

Some New Derivatives of Organozirconium(IV) and Organotitanium(IV) with Pyridinecarboxylic Acids

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Abstract

Reactions of dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) with pyridinecarboxylic acids *viz.* picolinic acid (HPicA), isonicotinic acid (HisonicA) and dipicolinic acid (DipicH₂) were carried out in different stoichiometric ratios. Complexes of the types Cp₂M(PicA)Cl, Cp₂M(PicA)₂, Cp₂M(IsonicA)Cl, Cp₂M(IsonicA)₂, Cp₂M(DipicH)Cl and Cp₂M(DipicH)₂ (where M = Zr or Ti) were obtained. These new complexes were characterized on the basis of their elemental analysis, electrical conductance, magnetic moment, ¹H NMR, IR and electronic spectral data.

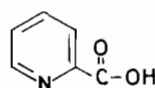
Introduction

Pyridinecarboxylic acids have been found on the basis of the reported X-ray molecular structures to be interesting and versatile ligands [1]. Some pyridinecarboxylic acids and their esters may be used as medicaments in the form of their complexes with MgCl₂, CaCl₂, Ca(NCS)₂ and SrCl₂ [2]. Some of the cobalt, zinc and copper complexes [3, 4] have also found practical application in medicine. More recently, Stelsenko *et al.* [5] have reported the preparation and study of the acidic properties of platinum(II) complexes with isonicotinic acid. Dipicolinic acid can function as a neutral, monobasic or dibasic tridentate chelating ligand. A large number of bivalent or trivalent transition metal and lanthanide(III) complexes of dipicolinic acid have been studied [6–9]. Recently, some cobalt(II) and cobalt(III) complexes of dipicolinic acid have been synthesized to explore the possibility of their use as models to explain some intricate reactions in biological systems [10, 11]. Dipicolinic acid and its derivatives are of biological interest [12, 13]. Sodium 2,6-pyridinedicarboxylate was tested with some success to inhibit the thermal denaturation of

proteins [14]. Ferric 2,6-pyridinedicarboxylate has been considered as a suitable compound for therapeutic injections against anemia [15]. The recent discovery by Köpf and Köpf-Maier [16] that titanocene-dichloride, Cp₂TiCl₂ is the most effective metallocene as an antitumour agent with a cure rate in the therapeutic range of over 80%, has generated much interest in the biological field. Zirconocene dichloride, Cp₂ZrCl₂ is a poor antitumour agent [17].

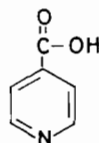
A survey of the literature reveals that no work has been carried out on the reactions of dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) with picolinic acid, isonicotinic acid and dipicolinic acid. It was, therefore, considered of interest to carry out the reactions of dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) with picolinic acid, isonicotinic acid and dipicolinic acid.

The structure of the pyridinecarboxylic acids used is given below



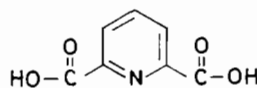
Picolinic acid

(2-pyridinecarboxylic acid)



Isonicotinic acid

(4-pyridinecarboxylic acid)



Dipicolinic acid

(2,6-pyridinedicarboxylic acid)

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Experimental

THF (Ferak, Berlin, F.R.G.) was dried according to the method described [18]. Triethylamine and n-hexane were dried by the standard method [19]. Dichlorobis(cyclopentadienyl)titanium(IV) was prepared by a known method [20]. CpNa and dichlorobis(cyclopentadienyl)zirconium(IV) were prepared as reported in the literature [21–23]. Picolinic acid (Aldrich) and isonicotinic acid (Aldrich) were used as supplied. Dipicolinic acid was dried under vacuum before use. Stringent precautions were taken to exclude moisture from the system. The reactions were carried out under dry nitrogen with the system well protected from atmospheric moisture by means of CaCl₂ guard tubes.

Analysis for carbon, hydrogen and nitrogen was carried out at the Central Micro-Analytical Laboratory of the Indian Institute of Technology, Kanpur. Zirconium and titanium were estimated gravimetrically as ZrO₂ and TiO₂. Chlorine was determined as AgCl. The IR spectra were recorded on a Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer

in the region 400–4000 cm⁻¹ in KBr pellets. The ¹H NMR spectra were recorded on a Jeol JNM-FX200 Fourier Transform Spectrometer, using CDCl₃ as solvent. 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 Cp₂ZrCl₂ and Cp₂TiCl₂ with picolinic acid (HPicA), isonicotinic acid (HisonicA) and dipicolinic acid (DipicH₂) which involved the mixing of the reactants in anhydrous tetrahydrofuran at room temperature in the presence of triethylamine. The reaction mixture was stirred for ~20–31 h. The precipitated Et₃N·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 Cp₂ZrCl₂ and Cp₂TiCl₂ with Pyridinecarboxylic Acids

Reactants			Molar ratio	Stirring time (h)	Product	Colour, melting point (°C)
Cp ₂ MCl ₂	Pyridinecarboxylic acid ^a	Et ₃ N				
Cp ₂ ZrCl ₂ 0.51 g, 1.75 mmol	HPicA 0.21 g, 1.71 mmol	0.18 g, 1.78 mmol	1:1:1	22	(C ₅ H ₅) ₂ Zr(PicA)Cl	brown, 135 (decomp. temp.)
Cp ₂ ZrCl ₂ 0.38 g, 1.30 mmol	HPicA 0.32 g, 2.60 mmol	0.26 g, 2.57 mmol	1:2:2	23	(C ₅ H ₅) ₂ Zr(PicA) ₂	brown, 125 (decomp. temp.)
Cp ₂ ZrCl ₂ 0.83 g, 2.84 mmol	HisonicA 0.35 g, 2.84 mmol	0.29 g, 2.87 mmol	1:1:1	25	(C ₅ H ₅) ₂ Zr(IsonicA)Cl	brown, 125 (decomp. temp.)
Cp ₂ ZrCl ₂ 0.44 g, 1.51 mmol	HisonicA 0.37 g, 3.01 mmol	0.31 g, 3.06 mmol	1:2:2	24	(C ₅ H ₅) ₂ Zr(IsonicA) ₂	brown, 92
Cp ₂ ZrCl ₂ 0.85 g, 2.91 mmol	DipicH ₂ 0.48 g, 2.87 mmol	0.29 g, 2.87 mmol	1:1:1	31	(C ₅ H ₅) ₂ Zr(DipicH)Cl	brown, 190
Cp ₂ ZrCl ₂ 0.49 g, 1.68 mmol	DipicH ₂ 0.56 g, 3.35 mmol	0.34 g, 3.36 mmol	1:2:2	30	(C ₅ H ₅) ₂ Zr(DipicH) ₂	grey, 200 (decomp. temp.)
Cp ₂ TiCl ₂ 1.60 g, 6.43 mmol	HPicA 0.79 g, 6.42 mmol	0.65 g, 6.42 mmol	1:1:1	24	(C ₅ H ₅) ₂ Ti(PicA)Cl	red, 108
Cp ₂ TiCl ₂ 0.82 g, 3.29 mmol	HPicA 0.81 g, 6.58 mmol	0.66 g, 6.52 mmol	1:2:2	24	(C ₅ H ₅) ₂ Ti(PicA) ₂	yellow, 102

(continued)

TABLE 1. (continued)

Reactants			Molar ratio	Stirring time (h)	Product	Colour, melting point (°C)
Cp ₂ MCl ₂	Pyridinecarboxylic acid ^a	Et ₃ N				
Cp ₂ TiCl ₂ 1.53 g, 6.14 mmol	HlsonicA 0.75 g, 6.09 mmol	0.62 g, 6.13 mmol	1:1:1	20	(C ₅ H ₅) ₂ Ti(IsonicA)Cl	brick red, 140 (decomp. temp.)
Cp ₂ TiCl ₂ 1.26 g, 5.06 mmol	HlsonicA 1.25 g, 10.15 mmol	1.02 g, 10.08 mmol	1:2:2	21	(C ₅ H ₅) ₂ Ti(IsonicA) ₂	brown, 125 (decomp. temp.)
Cp ₂ TiCl ₂ 0.86 g, 3.45 mmol	DipicH ₂ 0.58 g, 3.47 mmol	0.35 g, 3.46 mmol	1:1:1	24	(C ₅ H ₅) ₂ Ti(DipicH)Cl	brick red, 180 (decomp. temp.)
Cp ₂ TiCl ₂ 0.61 g, 2.45 mmol	DipicH ₂ 0.82 g, 4.91 mmol	0.50 g, 4.94 mmol	1:2:2	20	(C ₅ H ₅) ₂ Ti(DipicH) ₂	cream, 165 (decomp. temp.)

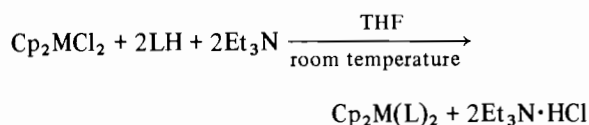
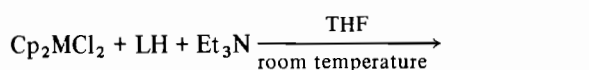
^aHPicA = picolinic acid; HlsonicA = isonicotinic acid; DipicH₂ = dipicolinic acid.

TABLE 2. Characterization Data

Complex	Analysis: found(calc.) (%)					C ₅ H ₅ ¹ H NMR (δ ppm)	λ _{max} (nm) (in CHCl ₃)
	M	C	H	N	Cl		
(C ₅ H ₅) ₂ Zr(PicA)Cl	24.1 (24.08)	50.36 (50.69)	3.39 (3.69)		9.23 (9.37)	6.36	265
(C ₅ H ₅) ₂ Zr(PicA) ₂	19.41 (19.60)	55.87 (56.74)	3.22 (3.86)	6.58 (6.01)		6.32	267.4
(C ₅ H ₅) ₂ Zr(IsonicA)Cl	23.95 (24.08)	51.09 (50.69)	3.82 (3.69)	3.18 (3.69)	9.26 (9.37)		246.8
(C ₅ H ₅) ₂ Zr(IsonicA) ₂	19.68 (19.60)	56.32 (56.74)	3.29 (3.86)	6.77 (6.01)			245.6
(C ₅ H ₅) ₂ Zr(DipicH)Cl	21.42 (21.57)	47.38 (48.24)	2.93 (3.31)		8.12 (8.39)		265.6
(C ₅ H ₅) ₂ Zr(DipicH) ₂	16.34 (16.48)	53.09 (52.03)	3.22 (3.25)	5.75 (5.05)			266.2
(C ₅ H ₅) ₂ Ti(PicA)Cl	14.18 (14.3)	56.82 (57.23)	4.08 (4.17)	4.28 (4.17)	10.45 (10.58)	6.64	254.4
(C ₅ H ₅) ₂ Ti(PicA) ₂	11.24 (11.37)	62.85 (62.56)	4.22 (4.27)	6.17 (6.64)		6.7	248.8
(C ₅ H ₅) ₂ Ti(IsonicA)Cl	13.99 (14.3)	56.84 (57.22)	4.26 (4.17)	4.63 (4.17)	10.43 (10.58)		254
(C ₅ H ₅) ₂ Ti(IsonicA) ₂	11.41 (11.37)		4.36 (4.27)				262.4
(C ₅ H ₅) ₂ Ti(DipicH)Cl	12.53 (12.62)	53.84 (53.75)	4.02 (3.68)	3.33 (3.68)	9.25 (9.35)		256.6
(C ₅ H ₅) ₂ Ti(DipicH) ₂	9.26 (9.39)	55.92 (56.45)		5.42 (5.49)			243.4

Results and Discussion

Reactions of dichlorobis(cyclopentadienyl)zirconium(IV), Cp_2ZrCl_2 and dichlorobis(cyclopentadienyl)titanium(IV), Cp_2TiCl_2 with different pyridinecarboxylic acids *viz.* picolinic acid (HPicA), isonicotinic acid (HisonicA) and dipicolinic acid (DipicH₂) in 1:1 and 1:2 molar ratios in anhydrous tetrahydrofuran in the presence of triethylamine at room temperature may be represented by the following general equations



where Cp = Cyclopentadienyl; M = Zr or Ti; LH = HPicA or HisonicA or DipicH₂.

All the complexes are crystalline, and extremely sensitive to hydrolysis. The complexes are soluble in tetrahydrofuran and chloroform, but insoluble in n-hexane and petroleum ether. Magnetic susceptibility values at room temperature of these complexes show their diamagnetic nature. The electrical conductance measurements of the complexes in acetone showed them to be non-electrolyte.

The IR spectra of the complexes invariably show the usual absorptions due to cyclopentadienyl groups at ~ 3100 [$\nu(\text{C-H})$], ~ 1435 [$\nu(\text{C-C})$], ~ 1020 [$\delta_{\text{i.p.}}(\text{CH})$] and ~ 810 [$\delta_{\text{o.p.}}(\text{CH})$] cm^{-1} [24]. The persistence of the bands of cyclopentadienyl rings in the complexes indicate that these groups remain delocalized and π -bonded to the metal and retain their aromatic character. In the IR spectra of free acids, picolinic acid and isonicotinic acid, the absorption bands due to $\nu(\text{OH})$ and $\nu(\text{C=O})$ appear in the regions 3000–2600 and 1710–1680 cm^{-1} respectively. The band due to $\nu(\text{OH})$ disappears in the complexes indicating the complete removal of the hydroxyl proton of the acids. The bands at 1710 and 1680 cm^{-1} due to $\nu(\text{C=O})$ exhibit a downward shift in the complexes and appear in the region 1606–1600 cm^{-1} indicating the coordination of carbonyl oxygen to the metal. The values of the $\nu(\text{COO})_{\text{asym}}$ and $\nu(\text{COO})_{\text{sym}}$ stretching vibrations of the complexes studied and of the sodium salts of pyridinecarboxylic acids are listed in Table 3. From the inspection of Table 3, it appears that in the complexes the $\Delta\nu$ value [$\Delta\nu = \nu(\text{COO})_{\text{asym}} - \nu(\text{COO})_{\text{sym}}$] is smaller by 120–70 cm^{-1} than that of the corresponding sodium salts. This suggests that bonding of

TABLE 3. Infrared Carbon–Oxygen Stretching Frequencies (cm^{-1})

Compound	$\nu(\text{COO})_{\text{asym}}$	$\nu(\text{COO})_{\text{sym}}$	$\Delta\nu^a$
PicANa	1605	1410	195
IsonicANa	1590	1410	180
DipicNa ₂	1610	1390	220
(C ₅ H ₅) ₂ Zr(PicA)Cl	1605	1480	125
(C ₅ H ₅) ₂ Zr(PicA) ₂	1600	1480	120
(C ₅ H ₅) ₂ Zr(IsonicA)Cl	1602	1525	77
(C ₅ H ₅) ₂ Zr(IsonicA) ₂	1601	1525	76
(C ₅ H ₅) ₂ Zr(DipicH)Cl	1600	1500	100
(C ₅ H ₅) ₂ Zr(DipicH) ₂	1605	1500	105
(C ₅ H ₅) ₂ Ti(PicA)Cl	1600	1475	125
(C ₅ H ₅) ₂ Ti(PicA) ₂	1605	1500	105
(C ₅ H ₅) ₂ Ti(IsonicA)Cl	1606	1500	106
(C ₅ H ₅) ₂ Ti(IsonicA) ₂	1603	1500	103
(C ₅ H ₅) ₂ Ti(DipicH)Cl	1650	1525	125
(C ₅ H ₅) ₂ Ti(DipicH) ₂	1645	1520	125

$$^a \Delta\nu = \nu(\text{COO})_{\text{asym}} - \nu(\text{COO})_{\text{sym}}$$

the carboxylate groups to the metal is bidentate in these complexes. The pyridine nitrogen is not involved in coordination since there is no upward shift of the pyridine (coupled) C=C and C=N stretch [25–28] in the complexes. All the acid derivatives show the breathing mode of the pyridine ring in the region 996–993 cm^{-1} [29, 30].

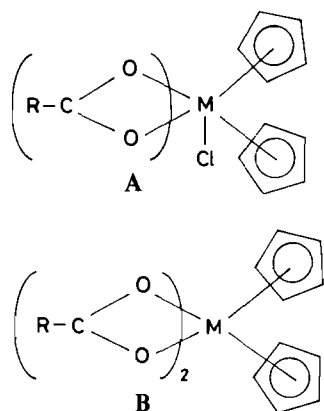
The IR spectral data for the dicarboxylate complexes show the presence of both the ‘free’ carboxylic and coordinated carboxylate groups at 1700 cm^{-1} and in the region 1650–1600 cm^{-1} respectively. This is strong evidence that only one of the two carboxylic acid groups is bonded to the metal. The pyridine stretch is observed at 1580 cm^{-1} in these complexes which indicates the non-involvement of the pyridine nitrogen in the coordination. All the complexes show the ring breathing mode of the pyridine at 998 cm^{-1} [29, 30].

The ring breathing vibrations of pyridine do not show shift to higher frequencies in these derivatives and occur almost at the same positions as in the free acids indicating that pyridine nitrogen is not involved in the bonding with the metal. The bands at ~ 450 cm^{-1} and in the region 485–460 cm^{-1} may be assigned to $\nu(\text{Zr-O})$ [31] and $\nu(\text{Ti-O})$ [32, 33] respectively.

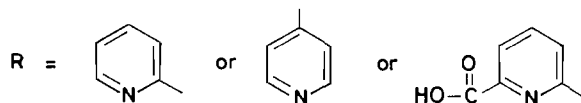
¹H NMR spectra of picolinic acid derivatives of dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) show a signal due to cyclopentadienyl groups in the region δ 6.7–6.32 ppm [34, 35]. (The different proton magnetic resonance signals are given in Table 2.) The spectra of the complexes show no signal at δ 11.94 ppm which indicates the complete removal of the hydroxyl proton of the carboxylic group.

The electronic spectra of all the complexes, recorded in chloroform, show fairly intense bands between 267.4 and 243.4 nm which can be attributed to the charge transfer band [36, 37]. (The positions of the absorption bands in the UV and visible regions of the electronic spectra of the complexes are given in Table 2.)

On the basis of elemental analyses, spectroscopic data, electrical conductance and magnetic susceptibility measurements, the following structures (A and B) may be tentatively assigned for $(C_5H_5)_2M(L)Cl$ and $(C_5H_5)_2M(L)_2$ complexes respectively.



(where $M = Zr$ or Ti ; $L = HPicA$, $HisonicA$ or $DipicH_2$)



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