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## SYNTHESIS AND CHARACTERIZATION OF TRANSITION METAL COMPLEXES WITH N, O-CHELATING HYDRAZONES

K.D. MISHRA, DEPARTMENT OF CHEMISTRY,  
AGRA COLLEGE, AGRA – 282002, INDIA

### Abstract:

The Reactions of hydrazones, derived by condensation of acetophenone, *o*-hydroxyacetophenone or salicylaldehyde with isonicotnoyl and nicotinoylhydrazides with bis(cyclopentadienyl) titanium (IV) dichloride have been studied in refluxing THF in the presence and absence of amine. Two types of derivatives are obtained depending upon the pH of medium  $[\text{Cp}_2\text{TiCIL}]_n$  and  $[\text{Cp}_2\text{TiCl}_2\text{L}]$  have been isolated in the presence and absence of amine respectively.

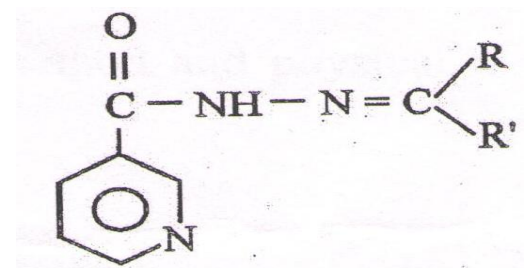
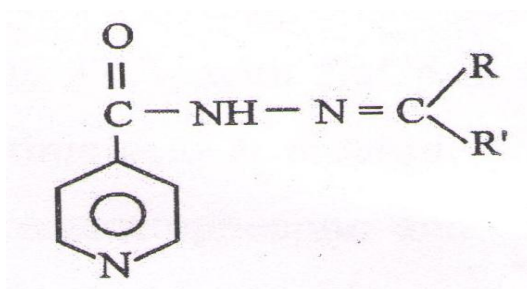
They are characterized by elemental analysis electrical conductance, Magnetic moment and spectral (electronic, IR,  $^1\text{H}$  NMR) studies.  $^1\text{H}$  NMR spectra reveals rapid rotation of the cyclopentadienyl ring around the metal-ring axis (NMR time scale) at  $25^\circ\text{C}$ . Probable structures for the complexes are proposed.

**Keywords :** Bis(Cyclopentadienyl), isonicotnoyl, nicotinoyaldeprotonation.

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## Introduction:

Hydrazones form stable complexes with transition metal ions, especially if the amine and/or the carbonyl group contain a second functional group sufficiently near the co-ordination site. In view of the diverse synthetic and structural aspects of these complexes, interest in them continues to increase. This paper describes the synthesis and structural features of bis(cyclopentadienyl) titanium (IV) derivatives with hydrazone derived from isonicotinic acid and nicotinic acid.



where



## Experimental:

All experiments were carried out under strictly anhydrous conditions THF (J.T. Baker, bp 65-66<sup>0</sup>C) was dried by stored over sodium wire overnight and then boiled under reflux, until it

gave the characteristic blue colour with benzophenone. It was finally dried by distilling over  $\text{LiAlH}_4$ .

Bis(cyclopentadienyl) titanium(IV) dichloride was prepared by reacting the appropriate  $\text{TiCl}_4$  with  $\text{NaCp}$  in  $\text{C}_6\text{H}_6$ . The Ligands were prepared from isonicotinic acid & nicotinic acid by condensation with acetophenone, o-hydroxyacetophenone and salicylaldehyde following the method of Efimovskiy and Rumpf<sup>2-4</sup> and Terunobu et al.<sup>5</sup>.

The analytical method and physical measurements details were described earlier.<sup>6,7</sup>

### **Preparation of Complexes:**

#### **$[\text{Cp}_2\text{TiClL}]_n$**

The reaction of bis(cyclopentadienyl) titanium(IV) dichloride (10m.mol) with appropriate isonicotinoyl and nicotinoylhydrazones (10m.mol) (molar ratio 1:1) have been carried out in anhydrous THF (60  $\text{cm}^3$ ) in the presence of n-butylamine (50 m. mol.). The mixture was stirred for 40-50 hrs. at room temperature and the resulting complex which precipitated was removed by filtration, washed thoroughly with THF and dried in vacuo.

#### **$[\text{Cp}_2\text{TiCl}_2\text{L}]$**

A mixture of bis(cyclopentadienyl) titanium(IV) dichloride (10m.mol) and appropriate hydrazones (10m.mol) were dissolved in anhydrous THF (50  $\text{cm}^3$ ) and the reaction mixture was boiled under reflux for 20-40 hrs. The solution was filtered and the volume reduced to ca 15 $\text{cm}^3$ . Dry petroleum ether (60-80 $^\circ\text{C}$ , 15  $\text{cm}^3$ ) was added and the mixture was set aside overnight. The coloured product thus obtained was filtered and dried in vacuo.

### **Results and Discussion:**

A systematic study of the reactions of bis(Cyclopentadienyl) titanium(IV) dichloride with appropriate isonicotinoyl and nicotinoylhydrazone (Molar ratio 1:1 and 1:3) have been carried out

in anhydrous THF in the presence and absence of n-butylamine. In the absence of amine molar ratio 1:1 have been carried out on refluxing in dichloromethane.

The complexes are light yellow to brown and orange coloured solids. The derivatives are insoluble in most of the common organic solvents but soluble in dimethylformamide and dimethylsulphoxide. The electrical conductance measurement in DMF indicate their non electrolytic nature. They decompose in the range 162-250<sup>0</sup>C without melting. Magnetic susceptibility values of these complexes at room temperature show their diamagnetic nature.

The Physical properties and analytical data for the complexes are given in table 1.

### **Electronic Spectra:**

The electronic spectra of all the isonicotinoyl complexes, recorded in nujol show a single band in the region 23200-23800 cm<sup>-1</sup> which can be assigned to the charge transfer band. For nicotinoyl complexes a single band is observed in the region 22500-23200 cm<sup>-1</sup> which can also be assigned<sup>8</sup> to the charge transfer band.

### **IR Spectra:**

The  $\nu(\text{NH})$  band appears at about 3200 cm<sup>-1</sup> in the ligand. The position of this band remains unaffected in the spectra of adducts type of complexes whereas it disappears in the spectra of deprotonated complexes. All these ligands show bands in the region 1675-1680, 1560-1550 and 1300 cm<sup>-1</sup> assignable<sup>9-14</sup> to amide I [ $\nu(\text{C}=\text{O})$ ], amide II [ $\nu(\text{CN}) + \delta(\text{NH})$ ] and amide III  $\{\delta(\text{NH})\}$  vibrations respectively. Negative shift of amide I ( $\sim 15\text{-}20$  cm<sup>-1</sup>) and amide II ( $\sim 20$  cm<sup>-1</sup>) in the spectra of adducts indicates co-ordination through the carbonyl oxygen<sup>9-12</sup>. These bands disappear in the deprotonated complexes suggesting enolization of the keto group by the formation of complexes through deprotonation. The spectra of strong characteristics bands  $\nu(\text{C}=\text{N})$  and  $\nu(\text{NCO}^-)$  in 1600-1585 and 1540-1530 cm<sup>-1</sup> regions respectively further support the enolization of the keto group<sup>15-17</sup>.

All these ligands show a weak bands at  $\sim 1635\text{-}1625\text{ cm}^{-1}$  which can assigned to  $\nu(\text{C}=\text{N})$  vibration of the azomethine linkage. The band due to  $\nu(\text{C}=\text{N})$  appears at a slightly lower wave number ( $\sim 1610\text{ cm}^{-1}$ ) in all the complexes suggesting that the nitrogen atom of the azomethine group is co-ordinated to titanium atom<sup>12,16</sup>.

The hydrazone derived from salicylaldehyde, o-hydroxyacetphenone show bands due to  $\nu(\text{OH})$  at about  $3400\text{ cm}^{-1}$ . This band disappears in their complexes indication the deprotonation of the phenolic group<sup>17</sup>.

The pyridine ring vibration appears at  $\sim 1570, 620, 410\text{ cm}^{-1}$  respectively in the free ligands. In all complexes except adducts, the position of these bands remain unaffected indication the nonparticipation of pyridine nitrogen in coordination. However in adducts type complexes these bands show upward shifts ( $\sim 10\text{-}20\text{ cm}^{-1}$ ) indicating pyridine nitrogen co-ordination<sup>12,18</sup>. Consequently, the ring nitrogen must coordinate with another titanium atom yielding polymeric structure.

The non-ligand bands in the spectra of the complexes in the  $480\text{-}460, 445\text{-}430$  and  $375\text{-}370\text{ cm}^{-1}$  assigned<sup>19</sup> to  $\nu(\text{Ti-O})$ (Ketonic),  $\nu(\text{Ti-N})$  and  $\nu(\text{Ti-Cl})$  modes respectively.

The absorption bands at  $\sim 3000\text{ cm}^{-1}$  (C-H Stretch),  $\sim 1435\text{ cm}^{-1}$  (C-C stretch) and  $\sim 810\text{ cm}^{-1}$  (C-H out of plane deformation) in all the complexes indicates the presence of cyclopentadienyl rings.

### **<sup>1</sup>H NMR Spectra:**

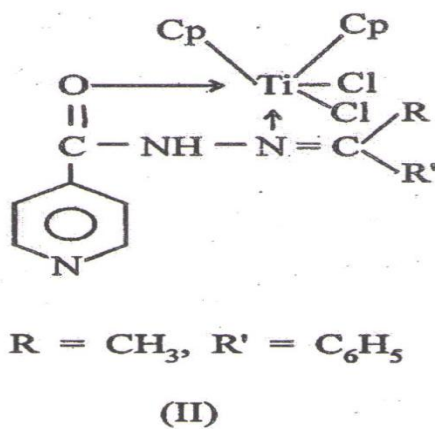
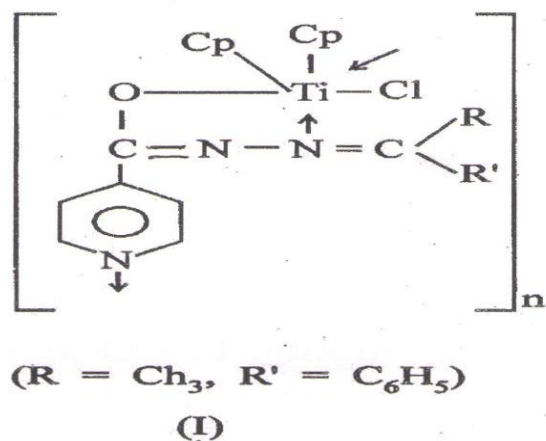
A Signal in all the derivatives at  $\delta 6.5\text{-}6.8$  may be assigned to the protons of the cyclopentadienyl rings.

The hydrazones display a signal at about  $\delta 11.3$  assignable to NH proton. This signal disappears in deprotonated complexes.

The phenolic proton signal of salicylaldehyde and o-hydroxyacetphenone at about  $\delta 12.4$  disappears in all the complexes. The signal due to pyridine proton in the spectra of different hydrazones appears at about  $\delta 8.0\text{-}8.9$ . This signal shifts down field in the adducts type complexes,

appears at  $\delta$  8.6-9.0, indicating the involvement of ring nitrogen in bonding with titanium. However, in all other complexes, the position of the signal remains almost the same.

The following structure are proposed for  $[\text{Cp}_2\text{TiCl.L}]_n$ (I) and  $[\text{Cp}_2\text{TiCl}_2\text{L}]$  (II) complexes on the basis of the above spectral evidences.



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**Table – 1: Reaction of Cp<sub>2</sub> TiCl<sub>2</sub> with different hydrazones in THF.**

Reactants taken (molar ratio)	Amine	Reflux Stirring time (h)	Product Colour Yield (%)	Found (Caled.) %				
				C	H	N	Cl	Ti
Cp <sub>2</sub> TiCl <sub>2</sub> + Ac INH-H (1:1)	BuNH <sub>2</sub>	60	{(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl(AcNH)} <sub>n</sub> , Brown (64)	63-6 (63.8)	4.6 (4.9)	9.0 (9.3)	7.6 (7.8)	10.5 (10.6)
Cp <sub>2</sub> TiCl <sub>2</sub> + S INH-H <sub>2</sub> (1:1)	BuNH <sub>2</sub>	40	{(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(SINH) <sub>2</sub> } <sub>n</sub> , Brown (40)	66.0 (66.1)	4.2 (4.5)	9.7 (10.0)	-	11.3 (11.4)
Cp <sub>2</sub> TiCl <sub>2</sub> + OIN-H <sub>2</sub> (1:1)	BuNH <sub>2</sub>	38	{(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(OINH)} <sub>n</sub> , Orange (62)	66.5 (66.5)	4.8 (4.9)	9.7 (9.7)	-	11.0 (11.1)
Cp <sub>2</sub> TiCl <sub>2</sub> + AcINH-H (1:1)	-	40	{(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub> (AcINH-H)}, Yellow (56)	58.8 (59.0)	4.5 (4.7)	8.5 (8.6)	14.5 (14.5)	9.7 (9.8)
Cp <sub>2</sub> TiCl <sub>2</sub> + SINH-H <sub>2</sub> (1:1)	-	30	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl (SINH-H), Yellowish Brown (70)	66.7 (66.8)	4.3 (4.4)	9.0 (9.2)	7.6 (7.8)	10.4 (10.5)
Cp <sub>2</sub> TiCl <sub>2</sub> + OINH-H <sub>2</sub> (1:1)	-	30	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl (OINH-H), Orange (62)	61.5 (61.6)	4.2 (4.7)	8.8 (8.9)	7.4 (7.5)	10.2 (10.2)
Cp <sub>2</sub> TiCl <sub>2</sub> + AcINH-H (1:1)	Et <sub>3</sub> N	40	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl (AcNH), Brown (45)	63.4 (63.8)	4.6 (4.9)	9.2 (9.3)	7.8 (7.8)	10.6 (10.6)
Cp <sub>2</sub> TiCl <sub>2</sub> + SNH-H <sub>2</sub> (1:1)	Et <sub>3</sub> N	20	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti SNH, Dark Brown (48)	66.0 (66.1)	4.1 (4.5)	9.7 (10.0)	-	11.4 (11.4)
Cp <sub>2</sub> TiCl <sub>2</sub> + ONH-H <sub>2</sub> (1:1)	Et <sub>3</sub> N	30	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti (ONH), Red (43)	66.6 (66.8)	4.6 (4.9)	9.6 (9.7)	-	11.0 (11.1)
Cp <sub>2</sub> TiCl <sub>2</sub> + AcNH-H (1:3)	Et <sub>3</sub> N	60	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti (AcNH) <sub>3</sub> , Brown (58)	68.0 (68.2)	4.5 (4.9)	15.0 (15.2)	-	5.7 (5.7)
Cp <sub>2</sub> TiCl <sub>2</sub> + AcNH-H (1:1)	-	40	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub> (AcNH-H), Light Brown (61)	58.6 (59.0)	4.4 (4.7)	8.5 (8.5)	14.5 (14.5)	9.8 (9.8)
Cp <sub>2</sub> TiCl <sub>2</sub> + SNH-H <sub>2</sub> (1:1)	-	20	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl (SNH-H), Yellowish Brown (50)	66.6 (66.8)	4.3 (4.4)	9.1 (9.2)	7.8 (7.8)	10.3 (10.5)
Cp <sub>2</sub> TiCl <sub>2</sub> + ONH-H <sub>2</sub> (1:1)	-	30	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> TiCl (ONH-H), Reddish Brown (54)	61.2 (61.6)	4.7 (4.7)	8.4 (8.9)	7.5 (7.5)	10.0 (10.2)



Where,

AcINH-H = Acetophenoneisoicotinoylhydrazone,

SINH-H<sub>2</sub> = Salicylaldehydeisonicotinoylhydrazone,

OINH-H<sub>2</sub> = o-Hydroxyacetophenoneisonicotinoylhydrazone,

AcNh-H<sub>2</sub> = Acetophenonenicotinoylhydrazone,

SNH-H<sub>2</sub> = Salicylaldehydenicotinoylhydrazone,

ONH-H<sub>2</sub> = o-Hydroxyacetophenonenicotinoylhydrazone,