

SYNTHESIS AND CHARACTERISATION OF [HgX₂.L¹⁻¹⁰] COMPLEXES

¹Vijay Kumar Chaudhary, ²Dhruv Kumar Agarwal, ²Anil Kumar, ²Mukesh Srivastava

¹Assistant Professor, ²Associate Professor

¹Department of Chemistry, Dayanand Vedic College, Orai, India

²Department of Chemistry, Bipin Bihari College, Jhansi, India

Email- vijay.chaudhary10@gmail.com

ABSTRACT:

Forty complexes of the type [HgX₂.L¹⁻¹⁰] (where X= Cl or Br or NO₃ or CH₃COO and L¹⁻¹⁰ = ten macrocyclic Schiff base ligands) have been synthesized and characterized by elemental analysis, molar conductance, IR and XPS data. An octahedral geometry was also established for each molar adduct.

Key words- Macrocyclic Ligands, elemental analysis, molar conductivity, IR and X-ray photoelectron spectra.

INTRODUCTION:

During last few decades macrocyclic compounds have considered to much interest due to their so many applications in coordination chemistry [11]; bioinorganic chemistry [12-14]; catalysts [15-21]; bio-coordination chemistry [22] due to their ability to bind different kinds of substrates. They form stable and selective complexes with a variety of inorganic and organic cations and with some anionic cations and neutral organic biological substrates provide supramolecular compounds with special properties and applications [23]. The unusual coordination properties of many synthetic and natural macrocyclic ligands have been studied extensively.

The studies of various complexes of Schiff base macrocyclic ligands with different size and number of donor atoms for coordination with a variety of metal centers have been extensively reported [24]. Many macrocyclic metal complexes are synthesized through template synthesis [25-27]. Many macrocyclic metal complexes work as enzymes or carriers in ligand environment [28-29] and used as modeling the active sites of metalloenzymes [30].

In this synthesis of [HgX₂.L¹⁻¹⁰] (where X= Cl or Br or NO₃ or CH₃COO and L¹⁻¹⁰ = ten macrocyclic Schiff base ligands) derived from condensation of trimestic acid with different aliphatic diamines[31], in this present research paper, the synthesis and characterization of [HgX₂.L¹⁻¹⁰] molar adducts (where X= Cl or Br or NO₃ or CH₃COO and L¹⁻¹⁰ = ten macrocyclic Schiff base ligands derived from condensation of aquiric acid i.e. 3,4- dihydroxy-3- cyclobutene-1-2-dione with different aliphatic diamines i.e. in L¹ = NH₂CH₂CH₂CH₂NH₂; in L² = NH₂CH₂CH(CH₃)CH₂NH₂; in L³ = NH₂CH₂NH(CH₂)₂NH₂; in L⁴ = NH₂CH₂C(CH₃)₂CH₂NH₂; in L⁵ = NH₂(CH₂)₆NH₂; in L⁶ = NH₂(CH₂)₇NH₂; in L⁷ = NH₂(CH₂)₈NH₂; in L⁸ = NH₂(CH₂)₉NH₂; in L⁹ = NH₂(CH₂)₁₀NH₂ and in L¹⁰ = NH₂(CH₂)₁₂NH₂; will be done and products structure and geometry will be establish on basis of various physicochemical techniques.

MATERIALS AND METHOD:

Hg(CH₃COO)₂; HgCl₂; Hg(NO₃)₂ and HgBr₂ were purchased and used from E. Merck (AR Grade) and re crystallized and dried before use. All the solvents were used from Ranbaxy (AR Grade) and used after purification and dried as given in literature [32-34]. Other chemicals like different aliphatic diamines and squaric acid i.e. 3-4-dihydroxy-3-cyclobutane-1-2-dione were used Aldrich and BDH (AR Grade) respectively and used after purification.

Elemental analysis for C, H, N and Cl or Br were determined in CDRI, Lucknow; India. Ir spectra were recorded on Perkin-Elmer 1000 IR spectrometer using CsI pellets. Molar conductance were measured in DMF using an Elico-CM82 conductivity bridge at room temperature. XPS were recorded on UG scientific ESCA-II spectrometer using AlK_α as source.

PREPARATION OF [HGX₂.L¹⁻¹⁰] COMPLEXES:

In 50 ml dry methanol squaric acid i.e. 3-4-dihydroxy-3-cyclobutene-1-2-dione (2mmol) was mixed with different aliphatic diamines (2mmol) i.e. NH₂CH₂CH₂CH₂NH₂ or NH₂CH₂CH(CH₃)CH₂NH₂ or NH₂CH₂NH(CH₂)₂NH₂ or NH₂CH₂C(CH₃)₂CH₂NH₂ or NH₂(CH₂)₆NH₂ or NH₂(CH₂)₇NH₂ or NH₂(CH₂)₈NH₂ or NH₂(CH₂)₉NH₂ or NH₂(CH₂)₁₀NH₂ and NH₂(CH₂)₁₂NH₂ in a three necked reflux flash and refluxed for two hours and then added into this solution HgX₂ (1mmol) and refluxed for another two hours. The red brick colored precipitate was found, filtered and re-crystallized by benzene : petether (9:1) and air- dried. (Fig.1).

RESULTS AND DISCUSSION:

The condensation of squaric acid i.e. 3-4-dihydroxy-3-cyclobutene-1-2-dione with different aliphatic diamines in 2:2 molar ratio given product of ten macrocyclic Schiff base ligands i.e. L¹ or L² or L³ or L⁴ or L⁵ or L⁶ or L⁷ or L⁸ or L⁹ or L¹⁰ (Fig. 1). Further when in each macrocyclic ligand HgX₂ (1mmol) (where X= Cl or Br or NO₃ or CH₃COO) was added and refluxed for another three hours, red brick colored precipitate was obtained.

All the precipitates were stable. For each [HgX₂.L¹⁻¹⁰], Hg, C, H, N and Cl or Br were found within ±0.5%. Each molecular adduct has shown molar conductivity below than 50 ohm⁻¹cm²mol⁻¹ in DMF at room temperature, suggesting non-ionic nature of each molecular adduct [35]. The $\vartheta_{\text{Hg-X}}$ and $\vartheta_{\text{Hg-N}}$ were observed in the range 340-315 [36] and 480-480 [37-38] respectively.

The binding energies (eV) for Hg 3P_{1/2,3/2}; Hg 3d_{3/2,5/2} and N1s photoelectron peaks for ligand, HgX₂ and [HgX₂.L¹⁻¹⁰] are listed in table I. Hg 3P_{1/2,3/2}; Hg 3d_{3/2,5/2} and N1s photoelectron peaks for HgX₂ (where X= Cl or Br or NO₃ or CH₃COO) have shown higher binding energies (eV) than

in prepared $[\text{HgX}_2\text{L}^{1-10}]$ molecular adducts (table I and Fig 2). This suggested that electron density is increased on mercury metal ion due to coordination of ligand in $[\text{HgX}_2\text{L}^{1-10}]$ molecular adduct [39].

Table I : Hg $3p_{1/2,3/2}$; Hg $3d_{3/2,5/2}$ and N1s binding energies (eV) in ligand, HgX_2 and $[\text{HgX}_2\text{L}]$ complexes.

Sr. No.	Ligand and Complex	Hg $3P_{1/2,3/2}$		Hg $3d_{3/2,5/2}$		N1s	
		Hg $3P_{1/2}$	Hg $3P_{3/2}$	Hg $3d_{3/2}$	Hg $3d_{5/2}$	Uncoord.	Coord.
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	280.8	848.8	386.8	296.8	-	-
12.	HgCl ₂ .L ¹	279.6	847.6	385.6	295.6	-	404.8
13.	HgCl ₂ .L ²	279.6	847.6	385.6	295.6	-	404.8
14.	HgCl ₂ .L ³	279.6	847.6	385.6	295.6	-	404.8
15.	HgCl ₂ .L ⁴	279.6	847.6	385.6	295.6	-	404.8
16.	HgCl ₂ .L ⁵	279.6	847.6	385.6	295.6	-	404.8
17.	HgCl ₂ .L ⁶	279.6	847.6	385.6	295.6	-	404.8
18.	HgCl ₂ .L ⁷	279.6	847.6	385.6	295.6	-	404.8
19.	HgCl ₂ .L ⁸	279.6	847.6	385.6	295.6	-	404.8
20.	HgCl ₂ .L ⁹	279.6	847.6	385.6	295.6	-	404.8
21.	HgCl ₂ .L ¹⁰	279.6	847.6	385.6	295.6	-	404.8
22.	HgBr ₂	280.6	848.6	386.6	296.6	-	-
23.	HgBr ₂ .L ¹	279.4	847.4	285.4	295.4	-	404.6
24.	HgBr ₂ .L ²	279.4	847.4	285.4	295.4	-	404.6
25.	HgBr ₂ .L ³	279.4	847.4	285.4	295.4	-	404.6
26.	HgBr ₂ .L ⁴	279.4	847.4	285.4	295.4	-	404.6
27.	HgBr ₂ .L ⁵	279.4	847.4	285.4	295.4	-	404.6
28.	HgBr ₂ .L ⁶	279.4	847.4	285.4	295.4	-	404.6
29.	HgBr ₂ .L ⁷	279.4	847.4	285.4	295.4	-	404.6
30.	HgBr ₂ .L ⁸	279.4	847.4	285.4	295.4	-	404.6
31.	HgBr ₂ .L ⁹	279.4	847.4	285.4	295.4	-	404.6
32.	HgBr ₂ .L ¹⁰	279.4	847.4	285.4	295.4	-	404.6
33.	Hg(NO ₃) ₂	280.4	848.4	386.4	296.4	-	-
34.	Hg(NO ₃) ₂ .L ¹	279.2	847.2	285.2	295.2	-	404.4
35.	Hg(NO ₃) ₂ .L ²	279.2	847.2	285.2	295.2	-	404.4
36.	Hg(NO ₃) ₂ .L ³	279.2	847.2	285.2	295.2	-	404.4
37.	Hg(NO ₃) ₂ .L ⁴	279.2	847.2	285.2	295.2	-	404.4
38.	Hg(NO ₃) ₂ .L ⁵	279.2	847.2	285.2	295.2	-	404.4
39.	Hg(NO ₃) ₂ .L ⁶	279.2	847.2	285.2	295.2	-	404.4
40.	Hg(NO ₃) ₂ .L ⁷	279.2	847.2	285.2	295.2	-	404.4
41.	Hg(NO ₃) ₂ .L ⁸	279.2	847.2	285.2	295.2	-	404.4
42.	Hg(NO ₃) ₂ .L ⁹	279.2	847.2	285.2	295.2	-	404.4
43.	Hg(NO ₃) ₂ .L ¹⁰	279.2	847.2	285.2	295.2	-	404.4
44.	Hg(CH ₃ COO) ₂	280.2	848.2	386.2	296.2	-	-
45.	Hg(CH ₃ COO) ₂ .L ¹	279.0	847.0	385.0	295.0	-	404.2
46.	Hg(CH ₃ COO) ₂ .L ²	279.0	847.0	385.0	295.0	-	404.2
47.	Hg(CH ₃ COO) ₂ .L ³	279.0	847.0	385.0	295.0	-	404.2
48.	Hg(CH ₃ COO) ₂ .L ⁴	279.0	847.0	385.0	295.0	-	404.2
49.	Hg(CH ₃ COO) ₂ .L ⁵	279.0	847.0	385.0	295.0	-	404.2
50.	Hg(CH ₃ COO) ₂ .L ⁶	279.0	847.0	385.0	295.0	-	404.2
51.	Hg(CH ₃ COO) ₂ .L ⁷	279.0	847.0	385.0	295.0	-	404.2
52.	Hg(CH ₃ COO) ₂ .L ⁸	279.0	847.0	385.0	295.0	-	404.2
53.	Hg(CH ₃ COO) ₂ .L ⁹	279.0	847.0	385.0	295.0	-	404.2

54.	Hg(CH ₃ COO) ₂ .L ¹⁰	279.0	847.0	385.0	295.0	-	404.2
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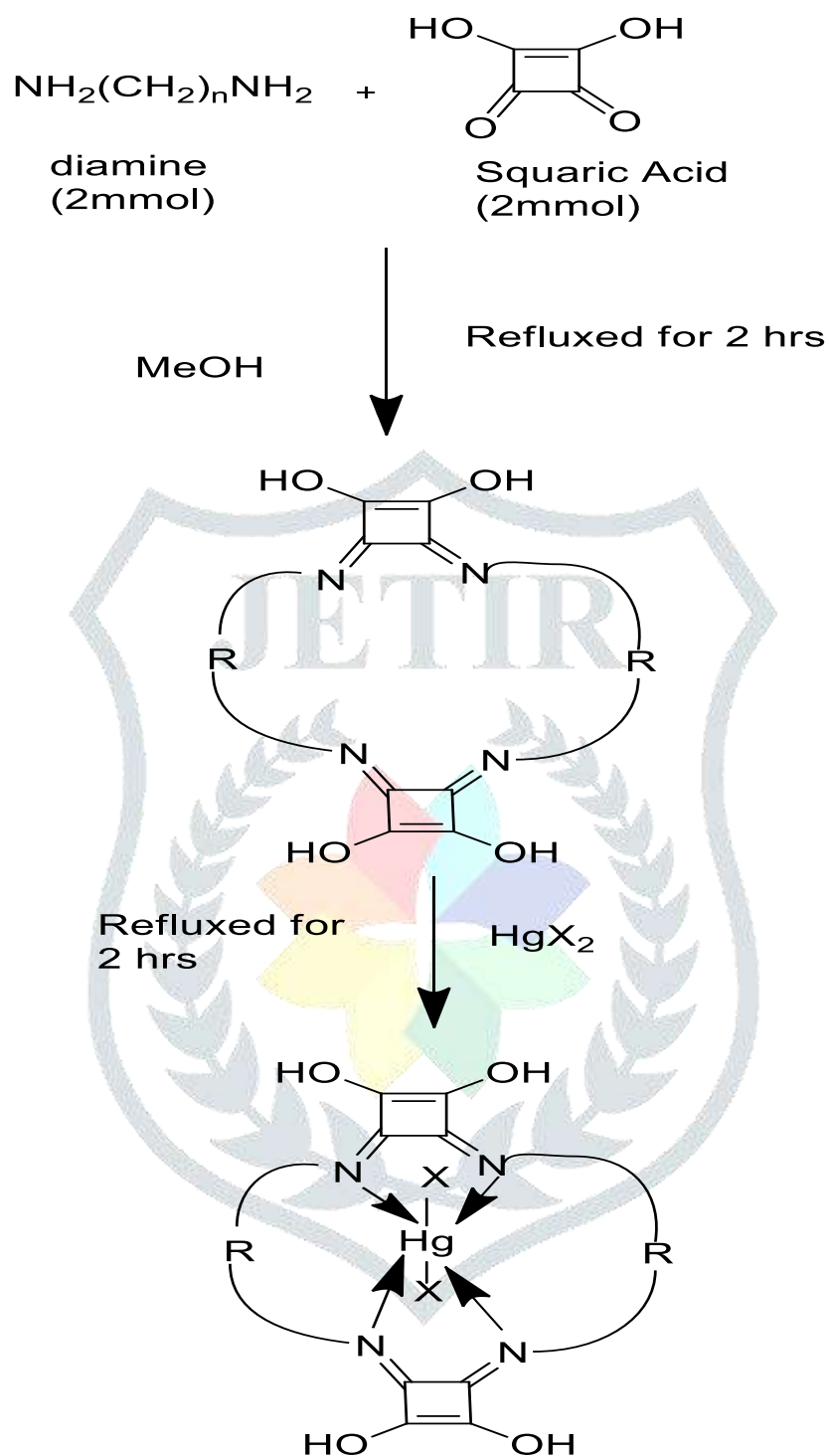


Fig 1: Preparation of [HgX₂.L¹⁻¹⁰] complexes where X=Cl or Br or NO₃ or CH₃COO and R= -CH₂CH₂CH₂-; -CH₂CH(CH₃)CH₂-; -CH₂NH(CH₂)₂-; -CH₂C(CH₃)₂CH₂-; -(CH₂)₆-; -(CH₂)₇-; -(CH₂)₈-; -(CH₂)₉-; -(CH₂)₁₀- and -(CH₂)₁₂-.

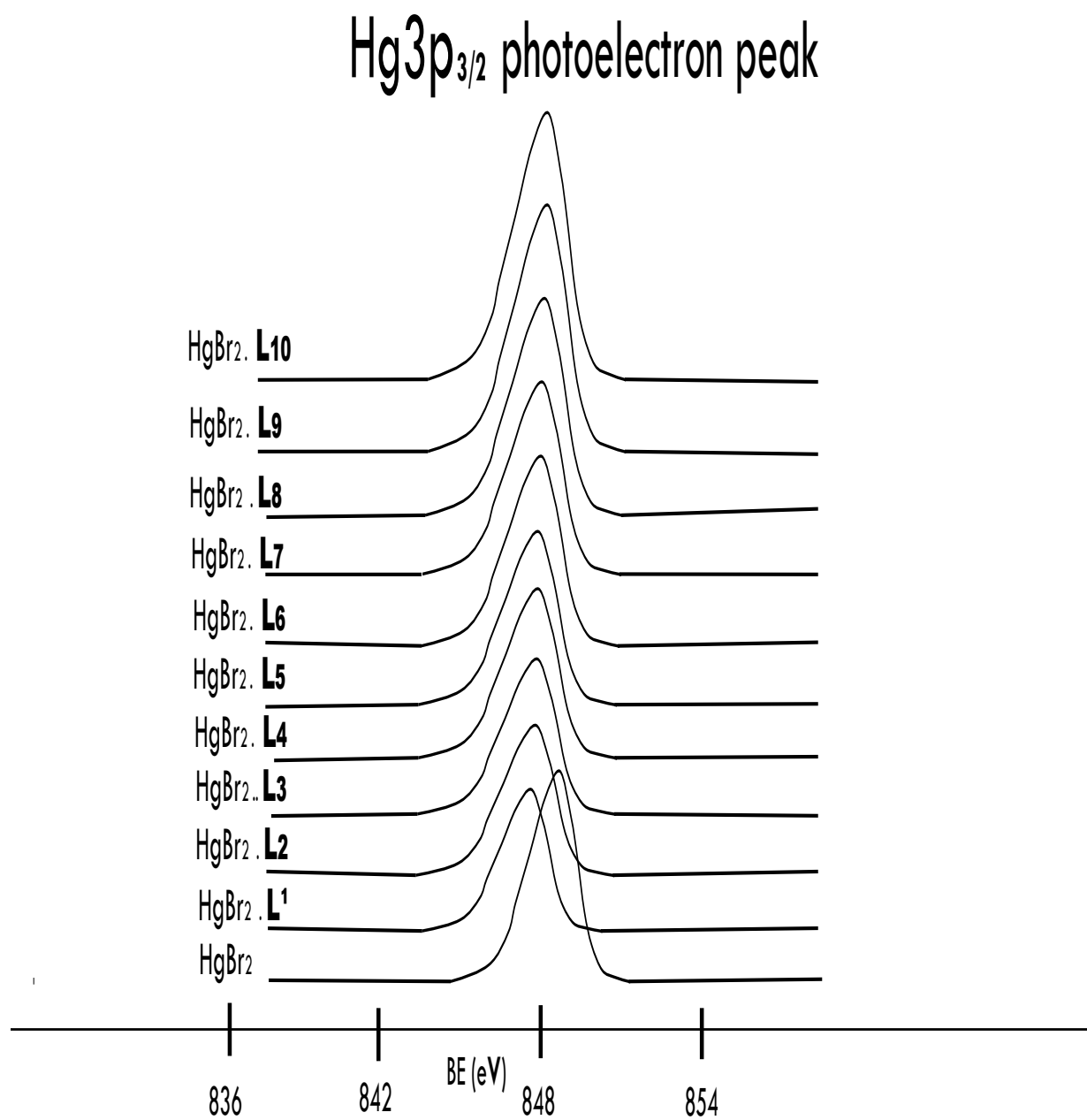


Fig2: Hg3p_{3/2} binding energies (ev) in HgBr₂ & [HgBr₂ L₁₋₁₀] complexes

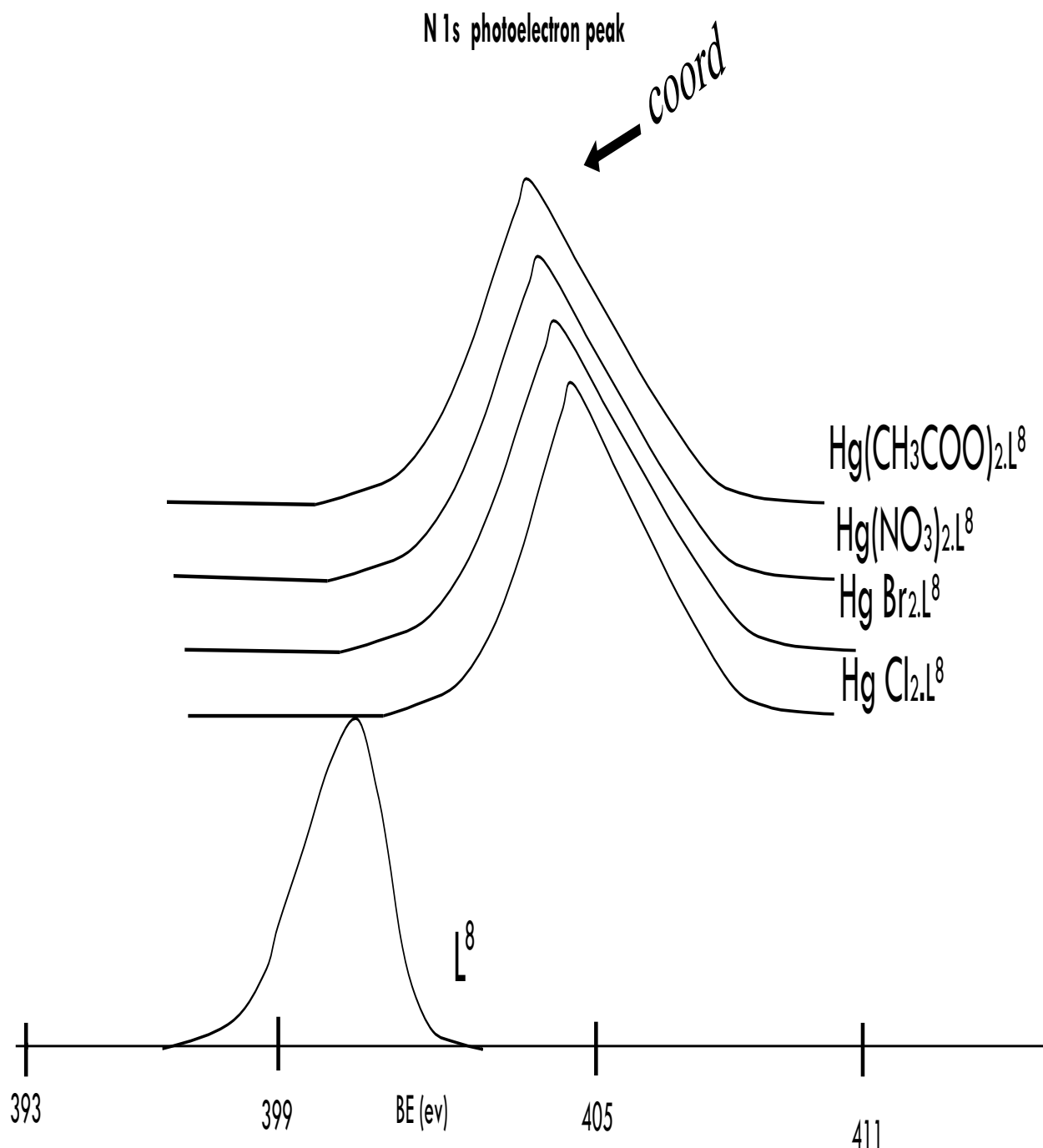


Fig 3 : N1s binding energies (ev) in L⁸ & [Hg X₂ L⁸] complexes

Furthermore, only one symmetrical peak was observed in each [HgX₂.L¹⁻¹⁰] molecular adduct towards higher binding energy (eV) side than N1s photoelectron peak in each ligand, suggesting all four nitrogen atoms are coordinated with mercury metal ion [10] (table I and Fig 3). The Hg 3S photoelectron peak in each [HgX₂.L¹⁻¹⁰] has shown a single symmetrical peak, suggesting each [HgX₂.L¹⁻¹⁰] molecular adduct is diamagnetic in nature.

CONCLUSION:

The structure of each molecular adduct [HgX₂.L¹⁻¹⁰] can be propose as given in Fig.1 on the basis of elemental analysis, molar conductance, IR and XPS data. An octahedral geometry may be also established.

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REFERENCES:

1. Chandra, S.; Kumar, R.; Spectrochem. Acta A, 2009, 66, 74.
2. Mertes, M. P.; Bontchev, P. R.; Coord. Chem. Rev. 1990, 23, 413.
3. Mitewa, M.; Bontchev, P. R.; Coord. Chem. Rev. 1994, 129, 135.
4. James, S.; Kumar D. S.; Alexander V. J.; Chem. Soc. Dalton Trans, 1999, 999, 1773.
5. Kong, D.; Huang, X.; Xie, Y.; Inorg. Chim. Acta, 2002, 340, 133.
6. Comba, P.; Luther, S. M.; Maas, O.; Pritzkow Vielfort; A.Inorg. Chem. 2001, 40, 2335.
7. Kumar, R.; Singh, R. Russian J. of Coord. Chem., 32, 192, 2006.
8. Malachowski, M. R.; Dorsey, B.T.; Parker, M. J.; Adams, M.E.; Kelly, R.S.; Polyhedron, 1998, 17(8), 1289.
9. Chaudhary, A.; Bansal, N.; Gajraj, A.; Singh, R.V.; J. Inorg. Biochem. 2003, 93, 393.
10. Valencia, L.; Adams, H.; Bastida, R.; Fenton, D.E.; Macias, A. Inorg. Chem. Acta, 2001, 317, 45.
11. Chandra, S.; Gupta, K.; Trans. Metal Chem. 2002, 27, 196.
12. Melson, G. A.; Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York, 1979.
13. Valencia, L.; Adams, H.; Bastida, R.; Fenton, D. E.; Macias, A.; Inorg. Chim. Acta, 2003, 343, 133.
14. Zhog, Z. J.; You, X-Z; Mark, T. C. W.; Polyhedron, 1994, 13, 2157.
15. Reddy, P. M.; Ho, Y. P.; Shanker, K.; Rohini, R.; Ravinder, V.; Eur. J. Med. Chem. 2009, 1-5, 104.
16. Reddy, P. M.; Prasad, A. V. S. S.; Rohini, R.; Ravinder, V.; Spectrochim. Acta, 2007, 68A, 1000.
17. Wolkert, W. A.; Hoffman, T. J.; Chem. Rev. 1999, 99, 2269.
18. Halma, M.; Bail, A.; Wypych, F.; Nakagaki, S. J.; Mol. Catal. (A) Chem. 2006, 44, 243.
19. Reddy, P. M.; Prasad, A. V. S. S.; Rohini, R.; Ravinder, V.; Spectrochim. Acta, 2008, 70A, 704.
20. Reddy, P. M.; Prasad, A. V. S. S.; Ravinder, V.; Trans. Met. Chem. 2007, 32, 507.
21. Reddy, M. B.; Shanker, K.; Usha Rani, P. Ind. Chem. Soc. 2007, 84, 971.
22. Anaconda, J. R.; Bastardo, E.; Camus, J.; Trans. Met. Chem. 1999, 24, 478.
23. Bozi, L.T.; Marotta, E.; Traldi, P. Polyhedron, 2007, 26, 1663.
24. Bertolo, E.; Bastida, R.; Blas, A. D.; Fenton, D. E.; Loderio, C.; Macias, A.; Rodriguez, A.; Rodriguez-Blas, T.; J. Inclusion Phenom. Macrocyclic Chem. 1999, 35, 191.
25. Niasri, M. S.; Davar, F.; Inorg. Chem. Commun. 2006, 9, 175.
26. Curtis, N. F.; Coord. Chem. Rev. 1968, 3, 3.
27. Chandra, S.; Singh, R.; Ind. J. Chem. 1995, 34(A), 1003.
28. Saleh, A. A.; J. Coord. Chem. 2005, 58(3), 255.
29. Kumar, D. S.; Alexander, V.; Polyhedron, 1991, 18, 1561.
30. Adel, A. A.; Emara, Azza, A. A.; Abou-Hussen; Spectrochim. Acta Part A, 2006, 64, 1010.
31. J.S. Wu, I.C. Hwang, K.S. Kim, Org. Lett. 9, 907(2007).
32. Vogel, A. I.; A Text Book Of Quantitative Inorganic Analysis, Longmans Green ELBS, London, 1991, 355.
33. Vogel, A. I.; A Text Book Of Quantitative Inorganic Analysis, Longmans Green ELBS, London, 1991, 302.
34. Vogel, A. I.; A Text Book Of Practical Organic Chemistry, 4 th Edition, Longmans, ELBS, London, 1991, 355.
35. Geary, W. L.; Coord. Chem. Rev. 1972, 1, 81.
36. Annigeri, S.M.; Naik, A. D.; Gangadharmath, U. B.; Revankar, V. K.; Mahale, V. B.; Trans. Met. Chem. 2002, 27, 316.
37. Mohapatra, B. B.; Saraf, S. K.; J. Ind. Chem. Soc. 2003, 80, 696.
38. Chaudhary, C. K.; Chaudhary, R. K.; Mishra, L. K.; J. Indian Chem. Soc. 2003, 80, 693.
39. Srivastava, S.; Applied Spectrosc. Rev. 1986, 22, 401.