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# Synthesis and Characterisation of Novel Mercuric Complexes

S.L. TURWATKAR and B.H. MEHTA*
*Department of Chemistry*
*University of Bombay*
*Vidyanagari, Bombay-400 098, India.*

The current interest in the coordination chemistry of azomethine group of various organic molecules arises from their wide ranging applications. The complexes were obtained from the interaction of mercuric(II) chloride with the different substituted Schiff bases. These complexes were characterised by using electrode absorption spectra and IR data. The results indicate that the metal ions coordinate with the azomethine nitrogen atom of the Schiff base. Assignments of the bands of the electronic absorption spectra are made and various ligand field parameters were calculated. Based on this diagnosis the complexes were assigned tetrahedral structure.

## INTRODUCTION

Although extensive work has been carried out for Schiff base complexes of transition metal ions but very few have beeen reported[1,2] to be of great utility in analytical, pharmacological and biological aspects. The transition metal complexes are also reported to possess good luminescence and pigmentation properties.[3] The aim of the present work is to investigate the coordination behaviour of various different substituted Schiff bases towards bivalent mercuric ion, to throw some light on stereochemistry of the isolated mercuric complexes, UV-visible and IR spectral data were recorded. The mercuric complexes of these Schiff bases were assigned a tetrahedral geometry.

## EXPERIMENTAL

The aromatic carbonyl compound and the diamine were mixed in ethanol and refluxed for 4 h. The solid compound formed after the refluxion was filtered, washed and dried. Four ligands were prepared by mixing 5-nitrosalicylaldehyde with *o*-toluidine, *o*-amino benzoic acid, *p*-toluidine, *p*-amino benzoic acid and named as $L_1$, $L_2$, $L_3$, $L_4$ respectively, while two more ligands $L_5$ and $L_6$ were obtained by mixing 2-hydroxy-1-naphthaldehyde with *o*-amino benzoic acid and *p*-amino benzoic acid respectively. Ligands were characterised after crystallising them from alcoholic solution. The mercuric complex $Hg(L_n)_2$, where n = 1, 2, 3, 4, 5, 6, was obtained by mixing metal ion with 1% alcoholic solution of the ligand in more than 1 : 2 metal : ligand stoichiometry. The mercuric(II) complexes were isolated by raising the pH to its optimum value 7. Each mercuric(II) complex was

recrystallised from its ethanolic solution and characterised by physico-chemical and spectroscopic data.

The microanalyses of the complexes were carried out on Carl Erba instrument. The molar conductance was measured on Toshniwal conductivity bridge using nitrobenzene solvent at room temperature. The diffused reflectance spectra were obtained using Carl-Zeiss VSU 2p spectrophotometer with reflectance attachment. The IR spectra of ligands as well as complexes were recorded on FTIR-4200 manufactured by Shimadzu Corporation, Japan using KBr pellet technique. The UV-visible spectra of ligands were recorded on UV-visible spectrophotometer. All the results of analytical and spectroscopic study are recorded in Tables 1 and 2.

TABLE-1
ANALYTICAL DATA OF LIGANDS AND THEIR METRIC COMPLEXES

| Compound | Mol. formulae / (colour) | Elemental analysis % Found (Calcd) | | | |
|---|---|---|---|---|---|
| | | C | H | N | Hg |
| $L_1$ | $C_{14}H_{12}N_2O_3$ (Yellow) | 64.84 (65.62) | 3.00 (4.68) | 9.71 (10.93) | — |
| $Hg(L_1)_2 \cdot H_2O$ | $Hg(C_{14}H_{12}N_2O_3)_2 \cdot H_2O$ (Brown) | 45.15 (46.12) | 3.00 (3.02) | 6.08 (7.69) | 26.15 (27.53) |
| $L_2$ | $C_{13}H_{10}N_2O_5$ (Orange) | 57.95 (58.74) | 3.30 (4.19) | 8.31 (9.79) | — |
| $Hg(L_2)_2 \cdot H_2O$ | $Hg(C_{13}H_{10}N_2O_5)_2 \cdot H_2O$ (Brown) | 42.45 (42.61) | 2.40 (2.54) | 6.85 (7.10) | 24.67 (25.44) |
| $L_3$ | $C_{14}H_{12}N_2O_3$ (Yellow) | 64.20 (65.62) | 3.65 (4.68) | 9.33 (10.93) | — |
| $Hg(L_3)_2 \cdot H_2O$ | $Hg(C_{14}H_{12}N_2O_3)_2 \cdot H_2O$ (Yellow) | 45.25 (46.12) | 2.92 (3.02) | 6.57 (7.69) | 26.58 (27.53) |
| $L_4$ | $C_{13}H_{10}N_2O_5$ (Yellow) | 57.71 (58.74) | 4.02 (4.19) | 8.81 (9.79) | — |
| $Hg(L_4)_2 \cdot H_2O$ | $Hg(C_{13}H_{10}N_2O_5)_2 \cdot H_2O$ (Yellow) | 42.15 (42.61) | 2.21 (2.54) | 6.20 (7.10) | 24.13 (25.44) |
| $L_5$ | $C_{18}H_{13}NO_3$ (Yellow) | 73.82 (74.22) | 3.89 (4.46) | 4.57 (4.81) | — |
| $Hg(L_5)_2 \cdot H_2O$ | $Hg(C_{18}H_{13}NO_3)_2 \cdot H_2O$ (Orange) | 53.22 (54.10) | 2.95 (3.26) | 2.25 (3.51) | 24.45 (25.12) |
| $L_6$ | $C_{18}H_{13}NO_3$ (Yellow) | 73.10 (74.22) | 3.82 (4.46) | 4.06 (4.81) | — |
| $Hg(L_6)_2 \cdot H_2O$ | $Hg(C_{18}H_{13}NOsub3)_2 \cdot H_2O$ (Orange) | 53.34 (54.10) | 2.89 (3.26) | 3.12 (3.51) | 24.86 (25.12) |

TABLE-2
KEY ELECTRONIC ABSORPTION AND IR/ VISIBLE BANDS OF LIGANDS AND THEIR MERCURIC COMPLEXES

| | IR band $cm^{-1}$ | | | | | | Electronic Absorption in kK | |
|---|---|---|---|---|---|---|---|---|
| Compound | $\nu_{OH}$ | $\nu_{(C=N)}$ | $\nu_{NO_2}$ asymmetric | $\nu_{NO_2}$ symmetric | $\nu_{(Hg-N)}$ | $\nu_{(Hg-O)}$ | Reflectance | Charge transfer transition |
| $L_1$ | 3094 | 1614 | 1465 | 1334 | — | — | 15.62, 19.23, 22.22, 22.72 | |
| $Hg(L_1)_2 \cdot H_2O$ | 3144 | 1632 | 1350 | 1280 | 600 | 420 | 15.87, 16.39, 17.54, 20.40, 22.72 | 16.39, 17.54 |
| $L_2$ | 3071 | 1635 | 1440 | 1329 | — | — | 16.39, 18.86, 19.60, 23.25 | |
| $Hg(L_2)_2 \cdot H_2O$ | 3410 | 1595 | 1358 | 1246 | 509 | 485 | 15.87, 16.94, 17.54, 18.51, 22.22 | 16.94, 17.54 |
| $L_3$ | 3123 | 1622 | 1510 | 1338 | — | — | 16.39, 16.66, 21.27, 23.25, 24.39 | |
| $Hg(L_3)_2 \cdot H_2O$ | 3441 | 1614 | 1500 | 1311 | 582 | 488 | 15.62, 16.66, 18.18, 21.27 | 16.66 |
| $L_4$ | 3098 | 1620 | 1568 | 1313 | — | — | 16.12, 16.66, 20.00 | |
| $Hg(L_4)_2 \cdot H_2O$ | 3296 | 1593 | 1500 | 1305 | 617 | 470 | 15.87, 18.51, 19.60, 20.40, 21.73 | 15.87 |
| $L_5$ | 3026 | 1615 | 1445 | 1320 | — | — | 16.12, 17.54, 19.23, 21.27, 22.72 | |
| $Hg(L_5)_2 \cdot H_2O$ | 3379 | 1587 | 1358 | 1251 | 515 | 420 | 16.39, 22.22 | 16.94 |
| $L_6$ | 3059 | 1626 | 1515 | 1352 | — | — | 16.12, 20.00, 21.27, 22.72 | |
| $Hg(L_6)_2 \cdot H_2O$ | 3340 | 1585 | 1365 | 1280 | 574 | 410 | 16.39, 18.51, 19.60, 21.73 | 16.39 |

## RESULTS AND DISCUSSIONS

On the basis of elemental analysis the complexes of Schiff bases have been assigned composition involving 1 : 2 metal : ligand stoichiometery. These complexes were thermally stable and decomposed at higher temperature without melting. The lower value of molar conductance (6.20–9.17 mhos $cm^2$ $mole^{-1}$) indicates the non-electrolytic nature of the complexes. All these complexes are moderately soluble in acetone, methanol, DMSO, DMF and nitrobenzene.

The Hg(II) complexes were also investigated for their magnetic behaviour at room temperature using Gouy balance method. The measurement of magnetic susceptibility suggests that all the complexes are diamagnetic in nature. The diamagnetic behaviour is accepted for Hg(II) compounds. It is reported[4] that diamagnetic mercuric salt generally crystallizes with tetrahedral geometry. Thus Hg(II) complexes under present investigation can also be suspected to be tetrahedral due to their diamagnetic behaviour at room temperature.

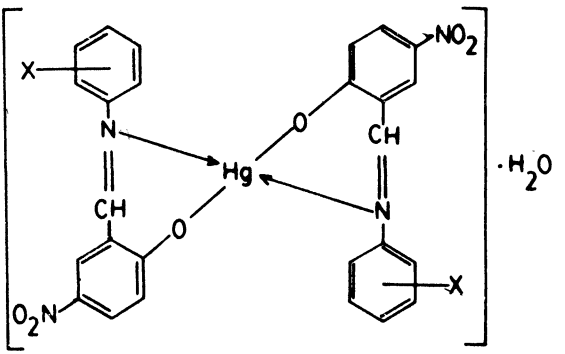
In the IR spectra of the ligands the bands *ca.* 3300 $cm^{-1}$ ν(OH) was lowered due to intramolecular O—H---N hydrogen bonding. The presence of these bands in metal complexes indicates that the metal : ligand stoichiometry is 1 : 2 since the mercury ion is coordinated with only one phenolic —OH group after deprotonation. The shifting of this $\nu_{OH}$ band suggests the bonding of oxygen atom to metal ion. The band pointed in the region 1678–1612 $cm^{-1}$ is assigned to $\nu_{(C=N)}$. The lowering of position of these bands into the region 1619 to 1588 $cm^{-1}$ in the corresponding mercury(II) conplexes suggest that the azomethine nitrogen atom of ligand is involved in coordination. Syamal *et al.*[5] have reported lowering in the $\nu_{(C=N)}$ stretching vibration by 60–20 $cm^{-1}$ when azomethine nitrogen coordinates with metal ion.

The asymmetric and symmetric stretching vibrations due to nitrochromophore appear in the range 1465 to 1352 $cm^{-1}$ in the spectra of ligands. Positions of these stretching vibrations remain unaffected in corresponding spectra of Hg(II) complexes.

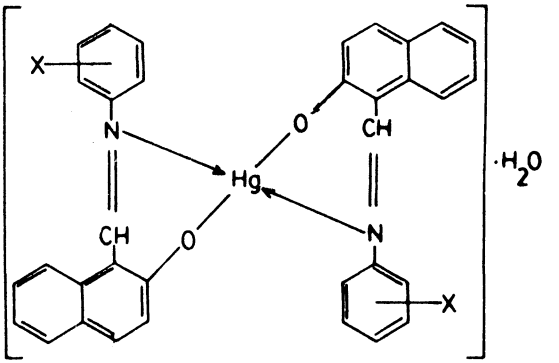
Nakamato[6] has reported that $\nu_{(M—N)}$ and $\nu_{(M—O)}$ stretching vibrations appear in the range of 600–500 $cm^{-1}$ and 500–400 $cm^{-1}$ respectively. The involvement of azomethine nitrogen and phenolic oxygen atom of the ligand in the complexation is further confirmed by appearance of new additional bands in the lower region of IR spectra. The absorption band in the range of 617 to 509 $cm^{-1}$ is assigned to $\nu_{(Hg—N)}$ while band appearing in the 488 to 410 $cm^{-1}$ is assigned to $\nu_{(Hg—O)}$.

The electronic absorption spectra of the Hg(II) complexes show band at 17.54–15.87 $cm^{-1}$ which can be assigned to d-d transition while absorption bands can be assigned to charge transfer transition.

Conclusively, the Hg(II) complexes synthesised using these novel Schiff bases can be designated as complexes with tetrahedral geometry. These complexes may be assigned the following structures.




Where X = $OCH_3$, p-$CH_3$, O-COOH or p-COOH.




Where X = o-COOH or p-COOH

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