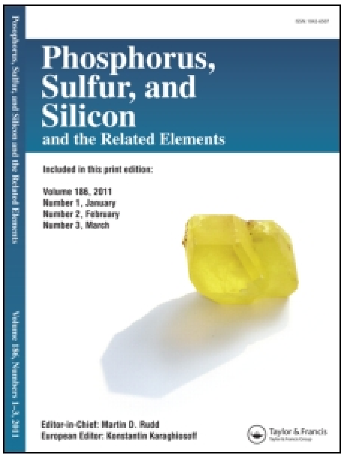

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SYNTHESIS AND CHARACTERISATION OF TITANIUM(IV) COMPLEXES OF BENZILMONOTHIOSEMICARBAZONE

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SYNTHESIS AND CHARACTERISATION OF TITANIUM(IV) COMPLEXES OF BENZILMONOTHIOSEMICARBAZONE

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Titanium(IV) derivatives of benzilmonothiosemicarbazone have been synthesised by the reaction of titanium tetrachloride with the sodium salt of benzilmonothiosemicarbazone (prepared *in situ*) in 1:1, 1:2, 1:3 and 1:4 molar ratios and have been characterised on the basis of elemental (C, H, N, S, Cl and Ti) analyses, molecular weight determinations and spectral (IR and PMR) studies.

Keywords: Titanium tetrachloride; benzilmonothiosemicarbazone; complexes; molecular weight spectral studies

The chemistry of stable organotitanium complexes have attracted the attention of chemists in the past few years as evidenced by a number of monographs[1–5] and reviews.[6] These titanium derivatives are becoming more and more important for industrial applications, and many organic syntheses have been improved by the use of them.[7,8] Various 1,2-diketones and derivatives acting as chelating agents with titanium[9] and the different pharmacological activities in the form of various metal complexes[10,11] have been reported. Titanium(IV) complexes have been cited as Lewis acid promotors in Diels-Alder reactions.[12] However, to the best of our knowledge, the complexes of benzilmonothiosemicarbazone with titanium(IV) have not been reported. In present paper we report the syntheses and characterisation of benzilmonothiosemicarbazone derivatives of titanium(IV).

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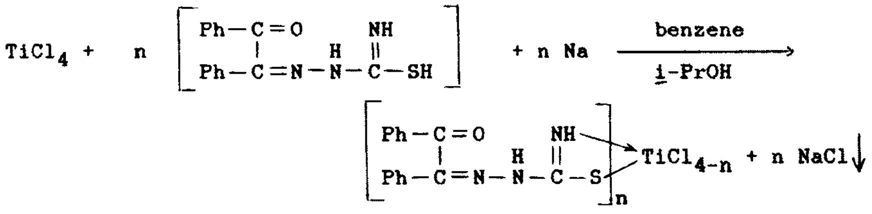


RESULTS AND DISCUSSION

The reaction of titanium tetrachloride with the sodium salt of benzilmonothiosemicarbazone (prepared *in situ*) in different stoichiometric ratios (i.e. 1:1, 1:2, 1:3 and 1:4) in dry benzene yields solid crystalline compounds identified as $TiCl_3L$, $TiCl_2L_2$, $TiClL_3$ and TiL_4, respectively. Intermolecular nucleophilic substitution with elimination of chloride ion (sodium chloride formed during the course of reaction was removed by filtration) led to the formation of products which were characterised on the basis of satisfactory elemental analyses, molecular weight determinations and spectral studies.

These new complexes are fairly soluble in common organic solvents like benzene, chloroform, carbontetrachloride, and dichloromethane as well as coordinating solvents like dimethylsulfoxide, dimethylformamide, etc. The complexes show an insoluble nature in aqueous solvents like water and lower alcoholic species (CH_3OH, C_2H_5OH), but are soluble in higher alcohols such as isopropanol and *n*-butanol. Where, n = 1, compd. (1); n = 2, compd. (2); n = 3, compd. (3); n = 4, compd. (4).

The molecular weight determination in chloroform solution shows the monomeric nature of these complexes at room temperature. These complexes are susceptible to hydrolysis[13] even by traces of moisture. Elemental analyses of carbon, hydrogen, nitrogen, sulfur, titanium, and chlorine suggest good agreement with the tentative structures proposed.

A close investigation of IR spectra revealed a band in the region 340–320 cm^{-1} which could be attributed to the formation of a titanium sulfur (Ti—S) bond.[14,15] This new band is not observed in the spectrum of the free ligand, and thus the formation of Ti-S bond is suggested. This is further confirmed by the disappearance of a band at 2600–2550 cm^{-1} [responsible for (S-H) in ligand] in the complexes. The comparison of IR spectra of these complexes with those of the ligand shows that a band at 1650–1640 cm^{-1} (due to ketocarbonyl group) is observed almost at the same position in both the ligand and in the complexes, indicating that the carbonyl group is not taking part in coordination. The band present in the overlapping region (1600–1585 cm^{-1})[16] of C=NH in the complexes is shifted downfield for about 20 cm^{-1} compared to the ligand (1610 cm^{-1}), inferring the involvement of the imino (C=NH) group in the coordination. The band present in the region 3415– 3225 cm^{-1} in the complexes is almost at the same position as in the ligand, suggesting noninvolvement of NH group in the bond formation (Table I).

The PMR spectra of these titanium(IV) derivatives exhibit usual features. The absorption positions of -SH and -NH protons are concentration dependent and are shifted to lower δ values in more dilute solutions. The signal for -SH proton at δ 2.20 in the free ligand is absent in the spectra of the complexes, again suggesting the metal bond formation through the sulfur atom of the -SH group. Since ^{32}S is non-magnetic, no coupling with this nucleus is observed. A signal at δ 3.60 for the proton of the -NH[16] is observed in the free ligand. In the spectra of the complexes, a signal is displayed at δ 4.50–4.20, showing the downfield shift of approximately δ 0.90 and indicating the involvement of C = NH group in the coordination. Hence, a bidendate structure is inferred. The aromatic protons present in the ligand and the complexes show a multiplet at δ 6.50–7.85 exhibiting a similar chemical environment (Table I). Thus, on the basis of above spectral studies it may be concluded that the ligand seems to be acting as a bidentate moiety involving thiol sulfur and imino nitrogen.

EXPERIMENTAL

All the melting points are uncorrected. The IR and PMR spectra are recorded on a Perkin-Elmer model 720 and JEOL JNM FX-90 Q spectrophotometers, respectively. Chemical shifts are recorded in ppm (δ) relative to TMS as an internal standard. Microanalyses, were performed by Coleman Carbon, Hydrogen, and Nitrogen analysers for C, H and N, respectively. Sulfur, titanium and chlorine have been estimated gravimetrically by the reported method and are in satisfactory agreement with the calculated values (Table II).

Synthesis of Benzilmonothiosemicarbazone

The ligand was prepared by adopting the general procedure for the synthesis of thiosemicarbazones.[17] To the boiling solution of thiosemicarbazide (3.46g, 0.40 mole) in ethanol (100 ml) was added benzil (8.40g, 0.40 mole) in a round bottomed flask. The contents were stirred and heated for one hour. After cooling, the thiosemicarbazone readily crystallised and was filtered off and dried under reduced pressure. It was recrystallised (ethanol) to give yellow coloured crystals,

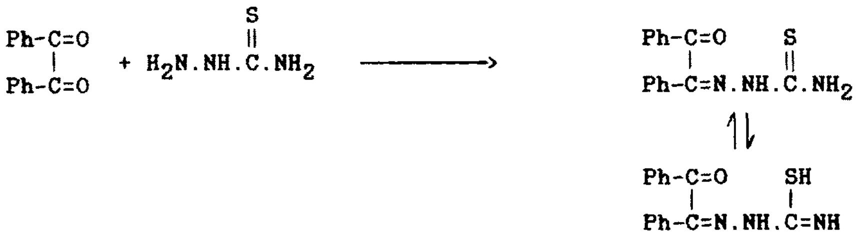
TABLE I Physical and spectral data of the ligand and the complexes

Compound/Mol. Wt. Calcd./(Found)	*Physical state*	*M.P. (°C)*	*IR (cm^{-1})*					*^1H MMR (δ ppm)*
			ν(C=O)	*ν(C=NH)*	*ν(NH)*	*ν(S-H)*	*ν(Ti-S)*	
$C_{15}H_{13}N_3OS$	Yellow	80	1640	1610	3515–3225	2600–2550	—	2.20(s,1 H, SH); 3.60 (s, 2H, NH);
283 (280)	crystals		(s)	(m)	(b)	(b)		6.50–7.85 (m, 10 H, arom.).
$C_{15}H_{12}N_3OSTiCl_3$	Brownish	195	1645	1585	3400–3220	—	320	4.20 (s,2 H, NH); 6.50–7.85
436.5 (441)	solid		(s)	(m)	(b)			(m, 10 H, arom.).
$C_{30}H_{24}N_6O_2S_2TiCl_2$	Brownish	215	1650	1590	3410–3210	—	330	4.40 (s, 4 H, NH); 6.50–7.80
683 (696)	solid		(s)	(m)	(b)			(m, 20 H, arom.).
$C_{45}H_{36}N_9O_3S_3TiCl$	Yellowish	205	1640	1600	3505–3225	—	325	4.45(s, 6 H, NH); 6.65–7.75
929.5 (932)	solid		(s)	(m)	(b)			(m, 30 H, arom.).
$C_{60}H_{48}N_{12}O_4S_4Ti$	Brownish	210	1650	1595	3415–3215	—	340	4.50(s, 8 H, NH); 6.55–7.85
1176 (1182)	solid		(s)	(m)	(b)			(m, 40 H, arom.).

(s = sharp; m = medium, b = broad)

TABLE II Synthetic and analytical data of the complexes 1–4

Compd. No.	*Reactants in g, (m mole)*			*Molar ratio*	*Yield in g, (%)*	*analyses % found/(Calcd.)*					
	TiCl$_4$	*Ligand*	*Sodium metal*			*C*	*H*	*N*	*S*	*Ti*	*Cl*
1.	0.95(5.0)	1.42(5.0)	0.12(5.0)	1:1:1	1.85(84)	41.23 (41.04)	2.75 (2.67)	9.62 (9.48)	7.33 (7.10)	10.99 (10.68)	24.39 (24.22)
2.	0.79(4.2)	2.36(8.4)	0.19(8.4)	1:2:2	2.01(71)	52.71 (52.68)	3.51 (3.39)	12.30 (12.08)	9.37 (9.12)	7.02 (7.22)	10.39 (10.14)
3.	0.85(4.5)	3.82(13.5)	0.30(13.5)	1:3:3	3.21(77)	58.09 (57.94)	3.87 (3.63)	13.55 (13.49)	10.30 (10.00)	5.16 (4.98)	3.81 (3.67)
4.	0.59(3.1)	3.53(12.4)	0.29(12.4)	1:4:4	2.90(79)	61.22 (61.08)	4.08 (3.86)	14.28 (14.04)	10.80 (10.60)	4.08 (4.22)	—



10.28g, (85.3%), mp 80°C. Analysis found: C,63.24; H,4.35; N,14.68; S,11.08 $C_{15}H_{13}H_3OS$ (283) requires: C,63.60; H,4.59; N,14.84; S,11.31%.

Reaction between Titanium(IV) Chloride and the Sodium Salt of Benzilmonothiosemicarbazone in a 1:1 Molar Ratio

0.12g, (5 mmole) of sodium metal and 20 ml of isopropanol were taken in a round bottom flask fitted with a dried and cooled water condenser and guard tube. It was refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling, 1.42g, (5 mmole) of benzilmonothiosemicarbazone was added and the mixture was further refluxed for two hours. 0.95g, (5 mmole) of titanium tetrachloride and 20 ml of dry benzene were added and the contents were boiled for an additional 2 hours to ensure the completion of the reaction. The desired product 1.85g, (84%) was isolated by evaporation of the solvent under reduced pressure, after filtering off the precipitated sodium chloride. The product was further purified by crystallisation using a benzene-petroleum ether (40°–60°) mixture. All other titanium(IV) derivatives of benzilmonothiosemicarbazone were synthesised analougsly. The pertinent data for this and other derivatives are tabulated in Table II.

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