

SYNTHESIS AND CHARACTERIZATION OF SOME TRANSITION METAL COMPLEXES WITH O, N- DONAR LIGANDS

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Abstract: The Reaction of BIS (cyclopentadienyl) titanium (IV) dichloride with acetophenone picolinoyl hydrazone (AcPH-H), salicylaldehyde picolinoyl hydrazone (SPH-H₂), O-hydroxyacetophenone picolinoyl hydrazone (OPH-H₂) have been carried out in anhydrous tetrahydrofuran under stirring in the presence and absence of amine. Three types of complexes are obtained depending upon the pH of the medium. [CpTiL]_n, [Cp₂TiClL] and [Cp₂TiCl₂L] have been isolated in the presence and absence of amine respectively. They are characterized by elemental analysis, electrical conductance, magnetic moment, and spectral (electronic, IR and ¹H.n.m.r) studies. ¹H.n.m.r spectra reveal rapid rotation of the cyclopentadienyl ring along the metal ring axis at 25°C.

Keywords: Bis(cyclopentadienyl), Picolinoyl, Deprotonation, Hydrazone, ¹H.n.m.r spectra.

I. INTRODUCTION

Hydrazones are important organic compounds usually formed by the action of hydrazine on ketones or aldehydes. It forms stable complexes with transition metal ions. Such complexes have diverse synthetic and structural aspects. The present paper describes the synthesis and structural characteristics of bis (cyclopentadienyl) titanium (IV) derivatives with hydrazones derived from picolinic acid.

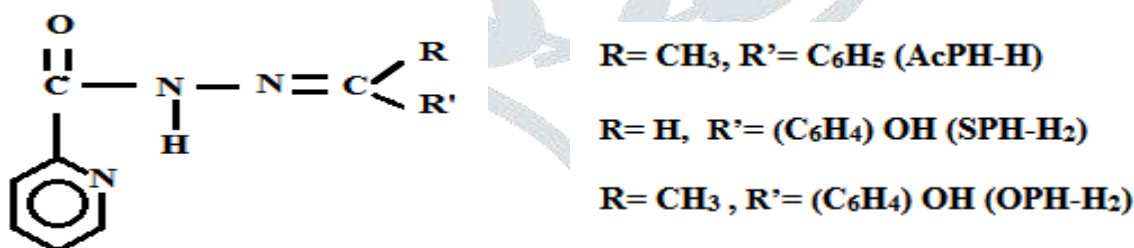


Figure: 01

II. EXPERIMENTAL

All reactions were carried out under strictly anhydrous condition. THF (Tetrahydrofuran, J.T. Baker, bp 65-66 °C) was dried and stored over sodium wire overnight and then boiled under reflux, until it gave the blue coloration with benzophenone. It was dried by distilling over LiAlH₄. Bis(cyclopentadienyl) titanium (IV) dichloride was prepared by reacting TiCl₄ with NaCp in C₆H₆ [1]. The Ligands were prepared from the picolinic acid by condensation with

acetophenone, O-hydroxyacetophenone and salicylaldehyde following the method of Efimousky and Rump [2-4] and Terunobu et.al [5]. The analytical method and physical measurement details were described [6, 7].

III. PREPARATION OF COMPLEXES

A mixture of bis(cyclopentadienyl) titanium (IV) dichloride (20m. mol) and appropriate hydrazones (20m.mol) were dissolved in anhydrous tetrahydrofuran (60ml) and also added triethylamine (20m.mol). The reaction mixture was stirred for 32-65 hours at room temperature. Triethylamine hydrochloride is precipitated which was removed by filtration and the solvent was taken out under reduced pressure. The colored complexes were crystallized from tetrahydrofuran and petroleum ether mixture.

IV. RESULTS AND DISCUSSION

A systematic study of the reactions of bis (cyclopentadienyl) titanium (IV) dichloride with acetophenone, O-hydroxyacetophenone and salicylaldehyde picolinoyl hydrazones (molar ratio1:1) in anhydrous tetrahydrofuran in presence and absence of triethylamine. The complexes are brown to yellowish brown and reddish brown colored solids. They are stable in air but their solution are hydrolysed on standing. Conductance measurement reveals that they are essentially non-electrolytes. Magnetic susceptibility value at room temperature shows the diamagnetic nature. These complexes decompose in the range 160-250°C.

The physical properties and analytical data for the complexes are given in **table 01**.

V. ELECTRONIC SPECTRA

The electronic spectra of all these complexes show a single band in the region of 22500-23200 cm^{-1} which can be assigned [8] to the charge transfer band.

VI. INFRA RED SPECTRA

The ν (NH) band appears at about 3200 cm^{-1} in the ligands. This band remains unaffected in the spectra of adducts type complexes but it disappears in the spectra of deprotonated complexes.

All ligands show bands in the region of 1675-1660 cm^{-1} , 1560-1550 cm^{-1} and 1300 cm^{-1} assignable [9-14] to amide I [ν (C=O)], amide- II [ν (CN) + δ (NH)] and amide- III { δ (NH)} vibrations respectively. Spectra of adducts shows negative shift of amide I (~15 – 20 cm^{-1}) and amide II (~20 cm^{-1}) which indicates the co-ordination through carbonyl oxygen [9-14]. Such type of bands disappears in the deprotonated complexes which indicate the enolization of the keto group. The strong characteristic bands of ν (C=N) and ν (NCO⁻) in the region of 1600-1585 cm^{-1} and 1540 -1530 cm^{-1} respectively further support the enolization of keto group [15].

A weak band at ~1635 - 1625 cm^{-1} in ligands which can assigned to ν (C = N) vibration of azomethine linkage. This band appears at a slightly lower wave number (~1610 cm^{-1}) in all the complexes. It indicates the nitrogen atom of the azomethine group is co-ordinated to titanium atom [12-16].

The ligands derived from salicylaldehyde and O- hydroxyacetophenone show bands at about 3400 cm^{-1} due to ν (OH) which disappears in their complexes indicating deprotonation of the phenolic group [17].

The free ligand shows vibrations at ~1570 cm^{-1} , 610 cm^{-1} , 420 cm^{-1} due to pyridine ring which remains unaffected in all complexes except adducts indicating non-participation of pyridine nitrogen in co-ordination. In adducts type complexes these bands show upward shift (~10 ~ 20 cm^{-1}) which indicates pyridine nitrogen co-ordination [12-18] with another titanium atom yielding polymeric structure.

The spectra of complexes show bands in the 480- 460 cm^{-1} , 445- 430 cm^{-1} and 375-370 cm^{-1} assigned [19] to ν (Ti-o) ketonic, ν (Ti- N) and ν (Ti- Cl) modes respectively.

All the complexes show bands at ~ 3000 cm^{-1} (C- H stretch), ~ 1435 cm^{-1} (C-C stretch) and ~ 810 cm^{-1} (C-H out of plane deformation) indicates the presence of cyclopentadienyl rings.

VII. ¹H.N.M.R

Signal appears at δ 6.5 - 6.8 in all the derivatives assigned to the proton of the cyclopentadienyl ring.

In deprotonated complexes the signal at about δ 11.3 disappears assignable to NH proton.

A signal at about δ 12.4 for phenolic proton of salicylaldehyde and O- hydroxyacetophenone disappears in all the complexes. The signal due to pyridine proton at about δ 8.0- 8.9 in all hydrazones shift down field in adduct type complexes. The signal appears at δ 8.6 - 9.0 indicating the involvement of ring nitrogen in bonding with titanium atom.

On the basis of the above structural evidences, the following structures are proposed-

(I) - $[\text{Cp}_2\text{TiCl}_2\text{L}]$ R= CH₃ R'= C₆H₅ (II) - $[\text{Cp}_2\text{TiClL}]$ R= CH₃ R'= C₆H₅ (III) - $[\text{CpTiL}]_n$ R= CH₃ R'= C₆H₅

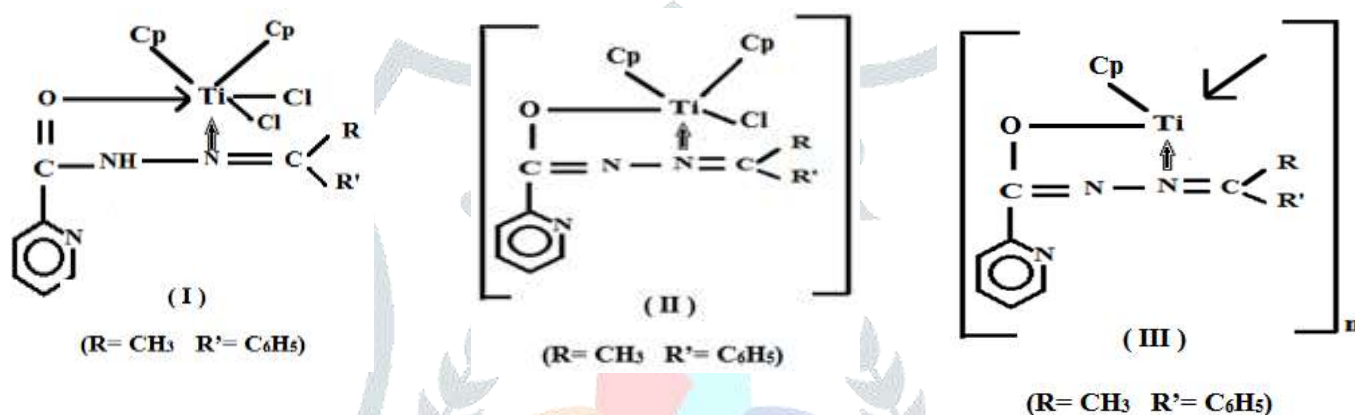


Figure: 02

VIII. ACKNOWLEDGEMENT

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Table 01: Reaction of Cp₂TiCl₂ with Picolinoyal hydrazones in THF

Reactants taken (molar ratio)	Amine	Reflux Stirring time (hrs)	Product Colour Yield (%)	Decomposition Temp (°C)	Found (Caled.) %				
					C	H	N	Cl	Ti
Cp ₂ TiCl ₂ + AcPH-H (1:1)	Et ₃ N	40	Cp ₂ TiCl ₂ (AcPH), Brown (58%)	≥250	63.6 (63.8)	4.5 (4.9)	9.2 (9.3)	7.8 (7.8)	10.5 (10.6)
Cp ₂ TiCl ₂ + SPH-H ₂ (1:1)	Et ₃ N	33	Cp ₂ Ti (SPH), Redish Brown (58%)	195	66.0 (66.1)	4.2 (4.5)	9.8 (10.0)	-	11.3 (11.4)
Cp ₂ TiCl ₂ + OPH-H ₂ (1:1)	Et ₃ N	40	Cp ₂ Ti (OPH), Brown (48%)	230	66.8 (66.8)	4.7 (4.9)	9.6 (9.7)	-	11.0 (11.1)
Cp ₂ TiCl ₂ + AcPH-H (1:3)	Et ₃ N	65	CpTi (AcPH) ₃ , Light Brown (54%)	220	68.0 (68.2)	4.8 (4.9)	15.1 (15.2)	-	5.7 (5.7)
Cp ₂ TiCl ₂ + AcPH-H (1:1)	-	50	Cp ₂ TiCl ₂ (AcPH-H), Brown (54%)	160	58.7 (59.0)	4.6 (4.7)	8.5 (8.6)	14.4 (14.5)	9.8 (9.8)
Cp ₂ TiCl ₂ + SPH-H ₂ (1:1)	-	30	Cp ₂ TiCl (SPH-H), Yellowish Brown (58%)	172	66.6 (66.8)	4.2 (4.4)	9.2 (9.2)	7.6 (7.8)	10.4 (10.5)
Cp ₂ TiCl ₂ + OPH-H ₂ (1:1)	-	32	Cp ₂ TiCl (OPH-H), Yellowish Brown (62%)	185	61.3 (61.6)	4.5 (4.7)	8.6 (8.9)	7.3 (7.5)	10.2 (10.2)

Where, *AcPH-H = Acetophenone Picolinoyal Hydrazone, *SPH-H₂ = Salicylaldehyde Picolinoyal Hydrazone, *OPH-H₂ = O- hydroxyacetophenone Picolinoyal Hydrazone

Source: Experimental Research Calculated by Researcher.

Table 02: ¹H .n.m.r. spectra data (δ scale, ppm) of bis (cyclopentadienyl) titanium (IV) derivatives with Hydrazones

Complex	η ⁵ -C ₅ H ₅	-NH	-C ₅ H ₅ N	Phenyl Ring	CH ₃	CH
Cp ₂ TiCl (AcPH)	6.75s	-	8.40s	7.55s	2.00(s)	-
Cp ₂ Ti (SPH)	6.50s	-	8.82s	7.50s	-	2.85(s)
Cp ₂ Ti (OPH)	6.60s	-	8.80s	7.40s	2.20(s)	-
CpTi (AcPH) ₃	6.80s	-	8.40s	7.45s	2.10(s)	-
Cp ₂ TiCl ₂ (AcPH-H)	6.80s	11.20s	8.35s	7.30s	2.10(s)	-
Cp ₂ TiCl (SPH-H)	6.60s	11.30s	8.80s	7.42s	-	2.90(s)
Cp ₂ TiCl (OPH-H)	6.60s	11.20s	8.80s	7.30s	2.10(s)	-

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