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Heterocarboxylates of bis(cyclopentadienyl)hafnium(IV) dichloride

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Abstract

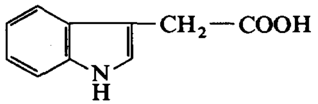
The reactions of dichlorobis(cyclopentadienyl)hafnium(IV) with 3-indoleacetic acid (IAH), 3-indole propionic acid (IPH), 3-indolebutyric acid (IBH) and 1-tryptophan (TRH) in various stoichiometric ratios have been studied, and the complexes of the type $Cp_2Hf(L)Cl$ and $CpHf(L)_2Cl$ (where L is the bidentate 3-indole carboxylate ion) were obtained. Magnetic susceptibility data that these complexes are diamagnetic.

Introduction

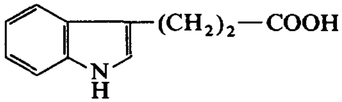
Monocarboxylic acid complexes of metals continue to provide interesting new types of coordination compounds because of the ability of carboxylate ions to adopt various (monodentate, bidentate or bridging) coordination modes [1,2].

Interest in 3-indole carboxylic acid derivatives of bis(cyclopentadienyl)hafnium (IV) arises from the use of 3-indoleacetic acid and 3-indole butyric acid as anticancer and antitumor agents [3]; the biological activity of these acids has been suggested to be considerably enhanced by binding with metals [4]. We report here the synthesis and characterisation of 3-indole carboxylic acid derivatives of bis(cyclopentadienyl)hafnium(IV) dichloride

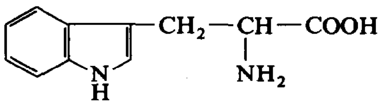
The structures of the 3-indole carboxylic acids used are as follows:



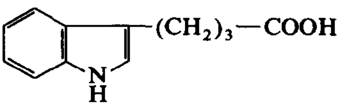
3-Indoleacetic acid (IAH)



3-Indolepropionic acid (IPH)



1-Tryptophan (TRH)



3-Indolebutyric acid (IBH)

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Experimental

All the manipulations were performed in Schlenk tubes under dry oxygen-free nitrogen. THF (E. Merck) was dried by storage over sodium wire overnight and then refluxed over the sodium until it gave blue colouration with benzophenone. n-Heptane and triethylamine were dried by standard methods [5]. Bis(cyclopentadienyl)hafnium(IV) dichloride was prepared as previously described [6]. Indole-3-acetic acid, indole-3-propionic acid, indole 3-butyric acid and 1-tryptophan (Aldrich) were used as supplied. All the solvents were degassed before being dried.

Hafnium was estimated gravimetrically as HfO_2. Chlorine was determined as AgCl. Carbon and hydrogen analyses were carried out at the microanalysis section, Chemistry department, Kurukshetra University, Kurukshetra. The IR spectra were recorded with KBr pellets on a Perkin–Elmer 842 spectrophotometer in the range 4000–400 cm^{-1}. The ^1H NMR spectra were recorded on a JEOL-JNM FX-200 Fourier Transform spectrometer with $CDCl_3$ as solvent. The electronic spectra of complexes in chloroform solution were recorded on a Shimadzu UV-260 spectrophotometer. The magnetic susceptibility was determined by the Faraday method.

Preparation of complexes

A general procedure for the preparation of the complexes of Cp_2HfCl_2 with 3-indolecarboxylic acids involved the mixing of reactants in THF at room temperature in presence of an excess of triethylamine which acts as a proton acceptor. The mixture was stirred for 25–30 h. The precipitated triethylammonium chloride was filtered off and the solvent removed in vacuo. The residue was washed with n-heptane and dried in vacuo. The yields were in the range of 70–75%. The relevant details of the preparative methods used, complexes obtained, and analytical data are given in Table 1.

Results and discussion

The reactions of dichlorobis(cyclopentadienyl)hafnium(IV) with 3-indole carboxylic acids in 1 : 1 and 1 : 2 molar ratios in dry THF in the presence of triethylamine are represented by the following general equations (where L represents the corresponding 3-indole carboxylate ion).

$$\underset{}{Cp_2HfCl_2} + HL + \underset{\text{(Excess)}}{(C_2H_5)_3N} \xrightarrow[\text{r.t.}]{\text{THF}} Cp_2Hf(L)Cl + (C_2H_5)_3N \cdot HCl$$

$$Cp_2HfCl_2 + 2\,HL + \underset{\text{(Excess)}}{(C_2H_5)_3N} \xrightarrow[\text{r.t.}]{\text{THF}} CpHf(L)_2Cl + C_5H_6 + (C_2H_5)_3N \cdot HCl$$

All the complexes are crystalline solids and extremely sensitive to hydrolysis. They are soluble in tetrahydrofuran and chloroform but insoluble in n-heptane and petroleum ether.

The IR spectra of the 3-indolecarboxylic acids show bands due to ν(OH), ν(C=O) and ν(N–H) groupings in the region 3040–2500, 1715–1690 and 3420–3370 cm^{-1}, respectively. 1-Tryptophan shows in addition a strong band at 3200 cm^{-1} which is assigned to ν(N–H) of NH_2 group [7].

The IR spectra of the complexes show no bands due to ν(OH) indicating that the

Table 1

Characterization data

Reactants (g)			Molar ratio	Stirring time (h)	Product, colour and decomposition temperature (°C)	Analysis, Found (calc.) (%)			
Cp_2HfCl_2	Ligand	$(C_2H_5)_3N$				C	H	Cl	Hf
Cp_2HfCl_2 0.85	IAH 0.39	$(C_2H_5)_3N$ Excess	1:1:Excess	25	$Cp_2Hf(IA)Cl$ Yellow, 97	46.20 (46.34)	3.63 (3.50)	6.62 (6.83)	34.23 (34.43)
Cp_2HfCl_2 0.52	IAH 0.48	$(C_2H_5)_3N$ Excess	1:2:Excess	30	$CpHf(IA)_2Cl$ Yellow, 103	47.40 (47.86)	3.30 (3.37)	5.60 (5.65)	28.40 (28.44)
Cp_2HfCl_2 0.70	IPH 0.35	$(C_2H_5)_3N$ Excess	1:1:Excess	26	$Cp_2Hf(IP)Cl$ Light brown, 101	47.60 (47.38)	3.28 (3.78)	6.53 (6.65)	33.45 (33.52)
Cp_2HfCl_2 0.48	IPH 0.48	$(C_2H_5)_3N$ Excess	1:2:Excess	30	$CpHf(IP)_2Cl$ Brown, 111	49.43 (49.47)	4.62 (3.84)	5.23 (5.40)	27.18 (27.23)
Cp_2HfCl_2 0.60	IBH 0.32	$(C_2H_5)_3N$ Excess	1:1:Excess	27	$Cp_2Hf(IB)Cl$ Light brown, 110	48.00 (48.36)	4.10 (4.05)	6.54 (6.48)	32.44 (32.66)
Cp_2HfCl_2 0.40	IBH 0.44	$(C_2H_5)_3N$ Excess	1:2:Excess	30	$CpHf(IB)_2Cl$ Light brown, 117	50.23 (50.96)	4.20 (4.27)	5.00 (5.18)	26.00 (26.11)
Cp_2HfCl_2 0.75	TRH 0.40	$(C_2H_5)_3N$ Excess	1:1:Excess	25	$Cp_2Hf(TR)Cl$ Yellow, 120	46.00 (46.08)	3.62 (3.87)	6.42 (6.47)	32.53 (32.60)
Cp_2HfCl_2 0.44	TRH 0.48	$(C_2H_5)_3N$ Excess	1:2:Excess	30	$CpHf(TR)_2Cl$ Yellow, 130	47.00 (47.30)	3.87 (3.97)	4.97 (5.17)	26.00 (26.04)

heterocarboxylic acids have been deprotonated. The bands at 1720–1690 cm^{-1} due to $\nu(C{=}O)$ show a downward shift of 125–150 cm^{-1} and appear in the region 1560–1520 cm^{-1}, indicating that carbonyl oxygen is coordinated to metal. The persistence of bands at 3420–3370 cm^{-1} due to ν(N–H) and at 740 cm^{-1} due to $\delta_{o.p.}$(C–H) as in the free acids indicate that hetero nitrogen is not involved in the coordination [1]. Since there is no change in the position of the ν(N–H) bond (3200 cm^{-1}) of the NH_2 group in the metal complexes formed by TRH, suggesting that the NH_2 group is free, and that the bonding of the carboxylate group to the metal is bidentate. Further, the low separation (Δ) value (100–110 cm^{-1}) rules out the possibility of unidentate coordination, and indicates a chelating or bridging mode. The presence of strong absorption band at 560 cm^{-1} ($\delta_{o.p.}$ (CO_2^-)) and absence of absorption band at 920–720 cm^{-1} ($\delta_{i.p.}$ (CO_2^-)) indicate the carboxylate ion adopts the chelating mode in the bis(cyclopentadienyl)hafnium(IV) chloride complexes of 3-indole carboxylic acids [2].

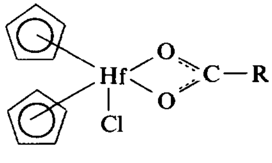
The IR spectra of metal complexes show the usual bands at ~ 3100 cm^{-1} (ν (C–H), ~ 1435 cm^{-1} (ν(C–C)), ~ 1020 cm^{-1} ($\delta_{i.p.}$(C–H)) and ~ 810 cm^{-1} ($\delta_{o.p.}$ (C–H)) which arise from the cyclopentadienyl groups [8]. The presence of these bands in the complexes indicates that these cyclopentadienyl ligands are π-bonded to metal and retain their aromatic character. Bands near ~ 430 cm^{-1} may be assigned to (Hf–O) [9].

^1H NMR spectra

The proton magnetic resonance spectra of 3-indolecarboxylic acids and their bis(cyclopentadienyl)hafnium(IV) chloride complexes show a sharp singlet at δ 6.4 ppm due to the protons of the cyclopentadienyl groups. Multiplets characteristic of 3-indole ring protons were observed at δ 6.9 to 8.2 ppm. The N–H signal appears at δ ~ 10.0 ppm in the spectrum of the ligand, and there is no appreciable change in its position in the metal complexes. There is no change in the position of the signals from the indole ring and N–H protons in the complexes, confirming that the hetero nitrogen atom is not involved in coordination. All the other protons give signals at the same positions as those for the free acids.

The electronic spectra of the carboxylates were recorded in DMSO, and showed charge transfer bands, in accordance with the $(n-1)d^{\circ}ns^{\circ}$ electronic configuration of hafnium in the complexes. Magnetic susceptibility data showed complexes to be diamagnetic.

The elemental analysis and spectral data indicate that indole 3-carboxylic acids behave as monofunctional bidentate $(\overset{\frown}{O\ O})$ chelating ligands, and structures I and II may be tentatively proposed for $Cp_2Hf(L)Cl$ and $CpHf(L)_2Cl$ (where L represents the corresponding bidentate mode of the 3-indole carboxylate ions).



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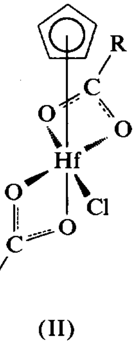

(II)

In structure II, the hafnium atom can be regarded being octahedrally coordinated in a *cis* configuration [10]. The loss of cyclopentadienyl group in the reaction of heterocarboxylic acid with Cp_2HfCl_2 has been accounted for in terms of the ease of electrophilic cleavage of the Hf–Cp bond [11].

Acknowledgements

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