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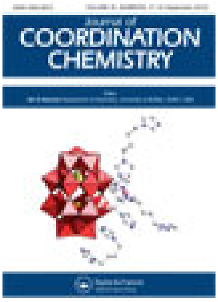

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Synthesis and characterization of new NNO ligands and some metal(II) complexes: crystal structures of $(BBH)_2Co$ and $(BIH)_2Ni$

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Synthesis and characterization of new NNO ligands and some metal(II) complexes: crystal structures of (BBH)$_2$Co and (BIH)$_2$Ni

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The ligands 2-acetylbenzimidazole benzoylhydrazone (HBBH) and 2-acetylbenzimidazole isonicotinoylhydrazone (HBIH) were prepared and characterized by elemental analysis, IR, NMR, and mass spectra. The complexes of these ligands with Co(II), Ni(II), Cu(II), and Zn(II) were prepared by the reaction of methanolic acetate salts with the ligands in methanol in a 1 : 2 metal : ligand mole ratio. M(II)L$_2$ were characterized based on elemental analysis, IR, NMR, MS, conductance, and electronic spectral measurements. Co(BBH)$_2$ and Ni(BIH)$_2$ were crystallographically characterized. They consist of two ligands that give six coordinate bonding to Co(II) and Ni(II) on a meridional plane through benzimidazole ring nitrogen, azomethine nitrogen, and benzoyl or isonicotinoyl oxygen, respectively. Co(BBH)$_2$ crystallizes in the triclinic space group $P\bar{1}$ and $Z = 2$ at 150 K with $a = 9.9010(3)$ Å, $b = 9.9705(4)$ Å, $c = 15.8141(6)$ Å, $\alpha = 96.424(2)^\circ$, $\beta = 94.1580(10)^\circ$, and $\gamma = 92.153(2)^\circ$. Ni(BBH)$_2$ crystallizes in the monoclinic space group $P2_1/n$ and $Z = 4$ at 100 K with $a = 14.3156(2)$ Å, $b = 24.7402(4)$ Å, $c = 19.8215(3)$ Å, $\alpha = 90^\circ$, $\beta = 98.7761(7)^\circ$, and $\gamma = 90^\circ$. The metal centers in these complexes have two ligands in a meridional, slightly distorted octahedron.

Keywords: Cobalt(II) complex; Nickel(II) complex; Schiff bases; NNO Tridentate ligands; Crystal structures

1. Introduction

Schiff bases have been used as pigments and dyes, catalysts, intermediates in organic synthesis, and polymer stabilizers. Coordination chemistry of these ligands through the selection of suitable amine and aldehyde substituents with different steric and electronic properties may bring about subtle structural and functional variations [1]. A large number of Schiff bases and their metal complexes have been synthesized for their properties [2], e.g., light emission diode (LED) [3], corrosion inhibitor [4], potentiometric sensors [5, 6], intermediates to obtain heterocyclic compounds [7], conjugate polymers containing azomethine [8], and their wide-spectrum biological activities [9–11].

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Acylhydrazones are capable of exhibiting keto-enol tautomerism and have interesting coordination properties to transition metals [12]. A class of hydrazones can be obtained by condensation of a functionalized aldehyde or ketone with properly substituted hydrazine to produce tridentate ligands containing donors such as NNO and SNO. Tridentate monoanionic NNO ligands have been employed for the preparation of complexes with many metals [13–18]. For example, transition metal(II) complexes of 2-acetylpyridine benzoylhydrazone [19] and a few 2-pyridinecarbaldehyde hydrazone [20] ligands containing the trifunctional N, N, O-donor system have been synthesized, and a few were crystallographically characterized.

The interesting properties of transition metal hydrazone complexes promoted us to synthesize two new hydrazones from the reaction of 1-(1-H-benz[d]imidazol-2-yl-1-ethanone) [21] with benzoylhydrazine and isonicotinoyl hydrazine. The resulting ligands were complexed with M(II) (M = Co, Ni, Cu, and Zn). The new ligands, 2-acetylbenzimidazole benzoylhydrazone (BBH) and 2-acetylbenzimidazole isonicotinoylhydrazone (BIH), and their complexes were characterized by elemental analysis and IR, ^{1}H, and ^{13}C NMR and mass spectral data. The structures of $Co(BBH)_2$ and $Ni(BIH)_2$ were determined by single-crystal X-ray diffraction. The ligands formed bis complexes and coordinated meridionally through their benzimidazole-N, imine-N, and carbonyl-O, forming distorted octahedral *cis*-CoN_4O_2 complexes.

2. Experimental

2.1. *Materials and methods*

2-Acetyl benzimidazole was prepared as described in [21]. Phenylenediamine, lactic acid, potassium permanganate, benzoylhydrazine, and isonicotinoyl hydrazine were obtained from Merck (Darmstadt, Germany). Reagent grade salts of all cations were purchased from Aldrich (St. Louis, MO, USA) and used as received. Commercially available solvents were used as received. FTIR spectra were recorded with a Thermoscientific FTIR spectrometer using KBr pellets. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. UV-Vis spectra of dimethylformamide (DMF) solutions of the complexes were recorded on a SHIMADZU UV-Vis spectrophotometer (UV-1601). Conductivity measurements were made on a PHYWE conductivity meter. C, H, N, and S microanalyses were performed at the Microanalytical Center, University of Montreal, Canada, using the ‘‘dynamic flash combustion method.’’ Accurate mass measurements were performed on an LC-MSD-TOF instrument from Agilent Technologies (Englewood, CO, USA) in a positive electrospray mode. Protonated molecular ions $(M+H)^+$ were used for empirical formula confirmation. NMR spectra were obtained using a Varian/Agilent VNMRS-500 spectrometer. ^{1}H- and ^{13}C-NMR spectra were acquired at 500 MHz for solutions in DMSO-d_6 at 21°C. Chemical shifts are in given in ppm relative to TMS.

Crystal structures were determined using a Bruker AXS (Madison, WI, USA), consisting of a Microsource MX copper source from Incoatec (Geesthacht, Germany) using a Quasar mirror and mounted on a Platform 3 circles goniometer with a fixed CHI.

The detector is a small area APEX II kept at 4 cm distance from the crystal along the data collection. It is usually done at 2θ positions using an omega scan mode, by fixing the detector at θ and omega scanning of 0.3° for each frame. That arrangement allows

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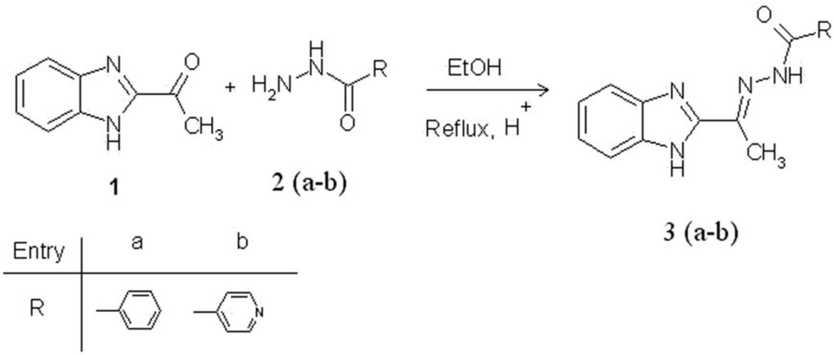
the scanning of 600 images for each phi orientations of the crystal. The crystal is kept at 100 K during data collection using a Kryoflex low-temperature system, also from Bruker. The structures were solved by SHELEXS and refined [22–24] with SHELXL by full-matrix least-squares on F^2. Graphics were drawn with Mercury and Platon for windows, the final look was performed with the assistance of POV-Ray program.

2.2. *Synthesis of ligands*

2.2.1. Preparation of 2-acetylbenzimidazole benzoylhydrazone (HBBH, 3a). 2-Acetyl benzimidazole (**1**) was condensed with benzoylhydrazine (**2a**) in a 1 : 1 mole ratio in ethanol and some drops of acetic acid were used as a catalyst. The reaction mixture was refluxed for 2 h. Cooling the solution precipitated the corresponding hydrazone in good yield (78%) (scheme 1). m.p. = 285°C. Its elemental analysis calculated for $C_{16}H_{14}N_4O$ is C, 69.04; H, 5.07; N, 20.14. Found: C, 69.06; H, 5.04; N, 20.14. The IR spectrum contains prominent peaks (in cm^{-1}) at 3400, 3100, 1670, 1570, corresponding to the two N–H, C = O, and C=N, respectively. The ^{1}H-NMR spectrum (in DMSO-d_6) contains peaks at 2.53 (s, 3H), 7.380–8.043 (multiplet, 9H), 13.131 (s, 1H, NH of benzimidazole), and 15.292 (s, 1H, NH of hydrazone). The mass spectrum contains the peak at 279 corresponding to $(M+1)^+$ and at 301 corresponding to $(M+Na)^+$. UV-Vis spectrum: 325 nm ($\log \varepsilon = 4.27$).

2.2.2. Preparation of 2-acetylbenzimidazole isonicotinoylhydrazone (HBIH, 3b). 2-Acetylbenzimidazole isonicotinoylhydrazone was prepared similarly by the condensation of 2-acetyl benzimidazole (**1**) and isonicotinoylhydrazine (**2b**). m.p. = 282°C. Its elemental analysis calculated for $C_{15}H_{13}N_5O$ is C, 64.50; H, 4.69; N, 25.08. Found: C, 64.52; H, 4.66; N, 25.09. The IR spectrum contains prominent peaks (in cm^{-1}) at 3400, 3100, 1670, 1560, corresponding to the two N–H, C=O, and C=N, respectively. The ^{1}H-NMR spectrum (in DMSO-d_6) contains peaks at 2.553 (s, 3H), 7.163–8.780 (multiplet, 9H), 11.210 (s, 1H), and 12.732 (s, 1H). The ^{13}C-NMR spectrum (in DMSO-d_6) contains peaks at 163.312, 150.603, 150.229, 149.607, 143.634, 141.325, 135.548, 124.204, 122.494, 122.217, 119.867, 112.606, and 14.209. The mass spectrum contains the peak at 280 corresponding to $(M+1)^+$. UV-Vis spectrum: 325 nm ($\log \varepsilon = 4.19$).



Scheme 1. Synthesis of the ligands: 2-acetylbenzimidazole benzoylhydrazone and 2-acetylbenzimidazole isonicotinoylhydrazone.

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2.3. *Preparation of metal complexes*

To a well-stirred suspension of the ligand (1.0 mmol) in methanol (25 mL), the metal acetate, $Co(OAc)_2 \cdot 4H_2O$, $Ni(OAc)_2 \cdot 4H_2O$, $Cu(OAc)_2 \cdot H_2O$, or $Zn(OAc)_2 \cdot 2H_2O$, (0.5 mmol) solid was added. The resulting solution was stirred for 24 h during which a solid appeared. The solid was collected by filtration, washed with methanol, diethyl ether, and dried.

Cis-bis[2-acetylbenzimidazole benzoylhydrazone]cobalt(II) [$Co(BBH)_2$] (**4a**) tan solid. Yield: 0.216 g (67%). The m.p. decomposes at 238–240°C, ESI MS: *m*/*z* 613.15 (M^+). Anal. Calcd for $(C_{16}H_{13}N_4O)_2Co \cdot CH_3OH$: C, 59.54; H, 4.65; N, 17.36. Found: C, 61.63; H, 4.91; N, 17.73. Λ_M (mMho cm^2 mol^{-1}): 26.23, and for DMSO solvent 8.46. UV-Vis (nm, log ε): 710 (1.94), 380 (3.71), and 265 (3.57). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1480, 1430, 1360, 1280, 1190, 1140, 1080, 970, 760, 720. Crystals of $Co(BBH)_2$ deposited in the undisturbed filtrate by slow evaporation at room temperature for a few days.

Cis-bis[2-acetylbenzimidazole benzoylhydrazone]nickel(II) [$Ni(BBH)_2$] (**5a**) tan solid. Yield: 0.159 g (52%). The m.p. decomposes at about 250°C. ESI MS: *m*/*z* 613.16 (M^+). Anal. Calcd for $(C_{16}H_{13}N_4O)_2Ni$: C, 62.66; H, 4.24; N, 18.27. Found: C, 62.15; H, 4.49; N, 18.07. Λ_M (Mho cm^2 mol^{-1}): 28.64. UV-Vis (nm, log ε): 250 (3.74), 275 (4.19), 325 (4.18), 395 (4.55), and 896 (1.38). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1470, 1430, 1360, 1290, 1220, 1160, 1070, 980, 760, 690.

Cis-bis[2-acetylbenzimidazole benzoylhydrazone]copper(II) [$Cu(BBH)_2$] (**6a**) olive green solid. Yield: 0.176 g (57%). The m.p. decomposes at 243–245°C. ESI MS: *m*/*z* 618.16 (M^+). Anal. Calcd for $(C_{16}H_{13}N_4O)_2Cu$: C, 62.18; H, 4.21; N, 18.13. Found: C, 61.96; H, 4.22; N, 17.93. Λ_M (mMho cm^2 mol^{-1}): 6.47. UV-Vis (nm, log ε): 650 (2.14), 400 (3.636), 330 (3.78), 265 (3.60). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1520, 1460, 1420, 1360, 1310, 1280, 1160, 1060, 970, 750, 720.

Cis-bis[2-acetylbenzimidazole benzoylhydrazone]zinc(II) [$Zn(BBH)_2$] (**7a**) yellow solid. Yield: 0.195 g (63%). The m.p. decomposes at 303°C. ESI MS: *m*/*z* 619.15 (M^+). Anal. Calcd for $(C_{16}H_{13}N_4O)_2Zn$: C, 61.99; H, 4.55; N, 18.08. Found: C, 61.34; H, 4.20; N, 17.94. Λ_M (Mho cm^2 mol^{-1}): 5.83. UV-Vis (nm, log ε): 330 (3.95) and 265 (3.64). ^{1}H-NMR (ppm): 13.42 (s, NH of benzimidazole), 7.09–8.14 (br, ArH), 2.75 (s, 3H, CH_3). ^{13}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. Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1490, 1460, 1430, 1355, 1290, 1190, 1060, 960, 820, 750, 710.

Cis-bis[2-acetylbenzimidazole isonicotinoylhydrazone]cobalt(II) [$Co(BIH)_2$] (**4b**) tan solid. Yield: 0.187 g (61%). The m.p. decomposes above 260°C. ESI MS: *m*/*z* 615.14 (M^+). Anal. Calcd for $(C_{15}H_{12}N_5O)_2Co$: C, 58.56; H, 3.90, N, 22.77. Found: C, 58.14; H, 4.28; N, 22.46. Λ_M (mMho cm^2 mol^{-1}): 5.54. UV-Vis (nm, log ε): 906 (1.45), 270 (4.37), 315 (4.13), 375 (4.35). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1540, 1470, 1370, 1330, 1210, 1150, 1070, 980, 850, 760, 700.

Cis-bis[2-acetylbenzimidazole isonicotinoylhydrazone]nickel(II) [$Ni(BIH)_2$] (**5b**) tan solid. Yield: 0.160 g (52%). The m.p. 224°C. ESI MS: *m*/*z* 615.15 (M^+). Anal. Calcd for $(C_{15}H_{12}N_5O)_2Ni$: C, 58.56; H, 3.90; N, 22.77. Found: C, 58.29; H, 4.31; N, 22.14. Λ_M (mMho cm^2 mol^{-1}): 6.44. UV-Vis (nm, log ε): 250 (3.74), 280 (4.14), 395 (4.42), 918 (1.92). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1470, 1350, 1240, 1180, 1060, 970, 840, 750, 690. Single crystals of $Ni(BIH)_2$ suitable for X-ray diffraction study

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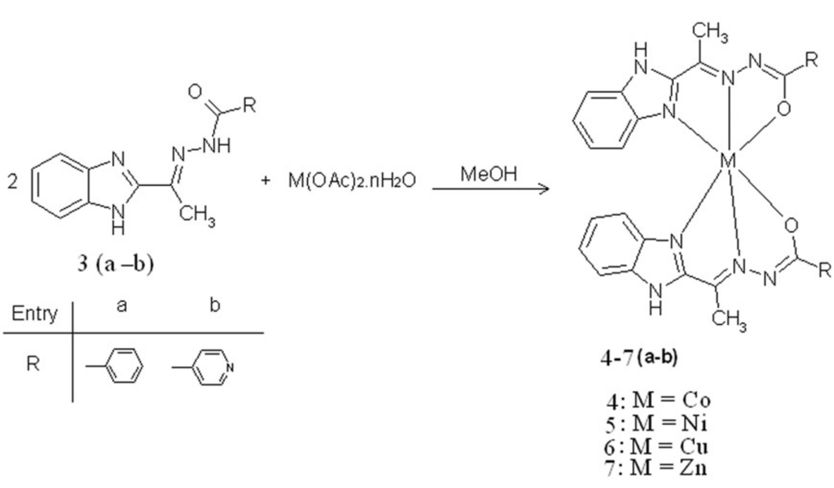
were obtained by slow evaporation of the filtrate of reaction at room temperature for about a week.

Cis-bis[2-acetylbenzimidazole isonicotinoylhydrazone]copperl(II) [Cu(BIH)$_2$] (**6b**) olive green solid. Yield: 0.173 g (56%). The m.p. decomposes at 290°C. ESI MS: *m/z* 620.14 (M$^+$). Anal. Calcd for $(C_{15}H_{12}N_5O)_2Cu$: C, 58.13; H, 3.87; N, 22.60. Found: C, 57.89; H, 4.19; N, 22.31. Λ_M (mMho cm^2 mol^{-1}): 9.68. UV-Vis (nm, $\log\varepsilon$): 275 (4.39), 340 (4.53), 395 (4.65), 686 (2.00). Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1500, 1460, 1360, 1300, 1170, 1130, 1040, 960, 820, 750, 680.

Cis-bis[2-acetylbenzimidazole isonicotinoylhydrazone]zinc(II) [Zn(BIH)$_2$] (**7b**) tan solid. Yield: 0.183 g (59%). The m.p. decomposes at 295°C. ESI MS: *m/z* 621.15 (M$^+$) Anal. Calcd for $(C_{15}H_{12}N_5O)_2Zn$: C, 57.96; H, 3.86; N, 22.54. Found: C, 57.54; H, 4.11; N, 22.25. Λ_M (mMho cm^2 mol^{-1}): 14.50. UV-Vis (nm, $\log\varepsilon$): 275 (4.65), 385 (4.49). ^{1}H-NMR (ppm): 11.121 (s, NH of benzimidazole), 7.063–8.598 (br, ArH), 2.776 (s, 3H, CH$_3$). ^{13}C-NMR: 172.013, 150.762, 150.248, 144.234, 142.220, 140.152, 135.507, 124.208, 123.838, 122.394, 116.995, 113.283, 13.124. Significant infrared bands (cm^{-1}): 3400, 3100, 1570, 1510, 1480, 1420, 1360, 1310, 1240, 1190, 1140, 1070, 1020, 970, 860, 830, 750, 700, 670.

3. Results and discussion

The Schiff base ligands (**3a**, **b**) used in this work were synthesized by the condensation of acid hydrazides (**2a**–**b**) with 2-acetylbenzimidazole (**1**) in a 1 : 1 mole ratio in ethanol (scheme 1). They were characterized based on physicochemical measurements. Results of elemental analysis, infrared, and ^{1}H-NMR as well as ^{13}C-NMR and mass spectral data are in accord with the expected structures. Metallation of these ligands with metal(II) acetate [metal(II) = Co(II), Ni(II), Cu(II), and Zn(II)] in a 2 : 1 ligand : metal mole ratio yielded six coordinate complexes **4**–**7**, in which the Schiff bases are N, N, O-tridentate ligands forming stable five-membered rings by binding with 2-acetylbenzimidazole-N, the imine-N, and the amide-O atoms (scheme 2).



Scheme 2. Synthesis of some metal(II) complexes of the present ligands.

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3.1. *Conductivity measurements*

Molar conductance of the complexes in DMSO 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 metal(II).

3.2. *IR spectra*

The IR spectra of the ligands have prominent bands at 3400 and 1670 cm^{-1} due to N–H and C=O stretching modes, respectively. The band due to C=O disappears on complexation and a new C–O band at 1040–1080 cm^{-1} appeared. Bands due to C=N and NH of benzimidazole are observed in all spectra of ligands and complexes.

3.3. *Mass spectra*

Mass spectra of the ligands show a peak due to the molecular mass plus a proton, $(M+H)^+$, consistent with the molecular structure of the ligand. Mass spectra of complexes show a peak due to ligand plus proton and the molecular ion peak of the complex, consistent with the proposed structure, and it also indicates that each ligand lost one proton upon complexation. The molecular ion peaks of the complexes contain individual peaks for isotopes of the metals with the known relative abundance of each metal as well as isotopic contributions for carbon and hydrogen which produce $(M+1)$ and $(M+2)$ peaks. Here is an explanation of the mass spectrometric data of one sample with this example being applicable for the other samples as well. In the case of sample **6b**, the value of the molecular ion would be $m/z=619$. Nevertheless, ESI-MS in the positive mode was used to measure these samples. Accordingly, the molecular ions $[M+H]^+$ were obtained each time instead of $[M]^+$, and thus, the value 620 instead of 619 was measured. Regarding the isotopic profile, one needs to keep in mind that the spectrum not only has the isotopic profile of Cu ions but also that of the ligand, which is connected twice to the Cu ion. Consequently, this compound contains a Cu atom, 30 C, 24 H, 10 N, and 2 O. Such a compound without Cu would have the isotopic profile: $[M+H]^+$, $[M+H+1]^+$, and $[M+H+2]^+$, respectively, with different intensities of course; the profile and the corresponding intensities can be calculated from automatic calculators in the website [25]. The addition of Cu to the ligands will lead to the constellation: $[M+H]^+$, $[M+H+1]^+$ and $[M+H+2]^+$, $[M+H+3]^+$, $[M+H+4]^+$. The first isotope of Cu would combine with the ligands resulting in the molecular ions: $[M+H]^+$, $[M+H+1]^+$, and $[M+H+2]^+$. The second isotope (which differs by $m/z=2$ from the first) would result in the profile: $[M+H+2]^+$, $[M+H+3]^+$, $[M+H+4]^+$. As both profiles share the molecular ion $[M+H+2]^+$, one obtains five peaks in the spectrum, with the third peak (which corresponds to $[M+H+2]^+$) having more intensity than the second peak, $[M+H+1]^+$. This reflects that the intensities of both $[M+H+2]^+$ peaks add up.

3.4. *NMR spectra*

^{1}H-NMR spectra for the ligands contain peaks corresponding to various protons. ^{13}C-NMR spectra for the ligands contain peaks for various carbons in each ligand. ^{1}H-NMR spectra for the complexes of Co(II), Ni(II), and Cu(II) were not helpful for

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identification due to their paramagnetism. ^{1}H-NMR spectra of the zinc complexes (**7a**, **b**) gave some information about these compounds. No peak was detected for NH of the amide, evidence for the involvement of nitrogen in coordination to zinc. Some changes in the aromatic region and its chemical shift can be observed, but the complexity of the signals does not allow interpretation. The ^{13}C-NMR spectra of **7a** and **b** show the correct number of signals, 14 signals from **7a** and 13 signals from **7b**, in accord with the suggested structures.

3.5. *Electronic spectra*

Absorption spectra were obtained in DMF and the resulting data are given in Section 2. A strong band at 375–400 nm and two or more moderately intense bands at 270–345 nm are observed. The intense band near 395 nm may be associated with a charge transfer (CT) transition. The bands below 345 nm are also observed in the free ligand (245–355 nm), and hence can be attributed to intraligand transitions. Zinc complexes, with d^{10} electronic configuration, have not allowed the d–d transition. The other complexes exhibited one weak and broad peak at 710, 896, and 650 nm for **4a**–**6a** and at 918, 906, and 686 nm for **4b**–**6b**, respectively. These observations are in line with common spectral features of d-block metal complexes. CT gives 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–n^* and n–n^* bands) often occur at higher energies than ‘d–d’ absorptions [26].

3.6. *Description of the crystal structures*

The crystal of $Co(BBH)_2$ has one CH_3OH in the asymmetric unit, but the crystal of $Ni(BIH)_2$ does not. The complexes display similar coordination geometry. ORTEP representations of the complexes are shown in figures 1 and 2. Selected bond lengths and angles are listed in table 1. The structure consists of two tridentate ligands coordinating cobalt(II) such that the deprotonated ligands produce a neutral cobalt(II) complex containing a CoN_4O_2 meridional coordination sphere (figure 1). Each of the two ligands provides benzimidazole-N, imine-N, and amide-O for coordination, forming two five-membered chelate rings upon chelation with cobalt(II).

The plane of the distorted octahedron is defined by two oxygen atoms and two nitrogen atoms, while the two apical positions are occupied by nitrogen atoms. Distortion of the coordination sphere is due to ligand rigidity, as observed in similar complexes [19, 20]. The angles at Co show deviations (figure 1 and table 1), for example, N_2–Co–O_1 angle: 81.57(5)° and N_2–Co–N_{22}: 82.77(5)° have deviation from 90°, while N_2–Co–N_2': 178.23(5)° and O_1–Co–N_{22}: 164.31(5)° deviate from an ideal 180°. The two ligands are almost equivalent in their bond angles and distances. Variations of the bond lengths are 0.004 Å at most. Intraligand distances conform with the enolate form of both ligands. The distances N_1–C_1, 1.330(2) and N_1'–C_1', 1.326(2) are short compared to a typical single bond (1.52 Å). C_1–O_1, 1.2955(19) and C_1'–O_1', 1.2998(19) are lengthened compared with the normal ketonic bond length of 1.23 Å.

Small deviations from planarity of the ligand in $Co(BBH)_2$ are obvious by looking at the torsion angles: N_1–N_2–C_2–C_{21} has a dihedral angle of 1.732°, C_2–N_2–N_1–C_1 an angle of 5.378°, N_2–N_1–C_1–C_{11} an angle of 4.362° in one ligand coordinated to cobalt,

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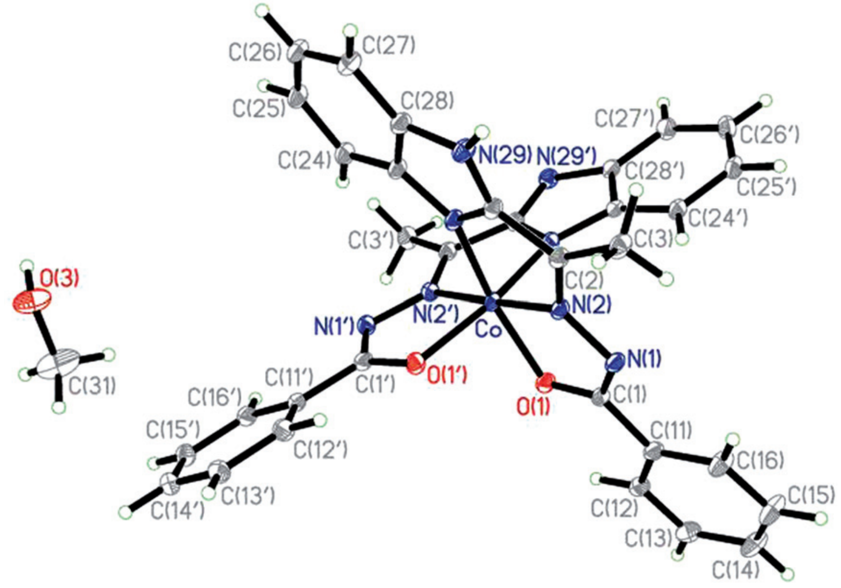

Figure 1. Structure of $Co(BBH)_2$ (ORTEP representation, 50% probability plot).

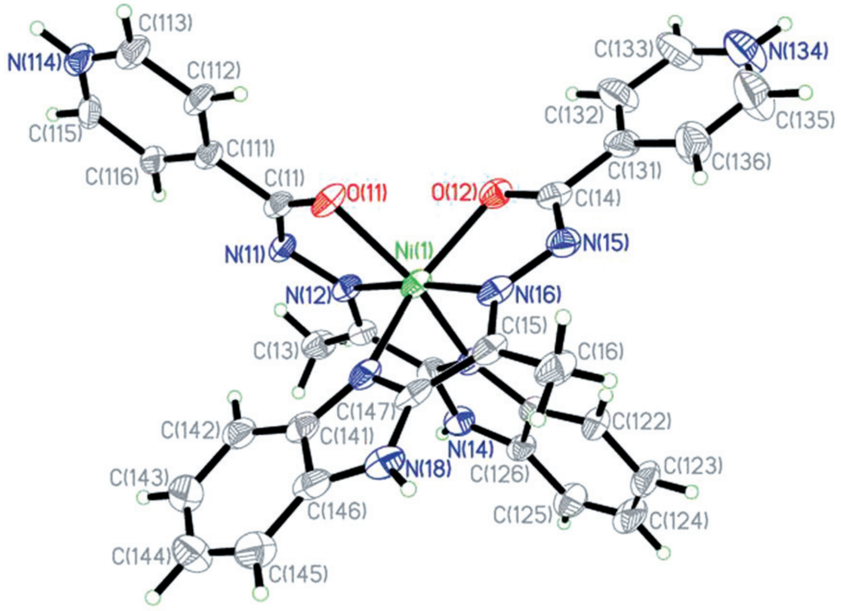

Figure 2. Structure of $Ni(BIH)_2$ (ORTEP representation, 50% probability plot).

and $N_{2'}$–$C_{2'}$–$C_{21'}$–$N_{22'}$ has a dihedral angle of 2.173°, $N_{1'}$–$N_{2'}$–$C_{2'}$–$C_{21'}$ an angle of 3.446°, $N_{2'}$–$N_{1'}$–$C_{1'}$–$C_{11'}$ an angle of 1.777° in the other.

The structure of $Ni(BIH)_2$ has the same general description, the same mode of bonding and the same pattern of distortion as $Co(BBH)_2$. Angles at Ni are similar to those in $Co(BBH)_2$ (figure 2). In $Ni(BIH)_2$ the two ligands are equivalent in binding

Table 1. Important bond lengths (Å) and angles (°) for Co(BBH)$_2$ and Ni(BIH)$_2$.

Co(BBH)$_2$		Ni(BIH)$_2$	
Co–N(2′)	1.8746(13)	Ni(1)–N(16)	2.013(3)
Co–N(2)	1.8752(14)	Ni–N(12)	2.016(3)
Co–N(22′)	1.9054(13)	Ni–N(17)	2.080(3)
Co–O(1′)	1.9070(11)	Ni(1)–N(13)	2.084(3)
Co–O(1)	1.9168(11)	Ni(1)–O(11)	2.108(2)
Co–N(22)	1.9222(13)	Ni(1)–O(12)	2.129(3)
O(1)–C(1)	1.2955(19)	O(11)–C(11)	1.255(4)
N(1)–C(1)	1.330(2)	N(11)–C(11)	1.342(4)
N(1)–N(2)	1.3721(18)	N(11)–N(12)	1.367(3)
N(2)–C(2)	1.297(2)	N(12)–C(12)	1.285(4)
N(22)–C(21)	1.336(2)	N(13)–C(127)	1.327(4)
C(2)–C(21)	1.453(2)	C(12)–C(127)	1.463(5)
N(2′)–Co–N(2)	178.23(5)	N(16)–Ni1–N(12)	174.08(11)
N(2′)–Co–N(22′)	82.98(6)	N(16)–Ni1–N(17)	78.48(13)
N(2)–Co–N(22′)	95.90(6)	N(12)–Ni1–N(17)	99.24(12)
N(2′)–Co–O(1′)	81.78(5)	N(16)–Ni1–N(13)	95.98(11)
N(2)–Co–O(1′)	99.37(5)	N(12)–Ni1–N(13)	78.61(11)
N(22′)–Co–O(1′)	164.69(5)	N(17)–Ni1–N(13)	92.80(11)
N(2′)–Co–O(1)	99.78(5)	N(16)–Ni1–O(11)	109.62(10)
N(2)–Co–O(1)	81.57(5)	N(12)–Ni1–O(11)	75.90(10)
N(22′)–Co–O(1)	89.70(5)	N(17)–Ni1–O(11)	94.54(10)
O(1′)–Co–O(1)	91.45(5)	N(13)–Ni1–O(11)	154.29(11)
N(2′)–Co–N(22)	95.89(6)	N(16)–Ni1–O(12)	75.77(12)
N(2)–Co–N(22)	82.77(5)	N(12)–Ni1–O(12)	106.83(11)
N(22′)–Co–N(22)	92.89(6)	N(17)–Ni1–O(12)	153.85(11)
O(1′)–Co–N(22)	90.12(5)	N(13)–Ni1–O(12)	94.32(10)
O(1)–Co–N(22)	164.31(5)	O(11)–Ni1–O(12)	89.86(10)

Table 2. Crystal data and structure refinement for Co(BBH)$_2$ and Ni(BIH)$_2$.

Empirical formula	$C_{33}H_{29}CoN_8O_3$	$C_{60}H_{51}N_{20}Ni_2O_4$
Formula weight	644.57	1233.63
Temperature (K)	150	100
Wavelength (Å)	1.54178	1.54178
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions (Å, °)		
a	9.9010(3)	14.3156(2)
b	9.9705(4)	24.7402(4)
c	15.8141(6)	19.8215(3)
α	96.424(2)	90
β	94.1580(10)	98.7761(7)
γ	92.153(2)	90
Volume (Å^3), Z	1545.60(10), 2	6938.01(18), 4
Calculated density (g cm^{-3})	1.385	1.181
Absorption coefficient (mm^{-1})	4.747	1.131
F(000)	668	2556
θ range for data collection (°)	2.82–69.68	2.88–71.04
Reflections collected	74,747	116,846
Independent reflection	5759 [R(int) = 0.042]	13,314 [R(int) = 0.058]
Max. and min. transmission	0.7887 and 0.5554	0.9558 and 0.8164
Parameters	410	779
Goodness-of-fit (GOF)[a] on F^2	1.048	0.846
Final R indices $[I > 2\sigma(I)]$[bc]	$R_1 = 0.0353$, $wR_2 = 0.0972$	$R_1 = 0.0593$, $wR_2 = 0.1510$

[a] $\mathrm{GOF} = [\Sigma[w(F_o^2 - F_c^2)^2]/M - N]^{1/2}$ (M = number of reflections, N = number of parameters refined).

[b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o$

[c] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

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to nickel. Details of the structures of the two complexes are included in table 2 for comparison.

4. Conclusion

Two tridenatate NNO-donor ligands, 2-acetylbenzimidazole benzoylhydrazone and 2-acetylbenzimidazole isonicotinoylbhydrazone, have been prepared and characterized. M(II)L_2 complexes (M = Co, Ni, Cu, and Zn) have been synthesized and characterized based on their analytical and spectral data. Crystal structure analyses of Co$(BBH)_2$ and Ni$(BIH)_2$ revealed that each metal is coordinated by two ligands, as monobasic NNO tridentate, through the benzimidazole ring nitrogen, azomethine nitrogen, and the carbonyl oxygen to form a distorted octahedral structure.

Supplementary material

Further details of the crystal structure determination can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Tel. +44 (0) 1223 762911, Email: kamila@ccdc.cam.ac.uk), by quoting the depository numbers CCDC 863-076 and CCDC 863-077.

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