in the coordinated complex, it has a frequency of 1188 cm^{-1}. There is a intensity band at 538 cm^{-1} due to M-O bonding, while the M-N bonds are responsible for the bands at 490 cm^{-1}. The [$SnH_{10}O_2N_2S_2$] complex's UV–Vis spectra show three prominent absorption bands at 267, 325, and 394nm. Both peaks, which exhibit themselves at 267nm and 325nm, respectively, the compound exhibited a strong band at 394nm of the azomethine chromophore, and a second band at 330nm. The –N=CH– signal can be seen in the ^{1}H NMR spectrum at 8.52(s), and the aromatic signal can be found in the range of 7.01–7.45 (m).

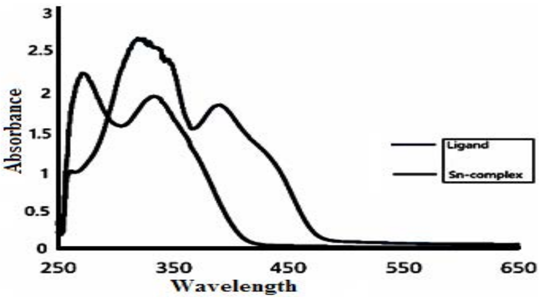


Fig. S6. Electronic spectra of Sn Complex

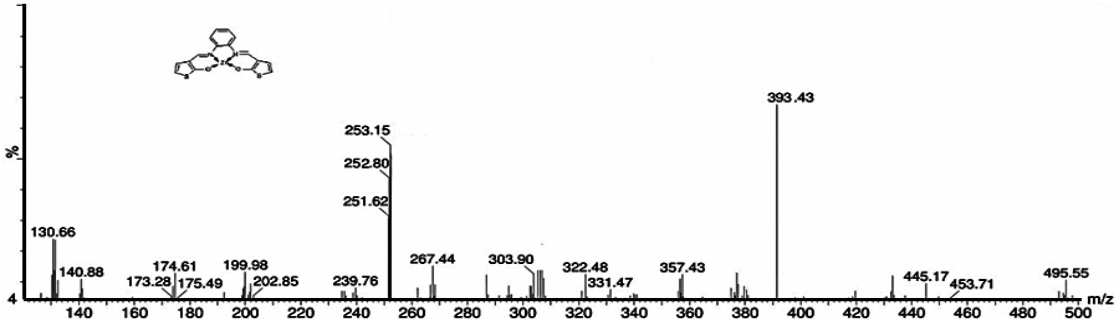


Fig. S7. Mass spectra of compound Sn Complex

Spectral data of [VO $C_{16}H_{10}O_2N_2S$] complex

The band that was previously located at 1614 cm^{-1} in VO(II) complexes shifted to 1606 cm^{-1} as a result of azomethine υ(C=N) stretching. For ligands in complex spectra, an increase in υ(C-O) stretching vibration from 1193 cm^{-1} to 1192 cm^{-1} shows that VO(II) has been coordinated by de protonated phenolic oxygen. M-O bonds produce the 542 cm^{-1} medium-intensity bands, where as M-N bonds generate the 486 cm^{-1} bands. Among other bands, the vanadyl complex exhibits the characteristic 980 cm^{-1}. The compound's UV–Vis spectra reveal strong absorption bands at 265, 323 and 400nm. There are two peaks in the absorption spectrum of azomethine nitrogen due to the single electron pair in its anti-bonding p orbital one at 265nm, There is a 400 nm absorption band for a charge transfer ligand. The –N=CH– signal can be seen in the ^{1}H NMR spectrum at 8.52(s), and the aromatic signal can be found in the range of 7.01–7.45 (m).

Spectral data of [Mg $C_{16}H_{10}O_2N_2S$] complex

In the spectra of the Mg(II) complex, the azomethine υ(C=N) stretching frequency shifted from 1614 cm^{-1} to 1609 cm^{-1}, pointing to the fact that coordination occurs via N atoms. Protonation of a phenolic oxygen in the free ligand is indicated by the change in the υ(C-O) stretching vibration from a 1193 cm^{-1} to 1181 cm^{-1} in the spectra of the coordinated complex, which indicates the synthesis of weaker C-O(Mg) bonds. The medium-intensity bands at 538 cm^{-1} and 466 cm^{-1} are like wise attributed to M-O and M-N bonds. Three prominent absorption bands, at 269, 297, and 338nm, may be seen in UV–Vis spectra of the [$MgH_{10}O_2N_2S$] complex. The 269nm ,$\pi \longrightarrow \pi^*$ transition peak is caused by the azomethine nitrogen lone pair of electrons in its antibonding p orbital, whereas the 297nm and 338nm peaks are attributed to the $n \longrightarrow \pi^*$ transition. An absorption band at 395nm was identified in the case of a ligand-to-metal charge transfer molecule. The –N=CH– signal can be seen in the ^{1}H NMR spectrum at 8.20(s), and the aromatic signal can be found in the range of 7.01–7.45 (m).

Antibacterial activity

Antibacterial susceptibility testing's primary aim is to discover pathogens that are resistant to commonly used antibiotics. Various species of *Bacillus cereus*, *Shigella boydii*, *Escherichia coli Enterobacter*, and *Shigella sonnei*, *Salmonella typhimurium*, used to test the antibacterial activities of free Schiff base ligands and their metal complexes. The paper disc diffusion technique was used to evaluate the compounds in DMSO solution at a level of 50 g/0.01 mL. Table 4 shows the diameter (in millimetres) of the zones of susceptibility. Susceptibility zones are disc penetration zones that are poisonous to microorganisms. Schiff base and metals inhibited the growth of all of the bacterial species studied (Table 4).

Table 4: Schiff base and metal complex antibacterial screening activities

Tested bacteria	Compounds' zone inhibition (mm)					Kanamycin (30µg/disc)
	$C_{16}H_{12}O_2N_2S_2$	$[ZnH_{10}O_2N_2S_2]$	$[SnH_{10}O_2N_2S_2]$	$[VOH_{10}O_2N_2S]$	$[MgH_{10}O_2N_2S]$	
Salmonella typhinium	12	13	10	12	12	25
Bacillus subtilis	10	10	12	10	12	25
Shigellaboydii	10	11	13	14	10	22
Shigellasonnei	8	11	-	12	12	22
E. coli	11	9	11	13	10	25
Enerobacter	10	9	12	10	10	24
Bacillus cereus	13	14	11	12	13	20
DMSO control	-	-	-	-	-	30

CONCLUSION

In this study, we report the Schiff base ligand and metals of Zn(II), Sn(II), VO(II), Mg(II), ions were synthesised and characterised in this work. IR spectroscopy revealed that the core metal atom is coordinated to N and O atoms. The tetrahedral-shaped complexes of $[ZnC_{16}H_{10}O_2N_2S_2]$, $[MgC_{16}H_{10}O_2N_2S]$ $[SnC_{16}H_{10}O_2N_2S_2]$, were suggested because of their high magnetic moments, UV-Vis absorption, and synthesis. Square planar geometry characterises the $[VOC_{16}H_{10}O_2N_2S]$. A comparison of the ligand and its metal complexes to a conventional antibiotic revealed mild to substantial antibacterial activity (Kanamycin). Metal complexes inhibited better than Schiff base ligand.

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Conflict of Interest

There are no competing interests between the authors and the publication in this work.

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