

**DESIGN AND SYNTHESIS OF NEW EFFICIENT
PYRIDINE-BASED CATALYSTS FOR ETHYLENE
POLYMERIZATION**

BY

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Dedication

This project is wholly dedicated to my late **PARENTS**. May Allah SWT grant them Jannatul-Firdaws.

Acknowledgement

Bismillah!

I would like to give all thanks and adorations to Almighty Allah for giving me an opportunity to diligently see the end of this thesis work. May His blessings and salutations be upon the universal Messenger, the Spirit of truth, Prophet Muhammad SAW.

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List of Abbreviations

PE	Polyethylene
PP	Polypropylene
PB-1	Poly(1-butene)
PO-1	Poly(1-octene)
P-4Mpen	Poly(4-methyl-1-pentene),
EPE	Ethylene-propylene elastomer
EPDR	Ethylene-propylene-diene rubber
PET	Polyethylene terephthalate
PVC	Polyvinyl chloride
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
LLDPE	Linear low-density polyethylene
UHMWPE	Ultrahigh molecular weight polyethylene
GDP	Growth domestic product
MWD	Molecular weight distribution
MW	Molecular weight
T_m	Melting temperature
NMR	Nuclear magnetic resonance
FT-IR	Fourier transform infrared spectroscopy
ESI-MS	Electrospray ionization mass spectrometry
DSC	Differential scanning calorimetry
TGA	Thermogravimetric analysis
SXRD	Single X-ray diffraction
GPC	Gel permeation chromatography
MHz	Megahertz
MMAO	Modified methylaluminoxane

BR	1-(6-bromopyridin-2-yl)-N-(2,6-diisopropylphenyl)methanimine
NLi	lithium (2,6-diisopropylphenyl)amine)
BR-NH	N-(2,6-diisopropylphenyl)-6-(((2,6-diisopropylphenyl)imino)methyl)pyridin-2-amine)
BR-NLi	Lithium N-(2,6-diisopropylphenyl)(6-(((2,6-diisopropylphenyl)imino)methyl)pyridin-2-yl)amide)
BL1	N-(2,6-diisopropylphenyl)-6-((2,6-diisopropylphenyl)imino)methyl)-N-((6-(2,6-diisopropylphenyl)imino)methyl)pyridin-2-yl)pyridin-2-amine)

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Abstract

Full Name: BISHIR IBRAHIM

Thesis Title: Design and Synthesis of New Efficient Pyridine-Based Catalysts for Ethylene Polymerization

Major Field: Chemistry

A sterically bulky ligand bearing pyridine-imine donors has been successfully synthesized and characterized. Further treatment of the ligand with the corresponding iron, cobalt, and nickel precursors afforded new monometallic, paramagnetic, six-coordinate octahedral complexes. The complexes were extensively characterized by various techniques, including IR spectroscopy, magnetic susceptibility measurement, ESI-MS, and single X-ray crystallography. Single-crystallographic evidence revealed how the coordinated donors provided the right steric effect to the catalytic center. On activation with MMAO as a co-catalyst, the complexes were very active in ethylene polymerization to Ultrahigh Molecular Weight Polyethylene (UHMWPE). Interestingly, exceptional catalytic activity of $5.54 \times 10^7 \text{ g (PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$ was obtained at 60 °C using cobalt catalyst. Thermal stability at 80 °C and the highest polymer molecular weight of $1.85 \times 10^6 \text{ g mol}^{-1}$ were obtained for iron catalyst, while nickel catalyst attained the highest catalytic activity of $1.26 \times 10^6 \text{ g of (PE) mol}^{-1} (\text{Ni}) \text{ h}^{-1}$ at its optimum polymerization temperature.

ملخص الرسالة

اسم الزهرة: بشر إبراهيم

عنوان الرسالة: تصميم وتوليف مجمعات جديدة فعالة قائمة على البيريدين لبلمرة الإيثيلين التحفيزي

المجال الرئيسي: الكيمياء

تم تصنيع وتوصيف ترابط ضخم بشكل استقيم يحمل مانحين من البيريدين إيمين بنجاح. أتاحت المعالجة الإضافية للترابط بسلانف الحديد والكوبالت والنيكل المقابلة مجمعات ثماني السطوح أحادية المعدن ومغناطيسية سداسية الإحداثيات. تميزت المجمعات على نطاق واسع بتقنيات مختلفة ، بما في ذلك التحليل الطيفي بالأشعة تحت الحمراء ، وقياس الحساسية المغناطيسية ، و MS-ESI ، وعلم البلورات أحادي الأشعة السينية. كشفت الأدلة البلورية المفردة كيف قدم المتبرعون المنسقون التأثير الفراغي الصحيح للمركز التحفيزي. عند التنشيط باستخدام MMAO كمحفز مساعد ، كانت المجمعات نشطة جدا في بلمرة الإيثيلين إلى البولي إيثيلين عالي الوزن الجزيئي (UHMWPE). ومن المثير للاهتمام ، أن النشاط التحفيزي الاستثنائي البالغ 5.54×10^7 جم (PE) $^{1-mol}$ (Co) $^{1-h}$ تم الحصول عليه عند 60 درجة مئوية باستخدام محفز الكوبالت. تم الحصول على الثبات الحراري عند 80 درجة مئوية وأعلى وزن جزيئي للبوليمر يبلغ 1.85×10^6 جم مول $^{-1}$ لمحفز الحديد ، بينما حقق محفز النيكل أعلى نشاط حفاز يبلغ 1.26×10^6 جم من (PE) $^{1-mol}$ (Ni) $^{1-h}$ عند درجة حرارة البلمرة المثلى.

CHAPTER ONE

INTRODUCTION

1.1 General Background

Globally, the largest class of synthetic polymeric materials which have prominent applications in daily lives are polyolefins [1]. Industrial production of these important materials, which led to one of the most recent advancements in the polyolefin industry, is attributed to the recent development in catalysis [2]. To synthesize polymeric materials, highly active and stable catalysts are crucial in the production process. Conventionally, ethylene polymerization is based on the early transition metal catalysts, which were first discovered by Ziegler-Natta in the early 1960s [3, 4]. This discovery led to a significant increase in research in the area heterogeneous catalysis. Apart from the difficulty in understanding the mechanism of action of the heterogeneous catalysts, some of the major drawbacks of using such catalysts include the production of polymers with broad molecular weight and their inability to tolerate polar monomer insertion due to their oxophilic nature [5, 6]. These effects in turn, render the absence of some desired features needed in polymers such as adhesion, electrical conductivity, miscibility, and rheological properties [7, 8].

Extensive theoretical and experimental work by Kaminsky and co-workers led to the discovery of single-site homogeneous catalysts which were based on metallocene [6]. Catalysis based on metallocene catalysts allows a more efficient control over polymer MWD, stereochemistry, and tacticity, thereby making a significant impact in polyolefin industries [9]. Since then, kinetics and mechanisms of metallocene catalysts have been continuously explored. Although metallocene catalysts can be used to polymerize strained cyclo-olefins such as norbornene, cyclopentene, and cyclobutene, which form polymers significant in the production

of optical and fiber materials, they cannot be used to polymerize olefinic monomers incorporated with polar functional groups [10]. As it can be inferred, both the Ziegler-Natta and the metallocene catalysts are based wholly on the early and mid-transition metals.

To overcome the drawbacks of polymerizing α -olefins with polar monomers, researchers centered their eyes on the applicability of late transition metal complexes as polymerization catalysts. The first attempt to make such exploration was made by Brookhart et al. in 1995, when Ni(II) and Pd(II) complexes were applied in α -olefin polymerization to form polymers with the desired structural morphology [11, 12].

The legendary discovery made by Brookhart and his co-workers paves the way for an immense development in the synthesis of homogeneous, single-site and active catalysts using the late transition metals for the polymerization of α -olefins. Apart from the ability of late metal complexes to polymerize ethylene effectively with high activity [13-16], these catalysts can also polymerize functional monomers with comparable turnover frequency relative to the ethylene monomers without polar functional groups, thereby given them a great catalytic advantage [17].

1.2 Statement of the Problem

A plethora of research papers and patents have been published on the applications of late transition metal complexes as homogeneous catalysts in olefin polymerization. Even though these catalysts received much attention as active and promising candidates for industrial polymerization, there is still a potential need to have new complexes that are thermally stable to produce unique polymers for wide variety of applications [18]. Additionally, the utilization of various donors in the synthesis of new metal complexes that are rationally designed for ethylene polymerization has achieved limited success [19], and thus there is a need to design and synthesize new catalysts for potential industrial applications. Herein, this research aims to design

new geometrically octahedral complexes bearing pyridine-imine donors and evaluate their applications for ethylene polymerization to ultra-high molecular weight polyethylene, an important material of choice for application in aerospace and defense industries and in the production of biomedical materials/devices.

As a general overview, this chapter provides information on the research background, chapter 2 contains relevant literature information on various polyolefins, historical development in polyolefin synthesis, and current trends entailing the use of transition metal catalysis. Furthermore, chapter 3 gives the details of the experiment and instrumental procedures, techniques, and data analysis. Chapter 4 includes the results and the discussion part. Chapter five contains summary, conclusion, and recommendations for future work.

1.3 Aim and Objectives of the Study

The aim of this research is to synthesize new, efficient and active catalysts of iron, cobalt, and nickel for ethylene polymerization. The objectives of the research are as follows:

- i. Synthesize and characterize new ligands from pyridine-based and aniline-based derivatives
- ii. Synthesize the corresponding complexes of Fe, Co, and Ni bearing the newly synthesized compounds
- iii. Characterize the complexes using various techniques including NMR, FT-IR, ESI-MS, magnetic susceptibility measurement, and single-crystallography
- iv. Evaluate the activity of the complexes in ethylene polymerization
- v. Characterize the polymers obtained and explore their potential applications

CHAPTER TWO

LITERATURE REVIEW

2.1 POLYOLEFINS

Basically, polyolefins are defined as polymers obtained from olefins, which principally include ethylene, propylene, 1-butene, 1-hexene, 1-octene, and other olefinic monomers. Polyolefins are regarded as waxy-like substances, containing only carbon and hydrogen atoms. The exceptional properties and less cost of production of polyolefins make them the building block of many chemical industries [20].

Historically, the scene behind polyolefins started in late 1890s when German chemist, Hans von Pechmann, confirmed that polymethylene containing a long chain of methylene units was synthesized from diazomethane [21]. About 40 years later, a resin with high molecular weight synthesized from $\text{CH}_2=\text{CH}_2$ and benzaldehyde at high pressure marked another beginning in polyolefin synthesis. Owing to the discovery of HDPE in 1953 by Ziegler and subsequently the synthesis of polypropene in 1954 by Giulio Natta, tremendous improvement was realized in polyolefin industries due to the development of industrial polymerization catalysts [2].

Polyolefins are thermoplastic polymers that have undergone tremendous growth as commercially available materials and are widely used in all aspects of human lives. Industrially, extrusion, calendaring, and molding (either by blow, injection, or compression) are the typical fabrication processes for polyolefins [22, 23]. These techniques, in addition to other factors, gave rise to several types polymeric materials such as homopolymers, copolymers, and polymer blends, with diverse range of applications [24].

The most widely available polymeric materials include PE, PP, PB-1, PO-1, poly(4-methyl-1-pentene), EPE, and ethylene-propylene-diene rubber (EPDR) [25]. Of all these, PE and

PP are the most commonest types of polymeric materials [26]. Saudi Arabia has become the center of polyolefins production such as PE, PP, PET and polyvinyl chloride, which positively contributes to its GDP [27].

The succeeding part briefly described some of the types of polyolefins, namely, polyethylene, polypropylene, and poly(but-1-ene). This will give the reader a glimpse of the vast applications of these important materials.

2.1.1 Polyethylene (PE)

Polyethylene refers to any polymer in which the building block is ethylene. Ethylene is a gaseous hydrocarbon, which is mainly produced through steam cracking of hydrocarbons at elevated temperatures [28]. Ethylene is made up of C=C bond, which under the influence of polymerization catalyst, the double bond can be broken into a single chain of long repeated units to form polyethylene.

When Eric and Gibson discovered a waxy solid, that was later identified to be polymer in 1933, the potential application of the material was shortly explored [29]. The solid, which was made up of highly branched units (low-density) was synthesized under high conditions of temperature and pressure. In 1953, Karl Ziegler and Erhard of Max Planck Institute jointly invented the first HDPE using organometallic catalysts [24].

PE is a semicrystalline polymeric material, whose properties depend on the relative proportion of the amorphous and the crystalline phases present in it [30]. At room temperature, part of polyethylene possesses a degree of structural crystallinity. The crystallinity of PE provides information on its structural constituents, while the amorphous phase provides information related to its elastic properties. Thus, these made polyethylene semi-crystalline

substance and one of the most important and most widely used polymers for making various plastic containers, wire cables for power transmission, insulation materials, pipes for construction, linings, and coating materials [24].

PE occurs in several types with varying molecular weight, polydispersity, density, crystallinity and degree of branching. As shown in **Figure 2.1**, there are three main classes of PE, namely, HDPE, LDPE, and LLDPE each with its unique molecular weight and polydispersity. MW and polydispersity in most situations depend on the degree of branching. Branching in polyethylene can either be short or long. Short chain branching arises due to comonomer incorporation, while long branches result from side reactions during the polyolefin production process.

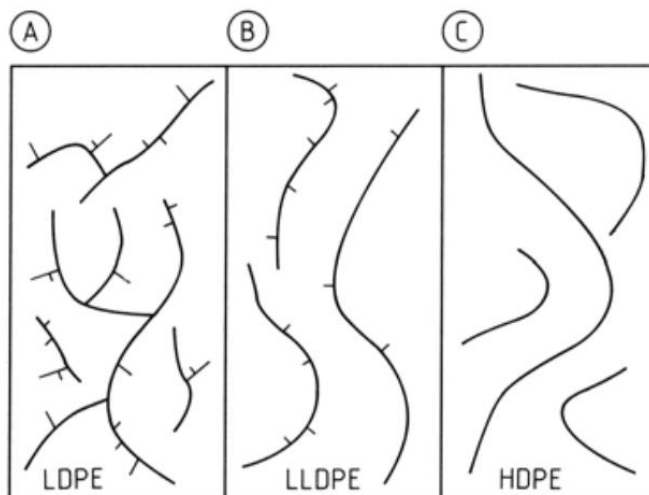


Figure 2.1: Schematic Molecular structures of polyethylene (A; LDPE; LLDPE; B;HDPE; C) [31].

2.1.1.1 LDPE

The structure of LDPE contains many long and short branches. The short branches, which are mainly one or two carbon atoms, are not uniformly arranged. There has been an assertion that ethyl branches probably occur in pairs in LDPE [32]. The clustering of branches in LDPE resulted to a density range of $0.91\text{-}0.94\text{ g/cm}^3$ [33]. As a result, the molecular mass distribution (MMD) of low-density polyethylene is moderately broad [34].

Low-density polyethylene was the first form of polyethylene to become commercially viable, and was discovered accidentally in 1933 at Imperial Chemical Industries by Fawcett et al. [29]. The value of the material was then quickly realized and exploited. For example, LDPE was used as cable insulation material for radar during the second world [35].

The production process of LDPE is via free radical reaction of supercritical ethylene using radical initiators at elevated temperature and pressure [36]. This kind of polyethylene

contains long branches, which are believed to give the low-density polyethylene a superior ease of processing as compared to high-density polyethylene [36].

2.1.1.2 HDPE

One of the major advancements in polyolefin industries was the discovery of catalysts that can produce linear polyethylene by Ziegler in 1953 [37, 38]. The results of this discovery showed that HDPE is more crystalline and therefore denser than LDPE due to the presence of long chains. HDPEs are produced using supported catalysts, which are in most cases, made up of titanium chloride supported by silica. The choice for heterogeneous catalytic process is attributed to the ease with which the catalyst can easily be recycled after the completion of the reaction [37]. Addition of chain transfer agents such as hydrogen can control the molecular weight of HDPE. Incorporating a small amount of comonomer such as 1-hexene or 1-butene, breaks the methylene units, and thus reduces the density leading to more flexibility on the kind of polymers to produce [39]. The density of HDPE ranges from 0.93 to 0.97 g/cm³ due to its less branching [33].

HDPE is widely used in the production of molded containers, detergent bottles, pipes for water distribution, high density fibers, bulletproof vehicles, medical devices, and many more [39].

2.1.1.3 LLDPE

LLDPE is a form of polyethylene possessing branches of uniform length. The branches are on average, equally and randomly distributed between chains, with the shorter chains having the highest concentration of branches [40]. The first method of producing LLDPE was fairly uneconomical, as it was based on solution process [39]. The expensive nature arises due to the

need to use additional steps to isolate the polymer from the solution. Currently, the most widely used method in the production of LLDPE was invented by the Union Carbide industry in late 1960s [41].

The process (Unipol process) utilizes fluidized bed reactors at low-pressure to produce polyethylene resins. The process simplifies the production process and reduces operational cost, leading to the production of large volume of polyethylene products [42]. In the solution-phase system, 1-octene or higher olefinic monomers can be incorporated as comonomers, whereas in the gas-phase system, propylene or 1-butene is mainly used as a comonomer [39].

The density of the product is controlled by the type and the amount of comonomer incorporated. The superior properties (mechanical) of LLDPE make its processing very difficult. It is very versatile and has good electrical properties.

2.1.2 Polypropylene (PP)

Polypropylene is a polymer containing propene monomers as the building block. It became commercially available around 1954 [27]. Similar to polyethylene, polypropylene has excellent properties, and it accounted for nearly 16% of the global plastic materials [27]. Due to the low cost of PP, it is one of the most widely used polymeric material for the fabrication of microporous membranes [43].

Among the plastic materials, polypropylene has the lowest density [27]. The crystallinity of polypropylene is controlled by how regularly the monomers are placed along the chain, and this determines the tacticity of polypropylene.

The first isotactic form of propylene was made by Natta and Phillips Petroleum Company in 1950s [37, 44]. As the name implies, both methyl groups and hydrogen are regularly arranged

on one side of the chain. Isotactic polypropylene is built in a folded fashion, and the desired isotactic property can be achieved by using suitable catalysts [37]. The next form of crystalline polypropylene is syndiotactic polypropylene. The stereoregularity in syndiotactic PP ensures that the CH₃ groups are alternated along the polymer chain. Syndiotactic PP was also synthesized by Natta, but it became commercially available when metallocene catalysts were discovered [39]. The final class of polypropylene is atactic polypropylene, which has no stereoregularity. Atactic polypropylene is amorphous and cheap, with applications mostly in manufacturing adhesives. The atactic polypropylene was first obtained as a byproduct during isotactic polypropylene synthesis [39]. Schematic structures of the three (3) types of polypropylenes are shown in Figure 2.2.

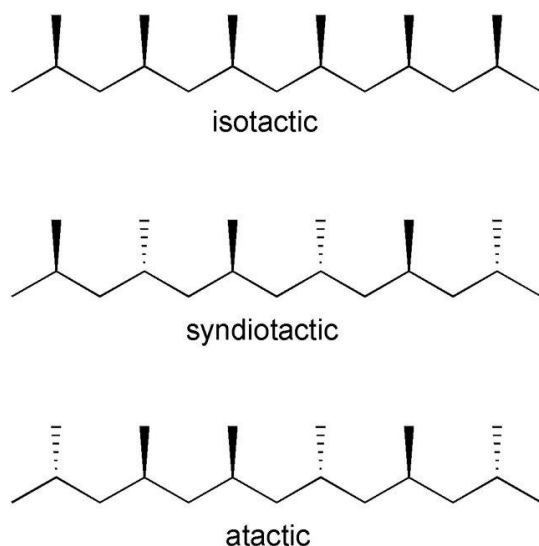


Figure 2.2: Tacticity in polypropylene

2.1.3 Poly-1-butene (PB-1)

This polyolefin contains 1-butene as a monomer. Although its wide applications are not comparable to those of lighter polyolefins, the supply has recently increased due to its demand as a comonomer in the production of LLDPE [45].

The exceptional properties of poly-1-butene that are more pronounced are its creep behavior and its ability to resist stress cracking even at elevated temperatures, which was assumed to be due to its high molecular mass [45]. The melting temperature of poly-1-butene and its stiffness are intermediate between those of HDPE and low-density PE, while its thermal stability is within that of PE and PP.

The main applications of poly-1-butene are in the manufacturing of pipes and tubes due to its high resistance to corrosion, as open-easy packaging material if blended with propylene or polyethylene in the modification of fibers, and in the production of films and sheets [46].

2.1.4 Poly-4-methylpentene

This is an isotactic, higher polyolefin containing methyl-pentene as the repeating unit [44]. The polymer was first commercialized in 1973 [47]. The polymeric materials made by this polymer are highly transparent and are widely used in the manufacture of medical devices [48]. The polymers made by poly-4-methylpentene also possess excellent electric insulation properties, high melting temperature and high degree of gas permeability [47].

2.2 Historical developments on catalysts in polyolefin production

2.2.1 Phillips catalysts

Phillips catalysts are heterogeneous catalysts that are produced by impregnating silica with chromium, followed by calcination at high temperature of about 800 °C [49]. The catalyst was discovered by Hogan and Banks in 1951 during an experiment on their attempt to dimerize propylene [49]. Instead of getting the dimer, high molecular weight polypropylene polymers were generated and the discovery was further applied to ethylene. The success of the research led

to the immediate commercialization of the catalysts. Phillips catalysts accounted for half the percentage of the world polyethylene [41].

After the discovery and licensing of the Phillips catalyst to nine different companies across the world, various operational plants producing homopolymers were built around 1956 [50]. Various polymer grades such as ethylene-butene copolymers and ethylene-hexene copolymers were produced using the Phillips catalysts in later years.

In the early years of the discovery, polymerization was carried out in a solvent medium, where the polymer is dissolved in a solvent as its formed. The need to improve the economic nature of the process led to the introduction of slurry process [51]. The slurry process uses a diluent instead of a solvent. The diluent is usually paraffin with low boiling point such as pentane, isopentane or isobutane. The need to produce LLDPE in 1980s led to another advancement in the reactor where fluidized-bed technology using mega-loop reactors was invented [49]. Polymerization based on this technology made it possible to produce HDPE or LLDPE with ease using the Phillips catalysts.

2.2.2 Ziegler-Natta catalysts

The discovery of one of the most widely used catalysts by Ziegler-Natta, led to the award of the 1963 Nobel Prize in Chemistry. Together with Phillips catalysts, these catalysts accounted for most of the global PE production. Similar to Phillips chromium oxide supported catalysts, Ziegler-Natta are heterogeneous catalysts, which are based on titanium chloride supported with main group metal alkyls [4].

Early Ziegler-Natta catalysts were based on titanium trichloride (TiCl_3), usually obtained together with about one-third of co-crystallized aluminium trichloride (AlCl_3) when TiCl_4 is

reduced with AlEt_2Cl or $\text{Al}_2\text{Et}_3\text{Cl}_3$ using AlEt_3 as co-catalyst [4]. Various kinetic studies revealed that early Ziegler-Natta catalysts were not very active, as only a small fractions of Ti atoms remain on the active crystalline surface [31]. Initial attempts to enhance the performance by supporting the transition metal catalysts on surface led to the optimum MgCl_2 supported Ziegler-Natta catalysts, which were very active and are the most widely used nowadays [52]. The presence of multiple sites in the catalysts result in the formation of polymers with dispersed structures between chains, leading to the high polydispersity of the polymers obtained using the catalysts [53].

2.2.3 Metallocene catalysts

Metallocenes are transition metal complexes containing bonded cyclopentadienyl ligand(s). The catalysts were first discovered at the university of Hamburg in 1970s [54]. Shortly after the discovery of metallocene catalysts, it was discovered that the catalysts can polymerize olefinic monomers in the presence of aluminium alkyl as a co-catalysts, but with low activity. The discovery of methylaluminoxane positively improved the performance of metallocene related catalysts, thereby improving the activity and the polymer yield [4, 9].

The discovery of metallocene catalysts revolutionized the polymerization industry due to their ability to incorporate various short and long chain comonomers such as styrene [55], 1-octadecene [56], isobutylene [57], norbornene [58], which conventional heterogeneous catalysts were unable to do so [59]. This ability of metallocene catalysts to copolymerize olefinic monomers can be affected by the ligand nature, substituents, and the metal type [59]. Figure 2.3 shows some metallocene catalysts reported in literature.

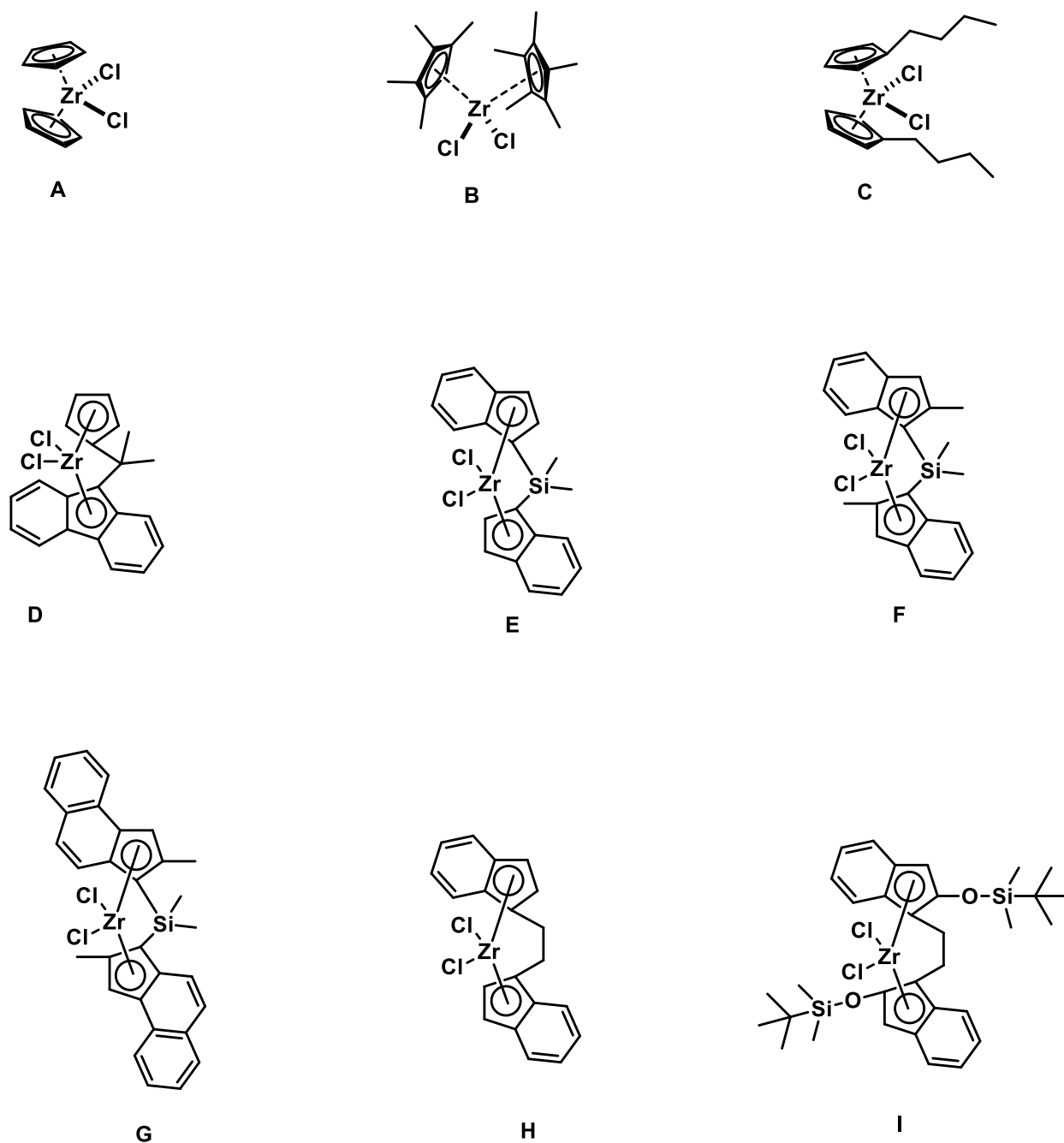


Figure 2.3: Previously reported metallocene catalysts

The first catalyst in Figure 2.3 is zirconocene. The catalysts, if activated with MAO, is very active towards ethylene monomers and mainly provides atactic polymers. Since the 1-olefin monomer can coordinate to the catalyst in any fashion, the polymer chain will be limited [9]. The increase in the steric bulk around the catalytic center significantly decreases the comonomer response [60], as present in the catalyst B (methyl substituted) and C (butyl substituted). The microstructure of the catalysts can also be

affected by the symmetry of the ligand. Catalysts with C_s symmetry such as **D** [61], enabled the synthesis of syndiotactic polypropylene. The reactivity of comonomer towards the catalyst was improved by using $\text{Si}(\text{Me})_2$ bridge catalyst (**E**), in which the molecular weight of polymer and tacticity were improved [62]. Similarly, the presence of substituent (2-methyl) at the indenyl ligand in **F**, resulted to enhancement of comonomer insertion, and the resulted polymers obtained were highly isotactic [63]. Further developments on catalyst **F** through rational catalyst design technique led to the discovery of catalyst **G** and its related types, which were extensively applied in ethylene copolymerization with 1- C_4H_8 and 1- C_8H_{16} [64].

2.2.4 Late transition metal catalysts

Recently, there has been a growing concern on the synthesis of new late transition metal complexes for their applications in the polymerization of readily available and inexpensive olefinic monomers [65]. For many years, one of the most important processes which utilizes the late transition metal homogeneous catalysis was Shell Higher Olefin Process (SHOP). The original catalyst bearing keto-phosphorus ligands and nickel as the central metal (**Figure 2.4A**) is primarily used to produce linear polyolefins [66]. Keim (2013), Soula et al. (2001) and Zhang (2018) uses Ni and Pd metals with donors bearing P-O type and P-PO type to generate linear polyethylene polymers [67-69]. Studies by Yu et al. in 2021 revealed that imine-based catalysts (**Figure 2.4B**) of the same metals (Ni and Pd) produce branched polymers and the catalysts have a tendency to enhance some specific desirable properties of the polyethylene polymers [70].

Among the imine-based catalysts, α -diimine-based catalysts (**Figure 2.4C**) were the first to be discovered and effectively examined for their application in ethylene polymerization [12, 71, 72]. Research conducted by D'Auria and co-workers on iminopyridine Ni catalysts (**Figure**

2.4D), revealed that when the pre-catalysts were activated with co-catalyst, mainly branched oligomers with low MW, which have potential application as lubricants were produced [73].

To enhance the performance and productivity of the designed catalysts, various synthetic methodologies were adopted. For example, symmetric axial shielding strategy which involves the restriction of rotation around the N-aryl moieties that led to the blockage and interlocking of the metal center from the axial position was reported to improve catalytic performance [18]. Wang and co-workers adopted this strategy and synthesized new Ni(II) α -diimine catalysts (**Figure 2.4E**) with high thermal stability and catalytic activity exceeding $10^6 \text{ gmol}^{-1} \text{ h}^{-1}$ [18]. Synergistic activity enhancement via the formation of mixed-nuclear metallic complexes greatly enhances catalytic activity as reported by Shen and Jordan on tetranuclear Pd catalysts [74], and on another studies by Nie and co-workers on several binuclear vanadium catalysts which were reported in both cases to exhibit higher activity than their analogous monometallic ones (**Figure 2.4F**) [75]. Careful manipulation of the backbone substituents as revealed in the studies conducted by Zou and co-worker on Ni and Pd catalysts (**Figure 2.4G**) is also critical in improving catalytic performance [76]. In the study, catalysts with methoxy substituent at ortho position of the acenaphthyl backbone exhibited exceptional catalytic performance. In another study, it was also reported that less electron-donating groups on the nickel catalysts and the presence of chelating ligands improve significant catalytic efficiency [77-79]. A study has also shown the possibility of fine-tuning and boosting catalytic performance of nickel phenoxy-imine catalysts having polyethylene glycol units by the aid of cationic species as co-additives [79]. Replacement of the polyethylene glycol units by chelating phenyl groups also resulted in a short distance between Ni and alkali metal ion in the catalyst which enhanced the catalysts` efficiency [80]. Of notable significance, in most of the catalysts having pyridine as a donor, presence of less

bulky substituent such as methyl on position 6 of the pyridine was reported by Laine et al. to give polymers with low branching and high molecular weight (**Figure 2.4H**) [81]. Presence of aryl substituent at the same position was reported to give rise to ethylene dimerization [82]. Another finding revealed that no direct relationship between the polymer MW and the nature of the substituents present in the pyridine ring [83].

In this study, six-coordinate octahedral complexes of Fe, Co, and Ni were synthesized (**Figure 2.4I**) and applied for ethylene polymerization to ultrahigh molecular weight polyethylene.

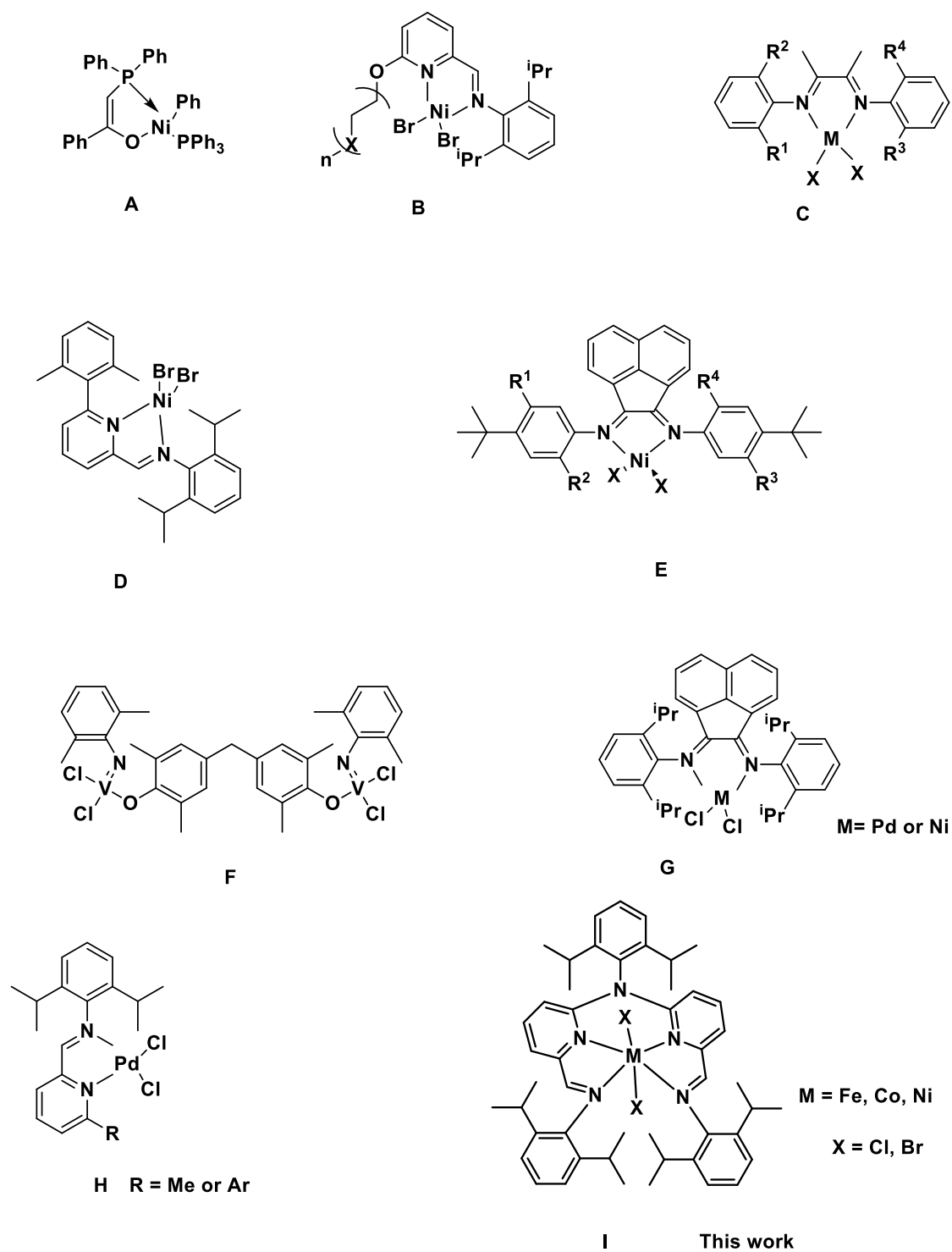


Figure 2,4 Previously reported late catalysts

CHAPTER THREE

RESEARCH METHODOLOGY

As a general overview, the following are the steps which this experimental work undergoes:

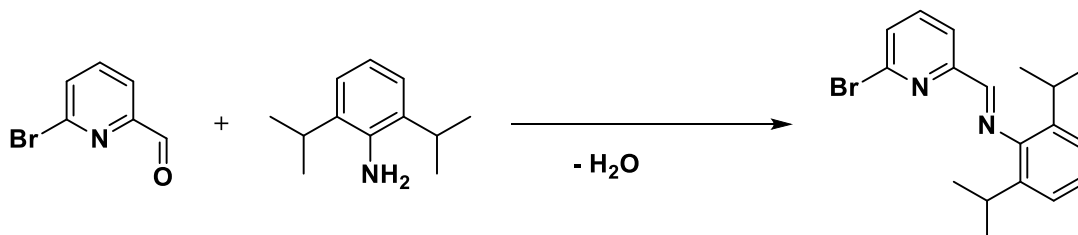
- (i) Synthesis of new bulky ligand bearing pyridine-imine donors and its characterization
- (ii) Treatment of the ligand with metal precursors to form complexes
- (iii) Characterization of the complexes using various spectroscopic techniques including IR spectroscopy, magnetic susceptibility measurement, and single X-ray crystallography
- (iv) Treatment of the complexes with co-catalyst to polymerize ethylene
- (v) Determination of the MW and T_m of the generated polymers

3.1 Materials and Chemicals

All chemicals were purchased from Sigma Aldrich Chemicals and used without further purification. The solvents used in synthetic methodologies and the polymerization were purified prior to use. Unless otherwise state, the synthesis of the complexes was carried out under inert conditions, with the use of Schlenk-tube techniques using standard experimental procedures as cited.

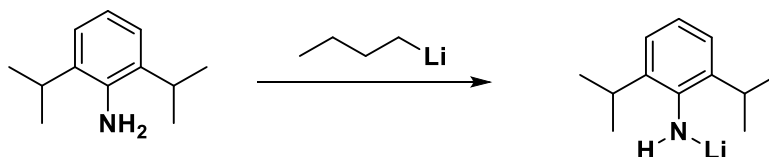
3.2 Synthesis of the first ligand

3.2.1 Imine-based intermediate (BR)



Prior to reaction, molecular sieves were freshly activated for 8 hr. After the activation, the condensation reaction proceeded under inert nitrogen environment. Succinctly, 17 mmol of 6-bromo-2-pyridinecarboxyaldehyde in toluene was added to an equimolar amount of 2,6-diisopropylaniline (17 mmol; 3.014g) and refluxed (16 h) at 70 °C under nitrogen. The mixture was then transferred to the glovebox for further treatment. It was filtered in vacuum and the filtrate was dried for 2 h, followed by treatment with n-hexane for recrystallization. Upon completion of the recrystallization, a solid yellow product was obtained [84].

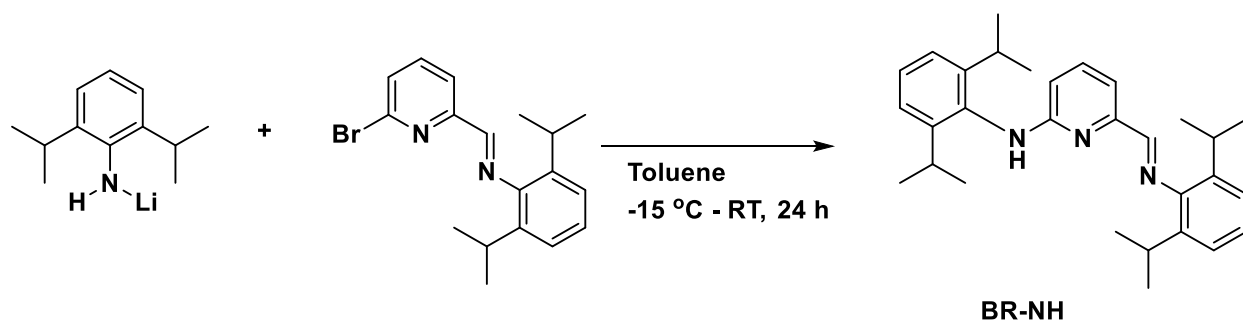
3.2.2 Synthesis of lithium salt of BR



Reaction was carried out for 4 h (from -15 °C to room temperature). Lithium salt (2,6-diisopropylaniline) was collected after vacuum filtration.

3.2.3 Synthesis of NH-BR

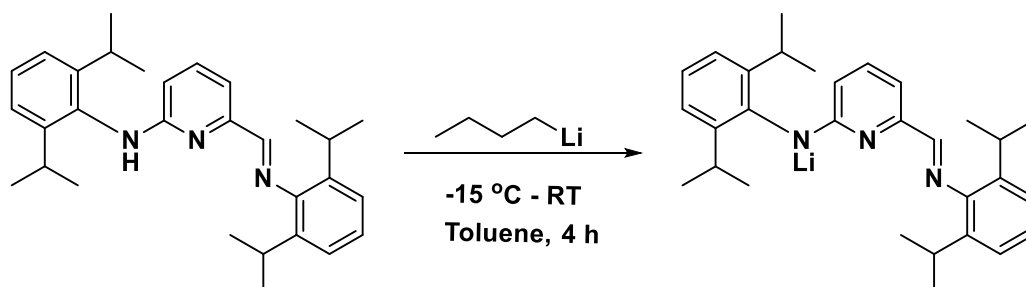
The BR amine-based intermediate was synthesized as follows:



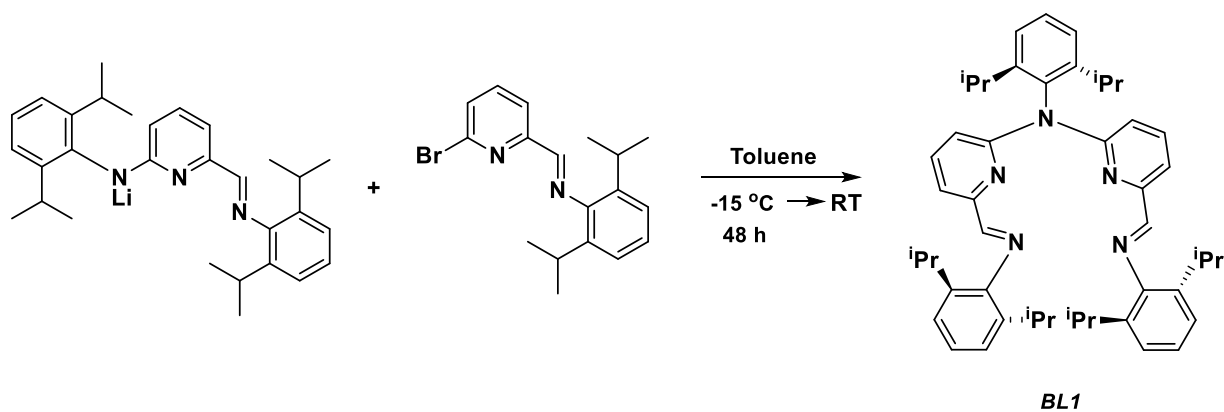
The recrystallized product obtained was filtered and dried under vacuum. It was further used in the next steps.

3.2.4 Synthesis of lithium BR-NLi

Further lithiation of NH-BR afforded the following:



3.2.5 Synthesis of BL1



3.3 Synthesis of the first series of metal complexes

3.3.1 Synthesis of Fe complex

Fe and Co complexes were synthesized according to the procedure as reported [85]. Succinctly, 0.060g of anhydrous FeCl_2 was carefully measured and dissolved in THF. The metal precursor was allowed to stir in the reaction flask for 30 min. 1.05 mol equivalent of BL1 in THF was transferred to the reaction flask containing the metal salt. Complexation was allowed for 48 hr. The mixture was then dried in vacuum and further treated with n-hexane for trituration. The final product was obtained after vacuum filtration and drying.

3.3.2 Synthesis of Co complex

For the cobalt complex, the same procedure was adopted, as in 3.3.1. In this case, 0.0367g of anhydrous CoCl_2 was measured and transferred to 15 mL of THF. 1.05 mol equivalent (0.210g) of BL1 was measured and dissolved in THF and was slowly transferred to the reaction flask. The same method of treatment was used as in 3.3.1.

3.3.3 Synthesis of Ni complex

For Ni complex, the complex was synthesized adopting the literature procedure [86]. 0.000181 mol (0.056g) of $\text{NiBr}_2(\text{DME})$ was measured and dissolved in toluene. 1.05 mol equivalent (0.134) of BL1 in toluene was slowly added to the reaction flask containing the $\text{NiBr}_2(\text{DME})$. Further treatment as in 3.3.1 was followed.

3.4 Synthesis of the second ligand

2.99 mmol (0.53g) of 2,6-diisopropylaniline in toluene was reacted with the mole equivalent (1.03g) of 1-(6-bromopyridin-2-yl)-N-(2,6-diisopropylphenyl)methanimine in

toluene. The reaction was allowed under constant stirring (at room temperature) for 8 h. The solvent was then dried, and the pale-yellow product was collected.

3.5 Synthesis of the second series of complexes

The second series of Fe, Co and Ni complexes was obtained following similar treatments with the respective metal precursors and the ligand as in 3.3.1-3.3.3.

3.6 Synthesis of the third ligand

4.22 mmol (1g) of 2,6-dibromopyridine in toluene was reacted with 2 mole equivalents of 2,6-diisopropylaniline at -15 °C. The mixture was allowed under constant stirring at room temperature for 16 h. After 16 h, the mixture was heated to 55 °C for an additional 4 h, after which it was cooled down to room temperature. The solvent was dried in vacuum and the mixture was further treated with n-hexane and placed inside the refrigerator for recrystallization. After some days, the white solid product was obtained after vacuum drying.

3.7 Synthesis of the third series of complexes

The third series of Fe, Co and Ni complexes was obtained following similar treatments with the respective metal precursors and the ligand as in 3.3.1-3.3.3.

3.8 Characterization of the synthesized ligands and their metal complexes

3.8.1 NMR spectroscopy

The NMR analysis of the ligand was conducted in deuterated benzene solution while for the synthesized complexes, deuterated chloroform solution was used. The NMR analyses was done using either of JEOL NMR of 600 MHz, 400 MHz or Bruker NMR of 400 MHz at the Department of Chemistry, King Fahd University of Petroleum and Minerals, Saudi Arabia.

3.8.2 IR Spectroscopy

The infrared spectra of the ligands and their complexes were recorded between 400-4000 cm^{-1} range by ATR technique using FT-IR spectrometer at the Polymer and Nanotechnology Lab, KFUPM, Saudi Arabia.

3.8.3 Single Crystal Analysis

Single crystals of NIBL1 were grown in suitable solvent(s) inside glovebox for some days. X-ray diffraction study was performed on a Bruker SMART APEX diffractometer ($\lambda = 0.71073 \text{ \AA}$) at 298 K. All structures were solved by direct method using SHELXT and refined by the use of the SHELXL-97 program in OL EX2 [87, 88].

3.8.4 Magnetic Susceptibility Measurement

The magnetic susceptibility of the complexes was measured using MSB mk1 magnetic susceptibility balance manufactured by Sherwood Scientific Limited at the Department of Chemistry.

3.8.5 Mass Spectrometry

The molecular mass of the catalysts was measured using Electrospray Ionization Mass Spectrometry at the Department of Chemistry.

3.9 Polymerization studies

The study of polymerization was conducted using a method analogous to [80]. Toluene/MMAO were used as solvent/co-catalyst. The reactor was prepared inside glovebox. Respective μmol of the catalysts, co-catalyst and the scavenger were weighed accurately and transferred to the reactor. The mixture was stirred for about 5 min and the reactor was then

purged with ethylene, kept at a specified temperature and desired time. 90/10 %v/v of CH₃OH/HCl was used to quench the reaction and precipitate the polymer. The reactor contents were cooled and filtered. The precipitated polymer was collected and dried at 60 °C for 2 h.

3.10 Characterization of the polymers

3.10.1 Differential Scanning Calorimetry

The DSC was done by heat/cool/heat method using Q1000 DSC series thermal analyzer at the Polymer and Nanotechnology Lab, King Fahd University of Petroleum and Minerals, Saudi Arabia.

3.10.2 Viscosimetric Analysis of the polymers obtained

3.10.2.1 Sample preparation for viscosity measurement

Respective solutions in g/mL were preferred by dissolving the appropriate mass of the polymer in a solvent. At the beginning, the solvent was heated to 150 °C. As the temperature reached the desired level, the polymer was gently transferred to the flask and the heating continued under constant stirring for 3 h. To avoid polymer degradation, 0.01% of an antioxidant was added.

3.10.2.2 Viscosity Measurement for the solvent

The set-up for the viscosity was organized in such a way that a stable temperature was maintained. In a closed system, a viscometer containing solvent was placed inside silicon oil. The oil was heated and maintained at 135 °C controlled by a digital thermometer. As the temperature equilibrated, and the solvent was passed to the measuring sphere, the measurement of the viscosity was conducted after the temperature equilibration was maintained for 5 min. The

flow time was recorded as the solvent flows from the upper timing mark to the lower timing mark. The measurement was repeated three times for consistency.

3.10.2.3 Viscosity measurement for the polymer solution

The viscosity of the polymer solution was measured after removing the solvent by vacuum. The viscometer was cooled to room temperature, washed with acetone and then dried inside oven for 2 h. After drying, the viscometer was brought to the set up and the measurement of the solution was conducted. Succinctly, the flask containing the polymer was placed inside silicon oil bath. As the temperature equilibrated to 135 °C, sufficient volume of the polymer solution was transferred to the viscometer. The viscosity measurement was conducted as on 3.10.2.2.

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents the results obtained from the experimental work that was carried out. Precisely, the physico-chemical properties, spectroscopic results and the results of the polymerization reactions are presented in this chapter.

4.1 Physico-chemical properties of the ligand (BL1) and its complexes

Table 4.1 shows the results of physical properties which were determined from the experimental result. The colors of BL1 ligand, FeBL1, CoBL1, and NiBL1 were obtained as yellow, blue, green and orange with the experimental yields of 91%, 96%, 81% and 93%, respectively.

Table 4.1: Physical properties of BL1 and its complexes

Compound	Mol. wt (g/mol)	Color	Yield (g)	T _d
BL1	706.04	Yellow	91	-
FeBL1	832.78	Blue	96	392.2
CoBL1	835.87	Green	81	371.2
NiBL1	924.54	Orange	93	372.6

KEY:

BL1 = as defined in the list of abbreviations

T_d = decomposition temperature

4.2 NMR Spectral Analysis of BR

The proton NMR spectrum of the imine-based intermediate was recorded at room temperature on a JEOL ECA-600 spectrometer, operating with a frequency of 600 MHz, using benzene-d₆ as the solvent. The spectrum of the ligand is consistent with its proposed structure as shown in figure 4.1.

Analysis; ^1H -NMR (600 MHz, BENZENE- D_6) 8.31 ppm [δ (imine CH) 1H, s], 7.99 ppm [δ (aromatic) dd, $J = 7.6, 0.6$ Hz, 1H), 7.13-7.09 ppm [δ (aromatic), m, 3H), 6.87 ppm [δ (aromatic) dd, $J = 7.8, 0.8$ Hz, 1H], 6.64-6.61 ppm [δ (aromatic) t, 1H)], 3.06-3.02 ppm [δ (CH) septet, 2H), 1.15-1.11 ppm δ (CH_3), d, 12H].

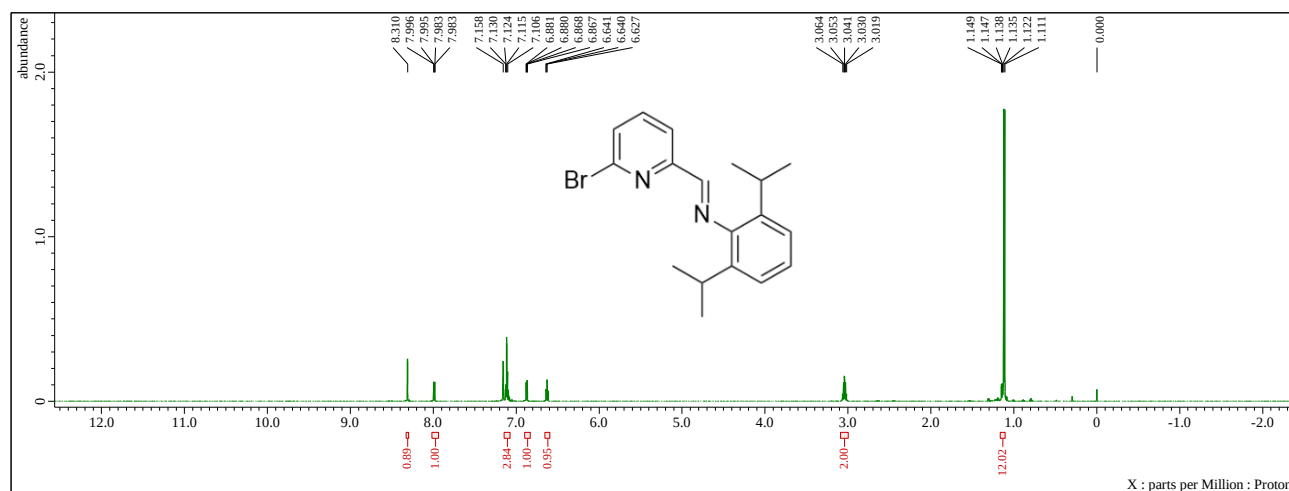


Figure 4.1: NMR spectrum of BR

4.3 NMR Spectral Analysis of the BL1 Ligand

The proton NMR spectrum of the ligand was recorded at room temperature on a JEOL ECA-600 spectrometer, operating with a frequency of 600 MHz, using benzene- d_6 as the solvent. The spectrum of the ligand is consistent with its proposed structure as shown in figure 4.2 and 4.3. **Analysis:** ^1H -NMR (600 MHz, benzene- d_6) 8.20 ppm [δ (imine CH) 2H, s], 7.98 ppm [δ (aromatic), 2H, dd], 7.27-7.21 ppm [δ (aromatic), 3H, m], 7.17-7.13 ppm [δ (aromatic), 7H, m], 7.13-7.11 ppm [δ (aromatic), 4H, m], 3.22 ppm [δ (CH), 2H, q], 3.11 ppm (δ (CH), 4H, septet), 1.14-1.09 ppm [δ (CH_3). 24H, d], 0.98 ppm [δ (CH_3), 12H, d].

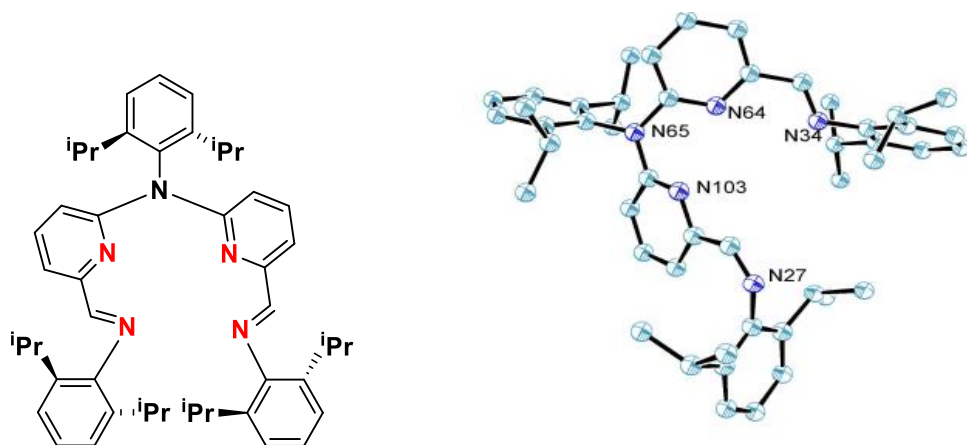


Figure 4.2: Molecular Structure and ORTEP structure of BL1

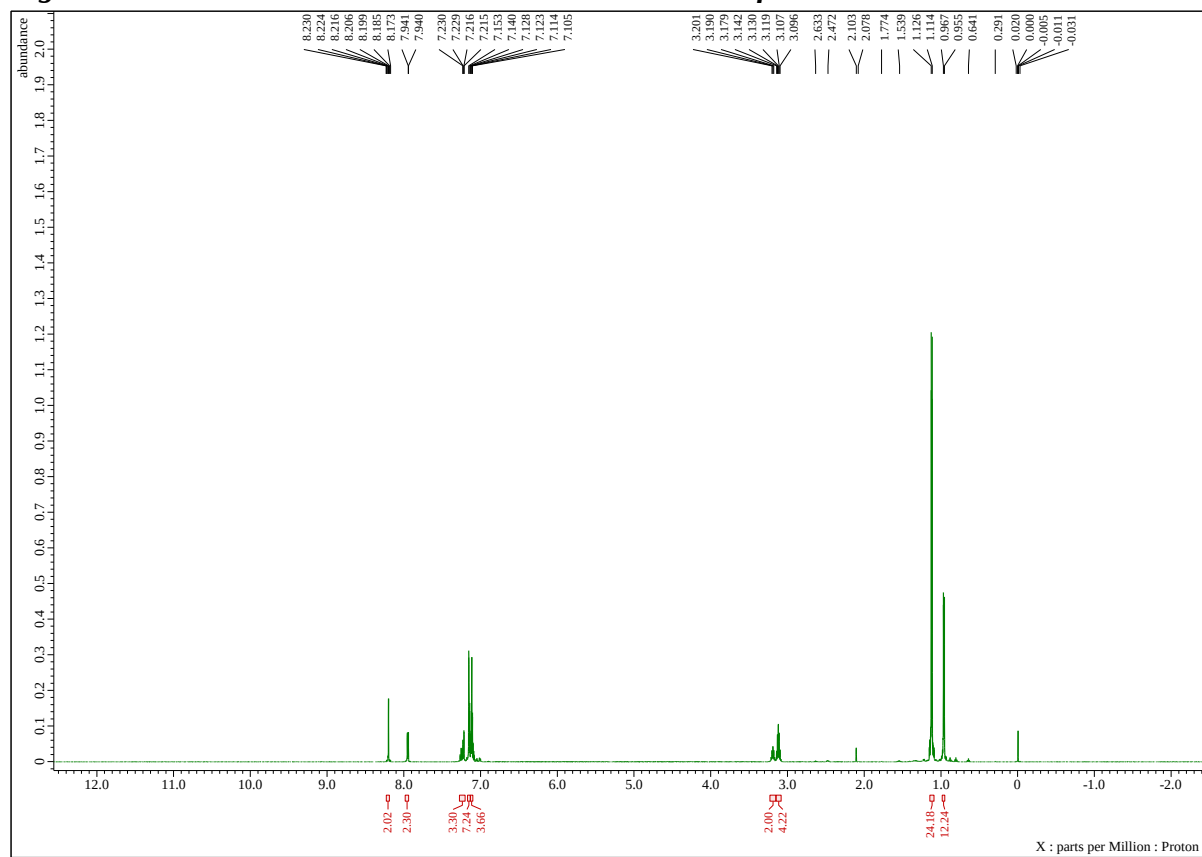


Figure 4.3: NMR spectrum of BL1

4.4 NMR Spectral Analysis of the complexes

Due to the paramagnetic nature of complexes, no significant information can be deduced from the recorded NMR spectra. The spectra confirmed the coordination between the ligand and the complexes. Appropriately, the complexes were thoroughly characterized as will be seen in the coming sections.

4.5 Infrared Spectral Analysis of the BL1 Ligand and its Complexes

The IR spectra of BL1 ligand and its corresponding Fe, Co and Ni complexes were recorded in the range of 4000–400 cm^{-1} . Stretching frequencies of the BL1 ligand and its metal complexes are given in Table 4.2. From the results, there exist similarities in the IR spectra of complexes to each other. There is an appearance of slight variations in the positions and the intensities of some few peaks due to the presence of different metal ions. Thus, this is an indication that the complexes possessed similar geometry.

Table 4.2. Important IR bands in (cm^{-1}) for the ligand and its metal complexes

Compound	$\nu(\text{sp}^2 \text{ C-H})$	$\nu(\text{sp}^3 \text{ C-H})$	$\nu(\text{C=N})$	$\nu(\text{aromatic C=N})$	$\nu(\text{CH}_3/\text{C=C})$	$\nu(\text{M-N})$
BL1	3080	2864	1645	1582	1435	-
FeBL1	3410	2957	1622	1596	1435	541
CoBL1	3063	2957	1628	1587	1436	542
NiBL1	3365	2958	1632	1588	1437	542

The IR spectrum of BL1 ligand shows characteristic band at 1645 cm^{-1} due to the $\nu(\text{C=N})$ stretching vibration of the imine group [89, 90]. The Vibrational frequencies in the ligand spectrum between 2960–2864 cm^{-1} are assignable to $\text{sp}^3 \text{ C-H}$ vibration. The broad band in the ligand's spectrum at 3080 cm^{-1} is due to the $\text{sp}^2 \text{ C-H}$ stretching of imine and/or C-H stretching

vibration of aromatic rings [91]. The vibrational frequency at 1435 cm^{-1} is due to the CH_3 antisymmetric bending vibration and/or aromatic $\text{C}=\text{C}$ ring stretching [92]. The strong band with vibrational frequencies between 790 is assignable to out-of-plane C-H bending [92].

After the complexation, there were some changes in the IR spectra of Fe, Co and Ni complexes. Both spectra of Fe, Co, and Ni exhibit characteristics $\text{C}=\text{N}$ bands between 1632 to 1620 cm^{-1} due to $\text{C}=\text{N}$ vibration. This shift to lower frequencies is an indication of the withdrawal of the electron density from the nitrogen atom due to the complexation to the metal center [93].

Additionally, the spectra of the complexes showed metal-nitrogen bands at the extreme ends of each spectrum between 545 to 540 cm^{-1} , attributed to metal-nitrogen coordination [93, 94]. This has also been confirmed by the existence of new vibrational bands around $2200\text{-}1950\text{ cm}^{-1}$ in the spectra of all complexes.

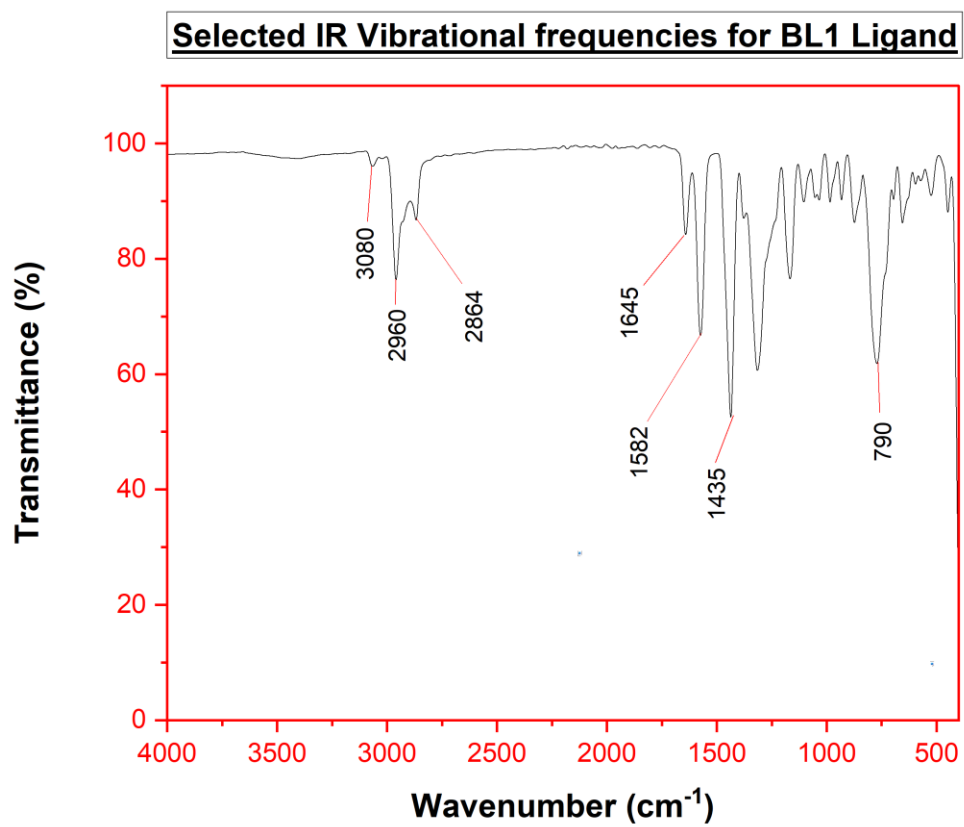


Figure 4.4: IR spectrum of BL1

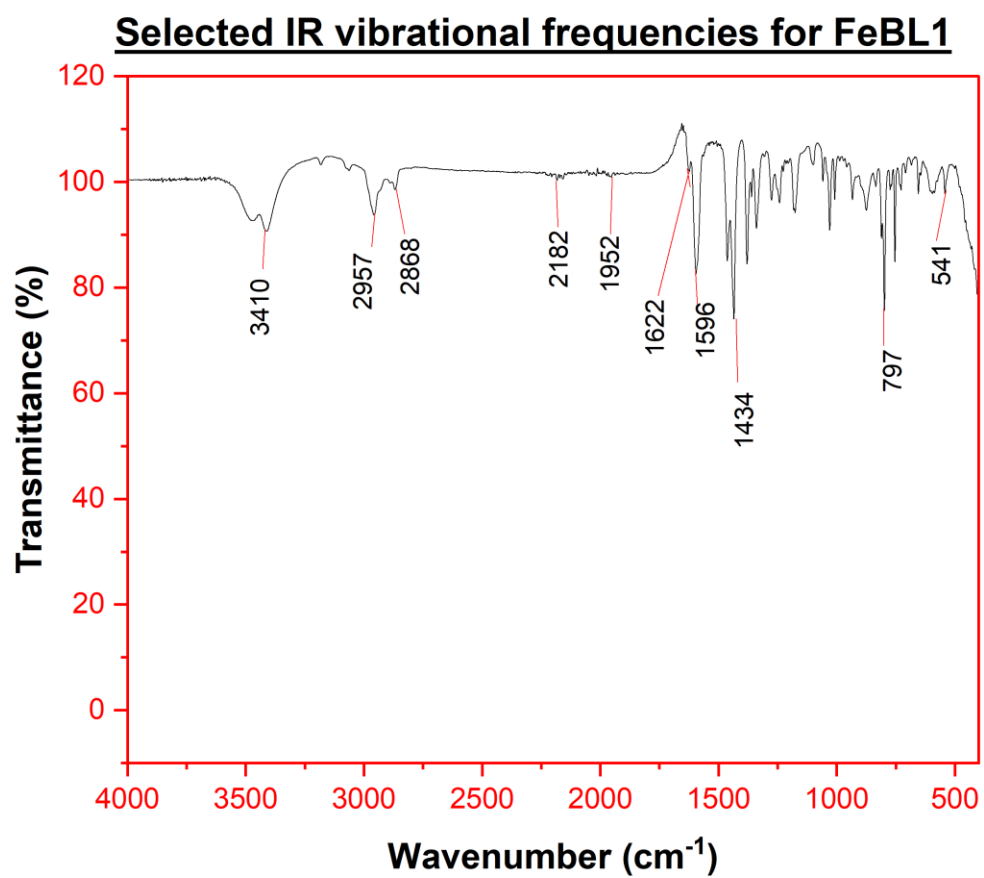


Figure 4.5: IR spectrum of FeBL1 complex

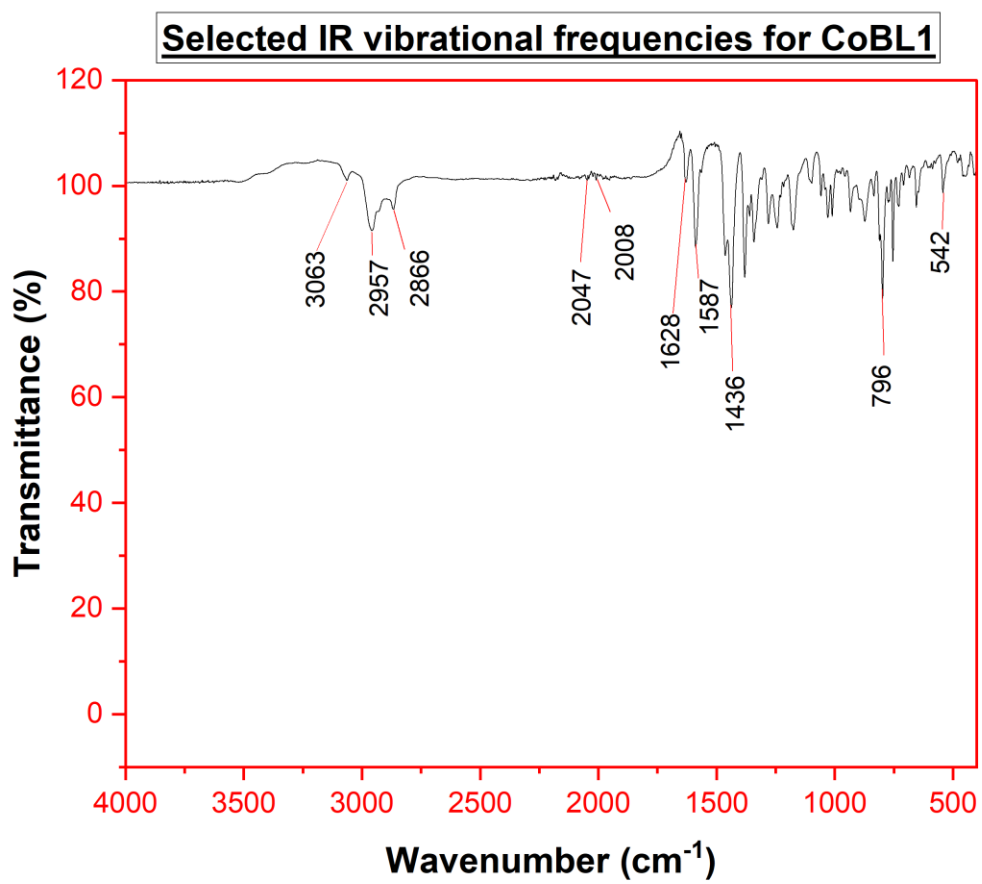


Figure 4.6: IR spectrum of CoBL1 complex

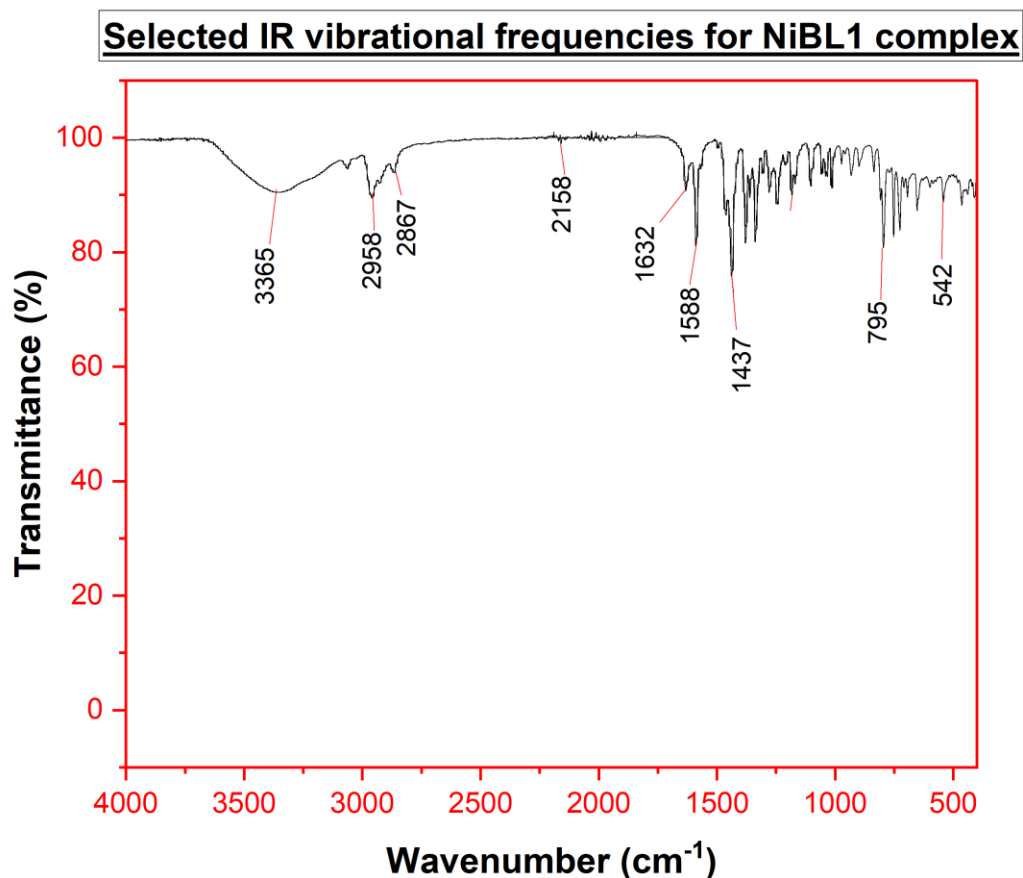


Figure 4.7: IR spectrum of NiBL1 complex

4.6 Thermogravimetric Analysis of the complexes

The simultaneous TGA/DTA of the synthesized complexes was obtained from room temperature to 900 °C by ramp method, under a controlled heating rate of 10.00 °C/min using alumina as reference compound.

4.6.1 Thermogravimetric Analysis of FeBL1 complex

As shown in figure 4.5a and 4.5b, the iron complex exhibited a multi-step degradation. The observed weight loss of 4.45% around 47 °C is due to the loss of two molecules of lattice water absorbed by the complex upon exposure to atmosphere [95]. This is evident as the Fe(II) complex synthesized, changes color from blue to brown if exposed to the air for sometime. The

second weight loss of 8.45% around 138 °C is attributed to the loss of chlorine molecule from the complex [96]. Other multistep decomposition processes observed may be due to the decomposition of other moieties in the complex, with a complete decomposition observed at a temperature of about 393 °C, as shown in the most intense peak of the DTA curve.

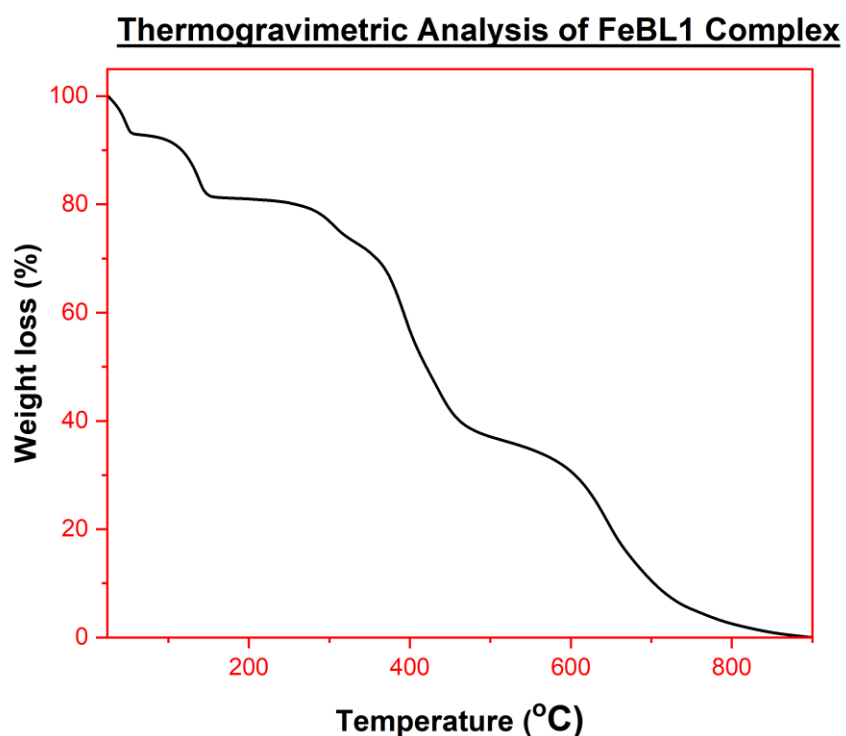


Figure 4.8a: TGA graph of FeBL1 complex

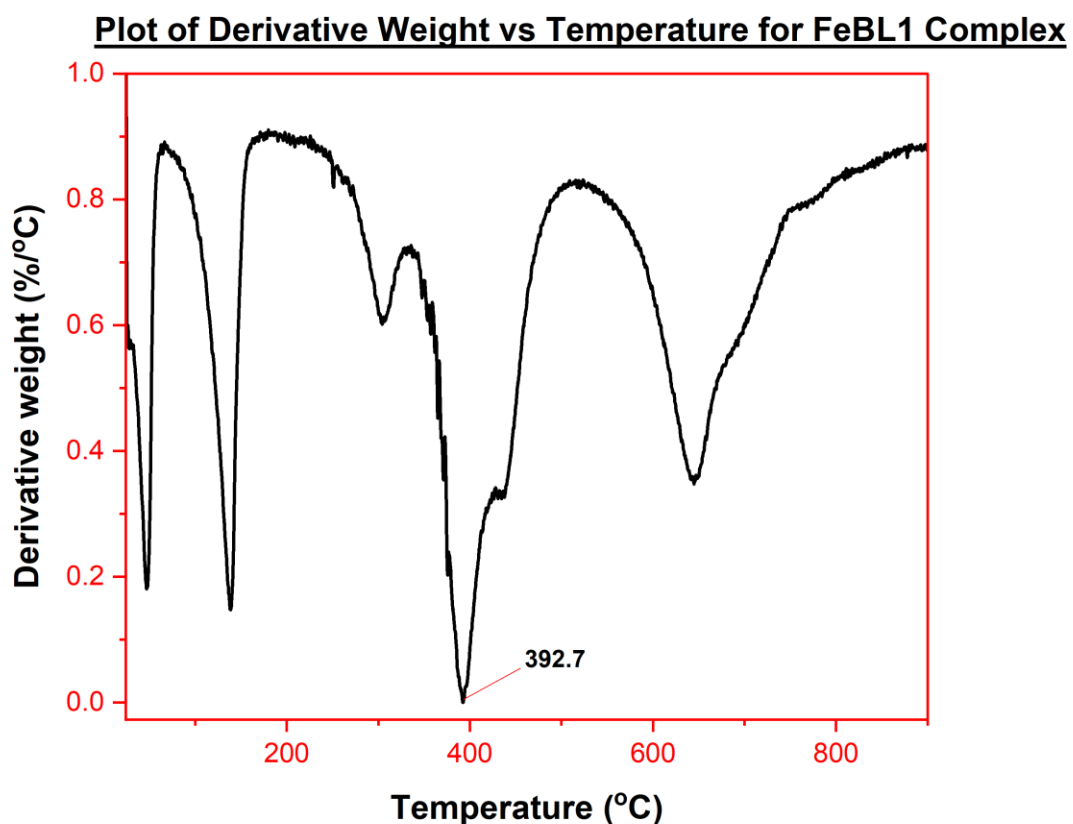


Figure 4,8b: DTA of FeBL1 complex

4.6.2 Thermogravimetric Analysis of CoBL1 complex

The thermogravimetric plot of cobalt complex shows a wet loss of 8.98% attributed to the loss of chlorine molecules near a temperature of 176 °C. The DTA curve of the complex shows an intense peak associated with the decomposition of the complex at a temperature of 371.2 °C, as shown in figure 4.6a and 4.6b

Thermogravimetric Analysis of CoBL1 Complex

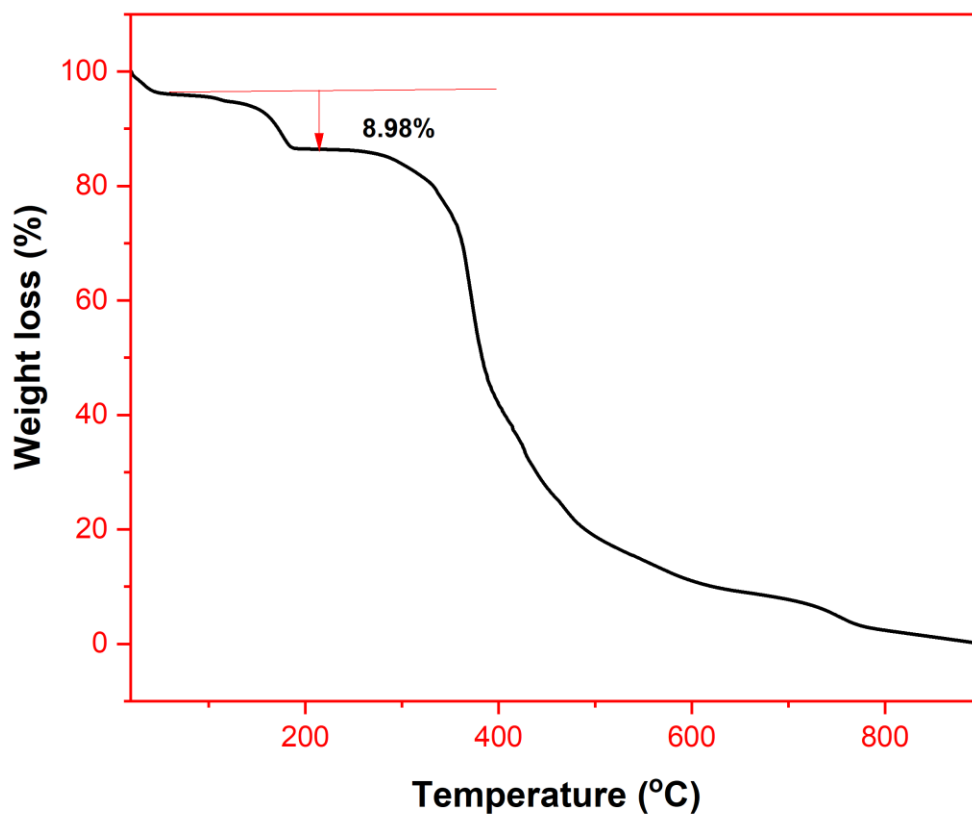


Figure.4.9a: TGA plot of CoBL1 Complex

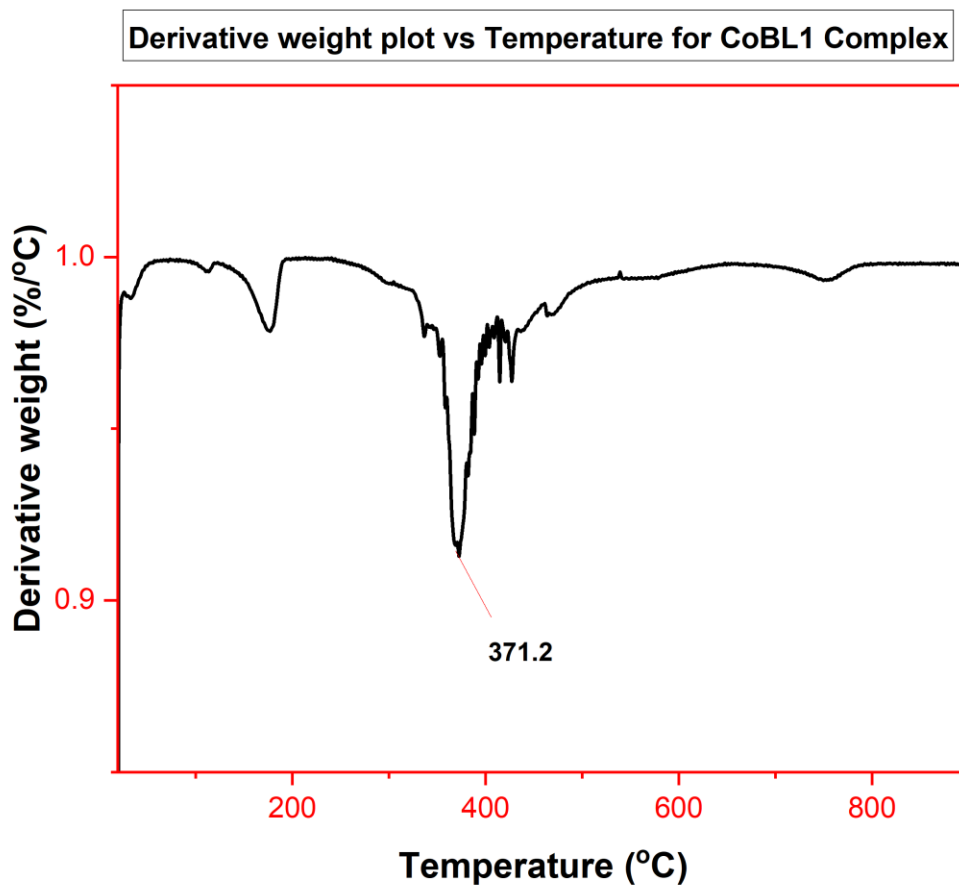


Figure 4.9b: DTA plot of CoBL1 Complex

4.6.3 Thermogravimetric Analysis of NiBL1 complex

The thermogravimetric plot of nickel complex shows that nickel catalyst underwent single step decomposition. The stable complex decomposed at a temperature of 372.6 °C as shown in the most intense peak of DTA curve in figure 4.7.

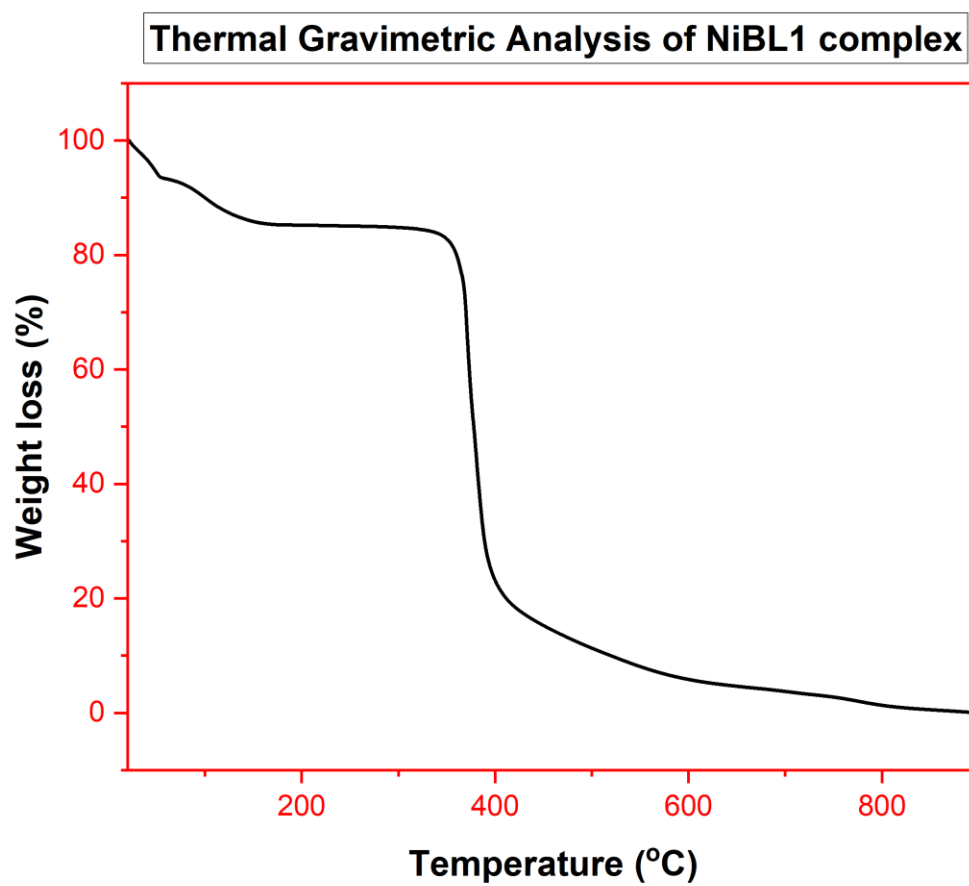


Figure 4.10a: TGA plot of NiBL1 Complex

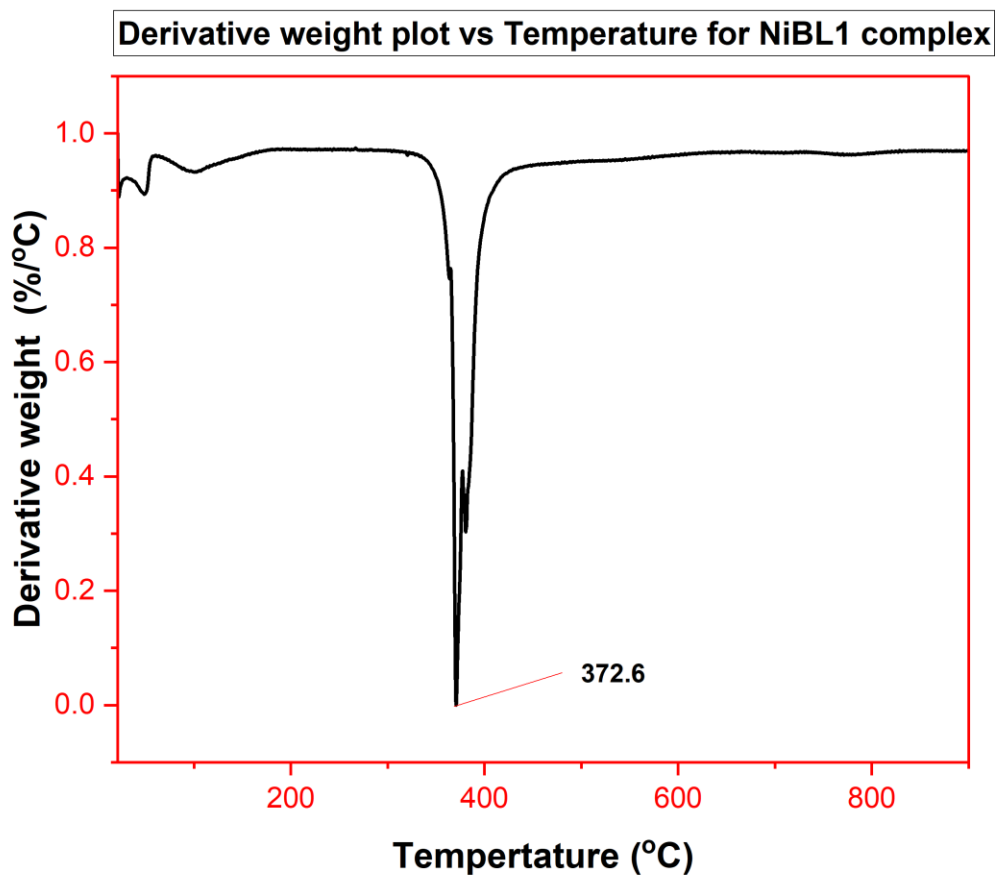


Figure 4.10b: DTA plot of NiBL1 Complex

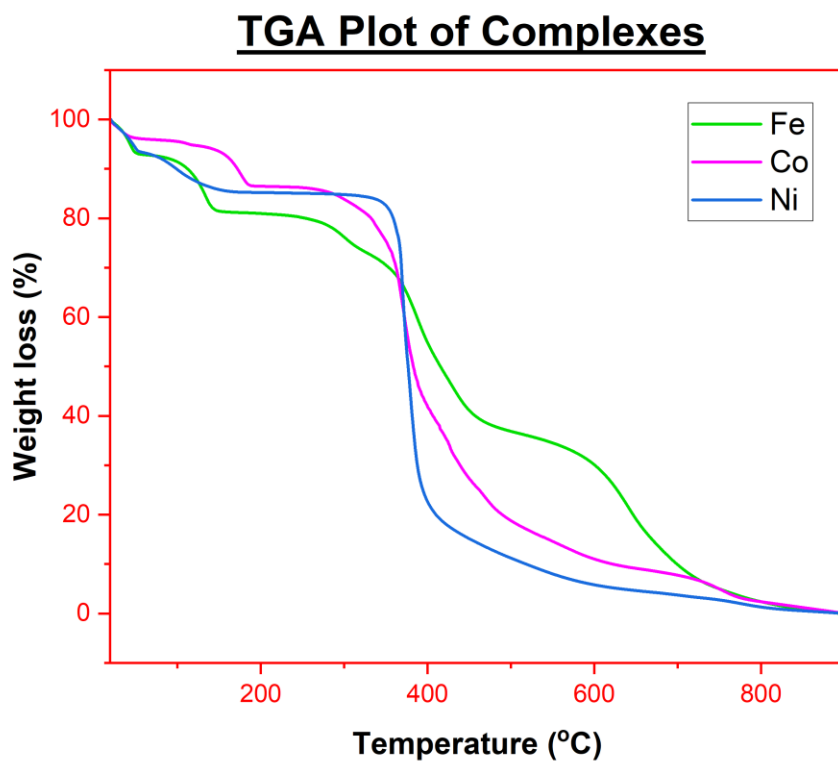
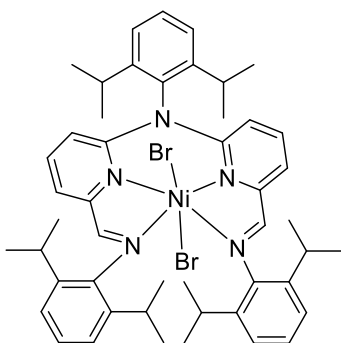


Figure 4. 11: Combined TGA plot of Fe, Co and Ni complexes

4.7 Single Crystallographic Analysis of the NiBL1 Complex



The results of single crystallographic analysis of NiBL1 complex are summarized in Table 4.3. The structure of the complex is also shown in figures 4.9 and 4.10.

The geometry around the nickel atom can is a slightly distorted octahedron, in which the two bromine atoms coordinated from the axial positions, while the four nitrogen atoms from

pyridine rings and the imines occupied the equatorial positions [89]. This nature of the coordination in the synthesized complex reflects the tendency of a d^8 nickel complex to form a stable and isolable 20 electron octahedral complexes, which are unambiguously rare.

Table 4.3: Summary of X-ray Crystallographic Data for NiBL1

Empirical formula	$C_{48}H_{59}Br_2N_5Ni$
Formula weight	924.54
Temperature	298 K
Crystal system	Monoclinic
Space group	Cc
α (Å)	90
β (Å)	107.961
γ (Å)	90
V (Å ³)	4901.6
Z	4
d_{calcd} (g · cm ⁻³)	1.253
Crystal size (mm)	0.46 x 0.13 x 0.03
abs coeff (mm ⁻¹)	2.061
$2\theta_{\text{max}}$ (deg)	25.499
No. of reflns collected	9099
No. of indep reflns	6573
No. of obsd reflns	9049
No. of variables	487
Final R indices	$R_1 = 0.0498$ $wR_2 = 0.1486$

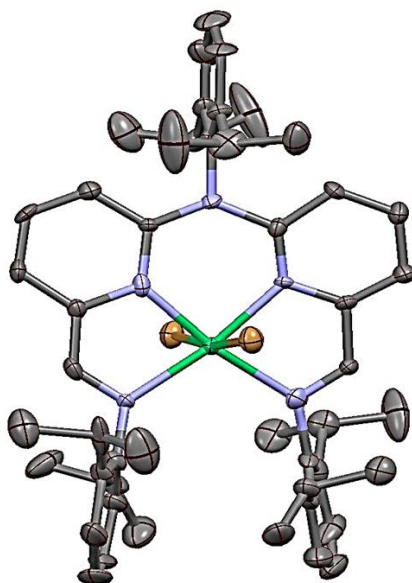


Figure 4.12: Structure of NiBL1 showing the coordinated ligands, with hydrogen atoms omitted for clarity.

Table 4.4 Selected Distances (Å) for the NiBL1 Complex
Bond lengths (Å)

Ni(02)–N(1)	1.992
Ni(02)–N(2)	2.059
Ni(02)–N(3)	2.168
Ni(02)–N(4)	2.143
Ni(02)–Br(01)	2.601
Ni(02)–Br(03)	2.611

Table 4.5 Selected Bond Angles (deg) for the NiBL1 Complex**Bond angles (°)**

N(1)-Ni(02)-N(3)	81.19
N(2)-Ni(02)-N(1)	89.37
Br(01)-Ni(02)-Br(03)	171.01
N(3)-Ni(02)-N(1)	81.19
N(4)-Ni(02)-N(2)	80.59
Br(01)-Ni(02)-N(2)	89.62
Br(03)-Ni(02)-N(1)	89.30

4.8 Magnetic susceptibility results

Magnetic susceptibility measurement was conducted by Evan`s method with $R_o = -38$, $C_{std} = 1165$ and $C_{bal} = 1.03$ at $20\text{ }^{\circ}\text{C}$, χ_{dia} in cm^3/mol for FeBL1, CoBL1, and NiBL1 = 4.16×10^{-4} , 4.18×10^{-4} , 4.62×10^{-4} respectively. The calculations took into account the correction of diamagnetic contributions from all atoms in the complexes [97]. The results are tabulated in Table 4.6.

Table 4.6: Magnetic susceptibility results for BL1 complexes

Comp.	Tube Mass(g)	Sample (g)	Length (cm)	R (x_1)	χ_{mass} (cm^3/g)	χ_{mol} (cm^3/mol)	χ_{para} (cm^3/mol)	μ_{eff} (BM)
FeBL1	0.8165	0.0465	1.95	277	1.36×10^{-5}	1.13×10^{-2}	1.09×10^{-2}	5.06
CoBL1	0.8211	0.0202	1.75	107	1.29×10^{-5}	1.08×10^{-2}	1.04×10^{-2}	4.93
NiBL1	0.8202	0.0321	1.95	073	6.76×10^{-6}	6.25×10^{-3}	5.79×10^{-3}	3.68

The effective magnetic moment of Fe(II) complex was found to be 5.06 BM, consistent with four unpaired electrons in an octahedral geometry. Similarly, magnetic moment of 4.93 BM was found for cobalt (II) complex indicating that the complex has high-spin octahedral geometry

with extremely high orbital contributions as a result of the three unpaired electrons [98, 99]. As for nickel complex, a magnetic moment of 3.68 BM was found, and that indicated the complex has an octahedral geometry with two unpaired electrons [100].

4.9 Electrospray Ionization Mass Spectrometry (ESI-MS) for the complexes

The ESI-MS of the complexes was recorded by dissolving 1 mg of the respective complexes in 5 mL of acetonitrile and then diluting 20% portion by serial dilution to 10 mL. The m/z and the proposed fragmentation pattern for the complexes are given in table 4.7.

Table 4.7. Magnetic susceptibility results for BL1 complexes

Complex	Fragmentation pattern	Calculated mol. wt.	Observed mol. wt.
FeBL1	$[\text{C}_{48}\text{H}_{59}\text{N}_5\text{FeCl}_2 + (\text{CH}_3\text{CN})_3]^+$	916.78	916
CoBL1	$[\text{C}_{48}\text{H}_{59}\text{N}_5\text{CoCl}_2 + \text{CH}_3\text{CN}]^+$	943.35	943
NiBL1	$[\text{C}_{48}\text{H}_{59}\text{N}_5\text{NiBr}_2 + \text{CH}_3\text{CN}]^+$	964.13	964

4.10 Polymerization results for FeBL1

4.10.1 Effect of temperature on the yield, activity and melting temperature using FeBL1

The performance of FeBL1 precatalyst was evaluated in the ethylene polymerization at various temperatures. The results obtained are summarized in Table 4.8. Figure 4.13 shows the trend between the temperature and the catalytic activity of FeBL1.

Table 4.8: Temperature effect on the activity and melting temperature using FeBL1

Run	Complex	Temp. (°C)	Pressure (psi)	Time (min)	Yield (g)	^c Activity	^d T _m
1	FeBL1	50	150	30	1.081	2.16 x 10 ⁶	129.10
2	FeBL1	60	150	30	1.401	2.80 x 10 ⁶	127.05
3	FeBL1	70	150	30	1.419	2.84 x 10 ⁶	123.97
4	FeBL1	80	150	30	1.683	3.37 x 10 ⁶	132.78
5	FeBL1	90	150	30	0.980	1.96 x 10 ⁶	124.70

^a Reaction conditions: 150 mL autoclave reactor; 1 μ mol of precatalyst in 40 mL of toluene, 2000 equivalent of MMAO; ethylene, 150 psi; 30 min, 800 rpm. ^c gram of PE produced per mol (Fe) h⁻¹. ^d Detected by DSC.

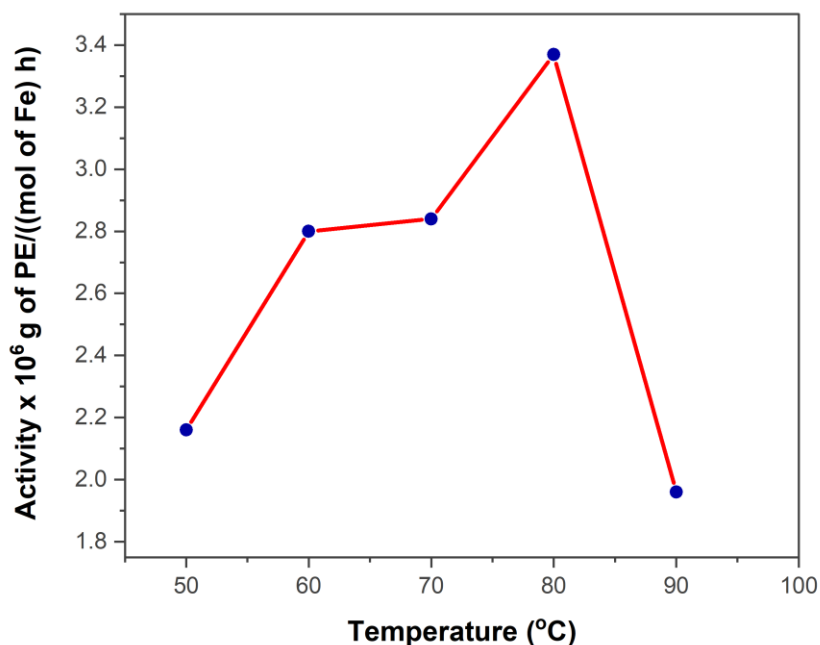


Figure 4.13: Plot of catalyst activity vs temperature using FeBL1

As shown in Figure 4.13, the catalytic performance of the new catalyst increased with an increase in temperature from 50 °C to 80 °C. As the polymerization temperature was raised to 90

°C, the catalytic performance decreased drastically. This drastic decrease in the catalytic activity can be attributed to the decomposition of the active species at elevated temperature [101, 102].

4.10.2 Effect of pressure on the activity and melting temperature using FeBL1

The effect of pressure on the catalytic performance of FeBL1 was evaluated at different pressures. The results are provided in Table 4.9. The dependence is also shown in Figure 4.14.

Table 4.9: Pressure effect on FeBL1 catalyst at 60 °C

Run	Complex	Pressure (psi)	Time (min)	Yield (g)	^c Activity	^d T _m
1	FeBL1	50	30	1.340	2.68 x 10 ⁶	131.39
2	FeBL1	100	30	1.382	2.76 x 10 ⁶	127.98
3	FeBL1	150	30	1.401	2.80 x 10 ⁶	127.05
4	FeBL1	200	30	0.270	5.40 x 10 ⁵	108.56
5	FeBL1	250	30	0.093	1.86 x 10 ⁵	119.13

^a Reaction conditions: 150 mL autoclave reactor; 1 μmol of precatalyst in 40 mL of toluene, 2000 equivalent of MMAO; ethylene, 30 min, 800 rpm. ^c gram of PE produced per mol of (Fe) h⁻¹. ^d Detected by DSC.

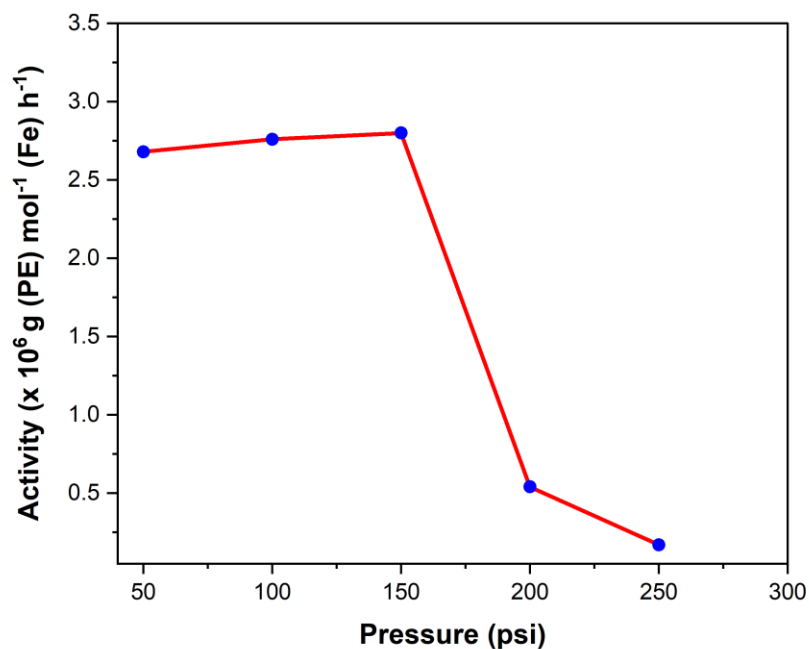


Figure 4.14: Plot of catalyst activity vs pressure using FeBL1

As shown in figure 4.14, there was an increase in the catalytic performance of the catalyst with an increase in pressure of up to 150 psi. This linear dependence of the activity on the pressure is consistent with the dependence of catalytic activity of similar iron polymerization catalysts reported [103]. The melting temperature of the polymers also remained considerably the same between 50-150 psi. As can be seen, in this system, the highest activity was observed at 150 psi. An increase in the reaction pressure to 200 psi and above led to a significant decrease in the activity of the FeBL1 catalyst associated with the possible decomposition of the active sites.

4.10.3 Effect of reaction time on the yield, activity, and melting temperature using FeBL1

The catalytic performance of FeBL1 was evaluated at various reaction times and the results are reported in Table 4.10. Figure 4.15 shows the relationship between catalyst activity and the reaction time.

The reaction time has significant effect on the activity and melting temperatures of the catalyst. The highest activity was observed at the lowest reaction time, which continued to decrease even though polymer yield continued to increase. This can be attributed to mass transfer limitations in which little polymer growth occurs at longer reaction times [101].

Table 4.10: Effect of reaction time on FeBL1 catalyst at 80 °C

Run	Complex	Pressure (psi)	Time (min)	Yield (g)	^c Activity	^d T _m
1	FeBL1	150	5	1.010	1.20 x 10 ⁷	112.46
2	FeBL1	150	10	1.260	7.56 x 10 ⁶	127.99
3	FeBL1	150	20	1.370	4.11 x 10 ⁶	128.01
4	FeBL1	150	30	1.683	3.37 x 10 ⁶	132.78
5	FeBL1	150	60	1.701	1.70 x 10 ⁶	114.13
6	FeBL1	150	120	1.731	8.65 x 10 ⁵	116.28

^a Reaction conditions: 150 mL autoclave reactor; 1 μmol of precatalyst in 40 mL of toluene, 2000 equivalent of MMAO; ethylene, 150 psi; 80 °C, 800 rpm. The yields are average of 2 runs. ^c gram of PE produced per mol of (Fe) h⁻¹. ^d Detected by DSC.

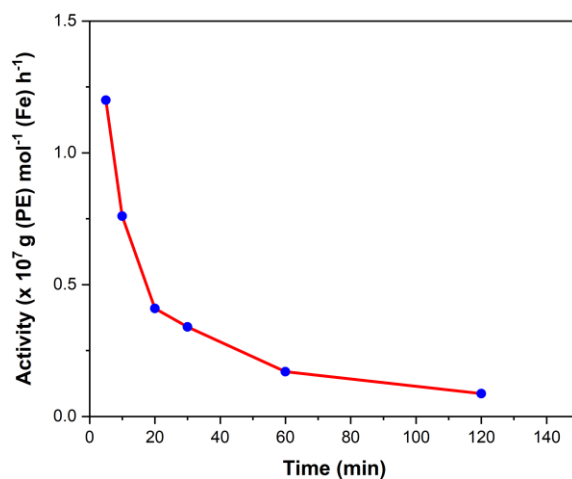


Figure 4.15: Plot of catalyst activity vs time using FeBL1

4.10.4 Effect of catalyst loading on the yield, activity, melting temperature using FeBL1

The performance of FeBL1 catalysts was evaluated at various loading of the catalyst. The results are tabulated in Table 4.11. As shown Table 4.11, decreasing the loading of the catalyst led to high catalytic activity and resulted to a significant decrease in the T_m of the generated polymers.

Table 4.11: Effect of catalyst loading on FeBL1 at 80 °C

Run	Complex	Cat. loa. (μmol)	Time (min)	Yield (g)	^c Activity	^d T_m
1	FeBL1	1.00	30	1.683	3.37×10^6	132.78
2	FeBL1	0.05	30	1.025	4.10×10^7	119.26
3	FeBL1	0.025	30	0.683	5.46×10^7	117.29

^a Reaction conditions: 150 mL autoclave reactor; respective μmol of precatalyst in 40 mL of toluene, 2000 equivalent of MMAO; ethylene, 150 psi; 80 °C, 800 rpm. ^c gram of PE produced per mol of (Fe) h^{-1} . ^d Detected by DSC.

4.10.5 Effect of MMAO loading on the yield, activity and melting temperature using FeBL1

The effect of co-catalyst loading on the performance of the catalyst was also investigated. The results are tabulated in Table 4.12. At low co-catalysts loading, the catalyst generated trace amounts of PE. Increasing co-catalyst loading led to an increase in the catalytic performance and the performance slightly reduced when 2500 equivalent of MMAO was used. Figure 4.15 shows the relationship between the activity and the co-catalyst loading.

Table 4.12: Effect of co-catalyst loading on FeBL1 at 80 °C

Run	Complex	Time (min)	MMAO equiv.	Yield (g)	^c Activity	^d T _m
1	FeBL1	30	500	Trace	-	-
2	FeBL1	30	1000	0.644	1.29 x 10 ⁶	128.22
3	FeBL1	30	1500	0.948	1.70 x 10 ⁶	131.56
4	FeBL1	30	2000	1.683	3.37 x 10 ⁶	132.78
5	FeBL1	30	2500	1.671	3.34 x 10 ⁶	131.65

^a Reaction conditions: 150 mL autoclave reactor; 1 µmol of catalyst in 40 mL of toluene, respective equivalent of MMAO; ethylene, 150 psi; 80 °C, 800 rpm. ^c gram of PE produced per mol of (Fe) h⁻¹. ^d Detected by DSC.

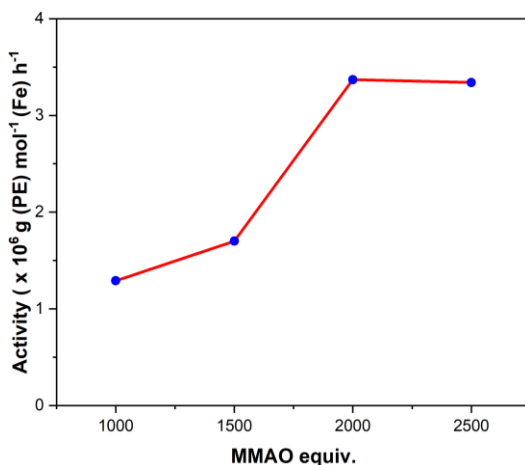


Figure 4.16: Plot of catalyst activity vs time using FeBL1

4.11 Polymerization results for CoBL1

4.11.1 Effects of reaction temperature and pressure on the catalytic performance of CoBL1

The catalytic performance of CoBL1 was evaluated at 50 and 150 psi at various temperatures. The results are tabulated in Table 4.13.

Table 4.13: Polymerization results at various temperatures and pressures for CoBL1

Run	Complex	Temp (°C)	Pressure (psi)	Time (min)	Yield (g)	^c Activity	^d T _m
1	CoBL1	50	150	30	Trace	Trace	Trace
2	CoBL1	60	150	30	1.817	3.63 x 10 ⁶	125.16
3	CoBL1	60	50	30	2.130	4.26 x 10 ⁶	130.58
4	CoBL1	70	150	30	1.023	2.04 x 10 ⁶	123.68
5	CoBL1	80	150	30	0.883	1.77 x 10 ⁶	128.35

^a Reaction conditions: 150 mL autoclave reactor; 1 μ mol of precatalyst in 40 mL of toluene, 2000 equivalent of MMAO; ethylene; 30 min, 800 rpm. ^c gram of PE produced per mol of (Co) h⁻¹. ^d Detected by DSC.

The catalytic performance of CoBL1 is superior to that of FeBL1. The CoBL1 catalyst showed excellent activity in the polymerization reaction, although it is less thermally stable compared with FeBL1. Figure 4.17 shows the relationship between the activity of CoBL1 against temperature.

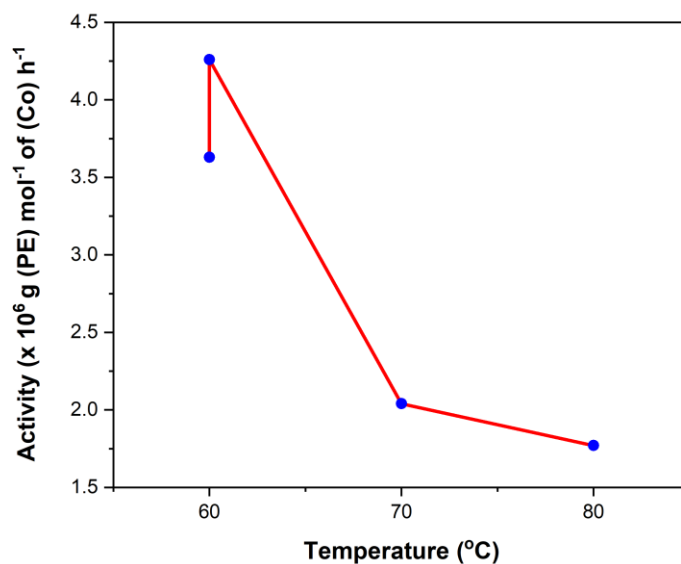


Figure 4.17: Plot of catalyst activity vs temperature using CoBL1

4.11.2 Effects of catalyst loading on the catalytic performance of CoBL1

The effect of catalyst loading on the catalytic performance of CoBL1 was also evaluated. The results are presented in Table 4.14. It is noteworthy to note that on decreasing the catalyst loading, the catalytic activity increased significantly.

Table 4.14: Effect of catalyst loading on catalytic performance of CoBL1 at 50 psi

Run	Complex	Cat. loa. (μmol)	Time (min)	Yield (g)	^c Activity	^d T _m
1	CoBL1	1.00	30	2.130	4.26×10^6	130.58
2	CoBL1	0.05	30	1.340	5.36×10^7	119.26
3	CoBL1	0.025	30	0.682	5.54×10^7	117.29

^a Reaction conditions: 150 mL autoclave reactor; respective μmol of precatalyst in 40 mL of toluene, 2000 equivalent of MMAO; ethylene, 50 psi; 60 °C, 800 rpm. ^c gram of PE produced per mol of (Co) h⁻¹. ^d Detected by DSC.

4.11.3 Effect of reaction time on the yield, activity and melting temperature using CoBL1

The catalytic performance of FeBL1 was evaluated at various reaction times and the results are reported in Table 4.15. The activity of CoBL1 was exceptional, and the polymer yield continued to increase overtime as shown in Figure 4.18.

Table 4.15: Effect of reaction time on CoBL1 catalyst

Run	Complex	Pressure (psi)	Time (min)	Yield (g)	^c Activity	^d T _m
1	CoBL1	50	5	1.569	1.88 x 10 ⁷	120.73
2	CoBL1	50	10	1.986	1.19 x 10 ⁷	122.54
3	CoBL1	50	20	2.018	6.05 x 10 ⁶	130.11
4	CoBL1	50	30	2.130	4.26 x 10 ⁶	130.78
5	CoBL1	50	60	2.372	2.37 x 10 ⁶	126.34
6	CoBL1	50	120	2.884	1.44 x 10 ⁶	127.12

. ^a Reaction conditions: 150 mL autoclave reactor; 1 μmol of precatalyst in 40 mL of toluene, 2000 equivalent of MMAO; ethylene, 50 psi; 60 °C, 800 rpm. ^c g of PE/mol of Co Comp. h⁻¹. ^d Detected by DSC.

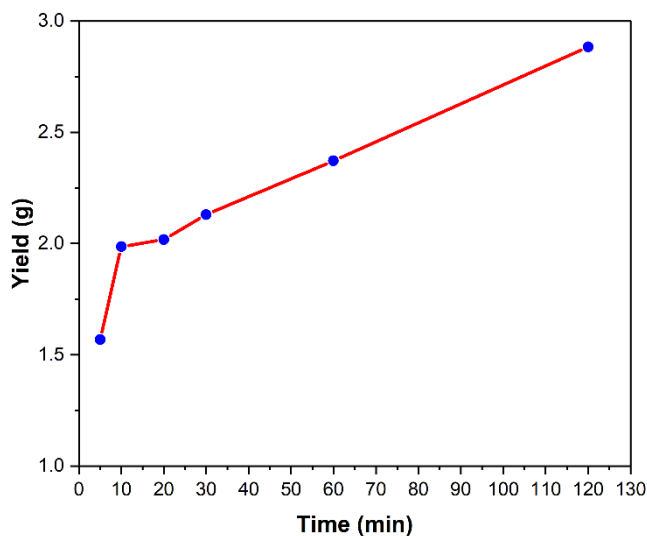


Figure 4.18: Plot of yield vs time using CoBL1

4.11.4 Effect of MMAO loading on the yield, activity and melting temperature by CoBL1

Table 4.16: Effect of MMAO on the performance of CoBL1

Run	Complex	Time (min)	MMAO equiv.	Yield (g)	^c Activity	^d T _m
1	CoBL1	30	500	Trace	-	-
2	CoBL1	30	1000	1.463	2.93 x 10 ⁶	129.84
3	CoBL1	30	1500	1.968	3.94 x 10 ⁶	128.56
4	CoBL1	30	2000	2.130	4.26 x 10 ⁶	130.58
5	CoBL1	30	2500	2.147	4.29 x 10 ⁶	130.24

^a Reaction conditions: 150 mL autoclave reactor; 1 μ mol of N₅CoCl₂ precatalyst in 40 mL of toluene; ethylene, 60 °C and 50 psi; 800 rpm. ^c gram of PE produced per mol of (Co) h⁻¹. ^d Detected by DSC.

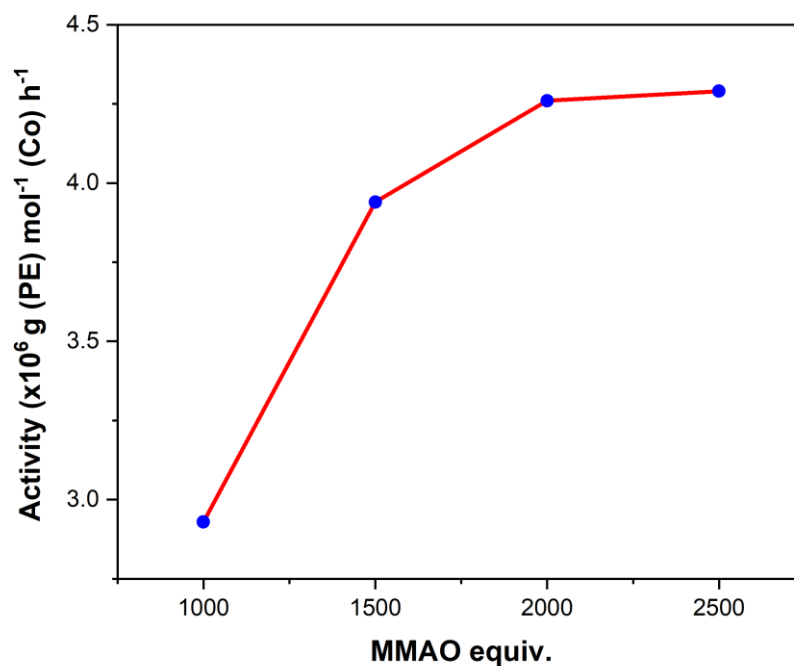


Figure 4.19: Plot of catalyst activity vs MMAO equivalent using CoBL1

4.12 Polymerization results for NiBL1

A thorough optimization at various polymerization conditions revealed that the optimum temperature for ethylene polymerization using 3 was 60 °C. When the reaction was conducted at either 50 °C or 60 °C with 150 psi, only trace amounts of polyethylene were generated.

Highest activity of 1.26×10^6 g of (PE) mol⁻¹ (Ni) h⁻¹ was obtained when we decreased the reaction pressure to 50 psi at 60 °C using NiBL1. The observed catalytic activity of the catalyst suggests that the rate of chain propagation using NiBL1 is not dependent on the concentration of ethylene gas during the polymerization.

Table 4.17: Effect of pressure and temperature on NiBL1 catalyst

Run	Complex	Temp (°C)	Pressure (psi)	Yield (g)	^c Activity	^d T _m
1	NiBL1	50	150	Trace	-	-
2	NiBL1	60	150	Trace	-	-
3	NiBL1	60	50	0.629	1.26 x 10 ⁶	115.95
4	NiBL1	80	50	0.389	7.78 x 10 ⁵	97.44

^a Reaction conditions: 150 mL autoclave reactor; 1 μmol of N₅NiBr₂ precatalyst in 40 mL of toluene; ethylene, 50 psi; 800 rpm. ^c gram of PE produced per mol of (Ni) h⁻¹. ^d Detected by DSC.

4.13 Viscosimetric results

In general, UHMWPE samples resist the desired solubility in different solvents, including 1,2,4-trichlorobenzene, THF, and toluene making it impractical to infer the molecular weight of UHMWPE [104-106] One of the recommended routine ways of inferring the molecular weight of UHMWPE is through intrinsic viscosity measurement using the Mark-Houwink equation [107, 108]. We employed the Standard ASTM D-4020 to determine the relative molecular weight of our synthesized polymers [109].

The viscosity measurements were conducted in decalin at 135 °C using Ubbelohde viscometer with type I capillary and a diameter of 0.63 mm. The results obtained are tabulated in Table 4.18

Details for polymer generated by FeBL1 at 80 °C and 150 psi

Mass of polymer: 0.0104g

Volume of solvent: 0.470 dL

Concentration of polymer: 0.022 g/dL

Solvent flow time (s): 189.34

Details for polymer generated by CoBL1 at 60 °C and 50 psi

Polymer Mass: 0.0134g

Volume of solvent: 0.605 dL

Concentration of polymer: 0.022 g/dL

Solvent flow time (s): 189.34

Details for polymer generated by NiBL1 at 60 °C and 150 psi

Polymer Mass: 0.0115g

Volume of solvent: 0.520 dL

Concentration of polymer: 0.022 g/dL

Solvent flow time (s): 189.34

Table 4.18: Relative molar mass from viscosity measurement

Sample	Fe @ 80-150	Co @ 60-50	Ni @ 60-50
Flow time (s)	249.43	236.16	230.02
	250.24	235.97	230.12
	250.36	235.59	229.94
Average flow time (s)	250.01	235.91	230.03
Relative viscosity	1.32	1.25	1.21
Specific viscosity	0.32	0.25	0.21
Reduced viscosity	14.55	11.36	9.55
Intrinsic viscosity (dL/g)	13.23	10.53	8.95
M_v (g/mol)	1.85 x 10⁶	1.35 x 10⁶	1.08 x 10⁶

As shown in Table 4.18, polyethylene produced by **FeBL1** at its optimum polymerization temperature has a relative molecular weight of $1.85 \times 10^6 \text{ g mol}^{-1}$. Also, the polymer produced by

CoBL1 at 60 °C when 50 psi was applied and that produced by **NiBL1** at their optimum temperature and pressure have relative molecular weights of $1.35 \times 10^6 \text{ g mol}^{-1}$ and 1.08×10^6 , respectively, as determined by viscosity measurements.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Conclusively, new octahedral complexes of iron, cobalt, and nickel have been successfully synthesized and characterized. The results obtained from the various spectroscopic analyses revealed various information related to the newly synthesized compounds. The complexes were applied for catalytic ethylene polymerization using MMAO as a co-catalyst to generate UHMWPEs. Comparatively, CoBL1 catalyst exhibited the highest catalytic activity of $5.54 \times 10^7 \text{ g (PE) mol}^{-1} (\text{Co}) \text{ h}^{-1}$ and was able to generate UHMWPE with a relative molecular weight of $1.35 \times 10^6 \text{ g mol}^{-1}$ at 60 °C. Excellent thermal stability and highest molecular weight ($1.85 \times 10^6 \text{ g mol}^{-1}$) were obtained using catalyst **FeBL1** at 80 °C during the polymerization screening in this system. On the other hand, catalyst **NiBL1** is the least active compared to the other catalysts, and gave polymer with a relative molecular weight of $1.08 \times 10^6 \text{ g/mol}$ at 60 °C and 50 psi. In particular, these appear to be the first stable and active octahedral complexes of iron, cobalt, and nickel capable of producing UHMWPE. The polymers are insoluble in many available solvents at room temperature, but only soluble in very few solvents such as decalin, DMF and DMSO at temperatures above 130 °C. Further exploration of the application of these new complexes for ethylene copolymerization is targeted.

5.2 Recommendations

Due to the findings from this thesis, the following recommendations are hereby forwarded:

- 1) The newly synthesized ligand should be complexed with chromium and applied for selective ethylene transformation to 1-octene or 1-hexene
- 2) The catalysts should also be applied for ethylene co-polymerization with polar monomers
- 3) The mechanical and thermal properties of the polymers should be explored to have information on their rheological properties
- 4) Bimetallic and monometallic four-coordinate structures should be synthesized and applied for ethylene polymerization

5.3 List of Publications and Patent

- 1) Bishir Ibrahim, Fakhre Alam, Jameel Raddah Al-thagfi. New Octahedral Fe(II), Co(II) and Ni(II) catalysts bearing pyridine-imine donors: Synthesis, Characterization and Ultra-High Molecular Weight Polyethylene (UHMWPE) production.
- 2) Bishir Ibrahim, Fakhre Alam, Jameel Raddah Al-thagfi. Thermal and Mechanical Properties of Ultra-High Molecular Weight Polyethylene (UHMWPE) produced by New Co(II) octahedral catalyst.
- 3) Bishir Ibrahim, Fakhre Alam, Jameel Raddah Al-thagfi. Crystal structure of 1-(6-bromopyridin-2-yl)-N-(2,6-diisopropylphenyl)methanimine.

Patent

Novel Geometrically Octahedral Fe(II), Co(II), and Ni(II) Catalysts Bearing Pyridine-Imine Donors for Ultrahigh Molecular Weight Polyethylene (UHMWPE) Production

References

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Vitae

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EDUCATIONAL BACKGROUND

Master of Science in Chemistry, 2023 – 2025

King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia.

Academic Standing: First Class

Bachelor of Science in Chemistry, 2018-2022

Umaru Musa Yar`adua University, Katsina, Nigeria.

Academic Standing: First Class

Nigeria Certificate in Education in Computer Science/Chemistry, 2014-2017

Federal College of Education, Katsina.

Grade: Distinction

TEACHING EXPERIENCE

Teaching Assistant 2023- 2025

King Fahd University of Petroleum and Minerals, Saudi Arabia.

- Taught undergraduate students, the principles of general chemistry
- Delivered lesson and administered quizzes on weekly basis
- Guided the conduct of experiments and graded the reports

Senior High School Teacher

Government Day Secondary School, Dandume, Katsina, Nigeria. 2018-2019

- Taught high school level chemistry to a class of 45 students
- Planned lesson note, organized and interacted with students for lesson delivery

Teaching Practice

Government Day Secondary School Dandume, Katsina, Nigeria. Feb. 2016 – Sept. 2017

- Taught Basic Science and Mathematics to junior students for six months
- Planned and delivered lesson, assessed and recorded the students` performance

LEADERSHIP EXPERIENCE

President – Students` Chemical Society of Nigeria (SCSN), 2019-2020

Umaru Musa Yar`adua University, Katsina.

President - Nigeria Association of Computer Science Students, 2016/2017

Federal College of Education, Katsina.

Coordinator- Alliance for Katsina Youth Development 2017-2020

AWARDS/HONORS

International Students` Scholarship, 2023 – 2025

King Fahd University of Petroleum and Minerals, Saudi Arabia.

Overall Best Graduating Student of the University, 2021

UMYU Class of 2020.

Best Graduating Student, 2021

Faculty of Natural & Applied Sciences, UMYU.

Best and Most Versatile Chemistry Student, 2021

SCSN 2020 Award,

PROFESSIONAL SKILLS

Instrumental Skills

- GC-MS
- HPLC
- DSC
- FT-IR
- UV-Vis
- TGA
- AAS

Computational Skills

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- OLEX2
- SHELXLE
- WinGX
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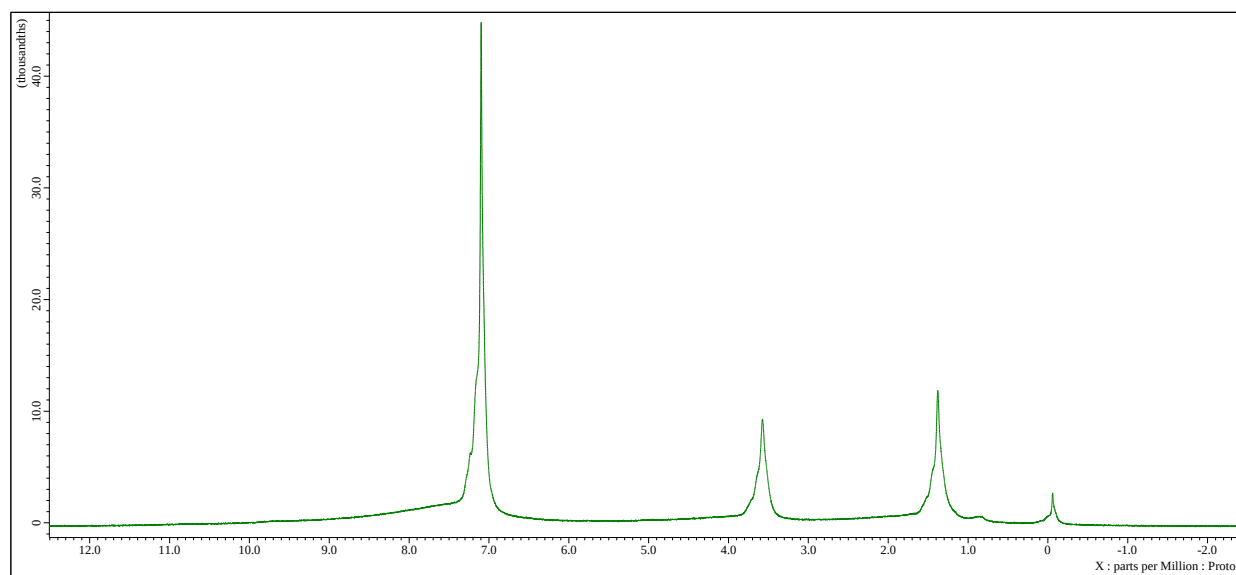
Dr. Nura Suleiman Gwaram

Senior Lecturer & Deputy Dean

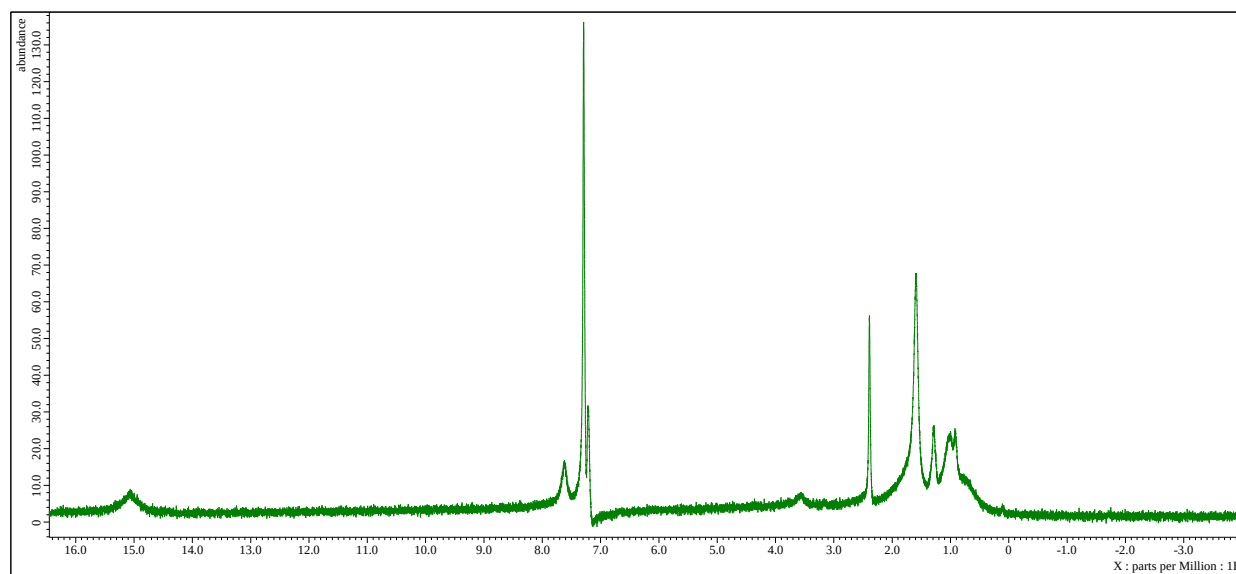
UMYU, Nigeria

nura.suleiman@umyu.edu.ng

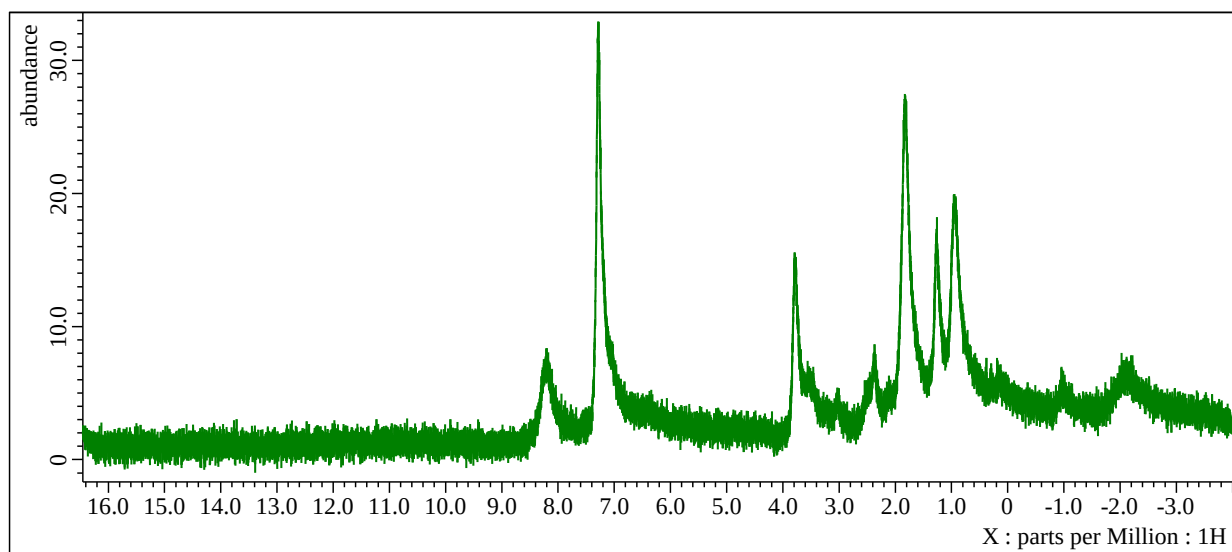
Appendices



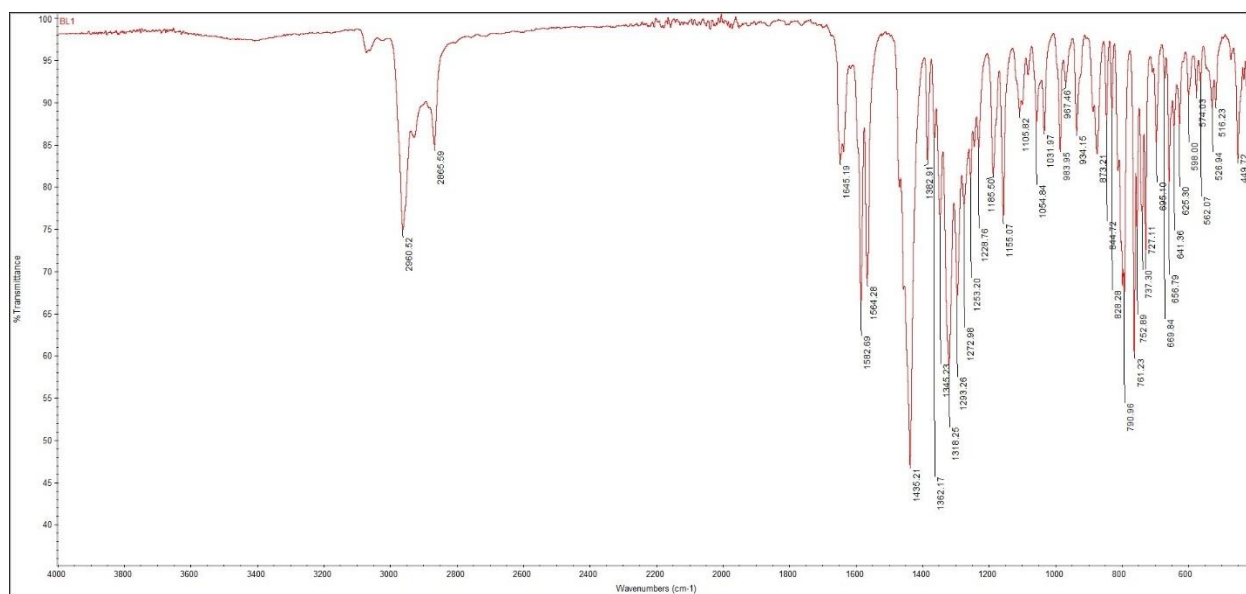
Appendix 1: NMR spectrum of FeBL1 complex



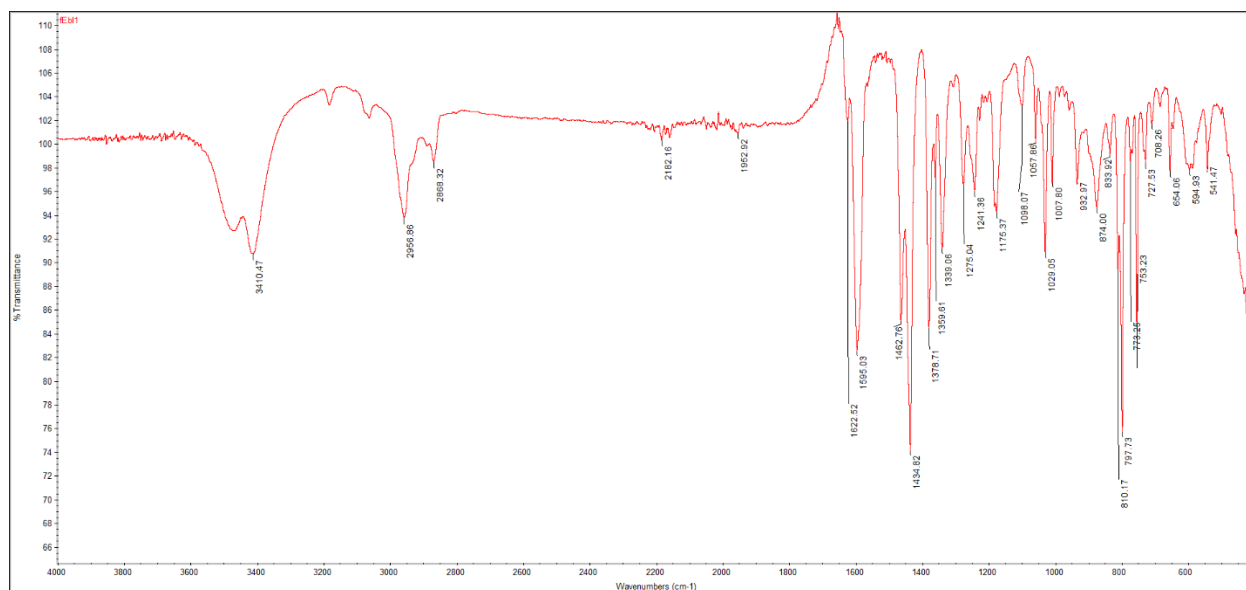
Appendix 2: NMR spectrum of CoBL1 complex



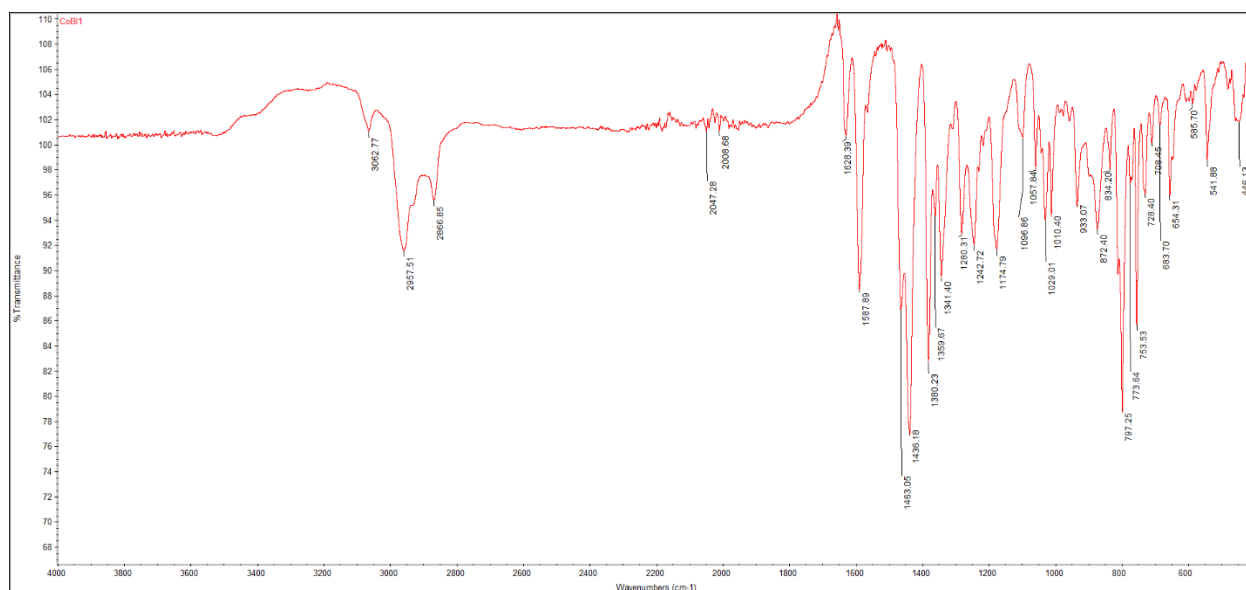
Appendix 3: NMR spectrum of NiBL1 complex



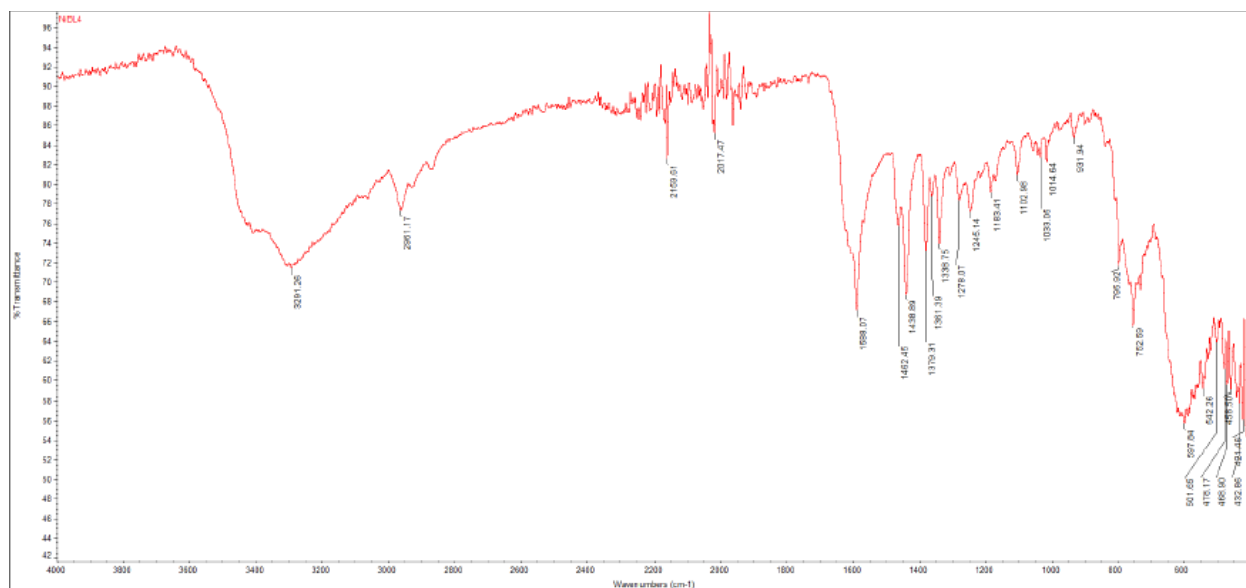
Appendix 4: FT-IR spectrum of BL1 complex



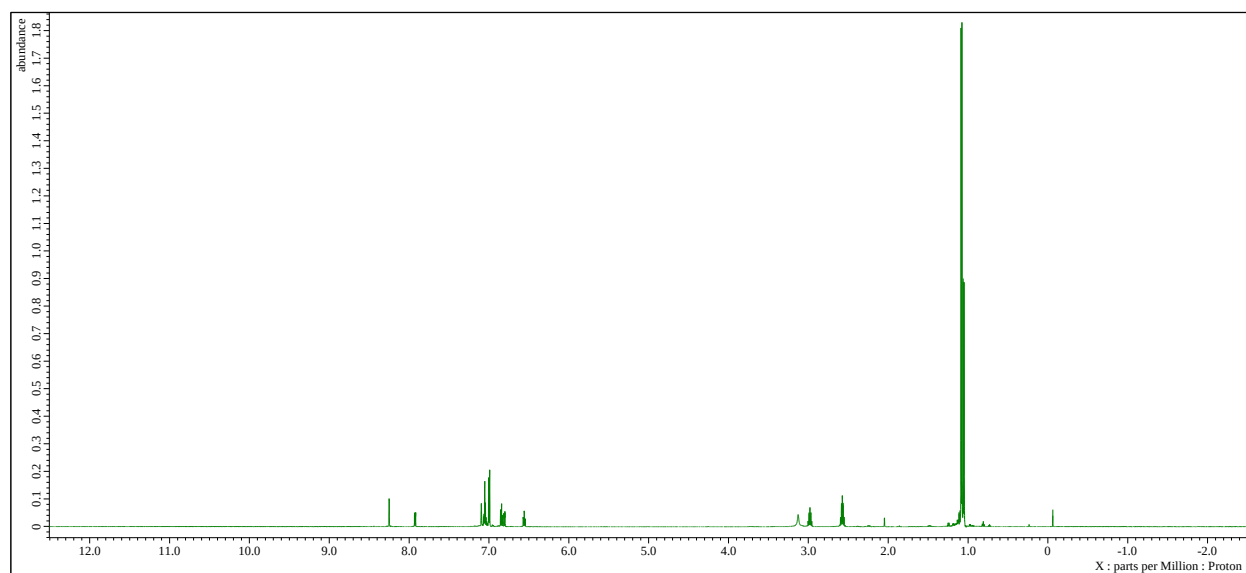
Appendix 5: FT-IR spectrum of FeBL1 complex



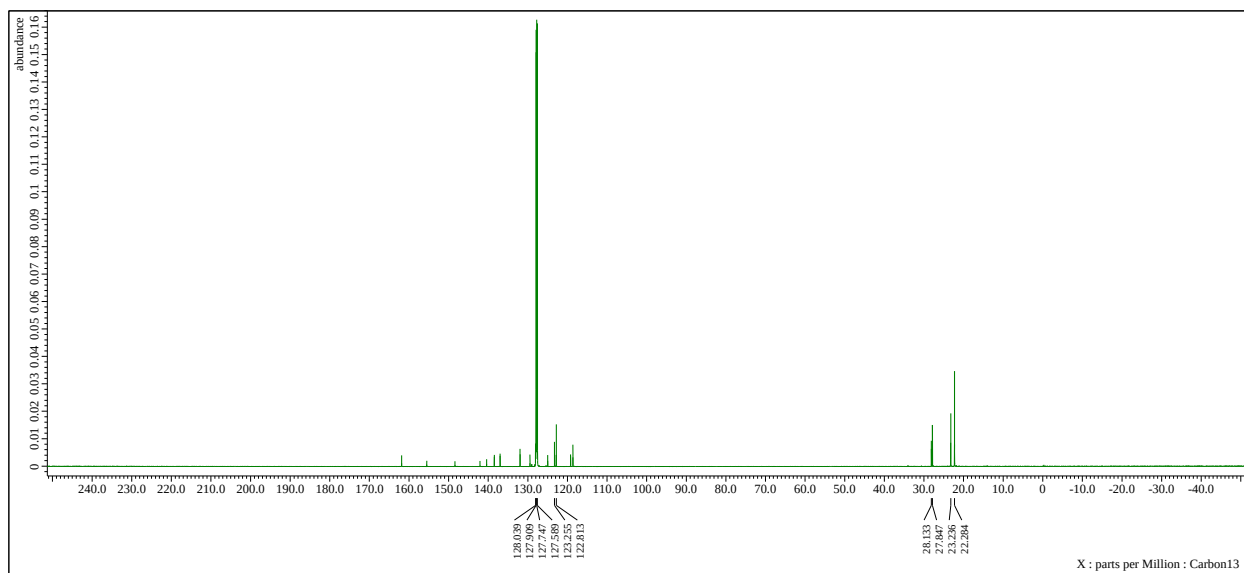
Appendix 6: FT-IR spectrum of CoBL1 complex



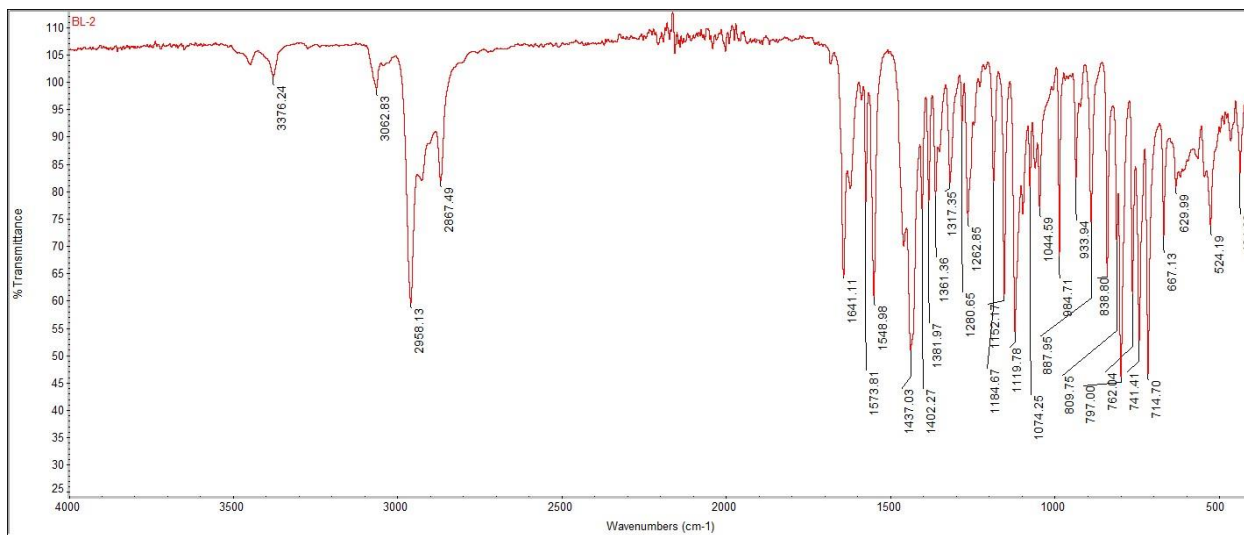
Appendix 7: FT-IR spectrum of NiBL1 complex



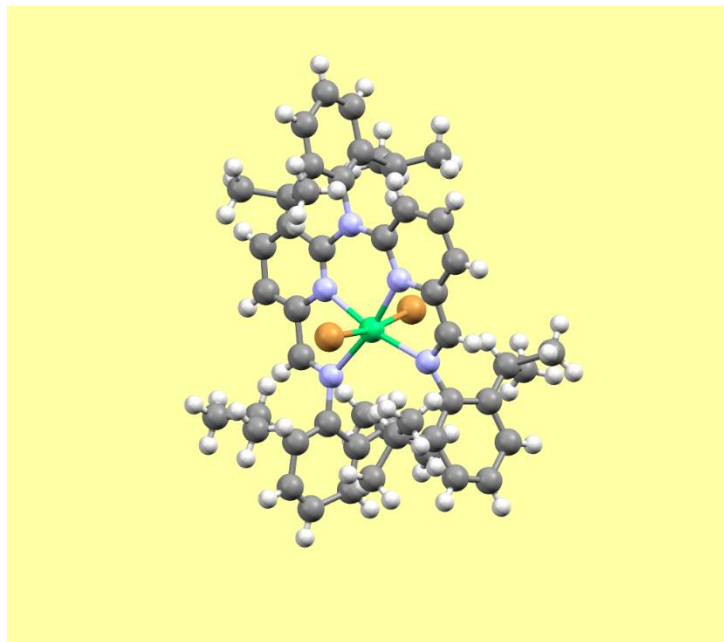
Appendix 8: ¹H NMR spectrum of BL2



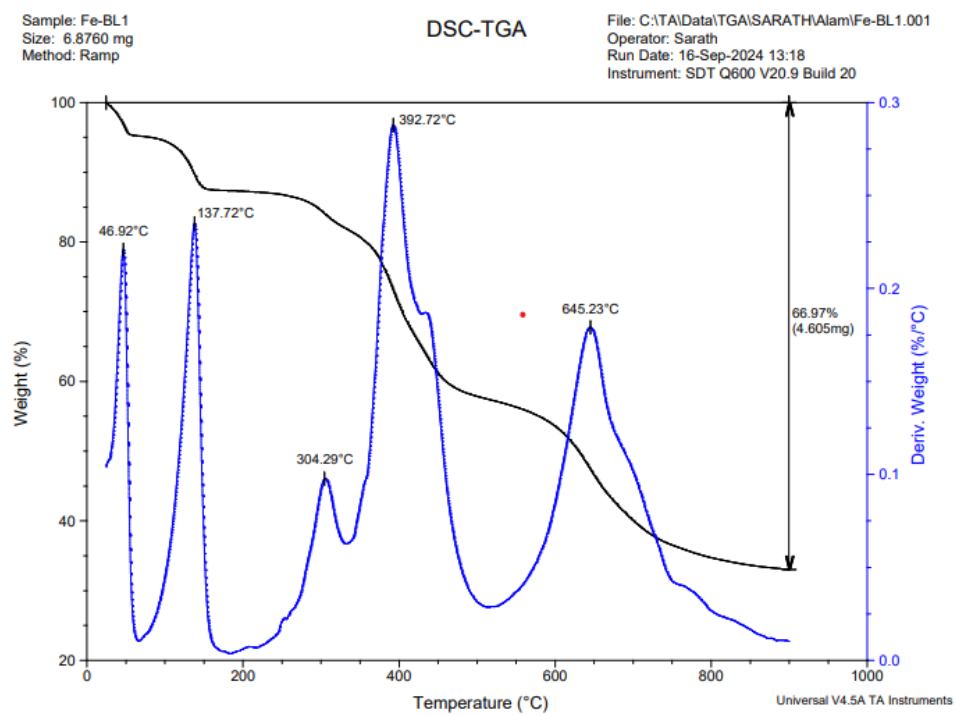
Appendix 9: ¹³C NMR spectrum of BL2



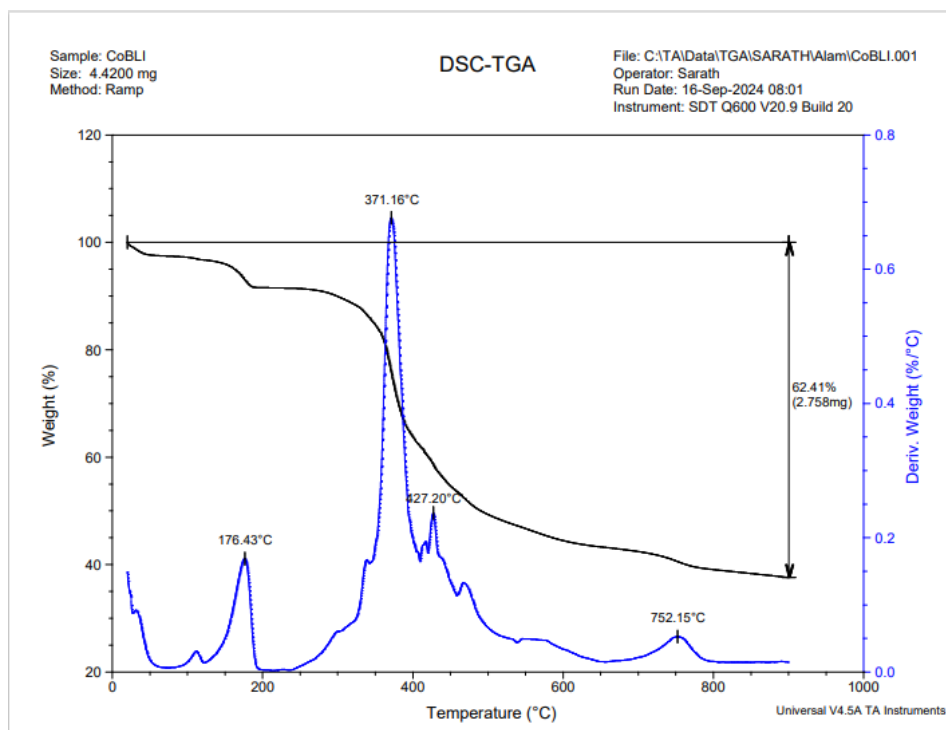
Appendix 10: FT-IR spectrum of BL2



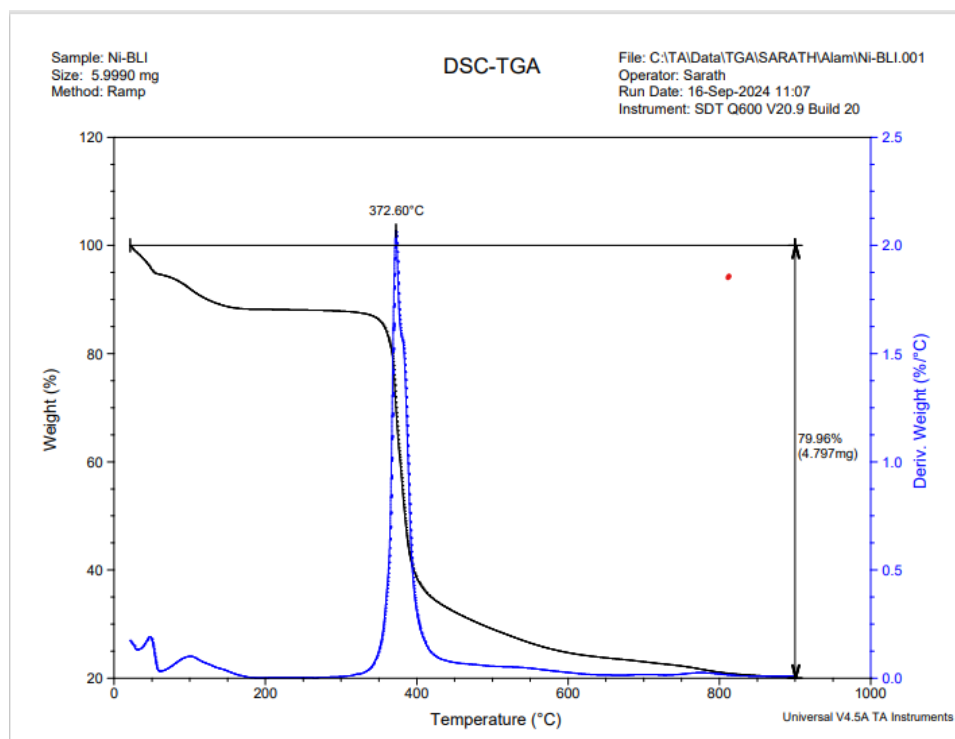
Appendix 11: Ball and stick picture of NiBL1 Xray structure



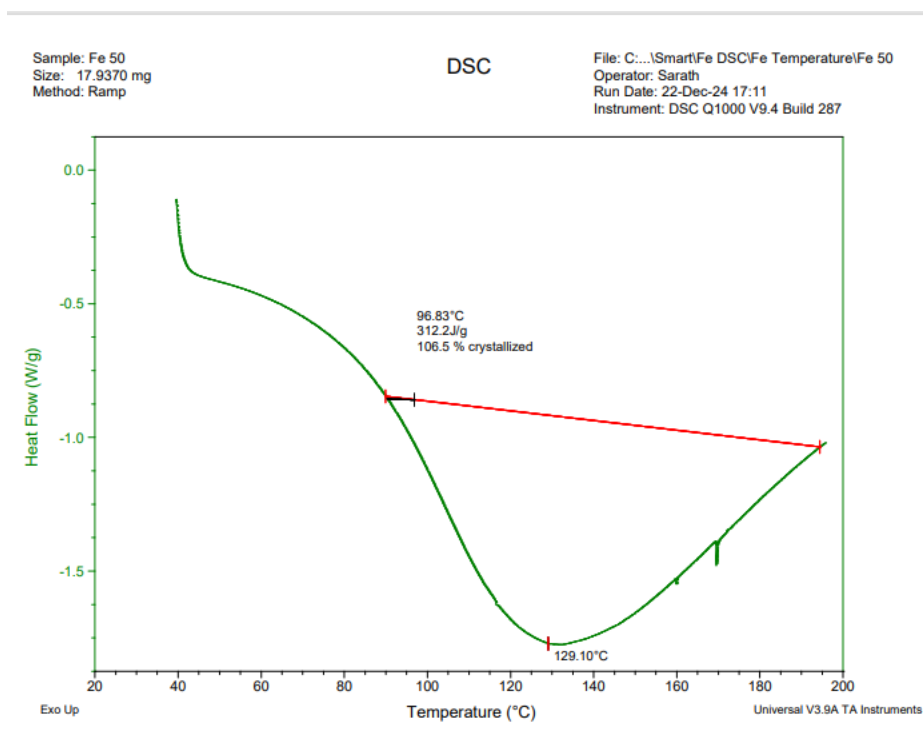
Appendix 12: DSC-TGA of FeBL1



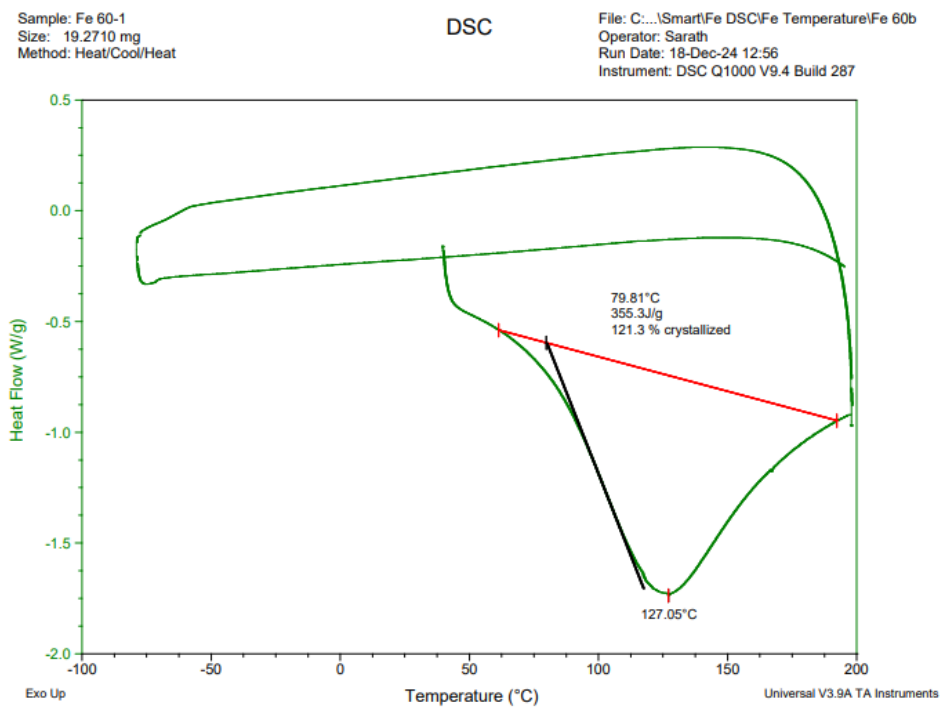
Appendix 13: DSC-TGA of CoBL1



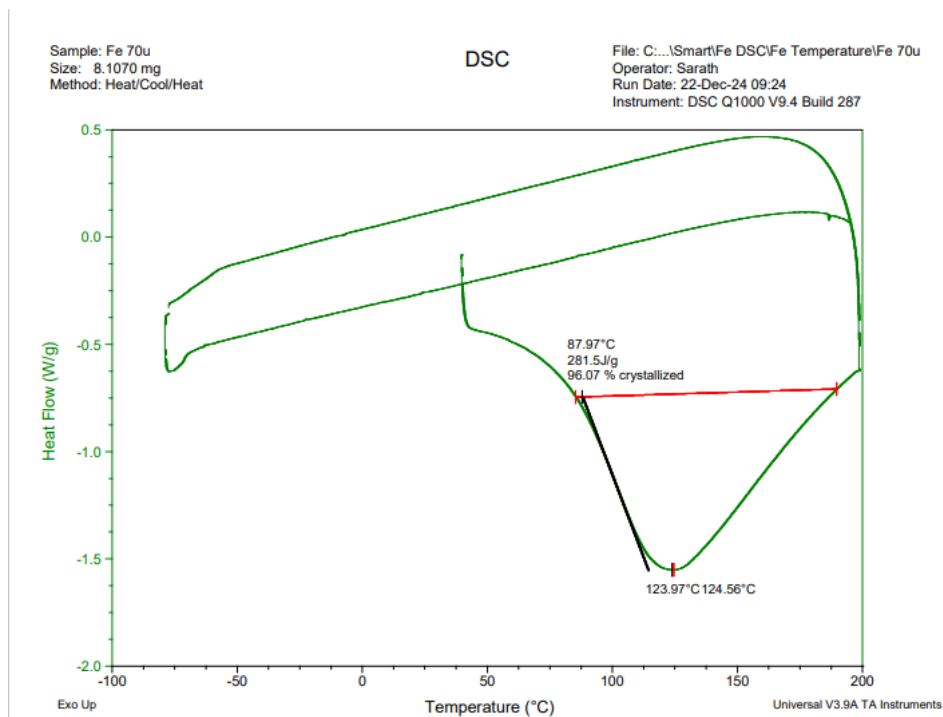
Appendix 14: DSC-TGA of NiBL1



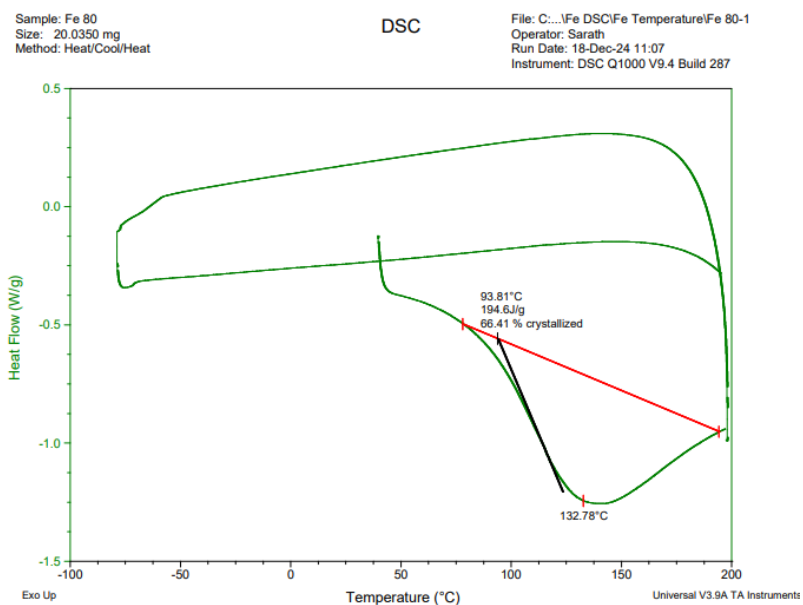
Appendix 15: DSC Fe 50-150



Appendix 16: DSC Fe 60-150



Appendix 17: DSC Fe 70-150

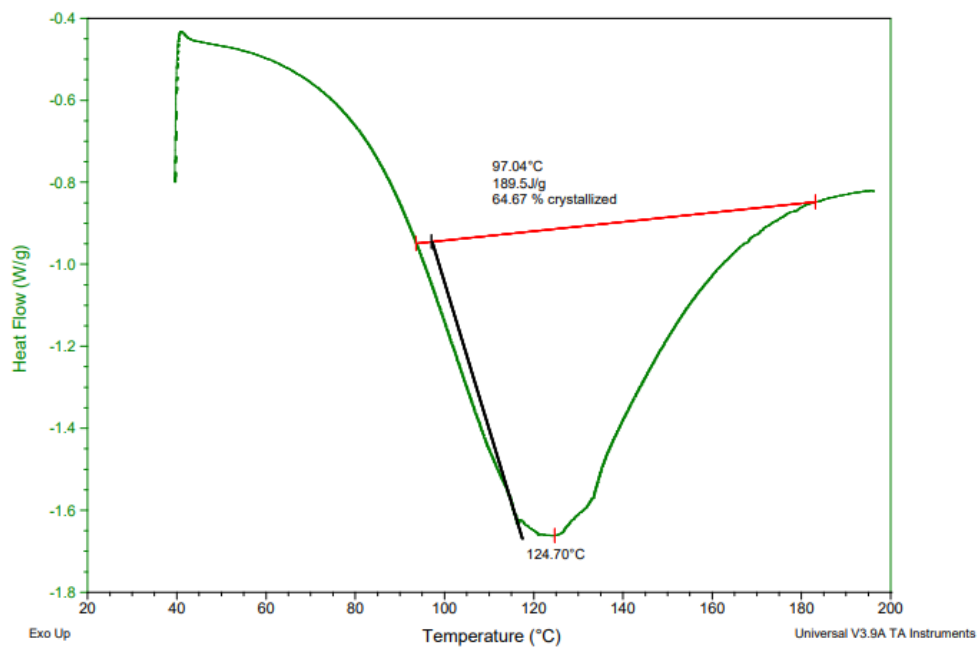


Appendix 18: DSC Fe 80-150

Sample: Fe 90
Size: 10.8620 mg
Method: Ramp

DSC

File: C:\...\Smart\Fe DSC\Fe Temperature\Fe 90
Operator: Sarath
Run Date: 22-Dec-24 17:31
Instrument: DSC Q1000 V9.4 Build 287

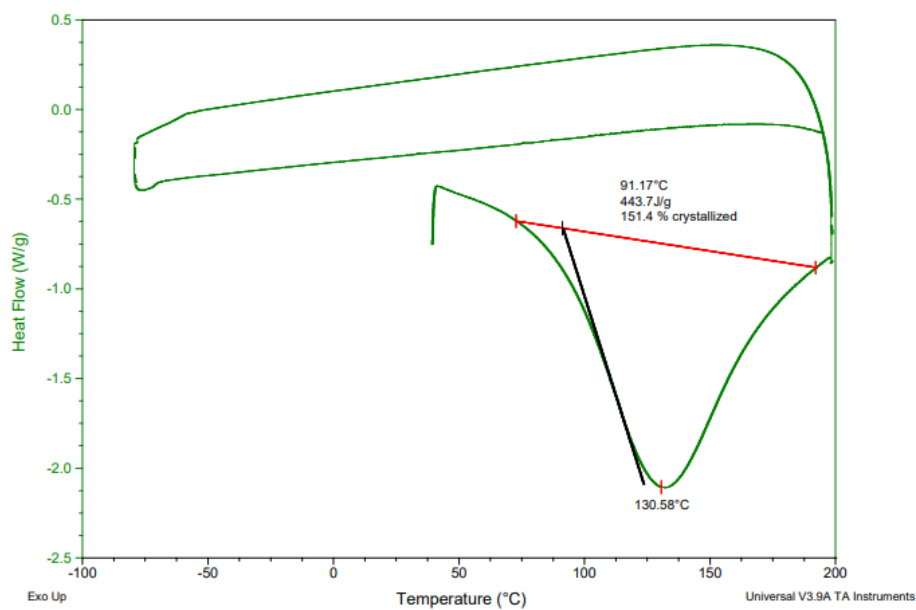


Appendix 19: DSC Fe 90-150

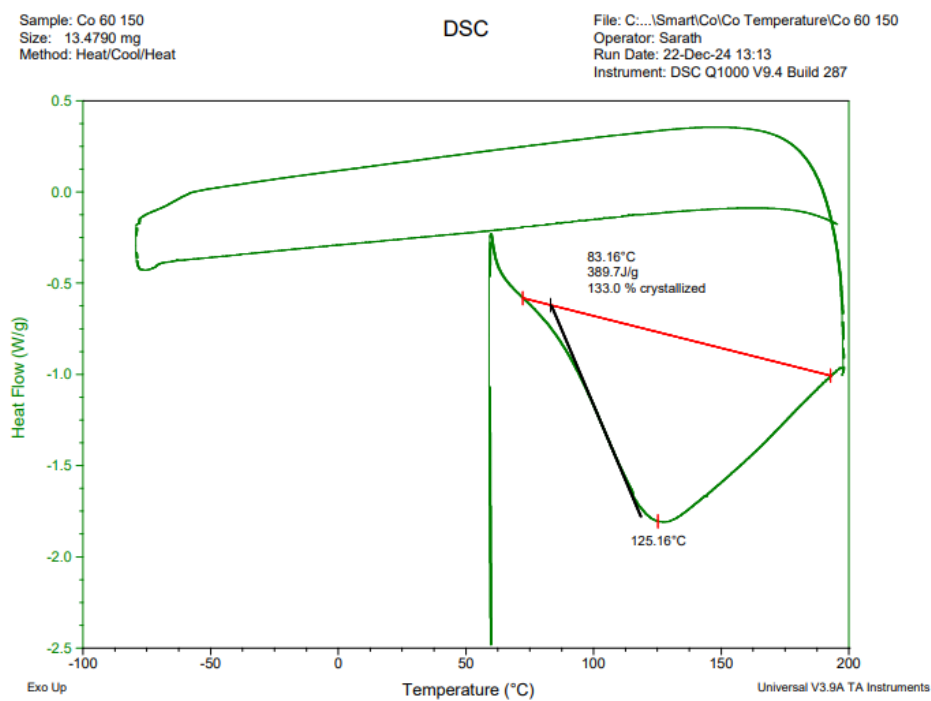
Sample: Co 60 50
Size: 13.6160 mg
Method: Heat/Cool/Heat

DSC

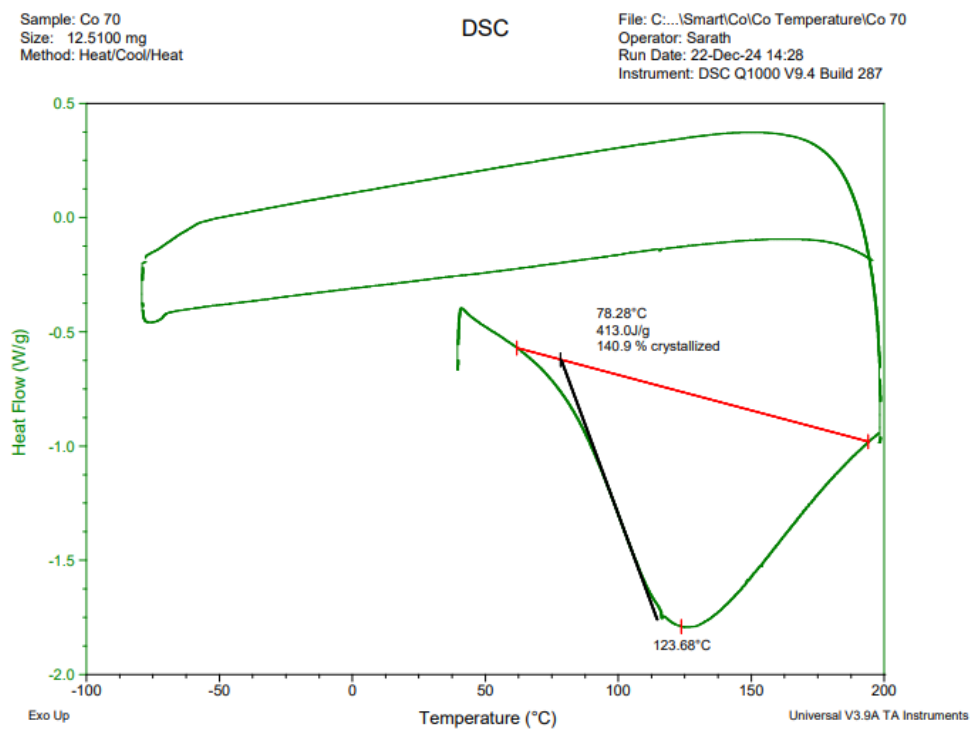
File: C:\...\Smart\Co\Co Temperature\Co 60 50
Operator: Sarath
Run Date: 22-Dec-24 11:57
Instrument: DSC Q1000 V9.4 Build 287



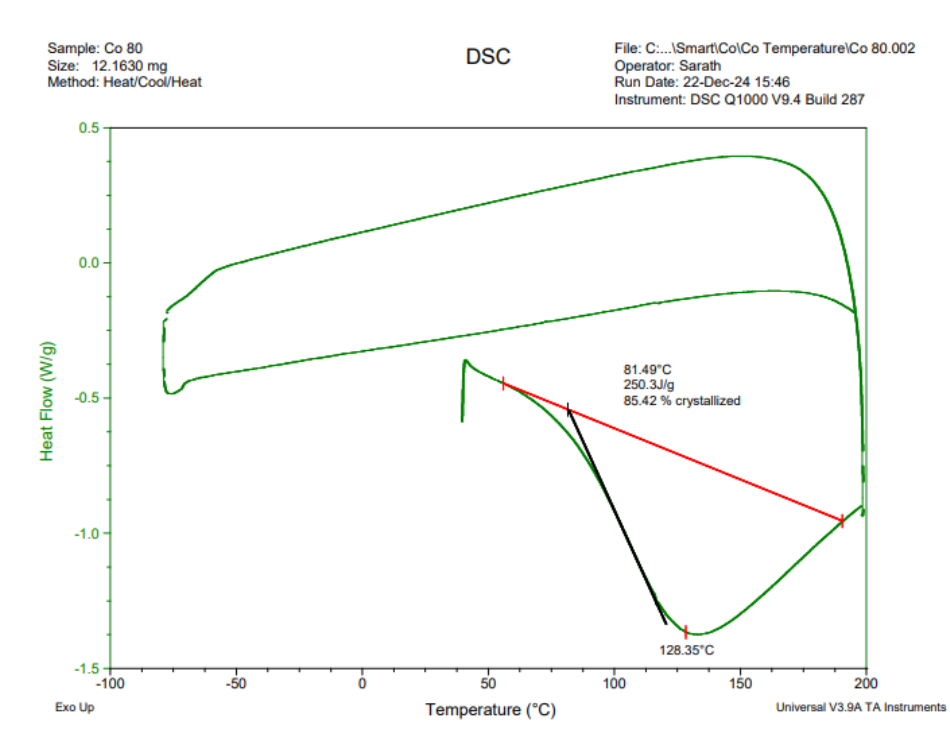
Appendix 20: DSC Co 60-50



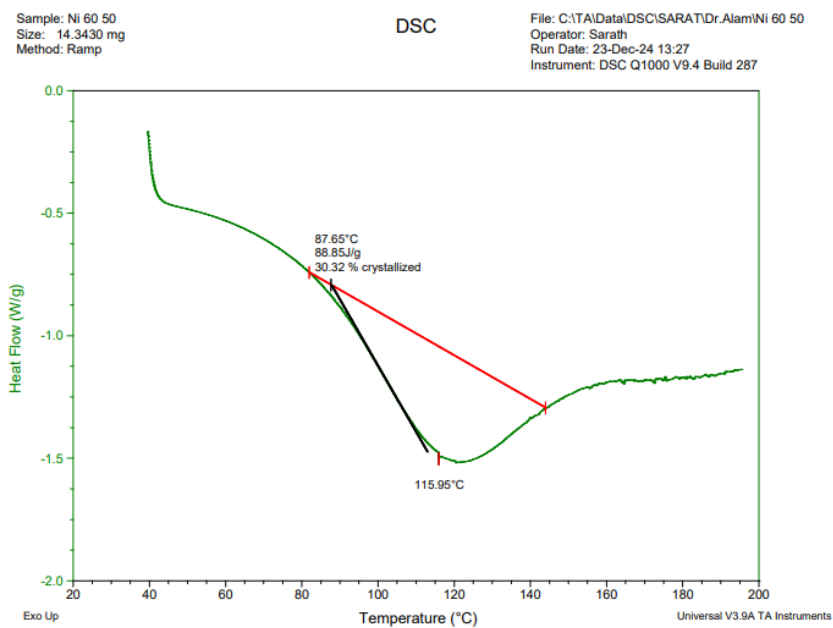
Appendix 21: DSC Co 60-150



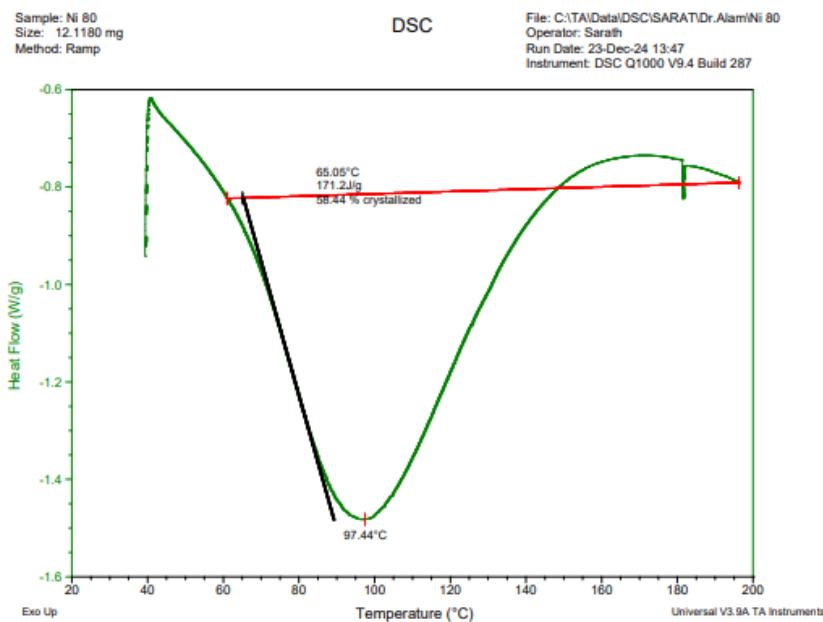
Appendix 22: DSC Co 70-50



Appendix 23: DSC Co 80-50

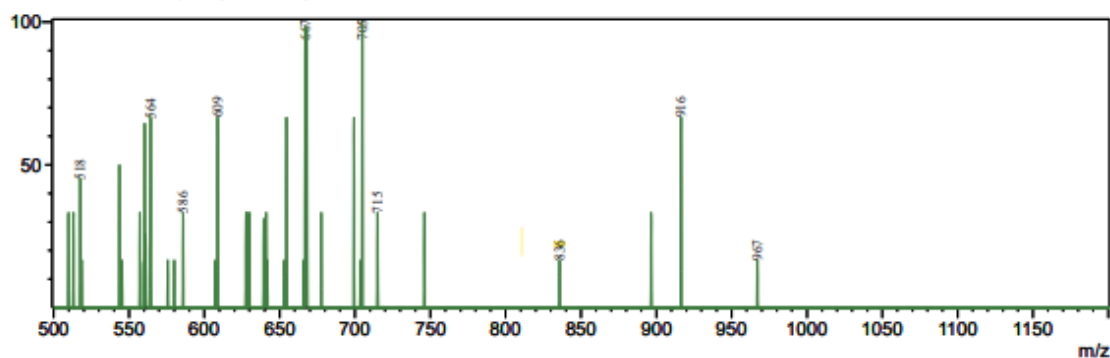


Appendix 24: DSC Ni 60-50



Appendix 25: DSC Ni 80-50

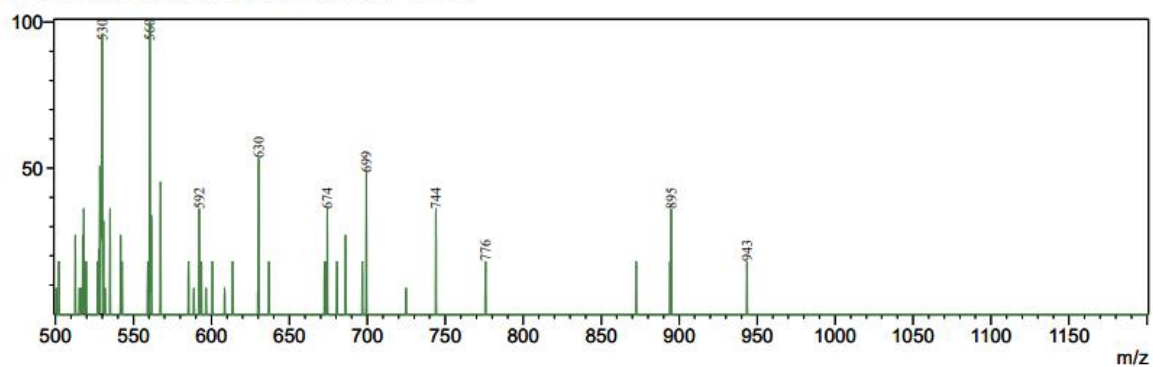
R. Time: 0.017 (Scan#: 2)
Mass Peaks: 37 Base Peak: 705 (10347)
Spectrum Mode: Single 0.017 (2)
BG Mode: None Polarity: Negative Segment 1 - Event 2



C:\Users\YU ser\Desktop\Yalam\data\3.bd

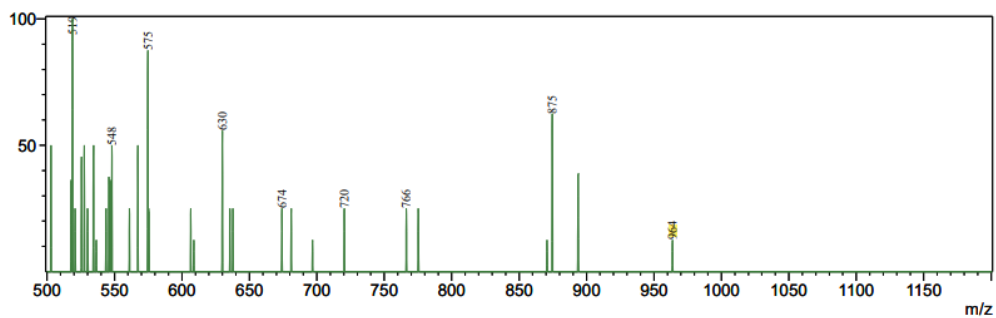
Appendix 26: ESI-MS of FeBL1

R.Time:0.017(Scan#:2)
 MassPeaks:45 BasePeak:560(19024)
 Spectrum Mode:Single 0.017(2)
 BG Mode:None Polarity:Negative Segment 1 - Event 2



Appendix 27: ESI-MS of CoBL1

R.Time:0.017(Scan#:2)
 MassPeaks:32 BasePeak:519(13800)
 Spectrum Mode:Single 0.017(2)
 BG Mode:None Polarity:Negative Segment 1 - Event 2



Appendix 28: ESI-MS of NiBL1