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Synthesis, Characterization and Antimicrobial Properties of Pd(II), Cr(III), Ni(II) and Co(II) Metal Complexes of Aniline and Sulphadiazine Schiff Bases as mixed Ligands.

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ABSTRACT

Novel Pd(II), Cr(III), Ni(II) and Co(II) metal complexes of Schiff bases were synthesized from the condensation reaction between salicylaldehyde and aniline (L1) and sulphadiazine (L2). They were characterized using FTIR and UV-Visible spectroscopy and subjected to conductivity, melting point and solubility measurements. The complexes are non-toxic, non-electrolytic and stable solids. The involvement of the azomethine nitrogen in coordination with the metals was confirmed by the IR and UV results. They showed good inhibitory activities against various microorganisms.

Keywords: Aniline Schiff bases, Sulphadiazine Schiff bases, Transition metal complexes, Antimicrobial properties, Synthesis, Spectral studies.

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Introduction

Schiff bases, synthesized from aliphatic or aromatic amines and carbonyl compounds are first reported in the 19th century by Hugo Schiff [1]. The chemistry of Schiff bases has opened up discoveries in the chemical and medical industries in past and recent times. They have been used as ligands to form coordination complexes with metal ions [2-4]. Coordination compounds of sulphur, oxygen and nitrogen, mostly from Schiff bases have been reported for their antimicrobial activities [4-6]. Some transition metal complexes (TMCs) of Schiff bases derived from salicylaldehyde have been studied and reported for antitumor, antibacterial and antifungal activities [7,8]. Our earlier work reported the synthesis, characterization, antibacterial and antifungi potentials of some TMCs of Cu(II), Mn(II), Fe(II) and Zn(II)[7].

TMCs have been characterized by different techniques like the Fourier-Transform Infra-red (FTIR) spectroscopy [2,7,9], Ultra-violet/visible spectroscopy (UV-Vis) [9,10], proton and carbon-13 nuclear magnetic resonance spectroscopy (^{1}H-and ^{13}C-NMR) [8,10], thermographic analysis (TGA) [2], molar conductivity [7,11], magnetic susceptibility measurements [11] and elemental analysis [11-13]. Antimicrobial studies reveal the potency of synthesized compounds against pathogens, necessitating the search for new drugs that combat drug resistant pathogens remains ongoing [7,14].

This project was aimed at synthesizing and characterizing some TMCs of Pd(II), Cr(III), Ni(II) and Co(II) ions using sulfadiazine and aniline mixed ligands and determining the medical value of the synthesized ligands and their respective TMCs by carrying out necessary antimicrobial studies.

MATERIALS AND METHODS

All reagents and solvents [sulfadiazine, aniline, salicyaldehyde, ethanol, dionized water and the salts of Pd(II), Cr(III), Ni(II) and Co(II)] are of analytical grade and they were used as supplied without further purification.

PREPARATION OF LIGANDS

The ligand was prepared using the same methods as in Maurya and co-workers and our earlier work [2,7].

Synthesis of Schiff Base Ligand (N-Salicylideneaniline) Using Aniline and Salicyaldehyde

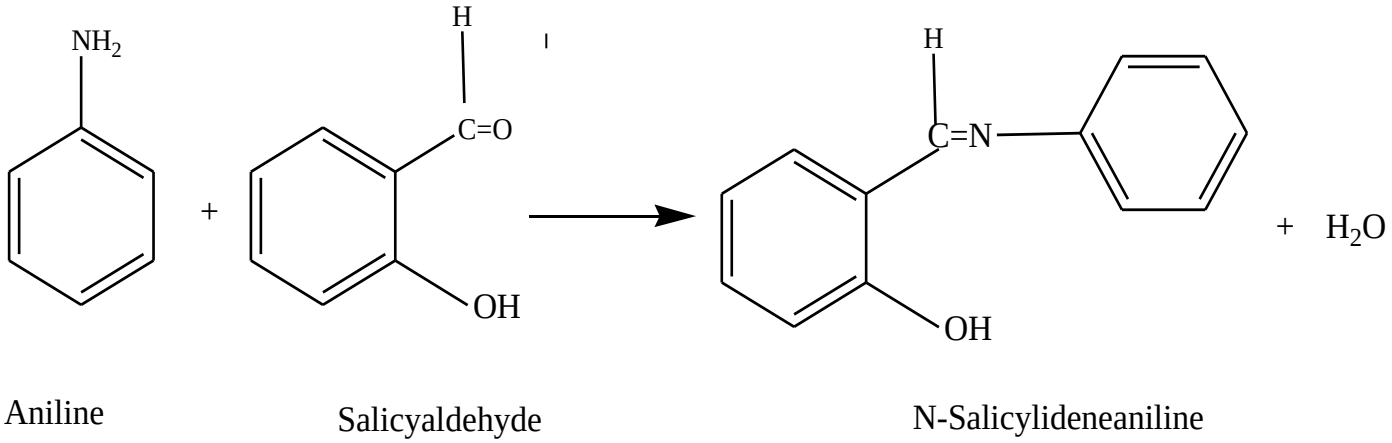

Fig. 1: Synthesis of aniline Schiff base ligand, L1

Synthesis of sulphadiazine Schiff base ligand using salicyaldehyde and sulphadiazine ligand

Equation of reaction:

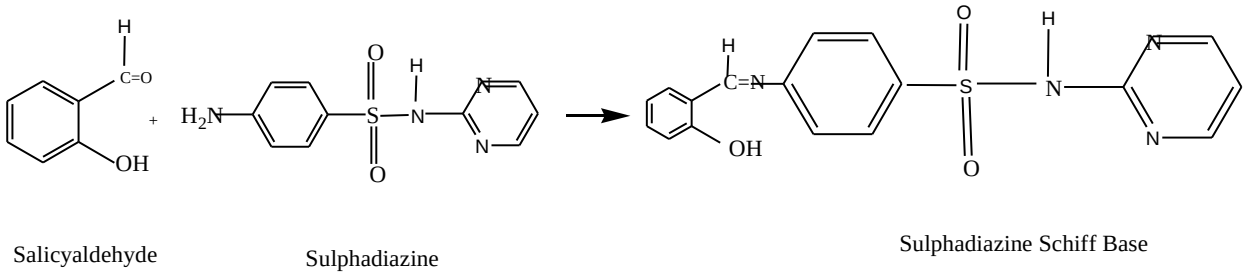

***Fig. 2: Synthesis of Sulfadiazine Schiff base ligand, L2*[7].**

Synthesis of the metal complexes

Equation of reaction:

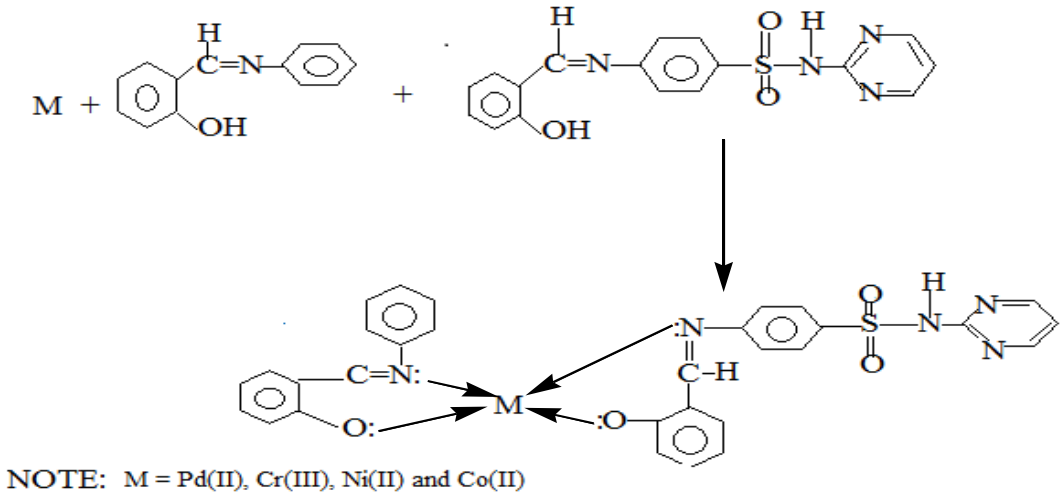

***Fig. 3: Synthesis of Metal complexes*[7].**

Evaluation of antibacterial activity

The investigated compounds were tested against *Pseudomonas aeruginosa* and *Staphylococcus aeures* etc on tables 4-7 via the disk diffusion techniques, using agar nutrient as the medium. The growths of the inoculated microorganisms were affected. The results were recorded by measuring the growth inhibition surrounding the disk.

RESULTS AND DISCUSSIONS

All synthesized ligands and their corresponding metal complexes are soluble in dimetyl sulphoxide **(**DMSO) and partially soluble in other organic solvents such as diethyl ether, hexane and methanol.

Conductivity measurement

Table 1: The conductivities and melting points of the Schiff base ligands and the metal complexes

Compound/complex	Conductivity ($\times 10^{-6}$) ($\mu seccm^{-1}$)	Melting points(ºC)
N-Salicylideneaniline (L1)	17	125
N-Salicylidenesulphadiazine(L2)	20	250
$[PdL1L2]Cl_2$	18	235-245
$K[CrL1L2(SO_4)_2]$	31	>300
$[NiL1L2]SO_4.6H_2O$	28	233
[CoL1L2]	22	255

IR spectroscopy

Table 2: IR results showing the bands of and corresponding functional groups of Schiff base ligands and metal complexes

Compound/Complex	υC=N	υC-O	$\upsilon SO_{2(as)}$	υN-H	$\upsilon SO_{2(s)}$
N-Salicylideneaniline (L1)	1613	1273	-	-	-
N-Salicylidenesulphadiazine(L2)	1618	1277	1338	3030	1187
$[PdL1L2]Cl_2$	1620	1276	1337	-	1186
$K[CrL1L2(SO_4)_2]$	1649	1260	1323	-	-
$[NiL1L2]SO_4.6H_2O$	1619	1277	1337	3030	1187
[CoL1L2]	1649	1260	1323	-	-

Electronic absorption spectra

The UV-Vis electronic spectra of the ligands and metal complexes were recorded in ethanol between 200-600 nm at room temperature. The electronic spectra of the synthesized metal complexes and the ligands are shown in Table 3.

Antimicrobial Studies

The antimicrobial studies of the ligands and their metal complexes were recorded in dimethyl sulphoxide against ten bacteria and ten fungi isolates, using Muller Hinton agar media. The results are given in the tables 4-7.

Table 3: The electronic spectra of the ligands and synthesized metal complexes and their corresponding transitions

Compound/Complex	λ_{max} value(nm)	Assignment
N-Salicylideneaniline (L1)	224	ICT
	264	π -π*
	298	π -π*
	338	n - π*
N-Salicylidenesulphadiazine (L2)	230	ICT
	270	π -π*
	344	n - π*
$[PdL1L2]Cl_2$	204	ICT
	228	π -π*
	294	n - π*
$K[CrL1L2(SO_4)_2]$	268	π -π*
$[NiL1L2]SO_4.6H_2O$	230	ICT
	270	π -π*
	344	n -π*
[CoL1L2]	268	π -π*

Table 4: Results of zones of inhibition in (mm) of the ligands and metal complexes against various bacteria isolates

Test organisms	**L1**	**L2**	$[PdL1L2]Cl_2$	$K[CrL1L2(SO_4)_2]$	$[NiL1L2]SO_4.6H_2O$	[CoL1L2]	Ampicillin	DMSO
Escherichia coli	13	10	NI	NI	10	12	15	NI
Pseudomonas aeruginosa	11	NI	NI	NI	NI	8	12	NI
Proteus vulgaris	12	9	NI	NI	9	NI	11	NI
Klebsiella pneumonia	NI	8	NI	9	11	NI	11	NI
Salmonella thypii	NI	11	NI	8	12	NI	11	NI
Bacillus cereus	NI	10	8	9	11	11	10	NI
Staphulococcus aureus	NI	13	7	9	10	10	12	NI
Streptococci feacalis	NI	12	NI	8	11	9	12	NI
Bacillus subtillis	8	10	8	8	10	11	10	NI
Staphylococcus epidermidis	14	11	6	8	11	10	9	NI

Key: NI=No inhibition, L1= N-Salicylideneaniline, L2= N-Salicylidenesulphadiazine

Table 5: Results of the zones of inhibition in (mm) of the ligands and metal complexes against various fungi isolates

Test organisms	**L1**	**L2**	$[PdL1L2]Cl_2$	$K[CrL1L2(SO_4)_2]$	$[NiL1L2]SO_4.6H_2O$	[CoL1L2]	Mycotine	DMSO
Aspergillus niger	13	15	NI	12	11	15	11	NI
Candida albicau	16	14	NI	14	12	18	15	NI
Mucor hiemalis	11	13	NI	12	9	14	11	NI
Fusarium oxysporium	11	13	9	11	9	12	9	NI
Candida krusei	14	14	NI	13	11	16	14	NI
Rhizopus stolonifer	11	12	9	11	NI	11	13	NI
Aspergillus flavus	12	11	NI	11	11	13	10	NI
Alternaria infectoria	10	11	9	12	11	9	12	NI
Aspergillus fumigutus	11	10	NI	9	12	11	11	NI
Fusarium solani	10	10	NI	12	11	12	10	NI

Key: NI=No inhibition, L1= N-Salicylideneaniline, L2= N-Salicylidenesulphadiazine

Table 6: Minimum Inhibitory Concentration (mg/ml) of the ligands and metal complexes against Bacteria

Name of test organisms	L1	L2	$[PdL1L2]Cl_2$	$K[CrL1L2(SO_4)_2]$	$[NiL1L2]SO_4.6H_2O$	[CoL1L2]	Ampicillin
Escherichia coli	10	20	NI	NI	20	20	5
Pseudomonas aeruginosa	10	NI	NI	NI	NI	20	10
Proteus vulgaris	10	20	NI	NI	20	NI	5
Klebsiella pneumonia	NI	20	NI	20	20	NI	5
Salmonella thypii	NI	20	NI	20	10	NI	5
Bacillus cereus	NI	20	20	20	10	20	5
Staphulococcus aureus	NI	10	20	20	20	20	5
Streptococci feacalis	NI	20	NI	20	20	20	5
Bacillus subtillis	20	20	20	20	20	20	5
Staphylococcus epidermidis	10	20	20	20	20	20	5

Key: NI=No inhibition, L1= N-Salicylideneaniline, L2= N-Salicylidenesulphadiazine

Table 7: Minimum Inhibitory Concentration (mg/ml) ligands and metal complexes against fungi

Name of test organisms	**L1**	**L2**	$[PdL1L2]Cl_2$	$K[CrL1L2(SO_4)_2]$	$[NiL1L2]SO_4.6H_2O$	[CoL1L2]	Mycotine
Aspergillus niger	10	10	NI	NI	20	20	10
Candida albicau	10	20	NI	NI	NI	20	5
Mucor hiemalis	20	20	NI	NI	20	NI	10
Fusarium oxysporium	20	20	NI	20	20	NI	10
Candida krusei	20	20	NI	20	10	NI	5
Rhizopus stolonifer	20	20	20	20	10	20	10
Aspergillus flavus	20	20	20	20	20	20	10
Mternaria infectoria	20	20	NI	20	20	20	10
Aspergillus fumigutus	20	20	20	20	20	20	10
Fusarium solani	20	20	20	20	20	20	10

Key: NI=No inhibition, L1= N-Salicylideneaniline, L2= N-Salicylidenesulphadiazine

DISCUSSIONS

Physical Parameters

The results suggest that the complexes are non-polar compounds, dissolve in solvents with relatively low dielectric constants. Their conductivities are appreciably low, meaning they are non-electrolytic. The Schiff base ligands are soluble in DMSO. The metal complexes are soluble in methanol and DMSO, partially soluble in hexane and diethylether, insoluble in chloroform. Their melting points are within the range of 235-300 ºC, indicating that they are all thermally stable.

Spectroscopic studies

Infra red spectroscopy

The IR spectra of the compounds were taken in the range 500-4000 cm^{-1}, in the regions of υO-H, υC=N, υN-H, υC-O, υSO_2(s and as) absorptions for symmetric and asymmetric bands, υM-N etc. vibrations. To confirm if complexation actually occurs, the IR spectra of the metal complex were compared with those of the free ligands.

The IR spectra of the ligands show an intense band in the region 1613-1618 cm^{-1}, assigned to υC=N. This band shows a shift in the spectra of all the metal complexes, indicating that azomethine nitrogen participated in coordination with metals. The elevation in stretching frequency may be due to an increase of the C=N bond order as a result of the M-N bond formation in the complexes. The bands appearing between 1520 and 1600 cm^{-1} are been assigned to aromatic υC=C while those appearing at 1323-1338 cm^{-1} have been assigned to υSO_2 asymmetric. Phenolic C-O stretching band is found in the range 1261-1277 cm^{-1}. Further evidence for bonding by nitrogen and oxygen atoms is provided by far IR spectra of complexes.

All the IR results confirm bonding between the metals and the Schiff bases through the phenolic oxygen and the imino-nitrogen, both acting as electron donors.

UV-Visible spectroscopy

The Schiff base ligand shows two type of transitions, π-π* and n-π*. These transitions are also present in the spectra of the complexes, but they shifted to lower intensity, confirming the co-ordination of the ligand to the metal ion. The lower wavelengths for the Schiff bases (204 nm-230 nm). These values were assigned to *Intra charge transfer* (ICT). The longer wavelengths (264 nm-298 nm) are assigned to π-π*. The wavelength range 338-344 nm is assigned to n-π*. The electronic absorption spectral bands of the complexes are summarized in Table 3.

Antimicrobial studies

The ligands and their metal complexes are positive against some of the selected bacteria and fungi isolates at various concentrations respectively. The two ligands and cobalt complex show high antifungal activities at MIC of 20mg/ml with three exceptions from the ligands in which their activities were at 10mg/ml. Their antibacterial activities are not as potent as their antifungal activities; L1 is active against only 5 of the bacteria, and L2 ligand against 9 bacteria isolates. [PdL1L2]Cl_2 was almost inactive against the bacteria and fungi isolates; and its zones of inhibition were low even. K[CrL1L2$(SO_4)_2$] showed low inhibition against the bacteria isolates too, in cases where it showed inhibition, of lower zones than reference drug (Ampicillin), its zones of inhibition proved active against the fungi isolates, and better than reference drug (Mycotine) with 6 of the fungi in table 5. [NiL1L2]$SO_4.6H_2O$ also inhibited most of the bacteria isolates and proved to be better than Ampicillin in 5 of them, it is active against the fungal isolates with more activities exhibited in 5 of them; more than Mycotine. [CoL1L2] is active against some of the bacterial isolates, however its antifungal activity is very strong against all of the isolates and proved to be better than Mycotine.

It is also evident that the complexes have lower antifungal activities than the free ligands, except for Co(II) complex. The highest activity from the complexes was that of the cobalt complex against *Candida albicau* (18mm), *Candida Krusei* (16mm), *Aspergillus niger* (15mm) and *Mucor biemalis* (14mm), all higher than that of the common antifungal compound (Mycotine). It also gave better inhibitory results than mycotine against most of the other fungi isolates. L1 gave better inhibitory potentials than mycotine against all the fungi except against *Rhizopus stolonifer* and *Mternaria infectoria.* L2 gave better inhibitory potentials than mycotine against all the fungi except against *Candida albicau, Rhizopus stolonifera, Mternaria infectoria* and *Aspergillus fumigutus*.

CONCLUSION

There is coordination of the bidentate Schiff base ligands to the metals through the phenolic oxygen that is deprotonated and the azomethine nitrogen. Also, the ligands coordinate to the metal complex through the same atoms, sulphate ions are still retained in the inner sphere of the metal complex causing an octahedral geometry for the complex. The new complexes are chelate complexes, hence; very stable.

Due to the strong potency of the ligands and their complexes against some of the selected test pathogens, the synthesized ligands and their metals complexes are recommended as modern-day drugs to combat drug resistant diseases or pathogens for pharmaceutical industries.

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