

# **Transport and Extraction of Au (III) using Thiourea Ligands**

**By**

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## **Declaration**

I, the undersigned, hereby declare that the work contained in this thesis is my original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Signature

Date

## Abstract

A series of di- and mono-substituted acyl(aryl) thioureas were examined for the extraction and transportation of Au(III). Two-phase metal ion extraction experiments were employed to investigate the extraction behaviour of these ligands. The effect of varying ligand concentration on the extraction trend of these ligands was investigated. The results show that the different substituent groups on the benzoyl ring can affect the extraction pattern of the metal. Furthermore, the alkyl substituents on the thiourea moiety and varying the ligand concentration have an influence on the percentage of metal ion extracted. With the exception of the  $H_2L^2$  (*N,N*-di-propyl-*N'*-benzoylthiourea) ligand the di-alkyl substituted thioureas were more efficient for the metal ion extraction than the mono-alkyl ligands. In almost all the experimental set ups there was reduction of the Au(III) to Au(I) and Au(0) but it was more pronounced with  $HL^3$  (*N,N*-di-(2-hydroxyethyl)-*N'*-benzoylthiourea).

Transport experiments were also conducted, the experimental set up for transportation was a concentric type cell involving a 3-phase system – 2 aqueous phases (source and receiving phase) separated by a chloroform membrane incorporating the ligand. The transport results however only gave a satisfactory result of about 5% of gold transported by the  $HL^1$  (*N,N*-dibutyl-*N'*-benzoylthiourea). All other ligands attempted resulted in metal ion being present in the organic phase, but no metal ion present in the receiving phase. To help drive the transport of the metal ion to the receiving phase  $CN^-$ ,  $S_2O_3^{2-}$  and perchloric acid were incorporated into the receiving phase. The transport results were not enhanced with these substances being present in the aqueous receiving phase. The aqueous source and receiving phases were analyzed by flame atomic absorption spectroscopy (FAAS).

Finally the *N,N*-diethyl-*N'*-camphanoylthiourea ( $HL^{10}$ ) ligand and its complex with Au(I) were synthesised. Single crystals of the complex were grown for X-ray crystallography and the crystal and molecular structure of the complex was determined. The complex crystallizes in the monoclinic space group  $P2_1$ . The cell parameters are  $a = 10.7356(7)\text{\AA}$   $b = 16.3443(11)\text{\AA}$   $c = 10.9268(7)\text{\AA}$   $\beta = 103.1450(10)^\circ$ , and final R-factor of 1.76%. The coordination sphere around Au(I) shows a nearly linear arrangement of sulphur and chloride.



## Opsomming

In hierdie proefskrif is 'n aantal mono- en di-gesubstitueerde asiel(ariel) thioureums ondersoek vir die transportasie en ekstraksie van Au(III). Twee-fase metaalioon vloeistof-vloeistof ekstraksie eksperimente is gebruik om die ekstraksie patroon van hierdie ligande te ondersoek. Die effek van verskillende ligand konsentrasies op die ekstraksie neiging van hierdie ligande is ondersoek. Resultate toon dat die verskillende substituentte op die benziel ring die ekstraksie patroon van die metaalioon beïnvloed. Verder, is gevind dat die alkiel substituentte op die thioureum saam met varierende ligand konsentrasies geensins die metaalioon ekstraksie beïnvloed nie. Met die uitsondering van  $H_2L^2$  (N,N-dipropiel-N'-benzielthioureum) is die di-alkiel gesubstitueerde ligande meer effektief vir metaalioon ekstraksie in vergelyking met die mono-alkiel ligande. In baie van die eksperimente is 'n reduksie van Au(III) na Au(I) en Au(0) gesien en dit is baie duidelik met ligand  $HL^3$  (N,N-di(2-hidroksie-etiel)N'-benzielthioureum). Alle waterige fases is ge-analiseer met gebruik van Atoomabsorpsie Spektroskopie (AAS).

Transportasie eksperimente is ook uitgevoer met gebruik van 'n drie-fase selsisteem. Twee waterige fases (bron- en ontvang-fase) is geskei met die chloroform membraan fase wat die ligande bevat. Hierdie eksperimente het net 'n 5% Au(III) transportasie getoon met  $HL^1$  (N,N-dibutiel-N'-benzielthioureum). Daar was geen transportasie van Au(III) met enige van die ander ligande. Analise van die twee waterige fases het getoon dat die metaalioon eindelik goed ge-ekstraer is en is teenwoordig in die membraan fase. Om die transportasie van Au(III) aan te spoor, is  $CN^-$ ,  $S_2O_3^{2-}$  en perchloorsuur in die ontvang-fase geïnkorporeer. Die resultate was geensins beïnvloed nie.

N,N-di-etiel-N'-kamfonieltioureum ( $HL^{10}$ ) ligande en die kompleks daarvan met Au(I) is ook gesintetiseer. Enkel-kristalle van die kompleks is verkry en X-straal kristallografiese analiese is onderneem. Hierdie kompleks kristalliseer in die monokliniese ruimtegroep  $P2_1$ , met  $a = 10.7356(7)\text{Å}$ ,  $b = 16.3443(11)\text{Å}$ ,  $c = 10.9268(7)\text{Å}$  en  $\beta = 103.1450(10)^\circ$ . Die finale R-faktor is 1.76%. Die koördinasie om Au(I) toon 'n liniêre geometrie met swael en chloor.



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## List of Abbreviations

Bu	Butyl
Pr	Propyl
Et	Ethyl
BLM	Bulk liquid membrane
ELM	Emulsion liquid membrane
SLM	Supported liquid membrane
AAS	Atomic Absorption Spectroscopy
NMR	Nuclear Magnetic Resonance Spectroscopy
$\text{CDCl}_3$	Deuterated chloroform
HL	Free ligand with one dissociable proton
$\text{H}_2\text{L}$	Free ligand with two dissociable protons.

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## Chapter one

### 1. Literature survey

#### 1.1. Introduction to membranes

A membrane is a thin semi-permeable barrier between two phases, whereby the permeation of metal ions across a concentration gradient is allowed. The separation of molecules by membranes have long been known in biological systems and have wide industrial applications [1]. Membranes are of two types

- a) Liquid membranes and
- b) Polymeric membranes
- a) Liquid Membranes

A liquid membrane is a membrane made purely of liquid. It is a simple membrane principle, just with a non-rigid material. The selectivity and rejection of these membranes towards certain solutes is what makes it remarkable studying these systems [2].

Because of the nature of a liquid, liquid membranes avoid problems other conventional membranes encounter. Furthermore, they give higher fluxes and selectivities compared with polymeric membranes [18]. Liquid membranes are relatively high in efficiency, and as such, sought after for industrial applications. Nevertheless, liquid membranes have their own class of problems. The major problem is stability in order to be effective, and if they are pushed out of the pores or ruptured in some way due to pressure differentials or turbulence, then they just do not work.

Liquid membrane transport has also additional distinct advantages over the other conventional methods of separation; low capital costs, space requirements and energy consumptions [4]. There are few carriers reported in the literature for the selective and efficient transport of transition or heavy metal ions; however, it is evident they are important from biological, medical, environmental and industrial

points of view [16]. Another fascinating feature of liquid membranes is the capability of simultaneous extraction and back extraction (stripping) of metal ions [3].

The developments in liquid membranes are replacing the solvent extraction, which is kinetically very slow and consequently requires a large interfacial area and hence a huge amount of solvent for the recovery of precious metals [21]. In addition, nowadays they have reached a pilot plant stage in many applications which has powerful implications for analytical purposes [16]. Transport of metal ions through liquid membranes has gained useful practical applications for the separation sciences.

#### b) Polymeric membranes

Synthetic polymeric membranes are either non-porous, microporous or macroporous. Solution-diffusion mechanism governs transport through non-porous polymers. In the latter two cases, transport and separation of substances is determined by sieving [58].

There are also polymeric membranes which have thermo sensitive permeability. They are characterized by a lower critical solution temperature (LCST) which provides hydrogels the possibility of having high swelling degrees at low temperatures and low swelling at high temperatures in a reversible way[59].

This thermo-shrinking behaviour reflects the hydrophilic/hydrophobic balance of the polymer chains. The hydrophobic interactions between polymer chains increase at elevated temperatures due to a decrease in the water structure around the hydrophobic groups in the polymer chains. This behaviour is reversible and occurs over a narrow temperature range [59]. A novel composite membrane, which is effective in the separation of an ethanol-water mixture by pervaporation, is an example [60]. Polymer membranes find applications in areas as varied as separation science, sensors and surface coatings. Particularly, surfactant–polymer systems are relevant to various areas, including formation of gels for use as thickeners, in textile and paper processing [60].

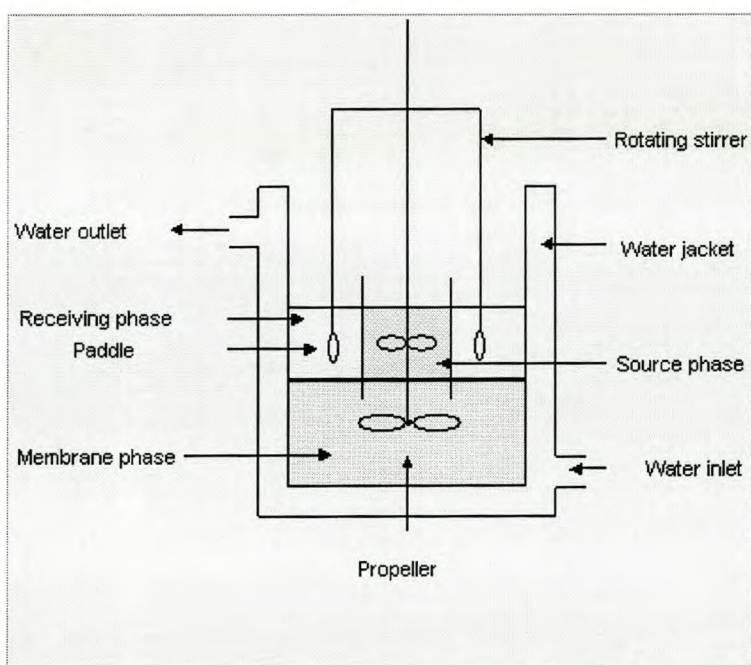


## 1.2. Types of liquid membranes

### 1.2.1. Bulk liquid membrane

This type of membrane is simple, inexpensive and uses a small amount of the carrier (ligand) and most of the time is used for the screening of ligands for other systems [2]. The choice of membrane solvent is most of the time determined by the factors like the low viscosity and low water solubility [1]. Solvents with relatively lower viscosity and water solubility are chosen most of the time. Practically, chloroform and dichloromethane are the ones used mainly because of their low dielectric constant in addition to the low viscosity and low water solubility, and univalent cations are extracted as ion pairs [1].

The most common configuration of bulk liquid membranes encountered in metal ion transport systems involves a three-phase arrangement; comprising two aqueous phases separated by an immiscible membrane phase [36]. The ligand is dissolved in the membrane solvent and is placed at the bottom of the cell. The source and the receiving phases are placed on top of it, and both the organic and the aqueous phases are stirred at a rate of 10 rpm to maintain the stability of the membrane. Figure 1.1 shows the schematic diagram of this transport cell system.



**Figure 1.1:** Diagram of the cell used

In bulk liquid membranes, the relatively thick membrane that separates the two aqueous phases could be responsible for the low transport of species transported by this kind of system. This low transport, the relatively large standard deviation and the difficulty to sort out surface effects makes them commercially unviable.

### **1.2.2 Supported liquid membranes**

Supported liquid membranes consist of an immobilized carrier in a porous polymer sheet. The support is usually a hydrophobic polymer such as polyethylene, polytetrafluoroethylene or polysulphone. The membrane is interposed between two aqueous phases (the source and the receiving phases) and the aqueous phase is then gently stirred. In this arrangement the source phase contains the metal to be transported and the receiving phase contains a complexing agent  $R'$ , which has a stronger affinity to trap the target metal ion than  $R$ . For fast transport, a thin film with high porosity is required.

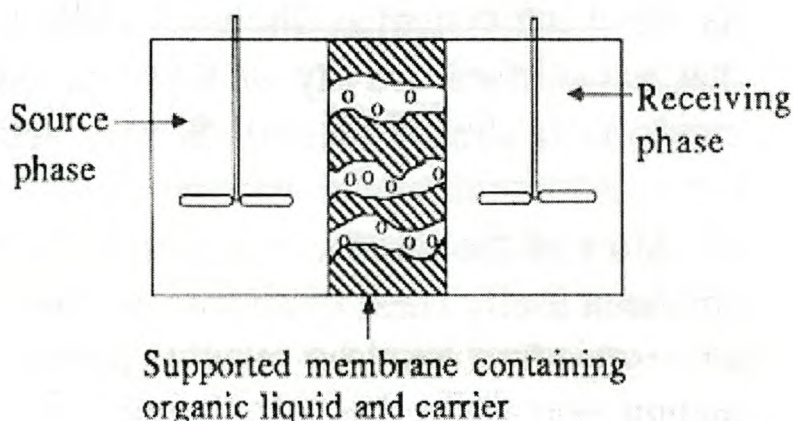
The process of metal ion transport in supported liquid membranes may be proton driven or counter ion driven. Nevertheless, the majority of the work done in the literature is based on the proton driven mechanism with most applications in industrial separations and recovery of target elements [25]. The main advantage of supported liquid membranes over traditional separations is the low inventory of the organic phase used. Consequently, only small quantities of chemicals are required as extractants, which can be exploited for the use of expensive and selective extractants [25]. Other advantages comprise the low capital and operating costs, simplicity of operation and low investment costs [25,37]. Supported liquid membranes can be used in various fields of science, technology, industry, clinical, pharmaceutical and environmental processes. It can be for example used in the recovery and enrichment of metals from hydrological samples, extraction of noble metals and removal of toxic metals and organic pollutants from wastewater [48, 47].

In spite of all these advantages, there are some limitations of the supported liquid



membranes. This is the fact that it is relatively hard to get rid of the organic liquid or the carrier of the pores of the support of the membrane after the end of the experiment. Nevertheless, there are two remedies for this problem. One is by evaporating the solvent and the second one creating a large pressure difference across the membrane, effectively pushing the fluid out.

The process of extraction using this type of membrane has the solute diffusing through the aqueous source phase layer and reacts at the interface with the carrier. Thus a metal carrier ligand complex is formed in the pores of the support. This complex then diffuses through the membrane to the receiving phase and at last, the carrier releases the metal ion at the liquid membrane interface [22]. A schematic diagram of a supported membrane is shown in figure 1.2



**Figure 1.2:** Carrier mediated transport across supported liquid membrane.

### 1.2.3. Emulsion liquid membranes

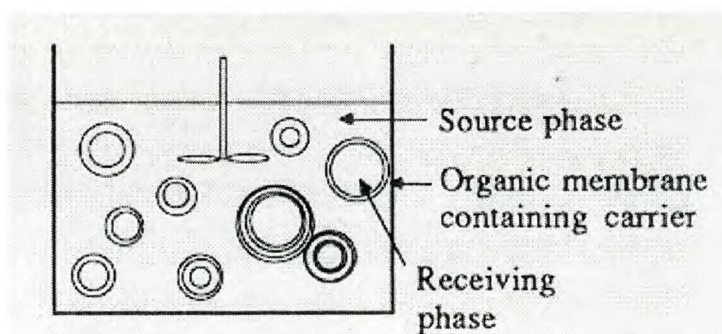
Emulsion liquid membranes are also called surfactant liquid membranes. They are prepared by dispersing an inner receiving phase in an immiscible liquid membrane phase to form an emulsion. A schematic diagram of the cell is shown in figure 1.3

This type of membrane has a thin membrane and a large surface area, which assists in the rapid rate of transport of metal ions. This membrane has been used for the



recovery of metal ions from wastewater [2,16]. They also have another advantage over supported and bulk liquid membranes in that they have the ability to enrich the transported metal ions up to ten fold since the ratio of the volumes of the receiving and source phase is ten to one [2].

In carrier mediated transport the metal ion present in the feed phase forms a complex with the ligand at the interface of the emulsion globule and the feed phase. The complex formed is then shuttled through the membrane to the membrane /strip interface and finally it is stripped to the bulk of the encapsulated strip phase. Emulsion stability is maintained by using a moderately hydrophobic membrane solvent and carrier molecules. Furthermore, the ionic strength and pH of the aqueous phases must be closely monitored. Compared to conventional liquid membranes the emulsion liquid membrane process has some attractive features such as simple operation, high efficiency, larger interfacial area and scope of continuous operation. The major disadvantage of emulsion liquid membranes is the formation of emulsions [48] and the need to break the emulsion to recover the receiving phase [49]. In comparison to bulk liquid membrane and supported liquid membranes, emulsion liquid membranes has been by far the most industrially used separation technique and has the greatest potential in the immediate future [48].



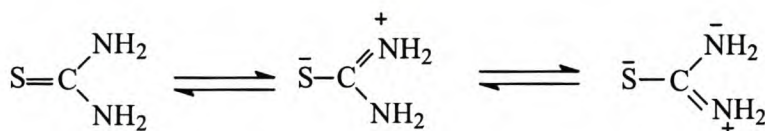
**Figure 1.3:** Carrier mediated transport across emulsion liquid membranes

### 1.3. The Chemistry of Thioureas and the Substituted Thioureas

#### 1.3.1. Simple Thioureas

Thioureas have been known to be good ligands for coordinating metal ions; Lewis basicity of the –CS– group dictates the suitability of these ligands as ionophores [23]. The simple monodentate thioureas have played a great role in the development of the coordination chemistry of the transition metal ions, particularly in the case of the noble metal ions [51]. They usually form coordinate bonds using both sulphur and nitrogen even though the low basicity of the ligand hinders the formation of nitrogen metal bonds. In acidic medium, however thioureas become protonated and the proton will bond to the sulphur atom thus giving the metal ion a chance to form a bond with the nitrogen [5].

Thioureas have also basic properties because of the presence of lone pairs of electrons on the nitrogen and sulphur atoms. These lone pairs of electrons have given them the power to coordinate (complex) with heavy metals. According to the Lewis structure of the canonical forms shown in figure 1.4, the coordination can be effected from the nitrogen or sulphur atoms [5]. However, thiourea and the substituted thioureas do not have the same mode of coordination [20].



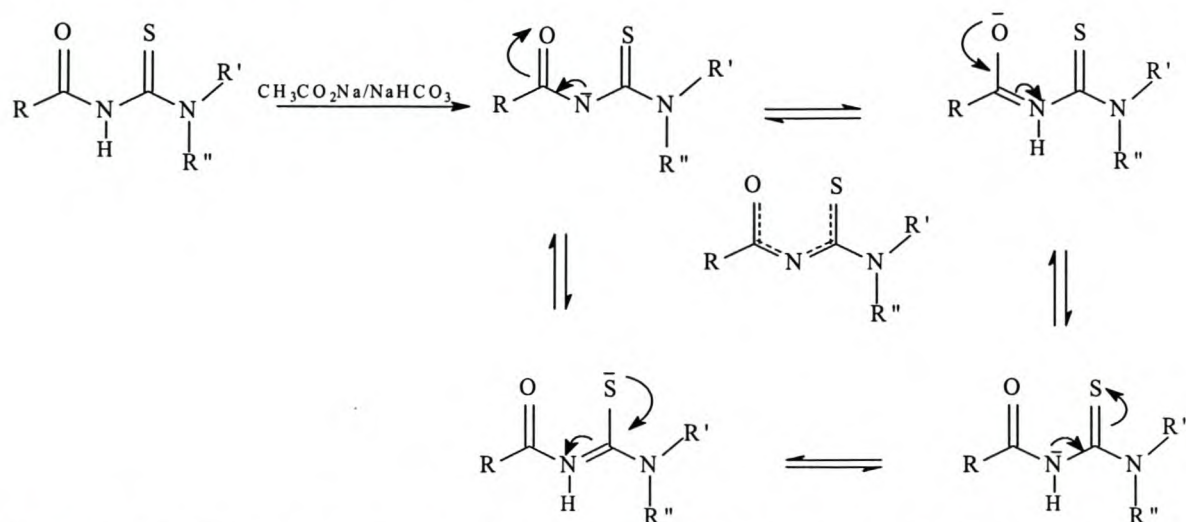
**Figure 1.4:** Canonical forms of thioureas

#### 1.3.2. The Aroyl and Acyl Thioureas

The NH proton in HL and H<sub>2</sub>L ligands is flanked by carbonyl and thiocarbonyl groups making the proton acidic. The acid dissociation constant [pK<sub>a</sub> (N-H)] of the proton in different environments of acyl and aroyl thiourea ligands was found to be between 7.5-10.9 in a water/dioxane mixture [20]. This acidic proton could easily be removed by a weak base like sodium acetate or sodium bicarbonate, to form an enolate ligand



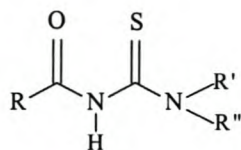
ion L<sup>-</sup>. This ionic ligand stabilizes its charge by resonance effects in the conjugated structure of the -C(O)NC(S)- moiety. The deprotonation and the resonance structures are shown in figure 1.5.



**Figure 1.5:** The deprotonation of HL ligand with a weak base and resonance structures.

It is sensible to think that the resonance of the charge between the oxygen and sulphur atoms as shown in figure 1.5 would greatly enhance the affinity of the enolate ion towards the metal complex formation. Schuster reported that the high pK<sub>a</sub> values of the enolate ion and the ability to increase the charge on the sulphur donor atom by means of resonance effects leads to very selective complex formation behaviour [38]. This is an indication that the resonance in the -C(O)NC(S)- moiety increases the stability of metal complexes that can be synthesized with such types of ligands. Any factor that hinders the freedom of this resonance will decrease the effectiveness of the complexing ability of the enolate ion with transition metal ions [38]. Consequently, the acyl thioureas are expected to form more stable complexes compared to the aroyl thioureas. The presence of the aromatic ring extends the resonance to the benzene ring which is outside the -C(O)NC(S)- moiety and thus reduces the resonance effect of the enolate ions in the -C(O)NC(S)- moiety. This in turn decreases the stability of the transition metal complexes of the aroyl thiourea ligands compared to the stability of the acyl thiourea ligands. Figure 1.6 shows the general structure of the aroyl and acyl thioureas.





**Figure 1.6:** General structure of aroyl and acyl thioureas

R = aryl or alkyl

R' R'' = alkyl; *N,N*-di-alkyl-*N'*- (aroyl) thiourea

R' = alkyl, R'' = H; *N*-alkyl-*N'*- (aroyl) thiourea

### 1.3.3. The mode of coordination of HL and H<sub>2</sub>L ligands to transition metals

Thiourea derivatives like *N,N*-dialkyl-*N'*-benzoylthioureas have attracted the interest of researchers for several reasons; the two main reasons are their ability to form complexes with precious metal ions [44], and the possibility to coordinate with harmful metal ions in an organism [11]. In HCl solutions, these ligands coordinate to Pt(II) or Pd(II) via their sulphur atoms and without the dissociation of the NH hydrogen's [20].

Beyer and Hoyer [54] were the first chemists to review the coordination chemistry of *N,N*-dialkyl-*N'*-aroylthioureas with a number of first and second row transition metal ions such as Ni(II), Co(II), Zn(II), Pd(II), Ag(I), and Cd(II). However, Koch [20] has recently done a detailed review of the coordination chemistry of HL and H<sub>2</sub>L aroyl thioureas.

This study has shown that the mode of coordination of HL and H<sub>2</sub>L ligands differs significantly for the two ligand types in some important aspects. Figure 1.7 shows the structure of these two ligands.



**Figure 1.7:** Structures of the HL and H<sub>2</sub>L Ligands.

In general, the HL ligand coordinates to  $d^8$  metal ions in a cis bidentate manner through the S, O atoms with the loss of a proton. As observed with nickel, *N,N*-diethyl-*N'*-benzoylthiourea for example binds in a bidentate fashion binding with both oxygen and sulphur atoms [17]. This is also in agreement with what Koning *et al.* have proposed about the formation of the Au(III) complex with *N,N*-diethyl-*N'*-benzoylthiourea [53].

Theoretically, the proton in the  $-C(S)NHR$  moiety forms an intramolecular hydrogen bond with the oxygen atom in the  $H_2L$  ligand [20,42,51]. Hence, these ligands are expected to be restricted to unidentate S atom coordination to the incoming transition metal ions [6,46]. However, there is the possibility that the HL ligand also binds itself in a unidentate fashion with the sulphur atom. W. Bensch and M. Schuster working on the structural analysis of *N,N*-diethyl-*N'*-benzoylthioureatogold(I) chloride found that the metal is bound to the sulphur in a linear fashion [19]. These observations have been accounted by Koch *et al.* [64]. In the coordination mode of these ligands with platinum, the ligand can be protonated by HCl and leads to the reversible opening of the 6-membered S-O chelate ring with one chloride ion attached to the metal.

#### 1.3.4. Structural contribution of the dialkyl and monoalkyl substituted thiourea ligands

An interesting observation made from X-ray diffraction results of the HL and the  $H_2L$  ligands, is that the average C-N bond distances of  $-(O)C-NH$ ,  $N'H-C(S)$  and  $(S)C-N(R/H)$  were  $1.327 \pm 0.006 \text{ \AA}$ ,  $1.374 \pm 0.016 \text{ \AA}$  and  $1.327 \pm 0.006 \text{ \AA}$  respectively [20,42,51]. These bonds were found to be shorter than a normal C-N single bond, which is indicative of the presence of partial double bond character [20,42,51]. It is also reported that upon coordination with metal ions the C=S and C=O bonds of such ligands become longer while the C-N bonds become shorter than their corresponding ligands in their free ligand state [44,17,54]. Moreover, Koch *et al.* have reported that rotation about the  $SC-N(CH_2R)_2$  bond is restricted due to resonance interaction between the electron pair of the N atom and the pi bond of the S=C group [20]. Due



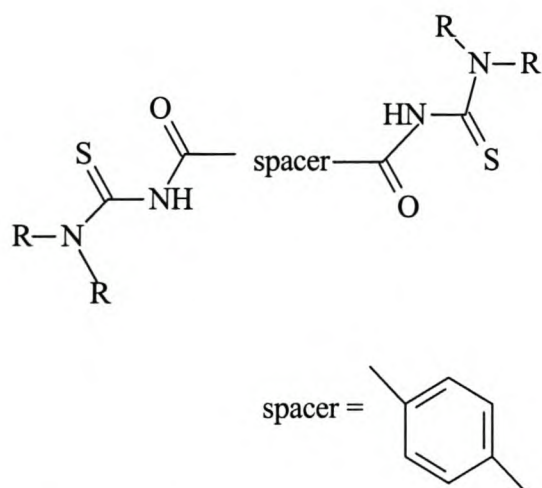
to this fact the two methylene protons in the SC-N (CH<sub>2</sub>R)<sub>2</sub> moiety have different chemical shifts on the proton NMR spectrum. For unsymmetrical *N, N*-dialkyl substituted HL ligands the restricted rotation about the bond helps to distinguish *E/Z* isomers in solution form [20, 54]. This situation leads to the difference in the coordination chemistry of the mono and di-substituted thiourea ligands.

### 1.3.5. Synthesis of ligands

Although the HL and H<sub>2</sub>L ligands were first prepared by Neucki in 1873 [61], their coordination chemistry has been explored to some extent in the last three decades. The facile synthesis of HL and H<sub>2</sub>L ligands, reported by Douglass and Dains [62] from readily available and inexpensive starting materials is one of the interesting features of these ligands. In general, ligands of the type that are derived from benzoyl chloride are very stable and relatively hydrophobic. This property makes these ligands suitable for transport and extraction studies.

### 1.3.6. The coordination chemistry of bipodal *N'*-acyl (aroyl) thioureas

The bipodal *N'*-acyl(aroyl)thioureas are ligands which have two –C(O)-NH-C(S)- moieties linked to each other with an aliphatic or aromatic spacer group as shown in figure 1.8. With rigid or short chain spacer groups, the two chelating moieties of these ligands coordinate to different metal centers.



**Figure 1.8:** Structure of bipodal *N'*-acyl (aroyl) thioureas.

A survey of the literature published [43] revealed that these ligands coordinate to Pt(II) and Pd(II) in a cis bidentate S, O chelating fashion in an overall metal to ligand stoichiometry of 1:1. On the other hand, it has also been reported that the bipodal ligand 3,3,3',3'-tetraethyl -1,1'-isophthaloylbisthiourea, coordinates to Ag(I) in a different coordination mode in which only the sulphur atoms of the ligands are coordinated forming an infinite one-dimensional chain leaving each Ag(I) coordinated in a highly distorted tetrahedral fashion[56,44].

### 1.3.7. Potential industrial applications of the HL and H<sub>2</sub>L ligands

The specific arrangement of the hetero atoms of the thiourea group of *N,N*-dialkyl-*N'*-benzoylthioureas leads to a series of significant changes in the chemical properties that can be exploited for analytical purposes. *N,N*-dialkyl-*N'*-benzoylthioureas have proved to be successful as selective complexing agents for heavy metal ions and for the enrichment of the platinum group metals even from strongly interfering matrices [43,41]. *N,N*-dialkyl-*N'*-benzoylthiourea ligands possess an unusually high redox stability and favourable toxicological properties which make them important for industrial applications [11]. Some of the applications are for the detoxification of wastewaters containing complexable heavy metals. These ligands also find potential applications in chromatographic separation of the PGMS as well as the separation of several soft transition metal ions like Cu(II), Hg(II) and Au(III) [20, 42, 45].

## 1.4. Recovery of precious metals

The conventional lexiavants like aqua regia produce chlorocomplexes of the noble metals except for silver, which forms a precipitate of silver chloride. Sorption methods have been widely used in the subsequent treatment of these solutions and anion exchange resins have proved to be very effective as collectors of related anionic chlorocomplexes. Nevertheless, the main problem with anion exchange resins is their low selectivity for noble metals that is the base metals eluting along with noble metals [24]. Furthermore, ion exchange technologies use resins, which are produced by polymerization processes and usually, have leachates or toxic chemicals contained within them by products from polymerization or unreacted reactants such as trichloro ethane. Moreover, ion exchange resins are unable to work in hard waters in which



case they become quickly exhausted. The use of either precipitation or coagulation requires harsh chemicals and is costly [57].

In particular, the recovery of gold from electronic scrap solutions and the recent development of the electronic industry make the recovery of gold crucial [12, 21]. Furthermore, the stabilization on the price of gold in recent years has led to the development of new extraction methods based on liquid membranes for the recovery of this precious metal [22]. The recovery of gold from different solutions has been by cementation, carbon adsorption, solvent extraction, etc. The solvent extraction of gold from acidic media is well documented and numerous studies have been made using different kinds of extractants such as basic extractants like amines, solvating ones like neutral organo phosphorus compounds and others containing sulphur as donor atoms[22].

## **1.5. The chemistry, occurrence and mining of gold**

### **1.5.1. Introduction**

Gold is called a noble metal for it possesses some exceptional properties such as resistance to chemical attack, heat and moisture. Mankind has tried to find ways to produce gold throughout the history. These include converting other metals into gold (no success yet), gravity techniques and chemical extraction. While various gravity techniques have been applied to recover gold for thousands of years, the techniques are not suitable or economical for gaining the metal from most gold deposits.

Gold is important for many industrial applications like catalysis, electrical and corrosion resistant alloys due to its specific physical and chemical characteristics. These same reasons make the extraction of this metal from its ores very difficult.

### **1.5.2. Occurrence**

Gold occurs in small quantities in clays, pyrite and in almost all silver, copper, bismuth, lead, zinc, tellurium and antimony ores. Therefore, recovery of gold requires their separation from other base metals [32].

There are few solvents to dissolve gold, and the chemicals that have been used in gold extraction are known to be extremely corrosive, toxic and hazardous to the environment. Cyanide is one of the few chemicals known to form a complex with gold and the reaction can be written as

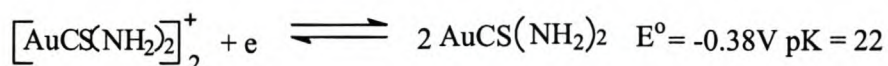


With the growing demand for gold, and other precious metals and the scarcity of high-grade ores, the need for highly selective and efficient separation methods and reagents for separation and recovery from secondary sources becomes crucial.

Following Pearson's principle of hard and soft acids and bases, sulphur-containing ligands have been the target for accomplishing this mission.

Thiourea is another reagent capable of extracting gold and is less toxic than cyanide, besides it has the potential advantage in the processing of gold ores which are not responsive to cyanide leaching [35]. It offers several other advantageous properties such as high gold recovery and low sensitivity to base metals (Pb, Cu, Zn, As, Sb) [12,4]. The dissolution of gold is strongly affected by pH, thiourea and oxidant concentration.

Thiourea also has several disadvantages in gold recovery. It can dissolve heavy metals in addition to gold, creating problems in handling and disposal of the effluent. It can easily be oxidized and consumed very rapidly under leaching conditions, giving rise to high reagent consumption [1,4].

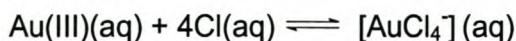


### 1.5.3. Chemistry

The chemistry of gold is enormous and the literature is full of resources. However, the tetrachloroaurate anion has attracted more attention from chemists than any other gold species. It is generally made by dissolving gold metal in aqua regia or in



HCl in the presence of other oxidizing agents like oxygen. A number of authors have determined the overall formation constant for the reaction. In aqueous solution the value of  $\beta_4$  obtained at 25<sup>0</sup>C, varies between 25 and 29.5

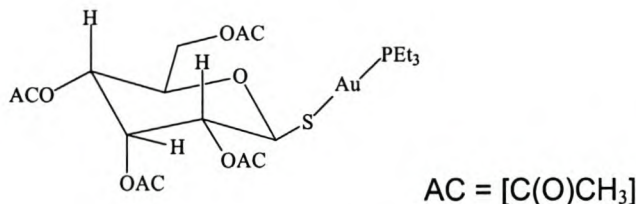


Au (III) in its reaction with most organic compounds is known to be reduced to Au(I) first and Au(0) later. Upon its reaction with sulphur containing ligands, Au(III) is reduced to Au(I) prior to its complexation [49]. The most common gold solution, Au(III) in  $\text{AuCl}_4^-$  form is hydrolyzed to a degree. The dominant hydrolyzed product is governed by the pH of the solution [46].

#### 1.5.4. Medicinal Applications

Sulphur is known to bond well to Au (III) and taking advantage of this are the gold sulphur drugs, which have been used in crysotherapy. Gold sulphur compounds have also been used for treatment of patients with tuberculosis; some showed improvement, but generally gave poor results.

For many years now, gold sulphur drugs are in use for the treatment of rheumatoid arthritis. However, Aurofin is the most common drug taken at present, which about 30% of patients take orally for the treatment of rheumatoid arthritis. The structure of Aurofin is shown in figure 1.9.



**Figure 1.9:** Structure of Aurofin

## 1.6. HASAB principle

According to Pearson, bases can be categorized into two categories, those that are polarizable and those, which are not. Those which are polarizable, were classified as soft and those, which are not as hard [10]. Hardness is associated with good proton binding, for example bases in which the coordinating atoms are from groups V, VI and VII having the atoms N, O, F being the hardest in each group and most basic to the proton. However, it is also possible that a base could be soft as well as strong binding to the proton, like the sulphide ion.

According to Pearson small size and high oxidation state contribute to those classified as hard Lewis acids and on the other hand lower or zero oxidation state and /large size contribute to those classified as soft acid/base. Those called soft acids are those metals like  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  and these metal ions bind soft donors in the following order  $\text{S} > \text{N} > \text{O}$  and on the other hand the hard metal ions bind to the hard donors in the following order  $\text{O} > \text{N} > \text{S}$ .

This hard acid and soft base principle is not a property, which merely depends upon the given atom but can be influenced by the neighbouring atoms [55]. The presence of a soft polarizable S atom next to an oxygen atom, can make the hard atom relatively softer. Electron withdrawing and electron releasing groups on adjacent atoms also play a role on the softness and hardness of the donor atoms.

## 1.7. Transport in bulk liquid membranes

### 1.7.1. Introduction

The main component in membrane transport is the ion recognition material, which is called the ionophore [23]. There are several articles in the literature about the selective transport of metal ions using synthetic ionophores. This has been the priority of researchers due to the vital role carrier mediated transport plays in biology, medicine and the environment [23]. Along with this has been active research on the use of macrocyclic compounds as carriers in liquid membrane systems, in view of their capacity for highly selective transport of metal ions [18].



Nowadays, ligands, which are relatively cheaper and facile to synthesize, are emerging and have been reported in the literature. One group of these ligands includes the acyl and aroyl thioureas. This group especially works well for those metal ions, which are classified as soft acids according to Pearson.

The transport of metal ions by ligands in liquid membranes is diffusion limited when neutral carriers are used and this is true even in those, which are relatively thin membranes like the supported and the emulsion membranes. Diffusion of the metal complex takes place at the hydrophobic liquid membrane from the feed phase to the receiving phase [13].

The transport of a metal by a proton ionisable ligand is also sometimes diffusion limited [2]. This kind of transport of metal ions is controlled by the physical and chemical parameters, which determine the transport rate. While the following are six factors that determine transport rate, cation selectivity in competitive transport systems are determined only by the first three factors [2]. These are:

1. the extraction constant which occurs at the membrane/source phase interface
2. the concentration gradient of the species being transported between the two aqueous phases
3. the equilibrium constants for any interactions occurring in the aqueous phases
4. the ligand distribution as determined by the ligand partition coefficient and the aqueous phase equilibrium constant for ligand metal interaction
5. the diffusion coefficient for neutral solutes in the membrane solvent and
6. the membrane diffusion path length

Most transport setups, which use bulk liquid membranes, involve a three-phase arrangement system, in which case the two aqueous phases are separated by a third and immiscible membrane phase. In the majority of bulk liquid membrane systems, the membrane phase is a water immiscible organic solvent like chloroform,

dichloromethane, toluene or hexanol . In our case, chloroform was employed as a membrane with aroyl and acyl thioureas as ionophores.

In the interfacial area where the organic and aqueous phases are in contact, solvent properties like dielectric constant are intermediate in between the two phases. The membrane phase will not allow diffusion of the metal ions from the source phase to the receiving phase in the absence of an ionophore. This kind of synthetic membrane thus resembles the lipid bi-layer membrane whereupon metal complexation, the inside of the molecule becomes hydrophilic while the outside is hydrophobic. This arrangement is then the reason why charged ions cannot pass through the membrane in the absence of ionophores. The lipid components of the biological membrane show the tendency that their polar groups face the membrane surfaces while the non-polar hydrocarbon portion occupies the internal part of the membrane.

The metal extraction chemistry in liquid membranes is governed by kinetics rather than chemical equilibrium between the phases [8], over which it has the advantage of concentrating the metal ions in the receiving phase [12]. On the contrary, the liquid membrane transport has problems of slow extraction kinetics, and reduction of the metal solution [8].

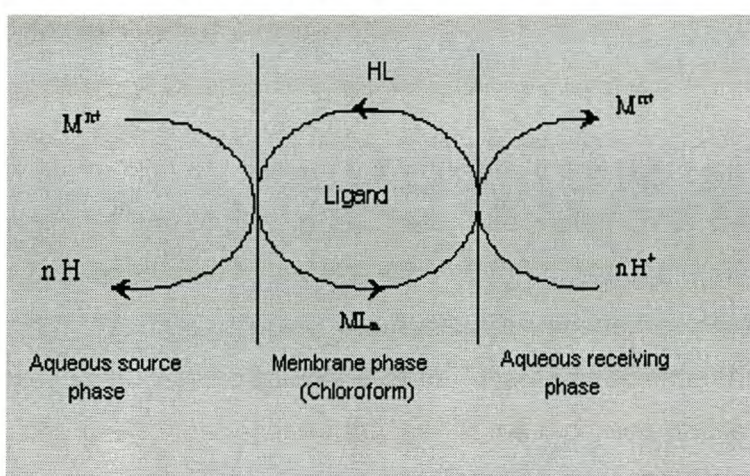
Theoretically, from Pearson, gold ion is expected to bind to the softer sulphur atom than to nitrogen, which has also been shown by the IR spectra of simple metal thiourea complexes [14], in which case the N-H absorption band is the same before and after the formation of the metal ligand complex.

### **1.7.2. Mechanisms of Transport**

There are several ways in which a liquid membrane setup can be configured to accomplish a task. To explain how the method works it is important to understand the rules governing diffusion. Diffusion systems can be classified as basic, active and passive, and depending on these systems one can then categorize the transport as active and passive transport.



The driving force in the case of our work was the pH gradient in which it is assumed that the ligand we employ is ionisable. The metal ion is coordinated to the donor atom of the ligand, and thus there is no need of pairing the anion. In other words, the metal ion transport is coupled with the back transport of protons [2]. The metal ion complexes with the anionic ligand at the source phase/membrane interface and it is then discharged to the receiving phase. At the receiving phase/membrane interface a chemical reaction occurs. The ligand takes away a proton with it and becomes again protonated and the metal ion is deposited in the receiving phase [2]. In consequence, any interference in one or more of these reactions can affect transport of the metal ion. Moreover, this interference can be affected by changing the pH of the source and/or the receiving phases [2]. Figure 1.10 shows the mechanism of transport.



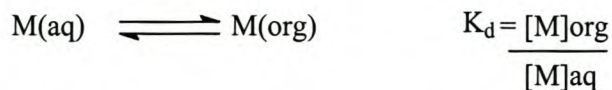
**Figure 1.10:** A schematic representation of the mechanism of transport of a metal ion across a chloroform membrane.

## 1.8. Principles of solvent extraction

Inorganic solvent extraction chemistry is concerned with multi component heterogeneous systems in a state of equilibrium. The types of equilibria encountered in any practical solvent extraction processes are highly diverse [63]. Generally, there are two important terms in dealing with the distribution of solute between two immiscible solvents [34].

a) **Distribution coefficient** is the equilibrium constant that describes the

distribution of solute between two immiscible solvents. That is for an aqueous solute M shaken with an organic solvent the equilibrium is expressed by the following equation.



Where  $K_d$  is the distribution coefficient.

**b) The distribution ratio** is the ratio of the total mass of a solute in the extract to that in the other phase. This is an experimental parameter and its value does not necessarily imply distribution equilibrium between the phases has been achieved.

### 1.8.1. Classification of extraction systems

Although equilibrium can be reached through a chemical reaction between the components, or a mere distribution of a compound between the two phases our interest in this dissertation will be focused on systems where extraction of an inorganic species occurs by virtue of chemical complexation.

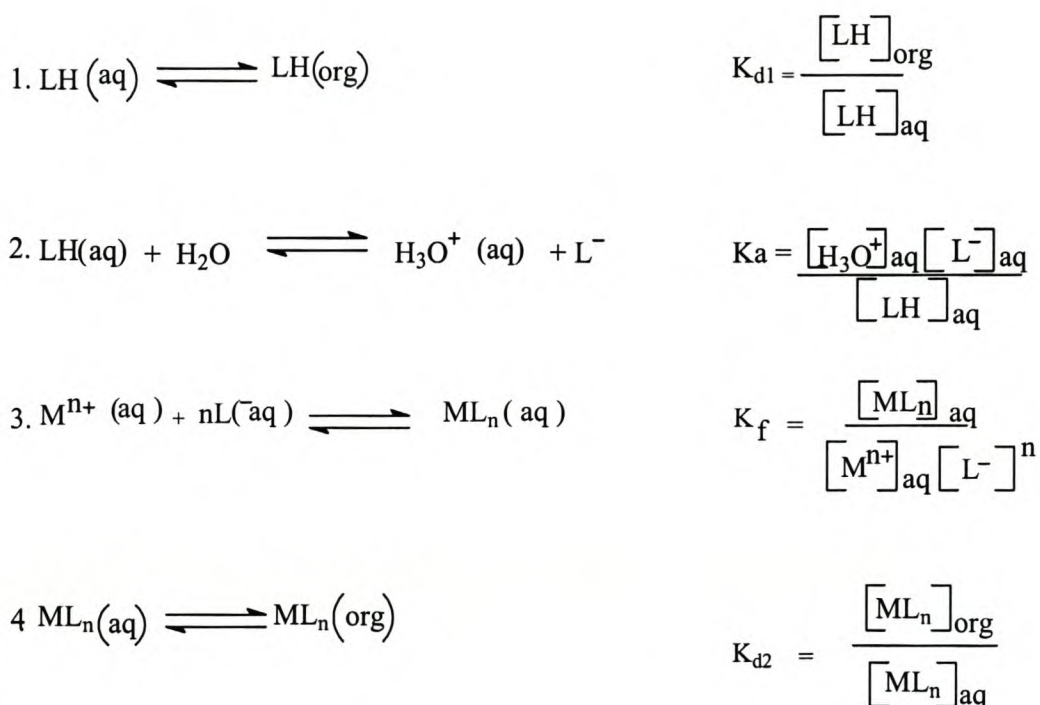
Four main common extraction systems are

1. distribution of simple molecules
2. extraction by complex formation, the extractants being chelating agents, carboxylic, alkyl and aryl sulphonic acids and acidic phosphorus esters
3. Extraction by solvation; extracting acids by solvating the hydrogen and the extractants are either carbon- bonded or phosphorus-bonded oxygen bearing extractants. Any other donor atom may replace the oxygen in these compounds.
4. Extraction by ion pair formation, the extractants being bulky ionic extractants of the polyphenyl metal-based type, polyalkyl-ammonium type and the salts of high molecular weight aliphatic amines. [63].



### 1.8.2. Extraction by chelating agents

Chelating reagents are more selective than solvating reagents and anion exchangers [9]. Several chelating agents have proved useful for the separation based upon the selective extraction of metal ions from buffered aqueous solution into a non-aqueous solvent containing these agents. Such processes involve several equilibria and several species. These are the undissociated ligand LH, its conjugate base and the metal ligand complex ML and the metal and hydronium ions [34]. The important equilibria are



Organic chelating agents as well as neutral metal complexes are usually highly soluble in organic solvents, so the distribution coefficients  $K_{d1}$  and  $K_{d2}$  are generally large numerically. Furthermore, the concentration of  $\text{M}^{n+}$  in the organic phase most of the time approaches zero. The selectivity of the reagent is determined by the relative magnitudes of the formation constants  $K_f$  for several cations. As we can see from equation 2, the concentration of the active reagents is pH dependent. Thus by controlling pH one can control the concentration of  $\text{L}^-$  and thus control which cations are extracted, and which are not.

Chelating agents have a broad application in analytical chemistry [24, 7] and the advancement in selective extractants for the separation and enrichment of noble metals has given rise to the need that these metals be recovered. For this purpose chelating extractants are found to be more selective than solvating ones [9]. According to Pearson's theory, the selectivity depends upon softness of the Lewis acid (metal) and softness of the Lewis base (ligand) [10] for this reason sulphur containing extractants are more effective.

## **1.9. Flame Atomic absorption spectroscopy**

### **1.9.1. Introduction**

Atomic absorption spectrometry is an instrumental technique used widely for the quantitative determination of metals at trace levels [33]. Several AAS techniques with different analytical scope, hardware sophistication, performance characteristics, sample pre-treatment requirements, throughput rates, economic parameters and other specific features can be distinguished [26] and these include: flame atomic absorption spectroscopy, electrothermal atomic absorption spectroscopy, vapour generation atomic absorption spectroscopy and hydride generation atomic absorption spectroscopy.

The flame AAS serves as a common, preferred routine technique in thousands of analytical laboratories owing to its unique combination of numerous positive assets. To mention some: remarkable selectivity and reliable interference control, large elemental coverage, relatively simple sample pre-treatment, very good precision, well established methodology, profound documentation, moderate, affordable price and low running costs, simple operation and easy maintenance; relatively fast and simple optimization, high sample throughput rates, and automation [27,30,31].

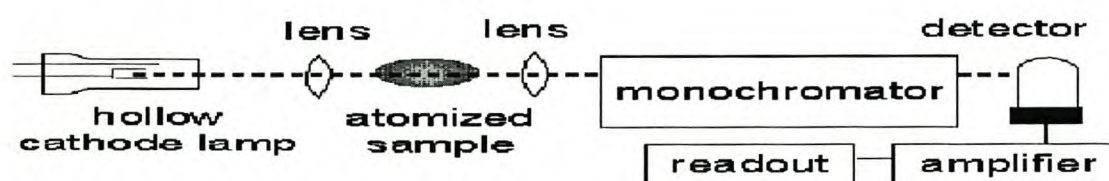
However, FAAS often lacks sensitivity at analyte levels below  $0.1\mu\text{g g}^{-1}$  and  $10\mu\text{g g}^{-1}$  in analyses of liquid and solid samples, respectively [26]. While the ETAAS has attractive features which are: excellent absolute and (less so) relative limit of detection in the  $\text{pg l}^{-1}$  and  $\mu\text{g l}^{-1}$  range, relatively simple pre-instrumental treatment of



samples, hence better contamination/blank control [26].

The last two are mostly employed for the analysis of mercury and metals like antimony, selenium, tin etc. In the case of flame atomic absorption, the sample solution is aspirated into a flame and the sample element is converted to atomic vapour. The flame then contains atoms of that element some are thermally excited by the flame, but most remain in the ground state. These ground-state atoms can absorb radiation given off by the special source made from that element. The wavelengths of radiation given off by the source are the same as those absorbed by the atoms in the flame [27].

The electrothermal atomic absorption uses an electrically heated furnace for vaporization and temperatures in the region of 2500K are achieved thus producing higher sensitivity to the technique of flame atomic absorption spectroscopy but results in lower precision [28] compared to the flame atomic absorption spectroscopy. Atomic absorption spectrometry follows Beer's law [27]. Beer's law states that the absorbance is directly proportional to the path length in the flame and to the concentration of atomic vapour in the flame. Both of these variables are difficult to determine, but the path length can be held constant and the concentration of atomic vapour is directly proportional to the concentration of the analyte in the solution being aspirated. The procedure used is to prepare a calibration curve of concentration in the solution versus absorbance. Figure 1.11 shows the schematic diagram of an atomic absorption spectrometer.



**Figure 1.11:** Schematic diagram of a flame atomic absorption spectrometer



### 1.9.2. Advantages and limitations of atomic absorption spectroscopy in the determination of gold ore

The main advantages of atomic absorption spectroscopic methods are as follows:

- ▶ The principle of measurement is straight forward and well understood.
- ▶ The technique is well suited to the measurement of gold and, gold pathfinders and base metals [26].
- ▶ There are relatively few matrix and other interference effects [26].
- ▶ Sample throughput is high especially with FAAS as each measurement can take only seconds when the instrument is calibrated [28].

### 1.9.3. Limitations of atomic absorption spectroscopy

- ▶ All measurements are made following chemical dissolution of the element of interest. Therefore, the measurement can only be as good as the quality of the sample digestion [27] particularly when FAAS is used.
- ▶ Occasionally interferences from other elements or chemical species can reduce atomization and depress absorbance, thereby reducing sensitivity [26].

Interferences occur at the analytical level and can be grouped as chemical, matrix, ionization, spectral, or as background absorption [26,31,27].

**A. Chemical interferences** occur when the element of interest combines with another species in the flame, thus altering the number of atoms available for absorption. In addition, this can result in either positive or negative bias in the results obtained. In addition, it can be controlled by using a hotter flame, or by the addition of a realizing agent, which inhibits the reaction between the metal and the interfering species.

**B. Matrix interferences** occur when the physical composition (viscosity, surface tension, etc) of the sample and the standard solutions differ considerably.

**C. Ionization interferences** occur when the flame temperature is sufficiently high to ionize the atoms of interest. This changes the absorption spectrum of the analyte and effectively removes atoms from the flame, causing loss of sensitivity. Ionization interferences are avoided by adding large amounts of an easily ionized metal such as Na, K, and Cs. The excess electrons released in the flame greatly reduce the degree of ionization of the metal being determined.



**D. Spectral interferences** occur when an element other than the one analyzed absorbs at the same wavelength. For gold, spectral interferences from Fe have been observed, as well as palladium and cyanide complexes are also reported interferences.

**E. Formation of compounds that do not dissociate in the flame**

The sample solution may contain a chemical, usually an anion that can form a refractory (heat stable) compound with the test element in the flame. The most common example is the formation of calcium and strontium phosphates. Refractory compound formation can be avoided by chemical competition by the use of high temperature flames [34].

**F. Background absorption interferences** include flame absorption and molecular absorption.

1. Flame absorption is most severe below 250nm. This absorption can be controlled by careful optimization of fuel and oxidant flow rates.
2. Molecular absorption is controlled by using hotter flames to break down molecular species.

### 1.10. Objectives of the research

Transport and extraction of metal ions has been dominated by macrocyclic and open chain polydentate ligands as carriers. There have been very few studies in transport and extraction of Au (III). Gold mines are looking for efficient and cost effective agents for the recovery of gold from ores and secondary sources. However, to the best of my knowledge there is no work done on the transport of Au(III) through bulk liquid membrane (BLM) using acyl (aroyl) thioureas of the type described in section 1.2. Hence, this project will focus on the examination of bulk liquid membrane transport and extraction of Au(III) ions using a series of acyl (aroyl) thioureas.

▲ The first part of this study will comprise transport. One of the important requirements for transport is the ligand must efficiently complex to the metal ion while still allowing the metal ion to be quantitatively stripped into the receiving phase. In order to meet this requirement, pH of the source phase and the receiving phase will be optimized and stripping agents, which complex very well with gold, e.g  $\text{CN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$

and perchloric acid would be used.

^ The second part will deal with extraction of the metal ion. Most of the reagents used in gold extraction are extremely corrosive, toxic, and hazardous to the environment. The traditional way of extraction of gold poses a challenge due to the strict environmental regulations and acyl (aroyl) thioureas could be an alternative. Thus, the extraction ability of the acyl (aroyl) thioureas for gold will be investigated.

^ Analysis of the aqueous source phase and aqueous receiving phase will be done by flame atomic absorption spectroscopy (FAAS). The extraction and transport results obtained will be rationalized using classical coordination chemistry arguments.

^ Lastly, an attempt will be made to grow crystals of the Au(I) complex with *N,N*-diethyl-*N'*-camphanoylthiourea. The crystal structure will be solved, and the coordination geometry around Au(I), bond lengths and other pertinent crystal structure data will be determined.

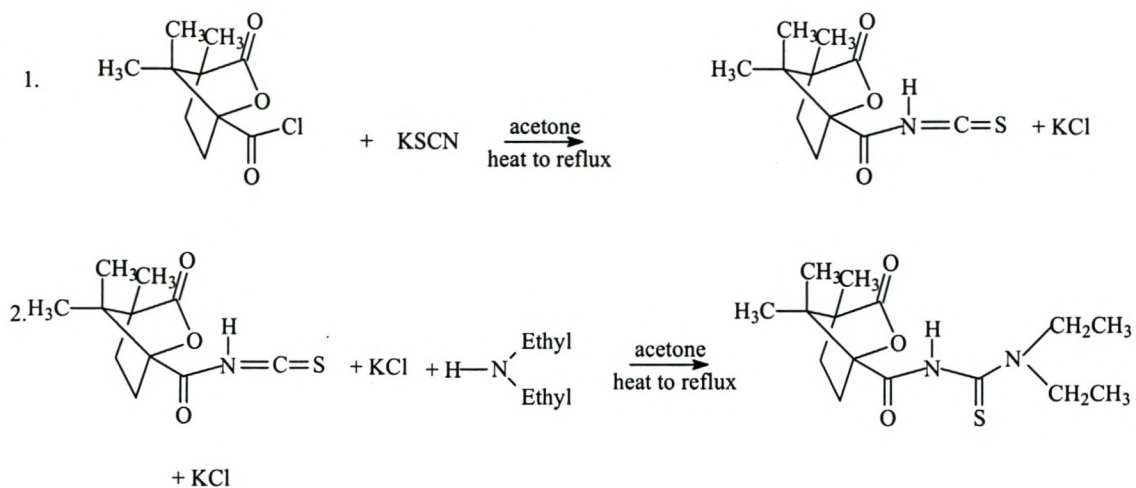


## Chapter Two

### 2.1. Synthesis of *N,N*-diethyl-*N'*-camphonylthiourea ligand

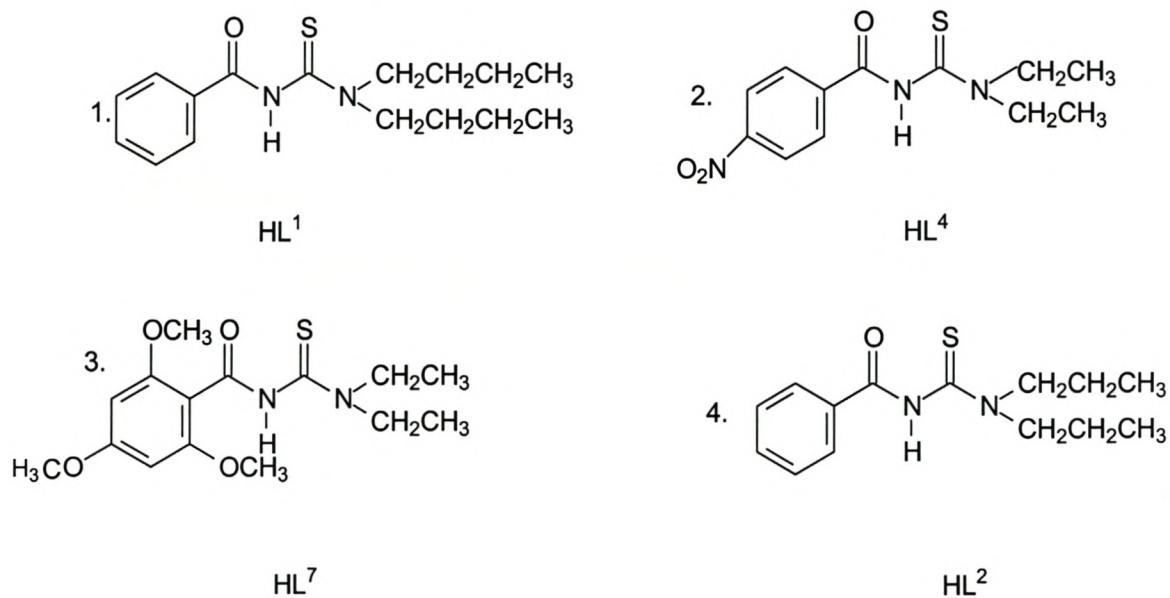
A pre-dried potassium thiocyanate 0.5g (5.3mmol) was dissolved in 50 ml of acetone in a two-necked round bottomed flask under nitrogen atmosphere. An equimolar amount of (S)-(-)-camphanic chloride was separately dissolved in the same volume of acetone and then added dropwise into the stirring potassium thiocyanate solution using a dropping funnel. After the addition was complete, the reaction mixture was heated to reflux for one hour at 50°C. Under these conditions, the formation of camphanoylthiocyanate was complete. The crude camphanoylthiocyanate was cooled to room temperature and insoluble potassium chloride was observed settling at the bottom of the flask.

After the reaction was cooled to room temperature, an equimolar amount of diethyl amine, dissolved in 50ml of anhydrous acetone was added dropwise into the camphanoylthiocyanate solution with stirring under nitrogen flush. There was no need to separate the insoluble potassium chloride at this stage, as it does not take part in any secondary reaction with the amine. The reaction mixture was heated to reflux for a further 45 minutes with stirring. The mixture was then cooled to room temperature and poured into a beaker containing 80ml of distilled water. The water has two purposes for dissolving the potassium chloride and precipitating the water insoluble ligand. The beaker was then left in a fume cupboard until the acetone evaporated. The resulting crude product was then collected by filtration, washed with water to remove any trapped salts and finally recrystallized from an acetone/water mixture. White crystals were obtained [67]. To remove any traces of water the product was dried under vacuum at 85°C for two hours and was finally identified and characterized by melting point determination, <sup>1</sup>H and <sup>13</sup>C NMR. All the reactions were carried out under a nitrogen atmosphere. The synthetic reaction scheme is as shown in fig 2.1

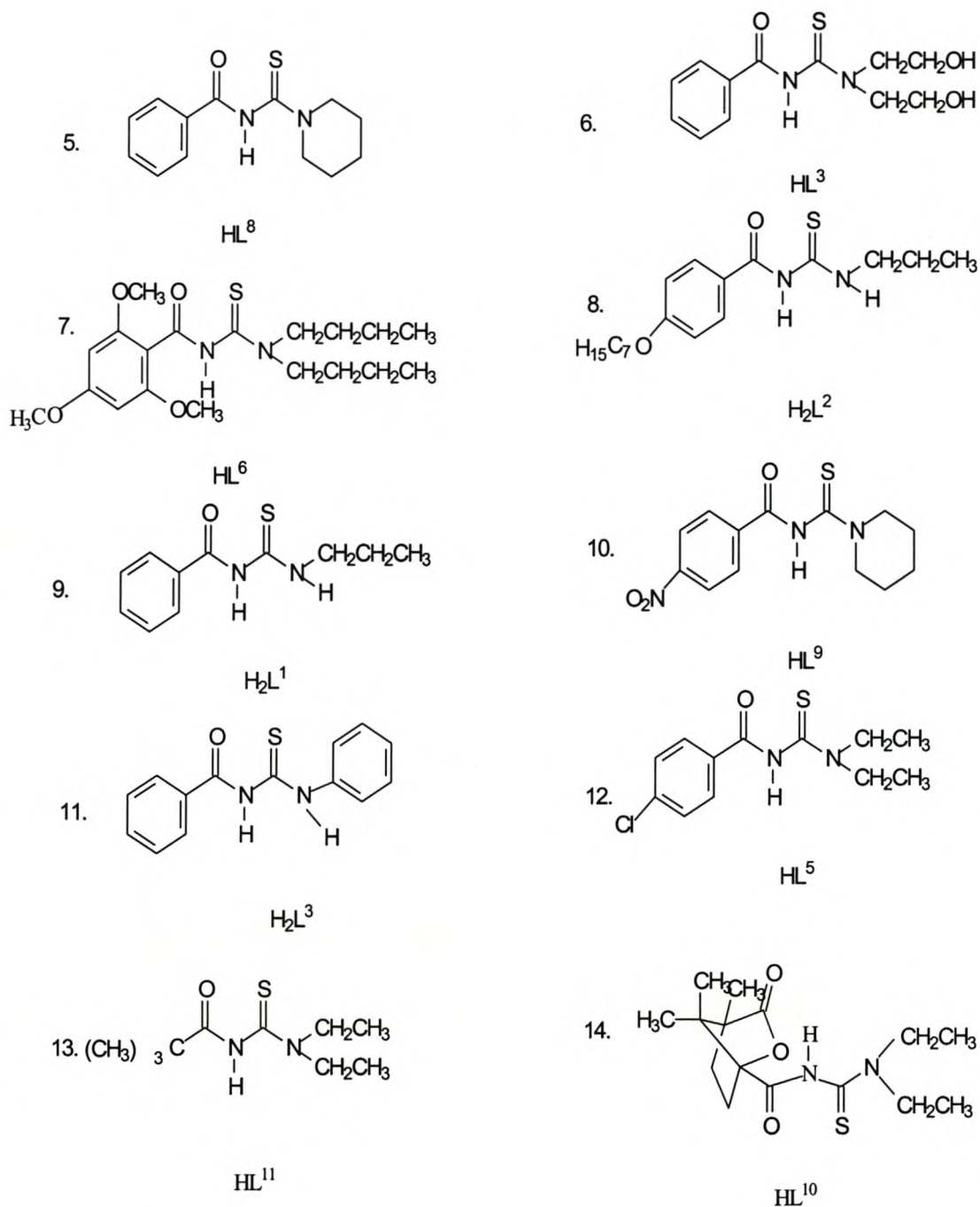


**Figure 2.1:** A reaction scheme for the synthesis of *N, N*-di-ethyl-*N'*-camphanoylthiourea.

## 2.2. Structure of the ligands studied



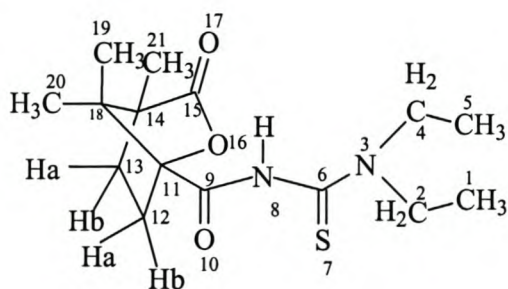




### 2.3. Experimental Details

All reagents were pure and were used without further purification. The ligands were fully characterized by melting point determination,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and elemental analysis by Michael Habtu [66], a previous group member.  $\text{HL}^{10}$  was the only ligand synthesized and checked for purity by melting point determination,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Melting point was determined using a Gallenkamp melting point apparatus in open capillaries. Nuclear magnetic resonance spectra ( $^1\text{H}$  and  $^{13}\text{C}$ )

were measured at 25°C in 5mm NMR tubes in CDCl<sub>3</sub> solution. The chemical shifts ( $\delta$ ) were referenced to tetra methylsilane (TMS) as internal standard. The melting point, recrystallised yield and selected chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR (see appendix for spectra) of the ligand, *N,N*-diethyl-*N'*-camphanoylthiourea, and the structure of the ligand with numbering are listed below. Recrystallised yield 70%; melting point 143°C-144°C



**Figure 2.2:** Structure of *N,N*-diethyl-*N'*-camphanoylthiourea with sequential numbering scheme.

$\delta_H$  (300MHz, CDCl<sub>3</sub>) 8.37 ( 1H, s, NH), 3.96 (2H, broad s ,H<sup>2</sup>), 3.53 (2H, broad s, H<sup>4</sup>), 2.48 (2H, ddd, <sup>2</sup>J<sub>12b,12a</sub>, <sup>3</sup>J<sub>12b,13b</sub>, <sup>3</sup>J<sub>12b,13a</sub>, 13.5, 10.5, 4.5HZ, H<sup>12b</sup>), 1.97 (2H, ddd, <sup>2</sup>J<sub>12a,12b</sub>, <sup>3</sup>J<sub>12a,13a</sub>, <sup>3</sup>J<sub>12a,13b</sub>, 13.5, 7.5, 3.3 HZ, H<sup>12a</sup> ), 1.93 (2H, ddd, <sup>2</sup>J<sub>13b,13a</sub>, <sup>3</sup>J<sub>13b,2b</sub>, <sup>3</sup>J<sub>13b,2a</sub> 13.5, 10.5, 3.3HZ, H<sup>13b</sup>), 1.26 (3H, t, <sup>3</sup>J<sub>1,2</sub> 6.3HZ, H<sup>1</sup>), 1.68 (2H, ddd, <sup>2</sup>J<sub>13a,13b</sub>, <sup>3</sup>J<sub>13a,12a</sub>, <sup>3</sup>J<sub>13a,12b</sub> 13.5, 7.5, 4.5 HZ, H<sup>13a</sup>), 1.26 (3H, t, <sup>3</sup>J<sub>4,5</sub> 6.3HZ H<sup>5</sup>), 1.09 (3H,s, H<sup>21</sup> ), 1.07 (3H, s H<sup>19</sup> ), 0.98 (3H,s, H<sup>20</sup>);  $\delta_C$  ( 150 MHz, CDCl<sub>3</sub>) 177.6 (C<sup>15</sup>), 177.5 (C<sup>6</sup>), 164.3 (C<sup>9</sup>), 92.1 (C<sup>11</sup>), 55.36 (C<sup>18</sup>), 55.0 (C<sup>14</sup>), 47.75 (C<sup>2</sup>), 47.48 (C<sup>4</sup>), 30.2 (C<sup>12</sup>), 28.67 (C<sup>13</sup>), 16.64 (C<sup>20</sup>), 16.4 (C<sup>19</sup>), 13.1(C<sup>1</sup>), 13.29(C<sup>5</sup>), 9.4 (C<sup>21</sup>).



## 2.4. Synthesis and characterization of Au(I) complex with N,N-diethyl-N'-camphanoylthiourealigand.

Tetrachloroaurate (III) in HCl matrix (0.172g, 1.0mmole) was prepared from a stock solution of tetrachloroaurate. To this solution is added the thiodiglycol (2,2'-thiodiethanol) with stirring slowly until the yellow colour of the solution is discharged. This is to reduce the Au(III) to Au(I). It is also possible to use the ligand itself as a reducing agent if it is not expensive and not difficult to synthesize. A solution of the ligand (0.312g, 1mmole) dissolved in 20ml of chloroform is added dropwise with stirring over 20minutes. The chloroform phase is separated and added dropwise to methanol (40ml) and a pale yellow metal ligand complex is precipitated. The precipitate is recrystallized from ether/chloroform (2:1) solution and the recrystallized material is redissolved in an ether/chloroform (2:1) solvent and crystals are grown by the slow solvent evaporation method. The crystals were then filtered and washed with ether and dried. The crystals were characterized by melting point determination, elemental(C, H, N, S) analysis and X-ray crystal structure determination. The general scheme of the reaction is given below [68].



Where R = CH<sub>2</sub>CH<sub>2</sub>OH and R' = N,N-diethyl-N'-camphanoylthiourea (HL<sup>10</sup>)

Mp: 174°C-175°C. (Found C, 33.32 H, 4.33 N, 5.16 S, 5.52; calculated for C<sub>15</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>SAuCl C, 33.05 H, 4.44 N, 5.14 S 5.89) the crystal structure of the complex is discussed in chapter 4.

## 2.5. Transport and extraction experiments

### 2.5.1. Reagents and Chemicals

Analytically pure (AR-grade) chloroform, obtained from Merck, was used in all transport and extraction experiments. Reagent grade AuCl<sub>4</sub><sup>-</sup> was obtained from Industrial Analytical and was used without further purification. AR- grade HCl (32% w/v) was obtained from Merck and used as receiving phase after appropriate dilution. NaCN, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, HClO<sub>4</sub> were all of analytical grade and obtained from Merck. All



aqueous solutions were prepared using deionised water.

### **2.5.2. Extraction experiments**

The extraction experiments were performed by taking 3ml of the aqueous solution and 15ml of the chloroform to mimic the transport processes and this was shaken in a labcon shaker at 120 rpm for 24 hours. The results were then analyzed with atomic absorption spectroscopy after appropriate dilution. The membrane phase contained the ligand dissolved in chloroform. pH of the gold solution was 1.0. All pH measurements were measured using a corning 425 pH meter with a combination glass electrode. The pH meter was calibrated using pH 4.0 and pH 7.0 standard buffer solutions.

### **2.5.3. Bulk Liquid membrane transport experiments**

The metal ion transport arrangement used in the present investigation is presented schematically in fig 1.1. The study involved metal ion transport from an aqueous source phase containing a solution of tetrachloroaurate into a solution of organic phase first containing the ligand and then to the aqueous receiving phase, against the back gradient of protons.

An aqueous source phase ( $10\text{cm}^3$ ) and an aqueous receiving phase ( $30\text{cm}^3$ ) were bridged by a presaturated chloroform membrane phase that contained the ligand ( $50\text{cm}^3$ ). The source/organic and organic/receiving phase contact areas were  $4.52$  and  $16.7\text{ cm}^2$ . Before any transport experiment was conducted, the cells were soaked overnight in concentrated  $\text{HNO}_3$  solution, rinsed with water and dried with acetone in the hood. The membrane phase, the source phase and the receiving phase were then gently transferred in that respective order into the cells. The cells were thermostated at  $25^\circ\text{C}$  and stirred at 10 rpm by means of a coupled single geared synchronous motor. 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. The cells were thereafter covered with cover slips in order to prevent evaporation of solvents over the 24-hour period. All transport runs were terminated after 24 hours and the amount of metal ion transported from the source phase to the receiving phase over that period was



determined by flame atomic absorption spectroscopy (FAAS).

#### **2.5.4. Analysis of solutions**

Samples were taken from both the source and receiving phases of each duplicate run after each experiment and diluted to the required concentration range with 0.1M HCl. The atomic absorption spectrometer was calibrated by a series of standards containing a solution of gold diluted with 0.1M HCl. The percentage metal ion transported was calculated based on the quantity of metal ions transported into the receiving phase in a 24-hour period. The transport results are quoted as the average values obtained from the duplicate runs carried out in parallel.

#### **2.5.5. Instrumentation**

The instrument used for the atomic absorption analysis was a varian type model, AA-1275. A specific wavelength at which gold absorbs and is free from spectral interferences was selected for analysis. An acetylene-air gas mixture was used as the flame source for the burner. By running a blank and a series of standard solutions in the linear response range of the detector, a standard calibration curve was drawn. For this specific instrument, calibration curves were found to be linear up to an absorbance reading of 1.0. As the analyte concentration increases the linearity of the instrument deviates. This deviation could be due to various factors, such as unabsorbed radiation, stray light, or disproportionate decomposition of molecules. Optimum experimental conditions for obtaining a linear dynamic response as recommended by the instrument supplier in the determination of gold is 242.8nm for concentration 5ppm- 20ppm. The slit width was one.

## Chapter Three

### 3. Results for metal ion extraction studies involving *N,N*-dialkyl-*N'*-acyl (aroyl) thioureas

#### 3.1. Introduction

In order to give us a better understanding of the transport results, parallel solvent extraction experiments were carried out. The transport experiments did not produce a high transport of Au (III) as we initially expected. The possible reasons and the results obtained of a ligand that was capable of transporting a small percent of Au(III) will be discussed at the end of this chapter. The ligands employed in the transport and extraction experiments were:

*N,N*-di-*n*-butyl-*N'*-benzoylthiourea(HL<sup>1</sup>), *N,N*-di-propyl-*N'*-benzoylthiourea (HL<sup>2</sup>), *N,N*-di-(2-hydroxyethyl)-*N'*-benzoylthiourea(HL<sup>3</sup>), *N,N*-diethyl-*N'*-4-nitrobenzoylthiourea(HL<sup>4</sup>), *N,N*-diethyl-*N'*-4-chlorobenzoylthiourea(HL<sup>5</sup>), *N,N*-dibutyl-*N'*-2,4,6-trimethoxybenzoylthiourea(HL<sup>6</sup>), *N,N*-diethyl-*N'*-2,4,6-trimethoxybenzoylthiourea(HL<sup>7</sup>), *N*-Piperidyl-*N'*-benzoylthiourea(HL<sup>8</sup>), *N*-Piperidyl-*N'*-4-nitrobenzoylthiourea(HL<sup>9</sup>), *N,N*-diethyl-*N'*-camphanoylthiourea (HL<sup>10</sup>), *N,N*-diethyl-*N'*-2,2-dimethylpropanoylthiourea(HL<sup>11</sup>), *N*-propyl-*N'*-benzoylthiourea (H<sub>2</sub>L<sup>1</sup>), *N*-propyl-*N'*-4-heptoxybenzoylthiourea(H<sub>2</sub>L<sup>2</sup>) and *N*-phenyl-*N'*-benzoylthiourea (H<sub>2</sub>L<sup>3</sup>).

Metal ion extraction depends upon a number of parameters, such as; structure of the ligand, stability of the individual metal/ligand complexes, type of solvent used, nature of the accompanying anion and pH of the aqueous phase during extraction. However, in this study, we have only focused on the effect of varying ligand structure on the extraction behaviour of the ligands. Moreover to see the effect of ligand concentration on the percentage metal ion extracted the metal to ligand (M:L) mole ratio was varied between 1:1, 1:0.5 and 1:0.25 and results of percentage metal ion extracted are reported.

#### 3.2. Experimental conditions

Two-phase solvent extraction experiments were carried out. In order to mimic the experimental conditions employed in the transport experiments, volumes of 3ml (aq)



and 15ml (org) were used in the extraction studies. This is important, for comparison purposes of the transport and extraction results. All extraction experiments were conducted at a fixed source phase pH while the effect of varying the ligand concentration was studied. For effective and convenient comparison, the ligands have been grouped together. The aqueous source phase (3ml) contained the metal ion at a concentration of 0.01M prepared by diluting the gold solution with 0.1M HCl. The organic phase contained the ligand dissolved in chloroform. The two phases were then enclosed in sample tubes and placed on a labcon oscillating shaker at 25°C, which was set at 120 rpm for 24 hours. All experiments were carried out in duplicate.

In all cases, the values between any two duplicate runs did not differ by more than 2%. Any extraction of small amounts of metal ions is ignored as it is deemed to be within experimental error. The sum of all experimental errors involved in all the measurements is assumed to be within  $\pm 5\%$ .

### **3.3. Assessment of experimental errors in data**

To minimize and control errors in measurements, it is essential to understand the origin, nature and type of error. There are always two types of errors, which can affect the precision, and accuracy of a measured quantity. These are determinate and indeterminate errors

#### **3.3.1. Determinate errors**

Determinate errors have a definite source that can usually be identified. They cause all the results from replicate measurements to be either high or low. They are divided into two, systematic and constant errors. The effect of such type of errors may be either constant or proportional. The magnitude of a constant error does not depend on the size of the quantity measured. However, proportional errors increase or decrease in proportion to the size of the sample taken for analysis. The main cause of proportional errors is the presence of interfering contaminants in the sample. This type of error affects accuracy of the measurements.

### Sources of determinate errors

There are three types of determinate error. These are

1. Lack of skill of the operator.
2. Systematic instrument errors are caused by the imperfections in measuring devices and instabilities in their power supply.
3. Method errors arise from non-ideal chemical or physical behaviour of analytical systems

#### 3.3.2. Indeterminate errors

Indeterminate errors, also called random errors, arise when a system of measurement is extended to its maximum sensitivity. They are caused by the many uncontrolled variables that are an inevitable part in every physical or chemical measurement. There are many sources of indeterminate errors, but none can be positively identified or measured because most of them are so small that they are undetectable. The cumulative effect of the indeterminate errors, however, causes the data from the set of replicate measurements to fluctuate randomly around the mean of the set. These mainly originate from inability to exactly reproduce physical conditions. This type of error affects the precision of the measurements.

### 3.4. Calculation

The percentage of metal ion extracted was calculated as follows

$$\% \text{ metal ion extracted} = \frac{n_a - n_b}{n_a} \times 100$$

Where

$n_a$  refers to the number of moles of the metal ion present in the aqueous source phase before extraction

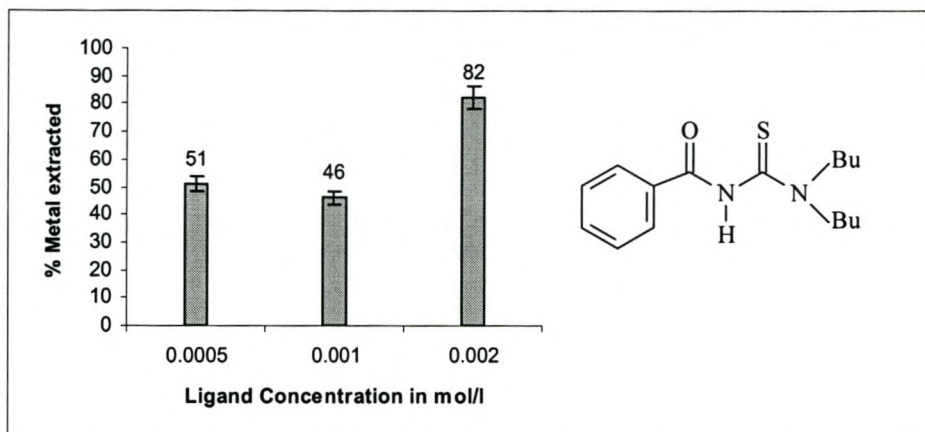
$n_b$  refers the number of moles of the metal ion present in the aqueous source phase after extraction.



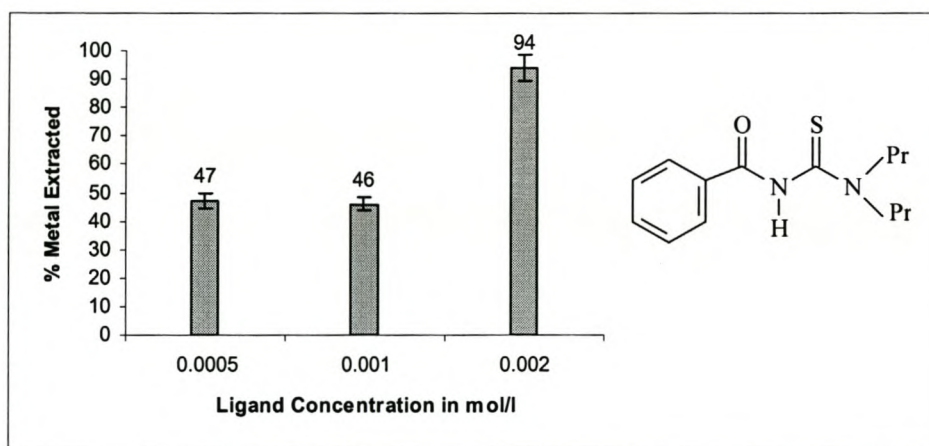
**Table 3.1:** Summary of the percentage metal ion extracted.

Ligand No	percentage metal extracted		
	1:1	1:0.5	1:0.25
	M:L (metal to ligand mol. ratio)		
HL <sup>1</sup>	82	46	51
HL <sup>2</sup>	94	46	47
HL <sup>3</sup>	97	90	63
HL <sup>4</sup>	93	89	44
HL <sup>5</sup>	84	83	53
HL <sup>6</sup>	85	72	53
HL <sup>7</sup>	95	77	48
HL <sup>8</sup>	93	76	44
HL <sup>9</sup>	32	23	23
HL <sup>10</sup>	92	55	31
HL <sup>11</sup>	94	83	56
H <sub>2</sub> L <sup>1</sup>	75	36	44
H <sub>2</sub> L <sup>2</sup>	100	79	85
H <sub>2</sub> L <sup>3</sup>	86	42	41

### 3.5. Metal ion extraction by *N,N*-di-*n*-butyl-*N'*-benzoylthiourea (HL<sup>1</sup>), *N,N*-di-propyl-*N'*-benzoylthiourea (HL<sup>2</sup>) and *N,N*-di-(2-hydroxyethyl)-*N'*-benzoylthiourea (HL<sup>3</sup>).

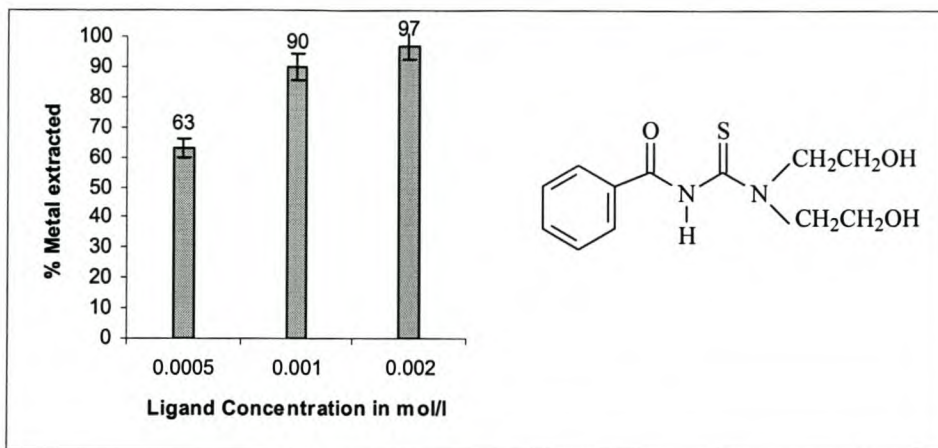


**Fig.3.1:** Percentage extraction of Au(III) ions involving HL<sup>1</sup>. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.



**Figure.3.2:** Percentage extraction of Au(III) ions involving HL<sup>2</sup>. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.





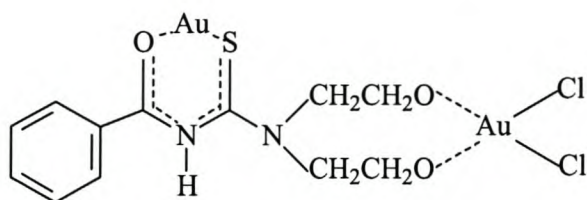
**Fig.3.3:** Percentage extraction of Au(III) ions involving HL<sup>3</sup>. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.

### 3.5.1. Comparison of metal ion extraction by N,N-di-n-butyl-N'-benzoylthiourea (HL<sup>1</sup>), N,N-di-propyl-N'-benzoylthiourea (HL<sup>2</sup>) ligands and N,N-di-(2-hydroxyethyl)-N'-benzoylthiourea (HL<sup>3</sup>).

These three ligands have similar structures and have been grouped together to evaluate the effect of the di alkyl substituents and the ethyl hydroxyls on the amount of metal ion extracted. HL<sup>1</sup> extracts 82% of the metal ion with a ligand concentration of 0.002M and this is at a 1:1 metal:ligand ratio. This value was reduced to about 46%, which is almost half the first result. Similarly, HL<sup>2</sup> extracted 94% of the Au(III) with 0.002M ligand concentration. When the ligand concentration was reduced to half, the amount of metal ion extracted has also been reduced to 46%. This extraction pattern of the ligands could be verified on the 1:1 mole ratio of the ligand metal ion in complex formation [19]. Thus, the percentage metal ion extracted is reduced by almost half when the ligand to metal mole ratio is 0.5:1. Reducing the ligand concentrations further to 0.0005M, gave an extraction value of 51% for HL<sup>1</sup> and 47% for HL<sup>2</sup>.

HL<sup>3</sup> extracts almost equally well as HL<sup>2</sup>, but it does not follow the same trend in reduction of percentage metal ion extracted when the the ligand concentration was reduced. It extracts about 97% of the metal ion when the ligand concentration is 0.002M which is 1:1 metal:ligand ratio and this was not reduced that much when the ligand concentration was reduced to 0.001M (90%). Two possible reasons could be

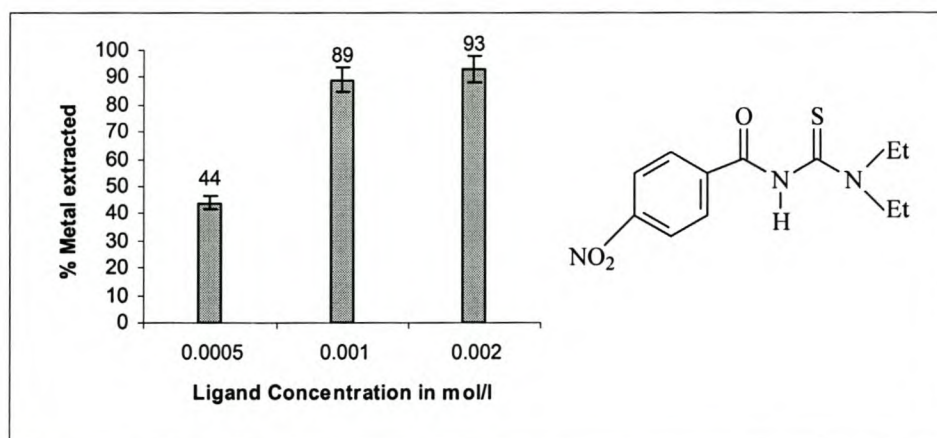
given for the higher extraction of HL<sup>3</sup> compared to HL<sup>1</sup> and HL<sup>2</sup>. Probably the two OH groups may bind another metal ion [65]. The probable structure is shown in fig. 3.4



**Figure 3.4:** A schematic diagram showing the probable binding of two metal ions involving the thiourea moiety and the hydroxyl oxygens as donor atoms.

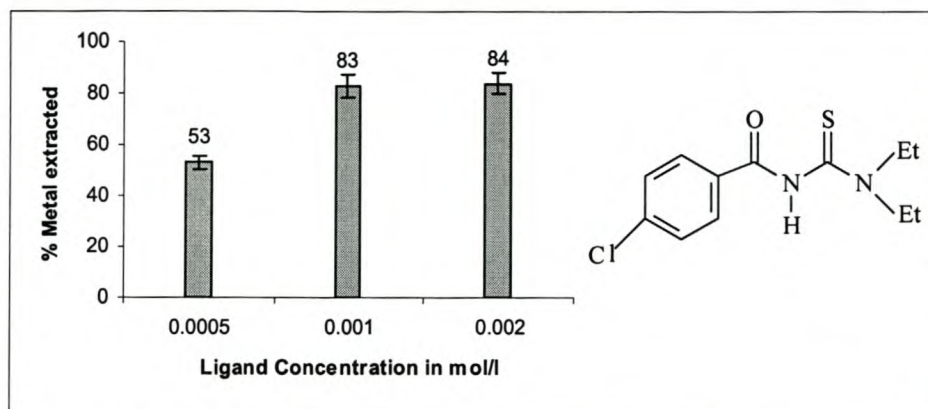
Secondly, the OH groups on the thiourea moiety may be enhancing the reduction of Au(III) to Au(0). Reducing the ligand concentration further to 0.0005M however reduces the metal ion extracted to 63%. The hydrophilic nature [39] of the ligand causes the ligand to bleed into the source phase, since it was seen that some of the metal ion was reduced in the source phase.

### 3.6. Metal ion extraction by *N,N*-diethyl-*N'*-4-nitrobenzoylthiourea (HL<sup>4</sup>) and *N,N*-diethyl-*N'*-4-chlorobenzoylthiourea (HL<sup>5</sup>) ligands.



**Figure 3.5:** Percentage extraction of Au(III) ions using (HL<sup>4</sup>). pH of the source phase = 1.0 and the concentration of the ligand was varied from 5x10<sup>-4</sup>M to 2x10<sup>-3</sup>M as shown in the figure.



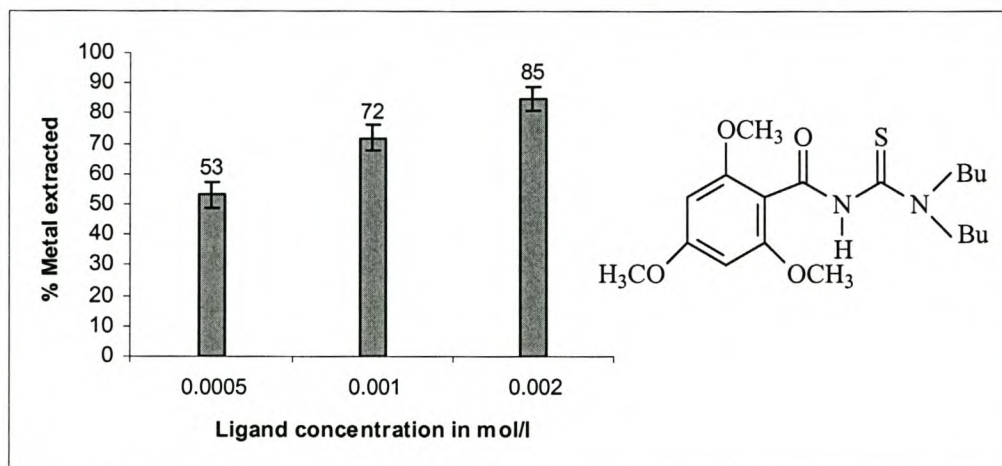


**Figure 3.6:** Percentage extraction of Au(III) using (HL<sup>5</sup>) ligand. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.

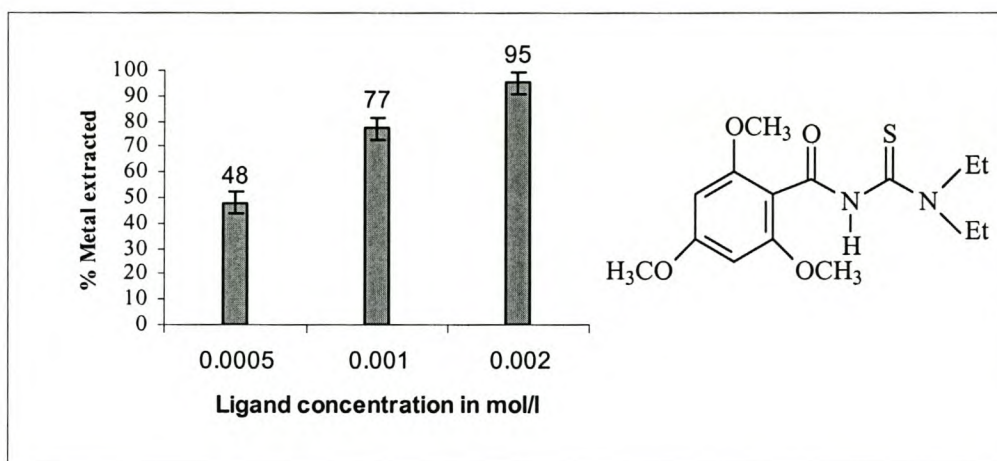
### 3.6.1. Comparison of metal ion extraction by N,N-diethyl-N'-4-nitrobenzoylthiourea (HL<sup>4</sup>) and N,N-diethyl-N'-4-chlorobenzoylthiourea (HL<sup>5</sup>) ligands.

These two ligands have electron withdrawing groups attached to the benzoyl ring. To see the effect of these substituents the two ligands have been grouped together. When the ligand to metal mole ratio is 1:1 this is at ligand concentration of 0.002 M HL<sup>4</sup> extracts 93% of the metal ion and HL<sup>5</sup> extracts 84%. The percentage metal ion extracted remains high when the ligand concentration is halved. This may probably be due to the electron withdrawing groups which decrease the electron density around the carbonyl in the thiourea moiety, thus making the oxygen atom relatively softer. This may provide the metal with two coordination sites, through S and O. This assumption however needs to be confirmed crystallographically or by complex formation or any other appropriate instrumental technique. Reducing the ligand concentration further to 0.0005 M, the percentage metal ion extracted decreases to 44% for HL<sup>4</sup> and 53% for HL<sup>5</sup>.

### 3.7. Metal ion extraction by *N,N*-dibutyl-*N'*-2,4,6-trimethoxybenzoylthiourea (HL<sup>6</sup>) and *N,N*-diethyl-*N'*-2,4,6-trimethoxybenzoylthiourea (HL<sup>7</sup>) ligands.



**Figure 3.7:** Percentage extraction of Au(III) using (HL<sup>6</sup>) ligand. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4} \text{M}$  to  $2 \times 10^{-3} \text{M}$  as shown in the figure.



**Figure 3.8:** Percentage extraction of Au(III) involving (HL<sup>7</sup>) ligand. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4} \text{M}$  to  $2 \times 10^{-3} \text{M}$  as shown in the figure.



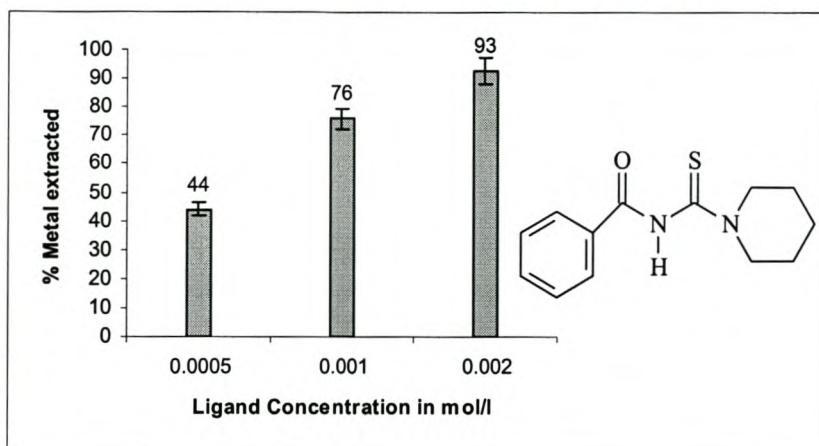
### 3.7.1. Comparison of metal ion extraction by N,N-dibutyl-N'-2,4,6-trimethoxybenzoylthiourea (HL<sup>6</sup>) and N,N-diethyl-N'-2,4,6-trimethoxybenzoylthiourea (HL<sup>7</sup>) ligands.

These two ligands have the methoxy electron releasing groups in their structures. The extraction would, thus, be expected to be quite similar to each other but opposite to HL<sup>4</sup> and HL<sup>5</sup>. The percentage of metal ion extracted by HL<sup>6</sup> was 85% and 95% for HL<sup>7</sup> at a ligand concentration of 0.002 which is at 1:1 metal:ligand mole ratio. Reducing the ligand concentration to half, 0.001M, the extraction results remain high at 72% and 77% for HL<sup>6</sup> and HL<sup>7</sup> respectively.

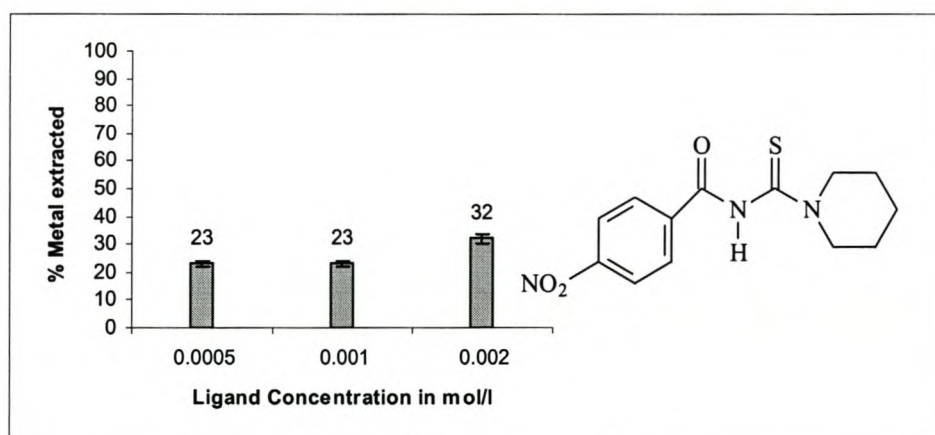
Sanna *et al.* have reported that despite the low affinity of gold for oxygen, some gold complexes with oxygen donors such as hydroxo and alkoxo (RO<sup>-</sup>; R= alkyl, aryl) groups are known [65]. Thus, the high extraction results of these ligands when the ligand concentration is halved may probably be attributed to the involvement of the oxygen atoms in the methoxy groups in binding another metal ion.

The relatively higher extraction of HL<sup>7</sup> compared to HL<sup>6</sup> may be due to the steric hindrance of the di-butyl groups compared to the di-ethyl groups in HL<sup>7</sup>. Another possibility for the higher metal ion extracted when ligand concentration is halved could be due to the reduction of Au(III) to Au(0) which was observed after terminating the extraction experiment. This reduction may be facilitated by the oxygen atoms in the methoxy groups in this pair of ligands. Since, the extraction patterns of HL<sup>5</sup> and HL<sup>6</sup>, are similar, it does not appear that the bulky dibutyl groups have an effect on the extraction.

### 3.8. Metal ion extraction by *N*-Piperidyl-*N'*-benzoylthiourea (HL<sup>8</sup>) and *N*-Piperidyl-*N'*-4-nitrobenzoylthiourea (HL<sup>9</sup>) ligands.



**Figure 3.9:** Percentage extraction of Au(III) using (HL<sup>8</sup>) ligand. pH of the source phase = 1.0 and concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.



**Figure 3.10:** Percentage extraction of Au(III) using (HL<sup>9</sup>) ligand. pH of the source phase = 1.0 and concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.

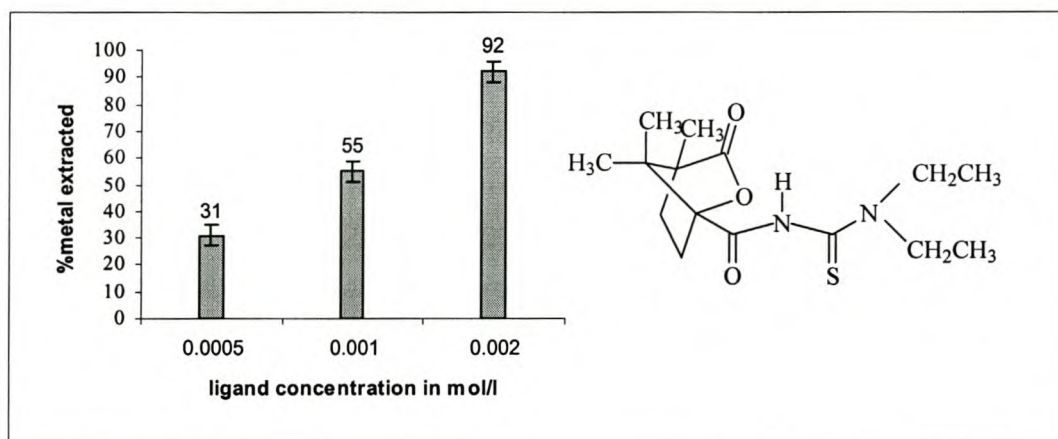
#### 3.8.1. Comparison of metal ion extraction by *N*-Piperidyl-*N'*-benzoylthiourea (HL<sup>8</sup>) and *N*-Piperidyl-*N'*-4-nitrobenzoylthiourea (HL<sup>9</sup>) ligands.

For these two ligands, one has an electron withdrawing group (NO<sub>2</sub> group) at the C<sub>4</sub>

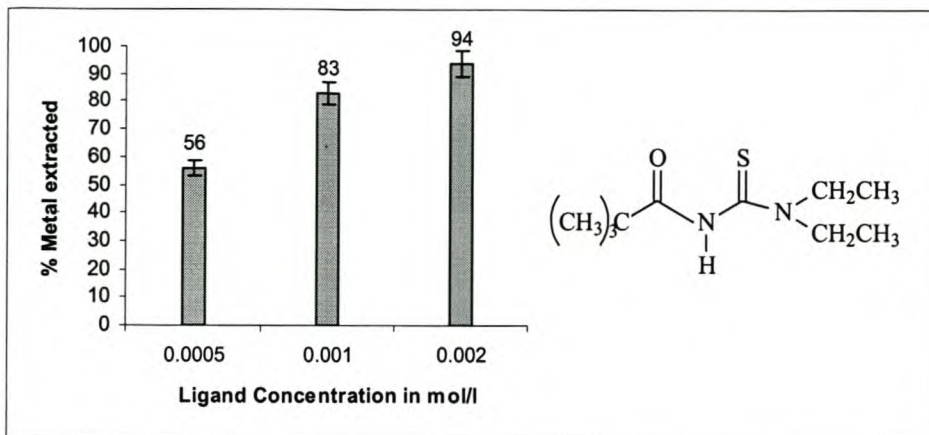


position and hence more metal ion would be expected to be extracted by this ligand as was seen by HL<sup>4</sup>. However, the results obtained reveal that it is quite the opposite. HL<sup>8</sup> extracts 93% of the metal ion when the ligand concentration was 0.002M the metal ligand ratio being 1:1 and was seen to drop to 76% when the ligand concentration was reduced by half. Reducing the ligand concentration further showed that the percentage metal ion extracted dropped down to 44%. With regard to HL<sup>9</sup> the metal ion extracted was 32% with 0.002M ligand concentration and it dropped to 23% when the ligand concentration was reduced to half the original. Reducing the ligand concentration further does not seem to have any effect on the percentage metal ion extracted, which remains 23% for (HL<sup>9</sup>). Habtu [66] mentioned that the extraction and transportation of (HL<sup>9</sup>) with Ag (I) showed similar, very low results. He hinted that it was possibly due to the low formation constant of the ligand with the metal ion.

### 3.9. Metal ion extraction by *N,N*-diethyl-*N'*-camphanoylthiourea (HL<sup>10</sup>) and *N,N*-diethyl-*N'*-2,2-dimethylpropanoylthiourea (HL<sup>11</sup>)



**Figure 3.11:** Percentage extraction of Au(III) using (HL<sup>10</sup>) ligand. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.



**Figure 3.12:** Percentage extraction of Au(III) using (HL<sup>11</sup>) ligand. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4}$  M to  $2 \times 10^{-3}$  M as shown in the figure.

### 3.9.1. Comparison of metal ion extraction by N,N-diethyl-N'-camphanoylthiourea (HL<sup>10</sup>) and N,N-diethyl-N'-2,2-dimethylpropanoylthiourea (HL<sup>11</sup>)

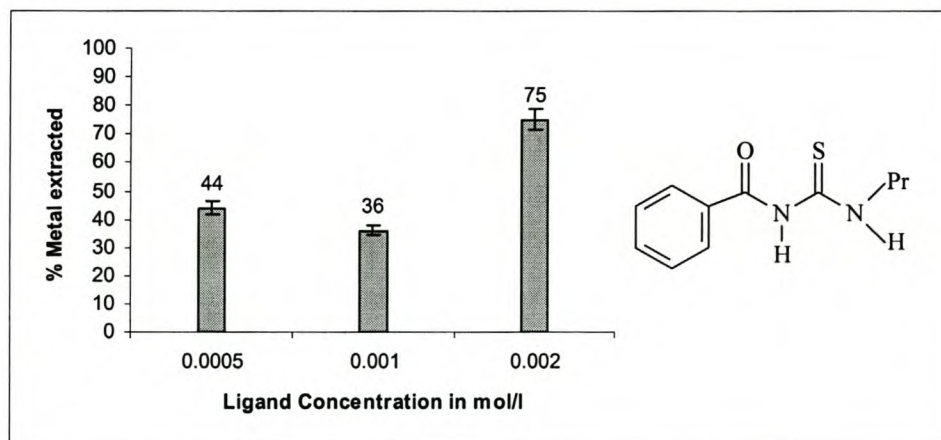
HL<sup>11</sup> is the only acyl thiourea ligand in the group of ligands studied and HL<sup>10</sup> is the only one with a different group other than the benzoyl group. Thus grouping them together and comparing the general extraction behaviour with that of the other ligands is of importance. HL<sup>11</sup> extracts 94% of the metal ion with 0.002 M ligand concentration which is at 1:1 metal:ligand ratio. Reducing the ligand concentration to half, the percentage metal ion extracted is decreased to 83%, which is still a very high value. Further reduction of the ligand concentration to 0.0005 M, the percentage of metal ion extracted drops to 56%. Thus, the acyl thiourea behaves exactly the same way as the aromatic ring substituted di-alkyl thioureas. Theoretically, the acyl thioureas are more powerful extracting agents than the benzoyl thioureas. The resonance in the  $-C(O)NC(S)-$  moiety increases the stability of metal complexes. This resonance is extended to the aromatic ring in the case of the benzoyl thioureas and decreases the stability of the resonance [38]. Thus, the high extraction of HL<sup>11</sup> may likely be attributed to this fact. HL<sup>10</sup> extracts about 92% when the ligand to metal mole ratio is 1:1 at ligand concentration of 0.002 M. The percentage metal ion extracted is reduced to 55% when the ligand concentration was reduced to half,



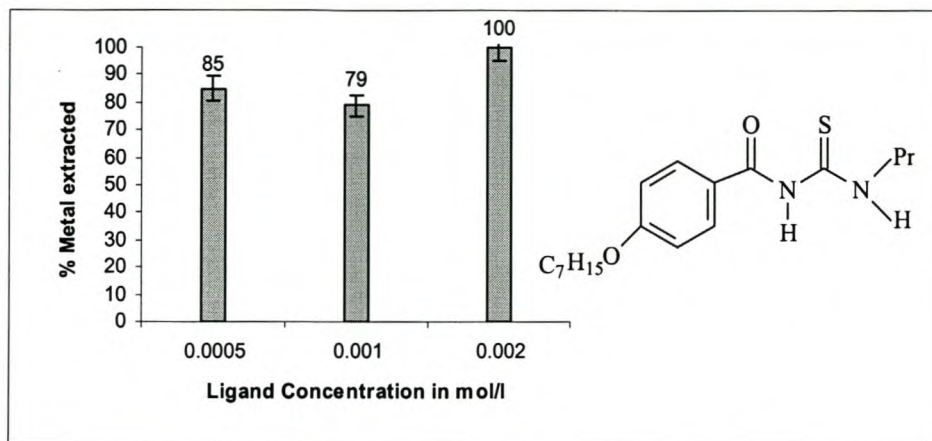
which is approximately half to the amount extracted when the ligand metal ratio is 1:1. Reducing the ligand concentration further to 0.0005M the percentage metal ion extracted drops to 31%.

The decrease in the percentage extraction of Au(III) by HL<sup>10</sup> with the decrease in ligand concentration could be verified from the crystal structure of HL<sup>10</sup> with Au(III) (see section 4.2). The crystal structure shows a 1:1 mole ratio ligand to metal during complex formation. Therefore, in the absence of determinate and indeterminate errors it is theoretically expected that decreasing the concentration by half would reduce the percentage metal ion extracted by half. However, slightly higher percentages of Au were extracted than theoretically expected with HL<sup>10</sup>.

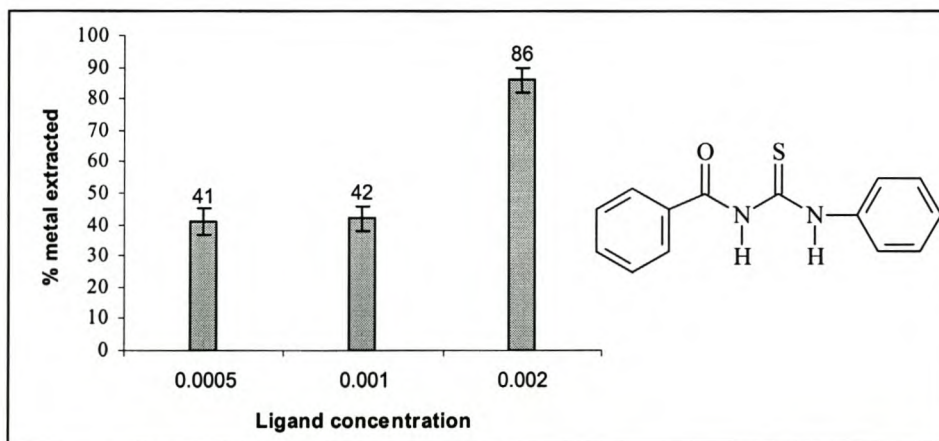
### 3.10. Metal ion extraction by *N*-propyl-*N'*-benzoylthiourea (H<sub>2</sub>L<sup>1</sup>), *N*-propyl-*N'*-4-heptoxybenzoylthiourea (H<sub>2</sub>L<sup>2</sup>) and *N*-phenyl-*N'*-benzoylthiourea (H<sub>2</sub>L<sup>3</sup>)



**Figure 3.13:** Percentage extraction of Au(III) using (H<sub>2</sub>L<sup>1</sup>) ligand. pH of the source phase = 1.0 and the concentration of the ligand was varied from 5x10<sup>-4</sup>M to 2x10<sup>-3</sup>M as shown in the figure.



**Figure 3.14:** Percentage extraction of Au(III) using ( $H_2L^2$ ) ligand. pH of the source phase = 1.0 and the concentration of the ligand was varied from  $5 \times 10^{-4} M$  to  $2 \times 10^{-3} M$  as shown in the figure.



**Figure 3.15:** Percentage extraction of Au (III) involving ( $H_2L^3$ ) ligand. pH of the source phase = 1.0 and concentration of the ligand was varied from  $5 \times 10^{-4} M$  to  $2 \times 10^{-3} M$  as shown in the figure

### 3.10.1. Comparison of metal ion extraction by N-propyl-N'-benzoylthiourea ( $H_2L^1$ ), N-propyl-N'-4-heptoxybenzoylthiourea ( $H_2L^2$ ) and N-phenyl-N'-benzoylthiourea ( $H_2L^3$ )

The hydrogen atom in the thiourea moiety is involved in intramolecular hydrogen bonding [20]. Hence, they are only capable of binding monodentately through the sulphur atom. The extraction results for  $H_2L^1$  and  $H_2L^3$  seem to be in agreement with



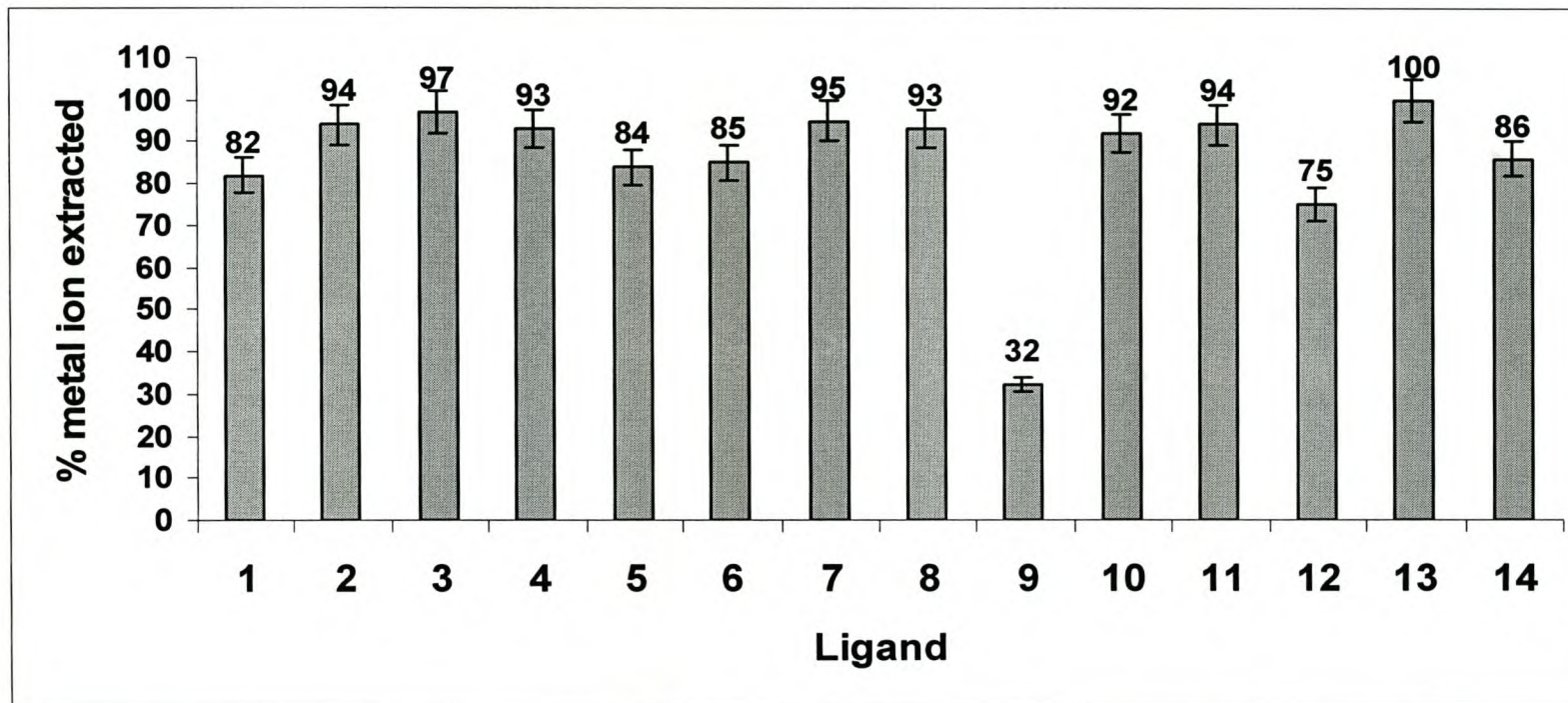
this argument.  $H_2L^3$  extracts 86% of the metal ion at a ligand to metal ratio of 1:1 this drops to 42% when the ligand concentration is halved and further reduction of the ligand concentration to 0.0005M results in percentage metal ion extraction of 41%.

$H_2L^1$  similarly extracts about 75% when the ligand concentration was 0.002M that is at a 1:1 metal to ligand mole ratio. The percentage metal ion extracted reduces to 36% with reduction of the ligand concentration to half. Further reduction of the ligand however, lead to percentage metal ion extraction of 44%.

$H_2L^2$  on the other hand extracts about 100% with 0.002M which is at a 1:1 metal to ligand mole ratio. This was seen to be reduced to 79% when the ligand concentration was halved to 0.001M. Further reduction of the ligand concentration to 0.0005M resulted in the percentage metal ion extracted to be 85%. The extremely high extraction of  $H_2L^2$  could be possibly due to the high lipophilicity of the ligand due to the  $-C_7H_{15}O$  group.

The fact that the ligand concentration is reduced from 0.002M to 0.001M produces an extraction value of 79% for  $H_2L^2$  is unexpected. When the ligand concentration is reduced further to 0.0005M, another unexpected result occurs, 85% and 44% of the metal ion is extracted by  $H_2L^2$  and  $H_2L^1$  respectively. Possible explanations for these could be that gold is reduced to Au(0) (as was seen after the 24 hour period elapsed) and the coordination site is available for more Au(III) to coordinate in solution.

Comparing the extraction results of these ligands with Ag(I) Habtu [66] found that they gave higher extraction results than the HL ligands, which is contrary to our findings with Au(III) except for  $H_2L^2$  which produces similar results to that of Habtu's.



**Fig 3.15:** Comparison of the extraction studies involving all the ligands studied: 1= HL1, 2 = HL2, 3 = HL3, 4 = HL4, 5 = HL5, 6 = HL6, 7 = HL7, 8 = HL8, 9= HL9, 10 = HL10, 11 = HL11, 12 = H2L1, 13 = H2L2, 14 = H2L3. pH of source phase = 1.0 and concentration of ligand =  $2 \times 10^{-3} \text{M}$ .



### 3.11. General discussion of the extraction results

All the above ligands were grouped by taking advantage of their close similarities. However, there are other minor similarities, which may need to be discussed below. Furthermore, some special features, which may have affected the extraction, are discussed below. Figure 3.15 shows a comparison of the percentage metal ion extracted by all the ligands.  $H_2L^2$  (*N*-propyl-*N'*-4-heptoxybenzoylthiourea) gave the highest value of percentage metal ion extracted which is probably due to the high lipophilicity brought by the  $-OC_7H_{15}$  group. On the other hand  $HL^9$  (*N*-Piperidyl-*N'*-4-nitrobenzoylthiourea) is the ligand to give the lowest percentage metal ion extracted which could probably be due to the cyclic structure on the nitrogen.

The  $NO_2$  group seems to have different effects with different substituents on the thiourea moiety. In the case of  $HL^4$  (*N,N*-diethyl-*N'*-4-nitrobenzoylthiourea) it seems to have produced a high extraction result contrary to  $HL^9$  where it seems that the extraction was highly depressed. It is most likely that the cyclic structure on the nitrogen and having  $NO_2$  in  $HL^9$  decreases the donor ability of oxygen and sulphur.

The lipophilicity of the ligand is one of the prerequisites of efficient transportation. In the case of the ligands studied, the more lipophilic ligands will be those with the di-butyl substituent on the thiourea moiety. However, it has been found to be different even though there is not such an exaggerated difference in the extraction results. Comparing the extraction results of  $HL^1$  (*N,N*-di-*n*-butyl-*N'*-benzoylthiourea) and  $HL^2$  (*N,N*-di-propyl-*N'*-benzoylthiourea),  $HL^1$  extracts slightly higher than  $HL^2$ .

The results of  $HL^{10}$  follow almost the same trend of metal ion extraction with the benzoylthioureas with the reduction of ligand concentration. The acyl thiourea  $HL^{11}$  is theoretically expected to extract higher than the aroyl thioureas for reasons mentioned in **section 3.9.1**. Its mode of extraction as a function of ligand concentration however was similar to those benzoyl thioureas with substituents in the aromatic ring.

### 3.12. Metal ion transport by aroyl (acyl) thiourea ligands

There are some important requirements for metal ion transport to be effective and for



a ligand to qualify as a suitable metal ion carrier in a liquid membrane system. These are:

1. it should be selective
2. it should display rapid metal exchange kinetics
3. it should be sufficiently lipophilic
4. It has to have a moderately high formation constant with the target metal ions to be transported.

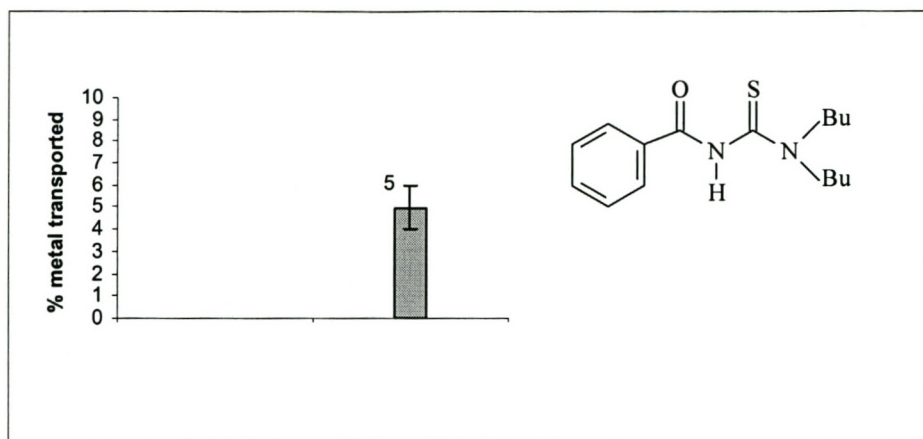
The above requirements thus need to be fulfilled for effective transport of metal ions within liquid membranes. However, the formation constants of the ligand metal complexes in our case, we assume were very high, that it was difficult for the metal ion to be stripped to the aqueous receiving phase using the pH gradient method. Other complexing agents were also incorporated into the receiving phase to strip the metal ion from the ligand but this did not help. The complexing agents  $\text{CN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ , and perchloric acid, however reduced the Au(III) to Au(0), in the membrane/receiving phase interface. This is most likely due to the presence of these complexing agents.

The low values of transport attributed to the high formation constant of the Au(III) thiourea complexes, is supported in an article by E. Hoyer *et al.* [69], where the formation constant of Au(III) with some acyl thioureas was found to be in excess of 30, which is extremely high for effective transport. The metal ion could thus not be transported to the receiving phase through the membrane after complexation.

The only ligand which was capable of transporting about 5% was the *N,N*-di-*n*-butyl-*N'*-benzoylthiourea. This result may be attributable to the longer alkyl chain of the butyl substituent of the thiourea moiety relative to others making the ligand relatively more lipophilic compared to the other ligands [12]. This result is also relatively low and may also be within the experimental error of the instrumentation used.

In all transport experiments the source phase pH was adjusted to 3.0 as hydrolysis of the  $\text{AuCl}_4^-$  may take place at higher pH values [46]. The receiving phase was HCl and the pH of it was adjusted to 1.0 and 0. In addition, concentrated HCl was also tried as a receiving phase but none of these could produce higher transport results.





**Figure 3.15:**Percentage metal ion transported by *N,N*-di-butyl-*N'*-benzoylthiourea ( $HL^1$ ) pH of the source phase =3.0 and the receiving phase pH = 0.

## Chapter Four

### 4. Crystal and molecular structure of *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride

#### 4.1. Crystallographic data

The *NN*-diethyl-*N'*-camphanoylthiourea gold (I) complex was synthesized as described in **section 2.4**. Single crystals of the complex were obtained from a 2:1 solvent mixture of ether/chloroform using the slow solvent evaporation method.

A suitable single crystal of the dimension 0.17 x 0.23 x 0.24 mm was used for the data collection. Data were collected on a smart Apex diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.7107$ ) in omega scans method, range of reflections  $1.91 \leq \theta \leq 26$ . 7272 reflections were collected and used in the refinement, with index range  $-13 \leq h \leq 13$ ,  $-13 \leq l \leq 13$ . A Lorentz-polarization correction was applied to the data.

The crystal structure was solved and refined using direct methods in SHELX97 [70] and developed via the aid of the interface program X-SEED. The final model included anisotropic refinement of all non-hydrogen atoms based on  $F^2$ . The diethyl hydrogens and the NH hydrogen were located in a different electron density map and refined isotropically. Other hydrogens were placed in geometrically calculated positions and refined with a common isotropic temperature factor. At convergence,  $wR = 0.0326$ , conventional  $R = 0.0150$  for 7131 reflections with  $I \geq 2\sigma I$ . The crystallographic data data are shown in table 4.1



**Table 4.1** The crystallographic data and structure refinement for *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) complex.

Empirical formula	C <sub>15</sub> H <sub>24</sub> Au Cl N <sub>2</sub> O <sub>3</sub> S
Chemical formula weight	544.84
Symmetry cell setting	monoclinic
Space group name H-M	P21
Cell length a	10.7356(7)
Cell length b	16.3443(11)Å
Cell length c	10.9268(7)
Cell angle alpha	90
Cell angle beta	103.1450(10)
Cell angle gamma	90
Cell volume	1867.0(2)
Cell formula units Z	4
Cell measurement temperature	100(2)
Exptl crystal density diffrn	1.938
Exptl crystal F 000	1056
Exptl absorpt coefficient mu	8.149
Diffrn ambient temperature	100(2)
Diffrn radiation wavelength	0.71073
Diffrn reflns theta min	1.91
Diffrn reflns theta max	26
Diffrn reflns limit h min	-13
Diffrn reflns limit h max	13
Diffrn reflns limit k min	-20
Diffrn reflns limit k max	20
Diffrn reflns limit l min	-13
Diffrn reflns limit l max	13
Reflns threshold expression	>2sigma(I)
Refine ls abs structure Flack	0.003(3)
Refine ls number reflns	7272
Refine ls number parameters	425
Refine ls number restraints	1
Refine ls R factor all	0.015
Refine ls R factor gt	0.0145
Refine ls wRfactor ref	0.0328
Refine ls wR factor gt	0.0326
Refine ls goodness of fit ref	0.8
Refine ls restrained S all	0.8

## 4.2. The crystal structure for *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride

The molecular structure of the complex *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride complex shows that the coordination sphere around Au(I) is nearly a linear arrangement of sulphur and chloride.

Berhe [67] worked on the same ligand complexing it with silver, nickel and copper. The choice for this ligand in synthesising the complex was the fact that it has a great variety of coordination modes that it exhibits which is attributed to the camphanoyl moiety, the relatively high extraction of Au(III) and to see how the metal ion of interest is coordinated to the ligand.

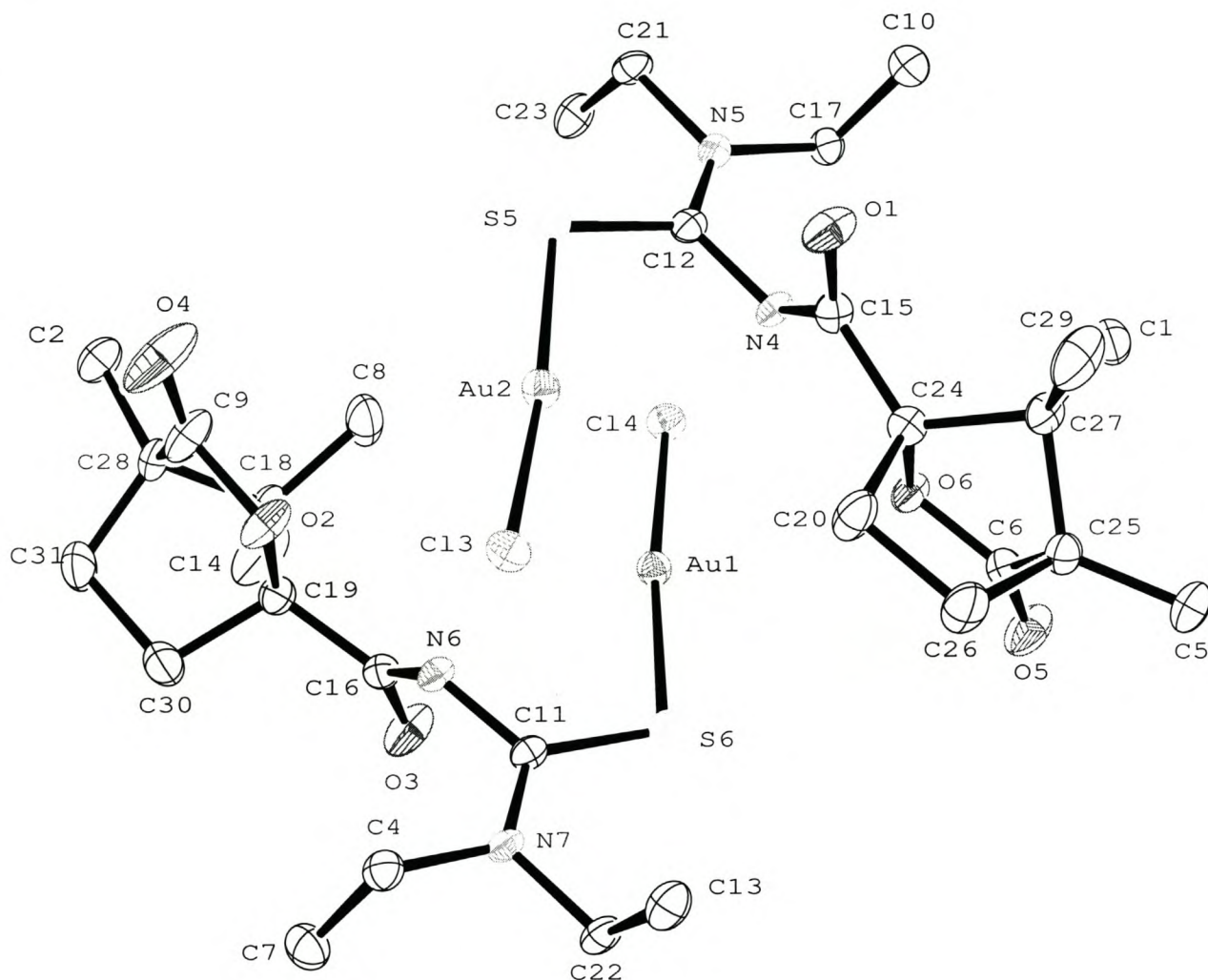
It is reported in the literature that a metal ion forms as many bonds to ligands as can be fitted into it [55]. It is also well known that bulky ligands favour lower coordination numbers due to the effects of the steric hindrance. Even in cases where square planar complexes are favoured for electronic reasons tetrahedral complexes can be formed when steric interactions between ligands are large [55]. The bulky camphonic group and two ethyl groups in HL<sup>10</sup> thus can affect the coordination mode of the ligand with the Lewis acid Au(III).

In our work the metal was directly bonded to the sulphur atom and one chloride atom attached to it as a counter ion. In similar work done by W. Bensch and M. Shuster, [19] the same mode of coordination is observed. Whereas this same ligand forms a metal chelate ring with Ag(I), Co(II), Cu(II), and Ni(II) yielding mononuclear complexes of Co(II), Cu(II), and Ni(II) while it forms a binuclear silver complex showing monodentate and bidentate modes of coordination within the same complex [67]. Hence, the ligand can be manipulated to have different coordination modes depending on the procedure of synthesis and the metal ion involved. The comparison of selected bond lengths of complexes of this ligand are summarized in table 4.4 and the crystal packing diagram is shown in figure 4.2.

The molecular structure also confirms the extraction results obtained by this ligand in which it was assumed that the ligand metal complex formation ratio was 1:1. The



extraction of the metal ion when the ligand mole ratio was equal to that of the metal ion was about 95%, which was seen to drop to 46% when the ligand concentration was halved. Figure 4.1 shows the molecular structure of *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride.



**Figure 4.1:** The molecular structure and numbering scheme of *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride

**Table 4.2** Selected bond lengths of *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride.

Bond	Length(Å)	Bond	length(Å)
Au1 S6	2.2559(9)	O5 C6	1.198(4)
Au1 Cl4	2.2823(8)	O2 C9	1.375(4)
Au2 S5	2.2570(9)	O6 C6	1.373(4)
Au2 Cl3	2.2849(9)	O6 C24	1.466(4)
S5 C12	1.716(3)	C5 C25	1.508(5)
S6 C11	1.705(3)	C6 C25	1.511(5)
O1 C15	1.217(4)	C8 C18	1.523(5)
O3 C16	1.210(4)	C21 C23	1.520(5)
N4 C15	1.360(4)	C22 C13	1.518(5)
N4 C12	1.403(4)	C14 C18	1.528(5)
N5 C12	1.304(4)	C24 C20	1.531(5)
N5 C21	1.474(4)	C24 C27	1.543(5)
N5 C17	1.480(4)	C25 C26	1.556(5)
N6 C16	1.356(4)	C25 C27	1.556(5)
N6 C11	1.407(4)	C18 C28	1.548(5)
N7 C11	1.316(4)	C26 C20	1.545(5)
N7 C22	1.476(4)	C1 C27	1.525(5)
N7 C4	1.479(4)	C2 C28	1.517(5)
C15 C24	1.515(5)	O4 C9	1.198(5)
C16 C19	1.509(5)	C4 C7	1.518(5)
C17 C10	1.515(5)	C27 C29	1.527(5)
C19 O2	1.471(4)	C28 C9	1.516(5)



C19 C30	1.529(5)	C28 C31	1.533(5)
C19 C18	1.548(5)	C30 C31	1.558(5)

**Table4.3** Selected bond angles of *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride

Bond	Angle	Bond	Angle
S6 Au1 Cl4	172.72(3)	O6 C24 C20	105.3(3)
S5 Au2 Cl3	173.34(3)	N7 C22 C13	111.1(3)
12 S5 Au2	108.23(12)	C15 C24 20	114.9(3)
C11 S6 Au1	107.98(12)	O6 C24 C27	102.1(2)
C15 N4 C12	122.4(3)	C15 C24 27	118.6(3)
C12 N5 C21	121.7(3)	C20 C24C27	105.3(3)
C12 N5 C17	123.0(3)	C5 C25 C6	115.2(3)
C21 N5 C17	115.3(3)	C5 C25 C26	115.3(3)
C16 N6 C11	122.7(3)	C6 C25 C26	103.4(3)
C11 N7 C22	120.7(3)	C5 C25 C27	119.6(3)
C11 N7 C4	123.6(3)	C6 C25 C27	98.7(3)
C22 N7 C4	115.7(3)	C26 C25 27	102.2(3)
N7 C11 N6	116.4(3)	C8 C18 C14	109.5(3)
N7 C11 S6	121.8(3)	C8 C18 C28	114.2(3)
N6 C11 S6	121.8(2)	C14 C18C28	113.8(3)
N5 C12 N4	117.4(3)	C8 C18 C19	113.2(3)
N5 C12 S5	121.4(3)	C14 C18 19	113.7(3)
N4 C12 S5	121.2(2)	C28 C18 19	91.6(3)
O1 C15 N4	123.1(3)	C20 C26C25	104.6(3)
O1 C15 C24	121.0(3)	C24 C20 26	100.7(3)
N4 C15 C24	115.8(3)	N7 C4 C7	111.9(3)
O3 C16 N6	123.7(3)	C1 C27 C29	109.1(3)
O3 C16 C19	121.6(3)	C1 C27 C24	112.8(3)
N6 C16 C19	114.5(3)	C29 C27C24	114.7(3)

N5 C17 C10	110.9(3)	C1 C27 C25	113.5(3)
O2 C19 C16	109.5(3)	C29 C27C25	114.4(3)
O2 C19 C30	105.5(3)	C24 C27 25	91.6(2)
C16 C19 C30	112.9(3)	C9 C28 C2	113.4(3)
O2 C19 C18	101.5(3)	C9 C28 C31	104.0(3)
C16 C19 C18	120.9(3)	C2 C28 C31	114.9(3)
C30 C19 C18	104.9(3)	C9 C28 C18	98.6(3)
C9 O2 C19	105.7(3)	C2 C28 C18	120.1(3)
C6 O6 C24	105.8(2)	C31 C28C18	103.5(3)
O5 C6 O6	121.5(3)	O4 C9 O2	121.2(4)
O5 C6 C25	131.2(3)	O4 C9 C28	131.8(4)
O6 C6 C25	107.2(3)	O2 C9 C28	107.0(3)
N5 C21 C23	110.2(3)	C19 C30 31	101.0(3)
O6 C24 C15	109.2(3)	C28 C31 30	103.9(3)

**Table 4.4** Comparison of the relevant bond lengths in [Å] of nickel, copper, silver complexes with *N,N*-diethyl-*N'*-camphanoylthiourea, *N,N*-diethyl-*N'*-benzoylthioureatogold(I)chloride and *N,N*-diethyl-*N'*-camphanoylthioureatogold(I)chloride.

Complex	C-S	C(12)-N(4)	C(11)-N(6)	C-O	M-S	Reference
1. AuClSC <sub>12</sub> H <sub>16</sub> N <sub>2</sub> O	1.70	1.38	1.42	1.20	2.26	[19]
2. C <sub>15</sub> H <sub>24</sub> Au Cl N <sub>2</sub> O <sub>3</sub> S	1.71	1.36	1.36	1.21	2.26	This work
3. [Ni(L-S,O) <sub>2</sub> ]	1.72	1.36	1.32	1.26	1.87	[67]
4. [Cu(L-S,O) <sub>2</sub> ]	1.73	1.36	1.30	1.26	1.91	[67]
5. Ag <sub>2</sub> [(HL-S) (L-μ-S,O)] <sub>2</sub>	1.71	1.37	1.38	1.27	2.45	[67]

As can be seen from the table, the C-S, C-O in the gold thiourea complexes are almost the same but are longer in the Ni, Cu and Ag, which is due to the partial single bond character of the metal chelate ring [67]. Similarly, the C-N bonds are relatively



shorter in the same complexes compared to the gold ligand complexes. The metal sulphur bonds in the gold thiourea complexes are the same.

Comparing the bond angles between the *N,N*-diethyl-*N'*-benzoylthioureatogold(I) chloride and *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride the S-Au-Cl bond angle is 177.1 and 172.72 respectively.

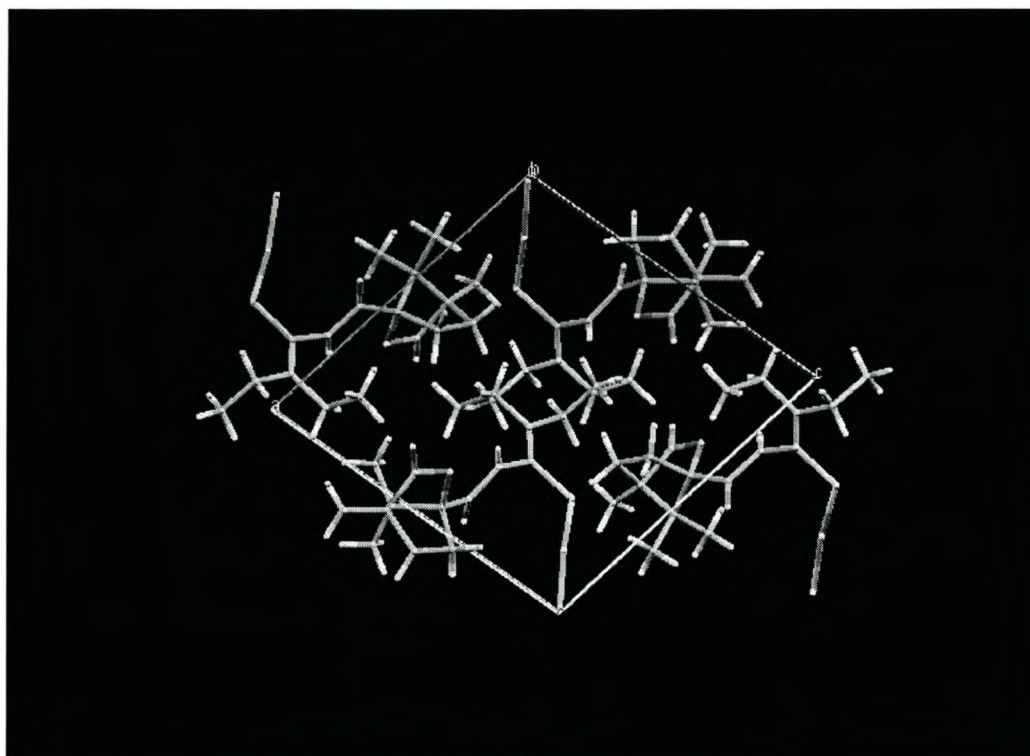


Figure 4.2 The crystal packing of *N,N*-diethyl-*N'*-camphanoylthioureatogold(I) chloride projected along the *c* axis.

## Chapter Five

### Conclusion and future work

One of the requirements, which plays a crucial role in membrane transport of metal ions, is moderately high formation constants of the metal ligand complexes formed. Gold thiourea complexes are known to have high formation constants, which have been determined potentiometrically [69]. These high formation constants of the metal thiourea complexes are probably the main reason for low or zero transport results in this study. Incorporating  $\text{CN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$  and perchloric acid into the receiving phase to help drive the metal into the receiving phase does not improve the transport results.

The liquid-liquid solvent extraction in the case of our work has revealed that these ligands are good for extraction but not for the transport of Au(III) ions. Ligands *N*-propyl-*N'*-4-heptoxybenzoylthiourea ( $\text{H}_2\text{L}$ ) and *N,N*-di-(2-hydroxyethyl)-*N'*-benzoylthiourea ( $\text{HL}^3$ ) were the best extracting ligands for Au (III). The high percentage extraction result in the former may be likely attributed to the increased lipophilicity brought about by the heptoxy group attached to the ring. Binding a second gold ion may probably be the reason for the high percentage extraction result of  $\text{HL}^3$ .

The di-alkyl-substituted thioureas have shown more affinity for gold than the monoalkyl-substituted thioureas. This is possibly due to the increased lipophilicity of the dialkyl thioureas imparted by the additional, alkyl group. Two of the monoalkyl ligands  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^3$  have shown experimental results which could be obtained by assuming a 1:1 metal to ligand mole ratio complexation on the formation of complexes. This may be supported by the drop of the metal ion percentage extracted to half when the ligand concentration was halved.

The electrochemistry of the metal thiourea complexes needs to be thoroughly examined. The reduction of Au(III) to Au(I) and Au(0) was observed in most of the ligands after 24 hours throughout the extraction and transport experiments, although the degree of reduction differs from one ligand to the next. Hence, the



electrochemistry of each ligand should be studied in future and the effect of the different substituents on the reduction behaviour of the ligands should be addressed. Some work has already been done [65] on the electrochemical behaviour of Au(III) with oxygen donor atoms although according to Pearson's principle of hard and soft acids, gold has a low affinity for hard donors like oxygen. These results showed that substituents like Cl<sup>-</sup> have more reducing character than the oxygen in hydroxyl groups in which more metal was reduced when the chlorides substitute the hydroxides. This effect has been described by mesomeric effects rather than induction effects only. Additionally, the methoxy groups have been known to have higher reduction potentials than the diacetates which has been described as methoxy groups being more prone to accept electrons than the diacetates. Bearing these facts in mind it will be worthy to study the electrochemical behaviour of the thiourea ligands with Au(III).

Finally, studying the electrochemical behaviour, stability constants and their full coordination chemistry, these ligands may be good candidates for the extraction of gold. The molecular structure of HL<sup>10</sup> with Au(III) shows that the Au metal is directly bonded to the sulphur atom and one chloride atom in a nearly linear fashion. This justifies the extraction results of the di-alkyl substituted thioureas. Not all the experimental results were however, explicable based on the extraction principles. It needs further studies on the electrochemistry and the x-ray diffraction studies of certain metal ligand complexes.

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## 6. Appendices

**Table 6.1: Atomic coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).  $U_{\text{eq}}$  is defined as one third of the orthogonalized  $U_{ij}$  tensor.**

	X	Y	Z	$U_{\text{eq}}$
Au1 Au	0.369911(12)	0.419688(7)	0.348558(12)	0.01823(3)
Au2 Au	0.160866(12)	0.580352(7)	0.126568(11)	0.01877(3)
Cl3 Cl	0.01710(8)	0.49102(5)	0.01107(8)	0.02113(18)
Cl4 Cl	0.52017(8)	0.50921(5)	0.45305(8)	0.02164(18)
S5 S	0.29838(9)	0.67801(6)	0.22069(8)	0.0245(2)
S6 S	0.22181(9)	0.32415(6)	0.26939(8)	0.0242(2)
O1 O	0.0586(2)	0.67592(15)	0.3845(3)	0.0294(6)
O3 O	0.4576(2)	0.31105(16)	0.1031(3)	0.0341(7)
N4 N	0.2490(2)	0.60958(16)	0.4318(2)	0.0158(6)
H4 H	0.2908	0.5676	0.4719	0.019
N5 N	0.3969(3)	0.71482(16)	0.4584(3)	0.0158(6)
N6 N	0.2687(3)	0.37809(16)	0.0483(3)	0.0167(6)
H6 H	0.229	0.4209	0.0086	0.02
N7 N	0.1159(3)	0.27679(16)	0.0375(3)	0.0171(6)
C11 C	0.2000(3)	0.3248(2)	0.1099(3)	0.0164(7)
C12 C	0.3172(3)	0.6685(2)	0.3803(3)	0.0171(7)
C15 C	0.1207(3)	0.6150(2)	0.4222(3)	0.0188(7)
C16 C	0.3935(3)	0.3662(2)	0.0477(3)	0.0196(7)
C17 C	0.4136(3)	0.7099(2)	0.5964(3)	0.0188(7)
H17A	0.5029	0.7243	0.6378	0.023
H17BH	0.3976	0.6532	0.6205	0.023
C19 C	0.4449(3)	0.4234(2)	-0.0375(3)	0.0195(7)
O5 O	0.1529(3)	0.37191(18)	0.6438(3)	0.0354(7)
O2 O	0.3496(2)	0.48718(16)	-0.0850(2)	0.0268(6)
O6 O	0.1555(2)	0.48016(14)	0.5180(2)	0.0210(5)
C5 C	-0.1177(3)	0.4146(3)	0.6464(3)	0.0263(8)
H5A H	-0.0798	0.4319	0.7327	0.04



H5B H	-0.1149	0.3548	0.6411	0.04
H5C H	-0.2067	0.4332	0.6225	0.04
C6 C	0.0959(3)	0.4268(2)	0.5831(3)	0.0230(7)
C8 C	0.5543(5)	0.5315(3)	0.1212(4)	0.0403(11)
H8A H	0.4766	0.5646	0.096	0.06
H8B H	0.6291	0.5675	0.1421	0.06
H8C H	0.5494	0.4985	0.1948	0.06
C10 C	0.3227(3)	0.7675(2)	0.6411(3)	0.0258(8)
H10A	0.2343	0.7525	0.6017	0.039
H10B	0.339	0.8238	0.6178	0.039
H10C	0.336	0.7636	0.7326	0.039
C21 C	0.4786(3)	0.7753(2)	0.4141(3)	0.0203(8)
H21A	0.4916	0.8233	0.471	0.024
H21B	0.4358	0.7943	0.3289	0.024
C22 C	0.0365(3)	0.2201(2)	0.0925(3)	0.0204(8)
H22AH	0.0828	0.2049	0.1785	0.024
H22B	0.0211	0.1695	0.0414	0.024
C13 C	-0.0907(3)	0.2589(2)	0.0974(3)	0.0269(8)
H13AH	-0.1343	0.2771	0.0131	0.04
H13B	-0.076	0.3059	0.1544	0.04
H13CH	-0.1442	0.2186	0.128	0.04
C14 C	0.6887(3)	0.4245(3)	0.0516(4)	0.0446(11)
H14A	0.6835	0.3897	0.1233	0.067
H14B	0.7625	0.4612	0.0753	0.067
H14CH	0.6984	0.3902	-0.0191	0.067
C23 C	0.6072(3)	0.7375(2)	0.4111(3)	0.0277(8)
H23AH	0.5945	0.6921	0.351	0.042
H23B	0.6481	0.7171	0.495	0.042
H23CH	0.6621	0.779	0.3854	0.042
C24 C	0.0569(3)	0.5386(2)	0.4577(3)	0.0180(7)
C25 C	-0.0432(3)	0.4515(2)	0.5586(3)	0.0203(8)
C18 C	0.5664(3)	0.4752(2)	0.0133(3)	0.0199(7)
C26 C	-0.0947(4)	0.4310(3)	0.4170(3)	0.0331(9)

H26A	-0.0736	0.374	0.3989	0.04
H26B	-0.1886	0.4383	0.3922	0.04
C20 C	-0.0262(4)	0.4924(3)	0.3469(3)	0.0298(9)
H20AH	0.0264	0.464	0.2963	0.036
H20B	-0.0878	0.5292	0.2918	0.036
C1 C	0.0477(3)	0.5814(3)	0.6804(3)	0.0295(8)
H1A H	-0.0027	0.5745	0.744	0.044
H1B H	0.0636	0.6398	0.6699	0.044
H1C H	0.1295	0.5527	0.7074	0
C2 C	0.6435(3)	0.5872(3)	-0.1295(3)	0.0282(8)
H2A H	0.6284	0.635	-0.0806	0.042
H2B H	0.6295	0.6023	-0.2184	0.042
H2C H	0.7317	0.5683	-0.0991	0.042
O4 O	0.3615(3)	0.6091(2)	-0.1759(3)	0.0540(10)
C4 C	0.0932(3)	0.2758(2)	-0.1012(3)	0.0216(8)
H4A H	0.1094	0.3311	-0.1312	0.026
H4B H	0.0026	0.2619	-0.1374	0.026
C27 C	-0.0257(3)	0.5460(2)	0.5557(3)	0.0191(7)
C28 C	0.5518(3)	0.5193(2)	-0.1146(3)	0.0205(7)
C7 C	0.1787(4)	0.2145(2)	-0.1468(3)	0.0264(9)
H7A H	0.1648	0.1599	-0.1152	0.04
H7B H	0.2684	0.2302	-0.1158	0.04
H7C H	0.1581	0.2137	-0.2389	0.04
C29 C	-0.1500(3)	0.5937(3)	0.5111(4)	0.0378(10)
H29A	-0.1303	0.6515	0.5008	0.057
H29BH	-0.2023	0.5888	0.5735	0.057
H29CH	-0.1972	0.5716	0.4305	0.057
C9 C	0.4146(4)	0.5479(2)	-0.1315(4)	0.0303(9)
C30 C	0.4694(4)	0.3807(3)	-0.1543(4)	0.0384(11)
H30AH	0.3885	0.3661	-0.214	0.046
H30B	0.5222	0.3309	-0.1321	0.046
C31 C	0.5433(4)	0.4487(2)	-0.2086(4)	0.0391(11)
H31AH	0.6296	0.4296	-0.2133	0.047



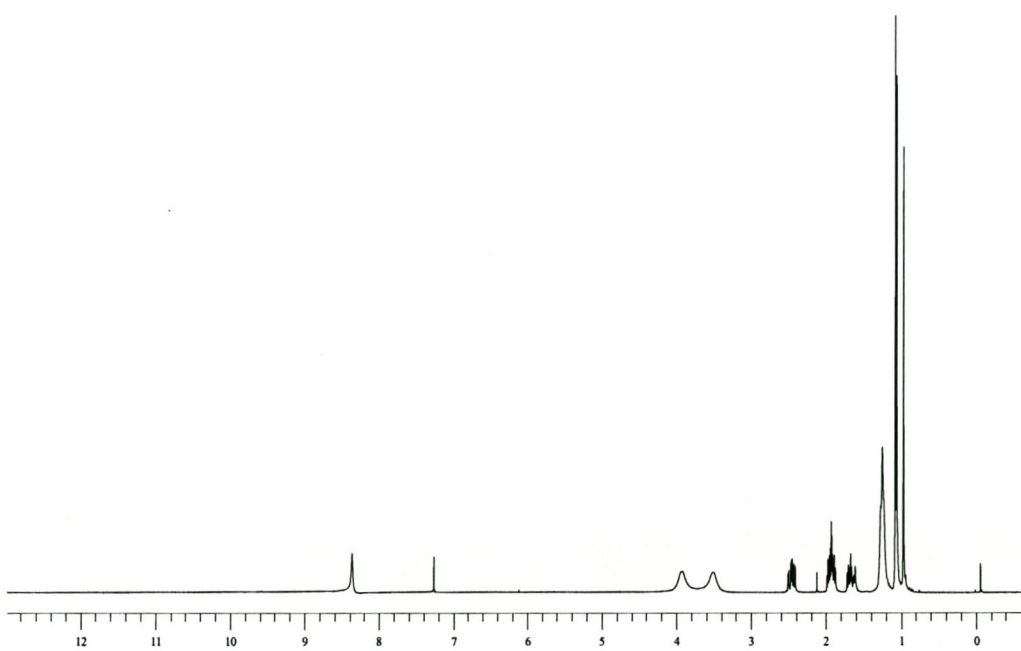
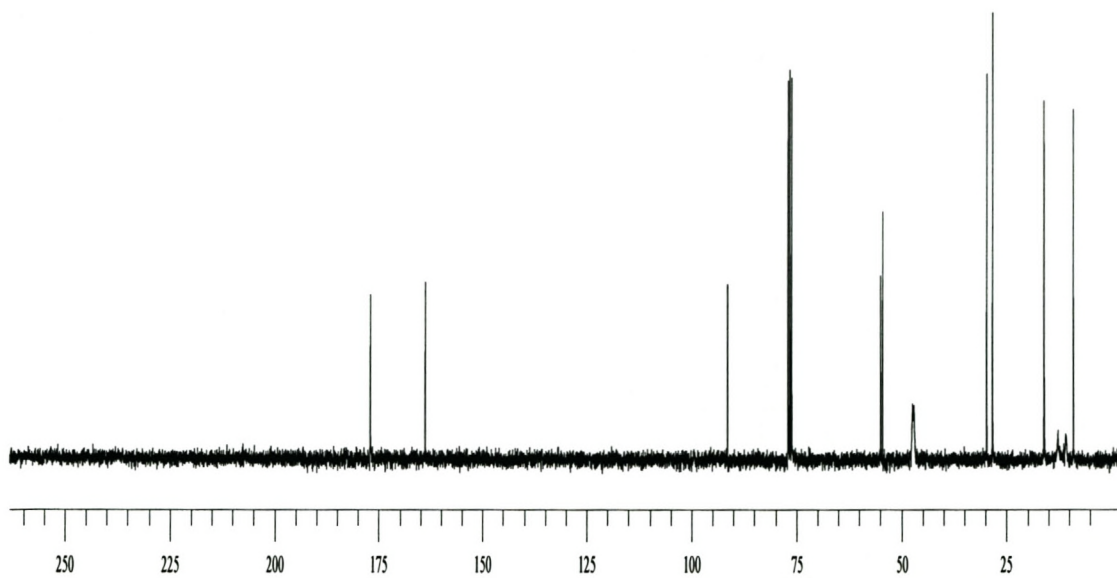
H31B    0.496            0.4656            -0.2935            0.047

**Table 6.2 Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ).**

	U11	U22	U33	U23	U13	U12
Au1	0.01817(6)	0.01915(7)	0.01728(6)	-0.00055(5)	0.00381(5)	-0.00033(6)
Au2	0.01721(6)	0.02132(7)	0.01702(6)	-0.00086(6)	0.00231(5)	-0.00101(6)
Cl3	0.0183(4)	0.0223(4)	0.0211(4)	-0.0025(3)	0.0011(3)	-0.0006(3)
Cl4	0.0199(4)	0.0220(4)	0.0216(4)	-0.0010(3)	0.0018(3)	-0.0024(3)
S5	0.0269(5)	0.0298(5)	0.0165(4)	0.0007(4)	0.0041(4)	-0.0114(4)
S6	0.0264(5)	0.0285(5)	0.0180(4)	0.0007(4)	0.0058(4)	-0.0095(4)
O1	0.0188(13)	0.0225(14)	0.0492(17)	0.0122(12)	0.0126(12)	0.0051(11)
O3	0.0251(14)	0.0305(15)	0.0514(18)	0.0203(13)	0.0189(13)	0.0126(12)
N4	0.0132(14)	0.0158(14)	0.0176(14)	0.0054(11)	0.0020(12)	-0.0010(11)
N5	0.0134(14)	0.0167(14)	0.0173(14)	0.0019(11)	0.0036(12)	0.0026(11)
N6	0.0147(14)	0.0146(14)	0.0213(15)	0.0039(11)	0.0052(12)	0.0009(11)
N7	0.0169(14)	0.0147(14)	0.0205(15)	0.0020(11)	0.0062(12)	-0.0030(11)
C11	0.0141(16)	0.0153(16)	0.0196(17)	0.0024(14)	0.0035(14)	0.0001(13)
C12	0.0148(16)	0.0150(16)	0.0222(17)	0.0027(14)	0.0060(14)	0.0035(14)
C15	0.0143(17)	0.0228(18)	0.0188(17)	-0.0009(14)	0.0029(14)	-0.0020(14)
C16	0.0202(18)	0.0184(18)	0.0207(18)	-0.0018(14)	0.0055(15)	-0.0029(14)
C17	0.0208(19)	0.0207(18)	0.0135(17)	0.0006(13)	0.0009(14)	0.0006(14)
C19	0.0182(16)	0.0207(16)	0.0198(16)	0.0015(16)	0.0047(13)	0.0003(16)
O5	0.0319(16)	0.0285(16)	0.0510(19)	0.0191(13)	0.0204(15)	0.0104(12)
O2	0.0138(13)	0.0303(14)	0.0344(14)	0.0162(12)	0.0014(11)	-0.0020(11)
O6	0.0171(12)	0.0185(12)	0.0306(14)	0.0076(10)	0.0122(11)	0.0052(10)
C5	0.0211(18)	0.032(2)	0.0283(18)	0.0056(18)	0.0094(15)	-0.0047(18)
C6	0.0249(18)	0.0211(18)	0.0262(17)	-0.0025(17)	0.0124(15)	0.0000(17)
C8	0.051(3)	0.049(3)	0.025(2)	-0.0114(19)	0.016(2)	-0.026(2)
C10	0.028(2)	0.0240(19)	0.0275(19)	-0.0018(16)	0.0099(17)	0.0007(16)
C21	0.0219(18)	0.0168(18)	0.0196(17)	-0.0001(14)	-0.0004(14)	-0.0077(14)
C22	0.0176(18)	0.0204(19)	0.0222(18)	0.0030(14)	0.0027(15)	-0.0070(14)
C13	0.0219(18)	0.030(2)	0.0294(19)	0.0037(17)	0.0076(16)	-0.0046(17)
C14	0.0185(19)	0.056(3)	0.059(3)	0.031(3)	0.0077(19)	0.006(2)

C23	0.0216(19)	0.031(2)	0.032(2)	0.0054(17)	0.0097(16)	-0.0058(16)
C24	0.0145(17)	0.0194(17)	0.0194(17)	0.0017(14)	0.0021(14)	0.0026(13)
C25	0.0185(18)	0.0227(18)	0.0208(18)	0.0005(14)	0.0068(15)	-0.0011(14)
C18	0.0157(17)	0.0241(18)	0.0202(18)	0.0041(14)	0.0048(14)	-0.0012(14)
C26	0.036(2)	0.039(2)	0.0234(18)	-0.0042(18)	0.0050(16)	-0.021(2)
C20	0.034(2)	0.036(2)	0.0184(18)	0.0021(16)	0.0021(17)	-0.0172(18)
C1	0.034(2)	0.0304(19)	0.0283(18)	-0.0082(19)	0.0152(16)	-0.0087(19)
C2	0.0220(18)	0.030(2)	0.0332(19)	0.0069(18)	0.0080(16)	-0.0051(17)
O4	0.0272(17)	0.053(2)	0.081(2)	0.0471(19)	0.0097(17)	0.0064(14)
C4	0.0234(19)	0.0210(18)	0.0190(17)	0.0021(14)	0.0021(15)	-0.0013(14)
C27	0.0125(17)	0.0216(17)	0.0240(18)	0.0024(14)	0.0055(14)	0.0013(13)
C28	0.0188(18)	0.0265(19)	0.0177(17)	0.0039(14)	0.0074(14)	-0.0030(15)
C7	0.029(2)	0.028(2)	0.0212(19)	-0.0027(15)	0.0024(16)	0.0007(16)
C29	0.0194(18)	0.043(3)	0.055(3)	0.021(2)	0.0177(18)	0.0083(18)
C9	0.020(2)	0.037(2)	0.033(2)	0.0158(18)	0.0046(17)	-0.0057(17)
C30	0.052(3)	0.036(2)	0.034(2)	-0.0145(18)	0.025(2)	-0.019(2)
C31	0.053(3)	0.042(2)	0.030(2)	-0.0093(18)	0.026(2)	-0.017(2)





$^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of *N,N*-diethyl-*N'*-camphanoylthiourea