

**Extraction and Recovery of Gold from both Primary and Secondary Sources by Employing
A Simultaneous Leaching and Solvent Extraction Technique and Gold Leaching In
Acidified Organic Solvents**

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By

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ABSTRACT

Gold extraction processes from both primary and secondary sources have changed little over the past centuries with cyanide remaining the preferred leach reagent used in 90% of gold mines, while aqua regia, which has been used for more than 1000 years, remains an unmatched gold leaching reagent for secondary sources. However, due to their extremely toxic nature, their continued use presents significant environmental risks and safety hazards for the work place. Therefore, considerable efforts have been made to find an alternative to cyanide and/or aqua regia, and variety of leaching reagents in aqueous media have been studied and proposed. Besides the reported leaching reagents in aqueous media, recently, a few preliminary investigations have also been done on non-aqueous solutions and in some cases, promising results have been achieved. However, among all reported leaching systems, none have been widely implemented on an industrial scale. The discovery of more efficient and benign gold extraction technologies is the main problem facing the gold industry today.

This thesis describes the discovery of two new recovery methods for selective extraction of gold from both primary and secondary sources which are promising for implementation on industrial scales. These two new methods are (i) simultaneous leaching and solvent extraction of gold and (ii) gold leaching in acidified water-miscible organic solvents. Gold recovery from gold ore by the simultaneous technique proved to be fast, efficient, and selective. In this method, the gold ore was contacted with a biphasic solution including an acidified aqueous phase and a water-immiscible organic solvent containing different derivatives of dithiobiuret-based ligands, and the resulting mixture was stirred for a short time to both leach and purify gold at the same time. It was demonstrated that the efficiency of this system was dependant on the concentrations of both acid and oxidizing agent in the aqueous phase, the type and concentration of ligand in the organic phase,

and the type of organic solvent. More than 94% of gold could be selectively extracted and recovered after 9 hours which was significantly faster than the current cyanidation process with 35 hours for just the leaching step.

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DEDICATION

I dedicate my dissertation work to my loving wife **Azhin Younesi**. A special feeling of gratitude to her who has been directly involved in any progress during my life with her great love and supports, and has never left my side over the last 8 years and has always been there during those difficult and trying times. I deeply appreciate all of what she has done for me since we have been in love.

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LIST OF ABBREVIATIONS

AAS	atomic absorption spectroscopy
aq	aqueous
AR	aqua regia
BFR	brominated flame retardant
β	complex stability constant
d	density
DBC	dibutyl carbitol
E-waste	electronic waste
E-scrap	electronic scrap
ICP-OES	inductively coupled plasma optical emission spectrometry
M	mol/lit
MIBK	methyl isobutyl ketone
org	organic
PCB	printed circuit board
ppm	part per million
RAM	random access memory
rt	room temperature
SX	solvent extraction
TBP	tributyl phosphate
TBPO	tributyl phosphine oxide
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction

CHAPTER 1

1. Introduction

1.1 Gold and Precious Metals

Gold belongs to the family of precious metals along with silver and the platinum group metals (platinum, palladium, osmium, rhodium, ruthenium and iridium). Precious metals are rare elements which are found in nature in metallic forms, as alloys, or in combination with sulfides, arsenides and other ores.¹ Gold and silver have been known and in use for millennia, while most of platinum group metals have been more recently discovered (since 500 years ago). Gold belongs to the same group of silver and copper in the periodic table with an average concentration of 0.005 ppm in the earth's crust, much smaller than silver and copper with 0.07 and 50 ppm concentrations respectively.² Besides their wide use in jewellery and decorative industries, precious metals have found some new applications in the past few decades due to their specific chemical and physical properties. For example, they are widely used in electronics, catalytic converters in automobiles, catalysis in chemical and petroleum refining industries, glass and aerospace industries, and medical science.³ Therefore, besides their natural sources, there is a viable source of recyclable precious metals, known as secondary sources.

1.1.1 Chemistry and Physical Properties of Gold

Like all of the precious metals, gold has a high density ($d = 19300 \text{ kg/m}^3$). Gold has an excellent conductivity for both electricity and heat without being tarnished when exposed to air and/or moisture. It is also the most ductile and malleable element and can thus be easily formed into extremely thin sheets or wires. All of these unique properties have made it an excellent candidate for jewelry and electronic applications.^{4,5} Gold has the lowest electrochemical potential among all metals in the periodic table which means in any cationic form it accepts electrons from almost any reducing agent to form metallic gold. It is also the most electronegative metal and has

high chemical and thermal stabilities. For instance, it is highly resistant against oxidation and corrosion and not affected by exposure to air, moisture, or most strong acids and bases.^{6,7}

1.1.2 Annual Production and Applications

The annual gold production in the mining industry was around 2500 tonnes in 2010 worldwide and it reached more than 3200 tonnes in 2015 (Fig. 1.1a) and expected to be the same for 2016. In addition, about 1200 tonnes of gold has been recycled from secondary sources like jewelry, electronic scraps, dentistry, and anode slime in 2015.⁸ Recycling gold from these secondary sources can substantially reduce gold extraction from virgin ores and extend the life of natural sources. Fig. 1.1b shows the main applications of gold in different areas.⁸ The majority of the produced gold (more than 50%) is used in the jewellery industry. Desirable features of gold including very high luster, attractive yellow color, tarnish resistance, and its ability to be drawn into different shapes make it highly suitable for manufacturing jewelry goods.^{5,8} However, pure gold is too soft to withstand against the applied stresses to many jewelry items, therefore it is alloyed with other metals such as copper, silver, palladium, and platinum to increase its durability. Thus, most gold which is used to make jewelry products is an alloy with one or more other metals.⁹

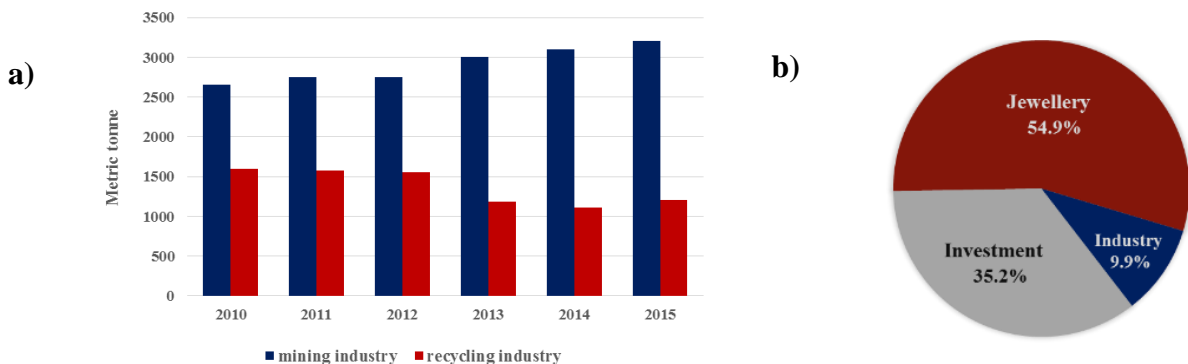


Figure 1.1⁸ a) Annual gold production in mining and recycling industries since 2010 to 2015 and b) gold applications.

Because of its high value, more than one third of the annually produced gold is used as investment and it is usually kept or traded in different forms of coins and bars. The other 10% of gold has some industrial applications of which the most important one is in the electronic industry.⁸ It also has some applications in medical sciences, dentistry and aerospace industries.

1.2 Gold Mining Industry

The average concentration of gold in the Earth's crust is 0.005 ppm and ore deposits with concentration of 0.5 ppm or higher are considered to be economically recoverable in gold mines. In other words, a minimum upgrading by a factor of 100 is required during ore formation processes in nature to reach commercial concentrations.² The current annual gold production in the mining industry is around 3200 tonnes worldwide, and Canada produces 160 tonnes per year which is the 5th largest gold producer in the world. On the other hand, more than 75% of gold companies are headquartered in Canada which has made the gold mining industry one of the major businesses in the country.⁸ Gold mineralogy and the whole recovery process starting from crushing and grinding till producing the final pure gold product will be discussed in detail in the following sections.

1.2.1 Gold Minerals and Ores

The characteristics of an ore deposit and the assemblies of its minerals determine the requirements for its extraction and recovery processes. Therefore, a good understanding of the ore mineralogy is necessary to design an optimum gold recovery process.

1.2.2 Gold Minerals

Since gold is an inert element at ambient temperatures and pressures, there are just a few minerals of the metal in nature. It usually has a tendency to concentrate with some other metals or sulfide minerals, as those rocks that are high in clays and low in carbonates are the best hosts for

gold. Native gold, which has also been known as gold nuggets, is one of the main gold minerals which can contain up to 99.8% Au, but usually its gold content is between 85% and 95%, with silver being the main impurity. Native gold can readily be recovered by gravity concentration techniques as it has a density of 15000 kg/m³ or higher, much denser than most common gangue minerals (e.g., quartz and silicates) with densities between 2700 to 3500 kg/m³. When the silver content of the gold mineral increases to 25-55%, it is called electrum. It has a light yellow color and a lower density (i.e., 13000 to 16000 kg/m³) than native gold.

Gold tellurides are another source of gold minerals with a density of 8000 to 10000 kg/m³. There are some other gold minerals which rarely occur in nature like those which are found with bismuth and copper. Gold as ultrafine solid particles can also occur in some sulfur minerals like arsenopyrite, pyrite, tetrahedrite, and chalcopyrite.^{2,10}

1.2.3 Gold Ores

The gold ore deposits are generally divided into two main categories; i) non-refractory ores which can directly be treated by the cyanidation process, and ii) refractory ores which need to be pretreated prior to leaching with cyanide.

1.2.3.1 Non-Refractory Ores

Non-refractory ores are those kind of gold deposits which can be directly (with or without crushing and grinding) treated with the cyanidation process, and in most cases more than 90% gold recovery is achieved.¹¹ The followings are the most common types of non-refractory ore deposits.

1.2.3.1.1 Placers

Placer gold ores are formed through gold liberation by some natural processes like weathering and hydraulic transportation of gold particles far from their original deposits. As the

gold has been liberated to a large extent, placer deposits do not usually need crushing and grinding prior to the leaching step. The gold concentration in placer ores is usually low, however, due to low capital and operation costs, they are often significant primary gold sources. Most of the gold placers have been already mined (especially in the 19th century), and today, the contribution of placer gold to annual gold production is estimated to be 2 to 5%.¹²

1.2.3.1.2 Free-Milling Ores

Free-milling ores are those types of gold deposits in which almost 95% of their gold content is extracted by cyanidation leaching (without a significant increase in reagent consumptions) when 80% of the ore particles are ground to less than 75 µm. Because the gold particles are unliberated and associated with other minerals, crushing and grinding is required to release the gold to a degree that allows effective gold extraction. However, the gangue minerals composition does not significantly affect the processing requirements, and usually some of the gold is recovered by gravity concentration prior to the cyanidation process. The gold grade is relatively high (5 to 15 g/t) in this type of ores, and they usually contain low concentrations of sulfide minerals. This type of ore is considered as a significant source of gold production in the mining industry.^{2,13}

1.2.3.1.3 Oxidized Ores

In an oxidized ore, the ore material has been oxidized to a high degree, leading to the breakdown of rock structure and increase in permeability. This usually leads to a high extraction efficiency by heap leaching, even in the case of large ore particles. However, in some cases, due to the presence of considerable amounts of some gangue minerals like poorly crystalline silica, clay minerals, sulfate salts, and other oxide compounds, the cyanide consumption increases significantly as some of these minerals have relatively high solubility in cyanide leaching solutions

due to their extremely large surface areas. Gold occurs either liberated (the degree of gold liberation is increased by oxidation) or usually associated with some iron oxides, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), and goethite (FeOOH).^{2,14}

1.2.3.1.4 Other Non-Refractory Ores

Silver rich gold ores are another type of non-refractory gold deposits which contain relatively high silver content (>10 g/t), and in some cases, the extraction process needs to be modified, especially the leaching and recovery steps. There are some other types of gold ores which contain some sulfide minerals, and they are classified as non-refractory ores if the gold particles are not captured inside the sulfide matrix and the presence of the sulfide minerals does not affect the extraction process.^{2,14}

1.2.3.2 Refractory Ores

These kind of ores are characterized by low gold recoveries and high reagent consumption (both cyanide and oxygen) when exposed to direct cyanidation leaching, due to one of the following reasons:

- a.** Gold particles are encapsulated in some gangue minerals, usually sulfides, and not able to be effectively liberated, even by fine grinding.
- b.** Gold occurs with those minerals that consume significant amounts of both oxygen and cyanide.
- c.** Gold is associated with carbonaceous materials which adsorb dissolved gold during leaching process.
- d.** Any combination of a to c.¹¹

The followings are some major refractory gold ores.

1.2.3.2.1 Sulfide Ores

As gold has a high affinity for sulfur, it is usually found in nature with some sulfur minerals such as iron sulfides, arsenic sulfides and copper sulfides. In the case of iron sulfides, gold is mostly unliberated in an iron sulfide matrix, or the behavior of the iron mineral(s) affects the gold extraction process. The major iron sulfide minerals are pyrite (FeS_2), marcasite (FeS_2), and pyrrhotite (Fe_{1-x}S where $x = 0.0$ to 0.2). Pyrite is a very common mineral in nature with a yellow color and metallic luster, and due to its high standard reduction potential, it stays unreacted in cyanide aqueous solutions. Therefore, the captured gold minerals in pyrite necessitate improved grinding and/or stronger oxidizing environment to liberate the gold particles. On the other hand, this unreactivity is a benefit as reagent consumptions are not increased during the leaching step.^{15, 16} Marcasite (FeS_2) has the same composition of pyrite, but in a different crystalline form (polymorphs). It is less common than pyrite, but it is decomposed easier in aqueous solutions. Marcasite is usually a major consumer of both cyanide and oxygen in the cyanidation process, and needs to be treated before the leaching step. Pyrrhotite is another iron sulfide compound which can associate with gold minerals in nature. Like marcasite, it can be oxidized in cyanide solutions and can be a significant cyanide and oxygen consumer.¹⁷

After pyrite, arsenopyrite (FeAsS) is another common sulfide host for gold which its gold content is significantly higher than pyrite and is more fragile too. There are some other types of arsenic sulfides like orpiment (As_2S_3) and realgar (As_2S_2) which have very minor importance in the gold mining industry.¹⁵

Copper sulfides are another types of sulfide minerals which can be associated with gold, however it is not common for gold to be found in association with just copper minerals, and usually some pyrite presents as well. Chalcopyrite (CuFeS_2) is the most common copper mineral in nature

and because the gold content of copper minerals is too low, gold is generally produced as a by-product of copper in copper mines. Chalcocite (Cu_2S) and covellite (CuS) are another important copper ore minerals which in some cases can contain gold.¹⁸

1.2.3.2.2 Carbonaceous Ores

This kind of ore contains carbonaceous components which adsorb the dissolved gold during leaching step, resulting in a significant decrease of gold extraction by cyanidation process. Although the exact nature of the carbonaceous compounds is not well understood, but in most cases they include hydrocarbons, humic acid, and activated elemental carbon which can adsorb gold from the cyanide leach solution. In some cases, a carbon content of just 0.1% may causes a preg-borrowing (a reversible adsorption of gold from the leaching solution) or preg-robbing (an irreversible adsorption of gold from the leaching solution) properties.¹⁹

1.2.3.2.3 Other Refractory Ores

Antimony sulfides can be associated with gold and affect the leaching conditions significantly. Aurostibnite (AuSb_3) and stibnite (Sb_2S_3) are the most common antimony minerals which can be found in some gold ores. Gold tellurides are another class of refractory ores and usually contain some native gold along with other metal tellurides. Calaverite (AuTe_2) is an example of gold telluride which can be found in some gold deposits.^{2,20}

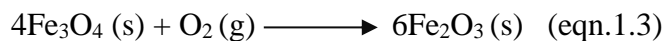
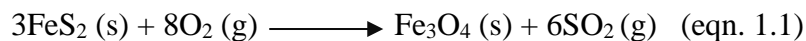
1.2.3.2.4 Pretreatment of Refractory Ores Prior to Cyanidation Leaching

Oxidative processes are the most common used techniques as a pretreatment for refractory ores to enhance the efficiency of gold extraction by the standard cyanidation process. The oxidation pretreatment is required if an unacceptable gold recovery is achieved by direct treatment with cyanide or the leaching process is uneconomical. In the case of sulfide ores, oxidation might

be needed to dissolve some or all of the sulfide components in order to expose gold minerals, and/or to form a passivation layer on their surfaces to prevent excessive consumption of leaching reagents.²¹ Oxidation pretreatment is also applied to carbonaceous ores to passivate the active surface of the carbonaceous materials to avoid adsorption of leached gold or to completely destroy them.²² Both hydrometallurgical and pyrometallurgical oxidation methods are applied to refractory ores in the mining industry. The most common methods include roasting, pressure oxidation, chlorination, and bio-oxidation.^{23,24}

In the absence of an oxidizing reagent and under ambient conditions, most sulfide minerals are highly stable and decompose very slowly in aqueous solutions over a wide range of pH. However, by adding an appropriate oxidizing agent like nitric acid, chlorine, or oxygen (under pressure), they can be readily decomposed.

Roasting in the presence of air or oxygen is the most common pretreatment method for oxidation of both refractory sulfide and carbonaceous ores. The main goal is converting iron sulfide minerals to porous iron oxides in which the gold is liberated, and the reagent consumption will also be minimized.²⁵ This method can be accomplished using a single (direct roasting of the material in an oxidizing environment) or two-stage (a first stage of operating under reducing conditions, followed by roasting under oxidizing atmosphere) processes. For example, pyrite, marcasite, and pyrrhotite are directly oxidized at 600 °C to magnetite and hematite under an oxidizing environment as follows:



An alternative option for pyrite is roasting under reducing conditions (in sulfur and sulfur dioxide-rich atmosphere) in which pyrite decomposes to pyrrhotite and sulfur in the first step (eqn. 1.4), followed by reaction under an oxidizing environment (eqn. 1.2).

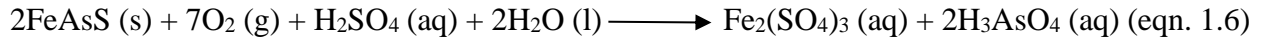


It is known that the two-stage process can produce a spongy, more porous product with a higher surface area compared to the single stage roasting method. In the case of arsenopyrite, the two-stage process is more favored as it is decomposed to pyrrhotite and elemental arsenic in the first stage (eqn. 1.5), and then can easily be converted to magnetite and arsenic trioxide in the second step.^{2,26}



Most of organic carbons in carbonaceous ores can be converted to carbon dioxide during the roasting process, resulting in losing their gold adsorption properties. The ideal temperature range during the roasting process is between 450–700 °C as at temperatures below 450 °C, the rate of sulfide mineral decomposition is very slow, and at temperatures higher than 700 °C, the porous iron oxide may capture gold particles, resulting in lower gold recovery (this phenomenon is often called “sintering”).^{2,26}

In recent years, pressure oxidation has been more popular in the industry instead of the traditional roasting methods due to both environmental reasons and higher gold recovery. Refractory sulfide ores are treated in autoclaves, usually under acidic conditions (including >0.1 M H₂SO₄) at high temperatures (100–210 °C) and pressures (700–2200 kPa).²⁷ Arsenopyrite for example can be decomposed as the following reaction during the pressure oxidation pretreatment:²⁸



Pressure oxidation can be accomplished in nonacidic media too, using similar conditions of temperatures and pressures to the acidic process, but under neutral or slightly basic pH. This process is suitable for the treatment of those refractory ores which contain large amounts of acid-consuming carbonates and low sulfide minerals and are therefore less appropriate to acidic oxidation pretreatments.²

Chlorination is another pretreatment method which is more suitable for carbonaceous gold ores to deactivate their preg-robbing or preg-borrowing properties.²⁹ Refractory ores with minor amounts of carbonaceous materials (usually less than 1%) can be treated effectively by adding a suitable surfactant like kerosene, and diesel oil to the ore prior to the cyanidation leaching (this process is sometimes termed “blinking” or “blinding” of the carbonaceous ores).² The ores with higher degree of carbonaceous components must be treated with chlorination (or roasting) for effective pretreatment before the leaching step. An aqueous solution including small amounts of chlorine gas is usually applied at 50 °C with pH being between 3 and 5, and the surface of the organic carbons are typically converted to mainly carboxyl groups (COOH). The formed carboxyl groups then can be deprotonated in cyanide alkaline solutions resulting in repelling the negatively charged $\text{Au}(\text{CN})_2^-$ ions. Due to high amounts of chlorine consumption, chlorination is not an appropriate pretreatment method for sulfide-bearing refractory ores, as ores including just 1% sulfide sulfur (~ 2% of pyrite) for example will consume 82 kg/t of Cl_2 .²

Some types of microorganisms like *Thiobacillus thio-oxidans* and *Thiobacillus ferro-oxidans* are able to catalyse mineral oxidation reactions during biological oxidation. These naturally occurring bacteria can effectively be used for pretreatment of the gold-bearing sulfide ores and concentrates, and they usually operate at near ambient temperatures (35°C - 45°C) and

within a pH range of 1.0 to 1.8. There are some other types of bacteria (e.g., *Sulfobacillus acidophilus*, *Sulfolobus*, etc) which can survive at even higher temperatures and have been applied increasingly to reach faster rates of oxidation in commercial systems.³⁰

Among different pretreatment methods, bacterial oxidation is the only process which can be operated to achieve controlled partial oxidation of sulfide minerals, leading to a significant decrease of the required oxygen and heat, and producing less acid, all of which can have substantial benefits. However, its practical application is limited to a few special ore types that have acceptable porosity and optimal sulfide content that are capable of sustaining bacteria through the oxidation cycle.²

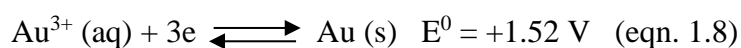
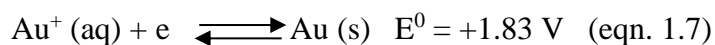
1.2.4 Gold Leaching

Metallic gold is highly resistant to oxidation and corrosion and usually harsh conditions are required for its fast dissolution. In the context of gold extraction, the process of gold (or any other metal) dissolution and its extraction from ore is called the leaching step in which metallic gold is oxidized and converted to a water-soluble complex by reacting with an appropriate ligand.³¹ Only a limited number of ligands can effectively react with gold and form stable soluble complexes. In the following section, common leaching reagents for gold are reviewed and their dissolution chemistry briefly discussed.

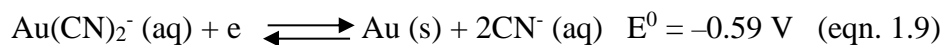
1.2.4.1 Cyanidation Process

For more than a century cyanidation has remained the dominant process for leaching and extraction of gold from ore,³² and every year more than 13% of the total produced cyanide is used in the gold mining industry. Cyanide is comprehensively used in gold mines as it is fairly cheap, highly efficient for gold leaching, and relatively selective for gold over base metals.³³ It is the only

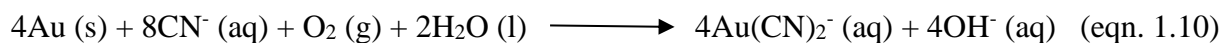
leaching reagent which can extract gold economically from the gold ores with extremely low gold content such as 0.5 gram per tonne. And because it has been used for a long time, its chemistry has extensively been studied. Metallic gold is highly resistant to oxidation, and in the absence of a ligand, the reduction potentials are extremely high for both Au(I) and Au(III) in water (eqn. 7 and 8).



However, gold can be readily oxidized and dissolved in an alkaline solution of potassium or sodium cyanide³⁴ (eqn. 1.9).



Although metallic gold is not oxidized with oxygen from the air, but in the presence of cyanide it is readily oxidized to Au(I) ($E^0 = -0.59 \text{ V}$) and forms a highly stable complex of dicyanoaurate, $\text{Au}(\text{CN})_2^-$, with β_2 of 2×10^{38} (β_2 represents the stability constant for complex ion $\text{Au}(\text{CN})_2^-$) because free cyanide ion is a strong σ -donor and very good π -accepter ligand which can form highly stable complexes with gold. The overall dissolution reaction in the presence of dissolved molecular oxygen has been shown in equation 1.10.³⁴



This reaction needs to be accomplished in basic conditions because over 99% of the cyanide will be converted to highly poisonous HCN gas in neutral or acidic environments, but by increasing pH it is converted to free cyanide ion, so that at pH of 9.3, CN^- and HCN are in equilibrium with 50% of each present, and at pH of 11 or higher, more than 99% of the cyanide remains in solution

as CN^- .³⁵ With stoichiometric ratios, gold dissolution in alkaline cyanide solution is extremely slow, but by increasing the cyanide concentration, the leaching rate will increase until a maximum is reached with 0.1% w/w of NaCN, and after that the rate of dissolution remains constant.³⁶ Indeed, at optimal concentration of cyanide, the amount of dissolved oxygen in solution is the rate limiting factor, and due to the low solubility of oxygen in aqueous solution (8.2 mg/L), the rate of gold dissolution is still slow ($4.6 \text{ gm}^{-2}\text{h}^{-1}$) with even high concentration of cyanide. Providing more oxygen under pressure can increase the rate of gold dissolution, as the maximum rate of $120 \text{ gm}^{-2}\text{h}^{-1}$ can be achieved by increasing the amount of dissolved O_2 to 32 mg/L.³⁷ Increasing temperature can also increase the gold dissolution kinetics, and the highest rate can be reached by elevating the temperature from 25 °C to 85 °C (Fig 1.2).^{2, 36} However, increasing temperature to more than 85 °C has a negative effect as the amount of dissolved oxygen will be significantly decreased. Before cyanide treatment, the gold ore is crushed and ground to decrease the size of ore particles to 75 microns or less, to provide a larger contact surface area between gold and the leaching solution, and/or in some cases, the gold particles need to be liberated from some minerals which have been encapsulated in their crystal structures. In the case of actual gold ores, the cyanide consumption varies from about 0.25 to 2 kg per tonne of ore, and the rate of gold dissolution in

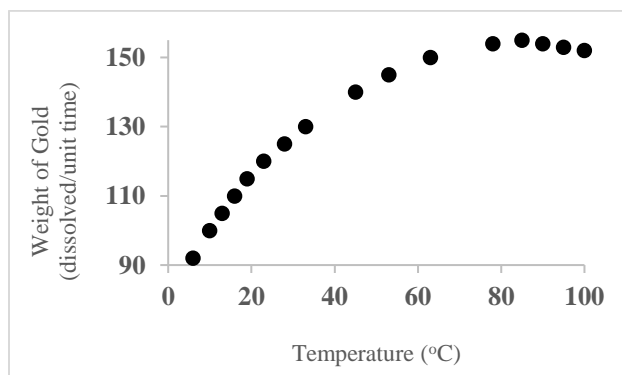


Figure 1.2.³⁶ Effect of temperature on the rate of gold dissolution (0.25% KCN solution).

cyanide solutions takes 16 to 48 hours.³⁶ During the cyanidation process, usually more than 90% of gold is extracted in the case of non-refractory ores. By increasing the refractoriness of gold ores, the percentage of extracted gold decreases while the cyanide consumption will increase. For example, copper minerals such as chalcocite and cuprite can form a variety of cyanide complexes such as CuCN , $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ and iron sulfides like pyrrhotite, pyrite and arsenopyrite form highly stable $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ complexes.³⁸ In addition, most of sulfide minerals have detrimental effects on gold leaching since they passivate the surface of gold and consume both cyanide and oxygen.³⁹ However, some other minerals such as galena (PbS) can improve gold leaching kinetics by preventing formation of a passivation layer on the gold surface.³⁷

Intensive cyanidation process is another type of cyanide leaching which is usually applied to higher-grade materials such as flotation and gravity concentrates. In this case, high reagent concentrations of both cyanide and oxygen are applied at often elevated temperatures and/or pressures to reach high rates of gold dissolution. The cyanide concentration of 5 to 25 kg/t (0.5% to 2.5% NaCN) is applied in practice under high temperature and pressures, and typically more than 97% gold extraction is reached in less than 24 hours.²

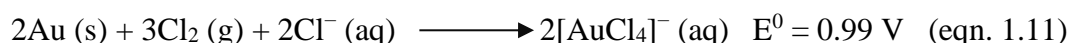
1.2.4.2 Alternative Leaching Reagents to Cyanide

Although cyanide is still the main leaching reagent for gold recovery in the mining industry, it suffers from several drawbacks, such as extremely high toxicity, slow leaching kinetics, and low gold extraction for refractory ores.^{34,40-41} In addition, due to some accidents and severe environmental regulations, the use of cyanide has been banned in some countries and there is a worldwide quest to find more suitable alternatives.⁴² For these reasons, considerable efforts have been made to find alternative leaching reagents to cyanide. Some of the best reported leaching

reagents are chlorine, thiosulfate, thiocyanite, thiourea, chloride/hypochlorite, and halogen based leaching reagents.

1.2.4.2.1 Chlorination

Gold leaching with chlorine in aqueous media is one of the known methods to dissolve gold effectively, and prior to the cyanidation process, chlorination was applied widely in the 19th century for the treatment of gold ores in gold mines.⁴³ An aqueous solution of chlorine gas with hydrochloric acid can provide a suitable media for gold dissolution in which metallic gold will be dissolved and form a stable complex with chloride (AuCl_4^- , $\beta_4 = 1 \times 10^{26}$) as follows:



Chlorine is one of the most suitable oxidants for gold, because besides being a strong oxidizing reagent, it also provides chloride ions for gold dissolution. At HCl concentration of less than 0.01 M, chlorine is decomposed to hypochlorous acid as the following reaction:

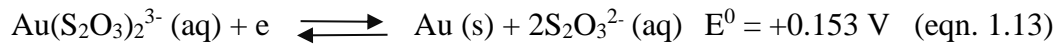


The generated HOCl is still a strong oxidizing reagent which can readily dissolve gold at the presence of appropriate amount of chloride ions.⁴⁴ In practice, the rate-determining step is the mass transport of chloride ions to the surface of gold, and because the solubility of chlorine in aqueous media is higher than oxygen, a higher rate of gold dissolution can be reached in chlorine leaching compared to cyanide ($33 \text{ gm}^{-2}\text{h}^{-1}$ in 1M HCl with 2mM Cl_2 at 12 °C).⁴⁵ By increasing the concentration of chlorine-chloride ions, much faster rates of gold dissolution can be obtained, and both HCl and NaCl can provide the required Cl^- ions in the solution. Except for silver and lead, most of the base metals (like iron, copper, and zinc) can dissolve in chloride media which can increase the reagent consumptions and decrease the selectivity of the process. The chlorination

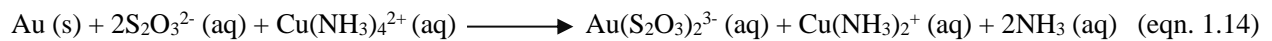
process is not used in the industrialization of gold production anymore due to relatively high reagent consumptions, challenges with corrosion–resistance of construction materials, handling problem of the chlorine gas, and some difficulties during gold recovery from chloride media.²

1.2.4.2.2 Thiosulfate Leaching

Thiosulfate is the most studied alternative leaching reagent to cyanide.⁴⁶ Gold can be oxidized and dissolved in an alkaline aqueous solutions of thiosulfate (eqn. 1.13) in the presence of an oxidizing agent like O₂ and copper(II) ions, forming a stable complex with β₂ of 5×10²⁸.



The rate of gold dissolution becomes slower in the absence of copper(II) ions.⁴⁷ Indeed, copper(II) can be maintained at a higher concentration in thiosulfate solution compared to dissolved oxygen, leading to a faster oxidation of metallic gold in this medium. Ammonia is also used to accelerate the rate of gold leaching in this media. It has an efficient role to stabilize the intermediate oxidation products of gold, preventing the formation of insoluble components like sulfides on the gold surface, keeping a high concentration of Cu²⁺ by forming Cu(NH₃)₄²⁺ during the leaching process, and preventing the formation of Cu(OH)₂.^{48,49} Oxygen has a dual role by oxidation of Cu⁺ to Cu²⁺ to complete the redox cycle and regenerate the oxidant, and/or direct oxidation of the gold surface. The overall balanced equation of gold dissolution in thiosulfate media has been shown in the following reaction:⁵⁰



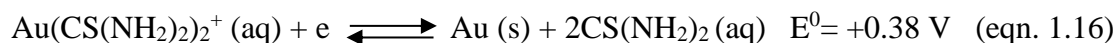
Thiosulfate leaching is typically carried out between pH 9 and 11. When pH is below 9, the Cu(I) triamine complex (Cu(NH₃)₃⁺) becomes predominant, making the copper species less effective as a catalyst during the gold leaching process. On the other hand, in highly alkaline

solutions, the stable $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ complexes are decomposed to gold hydroxide species. Thiosulfate concentrations of 0.05 to 2.0 M have been applied in practice for thiosulfate leaching system, and both sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) and ammonium thiosulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_3$) have been used with ammonium thiosulfate being more favoured as it can provide some of the required ammonia. The applied concentrations of copper and ammonia ranges from 0.0001 to 0.02 M, and 0.2 to 4 M respectively. Compared to the cyanidation process, thiosulfate leaching has some advantageous such as faster leaching kinetics ($27 \text{ gm}^{-2}\text{h}^{-1}$),⁵¹ lower toxicity, and higher gold recovery in the case of some refractory gold ores.⁵² However, it suffers from some major drawbacks, like complex chemistry, toxicity of used ammonia, ineffectiveness of activated carbon for adsorption of leached gold, thiosulfate oxidation to polythionates (for example, the decomposition products of polythionates can lead to the formation of elemental sulfur and CuS which may passivate the gold surface), and high consumption of thiosulfate. For example, in the latter case, the copper(II) itself consumes thiosulfate, resulting in high consumption of both thiosulfate and copper and gold passivation during the leaching process (reaction 1.15).^{53,54}



1.2.4.2.3 Thiourea

Thiourea is another promising leaching reagent which can dissolve gold in acidic media (pH of 1.4 to 1.8) in a relatively low potential and β_2 of 2×10^{23} .^{55,56}



The rate of gold dissolution with oxygen is slow, however, by using stronger oxidants like hydrogen peroxide, sodium peroxide, ozone and ferric ion, much higher gold dissolution rates will

be obtained. Among different oxidizing reagents, ferric ion shows the highest efficiency (eqn. 1.17).⁵⁷

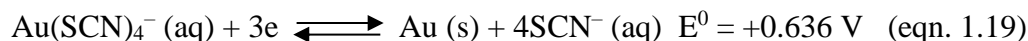
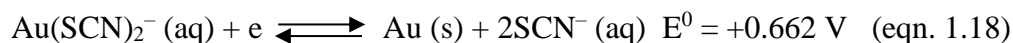


However, thiourea is not stable in the presence of most of oxidizing reagents and is oxidized very quickly during the leaching process.⁵⁸ Even in the presence of ferric ions in acidic media, thiourea can be decomposed to formamidine disulfide and then to elemental sulfur and cyanamide.⁵⁹ And, in the case of gold leaching from gold ores, it has been reported that the rate of thiourea decomposition is even faster, as potential and pH are more difficult to control during the leaching process. In addition, the presence of some minerals accelerates the rate of thiourea decomposition. For example, copper has a deleterious effect on consumption of thiourea and gold-leaching kinetics, as it not only oxidizes thiourea, but can also catalyse the oxidation of thiourea by ferric ions.⁵⁸ Addition of a reducing agent such as SO_2 , Na_2SO_3 , or $\text{Na}_2\text{S}_2\text{O}_5$ decreases the thiourea consumption by preventing its oxidation with Fe^{3+} ions.⁶⁰ The kinetics of gold leaching in thiourea solution is faster than the cyanidation process ($17 \text{ gm}^2\text{-h}^{-1}$) because of nongaseous ferric sulfate oxidants which have been used instead of oxygen which is the main oxidizing reagent in the cyanidation process.⁵¹ However, gold recovery and reagent consumption with cyanide is more economical than thiourea.⁶¹ Indeed, most of the other metals can also be dissolved in thiourea solution and form relatively stable complexes during the gold leaching process. This complexation with the other metals along with thiourea decomposition lead to high reagent consumption during the leaching process.⁵⁸ For optimized conditions, thiourea consumptions of 1 to 4 kg/t have been expected in practice, however, it can also be as high as 10 to 50 kg/t depending on different ore types. It has been shown that the addition of around 2.5 kg/t sodium sulfite (Na_2SO_3) to thiourea leach solutions can be beneficial by reducing thiourea consumption and increasing the rate of gold

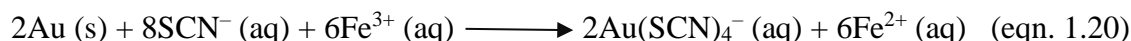
dissolution.⁶² Thiourea's commercial application has been hindered due to its high consumption and no existence of applicable industrial techniques for the recovery of gold from its solution. Although, thiourea has a lower toxicity compared to cyanide, it is suspected to be a carcinogen agent and must be treated with caution.²

1.2.4.2.4 Thiocyanate

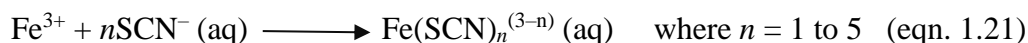
In acidic media, gold dissolves in an aqueous solution of thiocyanate (SCN^-)⁶³, and depending on the solution potentials, both stable Au(I) and Au(III) complexes can be formed (eqn. 1.18 and 1.19). Between these two complexes, $\text{Au}(\text{SCN})_4^-$ is more stable with β_4 of 1×10^{42} compared to β_2 of 1.3×10^{17} for $\text{Au}(\text{SCN})_2^-$.⁶⁴



In the presence of oxygen from the air, the rate of gold dissolution is extremely slow, but by adding a suitable oxidant like Fe^{3+} , the kinetics of gold dissolution improves significantly.⁶⁵ The following reaction shows the whole equation for gold dissolution in thiocyanate solution:

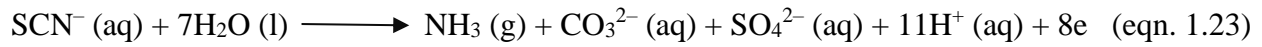
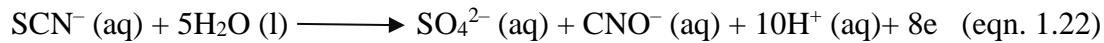


Thiocyanate is readily oxidized in the presence of stronger oxidizing agents like hydrogen peroxide. However, by adding Fe(III) to the solution, the stability of the thiocyanate ion is increased, presumably due to the formation of some stable complexes with Fe^{3+} as follows^{64,65}:



The optimum pH is between 1.5 to 2.5 as above about pH 3, Fe^{3+} is precipitated by hydrolysis to form $\text{Fe}(\text{OH})_3$, and below pH 1, thiocyanate is protonated to form HSCN .⁶⁶ The efficiency of gold

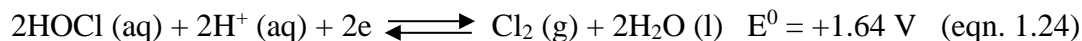
leaching is also highly dependent to the applied potential in the solution as satisfactory gold leaching rates are typically reached with a potential of more than 0.64 V, however, thiocyanate remains stable in the solution when the potential is below approximately 0.64 V. In practice, a compromise between these two requirements is needed to reach an acceptable gold leaching rates. At the same time, the applied conditions must be controlled to prevent oxidation of large amounts of thiocyanate to cyanate, ammonia, sulfate, and carbonate (eqn. 1.22 and 1.23).⁶⁷

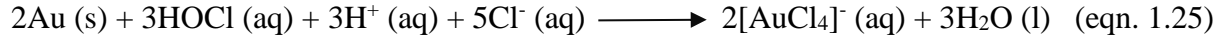


In practice, thiocyanate concentrations of 0.5 to 5 g/L and Fe(III) concentrations of 6 to 12 g/L have been used in laboratory scales. High reagent consumptions, and lack of suitable gold recovery processes from the leaching solution are the main barriers for the industrialization of thiocyanate leaching method.²

1.2.4.2.5 Chloride/Hypochlorite

Chloride/hypochlorite solutions have been recognized as another alternative leaching reagent to cyanide which can dissolve gold in a wide range of pH.⁶⁸ Depending on solution pH, three different oxidizing species can be formed in hypochlorite solutions. At pH > 7.5, hypochlorite ion (OCl^-) is the dominant species while for pH between 3.5 and 7.5, hypochlorous acid (HOCl) acts as oxidizing agent and when pH is below 3.5, HOCl is converted to chlorine gas. Among these three species, HOCl is the most effective oxidizing agent (eqn. 1.24) to leach gold as $[\text{AuCl}_4]^-$ (eqn. 1.25).

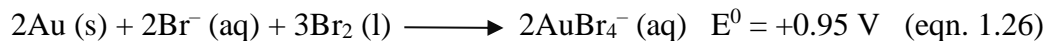




In a solution containing 100 g/L NaCl, this complex is stable in the pH range of 0–8 and potentials greater than 0.9 V.^{69,70} The chloride-hypochlorite solution is an effective leaching reagent especially for refractory gold ores, and because of low acidity, it does not produce a corrosion media; however the reagents consumption is still high. The main drawback of this lixiviant is that the percentage of leached gold is usually less than 85%.⁷¹

1.2.4.2.6 Other Lixiviants

Other halide systems, like a mixture of bromine–bromide⁷², and iodine–iodide³³ can also dissolve metallic gold efficiently (eqn. 1.26 and 1.27), and the dissolution kinetics are usually very fast.



These systems are strongly oxidizing, and both of bromide and iodide are strong ligands which can form stable complexes with gold, with β_4 of 1×10^{32} and 5×10^{47} for AuBr_4^- and AuI_4^- respectively.^{73,74} The rates of gold dissolution with these two leaching systems are typically much faster than those achieved with the cyanidation process. The gold dissolution rates in halide media are strongly dependent on the concentration of halide ligand and oxidizing reagent, and significantly increase at elevated temperatures. Although both of these reagents are effective leaching systems for gold and extract gold with high rates, but their commercial applications have been restricted by the high consumption of reagents and their high costs. In addition, there are some health issues associated with their use in large scales.^{2,75}

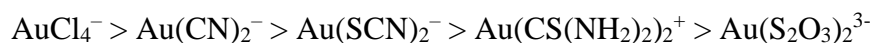
1.2.5 Solution Purification and Concentration

The purification and concentration processes are related to selective enrichment of dilute leach solutions containing e.g. 1 to 20 ppm dissolved gold to produce a more concentrated solution from which gold can be effectively recovered by those methods described in section 1.2.6. Dissolved gold is first separated from the impurities in leach solutions by selective adsorption onto activated carbon, or an ion exchange resin, or extracted into a water-immiscible organic solvent including an extractant during solvent extraction technique. The pregnant extractant is then separated from the leach solution, and the loaded gold is stripped from the extractant into a smaller volume of stripping solution, resulting in generation of a concentrated gold solution, suitable for metal recovery. The stripped extractant is regenerated during the purification and enrichment step, and then reused in the process. Besides gold adsorption on activated carbon as the major gold purification method, ion exchange resins and solvent extraction techniques have also been studied extensively in literature.

1.2.5.1 Carbon Adsorption

Activated carbon is a highly porous organic material with an extremely large surface area (1000 m²/g), and has been widely used in both gas and liquid separation industries.^{2,76} However, its use in the gold mining industry is relatively new and has only been widespread since about 35 years ago. After gold leaching in the cyanide solution, Au(CN)₂⁻ complex is adsorbed on the surface of activated carbon in the next step, thereby, gold is separated from the other metals and impurities. 0.1 to 1 Kg activated carbon per tonne of ore is usually applied in 4 to 8 steps for complete adsorption of Au(CN)₂⁻ complex ions from cyanide solutions. Typically, the complete gold-loading process takes 6 to 8 hours in which 5 to 10 kg Au is finally adsorbed on 1 tonne of

the activated carbon. Besides gold and silver, some other cyanide complexes of base metals such as Fe, Cu, Ni, Zn, and Hg are also adsorbed on the surface of activated carbon but to a smaller extent, leading to contamination of the final gold product, and competition with gold adsorption. After the gold adsorption step, the loaded activated carbon is washed with dilute HCl solution (1% to 5%) to remove some of the impurities which have been co-adsorbed with gold. In the next step, the dicyanoaurate(I) complex is removed from the activated carbon in an elution step by washing the loaded activated carbon with a fresh basic solution of sodium cyanide at elevated temperatures.^{35,42} There are typically three main industrial methods for the elution step:⁷⁷⁻⁷⁹ the Zadra process wherein the loaded activated carbon is washed with 0.1% of NaCN solution including 1% of NaOH at 95 °C, and the whole process takes 36 to 76 hours; the Pressure Zadra process in which a 0.2% of NaCN solution including 1% of NaOH is used to wash the loaded activated carbon at 135 – 140 °C and 400 - 500 kpa which takes 8 – 14 hours; and finally the AARL process where the loaded activated carbon is first presoaked with a 2 – 5% NaCN solution containing 1 – 2% NaOH followed by washing with water at 110 – 120 °C and 170 - 200 kpa, and the whole process can take 8 – 14 hours. Depending on the carbon quality and the applied reactivation technique, carbon can be reused between 100 and 400 adsorption–elution cycles. The desorbed NaAu(CN)₂ complex is finally reduced to the elemental gold by electrowinning or reduction.² Besides dicyanoaurate, tetrachloroaurate can also be effectively adsorbed by activated carbon, however, no effective adsorption of the other gold complexes have been observed, and the general trend for adsorption with activated carbon for different gold complexes is as follows⁸⁰:



Gold purification with activated carbon suffers from several drawbacks such as low selectivity, very long procedures, loss of some gold product, and high temperature requirements. Ion exchange

resins and solvent extraction techniques have been widely studied as potential alternatives to activated carbon for the purification and concentration step, and they are briefly discussed in the following sections.²

1.2.5.2 Ion Exchange Resins

The use of ion exchange resins as potential systems for the concentration and purification of gold from dilute cyanide solutions has been investigated for more than 70 years.⁸¹ Ion exchange resins are synthetic materials, made of an inert matrix like polystyrene and divinylbenzene crosslinked polymers⁸² which contain some surface functional groups, such as amines and esters which are able to exchange ions with some other similarly charged ionic species in solutions, and depending on the preference of a specific functional group, it can be completely selective for a specific ion.⁸³ This selectivity depends on some factors in the functional groups, such as their size, charge, and polarizability of the ions in the solution. Functional groups are generally classified into three different types; anion exchangers (basic), cation exchangers (acidic), and chelating functional groups. Among these three types, the first two are of more interest in gold extraction. Resins are typically produced in bead forms, generally with a 0.25 to 0.60 mm diameter.² Fig. 1.3 shows structures of some common studied resins for extraction of gold from cyanide solutions. The functional groups of strong-base and weak-base resins are quaternary, and primary-tertiary amines respectively which can extract gold from the cyanide solution as follows:

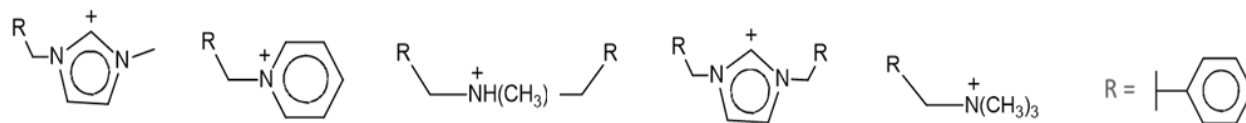
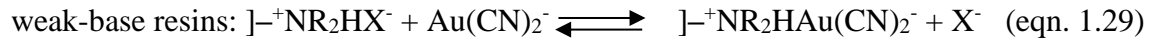
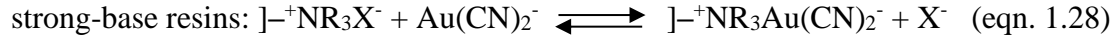


Figure 1.3 The structure of some common cations bonded to resins used for extraction of gold from cyanide solutions.



J^{-} = the inert portion of the resin

R = alkyl groups

X^{-} = an anion such as sulfate, bisulfate, etc.

In both cases, the rate of gold adsorption is faster than activated carbon. Furthermore, the gold-loading capacity is much higher than activated carbon, for example the loading capacity of >100 g pure Au per one liter of resin can be reached in the case of strong-base resins. However, in the presence of other metals and impurities, the loading capacity will decrease dramatically. Nevertheless, their selectivity is much lower than activated carbon, as other metal complexes such as zinc, iron, copper, nickel, cobalt, and silver can readily be adsorbed by these resins, with strong-base resins being less selective than weak-base ones.⁸⁴ After complete adsorption of gold from the leach solution, the loaded resins can be washed in the elution step with a solution containing high concentration of a competing anion like thiocyanate, chloride, bisulfate, or with a thiourea solution to convert the adsorbed gold ions to nonionic species.⁸⁵ Among the strong and weak-based resins, the former is more difficult to strip due to the greater strength of ion adsorption. After the elution step, the stripped resins can be reused for another cycle during the purification process, and the desorbed gold can be converted to metallic gold by electrowinning, or reduction with a reducing agent.

Although higher loading capacity and faster loading kinetics can be achieved with ion-exchange resins, they have been unable to compete with activated carbon in commercial scales

due to their poor selectivity, mechanical breakdown of the beads, and the requirements for the elution and regeneration processes.²

The application of ion-exchange resins have also been reported for the extraction of gold from non-cyanide media. For example, effective gold extraction using both strong and weak-based resins from chloride, bromide, thiosulfate, and thiourea solutions have been reported.²

1.2.5.3 Solvent Extraction

Solvent extraction is another potential alternative for activated carbon which can be used for purification and concentration of gold from dilute cyanide leach solutions. Solvent extraction techniques possess some advantages compared to activated carbon and ion exchange resins; such as faster extraction kinetics, higher selectivity, and high gold loadings.^{86,87} In this purification technique, gold is selectively extracted from an aqueous leach solution into a water-immiscible organic solvent containing an organic extractant. Depending on the efficiency of the extractant, a concentration of 10 to 20% of the extractant is typically used during the extraction step. The kinetics of solvent extraction method are much faster than both carbon adsorption and ion exchange resin methods, and complete gold extraction is typically attained within a few minutes. Nevertheless, the stripping stage is much slower, and 2 to 4 hours is usually needed to reach a satisfactory metal recovery. Gold loadings up to 200 g/L can be reached in the organic phase, however, the loading capacity is kept below 80 g/L (which is still 10 to 20 times higher than the loadings achieved by activated carbon or resin) to avoid any likely interferences during phase separations.^{2,87} Different types of extractants can be used during solvent extraction method, such as chelating ligands, solvating extractants, and those kind of extractants which form ion-pairs with the extracted metal in the organic phase.^{88,89} For instance, trioctylamine is a common example of a precious metals extractant which can form an ion-pair with the extracted metal, while

methyl isobutyl ketone (MIBK), and diethylene glycol dibutyl ether (DBC) are well-known solvating extractants for gold (Fig. 1.4). Both quaternary amines and guanidine-based extractants (such as LIX 7950) have been reported for efficient gold extraction from cyanide leach solutions, showing a high degree of selectivity.^{90,91} For example, LIX 7950 extractant is able to be protonated with water even at pH above 10, forming an ion-pair with $\text{Au}(\text{CN})_2^-$ and extract it into the organic phase in less than 5 min. DBC is another suitable extractant for gold, and it has been used for selective extraction of gold from acidic media for a long time. Indeed, DBC can selectively extract gold from hydrochloric acid solutions including even large amounts of platinum group and base metals. The extracted gold after scrubbing with 1-2 M HCl solution can be reduced to the metallic gold (with 99.99% purity) with a hot aqueous solution of oxalic acid (eqn. 1.30). Recently, an effective extraction of gold from cyanide solution has also been reported with DBC.⁹²



So far, no solvent extraction system has been applied in an industrial scale for extraction of gold from cyanide solutions. The major disadvantages of solvent extraction which have restricted its industrial applications are as follows: i) it must be applied to a clarified leach solution, resulting in an increase in the cost of purification steps ii) in some cases, the cost of extractant is

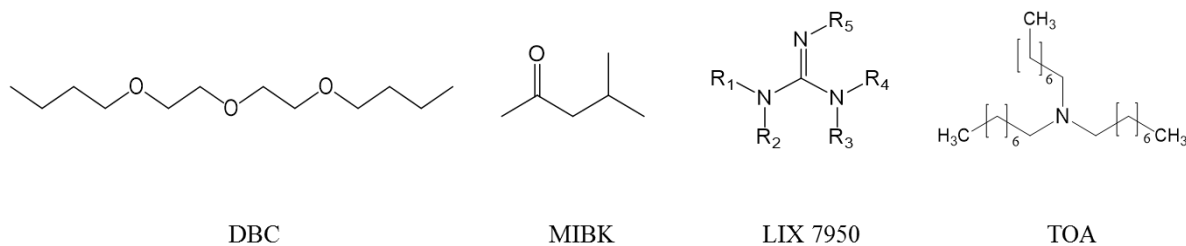


Figure 1.4 The structure of well-known extractants for selective extraction of gold from both acidic and basic media.

relatively high, and iii) some solvent (and gold) are always lost to the aqueous phase.²

1.2.6 Gold Recovery

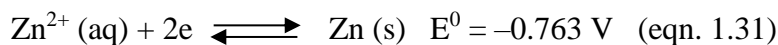
During the recovery process, concentrated gold obtained in the elution step is converted to metallic gold which can then either directly be sold or treated further by refining techniques (section 1.2.7) to reach higher grades. Prior to the extensive application of activated carbon for purification and concentration of dilute leach solutions in the late 1970s (section 1.2.5.1), zinc precipitation was the dominant process for direct recovery of gold from dilute cyanide leach solutions.^{91,93} Today, after enrichment and purification of gold with activated carbon, both electrowinning and zinc precipitation are used to treat concentrated gold in the elution step. The chemistry of both zinc precipitation and electrowinning processes are considered in the following sections.

1.2.6.1 Zinc Precipitation

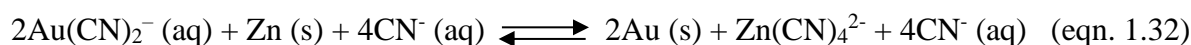
Gold precipitation with metallic zinc is one of the main two methods which has been widely used for gold recovery in the mining industry. The process, known as Merrill–Crowe, is a gold reduction method in which more than 99% of gold can be recovered from a dilute cyanide solution (including 0.5 to 10 ppm Au) by adding zinc powder to the solution.⁹⁴ In this method, the dilute cyanide solution must be deaerated to a dissolved oxygen concentration of less than 1.0 mg/L, to avoid undesirable side reactions which consume excess zinc and decrease the efficiency of the process. The amount of required zinc is between 5 to 30 times of the stoichiometric amount of dissolved gold, depending on the composition of solution and process operating efficiencies.⁹⁵ The purity of final gold precipitate will be between 25% and 40%, and the major impurities include 5% to 20% lead, 10% to 15% zinc, 1% to 15% silica/silicates, 0% to 8% sulfur, and 2% to 12% of

other metals (e.g., silver, mercury, iron, and copper).⁹⁶ This impure final product is sent for purification with one of the methods described in section 1.2.7. The Merrill–Crowe process was the major gold recovery technique from dilute cyanide solutions prior to exploration of the carbon adsorption process in 1981. This process is not applied on dilute cyanide solutions anymore, and instead, activated carbon is used to purify and concentrate the gold cyanide solution, and then zinc powder is applied in the hot concentrated eluates to precipitate gold.

The anodic oxidation of zinc in aqueous solutions is given by:



Gold cyanide can be reduced to the metallic gold by reacting with zinc powder as follows:

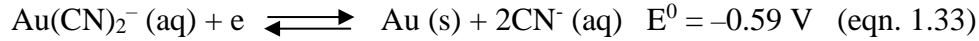


Typically, the temperature of solution obtained from the activated carbon elution step is between 60°C and 90°C, and appropriate amount of zinc is added to the solution which usually contains 50 to 200 ppm gold on average. The amount of free cyanide is also critical for effective gold reduction with zinc powder as at low concentration of CN^- , zinc hydroxide ($\text{Zn}(\text{OH})_2$) is formed which can passivate the surface of unreacted zinc powder, leading to ineffective gold precipitation. For example, the amount of required NaCN for treatment of a solution containing 50 to 100 ppm Au has been found to be 2 to 5 g/L. More than 99% gold recovery can be obtained during this process, and the final product generally contains higher grades of gold (50% to 75%), 10% to 25% silica, 5% to 10% zinc, and some other base metal impurities (5% to 15%).^{2,97}

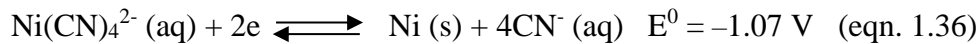
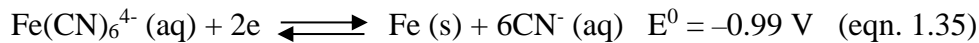
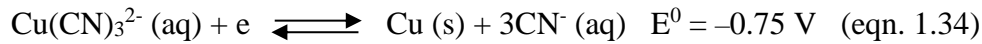
1.2.6.2 Electrowinning

Electrowinning is another major recovery process which is used for treatment of carbon eluates (high-grade gold solutions) to produce metallic gold in forms of loaded cathodes, and

cathode cell sludge which usually require relatively less refining. According to the following reaction, gold can electrolytically be displaced from an aqueous alkaline cyanide solution by acquiring one electron:



In practice, depending on the solution conditions, potentials below -0.7 V (typically between -0.7 and -1.1 V) must be applied for effective deposition of the metallic gold in cathode.⁹⁸ Besides gold cyanide, some other metal cyanide complexes can also be reduced to their metallic forms. For example, mercury, lead, and silver will be readily reduced at the potentials applied for gold reduction as their reduction potentials are bigger than that of gold (-0.33 , -0.38 , and -0.45 V respectively). Although the reduction potentials for copper, iron, and nickel are more negative (eqn. 1.34 – 1.36) than that for gold, their reduction is possible at applied potentials for gold reduction, and, depending on their concentration, they can significantly reduce the purity of final gold product.



In addition to metals, oxygen and water can also be reduced in cathode, and release hydroxide ion and hydrogen gas (eqn. 1.37 and 1.38).⁹⁹



Oxidation of water to oxygen is the major anodic reaction in electrowinning of gold in alkaline cyanide solutions. Cyanide may also be oxidized to cyanate at the anode which subsequently hydrolyzes to ammonia and carbon dioxide (eqn. 1.39). This reaction may explain the reason of the strong ammonia smell above many electrowinning cells.²



The produced solution by the carbon elution step usually contains an adequate concentration of sodium hydroxide to provide suitable conductivity, otherwise, conductivity needs to be adjusted by adding more sodium hydroxide as a suitable electrolyte to the solution. Electrowinning is implemented in cells, generally constructed of suitable non-conductive materials such as fiberglass or plastic which contains a number of stainless steel wool cathodes, and anodes, usually made of graphite or stainless steels. The final product usually contains 50% to 75% gold, large amounts of iron (10% to 25%), and 5 to 20% of other base metals. The impure gold is finally sent for refining to reach higher purities.¹⁰⁰

1.2.6.3 Gold Recovery from non-cyanide solutions

Both precipitation and electrowinning methods have been reported as effective techniques for gold recovery from non-cyanide leaching solutions. Aluminum for example, has been used efficiently to reduce gold in thiourea solutions with 99.5% efficiency.¹⁰¹ Aluminum has also been reported as an effective reducing agent for recovery of gold from chloride, thiocyanate, and thiosulfate solutions.² However, the purity of final gold precipitate is usually poor, and further purification steps are needed to reach high purities. Sodium borohydride has been reported as another suitable reducing agent to precipitate gold out of different leaching media including acidic thiourea, thiocyanate, chloride, and thiosulfate solutions, providing very fast kinetics.¹⁰² The final

gold product with relatively high purity can be obtained under controlled conditions and using stabilized sodium borohydride solutions (12% NaBH₄ in 40% NaOH solution). The electrolytic recovery of gold from chloride solutions has also been applied in industrial scales to produce highly pure gold in some refining operations, described in section 1.2.7.2.

1.2.7 Gold Refining

During refining processes, the impure gold products from the previous steps such as zinc precipitation process, loaded cathodes, electrowinning sludges, and any other products which contain more than 10% gold are processed by some purification techniques to first reach high purities, suitable for making bullions (with 90 – 99% purity), followed by further purifications to reach higher purities, mainly 99.6% for jewelry applications and gold bars, and 99.99% for production of coins. Electrolytic, hydrometallurgical and pyrometallurgical-based methods are applied in practice to refine impure gold products in the mining industry.

1.2.7.1 Pyrometallurgical Purification Methods

During roasting (which is also called “calcining” process), most of base metals such as iron, lead, zinc, and copper are converted to their corresponding oxides by applying temperatures above 600°C under air. In practice, the impure gold products are treated at elevated temperatures between 600°C to 700 °C for a period of 12 to 18 hours for effective conversion of base metals to their oxide forms. In some cases, temperatures more than 700 °C are also applied to decrease the roasting time. The formed oxide impurities will then be readily removed into a slag during subsequent smelting processes. During the roasting process, tiny amounts of sulfides, present in the feed materials are also oxidized. The color of the roasted product provides a useful indication

of the quality of the product, so that, a reddish-brown color shows an efficient oxidation, however, a black or dark gray color indicates unoxidized or poorly oxidized precipitates.^{2,97}

The roasted products are usually sent for smelting process in which most parts of base metals and other impurities are removed to finally produce a gold bullion typically with more than 95% purity. During the smelting process, almost all of base metals and impurities are separated into a slag by heating the materials in the presence of slag-forming fluxes at temperatures between 1,200 °C and 1,400°C for approximately 1.5 hours. The molten gold (and other precious metals) form an alloy which is heavier than the slag and stays at the bottom of the smelting vessel. A mixture of silica, sodium borate, and/or borax is one of the most common fluxes used in the smelting process.^{2,103} In some other cases, some oxidizing agents, like sodium nitrate and manganese dioxide, are added to the mixture which can facilitate the oxidation of unoxidized species. Once the smelting is completed, the slag is poured off, and the remaining precious metal alloy will be removed from the furnace.²

1.2.7.2 Pyrometallurgical Refining

The bullion produced by the process described in the previous section can be the starting material for the Miller refining (also called Miller chlorination) process to remove and separate silver and other remaining metal impurities from gold by bubbling chlorine gas into the molten metal at 1150 °C for 30 to 45 min.¹⁰⁴ Under these conditions, the remaining zinc, lead, and iron are converted to gaseous chloride complexes, while silver and copper form liquid chlorides which stay in the surface, and subsequently are removed. The molten gold is re-smelted a few times in the presence of some fluxes to produce the final gold product with 99.6% purity. Higher purities like > 99.9% can also be reached by the Miller chlorination method, however, a higher amount of

gold is lost due to volatilization, as the smelting time needs to be extended to remove the remaining impurities.²

1.2.7.3 Hydrometallurgical Purification Methods

Impure gold products are usually treated with some strong mineral acids to dissolve most of metal impurities which can be dissolved in acidic solutions. For example, high concentrations of sulfuric acid (10 - 70%) are used to dissolve most of zinc and iron contents in impure gold precipitates as both of these metals can be readily oxidized in H₂SO₄ solutions. During this reaction, hydrogen gas is formed and the existing arsenic and antimony in the precipitate are converted to the highly toxic gaseous hydrides (arsine (AsH₃) and stibine (SbH₃) respectively). Both HNO₃ and HCl can also be used for dissolving and removing most parts of base metals in gold precipitates. For instance, most of iron and zinc can be removed by treating the impure gold precipitate with 10% to 20% hydrochloric acid solutions at 60°C with a residence time of 12 to 24 h.⁹⁶

1.2.7.4 Hydrometallurgical Refining

The relatively high pure gold (typically with >90% purity) produced in the previous step can be treated with a boiling solution of sulfuric acid to reach >99.6% pure gold. This method which is called “parting” process has been used for the separation of silver and other impurities from crude gold bullions since the 19th century. As gold does not dissolve in sulfuric acid, while most of the other metals do, the large amounts of impurities can be washed from the gold bullion by this method. This process has largely been replaced by the other refining methods such as chlorination and electrolytic processes, and currently is not widely used anymore.²

The refining of crude gold bullion can also be implemented using chlorination leaching, followed by solvent extraction of gold from the chloride solution. An industrial solvent extraction process has been developed by Inco since 1972 in which DBC is used as the selective extractant for separation of gold from other metals and impurities in HCl media.¹⁰⁵ Extremely pure gold with more than 99.99% purity can be achieved by two steps for the solvent extraction of gold, followed by two to three steps for the scrubbing with 1 to 2 M HCl, and subsequently direct reduction of gold in the organic phase by applying a hot aqueous solution of oxalic acid. There are some difficulties associated with DBC which has limited its wide applications. The extractant must be used in pure form (without any solvent), the separation of DBC from the aqueous phase is only possible at elevated temperatures, and the solvent has relatively high solubility in the aqueous phase, resulting in loss of some extractant (and gold). No other known solvent extraction system has been implemented in industrial scales.

1.2.7.5 Electrolytic Refining

Very high-grade gold (99.99% purity) can also be acquired by electrolytic refining methods. The Wohlwill process is a well-known refining method in which tiny amounts of impurities such as copper, zinc, silver, and platinum group metals are removed. In this process, a gold bar with >99.6% purity is used as an anode, and 8% to 10% HCl solution containing 80 to 100 g/L Au (in AuCl_4^- form) is used as the electrolyte, and the solution temperature remains at approximately 60 °C. During this electrorefining process, the dissolved gold (removed from anode) is finally plated onto highly pure (99.99%) rolled gold cathodes.¹⁰⁶ Impurities such as copper, zinc, platinum, and palladium dissolve in the electrolyte during the process, contaminating the electrolyte solution. The cathode is then washed several times with a hot solution of sodium thiosulfate to remove remaining silver chloride, and is finally re-melted as the final pure product.

1.3 Gold Recycling Industry

Around a quarter of the annually produced gold comes from the gold recycling industry.¹⁰⁷ Because gold is highly resistant against oxidation, and does not tarnish and decay, all extracted gold still exists and is recyclable. It is estimated that around 176,000 tonnes of gold has been mined and extracted so far. Today, approximately 1200 tonnes of gold is recycled every year from both jewelry scraps and electronic wastes (e-wastes).⁸ Among these two sources, jewelry accounts for the majority of recycled gold. As was mentioned before in section 1.1.2, most gold used in jewelry is an alloy with one or more metals⁹, therefore, recycling and separating gold from these alloys is relatively straightforward, and is usually done by established pyrometallurgical techniques in both small and large scale operations. However, gold-bearing electronic scraps contain huge amounts of base metals (up to 60 different metals), around 60% by mass of plastic and ceramic, and 50 – 4000 ppm gold.¹⁰⁸ Therefore, recycling gold from this complicated mixture is much more difficult than jewelry scraps, and almost all of the implemented research in the gold recycling area has focused on gold recovery from electronic wastes. In the following section, different industrial methods for recycling gold from e-waste are explained, and the latest reported recycling methods in literature are reviewed.

1.3.1 Electronic Wastes and Global Production

Electronic wastes are those broken, unwanted, and obsolete electronic devices which have reached their end-of-life and been discarded by their original users.¹⁰⁹ Electronic wastes are a specific kind of waste as they contain large amounts of metals (including base, heavy, and precious metals), organic components, and ceramics. They are therefore considered as a valuable source of metals, and due to the presence of some hazardous organic material and heavy metals, they are also classified as dangerous wastes. Sustainable innovations in electrical and electronic

technologies, rapid growth in the economy, and the improvement in living standards have led to a dramatic increase in demand for electronic devices, and at the same time, shortened the useful life of electrical and electronic equipment.¹¹⁰ Therefore, the generation of electronic wastes has increased dramatically, making recycling e-wastes a major global and environmental issue. In addition, e-waste is considered as one of the fastest growing waste streams and accounts for around 8% of the municipal wastes.¹¹¹ The global production of e-waste is now around 50 million tonnes/year and expected to increase even more in the near future.¹¹² USA, Europe, Japan, and Australasia are the significant e-waste producers in the world now, however, China, along with some of the Latin American and Eastern Europe countries are expected to become major producers of electronic wastes in the next decade. Landfills are typically the final destination for most parts of e-waste, but disposing of these wastes can significantly contaminate the underground water and soil, and at the same time, a potential source of valuable metals is wasted. However, due to environmental pollution and global regulations, disposing of these wastes in landfills and/or exporting them overseas is not permitted anymore in most countries. Printed circuit boards (PCBs) which are one of the main components in most electronics (televisions, computers, mobile phones, laptops, etc), account for 3-5% of the total mass of generated e-waste, and due to their high precious metals content, they are considered as the most valuable components in e-wastes.^{113,114} As can be seen from Table 1.1, most PCBs contain huge amounts of base metals such as Cu, Ni, Fe, Zn, etc., and significant amounts of precious metals including Au, Pd, and Ag. Although the

Table 1.1 Metal compositions in printed circuit boards (PCBs) [120]

Metal	Cu	Fe	Ni	Al	Zn	Pb	Sb	Sn	Co (ppm)	Au (ppm)	Ag (ppm)	Pd (ppm)
(%)	6-27	1.2-8	0.3-5.4	2-7	0.2-2.2	1-4	0.1-0.4	1-5	1-4000	250-2050	110-4500	50-4000

amount of precious metals is negligible compared to huge amounts of base metals, they account for 80 to >90% of the total value in PCBs. Besides the environmental concerns, recovery of precious metals especially gold is the main driving force for recycling e-waste. Furthermore, using recycled materials instead of virgin resources can result in substantial energy savings.¹¹⁵ In addition to their large metal content, PCBs contain 60% by mass of plastics and ceramics (30% of each). Polymers such as polyethylene, polypropylene, PVC, epoxies, nylon, and polyesters are the main components of the plastic base, while the ceramic part is mainly composed of SiO₂, Al₂O₃, alkali- earth oxides, and titanates-micas.¹¹⁴ Brominated flame retardants (BFRs) are another organic compounds which are typically used in the plastic part to decrease the flammability of PCBs.¹¹⁶ Fig. 1.5 shows the sequence of three main metal layers in PCBs. As with most PCBs, the extremely thin layer of exposed gold is plated on top of nickel which is in turn layered on copper (Fig. 1.5a). Between these three main layers, dissolving the gold layer is the most difficult one as metallic gold is highly resistance against oxidation, and harsh conditions must be applied for its effective leaching and recovery. In the following section, the main industrial methods are explained for recovery of gold from e-waste.

1.3.2 E-Waste Processing

The e-waste recycling process includes three main steps: collection, preprocessing and end

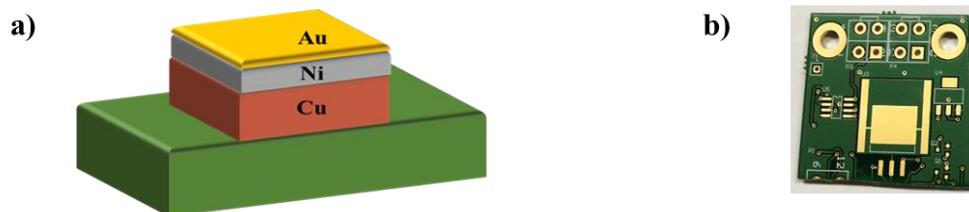


Figure 1.5. a) The sequence of three main metal layers in PCBs b) an example of actual PCB.

processing, all of which are essential for the recovery of metals and other components.¹¹⁴ The first step is usually implemented by some specific agencies and simplified by suitable government policies through installing several collection facilities at public places. After collecting the e-waste, they are sent for the preprocessing stage which is one of the important steps in the recycling process. During this stage, the obsolete equipment is manually or automatically dismantled, and different parts are isolated from e-wastes. Then, the isolated gold-bearing materials such as PCBs, memory RAMs, CPUs, connectors, etc. are sent for a shredding step in which the isolated pieces are mechanically crushed into smaller sizes (1–2 mm). Metals are then separated from non-metals by some magnetic and gravity-based techniques.^{117–119} The final step in the recycling process of e-waste is the end processing, where the separated non-metal and metal fractions are sent for further processing to recover valuable metals and components. In the following section, the most common industrial methods for recovery of precious metals, especially gold from PCBs and other types of gold-bearing e-scrap are discussed. Besides these industrial techniques, the recent hydrometallurgical methods reported in literatures are also reviewed.

1.3.2.1 Pyrometallurgical processes

Pyrometallurgical-based techniques such as smelting, incineration, and pyrolysis have been in use for the last two decades to recover both precious and base metals from different waste materials. Advanced smelters can extract and recover valuable metals and isolate most of the produced hazardous gases and substances during the process. Currently, pyrometallurgical techniques are the dominant recycling methods in industrial scales (Fig. 1.7a), and there are several massive smelting operations in some developed countries like Canada, Germany, Australia, Sweden, Belgium, and Japan.^{114,120} Generally, there are two different types of smelting operations for recovery of precious metals: copper, or lead smelters in which a mixture of e-waste/copper, or

e-waste/lead is fed into a furnace and after heating at high temperatures, precious metals are collected in a molten bath of copper or lead, and separated from the metal oxides in a slag phase. Between these two methods, the copper smelters are more popular as they are more environmentally friendly compared to the lead smelting operations that produce toxic fumes.^{121,122} The procedure for recovery of precious metals in both cases is similar. In copper smelters for example, the feed materials are subjected to a smelting furnace to melt all materials down at very high temperatures (>1200 °C) under super charged air conditions (up to 39% oxygen), forming two phases including a metallic layer of mainly copper (99.1%) containing small amounts of precious metals (0.9%) on the bottom, and a silica-based slag layer on the top including iron, lead and zinc oxides which is sent for grinding to recover its metal contents before disposal (Figure 1.6). Copper is then leached in the next step and recovered in a pure form by an electrowinning process. Next, the formed residue in the copper-electrowinning step is ground into a fine powder and processed in a series of hydrometallurgical steps to recover gold and the other precious metals including silver and palladium. The plastic part provides some part of the required energy in the furnace during the smelting process, and the emitted off gases are sent for another process to produce sulfuric acid.^{114,122} There are some major issues associated with pyrometallurgical methods which limit their applications, such as release of toxic dioxin gases, loss of precious metals in the slag phase (the total gold recovery is around 90%), long recycling processes, and requirement of large investments in heavy equipment.^{123,124}

1.3.2.2 Hydrometallurgical Processes

Although pyrometallurgical techniques are the dominant industrial processes for the recovery of precious metals, hydrometallurgical methods could be preferred due to the following reasons: i) they generate much less harmful and toxic gases like dioxins/furans, Cl₂, Br₂ and CO₂,

ii) they do not release volatile metals such as Pb and Hg, iii) they consume significantly less energy, and iv) the rate of precious metals recovery is much faster in some cases.^{125,126} Typically, the same traditional hydrometallurgical technologies of gold extraction from primary ores can be used for recovery of gold from electronic wastes. Similar leaching reagents like cyanide, halide, thiourea, and thiosulfate can be applied on gold-bearing e-scrap to leach the gold out of these waste materials. The dissolved gold in pregnant solutions can be then purified and separated from the other leached metals and impurities by adsorption, precipitation, or solvent extraction. The obtained gold precipitate can be finally sent for refining to reach high purities. However, just cyanide and aqua regia are practically used for gold recycling from e-wastes in industrial scales.¹²⁷ Indeed, in smaller scales than smelting operations, some companies use aqua regia (Fig. 1.7b) or cyanide as effective leaching reagents for recovery of gold from e-waste. Aqua regia, which is obtained by mixing three parts of concentrated HCl and one part of concentrated nitric acid, can dissolve gold (eqn. 1.40) with extremely high rates ($1850 \text{ gm}^{-2}\text{h}^{-1}$), and has been known for more than a millennia.¹²⁸



Aqua regia is prohibitively expensive to use for the treatment of gold ores due to high reagent and operation costs, however, it is considered as one of the most effective leaching reagents for gold recovery from e-scrap. Besides precious metals, almost all of base metals like Cu, Zn, Fe, Co, Ni, etc. also dissolve in aqua regia with extremely fast kinetics, resulting in extremely poor selectivity and a significant increase in reagent consumption. After metals leaching in aqua regia, gold can be purified and separated from the impurities with precipitation or solvent extraction. Although the rate of gold leaching from e-waste is faster in aqua regia, however, the reagent consumption in

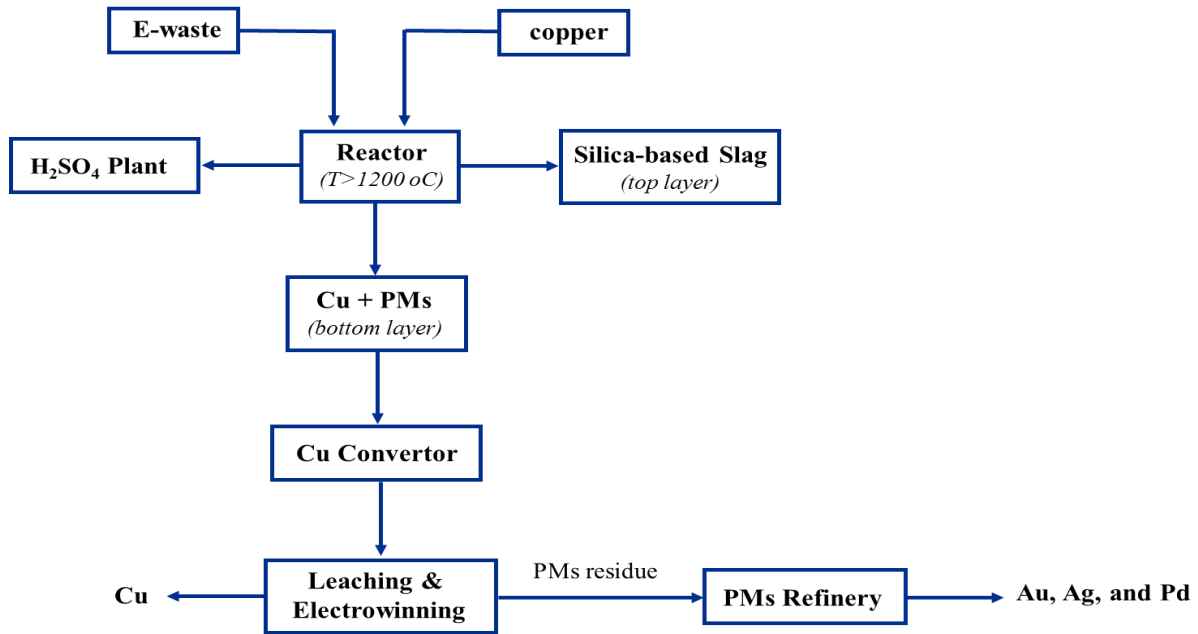
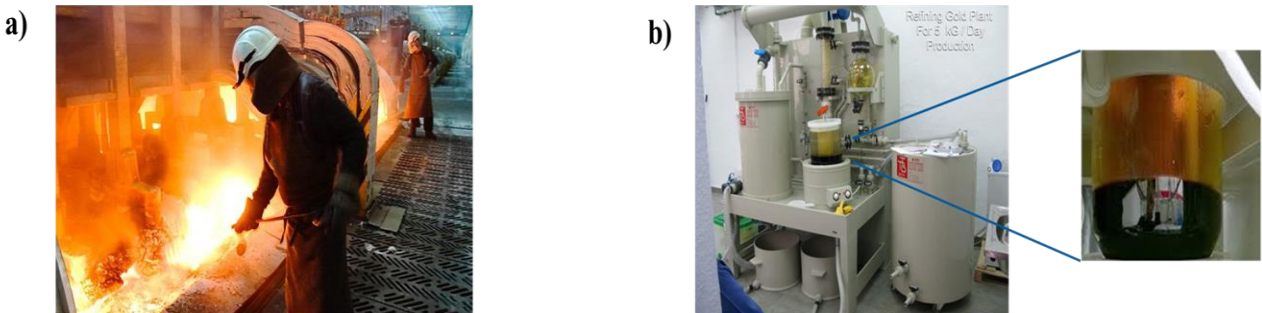


Figure 1.6 A general flowchart for recovery of precious metals from e-waste using copper smelters.

the cyanidation process is significantly less, and cyanide media is more selective for gold over base metals. In addition, aqua regia needs special stainless steel equipment to resist against its highly corrosive and oxidizing environment.¹²⁹ However, both of these methods are not so effective, use extremely toxic chemicals, and generate large amounts of toxic wastes. Beside these industrial methods, there are many family-run workshops which use similar recycling methods,



***Figure 1.7. a)** A smelting operation for recovery of gold from e-scrap **b)** an example of using aqua regia in industrial scales. [*http://www.rictec.com.sg/precious-metals-recovery/](http://www.rictec.com.sg/precious-metals-recovery/)

like aqua regia, cyanidation,¹²⁷ and open-burning of e-wastes¹³⁰ in some developing countries, but in unprotected ways (Fig. 1.8). In all cases, the rate of gold recovery is low, and there are thousands of people at high risk of exposure to toxic gases and working with extremely dangerous chemicals, resulting in lots of health issues for the workers and residents, living in the region. A well-known example is the city Guiyu in China where the attempts for extracting gold from e-waste by open burning and leaching with strong acids have caused an environmental disaster and serious health concerns. For instance, the lead and brominated flame retardants blood levels in Guiyu residents are much higher than the standard levels (BFR levels are 100 times higher than in Europe).¹³¹ All of these attempts to recycle gold from e-wastes have made severe environmental issues in some developing countries (Fig. 1.9). Several hydrometallurgical methods including the traditional gold leaching reagents, along with newer methods have been studied in recent years for recovery of gold from e-waste, however, none of them has found industrial applications as they suffer from similar drawbacks associated with current recycling methods. In the following section, some of the recently investigated hydrometallurgical systems for gold leaching from e-waste are reviewed.



***Figure 1.8.** Open-burning and using toxic chemicals such as aqua regia in developing countries to recover gold from e-scrap. * http://www.greenpeace.org/eastasia/news/stories/toxics/2005/20050817_exeter_report/

1.3.2.2.1 Investigated Hydrometallurgical Systems in Literature for Recovery of Gold from E-Wastes

Both cyanide and aqua regia are still the two main recycling systems which have been widely studied with some modifications to leach the gold out of the e-wastes. Aqua regia was used as a leaching reagent by Park and Fray with a ratio of 1:20 (metal wires: aqua regia), and after extraction of silver and palladium in the first stage, 97% of gold was recovered from the leach solution using solvent extraction in toluene.¹³² In another attempt, Sheng et al.¹³³ treated computer chips with nitric acid to first dissolve base metals, then they leached the residue with aqua regia (with 1:2 ratio of residue: aqua regia) to dissolve gold and the rest of remaining metals, and they finally precipitate gold out of the aqua regia solution with ferrous sulfate. In another study, PCBs were treated first with H₂SO₄ solution including an oxidant to dissolve Cu and Ag, followed by treating the residue with chloride solution to extract Pd and remaining Cu, and finally the gold content of PCBs were extracted by cyanide solution, resulting in 95% Au, 93% Ag and 99% Pd extractions.¹³⁴ In most cases, the gold-bearing e-scrap is first treated to remove the base metals, then their gold content is extracted using aqua regia or cyanide solutions. However, in all cases,



***Figure 1.9.** Environmental damages in developing countries caused by using toxic chemicals to recover precious metals from e-wastes. *<http://environmentalissuescomp1220uwiwe.weebly.com/>

the reagent consumption is high, and huge amounts of toxic wastes are finally generated. Thiosulfate has also been studied for gold recovery from e-waste. Ha et al. for example, treated grinded PCBs with 0.12 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ solution including 0.015 M Cu^{2+} and 0.2 M NH_3 , resulting in 90% of gold recovery after 10 hours.¹³⁵ In another study, Ficeriová et al. used a 0.5 M solution of thiosulfate (with S/L ratio of 1/12.5) containing 0.2 M Cu^{2+} and 1 M ammonia, and after stirring the mixture for 48 hours at 40 °C, more than 98% gold could be leached out from the PCBs.¹³⁶ Thiourea is another leaching reagent which has been widely investigated for recovery of gold from obsolete electronics. Birloaga et al.¹³⁷ used the following procedure for recovery of gold from PCBs: shredded PCBs (with <2 mm particle size) were treated three times with 2 M H_2SO_4 solution containing 5% H_2O_2 (with 1:10 PCB: solution ratio) for three hours, and more than 98% of copper was extracted from the treated PCBs. Then, the residue was treated with a solution (1/10 S/L ratio) containing 20 g/L thiourea, 6 g/L ferric ion, and 0.5 M H_2SO_4 for effective gold leaching. The leached gold was then precipitated by adding large amounts of zinc powder to the thiourea solution. Gurung et al. reported gold recovery from PCBs of spent mobile phones using acidified thiourea solution. Crushed and ground PCBs (<75 μm) were roasted at 750 °C, and then treated with thiourea solution (0.5M) containing 0.05 M H_2SO_4 , and 0.01 M Fe^{3+} at 45 °C (1/35 S/L ratio). After 2 hours, around 93% of gold could be leached from mobile phone PCBs, and dissolved gold was recovered with cementation with metallic copper.¹³⁸ Iodine has also been used as an effective leaching reagent for gold. In a study done by Xu et al. waste PCBs with 74-180 μm particle sizes were leached with an 1.2% iodine solution (with 1/10 ratio of solid/liquid, and $n(\text{I}_2):n(\text{I}^-) = 1:10$) containing 2% H_2O_2 concentration, and after 4 hours, 95% of gold was extracted at room temperature.¹³⁹ In another work, PCBs of waste mobile phones (<4 mm) were first pre-treated with supercritical water oxidation (SCWO) at 420 °C for 60 min, followed by a diluted hydrochloric

acid leaching to remove the copper content completely. Then the iodine–iodide leaching was subjected to the residue from the previous step under the following conditions; iodine/iodide mole ratio of 1:5, and a solid-to-liquid ratio of 1:10 at pH 9. After 2 hours, gold was completely leached into the iodine solution.¹⁴⁰ Kim and others have recovered gold from e-scrap (with 2–3 mm particle size) in a two-stage electro-generated chlorine process.¹⁴¹ In the first stage, 97% of copper was dissolved in 2 M HCl solution (with a solid: liquid ratio of 1:25) by electro-generation of chlorine at 25 °C for 165 min. In the second stage, 93% of gold was leached out from the residue of the first stage by the electro-generated chlorine in 0.1 M HCl (with a solid: liquid ratio of 1:6) after 10 min. Finally 95% of gold with 99.9% purity was recovered from the leach solution by selective adsorption of gold on Amberlite XAD-7HP resin. In another study, Alzate et al. recovered gold from e-scrap without any crushing and grinding.¹⁴² A solution of ammonium persulfate ((NH₄)₂S₂O₈) with concentration of 0.88M, oxygen concentration of 1 L/min, and S/L ratio of 1:25 was used to partially oxidize the Cu, Ni and Fe layers (19.56%) in electronic processors. During the leaching step, by partial oxidation of iron, nickel and copper, 99.43% of non-leaching gold was released from the substrate after 10 min (Fig. 1.10). Xu, and He have used chlorination as an effective leaching process for recovery of gold from PCBs.¹²⁷ During their

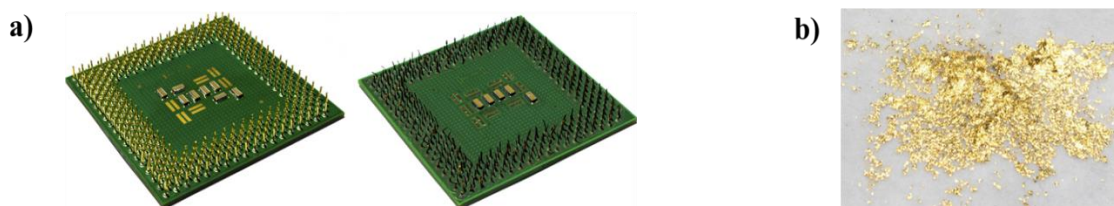


Figure 1.10. a) The untreated and treated e-scrap with ammonium persulfate solution and b) the released gold after treatment. Reprinted with permission from Alzatea, A.; Esperanza López, M.; Serna, C. *Waste Management* **2016**, 57, 113–120. Copyright © 2016 Elsevier Ltd.

process, they first treated crushed PCBs with 2.5 M H_2SO_4 solution including sodium chlorate (NaClO_3) as an oxidizing reagent for 3 hours at 85 °C. After removing around 90% of copper, the residue was subjected to a second leaching step with 1 M H_2SO_4 including 25 g/L NaClO_3 and 75 g/L sodium chloride at 40 °C for 90 min to recover 99% of gold. The whole leaching process has been simply shown in figure 1.11.

1.4 Gold Leaching in non-aqueous media

Besides aqueous-based leaching systems which have broadly been investigated, a few preliminary investigations have been recently reported in non-aqueous solutions, and in some cases, promising results have been achieved. For example, the dissolution of metallic gold has been reported in some organic solvents like acetonitrile including iodide ions, and iodine as an oxidizing reagent.¹⁴³ It has been known that in selected organic solvents, iodine can readily react with I^- , resulting in formation of the stable I_3^- ion which can subsequently react with metallic gold

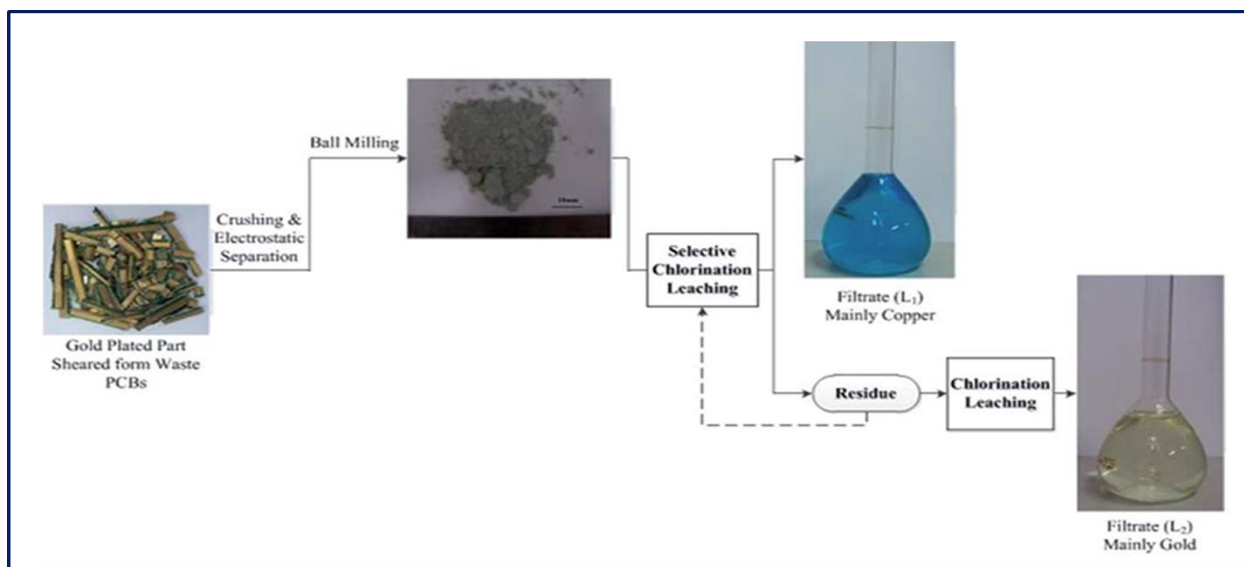
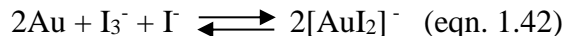
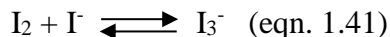
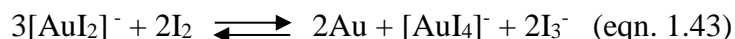


Figure 1.11. The whole recovery process to recover copper and gold by selective chlorination process. Reprinted with permission from He, Y.; Xu, Z. *RSC Adv.* **2015**, 5, 8957–8964. Copyright © 2014, Royal Society of Chemistry.

in the presence of I^- to form the stable $[AuI_2]^-$ complex (eqn. 1.41 and 1.42).



The gold dissolution rate of $189 \text{ gm}^{-2}\text{h}^{-1}$ was obtained in an acetonitrile solution including 0.15 M NEt_4I and 0.1 M I_2 at 80°C . However, the dissolved gold was not stable, and cooling the solution led to formation of both metallic gold and insoluble $[NEt_4][AuI_4]$ complex (eqn. 1.43).

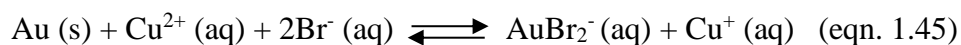


By cooling the solution to 20°C , 43% of gold precipitated out from the solution after one day.¹⁴³ However, refluxing the solution resulted to dissolution of the precipitated gold. A new mixture of thionyl chloride ($SOCl_2$) and some organic solvents/reagents such as pyridine, N,N-dimethyl formamide, or imidazole has been reported as an effective leaching solution for precious metals especially gold, silver and palladium.¹⁴⁴ This specific solution including 3:1(v/v) mixture of $SOCl_2$ and pyridine which has been named organic aqua regia, is able to dissolve gold, silver, and palladium at relatively high rates (59 , 157 , and $98 \text{ gm}^{-2}\text{h}^{-1}$ for gold, silver, and palladium respectively). Raman and X-ray photoelectron spectroscopy (XPS) techniques showed that the metallic gold is converted to $AuCl_4^-$ complex during reaction with a mixture of $SOCl_2$ and pyridine. Raman spectroscopy, and NMR studies showed that the oxidation of gold takes place through the formation of a charge-transfer complex ($SOCl_2$ -pyridine) which can activate thionyl chloride to oxidize the metallic gold. Calcination has been proposed for recovery of gold from the solution.¹⁴⁴ Yoshimura et al. has developed a new way to dissolve metallic gold in a non-aqueous media.¹⁴⁵ During their studies, a mixture of dimethyl sulfoxide (DMSO), potassium bromide, and copper (II) bromide was used as a new leaching solution for gold. The highest rate of gold dissolution,

370 gm⁻²h⁻¹, was obtained in a DMSO solution including 0.2M of CuBr₂ and 0.2 M of KBr at 75 °C. During the dissolution of gold, CuBr₂ acts as an oxidizing reagent, and it can also provide bromide ions to form a complex with the dissolved gold. It was shown that in the absence of KBr, the majority of gold dissolves as AuBr₄⁻ as follows:



By adding KBr to the solution, AuBr₂⁻ was proven to be the dominant dissolved gold species (eqn. 1.45).



To recover gold from the DMSO solution, water was added to the system, resulting in precipitation of gold from the solution. By adding water in 1:2 ratio (water: DMSO), around 87% of gold was reduced to the metallic gold and recovered after 24 hours. Along with gold, some copper was also reduced and precipitated out from the solution.¹⁴⁵

Regarding the gold leaching in non-aqueous media, none of the reported leaching methods to date have meet all of the requirements for an ideal industrial leaching system which can be summarized as follows: high dissolution rates, low toxicities, solution stability, recyclability and low costs. Besides, the efficiency of these systems has not been tested on actual gold ore and/or e-waste samples.

Although, the aqueous media has been widely studied for dissolution and recovery of gold, and several leaching reagents have been reported, the study of the non-aqueous solutions is a completely new area in the chemistry of gold extraction. With only a handful of papers in the literature regarding organic systems, the future for leaching and recovery of precious metals, especially gold from both primary and secondary sources, is a completely open field. Aqueous

systems for gold leaching have many problems associated with them as described above. With the right selection of organic solvents and additives, many of these problems could be overcome resulting in new systems that could outperform aqueous systems environmentally, economically and with higher leaching efficiencies.

1.5 Research Objectives

As discussed in previous sections, there are some major challenges to recover gold from both primary and secondary sources in industry, and none of the reported leaching systems in both aqueous and non-aqueous media meet all of the requirements to extract and recover gold from ores and electronic wastes efficiently in a safe manner. The main objective of my PhD work was to develop new gold extraction methods which could extract gold from ores and/or secondary sources like e-waste in a safer, faster and more suitable way than current methods. The following two proposals were investigated to reach the stated goals.

1) *Development of a simultaneous leaching and solvent extraction system for gold:* Aqua regia which is a mixture of three parts concentrated HCl and one part HNO₃ is one of the strongest solutions which can dissolve metallic gold with extremely fast kinetics. Decreasing the concentrations of hydrochloric and nitric acids (starting materials) results in a dramatic decrease in the rate of gold dissolution. Our hypothesis is that by performing leaching and solvent extraction steps simultaneously in the presence of an appropriate extractant, we can extract H₂AuCl₄ from the aqueous phase under mild conditions and thus push the gold dissolution equilibrium toward the formation of more H₂AuCl₄. Essential to this, very efficient extractants must be applied to extract even ppm amounts of leached gold under mild conditions into the organic phase. A simultaneous leaching and solvent extraction system has not previously been reported. Different derivatives of dithiobiuret ligands were studied during the simultaneous leaching and solvent extraction system

under mild acidic conditions. The main rationale of employing this class of ligands was that appropriate sulfur containing compounds can be one of the best candidates for extraction of gold, as in conformity with Pearson's concept of "hard acid / soft acid and hard base / soft base", precious metals such as gold are typically classified as soft acids while sulfur containing compounds are classified in soft bases, and appropriate sulfur containing ligands, especially chelating ligands, can have a strong interaction with gold and extract it selectively during the simultaneous process. Furthermore, by employing leaching and solvent extraction at the same time, gold could be leached and purified simultaneously in a single operation method.

2) Development of organic solvent based methodologies as viable alternatives to aqueous systems for the efficient leaching of gold

Another aim of my PhD thesis was to develop improved purification strategies to reach highly pure gold (i.e. >99.9% purity) that could be applied to the above proposed gold recycling systems to recover gold effectively from the resulting leaching solutions.

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CHAPTER 2

2. Simultaneous leaching and solvent extraction of gold

2.1 Introduction

The cyanidation technique has been in use for more than a century in gold mines to leach out gold from ores. However, cyanide leaching suffers from some major drawbacks such as slow reaction kinetics, extremely toxic nature of cyanide as well as major environmental costs like high water and energy consumptions.^{1,2} In addition, due to serious environmental accidents in various gold mines around the world, gold leaching by cyanidation has been prohibited in many countries in recent years.³ Therefore, considerable efforts have been made to find an alternative to cyanide and a variety of leaching reagents have been studied and proposed, such as thiourea, thiosulfate, thiocyanate and halides.⁴⁻¹² Between different halides, chloride (usually in the form of NaCl or hydrochloric acid) is one of the most promising leaching reagents which is usually applied with a strong oxidant like H₂O₂, HNO₃ or hypochlorite.¹³

In general, following the leaching step in the cyanidation process, gold is recovered mainly by activated carbon adsorption, or occasionally by the zinc cementation process which the earlier is considerably more common.¹⁴ In addition to the cyanide leaching step, gold recovery by activated carbon also suffers from several drawbacks, such as low selectivity, very long procedures, loss of gold product and high temperature requirements¹⁵, all of which bring additional costs during the gold recovery process. Solvent extraction techniques have been proposed as one of the viable alternatives for selective gold isolation from alkaline cyanide leach solution and has been studied extensively.¹⁶ By possessing fast extraction kinetics, and reaching high selectivity, solvent extraction is able to simplify the whole refining process.¹⁷⁻¹⁹ Different types of extractants have been studied and some of them have been proposed as effective extracting reagents like primary, secondary, tertiary and quaternary amines^{20,21}, dibutyl carbitol (DBC)²², organophosphorous derivatives²³ and guanidine-based extractants.²⁴ Although quaternary

amines^{25,26} and guanidine derivatives (especially LIX 7950)²⁷ have been reported as the most suitable extractants for selective extraction of gold from cyanide solution, the control of pH to avoid generation of highly toxic HCN gas makes the solvent extraction technique difficult in practice, and in addition to that, quaternary amines are also difficult to strip.²⁸ Indeed, these extractants are more suitable for neutral or acidic conditions, as they need to be protonated first to extract $\text{Au}(\text{CN})_2^-$ as an ion pair into the organic phase. As was mentioned earlier, chloride-based leaching has been proposed as an alternative to cyanide, and many extractants have also been investigated for selective extraction of gold from this media such as dibutyl carbitol (DBC)²⁹, sulfur-based extractants³⁰⁻³², tertiary and quaternary amines,³³ tributyl phosphate (TBP)³⁴, tributyl phosphine oxide (TBPO)³⁵, and primary amides.³⁶ Although considerable effort has been undertaken to replace cyanide and/or activated carbon, none of the reported leaching and extracting reagents has been used in the industrialization of gold production. Therefore, more effective leachants and extractants with higher efficiencies and lower toxicities need to be developed from both environmental and economical viewpoints.

2.2 Result and discussion

Appropriate sulfur containing compounds can be one of the best candidates for solvent extraction of gold, because in conformity with Pearson's concept of "hard acid / soft acid and hard base / soft base"³⁷, precious metals such as gold are typically classified as soft acids while sulfur containing compounds are classified in soft bases. Therefore, appropriate sulfur containing ligands, especially chelating ligands, can be used as highly selective extractants for extraction and recovery of gold. The general structure as shown in Fig. 2.1 will be an ideal system for selective extraction of gold from aqueous solutions. The ligand has two thiocarbonyl donor sites to bind to

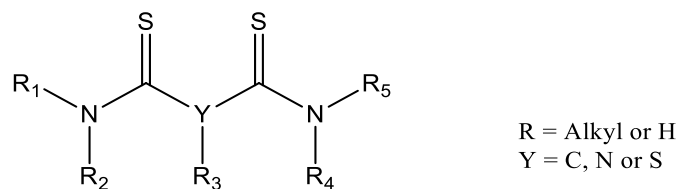


Figure 2.1 The general structure of proposed sulfur-based ligands for selective extraction of gold.

a metal center which potentially make it an excellent bidentate ligand, forming highly stable six-membered ring complexes with precious metals like gold. In addition, based on the resonance contributors depicted in Fig. 2.2, the nitrogen atoms could increase the Lewis basicity at the sulfur atoms, making the sulfur electrons more available to donate to the metal center (further resonance contributors exist when Y = N or S). Aqua regia is a well-known leaching reagent for gold and other transition metals, but high leaching efficiency is only achieved under harsh conditions (by applying high concentrations of acid and oxidant). For example the rate of gold dissolution in aqua regia is $1850 \text{ gm}^2\text{h}^{-1}$ while by decreasing the concentration of HCl and HNO_3 (from their concentrated forms) to 1 and 0.2 M, the rate will dramatically drops to around $1 \text{ gm}^2\text{h}^{-1}$. The reaction of gold with hydrochloric acid in the presence of an oxidant like HNO_3 is an equilibrium reaction (eqn. 2.1) in which formation of AuCl_4^- is favored by employing high concentrations of all reagents.

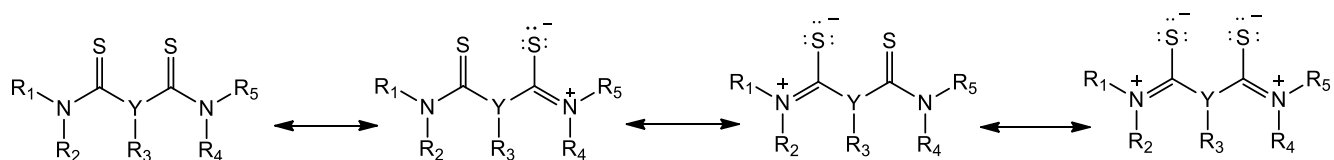
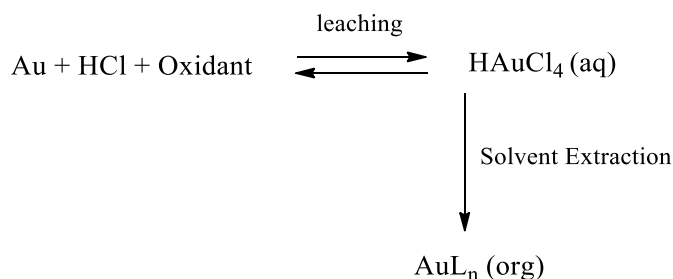


Figure 2.2 Different resonance contributors for the ligand shown in Fig. 2.1.



Decreasing the concentration of HCl and/or HNO₃ will push the equilibrium to the left and decreases the rate of gold dissolution. It will obviously be challenging to reach high dissolution rates for gold while maintaining the concentrations of the starting materials low. In all reported cases for gold recovery in acidic media, the solvent extraction stage is always accomplished after the leaching step which leads to applying harsh conditions and long process time for the leaching step, making the acidic media a non-economical leaching procedure with high environmental issues. A theoretical option to reach the fast gold dissolution kinetics at low concentrations of HCl/HNO₃ is removing the formed HAuCl₄ during the reaction which pushes forward the above equilibrium. Based on our hypothesis, combination of leaching and solvent extraction steps can remove the leached gold and withdraw it into the organic phase at the same time, leading to pushing the dissolution equilibrium to the right. As shown in Scheme 2.1, the whole process can be accomplished by forcing the reaction equilibrium to the right by withdrawing the dissolved gold from the aqueous solution containing small amounts of acid and oxidant into the organic phase containing an extractant. Essential to this, highly efficient extractants must be applied which are



Scheme 2.1 Simultaneous leaching and solvent extraction of gold in acidic media.

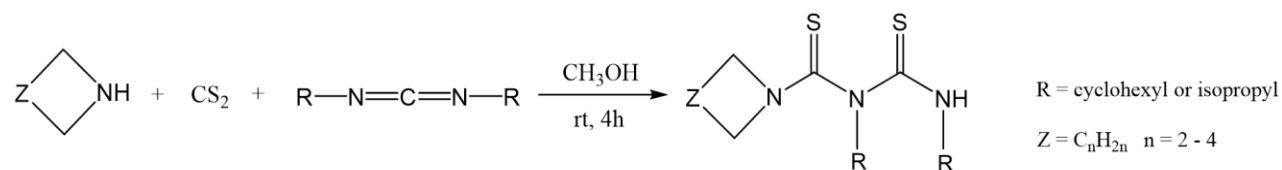


Figure 2.3 The reaction scheme to synthesize dithiobiurets, and their general structure as strong ligands for selective extraction of gold from HCl media.

able to extract even very small amounts of dissolved gold under mild conditions. As it was earlier mentioned, sulfur-based ligands can be a suitable candidate for this purpose as they have shown high efficiency to extract tiny amounts of gold selectively from acidic media. A good example is new synthesized derivatives of dithiobiuret, shown in Fig. 2.3 which have been proven to be very strong ligands for selective extraction of gold and palladium from hydrochloric acid media.³⁰ Different derivatives of dithiobiuret ligands, shown in Fig. 2.4, were chosen as effective extractants to test our hypothesis in practice. These derivatives were easily synthesized through a one-pot

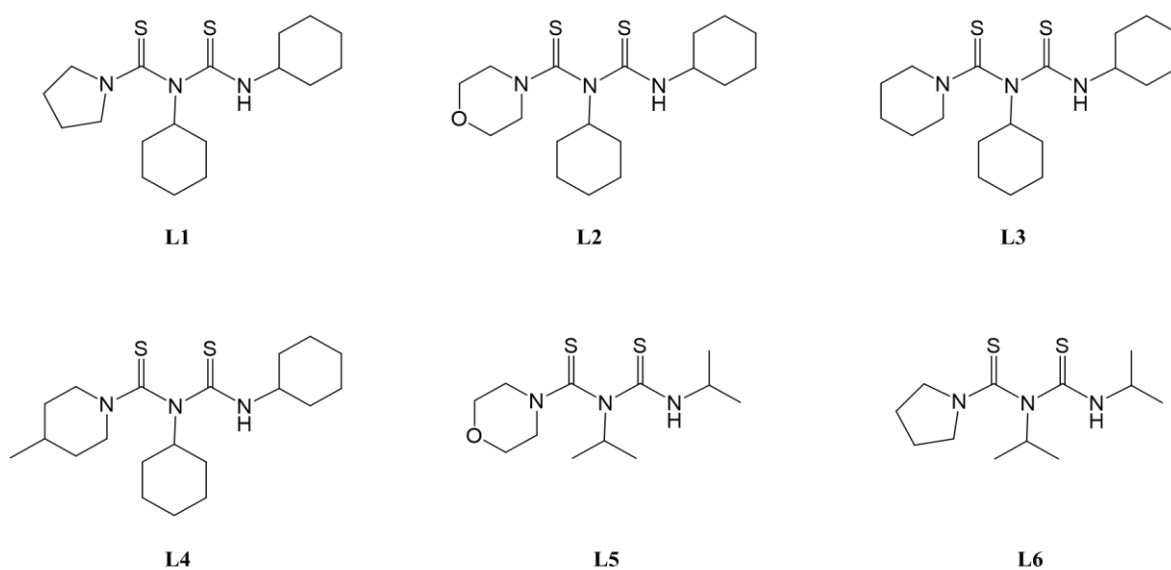


Figure 2.4 The structure of studied ligands employed for the simultaneous process.

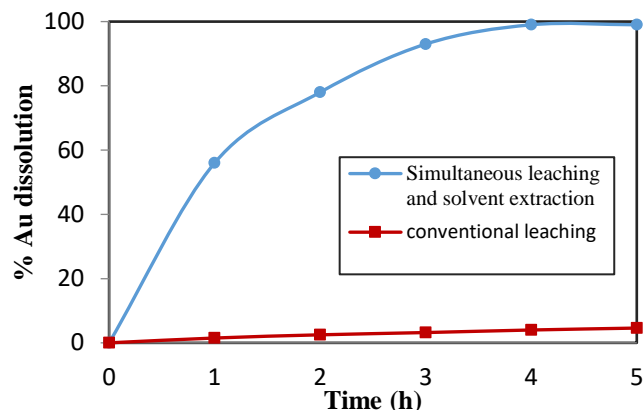


Figure 2.5 Simultaneous leaching and solvent extraction system vs conventional leaching in acidic solution. Conventional leaching conditions: 10.0 mg gold powder (200 mesh) in 5 ml HCl 1M, and HNO₃ 0.2M. Simultaneous leaching and solvent extraction: 10.0 mg gold powder (200 mesh) in 5 ml HCl 1M, and HNO₃ 0.2M, 71.7 mg L1 in 5 ml dichloromethane.

synthesis reaction of secondary cyclic amines with carbon disulfide and diisopropyl or dicyclohexylcarbodiimide in methanol. Stirring the reaction mixture at rt for 4 hours resulted in formation of a white precipitate as a final product with high yields (>85% for all derivatives). Fig. 2.5 shows that the rate of gold dissolution increases with the simultaneous leaching and extraction system until it reaches 99% after 4 hours and remains constant, which is substantially faster than the gold dissolution by conventional acidic leaching system with exactly the same amounts of HCl and HNO₃. In addition to a faster leaching step, the separation and purification of the dissolved gold is accomplished at the same time during our new recovery system, leading to significantly

Table 2.1 Gold recover by using different derivatives of dithiobiuret during the simultaneous process. Reaction condition: aq phase: 0.05 mmol gold powder in 5.0 ml HCl 1M, and HNO₃ 0.2M. org phase: 0.2 mmol ligand in 5.0 ml dichloromethane.

Ligand	L1	L2	L3	L4	L5	L6
Au recovery	>99%	70%	95%	96%	93%	72%

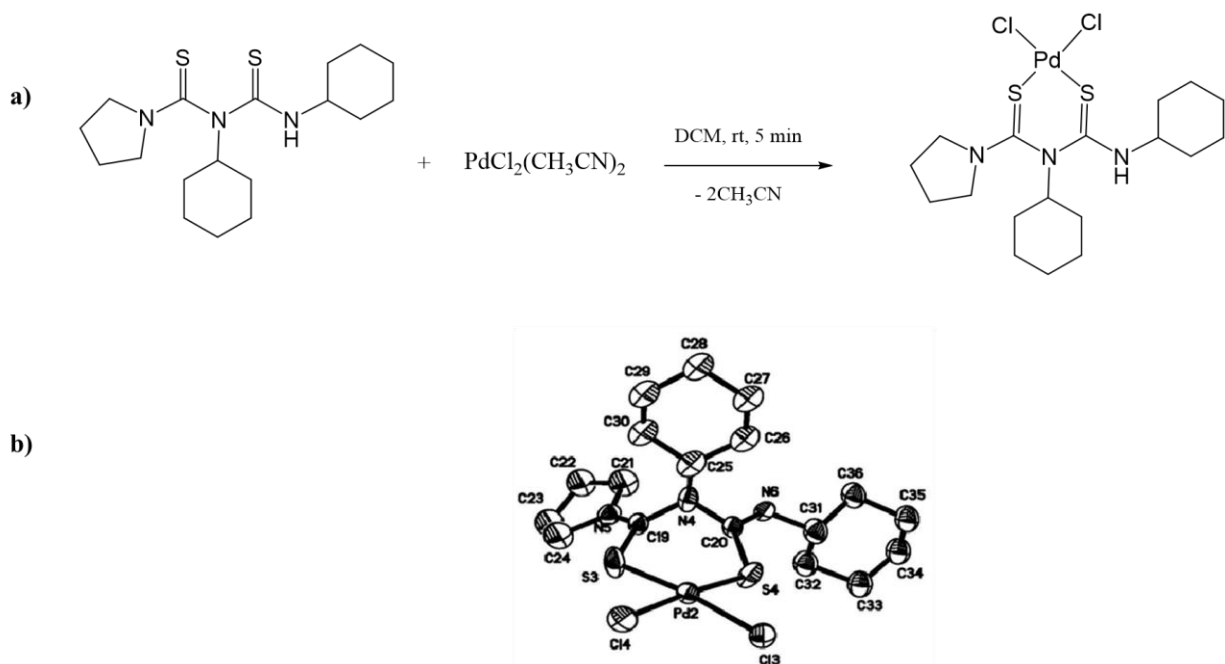


Figure 2.6 a) A reaction scheme to synthesize $[(L1)PdCl_2]$ complex and **b)** Molecular structure of $[(L1)PdCl_2]^*$. *The structure for the $[(L1)PdCl_2]$ was not completely solved as R value was too high. The attempts to grow better crystals was unsuccessful.

faster processing times than conventional recovery systems in which leaching and purification steps are performed separately. Between different derivatives of dithiobiuret, ligand L1 showed the highest efficiency during the simultaneous process (table 2.1). It seems, the dithiobiuret ligands with less polarity are more effective extractants during the simultaneous leaching and solvent extraction of gold. As was earlier mentioned, this class of ligands has been proven to be highly effective extractants for the selective extraction of gold and palladium during the solvent extraction process. To investigate the chemistry of interactions between this class of ligands with gold and palladium, they were directly reacted with chloride precursors of these metals in dichloromethane with different molar ratios. In the case of palladium, one or two equivalents of the dithiobiuret ligand was reacted with one equivalence of $PdCl_2(CH_3CN)_2$ in DCM, and the reaction mixture was

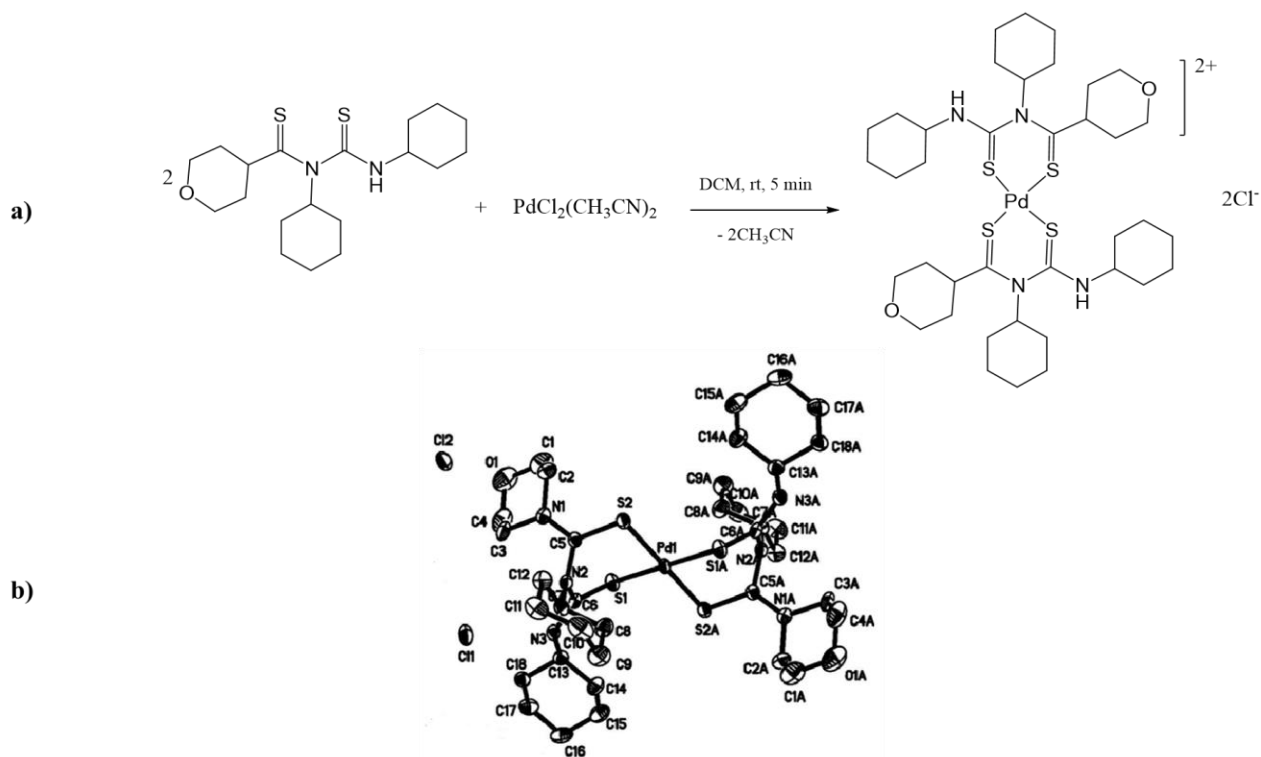


Figure 2.7 a) A reaction scheme to synthesize $[(L_2)_2Pd]Cl_2$ complex and **b)** Molecular structure of $[(L_2)_2Pd]Cl_2$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles for the L₂:Pd (2:1) complex: Pd1-S1 = 2.2898(10); Pd1-S1a = 2.2898(10); C1-S1 = 1.704(4); C1-N1 = 1.404(4); C1-N2 = 1.303(4); N2-C3 = 1.484(5); Pd1-S2 = 2.3033(10); Pd1-S2a = 2.3032(10); C2-S2 = 1.712(3); C2-N1 = 1.383(4); C2-N3 = 1.306(4); N3-C13 = 1.465(4); S1-Pd-S1a = 180.00(5); S1-Pd-S2a = 87.68(4); S1-Pd-S2 = 92.32(4); N1-C1-S1 = 124.2(3); N2-C1-S1 = 119.6(3); N2-C1-N1 = 116.0(3); N3-C2-S2 = 120.8(3); N1-C2-S2 = 123.1(3); N3-C2-N1 = 116.1(3). The crystal and structural refinement data can be found in Table 2.6.

stirred at rt for 5 min. A deep-red solution was obtained in both cases, and then the solvent was evaporated, and the resulting solid compounds re-dissolved in different solvent mixtures to grow crystals. The X-ray diffraction studies of the crystals showed a chelate formation between thiocarbonyl groups of the ligand and Pd in a square planar geometry in both cases of 1:1 and 1:2 (Pd: L) complexes, which was completely in agreement with our predictions (Fig. 2.6 and 2.7). The thiocarbonyl groups can readily replace chloride ligands, forming highly stable complexes with palladium. The dithiobiuret ligand was also reacted with NaAuCl₄ in DCM at rt, and an orange solution was formed promptly. Suitable crystals for a single-crystal X-ray analysis of the complex

Table 2.2. Crystal data and structure refinement for [(L2)₂Pd]Cl₂ complex.

Empirical formula	C ₄₀ H ₆₆ Cl ₁₄ N ₆ O ₂ Pd S ₄	
Formula weight	1393.92	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.1665(13) Å	α = 103.062(6)°.
	b = 13.4677(16) Å	β = 90.031(6)°.
	c = 23.644(3) Å	γ = 100.481(5)°.
Volume	3098.0(7) Å ³	
Z	2	
Density (calculated)	1.494 Mg/m ³	
Absorption coefficient	1.076 mm ⁻¹	
F(000)	1424	
Crystal size	0.370 x 0.240 x 0.190 mm ³	
Theta range for data collection	0.885 to 27.596°.	
Index ranges	-13<=h<=13, -17<=k<=17, -30<=l<=30	
Reflections collected	72069	
Independent reflections	14263 [R(int) = 0.0311]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6806	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14263 / 0 / 604	
Goodness-of-fit on F ²	1.036	
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.1610	
R indices (all data)	R1 = 0.0761, wR2 = 0.1745	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.993 and -1.467 e.Å ⁻³	

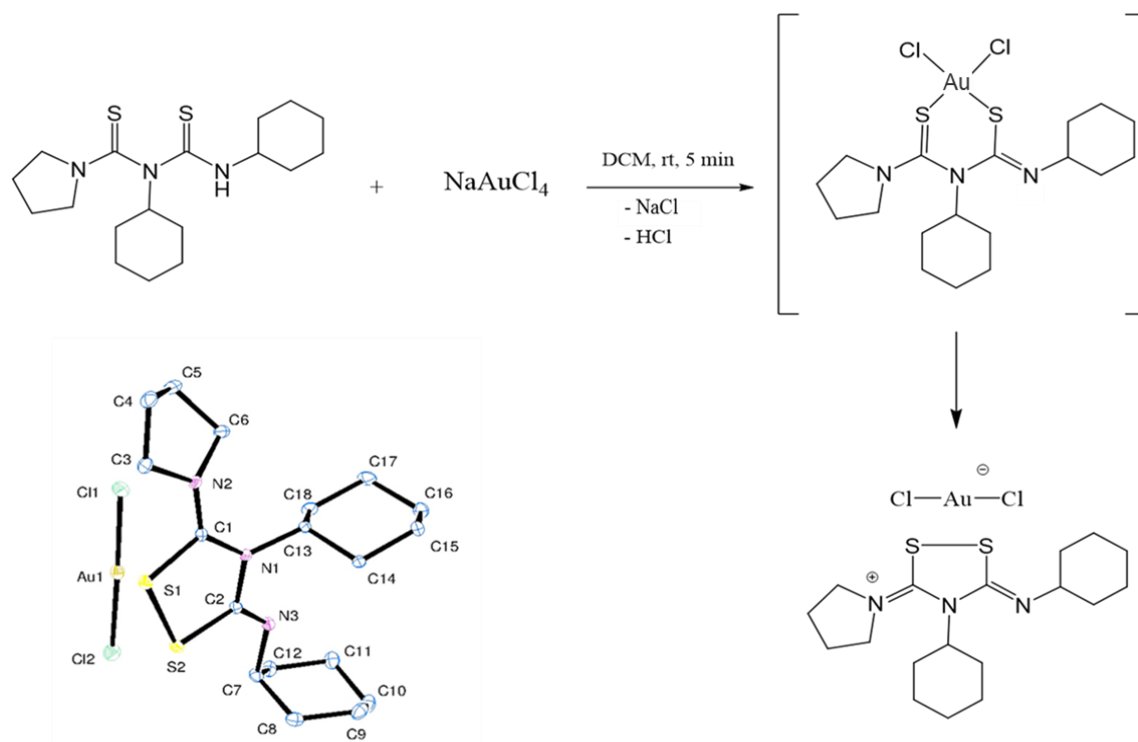


Figure 2.8. The reaction scheme for synthesizing $[(L1)AuCl_2]$ complex and its molecular structure with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles for the $[(L1)AuCl_2]$ complex: Au1-Cl1 = 2.2678(6); Au1-Cl2 = 2.2651(6); S1-S2 = 2.0579(7); C1-S1 = 1.7528(19); C1-N1 = 1.352(2); C1-N2 = 1.304(3); C1-S1 = 1.7528(19); C2-S2 = 1.7800(19); C2-N1 = 1.419(2); C7-N3 = 1.469(2); Cl1-Au1-Cl2 = 178.29(2); S2-S1-C1 = 95.08(7); S1-S2-C2 = 95.09(7); S1-C1-N2 = 116.40(14); S1-C1-N1 = 116.73(14); N2-C1-N1 = 126.87(17); S2-C2-N1 = 113.77(13); S2-C2-N3 = 124.75(15); N1-C2-N3 = 121.42(17). The crystal and structural refinement data can be found in Table 2.7.

of L1 with Au (1:1) was also obtained and its molecular structure could be solved (Figure 2.8). The obtained structure revealed a completely different interaction between the dithiobiuret ligands and gold for the 1:1 molar ratio. The structure indicated that Au(III) had been reduced to Au(I) while the ligand itself oxidized to form a sulfur-sulfur bond, leading to formation of an ion-pair complex, depicted in Fig. 2.8. The formation of the ion-pair between gold and L1 is presumably through the formation of a chelate complex similar to the palladium compound, shown in Fig. 6.2a, which is finally converted to the reduced gold product. The high affinity of Au(III) for reduction, and sulfur-based ligands to form disulfides are the two main driving forces for this type of

Table 2.3. Crystal data and structure refinement for [(L1)AuCl₂] complex.

Empirical formula	C18 H30 Au Cl2 N3 S2	
Formula weight	620.43	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.74850(10) Å	α = 88.8750(10)°.
	b = 8.6845(2) Å	β = 83.2720(10)°.
	c = 19.6624(5) Å	γ = 76.6150(10)°.
Volume	1113.31(4) Å ³	
Z	2	
Density (calculated)	1.851 Mg/m ³	
Absorption coefficient	7.043 mm ⁻¹	
F(000)	608	
Crystal size	0.200 x 0.200 x 0.070 mm ³	
Theta range for data collection	2.619 to 27.500°.	
Index ranges	-8<=h<=8, -11<=k<=10, -25<=l<=25	
Reflections collected	26203	
Independent reflections	5099 [R(int) = 0.0228]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5099 / 0 / 235	
Goodness-of-fit on F ²	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0155, wR2 = 0.0329	
R indices (all data)	R1 = 0.0172, wR2 = 0.0335	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.792 and -0.499 e.Å ⁻³	

reactions.³⁸

To characterize the molecular structure of extracted species during the simultaneous process, a mixture of gold powder, the dithiobiuret ligand in DCM, and an aqueous solution of HCl 1M and HNO₃ 0.2 M were stirred for 4 hours, and after isolation of the organic phase, the solvent was evaporated, and the resulting red precipitate re-dissolved in a mixture of THF and hexanes to grow the appropriate crystals. Single-crystal X-ray analysis of the isolated complex in the organic phase was performed (Figure 2.9). The obtained structure showed that one of the thiocarbonyl groups had been converted to carbonyl while the other one remained intact. This

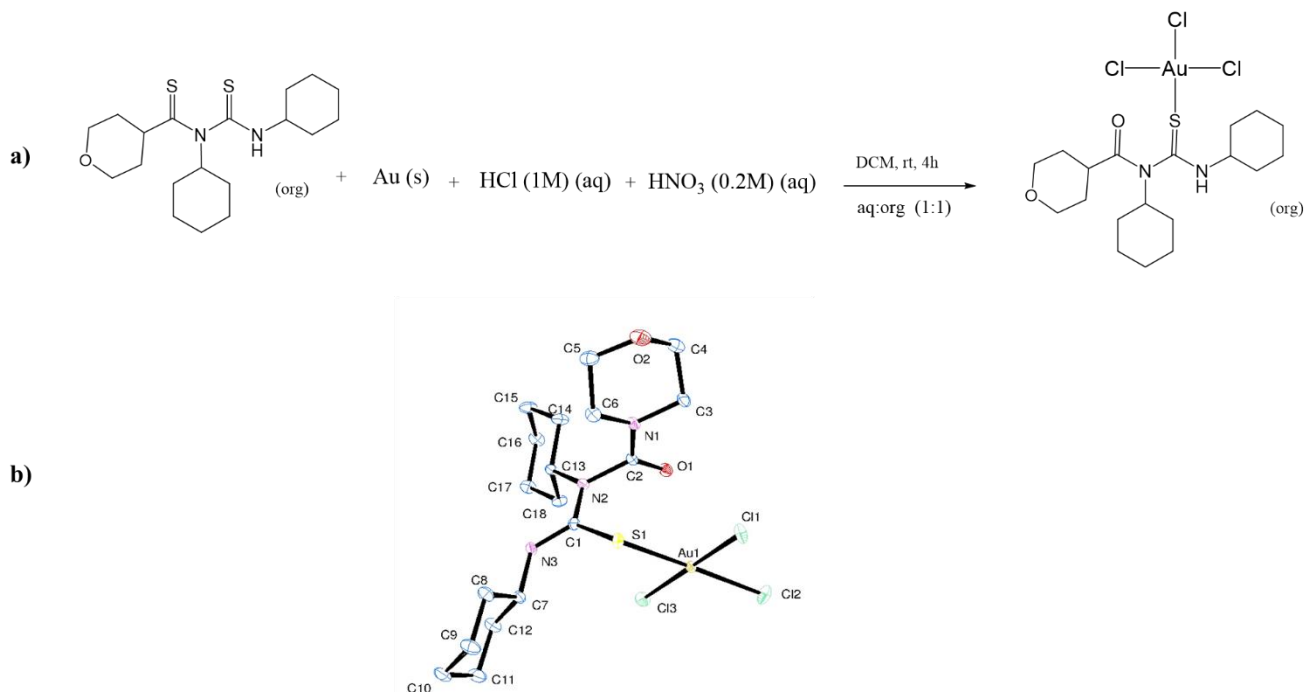


Figure 2.9 Molecular structure of the isolated gold species during the simultaneous leaching and solvent extraction of gold with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles for the complex: Au1-Cl1 = 2.2823(7); Au1-Cl2 = 2.3088(7); Au1-Cl3 = 2.2874(7); Au1-S1 = 2.3101(7); S1-C1 = 1.763(3); N2-C1 = 1.333(3); N3-C1 = 1.317(3); O1-C2 = 1.213(3); N1-C2 = 1.333(3); N2-C2 = 1.470(3); N3-C7 = 1.479(3). Cl1-Au1-Cl3 = 177.83(3); Cl1-Au1-Cl2 = 89.71(3); Cl3-Au1-Cl2 = 91.52(3); Cl1-Au1-S1 = 85.77(3); Cl3-Au1-S1 = 92.86(3); Cl2-Au1-S1 = 173.73(2); C1-S1-Au1 = 105.57(9); N3-C1-S1 = 118.6(2); N2-C1-S1 = 118.74(18); N3-C1-N2 = 122.3(2); O1-C2-N1 = 126.1(2); O1-C2-N2 = 119.2(2); N1-C2-N2 = 114.6(2). The crystal and structural refinement data can be found in Table 2.8.

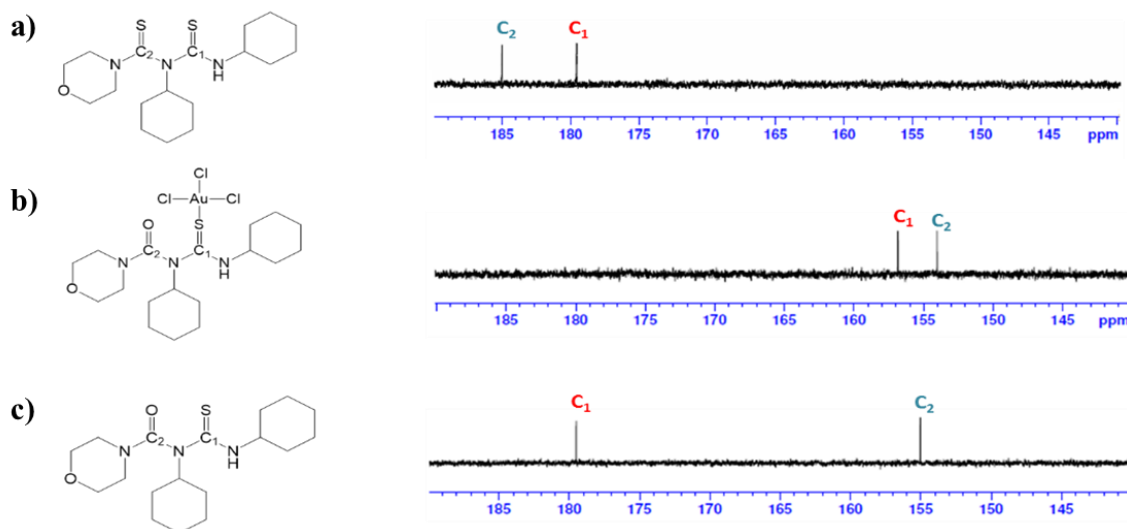


Figure 2.10 The ^{13}C NMR spectrums of **a)** the dithiobiuret free ligand (L2), **b)** extracted gold complex during the simultaneous process, and **c)** the stripped ligand after the simultaneous process (L2').

conversion during the simultaneous process is due to the presence of HNO_3 as a strong oxidant. Also, the metallic gold acts as a catalyst for this reaction as no conversion was observed in the absence of gold powder under exactly the same conditions. By forming a chelate between gold and the thiocarbonyl groups of the ligand, the thiocarbonyl will presumably be activated for a nucleophilic attack by water, followed by the conversion of sulfur to SO_3 or SO_4^{2-} (good leaving groups) by nitric acid³⁹, resulting in formation of the gold complex shown in Fig 2.9. The remaining thiocarbonyl group can still significantly interact with the leached gold in the aqueous solution and extract it into the organic phase. This interaction was indicated by significant chemical shifts in both ^1H and ^{13}C NMR spectrums of the isolated gold complex. ^{13}C NMR spectrum also clearly showed the thiocarbonyl conversion, as both signals corresponding to thiocarbonyl groups of the free ligand at 181 and 184 ppm shifted to up-field at 152 and 155 ppm respectively in the good complex (Fig. 2.10). After stripping the organic phase to recycle the ligand by a solution of thiourea in 1M sulfuric acid, the ^{13}C NMR showed a big chemical shift for one of the thiocarbonyl

Table 2.4. Crystal data and structure refinement for gold complex formed during the simultaneous leaching and solvent extraction process.

Chemical formula	$C_{19}H_{33}AuCl_5N_3O_2S$
Formula weight	741.76 g/mol
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal size	0.200 x 0.300 x 0.400 mm
Crystal habit	clear dark orange irregular chip
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	$a = 14.0845(4)$ Å $\alpha = 90^\circ$ $b = 14.0441(4)$ Å $\beta = 111.7160(10)^\circ$ $c = 14.6331(5)$ Å $\gamma = 90^\circ$
Volume	2689.06(14) Å ³
Z	4
Density (calculated)	1.832 g/cm ³
Absorption coefficient	6.067 mm ⁻¹
F(000)	1456
Index ranges	-19<=h<=20, -20<=k<=19, -19<=l<=20
Reflections collected	31432
Independent reflections	8214 [R(int) = 0.0238]
Coverage of independent reflections	99.1%
Absorption correction	multi-scan
Max. and min. transmission	0.7461 and 0.5550
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8214 / 0 / 280
Goodness-of-fit on F ²	1.023
Final R indices	6800 data; I>2σ(I) R1 = 0.0259, wR2 = 0.0587 all data R1 = 0.0360, wR2 = 0.0625
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0298P)^2+2.5529P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.921 and -1.084 eÅ ⁻³

Table 2.5. Selectivity studies for the simultaneous leaching and solvent extraction of gold in the presence of high concentrations of base metals.

	Fe	Cu	Zn	Ni	Co	Au
aq phase before extraction (ppm)	992	2140	543	562	523	113
aq phase after extraction (ppm)	991	2140	542	562	523	0.3
stripping solution (ppm)	0.4	<0.1	<0.1	<0.1	<0.1	112

peaks from 184 to 155 ppm which was attributed to conversion of one of the thiocarbonyl groups to a carbonyl group (Fig. 2.10c).

To investigate the role of ligand concentration on gold leaching, different ratios of ligand: metal were applied during the simultaneous system. With 1:1 ratio, only 42% of gold was recovered after 4 hours with optimized HCl and oxidant concentrations (1M HCl and 0.2 M HNO₃). Gold dissolution was increased with increasing the ligand concentration and reached 99.8% at 3:1 ratio (L1: Au). Further increasing the ligand concentration resulted to decrease in gold dissolution rate which is likely due to oxidant consumption by the ligand itself which is a competition reaction with gold dissolution at the same time. Different solvent systems including dichloromethane (DCM), chloroform, dichloroethane, chlorobenzene, 1,4-dichlorobenzene, and toluene were investigated as the organic phase during the simultaneous process. Between these solvents, DCM, 1,4-dichlorobenzene, and chloroform showed high efficiency, with DCM being the most effective one. So that, by employing L1, more than 99% gold was leached and extracted into the dichloromethane in less than 4 hours. However, most chlorinated solvents are not suitable solvent systems as there are some major safety issues associated with their use in large scales. However, by replacing ligand L1 with L4, high efficiency was obtained in toluene which is a more suitable organic solvent for industrial applications. Indeed, greater than 99% gold was leached and

extracted into toluene in around 5 hours when L4 was applied as the extractant (in 1:3 ratio (L4: Au)). In another experiment, the selectivity of the process was examined by dissolving metallic gold in the presence of some base metals including Fe, Co, Cu, Ni and Zn in their chloride forms. AAS analysis of both aqueous and stripping solutions revealed that less than 1 ppm of base metals was extracted into the organic phase which showed high efficiency of the method for leaching and selective extraction of gold even in the presence of high concentrations of base metals (Table 2.5). This high selectivity leads to a significant decrease in HCl and HNO₃ consumption, and recovery of gold with high purity in a single step operation. The efficiency of this new technique was examined on actual gold ore samples, provided by Claude Resources' Seabee Gold mine, with the average gold content of 10.4 ppm. By applying the optimized conditions on the ore (HCl 1M, HNO₃ 0.4 M, and ligand L1(0.017 M)), more than 94% of gold was recovered after stirring for 9 hours which was significantly faster than the cyanidation leaching which took 35 hours just for

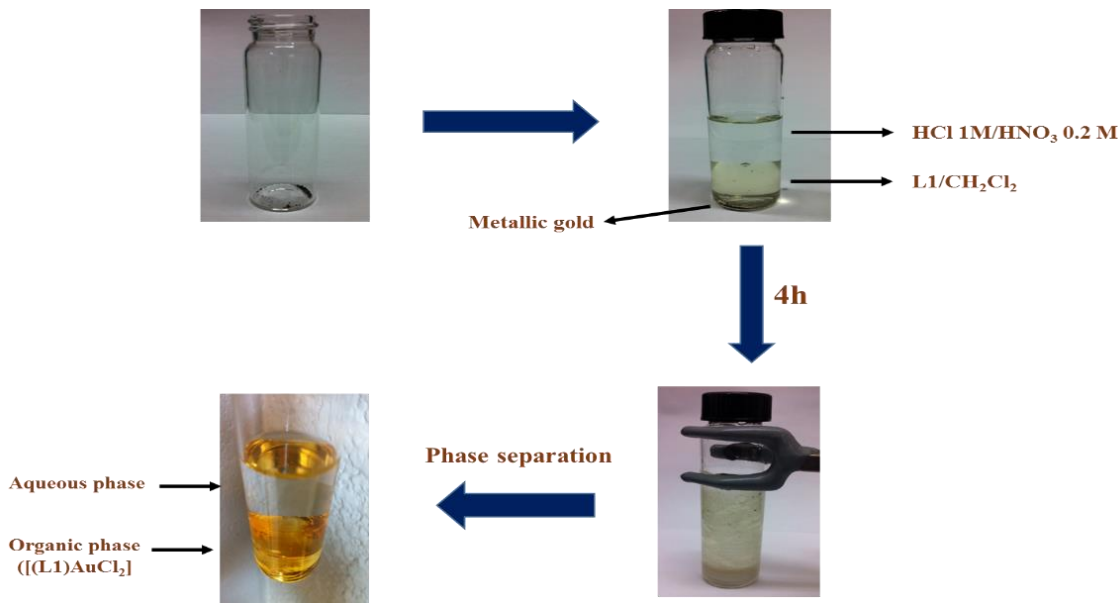


Figure 2.11 The simultaneous leaching and solvent extraction of gold.

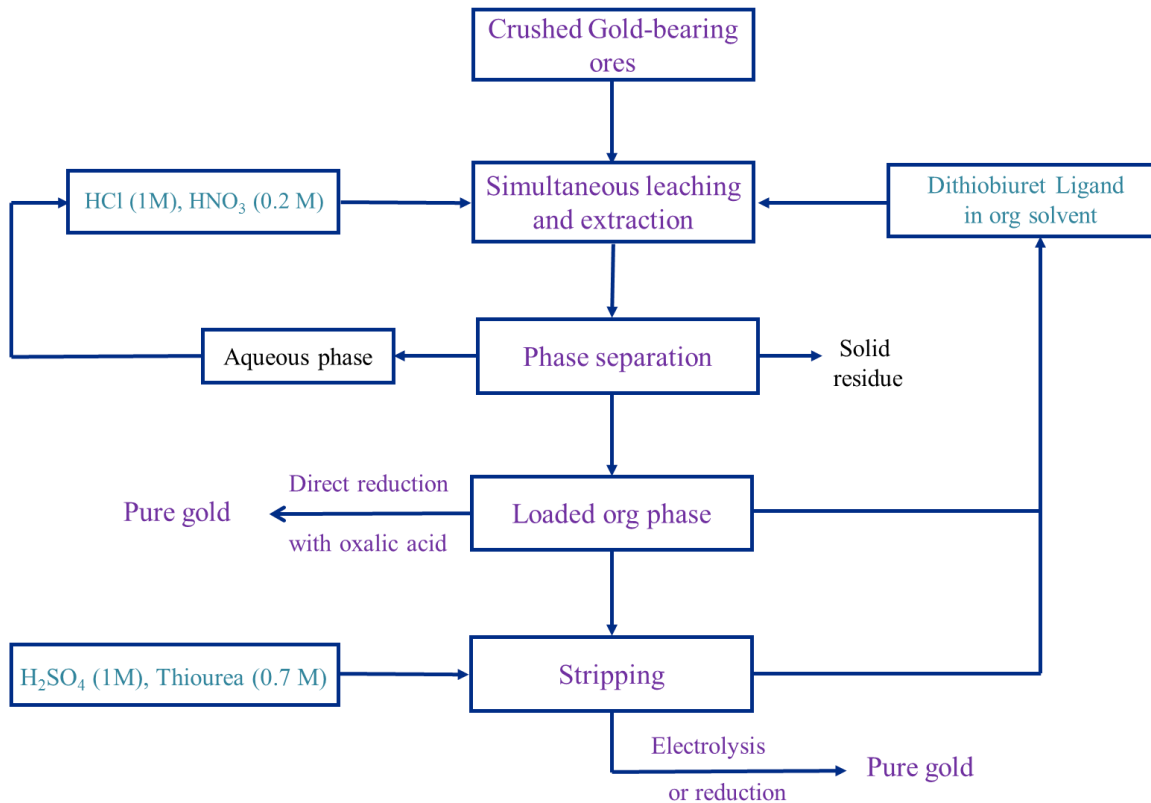


Figure 2.12 The proposed flowchart for gold ore treatment using the simultaneous leaching and solvent extraction system.

the leaching step for the same ore sample. In addition, in the simultaneous process, both leaching and purification were performed at the same time, resulting in a substantial reduction in the whole processing time. In the next step, after separation of the three phases (treated ore, aqueous and organic phases), the pregnant organic solution was stripped using a 1M sulfuric acid solution containing 0.7 M thiourea (1:1 ratio) for 15 min, leading to recycling the dithiobiuret ligand for another cycle of gold ore treatment. The same organic phase was reused 5 times to extract gold from fresh ore samples, showing the same degree of efficiency. Fig. 2.12 shows a proposed flowchart to recover gold from gold ore in industrial scales. Based on this diagram, gold ore can be treated with a mixture of an aqueous solution containing small amounts of HCl and HNO₃, and an organic phase containing the dithiobiuret ligands. After stirring the whole mixture for an

appropriate time, the aqueous phase is sent for a new extraction cycle (after adjusting the HCl and HNO₃ concentrations), and the organic phase will be isolated and stripped with a 1M H₂SO₄ solution containing thiourea to regenerate the organic phase for a new extraction cycle, and produce an aqueous solution of pure gold, suitable for reduction by electrolysis or direct reduction with a reducing agent such as sodium borohydride.

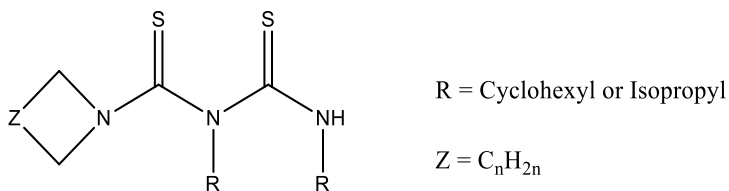
2.3 Conclusion

Modern gold extraction processes from primary sources have changed little over the past 100 years, and cyanide is still the preferred leaching reagent used in 90% of gold mines worldwide. However its continued use presents significant environmental risks. After the leaching step, gold is isolated by activated carbon method in which Au(CN)₂⁻ is adsorbed selectively during a very long process. Although a few alternatives have been reported to cyanide and activated carbon, none have been widely implemented, and the discovery of more efficient and benign gold extraction technologies is the main problem facing the gold industry today. During the present work, a new cyanide-free gold extraction method has been developed in which both the leaching and purification steps are simultaneously accomplished, resulting in improvement in leaching kinetics under substantially milder conditions. In this new method, the gold bearing materials are contacted with a biphasic solution including an acidified aqueous phase including small amounts of HCl and HNO₃, and a water-immiscible organic solvent containing a dithiobiuret-based ligand, and the resulting mixture is stirred for a short time to both leach and purify gold at the same time. The applied ligands during this work were proven to be highly selective for extraction of dissolved gold in acidic media, leading to a highly efficient and selective gold extraction process. The efficiency of this new technique was examined on gold ore samples, demonstrating 94% gold

recovery in less than 9 hours which was significantly shorter than the cyanidation process with 35 hours for only the leaching step.

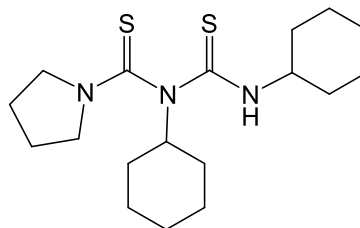
2.4 Experimental

2.4.1 Ligands Synthesis



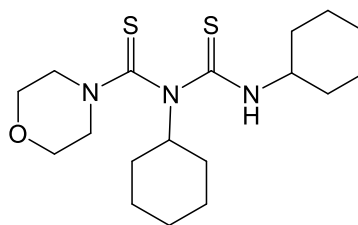
The ligands L1 – L6 were synthesized by following reported literature procedures.⁴⁰ In a round bottom flask, one equivalent of a substituted amine was added in small portions over a period of 1 hour to a mixture of 1.2 equivalents of CS₂ and 1 equivalent of carbodiimide in methanol at room temperature. The reaction mixture was stirred for 4 hours, and then the resulting white precipitate was separated from the solution by filtration. Finally, it was washed with water, brine, and methanol, and dried under vacuum.

2.4.1.1 Ligand L1 Synthesis



1.425 g pyrrolidine (20 mmol) was added in small portions to a mixture of 1.825 g CS₂ (24 mmol) and 4.125 g dicyclohexylcarbodiimide (20 mmol) in 50.0 ml methanol at room temperature. The reaction mixture was stirred for 4 hours, and then the resulting white precipitate was filtered and separated from the solution. Then, it was washed with water, brine (a 5% w/v NaCl solution), an methanol, and finally dried under vacuum, resulting in 6.223 g final product (yield = 88%). ¹H NMR (600.1 MHz, CDCl₃): δ 1.14 (m, 4H, 2CH₂), 1.38 (m, 4H, 2CH₂), 1.58 (m, 4H, 2CH₂), 1.78 (m, 4H, 2CH₂), 1.88 (m, 2H, CH₂), 1.97 (m, 6H, 3CH₂), 3.46 (br, 2H, CH₂), 3.75 (br, 2H, CH₂), 4.34 (m, 1H, CH), 4.92 (m, 1H, CH), 5.85 (d, J=6.9, 1H, NH). ¹³CNMR (150.9 MHz, CDCl₃): δ 24.5 (2CH₂), 24.9 (2CH₂), 25.4 (CH₂), 25.5 (CH₂), 25.9 (3CH₂), 30.4 (2CH₂), 32.5 (2CH₂), 33.0 (CH₂), 53.2 (CH), 60.5 (CH), 178.4 (C=S), 181.6 (C=S).

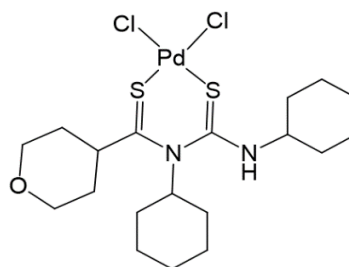
2.4.1.2 Ligand L2 Synthesis



1.745 g morpholine (20 mmol) was added in small portions to a mixture of 1.825 g CS₂ (24 mmol) and 4.125 g dicyclohexylcarbodiimide (20 mmol) in 50.0 ml methanol at room temperature. The reaction mixture was stirred for 4 hours at 600 rpm (stir plate setting), and then the resulting white precipitate was filtered and separated from the solution. Then, it was washed with water, brine, an methanol, and finally dried under vacuum, resulting in 6.710 g final product (yield = 91%). ¹H NMR (600.1 MHz, CDCl₃): δ 1.15 (m, 4H, 2CH₂), 1.38 (m, 4H, 2CH₂), 1.65 (m, 4H, 2CH₂), 1.78 (m, 4H, 2CH₂), 1.90 (m, 2H, CH₂), 2.02 (m, 2H, CH₂), 3.73 (m, 4H, 2CH₂), 3.90 (br, 4H, 2CH₂), 4.32 (m, 1H, CH), 4.97 (m, 1H, CH), 5.93 (d, J = 7.5, 1H, NH). ¹³CNMR (90 MHz, CDCl₃): ¹³CNMR (150.9 MHz, CDCl₃): δ 24.5 (2CH₂), 25.3 (CH₂), 25.4 (CH₂), 25.8 (2CH₂), 30.2 (2CH₂), 32.7 (2CH₂), 50.1 (2CH₂), 53.2 (CH), 60.5 (CH), 65.9 (2CH₂), 178.9 (C=S), 184.2(C=S).

2.4.2 Synthesis of gold and palladium complexes with dithiobiuret ligands

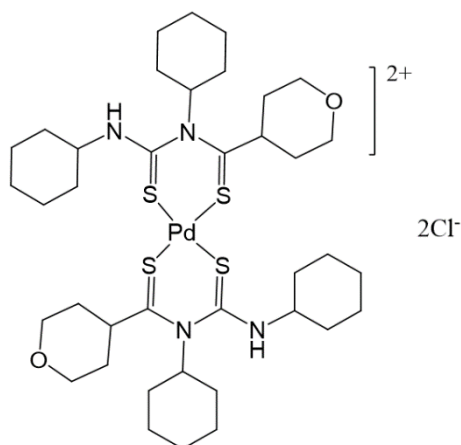
2.4.2.1 Synthesis of [(L2)PdCl₂] complex



208.0 mg Ligand L2 (0.564 mmol) and 146.3 mg [PdCl₂(CH₃CN)₂] (0.564 mmol) were mixed in 10 ml DCM, and the reaction mixture was stirred at 600 rpm for 5 min at room temperature. After completion of the reaction, a homogenous red solution was obtained, and after evaporating the solvent under vacuum, a reddish-orange precipitate was formed. The obtained

powder was then dried and analyzed by ^1H NMR, ^{13}C NMR, and CH&N elemental analysis without any further purification (yield = 95%). The related crystals were grown by re-dissolving the resulting precipitate in a mixture of chloroform and hexanes, followed by a slow evaporation in a freezer. ^1H NMR (600.1 MHz, CDCl_3) δ (ppm): 1.14 (d, $J=13$ Hz, CH_2 , 2H), 1.26-1.31 (m, 2CH_2 , 4H), 1.42 (t, $J=12.5$ Hz, CH_2 , 2H), 1.64 (d, $J=12$ Hz, 2CH_2 , 4H), 1.84-1.88 (m, 2CH_2 , 4H), 2.05 (d, $J=9$ Hz, CH_2 , 1H), 2.15 (d, $J=8$ Hz, CH_2 , 2H), 2.39 (d, $J=10.5$ Hz, CH_2 , 1H), 3.80-3.88 (m, NCH_2 , 4H), 3.94 (s, OCH_2 , 4H), 4.06 (s, NHCH_2 , 1H), 4.24 (t, $J=10$ Hz, NCH , 1H), 4.53 (d, $J=12$ Hz, NH , 1H). ^{13}C NMR (150.9 MHz, CDCl_3) δ (ppm): 24.9, 25.1, 25.8, 31.0, 31.2, 54.9, 59.5, 66.0, 67.3, 68.9, 179.2, 183.6. CH&N elemental analysis (%) calcd for $\text{C}_{18}\text{H}_{31}\text{ON}_3\text{S}_2\text{PdCl}_2$: C 39.5, H 5.71, N 7.68; found: C 39.3, H 5.61, N 7

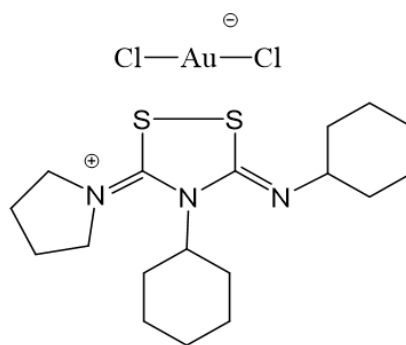
2.4.2.2 Synthesis of $[(\text{L}2)_2\text{Pd}]\text{Cl}_2$ complex



416.0 mg Ligand L2 (1.128 mmol) and 146.3 mg $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (0.564 mmol) were mixed in 10 ml DCM, and the reaction mixture was stirred at 600 rpm for 5 min at room temperature. After completion of the reaction, a homogenous red solution was obtained, and after evaporating the solvent under vacuum, a red precipitate was formed. The obtained powder was then dried and analyzed by ^1H NMR, Mass Spectrometry and CH&N elemental analysis without any further purification (yield = 91%). The related crystals were grown by re-dissolving the resulting precipitate in chloroform followed by a slow evaporation in a closed cap NMR tube. ^1H NMR (600.1 MHz, CDCl_3) δ (ppm): 1.09 (d, $J=12$ Hz, 4H, 2CH_2), 1.29 (s, 8H, 4CH_2), 1.64 (s, 8H,

4CH₂), 1.85 (s, 16H, 8CH₂), 2.41 (s, 4H, 2CH₂), 3.70-3.88 (m, 8H, 4CH₂), 3.95-4.06 (m, 8H, 4CH₂), 4.22-4.27 (m, 2H, 2CH), 4.60 (s, 2H, 2CH), 5.09 (d, J=8.5 Hz, 2H, 2NH). MS (TOF) m/z calcd for C₃₆H₆₂O₂N₆S₄Pd: 845.596; found: 845.290. CH&N elemental analysis (%) calcd for C₃₆H₆₂O₂N₆S₄PdCl₂: C 47.2, H 6.82, N 9.17; found: C 44.8, H 6.88, N 8.54.

2.4.2.3 Synthesis of [(L1)AuCl₂] complex



199.1 mg Ligand L2 (0.564 mmol) and 224.5 mg NaAuCl₄·2H₂O (0.564 mmol) were mixed in 10 ml DCM, and the reaction mixture was stirred at room temperature at 600 rpm for 5 min. After completion of the reaction, a grey solid (NaCl) was formed, and separated from a deep yellow solution by filtration. The solvent was then evaporated under vacuum, resulting in formation of a light orange precipitate (yield = 96%). The obtained powder was then dried and analyzed by ¹H NMR, ¹³C NMR. To grow the related crystals, the resulting light orange precipitate was re-dissolved in a mixture of THF and hexanes, and then slowly evaporated in a freezer. ¹H NMR (600.1 MHz, CDCl₃) δ (ppm): 1.24 (m, 2H, CH₂), 1.35 (d, J=12 Hz, 4H, 2CH₂), 1.54 (m, 6H, 3CH₂), 1.79 (m, 4H, 2CH₂), 2.04 (m, 4H, 2CH₂), 2.15 (m, 2H, CH₂), 2.24 (m, 2H, CH₂), 3.63 (t, J=6 Hz, 2H, CH₂), 3.93 (t, J=6.6 Hz, 2H, CH₂), 4.00 (m, 1H, CH), 10.19 (d, J=6.6 Hz, 1H, CH). ¹³C NMR (150.9 MHz, CDCl₃) δ (ppm): 24.4 (2CH₂), 25.1 (CH₂), 25.4 (CH₂), 26.0 (2CH₂), 31.8 (4CH₂), 51.3 (2CH₂), 53.7 (2CH₂), 58.1 (2CH), 175.5 (C=S), 176.2 (C=S).

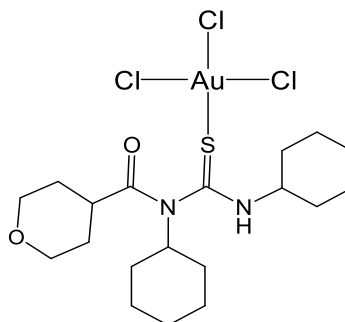
2.4.3 Preparing gold powder

Gold powder was prepared by adapting reported method from Jeffrey et al.⁴¹ 1.000 g pure (99.9% purity) metallic gold was dissolved in 4 mL aqua regia (3 mL HCl 37% / 1 mL HNO₃ 69%) and then diluted 5 times by adding distilled water. Sodium metabisulfite was gradually added to the solution while it was being stirred gently. Addition of Na₂S₂O₅ was continued until all of the gold was precipitated out from the solution (the color changed from a yellow to a colorless solution). The resulting precipitate was isolated, washed with 1M HCl and then with distilled water and finally dried in oven at 70 °C for 1 h. 0.975 g light brown gold powder was obtained (yield: 97%).

2.4.4 Simultaneous leaching and solvent extraction tests

10.0 mg gold powder (0.025 mmol) was added to a vial containing 5 ml aqueous solution including appropriate amounts of HCl and HNO₃. Then the proper amount of ligand was dissolved in a 5 ml water-immiscible organic solvent and added to the previous solution. The reaction mixture was stirred at 800 rpm for different periods of time. When reaction was completed, two phases were separated and organic phase was stripped with 5 ml 1 M H₂SO₄ solution containing 0.7 M thiourea for 15 min. Gold content of the strip solutions was analyzed by AAS.

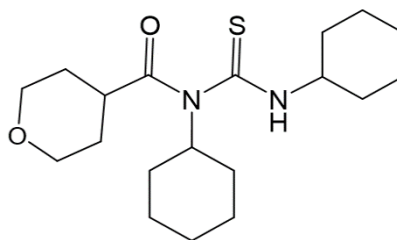
2.4.5 Synthesis of [(L2⁻)AuCl₃] complex



20.0 mg gold powder (0.10 mmol) was added to a vial containing 5 ml aqueous solution including 1.0 M HCl and 0.22 M HNO₃. Then 74.0 mg ligand L2 (0.20 mmol) was dissolved in 5

ml dichloromethane and added to the previous solution. The reaction mixture was stirred (600 rpm) for 6 hours and then the organic phase was isolated and the related crystals were grown by adding 5 drops of hexane to DCM solution followed by a slow evaporation in a freezer. The obtained crystals were then dried and analyzed by ^1H NMR, ^{13}C NMR and CH&N elemental analysis without any further purification. ^1H NMR (600.1 MHz, CDCl_3) δ (ppm): 1.12-1.24 (m, 6H, 3 CH_2), 1.40 (m, 4H, 2 CH_2), 1.66 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.98 (m, 2H, CH_2), 2.05 (m, 2H, CH_2), 3.56 (s, 4H, 2 CH_2), 3.67 (s, 4H, 2 CH_2), 4.33 (s, 1H, CH), 4.82 (s, 1H, CH), 6.28 (br, 1H, NH). ^{13}C NMR (150.9 MHz, CDCl_3) δ (ppm): 24.6 (CH_2), 25.1 (CH_2), 25.7 (2 CH_2), 26.4 (2 CH_2), 31.3 (2 CH_2), 33.4 (2 CH_2), 46.1 (2 CH_2), 56.6 (2 CH_2), 66.6 (CH), 66.9 (CH), 154.0 (C=O), 156.8 (C=S). CH&N elemental analysis (%) calcd for $\text{C}_{18}\text{H}_{31}\text{O}_2\text{N}_3\text{SAuCl}_3$: C 32.9, H 4.72, N 6.40; found: C 32.6, H 4.80, N 6.37.

2.4.6 L2` synthesis:



20.0 mg gold powder (0.05 mmol) was added to a vial containing 5 ml aqueous solution including 1.0 M HCl and 0.22 M HNO_3 . Then 74.0 mg ligand L2 (0.20 mmol) was dissolved in 5 ml dichloromethane and added to the previous solution. The reaction mixture was stirred at 600 rpm for 4 hours and then the organic phase was isolated and stripped with 5 ml H_2SO_4 (1 M) containing 0.7 M thiourea for 15 min. After separation of the two phases, the DCM was evaporated, resulting in formation of 69.4 mg white precipitate (yield: 91%). The resulting white precipitate was then analyzed by ^1H NMR, ^{13}C NMR, Mass Spectrometry and CH&N elemental analysis without any further purification. ^1H NMR (600.1 MHz, CDCl_3) δ (ppm): 1.10-1.18 (m,

4H, 2CH₂), 1.31-1.43 (m, 4H, 2CH₂), 1.53 (m, H, CH), 1.57 (m, H, CH), 1.65 (m, 2H, CH₂), 1.72 (m, 2H, CH₂), 1.82 (m, 2H, CH₂), 1.95 (m, 2H, CH₂), 2.08 (m, 2H, CH₂), 3.51 (t, J=6 Hz, 4H, 2CH₂), 3.68 (t, J=6 Hz, 4H, 2CH₂), 4.34 (m, 1H, CH), 4.60 (m, 1H, CH), 5.52 (d, J=8 Hz, 1H, NH). ¹³C NMR (150.9 MHz, CDCl₃) δ (ppm): 24.9 (2CH₂), 25.4 (CH₂), 25.6 (CH₂), 26.0 (2CH₂), 30.8 (2CH₂), 33.1 (2CH₂), 45.4 (CH₂), 53.9 (CH₂), 59.4 (2CH₂), 66.6 (2CH), 155.0 (C=O), 179.5 (C=S). MS (TOF) m/z calcd for C₁₈H₃₁O₂N₃S: 353.214; found: 353.223. CH&N elemental analysis (%) calcd for C₁₈H₃₁O₂N₃S: C 61.2, H 8.78, N 11.9; found: C 61.1, H 8.80, N 11.8.

2.4.7 Selectivity test

A mixture of different metals in chloride forms including FeCl₃ (14.5 mg), CuCl₂ (21.3 mg), ZnCl₂ (5.2 mg), NiCl₂ (5.6 mg), CoCl₂ (5.6 mg), and 0.5 mg gold powder was added to a vial containing 5 ml 1M HCl and 0.2M HNO₃. Then, 26.8 mg ligand L1 was dissolved in 5 ml dichloromethane and added to the previous solution. The reaction mixture was stirred at 800 rpm for 3 hours. When the reaction was completed, two phases were separated and then the organic phase was stripped with 5 ml H₂SO₄ (1 M) containing 0.7 M thiourea for 15 min. Metal content of the post extraction and strip solutions were analyzed by AAS.

2.4.8 Gold ore treatment

Crushed and ground gold ore with an average gold concentration of 10.4 ppm and an average particle size of 74 microns was provided to us by Claude Resources from their Seabee gold mine operation located in the La Ronge Mining District at the north end of Laonil Lake approximately 125 kilometres northeast of the town of La Ronge, Saskatchewan, Canada.

2.4.8.1 General experimental for simultaneous leaching and solvent extraction:

10.0 g crushed and ground gold ore with an average particle size of 74 microns was added to 10 ml 1M HCl solution in the presence of different concentrations of HNO₃. A solution of ligand L1 (35.0 mg) in 10 ml dichloromethane then added to the aqueous solution. The resulting triphasic reaction mixture was stirred at 800 rpm for different time periods. The mixture was then filtered and the organic phase was isolated. The organic phase was then stripped with 10 ml 1M H₂SO₄ solution containing 0.7 M thiourea for 15 min, and the gold content of the stripped solutions was analyzed by AAS.

Table 2.6. Bond lengths [Å] and angles [°] for [(L2)₂Pd]Cl₂ complex

Pd(1)-S(2)#1	2.3186(10)	Pd(1)-S(2)	2.3186(10)
Pd(1)-S(1)	2.3430(9)	Pd(1)-S(1)#1	2.3430(9)
Pd(2)-S(3)#2	2.3162(10)	Pd(2)-S(3)	2.3162(10)
Pd(2)-S(4)	2.3239(9)	Pd(2)-S(4)#2	2.3239(9)
S(1)-C(6)	1.722(4)	S(2)-C(5)	1.717(4)
S(3)-C(23)	1.710(4)	S(4)-C(24)	1.724(4)
O(1)-C(1)	1.413(7)	O(1)-C(4)	1.414(7)
O(2)-C(19)	1.420(6)	O(2)-C(22)	1.421(6)
N(1)-C(5)	1.309(5)	N(1)-C(3)	1.479(5)
N(1)-C(2)	1.480(5)	N(2)-C(6)	1.374(5)
N(2)-C(5)	1.420(5)	N(2)-C(7)	1.507(5)
N(3)-C(6)	1.313(5)	N(3)-C(13)	1.484(5)
N(3)-H(3)	0.8800	N(4)-C(23)	1.309(5)
N(4)-C(20)	1.472(5)	N(4)-C(21)	1.482(5)
N(5)-C(24)	1.364(5)	N(5)-C(23)	1.427(4)
N(5)-C(25)	1.506(4)	N(6)-C(24)	1.309(5)
N(6)-C(31)	1.476(5)	N(6)-H(6)	0.8800
C(1)-C(2)	1.522(6)	C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900	C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900	C(3)-C(4)	1.524(7)
C(3)-H(3A)	0.9900	C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9900	C(4)-H(4B)	0.9900
C(7)-C(8)	1.527(5)	C(7)-C(12)	1.528(6)
C(7)-H(7)	1.0000	C(8)-C(9)	1.533(6)
C(8)-H(8A)	0.9900	C(8)-H(8B)	0.9900
C(9)-C(10)	1.530(8)	C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900	C(10)-C(11)	1.524(7)
C(10)-H(10A)	0.9900	C(10)-H(10B)	0.9900
C(11)-C(12)	1.533(6)	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900	C(13)-C(14)	1.525(5)
C(13)-C(18)	1.526(5)	C(13)-H(13)	1.0000
C(14)-C(15)	1.530(6)	C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900	C(15)-C(16)	1.521(7)

C(15)-H(15A)	0.9900	C(15)-H(15B)	0.9900
C(16)-C(17)	1.513(6)	C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900	C(17)-C(18)	1.532(5)
C(17)-H(17A)	0.9900	C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9900	C(18)-H(18B)	0.9900
C(19)-C(20)	1.523(6)	C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-C(22)	1.519(6)
C(21)-H(21A)	0.9900	C(21)-H(21B)	0.9900
C(22)-H(22A)	0.9900	C(22)-H(22B)	0.9900
C(25)-C(26)	1.521(5)	C(25)-C(30)	1.528(5)
C(25)-H(25)	1.0000	C(26)-C(27)	1.529(6)
C(26)-H(26A)	0.9900	C(26)-H(26B)	0.9900
C(27)-C(28)	1.518(7)	C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900	C(28)-C(29)	1.530(7)
C(28)-H(28A)	0.9900	C(28)-H(28B)	0.9900
C(29)-C(30)	1.534(6)	C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900	C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900	C(31)-C(32)	1.508(6)
C(31)-C(36)	1.513(6)	C(31)-H(31)	1.0000
C(32)-C(33)	1.531(6)	C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900	C(33)-C(34)	1.528(8)
C(33)-H(33A)	0.9900	C(33)-H(33B)	0.9900
C(34)-C(35)	1.516(8)	C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900	C(35)-C(36)	1.538(6)
C(35)-H(35A)	0.9900	C(35)-H(35B)	0.9900
C(36)-H(36A)	0.9900	C(36)-H(36B)	0.9900
C(1S)-Cl(4)	1.748(6)	C(1S)-Cl(3)	1.757(5)
C(1S)-Cl(5)	1.763(6)	C(1S)-Cl(5')	1.796(7)
C(1S)-H(1S)	1.0000	C(2S)-Cl(7)	1.717(7)
C(2S)-Cl(8)	1.732(7)	C(2S)-Cl(6')	1.764(7)
C(2S)-Cl(6)	1.775(7)	C(2S)-Cl(8')	1.788(7)
C(2S)-H(2S)	1.0000	C(3S)-Cl(9')	1.755(6)
C(3S)-Cl(11)	1.756(5)	C(3S)-Cl(10)	1.758(6)
C(3S)-Cl(9)	1.771(6)	C(3S)-H(3S)	1.0000
C(4S)-Cl(12)	1.737(5)	C(4S)-Cl(13)	1.751(6)

C(4S)-Cl(14)	1.775(6)	C(4S)-H(4S)	1.0000
S(2)#1-Pd(1)-S(1)	85.83(3)	S(2)#1-Pd(1)-S(2)	180.0
S(2)#1-Pd(1)-S(1)#1	94.17(3)	S(2)-Pd(1)-S(1)	94.17(3)
S(1)-Pd(1)-S(1)#1	180.0	S(2)-Pd(1)-S(1)#1	85.83(4)
S(3)#2-Pd(2)-S(4)	85.63(3)	S(3)#2-Pd(2)-S(3)	180.0
S(3)#2-Pd(2)-S(4)#2	94.37(3)	S(3)-Pd(2)-S(4)	94.37(3)
S(4)-Pd(2)-S(4)#2	180.0	S(3)-Pd(2)-S(4)#2	85.63(3)
C(5)-S(2)-Pd(1)	99.84(12)	C(6)-S(1)-Pd(1)	100.75(12)
C(24)-S(4)-Pd(2)	103.59(12)	C(23)-S(3)-Pd(2)	101.79(12)
C(19)-O(2)-C(22)	110.7(4)	C(1)-O(1)-C(4)	111.2(4)
C(5)-N(1)-C(2)	124.1(3)	C(5)-N(1)-C(3)	124.3(3)
C(6)-N(2)-C(5)	115.9(3)	C(3)-N(1)-C(2)	110.7(3)
C(5)-N(2)-C(7)	119.7(3)	C(6)-N(2)-C(7)	121.5(3)
C(6)-N(3)-H(3)	116.8	C(6)-N(3)-C(13)	126.4(3)
C(23)-N(4)-C(20)	123.4(3)	C(13)-N(3)-H(3)	116.8
C(20)-N(4)-C(21)	110.8(3)	C(23)-N(4)-C(21)	125.2(3)
C(24)-N(5)-C(25)	121.3(3)	C(24)-N(5)-C(23)	117.2(3)
C(24)-N(6)-C(31)	126.1(3)	C(23)-N(5)-C(25)	119.8(3)
C(31)-N(6)-H(6)	117.0	C(24)-N(6)-H(6)	117.0
O(1)-C(1)-H(1A)	109.2	O(1)-C(1)-C(2)	112.1(4)
O(1)-C(1)-H(1B)	109.2	C(2)-C(1)-H(1A)	109.2
H(1A)-C(1)-H(1B)	107.9	C(2)-C(1)-H(1B)	109.2
N(1)-C(2)-H(2A)	110.2	N(1)-C(2)-C(1)	107.7(4)
N(1)-C(2)-H(2B)	110.2	C(1)-C(2)-H(2A)	110.2
H(2A)-C(2)-H(2B)	108.5	C(1)-C(2)-H(2B)	110.2
N(1)-C(3)-H(3A)	110.4	N(1)-C(3)-C(4)	106.7(4)
N(1)-C(3)-H(3B)	110.4	C(4)-C(3)-H(3A)	110.4
H(3A)-C(3)-H(3B)	108.6	C(4)-C(3)-H(3B)	110.4
O(1)-C(4)-H(4A)	109.4	O(1)-C(4)-C(3)	111.1(4)
O(1)-C(4)-H(4B)	109.4	C(3)-C(4)-H(4A)	109.4
H(4A)-C(4)-H(4B)	108.0	C(3)-C(4)-H(4B)	109.4
N(1)-C(5)-S(2)	123.1(3)	N(1)-C(5)-N(2)	115.5(3)
N(3)-C(6)-N(2)	117.8(3)	N(2)-C(5)-S(2)	121.4(3)
N(2)-C(6)-S(1)	120.7(3)	N(3)-C(6)-S(1)	121.4(3)
N(2)-C(7)-C(12)	110.9(3)	N(2)-C(7)-C(8)	111.0(3)
		C(8)-C(7)-C(12)	112.1(3)

N(2)-C(7)-H(7)	107.5	C(8)-C(7)-H(7)	107.5
C(12)-C(7)-H(7)	107.5	C(7)-C(8)-C(9)	110.1(4)
C(7)-C(8)-H(8A)	109.7	C(9)-C(8)-H(8A)	109.7
C(7)-C(8)-H(8B)	109.7	C(9)-C(8)-H(8B)	109.7
H(8A)-C(8)-H(8B)	108.2	C(10)-C(9)-C(8)	110.6(4)
C(10)-C(9)-H(9A)	109.5	C(8)-C(9)-H(9A)	109.5
C(10)-C(9)-H(9B)	109.5	C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	108.1	C(11)-C(10)-C(9)	110.3(4)
C(11)-C(10)-H(10A)	109.6	C(9)-C(10)-H(10A)	109.6
C(11)-C(10)-H(10B)	109.6	C(9)-C(10)-H(10B)	109.6
H(10A)-C(10)-H(10B)	108.1	C(10)-C(11)-C(12)	111.3(4)
C(10)-C(11)-H(11A)	109.4	C(12)-C(11)-H(11A)	109.4
C(10)-C(11)-H(11B)	109.4	C(12)-C(11)-H(11B)	109.4
H(11A)-C(11)-H(11B)	108.0	C(7)-C(12)-C(11)	109.3(4)
C(7)-C(12)-H(12A)	109.8	C(11)-C(12)-H(12A)	109.8
C(7)-C(12)-H(12B)	109.8	C(11)-C(12)-H(12B)	109.8
H(12A)-C(12)-H(12B)	108.3	N(3)-C(13)-C(14)	111.1(3)
N(3)-C(13)-C(18)	107.7(3)	C(14)-C(13)-C(18)	111.9(3)
N(3)-C(13)-H(13)	108.7	C(14)-C(13)-H(13)	108.7
C(18)-C(13)-H(13)	108.7	C(13)-C(14)-C(15)	110.6(3)
C(13)-C(14)-H(14A)	109.5	C(15)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5	C(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1	C(16)-C(15)-C(14)	111.5(4)
C(16)-C(15)-H(15A)	109.3	C(14)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15B)	109.3	C(14)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0	C(17)-C(16)-C(15)	110.2(4)
C(17)-C(16)-H(16A)	109.6	C(15)-C(16)-H(16A)	109.6
C(17)-C(16)-H(16B)	109.6	C(15)-C(16)-H(16B)	109.6
H(16A)-C(16)-H(16B)	108.1	C(16)-C(17)-C(18)	111.4(4)
C(16)-C(17)-H(17A)	109.3	C(18)-C(17)-H(17A)	109.3
C(16)-C(17)-H(17B)	109.3	C(18)-C(17)-H(17B)	109.3
H(17A)-C(17)-H(17B)	108.0	C(13)-C(18)-C(17)	110.8(3)
C(13)-C(18)-H(18A)	109.5	C(17)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5	C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	108.1	O(2)-C(19)-C(20)	112.0(4)
O(2)-C(19)-H(19A)	109.2	C(20)-C(19)-H(19A)	109.2

O(2)-C(19)-H(19B)	109.2	C(20)-C(19)-H(19B)	109.2
H(19A)-C(19)-H(19B)	107.9	N(4)-C(20)-C(19)	106.8(4)
N(4)-C(20)-H(20A)	110.4	C(19)-C(20)-H(20A)	110.4
N(4)-C(20)-H(20B)	110.4	C(19)-C(20)-H(20B)	110.4
H(20A)-C(20)-H(20B)	108.6	N(4)-C(21)-C(22)	107.7(3)
N(4)-C(21)-H(21A)	110.2	C(22)-C(21)-H(21A)	110.2
N(4)-C(21)-H(21B)	110.2	C(22)-C(21)-H(21B)	110.2
H(21A)-C(21)-H(21B)	108.5	O(2)-C(22)-C(21)	110.7(4)
O(2)-C(22)-H(22A)	109.5	C(21)-C(22)-H(22A)	109.5
O(2)-C(22)-H(22B)	109.5	C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	108.1	N(4)-C(23)-N(5)	114.7(3)
N(4)-C(23)-S(3)	124.0(3)	N(5)-C(23)-S(3)	121.2(3)
N(6)-C(24)-N(5)	117.6(3)	N(6)-C(24)-S(4)	121.3(3)
N(5)-C(24)-S(4)	121.1(3)	N(5)-C(25)-C(26)	110.3(3)
N(5)-C(25)-C(30)	112.1(3)	C(26)-C(25)-C(30)	111.2(3)
N(5)-C(25)-H(25)	107.7	C(26)-C(25)-H(25)	107.7
C(30)-C(25)-H(25)	107.7	C(25)-C(26)-C(27)	109.6(3)
C(25)-C(26)-H(26A)	109.8	C(27)-C(26)-H(26A)	109.8
C(25)-C(26)-H(26B)	109.8	C(27)-C(26)-H(26B)	109.8
H(26A)-C(26)-H(26B)	108.2	C(28)-C(27)-C(26)	111.0(4)
C(28)-C(27)-H(27A)	109.4	C(26)-C(27)-H(27A)	109.4
C(28)-C(27)-H(27B)	109.4	C(26)-C(27)-H(27B)	109.4
H(27A)-C(27)-H(27B)	108.0	C(27)-C(28)-C(29)	109.9(4)
C(27)-C(28)-H(28A)	109.7	C(29)-C(28)-H(28A)	109.7
C(27)-C(28)-H(28B)	109.7	C(29)-C(28)-H(28B)	109.7
H(28A)-C(28)-H(28B)	108.2	C(28)-C(29)-C(30)	111.5(4)
C(28)-C(29)-H(29A)	109.3	C(30)-C(29)-H(29A)	109.3
C(28)-C(29)-H(29B)	109.3	C(30)-C(29)-H(29B)	109.3
H(29A)-C(29)-H(29B)	108.0	C(25)-C(30)-C(29)	108.9(3)
C(25)-C(30)-H(30A)	109.9	C(29)-C(30)-H(30A)	109.9
C(25)-C(30)-H(30B)	109.9	C(29)-C(30)-H(30B)	109.9
H(30A)-C(30)-H(30B)	108.3	N(6)-C(31)-C(32)	111.3(3)
N(6)-C(31)-C(36)	108.1(3)	C(32)-C(31)-C(36)	111.8(4)
N(6)-C(31)-H(31)	108.5	C(32)-C(31)-H(31)	108.5
C(36)-C(31)-H(31)	108.5	C(31)-C(32)-C(33)	110.4(4)
C(31)-C(32)-H(32A)	109.6	C(33)-C(32)-H(32A)	109.6

C(31)-C(32)-H(32B)	109.6	C(33)-C(32)-H(32B)	109.6
H(32A)-C(32)-H(32B)	108.1	C(34)-C(33)-C(32)	110.7(5)
C(34)-C(33)-H(33A)	109.5	C(32)-C(33)-H(33A)	109.5
C(34)-C(33)-H(33B)	109.5	C(32)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	108.1	C(35)-C(34)-C(33)	110.8(4)
C(35)-C(34)-H(34A)	109.5	C(33)-C(34)-H(34A)	109.5
C(35)-C(34)-H(34B)	109.5	C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	108.1	C(34)-C(35)-C(36)	111.3(5)
C(34)-C(35)-H(35A)	109.4	C(36)-C(35)-H(35A)	109.4
C(34)-C(35)-H(35B)	109.4	C(36)-C(35)-H(35B)	109.4
H(35A)-C(35)-H(35B)	108.0	C(31)-C(36)-C(35)	110.8(4)
C(31)-C(36)-H(36A)	109.5	C(35)-C(36)-H(36A)	109.5
C(31)-C(36)-H(36B)	109.5	C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	108.1	Cl(4)-C(1S)-Cl(3)	108.3(3)
Cl(4)-C(1S)-Cl(5)	102.9(3)	Cl(3)-C(1S)-Cl(5)	113.2(3)
Cl(4)-C(1S)-Cl(5')	123.8(4)	Cl(3)-C(1S)-Cl(5')	106.1(3)
Cl(4)-C(1S)-H(1S)	110.7	Cl(3)-C(1S)-H(1S)	110.7
Cl(5)-C(1S)-H(1S)	110.7	Cl(7)-C(2S)-Cl(8)	117.6(4)
Cl(7)-C(2S)-Cl(6')	120.7(4)	Cl(7)-C(2S)-Cl(6)	100.1(4)
Cl(8)-C(2S)-Cl(6)	110.6(3)	Cl(7)-C(2S)-Cl(8')	95.0(4)
Cl(6')-C(2S)-Cl(8')	112.4(4)	Cl(7)-C(2S)-H(2S)	109.4
Cl(8)-C(2S)-H(2S)	109.4	Cl(6)-C(2S)-H(2S)	109.4
Cl(9')-C(3S)-Cl(11)	105.8(3)	Cl(9')-C(3S)-Cl(10)	103.4(3)
Cl(11)-C(3S)-Cl(10)	109.9(3)	Cl(11)-C(3S)-Cl(9)	112.2(3)
Cl(10)-C(3S)-Cl(9)	116.4(3)	Cl(11)-C(3S)-H(3S)	105.8
Cl(10)-C(3S)-H(3S)	105.8	Cl(9)-C(3S)-H(3S)	105.8
Cl(12)-C(4S)-Cl(13)	113.5(3)	Cl(12)-C(4S)-Cl(14)	108.3(3)
Cl(13)-C(4S)-Cl(14)	109.6(3)	Cl(12)-C(4S)-H(4S)	108.5
Cl(13)-C(4S)-H(4S)	108.5	Cl(14)-C(4S)-H(4S)	108.5

Table 2.7. Bond lengths [Å] and angles [°] for [(L1)AuCl₂] complex

Au(1)-Cl(2)	2.2651(6)	Au(1)-Cl(1)	2.2678(6)
S(1)-C(1)	1.7800(19)	S(1)-S(2)	2.0579(7)
S(2)-C(2)	1.7528(19)	N(1)-C(2)	1.352(2)
N(1)-C(1)	1.419(2)	N(1)-C(7)	1.503(2)
N(2)-C(2)	1.304(3)	N(2)-C(6)	1.488(2)
N(2)-C(3)	1.491(2)	N(3)-C(1)	1.258(2)
N(3)-C(13)	1.469(2)	C(3)-C(4)	1.518(3)
C(3)-H(3A)	0.9900	C(3)-H(3B)	0.9900
C(4)-C(5)	1.521(3)	C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900	C(5)-C(6)	1.518(3)
C(5)-H(5A)	0.9900	C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900	C(6)-H(6B)	0.9900
C(7)-C(12)	1.523(3)	C(7)-C(8)	1.524(2)
C(7)-H(7)	1.0000	C(8)-C(9)	1.531(3)
C(8)-H(8A)	0.9900	C(8)-H(8B)	0.9900
C(9)-C(10)	1.526(3)	C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900	C(10)-C(11)	1.520(3)
C(10)-H(10A)	0.9900	C(10)-H(10B)	0.9900
C(11)-C(12)	1.529(3)	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900	C(13)-C(18)	1.529(3)
C(13)-C(14)	1.533(3)	C(13)-H(13)	1.0000
C(14)-C(15)	1.528(3)	C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900	C(15)-C(16)	1.520(3)
C(15)-H(15A)	0.9900	C(15)-H(15B)	0.9900
C(16)-C(17)	1.518(3)	C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900	C(17)-C(18)	1.523(3)
C(17)-H(17A)	0.9900	C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9900	C(18)-H(18B)	0.9900
H(18A)-C(18)-H(18B)		Cl(2)-Au(1)-Cl(1)	178.29(2)
	107.9		
C(1)-S(1)-S(2)	95.09(7)	C(2)-S(2)-S(1)	95.08(7)
C(2)-N(1)-C(1)	117.64(15)	C(2)-N(1)-C(7)	122.93(15)
C(1)-N(1)-C(7)	119.14(15)	C(2)-N(2)-C(6)	128.67(16)

C(2)-N(2)-C(3)	119.89(16)	C(6)-N(2)-C(3)	110.42(15)
C(1)-N(3)-C(13)	119.78(16)	N(3)-C(1)-N(1)	121.42(17)
N(3)-C(1)-S(1)	124.75(15)	N(1)-C(1)-S(1)	113.77(13)
N(2)-C(2)-N(1)	126.87(17)	N(2)-C(2)-S(2)	116.40(14)
N(1)-C(2)-S(2)	116.73(14)	N(2)-C(3)-C(4)	103.65(16)
N(2)-C(3)-H(3A)	111.0	C(4)-C(3)-H(3A)	111.0
N(2)-C(3)-H(3B)	111.0	C(4)-C(3)-H(3B)	111.0
H(3A)-C(3)-H(3B)	109.0	C(3)-C(4)-C(5)	103.41(16)
C(3)-C(4)-H(4A)	111.1	C(5)-C(4)-H(4A)	111.1
C(3)-C(4)-H(4B)	111.1	C(5)-C(4)-H(4B)	111.1
H(4A)-C(4)-H(4B)	109.0	C(6)-C(5)-C(4)	102.71(17)
C(6)-C(5)-H(5A)	111.2	C(4)-C(5)-H(5A)	111.2
C(6)-C(5)-H(5B)	111.2	C(4)-C(5)-H(5B)	111.2
H(5A)-C(5)-H(5B)	109.1	N(2)-C(6)-C(5)	102.35(16)
N(2)-C(6)-H(6A)	111.3	C(5)-C(6)-H(6A)	111.3
N(2)-C(6)-H(6B)	111.3	C(5)-C(6)-H(6B)	111.3
H(6A)-C(6)-H(6B)	109.2	N(1)-C(7)-C(12)	111.51(14)
N(1)-C(7)-C(8)	112.27(15)	C(12)-C(7)-C(8)	112.49(15)
N(1)-C(7)-H(7)	106.7	C(12)-C(7)-H(7)	106.7
C(8)-C(7)-H(7)	106.7	C(7)-C(8)-C(9)	109.67(16)
C(7)-C(8)-H(8A)	109.7	C(9)-C(8)-H(8A)	109.7
C(7)-C(8)-H(8B)	109.7	C(9)-C(8)-H(8B)	109.7
H(8A)-C(8)-H(8B)	108.2	C(10)-C(9)-C(8)	111.26(16)
C(10)-C(9)-H(9A)	109.4	C(8)-C(9)-H(9A)	109.4
C(10)-C(9)-H(9B)	109.4	C(8)-C(9)-H(9B)	109.4
H(9A)-C(9)-H(9B)	108.0	C(11)-C(10)-C(9)	111.04(17)
C(11)-C(10)-H(10A)	109.4	C(9)-C(10)-H(10A)	109.4
C(11)-C(10)-H(10B)	109.4	C(9)-C(10)-H(10B)	109.4
H(10A)-C(10)-H(10B)	108.0	C(10)-C(11)-C(12)	111.39(17)
C(10)-C(11)-H(11A)	109.3	C(12)-C(11)-H(11A)	109.3
C(10)-C(11)-H(11B)	109.3	C(12)-C(11)-H(11B)	109.3
H(11A)-C(11)-H(11B)	108.0	C(7)-C(12)-C(11)	108.75(15)
C(7)-C(12)-H(12A)	109.9	C(11)-C(12)-H(12A)	109.9
C(7)-C(12)-H(12B)	109.9	C(11)-C(12)-H(12B)	109.9
H(12A)-C(12)-H(12B)	108.3	N(3)-C(13)-C(18)	106.77(16)
N(3)-C(13)-C(14)	110.77(16)	C(18)-C(13)-C(14)	111.09(17)

N(3)-C(13)-H(13)	109.4	C(18)-C(13)-H(13)	109.4
C(14)-C(13)-H(13)	109.4	C(15)-C(14)-C(13)	112.45(18)
C(15)-C(14)-H(14A)	109.1	C(13)-C(14)-H(14A)	109.1
C(15)-C(14)-H(14B)	109.1	C(13)-C(14)-H(14B)	109.1
H(14A)-C(14)-H(14B)	107.8	C(16)-C(15)-C(14)	111.51(18)
C(16)-C(15)-H(15A)	109.3	C(14)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15B)	109.3	C(14)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0	C(17)-C(16)-C(15)	110.83(18)
C(17)-C(16)-H(16A)	109.5	C(15)-C(16)-H(16A)	109.5
C(17)-C(16)-H(16B)	109.5	C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	108.1	C(16)-C(17)-C(18)	110.86(19)
C(16)-C(17)-H(17A)	109.5	C(18)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5	C(18)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	108.1	C(17)-C(18)-C(13)	111.76(17)
C(17)-C(18)-H(18A)	109.3	C(13)-C(18)-H(18A)	109.3
C(17)-C(18)-H(18B)	109.3	C(13)-C(18)-H(18B)	109.3

Table 2.8. Bond lengths [Å] and angles [°] for gold complex formed during the simultaneous leaching and solvent extraction process ($[(L2^+)AuCl_3]$).

Au1-Cl1	2.2823(7)	Au1-Cl3	2.2874(7)
Au1-Cl2	2.3088(7)	Au1-S1	2.3101(7)
S1-C1	1.763(3)	O1-C2	1.213(3)
O2-C5	1.417(4)	O2-C4	1.420(4)
N1-C2	1.333(3)	N1-C6	1.461(3)
N1-C3	1.466(3)	N2-C1	1.333(3)
N2-C2	1.470(3)	N2-C13	1.504(3)
N3-C1	1.317(3)	N3-C7	1.479(3)
N3-H3	0.88	C3-C4	1.514(4)
C3-H3A	0.99	C3-H3B	0.99
C4-H4A	0.99	C4-H4B	0.99
C5-C6	1.523(4)	C5-H5A	0.99
C5-H5B	0.99	C6-H6A	0.99
C6-H6B	0.99	C7-C8	1.518(4)

C7-C12	1.524(4)	C7-H7	1.0
C8-C9	1.516(4)	C8-H8A	0.99
C8-H8B	0.99	C9-C10	1.519(5)
C9-H9A	0.99	C9-H9B	0.99
C10-C11	1.514(5)	C10-H10A	0.99
C10-H10B	0.99	C11-C12	1.531(4)
C11-H11A	0.99	C11-H11B	0.99
C12-H12A	0.99	C12-H12B	0.99
C13-C18	1.515(4)	C13-C14	1.521(4)
C13-H13	1.0	C14-C15	1.533(4)
C14-H10	0.99	C14-H11	0.99
C15-C16	1.514(4)	C15-H15A	0.99
C15-H15B	0.99	C16-C17	1.521(4)
C16-H16A	0.99	C16-H16B	0.99
C17-C18	1.531(4)	C17-H17A	0.99
C17-H17B	0.99	C18-H18A	0.99
C18-H18B	0.99	C14-C19	1.753(5)
C15-C19	1.735(5)	C19-H19A	0.99
C19-H19B	0.99		
C11-Au1-C13	177.83(3)	C11-Au1-C12	89.71(3)
C13-Au1-C12	91.52(3)	C11-Au1-S1	85.77(3)
C13-Au1-S1	92.86(3)	C12-Au1-S1	173.73(2)
C1-S1-Au1	105.57(9)	C5-O2-C4	109.6(2)
C2-N1-C6	125.1(2)	C2-N1-C3	117.9(2)
C6-N1-C3	114.1(2)	C1-N2-C2	119.2(2)
C1-N2-C13	122.7(2)	C2-N2-C13	116.9(2)
C1-N3-C7	126.4(2)	C1-N3-H3	116.8
C7-N3-H3	116.8	N3-C1-N2	122.3(2)
N3-C1-S1	118.6(2)	N2-C1-S1	118.74(18)

O1-C2-N1	126.1(2)	O1-C2-N2	119.2(2)
N1-C2-N2	114.6(2)	N1-C3-C4	109.5(2)
N1-C3-H3A	109.8	C4-C3-H3A	109.8
N1-C3-H3B	109.8	C4-C3-H3B	109.8
H3A-C3-H3B	108.2	O2-C4-C3	111.4(3)
O2-C4-H4A	109.3	C3-C4-H4A	109.3
O2-C4-H4B	109.3	C3-C4-H4B	109.3
H4A-C4-H4B	108.0	O2-C5-C6	111.4(3)
O2-C5-H5A	109.4	C6-C5-H5A	109.4
O2-C5-H5B	109.4	C6-C5-H5B	109.4
H5A-C5-H5B	108.0	N1-C6-C5	110.3(2)
N1-C6-H6A	109.6	C5-C6-H6A	109.6
N1-C6-H6B	109.6	C5-C6-H6B	109.6
H6A-C6-H6B	108.1	N3-C7-C8	111.4(2)
N3-C7-C12	108.0(2)	C8-C7-C12	112.2(2)
N3-C7-H7	108.4	C8-C7-H7	108.4
C12-C7-H7	108.4	C9-C8-C7	110.5(3)
C9-C8-H8A	109.5	C7-C8-H8A	109.5
C9-C8-H8B	109.5	C7-C8-H8B	109.5
H8A-C8-H8B	108.1	C8-C9-C10	111.1(3)
C8-C9-H9A	109.4	C10-C9-H9A	109.4
C8-C9-H9B	109.4	C10-C9-H9B	109.4
H9A-C9-H9B	108.0	C11-C10-C9	110.6(3)
C11-C10-H10A	109.5	C9-C10-H10A	109.5
C11-C10-H10B	109.5	C9-C10-H10B	109.5
H10A-C10-H10B	108.1	C10-C11-C12	111.7(3)
C10-C11-H11A	109.3	C12-C11-H11A	109.3
C10-C11-H11B	109.3	C12-C11-H11B	109.3
H11A-C11-H11B	107.9	C7-C12-C11	110.2(3)

C7-C12-H12A	109.6	C11-C12-H12A	109.6
C7-C12-H12B	109.6	C11-C12-H12B	109.6
H12A-C12-H12B	108.1	N2-C13-C18	110.9(2)
N2-C13-C14	111.0(2)	C18-C13-C14	111.8(2)
N2-C13-H13	107.6	C18-C13-H13	107.6
C14-C13-H13	107.6	C13-C14-C15	109.8(2)
C13-C14-H10	109.7	C15-C14-H10	109.7
C13-C14-H11	109.7	C15-C14-H11	109.7
H10-C14-H11	108.2	C16-C15-C14	111.8(3)
C16-C15-H15A	109.3	C14-C15-H15A	109.3
C16-C15-H15B	109.3	C14-C15-H15B	109.3
H15A-C15-H15B	107.9	C15-C16-C17	110.5(2)
C15-C16-H16A	109.6	C17-C16-H16A	109.6
C15-C16-H16B	109.6	C17-C16-H16B	109.6
H16A-C16-H16B	108.1	C16-C17-C18	111.0(2)
C16-C17-H17A	109.4	C18-C17-H17A	109.4
C16-C17-H17B	109.4	C18-C17-H17B	109.4
H17A-C17-H17B	108.0	C13-C18-C17	110.4(2)
C13-C18-H18A	109.6	C17-C18-H18A	109.6
C13-C18-H18B	109.6	C17-C18-H18B	109.6
H18A-C18-H18B	108.1	C15-C19-C14	112.1(2)
C15-C19-H19A	109.2	C14-C19-H19A	109.2
C15-C19-H19B	109.2	C14-C19-H19B	109.2
H19A-C19-H19B	107.9		

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