

Synthesis And Characterization Of The Potassium Hydrotris(3-Methyl-4,5,6,7-Tetrahydro-2h-Indazol-2-Yl)Borate And Its Cobalt(Ii) And Zinc(Ii)Complexes

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Abstract :

The homoscorpionate ligand, hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borate $\text{KBH}(\text{C}_8\text{H}_{11}\text{N}_2)_3, \text{K}[\text{Tp}^{\text{Me,mt}^4}]$, has been synthesized by the reaction of KBH_4 with 3-methyl-4,5,6,7-tetrahydro-2H-indazole and isolated as a potassium salt. This was followed by the synthesis of its cobalt(II) complex, bis(hydrotris((3-methyl-4,5,6,7-tetrahydro-2H-indazol-

2-yl)borato)cobalt(II), $[\text{BH}(\text{C}_8\text{H}_{11}\text{N}_2)_3]_2\text{Co}$, which has been obtained from its reaction with cobalt(II) chloride in methanol. The zinc complex, $\text{BH}(\text{C}_8\text{H}_{11}\text{N}_2)_3\text{ZnCl}$ has been readily synthesized by the reaction of ZnCl_2 with potassium hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borate in methanol and isolated in good yields. The ligand and its complexes have been characterized by elemental analysis, mass spectrometry, IR spectroscopy, UV-visible spectroscopy and NMR spectroscopy.

Keywords :

Homoscorpionate; tris(pyrazolyl) borate; ligand; hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borate; complexes; cobalt; zinc.

1. Introduction :

Hydrotris(pyrazolyl)borate (Tp) ligands have been widely used in organometallic and coordination chemistry since their initial development by Trofimenko^[1]. The basic skeleton of the ligand involves pyrazole units bonded to a boron atom via the nitrogen atoms by the displacement of hydrogen. They behave as monoionic tridentate ligands, and the manner in which they combine with metal ions is similar to the grabbing and stinging

action of a scorpion, hence Trofimenko has given them the name “scorpionates”^[2].

Tris(pyrazolyl) borate ligands have proven to be extremely popular for coordination chemists in a wide range of applications because of their ease of synthesis, ease of functionalization, and the steric protection which they afford to transition metal centers^[3]. Furthermore, the steric and electronic properties of the pyrazolyl donors can be modified by variation of the 3 and 5 substituents and thus providing attractive properties for the Tp-metal complex. Tris(pyrazolyl)borate derivatives with bulky substituents at the pyrazolyl C-3 positions form four-coordinate pseudo-tetrahedral complexes in which a protective screen around the fourth coordination site allows the stabilization of low-coordinate complexes which would otherwise be inaccessible or highly reactive^[4]. Tris (pyrazolyl) borate ligands (generally abbreviated as Tp^x) are formally analogous to cyclopentadienyl (Cp⁻) ligand, in that both are six-electron (ionic model) or five-electron donor (covalent model) ligands. They are weak-field hard σ -N donors, which tend to form fac-octahedral complexes, while Cp ligands are typically $^5\eta$ π -donors and tend to form tetrahedral

complexes. Their overall donor properties are relatively weaker than those of the cyclopentadienyls^[2,5].

Scorpionate ligands have been used for a number of different purposes, including biomedical applications^[6,7], enzyme modeling^[8], ring-opening polymerization of lactides^[9], metal ion extraction^[10], polymerization of olefins^[11-13] and C–H activation^[14,15].

Several tris (pyrazolyl) borate complexes of Co(II), which are well-defined, have been reported. These include $[\text{CoTp}^{\text{tBu}}(\text{NCS})]^{[4]}$, $[\text{Tp}^{\text{Ant}}\text{CoNCS}]^{[16]}$, $\text{Co}[\text{Tp}^{\text{4Br}}]_2^{[17]}$, $[\text{CoTp}^{\text{Cy,4Br}}\text{Cl}]^{[18]}$, $[\text{Tp}^{\text{n-C3F7,Me}}\text{CoNO}_3]^{[19]}$, $[(\text{Tp}^{\text{t-Bu,4CN}})_2\text{Co}(\text{H}_2\text{O})_2(\text{CH}_3\text{OH})_2]^{[20]}$ and the cobalt(II) carboxylate complexes supported by Tp^{iPr_2} ligand^[21]. The use of zinc tris(pyrazolyl)borate complexes to model the active sites of a number of zinc-containing enzymes has been well established by the work of Trofimenko^[3]. The interaction between the transition metal ion Zn(II) and one or two anionic tridentate chelating donors, Tp^{Ms} , $\text{Tp}^{\text{MS*}}$, $\text{Tp}^{\text{An,Me}}$, $\text{Tp}^{\text{n-C3F7,Me}}$, $[\text{Tp}^{\text{4Br}}]^-$ and $[\text{Tp}^{\text{R}}]^-$ (hydrotris-{3-arylpyrazolyl}borate) have been reported^[17,19,22-24].

In this paper, we report the synthesis and structural characterization of mono-ligand zinc(II) and bis-ligand cobalt(II) complexes with the new tris (pyrazolyl)borate ligand obtained from 3-methyl-4,5,6,7-tetrahydro-2H-indazole.

2. Experimental :

2.1. Materials and Methods :

2-Acetylcyclohexanone was purchased from Alfa Aesar. N-hexane, CHCl_3 , MeOH, $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ and petroleum ether (40-60°C and 60-80°C) were obtained from Breckland Scientific Supplies. KBH_4 was obtained from Riedel DeHaen AG. All chemicals used were of analytical grade and were used without further purification. Syntheses of complexes were carried out in the open air at room temperature.

Infrared spectra were recorded on an FT-IR spectrometer Varian 660. ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 300 MHz. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS). The UV-Visible spectra were recorded on a Cary 5000 Varian spectrometer.

2.2. Syntheses :

2.2.1. Synthesis of 3-methyl-4,5,6,7-tetrahydro-2H-indazole {(C₈H₁₂N₂), (I)} :

Two methods were adopted in the synthesis of 3-methyl-4,5,6,7-tetrahydro-2H-indazole (C₈H₁₂N₂) (I):

Method A :

Hydrazine hydrate, 3.0cm³ (3.096g, 0.061mol), was added with stirring to a solution of 2-acetylcyclohexanone, 8.0cm³ (8.624g, 0.061mol), in 3.0cm³ of ethanol. The reaction mixture was refluxed for 3 hours. The ethanol was removed under vacuum giving 7.402g of a yellowish solid in 89.2% yield. [mp: 48–50°C; elemental analysis: calculated for C₈H₁₂N₂: C, 70.55; H, 8.88; N, 20.57%; found: C, 69.55; H, 8.61; N, 20.48%; IR (cm⁻¹): ν_(NH) 3207, ν_(CH) 2841, 2919; ¹H NMR(CDCl₃): δ 1.72-1.83 (4H, multiplet, CH₂-5, CH₂-6), δ 2.21 (3H, s, CH₃), δ 8.57 broad (1H, s, NH), δ 2.65(2H, t, CH₂-4), δ 2.42 (2H, t, CH₂-7); ¹³C NMR (CDCl₃) ppm: 10.05, 19.64, 21.98, 22.73, 23.12, 112.16, 139.72, 143.23; MS:m/z: 136[M]⁺(58%), 95[C₇H₁₂-1]⁺(88%)].

Method B :

Hydrazine hydrate, 14.5cm³ (14.964g, 0.299mol), was added dropwise to 2-acetylcyclohexanone, 26.0cm³ (28.028g, 0.199mol), with stirring. The mixture was stirred at room temperature for one hour. The resulting yellow solution was dried in vacuum to give a yellowish solid (27.0g, 99% yield); mp: 48–50°C. IR(cm⁻¹): $\nu_{(\text{NH})}$ 3207.

2.2.2 Synthesis of Potassium Hydrotris (3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl) borate {KBH(C₈H₁₁N₂)₃, (II)} :

A mixture of 2.5018g (0.0183mol) of 3-methyl-4,5,6,7-tetrahydro-2H-indazole and 0.2477g (4.59x10⁻³mol) of potassium tetrahydroborate was heated gradually to 240°C in 50mL flask by a heating mantle. The mixture was kept at this temperature for one hour until hydrogen gas evolution had stopped. The mixture was cooled and hot toluene (20.0cm³) was added. The product was filtered and washed several times with hot toluene and petroleum ether (40-60°C). The product was isolated as a white powder. (yield: 1.5332g, 73% yield); [mp: over 400°C; elemental analysis: calculated for C₂₄H₃₄BKN₆.2H₂O: C, 58.53; H, 7.78; N, 17.06%; found: C, 58.34; H, 12.81; N, 17.04%; IR (cm⁻¹): $\nu_{(\text{BH})}$ 2410, $\nu_{(\text{CH})}$ 2846, 2931; ¹H

NMR (CDCl₃): δ 2.63 (6H, t, CH₂-4), δ 2.43 (6H, t, CH₂-7), δ 2.19 (9H, s, CH₃), δ 1.72-1.80 (12H, m, CH₂-5, CH₂-6); MS: *m/z*: 135 [C₈H₁₁N₂]⁺, 490 [C₂₄H₃₈BKN₆O₂-2H]⁺.

2.2.3 Synthesis of Chloromonakis(hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borato)zinc(II){BH(C₈H₁₁N₂)₃ ZnCl, (III)} :

ZnCl₂ (0.0205g, 1.50x10⁻⁴mol) dissolved in 5.0cm³ of methanol was added slowly with stirring to a solution of KBH(C₈H₁₁N₂)₃ (0.07g, 1.53x10⁻⁴ mol) in 9.0cm³ of methanol to give a white precipitate. The product was washed with methanol and dried in vacuum (yield: 0.0593g, 74.78 %); mp: over 400°C; elemental analysis: calculated for C₂₄H₃₄BCIN₆Zn: C, 55.63; H, 6.61; N, 16.22%; found: C, 57.95; H, 12.16; N, 16.87%; IR (cm⁻¹): ν_(BH) 2486, ν_(CH) 2844, 2929; MS: *m/z*:518 [M]⁺, 383 [M-C₈H₁₁N₂]⁺,135 [C₈H₁₁N₂]⁺.

2.2.4 Synthesis of Bis (hydrotris (3- methyl -4,5,6,7- tetrahydro -2H-indazol-2-yl) borato)cobalt(II){[BH(C₈H₁₁N₂)₃]₂Co, (IV)} :

A solution of CoCl₂.6H₂O (0.0261g,1.09x10⁻⁴mol) in methanol (3.3mL) was added dropwiseto a stirred solution of KBH(C₈H₁₁N₂)₃ (0.1002g, 2.19x10⁻⁴mol) in methanol (15.0mL). A violet solution was

obtained. The reaction mixture was stirred for 24h at room temperature, and the solvent was removed under vacuum, leaving a violet powder. The product was washed with methanol and dried in vacuum (yield: 0.08g, 81%); [mp: over 400°C; elemental analysis: calculated for $C_{48}H_{68}B_2CoN_{12}.6H_2O$: C, 57.55; H, 8.05; N, 16.78%; Found: C, 57.92; H, 7.97; N, 16.49%; IR (cm^{-1}): $\nu_{(BH)}$ 2485, $\nu_{(CH)}$ 2845, 2928; MS: m/z : 893 $[M]^+$, 892 $[M-1]^+$, 135 $[C_8H_{11}N_2]^+$].

3. Results and Discussion :

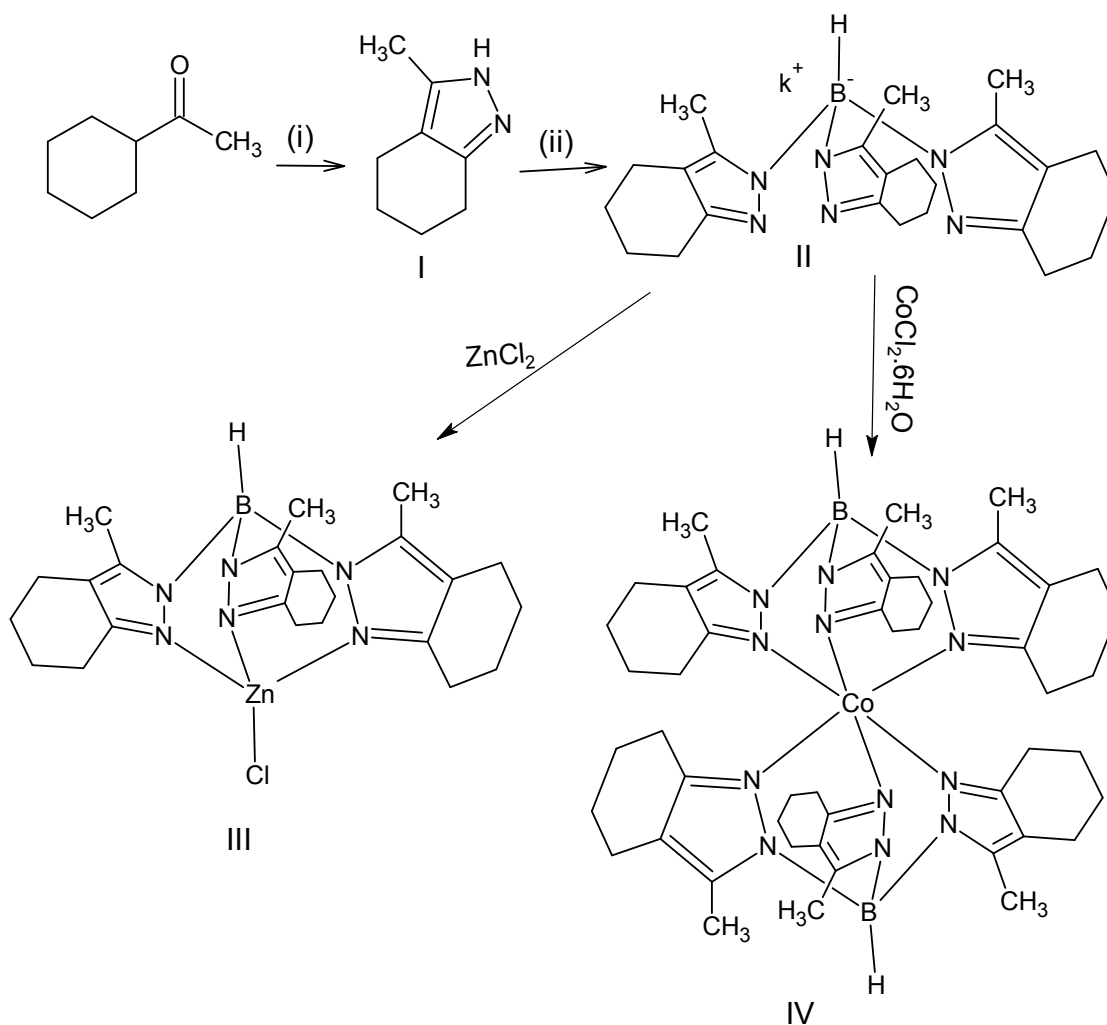
3.1. Synthesis :

3.1. Syntheses of Potassium Hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borate{ $KBH(C_8H_{11}N_2)_3$, (II)} :

The ligand was prepared according to the method outlined in scheme 1, (i) 3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-ylII was prepared by the condensation of 2-acetylcyclohexanone with hydrazine monohydrate in ethanol;(ii) the potassium salt of the ligand II was synthesized by melting the pyrazole with potassium tetrahydroborate at 240°C without any solvent. Slow heating rate at about three degrees per minute was preferred, because

when the melt was heated too quickly the pyrazole sublimates. The product was isolated by careful hot filtration from boiling toluene. The product solidifies on the filter paper during filtration. The identity of **II** was confirmed by mass spectrometry, IR, elemental analysis, and a ^1H NMR spectroscopy.

Treatment of ZnCl_2 with one equivalent of $\text{KBH}(\text{C}_8\text{H}_{11}\text{N}_2)_3$ in CH_3OH at room temperature afforded a four-coordinated zinc complex, $\text{BH}(\text{C}_8\text{H}_{11}\text{N}_2)_3\text{ZnCl}$ **III**. This complex was obtained in good yield and was found to be air-stable solid, soluble in chloroform and dichloromethane. The cobalt complex **IV** was synthesized in methanol at room temperature by the reaction of **II** with cobalt(II) chloride in a ligand to metal molar ratio of 2:1, as indicated in scheme 1. The complex was obtained in high yield. The ligand is soluble in water and methanol but slightly soluble in chloroform and dichloromethane. The cobalt complex is soluble in chloroform and dichloromethane. Identification of the complexes was established on the basis of elemental analysis, IR spectroscopy and by mass spectrometry.



Scheme 1: Synthesis of the potassium salt of the ligand and its complexes.

(i) NH₂-NH₂.H₂O in refluxing EtOH for 3 h;(ii):KBH₄,240 °C.

3.2. Characterization :

3.2.1.3-methyl-4,5,6,7-tetrahydro-2H-indazole ($C_8H_{12}N_2$) (I) :

The IR spectrum of compounds **I** shows bands at 3207cm^{-1} which is assigned to stretching vibration of the N-H group. The bands in the range $2841\text{-}2919\text{cm}^{-1}$ can be attributed to the stretching vibrations of the aliphatic C-H groups in all compounds. The ^1H NMR spectrum of **I** shows: (a) a slightly broad signal at 8.57ppm, attributed to the proton of the NH, (b) a triplet at 2.65ppm due to $\text{CH}_2\text{-4}$, (c) a triplet at 2.42ppm due to $\text{CH}_2\text{-7}$, (d) a signal at 2.21ppm for the methyl group, and (e) a multiplet at 1.72-1.83ppm due to $\text{CH}_2\text{-5}$ and $\text{CH}_2\text{-6}$. The ^{13}C NMR spectrum of **I** shows peaks at 10.05ppm due to (CH_3), 19.64ppm due to ($\text{CH}_2\text{-4}$), 21.98ppm due to ($\text{CH}_2\text{-5}$), 22.73ppm due to ($\text{CH}_2\text{-6}$), 23.12ppm due to ($\text{CH}_2\text{-7}$), 112.16ppm due to (C-3a), 139.72ppm due to (C-3) and 143.23ppm due to (C-7a). The mass spectrum of **I** showed parent ions $[\text{M}]^+$ and $[\text{M}+1]^+$ at m/z 136 and 137, respectively. The peak at m/z 109 was assigned to the fragment $[\text{C}_6\text{H}_9\text{N}_2]^+$. CHN elemental analysis results for compound **I** are quite close to those corresponding to the proposed molecular formula.

3.2.2. Potassium Hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borate {KBH(C₈H₁₁N₂)₃, (II)} :

The IR spectrum of compound **II** shows a band at 2410 cm⁻¹, which is assigned to the stretching vibration of the B-H group. This band represents an important feature of the IR spectra of this type of compounds, hydrotris(pyrazolyl)borate (Tp), and provides a good tool for identifying them. The bands in the range 2841-2960cm⁻¹ in the IR spectrum of compound **II** can be attributed to the stretching vibrations of the aliphatic C-H groups. The ¹H NMR spectrum of **II** shows a multiplet at 1.72-1.80ppm due to CH₂-5, CH₂-6, a signal at 2.19ppm due to CH₃, a triplet at 2.63ppm due to CH₂-4 and a triplet 2.43ppm due to CH₂-7.

The mass spectrum of **II** showed a series of peaks clearly representing the fragments derived from the parent ion. The peak at m/z 490 can be assigned to [C₂₄H₃₈BKN₆O₂-2H]⁺ and the peak at m/z 135 was assigned to the fragment [C₈H₁₁N₂]⁺. CHN elemental analysis results for compound **II** are quite close to those corresponding to the proposed molecular formula. However, the hydrogen content was not consistent with the proposed formula. This could be due to experimental errors since different results were obtained at two laboratories.

The UV-visible spectrum of the potassium salt of the ligand **II** has been recorded in dichloromethane. It shows very strong absorption bands at 234 and 248 nm, respectively, which can be assigned to the π - π^* transition of the ligand.

3.2.3 Chloromonakis(hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borato)zinc(II){BH(C₈H₁₁N₂)₃ ZnCl, (III)} :

The IR spectrum of compound **III** reveals a medium absorption at 2486 cm⁻¹, which can be attributed to the B-H stretching vibration; the same band in the case of Zn[HB(4-Brpz)₃]₂ was reported at 2460 cm⁻¹[14]. This band generally shifts to higher frequencies with respect to that of the potassium salt of the ligand K[HB(C₈H₁₁N₂)₃] (2410 cm⁻¹), and appears as a single peak. The bands at 2844-2929 cm⁻¹ are assigned to the stretching vibrations of the aliphatic C-H groups. The bands at 1564-1065 cm⁻¹ are assigned to the C=N and C=C vibrations from the pyrazole rings and finally the B-N stretching vibrations are observed at ca. 1400 cm⁻¹. The characteristic absorption bands of the pyrazole ring of the coordinated tris(pyrazolyl)borate of complex **III**, which are in the range of 1564-1064 cm⁻¹, are similar to the free hydrotris(pyrazolyl)borate ligand, including characteristic absorption of $\nu_{C=N}$, $\nu_{C=C}$, ν_{N-N} , but it was hard to identify the bands because the peaks were overlapped.

The mass spectrum of **III** gave its molecular ion $[M]^+$ at m/z 518. A series of peaks clearly representing the fragments derived from parent ion were detected and a peak due to the fragment $[C_8H_{11}N_2]$ was observed at m/z 135. CHN elemental analysis results for compound **III** are quite close to those corresponding to the proposed molecular formula. However, the hydrogen content was not consistent with the proposed formula. This could be due to experimental errors since different results were obtained at two laboratories.

3.2.4 Bis (hydrotris ((3-methyl -4,5,6,7- tetrahydro -2H-indazol-2-yl) borato)cobalt(II) $\{[BH(C_8H_{11}N_2)_3]_2Co, (IV)\}$:

In the IR spectrum of complex $[BH(C_8H_{11}N_2)_3]_2Co$ **IV**, the absorption band due to $\nu_{(B-H)}$ stretching, has been observed at 2485cm^{-1} . This band has shifted to higher frequencies with respect to that of the potassium ligand salt $K[HB(C_8H_{11}N_2)_3]$ (2410cm^{-1}) and appears as a single neat peak. The B–N stretching vibration was observed as medium intensity at ca. 1400cm^{-1} ^[25].

Mass spectrometry was used in the characterization of the cobalt complex **IV**. The mass spectrum of **IV** showed a parent ion $[M]^+$ peak at

m/z 893 corresponding to the molecular weight of the complex. The peak at m/z 312 was assigned to the fragment $[C_{14}H_{19}BCoN_4]^+$. The peak at m/z 135 was assigned to the fragment $[C_8H_{11}N_2]^+$. This peak was also observed in the mass spectrum of II. Another peak, observed at m/z 81, was assigned to the fragment $[C_4H_5N_2]^+$. CHN elemental analysis for compound **IV** are quite close to those corresponding to the proposed molecular formula.

The UV–Vis spectra of complexes **IV** (figure 1) shows very strong absorption bands at 234 and 248 nm, respectively, which can be assigned to the π - π^* transition of the ligand. Absorption bands could be observed in the region of 290–400 nm, suggesting (MLCT) transitions. In the visible region, two bands were observed at 550 and 612 nm; whereas, two absorption bands were observed at 470 and 512 nm for aqueous solution of $CoCl_2 \cdot 6H_2O$. In complex **IV**, the two bands at 550 and 612 nm are due to ν_3 (${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$), ν_2 (${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$), respectively, and the spin allowed band ν_1 (${}^4T_{1g} \rightarrow {}^4T_{2g}$) was not observed. From comparison between bands in the spectrum of $CoCl_2 \cdot 6H_2O$ and the spectrum of complex **IV** an octahedral geometry was suggested for the complex. Moreover, complex **IV** had a violet color.

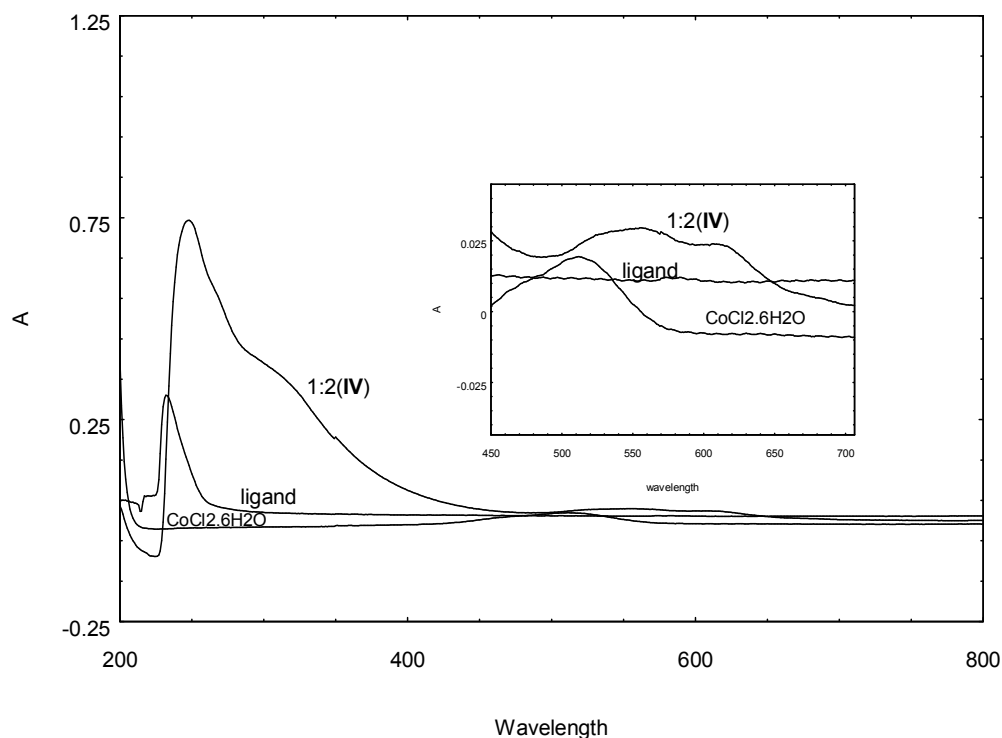


Figure.1. UV-Vis spectra of compounds **II**, **IV** and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, the wavelength is recorded in nm

4. Conclusion :

In this work, we have demonstrated that potassium hydrotris(3-methyl-4,5,6,7-tetrahydro-2H-indazol-2-yl)borate $\text{KBH}(\text{C}_8\text{H}_{11}\text{N}_2)_3$ $[\text{Tp}^{\text{Me,mt}4}]^-$, could be synthesized from the reaction of KBH_4 with 3-methyl-4,5,6,7-tetrahydro-2H-indazole and isolated in good yield. Zinc(II) and

cobalt(II) complexes have been obtained from reaction of $\text{KBH}(\text{C}_8\text{H}_{11}\text{N}_2)_3$ with the appropriate metal chloride in a 1:1 and 2:1 ligand to metal molar ratios, respectively. These complexes are stable in air at room temperature. The ligand and its metal complexes have been characterized by elemental analysis, mass spectrometry, IR spectroscopy, UV-visible spectroscopy and, in the case of the starting material and the ligand, ^1H NMR spectroscopy. Based on the UV-visible spectra and mass spectrum, an octahedral geometry was suggested for the cobalt complex. On the other hand, the zinc complex was proposed to have a tetrahedral geometry in which three sites around the zinc atom are occupied by the nitrogen atoms of the ligand and the fourth site is occupied by a chlorine atom.

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