

Synthesis Characterisation and Antimicrobial Studies of Zr (IV) Metal Complexes of New Schiff's Base derived from 2-aminophenol

Apeksha W. Walke^a and Niren E. Kathale^b

^aResearch Scholar, Department of Chemistry, Gondwana University, Gadchiroli-442 605, Maharashtra, India.

^bAssociate Professor, Department of Chemistry, Sardar Patel Mahavidyalaya, Chandrapur-442401, Maharashtra, India.

Abstract

New zirconium (IV) complexes were synthesized and characterised with Schiff's base ligands derived from p-hydroxybenzaldehyde, 4-nitrobenzaldehyde, p-chloroacetophenone and p-dimethylaminobenzaldehyde with o-aminophenol. Metal complexes are reported and characterized on the basis of elemental analysis, IR, UV-Vis, ¹H NMR, molar conductance. The prepared schiff base ligands and metal complexes have been examined against the growth of organism in vitro to assess their antimicrobial potential. The spectroscopic and other analytical data reveals that these Schiff's bases behave as O, N donor ligands and react with Zr in a 2:1 ratio.

KEYWORDS: Schiff's base, zirconium (IV), complexes, antimicrobial.

Introduction

Schiff's bases of azomethine nitrogen donor ligands are well known due to their wide range of applications in pharmaceuticals, agriculture and industrial fields. They have been found to act as antibacterial and antifungal agents. Many Schiff base complexes are synthesized and studied by the researcher which shows its great importance in the coordination chemistry. Varieties of metal complexes have been synthesized and many symmetrical complexes have been reported in the literature. Due to wide range of application, Schiff base metal complex were found increase human interest in its studies. Many of the Schiff's base metal complexes were biologically active. Many researchers have studied the transition metal complexes. In the view of the above, in the present study, we have focused on studied complexes derived from aldehyde and ketone with O-aminophenol (M=Zr (IV)) which are synthesized. Zirconium has most stable oxidation state +4 while +2 and +3 are not so stable.

Schiff's bases are the compounds having azomethine group (-C=N-). Aldehyde and ketone in which >C=O group is present which play an important role in the formation of metal schiffs base complexes. All the four ligands behave as bidentate co-ordinating through O, N donor. These types of Schiff's bases are also reported to be used as catalyst in pharmaceutical industry, such as antibiotics, anti-inflammatory agents, and industry as anti-corrosive, while metal complexes has diverse range of application, viz. treatment of cancer, antibacterial agents, antiviral agents, fungicidal agents. It is also applicable in the treatment of cancer. Para-dimethylaminobenzaldehyde (DMAB) is used as Ehrlich's reagent which has wide range of application for analytical, biochemical for the synthetic procedures. Aldehyde moiety of para-dialkylamino substituent is highly reactive towards

compounds. However it is used as a condensation reagent, oxidizable and reducible reagent in much of the reactions.

In this paper we are studying the synthesis and characterization of schiffs base (SB3,SB4,SB5,SB6) and metal complex (MC3,MC4,MC5,MC6) with Zr(IV). Antimicrobial activity of the schiff's base and its metal complex was also studied against some pathogenic bacteria and fungi.

Materials and Methods

All the chemicals and solvents were of A.R. grade and used without further purification. Zirconium (IV) oxychloride octahydrate used as supplied from Laboratories Pvt. Ltd. P-dimethylaminobenzaldehyde is procured from LOBA CHEHIE Pvt Ltd. While 2 aminophenol is procured from S D fine-chem. Limited. All the chemicals and solvents were of AR grade and used without further purification. The UV-visible spectra were recorded on Perkin-Elmer while IR spectra were recorded on Perkin-Elmer FTIR 400 SAIF Chandigarh. ¹H NMR spectra of ligand and complex in DMSO were recorded on Bruker Avance II 400NMR spectrometer. The microanalysis of C, H and N were carried out at SAIF IIT Bombay, India. Melting points were determined in electrical melting point apparatus. The digital conductivity meter (model no.EQ 660A) was used for measuring conductivity of schiffs base and synthesized complexes.

Synthesis of schiff's bases

Synthesis of 2-[(4-Nitro-benzylidene)-amino]-phenol (3a)

The Schiff base ligand was prepared as described by Raman *et al.*, 2004. This was done by the condensation of 4 Nitro-benzaldehyde (3.02 g,10mmol) was added with 2 aminophenol (2.18g,10mmol) in 20ml hot ethanol(1:1 molar ratio). The mixture was reflux for 8 hours. Then kept in freeze for 24 hours. The bright yellow coloured solid that separated out was filtered under reduced pressure. Recrystallise with ethanol.

Synthesis of 2-[(4-Dimethylamino-benzylidene)-amino]-phenol (4a)

A MeOH (20) mL solution of p-dimethylaminobenzaldehyde (2.984 g, 10mmol) was added to a hot solution of 2 aminophenol (2.182g, 10mmol). The mixture was reflux on a water bath for 8 h and then cooled in an ice bath. The yellow solid that separated out was filtered under reduced pressure, washed several times with hot ethanol and then dried in vacuum. The precipitate so obtained was recrystallized from MeOH.

Synthesis of [(4 hydroxybenzyl)-amino]-phenol (5a)

Schiff base ligand have been synthesized by adding 4 hydroxybenzaldehyde (2.44 g,10mmol) with ethanolic solution of 2 aminophenol (2.18g,10mmol) in equimolar ratio. Stir till the entire compound dissolved completely in ethanol. Mix both ethanol solution in each other and reflux for 8h. Now, stir solution in ice-bath for 2h till the brown coloured product obtained. The brown solid that separate out was filtered under reduced pressure, washed several times with hot EtOH and dried in vacuum.

Synthesis of 2-[(4chlorophenylmethylidene)-amino]-phenol (6a)

The schiff's base ligand was synthesized by adding p-chloroacetophenone (2.58g, 10mmol) with ethanolic solution of 2 aminophenol (2.18g, 10mmol) in equimolar ratio. Stir till the entire compound dissolved completely in ethanol. Mix both ethanol solution in each other and reflux for 3h. The brown solid that separate out was filtered under reduced pressure, washed several times with hot EtOH and dried in vacuum.

Synthesis of transition metal complexes

The sample of appropriate Schiff base ligand (10mmol) was dissolved in 20 mL of absolute ethanol and to this was added a hot ethanol solution of Zr(IV) oxychloride octahydrate (0.644 g, 10mmol) in 2:1 ratio with vigorous stirring. The reaction mixture was then refluxed on a water bath for half hr and the precipitate, which separated out from their respective solutions, were filtered under reduced pressure, washed several times with with hot EtOH and dried in vacuum.

Result and Discussion

The formula of complexes from analytical data (**Table I**) should be $[M(L_2)(H_2O)]$ where $M=Zr$. All the synthesized compounds were coloured, non hygroscopic, stable at room temperature. All these metal complexes were insoluble in water, partly soluble in ethanol and freely soluble in DMSO and DMF. Molar conductance of the 10^{-3} solution of complexes was measured in DMSO at room temperature whose value is in the range $10-20 \text{ ohm}^{-1}\text{cm}^3\text{mol}^{-1}$ which indicate that the complexes are non-electrolytic in nature.

Elemental analysis

The analytical data suggest that ligand co-ordinated to central metal atom in all the complexes while metal to ligand ratio is 1:2. All complexes are mononuclear. Their empirical formula have been computed and given in **table I**.

Electronic spectra

The UV-visible spectra are often helpful in the evaluation of results furnished by other methods of structural elucidation. As expected for d^0 systems, d-d transition were not observed. Ligands shows a broad band at 360nm of $>C=N$ which is due to $\pi-\pi$ transition. In metal complexes the bonding was shifted to lower wavelength due to co-ordination of nitrogen with central metal. Complex show a broad band in the region 400-430 nm compared to ligand which may be due to the ligand to metal charge transfer transition (LMCT).

Conductivity measurement

The molar conductivity values are given in table 1. The Schiff's bases and its metal complexes were soluble in DMSO while it measured at room temperature. Table I shows that the demonstrated that the complexes have low molar conductance value in the $19-20 \text{ Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ range. The low conductance values of schiffs bases and their metal complexes indicate their non-electrolytic nature.

Infrared spectra

A bands having medium intensity is observed in the region $1590-1611\text{cm}^{-1}$ indicating $\nu(\text{>C=N})$ vibrations. This band undergoes a shift to lower frequency in the complexes, which indicates that involvement of azomethine nitrogen atom in formation of co-ordinate bond with metal atom. All ligands exhibit a band at 3337cm^{-1} indicate the presence of phenolic (O-H) group. The appearance of broad band above 3400cm^{-1} in all complexes indicates the presence of water molecule as a co-ordinated ligand. All complexes exhibit new bands in the region $450-760\text{cm}^{-1}$ which is attributed due to M-O and M-N vibrations. The details are given in **Table II**.

^1H NMR spectra

The ^1H NMR spectral data of the ligands and complexes is given in **Table-III**. The ligands exhibits multiplet at 6.76-7.16ppm due to the aromatic protons. A single band at 8.17ppm belongs to one proton of hydroxyl group (OH) which disappears in metal complex. The singlet obtained at 8.51ppm due to NH proton in the spectrum of Schiff base which shifted downfield in the spectrum of metal complexes indicating complex formation.

Biological assay

The results from biological activity studies of schiffs bases and metal complexes are represented in **Table-IV**. The synthesized schiff bases and their reactive zirconium(IV) complexes were screened in vitro for antibacterial activity against gram positive(*Staphylococcus aureus*) and gram negative(*E.coli*) bacterial strain using well diffusion technique. The test was carried out in DMSO solution at $100\mu\text{g}$ using Muller Hinton Agar (Hi-Media). Piperacillin ($100\mu\text{g}$) was used as the standard drug which show activity against *E.coli* and *S.aureus* while Carbenicillin ($100\mu\text{g}$) was used as standard antibiotic against *A. Niger*.

Conclusion

The complexes were coloured powered and were characterized using IR spectra, electronic spectra, CHN elemental analysis, NMR and molar conductance. The proposed structure according to the analyses is shown in **figure 1**. The antimicrobial activity data show that Schiff base exhibit higher activity than the metal complexes. IR spectra shows that the complexes is O,N bidentate co-ordinating via phenolic oxygen and azomethine nitrogen atom. Conductivity measurement indicates that the schiffs bases and metal complexes are non-electrolytic in nature. From the analytical data we can say that metal complexe should be octahedral.

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Table I. Analytical Data of Tetravalent Zirconium Metal Complex and Schiff Base Ligands

Ligand/ Complex	Yield %	Colour	Λ_m° (ohm ⁻¹ cm ⁻¹ mol ⁻¹)	Melting Point	Elemental analysis				
					C	H	N	O	Zr
SB 3	78	Bright yellow	13	>220 ⁰ C	64.45	4.16	11.56	19.81	-
SB 4	59	Bright yellow	19	>180 ⁰ C	74.37 (74.43)	6.71 (6.60)	11.65 (11.71)	6.65	-
SB 5	68	Brown	19	>195 ⁰ C	73.22 (65.54)	5.19 (6.49)	6.56 (13.31)	15.00	-
SB 6	72	Brown	10	>250 ⁰ C	68.43 (71.52)	4.92 (5.28)	5.70 (5.77)	6.51	-
MC 3	48	Reddish brown	17	>280 ⁰ C	51.21	3.63	9.18	20.99	14.96 (14.18)
MC 4	25	Brown	20	>240 ⁰ C	62.35 (32.80)	5.93 (3.62)	4.82 (5.19)	11.07	15.77 (15.78)
MC 5	55	Green	20	>230 ⁰ C	56.81 (32.42)	4.03 (3.33)	5.09 (5.68)	17.46	16.73 (16.59)
MC 6	93	Grey	12	>240 ⁰ C	54.53 (38.54)	4.24 (4.09)	4.54 (2.87)	10.37	14.79 (14.64)

The values in the brackets are actual values and outside the bracket are calculated theoretically.

Table-II.
IR Spectral Data (cm⁻¹) Of Zirconium Tetravalent Complex

Symbols	Phenolic $\nu(\text{O-H})$	$\nu(\text{C=N})$	Aromatic $\nu(\text{C=C})$	Aromatic $\nu(\text{C-H})$	$\nu(\text{Zr-N})$	$\nu(\text{Zr-O})$
Ligand-3	3336	1611	1542,1588	-	-	-
Complex-3	-	1600	1492	-	450	598
Ligand -4	3337	1611	1484, 1542,1588	2909	-	-
Complex -4	-	1600	1491, 1546, 1589	3094	530	450
Ligand-5	3219	1608	1582,1514,1 489,1447	2925	-	-
Complex-5	-	1604	1516,1585	2931	761	699
Ligand-6	-	1600	1511.1	3019	-	-
Complex- 6	-	1592	1492.5	3064	510	440

Table III
NMR Spectral Data Of Zirconium Tetravalent Complex

Sr. No.	Symbols	Types of Proton	Chemical shift in ppm (δ)
1.	Ligand-3	Ar-OH Ar-H N=C-H	8.50ppm 6.76-7.16ppm 8.50ppm
2.	Complex-3	Ar-H N=C-H Ar-NO ₂	6.78-7.18ppm 8.52ppm 9.67ppm
3.	Ligand -4	Ar-OH Ar-H N=C-H N-(CH ₃) ₂	8.71 ppm 6.76-7.16 ppm 8.51 ppm 3.03 ppm
4.	Complex-4	Ar-H N=C-H CH ₃	6.76-7.16 ppm 7.68ppm 3.38ppm
5.	Ligand-5	Ar-OH(ortho) Ar-H N=C-H Ar-OH(para)	8.80ppm 6.79-7.15ppm 8.55ppm 10.09ppm
6.	Complex-5	Ar-H N=C-H	6.79-7.20ppm 8.60ppm
7.	Ligand -6	Ar-H	6.40-6.68ppm

		N=C-H	8.97ppm
8.	Complex – 6	Ar-H	4.56ppm
		N=C-H	8.95ppm

Table IV
Antimicrobial Activity Of Zirconium Tetravalent Transition Metal Complexes

Sr.no.	Compound	Conc(mg)	Control (DMSO)	Zone of Inhibition (mm)		
				Escherichia coli	Staphylococcus aureus	Aspergillus niger
	Ligand 3	100	-	11	10	12
	Complex 3	100	-	13	13	10
	Ligand 4	100	-	24	12	10
	Complex 4	100	-	28	14	19
	Ligand 5	100	-	12	12	13
	Complex 5	100	-	18	11	10
	Ligand 6	100	-	10	17	21
	Complex 6	100	-	11	13	23

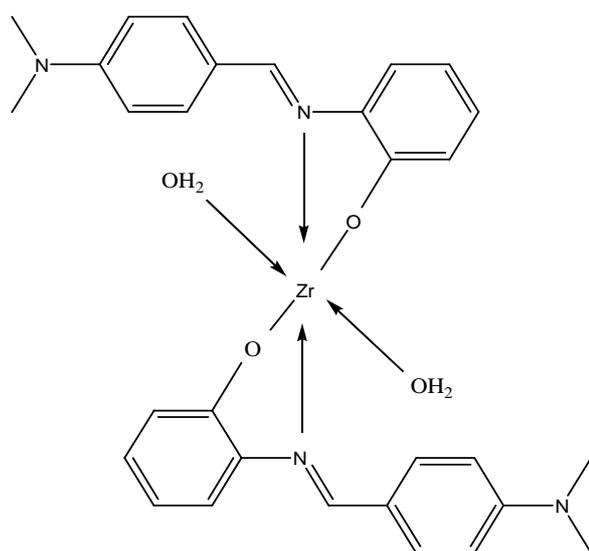


Fig.1.: Proposed structure of the Zr (IV) metal complex