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Synthesis and characterisation of $[HgX_2.L^{1-10}]_x$ complexes with macrocyclic ligands: An photoelectron spectroscopic study

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Abstract

A complex compound is an entity consisting of two or more molecular species, which interact in such manner that they are being held together in a physically characterisable structural relationship. Macrocyclic and macropolycyclic effects designate the great thermodynamic stability of macrocyclic ligand complexes compared to non- macrocyclic analogues. The design of novel macrocyclic ligands and their complexes is interesting in view of their use as models to elaborate the metal ions interaction and to get an insight of the coordinating sites in metalloproteins and in biological system. Hg(II) complexes of the type $[HgX_2L^{1-10}]_x$, where $X=Cl$ or NO_3 ; L = macrocyclic ligands derived from $C_6H_5COCOC_6H_5$ (2mmol) condensation with different aliphatic diamine (2mmol) have been synthesized and characterized by elemental analysis, molar conductance, IR spectra and X-ray photoelectron i.e. (XPS) spectra. An octahedral geometry is also established for each complex.

Keywords: Hg (II), IR spectra, Molar conductance, Macrocyclic ligand, XPS

Introduction

Mercury and its compounds are dangerous and insidious poison ^[1-4]. It is a protoplasmic poison. It can be absorb through skin and lungs and also through gastrointestinal tract. Mercury compounds are toxic and 0.5g may be fetal. Mercury (II) fulminate may induce dermatitis and mercury chloride may induce dermatitis. Mercury is used industrially to fill fluorescent tubular lamps, AC rectifiers. Compounds of mercury is also used in various ways e.g. mercury (II) fulminate is a detonator; mercury oxide as a germicide and fungicide mercury (I) chloride forms part of standard electrode system and various organo mercury derivative have pharmaceutical applications. Many scientific parts of equipment depend for their working on mercury due to its unique combination of properties; they are thermometer barometer, toiler pumps, temperature compensating pendulums, diffusion pumps, mercury electrode, standard cells; gas and pressure regulators. The few mercury (I) compounds are know but mercury (II) compounds are well known e.g. pseudo halogen mercury (II) complexes ^[5-10]; mercury hydride ^[11-14]; halogen complexes of mercury (II) ^[15-21]; mercury oxide and mixed metal oxides ^[22-23]; mercury alkoxide, mercury basic salts compounds ^[24-25]; mercury (II) sulphides and mixed metal mercury (II) sulphides ^[26-28]; mercury compounds linked with sulphur; mercury compound with nitrogen ^[29-31]; mercury(II) with Phosphorus, as donor mercury (II) with O-donors ^[32], Mercury (II) complexes with macrocyclic ligands and bimetallic compounds of mercury (II) have been synthesized and studied well. Recent literature survey of past few decades reveals that very few mercury (II) compounds with macrocyclic ligands are known e.g. mercury (II) complexes with N_4S_2 macrocycles ^[33]; structural studies of polyether to mercury (II) halides ^[34] synthesis and structural characterization of mercury complexes ^[35]; mercury macrocyclic complexes: synthesis and crystal structure ^[36]; mercury (II) complexes with macrocyclic ligands derived from 2, 6-diacetylpyridine; mercury (II) complexes with macrocyclic ligands derived from diaminopropane or diaminobutane and hexanedione; mercury (II) complexes and its dinuclear complexes with macrocyclic ligands derived from [2+2] condensation of 2, 6-diformyl -4-methylphenol with malanoyl dihydrazide. Few comprehensive reviews were also published on synthesis, characterization and applications of mercury (II) complexes with macrocyclic ligands ^[37-53]. Mukta *et al* have reported synthesis and spectral studies of

[HgX₂L¹⁻¹⁰] (where X=Cl or Br or I; L=macrocyclic ligands) derived from thio diglycolic acid and different aliphatic diamines. Very recently V. K. Choudhary *et al.* [54-55] have synthesized and characterized [HgX₂L¹⁻¹⁰] type of complexes with mercury ligands. This research paper deals with synthesis and characterization of Hg (II) complexes with macrocyclic ligands derived from C₆H₅COCOC₆H₅ and different aliphatic diamines.

Experimental

The chemical C₆H₅COCOC₆H₅ (BDH); NH₂CH₂CH₂NH₂ (BDH); NH₂ (CH₂)₃NH₂ (BDH); NH₂ (CH₂)₄NH₂ (BDH); NH₂ (CH₂)₅NH₂ (BDH); NH₂ (CH₂)₆NH₂ (BDH); NH₂ (CH₂)₇NH₂ (BDH); NH₂ (CH₂)₈NH₂ (BDH); NH₂ (CH₂)₉NH₂ (BDH); NH₂ (CH₂)₁₀NH₂ (BDH); NH₂ (CH₂)₁₂NH₂ (BDH); HgCl₂ (Aldrich); HgBr₂ (Aldrich); HgI₂ (Aldrich); Methanol (BDH) were used after purification, distillation and dried as given in literature. Melting points were measured by using in sealed capillary tubes on melting point apparatus. The C and H analysis were measured in CDRI Lucknow. The chlorine and nitrogen were determined by Volhard's [56] and Kjeldahl's method [57] respectively. Molar

conductance were performed at room temperature on systronic model 305 conductivity bridge in dry acetone/DMF. FTIR spectra were recorded on Shimadzu [58] FTIR spectrophotometer in the range of 4000-200 cm⁻¹ using CsI Pellets. VG scientific ESCA-II spectrometer was used for recorded X-ray photoelectron spectra using Alka as source [59]. All the peaks were corrected for charging with reference to C1s peak 284.8 eV and fitted with Shirley background and a combination of Gaussian and Lorentzian line-shapes using ESC Ape software.

Preparation of [HgX₂L¹⁻¹⁰] complexes (where X=Cl or Br or I)

In C₆H₅COCOC₆H₅ (2mmol) in methanol added different aliphatic diamines (2mmol) i.e. NH₂ (CH₂)₂NH₂ or NH₂ (CH₂)₃NH₂ or NH₂ (CH₂)₄NH₂ or NH₂ (CH₂)₅NH₂ or NH₂ (CH₂)₆NH₂ or NH₂ (CH₂)₇NH₂ or NH₂ (CH₂)₈NH₂ or NH₂ (CH₂)₉NH₂ or NH₂ (CH₂)₁₀NH₂ or NH₂ (CH₂)₁₂NH₂ and refluxed for 3hrs and then put HgX₂ (where X=Cl or Br or I) (1mmol) and refluxed again for 2hrs. The resulting precipitate was filtered and recrystallised into benzene-perethene and air-dried (Fig 1).

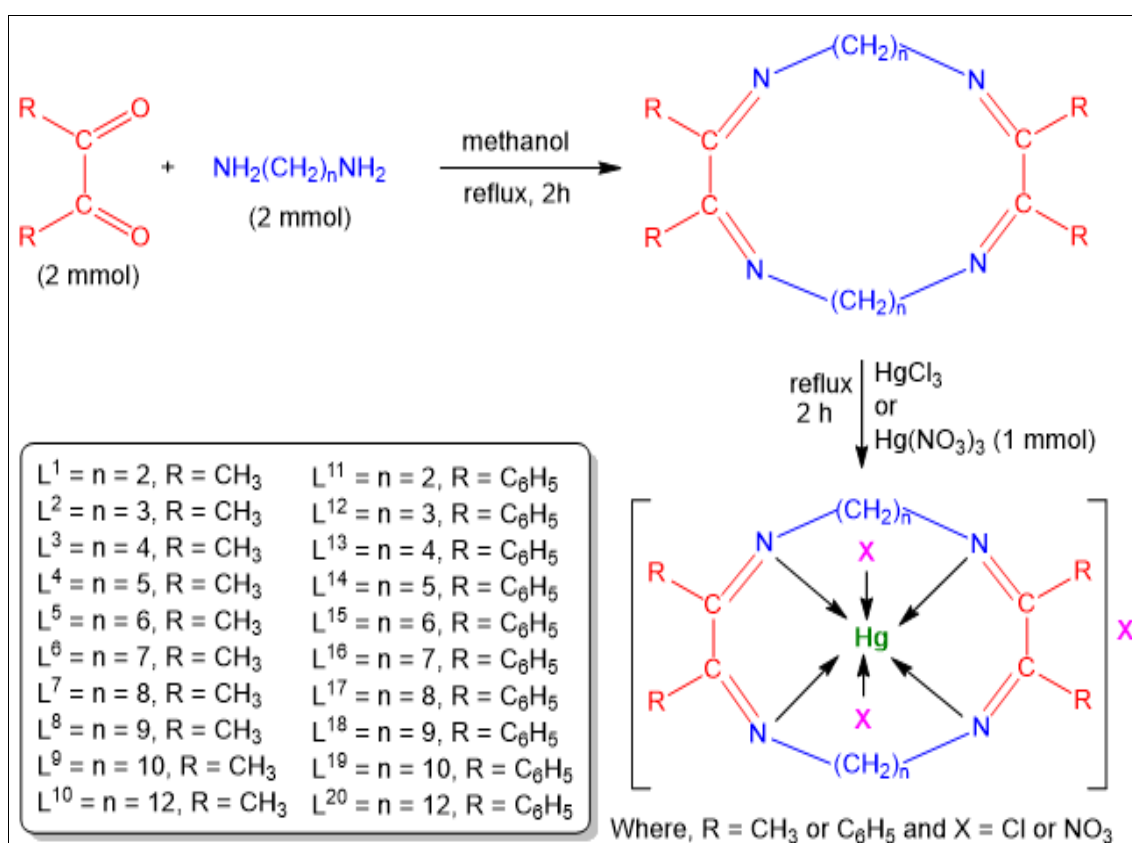


Fig 1: Preparation of [HgX₂L¹⁻¹⁰] X Complexes

Results and Discussion

These newly synthesized [HgX₂L¹⁻¹⁰] complexes were dark-red solid and stable at room temperature. The calculated and found elemental analysis for Hg, C, H and N were observed within ± 0.5% range. The molar conductance of each complex was found below 60 ohm⁻¹cm²mol⁻¹ in DMF at room temperature suggesting nature of each molecular adduct non-electrolyte. IR frequency for 9Hg-X and 9Hg-N were observed in the range of 340-315

cm⁻¹ and 478-420 cm⁻¹ respectively [60-61]. The binding energies (ev) for Hg3p_{1/2}; N1s and Xnp (Xbp=Cl_{2p} or Br_{3p_{1/2}} or I_{3p_{3/2}}) photoelectron peaks for ligands; HgX (where X= Cl or Br or I) and [HgX₂L¹⁻¹⁰] complexes are given in table I. Hg_{3p_{1/2,3/2}} photoelectron peaks binding energies in the starting material each starting material i.e. in HgX₂ (X=Cl or Br or I), suggested X is coordinated with HgX₂ (Fig.5-6).

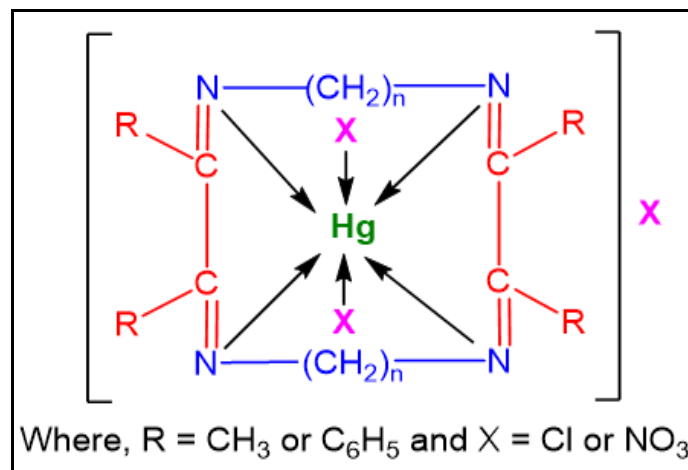


Fig 2: Proposed structure of octahedral complex

Table 1: Hg3p_{3/2}, 1/2; N1s and Xnp Diving Ligands and their Complexes [HgX₂.L¹⁻¹⁰]

Sr. No.	Ligand & Compound	Hg3p _{1/2,3/2}		N1s	Cl _{2p}	Br3p _{1/2}	I3p _{3/2}
		Hg3p _{1/2}	Hg3p _{3/2}				
1.	L ¹	-	-	400.8	-	-	-
2.	L ²	-	-	400.8	-	-	-
3.	L ³	-	-	400.8	-	-	-
4.	L ⁴	-	-	400.8	-	-	-
5.	L ⁵	-	-	400.8	-	-	-
6.	L ⁶	-	-	400.8	-	-	-
7.	L ⁷	-	-	400.8	-	-	-
8.	L ⁸	-	-	400.8	-	-	-
9.	L ⁹	-	-	400.8	-	-	-
10.	L ¹⁰	-	-	400.8	-	-	-
11.	HgCl ₂	279.8	847.8	-	201.8	-	-
12.	HgCl ₂ .L ¹	278.6	846.6	402.8	202.8	-	-
13.	HgCl ₂ .L ²	278.6	846.6	402.8	202.8	-	-
14.	HgCl ₂ .L ³	278.6	846.6	402.8	202.8	-	-
15.	HgCl ₂ .L ⁴	278.6	846.6	402.8	202.8	-	-
16.	HgCl ₂ .L ⁵	278.6	846.6	402.8	202.8	-	-
17.	HgCl ₂ .L ⁶	278.6	846.6	402.8	202.8	-	-
18.	HgCl ₂ .L ⁷	278.6	846.6	402.8	202.8	-	-
19.	HgCl ₂ .L ⁸	278.6	846.6	402.8	202.8	-	-
20.	HgCl ₂ .L ⁹	278.6	846.6	402.8	202.8	-	-
21.	HgCl ₂ .L ¹⁰	278.6	846.6	402.8	202.8	-	-
22.	HgBr ₂	279.0	847.8	-	-	189.6	-
23.	HgBr ₂ .L ¹	278.0	846.4	402.6	-	190.4	-
24.	HgBr ₂ .L ²	278.0	846.4	402.6	-	190.4	-
25.	HgBr ₂ .L ³	278.0	846.4	402.6	-	190.4	-
26.	HgBr ₂ .L ⁴	278.0	846.4	402.6	-	190.4	-
27.	HgBr ₂ .L ⁵	278.0	846.4	402.6	-	190.4	-
28.	HgBr ₂ .L ⁶	278.0	846.4	402.6	-	190.4	-
29.	HgBr ₂ .L ⁷	278.0	846.4	402.6	-	190.4	-
30.	HgBr ₂ .L ⁸	278.0	846.4	402.6	-	190.4	-
31.	HgBr ₂ .L ⁹	278.0	846.4	402.6	-	190.4	-
32.	HgBr ₂ .L ¹⁰	278.0	846.4	402.6	-	190.4	-
33.	HgI ₂	278.0	847.2	-	-	-	876.8
34.	HgI ₂ .L ¹	278.0	846.6	402.4	-	-	877.4
35.	HgI ₂ .L ²	278.0	846.6	402.4	-	-	877.4
36.	HgI ₂ .L ³	278.0	846.6	402.4	-	-	877.4
37.	HgI ₂ .L ⁴	278.0	846.6	402.4	-	-	877.4
38.	HgI ₂ .L ⁵	278.0	846.6	402.4	-	-	877.4
39.	HgI ₂ .L ⁶	278.0	846.6	402.4	-	-	877.4
40.	HgI ₂ .L ⁷	278.0	846.6	402.4	-	-	877.4
41.	HgI ₂ .L ⁸	278.0	846.6	402.4	-	-	877.4
42.	HgI ₂ .L ⁹	278.0	846.6	402.4	-	-	877.4
43.	HgI ₂ .L ¹⁰	278.0	846.6	402.4	-	-	877.4

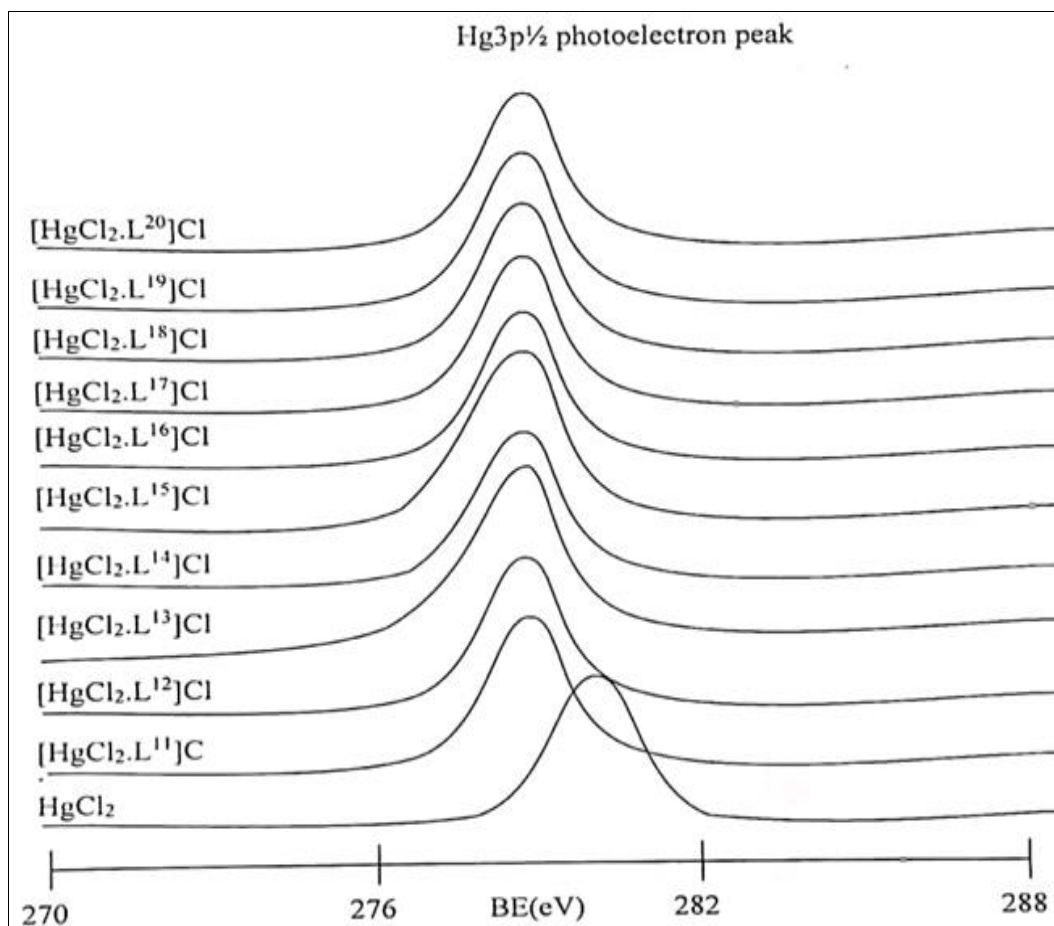


Fig 3: Hg3p_{1/2} binding energies (eV) of HgCl₂ and [HgCl₂.L¹⁻¹⁰] Complexes

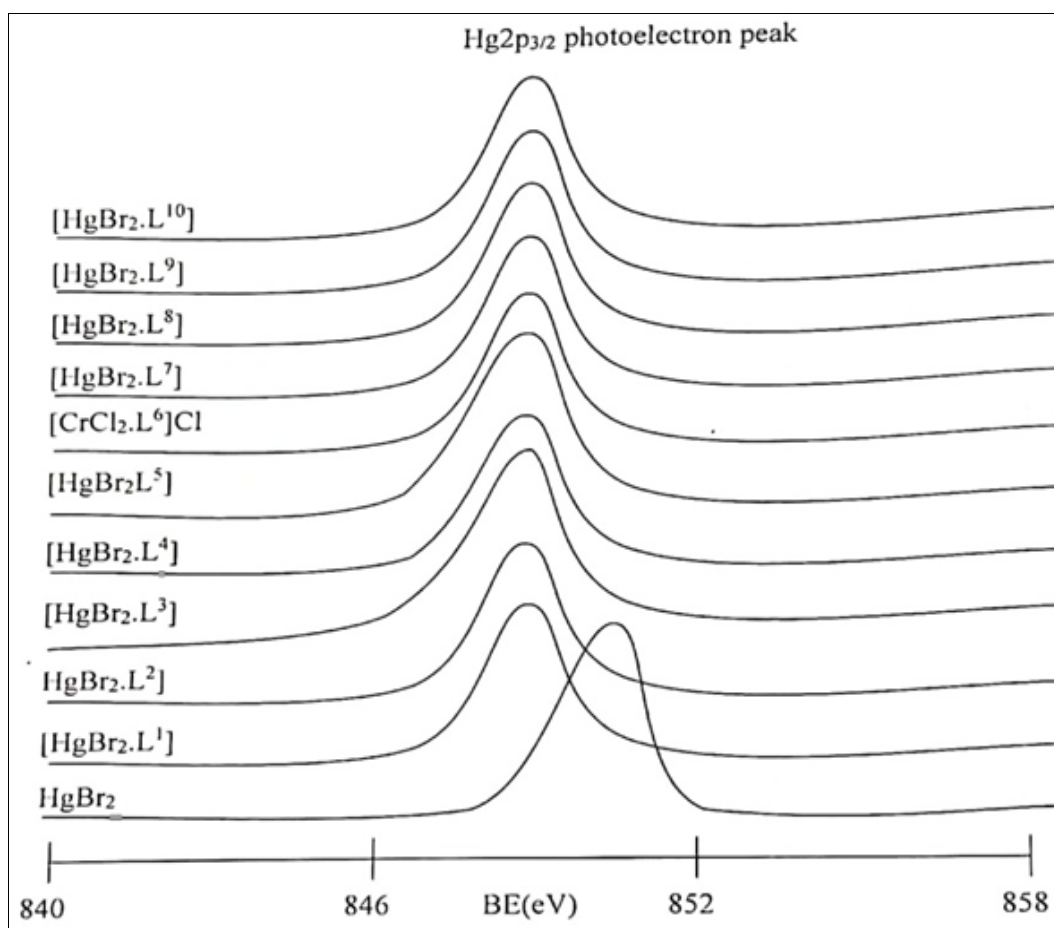


Fig 4: Hg2p_{3/2} binding energies (eV) of HgBr₂ and [HgBr₂.L¹⁻¹⁰] complexes

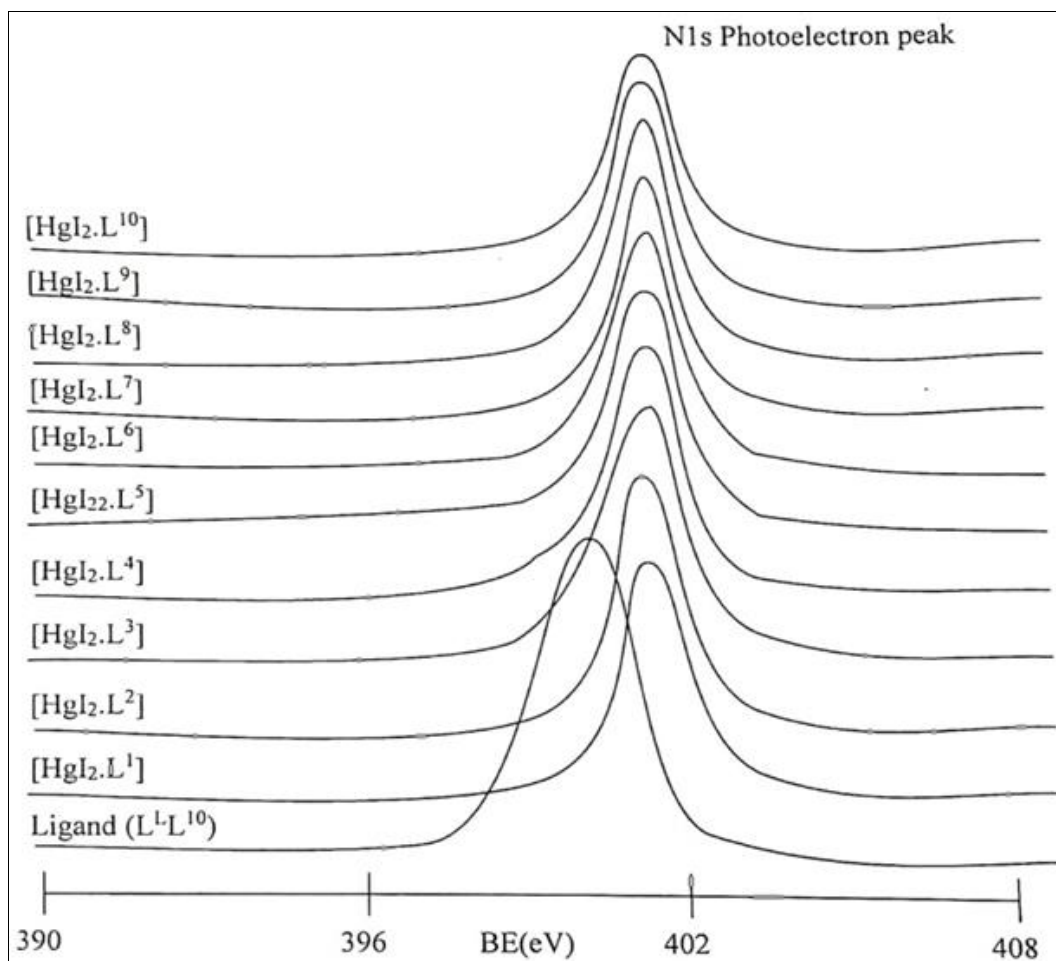


Fig 5: N1s binding energies (eV) of CrCl₃ and [CrCl₂L¹⁻¹⁰] complexes

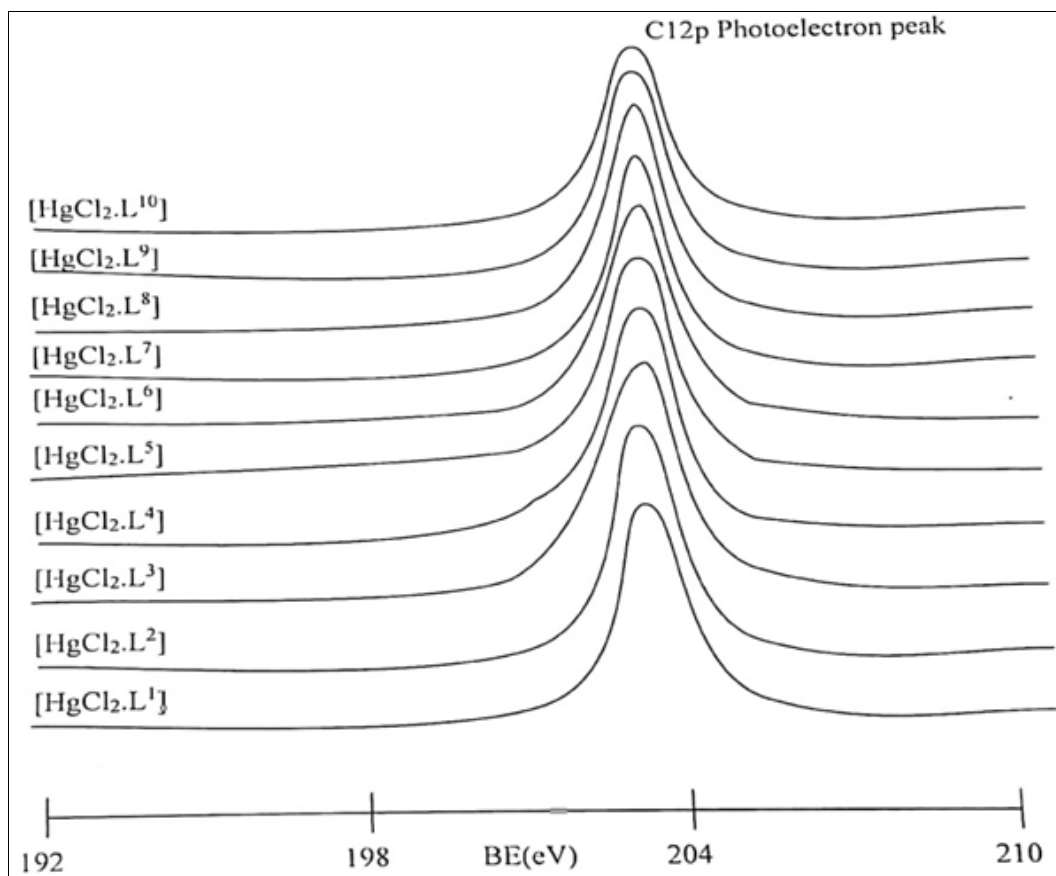


Fig 6: Cl2p binding energies (eV) of HgCl₂ and [HgCl₂L¹⁻¹⁰] complexes

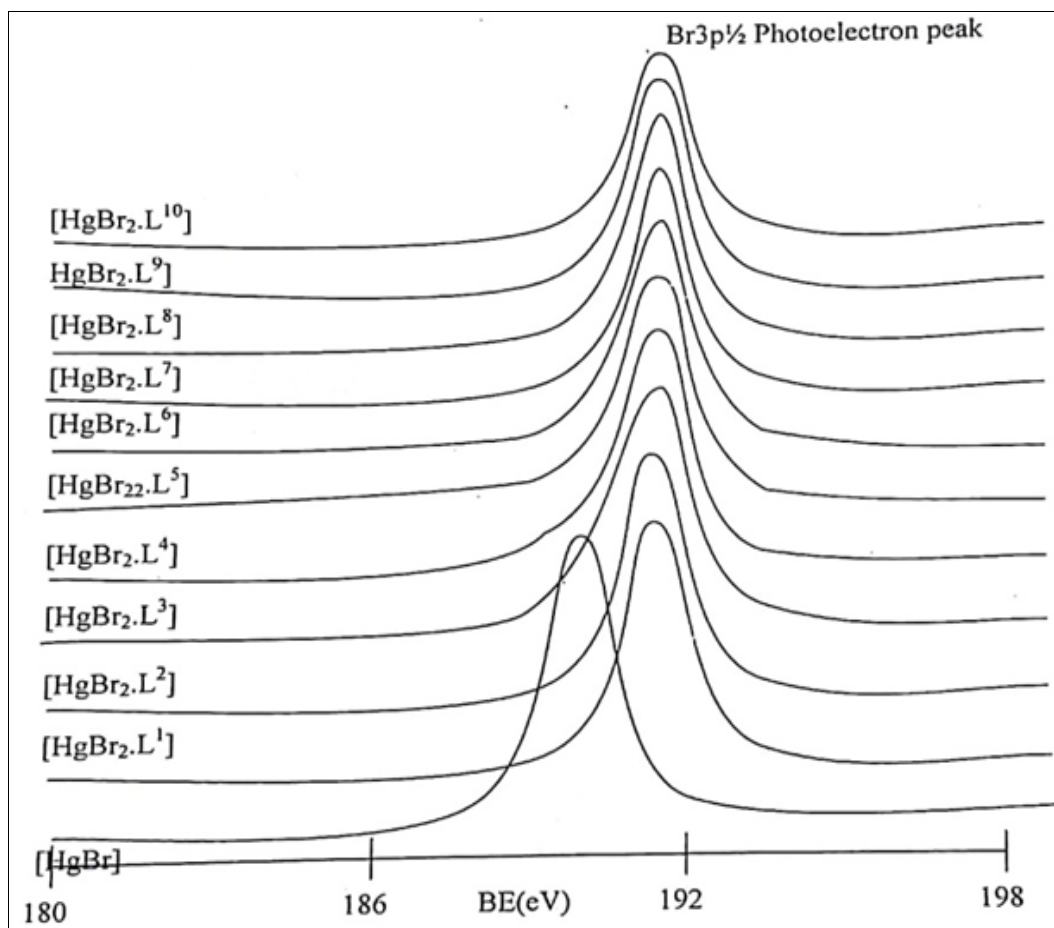


Fig 7: Br $3p_{1/2}$ binding energies (eV) of HgBr₂ and [HgBr₂.L¹⁻¹⁰] complexes

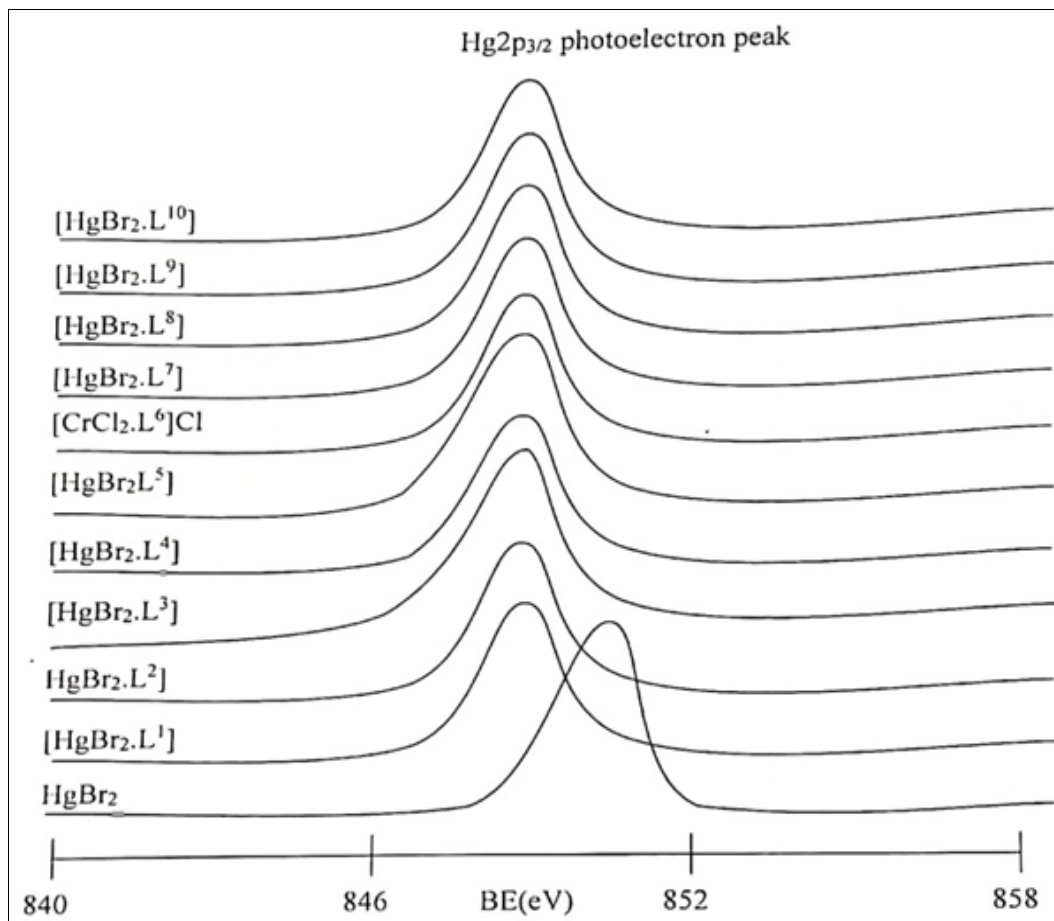


Fig 8: Hg $2p_{3/2}$ bindings energies (eV) of HgBr₂ and [HgBr₂.L¹⁻¹⁰] complexes

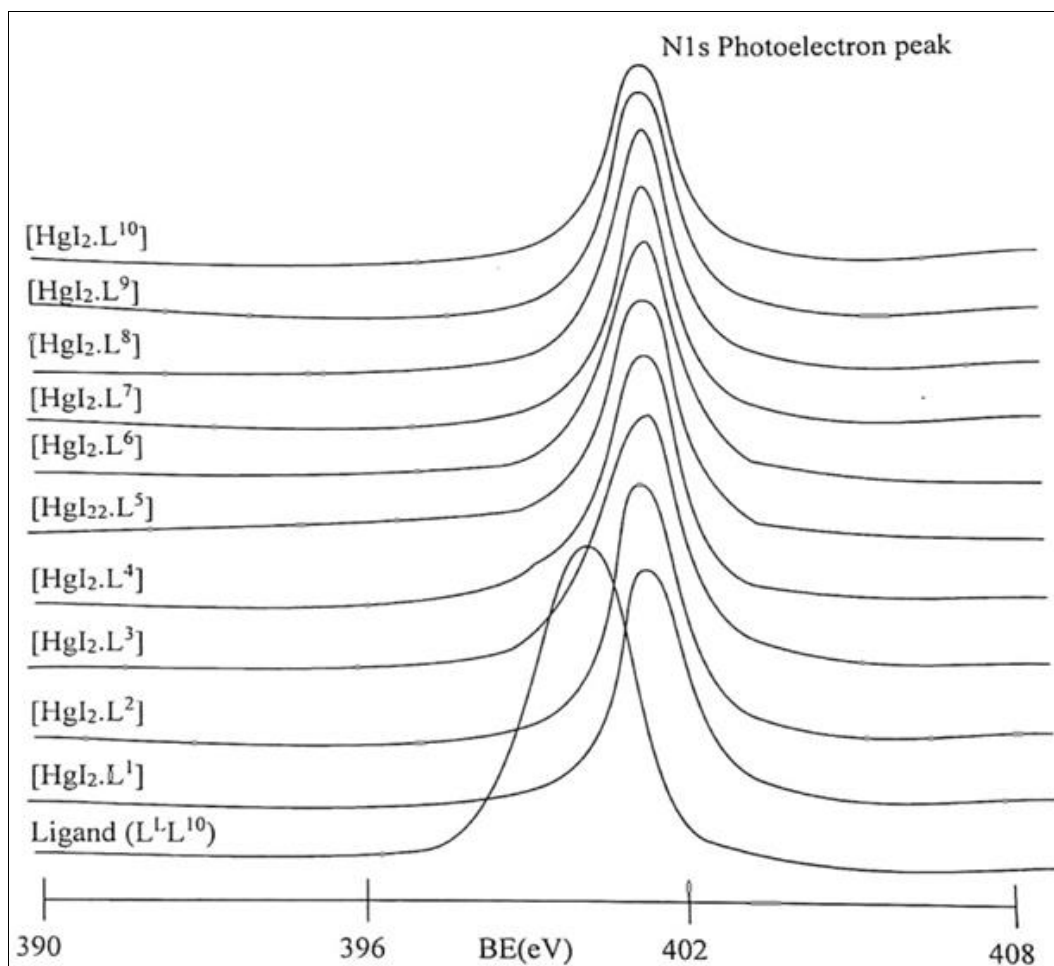


Fig 9: N1s binding energies (eV) of CrCl₃ and [CrCl₂L¹⁻¹⁰] complexes

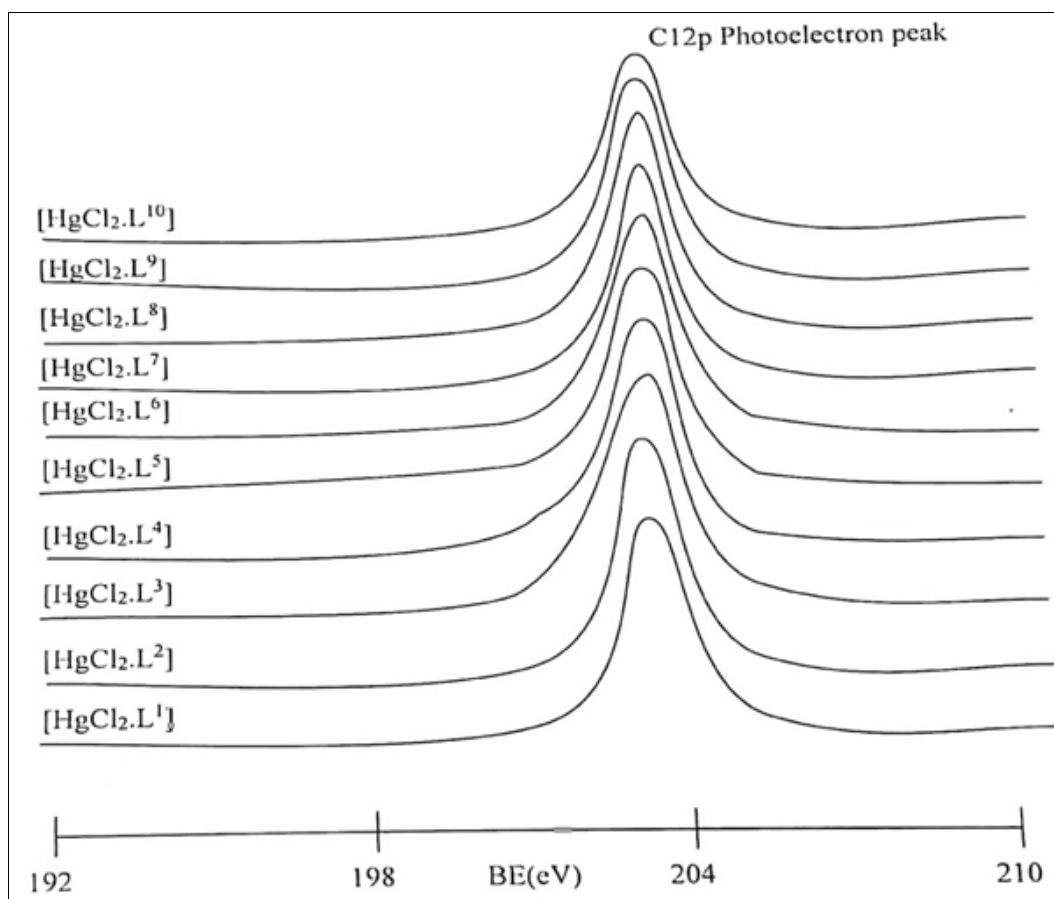


Fig 10: Cl2p binding energies (eV) of HgCl₂ and [HgCl₂L¹⁻¹⁰] complexes

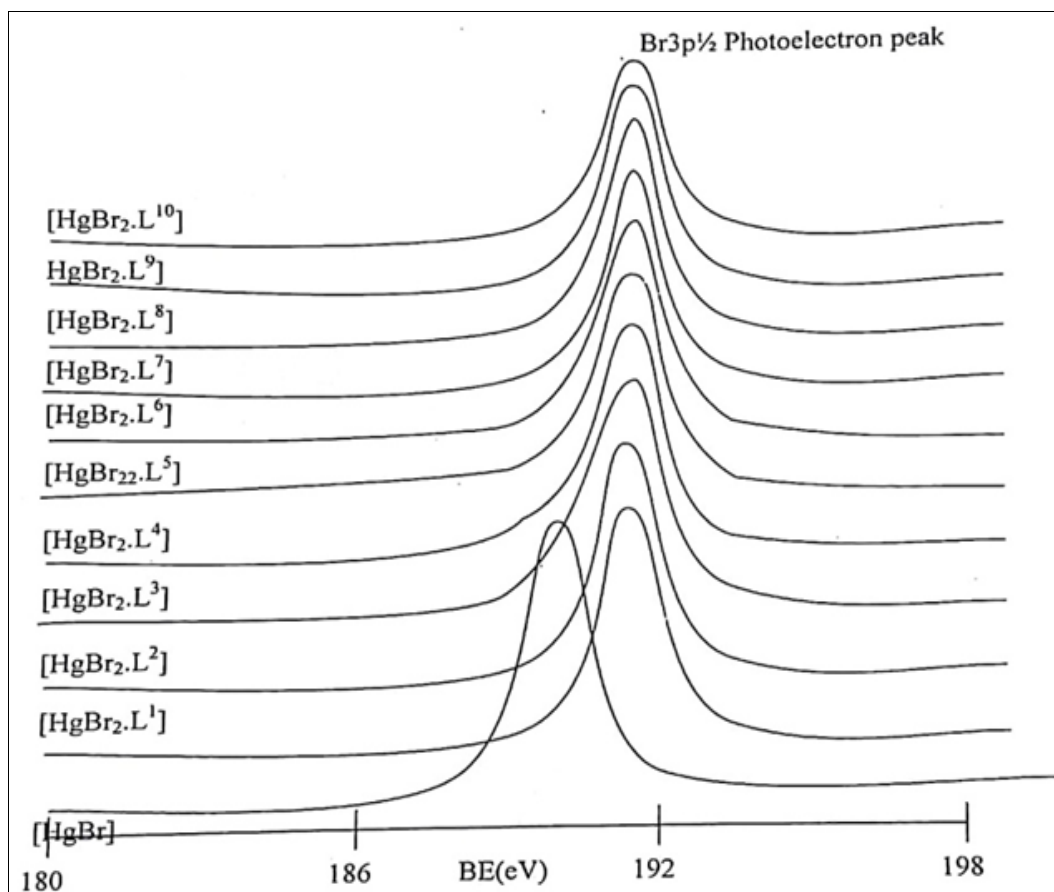


Fig 11: Br $3p_{1/2}$ binding energies (eV) of HgBr $_2$ and [HgBr $_2$.L $^{1-10}$] complexes

Conclusion

On the basis of elemental analysis, molar conductance, IR and XPS data, the structure of each complex may be proposed as given in fig.7.0 and an octahedral geometry may be established for each complex.

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