



CHAPTER V

DISCUSSION

The first and the foremost step in the study of any aspects of the chemical compounds is to ascertain that the prepared compounds are the desired ones. It is therefore worthwhile here to commence the discussion of the results with the interpretation of the experimental data which have direct or indirect relation to the properties of the complexes under study namely Ph_2TlBr , $\text{Ph}_2\text{TlBr} \cdot 2\text{pyridine}$, $\text{Ph}_2\text{TlBr} \cdot 1,10\text{-phenanthroline}$, PhHgBr , $\text{PhHgBr} \cdot 2\text{pyridine}$ and $\text{PhHgBr} \cdot 1,10\text{-phenanthroline}$.

The direct and obvious proof of the existence of the four complexes concerned is obtained from their DTA thermograms and the infrared spectra (Figures 4.7, 4.8 and 5.1) The shift in the absorption frequencies and the difference in melting point confirm the formation of those complexes through the preparation procedure used in this work.

Additionally, the presence of $\text{Ph}_2\text{TlBr} \cdot 1,10\text{-phenanthroline}$ and $\text{PhHgBr} \cdot 1,10\text{-phenanthroline}$ are indicated by the results obtained from

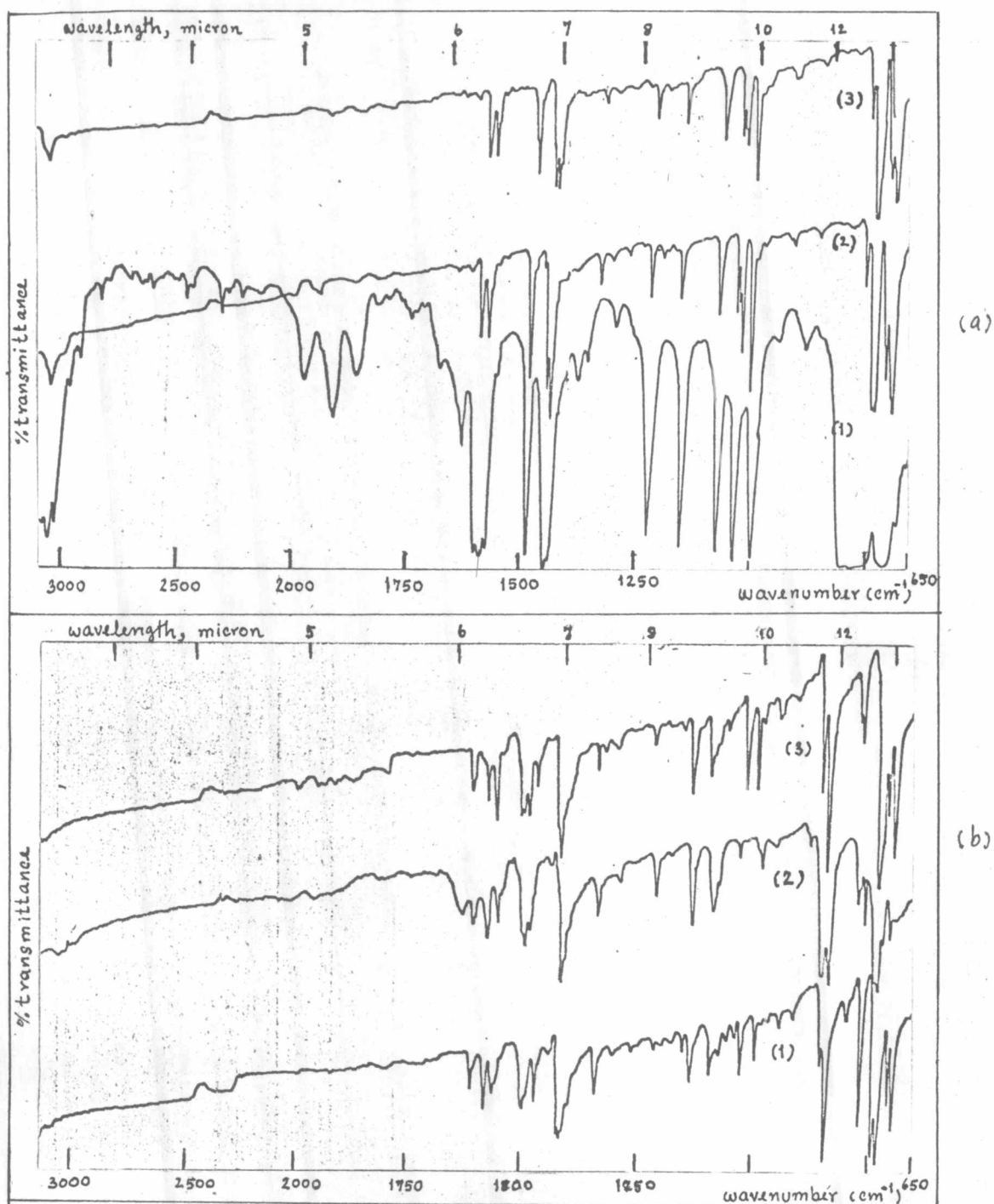


Figure 5.1 a) The infrared spectra of (1) Pyridine in 0.1 mm. solution cell. (2) $\text{Ph}_2\text{TlBr} \cdot 2\text{pyridine}$ and (3) $\text{PhHgBr} \cdot 2\text{pyridine}$ as KBr disks.

b) The infrared spectra of (1) $\text{Ph}_2\text{TlBr} \cdot \text{Phen}$ (2) 1,10-phenanthroline and (3) $\text{PhHgBr} \cdot \text{Phen}$ as KBr disks.

the conductometry and the NMR technique. The conductance of the ligand 1,10-phenanthroline is negligible in the solvent used. Hence an increase in the conductance of the product of the reaction between the organothallium and 1,10-phenanthroline or organomercury and 1,10-phenanthroline can be taken as a proof of the presence of a new species. (Table 4.1 page 35)

Similarly, the NMR spectra shown in Figure 4.3 (page 33) give the difference in the coupling constant of $Tl-H_{ortho}$ in $Ph_2TlBr \cdot 1,10\text{-phenanthroline}$ and Ph_2TlBr by the order of 10 Hz. The difference is sufficiently large to distinguish the two species from each other.

Unfortunately, however, that the sensitivity of the conductometry and NMR technique is concentration dependent. They could therefore not be used with the sparingly soluble compounds, Ph_2TlBr and $Ph_2TlBr \cdot 2\text{pyridine}$ in this case.

5.1 Structural Elucidation

As far as the discussion of the structure and the nature of the complexes are concerned uses can be made of informations obtainable from the physical measurements.

The plot of the molar conductance (Λ) against the square root of concentration (\sqrt{c}), or what is known as a phoreogram are shown in Figures 5.2, 5.3 and 5.4. The experimental points fit very nicely on the concave curve which was named by Fuoss⁽⁴⁷⁾ as anabatic phoreogram, the indication of the presence of weak electrolyte in the solution.

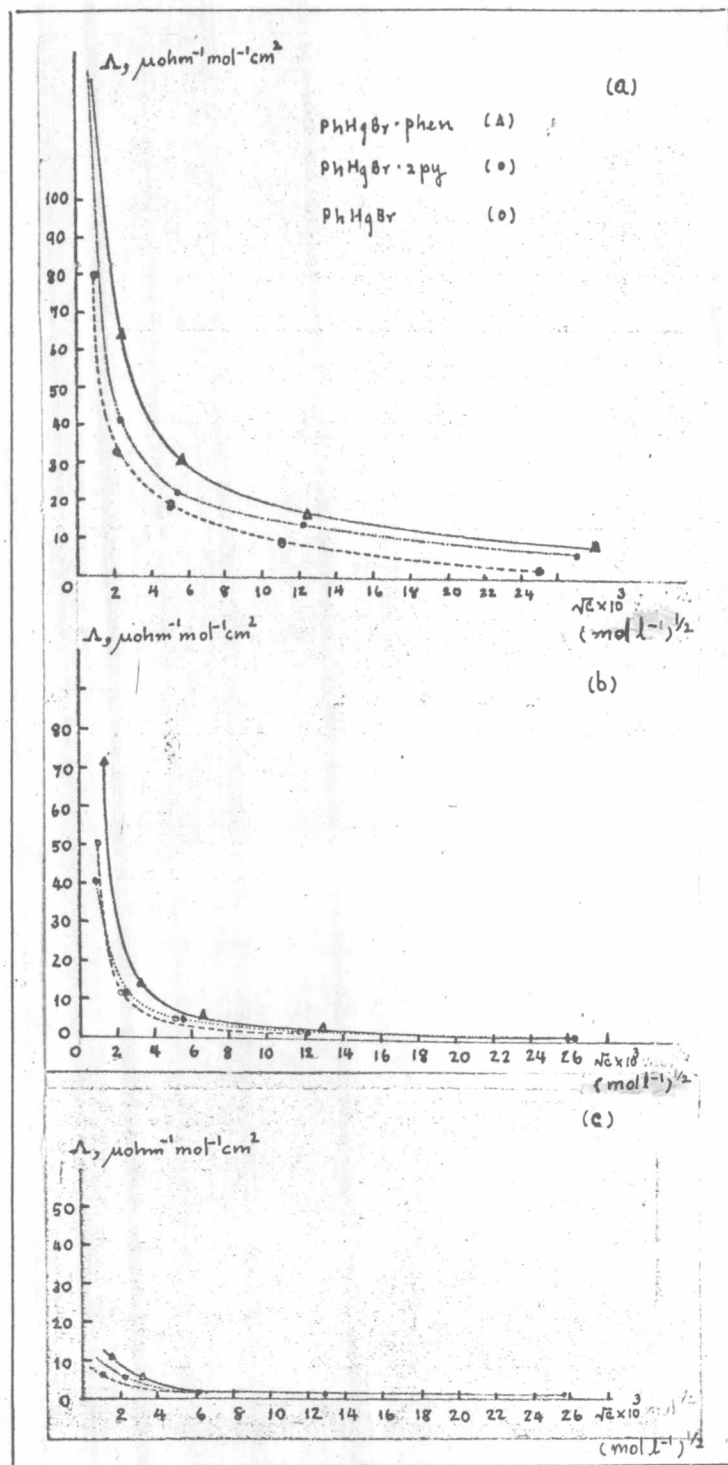


Figure 5.2 The phoreogram of PhHgBr and its derivatives in acetonitrile (a), acetone (b) and ethanol (c).

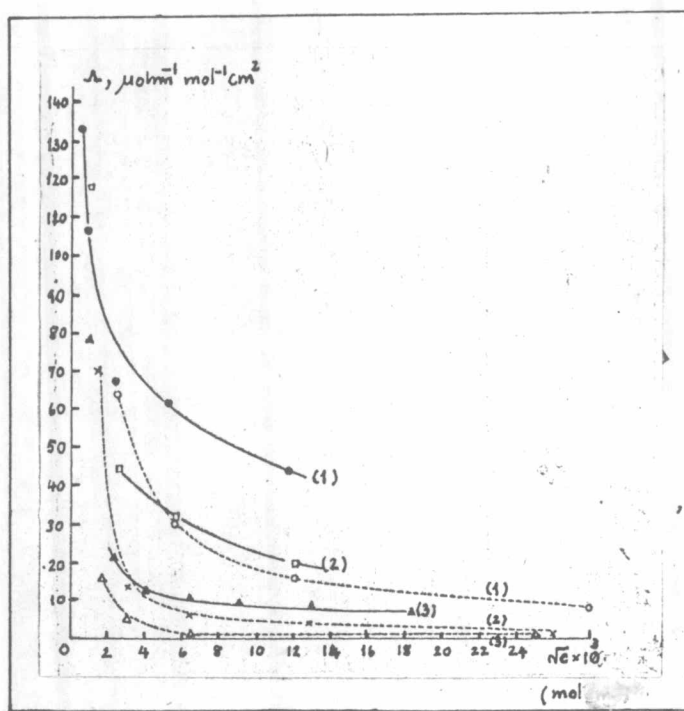


Figure 5.3 The phoreogram of $\text{Ph}_2\text{TlBr.Phen}$ (—) and PhHgBr.Phen (---) in acetonitrile (1), acetone (2) and ethanol (3).

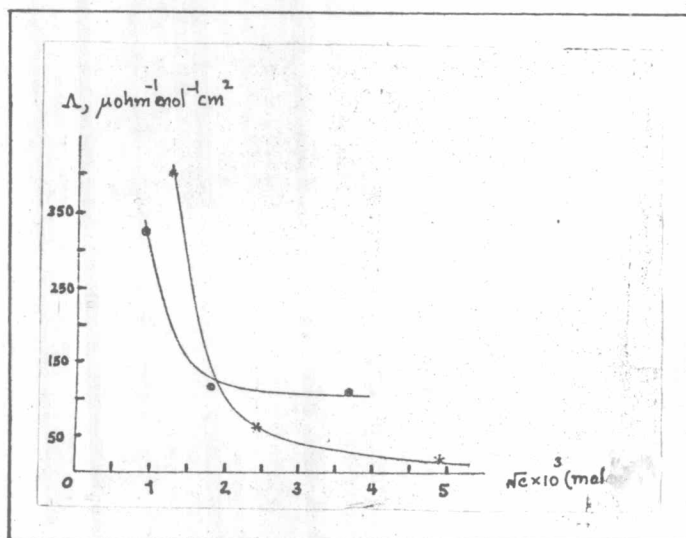


Figure 5.4 The phoreogram of $\text{Ph}_2\text{TlBr.Phen}$ (*) and PhHgBr.Phen (•) in water.

Table 5.1 shows that although the pyridine and 1,10-phenanthroline complexes of PhHgBr compound are weak electrolytes, they are stronger than the non-complexing organomercury compounds.

Table 5.1

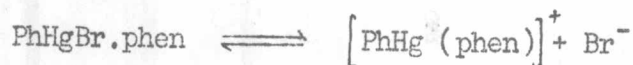
Molar conductance of the organometallic compounds in acetonitrile, acetone and ethanol.

	Acetonitrile		Acetone		Ethanol	
	A ^a	Cx10 ^{6b}	A	Cx10 ⁶	A	Cx10 ⁶
PhHgBr	10.08	1.28	1.66	1.50	0.70	1.53
PhHgBr.2py	14.04	1.49	1.81	1.04	0.76	1.38
PhHgBr.phen	16.32	1.57	2.81	1.70	0.98	1.66
Ph ₂ TlBr.phen	44.51	1.38	8.63	1.67	31.11	1.54
Ph ₂ TlBr	insoluble					
Ph ₂ TlBr.2py	insoluble					

a) Molar conductance (A) in $\mu\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$

b) Concentration (C) in mol l^{-1}

It is suggested therefore that the bromide ion is not strongly held in the complexes and that bonding in such complexes are slightly ionic. During the course of the experimental part, a single determination of molecular weight of PhHgBr.1,10-phenanthroline has been carried out, the result of which proves that this complex is a monomer. It may be possible to represent the dissociation reaction of PhHgBr.1,10-phenanthroline by the equation.



Due to the technical difficulty, the molecular weight of other complexes could not be obtained and the dissociation equation will not be shown here.

The infrared spectra of the organothallium and organomercury compounds have been examined in the region $2000-700 \text{ cm}^{-1}$. The spectra of the phenyl group attached to the heavy mass atom resemble that of iodobenzene which has been assigned in detail⁽⁴⁸⁾ and this is shown in Table 5.2. The spectra of Ph_2TlBr and PhHgBr compounds are shown in Figures 4.1 (a) and 4.1 (b) (page 31). The infrared spectra of the two compounds have also been investigated by Deacon⁽⁴⁹⁾ with which the observed frequencies from this work are in good agreement. In this work Deacon suggested that both Ph_2TlBr and PhHgBr have the symmetry groups C_{2v} but the former has a non-linear C-Tl-C bond whereas the C-Hg-Br in the latter is linear.

Table 5.2

Infrared absorption frequencies ($3100-650 \text{ cm}^{-1}$) for diphenylthallium bromide, phenylmercury bromide and iodobenzene.

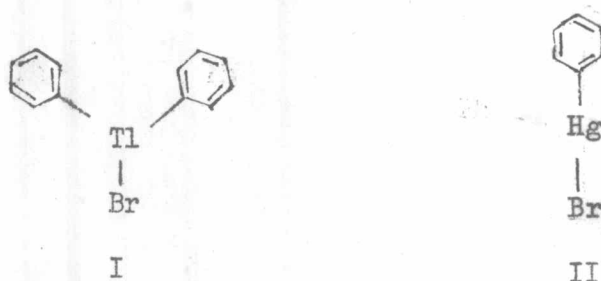
$(\text{C}_6\text{H}_5)_2\text{TlBr}$	$\text{C}_6\text{H}_5\text{HgBr}$	$\text{C}_6\text{H}_5\text{I}^a$	assignment
3100 m ^c (3068) ^b	3070-3090 w (3075)	3031-3064	$\nu(\text{C-H})$
1570 m (1568)	1575 m (1576)	1575	} $\nu(\text{C-C})$
1478 s (1473)	1480 s (1482)	1473s	
1430 s (1438)	1430 s (1434)	1435s	
1330 m (1328)	1330 m (1331)	1321	} $\delta(\text{C-H})$
1035 m (1017)	1035 m (1015)	1068	
1000 (997)	1000 m (998)	1015	
915 (906)	- (910)	904	
860 (855)	- -	835	
740 s (732)	730 s (726)	730s	} $\pi(\text{C-H})$
695 s (685)	699 s (693)	684s	

^a Values obtained from reference 11.

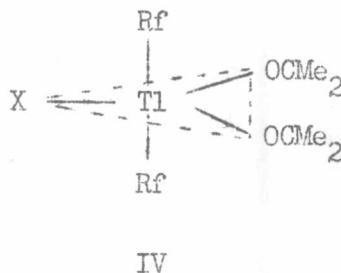
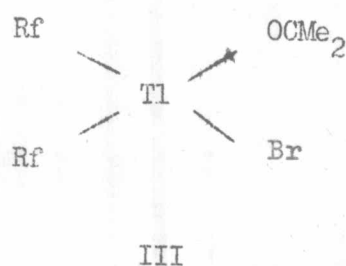
^b Values in parentheses obtained from reference 49.

^c All frequencies are assigned as a qualitative intensity of strong(s), medium(m) and weak(w).

In the same paper Deacon has proposed the following structures for Ph_2TlBr and PhHgBr as I and II



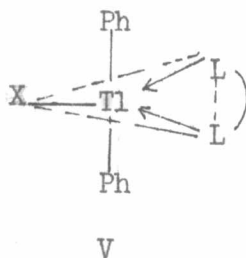
In 1965, Deacon⁽²⁰⁾ has carried out an investigation on the structure of $(\text{Rf})_2\text{TlBr}$ which is the analogue of Ph_2TlBr . Here, Rf represents pentafluorophenyl group. It was found that in acetone $(\text{Rf})_2\text{Tl X}$ (X is Cl or Br) existed as a monomer whereas a dimer form was formed when it dissolved in benzene. This finding indicated the rupture of a halogen bridging, perhaps due to coordination with acetone. Deacon proposed that either the tetrahedral species (Structure III) or the five-coordinate species (Structure IV) could be formed in acetone.



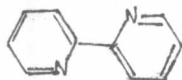
The isolation of $(\text{Rf})_2\text{Tl}(\text{py})_2\text{Br}$ from a solution of $(\text{Rf})_2\text{TlBr}$ in pyridine supported the validity of Structure IV.

Moreover Structure IV is favoured, since it would permit the $(R_f)_2Tl$ group to revert to the stable linear C-Tl-C stereochemistry.

It has been mentioned earlier that the compound Ph_2TlBr is analogous to $(R_f)_2TlBr$, hence the Structure IV can be used as a model for the pyridine and 1,10-phenanthroline complexes with only slight and appropriate adjustment. Pentafluorophenyl and acetone groups have to be replaced by phenyl groups and the ligands respectively, as shown below.



It is worth reported that the failure in the synthesis of 2,2'-bipyridyl complex of diphenylthallium bromide has been experienced during the course of the experimental part of this work. Fielding and Le Fevre⁽⁵⁰⁾ have proposed that the preferred configuration of 2,2'-bipyridyl is of the trans-type

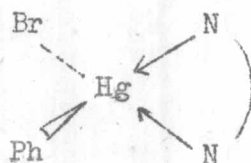


and a twisting out of the common plane by $20^\circ - 30^\circ$ should be easily accomplished.

If the structure of organothallium compound is according to Structure IV (page 55), obviously 2,2'-bipyridyl

cannot approach the ligand's position due to steric hindrance. Hence, this failure may be used to support the proposed structure of the complexes under study. The structure of $\text{PhHgBr} \cdot 2\text{pyridine}$ and $\text{PhHgBr} \cdot 1,10\text{-phenanthroline}$ can be interpreted in the same way as organothallium complexes since Hg atom is isoelectronic with Tl ion.

Thus PhHgBr complexes contain four-coordinate mercury atom as in VI



VI

The previous workers⁽³⁷⁾ also suggested that the bond C-Hg-Br is nearly linear.

From the NMR experiment, the $\text{Tl-H}_{\text{ortho}}$ coupling constant of Ph_2TlBr in DMSO-d_6 was found to be 456 Hz in comparison with 466 Hz of $\text{Ph}_2\text{TlBr} \cdot 1,10\text{-phenanthroline}$ in the same solvent. It is believed that the increase in the magnitude of Tl-H coupling constant is due to an increase in the s-character of the Tl-H bond in the phenanthroline complex. Based on Fermi contact term, the previous workers⁽⁵²⁾ have suggested that the increase in s-character occurred when the covalent character with the non-linear C-Tl-C bond is changed to a nearly ionic character. This could be reasonably expected if the complex dissociated in the solvents under study more than the non-complexing compound,

which was the case of the work reported here.

5.2 Physical Properties and Other Studies.

5.2.1 Physical properties

Table 5.3

Physical properties of diphenylthallium bromide, diphenylmercury bromide and their complexes.

Compound	M.P. °C	Color & Cryst. form	Solubility				Mol. wt. det.	Elect. cond.
			H ₂ O	Actn.	Acet.	Eth.		
Ph ₂ TlBr	315d.	wh.ndl.	i	i	i	i	-	wk.ele.
PhHgBr	275	wh.fl.	sl.s.	sl.s.	sl.s.	sl.s.	-	"
Ph ₂ TlBr.2py	320d.	wh.ndl. lus.	i	i	i	i	-	"
PhHgBr.2py	265	wh.fl. lus.	sl.s.	sl.s.	sl.s.	sl.s.	531 (537)	"
Ph ₂ TlBr.phen	230d.	wh.cb.	sl.s.	sl.s.	i	i	-	"
PhHgBr.phen	165	wh. powd.	sl.s.	sl.s.	sl.s.	sl.s.	-	"

abbreviations M.P. - melting point ; d - decompose
wh - white ; sl - slightly
ndl - needles ; s - soluble
fl. - flakes ; i - insoluble
lus - lustrous ; Actn - Acetonitrile
cb - cubes ; Acet - Acetone
powd - powder ; Eth - Ethanol

- Mol. wt. det - Molecular weight determination, value in parenthesis is the expected molecular weight for PhHgBr.phen
- Elect. cond. - Electrical conductivity
- wk - weak ; ele. - electrolyte

Physical properties of the compounds and complexes in question are tabulated in Table 5.3. Though this may not be regarded as a complete set of data, it should be sufficient in a way of the preliminary identification of such compounds and complexes.

5.2.2 Stability constants. The first formation constant of pyridine and phenanthroline complexes of the organometallic compounds at about 25°C in 100% dioxane solution were reported in Table 4.2 (page 42). For 1:1 phenanthroline complex, the stability constant of the diphenylthallium and phenylmercury are the same order of 10^6 which suggests the existence of the two complexes in dioxane solution. Besides these complexes have little or no difference in the strength of N-M coordinate covalent bonds.

The Kf value for the pyridine complexes of the organothallium and organomercury are 3.59×10^{11} and 1.54×10^9 respectively. The difference in the Kf values is remarkable and is not consistent with the values obtained from the phenanthroline complexes. This ambiguous result may be caused by the uncertainty of the concentration of pyridine used in the reaction. It is a well known fact that pyridine

has a low vapour pressure and the considerable loss of pyridine due to vapourisation should be expected even at room temperature. Hence the figures obtained for the pyridine complexes in Table 4.2 can be used only as the indication of the stability of the complexes in dioxane but cannot be used for a more quantitative purpose.

Since quite a few more informations obtainable from techniques other than described in this thesis will find useful in accomplishing the structural elucidation the following studies hence are recommended for a future work i.e., the far-infrared spectrophotometry, the molecular weight determination, X-ray spectrometry, and magnetic susceptibility measurement. In addition, it is thought necessary to do more precise work in NMR spectrometry.