

Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Complexes with an ONO- and an NNO-Functionalized Ligand

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Abstract: A new ligand was synthesized from condensation of 2-aminophenol and 2-acetylbenzimidazole. This ligand (HAPAB, **6**) was characterized based on elemental analysis, IR, ¹H-NMR and ¹³C-NMR and MS spectral spectra. The complexes of the ligands, HAPAB (**6**) and 2-acetylfruan benzoylhydrazone (HAFBH, **3**), with Co(II), Ni(II), Cu(II) and Zn(II), encoded **a-d**, were prepared by reaction of their methanolic acetate salts with the ligands in methanol in 1:2 metal to ligand mole ratio. These complexes, M(II)L₂, **7a-d** and **8a-d**, were similarly characterized based on their physicochemical data by elemental analysis, IR, ¹H-NMR and ¹³C-NMR, MS, molar conductance and electronic absorption spectra. The complexes consist of two ligands that give six coordinate bonding to each metal ion on a meridional plane through binding with the acetylfruan-O, the azomethine-N and the oxygen donor atom in the enol form of the hydrazone **3** and the 2-acetylbenzimidazole-N, the azomethine-N, and the phenoxo-O atoms of the imine **6** respectively. The ligands function as monobasic ONO- and NNO-trifunctional donor ligands where the deprotonated enolic form is preferred in the coordination producing distorted octahedral complexes.

Key words: metal (II) complexes, Schiff bases, NNO-tridentate ligand, ONO-tridentate ligand

تحضير وتشخيص معقدات الكوبلت (II) والنيكل (II) والنحاس (II) والزنك (II) مع متصلة ثلاثية جديدة من خلال ذرات (NNO) وأخرى بذرات (ONO)

ملخص: تم في هذا البحث تحضير متصلة ثلاثية جديدة بتفاعل التكثيف لمادة 2-أمينوفينول مع 2-أسيتايل بنزيميدازول وتم تشخيص المتصلة الناتجة بناء على التحليل العنصري الدقيق والقياسات الطيفية لها، ولهذه المتصلة قابلية الارتباط مع أيونات المعادن من خلال ذرات NNO وتم تحضير معقدات هذه المتصلة مع الكوبلت (II) والنيكل (II) والنحاس (II) والزنك (II) وتشخيصها وكذلك حضرت معقدات المتصلة 2-أسيتايل فيوران بنزويل هيدرازون مع الأيونات السابقة، ولهذه المتصلة قابلية الارتباط من خلال ذرات ONO. وتم تشخيص المعقدات الناتجة جميعها بناءً على تحاليلها الدقيقة ونتائج قياسات أطيفها: الأشعة تحت الحمراء والكتلة والرنين النووي المغناطيسي

والموصلية والامتصاص الإلكتروني. وبيّنت نتائج الفحوصات أن هذه المعقدات ثمانية الأوجه وذلك للتشابه بين خواص هذه المواد وتلك التي تمت دراستها بالأشعة السينية.

1. Introduction

Schiff base ligands have been extensively studied in coordination chemistry mainly due to their facile syntheses and tunable steric and electronic properties [1]. In recent years, transition metal complexes of asymmetrical Schiff base ligands have attracted enormous attentions due to their diversity of molecular structures [2-4] and important properties, such as catalysis, porosity, chirality, luminescence, non-linear optics, ferroelectrics, magnetism [5-8].

Imine is an important compound of Schiff-bases. Imine ligands have been used in the construction of sophisticated metallosupramolecular compounds and coordination polymers, as well as in the preparation of innumerable simple mononuclear complexes [9–12]. Hydrazone is another important compound of Schiff bases and a major polydentate ligand. Due to their variable bonding when forming complexes with metal ions, the coordination chemistry of hydrazones has been intensively investigated [13-16]. Tridentate ligands can be obtained by condensation of a functionalized aldehyde or ketone with properly substituted amine or hydrazine. The interesting properties of the transition metal complexes with Schiff bases promoted making this research in which two tridentate ligands and some of their metal(II) complexes were prepared and characterized. The ligands are the new imine, 2-[1-(2-hydroxyphenylimino)ethan-1-yl]-benzimidazole (APAB), and the hydrazone, 2-acetylfuran benzoylhydrazone (AFBH). The complexes are those of Co(II), Ni(II), Cu(II) and Zn(II). These compounds were prepared and fully characterized by elemental analysis and IR, ¹H-NMR and ¹³C-NMR and mass spectral data as well as electronic absorption spectra. It was found that the ligands formed bis complexes coordinated meridionally through their heteroatom donor sets. The distorted octahedral cis-N₄O₂ or cis-O₄N₂ complexes produced are similar to those formed with analogous monobasic ligands [17, 18].

2. Experimental

2.1. Material and methods

Phenylenediamine, lactic acid, potassium permanganate, benzoylhydrazine, 2-acetylfuran and 2-aminophenol were obtained from Merck. Reagent grade salts of all cations were purchased from Aldrich and used as received. Commercially available solvents were used as received. The FTIR was recorded with thermoscientific FTIR spectrometer using KBr pellets. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. UV–Vis spectra of DMF solutions of the complexes were

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recorded on a SHIMADZU UV-Vis spectrophotometer (UV-1601). Conductivity measurements were made on a PHYWE conductivity meter. Microanalysis of C, H and N was performed at the Microanalytical Center-University of Montreal- Canada, using the “dynamic flash combustion method”. Accurate mass measurements were performed on a LC-MSD-TOF instrument from Agilent Technologies in positive electrospray mode. Protonated molecular ions $(M+H)^+$ were used for empirical formula confirmation. NMR spectra were obtained using a Varian/Agilent VNMR-500 spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were acquired at 500 MHz for solutions in DMSO-d_6 at 21°C . Chemical shifts are in ppm relative to TMS.

2.2. Synthesis of the Schiff base ligands

2.2.1. Preparation of 2-acetylfuran benzoylhydrazone (HAFBH, 3)

This compound **3** was prepared from 2-acetyl furan (**1**) and benzoyl hydrazine (**2**) similar to that described in the literature [19].

Yellow solid, yield 84% (Scheme 1a). Anal. calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.21; H, 5.22; N, 12.19. IR (cm^{-1}): 3220 (s, NH), 1670 (m, C=O), 1600 (s, C=N) where s: sharp; m: medium. $^1\text{H-NMR}$ (DMSO-d_6) spectra 10.4 (s, 1H, NH), 6.4–8.1 (m, 8H, Ar-H), 1.94 (s, 3H, CH_3), $^{13}\text{C-NMR}$: 187.5 (C=O), 152.1 (C=N), 139.2, 129.5, 127.0, 125.2, 123.6, 121.4, 112.7, 104.9 (Ar-C), 15.6 (CH_3).

2.2.2. Preparation of 2-[1-(2-hydroxyphenylimino)ethan-1-yl]-benzimidazole (HAPAB) (6)

2-Acetyl bezimidazole (**4**) was prepared from phenylenediamine, lactic acid, potassium permanganate as described in the literature [20].

The imine, 2-[1-(2-hydroxyphenylimino)ethan-1-yl]-benzimidazole, (**6**), was made from the reaction of 1-(1-H-Benz[d]imidazol-2-yl-1-ethanone), i.e., 2-acetylbenzimidazole (**4**), with 2-aminophenol (**5**) in 1:1 mole ratio in ethanol and some drops of acetic acid were used as a catalyst. The reaction mixture was refluxed for 2 hours. Cooling the solution precipitated the corresponding imine in good yield (78%) (scheme 1b). Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$ is C: 71.10, H: 5.21, N: 16.72, and found: C: 70.89; H: 5.14; N: 16.64.

The IR spectrum contains prominent peaks (in cm^{-1}) at 3415 br. (O-H), 3105 (N-H), 1615 (C=N). The $^1\text{H-NMR}$ spectrum (in DMSO-d_6) contains peaks at 13.25 (s, OH), 11.92 (s, NH), 6.98-7.78 (m, 8H, phenyl protons), 2.75 (s, CH_3). $^{13}\text{C-NMR}$: 173.679, 151.088, 140.307, 139.633, 137.032, 135.344, 130.921, 128.557, 128.260, 123.960, 123.549, 117.013, 113.009.

2.3. Preparation of metal complexes

To a well-stirred suspension of each ligand (1.0 mmol) in methanol (25 mL) was added the metal acetate, namely $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, (0.5 mmol) solid. The resulting solution was stirred for 24 h during which a solid complex appeared. The solid was collected by filtration, washed with methanol, diethyl ether and dried.

Cis-Bis[2-acetylfuran benzoylhydrazone]cobalt(II) [Co(AFBH)₂] (7a): tan solid. Yield: 0.178 g (69%). mp. 245–7 °C. ESI MS: m/z 513 (M^+). Anal. calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{Co}$: C, 60.82; H, 4.32; N, 10.92. Found: C, 60.98; H, 4.37; N, 11.09. Λ_{M} (Mho $\text{cm}^2 \text{mol}^{-1}$): 0.43, and for chloroform solvent 0.46. UV–Vis. (nm, log ϵ): 715(1.73), shoulder at 583 nm (3.46), 355 (4.38), 260 (4.40). Significant infrared bands (cm^{-1}): 1575, 1500, 1365, 1148, 1065, 1018, 894, 710, 527.

Cis-Bis[2-acetylfuran benzoylhydrazone]nickel(II) [Ni(AFBH)₂] (7b): green solid. Yield: 0.192 g (74%). mp. > 300 °C (dec.). ESI MS: m/z 512 (M^+). Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{Ni}$: C, 60.85; H, 4.32; N, 10.92. Found: C, 60.94; H, 4.27; N, 11.14. Λ_{M} (Mho $\text{cm}^2 \text{mol}^{-1}$): 4.26. UV–Vis (nm, log ϵ): 879 (1.41), 403 (3.41), 315 (3.90), 250 (4.36). Significant infrared bands (cm^{-1}): 1587, 1513, 1476, 1365, 1294, 1169, 1067, 999, 924, 883, 797, 755, 717, 516.

Cis-Bis[2-acetylfuran benzoylhydrazone]copper(II) [Cu(AFBH)₂] (7c): olive green solid. Yield: 0.180 g (69%). mp. 225–227 °C (dec.). ESI MS: m/z 518 (M^+). Anal. calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{Cu}$: C, 56.15; H, 4.28; N, 10.82. Found: C, 60.20; H, 4.24; N, 10.75. Λ_{M} (Mho $\text{cm}^2 \text{mol}^{-1}$): 4.78. UV–Vis (nm, log ϵ): 652 (2.08), 372 (3.30), 352 (3.28), 258 (3.35). Significant infrared bands (cm^{-1}): 1586, 1519, 1378, 1301, 1171, 1067, 1019, 904, 792, 703, 435.

Cis-Bis[2-acetylfuran benzoylhydrazone]zinc(II) [Zn(AFBH)₂] (7d): yellow solid. Yield: 0.182 g (70%). mp. 250–252 °C (dec.). ESI MS: m/z 519 (M^+). Anal. calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_4\text{Zn}$: C, 60.07; H, 4.27; N, 10.78. Found: C, 60.10; H, 4.18; N, 10.85, Λ_{M} (Mho $\text{cm}^2 \text{mol}^{-1}$): 5.46. UV–Vis (nm, log ϵ): 326 (3.32) and 267 (3.12). Significant infrared bands: (cm^{-1}): 1581, 1491, 1425, 1372, 1305, 1167, 1068, 710, 454. NMR spectral data of $\text{Zn}(\text{AFBH})_2$: ^1H -NMR (ppm), 6.551–8.144 (br, ArH), 2.608 (s, 3H, CH_3) and ^{13}C -NMR: 170.706, 150.736, 149.755, 145.318, 135.884, 131.044, 128.475, 128.157, 115.836, 113.668, 15.378.

Cis-bis [2-[1-(2-hydroxyphenylimino)ethan-1-yl]-benzimidazole] cobalt(II) [Co(APAB)₂] (8a),

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tan solid. Yield: 0.196 g (69%). mp. decomposes at 245-247 °C, ESI MS: m/z 559 (M^+). Anal. calcd. for $C_{30}H_{24}N_6O_2Co$: C, 64.40; H, 4.32; N, 15.02. Found: C, 64.21; H, 4.23; N, 14.92, $\Lambda_M(\text{Mho cm}^2 \text{ mol}^{-1})$: 6.23, and for DMSO solvent 8.46. UV-Vis. nm (log ϵ): 912(1.89), 378 (3.69), 263 (3.54). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1480, 1430, 1360, 1280, 1190, 1140, 1080, 970, 760, 720.

Cis-bis [2-{1-(2-hydroxyphenylimino)ethan-1-yl}-benzimidazole] nickel(II) [Ni(APAB)₂] (8b),

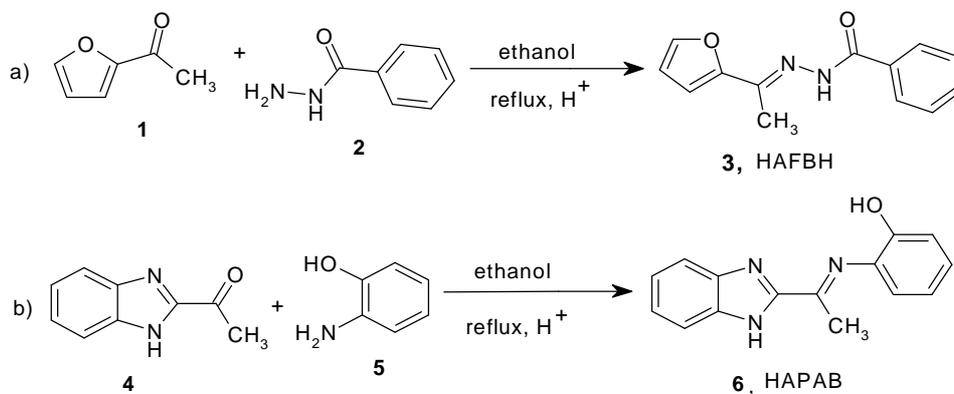
tan solid. Yield: 0.163 g (58%). mp. decomposes at 255 °C. ESI MS: m/z 558 (M^+) Anal. calcd. for $C_{30}H_{24}N_6O_2Ni$: C, 64.42; H, 4.33; N, 15.03. Found: C, 64.15; H, 4.26; N, 14.94. $\Lambda_M(\text{Mho cm}^2 \text{ mol}^{-1})$: 8.64. UV-Vis. nm (log ϵ): 253 (3.64), 278 (4.15), 328 (4.12), 393 (4.51) and 903(1.42). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1470, 1430, 1360, 1290, 1220, 1160, 1070, 980, 760, 690.

Cis-bis [2-{1-(2-hydroxyphenylimino)ethan-1-yl}-benzimidazole] copper(II) [Cu(APAB)₂] (8c), olive green solid. Yield: 0.152 g (54%). mp. decomposes at 225-227 °C. ESI MS: m/z 564 (M^+). Anal. calcd. for $C_{30}H_{24}N_6O_2Cu$: C, 63.87; H, 4.29; N, 14.90. Found: C, 63.69; H, 4.13; N, 14.81. $\Lambda_M(\text{Mho cm}^2 \text{ mol}^{-1})$: 5.47. UV-Vis. nm (log ϵ): 398 (3.629), 332 (3.68), 268 (3.55) and 682(1.98). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1520, 1460, 1420, 1360, 1310, 1280, 1160, 1060, 970, 750, 720.

Cis-bis [2-{1-(2-hydroxyphenylimino)ethan-1-yl}-benzimidazole] zinc(II) [Zn(APAB)₂] (8d), yellow solid. Yield: 0.184 g (65%). mp. decomposes at 253°C. ESI MS: m/z 565 (M^+). Anal. calcd. for $C_{30}H_{24}N_6O_2Zn$: C, 63.66; H, 4.27; N, 14.85. Found: C, 63.31; H, 4.11; N, 14.62. $\Lambda_M(\text{Mho cm}^2 \text{ mol}^{-1})$: 5.83. UV-Vis. nm (log ϵ): 335 (3.90) and 270 (3.62). $^1\text{H-NMR}$ (ppm), 11.92 (s, NH of benzimidazole), 6.98–7.82 (br, ArH), 2.75 (s, 3H, CH_3). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1490, 1460, 1430, 1355, 1290, 1190, 1060, 960, 820, 750, 710.

3. Results and discussion

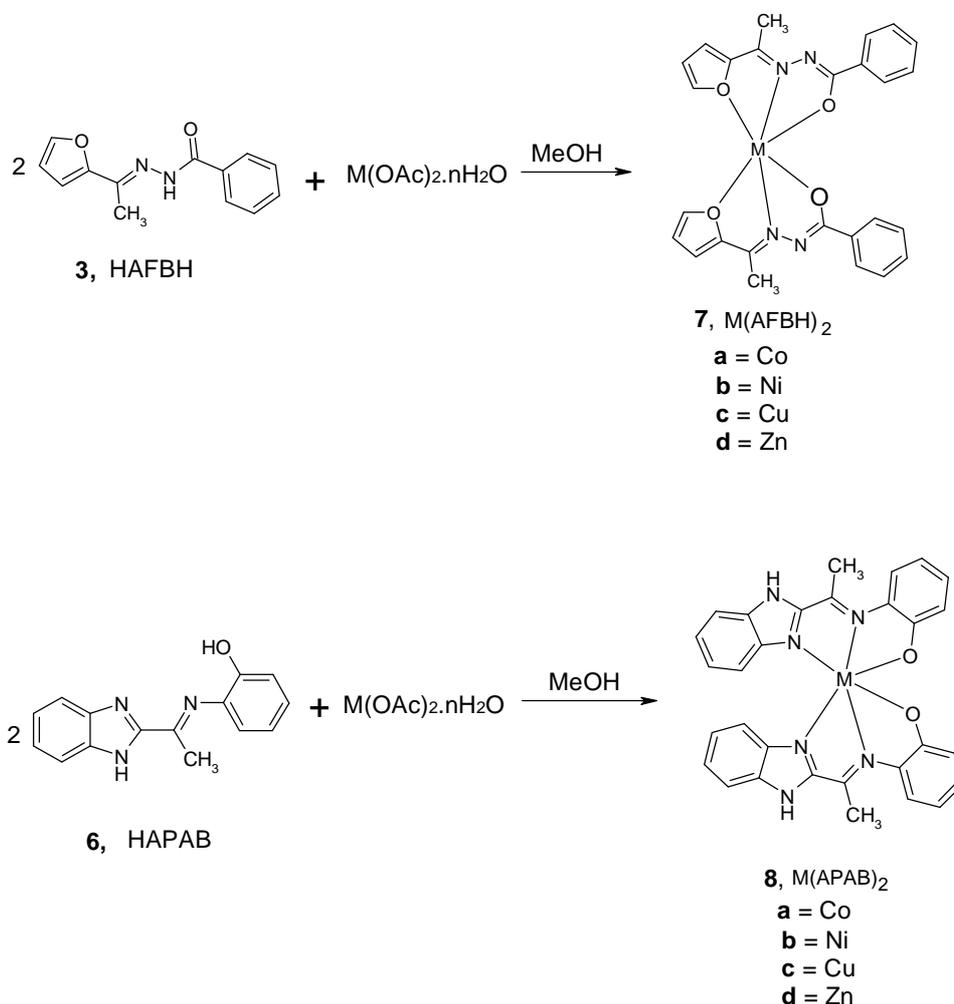
The Schiff base ligand (**3**) was prepared from 2-acetyl furan (**1**) and benzoyl hydrazine (**2**) and the imine (**6**) from the reaction of 2-acetylbenzimidazole (**4**) with 2-aminophenol (**5**) in 1:1 mole ratio in ethanol, Scheme 1.



Scheme 1

These ligands were characterized based on physicochemical measurements. Results of elemental analysis, infrared and $^1\text{H-NMR}$ as well as $^{13}\text{C-NMR}$ and mass spectral data are in accordance with the expected structures. The metallation of these ligands with metal(II) acetate [metal(II) = Co(II), Ni(II), Cu(II) and Zn(II)] in 2:1 ligand to metal mole ratio yielded six coordinate complexes, **7a-d** and **8a-d**, in which the hydrazone **3** and the imine **6** act as O, N, O- and N, N, O-tridentate ligands (Scheme 2).

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Scheme 2

They form stable 5-membered rings by binding with the acetylfuluran-O, the azomethine-N and the oxygen donor atom in the enol form of the hydrazone and the 2-acetylbenzimidazole-N, the azomethine-N, and the phenoxo-O atoms of the imine respectively. These formulations are in accordance with the data from elemental analysis and physicochemical measurements

3.1. Conductivity measurements

Molar conductance of the complexes determined in DMSO solution are almost negligible, indicating that the complexes are electrically non conductive. This suggests that each of these complexes is neutral with two uninegative ligands coordinated to the metal(II) ion.

3.2. IR spectra

The IR spectra of the ligands have several prominent bands appearing at 3400 and 1670 cm^{-1} due to N-H, O-H and C=O stretching modes, respectively. The band due to C=O disappeared on complexation and a new C-O band at 1040-1080 cm^{-1} appeared. The bands due to C=N and the NH of the hydrazone or benzimidazole are observed in all the spectra of the ligands and the complexes, **8a-d**, of the imine for the N-H bond of the benzimidazole ring is retained on complexation. However, the band due to O-H of the phenol as well as the band due to N-H in the hydrazone disappeared on complexation.

3.3. Mass spectra

The mass spectra of the ligands show a peak due to the molecular mass plus a proton ion, $(M+H)^+$, that is consistent with the molecular structure of the ligand. In addition, the mass spectra of complexes show a peak due to the complex plus proton ion and the molecular ion peak of the complex, which is in consistence with the proposed structure and it also ensures that each ligand lost one proton upon complexation. The molecular ion peaks of the complexes contain individual peaks for the isotopes of the metals with the known relative abundance of each metal.

3.4. NMR spectra

^1H -NMR spectra for the ligands contain peaks corresponding to the various types and the numbers of the existing protons. ^{13}C -NMR spectra for the ligands contain peaks corresponding to the number of various types of carbons in each ligand. ^1H -NMR spectra for the complexes of Co(II), Ni(II) and Cu(II) were not helpful for identification due to their paramagnetism. ^1H -NMR spectra of the zinc complexes (**7d**, **8d**) gave some information about these compounds. It is noted that no peak was detected for the (NH) proton of the amide and the phenol proton in these complexes. This observation is considered an evidence for involvement of the nitrogen of the hydrazone and the oxygen of the phenol in coordination to the central zinc ion after deprotonation. This fact suggests that the Schiff bases act as monobasic tridentate ligands. Some changes in the aromatic region and its chemical shift can be observed, but the complexity of the signals does not allow to interpret this in detail. The ^{13}C -NMR of (**7d**) show the correct number of signals, 11 signals.

3.5. Electronic spectra

Absorption spectra were obtained in DMF and the resulting data are given in the experimental section. A strong band in the range 375-400 nm, and two or more moderately intense bands in the range 270-345 nm are

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observed. The intense band near 395 nm may be associated with a charge transfer transition [21].

The last bands below 345 nm are also observed in the free ligand (245-355 nm) and hence can be attributed to intraligand transition bands. Zinc complexes, with d¹⁰ electronic configuration, have no allowed d-d transition. The other complexes exhibited one weak and broad peaks at 715, 879 and 652 nm for complexes 7a-c and at 912, 903 and 682 nm for complexes 8a-c respectively. They are assigned to d-d transitions in the octahedral coordination environment of Co(II)(d⁷), Ni(II)(d⁸) and Cu(II)(d⁹) [22]. These observations are in line with common spectral features of d block metal complexes. Charge transfer (CT) gives rise to intense absorptions, whereas 'd-d' bands are much weaker. In some spectra, CT absorptions mask bands due to 'd-d' transitions, although CT absorptions (as well as ligand-centered n-π* and π-π* bands) often occur at higher energies than 'd-d' absorptions [22].

On the basis of the above observations and considerations it is tentatively suggested that all of the complexes show an octahedral geometry (Scheme 2) in which the two ligands act as tridentate ligands where they possibly accommodate themselves around the metal atom in such a way that a stable chelate ring is formed giving, in turn, stability to the formed metal complexes. Therefore, the structure proposed to M^{II}L₂ complexes is justified. These results are the same as those found for the crystallographically determined and spectroscopically confirmed structures [17, 18].

4. Conclusions

Two tridentate ONO- and NNO-donor ligands, 2-acetylfuran benzoylhydrazone and 2-aminophenol 2-acetylbenzimidazole, have been prepared and characterized based on their physicochemical data. A number of their metal(II) complexes, M^{II}L₂ (M = Co, Ni, Cu, and Zn), have been synthesized and characterized based on their analytical and spectral data. The ligands behave as monobasic ONO- and NNO- tridentate, bonding to metal(II) through the acetylfuran-O, the azomethine-N and the oxygen donor atom in the enol form of the hydrazone and the 2-acetylbenzimidazole-N, the azomethine-N, and the phenoxo-O atoms of the imine to form distorted octahedral structures.

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