Asian Journal of Chemistry Vol. 19, No. 5 (2007), 3671-3676

Analytical and Crystallographic Parameters of Hg(II) Complexes Derived from Substituted Schiff Bases

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Mercury(II) complexes of type $Hg(L)_2 \cdot H_2O$, where L = substituted Schiff bases, prepared from condensation of 5-nitrosalicylaldehyde with *o*-toluidine, *p*-toluidine, *o*-amino benzoic acid, *p*-amino benzoic acid and are named as L_1, L_2, L_3 and L_4, respectively, while two ligands L_5 and L_6 were prepared by condensation of 2-hydroxy-1-naphthaldehyde with *o*-amino benzoic acid and *p*-amino benzoic acid respectively and n = 1,2,3,4,5,6 have been prepared and characterized by IR, X-ray, UV-visible etc. Molar conductivity measurements indicates that the complexes are non-electrolytic in nature. The metal complexes of schiff bases are assigned tetrahedral structure.

Key Words: Hg(II) complexes, Substituted Schiff bases.

INTRODUCTION

Transition metal compounds containing the schiff base ligands have been of interest for many years. These complexes play an important role in the developing of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures[1-3]. Schiff bases and its transitional complexes have been used in anticancer, antitubercular, antibacterial, antifungal, antihypertensive and hypothermic reagents[4,5]. The transitional metal complexes are also reported to possess good luminescence and pigmentation properties[6]. In this paper, the synthesis, characterization and crystal lattice parameters of Hg(II) complexes of Schiff base derived from 5-nitrosalicylaldehyde with *o*-toluidine, *p*-toluidine, *o*-amino benzoic acid, *p*-amino benzoic acid and 2-hydroxy-1-naphthaldehyde with *o*-amino benzoic acid, *p*-amino benzoic acid have been reported.

EXPERIMENTAL

All chemicals used for the synthesis were of AR grade. *o*-Toluidine, *p*-toluidine, *o*-amino benzoic acid, *p*-amino benzoic acid and Hg(II) salts were obtained from S.D. fine chemicals. 2-Hydroxy-1-naphthaldehyde was obtained from Fluka Ltd. Distilled solvents were used throughout the experiments.

Synthesis of schiff bases: The schiff bases L_1, L_2, L_3 and L_4 were prepared by refluxing 5-nitrosalicylaldehyde with *o*-toluidine/*p*-toluidine/*o*-amino benzoic acid/*p*-amino benzoic acid and schiff bases L_5 and L_6 were prepared by refluxing 2-hydroxy-1-naphthaldehyde with *o*-amino benzoic acid/*p*-amino benzoic acid in ethanol for 4 h. The resulting solution was concentrated then cooled to room temperature, filtered and washed with water and then by ethanol and dried under vacuum in oven. The Schiff bases were recrystallized in ethanol, m.p. are 162, 155, 264, 235, 189 and 210ºC, respectively.

Synthesis of mercury(II) complexes: The Hg(II) complexes were synthesized by mixing hot ethanolic solutions of ligands with hot ethanolic solution of Hg(II) salts in the ratio of 1:2 (M:L). The resulting mixture was refluxed for 4 h on a water bath and cooled to room temperature. The pH of the mixture was adjusted to 7 by adding alcoholic ammonia. Subsequently, mixture was digested on waterbath for 1 h whereby solid metal complexes were precipitated and filtered, washed with ethanol and dried in oven.

Physical measurements: The melting point of all complexes was determined by open capillary method. Elemental analysis was carried out in Carl Erba instrument. The metal content of all metal complexes was determined by reported method[7]. The complexes were examined for solubility using various solvents. Molar conductivity of ligands and complexes were recorded using 1×10^{-3} M solutions in DMF on Toshniwal TSM-15 conductivity meter. The electronic absorption spectra of ligands and complexes were recorded in UV-visible region using DMF as solvent on UV-visible 2100 spectrometer supplied by M/s Shimadzu corporation. Magnetic susceptibility measurements were made on Gouy's balance instrument, Pyris diamond TGA/DTG analyzer in static nitrogen atmosphere with heating rate of 10ºC/min. X-ray diffraction spectra were recorded on X-ray diffractometer supplied by M/s Phillips, Holland.

RESULTS AND DISCUSSION

Analytical parameters of ligands and complexes are given in Table-1. All complexes are coloured, stable in air and decompose at higher temperature. The elemental analysis of the metal complexes suggest 1:2 metal to ligand stoichiometry. The complexes were soluble in DMF, DMSO, *etc*. The lower value of molar conductance (6.10-9.15×10^{-3} S cm^2 mol^{-1}) indicates non-electrolytic nature of the complexes[8-10].

The TGA analysis of the complexes confirmed the presence of coordinated water molecule. All the complexes have water molecule coordinated to the metal.

TABLE-1
ANALYTICAL DATA OF LIGAND AND Hg(II) COMPLEXES

Compound	m.f.	m.w.	m.p. (°C)	Elemental Analysis Found (Calcd.) (%)			
				C	H	N	Hg
L_1	$C_{14}H_{12}N_2O_3$	256	162	64.93	3.76	9.87	-
				(65.62)	(4.68)	(10.93)	
$Hg(L_1)_2.H_2O$	$HgC_{28}H_{22}N_4O_6.H_2O$	728	190	45.22	2.98	6.15	26.32
				(46.12)	(3.02)	(7.69)	(27.53)
L_2	$C_{14}H_{12}N_2O_3$	256	155	64.47	3.70	9.53	-
				(65.62)	(4.68)	(10.93)	
$Hg(L_2)_2.H_2O$	$HgC_{28}H_{22}N_4O_6.H_2O$	728	210	45.37	2.95	6.77	26.47
				(46.12)	(3.02)	(7.69)	(27.53)
L_3	$C_{14}H_{10}N_2O_5$	286	264	57.83	3.84	8.62	-
				(58.74)	(4.19)	(9.79)	
$Hg(L_3)_2.H_2O$	$HgC_{28}H_{18}N_4O_{10}.H_2O$	788	240	42.30	2.42	6.88	24.58
				(42.61)	(2.52)	(7.10)	(25.55)
L_4	$C_{14}H_{10}N_2O_5$	286	235	57.94	3.77	8.72	-
				(58.74)	(4.19)	(9.79)	
$Hg(L_4)_2.H_2O$	$HgC_{28}H_{18}N_4O_{10}.H_2O$	788	192	42.39	2.27	6.51	24.29
				(42.61)	(2.54)	(7.1)	(25.44)
L_5	$C_{18}H_{13}NO_3$	291	189	75.09	4.11	4.15	-
				(74.22)	(4.46)	(4.81)	
$Hg(L_5)_2.H_2O$	$HgC_{36}H_{24}N_2O_6.H_2O$	798	200	53.87	3.19	2.44	24.60
				(54.10)	(3.26)	(3.51)	(25.12)
L_6	$C_{18}H_{13}NO_3$	291	210	73.83	4.27	3.78	-
				(74.22)	(4.46)	(4.81)	
$Hg(L_6)_2.H_2O$	$HgC_{36}H_{24}N_2O_6.H_2O$	798	194	53.56	2.28	2.17	24.31
				(54.10)	(3.26)	(3.51)	(25.12)

The measurements of magnetic susceptibility suggest that all the complexes are diamagnetic in nature. Mahapatra and Bhoi[11] have reported that diamagnetic mercuric salt generally crystallizes with tetrahedral geometry. Thus complexes under present investigation can also be suspected to be tetrahedral due to their diamagnetic behaviour at room temperature.

In IR spectra of ligand the band pointed in the region 1638-1620 cm^{-1} is assigned to $\nu(C=N)$. The lowering of position of these band in the region 1618-1587 cm^{-1} in corresponding mercury(II) complexes suggest that the azomethine nitrogen atom of ligand is involved in coordination. Mehta and Ghoghale[12] have reported that lowering in the $\nu(C=N)$ stretching vibration by 60-20 cm^{-1} when azomethine nitrogen is coordinated with metal ion. Syamal and Kale[13] have reported lowering of $\nu(C=N)$ frequency during chelation. The ligand exhibits $\nu(C-O)$ stretching vibration at 1468-1442 cm^{-1}.

TABLE-2
UV-VISIBLE AND IR SPECTRAL DATA OF LIGAND AND MERCURY(II) COMPLEXES

Ligands/ complexes	IR spectral data (cm^{-1})					Electronic spectral data (cm^{-1}) (ε = dm^3 mol^{-1}cm^{-1} × 10^4)		
	ν(OH)	ν(C=N)	ν(C-O)	ν(Hg-N)	ν(Hg-O)	Assignment for *d-d* transition		Change transfer
L_1	3100	1624	1468	-	-	32362	37593	41665
						(2.94)	(2.61)	(2.41)
$Hg(L_1)_2.H_2O$	3148	1615	1422	610	412	25445	37453	37878
						(4.68)	(1.18)	(1.25)
L_2	3085	1638	1442	-	-	31645	40816	46728
						(1.40)	(1.23)	(3.33)
$Hg(L_2)_2.H_2O$	3420	1590	1410	510	485	32051	36764	37594
						(2.66)	(2.56)	(2.11)
L_3	3125	1625	1452	-	-	31786	37735	41493
						(3.28)	(2.29)	(2.60)
$Hg(L_3)_2.H_2O$	3400	1618	1427	584	480	25834	300301	37313
						(2.46)	(1.91)	(1.38)
L_4	3095	1622	1449	-	-	28328	29067	38610
						(2.47)	(1.88)	(1.42)
$Hg(L_4)_2.H_2O$	3288	1595	1423	620	478	23148	26178	31348
						(2.53)	(2.50)	(2.41)
L_5	3030	1620	1448	-	-	43859	47393	47619
						(3.15)	(2.43)	(2.39)
$Hg(L_5)_2.H_2O$	3380	1590	1428	518	415	27027	28089	30674
						(2.33)	(2.60)	(3.24)
L_6	3059	1628	1456	-	-	43290	47680	48210
						(5.11)	(3.93)	(2.88)
$Hg(L_6)_2.H_2O$	3320	1587	1437	581	410	26246	303951	32573
						(2.96)	(2.86)	(3.78)

In metal complexes ν(C-O) phenolic absorption band appears at 1437-1410 cm^{-1}, which is 20-50 cm^{-1} lower than the corresponding ν(C-O) vibration of the free ligand. This indicates bonding of phenolic oxygen to the metal ion[14]. It is reported[15-17] that ν(Hg-N) and ν(Hg-O) stretching vibrations appears in the range of 600-500 cm^{-1} and 500-400 cm^{-1}. 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 620 to 510 cm^{-1} is assigned to ν(Hg-N) while band appearing in the range of 485 to 410 cm^{-1} is assigned to ν(Hg-O).

The electronic absorption spectra of Hg(II) complexes shows band at 30000-20000 cm^{-1} which is assigned to dd-transition while absorption band at 40000-30000 cm^{-1} can be assigned to charge transfer transition.

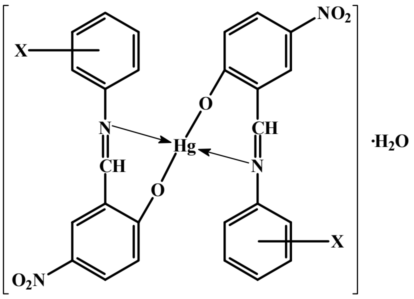
The crystal lattice parameters of the complexes are summarized in Table-3. All the complexes are monoclinic with space group $P_{2/m}$ and crystallized by 16 molecules (Z) per unit cell.

TABLE-3
CRYSTAL LATTICE PARAMETERS OF MERCURY(II) COMPLEXES

Complex	a	b	c	β°	Vol. Å^3	δ obs (g/cm^3)	δ cal (g/cm^3)	Porosity (%)
	Å	Å	Å					
Hg$(L_1)_2$.H_2O	18.9624 ± 0.0499	24.7004 ± 0.1656	31.9178 ± 0.2352	85.24	14949	1.2664	1.2944	2.16
Hg$(L_2)_2$.H_2O	18.8827 ± 0.0520	24.9614 ± 0.1726	32.1189 ± 0.1824	86.08	15103	1.2412	1.2812	3.12
Hg$(L_3)_2$.H_2O	18.8181 ± 0.0629	24.9653 ± 0.1515	33.2640 ± 0.2963	85.82	15586	1.2957	1.3438	3.58
Hg$(L_4)_2$.H_2O	19.4608 ± 0.0606	23.7506 ± 0.1635	30.4088 ± 0.3500	83.43	13962	1.4688	1.5001	2.08
Hg$(L_5)_2$.H_2O	19.4664 ± 0.0801	23.8403 ± 0.3263	29.1218 ± 0.3276	86.29	13488	1.4629	1.5725	6.97
Hg$(L_6)_2$.H_2O	20.2189 ± 0.6637	21.5493 ± 0.1671	30.1587 ± 0.1836	87.68	13074	1.5187	1.6223	6.38

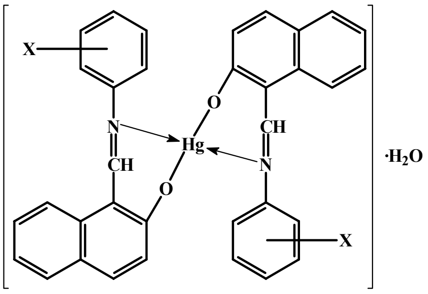
Conclusion

On basis of analytical data, magnetic measurements and spectral data the complexes may be assigned the following structures (a) and (b):



where X =*o*-CH$_3$, *p*-CH$_3$, *o*-COOH or*p*-COOH

(a)



where X =*o*-COOH or*p*-COOH

(b)

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(*Received*: 5 May 2006; *Accepted*: 28 February 2007) AJC-5466