



Synthesis and Characterization of Some Four Coordinated Zinc(II) and Mercury(II) Complexes

M. MONTAZEROZHORI¹, V. NOUROOZI², S. HASHEMI², Z. KAZEMI², S. JOOHARI^{1,*} and S.A. MUSAVI³

¹Department of Basic Science, Yasouj Branch, Islamic Azad University, Yasouj, Iran

²Department of Chemistry, Firoozabad Branch, Islamic Azad University, Firoozabad, Iran

³Young Researchers Club, Shiraz Branch, Islamic Azad University, Shiraz, Iran

*Corresponding author: E-mail: shjoohari@yahoo.com

(Received: 6 December 2010;

Accepted: 23 August 2011)

AJC-10293

Several new symmetrical bidentate Schiff base ligands ($L^1 = N,N$ -bis(4-chlorobenzylidene)ethane-1,2-diamine, $L^2 = N,N$ -bis(3-nitrobenzylidene)ethane-1,2-diamine and $L^3 = N,N$ -bis(4-nitrobenzylidene)ethane-1,2-diamine and their zinc(II) and mercury(II) complexes with general formula MLX_2 in which $X = Cl, Br$ and I and $M = Hg(II)$ and $Zn(II)$ have been prepared and characterized by elemental analysis, 1H NMR, ^{13}C NMR, Fourier transform-infrared and ultraviolet-visible spectra and molar conductance. All compounds are non-electrolytes in dimethylformamide. The molar conductance and spectral properties indicate coordination of halides ions to metal in pseudo-tetrahedral geometry.

Key Words: Schiff base, Zinc complex, Mercury complex, Bidentate, Symmetrical.

INTRODUCTION

Schiff base compounds containing an iminic groups ($-RC=N-$) are usually formed by the condensation of a primary amine with an active carbonyl^{1,2}. Schiff base complexes containing different central metal atoms have been studied in great detail because of their interesting and important properties, e.g. their ability to reversibly bind oxygen³, complexing ability towards certain toxic metals⁴, catalytic activity in hydrogenation of olefins⁵ and decarboxylation of arylacetic acids⁶, transfer of an amino group⁷, photochromic properties⁸. Schiff bases are potential biologically active compounds some of them are used as antibiotics, antiviral, antitumor agents because of their specific structures, agrochemicals, model systems for biological macromolecules, radiopharmaceuticals for cancer targeting, antidepressants, antimicrobial, antiphlogogistic, nematocide, catalysts and as dioxygen carriers⁹⁻¹⁷. The aim of this work is synthesis, physical and spectral characterization of the several new Schiff base ligand ($L^1 = N,N$ -bis(4-chlorobenzylidene)ethane-1,2-diamine, $L^2 = N,N$ -bis(3-nitrobenzylidene)ethane-1,2-diamine and $L^3 = N,N$ -bis(4-nitrobenzylidene)ethane-1,2-diamine) and their metal complexes with the general formula MLX_2 ($M = Zn(II), Hg(II)$ and $X = Cl, Br, I$).

EXPERIMENTAL

Ethane-1,2-diamine, 3-nitrobenzaldehyde, 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, zinc salts and mercury salt,

solvent and other chemicals were purchased from either Aldrich, Merck or BDH chemicals and were used without purification. Elemental analyses (CNHS) of complete dried samples were performed using a CHNS elemental analyzer. The IR spectra were recorded using KBr discs ($4000-400\text{ cm}^{-1}$) on a FT-IR (Burker Tensor 27) spectrometer. Electronic spectra in the 200-800 nm range were obtained in DMF solutions on a Perkin Elmer Lambda model spectrometer. Molar conductance of the Schiff base ligands and their metal complexes were determined in DMF ($1.0 \times 10^{-3}\text{ M}$) at room temperature using CTR 80 conductometer. 1H and ^{13}C NMR spectra were obtained using a Bruker DPX FT-NMR spectrometer at 500 MHz with the samples dissolved in $DMSO-d_6$ using TMS as internal standard. The melting points ($^{\circ}C$) of the complexes were recorded on BI Barnstead electrothermal instrument.

Synthesis of Schiff base ligand ($L = L^1, L^2$ and L^3):

The ethane-1,2-diamine (0.060 g, 1 mmol) was dissolved in 10 mL methanol and then added to the methanolic solutions of 4-chlorobenzaldehyde (0.281 g, 2 mmol) for L^1 , 3-nitrobenzaldehyde (0.302 g, 2 mmol) for L^2 and 4-nitrobenzaldehyde (0.302 g, 2 mmol) for L^3 and severely stirred for 2-3 h. After completion of the reactions the Schiff base ligands were filtered and washed twice with warm methanol. In final, ligands were dried under vacuum. Spectral data of the ligands are summarized as following:

L^1 : IR spectrum (KBr, cm^{-1}): 3424(m), 3022(w), 2915(m), 2854(m), 2361(m), 1909(w), 1803(w), 1643(vs), 1591(m),

1568(m), 1484(s), 1404(m), 1370(m), 1279(m), 1215(m), 1168(m), 1083(s), 1013(s), 978(m), 863(m), 819(s), 701(m). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 265(14110). 1H NMR spectrum (DMSO- d_6): 8.29(bs, 2H), 7.67(bs, 4H), 7.44(bs, 4H), 4.04(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.72, 136.06, 135.7, 130.30, 129.00, 61.87 ppm.

L²: IR spectrum (KBr, cm^{-1}): 3424(w), 3075(w), 2970(w), 2910(w), 2860(m), 2000(w), 1940(w), 1849(w), 1758(w), 1645(vs), 1615 (w), 1570(w), 1525(vs), 1500(m), 1475(w), 1350(vs), 1273(m), 1228(w), 1077(m) 1017(s), 974(w), 866(w), 812(m), 737(s), 677(s), 632(w). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 266(15149). 1H NMR spectrum (DMSO- d_6): 8.47(s, 2H), 8.46(s, 2H), 8.22(d, 2H, $J = 8.12$ Hz), 8.09(d, 2H, $J = 7.66$ Hz), 7.67(t, 2H, $J = 7.90$ Hz and $J = 7.93$ Hz), 3.93(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.25, 148.99, 138.40, 134.87, 131.22, 125.87, 122.68, 61.35 ppm.

L³: IR spectrum (KBr, cm^{-1}): 3441(w), 3100(w), 2911(m), 2885(m), 1645(vs), 1602(s), 1519(vs), 1462(m), 1372(m), 1339(vs), 1312(s), 1286(m), 1219(w), 1103(m), 1017(s), 959(w), 854(s), 839(s), 794(w), 748(s), 689(m), 503(w). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 286(26478). 1H NMR spectrum (DMSO- d_6): 8.48(s, 2H), 8.23(d, 4H, $J = 8.58$ Hz), 7.93(d, 4H, $J = 8.60$ Hz), 3.95(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.60, 149.44, 142.37, 129.73, 124.81, 61.57 ppm.

Preparation of ZnLX₂ (X = Br, I and L = L¹, L² and L³): A solution of 0.5 mmol ligand (L¹(0.153g), L² and L³ (0.163 g)) in 10 mL of chloroform was added drop wise under stirring to the solution of 0.5 mmol of ZnX₂ in methanol (20 mL). Complexes as a white precipitate were filtered and for purification washed twice with methanol. Then complexes were dried at (80-100 °C) under vacuum and were kept in a desiccator over silica-gel.

ZnL¹Br₂: IR spectrum (KBr, cm^{-1}): 3435(m), 3040(w), 2919(m), 1903(w), 1638(vs), 1591(s), 1488(m), 1431(m), 1391(m), 1333(m), 1304(m), 1219(m), 1178(m), 1090(s), 1032(m), 1011(m), 832(m), 591(m), 502(m). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 265(13650). 1H NMR spectrum (DMSO- d_6): 8.30(s, 2H), 7.68(d, 4H, $J = 6.6$ Hz), 7.42(d, 4H, $J = 6.48$ Hz), 3.83(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.68, 136.07, 135.75, 130.29, 129.60, 61.53 ppm.

ZnL¹I₂: IR spectrum (KBr, cm^{-1}): 3435(m), 3032(w), 2916(m), 1887(w), 1634(vs), 1590(s), 1488(m), 1428(m), 1391(m), 1334(m), 1304(m), 1219(m), 1178(m), 1090(s), 1031(m), 958(m), 827(m), 803(m), 589(m), 499(m), 428(m). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 265(17850). 1H NMR spectrum (DMSO- d_6): 8.30(s, 2H), 7.68(d, 4H, $J = 8.48$ Hz), 7.42(d, 4H, $J = 8.46$ Hz), 3.82(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.70, 136.04, 135.70, 130.31, 129.63, 61.55 ppm.

ZnL²Br₂: IR spectrum (KBr, cm^{-1}): 3282(m), 3222(w), 3081(m), 3033(w), 2919(w), 2000(w), 1940(w), 1871(w), 1758(w), 1644(vs), 1614(m), 1526(vs), 1443(s), 1400(m), 1351(vs), 1031(m), 998(m), 980(m), 816(s), 734(s), 677(s), 599(m), 434(w). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 264(13759). 1H NMR spectrum (DMSO- d_6): 8.46(s, 2H), 8.44(s, 2H), 8.20(d, 2H, $J = 8.07$ Hz), 8.07(d, 2H, $J = 7.57$ Hz), 7.66(t, 2H, $J = 7.58$ Hz and $J = 7.86$ Hz), 3.91(s, 4H)

ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.21, 148.95, 138.37, 134.87, 131.22, 125.85, 122.64, 61.34 ppm.

ZnL²I₂: IR spectrum (KBr, cm^{-1}): 3443(w), 3098(m), 3036(w), 2939(w), 2859(m), 2060(m), 1952(w), 1710(w), 1678(w), 1640(vs), 1608(w), 1530(vs), 1475(w), 1443(m), 1350(vs), 1223(m), 1098(m), 1031(m), 982(m), 819(m), 781(w), 734(m), 677(m), 560(w), 440(w). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 265(16598). 1H NMR spectrum (DMSO- d_6): 8.48(s, 2H), 8.45(s, 2H), 8.21(d, 2H, $J = 8.13$ Hz and $J = 1.54$ Hz), 8.09(d, 2H, $J = 7.67$ Hz), 7.67(t, 2H, $J = 7.90$ Hz and $J = 7.94$ Hz), 3.93(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.23, 148.96, 138.38, 134.90, 131.26, 125.86, 122.64, 61.31 ppm.

ZnL³Br₂: IR spectrum (KBr, cm^{-1}): 3468(w), 3108(w), 2970(w), 2853(m), 1642(vs), 1602(s), 1519(vs), 1487(w), 1436(w), 1341(vs), 1299(s), 1218(m), 1115(m), 1109(s), 956(w), 825(s), 815(w), 747(s), 690(m), 488(w), 477(w). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 278(20000). 1H NMR spectrum (DMSO- d_6): 8.48(s, 2H), 8.45(s, 2H), 8.21(d, 2H, $J = 8.13$ Hz and $J = 1.54$ Hz), 8.09(d, 2H, $J = 7.67$ Hz), 7.67(t, 2H, $J = 7.90$ Hz and $J = 7.94$ Hz), 3.93(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.23, 148.96, 138.38, 134.90, 131.26, 125.86, 122.64, 61.31 ppm.

ZnL³I₂: IR spectrum (KBr, cm^{-1}): 3440(m), 3096(w), 3065(m), 2909(w), 2831(w), 1639(vs), 1599(s), 1519(vs), 1445(m), 1376(w), 1345(vs), 1299(s), 1227(m), 1124(w), 1031(s), 981(w), 935(w), 847(s), 747(s), 697(w), 515(w), 454(w). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 284(17830). 1H NMR spectrum (DMSO- d_6): 8.47(s, 2H), 8.21(d, 4H, $J = 8.41$ Hz), 7.91(d, 4H, $J = 8.44$ Hz), 3.92(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 161.56, 149.37, 142.34, 129.74, 124.78, 61.57 ppm.

Preparation of HgLX₂ (X = Cl, Br, I and L = L¹, L² and L³): To the solution of mercury salt (HgCl₂(0.135 g, 0.5 mmol), HgBr₂ (0.180 g, 0.5 mmol) and HgI₂ (0.227 g, 0.5 mmol) in ethanol, solution of 0.5 mmol ligand (L¹(0.153 g), L² and L³ (0.163 g)) in 10 mL chloroform was added dropwise and stirred magnetically for 2-3 h. After this time, white precipitate was separated by filtration and washed with warm ethanol for purification. Complexes were dried at (80-100 °C) under vacuum and were kept in a desiccator over silica-gel.

HgL¹Cl₂: IR (KBr, cm^{-1}): 3443(m), 3112(w), 2926(m), 1919(w), 1636(vs), 1597(m), 1570(s), 1490(m), 1444(m), 1381(m), 1301(m), 1223(m), 1143(m), 1091(m), 1041(m), 1014(m), 818(s), 693(m), 556(m), 497(m). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 264(9200). 1H NMR spectrum (DMSO- d_6): 8.57(bs, 2H), 7.89(d, 4H, $J = 8.45$ Hz), 7.68(d, 4H, $J = 8.48$ Hz), 3.83(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 165.07, 136.08, 135.70, 131.29, 130.32, 61.57 ppm.

HgL¹Br₂: IR spectrum (KBr, cm^{-1}): 3444(m), 3111(w), 2880(m), 1996(w), 1635(vs), 1596(m), 1567(s), 1489(m), 1452(m), 1378(m), 1300(m), 1284(m), 1223(m), 1090(s), 1033(m), 1011(m), 965(m), 845(m), 818(s), 677(m), 555(m), 495(m). UV-VIS spectrum [(DMF), λ (nm) (ϵ , $M^{-1}cm^{-1}$): 265(15690). 1H NMR spectrum (DMSO- d_6): 8.59(bs, 2H), 7.90(d, 4H, $J = 8.46$ Hz), 7.69(d, 4H, $J = 7.48$ Hz), 3.83(s, 4H) ppm. ^{13}C NMR spectrum (DMSO- d_6): 165.32, 136.10, 135.67, 131.40, 130.32, 61.56 ppm.

HgL²Br₂: IR spectrum (KBr, cm⁻¹): 3441(m), 3081(w), 2992(w), 2910(w), 2862(w), 1978(w), 1914(w), 1736(w), 1700(w), 1640(vs), 1608(w), 1525(vs), 1473(w), 1441(m), 1351(vs), 1173(w), 1220(m), 1093(w), 1031(m), 972(w), 817(m), 735(m), 676(m), 580(w), 500(w). UV-VIS spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 266(16148)]. ¹H NMR spectrum (DMSO-*d*₆): 8.49(s, 2H), 8.47(s, 2H), 8.23(bd, 2H, *J* = 8.11 Hz), 8.10(d, 2H, *J* = 7.59 Hz), 7.68(t, 2H, *J* = 7.88 Hz), 3.93(s, 4H) ppm. ¹³C NMR spectrum (DMSO-*d*₆): 161.32, 148.99, 138.37, 134.88, 131.23, 125.90, 122.70, 61.34 ppm.

HgL²I₂: IR spectrum (KBr, cm⁻¹): 3429(w), 3066(w), 3035(w), 2914(w), 2838(w), 2060(w), 1998(w), 1938(w), 1877(w), 1756(w), 1635(vs), 1605(w), 1529(vs), 1468(w), 1438(m), 1349(vs), 1279(w), 1219(m), 1093(m), 1032(m), 973(m), 816(s), 734(s), 678(m), 501(w). UV-VIS spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 266(20157)]. ¹H NMR spectrum (DMSO-*d*₆): 8.49(s, 2H), 8.47(s, 2H), 8.23(dd, 2H, *J* = 8.14 Hz and *J* = 1.48 Hz), 8.09(d, 2H, *J* = 7.92 Hz), 7.68(t, 2H, *J* = 7.92 Hz and *J* = 7.92 Hz), 3.93(s, 4H) ppm. ¹³C NMR spectrum (DMSO-*d*₆): 161.31, 148.99, 138.37, 134.88, 131.23, 125.90, 122.71, 61.34 ppm.

HgL³Cl₂: IR spectrum (KBr, cm⁻¹): 3448(w), 3108(w), 2970(w), 2853(m), 1642(vs), 1602(s), 1519(vs), 1487(w), 1436(w), 1341(vs), 1299 (s), 1218(m), 1115(m), 1109(s), 956(w), 825(s), 815(w), 747(s), 690(m), 488(w), 447(w). UV-VIS spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 286(19373)]. ¹H NMR spectrum (DMSO-*d*₆): 8.47(s, 2H), 8.22(d, 4H, *J* = 8.58 Hz), 7.92(d, 4H, *J* = 8.60 Hz), 3.94(s, 4H) ppm. ¹³C NMR spectrum (DMSO-*d*₆): 161.62, 149.42, 142.34, 129.73, 124.78, 61.56 ppm.

HgL³Br₂: IR spectrum (KBr, cm⁻¹): 3465(w), 3080(w), 3048(w), 2920(m), 2823(w), 2360(m), 1641(vs), 1599(s), 1518(vs), 1452(m), 1364(w), 1343(vs), 1307(s), 1225(w), 1181(w), 1106(m), 1031(m), 1009(w), 934(w), 851(s), 749(s), 696(m), 499(w). UV-VIS spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 284(19366)]. ¹H NMR spectrum (DMSO-*d*₆): 8.47(s, 2H), 8.24(d, 4H, *J* = 8.62Hz), 7.93(d, 4H, *J* = 8.63 Hz), 3.95(s, 4H) ppm. ¹³C NMR spectrum (DMSO-*d*₆): 161.62, 149.43, 129.73, 124.80, 61.56 ppm.

HgL³I₂: IR spectrum (KBr, cm⁻¹): 3446(w), 3104(w), 2942(w), 2904(w), 2850(m), 1639(vs), 1600(s), 1519(vs), 1471(w), 1381(w), 1341(vs), 1317 (s), 1277(s), 1196(w), 1102(m), 1020(s), 937(w), 851(s), 749(s), 689(s), 504(w), 446(w). UV-VIS spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 283(33327)].

RESULTS AND DISCUSSION

The reaction of MX₂ (X = chloride, bromide and iodide, M = zinc and mercury) with ligands (L¹ = N,N-bis(4-chlorobenzylidene)ethane-1,2-diamine, L² = N,N-bis(3-nitrobenzylidene)ethane-1,2-diamine and L³ = N,N-bis(4-nitrobenzylidene)ethane-1,2-diamine) in a 1:1 (MX₂:L) molar ratio give complexes whose stoichiometries are confirmed by elemental analysis. Elemental analyses and other physical properties of the ligands and their complexes are summarized in Table-1. The compounds are stable under ordinary laboratory conditions. The low molar conductivities of 10⁻³M solutions of all complexes in DMF solvent at room temperature were in the range of 5-20 cm² Ω⁻¹M⁻¹ which shows them to be non-electrolytes^{18,19}.

The most characteristic absorptions of the bidentate Schiff base ligands are different from their complexes and ligands absorptions at different frequencies indicating the coordination of them. Characteristic absorption frequencies of the starting material including aldehydes and amine (ν_{sym} and ν_{asym} of (-NH₂) of 1,2-ethylenediamine) at 1700-1710 and 3100-3300 cm⁻¹ were not observed in the FT-IR spectrum of the ligands at all.

The FT-IR spectrum of ligands showed frequencies at 2970-3100, 2910-2915, 2854-2885 cm⁻¹ assigned to C-H of aromatic, aliphatic and iminic groups, respectively, smoothly affected by coordination of the ligands. The vibrational frequency at 1643, 1645 and 1645 cm⁻¹ can be assigned to azomethine group (C=N) for the ligands L¹, L² and L³ respectively²⁰⁻²³ and shifts by 1-11 cm⁻¹ to lower frequencies in the spectra of the related complexes indicating coordination through the azomethine nitrogen^{23,24}. The stretching frequency of -C=N is shifted to lower frequencies after coordination is attributed to the π-back bonding of metal to ligand. The band

TABLE-1
ELEMENTAL ANALYSIS, COLOUR, MELTING POINTS, %YIELD AND MOLAR CONDUCTIVITY OF THE LIGANDS AND THEIR COMPLEXES

Compound	m.w.	Colour	m.p. (°C)	Yield (%)	Found (Calcd.) (%)			Λ _M (cm ² Ω ⁻¹ M ⁻¹)
					C	N	H	
L ¹	305	White	135-137	86	62.90 (62.97)	9.17 (9.18)	4.58 (4.62)	5
L ²	326	White	146-148	91.5	58.70 (58.89)	17.30 (17.17)	4.30 (4.32)	5
L ³	326	Pale Yellow	198	79	58.70 (58.89)	17.30 (17.17)	4.30 (4.32)	5
ZnL ¹ Br ₂	530	White	254-256	78	36.24 (36.30)	5.28 (5.30)	2.64 (2.50)	9
ZnL ¹ I ₂	624	White	249-251	82	-	-	-	19
HgL ¹ Cl ₂	577	White	176-178	76	33.32 (33.40)	4.85 (4.70)	2.42 (2.50)	7
HgL ¹ Br ₂	666	White	150-152	78	-	-	-	7
ZnL ² Br ₂	552	White	312-314	72	34.70 (34.84)	10.20 (10.15)	3.60 (3.55)	10
ZnL ² I ₂	646	White	318-319	83	-	-	-	20
HgL ² Br ₂	687	White	178-179	79	-	-	-	6
HgL ² I ₂	781	Cream	178-180	69	24.50 (24.41)	7.20 (7.17)	1.70 (1.80)	8
ZnL ³ Br ₂	552	White	205	68	34.70 (34.84)	10.20 (10.15)	3.60 (3.55)	6
ZnL ³ I ₂	646	White	230	65	-	-	-	7
HgL ³ Cl ₂	598	White	200	69	-	-	-	10
HgL ³ Br ₂	687	White	210	72	-	-	-	8
HgL ³ I ₂	781	Cream	260	63	24.50 (24.41)	7.20 (7.17)	1.70 (1.80)	11

at 1370-1372 cm^{-1} present in the IR spectrum of the Schiff bases may be assigned to (C-N) stretching mode that is shifted to 1364-1400 cm^{-1} after coordination^{18,24,25}. In the FT-IR spectrum of L^1 the frequencies at 1083 cm^{-1} show C-Cl stretching vibration that is shifted to 1090-1091 cm^{-1} after coordination. In the spectrum of L^2 and L^3 the very strong bands at 1525, 1519 and 1350, 1339 cm^{-1} respectively, can be attributed to the asymmetric (ν_{asym}) and symmetric stretching (ν_{sym}) of $-\text{NO}_2$ groups that shifted a few wave numbers²⁶. The very strong out-of-plane bending of the aromatic C-H and C-C at 812-839 and 748-701 cm^{-1} are nearly unchanged or shifted to higher frequencies after coordination²⁷. Evidences for bonding in the complexes is also shown by observation of new bands in the spectra of the metal complexes at 428-502 cm^{-1} assigned to $\nu(\text{M-N})$.

Electronic spectra of the ligands and their complexes were recorded in DMF of 1.0×10^{-3} M at room temperature. The spectrum of the free Schiff bases exhibits one absorption bands at 265(L^1), 266(L^2) and 286(L^3) nm, attributed to $\pi-\pi^*$ transitions. In the complexes, the $\pi-\pi^*$ transitions are almost unchanged for all complexes except for entries 12 that is shifted to lower wavelength as a consequence of coordination. The suggested structure for complexes is pseudo-tetrahedral geometry²⁶ (Fig. 1).

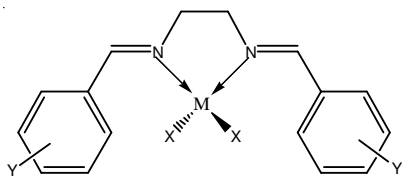


Fig. 1. Structural formula of complexes, where M= Zn(II), Hg(II), X = chloride, bromide and iodide and Y = 4-chloro, 3-nitro and 4-nitro

The ^1H NMR and ^{13}C NMR spectra of ligands and their complexes are summarized in experimental sections. The ^1H NMR of L^1 exhibits signals at 8.29 ppm (bs, 2H) for iminic group; 7.67(bs, 4H) and 7.44(bs, 4H) ppm for aromatic hydrogens and 4.04 ppm (s, 4H) for methylene groups. ^{13}C NMR spectrum shows signals at 161.72 ppm for iminic carbon, 136.06, 135.7, 130.30, 129.00 and 61.87 ppm for aromatic and aliphatic carbons. The ^1H NMR of L^2 exhibits signals at 8.47 ppm (s, 2H) for iminic group, 8.46(s, 2H), 8.22(d, 2H, $J = 8.12$ Hz), 8.09(d, 2H, $J = 7.66$ Hz), 7.67(t, 2H, $J = 7.90$ Hz and $J = 7.93$ Hz) ppm for aromatic hydrogens and 3.93(s, 4H) ppm for methylene groups. Again ^{13}C NMR spectrum shows signals at 161.25 ppm for iminic carbon, 148.99, 138.40, 134.87, 131.22, 125.87, 122.68 and 61.35 ppm for aromatic and aliphatic carbons. The ^1H NMR of L^3 exhibits signals at 8.48 ppm (s, 2H) for iminic group; 8.23(d, 4H, $J = 8.58$ Hz), 7.93(d, 4H, $J = 8.60$ Hz) ppm for aromatic hydrogens and the signal at 3.95 ppm (s, 2H) is related to methylene groups. Its ^{13}C NMR spectrum shows signals at 161.60 ppm for iminic carbon, 149.44, 142.37, 129.73, 124.81 and 61.57 ppm for aromatic and aliphatic carbons. After coordination of ligand L^1 , the iminic hydrogen downfield shifted considerably in mercury complexes while low down field shifting is observed

in zinc complexes. On the other hand the aromatic hydrogen signals that are shown as broad singlet in ligand spectrum have been appeared as doublet in the all complexes spectra. Ultimately the aliphatic hydrogen signals up field shifted in complexes with respect to ligand. Also the iminic carbon downfield shifted smoothly in mercury complexes. In zinc complexes, the considerable shifting was not shown. In the case of L^2 and L^3 , considerable changes of the hydrogen and carbon signals have not observed after coordination. This observation can be explained based on a balance between the induction and resonance effects in the molecules in opposite directions that lead to nearly unchanged chemical shifts. In other view, speed dissociation in the DMSO solvent may be responsible for this observation.

ACKNOWLEDGEMENTS

Partial supports of this work by Islamic Azad University, Firoozabad branch and Yasouj University is acknowledged.

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