

Ligand Design for the Selective Removal of Metal Ions from Industrial Streams and Wastewater

by Waheed Saban

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in Chemistry in the Department of Chemistry and Polymer Science,
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Supervisor: Dr. R.C. Luckay

Co-supervisor: Dr R. Malgas-Enus

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Declaration

By submitting this thesis electronically, I declare that the entirety of the work contained therein is my own original work, that I am the authorship owner thereof (unless to the extent explicitly otherwise stated) and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

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Date: December 2016

Abstract

This thesis reports the development of new types of solvent extractants for use in the hydrometallurgical recovery of base metals, and addresses the ligand design features which are needed to control the strength, transport efficiency and selectivity of these extractants.

The first section of the thesis deals with the synthesis of a new series of monocationic Schiff base ligands. The ligands are fully characterized using ^1H and ^{13}C NMR, FT-IR, mass spectrometry and elemental analysis. The extraction and bulk liquid membrane transport abilities of the ligands were evaluated by monitoring the extraction and transport of the metal ions Co(II) , Ni(II) , Cu(II) , Zn(II) , Cd(II) and Pb(II) over a 24-hour period. Palmitic acid was included in the organic phase. All ligands showed extraction of Cu(II) and Pb(II) ions, with 2 ligands being more selective towards the extraction of Cu(II) whereas the other 2 ligands extracted more Pb(II) . The extraction of Pb(II) is most likely due to a synergistic effect, since palmitic acid was added throughout the organic phase. In the transport studies, only Cu(II) ions were transported. pH-isotherms for both Cu(II) and Pb(II) were also carried out for all ligands. Interestingly Pb(II) is extracted better at lower pH's compared to Cu(II) in two cases. This study shows how these salen-type ligands, when used together with palmitic acid, show transport selectivity for Cu(II) , and in the extraction studies, extraction selectivity for Cu(II) and Pb(II) . Single crystals of two free ligands and two Cu(II) complexes were obtained and these were refined to acceptable levels. Extensive intramolecular and intermolecular hydrogen bonding is found in the free ligand structures. One Cu(II) complex is similar to that in the literature whilst the other

Cu(II) complex is novel, with Cu(II) being four co-ordinate in a structure producing a metallocycle.

The second section of this thesis describes the synthesis of several new salicylaldehyde scaffolds as well as the anchoring of substituents onto the Schiff bases in section one making them ditopic ligands. These ligands were fully characterized using ^1H and ^{13}C NMR, FT-IR, mass spectrometry and elemental microanalysis. Cu(II) was selectively extracted by all the ditopic ligands showing extraction percentages from 69% to 79%. Cu(II) and Pb(II) metal ions were transported throughout into the receiving phase by these ligands. Cu(II) complexes were synthesized using copper (II) acetate and these were characterized using FTIR and mass spectrometry. These Cu(II) complexes were then used in competitive extraction and transport studies of the anions nitrate, chloride and sulfate. Selective extraction and transport was obtained for nitrate and chloride in agreement with the Hofmeister bias.

The third section of this thesis aims to investigate how four different carboxylic acids attach to a Schiff base ligand (2-((E)-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethylamino)ethylimino)methyl)-4-tert-butylphenol); **L1** before complexation to the metal ion by using NMR studies. The extraction of both copper and lead was observed when palmitic and salicylic acid was used with the ligand. It was observed that the ligand palmitic acid assembly showed the highest uptake of lead ions above pH = 5. An extraction experiment involving palmitic acid and Pb(II) only gave 34% extraction. This behaviour is consistent with synergistic solvent extraction.

Conference Presentations

1. Oral Presentation titled, “Novel Cationic Schiff-Base Ligands for the Extraction and Transport of Transition Metal Ions” W. Saban, R. Malgas-Enus, R.C. Luckay, presented at SACI Young Symposium 2014, University of Cape Town, Cape Town, Western Cape, South Africa, October 2014.
2. Oral Presentation titled, “ Novel Schiff-base ligands for the selective extraction and transport of transition and post-transition metal ions”, W. Saban, H.F. Ogutu, R. Malgas-Enus, R.C. Luckay, presented at SACI Convention, Durban, South Africa, November 2015

Opsomming

Hierdie tesis rapporteer die ontwikkeling van nuwe ekstraermiddels vir die herwin van basis metale. Dit beklemtoon ligand ontwerpings besonderhede wat benodig word om die selektiwiteit en sterkte van hierdie ekstraermiddels te beheer.

Die eerste afdeling van hierdie skripsie behandel oor die sintese van 'n nuwe reeks monokationiese Schiff basis ligande. Die ligande word volledig gekarakteriseer met gebruik van ^1H en ^{13}C KMR, FT-IR, massa spektrometrie en elementele analise. Die ekstraksie en membraan vervoer vermoëns van die ligande is ge-evalueer deur die hoeveelheid van die metale Co(II), Ni(II), Cu(II), Zn(II), Cd(II) en Pb(II) te meet na 'n periode van 24 – uur. Palmitienseer is deurgaans in die organiese fase gevoeg. Alle ligande het ekstraksie van Cu(II) and Pb(II) getoon, met twee ligande meer selektief vir Cu(II) en die ander twee meer selektief vir Pb(II). Die ekstraksie van Pb(II) is waarskynlik weens 'n sinergistiese effek, want palmitiensuur is deurgaans in die organiese fase bygevoeg. In die vervoer studie is net Cu(II) in die ontvangs fase gevind. pH-isoterme vir beide Cu(II) en Pb(II) is gedaan vir al die ligande. Dit is interessant dat Pb(II) beter as Cu(II) ge-ekstraer word in twee gevalle. Hierdie studie toon hoe hierdie salen-tipe ligande, wanneer met palmitiensuur gebruik word, vervoer selektiwiteit vir Cu(II) toon en ekstraksie selektiwiteit vir Cu(II) en Pb(II). Enkel kristalle van twee vrye ligande en twee Cu(II) komplekse is verkry en hierdie is verfyn na aanvaarbare vlakke. Uitgebreide intramolekulêre en intermolekulêre waterstof bindings is gevind in die vrye ligand strukture.

Een Cu(II) kompleks is soortgelyk aan dit wat in die literatuur voorkom terwyl die ander Cu(II) kompleks nuut is. In hierdie een is Cu(II) gebind aan vier donor atome in 'n struktuur wat 'n metaalosiklus produseer.

Die tweede afdeling van hierdie skripsie beskryf die sintese van nege nuwe salisielaldoksiem steiers sowel as die ankerering van substituentte aan Schiff basis ligande om hulle ditopiese ligande te maak. Hierdie ligande is volledig gekarakteriseer met gebruik van ^1H en ^{13}C KMR, FT-IR, massa spectrometrie en elementele mikroanalise. Cu(II) is allenlik ge-ekstra-eer deur al die ligande met waardes vanaf 69% tot 79%. Cu(II) en Pb (II) metaal ione is deurgaans na die ontvangs medium vervoer. Cu(II) komplekse is ge-sintetiseer en hierdie is deur middel van FT-IR en massa spektrometrie gekarakteriseer. Hierdie komplekse is dan gebruik in mededingende ekstraksie en vervoer van die anione nitraat, chloride, en sulfaat. Selektiewe ekstraksie en vervoer is verkry vir nitraat en chloried wat in ooreenkoms is met die Hofmeister bias.

Die derde afdeling van hierdie skripsie se doel is om te ondersoek hoe vier verskillende karboksielsure aan 'n Schiff basis heg deur van KMR gebruik te maak. Die ekstraksie van beide koper en lood is waargeneem waneer palmitiensuur en salisielsuur tesame met die ligand gebruik word. Die ligand palmitiensuur kombinasie het die hoogste opname van lood getoon bokant pH 5.

'n Ekstraksie eksperiment met net palmitiensuur en Pb(II) het 'n resultaat van 34 % ekstraksie Pb(II) getoon. Hierdie gedrag is konsekwent met sinergistiese ekstraksie.

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List of Abbreviations/Glossary

C.A. – Carboxylic Acid

FTIR - Fourier Transform Infrared

HSAB - Hard and Soft Acid and Base

ICP-OES - Inductively Coupled plasma-Optical Emission Spectroscopy

L - Ligand

L1 - 2-((E)-(2-(2-((E)-5-tert-butyl-2-

hydroxybenzylideneamino)ethylamino)ethylimino)methyl)-4-tert-butylphenol

L2 - 2-((E)-(3-(3-((E)-5-tert-butyl-2-

hydroxybenzylideneamino)propylamino)propylimino)methyl)-4-tert-butylphenol

L3 - 2-((E)-(2-(2- (2-((E)-5-tert-butyl-2-

hydroxybenzylideneamino)ethylamino)ethylamino)ethylimino)methyl)-4-tert-

butylphenol

L4 - 2-((E)-(2-(2-((E)-5-tert-butyl-2-

hydroxybenzylideneamino)ethoxy)ethylimino)methyl)-4-tert-butylphenol

LH - chelating agent

LFSE- Ligand Field Stabilization Energy

LMCT – Ligand to metal charge transfer

MeOH - methanol

ML - Metal Ligand chelate

M^{n+} - metal cation with charge $n+$

N - donor - Nitrogen-donor

NMR - Nuclear Magnetic Resonance

O-donor - Oxygen-donor

PLS - Pregnant Leach Solution

rpm – revolution per minute

sal - salicylaldehyde

SSX - Synergistic Solvent Extraction

SX - Solvent Extraction

TGA – Thermogravimetric Analysis

via - by way of

XRD - X-Ray Diffraction

Chapter 1

Introduction and Objectives

1.1 General Introduction

Schiff base ligands are common organic molecules that have been named after Hugo Schiff and involves the reaction between an aldehyde with an amine resulting in the elimination of water molecules.^{1,2} The general structure of Schiff bases are shown in figure 1.1, where R represents a phenyl or alkyl group or a bridged Schiff base as presented in figure 1 (b), where X = alkyl or aryl and R' represents phenyl or substituted phenyl and R'' represents hydrogen or alkyl group.³

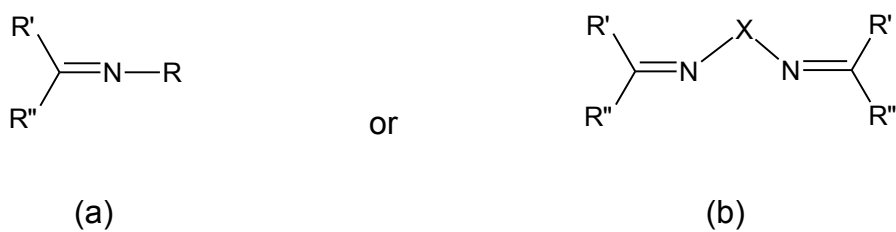


Figure 1.1: The representative structure of a Schiff base

Schiff bases are also called anils, imines, or azomethines. They exhibit interesting properties and have been used in many applications such as inorganic research, building new heterocyclic systems and for identification, detection, and determination of aldehydes and ketones. They have also been used for the purification of carbonyl or amino compounds and for the protection of these groups during complex formation or sensitive reactions. Other areas of interest include, coordination chemistry, pigments and dyes, polymer industries, vitamins and enzymes for model biomolecules.^{4,5}

Salicylaldehyde type (sal) ligands (figure 1.2) also known as 2-hydroxybenzaldehyde oxime can be modified by replacing the aldehydic hydrogen with a substituent or by placing substituents on the aromatic ring. These ligands have been used to produce metal complexes in which the phenolic proton is substituted, but it is also possible for the less acidic protons to be lost from the oximic oxygen atom. The interaction of Schiff base ligands with transition metal ions are dependent upon the presence of additional coordination donor atoms in the ligand moiety and the charge on the ligand.⁶ Schiff bases plays an important role in the formation of metal complexes owing to their ease of preparation, binding ability and the ability to extract transition metal ions.

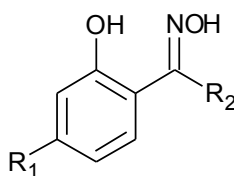


Figure 1.2: General form of a phenolic oxime ligand

Schiff bases are compounds consisting of carbon-nitrogen double bonds as a functional group, where the nitrogen atom is connected to aryl group or alkyl group (R) but not a hydrogen atom. The double bond attached to the nitrogen atoms enhances the basicity of both nitrogen atoms, which leads to increase in the stability of the complex formed. Although the Schiff bases are known to be easily synthesized and characterized, they are insoluble in aqueous solutions and they decompose easily in acidic solutions.⁷

1.2 The Chemistry of Schiff bases

The chemistry of Schiff bases and their coordination complexes have been explored for many years as a result of their interesting chemical nature. Schiff bases

are generally bi- or tridentate ligands and they are able to form stable complexes with transition metals. In organic synthesis, Schiff base reactions are useful in making carbon-nitrogen bonds.⁷ Schiff base ligands are considered to be good chelating agents,⁸ particularly when the hydroxyl functional group is in close vicinity to the azomethine group.⁹ Schiff bases are a special class of ligands with a variety of donor atoms exhibiting interesting coordination modes towards transition metals,¹⁰ while azomethine linkage is responsible for the biological activities.¹¹ Schiff bases derived from various amines¹² have produced interesting compounds that have been applied in many industrial applications such as in catalytic reactions, and materials chemistry.¹³ Schiff base complexes have resulted in many coordination geometries as a result of their different structural features and also display flexible oxidation states.¹⁴⁻¹⁶

Schiff base compounds are known to have certain unique properties such as thermal stabilities, abnormal magnetic properties, high synthetic flexibility, coordinating ability and medicinal utility. The various substituents appended to the benzene ring to produce different Schiff bases have electron-donating or electron-withdrawing properties and as such the selectivity towards certain metal ions is enhanced.

Schiff bases lacking hydrogen atoms α to the carbon-nitrogen double bond react with Grignard and organolithium reagents (alkyl and aryl) analogously to carbonyl compounds to yield adducts which on hydrolytic work-up afford secondary amines in good to excellent yields (60-90 %). Some examples of Schiff bases are shown in figure 1.3.

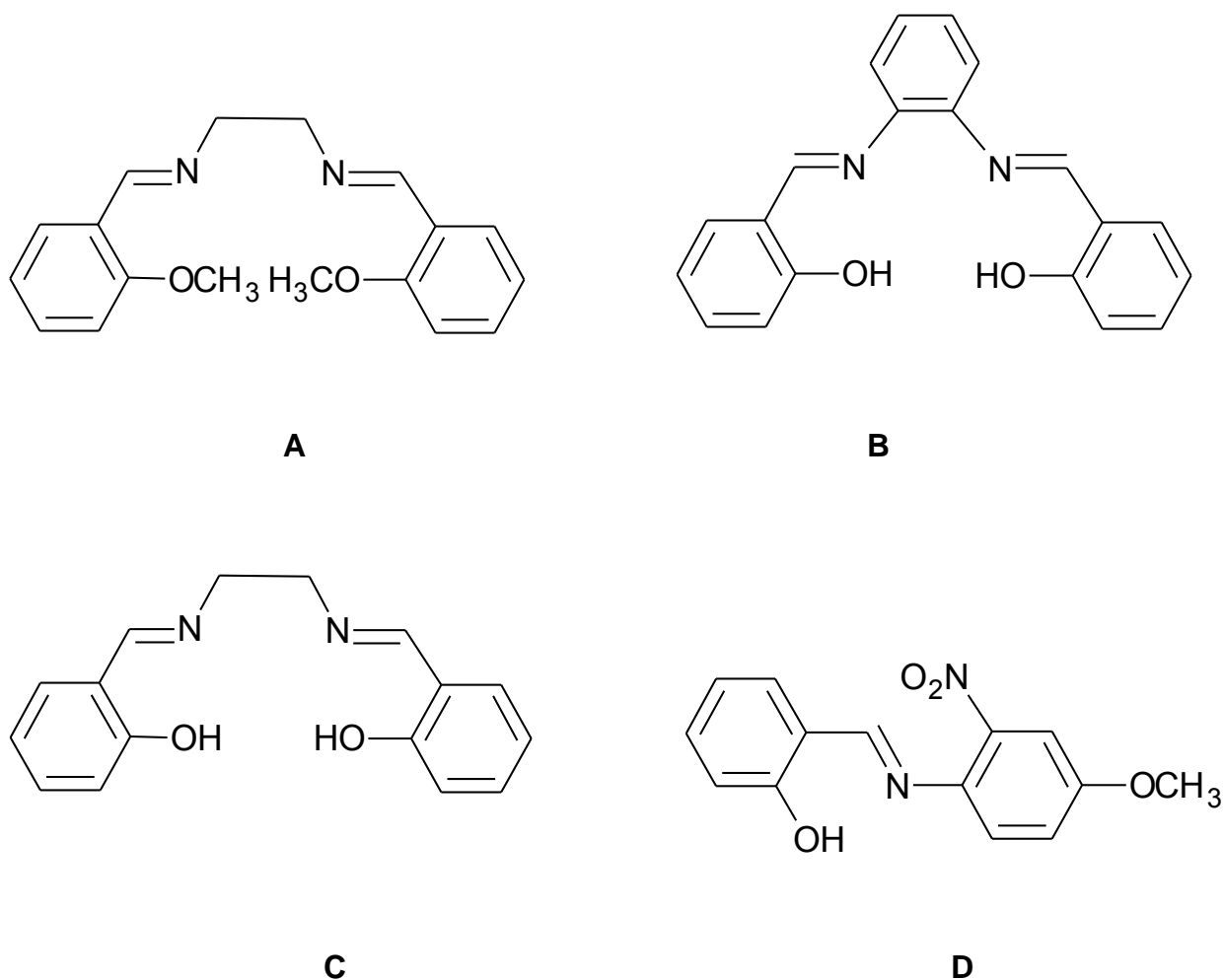


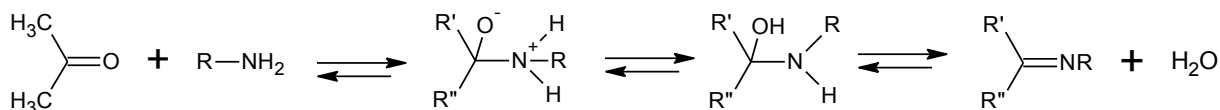
Figure 1.3: (A-D) Structure of Schiff bases¹⁷

Schiff base ligands possessing oxygen and nitrogen donor atoms in their structures have been used as good chelating agents for the transition and non-transition metal ions. The most well-known Schiff bases are those in which metal ions coordinate via O- or N-terminals and have exhibited unusual structural properties.¹⁸

1.3 Syntheses of Schiff-base ligands

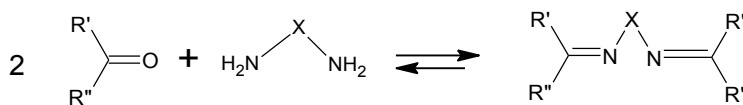
The synthesis of Schiff base ligands usually involves an acid catalysed condensation reaction of amine and aldehyde or ketone in various solvents under different reaction conditions (scheme 1.1). These are fairly straight forward reactions, although some reactants (usually as a result of electronic effects) can

require forcing conditions such as heating to reflux in a high boiling solvent and may include the use of a Dean-Stark apparatus or molecular sieves to remove the by-product, water.¹⁹



Scheme 1.1: Synthesis of Schiff base

The preparation of bridged Schiff bases follows the following route as outlined in scheme 1.2 below in which a diamine is required for 2 molecules of aldehyde or ketone.



Scheme 1.2: Synthesis of bridged Schiff base

Where R' = H or alkyl group, R'' = phenyl or substituted phenyl, X = alkyl or aryl

The most well-known of Schiff bases are derived from salicylaldehyde and diamines, commonly called salen ligands. The N₂O₂ coordination sphere is an excellent host for many metal ions. These ligands can use either aliphatic or aromatic R groups bound to the iminic carbon atom, with a heteroatom at the ortho position. The iminic nitrogen along with the heteroatom can form stable 6-membered chelate rings with a variety of metal centers.²⁰

The most common Schiff base reaction is an acid catalysed condensation reaction of an amine with an aldehyde or ketone under refluxing conditions. The first step in this reaction is an attack of a nucleophilic nitrogen atom from an amine, on the carbonyl carbon, resulting in a normally unstable carbinolamine intermediate. The reaction can reverse to the starting materials, or when the hydroxyl group is eliminated and a C=N bond is formed, the product is called imine.

Many factors affect the condensation reaction, for example the pH of the solution as well as steric and electronic effects of the carbonyl compound and amine. In acidic solutions the amine is protonated, thus it cannot function as a nucleophile and the reaction cannot proceed. Furthermore, in very basic reaction conditions the reaction is hindered as insufficient protons are not available to catalyse the elimination of the carbinolamine hydroxyl group. In general, aldehydes react faster than ketones in Schiff base condensation reactions as the reaction centre of aldehydes is sterically less hindered than that of a ketone. Furthermore, the extra carbon of the ketone donates electron density and thus makes the ketone less electrophilic compared to aldehyde.

1.4 Reactions of Schiff bases with metal ions

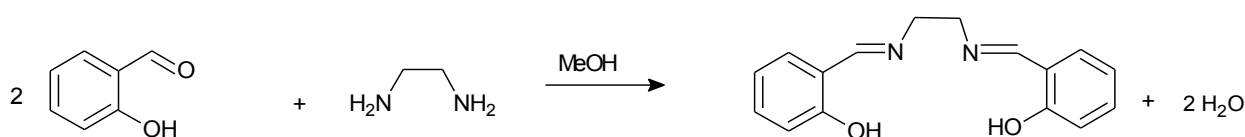
A Schiff base metal complex was first synthesized in 1933 by condensation of salicylaldehyde and ethylenediamine with various metal salts which was called a salen complex. The salicylaldimine ligand can be regarded as the half of a salen ligand and is synthesized by the reaction of equivalent salicylaldehyde with only one monoamino group. The imine functional group is prone to undergo an acid-catalyzed hydrolysis, reverting to the corresponding salicylaldehyde and amine reactants in the

presence of water. The stability of the Schiff base group increases considerably upon coordination with a metal ion and formation of the Schiff base-metal complex. These Schiff base-metal complexes can be used in wet solvents or even in aqueous media without undergoing decomposition.

The Salen type Schiff base complexes with transition metal ions have been extensively examined in coordination chemistry. These complexes have contributed to the development of contemporary coordination chemistry, catalysis, magnetism and medical imaging. They can be easily prepared and have the ability to complex with metal ions.²⁴

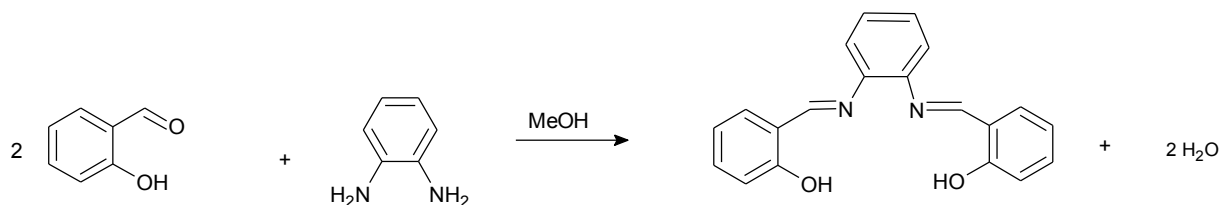
These Salen type Schiff base ligands comprise two oxygen and two nitrogen donor groups. The coordination sphere containing the carbon-chain linkage permits metal ions to find an easy approach to bind to the Schiff base. The steric interaction of these ligands resulting from the substituents on the aromatic ring makes an excellent host for both transition metals and the *f*-block elements.²⁴

The fundamental characteristic of the coordination chemistry of Schiff base complexes is how the metal is displaced out of the plane of the ligand core. These ligands tend to act as tetra-dentate ligands with two nitrogen atoms and two oxygen atoms with the metal ion coordinating through the four coordination sites (scheme 1.3).



Scheme 1.3: The formation of a salen Schiff base

Schiff bases that contain an aromatic moiety in the backbone have been synthesized by Kocyigit *et al.*⁴⁰ and takes place by means of a condensation reaction between the salicylaldehydes with *o*-phenylenediamine (scheme 1.4).



Scheme 1.4: The formation of a salophen Schiff base

The rapid progress of Schiff bases that are produced from salicylaldehyde and diamines are among the most relevant synthetic salen ligands with great potential applications in the field of catalysis. This is due to their low cost, ease of fabrication and their stability.²⁵

1.5 Co-ordination Chemistry of Schiff base ligands

The coordination chemistry of base metal ions with Schiff base extractants has played a major role in the improvements of the chemical processes in solvent extraction. The complexes formed as a result of Schiff bases with aliphatic amine linkers has resulted in the formation of strong chelates with main group metals at high pH.²¹ Schiff base ligands are able to stabilise a wide variety of transition metals in a range of oxidation states.²² Chelating ligands containing N, O and S donor atoms have been used to produce novel frameworks in which most transition metal ions are bonded. The π -system in a Schiff base often causes a geometrical constriction that affects the electronic structure. Schiff base ligands exhibit remarkable bioactivity and predictable physicochemical, stereochemical, electrochemical and structural properties. The properties of these compounds arise due to their diverse

condensation products of the amine-aldehyde reaction, but also due to the participation of the specific metal atoms and ligands.²³

1.6 Transition Metal Complexes of Schiff base ligands

Schiff base ligands have been used as frameworks for the preparation of a number of transition metal complexes. A transition metal complex is an aggregate of a Lewis acid (the metal) and Lewis bases (the ligands). The ligands may contain more than one donor atom (ligand denticity) and more than one type of donor atom (so there is the possibility of binding in different ways to different metals). The binding affinity of a specific donor atom for metal ions differs from one metal ion to another depending on the softness or hardness of the metal ion and the donor atom.

The physico-chemical properties of metal–ligand coordination compounds are determined mainly by the nature of ligands bound to the metal ion. The nitrogen donor atoms have a higher tendency to coordinate with metal ions than the oxygen atoms as a result of the increased softness over the oxygen atoms. The double bond, which is attached to the nitrogen atom, also contributes in enhancing the basicity of both nitrogen atoms.²⁶

1.7 Geometry of copper (II) Schiff base complexes

Metal complexes of Schiff bases have shown that they are capable of forming stable metal complexes with Cu(II). It is considered a borderline metal ion and easily coordinates with N and O. Cu(II) is a transition metal cation in 3d series and tends to form the coordination complexes displaying various geometries such as square planar, square pyramidal, trigonal bipyramidal, and octahedral with the coordination

number of four, five and six respectively. The characteristics exhibited by the Cu(II) metal ion are mainly due to it possessing a d^9 configuration. When Cu(II) is four coordinated, the geometry of the metal centre is square planar. When Cu(II) is five coordinated, the geometry of the metal centre lies somewhere between square distorted pyramidal and trigonal bipyramidal. The possible intermediate square pyramidal or trigonal bipyramidal geometry for the five coordinated Cu(II) centers is associated with the τ value ($\tau = \beta - \alpha/60$, where β and α are the two planar angles $> 90^\circ$) as introduced by Reedjik and co-workers (figure 1.4). The τ value of 0 and 1 basically is an indication of a geometry around Cu(II) ion, with former value indicating perfect square pyramid (C_{4v}) while the latter value represents a trigonal bipyramid (D_{3h}).²⁷

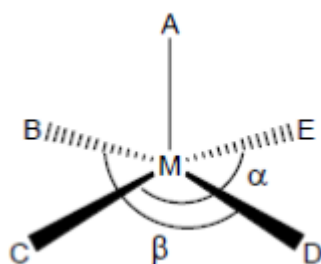


Figure 1.4: A diagram showing the definition of τ .²⁷

1.8 Carrier assisted transport of transition and post transition metal ions by means of a bulk liquid membrane (BLM)

The transport of metal ions using a membrane with a concentration gradient has gained increasing impetus in recent years.²⁸ A number of extractants/ionophores have been developed to achieve high transport efficiency and excellent selectivity of the extractant. Liquid membrane is a water-immiscible organic layer (bulk or supported on a microporous film) that separates two aqueous layers. This organic

layer contains a molecular system (carrier) able to extract a substrate from one of the aqueous layers (the source phase), and to release it to the other one (the receiving phase). The carrier works in a cyclic way, shuttling back and forth between the two membranes/aqueous phase interfaces. The process of transporting metal ions by means of bulk liquid membranes usually involves the separation of three phases, with two aqueous phases separated by an immiscible (organic) membrane phase (Figure 1.5). The ligands (carrier) are dissolved using suitable organic solvents (CHCl_3 , or CH_2Cl_2) and usually are located at the bottom of the cell.

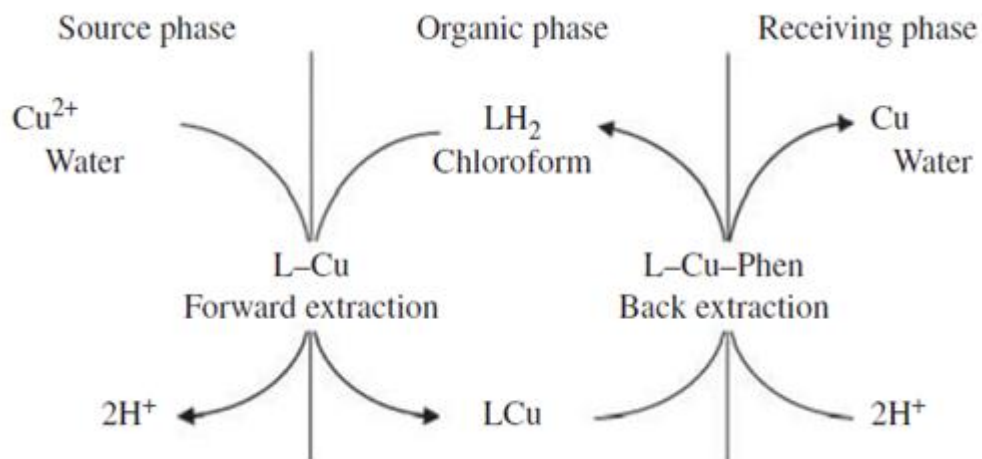


Figure 1.5: Schematic representation of transport of copper ions across a bulk liquid membrane

1.9 Hydrometallurgy

The processing of metal ores by pyrometallurgical techniques has been replaced largely by hydrometallurgical operations as shown in figure 1.6. This method of recovering valuable metal ions has several advantages over the former in that it does not lead to the release of toxic gases and does not require high temperatures.

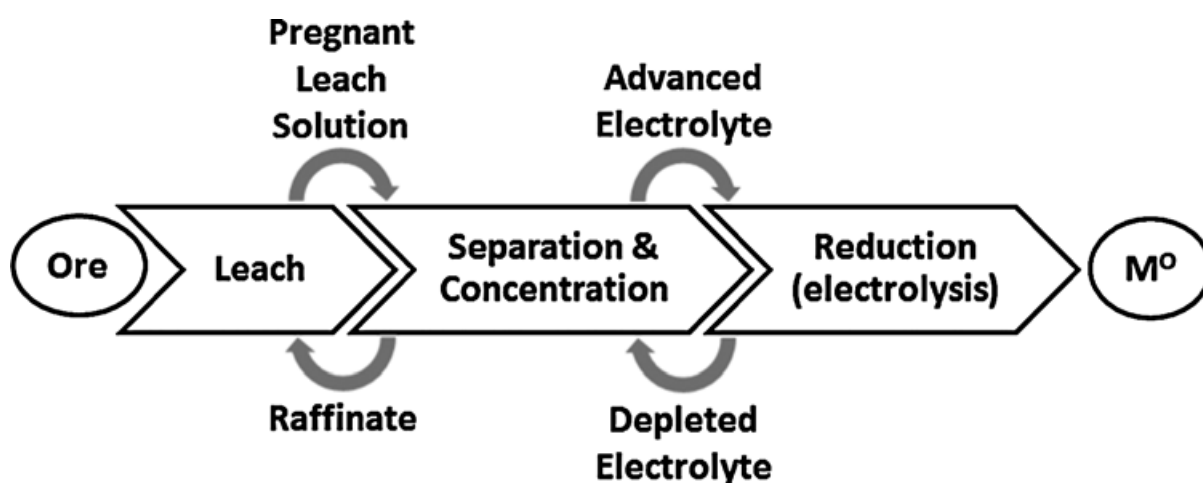


Figure 1.6: Hydrometallurgical operation for metal recovery²⁹

This had led to the development of a number of hydrometallurgical steps in which the essential metal ions are recovered. The main steps in a hydrometallurgical process for the recovery of metal ions involve leaching, extraction, stripping and finally electrowinning. The first phase of the process is called leaching, which is the selective dissolution of the metal and this is often carried out with sulfuric acid. The leaching process can be carried out in two ways viz; (i) simple leaching (at atmospheric temperature and pressure) and (ii) pressure leaching (pressure and temperature are increased to quicken the process). The next step is followed by the extraction and selective transport of metal ions into a non-polar organic phase by means of a hydrophobic ligand. The removal of the metal ions from the organic

phase is usually carried out by contacting this phase with an aqueous phase at lower pH than the leaching solution. This process ensures excellent materials and energy balances as reagents are recycled.³⁰

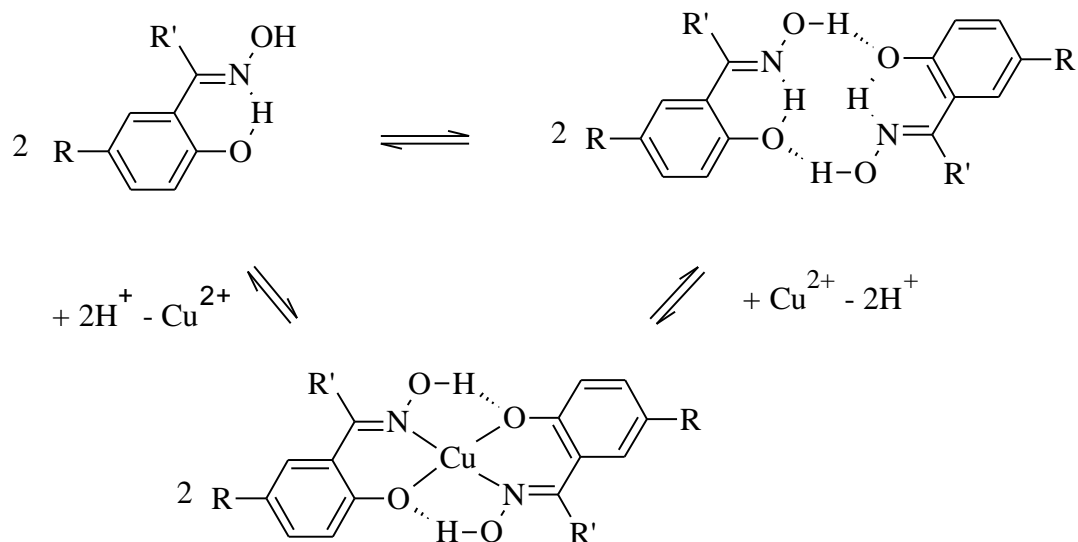


Figure 1.7: The formation of 14-membered pseudomacrocycle phenolic oxime

The process for extracting copper from sulfate streams by means of phenolic oxime reagents, has resulted in the production of 25% of copper supplies worldwide. The main reason for achieving high selectivity towards copper by using these reagents is due to 'goodness-of-fit' of the cavity which is generated by two deprotonated ligands. This is due to the formation of a square planar coordination environment containing a 14-membered pseudomacrocylic hydrogen bonded array (Figure 1.7), with the H-bonds between the oximic H and phenolate O atoms thought to impart additional stability to the complex.⁶

1.9.1 Solvent extraction

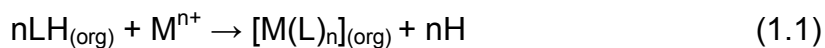
The most efficient way in which metal ions can be separated and concentrated from aqueous streams is solvent extraction (SX). Solvent extraction is also known as liquid-liquid extraction and it is a well-known process in the hydrometallurgical industry for separation and purification of several metals. The purification of a metal ion solution after the leaching process can be achieved by solvent extraction. This separation technique enables the extraction of important metal ions from pregnant leach (i.e. solution with dissolved valuable metals) or aqueous solutions. The extraction takes place by means of a chemical reaction between extracted metal ion prevailing in the aqueous phase and extractant from the organic phase.

Solvent extraction is a process of transferring a chemical compound from one liquid phase to a second phase that is immiscible with the first.³¹

The advantages of using this process are:

- Complete recovery of metals giving high purity products
- Low energy requirements
- Removal of air contaminants and
- Reduction of wastes

The recovery of metals by solvent extraction processes can be described by equation (1.1) in which the metal cation (M^{n+}) forms a chelate with the chelating agent (LH) to form a neutral molecule.



The amount of the metal extracted is equal to the moles of metal after extraction divided by the total number of moles of metal before extraction. This is calculated as a percentage according to equation 1.2 below:

$$\% E = \frac{T-A}{T} \times 100 \quad (1.2)$$

Where T = total number of moles of metal before extraction

A = total number of moles of metal after extraction

% extraction = is the number of moles which goes into the organic phase.

1.10 Reagents used for the hydrometallurgical separation of base metal ions

The development of hydrometallurgical reagents is very essential to meet the ever increasing demand to purify metals from low-grade ores, transition ores, and mixed metals. The benefits of this method are mainly due to the absence of high temperatures and toxic gases and also separating metal ions using aqueous solutions.

The donor atoms of the ligand are very important when extracting certain metal ions. A key requirement is that when synthesizing these ligands industrially is that they are cheap and easy to produce and relatively stable under the conditions employed. The other factor that is important when designing metal specific ligands is steric effects and high solubility in the organic phase. Schiff-base ligands with N,O-donor sets have often been used since the Schiff-base ligands may assemble coordination architectures directed by the transition metal ions.³²

1.10.1 Oxygen and Nitrogen donors

Oximes and Schiff bases are major extractants of metal ions in solvent extraction as a result of the formation of chelate complexes. The oxygen-donor ligands have been extensively used for the separation of base metal ions. As a rule increasing the number of oxygen donors, increases the selectivity of the ligand for large metal ions over small metal ions. Chelating agents such as nitrogen donors in Schiff base ligands have been used for the extraction of metal ions. Schiff base compounds play an important role in the coordination of metals because it consists of donor atoms which are capable of forming complexes with the transition metal ions.³²

The N-donor ligand forms stable complexes with most transition metals. Amines possessing nitrogen donor ligands have been used as extractants for separating metal ions. The basicity of both nitrogen atoms is enhanced as a result of the double bond, which is attached to the nitrogen atom. Cu(II) forms stable complexes with the N-donors and the most favourable coordination is tetrahedral or square-planar coordination.³²

1.11 Schiff base donor atom preference

The ability of Schiff bases to form stable metal complexes is dependent on a number of factors such as; **(i)** the number and type of donor atoms, **(ii)** the backbone structure of the ligand and its preferred co-ordination geometries with the respective metal ions (including the degree of 'preorganisation' present in the system), **(iii)** the number and size of the chelate rings formed on complexation, and **(iv)**, for transition-metal ions, crystal-field effects of the type underlying the Irving-Williams stability order. The donor capability and dielectric constant of the solvent as well as the shape and size are key parameters that determine the stability and selectivity of complexation.³³

Polydentate Schiff base ligands allow the selective extraction of metal ions by exploiting the multiple donor atoms and in addition the complex stability is increased compared with monodentate counterparts due to the chelate effect. This effect can be enhanced when the number and size of the chelate rings are optimized for the size of the cation by reducing the steric strain upon metal binding.³⁴

The affinity of metal ions towards certain donor atoms and the stability of metal-ligand bonds can be predicted according to the theory proposed by Pearson.³⁵ This theory states that hard acids prefer to combine with hard bases and soft acids prefer to combine with soft bases. It was found that the interaction of Cu(II) is normally more intense than any other divalent metal ions in the 3d series with Schiff base ligands. Pearson's classifications of metal ions (Lewis acids) and their ligands (Lewis bases) are shown in Table 1.1, which serves as a useful starting point for predicting the preference of metal ions for ligands with various donor groups.

Table 1.1 Classification of selected metal ions and donor atoms according to Pearson's HSAB

Principle		
Hard Lewis Acids	Borderline Acids	Soft Acids
H^+ , Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Sc^{3+} , Ti^{4+} , Zr^{4+} , Cr^{3+} , Al^{3+} , Ga^{3+} , La^{3+} , Gd^{3+} , Co^{3+} , Fe^{3+}	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Bi^{3+} , Rh^{3+} , Ir^{3+}	Cu^+ , Au^+ , Ag^+ , Tl^+ , Hg^+ , Pd^{2+} , Cd^{2+} , Pt^{2+} , Hg^{2+}
Hard Lewis Bases	Borderline Bases	Soft Bases
F^- , OH^- , H_2O , ROH , Cl^- , RO^- , R_2O , $CH_3CO_2^-$, NH_3 , RNH_2 , NH_2NH_2 , CO_3^{2-} , NO_3^- , O_2^- , SO_4^{2-} , PO_4^{3-} , ClO_4^-	NO_2^- , Br^- , N_3^- , N_2 , $C_6H_5NH_2$, pyridine, imidazole	RSH , RS^- , R_2S , S_2^- , CN^- , RNC , CO , I^- , R_3As , R_3P , C_6H_5 , C_2H_4 , H_2S , HS^- , H^- , R^-

The stability constants of these complexes with respect to divalent first row transition metal ions followed the order $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$. This order is in agreement with Irving-Williams series and shows a decrease in ionic radii across the series which leads to stronger metal-ligands bonds.³⁶ The complex stability increases as the ionic radius decreases across the series, but Cu^{2+} shows an increase in stability that can be attributed to ligand field stabilization energy (LFSE) obtained through Jahn-Teller distortion, and Zn^{2+} shows a diminished stability due to a lack of LFSE for its d^{10} configuration.

1.12 Factors associated with cation and anion recognition chemistry

The zwitterionic reagents that are commonly used in extractive metallurgy possess binding sites for both cations and anions. The loading and stripping operations can be controlled by varying the pH of the aqueous phase in contact with the reagent as shown in figure 1.8.

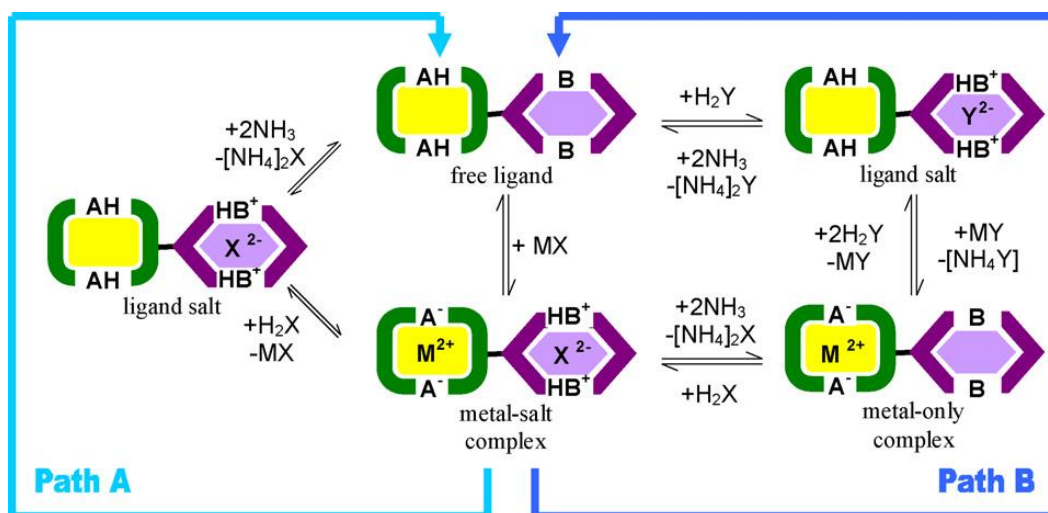


Figure 1.8: pH dependent interconversions of the ditopic ligand, its salts and its 'metal-only' and 'metal-salt' complexes³¹

The pendant amine groups can be protonated to provide the anion-binding site(s) while the deprotonated salicylaldimine units form a binding site with which a metal cation can complex. The crystal structure in figure 1.9 illustrates a key feature of the coordination chemistry of these systems, the cooperative binding of both the cation and anion.³¹

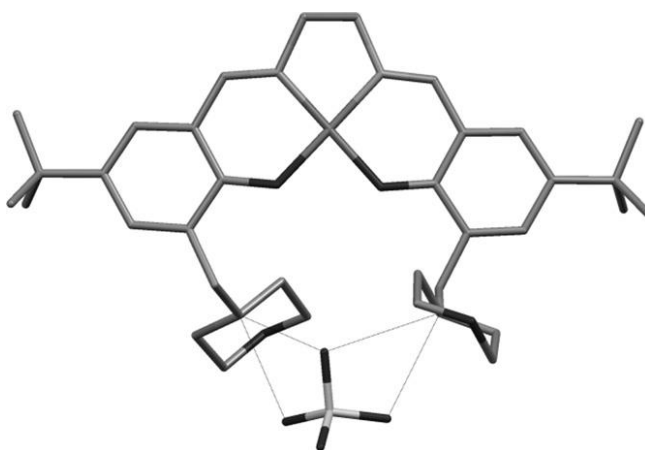


Figure 1.9: Crystal structure of the salen-type ligand bearing pendant morpholinomethyl groups³¹

1.13 X-ray Crystallography

Single-crystal X-ray diffraction is used to investigate structural properties of crystalline materials. This technique has enabled researchers to determine detailed structural information of metal-organic frameworks in different states.³⁶ X-ray diffraction has also been used to study the relationship between ligand and metal while also investigating possible hydrogen bonding interactions. The X-rays interact with the electron density of a particular atom.^{38, 39} X-ray crystallography has become an increasingly popular technique for analysing hydrogen bonding interactions because of the increasingly accessible and powerful diffractometers and computational facilities.³⁷

The biggest challenge using X-ray diffraction is, when investigating metal ligand interactions with Schiff-base ligands containing three or more donor atoms and long alkyl chain functionalities is to obtain single crystals suitable for XRD analysis.

1.14 Research Objectives

The research objectives in the following Chapters are aimed at the synthesis, characterization and application of novel Schiff bases towards the extraction and transport of transition and post transition metal ions from an aqueous phase into an immiscible organic phase in a solvent extraction process. The rapid demand for base metals has escalated over the past decade. Literature reports reveal that metal complexes of Schiff base ligands with N- and O- donor sites have successfully been used to complex various transition metal ions. The research objectives are divided into three sections.

Section 1

- I. The design and synthesis of a series of novel monocationic substituted salicylaldimine ligands with the aim of tuning their extractive ability towards transition metal ions.
- II. The characterisation of the ligands *via* FT-IR (ATR) spectroscopy, ^1H and ^{13}C NMR, melting point determination (where applicable), mass spectrometry, micro-elemental analysis and, where possible single-crystal XRD analysis.
- III. These ligands will be subjected to competitive extraction and competitive transport to determine the metal extraction strength and selectivity.
- IV. The addition of palmitic acid to help keep the ligand in the organic phase as well as determine whether it affects the competitive extraction of the metal ions.
- V. And finally, the effect of pH was investigated on the binding affinity of copper(II) and lead(II) on the series of Schiff base ligands *via* solvent extraction.

Section 2

- I. The second phase of the study will involve the design of novel ditopic Schiff base ligands (possessing both cation and anion binding sites).
- II. The synthesis and full characterization of the ditopic ligands by ^1H and ^{13}C NMR spectroscopy, FT-IR (ATR) spectroscopy, mass spectrometry, micro-elemental analysis and where possible single-crystal XRD analysis.
- III. The ditopic ligands will be used as extractants for the metal salt recovery processes (*via* solvent extraction) for the recovery of transition and post transition metal ions as well as selected anions. The metal cations that will be evaluated in this study include, Cu(II), Ni(II), Zn(II), Co(II), Cd(II), and Pb(II), and the selected anions in this study involve; Cl^- , NO_3^- , and SO_4^{2-} .
- IV. These ditopic ligands are examined for the anion extraction ability so as to overcome the Hofmeister bias.

Section 3

- I. The third phase of this study will be to evaluate on a molecular level how four different carboxylic acids interacts with the ligand before complexation to a metal ion by using NMR.
- II. Cu(II) and Pb(II) extraction studies will also be performed using the ligand with the various acids. ICP-OES will be employed to analyse the percentage copper and lead extracted at $\text{pH} = 5$.

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Chapter 2

2. Synthesis, Characterization and application of monotopic Schiff Base Ligands and Complexes

2.1 Introduction and Aims

This chapter describes the synthesis and characterization of novel monotopic Schiff base ligands. A series of new N-substituted 5-tert butyl salicylaldimines as shown in Figure 2.1 have been synthesized and investigated.

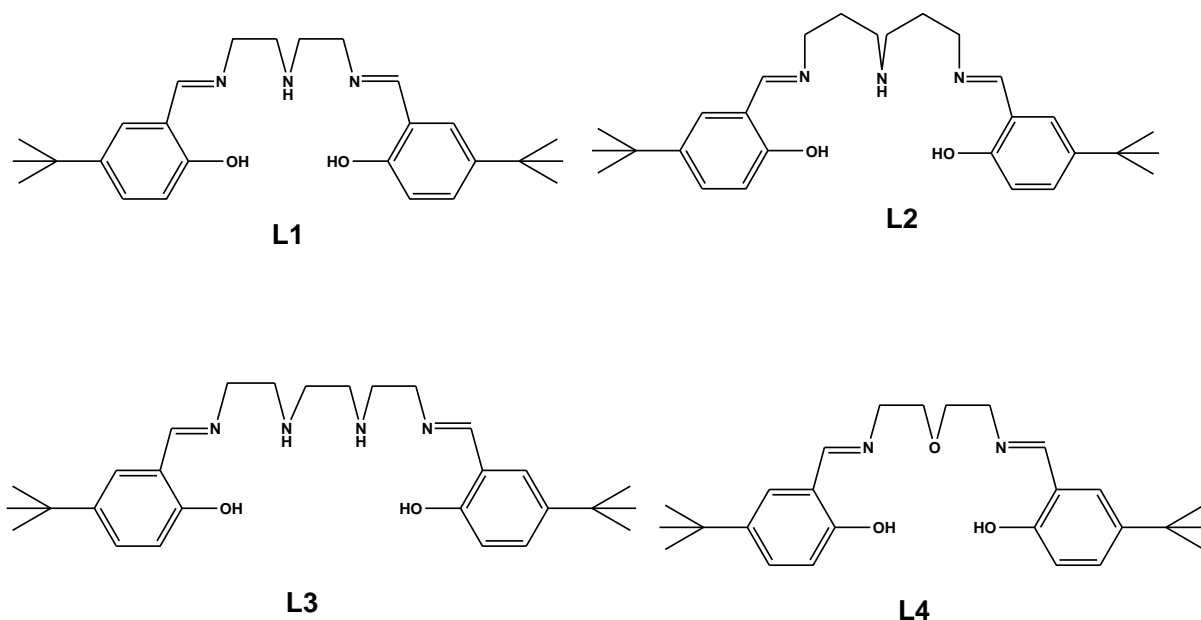


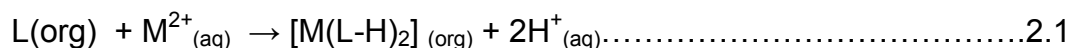
Figure 2.1: Schiff-base ligands investigated as potential metal ion extractants

Schiff base ligands are formed by the condensation of 5-tert butyl salicylaldehyde with various amine linkers containing nitrogen and oxygen donor atoms in their backbone. These were fully characterized using ^1H and ^{13}C NMR, FT-IR, mass spectrometry, elemental analysis and X-ray crystallographic techniques. The extraction and bulk liquid membrane transport abilities of the ligands were evaluated by monitoring the extraction and transport of the metal ions Co(II), Ni(II),

Cu(II), Zn(II), Cd(II) and Pb(II) over a 24-hour period. Palmitic acid was included in the organic phase to ensure that there is minimal ligand loss from the organic to the aqueous phase.

This chapter deals with the use of various amine linkers that forms the backbone of these salicylaldimine ligands, thus enabling them to function as cation exchange reagents according to Equation 2.1. Previous studies have reported good selectivity for Cu(II) and have shown that Schiff bases derived from the mono-condensation of diamines with carbonyl compounds consisting of N₂O₂ donor ligands readily react with transition metal ions (especially Cu(II)).¹

Equation 2.1



The incorporation of donor atoms such as nitrogen and oxygen atoms into the structure of organic compounds affects the behaviour towards metal ions as previously reported.^{2,3} The nitrogen and oxygen atoms act as the donors, or base, in which it readily donates its electron pairs to a metal ion. The functionality of these ligands and their metal complexes are the focus of much coordination and structural chemistry studies.^{4,5}

In this chapter and subsequently in Chapter 3, consideration is given to the interligand hydrogen bonding, the effect of changing the ligand backbone and its contribution to the extractive properties of ligands. Each ligand includes a 5-*tert*-butyl group to increase the solubility in non-polar solvents. The objective of the work in this

chapter was to vary the number of donor atoms in the amine linker to see whether selectivity of the ligands is changed for a metal ion other than Cu(II).

2.2 Materials and Methods

The following chemicals were purchased from Sigma-Aldrich: 4-tertbutylphenol, *bis*(3-aminopropyl)amine, triethylenetetraamine, and 2,2-oxydiethylamine dihydrochloride; and all these were used without any further purification. HNO₃ (0.1 M) was purchased from Fluka and deuterated chloroform and chloroform were purchased from Merck. The following chemical was purchased from Riedel-de-Haen: diethylenetriamine. All aqueous solutions were prepared using deionised water. Chloroform used for the membrane phase was presaturated with water by shaking a two phase water-chloroform mixture, then removing the aqueous phase.

Infrared spectra were obtained using a Nicolet Avatar 330 FT-IR instrument as neat samples, using an ATR accessory with a ZnSe/Diamond crystal. ¹H and ¹³C NMR were obtained using a 300 MHz Varian VNMRS, 400 MHz Varian Unity Inova or 600 MHz Varian Unity Inova NMR Instrument with deuterated solvents. Chemical shifts (δ) were recorded using the residual solvent peak or external reference (TMS). All chemical shifts are reported in parts per million and all spectra were obtained at 25 °C. Data was processed using Mestrenova file version 7.11. Melting points were recorded on a Stuart Scientific Melting Point apparatus SMP30, and are uncorrected. Standard resolution mass spectrometry was performed by CAF (Central Analytical Facility) at Stellenbosch University using a Waters Synapt G2 Spectrometer. Metal analysis was done using ICP-OES which was performed by CAF at Stellenbosch University using a Thermo Scientific iCAP 6000 Series instrument. Ion

chromatography data was obtained on a DIONEX DX-120 instrument. Elemental analyses were carried out using a Perkin-Elmer CHNS Elemental Analyzer model 2400 at the University of Kwazulu-Natal. UV-Vis spectroscopy was performed using a GBC 920 spectrometer. Fourier transform infrared spectroscopy was performed using a Thermo Nicolet Avatar 330 with a Smart Performer Zn/Se ATR accessory.

The X-ray data sets for compounds 1 and 2, were collected on an APEX 2⁶ diffractometer, using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K. The structure was solved by conventional Patterson and Fourier methods and refined through full matrix least squares calculations based on F2, using the software packages WinGX⁷ with SHELXL97⁸. All non hydrogen atoms were refined anisotropically, while the phenyl hydrogen atoms were calculated as riding on the adjacent carbon (aromatic C – H = 0.96 \AA). The program, Diamond⁹, was used for graphical representation of the crystal structures. Cell refinement: SAINTPlus; data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97; program(s) used to refine structure: SHELXL97; molecular graphics: DIAMOND; software used to prepare material for publication: WinGX and XSEED.¹⁰

2.3 Other Instruments

2.3.1 pH determinations

A Corning 425 pH meter with a glass electrode was used to measure the pH. It was calibrated before use, using a standard buffer solution of pH 4.0 and 7.0.

2.3.2 Labcon Shaker and KugelRohr distillation Apparatus

The Labcon Shaker (figure 2.2) was used for contacting the two phases in the solvent extraction experiments. This instrument was set at 220 rpm for a period of 24 hours. 24 hours was chosen since equilibrium is most likely reached after this time period. The KugelRohr distillation (figure 2.3) was used to purify the sample from unwanted impurities.



Figure 2.2: Labcon Platform Shaker



Figure 2.3: KugelRohr distillation Apparatus

2.4 Experimental

2.4.1 Preparation of 5-*t*-butyl-salicylaldehyde

In a typical experiment, 5-*tert*-butylsalicylaldehyde was prepared by adding 4-*tert*-butylphenol (37.56 g, 0.2500 mol) to a solution of magnesium methoxide (3.64 g, 0.150 mol, 300 ml dry MeOH) in a two neck 500 ml round bottom flask with a magnetic stirrer bar and the mixture was heated to reflux. The solution appeared light brown and stirred for a further 90 min under reflux. MeOH, 200 ml, was distilled off by fractional distillation after which 200 ml of toluene was added to the mixture under reflux. The azeotropic mixture of toluene and methanol was removed by fractional distillation. The solution appeared white at this stage with a precipitate. Paraformaldehyde (23.1 g, 0.770 mol) dissolved in toluene (50 ml) was added, resulting in the formation of a yellow colour. The solution changed to a light yellow colour indicating the formation of the aldehyde. H₂SO₄ (10 %) was added to the solution. The organic layer was separated from the aqueous layer (x2) and thereafter transferred to a rotary evaporator to remove the toluene.¹¹ The solution was further purified using a KugelRohr distillation apparatus to produce a pale yellow oil.

Characterization: Pale Yellow oil, yield 72 %. ¹H NMR (400 MHz, CHLOROFORM-*d*) δ ppm 0.8 -1.3 (s, 9H, C(CH₃)₃), 6.9 - 6.95 (d, *J* = 2.28 Hz, 1H, ArH), 7.50 – 7.58 (dd, *J* = 2.49 Hz, 2H, ArH), 9.95 (s, 1H, CHO), 11.05 (s, 1H, OH); ¹³C NMR (400 MHz, CHLOROFORM-*d*) δ ppm 31.08 (C(CH₃)₃), 34.60 (C(CH₃)₃), 118.13 (C_{Ar}H), 123.30 (C_{Ar}H), 134.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 162.40 (C_{Ar}OH), 192.40 (C_{Ar}CHO). IR (neat); 2952, 2863 (m, CH); 1653 (m, C=O); 1588 (s, C=C); 1490 (m, CH).

The characterization of this product corresponds to that found in literature.¹¹

2.4.2 Preparation of 2,2-oxydiethylamine: Approximately 1.04 g (0.0454 mol) of Na metal was allowed to dissolve completely in absolute ethanol to form sodium ethoxide in a 250 ml round bottom flask. (4.0 g, 0.023 mol) 2,2-oxydiethylamine dihydrochloride was thereafter added and allowed to stir for 3 hours upon which the solution turned yellow with a precipitate. The resulting precipitate was filtered using gravity filtration and the final product was stored in absolute ethanol. The yield was quantitative and the amine was subsequently used without further characterization.

2.4.3 General procedure of mono Schiff bases

A typical synthesis involves the reaction of 2 equivalents of 5-*t*-butylsalicylaldehyde in 30 cm³ absolute ethanol with one equivalent of the amine derivative. The mixture was allowed to reflux for 24 hours, after which the solvent was removed via rotary evaporation. The final product was dried further under high vacuum for 3 days.¹²⁻¹⁴

2.5 Ligand Characterization

Characterization of 2-((E)-(2-(2-((E)-5-*tert*-butyl-2-hydroxybenzylideneamino)ethylamino)ethylimino)methyl)-4-*tert*-butylphenol

(L1): Amine derivative used: *diethylenetriamine*:

Yellow solid, yield 54%; mp 66.0-66.9. Anal. Calcd. % for C₂₆H₃₇N₃O₂: C 73.73, H 8.80, N 9.92. Found: C 73.86, H 7.93, N 9.56. ¹H NMR (400MHz, CHLOROFORM-*d*) δ ppm 1.31 (s, 18H, C(CH₃)₃), 3.69 - 3.73 (t, *J* = 6.64 Hz, 4H, NCH₂CH₂), 6.92 – 6.94 (d, *J* = 8.50 Hz, 2H, ArH), 7.24 - 7.25 (d, *J*=2.28 Hz, 2H, ArH), 7.35 – 7.38 (dd, *J*=2.49 Hz, 2H, ArH), 8.39 (s, 2H, NCH), 13.23 (s, 2 H, OH); ¹³C NMR (400 MHz, CHLOROFORM-*d*) δ ppm 31.08 (C(CH₃)₃), 31.47 (NCH₂CH₂), 34.60 (C(CH₃)₃), 50.14

(ArCH₂N), 59.01 (NCH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 129.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 158.40(C_{Ar}OH), 167.41 (ArCN); IR (neat); 2952, 2863 (m, CH); 1631 (m, C=N); 1588 (s,C=C); 1490 (m, CH); 1264 cm⁻¹ (m, C-N); Expected MS : m/z (%) 423, (ES+):m/z (%) 424.3(100) [M+H]⁺, 425.3 (30) [M+2H]⁺; MS (ES-): m/z(%) 422.3 (100) [M-H]⁺, 423.59 (20) [M]⁺.

Characterization of 2-((E)-(3-(3-((E)-5-tert-butyl-2-hydroxybenzylideneamino)propylamino)propylimino)methyl)-4-tert-butylphenol (L2): Amine derivative used: *bis (3-aminopropyl)amine*:

Sticky orange oil; yield 66 %; Anal. Calcd. % for C₂₈H₄₁N₃O₂ (EtOH)_{1.5}(H₂O)_{0.5}: C 70.28, H 9.70, N 7.93. Found:, C 70.58, H 7.90, N 8.58; ¹H NMR (400MHz, CHLOROFORM-*d*) δ ppm 1.31 (s, 18H, C(CH₃)₃), 2.07-2.14 (t, J=6.64Hz, 2H, NCH₂CH₂), 3.69 - 3.73 (q, J = 6.64 Hz,4H, NCH₂CH₂), 6.92 – 6.94 (d, J = 8.50 Hz, 2H, ArH), 7.24 - 7.25 (d, J=2.28Hz, 2H, ArH), 7.35 – 7.38 (dd, J=2.49Hz, 2H, ArH), 8.39 (s, 2H, NCH); ¹³C NMR (400MHz, CHLOROFORM-*d*) δ ppm 31.08 (C(CH₃)₃), 31.47 (NCH₂CH₂), 34.60 (C(CH₃)₃), 48.14 (ArCH₂N), 58.01 (NCH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 131.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 158.40(C_{Ar}OH), 166.41 (ArCN); IR (neat); 2961, 2865 (m, CH); 1633 (m, C=N); 1589 (s, C=C); 1491 (m, CH); 1265 cm⁻¹ (m, C-N); Expected MS: m/z (%) 451 [M], (ES+): m/z (%) 452.33(100) [M+H]⁺, 453.33 (30) [M+2H]⁺.

Characterization of 2-((E)-(2-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethylamino)ethylamino)ethylimino)methyl)-4-tert-butylphenol (L3): Amine derivative used: *triethylenetetraamine*:

Sticky orange oil; yield 60 %; Anal. Calcd. % for C₂₈H₄₂N₄O₂ . (EtOH).(H₂O): C 67.89, H 9.5, N 10.56, Found: C 67.22, H 8.01, N 10.80; ¹H NMR (400MHz,

CHLOROFORM-*d*) δ ppm 1.31 (s, 18H, C(CH₃)₃) 2.62-3.03 (m, 8H, NCH₂CH₂CH₂), 3.69 - 3.73 (q, *J* = 6.64 Hz, 4H, NCH₂CH₂), 6.72 – 6.94 (dd, *J* = 8.50 Hz, 2H, ArH), 7.24 - 7.25 (d, *J*=2.28Hz, 2H, ArH), 7.35 – 7.38 (dd, *J*=2.49Hz, 2H, ArH), 8.39 (s, 2H, NCH); ¹³C NMR (400MHz, CHLOROFORM-*d*) δ ppm 31.08 (C(CH₃)₃), 31.47 (NCH₂CH₂), 34.60 (C(CH₃)₃), 48.14 (ArCH₂N), 58.01 (NCH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 131.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 158.40(C_{Ar}OH), 166.41 (ArCN); IR (neat); 2952, 2861 (m, CH); 1633 (m, C=N); 1588 (s, C=C); 1490 (m, CH); 1264 cm⁻¹ (m, C-N); Expected MS: *m/z* (%) 466 [M], MS (ES⁺):*m/z* (%) 467.33(60) [M+H]⁺, 468.34 (20) [M+2H]⁺.

Characterization of 2-((E)-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethoxy)ethylimino)methyl)-4-tert-butylphenol (L4):

Amine derivative used: *2,2-oxydiethylamine*:

Orange oil, yield 56%; Anal. Calcd. % for C₂₈H₄₂N₂O₃ . (EtOH)_{1.67}·(H₂O)_{1.67} : C 70.56, H 8.88, N 6.03. Found: C 70.74, H 7.68, N 5.50; ¹H NMR (400MHz, CHLOROFORM-*d*) δ ppm 1.31 (s, 18H, C(CH₃)₃), 3.71 - 3.78 (m, *J* = 6.54 Hz, 4H, NCH₂CH₂), 6.78 – 6.94 (dd, *J* = 8.50 Hz, 2H, ArH), 7.24 - 7.25 (d, *J*=2.28Hz, 2H, ArH), 7.35 – 7.38 (dd, *J*=2.49Hz, 2H, ArH), 8.39 (s, 2H, NCH), ¹³C NMR (400MHz, CHLOROFORM-*d*) δ ppm 31.08 (C(CH₃)₃), 31.47 (NCH₂CH₂), 34.60 (C(CH₃)₃), 50.14 (ArCH₂N), 59.01 (NCH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 129.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 158.40(C_{Ar}OH), 167.41 (ArCN); IR (neat); 2961, 2865 (m, CH); 1633 (m, C=N); 1589 (s, C=C); 1491 (m, CH); 1265 cm⁻¹ (m, C-N); Expected MS: *m/z*(%) 424 [M], (ES⁺):*m/z* (%) 425.28(100) [M+H]⁺, 426.28 (30) [M+2H]⁺.

2.6 Preparation of copper Schiff base complexes

[Cu(L1-2H)]

A solution of **L1** (0.12 mol) in absolute ethanol (30 cm³) and Cu(CH₃COO)₂·H₂O (0.12 mol) in ethanol (30 cm³) was stirred for 3 h. The solvent was thereafter removed *in vacuo* to yield a dark green oil. IR (neat): 2920 (m, CH), 1630 (m, C=N), 1476 (s, CH); Anal. Calcd. %: C 58.77, H 7.87, N 7.34, Found: C 58.85, H 7.89, N 7.34, (EtOH)·(H₂O)₂ Expected MS: m/z (%): 485.12, Found (ES+): m/z: 424.29 (95) [M-Cu]⁺, 485.21 (10) [M+Cu]⁺.

[Cu(L2-2H)]

A solution of **L2** (0.11 mol) in absolute ethanol (30 cm³) and Cu(CH₃COO)₂·H₂O (0.11 mol) in ethanol (30 cm³) was stirred for 3 h. The solvent was thereafter removed *in vacuo* to yield dark green oil. Vapour diffusion of diethyl ether into the resulting complex which was in a minimum amount of dichloromethane yielded green crystals suitable for single crystal XRD. IR (neat): 2957 (s, CH), 1626 (s, C=N), 1477 (s, CH) Anal. Calcd. %: C 64.1, H 8.0, N 7.6. Found: C 64.5, H 7.2, N 7.1. (EtO₂)_{0.33}(H₂O)_{0.67}. Expected MS: m/z (%): 513.17, Found (ES+): m/z: 452.33 (55) [M-Cu]⁺, 513.24 (10) [M+Cu]⁺.

[Cu(L4-2H)]

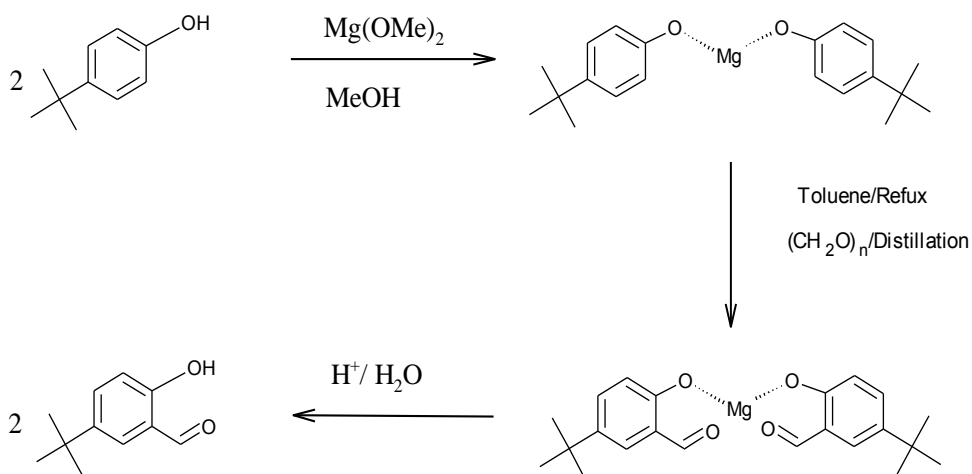
A solution of **L4** (0.12 mol) in absolute ethanol (30 cm³) and Cu(CH₃COO)₂·H₂O (0.12 mol) in ethanol (30 cm³) was stirred for 3 h. The solvent was thereafter removed *in vacuo* to yield a dark green oil. IR (neat): 2920 (s, CH), 1624 (s, C=N), 1470 (s, CH); Anal. Calcd. %: C 66.30, H 7.8, N 5.9, Found, C 65.91, H 9.2, N 6.8. Expected MS: m/z (%): 1120, Found (ES-): m/z: 1128 [M+H]⁺.

2.7 Results and discussion

2.7.1 Schiff base Condensation Reaction

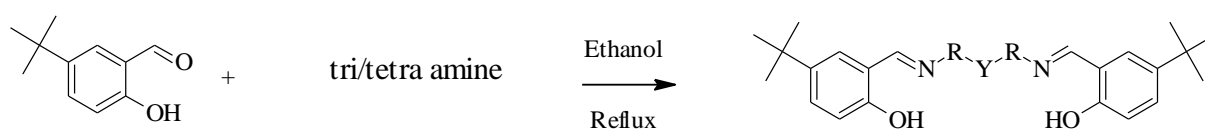
In the present investigation, the chapter aims to elaborate on all the synthetic aspects of monotopic ligands containing three or more donor atoms in the ligand backbone. Schiff base ligands **L1-L4** were synthesised and characterised as described previously in the experimental section 2.4 and 2.5 respectively. All the ligands were isolated as oils except **L1** which yielded a yellow solid. They were relatively stable in air, soluble in polar solvents such as methanol and ethanol. It was hoped that by increasing the length of the aliphatic chain linking the two iminophenol moieties enough flexibility would be introduced into the backbone of the ligand to enable donation into the metal from the nitrogen and oxygen donor atoms.

The prepared Schiff base ligands **L1-L4** all contained t-butyl substituents to minimise bleeding of ligands and complexes to the aqueous phase. The preferred method used in this thesis for the preparation of substituted salicylaldehydes was based on the methods employed by Levin and co-workers¹¹ involving magnesium-mediated formylation (Scheme 2.1) using magnesium methoxide and paraformaldehyde.



Scheme 2.1: Preparation of 5-tert butyl salicylaldehyde

The synthesis of the respective Schiff base ligands **L1-L4** (Scheme 2.2) was generated from the 5-tert butyl salicylaldehyde and the corresponding amine linker in a molar ratio of 2:1 under reflux in ethanol, giving products in moderate yields of (~ 60%). Finally the solvent was removed on a rotary evaporator and dried under high vacuum.

Scheme 2.2: Schiff base condensation of substituted salicylaldehydes to give ligands (**L1-L4**)

- L1 has** Y = NH
R = CH₂CH₂
- L2 has** Y = NH
R = CH₂CH₂CH₂
- L3 has** Y = NHCH₂CH₂NH
R = CH₂CH₂
- L4 has** Y = O
R = CH₂CH₂

2.7.2 IR Spectroscopy

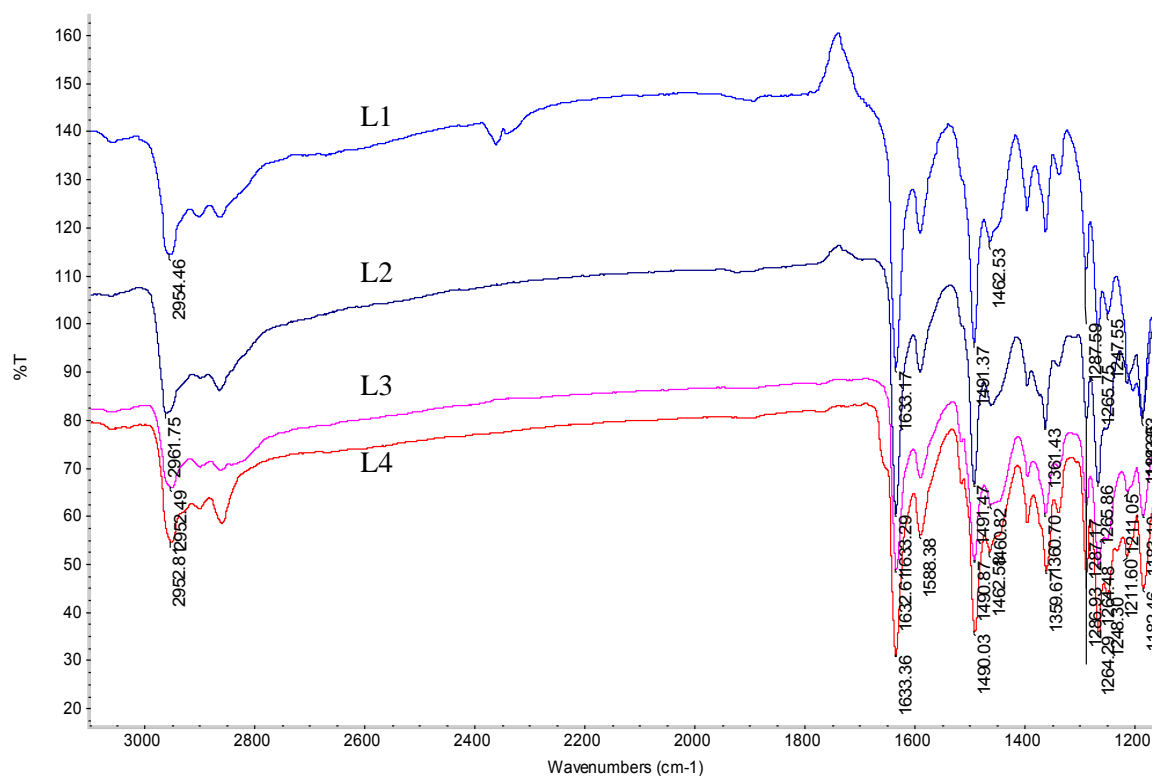


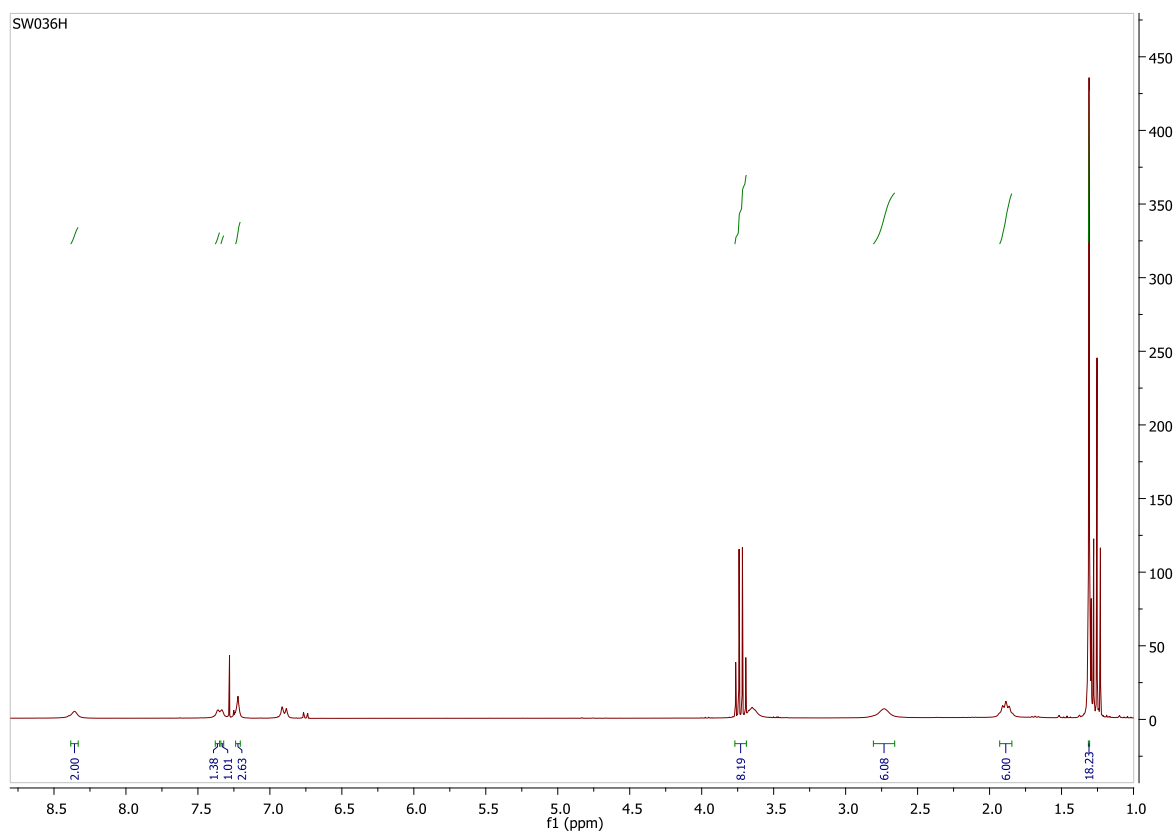
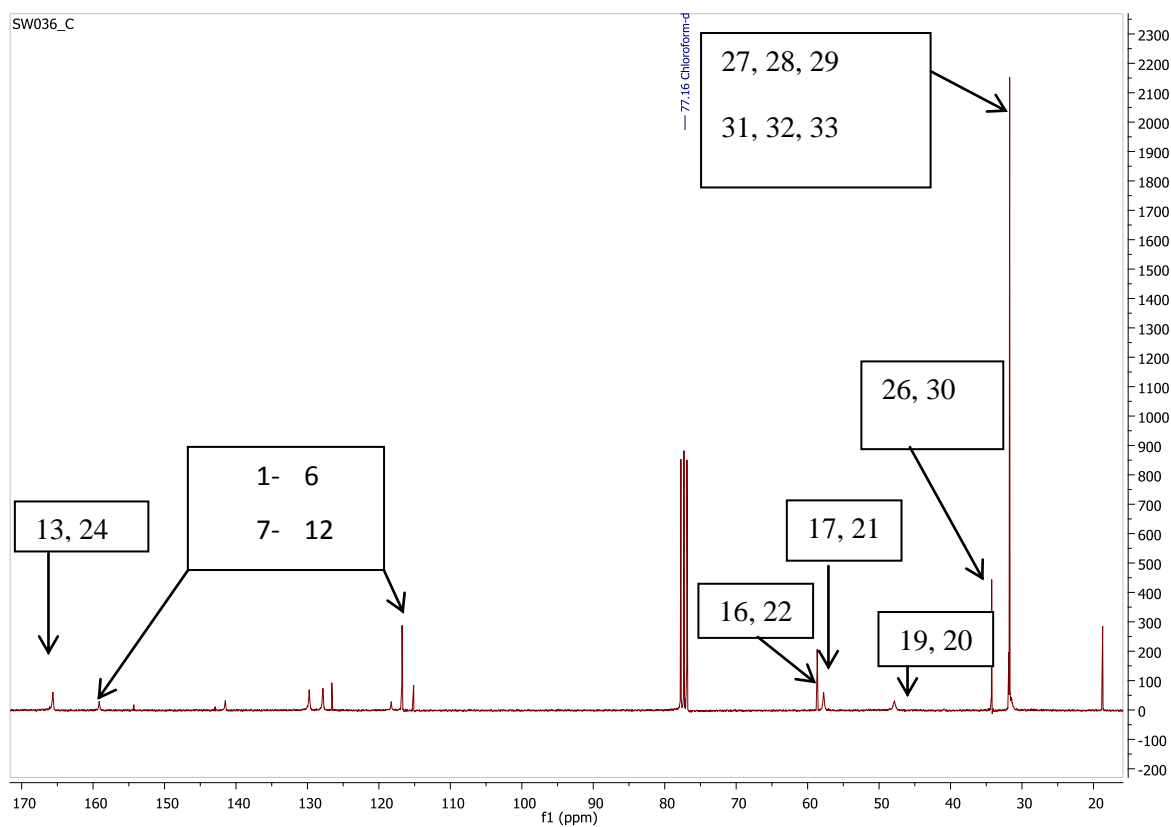
Figure 2.4: The IR spectrum of Schiff base ligands **L1-L4** containing a strong band for the imine bond at 1633 cm^{-1}

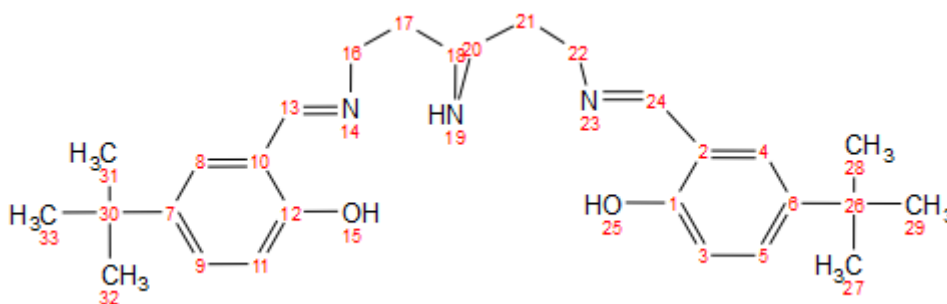
All the ligands and copper complexes have been characterized by FTIR spectroscopy. The IR spectra of the free ligands were carried out in the range from 3100–1200 cm^{-1} . The characteristic IR spectra of the four Schiff base ligands, **L1-L4**, have some similar features as is shown in the experimental section. In general, they show strong bands at 1626–1633 cm^{-1} that are assigned to the imine (C=N) stretching vibration which compares favourably with results obtained by Keypour *et al.*¹⁵ The aldehyde C=O stretch of 1654 cm^{-1} is absent and a C=N stretch is present which is indicative of the Schiff base condensation having occurred. The IR spectra of the ligands also show two weak bands in the region of 2960 cm^{-1} and 2860 cm^{-1} which can be attributed to C-H stretching vibration. The stronger band in the 1600–1500 cm^{-1} region is due to the skeleton stretching vibration of C=C of the benzene ring.¹⁷ The structures of the Schiff bases are illustrated in Figure 2.1.

The phenolic (C-O) bands appearing at 1286 cm^{-1} and 1288 cm^{-1} for the four Schiff base ligands, reflects the higher acidity of the OH group, which in turn affects the strength of the (C-O) bond. These values shifted towards lower frequency on coordination with metal ions, due to participation of oxygen in formation of the C-O-Cu bond. This shift can further be explained by the donation of electrons from nitrogen to the empty d-orbitals of the metal atom. The ring skeletal vibration (C=C) were constant in all derivatives and unaffected by complexation. The absence of a strong broad band in the 3479 cm^{-1} region, which is observed in the spectra of the metal complexes, is an indication of deprotonation of the intramolecular hydrogen bonded OH group on complexation and subsequent coordination of the phenolic oxygen to the metal ion.

As expected, these O-H and N-H absorption bands have vanished in the spectra of complexes, indicating that the coordination to the metal ion has taken place through both deprotonated oxygen atoms. In the low frequency region, observed in the complexes in the region $(415-453)\text{ cm}^{-1}$ was attributed to Cu-O and Cu-N bonds respectively. This showed that the coordination occurs through phenolic oxygen, and imino nitrogen. The observed FTIR results for the copper complexes shows successful metal complexation which is supported by the mass spectral results obtained. The infrared spectra of **L1**, **L2** and **L4** are very much consistent with their structures confirmed from single crystal X-ray diffraction. The existence of intramolecular hydrogen bonds between the hydroxyl and the nitrogen atoms is further corroborated by X-ray structural data. The observed FTIR vibration all show similar vibrational frequencies for both the ligands and complexes and this shows the inherent stability of these organic compounds.

2.7.3 NMR Spectroscopy

Figure 2.5: The ^1H NMR spectrum of Schiff base ligand L2Figure 2.6: The ^{13}C NMR spectrum of Schiff base ligand L2



All ligands and precursors were characterized by ^1H and ^{13}C spectroscopy. NMR spectroscopy was particularly useful for establishing the complete formation of the ligands and also to follow the processes which involved substitution on the aromatic rings. This was evident through observation of the decreasing number of protons on the ring from four in the alkyl-phenol to three in the 5-tert butyl salicylaldehyde. The disappearance of the aldehyde proton (9-10 ppm) and the observed resonance between 8.4 and 8.3 ppm is indicative of $\text{CH}=\text{N}$ - (imine) protons which confirms the formation of the Schiff base condensation product. The spectra also shows signals of both aromatic and aliphatic protons respectively. The intramolecular hydrogen bonding effect causes the phenol hydrogen peak to appear at the most downfield region. Similar ^1H and ^{13}C NMR chemical shifts were reported by Keypour *et al.*¹⁵ for Schiff base ligands.

The proton chemical shift of the OH group can only inform us about the presence of hydrogen bonding (a large downfield effect for the hydrogen-bonded structure) but cannot be used to decide where the proton is located in the H-bridge. The single crystal X-ray diffraction clearly shows hydrogen bonding in the Schiff base ligands. This fact can be further explained by Makal *et al.*¹⁶ from NMR experiments in which he states that the transfer of the hydrogen atom from the oxygen atom to the nitrogen atom produces a significant upfield shift of the imine nitrogen signal whilst at the same time a downfield shift of the signal of the C–OH atom is observed.

It is important to note that the hydroxyl group assists in the formation of a hydrogen H1N acceptor as an effective donor in intermolecular hydrogen bonds which help for crystal structure stabilization.¹⁶

2.7.4 Mass Spectrometry

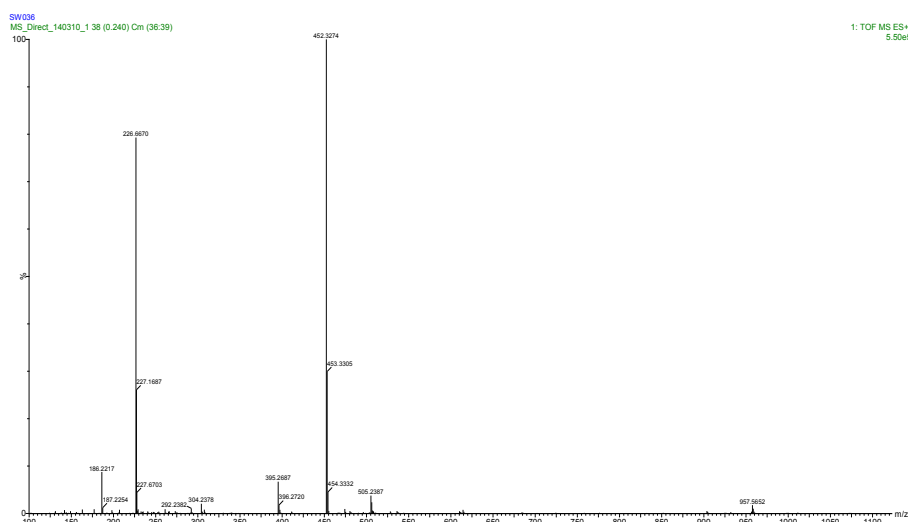


Figure 2.7: The mass spectrum of Schiff base ligand **L2** showing a peak at $m/z = 452.32$ for the free ligand (ES+)

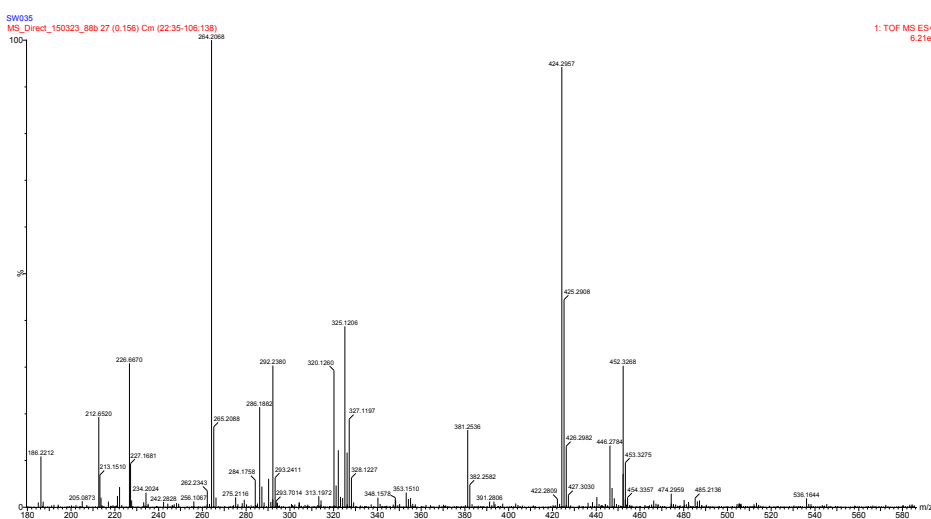
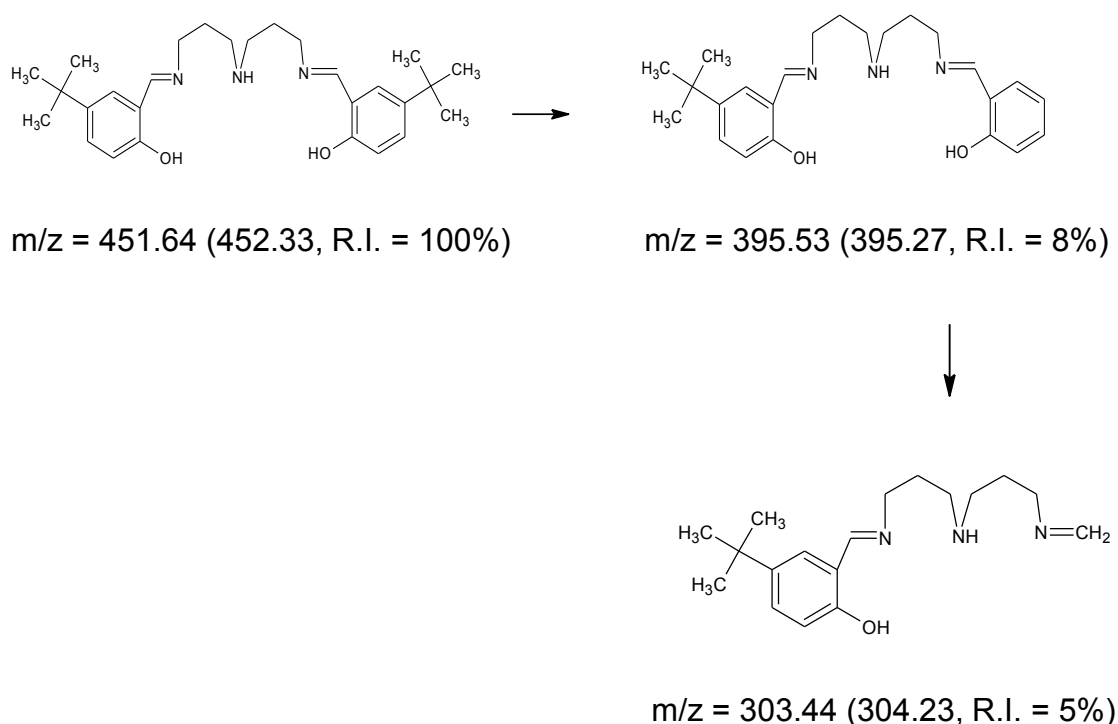


Figure 2.8: Mass spectra of metal complex Schiff base ligand (Cu complex **L1**) showing a peak at $m/z = 485.21$

Mass spectra of the newly synthesized Schiff base ligands **L1-L4** and the copper complexes all show similar spectra as shown for Schiff base ligand **L2** (Fig 2.7) and “metal-only” complexes (**L1_Cu**, Fig 2.8) indicates a metal to ligand ratio of 1:1. The molecular mass obtained from the mass spectra of all the compounds are shown in the experimental section and show intense molecular ion peaks with m/z 424.3, 452.33, 467.33, and 425.28 which is close to the calculated value for the structures of the Schiff bases (L1-L4). The fragments observed for L2 were in good agreement with the proposed fragmentation pattern (**Scheme 2.3**).



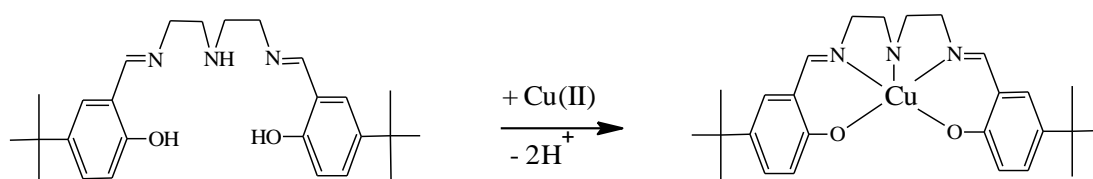
Scheme 2.3: Mass fragmentation pattern of **L2**

There was no evidence of any complexes containing more than one metal ion. Their intensity gives an idea of stability of fragments. All mass spectra of the ligands and complexes confirmed the presence of the molecular ions using ESI in the positive or negative mode. This confirms the condensation reaction of the aldehyde

group with the respective amine derivative to form the Schiff base ligand and also suggests successful metal ion complexation.

2.7.5 Copper(II) Complexes

Neutral “metal-only” complexes of Schiff base ligands **L1-L4** were prepared from metal(II) acetates. The symmetrical Schiff base metal complex derivatives can be easily obtained by reaction between the ligand and the metal acetate. In particular, the acetate ion deprotonates the phenolic groups of the ligand framework, so that the metal ion can be complexed. The achievement of the synthesized metal complexes can be carried out with or without heating under reflux. The synthesised copper(II) complexes of **L1-L4** were prepared by mixing stoichiometric amounts of the ligand and copper(II) acetate in ethanol as shown in the section 2.8. FTIR results as shown in table 2.1 confirm successful complexation, in that the stretching frequency of the imine band decreases as shown by Al-Obaidi *et al.*¹⁷ Colour changes, indicating complex formation were instantaneous. The changes were expected as H₂ salen-type complexes of these metals form a dark-green colour with copper(II). Precipitation occurred immediately, and the pure products were collected by removing the solvent on the rotary evaporator. All complexes were isolated as green powders. The metal-only complexes **ML1-ML4** were found to be soluble in chloroform and dichloromethane with very low solubility in water thus making them ideal for solvent extraction experiments.¹⁷



Scheme 2.4: The formation of the metal only complex [M(L-2H)]

Table 2.1 The imine stretching frequencies for Schiff base ligands **L1-L4** and their metal complexes (cm^{-1})

	L1 (cm^{-1})	L2 (cm^{-1})	L3 (cm^{-1})	L4 (cm^{-1})
L	1633	1633	1633	1633
Cu	1630	1626	-	1624

2.7.6 Electronic Absorption Spectroscopy

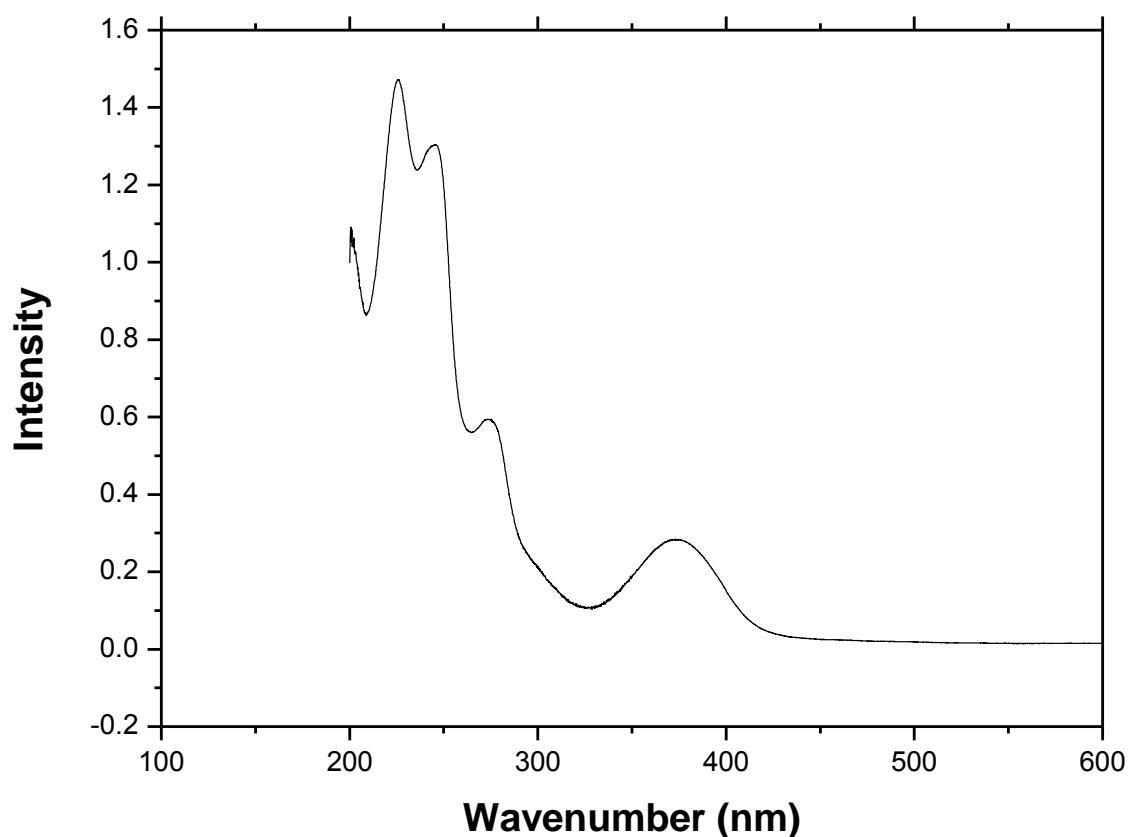


Figure 2.9: The electronic absorption spectrum of Schiff base ligand **L2** copper complex

The main reason for doing a UV-VIS for the Schiff base copper complex of **L2** (Figure 2.9) was to confirm the single crystal X-ray diffraction results, which showed trigonal bipyramidal geometry. Even though the electronic spectra of copper complexes with Schiff base ligands are not in general good indicators of geometry, they do help to support it. The fact that there is no evidence of a band between 500

nm and 800 nm provides further evidence to support the results obtained by XRD. The UV-Vis spectrum showed two bands at 285 and 370 nm which are assigned to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions respectively. In the spectra of the Schiff base complexes, the bands of the azomethine chromophore ($n\text{-}\pi^*$) transition are shifted to lower frequencies indicating that the imine nitrogen atom is involved in coordination to the metal ion. On the other hand, $\pi\text{-}\pi^*$ transition showed a shoulder at 285 nm due to the complexation of copper to the Schiff base ligand. These bands can be attributed to the ligand to Cu(II) charge transfer transition (LMCT).¹⁸ Also the d-d transition in this type of complexes may appear above 500 nm but does not appear due to the low intensity of the d-d transition.¹⁹

2.7.7 Elemental Analysis

The main reason for performing elemental analysis was firstly to establish the purity of the synthesized Schiff base ligands. The elemental analyses results complement the IR spectral studies. The results of elemental analyses of the ligand and its complexes are in good agreement with those required by the proposed formulae given in section 2.5 and also suggest that the metal and the ligands are coordinated in the ratio 1:1. The ligands were isolated as oils except for **L1** which turned out to be a solid. These oils were placed under high vacuum for 3 days whilst heating to ensure complete removal of volatile starting material as well as solvents present in the oils. It was not necessary to place **L1** under high vacuum as it yielded a solid. Some solvents from which the ligands were isolated were incorporated into the ligand structure as could be seen from the results obtained from elemental analysis. The standard on the analyser for hydrogen was not working well and as a result the found results for hydrogen were lower throughout.

2.8 Evaluation of metal ion binding strength by Solvent Extraction

Experiments were carried out to assess the extractive ability of the ligand series towards selected transition and post-transition metal ions. Stoichiometric quantities of the ligand in chloroform and an aqueous solution of mixed metal ions (figure 2.10) were shaken for 24 hours on a labcon shaker. The aqueous phase was separated afterwards, and measured by ICP-OES. The initial liquid-liquid extraction experiments indicated substantial bleeding of the ligand from the chloroform phase into the aqueous solution. This is most likely due to the additional amine group between the two phenyl rings which makes the ligand more polar and hence able to leach into the aqueous phase. Palmitic acid was then added to the organic phase and bleeding was dramatically reduced in all the subsequent solvent extraction experiments. The concentrations of metal ions present before and after extraction was determined by ICP-OES.

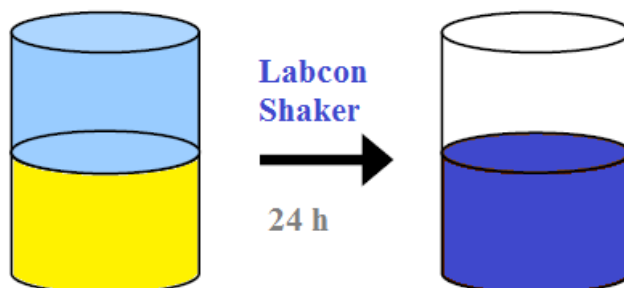


Figure 2.10: Schematic of competitive extraction of selected transition and post-transition metal ions by means of Schiff base ligand

All the extractions were carried out in a temperature controlled laboratory at $25 \pm 2^\circ\text{C}$. The aqueous source phase consisted of a buffer solution ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) at $\text{pH} = 4.90$ and contained an equimolar mixture of the 6 metal cations (Cu(II) , Zn(II) , Ni(II) , Co(II) , Pb(II) , and Cd(II)). Equal volumes (5 cm^3) of 0.01 M solution of each ligand and 0.04 M palmitic acid in chloroform was contacted

with a buffer solution containing a 0.01 M mixture of the metal ions (5 cm³) and shaken on a labcon-oscillating automated platform shaker at an optimised speed of 220 rpm for 24 h. Figure 2.11 shows the colour changes in the different phases before and after metal ion extraction. The results of the extraction are indicated in figure. 2.12. Duplicate results did not differ by more than 3 %. Any apparent extraction of a metal ion found to be within the experimental error was taken as zero and hence ignored in the treatment of results.

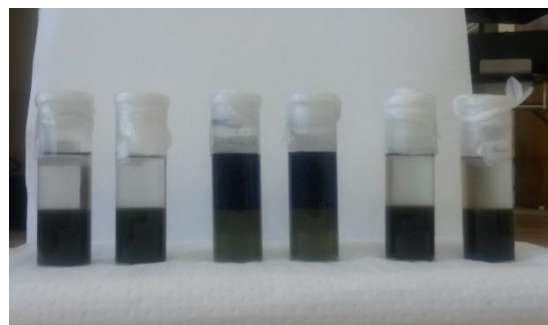
The percentage extractions (%E) of the metal ions were calculated from the concentrations of the metal ions in the aqueous phase using the equation below:

$$\% E = \frac{C_i - C_s}{C_i} \times 100 \quad (2.2)$$

where C_i is the initial metal ion solution concentration (mg/L) and C_s is the solution metal ion concentration after extraction.



(i)



(ii)

Figure 2.11: (i) Before and (ii) after images of solvent extraction using different metal ions for each of the ligands (performed in duplicate)

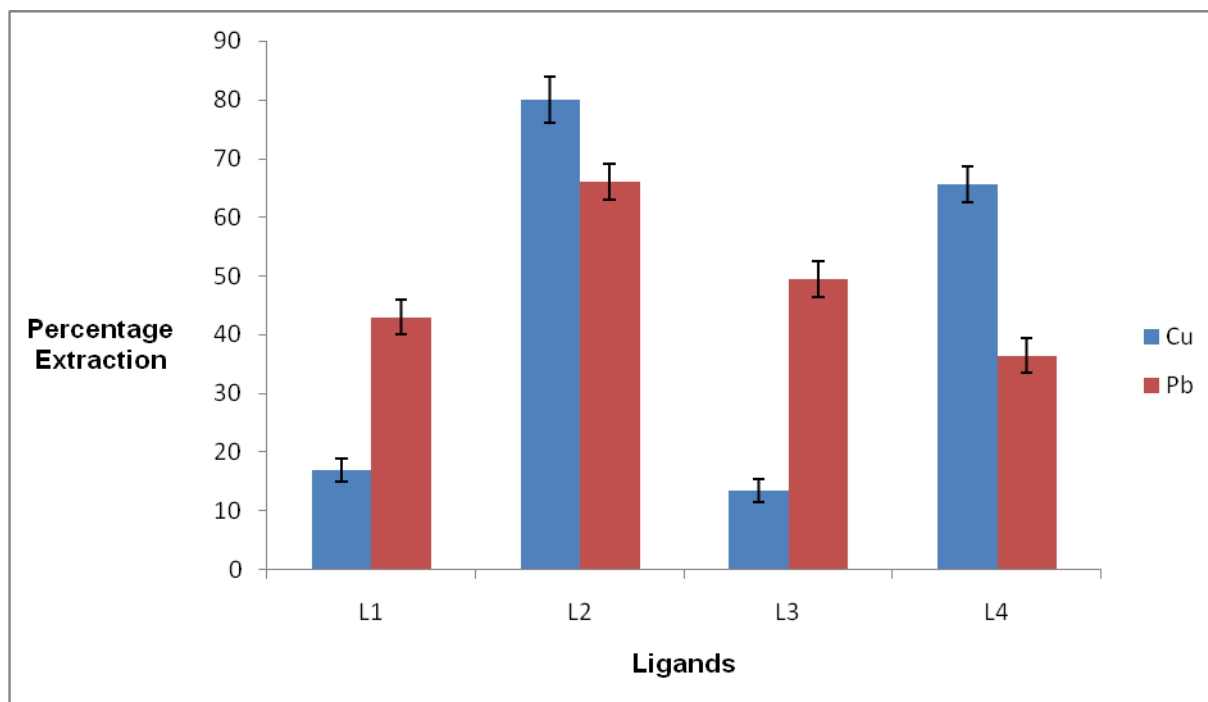


Figure 2.12: Percentage of metal ions extracted

When summarizing all the results of Cu(II) and Pb(II) extraction as shown in figure 2.12, it is apparent that **L2** has the highest extraction of both Cu(II) and Pb(II) followed by **L4** for Cu(II) and Pb(II) respectively. The four six-membered chelate rings as exhibited in **L2**, normally result in higher complex stability for small metal ions relative to large metal ions hence high extraction efficiency for copper(II) ions. **L4** contains an ethereal oxygen and nitrogen donor atoms in the chelate backbone, which appears to be favourable for complexation with Cu(II). The nitrogen and oxygen atoms induce two opposite electronic effects: the phenolate oxygen is regarded as a hard donor, while the imine nitrogen is a softer donor and this combination appears to favour the extraction of copper over other metal ions which correspond to the Irving-Williams series.²⁰ The Schiff base exhibits a synergistic effect (investigation reported later) with palmitic acid and experimentally shows an

increased uptake of lead ions. However, without the use of palmitic acid there was no metal extraction. It is observed that all the ligands show relatively high extraction of lead ions most likely due to the synergistic effect. The order for the extraction of Pb(II) is **L2 > L3 > L1 > L4**. The size of the coordination cleft in **L2** could suit the large sized Pb(II) more ideally. **L3** is even larger and has 6 donor atoms used for bonding to metal cations. This will tend to favour borderline metal ions such as Cu(II).²¹

2.9 Comparison of metal ion transport by **L1-L4**

The aqueous source phase solution consisted of an equimolar mixture of Cu(II), Zn(II), Co(II), Ni(II), Pb(II), and Cd(II) metal ions in a CH₃COONa/CH₃COOH buffer at pH = 4.90 which was separated by a presaturated aqueous chloroform layer that consisted of the respective Schiff base ligand (**L1-L4**) which was used separately as a carrier for the transport of metal ions across a bulk liquid membrane (BLM) phase. The receiving phase consisted of 30 cm³ of 0.1 M HNO₃ at pH 1.0. The concentration of the metal ions was (1x10⁻² mol dm⁻³) and that of the chosen ligand (1x 10⁻² mol dm⁻³) with 4 x 10⁻² mol dm⁻³ palmitic acid. The cell details are the same as those used by Lindoy *et al.*²².

All three phases in the transport cell were stirred at 10 rpm by using a coupled single gear synchronous motor at 25 °C using a water bath pump. The rate of stirring remained constant throughout the experimental process, and also the interface between the organic membrane phase and the two aqueous phases were very distinct. The cells were covered with cover slips to prevent evaporation of solvents and obstructions from surrounding dust over the 24 h period. The metal ion transport

is an effective way to establish the transport efficiency for a series of Schiff-base ligands. Before use, the transport cell was soaked in concentrated HNO_3 overnight, rinsed with distilled water, dried with acetone and covered.

The membrane phase, the source phase and the receiving phase were then gently transferred in this respective order into the cells. Under these conditions, not only was the stirring process consistent, but also the interfaces between the organic membrane and the two aqueous phases remained flat and well defined and transport allowed to take place, against a back gradient of protons (figure 2.13).



(i)



(ii)

Figure 2.13: (i) Before and (ii) after images of the membrane transport using different metal ions with **L1 – L4**

Samples of the source and receiving phases were taken and analysed by ICP-OES. Figure 2.13 indicates the phases before and after the transport studies. The transport experiment was terminated after 24 h.

The transport of Cu^{2+} ions can be elucidated according to the following explanation: at the source phase/membrane interface, the ligand selectively complexes the copper ion and forms an uncharged complex with the ligand having released its protons to the source phase. The complex which formed diffuses across the membrane and at the membrane/receiving phase interface it releases the Cu^{2+} ion into the receiving phase. Here the ligand re-protonates itself due to the pH of the receiving phase being 1.0. The pH gradient is used in order to facilitate the transport of the metal ions across the organic membrane by counter transport of protons. The free ligand diffuses back across the membrane to the source phase/membrane interface, where the cycle continues.²³

The results are quoted in Table 2.2 as the average value obtained from duplicate runs. Any apparent extractions of a metal ion less than 3% was assumed to be within experimental error and hence ignored in the final results. In all cases the values between the duplicate runs did not differ by more than 3%.

Table 2.2. $J / \text{mol h}^{-1} \times (10^{-7})$ values for the competitive metal ion transport studies involving **L1–L4**. The experimental conditions were: pH of the source phase = 4.9, pH of receiving phase = 1.0 and concentration of ligand = 0.01 mol dm^{-3} .

Metal ion transport, $J / \text{mol h}^{-1} \times 10^{-7}$

Ligand number	L1	L2	L3	L4
Co(II)	—	—	—	—
Ni(II)	—	—	—	—
Cu(II)	8.6	15.1	9.7	13.2
Zn(II)	—	—	—	—
Cd(II)	—	—	—	—
Pb(II)	—	—	—	—
${}^{\text{Cu}} T_r \%^{\text{a}}$	6.0	12.1	7.8	10.7
${}^{\text{Cu}} T_M \%$	19.6	26.0	25.3	34.1
${}^{\text{Pb}} T_r \%$	—	—	—	—
${}^{\text{Pb}} T_M \%$	9.4	18.6	62.4	12.8
$\eta(\text{Cu(II)/Pb(II)})^{\text{b}}$	∞	∞	∞	∞

^a ${}^{\text{Cu}} T_r \% =$ Percentage of Cu(II) transported into the receiving phase. ${}^{\text{Cu}} T_M \% =$ Percentage of Cu(II) transported into the membrane phase. ${}^{\text{Pb}} T_r \% =$ Percentage of Pb(II) transported into the receiving phase. ${}^{\text{Pb}} T_M \% =$ Percentage of Pb(II) transported into the membrane phase. ^b $\eta(\text{Cu(II)/Pb(II)}) = \frac{{}^{\text{Cu}} T_r \% / {}^{\text{Pb}} T_r \%}{}$

The transport results are consistent with the extraction results and complement it. No Pb(II) is transported into the receiving phase most likely because the ligand palmitic acid assembly holds onto Pb(II) strongly, not releasing it.

Schiff base ligands with nitrogen and oxygen donor atoms act as good chelating agents for transition and non-transition metal ions.^{23, 25, 26} Transport selectivity was achieved towards copper ions over lead, nickel, cobalt, cadmium and zinc ions in the transport experiments using the various Schiff base ligands as a carrier. The results presented in Table 2.2 represent the metal ions transported as well as the metal ions present in the membrane phase. The results confirm selectivity of these Schiff base ligands for the stripping of copper ions over other ions due to multi-ion competition or crowding effect amongst other reasons.^{6,7,24} Also, Pb(II) is more likely coordinated quite strongly to the ligand-palmitic acid assembly, thus not releasing it into the receiving phase under these conditions. Cu(II), on the other hand, is transported by all four ligands and **L2** shows the highest transport followed by **L4**. These results complement those obtained in the extraction studies, where ligands **L2** and **L4** showed the highest Cu(II) extraction.

2.10 Terminologies and Calculations

${}^{\text{Cu}} T_r\%$ = Percentage of Cu(II) transported into the receiving phase

${}^{\text{Cu}} T_M\%$ = Percentage of Cu(II) transported into the membrane phase

${}^{\text{Pb}} T_r\%$ = Percentage of Pb(II) transported into the receiving phase

${}^{\text{Pb}} T_M\%$ = Percentage of Pb(II) transported into the membrane phase

The selectivity factor for a specific ligand can be defined as

$$\eta (\text{Cu(II)/Pb(II)}) = {}^{\text{Cu}}T_r (\%) / {}^{\text{Pb}}T_r (\%)$$

The average cation flux rate is given by J values, which are based on the quantity of metal ion transported into the receiving phase, see equation 3.1.

$$J = \frac{C_{\text{receiving}} \times V}{t} \quad (3.1)$$

Where $C_{\text{(receiving)}}$ is the concentration of the cation in the receiving phase (mol dm^{-3}),

V is the volume of the receiving phase (30 cm^3), T is the transport time in hours

The percentage of metal ion transported from the aqueous phase to the receiving phase, ($T \%$), is calculated using the following equation:

$$(T \%) = (n_r / n_i) \times 100$$

Where n_r and n_i represent the number of moles of metal ion transported into the receiving phase and the initial moles of metal ion in the source phase respectively.

2.11 Solvent extraction of Cu(II) and Pb(II) at different pH values

The initial pH isotherm is essential to be studied as it describes the interactive behaviour between the metal ions and the ligand. One hopes to obtain steep pH isotherm curves which do not overlap which are indicative of a good separation. Different pH's of Cu(II) and Pb(II) ion solutions ranging from 2-6 were measured and subsequently used to study the maximum extraction of Schiff base ligands together with palmitic acid. Experiments were carried out by contacting chloroform solutions (5 cm^3) which contained the ligand and palmitic acid at concentrations of 0.01 mol dm^{-3} and 0.04 mol dm^{-3} respectively. The aqueous solutions (5 cm^3) contained either copper(II) nitrate or lead(II) nitrate at a concentration of 0.01 mol dm^{-3} . After adjusting the pH of the aqueous metal solutions using a few drops of either concentrated HNO_3 or concentrated NaOH the chloroform solution was added and placed on a shaker, shaking at 220 rpm for 24 h at room temperature. After 24 hours, 1 cm^3 aliquots of the aqueous phase were removed and diluted up to a volume of 10 ml with 0.1 M

HNO₃, and Cu(II) and Pb(II) ions were analysed respectively by ICP-OES. The calculated percentage of Cu(II) and Pb(II) uptake into the organic phase was plotted against the measured initial pH of the aqueous phase to give s-curves.

The pH isotherms presented in Figures 2.14 - 2.17 for Cu(II) and Pb(II) respectively shows that at low pH almost no extraction of the metal ions was detected whilst at higher pH the extraction efficiency increases. The selected pH isotherm for copper and lead ions was conducted to determine the optimal extraction efficiency for the respective metal ions. It is observed that both Cu(II) and Pb(II) ions were simultaneously extracted with high efficiency in the pH range of 5–6 for **L2** and **L4**. The most significant difference was observed between pH 3-4 where Cu²⁺ shows a higher extraction affinity over Pb²⁺ for **L2**. The increase in metal ion removal with an increased pH can be explained on the basis of a decrease in competition between H⁺ and positively charged metal ion (Pb²⁺ or Cu²⁺) at the surface sites which results in a lower electrostatic repulsion of the adsorbing metal ion and consecutively increased metal ion removal.²¹ By contacting the prepared Schiff base ligands in chloroform solutions with aqueous solutions of copper and lead solutions of varied pH values, much better material balances were obtained.

The main reason for the low extraction of copper ion at low pH is due to the protonated functional groups (hydroxyl and imine) and these results in the formation of positive sites. The low extractive ability of Schiff bases is due to the electrostatic repulsion between the positively charged Schiff base, copper ions and the protons (H⁺) present. Furthermore, complexation takes place at higher pH because the hydroxyl group is deprotonated creating a negatively charged ion that will attract copper (II) ions. Also the decrease in protons results in less competition between copper ion and protons. In this study, pH 6 was chosen as the highest extraction pH

because at higher pH, Cu(II) and Pb(II) ions will form the insoluble Cu(OH)₂ and Pb(OH)₂ precipitate.²⁷

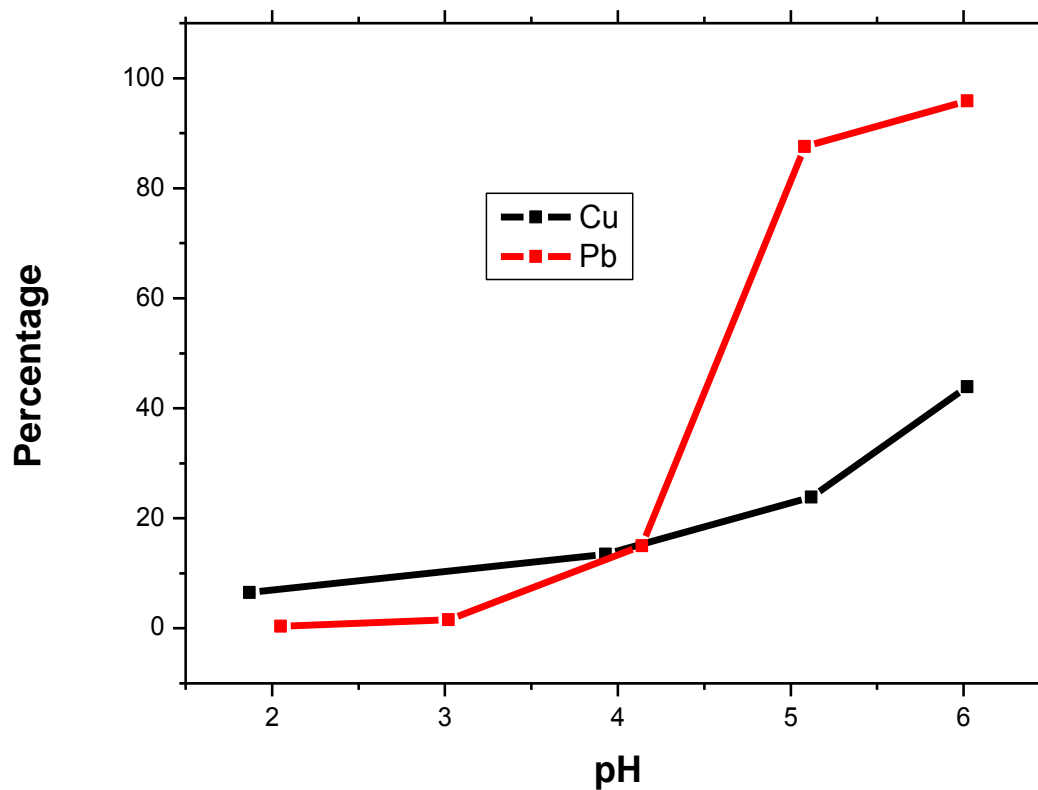


Figure 2.14: Extraction of Pb²⁺ and Cu²⁺ by L1 from an aqueous (pH 2-6) to organic phase

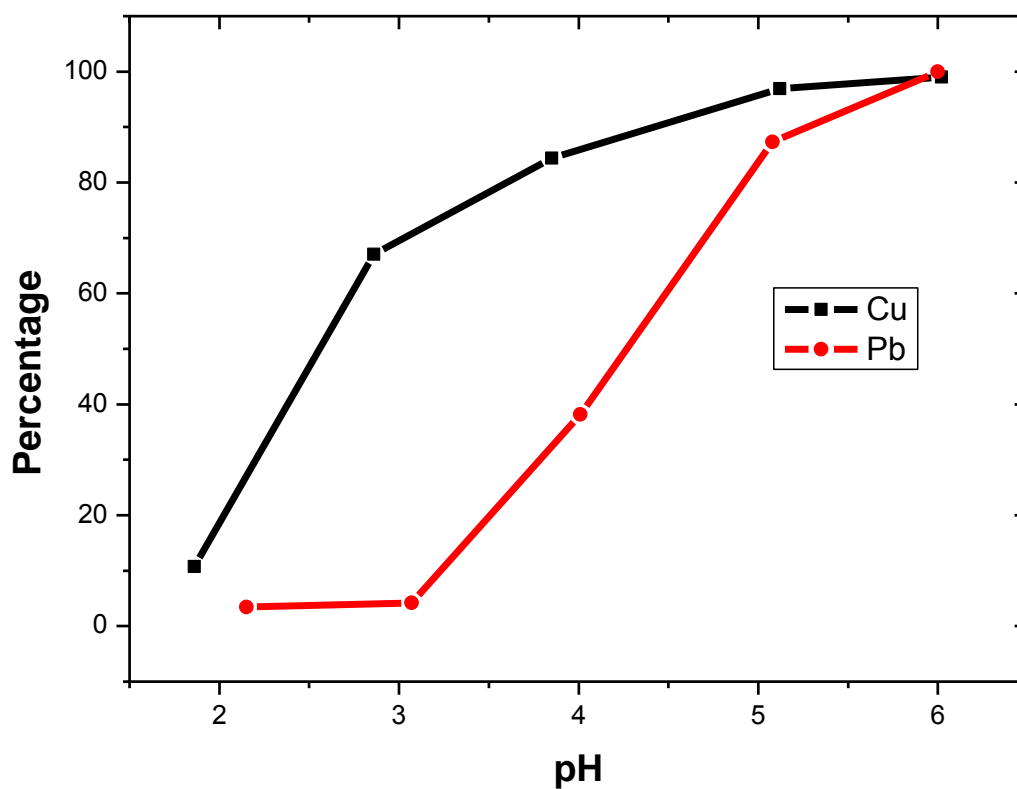


Figure 2.15: Extraction of Pb^{2+} and Cu^{2+} by L2 from an aqueous (pH 2-6) to organic phase

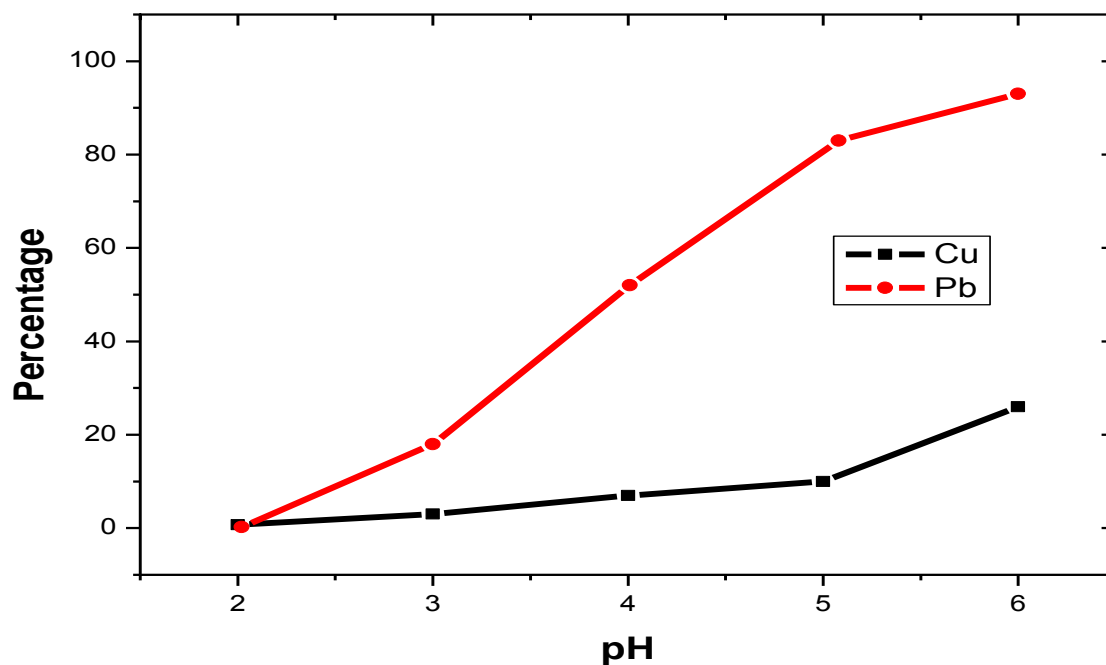


Figure 2.16: Extraction of Pb^{2+} and Cu^{2+} by L3 from an aqueous (pH 2-6) to organic phase

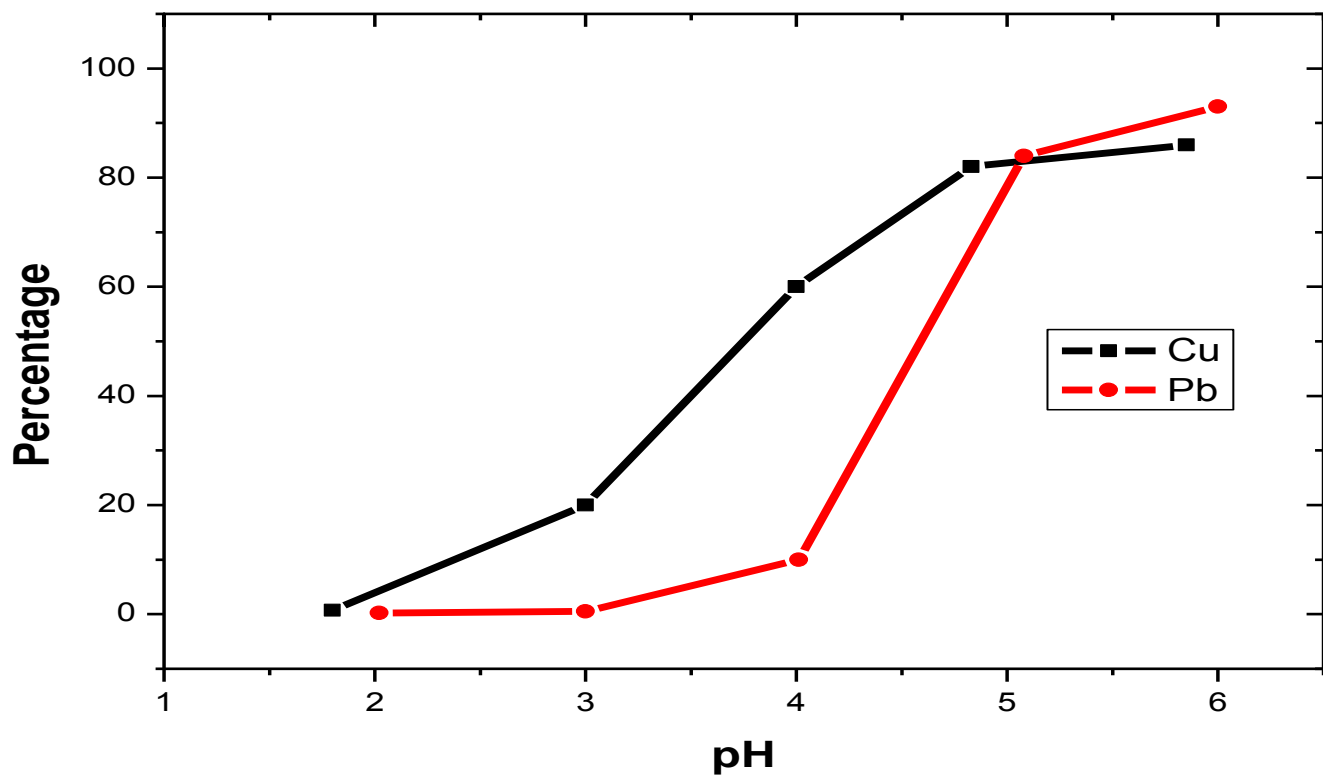
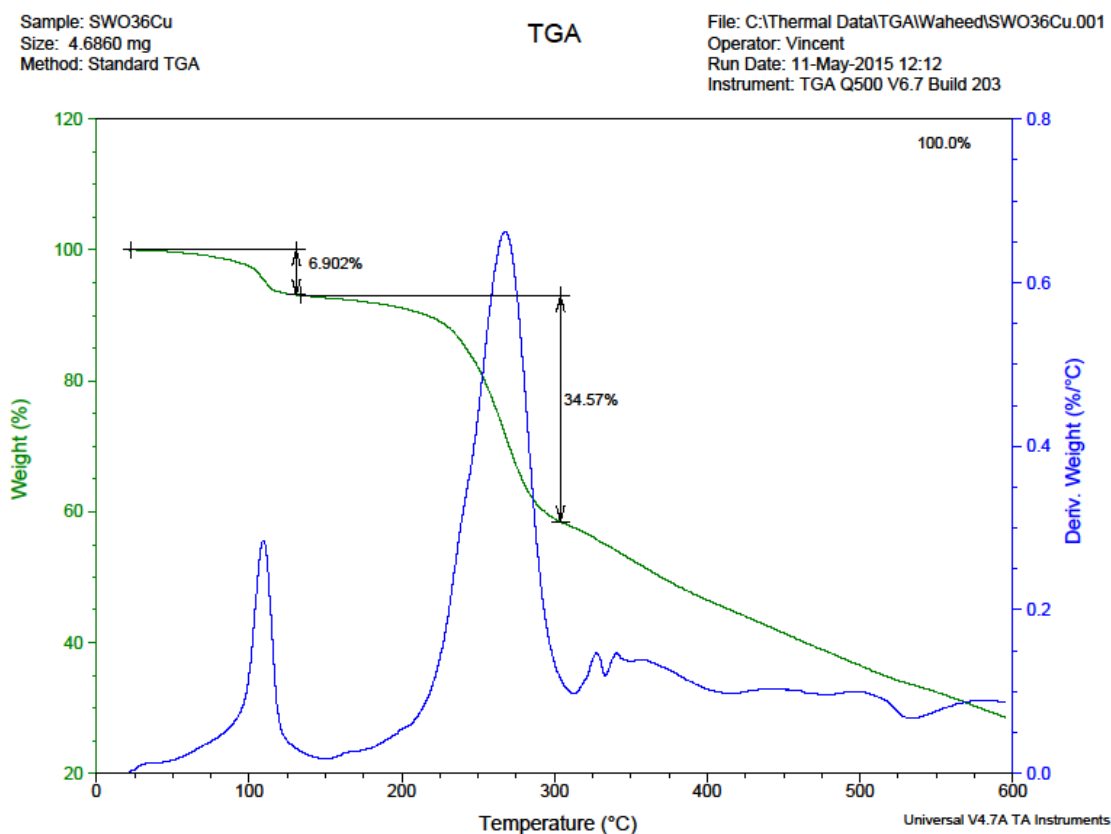


Figure 2.17: Extraction of Pb²⁺ and Cu²⁺ by L4 from an aqueous (pH 2-6) to organic phase

2.12 Thermogravimetric Analysis (TGA)

Figure 2.18: TGA of **L2**_Cu

The TGA plot of copper complexed with **L2** (Figure 2.18) shows 2 thermal events. The observed TGA for the copper **L2** complex shows a mass loss below 100 °C, likely due to encapsulated solvent (local maximum below 100 °C). It is observed that the first derivative plot of the Schiff base complex has an extra mass loss peak (local maximum at 225 °C). This mass loss corresponds to 6.9 % (solvent) of the total mass. This is most probably due to the loss of the acetate counter ion (8% of total mass of the proposed structure). A very large mass loss then occurs starting between 120 and 285 °C. This could be accounted for the decomposition of the Schiff base ligand which makes up for the majority of the mass. It appears that the Schiff base ligand decomposition takes place in two stages. The temperature range between 120-285 °C about 40% of the remaining mass decomposes. A further 15 %

of the total mass decomposes in the range 300-500°C resulting in the metal oxide at high temperatures (600°C). The Cu (II) complex was stable below 335 °C, after that it gradually decomposes to form the corresponding metal oxide at 600°C.

The TGA plot of copper complexed to **L4** (Figure 2.19) shows four thermal events. The observed TGA for the copper **L4** complex shows a mass loss below 100°C, likely due to encapsulated solvent (local maximum below 100°C). It is observed that the first derivative plot of the Schiff base complex has an extra mass loss peak (local maximum at 225 °C). Sharma *et al.*²⁸ observed similar results for the thermal stability of bidentate Schiff base copper complexes.

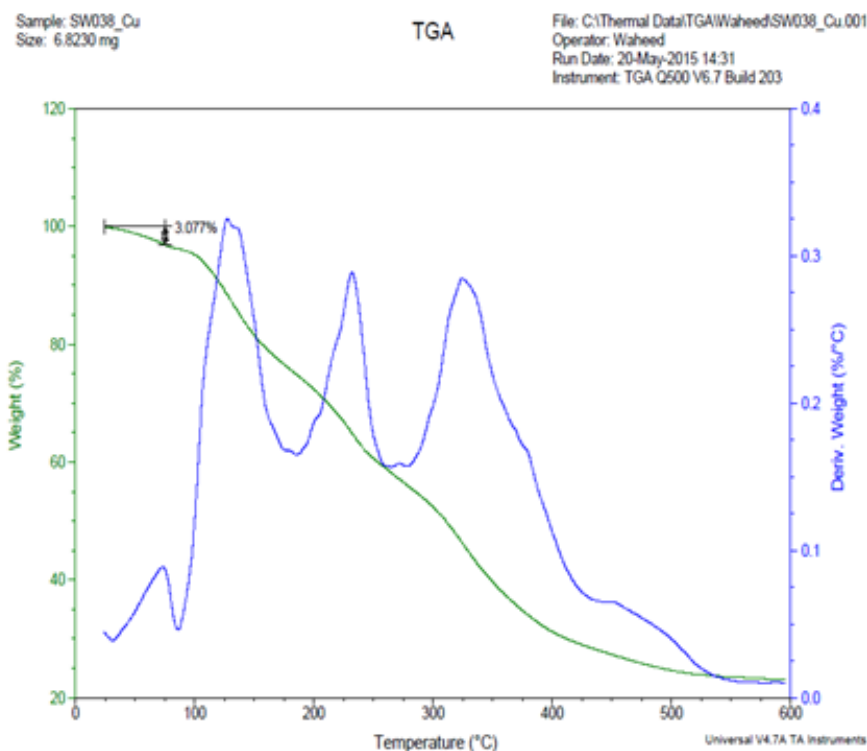


Figure 2.19: TGA of **L4**_Cu

Thermal analyses gives useful data about the thermal stability of the metal complexes and the metal ligand bonds. The thermal measurements (TG and DTG) were carried out within a temperature range from 25 up to 600 °C. The second stage is endothermic and represents the loss of two molecules of water one of them is

coordinated to the metal ion and the other exists in the crystal structure but without coordination to the metal ion. This step lies in the temperature range 95–180 °C. The third step lies in the range 200–250 °C. This step is endothermic and represents the loss of CO₂, acetate group, -OH, -CH₂NCCH₃. The last step lies in the temperature range 285–450 °C. This is possibly due to the decomposition of the ligand molecule.

2.14 X-ray Crystal Structures

Diffraction-quality single-crystals for X-ray structure investigation were obtained for compounds **L1** and **L4** by slow evaporation and vapour diffusion of diethylether into a saturated solution of the compound in ethanol/dichloromethane. Crystal structures for the copper complexes of **L2** and **L4** were obtained from a solution of the complex dissolved in dichloromethane, enclosed by diethylether in a sealed container. The experimental parameters are given in section 2.2.

2.14.1 Crystal structure of the free ligand **L1**

Light orange crystals of the free ligand **L1**, suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into a methanol solution at room temperature. The molecular structure of $[C_{26}H_{37}N_3O_2]$ is presented in Figure 2.20 and the selected bond angles and lengths are given in Tables 2.4 and 2.5 respectively. X-ray diffraction confirms the synthesis of **L1** and shows the atom connectivity in figure 2.20. The structure was solved in the monoclinic space group $C2/c$.

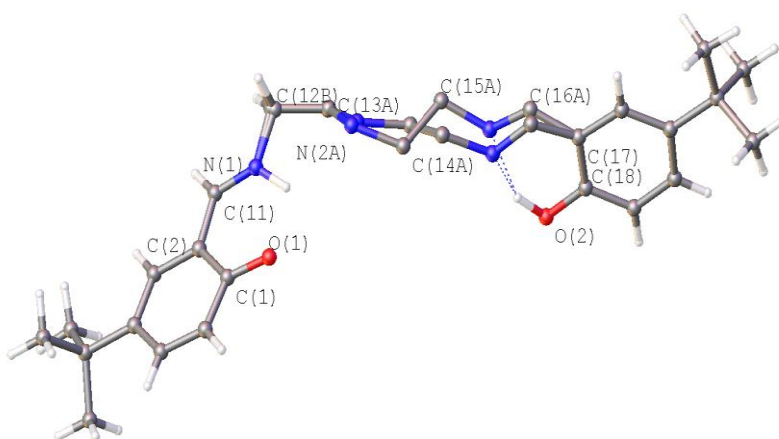


Figure 2.20: **L1** = 2-((E)-(2-(2-((E)-5-tert-butyl-2-

hydroxybenzylideneamino)ethylamino)ethylimino)methyl)-4-tert-butylphenol, Molecular diagram of Schiff base free ligand (**L1**), showing single chain amine section consisting of the three nitrogen atoms that are disordered. The ellipsoids are drawn at 50 % displacement probability.

This is a free ligand Schiff base consisting of three nitrogen donor atoms with an ethylene bridge and tertiary butyl substituents. The single-crystal X-ray diffraction analysis was used to confirm that the compound is an NNN Schiff base framework resulting from the mono-condensation of the 5-tert butyl salicylaldehyde and appropriate amine linker.

The asymmetric unit of **L1** consists of two phenyl rings that are approximately orthogonal to each other whilst the single chain amine section consisting of the three nitrogen atoms are disordered. The structure shows that the donor atoms are arranged in an approximately distorted square planar geometry. The molecule lies on a centre of symmetry with half of the molecule generated through symmetry. In figure 2.20 half of the molecule is generated through symmetry. The two hydroxyl atoms are in a *cis* configuration. This is due to internal hydrogen bonding between the imine nitrogen and the hydroxyl group. The crystal data and structure refinement parameters can be found in Table 2.3.

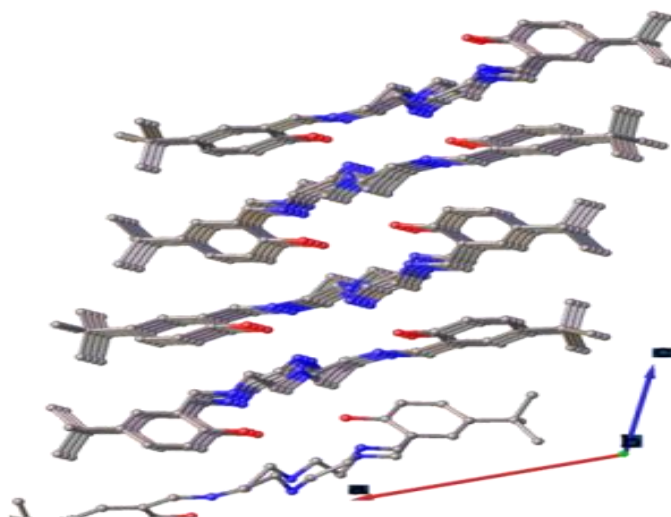


Figure 2.21: Packing diagram along the b axis showing the stratified format of **L1**

Table 2.3: Crystal data and structure refinement for L1

Identification code	L1
Name	2-((E)-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethylamino)ethylimino)methyl)-4-tert-butylphenol
Empirical formula	C ₂₆ H _{35.92} N ₃ O ₂
Formula weight	422.5
Temperature/K	102(2)
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	43.034(13)
<i>b</i> /Å	5.9964(18)
<i>c</i> /Å	20.776(6)
α /°	90
β /°	116.415(4)
γ /°	90
Volume/Å ³	4801(2)
Z	8
ρ_{calc} /cm ³	1.169
μ /mm ⁻¹	0.074
F(000)	1831
Crystal size/mm ³	0.15 × 0.12 × 0.09
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.92 to 56.38
Index ranges	-54 ≤ <i>h</i> ≤ 52, -7 ≤ <i>k</i> ≤ 7, -27 ≤ <i>l</i> ≤ 23
Reflections collected	13866
Independent reflections	5545 [<i>R</i> _{int} = 0.0468]
Data/restraints/parameters	5545/14/342
Goodness-of-fit on <i>F</i> ²	1.068
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0621, <i>wR</i> ₂ = 0.1428
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1064, <i>wR</i> ₂ = 0.1686
Largest diff. peak/hole / e Å ⁻³	0.44/-0.45

Table 2.4: Selected bond lengths for L1

Atom	Atom	Length/Å
O1	C1	1.280(2)
N1	C11	1.303(3)
N1	C12B	1.460(2)
O2	C18	1.352(3)

Table 2.5: Selected bond angles for L1

Atom	Atom	Atom	Angle/°
C11	N1	C12B	127.4(7)
C11	N1	C12A	123.4(4)

The packing diagram (Figure 2.21) shows the O atoms in a *trans*-conformer arrangement. The ligand is packed in uniform layers running parallel to the *a* direction, each molecule and its subsequent molecule stratified and organized from head to tail in the packed structure.

2.14.2 Crystal structure of the free ligand **L4**

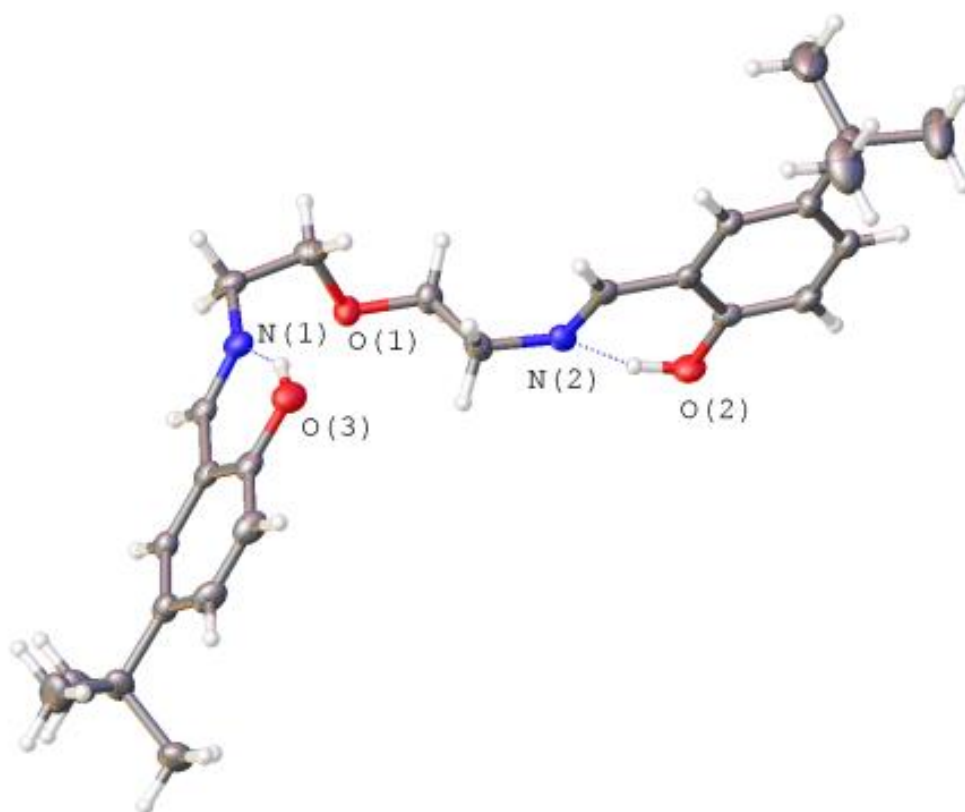


Figure 2.22: **L4** = 2-((E)-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethoxy)ethylimino)methyl)-4-tert-butylphenol, The ellipsoids are drawn at 50 % displacement probability.

Figure 2.22 shows the ligand, which was used to study the metal ion extraction and transport. This Schiff base consists of five donor atoms, two nitrogen and three oxygen donor atoms with an ethylene bridge and tertiary butyl substituents. The crystal data and structure refinement can be found in Table 2.6. Selected bond lengths and angles are shown in tables 2.7.

The crystal structure consists of discrete molecules held together by both intra- and intermolecular hydrogen bonding. A structure similar to that shown for **L1** is observed.

Table 2.6: Crystal data and structure refinement for L4

Identification code	L4
Name	2-((E)-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethoxy)ethylimino)methyl)-4-tert-butylphenol
Empirical formula	C ₂₆ H ₃₆ N ₂ O ₃
Formula weight	424.57
Temperature/K	100.03
Crystal system	Monoclinic
Space group	<i>C2/c</i>
<i>a</i> /Å	14.407(2)
<i>b</i> /Å	13.744(2)
<i>c</i> /Å	24.944(4)
α /°	90.00
β /°	91.152(2)
γ /°	90.00
Volume/Å ³	4938.2(13)
<i>Z</i>	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.142
μ/mm^{-1}	0.074
F(000)	1840.0
Radiation	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/°	3.26 to 53.04
Index ranges	-18 \leq <i>h</i> \leq 17, -12 \leq <i>k</i> \leq 17, -30 \leq <i>l</i> \leq 31
Reflections collected	14330
Independent reflections	5105 [<i>R</i> _{int} = 0.0274, <i>R</i> _{sigma} = 0.0339]
Data/restraints/parameters	5105/0/292
Goodness-of-fit on <i>F</i> ²	1.086
Final <i>R</i> indexes [<i>I</i> \geq 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0606, <i>wR</i> ₂ = 0.1679
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0786, <i>wR</i> ₂ = 0.1827
Largest diff. peak/hole / e Å ⁻³	0.80/-0.40

Table 2.7: Selected bond lengths for **L4**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C8	1.422(3)	C5	C23	1.406(3)
O1	C9	1.422(3)	C7	C8	1.503(3)
O2	C20	1.357(2)	C9	C10	1.523(3)
O3	C23	1.360(3)	C11	C12	1.456(3)
N1	C6	1.277(3)	C12	C13	1.394(3)
N1	C7	1.458(3)	C12	C20	1.411(3)
N2	C10	1.459(3)	C13	C14	1.389(3)
N2	C11	1.277(3)	C14	C15	1.529(3)
C1	C2	1.541(3)	C14	C18	1.398(3)
C2	C3	1.525(3)	C15	C16	1.511(4)
C2	C24	1.538(3)	C15	C17	1.574(4)
C2	C25	1.530(3)	C15	C26	1.506(4)
C3	C4	1.391(3)	C18	C19	1.387(3)
C3	C21	1.407(3)	C19	C20	1.386(3)
C4	C5	1.400(3)	C21	C22	1.378(3)
C5	C6	1.456(3)	C22	C23	1.386(3)

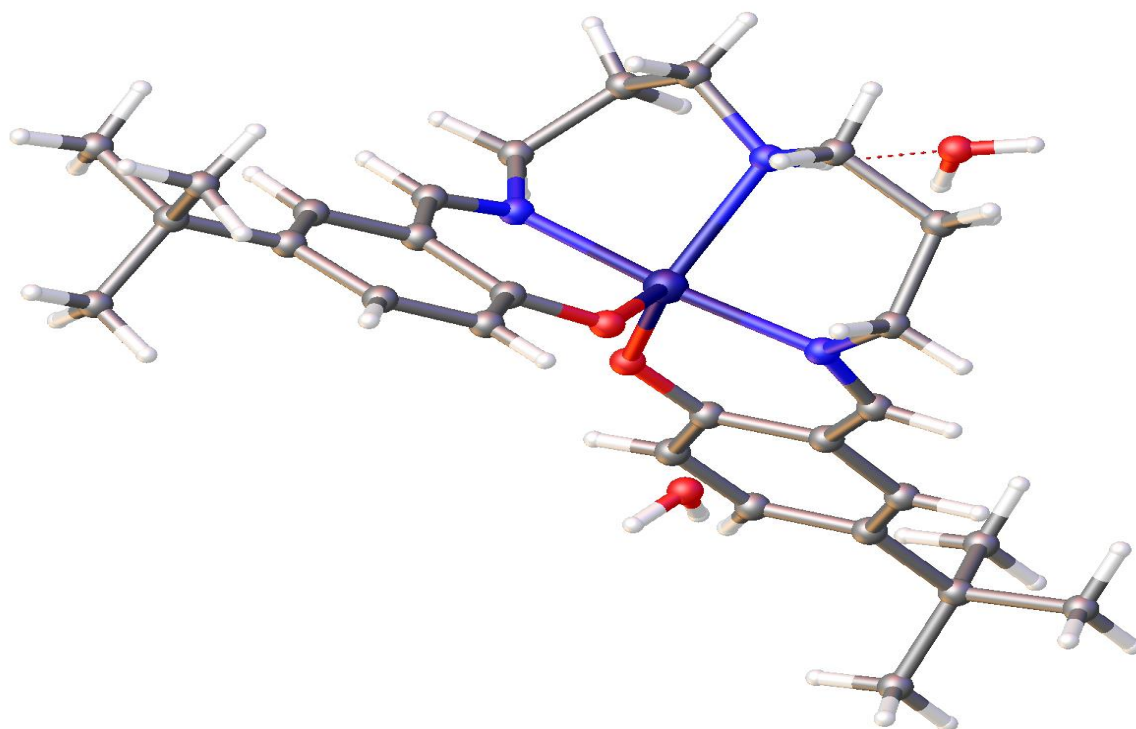
2.14.3 Crystal structure of $[\text{Cu}(\text{L2-2H})]\cdot 2\text{H}_2\text{O}(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)$ 

Figure 2.23: Cu-2-((E)-(3-(3-((E)-5-tert-butyl-2-hydroxybenzylideneamino)propylamino)propylimino)methyl)-4-tert-butylphenol, The ellipsoids are drawn at 50 % displacement probability.

Figure 2.23 shows the copper complex with ligand (**L2**), which was used to study the metal ion extraction and transport. Light green crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into a dichloromethane solution at room temperature. Crystallographic data and refinement parameters for the complex are shown in Table 2.8.

Table 2.8: Crystal data and structure refinement for Cu-L2

Identification code	Cu-L2
Name	Cu-2-((E)-(3-(3-((E)-5-tert-butyl-2-hydroxybenzylideneamino)propylamino)propylimino)methyl)-4-tert-butylphenol
Empirical formula	C _{28.59} H _{44.47} CuN ₃ O _{4.15}
Formula weight	560.10
Temperature/K	173(2)
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> /Å	13.9595(19)
<i>b</i> /Å	12.2346(16)
<i>c</i> /Å	35.383(5)
α /°	90.00
β /°	90.00
γ /°	90.00
Volume/Å ³	6043.0(14)
Z	8
ρ_{calc} /g/cm ³	1.231
μ /mm ⁻¹	0.759
F(000)	2393.4
Crystal size/mm ³	0.20 × 0.18 × 0.12
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.72 to 56.44
Index ranges	-17 ≤ <i>h</i> ≤ 18, -16 ≤ <i>k</i> ≤ 16, -45 ≤ <i>l</i> ≤ 46
Reflections collected	133255
Independent reflections	7307 [<i>R</i> _{int} = 0.0446, <i>R</i> _{sigma} = N/A]
Data/restraints/parameters	7307/112/442
Goodness-of-fit on <i>F</i> ²	1.289
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0723, <i>wR</i> ₂ = 0.1589
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0803, <i>wR</i> ₂ = 0.1622
Largest diff. peak/hole / e Å ⁻³	0.90/-1.88

The monotopic **L2** ligand coordinates to the Cu centre to form a monomeric complex (Cu-**L2**) with a disordered tertiary-butyl, disordered diethyl ether molecules and two water molecules. The Cu center is bound to three N-donor atoms and two O-atoms forming a trigonal bipyramidal coordinate structure. All the bond angles and bond lengths are systemic for a normal trigonal bipyramidal structure. However, the N3 atom that is in plane has been elongated and this is usually due to Jahn Teller distortion. The Cu atom is lifted off the plane to the axial N3 atom by the two O-atoms forming an angle of 123.13° with atomic bond lengths of $2.012(3)$ Å and $2.052(3)$ Å for O1 and O2 respectively. The in plane Cu-N average bond length is $1.959(3)$ Å at an angle of $87.67(14)^\circ$. Selected bond lengths and angles are shown in Tables 2.9 and 2.10 respectively.

The Cu(II) complexes synthesized by Addison *et al.* with nitrogen and sulfur donor atoms were found to be both trigonal bipyramidal and square pyramidal geometry in the asymmetric unit. Furthermore it was found that Cu(II) atom was coordinated to three nitrogen atoms of the Schiff base ligand. The τ values for these two geometries are 0.45 and 0.56 for Cu(1) and Cu(2), respectively which leads to trigonal bipyramidal and square pyramidal geometries. The Cu-N_{imine} distances fall in the range 1.951-2.136 Å. Jana *et al.* also reported similar bond lengths and angles for similar systems.²⁹ The N(1)-Cu(1)-N(3) bond angle is $175.12(14)^\circ$ and the axial Cu-N bonds are shorter than any of the equatorial Cu-N/Cu-O bonds, which is typical of copper(II) trigonal bipyramidal (TBP) geometries.³⁰

Table 2.9: Selected bond lengths for Cu-L2

Atom	Atom	Length/Å
C28	C25	1.531(6)
Cu1	O1	2.012(3)
Cu1	O2	2.052(3)
Cu1	N2	2.136(3)
Cu1	N1	1.959(3)
Cu1	N3	1.951(3)

Table 2.10: Selected bond angles for Cu-L2

Atom	Atom	Atom	Angle/°
O1	Cu1	O2	123.13(12)
O1	Cu1	N3	91.93(12)
O2	Cu1	N3	91.10.1(13)
N2	Cu1	O1	125.58(12)
N2	Cu1	O2	111.29(13)
N2	Cu1	N1	87.67(14)
N2	Cu1	N3	87.45(14)
N1	Cu1	O1	90.99(13)
N1	Cu1	O2	90.57(13)
N1	Cu1	N3	175.12(14)

2.14.4 Crystal structure of $[\text{Cu}(\text{L4-2H})] \cdot \text{xH}_2\text{O}(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3)$

The X-ray diffraction structure of copper complex of **L4** is shown in figure 2.24, and selected bond lengths and angles are given in Tables 2.12 and 2.13 respectively. The crystal has a triclinic unit cell and the space group is $P\bar{1}$. Light green crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature.

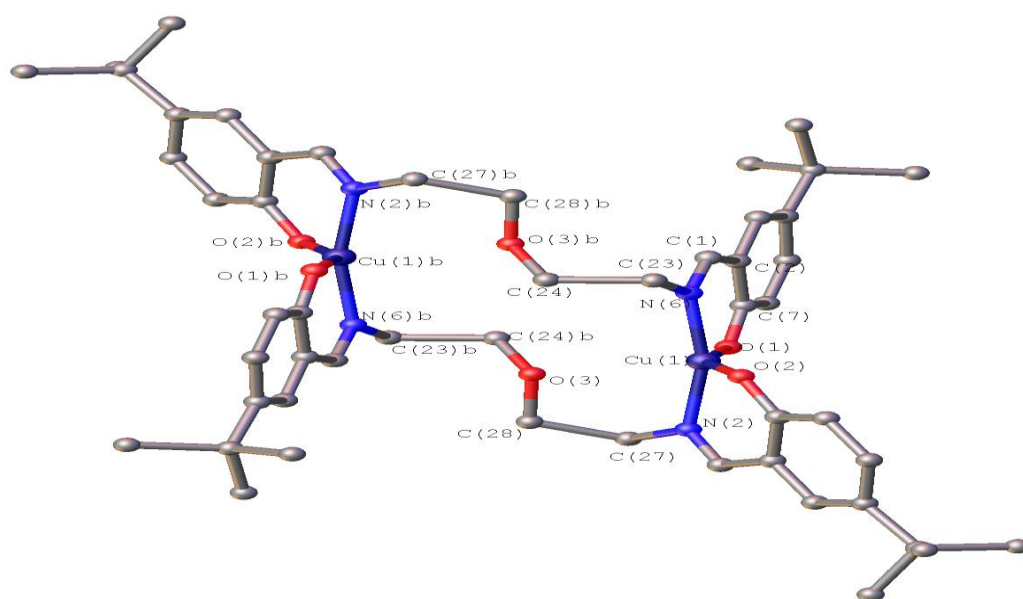


Figure 2.24: Diagram showing the asymmetric unit. Selected atoms have been labelled to show the general symmetry around the Cu atom. H-atoms have been omitted for picture clarity. The ellipsoids are drawn at 50 % displacement probability.

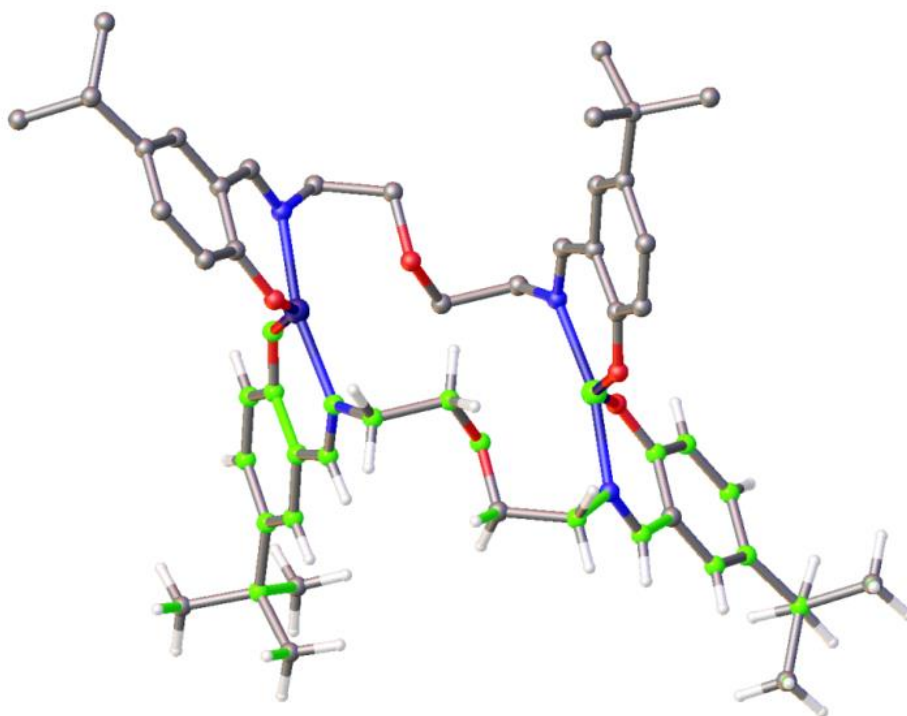


Figure 2.25: Cu-2-((E)-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethoxy)ethylimino)methyl)-4-tert-butylphenol, Diagram highlighting one ligand (shown in green) with hydrogen atoms attached and showing the metallocyclic ring. The other ligand is generated through symmetry and no hydrogen atoms are shown.

Figure 2.24 shows the asymmetric unit of the metallocycle. The Cu atoms have been labelled to show the generated symmetry and H-atoms have been omitted for clarity. The asymmetric unit consists of two metallocyclic units with the one metallocycle being twisted to almost 45° relative to the other. Two ligands are arranged in a *cis* conformation with the two ligands coordinating to the two Cu(II) centres. This is clearly shown in figure 2.25 which shows one metallocycle unit. This *cis* conformation ensures that N-donors are *trans* to each other and O-donors are *trans* to each other when coordinated to the copper (II) centre. An imine nitrogen and a phenoxy oxygen of two different ligands are coordinated to one Cu(II) centre in each case to produce a metallocycle. The etheral donor atoms are not coordinated to the Cu(II) centre. The metallocycle is a 16-membered ring made up of 2 copper (II) centres, 8 carbon atoms, 4 nitrogen atoms and 2 oxygen atoms. The cycle is flexible

and there is no solvent present in the cavity of the cycle, but diethyl ether and acetic acid are present as part of the packing. The average Cu-O bond length is 1.917 Å while that of Cu-N is 1.966 Å which coincides with that of the literature.³² The coordination geometry around the Cu(II) centre can be described as distorted square planar. One can see the distortion away from perfect square planar geometry by looking at the N-Cu-N and O-Cu-O bond angles which are 167.8° and 153.2° respectively. Some of the guest molecules could not be modelled and the e⁻ density was squeezed. The squeeze program was used to get rid of some of the solvent acetic acid molecules which were disordered. These were squeezed out resulting in the final R-factor coming down quite substantially.

To the best of our knowledge, this is the first example of this kind of copper metallocycle with a Schiff base ligand. There is only one other metallocycle in the literature of a similar ligand with the metal ion yttrium.³¹ The ligand is without t-butyl groups and yttrium forms a Y₂L₂ type structure. A four membered metallocyclic ring is formed in this case with one phenoxy oxygen coordinated to two Y(III) centres. Y(III) is eight coordinate in the structure having the other coordination sites occupied by two oxygen donors of a nitrate counterion.

Crystallographic data and refinement parameter for the complex is shown in Table 2.11.

Table 2.11: Crystal data and structure refinement for Cu-L4

Identification code	Cu-L4
Name	Cu- 2-((E)-(2-(2-((E)-5-tert-butyl-2-hydroxybenzylideneamino)ethoxy)ethylimino)methyl)-4-tert-butylphenol
Empirical formula	C ₆₀ H ₈₈ N ₄ O ₈ Cu ₂
Formula weight	1120.42
Temperature/K	100.15
Crystal system	Triclinic
Space group	P-1
a/Å	11.465(4)
b/Å	15.214(6)
c/Å	18.377(7)
α/°	81.299(5)
β/°	76.628(4)
γ/°	89.890(5)
Volume/Å ³	3081(2)
Z	2
ρ _{calc} /cm ³	1.208
μ/mm ⁻¹	0.743
F(000)	1196.0
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.7 to 56.5
Index ranges	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -24 ≤ l ≤ 24
Reflections collected	35575
Independent reflections	14183 [R _{int} = 0.0715, R _{sigma} = 0.1032]
Data/restraints/parameter	14183/0/683
Goodness-of-fit on F ²	0.958
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0607, wR ₂ = 0.1375
Final R indexes [all data]	R ₁ = 0.1058, wR ₂ = 0.1916
Largest diff. peak/hole / e Å ⁻³	1.95/-1.06

Table 2.12: Selected bond lengths of Cu-L4

Atom	Atom	Length/Å
Cu1	O1	1.909(2)
Cu1	N6	1.962(3)
Cu1	O2	1.925(2)
Cu1	N2	1.968(3)
Cu2	O5	1.910(2)
Cu2	N5	1.965(3)
Cu2	O6	1.926(2)
Cu2	N12	1.966(3)

Table 2.13: Selected bond angles of Cu-L4

Atom	Atom	Atom	Angle/°
O1	Cu1	N6	93.27(11)
O1	Cu1	O2	153.2(10)
O2	Cu1	N2	89.79(10)
N6	Cu1	N2	167.8(11)
O2	Cu1	N6	90.95(10)
O2	Cu1	N2	91.65(11)
O5	Cu2	N5	93.26(11)
O5	Cu2	O6	152.5(10)
O5	Cu2	N12	89.87(11)
N5	Cu2	N12	167.2(11)
O6	Cu2	N5	91.33(11)
O6	Cu2	N12	91.59(11)

2.15 Conclusions

The aim of the work in this chapter was to establish whether 5-tert-butyl-salicylaldehyde could produce a range of Schiff base analogues using a range of amine linkers. We also wished to evaluate the extraction efficiency towards selected base metal ions. We have synthesized and systematically characterized, using FT-IR, NMR, MS, EA and UV-vis absorption spectra, these novel pentadentate and 1 novel hexadentate Schiff base ligand.

Cu(II) and Pb(II) were extracted by all four ligands and some extract Cu(II) in preference to Pb(II) whilst the others extract Pb(II) in preference to Cu(II). Only Cu(II) was selectively transported throughout. The spectral data revealed that the Schiff base (**L2**) acts as a pentadentate ligand when complexed to Cu(II) and shows trigonal bipyramidal geometry. The Schiff base (**L4**) complexes with copper to form a metallocycle. It must be noted that obtaining crystals for the monotopic Schiff base ligands was not easy because of the extra donor atom in the ligands backbone. Furthermore various crystallization techniques were used to obtain crystals such as layering, slow evaporation, and vapour diffusion. The pH isotherms of Cu(II) and Pb(II) using **L1-L4** complement the results obtained in the competitive extraction and transport studies thus demonstrating high extraction efficiency for Pb(II) ions at pH \approx 6 for all the ligands.

In summary, these novel Schiff base ligands could be used as Cu(II) and Pb(II) extractants in hydrometallurgical recovery processes. The synergistic effect between the Schiff base ligand and palmitic acid has proved effective in tuning the extraction strength of lead ions.

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32. Ligands similar in structure to ours, 4 hits, DOYTUM, LEHGIQ, BAMXAP, TAQHUP from CCDC, December **2014** version

Chapter 3

3. Synthesis, Characterization and Application of N-donor Ditopic Schiff Base Ligands and Complexes

3.1 Introduction and Aims

This chapter describes the synthesis and characterization of six novel multiloading metal salt extractants and their ability to extract base metal ions and selected anions. The resulting ditopic Schiff base ligands formed by the condensation of substituted 5-tert butyl salicylaldehyde with various amine linkers containing nitrogen atoms in their backbone were fully characterized using ^1H and ^{13}C NMR, FT-IR, mass spectrometry, and elemental analysis. The extraction and bulk liquid membrane transport abilities of the ligands were evaluated by monitoring the extraction and transport of the metal ions Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II), as their nitrate salts over a 24-hour period. The Cu(II) metal complexes of these ligands are used in solvent extraction experiments to evaluate their selectivity towards Cl^- , NO_3^- and SO_4^{2-} . Extensive alkyl chain functionality was incorporated into all of the ligands to ensure exclusive solubility in the organic phase.

Ditopic zwitterionic ligands possess both positively and negatively charged binding sites and form overall charge-neutral complexes with metal *cations* and their attendant *anions* as shown in figure 3.1. These extractants can load metal cations *via* cation exchange, and attendant anions *via* anion exchange. This is achieved by the deprotonation of the hydroxyl protons and coordination to the donor atoms. The

protons are then transferred onto the tertiary amine groups and this contributes to the formation of the anion binding site.

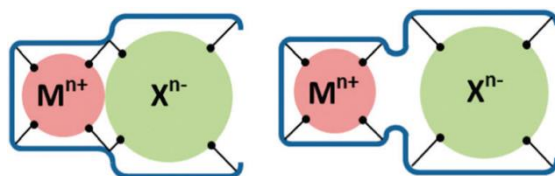


Figure 3.1: Illustration of two types of ditopic extractants of metal salts to accommodate contact ion pairs (left) and separated ion pairs (right).¹

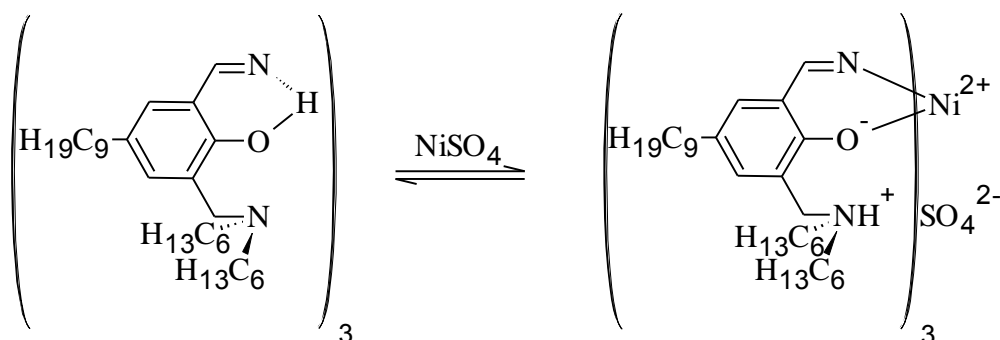
The synthesis of salen base ditopic ligands has been reported by the Tasker group for the extraction and transport of metal salts. The metal ions that were extracted were copper and while nickel and the selected anion was sulfate.¹

The binding sites form part of a zwitterionic form of the reagent which facilitates the loading and stripping of metal salts by varying the pH of the aqueous phase in contact with the reagent. The metal can be selectively removed from the metal salt complex by decreasing the pH, leaving the ligand salt. The free ligand can then be recovered by contacting the ligand salt with a basic aqueous phase.

3.2 Overcoming the Hofmeister bias

The Hofmeister bias essentially deals with the extraction of anions from aqueous solutions. This principle can be used to predict why certain anions will generally be extracted from aqueous media into a water-immiscible solvent. Anions such as SO_4^{2-} are usually more hydrophilic than Cl^- and NO_3^- , so it has a preference for the aqueous environment. The extraction of certain anions can also be related to their charge and distribution coefficients that can be predicted from the Gibbs free energies of solvation/hydration.⁶

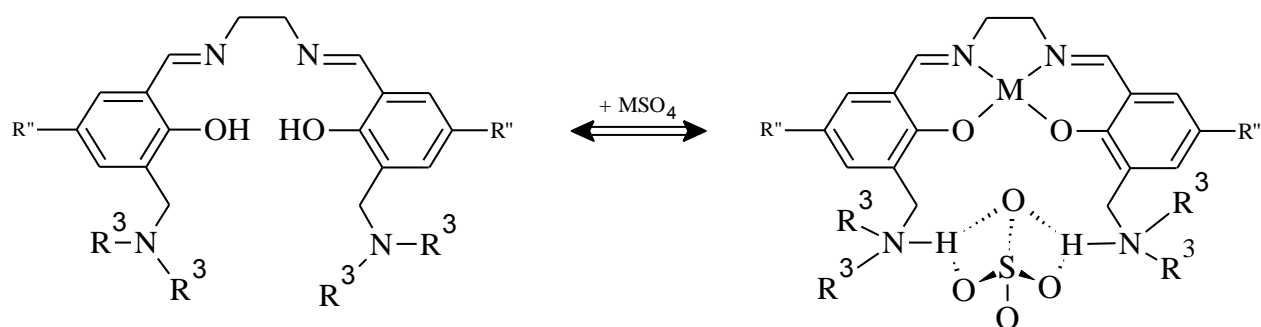
Salen derivatives were developed to overcome the Hofmeister bias.⁵ The synthesis of these ligands can be derived from precursors of commercial phenolic oxime extractants using Mannich reactions to append alkyl-aminomethyl groups. The use of tertiary amines such as the Alamine type as shown in scheme 3.1, seeks to overcome the separation and extraction of a sulfate salt from sulfate leach solutions.²



Scheme 3.1: Extraction of NiSO_4 by HNT to give a neutral complex $[\text{Ni}(\text{HNT})\text{SO}_4]$ containing a zwitterionic form of the ligand.²

3.3 Anion Selectivity

The design of organic compounds to achieve high selectivity and extraction of anions such as sulfate is challenging because sulfate is a weak inner sphere ligand and is essentially difficult to transport from an aqueous solution because of its high hydration energy. Cooperative binding has been successfully used by using cation complexation to facilitate anion binding. Intra- and intermolecular interactions, such as hydrogen bonds play a significant role and can be instrumental in controlling the efficiency of complexation and extraction of anions.³



Scheme 3.2: Example of ditopic ligands for the transport of metal sulfates⁴

The Schiff base ligands (Scheme 3.2) also possess two pendant tertiary amines that have the ability to capture protons released from the phenolic oxygen atoms upon metal complexation resulting in the formation of positive and negative sites within the ligand, and this is known as a zwitterionic ligand. The resulting anion-binding site has the capability to capture anions by means of the hydrogen bonds and the electrostatic interactions. This interaction allows selected anions to be extracted in solvent extraction processes.⁴

The removal of anions from the water immiscible organic phase is possible by raising the pH of the aqueous phase to deprotonate the extractant as shown in Equation 3.1.



The tetradentate ditopic ligands containing H₂salen type pendant tertiary amine groups have recently been synthesized for the solvent extraction and membrane transport of transition metal salts. These ligands undergo a zwitterionic transformation when they complex with metal salts and produce overall neutral assemblies that can be transported into non-polar, water-immiscible solvents.⁶

3.4 Experimental

3.4.1 Ligands and Metal Complexes

The ligands (Figure 3.2) and metal complexes synthesized for this chapter are summarised below (Table 3.1).

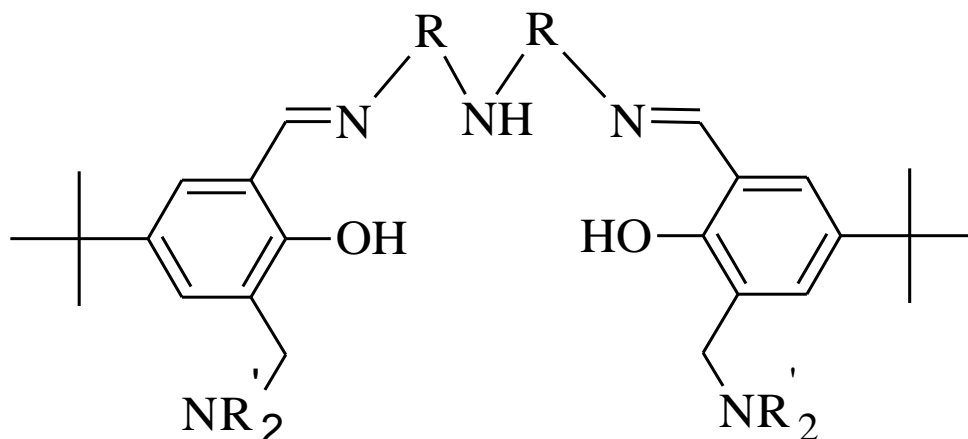
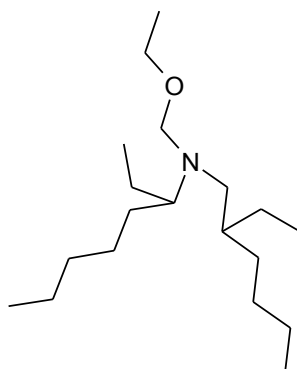


Figure 3.2: Prototype metal salt extractants; R = alkyl; R' = alkyl or aryl

Table 3.1 Ligands and metal complexes used and their designated reference numbers.

Ligands	R	NR' ₂	Metal complexes	
DL1	-(CH ₂) ₂ -	(n-C ₆ H ₁₃) ₂	C1	[Cu(DL1-2H)]
DL2	-(CH ₂) ₂ -	(n-CH ₂ C(C ₂ H ₄)C ₄ H ₉) ₂	C2	[Cu(DL2-2H)]
DL3	-(CH ₂) ₂ -	Piperidine	C3	[Cu(DL3-2H)]
DL4	-(CH ₂) ₃ -	(n-C ₆ H ₁₃) ₂	C4	[Cu(DL4-2H)]
DL5	-(CH ₂) ₃ -	(n-CH ₂ C(C ₂ H ₄)C ₄ H ₉) ₂	C5	[Cu(DL5-2H)]
DL6	-(CH ₂) ₃ -	Piperidine	C6	[Cu(DL6-2H)]

3.4.2 Ligand Precursors

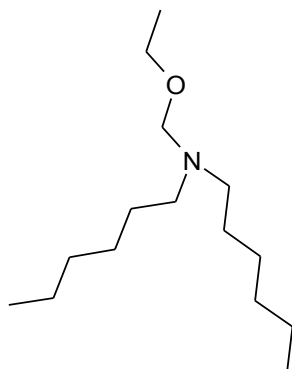


1

Ethoxy-*N*-bis(2-ethyl hexyl) aminomethane (1)

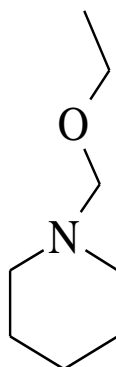
(24.2 g, 100 mmol) of secondary amine was added dropwise to a suspension of paraformaldehyde (3.75 g, 130 mmol) and anhydrous potassium carbonate (27.6 g, 200 mmol) in absolute ethanol (100 cm³) with external cooling in an ice bath and allowed to stir for 48 h. The solid was then filtered off and washed with dried diethyl ether (2 x 50 ml). The filtrate was then subjected to a rotary evaporator to remove the solvent and further subjected to kugelrohr distillation to remove residual solvents to afford the product as yellow-orange oil (21.5 g, 72.0%).

¹H NMR (CDCl₃, 400 MHz): δ 0.80 (t, 6H, N((CH₂)₅CH₃)₂), 1.09 (t, 3H, CH₂OCH₂CH₃), 1.20 (m, 12H, N(CH₂CH₂(CH₂)₃CH₃)₂), 1.37 (m, 4H, N(CH₂CH₂(CH₂)₂CH₃)₂), 2.53 (t, 4H, N(CH₂(CH₂)₄CH₃)₂), 3.35 (q, 2H, CH₂OCH₂CH₃), 4.06 (s, 2H, CH₂OCH₂CH₃). No CHN analysis was done.

**2****Ethoxy-*N*-dihexylaminomethane (2)**

(18.5 g, 100 mmol) of secondary amine was added dropwise to a suspension of paraformaldehyde (3.75 g, 130 mmol) and anhydrous potassium carbonate (27.6 g, 200 mmol) in absolute ethanol (100 cm³) with external cooling in an icebath. The mixture was then stirred vigorously for 48 h allowing the temperature to gradually reach ambient conditions. The solid was then filtered off and washed with dried diethyl ether (2 × 25 cm³). The filtrate was then concentrated *in vacuo* to give a colourless oil which was fractionally distilled through a Kugelrohr vacuum distillation apparatus affording the product (17.2 g, 71.0%).

¹H NMR (CDCl₃, 400 MHz) δ ppm 0.86 – 0.91 (m, 6 H, N(CH₂CH₂CH₂CH₂CH₂CH₃)₂), 1.16 – 1.20 (t, J = 7.16 Hz, 3 H, OCH₂CH₃), 1.26 – 1.34 (m, 12 H, N(CH₃CH₂CH₂CH₂CH₂CH₂)₂), 1.40 – 1.47 (m, 4 H, CH₃CH₂CH₂CH₂CH₂CH₂N), 2.59 – 2.64 (m, 4 H, CH₃CH₂CH₂CH₂CH₂CH₂N), 3.41 – 3.48 (q, J = 7.01 Hz, 2 H, OCH₂CH₃), 4.15 (s, 2 H, OCH₂N). No CHN analysis was done.

**3****1-(Ethoxymethyl)piperidine (3)**

Paraformaldehyde (3.75 g, 120 mmol) was added to potassium carbonate (27.6 g, 200 mmol). 100 ml absolute ethanol was added and the suspension was stirred. Piperidine (8.52 g, 100 mmol) was added dropwise and allowed to stir for 48h. The solid was then filtered off and washed with dried diethyl ether (2 x 50 ml). The filtrate was then subjected to solvent extraction and further subjected to Kugelrohr distillation to remove residual solvents. The product was obtained as a viscous yellow oil. The weight collected was 8.50 g (70.0% yield).

^1H NMR (CDCl_3 , 300 MHz) δ ppm 1.16 - 1.20 (t, $J = 7.16$ Hz, 3 H, OCH_2CH_3), 1.40 – 1.47 (m, 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.55 – 1.60 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.59 – 2.64 (m, 4 H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 3.41 – 3.48 (q, $J = 7.04$ Hz, 2 H, OCH_2CH_3), 4.15 (s, 2 H, NCH_2O).

No CHN analysis was done.

5-Tert-Butyl-3-[(dihexylamino)methyl]-2-hydroxybenzaldehyde (4)

A mixture of 5-tert-butyl-2-hydroxybenzaldehyde (3.49 g, 19.6 mmol) and N-hexylhexan-1-amine (5.00 g, 20.5 mmol) in acetonitrile (100 cm^3) was heated to reflux under a dinitrogen atmosphere for 90 h. After cooling to room temperature the solvent was removed *in vacuo* to yield the product as a dark yellow oil. No further purification was performed on the obtained oil.

^1H NMR (CDCl_3 , 400 MHz): δ 0.84 (t, 6H, $\text{N}(\text{CH}_2)_5\text{CH}_3$), 1.25 (m, 12H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.26 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.53 (m, 4H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.51 (t, 4H, $\text{NCH}_2(\text{CH}_2)_4\text{CH}_3$), 3.77 (s, 2H, ArCH_2N), 7.26 (d, 1H, Ar-H), 7.63 (d, 1H, Ar-H), 10.40 (s, 1H, CHO), 12.01 (s, 1H, OH); ^{13}C NMR (CDCl_3 , 400 MHz): δ 14.3 (2C, $\text{N}(\text{CH}_2)_5\text{CH}_3$), 22.9 (2C, $\text{N}(\text{CH}_2)_4\text{CH}_2\text{CH}_3$), 26.6 (2C, $\text{N}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 27.3 (2C, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 31.6 (3C, $\text{C}(\text{CH}_3)_3$), 32.0 (2C, $\text{N}(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{CH}_3$), 34.4 (1C, $\text{C}(\text{CH}_3)_3$), 53.8 (1C, $\text{CH}_2\text{N}(\text{CH}_2)_5\text{CH}_3$), 57.7 (2C, $\text{NCH}_2(\text{CH}_2)_4\text{CH}_3$), 122.7 (1C, Ar-C), 123.8 (1C, Ar-C), 124.0 (1C, Ar-C), 132.5 (1C, Ar-C), 141.7 (1C, Ar-C), 160.5 (1C, Ar-C), 191.4 (1C, CHO). No CHN analysis was done

5-Tert-Butyl-3-[(bis(2-ethylhexylamino)methyl]-2-hydroxybenzaldehyde (5)

A mixture of 5-tert-butyl-2-hydroxybenzaldehyde (3.56 g, 20.0 mmol) and N-(ethoxymethyl)-N-hexylhexan-1-amine (4.68 g, 22.0 mmol) in acetonitrile (100 cm^3) was heated to reflux under a dinitrogen atmosphere for 90 h. This reaction resulted in a yellow colour that changed to a dark orange colour as the reaction progressed. After cooling to room temperature the solvent was removed *in vacuo* to yield the product as a dark yellow oil. No further purification was performed on the obtained oil.

^1H NMR (CDCl_3 , 400 MHz) δ ppm 0.83 – 0.86 (m, 6 H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.26 (m, 20 H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$ & $\text{C}(\text{CH}_3)_3$), 1.50 – 1.54 (m, 4 H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$) 2.48 – 2.52 (m, 4 H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.77 (s, 2 H, NCH_2Ar), 7.24 – 7.25 (d, $J = 2.49$ Hz, 1 H, ArH), 7.62 – 7.63 (d, $J = 2.49$ Hz, 1 H, ArH), 10.40 (s, 1 H, CHO), 11.78 (s, 1 H, OH); ^{13}C NMR (400 MHz, CHLOROFORM-*d*) δ ppm 13.91 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 22.45 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 26.14 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 26.91 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 31.24 ($\text{C}(\text{CH}_3)_3$), 31.53 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$),

33.98 ($\text{C}(\text{CH}_3)_3$), 53.43 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 57.31 (ArCH_2N), 122.28 ($\text{C}_{\text{Ar}}\text{CH}_2$), 123.42 (C_{Ar}), 123.58 (C_{Ar}), 132.06 (C_{Ar}), 141.27 ($\text{C}_{\text{Ar}}\text{C}(\text{CH}_3)_3$), 160.06 ($\text{C}_{\text{Ar}}\text{OH}$), 191.01 (ArCHO). No CHN analysis was done.

5-*Tert*-Butyl-3-[(piperidin-1-ylmethyl)]-2-hydroxybenzaldehyde (6)

(10.0 g, 57.0 mmol) of the tertiary amine and (8.88 g, 62.0 mmol) aldehyde were refluxed in acetonitrile (200 cm³) under a nitrogen atmosphere for 90 h. After cooling to room temperature, the solvent was removed *in vacuo* and resulted in a sticky yellow oil. No further purification was performed on the obtained oil. ¹H NMR (CDCl_3 , 400 MHz): δ 1.28 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.52 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.66 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.54 (m, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 3.71 (s, 2H, NCH_2Ar), 7.25 (d, 1H, Ar-H), 7.65 (d, 1H, Ar-H), 10.42 (s, 1H, CHO), 11.30 (s, 1H, OH); ¹³C NMR (CDCl_3 , 400 MHz): δ 24.2 (2C, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 26.1 (1C, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 31.7 (3C, $\text{C}(\text{CH}_3)_3$), 34.4 (1C, $\text{C}(\text{CH}_3)_3$), 54.3 (1C, $\text{CH}_2\text{NCH}_2\text{CH}_2\text{CH}_2$), 61.8 (2C, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 122.7 (1C, Ar-C), 123.2 (1C, Ar-C), 124.1 (1C, Ar-C), 132.7 (1C, Ar-C), 141.8 (1C, Ar-C), 160.4 (1C, Ar-C), 191.5 (1C, CHO). No CHN analysis was done.

Characterization of 5-(*tert*-butyl)-2-hydroxy-3-(dihexylamino)methyl benzaldehyde (DL1): Amine derivative used: *diethylenetriamine*: Yellow-orange oil, yield 55.0%; Anal. Calcd. % for $\text{C}_{52}\text{H}_{91}\text{N}_5\text{O}_2$ (CHCl_3)_{0.67}(CH_3OH)_{0.67}; C 69.68, H 10.34, N 7.62. Found: C 69.24, H 10.59, N 7.55. ¹H NMR (CDCl_3 , 400 MHz) δ 0.87 (t, 12H, $\text{N}(\text{CH}_2)_5\text{CH}_3$), 1.27 (m, 24H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.33 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.52 (m, 8H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.48 (t, 8H, $\text{NCH}_2(\text{CH}_2)_4\text{CH}_3$), 2.95-2.98 (t, 4H, NCH_2CH_2), 3.69 - 3.73 (t, $J = 6.64$ Hz, 4H, NCH_2CH_2), 6.92 – 6.94 (d, $J = 8.50$ Hz, 2H, ArH), 7.24 - 7.25 (d, $J = 2.28$ Hz, 2H, ArH), 7.35 – 7.38 (dd, $J = 2.49$ Hz, 2H, ArH), 8.39 (s, 2H, NCH), ¹³C NMR (CDCl_3 , 400 MHz) δ ppm 10.5 (4C, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 14.8

(4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 23.3 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 24.2 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 25.3 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 26.1 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 31.08 (C(CH₃)₃), 31.47 (NCH₂CH₂), 34.60 (C(CH₃)₃), 50.14 (ArCH₂N), 59.01 (NCH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 129.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 158.40(C_{Ar}OH), 167.41 (ArCN); IR (neat); 2952, 2863 (m, CH); 1631 (m, C=N); 1490 (m, CH); 1264 cm⁻¹ (m, C-N); Expected MS: m/z (%) 818.72, Found (ES+):m/z (%) 818.72(100) [M]⁺.

Characterization of 5-(tert-butyl)-2-hydroxy-3-(bis(2-ethylhexylamino)methyl benzaldehyde (DL2): Amine derivative used: *diethylenetriamine*: Yellow-orange oil, yield 54.0%; Anal. Calcd. % for C₆₀H₁₀₇N₅O₂(CHCl₃)_{1.5}; C (66.57), H (9.86), N (6.31), Found: C (66.39), H (9.38), N (5.77). ¹H NMR (CDCl₃, 400 MHz) δ 0.80 (t, 12H, N(CH₂)₅CH₃), 1.27 (m, 24H, NCH₂CH₂(CH₂)₃CH₃), 1.29 (s, 18H, C(CH₃)₃), 1.34 (m, 8H, NCH₂CH₂(CH₂)₃CH₃), 2.28 (t, 8H, NCH₂(CH₂)₄CH₃),), 2.47 (m, 8H, NCH₂CH₂(CH₂)₂CH₂CH₃), 2.98 (t, 4H, NCH₂CH₂), 3.69 - 3.73 (t, J = 6.64 Hz, 4H, NCH₂CH₂), 6.92 – 6.94 (d, J = 8.50 Hz, 2H, ArH), 7.24 - 7.25 (d, J = 2.28 Hz, 2H, ArH), 7.35 – 7.38 (dd, J = 2.49 Hz, 2H, ArH), 8.39 (s, 2H, NCH), 13.23 (s, 2 H, OH); ¹³C NMR (CDCl₃, 400 MHz) δ ppm δ ppm 10.5 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 14.8 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 23.3 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 24.2 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂) (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 26.1 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 31.08 (C(CH₃)₃), 31.47 (NCH₂CH₂), 34.60 (C(CH₃)₃), 50.14 (ArCH₂N), 59.01 (NCH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 129.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 158.40(C_{Ar}OH), 167.41 (ArCN); IR (neat); 2954, 2924 (m, CH); 1632 (m, C=N); 1490 (m, CH); 1264 cm⁻¹ (m, C-N). Expected MS : m/z (%) 930.85, Found (ES+):m/z (%) 930.85(2) [M]⁺.

Characterization of 5-(tert-butyl)-2-hydroxy-3-(piperidin-1-yl)methyl benzaldehyde (DL3): Amine derivative used: *diethylenetriamine*: sticky yellow-orange oil, yield 62.0%. Anal. Calcd. % for $C_{38}H_{59}N_5O_2$ ($CHCl_3$)(H_2O); C(61.29), H(8.31),N(9.16), Found: C (61.08), H (7.52), N (9.19). 1H NMR ($CDCl_3$, 400 MHz) δ ppm 1.31 (s, 18H, $C(CH_3)_3$), 1.45 (m, 4H, $NCH_2CH_2CH_2$), 1.62 (m, 8H, $NCH_2CH_2CH_2$), 2.46 (t, 8H, $NCH_2CH_2CH_2$), 2.98 (t, 4H, NCH_2CH_2), (3.58 (s, 4H, NCH_2Ar), 3.69 - 3.73 (t, $J = 6.64$ Hz, 4H, NCH_2CH_2), 6.92 – 6.94 (d, $J = 8.50$ Hz, 2H, ArH), 7.24 - 7.25 (d, $J=2.28$ Hz, 2H, ArH), 7.35 – 7.38 (dd, $J=2.49$ Hz, 2H, ArH), 8.39 (s, 2H, NCH); ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm 24.2 (2C, $NCH_2CH_2CH_2$), 26.1 (1C, $NCH_2CH_2CH_2$), 31.08 ($C(CH_3)_3$), 31.47 (NCH_2CH_2), 34.60 ($C(CH_3)_3$), 50.14 ($ArCH_2N$), 59.01 (NCH_2CH_2), 116.13 ($C_{Ar}H$), 117.64 ($C_{Ar}CN$), 127.30 ($C_{Ar}H$), 129.21 ($C_{Ar}H$), 142.94 ($C_{Ar}C(CH_3)_3$), 158.40($C_{Ar}OH$), 167.41 ($ArCN$); IR (neat); 2929, 2851 (m, CH); 1629 (m, C=N); 1463 (m, CH); 1268 cm^{-1} (m, C-N); Expected MS: m/z (%) 617.91, Found (ES-):m/z (%) 617(20) $[M]^+$.

Characterization of 5-(Tert-Butyl)-2-hydroxy-3-(dihexylamino)methyl benzaldehyde (DL4): Amine derivative used: *N*-(3-aminopropyl)propane-1,3-diamine: yellow-orange oil, yield 58.0%. Anal. Calcd. % for $C_{54}H_{95}N_5O_2$; C(76.6), H(8.3), N(11.3), Found: C(76.3), H(8.3), N(10.9). 1H NMR ($CDCl_3$, 400 MHz) δ ppm 0.86 (t, 12H, $N(CH_2)_5CH_3$), 1.26 (m, 24H, $NCH_2CH_2(CH_2)_3CH_3$), 1.29 (s, 18H, $C(CH_3)_3$), 1.49 (m, 8H, $NCH_2CH_2CH_2CH_2CH_2CH_2$), 2.46 (t, 8H, $NCH_2CH_2CH_2$), 2.58 (t, 4H, $NCH_2CH_2CH_2$), 2.73 (s, 4H, NCH_2Ar), 3.63 - 3.68 (t, $J = 6.64$ Hz, 4H, $NCH_2CH_2CH_2$), 7.1 – 7.15 (d, $J = 8.50$ Hz, 2H, ArH), 7.42 – 7.59 (dd, $J = 2.49$ Hz, 2H, ArH), 8.39 (s, 2H, NCH).

^{13}C NMR (CDCl_3 , 400 MHz d) δ ppm 18.3 (4C, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 25.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 26.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 28.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 29.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 29.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 30.08 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 31.47 ($\text{C}(\text{CH}_3)_3$), 32.46 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 34.60 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 34.60 ($\text{C}(\text{CH}_3)_3$), 50.14 (ArCH_2N), 59.01 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 116.13 ($\text{C}_{\text{Ar}}\text{H}$), 117.64 ($\text{C}_{\text{Ar}}\text{CN}$), 127.30 ($\text{C}_{\text{Ar}}\text{H}$), 129.21 ($\text{C}_{\text{Ar}}\text{H}$), 142.94 ($\text{C}_{\text{Ar}}\text{C}(\text{CH}_3)_3$), 158.45 ($\text{C}_{\text{Ar}}\text{OH}$), 167.66 (ArCN); IR (neat); 2948, 2859 (m, CH); 1631 (m, C=N); 1463 (m, CH); 1268 cm^{-1} (m, C-N). Expected MS: m/z (%) 846.76, Found (ES-): m/z (%) 847.76 $[\text{M}+\text{H}]^+$.

Characterization of 5-(tert-butyl)-2-hydroxy-3-(bis(2-ethylhexylamino) methyl benzaldehyde (DL5): Amine derivative used: *N*-(3-aminopropyl)propane-1,3-diamine: yellow-orange oil, yield 64.3%. Anal. Calcd. % for $\text{C}_{62}\text{H}_{111}\text{N}_5\text{O}_2$ (H_2O); C(76.3), H(11.7), N(7.3), Found: C(76.1), H(10.7), N(7.6). ^1H NMR (CDCl_3 , 400 MHz) δ ppm 0.86 (t, 12H, $\text{N}(\text{CH}_2)_5\text{CH}_3$), 1.26 (m, 24H, $\text{NCH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.29 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.49 (m, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 2.46 (t, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.58 (t, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.73 (s, 4H, NCH_2Ar), 3.63 - 3.68 (t, $J = 6.64$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 7.1 - 7.15 (d, $J = 8.50$ Hz, 2H, ArH), 7.42 - 7.59 (dd, $J = 2.49$ Hz, 2H, ArH), 8.39 (s, 2H, NCH); ^{13}C NMR (CDCl_3 , 400 MHz) δ ppm 18.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 25.3 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 26.4 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 28.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 29.6 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 29.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 30.08 ($\text{C}(\text{CH}_3)_3$), 31.47 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 32.46 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 34.60 ($\text{C}(\text{CH}_3)_3$), 50.14 (ArCH_2N), 59.01 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 116.13 ($\text{C}_{\text{Ar}}\text{H}$), 117.59 ($\text{C}_{\text{Ar}}\text{CN}$), 126.90 ($\text{C}_{\text{Ar}}\text{H}$), 129.21 ($\text{C}_{\text{Ar}}\text{H}$), 142.94 ($\text{C}_{\text{Ar}}\text{C}(\text{CH}_3)_3$), 158.40 ($\text{C}_{\text{Ar}}\text{OH}$), 166.88 (ArCN). IR (neat); 2938, 2839 (m, CH); 1631 (m, C=N); 1466 (m, CH); 1274 cm^{-1} (m, C-N); Expected MS: m/z (%) 958.58, Found (ES-): m/z (%) 959.88 $[\text{M}+\text{H}]^+$.

Characterization of 5-(tert-butyl)-2-hydroxy-3-(piperidin-1-yl)methyl benzaldehyde (DL6): Amine derivative used: *N*-(3-aminopropyl)propane-1,3-diamine: sticky yellow-orange oil, yield 61.0%. Anal. Calcd. % for C₄₀H₆₃N₅O₂ (CH₃OH)₃; C (69.60) H (10.19) N (9.44), Found: C (70.09%), H(9.80%), N(8.60%).
¹H NMR (CDCl₃, 400 MHz) δ ppm 1.31 (s, 18H, C(CH₃)₃), 1.45 (m, 4H, NCH₂CH₂CH₂), 1.62 (m, 8H, NCH₂CH₂CH₂), 2.46 (t, 8H, NCH₂CH₂CH₂), 2.98 (t, 4H, NCH₂CH₂), (3.58 (s, 4H, NCH₂Ar), 3.69 - 3.73 (t, *J* = 6.64 Hz, 4H, NCH₂CH₂), 6.92 – 6.94 (d, *J* = 8.50 Hz, 2H, ArH), 7.24 - 7.25 (d, *J* = 2.28 Hz, 2H, ArH), 7.35 – 7.38 (dd, *J* = 2.49 Hz, 2H, ArH), 8.39 (s, 2H, NCH). ¹³C NMR (CDCl₃, 400 MHz) δ ppm 24.2 (NCH₂CH₂CH₂), 26.1 (NCH₂CH₂CH₂), 31.08 (C(CH₃)₃), 31.23 (NCH₂CH₂CH₂), 32.40 (NCH₂CH₂CH₂), 34.60 (C(CH₃)₃), 50.14 (ArCH₂N), 58.88 (NCH₂CH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H), 129.21 (C_{Ar}H), 142.94 (C_{Ar}C(CH₃)₃), 158.40(C_{Ar}OH), 167.41 (ArCN). IR (neat); 2929, 2851 (m, CH); 1629 (m, C=N); 1463 (m, CH); 1268 cm⁻¹ (m, C-N). Expected MS: m/z (%) 645.96, Found (ES⁻):m/z (%) 646.50 [M]⁺.

3.5 Discussion of Results

The synthesis of the ligands involved the reaction of the appropriate amine linker in MeOH (50 cm³) into a stirred solution of the appropriate aldehyde in CHCl₃ (50 cm³). After stirring for between 15-18 hrs the solvent was removed to give a yellow-orange oil which was thereafter redissolved in CHCl₃ (100 cm³) and washed with water (2 x 50 cm³). The organic phase was separated and dried with MgSO₄, filtered and the solvent was removed in vacuo to yield a yellow-orange viscous oil.

The synthesized Schiff base ligands were isolated in approximately 60% yield and were obtained as viscous yellow-orange oils after drying extensively under high vacuum for 3 days whilst heating in order to remove organic solvents. The reaction of the ligand and metal salt gave the corresponding metal complex and was stable and non-hygroscopic in nature. The ligands were found to be soluble in common organic solvents such as methanol, dichloromethane and chloroform.

The ¹H and ¹³C NMR for **DL3** are shown in figures 3.3 and 3.4 with all the peaks accounted for as shown in the characterization results.

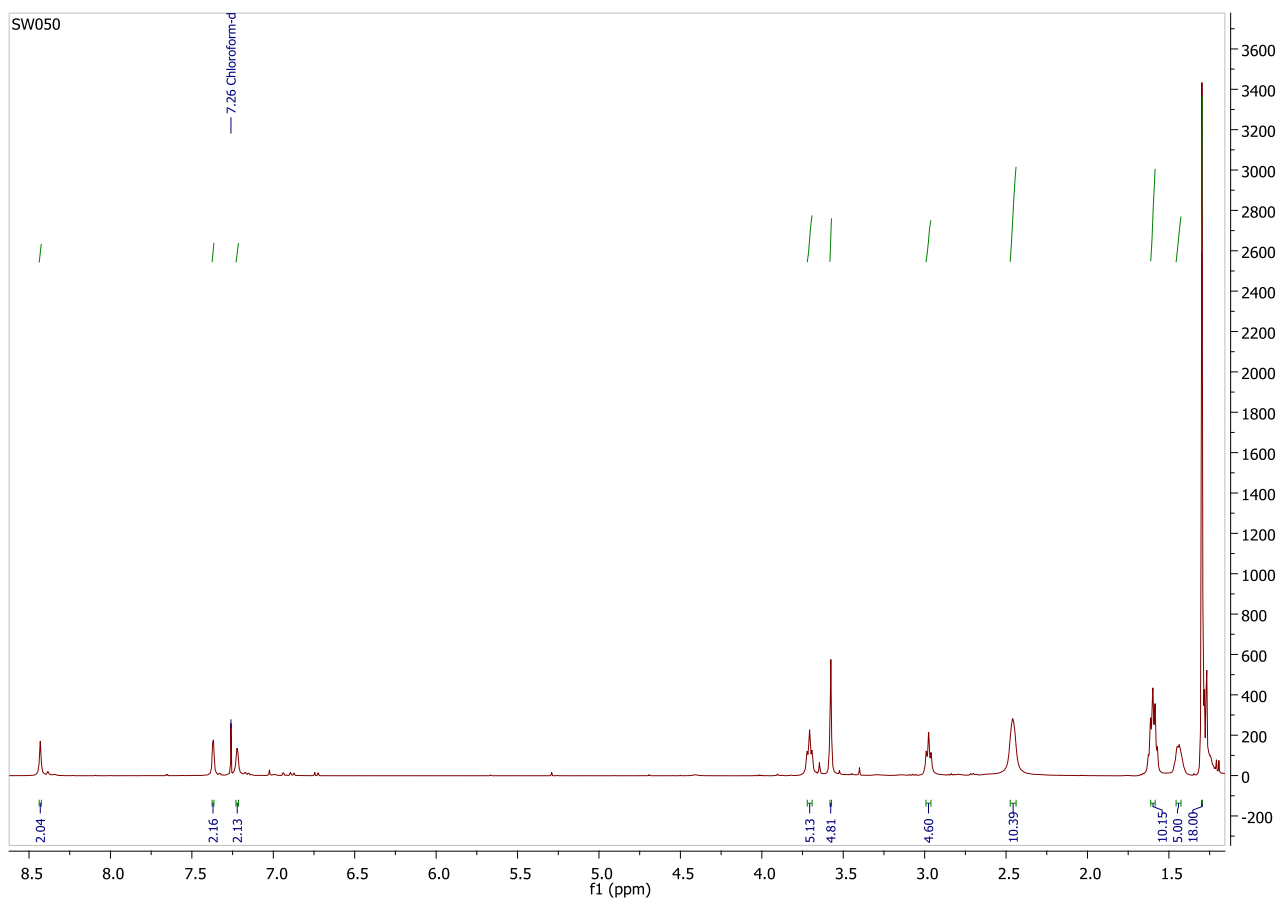


Figure 3.3: ^1H NMR of ditopic ligand (**DL3**).

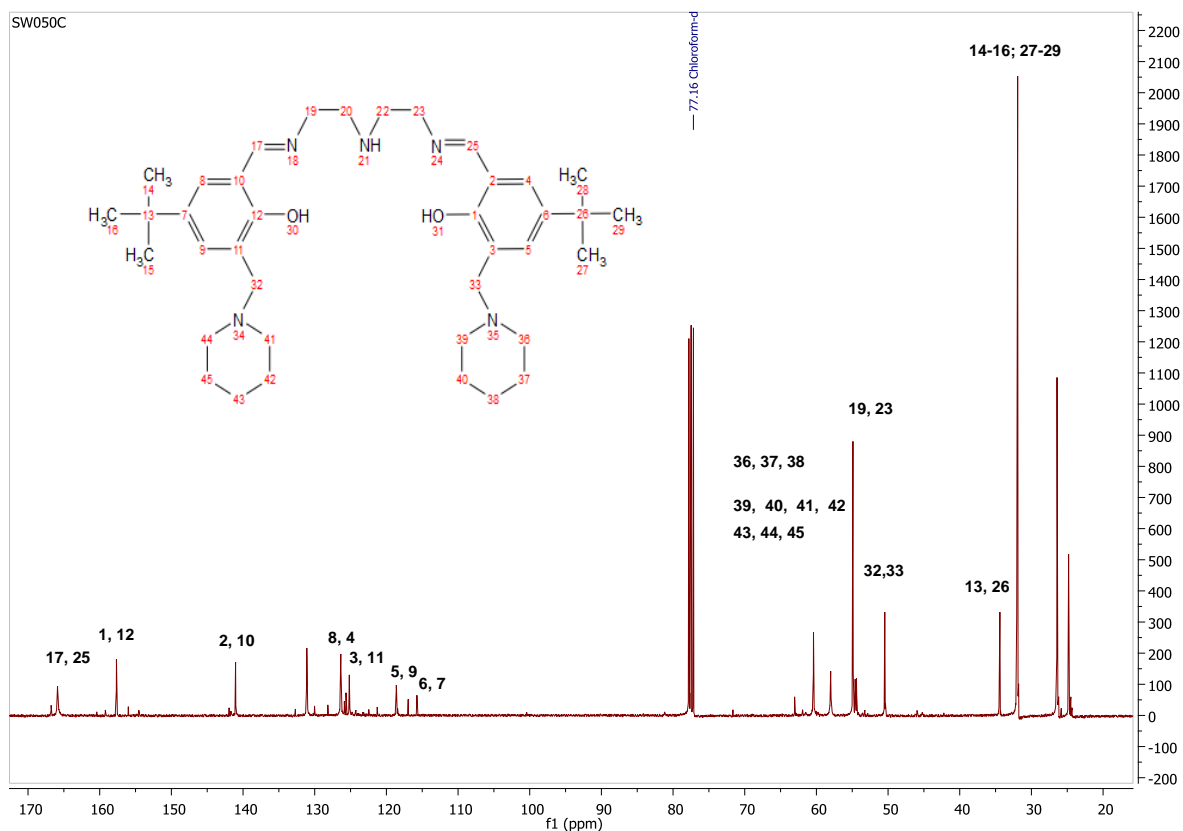


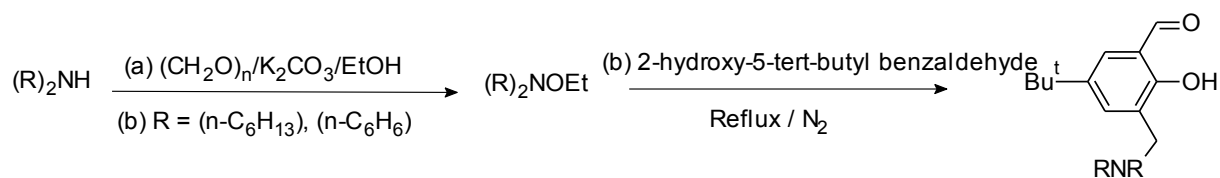
Figure 3.4: ^{13}C NMR of ditopic ligand (DL3).

3.5.1 Synthesis of Free Ligands

Ligands **DL1**, **DL2**, **DL4**, **DL5**, with longer alkyl chains, two n-hexyl groups and 2-ethyl hexyl groups respectively, were prepared to minimise bleeding of ligands and complexes to the aqueous phase. These were easily prepared by a four step convergent synthesis from tert-butyl substituted salicylaldehyde, paraformaldehyde, dihexylamine, *bis*(2-ethyl) hexylamine, and an amine of choice. The preferred method in this thesis for the preparation of substituted salicylaldehydes was based upon the industrial process developed by Levin and co-workers¹⁷

The 2-hydroxy-3-*N*-hexylaminomethyl-5-tert-butyl-benzaldehyde was synthesized in acetonitrile, under dinitrogen atmosphere (scheme 3.3). The product was obtained in a high yield. Dihexylamine and *bis*(2-ethylhexyl)amine was also used

as its hydrophobicity should increase solubility in non-polar solvents suitable for solvent extraction studies. Piperidine was also chosen as it is known to form crystalline material of both transition metal cation and metal salts.¹⁸



Scheme 3.3: Two step Mannich reaction used to append pendant dialkylaminomethyl arms to form the substituted t-butyl salicylaldehyde based metal salt extractants

3.6 Syntheses and Characterization of Cu(II) Complexes

Metal complexes were obtained through the reaction between metal ions and the Schiff base ligand at 1:1 (M: Schiff base ratio). The synthesized Schiff base ligand and its complexes are stable at room temperature. The Schiff base ligand and its metal complexes were soluble in chloroform and were used in solvent extraction experiments.

The copper(II) complexes of **DL1-DL6** were successfully synthesised by mixing stoichiometric amounts of the ligand and copper(II) acetate in ethanol. Precipitation occurred in the case of ligands (**DL3** and **DL6**), and the pure products were obtained by filtering off the green solid. The complexes of ligands (**DL1**, **DL2**, **DL4** and **DL5**) were isolated as green oils. The copper(II) complexes were characterised by IR analysis (Figure 3.5, Table 3.2) and ESI Mass Spectrometry. Molecular ion peaks corresponding to the ligands were observed, confirming the successful syntheses.

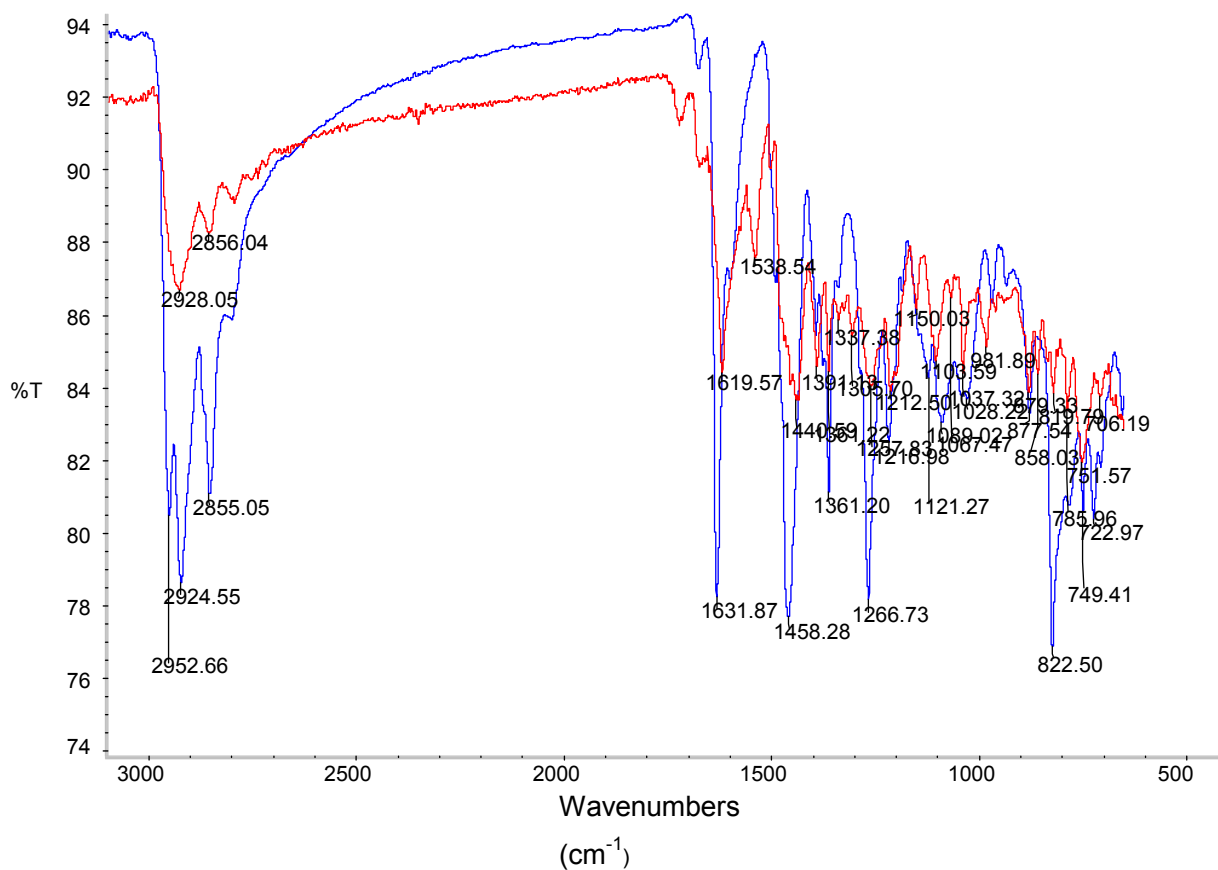


Figure 3.5: The IR Spectrum of Schiff base ligand (**DL1**) and the copper complex of (**DL3-Cu**) showing a strong imine band at 1632 cm^{-1} and stretches for C-H bonds at 2925 and 2855 cm^{-1} and the imine can be seen slightly lowered in energy at 1619 cm^{-1} for the copper complex (**DL3**)

Table 3.2: The imine stretching frequencies for ligands DL1-DL6 and their metal complexes (cm^{-1})

$\nu\text{ (cm}^{-1}\text{)}$	DL1	DL2	DL3	DL4	DL5	DL6
Free ligand	1631	1633	1630	1633	1630	1631
Cu-complex	1623	1624	1620	1622	1624	1622

3.7 Characterisation

3.7.1 FTIR Spectroscopy

The IR spectrum of all the ligands show a characteristic band between 1633-1630 cm^{-1} which is attributed to the $\nu(\text{C}=\text{N})$. This band is shifted to a lower frequency (1620-1624 cm^{-1}) when the ligand is complexed to Cu(II). The shift to lower wave numbers is an indication that the azomethine nitrogen is co-ordinated to the metal ion. Similar shifts were reported by Ketata *et al.* for tridentate Schiff base ligands.¹⁹

The absorption bands at 3073 cm^{-1} , 2917 cm^{-1} and 2849 cm^{-1} are assigned to aromatic $\nu_{\text{asym}}(\text{C}-\text{H})$, aliphatic $\nu_{\text{asym}}(\text{C}-\text{H})$, and $\nu_{\text{sym}}(\text{C}-\text{H})$ respectively. Furthermore, the absence of C=O vibration in the spectra of the ligands, related to aldehyde, indicate occurrence of Schiff base condensation.

The shift of $\nu(\text{C}-\text{O})$ band at 1283 cm^{-1} to a lower frequency for metal complexes suggests the weakening of $\nu(\text{C}-\text{O})$ and formation of M-O bond. Coordination of the Schiff base to the metal ions through the nitrogen atom is expected to reduce electron density in the azomethine link and lower the $\nu(\text{C}=\text{N})$ absorption frequency.

The weak to medium bands in the two ranges 580-615 cm^{-1} and 430-560 cm^{-1} , could be assigned to the stretching frequencies of the $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively. This provides further evidence that the bonding of the ligand to metal ions is achieved by the phenolic oxygen and azomethine nitrogen atom of the

ligand.¹² The FTIR spectra of the free ligands all exhibited similar stretching frequencies, which indicates the stability of these ligands.

3.7.2 NMR Spectroscopy

All ligands and precursors were fully characterised by both ^1H and ^{13}C NMR spectroscopy. ^1H NMR spectroscopy was used to monitor conversion of the aldehyde to the imine as described in Chapter 2. A sharp singlet at 8.45 ppm is assigned to the azomethine protons. Multiplets of aromatic protons appear in the region 6.95– 7.45 ppm. ^{13}C NMR spectra of these Schiff base ligands showed thirteen peaks instead of sixteen expected signals. The aromatic ring carbon corresponds to the region (115.908–155.037 ppm) as the resonances for these carbon atoms were similar. The imine carbon appears at 161.497 ppm. This data supports the formation of the synthesized Schiff base ligands.

3.7.3 Mass Spectrometry

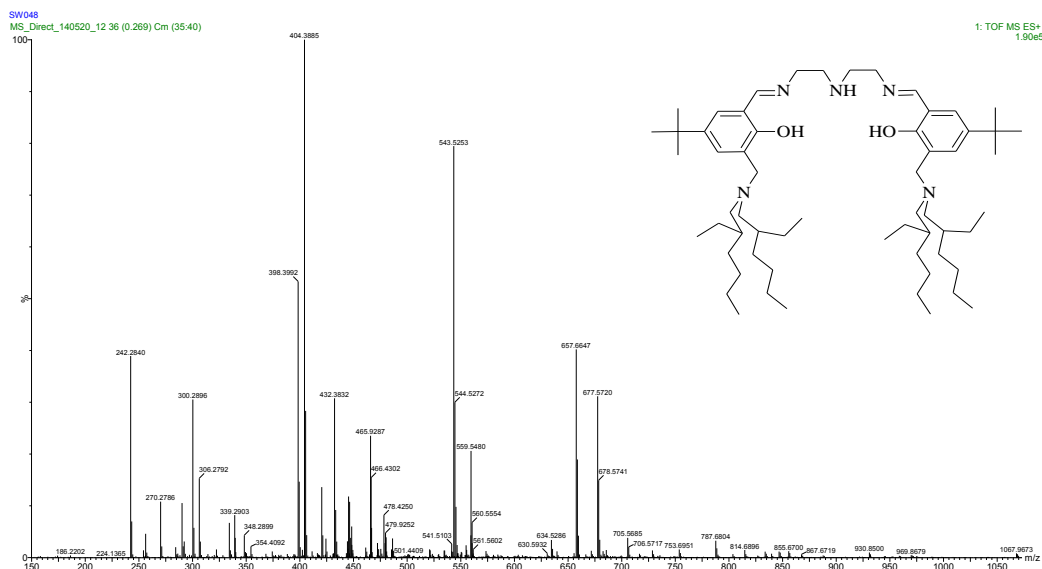


Figure 3.6: Mass Spectrum of **DL2** showing the molecular ion at 930.85 amu.

Mass spectra of each of the ligands showed a peak assignable to the free ligand. Molecular ion peaks and intensities for **DL2** (figure 3.6), is shown for the Schiff base ligand which confirms a successful condensation reaction. The molecular ion peaks of the synthesized Schiff base ligands are shown in the characterization section of this chapter. All copper(II) complexes were studied by IR and MS, and molecular ion peaks were seen in all cases confirming their successful synthesis.

3.7.4 Elemental Analysis

The percentage of C, H, and N of **DL1-DL6** were evaluated by elemental analysis and are presented in the section 3.4. Elemental analysis showed a clear consistency with the increasing amount of organic groups that were appended to the respective Schiff base ligand. The ligands were all obtained as oils and therefore they were subjected to high vacuum to ensure complete removal of any residual solvent. The values found were in agreement with the calculated values based on the inclusion of some solvents which were used for the condensation reaction. The standard on the analyser for hydrogen was not working well and as a result the found results for hydrogen were lower throughout.

3.8 Competitive Solvent Extraction of N-donor Ditopic Schiff Base Ligands for transition and post transition metal ions (Pb^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}).

A 0.01 M solution of each ligand in chloroform (5 cm^3) was contacted with a buffer solution at pH 5.09 containing a 0.01 M mixture of the Cu(II), Zn(II), Ni(II), Co(II), Pb(II) and Cd(II) metal ions (5 cm^3) and shaken on a labcon-oscillating shaker at 220 rpm for 24 h. Extraction was performed at 25°C . The aqueous phase was removed and a sample was taken and used for metal ion analysis by ICP-OES. The results are quoted as the average value obtained from duplicate runs. Any apparent extraction of a metal ion of less than 2.0% was assumed to be within the experimental error and regarded as zero and hence ignored in the treatment of results. The competitive extraction results are shown in Figure 3.7. In all cases the values between any two duplicate runs did not differ by more than 5%.

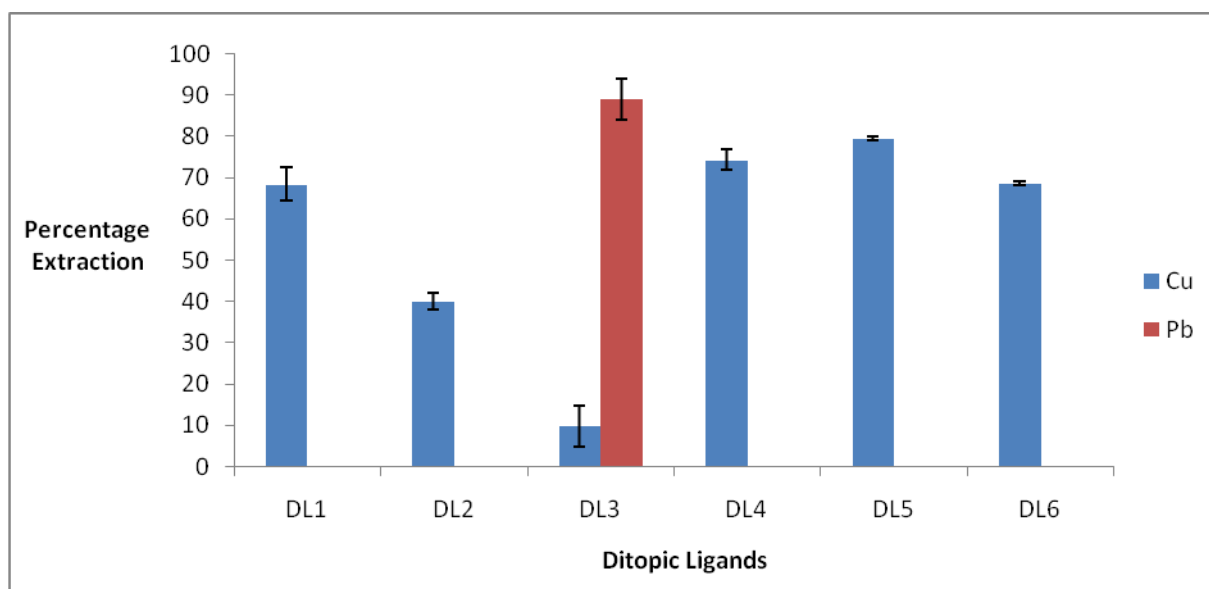


Figure 3.7: Competitive Solvent Extraction of **DL1-DL6** towards transition and post-transition metal ions

The findings for the solvent extraction of base metal ions using the ditopic Schiff base ligands (**DL1**, **DL2**, **DL3**, **DL4**, **DL5**, **DL6**) are consistent with relative stabilities of complexes formed by metal(II) cations predicted by the Irving-Williams series. The electronic properties of the donor atoms which bond to the copper atom and the substituents in the 3-position could also have a significant effect on the interligand hydrogen bonding which is thought to contribute to the stability of these copper ditopic complexes. The strong interligand H-bonds between imine nitrogen atoms and their neighbouring phenol oxygen atoms and the existence of a cavity favours the extraction Cu(II).¹

The order of extraction efficiency for Schiff base ligands for the extraction of copper(II) ions follows the order **DL5** > **DL4** > **DL6** > **DL1** > **DL2** > **DL3**. **DL4-DL6** shows a relatively higher extraction for copper(II) than **DL1-DL3** due to the formation of the six membered chelate rings as shown in Chapter 2 for **L2**. The reason for the extraction of lead by **DL3** is due to the addition of Palmitic acid. The function of palmitic acid was to ensure the ligand remains soluble in the organic phase. Palmitic acid has a carboxylic acid moiety which shows coordination towards Pb²⁺. Furthermore the extraction results obtained for all the monotopic Schiff base ligands as discussed in Chapter 2 is complemented by the results obtained for the ditopic Schiff base ligands. The nitrogen donor atoms in the ligand backbone play an important role, forming complexes with borderline metal ions such as copper. The extraction value of **L1** for copper was 16.9% (chapter 2) which is much lower than that obtained for **DL1 - DL3**. This suggests that the pendant amine group attached to the salicylaldimine moiety enhances the extraction of copper because of its improved solubility in the organic phase. The extraction value of **DL4** and **DL6** is only slightly

lower than **L2** (chapter 2) whilst **DL5** is similar to **L2**. This suggests that the 6 membered chelate rings is the sole determining factor for the extraction of copper.

3.9 Membrane transport of transition and post transition metal ions

The transport experiments for **DL1-DL6** were carried out according to the same experimental conditions as stated in section 2.9 of Chapter 2. The results are quoted in Table 3.3 as the average value obtained from duplicate runs. Any apparent extractions of a metal ion less than 3% was assumed to be within experimental error and regarded as zero and hence ignored in the final results. In all cases the values between the duplicate runs did not differ by more than 5%.

Table 3.3: $J / \text{mol h}^{-1} \times (10^{-7})$ values for the competitive metal ion transport studies involving **DL1–DL6**. The experimental conditions were: pH of the source phase = 5.09, pH of the receiving phase = 1.0 and concentration of ligand = $0.002 \text{ mol dm}^{-3}$.

Ligand number	DL1	DL2	DL3	DL4	DL5	DL6
Co(II)	—	—	—	—	—	—
Ni(II)	—	—	—	—	—	—
Cu(II)	3.23	2.12	1.69	1.35	1.79	1.84
Zn(II)	—	—	—	—	—	—
Cd(II)	—	—	—	—	—	—
Pb(II)	0.43	0.29	1.22	0.43	0.69	0.30
$^{Cu} T_r\%$	23.8	15.6	8.64	6.89	13.42	13.75
$^{Cu} T_M\%$	93.49	93.37	49.62	44.95	51.69	50.16
$^{Pb} T_r\%$	3.46	3.52	9.79	3.46	5.52	2.43
$^{Pb} T_M\%$	25.42	24.46	90.76	8.97	6.92	10.15
$\eta(\text{Cu(II)/Pb(II)})$	6.88	4.43	8.28	1.99	2.43	5.66

The competitive transport results of the metal ions Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) are reported in table 3.3. As seen from the table only Cu(II) and Pb(II) were transported into the receiving phase. The transport of copper follows the order; **DL3 > DL1 > DL2 > DL6 > DL5 > DL4**. The transport of copper complements the high extraction results obtained by these Schiff base ligands. Palmitic acid was added in the organic phase for the transport of transition metal ions involving ligand **DL3**. The selective transport of lead cation is possibly due to lead forming a stable complex with the respective Schiff base ligand-palmitic acid assembly in the membrane phase and thereafter releasing the lead ions into the receiving phase due to the pH gradient. Rounaghi *et al.* reported a similar result, in which lead was transported with relatively high efficiency across a bulk liquid membrane (BLM) containing dicyclohexano-18-crown-6 (DC18C6) as carrier.⁶ These types of ligands have a preference for Cd(II) and Pb(II) and other alkali or alkali earth metal ions, i.e. they have high selectivity for harder metal ions compared to the synthesized ligands **DL1-DL6** in this chapter which contains imine, amine and hydroxyl functionalities.

Habtu *et al.* reported a new series of *N,N*-substituted thiourea ligands and showed that all these ligands were highly effective and selective for extracting Ag(I) from a mixture of seven metal ions.¹⁰ Nezhadali *et al.*, synthesized a series of oxygen, nitrogen and sulfur donor macrocycles for the competitive metal ion extraction and transport of Cu(II), Mn(II), Zn(II), and Ni(II) as their nitrate salts. In this study it was shown that the ligands containing N,S-donor atoms selectively extracted copper(II) ions over other cations.¹¹

N,N-bis(salicylidene)diethylenetriamine (H₂saldien) Schiff base ligands which have the same backbone as **DL1-DL3** in this chapter was synthesized by Maurya *et*

al., which was used to complex metal ions such as copper, nickel and zinc. These complexes were used for the oxidation of phenols.¹²

Charef *et al.*, reported the chelating behaviour of divalent metal ions such as Cu^{2+} , Zn^{2+} , Ni^{2+} , and Pb^{2+} towards *N,N*-bis(salicylidenepropylenetriamine)-aminomethyl polystyrene Schiff base resin. It was found that the maximum adsorption was for copper. The Schiff base ligands **L2** in Chapter 2 and **DL4-DL6** in this Chapter also show extraction selectivity for copper(II) with the same ligand backbone.¹³

Butvin *et al.*, reported the high selectivity of Cu(II) extraction from a aqueous stock solution that contained Cu(II), Zn(II), Cd(II), Pb(II), Co(II), Ni(II), and Mn(II) using salicylideneethylimine Schiff base extractant. Furthermore the extraction of Cu(II) was compared with those that contained different alkyl chain length.²¹

Turkington *et al.*, concluded that the selectivity towards Cu(II) ions could be as a result of viz; (i) goodness of fit of the cavity of the macrocycle that produces a 14 – membered macrocycle due to the two deprotonated ligands and the strong hydrogen bonding interactions between the phenolate and oxime groups.¹

Nitrogen, sulfur and oxygen donor atoms in Schiff base ligands as reported by Al Zoubi *et al.*, show a relatively high transport of Cu(II) ions across a liquid membrane.¹⁴ Sadeghi *et al.* also published similar results in which he found the transport of Cu^{2+} ions by using Erythromycin derivative to the receiving phase in the presence of an equimolar mixture of some foreign cations in the source phase was almost quantitative after 5 hours.¹⁵

Taghdiri *et al.* also demonstrated an efficient and selective transport of Cu(II) through chloroform bulk liquid membranes using tetradentate Schiff base ligands.⁷

The work published by Black *et al.* using a Robson Schiff base free ligand showed high extraction and selectivity for Cu(II).⁸

Kazemi *et al.*, showed the transport selectivity for Pb(II) using macrocyclic crown ethers over other metal ions such as Cu(II), Zn(II), Cd(II), Co(II), and Ni(II) with a recovery factor of 91 % (after 2 h).²⁰

The research findings suggest that the synthesized NNN ditopic ligands in this chapter clearly illustrates the precedence of Irving Williams series as a determining factor over the chelate ring size and the number and type of donor atoms in terms of extracting copper over other metal ions.

3.10 Anion Solvent Extraction

Experiments were carried out to assess the relative “strengths” of copper(II) extractants of the ligand series. The copper complexes of **DL1-DL6** were prepared and thereafter characterized by FTIR and MS. These complexes were employed for the competitive solvent extraction and transport of the selected anions such as nitrates, chlorides and sulfates.

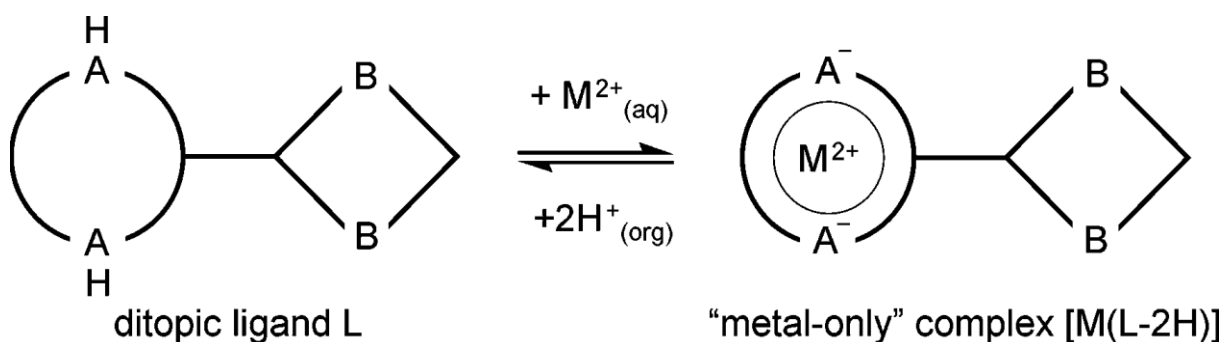


Figure 3.8: Schematic representation of ditopic ligands for metal salts extraction²²

The selectivity of Schiff base ligands possessing the $[N_2O_2]^{2-}$ donor set of the salen unit towards copper over other metal ions can be attributed to the ‘bite size’ in solid state structures of copper(II) complexes as shown in figure 3.8. The most important requirement needed by metal salt extractants is to obtain maximum loading of both cations and attendant anions within the same pH-range.

3.10.1 Competitive Solvent extraction of selected anions (SO_4^{2-} , NO_3^- , and Cl^-) by copper-only complexes

A 0.01 M solution of copper complex of **DL1-DL6** in chloroform (5 cm^3) was contacted with a solution containing a mixture of 0.01 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.01 M HNO_3 and 0.005 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at pH 2.15 (5 cm^3) and shaken on a labcon-oscillating shaker at 220 rpm for 24 h. Extraction was performed at 25°C . The aqueous phase was removed and a sample was taken and used for ion analysis by ion chromatography. The results are quoted in figure 3.9 as the average value obtained from duplicate runs. Any apparent extraction of an anion of less than 5.0% was assumed to be within the experimental error and regarded as zero and hence ignored in the treatment of results.

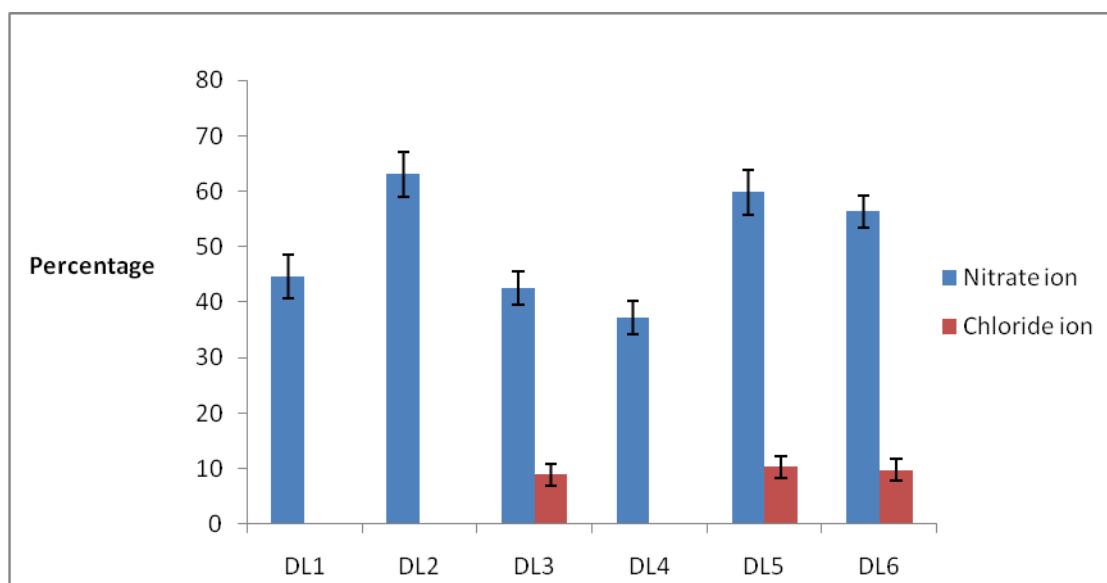


Figure 3.9: Results of competitive anion extraction of Schiff base copper complexes (**DL1-DL6**).

3.10.2 Competitive Anion Transport of selected anions (NO_3^- , Cl^- , SO_4^{2-}) by copper-only complexes

The competitive transport results for the respective Schiff base ligands (**DL1-DL6**) are shown in **Table 3.4**.

Table 3.4: $J / \text{mol h}^{-1} \times 10^{-7}$ values for the competitive anion transport studies involving **DL1-DL6**. The experimental conditions were: pH of the source phase = 3.2, pH of receiving phase = 6.5 and concentration of ligand = $0.002 \text{ mol dm}^{-3}$

Ligand number	DL1	DL2	DL3	DL4	DL5	DL6
NO_3^-	—	—	—	—	—	—
Cl^-	—	—	3.4	10.8	—	6.4
SO_4^{2-}	—	—	—	—	—	—
$\text{NO}_3^- T_r\%$	—	—	—	—	—	—
$\text{NO}_3^- T_M\%$	—	—	—	82.1	—	91.1
$\text{Cl}^- T_r\%$	—	—	9.6	30.8	—	18.4
$\text{Cl}^- T_M\%$	—	—	47.2	38.7	—	46.0
$\eta(\text{NO}_3^-/\text{Cl}^-)$	—	—	0	0	—	0

$\text{NO}_3^- T_r\%$ = Percentage of NO_3^- transported into the receiving phase

$\text{NO}_3^- T_M\%$ = Percentage of NO_3^- transported into the membrane phase

$\text{Cl}^- T_r\%$ = Percentage of Cl^- transported into the receiving phase

$\text{Cl}^- T_M\%$ = Percentage of Cl^- transported into the membrane phase

The selectivity factor for specific ligands can be defined as;

$$\eta(\text{NO}_3^-/\text{Cl}^-) = \text{NO}_3^- \text{ T}_r\% / \text{Cl}^- \text{ T}_r\%$$

The results shows the selective transport of chloride ions into the receiving phase (**DL4 > DL6 > DL3**). It has also been observed that no sulfate was transported and that no nitrate was present in the receiving phase. This is possibly due to the pH of the receiving phase being too high. The anion transport experiment was carried out by using a “metal only” complex as a carrier in a CHCl_3 bulk liquid membrane (BLM). Forgan *et al.* have also shown that by attaching dialkylaminomethyl arms to commercial phenolic oxime reagents, the extraction efficiency was improved for the recovery of both copper and chloride ions.⁹

Furthermore it was also established in this study that pendant dihexylaminomethyl arms provides good solubility of both the ligand and its complexes in water immiscible solvents which assist in the extraction of copper salts.⁷ It was also established by these authors that the use of hydrocarbons in solvent extraction processes result in the formation of hydrogen bonding between the ligands improving the stability of the metal complexes formed. The presence of the hydroxyl group in the aromatic ring and the imine nitrogen atom could result in hydrogen bonding interactions resulting in the formation of interesting chemical structures.¹

3.11 pH Isotherms of Schiff base ligands (DL1, DL2, DL4-DL6)

The selected pH isotherms using copper(II) metal ions and selected Schiff base ditopic ligands (DL1, DL2, DL4, DL5 & DL6) are presented in Figure 3.9. The main reason for performing pH isotherms of copper (II) was to establish at which pH copper is extracted the most.

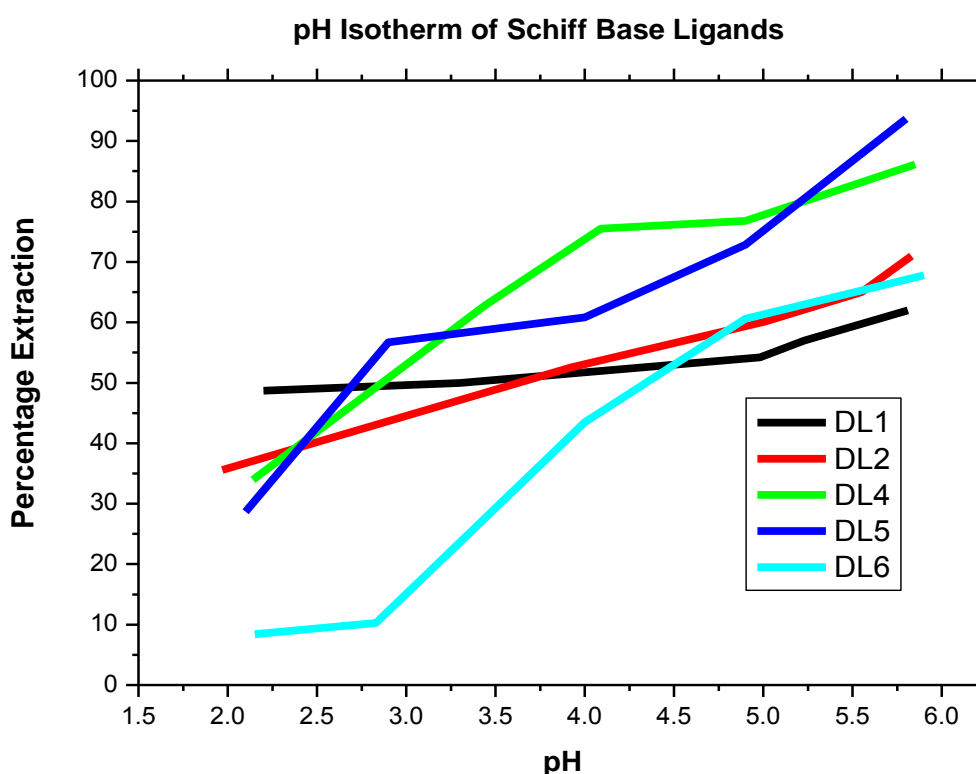


Figure 3.10: pH Isotherms for Schiff base ligands (DL1, DL2, DL4-DL6) for extraction of copper(II) ions

The extraction of Cu(II) was studied in the pH range of 2-6 as shown in figure 3.10. The highest extraction pH for the Schiff base extractants was observed above pH 5. From this figure it is obvious that the low extraction of copper(II) was observed at low pH whilst higher extraction was observed at high pH. The results obtained showed that it was profoundly influenced by the pH of the aqueous medium. It is observed that $DL5 > DL4$ and $DL2 > DL6 > DL1$ for the extraction of copper possibly

due to the alkyl chain length which makes the ligands more soluble in the organic phase. The results obtained from the pH isotherms complement those obtained in the extraction process. pH isotherm for the extraction of copper using Schiff base **DL3** was not done because the competitive extraction of copper was found to be approximately 9.8 % at pH = 5. Furthermore, the extraction was not done at a pH higher than 6 due to metal hydroxide formation.

3.12 Crystallography

The ^1H NMR spectra confirms the Schiff base condensation products, and with all crystallisation attempts unsuccessful, the structures of these ditopic complexes cannot be obtained crystallographically. However, elemental analyses support their formation, and the mass spectra exhibit molecular ions for the respective ligands. Furthermore numerous attempts were made to obtain crystals of both the ditopic ligands and their corresponding copper complexes *via* several techniques such as vapour diffusion, layering and slow evaporation which were unsuccessful. Small crystals were obtained with the copper complex of a ditopic ligand that possessed the piperidyl chain; however it was too small to be mounted for single crystal X-ray studies.

The Schiff base monotopic extractants investigated in Chapter 2 have a high degree of flexibility in the ligand backbone. On the other hand the Schiff base ditopic ligands possess long alkyl chains and a high flexibility in the ligand backbone that does not allow for straightforward crystallization since these ligands were obtained as oils or amorphous solids.

3.13 Conclusions

The work described in this chapter involved the synthesis, characterization and spectroscopic characterization of a new series of Schiff base ditopic ligands derived from an N-substituted 5-t-butyl salicylaldehyde and the appropriate amine derivative. The syntheses of **DL1-DL6** have shown that 3-substituted salicyaldimines can be prepared on the gram scale in moderate yields. These ligands were characterized by using different physicochemical techniques and they all complemented each other to elucidate the structure of each respective Schiff base ligand. The polytopic ligands described in this chapter are capable of extracting base metal chlorides or nitrates. Solvent extraction experiments have confirmed that **DL1-DL6** is effective for extracting copper(II). These results indicate that these ligands can be used for selectively extracting copper over metal ions and also nitrates over chloride and sulfate ions.

A very important aspect of this study is the comparison of the analytical techniques in structural elucidation. NMR results are obtained from synthesized ligands, complements the other spectroscopic techniques, whereas the X-ray method requires single crystals. In conclusion, on the basis of the IR measurements, it was possible to decide which atoms are involved in the complexation process. However, in order to obtain the exact structure, it would be necessary to perform X-ray structural investigations.

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Chapter 4

4. Synthesis of Ditopic (Oxo) Ligands for Metal Cation and Anion Extraction and Transport

4.1 Introduction

This chapter deals with the synthesis of a new class of metal salt extractants based on salicylaldimine ligands, and an initial investigation into their ability to extract both a metal cation and its attendant anion(s) into a water-immiscible solvent. This chapter extends the work of the previous chapter with a focus on anion analysis and anion selectivities of the polytopic ligands and their metal complexes. The selective transport of anions is an important requirement in hydrometallurgical flowsheets which involve the extraction of metal salts. The development of ditopic pro-ligands provides the possibility of changing the selectivity of the anion-binding site and the metal cation-binding sites in a solvent extractant.¹ The ditopic ligands that are synthesized in this study all possess imine functionalities which participates in metal ion coordination.

4.1.1 Factors influencing Anion Extraction

It has been reported by Moyer *et al.* that the factors that influence selective anion coordination are viz; (i) hydrogen bonding, (ii) conformational changes, (iii) electrostatic, (iv) dipole forces, and (v) topological complementarity.⁶ It has also been reported that hydrogen bonding is essential for the binding affinity of anions in Schiff base complexes.⁵ The d- and f-block metals form stable inner-sphere complexes with anions such as chloride and nitrate.

4.2 Experimental

4.2.1 Ligands and Metal Complexes

The ligands (Figure 4.1) and metal complexes synthesized for this chapter are summarised below (Table 4.1).

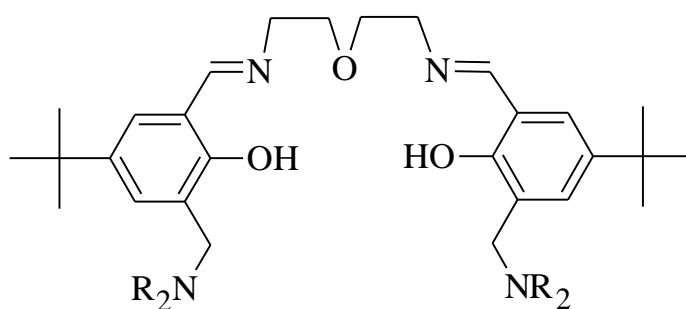


Figure 4.1: Prototype metal salt extractants; R = alkyl or aryl

Table 4.1: Ligands and metal complexes used and their designated reference numbers.

Ligands	NR ₂	Metal complexes	
DL7	(n-C ₆ H ₁₃) ₂	C7	[Cu(DL7 -2H)]
DL8	(n-CH ₂ C(C ₂ H ₅)C ₄ H ₉) ₂	C8	[Cu(DL8 -2H)]
DL9	Piperidine	C9	[Cu(DL9 -2H)]

4.3 Results and Discussion

The newly synthesized Schiff bases were stable at room temperature. The Schiff bases were soluble in common organic solvents such as ethanol, methanol and chloroform and partially soluble in hexane.

The synthesis of the ligands was performed according to the method of Galbraith *et al.*,⁴ involving the reaction of the appropriate amine linker in MeOH (50 cm³) into a stirred solution of the appropriate aldehyde in CHCl₃ (50 cm³). After stirring for between 15-18 hrs the solvent was removed to give a yellow-orange oil which was redissolved in CHCl₃ (100 cm³) and washed with water (2 x 50 cm³). The resulting solution was dried with MgSO₄, filtered and the solvent was removed in vacuo to yield a yellow-orange viscous oil.

Characterization of 5-(tert-butyl)-2-hydroxy-3-(dihexylamino)methyl benzaldehyde (DL7): Amine derivative used: 2,2-oxydiethylamine: Yellow-orange oil, yield 55.0%. Anal. Calcd. % for C₅₂H₉₀N₄O₃: C (76.23), H (11.07), N (6.84) Found: C (75.91), H (10.42) N (6.68). ¹H NMR (CDCl₃, 400 MHz) δ 0.87 (t, 12H, N(CH₂)₅CH₃), 1.27 (m, 24H, NCH₂CH₂(CH₂)₃CH₃), 1.33 (s, 18H, C(CH₃)₃), 1.52 (m, 8H, NCH₂CH₂(CH₂)₃CH₃), 2.48 (t, 8H, NCH₂(CH₂)₄CH₃), 2.95-2.98 (t, 4H, NCH₂CH₂), 3.69 - 3.73 (t, *J* = 6.64 Hz, 4H, NCH₂CH₂), 6.92 – 6.94 (d, *J* = 8.50 Hz, 2H, ArH), 7.24 - 7.25 (d, *J* = 2.28 Hz, 2H, ArH), 7.35 – 7.38 (dd, *J* = 2.49 Hz, 2H, ArH), 8.39 (s, 2H, NCH). ¹³C NMR (CDCl₃, 400 MHz) δ ppm 10.5 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 14.8 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 23.3 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 24.2 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 25.3 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 26.1 (4C, NCH₂CH₂CH₂CH₂CH₂CH₂), 31.08 (C(CH₃)₃), 31.47 (NCH₂CH₂), 34.60 (C(CH₃)₃), 50.14 (ArCH₂N), 59.01 (NCH₂CH₂), 116.13 (C_{Ar}H), 117.64 (C_{Ar}CN), 127.30 (C_{Ar}H),

129.21 ($C_{Ar}H$), 142.94 ($C_{Ar}C(CH_3)_3$), 158.40($C_{Ar}OH$), 167.41 (ArCN). IR (neat); 2952, 2863 (m, CH); 1631 (m, C=N); 1490 (m, CH); 1264 cm^{-1} (m, C-N). Expected MS: m/z (%) 819.29, Found (ES+):m/z (%) 819.72(100) $[M]^+$, 820.71 (30) $[M+H]^+$

Characterization of 5-(tert-butyl)-2-hydroxy-3-(bis(2-ethylhexylamino)methyl

benzaldehyde (DL8): Amine derivative used: 2,2-oxydiethylamine: Yellow-orange oil, yield 54.0%. Anal. Calcd. % for $C_{60}H_{106}N_4O_3$: C (77.36), H (11.47), N (6.01) Found: C (77.30) H(10.74) N(6.10). 1H NMR ($CDCl_3$, 400 MHz) δ 0.87 (t, 24H, $(N(CH_2(CH)CH_2CH_3)_2(CH_2)_3CH_3)$, 1.27 (m, 24H, $NCH_2CH_2(CH_2)_3CH_3$), 1.33 (s, 18H, $C(CH_3)_3$), 1.52 (m, 8H, $NCH_2CH_2(CH_2)_3CH_3$), 2.48 (t, 8H, $NCH_2(CH_2)_4CH_3$), 3.69 - 3.73 (t, $J = 6.64$ Hz, 4H, NCH_2CH_2), 6.92 – 6.94 (d, $J = 8.50$ Hz, 2H, ArH), 7.24 - 7.25 (d, $J = 2.28$ Hz, 2H, ArH), 7.35 – 7.38 (dd, $J = 2.49$ Hz, 2H, ArH), 8.39 (s, 2H, NCH), 13.23 (s, 2 H, OH). ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm δ ppm 10.5 (4C, $NCH_2CH_2CH_2CH_2CH_2CH_2$), 14.8 (4C, $NCH_2CH_2CH_2CH_2CH_2CH_2$), 23.3 (4C, $NCH_2CH_2CH_2CH_2CH_2CH_2$), 24.2 (4C, $NCH_2CH_2CH_2CH_2CH_2CH_2$) (4C, $NCH_2CH_2CH_2CH_2CH_2CH_2$), 26.1 (4C, $NCH_2CH_2CH_2CH_2CH_2CH_2$), 31.08 ($C(CH_3)_3$), 31.47 (NCH_2CH_2), 34.60 ($C(CH_3)_3$), 50.14 (Ar CH_2N), 59.01 (NCH_2CH_2), 116.13 ($C_{Ar}H$), 117.64 ($C_{Ar}CN$), 127.30 ($C_{Ar}H$), 129.21 ($C_{Ar}H$), 142.94 ($C_{Ar}C(CH_3)_3$), 158.40($C_{Ar}OH$), 167.41 (ArCN). IR (neat); 2954, 2924 (m, CH); 1632 (m, C=N); 1490 (m, CH); 1264 cm^{-1} (m, C-N). Expected MS: m/z (%) 931.5, Found (ES+):m/z (%) 931.85 (100) $[M]^+$, 932.83 (70) $M+H]^+$

Characterization of 5-(tert-butyl)-2-hydroxy-3-(piperidin-1-yl)methyl benzaldehyde (DL9): Amine derivative used: 2,2-oxydiethylamine: sticky yellow-orange oil, yield 62.0%. Anal. Calcd. % for $C_{38}H_{58}N_4O_3$ ($CHCl_3$)_{0.5}: C(68.14), H(8.69),N(8.26), Found: C (68.64), H (8.03), N (8.55). 1H NMR ($CDCl_3$, 400 MHz) δ ppm 1.31 (s, 18H, $C(CH_3)_3$), 1.45 (m, 4H, $NCH_2CH_2CH_2$), 1.62 (m, 8H, $NCH_2CH_2CH_2$), 2.46 (t, 8H, $NCH_2CH_2CH_2$), 3.58 (t, 4H, NCH_2CH_2), 3.72 (s, 4H, NCH_2Ar), 3.69 - 3.73 (t, $J = 6.64$ Hz, 4H, NCH_2CH_2), 7.24 - 7.25 (d, $J = 2.28$ Hz, 2H, ArH), 7.35 – 7.38 (dd, $J = 2.49$ Hz, 2H, ArH), 8.39 (s, 2H, NCH). ^{13}C NMR ($CDCl_3$, 400 MHz) δ ppm 24.2 (2C, NCH_2CH_2), 31.08 ($C(CH_3)_3$), 31.47 (NCH_2CH_2), 34.60 ($C(CH_3)_3$), 50.14 ($ArCH_2N$), 59.01 (NCH_2CH_2), 116.13 ($C_{Ar}H$), 117.64 ($C_{Ar}CN$), 127.30 ($C_{Ar}H$), 129.21 ($C_{Ar}H$), 142.94 ($C_{Ar}C(CH_3)_3$), 158.40($C_{Ar}OH$), 167.41 (ArCN). IR (neat); 2929, 2851 (m, CH); 1629 (m, C=N); 1463 (m, CH); 1268 cm^{-1} (m, C-N). Expected MS: m/z (%) 619, Found (ES-):m/z (%) 619(20) $[M]^+$, 620 (10) $[M+H]^+$

4.4. Characterization of Ditopic Ligands

The ligands synthesized in this chapter were fully characterized by ^1H and ^{13}C NMR spectroscopy, FTIR spectroscopy, mass spectrometry and elemental analysis. ^1H NMR spectra of the extractants **DL7-DL9** showed that the conversion of aldehyde to Schiff base was complete as indicated by the appearance of an azomethine signal and the absence of a carbonyl signal. ESI MS indicated the formation of the desired products by the presence of the expected parent ion ($\text{M}+\text{H}^+$).

4.4.1 FTIR Spectroscopy

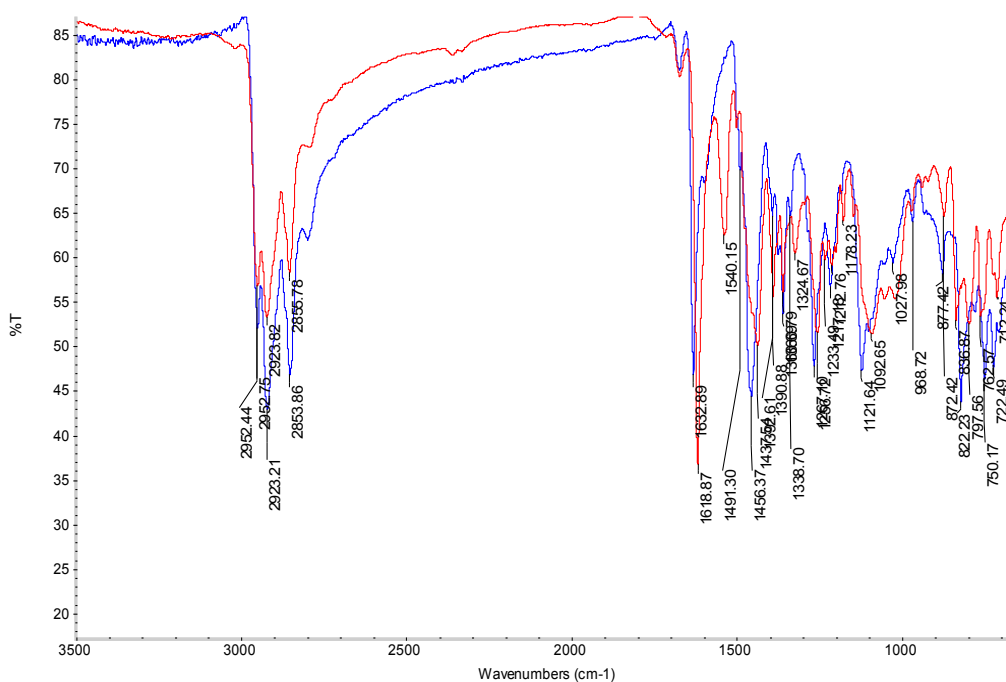


Figure 4.2: FTIR Spectrum of **DL7** and **DL7_Cu** showing the imine band slightly lowered due to metal complexation

All of the ligands and metal complexes have been characterised by FTIR spectroscopy. The observed stretches in figure 4.2 show the $\nu(\text{C-H})$ bands (2930-2980 cm^{-1}) for both **DL7** and the copper complex of **DL7**. The strong imine band

$\nu(\text{C}=\text{N})$ was also observed in all the spectra of the ligands ($1630 - 1635 \text{ cm}^{-1}$). The imine stretching vibration is slightly lowered upon metal complexation. This is an indication that the imine nitrogen is involved in metal binding.

4.4.2 NMR spectroscopy

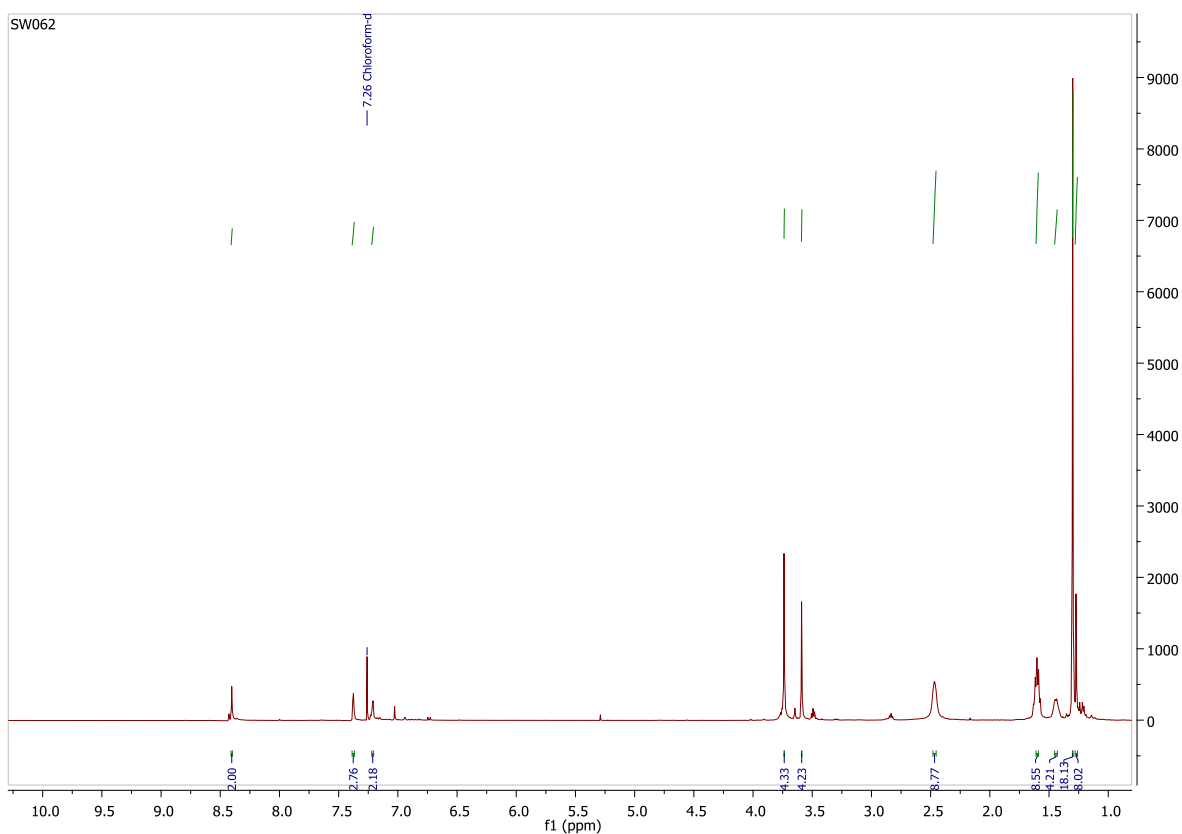


Figure 4.3: ^1H NMR spectrum of **DL9** in CDCl_3

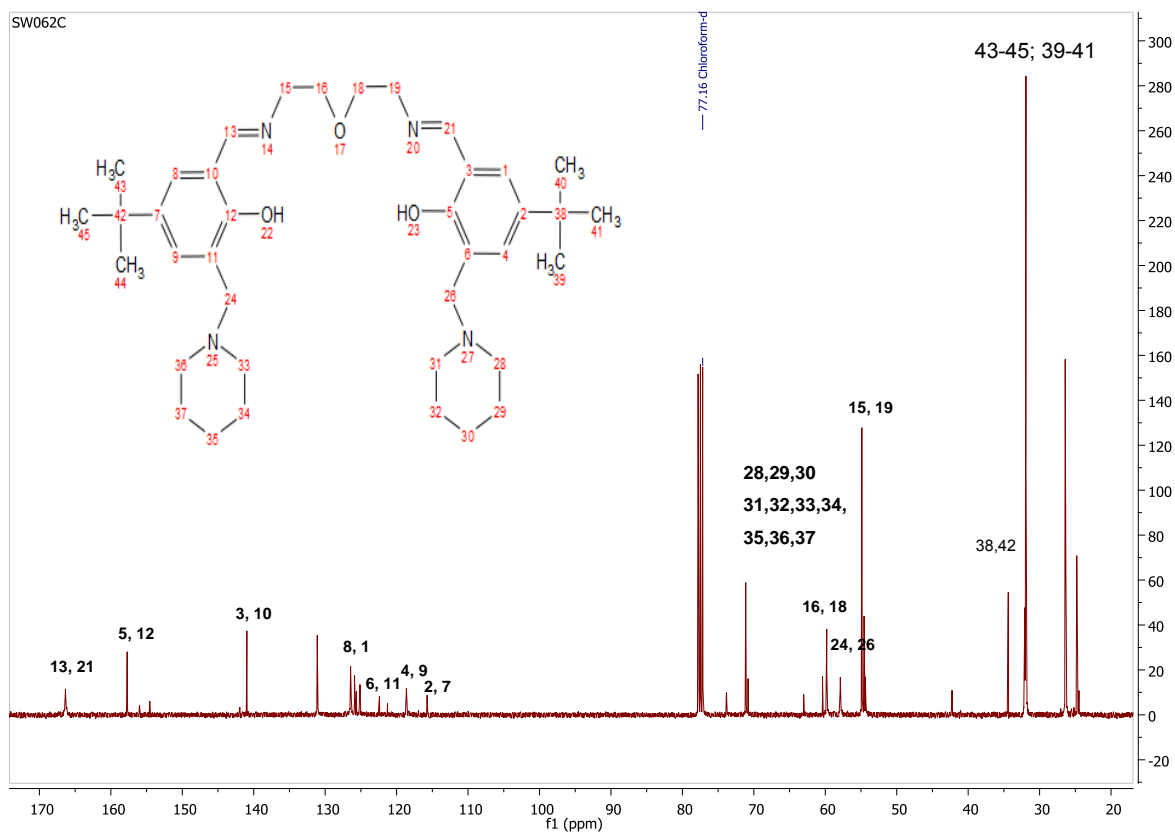


Figure 4.4: ^{13}C NMR spectrum of **DL9** in CDCl_3

The ^1H and ^{13}C NMR spectra of ligand (**DL9**) in CHCl_3 shows assignable peaks for the Schiff base ligands as shown in section 4.3. In the ^1H NMR, the peaks can be assigned to $\text{HC}=\text{N}$, aromatic CH , and the amine protons respectively which confirms the formation of the Schiff bases.

4.4.3 Mass Spectrometry

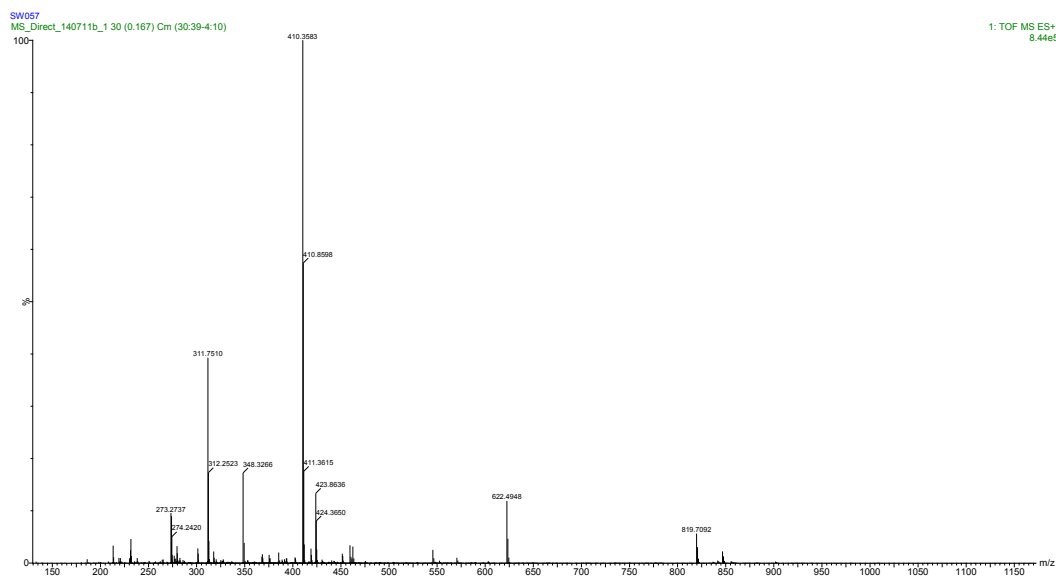


Figure 4.5: Mass Spectrum of **DL7**, molecular ion peak observed at 819.7 amu.

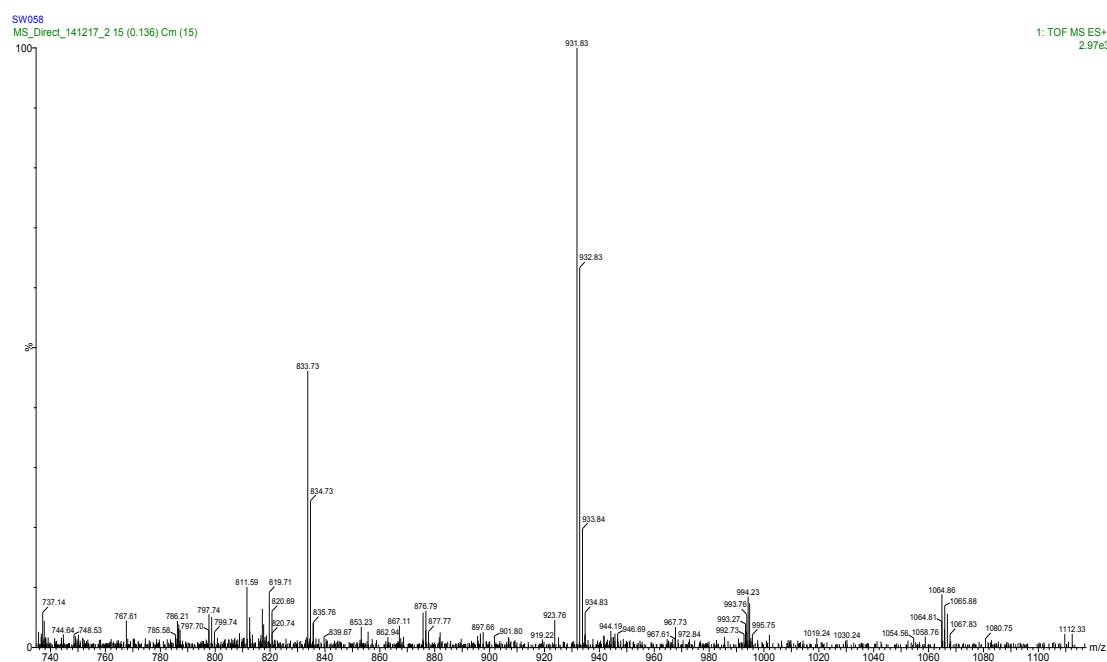


Figure 4.6: Mass Spectrum of **DL8_Cu**, molecular ion peak observed at 993 amu.

ESI MS was used to characterise all the ligands and copper complexes. Appropriate peaks were seen for each molecular ion (M^+) and ($M+H^+$) of the ditopic Schiff base ligand (**DL7**), indicating the successful condensation reaction. Figure 4.5 and figure

4.6 shows the molecular ion peak for **DL7** and the copper complex of **DL8** which confirms successful condensation reaction and copper complexation respectively. Similar spectra were observed for **DL8** and **DL9**.

4.4.4 Elemental Analysis

The physical data, elemental analyses are also given in section 4.3 for all the ligands synthesized. The elemental analysis data for all the ligands were complemented by the IR spectra and MS results. The purity of the extractant was further assured by the agreement of the elemental analysis results to the theoretical values. The hydrogen atoms were slightly high as the ligands were isolated as oils due to the incorporation of some solvent within the oil. The standard on the analyser for hydrogen was not working well and as a result the found results for hydrogen were lower throughout. Similar results were reported by Matthews *et al.* for N-alkyl-substituted *bis*(benzimidazole) ligands. A few of these ligands were also isolated as oils and the elemental analysis results for the hydrogen atoms were also found to be slightly higher.⁵

4.5 Cu(II) Complex Syntheses

General Procedure A solution of the ligand (1.4 mmol) in CHCl_3 (30 ml) and $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (1.4 mmol) in methanol were mixed and stirred overnight. Colour changes due to complex formation occurred immediately, along with precipitation. The solvent was removed in vacuo to give the pure product as a greenish black oil. This oil was redissolved in CHCl_3 (60 ml) and washed with pH 9 ammonia solution (2 x 30 ml). The resulting organic phase was dried with anhydrous MgSO_4 , filtered and then concentrated in vacuo to yield the metal complex which was used without further purification.⁴ The copper(II) complexes were characterised by FTIR and MS.

Data for [Cu-(DL7-2H)]: yield: 0.66 g, 79%; IR ν = 1618.87 (s), 1540, 1437, 1212, 750 cm^{-1} ; Expected MS: m/z: 880.8, Found MS: m/z: 881.1 $[\text{M}+\text{H}]^+$.

Data for [Cu-(DL8-2H)]: yield: 0.69 g, 98%; IR ν = 1619.9 (s), 1533, 1457, 1219, 725 cm^{-1} ; Expected MS: m/z: 993.0, Found MS: m/z: 994.2 $[\text{M}+\text{H}]^+$.

Data for [Cu-(DL9-2H)]: yield: 1.1 g, 98%; IR ν = 1621.57 (s), 1541, 1441, 1216, 708 cm^{-1} ; Expected MS: m/z: 680.4, Found MS: m/z: 681.4 $[\text{M}+\text{H}]^+$.

4.6. Solvent Extraction Experiments

4.6.1 Initial Competitive Extraction Experiment

Two-phase solvent extraction experiments were carried out by contacting 0.01 mol dm^{-3} chloroform solutions of Schiff base extractants (**DL7-DL9**) with equal molar metal ion solution and the aqueous source phase consisting of Pb^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} .

Table 4.2 Percentage metal ion extracted by **DL7-DL9**; The experimental conditions were: pH of the source phase = 4.9, concentration of ligand = 0.01 mol dm^{-3} , extraction time = 24 h.

Ligands	Extracted value Cu (%)
DL7	79 ± 3
DL8	64 ± 1
DL9	51 ± 2

The competitive extraction results for **DL7-DL9** show copper(II) is extracted in all three cases over other base metal ions. The selectivity shown in Table 4.2 is basically in accordance with the Irving-Williams series.⁵ The percentage errors are based on the average values of duplicate samples. The solvent extraction process

provides for an opportunity to selectively remove copper from the other base metals using the synthesized Schiff base ligands **DL7-DL9**. Similar findings were reported for the N-donor ditopic and monotopic ligands as shown in chapter 3 and chapter 2 respectively.

4.6.2 Initial Competitive Transport Experiment

Competitive metal ion transport experiments involving Schiff base ligands (**DL7-DL9**) were conducted and the results are summarized in Table 4.3

Table 4.3 *J* values for the competitive metal ion transport studies for 24 h, involving **DL7-DL9**. The experimental conditions were: pH of the source phase = 4.9, pH of receiving phase = 1.0 and concentration of ligand = 0.002 mol dm⁻³.

Ligand number	DL7	DL8	DL9
Co(II)	—	—	—
Ni(II)	—	—	—
Cu(II)	0.59	1.82	1.58
Zn(II)	—	—	—
Cd(II)	—	—	—
Pb(II)	1.97	6.57	0.17
^{Cu} <i>T_r</i> %	4.4	14.76	11.9
^{Cu} <i>T_M</i> %	27.78	41.65	58.81
^{Pb} <i>T_r</i> %	3.4	14.57	1.2
^{Pb} <i>T_M</i> %	11	18.1	8.8
$\eta(\text{Cu(II)/Pb(II)})$	1.29	1.01	9.92

Under these conditions it was assumed that the resulting pH gradient across the cell was favourable for the uptake of metal ions from the source phase into the membrane phase while promoting its loss to the receiving phase as shown in Table 4.3. These results are supported by Reddy *et al.* in which he demonstrated the efficient transport of copper ions in the presence of other metal ions by using oxime derivatives.⁸ Furthermore he stated that the transport of copper ions were not affected even in the presence of 10-fold concentration of these ions which suggest selectivity toward copper ions. This work is further supported by the transport of copper by the monotopic Schiff base ligands as shown in Chapter 2.

4.7 Selectivity for Copper ions with 10-fold Excess of the Ions (Pb, Co, Ni, Cd, Zn)

The competitive extraction studies of Schiff base ligands (**DL7-DL9**) were performed using mixed ion solutions and the results are summarized in Table 4.4. The concentration of the five metal ions was 10 times higher than that of copper(II). This was done to establish whether or not the ligand would still be selective for copper. pH = 5 was selected for all competitive extraction studies of **DL7-DL9**.

Table 4.4 Percentage copper ion extracted by **DL7-DL9** using 10 – fold excess of the Ions (Pb, Co, Ni, Cd, Zn); The experimental conditions were: pH of the source phase = 5.0, concentration of ligand = 0.01 mol dm⁻³, concentration of Cu = 0.01 mol dm⁻³, concentration of other metal ions = 0.1 mol dm⁻³, extraction time = 24 h.

Ligands	Extracted value, Cu (%)
DL7	70.8 ± 3
DL8	67.2 ± 4
DL9	69.2 ± 4

Under the conditions employed, *sole* extraction was observed for copper(II) as shown in Table 4.4, over the five other metal ions even in the presence of 10 fold concentration of other metal ions in the source phase. This indicates that these oxo donor ditopic ligands are very selective towards copper ions. The percentage errors are based on the average values of duplicate runs. This is consistent with the copper(II) complex of **DL7-DL9** being thermodynamically favoured in the organic phase. The expected complex stability of copper for these Schiff base ligands is in accordance with the expected Irving–Williams stability order for complexes of the present metal ion series. The extraction of copper has also been achieved by using phenolic oxime extractants.⁶ The intermolecular hydrogen bonds between the oxime OH groups and the phenolate oxygen atoms allows for the formation of copper complexes of high stability, which contribute to the high extraction efficiency.⁷ Dede *et al.*¹¹ reported a high extraction of copper(II) ions over metal ions including Mg²⁺, Pb²⁺, and Hg²⁺ ions.

4.8 Selected pH Isotherms of DL7-DL9

The pH isotherms for Schiff base ligands **DL7-DL9** are presented in figure 4.7 for extraction of copper ions. These isotherms were performed to establish the maximum extraction as well as $pH_{1/2}$ (the pH at which 50 % of Cu (II) is extracted) of copper of the Schiff bases **DL7-DL9**. The pH isotherms were also used to determine the stability of the Schiff base extractants in the selected pH range.

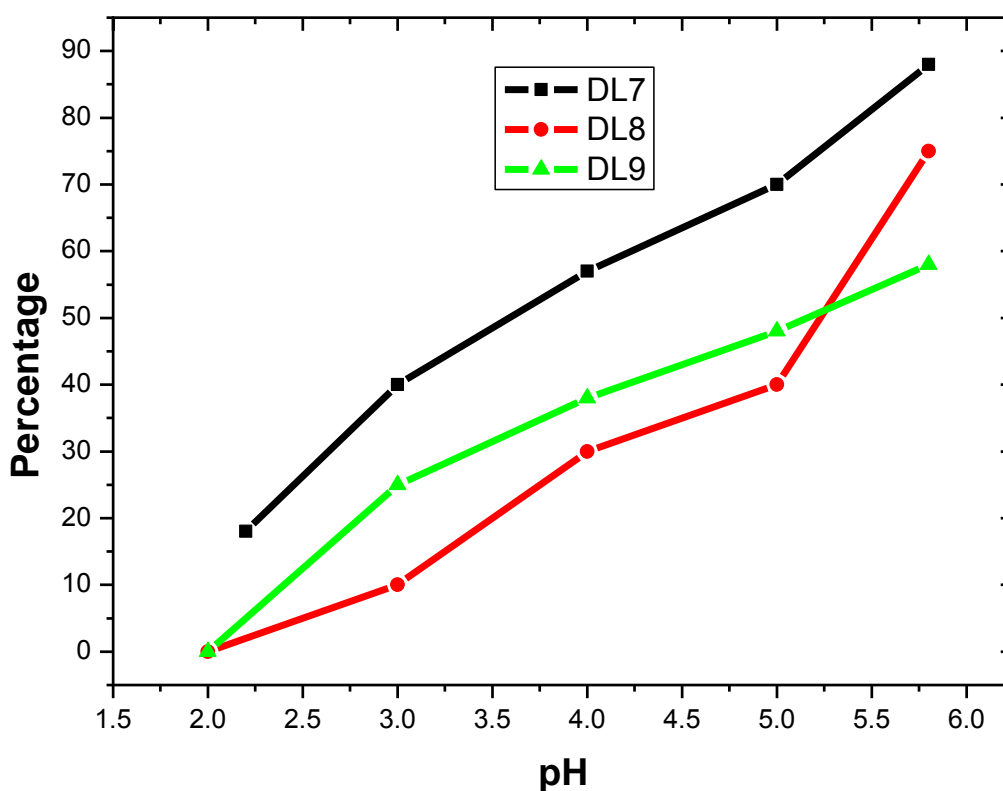


Figure 4.7: pH Isotherm for Schiff base ligands (**DL7-DL9**) for extraction of copper (II) ions

Figure 4.7 shows the pH isotherms obtained for copper(II) for **DL7-DL9**. It was observed that the extraction of copper(II) was the highest in the pH range 5-6 for **DL7-DL9**. The extraction data shows the order of extraction for the ligands **DL7>DL8>DL9**. These results indicate that the highest extraction efficiency for Cu(II)

was obtained for **DL7**. The results also suggest that the **DL7-DL9** is relatively stable above pH = 4 and shows consistency with the results obtained from the competitive extraction of the selected base metal ions. These Schiff base extractants could therefore potentially find application in copper recovery circuits working within the conventional pH ranges. These results are complemented by the extraction results for the monotopic and N-donor ditopic Schiff base ligands respectively which also shows selectivity towards copper.

4.9 Extraction of Anions

The competitive extraction of anions was carried out using three anions (Cl^- , NO_3^- , SO_4^{2-}). The experimental conditions used for the extraction of anions are shown in figure 4.8. It is quite a challenge to achieve selectivity of extraction of SO_4^{2-} over Cl^- and NO_3^- because sulfate has a higher hydration energy making it intrinsically more difficult to transport into a water-immiscible phase. The additional hydrogen bond donor groups at the anion binding site did not show high binding for sulfate as expected from the Hofmeister bias for its extraction into chloroform.^{9, 10} The extraction of sulfate is important and if these ligands did extract sulfate, it provides a new source of ligands for the extraction of sulfate.

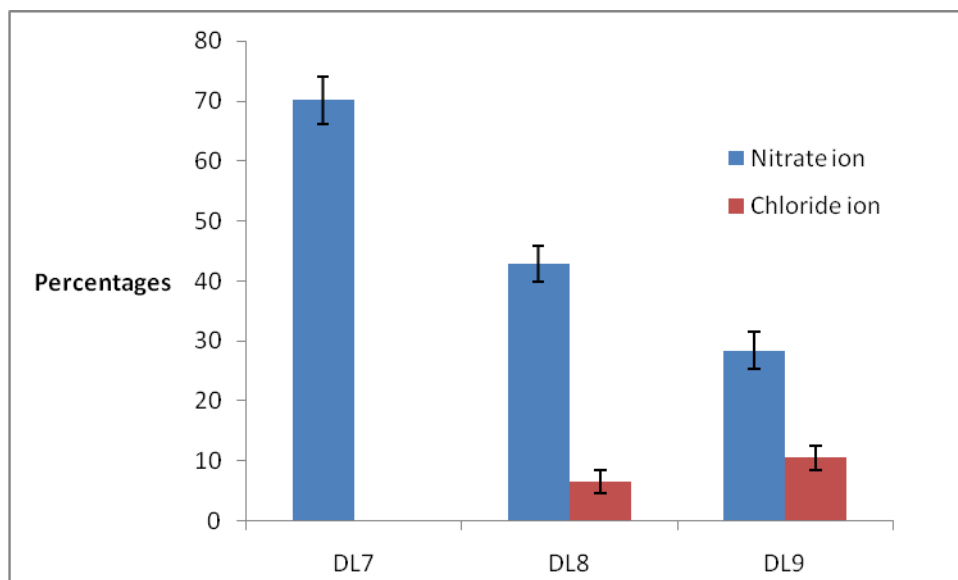


Figure 4.8: Competitive Extraction of selected anions using copper complexes of **DL7-DL9**. The experimental conditions used for the extraction of the anions are as follows; 0.01M ligand concentration, 0.01 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.005 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.01 M HNO_3 at pH = 2.15 on a labcon oscillating shaker for 24 h at 25 °C.

The results in figure 4.8 show that nitrates are favourably extracted over chloride and sulfates. The percentage errors are based on the average values of duplicate samples. The selective extraction of sulfate has not been widely published due to the hydrophilicity of sulfate which accounts for the low extractability into low polarity organic solvents. Galbraith *et al.*⁴ showed that the extraction of sulfate ions using Salen Schiff base derivatives was dependant on pH. They observed that the highest extraction of sulfate ions was observed at pH below 2 whilst a pH above 3 showed no extraction in the case of the free Schiff base ditopic ligand. Furthermore the increased basicity of the pendant dialkylaminomethyl arms allowed for the extraction of anions such as sulfate. The coextraction of copper and sulfate ions has been reported by Coxall *et al.*¹² using hydrophobic ditopic ligands. Plieger *et al.*¹³ found that the binding of sulfate ions was enhanced by using hexamethylene straps which was anchored to the pendant amine groups. The Schiff base ligands reported

in this chapter have pendant groups and this usually results in an increase in solubility in non-polar organic solvents that makes it suitable for solvent extraction studies. Hydrogen bonding interactions assist with the binding of anions and can assist in determining the structure-defining aspect in anion coordination chemistry. It has been reported by Moyer *et al.*⁶ that increasing the hydrogen-bond donor functionality can favour the extraction of larger, more complex anions such as sulfate over nitrate ions.

There was no transport of any anions into the receiving phase with **DL7-DL9**. The possible reason for no transport of any anions into the receiving phase was possibly due to the pH gradient between the source phase and receiving phase. The pH of the source and receiving phase were 3.1 and 6.5 respectively.

5. Conclusions

In conclusion, the synthesis of novel ditopic **DL7-DL9** ligands are reported which was used in competitive extraction and transport of selected metal ions. Furthermore anion extraction and transport were also evaluated to determine anion selectivity. The extraction and transport ability of these ligands towards copper(II) ions and nitrate anions were observed. The co-extraction of a metal cation with its attendant anion in the form of a metal salt by these types of ligands provides an alternative to conventional ion exchange reagents which have the disadvantage of adding components to the aqueous stream. The spectroscopic results of Schiff base ligands **DL7-DL9** have established the feasibility of preparing simple and inexpensive extractants based on salicylaldimine ligands to transport metal nitrates.

The ditopic ligands described in this chapter are capable of extracting copper nitrates. All the ligands possess metal cation binding and an anion binding component tethered in the same ligand. The advantage of these new ligands is that the extraction of metal salts will not create a major change in pH of the aqueous feed solution as they form metal salt complexes with zwitterionic forms of the ligands.

It is very clear that these ditopic ligands (oxo) are very selective for copper which is complemented by the monotopic ligands in Chapter 2 that also showed selectivity for both copper and lead as indicated by the extraction results. Similarly the N donor ditopic ligands in Chapter 3 also show selectivity towards copper except DL3 which extracts both copper and lead due to the presence of palmitic acid. However the best extraction of copper was observed with oxo (NON) donor ditopic ligands under the same conditions.

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Chapter 5

5. Interaction of Schiff base ligand and carboxylic acids

5.1 Introduction

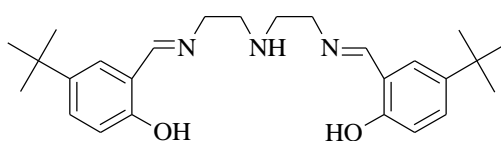
The extraction of metal ions using the four monotopic Schiff base ligands (Chapter 2) resulted in higher extraction for lead metal ions which were obtained with palmitic acid, hence the motivation for this further study.

The objective of this study was to determine the interaction of the Schiff base ligand with palmitic acid. This chapter aims to study the interaction of a Schiff base ligand with various carboxylic acids in chloroform by investigating the effect of such ligand assembly on the solvent extraction of copper(II) and lead(II) ions respectively. It is well-known that the supramolecular association between ligands may be employed to influence the selectivity and efficiency of separation processes. NMR titration experiments in the absence of a metal ion will be undertaken to confirm the formation of weak 1:1 and 1:2 (ligand:carboxylic acid) assemblies in CDCl_3 and DMSO. It has been reported previously that carboxylic acid assemblies of this type have been used as extractants in a series of solvent (water/chloroform) experiments. It was observed from previous work that the use of host guest assemblies for metal ion complexation resulted in enhanced metal ion binding (and concomitant enhanced metal ion extraction).¹

The acids that will be employed in this study are; (i) palmitic acid; (ii) salicylic acid; (iii) benzoic acid; (iv) heptanoic acid together with the monotopic Schiff base ligand prepared in Chapter 2. The monotopic Schiff base ligand contains three nitrogen donor atoms and bridged by two carbon atoms. It was found that the

synthesized ligand was appreciably soluble in the aqueous layer hence the addition of palmitic acid to make it less hydrophilic. It was observed that besides the ligand being selective for copper ions following the Irving-Williams series, lead was also extracted which came as a surprise. Further experiments were conducted to confirm the synergistic behaviour between the Schiff base ligand and palmitic acid. The solvent extraction of metal ions with palmitic acid in saturated chloroform showed extraction of only lead ions and no other metal ion. Surprisingly enough, the presence of palmitic acid with the Schiff base ligand resulted in an enhanced uptake of lead ions suggesting a cooperative action taking place.

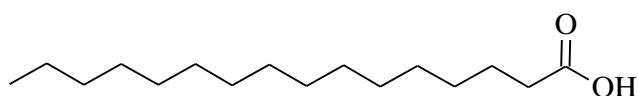
It was then decided to employ a range of carboxylic acids to study the influence of these acids on extraction behaviour. The solvent extraction of heptanoic and benzoic acids with the Schiff base ligand **L1** showed no extraction of lead ions. It was also observed that palmitic and salicylic acid together with the ligand resulted in the extraction of lead ions. It can thus be concluded that there is synergism between the ligand **L1** with palmitic and salicylic acids respectively for the uptake of lead ions.



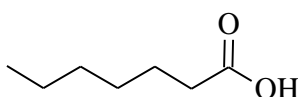
L1

5.2 Experimental

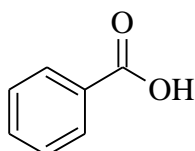
All reagents and solvents were of the highest commercial grade available and were used without further purification. The Schiff base ligand (**L1**) was prepared and characterised as described in Chapter 2 (section 2.5). Carboxylic acids were obtained commercially. All aqueous solutions were prepared using ultra-pure water; chloroform was presaturated with water before use in the solvent extraction experiments.



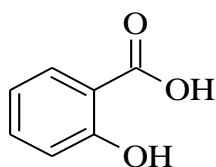
A = Hexadecanoic acid



B = Heptanoic acid



C = Benzoic acid



D = 2-hydroxybenzoic acid (salicylic acid)

Figure 5.1: Carboxylic Acids (A-D)

5.2.1 Proposed Linkage

The following is a proposed linkage between **L1** and palmitic acid which shows enhanced uptake of lead ions.

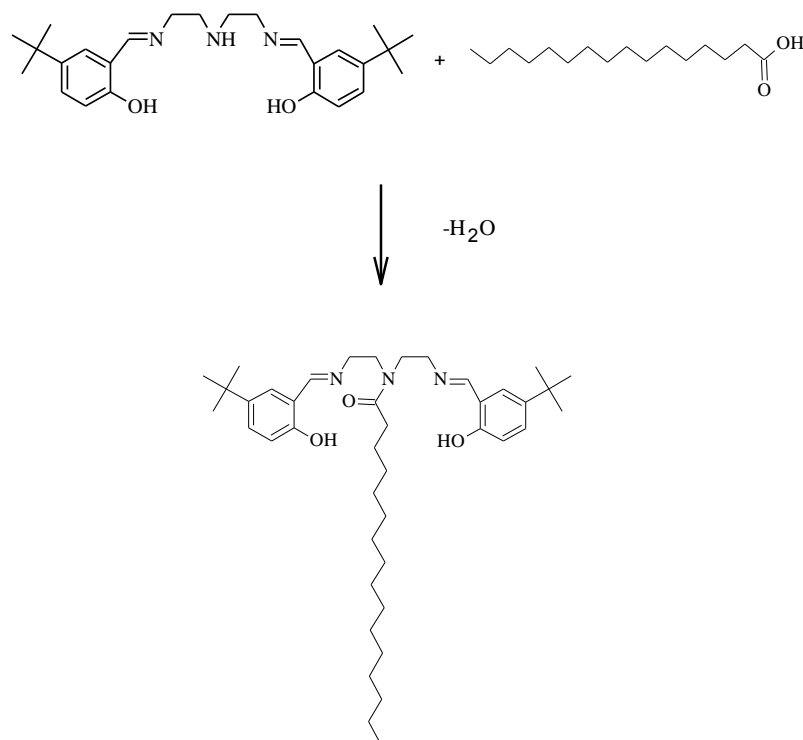


Figure 5.2: Proposed linkage between **L1** and palmitic acid²

5.2.2 FTIR Study

An FTIR study was conducted on the Schiff base ligand (**L1**) and the ligand assembly (palmitic acid) as shown in the section 5.3. The concentration of the palmitic acid was four times that of the ligand **L1**. The concentration of $\text{Pb}(\text{NO})_3$ was equivalent to that of **L1**.

5.2.3 NMR Titrations

The NMR titration experiments were carried out involving **L1** and different acids such as palmitic, salicylic, benzoic, and heptanoic acid. For the NMR titration studies, a weighed amount of the carboxylic acid was added incrementally to the respective Schiff base ligand (at $\sim 0.07 \text{ mol dm}^{-3}$) dissolved in either deuterated chloroform (0.5 cm^3) or DMSO- d_6 (0.5 cm^3) in the NMR tube. The amount added was determined by the weight difference before and after each addition. The ratio of ligand:acid that was used ranged from (1:1; 1:1.5; 1:2; 1:2.5; 1:3; 1:3.5; 1:4; 1:4.5; 1:5). This was done in order to probe how the structure of the ligand changes as the concentration of the respective acid increases. Chemical shift changes in the ^1H NMR spectra were recorded after each addition. The induced chemical shifts were plotted as a function of the mole ratio of palmitic, benzoic, heptanoic and salicylic acid to **L1** present at each titration point.¹

5.2.4 Solvent extraction experiments

Preliminary solvent extraction experiments confirm that the more lipophilic derivative **L1** with the carboxylic acids have a low propensity to bleed from chloroform to an aqueous phase when employed in the metal ion solvent extraction experiments under the present conditions.

Four series of solvent extraction (chloroform/water) experiments involving **L1** were undertaken during the present study. The aqueous phase consisted of copper(II) and lead(II) (each at an initial aqueous phase concentration of $1 \times 10^{-2} \text{ mol dm}^{-3}$) and was maintained at $\text{pH} = 5$ using a buffer solution (sodium acetate/acetic acid). The metal ion concentration after extraction was measured by ICP-OES and the experiments were performed in duplicate. These extractions were performed in

sealed glass vials containing a chloroform phase (5 cm³) and an aqueous phase (5 cm³). The chloroform phase consisted of **L1** (1x10⁻²) and a known concentration of palmitic, heptanoic, benzoic and salicylic acids (4x10⁻² mol dm⁻³).¹

5.3 Results and discussion

5.3.1 FTIR Results

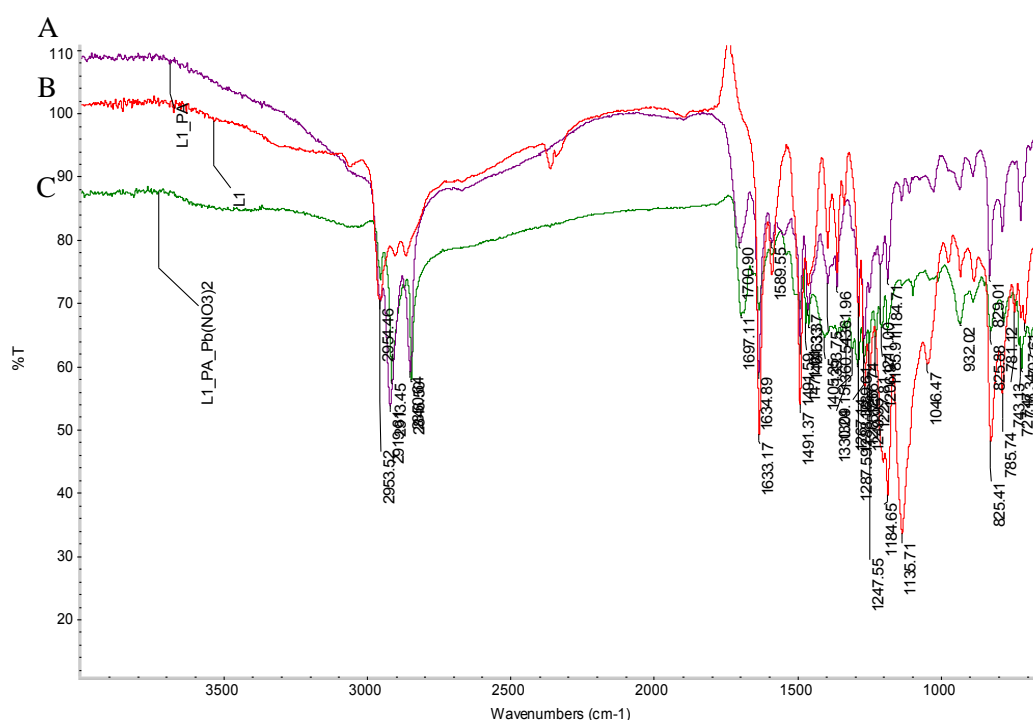


Figure 5.3: FTIR spectra of (A) = Schiff base ligand (**L1**)-palmitic acid, (B) = Schiff base ligand (**L1**), (C) = Schiff base ligand (**L1**)-palmitic acid -Pb(NO₃)₂

The spectra presented in figure 5.3 shows distinct bands for the Schiff base ligand (**L1**) and also the Schiff base ligand with palmitic and lead nitrate. It clearly shows that the imine band at 1633 cm⁻¹ has not shifted in the presence of palmitic acid and lead nitrate. However the C-H vibrational stretches shifted by approximately 40 cm⁻¹ which suggest that the palmitic acid interacts with the protons causing a shift in frequency.

5.3.2 NMR Results

The use of NMR titrations to investigate the interactions between the ligand and selected carboxylic acid assemblies have been previously investigated.³⁻⁵ It was found that metal ion extraction was associated with synergism relative to the extraction of the carboxylic acid (C.A).

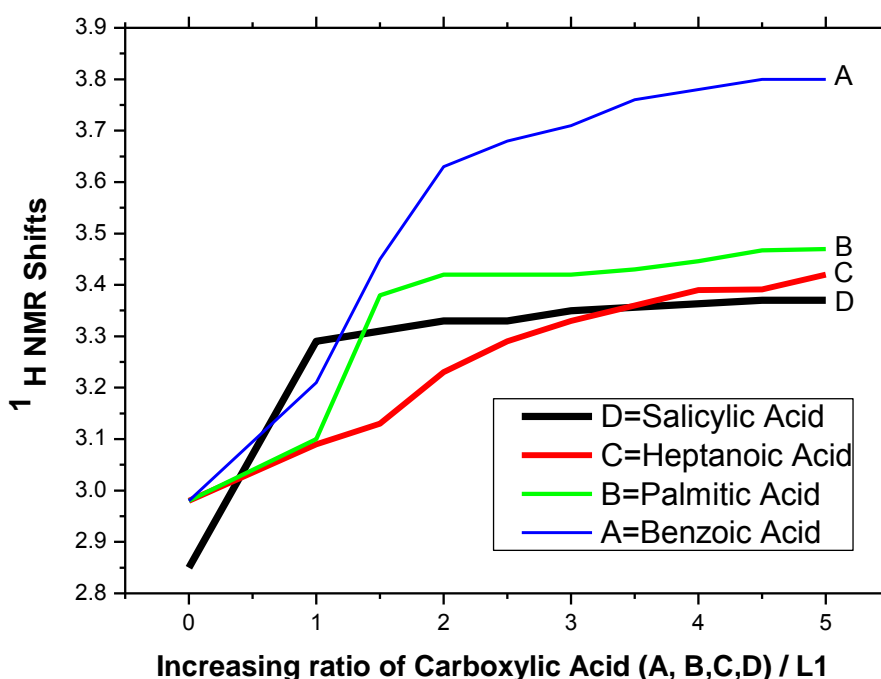


Figure 5.4: ^1H NMR Titration study of **L1** (**C=N-C-C-H**) with carboxylic acids (A-D), increasing ratio of carboxylic acid to ligand ratio

The ^1H NMR results for the four acids as shown in figure 5.4, shows the titration plot for the addition of the various carboxylic acids to **L1** in CDCl_3 and DMSO in the case of salicylic acid only. It is observed that for every addition of carboxylic acid to the ligand (**L1**) there is a shift in the ^1H NMR spectra. We only observed the changes in the ^1H NMR spectra at two particular shifts (ie. the $-\text{C}=\text{N}-\text{CH}_2-\text{C}-\text{H}$ and $-\text{C}=\text{N}-\text{CH}-\text{C}-\text{H}$). This could be due to the interactions between the amine protons and

the carboxylic acids as shown by the titration plot. It is also evident from figure 5.4 that incremental shifts of the amine protons were observed after every addition of the respective acids which indicates that there are less hydrogen atoms available for hydrogen bonding. The shifts are also confirmed by the FTIR study as reported in section 5.3.1. Similar shifts were observed in the aromatic region of the ^1H NMR spectrum which suggests possible steric interactions between the benzyl group and the carboxylic acid.

Therefore the NMR study confirms that the interaction between the carboxylic acids and **L1** causes the ligand to be more soluble in the organic phase. It was also observed that above the ratio of 4 C.A. to the ligand the curves levels which indicates that the optimum ratio of ligand:carboxylic acid assembly is 1:4 and therefore this ratio was used in subsequent solvent extraction experiments.

5.3.3 Synergistic Solvent extraction results of Copper(II) and Lead(II)

Synergistic separation is the process by which one extractant and one carboxylic acid (synergist) are used in combination to enhance the extraction of a certain metal ion. It has a much higher efficiency as compared to the normal additive effect of these extractants separately.⁶ Synergistic effects of mixed ligands on metal ion extraction is very interesting and also important from the scientific and industrial point of view.⁷

It is well known that Cu(II) coordinates with a number of Schiff base ligands due to a number of factors such as the hard soft acid base theory and also the Irving Williams series.^{8,9} As shown in figure 5.5, four experiments were conducted using **L1** and the respective carboxylic acids to determine the extraction efficiency towards copper and lead ions respectively.

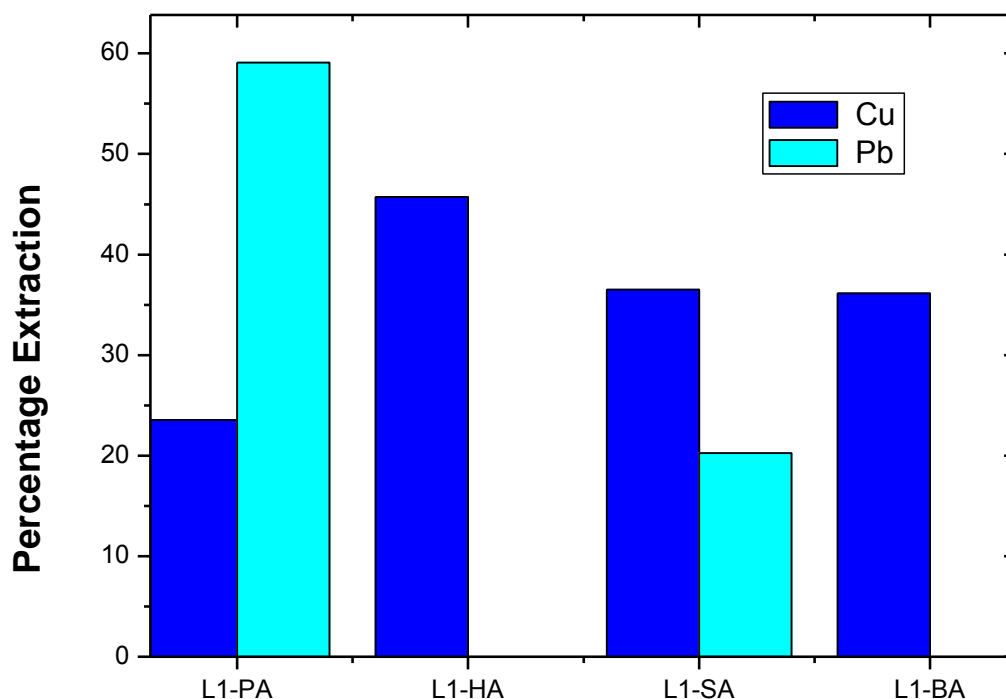


Figure 5.5: Solvent Extraction of the Ligand:Carboxylic Acid Assembly with Cu (II) and Pb (II);The experimental conditions were: pH of the metal ion solution = 5.0, concentration of ligand = 0.01 mol dm^{-3} , concentration of the carboxylic acids (PA, HA, SA, BA) = 0.04 mol.dm^{-3} , room temperature, extraction time = 24 h

The experiments (Figure 5.5) clearly illustrate the selectivity towards copper which also correlates well with the competitive extractions of selected transition metal ions in Chapter 2. However, when **L1** was employed in conjunction with palmitic and salicylic acid, lead extraction was significantly higher than for **L1** alone. The extraction of lead with palmitic acid alone resulted in 34% of lead extracted whilst no extraction of lead was observed for the other acids. The extraction of lead when salicylic acid was used in the presence of **L1** is possibly enhanced due to the chelate effect of the two hydroxyl groups. There is clear evidence of synergism in the case of palmitic and salicylic acid systems. However there is clear evidence for substantial

synergism for the palmitic acid system which is why lead is extracted to its greatest extent using the ligand-palmitic acid assembly.

The favourable extraction of copper by the Schiff base ligands **L2** and **L4** in this work is supported by the obtained crystal structures as shown in Chapter 2. This also suggests the stability of copper when complexing with these ligands. The extraction of copper(II) and silver(I) was also observed by other researchers such as Gasperov *et al.* using a similar ligand assembly.¹ They observed a similar synergistic behaviour towards the extraction of silver(I) in the presence of copper(II). Similarly, Dadfarnia *et al.* also found the cooperative behaviour between a macrocyclic ligand with palmitic acid for the efficient transport of copper across a bulk liquid membrane.¹⁰ Synergistic extraction of Pb(II) from water into 1,2 dichloroethane (DCE) was demonstrated by Kavallieratos *et al.* using a mixture of sulfonamide chelates and 2,2'-bipyridine.¹¹

Shiri-Yekta *et al.* demonstrated the efficient separation of Zn(II), Cd(II) and Pb(II) ions in an aqueous mixture by using a combination of 2,2'-bipyridine (bipy) and a disulfonamides in dichloroethane.¹² Similarly, synergistic behaviour of mixed ligands on metal extraction have also been reported by Koh *et al.* which showed a high uptake of metal ions (Cd^{2+} , Co^{2+} , Cu^{2+} , Pb^{2+} and Zn^{2+}) in supercritical CO_2 by using two organophosphorous ligands.¹³

5.4 Concluding Remarks

In this chapter a range of solvent extraction experiments (water/chloroform) involving ligand assemblies between Schiff base **L1** and selected carboxylic acids in the respective organic phases and copper(II) and lead(II) have been investigated. Metal ion extraction was associated with synergism using the carboxylic acid ligand assemblies.

The study demonstrates how the extraction efficiency of **L1** was improved towards lead based on the extraction experiments using the various acids, by way of the cooperative effect or synergism between the ligand assemblies.

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Chapter 6

6. Conclusions and Future work

The first section of the thesis (Chapter 2) involved the synthesis and characterization of monocationic Schiff base ligands. These ligands (**L1-L4**) were subjected to competitive extraction and transport of selected base metal ions. Cu(II) and Pb(II) were extracted by all four ligands whilst only copper was transported. Crystal structures were obtained for two free ligand structures and two complexes which indicated how Cu(II) is coordinated to the ligand. The copper complex crystal structure which forms a metallocycle with ligand (L4) has been reported for the first time.

The second objective of the thesis (Chapters 3 and 4) involved the synthesis and characterization of salicylaldimine ligands bearing pendant tertiary amine groups, **DL1 – DL9**, were used for the extraction and transport of selected base metal ions. The synthesized ditopic ligands were highly selective for extracting copper. Mass spectrometry proved invaluable in confirming the ligand:metal stoichiometry and molecular formulae. Efforts to isolate single crystals of ditopic copper complexes of the Schiff base ligands for X-ray structure determination were not as successful as those using the monotopic copper complexes. Furthermore the copper complexes of these ligands were subjected to competitive anion extraction and transport of selected anions. The anion selectivity follows the order $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. This is in agreement to the Hofmeister bias.

The third objective of this thesis (Chapter 5), was to investigate the binding action of the carboxylic acid to the Schiff base ligand (**L1**) before complexation. An NMR and

IR study was successfully employed to investigate interactions between the carboxylic acid and the Schiff base ligand. Solvent extraction of the palmitic acid with **L1** showed an enhanced uptake of lead ions which is most likely synergistic behaviour.

The following recommendations for future work can be proposed:

Section 1

1. Designing monocationic Schiff base ligands with a high solubility in the organic phase.
2. Changing the substituents on the amine linker of the Schiff base ligands thus making it more selective to other transition metal ions.
3. Investigate their suitability in industrial applications.

Section 2

1. Developing a more efficient synthesis methodology for the preparation of the ditopic Schiff base ligands.
2. It will be important to understand the coordination geometry around the metal centre of these complexes using single crystal X-ray crystallography. Therefore it will be required to investigate new ways of growing crystals of these ditopic Schiff base ligands.
3. The anchoring of different alkyl substituents to create an anion binding site should be investigated which will enable the extraction of sulfate.

Section 3

1. Further characterization techniques (e.g. different NMR techniques) have to be investigated which will provide a better understanding of how the carboxylic acids (including palmitic acid) coordinates to the ligand before complexation of the metal ion.