

## Synthesis and spectral investigation of some Zn (II), Hg (II), Co (II) and Cu (II) Schiff base complexes

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### Abstract

Three symmetrical Schiff base ligands of N, N'-bis (2-chlorobenzylidene) ethane-1, 2-diamine (BCBEN), N,N'-bis (2-nitrobenzylidene) ethane-1,2-diamine and N,N'-bis (3-phenylallylidene)-*o*-phenylenediamine and some zinc (II), mercury (II), cobalt (II) and copper (II) complexes were synthesized and characterized by elemental analyses, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, UV-Visible spectra, and molar conductance. All compounds were found to be non-electrolytes in the dimethylsulfoxide solutions.

**Keywords:** Schiff base complex, Thiocyanate, Spectral, Symmetrical.

### Introduction

A wide range of Schiff base ligands and transition metal complexes have been synthesized and reported in literature (Wang *et al.*, 2004; Habibi *et al.*, 2007a, 2007b, 2007c, 2007d, 2007e; Wu *et al.*, 2009; Zhang *et al.*, 2010). Schiff bases play a key role in the extension of coordination chemistry and introduce various effecting factors on coordination geometries (Birdsall, 1988; Sonmez *et al.*, 2003; Dolakia & Patel, 2004; Dehghanpour *et al.*, 2006; Zhu *et al.*, 2006; Chen *et al.*, 2007). Schiff bases are of interest, because of their versatility in coordinating to metals, flexibility in assuming different conformations, radiopharmaceuticals for cancer targeting, agrochemicals, as model systems for biological macromolecules, as catalysts and as oxygen carriers (Li & Chang, 1991; Berkessel *et al.*, 1997; Blower, 1998; Unaleroğlu *et al.*, 2001; Venkataraman *et al.*, 2005) and their use in analytical methods (Ghaedi *et al.*, 2008, 2010; Shokrollahi *et al.*, 2009). They can coordinate either in the neutral or in the anionic form. Furthermore, the possibility of tautomerization makes their investigation extremely interesting for inorganic chemists. In continuation our studies on four coordinated complexes (Montazerzohori *et al.*, 2008, 2009a, 2009b, 2009c) in this work we report the synthesis, physical and spectral characterization of ligands of N, N'-bis(2-chlorobenzylidene)ethane-1,2-diamine (BCBEN), N, N'-bis(2-nitrobenzylidene)ethane-1,2-diamine and N, N'-bis(3-phenylallylidene)-*o*-phenylenediamine and some zinc(II), mercury(II), cobalt(II) and copper(II) halide or pseudo halide complexes were synthesized and characterized by elemental analyses, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and UV-Visible spectra, and molar conductance.

### Experimental

2-chlorobenzaldehyde, 2-nitrobenzaldehyde, 3-phenylpropenal, *o*-phenylenediamine, 1,2-ethanediamine, zinc(II), mercury(II), cobalt(II) and copper (II) salts, solvent and other chemicals were purchased from either Aldrich, Merck or BDH Chemicals and were used without purification. IR spectra in the 4000-400 cm<sup>-1</sup> range were recorded as KBr pellets on a FT-IR (BRUKER TENSOR

27) model. UV-Vis spectra in the 200-800 nm range were recorded using a Perkin Elmer Lambda5 model spectrophotometer in DMF. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Bruker spectrometer at 400 MHz and 100 MHz respectively in DMSO-d<sub>6</sub>. Elemental analyses (CNHS) of complete dried samples were performed using a CHNS elemental analyzer. The melting points (°C) of the complexes were recorded on BI Barnstead electrothermal instrument. The molar conductivities of the ligand and their complexes were determined in DMF (1.0×10<sup>-3</sup> M) at room temperature using CTR 80 conductometer.

### Synthesis of Schiff base ligands

Schiff-bases of N,N-bis(2-chlorobenzylidene)ethane-1,2-diamine (BCBEN), N,N-bis(2-nitrobenzylidene)ethane-1,2-diamine (BNBEN) and N, N'-bis(3-phenylallylidene)-*o*-phenylenediamine (BPAPHEN) were synthesized by condensation of 2-chlorobenzaldehyde (0.562 g, 4 mmol) for BCBEN, 2-nitrobenzaldehyde (0.604 g, 4 mmol) for BNBEN with 1,2-diaminoethane (0.12 g, 2 mmol) in 20 mL methanol under rigorous stirring for 4 h. The Schiff bases precipitated and then the reaction mixtures were filtered and ligands were recrystallized from chloroform. N,N'-bis(3-phenylallylidene)-*o*-phenylenediamine (BPAPHEN) was synthesized by condensation of 3-phenylpropenal (0.529 g, 4 mmol) and *o*-phenylenediamine (0.216 g, 2 mmol) in 20 mL ethanol. The mixture was subjected to evaporation to obtain designed Schiff base. For more purification, the ligands were washed twice with *n*-heptane and dried under vacuum. Physical and spectral data of the ligands are summarized as following:

**BCBEN:** White color. %75 Yield. M.P (°C): 85-87. Λ<sub>M</sub> [(DMF), (cm<sup>-2</sup> Ω<sup>-1</sup> M<sup>-1</sup>): 0.6. IR(KBr, cm<sup>-1</sup>): 3426(w), 3037(w), 2918(w), 2854(w), 1637(s), 1591(m), 1466(m), 1437(s), 1371(m), 1270(m), 1052(m), 1015(m), 948(w), 759(vs), 705(w), 628(w). UV-Vis [(DMF), λ(nm) (ε, M<sup>-1</sup>cm<sup>-1</sup>): 272(20220). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 8.65(s, 2H), 7.95(d, 2H, J=9.00Hz), 7.47(m, 4H), 7.41(d, 2H, J=8.00Hz), 3.97(s, 4H) ppm. <sup>13</sup>C NMR(DMSO-d<sub>6</sub>): 158.84, 134.42, 133.10, 132.61, 130.26, 128.54, 127.88, 61.11

**BNBEN:** Light yellow color. % 64 Yield; M.P (°C): 109.  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 0.6 IR(KBr,  $\text{cm}^{-1}$ ): 3424(w), 2917(w), 2851(w), 1637(s), 1570(w), 1517(vs), 1368(w), 1340(vs), 1018(m), 846(w), 790(m), 747(m), 696(w). UV-Vis [(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 290(23961).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.60(S, 2H), 8.00(dd, 2H, J=8.00Hz, J=1.20Hz), 7.97(dd, 2H, J=7.6Hz, J=1.2Hz), 7.760(dt, 2H, J=7.60Hz, J=1.20Hz), 7.68(dt, 2H, J=7.60Hz, J=1.6Hz), 3.96(S, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 158.63, 149.23, 133.86, 131.68, 130.41, 129.87, 124.58, 61.05 ppm.

**BPAPHEN:** Yellow color. %70 yield.  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 0.7 IR(KBr,  $\text{cm}^{-1}$ ): 3407(w), 3057 (m), 3024(w), 2860 (m), 1624(s), 1496(m), 1451(s), 1275 (w) 1123(m), 969(w), 745(s), 698(w).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 1.4. UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 274(13203), 309(14976).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.25(bs, 2H), 7.62(m, 4H), 7.2(m, 10 H), 6.55(m, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 162.3, 148.1, 142.5, 134.1, 131.01, 128.9, 127.2, 126.8, 118.8 ppm.

**General procedure for preparation of  $M(\text{BCBEN})X_2$ ,  $M(\text{BNBEN})X_2$  ( $M = \text{Zn}$  and  $\text{Hg}$ ;  $X = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ) and  $M(\text{BPAPHEN})X_2$  ( $M = \text{Co}$  and  $\text{Cu}$ ;  $X = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$  and  $\text{SCN}$ ) complexes.** The M(II) complexes were prepared by

stepwise addition and stirring of the ligand (0.5 mmol) in methanol or ethanol (10 mL) to the respective 0.5 mmol of metal halides or freshly metal thiocyanate in methanol or ethanol (30 mL) for 2-5 h. The complexes so obtained were filtered, washed with EtOH twice and dried under vacuum. The precipitates were further purified from dichloromethane/ ethanol mixture and dried at (80-100°C) under vacuum and were kept in a desiccator over silica-gel.

**Zn(BCBEN)Cl<sub>2</sub>:** White color. %75 Yield. M.P (°C): 217-225(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 1.4. IR(KBr,  $\text{cm}^{-1}$ ): 3534(w), 3022(w), 1632(vs), 1592(s), 1472(w), 1435(m), 1388(w), 1339(w), 1291(w), 1218(w), 1036(m), 768(s), 701(w). UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 258(73000).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.63(S, 2H), 7.93(d, 2H, J=7.20Hz), 7.49(m, 4H), 7.43(dt, 2H, J=10.00Hz, J=3.3Hz), 3.96(S, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 158.90, 134.39, 133.08, 132.64, 130.27, 128.53, 127.90, 61.09 ppm.

**Zn(BCBEN)Br<sub>2</sub>:** White color. %64 Yield. M.P (°C): 205(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 3.9. IR(KBr,  $\text{cm}^{-1}$ ): 3049(w), 2942(w), 1632(vs), 1591(s), 1434(m), 1335(w), 1284(w), 1214(w), 1036(m), 765(s), 460(w). UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 256(20960).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.77(S, 2H), 8.10(d, 2H, J=7.2Hz), 7.46(m, 4H), 7.38(m, 2H), 3.97. (S, 4H) ppm.  $^{13}\text{C}$ NMR (DMSO- $d_6$ ): 160.31, 134.41, 133.08, 132.60, 130.25, 128.53, 127.87, 1.11 ppm.

**Zn(BCBEN)I<sub>2</sub>:** Cream color. %53 Yield. M.P (°C): 208-220(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 9.5. IR(KBr,  $\text{cm}^{-1}$ ): 3425(w), 3028(w), 2934(w), 1633(vs), 1592(m), 1436(m), 1288(w), 1035(m), 762(s). UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 264(22840).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.63(S, 2H), 7.93(d, 2H, J=7.20Hz), 7.49(m, 4H), 7.43(dt, 2H, J=10.00Hz,

J=3.3Hz), 3.96(s, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 158.90, 134.39, 133.08, 132.64, 130.27, 128.53, 127.90, 61.09 ppm.

**Hg(BCBEN)Cl<sub>2</sub>:** White color. %48 Yield. M.M.P (°C): 127-129(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 1.4. IR(KBr,  $\text{cm}^{-1}$ ): 3034(w), 2917(w), 2895(w), 2854(w), 1632(s), 1590(m), 1466(m), 1437(m), 1371(m), 1270(m), 1121(w), 1051(m), 1015(vs), 967(m), 865(w), 759(vs), 718(w), 705(m), 628(w). UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 268(21370).

**Hg(BCBEN)I<sub>2</sub>:** Cream color. %48 Yield. M.P (°C): 107(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 1.0. IR(KBr,  $\text{cm}^{-1}$ ): 3442(w), 3027(w), 2919(w), 2854(w), 1632(vs), 1590(m), 1568(w), 1467(w), 1438(s), 1372(w), 1270(w), 1051(m), 1061(m), 967(w), 758(vs), 703(w). UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 287(29300).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.93(s, 2H), 8.15(d, 2H, J=7.6Hz), 7.55(d, 2H, J=3.6Hz), 7.41(m, 4H), 3.97(4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 159.04, 134.67, 133.48, 132.66, 130.27, 128.58, 127.90, 59.21ppm.

**Zn(BNBEN)Br<sub>2</sub>:** White color. % 83 Yield. M.P (°C): 270(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 3.1. %C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>O<sub>4</sub>Br<sub>2</sub>Zn: Calc. C, 34.84; H, 2.56, N, 10.16; Found, C, 35.23; H, 2.90; N, 10.17. IR(KBr,  $\text{cm}^{-1}$ ): 3421(w), 3034(w), 2951(w), 2847(m), 1655(s), 1616(w), 1575 (w), 1523(vs), 1434(w), 1345(vs), 1212(w), 1090(w), 1041(m), 871(w), 794(m), 745(m), 701(w). UV-Vis [(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 298(29740).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.59(S, 2H), 8.01(d, 2H, J=8.00Hz), 7.96(6, 2H, J=7.6Hz), 7.77(t, 2H, J=7.2Hz), 7.69(t, 2H, J=7.6Hz), 3.95(S, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 158.67, 149.24, 133.89, 131.72, 130.39, 129.89, 124.59 ppm.

**Zn(BNBEN)I<sub>2</sub>:** White color. %94 Yield. M.P (°C): 317-320(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 8. IR(KBr,  $\text{cm}^{-1}$ ): 3426(w), 3024(w), 2941(w), 2857(m), 1654(s), 1650(w), 1530(w), 1523(vs), 1344(vs), 1039(m), 792(m), 743(m), 700(m). UV-Vis [(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 305(30740).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.58(S, 2H), 8.01(dd, 2H, J=8.00Hz, J=0.4Hz), 7.95(dd, 2H, J=7.6Hz, J=0.8Hz), 7.77(t, 2H, J=7.2Hz), 7.68(dt, 2H, J=8.0Hz, J=1.6Hz), 3.94(s, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 158.70, 149.20, 133.92, 131.75, 130.37, 129.89, 61.03 ppm.

**Hg(BNBEN)Br<sub>2</sub>:** White color. %80 Yield. M.P (°C): 190-195(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 2.2. IR(KBr,  $\text{cm}^{-1}$ ): 3447(m), 3098(w), 1650(s), 1612(w), 1571(w), 1527(vs), 1461(w), 1338(vs), 1229(w), 1206(w), 1079(w), 1040(m), 968(w), 847(w), 791(m), 740(m), 701(m). UV-Vis [(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1} \text{cm}^{-1}$ ): 286(27520).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.67(S, 2H), 8.02(d, 2H, J=7.6Hz), 7.94(d, 2H, J=6.8Hz), 7.78(t, 2H, J=7.20Hz), 7.70(t, 2H, J=6.8Hz), 3.98(S, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 159.51, 149.08, 134.65, 131.84, 130.49, 129.95, 124.64, 60.87 ppm.

**Hg(BNBEN)I<sub>2</sub>:** Cream color. %80 Yield. M.P (°C): 170-175(dec.).  $\Lambda_M$  [(DMF), ( $\text{cm}^{-2} \Omega^{-1} \text{M}^{-1}$ ): 1.2. IR(KBr,  $\text{cm}^{-1}$ ): 3442(m), 2923(w), 1652(s), 1615(w), 1557(w), 1523(vs), 1433(w), 1343(vs), 1208(w), 1040(m), 872(w), 792(m),

742(s), 702(m). UV-Vis [(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 307(31060).  $^1\text{H}$ NMR (DMSO- $d_6$ ): 8.68(s, 2H), 8.04(d, 2H,  $J=8.0\text{Hz}$ ), 7.94(d, 2H,  $J=7.20\text{Hz}$ ), 7.78(t, 2H,  $J=7.6\text{Hz}$ ), 7.70(t, 2H,  $J=7.2\text{Hz}$ ), 3.97(s, 4H) ppm.  $^{13}\text{C}$ NMR(DMSO- $d_6$ ): 159.7, 149.03, 134.09, 131.85, 130.52, 130.01, 124.67, 60.88 ppm.

**Co(BPAPHEN)Cl<sub>2</sub>**: Green color. 60.4% Yield. M.P ( $^{\circ}\text{C}$ ): 287(dec.).  $\Lambda_{\text{M}}$  [(DMF), ( $\text{cm}^{-2}\Omega^{-1}\text{M}^{-1}$ ): 2.1. IR(KBr,  $\text{cm}^{-1}$ ): 3423 (w), 3024(w), 1614 (vs), 1559 (vs), 1482(w), 1642 (s), 1448 (m), 1371(w), 1285(w), 1170(s), 995 (m), 947 (m), 749(s), 684(m). UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 307(29860), 358(24940), 600(350), 665(356).  $\% \text{C}_{24}\text{H}_{20}\text{N}_2\text{Cl}_2\text{Co}$ ; calc. C, 61.82; H, 4.32N, N, 6.01 ; Found, C, 60.61; H, 4.48; N, 6.17.

**Co(BPAPHEN)Br<sub>2</sub>**: Green color. %32.31 Yield. M.P ( $^{\circ}\text{C}$ ): 325(dec.).  $\Lambda_{\text{M}}$  [(DMF), ( $\text{cm}^{-2}\Omega^{-1}\text{M}^{-1}$ ): 8. IR(KBr,  $\text{cm}^{-1}$ ): 3420(w), 3054(w), 3024(w), 1612(vs), 1558(vs), 1482(m), 1449(m), 1374(m), 1318(w), 1285(m), 1225(w), 1171(s), 996(m), 947(m), 748(s), 685(s). UV-Vis (DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 305(3990), 314(37840), 370(32740), 425(19200).

**Co(BPAPHEN)I<sub>2</sub>**: Light Brownish Green color. %40.48 Yield. M.P ( $^{\circ}\text{C}$ ): 212(dec.).  $\Lambda_{\text{M}}$  [(DMF), ( $\text{cm}^{-2}\Omega^{-1}\text{M}^{-1}$ ): 12.1. IR(KBr,  $\text{cm}^{-1}$ ): 3422(w), 3054(w), 2850(w), 1639(s), 1613(vs), 1557(vs), 1519(m), 1432(vs), 1383(vs), 1281(m), 1225(m), 1169(m), 1044(w), 958(s), 844(w), 745(vs), 702(s), 685(s), 622(w). UV-Vis(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 310(30300), 369(26220).

**Co(BPAPHEN)(SCN)<sub>2</sub>**: Brownish Green color. %68.79 Yield. M.P ( $^{\circ}\text{C}$ ): 228(dec.).  $\Lambda_{\text{M}}$  [(DMF), ( $\text{cm}^{-2}\Omega^{-1}\text{M}^{-1}$ ): 7.2. IR(KBr,  $\text{cm}^{-1}$ ): 3425(w), 3097 (w), 3020(w), 2860(w), 2070(vs), 1621(s), 1572(s), 1523(w), 1480(w), 1446(m), 1378(w), 1280(w), 1164(m), 993(w), 958(w), 748 (s), 689 (w). UV-Vis(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 280(25100), 319(49400), 362(24000), 610(600).  $\% \text{C}_{26}\text{H}_{20}\text{N}_4\text{S}_2\text{Co}$ ; calc. C, 61.05; H, 3.94; N, 10.95 Found, C, 60.7; H, 3.8; N, 11.2.

**Cu(BPAPHEN)Cl<sub>2</sub>**: Green color. 38.91% Yield. M.P ( $^{\circ}\text{C}$ ): 128(dec.).  $\Lambda_{\text{M}}$  [(DMF), ( $\text{cm}^{-2}\Omega^{-1}\text{M}^{-1}$ ): 11.3. IR(KBr,  $\text{cm}^{-1}$ ): 3054(m), 1611(vs), 1559(vs), 1484 (m), 1448 (m), 1374(m), 1318(w), 1287(m), 1225(w), 1169(s), 980(s), 943 (m), 839(s), 749(vs), 685(s). UV-Vis(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 292 (2907), 365 (2821), 420(20000).  $\% \text{C}_{24}\text{H}_{20}\text{N}_2\text{Cl}_2\text{Cu}$ ; calc. C, 61.22; H, 4.28 N, 5.95; Found, C, 60.22; H, 4.1 N, 6.2.

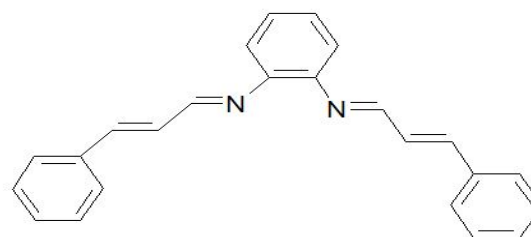
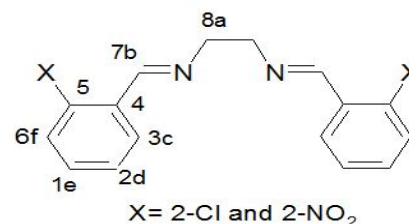
**Cu(BPAPHEN)Br<sub>2</sub>**: Brown color. 42.77% Yield. M.P ( $^{\circ}\text{C}$ ): 165(dec.).  $\Lambda_{\text{M}}$  [(DMF), ( $\text{cm}^{-2}\Omega^{-1}\text{M}^{-1}$ ): 15.5. IR(KBr,  $\text{cm}^{-1}$ ): 3423(w), 28540(w), 3054(m), 1609(vs), 1559(vs), 1488(m), 1448(s), 1374(m), 1284(m), 1171(s), 966(m), 749(vs), 696(s). UV-Vis(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 306 (29850), 359 (25760) .

**Cu(BPAPHEN)(SCN)<sub>2</sub>**: Light brown color. %42.83 Yield. M.P ( $^{\circ}\text{C}$ ): 189(dec.).  $\Lambda_{\text{M}}$  [(DMF), ( $\text{cm}^{-2}\Omega^{-1}\text{M}^{-1}$ ): 6.2. IR(KBr,  $\text{cm}^{-1}$ ): 3429(w), 3026(w), 2120(vs), 1620(vs), 1564(s), 1479(m), 1444(s), 1368(s), 1164(s), 976(s), 749(vs), 687(s). UV-Vis(DMF),  $\lambda(\text{nm})$  ( $\epsilon, \text{M}^{-1}\text{cm}^{-1}$ ): 308

(36700), 376 (28250), 395 (18250).  $\% \text{C}_{26}\text{H}_{20}\text{N}_4\text{S}_2\text{Co}$ ; calc. C, 60.50; H, 3.91; N, 10.85; Found, C, 59.30; H, 3.7; N, 11.1.

## Results and discussion

Scheme 1



### General

The structures of ligands are shown in Scheme 1. The BCBED and BNBEN ligands were synthesized by condensation reaction of 4-chlorobenzaldehyde and/or 2-nitrobenzaldehyde with 1,2-diaminoethane. BPAPHEN was synthesized by reaction of 3-phenylpropenal with *o*-phenylenediamine. They are soluble in dichloromethane, chloroform, acetone, dimethylsulfoxide, dimethylformamide while are non-soluble in methanol. The complexes were prepared by the reaction of the equimolar of the ligands and metal salts. Most of isolated complexes are non-soluble in alcohols such as methanol or ethanol. The elemental analyses of some selected complexes confirm 1:1 ratio of ligand to metal salts for all complexes. The analytical data along with some physical properties of the complexes have been brought in experimental section. Molar conductivity values of  $10^{-3}\text{M}$  solutions of the complexes in DMF at room temperature lies in the range of 0.6- 15.5  $\text{cm}^2\Omega^{-1}\text{M}^{-1}$  which indicates that are all non-electrolytes (Yu *et al.*, 2003; Saleh, 2005).

### Spectral investigation

Some important vibrational frequencies of the ligands and their complexes are summarized at experimental section. Vibrational frequencies attributed to the starting material were not observed in the IR spectra of the ligands. The IR spectrum of BCBEN shows very strong iminic peak at  $1637\text{cm}^{-1}$ . This iminic peak shifts to lower frequency in the complexes of BCBEN by 2-5  $\text{cm}^{-1}$ . This lowering is due to coordination of this ligand to metal center and  $\pi$ -back bonding. The absorption frequencies of ligand at 3022, 2918, 2854, are assigned to aromatic, aliphatic and iminic C-H groups that are shifted smoothly to higher values after coordination. The FT-IR spectrum of the Schiff base ligand of BNBEN showed the stretching

frequencies at (3053, 3022), 2917 and 2850  $\text{cm}^{-1}$  assigned to C-H of aromatic, aliphatic and iminic groups respectively. These frequencies are not affected notably during the coordination. The frequency at 1637  $\text{cm}^{-1}$  can be very safely assigned to asymmetric vibration of the azomethine group (C=N) (Sonmez *et al.*, 2003; Dehghanpour *et al.*, 2006; Birdsall, 2008). This band is shifted by 13-18  $\text{cm}^{-1}$  to higher frequencies in the spectra of the complexes, indicating well coordination of this ligand during the azomethine nitrogen atoms. The observed blue shifting is opposite to most cases, that stretching frequency of -C=N is shifted to lower frequencies after coordination. It seems that after coordination of BNBEN, the probable resonance in the ligand is restricted and therefore the bond order of -C=N is increased that leading to higher stretching frequency of iminic group. The peaks at 1517 and 1340  $\text{cm}^{-1}$  are attributed to asymmetric and symmetric stretching of  $\text{NO}_2$  that are smoothly shifted by 3-5  $\text{cm}^{-1}$  to higher energy after coordination. The IR spectrum of BPAPHEN shows very strong iminic peak at 1637  $\text{cm}^{-1}$ . This peak is red shifts by 3-15  $\text{cm}^{-1}$ . This can also be attributed to the  $\pi$ -back bonding of metal to ligand after  $\sigma$ -coordination of -C=N group (Yu *et al.*, 2003; Saleh, 2005). The absorption frequencies at 3057, 3024, and 2860  $\text{cm}^{-1}$  assigned to C-H of aromatic, olefinic and iminic groups respectively that are not considerably affected due to binding to metal. In the cobalt and copper thiocyanate complexes, the frequencies at 2070 and 2120  $\text{cm}^{-1}$  are observed that assigned to N-coordinated and S-coordinated mode of thiocyanate ion in the complexes respectively (Sabatini, 1966; Baer & Pike, 2010).

The UV-Visible spectrum of each of the ligands of BCBEN and BNBEN shows an absorption band at 272 and 290 nm respectively that may be related to  $\pi$ - $\pi^*$  transition of azomethine and aromatic ring together. This band is shifted to higher energy in BCBEN complexes and to lower energy in BNBEN complexes. The UV-Visible spectrum of BPAPHEN exhibits two absorption bands at 274 and 309 nm that may be assigned to  $\pi$ - $\pi^*$  transition of aromatic ring/olefinic moiety and azomethine respectively. Each two peaks move to longer wavelengths after coordination of this ligand to cobalt and copper probably due to strong back bonding of metal to  $\pi^*$  of ligand. In cobalt and copper complexes of BPAPHEN, d-d transition is expectable. This type of transitions are seen in the cobalt chloride and thiocyanate complexes at (610 and 665 nm) and 610 nm respectively (These transitions may be assigned to  ${}^4A_2$  -  ${}^4T_2$ ) that is in agreement with tetrahedral geometry around the cobalt (II) ion (Gavali & Hankarep, 2007). In other cases, this transition was not observed that may be due to its very low intensity.

The  ${}^1\text{H}$  NMR spectrum of the BCBEN includes signals at: 8.65(s, 2H), 7.95(d, 2H,  $J=9.00\text{Hz}$ ), 7.47(m, 4H), 7.41(d, 2H,  $J=8.00\text{Hz}$ ) and 3.97(S, 4H) ppm that are

assigned to the azomethine protons as functional group of ligand( $\text{H}_b$ ), aromatic hydrogens of  $\text{H}_c$ ,  $\text{H}_{ed}$  and  $\text{H}_f$  and aliphatic hydrogens of  $\text{H}_a$  respectively.  ${}^{13}\text{C}$  NMR spectrum of the BCBEN shows signals at 158.84, 134.42, 133.10, 132.61, 130.26, 128.54, 127.88, and 61.11 that may be related to  $\text{C}_7$ ,  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_3$ ,  $\text{C}_2$ ,  $\text{C}_6$ ,  $\text{C}_1$  and  $\text{C}_8$ . Azomethine protons and carbons in zinc and mercury complexes are appeared at 8.63-8.93 and 158.90-160.31 ppm. The  ${}^1\text{H}$  NMR spectrum of the BNBEN exhibits signals at 8.60(S, 2H), 8.00(dd, 2H,  $J=8.00\text{Hz}$ ,  $J=1.20\text{Hz}$ ), 7.97(dd, 2H,  $J=7.6\text{Hz}$ ,  $J=1.2\text{Hz}$ ), 7.760(dt, 2H,  $J=7.60\text{Hz}$ ,  $J=1.20\text{Hz}$ ), 7.68(dt, 2H,  $J=7.60\text{Hz}$ ,  $J=1.6\text{Hz}$ ), 3.96(S, 4H) ppm that again may be attributed to the azomethine protons as functional group of ligand( $\text{H}_b$ ), aromatic hydrogens of  $\text{H}_f$ ,  $\text{H}_c$ ,  $\text{H}_d$  and  $\text{H}_e$  and aliphatic hydrogens of  $\text{H}_a$  respectively. The signals at 158.63, 149.23, 133.86, 131.68, 130.41, 129.87, 124.58, 61.05 ppm are appeared in the  ${}^{13}\text{C}$  NMR spectrum of BNBEN that are chemical shifts of  $\text{C}_7$ ,  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_3$ ,  $\text{C}_2$ ,  $\text{C}_6$ ,  $\text{C}_1$  and  $\text{C}_8$  respectively. Azomethine protons and carbons in zinc and mercury complexes are shown at 8.58-8.68 ppm and 158.67- 159.7 ppm. As seen in NMR data, notable changes are not observed after coordination. This observation is due to weak binding of ligand to metal centers that leading to little changes and/or different coupling models in the spectral signals in complexes with respect to free ligands of BCBEN and BNBEN. The  ${}^1\text{H}$  NMR spectrum of the BPAPHEN depicts peaks at 8.25(bs, 2H) for azomethine, 7.62(m, 4H), 7.2(m, 10 H) for aromatic and 6.55(m, 4H) ppm for olefinic hydrogens. Peaks at 162.3 for azomethine and peaks at 148.1, 142.5, 134.1, 131.01, 128.9, 127.2, 126.8 and 118.8 ppm for aromatic and olefinic carbons are appeared in  ${}^{13}\text{C}$  NMR spectrum of this ligand. NMR recording of cobalt and copper complexes was not possible due to their paramagnetic properties. In final according to the evidences and with regard to our previous report on similar complexes (Habibi *et al.*, 2007c; Montazerzohori *et al.*, 2009c), the proposed geometry for these complexes is pseudo-tetrahedral.

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