12-2013

Synthesis and Characterization of a New Cyano-substituted Tris(pyrazolyl)borate and its Thallium(I) Complex

Bozumeh Som
East Tennessee State University

Recommended Citation
Som, Bozumeh, "Synthesis and Characterization of a New Cyano-substituted Tris(pyrazolyl)borate and its Thallium(I) Complex" (2013). *Electronic Theses and Dissertations.* Paper 2273. https://dc.etsu.edu/etd/2273

Synthesis and Characterization of a New Cyano-substituted Tris(pyrazolyl)borate and its Thallium(I) Complex

---

A thesis
presented to
the faculty of the Department of Chemistry
East Tennessee State University

In partial fulfillment
of the requirements for the degree
Master of Science in Chemistry

---

by
Bozumeh Som
December 2013

Ningfeng Zhao, Ph.D., Chair.
Cassandra Eagle, Ph.D.
Ismail Kady, Ph.D.

Keywords: Cyanoscorpionate, X-ray crystal structure, Poly(pyrazolyl)borate

ABSTRACT

Synthesis and Characterization of a New Cyano-substituted Tris(pyrazolyl)borate and its Thallium(I) Complex

by

Bozumeh Som

A new cyanoscorpionate - tris(4-cyano-3,5-diphenylpyrazolyl)borate ($Tp^{Ph2,4CN}$) has been synthesized and characterized. The thallium complex of this ligand $TlTp^{Ph2,4CN}$ has also been prepared and characterized by FT-IR, ^1H NMR, and single-crystal X-ray-diffraction. The complex $TlTp^{Ph2,4CN}$ crystalized in the monoclinic space group C2/c with unit cell a = 14.6697(10) Å, b = 13.9493(10) Å, c = 19.3347(12) Å, and β= 91.761(2)°. Structural comparison of $TlTp^{Ph2,4CN}$ with analogous complexes demonstrated the effects of both steric and electron-withdrawing substituents on coordination geometry and the electronic properties of the metal ion. There were short contacts between the cyano groups and neighboring thallium ions that also indicated the ligand's potential to form coordination polymers.

DEDICATION

To my late uncle, Mr. Francis D. Benia

ACKNOWLEDGEMENTS

First and foremost, I must thank God Almighty for guiding me through this journey. I hope His mercies and grace will continue to push me to greater heights.

My family and wife have been extremely supportive, even though we are thousands of miles apart. I must say you are highly appreciated for all the love you have shown me through these years.

Special thank you, to my advisor, Dr. Ningfeng Zhao, for all the guidance and mentorship given to me. You have helped me lay a very good foundation for scientific research through your wisdom, patience, and kindness. I would like to thank all the professors and staff of the Chemistry Department at East Tennessee State University (ETSU), especially my committee members Dr. Cassandra Eagle and Dr. Ismail Kady for all the helpful advice and assistance, and ETSU for financial support. I am also very grateful to Dr. Reza Mohseni for assisting with instrumentation and Dr. Curtis Moore of University of California, San Diego for help with X-ray crystallography.

Lastly, I would like to thank all of my fellow graduate students. Not only have I had a great time with everyone for the past 2 years, but I have also learned so much.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

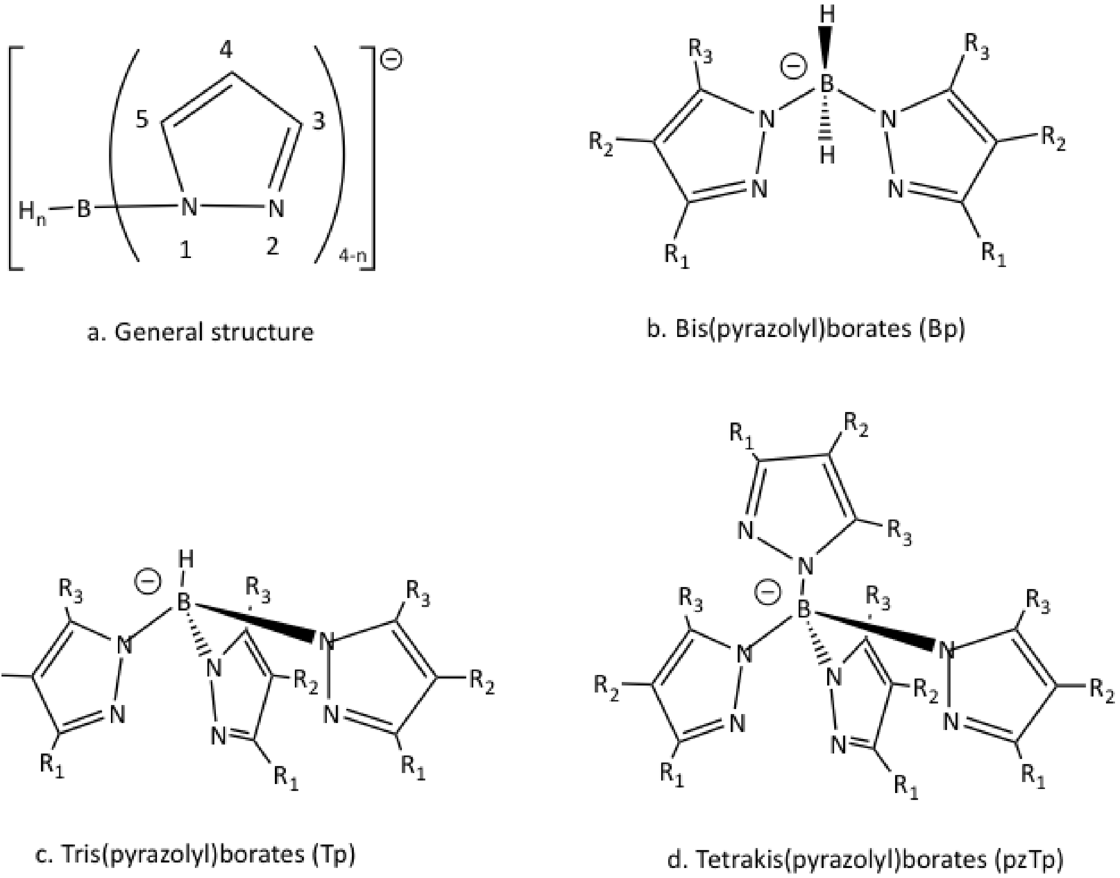
Figure Page

CHAPTER 1

INTRODUCTION

General Introduction

Poly(pyrazolyl)borates, from the time when they were invented by Trofimenko in 1966, have been an interesting and ever growing versatile system of ligands.[1] They consist of a tetra-substituted boron atom attached to two or more pyrazoles through one N atom of the ring (Figure 1). The other N atoms of the pyrazole rings become the donor atoms of the ligand. Because they always adopt a multi-dentate mode, poly(pyrazolyl)borates are also known as "scorpionate" ligands. In general, scorpionates are easy to make and hold a very bright future as a result of their wide applications.[2] Usually a controlled reaction of the pyrazole derivative with a borohydride ion can yield the three basic forms of scorpionates: dihydrobis(pyrazolyl)borates (Bp), hydrotris(pyrazolyl)borates (Tp), and tetrakis(pyrazolyl)borates (pzTp), all with a single negative charge (Figure 1). Applications of scorpionates range from cluster chemistry, bioinorganic chemistry, inorganic and organometallic chemistry, enzyme modeling, catalysis, and C–H bond activation to materials sciences.[1] In recent years, complexes of scorpionate ligands have been successfully used to mimic the active sites of metalloenzymes as a valuable resource for chemists and biologists investigating the properties of metal complexes in biological systems.[3] For example, vanadium complexes of general type $Tp^*VO(OAr)_2$ (note that $Tp^* = Tp^{Me2}$) have been considered as possible models for the active site in bromoperoxidase.[2] Also, a number of scorpionate ligand complexes have been used to catalyze a variety of chemical reactions including polymerization and oligomerization.[2] For instance, the complex Tp*W(=NPh)Br(=CHPh) and related complexes, when combined with $AlCl_3$, catalyzed the acyclic diene methathesis (ADMET) oligomerization of 1,9-decadiene and also the ring-opening metathesis (ROMP) polymerization of cyclooctene[1]. Because of the versatility and ease with which one can synthesize scorpionate ligands, they have also been electronically and sterically tuned to modify the coordination to the metal center in a desired fashion, leading to potential molecular materials with desired electronic and magnetic properties.[4]


a. General structure

b. Bis(pyrazolyl)borates (Bp)

c. Tris(pyrazolyl)borates (Tp)

d. Tetrakis(pyrazolyl)borates (pzTp)

Figure 1. General structure (a) of poly(pyrazolyl)borate anion, where n= 0, 1 or 2, and its three basic forms (b, c, d)

To fully understand and appreciate the chemistry of the scorpionate ligand system as well as their metal complexes, one will need to understand the nomenclature system and abbreviations employed in this text that have been developed over several decades of research. The nomenclature and abbreviations are based mainly on the substitution on the pyrazole rings of the scorpionate ligand. The “default” position in this abbreviation system is the 3-position on the pyrazole ring (Figure 1), which is denoted by a superscript “R”, that is, Bp^R or Tp^R. Thus, hydrotris(3-methylpyrazolyl)borate is denoted as Tp^{Me} and the 3-phenyl equivalent of Tp is written as Tp^{Ph}. [1] The 5-position substituent follows the 3-position substituent as a superscript separated by a comma. For instance, hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate is denoted as $Tp^{t\text{-}Bu,Me}$. When 3- and the 5-position substituents are identical, the superscript R is followed by a 2: for example hydrotris(3,5-diphenylpyrazolyl)borate is abbreviated as Tp^{Ph2}. In the case of the most commonly used ligand, hydrotris(3,5-dimethylpyrazolyl)borate, the systematic abbreviation would be Tp^{Me2} , although considering the long historical use of Tp*.[2] A substituent in the 4-position is denoted as a 4R superscript. Thus, hydrotris(4-cyano-3-methyl-pyrazolyl)borate is $Tp^{Me,4CN}$ and hydrotris(4-chloropyrazolyl)borate is Tp^{4Cl}. In the case of four identical pyrazolyl groups bound to the boron, as in tetrakis(3-methylpyrazolyl)borate, the ligand is denoted as $pzTp^{Me}$.

Tris(pyrazolyl)borates are the most widely used ligands of the scorpionate family, because they form a wide range of complexes with metal ions throughout the Periodic Table.[1] The tris(pyrazolyl)borates generally coordinate as tridentate ligands κ^3-N, N’, N’’ through three available N atoms of the pyrazole rings. The term “scorpionate” was actually coined, which provides an idea of how the ligand bonds. Almost always two pyrazolyl groups (claws) coordinate to the metal ion (Figure 2), and the resulting six-membered ring is in a deep boat form that brings the third pyrazolyl group (homoscorpionate) or other (H, OR, SR, NR_2) group (heteroscorpionate), like the tail of a scorpion, arching over and "stinging" the metal ion.[1] However, the "sting" is not mandatory, as the Tp ligand can sometimes be only bidentate (κ^2), as in complexes of Rh(I) and Pd(II).[2]

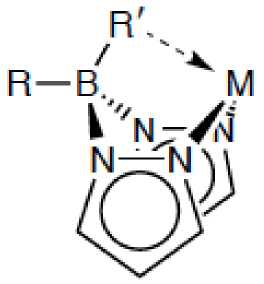


Figure 2. Bonding in a polypyrazolylborate–metal complex.[2] R' is a third pyrazolyl group, or other (H, OR, SR, NR_2) group. R = H or alkyl group

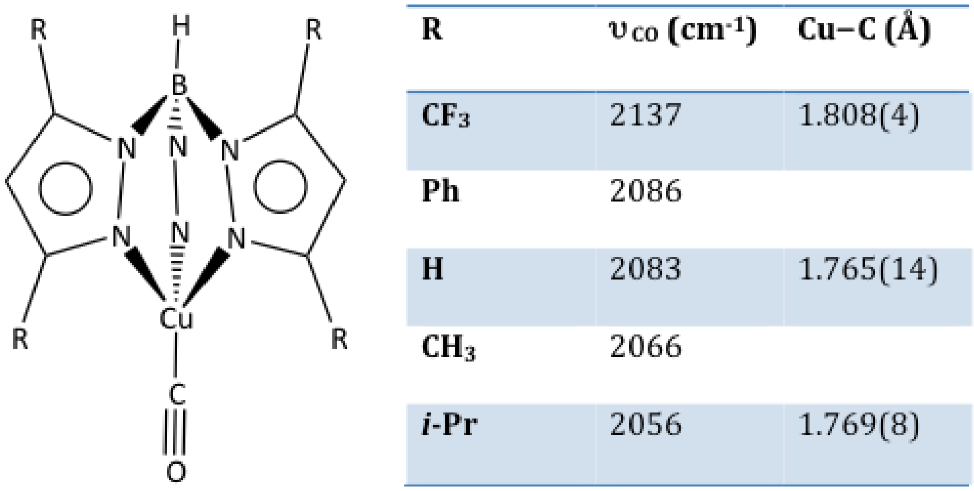
Numerous research work over the years produced several generations of scorpionate ligands. There is particular interest arising out of the ability of this family of ligands to modify or control the steric and electronic environment about the metal center by variation of the substituents on the pyrazolyl groups.[5] The first generation scorpionates consisted of homoscorpionate ligands (Tp, pzTp, and Tp*) bearing pyrazolyl or 3,5-dimethylpyrazolyl donor groups. These have been extensively used because they are easy to synthesize from readily available and inexpensive materials: pyrazole or 3,5-dimethylpyrazole and a borohydride salt.[1] However, to overcome their limitations of application in homogeneous catalysis, scientists developed the second-generation scorpionates that contain bulky substituents (e.g., Ph, *t*-Bu) on the 3-

positions of their pyrazolyl rings,[6] as well as those containing various combinations of substituents in the 3-, 4-, and 5-positions and on boron.[1] Incorporating a bulky substituent such as *t*-Bu group at the 3-position allows the selective formation of low-coordination molecules, as these bulky substituents prohibits the coordination of a second Tp ligand to the metal center.[7] Several studies have been carried out to determine the roles of these bulky substituents in relation to the structural and electronic properties of scorpionate metal complexes.[8,9] For example, coordination complexes involving iron (II) containing various substituted poly(pyrazolyl)borate ligands have displayed unusual temperature-dependent spin-state crossover behavior (Table 1).[8,10] The octahedral and pseudooctahedral complexes of iron(II) have been a model for the high-spin, low-spin, and spin-crossover compounds for the $3d^6$ electronic configuration. In a complex, there is a critical crystal field below which iron(II) has the $t_{2g}{}^4e_g{}^2$, high-spin ground state electronic configuration ($^5T_{2g}$) and above which it has the $t_{2g}{}^6$, low-spin ground state electronic configuration ($^1A_{1g}$).[10] Although Fe(II) compounds are known to exhibit spin-equilibrium characteristics, a change from $t_{2g}{}^6$, low-spin state to a $t_{2g}{}^4e_g{}^2$, high-spin state is believed to be accompanied by an expansion of metal-ligand bond length.[8] As shown in Table 1, the Fe –N distances within the set vary smoothly with the size of the ligand substituents, and the introduction of bulky phenyl substituents is capable of elongating the metal-ligand bond length, resulting in the high-spin complex.

Table 1. Structure and electronic properties of iron(II) complexes with poly(pyrazolyl)borate ligands.[8,9]

	$(Tp)_2Fe$	$(Tp^{Me2})_2Fe$	$(Tp^{Ph2})_2Fe$
Fe –N bond (Å)	1.97	2.17	2.25
Spin state	Spin crossover Tc > 395 K	Spin crossover Tc > 195 K	High-spin (for T > 2 K)
Redox potential	0.1 V	N/A	0.86 V

The term “third generation scorpionates” has been introduced to designate poly(pyrazolyl)borate ligands containing substituents that are electronically active, such as CF_3 and C≡N groups.[11-12] Despite the overwhelming research into the importance and usefulness of scorpionate ligands, relatively little is known about their moderate-to-strong electron-withdrawing or electron-donating properties. Over the years research has shown the effects of these substituents through the changes in the structural, electronic, and magnetic properties of their metal complexes. For example, it has been shown that the strongly electron-withdrawing CF_3 substituents can pull the electron density from the substituted pyrazolyl ring and weaken the metal-nitrogen bond, resulting in the reduced electron density around the coordinated metal ion.[12,13] Dias and others have compared the structural data of a related tris(pyrazolyl)boratocopper(I) carbonyl complexes (Figure 3). It was suggested that with CF_3 substituents, the coordinated copper has the lowest electron density among the analogous complexes, leading to the lowest Cu to CO π-back-bonding. The decreasing π-back-bonding from the d-orbital of the metal to the π* anti-bonding orbital of CO raises the CO stretching frequency. Electron-withdrawing substituents are also known to improve the volatility, oxidation resistance, thermal stability, and fluorocarbon solubility of their metal complexes.[14]



R	υ_{CO} (cm^{-1})	Cu–C (Å)
CF_3	2137	1.808(4)
Ph	2086	
H	2083	1.765(14)
CH_3	2066	
i-Pr	2056	1.769(8)

Figure 3. Tris(pyrazolyl)boratocopper(I) carbonyl complexes.[12]

Cyanoscorpionate as a Ligand in Coordination Polymers

Cyano-substituted poly(pyrazolyl)borates are also known as cyanoscorpionates and fall under the “third generation” scorpionates.[15] Rheingold and others first reported the simplest member of this ligand family, dihydrobis(4-cyanopyrazol-1-yl)borate, [Bp^{4CN}], and several of its complexes, by X-ray crystallography.[16] Thereafter several other cyanoscorpionates have been studied showing that the cyano group as a strong electron-withdrawing character also had the capability to coordinate a second metal center.[4,15] Thus, metal complexes of cyanoscorpionate ligands can potentially be linked together through coordination of another metal ion to the cyano groups of the complexes, with a fully conjugated pathway connecting the pyrazole- and cyano-coordinated metals.[17] Extension of this motif can potentially result in a coordination polymer in which the intermetallic communication might be expected to yield materials demonstrating useful bulk properties such as magnetism and conductivity.[17] The coordination behavior of the cyano group as shown by earlier reports depends on the presence of other ligands and steric hindrance.[16] For example, in complexes $M[Bp^{4CN}]_2$ with divalent metals the two open coordination sites are occupied by intermolecular C≡N–M bonds leading to intractable polymeric structures.[16] Furthermore, in Co^{2+}, Mn^{2+}, and Ni^{2+} complexes of $Tp^{t\text{-Bu},4CN}$, the only coordinating N atoms came from the cyano groups, leaving the pyrazole N atoms open for ligation to other metals, which could result in heterometallic complexes as well as coordination polymers.[4] These complexes also showed that the $Tp^{t\text{-Bu},4CN}$ anions coordinated on opposite sides to each other around the metal center, demonstrating the effect of steric hindrance imposed by the *t*-butyl substituents. The first isolated and crystallographically characterized examples of cyanoscorpionate coordination polymers are $[Tp^{Ph,4CN}Cu]_n$ and $[Tp^{t\text{-Bu},4CN}Cu]_n$.[15] In these polymers the tetrahedral coordination sphere of Cu is made up of the three-pyrazole N atoms of one Tp ligand and a cyano N atom of another Tp ligand. The versatility of the cyanoscorpionate ligands presents a great potential for crystal engineering, which deals with structural design and control of the architecture as well as the possibilities of making molecular magnets and conductive polymers.

The goal of this research was to synthesize and structurally characterize the first scorpionate ligand with symmetrical 3,5-substituents and a 4-C≡N group: tris(4-cyano-3,5-diphenylpyrazolyl)borate ($Tp^{Ph2,4CN}$) and its metal complexes. The steric bulk and electron withdrawing properties of the substituents were studied over the structural and electronic properties of the metal ion. The use of symmetric 3,5-disubstituted pyrazole offers several advantages over unsymmetrically substituted scorpionate ligands: (i) substitution at the 5-position provided a protective environment about the B-H group that prevented ligand degradation, (ii) monosubstituted and asymmetric 3,5-

disubstituted pyrazoles may give a mixture of tris(pyrazolyl)borate derivatives, depending on the selectivity of the reaction with the equivalent nitrogen centers of the pyrazole,[18] and (iii) asymmetric derivatives may rearrange in order to relieve steric congestion.[18] Clearly, such problems are avoided with the use of symmetric 3,5-disubstituted pyrazoles. It is also our intension to explore the potential of coordination polymers involving this class of ligands.

CHAPTER 2

EXPERIMENTAL

Materials and Methods

Unless otherwise stated, all solvents and reagents were used as received from Acros, Aldrich, Fisher Scientific, and TCI without further purification. Toluene was dried over sodium/benzophenone.[19] A BUCHI SWITZERLAND Rotavapor RII was used to remove solvents from solutions under reduced pressure. Glassware were soaked in a KOH/isopropanol/water base bath, rinsed with de-ionized water, and then dried over night at 80°C in a Fisher Scientific Isotemp Oven. All mass measurements were performed using a METTLER TOLEDO CLASSIC Plus PB403-S/FACT laboratory balance. Melting points were determined using Electrothermal MEL-TEMP melting point apparatus. FT-IR spectra were recorded on a FTIR Shimadzu (IRPrestige-21). GC-Mass spectra were measured on a Hewlett Packard 5890 SERIES II. ^{1}H NMR spectra were measured on a JEOL 400 MHz NMR spectrometer in $CDCl_3$ solution with TMS as internal standard. X-ray crystallographic data were obtained from the University of California, San Diego Crystallography Laboratory, where the crystals were sent and analyzed using a Bruker Kappa APEX-II CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å).

X-ray Crystallographic Analysis

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). A 0.135 x 0.122 x 0.087 mm piece of a colorless block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using Φ and ϖ scans.

The crystal-to-detector distance was 35 mm and the exposure time was 5 seconds per frame using a scan width of 2°. Data collection was 99.9% complete to 25.00° in θ. A total of 52,431 reflections were collected covering the indices, -22<=h<=22, -21<=k<=21, -24<=l<=29. A total of 7,186 reflections were found to be symmetry independent, with a R_{int} of 0.0565. Indexing and unit cell refinement indicated a *C*-centered, monoclinic lattice. The space group was found to be *C*2/c. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXS) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2013. Crystallographic data are summarized in Table 3.

Synthesis of 4-cyano-3,5-diphenylpyrazole, $Hpz^{Ph2,4CN}$ (4)

An outline of all the syntheses is given by the scheme in Figure 4. Sodium hydride (0.690 g, 17.24 mmol, 60% dispersion in mineral oil) was weighed into 100 mL dry toluene forming a suspension. This was put under nitrogen and cooled by means of an ice bath. To the suspension, benzoylacetonitrile , **2** (2.500 g, 17.24 mmol), was added resulting in the immediate appearance of bubbles. The mixture was stirred 18 h resulting in a cloudy viscous solution. To this was added benzoyl chloride, **1** (2.424 g, 17.24 mmol), dropwise. The reaction mixture became slightly yellow and was stirred overnight. A 100 mL of aqueous solution of 0.2 M sodium hydroxide was then added and the aqueous layer was separated from the organic layer using a separating funnel. The extraction was repeated with two more portions (100 mL each) of 0.2 M sodium hydroxide. The yellow aqueous layers were combined and acidified with concentrated HCl/H_2O (50/50) solution to neutralize the NaOH used for the extraction and also to fully protonate the product. A white precipitate appeared immediately when the concentrated HCl/H_2O (50/50) solution was added; the entire solution became turbid as a result of the white precipitates when it was acidified to pH $\approx$ 1. The acidified solution with precipitate was extracted with three portions of ethyl acetate (100 mL each), which were combined and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure yielded 3.088 g (72.10%) crude product. The product was then recrystallized from ethanol to yield slightly yellow 2-cyano-1,3-diphenyl-1,3-propanedione, **3** (1.503 g, 6.04 mmol, 35.01%). **3** was then reacted with hydrazine monohydrate (0.302 g, 6.04 mmol) in 100 mL of methanol under nitrogen and stirred overnight. The solvent was reduced to 25 mL and chromatographed using silica gel column (100-200 mesh) and 50/50 ethyl acetate/hexanes. TLC showed one spot and the same R_f value for the first 15 fractions, which were combined, and the solvent removed under reduced pressure. Recrystallization from dry toluene yielded 4-cyano-3,5-diphenylpyrazole (**4**) as white solid (0.32 g, 1.31 mmol, 21.68%). GC-MS confirmed the molecular mass of the compound (Figure 5). Infrared spectroscopy showed characteristic peaks at 3188 cm^{-1} and 2226 cm^{-1} for N–H and C≡N stretches respectively (Figure 6). The ^1H NMR (chloroform-d) showed peaks at 8.06 ppm (d, 4H), 7.64 ppm (t, 4H), and 7.54 ppm (t, 2H) (Figure 7-8).

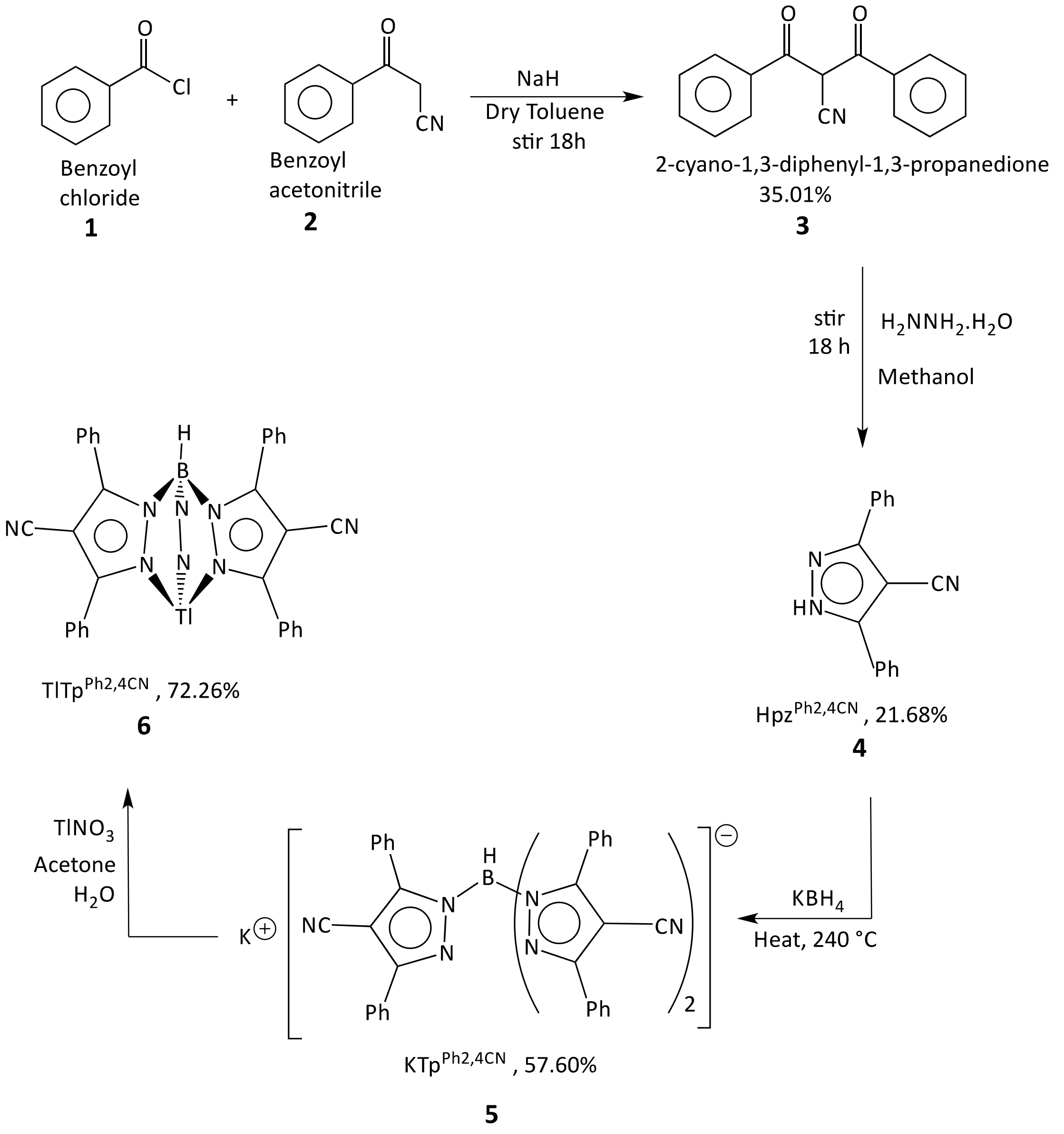


Figure 4. Syntheses of the ligand and complexes, Ph = phenyl substituent

Synthesis of Potassium Tris(4-cyano-3,5-diphenylpyrazolyl)borate, KTp^{Ph2,4CN} (5)

A portion of **4** (0.636 g, 2.59 mmol) and potassium borohydride (0.042 g, 0.78 mmol) (3.3:1 ratio) were combined in a 100 mL round bottom flask fitted with a reflux condenser. The mixture was then heated in an oil bath slowly to 240 °C whilst stirring. The pyrazole began to melt at 237 °C and reacted with KBH_4 producing hydrogen bubbles until it completely melted at 240 °C. After 45 minutes the mixture solidified and the resulting solid was then dissolved in 50 mL acetonitrile and filtered to remove any excess KBH_4. The solvent was then removed under reduced pressure and the residue was boiled in toluene to further remove any unreacted pyrazole. Upon filtration and drying, a fine white powder of **5** (0.352 g, 0.45 mmol, 57.60%) was obtained. FT-IR showed the B–H and C≡N stretches at 2359 cm^{-1} and 2228 cm^{-1} respectively (Figure 9). ^1H NMR (chloroform-d): 7.91 ppm (d, 12H), and 7.51 ppm (t, 18H) (Figure 10).

Synthesis of Thallium Tris(4-cyano-3,5-diphenylpyrazolyl)borate, $TlTp^{Ph2,4CN}$ (6)

A solution **5** (0.425 g, 0.54 mmol) in 20 mL of acetone was added to a solution of $TlNO_3$ (0.144 g, 0.54 mmol) in 20 mL of 50/50 acetone/H_2O in a 100mL round bottom flask and stirred for 1 hour (Figure 4). The solvent was then removed under reduced pressure resulting in a white precipitate of **6** (0.370 g, 0.44 mmol, 72.26%) that was collected and washed with water to remove any remaining nitrates. IR spectra showed the B–H and C≡N stretches at 2359 cm^{-1} and 2220 cm^{-1} respectively (Figure 11). The ^1H NMR (chloroform-d) showed peaks at 7.71 ppm (6H), 7.52 ppm (12H), 7.07 ppm (6H), and 7.01 (6H) (Figure 12-13). X-ray quality crystals were grown by carefully layering a 1/20 saturated solution of **5** in acetone on top of a saturated solution of $TlNO_3$ in 50/50 acetone/ H_2O (Figure 5). The solutions were allowed to diffuse for 2 weeks. When crystals started growing after the first week, the top covers were then removed from the tubes and the solvent was allowed to evaporate slowly, this produced colorless crystals. The air stable version of this technique was used to grow these crystals.

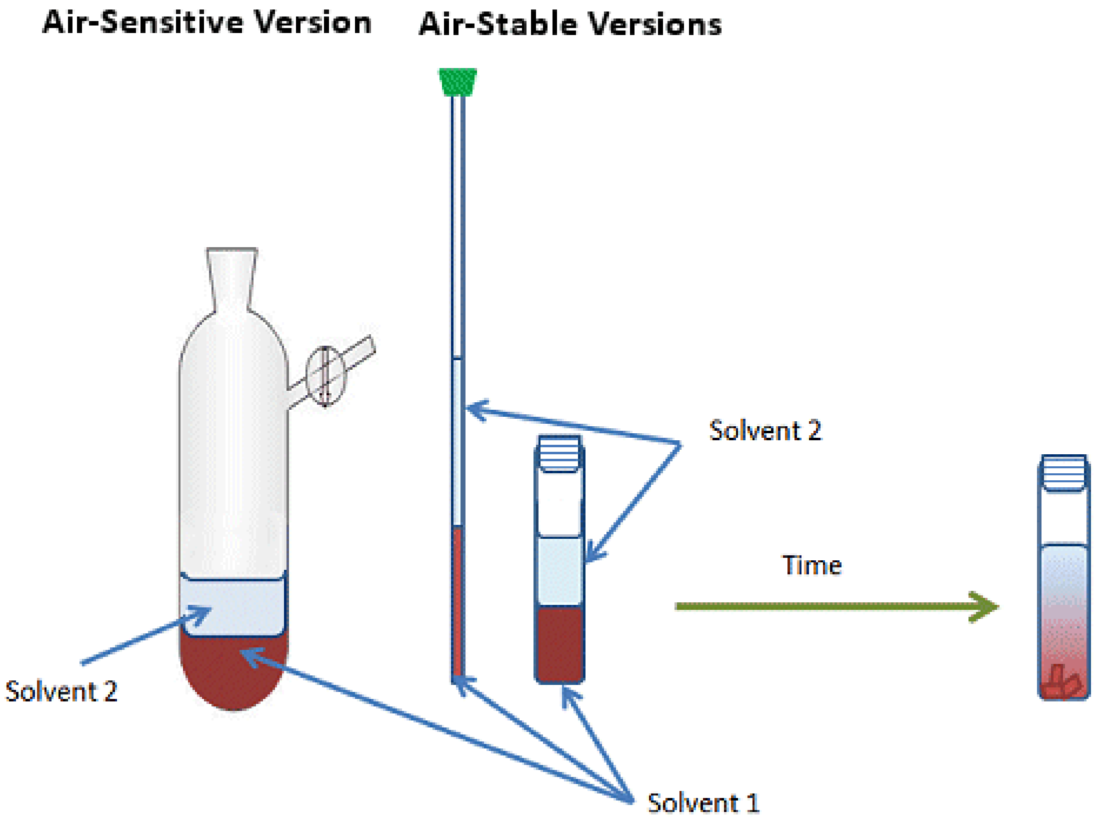


Figure 5. The liquid-liquid diffusion, or layering technique for growing crystals.[20]

Solvent 1 = $TlNO_3$ in 50/50 acetone/H_2O, Solvent 2 = $KTpPh^{2,4CN}$ in acetone

CHAPTER 3

RESULTS AND DISCUSSION

4-cyano-3,5-diphenylpyrazole, Hpz^{Ph2,4CN} (4)

Synthesis of **4,** as outlined in Figure 4, used one of the most prevalent methods of obtaining pyrazoles by reaction of 1,3-diketones with hydrazine and hydrazine derivatives.[21] The crude product of **4** obtained was a sticky mixture and recrystallized in dry toluene to give a white solid. Overall, the yield of **4** was low (21.68%) with a melting point of 226-230 °C. The molecular mass of the compound was confirmed by GC-MS as shown in Figure 6. The mass spectral fragmentation of the compound was found to give a characteristic pattern. For example, a base peak (the most intense peak signifying a stable fragment) of m/z = 245 was observed corresponding to the molecular ion, which had the same molar mass as the neutral molecule (245) and a stable phenyl cation (m/z = 77). The characteristic IR stretches for this compound came from the N–H and C≡N bonds that were observed at the frequencies of 3188 cm^{-1} and 2226 cm^{-1} respectively (see Figure 7). These were within the typical pyrazolyl N–H stretch (3100 – 3500 cm^{-1})[22] and C≡N stretch (2220 - 2240 cm^{-1}).[23] The peaks in the range of (1653-1455) cm^{-1} represent the aromatic ring stretches. The ^{1}H NMR (chloroform-d) spectrum of **4** (Figure 8-9) showed the phenyl ring protons at 8.06 ppm (d, 4H, ortho-protons), 7.64 ppm (t, 2H, para-protons), and 7.54 ppm (t, 4H, meta-protons), with a ratio of 2:1:2. This pattern showed the impact of cyano group on the phenyl protons. The ortho-protons that are much closer to the cyano groups were more deshielded, hence moving downfield, whilst meta-protons appeared farther upfield even than the para-protons that were supposed to be the least deshielded. This was probably due to the concentration of the π electron density at meta-positions than at the para-positions. The pyrazole N–H was not found and a peak at about 1.56 ppm was attributed to water.[24]

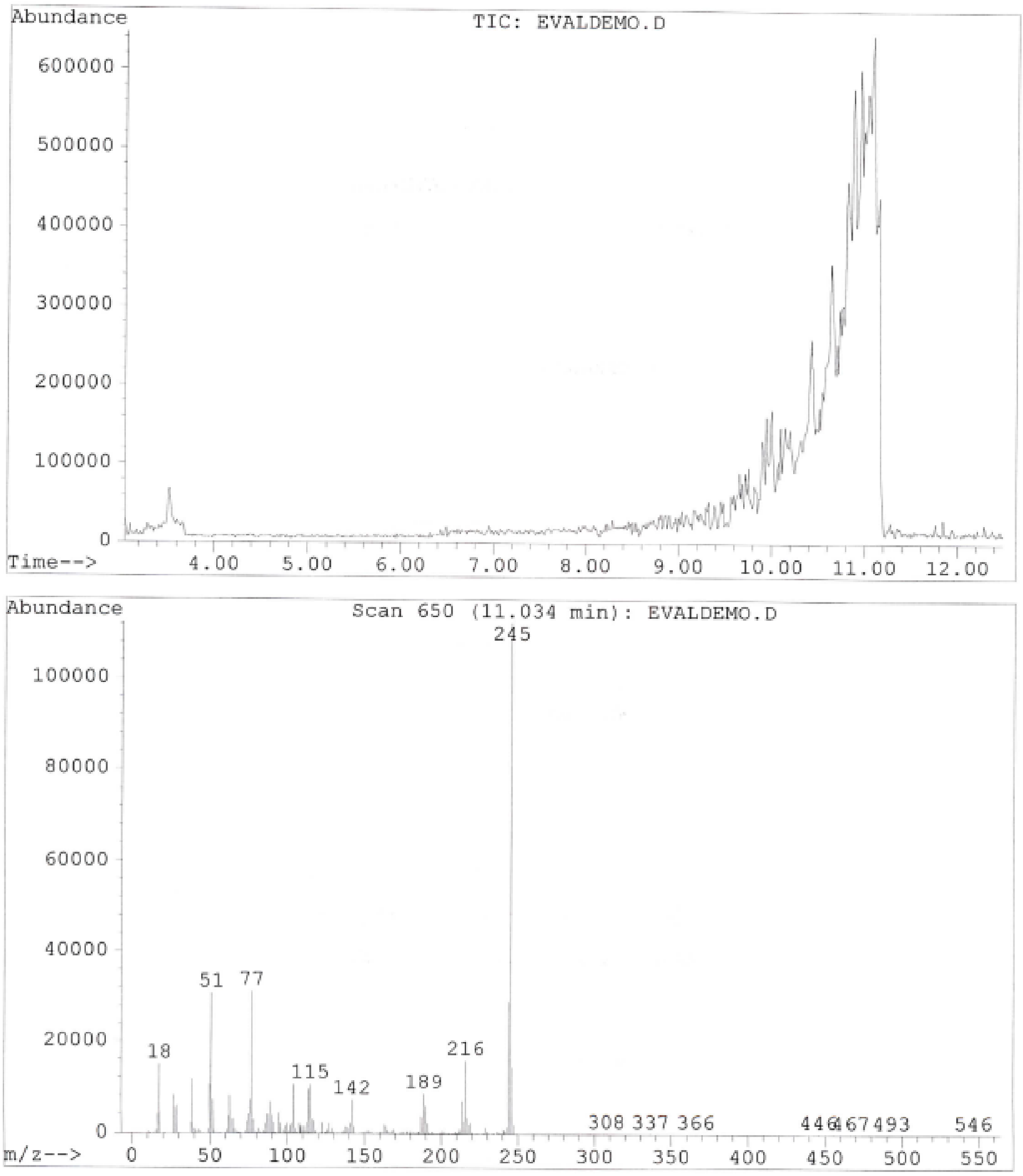


Figure 6. GC-Mass spectrum of $Hpz^{Ph2,4CN}$

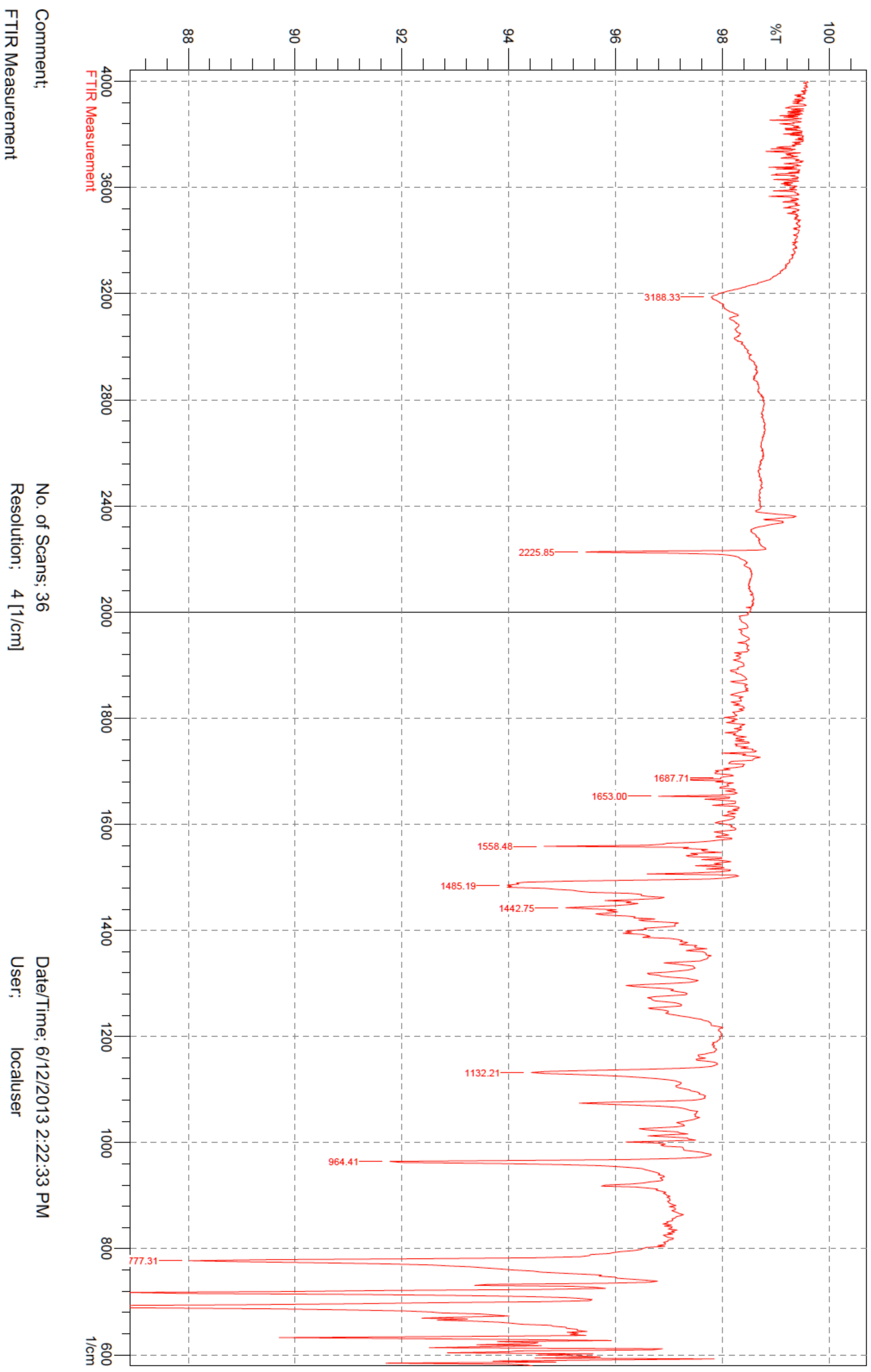


Figure 7. FT-IR spectrum of Hpz^{Ph2,4CN}

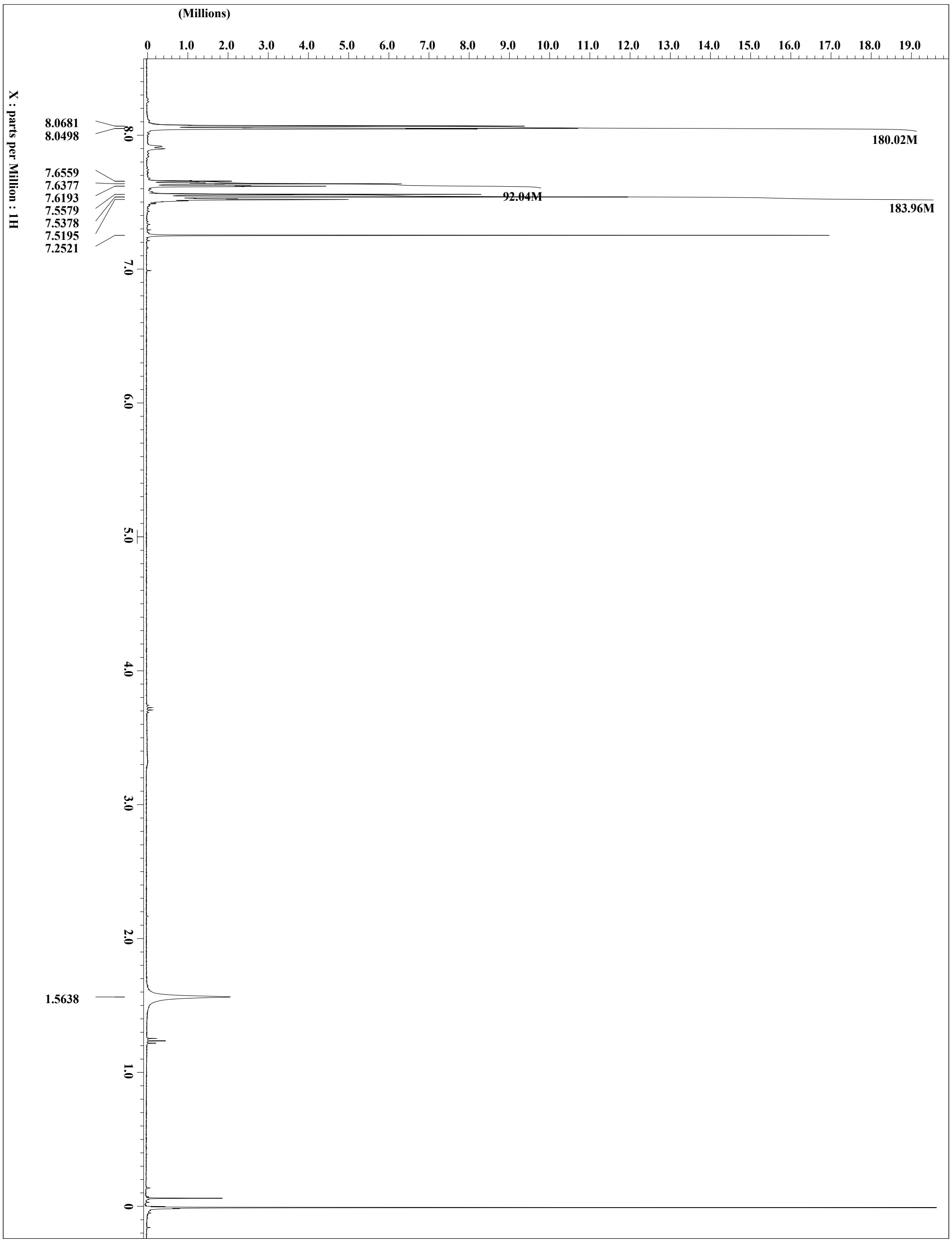


Figure 8. ^{1}H NMR spectrum of Hpz^{Ph2,4CN}

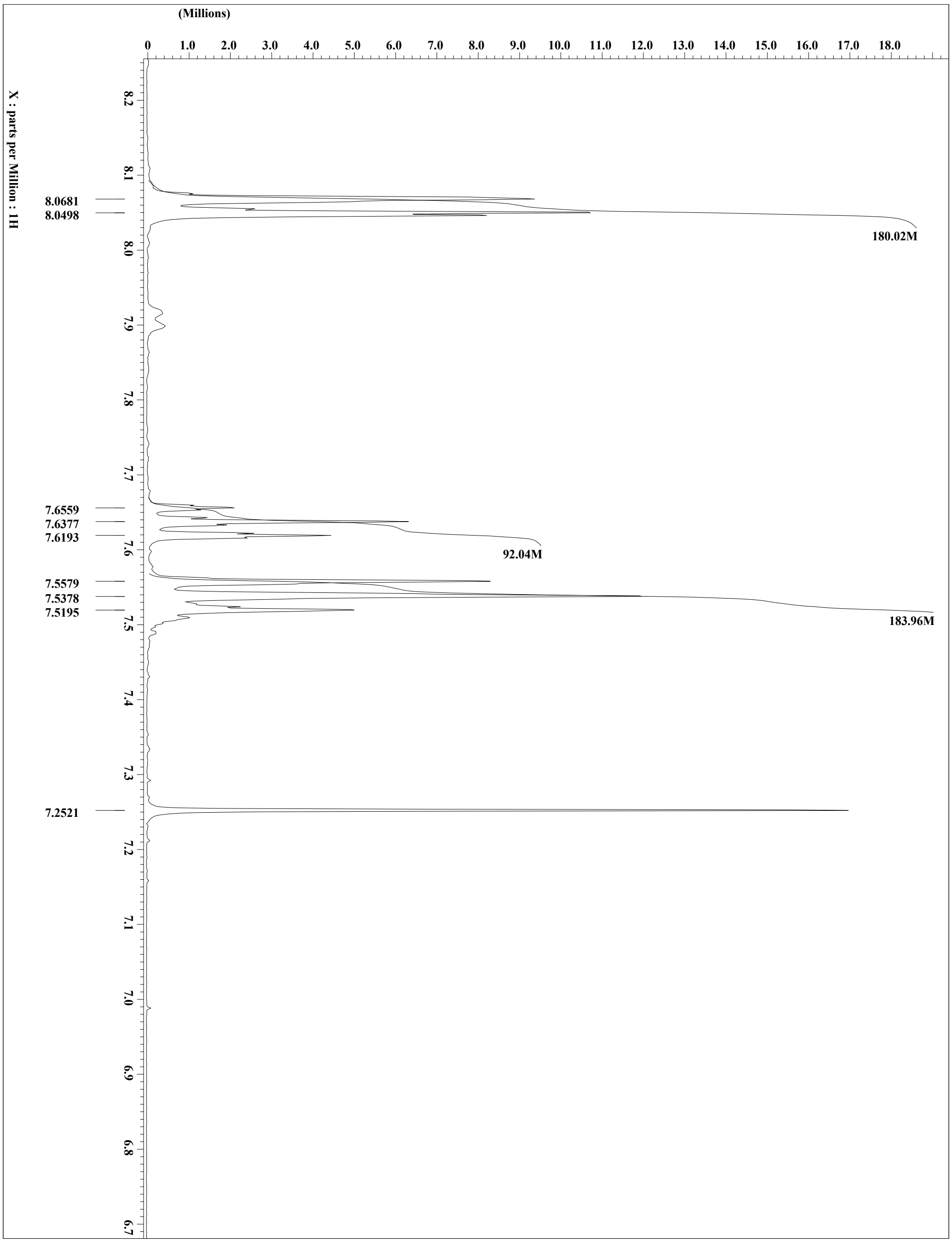


Figure 9. Magnified ^{1}H NMR spectrum of Hpz^{Ph2,4CN}

Potassium Tris(4-cyano-3,5-diphenylpyrazolyl)borates; KTp^{Ph2,4CN} (5)

KTp^{Ph2,4CN} was prepared according to the synthetic route (see Figure 4), which is the most general and convenient route to synthesize scorpionate ligands.[2] This was accomplished by heating a mixture of **4** and KBH_4 in a 3.3:1 ratio to a temperature slightly higher than the melting point of **4**. A slight excess of **4** was used to ensure that all the KBH_4 reacted resulting in the formation of the tris(pyrazolyl)borate **5**. No solvent was used and the reactions proceeded at high temperature and produced off hydrogen gas and KTp^{Ph2,4CN} (**5**) as the major products. The recorded IR spectrum (Figure 10) showed characteristic B-H and C≡N stretches for **5** at 2359 cm^{-1} and 2228 cm^{-1} respectively. The missing N-H stretching indicated the bonding between the pyrazole N atoms and the boron. Compared to analogous scorpionates (Table 2), the B-H stretching of **5** was the lowest (2359 cm^{-1}). This indicated a weaker B-H bond in **5** than those in the other scorpionates, possibly due to the 5-position substituents and the strong electron-withdrawing character of the cyano groups. The ^{1}H NMR (chloroform-d) spectrum of **5** (Figure 11) showed multiplets at 7.91 and 7.51 ppm, with an integration ratio of 2:3. The 7.91 ppm peak represented the ortho-protons (12H) on the phenyl rings, whilst the 7.51 ppm peak is a combined signal for both meta- and para-protons (18H).

Table 2. Comparison of characteristic B-H and –CN stretches of analogous scorpionates

	B-H (cm^{-1})	CN (cm^{-1})	Reference
KTp^{Ph2,4CN}	2359	2228	This work
KTp^{Ph,4CN}	2456	2230	[25]
KTp^{Ph2}	2527	---	[26]

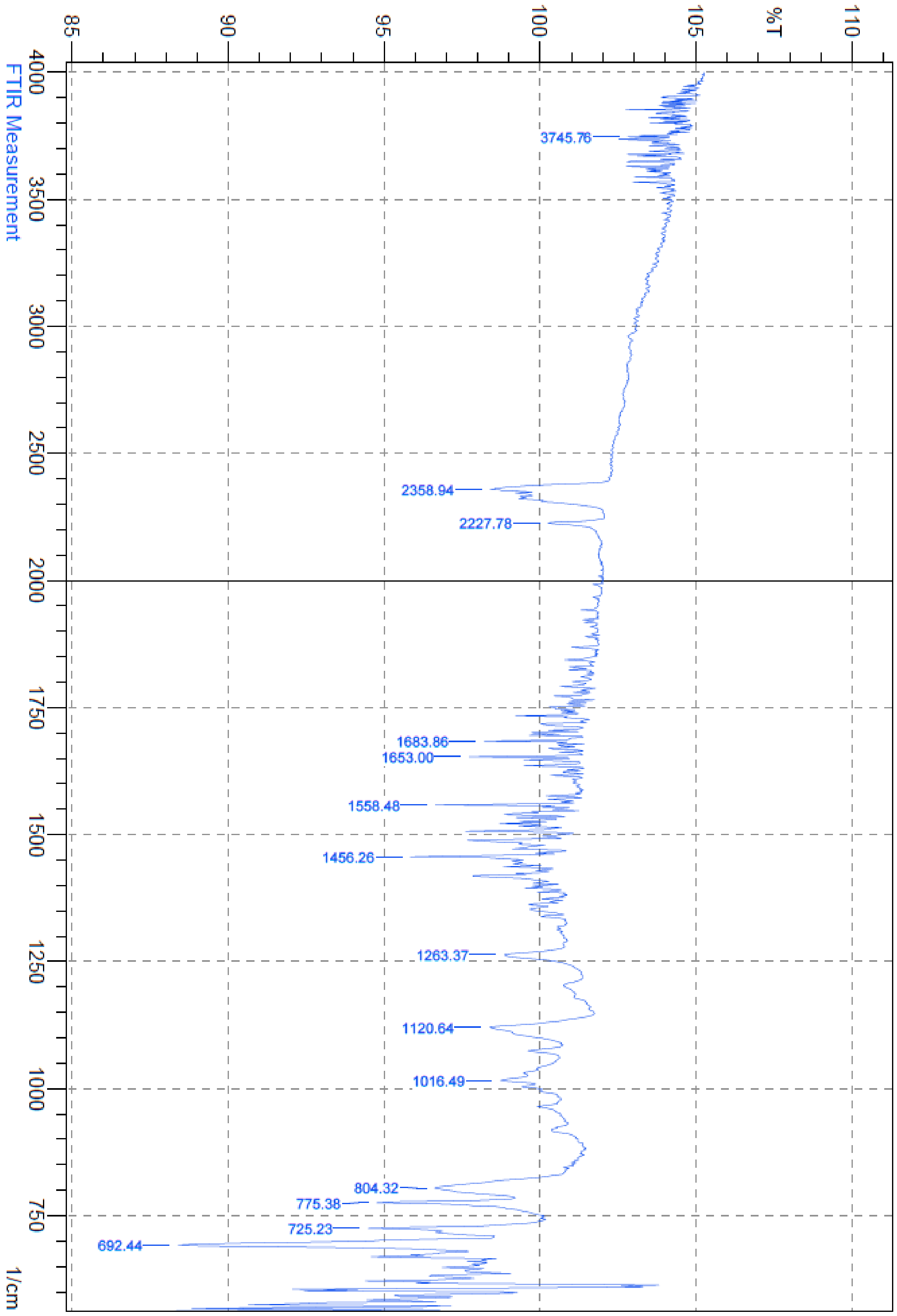


Figure 10. IR spectrum of $KTp^{Ph2,4CN}$

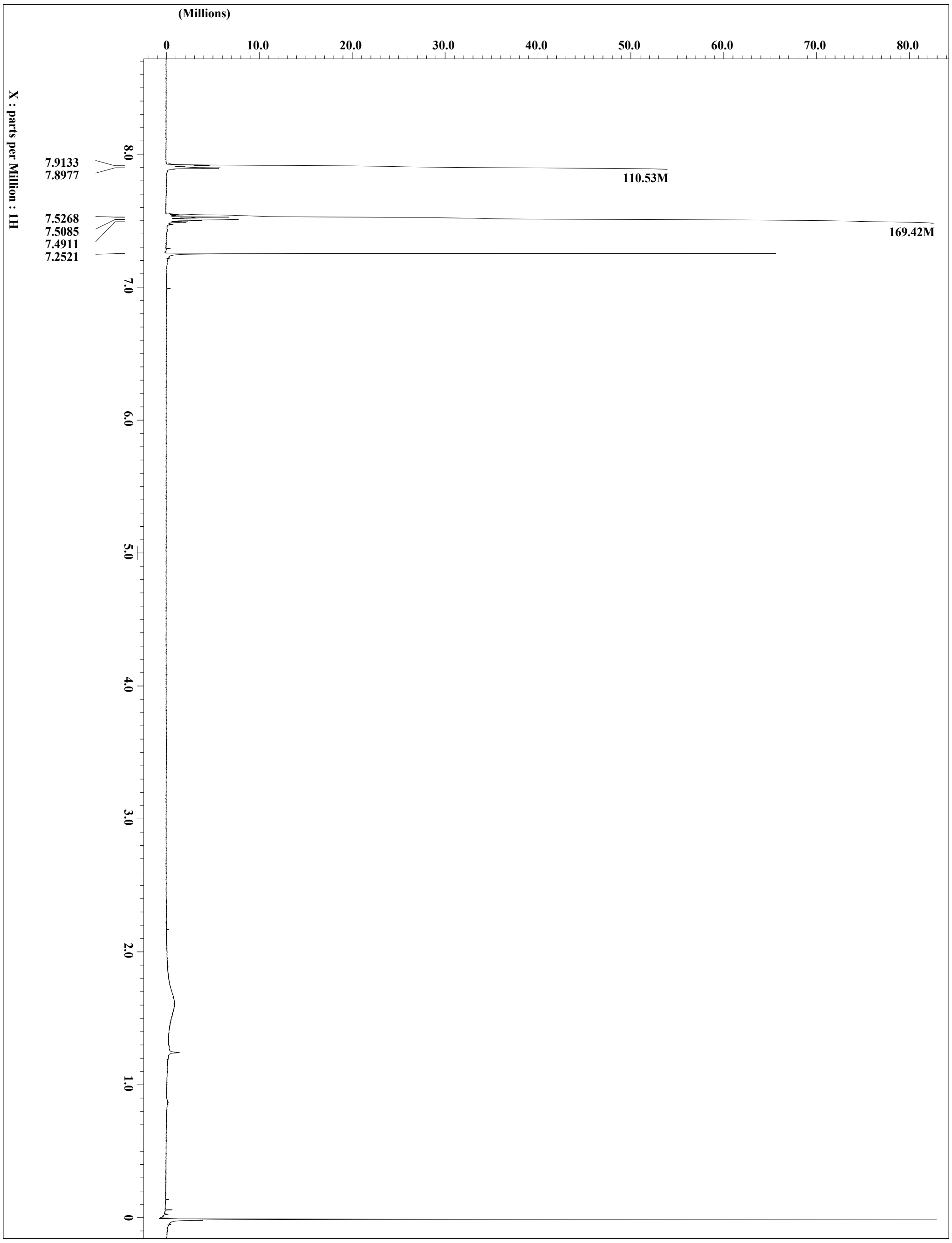


Figure 11. ^{1}H NMR spectrum of KTp^{Ph2,4CN}

Thallium Tris(4-cyano-3,5-diphenylpyrazolyl)borate, $TlTp^{Ph2,4CN}$ (6)

Thallium (I) complexes of poly(pyrazolyl)borates are used for purification and characterization of new scorpionate ligands and as a mild and often more stable ligand transfer reagent.[27,28] $TlTp^x$ species (where x is any substituent) are soluble in organic solvents and almost always afford monomeric crystals.[2] Reaction of **5** with $TlNO_3$ (Figure 4) allowed the isolation of **6**. Due to the highly insoluble nature of the cyanoscorpionate ligand (**5**) in water, it was dissolved in acetone whilst $TlNO_3$ was dissolved in an acetone/water mixture for the reaction. However, because of the limited solubility of **5** in acetone, there was possibly unreacted **5** in the raw product. The IR spectrum was fairly similar to that of **5** (Figure 12) with the characteristic B-H and C≡N stretches at 2359 cm^{-1} and 2220 cm^{-1} respectively. In general, when the same ligand is involved in a set of compounds, the differences in IR spectra were attributed to the differences in the ionic radii of the metal ions and the molecular geometry of the compounds.[29] The major difference between the spectra of the two salts was a slight shift of the C≡N stretching frequency. The IR peaks of the C≡N group in compounds **5** and **6** were observed at 2228 and 2220 cm^{-1} respectively, while the B-H stretch was the same for both (2359 cm^{-1}). The ^1H NMR (chloroform-d) spectra of **6** (shown in Figures 13-14) have multiplets at 7.71, 7.52, 7.34, 7.07, and 7.01 ppm. However, after careful examination and comparison with the ^1H NMR spectrum of $KTp^{Ph2,4CN}$, it was clear that the peaks at 7.71 and 7.52 came from the $KTp^{Ph2,4CN}$ that was used to synthesize the $TlTp^{Ph2,4CN}$. Integration of the peaks representing 6H(para), 12H(meta), and 12H(ortho) gave a ratio of 1:2:2 that were observed at 7.34, 7.07, and 7.01 ppm respectively. The presence of acetone and water was indicated by the peaks at 2.16 and 1.56 ppm respectively.[24]

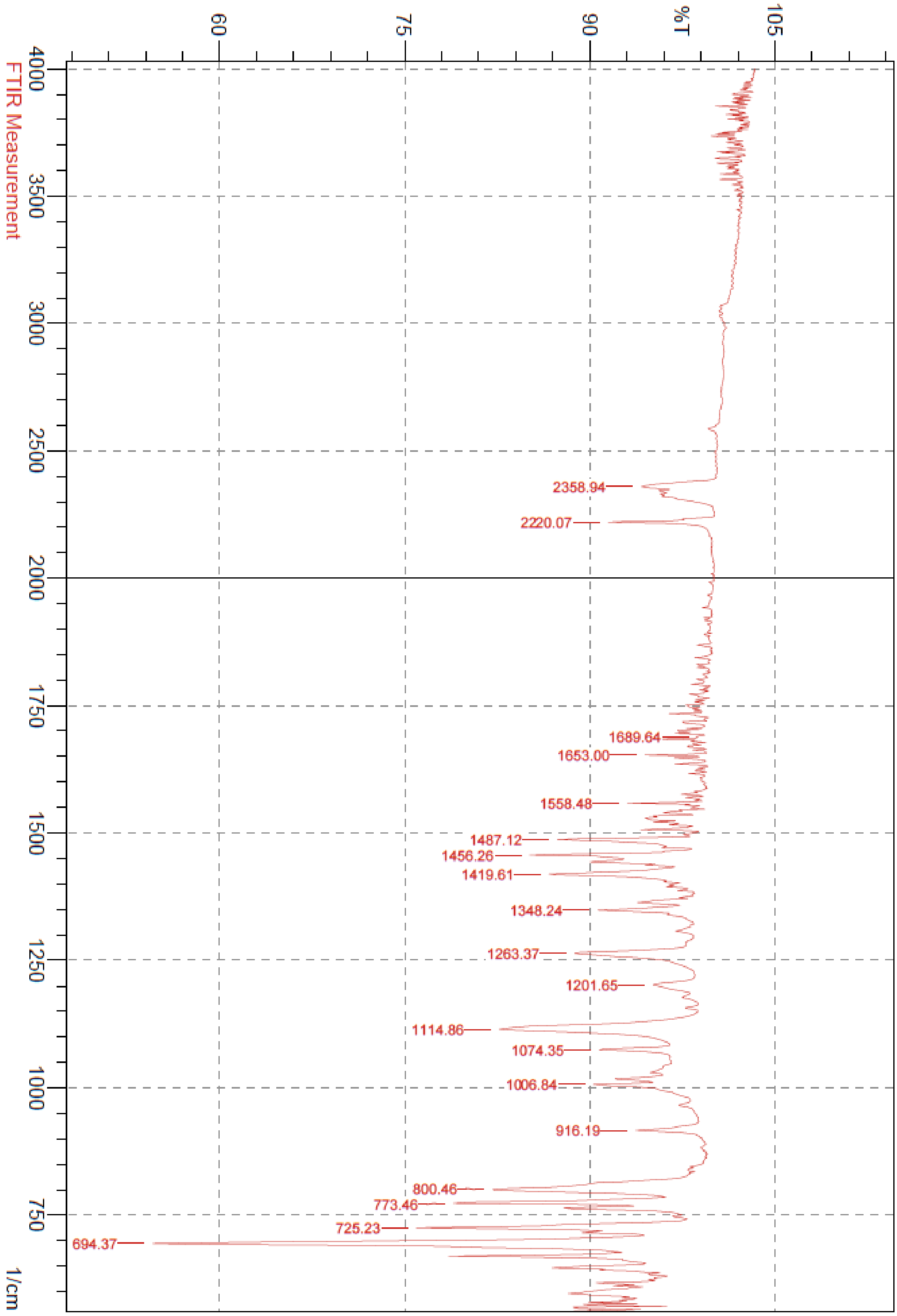


Figure 12. IR spectrum of $TlTp^{Ph2,4CN}$

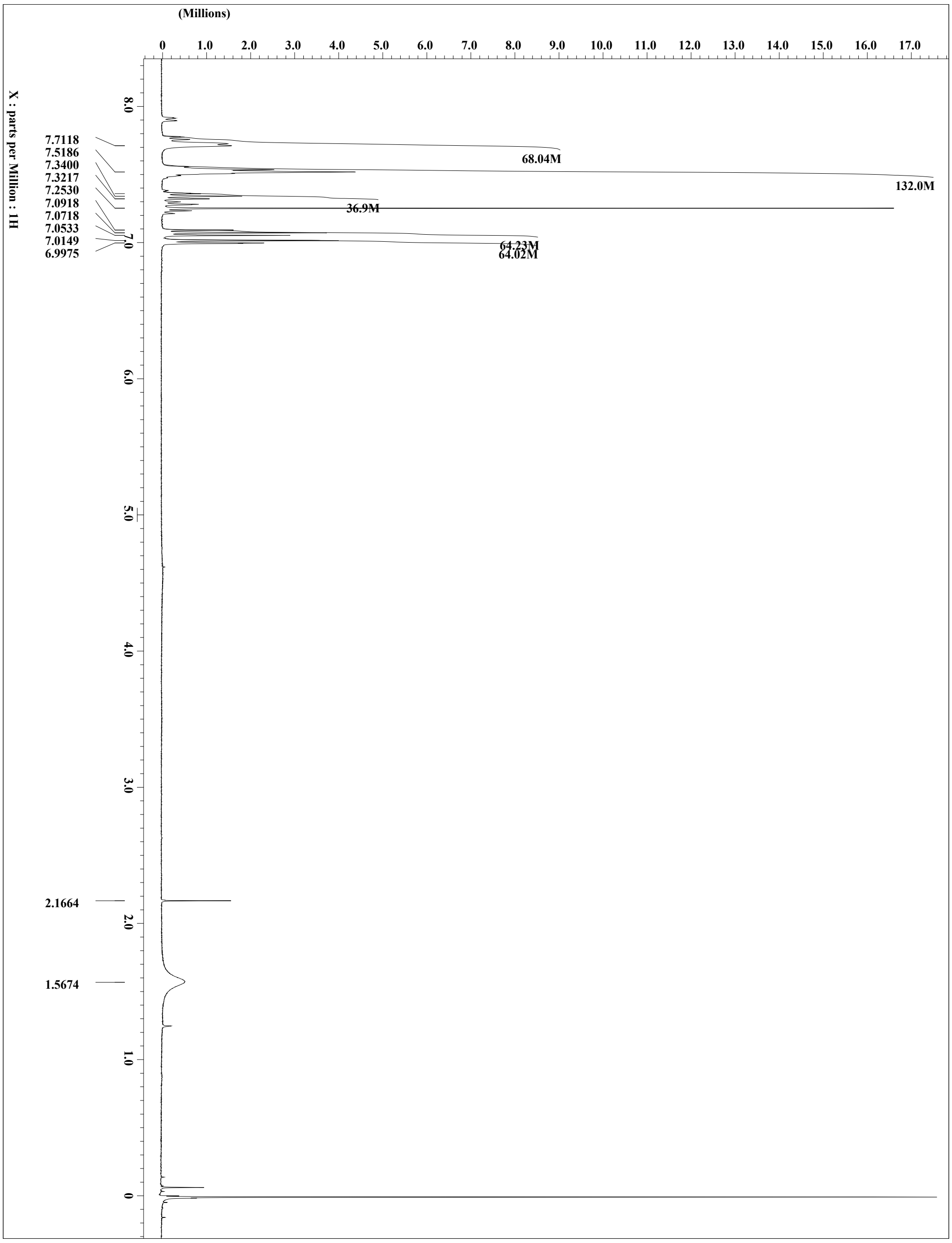


Figure 13. ^{1}H NMR spectrum of $TlTp^{Ph2,4CN}$

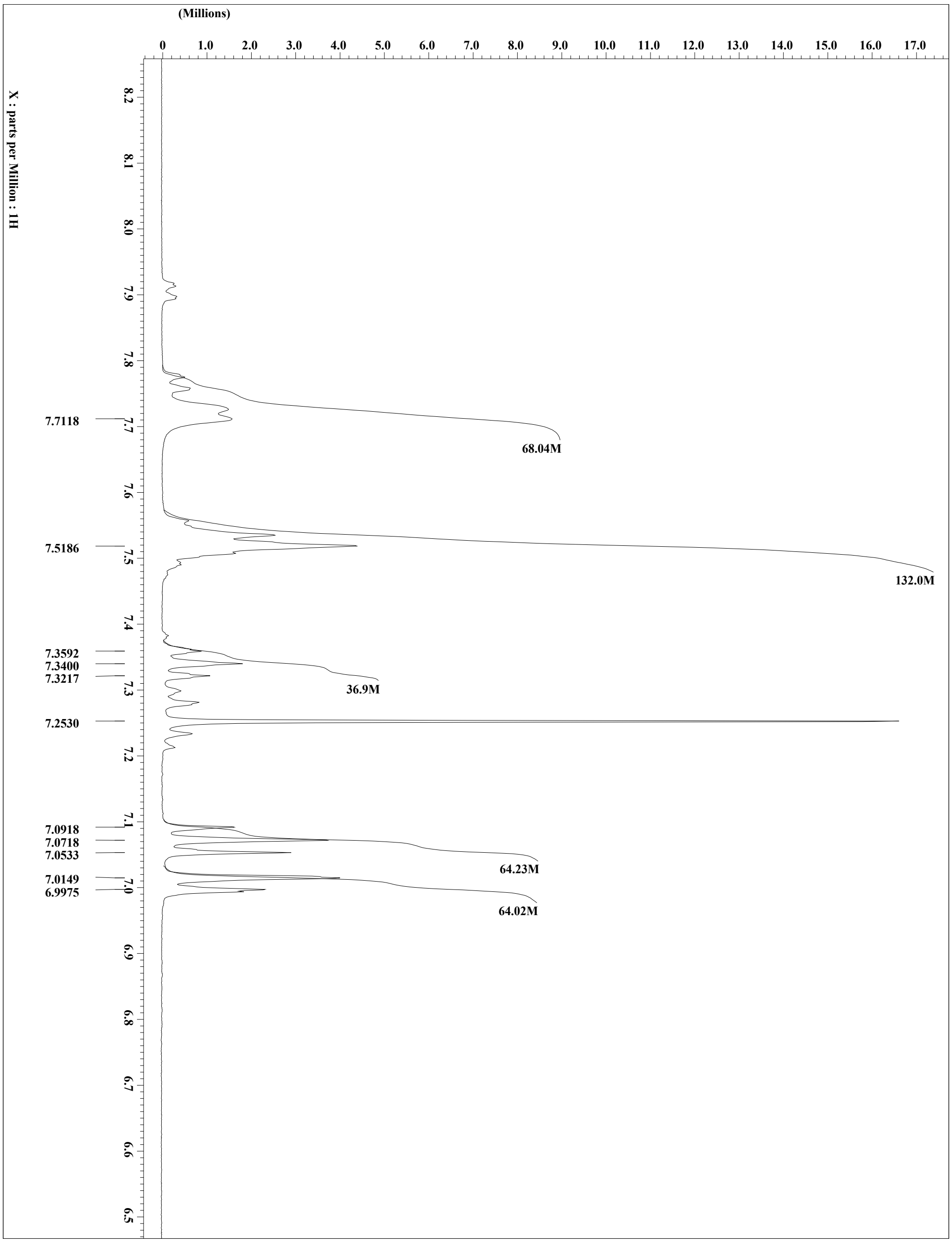


Figure 14. Magnified ^{1}H NMR spectrum of $\mathrm{TlTp^{Ph2,4CN}}$

Using the liquid-liquid diffusion, or layering technique, X-ray quality crystals have been successfully grown to allow for structural characterization. The molecular structure of $TlTp^{Ph2,4CN}$ has been determined by single crystal X-ray diffraction as illustrated in Figure 15, with data collection and refinement parameters in Table 3, and important bond lengths and angles in Table 4. $TlTp^{Ph2,4CN}$ crystallized in the monoclinic space group of C2/c.

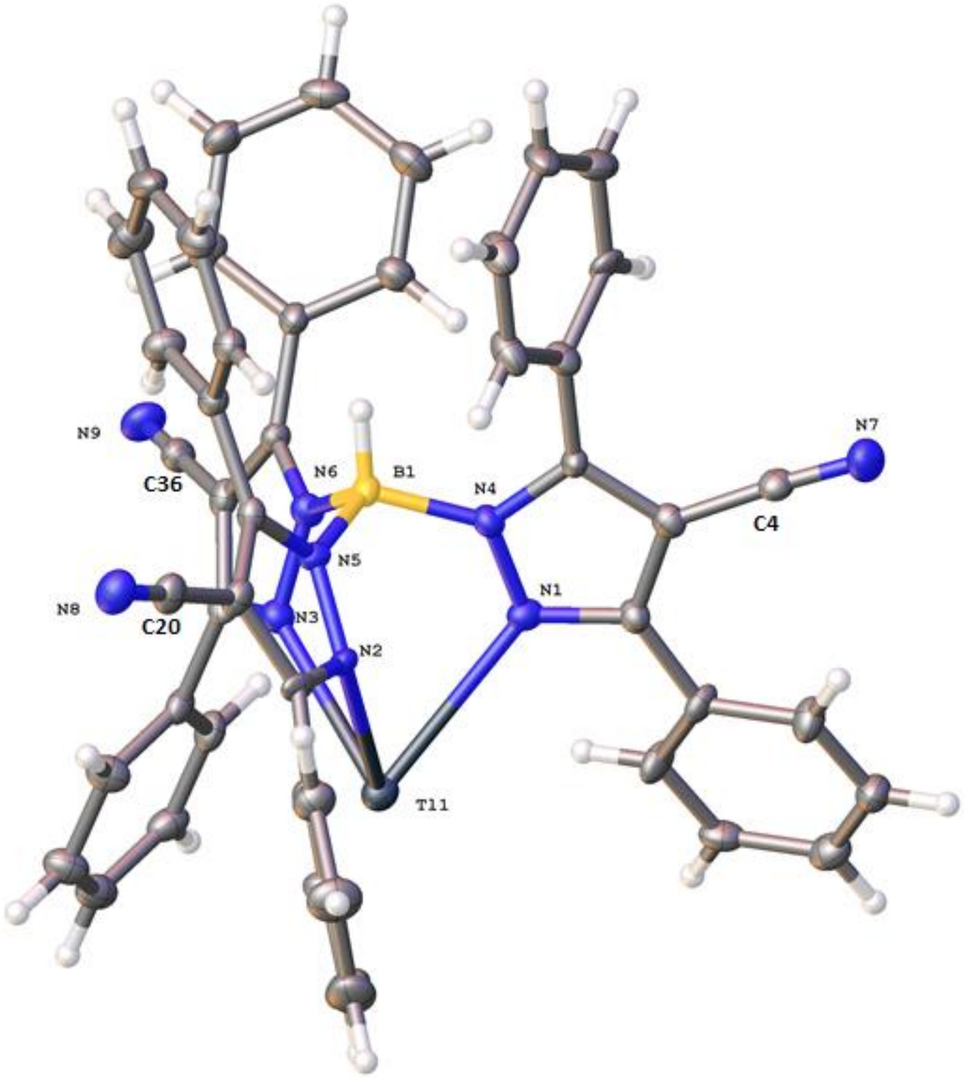


Figure 15. X-ray crystal structure of $TlTp^{Ph2,4CN}$. Displacements of ellipsoids are drawn at the 50% probability level. Hydrogen atoms are shown at arbitrary radii

Table 3. X-ray crystal data and structure refinement

Thallium Hydrotris(4-cyano-3,5-diphenylpyrazolyl)borate [TlTp^{Ph2,4CN}]		
Empirical formula	$C_{48}H_{31}BN_9Tl$	
Molecular formula	$C_{48}H_{31}BN_9Tl$	
Formula weight	949.00	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.6697(10) Å	α= 90°.
	b = 13.9493(10) Å	β= 91.761(2)°.
	c = 19.3347(12) Å	γ= 90°.
Volume	3954.6(5) Å^3	
Z	4	
Density (calculated)	1.594 Mg/m^3	
Absorption coefficient	4.132 mm^{-1}	
F(000)	1872	
Crystal size	0.135 x 0.122 x 0.087 mm^3	
Crystal color, habit	Colorless Block	
Theta range for data collection	2.015 to 33.158°.	
Index ranges	-22<=h<=22, -21<=k<=21, -24<=l<=29	
Reflections collected	52431	
Independent reflections	7186 [R(int) = 0.0565]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. & Min. transmission	0.0734 and 0.0350	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7186 / 12 / 456	
Goodness-of-fit on F^2	1.247	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1469	
R indices (all data)	R1 = 0.0517, wR2 = 0.1482	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.759 and -4.919 e.Å^{-3}	

Table 4. Selected bond lengths (Å) and angles (°) for $TlTp^{Ph2,4CN}$

Tl(1)-N(1)	2.814(9)
Tl(1)-N(2)	2.773(9)
Tl(1)-N(3)	2.658(9)
N(4)-B(1)	1.551(14)
N(5)-B(1)	1.536(15)
N(6)-B(1)	1.558(15)
N(7)-C(4)	1.153(15)
N(8)-C(20)	1.161(15)
N(9)-C(36)	1.159(15)
N(2)-Tl(1)-N(1)	68.6(3)
N(3)-Tl(1)-N(1)	71.5(3)
N(3)-Tl(1)-N(2)	74.5(3)
N(4)-B(1)-N(6)	110.3(8)
N(5)-B(1)-N(4)	109.1(9)
N(5)-B(1)-N(6)	112.2(8)

The three available pyrazole N atoms of the Tp ligand coordinated to the Tl(I) ion similarly as found in related complexes. The Tl(I) adopted a pyramidal geometry with respect to the three N-donors N1, N2, and N3.[30] A view of the crystal structure of $TlTp^{Ph2,4CN}$ down the Tl-B axis (Figure 16) showed twisting of the pyrazolyl groups, resulting in a propeller-like ligand. This twisting alleviated steric interactions among the 5-phenyl groups and also between the 5-phenyl groups and the B-H moiety.[31]

The Tl-N bond lengths of $TlTp^{Ph2,4CN}$ ranged from 2.658 – 2.814 Å (Table 4) with an average of 2.748(5) Å, which was shorter than the related cyanoscorpionate complex $TlTp^{Ph,4CN}$ (2.804(5) Å), as shown in Table 5. It was suggested that due to the orientation of additional 5-position substituents of the pyrazole rings, the N donor atoms have been forced towards the Tl atom, resulting in a reduced Tl–N bond length. Additionally, the N-Tl-N and N–B–N bond angles in $TlTp^{Ph2,4CN}$ were also smaller than those of $TlTp^{Ph,4CN}$, which further supported the effect of additional 5-position substituents in $TlTp^{Ph2,4CN}$. Similar comparisons have been observed for analogous complexes of $\mathrm{TlTp}^{t\text{-}\mathrm{Bu2}}$ and $\mathrm{TlTp}^{t\text{-}\mathrm{Bu}}$. When compared with $\mathrm{TlBp}^{\mathrm{Ph,4CN}}$, the much shorter Tl-N bond length in $\mathrm{TlTp}^{\mathrm{Ph2,4CN}}$ highlighted the effect of the additional 3-position substituents. This formed a "pocket" to facilitate the coordination of the metal ion. On the other hand, the difference of Tl-N bond length was more significant when comparing $\mathrm{TlTp}^{\mathrm{Ph2,4CN}}$ (2.748(5) Å)with $\mathrm{TlTp}^{\mathrm{Ph}}$ (2.605(6) Å), which showed the electron-withdrawing effects of cyano substituents that reduced the electron density on the N donors.

Table 5. Bond lengths and short contacts (Å) and angles (°) of related thallium complexes

Average	$\mathrm{TlTp}^{\mathrm{Ph2,4CN}}$	$\mathrm{TlTp}^{\mathrm{Ph,4CN}}$	$\mathrm{TlTp}^{\mathrm{Ph}}$	$\mathrm{TlTp}^{t\text{-}\mathrm{Bu2}}$	$\mathrm{TlTp}^{t\text{-}\mathrm{Bu}}$	$\mathrm{TlBp}^{\mathrm{Ph,4CN}}$
Tl–N	2.748(5)	2.804(5)	2.605(6)	2.57(3)	2.58(1)	2.874(4)
N–Tl–N	71.50(2)	72.83(26)	75.14(24)	78.07(3)	78.00(3)	69.56(9)
N–B–N	110.50(5)	111.50(14)	n/a	109.00(12)	n/a	110.40(3)
Tl---N≡C	3.330	3.211	----	----	----	3.215
Tl---H–B	----	3.071	n/a	n/a	n/a	2.64
Reference	This work	[25]	[27]	[31]	[31]	[32]

There were no short contacts between Tl and H atoms bound to the boron, as have been reported for the $\mathrm{TlTp}^{\mathrm{Ph,4CN}}$ and $\mathrm{TlBp}^{\mathrm{Ph,4CN}}$ (Table 5). This was because substituents at 5-position of the pyrazole rings, particularly in tris(pyrazolyl)borates, are known to play a protecting role over the B-H groups against attack by electrophiles.[30] In addition, the phenyl groups at the 3-positions of the pyrazole rings have created another "pocket" around the Tl , which limited both frontal and side-on access to this atom.[1] From the crystal structure it can be seen that the "pocket" created around the B-H bond was "tighter" than that around the Tl atom. This resulted in its inability to interact with neighboring atoms. The structural data also showed that there were close contacts (Figure 17) between three neighboring cyano nitrogen atoms and thallium ion, which afforded a distorted trigonal anti-prism structure around the Tl ion. These short contacts demonstrated the ligand's potential to form coordination polymers. The short contacts of Tl---N≡C in analogous cyanoscorpionate complexes are listed in Table 5. The average short contacts of Tl---N≡C in $TlTp^{Ph2,4CN}$ were longer than those of $TlTp^{Ph,4CN}$ and $TlBp^{Ph,4CN}$. This confirmed the effects brought by the symmetrical substituents of the phenyl groups, as described above.

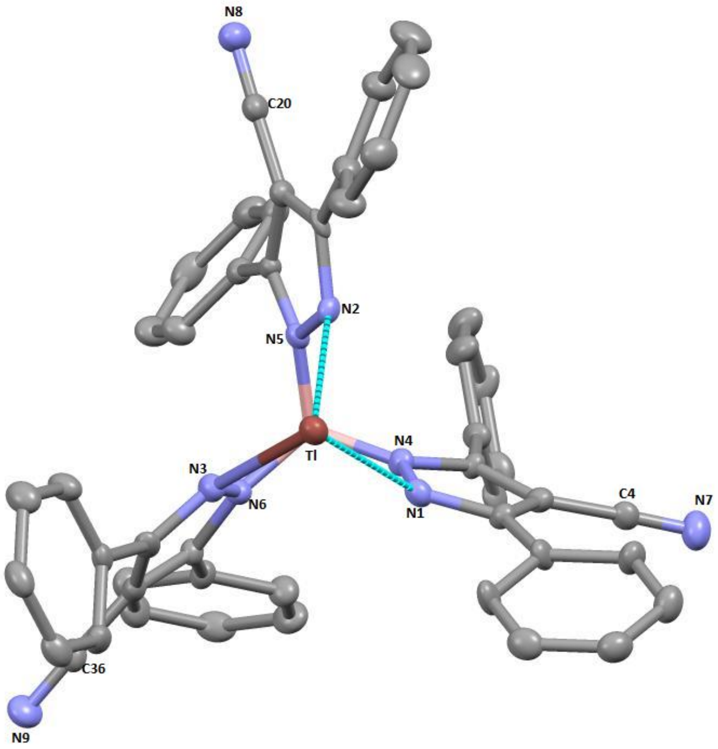


Figure 16. View of $TlTp^{Ph2,4CN}$ down Tl---B axis. Hydrogen atoms have been omitted for clarity

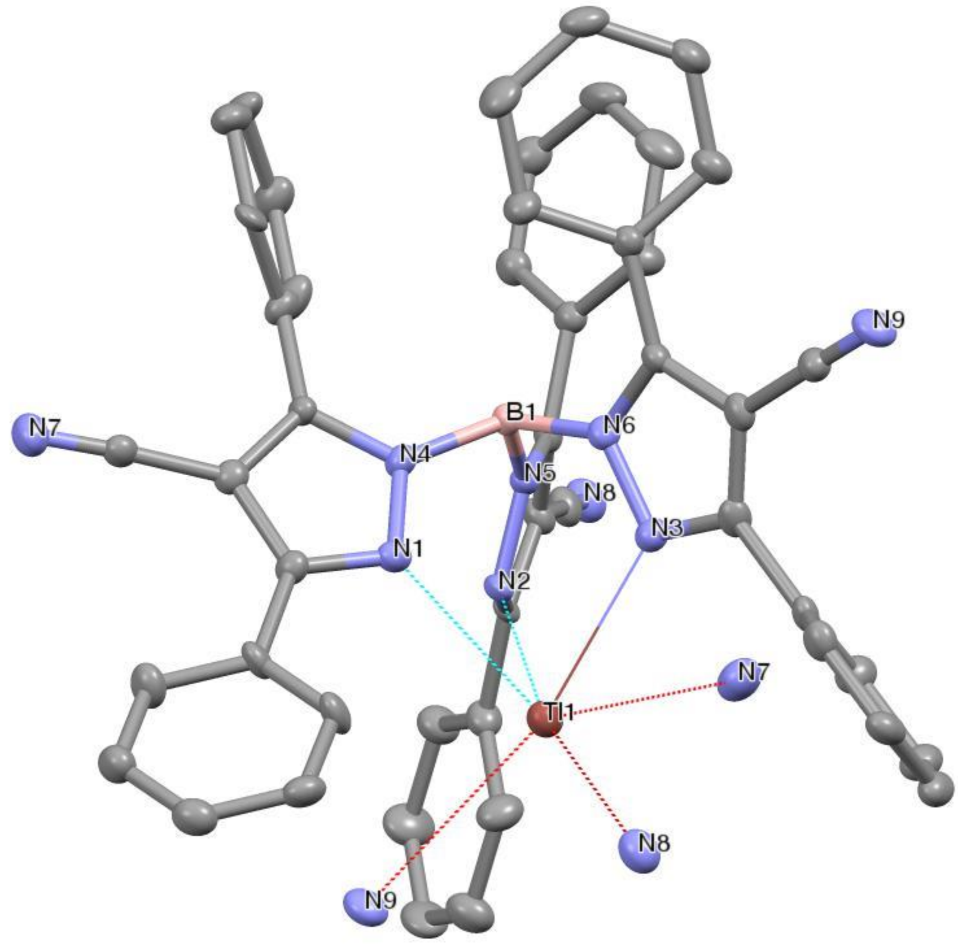


Figure 17. Mercury drawing of TlTp^{Ph2,4CN} showing short contacts between cyano nitrogen atoms and thallium ion. Hydrogen atoms have been omitted for clarity

CHAPTER 4

CONCLUSIONS

In summary, 4-cyano-3,5-diphenylpyrazole has been synthesized and applied to prepare the first symmetrically substituted cyanoscorpionate. The thallium complex of $Tp^{Ph2,4CN}$ has been synthesized and structurally characterized by X-ray crystallography. The successful synthesis of this new ligand $Tp^{Ph2,4CN}$ have further expanded the class of cyanoscorpionate ligands. Steric effects of the bulky substituents were observed in addition to intermolecular short contacts between the cyano substituents and the Tl ion. A dramatic difference in Tl-N bond lengths between $TlTp^{Ph2,4CN}$ and $TlTp^{Ph}$, and relatively smaller difference with analogous cyanoscorpionate complexes($TlTp^{Ph,4CN}$, $TlBp^{Ph,4CN}$), demonstrated how both electronically active and sterically bulky substituents can affect the electronic properties and coordination geometries of metal atoms. Using bulky substituents in the 3- and 5-position of the pyrazolyl ring, one can control the accessibility of the metal ion and the B-H moiety respectively. This was consistent with the longer Tl---N≡C short contacts and no Tl---HB short contacts observed in $TlTp^{Ph2,4CN}$. The Tl---N≡C short contacts indicated the ligand's potential to form coordination polymers, which have a promising future with respect to electronic/magnetic materials and catalytic applications.[17,15]

In investigating this cyanoscorpionate ligand further, it will be necessary to find a way of improving the yield of $Hpz^{Ph2,4CN}$, which was the main material for its synthesis. The characterizations of the transition metal complexes of the new ligand by X-ray crystallography is to be pursued in future work that might provide more insight into the structural arrangements of and coordination behavior of the ligand within the crystals. Also, investigation of the properties of these complexes is recommended in future studies. This will allow for further exploration of the potential of the cyano substituent in forming coordination polymers as well as the production of molecular material involving scorpionate metal complexes.

REFERENCES

1. Trofimenko, S., *Scorpionates: The Coordination Chemistry of Polypyrazolylborates Ligands*. Imperial College Press: London, 1999.
2. Trofimenko, S., Polypyrazolylborates: Scorpionates. *Journal of Chemical Education* **2005,** *82* (11), 1715.
3. Pellei, M.; Santini, C., Biomimetic Applications of Metal Systems Supported by Scorpionates. In *Biomimetic Based Applications*, Cavrak, M., Ed. InTech: 2011; pp 385-428.
4. Bullinger, J. C.; Eichhorn, D. M., Cyanoscorpionates: Co(II), Mn(II), and Ni(II) complexes coordinated only through the cyano group. *Inorganica Chimica Acta* **2009,** *362* (12), 4510-4516.
5. Pellei, M.; Papini, G.; Lobbia, G. G.; Ricci, S.; Yousufuddin, M.; Rasika Dias, H. V.; Santini, C., Scorpionates bearing nitro substituents: mono-, bis- and tris-(3-nitro-pyrazol-1-yl)borate ligands and their copper(i) complexes. *Dalton Transactions* **2010,** *39* (38), 8937-8944.
6. Trofimenko, S.; Calabrese, J. C.; Thompson, J. S., Novel polypyrazolylborate ligands: coordination control through 3-substituents of the pyrazole ring. *Inorganic Chemistry* **1987,** *26* (10), 1507-1514.
7. Brunker, T. J.; Hascall, T.; Cowley, A. R.; Rees, L. H.; O'Hare, D., Variable Coordination Modes of Hydrotris(3-isopropyl-4-bromopyrazolyl)borate (Tp‘) in Fe(II), Mn(II), Cr(II), and Cr(III) Complexes: Formation of MTp‘Cl (M = Fe and Mn), Structural Isomerism in CrTp‘2, and the Observation of Tp‘ - as an Uncoordinated Anion. *Inorganic Chemistry* **2001,** *40* (13), 3170-3176.

8. Oliver, J. D.; Mullica, D. F.; Hutchinson, B. B.; Milligan, W. O., Iron-nitrogen bond lengths in low-spin and high-spin iron(II) complexes with poly(pyrazolyl)borate ligands. *Inorganic Chemistry* **1980,** *19* (1), 165-169.

9. Eichhorn, D. M.; Armstrong, W. H., M{Hydrotris(3-phenylpyrazol-1-yl)borate}$_2$: sterically encumbered iron(II) and manganese(II) complexes. *Inorganic Chemistry* **1990,** *29* (18), 3607-3612.

10. Hannay, C.; Hubin-Franskin, M.-J.; Grandjean, F.; Briois, V.; Polian, A.; Trofimenko, S.; Long, G. J., X-ray Absorption Spectroscopic Study of the Temperature and Pressure Dependence of the Electronic Spin States in Several Iron(II) and Cobalt(II) Tris(pyrazolyl)borate Complexes. *Inorganic Chemistry* **1997,** *36* (24), 5580-5588.

11. Reger, D. L.; Gardinier, J. R.; Gemmill, W. R.; Smith, M. D.; Shahin, A. M.; Long, G. J.; Rebbouh, L.; Grandjean, F., Formation of Third Generation Poly(pyrazolyl)borate Ligands from Alkyne Coupling Reactions of $Fe[(p\text{-}IC_6H_4)B(3\text{-}Rpz)_3]_2$ (R = H, Me; pz = Pyrazolyl): Pathways toward Controlling an Iron(II) Electronic Spin-State Crossover. *Journal of the American Chemical Society* **2005,** *127* (7), 2303-2316.

12. Dias, H. V. R.; Lu, H.-L., Copper(I) Carbonyl Complex of a Trifluoromethylated Tris(pyrazolyl)borate Ligand. *Inorganic Chemistry* **1995,** *34* (21), 5380-5382.

13. Dias, H. V. R.; Jin, W., Low-Valent Gallium, Indium, and Tin Compounds That Contain a Highly Fluorinated Tris(pyrazolyl)borate Ligand: Syntheses and Characterization of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ga$, $[HB(3,5\text{-}(CF_3)_2Pz)_3]In$, and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Sn(CF_3SO_3)$. *Inorganic Chemistry* **2000,** *39* (4), 815-819.

14. Rasika Dias, H. V.; Goh, T. K. H. H., Fluorinated tris(pyrazolyl)borates. Syntheses and characterization of sodium and copper complexes of $[HB(3\text{-}(CF_3),5\text{-}(Ph)Pz)_3]^-$. *Polyhedron* **2004,** *23* (2–3), 273-282.

15. Zhao, N.; Bullinger, J. C.; Van Stipdonk, M. J.; Stern, C. L.; Eichhorn, D. M., Cyanoscorpionates: Synthesis and Crystallographic Characterization of One-Dimensional Cu(I) Coordination Polymers. *Inorganic Chemistry* **2008,** *47* (13), 5945-5950.

16. Rheingold, A. L.; Incarvito, C. D.; Trofimenko, S., Dihydrobis(4-cyanopyrazol-1-yl)borate, [Bp4CN], a Functionalized Heteroscorpionate Ligand with Cross-Linking Potential†. *Inorganic Chemistry* **2000,** *39* (24), 5569-5571.

17. Siemer, C. J.; Goswami, N.; Kahol, P. K.; Van Stipdonk, M. J.; Eichhorn, D. M., Dihydrobis(4-cyano-3-phenylpyrazol-1-yl)borate: Homoleptic Mononuclear Cobalt(II) and Copper(II) Complexes with a Cyano-Substituted Scorpionate Ligand. *Inorganic Chemistry* **2001,** *40* (16), 4081-4084.

18. Libertini, E.; Yoon, K.; Parkin, G., The synthesis of $[HB[3,5\text{-}(Bu^tph)_2pz]_3]^-$ (Bu^tph = p-$C_6H_4Bu^t$), a new tris(pyrazolyl)hydroborato ligand: the crystal and molecular structure of Tl{η3-HB[3,5-(Butph)2pz]3}. *Polyhedron* **1993,** *12* (20), 2539-2542.

19. Zhao, N.; Van Stipdonk, M. J.; Eichhorn, D. M., Syntheses and crystal structures of 3-tert-butyl-4-cyano pyrazole and its complexes with cobalt(II), manganese(II), and copper(II). *Polyhedron* **2007,** *26* (12), 2449-2454.

20. Millar, S. Tips and Tricks for the Lab: Growing Crystals Part 3. http://www.chemistryviews.org/details/education/2538941/Tips_and_Tricks_for_the_Lab_Growing_Crystals_Part_3.html (accessed September 30, 2013).

21. Heller, S. T.; Natarajan, S. R., 1,3-Diketones from Acid Chlorides and Ketones: A Rapid and General One-Pot Synthesis of Pyrazoles. *Organic Letters* **2006,** *8* (13), 2675-2678.

22. Zerbi, G.; Alberti, C., Infrared spectra of pyrazoles—I: Pyrazoles mono-alkyl substituted. *Spectrochimica Acta* **1962,** *18* (3), 407-423.

23. Stuart, B., *Infrared Spectroscopy : Fundamentals and Applications*. J. Wiley: Chichester, England, 2004.

24. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010,** *29* (9), 2176-2179.

25. Zhao, N.; Van Stipdonk, M. J.; Bauer, C.; Campana, C.; Eichhorn, D. M., Sandwich Compounds of Cyanotrispyrazolylborates: Complexation-Induced Ligand Isomerization. *Inorganic Chemistry* **2007,** *46* (21), 8662-8667.

26. Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Morooka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A., A new model for dioxygen binding in hemocyanin. Synthesis, characterization, and molecular structure of the μ-η^2:η^2 peroxo dinuclear copper(II) complexes, [Cu(HB(3,5-R2pz)3)]2(O2) (R = isopropyl and Ph). *Journal of the American Chemical Society* **1992,** *114* (4), 1277-1291.

27. Ciunik, Z.; Ruman, T.; Lukasiewicz, M.; Wolowiec, S., Complexes of heteroscorpionate trispyrazolylborate ligands. Part XI. Weak CH/π interactions in crystals of hydrotris(3-phenylpyrazolyl)boratothallium(I) and hydrobis(5-methyl-3-phenylpyrazolyl)(3,5-dimethylpyrazol-yl)boratothallium(I) studied by X-ray crystallography. *Journal of Molecular Structure* **2004,** *690* (1–3), 175-180.

28. Craven, E.; Mutlu, E.; Lundberg, D.; Temizdemir, S.; Dechert, S.; Brombacher, H.; Janiak, C., Thallium(I) complexes with modified poly(pyrazolyl)borate ligands—metal-ligand coordination and crystal packing. *Polyhedron* **2002,** *21* (5–6), 553-562.

29. Trofimenko, S., Boron-pyrazole chemistry. II. Poly(1-pyrazolyl)-borates. *Journal of the American Chemical Society* **1967,** *89* (13), 3170-3177.

30. Renn, O.; Venanzi, L. M.; Marteletti, A.; Gramlich, V., High-Yield Syntheses of Sodium, Potassium, and Thallium Hydrotris[3,5-bis(trifluoromethyl)pyrazolyl]borates and the X-ray crystal structure of {hydrotris[3,5-bis(trifluoromethyl)pyrazolyl]borato} thallium(I). *Helvetica Chimica Acta* **1995,** *78* (4), 993-1000.

31. Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Trofimenko, S., Hydridotris(3-t-butylpyrazolyl)boratothallium(I). A spectroscopic and structural study. *Journal of Organometallic Chemistry* **1989,** *365* (1–2), 19-22.

32. Johnson, D.; Eichhorn, D.; Moore, C.; Mwania, T.; Zhao, N., Thallium(I) Complexes of Cyano-Substituted Bispyrazolylborate Ligands. *J Chem Crystallogr* **2012,** *42* (7), 746-751.

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for TlTp^{Ph2,4CN}. U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Tl(1)	5000	4168(1)	2500	22(1)
N(1)	5107(6)	4620(7)	3918(5)	19(2)
N(2)	3762(6)	5588(6)	2828(4)	16(2)
N(3)	5981(6)	5759(7)	2665(5)	19(2)
N(4)	4880(6)	5542(7)	4097(5)	18(2)
N(5)	4139(6)	6415(6)	3090(4)	15(1)
N(6)	5885(6)	6376(7)	3228(5)	19(2)
N(7)	4214(8)	4075(9)	6228(6)	32(2)
N(8)	1564(7)	7841(8)	1966(6)	28(2)
N(9)	8927(7)	7197(8)	2734(6)	29(2)
C(1)	4957(7)	4051(8)	4461(5)	18(2)
C(2)	4626(7)	4620(8)	5004(5)	19(2)
C(3)	4582(7)	5562(7)	4757(5)	16(2)
C(4)	4389(7)	4347(7)	5684(6)	20(2)
C(5)	5160(6)	3014(4)	4451(5)	21(3)
C(10)	4794(5)	2397(5)	4934(4)	27(2)
C(9)	5084(6)	1449(5)	4971(4)	28(2)
C(8)	5740(6)	1119(4)	4525(4)	27(2)
C(7)	6106(5)	1737(6)	4043(4)	26(3)
C(6)	5816(6)	2684(6)	4005(4)	25(3)
C(11)	4274(5)	6439(5)	5104(4)	20(2)
C(12)	3515(5)	6946(6)	4859(3)	28(2)
C(13)	3245(5)	7775(6)	5195(4)	30(3)
C(14)	3734(7)	8098(5)	5776(4)	29(3)
C(15)	4493(6)	7591(6)	6022(4)	29(3)
C(16)	4763(5)	6762(6)	5686(4)	20(3)
C(17)	2978(12)	5841(19)	2505(15)	17(3)

C(18)	2848(7)	6836(8)	2549(6)	20(2)
C(19)	3598(7)	7177(7)	2937(5)	16(2)
C(20)	2149(8)	7398(9)	2228(6)	23(2)
C(21)	2354(4)	5137(5)	2148(4)	23(2)
C(22)	1419(5)	5299(5)	2151(5)	27(2)
C(23)	820(4)	4619(7)	1872(5)	36(3)
C(24)	1156(6)	3777(6)	1591(5)	35(3)
C(25)	2091(6)	3616(5)	1589(5)	32(5)
C(26)	2690(4)	4296(6)	1867(5)	29(2)
C(27)	3753(5)	8173(4)	3190(4)	18(2)
C(32)	3021(4)	8638(5)	3483(5)	23(4)
C(31)	3125(5)	9565(6)	3737(5)	29(2)
C(30)	3961(6)	10028(4)	3697(4)	32(3)
C(29)	4693(4)	9563(5)	3404(5)	31(3)
C(28)	4589(4)	8635(5)	3151(4)	25(2)
C(33)	6812(14)	5941(19)	2441(16)	20(4)
C(34)	7277(7)	6595(8)	2850(6)	19(2)
C(35)	6660(7)	6888(7)	3345(5)	17(2)
C(36)	8179(9)	6942(9)	2783(6)	23(2)
C(37)	7148(5)	5379(5)	1822(3)	18(2)
C(42)	7950(4)	4849(5)	1872(3)	22(2)
C(41)	8247(4)	4345(5)	1301(4)	25(2)
C(40)	7743(5)	4371(6)	681(3)	27(3)
C(39)	6942(5)	4901(6)	631(3)	28(2)
C(38)	6644(4)	5405(5)	1202(4)	25(2)
C(43)	6812(5)	7601(5)	3899(3)	18(2)
C(48)	7224(6)	8462(5)	3727(3)	26(2)
C(47)	7431(6)	9135(4)	4238(4)	27(3)
C(46)	7224(6)	8947(5)	4922(4)	28(2)
C(45)	6812(6)	8086(6)	5094(3)	30(2)
C(44)	6606(5)	7413(5)	4582(3)	24(2)
B(1)	4961(8)	6411(8)	3602(6)	17(2)

Table 7. Bond lengths [Å] and angles [°] for TlTp^{Ph2,4CN}

Tl(1)-N(1)	2.814(9)	C(12)-H(12)	0.9500
Tl(1)-N(2)	2.773(9)	C(12)-C(13)	1.3900
Tl(1)-N(3)	2.658(9)	C(13)-H(13)	0.9500
N(1)-N(4)	1.374(13)	C(13)-C(14)	1.3900
N(1)-C(1)	1.340(13)	C(14)-H(14)	0.9500
N(2)-N(5)	1.371(11)	C(14)-C(15)	1.3900
N(2)-C(17)	1.34(2)	C(15)-H(15)	0.9500
N(3)-N(6)	1.398(13)	C(15)-C(16)	1.3900
N(3)-C(33)	1.33(3)	C(16)-H(16)	0.9500
N(4)-C(3)	1.362(13)	C(17)-C(18)	1.40(3)
N(4)-B(1)	1.551(14)	C(17)-C(21)	1.50(2)
N(5)-C(19)	1.354(13)	C(18)-C(19)	1.396(15)
N(5)-B(1)	1.536(15)	C(18)-C(20)	1.419(15)
N(6)-C(35)	1.356(13)	C(19)-C(27)	1.488(12)
N(6)-B(1)	1.558(15)	C(21)-C(22)	1.3900
N(7)-C(4)	1.153(15)	C(21)-C(26)	1.3900
N(8)-C(20)	1.161(15)	C(22)-H(22)	0.9500
N(9)-C(36)	1.159(15)	C(22)-C(23)	1.3900
C(1)-C(2)	1.415(14)	C(23)-H(23)	0.9500
C(1)-C(5)	1.476(12)	C(23)-C(24)	1.3900
C(2)-C(3)	1.399(14)	C(24)-H(24)	0.9500
C(2)-C(4)	1.421(15)	C(24)-C(25)	1.3900
C(3)-C(11)	1.473(11)	C(25)-H(25)	0.9500
C(5)-C(10)	1.3900	C(25)-C(26)	1.3900
C(5)-C(6)	1.3900	C(26)-H(26)	0.9500
C(10)-H(10)	0.9500	C(27)-C(32)	1.3900
C(10)-C(9)	1.3900	C(27)-C(28)	1.3900
C(9)-H(9)	0.9500	C(32)-H(32)	0.9500
C(9)-C(8)	1.3900	C(32)-C(31)	1.3900
C(8)-H(8)	0.9500	C(31)-H(31)	0.9500
C(8)-C(7)	1.3900	C(31)-C(30)	1.3900
C(7)-H(7)	0.9500	C(30)-H(30)	0.9500
C(7)-C(6)	1.3900	C(30)-C(29)	1.3900
C(6)-H(6)	0.9500	C(29)-H(29)	0.9500
C(11)-C(12)	1.3900	C(29)-C(28)	1.3900
C(11)-C(16)	1.3900	C(28)-H(28)	0.9500

C(33)-C(34)	1.38(3)
C(33)-C(37)	1.52(3)
C(34)-C(35)	1.399(15)
C(34)-C(36)	1.418(16)
C(35)-C(43)	1.473(11)
C(37)-C(42)	1.3900
C(37)-C(38)	1.3900
C(42)-H(42)	0.9500
C(42)-C(41)	1.3900
C(41)-H(41)	0.9500
C(41)-C(40)	1.3900
C(40)-H(40)	0.9500
C(40)-C(39)	1.3900
C(39)-H(39)	0.9500
C(39)-C(38)	1.3900
C(38)-H(38)	0.9500
C(43)-C(48)	1.3900
C(43)-C(44)	1.3900
C(48)-H(48)	0.9500
C(48)-C(47)	1.3900
C(47)-H(47)	0.9500
C(47)-C(46)	1.3900
C(46)-H(46)	0.9500
C(46)-C(45)	1.3900
C(45)-H(45)	0.9500
C(45)-C(44)	1.3900
C(44)-H(44)	0.9500
B(1)-H(1)	1.0000

N(2)-Tl(1)-N(1)	68.6(3)
N(3)-Tl(1)-N(1)	71.5(3)
N(3)-Tl(1)-N(2)	74.5(3)
N(4)-N(1)-Tl(1)	116.6(6)
C(1)-N(1)-Tl(1)	128.7(7)
C(1)-N(1)-N(4)	108.1(8)
N(5)-N(2)-Tl(1)	115.2(6)
C(17)-N(2)-Tl(1)	129.9(13)
C(17)-N(2)-N(5)	106.3(13)
N(6)-N(3)-Tl(1)	122.7(6)
C(33)-N(3)-Tl(1)	128.2(14)
C(33)-N(3)-N(6)	104.5(15)
N(1)-N(4)-B(1)	123.5(8)
C(3)-N(4)-N(1)	110.0(8)
C(3)-N(4)-B(1)	126.5(9)
N(2)-N(5)-B(1)	122.3(8)
C(19)-N(5)-N(2)	110.6(8)
C(19)-N(5)-B(1)	126.1(9)
N(3)-N(6)-B(1)	119.4(8)
C(35)-N(6)-N(3)	110.6(8)
C(35)-N(6)-B(1)	130.0(9)
N(1)-C(1)-C(2)	108.5(9)
N(1)-C(1)-C(5)	122.2(9)
C(2)-C(1)-C(5)	129.3(9)
C(1)-C(2)-C(4)	129.5(10)
C(3)-C(2)-C(1)	106.7(9)
C(3)-C(2)-C(4)	123.9(10)
N(4)-C(3)-C(2)	106.7(9)
N(4)-C(3)-C(11)	123.8(9)
C(2)-C(3)-C(11)	129.5(9)
N(7)-C(4)-C(2)	176.2(12)
C(10)-C(5)-C(1)	121.0(6)
C(10)-C(5)-C(6)	120.0
C(6)-C(5)-C(1)	118.5(6)
C(5)-C(10)-H(10)	120.0
C(9)-C(10)-C(5)	120.0
C(9)-C(10)-H(10)	120.0
C(10)-C(9)-H(9)	120.0
C(10)-C(9)-C(8)	120.0
C(8)-C(9)-H(9)	120.0
C(9)-C(8)-H(8)	120.0
C(7)-C(8)-C(9)	120.0
C(7)-C(8)-H(8)	120.0
C(8)-C(7)-H(7)	120.0
C(8)-C(7)-C(6)	120.0
C(6)-C(7)-H(7)	120.0
C(5)-C(6)-H(6)	120.0

C(7)-C(6)-C(5)	120.0
C(7)-C(6)-H(6)	120.0
C(12)-C(11)-C(3)	121.3(6)
C(12)-C(11)-C(16)	120.0
C(16)-C(11)-C(3)	118.7(6)
C(11)-C(12)-H(12)	120.0
C(11)-C(12)-C(13)	120.0
C(13)-C(12)-H(12)	120.0
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-C(12)	120.0
C(14)-C(13)-H(13)	120.0
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-C(13)	120.0
C(15)-C(14)-H(14)	120.0
C(14)-C(15)-H(15)	120.0
C(14)-C(15)-C(16)	120.0
C(16)-C(15)-H(15)	120.0
C(11)-C(16)-H(16)	120.0
C(15)-C(16)-C(11)	120.0
C(15)-C(16)-H(16)	120.0
N(2)-C(17)-C(18)	110.5(15)
N(2)-C(17)-C(21)	123(2)
C(18)-C(17)-C(21)	126.4(17)
C(17)-C(18)-C(20)	128.2(13)
C(19)-C(18)-C(17)	105.3(12)
C(19)-C(18)-C(20)	126.4(11)
N(5)-C(19)-C(18)	107.3(9)
N(5)-C(19)-C(27)	125.2(9)
C(18)-C(19)-C(27)	127.3(9)
N(8)-C(20)-C(18)	178.4(13)
C(22)-C(21)-C(17)	118.8(11)
C(22)-C(21)-C(26)	120.0
C(26)-C(21)-C(17)	121.0(11)
C(21)-C(22)-H(22)	120.0
C(21)-C(22)-C(23)	120.0
C(23)-C(22)-H(22)	120.0
C(22)-C(23)-H(23)	120.0
C(22)-C(23)-C(24)	120.0
C(24)-C(23)-H(23)	120.0
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-C(23)	120.0
C(25)-C(24)-H(24)	120.0
C(24)-C(25)-H(25)	120.0
C(24)-C(25)-C(26)	120.0
C(26)-C(25)-H(25)	120.0
C(21)-C(26)-H(26)	120.0
C(25)-C(26)-C(21)	120.0
C(25)-C(26)-H(26)	120.0
C(32)-C(27)-C(19)	117.2(6)
C(32)-C(27)-C(28)	120.0
C(28)-C(27)-C(19)	122.8(6)
C(27)-C(32)-H(32)	120.0
C(31)-C(32)-C(27)	120.0
C(31)-C(32)-H(32)	120.0
C(32)-C(31)-H(31)	120.0
C(30)-C(31)-C(32)	120.0
C(30)-C(31)-H(31)	120.0
C(31)-C(30)-H(30)	120.0
C(29)-C(30)-C(31)	120.0
C(29)-C(30)-H(30)	120.0
C(30)-C(29)-H(29)	120.0
C(28)-C(29)-C(30)	120.0
C(28)-C(29)-H(29)	120.0
C(27)-C(28)-H(28)	120.0
C(29)-C(28)-C(27)	120.0
C(29)-C(28)-H(28)	120.0
N(3)-C(33)-C(34)	113(2)
N(3)-C(33)-C(37)	119(2)
C(34)-C(33)-C(37)	128.7(19)
C(33)-C(34)-C(35)	105.5(14)
C(33)-C(34)-C(36)	128.4(15)
C(35)-C(34)-C(36)	126.0(10)
N(6)-C(35)-C(34)	106.7(9)
N(6)-C(35)-C(43)	125.8(9)
C(34)-C(35)-C(43)	127.5(9)
N(9)-C(36)-C(34)	177.8(14)

C(42)-C(37)-C(33)	120.8(8)
C(42)-C(37)-C(38)	120.0
C(38)-C(37)-C(33)	119.2(8)
C(37)-C(42)-H(42)	120.0
C(41)-C(42)-C(37)	120.0
C(41)-C(42)-H(42)	120.0
C(42)-C(41)-H(41)	120.0
C(42)-C(41)-C(40)	120.0
C(40)-C(41)-H(41)	120.0
C(41)-C(40)-H(40)	120.0
C(39)-C(40)-C(41)	120.0
C(39)-C(40)-H(40)	120.0
C(40)-C(39)-H(39)	120.0
C(40)-C(39)-C(38)	120.0
C(38)-C(39)-H(39)	120.0
C(37)-C(38)-H(38)	120.0
C(39)-C(38)-C(37)	120.0
C(39)-C(38)-H(38)	120.0
C(48)-C(43)-C(35)	117.8(6)
C(48)-C(43)-C(44)	120.0
C(44)-C(43)-C(35)	122.1(6)
C(43)-C(48)-H(48)	120.0
C(47)-C(48)-C(43)	120.0
C(47)-C(48)-H(48)	120.0
C(48)-C(47)-H(47)	120.0
C(48)-C(47)-C(46)	120.0
C(46)-C(47)-H(47)	120.0
C(47)-C(46)-H(46)	120.0
C(45)-C(46)-C(47)	120.0
C(45)-C(46)-H(46)	120.0
C(46)-C(45)-H(45)	120.0
C(46)-C(45)-C(44)	120.0
C(44)-C(45)-H(45)	120.0
C(43)-C(44)-H(44)	120.0
C(45)-C(44)-C(43)	120.0
C(45)-C(44)-H(44)	120.0
N(4)-B(1)-N(6)	110.3(8)
N(4)-B(1)-H(1)	108.4
N(5)-B(1)-N(4)	109.1(9)
N(5)-B(1)-N(6)	112.2(8)
N(5)-B(1)-H(1)	108.4
N(6)-B(1)-H(1)	108.4

Table 8. Anisotropic displacement parameters ($Å^2$x 10^3) for $TlTp^{Ph2,4CN}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tl(1)	20(1)	21(1)	25(1)	0	3(1)	0
N(1)	18(4)	18(4)	22(4)	-3(3)	3(3)	-1(3)
N(2)	21(4)	11(3)	16(4)	1(3)	0(3)	-3(3)
N(3)	20(4)	21(4)	18(4)	-1(3)	2(3)	0(3)
N(4)	20(4)	20(4)	15(4)	-1(3)	2(3)	1(3)
N(5)	15(3)	14(3)	17(4)	-2(3)	3(3)	-1(3)
N(6)	17(4)	21(4)	18(4)	0(3)	0(3)	-1(3)
N(7)	38(6)	31(5)	27(5)	3(4)	4(4)	-8(5)
N(8)	24(5)	26(5)	34(5)	5(4)	-1(4)	0(4)
N(9)	25(5)	26(5)	36(6)	-2(4)	-3(4)	-8(4)
C(1)	20(4)	19(5)	16(4)	1(3)	0(3)	3(4)
C(2)	18(4)	21(5)	18(4)	0(4)	-1(3)	2(4)
C(3)	20(4)	13(4)	13(4)	1(3)	1(3)	1(3)
C(4)	20(4)	16(4)	22(5)	-2(3)	3(4)	2(3)
C(5)	20(5)	14(6)	30(6)	5(5)	6(4)	-3(4)
C(10)	30(6)	22(5)	29(5)	9(4)	5(4)	4(4)
C(9)	38(6)	21(5)	25(5)	2(4)	3(5)	-2(5)
C(8)	29(6)	21(5)	32(6)	-1(4)	-4(5)	2(4)
C(7)	26(6)	25(6)	26(7)	-10(5)	1(5)	2(5)
C(6)	24(6)	17(6)	35(6)	6(5)	12(5)	-2(4)
C(11)	20(4)	24(5)	16(4)	-3(4)	3(3)	3(4)
C(12)	30(6)	37(6)	17(5)	2(4)	1(4)	10(5)
C(13)	38(6)	30(6)	23(5)	2(4)	3(5)	13(5)
C(14)	48(9)	23(6)	16(6)	-4(5)	4(5)	6(6)
C(15)	37(8)	26(7)	26(6)	-10(5)	7(5)	-5(5)
C(16)	22(5)	12(5)	25(6)	-1(5)	3(4)	-8(4)
C(17)	15(7)	15(6)	20(6)	-3(5)	7(6)	-8(6)
C(18)	18(4)	17(4)	24(5)	4(4)	1(4)	-2(3)
C(19)	14(4)	18(4)	17(4)	4(3)	1(3)	1(3)
C(20)	20(5)	23(5)	25(5)	5(4)	1(4)	-3(4)
C(21)	20(5)	26(5)	22(5)	1(4)	-2(4)	-5(4)

C(22)	22(5)	26(5)	32(6)	-1(4)	-2(4)	-3(4)
C(23)	21(5)	39(7)	47(8)	-8(6)	-1(5)	-7(5)
C(24)	32(6)	37(7)	33(6)	-5(6)	-8(5)	-15(6)
C(25)	33(8)	22(10)	40(10)	1(8)	-5(8)	-2(7)
C(26)	24(5)	35(7)	27(5)	-9(5)	-4(4)	0(5)
C(27)	21(4)	17(4)	17(4)	1(3)	-1(3)	0(4)
C(32)	27(7)	21(9)	21(7)	3(6)	0(6)	0(6)
C(31)	35(6)	28(6)	24(5)	0(4)	-3(5)	7(5)
C(30)	54(8)	17(5)	25(5)	-2(4)	-7(5)	-1(5)
C(29)	26(6)	25(6)	42(7)	2(5)	-9(5)	-7(5)
C(28)	21(5)	22(5)	30(6)	-5(4)	-1(4)	-2(4)
C(33)	18(8)	16(7)	25(7)	4(5)	5(7)	7(6)
C(34)	19(4)	18(4)	21(5)	6(4)	1(4)	1(3)
C(35)	18(4)	15(4)	17(4)	1(3)	1(3)	-3(3)
C(36)	27(5)	22(5)	19(5)	-1(4)	3(4)	-4(5)
C(37)	19(4)	15(4)	21(4)	4(3)	7(3)	0(3)
C(42)	23(5)	19(5)	25(5)	7(4)	2(4)	3(4)
C(41)	24(5)	17(5)	34(6)	-4(4)	6(4)	-3(4)
C(40)	27(6)	29(7)	25(6)	-6(5)	7(5)	-9(5)
C(39)	25(5)	33(6)	25(5)	-8(5)	0(4)	-3(5)
C(38)	18(4)	31(6)	26(5)	-5(4)	0(4)	0(4)
C(43)	23(4)	15(4)	18(4)	1(3)	1(3)	1(4)
C(48)	28(5)	18(5)	31(6)	0(4)	1(4)	-3(4)
C(47)	29(6)	19(6)	32(6)	-1(5)	2(5)	-6(6)
C(46)	26(5)	27(6)	30(6)	-13(4)	-4(4)	2(4)
C(45)	32(6)	40(7)	18(5)	-3(5)	-4(4)	0(5)
C(44)	26(5)	27(5)	19(5)	-3(4)	-1(4)	-3(4)
B(1)	21(5)	14(4)	16(4)	2(4)	2(4)	1(4)

Table 9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for $TlTp^{Ph2,4CN}$

	x	y	z	U(eq)
H(10)	4346	2623	5238	32
H(9)	4834	1027	5301	34
H(8)	5939	471	4551	33
H(7)	6555	1511	3738	31
H(6)	6066	3106	3676	30
H(12)	3181	6725	4461	34
H(13)	2726	8121	5027	36
H(14)	3550	8664	6006	35
H(15)	4828	7811	6419	35
H(16)	5282	6416	5854	24
H(22)	1189	5874	2343	32
H(23)	181	4729	1874	43
H(24)	747	3313	1401	41
H(25)	2321	3041	1397	38
H(26)	3329	4185	1866	35
H(32)	2449	8322	3511	27
H(31)	2625	9883	3937	35
H(30)	4032	10662	3870	39
H(29)	5264	9879	3377	38
H(28)	5089	8318	2950	30
H(42)	8294	4831	2296	27
H(41)	8795	3982	1335	30
H(40)	7947	4026	291	32
H(39)	6597	4918	207	33
H(38)	6096	5767	1168	30
H(48)	7365	8591	3259	31
H(47)	7712	9724	4121	32
H(46)	7365	9407	5271	33
H(45)	6671	7957	5561	36

H(44)	6324	6824	4700	29
H(1)	4944	7011	3884	21

VITA

BOZUMEH SOM

Personal Data	Date of Birth: September 04, 1982 Place of Birth: Cape Coast, Ghana Marital Status: Married
Education	Master of Science (MS) Chemistry, Dec. 2013, East Tennessee State University(ETSU), Johnson City, TN Master of Science (MSc) Natural Resources Management, June 2011, Norwegian University of Science & Technology Trondheim (Norway) Bachelor of Science (BSc) Chemistry, May 2007, University of Cape Coast, Cape Coast (Ghana)
Related Experience	Graduate Assistant, Department of Chemistry, East Tennessee State University (ETSU), Johnson City, TN, 2012 – 2013 Chemistry Tutor, Wesley Girls' High School, Cape Coast (Ghana), 2008 – 2009 Teaching Assistant, Department of Chemistry, University of Cape Coast, Cape Coast (Ghana), 2007 – 2008

Professional Development	15th International Conference on Heavy Metals in the Environment, Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology Gdansk, Poland, September 2010
Honors and Awards	Michael and Karen Fallgatter Scholarship, East Tennessee State University (ETSU), 2013 Norwegian Quota Scholarship Scheme, Norwegian University of Science and Technology, Norway - Trondheim, 2009 – 2011