CHAPTER III

EXPERIMENTAL
1. **Experimental techniques and materials**

As a precaution against any hydrolytic decomposition, all the reactions and other operations like filtration, concentration etc., except otherwise stated, were carried out under purified and dry nitrogen atmosphere. Nitrogen gas was always used to break vacuum when solutions were concentrated or substances were dried under reduced pressure. Various organic solvents used were all purified and dried by standard procedures available in literature. The various starting materials were either pure and used as such or purified, wherever necessary, as stated in the experimental descriptions below.

On the analytical side, carbon, hydrogen, nitrogen and sulphur were determined microanalytically. Titanium was determined, except where stated otherwise below, by fusing the compounds with concentrated sulphuric and nitric acids till complete decomposition, precipitating the metal with cupferron and igniting the precipitate to oxide TiO$_2$. Other metals were determined as stated in the experimental descriptions. The chloride content, wherever present, was estimated by fusing the compound with appropriate quantity of sodium carbonate, dissolving the carbonate melt in water and titrating the solution, after acidification with dilute nitric acid and filtration, according to Volhard's method.
As regards the physical studies, Perkin-Elmer Infracord Spectrophotometer, Models 137-B and 137-E, and in certain cases, Model 221 Spectrophotometer with sodium chloride optics were used for recording the infrared spectra of the compounds in the region 4000-700 cm\(^{-1}\). NMR spectra were recorded using Varian A-60 Spectrophotometer. Mass spectra were recorded at 70 eV with CEC 21-110B Model Mass Spectrometer. A thermogravimetric balance using McBain-Bakr type quartz spring was used for the thermogravimetric study, measuring the extension of the spring with a travelling microscope every 4 minutes keeping the heating rate at 4°C per minute.

2. Synthesis of bis-\(\pi\)-cyclopentadienyl-titanium(IV) dichloride

Bis-\(\pi\)-cyclopentadienyltitanium(IV) dichloride, which formed the starting material in other experiments, was synthesized following essentially the methods described in literature\(^{21,70}\).

2.1. By reaction of titanium tetrachloride with sodium cyclopentadienide

2.1.1. Preparation of cyclopentadiene monomer

Preparation of cyclopentadiene monomer is best accomplished by thermal depolymerization of dicyclopentadiene at temperatures above 150°C. Cyclopentadiene monomer is unstable at room temperature and therefore must be stored at low temperatures.
to prevent dimerization to dicyclopentadiene. The rate of
dimerization is about 0.05 per cent per hour at -20°C and 1 per
cent per hour at 10°C. A convenient laboratory apparatus for
the depolymerization of cyclopentadiene is shown in Fig. 33.
In the flask A of one litre capacity was placed purified BOC white
oil (b.p. > 300°C) which served as a heat transfer medium for the
depolymerization process. Heating the oil to about 200-220°C and
keeping a stream of steam passing through the condenser C,
dicyclopentadiene was slowly dropped (at the rate of 100-150 ml.
per hour) onto the heated oil. Depolymerization was nearly
instantaneous and the vapours which passed through the condenser
C were condensed in the second ice-water condenser D and cyclo-
pentadiene monomer was collected in the receiver flask B cooled
with ice-salt mixture. The condenser C prevented contamination
of the cyclopentadiene with the white oil by condensing the
latter and returning it to the flask. Yield was about 90% of
the theoretical.

2.1.2. Preparation of sodium cyclopentadienide

A 500 ml. three-neck flask was fitted with a
mechanical stirrer, a dropping funnel, a reflux condenser provided
with a guard tube and a nitrogen inlet. In the flask was placed
6.3 g. of fine sodium metal sand which contained 6 g. of active
sodium metal and 100 ml. of tetrahydrofuran. The sodium metal
fine sand was prepared by vigorously stirring with a high speed
FIG. 33. APPARATUS FOR DEPOLYMERIZATION OF CYCLOPENTADIENE
stirrer molten sodium in kerosene to obtain a sodium dispersion, subsequently washing repeatedly the dispersion with petroleum ether (b.p. 40-50°) till free of kerosene and drying under vacuum. In the dropping funnel was placed an ice-cooled mixture of 23 ml. cyclopentadiene monomer and 25 ml. tetrahydrofuran. Keeping the sodium metal suspension stirred, the cyclopentadiene mixture was slowly dropped in the course of about 30 minutes while the temperature inside the flask was maintained between 30-40°C by external cooling. After complete addition of cyclopentadiene, stirring was continued for another three hours and an orange coloured solution obtained was subsequently filtered. The yield was nearly quantitative.

2.1.3. Reaction of titanium tetrachloride with sodium cyclopentadienide - synthesis of bis-\( \eta^2 \)-cyclopentadienyltitanium dichloride

In a 500 ml. three-neck flask fitted likewise as in (2.1.2) above, was placed 150 ml. of tetrahydrofuran. The flask was surrounded with ice and, keeping the solvent stirred, titanium tetrachloride (18.7 g., 0.1 mole) from the dropping funnel was slowly added. An yellow coloured suspension was obtained. The dropping funnel was replaced by another which contained the sodium cyclopentadienide solution prepared above. While the suspension in the flask was stirred, cyclopentadienide solution was slowly added, carefully controlling the rate of
addition as the reaction was vigorous. The flask was kept cooled throughout by surrounding with ice. After the addition was complete, stirring was continued for three hours. Subsequently, the solvent was removed under reduced pressure and the dry residue obtained was repeatedly extracted with boiling chloroform through which was passed a slow stream of hydrogen chloride. The extract was evaporated and the residue was re-extracted with chloroform saturated with hydrogen chloride. The product obtained after evaporating the second extract, was recrystallized from toluene. Deep red crystalline product, m. p. 287-88°C with decomposition, was obtained. Yield, 8.5 g. (35%).

Found: Ti, 19.13; Cl, 29.02; C, 47.96; H, 3.89%. Calculated for C_{10}H_{10}TiCl_{2}: Ti, 19.24; Cl, 28.51; C, 48.19; H, 4.01%.

2.2. By reaction of titanium tetrachloride with cyclopentadiene in presence of base diethylamine

The cyclopentadiene monomer was prepared as in 2.1.1 above.

A three-neck flask was fitted with a mechanical stirrer, a condenser provided with a calcium chloride guard tube and a pressure equalizer addition funnel. In the flask and the addition funnel were placed respectively 300 ml. of tetrahydrofuran and 60 g. (0.31 mole) of titanium tetrachloride. The titanium tetrachloride was then carefully added to the tetrahydrofuran with good mixing and cooling. To this mixture was then added 100 ml. (1 mole) of diethylamine followed by 120 ml. (1.4 mole) of
cyclopentadiene monomer. Subsequently, the whole mixture, while being stirred, was heated under reflux for 8 hours. Cooling to 5°C, it was filtered through a sintered disc. No nitrogen gas blanket was provided during this filtration and subsequent operations. The precipitate collected on the sinter was washed with tetrahydrofuran and petroleum ether (40-60 fraction), and dried in air. The dried precipitate was then added to 200 ml. of 4N hydrochloric acid and the resulting slurry was stirred for fifteen minutes and filtered. The red solid collected on the filter (sintered disc) was washed with ice-water and methanol and then dried. It was subsequently crystallized from toluene. Yield, 46 g. (60%); m. p. 287-289° with decomposition. Found: Ti, 19.18; Cl, 29.13; C, 47.89; H, 4.10%.

3. Reactions of bis-π-cyclopentadienyltitanium(IV) dichloride with sulphur-containing ligands in presence of gaseous ammonia

Only those experiments in which pure compounds were isolated have been described. The simple reaction apparatus used in these experiments consisted of a three-neck flat-bottomed flask of suitable size. One of the side necks was used for the nitrogen inlet, while the ammonia gas inlet tube was introduced through the central neck and dipped in the solution. The other side neck provided with a calcium guard tube, served as the outlet for gases. Stirring was provided by means of a magnetic stirrer. Ammonia gas used from a cylinder was dried by passing through a column packed
with potassium hydroxide pellets. The ligands thiophanol (Koch-Light), toluene-3,4-dithiol (EDH), ethane-1,2-dithiol (Koch-Light) and thiosalicylic acid (Fluka AG) were of pure quality and used as such without further purification. o-Aminothiophenol (Koch-Light) was purified by distillation under reduced pressure (b.p. 76\(^{\circ}\) at 2 mm.) under nitrogen atmosphere. Skin contact had to be avoided since it caused severe dermatitis.

3.1. Reactions with mercaptans and dimercaptans

3.1.1. Reaction with thiophenol, \(\text{C}_6\text{H}_5\text{SH}\)

Ammonia gas was passed through a stirred solution of bis-\(\pi\)-cyclopentadienyltitanium dichloride (1.866 g., 0.0075 mole) and thiophenol (2.613 g., 0.0237 mole) in 200 ml. benzene for 2.5 hours. A deep magenta coloured solution was obtained along with a white precipitate of ammonium chloride. The solution was filtered and the filtrate was concentrated under reduced pressure at room temperature to about 20 ml. Further concentration was effected by passing a slow stream of nitrogen till appreciable quantity of solid appeared. The solid was collected on a frit, washed with small quantities of benzene followed by hexane and dried under vacuum to give a magenta coloured compound. Yield, 2 g.; m.p. 199\(^{\circ}\)C. Found: C, 67.97; H, 5.46; Ti, 12.12%. Required for \((\text{C}_6\text{H}_5)_2\text{Ti} (\text{SC}_6\text{H}_5)_2\) i.e. \(\text{C}_{22}\text{H}_{20}\text{S}_2\text{Ti}\); C, 66.67; H, 5.05; Ti, 12.12%.
3.1.2. Reaction with ethyl alcohol and of the product thereof with thiophenol

A benzene solution containing bis-\(\pi\)-cyclopentadienyl(ethoxy)titanium(IV) chloride was obtained by reacting 1.88 g. (0.0076 mole) dichloride with 0.84 g. (0.018 mole) ethyl alcohol in presence of 1.04 g. (0.01 mole) triethylamine in benzene, following essentially the procedure described in literature. To this solution, on filtering off the precipitate of triethylamine hydrochloride (1.01 g.) was added 0.97 g. (0.0088 mole) of thiophenol and keeping it stirred, ammonia gas was passed through it. A magenta coloured solution obtained was filtered and concentrated under vacuum to a small volume till appreciable quantity of magenta coloured solid was formed. The solid was collected on a frit, washed with small quantities of benzene and dried under vacuum. Yield, 1.2 g.; m.p. 198-199°C. Found: Ti, 12.67%. The solid was confirmed as the bis-\(\pi\)-cyclopentadienyl-bis(thiophenolato)titanium(IV) from its NMR spectrum.

3.1.3. Reaction with toluene-3,4-dithiol, \(\text{HSC}_6\text{H}_3(\text{CH}_3)\text{SH}\)

A deep green coloured solution was obtained when ammonia gas was passed through a stirred solution of the dichloride (1.25 g., 0.005 mole) and toluene-3,4-dithiol(0.927 g., 0.0059 mole) in 125 ml. chloroform. The reaction was slightly exothermic and ammonia passing was discontinued a few minutes after the solution had reattained the room temperature. The green solution
was centrifuged to remove the precipitated ammonium chloride, put under vacuum at room temperature for some time to remove excess ammonia, filtered and evaporated to dryness under reduced pressure at room temperature. The deep green solid obtained was thrice washed with hexane to remove excess of the ligand and dried under vacuum. Yield, 1.61 g.; m. p. 168-60°.

Found: C, 61.75; H, 5.17; Ti, 13.98%. Required for (C₅H₅)₂Ti(S₂C₇H₅) i.e. C₁₇H₁₆S₂Ti : C, 61.45; H, 4.82; Ti, 14.45%.

**3.1.4. Reaction with ethane-1,2-dithiol**

The dichloride (1.9 g., 0.0076 mole) and the ligand (1.55 g., 0.0165 mole) were taken in 175 ml. chloroform and dry ammonia gas was passed through the stirred solution. The reaction was exothermic and there was change in the colour of the solution. The passage of ammonia was discontinued some minutes after the solution had reattained the room temperature. The deep violet coloured solution obtained was separated from the precipitated ammonium chloride and concentrated, by distilling off the solvent under nitrogen at ordinary pressure, till some solid appeared. After allowing to stand overnight at 10°C, the dark violet coloured solid was collected on a frit, washed with small quantities of cooled chloroform followed by dry tetrahydrofuran and dried under vacuum. Yield, 0.525 g. Found: C, 53.27; H, 5.48; S, 23.60; Ti, 17.56%. Required for (C₅H₅)₂Ti(SCH₂CH₂S) i.e.
The compound is insoluble in benzene as well as in ether and very slightly soluble in tetrahydrofuran. It is stable in air and starts decomposing without melting at 140°C.

3.2. Reactions with mercaptocarboxylic acids

3.2.1. Reaction with thiosalicylic acid, \( \text{HSC}_6\text{H}_4\text{COOH} \)

On passing ammonia gas through a stirred solution of the dichloride (1.72 g., 0.0068 mole) and thiosalicylic acid (1.12 g., 0.0072 mole) in 175 ml. benzene, the colour of the red solution immediately turned to green along with the precipitation of ammonium chloride. The reaction was exothermic and ammonia passing was discontinued some minutes after the solution had reattained the room temperature. On separating the precipitated ammonium chloride by centrifugation, the deep green solution obtained was evaporated to dryness under reduced pressure at room temperature. The deep green solid obtained was redissolved in benzene, the solution was filtered and concentrated, by distilling off the solvent under nitrogen at ordinary pressure, till appreciable quantity of solid crystallized out. On cooling and allowing to stand overnight, the recrystallized deep green solid was collected on a frit, washed with small quantities of benzene and dried under vacuum. Yield, 0.845 g. Found: C, 61.94; H, 5.21; S, 10.30; Ti, 15.06%. Required for \( (\text{C}_6\text{H}_5)\text{Ti(SC}_6\text{H}_4\text{COO}) \) i.e. \( \text{C}_{17}\text{H}_{14}\text{O}_2\text{STi} \): C, 61.81; H, 4.24; S, 9.69; Ti, 14.55%.
The compound is soluble in chloroform, to a less extent in tetrahydrofuran and slightly soluble in ether. It starts decomposing in air without melting at about 145°C.

3.3. Reactions with mercaptamines

3.3.1. Reaction with o-aminothiophenol, \( \text{H}_2\text{NC}_6\text{H}_4\text{SH} \)

Treatment of a solution of the dichloride (2.017 g., 0.0081 mole) and o-aminothiophenol (2.215 g., 0.0177 mole) in 200 ml. chloroform, kept stirring, with gaseous ammonia for 1.5 hr., resulted in giving a magenta coloured solution and ammonium chloride precipitate. After allowing to stand overnight, the ammonium chloride was separated by centrifugation and filtration. The filtrate was concentrated to two-third of its volume under reduced pressure at room temperature, filtered again and further concentrated to a small volume. When 50 ml. of hexane (B.R. 63-65°C) was added to the concentrate a dark magenta coloured thick liquid separated out from the pale magenta coloured hexane solution. The hexane solution was decanted off and the thick liquid was retreated with hexane repeatedly (6 x 15 ml.). The thick liquid solidified when put under reduced pressure at room temperature for several hours. Yield, 3 g., m.p. 93-95°C. Found: C, 60.73; H, 5.33; S, 17.00; N, 7.07; Ti, 8.66%. Required for \((\text{C}_6\text{H}_5)_2\text{Ti(ScH}_4\text{NH).2HNC}_6\text{H}_4\text{SH}\) i.e. \(\text{C}_{28}\text{H}_{29}\text{S}_3\text{N}_3\text{Ti}\) : C, 60.96; H,5.26; S,17.43; N,7.62; Ti,8.71%. Molecular weight determined ebulliometrically in benzene was found to be 536.
4. **Reactions of bis-$\Pi$-cyclopentadienyl-titanium(IV) dichloride with sulphur-containing ligands in presence of divalent metals**

The ligands were of pure quality and used as such.

The metals used were of analytical reagent grade.

4.1. **Reactions in presence of zinc**

4.1.1. **Reaction with thiosalicylic acid, $\text{HSC}_{6}\text{H}_{4}\text{COOH}$**

To a solution of 1.246 g. (0.005 mole) of the dichloride and 1.699 g. (0.011 mole) of thiosalicylic acid in 75 ml. of pure dry acetone, 0.67 g. (0.01 mole) of zinc metal powder was added and the solution was heated under reflux for three hours. The original red colour of the solution turned to deep green. On filtering the solution from excess of zinc and evaporating it to dryness under vacuum at room temperature, a deep green solid was obtained. This solid was treated for half an hour with 60 ml. of pure dry ether (in which it was slightly soluble) under reflux. The ether solution, on cooling, was filtered off and the process was repeated three times. The solid was further washed with ether (3 x 20 ml.), dried under vacuum at room temperature and recrystallized from acetone-benzene solution. For recrystallisation, the solid (1.7 g.) was dissolved in 220 ml. of acetone-benzene (1:4) mixture and the solution, on filtering to remove the insoluble, was concentrated to about 20 ml. by distilling off the solvent at ordinary pressure. After allowing
to stand overnight at 15°C, the deep green solid that had crystallized out was collected on a frit, washed with small quantities of acetone-benzene mixture and dried under vacuum at room temperature. Yield, 0.9 g.; m. p. 128-130°C. Found: C, 45.55; H, 4.10; S, 6.37; Cl, 13.80; Ti, 8.44; Zn, 11.79%. Required for C_{20}H_{20}O_{3}SCl_{2}TiZn: C, 45.81; H, 3.82; S, 6.11; Cl, 13.55; Ti, 9.16; Zn, 12.40%. The solubility of the compound in benzene and other non-polar solvents was very low.

In another experiment, 1.336 g. (0.0053 mole) of the dichloride, 1.323 g. (0.0118 mole) of thiosalicylic acid and 0.80 g. (0.012 mole) zinc metal powder were taken in 60 ml. of pure dry tetrahydrofuran and the solution was heated under reflux for six hours. A deep green solid obtained on filtering the solution and evaporating off the solvent under vacuum at room temperature, could not be recrystallized. It was purified by treating with ether as in the previous experiment, redissolving in tetrahydrofuran and evaporating the solution to dryness; the process having been repeated once again. Yield, 1.63 g.; Found: C, 45.47; H, 4.61; S, 7.49; Cl, 12.68; Ti, 8.32; Zn, 11.74%. Required for C_{21}H_{22}O_{3}SCl_{2}TiZn: C, 46.84; H, 4.09; S, 5.95; Cl, 13.20; Ti, 8.92; Zn, 12.08%.

The above experiment was repeated using acetonitrile instead of tetrahydrofuran. However, the elemental analysis of the deep green solid isolated did not conform to any definite composition.
4.1.2. Reaction with toluene-3,4-dithiol
\[ \text{HSC}_6\text{H}_3(\text{CH}_3)\text{SH} \]

To a solution of 1.25 g. (0.005 mole) of the dichloride and 1.58 g. (0.01 mole) of toluene-3,4-dithiol in 70 ml. acetone, 0.68 g. (0.01 mole) of zinc metal powder was added and the solution was refluxed for four hours. A deep green solution obtained was, on cooling, filtered from excess zinc and evaporated to dryness in vacuo at room temperature. The deep green solid obtained was washed with ether several times (7 x 15 ml.) and dried. Attempts to recrystallize the solid did not succeed. The compound was dissolved in acetone and, on filtration, the solution was evaporated to dryness under vacuum at room temperature, this process having been repeated once again. The solid was well-dried under vacuum at room temperature. Yield, 2.05 g.; Found: C, 44.70; H, 4.63; S, 13.28; Cl, 12.50; Ti, 8.33; Zn, 12.87%. Required for \( \text{C}_{20}\text{H}_{22}\text{S}_2\text{OCl}_2\text{TiZn} \): C, 45.62; H, 4.12; S, 12.17; Cl, 13.50; Ti, 9.12; Zn, 12.33%.

In the above compounds, zinc was estimated from the quantity of ZnO determined by subtracting the quantity of TiO\(_2\) (determined by cupferron precipitation etc.) from the total metal oxides obtained on ignition of a known quantity of the substance.

4.1.3. Reaction with ethane-1,2-dithiol, \( \text{HSC}_2\text{CH}_2\text{SH} \)

To a solution of 1.25 g. (0.005 mole) of the dichloride and 1.09 g. (0.012 mole) of ethane-1,2-dithiol in
75 ml. acetone, 0.69 g. (0.011 mole) zinc metal powder was added and the solution was heated under reflux for six hours. The red coloured solution, on cooling, was filtered from the zinc metal and concentrated under vacuum at room temperature, till a good quantity of red coloured solid crystallized out. The solid was collected on a frit, washed with small quantities of acetone and dried under vacuum at room temperature. Yield, 1.1 g. Found: Ti, 18.82; Cl, 27.91%. No sulphur and zinc were detected in the solid which was identified as \((\text{C}_6\text{H}_4)_2\text{TiCl}_2\) from the infrared spectrum and the melting point.

4.2. Reactions in presence of magnesium

4.2.1. Reaction with thiosalicylic acid

A solution obtained by dissolving 1.62 g. (0.0065 mole) dichloride and 2.29 g. (0.015 mole) thiosalicylic acid in 100 ml. acetone and to which 0.4 g. (0.016 mole) magnesium metal powder was added, was heated under reflux for sixteen hours. A deep green coloured solution obtained was, on cooling and filtering, evaporated to dryness under vacuum at room temperature. The deep green coloured solid was repeatedly treated with ether (6 x 25 ml.) in which it was slightly soluble. On drying, it was dissolved in 80 ml. of xylene-acetone (1:5) solvent mixture and the filtered solution was concentrated by distilling off the solvent (max. b.p. 50°C) at ordinary pressure till appreciable quantity of solid had crystallized out. After allowing to stand
overnight at room temperature, the mother liquor was filtered off and the solid was washed with small quantities of xylene followed by hexane. The deep green solid was dried under vacuum at room temperature. Yield: 0.9 g.; Found: C, 59.67; H, 4.77; S, 10.85; Ti, 9.93; Mg, 2.15%. Required for C_{44}H_{38}O_{7.3}Ti_{2}Mg: C, 59.06; H, 4.25; S, 10.74; Ti, 10.74; Mg, 2.68%.

Magnesium in the compound was determined as follows: The filtrate and washings obtained after separation of titanium by precipitation with cupferron, were mixed and the solution was evaporated to a small volume. After destroying the organic matter (cupferron) by treating with nitric acid, the solution was neutralized with sodium hydroxide solution and titrated with standard EDTA solution following the usual procedure.

4.2.2. Reaction with toluene-3,4-dithiol

To a solution obtained by dissolving 1.5 g. (0.006 mole) dichloride and 1.016 g. (0.0065 mole) toluene-3,4-dithiol in 100 ml. acetone, was added 0.4 g. (0.016 mole) magnesium metal powder. The solution was heated under reflux for sixteen hours. A deep green solution obtained was filtered and evaporated to dryness under vacuum at room temperature. The solid obtained, which was somewhat sticky in nature, was dissolved in 100 ml. of acetone-hexane (1:2) solvent mixture and the filtered solution was concentrated to almost one-third of its original volume by
distilling off the solvent at ordinary pressure. The solid that had crystallized out was collected on a frit, washed with little quantities of acetone-hexane mixture followed by hexane and dried under vacuum at room temperature. Yield, 1.22 g.; m. p. 144-146°. Found: C, 60.02; H, 5.30; S, 16.44; Cl, 3.49; Ti, 14.94%. Required for \((C_5H_5)_2Ti(S_2C_6H_3CH_2) + 0.2[(C_5H_5)_2TiCl_2]\): C, 59.68; H, 4.72; S, 16.75; Cl, 3.72; Ti, 15.08. A mixture prepared artificially by mixing well bis-\(\pi\)-cyclopentadienyl (toluene-3,4-dithiolato)titanium(IV) and bis-\(\pi\)-cyclopentadienyl-titanium dichloride in respective molar ratio of 5:1, also melted at 144-146°.

In another experiment, the quantities of the reactants and solvent were: dichloride, 1.22 g. (0.0049 mole); toluene-3,4-dithiol, 1.54 g. (0.0099 mole); magnesium powder, 0.39 g. (0.016 mole); acetone, 100 ml. Rest of the conditions of reaction and isolation of the product were the same as described above. A deep green solid obtained (yield, 1.3 g., m. p. 159°C; Ti, 14.01%) was identified as the pure bis-\(\pi\)-cyclopentadienyl(toluene-3,4-dithiolato)titanium(IV) from its NMR spectrum in deuterochloroform.

4.3. Reactions in presence of tin

4.3.1. Reaction with thiosalicylic acid

A red coloured solution obtained by dissolving 1.42 g. (0.0057 mole) dichloride and 2.1 g. (0.0136 mole) thiosalicylic acid in 100 ml. acetone and to which was added 1.43 g. (0.012 mole)
tin metal granules, was heated under reflux for 57 hours during which period it gradually turned to deep green. The solution was filtered and evaporated to dryness under vacuum at room temperature. It was noticed that the green colour of the solution was not stable and gradually changed to brown red during the process of evaporation. A brown red solid obtained was stirred for half an hour with 25 ml. of ether in which it was slightly soluble and filtering off the ether solution, the ether treatment process was repeated several times (10 x 20 ml.). The ether-washed solid, on drying, was redissolved in 80 ml. acetone and the filtered solution was re-evaporated to dryness under vacuum at room temperature. Again treating the solid so obtained with ether (6 x 10 ml.) it was redissolved in 50 ml. acetone and the filtered solution was again evaporated to dryness as above, to yield, on powdering, an orange coloured solid. Yield, 1.02 g.; Found: C, 40.28; H, 3.69; S, 7.57; Cl, 9.72; Ti, 11.31; Sn, 14.43%. Required for \( C_{27}H_{24}S_2O_6Cl_2Ti_2Sn \): C, 40.81; H, 3.02; S, 8.06; Cl, 8.95; Ti, 12.09; Sn, 14.98%.

For determining the tin and titanium contents, the compound was decomposed by fuming with conc. sulphuric and nitric acids and the metals were brought into a 10% (v/v) sulphuric acid solution. Treating the solution with hydrogen sulphide, tin was precipitated as stannic sulphide which was ignited to oxide. Titanium contained by the filtrate (plus washings) thereof was precipitated with supferron and ignited to oxide as usual.
4.3.2. Reaction with toluene-3,4-dithiol

A solution of 1.52 g. (0.0061 mole) dichloride and 1.03 g. (0.0066 mole) toluene-3,4-dithiol in 100 ml. of acetone to which was added 1.58 g. (0.013 mole) tin granules, was heated under reflux for 18 hours during which period it turned to dark green colour. However, the green colour of the solution was unstable and reverted to the red colour during filtration even though the filtration was carried out under nitrogen atmosphere as usual. The solution on concentration to a very small volume gave a red crystalline solid (1.42 g.) which was identified from the elemental analysis and infrared spectrum as the bis-Π-cyclopentadienyltitanium dichloride.

5. Reactions of bis-Π-cyclopentadienyltitanium dichloride with monofunctional bidentate ligands

Experiments involving the reactions of the dichloride with 8-quinolinol, acetoacetanilide and dibenzoylmethane, in which pure compounds were isolated, have only been described. The ligands which were prepared by the fine chemicals section of this laboratory, were of pure quality as checked by melting points and elemental analysis.

5.1. Reaction with 8-quinolinol, C₉H₇ON

To a solution of 1.425 g. (0.0098 mole) of 8-quinolinol in 80 ml. of benzene, 1.13 g. (0.00454 mole) of the dichloride was added and the mixture heated under reflux when a clear red coloured
solution was obtained. Heating under reflux was continued for 150 hours till evolution of HCl ceased. On cooling overnight and filtering, a red coloured filtrate and dark brown residue were obtained. The brown residue was treated thrice at the reflux temperature with benzene (40 ml. each time) and the benzene extracts mixed with the filtrate. On concentrating the solution (1/3 volume) by distilling off the solvent under reduced pressure and standing overnight, a red coloured solid was obtained. This was collected on a frit, washed several times with small quantities of benzene and finally with petroleum ether (BR 63-65°C), and dried under vacuum. Yield, 37% on the basis of dichloride taken. Found: C, 62.61; H, 3.93; N, 6.63; Ti, 11.75; Cl, 8.50%. Required for \((\text{C}_6\text{H}_5)\text{Ti(C}_6\text{H}_5\text{ON})_2\text{Cl}\) i.e. \(\text{C}_{23}\text{H}_{17}\text{O}_2\text{N}_2\text{ClTi} \): C, 63.23; H, 3.89; N, 6.41; Ti, 11.02; Cl, 8.13%.

The compound was moderately soluble in benzene and chloroform.

5.2. Reaction with acetoacetanilide, \(\text{CH}_3\text{COCH}_2\text{CONHC}_6\text{H}_5\)

To a solution of 1.86 g. (0.0105 mole) acetoacetanilide in 80 ml. benzene, 1.312 g. (0.0053 mole) of the dichloride was added and the mixture was heated under reflux. A clear solution was obtained after sometime and heating under reflux was continued for nearly 300 hours till evolution of HCl ceased. A red coloured substance was found to have been deposited on the sides of the reaction flask. On cooling and filtering, a red coloured solid
and a red coloured filtrate were obtained. The filtrate was concentrated and the crystals obtained on cooling were found to be unreacted dichloride. The solid was heated with 60 ml. of benzene to the reflux temperature for 3 hours, filtered when cooled, washed several times with small quantities of benzene and finally with petroleum ether (BR 63-65°C) and dried under vacuum. Yield, 20% on the basis of dichloride taken; m. p. 239-40°C with decomposition. Found: C, 61.56; H, 4.88; N, 4.06; Ti, 12.77; Cl, 9.71%. Required for \((\text{C}_6\text{H}_5)_2\text{Ti}(\text{C}_{10}\text{H}_{10}\text{O}_2\text{N})\text{Cl}\) i.e. \(\text{C}_{20}\text{H}_{20}\text{O}_2\text{NClTi}\): C, 61.61; H, 5.13; N, 3.59; Ti, 12.32; Cl, 9.11%.

The compound was very slightly soluble in benzene and insoluble in chloroform.

5.3. Reaction with dibenzoylmethane, \(\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5\)

To a solution of 2.675 g. (0.012 mole) dibenzoylmethane in 80 ml. benzene, 1.49 g. (0.006 mole) of the dichloride was added and the mixture was heated under reflux to give a clear solution. Heating under reflux was continued for about 380 hours, till HCl evolution ceased. The red solution turned dark brown in colour and a deep orange coloured solid was deposited on the sides of the reaction flask. The solid was collected on a frit, washed several times with small quantities of benzene followed by petroleum ether (BR 63-65°C) and dried under vacuum. Yield, 22% on the basis of dichloride taken. Found: C, 68.61; H, 4.47;
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Ti, 10.35; Cl, 7.57%. Required for \((C_5H_5)_2Ti(C_{15}H_{11}O_2)Cl\) i.e. \(C_{25}H_{21}O_2ClTi\): C, 68.72; H, 4.81; Ti, 10.99; Cl, 8.12%. The compound was very slightly soluble in benzene and chloroform. The filtrate on concentration gave red crystals which were identified as unreacted bis-cyclopentadienyltitanium dichloride.

6. Reactions of bis-\(\pi\)-cyclopentadienyltitanium dichloride with thallium(I) derivatives of acetylacetone and benzoylacetonone

6.1. Syntheses of thallium derivatives

The thallium(I) derivatives of acetylacetone and benzoylacetonone were prepared in the laboratory as described below, following with some modifications, the methods reported in literature\(^\text{153}\).

6.1.1. Synthesis of thallous acetylacetonate

To a solution of 8 g. thallous nitrate in 7 ml. water, 7.8 g. sodium hydroxide was added. The mixture was stirred well and on cooling to room temperature, the yellow thallous hydroxide formed was collected on a frit, washed with small quantities of benzene and dried by sucking dry nitrogen gas through it. The thallous hydroxide was then transferred to a flask through which nitrogen gas was being passed. About 8 ml. of ethyl alcohol was added and the mixture was stirred well till all the yellow solid disappeared. The thallous ethoxide formed was selectively extracted with benzene repeatedly (4 x 10 ml.). The extract was
filtered under nitrogen and was treated with a solution of
3.2 g. acetylacetone in 20 ml. benzene. A white crystalline
solid precipitated out immediately on mixing the solutions.
The solid was collected on a frit, washed with small quantities
of benzene and dried under vacuum. Yield, 3.5 g.; m. p. 153-154°C
which was identical to that reported in literature. The mother
liquor on concentration under vacuum at room temperature gave
a further crop of crystals.

6.1.2. Synthesis of thallous benzoylacetonate

To a solution of 5.3 g. of thallous nitrate in
5 ml. water, 5.26 g. of sodium hydroxide was added. After
stirring the mixture well and on cooling to room temperature,
the yellow thallous hydroxide was collected on a frit, washed
with benzene and rendered dry by sucking dry nitrogen through
it. The hydroxide was then treated with 5 ml. ethyl alcohol and
the ethoxide formed was extracted with benzene, as in the above.
To the filtered benzene extract was then added a solution of
3.25 g. benzoylacetonate in 20 ml. benzene. After mixing well,
the solution was evaporated to dryness under vacuum at room
temperature. The crude product obtained was recrystallized as
follows: It was dissolved in 25 ml. benzene and to the filtered
solution 25 ml. heptane was added. Scratching the sides of the
flask was necessary to induce crystallization. After allowing to stand
for two hours, the crystals were collected on a frit, washed with
benzene-heptane (1:1.5) mixture followed by hexane and dried under vacuum at room temperature. Yield, 4.85 g.; m. p. 101-102°C which agreed with the literature value.

6.2. Reactions of the dichloride with the thallium derivatives

6.2.1. Reaction with thallous acetylacetonate

On adding a solution of 3.11 g. (0.01 mole) of thallous acetylacetonate in 50 ml. benzene to a solution of 1.27 g. (0.005 mole) dichloride in 130 ml. benzene and stirring well the mixture for four hours, a dark brown coloured solution and a white precipitate were obtained. The solution and the precipitate were separated by centrifugation and filtration. The white precipitate was washed with benzene and dried at 110°C. It was identified as the thallous chloride (Tl, 84.67; Cl, 13.93%) and weighed 2.41 g. (0.01 mole). The solution was evaporated to dryness under vacuum at room temperature. A dark brown solid obtained, free of chloride, was found to be impure as was indicated by the elemental analysis. Attempts to purify it were not successful due to its very high solubility in various organic solvents.

In another experiment, a solution of 1.876 g. (0.0062 mole) thallium acetylacetonate in 50 ml. tetrahydrofuran was mixed with a solution of 1.51 g. (0.0061 mole) dichloride in 125 ml. tetrahydrofuran and the mixture was stirred for four hours. A white precipitate formed and collected as in the above
experiment, which was identified as the thallous chloride, weighed 1.46 g. (0.0061 mole). The brown red solution obtained was concentrated to about one-fourth its original volume and adding to it 25 ml. benzene, the solution was again concentrated to a small volume when some red solid crystallized out. This red solid (0.31 g.) was identified as the bis-\( \pi \)-cyclopenta-dienyltitanium dichloride.

6.2.2. Reaction with thallous benzoylacetonate

A solution of 4.14 g. (0.0113 mole) thallous benzoylacetonate in 75 ml. benzene was added to a solution of 1.25 g. (0.006 mole) dichloride in 150 ml. benzene and the mixture was stirred well for five hours. A white precipitate and a dark brown coloured solution were obtained. The white precipitate was separated from the solution by centrifugation and filtration, washed thoroughly with benzene and dried at 110°C. It was identified as the thallous chloride (Tl, 84.51; Cl, 14.06%) and weighed 2.40 g. (0.01 mole). The solution was evaporated to dryness under vacuum. The brown solid obtained, however, could not be purified due to its high solubility in various organic solvents.

In another experiment, a solution of 1.89 g. (0.0052 mole) thallous benzoylacetonate in 50 ml. tetrahydrofuran was added to a solution of 1.245 g. (0.005 mole) dichloride in 125
ml. tetrahydrofuran. After stirring the mixture for five hours, the white precipitate of thallous chloride formed was separated and dried as in the above experiment. It weighed 1.23 g. (0.0051 mole). The solution was evaporated to dryness under vacuum to a red solid. The benzene solution of the red solid on concentration yielded crystals of \((\text{C}_6\text{H}_5)_2\text{TiCl}_2\).

7. Syntheses of some titanoxane polymers containing cyclopentadienyl and chelate groups

7.1. Reaction between bis-\(\pi\)-cyclopentadienylltitanium(IV) perchlorate, \((\pi-\text{C}_5\text{H}_5)_2\text{Ti(ClO}_4)_2\), and 8-quinolinol

A solution of 2.45 g. (0.012 mole) silver perchlorate in 25 ml. water was added to a suspension of 1.332 g. (0.0064 mole) dichloride in 50 ml. (dist.) water. The mixture was stirred well and filtered to give an aqueous solution containing bis-\(\pi\)-cyclopentadienyltitanium(IV) perchlorate. To this solution, which was kept stirring by a magnetic stirrer, was added a solution of 1.55 g. (0.011 mole) 8-quinolinol in 20 ml. tetrahydrofuran. An orange yellow precipitate immediately separated out. The mixture was kept stirring for 15 hours after which the solid was collected on a frit, washed with tetrahydrofuran, then with ice cold water and finally with ether before drying under vacuum at room temperature. Yield, 1.36 g. Found: C, 53.52; H, 3.47; N, 4.81; Cl, 1.58; Ti, 15.18%. Required for
The compound was found insoluble in any of the organic solvents.

7.2. Reaction between bis-T-cyclopentadienyl-titanium(IV) perchlorate and acetoacetanilide

To a solution of bis-T-cyclopentadienyltitanium perchlorate obtained by treating a suspension of 1.51 g. (0.0061 mole) dichloride in 75 ml. water with a solution of 2.72 g. (0.014 mole) silver perchlorate in 25 ml. water, was added a solution of 2.16 g. (0.0122 mole) acetoacetanilide in 10 ml. tetrahydrofuran. A red thick liquid and an yellow precipitate were formed. The yellow precipitate disappeared after stirring the mixture for considerable time. On allowing to stand for three days the red thick liquid solidified. It was collected on a frit, washed with tetrahydrofuran, then with cold water and finally with ether. On drying under vacuum at room temperature an orange coloured substance was obtained. Yield, 1.26 g. Found: C, 44.98; H, 4.03; N, 4.05; Cl, 3.19; Ti, 15.30%. Required for

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\begin{align*}
\text{C}_5\text{H}_5 \quad \text{ClO}_4 \quad \text{C}_5\text{H}_5
\end{align*}
\]

C, 44.73; H, 3.73; N, 4.91; Cl, 3.12; Ti, 16.83%.