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Schiff base metal complex synthesis, characterization, and antimicrobial application

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There is a wide variety of biological activity that may be shown by complexes of mixed ligands with transition metal ions. Schiff bases, which are compounds that include an azomethine (C=N) group and amino acids, are very versatile molecules that may be used in the construction of ternary complexes. All three novel metal complex derivatives from the 4-(5-((2-hydroxybenzylidene)amino)-1,3,4-thiadiazol-2-yl)benzonitrile in alcoholic medium have been effectively synthesised by combining HL with the metal ions Mg(II), Zn(II) and Sn(II). Elemental analysis, molecular weight, magnetic moment and spectroscopic methods have been used to characterise the prepared complexes. Biological evaluation of the ligand and its metal complexes has demonstrated weak to significant antibacterial activity, relative to the standard antibiotic (Kanamycin). The prepared metal bound complexes are bactericidal to a greater extent than the corresponding unbounded Schiff base ligand.

Keywords: Mixed ligand complex, Azomethine, Antibacterial

In the main group and transition metal coordination chemistry, Schiff base complexes are regarded as one of the most prominent stereochemical models owing to their permeability and structural complexity. As ligands, Schiff bases have been extensively employed due to their higher tensile strength and ease of saturation in standard solvents[1].

In addition to its antimicrobial, antifungal, antiviral, antiinflammatory, antimalarial, antiproliferative, and antipyretic characteristics[2-8], Schiff bases have been shown to exhibit a wide variety of other biological actions[9]. Due to their easy interaction with metallic ions and their ability to form complexes, multi-dentate Schiff bases are often utilized as ligands[10]. Significant interest has been shown by researchers over the last several decades in the development of applications using transition metal complexes with N, O-donor ligands[11,12]. Scientists often use N, O-donor ligands using the well-known Schiff base condensation process[13,14].

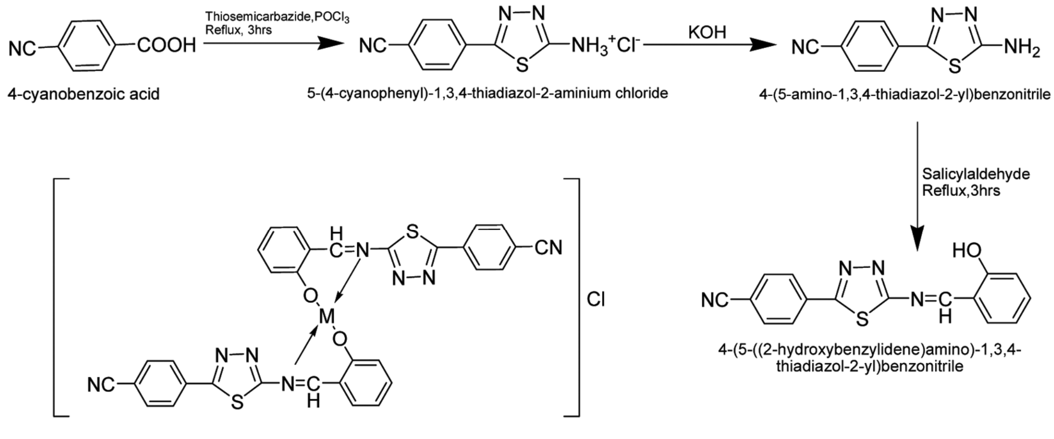
Consequently, the structural-activity connection investigation of 1,3,4-thiadiazoles might develop in the near future[15]. As the continuation interest of our study of transition metal complexes These new 2-(((5-(4-aminophenyl)-1,3,4-thiadiazol-2-yl)imino)methyl)phenol complex compounds are described in this paper[16]. This article also includes preliminary *in vitro* antibacterial screening results for the complexes generated[17].

Results and Discussion

Preparation of 2N-salicylidene-5-(*p*-cyanophenyl)-1,3,4-thiadiazole, HL

An aqueous solution of 4-aminobenzoic acid (0.01 mol), thiosemicarbazide (0.01 mol), and phosphorus oxychloride (5.0 mL) was heated under reflux for three hours. It was allowed to cool before being re-heated with 50 mL of distilled water over a 4-hour period at reflux. Finally, potassium hydroxide was added to neutralize the filtrate. The precipitate purged with cold distilled water and then recrystallized in an ethanol-water solvent mixture to get 5-(4-cyanophenyl)-1,3,4-thiadiazol-2-amine. A solution of 5-(4-cyanophenyl)-1,3,4-thiadiazol-2-amine and salicylaldehyde was heated for three hours under reflux to produce the yellow precipitate. The 2N-sulfonyl-5-(p-cyanophenyl)-1,3-thiadiazole ligand was produced through filtering and crystallization from the solution in ethanol. The simplified steps required to synthesize the ligand HL are shown in Scheme 1.

HL showed two distinct stretching bands at 1646 cm^{-1} in complexes **1-3** these were attributed to the ligand's υ(CN) atoms. Complexes **1–3** were found



M=Mg, Zn, Sn

Scheme 1 — The structure of HL and the proposed structure of complexes

Table 1 — Selected infrared data of HL and complexes **1**–**3**

Compd	Wavenumber (cm^{-1})		
	υ (C=N)	υ (M-O)	υ (M-N)
HL	1646	–	–
Mg(L)$_2$, **1**	1684	509	485
Zn(L)$_2$, **2**	1606	507	482
Sn(L)$_2$, **3**	1609	518	475

to have a lower υ(CN) number than their nitrogen atom, suggesting that the ligand HL was involved in their coordination. Metal-ligand complexes were identified in the spectral regions extending from 509 to 485 cm^{-1},507 to 482 cm^{-1}, 518-475 respectively, indicating that the ligand's oxygen and nitrogen atoms are involved. Table 1 provides the most relevant infrared data for the ligand HL and the complexes **1-3**.

The complexes were typically made by heating the appropriate metal salts with a ligand, HL, in a 1:2 molar ratio while maintaining a constant reflux.TLC using silica gel-G as an adsorbent was used to examine the purity of the ligand, HL, and complexes **1–3**. A rapid melting point was recorded for complexes **1–3**, suggesting the isolation of relatively pure complexes. The obtained complexes molecular weights and micro-elemental analyses of carbon, hydrogen, nitrogen, and sulfur corroborated those expected for complexes **1-3**. A schematic representation of the suggested structure for complexes **1–3** and ligand, HL is shown in Scheme 1. Melting point, microelement analysis, and m/z values are listed in Table 2.

The identification of extremely drug-resistant strains of pathogenic microbes is the primary purpose of antibacterial susceptibility testing. The antibacterial properties of free Schiff base ligands and their metal complexes were put to the test using a variety of bacterial strains, including *Bacillus cereus*, *Salmonella typhimurium*, *Shigella boydii*, *Escherichia coli*, *Enterobacter* and *Shigella sonnei* among others. The compounds were examined by using a method known as paper disc diffusion at a concentration of fifty grams per milliliter of DMSO solution. The findings of a measurement that was performed on the diameter (in mm) of the susceptibility zones are shown in Table 3. The areas of disc penetration that contained bacteria-killing toxins were referred to as susceptibility zones. The levels of growth inhibition shown by the various Schiff base and metal complexes were different across all of the bacterial species that were examined (Table 3).

Experimental Section

Spectral data of [$C_{32}H_{18}MgN_8O_2S_2$] complex

The azomethine (C=N) stretching frequency band at 1684 cm^{-1} in the spectrum of the free ligand shifted to a lower frequency at 1609 cm^{-1} in the spectrum of the Mg(II) complex, indicating coordination through N atoms. The development of a weaker C-O(Mg) bond compared to C-O confirms that the ligand coordinates to Mg(II) through deprotonated phenolic oxygen in the spectra of the coordinated complex, where it moves from 1193 cm^{-1} in the free ligand spectrum to 1181 cm^{-1} in the coordinated complex spectrum (H). M-O and M-N bonds are also responsible for the medium-intensity bands seen at 509 cm^{-1} and 485 cm^{-1}. In UV-Vis spectra of the [$C_{32}H_{18}MgN_8O_2S_2$] complex, three significant absorption bands can be detected at 269, 297, and

Table 2 — Melting points, elemental analytical data (%) and *m/z* value of HL and complexes **1**–**3**

Compd	Physical Appearence	m.p. (°C)	Elemental Analysis (%)				(M) metal	*m/z*
			C	H	N	S		
HL	Yellow	112–114	62.73 (62.74)	3.29 (3.32)	18.29 (18.32)	10.93 (10.95)	–	306.34
$Mg(L)_2$, **1**	Deep Orange	194–196	60.53 (60.55)	2.86 (2.88)	17.69 (17.73)	10.10 (10.13)	14.16 (14.20)	634.08
$Zn(L)_2$, **2**	Blue	98–101	56.85 (56.87)	2.68 (2.70)	16.57 (16.62)	9.49 (9.52)	9.67 (9.70)	674.03
$Sn(L)_2$, **3**	Green	207–209	52.69 (52.72)	2.49 (2.52)	15.36 (15.40)	18.79 (18.80)	16.28 (16.30)	730.28

Table 3 — Schiff base and metal complex antibacterial screening activities

Tested Bacteria	Diameter of zone inhibition(mm) of tested compounds				Kanamycin (30 μg/disc)
	$C_{16}H_{12}O_2N_2S_2$	$[C_{32}H_{18}MgN_8O_2S_2]$	$[C_{32}H_{18}N_8O_2S_2Zn]$	$[C_{32}H_{18}N_8O_2S_2Sn]$	
Salmonella typhinium	13	12	11	13	26
Bacillus subtilis	11	11	13	13	26
Shigella boydii	11	12	14	11	23
Shigella sonnei	9	12	–	13	23
E. coli	10	8	12	11	26
Enerobacter	11	8	13	11	25
Bacillus cereus	12	15	12	14	21
DMSO control	–	–	–	–	30

338 nm. The 269 nm $\pi\rightarrow\pi^*$ transition peak, together with the 297 nm and 338 nm peaks, are attributed to the $n\rightarrow\pi^*$ transition, which is caused by a lone pair of electrons in the antibonding p orbital of nitrogen in azomethine. An absorption band at 395 nm was seen for the molecule that was identified as a ligand-to-metal charge transfer (Table 4). The -OH is detected at 8.20(s) in ^{1}H NMR spectra, whereas aromatic compounds are found between δ 7.01 and 7.45 (m).

Spectral data of $[C_{32}H_{18}N_8O_2S_2Zn]$ complex

The azomethine (C=N) stretching frequency of the free ligand contributed to a significant absorption band in the ligand spectra at 1614 cm-1. The band at 1606 cm^{-1} was identified as belonging to the hydroxyl (O-H) group. One can tell that the Schiff base ligand has a C-O bond because of the strong band at 1193 cm-1 for carbon monoxide (C-O). The Zn(II) complex's UV-Vis spectra reveal three notable absorption bands at 265, 296 and 321 nm. The UV spectra of the bound ligand at 277 nm and 339 nm are modified when Zn(II) is present. We may attribute the 265nm and 296nm peaks to the $\pi\rightarrow\pi^*$ transition and the 321 nm peak to the $n\rightarrow\pi^*$ transition based on the spectral shape of the transitions (Table 4). The –N=CH– signal may be seen at δ 8.51 (s) in ^{1}H NMR spectra, whereas aromatic peaks can be seen around δ 7.01 (s) to 7.45 (s) (m).

Table 4 — Ligands and metals electronic spectra and magnetic moments

Compd	λ_{max} (nm)	Wavenumber (cm^{-1})	μ_{eff} /BM	Assignment
HL	277	36101	–	$\pi\rightarrow\pi^*$
	339	25062		$n\rightarrow\pi^*$
$Mg(L)_2$, **1**	269	29585	0.48	$n\rightarrow\pi^*$
	297	37174		$\pi\rightarrow\pi^*$
	338	33670		$\pi\rightarrow\pi^*$
	395	24691		CT (M→L)
$Zn(L)_2$, **2**	265	31152	0.86	$n\rightarrow\pi^*$
	296	37735		$\pi\rightarrow\pi^*$
	321	33783		$\pi\rightarrow\pi^*$
	395	24691		CT (M→L)
$Sn(L)_2$, **3**	267	37453	0.60	$\pi\rightarrow\pi^*$
	325	30769		$n\rightarrow\pi^*$
	394	25380		CT (M→L)

Spectral data of $[C_{32}H_{18}N_8O_2S_2Sn]$ complex

As Sn(II) complex forms, the 1614 cm^{-1} band, induced by the free ligand azomethine (C=N) stretching frequency, moves to a lower frequency at 1609 cm^{-1}. This means that there is no (O-H)-induced 3466 cm-1 band. Another piece of evidence is that the (C-O) stretching vibration shifts from 1193 cm^{-1} in the free ligand spectrum to 1188 cm^{-1} in the spectrum of the coordinated complex. There were other bands found at 475 cm^{-1}, thought to be associated with M-N bonds, and 518 cm^{-1}, thought to be associated with M-O bonds. Important absorption bands can be seen in the UV-Vis spectra of the $[SnH_{10}O_2N_2S_2]$ complex at 267, 325, and 394 nm. The lone pair of electrons on the nitrogen atom in an azomethine is responsible for both peaks: the $\pi\rightarrow\pi^*$ transition at 267 nm and the $n\rightarrow\pi^*$ transition at 325 nm. The $n\rightarrow\pi^*$ transition of the azomethine chromophore contributed a prominent band at 394 nm to the spectrum of this molecule, and a second band at 330 nm may be due to a charge transfer (Table 4). –N=CH– is detected at δ 8.52(s) in ^{1}H NMR spectra, while aromatic compounds are detected between δ 7.01 and 7.45 (m).

Conclusion

This work describes the synthesis and coordination chemistry of Mg(II), Zn(II), and Sn(II) complexes with the Schiff base ligand 4-(5-((2-hydroxybenzylidene)amino)-1,3,4-thiadiazol-2-yl) benzonitrile. According to infrared spectroscopy, the central metal atom is coordinated to nitrogen and oxygen. High magnetic moments (Table 4) resulted in the creation of the tetrahedral-shaped complexes [$ZnC_{16}H_{10}O_2N_2S_2$], [$SnC_{16}H_{10}O_2N_2S_2$], and [$MgC_{16}H_{10}O_2N_2S$]. The ligand and its metal complexes showed moderate to strong antibacterial activity in comparison to the standard antibiotic in biological evaluations (Kanamycin). Metal complexes were more effective as bactericides than their equivalent Schiff base ligands.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

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Conflict of interest

The authors of this work do not have any conflicting interests that might be affected by the publishing of this work.

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