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SPECTROSCOPIC CHARACTERIZATION OF SCHIFF BASE METAL (II) COMPLEXES DERIVED FROM 2-HYDROXYBENZALDEHYDE AND 1,8-DIAMINONAPHTHALENE

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ABSTRACT

Schiff base ligand (HL) derived from 2-hydroxybenzaldehyde with 1,8 diaminonaphthalene was synthesized and characterized by elemental analysis, melting point and IR. The elemental analysis revealed a 1:2 molar ratio (amine: aldehyde) for the ligand. IR spectra showed the azomethine (>C=N) bond at around 1624 cm^{-1} in the ligand. The Schiff base (HL) is coordinated with Hg(II), Pb(II), and Cd(II) to form the corresponding metal complexes. These complexes were characterized by elemental analysis, melting point, solubility, conductivity, Infra-Red, and electronic spectra. The purity and composition of both the Schiff base and the metal complexes were established by elemental analysis. The complexes showed various colours ranging from brown to dark brown and grey.

Keywords: Spectroscopy; Complexes; 2-hydroxybenzaldehyde; 1,8-diaminonaphthalene

INTRODUCTION

Schiff bases' coordination with transition metals, main group metals, and main group organometallics has gotten a lot of attention recently [1]. Based on the coordinating potential of the ligand under consideration, the aforementioned metallic derivatives of Schiff bases have displayed a broad variety of structural motifs. Due to their wide range of uses as ligands in the synthesis of metal complexes in the elemental, spectral, nanomaterial, biological, and pharmaceutical application. Schiff bases and their derivative products have attracted a lot of interest [1]. The presence of more than one type of ligand in a complex increases the chance of variation in properties expected for the complex. The synthesis and characterization of mixed ligands are gaining attention day by day. The increased interest in this research area has motivated many researchers to get involved in this field [2]. One of the main goals of present-day inorganic coordination chemists and pharmaceutical investigation is the discovery and development of better drugs to fight diseases, which has led to numerous studies on drug-metal complexes [3].

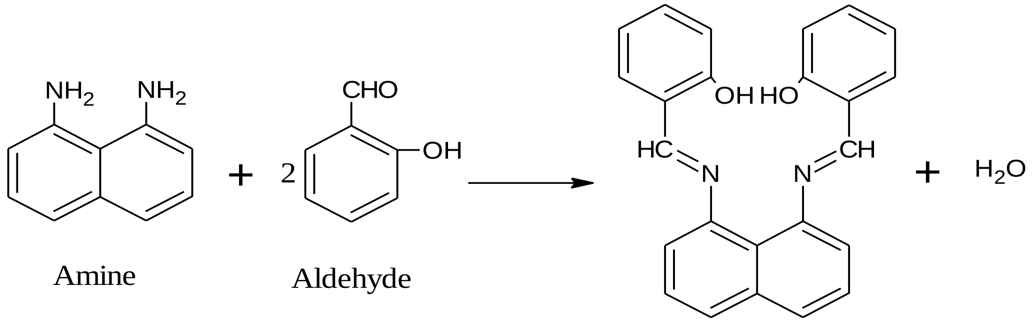
Mercury is one of the most toxic heavy metals on earth. For example, methylmercury is more toxic than elemental mercury and other inorganic mercury compounds. Mercury containing ligands are known to form stable complexes with metal ions, such as gold (I) and Se(II), because mercury is considered to be a soft lewis base [4, 5]. The coordination chemistry of mercury(II) differs from most other transition metals due to its large size and d10 configuration. Its interference in biological system and its potential as a toxin or as a medicine require a better understanding of its coordination properties [6]. Medicinal inorganic chemistry can exploit the unique properties of metal ions for the design of new drugs. This has for instance, led to the clinical application of chemotherapeutic agents for cancer treatment, such as cisplatin. The therapeutic use of metal complexes in cancer and leukemia were reported since sixteenth century. In 1960, an inorganic complex, cisplatin was discovered, today more than 50 years, it is still one of the world's best-selling anticancer drug [7].

MATERIALS AND METHODS

The reagents deployed in this research are analytical grade and purchased from Sigma Aldrich 99%. These reagents were used without any purification. They include: 2-hydroxybenzaldehyde, 1,8-diaminonaphthalene, ethanol, methanol, diethyl ether, chloroform, hexane, acetone, sulfuric acid, mercury chloride, lead chloride and cadmium chloride. All weighing was observed on the electrical balance model AB 54. A Griffin melting point apparatus was used to determine the melting point and decomposition temperature. Microanalysis was performed on a Thermo Flash EA CHNS-O elemental analyzer. The infrared (IR) spectra were recorded on the FTIR–84005 Model in the range of 4000–350 cm^{-1} for the ligand and complexes. The electronic absorption spectra of the ligand and the complexes were obtained on the UV/Visible Spectrophotometer Model 721. The conductivity of the complexes determined at room temperature (30 ^{o}C) on freshly prepared 10^{-3} MeOH solutions using an estick (R) Series Model EC 500/Conductivity and Temperature Meter. The antibacterial activities of the ligand and metal complexes were screened against two strains of gram-positive bacteria *(Staphylococcus aureus, Streptococcus pyogenes)* and two gram-negative *(Escherichia* *coli*, *Klebsiella pneumoniae)* and two fungi *(Aspergillus niger* and *Candida albicans) using the* filter paper disc agar diffusion method.

Preparation of the Schiff Base Ligand

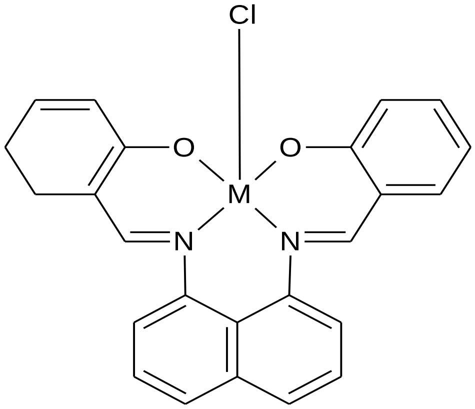
The Schiff base formed from 2-hydroxybenzaldehyde and 1,8-diaminonaphthalene was prepared by adding 30 ml of ethanolic solution of 2-hydroxybenzaldehyde (20 mmol, 2.44 g) to the same volume of ethanolic solution of 1,8-diaminonaphthalene (10 mmol, 1.582 g) after which 2-3 drops of conc. H_2SO_4 was added. The mixture was refluxed for 3 hours in a quick-fit flat bottom flask. After refluxing, the mixture was left to stand for 2-3 days. The product formed was filtered, washed several times with ethanol, and dried in a desiccator over calcium chloride. ($CaCl_2$) [8,9].



Scheme 1: Synthesis of the Schiff base ligand

Preparation of the Schiff Base Metal Complexes

The metal complexes were prepared by adding a mixture of the Schiff base (HL) under investigation (1 mmol, 0.3664g) in 30 ml of ethanolic solution and 30 ml of ethanolic solution of Hg (II) salt (1 mmol, 0.1979g) were refluxed for 2 hours, after which they were cooled, filtered, and the product obtained was dried in a desiccator containing calcium chloride ($CaCl_2$) as a desiccant. The same procedure was applied to each metal salt. The masses of the products obtained were determined by weighing after drying and percentage (%) yields were calculated [8,9].



Scheme 2: Synthesis of the metal complex

Where M = Hg (II), Pd (II) and Cd (II)

RESULTS AND DISCUSSION

All the metal complexes are coloured solids, stable towards the air, and have high melting points in the range of 210-340 °C A similar observation was reported by [6]. The complexes are insoluble in water and common organic solvents. The conductivities of solutions of the complexes in methanol are shown below. Analytical data suggests that the metal-to-ligand ratio in all the complexes is 1:1 (Table 1). Because of their low conductivity values, all the complexes are non-electrolytes.

Table 1: Physical properties and some analytical data of the Schiff base ligand and its metal complexes

S/N	Compound	Colour	Yield g (%)	M.P. (°C)	Λ_m (Scm^2 mol^{-1})
1	HL	Brown	5.08 (69)	255	-
2	[Hg(HL)Cl]	Dark brown	1.24 (68)	230	20.00
3	[Pb(HL)Cl]	Dark brown	1.37 (74)	340(d)	18.70
4	[Cd(HL)]	Grey	0.395 (85)	210	16.80

IR Spectra

The IR spectral bands for the ligand and its complexes are given in Table 2. The characteristic absorption bands in the spectra of the ligand (HL) at 3402 cm^{-1} is attributed to OH group. The υ (C=N) band was observed at 1631 cm^{-1} for the HL ligand. In the spectra of the metal complexes υ (C = N) shifted to higher frequency of 1639 cm^{-1} [7]. In the spectra of the ligand, the C = C band appears at 1485 cm^{-1} as a broad band due to aromatic C=C vibrations. In the spectra of the complexes, this band shifted to both higher and lower frequencies on coordination with the metal ions. This shift indicates that there is coordination between the ligand and the metal ions. The lower frequency shift was observed in Pb(HL)Cl at 1411 cm^{-1}, while the higher frequency was observed at 1496 for both Hg(II) and Cd(II) complexes. The υ (C-O) band observe in the spectrum of the ligand and Cd(II) complex at 1411 cm^{-1} as a weak medium bands respectively. However, these bands shifted to lower frequencies of 1350 and 1319 cm^{-1} for Hg(II) and Pb(II) complexes, confirming the involvement of the phenolic group in complex formation. Wahab and Adedibu reported the infra-red spectra of Co (II), Cu (II) and Ni (II) complexes of bis(2-hydroxy-4-methoxy acetophenone with ethylenediamine in the range of 1320-1336 cm^{-1}, which was attributed to υ (C-O). The lower frequency observed in all the spectra of the metal complexes is attributed to M-O in the range of 617-844 cm^{-1} and M-N in the range of 455-540 cm^{-1}, respectively.

Table 2: The Relevant infrared frequencies (cm^{-1}) for the Schiff base ligand and its metal complexes

S/N	Compounds	υ (OH)	υ (C=N)	υ (C-O)	υ (C=C)	M-O	M-N
1	HL	3402s	1631m	1411w	1485b	-	-
2	[Hg(HL)Cl]	3402m	1639m	1350b	1496b	844w	455w
3	[Pb(HL)Cl]	3402s	1639m	1319w	1411m	663b	451b
4	[Cd(HL)]	3402s	1639m	1411m	1496b	617b	455w

UV-Visible Spectra

The primary use of UV-Vis spectra for transition metal complexes is the elucidation of electronic structure parameters. Two absorption bands at 27777 cm^{-1} and 25641 cm^{-1} were observed due to π - $\pi^*$and n - π^* transitions in the spectra of the HL ligand [10]. Pb(HL)Cl showed two absorption bands at 25641 cm^{-1} and 25000 cm^{-1} attributed to charge transfer transition either from ligand to metal or metal to ligand charge transfer transitions. Cd(II) complex had two absorption bands in the U-V region at 22222 and 15607 cm^{-1} which is attributed to $^5T_2g(E) \rightarrow {}^5Eg$ transitions [11].

Table 3: Electronic spectra of the Schiff base ligand and its metal complexes

S/N	Compound	λ_{max} nm	λ_{max} cm^{-1}	A	Σ	Assignment
1	HL	360	27777	0.880	8800	n - π^*
		390	25641	1.366	1366	π - π^*
2	[Hg(HL)Cl]	480	20833	1.284	1284	$^4A_2g(F) \rightarrow {}^4T_2g(F)$
		610	16393	1.906	1.906	
3	[Pb(HL)Cl]	390	25641	1.253	1253	MLCT
		400	25000	0.885	885	MLCT
4	[Cd(HL)]	450	22222	1.115	1115	$^5T_2g(E) \rightarrow {}^5Eg$
		510	15607	0.950	950	$^5T_2g(E) \rightarrow {}^5Eg$

Microanalysis

The results of the microanalysis of the ligand and some of the metal complexes are presented in Table 3. The results of microanalysis (CHN) indicated that the experimental data is in close agreement with the theoretical values in most cases and agrees with the formation of a 1:1 (M:L) molar ratio for the complexes. Similar observations are reported by [9].

Table 4: Microanalysis of the Schiff base ligand and some of the metal complexes

S/N	Compound	%C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% M Found (Calcd)
1	$C_{24}H_{18}N_2O_2$	78.33	4.86	7.35	-
	(366.44)	(78.59)	(4.91)	(7.64)	-
2	$Hg(C_{24}H_{18}N_2O_2)Cl$	47.55	2.33	4.91	33.76
	(602.92)	(47.76)	(2.98)	(4.64)	(33.33)
3	$Cd(C_{24}H_{18}N_2O_2)$	60.94	3.71	5.20	23.49
	(478.94)	(60.13)	(3.75)	(5.84)	(23.40)
4	$Cr(C_{24}H_{18}N_2O_2)$	68.33	4.52	6.29	12.43
	(418.44)	(68.82)	(4.32)	(6.69)	(12.48)

Antimicrobial Activity

The antimicrobial activity of the Schiff base ligand derived from 2-hydroxybenzaldehyde with 1,8-diaminonapthalene showed no activity against both bacteria and fungi species. On chelation with Hg(II) complex showed activity against all the tested organisms. On *E. coli* and *A. niger,* which showed no activity at 200 mg/ml and 100 mg/ml. Based on the findings, as the concentration decreased, the activity also decreased as observed in the Hg(HL)Cl complex, similar observation was reported by [11] the more the concentrations the higher the susceptibility test. Pb(II) and Cd(II) complexes displayed no activity on the tested microorganisms.

Table 6: Antimicrobial activities of the Schiff base ligand (HL) and its metal complexes

Compounds	Concentration (mg/ml)	Antimicrobial activity with zone of inhibition (mm)					
		Staphylococcus aureus	*Streptococcus Pyogenes*	*Escherichia coli*	*Klebsiella pneumonia*	*Candida albicans*	*Aspergillus niger*
HL	400	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	300	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	200	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	100	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
[Hg(HL)Cl]	400	13.67±0.58^{b}	18.67±0.58^{b}	10.0±0.00^{b}	16.0±0.00^{b}	20.0±0.00^{b}	10.67±0.58^{b}
	300	11.0±0.00^{c}	15.0±0.00^{c}	7.67±0.58^{c}	12.33±0.58^{c}	16.33±0.00^{c}	8.0±0.00^{c}
	200	9.0±0.00^{d}	11.33±0.58^{d}	0.00±0.00^{d}	9.66±0.58^{d}	12.0±0.00^{d}	0.00±0.00^{a}
	100	7.0±0.00^{e}	9.0±0.00^{e}	0.00±0.00^{e}	7.0±0.00^{e}	9.0±0.00^{e}	0.00±0.00^{a}
[Pb(HL)Cl]	400	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	300	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	200	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	100	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
[Cd(HL)]	400	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	300	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	200	0.00±0.00a	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	100	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
[Cr(HL)]	400	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	300	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	200	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
	100	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}	0.00±0.00^{a}
Cipro	400	20.66±0.58^{f}	35.00±0.00^{f}	18.00±0.00^{f}	17.33±0.58^{f}	-	-
Amph. B		-	-	-	-	22.33±0.58^{f}	32.00±0.00^{d}

Different superscript letters along the same column are significantly ($P<0.05$) different.

Cipro = Ciprofloxacin, Amph. = Amphotericin

CONCLUSION

All the compounds are air-stable and were formed in good yields with various colours ranging from brown to dark brown and grey. The compounds showed a high melting point, which indicates that they are stable. Some of them, however, decomposed before melting. The ligand is soluble in most of the solvents, while the complexes are not soluble in the solvents used. The molar conductivity of the complexes indicates that they are non-electrolytes. The ratio of amine to aldehyde in the (HL) ligand observed agrees with the 1:2 molar ratios. The IR results showed that the Schiff base coordinates with the metal ion through the phenolic oxygen and azomethine nitrogen atoms. The electronic spectral measurements of the complexes in methanol suggest the complexes to be either four or five coordinated. The stoichiometric compositions of the complexes are reported based on the microanalysis results and also the purity. The antimicrobial activity of the Schiff base ligand showed no activity against both bacteria and fungi species. On chelation with Hg(II) complex displayed activity against all the tested organisms while Pb(II) and Cd(II) complexes show no activity on the tested microorganisms these complexes are not potent antimicrobial.

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