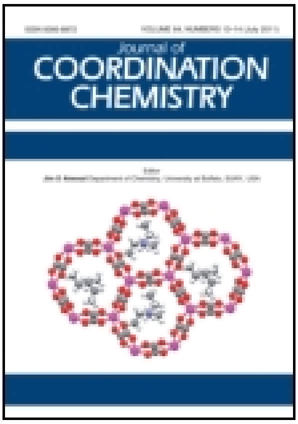


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Zinc(II) and mercury(II) complexes with Schiff bases: syntheses, spectral, and structural characterization

R.K. Dubey [a] , P. Baranwal [a] & A.K. Jha [b]

[a] Synthetic Inorganic and Metallo-organic Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad - 211 002, Uttar Pradesh, India

[b] Department of Chemistry, G.B. College Naugachia, T.M. Bhagalpur University, Bhagalpur - 853204, Bihar, India

To cite this article: R.K. Dubey, P. Baranwal & A.K. Jha (2012): Zinc(II) and mercury(II) complexes with Schiff bases: syntheses, spectral, and structural characterization, Journal of Coordination Chemistry, 65:15, 2645-2656

To link to this article: http://dx.doi.org/10.1080/00958972.2012.699634

Journal of Coordination Chemistry
Vol. 65, No. 15, 10 August 2012, 2645–2656

Zinc(II) and mercury(II) complexes with Schiff bases: syntheses, spectral, and structural characterization

R.K. DUBEY*†, P. BARANWAL† and A.K. JHA‡

†Synthetic Inorganic and Metallo-organic Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad – 211 002, Uttar Pradesh, India
‡Department of Chemistry, G.B. College Naugachia, T.M. Bhagalpur University, Bhagalpur – 853204, Bihar, India

(*Received 9 August 2012; in final form 26 April 2012*)

Schiff bases *o*-vanilidene-1-aminobenzene (HL^1) and *o*-vanilidene-2-methyl-1-aminobenzene (HL^2) lead to the formation of mono- and bis-[(Cl)Zn(L^1)] (**1**), [(Cl)Zn(L^2)] (**2**), [(Cl)Hg(L^1)] (**3**), [(Cl)Hg(L^2)] (**4**), [Zn(L^1)$_2$] (**5**), [Zn(L^2)$_2$] (**6**), [Hg(L^1)$_2$] (**7**), and [Hg(L^2)$_2$] (**8**) complexes by reactions of zinc(II) and mercury(II) chlorides in different mole ratio(s). Complexes **1**–**8** have been characterized by elemental analyses (Zn, Hg, C, H, Cl, and N), melting point and spectral (IR, ^{1}H-NMR), PXRD, molar conductivity measurement, and TGA. Conductivity measurements suggest non-electrolytes. Structural compositions have been assigned by mass spectral studies. Four-coordinate geometry may be assigned to these complexes tentatively. Structural study reveals that in **1**–**4** two metal centers are held together by two bridged (μ_2-Cl) chlorides, whereas **5**–**8** contain two bidentate Schiff-base ligands around one metal-producing monomers.

Keywords: Synthesis; Schiff bases; Zn(II) and Hg(II) complexes; IR; NMR; FAB-MS; TOF-MS; PXRD; TGA; Conductivity measurement

1. Introduction

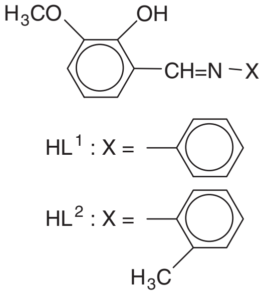
Group 12 metal complexes of Schiff bases have interest [1] for the ease of synthesis, versatility, and wide range of complexing ability [2]. They can be used as corrosion inhibitors for metals and alloys and for potential antibacterial, antiviral, and antitumor effects [3–5]. Metal complexes of biologically important ligands are sometimes more effective than free ligand [3]. Schiff bases are potential anticancer drugs [6] and when administered as their metal complexes, anticancer activity is enhanced in comparison to free ligand [7]. Two new series of complexes of zinc(II) and mercury(II) with new Schiff

---

*Corresponding author. Email: rajalkoxy@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.699634

bases, HL^1 and HL^2, are of interest.



Zinc is involved in a number of enzymatic functions, fulfilling both structural and catalytic roles [8]. Mercury has been used as a constituent in bactericides, antiseptics, skin ointment, and laxatives [9, 10]; toxicity of mercury and its compounds are well known [11]. As part of our [12–14] interest in the synthesis and coordination chemistry of group 12 metal complexes containing Schiff bases, we describe the synthesis and characterization of new [(Cl)M(L)] and $[M(L)_2]$ complexes with HL^1 (*o*-vanilidene-1-aminobenzene) and HL^2 (*o*-vanilidene-2-methyl-1-aminobenzene), where M = Zn(II) and Hg(II).

2. Experimental

All materials and solvents were purified by standard procedures [15]. Zinc and mercury chloride were purchased from Merck and used without purification. Elemental analyses for C, H, and N were performed on a Heraceous Carlo Erba 1108 elemental analyzer. Zinc(II) and mercury(II) were estimated by reported methods [16]. Infrared spectra of ligands and complexes, 4000–200 cm^{-1}, were recorded in KBr pellets on a Perkin-Elmer 1000 FT-IR spectrophotometer. NMR spectra of the ligands and the complexes were recorded in $CDCl_3$ and DMSO-d_6, respectively, on a Bruker DRX-300 spectrometer at a sweep width of 300 MHz and a sweep time of 300 s. Molar conductances of the complexes were measured in DMSO (10^{-3} mol L^{-1}) using a Coronation Digital Conductivity Meter. FAB-MS spectra were recorded on a JEOLSX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas and TOF-MS spectra were recorded on a Q-TOF MS instrument. The thermogravimetric (TG) analysis of the solid complex was performed using a TGA 50H thermogravimetric analyzer (Shimadzu) from ambient to 800°C with a 20°C min^{-1} heating rate using N_2. X-ray powder diffraction of the complexes was recorded on a Rigaku Model D/Max-2200 PC using Cu-Kα_1 radiation ($\lambda = 1.5406$ Å).

2.1. *Syntheses*

2.1.1. Preparation of ligands

2.1.1.1. *o-Vanilidene-1-aminobenzene (HL^1).* Equimolar amounts of *o*-vanillin (5 g, 33.0 mmol) and aniline (3.060 g, 33.0 mmol) in methanol (~30 cm^3) were refluxed on a water bath for ~5 h. The analytically pure light yellow ligand was obtained. The yield of HL^1 was 5.42 g (72.6%); m.p. = 250°C. For $C_{14}H_{13}NO_2$ Anal. Calcd (%): C, 73.92; H, 5.72; N, 6.16. Found (%): C, 73.88; H, 5.65; N, 6.11.

The ^{1}H-NMR spectrum, δ (ppm): 7.69–6.94 (m, 8H, CH_{ar}), 3.92 (t, 3H, OCH_3), 8.3 (s, 1H, HC=N), 13.26 (s, 1H, OH). IR spectrum, ν (cm^{-1}): 1615 (C=N), 1274 ($(C–O)_{phenolic}$), 3445 ($\nu(OH_{stretching})$), 1352 ($\delta(OH_{deformation})$).

2.1.1.2. *o-Vanilidene-2-methyl-1-aminobenzene (HL^2).* Equimolar amounts of *o*-vanillin (5 g, 33.0 mmol) and *o*-toluidine (3.54 g, 33.0 mmol) in methanol (~30 cm^3) were refluxed on a water bath for ~5 h. The analytically pure light yellow ligand was obtained as 5.98 g (75.4%); m.p. = 231°C. For $C_{15}H_{15}NO_2$ Anal. Calcd (%): C, 74.59; H, 6.23; N, 5.80. Found (%): C, 74.50; H, 6.17; N, 5.73.

The ^{1}H-NMR spectrum, δ (ppm): 7.9–6.8 (m, 7H, CH_{ar}), 3.9 (t, 3H, OCH_3), 2.60 (t, 3H, CH_3), 8.3 (s, 1H, HC=N), 13.16 (s, 1H, OH). IR spectrum, ν (cm^{-1}): 1617 (C=N), 1272 ($(C–O)_{phenolic}$), 3464 ($\nu(OH_{stretching})$), 1355 ($\delta(OH_{deformation})$).

2.1.2. Synthesis of complexes

2.1.2.1. *$[(\mu\text{-}Cl)_2Zn_2(L^1)_2]$ (**1**).* To a suspension/solution of $ZnCl_2$ (0.640 g, 4.69 m mol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (1.170 g, 4.69 mmol) was added with constant stirring. The reaction mixture was refluxed for ~4 h, filtered to remove NaCl, and filtrate was concentrated by distillation under reduced pressure. The product so obtained was purified by recrystallization from THF (purity was further checked by TLC) to afford brown crystalline solid. The yield of the complex was 1.109 g (72.2%); decomposition point = 280°C. For $C_{28}H_{24}N_2O_4Cl_2Zn_2$ Anal. Calcd (%): C, 51.40; H, 3.70; N, 4.28; Cl, 10.84; Zn, 20. Found (%): C, 51.33; H, 3.65; N, 4.26; Cl, 10.82; Zn, 19.96.

The ^{1}H-NMR spectrum, δ (ppm): 7.83–6.56 (m, 8H, CH_{ar}), 4.59 (t, 3H, OCH_3), 8.74 (s, 1H, HC=N). IR spectrum, ν (cm^{-1}): 1592 (C=N), 1292 ($(C–O)_{phenolic}$), 1031 (OCH_3), 460 (Zn–N), 348 (Zn–O), 244 ($(Zn–Cl)_{bridging}$), TOF-MS: 652.18 *m*/*z*; calculated mass (649.97), molar conductivity: 10.34 $\Omega^{-1} mol^{-1} cm^2$.

2.1.2.2. *$[(\mu\text{-}Cl)_2Zn_2(L^2)_2]$ (**2**).* To a hot suspension/solution of $ZnCl_2$ (0.729 g, 5.35 mmol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (1.408 g, 5.35 mmol) was added with constant stirring. The product was obtained by the similar procedure used for **1**. The product was formed as a yellow powder, 1.289 g (70.6%); decomposition point = 295°C. For $C_{30}H_{28}N_2O_4Cl_2Zn_2$ Anal. Calcd (%): C, 52.81; H, 4.14; N, 4.11; Cl, 10.39; Zn, 19.17. Found (%): C, 52.75; H, 4.07; N, 4.05; Cl, 10.39; Zn, 19.13.

The ^{1}H-NMR spectrum, δ (ppm): 8.11–7.06 (m, 7H, CH_{ar}), 4.51 (t, 3H, OCH_3), 2.77 (t, 3H, CH_3), 8.69 (s, 1H, HC=N). IR spectrum, ν (cm^{-1}): 1591 (C=N), 1295 ($(C–O)_{phenolic}$), 1029 (OCH_3), 462 (Zn–N), 352 (Zn–O), 249 ($(Zn–Cl)_{bridging}$), FAB-MS: 681 *m*/*z*; calculated mass (678), molar conductivity: 8.97 $\Omega^{-1} mol^{-1} cm^2$.

2.1.2.3. *$[(\mu\text{-}Cl)_2Hg_2(L^1)_2]$ (**3**).* To a solution of $HgCl_2$ (1.45 g, 5.35 mmol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (1.33 g, 5.35 mmol) was added with constant stirring. The product was obtained by the above process as a reddish brown crystalline solid. The yield was 1.812 g (73.3%); decomposition point = 285°C. For $C_{28}H_{24}N_2O_4Cl_2Hg_2$ Anal. Calcd (%): C, 36.37; H, 2.62; N, 3.03; Cl, 7.67; Hg, 43.39. Found (%): C, 36.32; H, 2.62; N, 3.01; Cl, 7.63; Hg, 43.38.

The ^{1}H-NMR spectrum, δ (ppm): 8.71–6.66 (m, 8H, CH_{ar}), 4.46 (t, 3H, OCH_3), 8.61 (s, 1H, HC=N). IR spectrum, ν (cm^{-1}): 1588 (C=N), 1282 ($(C–O)_{phenolic}$), 1031 (OCH_3), 413 (Hg-N), 320 (Hg–O), <200 ($(Hg–Cl)_{bridging}$), FAB-MS: 928 m/z; calculated mass (926.05), molar conductivity: 11.64 $\Omega^{-1}\,mol^{-1}\,cm^2$.

2.1.2.4. *[(μ-Cl)$_2$Hg$_2$(L^2)$_2$] (**4**).* To a solution of $HgCl_2$ (1.23 g, 4.48 mmol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (1.18 g, 4.48 mmol) was added with constant stirring. The product was obtained as above as a blackish brown crystalline solid, 1.611 g (75%); decomposition point = 292°C. For $C_{30}H_{28}N_2O_4Cl_2Hg_2$ Anal. Calcd (%): C, 37.82; H, 2.96; N, 2.94; Cl, 7.44; Hg, 42.11. Found (%): C, 37.69; H, 2.91; N, 2.90; Cl, 7.45; Hg, 42.07.

The ^{1}H-NMR spectrum, δ (ppm): 7.79–6.83 (m, 7H, CH_{ar}), 4.39 (t, 3H, OCH_3), 2.69 (t, 3H, CH_3), 8.57 (s, 1H, HC=N). IR spectrum, ν (cm^{-1}): 1590 (C=N), 1278 ($(C–O)_{phenolic}$), 1029 (OCH_3), 411 (Hg–N), 318 (Hg–O), <200 ($(Hg–Cl)_{bridging}$), FAB-MS: 952 m/z; calculated mass (954.08), molar conductivity: 12.86 $\Omega^{-1}\,mol^{-1}cm^2$.

2.1.2.5. *[Zn(L^1)$_2$] (**5**).* To a solution of $ZnCl_2$ (0.290 g, 2.13 mmol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (1.061 g, 4.26 mmol) in 1 : 2 molar ratio was added with constant stirring; separated NaCl was removed by filtration. The product was recrystallized from THF (purity further checked by TLC). A brown crystalline solid complex was obtained, 0.803 g (72.9%); decomposition point = 303°C. For $C_{28}H_{24}N_2O_4Zn$ Anal. Calcd (%): C, 64.93; H, 4.67; N, 5.41; Zn, 12.63. Found (%): C, 64.86; H, 4.66; N, 5.40; Zn, 12.62.

The ^{1}H-NMR spectrum, δ (ppm): 7.91–6.54 (m, 8H, CH_{ar}), 4.43 (t, 3H, OCH_3), 8.68 (s, 1H, HC=N). IR spectrum, ν (cm^{-1}): 1588 (C=N), 1289 ($(C–O)_{phenolic}$), 1030 (OCH_3), 463 (Zn–N), 359 (Zn–O), FAB-MS: 517 m/z; calculated mass (516.10), molar conductivity: 9.14 $\Omega^{-1}\,mol^{-1}\,cm^2$.

2.1.2.6. *[Zn(L^2)$_2$] (**6**).* To a solution of $ZnCl_2$ (0.246 g, 1.81 mmol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (0.950 g, 3.61 mmol) in 1 : 2 molar ratio was added with constant stirring. The product was obtained by analogous procedure to that used for **5**. The product formed as a dark brown crystalline solid, 0.743 g (73%); decomposition point = 317°C. For $C_{30}H_{28}N_2O_4Zn$ Anal. Calcd (%): C, 66.00; H, 5.17; N, 5.13; Zn, 11.98. Found (%): C, 65.72; H, 5.08; N, 5.06; Zn, 11.94.

The ^{1}H-NMR spectrum, δ (ppm): 8.13–7.09 (m, 7H, CH_{ar}), 4.39 (t, 3H, OCH_3), 2.82 (t, 3H, CH_3), 8.64 (s, 1H, HC=N). IR spectrum, ν(cm^{-1}): 1593 (C=N), 1290 ($(C–O)_{phenolic}$), 1029 (OCH_3), 464 (Zn–N), 366 (Zn–O), FAB-MS: 545 m/z; calculated mass (544.13), molar conductivity: 14.26 $\Omega^{-1}\,mol^{-1}\,cm^2$.

2.1.2.7. *[Hg(L^1)$_2$] (**7**).* To a solution of $HgCl_2$ (0.673 g, 2.48 mmol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (1.236 g, 4.96 mmol) in 1 : 2 molar ratio was added with constant stirring. The product was obtained by analogous procedure as for **5**. The product formed as a brownish black crystalline solid, 1.192 g (73.6%); decomposition point = 305°C. For $C_{28}H_{24}N_2O_4Hg$ Anal. Calcd (%): C, 51.49; H, 3.70; N, 4.29; Hg, 30.71. Found (%): C, 51.40; H, 3.65; N, 4.31; Hg, 30.67.

The ^{1}H-NMR spectrum, δ (ppm): 8.04–6.98 (m, 8H, CH_{ar}), 4.33 (t, 3H, OCH_3), 8.49 (s, 1H, HC=N). IR spectrum, ν (cm^{-1}): 1584 (C=N), 1288 ($(C\text{–}O)_{phenolic}$), 1031 (OCH_3), 407 (Hg–N), 315 (Hg–O), TOF-MS: 650.42 m/z; calculated mass (654.14), molar conductivity: 17.17 $\Omega^{-1}\,mol^{-1}\,cm^2$.

2.1.2.8. *[Hg(L^2)$_2$] (**8**).* To a solution of $HgCl_2$ (0.703 g, 2.59 mmol) in THF (~30 mL), a methanolic solution of the sodium salt of Schiff base (1.363 g, 5.17 mmol) in 1 : 2 molar ratio was added with constant stirring. The product was obtained as above as a brownish black crystalline solid, 1.248 g (70.8%); decomposition point = 314°C. For $C_{30}H_{28}N_2O_4Hg$ Anal. Calcd (%): C, 52.90; H, 4.14; N, 4.11; Hg, 29.45. Found (%): C, 52.82; H, 4.13; N, 4.31; Hg, 29.41.

The ^{1}H-NMR spectrum, δ (ppm): 7.53–6.55 (m, 7H, CH_{ar}), 4.28 (t, 3H, OCH_3), 2.75 (t, 3H, CH_3), 8.44 (s, 1H, HC=N). IR spectrum, ν (cm^{-1}): 1589 (C=N), 1289 ($(C\text{–}O)_{phenolic}$), 1029 (OCH_3), 410 (Hg–N), 321 (Hg–O), FAB-MS: 681 m/z; calculated mass (682.18), molar conductivity: 15.54 $\Omega^{-1}\,mol^{-1}\,cm^2$.

3. Results and discussion

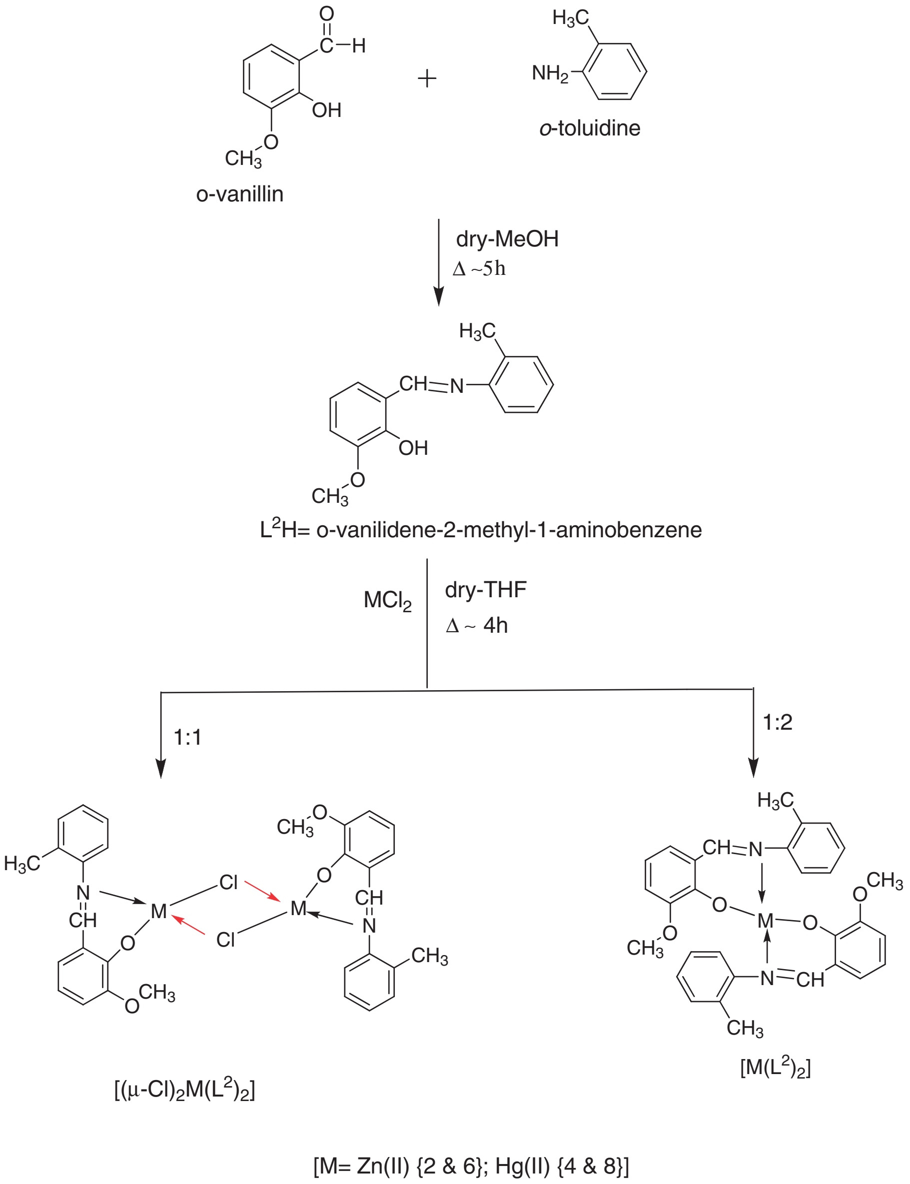
Zinc(II) and mercury(II) complexes have been synthesized by interactions of $ZnCl_2$ and $HgCl_2$ with sodium salt of the *o*-vanilidene-1-aminobenzene (HL^1) and *o*-vanilidene-2-methyl-1-aminobenzene (HL^2) in different molar ratio to yield mono (chloro) (**1**–**4**) and bis complexes **5**–**8**. The detailed synthetic procedures of both ligands and all complexes are given in schemes 1 and 2.

These complexes are colored, non-hygroscopic solids, soluble in polar solvents such as DMF, DMSO, and pyridine. The complexes have been characterized by elemental analyses, spectral studies, and molar conductivity measurements with some studied by PXRD and thermogravimetric analysis. Conductivity measurements indicate the characteristics of nonelectrolytes, 8.97–17.17 $\Omega^{-1}\,mol^{-1}\,cm^2$, for all the studied complexes [17].

3.1. *IR spectra*

The tentative assignments of IR spectral bands for HL^1, HL^2, monochloro-, and bis-complexes are given in section 2. The ligands possess two potential donor sites, the phenolic oxygen and the azomethine nitrogen.

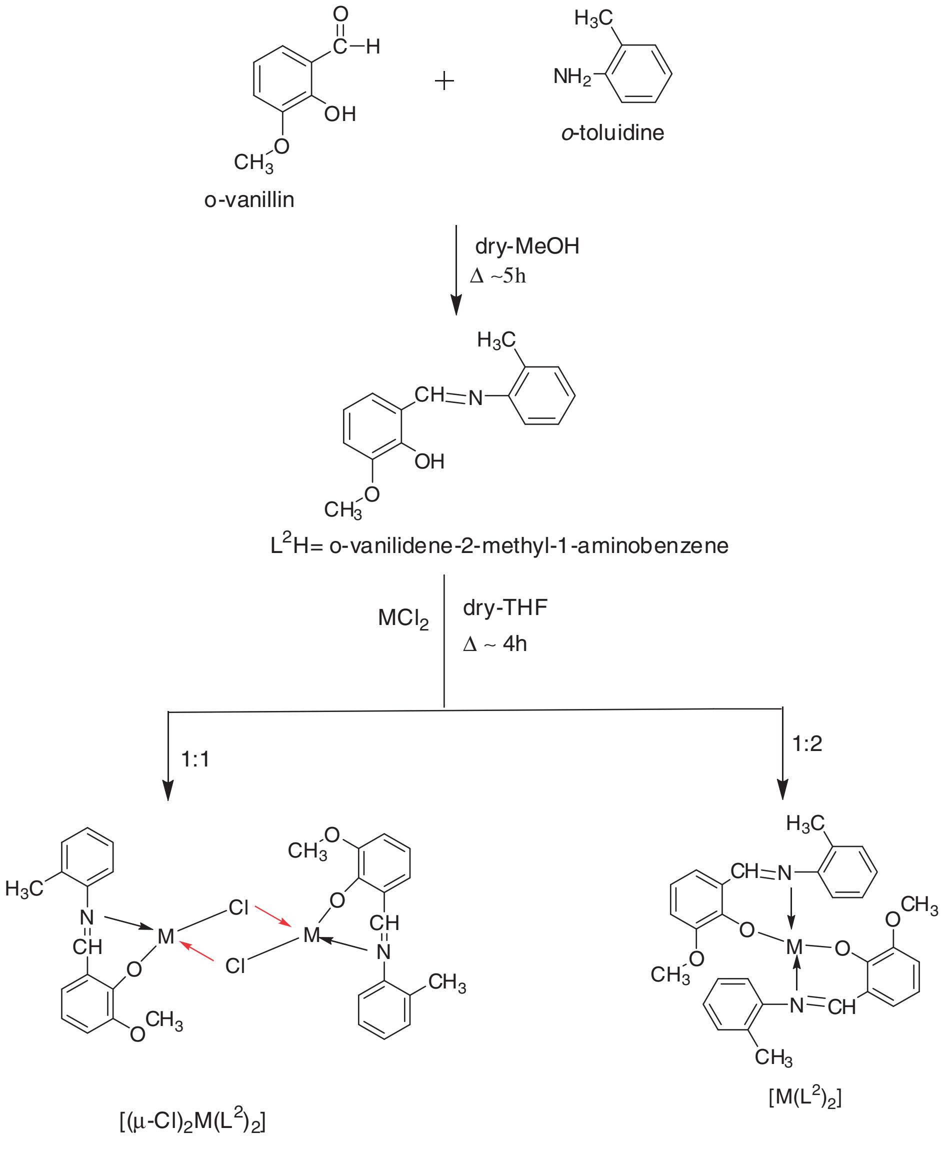
The ligands exhibit characteristic bands for ν(C=N) at 1615 and 1617 cm^{-1}, respectively. Bonding of the azomethine [18, 19] is indicated by the shift of ν(C=N) to lower frequency 1595–1584 cm^{-1} in the complexes. Bonding through phenolic oxygen after deprotonation is revealed by the disappearance of ν(OH) phenolic bands at 3445 and 3464 cm^{-1} for HL^1 and HL^2, respectively, and the appearance of bands [20, 21] due to ν(C–O) at much lower frequencies (1295–1278 cm^{-1}) in the complexes. Coordination of azomethine nitrogen and phenolic oxygen is further supported by two bands [22, 23]



Scheme 1. Synthesis of L^1H and complexes.

at 366–315 cm^{-1} and 464–407 cm^{-1} due to ν(M–O) and ν(M–N), respectively. HL^1 and HL^2 exhibit bands for ν(OCH_3) at 1031 and 1029 cm^{-1}, respectively, which remain unchanged in the complexes [24], indicating that this group does not participate in coordination.

In zinc(II) chloro complexes for bridging zinc chloride ν(Zn–Cl) occurred at 249–244 cm^{-1} due to delocalization of electrons in the chelate ring. This band suggests bridging chloride between two zinc(II) centers; in the mercury(II) chloro complexes bridging ν(Hg–Cl) occur much lower [25], <200 cm^{-1}, as expected [26].



[M= Zn(II) {2 & 6}; Hg(II) {4 & 8}]

Scheme 2. Synthesis of L^2H and complexes.

3.2. ^{1}*H-NMR spectra*

For further evidence regarding the coordination of HL^1 and HL^2, ^{1}H-NMR spectra of the ligand and complexes (**1**–**8**) were recorded in DMSO-d_6. Comparison of the chemical shifts shows that the signal due to the phenolic proton (OH) is absent in the complex, suggesting coordination of the phenolic oxygen to the metal

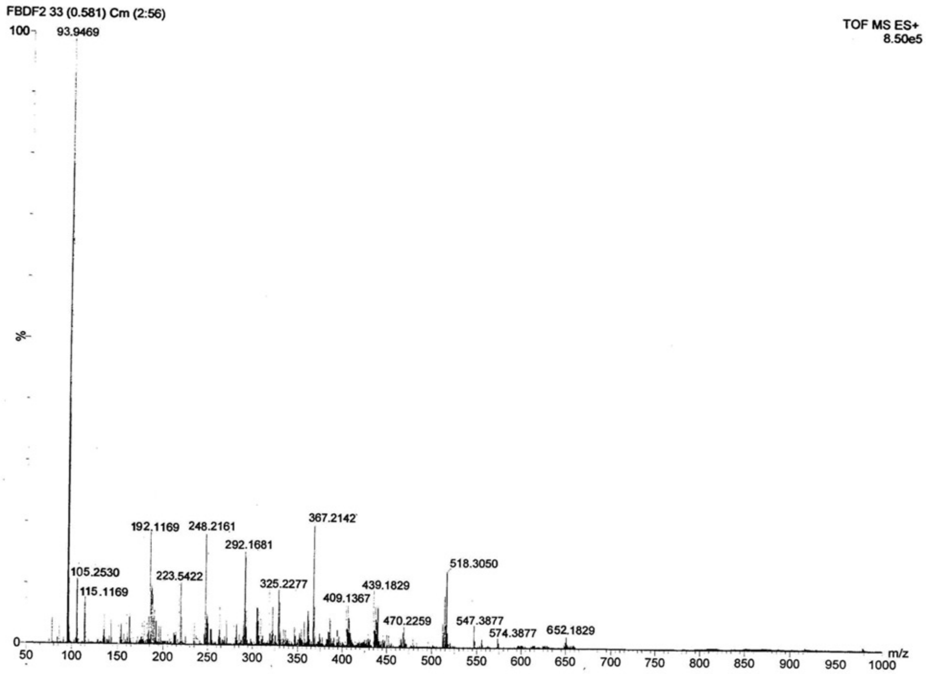


Figure 1. TOF-MS spectrum of [(μ-Cl)$_2$Zn$_2$(L^1)$_2$] (**1**).

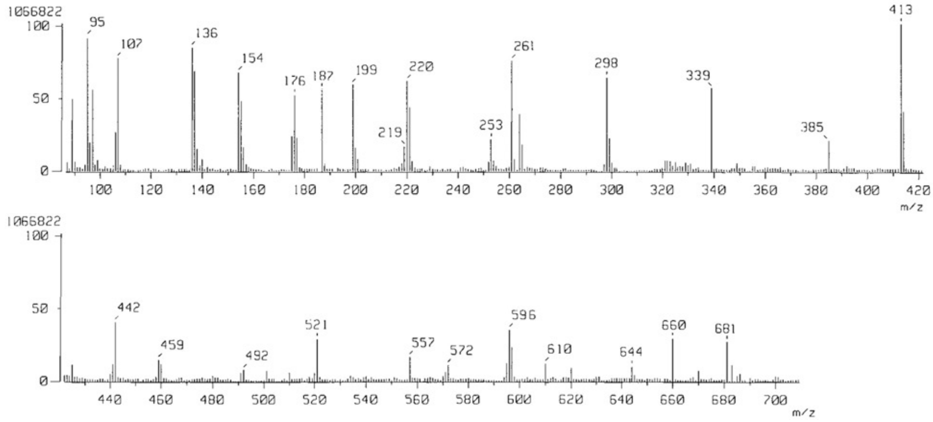


Figure 2. FAB-MS spectrum of [(μ-Cl)$_2$Zn$_2$(L^2)$_2$] (**2**).

after deprotonation. The azomethine proton at 8.38–8.31 ppm in the ligand appeared at 8.74–8.44 ppm in the complexes [27, 28], this supports the coordination of azomethine nitrogen to metal. These conclusions are also supported by IR spectral data. A strong signal at δ13.26, δ13.16 ppm may be attributed to phenolic proton of HL^1 and HL^2, respectively, whereas ^{1}H-NMR spectra of the corresponding metal complexes of Zn(II) and Hg(II) are devoid of signals due to OH.

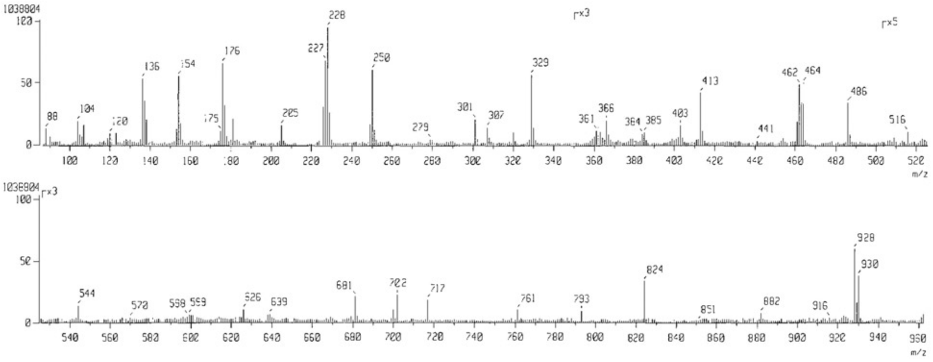


Figure 3. FAB-MS spectrum of $[(\mu\text{-Cl})_2Hg_2(L^1)_2]$ (**3**).

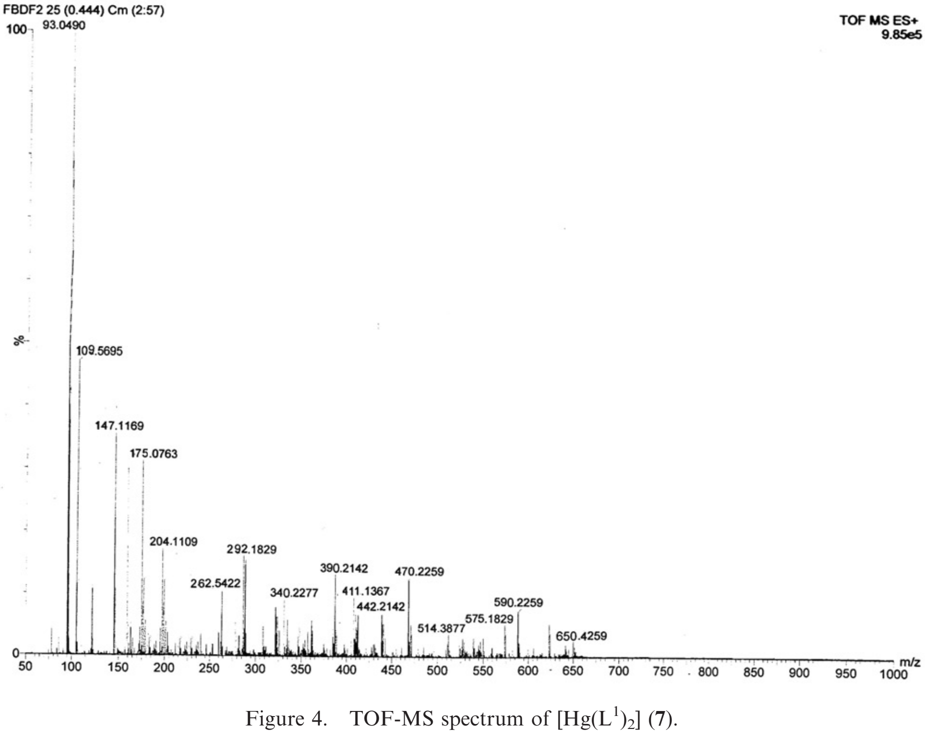


Figure 4. TOF-MS spectrum of $[Hg(L^1)_2]$ (**7**).

3.3. *Mass spectrum*

The mass spectra of zinc(II) and mercury(II) complexes exhibit molecular ion peaks (*m*/*z*) corresponding to their molecular association, representing monomeric and dimeric complexes. The *m*/*z* values for the eight complexes are given in section 2, whereas mass spectra for **1**, **2**, **3**, and **7** are given as figures 1–4. Spectra **1** and **4** are obtained by TOF-MS whereas **2** and **3** were recorded by FAB-MS spectrometry. In **1** and **7**, most fragment ions were observed as a group of peaks due to the presence of

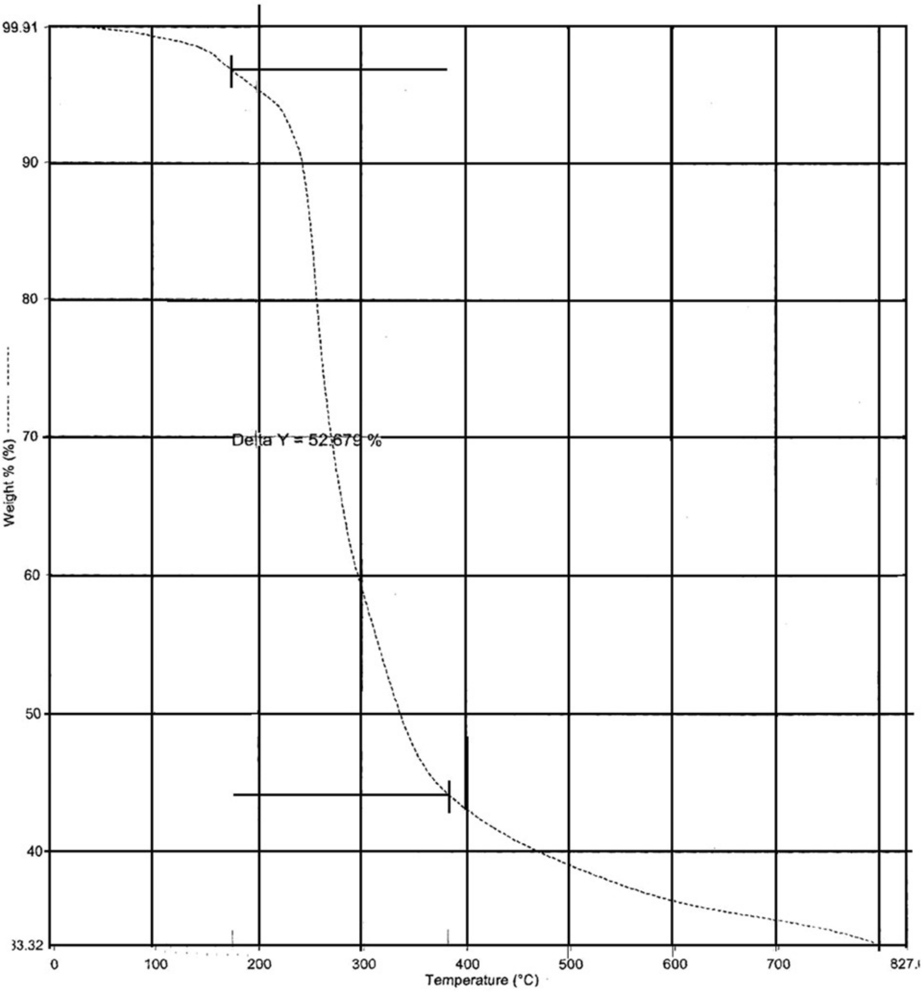


Figure 5. TGA curve of [(Cl)Hg(L^2)] (**4**).

various isotopes of these metals and chlorides. The mass fragmentation pattern (Supplementary material) of [(μ-Cl)$_2$Zn$_2$(L^1)$_2$], [(μ-Cl)$_2$Hg$_2$(L^1)$_2$], and [Hg(L^1)$_2$] confirm the composition and structure of these complexes. FAB-MS spectrum [29, 30] of **3** showed characteristic molecular ion peak for dimer [($C_{28}H_{24}N_2O_4Cl_2Hg_2$) Calcd mass 926.05] at 928 m/z due to various isotopes including mercury and chloride [12]. Various peaks represent successive degradation of the complex by formation of a monomer, for which a molecular ion peak was observed at 464 m/z. The TOF-MS spectra of **1** and **7** show molecular ion peaks at 652.18 (Calcd 649.97) and 650.42 (Calcd 654.14), respectively. Other important peaks were also observed at m/z 572.93, 546.93, 516.92, 346.84, 423.88, 362.84, 290.83, 247.95, 221.94, 213.79, 191.93, and 114.89 due to the formation of various radicals $C_{14}H_{12}ClNHO_2Zn^\bullet$, $C_6H_5^\bullet$, HCN, $ZnCl^\bullet$, $OCH_3^\bullet$, $C_6H_5O^\bullet$, $O^\bullet$, in **1**, whereas **7** showed some prominent peaks at m/z 623.07, 593.04, 577.00, 549.97, 515.94, 472.87, 446, 438.83, 416.82, 412.81, 386.80, and 293.69 due to the formation of various radicals $C_6H_5^\bullet$, $CH_3^\bullet$, HCN, $Hg^\bullet$.

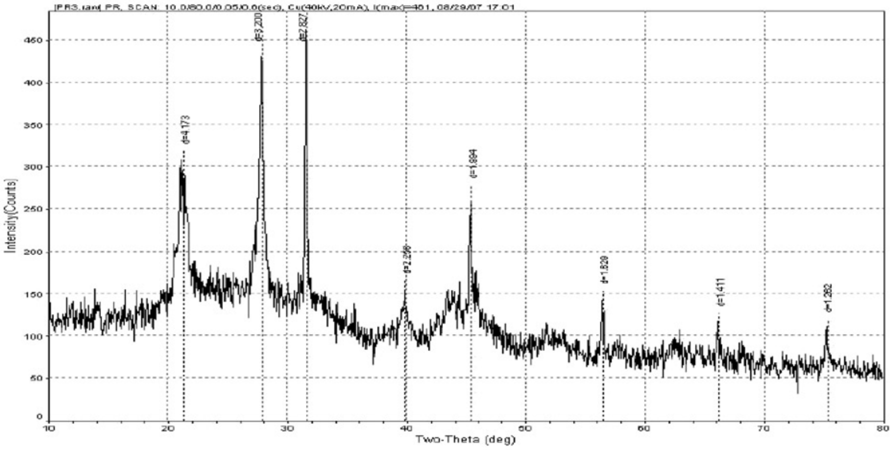


Figure 6. The powdered X-ray diffraction spectrum of [(Cl)Hg(L^2)] (**4**).

3.4. *Thermogravimetric analysis*

The thermal analysis [13] of [(μ-Cl)$_2$Hg$_2$(L^2)$_2$] (**4**) ($C_{30}H_{28}N_2O_4Cl_2Hg_2$) was performed from 50°C to 800°C in dynamic nitrogen. Figure 5 exhibits weight loss between 170.5°C and 380°C. The molecular mass of **4** is 954.62 and the % weight loss of the complex is 52.679%, which is equal to the approximate weight of the complex 511.31 (53.56%). It is clear that elimination of one coordinated ligand, one mercury along with two chlorines from the complex takes place. Thereafter the weight of residue 443.31 [$HgC_{15}H_{14}O_2N$] was obtained. Thermogram of **7** from ambient to 900°C shows that total % weight loss of the complex is 66.7688%, equal to approximate weight of the complex 441 (67.5345 %) leaving HgO as residue at 217 m/z after elimination of ligands.

3.5. *PXRD studies*

X-ray diffraction [13] spectrum of solid powder of **4** clearly showed the crystalline material (figure 6). Diffraction pattern comprises a number of sharp Bragg's reflections corresponding to different orientation of crystallites. Broadening of the diffraction pattern beyond that expected from instrumental factors is generally attributed to crystallite size [31]. Non-uniform broadening of lines is attributed to anisotropic crystallites [32, 33]. Line broadening is used here to calculate the crystallite size using the Debye Scherrer formula [34]. The crystallite size is 328.14 Å.

4. Conclusion

Eight Schiff-base complexes of Zn(II) and Hg(II) have been synthesized containing bidentate ligands. The structural composition has been tentatively proposed by mass spectral studies, showing isotopic molecular ion peaks. The position of the molecular ion peak in the mass spectrum is consistent with the empirical molecular formula as indicated from the elemental analysis. Thermal analysis of [(μ-Cl)$_2$Hg$_2$(L^2)$_2$] (**4**) and

[Hg(L^1)$_2$] (**7**) confirm the dimeric and monomeric molecular association. Molar conductivity measurement indicates that the complexes are non-electrolytes.

Acknowledgments

The authors are grateful to Director, C.D.R.I., Lucknow, for providing spectral and analytical data and also IIT, Delhi, for thermal analysis. Nanophosphor Application Center, University of Allahabad, is also acknowledged for PXRD studies of one of the compounds.

References

[1] Z.L. You, H.L. Zhu, W.S.Z. Liu. *Anorg. Allg. Chem.*, **630**, 1617 (2004); (b) Z.L. You, H.L. Shu. *Anorg. Allg. Chem.*, **630**, 2754 (2004).
[2] R.H. Holm. *J. Am. Chem. Soc.*, **82**, 5632 (1960).
[3] S. Yurdakul, M. Kurt. *J. Mol. Struct.*, **650**, 181 (2003).
[4] F. Saczewski, E. Dziemidowicz-Borys, P.J. Bednarski, R. Grunert, M. Gdaniec, P. Tabin. *J. Inorg. Biochem.*, **100**, 1389 (2006).
[5] P. Kopel, J. Kamenieek, V. Petrieek, A. Kureeka, B. Kalinska, J. Mrozinski. *Polyhedron*, **26**, 535 (2007).
[6] (a) D. Kessel, A.F.A. Sayyab, E.M.H. Jaffar, A.H.H.A. Lanil. *Iraqi J. Sci.*, **22**, 312 (1981); (b) E.M. Hodnett, W.J. Dunn. *J. Med. Chem.*, **13**, 768 (1970).
[7] (a) E.M. Hodnett, W.J. Dunn. *J. Med. Chem.*, **15**, 339 (1972); (b) J. Chakraborty, R.N. Patel. *J. Indian Chem. Soc.*, **73**, 191 (1996).
[8] B.L. Vallee, D.S. Auld. In *Interface Between Chemistry & Biology*, P. Jolles, H. Jornvall (Eds), p. 259, Verlag, Basel (1995).
[9] A.K. Das, S. Seth. *J. Inorg. Biochem.*, **65**, 207 (1977).
[10] J.J. Vostal, R.W. Clarkson. *J. Occup. Med.*, **15**, 649 (1973).
[11] L. Magos. In *Handbook of Toxicity of Inorganic Compounds*, H.G. Seiler, H. Sigel, A. Sigel (Eds), Marcel Dekker, New York (1998).
[12] R.K. Dubey, P. Baranwal, S.K. Dwivedi, U.N. Tripathi. *J. Coord. Chem.*, **64**, 2649 (2011).
[13] R.K. Dubey, P. Baranwal. *Main Group Met. Chem.*, **32**, 321 (2009).
[14] P. Baranwal, D. Phil. Thesis, A.U., Allahabad (2009).
[15] W.L.F. Argarego, D.D. Perrin. *Purification of Laboratory Chemicals*, 4th Edn, Butterworth, Henemann, Oxford (1997).
[16] A.I. Vogel. *A Text Book of Quantitative Inorganic Analysis*, 4th Edn, Longmans Green Co. Ltd., London (1972).
[17] (a) W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971); (b) S. Srivastava, A. Kalam, H.S. Gupta, D. Gupta. *J. Indian Chem. Soc.*, **77**, 371 (2007); (c) D. Feng, B. Feng. *Trans. Met. Chem.*, **18**, 101 (1993).
[18] S.I. Mostafa, T.H. Rakha, M.M.E.L. Agex. *Indian J. Chem.*, **39A**, 1301 (2000).
[19] R.K. Dubey, A.N. Mishra, C.M. Mihsra. *Proc. Nat. Acad. Sci. India*, **75A**, 239 (2005).
[20] N.S. Biradar, N.A. Pujar, V.R. Marathe. *Indian J. Chem.*, **9A**, 712 (1971).
[21] P.B. Chakrawarti, P. Khanna. *J. Indian Chem. Soc.*, **61**, 112 (1984).
[22] A. Majumder, G.M. Rosair, A. Mallick, N. Chatopadhyay, S. Mitra. *Polyhedron*, **25**, 1753 (2006).
[23] S. Basak, S. Sen, S. Banerjee, S. Mitra, G. Rosair, M.T. Garland Rodriguez. *Polyhedron*, **26**, 5104 (2007).
[24] M.S. Singh, P. Nanayan. *Indian J. Chem.*, **411**, 89 (1991).
[25] I.S. Ahuja, R. Singh, C.L. Yadava. *Curr. Sci.*, **50**, 317 (1981).
[26] S.C. Jain, R. Rivest. *Inorg. Chim. Acta*, **4**, 291 (1970).
[27] T.N. Srivastava, A.K.S. Chauhan, B.K. Dwivedi. *Indian J. Chem.*, **19A**, 269 (1980).
[28] R. Malhotra, S. Kumar, K.S. Dhindsa. *Indian J. Chem.*, **36A**, 321 (1997).
[29] (a) R.K. Dubey. *J. Indian Chem. Soc.*, **83**, 1087 (2006); (b) R.K. Dubey, C.M. Mishra, P. Baranwal. *J. Indian Chem. Soc.*, **85**, 387 (2008); (c) R.K. Dubey, U.K. Dubey, C.M. Mishra. *Trans. Met. Chem.*, **31**, 849 (2006); (d) R.K. Dubey, A.K. Mishra, A. Mariya, N. Kumari. *J. Indian Chem. Soc.*, **87**, 1047 (2010).
[30] S.S. Haggag. *Indian J. Chem.*, **46A**, 582 (2007).
[31] A.R. West. *Solid Chemistry and its Application*, p. 173, John Wiley and Sons, New Delhi (1998).
[32] M.C. Bernard, R. Cortes, M. Keddom, H. Takenouti, P. Bernard, S. Senyarich. *J. Power Resources*, **63**, 247 (1996).
[33] Y. Ding, G. Zhang, H. Wu, B. Hai, I. Wang, Y. Qian. *Chem. Mater.*, **13**, 435 (2001).
[34] B.D. Cullity. *Elements of X-ray Diffraction*, Addison-Wesley, Reading (1978).