Inorganica Chimica Acta, *90* (1984) 91–96

Mono(cyclopentadienyl)titanium(IV) Derivatives with Heterocyclic Thiones

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Received February 22, 1984

The reactions of mono(cyclopentadienyl)titanium(IV) trichloride with three important series of heterocyclic thiones, viz., triazoline thiones (3-trifluoromethyl-4-amino-1,2,4-triazoline-5-thione (HAFT), 3-trifluoromethyl-4-benzylidene-1,2,4-triazoline-5-thione (HFBT), 3-trifluoromethyl-4-furylidene-1,2,4-triazoline-5-thione (HFFT) and 3-trifluoromethyl-4-salicylidene-1,2,4-triazoline-5-thione (H_2FST)), quinazolone thiones (3-methyl-quinazol-4-one-2-thione (MQztH), 3-phenyl-quinazol-4-one-2-thione (PQztH) and 3-tolyl-quinazol-4-one-2-thione (TQztH)) and oxadiazole thiones (5-phenyl-1,3,4-oxadiazole-2-thione (BOxtH), 5-p-nitrophenyl-1,3,4-oxadiazole-2-thione (POxtH) and 5-o-chlorophenyl-1,3,4-oxadiazole-2-thione(COxtH)), 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. Proton NMR spectra indicate that there is rapid rotation of the cyclopentadienyl ring around the metal ring axis on the NMR time scale at 28 °C.

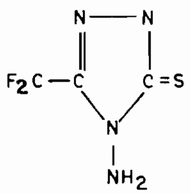
Introduction

Although the preparation of mono(cyclopentadienyl)titanium(IV) trichloride was prepared [1] by Gorsich as early as 1960, its coordination behaviour with chelating agents is still practically unknown. Some papers have appeared on mono(cyclopentadienyl)titanium(IV) compounds containing carboxylic acids [2, 3], dithiocarbamates [4], thione [5] or β-diketones [6, 7] as ligands, but they are mostly derived by the oxidation of $CpTiCl_2$ or removal of one cyclopentadienyl moiety from Cp_2TiCl_2 derivatives. Recently, some papers appeared dealing with the reactions of $CpTiCl_3$ with dithiocarbamates [8], Schiff bases [9], *o*-phenanthroline [10], *o*-phenylenebis(dimethylarsine) and 2,2'-bipyridyl [11].

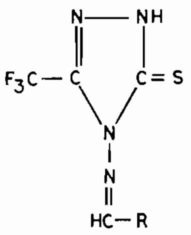
In this paper we report the syntheses and characterization of mono(cyclopentadienyl)titanium(IV) derivatives containing heterocyclic thiones as chelating agents. These ligands, containing the thioamide bond and capable of undergoing thione–thiol (HN–C=S ⇌ N=C–SH) tautomerism, can coordinate to a metal atom through nitrogen or through sulphur, or simultaneously through nitrogen and sulphur. The chemistry of transition metal complexes with heterocyclic thiones continues to be of interest, because of the striking structural features presented by this class of compounds and also due to their biological importance [12–16].

The structures of the ligands are given below:

(a) TRIAZOLINE THIONE

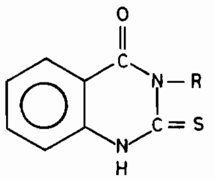


(HAFT)



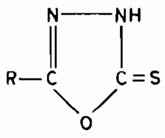
R= C_6H_5 (HFBT)
R= C_4H_3O (HFFT)
R= C_6H_4 (OH) (H_2FST)

(b) QUINAZOLONE THIONE



R= CH_3 (MQztH)
R= C_6H_5 (PQztH)
R= C_6H_4. CH_3 (o) (TQztH)

(c) OXADIAZOLE THIONE



R= C_6H_5 (BOxtH)
R= C_6H_4 NO_2 (p) (POxtH)
R= C_6H_4Cl (o) (COxtH)

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0020-1693/84/$3.00

TABLE I. Reactions of $CpTiCl_3$ with Heterocyclic Thiones in Dichloromethane.

Reactants taken (g) $CpTiCl_3$ (1)	Ligand (2)	Refluxing time (h) (3)	Product, yield (%) (4)	colour,	Decomp. temp. (°C) (5)
1.0	HAFT, 0.9	20	$CpTiCl_2(AFT)$, 58	yellow,	252
1.0	HAFT, 1.8	28	$CpTiCl(AFT)_2$, 54	brown,	232
0.52	HAFT, 1.3	38	$CpTi(AFT)_3$, 62	brown,	280
1.1	HFBT, 1.3	25	$CpTiC_2(FBT)$, 65	yellow,	262
0.6	HFBT, 1.2	35	$CpTiCl(FBT)_2$, 55	orange,	300
0.5	HFBT, 2.0	45	$CpTi(FBT)_3$, 60	orange,	275
1.0	HFFT, 1.3	30	$CpTiCl_2(FFT)$, 68	yellow,	180
1.0	HFFT, 2.5	40	$CpTiCl(FFT)_2$, 65	yellow,	210
0.5	HFFT, 1.85	50	$CpTi(FFT)_3$, 50	orange,	300
1.0	H_2FST, 1.45	20	$CpTi(FST)Cl$, 68	orange,	245
1.1	MQztH, 1.0	22	$CpTiCl_2(MQzt)$, 65	yellow,	200
1.0	MQztH, 1.9	28	$CpTiCl(MQzt)_2$, 50	brown,	182
0.5	MQztH, 1.4	45	$CpTi(MQzt)_3$, 52	orange,	300
1.0	PQztH, 1.2	28	$CpTiCl_2(PQzt)$, 68	yellow,	165
1.0	PQztH, 2.5	38	$CpTiCl(PQzt)_2$, 58	orange,	295
1.0	PQztH, 3.5	50	$CpTi(PQzt)_3$, 64	orange,	218
1.0	TQztH, 1.3	28	$CpTiCl_2(TQzt)$, 58	orange,	248
0.5	TQztH, 1.25	38	$CpTiCl(TQzt)_2$, 62	brown,	300
0.5	TQztH, 1.82	45	$CpTi(TQzt)_3$, 45	brown,	278
1.1	BOxtH, 0.7	22	$CpTiCl_2(BOxt)$, 60	yellow,	162
0.6	BOxtH, 0.8	30	$CpTiCl(BOxt)_2$, 58	brown,	235
0.5	BOxtH, 1.6	48	$CpTi(BOxt)_3$, 52	dark brown	193
1.0	POxtH, 0.9	28	$CpTiCl_2(POxt)$, 60	brown,	193
1.0	POxtH, 1.8	37	$CpTiCl(POxt)_2$, 54	orange brown	198
0.5	POxtH, 1.5	50	$CpTi(POxt)_3$, 60	yellowish brown,	215
1.0	COxtH, 0.9	28	$CpTiCl_2(COxt)$, 60	light brown,	214
1.0	COxtH, 1.8	35	$CpTiCl(COxt)_2$, 52	yellowish brown,	186
0.5	COxtH, 1.6	50	$CpTi(COxt)_3$, 70	brown,	206

Experimental

The ligands triazoline thiones, quinazolone thiones and oxadiazole thiones were prepared as mentioned in the literature [17–19]. Mono(cyclopentadienyl)-titanium(IV) trichloride was prepared from Cp_2TiCl_2 and $TiCl_4$ in *p*-xylene [1]. 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.

Titanium was determined gravimetrically as TiO_2 and chloride as AgCl. Sulphur was estimated as $BaSO_4$. The carbon and hydrogen analyses were carried out at the Central Drug and Research Institute, Lucknow.

The details of physical measurements are as described earlier [20].

Preparation of Complexes

All these complexes were prepared by reacting mono(cyclopentadienyl)titanium(IV) trichloride with the corresponding ligand in appropriate molar ratios 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 at 80 °C.

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

Results and Discussion

The analytical data of the complexes are given in Table 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 above ~150 °C without melting. 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 23500–24400 cm^{-1}, which can be assigned [20] to the charge transfer band and which is in accordance with the $(n - 1)d^0\ n\ s^0$ electronic configuration of titanium. In addition, the ligands and the complexes show bands around 32000 cm^{-1} which are assigned to $\pi \rightarrow \pi^*$ transition of the azomethine linkages.

Infrared Spectra

Triazoline Thione Derivatives

The assignments of infrared spectral bands of the ligands and the complexes are based on an earlier study of similar ligands [21–24]. The ligands show four bands at *ca.* 1560–1550, 1250, 1090–1080 and 790–780 cm^{-1} which are assigned [22] to thioamide I, II, III and IV vibrations. 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 titanium complexes these bands disappear, indicating that mixing of ν(C–N), δ(N–H) and ν(C=S) vibrations may be absent and that the ligand is coordinating to the metal atom through a deprotonated thiol sulphur atom. A weak band at *ca.* 2550–2480 cm^{-1} in the spectra of the ligands due to the SH group vibration further suggests the thione ⇌ thiol tautomerism. However, in the spectra of the complexes, this band disappears indicating the coordination through sulphur after deprotonation. The ν(Ti–S) vibrations appear at *ca.* 380–340 cm^{-1} [25].

The bands observed around 3250–3150 (in HAFT), 1630 in (HFBT, HFFT and H_2FST), 1580–1565 and 1500 cm^{-1} in the spectra of the ligands may be assigned [21] to ν(N–H), ν(C=N), (N–N=C–), ν(C=N) (ring) and ν(C=C) (phenyl) vibrations, respectively. The spectra of the complexes show the shifting of ν(C=N) band (~1630 cm^{-1}) to lower frequency (~25 cm^{-1}), indicating the coordination of the azomethine nitrogen to a metal atom. The IR band in the region 3250–3200 cm^{-1} in the ligand HFAT due to ν(NH) of the primary amino group is shifted towards the lower wavenumber (~50 cm^{-1}) in its complexes, which indicate [26] the coordination of the amido nitrogen to the metal atom. The bands observed at *ca.* 450–430 cm^{-1} may be assigned [25] to ν(Ti–N).

The ligand H_2FST shows one band at *ca.* 3400 cm^{-1} which may be assigned [26] to ν(OH) of phenolic group. In the complex this band disappears, indicating the coordination of phenolic oxygen to the metal atom through deprotonation. The bands at 500 cm^{-1} in the complex can be assigned [20] to ν(Ti–O).

Thus, the infrared spectra reflect that the ligand HAFT acts as a monobasic bidentate ligand having coordination sites at thiol sulphur and amino nitrogen, the ligands HFBT and HFFT coordinate through thiol sulphur and azomethine nitrogen, and the ligand H_2FST behaves as dibasic tridentate ligand coordinating through thiol sulphur, phenolic oxygen and azomethine nitrogen.

Quinazolone Thione Derivatives

The IR spectra of the ligands, 3-substituted-quinazol-4-one-2-thiones, show sharp bands at 3400

TABLE II. Analytical Data of the Complexes.

Complex	Calc. (Found (%)				
	C	H	S	Ti	Cl
(1)	(2)	(3)	(4)	(5)	(6)
$CpTiCl_2(AFT)$	26.1	1.9	8.7	13.0	19.3
	(26.0)	(1.7)	(8.5)	(13.0)	(19.2)
$CpTiCl(AFT)_2$	25.6	1.7	12.4	9.3	6.9
	(25.4)	(1.7)	(12.2)	(9.0)	(6.8)
$CpTi(AFT)_3$	25.3	1.6	14.5	7.2	
	(25.3)	(1.4)	(14.2)	(7.2)	
$CpTiCl_2(FBT)$	39.5	2.4	7.0	10.5	15.6
	(39.3)	(2.4)	(6.8)	(10.5)	(15.3)
$CpTiCl(FBT)_2$	43.4	2.4	9.2	6.9	5.1
	(43.2)	(2.1)	(9.0)	(6.7)	(5.1)
$CpTi(FBT)_3$	45.3	2.4	10.3	5.1	
	(45.3)	(2.2)	(10.1)	(5.1)	
$CpTiCl_2(FFT)$	35.0	2.0	7.1	10.7	15.9
	(35.0)	(1.8)	(7.0)	(10.7)	(15.9)
$CpTiCl(FFT)_2$	37.5	1.9	9.5	7.1	5.2
	(37.3)	(1.9)	(9.2)	(7.1)	(5.2)
$CpTi(FFT)_3$	38.8	2.1	10.7	5.3	
	(38.6)	(2.0)	(10.7)	(5.3)	
$CpTi(FST)Cl$	41.4	2.5	7.3	11.0	8.1
	(41.2)	(2.3)	(7.3)	(10.9)	(8.1)
$CpTiCl_2(MQzt)$	46.2	3.3	8.8	13.1	19.5
	(46.0)	(3.0)	(8.7)	(13.0)	(19.5)
$CpTiCl(MQzt)_2$	54.5	3.7	12.6	9.4	7.0
	(54.2)	(3.7)	(12.4)	(9.3)	(7.0)
$CpTi(MQzt)_3$	59.0	4.0	14.7	7.3	
	(59.0)	(3.8)	(14.6)	(7.3)	
$CpTiCl_2(PQzt)$	52.1	3.2	7.3	10.9	16.2
	(52.0)	(3.1)	(7.3)	(10.9)	(16.1)
$CpTiCl(PQzt)_2$	60.5	3.5	9.7	7.3	5.4
	(60.5)	(3.2)	(9.7)	(7.3)	(5.2)
$CpTi(PQzt)_3$	64.6	3.6	11.0	5.4	
	(64.4)	(3.3)	(11.0)	(5.4)	
$CpTiCl_2(TQzt)$	53.2	3.5	14.1	10.6	15.7
	(53.0)	(3.5)	(14.0)	(10.4)	(15.7)
$CpTiCl(TQzt)_2$	61.5	3.6	9.3	7.0	5.2
	(61.5)	(3.6)	(9.0)	(7.0)	(5.1)
$CpTi(TQzt)_3$	65.6	3.8	10.5	5.2	
	(65.6)	(3.7)	(10.5)	(5.0)	
$CpTiCl_2(BOxt)$	43.1	2.7	8.8	13.2	19.6
	(43.0)	(2.5)	(8.8)	(13.0)	(19.6)
$CpTiCl(BOxt)_2$	50.1	2.9	12.7	9.5	7.0
	(50.1)	(2.9)	(12.5)	(9.4)	(7.0)
$CpTi(BOXt)_3$	54.0	3.1	14.9	7.4	
	(54.0)	(3.0)	(14.9)	(7.3)	
$CpTiCl_2(POxt)$	38.4	2.2	7.8	11.8	17.4
	(38.4)	(2.0)	(7.8)	(11.6)	(17.4)
$CpTiCl(POxt)_2$	42.5	2.1	10.8	8.0	5.9
	(42.4)	(2.1)	(10.7)	(7.8)	(5.9)
$CpTi(POxt)_3$	44.6	2.1	12.3	6.1	
	(44.4)	(2.1)	(12.3)	(6.0)	
$CpTiCl_2(COxt)$	39.4	2.2	8.0	12.1	26.9
	(39.2)	(2.2)	(8.0)	(12.0)	(26.7)
$CpTiCl(COxt)_2$	44.1	2.2	11.2	8.3	18.6
	(44.0)	(2.2)	(11.2)	(8.3)	(18.4)
$CpTi(COxt)_3$	46.5	2.2	12.8	6.4	14.2
	(46.4)	(2.2)	(12.8)	(6.4)	(14.1)

cm^{-1} and 1650 cm^{-1} which may be assigned [26] to ν(NH) and δ(NH), respectively. However, in the spectra of the complexes these bands disappear indicating the displacement of N–H hydrogen by metal ion. This is further confirmed by the appearance of new bands around 470–440 cm^{-1}, assignable [25] to ν(Ti–N). A sharp band appearing at 1720–1700 cm^{-1} (due to νC=O) in the ligands appears at the same place in the spectra of the complexes, ruling out the possibility of coordination through carbonyl groups. The ligands quinazol-4-one-2-thione contains a thioamide group.

The four thioamide bands, I, II, III and IV, are typical of molecules containing H–N–C=S skeleton and are found at *ca.* 1500, 1400–1300, 1000 and 850–700 cm^{-1}, respectively. The appearance of four thioamide bands and the absence of any band near 2500 cm^{-1} (due to νS–H), indicates [16] the existence of the ligands in the thione form. The thioamide III and IV bands, having main contribution from ν(C=S), are shifted towards lower energies in the complexes indicating [21] the coordination of thioketo sulphur to a titanium atom. The ν(Ti–S) vibrations appear at 390–360 cm^{-1}. Thus, it becomes evident that the ligands 3-substituted quinazol-4-one-2-thiones act as bidentate chelating agents, coordinating through thione sulphur and amino nitrogen (through deprotonation).

Oxadiazole Thione Derivatives

The ν(NH) and δ(NH) vibration bands, which appear at *ca.* 3350 and 1630 cm^{-1} in the ligands, disappear in the complexes indicating [26] the coordination of amino nitrogen to the titanium atom through deprotonation. This is confirmed by the appearance of new bands at *ca.* 480–440 cm^{-1}, assignable [25] to ν(Ti–N). The thioamide III and IV vibrations, which have their largest contribution from ν(C=S), undergo a red shift in the complexes suggesting the coordination of sulphur atom to the titanium atom in the thione form [21]. The ν(Ti–S) vibrations appear at 400–370 cm^{-1}. The position of IR bands due to phenyl and oxadiazole group (C–O–C) [22] do not change in the complexes, indicating the non-coordination of the oxygen atom. The above observations indicate that the bonding in titanium complexes is possibly through amino nitrogen and thiocarbonyl sulphur.

In addition, absorption bands occurring at ~3000 cm^{-1} ν(C–H), ~1430 cm^{-1} ν(C–C) and ~1020 cm^{-1} δ(C–H) in all the complexes indicate the presence of cyclopentadienyl rings. All these bands are similar to those of mono(cyclopentadienyl)titanium(IV) [27]. Davison and Rakita have pointed out [28] that at 3000 cm^{-1}, η^1-C_5H_5 should show four bands whereas η^5-C_5H_5 should show only one. 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 some of these complexes have been recorded in deuterated chloroform and dimethylformamide. The intensities of all the resonance lines were determined by planimetric integration. The following conclusions can be derived by comparing the spectra of ligands and their corresponding complexes.

(i) A signal in all derivatives at δ ~6.5–6.8 ppm may be assigned to the protons of cyclopentadienyl ring. The appearance of a single, sharp cyclopentadienyl resonance is attributed to the rapid rotation of the ring around the metal ring axis.

(ii) The two kinetic possibilities, *viz.*, metal-centered rearrangement is slow or fast, can be distinguished by the analysis of NMR spectra. In the spectra of 1:3 complexes, CpTi(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 one signal has been observed for ligand proton groups.

(iii) In the NMR spectra of mercapto triazoles, the signal due to SH proton appears at about δ 4.4 ppm which disappears in the corresponding complexes indicating the deprotonation of thiol proton. Further, the ligand H$_2$FST shows one signal at δ 9.8 ppm due to phenolic proton. This signal disappears in its complex indicating the deprotonation of the phenolic group.

(iv) The spectra of quinazolone thione and oxadiazole thione show one sharp signal at δ 4.8–4.9 ppm due to the NH proton which disappears in their corresponding complexes suggesting the coordination of amino nitrogen to titanium atom through deprotonation.

Acknowledgement

The authors are thankful to the Indian National Science Academy for financial assistance.

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