مجلة جامعة الزاوية للعلوم الطبيعية
University of Zawia Journal of Natural Sciences *(UZJNS)*
https://journals.zu.edu.ly/index.php/UZJNS ISSN: 3078-4999

Synthesis and Characterization of a Fluorinated Tris(pyrazolyl)Borate Ligand and its Cobalt, Nickel and Zinc Complexes

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Received 04 Jan 2025 | Accepted 09 Feb 2025 | Available online 15 Mar 2025 | DOI: 10.26629/uzjns.2025.02

ABSTRACT

Potassium salt of the fluorinated tris(pyrazolyl)borate ligand $[HB(3-(CF_3)Pz)_3]^-$ has been synthesized in a high yield by the reaction of the corresponding pyrazole with KBH_4. First, a series of new zinc (II), nickel (II), and cobalt (II) complexes of the fluorinated tris(pyrazolyl)borate ligand were prepared by reaction of the ligand with the corresponding metal chloride in methanol. Characterization of the complexes revealed that the reaction of the zinc salt with the Tp ligand gave a 1:1 metal to ligand complex [MLCl], whereas cobalt and nickel complexes were a 2:1 ligand to metal complex $[ML_2]$. All the compounds prepared in this work were characterized by elemental analysis, thermal and thermogravimetric (TGA)analysis, FT-IR spectroscopy, H^1 NMR, C^{13}NMR spectroscopy and mass spectrometry.

Keywords: *Synthesis, fluorinated, trispyrazolyl, borate, complexes, characterization.*

تخليق وتوصيف متصلة ثلاثي بايرازولايل البورات المُفلورة ومركباتها التناشقية مع الكوبلت والنيكل والزنك

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الملخص

تم تحضير ملح البوتاسيوم للمتصلة ثلاثي بايرازولايل البورات المفلورة [$(HB(3-CF_3)Pz)_3$] بنسبة إنتاجية عالية من تفاعل البايرازول المناظر مع KBH_4. هذه المتصلة تحتوي على مستبدلات (مجموعات) ساحبة للإلكترونات تجعل من الفلز المرتبط بها يمتلك خواص الكترونية وفراغية مختلفة عن نظائرها غير المفلورة.
سلسة المركبات التناسقية الأولى للخارصين و النيكل و الكوبلت تم تحضيرها من التفاعل المباشر بين المتصلة و كلوريد الفلز المناظر في الميثانول. تشخيص هده المركبات (المعقدات)، اثبت أن معقد الخارصين يتكون بنسبة 1:1 من الفلز الى المتصلة (MLCl) بينما الكوبلت و النيكل فتكون مركباتها بنسبة 1 :2 من الفلز إلى المتصلة (ML_2) رغم أن التفاعل كان على أساس النسبة 1:1.
كل المركبات التي حُضرت تم تشخيصها بالتقنيات التحليلية الاتية:
Elemental analysis, Thermal and Thermo gravimetric (TGA)analysis, FT-IR spectroscopy, ^1H spectroscopy and mass spectrometry NMR, ^{13}C NMR.

الكلمات المفتاحية: التخليق، المفلورة، تريسبيرازوليل، بورات، المركبات التناسقية، التوصيف

1. Introduction

The development of multidentate ligands to explore the coordination chemistry of metal ions in solution and the solid state and to control their reactivities in catalysis is one of the most compelling and challenging activities in chemical research [1-5].

Very little has been done on systems which contain electron-withdrawing substituent [6], i.e., tris(pyrazolyl)borate systems featuring fluorinated substituents on the pyrazolyl groups are still relatively uncommon [7].

Fluorinated ligands contain substituents with avarying degreess of steric and electronic properties [8], and their metal adducts often show properties very different from their nonfluorinated counterparts [9]. For example, the CF_3 substituent, as a good electron-withdrawing group, has been shown to have a large effect on the electronic properties of the coordinated metal [10]. Fluorinated tris(pyrazolyl)borate ligands are significantly weaker donors compared to tris(pyrazolyl)borates with hydrocarbon substituents [11].

2. EXPERIMENTAL

2.1 Materials:

All purchased materials were used without any further purification.

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2.2. Measurements:

The purity of the synthesized compounds was checked by performing TLC. The NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer. ^{1}HNMR spectra were run at 300 MHz in DMSO, at 30.0°C, ^{13}C NMR spectra were run at 125.78 MHz in DMSO (chemical shifts in δ, ppm), FT-IR spectra were recorded on a Nicolet 710 FT-IR spectrophotometer. Mass spectroscopic data were recorded on Shimdzu Qp-2010 plus. Elemental analyses were performed in a Micro analysis unit at the faculty of Science ASU and in the organic Micro analyses section OMAS on Vario EI Elementar. Thermal analysis was performed in the Central Laboratory of faculty of Science ASU.

2.3. Synthesis

2.3.1. Synthesis of fluorinated tris(pyrazolyl)borate (Tp^{CF3}):

3-(Trifluoromethyl)pyrazole Pz^{CF3}(1.00g, 7.35mmol) was added to KBH_4(0.100g, 1.83mmol). The two solids were ground together and placed into a round bottom flask and were heated in an oil bath to 165°C under nitrogen gas until about 246mL hydrogen gas had evolved. The reaction mixture was left at 165^{o}C overnight. A white solid was formed and was washed with n-hexane and dried under a vacuum. Tp^{CF3} was obtained in a yield of 0.35g (41.47%), mp:249-251^{o}C.

2.3.2. Synthesis of $[HB(3-(CF_3)Pz)_3]ZnCl$ complex :

A solution of $K[HB(3-(CF_3)Pz)_3]$(0.100g, 0.219mmol) in15.0mL of methanol was added dropwise with stirring to a solution of $ZnCl_2$ (0.030g, 0.219mmol) in 10.0mL of methanol for a period of 5min. The mixture was stirred for one hour. A white solid was formed and was collected by filtration and dried. It was obtained in a yield of 0.037g (32.74%), mp: 298-300^{o}C.

2.3.3. Synthesis of $[HB(3-(CF_3)Pz)_3]_2Ni$ complex :

$K[HB(3-(CF_3)Pz)_3]$(0.100g, 0.219 mmol) dissolved in 15.0mL of methanol was added slowly to a solution of $NiCl_2.6H_2O$ (0.0521g, 0.219mmol) dissolved in 10.0mL of methanol. The resulting mixture was stirred for two hours at room temperature. A pale blue precipitate was formed and was collected by filtration. The product, $[HB(3-(CF_3)Pz)_3]_2Ni$,was obtained in a yield of 0.097g(51.63%), mp:319^{o}C.

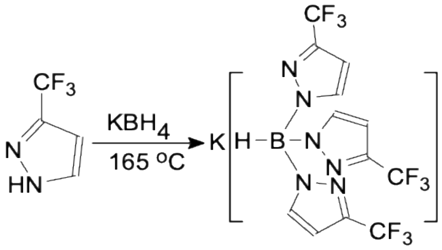
2.3.4. Synthesis of TpCF^{3}Co complex:

$K[HB(3-(CF_3)Pz)_3]$(0.100g, 0.219 mmol) dissolved in 10.0mL of methanol was added slowly to a solution of $CoCl_2.6H_2O$ (0.052g, 0.219 mmol) in 10.0mL of methanol. The resulting mixture was stirred for two hours at room temperature. A pink precipitate was obtained and collected by filtration. $[HB(3-(CF_3)Pz)_3]_2Co$ was obtained in a yield of 0.14g (73.68%), mp:205-207^{o}C.

3. Results and Discussion:

3.1. Synthesis of fluorinated tris(pyrazolyl)borate (Tp^{CF3}):

The ligand 3-(Trifluoromethyl)pyrazole (Pz^{CF3}) was synthesized according to the reaction shown in Scheme 1:



Scheme 1. preparation of $K[HB(3-(CF_3)Pz)_3]$

It was characterized by five techniques, which included elemental analysis, which showed that the C, H, and N contents were 28.83%, 1.32%, and 16.63%, respectively. This is in agreement with the calculated values for formula $[C_{12}H_7BF_9N_6K].3H_2O$: C, 28.22; H,1.37; N, 16.46%. The results of differential thermal analysis and thermogravimetric (TGA) showed a loss of weight at approximately 90^{o}C and ΔTGA = 3.825%, revealing a loss of one molecule of hygroscopic and/or crystallization water at around 90^{o}C. FT-IR spectrum, shown in Figure 1, showed an absorption band at 2436cm^{-1} for the B–H stretching vibration; this band is characteristic of these kinds of ligands and is very important in

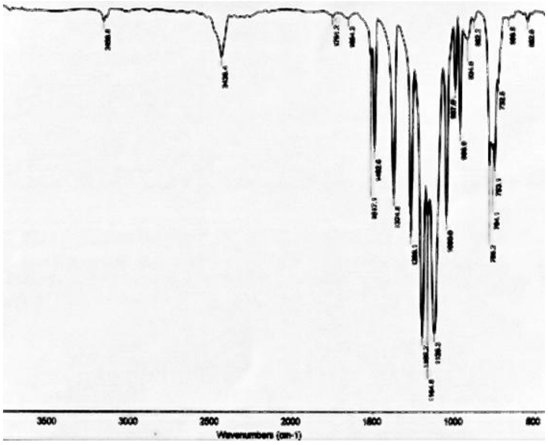


Figure 1 FT-IR spectrum of the ligand (Tp^{CF3})

confirming the formation of the Tp ligand. Bands at 1517cm^{-1} and 1493cm^{-1} are associated with the pyrazolyl ring (C=N, C=C). The CF_3 group stretching vibrations appear at 1268cm^{-1}**.**

^1H NMR spectrum, Figure 2, was run at 300 MHz at 30.0°C in dimethylsulphoxide (DMSO). It shows two peaks at δ 6.5ppm (d, 3H, J=2.1Hz) and δ 7.5ppm (d, 3H, J=0.6Hz) The peaks at 2,5 and 3.4ppm are due to the solvent.

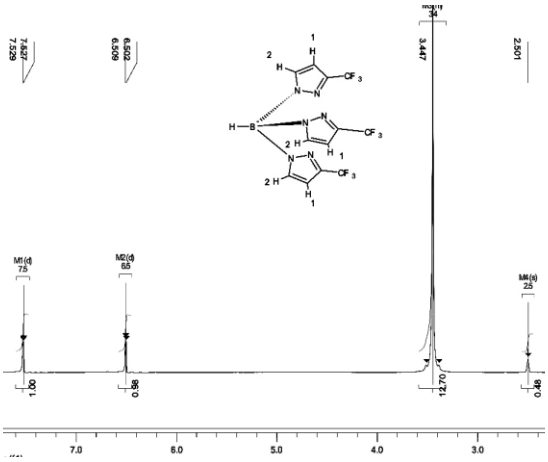


Figure 2 ^{1}HNMR spectrum of the ligand (Tp^{CF3})

^{13}C NMR spectrum, Figure 3, was run at 125.8 MHz at 30.0°C in dimethylsulphoxide (DMSO). It shows four peaks at δ 103.4ppm (s,CH),123ppm (q,CF_3,$^1J_{(C,F)}$= 267.3Hz),135.5ppm(S,CH), and 141.9ppm (q, CCF_3, $^2J_{(C,F\ )}$= 35.6Hz).

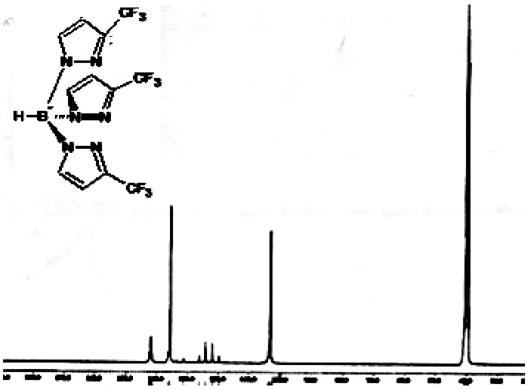
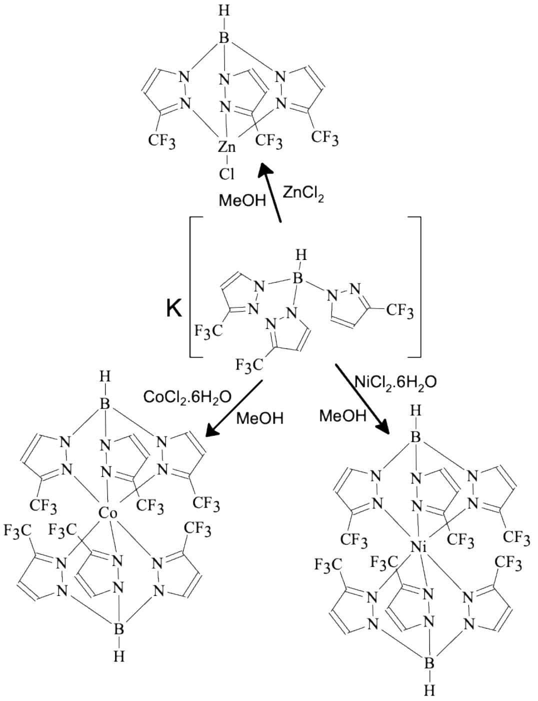


Figure 3 ^{13}C NMR spectra of the ligand (Tp^{CF3})

The electrospray ionization (ESI) mass spectrum of the ligand is shown a peak at m/z(%):495.17(16.78) $[HB(3\text{-}(CF_3)Pz)_3K.2H_2O]^+$. The base peak in the ESI spectrum occurs at m/z 455.20(100) and corresponds to $[M\text{-}H]^+$, m/z 213.17(6.00) for $[H_2B(3\text{-}(CF_3)Pz)_2\text{-}CF_3]^+$, m/z 136.13(7.00) for $[Pz^{CF3}]^+$ and at m/z 69.07(47.50) for $[CF_3]^+$.

3.2. Complexes of fluorinated tris(pyrazolyl)borate (Tp^{CF3}):

three complexes of the fluorinated tris(pyrazolyl)borate (Tp^{CF3}) with nickel, cobalt and zinc have been synthesized by direct reaction of the ligand with metal chloride in methanol. The syntheses are summarized in Scheme 2.



Scheme 2: preparation of complexes of fluorinated tris(pyrazolyl)borate

3.2.1. $[HB(3\text{-}(CF_3)Pz)_3]ZnCl$ complex :

The zinc complex, $[HB(3\text{-}(CF_3)Pz)_3]ZnCl$, was characterized by elemental analysis, thermal analysis, FT-IR spectroscopy, mass spectrometry and ^{13}C NMR spectroscopy. Elemental analysis showed that the C, H, and N contents were C, 27.02; H, 1.31; N, 15.68%**.** These are in good agreement with the calculated values: C, 27.80; H,1.35; N,16.20%. The results of differential thermal

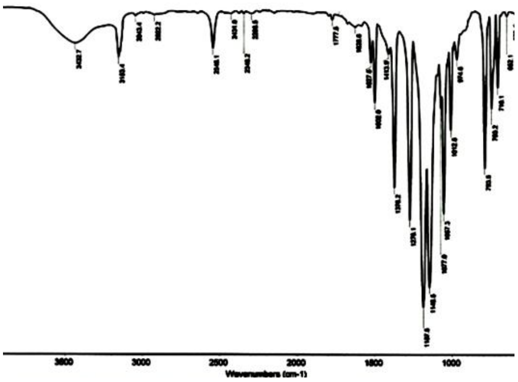


Figure 4 FT-IR spectrum of $[HB(3\text{-}(CF_3)Pz)_3]ZnCl$

analysis and thermogravimetric (TGA) are consistent with the elemental analysis through the absence of peaks under 100ºC due to the water evaporation. They show no weight loss at approximately 100ºC, which means that the complexes do not lose hygroscopic and/or crystallization water. The FT-IR spectrum, Figure 4, reveals the following characteristic absorption bands: υ(CH) (3153cm^{-1}), υ(BH) (2546cm^{-1}), υ(C=C, C=N) (1528,1502cm^{-1}) and υ(CF_3) (1276cm^{-1}).

3.2.2. Synthesis of [HB(3-(CF_3)Pz)$_3$]$_2$Ni complex:

The nickel complex, **[HB(3-(CF_3)Pz)$_3$]$_2$Ni**, was characterized by elemental analysis, thermal analysis, FT-IR spectroscopy, and mass spectrometry. Elemental analysis for $C_{24}H_{14}B_2F_{18}N_{12}Ni$ showed that the C, H, and N contents were C, 31.24; H, 1.76; N, 18.27%, These are in good agreement with the calculated values C, 32.26; H,1.56; N,18.80. The results of differential thermal analysis and thermogravimetric (TGA) are consistent with the elemental analysis. These results show no weight loss at approximately 100ºC, which means that the complexes don't lose hygroscopic and/or crystallization water. The FT-IR spectrum, Figure 5, reveals the following characteristic absorption bands: υ(CH) (3164cm^{-1}), υ(BH)(2511cm^{-1}), υ(C=C, C=N) (1523,1496cm^{-1}), υ(CF_3) (1281cm^{-1}).

(ESI) mass spectrum shows the following peaks: m/z(%):893.9(4.01) [M]$^+$, m/z(%):757.0(27.48) [M-Pz]$^+$, m/z: 136.0(4.69) [Pz^{CF3}]$^+$.

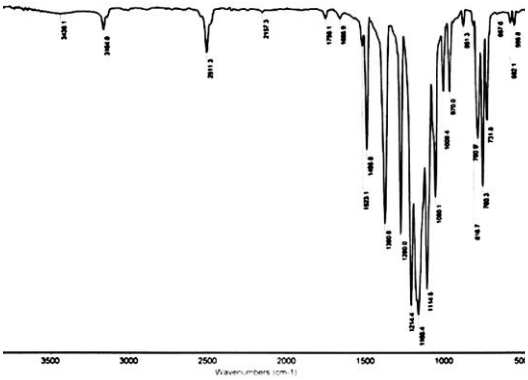


Figure 5 FT-IR spectrum of [HB(3-(CF_3)Pz)$_3$]$_2$Ni

3.2.3 Synthesis of Tp^{CF3}Co complex:

The cobalt complex, (Tp^{CF3})$_2$Co, was characterized by elemental analysis, thermal analysis, FT-IR spectroscopy, and mass spectrometry. Elemental analysis for $C_{24}H_{14}B_2F_{18}N_{12}Co$, anal.calc : C, 32.25 ; H,1.95; N,17.54. Found: C, 31.21; H, 1.56; N, 18.81. The results of differential thermal and thermogravimetric (TGA) analyses are consistent with the elemental analysis. These results show no weight loss at approximately 100ºC, which means that the complexes don't lose hygroscopic and/or crystallization water. The FT-IR spectrum, Figure 6, reveals the following characteristic absorption bands: υ(CH) (3164cm^{-1}), υ(BH)(2509cm^{-1}), υ(C=C, C=N) (1523,1498cm^{-1}), υ(CF_3) (1279cm^{-1}).

(ESI) mass spectrum shows peaks at: m/z(%):893.5(11.0) [M]$^+$, m/z(%): 757.4(8.0) [M-Pz]$^+$, m/z: 136.0(11.0) [Pz^{CF3}]$^+$.

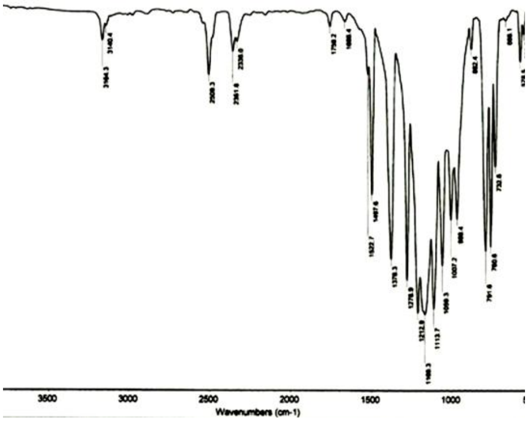


Figure 6 FT-IR spectrum of [HB(3-(CF_3)Pz)$_3$]$_2$Co

4. Conclusion:

The aim of this search was the synthesis and characterization of a fluorinated tris(pyrazolyl)borate ligand and its metal complexes. These compounds are important in coordination chemistry, biological studies, and catalysis. The synthesis of ligand required specific conditions different from its nonfluorinated counterparts to obtain a high yield, such as raising the reaction temperature stepwise at a slow rate, avoiding complex decomposition, and carrying out the reaction under nitrogen gas. Many techniques were used to characterize and confirm the structures of these compounds. The results were identical to the expected for the proposed structures, where the ligand was tripodal and behaved as tridentate through three nitrogen atoms of the pyrazole rings η^3-N, N’, N". In all complexes that were prepared, bonding with ligands was through the three nitrogens, as expected.

Acknowledgements

This work was carried out at the Department of Chemistry at Zawia University, Libyan Medical

Research Center in Zawia and Polymer Research Center in Tripoli. The authors would like to express their gratitude for providing support to this work.

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