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RESEARCH ARTICLE

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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES OF 2-[(2-HYDROXY-5-NITRO BENZYLIDENE)-AMINO]-4-METHYL-PHENOL WITH Ti(IV) AND Zr(IV) COMPLEXES

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ABSTRACT

A new Schiff base derived from 2-amino, 4-methyl phenol with 5-nitro salicylaldehyde (AMPNSA) and their Ti(IV) and Zr(IV) metal complexes. The metal chelates were characterized on the basis of infrared spectra, elemental analysis, electronic spectral data, conductance and ¹H NMR spectral analysis. The complexes confirm to 1:1 stoichiometry and are electrolyte in nature. The coordination of the ligand to the metal ions is found to be through azomethine nitrogen, phenoxide oxygen and phenolic – OH of the Schiff base in the octahedral environment. The Schiff base and its metal complexes have been tested for their antimicrobial activity using disc diffusion methods and the results discussed.

KEYWORDS

Schiff base, Metal complexes, Spectral studies and Anti-microbial activity.

INTRODUCTION

Transition metal complexes with Schiff base as ligand have been amongst the widely studied coordination compounds in the past few years, since they are found to be widely applicable in many fields such as biochemical¹, analytical² and antimicrobial fields³.

Schiff base ligand formed from salicylaldehyde or substituted salicylaldehyde with various aromatic amines⁴⁻⁵. They have actively associated with antibacterial⁶, antifungal⁷, antitubercular⁸ and anticancer activities⁹.

Our purpose was to synthesize metal chelates of 2-[(2-Hydroxy-5-nitrobenzylidene)-amino]-4-methyl-phenol with Ti(IV) and Zr(IV) metal ions.

MATERIALS AND METHODS

All the chemicals and solvents used were A.R. grade. All the metals were used as their chloride salts. Elemental analysis was done on instrument Egar-300 analyzer. Infrared and UV spectra were recorded on Perkin Elmer spectrum 100 and UV-Vis spectro photometer 119 in the 200-1000 nm range in DMF solution (10^{-3}). Conductance of the metal complexes was determined in DMF on conductivity meter Equip-tronics model No-EQ665. Melting points were recorded by open capillary method and are uncorrected. ¹H-NMR spectra of Schiff base and its metal complexes recorded on Bruker 300 MHz spectro meter in DMSO-d₆.

In our present studies we have conducted some microbial activity to see whether chelating agent (Schiff base) and metal complexes have any action on microbial activities. Bacteria species like Escherichia coli, Bacillus subtilis, Aspergillus flavus and Aspergillus niger.

Synthesis of Schiff base

The Schiff base were prepared by condensing of 2-amino, 4-methyl phenol and 5-nitro salicylaldehyde in ethanol by refluxing on water bath for two to three hours in presence of 2-3drops of glacial acetic acid. The reaction mixture were poured in crushed ice, where by brown orange precipitate was obtained. It was suction filtered, washed with distilled water and ethanol.

Then it is dried in vacuum dessicator. The pure Schiff base was recrystallized from ethanol. The purity of the Schiff base was checked by TLC. Further the structure of Schiff base was confirmed by subjecting them to infrared spectra, elemental analysis and NMR spectra.

Synthesis of Metal Complexes

To warm ethanolic solution of AMPNSA (0.01M) and ethanolic solution of the corresponding metal chloride (0.01M) in the ratio 1:1 were added drop wise with constant stirring. The P^H of the solution was adjusted in the range of 6.8 to 7.1 by adding alcoholic ammonia. The reaction mixture was refluxed for four hours on water bath. The dark reddish brown precipitate appeared at the end was digested, separated by filtration washed with warm alcohol. The complexes is dried in vacuum at room temperature and stored in a glass bottle.

RESULTS AND DISCUSSION

All the metal complexes were intense coloured, they were soluble in DMF, DMSO. All the results of elemental analysis are given in the table. For the estimation of chloride by

Volhard's method is used¹⁰, metal ion percentage is determined by standard method¹¹.

Presence of lattice water molecules present in the metal complexes was recorded by keeping the known weight of the complex in previously weighed crucible in oven at 110°C for one hour. The difference in weight gives the amount of lattice water in the complexes.

All compounds give satisfactory elemental analysis. Values are in close agreement with the values calculated for expected molecular formulae assigned to these complexes, suggesting 1:1 for Ti(IV) and Zr(IV) complexes. The molar conductance of Ti(IV) and Zr(IV) complexes in DMF reveals their electrolytic nature¹²⁻¹³

Table-1
Analytical data and other physical properties of (AMPNSA) ligand and metal complexes.

Ligand / Metal Complex Empirical Formula	Mol. Wt. Colour/ D.P.°C	M:L Ratio/Yield (%)	Molar Cond. (Ohm ⁻¹ cm ² mol ⁻¹)	Elemental analysis % Cal (Obs)				
				C	H	N	M	Cl
AMPNSA C ₁₄ H ₁₂ N ₂ O ₄	272.72 Brown Orange (166)	- 88	-	61.60 (60.05)	4.40 (4.32)	10.26 (10.31)	-	-
[Ti(AMPNSA)H ₂ O.Cl ₂]Cl.H ₂ O Ti(C ₁₄ H ₁₅ N ₂ O ₆ Cl ₃)	461.40 Dark reddish brown (>300)	1:1 69	65	36.41 (36.11)	3.25 (3.04)	6.06 (6.19)	10.38 (10.26)	23.08 (22.79)
[Zr(AMPNSA)H ₂ O.Cl ₂]Cl.2H ₂ O Zr(C ₁₄ H ₁₇ N ₂ O ₇ Cl ₃)	522.72 Yellow (275)	1:1 57	50	32.13 (32.29)	3.25 (3.17)	5.35 (5.08)	17.45 (17.33)	20.37 (20.03)

The UV electronic spectra of Ti(IV) and Zr(IV) complexes indicates, the transition is shifted towards higher or lower frequencies which confirm the coordination of the ligand to the metal ions. Also, electronic spectra of Ti(IV) and Zr(IV) complexes display absorption band at 24154cm⁻¹, 23391cm⁻¹ assigned ligand to metal charge transfer band¹⁴.

The IR spectra of the free ligand AMPNSA shows a band in the region 3090cm⁻¹ due to ν (OH) stretching vibration. This band is disappeared in the complexes, indicating deprotonation of this group¹⁵. Similarly a band observed around 1389cm⁻¹ is due to the bond bending vibration of -OH group shifted at 1378cm⁻¹ to 1379cm⁻¹ in Ti(IV) and Zr(IV) complexes, suggesting the involvement in metal

coordination. This is further reflected by the appearance of phenolic ν (C-O) at 1269cm⁻¹ in ligand. This band in the complexes was shifted to higher stretching frequency¹⁶. Further, the band observed at 1625cm⁻¹ due to ν (C=N) azomethine group in ligand is shifted towards lower frequency by 15-20cm⁻¹ in the spectra of complexes indicate, that azomethine group involved in coordination with metal ion¹⁷.

New broad bands at 3418cm⁻¹ Ti(IV) complex and 3421cm⁻¹ in Zr(IV) complex indicate the presence of coordinated water molecules¹⁸⁻¹⁹. The new bands found in the spectra of Ti(IV) and Zr(IV) metal ion complexes at 530-535cm⁻¹ and 595-610cm⁻¹ due to new bonding i.e, ν (M-N)²⁰ and ν (M-O)²¹⁻²².

Table-2
Infrared spectral data of ligand (AMPNSA) and their metal complexes.

Compounds	$\nu(\text{H}_2\text{O})$	$\nu(\text{OH})$	$\nu(\text{OH})$	$\nu(\text{C-O})$	$\nu(\text{CH=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
AMPNSA	-	3090	1389	1269	1625	-	-
[Ti(AMPNSA)H ₂ O.Cl ₂] Cl.H ₂ O	3418	-	1378	1285	1610	535	610
[Zr(AMPNSA)H ₂ O.Cl ₂] Cl.2H ₂ O	3421	-	1379	1309	1605	530	595

The ¹H-NMR spectrum of the ligand AMPNSA indicated signals at δ 2.23ppm (s) for methyl protons, δ 6.8-7.59 (m, 7H) due to aromatic protons, δ 8.10ppm (s, 1H) for azomethine proton, δ 9.41 (s, 1H) Ar-OH²³ and δ 13.30 (s, 1H) for Ar-OH.

In Ti(IV) and Zr(IV) complexes phenolic –OH peak have been shifted to down field at δ 9.78ppm and δ 9.93ppm respectively. A signal corresponding to azomethine in free ligand at δ 8.10ppm is shifted to down field region in metal

complexes²⁴. The disappearance of peak at δ 13.30 ppm due to phenolic OH may be attributed to deprotonation of this group on involvement in bonding²⁵.

A new peak observed at δ 2.0ppm in Ti(IV) and Zr(IV) complexes due to corresponding coordinated water molecules²⁶. Thus, AMPNSA molecule seems to be coordinated to the metal ions through azomethine nitrogen, phenoxide oxygen and phenolic –OH.

Proposed structural formulae of the investigated metal complexes:

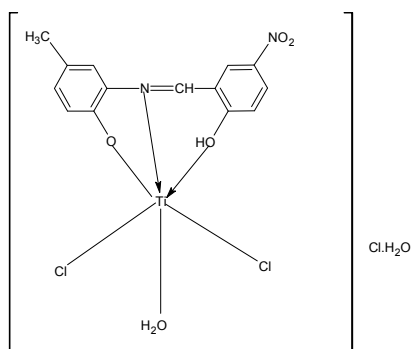


Figure 1

On the basis of the above observation it is, therefore, proposed that [Ti(IV) AMPNSA] and [Zr(IV) AMPNSA] complexes shows octahedral geometry in which ligand is uninegative tridentate in nature.

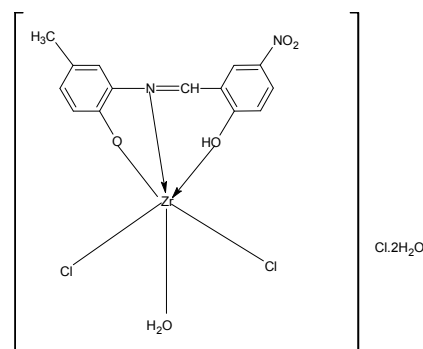


Figure 2

Antimicrobial Activity

The ligand (AMPNSA) and their [Ti(IV) AMPNSA] and [Zr(IV) AMPNSA] complexes antimicrobial tests were performed by the standard disc diffusion method²⁷. The antibacterial and antifungal activity is found in vitro against Escherichia coli, Bacillus subtilis, Aspergillus flavus and Aspergillus niger.

Table No.3
Result of antibacterial study of Ti(IV) and Zr(IV) complexes

Sr. No.	Compounds	Escherichia coli	Bacillus subtilis
1	AMPNSA	8 mm	6 mm
2	[Ti(IV) AMPNSA]	-ve	-ve
3	[Zr(IV) AMPNSA]	-ve	6 mm
4	Streptomycin	24 mm	30 mm
5	Control (DMSO)	10 mm	14 mm

-ve –No antibacterial activity, zone of inhibition -----mm.

Table No.4
Result of antifungal study of Ti(IV) and Zr(IV) complexes

Sr. No.	Compounds	Aspergillus flavus	Aspergillus niger
1	AMPNSA	6 mm	-ve
2	[Ti(IV) AMPNSA]	-ve	-ve
3	[Zr(IV) AMPNSA]	-ve	-ve
4	Fluconazole	15 mm	10 mm
5	Control (DMSO)	-ve	-ve

-ve –No antifungal activity, zone of inhibition -----mm.

After observing the petridish and zone of inhibition towards metal complexes shows that only [Zr(IV) AMPNSA] complex have very less zone of inhibition towards Bacillus subtilis. But [Ti(IV) AMPNSA] metal ion complex have negative zone of inhibition.

2-[(2-Hydroxy-5-nitrobenzylidene)-amino]-4-methyl-phenol (AMPNSA) produces zone of inhibition 6 mm for Aspergillus flavus. Aspergillus niger does not form zone of inhibition. The result indicates that Ti(IV) and Zr(IV) metal complexes do not form zone of inhibition towards

Aspergillus flavus and Aspergillus niger indicating negative antifungal activity.

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