

***N*-(Aryl)-2-mercaptoacetamide derivatives of dichlorobis(cyclopentadienyl)hafnium(IV)**

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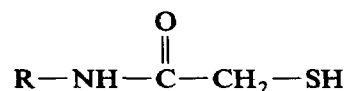
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Abstract

Dichlorobis(cyclopentadienyl)hafnium(IV) in THF in the presence of triethylamine reacts with *N*-(α -naphthyl)-2-mercaptoacetamide (NMAH), *N*-phenyl-2-mercaptoacetamide (PMAH), *N*-(*o*-tolyl)-2-mercaptoacetamide (*o*-TMAH), *N*-(*m*-tolyl)-2-mercaptoacetamide (*m*-TMAH), *N*-(*p*-tolyl)-2-mercaptoacetamide (*p*-TMAH) and *N*-(3,5-dimethylphenyl)-2-mercaptoacetamide (DMPMAH) in various stoichiometric ratios, to give complexes of the types $\text{Cp}_2\text{Hf}(\text{MA})\text{Cl}$ and $\text{Cp}_2\text{Hf}(\text{MA})_2$ (where MA^- represents the anion of corresponding bidentate mercaptoacetamide). These were characterized by elemental analysis, and IR, PMR and electronic spectroscopy. Magnetic susceptibility data show that the complexes are diamagnetic.

Introduction

In recent years transition metal complexes containing nitrogen-oxygen-sulphur chelating ligands have received considerable attention because of ability of these ligands to adopt various coordination modes (monodentate, bidentate or tridentate) [1,2]. Further, these complexes can be carcinostatic and antiviral [3,4]. Recently, antitumor activity of titanocene has been reported [5]. Mercaptoacetamides have extensively been used in qualitative analysis and as specific precipitating reagents [6]. We report here the results of a study of the reaction of *N*-(aryl)-2-mercaptoacetamide with Cp_2HfCl_2 aimed at establishing the mode of coordination of the mercaptoacetamides in the complexes. The *N*-(aryl)-2-mercaptoacetamides used were as follows:



R = α -naphthyl (NMAH); phenyl (PMAH); *o*-tolyl (*o*-TMAH); *m*-tolyl (*m*-TMAH); *p*-tolyl (*p*-TMAH), and 3,5-dimethyl phenyl (DMPMAH).

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods [7] and freed from oxygen by repeated degassing. Dicyclopentadienyl hafnium(IV) chloride was used as purchased from Aldrich. Mercaptoacetamides were made by condensation of thioglycolic acid with an equimolar amount of the appropriate aryl amine [8]. Elemental analyses were performed in the microanalytical division, Department of Chemistry, Kurukshetra University, Kurukshetra. Chlorine was determined as AgCl. Hafnium was estimated as HfO₂. The IR spectra were recorded in KBr pellets on a Perkin-Elmer 842 spectrophotometer in 4000–400 cm⁻¹ range. Magnetic susceptibility was determined by the Faraday method. The ¹H NMR spectra were recorded on a JEOL-JNM-FX-200 Fourier-Transform spectrometer with CDCl₃ as solvent. The electronic spectra were recorded on a Shimadzu UV-260 spectrophotometer.

Preparation of complexes

The preparation of the complexes of Cp₂HfCl₂ with *N*-(aryl)-2-mercaptoacetamide involved mixing the reactants in tetrahydrofuran in the presence of triethylamine at room temperature. The mixture was stirred for 25–30 h and the precipitate of (C₂H₅)₃N · HCl was then filtered off and the solvent was removed in vacuo. The residue was washed with *n*-heptane and dried in vacuo. The yields were in the range of 70–75%. Details of the procedures used, the yields of the complexes obtained, and the analytical data are given in Table 1.

Results and discussion

The reactions of dichlorobis(cyclopentadienyl)hafnium(IV) with *N*-(aryl)-2-mercaptoacetamides in 1:1 and 1:2 molar ratio in dry THF in the presence of triethylamine are represented by the following general equations (where MA⁻ represents the anion of corresponding mercaptoacetamide).



All the complexes are crystalline solids and are sensitive to hydrolysis. They are soluble in many common organic solvents, such as tetrahydrofuran, chloroform, and benzene, but insoluble in *n*-heptane and petroleum ether. Magnetic susceptibility data reveal the diamagnetic nature of these complexes.

The IR spectra of the ligands show medium intensity bands in the region 3270–3240 cm⁻¹ and 2550–2500 cm⁻¹ which are assigned to ν(NH) and ν(SH) respectively [9]. Strong bands in the regions 1650–1640, 1540–1530, 1280–1270, 720–685 and 610–590 cm⁻¹ may be assigned to amide-I [ν(C=O)], amide-II [ν(CN) + δ(NH)], amide-III [ν(CN) + δ(NH)], amide-V [δ_{o.p.}(C=O)] and amide-IV [δ_{i.p.}(C=O)], respectively [10].

The IR spectra of complexes show no band in the region 2550–2500 cm⁻¹ indicating that the thiol group (–SH) has been deprotonated [11]. The appearance of a band of ν(N–H) at the same position at 3270–3240 cm⁻¹ indicates that amide-

Table 1

Reactants (g)		Ligand	$(C_2H_5)_3N$	Molar ratio	Stirring time (h)	Product, colour and decomposition temperature ($^{\circ}C$)	Analysis, (Found (calc.) (%))				
Cp_2HfCl_2							C	H	N	Cl	Hf
Cp_2HfCl_2 0.76	NMAH 0.43		$(C_2H_5)_3N$ 0.21	1:1:1	30	$(C_3H_5)_2Hf(NMA)Cl$ brown (165)	46.98 (47.16)	3.00 (3.59)	2.16 (2.50)	6.25 (6.32)	31.67 (31.85)
Cp_2HfCl_2 0.66	NMAH 0.76		$(C_2H_5)_3N$ 0.36	1:2:2	26	$(C_3H_5)_2Hf(NMA)_2$ brown (150)	54.68 (55.10)	4.36 (4.08)	3.26 (3.78)	-	23.59 (24.08)
Cp_2HfCl_2 0.70	PMAH 0.31		$(C_2H_5)_3N$ 0.20	1:1:1	25	$(C_3H_5)_2Hf(PMA)Cl$ grey (115)	41.76 (42.36)	3.85 (3.56)	2.40 (2.75)	6.72 (6.95)	34.18 (34.97)
Cp_2HfCl_2 0.64	PMAH 0.56		$(C_2H_5)_3N$ 0.35	1:2:2	30	$(C_3H_5)_2Hf(PMA)_2$ grey (131)	48.50 (48.71)	4.47 (4.09)	4.00 (4.37)	-	27.42 (27.84)
Cp_2HfCl_2 0.60	<i>o</i> -TMAH 0.29		$(C_2H_5)_3N$ 0.17	1:1:1	27	$(C_3H_5)_2Hf(o-TMA)Cl$ orange (145)	43.23 (43.52)	3.26 (3.84)	2.23 (2.67)	6.46 (6.76)	33.64 (34.04)
Cp_2HfCl_2 0.53	<i>o</i> -TMAH 0.51		$(C_2H_5)_3N$ 0.29	1:2:2	30	$(C_3H_5)_2Hf(o-TMA)_2$ orange (160)	50.00 (50.27)	4.30 (4.52)	3.94 (4.19)	-	26.62 (26.68)
Cp_2HfCl_2 0.68	<i>m</i> -TMAH 0.33		$(C_2H_5)_3N$ 0.19	1:1:1	26	$(C_3H_5)_2Hf(m-TMA)Cl$ brown (150)	42.12 (43.52)	3.63 (3.84)	2.42 (2.67)	6.32 (6.76)	34.00 (34.04)
Cp_2HfCl_2 0.50	<i>m</i> -TMAH 0.48		$(C_2H_5)_3N$ 0.28	1:2:2	30	$(C_3H_5)_2Hf(m-TMA)_2$ brown (162)	49.96 (50.27)	4.26 (4.52)	4.04 (4.19)	-	26.00 (26.68)
Cp_2HfCl_2 0.70	<i>p</i> -TMAH 0.34		$(C_2H_5)_3N$ 0.20	1:1:1	28	$(C_3H_5)_2Hf(p-TMA)Cl$ brown (157)	42.74 (43.52)	4.00 (3.84)	2.24 (2.67)	6.58 (6.76)	33.78 (34.04)
Cp_2HfCl_2 0.57	<i>p</i> -TMAH 0.55		$(C_2H_5)_3N$ 0.32	1:2:2	29	$(C_3H_5)_2Hf(p-TMA)_2$ brown (180)	50.00 (50.27)	4.26 (4.52)	3.78 (4.19)	-	25.98 (26.68)
Cp_2HfCl_2 0.80	DMPMAH 0.41		$(C_2H_5)_3N$ 0.22	1:1:1	25	$(C_2H_5)_2Hf(DMPMA)Cl$ brown (180)	44.00 (44.63)	4.34 (4.12)	2.32 (2.60)	6.24 (6.58)	32.70 (33.16)
Cp_2HfCl_2 0.46	DMPMAH 0.48		$(C_2H_5)_3N$ 0.22	1:2:2	30	$(C_3H_5)_2Hf(DMPMA)_2$ brown (190)	51.28 (51.70)	4.42 (4.91)	3.94 (4.02)	-	24.86 (25.61)

NMAH = *N*-(α -naphthyl)-2-mercaptoacetamide; PMAH = *N*-(phenyl)-2-mercaptoacetamide; *o*-TMAH = *N*-(*o*-tolyl)-2-mercaptoacetamide; *m*-TMAH = *N*-(*m*-tolyl)-2-mercaptoacetamide; *p*-TMAH = *N*-(*p*-tolyl)-2-mercaptoacetamide; DMPMAH = *N*-(3,5-dimethylphenyl)mercaptoacetamide.

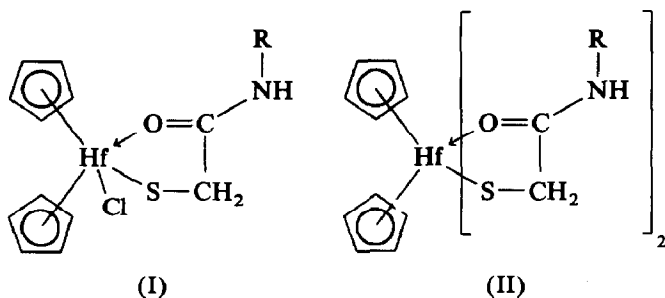
nitrogen is not involved in coordination. The appearance of the $[\nu(\text{C}=\text{O})]$ band at lower frequencies ($30\text{--}50\text{ cm}^{-1}$) indicates a decrease in carbon-oxygen bond order and coordination of the carbonyl oxygen of the amide group to the metal. The bands at $\sim 3100\text{ cm}^{-1}$ $[\nu(\text{C}-\text{H})]$, $\sim 1435\text{ cm}^{-1}$ $[\nu(\text{C}-\text{C})]$, $\sim 1020\text{ cm}^{-1}$ $[\delta_{\text{i.p.}}(\text{CH})]$ and $\sim 810\text{ cm}^{-1}$ $[\delta_{\text{o.p.}}(\text{CH})]$ are assigned to cyclopentadienyl groups [12], and indicate that these groups are π -bonded to the metal. The bands at $\sim 430\text{ cm}^{-1}$ can be assigned to $\nu(\text{Hf}-\text{O})$ [13].

^1H NMR spectra

The ^1H NMR spectra of all the complexes show a signal due to cyclopentadienyl group at $\sim \delta 6.3\text{ ppm}$ [14,15]. The ^1H NMR spectra of mercaptoacetamides in CDCl_3 show a triplet in the region $\delta 2.2\text{--}1.9\text{ ppm}$ due to the $-\text{SH}$ proton and this signal is absent in the corresponding complexes. However, the presence of a singlet in the region $\delta 8.3\text{--}8.0\text{ ppm}$ for both the ligands and the complexes confirms that $-\text{NH}$ group is present in the latter.

The electronic spectra of all the complexes in chloroform show charge transfer bands, in accord with the $(n-1)d^0ns^0$ electronic configuration of hafnium in the complexes.

The elemental analysis and spectroscopic data indicate that mercaptoacetamide behaves as a bidentate (OS) chelating ligand. The following structures (I and II) are tentatively proposed for $\text{Cp}_2\text{Hf}(\text{MA})\text{Cl}$ and $\text{Cp}_2\text{Hf}(\text{MA})_2$ (where MA^- represents the anion of the corresponding bidentate mercaptoacetamide).



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References

- 1 M. Akbar Ali, S.E. Livingstone and D.J. Phillips, *Inorg. Chim. Acta*, 7 (1973) 179.
- 2 M. Das and S.E. Livingstone, *Inorg. Chim. Acta*, 19 (1976) 5.
- 3 M. Akbar Ali and S.E. Livingstone, *Coord. Chem. Rev.*, 13 (1974) 101.
- 4 M.J. Cleare, *Coord. Chem. Rev.*, 12 (1974) 349.
- 5 P. Köpf-Maiert, T. Klapötke and H. Köpf, *Inorg. Chim. Acta*, 153 (1988) 119.
- 6 F. Feigl, *The Chemistry of Specific, Selective and Sensitive Reactions*, Academic Press, New York, 1948.
- 7 A.I. Vogel, *A Textbook of Practical Organic Chemistry*, Longman, Green, London, 1948.
- 8 R.N. Misra and S.S. Guha-Sirkar, *J. Indian Chem. Soc.*, 32 (1955) 127.
- 9 K. Nag and D.S. Joardar, *Inorg. Chim. Acta*, 14 (1975) 133.

- 10 L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, Reprinted, 1978.
- 11 M. Chaudhury, *J. Chem. Soc., Dalton Trans.*, (1984) 115.
- 12 H.P. Fritz, *Adv. Organomet. Chem.*, 1 (1964) 262.
- 13 K.C. Malhotra and S.C. Chaudhary, *Aust. J. Chem.*, 27 (1974) 79.
- 14 P.C. Wailes, H. Weigold and A.P. Bell, *J. Organomet. Chem.*, 33 (1971) 181.
- 15 E. Samuel, *Bull. Soc. Chim. Fr.*, (1966) 3548.