COORDINATION CHEMISTRY AND LIQUID-LIQUID EXTRACTION OF ZINC(II), CADMIUM(II) AND LEAD(II) CATIONS WITH (PYRAZOL-1-YLMETHYL)PYRIDINE LIGANDS

BY

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ABSTRACT

Amongst the countless man-made contaminants that infiltrate our water sources are heavy metals, usually as by-products of industrial processes. Many metals, particularly heavy metals are toxic. Metal contamination (e.g. Hg, Pb, Cd, etc.) can be addressed by using filters/sorbents (e.g. gamma alumina), and flocculation/precipitation, but these methods are non-specific and best suited to contaminants at high concentrations. Chelating extraction is a potential technology of remediation for heavy metals-contaminated water and as such considerable attention has been devoted to the development of chelating agents for liquid-liquid extraction of metal ions. The ligands 2,6-bis(pyrazol-1-ylmethyl)pyridine (**L1**), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**), 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L3**), 2-(pyrazol-1-ylmethyl)pyridine (**L4**), 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L5**) and 2-(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L6**) were prepared and their coordination chemistry with zinc and cadmium metal ions investigated prior to their applications as chelating agents to remove heavy metals from water. Ligands **L2**, **L5** and **L6** reacted with either $Zn(NO_3)_2$, $ZnCl_2$, $Cd(NO_3)_2$ or $CdCl_2$ to form monometallic complexes $[Zn(NO_3)_2(\mathbf{L5})]$ (**C1**), $[Zn(NO_3)_2(\mathbf{L6})]$ (**C2**), $[ZnCl_2(\mathbf{L5})]$ (**C3**), $[Cd(NO_3)_2(\mathbf{L5})]$ (**C4**), $[Cd(NO_3)_2(\mathbf{L6})]$ (**C5**), $[CdCl_2(\mathbf{L5})]$ (**C6**), $[Zn(NO_3)_2(\mathbf{L2})]$ (**C7**), $[ZnCl_2(\mathbf{L2})]$ (**C8**), $[Cd(NO_3)_2(\mathbf{L2})]$ (**C9**), $[CdCl_2(\mathbf{L2})]$ (**C10**). All the new compounds prepared were characterized by ^1H NMR and elemental analyses. Single crystal X-ray crystallography of complexes **C1**, **C3**, **C4**, **C5**, **C7** and **C9** has been used to confirm the solid state structure of the complexes. **L5** and **L6** adopts bidentate coordination mode through the pyridine nitrogen and one pyrazolyl nitrogen atom as confirmed by single crystal X-ray crystallography of complexes **C1**, **C3**, **C4** and **C5**. The tridentate coordination of **L2** has also been established by the solid state structures of **C7** and **C9**. The abilities of 2,6-bis(pyrazol-1-ylmethyl)pyridine (**L1**), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**), 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L3**), 2-(pyrazol-1-ylmethyl)pyridine (**L4**), and 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L5**) to extract heavy metal ions, (lead(II), cadmium(II) and zinc(II)) were examined by liquid-liquid extraction experiments using dichloromethane-water biphasic system. Extraction efficiency was found to be dependent on the type of metal cations. All the ligands showed greater extraction efficiency for zinc (88-99%) and lowest extraction for cadmium (19-31%). The ligand architecture as well as experimental conditions such as metal:ligand ratio, time of reaction influenced the extraction efficiency of the ligands. Theoretical studies using Density Functional Theory by Gassian03 have been used to explain the observed experimental trends.The theoretical results were consistent with the experimental results with zinc(II) giving the highest negative enthalpy followed by lead(II) and cadmium(II) giving the lowest.

CHAPTER ONE

INTRODUCTION: HEAVY METAL POLLUTION OF WATER AND METHODS OF REMEDIATION

1.1 General remarks

Pure, clean drinking water is arguably the most important factor in determining quality of life (Glen *et al.*, 2007). Biological and chemical contaminations are the two primary concerns for drinking-water contamination. Biological contamination can be effectively treated by using any of a number of existing technologies (e.g. chlorination, ozone, UV, etc.), but chemical contamination is a more challenging hurdle, particularly heavy-metal contamination (Glen *et al.*, 2007).

1.2 Heavy metal pollution

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are natural components of the Earth's crust. Nowadays, anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem. Toxic metals enter waterways from two main sources: industrial waste discharges and particulates in the atmosphere that settle and are carried in run-off (James, 2005).

Metals and metalloids have long been mined, industrially processed, and used in numerous applications. This has led to regional and global redistribution to more or less hazardous levels in the upper part of the earth's crust. Therefore, in the plough-layer of soils, in plants, animals, lakes, rivers, and even in the oceanic regions the levels of a variety of elements have substantially increased over time (Chao *et al.*, 1998). Ingestion of metals such as lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), barium (Ba), and chromium (Cr), may pose great risks to human health. Heavy metal toxicity can result in damaged or reduced mental and central nervous functions, lower energy levels, altered blood composition and damage to lungs, kidneys, liver, and other vital organs. Trace metals such as lead and cadmium interfere with essential elements such as calcium and zinc which are responsible for coordination.

During the last years, most of the nutrition research on zinc has focused on its essential roles in the body. Relatively little attention has been directed toward toxic properties of zinc other than where there has been a clear industrial hazard, such as with metal-fume fever due to inhalation of zinc oxide fumes or as a consequence of severe pollution of a localized environment. Even though zinc is a very essential requirement for a healthy body, excess zinc can be harmful, and cause zinc toxicity.

The U.S. Food and Drug Administration (FDA) has stated that zinc damages nerve receptors in the nose, which can cause anosmia. On June 16, 2009, the FDA said that consumers should stop using zinc-based intranasal cold products and ordered their removal from store shelves. The FDA said the loss of smell can be life-threatening because people with impaired smell cannot detect leaking gas or smoke and cannot tell if food has spoiled before they eat it (FDA, 2009). According to the Kenya Bureau of Standards (KEBS, 1996), safe drinking water should contain at most 5 ppm of zinc.

In order to alleviate heavy metal pollution in water, a variety of techniques have been investigated and developed for the removal of these pollutants. These techniques include ion exchange, electrodeionization and flocculation/precipitation. However, these methods are either non-specific (meaning that they remove all metal ions including the essential metal ions like calcium(II), magnesium(II)), or are not suited to contaminants at low concentrations (Glen, 2007). It is thus important that new and efficient methods for metal ion extraction from waste and drinking water are investigated. One such method is the use of organic chelating agents to sequester the metal cations from domestic water.

1.3 Metal chelating agents

A ligand is an ion or molecule which exists independently of any complex that it might form. In the complex $[Co(NH_3)_6]^{3+}$, the ammonia molecules, which can exist outside of the complex, are acting as ligands. Ligands can be divided into three categories: unidentate, bidentate and multidentate. Unidentate ligands can form one coordinate bond with a central metal ion. Bidentate ligands can form two coordinate bonds with a central metal ion while those ligands that can form three or more coordinate bonds with a central metal ion are called multidentate ligands (Wiki books, 2009).

Another type of ligand is an ambidentate ligand. An ambidentate ligand contains more than one potential donor atom such as the thiocyanate ion, NCS^-, which can bind to the metal center via either the nitrogen or sulphur atoms. Chelating ligands are those multidentate ligands which can form a ring including the metal atom. This process of ring formation is known as *chelation*. An example is the complex formed between ethylenediaminetetraacetic acid (EDTA) and various metals such as lead(II), zinc(II), copper(II) and magnesium(II) (Figure 1.1).

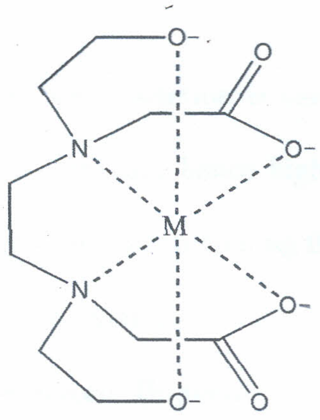


Figure 1.1: Metal-EDTA chelate

When the EDTA ligand comes into contact with positively charged metal ions such as ions of lead, iron, copper, magnesium, zinc, platinum and manganese, it grabs them and thus removes them (Cotton and Wilkinson, 1980). Hence, chelation is the binding or complexation of a bi- or multidentate ligand with a metal cation. Chelating extraction is a potential technology of remediation of heavy metal-contaminated water.

1.4 Factors affecting the stability of chelate complexes

The ability of a chelate ligand to bind to a metal cation is governed by the stability of the resultant complex. This is called the formation constant, K_f, and refers to the ease of formation and stability of the complex (Equation 1.1). The larger the value of K_f, the greater the stability of the resulting complex (Bell, 1977),

$$M^{n+} + L \rightleftharpoons [ML]^{n+} \qquad K_f = \frac{[ML]^{n+}}{[M]^{n+}[L]} \qquad (1.1)$$

1.4.1 Number of chelate rings

The enhanced stability associated with chelation is called *the chelate effect*. Increased chelation results in high formation constant hence higher stability of the complex. An example of the chelate effect is provided by comparing the reaction between cadmium(II) ions and the monodentate ligand methylamine (Equation 1.2) with that of the chelating bidentate ligand ethane-1,2-diamine,en (Equation 1.3). The formation constant of tetramethylamminecadmium(II), $[Cd(MeNH_2)_4]^{2+}$, in aqueous media is $10^{6.52}$, but the formation constant for the chelate analogue bis(ethylenediamine)cadmium(II), $[Cd(en)_2]^{2+}$, is $10^{10.6}$, some four orders of magnitude larger (Jones, 2002).

$$Cd^{2+}_{(aq)} + 4MeNH_{2(aq)} \rightleftharpoons [Cd(MeNH_2)_4]^{2+}_{(aq)} \qquad (1.2)$$

$$Cd^{2+}_{(aq)} + 2en_{(aq)} \rightleftharpoons [Cd(en)_2]^{2+}_{(aq)} \qquad (1.3)$$

The chelating effect is also affected by thermodynamic contributions (Hartley *et al*, 1980). In general, the following thermodynamic expression is used:-

$$\Delta G^0 = -RT \ln \beta \qquad (1.4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (1.5)$$

Where ΔG^0 is the standard free energy, R is the gas constant, T is the temperature in Kelvin, β is the equilibrium constant, ΔH^0 is the standard enthalpy and ΔS^0 is the standard entropy.

The enthalpy change (ΔH^0) and entropy change (ΔS^0) factors can have positive or negative values but their sum can have a decisive effect. The quantity β is positive ($\beta > 0$

always). With increasing β, ΔG^0 becomes more negative. More negative enthalpy or more positive entropy terms contributes to a more negative value of ΔG^0.

The size of the ring can affect the stability of the chelate complex. The rings usually have five or more members, smaller rings are possible only on rare occasions. Bond distortions are generally lowest in five- and six-membered rings, and these ring sizes are usually favoured. Five- and six-membered chelate rings are commonly considered to form the most stable complexes, with the five-membered rings rated more stable than the six. However, it is pointed out that five-membered chelate rings are better preorganized for coordinating with large metal ions, and six-membered chelate rings for coordinating with small metal ions. This tendency is valid irrespective of the hard or soft acid character of the metal ion because it is related to donor-metal-donor angles and to steric strain with different metal ions and chelate ring sizes (Hancock and Martell, 1989; Hancock *et al.*, 1989). Besides these effects, a chelating ligand generates a larger crystal field splitting than do otherwise similar monodentate ligands, and this enables the formation of more stable complexes.

1.4.2 Size and charge of the metal cation

Several properties such as electronic structure, size, oxidation state and coordination number of the metal ion affect chelate formation. The nature of the bond between metal and ligand may vary from essentially electrostatic to almost purely covalent (Bell, 1977). The relative sizes of metal ion and ligand are reported to affect the hardness of the metal ion and thereby the strength of complexation (Hancock and Martell, 1989; Hancock *et* *al.*, 1984). According to the Irving-Williams series, the general stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands is:

$$\mathrm{Mn(II)} < \mathrm{Fe(II)} < \mathrm{Co(II)} < \mathrm{Ni(II)} < \mathrm{Cu(II)} > \mathrm{Zn(II)}$$

This trend is essentially independent of the ligand.

The size of a metal ion is not invariant, but is affected by several factors, including coordination number, nature of the linked molecules and bonding, and in the case of transition metals, spin state (high/low spin).

1.4.3 Hard-Soft Acid Base (HSBA) relationship

Since metal ions behave as Lewis acids (electron pair acceptor) and ligands as Lewis bases (electron pair donor), the hardness/softness of metal ions and ligands offers away to classify them. Stable complexes result from interactions between hard acids and hard bases or between soft acids and soft bases. Ligands containing highly electronegative donor atoms, which are difficult to polarize, are classified as hard bases. Hard metal ions retain their valence electrons strongly and are not easily polarized. Ions that are small in size and possess high charge are classified as hard. Soft metal ions in turn are relatively large, do not retain their valence electrons firmly and are easily polarized (Pearson, 1968; Pearson, 1968; Pearson and Parr, 1983).

According to the hardness parameter derived from electronegativity by Parr and Pearson, (Pearson and Parr, 1983) the hardness order of the studied metal ions is $Mg^{2+} > Ca^{2+} > La^{3+} > Fe^{3+} > Zn^{2+} > Cd^{2+} > Mn^{2+} > Pb^{2+} > Cu^{2+} > Hg^{2+}$. A hardness order similar to this, expressed by Hancock and Marsicano, (Hancock and Marsicano, 1978; Hancock and Marsicano, 1980), as relative ionicity versus covalence in the M-L bond, gives the series

$Ca^{2+} > Mg^{2+} > La^{3+} > Fe^{3+} > Mn^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Cu^{2+} > Hg^{2+}$. Table 1.1 lists the hard/borderline/soft designation for the metal ions with a few other examples included in this thesis.

Table 1.1: The hard and soft acids and bases (HSAB) theory. The Lewis acids and bases presented in this thesis are included with a few examples as listed by Pearson (R = carbon chain of undetermined length).

Hard Lewis acids	**Borderline Lewis acids**	**Soft Lewis acids**
H^+, Na^+, K^+	Fe^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}	Cu^+, Ag^+, Au^+
Be^{2+}, Mg^{2+}, Sr^{2+}		Cd^{2+}, Pd^{2+}, Pt^{2+}
Sc^{3+}, Fe^{3+}, Ln^{3+}		Tl^{3+}
Hard Lewis bases	**Borderline Lewis bases**	**Soft Lewis bases**
H_2O, NH_3, R_2O	$C_6H_5NH_2$, C_5H_5N, N_2	RSH, R_2S
Cl^-, NO_3^-,		I^-, CN^-

1.4.4 Steric effects

Besides the ionic contribution and the strength of covalence of Lewis acid and base, steric hindrance may affect the formation of the M-L bond. Steric effects arise from the fact that each atom within a molecule occupies a certain amount of space. If atoms are brought too close together, there is an associated cost in energy due to overlapping electron clouds, and this may affect the molecule's preferred shape (conformation) and reactivity (Weinhold and Frank, 2001).

Steric hindrance or steric resistance occurs when the size of groups within a molecule prevents chemical reactions that are observed in related smaller molecules. Although steric hindrance is sometimes a problem, it can also be a very useful tool, and is often exploited by chemists to change the reactivity pattern of a molecule by stopping unwanted side-reactions (steric protection). When the size of the metal ion and donor atom are large, steric effects increase (Hancock and Marsicano, 1978; Hancock and Marsicano, 1980). In order for the metal complex to be stable, the ligand set must effectively occupy the metal ion coordination sphere.

1.5 Problem Statement

Heavy metals constitute a majority of the contaminants that infiltrate our water sources usually as byproducts of industrial processes (James, 2005). If ingested in even trace amounts, these materials pose many serious health risks to humans, risks that include damage to internal organs, the central nervous system and the reproductive system, as well as side effects such as nausea and vomiting. The existing water purification technologies such as ion exchange, electro-deionization are quite expensive to be readily adopted in developing countries and very few result in the complete extraction of the toxic heavy metal ions. To help advance the search for better alternative heavy metal removal from water, it is thus important to pursue methods that are cost effective, efficient and specific.

1.6 Justification of the research

The design and development of cheap and effective methods of water purification is of great significance considering the increasing level of water contamination from industrial processes. One such approach is the design of chelating ligands that are chemically specific and capable of permanently sequestering toxic heavy metal ions, even at trace levels, from drinking water.

Ideally, these ligands would work quickly, have a high binding capacity for the target analyte, and would not release its toxic bound metal ions easily. It is against this background that the extraction capability of (pyrazol-1-ylmethyl)pyridine ligands was investigated in this research work. The coordination chemistry and behavior of various metal ions towards each ligand system was investigated. This is useful in rational ligand design to target specific metal cations for selective and controlled extraction.

1.7 Significance of Study

Purification of water remains one of the major challenges in modern society. This is because the provision of clear and safe domestic water is vital for mankind. Thus, the development of chelating agents that can remove heavy metals from water is of great significance.

1.8 Objectives of the study

The main objectives of this research were:-

(i) To investigate the coordination chemistry of the (pyrazol-1-ylmethyl)pyridine lead(II), cadmium(II), and zinc(II) complexes, and

(ii) To study the ability of the pyrazolyl ligands to extract lead(II), cadmium(II), and zinc(II) cations from water.

1.9 Specific Objectives

The specific objectives of this research were:-

(i) To synthesize and characterize (pyrazol-1-ylmethyl)pyridine cadmium(II), zinc(II) and lead(II) metal complexes.

(ii) To investigate the coordination chemistry of the ligands with cadmium(II), lead(II), and zinc(II) cations.

(iii) To investigate the extracting properties of the chelating ligands with zinc(II), cadmium(II) and lead(II) metal cations.

(iv) To study the factors that control the extraction efficiency of metal cations by the pyrazolyl ligands.

(v) To use Density Functional Theory to investigate the binding properties of the ligands to cadmium(II), zinc(II) and lead(II) metal cations in order to understand the observed experimental results.

1. 10 Hypotheses

1. It is hypothesized that these chelating (pyrazol-1-ylmethyl)pyridine ligands would be effective in extraction of heavy metal ions from water due to their good donor abilities suitable for binding most heavy metal ions.

2. The bidentate and tridentate coordination mode of bis(pyrazolylmethyl)pyridine ligands would result in very stable metal complexes and hence avoid leaching of the metal ions once chelated.

3. Density Functional Theory results could be used to investigate the binding properties of the ligands to cadmium(II), zinc(II) and lead(II) metal cations in order to understand the observed experimental results.

CHAPTER TWO

LITERATURE REVIEW: COORDINATION CHEMISTRY AND EXTRACTION OF ZINC(II), CADMIUM(II) AND LEAD(II) USING CHELATING AGENTS

2.1 Introductory remarks

The rich diversity of transition metal coordination chemistry provides exciting prospects for the design and development of novel ligand systems having unique structures and valuable functional characteristics (Gardner *et al.*, 1995; Venkataraman *et al.*, 1995; Yaghi *et al.*, 1996; Hennigar *et al.*, 1997; Vatsadze *et al.*, 2005; Lee *et al.*, 1999; Bouabdallah *et al.*, 2006). Significant efforts directed towards the design of specific ligand architecture have been carried out in a number of fields of synthetic chemistry (Trofimenko, 1996). Heavy metal cations are an important group of elements due to their varied roles in biological systems ranging from essential elements to toxic compounds. It is thus important that their coordination chemistry is fully understood in order to design molecules to play specific functions. This includes design of molecules that can mimic enzymes as well as those that can remove the toxic elements from the biological systems (Zandile, 2008; Mukherjee, 1999). One such area is the use of chelating agents to remove the toxic heavy metal cations from water as complexes and insoluble precipitates.

To design suitable ligands for a specific metal cation, it is imperative that the coordination chemistry of the complexes formed be understood (Comba, 1993, Brown and Lee, 1993). This chapter therefore reviews (i) the coordination chemistry of the zinc(II), cadmium(II) and lead(II) metal cations with various donor atoms or ligands and

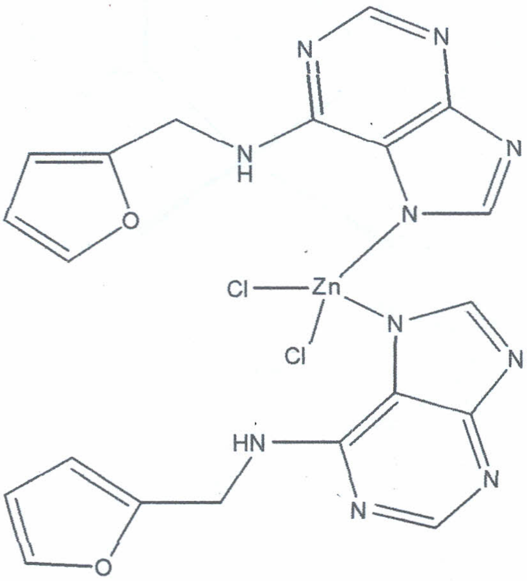
(ii) the use of chelating ligands for liquid-liquid extraction of the zinc(II), cadmium(II) and lead(II) metal cations from water.

2.2 Coordination chemistry of zinc(II), cadmium(II) and lead(II)

2.2.1 Coordination Chemistry of Zinc(II)

The role of zinc metal in living organisms is an emerging area of bioinorganic chemistry (Chao *et al.*, 1998; Tshuva and Lippard, 2004; Barondeau and Getzoff, 2004; Tainer *et al.*, 1991). It has become quite apparent over the last several years that the zinc ion plays a critical role with many divergent functions, both structural and catalytic. Examples of the structural importance of zinc include: aspartate transcarbamoylase, the zinc fingers, or the coenzyme domain of liver alcohol dehydrogenase (Lipscomb and Straeter, 1996). Typically, when playing a structural role, the metal ion is four coordinate surrounded by donor atoms originating from amino acid side chains. Thus the synthesis and characterization of model zinc compounds can provide better insight into the design of various models to perform specific tasks.

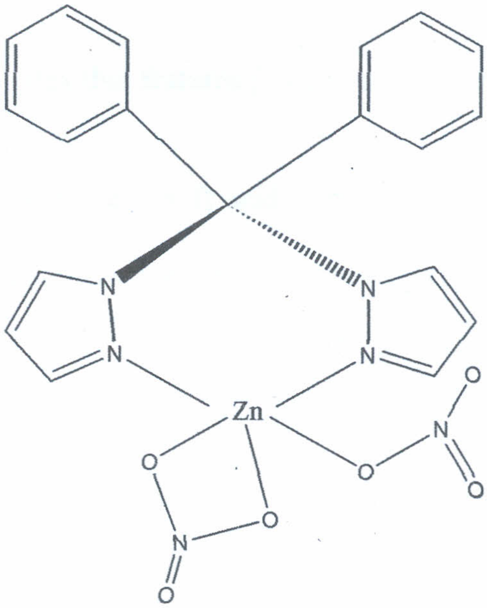
Since there is no ligand field stabilization effect in zinc(II) ions because of its fully filled 3*d* sub shell, its stereochemistry is determined solely by considerations of size, electrostatic forces, and covalent forces. Zinc has two *s* electrons outside the filled 3*d* shell ($3d^{10}4s^2$), and there is no evidence of zinc having an oxidation state higher than II (Cotton and Wilkinson, 1972). It forms a number of complexes which may be linear (*sp hybridization*) e.g. $Zn(CH_3)_2$; tetrahedral (*sp^3 hybridization*) e.g. $[Zn(NH_3)_4]^{2+}$; square pyramidal (sp^3d) e.g. $[Zn(acac)_2.H_2O]^0$ and octahedral (*sp^3d^2 hybridization*) e.g. $[Zn(en)_3]^{2+}$. However, zinc(II) normally prefers tetrahedral geometry and coordination number four is common owing to its small ionic and atomic size (Al-Jeboori *et al.*, 2010). For example, Novotná *et al.* have reported the synthesis of a zinc(II) complex of N6-furfuryladenine (**2.1**) in which the zinc(II) centre is four coordinated by two N atoms of the purine moieties of two N6-furfuryladenine molecules and two chloride ligands forming ZnN_2Cl_2 chromophore (Novotná, *et al.*, 2010).



2.1

Figure 2.1: Zinc(II) complex of N6-Furfuryladenine

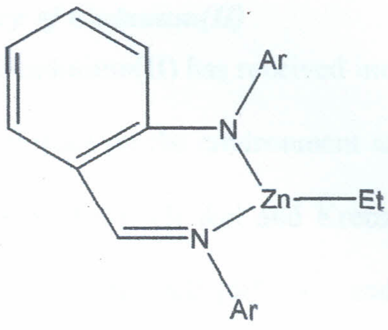
The coordination geometry in the vicinity of the central atom can be described as a distorted tetrahedron. It has been shown that the type of metal precursor (e.g. $ZnCl_2$ or $Zn(NO_3)_2$) might have a profound effect on the coordination behavior of the metal ion and this can lead to varied coordination geometries depending on the nature of the anion. For example, Shaw *et al.* have reported the synthesis of a diphenyldipyrazolylmethane complex of zinc(II) (Shaw *et al.*, 2009), in which the zinc(II) center is five coordinate, and the geometry at the metal is distorted square pyramidal (**2.2**). One NO_3 ligand displays anisodentate binding mode while the other displays a monodenticity. This is due to the flexibility of the coordination behaviour of the nitrate ligand, which resembles the bicarbonate ligand (Crichton, 2008; Kraatz and Metzler-Nolte, 2006; Parkin, 2004; Vahrenkamp, 1999; Addison *et al.*, 1984).



2.2

Figure 2.2: Diphenyldipyrazolylmethane complex of Zinc(II)

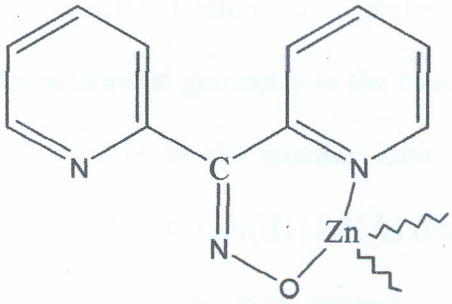
Moreover, the steric properties of the ligand profoundly affect the coordination chemistry of the metal centre as illustrated by the zinc(II) complex that features β-diketiminato and anilido-imine ligands (**2.3**) (Pang *et al.*, 2010). Due to the steric bulk of the substituents on the ligand, the zinc(II) metal center adopts a three coordinate trigonal planar geometry. Hence, control of the steric requirements of the ligand design can be used to enforce a desired geometry at the metal center.



2.3

Figure 2.3: Zinc(II) complex that features β-diketiminato and anilido-imine ligands

Zinc being on the borderline of hard-soft acids, shows strong affinity for the medium bases and also readily binds to the hard bases such as oxygen containing ligands. For example, stable tetranuclear zinc(II) complexes of the 2-pyridyl oxime chelating ligands (**2.4**) have been isolated and structurally characterized by Martinez *et al.* (Martinez *et al.*, 2008). The encapsulation of anions such as hydroxyl groups into the cavity of the tetranuclear cluster is an indication of zinc's affinity to the oxygen containing ligands.



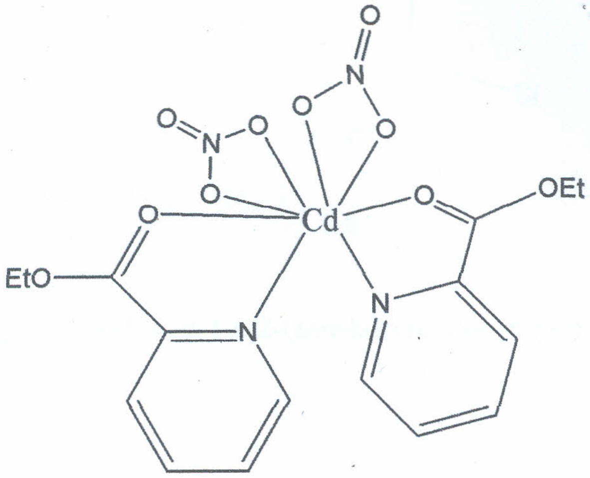
2.4

Figure 2.4: Zinc(II) complex of the 2-pyridyl oxime

2.2.2 Coordination Chemistry of Cadmium(II)

The coordination chemistry of cadmium(II) has received increased attention lately, in part due to concerns regarding its impact on the environment and its toxicological effects on health (Waalkes, 2000; Waalkes, 2003; Henkel and Krebs, 2004). Cadmium, like zinc, has two *s* electrons outside the filled *4d* shell ($4d^{10}5s^2$), and since there is no ligand field stabilization effect in cadmium(II) ions because of its completed *4d* sub shell, its stereochemistry is determined solely by considerations of size, electrostatic forces, and covalent forces. In fact, the toxic effect of cadmium is associated with the fact that it often competes with zinc for a variety of important binding sites in cells, including sites potentially important in gene regulation (Pons *et al.*, 2007). This has enhanced interests in comparative investigation of cadmium and zinc coordination chemistry with various ligands.

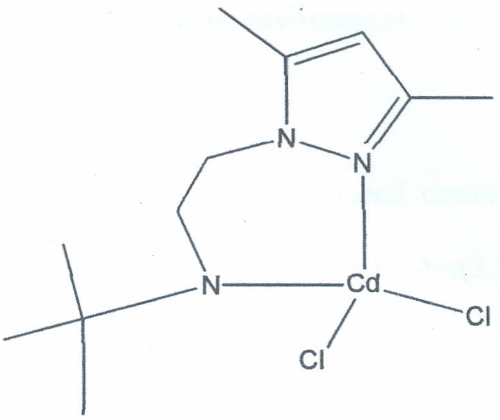
In the literature, it is observed that there are significant differences between the tetrahedral/octahedral geometry of zinc(II) and cadmium(II) (both cations are d^{10}-configured metals). While zinc(II) complexes prefer tetrahedral geometry, in cadmium(II) complexes, the octahedral geometry is the most common. This difference in coordination number is attributed to the smaller ionic radius of zinc(II) (1.38Å) compared to the larger ionic size of cadmium(II) (1.71Å) (Pons *et al.*, 2007; Pons *et al.*, 2009; Lipscomb and Straeter, 1996) . One such example in which the cadmium atom exhibits a higher coordination number of eight is the reaction of $Cd(NO_3)_2.4H_2O$ with ethyl-2-pyridinecarboxylate to give the complex $[Cd(NO_3)_2(C_5H_4NCOOEt)_2]$ **(2.5)** (Pons *et al.*, 2007) . The cadmium coordination sphere consists of bidentate nitrate anions and two bidentate ethyl picolinate ligands, to give an eight-coordinated cadmium metal center. The coordination polyhedron can thus be described as an antiprism. More than 80 eight-coordinated cadmium(II) structures have been reported in literature (Allen, 2002).



2.5

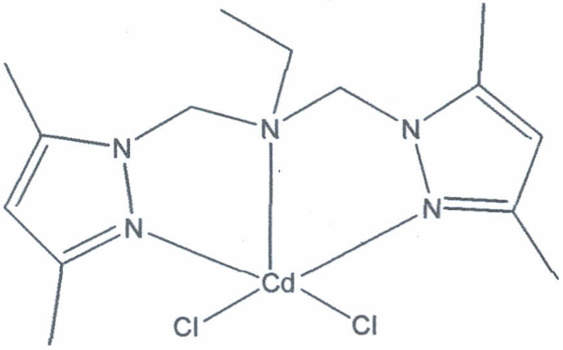
Figure 2.5: Cadmium(II) complex of ethyl-2-pyridinecarboxylate

The coordination sphere around the cadmium metal centre is largely controlled by the choice of the ligand as previously demonstrated by Pons *et al.* in the synthesis of cadmium(II) complexes of 1-[(2-(*tert*-butylamino)ethyl)-3,5-dimethylpyrazole (**deat**), (**2.6**)), and bis-[(3,5-dimethylpyrazolyl)methyl]ethylamine (**bdmae**) (**2.7**) (Pons *et al.*, 2009).



2.6

Figure 2.6: Cadmium(II) complex of 1-[(2-(*tert*-butylamino)ethyl)-3,5-dimethylpyrazole (**deat**).

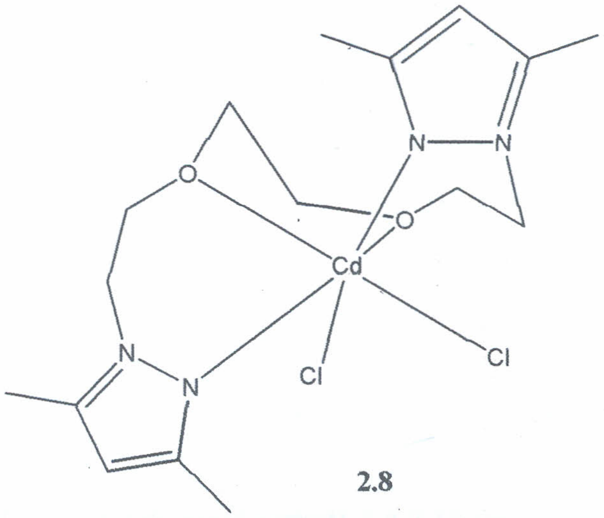


2.7

Figure 2.7: Cadmium(II) complex of bis-[(3,5-dimethylpyrazolyl)methyl]ethylamine (**bdmae**).

While in complex **2.6** the **deat** ligand showed bidentate coordination (NN′) to give a four coordination number around the metal atom, in complex **2.7**, the **bdmae** ligand is tridentate producing a five coordinate geometry. The coordination geometry in complex **2.6** is a distorted tetrahedral with bond angles (N/Cl–Cd–N/Cl) varying from 91.83(9)° to 123.66(7)°. The molecular structure of complex **2.7** consists of discrete [CdCl$_2$ (**bdmae**)] molecules linked by van der Waals forces. The central cadmium atom is pentacoordinated and surrounded by a N_3Cl_2 environment, adopting a distorted trigonal bipyramidal geometry.

A number of complexes in which the cadmium metal center adopts a six coordinate geometry have also been reported. An example is the 1,8-bis(3,5-dimethyl-1H-pyrazol-1-yl)-3,6-dioxaoctane cadmium(II) complex **(2.8)** where the cadmium centre adopts distorted octahedral coordination geometry (Pons *et al.*, 2009). The cadmium atom is coordinated to two pyrazolic nitrogen atoms and two ether oxygen atoms to form two six-membered rings and one five-membered ring.

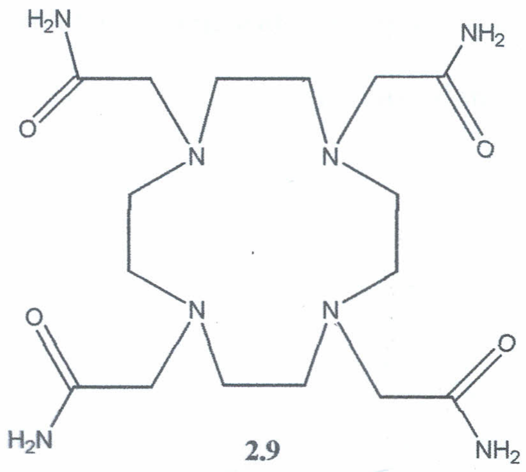


2.8

Figure 2.8: 1,8-bis(3,5-dimethyl-1H-pyrazol-1-yl)-3,6-dioxaoctane cadmium(II) complex **(2.8)**

2.2.3 Coordination Chemistry of lead(II)

Lead(II) has electronic properties resulting in a rich coordination chemistry, giving it the ability to mimic both zinc(II) and calcium(II) ions in biological systems. On the scale between hard and soft acids, it is considered as an intermediate. Therefore it has the ability to bind to different donor atoms e.g. O, N, S and P (Jones, 2002). Lead(II) ion has the tendency to form linear complexes where one of the coordination sites is occupied by the lone pair of electrons and its structures can range from those where the lone pair appears to have no steric effects, i.e., be sterically inactive or holodirected or can show steric effects, and be hemidirected (Hueso-Urená *et al.*, 1998; Cláudio, 2003; Glusker *et al.*, 1998). An example of where there is the lone pair was reported for the lead complex of the Pendant-Donor Macrocycle DOTAM (1,4,7,10-Tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane) ligand **(2.9)** (Hancock *et al.*, 2004).

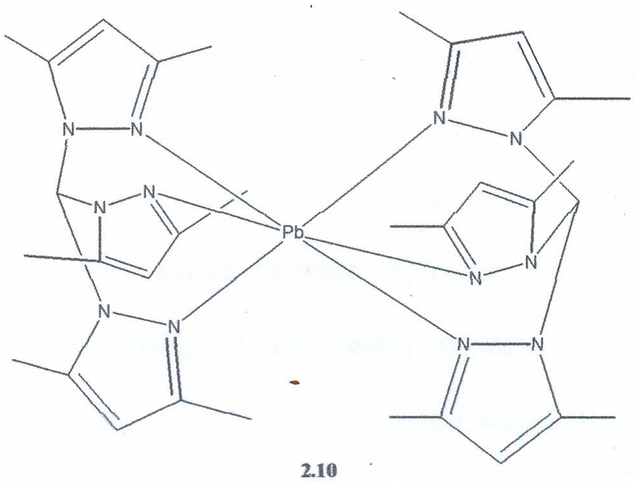


2.9

Figure 2.9: 1,4,7,10-Tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane ligand.

In the holodirected case, all Pb-L bonds are of intermediate length, and there are no marked differences in the Pb-L bond lengths, once corrected for differences in ionic radii of the donor atoms. In the hemidirected case, the characteristics of the sterically active lone pair are that (1) the Pb-L bonds on the side of the lead away from the proposed site of the lone pair are shorter than in the rest of the complex, and may be usually short for a Pb-L bond of that type; (2) there may be a gap in the coordination geometry at the site of the lone pair, or very long Pb-L bonds at this site, and (3) Pb-L bonds become progressively longer as one moves from the site opposite the lone pair to the position of the lone pair (Hancock *et al.*, 2004). According to Glusker *et al.* (Glusker *et al.*, 1998), lead(II) complexes with oxygen donor ligands and high coordination number are more likely to be holodirected, while hemidirected complexes are more likely to be of low coordination number and involve nitrogen or carbon donor ligands.

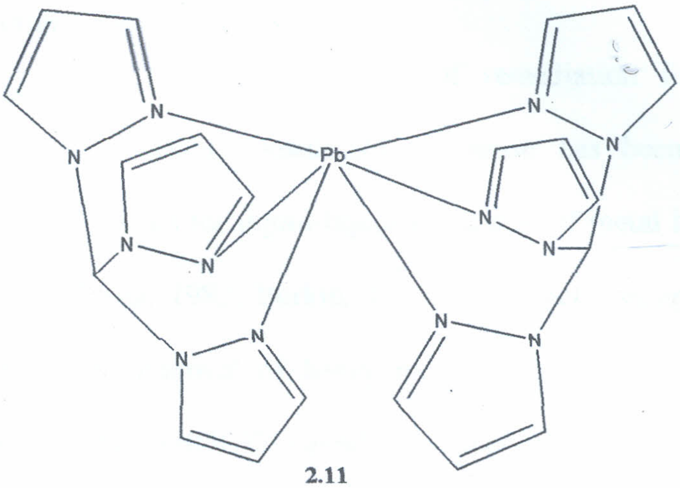
Indeed Reger *et al.* (Reger *et al.*, 1997) reported the synthesis of {[HC(3,5-$Me_2pz)_3]_2Pb$}$(BF_4)_2$ **(2.10)** and {$[HC(pz)_3]_2Pb$}$(BF_4)_2$ **(2.11)**. In **2.10**, the lead(II) ion sits on a crystallographic center of inversion with the planes formed by the three nitrogen atoms of each ligand being parallel yielding a structure of the cation that is a trigonally distorted octahedron.



2.10

Figure 2.10: An example of a lead complex with stereochemically inactive lone pair on lead(II)

Intraligand N-Pb-N bonds angles are restrained to 72.4(3)° by the chelate rings with cis interligand N-Pb-N bond angles of 107.6(3)°. All *trans* N-Pb-N angles are 180°, as required by the symmetry (Reger *et al.*, 1997). Clearly, the lone pair on lead(II) is stereochemically inactive.



2.11

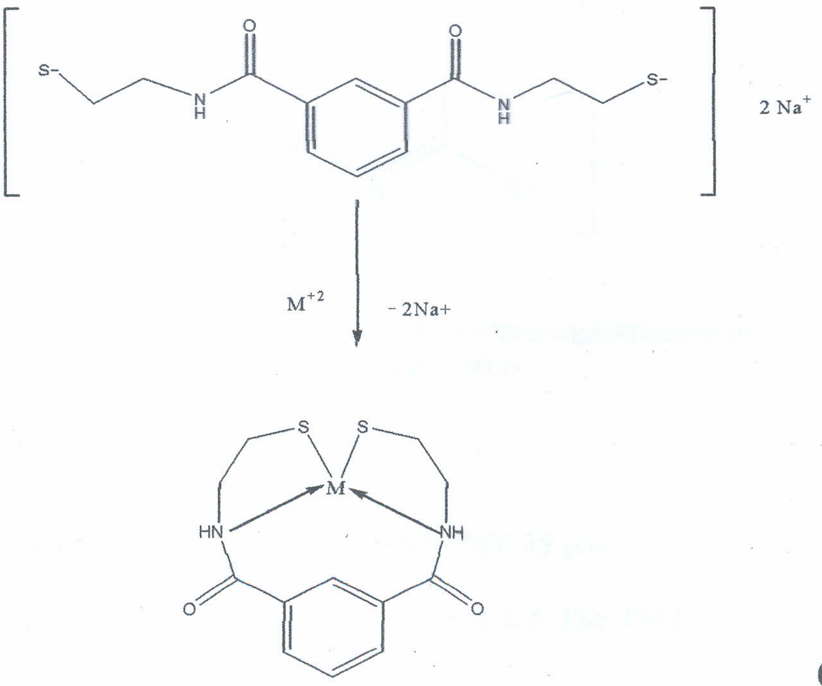
Figure 2.11: An example of a lead complex with a stereoactive lone pair on the lead(II) center

In **2.11**, the lead(II) is six coordinate but the arrangement of the nitrogen donor atoms is highly asymmetric with three pairs of Pb-N bonds of average distance 2.69Å (Reger *et al.*, 1997).The intraligand bond angles are fairly similar ranging from 65.5(2)° to 69.8(2)°; however the interligand bond angles between equivalent nitrogen atoms vary from 72.0(2)° to 140.9(2)°. These interligand bond angles correlate with the bond distances in that the longer bond distances are associated with larger angles (Reger *et al.*, 1997). The structure of **2.11** is highly distorted from a regular six-coordinate geometry and this distortion can be attributed to a stereoactive lone pair on the lead(II) center. In general, in higher coordinate lead structures, bonds adjacent to the presumed location of the lead(II) lone pair are generally longer than bonds remote from the lone pair (Harrison, 1987;

Lawton and Kokotallo, 1972). The "open" space in the structure correlates with longer adjacent bond distances.

2.3 Chelate extraction of metal cations

Chelating extraction is a potential technology of remediation for heavy metals-contaminated water and as such considerable attention has been devoted to the development of chelating agents for liquid-liquid extraction of metal ions (Lucky *et al.*, 1997; Hudson, 1982; Habashi, 1982; Burkin, 1983). One chelating agent that has been widely investigated for the removal of heavy metal cations from water is the 1, 3-benzenediamidoethanethiolate (BDET) ligand developed by Atwood and co-workers (Atwood *et al.*, 2000). The BDET ligand (Figure 2.1) exhibits a high affinity for soft heavy metals and produces insoluble complexes which are stable under low and high pH. The proposed mechanism of binding of the cations by the BDET ligand to form the insoluble complexes is represented in equation 2.1.



(2.1)

In equimolar mixture of the metal and BDET solutions, the ligand shows preferential binding to the mercury(II) cation . However, for solutions containing low mercury levels and high concentrations of other soft heavy metals, Hg binding by BDET may be kinetically impeded (Matlock *et al.*, 2002).

Another chelating agent that has been investigated for its ability to remove heavy metal cations from water is, 2, 4, 6-trimercaptotriazine, trisodium salt, nonahydrate ($Na_3S_3C_3.9H_2O$), commonly abbreviated as TMT-55 (Figure 2.12). This ligand precipitates mercury and other divalent and univalent heavy metals (e.g. cadmium, copper, lead and zinc) from water (Degussa Corporation, 1993; Henke, 1997).

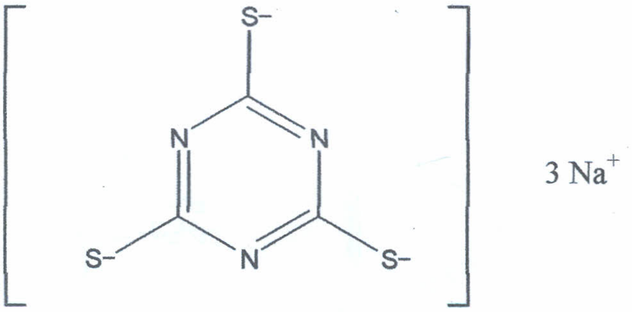


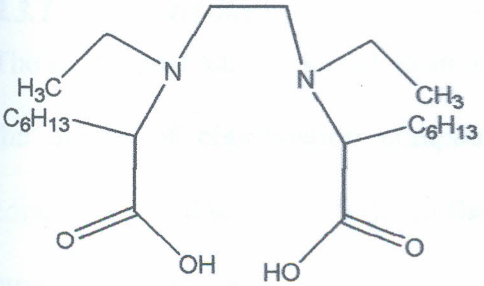
Figure 2.12: The chemical structure for 2, 4, 6-trimercaptotriazine in TMT-55 ($Na_3S_3C_3.9H_2O$) (after Degussa Corporation, 1993).

Degussa Corporation (1993) postulated that TMT-55 precipitates divalent mercury from aqueous solutions as given in equations **2.2** and **2.3**. The TMT heavy metal precipitates are described as being insoluble like metal sulfides.

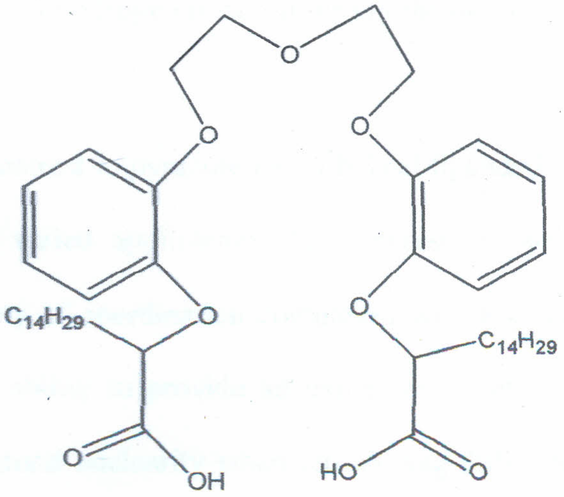
$$Na_3C_3N_3S_3.nH_2O + H_2O \longrightarrow 3Na^+ + (C_3N_3S_3)^{3-} \qquad (2.2)$$

$$2(C_3N_3S_3)^{3-} + 3Hg^{2+} \longrightarrow Hg_3(C_3N_3S_3)_2 \qquad (2.3)$$

Mixed nitrogen- and oxygen-donor ligands such as acyclic polyethers have been considerably studied due to their excellent complexation behavior with several metal ions as do cyclic polyethers (Henke *et al.*, 1997; Lindoy, 1987; Cleij *et al.*, 1997). For instance the extraction efficiency of N,N-diethyl-2,7-dihexyl-3,6-diazaoctanoic acid (Figure 2.13(**2.12**)), which contains dicaboxylate functional end-groups was investigated for aluminium(III), chromium(III), iron(III), cadmium(II), lead(II), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II) and silver(I) metal ions using a water-chloroform biphasic system (Lee *et al.*, 1999).



2.12



2.13

Figure 2.13: Structures of N, N-diethyl-2, 7-dihexyl-3, 6-diazaoctanoic acid (**2.12**) and 1,5- bis[2-(2'-carboxypentadecyloxy)phenoxy]-3-oxapentane (**2.13**)

The extraction efficiency was found to be independent of pH over the range of 2.0-10.0. Compound **(2.12)** showed very high selectivity and extractability of silver ions (95.2%) over the other 10 elements investigated due to the enhanced dynamic structural adaptability and the formation of 2:1 metal ion-acyclic multidentate complexes (Henke, *et al.*, 1997). In general, acyclic polyethers have lower stability and less ability to extract metal cations from aqueous solution compared to cyclic polyethers (Hancock, 1992).

Comparative work on the extraction efficiency of compound **(2.12)** and compound **(2.13)** was investigated for silver(I), lead(II) and nickel(II) metal ions. Ligand **(2.13)** showed excellent extraction efficiency for alkali and alkaline earth metal ions especially for calcium cations a feature attributed to the hard oxygen donor atom compared to the softer nitrogen atoms in ligand **(2.12)** (Kim *et al.*, 1998; Hancock, 1992). Compound **(2.12)** on the other hand showed higher efficiency than compound **(2.13)** especially for silver(I) ion possibly due to the presence of the moderately soft nitrogen donor groups in the motif.

2.3.1 Pyrazolyl-Based Chelating Ligands

The recent past has witnessed an increasing interest in pyrazole-based hybrid ligands for the design of coordination compounds of varied application. The interest in such compounds is due, first of all, to their variety of coordination complexes with a great number of metal ions and, second, to their ability to provide an extensive variety of coordination geometries and significant structural nuclearity when introducing different kinds of heteroatoms (Halcrow, 2009). Moreover, the past few years have seen a considerable rise in interest in the design of various pyrazole-based ligands as well as the study of their structural properties to serve specific stereochemical requirements for a particular metal-binding site (Halcrow, 2005; Bigmore *et al.*, 2005; Radi *et al.*, 2009).

Pyrazole compounds were known as early as in 1884, when Knorr discovered the antipyretic action of a pyrazole derivative in man (Acheson, 1967). This stimulated interest for pyrazole chemistry with its initial use in pharmaceuticals and dyestuffs. Figure 2.14 shows the structure of pyrazole which is a five-membered heterocycle that contains two nitrogen atoms bonded to each other with one of the nitrogens bearing a hydrogen atom.

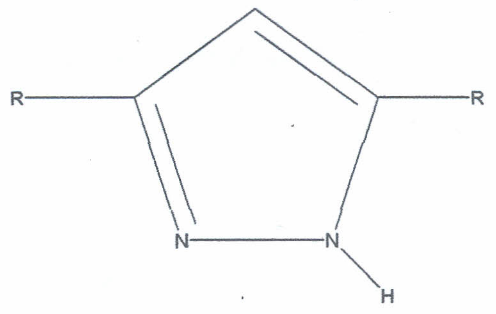
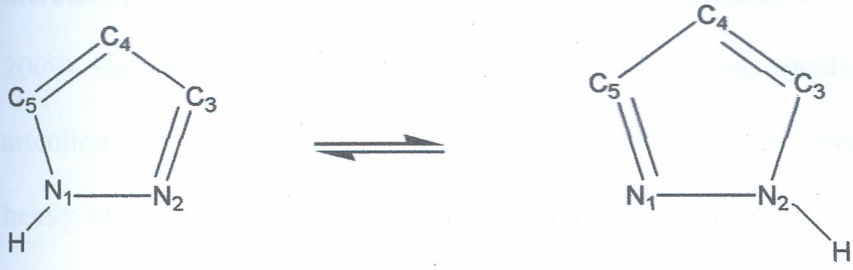


Figure 2.14: General structure of pyrazole (R=H, Me, ^{t}Bu, Ph, CF_3)

Pyrazole is tautomeric since either of the two nitrogens on the ring can bear the hydrogen atom (Equation 2.4). The nucleophilicity of the nitrogen atoms in pyrazole and their accessibility to bind metals are usually varied through an appropriate choice of substituents on the ring normally at 3-C and 5-C positions of the ring. A substituent in position 3 introduces steric hindrance and limits the number of pyrazole ligands that can be coordinated via the 2-N to the metal. To circumvent steric hindrance, 3-methylpyrazole tautomerises to 5-methylpyrazole before coordination (Trofimenko, 1993; Mukherjee, 2000), however, when pyrazole has substituents on 1-N the steric effect produced could lead to different mode of coordination and a modification of electronic properties of metal complexes formed. This class of ligands is referred to as pyrazolyl-based ligands.

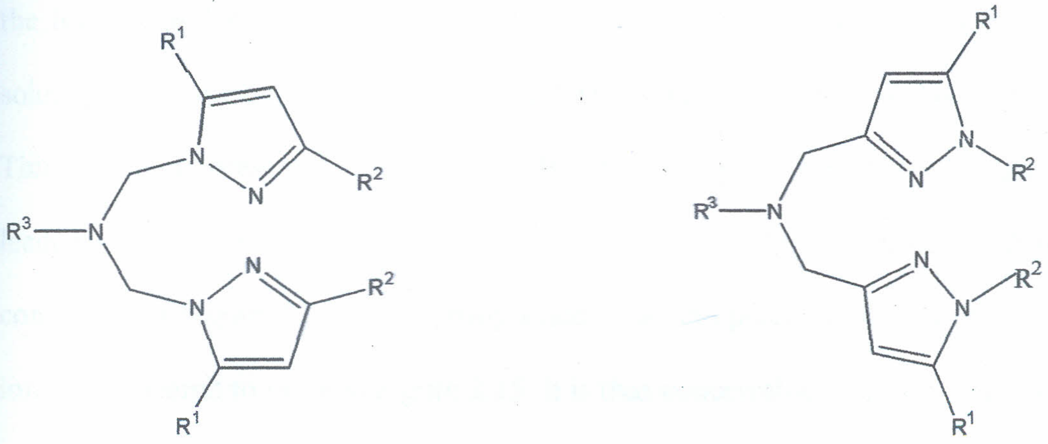


2.4

Pyrazoles and their derivatives are attractive ligands as their steric and electronic properties can be fine tuned by the appropriate choice of substituents on the 1-N, 3-C, 4-C and 5-C atoms of the pyrazole ring (Simphiwe, 2007). As a ligand, pyrazole coordinates to metals through the N-atom that does not bear the proton but when it is deprotonated it can coordinate through both N atoms as a bidentate ligand. Substituents at different positions on the pyrazole ring lead to different bonding modes, which results in a variety of pyrazolyl complexes (Mukherjee, 2000). That is, the substituents at the pyrazole ring determine the nucleophilicity of the nitrogen atoms (the bonding of the ligand to the metal centre).

Unlike some six-membered rings such as 2,2-bipyridine, which have π-electron deficiency making them π-acceptors that provide soft sites for metal coordination, pyrazoles act as hard α-donor sites (Mukherjee, 2003). Pyrazole molecules are thus good candidates for the preparation of N^N' and N^N'^N mixed ligands owing to their ease of synthesis and the possibility of electronic and steric variation of their properties (Panella *et al.*, 2006). These compounds have a linker between the pyridine and pyrazole rings.

Over the past decade, many reports on the use of pyrazole and pyrazolyl ligands in the formation of metal complexes and their application in catalysis have appeared in literature (Ojwach *et al.*, 2010; Ojwach *et al.*, 2007; Simphiwe *et al.*, 2008; Ojwach *et al.*, 2009). However, the use of pyrazolyl ligands as chelating agents has not received major attention. To date, few examples where pyrazolyl ligands have been used to remove heavy metal cations from water have been reported. One such example is the use of potential tridentate N,N-bis[(3,5-dimethylpyrazol-1-yl)methyl]-amine Figure 2.15 **(2.14)** and N,N-bis[(1,5-dimethylpyrazol-3-yl)methyl]-amine, Figure 2.15 **(2.15)**, ligands to remove Hg(II), Cu(II) and Pb(II) metals ions from water when anchored on silica (Bouabdallah *et al.*, 2006).



(2.14) **(2.15)**

Figure 2.15: Structures of N, N-bis[(3, 5-dimethylpyrazol-1-yl)methyl]amines **(2.14)** and N,N-bis[(1,5-dimethylpyrazol-3-yl)methyl]amines **(2.15)**.

Ligands of type **(2.15)** showed greater liquid-liquid extraction ability for all the metal ions compared to ligand **(2.14)**. For example, while ligand **(2.14)** (R = ph) exhibits 80%

extraction of copper(II) ions, the corresponding ligand **(2.15)** gave extraction of only 22%. However, low extraction percentages were shown depending on the R^3 substituent. It is thus evident that the linker between the two pyrazolyl units plays a role, where the N-C-C linker results in lower extraction than the N-C-N linkage. It was also observed that changing the R^3 group significantly alters the extraction efficiencies of the ligands. For instance, changing R^3 from ph to CH_2CH_2OH lowers the copper(II) extraction from 62 % to 25% (Bouabdallah, 2006). Generally both chelates show more affinities towards copper(II) and lead(II) than cadmium(II). This indicates the ligands display hard-base property thus showing poor affinity towards the soft cadmium(II) ions.

In a similar work, two different series of N-donor pyrazole ligands were investigated in the liquid-liquid extraction of copper(II), cadmium(II) and lead(II) ions from aqueous solution using methylene chloride as a solvent (Figure 2.16) (Bouabdallah *et al*, 2006). This compound presents a fair extractive affinity for copper(II) (44%) in comparison with lead(II) (9%) and poor extraction of cadmium(II) (4%). The low extraction ability of the compound in Figure 2.16 is interesting since it has the potential to coordinate two metal ions as compared to those in Figure 2.15. It is thus conceivable that steric hindrance plays a major role in determining the dynamics of coordination of the metal atoms to the ligand prior to extraction.

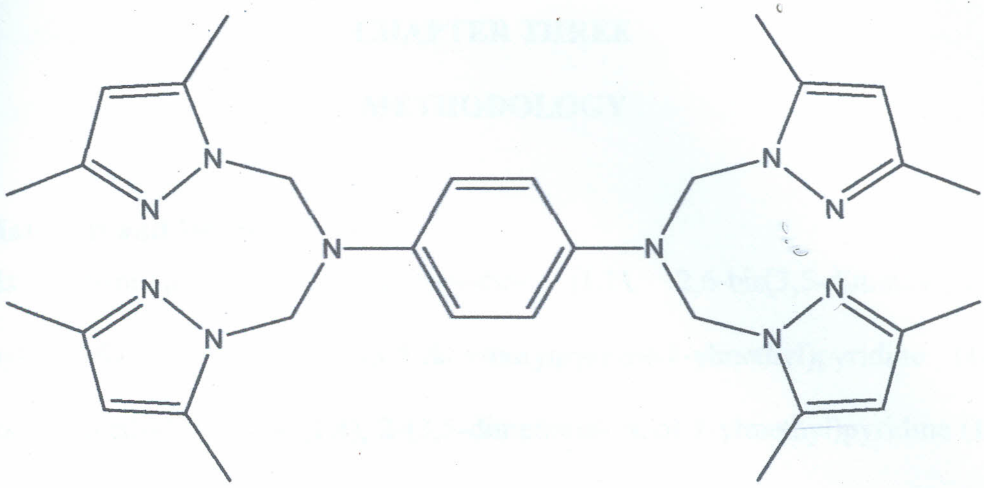


Figure 2.16: Multidentate pyrazolyl ligand used for the extraction of copper(II), lead(II) and cadmium(II) cations.

From this review, it is thus clear that pyrazole and pyrazolyl ligands can form potential chelate systems for the removal of heavy metal cations from water. Their ability to coordinate metal cations to form stable complexes can be exploited to design suitable metal chelating agents. Through careful modification of the ligand moiety, the electronic and steric properties can be fine-tuned to target specific metal ions. Due to the hard-donor property of the pyrazole ligand, it is thus expected that the pyrazolyl ligands would show preference to hard-acids (Group 1, 2 and early transition elements). In this research, we intended to modify the donor-ability of the pyrazole motif by incorporating a soft-donor, pyridine group, to the chelate system. This was expected to impart moderate donor abilities in the ligand to allow greater affinity to the moderate and soft metal cations such as zinc(II), lead(II) and cadmium(II) metals. The synthesis, characterization of the (pyrazolylmethyl)pyridine zinc(II), lead(II) and cadmium(II) complexes and the use of the pyrazolyl ligands to remove these metal cations from water by liquid-liquid extraction are described in chapters 3 and 4.

CHAPTER THREE

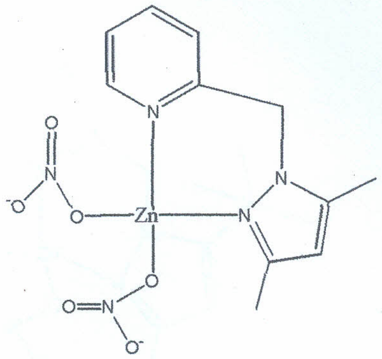
METHODOLOGY

3.1 Materials and Instrumentation

Ligands: 2,6-bis(pyrazol-1-ylmethyl)pyridine (**L1**), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**), 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L3**), 2-(pyrazol-1-ylmethyl)pyridine (**L4**), 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L5**) and 2-(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L6**) were prepared according to the methods cited in literature (Steel *et al.*, 1987; Ojwach *et al.*, 2007). The solvents and chemicals: dichloromethane (CH_2Cl_2), toluene, methanol (CH_3OH), chloroform ($CDCl_3$), hexane, pyrazole, 3,5-dimethylpyrazole, tetrabutylammonium bromide, 2-picolylchloride hydrochloride, 2,6-bis(chloromethyl)pyridine, sodium hydroxide, lead nitrate, zinc nitrate and cadmium nitrate were obtained from Sigma–Aldrich and were used as received. NMR spectra were recorded on a Bruker instrument at room temperature in $CDCl_3$ at the University of Johannesburg (^1H at 400 MHz) and on a Varian instrument at the University of Nairobi (^1H at 200 MHz). Chemical shifts are reported in δ (ppm) and referenced to the residual solvent peak of $CDCl_3$ (δ= 7.26). Coupling constants are measured in Hertz (Hz). ^1H NMR data are listed in the order: chemical shift, multiplicity, number of protons, assignment, coupling constant (J, in Hertz). Elemental analysis was performed at the Department of Chemistry, Rhodes University, South Africa. Metal determinations were measured using Atomic Absorption Spectrophotometry, on a SpectrAA-10 Varian spectrophotometer at the Department of Mines and Geology, Nairobi and Shimadzu AAS 6200 at the Department of Chemistry, Maseno University.

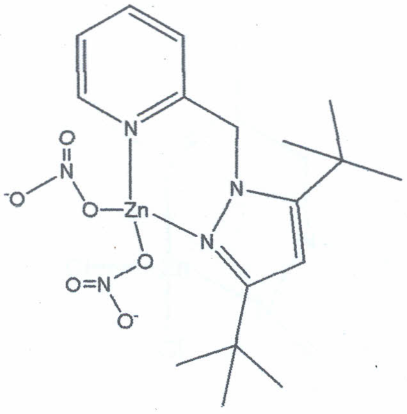
3.2 Synthesis of Zinc(II) and Cadmium(II) complexes

3.2.1 Synthesis of [2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dinitrato]zinc(II) (C1)



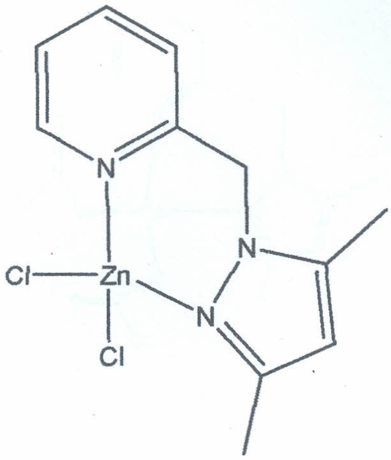
To a solution of the ligand 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L5**) (0.12g, 0.63 mmol) in methanol (10 mL) was added a solution of $Zn(NO_3)_2.4H_2O$ (0.17g, 0.63 mmol) in methanol (10 mL). The mixture was stirred for 15 h to give a clear solution. The solvent was evaporated under reduced pressure to afford an off-white (pale white) solid. Yield: 0.14g (59%). The crude product was recrystallized from CH_2Cl_2 to afford crystals suitable for single crystal X-ray analysis. Yield = 0.08g (34%). ^1H NMR: (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3, pz); 2.41 (s, 3H, CH_3, pz); 5.34 (s, 2H, CH_2); 6.03 (s, 1H, pz); 7.60 (d, 1H, py, $^3J_{HH}$ = 8.0 Hz); 7.66 (t, 1H, py, $^3J_{HH}$ = 5.6 Hz); 8.09(t, 1H, py, $^3J_{HH}$ = 7.6 Hz); 8.86(d,1H,py, $^3J_{HH}$ = 4.8 Hz). Anal. Calc for $C_{11}H_{13}N_5O_6Zn$: C, 35.08; H, 3.48; N, 18.59. Found: C, 35.33; H, 3.40; N, 18.90.

3.2.2 Synthesis of [2-(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine-dinitrato]zinc(II) (C2)



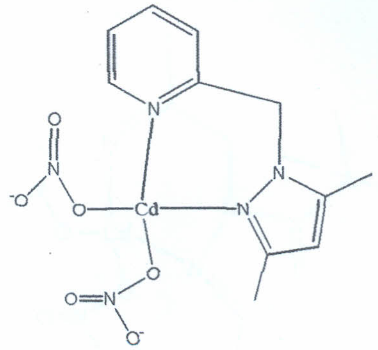
To a solution of the ligand, 2-(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L6**), (0.10g, 0.36 mmol) in methanol (10 mL) was added a solution of $Zn(NO_3)_2.4H_2O$ (0.10g, 0.36 mmol) in methanol (10 mL). The resultant clear solution was stirred for 15 h. The solvent was evaporated under reduced pressure to afford a white solid. Recrystallization from a solution of hexane/CH_2Cl_2, gave an analytically pure white compound. Yield = 0.05g (32%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 1.35 (s, 9H, ^{t}Bu, pz); 1.48 (s, 9H, ^{t}Bu, pz); 5.62 (s, 2H, CH_2); 6.12 (d, 1H, py, $^3J_{HH}$ = 17.6 Hz); 7.66 (s, 1H, pz); 8.11 (t, 1H, py, $^3J_{HH}$ = 7.2 Hz); 8.81 (d, 1H, py, $^3J_{HH}$ = 4.4 Hz). Anal. Calc for $C_{17}H_{25}N_5O_6Zn$: C, 44.31; H, 5.47; N, 15.20. Found: C, 44.21; H, 5.27; N, 15.40.

3.2.3 Synthesis of [2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dichlorido]zinc(II) (C3)



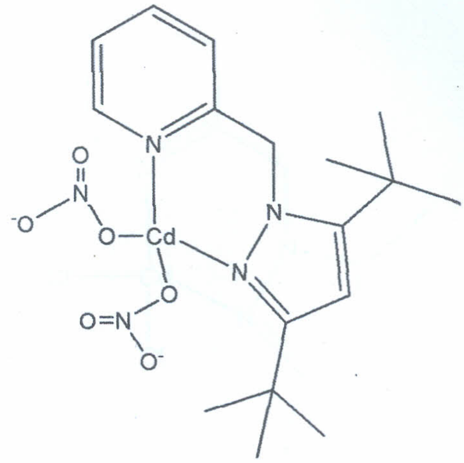
This complex was synthesized according to the procedure described for complex **C1** using ligand 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine **(L5)** (0.13g, 0.74 mmol) and $ZnCl_2$ (0.10g, 0.74 mmol). Recrystallization of the crude product from CH_2Cl_2 gave crystals suitable for single crystal X-ray analysis. Color: white solid. Yield = 0.15g (75%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.38 (s, 3H, CH_3, pz); 2.47 (s, 3H, CH3, pz); 5.49 (s, 2H, CH_2); 5.98 (s, 1H, pz); 7.56 (d, 1H, py, $^3J_{HH}$ = 7.6 Hz); 7.63 (t, 1H, py, $^3J_{HH}$ = 6.8 Hz); 8.04 (t, 1H, py, $^3J_{HH}$ = 8.0 Hz); 8.96 (d, 1H, py, $^3J_{HH}$ = 4.8 Hz). Anal. Calc for $C_{11}H_{13}Cl_2N_3Zn$: C, 40.85; H, 4.05; N, 12.99. Found: C, 40.55; H, 3.90; N, 12.62.

3.2.4 *Synthesis of [2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dinitrato]cadmium(II) (C4)*



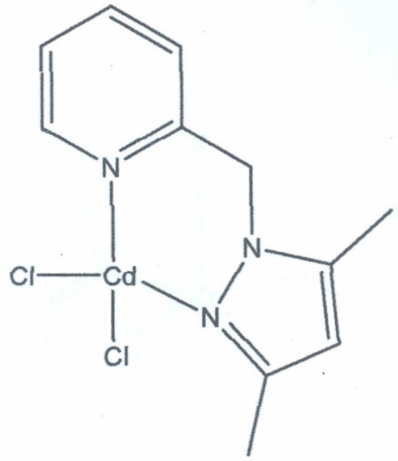
To a solution of the ligand, 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine, (0.10g, 0.54 mmol) in methanol (10 mL) was added a solution of $Cd(NO_3)_2.4H_2O$ (0.16g, 0.54 mmol) in methanol (10 mL). The resultant mixture was stirred for 15 h to give a clear solution. Slow evaporation of the methanol solvent afforded white crystals suitable for single crystal X-ray analysis. Yield: 0.20g (80%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.14 (s, 3H, CH_3, pz); 2.33 (s, 3H, CH3, pz); 5.42 (s, 2H, CH_2); 5.90 (s, 1H, pz); 7.42 (d, 1H, py, $^3J_{HH}$ = 7.6 Hz); 7.86 (t, 1H, py, $^3J_{HH}$ = 6.0 Hz); 7.88 (t, 1H, py, $^3J_{HH}$ = 6.0); 8.62 (d, 1H, py, $^3J_{HH}$ = 4.4 Hz). Anal. Calc for $C_{11}H_{13}CdN_5O_6$: C, 31.18; H, 3.09; N, 16.53. Found: C, 30.94; H, 3.05; N, 16.37.

3.2.5 Synthesis of [2-(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine-dinitrato]cadmium-(II) (C5)



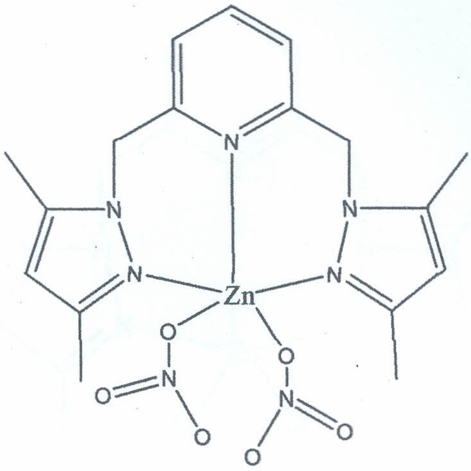
Compound **C5** was prepared following the procedure described for **C4** using **L6** (0.10g, 0.36 mmol and $Cd(NO_3)_2.4H_2O$ (0.11g, 0.36 mmol). Recrystallization from hexane/CH_2Cl_2 afforded **C5** as a pure pale yellow solid. Single crystals suitable for X-ray crystallography were grown by slow evaporation of $CHCl_3$ used for the ^1H NMR analysis. Yield: ^1H NMR: (400 MHz, $CDCl_3$): δ 1.25 (s, 9H, ^{t}Bu, pz); 1.47 (s, 9H, ^{t}Bu, pz); 5.58 (s, 2H, CH_2); 6.15 (d, 1H, py, $^3J_{HH}$ = 17.2 Hz); 7.64 (s, 1H, pz); 8.15 (t, 1H, py, $^3J_{HH}$ = 7.6 Hz); 8.85 (d, 1H, py, $^3J_{HH}$ = 4.8 Hz). Anal. Calc for $C_{17}H_{25}N_5O_6Cd$: C, 40.21; H, 4.96; N, 13.79. Found: C, 40.31; H, 5.17; N, 13.40.

3.2.6 Synthesis of [2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dichlorido] cadmium-(II) (C6)



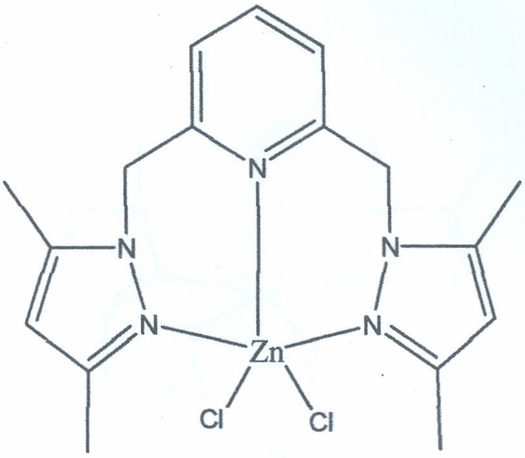
To a solution of the ligand, 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L5**), (0.10g, 0.54 mmol) in methanol (10 mL) was added a solution of $CdCl_2$ (0.11g, 0.54 mmol) in methanol (10 mL) to form a white precipitate. The resultant mixture was stirred for 15 h and filtered to give a white solid. Yield: 0.18g (90%) ^{1}H NMR: ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.28 (s, 3H, CH_3, pz); 2.51 (s, 3H, CH_3, pz); 5.45 (s, 2H, CH_2); 5.89 (s, 1H, pz); 7.61 (d, 1H, py, $^3J_{HH} = 7.6$ Hz); 7.13 (t, 1H, py, $^3J_{HH} = 7.2$ Hz); 8.11 (t, 1H, py, $^3J_{HH} = 8.4$ Hz); 8.89 (d, 1H, py, $^3J_{HH} = 4.4$ Hz). Anal. Calc for $C_{11}H_{13}CdN_3Cl_2$: C, 35.65; H, 3.54; N, 11.34. Found: C, 35.94; H, 3.25; N, 11.07.

3.2.7 Synthesis of [2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dinitrato]zinc(II) (C7)



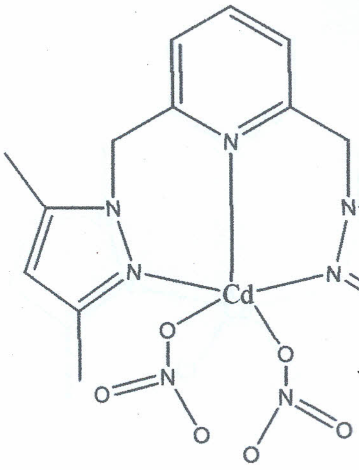
To a solution of 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**) (0.10g, 0.34 mmol) in methanol (10 mL) was added a solution of $Zn(NO_3)_2.4H_2O$ (0.10g, 0.34 mmol) in methanol (10 mL). The clear solution was stirred for 15 h and the solvent removed under reduced pressure to afford an off- white (yellowish) solid. Recrystallization from CH_2Cl_2 at ambient temperature afforded crystals suitable for single crystal X-ray analysis. Yield: 0.10g (60%) ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.31 (s, 6H, CH_3, pz); 2.35 (s, 3H, CH3, pz); 5.51 (s, 4H, CH_2); 5.84 (s, 2H, pz); 7.45 (d, 2H, py, $^3J_{HH}$ = 7.6 Hz); 7.86 (t, 2H, py, $^3J_{HH}$ = 8.2 Hz).

3.2.8 Synthesis of [2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dichlorido]zinc-(II) (C8)



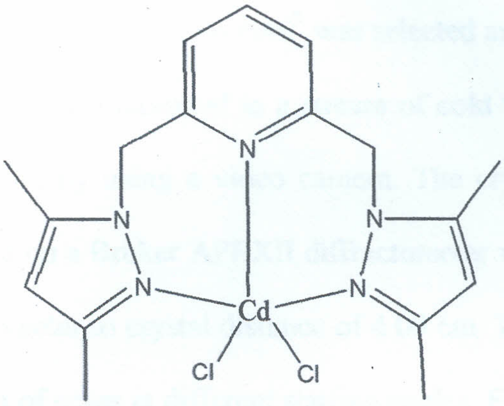
To a solution of the ligand, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine, (0.10g, 0.34 mmol) in methanol (10 mL) was added a solution of $ZnCl_2$ (0.05g, 0.34 mmol) in methanol (10 mL) to form a white precipitate. The mixture was stirred for 15 h and filtered to give a white compound. This was then washed with CH_2Cl_2 to remove excess ligand to give **C8** as an analytically pure white compound. Yield: 0.09g (59%) ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.31 (s, 6H, CH_3, pz); 2.44 (s, 3H, CH3, pz); 5.52 (s, 4H, CH_2); 5.78 (s, 2H, pz); 7.44 (d, 2H, py, $^3J_{HH}$ = 7.6 Hz); 7.96 (t, 2H, py, $^3J_{HH}$ =. Anal. Calc for $C_{17}H_{21}CdN_5Cl_2$: C, 47.30; H, 4.90; N, 16.22. Found: C, 47.65; H, 5.15; N, 16.55.

3.2.9 *Synthesis of [2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dinitrato] cadmium(II) (C9)*



To a solution of the ligand, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine, (0.20g, 0.68 mmol) in methanol (10 mL) was added a solution of $Cd(NO_3)_2.4H_2O$ (0.21g, 0.68 mmol) in methanol (10 mL). The resultant white suspension was stirred for 15 h to give an off -white precipitate. The precipitate was filtered, washed with methanol (10mL) and dried. Recrystallization from CH_2Cl_2 at room temperature afforded crystals suitable for single crystal X-ray analysis. Yield = 0.21g (58%) ^{1H} NMR: (400 MHz, $CDCl_3$): δ 2.33 (s, 6H, CH_3, pz); 2.39 (s, 3H, CH3, pz); 5.41 (s, 4H, CH_2); 5.94 (s, 2H, pz); 7.47 (d, 2H, py, $^3J_{HH}$ = 7.6 Hz); 7.96 (t, 2H, py, $^3J_{HH}$ = 8.0 Hz). Anal. Calc for $C_{17}H_{21}CdN_7O_6$: C, 38.39; H, 3.98; N, 18.44. Found: C, 38.73; H, 3.88; N, 18.13

3.2.10 Synthesis of [2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine-dichlorido]-cadmium(II) (C10)



To a solution of the ligand, 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine, (0.10g, 0.34 mmol) in methanol (10 mL) was added a solution of $CdCl_2$ (0.07g, 0.34 mmol) in methanol (10 mL). The resultant mixture was stirred for 15 h to give a white precipitate. Yield: 0.10g (61%) ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.30 (s, 6H, CH_3, pz); 2.54 (s, 3H, CH3, pz); 5.62 (s, 4H, CH_2); 5.85 (s, 2H, pz); 7.44 (d, 2H, py, $^3J_{HH}$ = 7.6 Hz); 7.91 (t, 2H, py, $^3J_{HH}$ =. Anal. Calc for $C_{17}H_{21}CdN_5Cl_2$: C, 42.65; H, 4.42; N, 14.63. Found: C, 42.25; H, 4.15; N, 14.95

3.3 X-ray Crystallography section

A typical data collection and structure refinement is described using complex **C5**.

3.3.1 Data Collection

A crystal of dimensions 0.23 x 0.16 x 0.06 mm^{-3} was selected and glued on to the tip of a glass fibre. The crystal was then mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker APEXII diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation and diffractometer to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite (Bruker-AXS, 2009). The final cell constants were calculated from a set of 6460 strong reflections from the actual data collection. The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. A total of 6792 data were harvested by collecting 2984 frames at intervals of 0.5° scans in ω and φ with exposure times of 10 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.

3.3.2 Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1/c$ that yielded chemically reasonable and computationally stable results of refinement (SUPERFLIP Palatinus and Chapuis, 2007; Farrugia, 1999; Farrugia, 1997; Sheldrick, 2008; Altomare *et al*, 1999; Burla *et al*, 2003; Burnet and Johnson, 1996;

SAINT, 1995; SADABS, 1996; Frisch *et al*, 1998). A successful solution by the direct methods of SHELXS97 (Sheldrick, 2008; SUPERFLIP Palatinus and Chapuis, 2007; Farrugia, 1999; Farrugia, 1997; Sheldrick, 2008; Altomare *et al*, 1999; Burla *et al*, 2003; Burnet and Johnson, 1996; SAINT, 1995; SADABS, 1996; Frisch *et al*, 1998) provided all non-hydrogen atoms from the *E*-map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms except those on the solvent water molecules were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The final least-squares refinement of 283 parameters against 6792 data resulted in residuals R (based on $F2$ for $I \geq 2\sigma$) and wR (based on $F2$ for all data) of 0.0328 and 0.0736, respectively. The final difference Fourier map was featureless. The molecular diagrams are drawn with 50% probability ellipsoids. The complex crystallizes with two molecules (complex molecule and a solvent molecule) in the asymmetric unit. The ligand coordinates through two N atoms in bidentate manner and to five O atoms, two each from two nitrate anions and one from a water molecule.

3.4 Extraction of metal ions

3.4.1 Extraction experiments

The extraction of metal ions was investigated using metal nitrate salts dissolved in distilled water to give concentrations of 1000 ppm. The organic solutions were made by dissolving a weighed amount of the ligand in dichloromethane to give ratios of the aqueous solution of the metal ions to the organic solution (M: L) of 1:1.For example, in the extraction of lead(II) by **L5**, lead(II) (20.0 mg, 0.097 mmol) in (20 ml) of 1000 ppm lead (II) nitrate solution was added to (20 ml) dichloromethane solution of **L5** (18.1 mg, 0.097 mmol). Solvent extractions were carried out by vigorously shaking the equal volumes (20 ml) of the metal cations in aqueous solution and the organic ligands in dichloromethane solution for 2 hours. The temperature was maintained constant at 25 °C during all experiments and pH of 7.00. The aqueous phase was separated and the extraction efficiency of each ligand was determined from the decrease of metal ion concentration in the aqueous phase by atomic absorption spectrometry.

3.4.2 AAS analysis

The aqueous phase obtained after the extraction was diluted 100-fold for AAS analysis. Single element standards were prepared for these metals from a Merck 1000 μg/mL stock solutions. All standards were made sufficiently acidic to avoid metal hydrolysis and to match content in the sample using nitric acid 65% Suprapur from Merck. Each metal ion concentration in the aqueous solution was calculated using an established calibration curve with five different corresponding standard solutions and the values obtained thereafter multiplied by the dilution factor. Percentage extractions were then calculated using the following formula:-.

$$\% Extraction = \frac{Initial\ concentrat\ ion - Final\ concentrat\ ion}{Initial\ concentrat\ ion} X100 \qquad 3.1$$

3.5 Molecular modeling

Molecular modeling experiments were performed using Gaussian03 (Sheldrick, 2008). Geometry and energies of the reactants, intermediates and products were computed using a hybrid density functional theory at the B3LYP/LANL2DZ level of theory. All calculations were performed using restricted Hartree-Fock approximations and all structures were optimized without symmetry constraints. The basis set LANL2DZ was used as a standard basis set and was not augmented. The enthalpies of formation of the complexes were computed by calculating the enthalpies of formation of the respective metal chloride salts, MCl_2, (H_1), the ligand, **L**, (H_2) and the complex, $[MLCl_2]$, (H_3). Then enthalpy of formation (ΔH_f) was thus obtained using the following equation:-

$$\Delta H_f = H_3 - (H_1 + H_2). \qquad 3.2$$

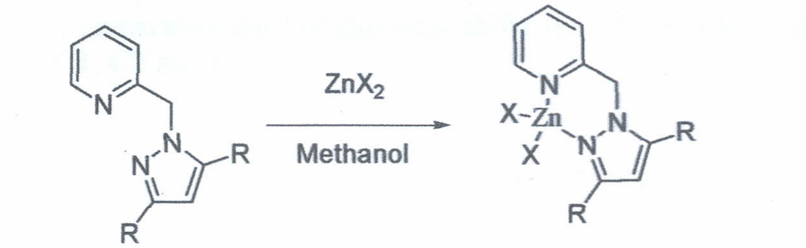
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Synthesis and characterization of zinc(II) and cadmium(II) complexes

4.1.1 Synthesis and characterization of (pyrazol-1-ylmethyl)pyridine zinc(II) complexes

The reaction of compounds **L5** and **L6** with either $Zn(NO_3)_2$ or $ZnCl_2$ in a 1:1 mole ratio resulted in the formation of the corresponding complexes **C1, C2** and **C3**. The complexes were isolated as white solids in moderate to good yields, 32-75%, (Scheme 4.1).



4.1

R = Me, X = NO$_3$ **(C1)**; R = ^{t}Bu, X = NO$_3$ **(C2)**; R = Me, X =Cl **(C3)**

Scheme 4.1: Synthesis of (pyrazol-1-ylmethyl)pyridine zinc(II) complexes

All the compounds synthesized were characterized by ^{1}H NMR, elemental analyses and in the case of **C1** and **C3**, single crystal X-ray crystallography. The ^{1}H NMR spectra of all the complexes were used as evidence of complexation. This was diagnosed by comparing the signature peaks in the free ligands and the complexes. For example, while the ^{1}H NMR spectrum of **L5** gave signature peaks of the two methyl groups at 2.17 and 2.25 ppm, the ^{1}H NMR spectrum of the corresponding complex **C1** showed a downfield shift in the peaks at 2.36 and 2.41 ppm respectively (Figure 4.1). A similar trend was observed in the four pyridine peaks which were reported at 6.78, 7.16, 7.58 and 8.54 ppm in **L5** and 7.60, 7.66, 8.09 and 8.86 ppm in the corresponding complex **C1**. These shifts were indicative of ligand coordination to the zinc metal atom. Selected ^{1}H NMR peak frequencies of ligands **L5** and **L6** and their corresponding complexes **C1, C2** and **C3** are given in Table 4.1. In contrast to previously reported palladium complexes of **L5** which showed the CH_2 linker protons as two doublets (Ojwach *et al.*, 2009), in **C1**, the CH_2 linker protons were observed as a singlet at around 5.34 ppm. In addition, the micro-analyses data of all the complexes were consistent with the expected complex structures as proposed in Scheme 4.1 (Table 4.2).

Table 4.1: Comparative data of chemical shifts for **L5** and **L6** versus the corresponding complexes **C1**, **C2** and **C3**

	Chemical shift (ppm)						
	-CH_2 linker	CH_3-pz	CH_3-pz	1H-py	2H-py	3H-py	4H-py
L5	**5.33**	**2.17**	**2.25**	**6.78**	**7.16**	**7.58**	**8.54**
C1	5.34	2.36	2.41	7.60	7.66	8.09	8.86
C3	5.49	2.38	2.47	7.56	7.63	8.04	8.96
	-CH_2 linker	^{t}Bu-pz	^{t}Bu-pz	1H-py	2H-py	3H-py	4H-py
L6	**5.58**	**1.24**	**1.32**	**6.49**	**7.12**	**7.55**	**8.52**
C2	5.62	1.35	1.48	7.66	8.07	8.11	8.81

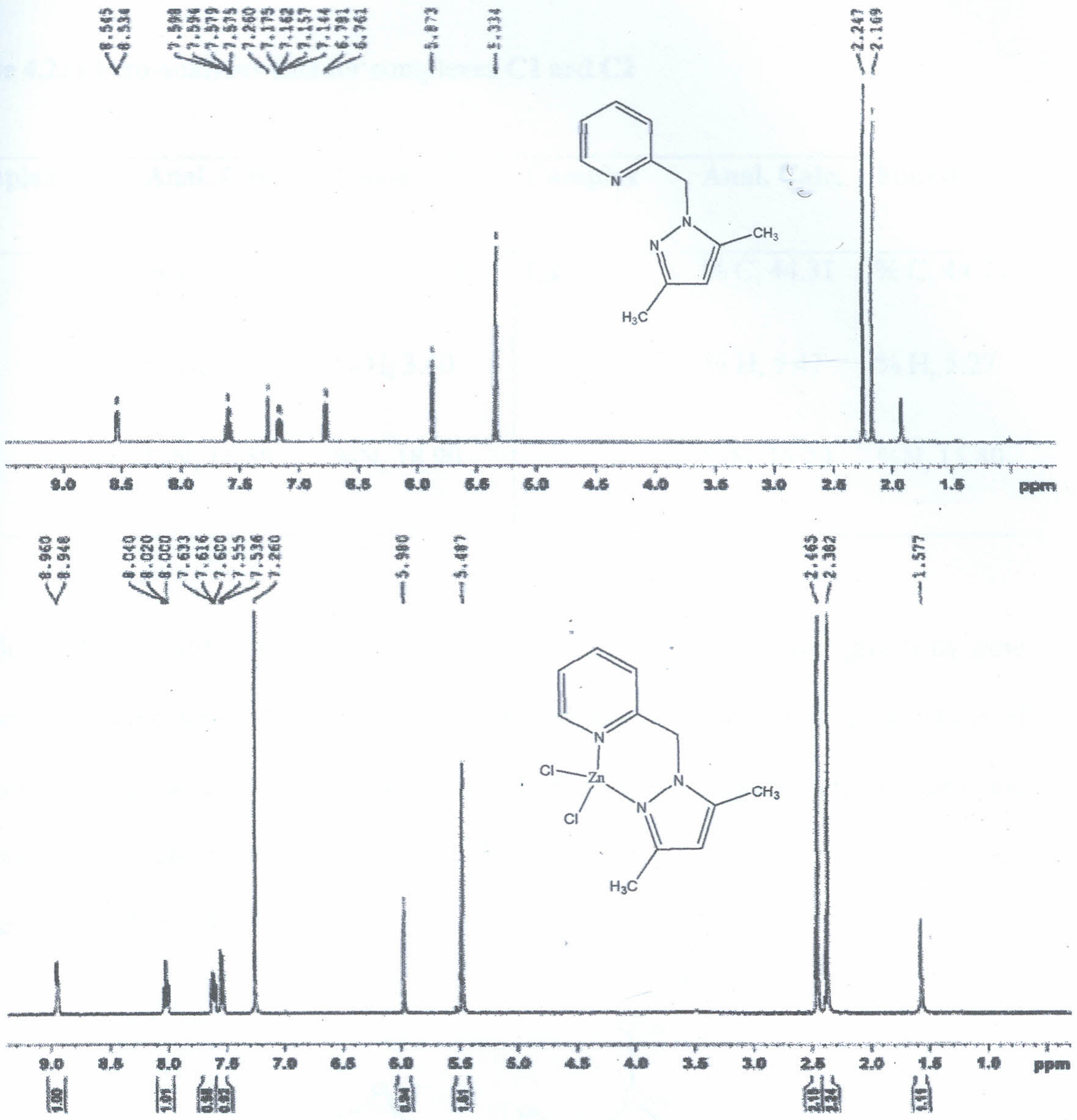


Figure 4.1: ^{1}H NMR spectra of **L5** (above) and its corresponding complex **C3** (below) showing the downfield shifts of the signals in **C3** with respect to **L5**.

Table 4.2: Micro-analyses data for complexes **C1** and **C2**

Complex	Anal. Calc.	Found	Complex	Anal. Calc.	Found
C1	% C, 35.08	% C, 35.33	**C2**	% C, 44.31	% C, 44.21
	% H, 3.48	% H, 3.40		% H, 5.47	% H, 5.27
	%N, 18.59	%N, 18.90		%N, 15.20	%N, 15.40

Single crystals suitable for X-ray analysis of complexes **C1** and **C3** were grown by slow evaporation of dichloromethane solvent at room temperature. The solid state structures of **C1** and **C3** are shown in Figures 4.2 and 4.3 respectively. Crystallographic data and structure refinement parameters are given in Table 4.3 while selected bond lengths and angles are listed in Table 4.4.

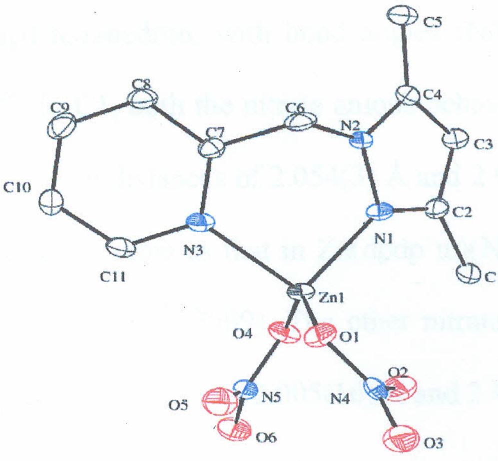


Figure 4.2: Molecular structure of the zinc(II) complex C1 shown with 50% probability ellipsoids

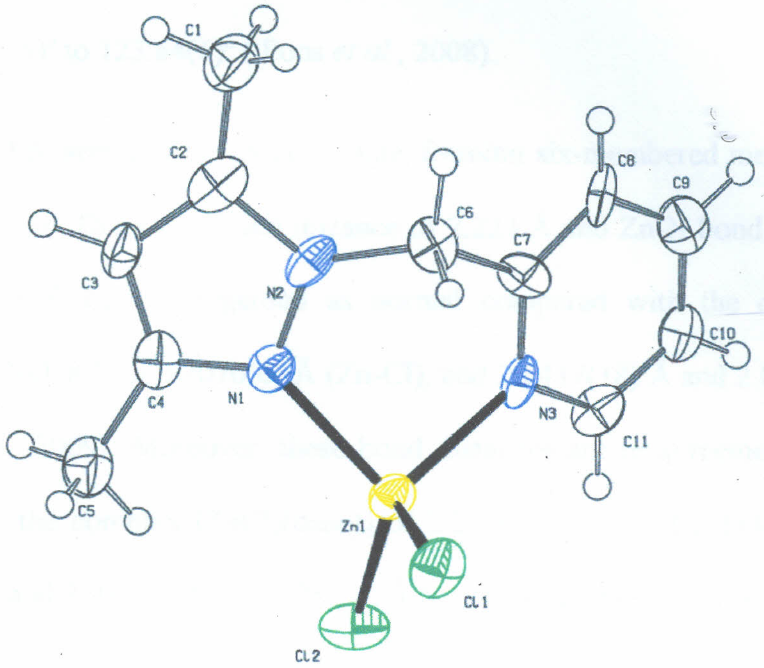


Figure 4.3: Molecular structure of complex **C3** shown with 50% probability ellipsoids

The zinc(II) atom in **C1** is four-coordinated with one bidentate ligand **L5** and two monodentate nitrate anions forming the coordination sphere. The coordination geometry is described as a distorted tetrahedron, with bond angles (N/O-Zn-N/O) varying from 95.02(13)° to 136.49(10)°. In **C1**, both the nitrate anions behave as monodentate ligands with Zn-O(1) and Zn-O(4) bond distances of 2.054(3) Å and 2.040 Å respectively. These distances are approximately the same as that in Zn(dpdp'm)$(NO_3)_2$ of 1.9605(17) Å of the monodentate nitrate (Shaw *et al.*, 2009). The other nitrate in Zn(dpdp'm)$(NO_3)_2$ is anisobidentate with Zn-O bond distances of 2.005(16) Å and 2.4730(18) Å.

The zinc ion in **C3** is four coordinated with two Zn-N bonds and two Zn-Cl bonds and the coordination geometry is also distorted tetrahedral with bond angles (N/Cl-Zn-N/Cl) varying from 92.1(5)° to 116.7(4)°. This compares well with [$ZnCl_2$(deae)] in which the zinc(II) ion is four coordinated with two Zn-N bonds and two Zn-Cl bonds resulting in a distorted tetrahedral coordination geometry with bond angles (N/Cl-Zn-N/Cl) varying from 96.64(15)° to 123.84(6)° (Pons *et al.*, 2008).

The ligand, **L5**, acts as a bidentate chelate, forming six-membered metallocyclic rings in both complexes. The Zn-Cl bond distance of 2.223 Å and Zn-N bond distances of 2.023 Å and 2.066 Å can be regarded as normal compared with the distances found in Zn(dpdpm)(NO_3)Cl of 2.2070(6) Å (Zn-Cl), and 2.0417(18) Å and 2.0179(18) Å (Zn-N) (Shaw *et al.*, 2009). Moreover, these bond distances are in agreement with the values reported for the complex [$ZnCl_2$(deae)] of 2.2206 (16) Å and 2.2346(16) Å for Zn-Cl bond length and 2.035(4) Å and 2.050(4) Å for Zn-N bond length (Pons *et al.*, 2008).

Table 4.3: Crystal data and structure refinement parameters for complexes **C1** and **C3**

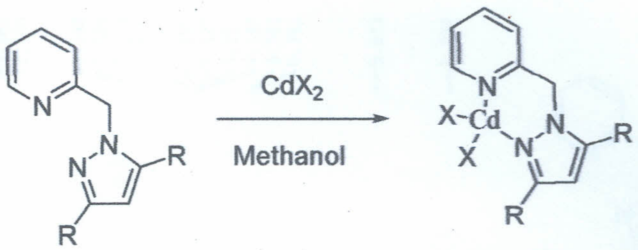
Parameter	**C1**	**C3**
Empirical formula	$C_{11}H_{13}N_5O_6Zn$	$C_{11}H_{13}Cl_2N_3Zn$
Formula weight	376.63	323.56
Temperature(K)	100(2)K	100(2) K
Wavelength	0.71069 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/c}$	$P2_{1/c}$
a/ Å	12.169(5)	9.959(5) Å
b/ Å	16.839(5)	13.023(5) Å
c /Å	18.493(5)	13.347(5) Å
α	90°.	90°
β	131.150(16)°	130.95(2)°
γ	90°	90°
Volume	2853.4(16) $Å^3$	1307.4(10) $Å^3$
Z	8	4
Density (calculated)	1.753 Mg/m^3	1.463 Mg/m^3
Absorption coefficient	1.763 mm^{-1}	2.059 mm^{-1}
F(000)	1536	588
Reflections collected	23180	24415
Completeness to theta	85.2 %	99.5 %
Goodness-of-fit on F^2	0.913	2.815
Largest diff. peak and hole	1.539 and -0.602 e.$Å^{-3}$	3.859 and -3.211 e.$Å^{-3}$

Table 4:4 Selected bond lengths [Å] and angles [°] for complex **C1** and **C3**.

Bond lengths [Å]		**Angles [°]**	
C1			
O(1)-Zn(1)	2.054(3)	N(1)-Zn(1)-O(4)	99.54(12)
O(4)-Zn(1)	2.040(3)	N(1)-Zn(1)-N(3)	95.02(13)
Zn(1)-N(1)	2.007(3)	O(4)-Zn(1)-N(3)	107.33(13)
Zn(1)-N(3)	2.051(3)	N(1)-Zn(1)-O(1)	112.58(13)
C3			
Zn(1)-N(1)	2.023(13)	N(1)-Zn(1)-N(3)	92.1(5)
Zn(1)-N(3)	2.066(13)	N(1)-Zn(1)-Cl(2)	108.2(4)
Zn(1)-Cl(2)	2.223(6)	N(3)-Zn(1)-Cl(2)	111.0(4)
Zn(1)-Cl(1)	2.223(5)	N(1)-Zn(1)-Cl(1)	116.7(4)

4.1.2 Synthesis and characterization of neutral (pyrazol-1-ylmethyl)pyridine cadmium complexes

The reaction of **L5** and **L6** with either Cd $(NO_3)_2$ or $CdCl_2$ in a 1:1 mole ratio resulted in the formation of the corresponding complexes **C4, C5** and **C6** in quantitative yields (Scheme 4.2**)**. The cadmium complexes were isolated as white solids. All the compounds synthesized were characterized by ^{1}H NMR, elemental analyses and in the case of **C4** and **C5**, single crystal X-ray crystallography. The complexes gave satisfactory C, H and N elemental analyses in agreement with mononuclear complexes as proposed in Scheme 4.2. The ^{1}H NMR spectra of all the complexes were different from those of the respective ligands indicating complexation.



4.2

R = Me, X = NO_3, **(C4)**; R = ^{t}Bu, X = NO_3; **(C5)**R = Me, X =Cl, **(C6)**

Scheme 4.2: Synthesis of neutral (pyrazol-1-ylmethyl)pyridine cadmium complexes

For instance, the ^{1}H NMR spectrum of **L5** gave signature peaks of the –CH_2 linker proton as a singlet at 5.33 ppm and typical peaks of the two methyl groups appearing at 2.17 and 2.25 ppm respectively. In the corresponding complex **C4**, the –CH_2 linker proton was observed as a singlet at 5.42 ppm and the methyl peaks at 2.14 and 2.33 ppm respectively (Figure 4.4). Similar observation was made in the four pyridine peaks. The shift of these peaks compared to those of the free ligand **L5** confirms complexation of **L5** to cadmium(II) ion. Table 4.5 contains selected ^{1}H NMR signals of ligands **L5** and **L6** and their corresponding complexes **C4, C5** and **C6**.

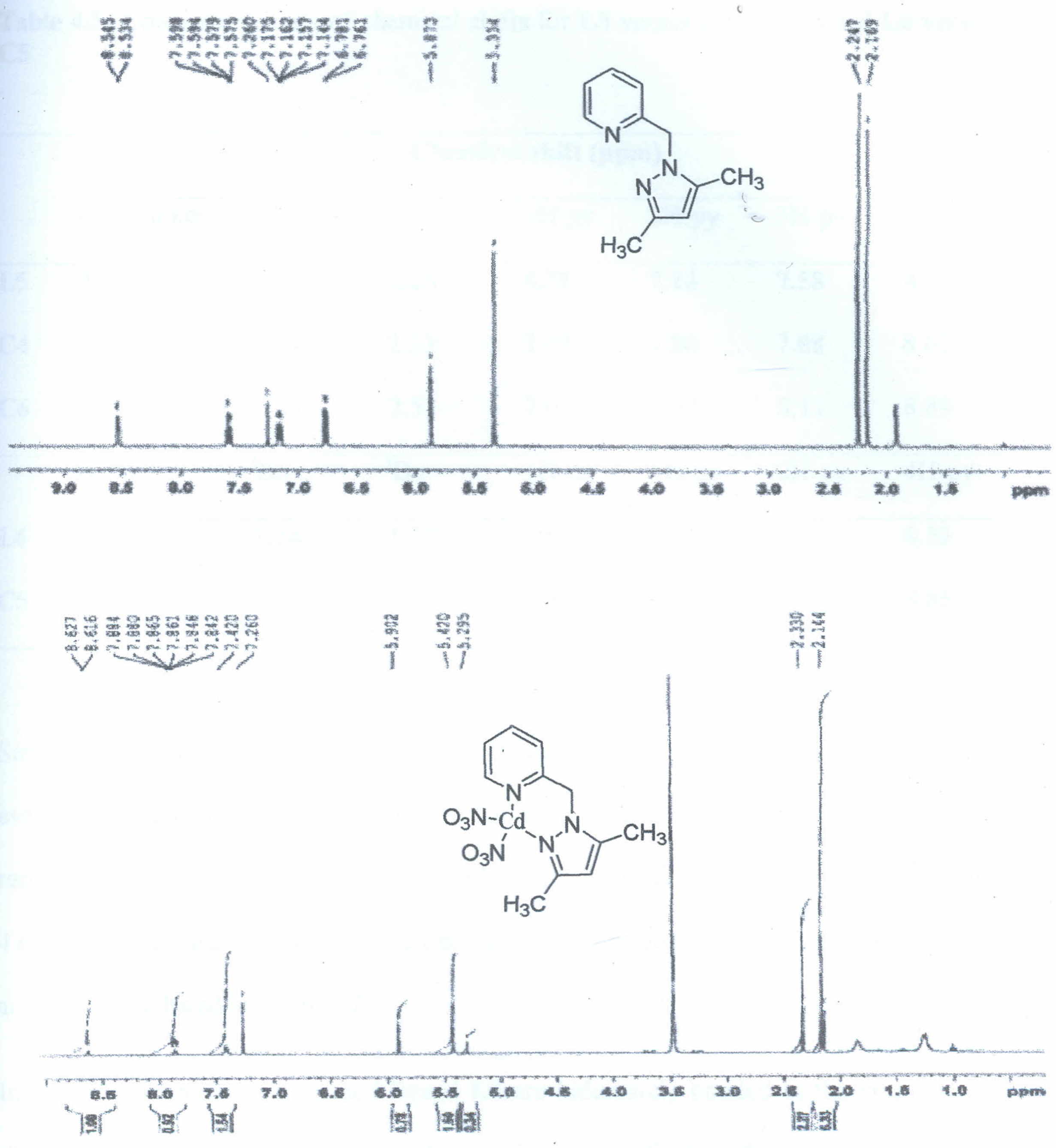


Figure 4.4: ^{1}H NMR spectra of **L5** (above) and complex **C4** (below) showing the downfield shifts of the signals in **C4** with respect to **L5**.

Table 4.5: Comparative data of chemical shifts for **L5** versus **C4** and **C6** and **L6** versus **C5**

	Chemical shift (ppm)						
	-CH_2 linker	CH_3-pz	CH_3-pz	1H-py	2H-py	3H-py	4H-py
L5	**5.33**	**2.17**	**2.25**	**6.78**	**7.16**	**7.58**	**8.54**
C4	5.42	2.14	2.33	7.42	7.86	7.88	8.62
C6	5.45	2.28	2.51	7.61	7.13	8.11	8.89
	-CH2	^{t}Bu	^{t}Bu	1H-pz	1H-py	2H-py	4H-py
L6	**5.58**	**1.24**	**1.32**	**5.94**	**6.49**	**7.57**	**8.52**
C5	5.58	1.25	1.47	7.64	6.15	8.15	8.85

Single crystals suitable for X-ray analysis of complexes **C4** and **C5** were grown by slow evaporation of methanol and chloroform solutions of **C4** and **C5** at room temperature respectively. The solid state structures of **C4** and **C5** are shown in Figure 4.5 and Figure 4.6 respectively and crystallographic data are given in Table 4.6. Selected bond lengths and angles are listed in Table 4.7.

In **C4,** the two nitrate anions and ligand **L5** are bidentately bonded to the metal centre giving two four and six-membered chelate rings respectively. The metal coordination sphere also consists of one methanol molecule, which is severely distorted resulting in a seven coordination number around the cadmium centre. The coordination polyhedron can thus be described as pentagonal bipyramid (Figure 4.5). The inter-atomic Cd-N distances of 2.293(3) and 2.337(2) Å are approximately the same as Cd-N distances of [$CdCl_2$(L)] (L= 1,8-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-3,6-dioxaoctane) (2.3111 Å) (Pons *et al.*, 2009). On the other hand, the two oxygen atoms of the bidentate nitrate groups bind to the Cd centre in a non-symmetrical manner. The Cd-O$_{nitrate}$ distances of 2.356(2) and 2.511(2) Å are of the same order as those reported for the complex [Cd(NO$_3$)$_2$(C$_5$H$_4$NCOOEt)$_2$]: (2.362(4) and (2.476(4) Å (Pons *et al.*, 2007). Moreover, these distances are compatible with those reported for Cd(NO$_3$)$_2$. 4H$_2$O (2.44(2) Å and 2.59(2) Å) (Matkovic *et al.*, 1966). They are all short enough to indicate definite Cd-O bonding interactions. The angle subtended at Cd is 52.64(8)° for O1-Cd1-O2 and is comparable to the one reported for the complex [Cd(NO$_3$)$_2$(C$_5$H$_4$NCOOEt)$_2$] (52.50(13)° (Pons *et al.*, 2007).

In **C5,** the nitrate anions are also bidentately bonded to the metal centre giving a four-membered chelate ring. The metal centre is also coordinated to a water molecule resulting in a seven coordination number around the cadmium centre. The coordination polyhedron can also be described as a pentagonal bipyramid (Figure 4.6). The Cd-N bond distances of 2.304(3) and 2.345(2) Å are comparable to those of complex **C4**; indicating less trans effect by the ligands **L5** and **L6.** On the other hand, Cd-O$_{nitrate}$ distances of 2.4422(17); 2.4589(17) and 2.4864(17); 2.3527(16) Å are of the same order as those reported for the complex [Cd(NO$_3$)$_2$(C$_5$H$_4$NCOOEt)$_2$] of (2.362(4) and (2.476(4) Å (Pons *et al.*, 2007).

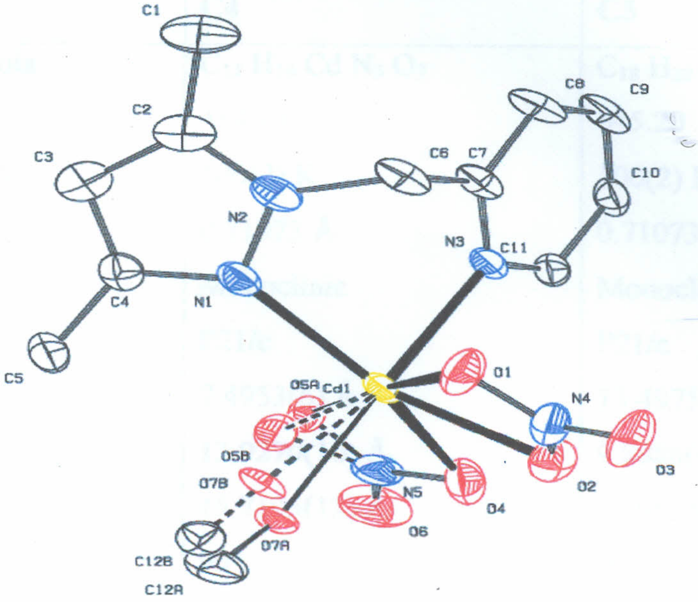


Figure 4.5: Molecular structure of **C4** shown with 50% probability ellipsoids

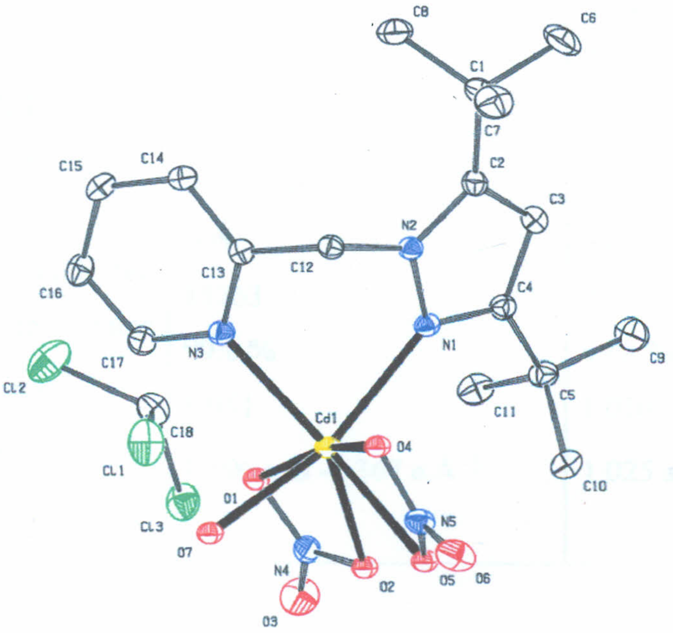


Figure 4.6: Molecular structure of **C5** shown with 50% probability ellipsoids

Table 4.6: Crystal data and structure refinement parameters for complexes **C4** and **C5**

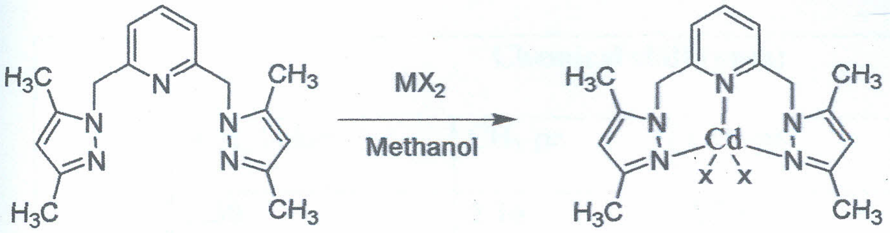
Parameter	**C4**	**C5**
Empirical formula	$C_{12} H_{16} Cd N_5 O_7$	$C_{18} H_{28} Cd Cl_3 N_5 O_7$
Formula weight	454.70	645.20
Temperature(K)	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/c
a/ Å	7.4953(6) Å	15.4975(7) Å
b/ Å	13.9270(10) Å	9.8086(4) Å
c /Å	15.7195(12) Å	19.9825(7) Å
α	90°	90°
β	92.078(2)°	117.010(3)°
γ	90°.	90°
Volume	1639.8(2) $Å^3$	2706.20(19) $Å^3$
Z	4	4
Density (calculated)	1.842 Mg/m^3	1.584 Mg/m^3
Absorption coefficient	1.379 mm^{-1}	1.148 mm^{-1}
F(000)	908	1304
Reflections collected	15763	70947
Completeness to theta	99.8 %	99.8 %
Goodness-of-fit on F^2	1.051	1.030
Largest diff. peak and hole	1.196 and -2.367 e.$Å^{-3}$	1.025 and -2.729 e.$Å^{-3}$

Table 4.7: Selected bond lengths [Å] and angles [°] for complexes **C4** and **C5**.

Bond lengths [Å]		**Angles [°]**	
C4			
N(1)-Cd(1)	2.293(3)	N(1)-Cd(1)-N(3)	81.90(9)
N(3)-Cd(1)	2.337(2)	N(1)-Cd(1)-O(2)	142.86(9)
O(1)-Cd(1)	2.511(2)	N(3)-Cd(1)-O(2)	94.90(8)
O(2)-Cd(1)	2.356(2)	N(1)-Cd(1)-O(4)	141.83(9)
O(4)-Cd(1)	2.451(3)	N(1)-Cd(1)-O(1)	90.47(9)
O(5A)-Cd(1)	2.626(5)	N(1)-Cd(1)-O(5A)	93.09(11)
		O(2)-Cd(1)-O(1)	52.64(8)
C5			
Cd(1)-N(3)	2.304(2)	N(3)-Cd(1)-N(1)	81.76(7)
Cd(1)-N(1)	2.345(2)	N(3)-Cd(1)-O(2)	134.90(7)
Cd(1)-O(2)	2.3527(16)	N(1)-Cd(1)-O(2)	110.75(6)
Cd(1)-O(4)	2.4422(17)	N(3)-Cd(1)-O(4)	100.50(6)
Cd(1)-O(5)	2.4589(17)	N(1)-Cd(1)-O(4)	85.60(6)
Cd(1)-O(1)	2.4864(17)	O(2)-Cd(1)-O(4)	122.94(6)

4.1.3 Synthesis and characterization of bis-(pyrazol-1-ylmethyl)pyridine zinc(II) and Cadmium(II) complexes

Reactions of **L2** with zinc or cadmium nitrate and chloride salts in a 1:1 mole ratio resulted in the formation of the corresponding complexes **C7** - **C10** (Scheme 4.3). The complexes were isolated as white solids in good yields (59-60%).



4.3

M = Zn, X = NO_3 (**C7**); M = Zn, X = Cl (**C8**)
M = Cd; X = NO_3 (**C9**); M = Cd, X = Cl (**C10**)

Scheme 4.3: Synthesis of bis-(pyrazol-1-ylmethyl)pyridine zinc(II) and Cadmium(II) complexes

The compounds synthesized were characterized by ^{1}H NMR, elemental analyses and in the case of **C7** and **C9**, single crystal X-ray crystallography. All the compounds gave satisfactory C, H and N elemental analyses. The ^{1}H NMR spectrum of **L2** gave signature peaks of the –CH_2 linker proton as a singlet at 5.30 ppm and typical peaks of the four methyl groups appearing at 2.16 and 2.24 ppm respectively. The pyrazole protons appeared at 5.87 ppm. These peaks were diagnostic in the next step to confirm that complexation of the ligands with the cadmium(II) had occurred (Table 4.8). The ^{1}H NMR spectrum of **C9** in general showed downfield shifts in comparison to **L2** (Figure 4.7). For instance, the –CH_2 linker proton were observed as a singlet at 5.41 ppm (5.30 ppm in **L2**) and the methyl peaks at 2.33 and 2.39 ppm (2.16 and 2.24 ppm in **L2**). The pyrazole protons of **C9** appeared at 5.94 ppm in comparison to 5.87 ppm in **L2**. Similarly, the ^{1}H

NMR spectrum of **C10** showed downfield shifts (Table 4.8). The shift of these peaks in complexes compared to those of the free ligand **L2** confirmed complexation. The micro-analyses data of complexes **C7** – **C10** were consistent with the proposed structures in Scheme 4.3.

Table 4.8: Comparative data of chemical shifts for **L2** versus complexes **C9** and **C10**

	Chemical shift (ppm)			
	-CH_2 linker	CH_3-pz	CH_3-pz	^1H-pz
L2	**5.30**	**2.16**	**2.24**	**5.87**
C9	5.41	2.33	2.39	5.94
C10	5.62	2.30	2.54	5.85

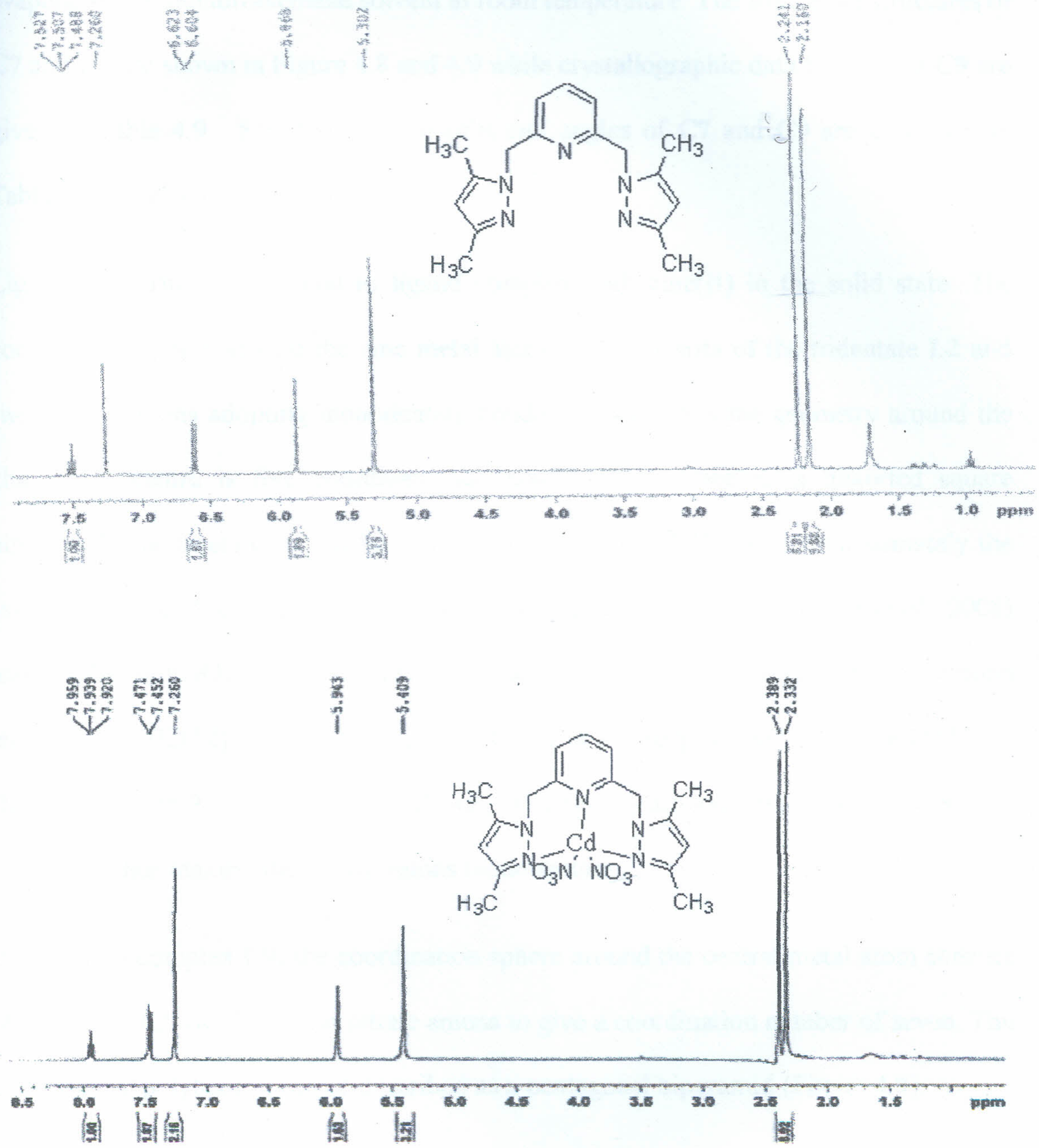


Figure 4.7: ^{1}H NMR spectra of ligand **L2** (above) and the corresponding complex **C9** (below) showing significant shifts in the **C9**.

Single crystals suitable for X-ray analysis of complexes **C7** and **C9** were grown by slow evaporation of dichloromethane solvent at room temperature. The solid state structures of **C7** and **C9** are shown in Figure 4.8 and 4.9 while crystallographic data for **C7** and **C9** are given in Table 4.9. Selected bond lengths and angles of **C7** and **C9** are contained in Tables 4.10 and 4.11 respectively.

Ligand **L2** forms a 1:1 metal to ligand complex with zinc(II) in the solid state. The coordination sphere around the zinc metal atom in **C7** consists of the tridentate **L2** and two nitrate anions adopting monodentate bonding mode. Thus the geometry around the zinc metal centre is five coordinate and could be described as a distorted square bipyramid. The interatomic Zn-N_{pz} bond distances (2.0837(12) Å) is approximately the same as the ones found for the complexes [$ZnCl_2$(deae)], 2.035(4) Å, (Pons *et al.*, 2008) and Zn(dpdpm)(NO_3)Cl, 2.0417(18) Å, (Pons *et al.*, 2009). However, the Zn-O bond length of 2.2072(12) Å is longer than that found in Zn(dpdp'm)$(NO_3)_2$ of 1.9605(17) Å (Shaw *et al.*, 2009). The Zn-O_2 and Zn-O_{2a} (Figure 4.8) are too long to be considered as real bonds thus making the nitrate anions monodentate.

In cadmium complex **C9,** the coordination sphere around the central metal atom consists of tridentate **L2**, two bidentate nitrate anions to give a coordination number of seven. The coordination polyhedron can be described as a pentagonal bipyramid (Figure 4.9).

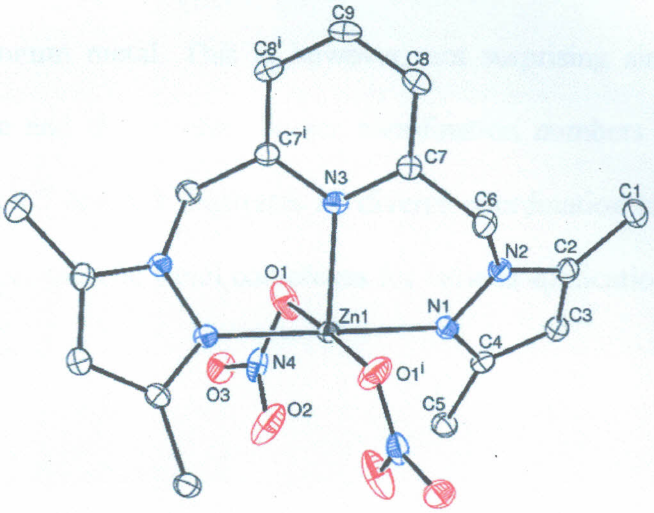


Figure 4.8: Molecular structure of the zinc complex **C7** drawn with ellipsoids at 50% probability level.

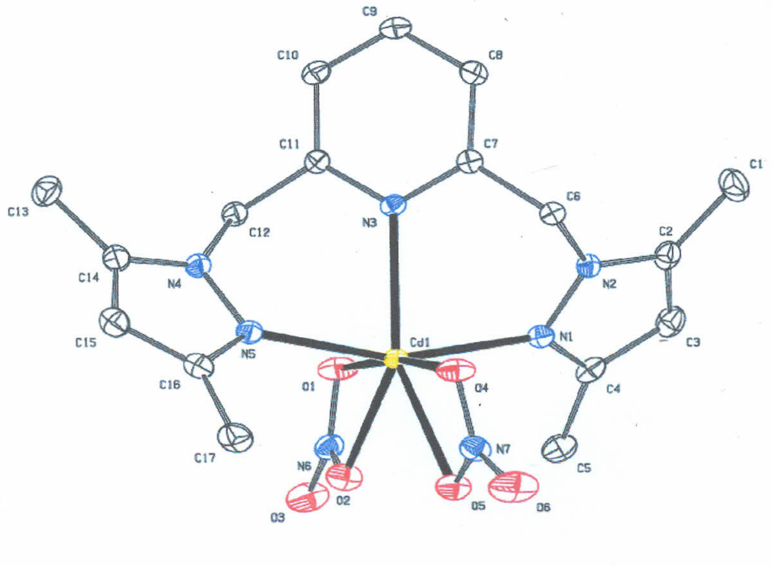


Figure 4.9: Molecular structure of the cadmium complex **C9** drawn with ellipsoids at 50% probability level

It is worth noting that while in the zinc complex (**C7**) the nitrate anions are monodentate, in the cadmium complex (**C9**), they are bidentate to afford higher coordination number around the cadmium metal. This is however, not surprising since cadmium(II) has a larger ionic size and thus prefers higher coordination numbers. The behaviour of the nitrate ligand in **C7** and **C9** illustrates its diverse coordination chemistry which can be exploited to model specific metal complexes for various applications.

Table 4.9: Crystal data and structure refinement information for complex **C7** and **C9**

Parameter	**C7**	**C9**
Empirical formula	$C_{17} H_{21} N_7 O_6 Zn$	$C_{17} H_{21} Cd N_7 O_6$
Formula weight	484.78	531.81
Temperature(K)	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P21/c
a/ Å	17.215(3) Å	14.967(5) Å
b/ Å	10.3340(17) Å	8.803(5) Å
c /Å	11.5280(19) Å	17.490(4) Å
α	90°.	90°.
β	106.607(4)°.	115.37(2)°.
γ	90°.	90°
Volume	1965.3(6) Å^3	2082.1(15) Å^3
Z	4	4
Density (calculated)	1.638 Mg/m^3	1.696 Mg/m^3
Absorption coefficient	1.303 mm-1	1.099 mm^{-1}
F(000)	1000	1072
Reflections collected	20309	51226
Completeness to theta	99.6 %	99.8 %
Goodness-of-fit on F^2	1.081	1.126
Largest diff. peak and hole	0.393 and -0.235 e.Å^{-3}	1.482 and -1.147 e.Å^{-3}

Table 4.10: Selected bond lengths [Å] and angles [°] for complex **C7**

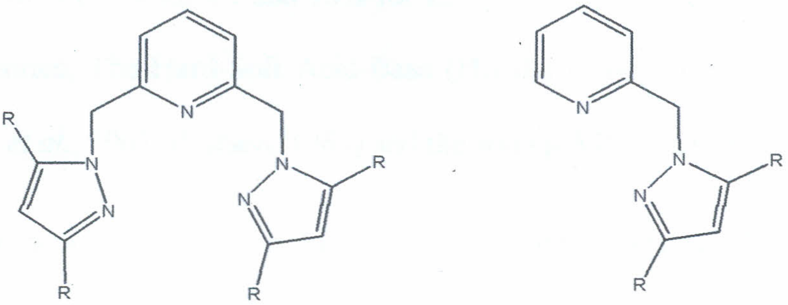
Bond lengths [Å]		**Angles [°]**	
N(1)-Zn(1)	2.0837(12)	N(1)-Zn(1)-O(1)	90.05(5)
N(3)-Zn(1)	2.1795(16)	N(3)-Zn(1)-O(1)	91.33(3)
O(1)-Zn(1)	2.2072(12)	N(1)-Zn(1)-O(1)#1	89.96(5)
		N(3)-Zn(1)-O(1)#1	91.33(3)
		O(1)-Zn(1)-O(1)#1	177.35(7)

Table 4.11: Selected bond lengths [Å] and angles [°] for complex **C9**

Bond lengths [Å]		**Angles [°]**	
Cd(1)-N(5)	2.2789(18)	N(5)-Cd(1)-N(1)	160.26(6)
Cd(1)-N(1)	2.2815(18)	N(5)-Cd(1)-O(2)	90.58(6)
Cd(1)-O(2)	2.3346(17)	N(1)-Cd(1)-O(2)	103.75(6)
Cd(1)-N(3)	2.4100(16)	N(5)-Cd(1)-N(3)	79.20(6)
Cd(1)-O(4)	2.4413(16)	N(1)-Cd(1)-N(3)	81.14(6)
Cd(1)-O(5)	2.4463(14)	O(2)-Cd(1)-N(3)	141.02(5)

4.2 Extraction of metal ions

The extraction efficiencies of 2,6-bis(pyrazol-1-ylmethyl)pyridine (**L1**), 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L2**), 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L3**), 2-(pyrazol-1-ylmethyl)pyridine (**L4**), and 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine (**L5**) (Figure 4.10) and various heavy metal ions lead(II), cadmium(II) and zinc(II)) were investigated by solvent extraction using dichloromethane-water biphasic system.



R = H (**L1**)
R = Me (**L2**)
R = ^{t}Bu (**L3**)

R = H (**L4**)
R = Me (**L5**)
R = ^{t}Bu (**L6**)

Figure 4.10: Pyrazol-1-ylmethylpyridine ligands

An aqueous phase of metal nitrate solution was employed as an aqueous phase while a dichloromethane solution of the ligand was used as an organic phase. The organic solution of the ligand was equilibrated against the aqueous phase and the amount of metal extracted in dichloromethane was determined using AAS. Extraction selectivity was investigated by mixing an aqueous solution containing zinc(II), cadmium(II) and lead(II) and an organic solution of the ligand in dichloromethane. Relative extraction efficiencies of the metal ions were determined in percentages based on total extracted metal ion concentrations.

4.2.1 Effect of metal cations

The ability of the pyrazolyl ligands to remove the heavy metal cations, zinc(II), cadmium(II) and lead(II) from water was preliminarily investigated using the potentially tridentate ligand **L1** and the bidentate ligand **L5**. This was to determine the relative affinities of the two ligand types towards different metal cations (Table 4.12). Extraction efficiency was found to be dependent on the type of metal cation, with zinc showing the highest affinity (99% for **L1** and 88% for **L5**), followed by lead, and cadmium displaying the poorest affinity (31% for **L1** and 16% for **L5**). This observed trend can be explained using two theories; The Hard-Soft Acid-Base (HASB) theory (Alexandratos and Zhu, 2005; Misono *et al.*, 1967; Pearson, 1963) and the Irving-Williams stability theory.

Using the first theory, zinc(II) is on the borderline (moderate acid, neither soft nor hard). The higher affinities of zinc(II) towards ligands **L1** and **L5** thus indicate that the ligands are also moderate (borderline) bases. It is thus conceivable that the combination of pyrazole, a hard-donor, and pyridine, a soft-donor in the ligand motif results in moderation of the donor abilities of the (pyrazolylmethyl)pyridine ligands. It is therefore reasonable that cadmium, a soft acid, showed poor binding affinity towards **L1** (31%) and **L5** (16%). These results are consistent with earlier literature reports. For example, in the structure of $[M(SCN)_4]^{2-}$ where M = cadmium(II) or zinc(II), cadmium(II) preferentially binds to the S-atom which is a soft base, while zinc(II) binds to the N-atom, which is relatively hard base (borderline) (Greenwood and Earnshaw, 1984).

The Irving-Williams stability, where a larger atomic size result in decreased stability constant of the resultant complex is also consistent with the greater affinity of zinc(II) compared to cadmium(II) cations. Zinc(II) has a smaller ionic size of 1.38 Å (Emsley,

1992) compared to cadmium (1.71 Å); hence the higher extraction efficiency by **L1** of 99% compared to 31% for cadmium follows the Irving-William series. However, an opposite trend is observed for lead(II) and cadmium(II). Lead(II) has greater ionic size (1.75Å) than cadmium(II) (1.71Å), and is expected to form a less stable complex with either **L1** or **L5** than cadmium(II). Higher extraction efficiencies of lead(II) by **L1** and **L5** in comparison to cadmium(II) therefore points that the Hard-Soft Acid Base theory plays a more significant role than the Irving-William series.

Table 4.12: Comperative profile for the extraction of zinc(II), lead(II) and cadmium(II) ions by **L1** and **L5**[a]

Entry	Ligand	Metal ion(M^{2+})	Final Conc.(ppm)[b]	% Extraction
1	**L1**	Zn	10	99
2	**L1**	Pb	345	66
3	**L1**	Cd	687	31
4	**L5**	Zn	123	88
5	**L5**	Pb	482	52
6	**L5**	Cd	845	16
7	**L5**[c]	Zn	212	36
8	**L5**[c]	Pb	269	18
9	**L5**[c]	Cd	312	5

[a](M:L=1:1), time of mixing, 2 hours, original concentration of metal solution, 1 000 ppm. Solvent system, dichloromethane (20 mL) and water (20 mL) [b]Determined by AAS. [c]Extraction of a mixture of metal ions of 330 ppm.

In an attempt to investigate the selective binding of the metal in a mixture that could mimic real water samples, **L5** was used to perform the extraction in a solution containing zinc, cadmium and lead metal metals (Table 4.12, entries 7-9). In deed, **L5** showed greater selectivity towards zinc(II) (36%), followed by lead(II) (18) and poor selectivity towards cadmium(II) (5%). It is worth noting that the ability of **L5** to remove the heavy metals drastically dropped when a mixture of the cations was used compared to pure metal solutions. This behavior could arise from competition for the ligand by the respective metal ions. The extraction efficiencies of the three metal cations, zinc(II), cadmium(II) and lead(II) were further investigated using the other ligands **L2, L3** and **L4.** The results are represented in Figure 4.11. Similar trend as discussed for **L1** and **L5** was observed.

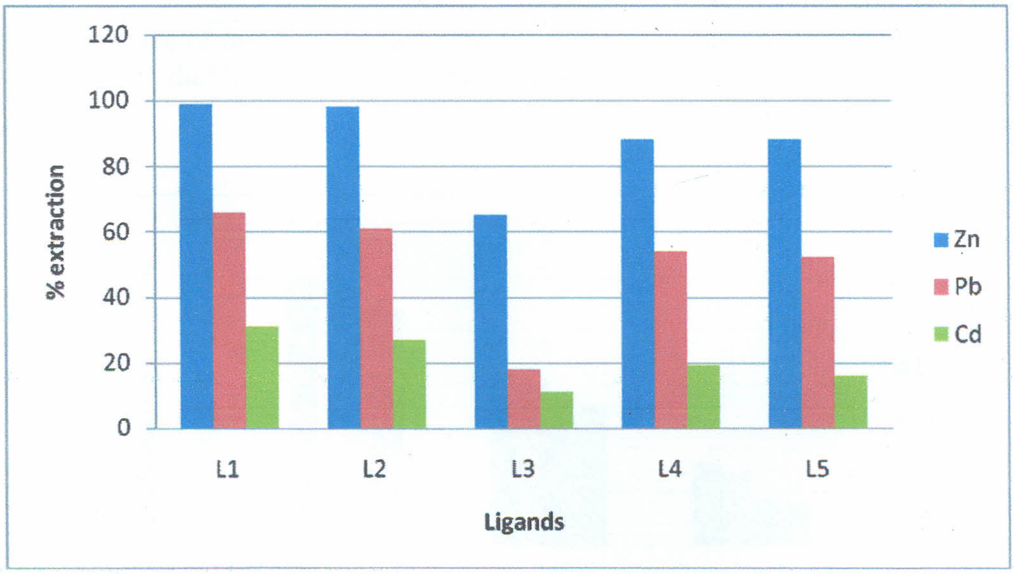


Figure 4.11: Comparative profile for the extractions of zinc(II), lead(II) and cadmium(II) cations by **L1- L5**.

4.2.2 Effect of Ligand structure on extraction efficiency of the metal cations

The effect of the nature of the chelating agents, **L1 - L5**, on the extraction efficiency for Zinc(II), lead(II) and cadmium(II) metal ions was also investigated. **L1** and **L2** are potential tridentate ligands while **L4** and **L5** are potential bidentate ligands. The profiles for the extraction of zinc(II), lead(II) and cadmium(II) by the ligands is shown in Table 4.13 and Figure 4.12.

Table 4.13: Effect of ligand structure on extraction efficiency of the metal ions.[a]

Metal/Ligand	**L1**	**L2**	**L4**	**L5**
Zinc(II)	99	98	88	88
Cadmium(II)	31	27	19	16
Lead(II)	66	61	54	52

[a](M:L=1:1), time of mixing, 2 hours, original concentration of metal solution, 1 000 ppm. Solvent system, dichloromethane (20 mL) and water (20 mL)

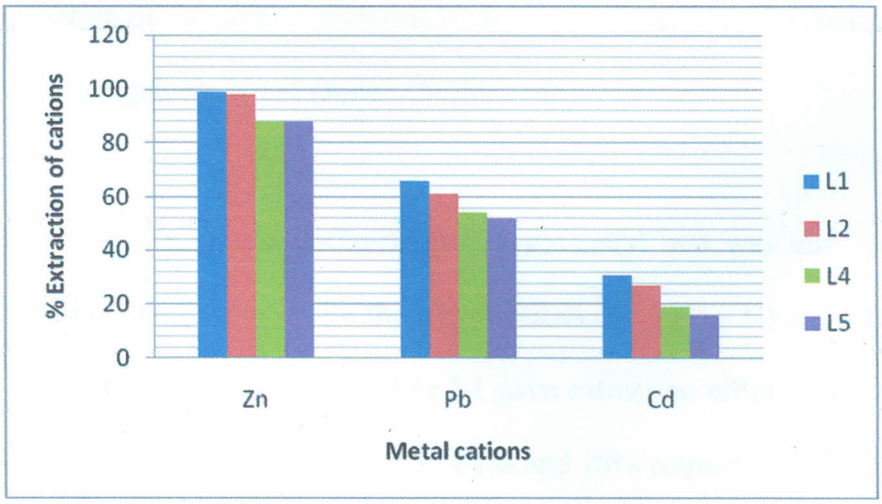


Figure 4.12: Comparative profile of ligands **L1**, **L2**, **L4** and **L5 for the extractions of** zinc(II), lead(II) and cadmium(II) **metal cations.**

The potential tridentate ligands **L1** and **L2** gave higher extraction efficiencies than the corresponding bidentate ligands **L4** and **L5** for all the metal cations. For example, **L1** had a higher extraction efficiency of 99% for zinc(II) as compared to 88% exhibited by **L4**. Similarly, **L2** had a higher extraction efficiency (98%) than **L5** (88%) for the same zinc(II) cation. This feature can be attributed to the chelate effect; the stability constant of a tridentate ligand is higher than that of a bidentate ligand due to increased chelation. An example of chelate effect is provided by the reaction between cadmium(II) ions and the unidentate ligand methylamine (Equation 4.4) or the chelating bidentate ligand ethane-1,2-diammine, en (Equation 4.5).

$$Cd^{2+}{}_{(aq)} + 4MeNH_{2\,(aq)} \rightleftharpoons [Cd(MeNH_2)_4]^{2+}{}_{(aq)} \qquad \textbf{4.4}$$

$$Cd^{2+}{}_{(aq)} + 2en_{(aq)} \rightleftharpoons [Cd(en)_2]^{2+}{}_{(aq)} \qquad \textbf{4.5}$$

The stability constant for the formation of $[Cd(MeNH_2)_4]^{2+}$ in aqueous media is $10^{6.52}$, but for the formation of the chelate analogue $[Cd(en)_2]^{2+}$ the stability constant is $10^{10.6}$, some four orders of magnitude larger (Jones, 2002).

The influence of the alkyl substituent on the pyrazolyl unit was also investigated by comparing the binding affinities for the metal cations of **L1** (R = H) and **L2** (R = Me) and **L3** (R = ^{t}Bu). It was observed that while **L1** gave extraction efficiency of 66% for lead, **L2** and **L3** gave extraction percentages of 61% and 18% respectively for the same metal cation (Figure 4.11). A similar trend was observed for **L4** and **L5** and for all the metal cations studied. This trend could be ascribed to two reasons; steric effect and water solubility. **L1** is sterically less demanding while **L3**, containing the bulkier tert-butyl groups, is sterically hindered. The less bulky ligands, **L1** and **L4**, can thus access the metal coordination sphere more easily as compared to the sterically hindered ligands **L2**, **L3** and **L5**. The ease of coordination enhances the binding affinities of the chelates to the metal atoms and thus greater extraction efficiencies reported for **L1** and **L4** compared to **L2**, **L3** and **L5**. In addition, it has also been revealed that increased steric hindrance lowers the stability of the resultant metal complexes (Ilia, 2006, Ojwach 2007). It is therefore conceivable that the lower extraction abilities of the bulkier **L3** ligand could result from the reduced formation constants of its metal complexes.

Reduced solubility of **L3** in aqueous media due to the presence of more bulky *di*-tertiary butyl groups could also be responsible for its lower extraction ability in relation to the relatively more water soluble **L1**. This can be explained from the reduced amount of **L3** entering the aqueous phase (in the interface) prior to coordination to the metal cations.

4.2.3 Effect of time and metal:ligand ratio on the extraction efficiencies of the metal cations.

The influence of various experimental parameters such as metal:ligand ratio, mixing time was studied using **L5** for the metal cations. First, the effect of metal:ligand ratio was investigated by varying the metal:ligand ratios from 1:1 to 1:2 (Table 4.14). The extraction efficiency of zinc(II) by **L5** with M:L=1:1 was 88% while that of M:L=1:2 was 87%; lead(II) by **L5** with M:L=1:1 was 52% while M:L=1:2 was 53% and for cadmium(II), M:L=1:1 was 16% while M:L=1:2 was 10%.

Table 4.14: Influence of metal:ligand ratio and time of mixing on the extraction efficiency of **L5**.

Entry	**Metal ion**	**M:L Ratio**	**Time of mixing (Hrs)**	**Final Concentration**	**% Extraction**
1	Zn	1:1	.5	180	82
2	Zn	1:1	1	107	87
3	Zn	1:1	2	123	88
4	Zn	1:2	2	107	87
5	Cd	1:1	2	845	16
6	Cd	1:2	2	893	10
7	Cd	1:1	12	770	23
8	Cd	1:1	24	730	27
9	Pb	1:1	2	482	52
10	Pb	1:2	2	474	53

[a] Original concentration of metal solution, 1 000 ppm. Solvent system, dichloromethane (20 mL) and water (20 mL).

It is evident from the results that increasing the amount of ligand (M:L = 1:2) did not improve the extraction efficiency. This indicates that monometallic complexes were formed and the metal: ligand ratio was 1:1. This phenomenon had been unequivocally confirmed by the solid state structures of the complexes as described earlier in section 4.1. The effect of time of mixing was also studied. This was done by varying the reaction time from 0.5 h to 2 h for zinc(II) and from 2 h to 24 h for cadmium(II). It was found that by increasing the mixing time from 30 min to 2 h, the extraction efficiency of zinc by **L5** increased marginally from 82% to 88%. (Table 4.14, entries 1-3). It was also found that by varying the reaction time for cadmium from 2 h to 24 h, the percentage extractions showed gradual increase from 16% to 27% (Table 4.14, entries 5,7,8). It is evident from the results that percentage extraction is affected by time variation and that there is a slight increase in extraction efficiency with increase in time.

4.3 Density functional theory (DFT) studies on the extraction abilities of bis(pyrazolylmethyl)pyridine and (pyrazolylmethyl)pyridine ligands.

In order to understand the variation in the extraction abilities of the bidentate and tridentate ligands towards various metal ions (zinc, cadmium and lead), density functional theory studies were performed at B3LYP/LANL2DZ level of theory to determine the energies of formation of the respective complexes (enthalpy of formation). It is believed that the greater the enthalpy of formation (greater formation constant), the higher the binding affinity hence the greater the extraction efficiency of a given metal cation by the respective ligand. In a typical chemical reaction, a negative free energy change would mean that the reaction is feasible (spontaneous) while a positive free energy implies that the process is not feasible. Tables 4.15 and 4.16 show DFT data obtained using ligand **L1** and **L4** and zinc, cadmium, lead and mercury cations. **L1** and **L4** were chosen due to their small size and thus reduced time of the experiment and better accuracy.

Table 4.15: Enthalpies and Gibbs free energies of coordination of metal ions to ligand **L1**

Metal ion (M^{2+})	**$\Delta H_{coordination}$ Kcal/mol[a]**	**$\Delta G_{coordination}$ Kcal/mol[a]**	**% Extracted[b]**
Zn	-116.75	-101.23	99
Cd	-107.24	-92.89	31
Pb	-109.25	-97.72	66
Hg	-91.21	-77.93	-

[a]Determined by calculation of the respective energies of **L1**, metal dichloride salts, and the complexes using DFT at the B3LYP/LANL2DZ level of theory. [b]Determined by liquid-liquid extraction of metal ions using **L1**:M ratio of 1:1; water/CH_2Cl_2 system, Time, 2 h of mixing.

Table 4.16: Enthalpies and Gibbs free energies of coordination of metal ions to ligand **L4**

Metal ion (M^{2+})	**$\Delta H_{coordination}$ Kcal/mol[a]**	**$\Delta G_{coordination}$ Kcal/mol[a]**	**% Extracted [b]**
Zn	-87.43	-75.03	88
Cd	-76.02	-64.02	19
Pb	-84.70	-76.02	54
Hg	-63.05	-52.29	-

[a]Determined by calculation of the respective energies of **L4**, metal dichloride salts, and the complexes using DFT at the B3LYP/LANL2DZ level of theory. [b]Determined by liquid-liquid extraction of metal ions using **L4**:M ratio of 1:1; water/CH_2Cl_2 system, and 2 h of mixing.

The negative free energy change values obtained indicates that the ligands easily coordinate to the metal cations. In both cases (Tables 4.15 and 4.16), zinc(II) had the highest negative enthalpy followed by lead(II) and cadmium(II). This is consistent with the extraction results given in Tables 4.13, 4.14 and 4.15 where zinc(II) had the highest extraction efficiency. In addition, the less negative values obtained for mercury(II) further augments our observed experimental results since mercury(II) is a softer metal cation than cadmium(II). From DFT results, it is therefore expected that the use of chelating ligands **L1-L5** to remove mercury(II) from water would give lower extraction percentages than those of cadmium(II) (less than 31% for **L1** and less than 19% for **L4**). Figure 4.16 shows selected optimized structures from DFT studies.

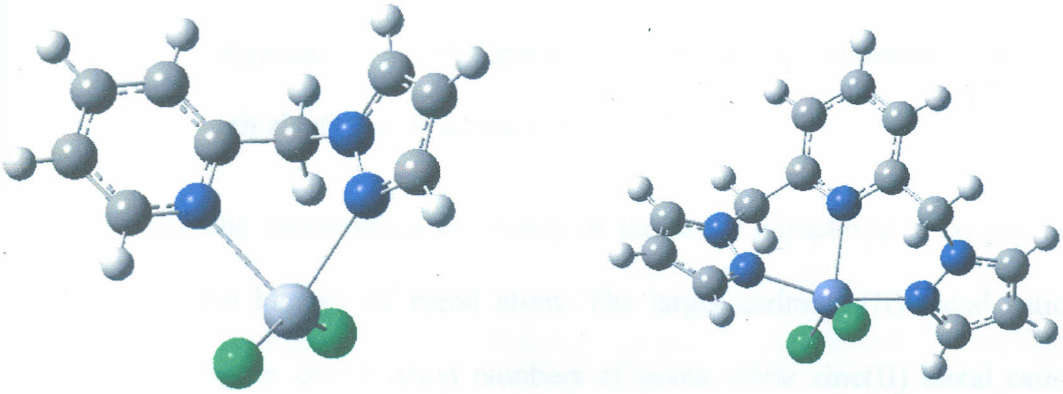


Figure 4.13: Selected optimized structures from DFT calculations

CHAPTER FIVE

CONCLUSIONS AND FUTURE PROSPECTS

5.1 Conclusions

1. Zinc(II) and cadmium(II) complexes of (pyrazol-1-ylmethyl)pyridine and bis-(pyrazol-1-ylmethyl)pyridine were synthesized and characterized using ^{1}H NMR, micro-analyses and single crystal X-ray crystallography.

2. The 2,6-bis(pyrazol-1-ylmethyl)pyridine and 2-(pyrazol-1-ylmethyl)pyridine ligands react with either $Zn(NO_3)_2$, $ZnCl_2$, $Cd(NO_3)_2$ or $CdCl_2$ to form monometallic complexes containing one ligand motif.

    i) The 2,6-bis(pyrazol-1-ylmethyl)pyridine ligands adopt tridentate binding mode with both the zinc(II) and cadmium(II) metal cations.

    ii) 2-(pyrazol-1-ylmethyl)pyridine ligands display bidentate coordination fashion with zinc(II) and cadmium(II) metal cations.

    iii) The coordination chemistry of the metal complexes is largely controlled by the identity of metal atom. The larger cadmium(II) metal cation preferred higher coordination numbers of seven while zinc(II) metal cation exhibited lower coordination numbers of four and five.

    iv) In zinc(II) complexes, the nitrate anion displayed monodenticity while in the cadmium(II) complexes, the nitrate anion displayed bidenticity. The coordination chemistry of these metal complexes highlighted the diverse binding modes of the nitrate ligand from monodentate, ambidentate to bidentate.

3. The relative affinities of 2,6-bis(pyrazol-1-ylmethyl)pyridine (**L1**), 2,6-bis(3,5-dimethyl- pyrazol-1-ylmethyl)pyridine (**L2**), 2,6-bis(3,5-ditertbutylpyrazol-1-ylmethyl)pyridine (**L3**), 2-(pyrazol-1-ylmethyl)pyridine (**L4**), and 2-(3,5-dimethylpyrazol-1-ylmethyl)- pyridine (**L5**) for lead(II), cadmium(II) and zinc(II)) by solvent extraction using dichloromethane-water biphasic system was found to be in the sequence zinc(II) > lead(II) > cadmium(II).

4. (a) The nature of the metal ion influenced the extraction ability of the ligands and the extraction sequence of $Zn^{2+} > Pb^{2+} > Cd^{2+}$ can be qualitatively interpreted by hard and soft acids and bases (HASB) theory. This therefore demonstrates that the Pyrazolyl ligands used in this study are hard bases according to HASB theory.

   (b) The ligand architecture influences the extraction efficiency of metal cations; the tridentate ligands (**L1** and **L2**) showed greater extraction efficiency than the bidentate ligands (**L4** and **L5**). It can thus be concluded that greater chelation results in enhanced stability of the coordination compounds hence greater extraction efficiency. Steric factors also control the extraction efficiency albeit with less pronounced effect; **L1** displayed greater extraction efficiency than **L3,** particularly of lead(II).

5. Theoretical calculations results obtained from Density Functional Theory on the binding affinities of the ligands to the zinc(II), cadmium(II), lead(II) and mercury(II) cations were consistent with the experimental extraction results and supported the observed experimental trends.

5.2 Recommendations

- ✓ Extend the extraction experiments to real water samples as the ligands are promising chelating agents of heavy metals from water.

- ✓ Modify the ligands so as to fine tune their donor properties to selectively target lead(II) and cadmium(II) by, for example, incorporating O and S donor atoms which would have an optimal hard/soft Lewis basicity to match the preference of the lead(II) and cadmium(II) ions.

5.3 Future prospects

- ✓ Widen the extraction of metal ions to include more heavy metals like copper(II) and mercury(II).

- ✓ To investigate the coordination chemistry of lead(II) with the pyrazolyl ligands.

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