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PREPARATION AND CHARACTERIZATION OF β-DIKETONATE PYRAZOLE COMPLEXES WITH COBALT AND NICKEL

Jittima Thisuwan

A Thesis Submitted in Partial Fulfillment of the Requirements for the

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PREPARATION AND CHARACTERIZATION OF β-DIKETONATE PYRAZOLE COMPLEXES WITH COBALT AND NICKEL

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งานวิจัยนี้มุ่งเน้นที่การเตรียมลิแกนด์ไพราโซลที่มีหมู่แทนที่ในตำแหน่งที่ 3 และ 5 และลิแกนด์เบตา-ไดคีโตเนท และการเกิดสารประกอบเชิงซ้อนผสมของลิแกนด์ทั้งสองกับโคบอลต์และนิกเกิลผลิตภัณฑ์ของลิแกนด์ผสมทำให้บริสุทธิ์ได้ด้วยการตกผลึกโดยปล่อยให้ตัวทำละลายผสมของ CH_2Cl_2 และ MeOH ที่อุณหภูมิห้อง ผลิตภัณฑ์ที่ได้จาก 8 ปฏิกิริยาที่ประสบผลสำเร็จซึ่งเป็นสารประกอบเชิงซ้อนของ 1,3-diphenylpropane-1,3-dionate กับโลหะ {โลหะ = โคบอลต์, นิกเกิล} ด้วยลิแกนด์ไพราโซลที่มีหมู่แทนที่ในตำแหน่งที่ 3 และ 5 {3,5-dimethylpyrazole (Hpz^{Me2}), 3,5-diphenylpyrazole (Hpz^{Ph2}), 3,5-bis(trifluoromethyl)pyrazole ($Hpz^{(CF3)2}$) และ 3,5-di-*tert*-butylpyrazole ($Hpz^{(t\text{-}Bu)2}$)} เป็นสารใหม่จากทั้งหมด 24 ปฏิกิริยาซึ่งเก็บในสารละลายผสม นำมาแยกและพิสูจน์เอกลักษณ์ด้วยเทคนิคฟูเรียร์ทรานฟอร์มอินฟาเรด อัลตราไวโอเลต-วิสิเบิล โปรตอน-นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี และการวิเคราะห์เชิงความร้อน

สีของผลึกของโคบอลต์คือแดง/ส้ม และผลึกของนิกเกิลคือเขียว สเปกตราอินฟาเรดและอิเล็กทรอนิกส์ของผลิตภัณฑ์แตกต่างจากสารตั้งต้นอย่างมีนัยสำคัญ การเปรียบเทียบระหว่างสารประกอบเชิงซ้อนของโคบอลต์และนิกเกิลพบว่าไม่มีการเปลี่ยนแปลงอย่างมีนัยสำคัญในคุณสมบัติทางสเปกโทรสโกปิก สเปกตราอินฟราเรดแสดงแบนด์ที่มีลักษณะเฉพาะของคีเลตติงใน dbm และบริดจิงในไพราโซล สเปกตราอิเล็กทรอนิกส์แสดงค่า λ_{max} ในสองและสามแบนด์สำหรับสารประกอบเชิงซ้อนเหล่านี้ ในขณะที่สารตั้งต้นแสดงเพียงหนึ่งแบนด์ สเปกตราโปรตอน-นิวเคลียร์แมกเนติกเรโซแนนซ์ แสดงให้เห็นว่าโลหะโคออร์ดิเนตกับน้ำ dbm และไพราโซล การเปลี่ยนแปลงที่สำคัญในสารประกอบเชิงซ้อนแบบโมโนเมอริคของนิกเกิลไพราโซลิล $[Ni(dbm)_2(Hpz^{R2})_2]$ คือลักษณะแบนด์ของ N–H สเตรทชิงในลิแกนด์ไพราโซลแบบโมโนเดนเทตที่มีหมู่แทนที่เป็นเมทิล และที-บิวทิล และการเกิดเป็นบริดจิงไพราโซลในโครงสร้างแบบไดเมอริคในสารประกอบเชิงซ้อนอีกหกตัว $[M_2(dbm)_2(\mu\text{-}pz^{R2})_2(H_2O)_4]$ ซึ่งการระบุสูตรสอดคล้องกับผลของการวิเคราะห์เชิงความร้อน

สาขาวิชาเคมี ลายมือชื่อนักศึกษา________________________
ปีการศึกษา 2553 ลายมือชื่ออาจารย์ที่ปรึกษา___________________

JITTIMA THISUWAN : PREPARATION AND CHARACTERIZATION OF β-DIKETONATE PYRAZOLE COMPLEXES WITH COBALT AND NICKEL. THESIS ADVISOR : ASSOC. PROF. KENNETH J. HALLER, Ph.D. 88 PP.

COBALT/NICKEL/PYRAZOLE LIGANDS/β-DIKETONATE LIGANDS/MIXED LIGANDS

The research focused on the preparation of 3,5-disubstituted pyrazole and β-diketonate ligands and formation of their mixed complexes with cobalt and nickel. The mixed ligand products were purified by recrystallization by slow evaporation at room temperature from CH_2Cl_2:MeOH solutions. Products from the eight successful reactions of 1,3-diphenylpropane-1,3-dionate metal complexes {metal = cobalt, nickel} with 3,5-disubstituted pyrazoles {3,5-dimethylpyrazole (Hpz^{Me2}), 3,5-diphenylpyrazole (Hpz^{Ph2}), 3,5-bis(trifluoromethyl)pyrazole (Hpz$^{(CF3)2}$), and 3,5-di-*tert*-butylpyrazole (Hpz$^{(t\text{-}Bu)2}$)}, obtained from 24 attempted reactions stored in their mother liquor, were isolated and were characterized by FT-IR, UV-Vis, ^{1}H NMR, and TGA techniques.

The color of the adduct crystals is red/orange for cobalt and green for nickel. The infrared and electronic spectra of the products are significantly different from those of the starting materials. Comparison of the spectra of the cobalt and nickel complexes indicates their similarity. The infrared spectra show characteristic bands of chelating dbm and pyrazole ligands. The electronic spectra give two and three bands for product complexes, while the starting materials show only one band in their spectra. ^{1}H NMR spectra are consistent with metal coordinated with water, dbm, and pyrazole. The major differences are attributed to bands for N–H stretching in the monodentate pyrazole ligand of the monomeric methyl and *t*-butyl substituted pyrazolyl nickel complexes, $[Ni(dbm)_2(Hpz^{R2})_2]$, and their lack in the bridging pyrazoles of the dimeric structures, $[M_2(dbm)_2(\mu\text{-}pz^{R2})_2(H_2O)_4]$, of the other six complexes. The assigned formula are consistent with thermal analysis results.

School of Chemistry Student's Signature_____________________

Academic Year 2010 Advisor's Signature_____________________

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Jittima Thisuwan

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LIST OF ABBREVIATIONS

β-dkt	β-diketonates
δ	chemical shift (part per million)
λ	lambda
ν	frequency (per centimeter)
π	pi
ºC	degree Celcius
Å	angstrom
acac	acetylacetonate (2,4-pentanedione)
bipy	bipyridine
dbm	1,3-diphenyl-1,3-propanedione
DCM	dichloromethane solvent
dmae	dimethylethanolamine
e.g.	*exempli gratia*, Latin meaning “for example”
etc.	*et cetera*, Latin meaning “and so forth”
EtOH	ethanol
FT-IR	Fourier Transform Infrared spectroscopy
^{1}H-NMR	proton nuclear magnetic resonance spectroscopy
hfac	hexafluoroacetylacetonate
Hpz	pyrazoles
Hpz$^{(CF3)2}$	3,5-bis(trifluoromethyl)pyrazole

LIST OF ABBREVIATIONS (Continued)

Hpz$^{\mathrm{Me2}}$	3,5-dimethylpyrazole
Hpz$^{\mathrm{Ph2}}$	3,5-diphenylpyrazole
Hpz$^{\mathrm{R2}}$	3,5-disubstituted pyrazole
Hpz$^{t\text{-}\mathrm{Bu2}}$	3,5-dimethylpyrazole
hr	hour
IUPAC	International Union of Pure and Applied Chemistry
MeOH	methanol
MHz	megahertz
min	minute
mmol	millimole
M−N−O	metal nitrosyl triatomic moiety
MW	molecular weight
NCS	isocyanate
nm	nanometer
NO	nitrosyl
NMR	nuclear magnetic resonance spectroscopy
phen	phenanthroline
PTFE	polytetrafluoroethylene
sec	second
SEM	scanning electron microscope

LIST OF ABBREVIATIONS (Continued)

TGA	thermogravimetric analysis
tmhd	2,2,6,6-tetramethyl-3,5-heptanedione
Tp^{Ph2}	hydrotris(3,5-diphenylpyrazolyl)borate
UV-Vis	ultraviolet-visible spectroscopy

CHAPTER I

INTRODUCTION

1.1 General introduction

The molecular structure of a discrete chemical entity is the result of the total of the attractive and repulsive interactions among all the electrons and nuclei of the entity. The electronic structure of the entity is related to the number and distribution of the electrons about the nuclei, and is commonly modeled and discussed in terms of atomic and molecular orbitals. The spatial distribution of the electrons determines chemical reactivity and other important properties of the chemical entity.

From a model point of view, the arrangement of the nuclei is determined by the interplay of the intra-entity electrostatic interactions, the atomic orbitals forming the molecular orbitals, and the steric interactions between adjacent noncovalently bound atoms or groups of atoms. According to the International Union of Pure and Applied Chemistry (IUPAC, 1997), steric effects, “arise from contributions ascribed to strain as the sum of (1) nonbonded repulsions, (2) bond angle strain, and (3) bond stretch or compression.” An effect in which the chemical reaction is slowed down or prevented depends on the size or arrangement of groups in a molecule as large groups on a reactant molecule may hinder the approach of other reactant molecules.

Steric and electronic effects are often interrelated and results from the various spectroscopic techniques are often explained in terms of the electronic effects that occur as the substituents on either ligands or metal atoms in the complexes and/or the stereochemical structures of the complexes are changed (Tolman, 1977; Hasan and Ali, 1985). Structural correlations are also often interpreted in terms of the steric and/or electronic effects of these same changes. Steric bulk can be readily altered, the only constraint being that the modified ligand does not preclude the formation of the principal metal-ligand bond. Although electronic properties are more complex, ultimately the main concern is usually the donor strength of the ligands. These properties can be influenced by inductive effects (basicity) and by the donor/acceptor properties of the ligand as well (Schwalbe, Andrikopoulos, Armstrong, Reglinski, and Spicer, 2007). While steric and electronic effects are interrelated, their dominant effects generally alter distances or angles, respectively, as shown schematically in Figure 1.1.

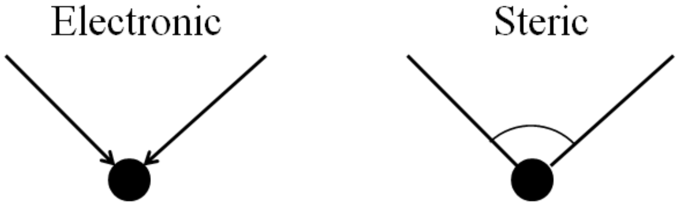

Figure 1.1 Schematic illustration of the essential difference between electronic and steric effects.

An example of electronic effects can be seen in the concept of stereochemical control of valence, which predicts that the stereochemistry of the nickel nitrosyl triatomic moiety in four-coordinate $\{Ni{-}N{-}O\}^{10}$ nickel mono-nitrosyl complexes[1] will be dictated by the overall coordination stereochemistry of the complex formed, leading to limiting geometries ranging from linear, 180º, to strongly bent, 120º, geometries (Enemark and Feltham, 1974). This prediction has been demonstrated in

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[1] The $\{M{-}N{-}O\}^n$ notation, introduced by Enemark and Feltham, is used herein to avoid ambiguity in assigning formal oxidation states in metal nitrosyls. The n corresponds to the total number of metal *d* and nitrosyl π^* electrons in the complexes for nitric oxide assumed to be coordinated as a +1 ligand.

the structural determinations of $Ni(NCS)(NO)(P(C_6H_5)_3)_2$ (Haller and Enemark, 1978) with intermediate pseudo C_s geometry, [Ni–N–O] = 161° (formally Ni^{+1} and NO^0), and the cationic tripod ligand complex, $\{Ni(NO)((P(C_6H_5)_2(CH_2))_3CCH_3)\}^+$ (Berglund and Meek, 1972), with pseudo C_{3v} geometry, and linear $\{Ni–N–O\}^{10}$. $Ni(NO)((Tp^{Ph2})_3)BH$ (Harding, Harding, Adams, and Tuntulani, 2007) also shows a C_{3v}, linear $\{Ni–N–O\}^{10}$ stereochemistry, as demonstrated by IR spectroscopy.

The geometry of the M–N–O triatomic moiety changes from linear NO^+ to strongly bent NO^- as electrons are transferred from the metal based *d* orbitals into the π^* orbitals of the nitrosyl ligand. Thus, as the effective oxidation-reduction reaction occurs, the geometry of the M–N–O triatomic moiety changes as illustrated schematically in Figure 1.2. Study of complexes containing ligands such as this, which are stereochemically active towards redox reactions, are of interest in our group.

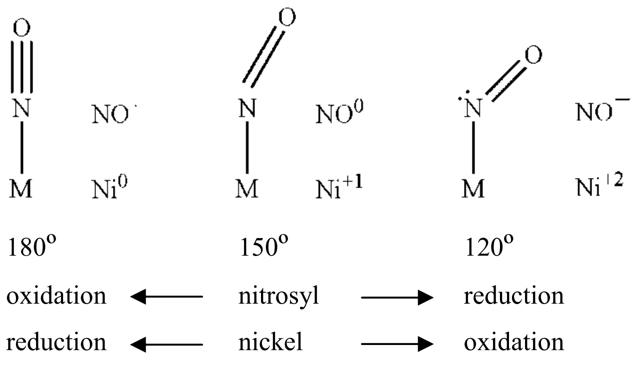

Figure 1.2 Schematic representation of the change in geometry of the M–N–O triatomic moiety.

1.2 Coordination chemistry

Specific properties of coordination compounds such as color and shape, *etc.*, can be changed by the coordination environment, and thus can easily be affected in the design of new structures. Furthermore, metal ions, especially transition metal ions, play an important role in biological systems. For example, several enzymes are metal complexes where the coordination environment of the catalytically active metal ion may alter the electronic structure of the metal ion or ligand(s) and thereby, may alter the activity of a specific enzyme.

Through the appropriate choice of ligands, we can generally design and synthesize coordination compounds having particular specified properties. Moreover, because of the intrinsic complexity of many of the bridging-group derivative ligands, unexpected modes of coordination may sometimes occur, and reactions may follow undesired routes.

Complexes containing chelate ligands generally possess enhanced stability when compared to similar complexes containing monodentate ligands. The concepts generally used to explain the increased stability of these chelate complexes include: 1) the closeness of the other ligand atoms of the chelate once the first metal ligand bond is formed, and 2) the more positive entropy of the formation of the chelate complex. The first concept is based on geometrical considerations and is rather qualitative, while the second concept is based on the fact that more monodentate ligands are liberated than chelating ligands are used in the putative reaction. However, a major shortcoming of this concept is that it does not consider changes in solvation that are intimately associated to the reaction and affect both its enthalpy and entropy (Emmenegger, Schlaepfer, Stoeckli-Evans, Piccand, and Piekarski, 2001).

1.3 Summary of β-diketonates and pyrazoles

Generally, nitrogen and oxygen containing heterocyclic compounds are of special interest as electron donors because they can function as π-electron donors or acceptors (Katritzky, Ramsden, Joule, and Zhdankin, 2010). The pyrazole ligands are of this type. Many chelate systems also undergo some degree of delocalization in forming planar five- and six-membered chelate ring systems. The β-diketonate ligands form such planar six-membered ring systems. Thus, the current work is focused on the interplay of two such types of ligands, pyrazole ligands and β-diketonate ligands in complexes with nickel and cobalt ions.

Pyrazole ligands

Pyrazoles, often abbreviated as Hpz^{R2}, are usually produced by the reaction of a β-diketonate with hydrazine. Pyrazoles are isomeric delocalized five-membered heterocyclic molecules containing two nitrogen atoms (Figure 1.3). One nitrogen atom has a localized lone electron pair on an in-plane orbital, while the other has an in-plane hydrogen atom attached. They also feature empty low-energy orbitals, the π* antibonding orbitals of the aromatic system located above and below the molecular plane. Hence, electronically, there are both σ-donor and π-acceptor ligands. (Reedijk, 1987). Due to their small size and the rigidity of the five-membered ring, the structure and vibrational spectra of this molecule have drawn much attention both experimentally and theoretically (El-Azhary, 2003).

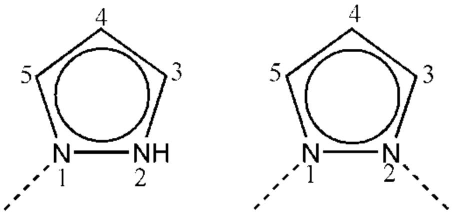

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Figure 1.3 Schematic diagrams of the molecular formula and atom numbering system used for pyrazole (1) monodentate coordination; (2) bridging coordination.

In pyrazoles, the number 1 atom is that bearing the substituent, either H or R. In the case of free pyrazole, rapid tautomerism leads to switching of the hydrogen atom from one nitrogen to the other as illustrated in Figure 1.4, resulting in inevitable mixtures of the 3- or 5-monosubstituted pyrazoles. Nomenclature to signify this has been developed (Krichhoff, 1967; Joule and Mills, 2010). For example, for 3-methylpyrazole and 5-methylpyrazole, the mixtures would be denoted (3,5)-methylpyrazole.

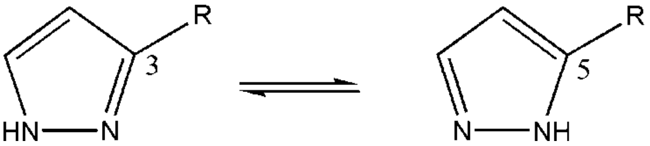

Figure 1.4 Tautomerization reaction producing 5-methylpyrazole from 3-methylpyrazole.

Synthesis of pyrazole rings with electron-donating or electron-withdrawing substituents on the carbon atoms will modify the nucleophilicity of the 2-N $(sp^2)^2$ position, thereby modifying the acid character of the pyrazole proton. Sterically demanding alkyl or aryl substituents at positions 3, 4 and 5 of the pyrazole ring can modify the steric bulk of the ligand (Catalan and Elguero, 1987; Chadghan, Pons,

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[2] Nitrogen atom at 2 position with sp^2 hybridization.

Caubet, Casabó, Ros, Larena, and Piniella, 2000; Zhao, Stipdonk, and Eichhorn, 2007). The most interesting aspect of this is in the possibility of designing new pyrazole ligands offering the opportunity of control of the electronic and steric properties in their metal complexes. The planarity of these aromatic molecules makes them relatively unhampered ligands from a steric point of view. However, the exact steric profile is highly dependent on the presence of substituents, their size, and their position on the ring (Reedijk, 1987).

The molecular and crystal structure of pyrazole ligands is well known (Nygaard, Christen, Nielsen, Pedersen, Snerling, Vestergaard, and Sørensen, 1974; Larsen, Lehmann, Søtofte, and Rasmussen, 1970). The pyrazole ligand can exhibit three coordination modes: (1) as neutral pyrazole ligands they have only one coordination site. When deprotonated, pyrazole becomes the pyrazolide ion, which can then coordinate as (2) a monodentate ligand using one of the nitrogen atom sites, or as (3) an exobidentate[3] ligand of approximate C_{2v} symmetry using both nitrogen atom sites (Trofimenko, 1972). In most cases, the pyrazolate ligand coordinates in an exobidentate fashion, thus linking two metal centers that may be identical or different (Pons, Chadghan, Alvarez-Larena, Piniella, and Rose, 2001). The nucleophilicity and steric accessibility of the coordinating nitrogen atom may be varied through ring substitution. A wide variety of substituted pyrazoles have been reported (Zhao, Stipdonk, and Eichhorn, 2007). A substituent in the 3 position introduces steric hindrance and makes it difficult to have six 3-substituted pyrazoles coordinated via the 2-N position to a metal. This difficulty can be circumvented by coordination

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[3] An exobidentate ligand bonds to two separate metals or metalloids.

through a tautomeric 5-substituted structure, where steric hindrance is minimized (Trofimenko, 1972).

Pyrazoles have been of wide interest for applications in synthesis (Elugero, Yranzo, Laynez, Jiménez, Menéndez, Catalán, de Paz, Anvia, and Taft, 1991), organometallic chemistry (Sadimenko and Basson, 1996; Mukherjee, 2000), precursors for chemical vapor deposition and luminescent properties (Dias, Diyabalanage, Eldabaja, Elbjeirami, Rawashdeh-Omary, and Omary, 2005; Omary, Rawashdeh-Omary, Gonser, Elbjeirami, Grimes, and Cundari, 2005; Hu, Gahungu, and Zhang, 2007), and biological systems (Katritzy and Lagowski, 1984; Trofimenko, 1999). Moreover, these can be integrated as part of many polydentate ligands (Mukherjee, 2000).

Tris(pyrazolyl)borate (scorpionate) complexes have been studied as ligands for the construction of bioinorganic models duplicating the spectral properties or the activity of various molybdenum and tungsten oxidase/reductase enzymes (Trofimenko, 1999) as well as for their own oxidation/reduction behavior. Coordination of the scorpionate ligands is through the pyrazole groups, and presumably the redox activity of these ligands is partially due to their ability to accept electrons from and return electrons to the coordinating metal atom.

For coordination purposes, the functionalization of the three position is particularly attractive as it may lead to the introduction of further coordinating functionalities. These substituted pyrazoles can alter the coordination geometries and electronic properties of transition metal complexes through steric interactions and have the potential for inductive effects on the electronic characteristics of the coordinated metal atoms (Zhao, Stipdonk, and Eichhorn, 2007). Pyrazoles are components of many drugs, herbicides, and fungicides and are well known to coordinate with metal ions (Bandini, Banditelli, Bonati, Minghetti, and Pinillos, 1985; Schoonhoven, Driessen, Reedijk, and Verschoor, 1984).

Transition metal complexes of pyrazoles and pyrazole-derived ligands have attracted attention because of their versatile structures and properties (Zhao, Stipdonk, and Eichhorn, 2007). The most studied type of pyrazole complex is $M(Hpz)_nX_m$ where M is a transition metal, Hpz is a pyrazole ligand, X is a counter ion, and m is the valence of the transition metal. For example, maximal coordination of pyrazole is found when X is a noncoordinating anion such as NO_3^-, BF_4^-, or ClO_4^-, and M = $Fe^{II,\ III}$, Co^{II}, Ni^{II}, Zn^{II}, and Cd^{II} (Daugherty and Swisher, 1968). These compounds allow octahedral complexes with four pyrazole ligands and two axial ligands (Zhao, Stipdonk, and Eichhorn, 2007; Nelana, Darkwa, Guzei, and Mapolie, 2004), square planar complexes with two pyrazole ligands and two additional ligands (Spencer, Guzei, Ojwach, and Darkwa, 2006), and tetrahedral complexes with two pyrazole ligands and two additrional ligands (Nelana, Darkwa, Guzei, and Mapolie, 2004). In addition, dimeric and trimeric arrangements with bridging pyrazole groups are also known (Rettig, Storr, Summers, Thomson, and Trotter, 1997).

β-diketonate ligands

The ligating ability of the β-diketonate moiety has been extensively studied over the years because of its rich coordinating ability to metal centers. Both oxygen atoms interact with the metal to form a six-membered chelate ring. β-diketonates form anions as a result of enolization and ionization after α-proton extraction by a base. The β-diketonate anion has been shown to undergo keto to enol tautomerization with the enol form dominating and existing in two resonance forms (Figure 1.5), leading to a delocalized anion that results in planarity of the the six-membered chelate ring. These β-diketonate ions form very stable complexes with metal ions (Thornton, 1990; Burton, 2006). The chemical and physical properties of these ligands can be varied systematically by changing the organic substituents, allowing manipulation of their oxidation and chelating reactions (Cotton and Soderberg, 1964; Graddon, 1969).

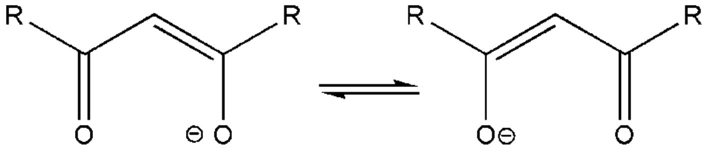

Figure 1.5 Resonance forms of the enol tautomer of the β-diketonate anion.

The presence of bulky substituents such as *tert*-butyl groups on the β-diketonate has been shown to sterically impede oligomerization and monomers are generally formed (Burton, 2006).

Metal β-diketonate complexes of acetylacetonate (acac), hexafluoroacetyl-acetonate (hfac), 1,3-diphenyl-1,3-propanedionate (dbm), and 2,2,6,6-tetramethyl-heptane-3,5-dionate (tmhd), (M = Mn, Co, Ni, Cu, and Zn) form bis- and tris-complexes with M^{II} and M^{III}, respectively (Cotton, Wilkinson, Murillo, and Bochmann, 1999). These investigations have revealed that in the presence of additional ligands the metal will frequently expand its coordination number from 4 to 6 (Emmenegger, Schlaepfer, Stoeckli-Evans, Piccand, and Piekarski, 2001). They have been the subject of many different investigations ranging over synthesis (Gnanasoundari and Natarajan, 2005), magnetic properties (Addison and Graddon, 1968; Collins and Henneike, 1973; Cotton and Soderberg, 1964; Koyama, Watanabe, Ishida, Nogami, and Kogane 2009), coordination (Izumi, Kurosawa, Kawamoto, and Akaiwa, 1975; Fondo, Garcia-Deiba, Ocampo, Sanmartin, Bermejo, and Llamas-Saiz, 2006), precursor materials (Fischer, Atakan, and Kohse-Höinghaus, 2001; Hubert-Pfalzgraf, 2003), photochemical behavior (Kutal, Yang, and Ferraudi, 1980), and supramolecular chemistry (Aakeröy, Scott, Smith, Urbina, and Desper, 2009). A recent study has explored electron delocalization in the β-diketonate chelate ring and the change in acidity of hydrogen atoms bonded to the chelate ring, thereby suggesting that β-diketonate chelate rings may possess some measure of ability to act as an electron reservoir in coordination complexes as well (Milčič, Medaković, Sredojević, Juranić, and Zarić, 2006).

Special attention has been paid to the dependence of the geometry, physical properties, and structure of complexes on the nature of the β-diketonate and pyrazole ring substituents and the coordination ions. This work is focused on cobalt and nickel ions for the metal and three β-diketonate ligands, 2,4-pentanedione (acac), 1,3-diphenyl-1,3-propanedione (dbm), and 2,2,6,6-tetramethyl-3,5-heptanedione; and four pyrazole ligands, 3,5-dimethylpyrazole (Hpz$^{\mathrm{Me2}}$), 3,5-diphenylpyrazole (Hpz$^{\mathrm{Ph2}}$), 3,5-di-*tert*-butylpyrazole (Hpz$^{(t\text{-}\mathrm{Bu})2}$), and 3,5-bis(trifluoromethyl)pyrazole (Hpz$^{(\mathrm{CF3})2}$) as illustrated in Figure 1.6.

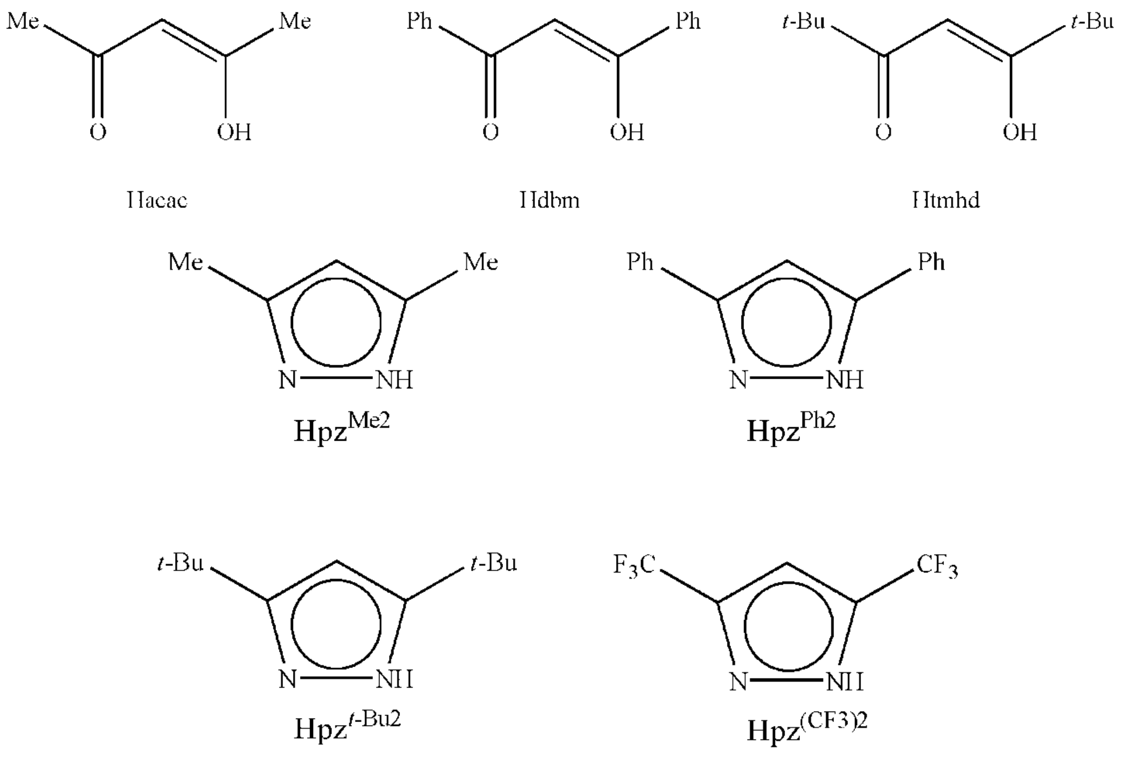

Figure 1.6 The β-diketonate and pyrazole ligands used in this study.

1.4 Spectroscopic techniques

Any compound having bonds, whether organic or inorganic, will absorb radiation of appropriate energies. Spectroscopy also involves the interactions of other types of particles, such as neutrons, electrons, and protons. There are a number of possible classifications according to the radiation used and the state of the matter (solid, liquid, or gas) interacting with the radiation. Radiation ranges are provided in Figure 1.7, and information on the energy transitions is collected in Table 1.1. There are generate in range of X-ray, visible and ultraviolet light, infrared, microwave, and radio wave (arrange from high to low energy) (Pavia, Lampman, and Kriz, 2001).

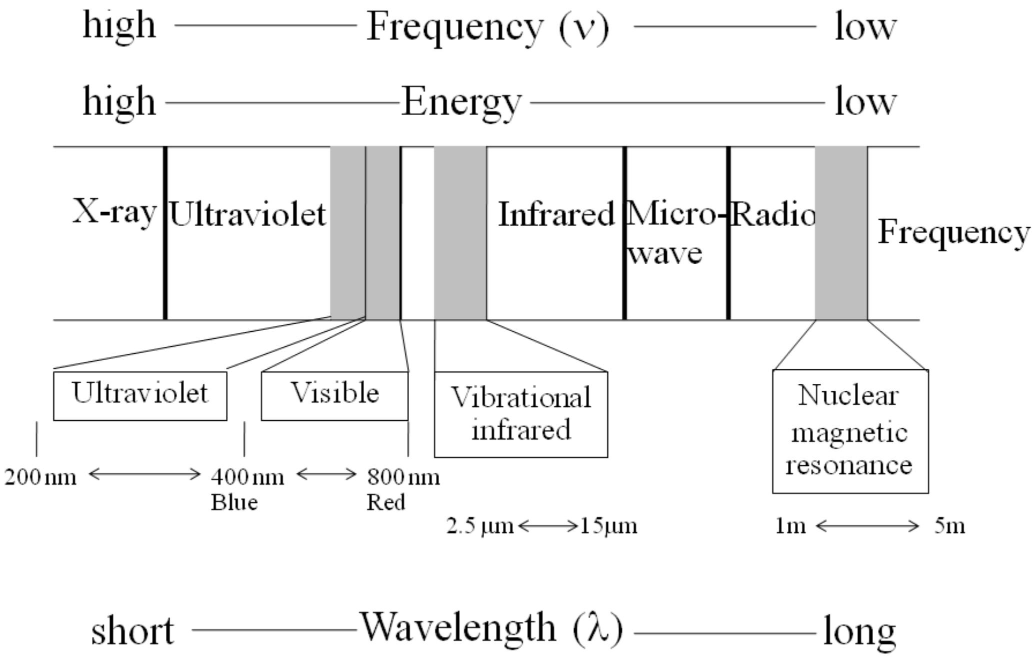

Figure 1.7 The types of electromagnetic radiation.

The radio, infrared, and ultraviolet spectral ranges are of great importance in this work. Radio waves are used in nuclear magnetic resonance to induce transitions between different nuclear spin states. This technique is of great relevance in the study of molecular structures. Atoms in solids vibrate at frequencies of approximately 10^{12}-10^{13} Hz. Thus, vibrational modes can be excited to higher energy states by radiation in this frequency range. Infrared absorption is the most relevant vibrational spectroscopy technique and is very useful for identifying functional groups and characterizing complexes in different materials as well as for characterizing structural changes in solids. Electronic energy levels involve transitions in a range of energy values. The valence electrons can be excited with appropriate ultraviolet and visible radiation in the wavelength range from about 200 nm to about 3000 nm. These electrons are responsible for a great number of physical and chemical properties; for example, the formation of molecules and solids (Solé, Bausá, and Jaque, 2005).

Table 1.1 Types of energy transition in each region of the electromagnetic spectrum.

Region of spectrum	Energy transition
X-rays	Bond breaking
Ultraviolet/visible	Electronic
Infrared	Vibrational
Microwave	Rotational
Radiofrequencies	Nuclear spin (Nuclear magnetic resonance)
	Electronic spin (Electronic spin resonance)

1.5 Solvent effects

Solvent effects are rarely studied and often operate in complex combinations. The solvent plays an important role in recognition processes. If the solvent strongly solvates either host, guest or complex, or if the solvent interacts strongly with itself, it can have dramatic effects on the host-guest equilibrium. Desolvation possesses have unfavorable enthalpy and favorable entropy (Beer, Gale, and Smith, 1999).

The donor-acceptor ability of the solvent also plays a significant role in controlling molecular recognition. The donor-acceptor is also of great importance in hydrogen bonding recognition. A good electron pair donor will readily accept a hydrogen bond, while a more acidic proton will usually be a good hydrogen bond donor (Beer, Gale, and Smith, 1999).

1.6 Crystallizations

Development of a crystal depends on the relative rates of nucleation and growth. If the rate of nucleation is larger than the rate of growth, the results will be agglomerates of small crystallites. On the other hand, too rapid rate of growth may result in the inclusion of many faults in the crystal. Crystallization can occur through solid state transition, liquid to solid state transition (melt growth), gas to solid state transition (sublimation growth), or from solution (crystallization or recrystallization). Crystal growth from solution will be discussed here.

Crystal growth from solution: The important advantages of solution growth are the control of temperature and viscosity, the simplicity of the equipment, and the general high degree of crystal perfection obtained since the crystals grow at a temperature well below their melting point. Solution growth can be divided into three types depending upon the temperature, the nature of solvent and solute, and the pressure: low-temperature solution growth, superheated solution growth, and high-temperature solution growth. Room-temperature solution growth is focused here.

The substance to be crystallized should be only moderately soluble. The most common procedure is the slow cooling of a saturated solution, often by placing the container in a polystyrene jacket or a Dewar flask in order to allow it to cool very slowly. In order to reduce the number of nucleation sites, new and smooth glass or PTFE vessels are the best. The setup should be allowed to stand in a vibration free environment, *e.g.* not near a working pump. When possible, higher temperatures are preferable to lower ones, *e.g.* in a refrigerator or deep freeze, as they minimize the chance of including unwanted solvent in the crystals formed. Often, a small temperature gradient is useful, perhaps by placing the glass vessel in a sloping hole in a slowly cooled metal block so that the upper part of the solution remains outside. Convection will then transport material through the solution. If the compound is synthesized by the mixing of two reagents in different solvents, in favorable cases, direct crystallization will occur at the solvent interface. Good crystals are obtained when the solvents diffuse slowly into one another. Solution growth can be classified into several groups according to the method by which supersaturation is achieved (Figure 1.8):

1) Crystallization by changing the solution temperature
2) Crystallization by changing the composition of the solution (solvent evaporation or nonsolvent addition)
3) Crystallization by chemical reaction (Dhanaraj, Byrappa, Prasad, and Dudley, 2010)

Solution growth   Solid + Solvent $\xrightarrow{T}$ Crystal(s)

Evaporation
Slow cooling
Boiling solutions

Figure 1.8 Represent of solution growth process.

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CHAPTER II

EXPERIMENTAL

2.1 Instrumentation

2.1.1 Fourier transform infrared (FT-IR)

Infrared spectra were recorded on a Perkin-Elmer spectrum GX FTIR spectrophotometer in the range of 4000-400 cm^{-1}, using KBr pellets. The spectra were obtained with a resolution of 4 cm^{-1} with co-addition of 10 scans. KBr was dried at 110 ºC for 2 hr before obtaining the spectra. The sample and KBr were ground together with a mortar and pestle, and the ground powder was pressed into a transparent disk using a hydraulic pressing machine with an equivalent weight of about 10 tons for 1 min.

2.1.2 Electronic spectra (UV-Vis)

Electronic spectra were recorded on a Varian Cary 1E spectrometer at 25 ºC within the wavelength range 200-900 nm in dichloromethane, DCM, and methanol, MeOH, solutions, and with a quartz cell of 1 cm path length and 3 mL samples. The samples were separated from the mother liquid then dissolved in fresh DCM:MeOH solution.

2.1.3 Thermogravimetric analysis (TGA)

Thermal analyses were recorded on a Mettler-Toledo TGA/DSC1 Module under static air atmospheric pressure with nitrogen flow at a heating rate of 10 ºC min^{-1} over the range of 50-600 ºC. The STARe software system was utilized to analyze the spectra. The samples were isolated and washed with the mother liquid before characterization.

2.1.4 ^{1}H Nuclear magnetic resonance (^{1}H NMR)

Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 300 MHz Varian Unity Inova system at 30 ºC in freshly prepared $CDCl_3$ solutions with TMS added as an internal standard. The samples were isolated, washed with the mother liquors, and dried under a purge of N_2 before being dissolved in $CDCl_3$.

2.1.5 Scanning electron microscopy (SEM)

Scanning electron micrographs (SEM) were recorded with an accelerating voltage of 10 kV on a JEM-6400 instrument. The samples were dried by using UV light for 10 min, and then coated with a layer of gold approximately 20-25 Å thick with a Balzer sputtering coater to make them conductive.

2.2 Materials and methods

2.2.1 Chemicals and solvents

All chemical reagents and solvents were used as received without further purification.

Chemicals:

- 2,4-pentanedione ($C_5H_8O_2$), Fluka, 98%, analytical grade, MW 100.12
- 1,3-diphenyl-1,3-propanedione ($C_{15}H_{12}O_2$), Aldrich, 98%, purum grade, MW 224.06
- 2,2,6,6-tetramethyl-3,5-heptanedione ($C_{11}H_{20}O_2$), Fluka, 98%, analytical grade, MW 184.28
- Cobalt(II) acetylacetonato ($C_{10}H_{14}CoO_4$), Acros, 99%, AR grade, MW 257.15

- Cobalt(II) acetate tetrahydrate ($C_4H_6CoO_4 \cdot 4H_2O$), Fluka, ~99%, ACS grade, MW 249.09

- Hydrazine hydrate ($H_4N_2 \cdot H_2O$), PRS (panreac), 80%, reagent grade, MW 50.06

- Nickel(II) acetate tetrahydrate ($C_4H_6NiO_4 \cdot 4H_2O$), Fluka, 99%, purum grade, MW 248.86

- Nickel(II) acetylacetonato ($C_{10}H_{14}NiO_4$), Fluka, ~90%, technical grade, MW 256.93

- Sodium hydroxide ($NaOH$), Merck, 99%, reagent grade, MW 40.01

Solvents:

- Acetone ($(CH_3)_2CO$), RPE-ACS grade, Carlo Erba Reagent
- Dichloromethane (CH_2Cl_2), AR grade, BDH
- Ethanol (C_2H_5OH), ACS-Iso for analysis, Carlo Erba Reagent
- Methanol (CH_3OH), ACS-Iso for analysis, Carlo Erba Reagent

2.2.2 Recrystallization method

Slow evaporative crystallization is one of the simplest ways to grow crystals. The compound is dissolved in pure solvent or in a mixture of solvents and left for slow evaporation. The type of container can be purpose suited, but test tubes, NMR tubes, or similar containers are common. It is often suggested to place the crystallization in a location that minimizes air and/or mechanical disturbance. However, it has also been noted that beautiful crystals are often obtained from the rapidly boiling flask of a Soxhlet extractor. The rate of evaporation can be controlled by covering with parafilm or aluminum foil with a few small perforations or in an inert atmosphere by changing the rate of flow of the inert gas. Evaporation experiments are also profoundly affected by the temperature and the pressure of the atmosphere above the solution.

2.3 Syntheses

The pyrazole ligands, 3,5-dimethylpyrazole (Hpz^{Me2}), 3,5-diphenylpyrazole (Hpz^{Ph2}), 3,5-di-*tert*-butylpyrazole ($\text{Hpz}^{t\text{-Bu2}}$), and 3,5-bis(trifluoromethyl)pyrazole ($\text{Hpz}^{(\text{CF3})2}$) were prepared in a similar fashion to the published procedure (Wiley and Hexner, 1951; Quin and Tyrell, 1928; Fernández-Castaño, Foces-Foces, Jagerovic, and Elguero, 1995; Renn, Venanzi, Marteletti, and Gramlich, 1995). The diaqua(β-diketonate) metal complex starting materials, where metal = cobalt and nickel, β-diketonate = 2,4-pentanedione (Hacac) (Cotton, Wilkinson, Murillo, and Bochmann, 1999; Fernelius and Bryant, 1957), 1,3-diphenyl-1,3-propanedione (Hdbm) (Moeller, 1957; Soldatov, Henegouwen, Enright, Ratcliffe, and Ripmeester, 2001), 2,2,6,6-tetramethyl-3,5-heptanedione (Htmhd) (Barreca and Massignan, 2001; Collin and Hemmeike, 1973) were also prepared by literature methods. The diaqua(β-diketonate) metal complexes were then reacted with the 3,5-disubstituted pyrazole ligands.

2.3.1 Preparation of pyrazole ligands

The reaction for preparation of pyrazole ligands is presented in Figure 2.1. The resulting mixtures are different for the different β-diketonate starting materials.

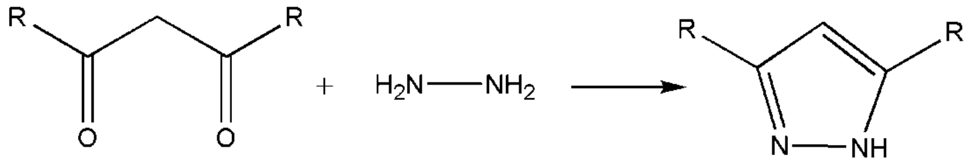

Figure 2.1 Preparation of 3,5-disubstituted pyrazoles.

3,5-dimethylpyrazole: MeOH (30 mL), Hacac (5.66 mL, 55.00 mmol), and hydrazine hydrate (3.90 mL, 75.0 mmol) were refluxed together for 2 hrs. The white powder was filtered under vacuum. Yield 62%. IR spectrum (ν/cm^{-1}): 3203 (νN–H); 3132-2878 (νC–H); 1659-1550 (νC=C, νC=N); 1465 (δC–H); 1327-1267 (δC–N). UV-Vis spectrum shows λ_{max} at 227 nm. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): 2.27, 2.48 [s, s, ($C(CH_3)_3)_2$], 5.96 [s, CH], 6.05 [s, NH].

3,5-diphenylpyrazole: EtOH (30 mL), Hdbm (4.48 g, 20.0 mmol), and hydrazine hydrate (1.40 mL, 27.0 mmol) were stirred together at room temperature for 2 hrs. The pale yellow/white powder was purified by vacuum sublimation. Yield 60%. IR spectrum (ν/cm^{-1}): 3184 (νN–H); 3133-2857 (νC–H); 1695-1571 (νC=C, νC=N); 1462 (δC–H); 1327-1272 (δC–N); 1074-915 (νC=C/Ph). UV-Vis spectrum shows λ_{max} at 282 nm. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): 6.83 [s, CH], 7.00 [s, NH], 7.46-8.04 [m, Ph].

3,5-di-(*tert*-butyl)pyrazole: EtOH (30 mL), Htmhd (5.00 mL, 2.40 mmol), and hydrazine hydrate (2.00 mL, 40.0 mmol) were refluxed together for 10 hrs. The pale yellow/white powder was purified by vacuum sublimation. Yield 52%. IR spectrum (ν/cm^{-1}): 3237 (νN–H); 3110-2867 (νC–H); 1634-1571 (νC=C, νC=N); 1488-1463 (δC–H); 1285-1251 (δC–N). UV-Vis spectrum shows λ_{max} at 229 nm. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): 1.24, 1.51 [s, s, ($C(CH_3)_3)_2$], 5.97 [s, CH], 6.21 [s, NH].

3,5-bis(trifluoromethyl)pyrazole: A solution of hydrazine hydrate (1 mL, 20.6 mmol) in EtOH (35 mL) was prepared, and hfac was added by dropping funnel. The mixture was refluxed for 19 hrs. The EtOH was distilled off and the resulting mixture was transferred to a round bottomed distillation flask connected to a Vigreux column pointing downward through a 120° bent glass adapter. A Schlenk tube, cooled in an ice bath, was connected to the Vigreux column through a 60° bent adapter. The oil bath was heated to 180° and the colorless product was distilled off. The distillation was stopped when a solid orange material remained in the distillation flask. The glassware was thoroughly washed with CH_2Cl_2, and the clear colorless solution was dried overnight (Na_2SO_4) and filtered. The solvent was removed by rotary evaporation. The colorless, crystalline product with a distinctive odor was stored at room temperature under Ar. IR spectrum (ν/cm^{-1}): 3195 (νN–H); 3157-3048 (νC–H); 1673-1591 (νC=C, νC=N); 1484 (δC–H); 1330-1235 (δC–N); 1330-1072 (δC–F). UV-Vis spectrum shows λ_{max} at 282 nm. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): 5.61 [s, CH], 6.94 [s, NH].

2.3.2 Preparation of diaqua(β-diketonate) metal complexes

The reactions for preparation of diaqua(β-diketonate) metal complexes are presented in Figures 2.2 and 2.3 for the cobalt and nickel complexes, respectively. The resulting mixtures are different for the different β-diketonate ligands and metals.

$Co(tmhd)_2(H_2O)_2$: A solution of Htmhd (2.06 mL, 10.0 mmol) was added to $Co(OAc)_2 \cdot 4H_2O$ (1.25 g, 5.00 mmol) in ethanol (25 mL) followed by addition of NaOH (2.00 mL, 0.0500 mmol). Although a pink precipitate formed immediately, the reaction mixture was stirred for 30 min. The pink product was then collected by paper filtration under vacuum, and washed by ethanol and ether. Yield 63%. IR spectrum (ν/cm^{-1}): 3417 (νO–H); 2961-2869 (νC–H); 1671 (νC–O); 1568 (νC=C); 1460-1361 (δC–H). UV-Vis spectrum shows λ_{max} at 281-282 nm. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): 1.16, 1.57 [s, s, $(C(CH_3)_3)_2$], 5.59 [s, CH].

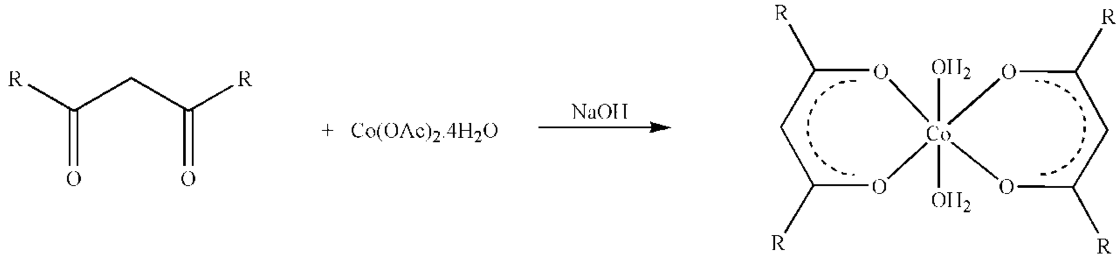

Figure 2.2 Preparation of diaquabis(β-diketonate) cobalt complexes.

$Co(dbm)_2(H_2O)_2$: Preparation was similar to that for $Co(thmd)_2(H_2O)_2$ by substituting Htmhd with Hdbm (1.12 g, 5.00 mmol). Yield 76%. IR spectrum (ν/cm^{-1}): 3387 (νO–H); 3087-2959 (νC–H); 1658 (νC–O); 1594 (νC=C); 1480-1394 (δC–H); 1072-789 (νC=C/Ph). UV-Vis spectrum shows λ_{max} at 353 nm. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): 6.39 [s, CH], 7.45-8.01 [m, Ph].

$Ni(tmhd)_2(H_2O)_2$: A solution of Htmhd (10.3 mL, 50.0 mmol) was added to $Ni(OAc)_2{\cdot}4H_2O$ (6.22 g, 25.00 mmol) in methanol (20 mL) followed by addition of NaOH (2.00 mL, 0.0500 mol). Although a lime green precipitate formed immediately, the reaction mixture was stirred for 30 min. The lime green product was then collected by paper filtration under vacuum, and washed by ethanol and ether. Yield 57%. IR spectrum (ν/cm^{-1}): 3436 (νO–H); 2963-2870 (νC–H); 1685 (νC–O); 1567 (νC=C); 1412 (δC–H). UV-Vis spectrum shows λ_{max} at 227 nm. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz): 1.13, 1.33 [s, s, $(C(CH_3)_3)_2$], 5.59 [s, CH].

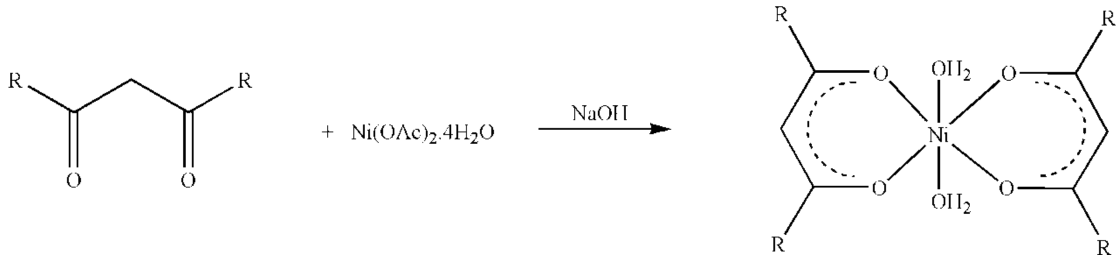

Figure 2.3 Preparation of diaquabis(β-diketonate) nickel complexes.

Ni(dbm)$_2$(H$_2$O)$_2$: Preparation was similar to that for Ni(tmhd)$_2$(H$_2$O)$_2$ by substituting Htmhd with Hdbm (11.21 g, 50 mmol). Yield 62%. IR spectrum (ν/cm^{-1}): 3412 (νO–H); 3090-3029 (νC–H); 1641 (νC–O); 1595 (νC=C); 1480-1395 (δC–H); 1072-791 (νC=C/Ph). UV-Vis spectrum shows λ_{max} at 344-345 nm. ^{1}H NMR spectrum (CDCl$_3$, 300 MHz): 6.40 [s, CH], 7.45-8.01 [m, Ph].

2.3.3 Adducts of cobalt complexes

1-4A: The 3,5-disubstituted pyrazole ligands, Hpz^{R2}, 0.200 mmol (Hpz^{Me2}, 0.0192 g; Hpz^{Ph2}, 0.0441 g; Hpz$^{(CF3)2}$, 0.0408 g; Hpz$^{(t\text{-Bu})2}$, 0.0361 g) were added to solutions of Co(acac)$_2$ (0.0257 g, 0.100 mmol) in 10 mL of 1:1 DCM:MeOH. Upon addition, no appreciable change in color was observed. The mixtures were allowed to stand at room temperature for several days but no crystalline products formed.

5-8A: The 3,5-disubstituted pyrazole ligands, Hpz^{R2}, 0.200 mmol (Hpz^{Me2}, 0.0192 g; Hpz^{Ph2}, 0.0441 g; Hpz$^{(CF3)2}$, 0.0408 g; Hpz$^{(t\text{-Bu})2}$, 0.0361 g) were added to solutions of Co(dbm)$_2$(H$_2$O)$_2$ (0.0541 g, 0.100 mmol) in 10 mL of 1:1 DCM:MeOH. Upon addition, no appreciable change in color was observed. The mixtures were allowed to stand at room temperature for several days to yield crystalline products of similar red-orange color: **5A**, needle shaped, 45% yield; **6A**, rectangular-shaped, 42% yield; **7A**, rod shaped, 51% yield; and **8A**, needle shaped, 39% yield.

9-12A: The 3,5-disubstituted pyrazole ligands, Hpz^{R2}, 0.200 mmol (Hpz^{Me2}, 0.0192 g; Hpz^{Ph2}, 0.0441 g; $Hpz^{(CF3)2}$, 0.0408 g; $Hpz^{(t\text{-Bu})2}$, 0.0361 g) was added to solutions of $Co(tmhd)_2(H_2O)_2$ (0.0461 g, 0.100 mmol) in 10 mL of 1:1 DCM:MeOH. Upon addition, no appreciable change in color was observed. The mixtures were allowed to stand at room temperature for several days but no crystalline products formed (Figure 2.4).

2.3.4 Adducts of nickel complexes

The adducts of the nickel complexes were prepared in a similar manner to those of the cobalt complexes:

For **1-4B, 9-12B:** No crystalline products formed.

For **5-8B: 5B** and **8B** gave needle-shaped crystal with 45% and 39% yields, respectively; **6B** gave rectangular-shaped crystals with 42% yield, and **7B** gave rod shaped crystals with 51% yield. These crystals have similar green color (Figure 2.5).

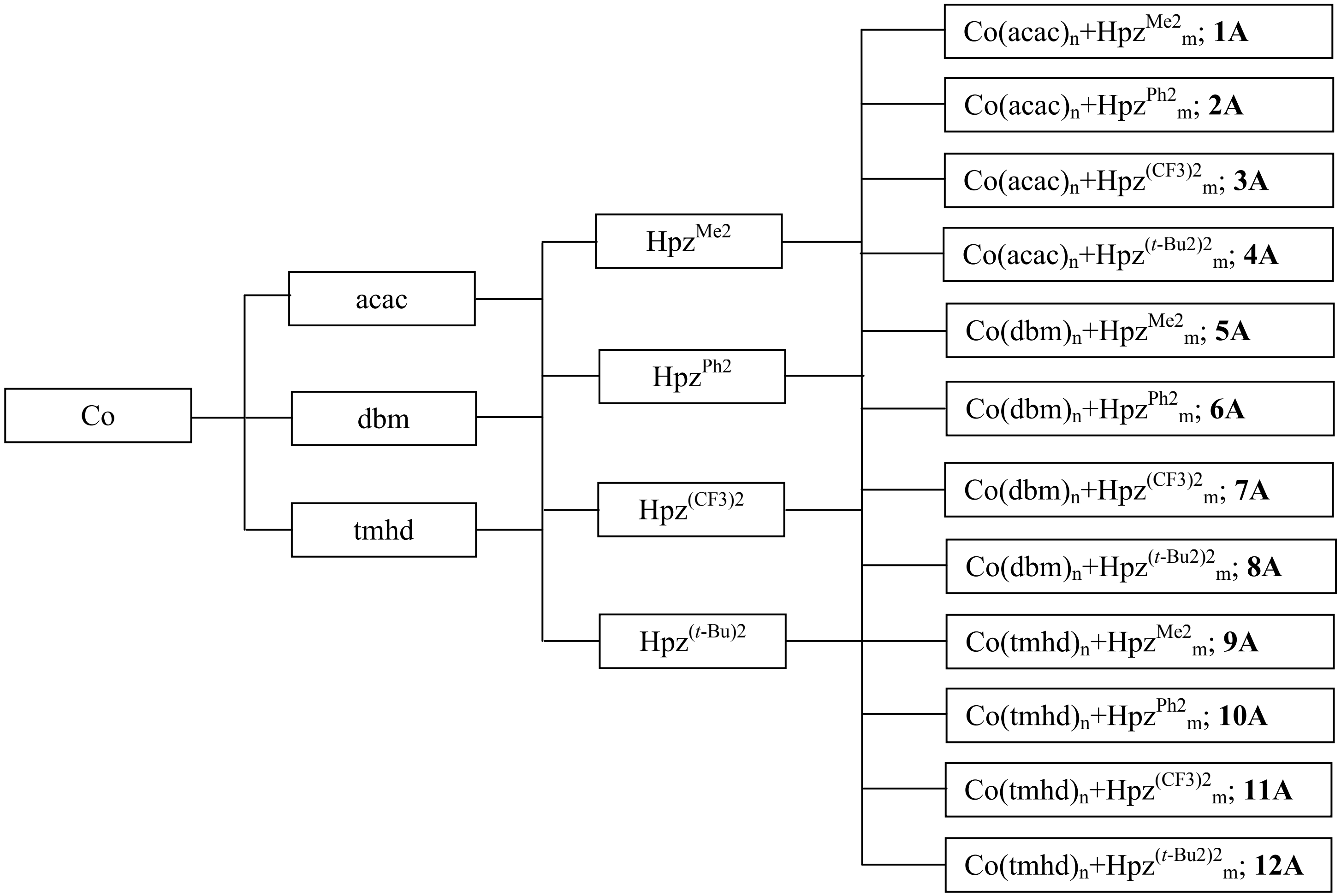

Figure 2.4 Matrix of attempted reactions between cobalt β-diketonate complexes and 3,5-disubstituted pyrazoles.

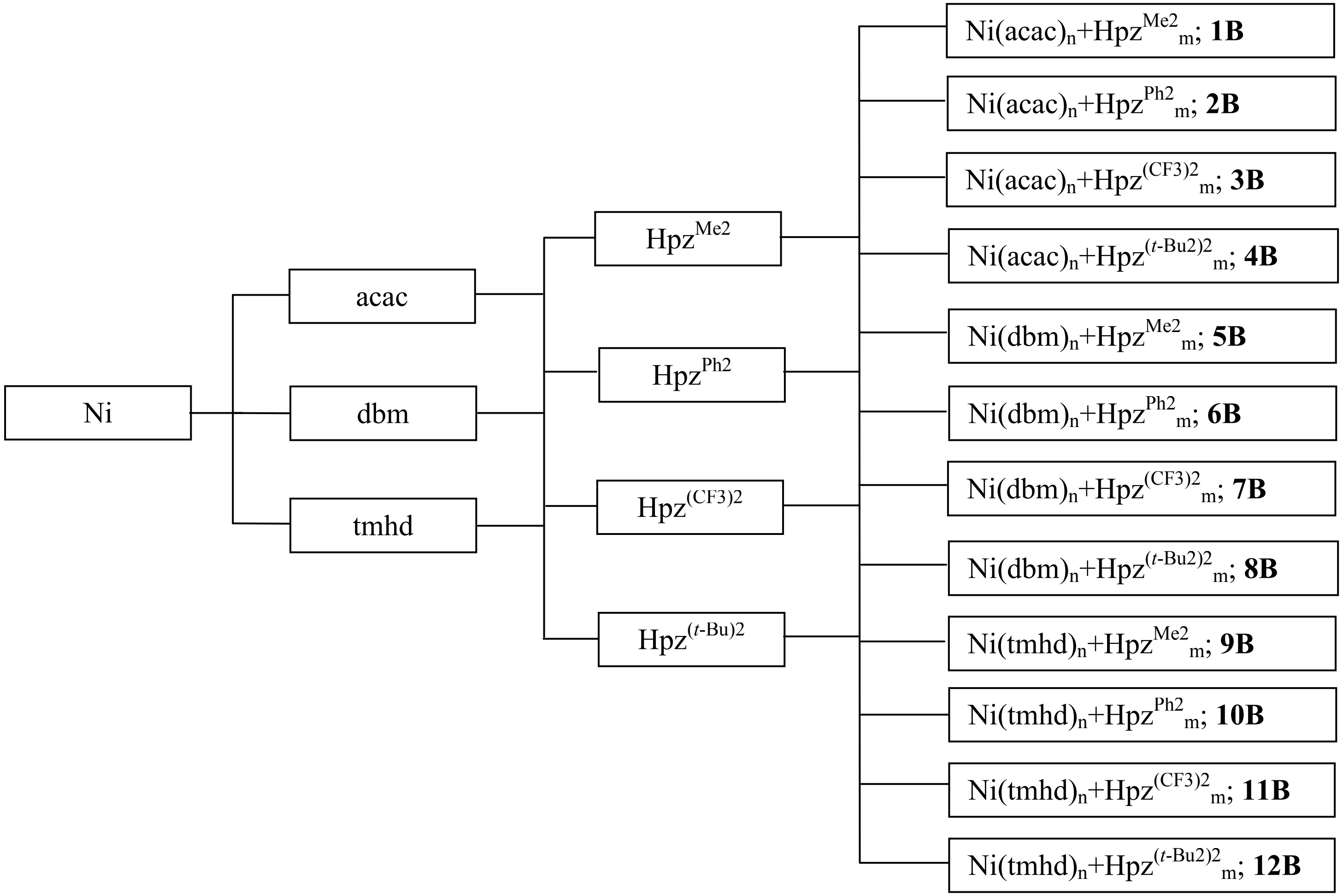

Figure 2.5 Matrix of attempted reactions between nickel β-diketonate complexes and 3,5-disubstituted pyrazoles.

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CHAPTER III

CHARACTERIZATION OF (1,3-DIPHENYL-1,3-PROPANEDIONATE) COBALT COMPLEXES WITH 3,5-DISUBSTITUTED PYRAZOLE LIGANDS

3.1 Introduction

Changes in electronic effects on changing ligands and substituents on ligands, in coordination complexes are often studied by spectroscopic techniques. Most transition metals easily form coordination complexes with β-diketonate ligands wherein both oxygen atoms interact with the metal to form a six-membered chelate ring (Cotton and Elder, 1966; Collins and Heneike, 1973; Lukeheart and Torrence, 1979; Chisholm, Folting, and Putilina, 1992; Fahlman and Barron, 2000). The chemical and physical properties of the β-diketonate ligands can be varied systematically by changing their organic substituents, allowing manipulation of their redox and chelation reactions (Cotton, Wilkinson, Murillo, and Bochmann, 1999; Ramsden, Seriven, and Taylor, 2008; Gnanasoundari and Natarajan, 2005; Cotton and Soderberg, 1964). Synthesis (Gnanasoundari and Natarajan, 2005), magnetic properties (Cotton and Soderberg, 1964), and precursor materials (Fischer Rivera, Atakan, and Kohse-Höinghaus, 2001) of cobalt β-diketonate complexes have been investigated with many organic ligands such as pyridine (Elder, 1968), quinoline (Hursthouse and Malik, 1978), and piperazine (Dunstan, 1997), but cobalt β-diketonate complexes with pyrazole ligands have not previously been reported. Pyrazole ligands have been studied as N-donor ligands to metals relating to bioinorganic chemistry (Trofimenko, 1999), and can exhibit three coordination modes. As neutral pyrazole ligands they have only one N-donor coordination site, while as deprotonated pyrazolide ions, they can coordinate as monodentate ligands using one of the N-donor sites, or as bidentate (usually bridging) ligands using both N-donor sites (Trofimenko, 1972).

This work reports preparation of 3,5-dimethyl and 3,5-diphenyl pyrazole ligands and their reactions with diaquabis(1,3-diphenyl-1,3-propanedionate)cobalt(II) at room temperature. The complexes were characterized by Fourier transform infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-Vis), ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR), and thermal analysis.

3.2 Experimental

Synthesis of adduct cobalt complexes

The 3,5-dimethylpyrazole (Hpz^{Me2}) (Wiley and Hexner, 1951), 3,5-diphenylpyrazole (Hpz^{Ph2}) (Quin and Tyrell, 1928), 3,5-bis(trifluoromethyl)pyrazole (Hpz$^{(CF3)2}$) (Renn, Venanzi, Marteletti, and Gramlich, 1995), and 3,5-di-*tert*-butylpyrazole (Hpz$^{(t\text{-Bu})2}$) (Fernández-Castaño, Foces-Foces, Jagerovic, and Elguero, 1995), diaquabis(1,3-diphenyl-1,3-propanedionate)cobalt complex (Cotton and Elder, 1966) were prepared following procedure reported previously. All chemicals were purchased from commercially available sources and were used without further purification.

Characterization of adduct cobalt complexes

Scanning electron microscopy (SEM) were recorded with an accelerating voltage of 10 kV on a JEM-6400 instrument.

Fourier transform infrared spectroscopy (FT-IR), spectra were recorded on a Perkin-Elmer Spectrum One infrared spectrometer for the range 4000-400 cm^{-1} using KBr pellets. The spectra were obtained with a resolution of 4 cm^{-1} and co-addition of 10 scans.

Electronic absorption spectra (UV-Vis), were recorded on a Varian Cary 1E spectrometer at 25 ºC between 200-900 nm in DCM and MeOH solutions.

^{1}H Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Unity Inova at 30 ºC in freshly prepared $CDCl_3$ solutions with TMS added as an internal standard. The samples were isolated from the mother liquid and dried with N_2 before dissolving in $CDCl_3$.

Thermogravimetric analysis (TGA) spectra were recorded on a Mettler-Toledo TGA/DSC1 Module over the range 50-600 ºC and analyzed with the STARe software system.

3.3 Results and discussion

The reactions of pyrazole with $Co(dbm)_2(H_2O)_2$ complex in DCM:MeOH solution gives good yields for **5A-8A**. Suitable crystals were obtained by slow evaporation of solvent. The color of the solution after crystallization is colorless for **5A** and **6A**, and red/orange for **7A** and **8A**. Crystals of these complexes are stable when kept in the mother liquor, but when a crystal is removed from the solution the surfaces rapidly become cloudy and the color intensity decreases, observations that generally indicate decomposition or solvent loss. As the complexes are air stable solvent loss seems the more probable explanation.

SEM images of the adduct cobalt complexes **5A-8A** are given in Figure 3.1. Morphologically, **5A**, **7A**, and **8A** exhibit a needle shape, and **6A** has a rectangular shape. Typical crystals are about 0.01-0.05 mm diameter and 0.10-0.15 mm in length for **5A**, **7A**, and **8A**, and about 0.05 x 0.10 x 0.20 mm for **6A**. These crystals are red/orange for **5A-7A** and rose colored for **8A**. They are frail and prone to fragmentation into stacks when separated from the mother liquor. The surfaces of crystals of **8A** have a poorer appearance when compared to the other complexes, possibly due to solvent loss.

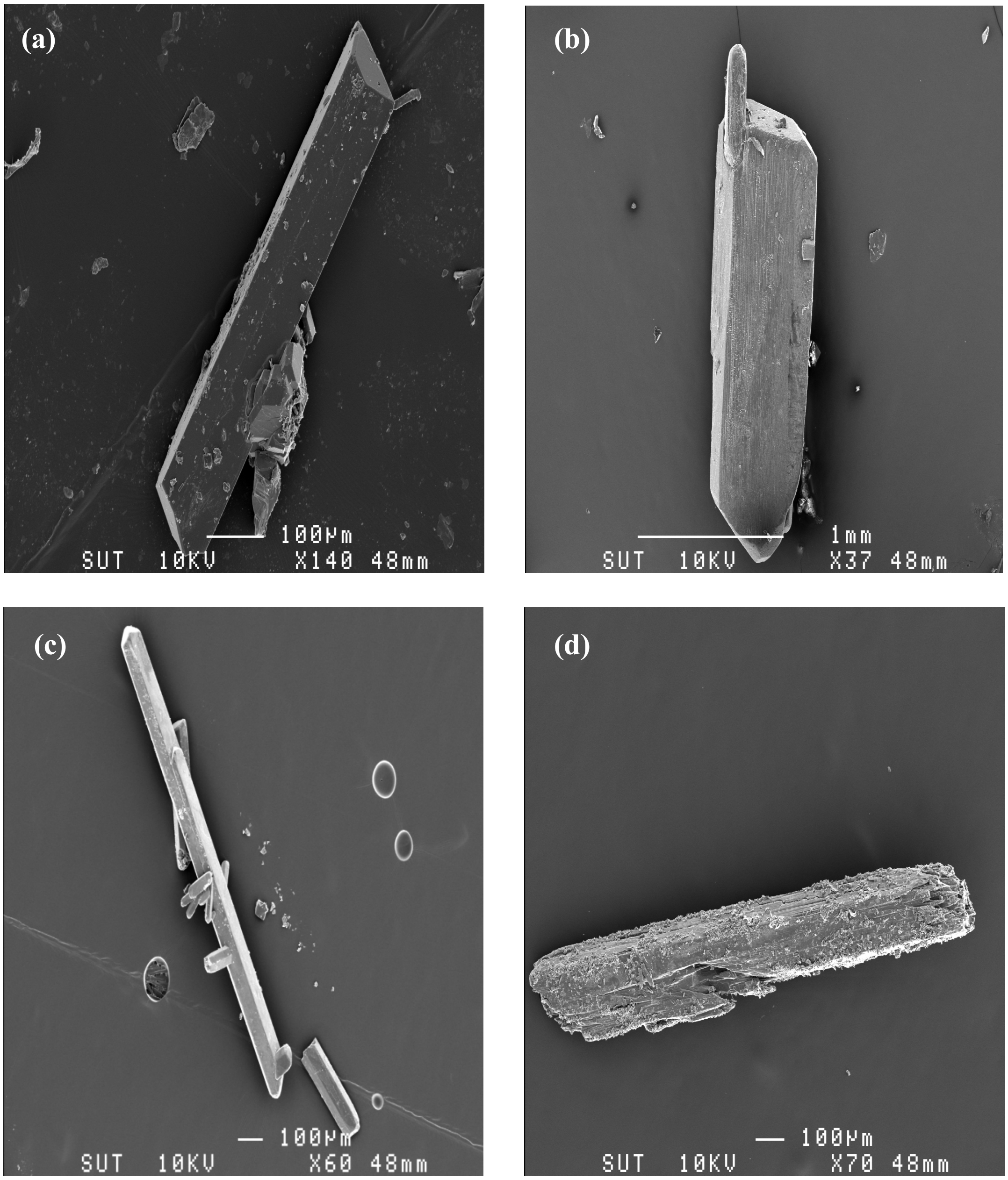


Figure 3.1 SEM micrographs of cobalt adduct complexes. (a) for **5A**, (b) for **6A**, (c) for **7A**, and (d) for **8A**.

The FT-IR spectra of the products are shown in Figure 3.2. Selected vibrational frequencies are assigned based on previous work (Kuzmany, 2009; Mistry, 2009) and are tabulated in Table 3.1. The Co–O stretching of the four complexes occurs around 450-480 cm^{-1} (Nakamoto, McCarthy, and Martell, 1961; Nakamoto, 2009). They are observed to be shifted to higher frequencies in the adducts and much more marked than those of the cobalt dbm chelate, indicating that the pyrazoles are bonded to the cobalt ion. The C–O stretching around 1670 cm^{-1} for **5A** and **8A**, and 1620 cm^{-1} for **6A** and **7A** indicates that the dbm ligand adopts a chelating coordination mode (Nakamoto, 2009). The above results revealed that adduct formation causes shifts of about 10 cm^{-1} to higher frequency and shifts of about 40 cm^{-1} to lower frequency. The C–H stretching for the dbm and pyrazole ligands are observed about 3190-2830 cm^{-1}. The C=C stretching of ring and the C–N bending of pyrazole ligand is observed about 1595-1520 cm^{-1}, while no N–H stretching is observed for all complexes. The O–H stretching of water is found between 3380-3300 cm^{-1}. The FT-IR spectrum of the cobalt complex has come under thorough investigation by Nakamoto and co-workers (Nakamoto, McCarthy, and Martell, 1961) and their spectra are significantly different from those of the starting materials and confirm the presence of chelating dbm and bridging pyrazole ligands in the metal coordination complexes. In all free ligands these vibrations have been observed in the higher frequency region.

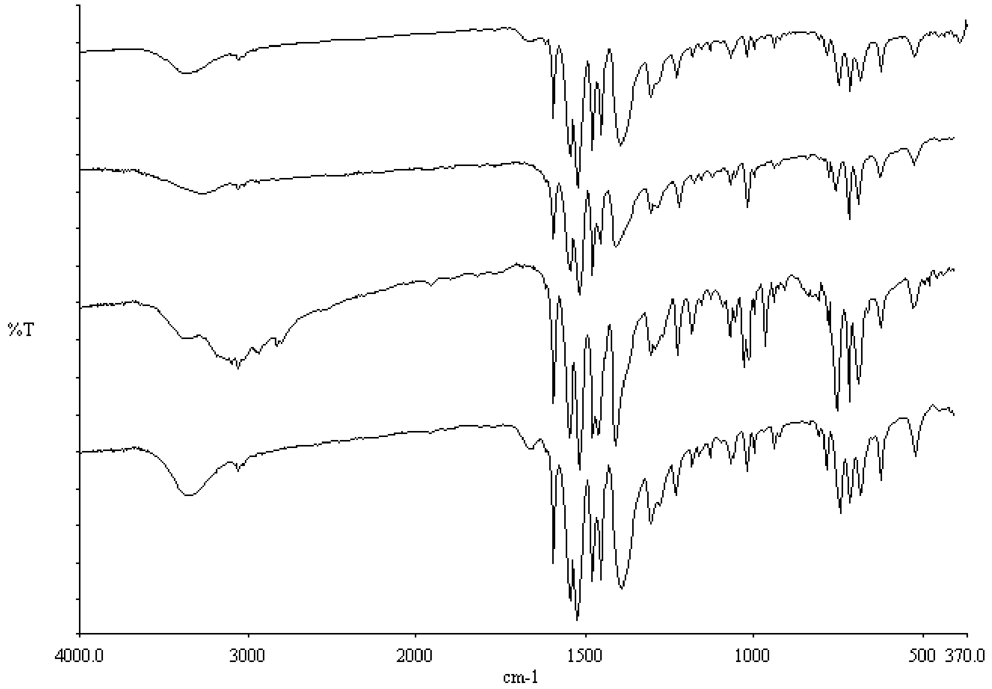


Figure 3.2 IR spectra of the cobalt adduct complexes. **5A-8A** from bottom to top.

Table 3.1 Selected vibrational frequencies (cm^{-1}) and assignments for the cobalt adduct complexes.

Assignment	Complexes			
	5A	**6A**	**7A**	**8A**
ν(O–H)	3358	3369	3263	3369
ν(C–H)	3091-3025	3188-2831	3099-2832	3088-2963
$\nu(\mathrm{C}\overset{\cdot\cdot}{-}\mathrm{O})$	1668	1619	1619	1667
ν(C=C+C=N)	1594-1521	1595-1523	1596-1524	1595-1522
δ(C–H)	1478-1395	1479-1410	1479-1408	1479-1396
δ(C–N)	1308-1228	1310-1227	1310-1230	1310-1230
ν(C=C/Ph)	1071-787	1073-788	1071-792	1071-786
ν(C–F)	-	-	1310-1133	-
δ(CF_3)	-	-	760, 527	-
νCo-O	454	461-484	456	456-486

The symbols of ν and δ indicate stretching and bending modes, respectively.

The electronic spectra of the complexes **5A**, **6A**, **7A**, and **8A** in DCM:MeOH are very similar (Figure 3.3). The bands at 253-279 and 343-363 nm represent n→σ* and π→π* transitions (Chisholm, Folting, and Putilina, 1992; Chavez, Briones, Olmstead, and Mascharak, 1999). The spectra of **5A** and **8A** show bathochromic shifts, indicating that the methyl and *tert*-butyl groups on the pyrazole ligand are electron donating groups, while that of **6A** shows a hypsochromic shift, corresponding to the electron withdrawing nature of the phenyl groups substituted on the pyrazole ligand, and the spectrum of **7A** shows a hypsochromic shift for the first peak, consistent with trifluoromethyl groups having an effective withdrawing nature on the pyrazole ligand. Selected λ_{max} for **5A-8A** are given in Table 3.2.

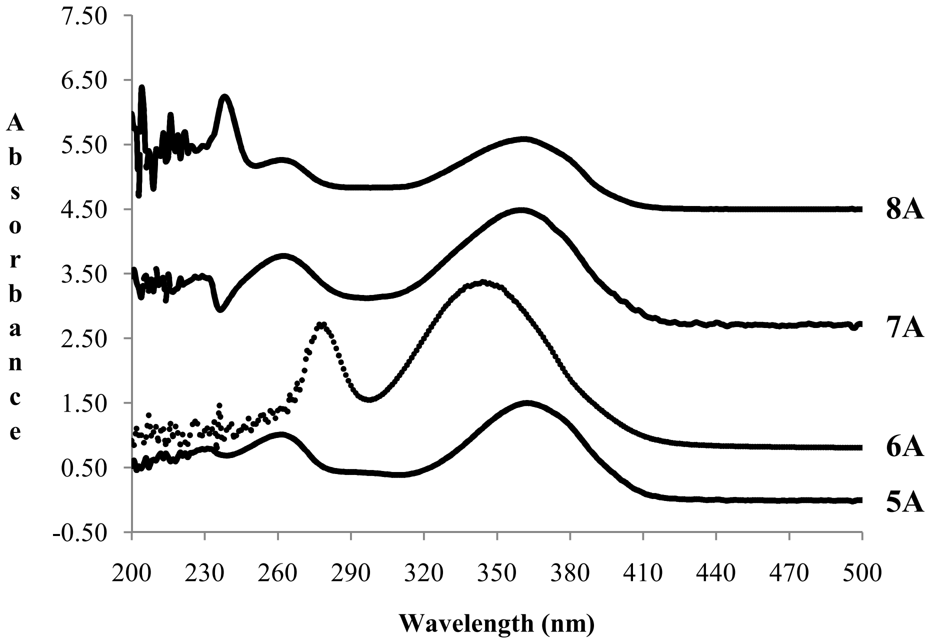


Figure 3.3 UV-Vis spectroscopic data of the cobalt adduct complexes.

Table 3.2 Selected λ_{max} (nm) for the cobalt adduct complexes.

Complexes	Wavenumber, λ_{max} (nm)
5A	261, 344
6A	279, 361-364
7A	262-263, 359-361
8A	238-239, 260-263, 360-362

^{1}H NMR spectra are given in Figure 3.4 and assignments of selected chemical shifts are given in Table 3.3.

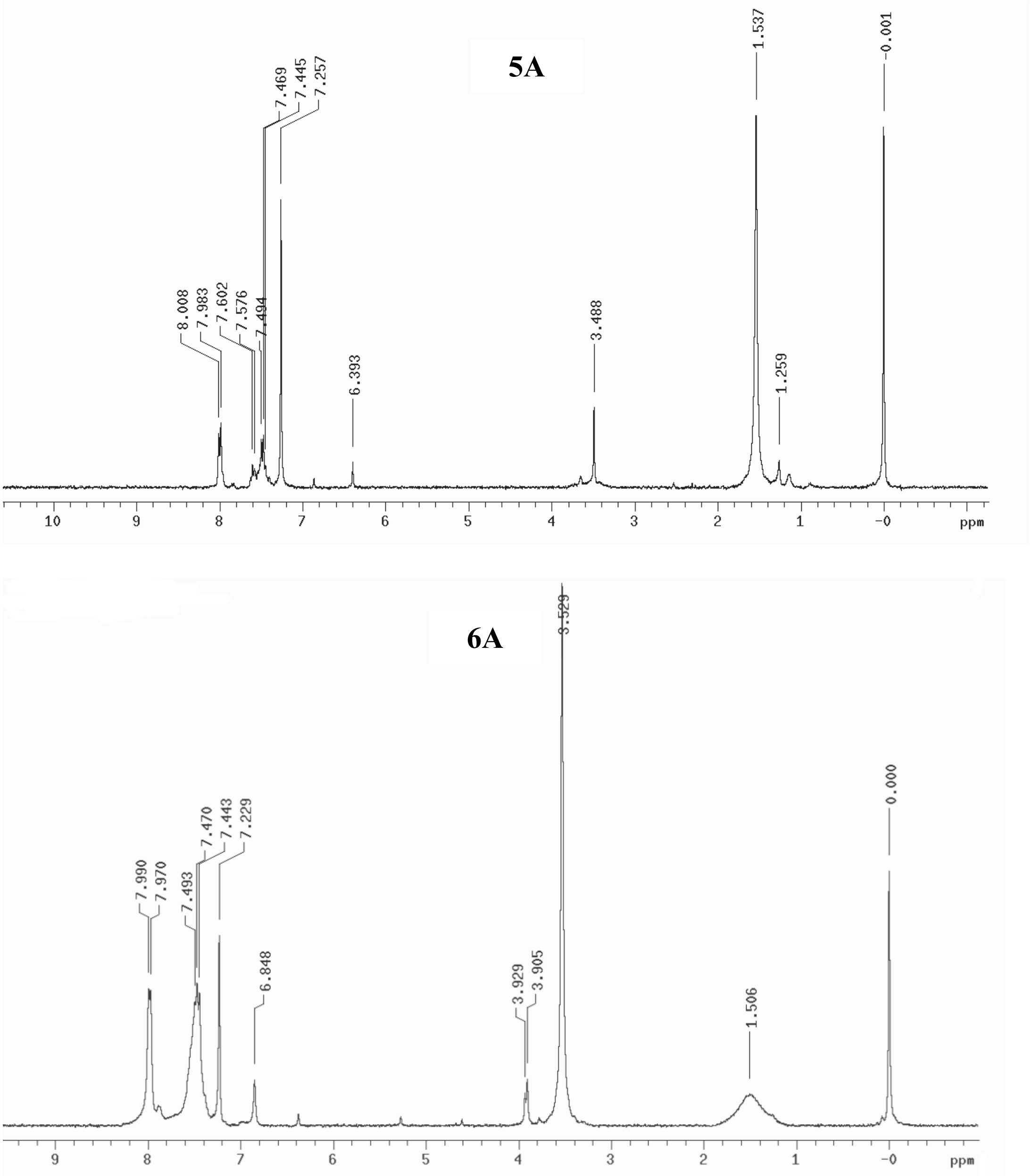


Figure 3.4 The 300-MHz ^{1}H NMR spectra recorded of the cobalt adduct complexes.

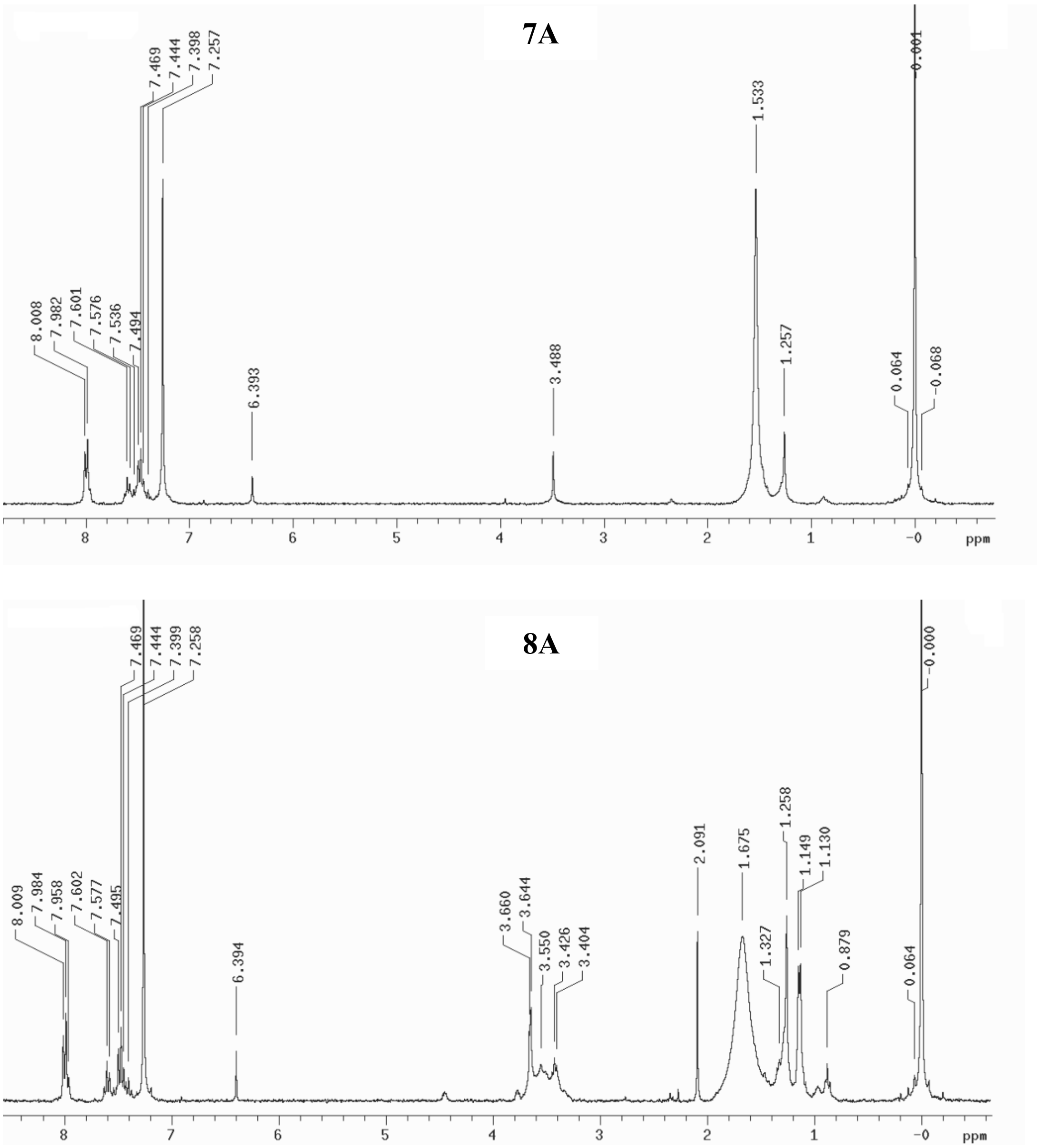


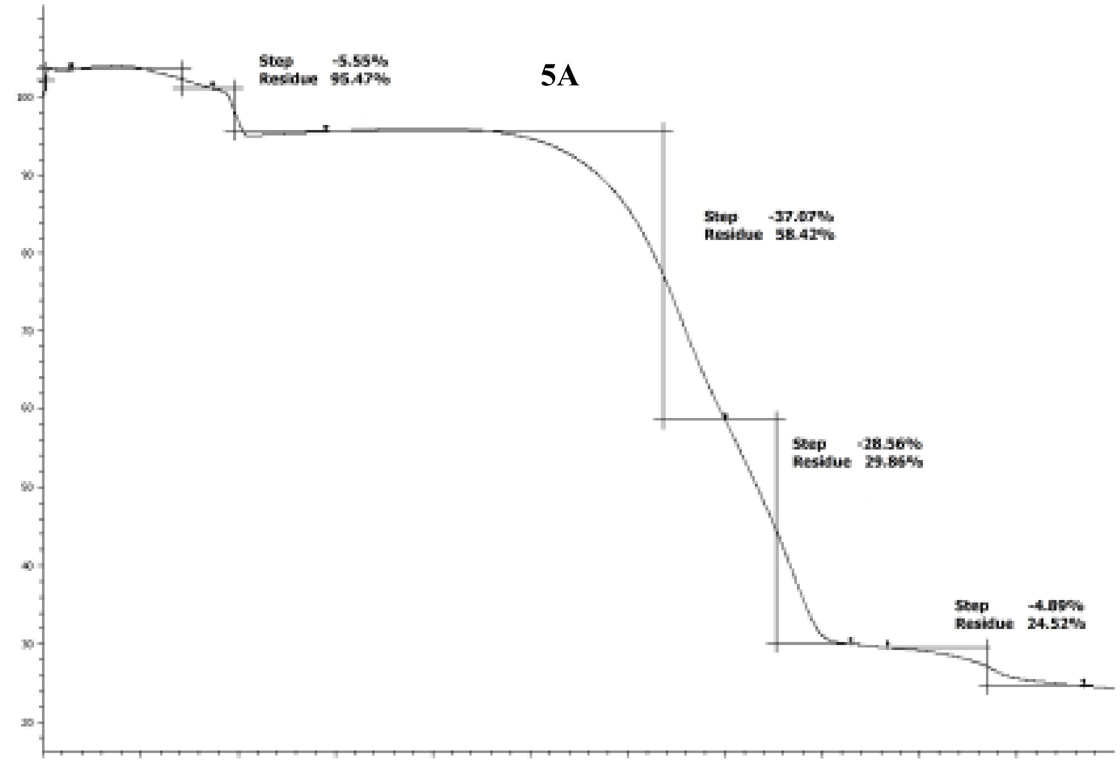
Figure 3.4 (continued) The 300-MHz ^{1}H NMR spectra recorded of the cobalt adduct complexes.

Table 3.3 Selected chemical shifts (ppm) and assignments for the cobalt adduct complexes.

Assignment	Chemical shift of adduct (ppm) [Integration number]			
	5A	**6A**	**7A**	**8A**
CH_3 in pz	1.13, 1.26 [1.73, 2.80]	-	-	-
t-Bu in pz	-	-	-	1.13-1.15, 1.26-1.33 [3.07, 4.05]
CH in dbm	3.55 [0.93]	3.91-3.93 [0.99]	3.49 [0.80]	3.55 [1.45]
CH in pz	6.39 [1.00]	6.80 [1.00]	6.39 [0.31]	6.39 [0.22]
Ph in dbm	7.45-7.60, 7.98-8.01 [10.38, 5.95]	7.44-7.49, 7.97-7.99 [9.42, 5.12]	7.40-7.49, 7.54-7.60, 7.98-8.01 [2.28, 0.70, 1.71]	7.40-7.49, 7.58-7.60, 7.98-8.01 [1.39, 0.67, 1.28]
Ph in pz	-	7.36-7.56, 7.73-7.85, 7.91-8.01	-	-

The multiplet observed in the δ 7.40-8.01 ppm region has been assigned to the protons of phenyl groups present in dbm in all cobalt complexes (Chavez, Briones, Olmstead, and Mascharak, 1999; Sato, Taniguchi, Nakahashi, Monde, and Yamagishi, 2007). The substituents on the pyrazoles were observed at δ 1.13 and 1.26 ppm for the methyl groups (Llamas, Lamoneda, Carmona, Hernandez, and Toscano, 2006), δ 7.36-7.85 ppm for phenyl groups (Yu, Korolev, Heeg, and Winter, 2002), δ 1.13-1.33 ppm for *tert*-butyl groups (Llamas, Lamoneda, Carmona, Hernandez, and Toscano, 2006). The CH for the pyrazoles were observed at δ 6.39, 6.85, 6.39, and 6.39 ppm (Maekawa, 1993), and shifted to upfield from the free pyrazole ligands. The CH in dbm are observed at δ 3.49, 3.95, 3.49, and 3.65 ppm and shifted to downfield from cobalt dibenzoylmethane. The chemical shifts for the substituent groups on the pyrazole ligands show peaks shifted to downfield, indicating that the pyrazoles are bonded to the cobalt atom. Chemical shifts of the phenyl groups on the pyrazole ligand are overlapped with the phenyl groups on dbm. Significant changes in the chemical shifts relative to the starting materials also confirm complexation.

Thermal analyses of the cobalt complexes are shown in Figure 3.5. These complexes show decomposition with weight loss of 5% in the temperature range of 120-140 ºC, indicating two water molecules. Decomposition about 200 ºC corresponds to the loss of the phenyl groups on the dbm ligands, and near 400 ºC corresponds to decomposition of the pyrazole bridging ligand. The last step is assigned to the formation of cobalt oxide (Dunstan, 1997; Sadeek, 2005).



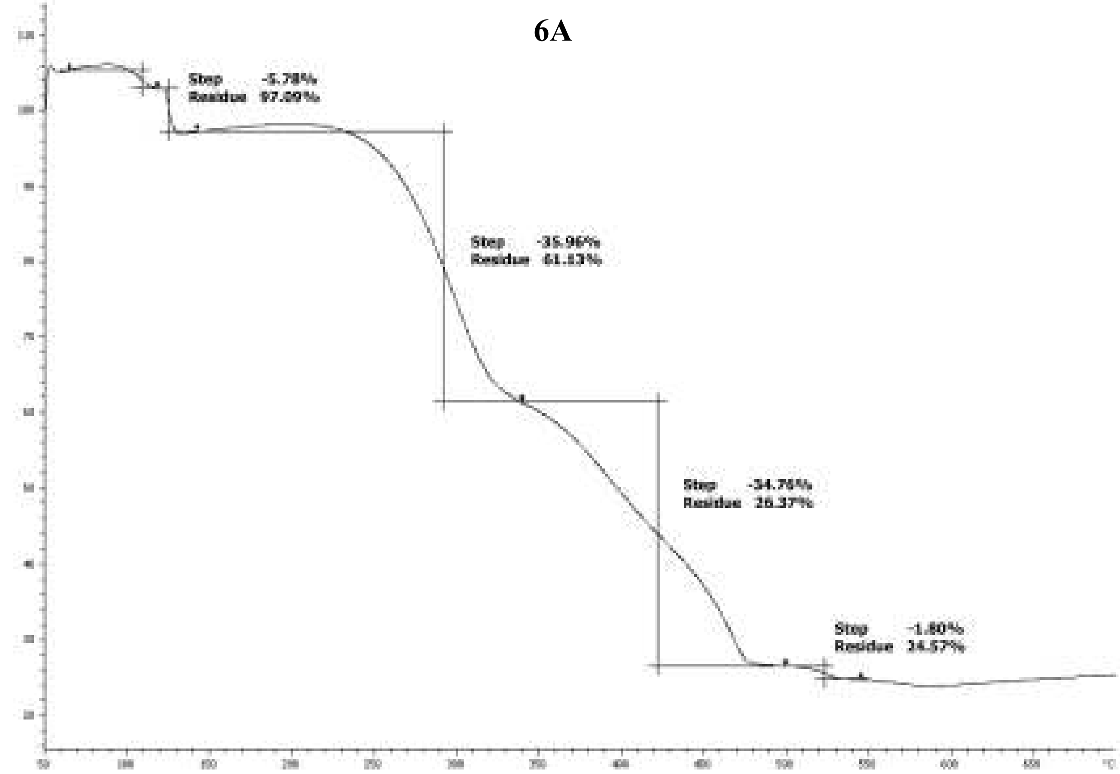


Figure 3.5 Thermal analyses of **5A** and **6A**.

The proposed structural formula, $[Co_2(dbm)_2(\mu\text{-}pz^{R2})_2(H_2O)_4]$ is consistent with the FT-IR, UV-Vis, and NMR spectroscopic and thermal analysis results. The pyrazole ligands most likely act as bridges as no N–H stretch is observed in the FT-IR and NMR spectra. The $\mu\text{-}pz^{R2}$ ligand coordinated to the cobalt metal is possible due to the steric effect of the phenyl groups on the dbm ligand and the substituents on the pyrazole ring.

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CHAPTER IV

CHARACTERIZATION OF (1,3-DIPHENYL-1,3-PROPANEDIONATE) NICKEL COMPLEXES WITH 3,5-DISUBSTITUTED PYRAZOLE LIGANDS

4.1 Introduction

Many properties of the β-diketonate complexes of nickel have been investigated, including structural properties (Zhou, Han, Chu, and Huang, 2001; Polyakov, 2001; Metin, Yildirm, and Özkar, 2007), magnetic properties (Yoshida, Suzuki, Kanamori, and Kaizaki, 1999; Fondo, García-Delba, Ocampo, Sanmartín, Bermejo, and Llamas-Saiz, 2006), spectroscopic properties (Shintani, Sone, Fukada, and Ohashi, 1991; Murata, Arakawa, Nakao, Satoh, and Fukuda, 2007), and electrochemical and thermochemical properties (Dunstan, 1998), *etc*. The structure of nickel 2,4-pentanedionate complex with 3,5-dimethylpyrazole ligand was reported in 1993 (Maekawa, 1993). He found that two 3,5-dimethylpyrazole ligands react with the nickel 2,4-pentanedionate complex to form a trinuclear complex.

Another very common and easily accessible β-diketonate coordination complex is the nickel (1,3-diphenyl-1,3-propanedionate) complex (Soldatov, Henegoumen, Enright, Ratcliffe, and Ripmeester, 2001). A wide variety of adducts of NiL_mA_n have been reported with A as nitrogen donor ligands such as piperidine, piperazine, methylpiperazine, and morpholine (Marcotrigiano, Battistuzzi, and Pellacani, 1972) and phen, dmae, and 2,2′-bpy (Harding, Harding, Phonsri, Saithong, and Phetmung, 2009) but nickel 1,3-diphenyl-1,3-propanedionate complexes with pyrazole ligands have not previously been reported.

We report the characterization of products of the reaction of nickel 1,3-diphenyl-1,3-propanedionate complexes and 3,5-disubstituted pyrazole ligands by SEM, FT-IR, UV-Vis, ^{1}H NMR, and TGA techniques.

4.2 Experimental

Synthesis of adduct nickel complexes

The 3,5-disubstituted pyrazole ligands (Wiley and Hexner, 1951; Quin and Tyrell, 1928; Renn, Venanzi, Marteletti, and Gramlich, 1995; Fernández-Castaño, Foces-Foces, Jagerovic, and Elguero, 1995) and diaquabis(1,3-diphenyl-1,3-propanedionate) nickel complex (Soldatov, Henegoumen, Enright, Ratcliffe, and Ripmeester, 2001) were prepared following procedures reported previously.

Characterization of adduct nickel complexes

The adducts of the nickel dbm complexes were characterized by the instrumentation described in Chapter III.

4.3 Results and discussion

The reaction of pyrazole with nickel (1,3-diphenyl-1,3-propanedionate) complexes was conducted in DCM:MeOH solution to give good yields of **5B-8B**. Attempts to obtain crystalline products by changing the β-diketonate nickel compound to nickel (2,4-pentanedionate) and nickel (2,2,6,6-tetramethyl-3,5-heptanedionate) using the same procedure were unsuccessful. Colorless solutions remained after crystallization of **5B**, **6B**, and **7B**, and a green solution remained after crystallization of **8B**. Crystals of these complexes are stable when kept in the mother liquor, but when a crystal is removed from the solution the surfaces rapidly become cloudy and the color intensity decreases, observations that generally indicate solvent loss, or air oxidation. Since the complexes appear to be air stable, it is more likely that the loss of crystal integrity is due to solvent loss.

The SEM images of the nickel adduct complexes are given in Figure 4.1.

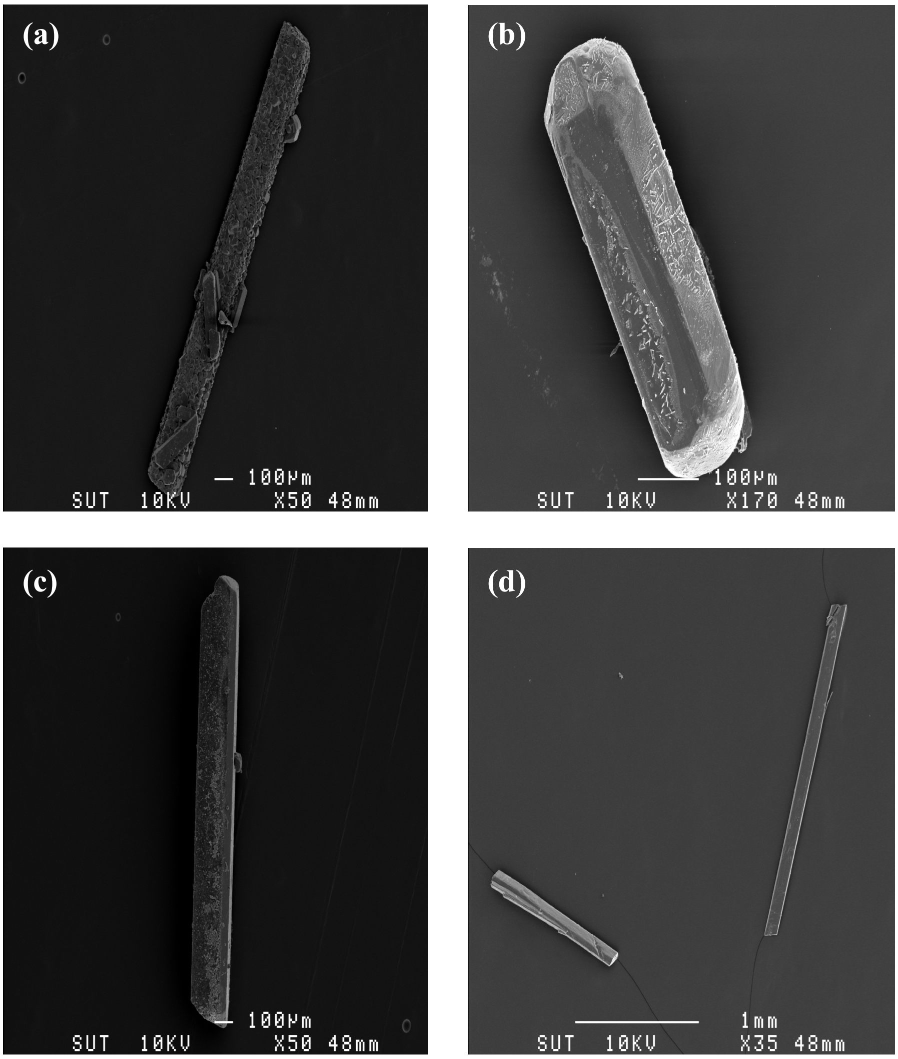

Figure 4.1 SEM micrographs for the nickel adduct complexes. (a) for **5B**, (b) for **6B**, (c) for **7B**, and (d) for **8B**.

Morphologically, **5B, 7B**, and **8B** crystals exhibit rod shapes, and **6B** shows a rhombic pyramidal shape. Typical crystals are about 0.01-0.03 mm diameter and 0.15 mm length for **5B** and **7B**, and 0.20 mm for **8B**, and about 0.05 x 0.10 x 0.20 mm for **6B**. The colors of the crystals are light-green, green (banana leaf), emerald, and pale yellowish green for **5B-8B**, respectively. They are delicate crystals, brittle and prone to fragmentation into stacks when separated from the mother liquor. **5B** appears to have crystals with continuous growth on the surfaces when stored a long time.

The FT-IR spectra of the nickel adducts are shown in Figure 4.2 and selected vibrational frequencies are collected in Table 4.1 with assignments based on similar complexes (Kuzmany, 2009; Mistry, 2009). The Ni–O stretching of the four complexes occurs around 520-530 cm^{-1} (Dunstan, 1998; Nakamoto, McCarthy, and Martell, 1961), shifted to higher frequencies and much more marked than those of the nickel 1,3-diphenyl-1,3-propanedionate chelate, indicating that the pyrazole ligand has bonded to the nickel ion. The C–O stretching around 1620 cm^{-1} indicates that the dbm ligand adopts a chelating coordination mode (Nakamoto, 2009). These results reveal that adduct formation causes a shift to lower frequency of about 20-60 cm^{-1}, consistent with effects from pyrazoles coordinated with nickel. The C–H stretching for the dbm and pyrazole ligands are observed about 3150-2830, 3100-2860, and 3060-3025 cm^{-1}, respectively. The C=C stretching in dbm and pyrazole ligands, and C–N bending are observed about 1670-1620 cm^{-1} and 1595-1520 cm^{-1}. The N–H stretching is observed about 3400 cm^{-1} and 3600 cm^{-1} for **5B** and **8B,** while no N–H stretching is observed for complexes **6B** and **7B**. The O–H stretching of water is found at 3380-3300 cm^{-1}. The FT-IR spectra are significantly different from those of the starting materials and the spectra of the four compounds show the bands expected for the organic ligands coordinated to the nickel center to confirm the presence of chelating dbm and bridging pyrazole ligands of two complexes, and monomer pyrazole of the other two complexes (Dunstan, 1998).

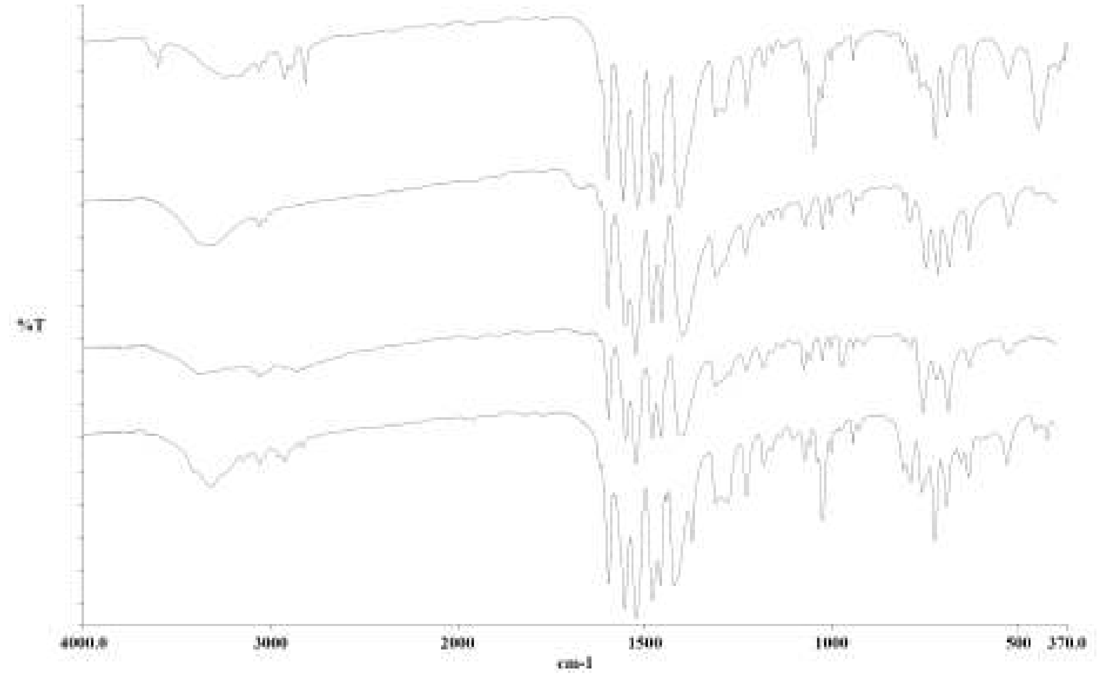

Figure 4.2 IR spectra of the nickel adduct complexes. **5B-8B** from bottom to top.

Table 4.1 Selected vibrational frequencies (cm^{-1}) and band assignments for the nickel adduct complexes.

Assignment	Complexes			
	5B	**6B**	**7B**	**8B**
ν(O–H)	3320	3371	3342	3243
ν(C–H)	3148-2828	3098-2863	3060-3342	3061-2813
$\nu(\mathrm{C}\overset{..}{-}\mathrm{O})$	1619	1619	1619	1619
ν(C=C+C=N)	1594-1521	1595-1523	1596-1524	1597-1519
δ(C–H)	1478-1372	1479-1398	1479-1396	1479-1406
δ(C–N)	1308-1228	1310-1227	1310-1230	1311-1226
ν(C=C/Ph)	1071-787	1073-788	1071-792	1071-786
ν(C–F)	-	-	1307-1102	-
δ(CF_3)	-	-	747, 525	-
ν(Ni–O)	532	526	526	524

The symbols ν and δ indicate stretching and bending modes, respectively.

The electronic spectra of the complexes **5B-8B** dissolved in DCM:MeOH are shown in Figure 4.3 and selected λ_{max} are given in Table 4.2. Bands at 251-276 and 350-364 nm represent n→σ* and π→π* transitions, respectively (Chisholm, Folting, and Putilina, 1992; Chavez, Briones, Olmstead, and Mascharak, 1999). The first peak on the spectra of the **5B** and **8B** complexes shows a bathochromic shift, indicating that the methyl and *tert*-butyl groups on the pyrazole ligand are electron donating groups, while the spectra of the **6B** and **7B** complexes shows a hypsochromic shift, corresponding to the electron withdrawing nature of the phenyl and trifluoromethyl groups substituted on the pyrazole ligand. Only the **7B** complex shows a weak shoulder at about 295-330 nm.

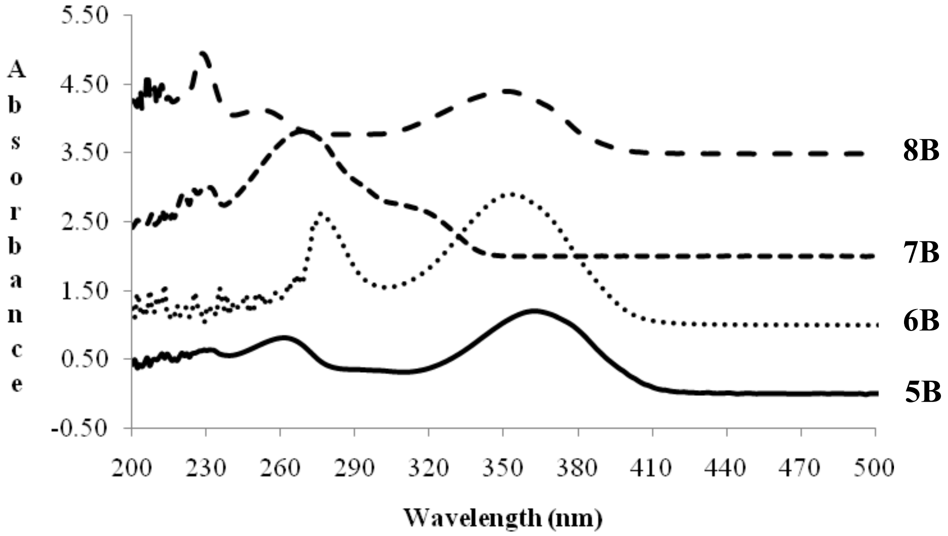

Figure 4.3 UV-Vis spectroscopic data of the nickel adduct complexes **5B-8B**.

Table 4.2 The selected λ_{max} (nm) for **5B-8B**.

Complexes	Wavenumber, λ_{max} (nm)
5B	259-263, 361-364
6B	276, 352-354
7B	267-268, 302-313
8B	228, 251-253, 350-352

The ^1H NMR spectra are shown in Figure 4.4 and selected chemical shift data in Table 4.3. The multiplet observed in the δ 7.40-8.01 ppm region has been assigned to the protons of the phenyl groups present in dbm in all four nickel complexes

(Chavez, Briones, Olmstead, and Mascharak, 1999; Sato, Taniguchi, Nakahashi, Monde, and Yamagishi, 2007). The substituents on the pyrazoles were observed at δ 1.13, 1.26 ppm for methyl groups (Llamas, Lamoneda, Carmona, Hernandez, and Toscano, 2006), δ 7.36-7.85 ppm for phenyl groups (Yu, Korolev, Heeg, and Winter, 2002), and δ 1.13-1.33 ppm for *tert*-butyl groups (Llamas, Lamoneda, Carmona, Hernandez, and Toscano, 2006). The pyrazole CH peak occurs at δ 6.86, 6.40, 6.39, and 6.39 ppm (Maekawa, 1993; Rettig, Storr, Summers, Thomson, and Trotter, 1997), shifted upfield from the free pyrazole ligand, while the dbm CH peak occurs at δ 3.49, 3.95, 3.49, and 3.65 ppm, shifted downfield from nickel 1,3-diphenyl-1,3-propanedionate. The substituted effect on pyrazole ligands show chemical shifts into downfield shifts indicating that the pyrazoles are bonded to the nickel center atom. The chemical shifts of phenyl groups on the pyrazole ligand overlap with the phenyl groups on dbm. Significant changes in the chemical shifts relative to the starting materials also confirm complexation.

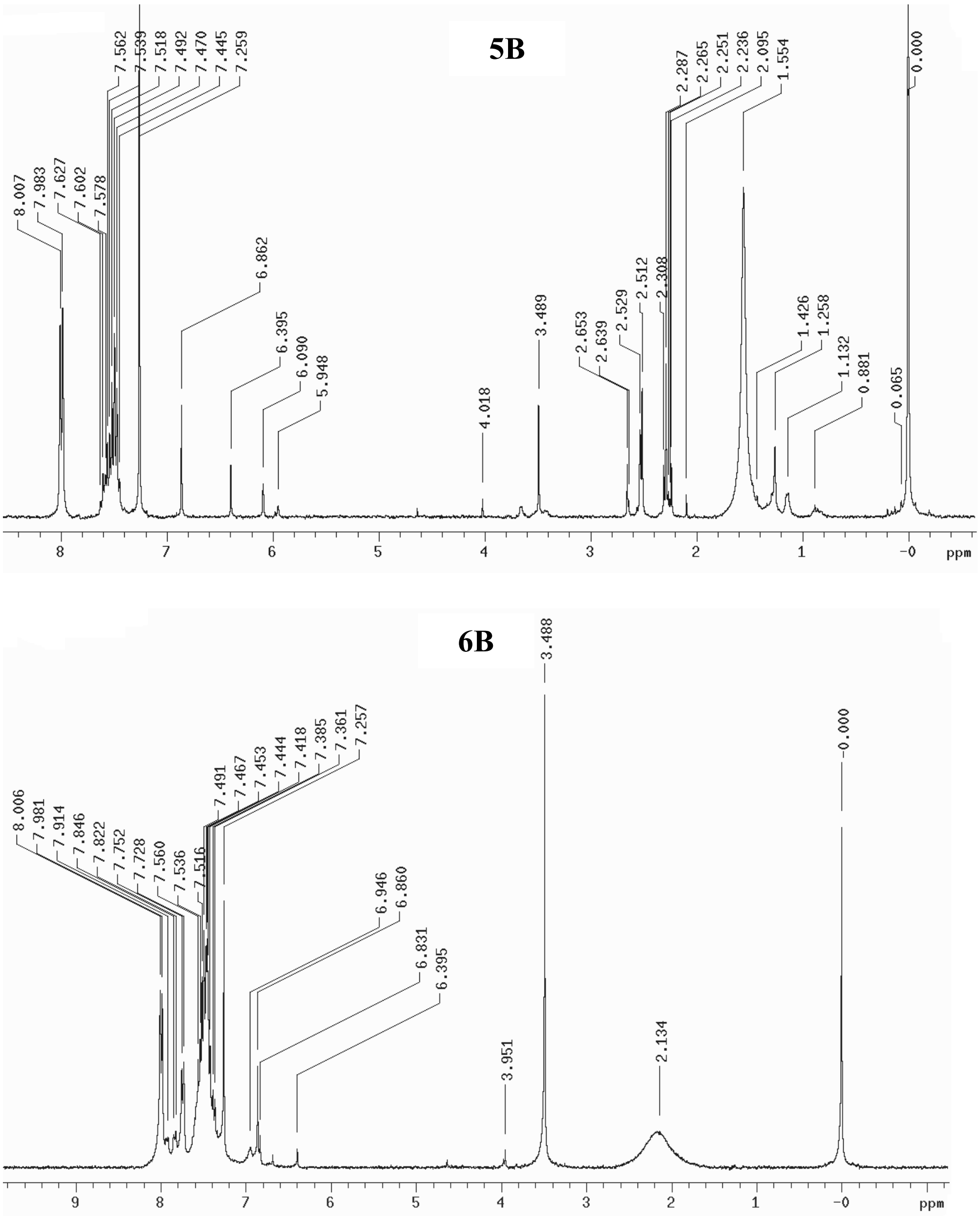

Figure 4.4 The 300-MHz ^{1}H NMR spectra recorded for the nickel adduct complexes.

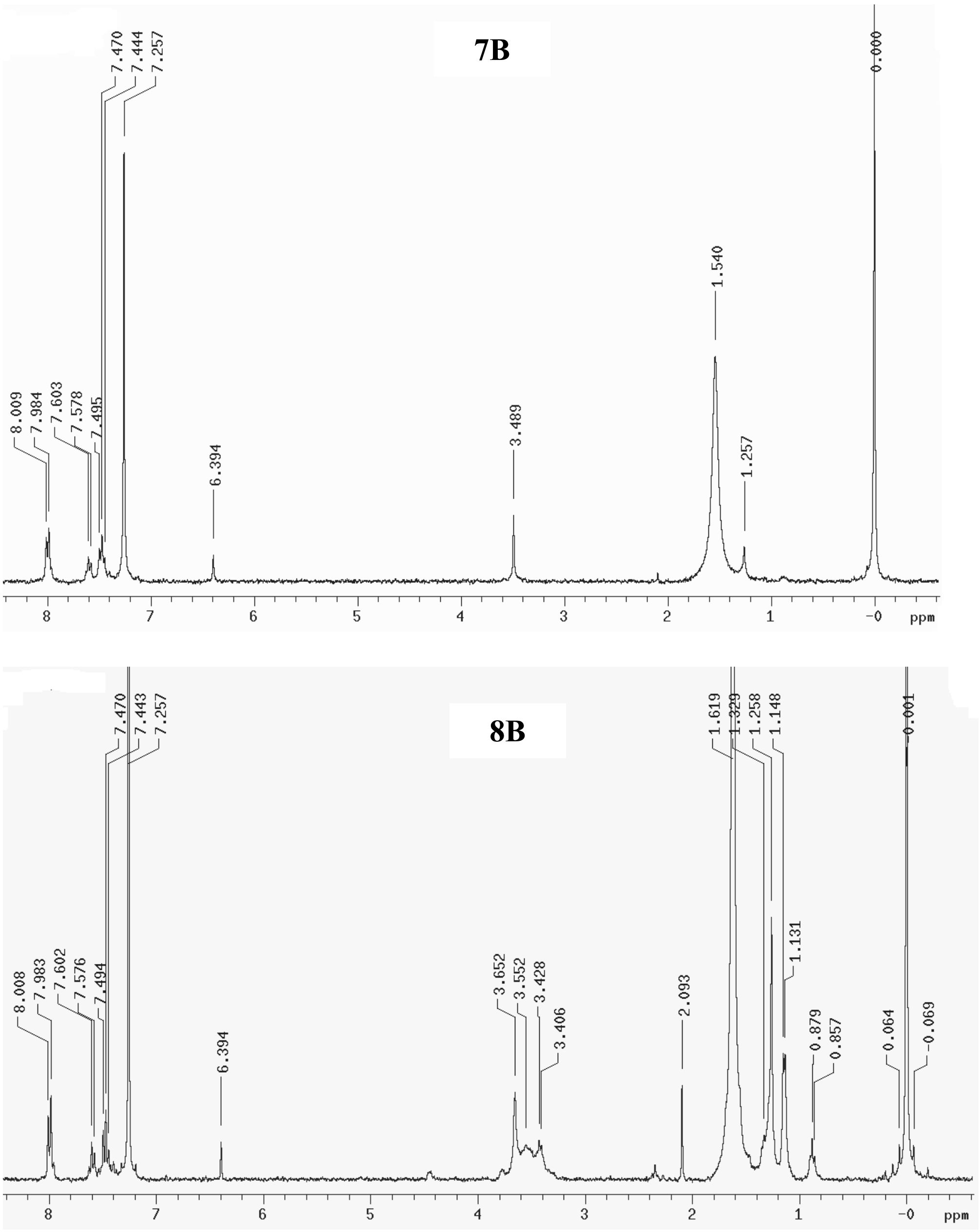

Figure 4.4 (continued) The 300-MHz ^{1}H NMR spectra recorded for the nickel adduct complexes.

Table 4.3 Selected chemical shifts (ppm) and assignments for **5B-8B**.

Assignment	Chemical shift of adduct (ppm) [Integration number]			
	5B	**6B**	**7B**	**8B**
CH_3 in pz	1.13, 1.26 [0.82, 1.80]	-	-	-
t-Bu in pz	-	-	-	1.13-1.15, 1.26-1.33 [1.97, 3.35]
CH in dbm	3.49 [0.87]	3.95 [0.94]	3.49	3.55 [1.03]
CH in pz	6.86 [0.72]	6.40 [1.00]	6.39	6.39 [0.15]
Ph in dbm	7.45-7.63, 7.98-8.01 [7.16, 4.39]	7.36-7.56, 7.73-7.85, 7.91-8.01 [108.17, 26.51, 37.71]	7.44-7.50, 7.58-7.60, 7.98-8.01	7.44-7.49, 7.58-7.60, 7.98-8.01 [1.04, 0.40, 0.82]
Ph in pz	-	7.36-7.56, 7.73-7.85, 7.91-8.01	-	-

Thermal analyses of the nickel complexes are shown in Figure 4.5. These complexes show decomposition with weight loss of 2 and 11% in the temperature range of 120-140 ºC for **6B** and 70-240 ºC for **7B**, indicating two water molecules.

Decomposition about 200 ºC corresponds to the loss of the phenyl groups on the dbm ligands, and near 400 ºC corresponds to decomposition of the pyrazole bridging ligand. The last step is assigned to the formation of nickel oxide (Dunstan, 1998).

The proposed structural formula, $[Ni_2(dbm)_2(\mu\text{-}pz^{R2})_2(H_2O)_4]$ for **6B** and **7B**, and $[Ni(dbm)_2(Hpz^{R2})_2]$ for **5B** and **8B** is consistent with the thermal analysis and the FT-IR, UV-Vis, and ^{1}H NMR spectroscopic results. The pyrazole ligands act as bridges as no N–H stretch is observed in the FT-IR or ^{1}H NMR spectra for **6B** and **7B**. The N–H protons of neutral monodentate pyrazole ligands in **5B** and **8B** can be observed in FT-IR, but are not observed in ^{1}H NMR suggesting that the protons are exchanging in solution.

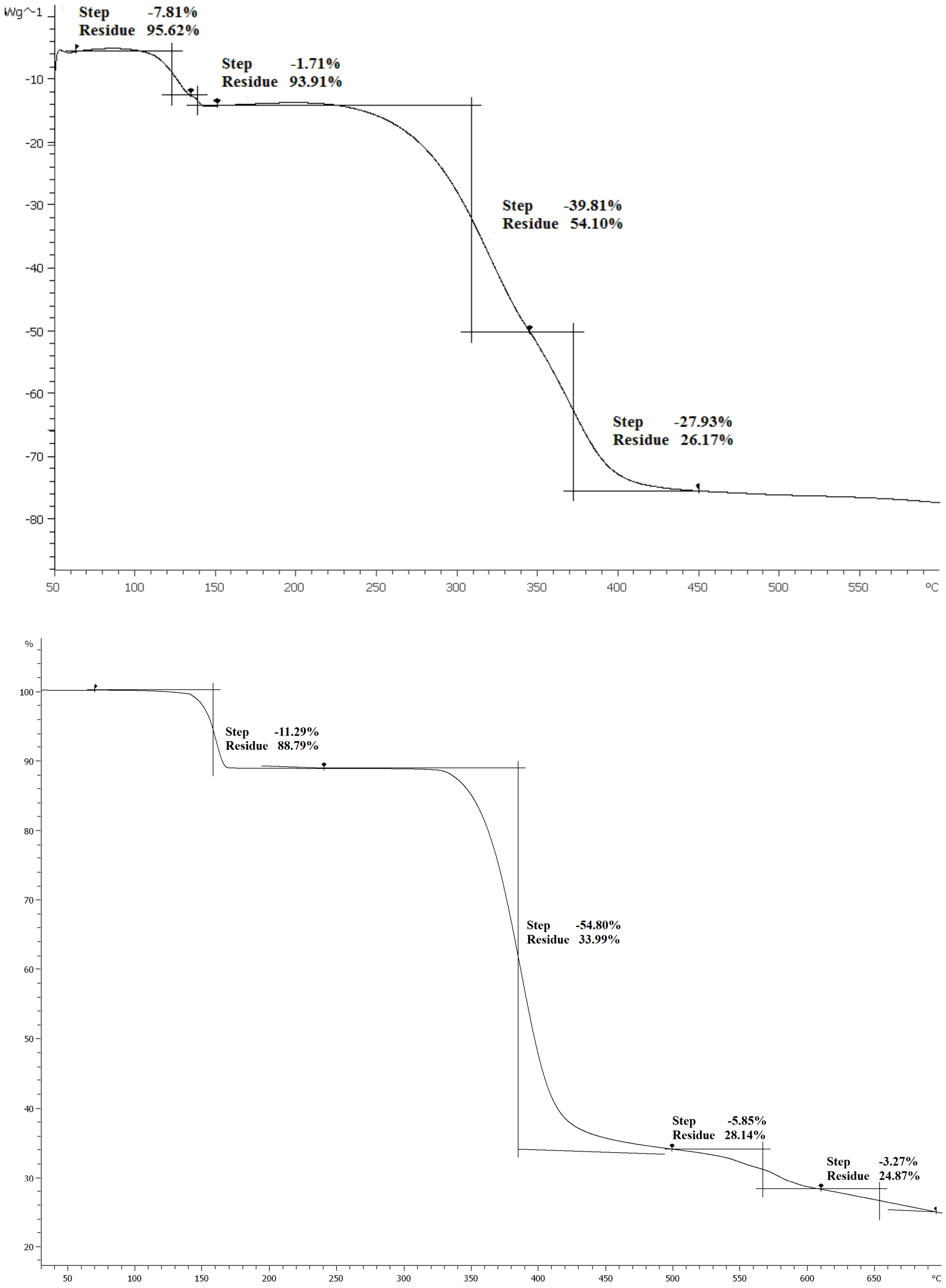

Figure 4.5 Thermal analyses of **6B** and **7B** (top to bottom).

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CHAPTER V

CONCLUSION

This research investigates potential reaction at room temperature of nickel and cobalt with β-diketonate and pyrazolyl ligands. Two series, one nickel and one cobalt, containing dbm with pz^{R2}, R = $-CH_3$, –Ph, $-CF_3$, and –*t*-Bu, gave crystalline products and were characterized by spectroscopic techniques. FT-IR spectroscopy was utilized to study vibrational frequencies, and UV-Vis spectroscopy to study the change in transition energies of the metal based bands as a function of different electron-donating and electron-withdrawing substituents on the pyrazolyl ligand. ^1H NMR spectroscopy was used to confirm the presence of pyrazolyl and β-diketonate, and thermogravimetric analysis to study weight loss correlations with ligands and/or compositions.

Four cobalt and four nickel complexes were obtained in good yield from a 1:2 ratio of metal dbm and pyrazole by slow evaporation at room temperature in CH_2Cl_2:MeOH. Red/orange crystals were produced from the cobalt reactions and varying shades of green crystals were produced from the nickel reactions. The integrity of some samples was lost on removal from the mother liquor, presumably due to solvent loss.

The IR, UV-Vis, and ^1H NMR spectra of the eight complexes are significantly different from the starting materials. The infrared spectra of all complexes show characteristic bands of chelating dbm at 1670 and 1620 cm^{-1}. Nickel complexes show the methyl and *t*-butyl N–H stretching at 3400 and 3600 cm^{-1} for monodentate pyrazolyl ligand, but the other six complexes contain bridging pyrazolide ligands with no observed N–H band. The ^1H NMR chemical shifts of the substituent functional groups on the pyrazolyl ligands are in good agreement with similar complexes, and are consistent with metal centers coordinated with water, dbm, and pyrazole. Even through, no observed N–H group in ^1H NMR due to the N–H proton exchanging in solution. The electronic spectra gives three bands for the methyl and *tert*-butyl substituted pyrazolyl cobalt and nickel complexes, and two bands for the other six complexes, while the starting materials show only one band in their spectra.

Based on spectroscopic results, the proposed structural formula for the methyl and *t*-butyl substituted pyrazolyl nickel complexes is $[Ni(dbm)_2(Hpz^{R2})_2]$, and for the other complexes is $[M_2(dbm)_2(\mu\text{-}pz^{R2})_2(H_2O)_4]$. These formula are also consistent with the thermogravimetric results.

Further work: The quality of the crystalline products appears adequate for single crystal X-ray diffraction studies. Such studies would allow unambiguous assignment of the structures, especially with regard to the difficulty of interpreting the ^1H NMR and IR results on whether the pyrazolyl ligand is bridging or terminal.

APPENDICES

APPENDIX A

SUPPORTING INFORMATION FOR CHAPTER II

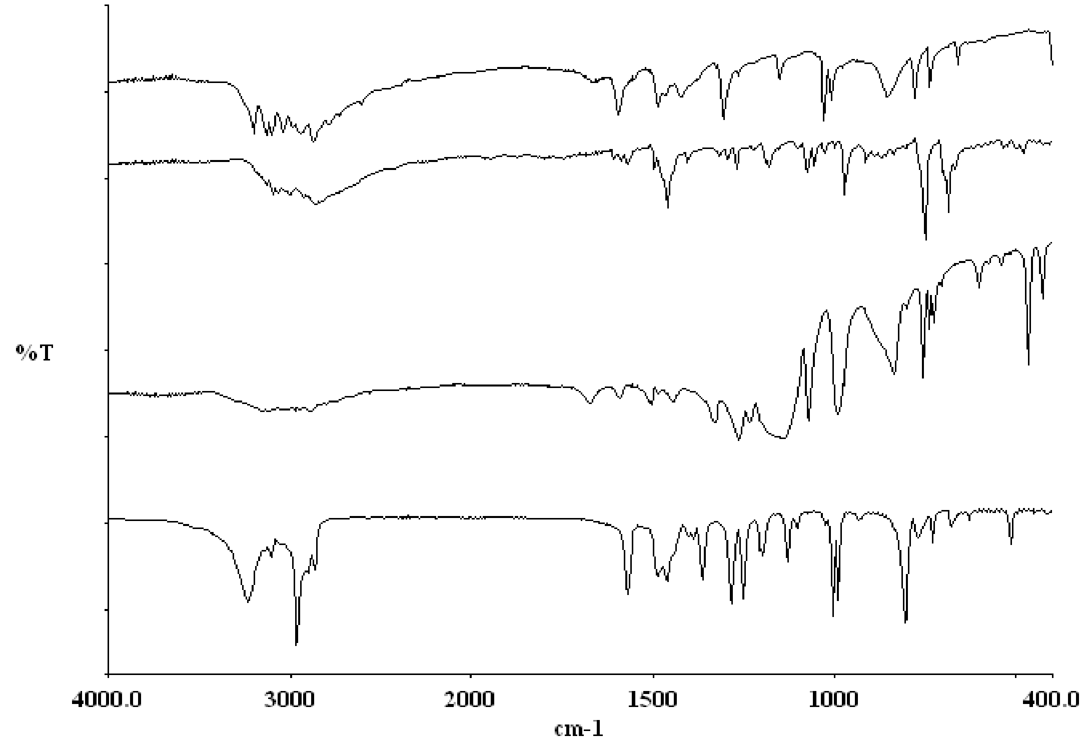

Figure A.1 The FT-IR spectra of Hpz^{Me2}, Hpz^{Ph2}, $Hpz^{(CF3)2}$, and $Hpz^{(t\text{-Bu})2}$ (top to bottom).

Table A.1 The observed FT-IR band (cm^{-1}) and assignment for 3,5-disubstituted pyrazole ligands.

Pyrazole Ligands	Wavenumber (cm^{-1})and Assignment						
	ν(N–H)	ν(C–H)	ν(C=C+C=N)	δ(C–H)	δ(C–N)	ν(C=C/Ph)	δ(C–F)
Hpz^{Me2}	3203	3132-2878	1595-1550	1465	1327-1267	-	-
Hpz^{Ph2}	3184	3133-2857	1605-1571	1462	1327-1272	1074-915	-
Hpz$^{(CF3)2}$	3195	3157-3048	1591 1571	1484	1330-1235	-	1330-1072
Hpz$^{(t\text{-Bu})2}$	3237	3110-2867		1488-1463	1285-1251	-	-

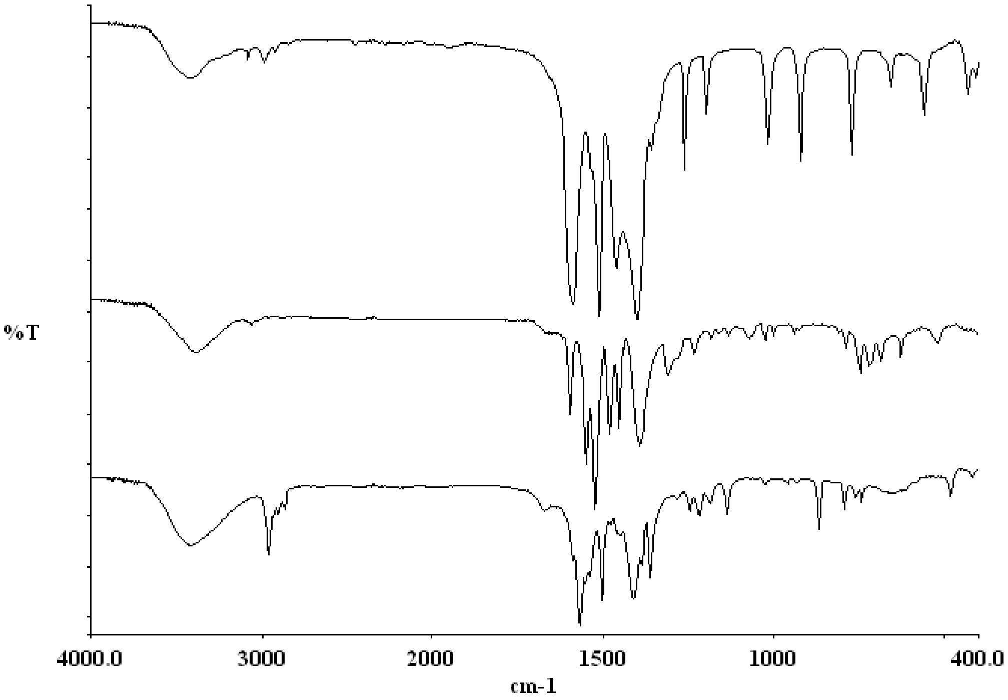

Figure A.2 The FT-IR spectra for cobalt complexes of Co(acac)$_2$, Co(dbm)$_2$(H$_2$O)$_2$, and Co(tmhd)$_2$(H$_2$O)$_2$ (top to bottom).

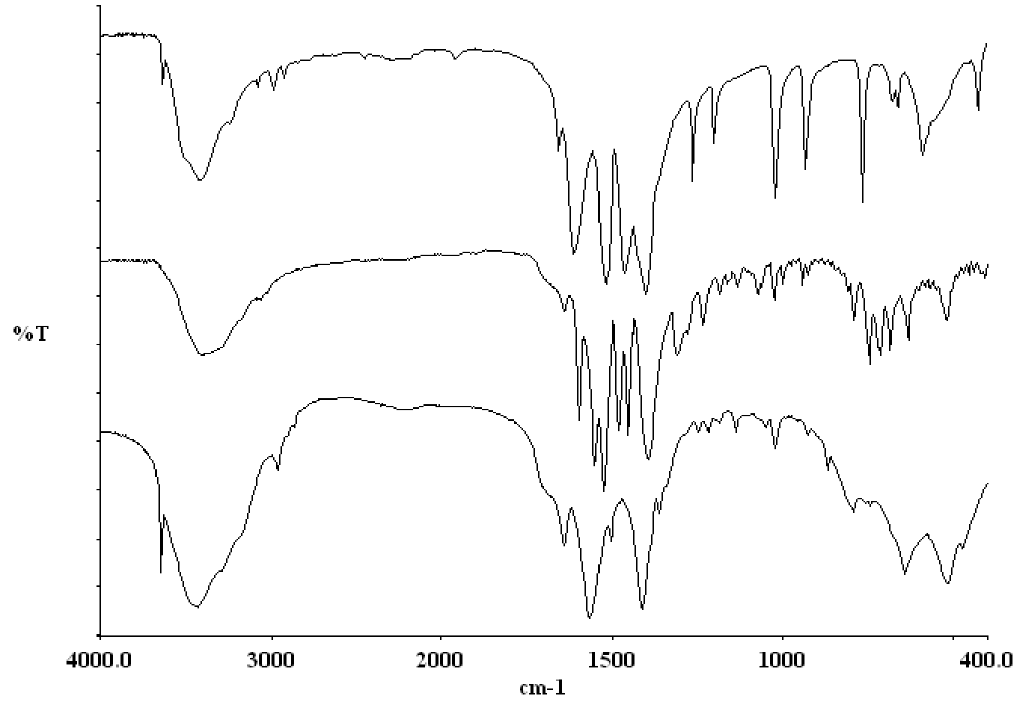

Figure A.3 The FT-IR spectra for nickel complexes of Ni(acac)$_2$, Ni(dbm)$_2$(H$_2$O)$_2$, and Ni(tmhd)$_2$(H$_2$O)$_2$ (top to bottom).

Table A.2 The observed FT-IR band (cm^{-1}) and assignment for diaquabis(β-diketonate) complexes with cobalt and nickel.

Complexes	Wavenumber (cm^{-1})and Assignment						
	ν(O–H)	ν(C–H)	ν(C=O)	ν(C=C)	δ(C–H)	ν(C=C/Ph)	ν(M–O)
Co(acac)$_2$	3420	3079-2925	1658	1587	1463-1403	-	431
Co(dbm)$_2$(H$_2$O)$_2$	3387	3087-2959	1658	1594	1480-1394	1072-789	454
Co(tmhd)$_2$(H$_2$O)$_2$	3417	2961-2869	1671	1568	1460-1361	-	482
Ni(acac)$_2$	3423	3075-2925	1655	1520	1465-1403	-	591
Ni(dbm)$_2$(H$_2$O)$_2$	3412	3090-3029	1641	1595	1480-1395	1072-791	522
Ni(tmhd)$_2$(H$_2$O)$_2$	3436	2963-2870	1685	1567	1412	-	519

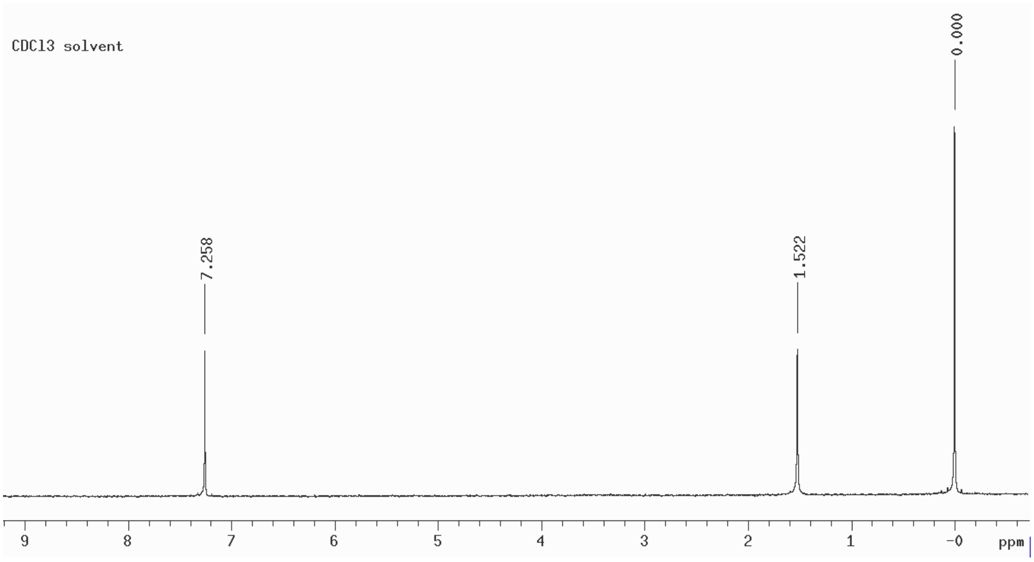

Figure A.4 The ^{1}H NMR spectrum of $CDCl_3$ solvent.

Table A.3 The observed chemical shift (ppm) for 3,5-disubstituted pyrazole ligands.

Pyrazole Ligands	Chemical shift (ppm) and Assignment				
	NH in pz	CH in pz	CH_3 in pz	Ph in pz	*t*-Bu in pz
Hpz^{Me2}	6.05	5.97	2.27-2.28, 2.48	-	-
Hpz^{Ph2}	7.00	6.83	-	7.46-8.04	-
$Hpz^{(CF3)2}$	6.94	5.61	-	-	-
$Hpz^{(t\text{-Bu})2}$	6.21	5.97	-	-	1.24-1.38 1.40-1.51

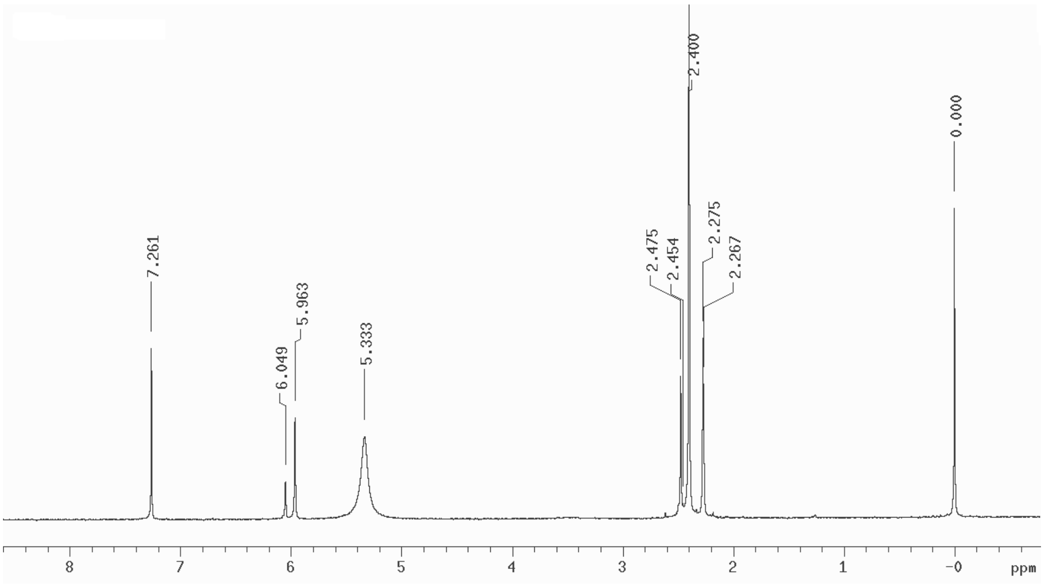

Figure A.5 The ^{1}H NMR spectrum of Hpz^{Me2} ligand.

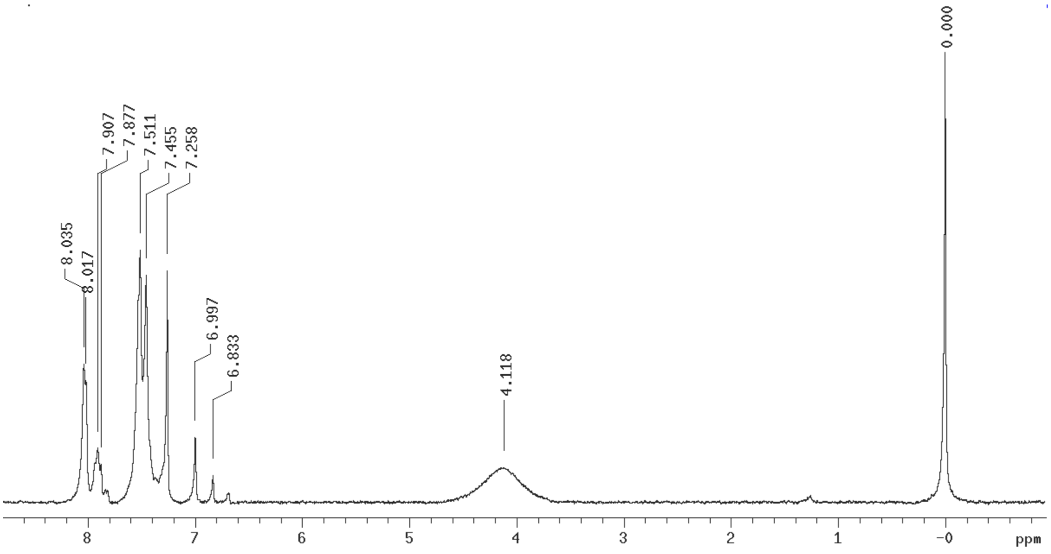

Figure A.6 The ^{1}H NMR spectrum of Hpz^{Ph2} ligand.

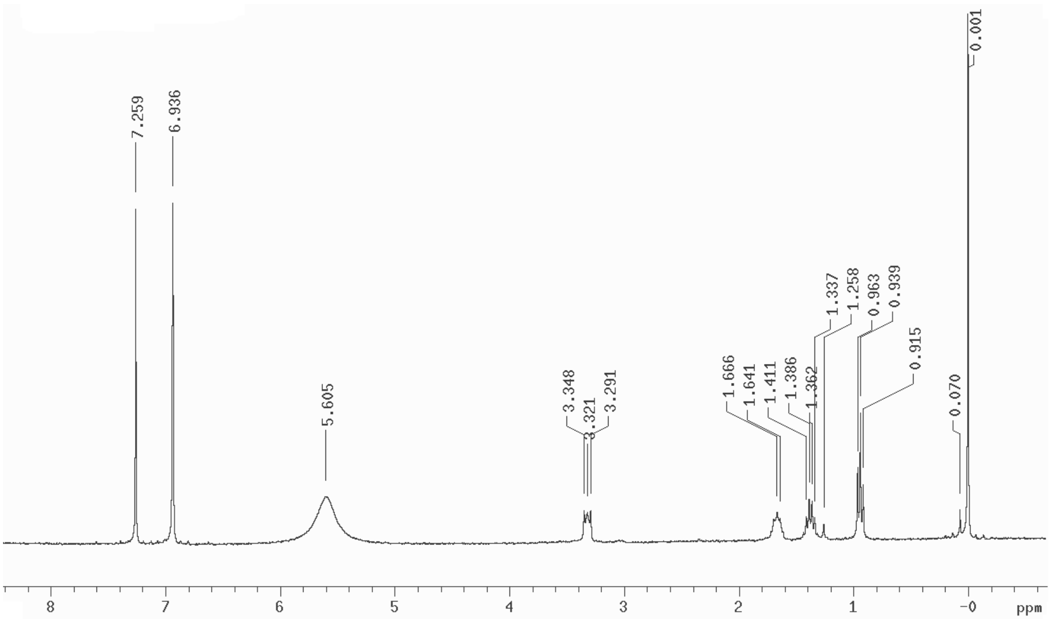

Figure A.7 The ^{1}H NMR spectrum of Hpz$^{(CF3)2}$ ligand.

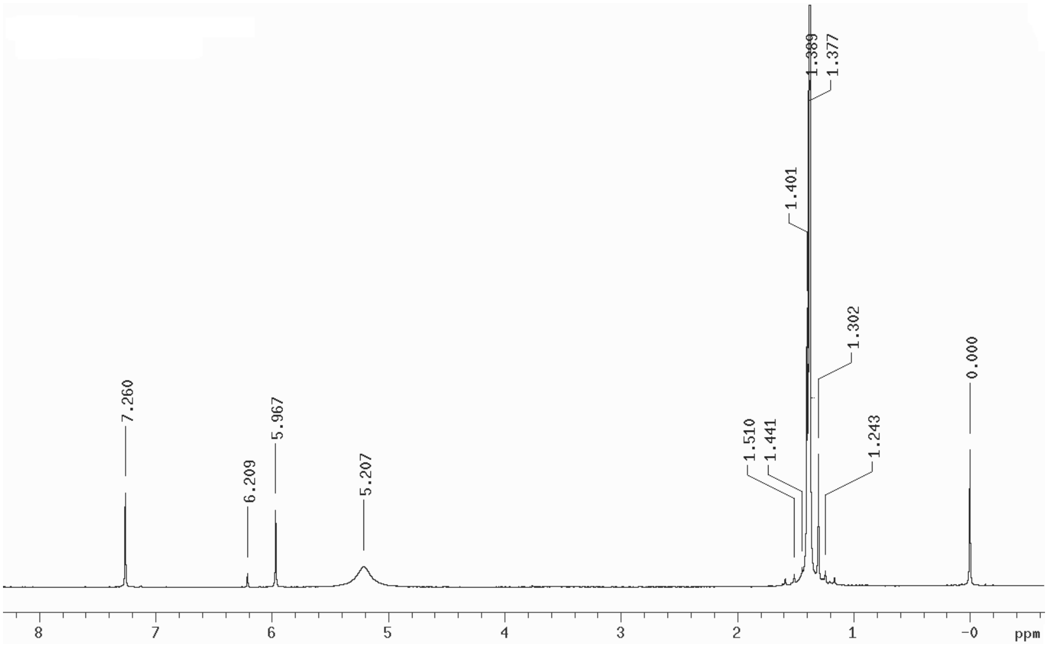

Figure A.8 The ^{1}H NMR spectrum of Hpz$^{(t\text{-Bu})2}$ ligand.

Table A.4 The observed chemical shift (ppm) for diaquabis(β-diketonate) complexes with cobalt and nickel.

Complexes	Chemical shift (ppm) and Assignment			
	CH in dike	Ph in dike	*t*-Bu in dike	H_2O
$Co(dbm)_2(H_2O)_2$	6.39	7.45-7.50, 7.58-7.60, 7.98-8.01	-	1.54
$Co(tmhd)_2(H_2O)_2$	5.59	-	1.16-1.26	1.56
$Ni(dbm)_2(H_2O)_2$	6.40	7.33-7.54, 7.58-7.63, 7.96-8.01	-	1.57
$Ni(tmhd)_2(H_2O)_2$	5.59	-	1.13-1.33	1.72

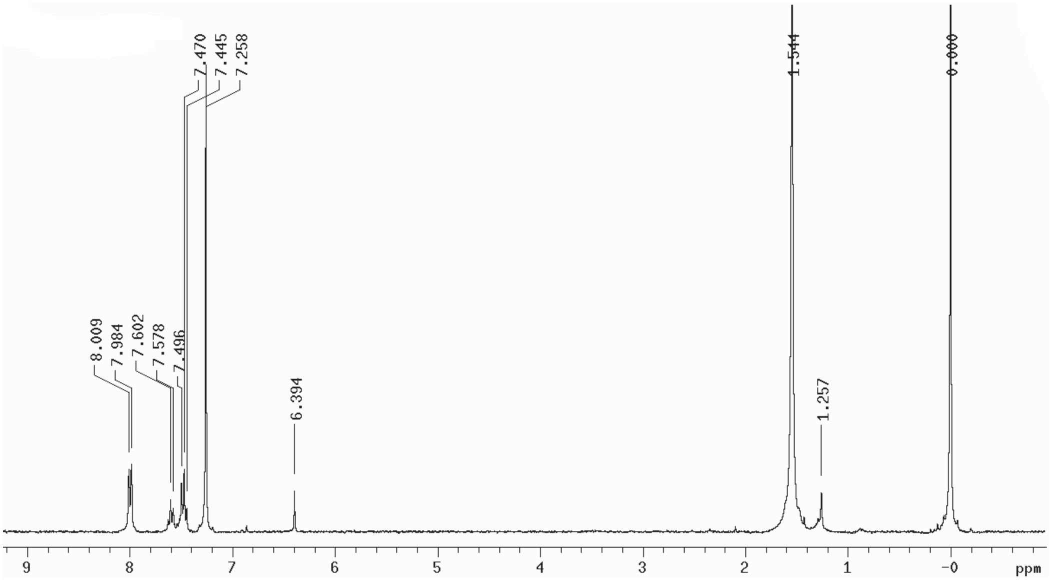

Figure A.9 The ^1H NMR spectrum of $Co(dbm)_2(H_2O)_2$ complex.

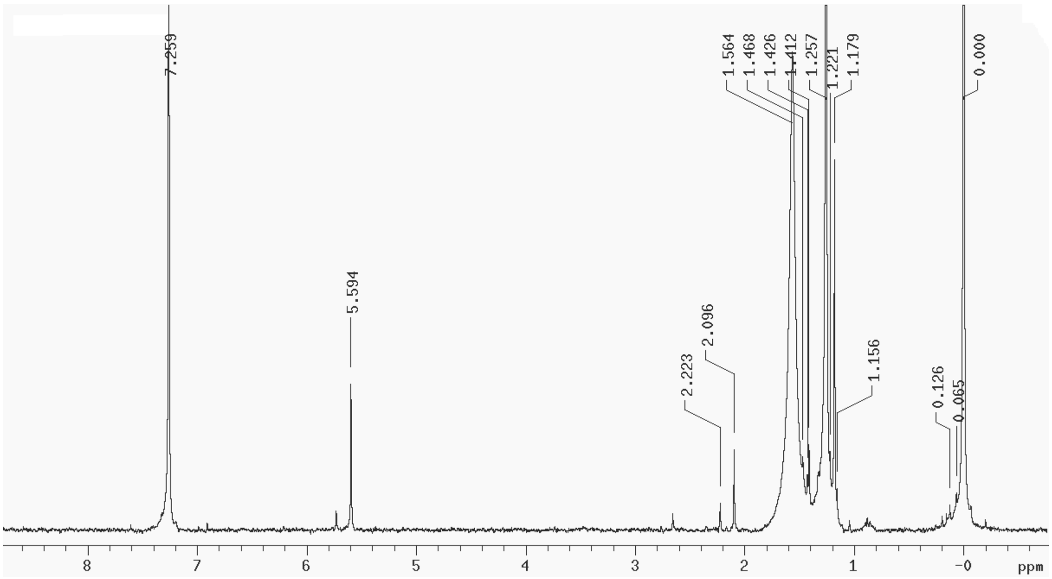

Figure A.10 The ^1H NMR spectrum of $Co(tmhd)_2(H_2O)_2$ complex.

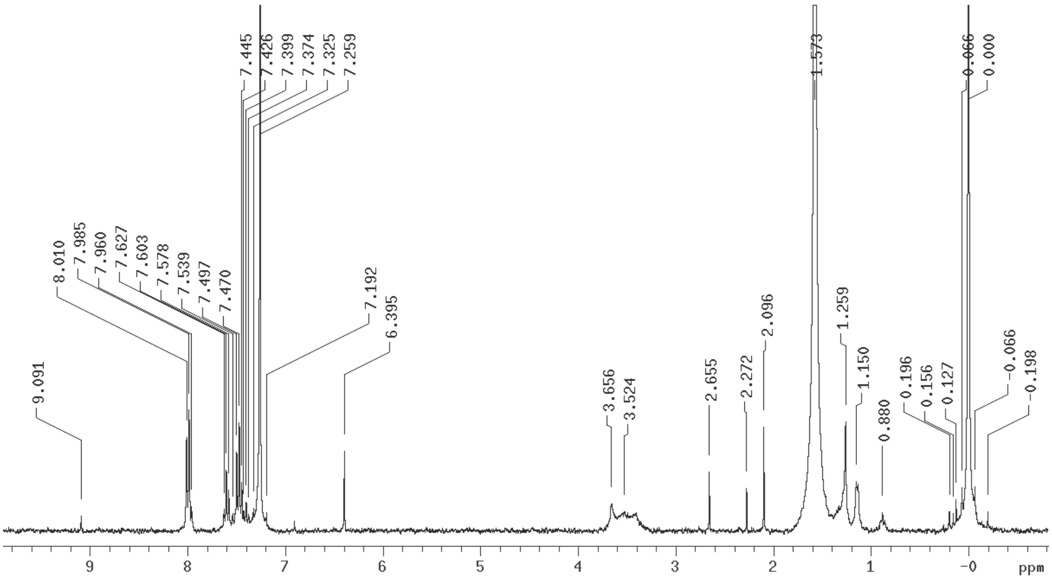

Figure A.11 The ^1H NMR spectrum of $Ni(dbm)_2(H_2O)_2$ complex.

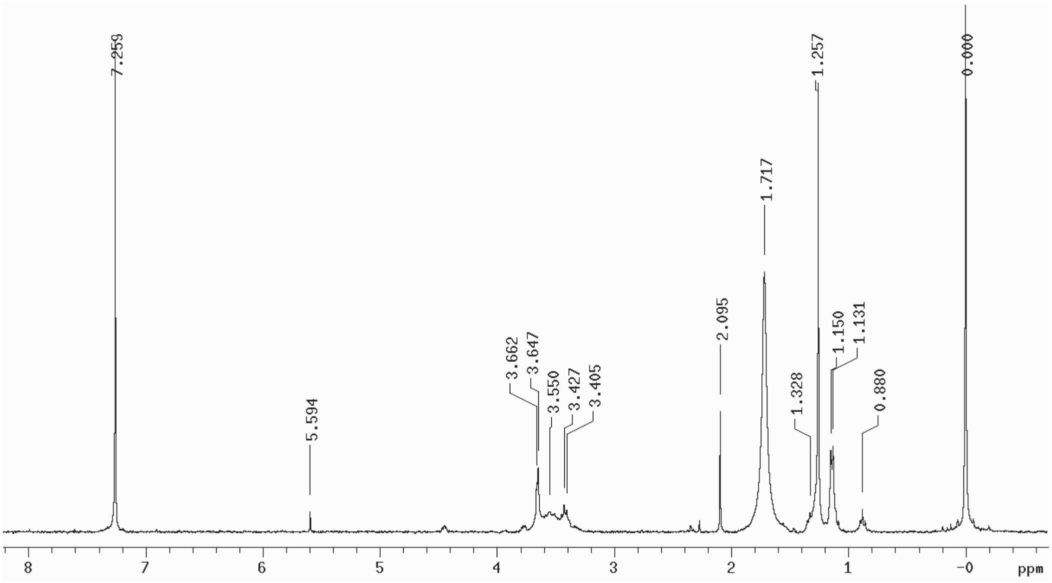

Figure A.12 The ^{1}H NMR spectrum of $Ni(dbm)_2(H_2O)_2$ complex.

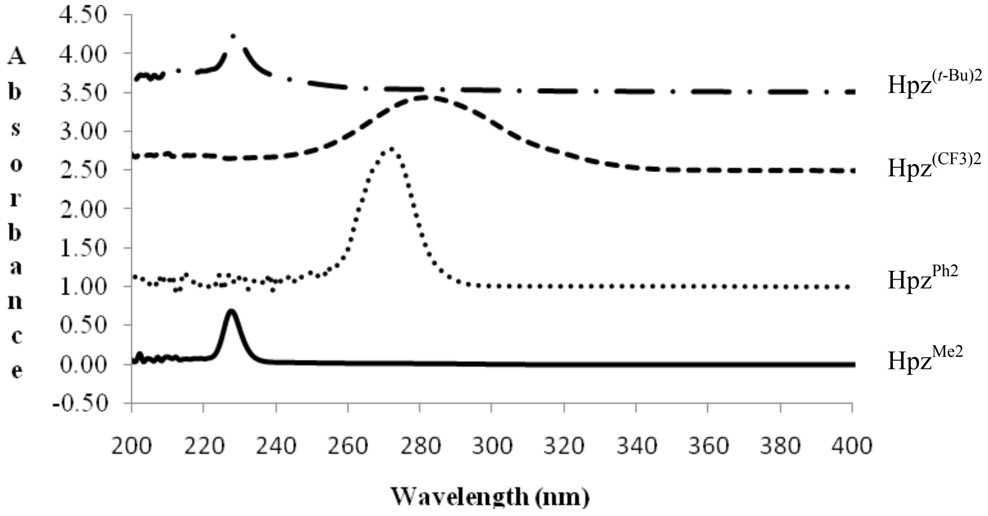

Figure A.13 The electronic spectra of Hpz^{Me2}, Hpz^{Ph2}, $Hpz^{(CF3)2}$, and $Hpz^{(t\text{-}Bu)2}$ (top to bottom).

Table A.5 The observed λ_{max} (nm) in 3,5-disubstituted pyrazole ligands.

Pyrazole Ligands	Wavenumber, λ_{max} (nm)
Hpz^{Me2}	227
Hpz^{Ph2}	282
$Hpz^{(CF3)2}$	282
$Hpz^{(t\text{-}Bu)2}$	229

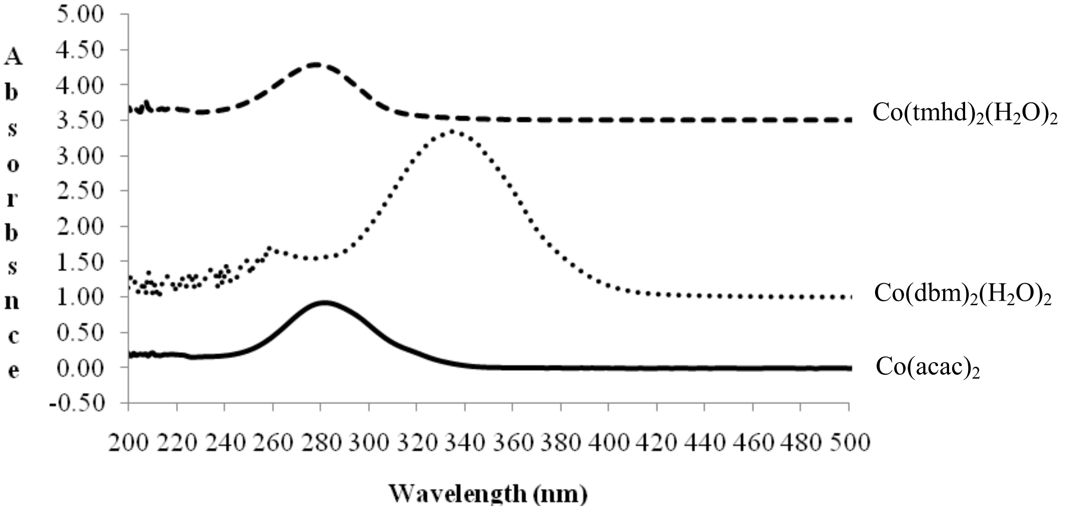

Figure A.14 The electronic spectra for cobalt complexes of $Co(acac)_2$, $Co(dbm)_2(H_2O)_2$, and $Co(tmhd)_2(H_2O)_2$ (top to bottom).

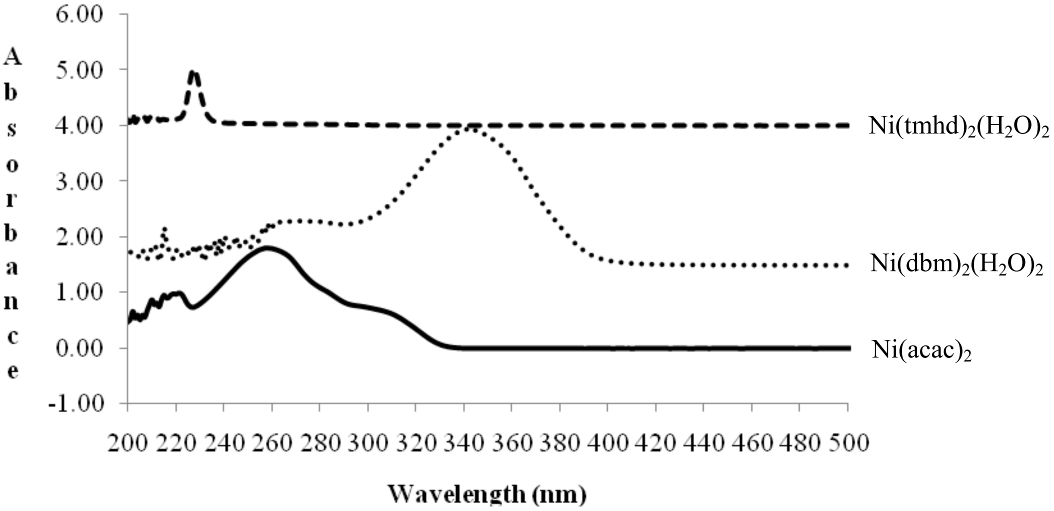

Figure A.15 The electronic spectra for nickel complexes of Ni(acac)$_2$, Ni(dbm)$_2$(H$_2$O)$_2$, and Ni(tmhd)$_2$(H$_2$O)$_2$ (top to bottom).

Table A.6 The observed λ_{max} (nm) diaquabis(β-diketonate) complexes with cobalt and nickel.

Complexes	Wavenumber, λ_{max} (nm)
Co(acac)$_2$	280-283
Co(dbm)$_2$(H$_2$O)$_2$	353
Co(tmhd)$_2$(H$_2$O)$_2$	281-282
Ni(acac)$_2$	280-283
Ni(dbm)$_2$(H$_2$O)$_2$	353
Ni(tmhd)$_2$(H$_2$O)$_2$	281-282

APPENDIX B

LIST OF ABSTRACTS AND PROCEEDINGS

Abstracts

Thisuwan, J. and Haller, K. J. Synthesis and Characterization of an Adduct of Dimethylglyoxime and Hexamethylenetetramine. *The 33rd Congress on Science and Techonology Thailand.*18-20 October 2007, Walailak University, Nakhon Si Thammarat, Thailand.

Thisuwan, J., Haller, K. J., Harding, D. J., and Harding, P. Synthesis and Characterization of Bis(1,3-Diphenylpropane-1,3-dionate), Bis(3,5-Diphenylpyrazole), Metal Complexes, $[M(dbm)_2(Hpz^{Ph2})_2]$; (M = Co, Ni). *German-Thai Symposium on Nanoscience and Nanotechnology.* 21-22 September 2009, Chiang Mai Orchid Hotel, Chiang Mai, Thailand.

Thisuwan, J., Haller, K. J., Harding, D. J., and Harding, P. Investigation of $Co(dbm)_2$ Complexes with 3,5-Disubstituted Pyrazole Ligands (dbm = dibenzoylmethane). *The 3rd SUT Graduate Conference.* 21-23 November 2010, Surasammanakhan, Suranaree University of Technology, Nakhon Ratchasima, Thailand.

Proceeding

Thisuwan, J. and Haller, K. J. Synthesis and Characterization of a Dimethylglyoxime and Hexamethylenetetramine. *The 1st SUT Graduate Conference.* 1-2 November 2007. Surasammanakhan, Suranaree University of Technology, Nakhon Ratchasima, Thailand.

Thisuwan, J., Haller, K. J., Harding, D. J., and Harding, P. Syntheses and Characterization of Dibenzoylmethane Cobalt complexes with 3,5-Disubstituted Pyrazole Ligands. *The 3rd Science Research Conference.* 14-15 March 2011. Naresuan University, Phitsanulok, Thailand.

Extended Conferences

The 6th National Symposium on Graduate Research. 7-8 September 2007. Mahidol University, Salaya Campus, Kakhonphatom, Thailand.

The 34th Congress on Science and Techonology Thailand. 31 October-2 November 2008. Queen Sirikit National Convention Center, Bangkok, Thailand.

Pure and Applied Chemistry International Conference (PACCON 2009). 14-16 January 2009. Naresuan University, Phitsanulok, Thailand.

The 35th Congress on Science and Techonology Thailand. 15-17 October 2009. Burapha University, Chonburi, Thailand.

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Relevant Experience	
2007	Research Assistance, Applied Surface and Crystallography Unit members, Suranaree University of Technology, Thailand
2007-2010	Teaching Assistance, School of Chemistry, Institute of Science, Suranaree University of Technology, Thailand
Fellowships	
2009	Research at Molecular Technology Research Unit, School of Science, Walailak University, Thailand