

Synthesis and characterization of some new four coordinated IIB transition metal ion complexes

M. Montazerzohori¹, S. Jooari^{2*}, V. Nouroozi³, S. Hashemi³, Z. Kazemi³ and S.A. Musavi¹

¹Department of Chemistry, Yasouj University, Yasouj 75918-74831, Iran

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

³Department of Basic Science, Islamic Azad University, firozabad Branch, Firoozabad, Iran.
mmzohory@yahoo.com, shjooari@yahoo.com*

Abstract

Complexes of Zn(II) and Hg(II) with new Schiff bases ligands of (N,N-bis(4-chlorobenzylidene)propane-1,2-diamine(L¹), N,N-bis(3-nitrobenzylidene)propane-1,2-diamine(L²) and N,N-bis(4-nitrobenzylidene)propane-1,2-diamine(L³)) with general formula MLX₂ in which X= Cl⁻, Br⁻ and I⁻ have been prepared using 1:1 metal-to-ligand ratios and characterized by elemental analysis, FT-Infrared and Ultraviolet-Visible spectra, ¹H NMR (Nuclear Magnetic Resonance), ¹³C NMR and molar conductance. All compounds are non-electrolytes in DMF. The complexes exhibit a pseudo tetrahedral geometry around the metal center.

Keywords: Schiff base, Zinc complex, Mercury complex, Bidentate, asymmetrical.

Introduction

In recent years among the chemical compounds, some Schiff bases and their complexes because of their ability as biologically activities such as antimicrobial, antifungal, antiviral and antitumor have been found to be very important and usefulness of these compounds are not covered by anyone (Saxena & Shrivastava, 1987; Kumar *et al.*, 2009). Schiff bases usually have variable donation sites, e.g., nitrogen, sulfur and/or oxygen markedly affected the activity of the compounds. They could be monodentate, bidentate, tridentate or tetradentate forming mono- or polynuclear complexes (Bray & George, 1985; George *et al.*, 1986; Singh *et al.*, 1997; Costamagna *et al.*, 1992; Guerriero, 1995). Also for this class of compounds, many applications such as antidepressants, antiphlogogistic, antinematocide, and other medicinal agents have been reported (Wu *et al.*, 1993; Song *et al.*, 1994; Ren *et al.*, 2002; Tarafder *et al.*, 2000). Schiff base metal complexes have good ability to reversibly bind oxygen in epoxidation reactions (El-Medani *et al.*, 2005), catalytic role in hydrogenation of olefins (Colman & Hegedu, 1980; Zhao *et al.*, 2001) and photochromic properties (Liu *et al.*, 2004). Schiff bases can be used to obtain optical materials and conducting polymers (Palys *et al.*, 1997; Aly & El-Shaieb, 2004). In the present paper, preparation and identification of several new Schiff base ligands and their metal complexes have been described. The general formula of these complexes are MLX₂ in which M= Zn(II) and Hg(II) and X= chloride, bromide and iodide, and L= N,N-bis(4-chlorobenzylidene)propane-1,2-diamine(L¹), N,N-bis(3-nitrobenzylidene)propane-1,2-diamine(L²) and N,N-bis(4-nitrobenzylidene)propane-1,2-diamine(L³). The Schiff bases and their complexes have been characterized by elemental analyses, IR, UV-Vis, ¹H NMR and ¹³C NMR and conductivity.

Experimental

3-nitrobenzaldehyde, 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, propane-1,2-diamine, zinc and mercury salts, solvent and other chemicals were purchased from either Aldrich, Merck and/or BDH Chemicals and were used without more purification. Elemental analyses (CHN) were performed on a elemental analyzer. The IR spectra were recorded using KBr discs (4000-400 cm⁻¹) on a FT-IR (BRUKER TENSOR 27) spectrometer. UV-Vis spectra in the 200-800 nm range were recorded using a Perkin Elmer Lambda5 model spectrophotometer in DMF. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer at 500 MHz with the samples dissolved in DMSO-*d*₆ using TMS as internal standard. Molar conductance of the Schiff base ligands and their transition metal complexes were determined in DMF (1.0 × 10⁻³ M) at room temperature using CTR 80 conductometer. The melting points (°C) of the complexes were recorded on BI Barnstead electrothermal instrument.

Synthesis of Schiff base ligands (L¹, L² and L³)

The new Schiff-bases of N,N-bis(4-chlorobenzylidene)propane-1,2-diamine (L¹), N,N-bis(3-nitrobenzylidene)propane-1,2-diamine (L²) and N,N-bis(4-nitrobenzylidene)propane-1,2-diamine (L³) were prepared by condensation of 4-chlorobenzaldehyde (0.281 g, 2 mmol) for L¹, 3-nitro benzaldehyde (0.302 g, 2 mmol) for L² and 4-nitro benzaldehyde (0.302 g, 2 mmol) for L³ with 1,2-diaminopropane (0.074 g, 1 mmol) in 20 mL methanol under rigorous stirring for 3-4 h. The Schiff bases precipitated and then the reaction mixtures were filtered and ligands were separated. For more purification, the ligands were washed twice with methanol and dried under vacuum. Spectral data of the ligands are summarized as following:

L¹: IR(KBr, cm⁻¹): 3419(m), 3024(w), 2961(m), 2840(s), 1903(w), 1643(vs), 1592(m), 1484(s), 1450(m), 1403(m), 1369(m), 1277(m), 1212(m), 1080(s), 1028(m), 1008(m), 975(m), 880(m), 817(s), 700(m), 499(m), 446(m). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 263(14516). ¹H-NMR spectrum (DMSO-d₆): 8.26(s, 1H), 8.23(s, 1H), 7.66(t(2d), 4H, J= 8.06Hz and J= 7.43Hz), 7.41(d, 4H, J= 8.22Hz), 3.74(dd, 1H, J= 11.09Hz and J= 4.62Hz), 3.65(sixtet, 1H, J= 6.02Hz), 3.58(dd, 1H, J= 7.42Hz and J= 11.00Hz), 1.22(d, 3H, J= 6.18Hz) ppm. ¹³C-NMR spectrum (DMSO-d₆): 161.59, 159.65, 136.06, 136.00, 135.77, 135.72, 130.29, 130.26, 129.60, 129.57, 67.64, 66.40, 21.26 ppm.

L²: IR spectrum (KBr, cm⁻¹): 3423(w), 3085(m), 3038(w), 2968(m), 2954(w), 2862(s), 2327(w), 1964(w), 1903(w), 1827(w), 1646(vs), 1600(w), 1568(w), 1530(vs), 1471(w), 1441(m), 1346(vs), 1267(w), 1215(m), 1078(m), 1033(m), 979(m), 826(m), 805(m), 734(s), 679(s), 438(w). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 262(16388). ¹H-NMR spectrum (DMSO-d₆): 8.47(bs, 2H), 8.44(s, 1H), 8.43(s, 1H), 8.21(bd, 2H, J= 6.02Hz), 8.09(d, 1H, J= 4.43Hz), 8.08(d, 1H, J= 6.04Hz), 7.67(t, 1H, J= 7.59Hz and J= 7.79Hz), 7.66(t, 1H, J= 7.93Hz and J= 7.68Hz), 3.85(dd, 1H, J= 11.18Hz and J= 4.80Hz), 3.79(Sixted, 1H, J= 6.08Hz and J= 7.17Hz), 3.70(dd, 1H, J= 11.14Hz and J= 7.17Hz), 1.28(d, 3H, J= 6.20Hz) ppm. ¹³C-NMR spectrum (DMSO-d₆): 160.20, 159.31, 148.99, 138.47, 138.41, 134.97, 134.83, 132.22, 125.88, 125.83, 122.68, 122.58, 67.34, 66.20, 21.17 ppm.

L³: IR spectrum (KBr, cm⁻¹): 3436(w), 3096(w), 3048(w), 2968(w), 2853(m), 1641(vs), 1598(s), 1518(vs), 1438(m), 1390(w), 1342(vs), 1280(s), 1218(w), 1102(s), 1029(m), 975(w), 849(s), 747(s), 688(m), 510(w), 484(w), 434(w). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 284(33610). ¹H-NMR spectrum (DMSO-d₆): 8.44(s, 1H), 8.41(s, 1H), 8.20(d, 2H, J= 8.58Hz), 8.19(d, 2H, J= 8.78Hz), 7.90(t(2d), 4H, J= 9.35Hz and J= 9.02Hz), 3.86(dd, 1H, J= 11.36Hz and J= 4.70Hz), 3.79(sextet, 1H, J= 6.56Hz), 3.70(dd, 1H, J= 11.34Hz and J= 7.32Hz), 1.27(d, 3H, J= 6.25Hz) ppm. ¹³C-NMR spectrum (DMSO-d₆): 161.47, 159.56, 149.38, 149.35, 142.45, 142.35, 129.70, 129.66, 124.74, 67.57, 66.47, 21.1 ppm.

Preparation of ZnLX₂ (X= Br⁻, I⁻ and L= L¹, L² and L³): Solution of 0.5 mmol ligand (L¹(0.160g), L²(0.170g) and L³(0.170g)) in 10 mL chloroform was added drop wise to the solution of 0.5 mmol of ZnX₂ (ZnBr₂(0.113g) and ZnI₂(0.159g)) in methanol (20 mL) and the mixture was stirred for 3-5 h. Complexes as a white precipitate were filtered and for more purification washed twice with methanol. Then complexes were dried at (80-100 °C) under vacuum and kept in a desiccator over silica-gel.

ZnL¹Br₂: IR spectrum (KBr, cm⁻¹): 3443(m), 3024(w), 2913(m), 1919(w), 1638(vs), 1592(s), 1487(m), 1435(m), 1387(m), 1354(m), 1286(m), 1218(m), 1089(s), 997(m), 824(m), 701(m), 507(m), 472(m). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 264(20000). ¹H-NMR spectrum (DMSO-d₆): 8.27(s, 1H), 8.24(s, 1H), 7.65(t(2d),

4H, J= 8.28Hz and J= 7.02Hz), 7.42(d, 4H, J= 8.22Hz), 3.75(dd, 1H, J= 11.16Hz and J= 4.80Hz), 3.65(sixtet, 1H, J= 6.10Hz), 3.59(dd, 1H, J= 11.09Hz and J= 7.39Hz), 1.22(d, 3H, J= 6.20Hz) ppm. ¹³C-NMR spectrum (DMSO-d₆): 161.63, 159.68, 136.06, 136.00, 135.71, 130.31, 130.27, 129.61, 129.58, 67.61, 66.38, 21.27 ppm.

ZnL¹I₂: IR spectrum (KBr, cm⁻¹): 3445(m), 3016(w), 2909(m), 1903(w), 1633(vs), 1591(s), 1487(m), 1435(m), 1386(m), 1290(m), 1217(m), 1089(s), 993(m), 822(m), 693(m), 505(m), 467(m). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 264(13770). ¹H-NMR spectrum (DMSO-d₆): 8.28(s, 1H), 8.25(s, 1H), 7.66(t(2d), 4H, J= 8.05Hz and J= 7.00Hz), 7.43(d, 4H, J= 18.18Hz), 3.75(dd, 1H, J= 11.18Hz and J= 4.76Hz), 3.66(sixtet, 1H, J= 6.12Hz), 3.59(dd, 1H, J= 11.07Hz and J= 7.37Hz), 1.22(d, 3H, J= 6.18Hz) ppm. ¹³C-NMR spectrum (DMSO-d₆): 161.63, 159.68, 136.03, 135.98, 135.77, 135.73, 130.31, 130.27, 129.62, 129.60, 67.60, 66.36, 21.27 ppm.

ZnL²Br₂: IR spectrum (KBr, cm⁻¹): 3445(m), 3076(w), 3030(w), 2966(w), 2919(m), 2857(w), 2361(m), 2000(w), 1938(w), 1751(w), 1704(w), 1642(vs), 1531(vs), 1492(w), 1446(m), 1350(vs), 1281(w), 1219(m), 1173(w), 1098(m), 995(m), 815(m), 739(m), 672(m), 490(w). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 270(19864). ¹H-NMR spectrum (DMSO-d₆): 8.47(bs, 2H), 8.45(s, 1H), 8.44(s, 1H), 8.22(bd, 2H, J= 8.12Hz), 8.09(t(2d), 2H, J= 4.00Hz and J= 6.40Hz), 7.67(t, 1H, J= 8.00Hz and J= 7.66Hz), 7.66(t, 1H, J= 7.00Hz and J= 7.90Hz), 3.84(dd, 1H, J= 11.12Hz and J= 4.63Hz), 3.78(Sixted, 1H, J= 6.30Hz), 3.70(dd, 1H, J= 11.14Hz and J= 7.17Hz), 1.27(d, 3H, J= 6.11Hz) ppm. ¹³C-NMR spectrum (DMSO-d₆): 161.21, 159.31, 148.99, 138.47, 138.41, 134.99, 134.84, 131.23, 125.88, 125.84, 122.64, 122.55, 67.33, 66.20, 21.18 ppm.

ZnL²I₂: IR spectrum (KBr, cm⁻¹): 3458(w), 3071(m), 3039(w), 2975(w), 2910(w), 2861(w), 1991(w), 1927(w), 1750(w), 1637(vs), 1611(m), 1557(w), 1530(vs), 1477(w), 1445(m), 1350(vs), 1281(m), 1218(m), 1170(w), 1122(w), 1098(m), 994(m), 815(s), 735(s), 676(m), 471(w). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 265(14952). ¹H-NMR spectrum (DMSO-d₆): 8.47(bs, 2H), 8.46(s, 1H), 8.45(s, 1H), 8.22(bd, 2H, J= 8.14Hz), 8.09(d, 1H, J= 4.00Hz), 8.07(d, 1H, J= 4.13Hz), 7.64(t, 1H, J= 7.96Hz), 7.66(t, 1H, J= 7.90Hz), 3.84(dd, 1H, J= 11.18Hz), 3.78(Sixted, 1H, J= 6.00Hz), 3.69(dd, 1H, J= 11.10Hz and J= 7.00Hz), 1.26(d, 3H, J= 6.18Hz) ppm. ¹³C-NMR spectrum (DMSO-d₆): 161.19, 159.30, 148.96, 138.46, 138.40, 135.00, 134.85, 131.25, 125.87, 125.82, 122.64, 122.55, 67.31, 66.16, 21.17 ppm.

ZnL³Br₂: IR spectrum (KBr, cm⁻¹): 3445(w), 3070(w), 2927(w), 1647(vs), 1602(s), 1521(vs), 1422(w), 1389(m), 1344(vs), 1313(s), 1218(m), 1109(m), 1000(m), 854(s), 750(s), 705(w), 672(w), 485(w), 455(w). UV-Vis spectrum [(DMF), λ(nm) (ε, M⁻¹cm⁻¹): 287(23490). ¹H-NMR spectrum (DMSO-d₆): 8.54(s, 1H), 8.43(s, 1H), 8.22(d, 2H, J= 8.52Hz), 8.21(d, 2H, J= 8.75Hz), 7.91(t(2d), 4H, J= 8.68Hz and J= 8.78Hz), 3.87(dd, 1H, J= 4.67Hz and

J= 11.42Hz), 3.79(sixted, 1H, J= 6.00Hz), 3.70(dd, 1H, J= 11.32Hz and J= 7.38Hz), 1.28(d, 3H, J= 6.24Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.52, 159.61, 149.42, 149.38, 142.46, 142.36, 129.73, 129.69, 124.80, 67.86, 66.46, 21.14 ppm.

ZnL^3I_2 : IR spectrum (KBr, cm^{-1}): 3445(w), 3130(w), 3096(w), 2957(w), 1643(vs), 1601(s), 1519(vs), 1437(w), 1388(m), 1343(vs), 1321(s), 1216(m), 1109(m), 997(m), 853(s), 749(s), 671(w), 494(w), 455(w). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$): 278(26891). ^1H -NMR spectrum (DMSO- d_6): 8.45(s, 1H), 8.42(s, 1H), 8.21(d, 2H, J= 8.24Hz), 8.19(d, 2H, J= 8.68Hz), 7.89(t(2d), 4H, J= 8.59Hz and J= 8.77Hz), 3.85(dd, 1H, J= 11.38Hz and J= 4.62Hz), 3.79(sixted, 1H, J= 6.12Hz), 3.70(dd, 1H, J= 7.62Hz and J= 7.36Hz), 1.26(d, 3H, J= 6.18Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.48, 159.56, 149.36, 149.33, 142.45, 142.3, 129.73, 129.69, 124.75, 67.52, 66.42, 21.13 ppm.

Preparation of HgLX_2 (X= Cl $^-$, Br $^-$, I $^-$ and L= L 1 , L 2 and L 3):

To a solution of mercury salt (HgCl_2 (0.135g, 0.5 mmol), HgBr_2 (0.180g, 0.5 mmol) and or HgI_2 (0.227g, 0.5 mmol)) in ethanol, solution of 0.5 mmol ligand (L 1 (0.160g), L 2 and L 3 (0.170g)) in 10 mL chloroform was added drop wise and stirred magnetically for 2-3 hours. After this time, precipitate was separated by filtration and washed with warm ethanol for purification. Complexes were dried at (80-100 $^\circ\text{C}$) under vacuum and were kept in a desiccator over silica-gel.

HgL^1Cl_2 : IR spectrum (KBr, cm^{-1}): 3435(m), 3080(w), 2892(m), 1903(w), 1638(vs), 1592(s), 1487(m), 1435(m), 1380(m), 1354(m), 1290(m), 1218(m), 1089(s), 992(m), 821(m), 701(m), 500(m), 468(m). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$): 265(17247). ^1H -NMR spectrum (DMSO- d_6): 8.31(s, 1H), 8.28(s, 1H), 7.69(d, 2H, J= 8.22Hz), 7.67(d, 2H, J= 8.20Hz), 7.44(d, 4H, J= 8.32Hz), 3.76(dd, 1H, J= 11.30Hz and J= 4.72Hz), 3.69(sixtet, 1H, J= 5.96Hz), 3.60(dd, 1H, J= 11.22Hz and J= 7.16Hz), 1.23(d, 3H, J= 6.27Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.80, 159.84, 136.10, 136.04, 135.72, 135.67, 130.33, 130.30, 129.64, 129.61, 67.57, 66.35, 21.25 ppm.

HgL^1Br_2 : IR spectrum (KBr, cm^{-1}): 3442(m), 3096(w), 2890(m), 1903(w), 1639(vs), 1592(s), 1487(m), 1435(m), 1378(m), 1290(m), 1090(s), 992(m), 823(m), 685(m), 507(m), 435(m). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$): 266(20000). ^1H -NMR spectrum (DMSO- d_6): 8.31(s, 1H), 8.28(s, 1H), 7.69(d, 2H, J= 6.45Hz), 7.66(d, 2H, J= 6.44Hz), 7.44(d, 4H, J= 8.32Hz), 3.77(dd, 1H, J= 11.30Hz and J= 4.72Hz), 3.69(sixtet, 1H, J= 5.96Hz), 3.60(dd, 1H, J= 11.29Hz and J= 7.16Hz), 1.23(d, 3H, J= 6.26Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.94, 160.00, 136.15, 136.10, 135.68, 135.62, 130.35, 130.32, 129.65, 129.62, 67.53, 66.31, 21.23 ppm.

HgL^2Br_2 : IR spectrum (KBr, cm^{-1}): 3446(w), 3079(w), 3031(w), 2966(m), 2885(w), 2869(w), 1860(w), 1832(w), 1825(w), 1731(w), 1635(vs), 1530(vs), 1475(m), 1443(w), 1350(vs), 1276(w), 1216(m), 1134(m), 1089(m), 992(m),

812(s), 735(s), 675(m), 449(m). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$): 265(19418). ^1H -NMR spectrum (DMSO- d_6): 8.47(bs, 2H), 8.44(bs, 2H), 8.22(bd, 2H, J= 8.08Hz), 8.07(t(2d), 2H, J= 4.44Hz and J= 6.64Hz), 7.66(t, 1H, J= 7.94Hz and J= 7.73Hz), 7.65(t, 1H, J= 7.80Hz and J= 7.90Hz), 3.84(dd, 1H, J= 11.18Hz and J= 4.70Hz), 3.78(sixted, 1H, J= 6.34Hz), 3.71(dd, 1H, J= 11.04Hz and J= 7.04Hz), 1.2(d, 3H, J= 6.13Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.30, 159.40, 146.96, 138.43, 138.35, 134.96, 134.83, 131.20, 125.90, 122.85, 122.70, 122.60, 67.31, 66.17, 21.15 ppm.

HgL^2I_2 : IR spectrum (KBr, cm^{-1}): 3442(m), 3072(m), 3023(w), 2976(w), 2911(w), 2862(w), 2370(w), 1940(w), 1887(w), 1758(w), 1633(vs), 1527(vs), 1471(w), 1439(m), 1348(vs), 1275(w), 1215(m), 1135(w), 1087(m), 990(s), 811(s), 734(s), 672(s), 447(m). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$): 270(20000). ^1H -NMR spectrum (DMSO- d_6): 8.47(bs, 2H), 8.44(bs, 2H), 8.22(bd, 2H, J= 8.16Hz), 8.07(t(2d), 2H, J= 4.31Hz and J= 6.43Hz), 7.67(t, 2H, J= 7.98Hz and J= 7.89Hz), 3.84(dd, 1H, J= 11.17Hz and J= 4.78Hz), 3.78(sixted, 1H, J= 6.36Hz), 3.69(dd, 2H, J= 11.13Hz and J= 7.10Hz), 1.27(d, 3H, J= 6.16Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.28, 159.38, 148.98, 134.8, 138.44, 138.37, 134.98, 134.84, 131.22, 125.89, 125.85, 122.70, 122.60, 67.33, 66.19, 21.18 ppm.

HgL^3Cl_2 : IR spectrum (KBr, cm^{-1}): 3444(w), 3048(w), 2952(w), 2888(w), 2850(m), 1643(vs), 1599(s), 1519(vs), 1456(w), 1360(w), 1345(vs), 1298(s), 1235(w), 1108(m), 990(m), 854(s), 750(m), 703(m), 515(w), 477(w). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$): 287(24911). ^1H -NMR spectrum (DMSO- d_6): 8.45(s, 1H), 8.42(s, 1H), 8.21(d, 2H, J= 8.75Hz), 8.20(d, 2H, J= 8.78Hz), 7.91(t(2d), 4H, J= 8.90Hz and J= 8.87Hz), 3.87(dd, 1H, J= 11.39Hz and J= 3.65Hz), 3.79(sixted, 1H, J= 6.56Hz), 3.71(dd, 1H, J= 11.49Hz and J= 7.32Hz), 1.28(d, 3H, J= 6.27Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.53, 159.61, 149.41, 149.38, 142.45, 142.35, 129.72, 129.69, 124.78, 67.56, 66.46, 21.13 ppm.

HgL^3Br_2 : IR spectrum (KBr, cm^{-1}): 3429(w), 3056(w), 2969(w), 2905(m), 2850(w), 1642(vs), 1598(s), 1516(vs), 1447(w), 1366(m), 1345(vs), 1304(s), 1218(w), 1139(w), 1108(m), 991(m), 853(s), 750(m), 703(w), 515(w), 477(w). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$): 277(26234). ^1H -NMR spectrum (DMSO- d_6): 8.45(s, 1H), 8.42(s, 1H), 8.21(d, 2H, J= 7.98Hz), 8.20(d, 2H, J= 8.74Hz), 7.91(t(2d), 4H, J= 8.46Hz and J= 8.86Hz), 3.87(dd, 1H, J= 11.39Hz and J= 4.71Hz), 3.79(sixted, 1H, J= 6.4Hz), 3.71(dd, 1H, J= 11.32Hz and J= 7.39Hz), 1.28(d, 3H, J= 6.24Hz) ppm. ^{13}C -NMR spectrum (DMSO- d_6): 161.5, 159.63, 149.41, 149.37, 142.44, 142.34, 129.72, 129.68, 124.76, 67.55, 66.46, 21.13 ppm.

HgL^3I_2 : IR spectrum (KBr, cm^{-1}): 3436(w), 3064(w), 2978(w), 2893(w), 2848(w), 1637(vs), 1596(s), 1515(vs), 1467(m), 1386(w), 1342(vs), 1311(s), 1232(m), 1137(w), 1106(s), 988(s), 897(w), 851(s), 748(s), 701(m), 497(w), 450(w). UV-Vis spectrum [(DMF), $\lambda(\text{nm})$ ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$):

290(33798). $^1\text{H-NMR}$ spectrum (DMSO-d_6): 8.45(s, 1H), 8.41(s, 1H), 8.20(d, 2H, $J = 7.54\text{Hz}$), 8.19(d, 2H, $J = 8.60\text{Hz}$), 7.89(t(2d), 4H, $J = 8.38\text{Hz}$ and $J = 8.84\text{Hz}$), 3.86(dd, 1H, $J = 4.62\text{Hz}$ and $J = 11.33\text{Hz}$), 3.78(sixtet, 1H, $J = 6.22\text{Hz}$), 3.70(dd, 1H, $J = 7.34\text{Hz}$ and $J = 11.20\text{Hz}$), 1.27(d, 3H, $J = 6.08\text{Hz}$) ppm. $^{13}\text{C-NMR}$ spectrum (DMSO-d_6): 161.54, 159.63, 149.38, 143.41, 142.30, 129.72, 129.69, 124.75, 67.55, 66.45, 21.14 ppm.

ligands. The frequencies at 1643(L^1), 1646(L^2) and 1641(L^3) cm^{-1} can be assigned to asymmetric vibration of the azomethine group (C=N). This band in ligands L^1 and L^2 are shifted by 4-10 and 4-13 cm^{-1} , respectively, to lower frequencies in the spectra of the complexes (Yu *et al.*, 2003; Montazerzohori *et al.*, 2009) but for ligand L^3 is shifted by 2-6 cm^{-1} to higher frequencies (Montazerzohori & Musavi, 2008; Tümer *et al.*, 1999)

Table 1. Elemental analysis, color, melting points, %yield and molar conductivity of the ligands and their complexes

	Compound	Mol. wt.	Color	M.p.($^{\circ}\text{C}$)	Yield (%)	Found (Calcd.) (%)			Λ_{M} ($\text{cm}^2 \Omega^{-1} \text{M}^{-1}$)
						C	N	H	
1	L^1	320	white	57	82	63.98 (63.96)	8.77 (8.78)	5.01 (5.05)	3
2	L^2	340	White	121-123	91	59.90 (59.99)	16.50(16.46)	4.70 (4.74)	2
3	L^3	340	Pale Yellow	145	75	59.90 (59.99)	16.50(16.46)	4.70 (4.74)	4
4	ZnL^1Br_2	544	White	149-151	82	37.51 (37.50)	5.14 (5.15)	2.93 (2.96)	9
5	ZnL^1I_2	638	White	238-240	77	-	-	-	15
6	HgL^1Cl_2	591	White	174-176	80	34.54 (34.56)	4.75 (4.74)	2.74 (2.73)	5
7	HgL^1Br_2	680	White	146-148	78	-	-	-	8
8	ZnL^2Br_2	566	White	290-291	82	-	-	-	7
9	ZnL^2I_2	660	White	178-180	85	30.80 (30.96)	8.60 (8.49)	2.30 (2.45)	3
10	HgL^2Br_2	701	White	190-192	74	29.30 (29.14)	7.90 (8.00)	2.20 (2.30)	4
11	HgL^2I_2	795	cream	196-198	78	-	-	-	4
12	ZnL^3Br_2	566	White	260	78	-	-	-	7
13	ZnL^3I_2	660	White	250	76	30.80 (30.96)	8.60 (8.49)	2.30 (2.45)	8
14	HgL^3Cl_2	612	White	192	83	-	-	-	6
15	HgL^3Br_2	701	White	198-200	86	29.30 (29.14)	7.90 (8.00)	2.20 (2.30)	13
16	HgL^3I_2	795	cream	314	68	-	-	-	12

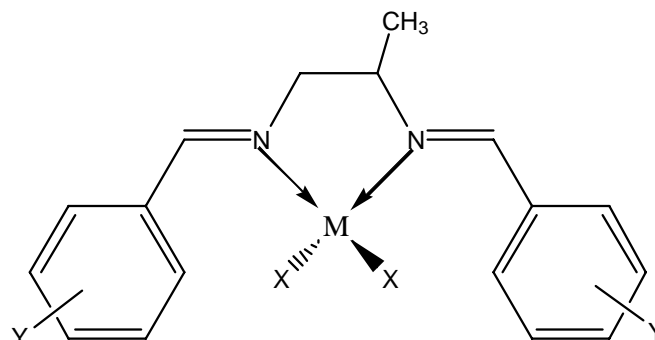
Results and discussion

Elemental analyses and other physical properties of the ligands and their complexes are summarized in Table 1. The new complexes were prepared by reaction between zinc and mercury salts (MX_2 ($X = \text{chloride}$, bromide and iodide)) and ligands ($L^1 = \text{N,N-bis(4-chlorobenzylidene)propane-1,2-diamine}$, $L^2 = \text{N,N-bis(3-nitrobenzylidene)propane-1,2-diamine}$ and $L^3 = \text{N,N-bis(4-nitrobenzylidene)propane-1,2-diamine}$) in a 1:1 ($\text{MX}_2:L$) molar ratio. The stoichiometries of ligands and some complexes are confirmed by elemental analysis. The ligands melt at 57-145 $^{\circ}\text{C}$ and the complexes decompose at 146-314 $^{\circ}\text{C}$. The ligands containing nitro group and their complexes are almost decomposed at higher temperature than chloro-derivative Schiff base. The low molar conductivities of 10^{-3}M solutions of all complexes in DMF solvent at room temperature were in the range of 2-15 $\text{cm}^2 \Omega^{-1} \text{M}^{-1}$ which show them to be non-electrolytes so that anions are coordinated to the metal ion (Yilmaz & Ukurovali, 2003; Saleh, 2005). Among the complexes, zinc iodide complex of L^1 has highest conductivity.

Any vibration frequencies assigned to used aldehydes and 1,2-propanediamine at 1700-1710 and 3100-3300 cm^{-1} were not observed in the IR spectrum of the ligands. The FT-IR spectrum of the Schiff bases ligands showed the stretching frequencies at (3096-3085, 3024-3048), (2920-2954) and 2840-2853 cm^{-1} assigned to C-H of aromatic, aliphatic and iminic groups, respectively, smoothly affected by coordination of the

except for entry 16 that is shifted to lower frequencies, indicating coordination through the azomethine nitrogens (Fig. 1). It seems that three agents affect the shifting of iminic bonds, a) coordination of nitrogen to metal b) intra molecular resonance of ligand and c) π -back bonding of metal to ligand. Third agent can be affected by various halides in the complexes. Final valance between these agents determine shifting of iminic frequencies to higher or lower absorption frequencies. In the FT-IR spectrum of L^1 the frequencies at 1080 cm^{-1} shows C-Cl stretching vibration that is shifted to 1089-1090 cm^{-1} after coordination. In the spectrum of L^2 and L^3 the very strong bands at 1530, 1518 and 1346, 1342 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

Fig. 1. Structural formula of complexes in which $M = \text{Zn(II)}$ and Hg(II) , $X = \text{chloride}$, bromide and iodide and $Y = 4\text{-Chloro}$, 3-Nitro and 4-Nitro .



numbers (Montazerzohori & Musavi *et al.*, 2008). The very strong out-of-plane bending of the aromatic C-H and C-C at 817-849 and 700-747 cm^{-1} are shifted to higher or lower frequencies after coordination (Pavia *et al.*, 2001). Evidences for bonding in the complexes is also shown by observation of some new weak bands in the spectra of the metal complexes at 485-515 cm^{-1} assigned to $\nu(\text{M-N})$ (Montazerzohori *et al.*, 2009).

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 263(L¹), 262(L²) and 284(L³) nm, attributed to $n \rightarrow \pi^*$ transitions. In the complexes, the $n \rightarrow \pi^*$ transitions are nearly unchanged or shifted to higher wavelength (entries 8,11 and 16) or lower wavelength (entries 13 and 15) as a consequence of coordination, confirming the formation of Schiff bases metal complexes. The suggested structure for complexes is pseudo-tetrahedral geometry (Fig.1). Some reports in literatures confirm this geometry for the d^{10} metal ion complexes containing bidentate ligands (Montazerzohori & Musavi *et al.*, 2008; Habibi *et al.*, 2005, 2007a, 2007b, 2007c; Barati *et al.*, 2009).

The ¹H-NMR and ¹³C-NMR spectra of asymmetric ligands and their complexes are summarized in experimental sections. The ¹H-NMR of L¹ exhibits signals at 8.26 and 8.23 ppm for iminic groups, 7.66 and 7.41 for aromatic hydrogens, 3.74, 3.65 and 3.58 ppm for hydrogen of methylene groups and 1.22 ppm for methyl group. The ¹³C-NMR spectrum shows signals at 161.59 ppm for iminic carbon, 159.65, 136.06, 136.00, 135.77, 135.72, 130.29, 130.26, 129.60, 129.57, 67.64, 66.40 and 21.26 ppm for aromatic and aliphatic carbons. The ¹H-NMR of L² exhibits signals at 8.47 ppm as broad for iminic groups and signals of 8.44, 8.43, 8.21, 8.09, 8.08, 7.67 and 7.66 ppm for aromatic hydrogens, 3.85, 3.79 and 3.70 ppm for hydrogen of methylene groups and 1.28 ppm for methyl group. Again, ¹³C-NMR spectrum shows signals at 160.20 ppm for iminic carbons, 159.31, 148.99, 138.47, 138.41, 134.97, 134.83, 132.22, 125.88, 125.83, 122.68, 122.58, 67.34, 66.20 and 21.17 ppm for aromatic and aliphatic carbons. The ¹H-NMR of L³ exhibits signals at 8.44 and 8.41 ppm for iminic groups, 8.20, 8.19 and 7.90 ppm for aromatic hydrogens, 3.86, 3.79 and 3.70 ppm for hydrogen of methylene groups and 1.27 ppm for methyl group. Its ¹³C-NMR spectrum shows signals at 161.47 ppm for iminic carbons, 159.56, 149.38, 149.35, 142.45, 142.35, 129.70, 129.66, 124.74, 67.57, 66.47 and 21.1 ppm for aromatic and aliphatic carbons. After coordination of ligands considerable changes of the hydrogen and carbon signals have not observed after coordination, only in some cases hydrogen signals that are shown as broad singlet or signals appeared as t(2d) in ligands spectra have been appeared as doublet or split into several signals in the complexes spectra. Not considerable changes in complexes spectra with respect to ligands ones can be explained based on a balance

between the induction and resonance effects in the ligand molecules in opposite directions that lead to nearly unchanged chemical shifts in NMR. On the other hand, speed dissociation in the DMSO solvent may be responsible for this observation.

Acknowledgement

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

References

1. Kumar S, Dhar DN and Saxena PN (2009) Applications of metal complexes Schiff bases. *J. Sci. Ind. Res.* 68, 181-187.
2. Saxena CG and Shrivastava SV (1987) Mn(II), Co(II), Ni(II) and Cu(II) complexes with p-toly-2-furylgloxalimine. *J. Indust. Chem. Soc.* 64. 685-686.
3. Dikumar EA and Kozlov NG (2006) Synthesis of Schiff bases from 1-naphthylamine and vanillin, vanillal, and their O-acyl derivatives. *Russ. J. Org. Chem.* 42, 369-375.
4. Bray RC and George GN (1985) Electron-paramagnetic-resonance studies using pre-steady-state kinetics and substitution with stable isotopes on the mechanism of action of molybdoenzymes. *Biochem. Soc. Trans.* 13, 560-567.
5. George GN, Bray RC and Cramer SP (1986) Extended x-ray absorption fine-structure studies of transient species during xanthine-oxidase turnover by using rapid freezing. *Biochem. Soc. Trans.* 14, 651-652.
6. Singh RV, Jadon SCS and Gupta N (1997) A New Series of Biologically Potent *cis*-Dioxomolybdenum(VI) Complexes of Fluoroimines. *Synth. React. Inorg. Met.-Org. Chem.* 27, 759-773.
7. Costamagna J, Vargas J, Latorre R, Alvarado A and Mena G (1992) Coordination compounds of copper, nickel and iron with Schiff bases derived from hydroxynaphthaldehydes and salicylaldehydes. *Coord. Chem. Rev.* 119, 67-88.
8. Guerriero P (1995) From mononuclear to polynuclear macro cyclic or macro acyclic complexes. *Coord. Chem. Rev.* 139, 17-23.
9. Wu JG, Deng RW and Chen ZN (1993) Transition metal complexes of 2-thenoyltrifluoroacetone isonicotinoyl hydrazone. *Transit. Met. Chem.* 18, 23-26.
10. Song QB, Wu XL, Liang YM and Ma YX (1994) Acylferrocene 2-furoyl hydrazones and their transition metal(II) complexes. *Polyhedron.* 13, 2395-2400.
11. Ren S, Wang R, Komastu K, Krause PB, Zyrianov Y, McKenna CE, Csipke C, Tokes ZA and Lien EJ (2002) Synthesis, Biological Evaluation, and Quantitative Structure-Activity Relationship Analysis of New Schiff Bases of Hydroxysemicarbazide as



- Potential Antitumor Agents. *J. Med. Chem.* 45, 410-419.
12. Tarafder MTH, Ali MA, Saravana N, Weng WY, Kumar S, Tsafe NU and Crouse KA (2000) Coordination chemistry and biological activity of two tridentate ONS and NNS Schiff bases derived from S-benzylidithiocarbamate. *Trans. Met. Chem.* 25, 295-298.
 13. El-Medani SM, Omyana AMA and Ramaden RN (2005) Photochemical reactions of group 6 metal carbonyls with N-salicylidene-2-hydroxyaniline and bis-(salicylaldehyde) phenylenediimine. *J. Mol. Struct.* 738, 171-177.
 14. Colman J, Hegedu LS (1980) Principles and applications of organotransition metal chemistry. University Science Book, California.
 15. Zhao J, Zhao B, Liu J, Xu WJ and Wang Z (2001) Spectroscopy study on the photochromism of Schiff Bases N,N'-bis(salicylidene)-1,2-diaminoethane and N,N'-bis(salicylidene)-1,6-hexanediamine. *Spectrochim. Acta: Part A* 57, 149-154.
 16. Liu WL, Zou Y, Li Y, Yao YG and Meng QJ (2004) Synthesis and characterization of copper(II) Schiff base complexes derived from salicylaldehyde and glycylglycylglycine. *Polyhedron* 23, 849-855.
 17. Palys BJ, Bukowska J and Jackowska K (1997) SERS of 1,8-diaminonaphthalene on gold, silver and copper electrodes polymerisation and complexes formed with the electrode material. *J. Electroanal. Chem.* 428, 19-24.
 18. Aly AA and El-Shaieb KM (2004) Reaction of 1,8-diaminonaphthalene with some selected π -acceptors; prospective optically active non-linear cyanovinylated naphthalenes as well as synthesis of novel perimidin and pleiadene derivatives. *Tetrahedron.* 60, 3797-3802.
 19. Saleh AA (2005) Synthesis and spectroscopic studies of novel mononuclear complexes of cyclic and acyclic Schiff-base derivatives of tridentate and tetradentate coordination with some bivalent transition metal ions. *J. Coord. Chem.* 58, 255-270.
 20. Yilmaz I and Ukurovali AC (2003) Synthesis, characterization and antimicrobial activity of the Schiff bases derived from 2,4-disubstituted thiazoles and 3-methoxysalicylaldehyde, and their cobalt(II), copper(II), nickel(II) and zinc(II) complexes. *Transition Met. Chem.* 28, 399-404.
 21. Montazerzohori M, Joohari S and Musavi SA (2009) Synthesis and spectroscopic studies of some cadmium(II) and mercury(II) complexes of an asymmetrical bidentate Schiff base ligand, *Spectrochim. Acta Part A.* 73, 231-237.
 22. Yu T, Lu G, Yan L and Yang R (2003) Synthesis, Characterization, and Fluorescence Studies of a Novel Schiff Base Ligand and Its Zn(II), Ni(II), Co(II), Cu(II) Complexes, *Synth. React. Inorg. Met. Org. Chem.* 33, 1623-1633.
 23. Tümer M, Celik C, Köksal H and Serin S (1999) Transition Metal Complexes of Bidentate Schiff Base Ligands, *Trans. Met. Chem.* 24, 525-532.
 24. Montazerzohori M and Musavi SA (2008) Synthesis and spectral characterization of a new symmetric bidentate Schiff-base and its zinc complexes, *J. Coord. Chem.* 61(24), 3934-3942.
 25. Pavia DL, Lampman GM and Kriz GS (2001) Introduction to spectroscopy. 3rd Edn, Brooks/Cole, London.
 26. Habibi MH, Montazerzohori M, Barati K, Harrington RW and Clegg W (2007a) Bis[N,N-(2-chlorobenzylidene)ethylenediamine- κ^2 N,N]copper(I) dichloridocuprate(I) acetonitrile solvate. *Acta Cryst.* C63, m592-m594.
 27. Habibi MH, Lalegani A, Mokhtari R and Suzuki T (2007b) (Bromido)[N,N-bis(2nitrocinnam aldehyde) ethylenediamine](triphenylphosphine)copper(I). *Acta Cryst.* E63, m2479.
 28. Habibi MH, Lalegani A, Mokhtari R and Suzuki T (2007c) [N,N-Bis[3-(2-nitrophenyl)prop-2-enylidene]ethylenediamine κ^2 N,N]iodide(triphenyl phosphane- κ^3 P)copper(I). *Acta Cryst.* E63, m2472.
 29. Habibi MH, Tangestaninejad S, Fallah-Shojaie A, Mohammadpoor-Baltork I, Tayyari S F, Emtiazi G and Hamidimotlagh R (2005) Preparation and spectral investigation of bis[N- (substituted-phenyl)thiobenzamidato]mercury(II) complexes. *J. Coord. Chem.* 58(11), 955-962.
 30. Barati K, Habibi MH, Montazerzohori M, Shafieyan H, Harrington R and Clegg W (2009) Synthesis, crystal structure and photo-induced isomerization of [N,N'-bis(4-fluorobenzylidene) ethylenediamine] bromo(triphenylphosphine)copper(I) complex. *J. Coord. Chem.* 62(3), 417-426.