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BIS(Cyclopentadienyl)Titanium (IV) Derivatives With schiffbases Derived from 4-Amino-3-HYDRAZINO-6-METHYL-5-OXO-1,2,4-TRIAZINE

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Abstract*—A series of metal complexes of Bis(Cyclopentadienyl)Titanium(IV) Derivatives With Schiff Bases Derived From 4-Amino-3-Hydrazino-6-Methyl-5-Oxo-1, 2,4-Triazine were prepared and characterized on the basis of Elemental analyses, Electrical Conductance, Magnetic moment and spectral data (Electronic spectra, infrared spectra, proton magnetic resonance spectra, ^{13}C NMR spectra) the antibacterial activity of Bis(Cyclopentadienyl)Titanium(IV) Derivatives With Schiff Bases Derived From 4-Amino-3-Hydrazino-6-Methyl-5-Oxo-1, 2,4-Triazine screening against gram positive *Bacillus subtilis* and gram negative *Escherichia coli.

I. INTRODUCTION

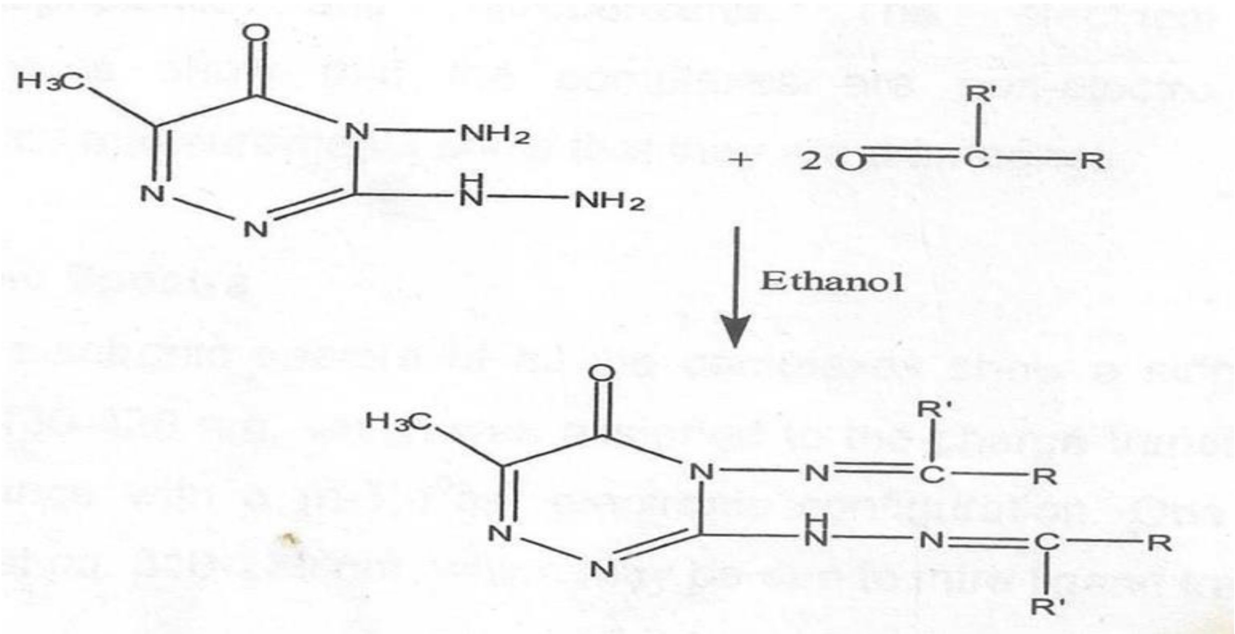
Hugo Schiff's described the condensation between an aldehyde andan amine leading to a Schiff base in 1854 Schiff bases, in general, arecharacterized by the structure RR'C=NR" in which >C=N is the azomethinegroup, RR'C= represents an aldehyde or ketone residue and =NR" is the aminoresidue of the primary amine. These compounds are also referred to as imines, azomethines or anils. There has been a growing interest in the synthesis ofmetal complexes of Schiff bases and their structural characterization in thecoordination chemistry. The systematic studies of Schiff bases were initiated byPfeiffer et. al. [1-5], who studied the general methods of their synthesis, metalexchange, ligand replacement and stereochemistry of their metal complexes. Inrecent years, considerable interest has been shown in the study of Schiff basecomplexes of non-transition [6-15], transition [16-28] and inner-transition metals" due to their striking structural features and also on account of their variedutility particularly in analytical, biological, pharmaceutical and industrial fields.

Mashaly at al. synthesized[29]oxorhenium(V) complexes with 3-hydrazino-5, 6-diphenyl-1, 2, 4-triazine, benzimidazolethion and 2-hydrazinobenzimidazole. The antifungal activities of these metal complexestowards Alternariaalternata and Aspergillusniger were tested and showedcomparable behavior with some well-known antibiotics. Shaban et alreported[130] sterically controlled regiospecificheterocyclization of 3-hydrazino-5-methyl-1,2,4-triazino- [5, 6-b] indole.

Thepresent paperdealswith the reactions ofbis(cyclopentadienyl)titanium (IV) dichloride with Schiff bases derived from 4-amino – 3 – hydrazine – 6 – methyl – 5 – oxo-1,2,4-triazine

A. Structure of ligands

The condensation of 4-amino-3-hydrazino-6-methyl-5-oxo-1, 2, 4-triazinewith 2-hydroxyacetophenone/ 4-hydroxyacetophenone/ salicylaldehyde/ 4-hydroxybenzaldehyde in ethanol in 1:2 molar ratio gives rise to Schiff bases asshown below



R	R’	Abbreviation
(2-OH) C_6H_4	CH_3	$OATzH_2$
(4-OH) C_6H_4	CH_3	$PATzH_2$
(2-OH) C_6H_4	H	$STzH_2$
(4-OH) C_6H_4	H	$BTzH_2$

B. Preparation of complexes

The reactions of bis(cyclopentadienyl)titanium (IV) dichloride with Schiffbases (LH_2) derived from 4-amino-3-hydrazino-6-methyl-5-oxo-1, 2, 4-triazine (molar ratio 2:1) in anhydrous THF in the presence of n-butylamine may berepresented by the following equation.

$2(n^5\text{-}C_5H_5)_2TiCl_2+LH_2+2n\text{-}BuNH_2$ $[\{(n^5\text{-}C_5H_5)2TiCl_2\}$ L] + $2n\text{-}BuNH_2.HCI$

(LH_2= $OATzH_2$, $PATzH_2$, $STzH_2$, $BTzH_2$)

The methods used for the preparation and isolation of these compoundsgave materials of good purity as supported by their analyses. All thesecompounds are colored solid, soluble in dimethylformamide. dimethylsulphoxide, and nitrobenzene. The electrical conductancemeasurements show that the complexes are non-electrolytes Magneticsusceptibility measurements show that they are diamagnetic

C. Electronic Spectra

The electronic spectra of all the complexes show a single band in theregion of 430-420 nm, which was assigned to the charge transfer band and isin accordance with a (n-1) d°ns° electronic configuration. One more band isobserved at ca. 310-280 nm, which may be due to intra ligand transition.

D. Infrared Spectra

The infrared spectrum of the parent triazine shows band at 1660 cm^1 dueto v(C=O) In the complexes, the position of v(C=O) band does not changeappreciably indicating the non-coordination of carbonyl oxygen to the metal ion. The ligands also show one broad band at 3300 cm^{-1} which may be due to v(NH) vibration of the amine group. In the complexes this band remains almostat the same position due to non-coordination of amino group to the metal. Bandat ca. 1620-1605 cm^{-1} due to the v(C=N) vibration of the azomethine group was observed. In the complexes, this band shifts to lower frequency (~15-10 cm^{-1} indicating the coordination of azomethine nitrogen to metal ion. This is furtherconfirmed by the appearance of v(Ti-N) band at ca 440-460 cm The Schiffbases show a broad band at ca 2650 cm^{-1}due to intramolecular H-bonded OHThis band is absent in their corresponding titanium (IV) complexes indicating thecoordination of phenolic oxygen through deprotonation This is furthersupported by the shift of phenolic C-O bond from 1280 cm^{-1} (in the free ligands)to ca. 1350 cm^{-1} in the complexes. The coordination through deprotonatedphenolic oxygen is confirmed by a new band at ca 480-470 cm^{-1} assignable tov(Ti-O).

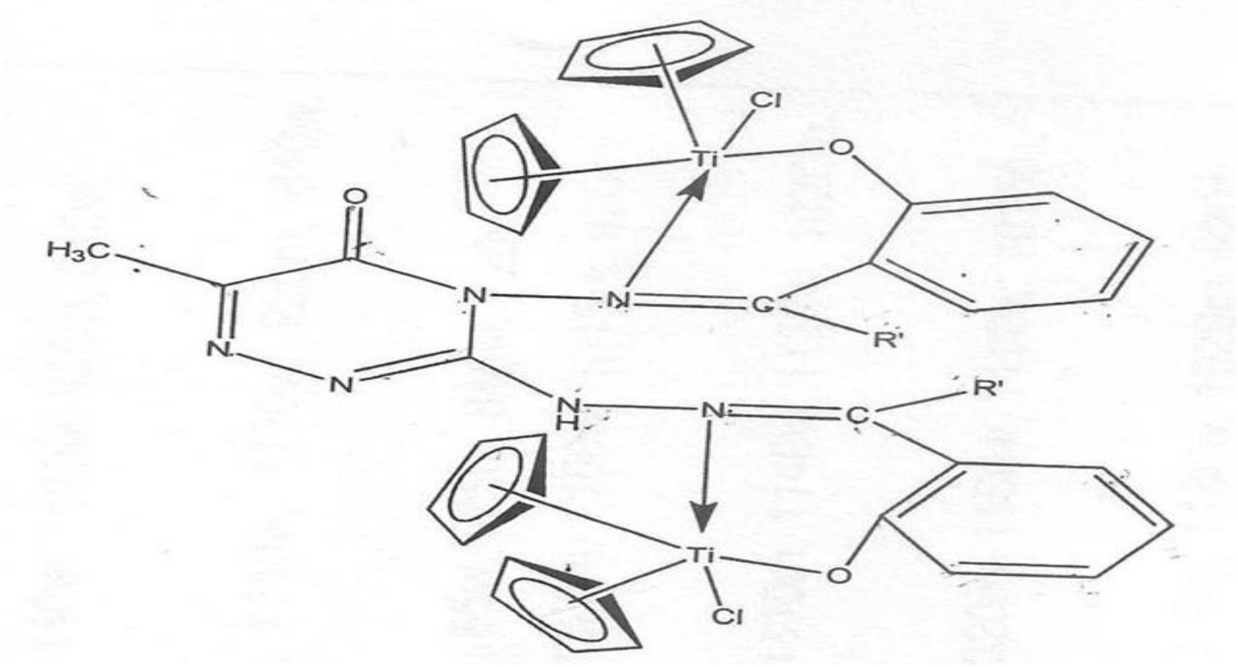
Bands at 3000 cm^{-1} for v(C-H), ca. 1420 cm^{-1} for v(C-C), ca. 1015 cm^{-1} and 800cm^{-1} for (C-H out of plane deformation) in the complexes are due to thecyclopentadienyl ring. These bands are similar to those similar forbis(cyclopentadienyl)titanium (IV) dichloride and their appearance indicates thatthe (n^5-C_5H_5) group persists in the complexes.

E. Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra of the ligands and theircorresponding complexes were recorded in deuterateddimethylsulphoxide.

1. A signal in all derivatives at 6.55-6.80 may be assigned to theprotons of cyclopentadienyl rings and indicate the rapid rotation of thering about the metal-ring axis.
2. All the ligands gave multiplet at 7.90-7 50 integrating for aromaticgroup protons. This signal shift only slightly upon coordination.
3. The ligands and the complexes show a singlet at ca.11.05-11.07 dueto the proton of -NH group.
4. All the ligands and complexes show a singlet at ca. 2.2 due to threeprotons of methyl group attached at 6th position of triazine ring. Inaddition to this, ligands $OATzH_2$ and $PATzH_2$ and their correspondingcomplexes show a singlet at 2.95 due to methyl group ofacetophenone

Thus, on the basis of above studies, the following structure may be proposed for[$\{(C_5H_5)_2TiCI\}_2$ (L)]



II. ANTIBACTERIAL ACTIVITY

Transition metals and their complexes have evolved great interestdue to their biological potential, unusual structural aspects, uniquestereo and magneto chemistry. Azomethines constitute one of the mostimportant classes of biologically active ligands providing potentialbinding sites through nitrogen and sulphur/oxygen donor atoms. Thecase of formation of a variety of metal complexes from these ligands likethiosemicarbazones, semicarbazones, dithiocarbazates andbenzothiazolines speak for their spectacular progress in bioinorganicchemistry. The different modes of bonding produce appreciable changesin biochemical properties of metal and are of tremendous interest due tothe current focus in the study of sulphur nitrogen donor ligands and theircomplexes[33-40].Azomethines and their derivatives are known to exhibit awide range of pharmacological properties such as anticancerous andantibacterial

The antibacterial activity was focused against two bacteria, viz,

Gram- positive Bacillus subtilis and Gram-negative Escherichia coli.

A. Bacillus subtilis

Bacillus subtilis, known as the Hay bacillus or Grass bacillus, is aGram- positive, catalase-positive bacterium commonly found in soil. Amember of the genus Bacillus, B. subtilis is rod shaped and has theability to form a tough, protective endospore, allowing the organism totolerate extreme environmental conditions. It is not considered a humanpathogen; it may contaminate food rarely causes food poisoning B. subtilis produces the proteolytic enzymesubtilism B subtilis spores can survive the extreme heating that is oftenuse to cook food, and it is responsible for causing Ropiness- a sticky, stringy consistency caused by bacterial production of long chainpolysaccharides

B. Escherichia coli

Escherichia coli, commonly known as E. coli is a Gram-negativebacterium that is commonly found in the lower intestine of warm-bloodedorganisms (endotherms). Serotype 0157:H7, strain of E.coll causesserious food poisoning in humans, and are occasionally responsible forcostly product It is a facultative anaerobic and non-sporulating, cells aretypically rod shaped and are about 2 µm long and 0.5 µm in diameter,with a cell volume of 0.6-0.7 µm. Virulent strains of E.coli can causegastroenteritis, urinary tract infections and neonatal meningitis. In rarecases, virulent strains are also responsible for hemolytic-uremicsyndrome (HUS). peritonitis, mastitis, septicemia and Gram-negativepneumonia.

The antibacterial activity was evaluated by the paper -disc plate

method The nutrient agar medium (peptone, NaCl and agar agar) and5mm diameter paper discs of Whatmann No. 1 were used. Thecompounds were dissolved in a suitable solvent at 1000 ppmconcentrations. The filter paper discs were soaked in different solution ofthe compounds, dried and then placed in the petriplates previouslyseeded with the test organism (Gram-positive Bacillus subtilis and Gram-negative Escherichia coli. The plates were incubated for 24h at 30±1°Cand the inhibition around each disc was measured in mm.

The results show that activity increases on chelation. The activityof the ligands is affected by the nature of substituent relation to thelipophilicity of the ligands and their membrane permeability, a key factorin determining their entry inside the cell.

The results lead to following conclusions.

a) The complexes are slightly more toxic than the parent ligands

b) The compounds exhibit a better effect on the Gram-negative form

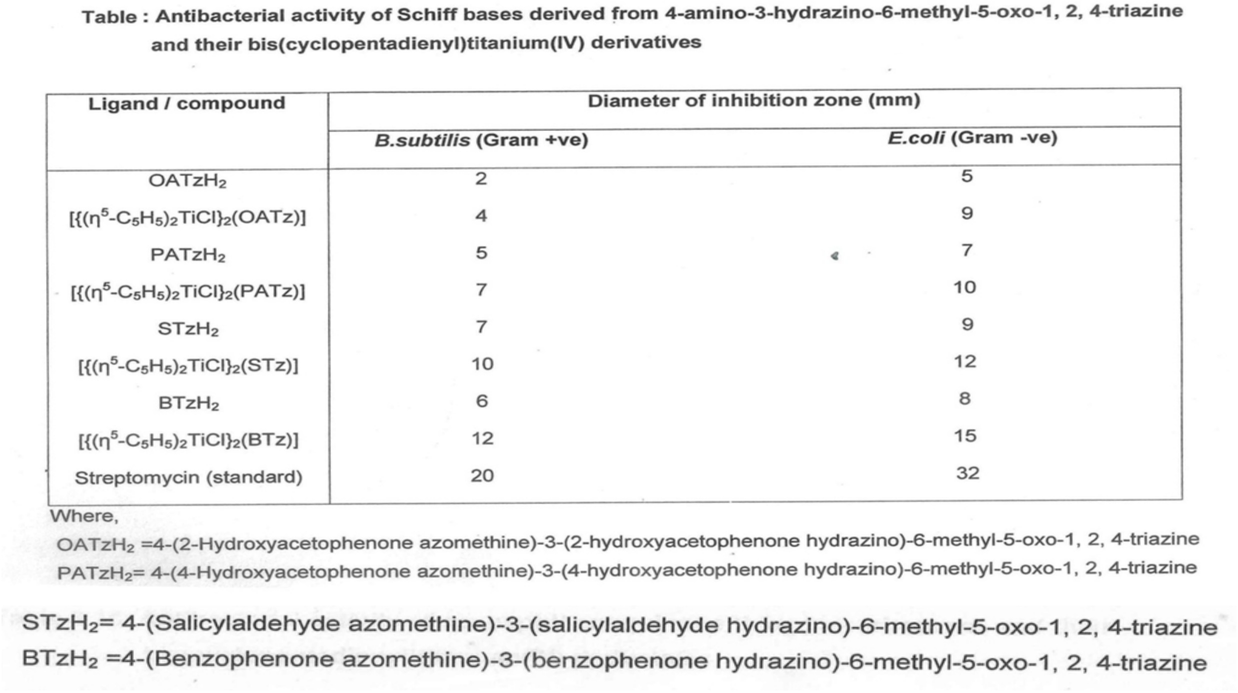


Table : Antibacterial activity of Schiff bases derived from 4-amino-3-hydrazino-6-methyl-5-oxo-1, 2, 4-triazine and their bis(cyclopentadienyl)titanium(IV) derivatives

Ligand / compound	Diameter of inhibition zone (mm)	
	B.subtilis (Gram +ve)	*E.coli* (Gram -ve)
$OATzH_2$	2	5
$[\{(\eta^5\text{-}C_5H_5)_2TiCl\}_2(OATz)]$	4	9
$PATzH_2$	5	7
$[\{(\eta^5\text{-}C_5H_5)_2TiCl\}_2(PATz)]$	7	10
$STzH_2$	7	9
$[\{(\eta^5\text{-}C_5H_5)_2TiCl\}_2(STz)]$	10	12
$BTzH_2$	6	8
$[\{(\eta^5\text{-}C_5H_5)_2TiCl\}_2(BTz)]$	12	15
Streptomycin (standard)	20	32

Where,

$OATzH_2$ =4-(2-Hydroxyacetophenone azomethine)-3-(2-hydroxyacetophenone hydrazino)-6-methyl-5-oxo-1, 2, 4-triazine

$PATzH_2$= 4-(4-Hydroxyacetophenone azomethine)-3-(4-hydroxyacetophenone hydrazino)-6-methyl-5-oxo-1, 2, 4-triazine

$STzH_2$= 4-(Salicylaldehyde azomethine)-3-(salicylaldehyde hydrazino)-6-methyl-5-oxo-1, 2, 4-triazine

$BTzH_2$ =4-(Benzophenone azomethine)-3-(benzophenone hydrazino)-6-methyl-5-oxo-1, 2, 4-triazine

III. ACKNOWLEDGEMENTS

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