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Synthesis and characterisation of $[HgX_2.L^{1-10}]$ Complexes

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Abstract: Forty complexes of the type $[HgX_2 . L^{1-10}]$ (where X = Cl or Br or NO_3 or CH_3COO and L^{1-10} i.e. 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 or L^{10} macrocyclic ligands) have been synthesized and characterized by elemental analysis, molar conductance, IR and X-ray photoelectron spectra data. An octahedral geometry was also established for each $[HgX_2 .L^{1-10}]$ complexes.

(Keywords: Macrocyclic Ligands, Elemental analysis, Molar conductance, IR and X-ray photoelectron spectra.)

Introduction

In the synthesis and characterization of $[HgX_2 .L^{1-10}]$ complexes where X= Cl or Br or NO_3 or CH_3COO and L^{1-10} i.e. 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 or L^{10} macrocyclic Schiff base ligands derived from condensation of benzene 1,3,5-tricarboxylic acid and various aliphatic diamines [1], in this research paper, $[HgX_2 .L^{1-10}]$ molecular adducts synthesis and characterization (where X = Cl or Br or NO_3 or CH_3COO and L^{1-10} i.e. 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 or L^{10}) macrocyclic ligands derived from condensation of p-thathalic acid i.e. terephthalic acid with different diamines i.e. in $L^1 = NH_2CH_2CH_2CH_2NH_2$; in $L^2 = NH_2CH_2CH(CH_3)CH_2NH_2$; in $L^3 = NH_2CH_2NH(CH_2)_2NH_2$; in $L^4 = NH_2CH_2C(CH_3)_2CH_2NH_2$; in $L^5 = NH_2(CH_2)_6NH_2$; in $L^6 = NH_2(CH_2)_7NH_2$; in $L^7 = NH_2(CH_2)_8NH_2$; in $L^8 = NH_2(CH_2)_9NH_2$; i n $L^9 = NH_2(CH_2)_{10}NH_2$; and in $L^{10} = NH_2(CH_2)_{12}NH_2$ will be conducted and their structure will be propose on basis of elemental analysis, molar conductance, IR and XPS data.

Experimental

$Hg(NO_3)_2$; $HgCl_2$; $Hg(CH_3COO)_2$ and $HgBr_2$ were used (E. Merck) (AR Grade) and recrystallised ; air-dried before use. All used solvents were from Ranbaxy (AR Grade); purified; air- dried before used. Different aliphatic diamines were purchased from BDH (AR Grade) used before purification.

Melting points were measured on melting points apparatus. The C, N, H and Cl or Br were determined by CDRI Lucknow India. Molar conductances were determined on conductivity bridge in DMF at room temperature. Infra red spectra recorded on Perkin- Elmer Infra–red spectrometer using Cs pellets. X-ray photoelectron spectra i.e. (XPS) were determined on UG Scientific ESCA-II spectrometer using AlKα as X-ray source.

Terephthalic acid or p-thathalic acid (2mmol) in 50 ml dry ethanol mixed with different aliphatic diamines (2mmol) i.e. $NH_2CH_2CH_2CH_2NH_2$ or $NH_2CH_2CH(CH_3)CH_2NH_2$ or $NH_2CH_2NH(CH_2)_2NH_2$ or $NH_2CH_2C(CH_3)_2CH_2NH_2$ or $NH_2(CH_2)_6NH_2$ or $NH_2(CH_2)_7NH_2$ or $NH_2(CH_2)_8NH_2$ or $NH_2(CH_2)_9NH_2$ or $NH_2(CH_2)_{10}NH_2$ or $NH_2(CH_2)_{12}NH_2$ in a three neck flask and refluxed for three hours and then added into this solution HgX_2 (1m mol) in 50 ml and refluxed again for another two hours. The precipitate was found, filtered and recrystallised by benzene: pet-ether (9:1) and dried on vacuum.

Results and Discussion

By condensation of p-thathalic acid with different aliphatic diamines i.e. $NH_2CH_2CH_2CH_2NH_2$ or $NH_2CH_2CH(CH_3)CH_2NH_2$ or $NH_2CH_2NH(CH_2)_2NH_2$ or $NH_2CH_2C(CH_3)_2CH_2NH_2$ or $NH_2(CH_2)_6NH_2$ or $NH_2(CH_2)_7NH_2$ or $NH_2(CH_2)_8NH_2$ or $NH_2(CH_2)_9NH_2$ or $NH_2(CH_2)_{10}NH_2$ or $NH_2(CH_2)_{12}NH_2$ in 2:2 molar ratio, given ten macrocyclic Schiff base ligands i.e. 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 or L^{10} (Fig. 1). In each prepared macrocyclic ligand (1mmol) of HgX_2 (X= Cl or Br or NO_3 or CH_3COO) added and refluxed for another two hours, precipitate was obtained called molecular adduct i.e. [HgX_2 .L^{1-10}] were solid, stable and dark brick red in colour. The elemental analysis for Hg, C, N, H and Cl or Br were found within +/- 0.5%. The molar conductance of each molecular adduct were found below 50 $ohm^{-1}cm^2mol^{-1}$ in DMF at room temperature, suggesting nonelectrolyte [2]. IR frequency for $^9N_{Hg-N}$ and $^9N_{Hg-X}$ were observed in the range of 479-417 cm^{-1} [3-4] and 340-320 cm^{-1} respectively. The binding energies (eV) for Hg $3P_{1/2,3/2}$ and N1s photoelectron peaks for ligands, HgX_2 and [HgX_2 .L^{1-10}] molecular adducts (where X= Cl or Br or NO_3 or CH_3COO and L^{1-10} = macrocyclic ligands) are listed in Table-1.

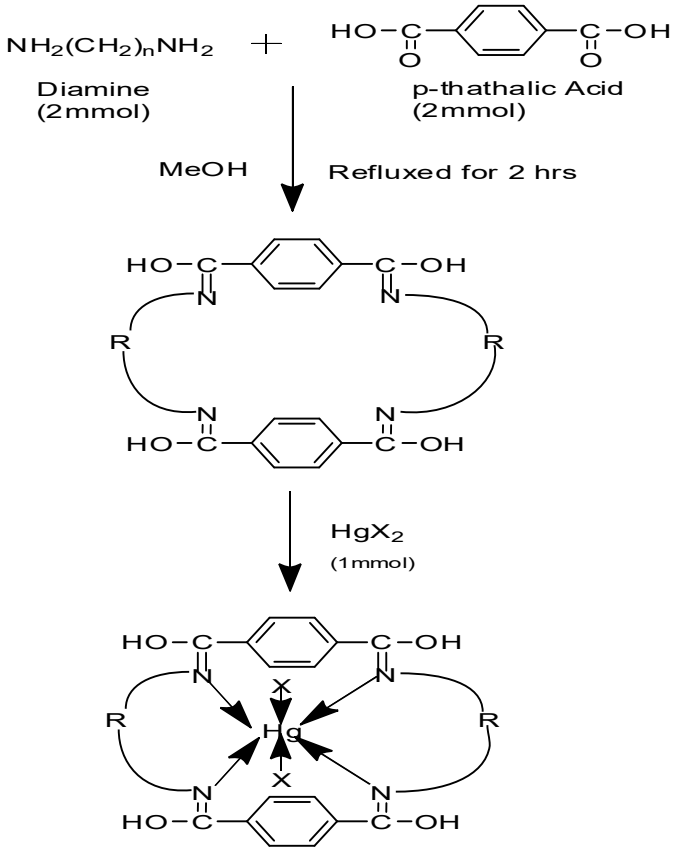

Fig. 1 Preparation of [HgX_2.L] complexes where X= Cl or Br or NO_3 or CH_3COO $NH_2CH_2NH(CH_2)_2NH_2$; $NH_2CH_2C(CH_3)_2CH_2NH_2$; $NH_2(CH_2)_6NH_2$; $NH_2(CH_2)_7NH_2$; $NH_2(CH_2)_8NH_2$; $NH_2(CH_2)_9NH_2$; $NH_2(CH_2)_{10}NH_2$ and $NH_2(CH_2)_{12}NH_2$.

In HgX_2 starting material, $Hg3P_{1/2,3/2}$ and Hg $3d_{3/2,5/2}$ photoelectron peaks are higher than in synthesized [$HgX_2.L^{1-10}$] molecular adducts. (Table I and Fig. 1). From these XPS data it is confirm that electron density is increased on $Hg3P_{1/2,3/2}$ and Hg $3d_{3/2,5/2}$ in [$HgX_2.L^{1-10}$] due to coordination of ligand[6]. Furthermore, in all these molecular adducts [$HgX_2.L^{1-10}$]; only one single symmetrical N1s photoelectron peak is observed to higher binding energy side than their each macrocyclic ligand (Table I and Fig.3) ; suggesting all four nitrogen atoms of each macrocyclic ligand is coordinated with mercury metal ion [6]. The Hg 3s photoelectron peak in each [$HgX_2.L^{1-10}$] molecular adduct has shown a single symmetrical photoelectron peak, suggested each are diamagnetic [5].

Table - 1

Hg $3p_{1/2,3/2}$; Hg $3d_{3/2,5/2}$ and N1s binding energies (eV) in ligand, HgX_2 and [HgX_2.L] complexes

Sr. No.	Ligand and Complex	Hg $3P_{1/2,3/2}$		$Hg3d_{3/2,5/2}$		N1s	
		$Hg3P_{1/2}$	$Hg3P_{3/2}$	$Hg3d_{3/2}$	$Hg3d_{5/2}$	Uncoord.	Coord.
1.	L^1	-	-	-	-	401.0	-
2.	L^2	-	-	-	-	401.0	-
3.	L^3	-	-	-	-	401.0	-
4.	L^4	-	-	-	-	401.0	-
5.	L^5	-	-	-	-	401.0	-
6.	L^6	-	-	-	-	401.0	-
7.	L^7	-	-	-	-	401.0	-
8.	L^8	-	-	-	-	401.0	-
9.	L^9	-	-	-	-	401.0	-
10.	L^{10}	-	-	-	-	401.0	-
11.	$HgCl_2$	280.8	848.8	386.8	296.8	-	-
12.	$HgCl_2.L^1$	279.8	847.8	385.8	295.8	-	404.8
13.	$HgCl_2.L^2$	279.8	847.8	385.8	295.8	-	404.8
14.	$HgCl_2.L^3$	279.8	847.8	385.8	295.8	-	404.8
15.	$HgCl_2.L^4$	279.8	847.8	385.8	295.8	-	404.8
16.	$HgCl_2.L^5$	279.8	847.8	385.8	295.8	-	404.8
17.	$HgCl_2.L^6$	279.8	847.8	385.8	295.8	-	404.8
18.	$HgCl_2.L^7$	279.8	847.8	385.8	295.8	-	404.8
19.	$HgCl_2.L^8$	279.8	847.8	385.8	295.8	-	404.8
20.	$HgCl_2.L^9$	279.8	847.8	385.8	295.8	-	404.8
21.	$HgCl_2.L^{10}$	279.8	847.8	385.8	295.8	-	404.8
22.	$HgBr_2$.	280.6	848.6	386.6	296.6	-	-
23.	$HgBr_2.L^1$	279.6	847.6	385.6	295.6	-	404.6
24.	$HgBr_2.L^2$	279.6	847.6	385.6	295.6	-	404.6
25.	$HgBr_2.L^3$	279.6	847.6	385.6	295.6	-	404.6
26.	$HgBr_2.L^4$	279.6	847.6	385.6	295.6	-	404.6
27.	$HgBr_2.L^5$	279.6	847.6	385.6	295.6	-	404.6
28.	$HgBr_2.L^6$	279.6	847.6	385.6	295.6	-	404.6
29.	$HgBr_2.L^7$	279.6	847.6	385.6	295.6	-	404.6
30.	$HgBr_2.L^8$	279.6	847.6	385.6	295.6	-	404.6
31.	$HgBr_2.L^9$	279.6	847.6	385.6	295.6	-	404.6
32.	$HgBr_2.L^{10}$	279.6	847.6	385.6	295.6	-	404.6
33.	$Hg(NO_3)_2$	280.4	848.4	386.4	296.4	-	-
34.	$Hg(NO_3)_2.L^1$	279.4	847.4	385.4	295.4	-	404.4
35.	$Hg(NO_3)_2.L^2$	279.4	847.4	385.4	295.4	-	404.4
36.	$Hg(NO_3)_2.L^3$	279.4	847.4	385.4	295.4	-	404.4

37.	$Hg(NO_3)_2.L^4$	279.4	847.4	385.4	295.4	-	404.4
38.	$Hg(NO_3)_2.L^5$	279.4	847.4	385.4	295.4	-	404.4
39.	$Hg(NO_3)_2.L^6$	279.4	847.4	385.4	295.4	-	404.4
40.	$Hg(NO_3)_2.L^7$	279.4	847.4	385.4	295.4	-	404.4
41.	$Hg(NO_3)_2.L^8$	279.4	847.4	385.4	295.4	-	404.4
42.	$Hg(NO_3)_2.L^9$	279.4	847.4	385.4	295.4	-	404.4
43.	$Hg(NO_3)_2.L^{10}$	279.4	847.4	385.4	295.4	-	404.4
44.	$Hg(CH_3COO)_2$	280.2	848.2	386.2	296.2	-	-
45.	$Hg(CH_3COO)_2.L^1$	279.2	847.2	385.2	295.2	-	404.2
46.	$Hg(CH_3COO)_2.L^2$	279.2	847.2	385.2	295.2	-	404.2
47.	$Hg(CH_3COO)_2.L^3$	279.2	847.2	385.2	295.2	-	404.2
48.	$Hg(CH_3COO)_2.L^4$	279.2	847.2	385.2	295.2	-	404.2
49.	$Hg(CH_3COO)_2.L^5$	279.2	847.2	385.2	295.2	-	404.2
50.	$Hg(CH_3COO)_2.L^6$	279.2	847.2	385.2	295.2	-	404.2
51.	$Hg(CH_3COO)_2.L^7$	279.2	847.2	385.2	295.2	-	404.2
52.	$Hg(CH_3COO)_2.L^8$	279.2	847.2	385.2	295.2	-	404.2
53.	$Hg(CH_3COO)_2.L^9$	279.2	847.2	385.2	295.2	-	404.2
54.	$Hg(CH_3COO)_2.L^{10}$	279.2	847.2	385.2	295.2	-	404.2

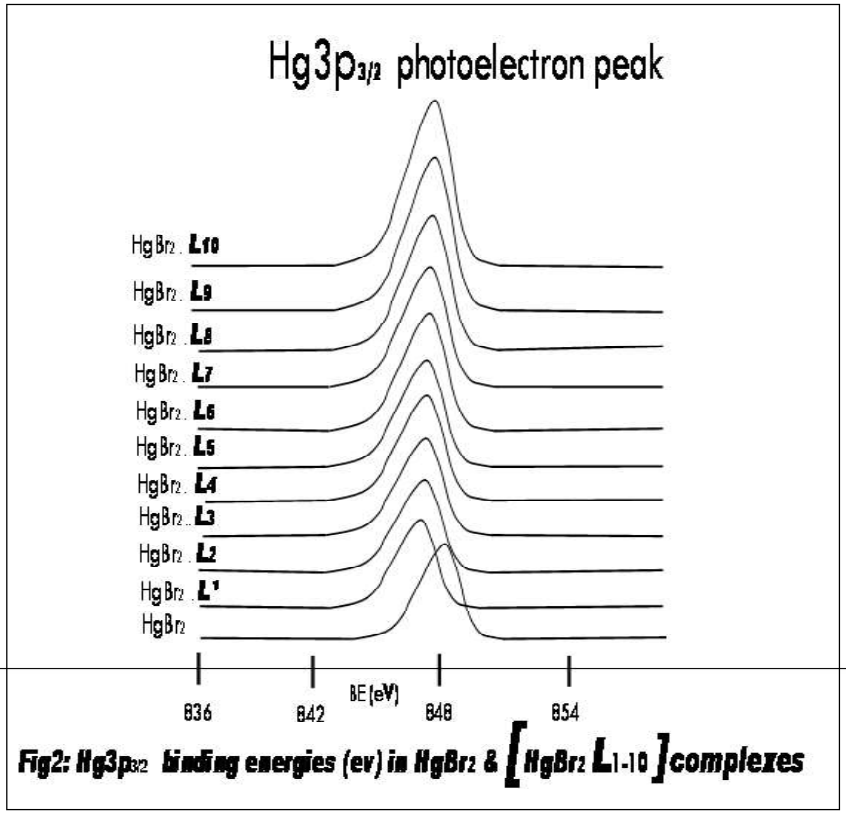

Fig2: $Hg3p_{3/2}$ binding energies (ev) in $HgBr_2$ & $[HgBr_2 L_{1-10}]$ complexes

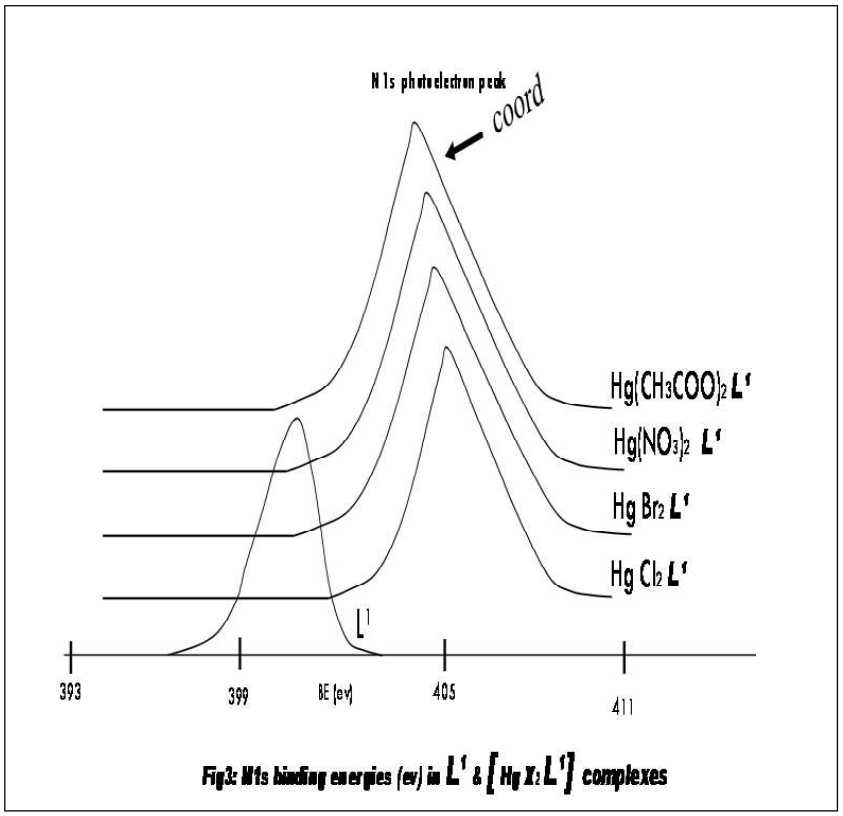

Fig3: N1s binding energies (ev) in L' & [Hg X2 L'] complexes

Conclusion

On the basis of elemental analysis, molar conductance, IR and XPS data, the structure of each molecular adduct may be propose as given in fig:1 and an octahedral geometry may be established for each [$HgX_2.L^{1-10}$].

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