

SOME NEW ORGANO THALLIUM (III) MOLECULAR ADDUCTS WITH BIDENTATE SCHIFF BASE LIGANDS, A PHOTOELECTRON SPECTROSCOPIC STUDY

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ABSTRACT

The thallium metal which has outer electronic configuration $6S^2, 6P^1$ shows formal oxidation state of (I) and (III), Thallium (III) compounds have sp^2 Hybridisation[1]. A literature survey reveals that so many organothallium (III) compounds have been synthesized ,but organothallium (III) complexes with bidentate and tetradentate Schiff base ligands are less known. The acceptor properties of $PhTlCl_2$ and Ph_2TlCl with various bidentate and tetradentate Schiff base ligands have been studied. It was observed that due to presence of one vacant p -orbital and five vacant d -orbitals, it accept lone pairs from various bidentate Schiff base ligands. Several $PhTlCl_2SB$ and $Ph_2TlCl SB$ have been synthesized and characterised by elemental analysis, molar conductance, UV-visible IR, Magnetic Moment and XPS data to establish their structure and geometry.

X -ray Photoelectron technique has been used known site of coordination in all prepared molecular adducts. [9], $Tl 4f$ Photoelectron peaks in all prepared molecular adducts are less than starting material. Which proved the coordination of ligands to central metal(thallium)ion. $3s$ Photoelectron peaks in all prepared molecular adducts have shown single symmetrical peak without any splitting in photoelectron peak which confirmed diamagnetic nature of all prepared molecular adducts [9].

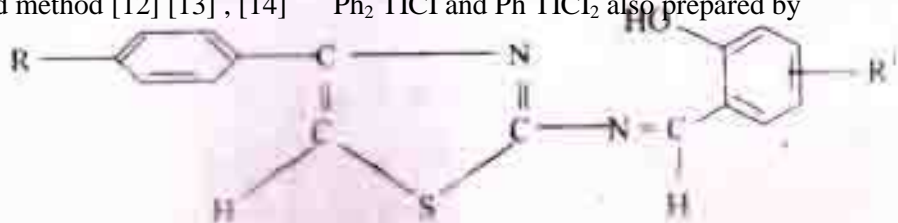
Keywords :- Schiff base ligand, diamagnetic, organothallium, (III) compound, and molecular adduct

I. INTRODUCTION

As literature survey reveals that the organ metallic chemistry of (III) B group of metals like gallium indium and Thallium not studied in detailed as that of boran and aluminum during last few year organ metallic stated of heavy metal widely study and found useful application in production of metal carbonyl [17]. metal cyclopentadienyls [18] . antiknock reagent etc.

Poisoned food technique has recently employed to determine the fungicidal activity of these compound preliminary evaluation of biocidal activity of some of these compounds against tomato seedlings has indicated that organothallium (III) SB are potential fungicides [19]

Eight organothallium (III) molecular adducts of the type $\text{Ph}_2\text{TlCl.SB}$ and $\text{PhTlCl}_2.\text{SB}$ have been synthesized and characterized & established their geometry. first of all we prepared four bidentate Schiff base ligand in reported method [12] [13] , [14] Ph_2TlCl and PhTlCl_2 also prepared by reported method [10] [11]



II Fig

Prepared Schiff Bases :

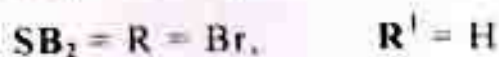


TABLE I: ELEMENTAL ANALYSIS AND CONDUCTANCE DATA OF

$\text{PhTlCl}_2.\text{SB}$ AND $\text{Ph}_2\text{TlCl.SB}$ COMPLEXES(SB= Bidentate Schiff base ligands)

Sr. No.	Compound	Elemental analysis % Found (Cal.)			Molecular Conductance in acetone $\text{Q}^{-1} \text{cm}^2 \text{mol}^{-1}$
		C	H	N	
1	$\text{PhTlCl}_2.\text{SB}_1$	42.70 (42.50)	2.93 (2.5)	4.33 (4.0)	15
2	$\text{PhTlCl}_2.\text{SB}_2$	41.81 (41.4)	2.53 (2.2)	4.43 (4.0)	22
3	$\text{PhTlCl}_2.\text{SB}_3$	38.05 (38.0)	2.48 (3.4)	3.86 (3.4)	20
4	$\text{PhTlCl}_2.\text{SB}_4$	35.39	2.01	3.75	24

		(35.4)	(2.0)	(3.4)	
5	Ph ₂ TiCl.SB ₁	50.59 (50.4)	3.489 (3.2)	4.07 (4.0)	18
6	Ph ₂ TiCl.SB ₂	45.38 (45.2)	2.99 (2.4)	3.65 (3.3)	16
7	Ph ₂ TiCl.SB ₃	45.38 (45.2)	2.99 (2.4)	3.65 (3.3)	15
8	Ph ₂ TiCl.SB ₄	42.67 (42.2)	2.54 (2.4)	3.55 (3.2)	14

Table II: Ti4f Binding Energies (eV) in PhTiCl₂.SB and Ph₂TiCl.SB

Sr. No	Complexes	Ti4f
1	PhTiCl ₂	119.8
2	PhTiCl ₂ SB ₁	116.4
3	PhTiCl ₂ SB ₂	116.2
4	PhTiCl ₂ SB ₃	116.0
5	PhTiCl ₂ SB ₄	116.0
6	Ph ₂ TiCl	119.6
7	Ph ₂ TiCl.SB ₁	116.2
8	Ph ₂ TiCl.SB ₂	116.0
9	Ph ₂ TiCl.SB ₃	116.0
10	Ph ₂ TiCl.SB ₄	116.0

Table III N1s, O1s and S2P Binding Energies (eV) in, ligand, Ph TiCl₂. SB and Ph₂ TiCl. SB Complexes

Sr no	Ligand & Compound	N 1s	O 1s	S2p
1	SB1	400.8	532.4	116.4
2	PhTiCl ₂ .SB ₁	402.8	532.4	167.2
3	PhTiCl ₂ .SB ₂	402.6	532.4	167.2
4	SB2	400.6	532.4	167.2
5	PhTiCl ₂ .SB ₂	402.6	532.4	167.0
6	Ph ₂ TiCl. SB ₂	402.6	532.4	167.0
7	SB3	400.6	532.4	167.0
8	Ph TiCl ₂ .SB ₃	402.6	532.4	167.2
9	Ph ₂ TiCl.SB ₃	402.6	532.4	167.2

10	SB ₄	400.6	532.4	167.0
11	PhTICl ₂ .SB ₄	402.6	532.4	167.2
12	Ph ₂ TICl.SB ₄	402.6	532.4	167.2

III EXPERIMENTAL Preparation of Ph₂ TICl.SB and PhTICl₂SB. Complexes : A mixture of 1 mmol of Ph₂TICl. and PhTICl₂ was mixed with 1mmol of SB₁ to SB₂ bidentate Schiff base ligands in dry chloroform. the mixture was refluxed above 3 hrs. The solid evaporation was purified wet ether (bp. 60 – 800) and dried.The micro analysis of the complexes were carried out at CDRI, LKQ. conductance were measured in acetone at RT using a digisum electronic conductivity bridges. IR spectra (QI) were recorded on a Perkin-Elmer.457 spectrophotometer. The X-ray Photoelectron Spectra were recorded on VU scientific ESCA-3mk 11 electron spectrometer.

IV. RESULTS AND DISCUSSION:

The elemental analysis of all the molecular adducts were found satisfactory. The molecular conductance of all the complexes in acetone range (10-30Q⁻¹ cm²m⁻¹) suggest their non-electrolyte [5]. [Table – I]. IR spectra of all the adducts exhibited νC = N band at 1620-1610 cm⁻¹ which appeared at 1640 – 1650 cm⁻¹ in the free ligands. the lowering of this band in the complexes coordination of nitrogen atom indicates the of azomethine groups to the thallium [6] ,[7] , Phenolic .OH, intra molecular H-bonded appeared at-2900 cm⁻¹ in both ligand and prepared molecular adducts, suggesting non-involvement of oxygen of phenolic. OH in the coordination to the thallium metal ion [8]. The far IR spectra exhibited bands at 600-200 cm⁻¹ for ν TI- C [3], [4].It was observed that the binding energy of TI4f in the starting material Ph TICl₂ or Ph₂ TICl was higher than their prepared molecular adducts.

These observation concluded that the electron density on TI metal ion has been increased by the coordination of Schiff base ligand with thallium Metal ion[9] (Table – II). It was noticed that O1s binding energy in PhTICl₂.SB or Ph₂ TICl.SB (where SB = Schiff base ligands) molecular adducts Were same as in their Schiff base ligands this observation concludes that oxygen atoms of Schiff base ligands is not bonded with thallium metal ion [9] (Table – III). The N1s photoelectron peak in all these molecular adducts have shown much higher binding energy than in their Schiff base ligands, suggesting nitrogen atom of Schiff base ligands in coordinated to thallium metal ion [9] (Table – III) The S2p_{1/2} , 3/2 photo electron peaks in all these molecular adducts have also shown higher binding energy than in their Schiff base ligands (Table –III) The TI3s photoelectron peak of all prepared molecular adducts have shown single symmetrical peak without any splitting In photoelectron peak.

This observation confirms the diamagnetic nature of molecular adducts [9] On the basis of elemental analysis, conductivity data, showing the complexes to be non-ionic and IR and X-ray photoelectron (XPS) identifying the site of coordination. It is possible to concluded that Ph $TiCl_2$.SB & Ph₂TiCl.SB are trigonal bipyramidal (Sp³d hybridization)

V. Conclusion :

In continuation of our study [3],[4],[9], [15]. we report in previous PhTiCl₂ SB & Ph₂TiCl. SB were synthesised & characterized by elemental analysis, XPS data etc. many of such complexes have been used in medicine, Antibacterial activity [2], [19]. it was toxicological study [2], [16].

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