Pyridinedicarboxylic Acid Derivatives of Dichlorobis(cyclopentadienyl)titanium(IV)

SATISH C. DIXIT* and ROHIT K. SINGH

*Deptt. of Chemistry, D.B.S.(P.G.) College, Kanpur-208006, India

Deptt. of Chemistry, Pt. J.L.N. College, Banda(U.P.), India

satishdixit1@gmail.com

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Abstract: Reactions of dichlorobis(cyclopentadienyl)titanium(IV) with pyridine dicarboxylic acids *viz.* quinolinic acid (QAH₂), 2,4-pyridine dicarboxylic acid (PAH₂), isocinchomeric acid (IAH₂), cinchomeric acid (CAH₂) and dinicotinic acid (DAH₂) were carried out in different stoichiometric ratios. Complexes of the type Cp₂Ti(QAH)Cl, Cp₂Ti(QAH)₂, Cp₂Ti(PAH)Cl, Cp₂Ti(PAH)₂, Cp₂Ti(IAH)Cl, Cp₂Ti(IAH)₂, Cp₂Ti(CAH)Cl, Cp₂Ti(CAH)₂, Cp₂Ti(DAH)Cl and Cp₂Ti(DAH)₂ were obtained. These new complexes were characterized on the basis of their elemental analyses, electrical conductance, magnetic moment and spectral data.

Keywords: Cp₂TiCl₂, Pyridinedicarboxylic Acids, Synthesis, Characterization, Complex

Introduction

Pyridine dicarboxylic acids form stable chelates with simple metal ions and oxometal cations¹⁻⁶. A very important characteristic of these ligands is their diverse biological activity⁷⁻⁸. Considerable work has been performed in developing therapeutic analogues of Cp₂TiCl₂ by varying the central metal, the labile ligands (Cl) and the bis-cyclopentadienyl moiety. In particular, small changes to the Cp ligand can strongly affect the hydrolytic stability and water solubility properties of the metallocenes and have an impact on the cytotoxic activity. Most of the analysed titanocene complexes have polar substituents on the cyclopentadienyl ring such as alkoxo, amino or electron – withdrawing groups as carboxylic acid and esters which have demonstrated in some cases a very high activity in antitumoral tests⁹⁻¹⁶.

A survey of the literature reveals that no work has been carried out on the reactions of Cp₂TiCl₂ with quinolinic acid, 2,4-pyridinedicarboxylic acid, isocinchomeric acid, cinchomeric acid and dinicotinic acid. It was, therefore, considered of interest to carry out

the reactions of dichlorobis(cyclopentadienyl)titanium(IV) with quinolinic acid, 2,4-pyridine dicarboxylic acid, isocinchomeric acid, cinchomeric acid and dinicotinic acid. The structure of the ligands used is given below:

Figure 1. Structure of the ligands used

Experimental

THF (Ferak, Berlin, FRG) was dried according to the method described¹⁷. Triethylamine and *n*-hexane were dried by the standard method¹⁸. Dichlorobis(cyclopentadienyl) titanium(IV) (Aldrich), quinolinic acid (Aldrich), 2,4-pyridinedicarboxylic acid (Aldrich), isocinchomeric acid (Aldrich), cinchomeric acid (Aldrich) and dinicotinic acid (Aldrich) were used as supplied. Stringent precautions were taken to exclude the moisture from the system. The reactions were carried out under dry nitrogen with system well protected from atmospheric nitrogen by means of calcium chloride guard tubes.

Analysis for carbon, hydrogen and nitrogen was carried out at the Central Micro Analytical Laboratory of IIT, Kanpur. Titanium was estimated gravimetrically as TiO_2 . Chlorine was determined as AgCl . The IR spectra were recorded on a Perkin-Elmer 1710 infrared Fourier Transform spectrometer in the region $400\text{--}4000\text{ cm}^{-1}$ in KBr pellets. The electronic spectra of the complexes in chloroform were recorded on a Shimadzu UV-260 spectrophotometer.

Preparation of complexes

A general procedure was followed to synthesize the complexes of Cp_2TiCl_2 with quinolinic acid; 2,4-pyridinedicarboxylic acid; isocinchomeric acid; cinchomeric acid and dinicotinic acid which involved the mixing of the reactants in anhydrous tetrahydrofuran at room temperature in the presence of triethylamine. The reaction mixture was stirred for ~ 32-42 h. The precipitated $\text{Et}_3\text{N}\cdot\text{HCl}$ was filtered off and the solvent was removed under reduced pressure. The product so obtained was recrystallized from a *n*-hexane/ THF mixture. The relevant details of the preparative method used and the complexes obtained are summarized in Table 1. The analytical data of these complexes are tabulated in Table 2.

Table 1. Reactions of Cp_2TiCl_2 with pyridinedicarboxylic Acids

Reactants, g			Molar Ratio	Stirring Time, h	Product	Colour, Decompo. Temp °C
Cp_2TiCl_2	Acid	Et_3N				
0.69	QAH ₂ , 0.46	0.28	1:1:1	32	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{QAH})\text{Cl}$	Dark red, 112
0.85	QAH ₂ , 1.14	0.69	1:2:2	35	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{QAH})_2$	Dark red, 118(M.P.)
0.79	PAH ₂ , 0.53	0.32	1:1:1	40	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{PAH})\text{Cl}$	Red, 115
0.75	PAH ₂ , 1.01	0.61	1:2:2	42	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{PAH})_2$	Red, 118
0.74	IAH ₂ , 0.50	0.30	1:1:1	38	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{IAH})\text{Cl}$	Reddish brown, 125
0.71	IAH ₂ , 0.95	0.58	1:2:2	39	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{IAH})_2$	Red, 135(M.P.)
0.80	CAH ₂ , 0.54	0.33	1:1:1	30	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CAH})\text{Cl}$	Dark red, 125
0.83	CAH ₂ , 1.11	0.67	1:2:2	32	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CAH})_2$	Red, 122(M.P.)
0.74	DAH ₂ , 0.50	0.30	1:1:1	35	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{DAH})\text{Cl}$	Dark red, 118
0.85	DAH ₂ , 1.14	0.69	1:2:2	36	$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{DAH})_2$	Light red, 125

Where QAH₂= quinolinic acid; PAH₂= 2,4 -pyridinedicarboxylic acid, IAH₂= isocinchomeric acid; CAH₂= cinchomeric acid, DAH₂= dinicotinic acid

Table 2. Characterization data

Complex	Analysis: found (calc.), %					λ_{max} , nm (in CHCl_3)
	Ti	C	H	N	Cl	
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{QAH})\text{Cl}$	12.7 (12.63)		3.67 3.69	3.56 3.69	9.3 9.36	245.4
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{QAH})_2$	9.36 (9.39)	55.16 56.48	3.5 3.53		--	243.2
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{PAH})\text{Cl}$	12.66 (12.63)	52.5 53.77			9.32 9.36	250.4
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{PAH})_2$	9.35 (9.39)		3.5 3.53	5.1 5.49	--	254.2
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{IAH})\text{Cl}$	12.64 (12.63)		3.64 3.69	3.5 3.69	9.31 9.36	258.0
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{IAH})_2$	9.35 (9.39)	55.7 56.48	3.49 3.53		--	262.2
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CAH})\text{Cl}$	12.8 (12.63)	53.18 53.77			9.4 9.36	258.2
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CAH})_2$	9.35 (9.39)	55.9 56.48			--	262.4
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{DAH})\text{Cl}$	12.59 (12.63)		3.61 3.69	3.57 3.69	9.32 9.36	248.6
$(\text{C}_5\text{H}_5)_2\text{Ti}(\text{DAH})_2$	9.41 (9.39)	55.6 56.48		5.38 5.49	--	250.0

Results and Discussion

Reactions of Cp_2TiCl_2 with different pyridine dicarboxylic acids viz. quinolinic acid; 2,4-pyridinedicarboxylic acid; isocinchomeric acid; cinchomeric acid and dinicotinic acid in 1:1 and 1:2 molar ratios in anhydrous THF in the presence of triethylamine at room temperature may be represented by the following general equation:

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