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 \([HgLX.L_2]^{1-10}X\), where \(X=Cl\) or \(NO_3\); \(L=\) macrocyclic ligands derived from \(C_6H_4(COOC)CH_2\) (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, Macroyclic 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 fatal. 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 known 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) sulphones 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 \(N_2S_2\) macrocycles \([33]\); structural studies of polymer 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-diacyethylpyridine; mercury (II) complexes with macrocyclic ligands derived from dianinopropane or dianinobutane and hexanedione; mercury (II) complexes and its dinuclear complexes with macrocyclic ligands derived from \([24+2]\) 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 \textit{et al} have reported synthesis and spectral studies of...
Experimental

The chemical C₆H₄COCOC₆H₄ (BDH); NH₂(CH₂)₄NH₂ (BDH); NH₂(CH₂)₆NH₂ (BDH); NH₂(CH₂)₈NH₂ (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 [58] 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 Shimedzu [56] 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 [55]. All the peaks were corrected for charging with reference to Cls peak 284.8 eV and fitted with Shirley background and a combination of Gaussian and Lorentzian line-shapes using ESC Ape software.

Preparation of [HgX₂L⁻¹⁰] complexes (where X=Cl or Br or I)

In C₆H₄COCOC₆H₄ (2mmol) in methanol added different aliphatic diamines (2mmol) i.e. NH₂(CH₂)₄NH₂ or NH₂(CH₂)₆NH₂ or NH₂(CH₂)₈NH₂ 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-per-ethene and air-dried (Fig 1).

Results and Discussion

These newly synthesized [HgX₂L⁻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⁻¹cm⁻¹mol⁻¹ in DMF at room temperature suggesting nature of each molecular adduct non-electrolyte. IR frequency for δHg-X and δHg-N were observed in the range of 340-315 cm⁻¹ and 478-420 cm⁻¹ respectively [60-61]. The binding energies (ev) for Hg3pₓ/₂; N1s and Xnp (Xbp=Clpery or Brpery or Ipery) photoelectron peaks for ligands; HgX (where X= Cl or Br or I) and [HgX₄L⁻₁⁰] complexes are given in table I. Hg₃pₓ/₂, 3d 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).
Table 1: Hg\(_{3\text{p}3/2, \frac{1}{2}}\); N1s and X\(\text{p}\) Diving Ligands and their Complexes [Hg\(\text{X}_{2}:L^{1-10}\)]

<table>
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<tr>
<th>Sr. No.</th>
<th>Ligand &amp; Compound</th>
<th>Hg(_{3\text{p}3/2, \frac{1}{2}})</th>
<th>N1s</th>
<th>Cl(_{3\text{p}})</th>
<th>Br(_{3\text{p}3/2})</th>
<th>I(_{3\text{p}3/2})</th>
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Fig 3: Hg3p½ binding energies (eV) of HgCl₂ and [HgCl₂:L₁⁻¹⁰] Complexes

Fig 4: Hg2p½ 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: Br3p½ binding energies (eV) of HgBr₂ and [HgBr₂L₁⁻¹⁰] complexes

Fig 8: Hg2p½ binding energies (eV) of HgBr₂ and [HgBr₂L₁⁻¹⁰] complexes
Fig 9: N1s binding energies (eV) of CrCl$_3$ and [CrCl$_2$L$_{1-10}$] complexes

Fig 10: Cl2p binding energies (eV) of HgCl$_2$ and [HgCl$_2$L$_{1-10}$] complexes
Conclusion
On the basis of elemental analysis, molar conductance, IR and XPS data, the structure of each complex may be propose as given in fig. 7.0 and an octahedral geometry may be established for each complex.

References