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Synthesis and Spectroscopic Studies of Mono(cyclopentadienyl)titanium(IV) Derivatives with Heterocyclic Thioketones

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Abstract

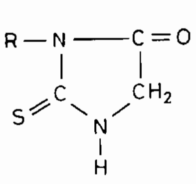
The reactions of mono(cyclopentadienyl)titanium(IV) trichloride with two different classes of heterocyclic thioketones *viz.* 1-substituted-2-thiohydantoins and 1-substituted tetrazoline-5-thione, were studied in anhydrous dichloromethane. The reaction products were characterized on the basis of elemental analyses electrical conductance, magnetic susceptibility and spectral (electronic, infrared and ^{1}H NMR) data.

Introduction

The chemistry of transition metal complexes with heterocyclic thioketones continues to be of unabated interest on account of the striking structural features presented by this class of compounds and also because of their biological importance [1–6]. These ligands containing a thioamide bond and capable of undergoing thione ⇌ thiol (NH–C=S ⇌ N=C–SH) tautomerism can coordinate to a metal atom through nitrogen or through sulphur or simultaneously through nitrogen and sulphur. In the present communication, the synthesis and characterization of mono(cyclopentadienyl)titanium(IV) derivatives containing heterocyclic thioketones as chelating agents are reported.

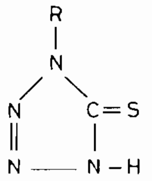
The structures of the ligands are given below:

1-Aryl-2-thiohydantoin



R = C_6H_5 (PThtH)
R = $C_6H_4CH_3$ (TThtH)
R = $C_6H_5CH_2$ (BThtH)
R = $C_6H_4CH_3O$-*p*(MPThtH)
R = $C_6H_4CH_3O$-*o* (MOThtH)
R = $C_{10}H_7$ (NThtH)

1-Substituted-tetrazoline-5-thione



R = C_6H_5 (PTth)
R = C_6H_4,CH_3O-*p* (MTtH)
R = $C_6H_4 \cdot Cl$-*p* (CTtH)
R = $C_6H_4 \cdot CH_3$-*o* (TTtH)

Experimental

The ligands thiohydantoins and tetrazoline thiones were prepared as mentioned in the literature [7, 8]. Mono(cyclopentadienyl)titanium(IV) chloride was prepared from Cp_2TiCl_2 and $TiCl_4$ in *p*-xylene. Dichloromethane was dried by refluxing for 30 h over calcium hydride. Most of the derivatives prepared and studied are susceptible to hydrolysis. Hence, all operations were carried out under strict anhydrous conditions, and glass apparatus with standard interchangeable joints was used throughout the work.

The details of analyses and physical measurements are the same as described earlier [9].

Preparation of Complexes

All these complexes were prepared by reacting mono(cyclopentadienyl)titanium(IV) trichloride with the corresponding ligand in 1:1, 1:2 or 1:3 molar ratios, respectively, and adding about 60 ml of dichloromethane followed by a reflux time of 20–50 h. The solutions were then filtered and their volume reduced to about 20 ml. Further, addition of dry petroleum ether (60–80 °C, 20 ml) to the above solutions and allowing them to stand overnight gave yellow to brown crystals, which were filtered and dried in an oven at 80 °C.

The details of the amount of reactants taken for the preparation of the complexes, refluxing time, yield and colour of the products are given in Tables I and II.

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TABLE I. Reactions of CpTiCl$_3$ with Thiohydantoins in Dichloromethane

Reactants (g)		Refluxing time (h)	Product, yield (%)	Colour	Found (Calculated) (%)				
CpTiCl$_3$	Ligand				C	H	N	Ti	Cl
2 1	PThtH 1.8	20	CpTiCl$_2$(PTht)	yellow	44.6	3.1	7.4	12.8	18.9
			54		(44.8)	(3.2)	(7.5)	(12.8)	(18.9)
1.0	pThtH, 1.9	25	CpTiCl(PTht)$_2$	brown	52.0	3.4	10.2	9.0	6.6
			62		(52.0)	(3.6)	(10.5)	(9.0)	(6.7)
1.1	PThtH, 2.8	32	CpTi(PTht)$_3$	brown	55.9	3.6	12.2	7.0	
			60		(56.0)	(3.8)	(12.2)	(7.0)	
2.0	TThtH, 2.0	25	CpTiCl$_2$(TTht)	yellow	46.2	3.4	7.0	12.3	18.1
			50		(46.3)	(3.6)	(7.2)	(12.3)	(18.2)
1.0	TThtH, 2.0	30	CpTiCl(TTht)$_2$	orange	53.4	4.0	10.0	8.6	6.2
			48		(53.7)	(4.1)	(10.0)	(8.6)	(6.3)
0.52	TThtH, 1.5	45	CpTi(TTht)$_3$	brown	57.4	4.3	11.4	6.6	
			58		(57.7)	(4.4)	(11.5)	(6.6)	
1.0	BThtH, 1.0	35	CpTiCl$_2$(BTht)	yellow	46.3	3.4	7.0	12.3	18.0
			62		(46.3)	(3.6)	(7.2)	(12.3)	(18.2)
1.0	BThtH, 2.0	45	CpTiCl(BTht)$_2$	yellow	53.5	4.0	10.0	8.6	6.2
			60		(53.7)	(4.1)	(10.0)	(8.6)	(6.3)
0.55	BThtH, 1.5	50	CpTi(BTht)$_3$	orange	57.7	4.2	11.4	6.6	
			64		(57.7)	(4.4)	(11.5)	(6.6)	
1.1	MPThtH, 1.2	28	CpTiCl$_2$(MPTht)	brown	44.2	3.2	6.8	11.8	17.5
			58		(44.4)	(3.4)	(6.9)	(11.8)	(17.5)
1.0	MPThtH, 2.5	30	CpTiCl(MPTht)$_2$	yellowish-brown	50.6	3.9	9.4	8.0	6.0
			52		(50.8)	(3.9)	(9.5)	(8.1)	(6.0)
0.54	MPThTH, 1.7	38	CpTi(MPTht)$_3$	dark-brown	54.0	4.1	10.7	6.2	
			55		(54.1)	(4.1)	(10.8)	(6.2)	
1.0	MOThtH, 1.2	22	CpTiCl$_2$(MOTht)	orange–brown	44.3	3.2	6.7	11.8	17.5
			70		(44.4)	(3.4)	(6.9)	(11.8)	(17.5)
1.0	MOThtH, 2.4	26	CpTiCl(MOTht)$_2$	orange	50.7	3.9	9.3	8.0	6.0
			68		(50.8)	(3.9)	(9.5)	(8.1)	(6.0)
0.50	MOThtH, 1.6	32	CpTi(MOTht)$_3$	dark-brown	54.0	4.1	10.6	6.2	
			55		(54.1)	(4.1)	(10.8)	(6.2)	
1.1	NThTh, 1.3	28	CpTiCl$_2$(NTht)	light-brown	50.6	3.1	6.6	11.3	16.7
			65		(50.8)	(3.3)	(6.6)	(11.3)	(16.7)
1.0	NThtH, 2.4	35	CpTiCl(NTht)$_2$	yellowish-brown	58.8	3.6	8.8	7.6	5.5
			58		(59.0)	(3.6)	(8.9)	(7.6)	(5.6)
1.0	nThtH, 3.6	50	CpTi(NTht)$_3$	brown	63.2	3.7	9.9	5.7	
			63		(63.2)	(3.8)	(10.0)	(5.7)	

TABLE II. Reactions of CpTiCl$_3$ with Tetrazoline Thiones in Dichloromethane

Reactants (g)		Refluxing time (h)	Product yield (%)	Colour	Found (Calculated) (%)				
CpTiCl$_3$	Ligand				C	H	N	Ti	Cl
2.1	PTtH, 1.8	28	CpTiCl$_2$(PTt)	yellow	39.8	2.7	15.3	13.3	19.7
			60		(39.9)	(2.8)	(15.5)	(13.3)	(19.7)
1.0	PtTH 1.82	38	CpTiCl(PTt)$_2$	yellowish-brown	54.4	3.0	22.1	9.3	7.0
			52		(45.4)	(3.0)	(22.3)	(9.5)	(7.1)
1.0	PTtH 2.7	48	CpTi(PTt)$_3$	brown	48.2	3.0	26.0	7.4	
			70		(48.4)	(3.1)	(26.1)	(7.4)	
1.1	MTtH, 1.0	22	CpTiCl$_2$(MTt)	orange	39.7	3.0	14.2	12.2	18.0
			68		(39.9)	(3.1)	(14.3)	(12.2)	(18.2)
1.0	MTtH, 2.0	30	CpTiCl(MTt)$_2$	yellow	44.7	3.2	19.7	8.3	6.3
			58		(44.8)	(3.4)	(19.9)	(8.5)	(6.3)

(continued)

TABLE II. *(continued)*

Reactants (g)			Refluxing time (h)	Product, yield (%)	Colour	Found (Calculated) (%)				
$CpTiCl_3$	Ligand					C	H	N	Ti	Cl
0.54	MTtH,	1.6	40	$CpTi(MTt)_3$ 64	yellow	47.4 (47.4)	3.2 (3.5)	22.7 (22.9)	6.2 (6.5)	
1.2	CTtH	1.1	20	$CpTiCl_2(CTt)$ 65	yellow	36.1 (36.4)	2.2 (2.3)	14.2 (14.2)	12.1 (12.1)	26.7 (26.9)
1.0	CTtH,	2.1	28	$CpTiCl(CTt)_2$ 50	brown	39.7 (39.9)	2.1 (2.3)	19.4 (19.6)	8.4 (8.4)	12.4 (12.4)
1.0	CTtH,	3.2	40	$CpTi(CTt)_3$ 52	orange	41.7 (41.7)	2.2 (2.3)	22.4 (22.5)	6.4 (6.4)	4.6 (4.7)
2.1	TTtH,	1.9	25	$CpTiCl_2(TTt)$ 55	light-yellow	41.6 (41.6)	3.1 (3.2)	14.7 (14.9)	12.8 (12.8)	18.9 (18.9)
1.0	TTtH,	2.0	32	$CpTiCl(TTt)_2$ 60	yellowish-orange	47.2 (47.5)	3.5 (3.6)	21.0 (21.1)	9.0 (9.0)	6.7 (6.7)
0.55	TTtH,	1.5	50	$CpTi(TTt)_3$	brown	50.7 (50.7)	3.6 (3.8)	24.4 (24.5)	7.0 (7.0)	

Results and Discussion

The analytical data of the complexes are given in Tables I and II. The methods used for preparation and isolation of these compounds give materials of good purity, as supported by their analyses and TLC. All these complexes are coloured. They are thermally stable but decompose in the temperature range 140–275 °C. They are quite stable in air but their solutions are hydrolysed on standing. Conductance measurements reveal that they are essentially non-electrolytes. Magnetic susceptibility values at room temperature show the diamagnetic nature of the complexes. The electronic spectra of all these complexes show a band in the region 23 000–24 800 cm^{-1}, which can be assigned [9] to the charge-transfer band an is in accordance with the $(n-1)d^0\ ns^0$ electronic configuration of titanium.

Infrared Spectra

(a) Thiohydantoin derivatives

The infrared spectra of 1-aryl-2-thiohydantoin ligands show sharp bands at *ca.* 3300 and 1650 cm^{-1} which may be assigned [10] to ν(N–H) and δ(N–H), respectively. However, in the titanium complexes, these bands disappear indicating the displacement of N–H hydrogen by titanium ion. This is further confirmed by the appearance of new bands around 450–430 cm^{-1} assignable [11] to ν(Ti–N). A sharp band appearing at 1720–1700 cm^{-1} due to ν(C=O) in the spectra of ligands appears at the same place in the spectra of the complexes, ruling out the possibility of coordination through the carbonyl group. Organic compounds having a thioamide group (HNC=S) give rise to four thioamide bands in the IR spectra [5, 6]. These are thioamide-I at about 1560–1550 cm^{-1}, band-II at about 1400–1300 cm^{-1}, band-III at about 1090–1080 cm^{-1} and band-IV at about 850–700 cm^{-1}. These bands have contributions from δ(C–H) + δ(N–H), ν(C=S) + ν(C=N) + δ(C–H), ν(C–N) + ν(C=S) and ν(C=S) modes of vibrations, respectively. In the present ligands, these bands appear at *ca.* 1500, 1400–1250, 1000 and 880–740 cm^{-1}, respectively. These bands are expected to be affected differently by different modes of coordination after complexation with the metal ions [6]. The thioamide-III and IV vibrations, which have the largest contribution from ν(C=S), undergo a red shift in the titanium(IV) complexes, suggesting coordination of the sulphur atom to the titanium atom in the thione form. The ν(Ti–S) vibration appears at 400–370 cm^{-1} [9]. Thus, it becomes evident that the thiohydantoin ligands act as bidentate chelating agents, coordinating through thione sulphur and amino nitrogen.

(b) Tetrazoline thione derivatives

The infrared spectra of ligands tetrazoline thiones and their complexes are quite similar to thiohydantoin derivatives. The ν(N–H) and δ(N–H) vibration bands, which appear at *ca.* 3350 and 1630 cm^{-1} in the spectra of ligands, disappear in the spectra of the complexes indicating the coordination of amino nitrogen through deprotonation. The four thioamide bands, thioamide-I, II, III and IV, typical of molecules containing a HN–C=S skeleton are found at *ca.* 1510–1500, 1280, 985–970 and 780–700 cm^{-1}, respectively. The appearance of four thioamide bands and the absence of any band near 2500 cm^{-1} due to ν(S–H) indicate the existence of the ligands in the thione form [12]. The thioamide-III and -IV bands, having their main contributions from ν(C=S), are shifted towards lower energies in the complexes, indicating the coordination of thioketo sulphur to the titanium atom [9, 13]. The ν(Ti–N) and ν(Ti–S) vibrations appear at *ca.* 480–460 and 400–380 cm^{-1}, respectively [9, 11]. The above observations indicate that possibly the bonding in titanium complexes is through the amino nitrogen and thiocarbonyl sulphur.

In addition, absorption bands occurring at ~3000 cm^{-1} ν(C–N), ~1430 cm^{-1}, ν(C–C) and ~1020 cm^{-1} δ(C–H) in all the complexes indicate [14] the presence of cyclopentadienyl ring. All these bands are similar to those of mono(cyclopentadienyl)-titanium(IV). Davison and Rakita have pointed out that at 3000 cm^{-1}, η^1-C_5H_5 should show four bands whereas η^5-C_5H_5 should show only one [15]. In the complexes reported in this paper, only one band at 3000 cm^{-1} indicates the pentahapto nature of cyclopentadienyl ring.

^{1}H NMR Spectra

The proton NMR spectra of these complexes were recorded in deuterated chloroform and dimethylformamide; the intensities of all the resonance lines were determined by planimetric integration. In general, a low-field shift of the resonance signals of various protons (R) in these complexes, in comparison with the respective proton signals in the free ligands, may be attributed to deshielding upon coordination. The resonance line for the protons on the $C_5H_5^-$ ring always falls near δ 6.5–6.8 ppm. The two kinetic possibilities, *viz.*, metal centred rearrangement is slow or fast, can be distinguished by analysis of the NMR spectra. In the spectra of the 1:3 derivatives $(C_5H_5)Ti(L)_3$, two distinct resonance lines for the protons of the ligands are observed which must result from the non-equivalent environments for the different ligands. However, in the 1:2 derivatives, $CpTi(L_2)Cl$, the ligand groups are equivalent since only one signal has been observed for ligand proton groups. The spectra of thiohydantoins and tetrazoline thiones show one sharp signal at δ 4.8–4.9 ppm due to the NH proton which disappears in the corresponding complexes. The integrated proton ratio corresponds to the proposed formulae.

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