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# Synthesis and spectral studies of some new dimeric $[(\mu-Cl)_2M_2(L)_2 \cdot xTHF]$ [M = Zn(II) and Hg(II)] complexes containing Schiff-base ligands

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A series of binuclear Schiff-base complexes of zinc(II) and mercury(II) containing bidentate ligands (HL) [HL = salicylidene-2-methyl-1-aminobenzene (HL<sup>1</sup>), salicylidene-2-aminopyridine (HL<sup>2</sup>), and salicylidene-3-nitro-1-aminobenzene (HL<sup>3</sup>)] with "N" and "O" donors have been synthesized by simple metathetic reactions of anhydrous metal chlorides with sodium salts of Schiff bases (in tetrahydrofuran (THF)/MeOH) in equimolar ratio to produce  $[(\mu-Cl)_2M_2(L)_2 \cdot xTHF]$  [where M = Zn(II) and Hg(II);  $L = HL^1$ ,  $HL^2$ , and  $HL^3$ ; x = 0 for (1), (4), (6) and x = 2 for (2), (3), (5)]. The main emphasis on the complexes  $[(\mu-Cl)_2M_2(L)_2 \cdot 2THF]$  (2), (3), and (5) is given due to their five-coordinate environment around metal ions. The complexes have been characterized by elemental analyses (M, Cl, C, H, N), melting point, and spectral (FT-IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR) studies. FAB-MS showed the isotopic molecular ion peak [M<sup>+</sup>] and fragments supporting the formulation. Powder X-ray diffraction study of 6 is also reported showing the crystallite size (404.5 Å) of the complexe.

Keywords: Synthesis, Schiff bases; Metal complexes; IR; NMR; FAB-MS; PXRD

#### 1. Introduction

The chemistry of Schiff bases has developed because of their facile syntheses, electronic properties, and fair solubility in common organic solvents [1]. Metal complexes of Schiff base are of interest in biomedical research [2–5] and chelation therapy for the treatment of heavy-metal poisoning [6]. Schiff bases containing oxygen and nitrogen donors have a variety of ways in which they are bonded to metal ions [7, 8]. Zinc can function as the active site of hydrolytic enzymes and is an important co-factor in biological molecules, either as a structural template in protein folding or as a Lewis acid catalyst that can readily adopt coordination numbers of four, five, or six [9–11]. The variety of possible Schiff-base metal complexes has prompted us to undertake research in this area.

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In this work, we synthesize and study the mode of coordination of chelates of salicylidene-2-methyl-1-aminobenzene (HL<sup>1</sup>), salicylidene-2-aminopyridine (HL<sup>2</sup>), and salicylidene-3-nitro-1-aminobenzene (HL<sup>3</sup>) Schiff bases with Zn(II) and Hg(II). This article focuses, for the first time, on binuclear chloro-bridged ( $\mu$ -Cl) Zn(II) and Hg(II) complexes of Schiff bases.

# 2. Experimental

Reagent grade (BDH) precursors to ligands and solvents were purified by standard procedures [12]. Mercury(II) chloride was purchased from E. Merck and used without purification. All other chemicals were purchased from commercial sources and used as received. Elemental analyses (C, H, and N) were performed on a Heraceous Carlo Erba 1108 elemental analyzer. Mercury was estimated by standard method [13]. Infrared (IR) spectra of ligands and complexes from 4000 to  $200 \text{ cm}^{-1}$  were recorded in KBr pellets on a Perkin-Elmer 1000 FT-IR spectrophotometer. NMR spectra of the ligands and complexes were recorded in CDCI<sub>3</sub> and DMSO-d<sub>6</sub>, respectively, on a Bruker DRX-300 spectrometer at the sweep width of 300 MHz and a sweep time of 300 s. FAB-MS spectra were recorded on JEOLSX 102/DA-6000 mass spectrometer/data system using argon/xenon (6kV, 10 mA) as the FAB-gas. Powder X-ray diffraction (PXRD) was recorded on a Rigaku model D/Max-2200 PC using Cu-K $\alpha_1$  radiation ( $\lambda = 1.5406 \text{ Å}$ ).

# 2.1. Syntheses

**2.1.1. Synthesis of ligands.** Salicylidene-2-methyl-1-aminobenzene (HL<sup>1</sup>) was prepared by refluxing ( $\sim$ 4–5 h) equimolar salicylaldehyde (5.73 g, 47.0 mmol) and *o*-toluidine (5.06 g, 47.0 mmol) in methanol ( $\sim$ 30 cm<sup>3</sup>). After recrystallization bright yellow solid product was obtained. [Yield (7.73 g, 78%); Anal. Calcd for C<sub>14</sub>H<sub>13</sub>NO (%): C, 79.58; H, 6.20; N, 6.61. Found (%): C, 79.64; H, 6.25; N, 6.67].

Similar procedure was adopted for the preparation of salicylidene-2-aminopyridine [14] (HL<sup>2</sup>) and salicylidene-3-nitro-1-aminobenzene [14] (HL<sup>3</sup>) using equimolar amounts of salicylaldehyde and 2-aminopyridine/3-nitro-1-aminobenzene in methanol. Sodium salts, Na(L<sup>1</sup>), Na(L<sup>2</sup>), and Na(L<sup>3</sup>), were prepared by dissolving equimolar amounts of sodium metal and salicylidene-2-methyl-1-aminobenzene, salicylidene-2-aminopyridine, and salicylidene-3-nitro-1-aminobenzene in methanol, respectively.

#### 2.1.2. Synthesis of metal complexes

2.1.2.1.  $[(\mu-Cl)_2Zn_2(L^1)_2]$  (1). To a suspension/solution of zinc(II) chloride (0.646 g, 4.74 mmol) in tetrahydrofuran (THF; ~20 mL) was added a methanolic solution of Na(L<sup>1</sup>) (1.105 g, 4.74 mmol) dropwise with constant stirring. The reaction mixture was allowed to reflux for ~4 h. NaCl was removed by filtration and filtrate was concentrated by distillation. The product was dried under reduced pressure and purified by recrystallization from THF–MeOH mixture (purity was further checked by TLC) to afford greenish yellow powdered solid. [Yield (1.112 g, 75.4%); Anal. Calcd for

C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub>Zn<sub>2</sub> (%): Zn, 21.02; Cl, 11.41; C, 54.01; H, 3.86; N, 4.50. Found (%): Zn, 21.08; Cl, 11.43; C, 54.02; H, 3.81; N, 4.49].

Similar procedure was adopted for the synthesis of  $[(\mu-Cl)_2Hg_2(L^1)_2]$  (4) and  $[(\mu-Cl)_2Hg_2(L^3)_2]$  (6).

2.1.2.2.  $[(\mu-Cl)_2M_2(L)_2 \cdot 2THF]$  (2), (3) and (5). Zinc(II) and mercury(II) complexes  $[(\mu-Cl)_2Zn_2(L^2)_2 \cdot 2THF]$  (2),  $[(\mu-Cl)_2Zn_2(L^3)_2 \cdot 2THF]$  (3), and  $[(\mu-Cl)_2Hg_2(L^2)_2 \cdot 2THF]$  (5) have been prepared by adopting similar procedure as described above for the preparation of mono(chloro) complexes of the type  $[(\mu-Cl)_2M_2(L)_2]$ . For the sake of brevity, all details are collected in table 1.

#### 3. Results and discussion

The Schiff-base complexes, [(Cl)M(L)] and  $[(Cl)M(L) \cdot 2THF]$ , have been prepared by the reaction of metal chlorides with sodium salts of corresponding Schiff bases in MeOH and THF:

$$MCl_2 + Na(L) \rightarrow [(Cl)M(L)] + NaCl \downarrow \\ \underset{1,4,\text{and } 6}{\text{MCl}} \rightarrow$$

$$MCl_2 + Na(L) \xrightarrow{THF/MeOH} [(Cl)M(L) \cdot 2THF] + NaCl \downarrow$$

where M = Zn(II), Hg(II);  $L = HL^1$ ,  $HL^2$ , and  $HL^3$ ; x = 2.

All these metal complexes are soluble in polar solvents such as THF, DMF, and DMSO but insoluble in water, methanol, ethanol, pyridine, etc. The physical and analytical details are given in table 1.

The tentative structures of the Schiff-base ligand and the metal complexes have been suggested by IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, and elemental analysis, and structural composition determined by FAB-MS spectral studies.

#### 3.1. IR spectra

The IR spectra of the ligand showed bands at 1620 to  $1622 \text{ cm}^{-1}$  attributed to  $v_{(C=N)}$  [15], which is shifted to lower frequency 1598 to  $1610 \text{ cm}^{-1}$  in the zinc(II) and mercury(II) complexes (table 2), indicating that bonding takes place through the azomethine nitrogen. The  $v_{(C-O)}$  (phenolic) stretching frequencies of the ligands were observed at  $1269-1277 \text{ cm}^{-1}$  and shift to  $1274-1289 \text{ cm}^{-1}$  in complexes, indicating bonding through phenolic oxygen [14, 16].

In  $[(\mu-Cl)_2Zn_2(L^2)_2 \cdot 2THF]$  (2),  $[(\mu-Cl)_2Zn_2(L^3)_2 \cdot 2THF]$  (3), and  $[(\mu-Cl)_2Hg_2(L^2)_2 \cdot 2THF]$  (5), asymmetric and symmetric C–O–C stretching frequencies, due to the presence of THF, were observed at ~897, 905, and 891 cm<sup>-1</sup> (THF asymmetric), and 761, 770, and 765 cm<sup>-1</sup> (THF symmetric) [17] as compared to ~1025–1015 cm<sup>-1</sup> (THF asymmetric) and 860–850 cm<sup>-1</sup> (THF symmetric) in free THF. Such shifting to lower frequency in the complexes suggests coordination by oxygen of THF. Zinc(II) and mercury(II) form dimeric four/five-coordinated [18] complexes where the

						% Analys	iis: Found (	Calcd)	
No.	Reactants (g, mmol)	Product (g, % yield)	Physical state	point (°C)	Zn/Hg	Cl	С	Н	z
1	$\operatorname{ZnCl}_2 + \operatorname{Na}(L^1)$ (0.646 4.74) (1.105 4.74)	$[(\mu-Cl)_2 Zn_2(L^1)_2] (1)$	Greenish yellow nowdered solid	234	21.08	11.43	54.02 (54.01)	3.81 (3.86)	4.49 (4.50)
7	$ZnCl_2 + Na(L^2)$ (0.670 4.01) (1.082 4.01)	$[(\mu-Cl)_2 Zn_2(L^2)_2 \cdot 2THF] (2)$	Green crystalline solid	239	17.63	9.53	(51.85 51.85 (51.80)	4.59	7.56
3	(0.070, 4.91) (1.062, 4.91) ZnCl <sub>2</sub> + Na(L <sup>3</sup> ) (0.829, 6.09) (1.615, 6.09)	$[(\mu-CI)_2Zn_2(L^3)_2 \cdot 2THF] (3)$	Yellowish brown crystalline solid	225	(15.79) (15.79)	(%5.7) 8.59 (8.57)	(49.29 (49.27)	(4.11) (111) (111)	(7.0) 6.76) (6.76)
4	$HgCl_2 + Na(L^1)$ (1.204. 4.43) (1.035. 4.43)	$[(\mu-CI)_2Hg_2(L^1)_2] (4)$ (1.48, 74, 8)	Light yellow powdered solid	265	44.91 (44.95)	7.90	37.65 (37.64)	2.68 (2.69)	3.56 (3.59)
Ś	$HgCl_2 + Na(L^2)$ (1.42. 5.22) (1.149. 5.22)	$[(\mu-Cl)_2Hg_2(L^2)_2 \cdot 2THF] (5)$	Brown crystalline solid	274	39.71 (39.70)	7.09	38.03 (38.00)	3.33 3.36)	5.51 (5.54)
9	$HgCl_2 + Na(L^3)$ (1.36, 5.0) (1.321, 5.0)	$[(\mu-Cl)_2Hg_2(L^3)_2] (6) (1.803, 75.6)$	Light brown crystalline solid	259	42.01 (42.03)	7.42 (7.44)	32.67 (32.69)	1.86 (1.89)	5.83 (5.87)

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Compound	$\nu_{(M-Cl)}$ (bridging)	v <sub>(M-N)</sub>	V(M-O)	$v_{(C-O)}$ (phenolic)	v <sub>(C=N)</sub>	v <sub>NO2</sub>	ν <sub>(C-O-C)</sub>
1 2	236 220	455 459	376 365	1282 1289	1604 1598	-	897(as)
3	240	457	359	1277	1602	1419(as) 1385(sv)	905(as) 770(sv)
4 5	<200 <200	421 415	310 305	1280 1274	1610 1599		891(as) 756(sv)
6	<200	419	302	1279	1609	1417(as) 1380(sy)	_

Table 2. IR spectral data (cm<sup>-1</sup>) of monochloro complexes of 1-6.

chloride forms bridges between two metal centers  $[M \leftarrow CI \leftarrow M]$ . This is supported by FAB-MS spectral studies showing dimeric nature of the complexes.

The bands [19, 20] at 366–315 and 464–407 cm<sup>-1</sup> are attributed to  $\nu_{(M-O)}$  and  $\nu_{(M-N)}$ , respectively. An intense band at ~220–240 cm<sup>-1</sup> has been assigned for  $\nu_{(Zn-Cl)}$ , characteristic of bridging chloride. In mercury(II) chloro complexes,  $\nu_{(Hg-Cl)}$  for bridging mercury chloride occurred [21] at <200 cm<sup>-1</sup> [22].

# 3.2. Nuclear magnetic resonance (NMR) spectra

**3.2.1.** <sup>1</sup>**H-NMR spectra.** The complexes exhibited signals at 9.50–8.77 ppm because of deshielding on complex formation, which suggest the involvement of azomethine nitrogen in coordination. In the complexes, the absence of a signal due to phenolic proton (–OH) at 12.65–12.40 ppm further supports the IR spectral observations. NMR spectra of all the ligands exhibited signals due to CH aromatic protons at 7.84–6.35 ppm (a multiplet range), shifted downfield in comparison to free ligands due to distortion of the aromatic rings as a result of complex formation [23] (tables 3 and 4). In <sup>1</sup>H-NMR spectra of **2**, **3**, and **5** the signal due to coordinated THF shows small upfield [24] shifts compared to free THF (3.10 and 1.53 ppm).

**3.2.2.** <sup>13</sup>C-NMR spectra. The <sup>13</sup>C-NMR spectra provide direct information about the skeleton of the ligand and complexes [25] (table 5). In <sup>13</sup>C-NMR spectra of ligands signals [26] at 150.38–149.30 and 149.31–148.59(d) ppm are assigned to azomethine, signals at 170.65–167.69 ppm suggest phenolic oxygen coordination.

The <sup>13</sup>C-NMR spectra of **2**, **3**, and **5** indicate coordination of THF to zinc. Signals at 67.06, 65.46, 64.74(t) ppm are assigned to  $C_1$  of THF;  $C_2$  of THF are at 26.77, 25.40, 24.27(t) ppm.

#### 3.3. FAB-MS spectra

The FAB-MS spectrum [27–29] of HL<sup>2</sup> shows a characteristic molecular ion (M<sup>+</sup>) peak at m/z 199. In the zinc(II) complex, [( $\mu$ -Cl)<sub>2</sub>Zn<sub>2</sub>(L<sup>2</sup>)<sub>2</sub> · 2THF] (**2**), molecular ion peaks

$3 \xrightarrow{4} a$ $2 \xrightarrow{CH=N-X} HL^{1}; X = - \underbrace{5}_{H_{0}C} \xrightarrow{6} 7$ $HL^{3}; X = - \underbrace{5}_{D} \xrightarrow{6} 7$				complex 1 complex	,4; M=Zn; X= $-5^{5}_{H_3C}^{6}$ 7 H <sub>3</sub> C 6; M=Hg; X= $-5^{5}_{b}^{6}$ 7 NO <sub>2</sub>
Schiff base/complex	$\delta$ OH (s)	$\delta$ H <sub>a</sub> (s)	$\begin{array}{c} \delta \ \mathrm{H_b} \\ (\mathrm{3H, t, H_b}) \end{array}$	$\begin{array}{c} \delta \ \mathrm{H_{c}} \ (\mathrm{s}) \\ (\mathrm{1H}, \ \mathrm{s}, \ \mathrm{H_{c}}) \end{array}$	δ H (m)
HL <sup>1</sup> HL <sup>3</sup> 1 4 6	12.40 12.62 	8.47 8.51 8.97 8.77 8.93	2.32 2.43 2.41	7.98  8.38	7.33–6.79(8H, m, H <sub>1</sub> –H <sub>8</sub> ) 7.84–6.35(7H, m, H <sub>1</sub> –H <sub>7</sub> ) 7.77–6.60(8H, m, H <sub>1</sub> –H <sub>8</sub> ) 7.80–6.72(8H, m, H <sub>1</sub> –H <sub>8</sub> ) 7.89–6.57(7H, m, H <sub>1</sub> –H <sub>7</sub> )

Table 3. <sup>1</sup>H-NMR chemical shifts ( $\delta$  ppm) for the Schiff base and 1, 4, and 6 in DMSO-d<sub>6</sub>.

Table 4. <sup>1</sup>H-NMR chemical shifts ( $\delta$  ppm) for the Schiff base and 2, 3, and 5 in DMSO-d<sub>6</sub>.

$a$ $CH=N-X$ $HL^{2}; X = - \underbrace{\bigcirc}_{b}^{5} \underbrace{\bigcirc}_{NO_{2}}^{6} 7$ $HL^{3}; X = - \underbrace{\bigcirc}_{b}^{5} \underbrace{\bigcirc}_{NO_{2}}^{6} 7$			2 -CH=N-X -CH=N-X -CH=CH -CH=CH		complex 2,5; M=Zn,Hg; X= $-\underbrace{50}_{8}^{5}$ 7 complex 3; M=Zn; X= $-\underbrace{50}_{6}^{5}$ 7		
Schiff base/complex	δ OH (s)	$\delta$ H <sub>a</sub> (s)	$\begin{array}{c} \Delta \ H_b \ (s) \\ (1H, \ s, \ H_b) \end{array}$	δ H (THF)	δ H (m)		
HL <sup>2</sup>	12.65	8.59	_	_	7.52–6.86(8H, m, H <sub>1</sub> –H <sub>8</sub> )		
HL <sup>3</sup>	12.62	8.51	7.98	-	$7.84-6.35(7H, m, H_1-H_7)$		
2	-	9.37	-	3.81-3.48(H <sub>c</sub> )	8.09-6.46(8H, m, H <sub>1</sub> -H <sub>8</sub> )		
				$1.91 - 1.83(H_d)$			
3	—	9.10	8.72	3.84-3.51(H <sub>c</sub> )	8.32-7.03(7H, m, H <sub>1</sub> -H <sub>7</sub> )		
				$1.95 - 1.87(H_d)$			
5	_	9.50	_	3.98–3.57(H <sub>c</sub> ) 1.96–1.89(H <sub>d</sub> )	7.94–6.48(8H, m, H <sub>1</sub> –H <sub>8</sub> )		

Schiff bases/complexes	HC=N (d)	C–O (phenolic)	Aromatic carbons	CH <sub>3</sub>	$\begin{array}{c} THF \\ (C_1 - C_2) (t) \end{array}$
$HL^1$	150.20, 149.31	161.12	133.05-117.12	18.17	_
$HL^2$	149.30, 148.59	160.74	133.80-115.21	_	_
HL <sup>3</sup>	150.38, 149.23	160.19	134.13-114.89	_	_
1	149.13, 146.89	170.65	149.13-109.47	17.83	_
2	148.79, 146.66	167.69	139.00–136.27(py) 123.03–109.18	—	67.06, 65.46, 64.74(C <sub>1</sub> ) 25.16, 24.60, 23.09(C <sub>2</sub> )
3	148.39, 146.53	168.37	150.77-109.18	_	66.87, 66.06, 65.73(C <sub>1</sub> ) 26.77, 25.40, 24.27(C <sub>2</sub> )

Table 5. <sup>13</sup>C-NMR data ( $\delta$  ppm) of Schiff bases and complexes.



Figure 1. FAB-MS spectrum of  $[(\mu-Cl)_2Zn_2(L^2)_2 \cdot 2THF]$  (2).

observed at m/z 742 and m/z 740 correspond to the molecular mass [(C<sub>32</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>Cl<sub>2</sub>Zn<sub>2</sub>); calculated mass = 740.04] due to isotopic pattern including zinc and chlorine [30]. Therefore, the position of molecular ion peak in the mass spectrum (figure 1) is consistent with the empirical molecular formula [31]. Peaks at m/z 596 and 298 are indicative of release of two THF molecules and fragmentation from dimer to monomer species, respectively. After fragmentation of the complex, several other peaks (Supplementary material) were also observed at m/z 670, 521, 493, 385, 321, 261, 221, 197 186, 106. The base peak with m/z 413 represents C<sub>13</sub>H<sub>9</sub>NO<sub>2</sub>Zn<sub>2</sub>Cl<sub>2</sub> as residue.

 $[(\mu-Cl)_2Zn_2(L^3)_2 \cdot 2THF]$  (3) showed molecular ion peak at m/z 828 (Supplementary material), confirming the proposed formula [32]. Peaks at m/z 684 and 342 observed due to the release of two THF and dimer to monomer species, respectively [33]. The spectrum exhibited prominent molecular ion peaks at m/z 756, 638, 563, 534, 518, 458, 426, 397, 321, 294, 242, 221, 207, 123, 97, 94 (Supplementary material). The base peak [34] m/z 413 represents  $C_{13}H_{10}NO_2Zn_2Cl_2$  as residue.

Mercury(II) complex  $[(\mu-Cl)_2Hg_2(L^3)_2 \cdot 2THF]$  (5) exhibited molecular ion peaks (Supplementary material) at m/z 1010 and m/z 1029, which are consistent with the

combination of mercury and chlorine isotopic distribution [35]. Two important peaks  $(m/z \ 938 \ and \ 866)$  have also been observed, corresponding to release of two THFs and dimer  $(m/z \ 860)$  to monomer  $(m/z \ 433)$  species. The spectrum showed prominent peaks (Supplementary material) at  $m/z \ 788$ , 685, 669, 505, 398, 355, 328, 105. The base peak with  $m/z \ 198$  corresponds to HL<sup>2</sup> (C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>O).

# 3.4. PXRD studies

PXRD [36] is widely used to characterize a crystalline solid. XRD spectrum of **6** clearly showed crystalline material (Supplementary material). Diffraction pattern comprises a number of sharp Bragg's reflections corresponding to different orientation of crystallites. Non-uniform broadening of lines is attributed to anisotropic crystallites, used here to calculate the crystallite size using Debye Scherrer formula [37]. The crystallite size of prepared materials is 404.5 Å by using Rigaku JADE 6.0 software.

# 4. Conclusion

Six Schiff-base complexes, [(Cl)M(L)] and  $[(Cl)M(L) \cdot 2THF]$  [where M = Zn(II) and Hg(II); L = salicylidene-2-methyl-1-aminobenzene (HL<sup>1</sup>), salicylidene-2-aminopyridine (HL<sup>2</sup>), and salicylidene-3-nitro-1-aminobenzene (HL<sup>3</sup>); x = 0 for (1), (4), (6) and x = 2 for (2), (3), (5)], have been synthesized by the reactions of metal chlorides with sodium salts of corresponding Schiff bases in the mixture of MeOH and THF in equimolar ratio. These chloro-bridged dimeric complexes have been characterized by elemental analyses (M, Cl, C, H, N), melting point, and spectroscopic (FT-IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR) data as well as PXRD study. The complexes have also been proposed by FAB-MS spectral studies.

The formulae are  $[(\mu-Cl)_2Zn_2(L^1)_2](1)$ ,  $[(\mu-Cl)_2Hg_2(L^1)_2](4)$ , and  $[(\mu-Cl)_2Hg_2(L^3)_2](6)$  confirmed by FAB-mass spectra whereas **2**, **3**, and **5** are dimers with two THF molecules,  $[(\mu-Cl)_2Zn_2(L^2)_2 \cdot 2THF]$ ,  $[(\mu-Cl)_2Zn_2(L^3)_2 \cdot 2THF]$ , and  $[(\mu-Cl)_2Hg_2(L^2)_2 \cdot 2THF]$ , which have been clearly indicated in the FAB-mass spectra (figure 1 and Supplementary material) containing five-coordinate Zn(II)/Hg(II).

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