IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 16, Issue 7 Ser. I (July 2023), PP 01-11
www.iosrjournals.org

Synthesis And Characterisation Of Biologically Important Organothallium Complexes With N_4 And N_6 Macrocyclic Ligands

Y. Pandey[1] , D.K.Singh[2] V.P.Shukla[3]*, and S.Bhatiya[4]
[1,2,4] *Department of Chemistry, Bipin Bihari College,Jhansi, U.P. 284001, India*
[3*] *Department of Chemistry, Bipin Bihari College, Jhansi, U.P. 284001, India*

Abstract
Metal Macrocycles Are Widely Studied Due To Their Special Physicochemical Properties And Their Potential Applications In Various Fields. The Novel Complexes Of [Phtlcl$_2$] And [Ph$_2$TlCl] Were Explored With Macrocyclic Tetradentate (N_4) And Hexadentate (N_6) Ligands. The Synthesized Complexes Were Characterized By Elemental Analysis, Molar Conductance, IR, And XPS Spectral Studies. The Ligands And Their Metal Complexes Were Screened For Photoelectron Peaks And Geometry Of Complexes. The Result Show That The Activity Of Ligands Towards Chelating Activity Becomes More Pronounced And Significant When Coordinated To The Bioactive Metal Ion. The Proposed Structure Of Complexes With Said Ligands Have Been Compared And Discussed.

Key Words: *Metal Macrocycles / Physicochemical / Molar Conductance / Spectral Parameters*

Date of Submission: 06-07-2023 Date of Acceptance: 16-07-2023

I. Introduction

The Chelation chemistry of macromolecules predecessor is a charming area which has attracted the attention of inorganic and organic chemists. Macrocyclic complexes of bioactive metals have been of great interest due to their importance in view of their various applications in the production of metal carbonyls[1-3], antimicrobial[4-6], biochemistry [7,8], organometallic chemistry[9-14]. Chelation activity of amino acid, peptides, Schiff bases and their derivatives with biologically active metal ions are of great significance as many complex metal macrocyclic ligands equilibria occurring in enzymatic process [15-18]. A enormous number of organothallium(III) complexes with a macrocyclic ligand have been reported [19-22]. Various macrocyclic bioactive metal complexes have been used as in anticancerous [23], antifungal [24], antitumor [25], metal ion separation [26], photosenstizer [27] chelation therapy [28-31] and as NMR shift and relaxation agents [32]. Macrocyclic complexes [33,34] are also advantageous in terms of selectivity, since they have stringent structures and can thus exact special coordination geometry to the metal ion. In this communication, we report here the synthesis of [$PhTlCl_2$] and [Ph_2TlCl] complexes with N_4 and N_6 macrocyclic ligands. These complexes were characterised on the basis of elemental analysis, molar conductance IR and XPS spectral studies.

II. Materials And Method

All reagents used were of A.R. Grade (Aldrich). Solvents were distilled from relevant drying agent immediately in earlier of used metal complexes prepared by published method. The elemental analysis like C and H were determined by CDRI Lucknow, India, Nitrogen and halogen were determined by kjeldhal's and Volhard's methods respectively. The melting point were evaluated by using in sealed capillary tube on melting point apparatus. Molar conductivity of complex was measured on Digisum Electronic conductivity bridge in DMF at room temp. The infrared spectra of complexes and ligands were recorded on Perkin-Elmer 457 spectrometer at room temp in KBr/CsCl pellets. Kratos analytical axis supra ESCA ie. X-ray photoelectron spectra (XPS) nstrument equipped with monochromatised AlK_α (1486.6 ev.) source is used. All the peaks were rectified [35] for charging with reference to C_1S peak 284.8 ev and countered with Shirley background and a union of Gaussian and Lorentz an line-shapes, using ESCAPe computer software.

Preparation of $PhTlCl_2$ and Ph_2TlCl macrocyclic complexes with L^1, L^2, L^3, L^4, L^5, L^6, L^7: $PhTlCl_2$ and Ph_2TlCl (1 mmol) was dissolved in 20 ml of C_2H_5OH and to this a solution of 3,4 hexanedione (2 mmol) was added dropwise with constant stirring. This was followed by dropwise addition of 1,3-diaminopropane (2 mmol) in C_2H_5OH (20 ml) with stirring which was continued for 5 hrs. A white solid appeared which was filtered, washed with C_2H_5OH and dried under vacuum (with L^1 Ligand). A similar procedure was adopted for the synthesis of $PhTlCl_2$ and Ph_2TlCl complexes of macrocycles derived from 3,4-

hexanedione with 1,4-diaminobutane (L^2), 1,5-diaminopentane (L^3), 1,7-diaminoheptane (L^4), 1,8-diaminooctane (L^5), 1,9-diaminononane (L^6) and 1,10-diaminoecane(L^7).

Synthesis of macrocyclic $PhTlCl_2$ and Ph_2TlCl complexes with L^8 and L^9: $PhTlCl_2$ and Ph_2TlCl (1 mmol) was dissolved in 20ml C_2H_5OH with stiring and (2 mmol) of 2,3-hexanedione in 15 ml of (C_2H_5OH) was added. A solution of 1,9-diaminononane or 1,10-diaminodecane (2 mmol) in 15ml C_2H_5OH was added dropwise with constant stirring (5hrs). The solid product was filtered, washed with C_2H_5OH and dried under reduced pressure.

Synthesis of Ligand L^{10}: In aqueous (50ml) solution of semicarbazide hydrochloride (0.02mol, 1.5g) and 2,3-pentanedione (0.02 mol,2.08ml) were added slowly with constant stirring for 15-20 minutes. Both diamine and diketone were mixed in 1:1 molar concentration ratio. Mixture was cooled upto 5^0C and kept undisturbed for 12 hrs. On cooling white precipitate was filtered , washed with distilled water and dried under vaccum over P_4O_{10}. M.p. 240^0C, Found C=51.7, H=6.4, N=30.0, Calculated C=51.79, H=6.47, N=30.12

Synthesis of Ligand L^{11}: Hot ethanolic solution (50 ml) thiosemicabazide (0.02 mol, 1.8g) and 2,3-pentanedione (0.02 mol, 2.08 ml) were mixed slowly with constant stirring. The mixture was refluxed at 80^0C for 6-8 hrs. on cooling upto 5^0C cream coloured was filtered washed with cold C_2H_5OH and dried over $P_4O_{10,}$ m.p. 220^0C, Found C=46.4, H=5.8, 27.0, Calculated C=46.48,H=5.82, N=27.2

Synthesis of Ligand L^{12}: Semicarbazide (0.02 mol,3.82g), hot ethanolic solution (50 ml) furil (0.02mol, 3.82 g) and hot aqueous solution (50 ml) were added slowly with constant stirring. The mixture was refluxed at 80^0C for 6-8 hrs. On cooling upto 5^0C, cream coloured precipitate was filtered , washed with cold C_2H_5OH and dried under vaccum over P_4O_{10} . m.p. 220^0C, Found= 57.5, H=3.0, N=18.12, Calculated C=57.64, H=3.05,N=18.34

Synthesis of Ligand L^{13}: Thiosemicabazide (0.02 mol, 1.83g), hot ethanolic solution of furil (0.02 mol, 3.82 g) and hot ethanolic solution (50 ml) were mixed slowly with constant stirring. The mixture was refluxed at 80^0C for 6-8 hrs. On cooling upto 5^0C, coloured precipitate was filtered, washed with cold C_2H_5OH and dried under vaccum over P_4O_{10},m.p. 236^0C. Found C=54.12, H=2.78, N=17.14; Calculated C=54.32, H=2.88, N=17.28

Preparation of [$PhTlCl_2$] and [$Ph_2Tl.L$] complexes (where L=L^{10} to L^{13}): [$PhTlCl_2$] or [Ph_2TlCl] (1 mmol) was dissolved in 20 ml C_2H_5OH with constant stirring and 1 mmol of prepared macrocyclic ligand (L^{10} or L^{11} or L^{12} or L^{13}) in 15 ml of C_2H_5OH was added. The stirring was continued for 5 hrs. The solid product was filtered, washed with C_2H_5OH and dried over vaccum.

Preparation of complexes with L^{14}, L^{15},L^{16},L^{17},L^{18} macrocyclic ligands: All the complexes were prepared by template method. Hot ethanolic solution (10 ml) of [$PhTlCl_2$] or [Ph_2TlCl] (0.001 mol), hot ethanolic solution (10ml) of diamine i.e. diethylene triamine (L^{14} or L^{15} or L^{16} or L^{17}) (0.002 mol) and ethanolic solution of carbonyl compounds i.e. benzaldehyde or salicylaldehyde or cyclohexanone or glutaric anhydride (0.002 mol) are mixed together and the mixture was refluxed for 4-5 hrs. on cooling coloured precipitate filtered, washed with ethanol and dried over P_4O_{10} under vaccum . A hot ethanolic solution of glutaric acid (0.01 mol) is added to an etanolic solution of 2,6-diaminopyridine (0.01 mol) L^{18} and the resulting solution was refluxed for one hour. A solution of $PhTlCl_2$ or Ph_2TlCl (0.005 mol) was then added to the above solution and refluxed for 4-6 hrs. On cooling the solution a crystalline compound separates out. It is then filtered, washed with ethanol and dried under vaccum over P_4O_{10}.

III. Result and Discussion

These newly synthesized [$PhTlCl_2$] and [Ph_2TlCl] complexes were while solid and stable at room temperature. The elemental analysis and molar conductance data are listed in table-1. The low molar conductance in DMF 20-30 $ohm^{-1}cm^2mol^{-1}$ of these complexes indicate that all these complexes indicate that all these are nonelectrolyte.

Characterisation of [$PhTlCl_2$.L] and [Ph_2TlCl.L] complexes , Where, L=L^1 or L^2 or L^3 or L^4 or L^5 or L^6 or L^7 or L^8 or L^9 : In the IR spectra of the macrocyclic complexes, no absorption band was observed at 1700 and 3200-3400 cm^{-1} indicating the absence of unreacted > C=O or $–NH_2$ group. Thus > C=O or $–NH_2$ groups have condensed to give C=N linkage. All the complexes synthesised during present investigations show one peak and one strong absorption bands in the region 1520-1540 cm^{-1} and 1580-1630 cm^{-1} respectively which can be attributed to the uncoordinated >C=N group and coordinated >C=N group. The bands at 409-413 cm^{-1} are due to coordinated chloro coordinated group behaving as a monodentate ligand. ^{1}HNMR spectrum of one representative [$PhTlCl_2$] and [Ph_2TlCl] complexes have been recorded. The α-CH_2 protons of the amine residue give a triplet at δ 2.63 ppm due to coupling with the β -CH_2 protons. The β -CH_2 protons of the amine residue give a broad peak at δ1.50 ppm. The remaining metylene protons (γ and other) of the amine residue give rise to a broad peak at δ1.32 ppm. In macrocyclic precursor, 1,2,8,9-tetraphenyl-3,7-diazaduohepta-2,7-diene 1,9-diene 1,9-dione(KIM) the α-CH_2 protons have been reported to appear as a triplet at δ3.63 ppm and β-CH_2 protons as a quintet at δ2.11 ppm.The free macrocycle has not been isolated during the present investigation but it is

expected to exhibit the α and β-CH_2 protons almost at the same position as reported for KIM. As compared to KIM, in the [$PhTlCl_2$] and [Ph_2TlCl] complex of the macrocycle these peaks observed at higher field. The high field shifting of these protons confirms the coordination of the nitrogen atom of the macrocycle to thallium ion. The CH_3^a protons of the ketone residue give rise to a triplet at δ0.99 ppm due to coupling with the CH_2^b protons. The peaks due to CH_2^b protons of the ketone residue merge with the peaks of the CH_2 (β and others) protons of the amine residue.

Characteriation of [$PhTlCl_2.L^{10}$] and [$Ph_2TlCl.L^{10}$] complexes: The infrared spectrum of ligand L^{10} does not exhibit any characteristic for free –NH and OH groups indicating the absence of free primary diamine and hydroxyl group, which suggest the complete condensation of keto group with amino group. In this spectrum, appearance of new bands characterstic of thioamide group at 1690ϑ (C=O) amide I, 1579ϑ (CO-NH), 1438ϑ (C-N) + δ (NH) amide II, 1262 δ (N-H) amide III and 728 φ cm^{-1}amide IV [5-7], which support the macrocyclic species. A sharp band observed in the region 3346 cm^{-1} and 3490 cm^{-1} may be assigned to ϑ (N-H) of secondary amino group. IR spectra of all [$PhTlCl_2.L^{10}$]and [$Ph_2TlCl.L^{10}$] complexes have shown the shifting in $\vartheta_{c=n}$, to lower side than ligand, an uncoordinated peak appear on same position as in ligand and there is no change in $\vartheta_{(C=O)}$ and $\vartheta_{(NH)}$ absorption bands in all [$PhTlCl_2.L^{10}$) and [$Ph_2TlCl.L^{10}$] complexes than ligand confirms that coordination takes place through the nitrogen of $\vartheta_{C=N}$ group, oneC=N is uncoordinated but not through $\vartheta_{C=O}$ and –NH goups.

Characterisation of [$PhTlCl_2.L^{11}$] and [$Ph_2TlCl.L^{11}$] complexes: The infrared spectrum of ligand L^{11} does not exhibit any band around 3400 cm^{-1} characteristic for free –NH groups, indicating the absence of free primary amine and hydroxyl group which suggest complete condensation of keto group with amino group. In this spectrum, appearance of new band characteristic of thioamide groups at 1607 ϑ (CS-NH), 1516 ϑ (C-N) + δ(N-H), 1263 δ(N-H), which support the macrocyclic species. A broad band observed in the region 3168 cm^{-1} due to ϑ (N-H) of secondary amino group. IR spectra of all [$PhTlCl_2.L^{11}$] and [$Ph_2TlCl.L^{11}$] complexes have shown the shifting in $\vartheta_{C=N}$ to lower side than ligand but one $\vartheta_{C=N}$ peak on same position as in ligand and there is no change in $\vartheta_{C=S}$ and ϑ_{N-H} absorption bands in all [$PhTlCl_2.L^{11}$] and [$Ph_2TlCl.L^{11}$] complexes than ligand, confirms that coordination takes place through the nitrogen of $\vartheta_{C=N}$ group, but not through –C=S and –NH groups.

Characterisation of [$PhTlCl_2.L^{12}$] and [$Ph_2TlCl.L^{12}$] complexes : The infrared spectrum of ligand L^{12} does not exhibit any characteristic bands for free –NH groups and the appearance of new bands characteristic of amide group at 1685ϑ $_{(C=O)}$ amideI, 1603 ϑ $_{(CONH)}$, 1507ϑ $_{(CN)}$ + δ $_{(NH)}$ amide II, 669$\varphi_{(C=O)}$ cm^{-1} and a bandat 2921 cm^{-1} shows C-H stretching , which support the macrocyclic species. Bands observed in the region 3293-3049 cm^{-1} due to ϑ $_{(NH)}$ of secondary amino group. IR spectra of all [$PhTlCl_2.L^{12}$] and [$Ph_2TlCl.L^{12}$] complexes have shown the shifting in $\vartheta_{C=N}$, to lower side than ligand but one $\vartheta_{C=N}$ on same position as in ligand and there is no change in $\vartheta_{(C=O)}$ and $\vartheta_{(NH)}$ absorption bands in all [$PhTlCl_2.L^{12}$] and [$Ph_2TlCl.L^{12}$] complexes than ligand, confirms that coordination takes place through the nitrogen of $\vartheta_{C=N}$ group but not through -C=O and –NH groups.

Characterisation of [$PhTlCl_2.L^{13}$] and [$Ph_2TlCl.L^{13}$] complexes: The infrared spectrum of ligand L^{13} does not exhibit any characteristics band for free –NH group, and the appearance of new bands characteristics to thioamide group at 1644 ϑ ($_{C=S}$) amide I, 1619 ϑ ($_{CS-NH}$), 1531 $\vartheta_{(C-N)}$ + $^{\delta}_{(N-H)}$, 1284 $^{\delta}_{(N-H)}$ and 646 $\Phi_{(C=S)}$[35-36] , which support macrocyclic . A sharp band observed in the region 3262-3177 cm^{-1} due to $\vartheta_{(N-H)}$ of secondary amino group[37]. IR spectra of all [$PhTlCl_2.L$] and [$Ph_2TlCl.L$] complexes have shown the shifting in $\vartheta_{C=S}$ to lower side than ligand but one $\vartheta_{C=N}$ peak on same position as ligand and there is no change in $\vartheta_{C=S}$ and ϑ_{N-H} in all [$PhTlCl_2.L$] and [$Ph_2TlCl.L$] complexes than ligand, confirms that coordination takes place through the nitrogen of $\vartheta_{C=N}$ group but not through -C=S and –NH groups.

Characterisation of [$PhTlCl_2.L^{13}$] and [$Ph_2TlCl.L^{13}$] complexes (where L=L^{14}, L^{15}, L^{16}, L^{17} and L^{18}) : An examination of the IR spectra of [$PhTlCl_2.L$] and [$Ph_2TlCl.L$] (where L=L^{14}, L^{15}, L^{16}, L^{17} and L^{18}) have shown the absence of absorption around 3400 cm^{-1}. This shows the absence of a free amino group. The presence and the shifting of the $\vartheta_{C=N}$ bands 1620 cm^{-1} towards lower side in all these metal complexes and one $\vartheta_{C=N}$ peak present on same position as in ligand indicates that coordination takes place through the nitrogen of the $\vartheta_{C=N}$ group and one $\vartheta_{C=N}$ is uncoordinated .The IR spectra of [$PhTlCl_2.L$] and [$Ph_2TlCl.L$] have shown absorption band at 403-413 cm^{-1}.

The Tl4f and N 1_S binding energies (ev) data of [$PhTlCl_2$] or[Ph_2TlCl] and [$PhTlCl_2.L$] or [$Ph_2TlCl.L$] where L= L^1, L^2, L^3, L^4, L^5,L^6, L^7,L^8, L^9, L^{10}, L^{11}, L^{12}, L^{13}, L^{14}, L^{15}, L^{16}, L^{17} and L^{18} are listed in table 2-4 . It may be seem that Tl4f photoelectron peaks binding energy values were observed more in metal salts than in metal complexes. It suggested that thallium ions have more electron density in metal complexes than [Ph_2TlCl] or [$PhTlCl_2$] due to involvement of metal ion in coordination. Further, $N1_S$ have shown two symmetrical peaks one with higher binding energy in [$PhTlCl_2.L$] or [$Ph_2TlCl.L$] complexes than free nitrogen atom $N1_S$ photoelectron peak as in free ligand other on same BE as in ligand in 3:1 intensity ratio ,while in complexes intensity ratio 3:3.

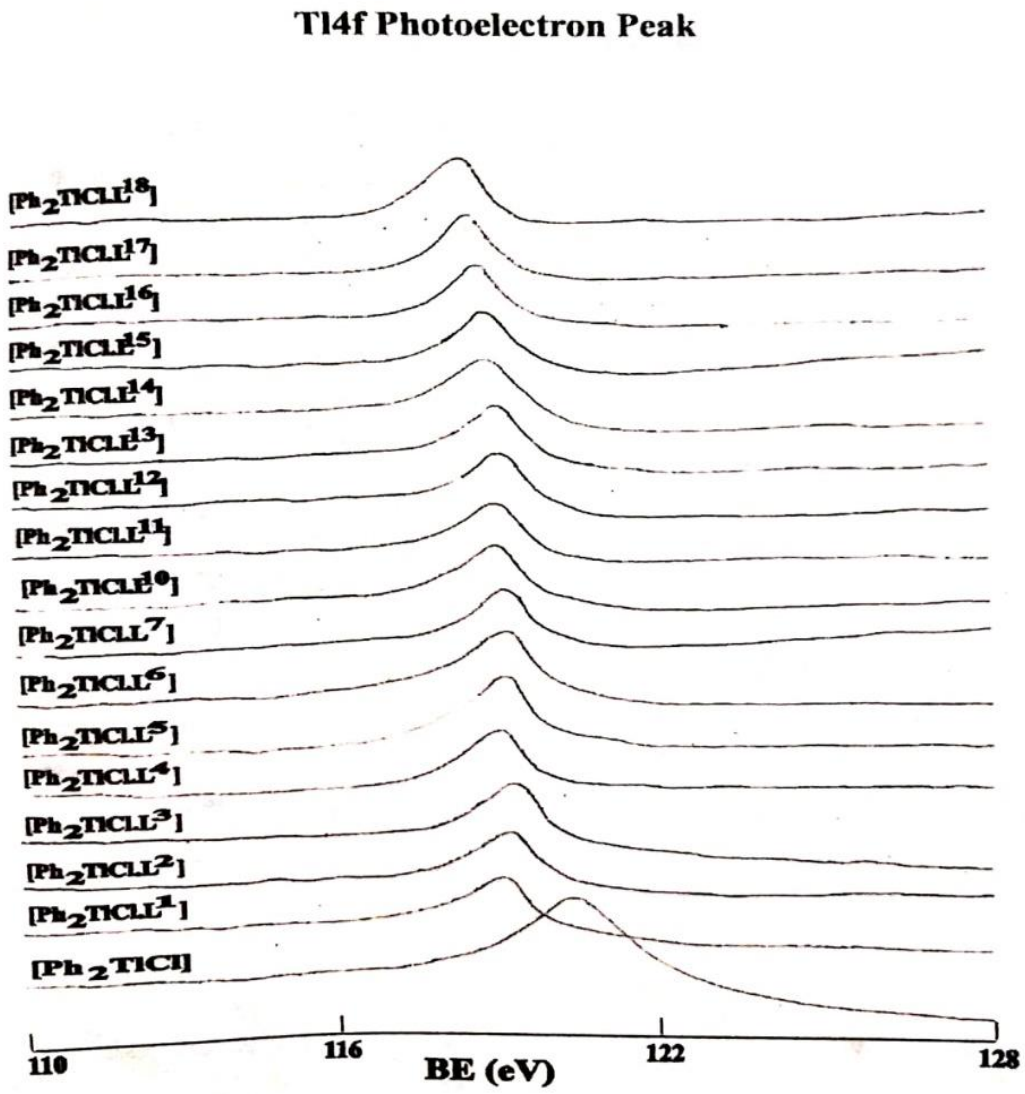

Fig. 1.0 Tl4f binding energies (ev) [Ph_2TlCl] and [$Ph_2TlCl.L$] complexes

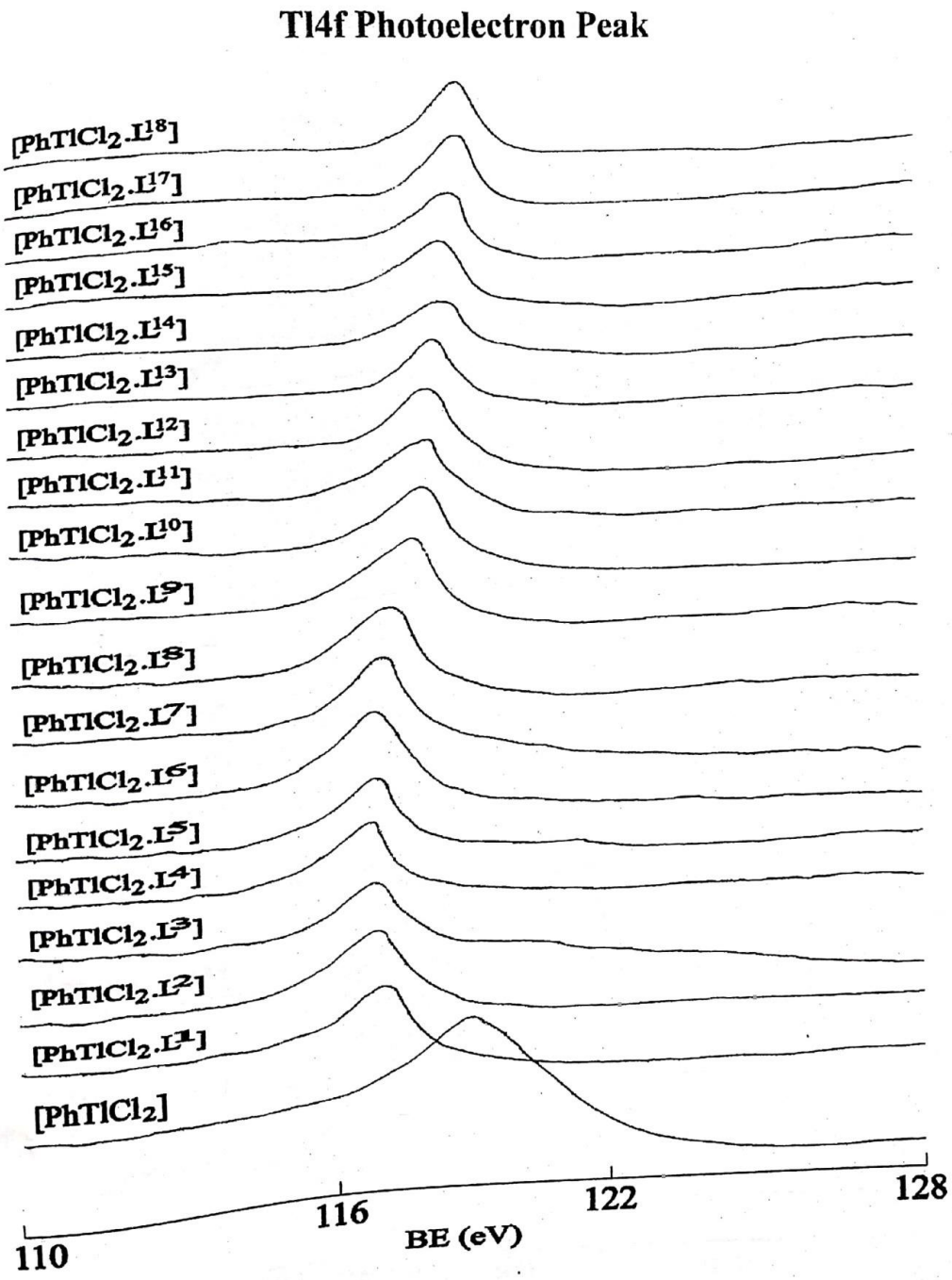

Fig. 2.0 Tl4f binding energies (ev) [$PhTlCl_2$] and [$PhTlCl_2$.L] complexes

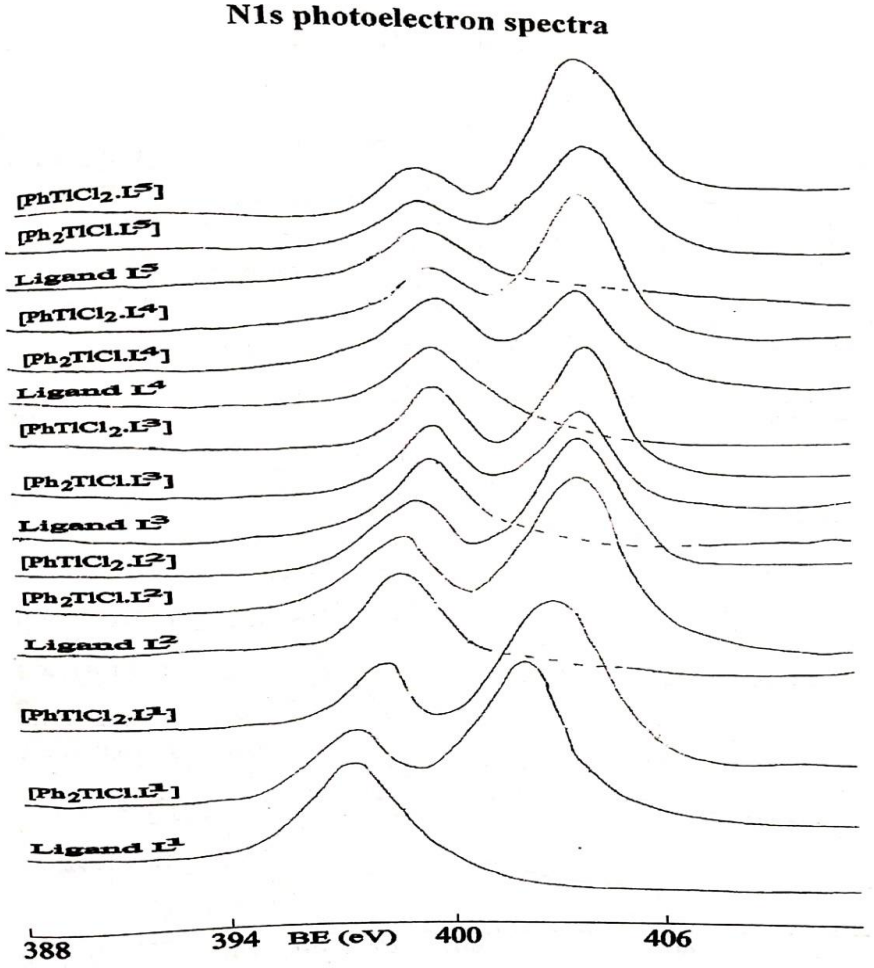

Fig.3.0 N1s binding energies (ev) in ligand [$Ph_2TlCl.L$] and [$PhTlCl_2.L$] complexes

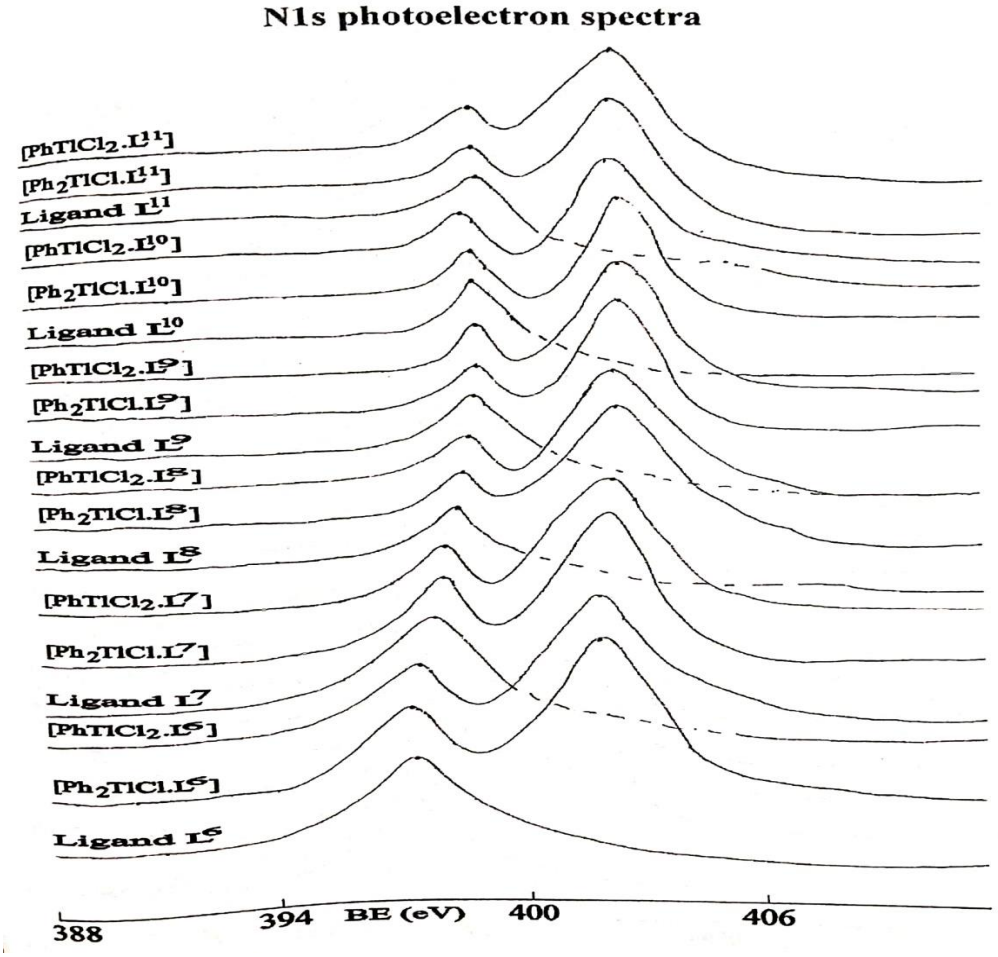

Fig. 4.0 N1s binding energies (ev) in ligand , [$Ph_2TlCl.L$] and [$PhTlCl_2.L$] complexes

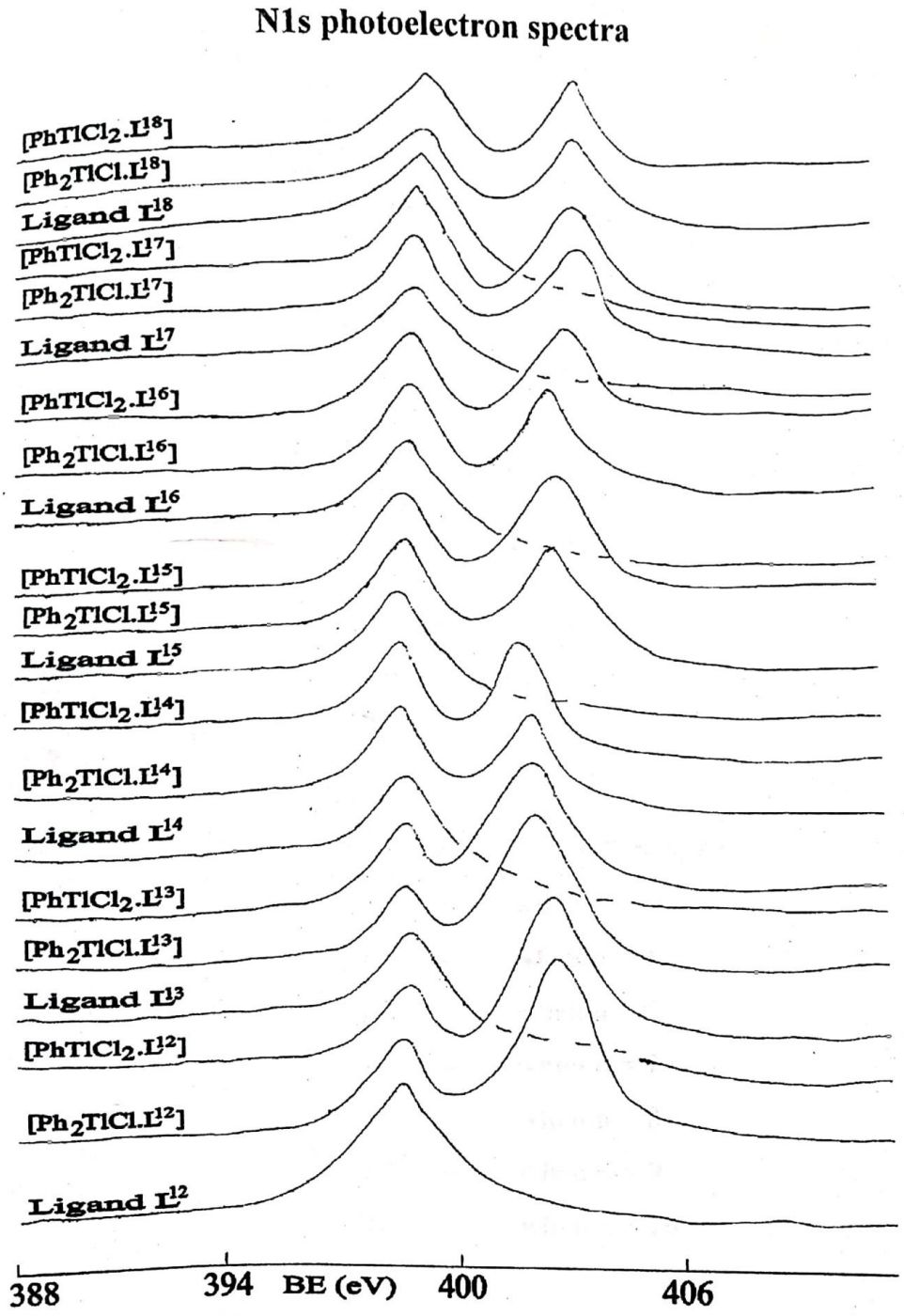

Fig. 5.0 N1s binding energies (ev) in ligand, [$Ph_2TlCl.L$] and [$PhTlCl_2.L$] complexes

Table-1.0
Elemental Analysis and Molar Conductance of [$Ph_2TlCl.L$] and [$PhTlCl_2.L$] Complexes

Sr.No.	Complexes	Found (Calc %)			Molar Conductance $ohm^{-1}cm^2mol^{-1}$
		C	H	N	
1	[$Ph_2TlCl.L^1$]	48.6 (48.7)	5.4 (5.6)	7.4 (7.5)	18
2	[$Ph_2TlCl.L^2$]	52.8 (52.9)	6.2 (6.3)	7.4 (7.7)	16
3	[$Ph_2TlCl.L^3$]	54.0 (54.1)	6.4 (6.6)	7.2 (7.4)	20
4	[$Ph_2TlCl.L^4$]	55.0 (55.2)	6.8 (6.9)	7.0 (7.1)	22

5	$[Ph_2TlCl.L^5]$	57.0 (57.2)	7.2 (7.4)	6.4 (6.6)	18
6	$[Ph_2TlCl.L^6]$	58.0 (58.2)	7.4 (7.6)	6.2 (6.4)	14
7	$[Ph_2TlCl.L^7]$	59.0 (59.0)	7.6 (7.8)	6.0 (6.2)	16
8	$[Ph_2TlCl.L^8]$	63.2 (63.3)	6.4 (6.6)	5.4 (5.6)	20
9	$[Ph_2TlCl.L^9]$	59.2 (59.0)	7.6 (7.8)	6.0 (6.2)	18
10	$[Ph_2TlCl.L^{10}]$	44.0 (44.5)	4.4 (4.6)	4.8 (4.9)	20
11	$[Ph_2TlCl.L^{11}]$	40.6 (40.8)	4.1 (4.2)	11.8 (11.9)	18
12	$[Ph_2TlCl.L^{12}]$	47.6 (47.8)	2.6 (2.8)	9.6 (9.8)	20
13	$[Ph_2TlCl.L^{13}]$	46.0 (46.1)	2.6 (2.7)	9.4 (9.5)	23
14	$[Ph_2TlCl.L^{14}]$	60.4 (60.5)	5.2 (5.3)	8.4 (8.8)	28
15	$[Ph_2TlCl.L^{15}]$	56.6 (56.7)	5.0 (5.0)	8.0 (8.2)	18
16	$[Ph_2TlCl.L^{16}]$	59.2 (59.0)	7.4 (7.6)	8.4 (8.6)	15
17	$[Ph_2TlCl.L^{17}]$	46.0 (46.2)	4.4 (4.6)	11.4 (11.5)	20
18	$[Ph_2TlCl.L^{18}]$	48.4 (48.6)	3.0 (3.2)	11.2 (11.3)	12
19	$[PhTlCl_2.L^1]$	43.4 (43.8)	5.4 (5.6)	8.4 (8.5)	20
20	$[PhTlCl_2.L^2]$	44.8 (44.9)	5.8 (5.9)	8.0 (8.0)	12
21	$[PhTlCl_2.L^3]$	47.0 (47.1)	6.2 (6.3)	7.4 (7.8)	22
22	$[PhTlCl_2.L^4]$	75.4 (75.6)	6.4 (6.6)	7.4 (7.5)	16
23	$[PhTlCl_2.L^5]$	51.0 (51.2)	7.0 (7.1)	7.0 (7.0)	18
24	$[PhTlCl_2.L^6]$	52.2 (52.3)	7.2 (7.4)	6.4 (6.7)	24
25	$[PhTlCl_2.L^7]$	53.4 (53.5)	7.4 (7.6)	6.4 (6.5)	12
26	$[PhTlCl_2.L^8]$	58.2 (58.4)	6.2 (6.4)	5.8 (5.9)	14
27	$[PhTlCl_2.L^9]$	53.4 (53.5)	7.4 (7.6)	6.4 (6.5)	18
28	$[PhTlCl_2.L^{10}]$	35.4 (35.7)	4.0 (4.1)	9.0 (9.2)	24
29	$[PhTlCl_2.L^{11}]$	32.4 (32.5)	3.6 (3.7)	12.4 (12.6)	22
30	$[PhTlCl_2.L^{12}]$	41.0 (41.4)	2.2 (2.3)	10.2 (10.3)	16
31	$[PhTlCl_2.L^{13}]$	39.4 (39.8)	2.0 (2.2)	9.8 (9.9)	18
32	$[PhTlCl_2.L^{14}]$	55.0 (55.4)	5.0 (5.0)	9.0 (9.2)	12
33	$[PhTlCl_2.L^{15}]$	51.6 (51.7)	4.6 (4.7)	8.4 (8.6)	14
34	$[PhTlCl_2.L^{16}]$	54.0 (54.0)	7.4 (7.5)	9.0 (9.0)	18
35	$[PhTlCl_2.L^{17}]$	38.4 (38.5)	4.0 (4.2)	12.0 (12.2	16
36	$[PhTlCl_2.L^{18}]$	41.0 (41.2)	2.6 (2.7)	12.0 (12.0)	12

Table-2.0
Tl4f Binding Energies (ev) In [Ph_2TlCl] and [$Ph_2TlCl.L$]

Sr.No.	Compound	Tl4f
1	[Ph_2TlCl]	119.8
2	[$Ph_2TlCl.L^1$]	116.4
3	[$Ph_2TlCl.L^2$]	116.4
4	[$Ph_2TlCl.L^3$]	116.4
5	[$Ph_2TlCl.L^4$]	116.4
6	[$Ph_2TlCl.L^5$]	116.4
7	[$Ph_2TlCl.L^6$]	116.4
8	[$Ph_2TlCl.L^7$]	116.4
9	[$Ph_2TlCl.L^{10}$]	116.4
10	[$Ph_2TlCl.L^{11}$]	116.4
11	[$Ph_2TlCl.L^{12}$]	116.4
12	[$Ph_2TlCl.L^{13}$]	116.4
13	[$Ph_2TlCl.L^{14}$]	116.4
14	[$Ph_2TlCl.L^{15}$]	116.4
15	[$Ph_2TlCl.L^{16}$]	116.4
16	[$Ph_2TlCl.L^{17}$]	116.4
17	[$Ph_2TlCl.L^{18}$]	116.4

Table-3.0
Tl4f Binding Energies (ev) In [$PhTlCl_2$] and [$PhTlCl_2.L$] Complexes

Sr.No.	Compound	Tl4f
1	[$PhTlCl_2$]	119.6
2	[$PhTlCl_2.L^1$]	116.2
3	[$PhTlCl_2.L^2$]	116.2
4	[$PhTlCl_2.L^3$]	116.2
5	[$PhTlCl_2.L^4$]	116.2
6	[$PhTlCl_2.L^5$]	116.2
7	[$PhTlCl_2.L^6$]	116.2
8	[$PhTlCl_2.L^7$]	116.2
9	[$PhTlCl_2.L^8$]	116.2
10	[$PhTlCl_2.L^9$]	116.2
11	[$PhTlCl_2.L^{10}$]	116.2
12	[$PhTlCl_2.L^{11}$]	116.2
13	[$PhTlCl_2.L^{12}$]	116.2
14	[$PhTlCl_2.L^{13}$]	116.2
15	[$PhTlCl_2.L^{14}$]	116.2
16	[$PhTlCl_2.L^{15}$]	116.2
17	[$PhTlCl_2.L^{16}$]	116.2
18	[$PhTlCl_2.L^{17}$]	116.2
19	[$PhTlCl_2.L^{18}$]	116.2

IV. Conclusion

On the basis of elemental analysis, molar conductance measurement , IR and XPS data and the subsequent discussion for the complexes the geometry as shown below.

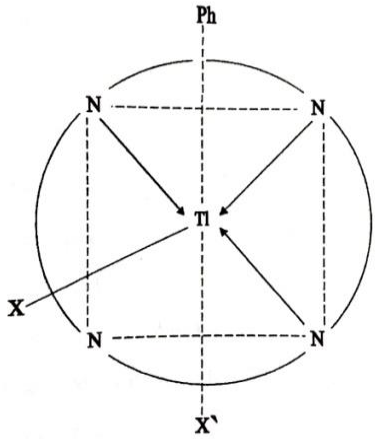

Fig:7.0 Octahedral Geometryof [$Ph_2TlCl.L$] complexes, Where In [$Ph_2TlCl.L$]= X=Cl; X^1= Ph, In[$PhTlCl_2.L$] = X= Cl; X^1=Cl

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