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Heterocarboxylates of Dichlorobis(cyclopentadienyl)zirconium(IV) and Dichlorobis(cyclopentadienyl)titanium(IV)

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Abstract

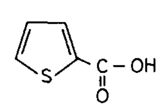
Reactions of dichlorobis(cyclopentadienyl)zirconium(IV) and dichlorobis(cyclopentadienyl)titanium(IV) with 2-thiophenecarboxylic acid (2-TCH), 2-thiopheneacetic acid (2-TAH) and nicotinic acid (HNicA) were carried out in different stoichiometric ratios. The complexes of the type $Cp_2M(2\text{-TA})Cl$, $Cp_2M(2\text{-TA})_2$, $Cp_2M(2\text{-TC})Cl$, $Cp_2M(2\text{-TC})_2$, $Cp_2M(NicA)Cl$ and $Cp_2M(NicA)_2$ (where M = Ti or Zr) were obtained. These were characterized by their elemental analysis, ^1H NMR, IR, mass spectra and electronic spectral data. Magnetic susceptibility data reveals their diamagnetic nature.

Introduction

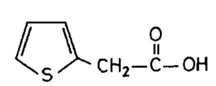
In recent years, metal carboxylates have received renewed interest in the field of coordination chemistry because of the ability of carboxylate ions to employ various (monodentate, bidentate or bridging) coordinating sites [1]. Wailes and Weigold [2] prepared $Cp_2Zr(O_2CCF_3)_2$ and $CpZr(O_2CCH_3)_3$ by treating the dihydride Cp_2ZrH_2 with excess acid. King and Kapoor [3] prepared the volatile bis(trifluoroacetate) and bis(heptafluoropropionate) in over 70% yield by the reaction of Cp_2ZrCl_2 with the silver salt of the acid. More recently, Xu *et al.* [4] reported the synthesis of perfluoro-organic acid derivatives of titanocene and also investigated their anticancer behaviour in mice.

Sankhla and coworkers [5] studied the reactions of heterocyclic carboxylic acids with lanthanide elements and obtained interesting results. Nicotinic acid forms a whole series of salts with heavy metals [6]. Neodymium and samarium nicotinates are used in medicine to prevent intravenous clotting [7]. In view of the interesting results obtained with lanthanides, it was considered of interest to investigate the reactions of 2-thiopheneacetic acid, 2-thiophenecarboxylic acid and nicotinic acid with dichlorobis(cyclopentadientyl)zirconium(IV), Cp_2ZrCl_2 and dichlorobis(cyclopentadienyl)titanium(IV), Cp_2TiCl_2.

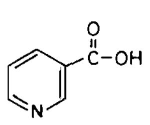
The structure of the ligands used is given below:



2-Thiophenecarboxylic acid



2-Thiopheneacetic acid



Nicotinic acid

Experimental

THF (Ferak, Berlin, F.R.G.) was dried by storage over sodium wire overnight and was then refluxed until it gave a blue coloration with benzophenone. It was finally dried by distilling over $LiAlH_4$. n-Hexane and triethylamine were dried by the reported method [8]. CpNa and bis(cyclopentadienyl)zirconium(IV) chloride were prepared as reported in the literature [9, 10]. Dichlorobis(cyclopentadienyl)titanium(IV) was prepared by a known method [11]. 2-Thiopheneacetic acid (Aldrich), 2-thiophenecarboxylic acid (Aldrich) and nicotinic acid (Aldrich) were used as supplied. Glass apparatus with interchangeable standard joints was used throughout this work; stringent precautions were taken to exclude moisture from the system. The reactions were carried out under nitrogen and the system was well protected from atmospheric moisture by means of $CaCl_2$ guard tubes.

Zirconium and titanium were estimated gravimetrically as ZrO_2 and TiO_2. Carbon, hydrogen and nitrogen were analysed at the central Micro-Analytical Laboratories of the I.I.T., Kanpur and Delhi. Chlorine was estimated as AgCl. The IR spectra were recorded in KBr pellets on a Shimadzu IR-435

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spectrophotometer in the range 400–4000 cm^{-1}. The ^{1}H NMR spectra were recorded on a JEOL-JNM-FX200 Fourier Transform spectrometer, using $CDCl_3$ as solvent. The electronic spectra of the complexes in chloroform solution were recorded on a Shimadzu UV-260 spectrophotometer. The mass spectra were recorded in the University of Texas at Austin (U.S.A.).

Preparation of Complexes

A general procedure adapted for the preparation of the complexes of Cp_2ZrCl_2 and Cp_2TiCl_2 with 2-thiopheneacetic acid, 2-thiophenecarboxylic acid and nicotinic acid involved mixing of the reactants in tetrahydrofuran in the presence of triethylamine at room temperature. The reaction mixture was stirred for ~30–35 h. The precipitated $Et_3N \cdot HCl$ was filtered off and the solvent was removed *in vacuo*. The product so obtained was recrystallized from n-hexane/THF mixture. The relevant details of the preparative method used and the complexes obtained are summarized in Table I. The analytical data of these complexes are given in Table II.

Results and Discussion

Reactions of Cp_2ZrCl_2 and Cp_2TiCl_2 with different heterocarboxylic acids, *viz.* 2-thiopheneacetic acid (2-TAH), 2-thiophenecarboxylic acid (2-TCH) and nicotinic acid (HNicA) in anhydrous THF in the presence of triethylamine may be represented by the following general equations:

$$Cp_2MCl_2 + LH + Et_3N \xrightarrow[\text{room temperature}]{\text{THF}} Cp_2M(L)Cl + Et_3N \cdot HCl$$

$$Cp_2MCl_2 + 2LH + 2Et_3N \xrightarrow[\text{room temperature}]{\text{THF}} Cp_2M(L)_2 + 2Et_3N \cdot HCl$$

where Cp = cyclopentadienyl; M = Zr, Ti; LH = 2-TAH, 2-TCH, HNicA

All these complexes are crystalline solids and extremely sensitive to hydrolysis. They are soluble in tetrahydrofuran and chloroform but insoluble in n-hexane and petroleum ether. Magnetic susceptibility values at room temperature of these complexes show that all are diamagnetic in nature.

The IR spectra of the complexes invariably exhibit the usual absorptions due to cyclopentadienyl groups at ~3100 cm^{-1} [ν(C–H)], ~1435 cm^{-1} [ν(C–C)], ~1020 cm^{-1} [$\delta_{i.p.}$(–CH)] and ~810 cm^{-1} [$\delta_{o.p.}$(–CH)] [12, 13]. The persistence of

TABLE I. Reactions of Cp_2ZrCl_2 and Cp_2TiCl_2 with Heterocarboxylic Acids

Reactants (g)			Molar ratio	Stirring time (h)	Product	Colour, decomposition temperature (°C)
Cp_2MCl_2	Heterocarboxylic acid[a]	Et_3N				
Cp_2ZrCl_2 0.66	2-TAH 0.32	0.23	1:1:1	30	$(C_5H_5)_2Zr(2\text{-}TA)Cl$	light brown, 120
Cp_2ZrCl_2 0.51	2-TAH 0.49	0.35	1:2:2	31	$(C_5H_5)_2Zr(2\text{-}TA)_2$	light brown, 115
Cp_2ZrCl_2 0.74	2-TCH 0.32	0.26	1:1:1	30	$(C_5H_5)_2Zr(2\text{-}TC)Cl$	light brown, 165
Cp_2ZrCl_2 1.01	2-TCH 0.88	0.70	1:2:2	35	$(C_5H_5)_2Zr(2\text{-}TC)_2$	brown, 180
Cp_2ZrCl_2 1.27	HNicA 0.53	0.44	1:1:1	32	$(C_5H_5)_2Zr(NicA)Cl$	light brown, 145
Cp_2ZrCl_2 0.97	HNicA 0.82	0.67	1:2:2	30	$(C_5H_5)_2Zr(NicA)_2$	brown, 175
Cp_2TiCl_2 1.50	2-TAH 0.86	0.61	1:1:1	32	$(C_5H_5)_2Ti(2\text{-}TA)Cl$	dark red, 105
Cp_2TiCl_2 0.58	2-TAH 0.67	0.47	1:2:2	30	$(C_5H_5)_2Ti(2\text{-}TA)_2$	brown, 105
Cp_2TiCl_2 0.78	2-TCH 0.40	0.32	1:1:1	29	$(C_5H_5)_2Ti(2\text{-}TC)Cl$	orange, 120
Cp_2TiCl_2 0.81	2-TCH 0.84	0.66	1:2:2	30	$(C_5H_5)_2Ti(2\text{-}TC)_2$	orange, 135
Cp_2TiCl_2 0.73	HNicA 0.36	0.30	1:1:1	33	$(C_5H_5)_2Ti(NicA)Cl$	brick red, 140
Cp_2TiCl_2 0.99	HNicA 0.98	0.81	1:2:2	35	$(C_5H_5)_2Ti(NicA)_2$	brown, 170

[a] 2-TAH = 2-thiopheneacetic acid; 2-TCH = 2-thiophenecarboxylic acid; HNicA = nicotinic acid.

TABLE II. Characterization Data

Complex	Analysis, found(calc) (%)					λ_{max} (nm) (in $CHCl_3$)	^{1}H NMR (δ ppm) (C_5H_5)	Molecular weight found(calc.)
	M	C	H	Cl	N			
$Cp_2Zr(2\text{-}TA)Cl$	22.74		3.85	8.58		248.4	6.2	429
	(22.93)		(3.77)	(8.92)				(397.72)
$Cp_2Zr(2\text{-}TA)_2$	18.09		4.47			251.4	6.54	
	(18.12)		(3.97)					
$Cp_2Zr(2\text{-}TC)Cl$	23.8	45.37	3.26	8.94		271.2	6.32	
	(23.77)	(46.9)	(3.38)	(9.25)				
$Cp_2Zr(2\text{-}TC)_2$	18.9	54.46	3.44			271.2	6.32	
	(19.2)	(50.50)	(3.37)					
$Cp_2Zr(NicA)Cl$	24.19	46.32	3.63	9.15		261.4	6.48	
	(24.08)	(50.69)	(3.69)	(9.37)				
$Cp_2Zr(NicA)_2$	19.84		4.26		5.87	263.2	6.52	497
	(19.60)		(3.86)		(6.01)			(465.22)
$Cp_2Ti(2\text{-}TA)Cl$	13.33	49.94	4.06	9.8		259.6	6.64	
	(13.54)	(54.16)	(4.23)	(10.01)				
$Cp_2Ti(2\text{-}TA)_2$	10.77		4.47			245.4	6.6	
	(10.43)		(4.34)					
$Cp_2Ti(2\text{-}TC)Cl$	14.42	48.82	4.02	10.00		251.6	6.64	
	(14.09)	(52.86)	(3.82)	(10.42)				
$Cp_2Ti(2\text{-}TC)_2$	10.99	53.9	4.3			249.4	6.72	447
	(11.1)	(55.55)	(3.7)					(432.00)
$Cp_2Ti(NicA)Cl$	14.4	54.78		10.26	4.79	254.5	6.52	
	(14.3)	(57.22)		(10.58)	(4.17)			
$Cp_2Ti(NicA)_2$	11.19	62.07	3.9		7.26	256.6	6.6	
	(11.37)	(62.56)	(4.27)		(6.64)			

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 the free acids, 2-thiophenecarboxylic acid and 2-thiopheneacetic acid, the bands due to ν(OH) and ν(C=O) appear in the region 3140–3120 cm^{-1} and 1690–1720 cm^{-1} respectively. The band due to ν(OH) disappears in the complexes indicating the complete removal of the hydroxyl proton of the acids. The bands at 1690 and 1720 cm^{-1} due to ν(C=O) show a downward shift of ~125 cm^{-1} and appear in the region 1610–1560 cm^{-1} indicating that the carboxyl oxygen is coordinated to the metal. This suggests that bonding of the carboxylate group to the metal is bidentate in heterocarboxylates of Cp_2ZrCl_2 and Cp_2TiCl_2. All the acid derivatives show the usual IR absorptions of 2-substituted thiophene with the ring breathing mode in the region 860–858 cm^{-1} [14]. The ring breathing vibrations of thiophene do not show any appreciable positive shift in these derivatives and occur almost at the same positions as in free acids indicating that heterosulphur is not involved in the coordination. The absorption bands in the region 580–440 cm^{-1} are assigned to metal–oxygen stretching vibration [15].

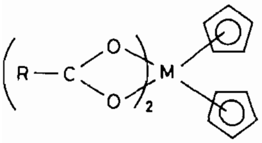
The asymmetric mode of the COO group at 1700 cm^{-1} in nicotinic acid is shifted to 1640 cm^{-1} in the complexes indicating coordination of the COO$^-$ anion to the metal. The pyridine nitrogen is not involved in coordination since there is no upward shift of the pyridine (coupled) C=C and C=N stretch [16–19] in the complexes. This argument is confirmed by the absence of the ν(M–N) band (where M = Zr, Ti) [20]. The band at ~450 cm^{-1} may be assigned to ν(M–O) [21].

^{1}H NMR spectra of all the complexes show a signal due to cyclopentadienyl groups in the region δ ~6.2–6.94 (The different proton magnetic resonance signals are given in Table II.) The spectra of the complexes show no signal in the region δ 13.43–11.0 which indicates complete removal of the hydroxyl proton of the carboxylic groups.

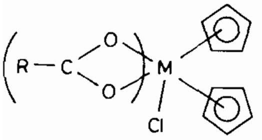
The electronic spectra of all complexes are recorded in chloroform. (The positions of the absorption bands in the UV and visible regions of the electronic spectra of the complexes are given in Table II.) The fairly intense bands between 248 and 301 nm can be assigned to the charge transfer band [22] and is in accord with their $(n-1)d^0$, nS^0 electronic configurations.

The values of molecular weight of the complexes calculated from their empirical formulae are in good agreement with the values obtained from their mass spectra. The values clearly indicate the monomeric nature of these complexes. The values of molecular weight obtained from mass spectra are given in Table II.

On the basis of elemental analysis and spectroscopic data, the following structures (**I** and **II**) may be tentatively proposed for $(C_5H_5)_2M(L)Cl$ and $(C_5H_5)_2M(L)_2$ complexes respectively.

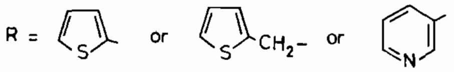


I



II

where M = Zr or Ti, L = 2-TCH or 2-TAH or HNicA



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References

1 C. Oldham, 'Progress in Inorganic Chemistry', Vol. 10, Interscience, New York, 1968, p. 223.
2 P. C. Wailes and H. Weigold, *J. Organomet. Chem., 24,* 413 (1970).
3 R. B. King and R. N. Kapoor, *J. Organomet. Chem., 15,* 457 (1968).
4 W. Xu, P. Lu, J. Lu, Y. Yang, X. Zhang, S. Zhand and B. Xu, *Youji Huascue, 366* (1984); *Chem. Abstr., 102,* 79039 (1985).
5 K. S. Gharia, Megh Singh, S. Mathur and B. S. Sankhla, *J. Indian Chem. Soc., LX,* 315 (1983).
6 J. Houben and T. Weyl, 'Die Methoden der Organischen Chemie', Vol. 4, No. 1, Book 2, 1949, p. 936.
7 V. V. Serebrennikov, 'Khimiya Redkozemel' nykh Elementov' (The Chemistry of the Rare-Earth Elements), Vol. 1, 1959, p. 20.
8 A. I. Vogel, 'A Text Book of Practical Organic Chemistry', Longman Green, London, 1948.
9 W. L. Jolly, 'Synthetic Inorganic Chemistry', Prentice Hall India (Pvt.) Ltd., New Delhi, 1965, p. 176.
10 G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc., 76,* 4281 (1954).
11 J. J. Eisch and R. B. King, 'Organometallic Synthesis', Vol. 1, Academic Press, New York, 1965.
12 H. P. Fritz, *Adv. Organomet. Chem., 1,* 279 (1964).
13 S. A. Gidding and R. J. Bert, *J. Am. Chem. Soc., 83,* 2393 (1961).
14 A. R. Katritzky and A. J. Boulton, *J. Chem. Soc.,* 3500 (1959).
15 C. Y. Liang, E. J. Schimtschek and J. A. Trias, *J. Inorg. Nucl. Chem.,* 1970, 32, 811.
16 A. J. Canty and G. B. Deacon, *Aust. J. Chem., 24,* 489 (1971).
17 M. Phytzenopoulas, G. Pnenmatikakis, N. Hadjliadis and D. Katakis, *J. Inorg. Nucl. Chem., 39,* 965 (1977).
18 M. M. daMota, J. Rodgers and S. M. Nelson, *J. Chem. Soc., A,* 2036 (1969)
19 R. C Paul, R. S. Chopra and G. Singh, *Inorg. Chim. Acta, 14,* 105 (1975).
20 K. Brodersen and H. J. Becher, *Chem. Ber., 89,* 1487 (1956).
21 K. C. Malhotra and S. C. Chaudhary, *Aust. J. Chem., 27,* 79 (1974).
22 P. B. Dorain, H. H. Patterson and P. C. Jordon, *J. Chem. Phys., 49,* 3845 (1968).