Synthesis, Reactions and Spectroscopic {UV-Visible, IR, NMR (^{1}H- & ^{13}C-), FAB-MS, TGA and XRD} Studies of New Mercury(II) Complexes Containing Various Mixed Ligand Schiff Bases

Raj Kumar Dubey and Pragya Baranwal

Synthetic Inorganic and Metallo-organic Research Laboratory
Department of Chemistry, University of Allahabad,
Allahabad-211 002 (India)
E-mail: rajalkoxy@yahoo.com

ABSTRACT

A series of new and novel complexes of the types [(Cl)Hg(L)] and [Hg(L)$_2$] [where L= Schiff bases; salicylidene-2-methyl-1-aminobenzene (smabH) and vanilidene-1-aminobenzene (vabH)] of mercury(II) have been synthesized by the interactions of mercury(II) chloride with sodium salts of Schiff bases in the presence of THF-MeOH mixture, in 1:1 and 1:2 molar ratio(s) respectively, to produce complexes; [(μ-Cl)$_2$Hg$_2$(smab)$_2$] **(1)**, [Hg(smab)$_2$] **(2)**, [(μ-Cl)$_2$Hg$_2$(vab)$_2$] **(3)** and [Hg(vab)$_2$] **(4)**. Further, complex [(μ-Cl)$_2$Hg$_2$(smab)$_2$] **(1)** has been treated with various aryloxo-, alkoxo-, tetraisopropoxyaluminate, benzoxazolato- and benzimidazolato- salts of sodium in equimolar ratio, to produce new mixed ligand complexes such as, [(μ-OAr)$_2$Hg$_2$(smab)$_2$]**(5)**, [(μ-OPr^i)$_2$Hg$_2$(smab)$_2$] **(6)**, [{(μ-OPr^i)$_2$Al(OPr^i)$_2$}Hg(smab)] **(7)**, [{η^2-(pbox)}Hg(smab)] **(8)** and [{η^2-(pbz)}Hg(smab)] **(9)**.

These complexes have been characterized by elemental analysis (Hg, Cl, C, H & N), melting points and spectral (UV-vis, FT-IR, ^{1}H-, ^{13}C-NMR and FAB-MS) data, whereas the structure of the complexes have been tentatively determined by FAB-MS spectral studies. A thermogravimetric analysis (for complex **4**) and X-ray powder diffraction studies (for complex **3**) are also reported herein.

INTRODUCTION

Schiff base complexes play a vital role in the field of coordination chemistry, due to their preparation, accessibility, diversity, structural variability /1/, and are extensively studied in coordination chemistry mainly

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*Author for correspondence
#This article is dedicated to my mentor (Late) Prof. R. C. Mehrotra; "Father of Metal Alkoxide" on his 88th Birthday.

due to their facile syntheses, easily tunable steric, electronic properties and good solubility in polar solvents. The studies on Schiff base complexes of mercury(II) are limited, probably due to the toxic nature of mercury which has long been known /2/.

Mercury toxicity causes autoimmune disorder, and its multiple adverse effects on the immune system, nerve tissue and connective tissue can only account for its wide range of symptoms in general /3, 4/. The coordination chemistry of mercury(II) differs from most transition metals due to its large size and d^{10} configuration, which causes it to be considered, by many authors, as a main group iron-transition metal.. Its interference in biological systems, and its potential as a toxin or as a medicine, has required a better understanding of its coordinative properties /5, 6/.

Although mercury has been used as a constituent of drugs such as bactericides, diuretics, antiseptics, skin ointment and laxatives /7, 8/, the toxicity of mercury and its compounds to living system is well known /9/. The chemistry of mercury Schiff base complexes has a great role in the field of bioinorganic chemistry. A detailed study of mixed ligand Schiff base complexes of later '3d' transition metals has already been explored in our laboratories /10-13/.

In view of the above facts we focus our attention on the synthesis and characterization [by means of spectral (IR, NMR, FAB-MS, XRD) and thermogravimetric studies] of mercury(II) complexes with Schiff bases containing oxygen and nitrogen donor atoms.

EXPERIMENTAL

Materials and Methods

Reagent grade (BDH) precursors to ligands and solvents were purified by the standard procedures /14/. Mercury(II) chloride was purchased from E. Merck and used without further purification. All other chemicals were purchased from commercial sources and used as such.

Elemental analyses for C, H and N were performed on a Heraeus Carlo Erba 1108 elemental analyser. Mercury was estimated by standard literature method /15/. The electronic spectra of the compounds were recorded in dimethyl formamide using a 10 mm quartz cell on a Perkin-Elmer Lambda 15 UV-vis spectrophotometer. The infrared spectra of ligands and the complexes, in the range 4000-200 cm^{-1}, were recorded in KBr pellets on a Perkin-Elmer 1000 FT-IR spectrophotometer. The NMR spectra of the ligands and the complexes were recorded in $CDCl_3$ and DMSO-D_6 solvents respectively, on Bruker DRX-300 spectrometer, at the sweep width of 300 MHz and a sweep time of 300 sec. The FAB-MS spectra were recorded on JEOLSX 102/DA-6000 mass spectrometer/data system using argon/xenon (6kV, 10mA) as the FAB-gas. The thermogravimetric (TG) analysis of the solid complex was performed using a TGA-50H thermogravimetric analyzer (Shimadzu) from ambient temperature to 800°C with a 20°C min^{-1} heating rate, using N_2 atmosphere. X-ray powder diffraction of the complex was recorded on a Rigaku Model D/Max-2200 PC, using Cu-$K\alpha_1$ radiation (λ = 1.5406 Å).

Preparation of Ligands

The Schiff base, salicylidene-2-methyl-1-aminobenzene (smab**H**) was prepared by refluxing (~4-5 h) equimolar amounts of salicylaldehyde (12.21 g, 10.6 ml) and o-toluidine (10.7 g, 10.6 ml) in methanol (~30 cm^3). A similar procedure was adopted for the preparation of vanilidene-1-aminobenzene (vab**H**) using equimolar amounts of vanillin and aniline in methanol.

Further, sodium salt of salicylidene-2-methyl-1-aminobenzene, Na(smab), was prepared by dissolving equimolar amounts of sodium metal and salicylidene-2-methyl-1-aminobenzene in methanol. Vanilidene-1-aminobenzene and its sodium salt, Na(vab), were prepared by the identical method.

2-aminosodium phenolate, $[Na(O\text{-}C_6H_4NH_2)]$, was prepared by refluxing (~1h) equimolar amount of 2-aminophenol and sodium metal in THF, whereas sodium tetraalkoxyaluminate, $[Na\{Al(OPr^i)_4\}]$ was prepared by standard literature procedure /16/.

The ligands 2-(o-hydroxyphenyl)-benzoxazole (pbox**H**) and 2-(o-hydroxyphenyl)-benzimidazole (pbz**H**) were prepared by standard literature procedure /17, 18/.

Synthesis of mono(chloro) complex of mercury(II), $[(\mu\text{-}Cl)_2Hg_2(smab)_2]$ (1)

To a suspension/ solution of mercury(II) chloride (1.204 g, 4.43 mmol) in tetrahydrofuran (~20 ml) a methanolic solution of Na(smab) (1.035 g, 4.43 mmol) was added dropwise with constant stirring. The reaction mixture was allowed to reflux for ~4h. The separated NaCl was removed by filtration and the filtrate was concentrated, removing the excess of solvent by distillation. The product was dried under reduced pressure, purified by recrystallization from THF-MeOH mixture (purity was further checked by TLC) to afford light yellow crystalline solid. The product $[(\mu\text{-}Cl)_2Hg_2(smab)_2]$ **(1)** on analysis was found to have Hg, 44.9 %; Cl, 7.93 %; (calcd): Hg, (44.9 %); Cl, (7.95 %).

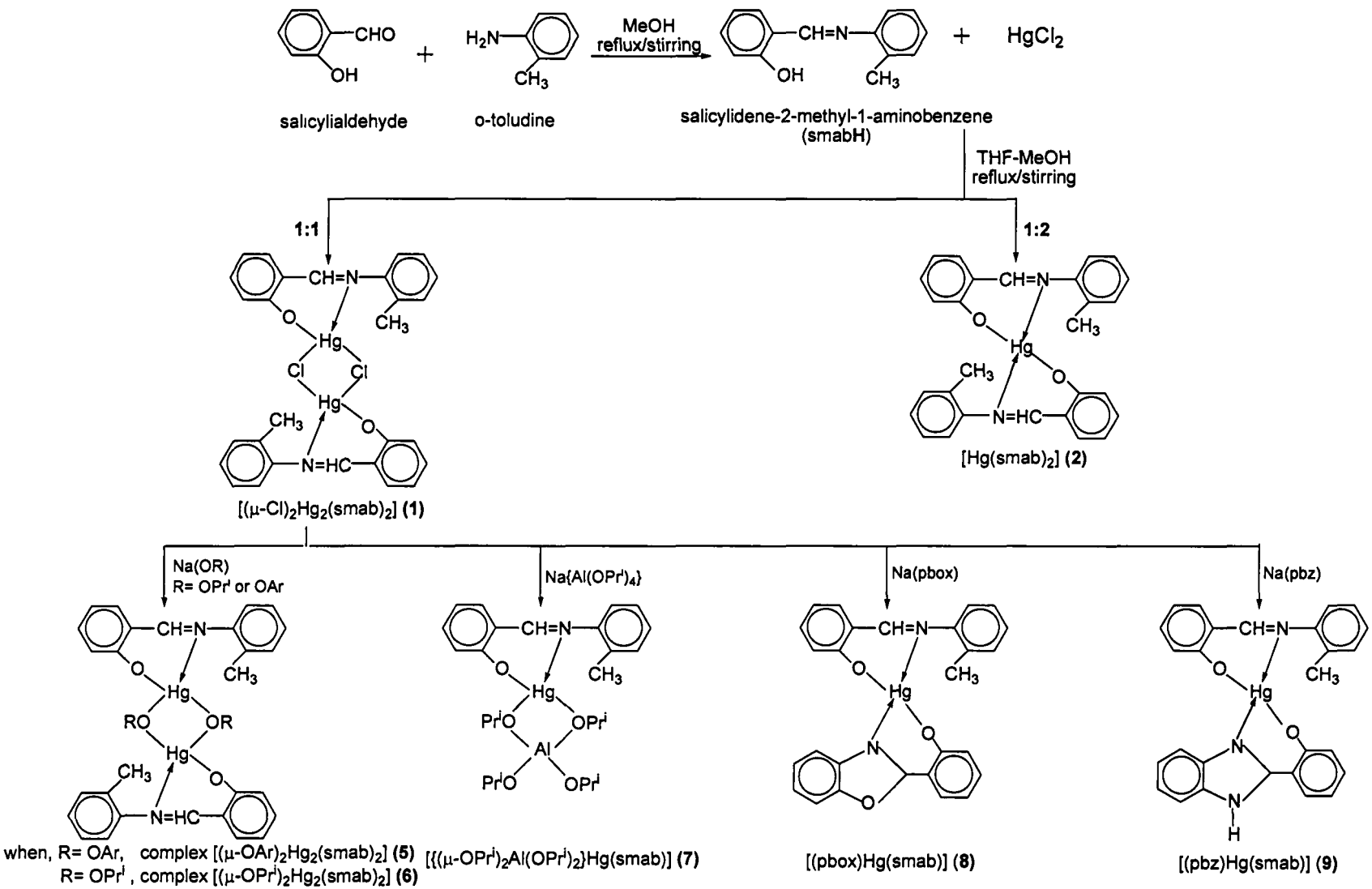
A similar procedure was adopted for the synthesis of complex $[(\mu\text{-}Cl)_2Hg_2(vab)_2]$ **(3)**.

Synthesis of complexes $[Hg(smab)_2]$(2) and $[Hg(vab)_2]$ (4)

The bis complexes $[Hg(smab)_2]$ **(2)** and $[Hg(vab)_2]$ **(4)** have also been prepared by adopting the similar procedure as described for monochloro complex by interaction of mercury(II) chloride and sodium salts of Schiff bases in 1:2 molar ratio. For the sake of brevity, all details are collected in Table 1.

Synthesis of mixed ligand complexes

To a mixture of sodium salt of o-aminophenol (0.245 g, 1.87 mmol) in methanol the THF solution of monochloro complex $[(\mu\text{-}Cl)_2Hg_2(smab)_2]$ **(1)** (0.834 g, 1.87 mmol) was added with constant stirring. The reaction mixture was allowed to reflux for ~4 h. The resulting brown coloured solution was filtered. The filtrate was concentrated and dried under reduced pressure to afford product $[(\mu\text{-}OAr)_2Hg_2(smab)_2]$ **(5)** (0.149 g, 71%)



Scheme 1: Synthesis & reactions of monochloro complex $[(\mu\text{-Cl})_2Hg_2(smab)_2]$ (1)

Table 1

Synthetic, analytical details and melting points of mercury(II) complexes

S. No.	Reactants (g, mmol)	Product (g, %yield)	Physical state	Decomposition point (°C)	% Analysis found (calcd)				
					Hg	Cl/Al	C	H	N
1.	$HgCl_2$ + smabH	[(Cl)Hg(smab)] (1)	Light Yellow	265	44.91	7.93	37.65	2.68	3.56
	(1.204, 4.43) (0.937, 4.43)	(1.48, 74)	Powdered Solid		(44.95)	(7.95)	(37.64)	(2.69)	(3.59)
2.	$HgCl_2$ + 2smabH	$[Hg(smab)_2]$ (2)	Light Green	289	32.32	–	54.07	3.85	4.50
	(0.691, 2.54) (1.075, 5.09)	(1.247, 78)	Powdered Solid		(32.30)		(54.01)	(3.86)	(4.51)
3.	$HgCl_2$ + vabH	[(Cl)Hg(vab)] (3)	Reddish brown	314	43.38	7.63	36.32	2.62	3.01
	(1.45, 5.35) (1.33, 5.35)	(1.812, 73.3)	Powdered Solid		(43.39)	(7.68)	(36.34)	(2.60)	(3.03)
4.	$HgCl_2$ + 2vabH	$[Hg(vab)_2]$ (4)	Brownish black	287	30.71	–	51.46	3.65	4.31
	(0.673, 2.48) (1.236, 4.96)	(1.192, 73.6)	sticky solid		(30.72)		(51.45)	(3.68)	(4.29)
5.	1 + Na(OAr)	[(OAr)Hg(smab)] (5)	Brown	245	38.59	–	46.23	3.49	5.37
	(0.834, 1.87) (0.245, 1.87)	(0.612, 63.09)	Powdered Solid		(38.66)		(46.25)	(3.47)	(5.40)
6.	1 + $Na(OPr^i)$	$[(OPr^i)Hg(smab)]$ (6)	Dirty Yellow	238	42.65	–	43.40	4.01	2.94
	(1.125, 2.52) (0.058, 2.52)	(0.803, 67.82)	Powdered Solid		(42.70)		(43.42)	(4.04)	(2.98)
7.	1 + $Na\{Al(OPr^i)_4\}$	$[\{Al(OPr^i)_4\}Hg(smab)]$ (7)	Mustard Yellow	229	29.72	3.99	–	–	–
	(0.952, 2.13) (0.608, 2.13)	(0.881, 61.39)	Powdered Solid		(29.82)	(4.01)			
8.	1 + Na(pbox)	[(pbox)Hg(smab)] (8)	Orangish Yellow	293	32.26	–	52.13	3.19	4.54
	(1.068, 2.39) (0.558, 2.39)	(0.936, 62.99)	Powdered Solid		(32.30)		(52.17)	(3.22)	(4.51)
9.	1 + Na(pbz)	[(pbz)Hg(smab)] (9)	Pale Yellow	299	32.28	–	52.22	3.33	6.75
	(1.030, 2.30) (0.536, 2.30)	(0.917, 64.08)	Powdered Solid		(32.35)		(52.25)	(3.39)	(6.77)

In a similar manner the other complexes [(μ-OPr^i)Hg(smab)] (**6**), [{(μ-Cl)$_2$Al(OPr^i)$_4$}Hg(smab)] (**7**), [{η^2-pbox)}Hg(smab)] (**8**) and [{η^2-pbz)}Hg(smab)] (**9**) have been synthesized. The synthetic, physical and analytical details are collected in Table 1.

RESULTS AND DISCUSSION

The new complexes, [(Cl)Hg(L)] and [Hg(L)$_2$], have been synthesized by the reaction of $HgCl_2$ with sodium salts of corresponding Schiff bases in methanolic solution, which can be represented by the following chemical equations:

$$HgCl_2 + Na(L) \xrightarrow[\Delta,\ \text{stirred}]{\text{THF/MeOH}} [(Cl)Hg(L)] + NaCl\downarrow$$

$$HgCl_2 + 2Na(L) \xrightarrow[\Delta,\ \text{stirred}]{\text{THF/MeOH}} [Hg(L)_2] + 2NaCl\downarrow$$

[Where L= Schiff base, salicylidene-2-methyl-1-aminobenzene (smab**H**) and vanilidene-1-aminobenzene (vab**H**)].

All these complexes are light-coloured solids and are soluble in polar solvents like THF, DMF and DMSO, but insoluble in water, methanol, ethanol and pyridine etc.

The monochloro complex [(Cl)Hg(smab)] (**1**) has been treated with sodium salts of aryloxo-/alkoxo- and tetraisopropoxyaluminate in equimolar ratio:

$$[(Cl)Hg(smab)] + Na(OR) \xrightarrow[\Delta,\ \text{stirred}]{\text{THF}} [(OR)Hg(smab)] + NaCl\downarrow$$

(where R= $NH_2C_6H_4$ or Pr^i)

$$[(Cl)Hg(smab)] + Na\{Al(OPr^i)_4\} \xrightarrow[\Delta,\ \text{stirred}]{\text{THF}} [\{Al(OPr^i)_4\}Hg(smab)] + NaCl\downarrow$$

whereas mixed ligand complexes, [(pbox)Hg(smab)] and [(pbz)Hg(smab)], have been prepared by using complex (**1**) and sodium salts of 2-(o-hydroxyphenyl)-benzoxazole (pbox**H**) and 2-(o-hydroxyphenyl)-benzimidazole (pbz**H**) in 1:1 molar ratio:

$$[(Cl)Hg(smab)] + Na(pbox) \xrightarrow[\Delta,\ \text{stirred}]{\text{THF}} [(pbox)Hg(smab)] + NaCl\downarrow$$

$$[(Cl)Hg(smab)] + Na(pbz) \xrightarrow[\Delta,\ \text{stirred}]{\text{THF}} [(pbz)Hg(smab)] + NaCl\downarrow$$

All these complexes are non-hygroscopic in nature. The physical and analytical details are collected in Table 1.

The structures and purities of the Schiff base ligand and the metal complexes were confirmed by IR, ^{1}H-, ^{13}C-NMR and elemental analysis. Further, the structure of ligand and complexes are confirmed by FAB-MS spectra, thermogravimetric analysis and X-ray powder diffraction studies.

Electronic Spectra

The electronic spectra of mercury(II) complexes formed by Schiff base ligand do not show any significant band which could help in elucidating their structure. The bands observed at 24330±260, 28310±150 and 32000±281 cm^{-1} may be due to their n-π*, π- π* and n-σ* transition /19/.

Infrared Spectra

The characteristic IR bands for the ligands, when compared with those of its mercury(II) complexes, provide positive indications with respect to the bonding sites of the ligands.

The characteristic $\nu_{(C-O)}$ phenolic stretching frequencies, appearing at 1275, 1265 cm^{-1} in the ligands smab**H** and vab**H**, respectively, were shifted to higher frequency region at 1289, 1273 cm^{-1} and showed that bonding with the neutral metal ion has taken place through the phenolic oxygen /10, 11/ of Schiff bases.

The medium band appearing at 1628-1624 cm^{-1} in the ligands, due to $\nu_{(C=N)}$ /20/, was shifted to lower frequency regions 1605-1584 cm^{-1} in the complexes, indicating coordination of the azomethine nitrogen to the metal.

The appearance of the new bands in the regions 324-310 and 426-407 cm^{-1} can be assigned to $\nu_{(Hg-O)}$ and $\nu_{(Hg-N)}$ /21/, respectively. The $\nu_{(M-Cl)}$ stretching frequency showed bridging between two metal atoms through (μ-Cl) by lowering in frequency. In mercury(II) chloro complexes with bridging mercury chloride, $\nu_{(Hg-Cl)}$ stretching frequencies occurred in the much lower range <200 cm^{-1} /22/, which would be expected to absorb /23/ below range 200 cm^{-1}.

The presence of bridging isopropoxy and aryloxy group, bands appeared at 914 and 1202 cm^{-1} respectively in the complexes. The IR spectra of alkoxo bridged (bimetallic) complexes exhibited characteristics frequencies for metal alkoxy group $\nu_{[(C-O)-Al]}$ in the range 1114 cm^{-1} for terminal isopropoxy group, and the band at 616 cm^{-1} has been assigned for bridging isopropoxy groups $\nu_{(Al-O)}$ /24/.

The stretching vibration $\nu_{(C=N)}$ of benzoxazole and benzimidazole ring shifted to lower frequencies region at 1598 and 1591 cm^{-1} in relation to the free ligand (range at 1617, 1622). The bands at 321 and 432 cm^{-1} can be attributed to $\nu_{(Hg-O)}$, $\nu_{(Hg-N)}$ (benzoxazole) respectively (vibrations for the complexes **8** and **9**), whereas other bands, appearing at 329 and 435 cm^{-1}, are attributed to $\nu_{(Hg-O)}$, $\nu_{(Hg-N)}$ (benzimidazole) respectively (vibrations for the complexes **8** and **9**).

NMR

^{1}H- NMR Spectra

^{1}H- NMR spectra have been recorded in deuterated dimethylsulfoxide (DMSO-d_6) and in deuterated chloroform ($CDCl_3$), using TMS as internal standard, and the resulting data showed expected multiplicity of the signals and shifting relative to their positions in the spectra of the corresponding ligands /25,26/. The integrated proton ratios correspond to the respective stoichiometric formulae of the complexes. In the spectra of the Schiff base ligands, smab**H** and sap**H**, sharp signals observed at δ8.47, δ8.38 ppm, respectively,

correspond to the azomethine proton, which on complexation undergoes some shielding due to a change in the environment surrounding the proton, and gave signals at δ8.69–8.49 ppm /27,28/ in the corresponding complexes. A strong signal appeared in the region δ12.40, δ6.51 ppm, which may be attributed to the phenolic proton (OH) of ligands, whereas ^{1}H-NMR spectra of the corresponding metal complexes of Hg(II) are devoid of signals due to OH proton, indicating bonding to metal through phenolic oxygen after deprotonation.

The NMR spectra of ligands exhibited signals due to OH aromatic protons in the region δ7.90–6.08 ppm, which are shielded compared to the free ligands, probably due to high order of distortion of the aromatic rings as a result of the complex formation with metal. All data are collected in Tables 2 and 3.

^{13}C- NMR Spectra

^{13}C-NMR spectra were recorded in DMSO–d_6 and the spectra exhibited characteristic resonance signals due to the presence of various groups, like hydroxyl, methoxy, carboxy, phenyl and azomethine.

The ^{13}C-NMR spectra of ligands signal observed in the region δ159.92–156.51 ppm, assigned to the azomethine carbon, which was shifted upfield in the range δ157.45–151.28 ppm in the complexes, suggests coordination of azomethine nitrogen to the metal atom /29/.

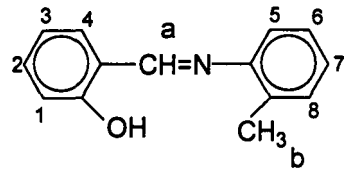
The signal appearing at around δ151.56–148.28 ppm in the spectra of ligands, corresponding to the phenolic carbon, shifted downfield to the region δ160–158.76 ppm, indicating bonding through phenolic oxygen after deprotonation of the OH proton, resulting in formation of an Hg-O bond /29/. The ligands exhibited signals in the regions δ125.36 ppm, 141.65 ppm and 122.6 ppm in their ^{13}C-NMR spectra, which may be attributed to the three different carbon atoms of the benzene ring; these did not show any appreciable change in complexation /29/.

FAB-MS Spectra

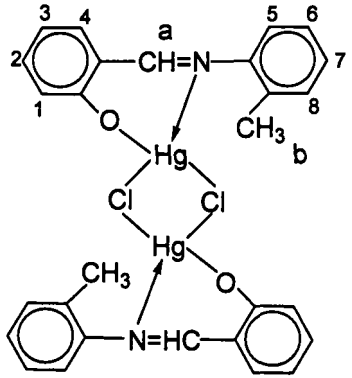
The FAB-MS spectrum /13/ of the ligand (smab**H**) shows [Fig. 1, Scheme 2] a characteristic molecular ion (M+) peak at m/z 213, which corresponds to the molecular weight of the ligand. The representative complexes of mercury(II), $[(\mu\text{-Cl})_2Hg_2(smab)_2]$ **(1)** (Fig. 2) and $[Hg(smab)_2]$ **(2)** (Fig. 3), show a characteristic molecular ion peak at m/z 894 and 622, respectively. **(1)** corresponds to the molecular weight of the complex $[(C_{28}H_{24}N_2O_2Cl_2Hg_2)$; calculated mass= 892.56] for a dimeric structure. The mass spectrum shows multiple peaks representing successive degradation of the complex molecule by the formation of monomer, and their ion peak was observed at m/z 447 (base peak); other important peaks were also observed due to formation of various radicals 879, 804, 777, 701, 685, 670, 594, 567, 471, 412, 329, 294, 253, 211, 119, 118, 92. The fragmentation pattern showing the structure is given in Scheme 3. On the other hand, complex **(2)** shows some prominent peaks corresponding to various fragments of the complex. The molecular ion peak at m/z 622 $[(C_{28}H_{24}N_2O_2Hg_2)$; calcd. mass= 621.06] represents the molecular ion peak of the complex. The base peak with m/z 387 represents the $(C_{12}H_8O_2Hg)$ as residue. Other important peaks at m/z 607, 532, 517, 505, 443, 413, 312, 235, 211, 195, 119, 118, 92 have been observed, which are exhibited in Scheme 4; confirming the structure of the complex.

Table 2

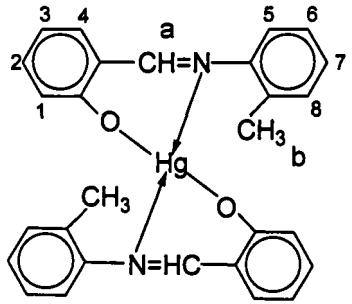
^{1}H-NMR, chemical shifts (δ, ppm) for the Schiff base, (smab**H**), their mercury(II) complexes **1**, **2** in DMSO-d_6 with their assignments



salicylidene-2-methyl-1-aminobenzene (smab**H**)



[(μ-Cl)$_2$Hg$_2$(smab)$_2$] **(1)**

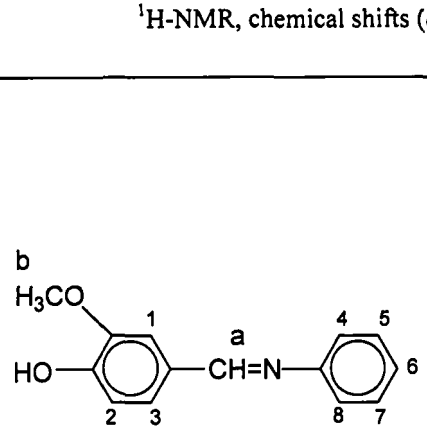


[Hg(smab)$_2$] **(2)**

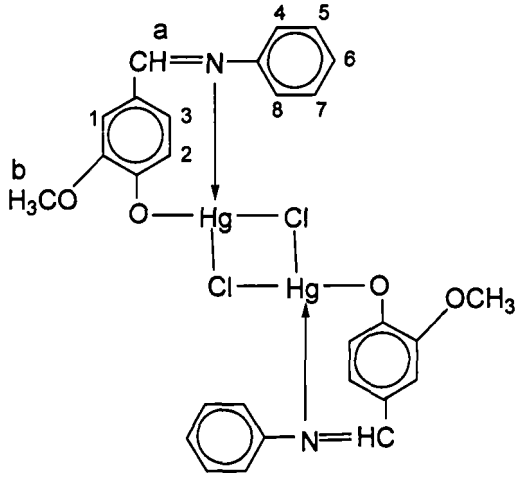
Schiff base/complex	δ OH (s)	δ H_a (s)	δ H_b (3H, t, H_b)	δ H (m) (8H, m, H_1-H_8)
Ligand (smab**H**)	12.40	8.47	2.32	7.33-6.79
[(Cl)Hg(smab)] **(1)**		8.77	2.41	7.80-6.72
[Hg(smab)$_2$] **(2)**		8.69	2.39	7.69-6.61

Table 3

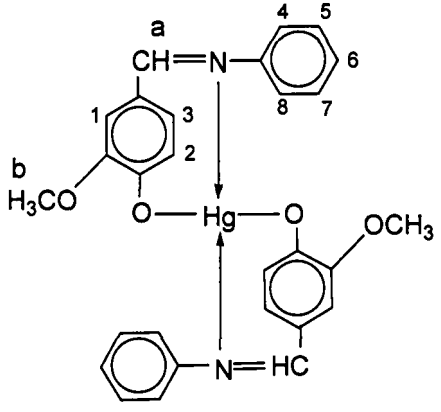
^{1}H-NMR, chemical shifts (δ, ppm) for the Schiff base, (vab**H**), their mercury(II) complexes **3**, **4** with their assignments



vanilidene-1-aminobenzene
(vabH)



[(μ-Cl)$_2$Hg$_2$(vab)$_2$] **(3)**



[Hg(vab)$_2$] **(4)**

Schiff base/complex	**δ OH (s)**	**δ H$_a$ (s)**	**δ H$_b$ (3H, t, H$_b$)**	**δ H (m) (8H, m, H$_1$-H$_8$)**
Ligand (vabH)	6.51	8.38	3.92	7.69-6.94
[(Cl)Hg(vab)] **(3)**		8.61	4.46	8.71-6.66
[Hg(vab)$_2$] **(4)**		8.49	4.33	8.04-6.98

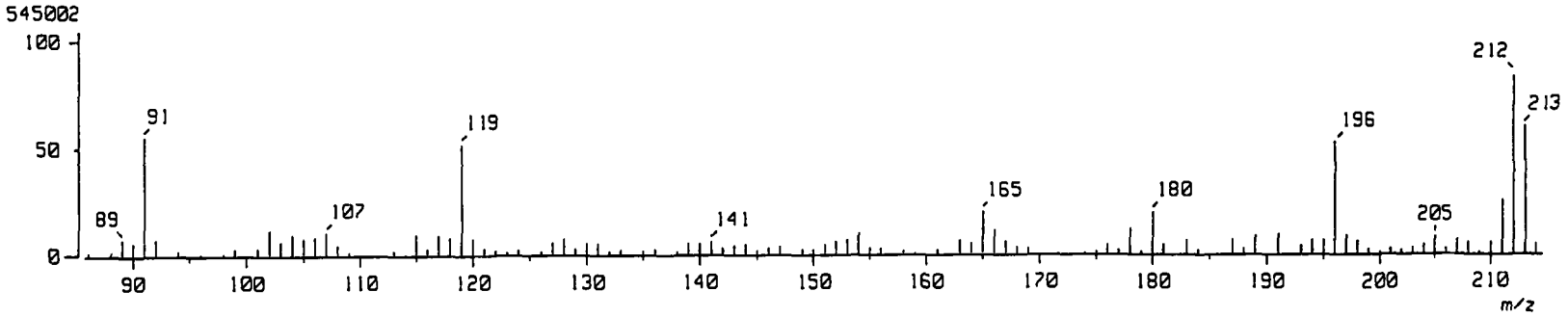
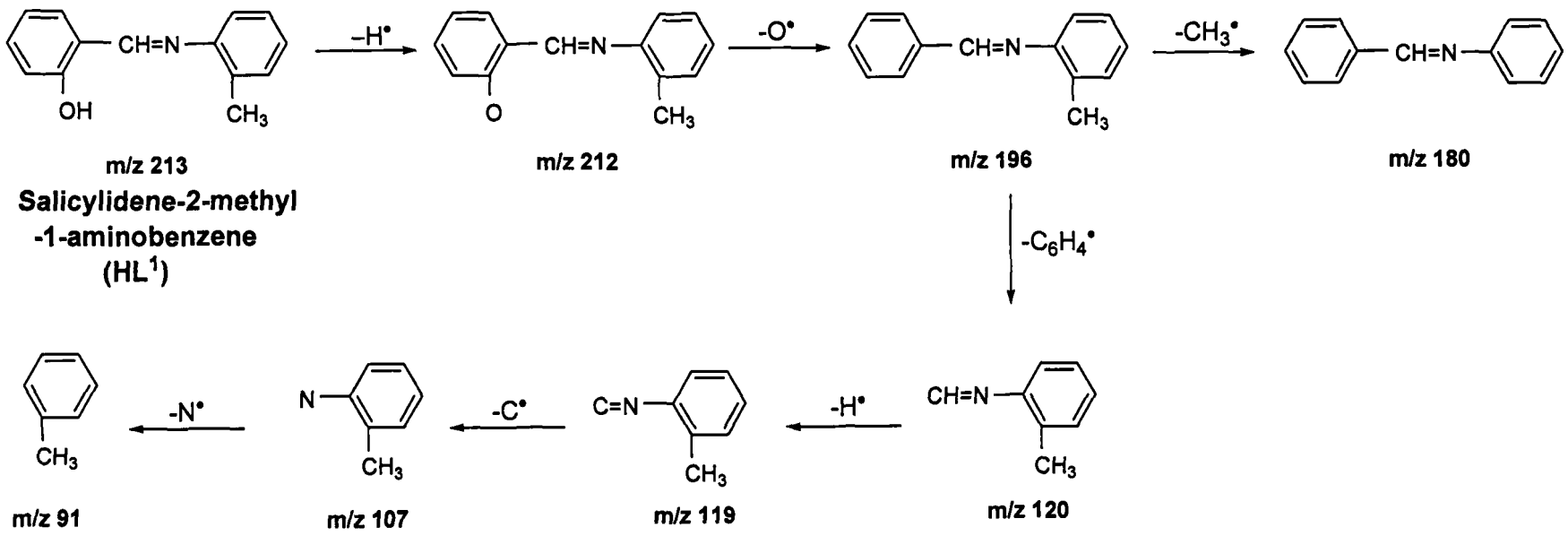


Fig. 1: FAB-MS spectra of smab**H**



Scheme 2 Fragmentation pattern of smab**H** using FAB-MS spectrum

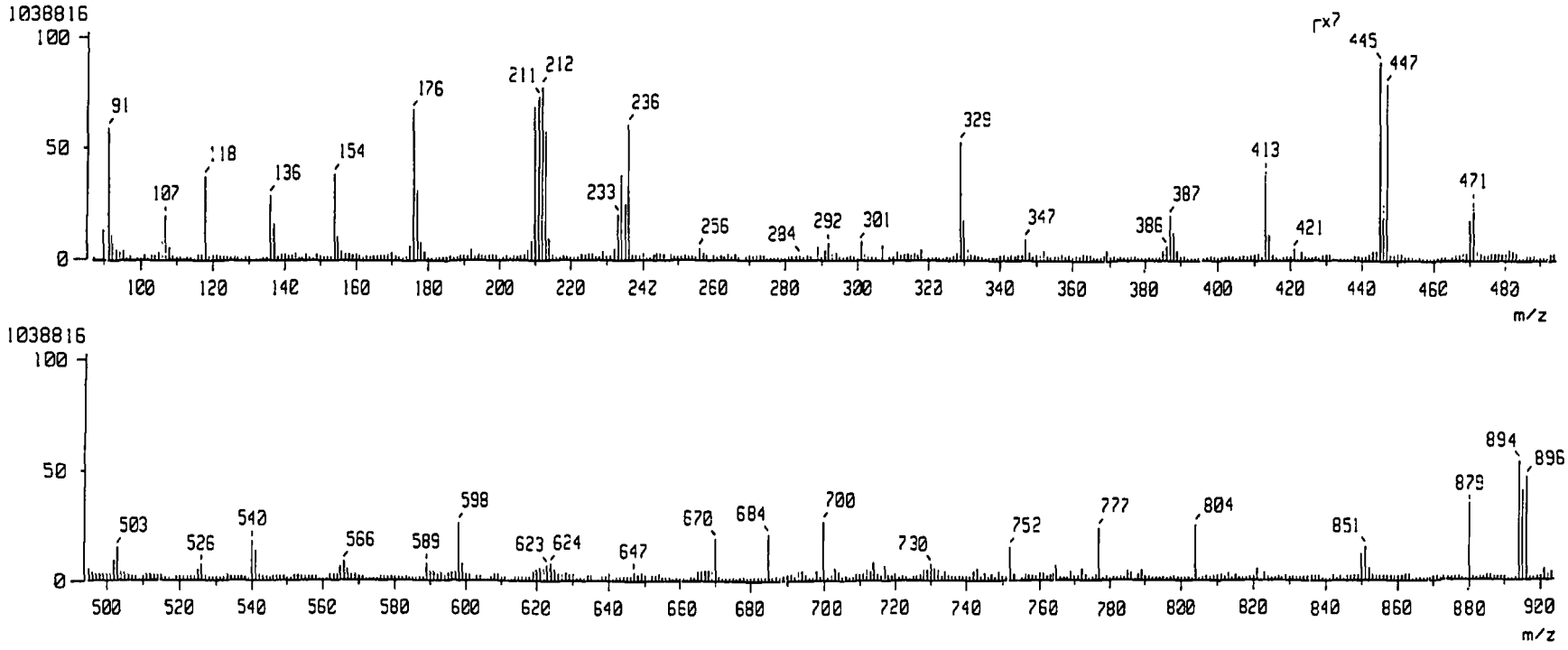
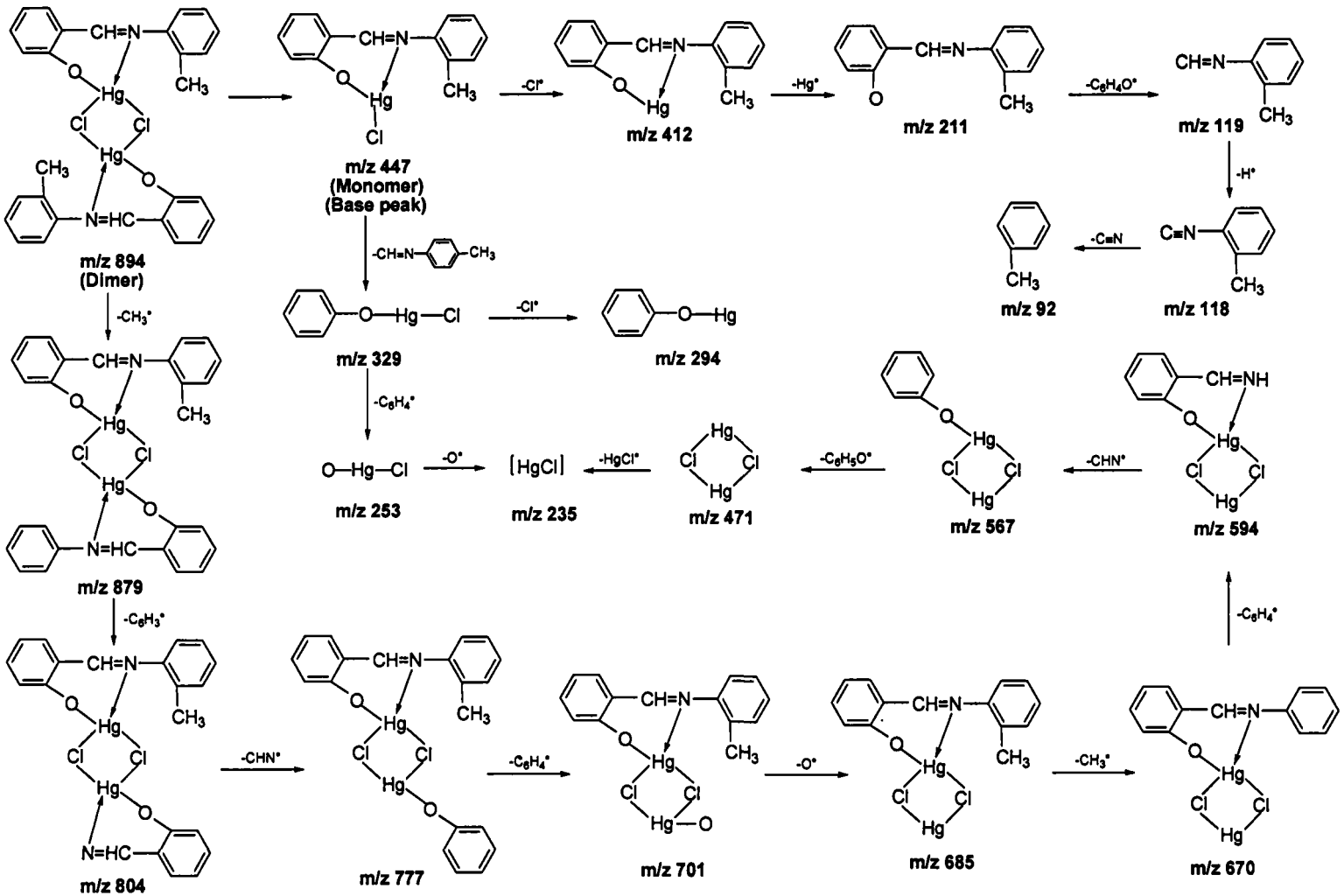


Fig. 2 FAB-MS spectra of $[(\mu\text{-Cl})_2Hg_2(smab)_2]$ (1)



Scheme 3: Fragmentation pattern of $[(\mu\text{-}Cl)_2Hg_2(smab)_2]$ (1) using FAB-MS spectrum

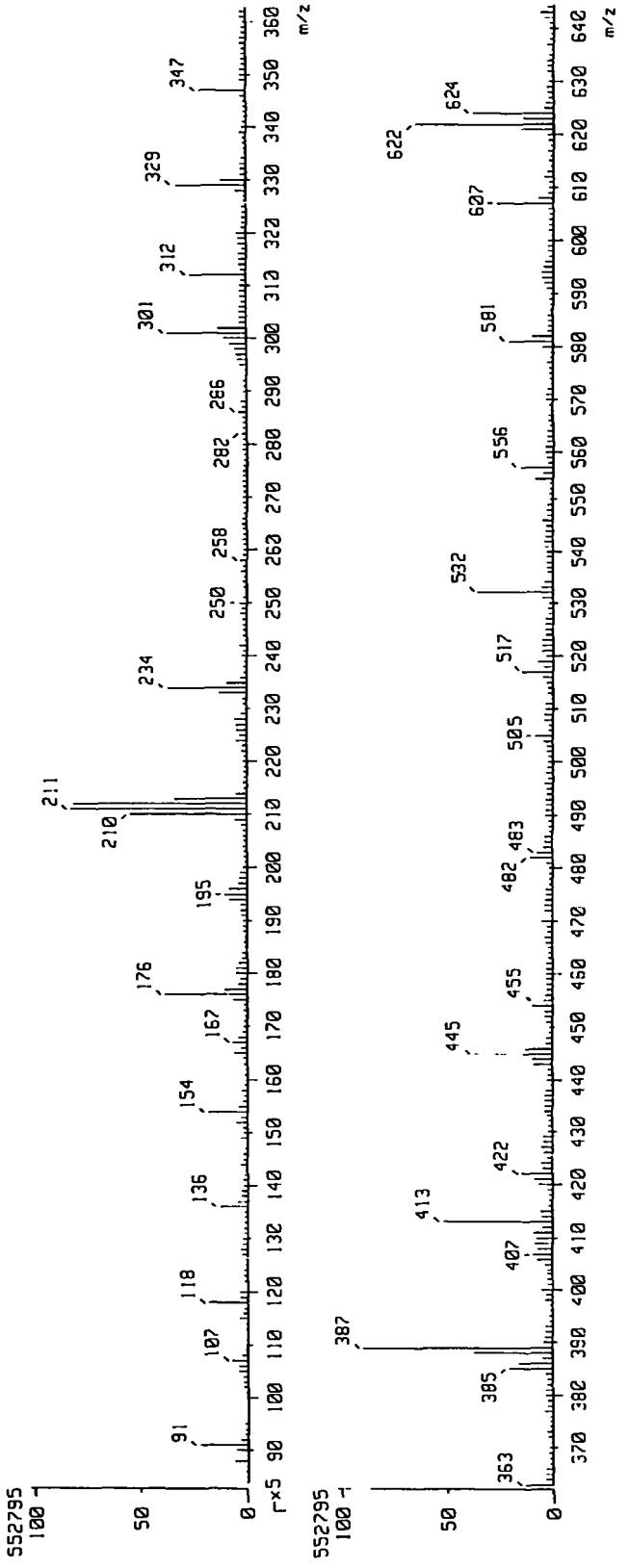


Fig. 3 FAB-MS spectra of [Hg(smab)$_2$] (2)

Thermogravimetric Analysis

Thermogravimetric analysis for the complex $[Hg(vab)_2]$ (**4**) ($C_{28}H_{24}O_4N_2Hg$), Fig. 4, shows a curve which was carried out within a temperature range 40 °C to 800 °C. The molecular mass of the complex is 655.06 and the % weight loss of the complex is 47.551% which amounts to 311.4875 mass of the complex. It is clear the complete elimination of one coordinated ligand from the complex and another from ligand C_6H_5N have occurred. Thereafter weight of the residue is 343.5725 [$HgC_8H_7O_2$].

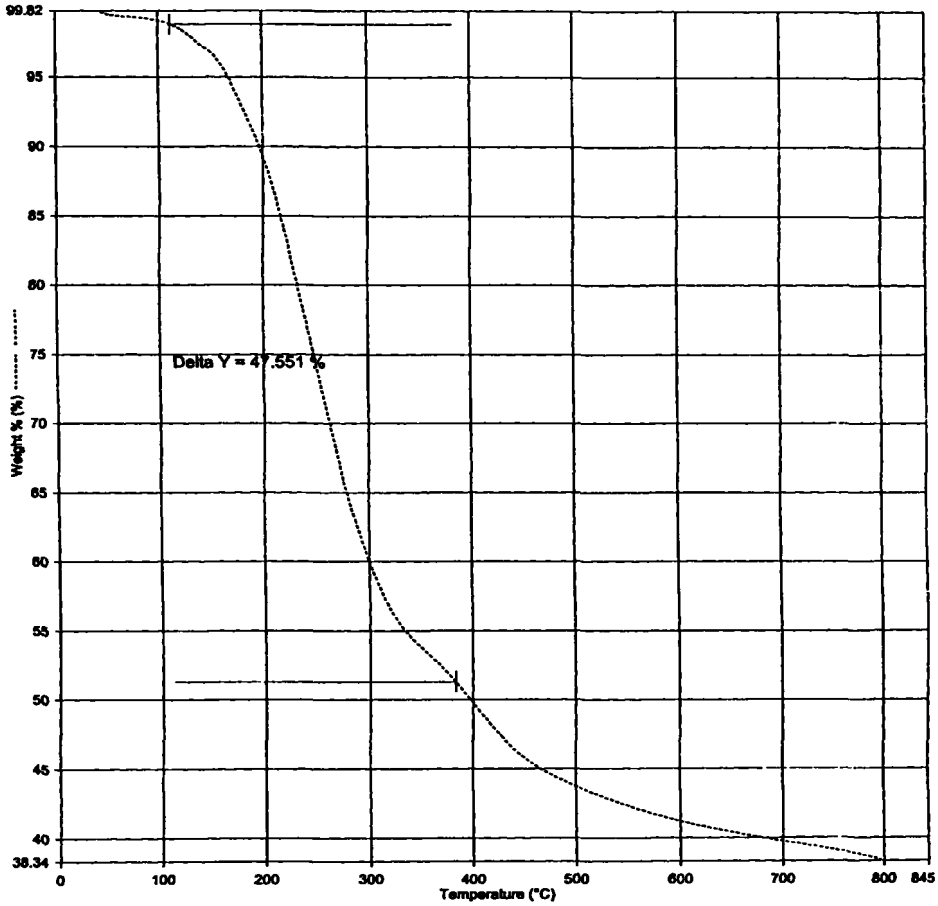
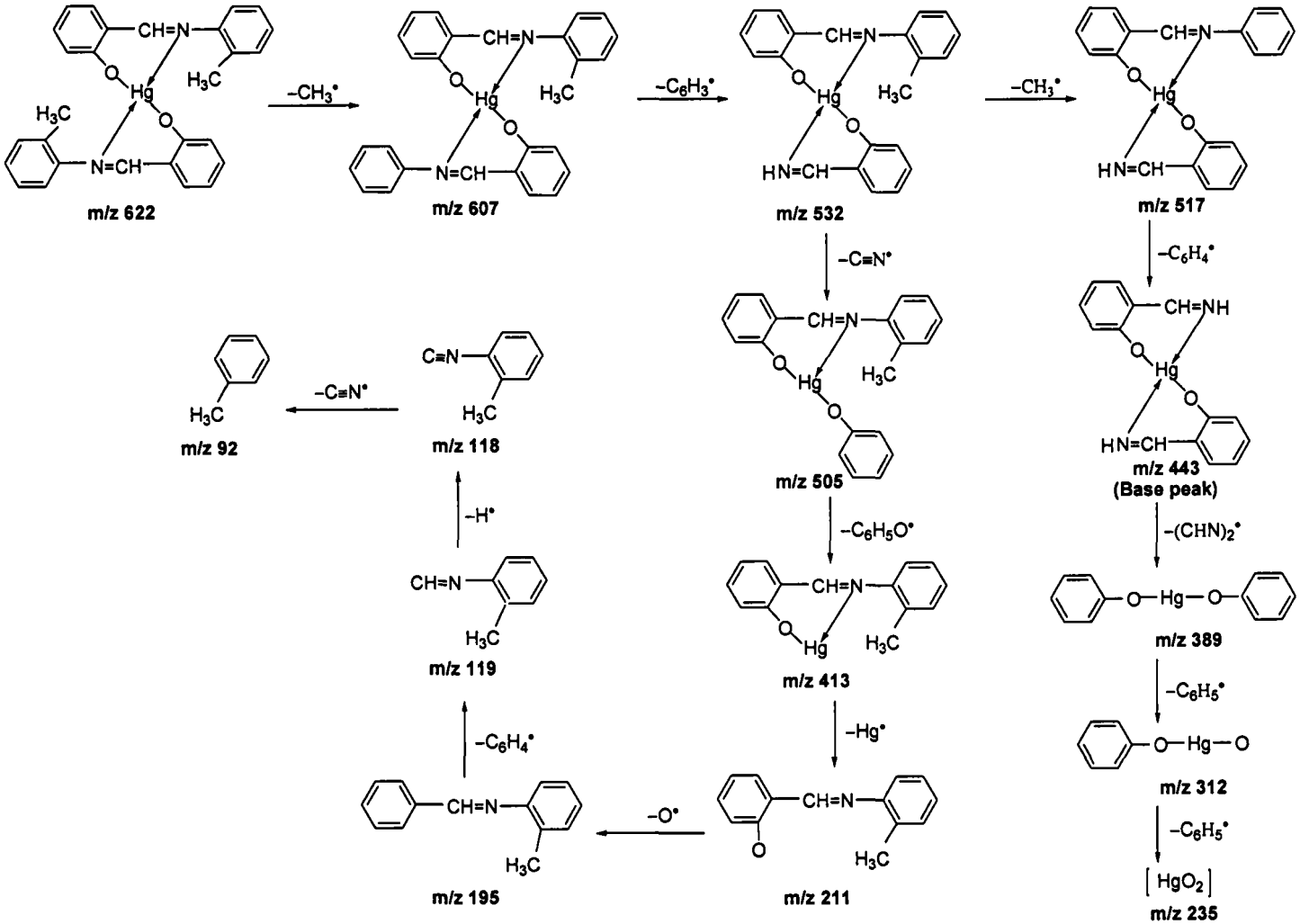


Fig. 4 TGA Curve of the Complex $[Hg(vab)_2]$ (4)

Table 4

Parameters of Mercury(II) Complex

Parameters	[(Cl)Hg(vab)] 3
Crystallite size	204.33333 Å
Empirical formula	$(C_{14}H_{12}O_2NHgCl)_2$
Formula weight	928
Powder used	0.8 Kw
Wave length	1.506 Å



Scheme 4 Fragmentation Pattern of [Hg(smab)$_2$] (2) Using FAB-MS Spectrum

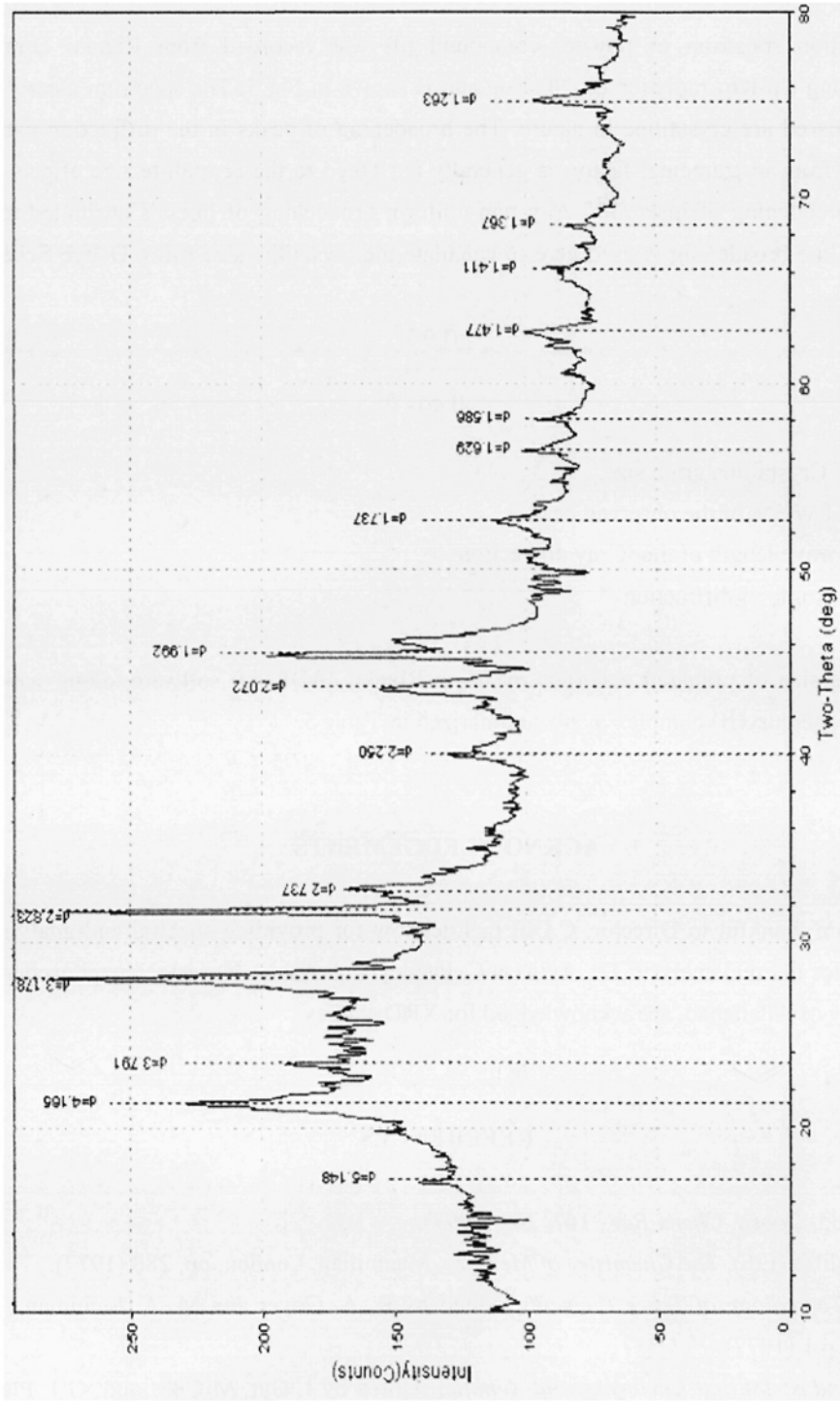


Fig. 5 PXRD Patterns of the Complex $[(\mu\text{-Cl})_2Hg_2(vab)_2]$ (3)

X-ray Powder Diffraction Studies

X-ray diffraction spectrum of powder compound **(3)** was recorded from Rigaku D/max-2200 PC diffractometer using Cu-$K\alpha_1$ radiation on 2θ scale and is shown in Fig 5. The spectrum clearly showed that the materials prepared are crystalline in nature. The broadening of peaks in the diffraction pattern, beyond what is expected from instrumental factor, is generally attributed to the crystallite size effects. This is also called Scherrer broadening of lines /30/. Any non-uniform broadening of lines is attributed to anisotropic crystallites. This line broadening is used here to calculate the crystallite size using Debye Scherrer formula /31/.

$$D = \frac{0.9\,\lambda}{\beta \cos 0}$$

where D = Crystalline grain size.
β = FWHM of the observed peak.
λ= wave length of the X-ray diffraction
0 = Angle of diffraction

The crystallite size of prepared materials by using Rigaku JADE 6.0 software, along with parameters calculated for the mercury(II) complex **3**, are summarized in Table 5.

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