SYNTHESIS CHARACTERISATION AND ANTIMICROBIAL ACTIVITY OF ZR(IV) METAL COMPLEX HAVING O,N DONOR LIGANDS

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ABSTRACT

New zirconium(IV) complexes were synthesized and characterised with schiff's base ligands derived from p-hydroxybenzaldehyde, p-dimethylaminobenzaldehyde with o-aminophenol.Metal complexes are reported and characterized based on the basis of elemental analysis, IR,UV-Vis, 1H NMR, molar conductance.The prepared schiffs base ligand and metal complexes has been examined against the growth of organism in vitro to assess their antimicrobial potential$_{49}$.The spectroscopic and other analytical data reveals that these schiff's bases behave as O,N donor ligands and react with [Zr(L2)H2O] in a 2:1 ratio.

Keywords: Schiffs base, zirconium (IV), complexes, antimicrobial.

Introduction

Schiffs bases of azomethine nitrogen donor ligand 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.In the present study we studied complexes derived from aldehyde and ketone with O-aminophenol (M=Zr(IV)) which are synthesized.. Aldehyde and ketone in which > C=O group is present which play an important role in the formation of metal schiffs base complexes. Two ligands behave as bidentate co-ordinating through O,N donor. These type of Schiffs bases are also reported to be used as catalyst in pharmaceutical industry, such as antibiotics, anti-inflammatory agents, industry as anti-corrosive. While metal complexes has diverse range of application for their metal complexes 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 proceduresThis paper review the synthesis and characterization of schiffs base(ligand 4,ligand 6) and metal complex(metal 4,metal 6) with Zr(IV). Antimicrobial activity of the schiffs base and its metal complex was also screened against some pathogenic bacteria and fungi.

Experimental

All the chemicals used were of A.R.Grade. Zirconium (IV) oxychlorideoctahydrate used as supplied from Laboratories Pvt. Ltd. Para-dimethylaminobenzaldehyde is procured from LOBA CHEMIE Pvt Ltd. While 2 aminophenol is procuredfromS 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.[1]H NMR spectra of ligand and complex in DMSO were recorded on BrukerAvancell 400 NMR spectrometer. The microanalysis of C,H and N were carried out at SAIF IIT Bombay, India. Melting point 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 2- [(4-Dimethyl amino-benzylidine) -amino]-phenol(Ligand 4)

A MeOH (20) mL solution of p-dimethylamino benzaldehyde (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 vaccum. The precipitate so obtained was recrystallized from MeOH.

Synthesis of 2-[(4chlorophenylmethylidine)-amino]-phenol(Ligand 6)

The schiffs base ligand was synthesized by adding p-chloroacetohenone(2.58g,10mmol) with ethanolic solution of 2 aminophenol (2.18g,10mmol) in equimolar ratio. Stir till all the 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 vacccum.

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 ethanolic solution of Zr(IV) oxychlorideoctahydrate (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 vaccume.

Result And Discussion

The formula of complexes from analytical data (Table 1) should be $[M(L_2)H_2O]$ where M=Zr. All the synthesized compounds were coloured, non hydroscopic, 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 complexes was measured in DMSO at room temperature whose value in the range 10-20 $ohm^{-1}cm^3mol^{-1}$ 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 is1:2. All complexes are mononuclear. Their empirical formula have been computed and given in table 1.

Table1

Ligand/ Complex	Yield	Colour	Molecular formula	Molecular Weight	Melting point	Elemental analysis				
						C	H	N	O	Zr
Ligand 4	59%	Bright yellow	$C_{15}H_{16}N_2O$	240	>180^{0}C	74.37 (74.43)	6.71 (6.60)	11.65 (11.71)	6.65	-
Ligand 6	72%	Brown	$C_{14}H_{12}ONCl$	245	250^{0}C	68.43 (71.52)	4.92 (5.28)	5.70 (5.77)	6.51	-
Complex 4	25%	Brown	$C_{30}H_{34}N_2O_4Zr$	577	>240^{0}C	62.35 (32.80)	5.93 (3.62)	4.82 (5.19)	11.07	15.77 (15.78)
Complex 6	93%	Grey	$C_{28}H_{26}N_2O_4Cl_2Zr$	617	>240^{0}C	54.53 (38.54)	4.24 (4.09)	4.54 (2.87)	10.37	14.79 (14.64)

Conductivity measurement

The molar conductivity values are given in table.2. The schiffs bases and its metal complexes were soluble in DMSO while it measured at room temperature. Table shows that the demonstrated that the complexes have low molar conductance value in the 19-20Ohm$^-$

^{1} cm^2mol^{-1} range.The low conductance values of schiffs bases and their metal complexes indicate their non-electrolytic nature.

Table 2

Compound	Molar conductance $Ohm^{-1} cm^2mol^{-1}$
Ligand 4	19
Ligand 6	10
Complex 4	20
Complex 6	12

Infrared spectra

A group of three bonds having medium intensity observed in the region 1590- 1611cm^{-1} indicating υ(>C=N) vibrations.This band undergoes a shift to lower frequency in the complexes, indicates that involvement of nitrogen atom with metal atom. Ligands exhibit a band at 3337cm^{-1} indicate the presence of phenolic υ(O-H) group. The appearance of broad band above 3400 cm^{-1} in all complexes indicates the presence of water molecule as a co-ordinated ligand. All complexes exhibit a new bands in the region 450-760 cm^{-1} have assigned to M-O and M-N vibrations.

Table (3)

Symbols	Phenolic υ(O-H)	υ(C=N)	Aromatic υ(C=C)	Aromatic υ(C-H)	υ(Zr-N)	υ(Zr-O)
Ligand –4	3337	1611	1484, 1542,1588	2909	-	-
Complex -4	-	1600	1491, 1546, 1589	3094	530	450
Ligand-6	-	1600	1511.1	3019	-	-
Complex- 6	-	1592	1492.5	3064	510	440

^{1}H NMR spectra

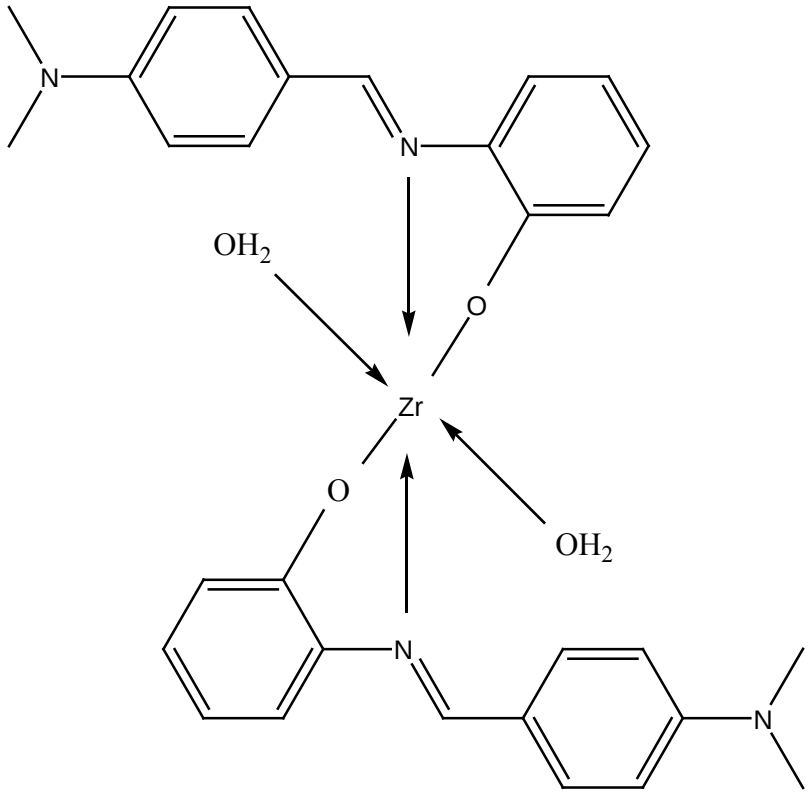
The ^{1}H NMR spectra data (Table-4) of the ligands exhibits multiplate at 6.76-7.16ppm due to the aromatic protons. A single band at 8.17ppm belong to one proton of hydroxyl group(OH) which disappears in metal complex . The singlet obtained at 8.51ppm due to >C=N group in the spectrum of Schiff base which shifted downfield in the spectrum of metal complexs.

Table (4)

Sr. No.	Symbols	Types of Proton	Chemical shift in ppm (δ)
1.	Ligand -4	Ar-OH	8.71 ppm
		Ar-H	6.76-7.16 ppm
		N=C-H	8.51 ppm
		N-$(CH_3)_2$	3.03 ppm
2.	Ligand -6	Ar-H	6.40-6.68ppm
		N=C-H	8.97ppm
3.	Complex -4	Ar-H	6.76-7.16 ppm
		N=C-H	8.60 ppm
		CH_3	3.38 ppm
4.	Complex - 6	Ar-H	4.56ppm
		N=C-H	8.95ppm

Electronic spectra

The UV-visible spectra are often helpful in the evaluation of results furnished by other methods of structural elucidation. As expected for $4d^0$system, d-d transition were not observed. Ligands shows a broad band at 360nm of>C=N which is due to π-π 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).



Structure of Zr(IV) metal complex

Biological assay

The results from biological activity studies of schiffs bases and metal complexes are represented in (Table-5).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 100µgusing Mullar Hinton Agar (Hi-Media).Piperacillin (100µg) was used as the standard drug which show activity against E.coli and S.aureus while Fluconozole (100µg) was used as standard antibiotic against A. Niger.

Table 5

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

Conclusion

The complexes were coloured powered and were characterized using IR spectra, electronic spectra, CHN elemental analysis, NMR and molar conductance.rom the antimicrobial activity data show that Schiff base exhibit higher activity than the metal complexes.IR spectra shows that the complexes is O,Nbidentate co-ordinating via phenolic oxygen and azomethine nitrogen atom.Conductiviy 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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