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

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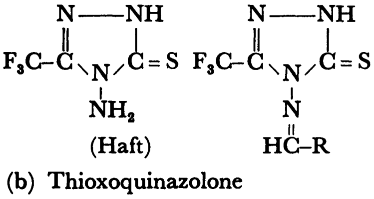
The reactions of mono(cyclopentadienyl)titanium(IV) trichloride with three important series of heterocyclic thioketones, *viz.*, triazolinethiones 4-amino-, 4-benzylideneamino-, 4-furfurylideneamino-, and 4-salicylideneamino-5-trifluoromethyl-1,2,4-triazoline-3-thiones, thioxoquinazolones (3-methyl-, 3-phenyl-, and 3-(*o*-tolyl)-2-thioxo-4-quinazolones), and oxadiazolethiones (5-phenyl-, 5-(*p*-nitrophenyl), and 5-(*p*-chlorophenyl)-1,3,4-oxadiazole-2-thiones, have been studied in anhydrous dichloromethane. The reaction products have been 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.

Although the preparation of mono(cyclopentadienyl)titanium(IV) trichloride was reported[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] thiols[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] 1,10-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 thioketones as chelating agents. These ligands, containing thioamide bond and capable of undergoing thione-enethiol (HN-C=S$\rightleftharpoons$N=C-SH) tautomerism, can coordinate to a metal atom through nitrogen or through sulfur or simultaneously through nitrogen and sulfur. 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 due to their biological importance.[12–16]

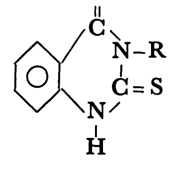
The structures of the ligands are given below:

(a) Triazolinethione



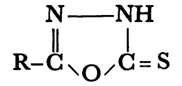
R = C_6H_5(Hfbt)
R = C_4H_3O(Hfft)
R = $C_6H_4(OH)$(H_2fst)

(b) Thioxoquinazolone



R = CH_3(mqztH)
R = C_6H_5(pqztH)
R = $C_6H_4CH_3$-*o*(tqztH)

(c) Oxadiazolethione



R = C_6H_5(boxtH)
R = $C_6H_4NO_2$-*p*(poxtH)
R = C_6H_4Cl-*o*(coxtH)

Experimental

The ligands triazolinethiones, thioxoquinazolones, and oxadiazolethiones were prepared as mentioned in 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 it for 30 h over calcium hydride.

Most of derivatives prepared and studied are susceptible to hydrolysis. Hence, all operations were carried out under strictly 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 Central Drug and Research Institute, Lucknow.

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

Preparation of Complexes. All these complexes were prepared by taking mono(cyclopentadienyl)titanium(IV) trichloride and respective 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 solution and allowing them to stand for overnight resulted yellow to brown crystals of the products which were filtered and dried in oven 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 1.

Results and Discussion

The analytical data of the complexes are given in Table 1. 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 hydrolyzed on standing. Conductance measurements reveal that they are essentially nonelectrolytes. Magnetic susceptibility values at room temperature show the diamagnetic nature of the complexes. The electronic spectra of all these complexes show a

TABLE 1. REACTIONS OF (cp)TiCl$_3$ WITH HETEROCYCLIC THIOKETONES IN DICHLOROMETHANE

Reactants	Molar ratio	Refluxing time/h	Product, colour, decomp temp/°C, yield/%	Found(Calcd)				
				C	H	S	Ti	Cl
(cp)TiCl$_3$+Haft	1:1	20	(cp)TiCl$_2$(aft), yellow, 252, 58	26.0 (26.1)	1.7 (1.9)	8.5 (8.7)	13.0 (13.0)	19.2 (19.3)
(cp)TiCl$_3$+Haft	1:2	28	(cp)TiCl(aft)$_2$, brown, 232, 54	25.4 (25.6)	1.7 (1.7)	12.2 (12.4)	9.0 (9.3)	6.8 (6.9)
(cp)TiCl$_3$+Haft	1:3	38	(cp)Ti(aft)$_3$,brown, 280, 62	25.3 (25.3)	1.4 (1.6)	14.2 (14.5)	7.2 (7.2)	— —
(cp)TiCl$_3$+Hfbt	1:1	25	(cp)TiCl$_2$(fbt), yellow, 262, 65	39.3 (39.5)	2.4 (2.4)	6.8 (7.0)	10.5 (10.5)	15.3 (15.6)
(cp)TiCl$_3$+Hfbt	1:2	35	(cp)TiCl(fbt)$_2$, orange, 300, 55	43.2 (43.4)	2.1 (2.4)	9.0 (9.2)	6.7 (6.9)	5.1 (5.1)
(cp)TiCl$_3$+Hfbt	1:3	45	(cp)Ti(fbt)$_3$, orange, 275, 60	45.3 (45.3)	2.2 (2.4)	10.1 (10.3)	5.1 (5.1)	— —
(cp)TiCl$_3$+Hfft	1:1	30	(cp)TiCl$_2$(fft), yellow, 180, 68	35.0 (35.0)	1.8 (2.0)	7.0 (7.1)	10.7 (10.7)	15.9 (15.9)
(cp)TiCl$_3$+Hfft	1:2	40	(cp)TiCl(fft)$_2$, yellow, 210, 65	37.3 (37.5)	1.9 (1.9)	9.2 (9.5)	7.1 (7.1)	5.2 (5.2)
(cp)TiCl$_3$+Hfft	1:3	50	(cp)Ti(fft)$_3$, orange, >300, 50	38.6 (38.8)	2.0 (2.1)	10.7 (10.7)	5.3 (5.3)	— —
(cp)TiCl$_3$+H$_2$fst	1:1	20	(cp)TiCl(fst), orange, 245, 68	41.2 (41.4)	2.3 (2.5)	7.3 (7.3)	10.9 (11.0)	8.1 (8.1)
(cp)TiCl$_3$+mqztH	1:1	22	(cp)TiCl$_2$(mqzt), yellow, 200, 65	46.0 (46.2)	3.0 (3.3)	8.7 (8.8)	13.0 (13.1)	19.5 (19.5)
(cp)TiCl$_3$+mqztH	1:2	28	(cp)TiCl(mqzt)$_2$, brown, 182, 50	54.2 (54.5)	3.7 (3.7)	12.4 (12.6)	9.3 (9.4)	7.0 (7.0)
(cp)TiCl$_3$+mqztH	1:3	45	(cp)Ti(mqzt)$_3$, orange, >300, 52	59.0 (59.0)	3.8 (4.0)	14.6 (14.7)	7.3 (7.3)	— —
(cp)TiCl$_3$+pqztH	1:1	28	(cp)TiCl$_2$(pqzt), yellow, 165, 68	52.0 (52.1)	3.1 (3.2)	7.3 (7.3)	10.9 (10.9)	16.1 (16.2)
(cp)TiCl$_3$+pqztH	1:2	38	(cp)TiCl(pqzt)$_2$, orange, 295, 58	60.5 (60.5)	3.2 (3.5)	9.7 (9.7)	7.3 (7.3)	5.2 (5.4)
(cp)TiCl$_3$+pqztH	1:3	50	(cp)Ti(pqzt)$_3$, orange, 218, 64	64.4 (64.6)	3.3 (3.6)	11.0 (11.0)	5.4 (5.4)	— —
(cp)TiCl$_3$+tqztH	1:1	28	(cp)TiCl$_2$(tqzt), orange, 248, 58	53.0 (53.2)	3.5 (3.5)	14.0 (14.1)	10.4 (10.6)	15.7 (15.7)
(cp)TiCl$_3$+tqztH	1:2	38	(cp)TiCl(tqzt)$_2$, brown, >300, 62	61.5 (61.5)	3.6 (3.6)	9.0 (9.3)	7.0 (7.0)	5.1 (5.2)
(cp)TiCl$_3$+tqztH	1:3	45	(cp)Ti(tqzt)$_3$, brown, 278, 45	65.6 (65.6)	3.7 (3.8)	10.5 (10.5)	5.0 (5.2)	— —
(cp)TiCl$_3$+boxtH	1:1	22	(cp)TiCl$_2$(boxt), yellow, 162, 60	43.0 (43.1)	2.5 (2.7)	8.8 (8.8)	13.0 (13.2)	19.6 (19.6)
(cp)TiCl$_3$+boxtH	1:2	30	(cp)TiCl(boxt)$_2$, brown, 235, 58	50.1 (50.1)	2.9 (2.9)	12.5 (12.7)	9.4 (9.5)	7.0 (7.0)
(cp)TiCl$_3$+boxtH	1:3	48	(cp)Ti(boxt)$_3$, dark brown, 193, 52	54.0 (54.0)	3.0 (3.1)	14.9 (14.9)	7.3 (7.4)	— —
(cp)TiCl$_3$+poxtH	1:1	28	(cp)TiCl$_2$(poxt), brown, 193, 60	38.4 (38.4)	2.0 (2.2)	7.8 (7.8)	11.6 (11.8)	17.4 (17.4)
(cp)TiCl$_3$+poxtH	1:2	37	(cp)TiCl(poxt)$_2$, orange brown, 188, 54	42.4 (42.5)	2.1 (2.1)	10.7 (10.8)	7.8 (8.0)	5.9 (5.9)
(cp)TiCl$_3$+poxtH	1:3	50	(cp)Ti(poxt)$_3$, yellowish brown, 215, 60	44.4 (44.6)	2.1 (2.1)	12.3 (12.3)	6.0 (6.1)	— —
(cp)TiCl$_3$+coxtH	1:1	28	(cp)TiCl$_2$(coxt), light brown, 214, 60	39.2 (39.4)	2.2 (2.2)	8.0 (8.0)	12.0 (12.1)	26.7 (26.9)
(cp)TiCl$_3$+coxtH	1:2	35	(cp)TiCl(coxt)$_2$, yellowish brown, 186, 52	44.0 (44.1)	2.2 (2.2)	11.2 (11.2)	8.3 (8.3)	18.4 (18.6)
(cp)TiCl$_3$+coxtH	1:3	50	(cp)Ti(coxt)$_3$, brown, 206, 70	46.4 (46.5)	2.2 (2.2)	12.8 (12.8)	6.4 (6.4)	14.1 (14.2)

band in the region 23500—24400 cm^{-1}, which can be assigned[20] to the charge transfer band and is in accordance with the $(n-1)$ d^0 ns^0 electronic configuration of titanium. In additon, 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. *(a) Triazolinethione Derivatives*: The assignments of infrared spectral bands of the ligands and the complexes are based on an earlier study of similar ligands.[21] Organic compounds having a thioamide group (H–N–C=S) give rise to four thioamide bands in the IR spectra.[22] These are thioamide band I at about 1500 cm^{-1}, band II at about 1300—1400 cm^{-1}, band III at about 1000 cm^{-1} and band IV at about 700—850 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 our ligands, these bands appear in the region 1560—1550, 1250, 1090—1080, and 790—780 cm^{-1}. These bands are expected to be affected differently by different modes of coordination after complexation with the metal ions.[21,23,24] However, in our complexes, these bands disappear indicating that mixing of ν(C-N), δ(N-H), and ν(C=S) vibrations may be absent and ligand is coordinating to the metal atom through a deprotonated thiol sulfur atom. A weak band at $\approx$2550 —2480 cm^{-1} in the spectra of the ligands due to the -SH group vibration, further suggests the thione$\rightleftharpoons$enethiol tautomerism. However, in the spectra of the complexes, this band disappears indicating the coordination through sulfur after deprotonation. This is further confirmed by the appearance of new band in the far IR region 380—340 cm^{-1} which can be assigned to the ν(Ti-S) vibration.[25]

The bands observed around 3250—3150 (in Haft), 1630 in (Hfbt, Hfft, and H$_2$fst), 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. Strong vibrations in the region 1600—1550 cm^{-1} are usually associated with phenyl and C=N groups and it is not usually possible to identify such bands with particular C=C or C=N linkage. However, a stringent assignment of the C=N group can be made by comparing the spectrum of the ligand Haft containing N-NH$_2$ group with that of the ligands Hfbt, Hfft, and H$_2$fst in which it is replaced by N-N=CH group. Following this method, the strong band observed around 1630 cm^{-1} is assigned to the ν(C=N) vibration. However, the spectra of the complexes show the shifting of this band to lower frequency ($\approx$25 cm^{-1}) indicating the coordination of the azomethine nitrogen to metal atom. The IR band in the region 3250—3200 cm^{-1} in the ligand Hfat due to ν(NH) of the amino group is shifted towards the lower wave number ($\approx$50 cm^{-1}) in its complexes which indicate[26] the coordination of the amino nitrogen to the metal atom. The bands observed in the region 450—430 cm^{-1} may be assigned[25] to ν(Ti-N).

The ligand H$_2$fst shows one band at $\approx$3400 cm^{-1} which may be assigned[26] to ν(OH) of phenolic hydroxyl group. However, in its 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 to ν(Ti-O).[20]

Thus, the infrared spectra reflect that the ligand Haft acts as monobasic bidentate ligand having coordination sites at thiol sulfur and amino nitrogen, the ligands Hfbt and Hfft coordinate through thiol sulfur and azomethine nitrogen and the ligand H$_2$fst behaves as dibasic tridentate ligand coordinating through thiol sulfur, phenolic oxygen, and azomethine nitrogen.

(b) Thioxoquinazolone Derivatives: The IR spectra of the ligands, 3-substituted 2-thioxo-4-quinazolones, show one sharp band at 3400 cm^{-1} which may be assigned[26] to ν(NH). The δ(NH) mode is observed at 1650 cm^{-1}. However, in the spectra of 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} in the ligands may be assigned to ν(C=O) which appears at the same place in the spectra of the complexes, ruling out the possibility of coordination through carbonyl group. The ligands 2-thioxo-4-quinazol-one contains a thioamide group. The four thioamide bands, I, II, III, and IV typical of molecules containing H-N-C=S skeleton are found at $\approx$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 ν(S-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 thioxo sulfur to titanium atom. The ν(Ti-S) vibrations appear at 390—360 cm^{-1}. Thus, it becomes evident that the ligands, 3-substituted 2-thioxo-4-quinazolone, act as bidentate chelating agents, coordinating through thione sulfur and amino nitrogen (through deprotonation).

(c) Oxadiazolethione Derivatives: The ligands, 5-substituted 1,3,4-oxadiazole-2-thione, have one phenyl, one oxadiazole rings and $\rangle$C=S group resulting in the presence of four donor sites (two nitrogen atoms, one oxygen atom and one sulfur atom). Its infrared spectra should, therefore, show characteristic bands of phenyl, oxadiazole rings and of $\rangle$C=S groups. Although the spectra of the ligand and the complexes are quite complicated owing to the overlap of various bands and the coupling of various modes of vibrations. However, the systematic shifts in the positions of a few bands relative to those present in the spectrum of the ligand, give clue to the mode of bonding in the complexes.

The ν(NH) and δ(NH) vibration bands, which appear in the region 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 about 480—440 cm^{-1}, assignable[25] to ν(Ti-N). The thioamide III and IV vibrations, which have largest contribution from ν(C=S), undergo a red shift in the complexes suggesting the coordination of sulfur 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 oxadiazolyl group

(C–O–C)[22] do not change in the complexes indicating the non-coordination of oxygen atom. The above observations indicate that possibly the bonding in titanium complexes is through amino nitrogen and thioxo sulfur.

In addition, absorption bands occurring at $\approx$3000 cm^{-1} ν(C–H), $\approx$1430 cm^{-1} ν(C–C), and 1020 cm^{-1} ν(C–H) in all the complexes indicate the presence of cyclopentadienyl ring. 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'-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} indicate 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 *N,N*-dimethyl-formamide. 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 $\delta\approx$6.5—6.8 ppm may be assigned to the protons of cyclopentadienyl ring. The value is in the range reported[2] for other (C_5H_5) Ti^{IV} complexes with chelating ligands and is significantly separated from the position of (C_5H_5)$TiCl_3$ ($\approx$7.07 ppm). The appearance of a single, sharp cyclopentadienyl resonance is attributed to 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, (cp)Ti(L)$_3$, two distinct resonance lines for the protons of the ligands are observed which must result from the nonequivalent environments for the different ligands. However in the 1:2 derivatives, (cp)Ti(L)$_2$Cl, the ligand groups are equivalent since one signal have been observed for ligand proton groups.

(iii) In NMR spectra of mercaptotriazoles, 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 hydroxyl group.

(iv) The spectra of thioxoquinazolone and oxadiazolethione show one sharp signal at δ=4.8—4.9 ppm due to -NH proton which disappear in their corresponding complexes suggesting the coordination of amino nitrogen to titanium atom through deprotonation.

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