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## Synthesis and Characterization of Hg (II) Complexes with Macrocyclic Ligand

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### ABSTRACT

This paper deals with the synthesis and characterization of a macrocyclic complex compounds of the general formula  $[M-LX_2]$  where M= Hg(II) resulted from the condensation reaction of diaminopropane/ diaminobutane and hexanedione with mercury in ethanolic solution. The coordination compounds are formulated according to the chemical analysis, electronic, infrared, <sup>1</sup>HNMR and mass spectra, as well as molar conductance values.

**Key words:** Metal complexes, Hg(II) metals, Spectroscopy.

### INTRODUCTION

The coordination chemistry of multidentate macrocycles has been a field of intensive research over the past many years. The tetraazamacrocyclic ligands and their metal complexes have attracted growing interest among coordination chemists followed by many workers on the metal controlled template synthesis of macrocyclic species<sup>1,2</sup>. The chemistry of synthetic macrocyclic polyamines and macrocyclic dioxopolyamines has been drawing much interest<sup>3-6(88-91)</sup>. These macrocycles form much more stable and selective complexes with various transition metal ions than do open chain analogue having the same donor arrangements. These macrocyclic ligands used as models for protein metal binding sites, pigments, vitamin B<sub>12</sub>,

photosynthesis, dioxygen, sodium and potassium ion transport<sup>7,8</sup>. In biomedical systems<sup>9-12</sup> they are used as therapeutic reagents<sup>13-15</sup> in chelate therapy for the treatment of metal intoxication, as anti-HIV agents<sup>16-18</sup> and as cyclic antibiotic activity is because of specific metal complexation. In the present investigation, the synthesis and structural elucidation of complexes from the reaction of hexanedione with diaminoalkane with Hg(II) metal ions are synthesized and characterized.

### EXPERIMENTAL

All solvents were reagent grade and purified as described else where prior to use. HgCl<sub>2</sub>, Hg(NO<sub>3</sub>)<sub>2</sub>, 3,4-hexanedione, diaminopropane and diaminobutane were purchased from Aldrich

Chemical and used after purification<sup>19</sup>. Elemental analyses were made by the microanalytical laboratory obtained from CDRI, Lucknow, India. Metals and chloride were determined volumetrically<sup>20</sup> and gravimetrically<sup>21</sup> respectively. The IR spectra (4000-200cm<sup>-1</sup>) of all prepared complexes in Csl pellets were recorded with a Perkin Elmer 621 spectrophotometer. The electrical conductivity of 10<sup>-3</sup>M solution in DMF was obtained with Digisum Electronic Conductivity Bridge at room temperature. <sup>1</sup>H NMR spectra, recorded in DMSO-d<sub>6</sub> using a Bruker AC 200E spectrometer with Me<sub>4</sub>Si as an internal standard, were obtained at the IIT Kanpur, India.

#### Synthesis of the Tetraazamacrocyclic complexes

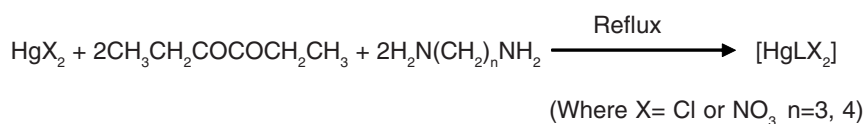
To ethanolic solution (20ml) of HgX<sub>2</sub> (X=Cl,

NO<sub>3</sub>) (1mmol) a solution of 3,4-hexanedione (2mmol) was added dropwise with constant stirring. This was followed by dropwise addition of 1,3-diaminopropane (2mmol) in ethanol (20ml) with constant stirring for 5hrs. A white solid appeared which was filtered, washed with ethanol and dried under vacuum over CaCl<sub>2</sub>. [HgL<sup>1</sup>X<sub>2</sub>] (Scheme 1).

A similar procedure was adapted for the synthesis of Hg(II) complexes of macrocycles derived from 3,4 hexanedione with 1,4-diaminobutane [HgL<sup>2</sup>X<sub>2</sub>].

#### Reflux

The complex may be synthesised by the following general method:



#### Scheme 1. Synthesis of macrocyclic complexes

#### RESULTS AND DISCUSSION

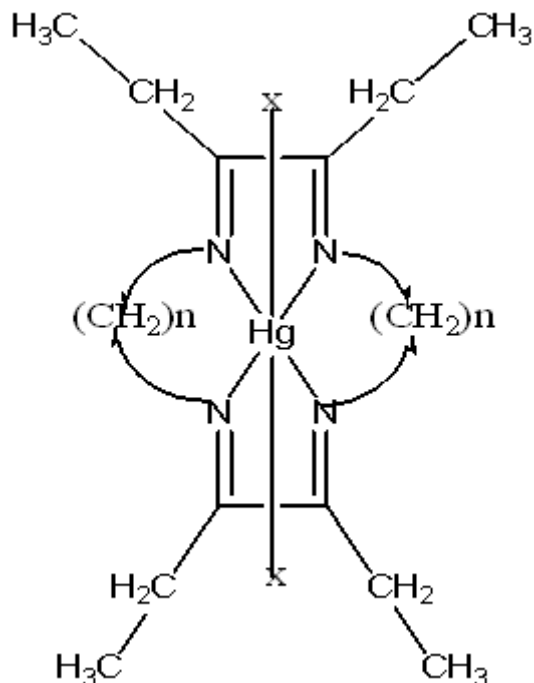
These synthesised complexes were white solid and stable at room temperature. All the complexes have showed high melting points. Elemental analysis were within ±0.5% for C, H, N, Hg and Cl. The elemental analysis and molar

conductance data are represented in Table 1. The molar conductance measurements of the complexes in DMF correspond to non-electrolyte nature<sup>22</sup>.

The infrared spectra of the metal complexes shown the absence of the stretching modes of functional groups (NH<sub>2</sub> and C=O), and the

Table 1: Elemental analysis and Molar Conductivity of [HgLX<sub>2</sub>]

S. No.	Compound	Found (Calcd) %			Molar Conductivity ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> (in DMF)
		C	H	N	
1.	[HgL <sup>1</sup> Cl <sub>2</sub> ]	34.2 (34.5)	5.4 (5.5)	9.6 (9.7)	20
2.	[HgL <sup>2</sup> Cl <sub>2</sub> ]	39.6 (39.7)	5.6 (5.9)	9.0 (9.2)	22
3.	[HgL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	34.0 (34.1)	5.0 (5.0)	13.2 (13.3)	16
4.	[HgL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	36.4 (36.5)	5.2 (5.4)	12.2 (12.4)	14



Where

$L^1 = n = 3$

$L^2 = n = 4$

$X = Cl, NO_3$

**Fig. 1: Proposed structure of macrocyclic metal complexes**

appearance of bands characteristics of imine group<sup>23-25</sup>. The major changes observed in the spectra of the metal complexes are the absence of stretching and deformation vibrations of  $NH_2$  group, indicating their deprotonation and the appearance of strong bands due to coordinated  $\nu(C=N)$  vibrations in the range  $1626-1605cm^{-1}$ <sup>23</sup>. Strong and sharp band

for C-H bending vibrations appear at ca.  $1460-1500 cm^{-1}$ <sup>23</sup>. The presence of new bands in the spectra of the metal complexes in the region at  $4387-457cm^{-1}$  due to  $\nu(Hg-N)$  vibration supports the coordination of the imine nitrogen to the mercury ion<sup>26</sup>. In the spectrum of the complexes the bands at  $cm^{-1}$  are observed, which may be assigned to coordinated chloro and nitrate group respectively<sup>23-25</sup>.

$^1H$  NMR spectrum of one representative Hg(II) complex has been recorded. The  $\alpha-CH_2$  protons of the amine residue give a triplet  $\delta-2.63$  ppm due to coupling with the  $\beta-CH_2$  protons. The  $\beta-CH_2$  protons of the amine residue give a broad peak at  $\delta-1.50$  ppm. The remaining methylene protons of the amine residue give rise to a broad peak at  $\delta-1.32$  ppm. In macrocyclic precursor, 1,2,8,9-tetraphenyl-3,7-diazaduohepta-2,7-diene-1,9-dione(KIM,3) the  $\alpha-CH_2$  protons have been reported to appear as a triplet at  $\delta-3.63$  ppm and  $\beta-CH_2$  protons as a quintet at  $\delta-2.11$  ppm<sup>27</sup>.

## CONCLUSION

From the reported data, the following chemical structures for the synthesis mixed ligand complexes are proposed.

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