

CHAPTER IV

RESULTS



4.1 Structural Studies of the Complexes.

In order to facilitate the study of the structure and to understand the nature of the bonding of organothallium and organomercury compounds, the infrared, and the nuclear magnetic resonance spectra together with other physical measurements of these compounds were examined.

4.1.1 Infrared spectra. The infrared spectra of organo-metallic compounds are roughly divided into two regions, the high frequency ($4000-650\text{ cm}^{-1}$) and the far-infrared region ($400-200\text{ cm}^{-1}$). The bands due to the organic moiety appear mainly in the former region, and those due to the skeleton containing the metal-carbon coordinate bonds appear in the latter region. Thus the former is a ligand-sensitive and is important in characterising the organic moiety, whereas the latter is metal-sensitive and is useful in characterising the metal involved.

Unfortunately, at present the spectrophotometer with the far-infrared region is not available in this laboratory and elsewhere

in Thailand, thus, the discussion on the metal-carbon vibrational frequencies is not included in this report.

The infrared spectra of the organometallic compounds and their complexes are shown in Figure 4.1 and Figure 4.2.

4.1.2. Nuclear Magnetic Resonance (NMR) spectra. **Thallium** possesses two magnetic isotopes Tl^{205} and Tl^{203} both with spin of $1/2$ and with natural abundance of 70.5% and 29.5% respectively. Accordingly, the spectra of the alkyl and aryl compounds consist of the peaks produced by the spin coupling of the proton belonging to the alkyl or aryl with both Tl^{205} and Tl^{203} nuclei. However, since the $Tl^{205}-H^1$ coupling constant is only slightly larger than the $Tl^{203}-H^1$ value (by a factor $\gamma^{205}/\gamma^{203} = 1.0098$)⁽¹¹⁾, lines due to $Tl^{203}-H^1$ coupling, therefore appear as distinct shoulders on the more intense lines produced by the $Tl^{205}-H^1$ coupling interaction.

The NMR spectra of diphenylthallium bromide and diphenylthallium bromide · 1,10-phenanthroline are shown in Figure 4.3. It is noticeable that only slight shifts in the peak position occur. These shifts (of the order 1-2 Hz.) indicate that the proton of the phenyl group are weakly influenced by the coordination of 1,10-phenanthroline to the organothallium compound.

4.1.3 Conductivity measurements. The molar conductance (Λ) of any solution is related to the square root of concentration (\sqrt{c}) according to the Onsager equation,

$$\Lambda = \Lambda^{\circ} + A \sqrt{c}$$

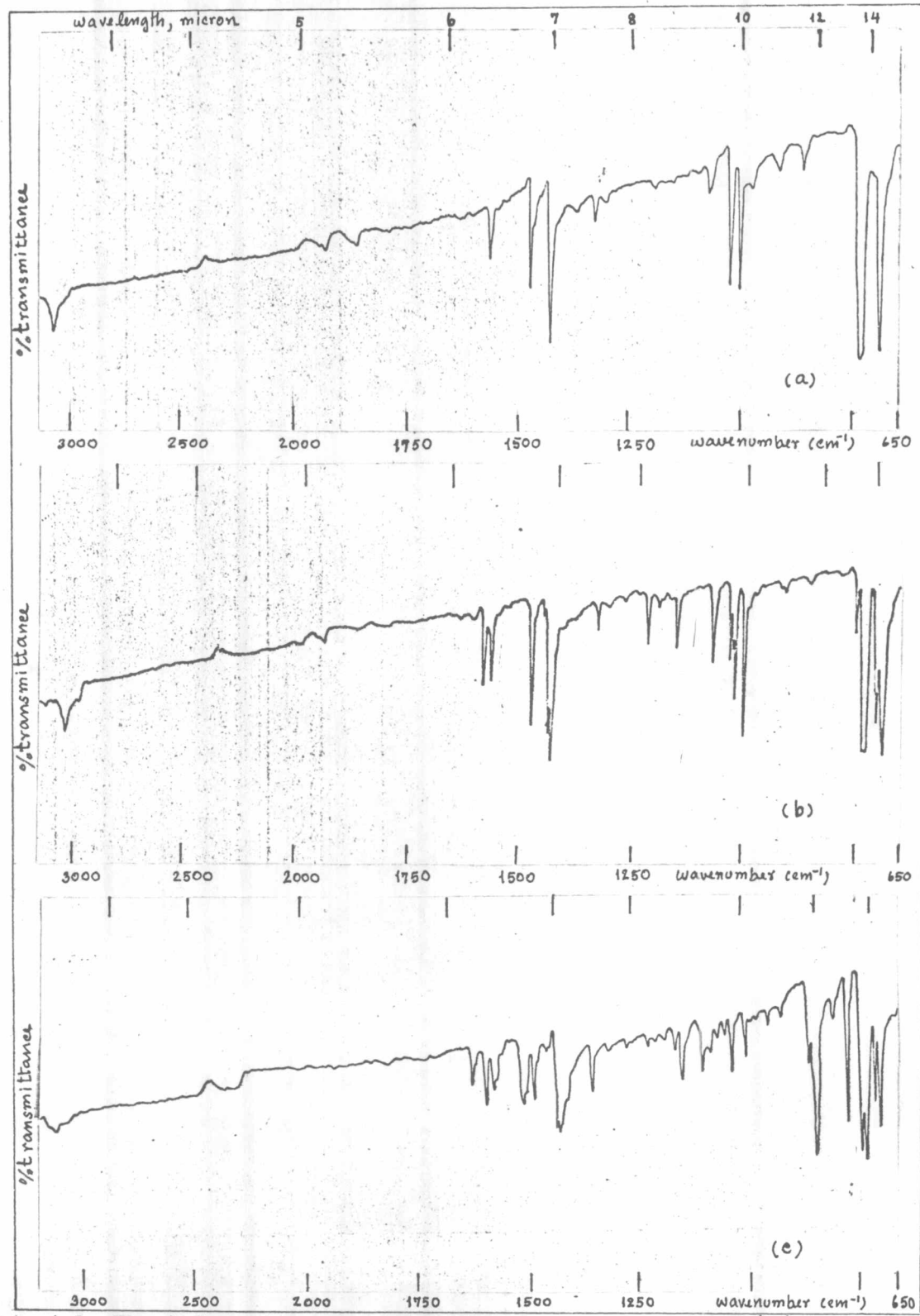


Figure 4.1 The infrared spectra of diphenylthallium bromide (a) diphenylthallium bromide.2pyridine (b) and diphenylthallium bromide.1,10-phenanthroline (c) as KBr disks.

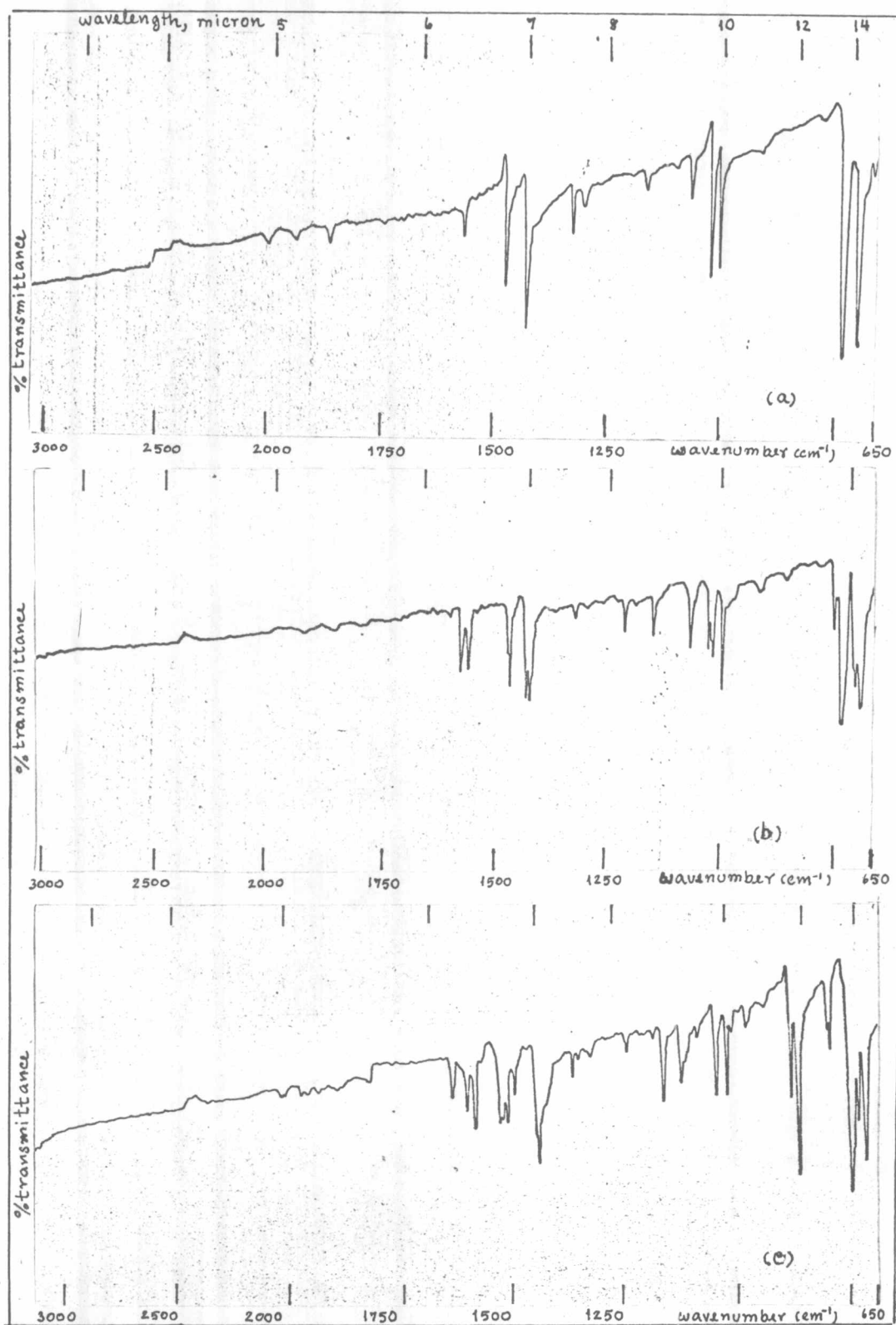


Figure 4.2 The infrared spectra of phenylmercury bromide (a) phenylmercury bromide.2pyridine (b) and phenylmercury 1,10-phenanthroline (c) as KBr disks.

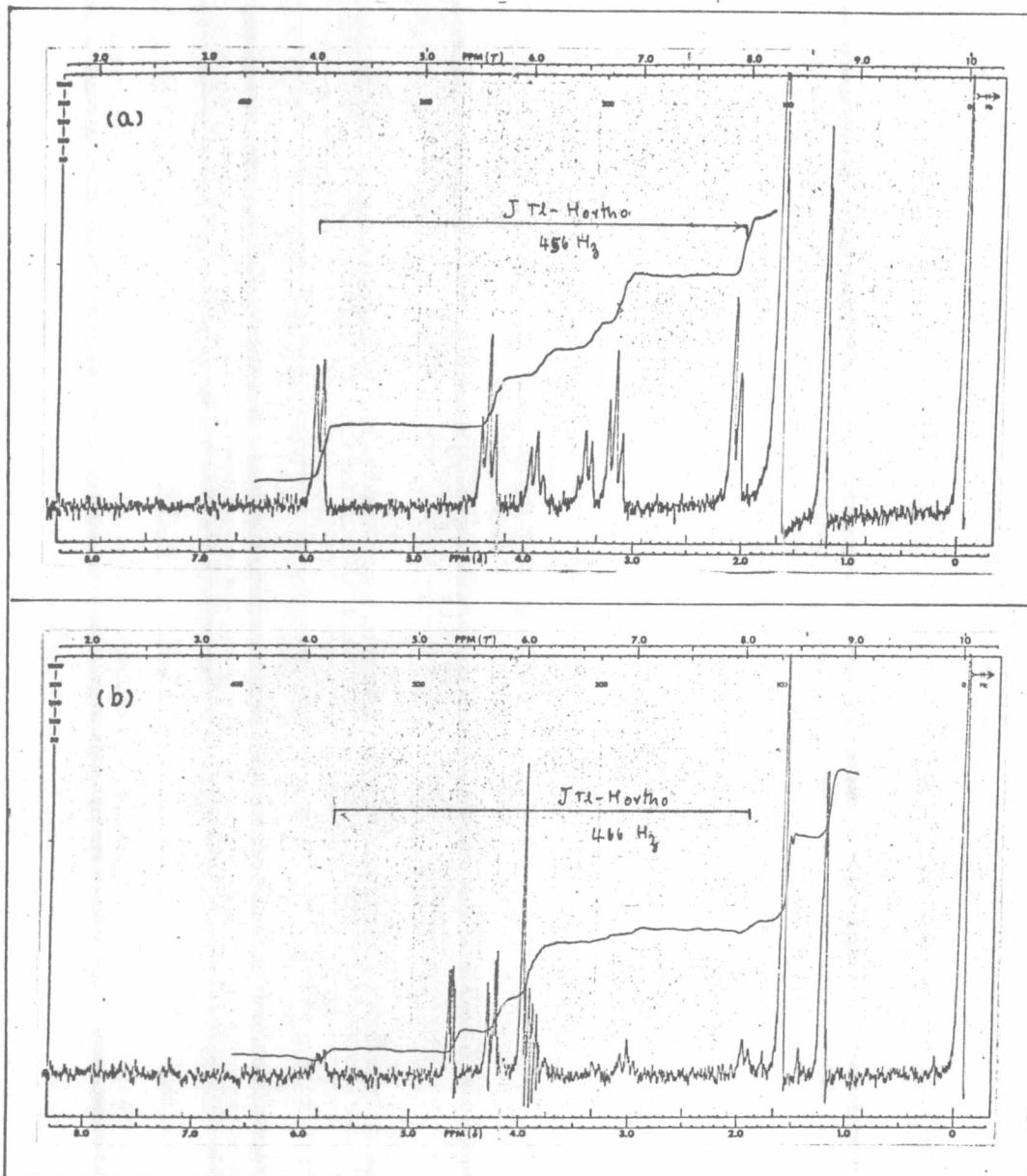


Figure 4.3 The NMR spectra of diphenylthallium bromide (a) and diphenylthallium bromide.1,10-phenanthroline in deuterated dimethylsulfoxide (DMSO-d_6).

Where Λ° is the molar conductance at infinite dilution and A is a numerical constant which involves the temperature as well as a number of terms characteristic of both the solvent and the solute.

Table 4.1 gives molar conductance of the compounds under study in acetonitrile, acetone and ethanol. The compounds exhibit very low conductances in organic solvents.

Table 4.1

Molar conductance of the organometallic compounds^a in acetonitrile, acetone, and ethanol at 25° C.

	PhHgBr		PhHgBr.2py.		PhHgBr.phen		Ph ₂ TlBr.phen	
	Λ^b	$C \times 10^{6c}$	Λ	$C \times 10^6$	Λ	$C \times 10^6$	Λ	$C \times 10^6$
Acetonitrile	2.12	642.15	6.34	748.65	7.78	788.36	44.51	138.84
	10.08	128.43	14.04	149.73	16.32	157.67	60.94	27.77
	19.88	25.68	22.19	29.95	30.59	31.53	69.21	5.55
	33.83	5.14	41.42	5.99	64.46	6.31	109.60	1.11
	80.48	1.03	200.06	1.20	313.20	1.26	134.42	0.22
Acetone	0.88	753.04	0.93	702.56	0.93	680.90	6.58	671.05
	1.66	150.61	1.81	104.51	2.81	170.22	8.63	167.76
	4.68	30.12	4.93	28.10	5.97	42.56	12.18	41.90
	11.31	6.02	11.17	5.62	14.46	10.64	20.32	10.44
	39.40	1.20	51.76	1.12	71.24	2.13		
Ethanol	0.50	765.28	0.62	693.51	0.83	665.03	25.71	772.79
	0.70	153.06	0.76	138.70	0.98	166.26	31.11	154.56
	1.28	30.61	1.49	27.74	1.75	41.57	44.46	30.91
	30.12	6.25	6.21	5.55	10.61	2.60	118.19	6.18
Water	—	—	—	—	25.76	24.52	123.50	13.14
					64.57	6.13	115.58	3.29
					401.67	1.53	327.17	0.82

- a) The solubility of Ph₂TlBr and Ph₂TlBr.2pyridine are too low to observe the conductance value.
- b) Molar conductance (Λ) in $\mu\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$
- c) Concentration (C) in mol l^{-1}

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4.1.4 Differential Thermal Analysis (DTA). In this technique peaks observed in the thermogram are caused by heat changes in the compounds with temperature. The number and the position of the peaks are characteristic of the compounds and therefore may be used as a mean for the qualitative identification of the substances. The DTA thermograms of each sample for the temperature range of 25° - 300° C are shown in Figure 4.4.

In the ordinary atmospheric system, the bromides, Ph_2TlBr and PhHgBr give the exothermic peaks due to melting with and without decomposition at 315° C and 275° C respectively. The low temperature peaks in Ph_2TlBr , DTA curve near 75° C is an exothermic peak due to dehydration. The pyridine complexes of Ph_2TlBr and PhHgBr , loose water near 50° C, after which the former begins to give up pyridine molecule near 140° C. The latter also shows a similar trend by evolution of its pyridine molecule near 120° C and melts with decomposition at 265° C.

The complexes $\text{Ph}_2\text{TlBr} \cdot 1,10\text{-phenanthroline}$ and $\text{PhHgBr} \cdot 1,10\text{-phenanthroline}$ begin to dehydrate near 50° C and give the endothermic peaks due to melting of the complexes at 230° C and 165° C respectively, and the former gives another exothermic peak due to the decomposition at 250° C.

4.2 Studies on the Complexes Formation

4.2.1 Spectrophotometric studies of the complexes. The absorption spectra of the series of solution prepared as described previously in Table 3.2 were measured over the spectral range

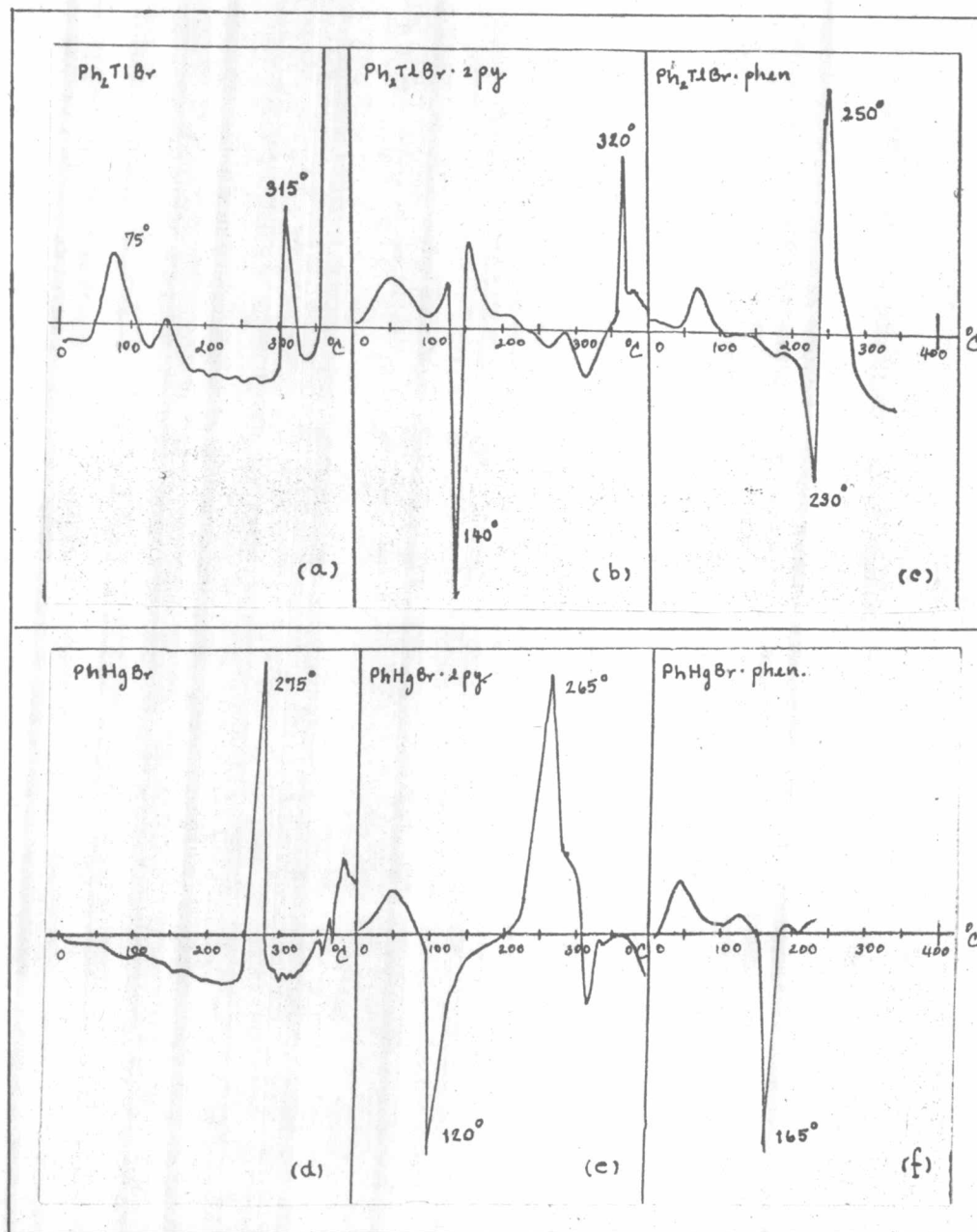


Figure 4.4 The DTA curves of the organothallium (a-c) and the organomercury (d-f) derivatives.

180-330 nm, using the pure dioxane as blank. The maximum absorption of $\text{Ph}_2\text{TlBr} \cdot 1,10\text{-phenanthroline}$ complex occurs at 225 nm as shown in Figure 4.5 (a).

Figures 4.5 (b), (c) and (d) also show the maximum absorption of the series of dioxane solution of $\text{PhHgBr} \cdot 1,10\text{-phenanthroline}$, $\text{Ph}_2\text{TlBr} \cdot 2\text{pyridine}$ and $\text{PhHgBr} \cdot 2\text{pyridine}$ complexes which occur at 223, 225 and 252 nm respectively.

In order to determine the stoichiometric formulae of the complexes, the plot of the absorbance of each aliquot against the mole ratio of the metal to ligand have been constructed.

It can be seen from Figure 4.6 (a) that the 1:1 complex is formed between the organometallic compounds and 1,10-phenanthroline since the straight lines of the two curves intersect at the mole ratio of 1:1, whereas Figure 4.6 (b) shows that the 1:2 complexes are observed for the organometallic compound -pyridine system. The formation constant of the complexes are calculated by the method of Meites and Thomas (Appendix II) and tabulated in Table 4.2.

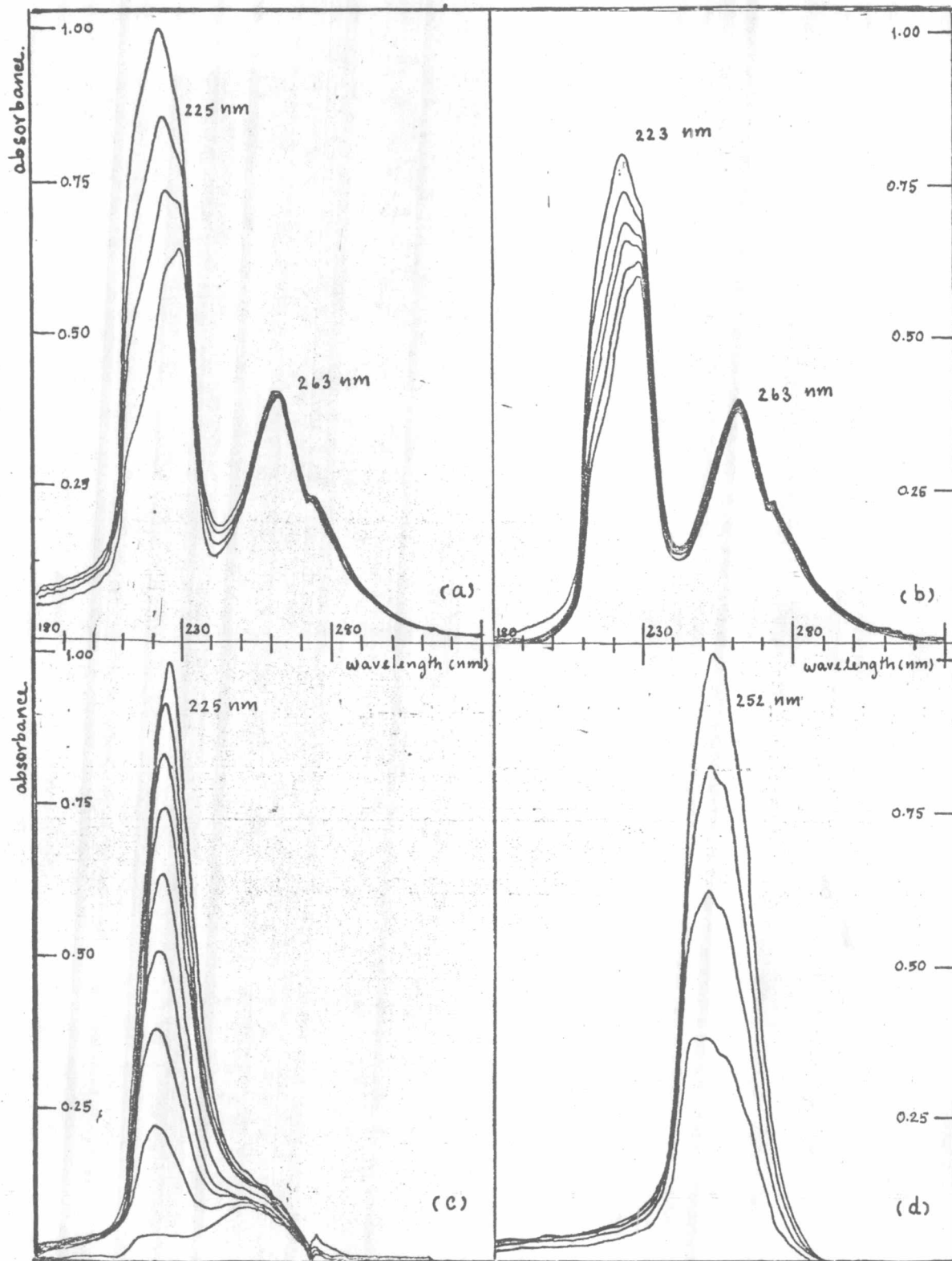


Figure 4.5 The UV spectra of the series of dioxane solution of the mixtures of pyridine, 1,10-phenanthroline with diphenylthallium bromide (a,c) and phenylmercury bromide (b,d).

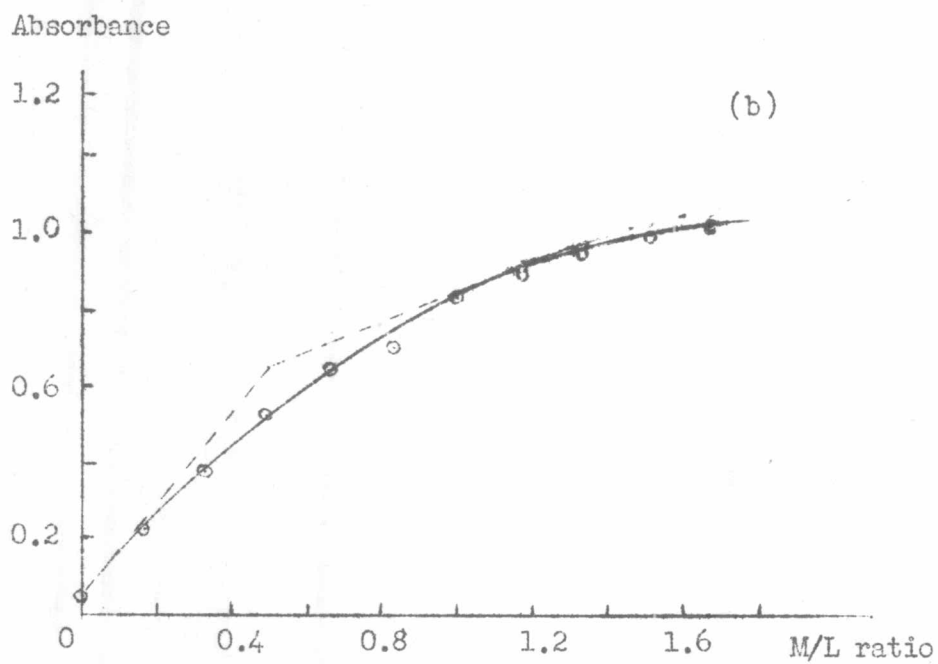
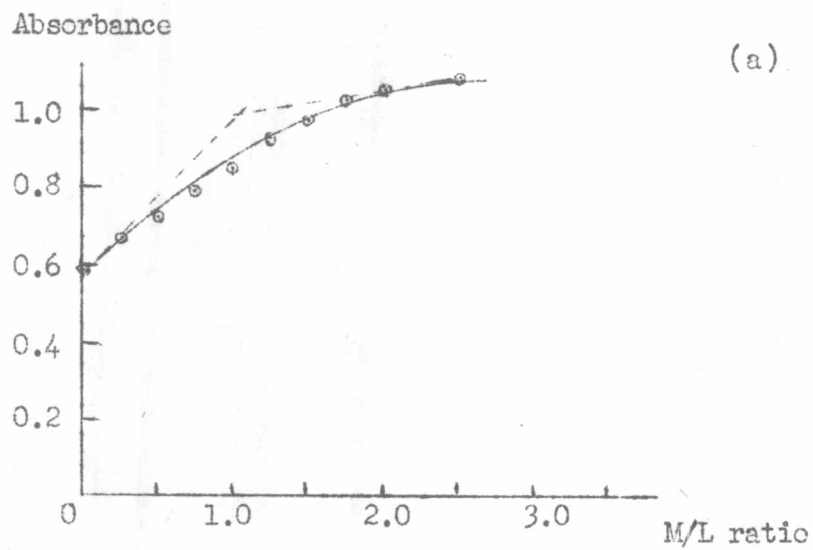


Figure 4.6 Mole ratio plots for (a) 1:1 complex of Ph_2TlBr : 1,10-phenanthroline and (b) 1:2 complex of Ph_2TlBr : Pyridine.

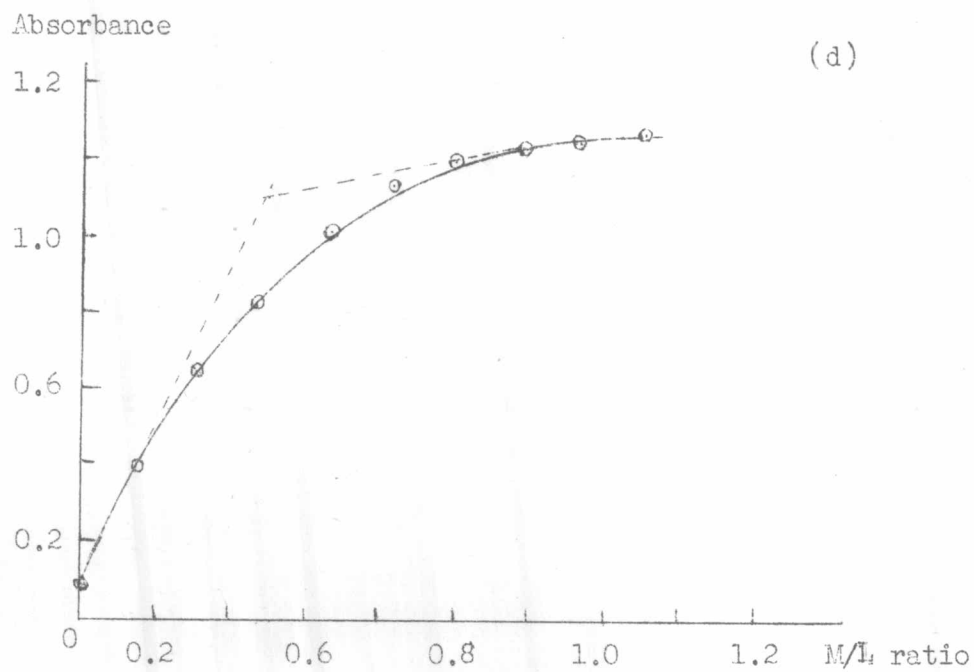
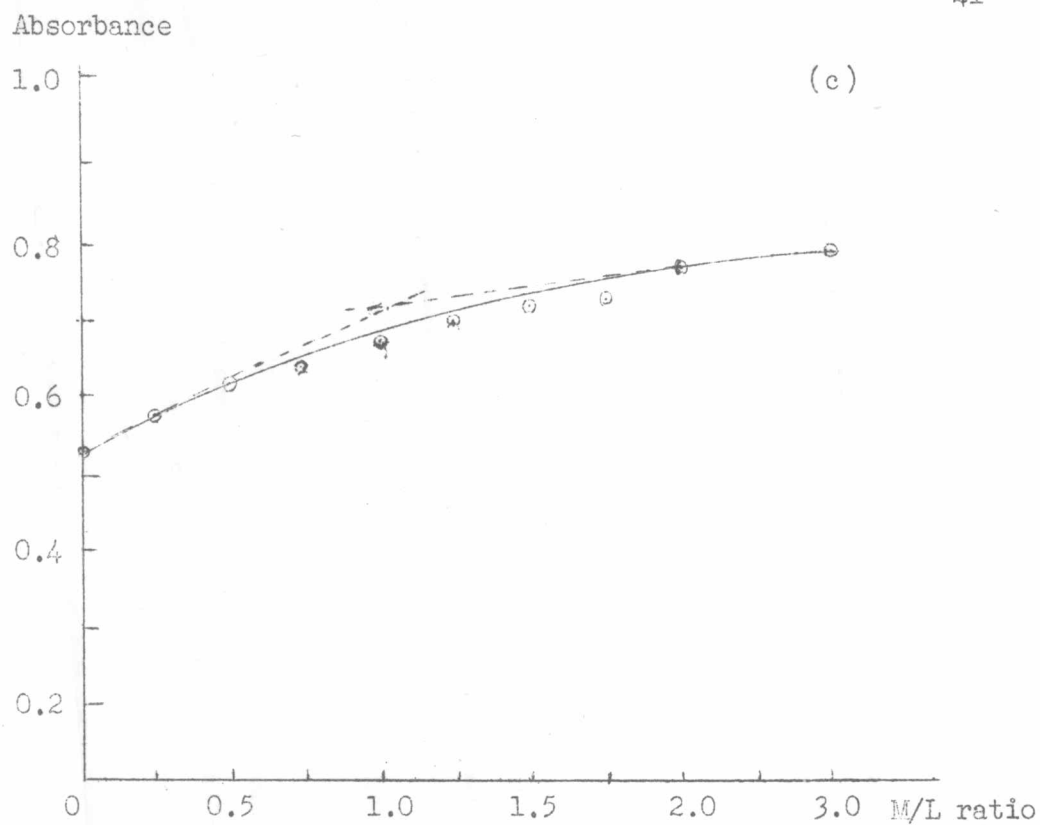


Figure 4.6 Mole ratio plots for (c) 1:1 complex of PhHgBr: 1,10-phenanthroline and (d) 1:2 complex of PhHgBr:Pyridine.

Table 4.2

Formation constants (Kf) of the organometallic compounds (M) with pyridine and 1,10-phenanthroline (L).

Ph ₂ TlBr + 1,10-phen		PhHgBr + 1,10-phen		Ph ₂ TlBr + py.		PhHgBr + py	
M/L	Kf x 10 ⁻⁶	M/L	Kf x 10 ⁻⁶	M/L	Kf	M/L	Kf
0	-	0	-	0	-	0	-
0.25	-	0.25	-	0.17	-	0.17	-
0.50	-	0.50	-	0.33	-	0.33	-
0.75	-	0.75	-	0.50	3.59x10 ¹¹	0.50	1.54x10 ⁹
1.00	1.34	1.00	2.32	0.67	-	0.67	-
1.25	1.29	1.25	1.34	0.80	-	0.80	-
1.50	1.46	1.50	1.33	1.00	-	1.00	-
1.75	2.78	1.75	1.18	1.17	-	1.17	-
2.00	2.87	2.00	2.87	1.33	-	1.33	-
2.50	-	2.50	-	1.50	-	1.50	-
average Kf 1.95x10 ⁶		1.81x10 ⁶		3.59x10 ¹¹		1.59x10 ⁹	

4.2.2 The molecular interaction of the organometallic compounds and 1,10-phenanthroline by DTA technique. The samples were prepared by mixing the two compounds thoroughly at varying ratio as indicated in Table 3.3. After the samples were heated and the subsequent melting behavior of such mixtures were recorded and are shown in Figure 4.7.

The results of this experiment support the evidence from the spectrophotometric determination which found that the 1:1 and 1:2 complexes were formed for the ligands 1,10-phenanthroline and pyridine respectively.

The DTA curves of phenanthroline- Ph_2TlBr system in Figure 4.7 show that the 1,10-phenanthroline alone gave an endothermic peak at 110°C due to melting. The addition of Ph_2TlBr to the ligand resulted in the appearance of a second endothermic peak near 125°C . With increasing amount of Ph_2TlBr the high temperature peak slightly increases as the low temperature one decreases. The system of 31.20% of 1,10-phenanthroline and 68.80% of Ph_2TlBr corresponds to the mole ratio of 1:1. Comparing the DTA thermograms Figure 4.7 (e) and 4.4 (c) (Page 37), the additional peak near 125°C in Figure 4.7 (e) strongly indicates the interaction between 1,10-phenanthroline and Ph_2TlBr to form a complex at mole ratio 1:1. Once the complex is formed the characteristic peak due to melting appears near 275°C as in Figure 4.4 (c).

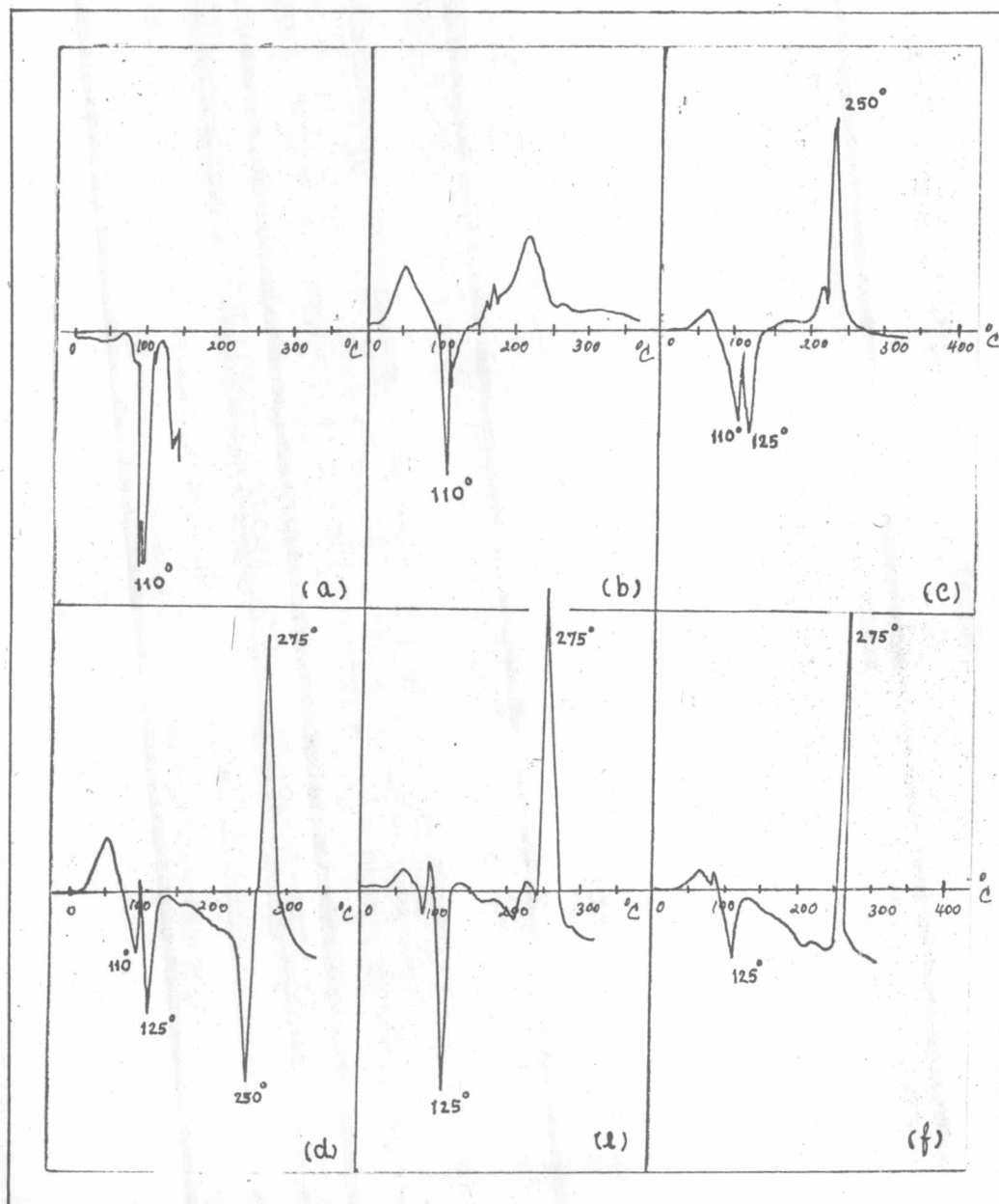


Figure 4.7. The DTA curves of the mixtures of 1,10-phenanthroline- Ph_2TlBr system. 100% Phen (a); 80% Phen & 20% Ph_2TlBr (b); 60% Phen. & 40% Ph_2TlBr (c); 50% Phen. & 50% Ph_2TlBr (d); 31.21% Phen. & 68.80% Ph_2TlBr (e); 18.44% Phen. & 81.56% Ph_2TlBr (f).

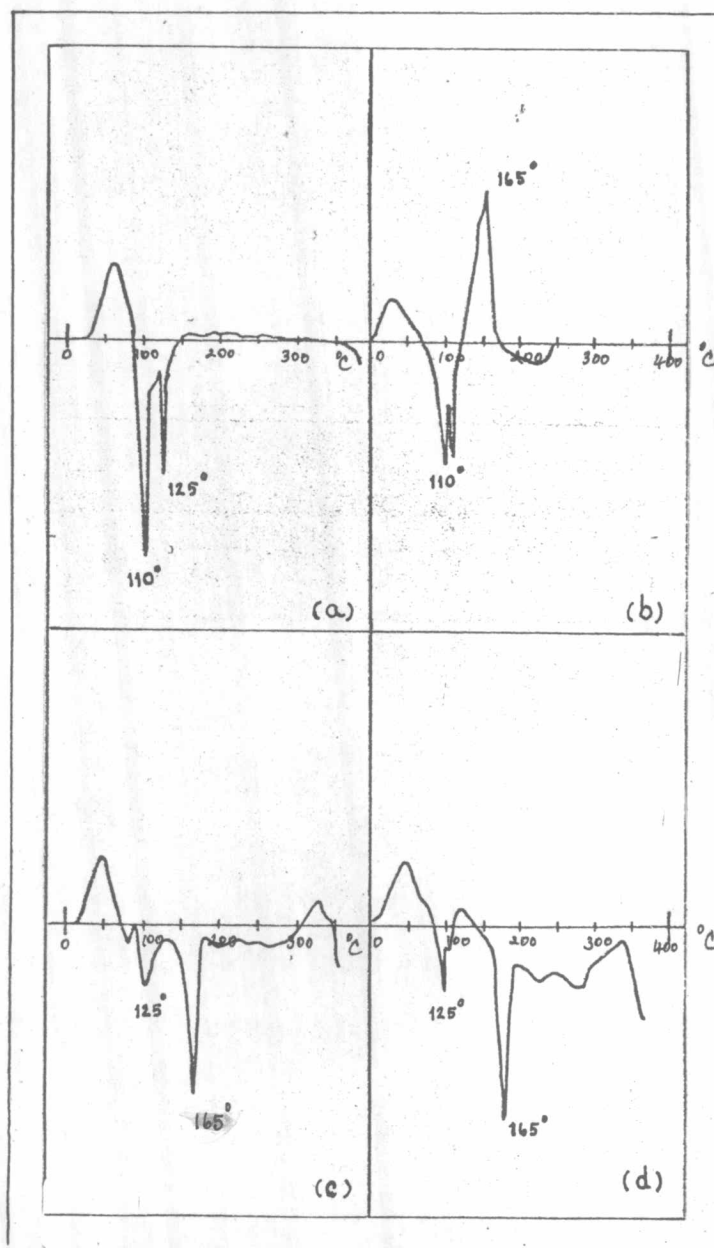


Figure 4.8 The DTA curves of the mixtures of 1,10-phenanthroline-PhHgBr system. 80% Phen. & 20% PhHgBr (a); 52.57% Phen. & 47.43% PhHgBr (b); 35.66% Phen. & 66.34% PhHgBr (c); 21.70% Phen. & 78.30% PhHgBr (d).

DTA curves for the system 1,10-phenanthroline-PhHgBr are shown in Figure 4.8. The results are similar to those of the organothallium analogue previously described. Again the complex is formed at the mole ratio 1:1 corresponding to 35.66% of 1,10-phenanthroline and 66.34% of Ph_2TlBr . The peak near 125°C indicates the complex formation and the characteristic peak due to melting appears near 165°C .