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RESEARCH ARTICLE

DESIGN AND SYNTHESIS OF ZINC(II) COMPLEXES WITH SCHIFF BASE DERIVED FROM 6-AMINOPENICILLANIC ACID AND HETEROCYCLIC ALDEHYDES

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Abstract

Reaction of Zinc(II) acetate with Schiff's bases derived from the condensation of benzaldehyde or indole-3-carboxyaldehyde with (2S,5R,6R)-6-Amino-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid (6-Aminopenicillanic Acid) in 1:1 molar ratio gave a new series of Zinc(II) complexes. The coordination behavior of Schiff's bases towards Zinc atom has been investigated by elemental analysis, conductance measurements, molecular weight determinations, IR, UV and ¹H NMR spectral studies.

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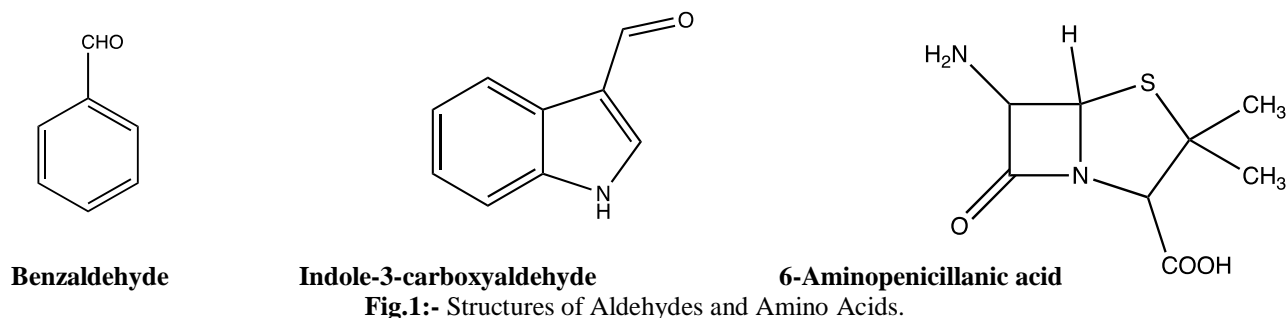
Introduction:-

The Schiff's bases derived from the condensation of amino acids with the carbonyl compounds constitute another series of ligand with-NH donor system and their metal complexes have been studied with intense interest [1-6]. It was therefore, considered of interest to synthesize Zn(II) derivatives of Schiff bases derived by the condensation of benzaldehyde and indole-3-carboxyaldehyde with amino acids. In this paper, we are communicating the results of these studies. The structures of the starting materials are shown in fig. 1. Research has been done in which a novel heterocyclic methyl-substituted pyridine Schiff base transition metal complexes of various metal complexes designed and synthesized by reacting their metal acetates with the heterocyclic ligand. All newly synthesized metal complexes were characterized by spectroscopic data and screened for elemental analysis, IR, ESR, magnetic susceptibility which indicated square planar and octahedral geometry with (N, H) group acting as a bidentate ligand. Their antimicrobial and antioxidant activities of synthesized metal complexes indicates moderate to good results [7]. The condensation of nicotinohydrazide with various heterocyclic aldehydes, followed by metalation with Co (II) and Cu (II) metal ions, has resulted in a new family of heterocyclic Schiff base complexes. Elemental analysis, Fourier transform infrared spectroscopy, proton nuclear magnetic resonance, ultraviolet-visible spectroscopy, and magnetic susceptibility were used to analyze the chemical structures of the produced compounds. The chemical structures of Cu (II) and Co (II) complexes were validated by spectral and magnetic data, and the geometry of Cu (II) and Co (II) complexes was square planar or deformed tetrahedral. The crystalline structures of the metal complexes were supported by X-ray diffraction measurements rather than the amorphous form of the parent Schiff bases. Thermogravimetric research found that metal complexes have improved heat stability over their Schiff base ligands. The antimicrobial efficacies of the Schiff base ligands and their metal complexes were tested against Gram-positive bacteria such as *Staphylococcus aureus* and *Bacillus subtilis*, Gram-negative bacteria such as *Escherichia*

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coli and *Proteus vulgaris*, and fungi such as *Aspergillus flavus* and *Candida albicans*. The antimicrobial inhibitory data demonstrated that metal complexes have stronger antibacterial activity than their Schiff base ligands.

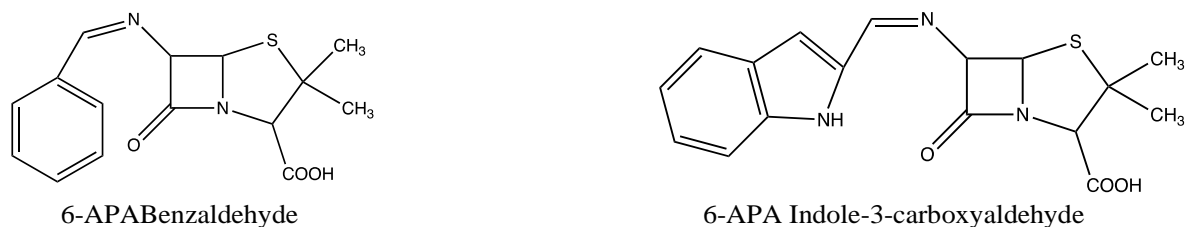


Experimental

The entire chemicals used in this work are of AR grade, the solvents were dried by standard method and all reactions were carried out under an anhydrous and oxygen free atmosphere.

Synthesis of ligands

The Schiff's bases were synthesized by the condensation of benzaldehyde and indole-3-carboxyaldehyde with (2*S*,5*R*,6*R*)-6-Amino-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid (6-aminopenicillanic Acid) in 1:1 molar ratio using methanol as the reaction medium and were then refluxed for 6h. On cooling, crystals of the Schiff bases separated out which were washed with methanol. These were dried and recrystallized from acetone. The structures of ligands prepared are shown below in Fig.2. The main characteristics and analysis of these Schiff bases were recorded in Table 1.



Synthesis of Zinc(II) Complexes

The ligand with Zinc (II) acetate were mixed in 1:2 molar ratio in methanol as the reaction medium. The contents were refluxed for 6-8 hours and the progress of the reaction was monitored by the estimation of acetic acid in the azeotrope. The solvent was removed and the products were washed many times with dry cyclohexane followed by drying in vacuo. The main characteristics and analysis of these compounds were recorded in Table 2. Reaction of Zinc(II) acetate with the ligands and methanol in 1:2 molar ratio may be represented as follows:



Where $\sim\text{NH}$ represent the bi-functional tridentate Schiff base ligand. The resulting complexes are colored solids (Table 2), which are soluble in DMSO and DMF. These are however susceptible to moisture and aerial oxidation. The conductance values of the synthesized compounds were below $50 \text{ Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$, indicating their non-electrolytic nature⁹⁻¹¹. Their monomeric nature was indicated by the Rast Camphor Method, which also determines the molecular weight of the complexes.

Results and discussion:-

IR Spectra

On comparing the IR spectra of the ligands as well as their corresponding Zinc complexes, it can be concluded that the chelate formation takes place through the oxygen and nitrogen of the ligand moieties. In the infrared spectra of the ligands, medium intensity bands appearing in the region, $\sim 3300 \text{ cm}^{-1}$ was

assigned to the hydrogen bonded ν OH vibrations¹²⁻¹⁴, which disappear in the resulting complex suggesting the possible deprotonation on complexation and the formation of Zn-O bond.

All the ligands display sharp and strong band in the region, 1610-1625 cm^{-1} and which is due to the ν C=N stretching frequency in the free ligands¹⁵. It gets shifted to the lower frequency region ($\sim 10 \text{cm}^{-1}$) in the spectra of complexes. The lowering in the frequency may be attributed to the decrease in the C=N bond order as a result of Zn-N bond formation. The low frequency region of the spectra indicated the presence of two new medium intensity bands at about 450 cm^{-1} to 470 cm^{-1} due to $\nu_{\text{M-O}}$ vibrations and at 530 cm^{-1} to 550 cm^{-1} due to $\nu_{\text{M-N}}$ vibrations¹⁶⁻¹⁷.

A strong band at $\sim 1280 \text{cm}^{-1}$ in the ligands may be due to the phenolic C-O stretching vibrations. In the resulting complexes, a shift of this band to the higher frequency ($\sim 1300 \text{cm}^{-1}$) indicates the bonding of the ligand through the phenolic oxygen.

In addition, the formation of Zinc complex with methanol, a sharp band at 1600 cm^{-1} was observed due to ν C=N vibration.

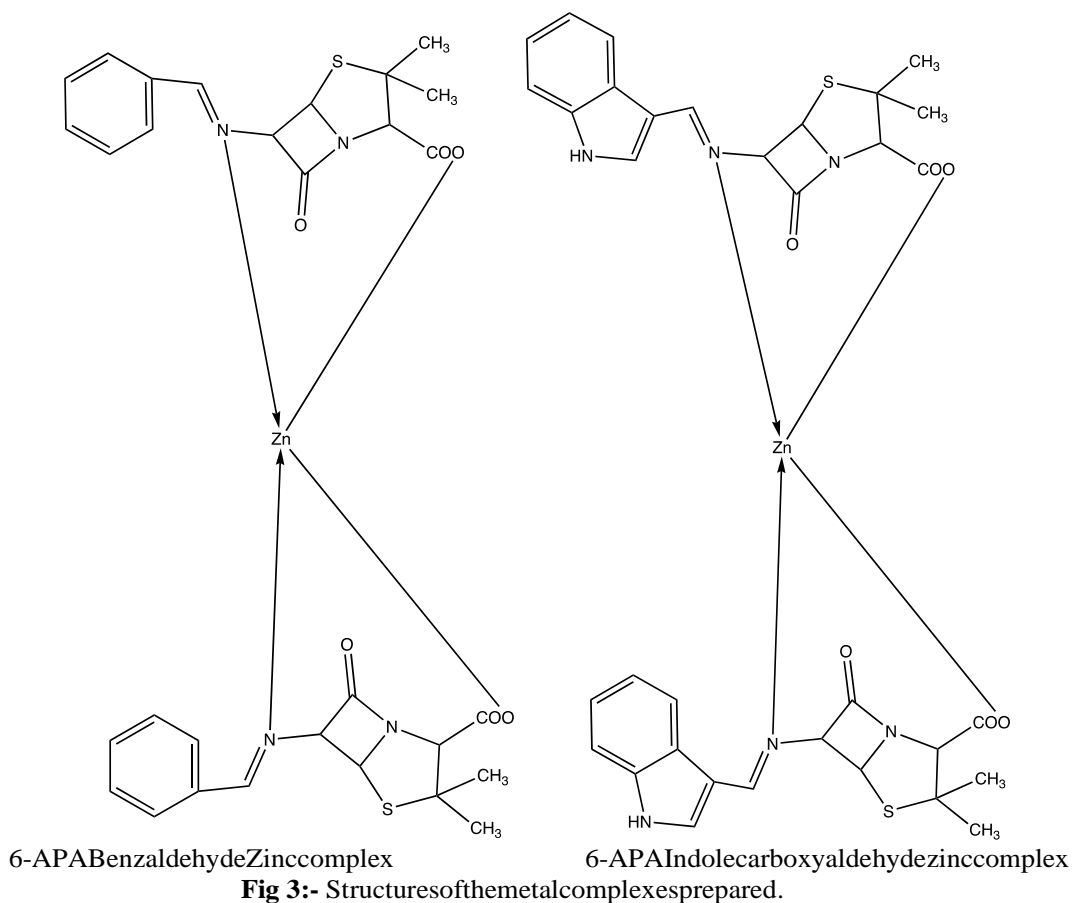
¹H NMR Spectra

The diamagnetic nature of Zn(II) metal complexes made possible to scan ¹H NMR spectrum in DMSO-*d*⁶. Diamagnetic zinc metal complexes do not interfere in magnetic field of NMR instrument whereas paramagnetic does interfere in magnetic field of NMR instrument. The spectrum of ligands exhibit -OH proton signal at $\delta 3.70$ ppm and the -COOH proton signals at $\delta 11.00$ ppm, respectively. These absorptions disappear in the corresponding metal complexes. In the case of the ligand, the proton signal for the azomethine proton signals at $\delta 8.80$ ppm shifts downfield in the spectra of the corresponding metal complexes due to the formation of a coordinate linkage between the nitrogen and metal atom. The ligand shows a complex multiplet signal in the region at $\delta 7.65$ to $\delta 6.80$ ppm for the aromatic protons and it remains in almost the same position [-CH₂, -CH(CH₃)₂, -CH(CH₃)-CH₂-CH₃ at $\delta 3.2$ ppm, $\delta 2.8$ ppm and $\delta 1.45$ - $\delta 3.15$ ppm in the metal complexes respectively.

Electronic Spectra

The electronic spectra of ligands and their Zinc complexes have also recorded in DMF. The spectra of ligands show broadband at $\sim 370 \text{nm}$ and $\sim 350 \text{nm}$ and which can be assigned to n- π^* transition of azomethine group. This band shifts in the Zinc complexes and appears at $\sim 415 \text{nm}$ and $\sim 400 \text{nm}$ respectively indicating the coordination of azomethine nitrogen to Zinc atom.

On the basis of spectral data and element analysis the following structure can be assigned to these newly synthesized derivatives as shown below:



Measurements:-

Nitrogen was estimated by Kjeldahl's method. The complexes were analyzed as reported earlier¹². The infrared spectra were recorded on a Perkin-Elmer-577 spectrophotometer in the region 4000 – 667 cm^{-1} using KBr disks. A Perkin-Elmer Mode RB-12 spectrometer was used for obtaining the PMR spectra employing DMSO- d_6 as the solvent and TMS as internal standard. Molar conductance measurements were made in anhydrous

DMF at $36 \pm 1^\circ\text{C}$ using a systronic conductivity bridge model. Molecular weight determinations were carried out by the Rast camphor method.

Table 1:- Elemental analysis of Ligands.

Sr. No.	Name of the Ligand (Molecular formula)	Molecular Weight	Melting Point ($^\circ\text{C}$)	Colour of the ligand	% of carbon found (Calc.)	% of hydrogen found (Calc.)	% of nitrogen found (Calc.)	% of oxygen found (Calc.)	% of sulphur found (Calc.)
01	6-APA	304.34	118	Light	59.19	5.30	9.20	15.77	10.53
	Benzaldehyde ($\text{C}_7\text{H}_6\text{O}$)			Yellow	(58.94)	(5.26)	(9.03)	(15.65)	(10.49)
02	6-APA	343.37	162	Light	59.46	4.99	12.24	13.98	9.34

	Indolecarboxy			Green	(59.37)	(4.85)	(12.04)	(13.45)	(9.02)
	aldehyde								
	(C ₁₇ H ₁₇ N ₃ O ₃ S)								

Table2:- Elemental Analysis of Zinc(II) complexes.

Sr. No.	Name of the Complex (Molecular formula)	Molecular Weight	Melting Point (°C)	Colour of the complex	% of carbon (Calc.)	% of hydrogen (Calc.)	% of nitrogen (Calc.)	% of oxygen (Calc.)	% of sulphur (Calc.)	% of Zinc (Calc.)
01	6-APA Indolecarboxy aldehyde Zinc Complex (C ₃₄ H ₃₂ N ₆ O ₆ S ₂ Zn)	750.17	210	Brown	54.44 (54.03)	4.30 (4.07)	11.20 (11.09)	12.80 (12.56)	8.55 (8.12)	8.25 (8.12)
02	6-APA Benzaldehyde Zinc Complex (C ₃₀ H ₃₀ N ₄ O ₆ S ₂ Zn)	670.09	154	Light Brown	53.61 (53.11)	4.50 (4.44)	8.34 (8.04)	14.28 (14.02)	9.54 (9.01)	9.73 (9.42)

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