CHAPTER III

EXPERIMENTALS

หอสมุดกลาง จุฬาลงกรณมหาวิทยาลัย

3.1 Materials

Chemicals and solvents used are of reagent and analar grades. No further purification of these compounds were made unless otherwise stated.

3.1.1 Thallium (I) chloride. This compound is the laboratory reagent grade of the British Drugs House Chemicals Ltd., England. It was used as a starting material for the preparation of thallium (III) chloride.

3.1.2 Acetonitrile. The Baker analar reagent grade acetonitrile was kept over activated molecular sieves for 48 hours, and then distilled over anhydrous calcium chloride. The fraction distilled off at 80°C was collected and kept over molecular sieves before use.

3.1.3 Pyridine. The Mallinkrodt analar reagent grade pyridine was distilled from aluminium (III) chloride. The distillate was then refluxed over aluminium oxide and finally fractionated off. Pyridine obtained in this manner had specific conductivity in the

range of 3.8×10^{-8} ohm^{-1} cm^{-1} at $25^{o}C$.

3.1.4 Conductivity water. The conductivty water was obtained by passing the double distilled water to the ion exchange resin to give a final specific conductance about 0.75×10^{-6} $ohm^{-1}cm^{-1}$ at $25^{o}C$.

3.2 Preparations of the Compounds.

3.2.1 Diphenylthallium bromide.[1] This compound was obtained via a reaction taking place between thallium (III) chloride and the Grignard reagent at low temperature according to the reaction,

$$4\ C_6H_5MgBr + 2\ TlCl_3 \longrightarrow 2\ (C_6H_5)_2TlBr + MgBr_2 + 3\ MgCl_2.$$

In the actual preparation, 50 cm^3 of solution containing 10.3 g (0.003 mole) of thallium(III) chloride in dry ether, was slowly added to phenylmagnesium bromide. (Appendix I) The mixture was cooled in ice during the addition of thallium(III) chloride and was then heated on a water bath for 30 minutes, cooled and decomposed with water. The residue was filtered off, dried and extracted with pyridine. After several crystallization in pyridine, the pure white needle crystal which was characterized later as the pyridine complex, $Ph_2Tl(py)_2Br$, was obtained. The subsequent air drying of the mentioned complex in the oven at $110^{o}C$ was found to yield the desirable compound namely, Ph_2TlBr, accompanied by the evolving of pyridine. This compound does not melt but decomposes above $300^{o}C$. The final yield was 7.57 g (52 %)

3.2.2 Phenylmercury bromide.[43] Mercury(II) bromide (18 g, 0.05 mole) was added in a small portion and with vigorous shaking to

7.2 g (0.04 mole) of phenylmagnesium bromide in 100 cm^3 of ether and the mixture was refluxed for 4 hours. The phenylmagnesium bromide was then decanted and the residue boiled three times with 1 % HBr to remove the unreacted mercury(II) bromide. It is then thoroughly washed with hot water, ethanol and ether, and dried at 110°C. The yield of the crude product is 15.1 g (56 %). After recrystallization from pyridine the pure compound was obtained as a white, flake crystal with melting point of 275°C.

3.2.3 Diphenylthallium(pyridine)$_2$ bromide. The $Ph_2Tl(py)_2Br$ complex was obtained during the step of recrystallization of Ph_2TlBr compound from the pyridine solution as described in 3.2.1

3.2.4 Phenylmercury(pyridine)$_2$ bromide. This complex was prepared in the same maner as the preparation of $Ph_2Tl(py)_2Br$ complex.

3.2.5 Diphenylthallium(1,10-phenanthroline) bromide.[44] 0.44 g (0.001 mole) of diphenylthallium bromide and 0.06 g (0.003 mole) of 1,10-phenanthroline were dissolved in 75 cm^3 of dioxane. The mixture was boiled for 5 minutes and was filtered off. The filtrate was left standing at room temperature to evaporate the solvent until the white crystal was obtained. The product was washed several times with ethanol and ether. The product yields 0.9 g (30 %) and melts with decomposition at 25°C.

3.2.6 Phenylmercury (1,10-phenanthroline) bromide. 0.36 g (0.001 mole) of phenylmercury bromide and 0.40 g (0.002 mole) of

1,10-phenanthroline were mixed in 25 cm^3 dioxane and the subsequent reactions were carried out in the same manner as has been described in 3.2.5. 1.68 g (66 %) of white crystal product was obtained. It melts with decomposition at 165°C.

The results of the elemental analysis of the compounds mentioned above were shown together with the calculated values in Table 3.1

Table 3.1

The elemental analysis of the synthetic compounds

Compound	% Carbon		% Hydrogen	
	found	cal.	found	cal.
Ph_2TlBr	32.79	32.85	2.35	3.30
PhHgBr	20.56	20.13	1.83	1.40
$Ph_2Tl(phen)Br$	59.55	46.58	3.19	2.91
PhHg(phen)Br	38.29	40.19	1.91	2.44

3.3 Apparatus and Procedures

3.3.1 Conductivity measurement. The conductivity cell in conjunction with the A.C. conductivity bridge, oscillator and detector, manufactured by Beckmann Instruments, Inc., Type RC. 18A were used throuhgout this research.

The experiments were carried out in a thermostat bath whose temperature was maintained at 25±0.01°C by means of a Beckmann contact thermometer. The cell was thoroughly cleaned with dilute

cleaning solution, followed by rinsing with conductivity water, and finally with acetone and dried before use. In each measurement the thermal equilibrium between the cell solution and the bath temperature was attained before any conductivity measurement was performed. The cell constant of each cell used in this work was determined[45] with 0.001 D aqueous solution of potassium chloride. The cell constant value of 0.0765623 cm^{-1} was obtained.

3.3.2 Intrared spectrophotometer. All of the spectra were recorded in the region 4000-600 cm^{-1} on a Unicam SP 200 G grating Infrared Spectrophotometer. The solid sample was prepared as the potassium bromide pellet and the nujol mull. The solution spectra were recorded in the 0.1 mm. solution cell.

3.3.3 Spectrophotometric determination of stability constants and the formulae of the complexes. In this experiment the formula of the complex ion formed between organometallic ions and amine ligands were determined by using spectrophotometric measurement. The method employed is one that is widely used in cases where only a single complex is formed between the reacting species. Consider the case where a cation M^{2+} reacts with a ligand, X to form a complex $[MX_n]^{2+}$

$$M^{2+} + nX \rightleftharpoons [MX_n]^{2+}$$

In order to determine the formula of the complexes, n, the number of ligand bound to a metal ions, must be known. The mole-ratio method[46] is usually employed in the evaluation of n. In this method a series of solutions in which the concentration of one reactant, the ligand, is arbitrarily kept constant and that of the organo-metallic compound is varied. In this technique the absorbance increases to maximal value at a mole ratio of the complex formed and then levels off. Usually an abrupt change in the slope of the graph does not occur. Instead it exhibits a curvature just before the plateau starts and the straight line portions can be extrapolated until they intersect. Typical mole-ratio plots are shown in Figure 3.1

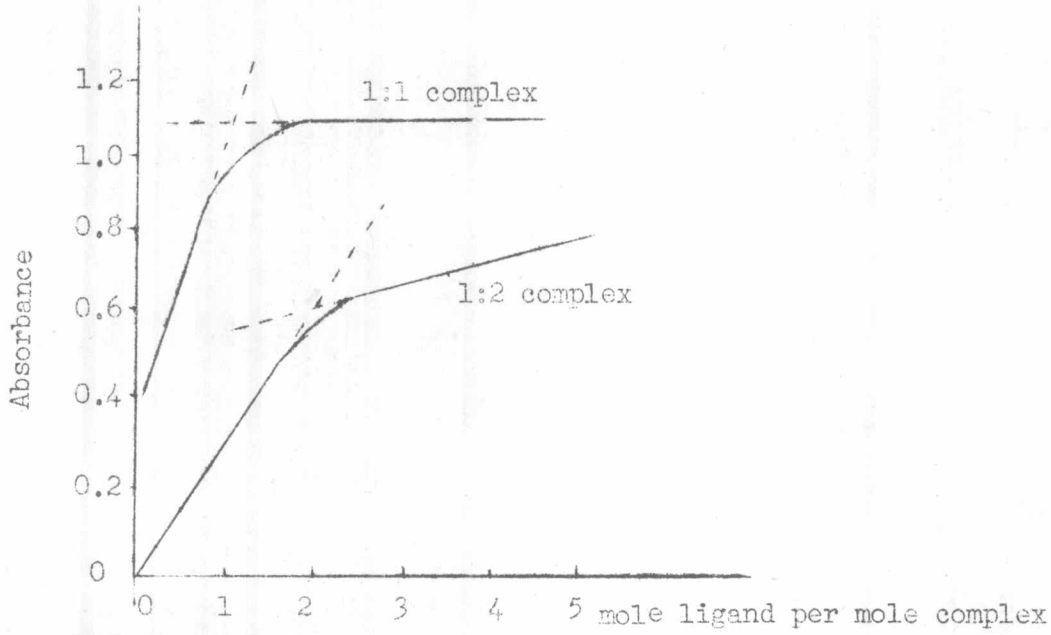

Figure 3.1 Mole-ratio plots for a 1:1 complex and a 1:2 complex.

In this work, stock solutions of 6×10^{-4} mol l^{-1} 1,10-phenanthroline and 3×10^{-4} mol l^{-1} orgnometallic compound were prepared in dioxane solvent. The testing solutions from the above stock solutions were prepared at various proportions as shown below.

Table 3.2

A series of solution made for the absorption measurements

Solution no.	cm^3 of Organo-metallic compound	cm^3 of 1,10-phen	cm^3 of Dioxane
1	5.0		15.0
2	7.5		12.5
3	10.0	5.0	10.0
4	12.5		7.5
5	15.5		5.0
6	17.5		2.5
7	20.0		0.0

The solutions obtained were made up to the final volume of 25 cm^3 in a volumetric flask and the absorbance of each solution was recorded in the wavelength range of 180-330 nm. Dioxane was used in the reference cell. The absorbance was recorded with a Varian-Techtron ultraviolet-visible spectrophotometer, model 635 with match cells of 10 mm path length.

3.3.4 Nuclear Magnetic Resonance

The spectra were recorded on a Varian Techtron spectrometer model 60 A operating at 60 MHz at 27°C. The compounds were mainly dissolved in deuterated dimethyl sulfoxide, the concentrations of the organometallic compounds in this solvent varied from 1-5 % by weight.

3.3.5 Differential Thermal Analysis (DTA)

DTA is the technique of measuring the heat effects associated with physical or chemical changes that take place as a substance is heated at a uniform rate. Heat changes, either exothermic or endothermic, are caused by the phase transition such as fusion, crystal structure inversion, boiling, sublimation, vaporization, dehydration, decomposition, oxidation and reduction, destruction of crystalline lattice; chemical reaction. Generally speaking, vaporization, dehydration, fusion, inversion, sublimation, boiling, decomposition, dehydration and reduction reactions produce endothermic heat effects, whereas crystallization and oxidation reactions produce exothermic effects. The heat effects occuring during these chemical and physical changes are measured by a "differential" method. A furnace used in this analysis contains a sample holder with two symmetrically located and identical chambers, each of which carries an identical thermocouple. The sample to be investigated is placed in one chamber and a thermally inert substance such as α - alumina is placed in the other. The sample and the alumina are then heated at a uniform rate and the temperature difference between them, as detected by the

two thermocouples, is recorded as a function of time or of the furnace temperature. If the chemical or physical change causes the sample thermocouple to be cooler than the reference thermocouple, a peak in the downward direction will be obtained and vice versa. The typical endothermic and exothermic peaks are illustrated in Figure 3.2

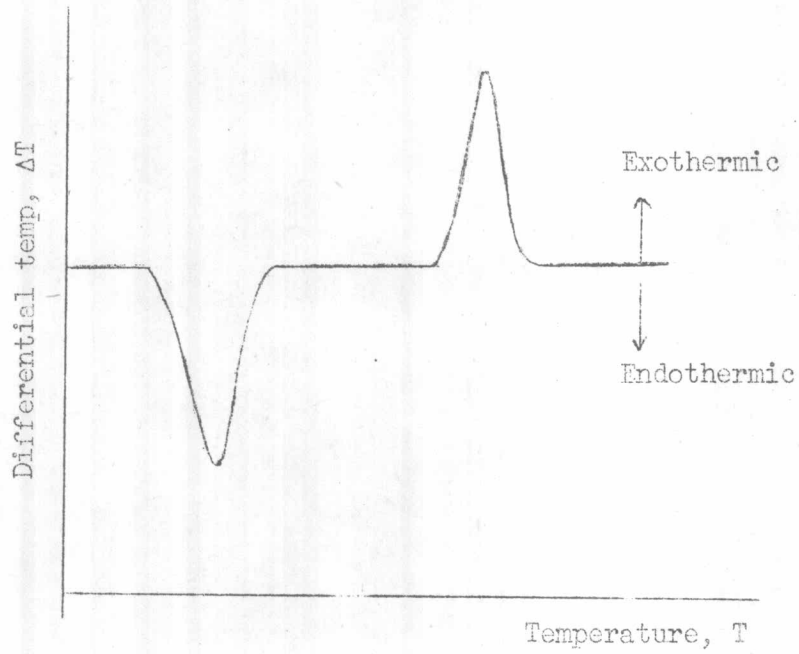

Figure 3.2 Typical differential thermal analysis curve.

In this work the thermograms were recorded on the Fischer Differential Thermal Analysis apparatus series 200 A, which was furnished with platinel thermocouples. The technique is divided into two parts.

1. Study of the thermal decomposition of the compounds. The exact known weight sample of the order 0.1 g. was placed in the quartz sample cell, and inserted in the sample well of the sample holder, along with the reference cell which contained alumina of the same weight as the sample. The sample was run under the atmospheric pressure, at the heating rate of 10 degrees per minute, and the temperature was increased from the room temperature up to 300°C.

2. Study of the molecular interaction between the organometallic compounds and 1, 10-phenanthroline. Specimens were prepared by heating small amount of the neutral ligand and the organometallic compound, at varying ratio, at room temperature up to 300°C , other experimental conditions were the same as described in the previous experiment.

The weight ratio of the organometallic compounds and 1, 10-phenanthroline of each specimen was shown in Table 3.3

Table 3.3

The weight ratio of the organometallic compounds (M) and 1,10-phenanthroline (L)

Compound	Sample no.	M(%)	L(%)	mole ratio
Ph_2TlBr : 1,10-phen	1	0.00	100.00	0
M : L	2	20.00	80.00	1:10
	3	40.00	60.00	1:3.3
	4	50.00	50.00	1:2.5
	5	68.80	31.20	1:1
	6	52.00	48.00	1:2
	7	81.56	18.44	2:1
PhHgBr : 1,10-phen	1	0	100.00	0
M : L	2	20.00	80.00	1:8
	3	47.43	52.57	1:2
	4	66.34	35.66	1:1
	5	78.30	21.70	2:1