

Comparative Study of Microwave Assisted and Conventional Synthesis of Tp*-Complexes

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Abstract: Cobalt, copper and nickel complexes with tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate (Tp*) were synthesized by the reaction of potassium tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate (KTp*) with the corresponding metal(II) chloride by using conventional reflux methods and microwave methods. The two methods were compared and the microwave method was found to be less time consuming and gave higher yields.

Keywords: Pz* [3,5-dimethyl-1H-pyrazol-1-yl], KTp* [potassium tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate], Tp*-complexes, [tris(3,5-dimethyl-1H-pyrazol-1-yl)hydroborate complexes]

1. Introduction

Pyrazole-derived ligands, known collectively as poly(pyrazolyl) ligands, are derived from two or more N-deprotonated pyrazole rings bound to a main group atom through one of the ring nitrogens [1]. The basic skeleton of the ligand involves pyrazole units bonded to a main group apex via the nitrogen atoms at the displacement of hydrogen [2]. Tris(pyrazolyl) borate (Tp^x) ligands, known as scorpionates, have attracted considerable attention and proven to be extremely popular ligands since their introduction by Trofimenko in 1967 [3-4]. They constitute one of the most widely used group of ligands in chemistry. The reaction of KTp* ligands with metal ions is expected to give either tetrahedral or octahedral complexes depending on the reactant ratios and the nature of the metal ion.

Reactions of Tp complexes have been investigated. Studies included the synthesis of complexes containing Tp in addition to other ligands with some metals such as Ni(II), Co(II) and Mn(II).

Michiue and Jordan have shown that reaction of the TITpMs and TITpMs* With MCl₄ (M=Zr, Hf) in toluene affords [ZrTpMsCl₃], [ZrTpMs*Cl₃] and [HfTpMs*Cl₃]. The complex [ZrTpMsCl₃] exhibits extremely high activity for ethylene polymerization and ethylene/hexane

copolymerization. Also, a series of TpxMCl₃ complexes (M=Ti, Zr, Tpx=TpNp, TpPh, TptBu) have been synthesized [5]. The heteroleptic picolinic acid N-oxide complexes, [Ln(Tp)₂(pnx)], (Ln=Y, Eu, Gd, Tb, Er, Yb or Lu,) have been prepared and characterized [6]. [Tp*VCl₂L] L=4-substituted pyridine N-C₅H₄-R (R= H, CH₃, C₂H₅, Ph) were prepared by replacing the dimethylformamide ligand in Tp*VC₁₂(DMF) by various N-containing heterocycles [7]. Xing and co-workers have prepared the new oxovanadium(IV) complexes VO(HB(Pz)₃)(H₂B(Pz)₂) and VO(B(Pz)₄) [8]. Chromium(III) complexes containing Tp ligands [Cr(Tp)₂][CrCl₃(Tp)], [CrCl₂(Tp)(THF)] and [HPMe₃][CrCl₃(Tp)] have been synthesized [9].

The compound Tp*MoI(CO)₂.2CH₃CN has been isolated from the reaction between [MoI₂(CO)₃(MeCN)₂] and KTp*, and has been described as a diamagnetic compound, showing well-defined ¹H NMR spectroscopic properties [10]. Carrillo and co-workers have reported the synthesis of [TpxMo(NNPhR)₂Cl] R=Ph, Me, TpX=Tp, Tp* [11].

[Tp*W(OPh){S₂C₂(CO₂Me)₂] and [Tp*W(SePh){S₂C₂(Ph)(2-quinoxaliny)] have been synthesized and determined by X-ray crystallography [12]. Zn(Tp*)Cl (Tp* = tris(3,5-dimethyl-1-pyrazolyl)borate) was investigated [13]. (3-NH(t-butyl)-5-methyl-pyrazole)_nMX₂ (M = Zn, Ni, Co, Mn; n = 3, 4; X = Cl, Br) have been synthesized [14]. [Cu(NCS)₂L¹], [Mn(NCS)₂L¹],

[Mn(NCS)₂L²] and [Zn(NCS)L²]₂[Zn(NCS)₄] complexes have been synthesized, L¹ = bis(1-(3,5-dimethylpyrazolyl)methyl)amine, L² = tris(1-(3,5-dimethylpyrazolyl)methyl)amine [15]. The V(III) complex [V(Tp^{tBu2})Cl₂] has been synthesized by the reaction of [VCl₃(THF)₃] (prepared in situ) and K(Tp^{tBu2}), Tp^{tBu2} = hydrotris(3,5-di-tert-butylpyrazolyl)borate [16].

Microwave-assisted synthesis is, in many ways, superior to traditional heating. The ability to elevate the temperature of a reaction well above the boiling point of the solvent increases the speed of reactions. Reactions are thus completed in minutes or even seconds. Yields are generally higher and the technique may provide a means of synthesizing compounds that is not available conventionally.

In a dedicated microwave reactor, reactions can be run in sealed vials under carefully controlled conditions at temperatures up to 200°C and pressures up to 20 bar. This provides the means to heat reactions much higher than conventional open-vessel conditions, in which the maximum temperature is limited to the boiling point of the solvent.

High-speed synthesis with microwaves has attracted considerable amount of attention in recent years [17]. More than 2000 articles have been published in the area of microwave assisted organic synthesis (MAOS) since the first reports on the use of microwave heating to accelerate organic

chemical transformations by the groups of Gedye and Giguere/ Majetich in 1986 [18-19]. The initial slow uptake of the technology in the late 1980s and early 1990s has been attributed to its lack of controllability and reproducibility, coupled with a general lack of understanding of the basics of microwave dielectric heating. The risks associated with the flammability of organic solvents in a microwave field and the lack of available systems for adequate temperature and pressure controls were major concerns [20].

In this work, we present a method for synthesizing complexes containing (KTp*) ligand and some transition metal atoms, (Tp*-Metal), using reflux methods and microwave techniques with a comparison between the two methods.

2. Experimental

2.1. Chemicals and Materials

All solvents used (N-hexane, petroleum ether, Chloroform, Methanol, Toluene, Ether and Acetone) were obtained from different companies and they were dried by standard methods and distilled prior to use.

The chemicals used for the synthesis were reagent grade (Table 1).

Table 1. List of chemicals used for the synthesis.

Chemicals	Formula	Molecular weight	Company
Coppr chloride dihydrate	CuCl ₂ .2H ₂ O	170.48	BDH chemicals Ltd Poole England
Cobalt chloride hexahydrate	CoCl ₂ .6H ₂ O	237.93	Avonchem - Khem King
Nickel chloride hexahydrate	NiCl ₂ .6H ₂ O	237.69	Khem King
Potassium tetraborohydrate	KBH ₄	170.4	Rledel-dehaen AG seelze-Hannover
Hydrazine sulphate	H ₆ N ₂ SO ₄	130.12	BDH chemicals Ltd Poole England
2,4-pentanedione	C ₅ H ₈ O ₂	100.12	Avocado Research chem. calsltd
Potassium carbonate	K ₂ CO ₃	138.21	Alfa Aesar

2.2. Instrumentations

Melting points were determined by using Electrothermal Digital Melting Point Apparatus model IA 9100.

Infrared spectra were recorded on IR spectrometer Varian 660. All the Tp*-Complexes were in KBr pellet for the measurement.

Mass spectra and Elemental analyses (C, H, N) were performed at the micro analytical center of Cairo University.

¹³C NMR and ¹H NMR spectra were recorded on a Bruker at 400 MHz spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS).

Microwave assisted syntheses were carried out by using Milestone Microwave.

2.3. Syntheses

2.3.1. The Ligand; Potassium Tris(3,5dimethyl pyrazolyl) Hydroborate (KTp*)

Potassium tris(3,5dimethyl pyrazolyl) hydroborate (KTp*) was synthesized with the use of microwave according to the method described in a previous publication [21]. (Yield: 90 %); m.p: >380°C. IR (cm⁻¹): ν(BH) 2436, ν(CH) 2862,

2925, 2960; ¹H NMR (DMSO): δ 2.05 (9H, CH₃), δ 3.17 (9H, CH₃), δ 5.53 (3H, CH), δ 8.53 (1H, BH); ¹³C NMR (DMSO): δ 12.4 (C4), 13.7(C5), 103.2 (C2),141.9 (C1), 144.6 (C3).

2.3.2. Synthesis of Metal-Tp* Complexes

(i) Complex of Tp* with Cobalt (II) Chloride (HI)

Two methods were adopted in the synthesis of complex (HI):

Method A (reflux):

A solution of 0.6022g of KTp* (1.79mmole, 10ml MeOH) was added drop wise to a stirred solution of 0.4822g of cobalt (II) chloride (2.02mmole, 10ml MeOH) in a 50 mL round bottom flask. The flask was fitted with a condenser and the mixture was stirred at room temperature for 5h. A blue precipitate was obtained. Recrystallization of the product was carried out in chloroform. Blue crystalline solid was obtained, 83% yield. (m.p: 170°C); IR (cm⁻¹): ν (BH) 2511.58, ν (CH) 2923.18. MS: m/z: 391[M]⁺, 95[C₅H₇N₂]⁺, 107[BH(C₅H₇N₂)]⁺, 356[BH(C₅H₇N₂)₃Co]⁺.

Method B (microwave):

A powder mixture of cobalt (II) chloride (0.3215g,

1.35mmole) and KTp* (0.4015g, 1.19mmole) was heated in a glass tube in TFM vessel on the rotating balance plate inside the microwave at 750 watt and 80°C for 17min. The rotor was cooled to room temperature. Chloroform was added to the reaction mixture and the product was washed several times with chloroform and filtered. The product was isolated as a blue powder. (Yield: 92%); m.p: 170°C; IR (cm⁻¹): ν (BH) 2511, ν (CH) 2923.

(ii) Synthesis of Nickel-Tp* Complex (H2)

Two methods were adopted in the synthesis of complex (H2):

Method A (reflux):

A solution of 0.4099g of KTp* (1.21mmole, 10ml MeOH) was added drop wise to a stirred solution of 0.3279g of nickel (II) chloride (1.37mmole, 10ml MeOH) in a 50 mL round bottom flask. The flask was fitted with a condenser and the mixture was stirred at room temperature for 5h. A purple precipitate was obtained. Recrystallization of the product was carried out in chloroform. Purple crystalline solid was obtained, 78% yield. (m.p: >380°C); IR (cm⁻¹): ν (BH) 2512.62, ν (CH) 2923.14. MS: m/z : 391[M]⁺, 95[C₅H₇N₂]⁺, 107[BH(C₅H₇N₂)]⁺, 355[BH(C₅H₇N₂)₃Ni]⁺.

Method B (microwave):

A powder mixture of nickel (II) chloride (0.3279g, 1.37mmole) and KTp* (0.4099g, 1.21mmole) was heated in a glass tube in TFM vessel on the rotating balance plate inside the microwave at 750 watt and 80°C for 17min. The rotor was cooled to room temperature. Chloroform was added to the reaction mixture and the product was washed several times with chloroform and filtered. The product was isolated as a purple powder. (Yield: 92%); m.p: > 380°C; IR (cm⁻¹): ν (BH) 2512, ν (CH) 2923.

(iii) Synthesis of Copper-Tp* Complex (H3)

Two methods were adopted in the synthesis of complex

(H3):

Method A (reflux):

A solution of 0.5954g of KTp* (1.77mmole, 10ml MeOH) was added drop wise to a stirred solution of 0.3416g of copper (II) chloride (2.00mmole, 10ml MeOH) in a 50 mL round bottom flask. The flask was fitted with a condenser and the mixture was stirred at room temperature for 5h. A green precipitate was obtained. Recrystallization of the product was carried out in chloroform. Dark-green crystalline solid was obtained, 80% yield. (m.p: 295°C); IR (cm⁻¹): ν (BH) 2513.10, ν (CH) 2922.88. MS: m/z : 391[M]⁺, 95[C₅H₇N₂]⁺, 107[BH(C₅H₇N₂)]⁺, 360[BH(C₅H₇N₂)₃Cu]⁺.

Method B (microwave):

A powder mixture of copper (II) chloride (0.3416g, 2.00mmole) and KTp* (0.5954g, 1.77mmole) was heated in a glass tube in TFM vessel on the rotating balance plate inside the microwave at 750 watt and 80°C for 17min. The rotor was cooled to room temperature. Chloroform was added to the reaction mixture and the product was washed several times with chloroform and filtered. The product was isolated as a dark-green powder. (Yield: 90%); m.p: 295°C; IR (cm⁻¹): ν (BH) 2513, ν (CH) 2922.

3. Results and Discussion

3.1. Metal-Tp* Complexes

The Co, Ni, Cu complexes (H1 to H3) were synthesized by reaction of the ligand (KTp*) with the appropriate metal (II) chloride by using conventional reflux methods and microwave methods as shown in figure 1. In the conventional reflux method, all reactions were carried out in methanol where the ligand-metal ratio was 1:1 at room temperature. The complexes were obtained in high yield percentage.

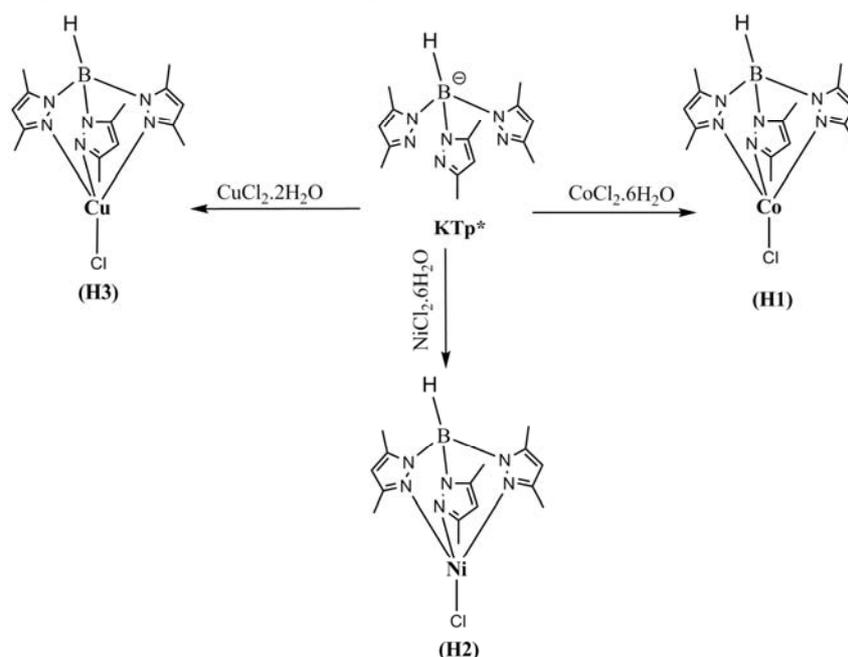


Figure 1. Synthesis of Tp* Complexes (H1 to H3).

Table 2 shows a comparison between the reflux method and the microwave method in the synthesis of various compounds prepared in this work. This comparison is made in terms of reaction yield and reaction time. As can be seen

from the table, it is evident that the microwave method gives higher yields and takes less time. In addition, the microwave method required no solvents. This made the reactions cleaner and the time required to evaporate has been saved.

Table 2. Comparison between the microwave and reflux method.

Compound	Microwave		Reflux	
	Reaction Time	%Yield	Reaction Time	%Yield
H1 - BH(C ₅ H ₇ N ₂) ₃ CoCl	17min	92%	5h	83%
H2 - BH(C ₅ H ₇ N ₂) ₃ NiCl	17min	92%	5h	78%
H3 - BH(C ₅ H ₇ N ₂) ₃ CuCl	17min	90%	5h	80%

3.2. IR Spectroscopy

Infrared spectroscopy was used in characterization of all compounds synthesized in this work. The IR spectrum of compound (KTp*), figure 2, shows a band at 2436cm⁻¹ that was assigned to the stretching vibration, $\nu_{(B-H)}$, of the B-H

group. The C=N group stretching frequency, $\nu_{(C=N)}$, occurs at 1537cm⁻¹, and the C-N group stretching frequency, $\nu_{(C-N)}$, occurs at 1028cm⁻¹. At 978cm⁻¹ band due to N-N group stretching frequency, $\nu_{(N-N)}$. The bands at 2862, 2925 and 2960cm⁻¹ can be attributed to the stretching vibrations of the aliphatic and aromatic C-H groups.

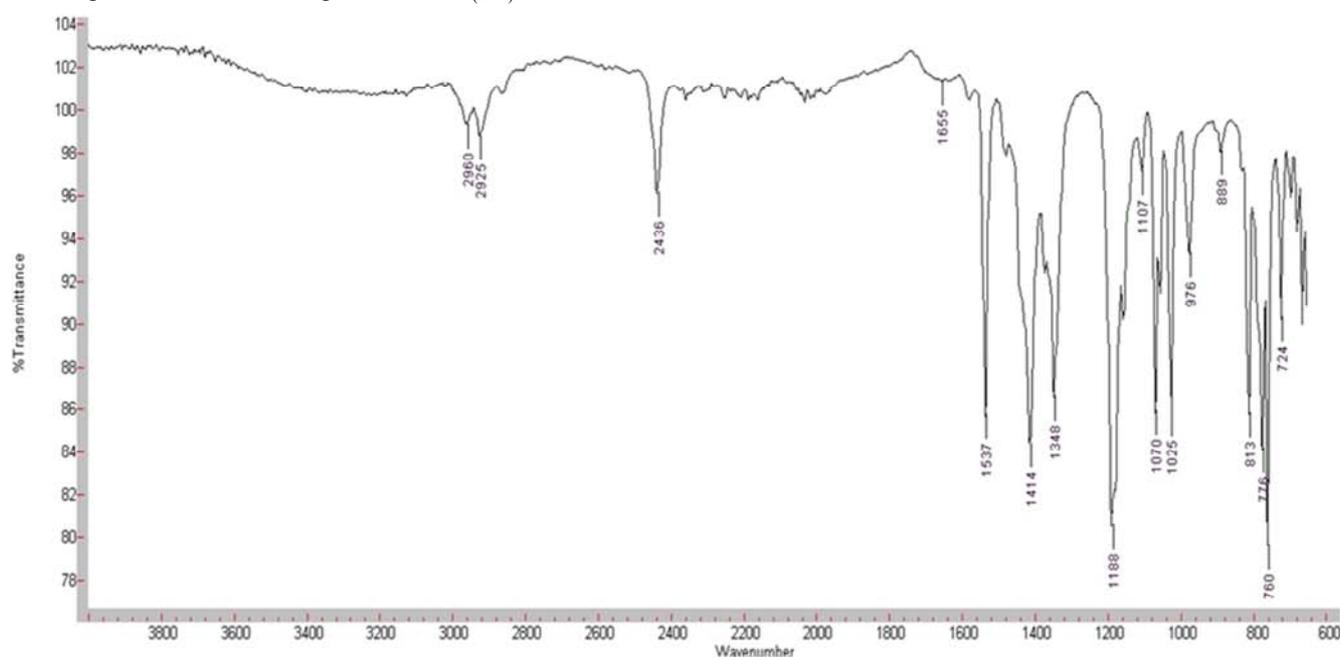


Figure 2. Infrared spectrum of (KTp*) At 1000 and 900watt.

The IR spectra of Tp* complexes, H1 to H3, figures 3, 4 and 5, respectively, are characterized an absorption band that occurs in the range 2507-2513cm⁻¹, as a single neat peak, due to $\nu_{(B-H)}$ stretching, table 3. The bands due to the 'breathing' of the pyrazole rings in the complexes occurred at unusually

high frequencies, in the range between 1540 and 1630cm⁻¹. The $\nu_{(M-N)}$ and $\nu_{(M-Cl)}$ stretching absorptions expected between 200 and 400cm⁻¹ were not observed because the infrared spectra were recorded from 600 to 4000cm⁻¹.

Table 3. IR data of Tp* complexes H1 to H3.

Complex	$\nu_{(B-H)}$	$\nu_{(C=N)}$	$\nu_{(C-N)}$	$\nu_{(N-N)}$
KTp* - K BH(C ₅ H ₇ N ₂) ₃ Ligand	2436	1537	1028	978
H1 - BH(C ₅ H ₇ N ₂) ₃ CoCl	2511	1541	1056	981.8
H2 - BH(C ₅ H ₇ N ₂) ₃ NiCl	2512	1542	1055	981.3
H3 - BH(C ₅ H ₇ N ₂) ₃ CuCl	2513	1541	1058	978.8

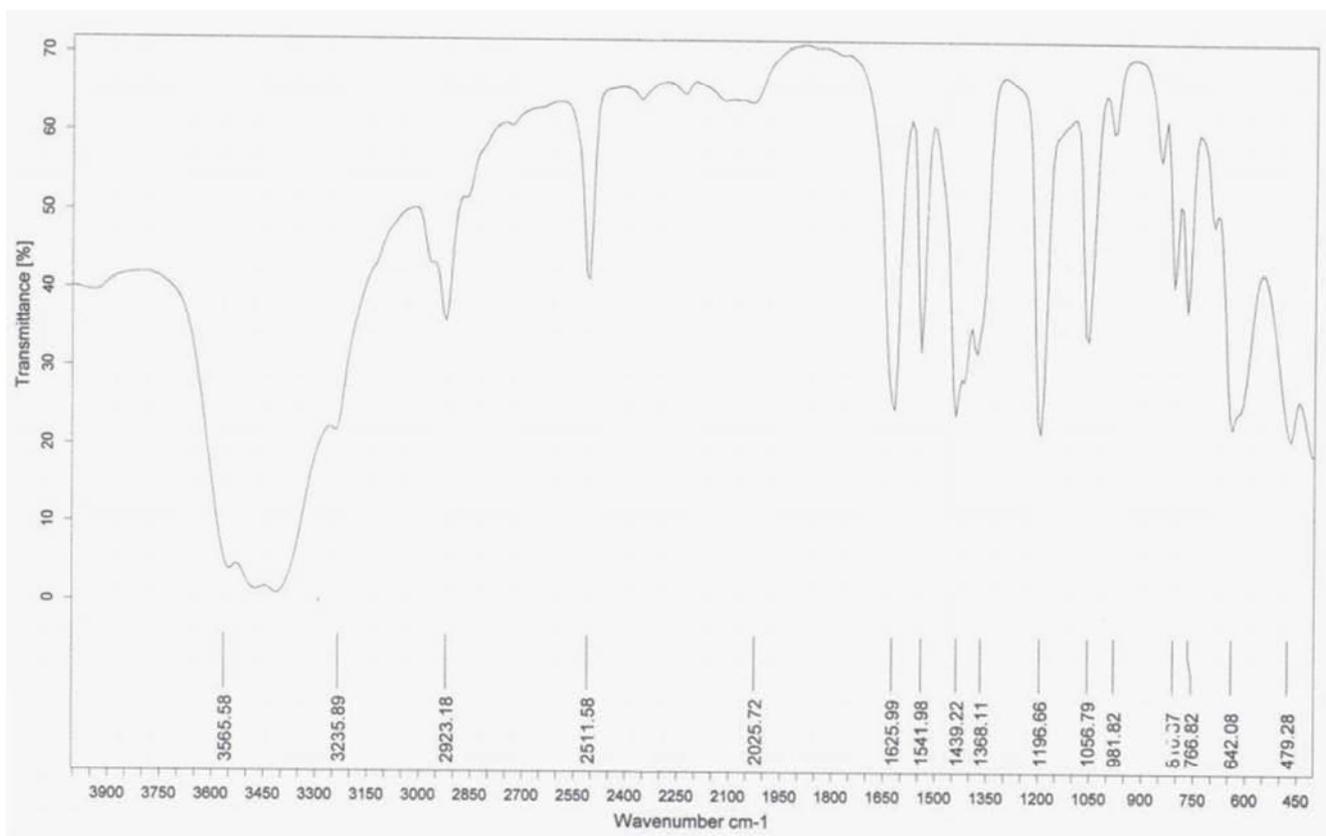


Figure 3. Infrared spectrum of (Tp*-Co) complex (H1).

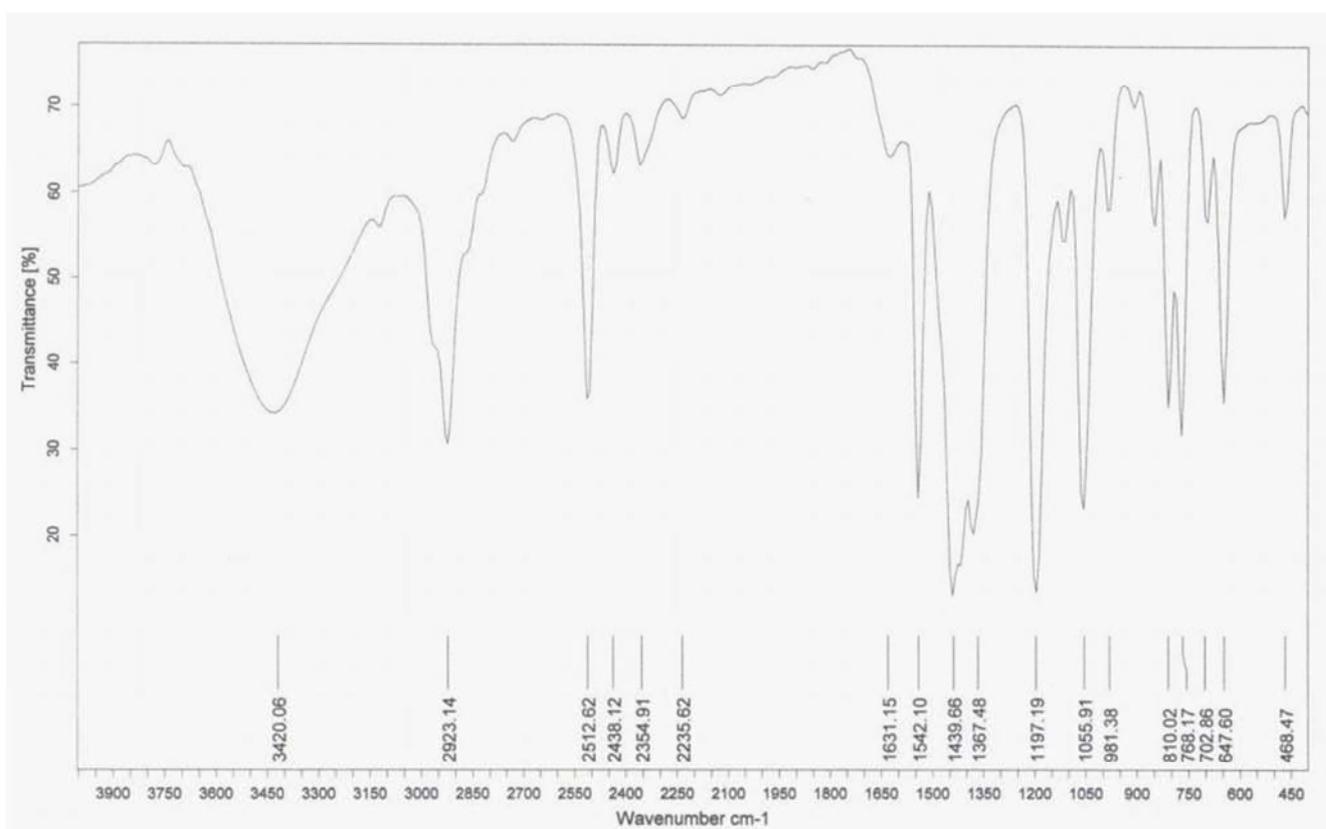


Figure 4. Infrared spectrum of (Tp*-Ni) complex (H2).

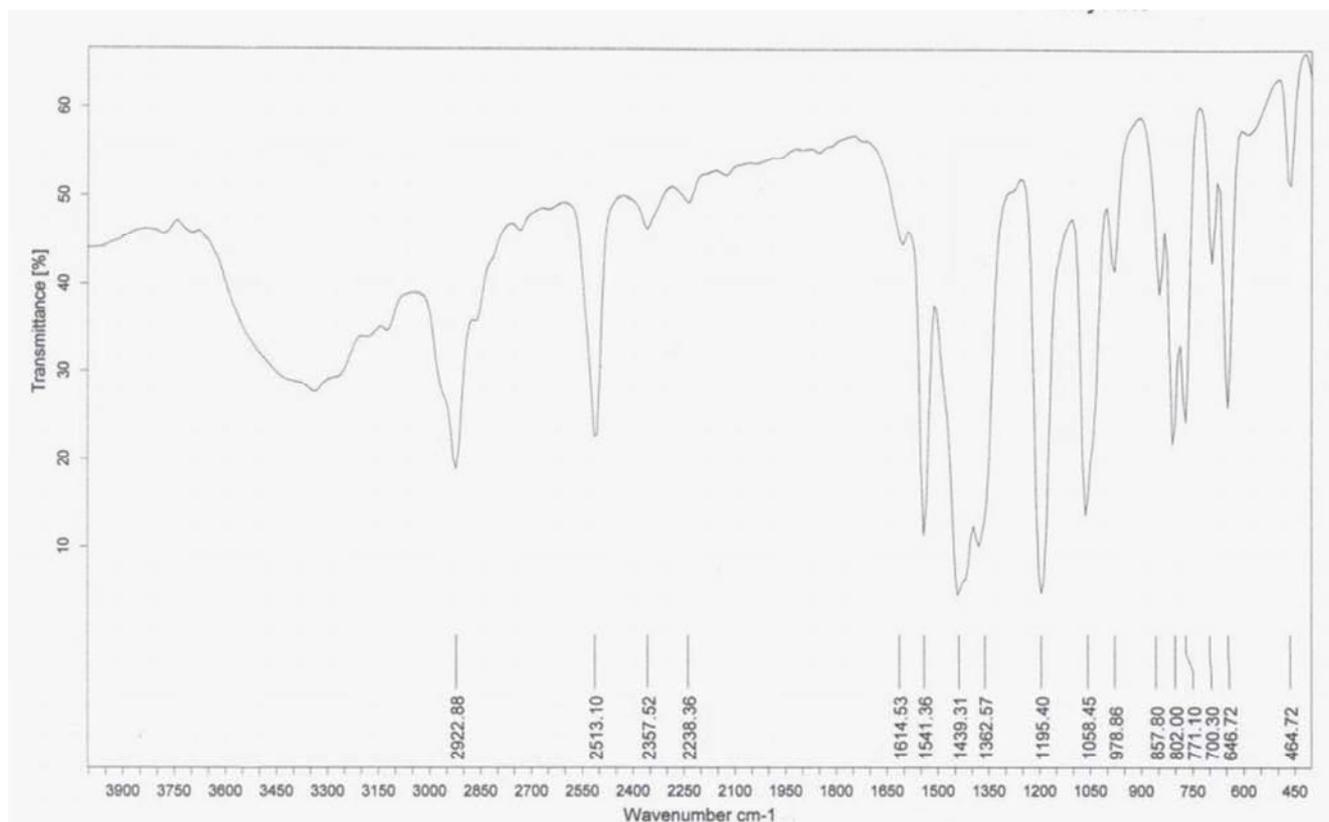


Figure 5. Infrared spectrum of (Tp^*-Cu) complex (H3).

3.3. Elemental Analysis Data

Elemental analysis of carbon, hydrogen and nitrogen was used in the characterization of all of the complexes synthesized in this work. The experimental and calculated C, H and N contents for these complexes are presented in the table 4.

Table 4. Elemental analysis data of complexes H1 to H3.

Complex	Elemental analysis			
		C	H	N
H1 - $BH(C_5H_7N_2)_3CoCl$	Cal.	46.01	5.66	21.46
	Found	46.03	5.75	21.58
H2 - $BH(C_5H_7N_2)_3NiCl$	Cal.	46.04	5.67	21.48
	Found	46.04	5.67	21.48
H3 - $BH(C_5H_7N_2)_3CuCl$	Cal.	45.47	5.60	21.21
	Found	46.09	5.69	21.22

4. Conclusion

The synthetic and characterization results obtained in this work lead to the conclusion that the $(Tp^* \text{ complexes})$ can be synthesized in a solid form using reflux and microwave method in a 1:1 ratio between metal chloride and (KTp^*) . The microwave method was easier than reflux method and it gives higher percentage yield, and saves time and solvent.

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